Soluzioni ai problemi proposti nell'Eserciziario

Capitolo 1

1.1 Il numero di massa è il numero dei protoni e dei neutroni. Il numero atomico è il numero dei protoni ed è identico per tutti gli isotopi.

a. Numero dei protoni = numero atomico per O = 8
b. Numero dei neutroni = numero di massa – numero atomico
c. Numero degli elettroni = numero dei protoni
d. Il numero di gruppo è lo stesso per tutti gli isotopi

1.2 I legami ionici si formano quando un elemento della parte sinistra della tavola periodica trasferisce un elettrone ad un elemento della parte destra della tavola periodica. I legami covalenti si originano quando due atomi condividono elettroni

1.3 Atomi con 1, 2 o 3 elettroni di valenza formano 1, 2 o 3 legami rispettivamente. Atomi con quattro o più elettroni di valenza formano [8 – (numero degli elettroni di valenza)] legami

1.4 Usare le regole di formazione dei legami della risposta 1.2.

1.5 [1]. Sistemare gli atomi con gli idrogeni sull'esterno
[2]. Contare gli elettroni di valenza
[3]. Sistemare gli elettroni attorno agli atomi. Assegnare prima due elettroni agli idrogeni, poi completare gli ottetti degli altri atomi.
4. Assegnare le cariche formali (Sezione 1.3C)

1.6 Segui il procedimento della risposta 1.5

1.7 Carica formale = numero di elettroni di valenza – [numero di elettroni non condivisi + ½ (numero di elettroni condivisi)]

1.8

1.9

1.10 Carica formale = numero di elettroni di valenza – [numero di elettroni non condivisi + ½ (numero di elettroni condivisi)]. Il C è nel gruppo 4A.

1.11 Carica formale = numero di elettroni di valenza – [numero di elettroni non condivisi + ½ (numero di elettroni condivisi)]. L'N è nel gruppo 5A e l'O nel gruppo 6A.

1.12 Seguire i passaggi della risposta 1.4 per disegnare le strutture di Lewis.

1.13 Seguire i passaggi della risposta 1.4 per disegnare le strutture di Lewis.

1.14 Due differenti definizioni:

. Gli isomeri hanno la stessa formula molecolare ed una *differente* posizione degli atomi.

. Le strutture di risonanza hanno la stessa formula molecolare e la stessa posizione degli atomi.

1.15 La notazione della freccia curva mostra il movimento di una coppia elettronica. La coda si posiziona presso una coppia elettronica (un legame o una coppia solitaria) e la testa punta dove gli elettroni si devono muovere. Confrontare le strutture di risonanza per vedere quali elettroni si sono “mossi”. Usare la freccia curva per mostrare il movimento di ogni coppia elettronica.

1.16 Confrontare le strutture di risonanza per vedere quali elettroni si sono “mossi”. **Usare una freccia curva per mostrare il movimento di ogni coppia elettronica.**

1.17 Per disegnare un’altra struttura di risonanza, muovere solamente gli elettroni dei legami multipli e le coppie solitarie e mantenere costante il numero degli elettroni spaiati.

1.18 Per disegnare un ibrido di risonanza:

. Usare linee intere per i legami che sono presenti in entrambe le strutture di risonanza e linee tratteggiate per i legami che sono presenti in una sola delle strutture di risonanza.

. Usa cariche parziali quando la carica è su più atomi nelle strutture di risonanza.

1.19 Una struttura di risonanza “migliore” è quella che presenta un numero maggiore di legami ed un numero minore di cariche. La struttura “migliore” è il maggior contribuente, mentre le altre sono contribuenti minori. Per disegnare l’ibrido di risonanza, usare le regole della risposta 1.13.

1.20 Gli isomeri devono avere una diversa posizione degli atomi.

1.21

1.22 Usare la definizione di isomeri e di strutture di risonanza della risposta 1.14.

1.23 Usare la definizione di isomeri e di strutture di risonanza della risposta 1.14.

1.24 Confrontare le strutture di risonanza per vedere quali elettroni si sono “mossi”. **Usare una freccia curva per mostrare il movimento di ogni coppia elettronica**.

1.25 La notazione della freccia curva mostra il movimento di una coppia elettronica. La coda comincia presso una coppia elettronica (un legame o una coppia elettronica solitaria) e la testa punta nella direzione del movimento elettronico.

1.26 Usare le regole della risposta 1.17.

1.27 Per disegnare un ibrido di risonanza, usare le regole della risposta 1.18.

1.28 Per i composti per cui non è data la struttura, prima disegnare una struttura di Lewis. Successivamente usare le regole della risposta 1.17.

1.29 Per disegnare un ibrido di risonanza, usare le regole della risposta 1.18.

1.30 Una struttura di risonanza "migliore" è quella che presenta maggior numero di legami e minor numero di cariche. La migliore struttura rappresenta il contribuente maggiore e tutte le altre i contribuenti minori.

1.31 Seguire i passaggi della risposta 1.5 per disegnare le strutture di Lewis.

1.32 Tutte le rappresentazioni presentano un carbonio con due legami nel piani della pagina, uno verso l'osservatore (linea a cuneo) ed uno verso il retro della pagina (linea tratteggiata). Quattro possibilità:

1.33 Per predire la geometria attorno ad un atomo, **conta il numero dei gruppi (atomi + coppie solitarie),** facendo attenzione a disegnare ogni coppia solitaria necessaria o atomi di idrogeno: 2 gruppi = lineare, 3 gruppi = trigonale planare, 4 gruppi = tetraedrico.

1.34 Per predire l'angolo di legame attorno ad un atomo, **contare il numero dei gruppi (atomi + coppie solitarie),** facendo attenzione a disegnare ogni coppia solitaria necessaria o atomi di idrogeno: 2 gruppi = 180°, 3 gruppi = 120°, 4 gruppi = 109,5°.

1.35 Per predire la geometria attorno ad un atomo, usare le regole della risposta 1.33.

1.36 Usare le regole della risposta 1.34

1.37 Per predire la geometria attorno ad un atomo, usare le regole della risposta 1.33.

1.38 Ogni carbonio presenta due legami nel piano della pagina, uno davanti alla pagina (cuneo solido) ed uno dietro la pagina (linea tratteggiata).

1.39 Andando da destra a sinistra, disegna la molecola come una struttura di Lewis. Controlla sempre che il carbonio abbia quattro legami e tutti gli eteroatomi abbiano l'ottetto, aggiungendo se necessario le dovute coppie elettroniche libere.

1.40 Nelle strutture segmentate, tutte le giunzioni o estremità di ogni segmento rappresentano atomi di carbonio. I carboni sono tutti tetravalenti.

1.41 Nelle strutture segmentate, tutte le giunzioni o estremità di ogni segmento rappresentano atomi di carbonio. Convertire scrivendo tutti i carboni, e successivamente aggiungendo gli atomi di idrogeno per rendere i carboni tetravalenti.

1.42 Una carica presente su un atomo prende il posto di un atomo di idrogeno. Un C carico negativamente presenta una coppia libera, un C carico positivamente non ne ha.

1.43

1.44 Nelle strutture segmentate, tutte le giunzioni o termini di riga rappresentano atomi di carbonio. I carboni sono tutti tetravalenti.

1.45 Nelle strutture segmentate, tutte le giunzioni o termini di riga rappresentano atomi di carbonio. Convertire scrivendo tutti i carboni, e successivamente aggiungendo gli atomi di idrogeno per rendere i carboni tetravalenti.

1.46 Nelle strutture segmentate, non disegnare i carboni e gli idrogeni eccetto quelli legati ad eteroatomi.

1.47 Relativamente alle strutture di Lewis, tutti gli atomi compresi gli H e tutte le coppie solitarie devono essere disegnate.

1.48 Una carica su un atomo di C prende il posto di un atomo di H. Un C carico negativamente presenta una coppia libera, ed un carbonio carico positivamente non ne presenta nessuna.

1.49 Per determinare gli orbitali usati nei legami, contare il numero dei gruppi (atomi + coppie solitarie): 4 gruppi = sp^3, 3 gruppi = sp^2, 2 gruppi = *sp*, atomo di idrogeno =*1s* (nessuna ibridazione). Tutti i legami singoli covalenti sono σ, e tutti i doppi legami contengono un legame σ ed uno π.

1.50 [1] Disegnare una valida struttura di Lewis per ogni molecola.

[2] Contare il numero dei gruppi attorno ad ogni atomo: 4 gruppi = sp^3, 3 gruppi = sp^2, 2 gruppi = *sp*, atomo di idrogeno =*1s* (nessuna ibridazione).

Nota: **Be e B** (Gruppi 2A e 3A) non hanno sufficienti elettroni di valenza per formare un ottetto, **e non formano un ottetto in molecole neutre**.

1.51 Per determinare l'ibridazione attorno agli atomi indicati, usare le procedure della risposta 1.54.

1.52 Per determinare quali orbitali sono coinvolti nei legami, usare la procedura della risposta 1.49.

1.53 Per determinare quali orbitali sono coinvolti nei legami, usare la procedura della risposta 1.49.

1.54 Per determinare l'ibridazione, **contare il numero dei gruppi** attorno ad ogni atomo: 4 gruppi = sp^3, 3 gruppi = sp^2, 2 gruppi = sp, atomo di idrogeno =*1s* (nessuna ibridazione).

1.55 Tutti i legami singoli sono σ. I legami multipli contengono un legame σ, e tutti gli altri sono legami π.

1.56

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1.58 Lunghezza di legame e forza di legame sono inversamente proporzionali: **legami più lunghi sono legami più deboli.** I legami singoli sono più deboli e più lunghi di quelli doppi, che sono più deboli e più lunghi di quelli tripli.

1.59 Lunghezza di legame e forza di legame sono inversamente proporzionali: **legami più lunghi sono legami più deboli.** I legami singoli sono più deboli e più lunghi di quelli doppi, che sono più deboli e più lunghi di quelli tripli. L'aumento del carattere *s* aumenta la forza di legame e diminuisce la lunghezza.

1.60 Per determinare le lunghezze di legame relative, usare le regole della risposta 1.59.

1.61 Per determinare le lunghezze di legame relative, usare le regole della risposta 1.59.

1.62 La percentuale di carattere *s* determina la lunghezza di un legame. Maggiore la percentuale di carattere *s*, minore la lunghezza del legame. In relazione a questa domanda, determinare la percentuale di carattere *s* attraverso l'individuazione dell'ibridazione di ogni atomo coinvolto nel legame. *sp* = 50 % di carattere *s*, sp^2 = 33 % di carattere *s*; sp^3 = 25% di carattere *s.*

1.63 Usare la regola della percentuale del carattere *s* e della lunghezza di legame della risposta 1.66 e ricordare che legami più corti sono legami più forti. Un legame formato da due C ibridi sp^2 è più forte di un legame σ formato da due C ibridi sp^3 perchè i C ibridi sp^2 presentano un orbitale a maggior carattere s

1.64 La percentuale di carattere *s* determina la forza di un legame. Maggiore la percentuale di carattere *s* di un orbitale usato nella formazione di un legame, maggiore la forza del legame.

1.65 **L'elettronegatività aumenta lungo una riga della** tavola **periodica e diminuisce lungo una colonna.** Controllare la posizione relativa degli atomi per determinare la loro elettronegatività relativa**.**

1.66 **L'elettronegatività aumenta lungo una riga della** tavola **periodica e diminuisce lungo una colonna.** Controllare la posizione relativa degli atomi per determinare la loro elettronegatività relativa**.**

1.67 Le molecole polari si originano dalla presenza di un dipolo netto. Per determinare la polarità, disegnare la molecola in tre dimensioni attorno ad ogni legame polare, disegnare i dipoli, e cercare di vedere se i dipoli si sommano o si sottraggono.

Nota: bisogna disegnare la molecola tridimensionalmente per osservare il dipolo. Nella struttura di Lewis, sembra che i dipoli si sottraggano, quando in realtà si sommano e formano una molecola polare.

1.68 I dipoli si originano da una ripartizione disuguale degli elettroni nei legami covalenti. Gli atomi più elettronegativi attraggono la densità elettronica verso di loro, originando un dipolo. Le frecce del dipolo sono dirette dalla densità elettronica più bassa (δ^+) a quella più alta (δ^-).

1.69 Usare le indicazioni della risposta 1.67.

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1.76 I legami polari si originano da una non uguale ripartizione degli elettroni nei legami covalenti. Normalmente noi pensiamo che gli atomi più elettronegativi "attraggano" la densità elettronica verso di loro, originando un dipolo. Osservando un legame Csp^2–Csp^3 , l'atomo con una maggior percentuale di carattere s "attrarrà" maggiormente la densità elettronica verso di sé, originando un piccolo dipolo.

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1.79

Capitolo 2

2.1 Gli acidi di Brønsted–Lowry sono **donatori di protoni** e devono contenere una atomo di idrogeno. **Le basi di Brønsted–Lowry** sono **accettori di protoni** e devono avere una coppia di elettroni disponibile (sia una coppia solitaria che un legame π).

a. $H\ddot{\underset{..}{Br}}:$ **acid** — $\ddot{N}H_3$ **acid** — CCl_4 not an acid—no H

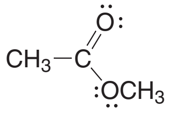
b. CH_3CH_3 no lone pairs or π bonds not a base — $(CH_3)_3C\ddot{\underset{..}{O}}:^-$ lone pairs on O **base** — $H{-}C{\equiv}C{-}H$ **base**—π bonds

c. $CH_3CH_2CH_2\ddot{\underset{..}{O}}H$

base—lone pairs on O
acid—contains H atoms

$CH_3CH_2CH_2CH_3$

not a base—no lone pairs or π bonds
acid—contains H atoms



base—lone pairs on O's, π bond
acid—contains H atoms

2.2 Per disegnare l'acido coniugato di una base di Brønsted–Lowry, **addizionare un protone alla base**.

a. $H_2\ddot{O}: \xrightarrow{H^+} H_3\ddot{O}^+$

b. $^-:\ddot{N}H_2 \xrightarrow{H^+} \ddot{N}H_3$

c. $HCO_3^- \xrightarrow{H^+} H_2CO_3$

d. $CH_3CH_2\ddot{N}HCH_3 \xrightarrow{H^+} CH_3CH_2\overset{+}{N}H_2CH_3$

e. $CH_3\ddot{\underset{..}{O}}CH_3 \xrightarrow{H^+} CH_3{-}\overset{H}{\underset{..}{\overset{|+}{O}}}{-}CH_3$

f. $CH_3COO^- \xrightarrow{H^+} CH_3COOH$

2.3 Per disegnare la base coniugata di un acido di Brønsted–Lowry, **rimuovere un protone dall'acido**.

a. $HCN \xrightarrow{-H^+} {}^-CN$

b. $HCO_3^- \xrightarrow{-H^+} CO_3^{2-}$

c. $(CH_3)_2\overset{+}{N}H_2 \xrightarrow{-H^+} (CH_3)_2NH$

d. $HC{\equiv}CH \xrightarrow{-H^+} HC{\equiv}C^-$

e. $CH_3CH_2COOH \xrightarrow{-H^+} CH_3CH_2COO^-$

f. $CH_3SO_3H \xrightarrow{-H^+} CH_3SO_3^-$

2.4 Una base di Brønsted–Lowry accetta un protone per formare l'acido coniugato. Un acido di Brønsted–Lowry perde un protone per formare la base coniugata.

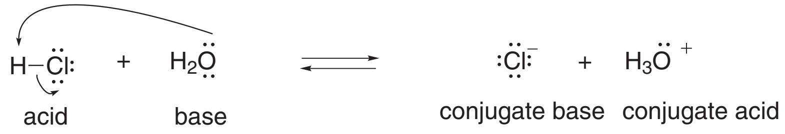
a. $NH_3 \longrightarrow NH_4^+$
$Cl^- \longrightarrow HCl$
$(CH_3)_2C{=}O \longrightarrow (CH_3)_2C{=}\underset{..}{\overset{+}{O}}H$

b. $HBr \longrightarrow Br^-$
$HSO_4^- \longrightarrow SO_4^{2-}$
$CH_3OH \longrightarrow CH_3O^-$

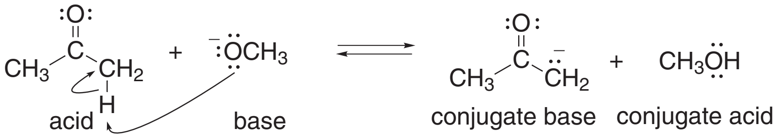
2.5 Usare le definizioni della risposta 2.2.

2.6 La base di Brønsted–Lowry accetta un protone per formare l'acido coniugato. L'acido di Brønsted–Lowry perde un protone per formare la base coniugata. Usare le frecce curve per mostrare il movimento di elettroni (***NON di protoni***). Se necessario ridisegnare il materiale di partenza per chiarire il movimento degli elettroni.

a.



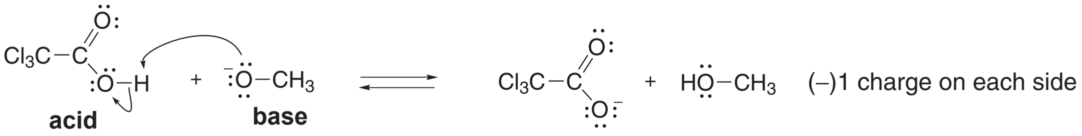
b.



2.7 Per disegnare i prodotti:

[1] Individuare l'acido e la base.
[2] Trasferire un protone dall'acido alla base.
[3] Controllare che le cariche su ogni lato delle frecce siano bilanciate.

a.



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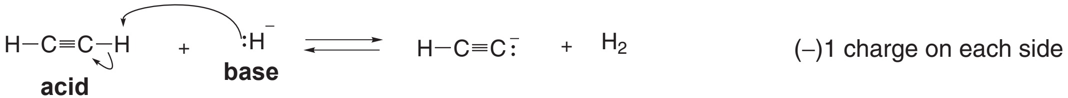

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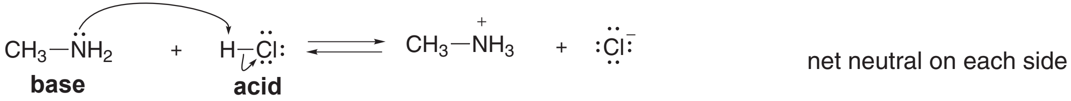

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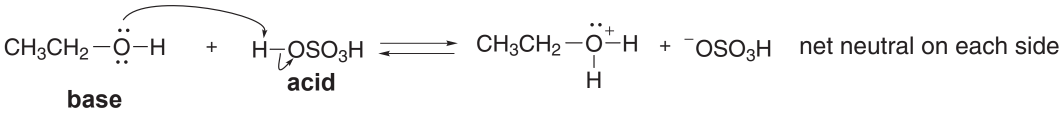
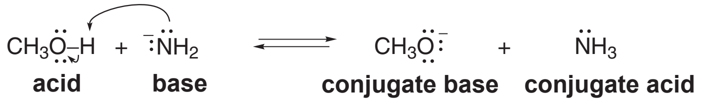


2.8 Individuare l'acido di Brønsted–Lowry e la base di Brønsted–Lowry nei composti di partenza e **trasferire un protone dall'acido alla base** per i prodotti.

a.


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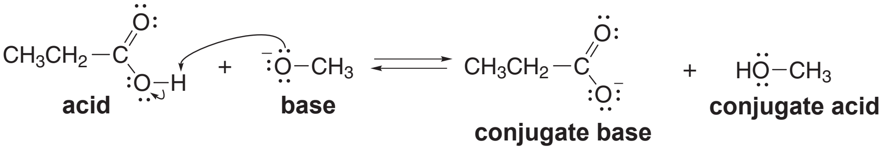

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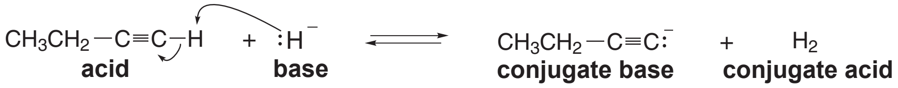

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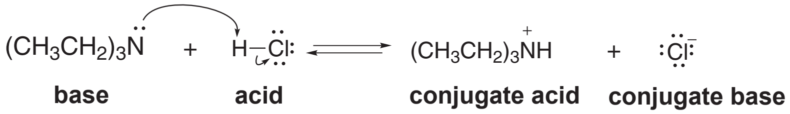
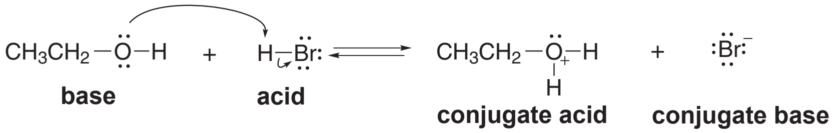
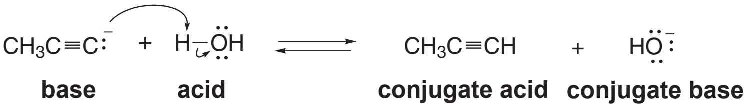
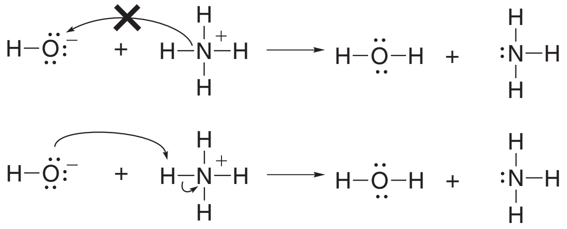


e.


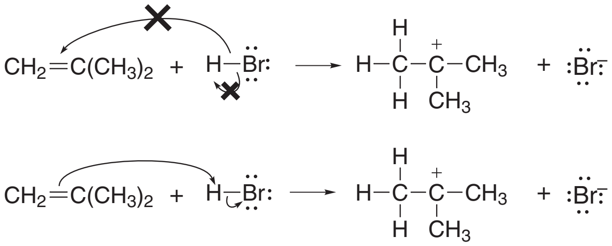
f.


2.9 Le frecce curve mostrano il movimento degli elettroni, **dalla coppia di elettroni**.

Incorrect. Arrow must flow from attacking electron pair on O to the proton.

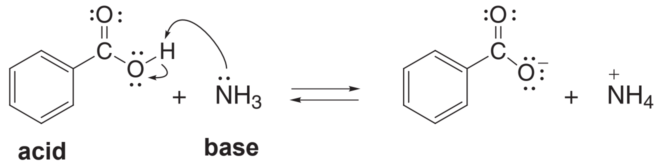
a.


Incorrect. Arrow must flow from the double bond to the proton it attacks.

b.


2.10 Individuare l'acido e la base nei composti di partenza e quindi disegnare i prodotti di trasferimento del protone dall'acido alla base.

a.



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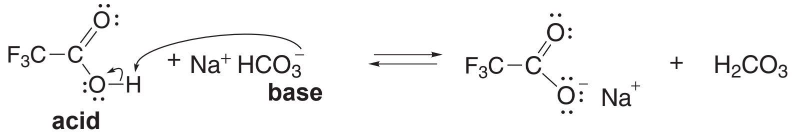

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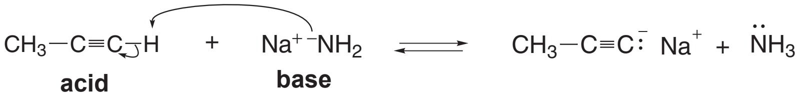

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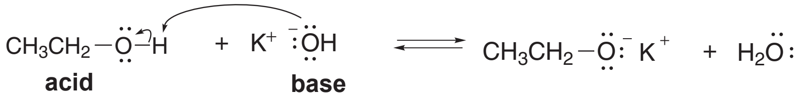
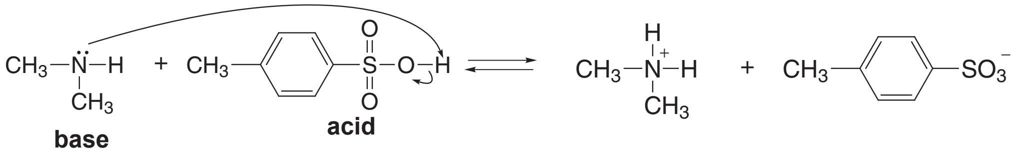
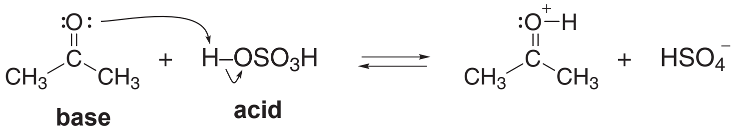


e.



f.



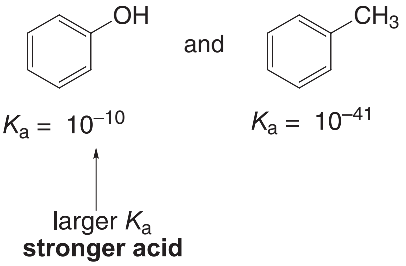
2.11 Più piccolo è il valore di pK_a, più forte è l'acido. Più grande è il K_a, più forte è l'acido.

a. $CH_3CH_2CH_3$ and CH_3CH_2OH

$pK_a = 50$ $pK_a = 16$

smaller pK_a **stronger acid**

b.



2.12 Per convertire K_a a pK_a, considerare il (–) log della K_a. **pK_a = -logK_a**
Per convertire pK_a a K_a, considerare l'antilog di (–) pK_a.

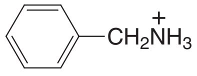
a. $K_a = 10^{-10} \rightarrow pK_a = 10$ $K_a = 10^{-21} \rightarrow pK_a = 21$ $K_a = 5.2 \times 10^{-5} \rightarrow pK_a = 4.3$

b. $pK_a = 7 \rightarrow K_a = 10^{-7}$ $pK_a = 11 \rightarrow K_a = 10^{-11}$ $pK_a = 3.2 \rightarrow K_a = 6.3 \text{ X } 10^{-4}$

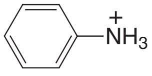
2.13 Per convertire pK_a in K_a, considerare l'antilog di (–) il pK_a.

a. H_2S	b. $ClCH_2COOH$	c. HCN
$pK_a = 7.0$	$pK_a = 2.8$	$pK_a = 9.1$
$K_a = 10^{-7}$	$K_a = 1.6 \times 10^{-3}$	$K_a = 7.9 \times 10^{-10}$

2.14 Per convertire da K_a in pK_a, considerare il (–) log di K_a. **pK_a = -logK_a**

a. 

$K_a = 4.7 \times 10^{-10}$
$pK_a = 9.33$

b. 

$K_a = 2.3 \times 10^{-5}$
$pK_a = 4.64$

c. CF_3COOH
$K_a = 5.9 \times 10^{-1}$
$pK_a = 0.23$

2.15 Un acido può essere deprotonato dalla base coniugata di ogni acido con un maggiore pK_a.

a. **H_2O**
$pK_a = 15.7$
Any base with a conjugate acid having a pK_a higher than 15.7 can deprotonate it.

Acid	**pK_a**	**Conjugate base**
CH_3CH_2OH	16	$CH_3CH_2O^-$
$HC\equiv CH$	25	$HC\equiv C^-$
H_2	35	H^-
NH_3	38	$^-NH_2$
$CH_2{=}CH_2$	44	$CH_2{=}CH^-$
CH_4	50	CH_3^-

Strong enough to deprotonate H_2O.

c. **CH_4**
$pK_a = 50$
There is no base with a conjugate acid having a pK_a higher than 50 in the table.

b. **NH_3**
$pK_a = 38$
Any base with a conjugate acid having a pK_a higher than 38 can deprotonate it.

Acid	**pK_a**	**Conjugate base**
$CH_2{=}CH_2$	44	$CH_2{=}CH^-$
CH_4	50	CH_3^-

Strong enough to deprotonate NH_3.

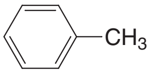
2.16 ^-OH può deprotonare ogni acido con un pK_a < 15.7.

a. HCOOH

$pK_a = 3.8$
stronger acid
deprotonated

b. H_2S

$pK_a = 7.0$
stronger acid
deprotonated

c. 

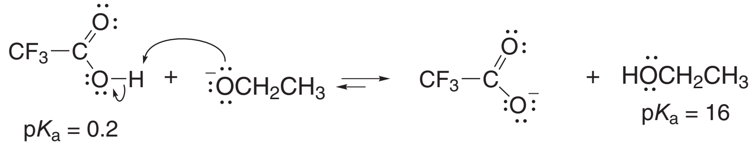
$pK_a = 41$
weaker acid

d. CH_3NH_2

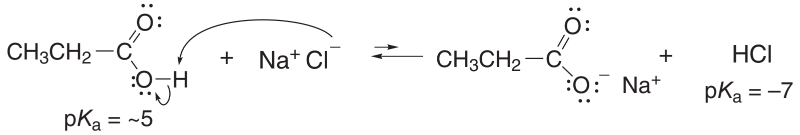
$pK_a = 40$
weaker acid

These acids are too weak to be deprotonated by ^-OH.

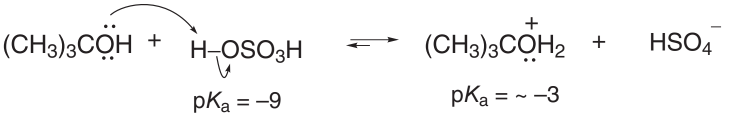
2.17 Disegnare i prodotti e quindi confrontare il pK_a dell'acido a sinistra, e l'acido coniugato a destra. **L'equilibrio è spostato verso la parte che ha l'acido con il maggiore pK_a (acido più debole).**

a. 

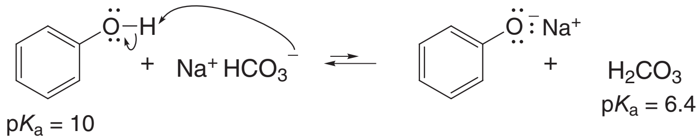
products favored

b. 

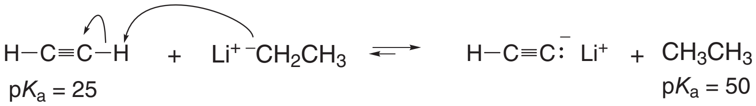
starting material favored

c. 

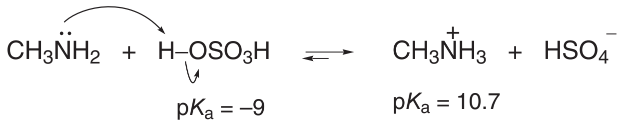
products favored

d.


starting material favored

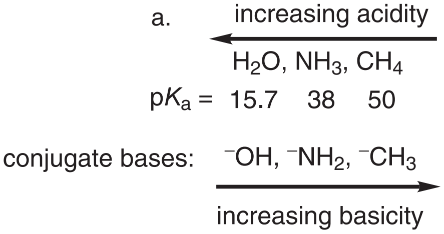
e.


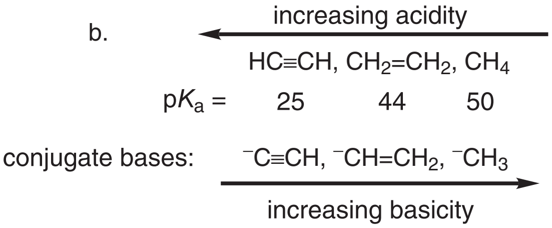
products favored

f.


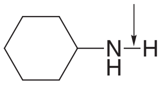
products favored

2.18 Poiché **acidi forti formano basi coniugate deboli**, la basicità delle basi coniugate aumenta all'aumentare del pK_a dei loro acidi. Trovare il pK_a di ogni acido in Tabella 2.1 e quindi ordinare gli acidi in ordine di pK_a crescente. Questo sarà anche l'ordine di basicità crescente delle loro basi coniugate.

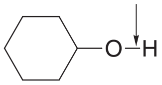
a.


b.


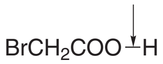
2.19 Per valutare il pK_a dei legami indicati, individuare un legame simile nella Tabella dei valori di pK_a (H legati allo stesso atomo con la stessa ibridazione).

a.


For NH_3, pK_a is 38.
estimated pK_a = 38

b.


For CH_3CH_2OH,
pK_a is 16.
estimated pK_a = 16

c.


For CH_3COOH, pK_a is 4.8.
estimated pK_a = 5

2.20 Individuare l'acido e la base e quindi trasferire un protone dall'acido alla base. Per determinare se la reazione procede come scritto, confrontare il pK_a dell'acido a sinistra con l'acido coniugato a destra. **L'equilibrio favorisce sempre la formazione dell'acido più debole e della base più debole.**

a.

$$H{-}C{\equiv}C{-}H \;+\; H\!:^{-} \;\rightleftharpoons\; H{-}C{\equiv}C\!:^{-} \;+\; H_2$$

$H{-}C{\equiv}C{-}H$	$H:^-$	$H{-}C{\equiv}C:^-$	H_2
acid	base	conjugate base	conjugate acid
$pK_a = 25$			$pK_a = 35$
			weaker acid

Equilibrium favors the **products.**

b.

$$CH_4 \;+\; {}^{-}\!:\!\ddot{O}H \;\rightleftharpoons\; {}^{-}\!:\!CH_3 \;+\; H_2\ddot{O}\!:$$

CH_4	$^-:\ddot{O}H$	$^-:CH_3$	$H_2\ddot{O}:$
acid	base	conjugate base	conjugate acid
$pK_a = 50$			$pK_a = 15.7$
weaker acid			

Equilibrium favors the **starting materials.**

c.

$$CH_3COOH \;+\; CH_3CH_2\ddot{O}\!:^{-} \;\rightleftharpoons\; CH_3COO^{-} \;+\; CH_3CH_2\ddot{O}H$$

CH_3COOH	$CH_3CH_2\ddot{O}:^-$	CH_3COO^-	$CH_3CH_2\ddot{O}H$
acid	base	conjugate base	conjugate acid
$pK_a = 4.8$			$pK_a = 16$
			weaker acid

Equilibrium favors the **products.**

d.

$$:\!\ddot{Cl}\!:^{-} \;+\; CH_3CH_2\ddot{O}H \;\rightleftharpoons\; H\ddot{Cl}\!: \;+\; CH_3CH_2\ddot{O}\!:^{-}$$

$:\ddot{Cl}:^-$	$CH_3CH_2\ddot{O}H$	$H\ddot{Cl}:$	$CH_3CH_2\ddot{O}:^-$
base	acid	conjugate acid	conjugate base
	$pK_a = 16$	$pK_a = -7$	
	weaker acid		

Equilibrium favors the **starting materials.**

2.21 Un acido può essere deprotonato dalla base coniugata di ogni acido con un pK_a maggiore.

CH_3COOH

pK_a = 4.8

Any base having a conjugate acid with a pK_a higher than 4.8 can deprotonate this acid.

Acid	**pK_a**	**Conjugate base**	
HCl	–7	Cl^-	not strong enough
HC≡CH	25	$HC{\equiv}C^-$	strong enough
H_2	35	H^-	strong enough

HC≡CH

pK_a = 25

All of these acids have a higher pK_a than HC≡CH, and a conjugate base that can deprotonate HC≡CH.

Acid	**pK_a**	**Conjugate base**
H_2	35	H^-
NH_3	38	$^-NH_2$
$CH_2{=}CH_2$	44	$CH_2{=}CH^-$
CH_4	50	CH_3^-

2.22 L'acidità di H–Z **aumenta attraverso una riga e scendendo lungo una colonna** nella tavola periodica.

a. NH_3, H_2O

O is further to the right in the periodic table.
stronger acid

b. HBr, HCl

Br is further down the periodic table.
stronger acid

c. H_2S, HBr

Br is further across and down the periodic table.
stronger acid

2.23 Considerare l'elemento legato all'H acido e stabilire la sua acidità in base agli andamenti nella tavola periodica. **Sono più acidi quelli su elementi più a destra e più in basso nella tavola periodica.**

a. $CH_3CH_2CH_2CH_2O\mathbf{H}$ ← most acidic
Molecule contains C–H and O–H bonds.
O is further right; therefore, O–H hydrogen is the most acidic.

b. $\mathbf{H}OCH_2CH_2CH_2NH_2$ ← most acidic
Molecule contains C–H, N–H and O–H bonds.
O is furthest right; therefore, O–H hydrogen is the most acidic.

c. $(CH_3)_2NCH_2CH_2CH_2N\mathbf{H_2}$ ← most acidic
Molecule contains C–H and N–H bonds.
N is further right; therefore, N–H hydrogen is the most acidic.

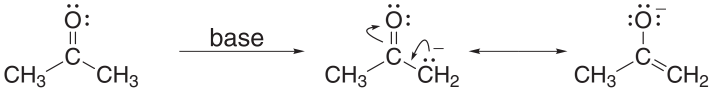
2.24 Gruppi più elettronegativi stabilizzano la base coniugata, rendendo l'acido più forte. Confrontare i gruppi elettron attrattori negli acidi seguenti per decidere quale è l'acido più forte. (**gruppi più elettronegativi = più acido).**

a. $ClCH_2COOH$ and FCH_2COOH more acidic
F is more electronegative than Cl making the O–H bond in the acid on the right **more acidic.**

b. Cl_2CHCH_2OH and $Cl_2CHCH_2CH_2OH$
Cl is closer to the acidic O–H bond. **more acidic**
Cl is further from the O–H bond.

c. CH_3COOH and O_2NCH_2COOH more acidic
NO_2 is electron withdrawing making the O–H bond in the acid on the right **more acidic.**

2.25 L'acidità di un acido aumenta quando la base coniugata è stabilizzata per risonanza. Confrontare le basi coniugate dell'acetone e del propano per spiegare perché l'acetone è più acido.



acetone
pK_a = 19.2

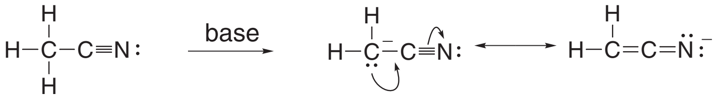
2 resonance structures
more stable conjugate base
Acetone is more acidic.

$CH_3CH_2CH_3 \xrightarrow{\text{base}} CH_3CH_2\overset{-}{\ddot{C}}H_2$ only one Lewis structure
less stable conjugate base

propane
pK_a = 50

(Any C–H bond in the starting material can be removed.)

2.26 L'acidità di un acido aumenta quando la base coniugata è stabilizzata per risonanza. L'acetonitrile ha una base coniugata stabilizzata per risonanza, che spiega la sua acidità.

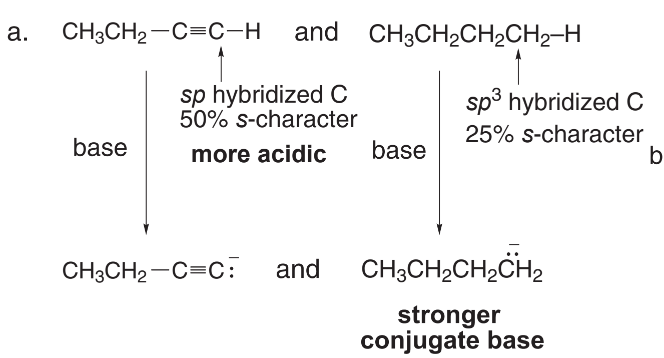


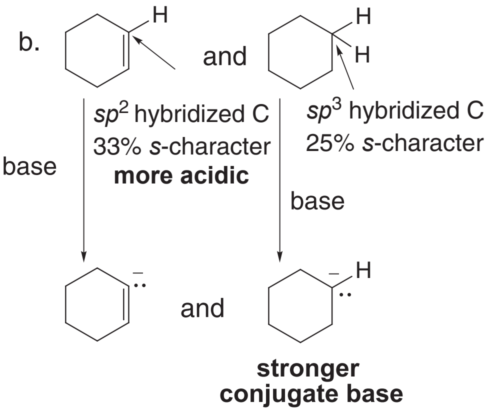
acetonitrile
(one Lewis structure)

The negative charge is stabilized by delocalization on the C and N atoms.

2 resonance structures for the conjugate base

2.27 L'aumento della percentuale di carattere *s* rende un acido più acido. Paragonare la percentuale di carattere *s* degli atomi di carbonio in ciascuno dei legami C–H in questione. Un acido più forte ha una base coniugata più debole.





2.28 Per confrontare gli acidi, prima **considerare gli effetti dell'elemento**. Quindi identificare i gruppi elettron attrattori, la risonanza o le differenze di ibridazione.

a. $CH_3CH_2CH_3$ — C is furthest left in the periodic table. **CH bond is least acidic.**

$CH_3CH_2NH_2$ — **intermediate acidity**

CH_3CH_2OH — O is furthest right in the periodic table. **OH bond is most acidic.**

c. $(CH_3)_3N$ — C is furthest left in the periodic table. **CH bond is least acidic.**

$CH_3CH_2NH_2$ — **intermediate acidity**

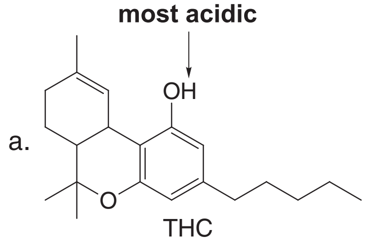
CH_3CH_2OH — O is furthest right in the periodic table. **OH bond is most acidic.**

b. $CH_3CH_2CH_2OH$ — OH group **least acidic**

CH_3CH_2COOH — **intermediate acidity**

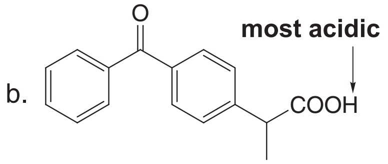
$BrCH_2COOH$ — Br is electron withdrawing and the conjugate base is resonance-stabilized. **most acidic**

2.29 Guardare l'elemento legato all'H acido e stabilire la sua acidità in base agli andamenti nella tavola periodica. **Sono più acidi quelli su elementi più a destra e più in basso nella tavola periodica.**



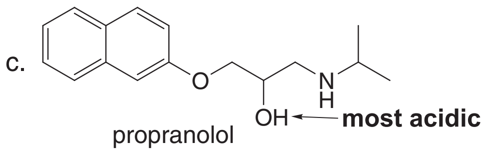
THC
tetrahydrocannabinol

The molecule contains C–H and O–H bonds.
O is further right; therefore,
O–H hydrogen is the most acidic.



ketoprofen

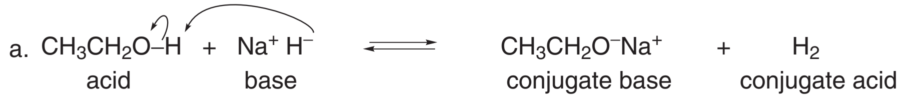
The molecule contains C–H and O–H bonds.
O is further right; therefore,
O–H hydrogen is the most acidic.

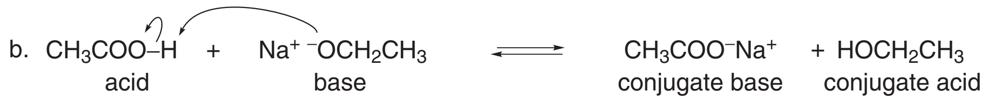


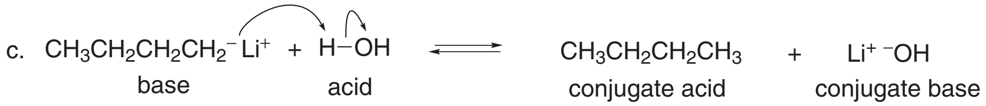
propranolol

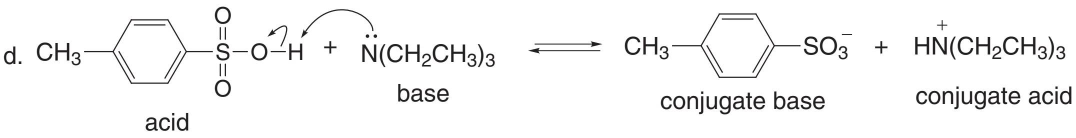
The molecule contains C–H, N–H and O–H bonds.
O is furthest right; therefore,
O–H hydrogen is the most acidic.

2.30 Individuare l'acido e la base nei reagenti e quindi disegnare i prodotti di trasferimento di protoni dall'acido alla base.









2.31 Confrontare prima gli effetti dell'elemento e quindi la risonanza, l'ibridazione e i gruppi elettron attrattori per determinare la forza relativa degli acidi.

a. Acidity increases across a row:
$NH_3 < H_2O < HF$

b. Acidity increases down a column:
$HF < HCl < HBr$

c. increasing acidity: $^-OH < H_2O < H_3O^+$

d. increasing acidity: $NH_3 < H_2O < H_2S$

Compare NH and OH bonds first:
acidity increases across a row.
OH is more acidic.

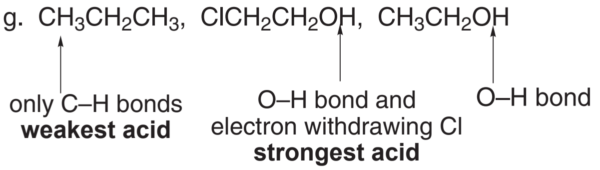
Then compare OH and SH bonds:
acidity increases down a column.
SH is more acidic.

e. Acidity increases across a row:
$CH_3CH_3 < CH_3NH_2 < CH_3OH$

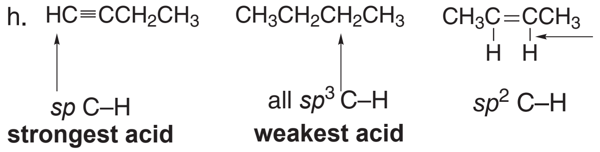
f. increasing acidity: $H_2O < H_2S < HCl$

Compare HCl and SH bonds first:
acidity increases across a row.
H–Cl is more acidic.

Compare OH and SH bonds:
acidity increases down a column.
SH is more acidic.



increasing acidity: $CH_3CH_2CH_3 < CH_3CH_2OH < ClCH_2CH_2OH$



increasing acidity: $CH_3CH_2CH_2CH_3 < CH_3CH{=}CHCH_3 < HC{\equiv}CCH_2CH_3$

2.32 L'acido più forte ha la base coniugata più debole.

a. Draw the conjugate acid.

Increasing acidity of conjugate acids:

$CH_3CH_3 < CH_3NH_2 < CH_3OH$

increasing basicity: $CH_3O^- < CH_3\overset{-}{N}H < CH_3\overset{-}{C}H_2$

b. Draw the conjugate acid.

Increasing acidity of conjugate acids:

$CH_4 < H_2O < HBr$

increasing basicity: $Br^- < HO^- < {}^-CH_3$

c. Draw the conjugate acid.

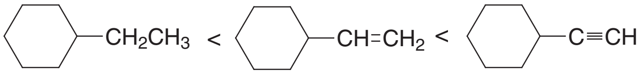
Increasing acidity of conjugate acids:

$CH_3CH_2OH < CH_3COOH < ClCH_2COOH$

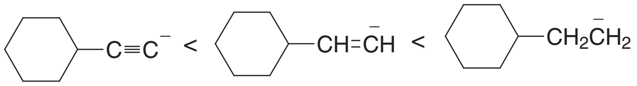
increasing basicity: $ClCH_2COO^- < CH_3COO^- < CH_3CH_2O^-$

d. Draw the conjugate acid.

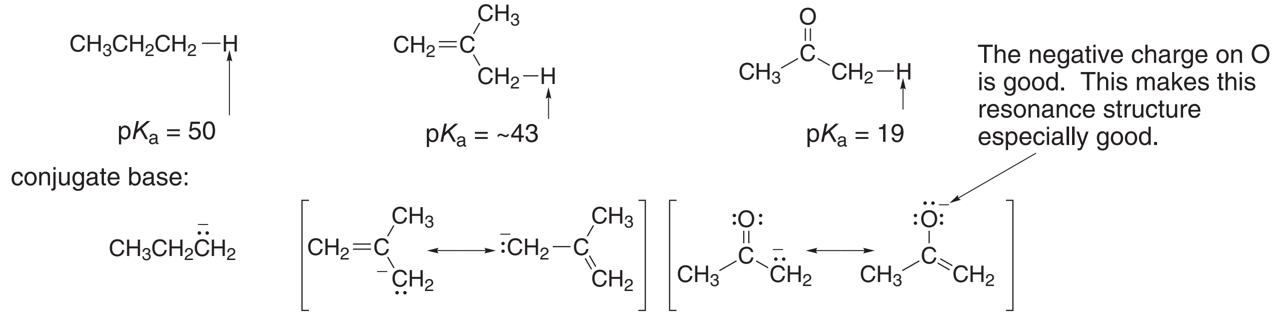
Increasing acidity of conjugate acids:



increasing basicity:



2.33



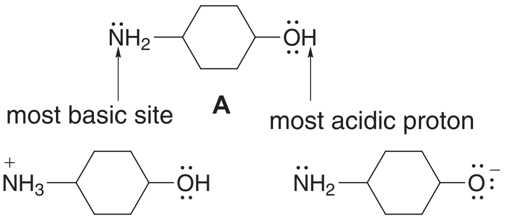
The negative charge on O is good. This makes this resonance structure especially good.

one resonance structure
weakest acid

two resonance structures
negative charge delocalized
on two carbons

two resonance structures
negative charge delocalized
on one O and one C
strongest acid

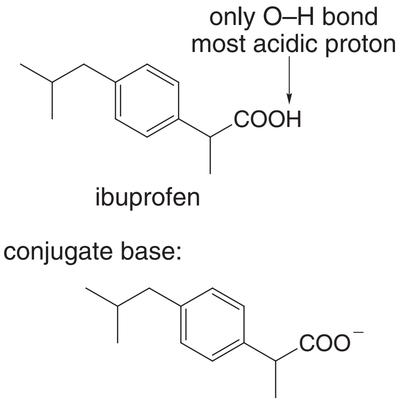
2.34 Per disegnare l'acido coniugato, individuare il punto più basico e protonarlo. Per disegnare la base coniugata, individuare il punto più acido e rimuovere un protone.

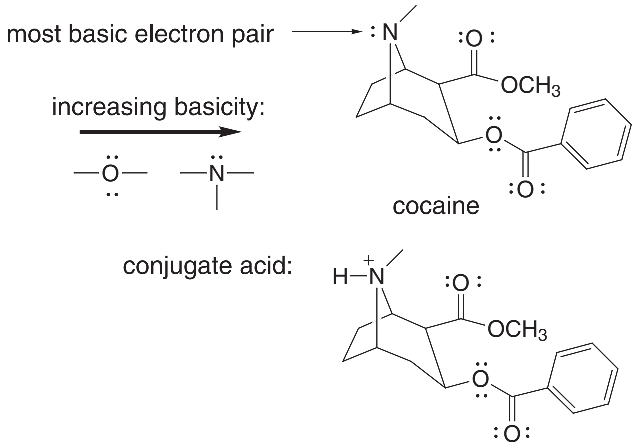


conjugate acid

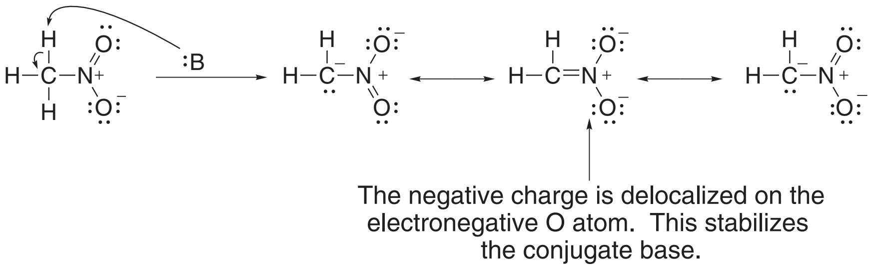
conjugate base

2.35 Rimuovere il protone più acido per formare la base coniugata. Protonare la coppia elettronica più basica per formare l'acido coniugato.

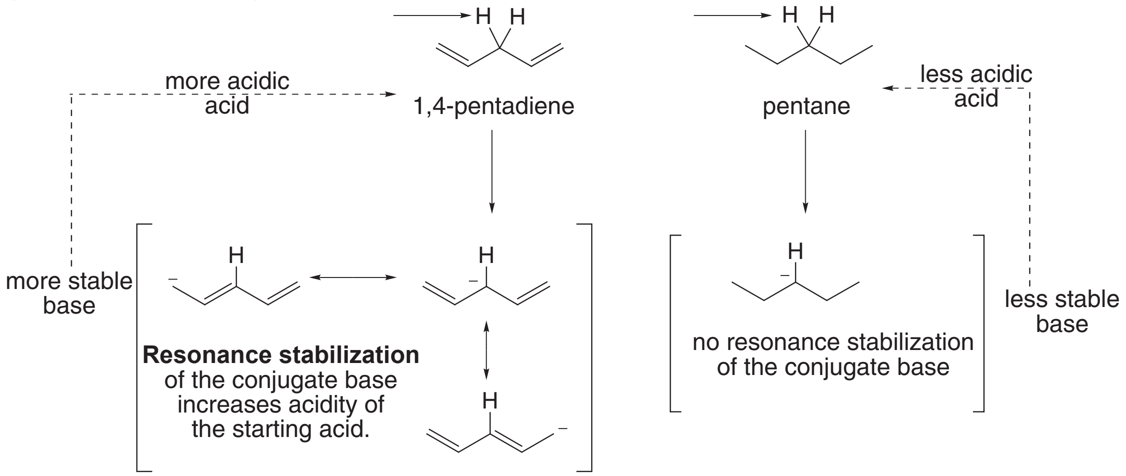




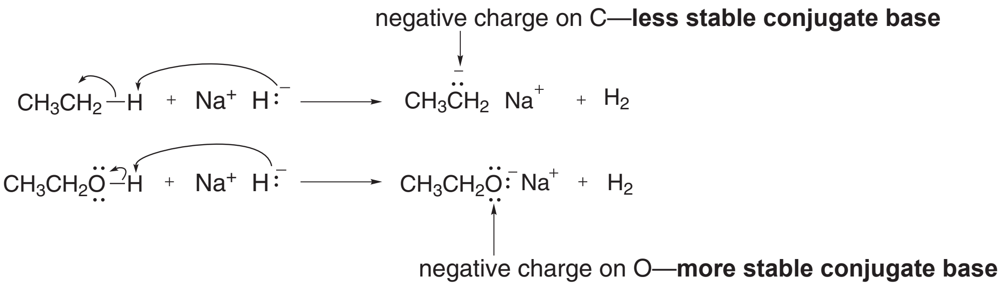
2.36 Un basso valore di pK_a significa acido più forte. Il pK_a è basso per il legame C–H in CH_3NO_2 a causa della stabilizzazione per risonanza della base coniugata.



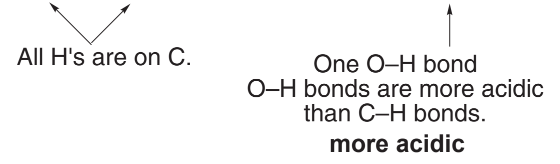
2.37 Disegnare le basi coniugate e confrontarle.



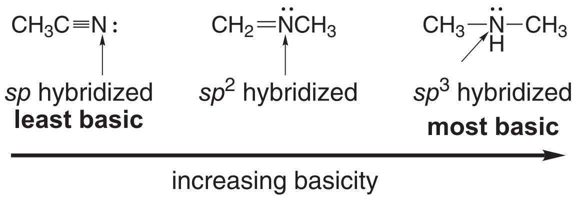
2.38 Confrontare CH_3CH_2OH e CH_3CH_3. La reazione di NaH avverrà più facilmente con un acido più forte. CH_3CH_2OH ha un legame O–H più acido, mentre CH_3CH_3 ha solo legami C–H. Quindi, questa reazione avverrà più velocemente rispetto alla reazione con CH_3CH_3.



2.39 Confrontare gli isomeri.



2.40 Ricordare che per un atomo A passando da ibridazione *sp* a *sp*^{2} e *sp*^{3}, H–A diventa meno acido e A:$^-$ diventa più basico.



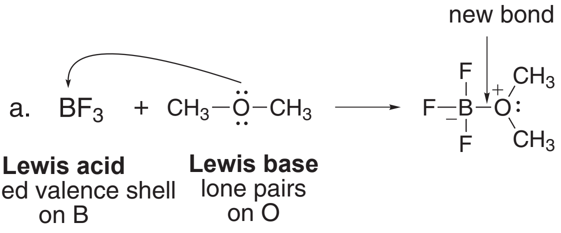
2.41 Le basi di Lewis sono donatori di una coppia di elettroni: esse contengono una coppia solitaria o un legame π.

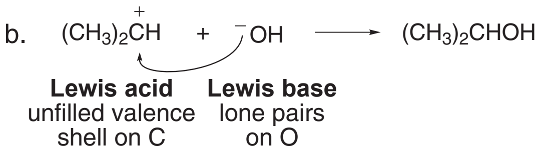
a. $\ddot{N}H_3$	b. $CH_3CH_2CH_3$	c. $H\colon^-$	d. H−C≡C−H
yes - has lone pair	**no** - no lone pair or π bond	**yes** - has lone pair	**yes** - has 2 π bonds

2.42 **Gli acidi di Lewis sono accettori di una coppia di elettroni.** La maggior parte di acidi di Lewis contiene un protone o un livello di valenza non completo di elettroni.

a. BBr_3	b. CH_3CH_2OH	c. $(CH_3)_3C^+$	d. Br^-
yes unfilled valence shell on B	**yes** contains a proton	**yes** unfilled valence shell on C	**no** no proton no unfilled valence shell

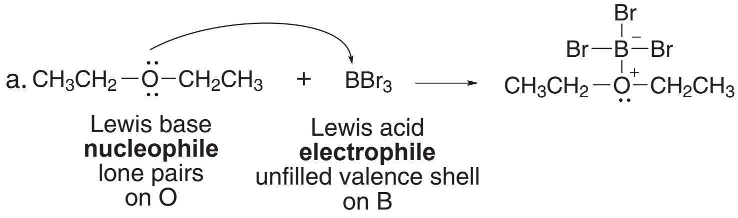
2.43 Individuare l'acido di Lewis e la base di Lewis, e disegnare le frecce curve.

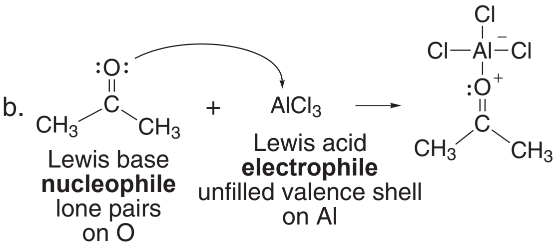




2.44

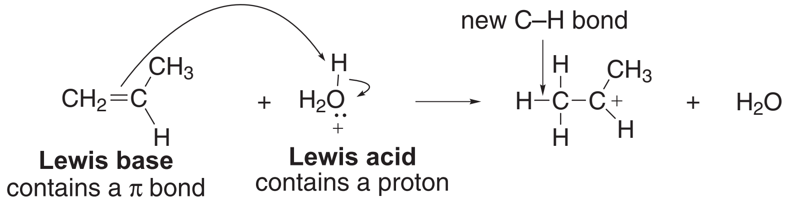
Un acido di Lewis è chiamato anche un **elettrofilo**. Quando una base di Lewis reagisce con un elettrofilo diverso da un protone, è chiamata anche un **nucleofilo**. Individuare l'elettrofilo e il nucleofilo nei reagenti, e quindi disegnare i prodotti.



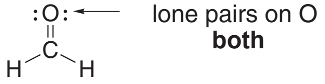


2.45

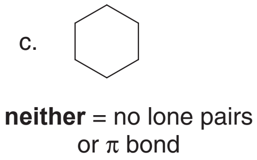
Le frecce curve iniziano dalla base di Lewis e sono dirette verso l'acido di Lewis.

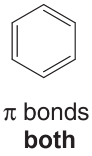


2.46 ***Le basi di Lewis* sono donatori di una coppia di elettroni**: contengono una coppia solitaria o un legame π. ***Le basi di Brønsted–Lowry* sono accettori di protoni**: per accettare un protone hanno bisogno di una coppia solitaria o di un legame π. Questo significa che tutte le basi di Lewis sono basi di Brønsted–Lowry.

a.


b.

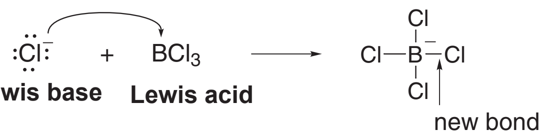

c.


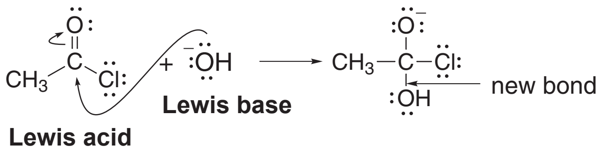
d.


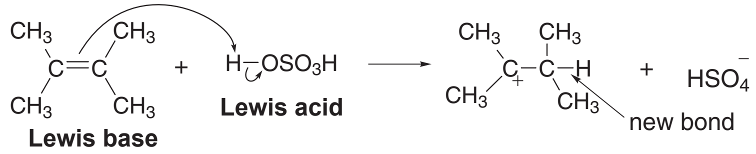
2.47 Un ***acido di Lewis* è un accettore di una coppia di elettroni** e generalmente contiene un protone o un livello di valenza non completo di elettroni. Un ***acido di Brønsted–Lowry* è un donatore di protoni** e deve contenere un atomo di idrogeno. Tutti gli acidi di Brønsted–Lowry sono acidi di Lewis, ma il contrario non è sempre vero.

a. H_3O^+	b. Cl_3C^+	c. BCl_3	d. BF_4^-
both - contains a H	**Lewis acid** - unfilled valence shell on C	**Lewis acid** - unfilled valence shell on B	**neither** - no H or unfilled valence shell

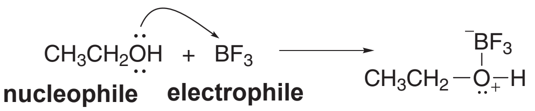
2.48 Individuare l'acido di Lewis e la base di Lewis, e quindi disegnare i prodotti.

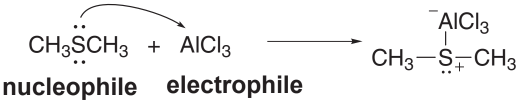
a.


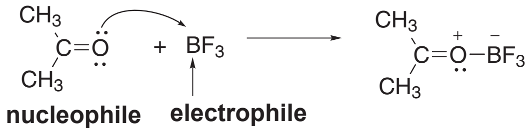
c.


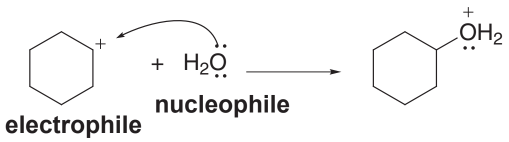
b.


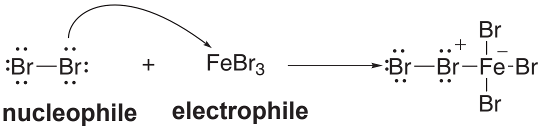
2.49 Un acido di Lewis è chiamato anche un **elettrofilo**. Quando una base di Lewis reagisce con un elettrofilo diverso da un protone, è chiamata anche un **nucleofilo**. Individuare l'elettrofilo e il nucleofilo nei composti di partenza, e quindi disegnare i prodotti.

a.


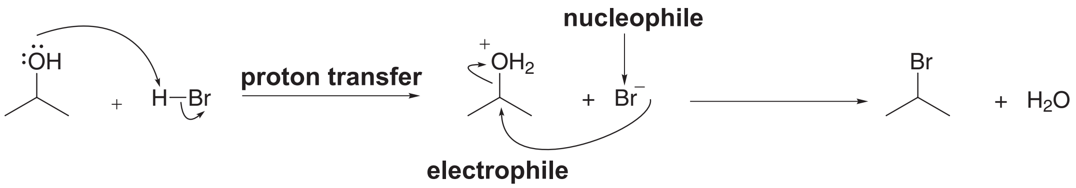
b.


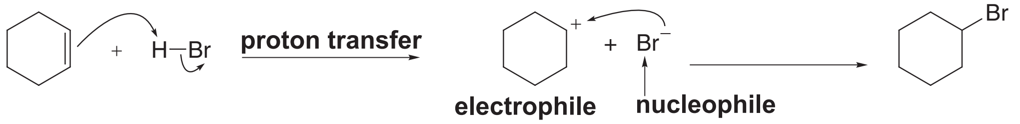
c.


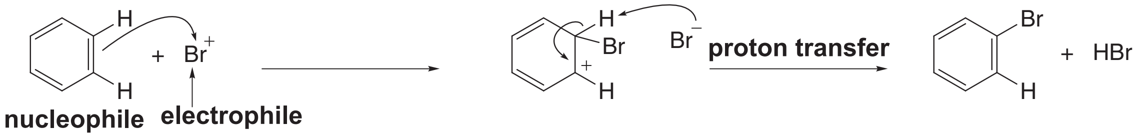
d.


e.


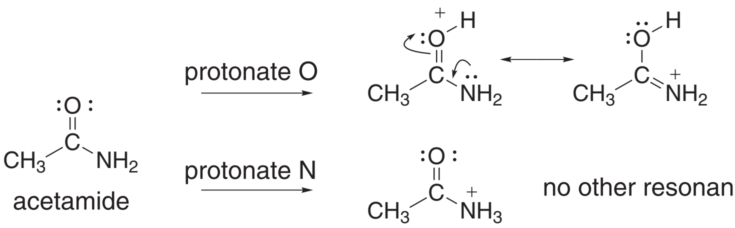
2.50

a.


b.


c.


2.51 Disegnare i prodotti di protonazione sia di O che di N e confrontare gli acidi coniugati.

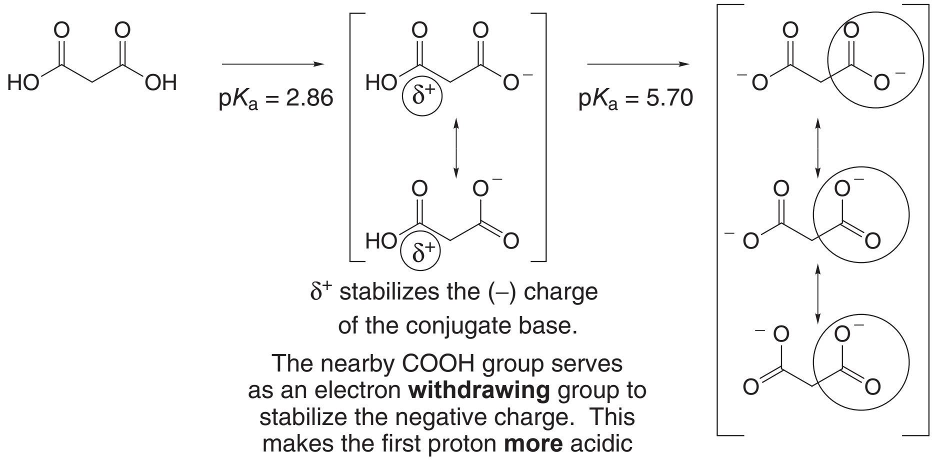


resonance stabilization of the + charge
O is more readily protonated
because the product is
resonance-stabilized.

no other resonance structure

When acetamide reacts with an acid, the O atom is protonated because it results in a resonance-stabilized conjugate acid.

2.52



This group destabilizes the second negative charge.

δ⁺ stabilizes the (–) charge of the conjugate base.

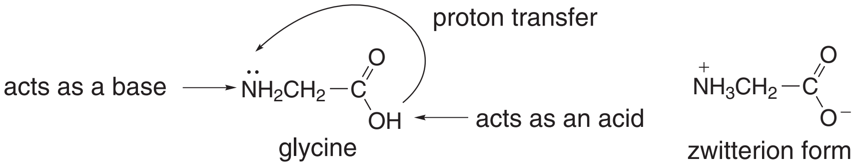
The nearby COOH group serves as an electron **withdrawing** group to stabilize the negative charge. This makes the first proton **more** acidic than CH_3COOH.

COO^- now acts as an electron **donor** group which destabilizes the conjugate base, making removal of the second proton more difficult and **less** acidic than CH_3COOH.

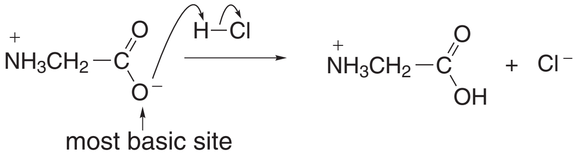
2.53

The COOH group of glycine gives up a proton to the basic NH_2 group to form the zwitterion.

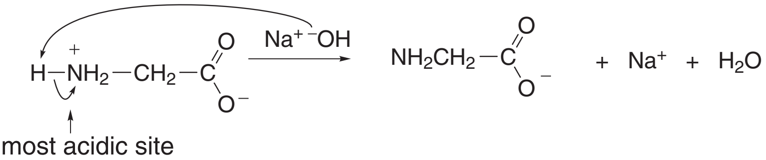
a.



b.

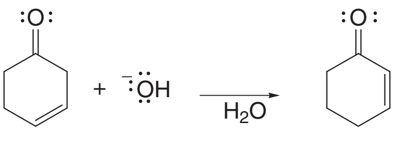


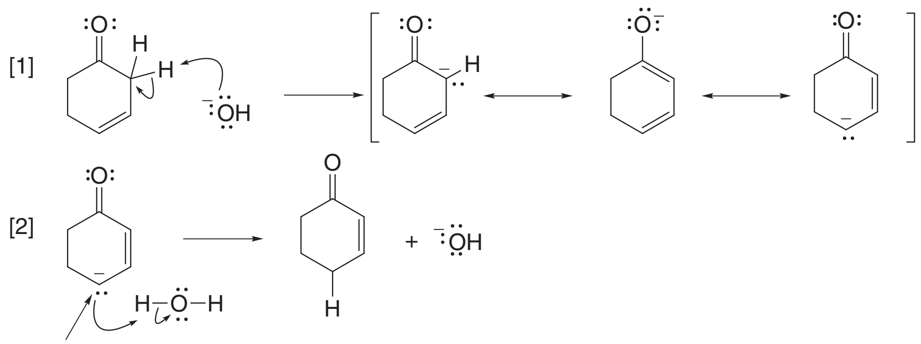
c.



2.54 Usare le frecce curve per mostrare come avviene la reazione.

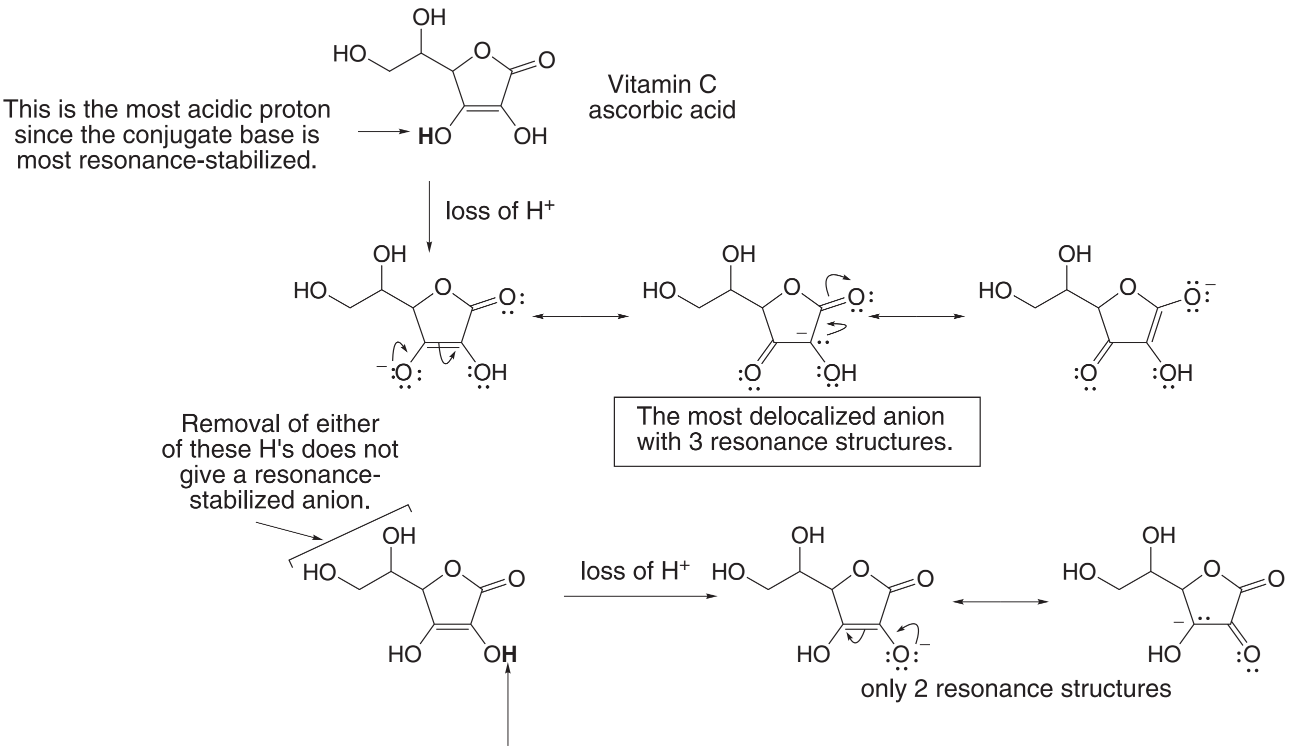
Overall reaction:





Protonate the negative charge on this carbon to form the product.

2.55 Confrontare i legami OH nella Vitamina C e decidere quale è il più acido.



This is the most acidic proton since the conjugate base is most resonance-stabilized.

The most delocalized anion with 3 resonance structures.

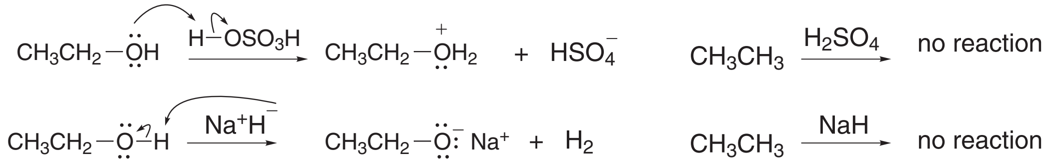
Removal of either of these H's does not give a resonance-stabilized anion.

only 2 resonance structures

This proton is less acidic since its conjugate base is less resonance-stabilized.

Capitolo 3

3.1

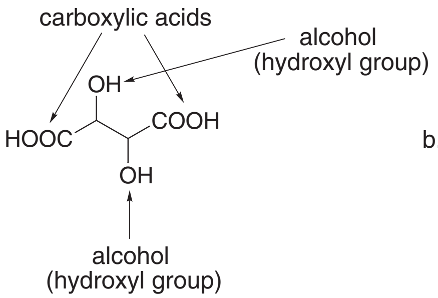


$$CH_3CH_2-\ddot{\underset{\cdot\cdot}{O}}H \xrightarrow{H-OSO_3H} CH_3CH_2-\overset{+}{\underset{\cdot\cdot}{O}}H_2 + HSO_4^- \qquad CH_3CH_3 \xrightarrow{H_2SO_4} \text{no reaction}$$

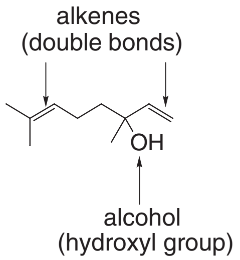
$$CH_3CH_2-\ddot{\underset{\cdot\cdot}{O}}-H \xrightarrow{Na^+H^-} CH_3CH_2-\ddot{\underset{\cdot\cdot}{O}}{:}^-\ Na^+ + H_2 \qquad CH_3CH_3 \xrightarrow{NaH} \text{no reaction}$$

3.2 Identificare i gruppi funzionali basandosi sulle tabelle 3.1, 3.2 e 3.3.

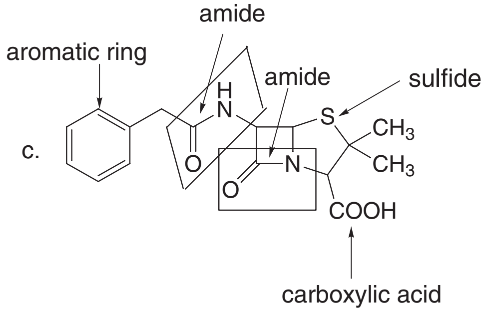
a.



b.

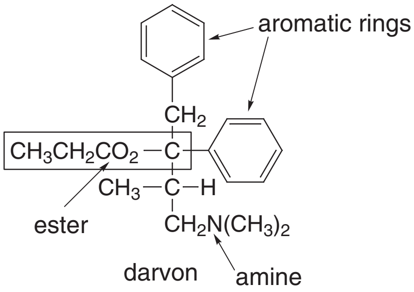


c.

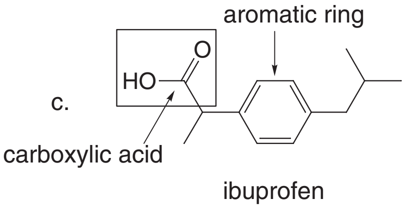


3.3 Identificare i gruppi funzionali facendo uso delle tabelle 3.1, 3.2 e 3.3.

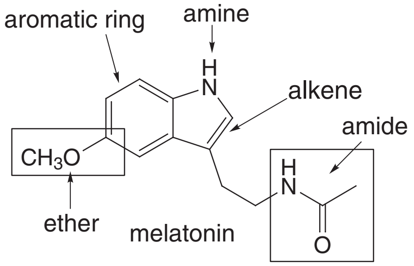
a.



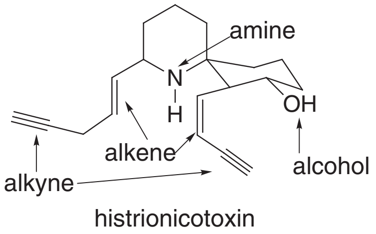
c.



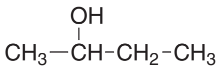
b.



d.



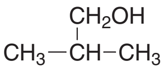
3.4


$\mathrm{CH_3-\overset{OH}{CH}-CH_2-CH_3}$

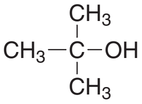
alcohol

$\mathrm{CH_3CH_2CH_2CH_2-OH}$

alcohol


$\mathrm{CH_3-\overset{CH_2OH}{CH}-CH_3}$

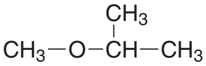
alcohol


$\mathrm{CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH}$

alcohol

$\mathrm{CH_3CH_2-O-CH_3CH_2}$

ether


$\mathrm{CH_3-O-\overset{CH_3}{CH}-CH_3}$

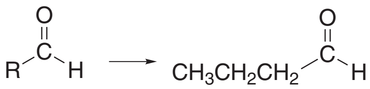
ether

$\mathrm{CH_3-O-CH_2CH_2CH_3}$

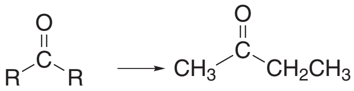
ether

3.5 Una possibile struttura per ogni gruppo funzionale:

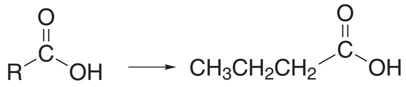
a. aldehyde =



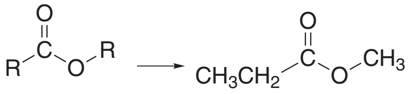
b. ketone =



c. carboxylic acid =



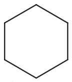
d. ester =



3.6 Riassunto delle forze:

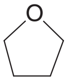
- **Tutti i composti mostrano forze di van der Waals (VDW)**.
- **Le molecole polari presentano interazioni dipolo-dipolo (DD)**.
- **I legami idrogeno (legami H) si possono formare solo quando un H è legato ad un O, N, o F.**

a.



only nonpolar C–C and C–H bonds
VDW only

b.



- **VDW forces**
- 2 polar C–O bonds and a net dipole - **DD**
- no H on O so no H-bonding

c. $\mathrm{(CH_3CH_2)_3N}$

- **VDW forces**
- polar C–N bonds - **DD**
- no H on N so no H-bonding

d. $\mathrm{CH_2{=}CHCl}$

- **VDW forces**
- polar C–Cl bond - **DD**

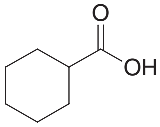
e. $\mathrm{CH_3CH_2CH_2COOH}$

- **VDW forces**
- polar C–O bonds and a net dipole - **DD**
- H bonded to O - **H-bonding**

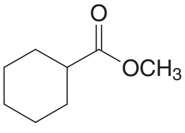
f. $\mathrm{CH_3-C{\equiv}C-CH_3}$

only nonpolar C–H and C–C bonds
VDW only

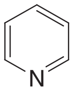
3.7 Usare le regole della risposta 3.3.

a.


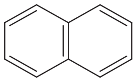
VDW
dipole-dipole
H-bonding (O–H bond)

b.


VDW
dipole-dipole
no H-bonding (no O–H bond)

c.


VDW
dipole-dipole
no H-bonding (no N–H bond)

d.


VDW
no dipole-dipole
(nonpolar C–C, C–H bonds)
no H-bonding (no O, N, F)

3.8 Aumento delle forze intermolecolari: van der Waals < dipolo-dipolo < legame H

a. **increasing intermolecular forces:**

$CH_3CH_3 < CH_3Cl < CH_3NH_2$

CH_3CH_3 ↑ VDW
CH_3Cl ↑ VDW, dipole-dipole
CH_3NH_2 ↑ VDW, dipole-dipole, H-bonding

b. **increasing intermolecular forces:**

$CH_3Cl < CH_3Br < CH_3I$ ⟶

increasing polarizability
stronger intermolecular forces

c. **increasing intermolecular forces:**

$(CH_3)_2C{=}C(CH_3)_2 < (CH_3)_2CHCOCH_3 < (CH_3)_2CHCOOH$

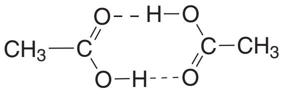
$(CH_3)_2C{=}C(CH_3)_2$ ↑ VDW
$(CH_3)_2CHCOCH_3$ ↑ VDW, dipole-dipole
$(CH_3)_2CHCOOH$ ↑ VDW, dipole-dipole, H-bonding

d. **increasing intermolecular forces:**

$CH_3Cl < CH_3OH < NaCl$

CH_3Cl ↑ VDW, dipole-dipole
CH_3OH ↑ VDW, dipole-dipole, H-bonding
$NaCl$ ↑ ionic

3.9



hydrogen bonding between
2 acetic acid molecules

3.10 **A** = forze di VDW; **B** = legami H; **C** = interazioni ione-ione; **D** = legami H ; **E** = legami H ; **F** = forze di VDW.

3.11 Un principio governa i punti di ebollizione:

- **Forze intermolecolari più forti = maggior p.e.**
  Aumento delle forze intermolecolari: van der Waals < dipolo-dipolo < legame idrogeno

Due fattori influenzano la forza delle forze di van der Waals , influenzando così i p.e.:

- **Aumento dell'area della superficie = aumento del p.e.**
  Molecole più lunghe hanno maggior area superficiale. Ogni ramificazione diminuisce l'area superficiale di una molecola.
- **Aumento della polarizzabilità = aumento del p.e.**

a. $(CH_3)_2C{=}CH_2$ and $(CH_3)_2C{=}O$

only VDW

VDW and DD
polar, stronger intermolecular forces
higher boiling point

b. CH_3CH_2COOH and CH_3COOCH_3

VDW, DD, and H-bonding
stronger intermolecular forces
higher boiling point

no H-bonding

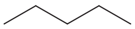
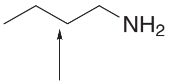
c. $CH_3(CH_2)_4CH_3$ and $CH_3(CH_2)_5CH_3$

longer molecule, more surface area
higher boiling point

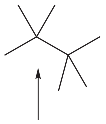
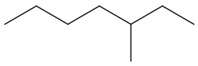
d. $CH_2{=}CHCl$ and $CH_2{=}CHI$

I is more polarizable.
higher boiling point

3.12

a.  and 

more polar
stronger intermolecular forces
(H-bonding)
higher mp

b.  and 

more spherical
packs better
higher mp

3.13 Nella fase solida che è più ordinata, le molecole sono molto più vicine l'una all'altra rispetto alla fase liquida meno ordinata. La forma di una molecola determina quanto si disponga ordinatamente in fase solida rendendo importante la simmetria. Nella fase liquida, le molecole sono più distanti tra loro, quindi la simmetria è meno importante e non influenza il punto di ebollizione.

3.14 Usare i concetti della risposta 3.4.

a. $CH_3(CH_2)_4{-}I$ $\quad$ $CH_3(CH_2)_5{-}I$ $\quad$ $CH_3(CH_2)_6{-}I$

$\longrightarrow$ increasing size, increasing surface area, increasing boiling point

b. $CH_3CH_2CH_2CH_3 < (CH_3)_3N < CH_3CH_2CH_2NH_2$

$CH_3CH_2CH_2CH_3$	$(CH_3)_3N$	$CH_3CH_2CH_2NH_2$
VDW	VDW dipole-dipole	VDW dipole-dipole H-bonding

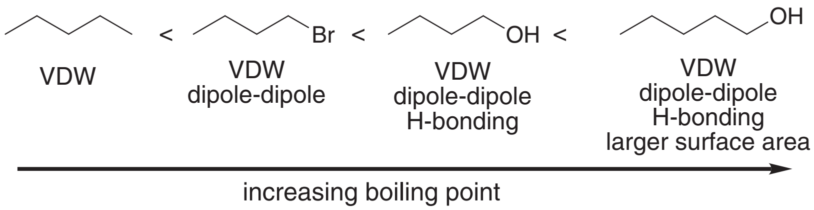
$\longrightarrow$ increasing boiling point

c. $(CH_3)_3COC(CH_3)_3 < CH_3(CH_2)_3O(CH_2)_3CH_3 < CH_3(CH_2)_7OH$

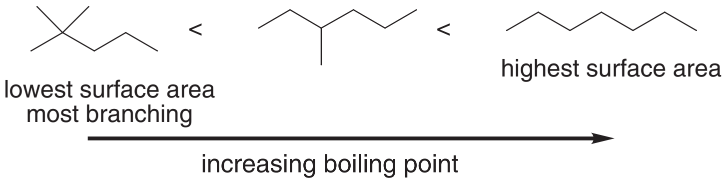
$(CH_3)_3COC(CH_3)_3$	$CH_3(CH_2)_3O(CH_2)_3CH_3$	$CH_3(CH_2)_7OH$
VDW dipole-dipole smaller surface area	VDW dipole-dipole larger surface area	VDW dipole-dipole H-bonding highest bp

$\longrightarrow$ increasing boiling point

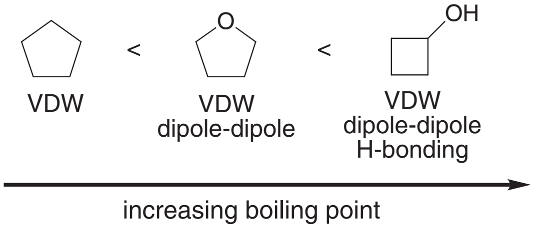
d.



e.



f.



3.15 In $CH_3CH_2NHCH_3$, è presente un legame N–H e conseguentemente la molecola mostra un legame idrogeno intermolecolare, mentre in $(CH_3)_3N$ l' N è legato solo al carbonio, e nessun legame idrogeno. Il legame idrogeno in $CH_3CH_2NHCH_3$ fa sì che le **forze intermolecolari siano più forti** che in $(CH_3)_3N$. All'aumentare delle forze intermolecolari, il punto di ebollizione di una molecola con lo stesso peso molecolare aumenta.

3.16 Forze maggiori, maggior p.f. Maggior simmetria dei composti, maggior p.f.

a. $(CH_3)_3CH$ < $(CH_3)_2C{=}O$ < $(CH_3)_2CHOH$

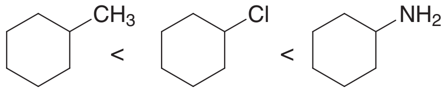
$(CH_3)_3CH$	$(CH_3)_2C{=}O$	$(CH_3)_2CHOH$
VDW	VDW DD	VDW DD H-bonding

$$\xrightarrow[\text{increasing melting point}]{\text{increasing intermolecular forces}}$$

b. CH_3F < CH_3Cl < CH_3I

$$\xrightarrow[\text{increasing melting point}]{\text{increasing polarizability}}$$

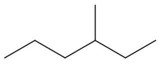
c.



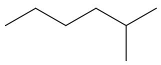
VDW	VDW DD	VDW DD H-bonding

$$\xrightarrow[\text{increasing melting point}]{\text{increasing intermolecular forces}}$$

3.17

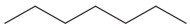


–119 °C
not symmetrical



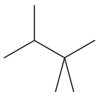
–118 °C
not symmetrical

In both compounds the CH_3 group dangling from the chain makes packing in the solid difficult, so the mp is low.



–91 °C
symmetrical
higher mp

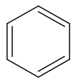
This molecule can pack somewhat better since it has no CH_3 group dangling from the chain, so the mp is somewhat higher. It also has the most surface area and this increases VDW forces compared to the first two compounds.



–25 °C
most spherical
highest mp

This compound packs the best since it is the most spherical in shape, increasing its mp.

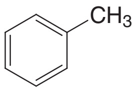
3.18 **Il punto di ebollizione è determinato solamente dall'intensità delle forze intermolecolari.** Poiché il benzene ha una dimensione più piccola, presenta una minor area superficiale e interazioni VDW più deboli, e conseguentemente un punto di ebollizione minore del toluene. L'aumento del punto di fusione per il benzene può essere spiegato dalla simmetria: il benzene è molto più simmetrico del toluene. Molecole più simmetriche so possono impacchettare più strettamente, con aumento del punto di fusione. La simmetria non ha nessun effetto sul punto di ebollizione.



benzene
bp = 80 °C
mp = 5 °C

very symmetrical
closer packing in solid form
higher mp

and



toluene
bp = 111 °C
mp = –93 °C

less symmetrical
lower mp

3.19 Un composto è solubile in acqua se è ionico oppure se possiede un atomo di O o uno di N e ≤ 5 Carboni.

a. $CH_3CH_2OCH_2CH_3$
↑
an O atom that
can H-bond with water
≤ 5 C's
water soluble

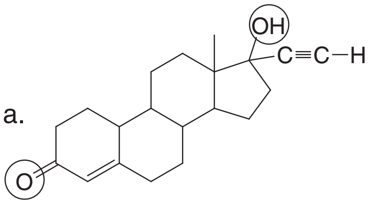
b. $CH_3CH_2CH_2CH_2CH_3$
↑
nonpolar
not water soluble

c. $(CH_3CH_2CH_2CH_2)_3N$
↑
an N atom that can
H-bond to H_2O, but
> 5 C's
not water soluble

3.20 **Le porzioni idrofobiche saranno principalmente catene idrocarburiche**. Le porzioni idrofile saranno polari.

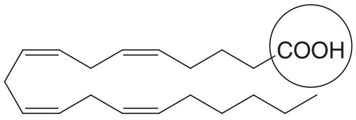
Circled regions are **hydrophilic** because they are polar.
All other regions are **hydrophobic** since they have only C and H.

a.



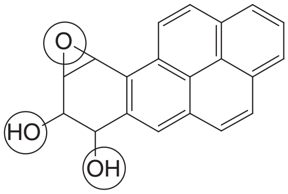
norethindrone

b.



arachidonic acid

c.



benzo[a]pyrene derivative

3.21 Aumento della polarità = aumento della solubilità in acqua.

Neither compound is very H_2O soluble.

a. $CH_3CH_2CH_2CH_3 < (CH_3)_3CH < CH_3OCH_2CH_3 < CH_3CH_2CH_2OH$

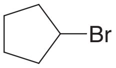
$CH_3CH_2CH_2CH_3$: VDW

$(CH_3)_3CH$: VDW
more spherical
(This nonpolar, hydrophobic
molecule is more compact,
making it more water soluble than its
straight chain isomer, drawn to the left.)

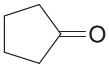
$CH_3OCH_2CH_3$: VDW
DD

$CH_3CH_2CH_2OH$: VDW
DD
H-bonding

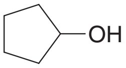
b.



polar
no H-bonding



polar
H-bonding to H_2O,
not itself



polar and
H-bonding
More opportunities
for H-bonding with its
O atom and its H on O.

3.22 Fare attenzione a due fattori:

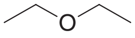
- Per formare legami idrogeno con un’altra molecola, la molecola deve contenere un **H legato a O, N, o F**.
- Per formare legami idrogeno con water, una molecola necessita **solamente di contenere un O, N, o F**.

These can H-bond to another molecule like itself:
Both compounds have N–H bonds.
b. CH_3NH_2, e. $CH_3CH_2CH_2CONH_2$

These can H-bond with water:
All of these molecules have an O or N atom.
b. CH_3NH_2, c. CH_3OCH_3, d. $(CH_3CH_2)_3N$,
e. $CH_3CH_2CH_2CONH_2$, g. CH_3SOCH_3,
h. $CH_3CH_2COOCH_3$

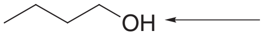
3.23 Disegnare la molecola in oggetto e individuare le forze intermolecolari coinvolte.

no H bonded to O



diethyl ether

VDW forces
dipole-dipole forces



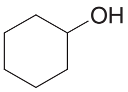
H bonded to O:
hydrogen bonding

1-butanol

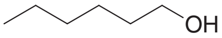
VDW forces
dipole-dipole forces
H-bonding

- Both have ≤ 5 C's and an electronegative O atom, so they can H-bond to water, making them soluble in water.
- Only 1-butanol can H-bond to another molecule life itself, and this increases its boiling point.

3.24



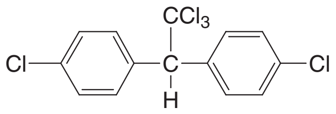
cyclohexanol
The nonpolar hydrocarbon part is more compact, so it is easier for the OH group to solubilize it in water.



1-hexanol

3.25 Usare la regola della solubilità della risposta 3.7.

a.

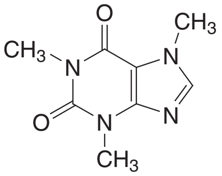


DDT

no N or O

not water soluble

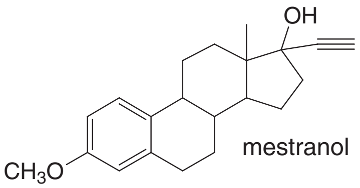
b.



caffeine

many polar bonds with N and O atoms
Many opportunities for H-bonding.
water soluble

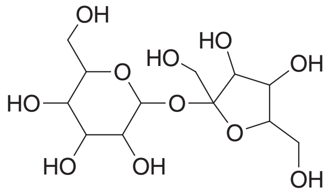
c.



mestranol

2 polar functional groups
but > 10 C's
not water soluble

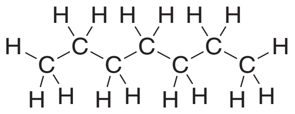
d.



sucrose

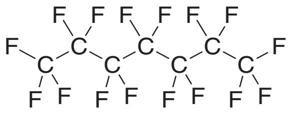
many polar bonds with O
11 O's and 12 C's
Many opportunities for H-bonding with H_2O.
water soluble

3.26



heptane
bp = 98°C

molecular weight = 100 g/mol



perfluoroheptane
bp = 82–84°C

molecular weight = 388 g/mol

F atoms are very electronegative and small, and their electron clouds are held tightly making them very poorly polarizable. This means there is little force of attraction between polyflourinated molecules, giving them much lower bp's than you would expect based on their molecular weights.

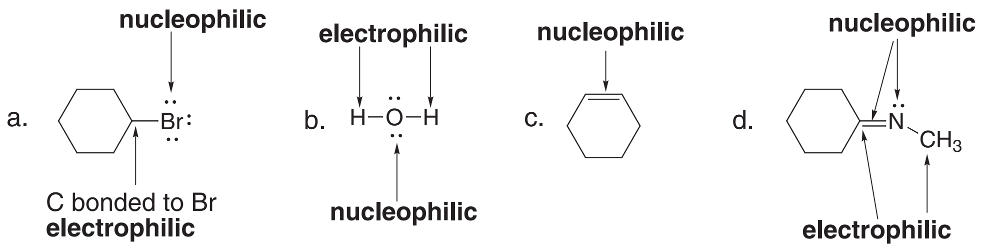
3.27

$(CH_3)_2CHCH(CH_3)_2$	$CH_3(CH_2)_4CH_3$	$CH_3(CH_2)_5CH_3$	$CH_3(CH_2)_6CH_3$
B	**C**	**D**	**A**
6 C's	6 C's	7 C's	8 C's
Branching makes less surface area, weaker VDW. **lowest bp**	no branching		**highest bp**

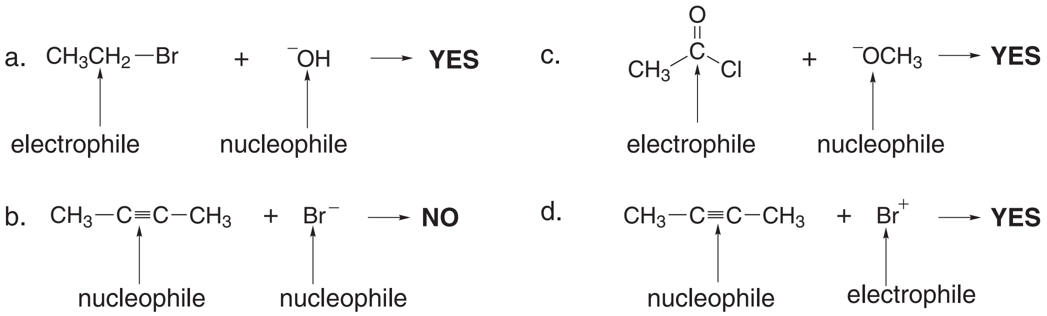
C, **D**, and **A** are all long chain hydrocarbons,
but the size increases from **C** to **D** to **A**, increasing
the VDW forces and increasing bp.

3.28 Eteroatomi elettronegativi come N, O o X fanno di un carbonio un *elettrofilo*.

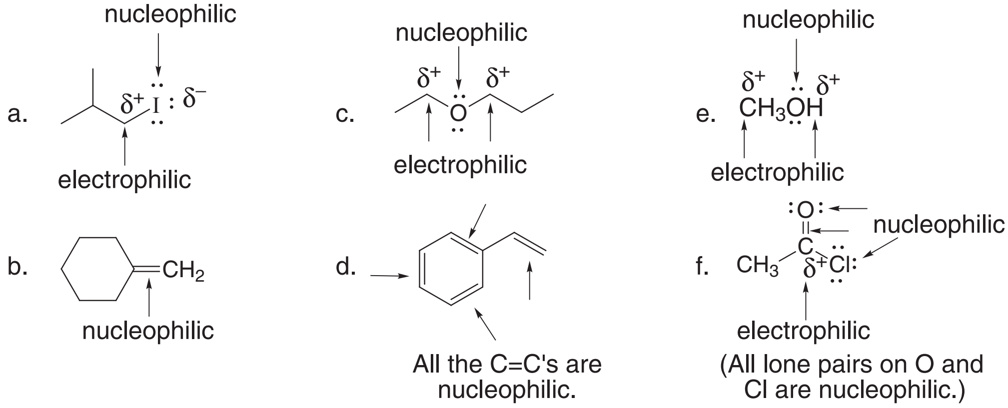
Una coppia elettronica solitaria su un eteroatomo lo rende basico e nucleofilo. I legami π creano siti *nucleofili* e sono più facilmente scissi dei legami σ.



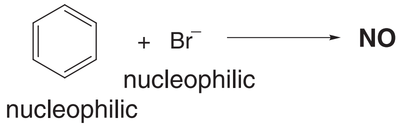
3.29 Gli elettrofili ed i nucleofili reagiscono l'uno con l'altro.

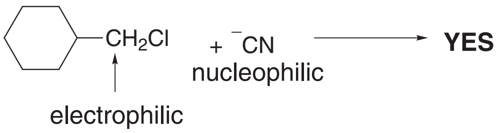


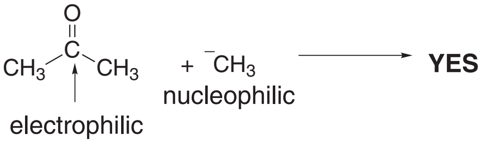
3.30 Usare la regola della risposta 3.12.

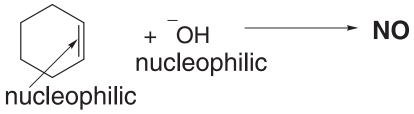


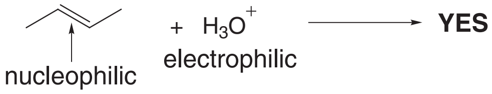
3.31

a.


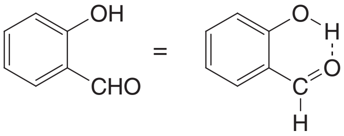
b.


c.


d.


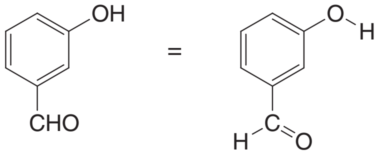
e.


3.32



A

These two functional groups are close enough that they can intramolecularly H-bond to each other. Since the two polar functional groups are involved in intramolecular H-bonding, they are less available for H-bonding to H_2O. This makes **A** less H_2O soluble than **B**, whose two functional groups are both available for H-bonding to the H_2O solvent.

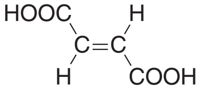


B

The OH and the CHO are too far apart to intramolecular H-bond to each other, leaving more opportunity to H-bond with solvent.

3.33

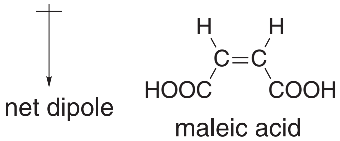
a. melting point



fumaric acid

Fumaric acid has its two larger COOH groups on opposite ends of the molecule, and in this way it can pack better in a lattice than maleic acid, giving it a **higher mp**.

b. solubility



maleic acid

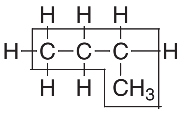
Maleic acid is more polar, giving it greater **H_2O solubility.**

Capitolo 4

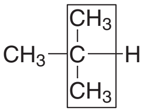
4.1 La formula generale per un alcano aciclico è $\mathbf{C_nH_{2n+2}}$.

a. $C_{12}H_{26}$	b. C_8H_{16}	c. $C_{30}H_{64}$
$2n + 2$ = # H's	$2n + 2$ = # H's	$2n + 2$ = # H's
$2(12) + 2 = 26$	$2(8) + 2 = 18$	$2(30) + 2 = 62$
yes	**no**	**no**

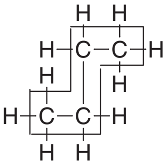
4.2 **Il butano** ha 4 Carboni in fila. **L'isobutano** ha 3 Carboni in fila ed 1 carbonio in catena laterale.

a.


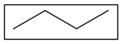
4 C's in a row.
butane

b. $(CH_3)_3CH$


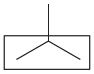
3 C's in a row.
isobutane

c.


4 C's in a row.
butane

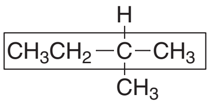
d.


4 C's in a row.
butane

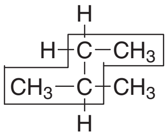
e.


3 C's in a row.
isobutane

4.3 L'isopentano ha 4 carboni in fila ed 1 carbonio in catena laterale.

a.


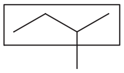
isopentane

b.


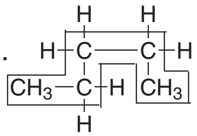
isopentane

c. $CH_3CH_2CH(CH_3)_2$

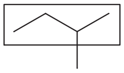
redraw



isopentane

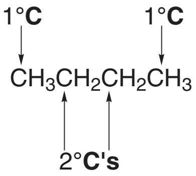
d.


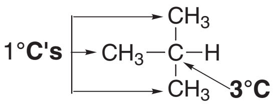
5 C's in a row.
pentane

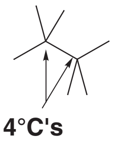
e.


isopentane

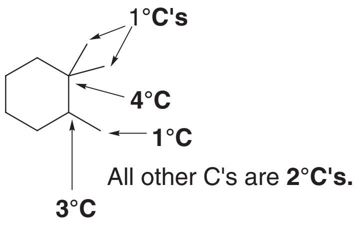
4.4 Per classificare un atomo di carbonio come 1°, 2°, 3° o 4° **determinare a quanti atomi di carbonio è legato** (**1° C** = legato ad **un** altro C, **2° C** = legato a due altri C, **3° C** = legato a tre altri C, **4° C** = legato a quattro altri C). Ridisegnare se necessario per osservare ogni carbonio chiaramente.

a.


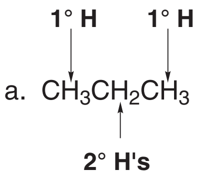
b. $(CH_3)_3CH$


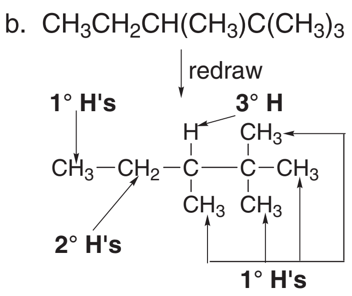
c.


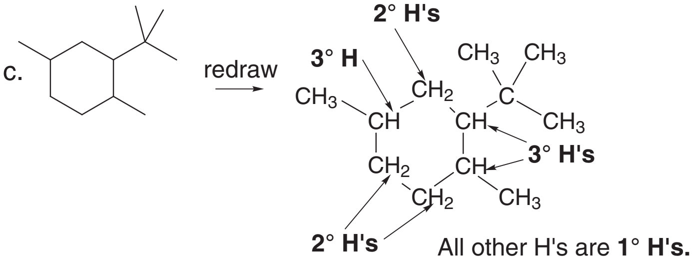
4°C's
All other C's are **1°C's.**

d.


4.5 Per classificare un atomo di idrogeno come 1°, 2°, or 3°, **determinare se è legato ad un carbonio 1°, 2° o 3° C (un H 1° è legato ad un C 1°, un H 2° è legato ad un C 2°**, un H **3° è legato ad un C 3°).** Ridisegnare se necessario.







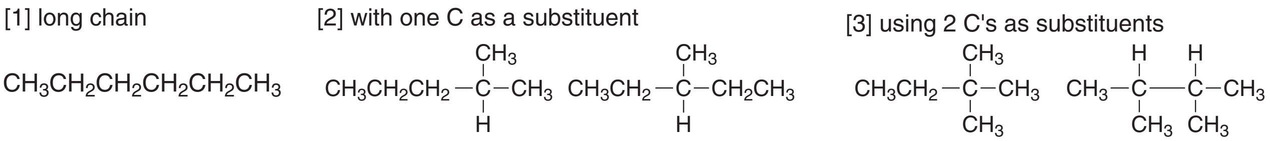
4.6 Gli isomeri costituzionali differiscono nel modo in cui gli atomi sono legati tra di loro. Per disegnare tutti gli isomeri costituzionali:

[1] Disegnare tutti i carboni della catena principale.

[2] Togliere un C ed usarlo come sostituente. (Non aggiungerlo al carbonio terminale: questo rigenera la catena precedente.)

[3] Togliere due C ed usarli come sostituenti, etc.

Five **constitutional isomers** of molecular formula C_6H_{14}



[1] long chain

$CH_3CH_2CH_2CH_2CH_2CH_3$

[2] with one C as a substituent

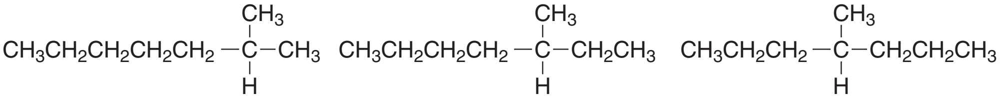
$CH_3CH_2CH_2-\underset{H}{\overset{CH_3}{C}}-CH_3$ $CH_3CH_2-\underset{H}{\overset{CH_3}{C}}-CH_2CH_3$

[3] using 2 C's as substituents

$CH_3CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$ $CH_3-\underset{CH_3}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}-CH_3$

4.7

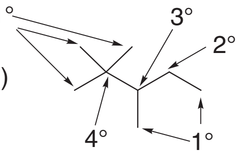
Molecular formula C_8H_{18} with one CH_3 substituent.



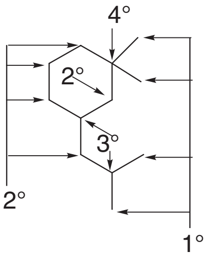
$CH_3CH_2CH_2CH_2CH_2-\underset{H}{\overset{CH_3}{C}}-CH_3$ $CH_3CH_2CH_2CH_2-\underset{H}{\overset{CH_3}{C}}-CH_2CH_3$ $CH_3CH_2CH_2-\underset{H}{\overset{CH_3}{C}}-CH_2CH_2CH_3$

4.8 Usare le regole delle risposte 4.4 e 4.5.

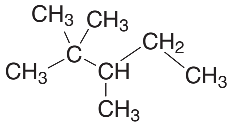
a. 1)



2)

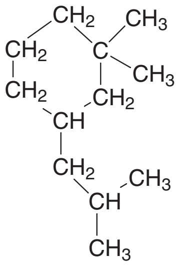


b. 1)



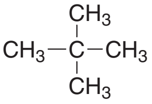
All CH_3's have 1° H's.
All CH_2's have 2° H's.
All CH's have 3° H's.

2)

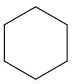


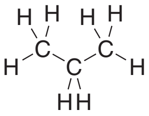
4.9

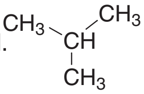
One possibility:

a. 

$CH_3-C(CH_3)_2-CH_3$

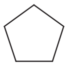
b. 

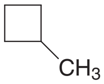
c. 

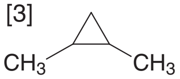
d. 

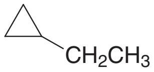
4.10 Usare i passaggi della risposta 4.6 per disegnare gli isomeri costituzionali.

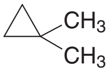
Five **constitutional isomers** of molecular formula C_5H_{10} having one ring

[1] 

[2] 

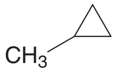
[3] 



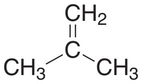


4.11 **I cicloalcani hanno formula molecolare C_nH_{2n}.** Per un cicloalcano con 288 carboni, ci sarebbero 2(288) = 576 H. Formula molecolare = **$C_{288}H_{576}$.**

4.12 a. Five consitutional isomers of molecular formula C_4H_8:



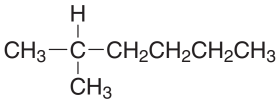
$CH_3CH{=}CHCH_3$ $CH_2{=}CHCH_2CH_3$



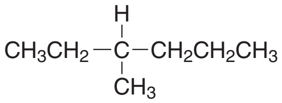
$$\underset{CH_3\quad CH_3}{\overset{CH_2}{\overset{\|}{C}}}$$

b. Nine constitutional isomers of molecular formula C_7H_{16}.

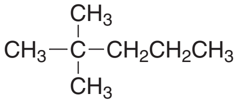
$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$



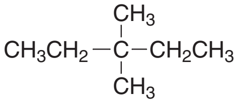
$$CH_3-\underset{CH_3}{\overset{H}{C}}-CH_2CH_2CH_2CH_3$$



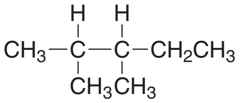
$$CH_3CH_2-\underset{CH_3}{\overset{H}{C}}-CH_2CH_2CH_3$$



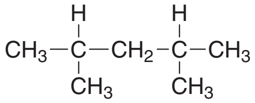
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2CH_2CH_3$$



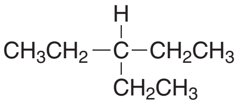
$$CH_3CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2CH_3$$



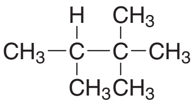
$$CH_3-\underset{CH_3}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}-CH_2CH_3$$



$$CH_3-\underset{CH_3}{\overset{H}{C}}-CH_2-\underset{CH_3}{\overset{H}{C}}-CH_3$$

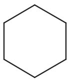


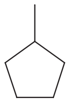
$$CH_3CH_2-\underset{CH_2CH_3}{\overset{H}{C}}-CH_2CH_3$$

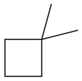


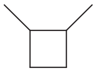
$$CH_3-\underset{CH_3}{\overset{H}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

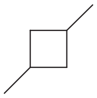
c. Twelve constitutional isomers of molecular formula C_6H_{12} containing one ring.

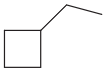


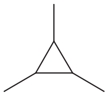


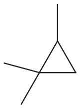


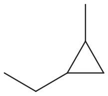


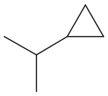


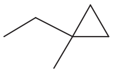


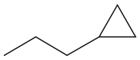












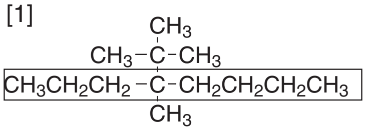
4.13 Seguire questi passaggi per attribuire il nome ad un alcano:

[1] **Attribuire il nome alla catena principale** attraverso l'individuazione della catena carboniosa più lunga.

[2] **Numerare la catena** in modo che il primo sostituente abbia il numero più basso. Successivamente **nominare e numerare tutti i sostituenti**, assegnando a sostituenti simili un prefisso (di, tri, etc.).

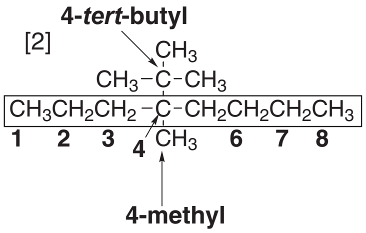
[3] **Combinare tutte le parti**, ordinando sostituenti in ordine alfabetico, ignorando tutti i prefissi eccetto *iso*.

a. [1]



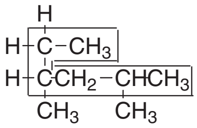
8 carbons = **octane**

[2]



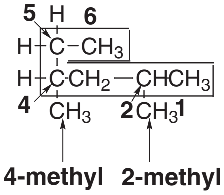
[3] **4-*tert*-butyl-4-methyloctane**

b. [1]



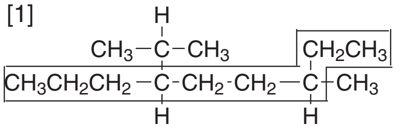
6 carbons = **hexane**

[2]



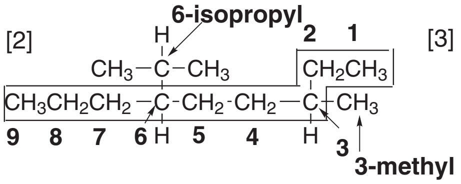
[3] **2,4-dimethylhexane**

c. [1]



9 carbons = **nonane**

[2]

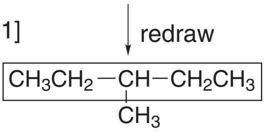


[3] **6-isopropyl-3-methylnonane**

4.14 Usare i passaggi della risposta 4.10 per assegnare il nome ad ogni alcano.

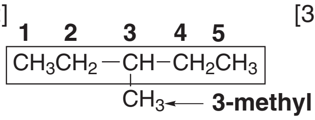
a. $CH_3CH_2CH(CH_3)CH_2CH_3$

[1]



5 carbons = **pentane**

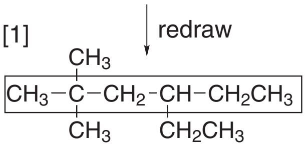
[2]



[3] **3-methylpentane**

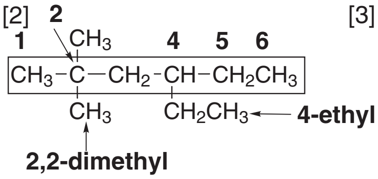
b. $(CH_3)_3CCH_2CH(CH_2CH_3)_2$

[1]



6 carbons = **hexane**

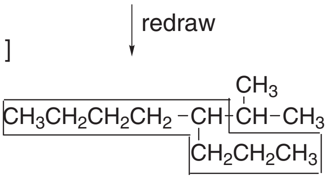
[2]



[3] **4-ethyl-2,2-dimethylhexane**

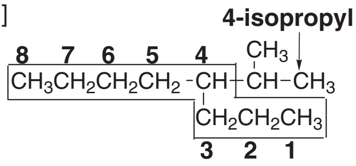
c. $CH_3(CH_2)_3CH(CH_2CH_2CH_3)CH(CH_3)_2$

[1]



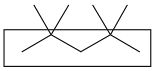
8 carbons = **octane**

[2]



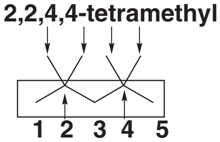
[3] **4-isopropyloctane**

d. [1]



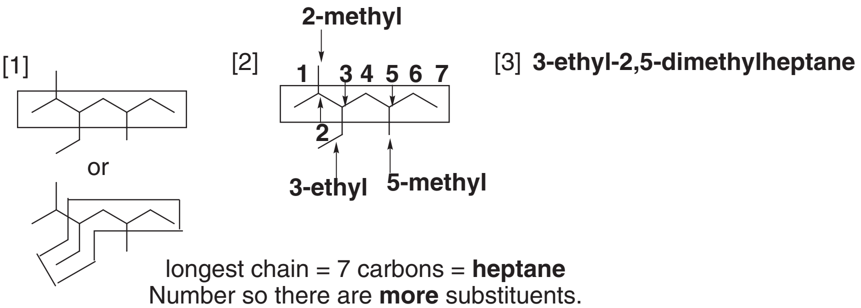
5 carbons = **pentane**

[2]



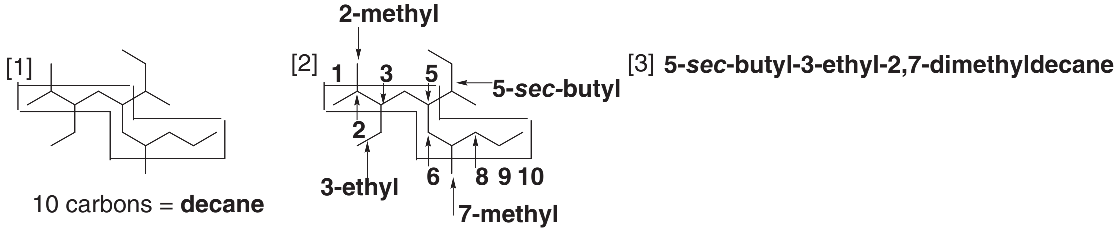
[3] **2,2,4,4-tetramethylpentane**

e.



longest chain = 7 carbons = **heptane**
Number so there are **more** substituents.
Pick the upper option.

f.



10 carbons = **decane**

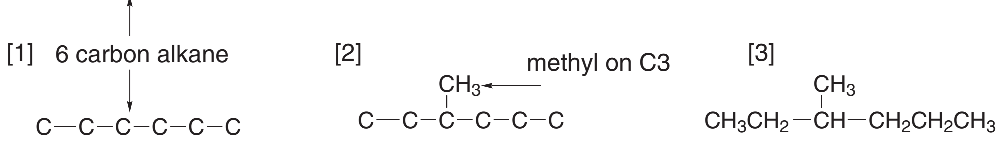
4.15 Per disegnare una struttura dal nome:

[1] Trovare la radice corrispondente e disegnare il numero di atomi di carbonio. Usare il suffisso per identificare il gruppo funzionale. **(-ano = alcano)**

[2] Numerare arbitrariamente gli atomi di C nella catena. Aggiungere i sostituenti ai carboni appropriati.

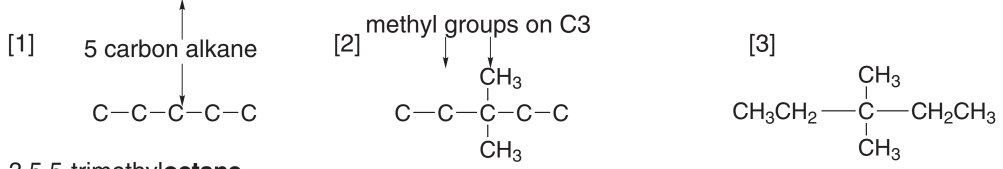
[3] Ridisegnare con gli H in modo che i carboni abbiano 4 legami.

a. 3-methyl**hexane**



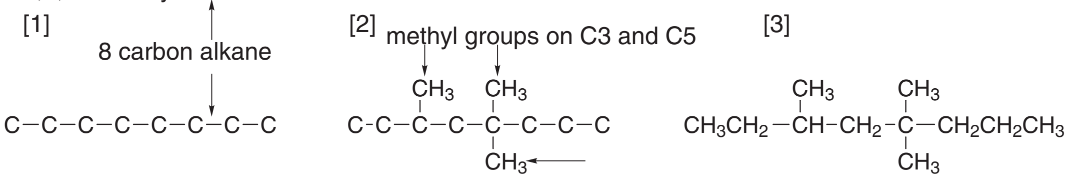
$$CH_3CH_2-\overset{CH_3}{\overset{|}{C}}H-CH_2CH_2CH_3$$

b. 3,3-dimethyl**pentane**



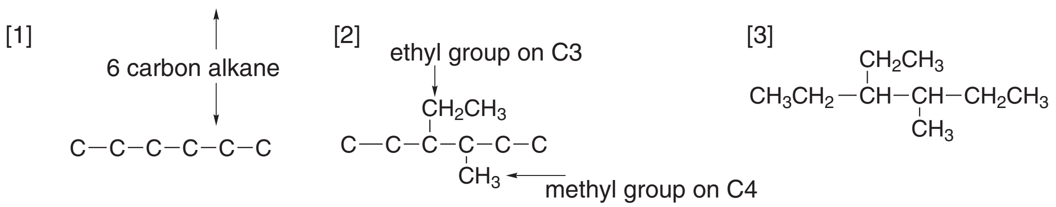
$$CH_3CH_2-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2CH_3$$

c. 3,5,5-trimethyl**octane**

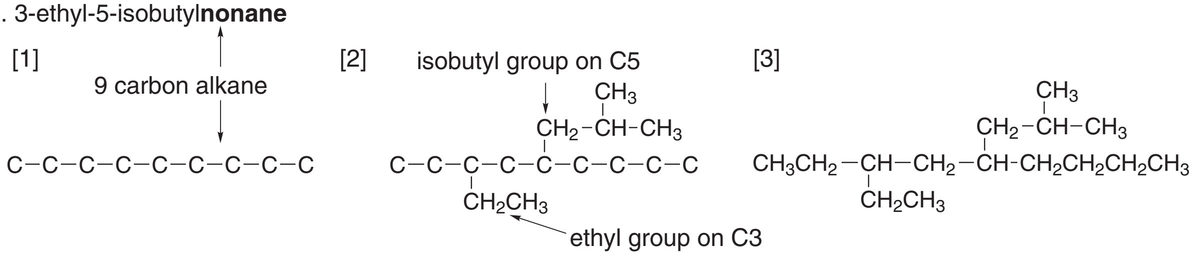


$$CH_3CH_2-\overset{CH_3}{\overset{|}{C}}H-CH_2-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2CH_2CH_3$$

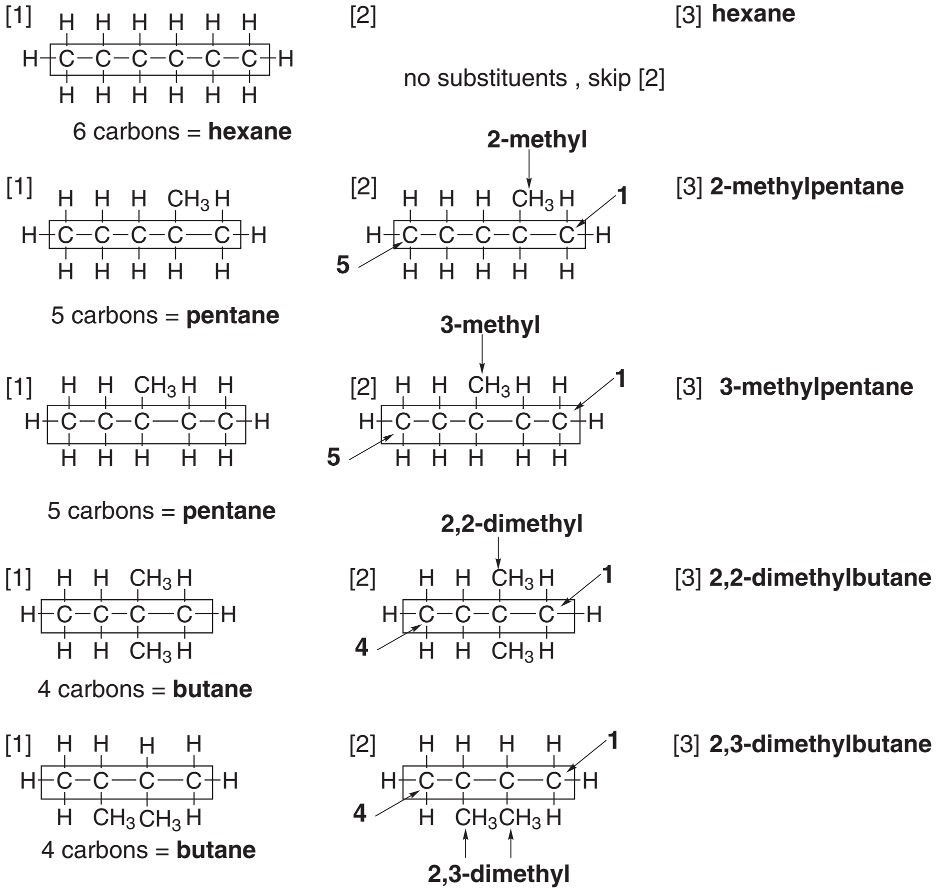
d. 3-ethyl-4-methyl**hexane**



e. 3-ethyl-5-isobutyl**nonane**



4.16 Usare i passaggi della risposta 4.10 per assegnare il nome ad ogni alcano.



4.17 Seguire questi passaggi per assegnare il nome ad un cicloalcano:

[1] Assegnare il nome alla radice del cicloalcano contando i carboni dell'anello ed aggiungendo ciclo-.

[2] **Numerazione:**

[2a] Numerare l'anello iniziando da un sostituente ed assegnando al secondo sostituente il numero più basso.

[2b] Assegnare il numero più basso al sostituente che precede in ordine alfabetico.

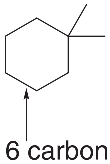
[2c] Denominare e numerare tutti i sostituenti, assegnando ai sostituenti uguali un prefisso (di, tri, ecc.).

[3] **Combinare tutte le parti**, disponendo in ordine alfabetico tutti i sostituenti, ed ignorando tutti I prefissi ad eccezione di *iso*.

(Ricordare: se una catena carboniosa ha più carboni dell'anello, la catena diventa la radice e l'anello un sostituente.)

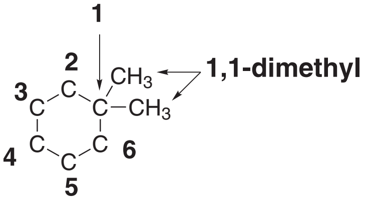
a.

[1]



6 carbons in ring = **cyclohexane**

[2]

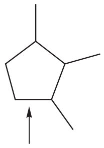


Number so the substituents are at C1.

[3] **1,1-dimethylcyclohexane**

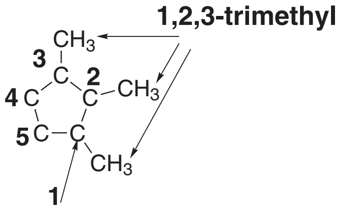
b.

[1]



5 carbons in ring = **cyclopentane**

[2]

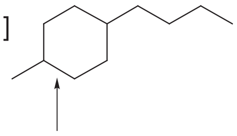


Number so the first substituent is at C1, second at C2.

[3] **1,2,3-trimethylcyclopentane**

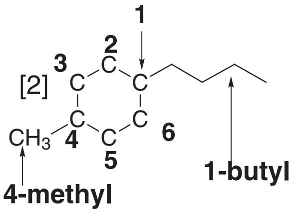
c.

[1]



6 carbons in ring = **cyclohexane**

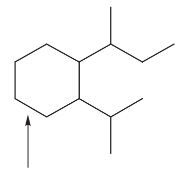
[2]



Number so the earliest alphabetical substituent is at C1, **b**utyl before **m**ethyl.

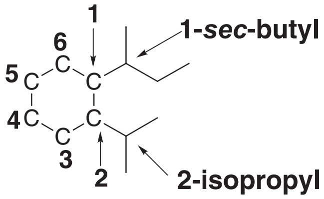
[3] **1-butyl-4-methylcyclohexane**

d. [1]



6 carbons in ring = **cyclohexane**

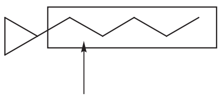
[2]



Number so the earliest alphabetical substituent is at C1, **b**utyl before **i**sopropyl.

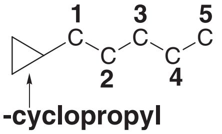
[3] **1-*sec*-butyl-2-isopropylcyclohexane**

e. [1]



longest chain = 5 carbons = **pentane**

[2]



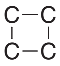
Number so the cyclopropyl is at C1.

[3] **1-cyclopropylpentane**

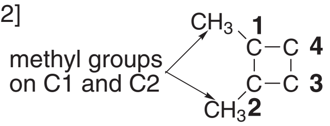
4.18 Per disegnare le strutture, usare i passaggi della risposta 4.15.

a. 1,2-dimethyl**cyclobutane**

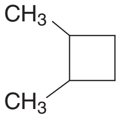
[1] 4 carbon cycloalkane



[2]

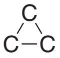


[3]

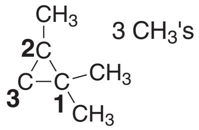


b. 1,1,2-trimethyl**cyclopropane**

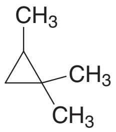
[1] 3 carbon cycloalkane



[2]

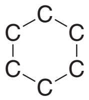


[3]

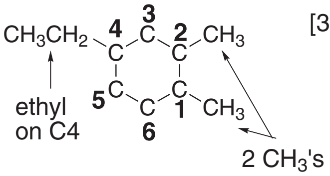


c. 4-ethyl-1,2-dimethyl**cyclohexane**

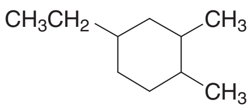
[1] 6 carbon cycloalkane



[2]

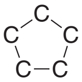


[3]

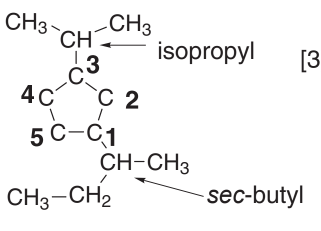


d. 1-*sec*-butyl-3-isopropyl**cyclopentane**

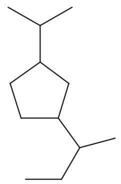
[1] 5 carbon cycloalkane



[2]

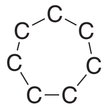


[3]

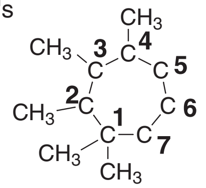


e. 1,1,2,3,4-pentamethyl**cycloheptane**

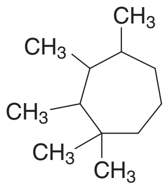
[1] 7 carbon cycloalkane



[2] 5 CH_3's

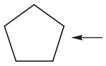


[3]



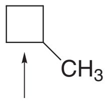
4.19 Per assegnare il nome ai cicloalcani, usare i passaggi della risposta 4.17.

[1]



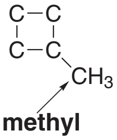
5 carbons in ring =
cyclopentane

[1]



4 carbons in ring =
cyclobutane

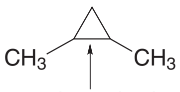
[2]



methyl

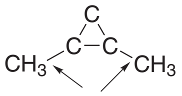
[3] **methylcyclobutane**

[1]



3 carbons in ring =
cyclopropane

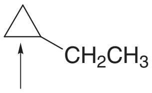
[2]



1,2-dimethyl

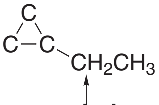
[3] **1,2-dimethylcyclopropane**

[1]



3 carbons in ring =
cyclopropane

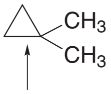
[2]



ethyl

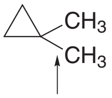
[3] **ethylcyclopropane**

[1]



3 carbons in ring =
cyclopropane

[2]

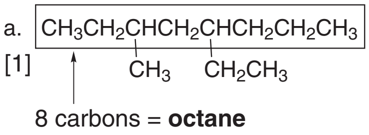


1,1-dimethyl

[3] **1,1-dimethylcyclopropane**

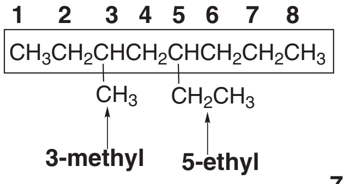
4.20 Usare I passaggi delle risposte 4.13 e 4.17 per dare il nome agli alcani.

a. [1]



$\boxed{CH_3CH_2\underset{CH_3}{CH}CH_2\underset{CH_2CH_3}{CH}CH_2CH_2CH_3}$

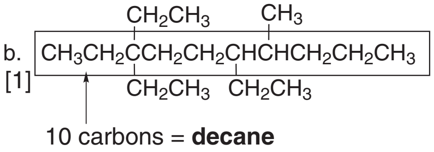
[2]



$\boxed{CH_3CH_2\underset{CH_3}{CH}CH_2\underset{CH_2CH_3}{CH}CH_2CH_2CH_3}$

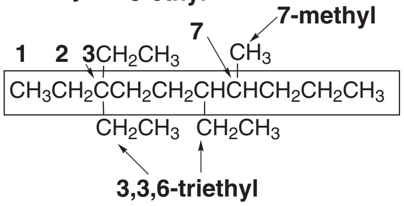
[3] **5-ethyl-3-methyloctane**

b. [1]



$\boxed{CH_3CH_2\overset{CH_2CH_3}{\underset{CH_2CH_3}{C}}CH_2CH_2\underset{CH_2CH_3}{CH}\overset{CH_3}{CH}CH_2CH_2CH_3}$

[2]

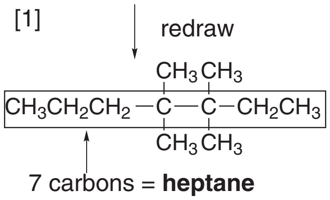


$\boxed{CH_3CH_2\overset{CH_2CH_3}{\underset{CH_2CH_3}{C}}CH_2CH_2\underset{CH_2CH_3}{CH}\overset{CH_3}{CH}CH_2CH_2CH_3}$

[3] **3,3,6-triethyl-7-methyldecane**

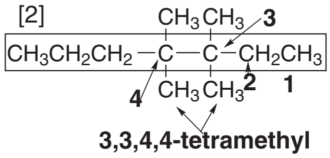
c. $CH_3CH_2CH_2C(CH_3)_2C(CH_3)_2CH_2CH_3$

[1]



$\boxed{CH_3CH_2CH_2-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_2CH_3}$

[2]

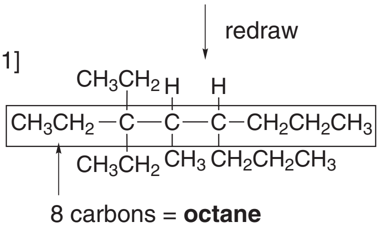


$\boxed{CH_3CH_2CH_2-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_2CH_3}$

[3] **3,3,4,4-tetramethylheptane**

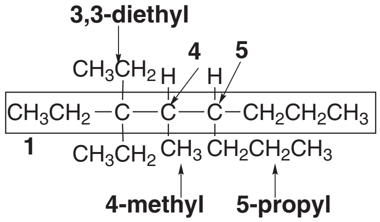
d. $CH_3CH_2C(CH_2CH_3)_2CH(CH_3)CH(CH_2CH_2CH_3)_2$

[1]



$\boxed{CH_3CH_2-\overset{CH_3CH_2}{\underset{CH_3CH_2}{C}}-\overset{H}{\underset{CH_3}{C}}-\overset{H}{\underset{CH_2CH_2CH_3}{C}}-CH_2CH_2CH_3}$

[2]

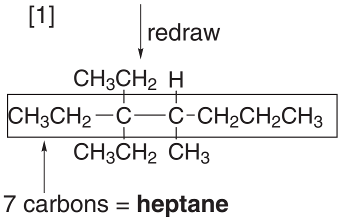


$\boxed{CH_3CH_2-\overset{CH_3CH_2}{\underset{CH_3CH_2}{C}}-\overset{H}{\underset{CH_3}{C}}-\overset{H}{\underset{CH_2CH_2CH_3}{C}}-CH_2CH_2CH_3}$

[3] **3,3-diethyl-4-methyl-5-propyloctane**

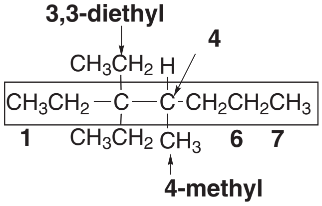
e. $(CH_3CH_2)_3CCH(CH_3)CH_2CH_2CH_3$

[1]



$\boxed{CH_3CH_2-\overset{CH_3CH_2}{\underset{CH_3CH_2}{C}}-\overset{H}{\underset{CH_3}{C}}-CH_2CH_2CH_3}$

[2]

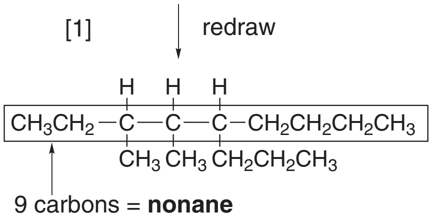


$\boxed{CH_3CH_2-\overset{CH_3CH_2}{\underset{CH_3CH_2}{C}}-\overset{H}{\underset{CH_3}{C}}-CH_2CH_2CH_3}$

[3] **3,3-diethyl-4-methylheptane**

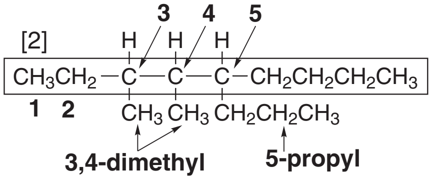
f. $CH_3CH_2CH(CH_3)CH(CH_3)CH(CH_2CH_2CH_3)(CH_2)_3CH_3$

[1]



$\boxed{CH_3CH_2-\overset{H}{\underset{CH_3}{C}}-\overset{H}{\underset{CH_3}{C}}-\overset{H}{\underset{CH_2CH_2CH_3}{C}}-CH_2CH_2CH_2CH_3}$

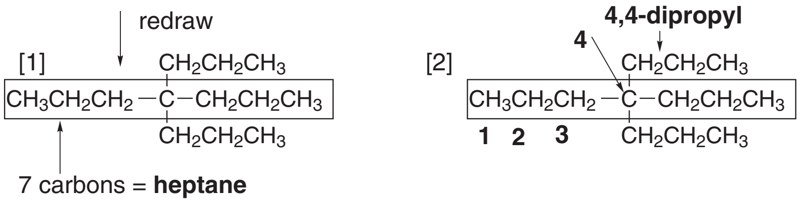
[2]



$\boxed{CH_3CH_2-\overset{H}{\underset{CH_3}{C}}-\overset{H}{\underset{CH_3}{C}}-\overset{H}{\underset{CH_2CH_2CH_3}{C}}-CH_2CH_2CH_2CH_3}$

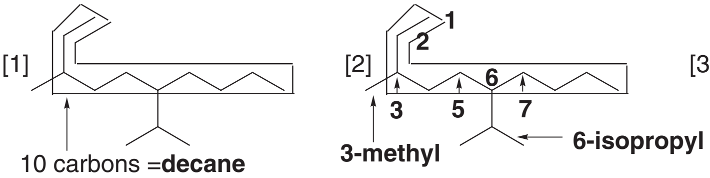
[3] **3,4-dimethyl-5-propylnonane**

g. $(CH_3CH_2CH_2)_4C$



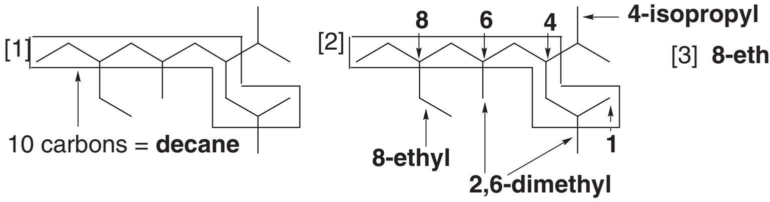
[3] **4,4-dipropylheptane**

h.



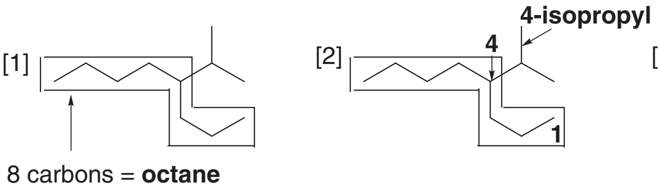
[3] **6-isopropyl-3-methyldecane**

i.



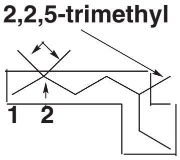
[3] **8-ethyl-4-isopropyl-2,6-dimethyldecane**

j.



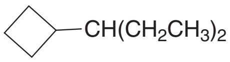
[3] **4-isopropyloctane**

k.

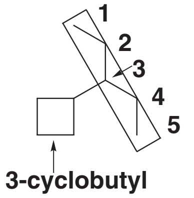


2,2,5-trimethylheptane

l.

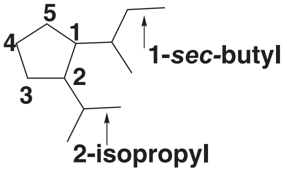


=



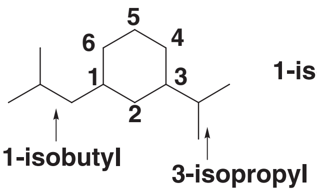
3-cyclobutylpentane

m.



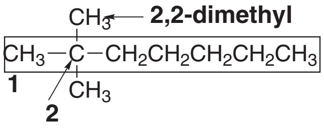
1-*sec*-butyl-2-isopropylcyclopentane

n.

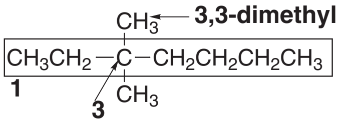


1-isobutyl-3-isopropylcyclohexane

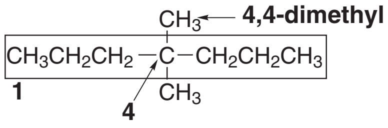
4.21



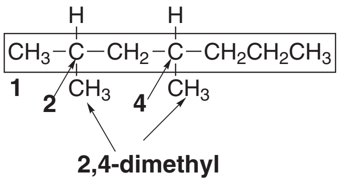
2,2-dimethylheptane



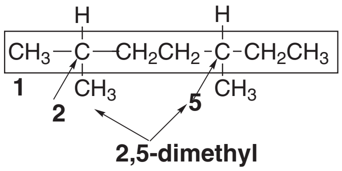
3,3-dimethylheptane



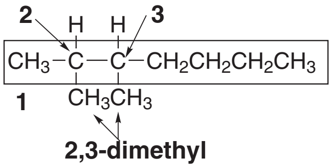
4,4-dimethylheptane



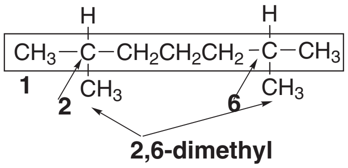
2,4-dimethylheptane



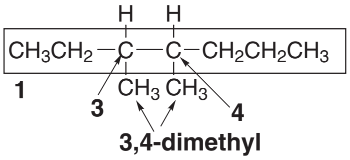
2,5-dimethylheptane



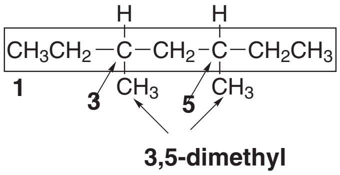
2,3-dimethylheptane



2,6-dimethylheptane



3,4-dimethylheptane

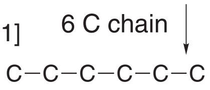


3,5-dimethylheptane

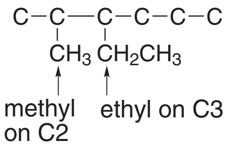
4.22 Usare i passaggi della risposta 4.15 per disegnare le strutture.

a. 3-ethyl-2-methyl**hexane**

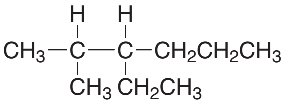
[1]



[2]

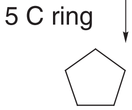


[3]

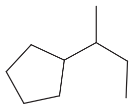


b. *sec*-butyl**cyclopentane**

[1]

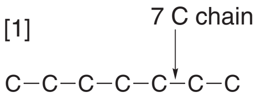


[2]

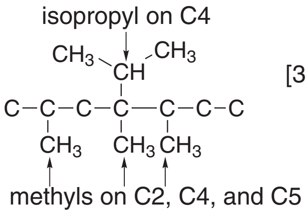


c. 4-isopropyl-2,4,5-trimethyl**heptane**

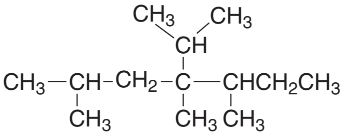
[1]



[2]

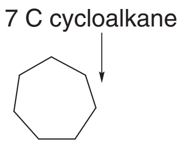


[3]

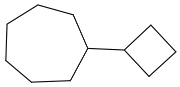


d. cyclobutyl**cycloheptane**

[1]

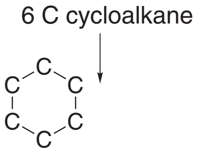


[2]

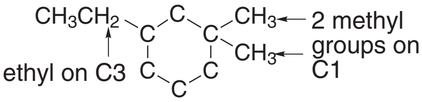


e. 3-ethyl-1,1-dimethyl**cyclohexane**

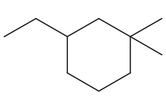
[1]



[2]

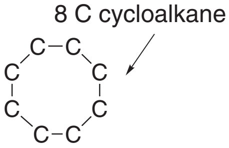


[3]

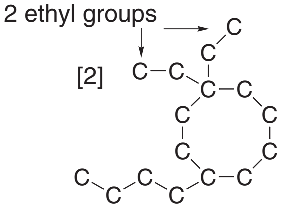


f. 4-butyl-1,1-diethyl**cyclooctane**

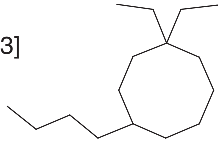
[1]



[2]

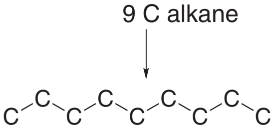


[3]

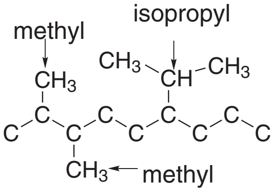


g. 6-isopropyl-2,3-dimethyl**nonane**

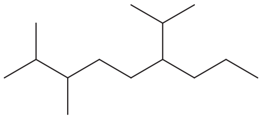
[1]



[2]

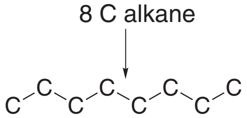


[3]

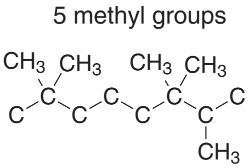


h. 2,2,6,6,7-pentamethyl**octane**

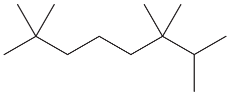
[1]



[2]

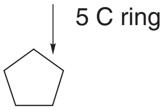


[3]

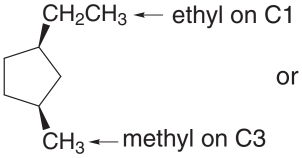


i. *cis*-1-ethyl-3-methyl**cyclopentane**

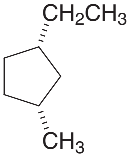
[1]



[2]

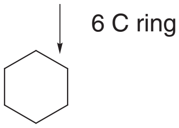


or

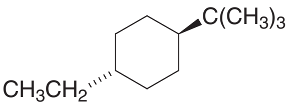


j. *trans*-1-*tert*-butyl-4-ethyl**cyclohexane**

[1]



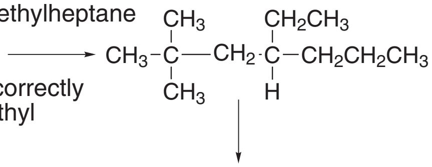
[2]



4.23 Disegnare i composti.

a. 2,2-dimethyl-4-ethylheptane

alphabetized incorrectly
ethyl before **m**ethyl

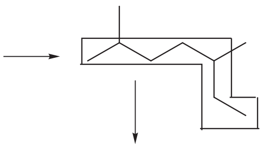


$CH_3-C(CH_3)_2-CH_2-CH(CH_2CH_3)-CH_2CH_2CH_3$

4-ethyl-2,2-dimethylheptane

b. 5-ethyl-2-methylhexane

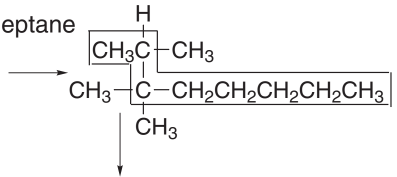
Longest chain was not
chosen = **heptane**



2,5-dimethylheptane

c. 2-methyl-2-isopropylheptane

longest chain was not
chosen = **octane**

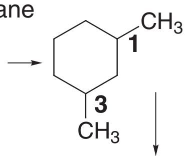


$CH_3-C(CH_3)(CH(CH_3)_2)-CH_2CH_2CH_2CH_2CH_3$

2,3,3-trimethyloctane

d. 1,5-dimethylcyclohexane

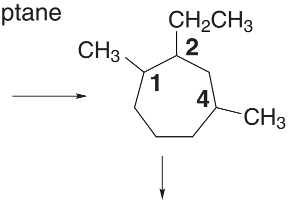
Numbered incorrectly.
Renumber so methyls
are at C1 and C3.



1,3-dimethylcyclohexane

e. 1-ethyl-2,6-dimethylcycloheptane

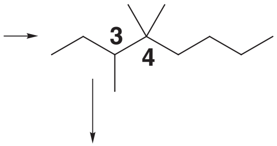
Numbered incorrectly.
Renumber so methyls
are at C1 and C4.



2-ethyl-1,4-dimethylcycloheptane

f. 5,5,6-trimethyloctane

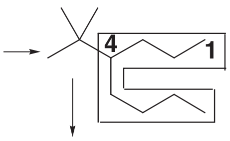
Numbered incorrectly.
Renumber so methyls
are at C3 and C4.



3,4,4-trimethyloctane

g. 3-butyl-2,2-dimethylhexane

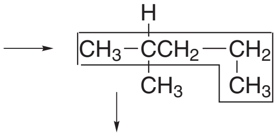
longest chain not
chosen = **octane**



4-*tert*-butyloctane

h. 1,3-dimethylbutane

longest chain not
chosen = **pentane**



$CH_3-CH(CH_3)-CH_2-CH_2-CH_3$

2-methylpentane

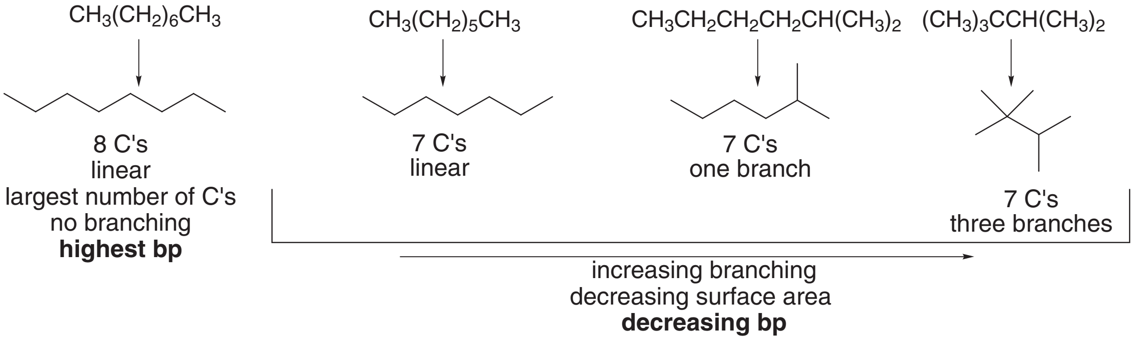
4.24 Confrontare i pesi molecolari per determinare i punti di ebollizione relativi.

gasoline: C_5H_{12} - $C_{12}H_{26}$	**kerosene:** $C_{12}H_{26}$ - $C_{16}H_{34}$	**diesel fuel:** $C_{15}H_{32}$ - $C_{18}H_{38}$
lowest molecular weight: **lowest boiling point**	middle molecular weight: **intermediate boiling point**	highest molecular weight: **highest boiling point**

4.25 Confrontare i numeri dei carboni e l'area superficiale per determinare I punti di ebollizione relativi. Regole:

[1] Aumento del numero dei carboni = aumento del punto di ebollizione.

[2] Aumento dell'area superficiale = aumento del punto di ebollizione (la ramificazione diminuisce l'area superficiale).



increasing boiling point: $(CH_3)_3CCH(CH_3)_2 < CH_3CH_2CH_2CH_2CH(CH_3)_2 < CH_3(CH_2)_5CH_3 < CH_3(CH_2)_6CH_3$

4.26 Usare le regole della risposta 4.25.

a. $CH_3CH_2CH_3$, $CH_3CH_2CH_2CH_3$, $CH_3CH_2CH_2CH_2CH_3$

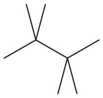
$CH_3CH_2CH_3$,	$CH_3CH_2CH_2CH_3$,	$CH_3CH_2CH_2CH_2CH_3$
3C's **lowest boiling point**	4 C's	5 C's **highest boiling point**

b.

$(CH_3)_2CHCH(CH_3)_2$,	$CH_3CH_2CH_2CH(CH_3)_2$,	$CH_3(CH_2)_4CH_3$
most branching **lowest boiling point**		least branching **highest boiling point**

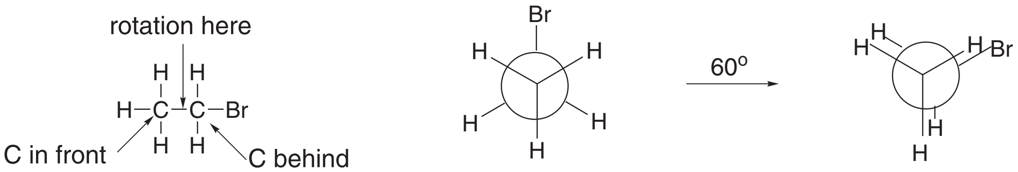
4.27

$CH_3(CH_2)_6CH_3$
no branching = higher surface area
higher boiling point



$(CH_3)_3C(CH_3)_3$
branching = lower surface area
lower boiling point
more spherical, better packing =
higher melting point

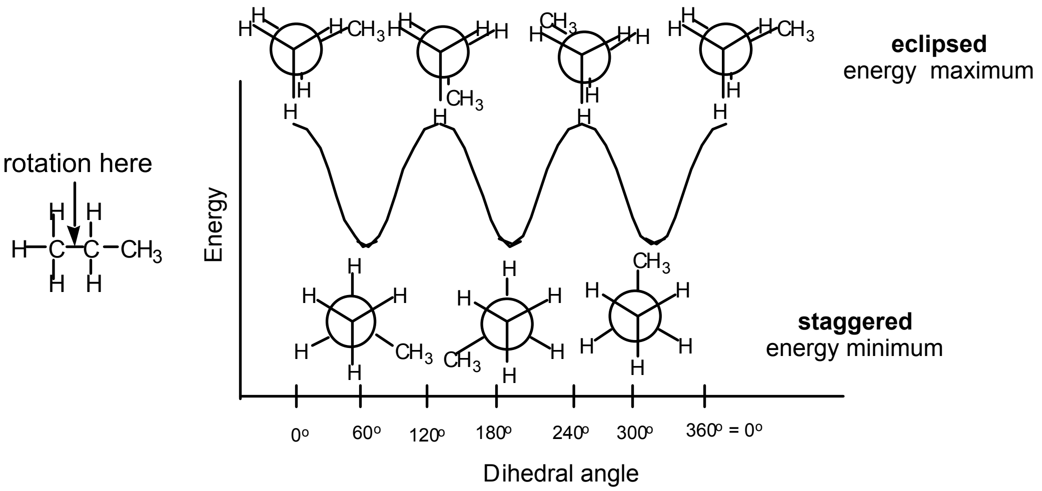
4.28 Per disegnare una proiezione di Newman, visualizzare i carboni come uno davanti ed uno dietro rispettivamente. Il legame C–C non viene disegnato. C'è una sola conformazione sfalsata ed una eclissata.



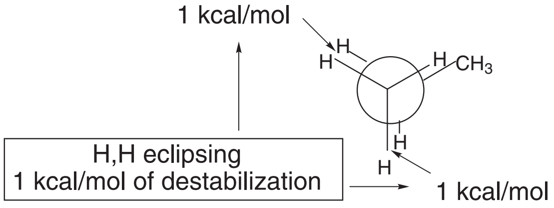
1 staggered

2 eclipsed

4.29 Le conformazioni sfalsate sono più stabili delle conformazioni eclissate.



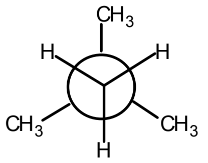
4.30



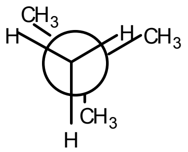
To calculate H,CH_3 destabilization:

3.5 kcal/mol (total) –
2 kcal/mol for 2 H,H eclipsing interactions
= **1.5 kcal/mol** for one H,CH_3 eclipsing interaction

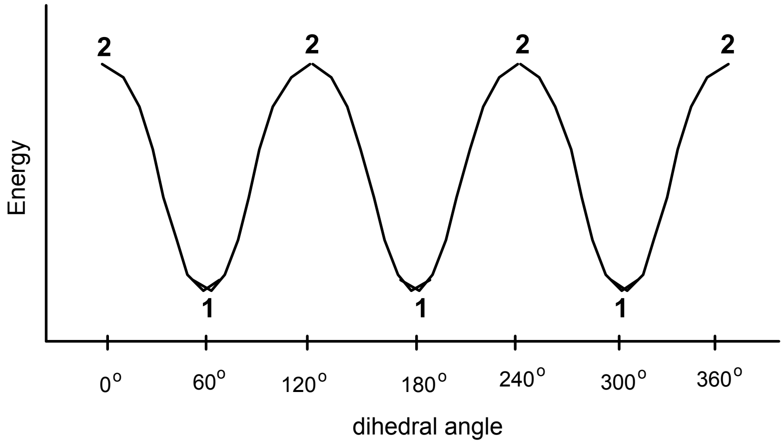
4.31 Per determinare l’energia dei conformeri ricordare due fattori:
[1] I conformeri eclissati sono più stabili di quelli eclissati.
[2] Minimizzare le interazioni steriche mettendo I gruppi più ingombranti lontano uno dall’altro.
La conformazione a più alta energia è la conformazione eclissata in cui i due gruppi più ingombranti sono eclissati. La conformazione a minore energia è la configurazione sfalsata in cui i due gruppi più ingombranti sono anti.



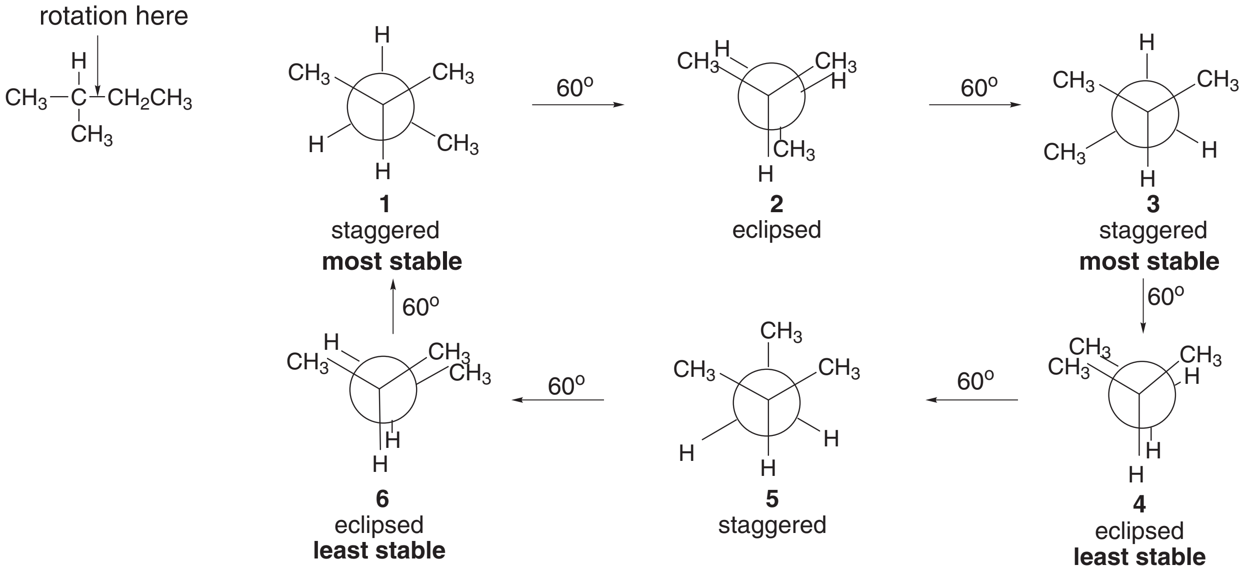
most stable
1



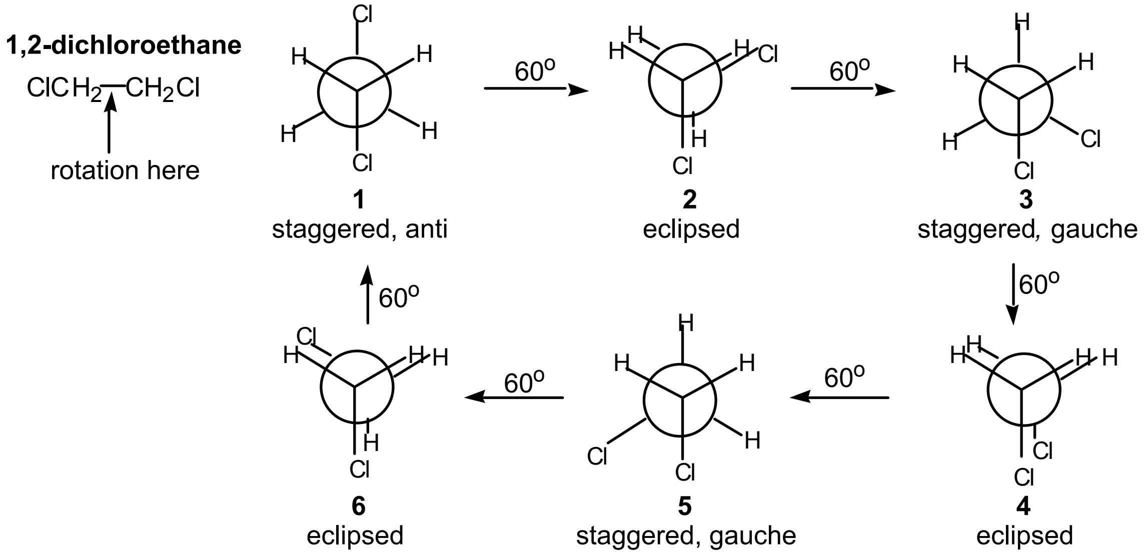
least stable
2

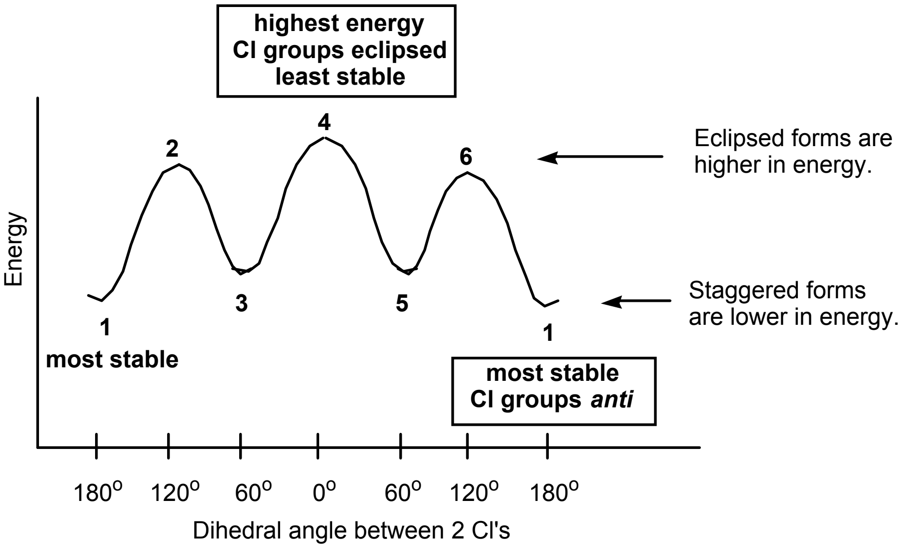


4.32 Per determinare i conformeri più stabili e quelli meno stabili, usare le regole della risposta 4.31.



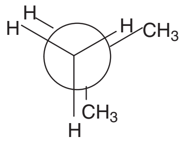
4.33 Per determinare i conformeri più stabili e quelli meno stabili, usare le regole della risposta 4.31.





4.34 Aggiungere l'aumento di energia per ogni interazione eclissata per determinare la destabilizzazione.

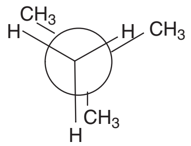
a.



1 H,H interaction = 1 kcal/mol
2 H,CH_3 interactions (2 x 1.5 kcal/mol) = 3 kcal/mol

Total destabilization = 4 kcal/mol

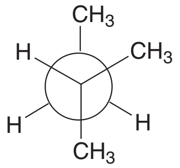
b.



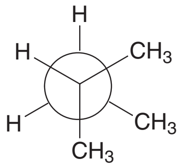
3 H,CH_3 interactions
(3 x 1.5 kcal/mol) = **4.5 kcal/mol**
Total destabilization

4.35

a.



and

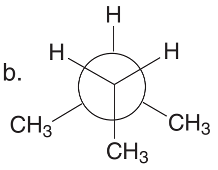


1 gauche CH_3,CH_3
= 0.9 kcal/mol
of destabilization

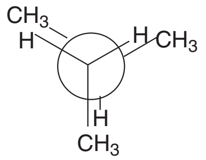
higher energy
2 gauche CH_3,CH_3
0.9 kcal/mol x 2 = 1.8 kcal/mol
of destabilization

Energy difference =
1.8 kcal/mol – 0.9 kcal/mol = **0.9 kcal/mol**

b.



and



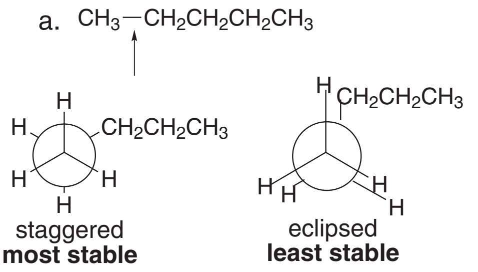
2 gauche CH_3,CH_3
0.9 kcal/mol x 2 =
1.8 kcal/mol
of destabilization

higher energy
3 eclipsed H,CH_3
1.5 kcal/mol x 3 = 4.5 kcal/mol
of destabilization

Energy difference =
4.5 kcal/mol – 1.8 kcal/mol = **2.7 kcal/mol**

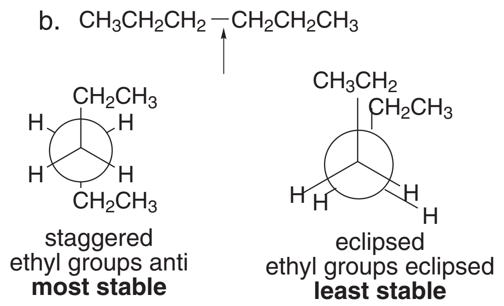
4.36 Usare le regole della risposta 4.31 per determinare i conformeri più stabili e meno stabili.

a.



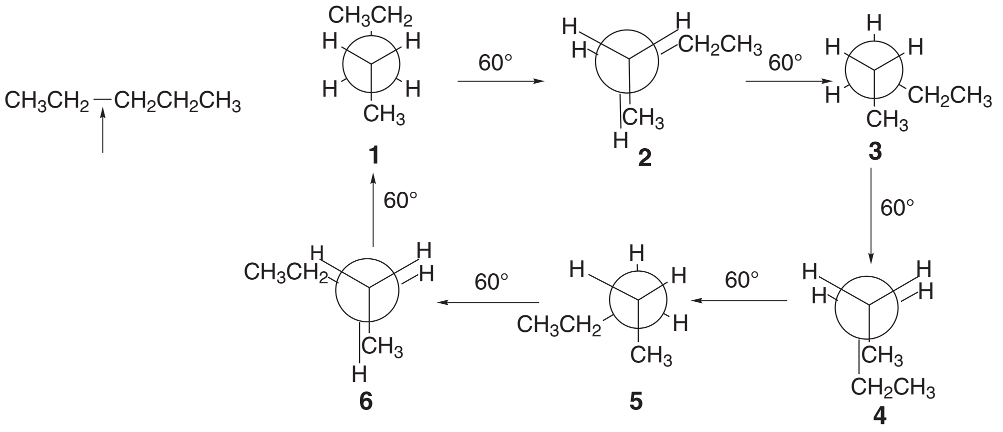
All staggered conformers are equal in energy.
All eclipsed conformers are equal in energy.

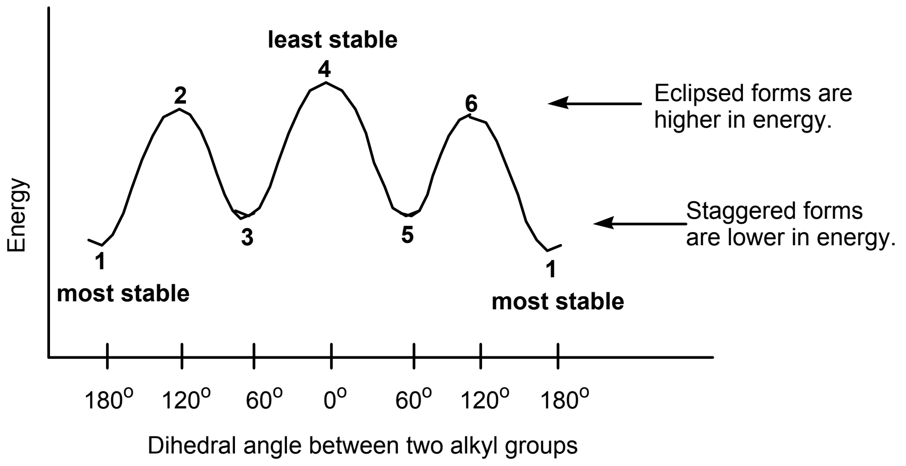
b.



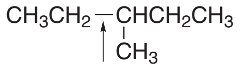
4.37

(1)

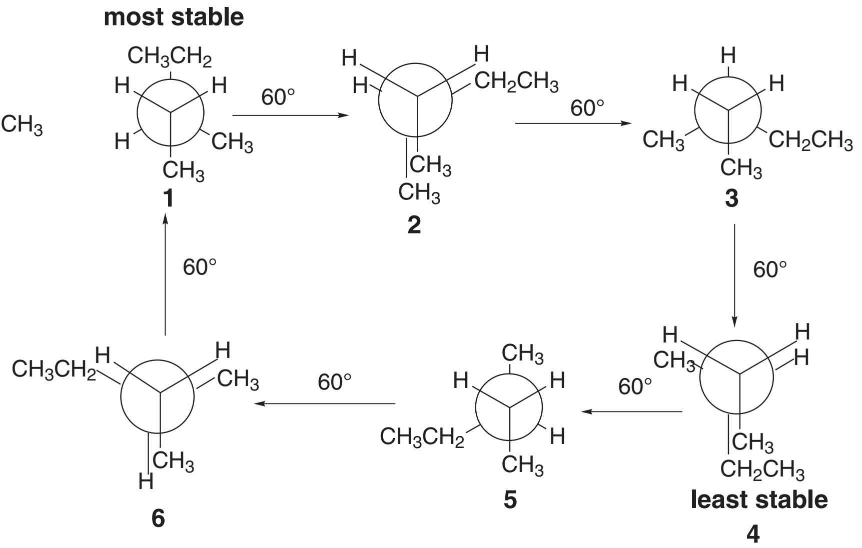


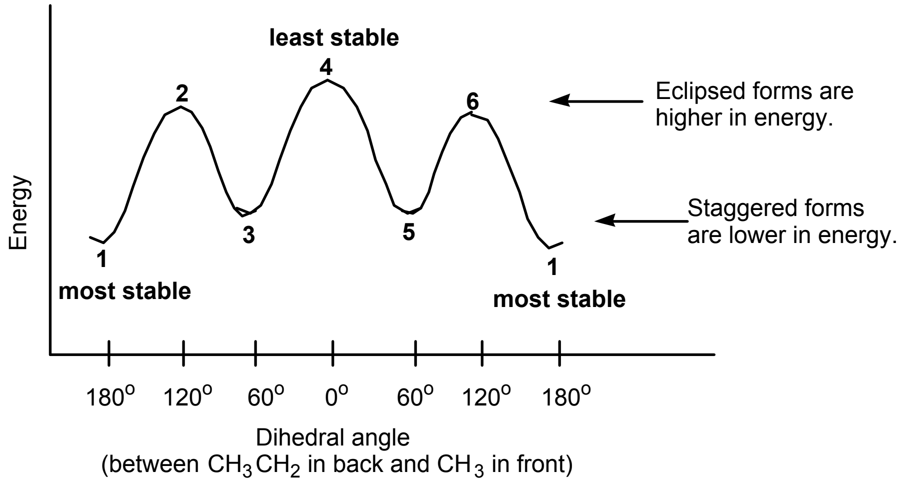


(2)



$CH_3CH_2\!-\!\underset{CH_3}{CHCH_2CH_3}$

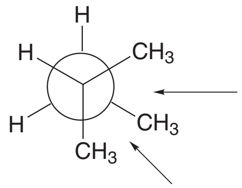




4.38 Due tipi di tensione:

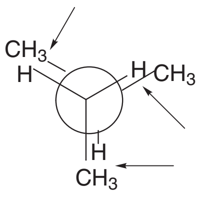
- *La tensione torsionale* è dovuta a gruppi eclissati su atomi di carbonio adiacenti.
- *La tensione sterica* è dovuta a sovrapposizione delle nuvole elettroniche di gruppi voluminosi (es: interazioni gauche).

a.



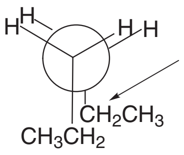
two sites
three bulky methyl groups close =
steric strain

b.



eclisped conformation=
torsional strain

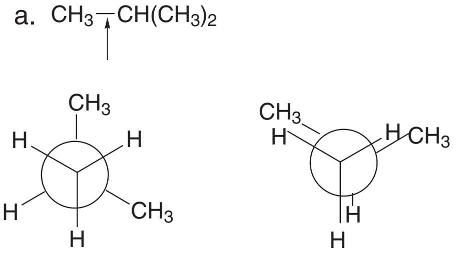
c.



two bulky ethyl groups close =
steric strain
eclipsed conformation =
torsional strain

4.39 La barriera di energia rotazionale è uguale alla differenza di energia tra la più alta energia eclissata e la più bassa energia sfalsata della molecola.

a.



most stable least stable

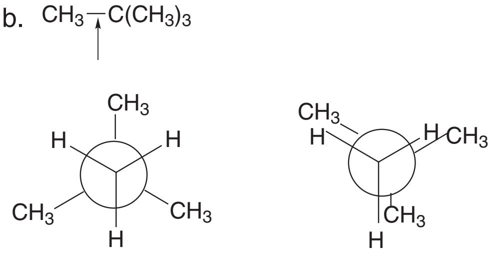
Destabilization energy =

2 H,CH_3 eclipsing interactions
2(1.5 kcal/mol) = 3 kcal/mol
1 H,H eclipsing interaction = 1 kcal/mol

Total destabilization = **4 kcal/mol**

4 kcal/mol = rotation barrier

b.



most stable least stable

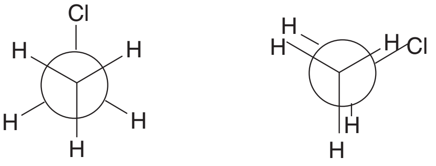
Destabilization energy =

3 H,CH_3 eclipsing interactions
3(1.5 kcal/mol) = 4.5 kcal/mol

Total destabilization = **4.5 kcal/mol**

4.5 kcal/mol = rotation barrier

4.40



most stable least stable

2 H,H eclipsing interactions = 2(1 kcal/mol) = 2 kcal/mol

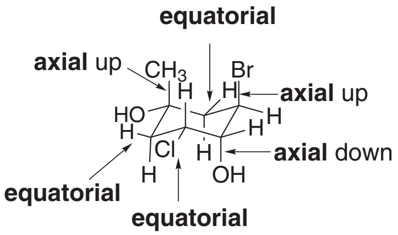
Since the barrier to rotation is 3.7 kcal/mol, the difference between this value and the destabilization due to H,H eclipsing is the destabilization due to H,Cl eclipsing.

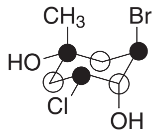
3.7 kcal/mol - 2 kcal/mol = **1.7 kcal/mol**
destabilization due to H,Cl eclipsing

4.41 Il conformero gauche può formare un legame idrogeno intramolecolare, che lo rende il conformero più stabile.

4.42 Due punti:

- I legami assiali sono direzionati in alto o in basso, mentre quelli equatoriali verso l'esterno.
- Un carbonio *in alto* ha un legame assiale *in alto*, ed un carbonio *in basso* ha un legame assiale *in basso*.

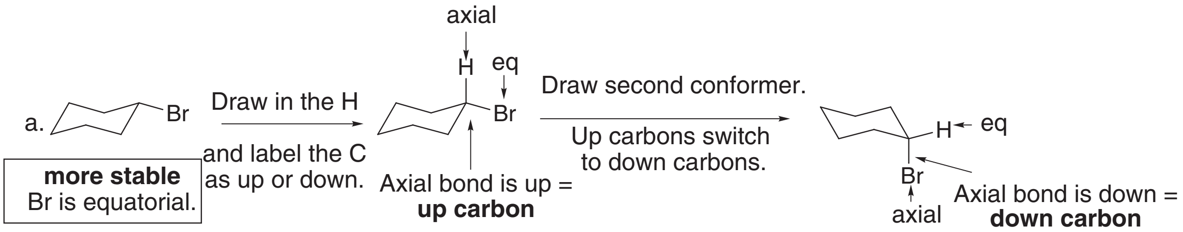


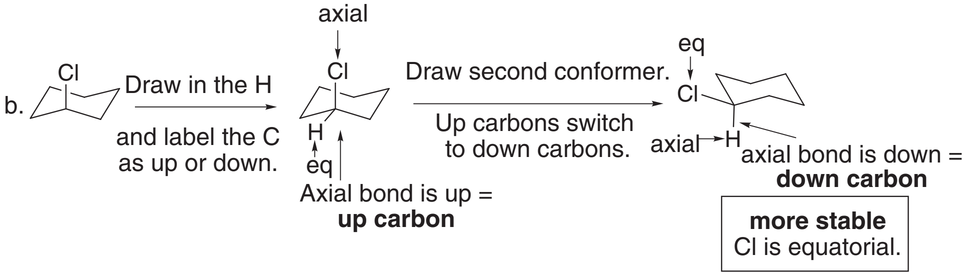


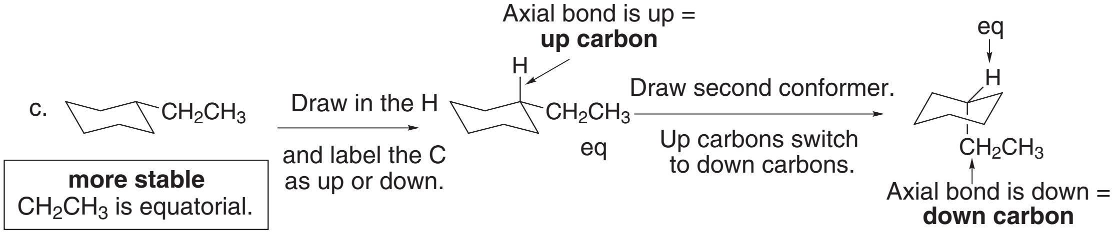
Up carbons are dark circles.
Down carbons are clear circles.

4.43 Disegnare un secondo conformero a sedia per inversione dell'anello**.**

- **I carboni *in alto* diventano carboni *in basso*, e i legami assiali diventano legami equatoriali.**
- **I legami assiali diventano equatoriali, ma i legami *in alto* rimangono *in alto***; cioè un legame assiale *in alto* diventa un legame equatoriale *in alto*.
- Il conformero con **i gruppi più ingombranti in posizione equatoriale è più stabile** ed è presente in maggior concentrazione all'equilibrio.

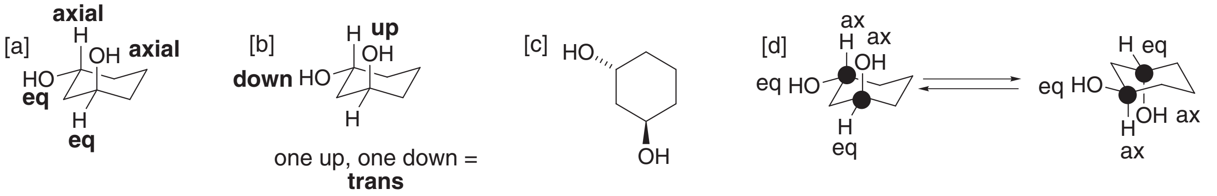




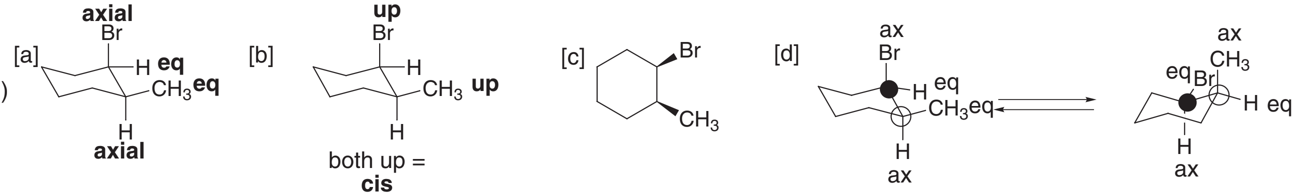


4.44

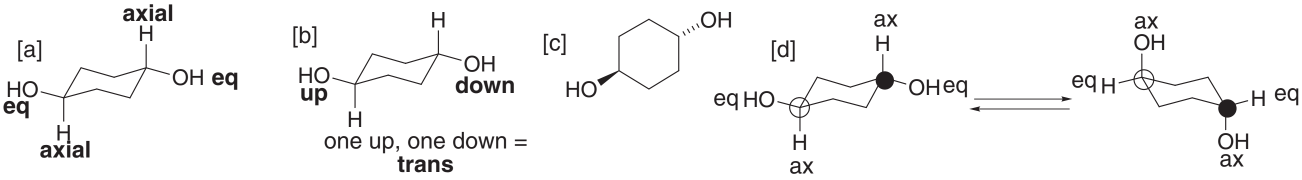
(1)



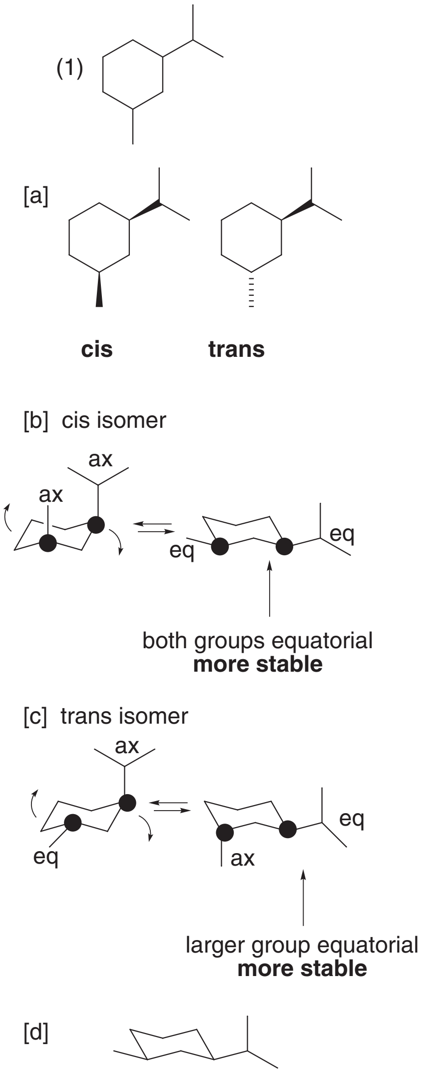
(2)



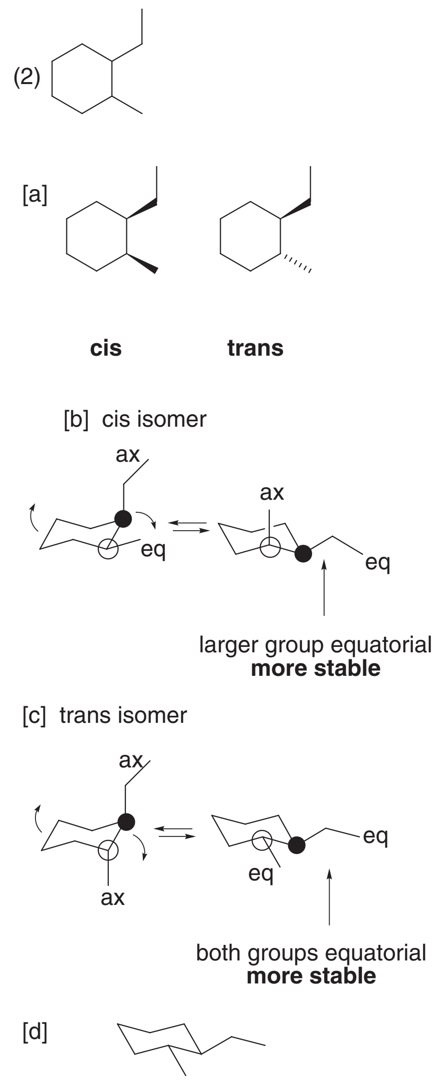
(3)



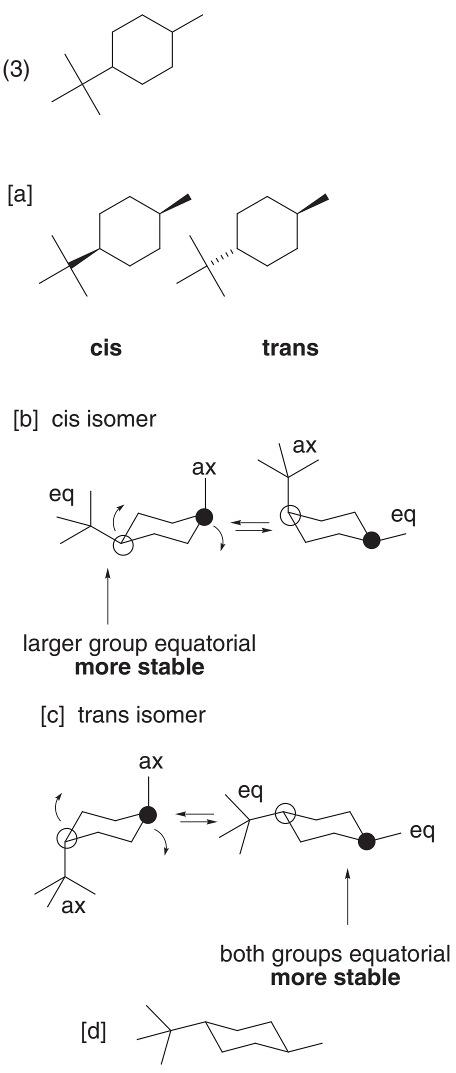
4.45 Un **isomero cis** ha due gruppi dalla **stessa parte** dell'anello. I due gruppi possono essere disegnati entrambi su sia entrambi giù. Viene rappresentata solo una possibilità. Un **isomero trans** ha un gruppo su una parte dell'anello ed uno dalla parte opposta. Ciascun gruppo può essere disegnato da ciascun lato. Viene rappresentata solo una possibilità.



The cis isomer is more stable than the trans since one conformer has both groups equatorial.



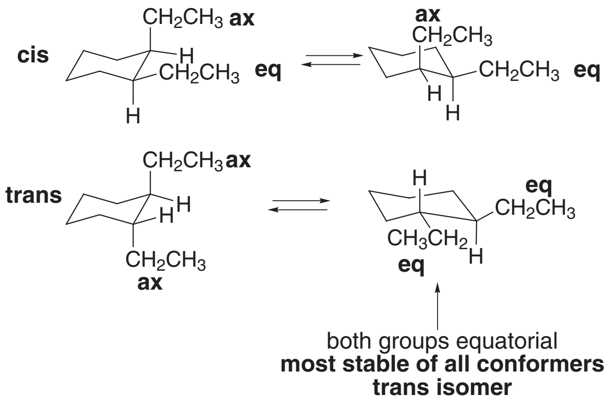
The trans isomer is more stable than the cis since one conformer has both groups equatorial.



The trans isomer is more stable than the cis since one conformer has both groups equatorial.

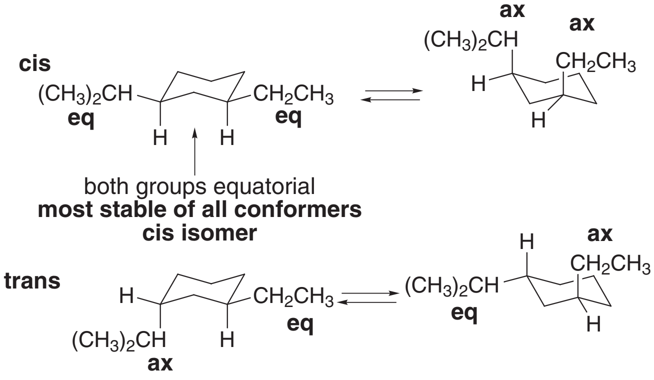
4.46 Confrontare gli isomeri disegnandoli nella conformazione a sedia. I sostituenti equatoriali sono più stabili. Confrontare le definizioni del problema 4.53.

(a) **1,2-diethylcyclohexane**



The trans isomer is more
stable than the cis isomer
because its more stable
conformer has two groups equatorial.

(b) **1-ethyl-3-isopropylcyclohexane**

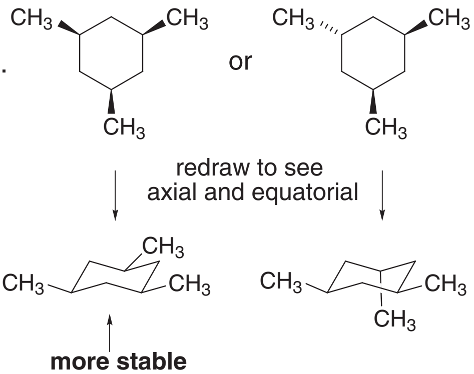


The cis isomer is more
stable than the trans isomer
because its more stable
conformer has two groups equatorial.

4.47

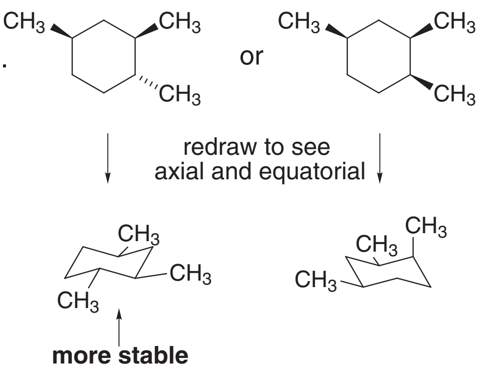
Only the more stable conformer of each compound is drawn.

a.



more stable
substituents on C1, C3, C5=
all equatorial

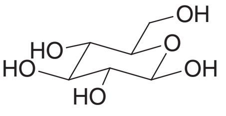
b.



more stable
can all be equatorial

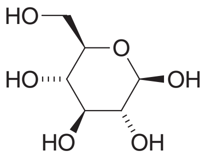
4.48

a.



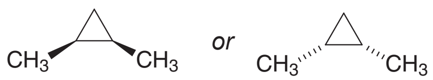
most stable
all groups are equatorial

b.



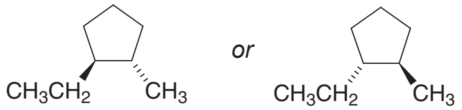
4.49 I cunei indicano gruppi “sopra” alla pagina, e i trattini sono “sotto” dietro alla pagina. I gruppi cis sono dalla stessa parte dell’anello, i gruppi trans da parti opposte.

***cis*-1,2-dimethylcyclopropane**



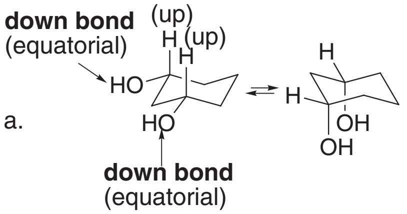
cis = same side of the ring
both groups on wedges or
both on dashes

***trans*-1-ethyl-2-methylcyclopentane**

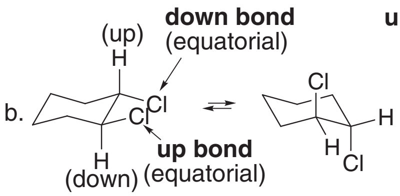


trans = opposite sides of the ring
one group on a wedge,
one group on a dash

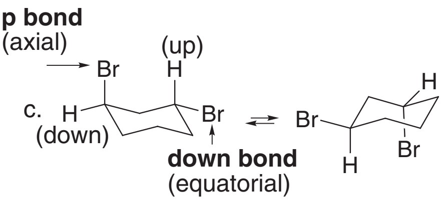
4.50 Per classificare un composto come isomero cis o trans, **classificare ogni gruppo diverso dall'idrogeno come su o giù. Gruppi dalla stessa parte = isomero cis, gruppi da parti opposte = isomero trans.**



both groups down =
cis isomer

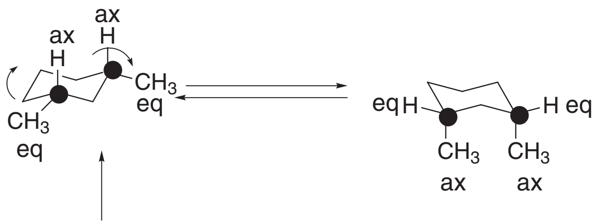


one group up, one down =
trans isomer



one group up, one down =
trans isomer

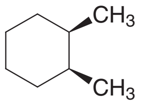
4.51



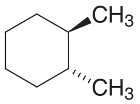
both groups equatorial
more stable

4.52

a.

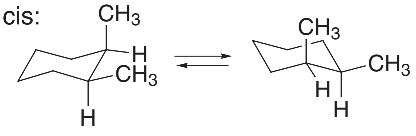


groups on same side
cis isomer



groups on opposite sides
trans isomer

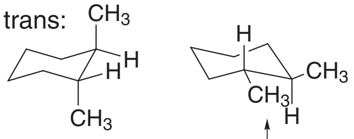
b.



two chair conformers for the **cis isomer**

Same stability since they are identical groups with one equatorial, one axial.

c.

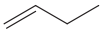


both groups equatorial
more stable
two chair conformers for the **trans isomer**

d. The **trans isomer is more stable** because it can have both methyl groups in the more roomy **equatorial** position.

4.53

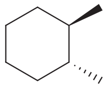
a.



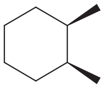
and

same molecular formula C_4H_8
different connectivity
constitutional isomers

b.

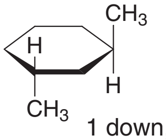


and

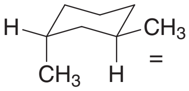


different arrangement in three dimensions
stereoisomers

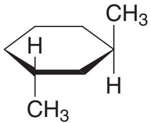
c.



and



=

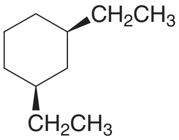


1 down, 1 up =
trans

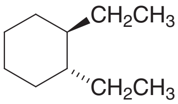
1 down, 1 up =
trans

same arrangement in three dimensions
identical

d.

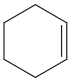


and

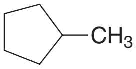


same molecular formula $C_{10}H_{20}$
different connectivity
constitutional isomers

e.



and

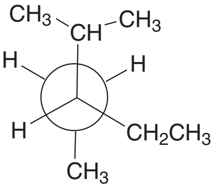


molecular formula: C_6H_{10}

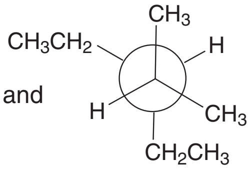
molecular formula: C_6H_{12}

different molecular formulas
not isomers

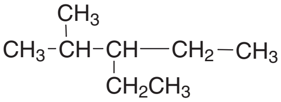
f.



and

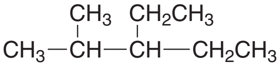


redraw



$$CH_3-\overset{\overset{CH_3}{|}}{CH}-\underset{\underset{CH_2CH_3}{|}}{CH}-CH_2-CH_3$$

3-ethyl-2-methylpentane

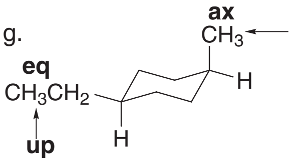


$$CH_3-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_2CH_3}{|}}{CH}-CH_2CH_3$$

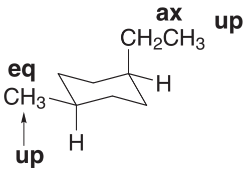
3-ethyl-2-methylpentane

same molecular formula
same name
identical molecules

g.

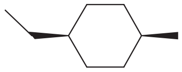


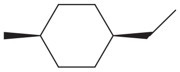
and



both up = **cis**

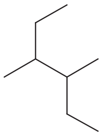
both up = **cis**



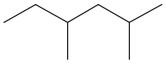


same arrangement in three dimensions
identical

h.



and

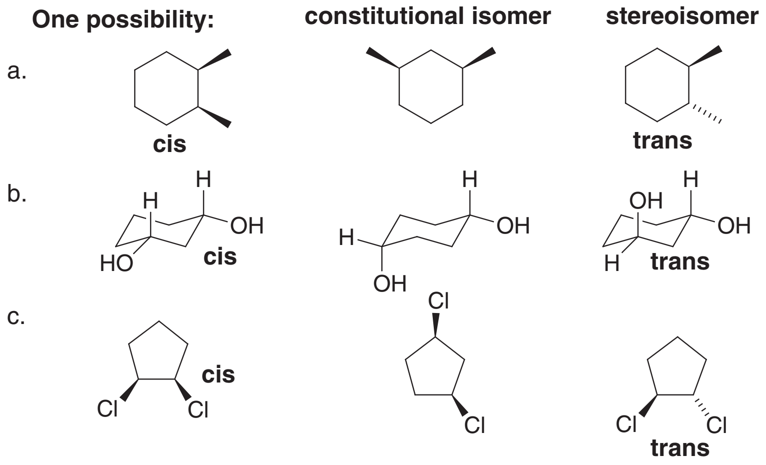


3,4-dimethylhexane

2,4-dimethylhexane

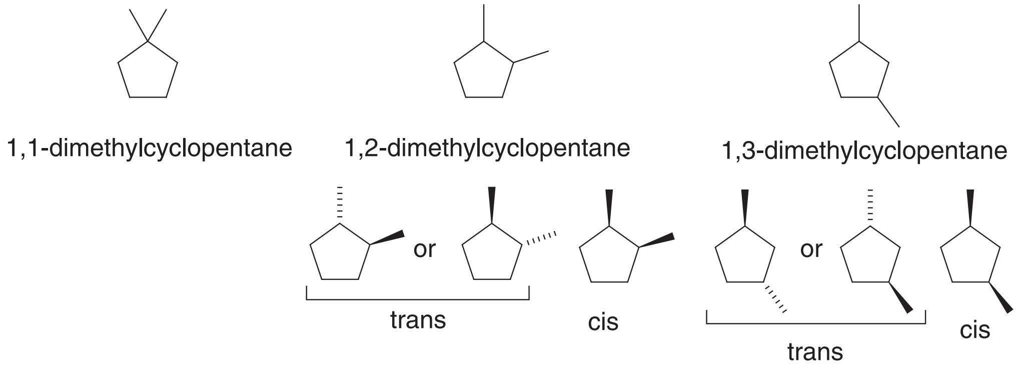
same molecular formula C_8H_{18}
different IUPAC names
constitutional isomers

4.54



4.55

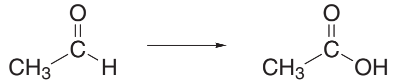
Three constitutional isomers of C_7H_{14}:



4.56 *L' ossidazione* provoca un *aumento* del numero di legami C–Z, o *in una diminuzione* del numero di legami C–H.

La riduzione provoca una *diminuzione* del numero di legami C–Z, o un *aumento* del numero di legami C–H.

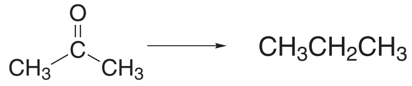
a.



$CH_3C(=O)H \longrightarrow CH_3C(=O)OH$

Decrease in the number of C–H bonds.
Increase in the number of C–O bonds.
Oxidation

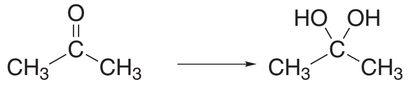
b.



$CH_3C(=O)CH_3 \longrightarrow CH_3CH_2CH_3$

Decrease in the number of C–O bonds.
Increase in the number of C–H bonds.
Reduction

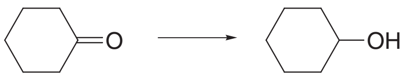
c.



$CH_3C(=O)CH_3 \longrightarrow CH_3C(OH)_2CH_3$

No change in the number of C–O or C-H bonds. **Neither**

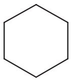
d.



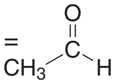
Decrease in the number of C–O bonds.
Increase in the number of C–H bonds.
Reduction

4.57 I prodotti della combustione di un idrocarburo sono sempre gli stessi: **CO_2 e H_2O.**

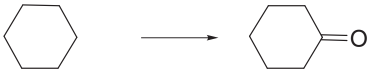
a. $CH_3CH_2CH_3 + 5\ O_2 \xrightarrow{\text{flame}} 3\ CO_2 + 4\ H_2O + \text{heat}$

b.  $+\ 9\ O_2 \xrightarrow{\text{flame}} 6\ CO_2 + 6\ H_2O + \text{heat}$

4.58 Usare le definizioni della risposta 4.56 per classificare le reazioni.

a. CH_3CHO =  $\longrightarrow CH_3CH_2OH$

Decrease in the number of C–O bonds. **Reduction**

b. 

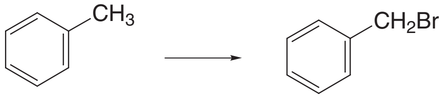
Increase in the number of C–O bonds. **Oxidation**

c. $CH_2{=}CH_2 \longrightarrow HOCH_2CH_2OH$

Two new C–O bonds. **Oxidation**

d. $CH_2{=}CH_2 \longrightarrow H{-}C{\equiv}C{-}H$

Decrease in the number of C–H bonds. **Oxidation**

e. 

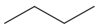
Increase in the number of C–Z bonds. **Oxidation**

f. $CH_3CH_2OH \longrightarrow CH_2{=}CH_2$

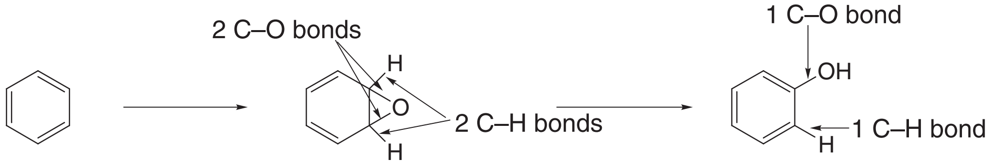
Loss of one C–O bond *and* one C–H bond. **Neither**

4.59 Usare la regola della risposta 4.57.

a. $CH_3CH_2CH_2CH_2CH(CH_3)_2 \xrightarrow[11\ O_2]{\text{flame}} 7\ CO_2 + 8\ H_2O + \text{heat}$

b.  $\xrightarrow[(13/2)\ O_2]{\text{flame}} 4\ CO_2 + 5\ H_2O + \text{heat}$

4.60

a. 

benzene **an arene oxide** **phenol**

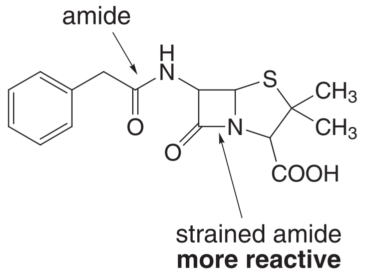
increase in C–O bonds
oxidation reaction

loss of 1 C–O bond,
loss of 1 C–H bond
neither

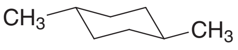
b. Phenol is more water soluble than benzene because it is **polar (contains an O–H group) and can hydrogen bond with water,** whereas benzene is nonpolar and cannot hydrogen bond.

4.61 L'ammide del ciclo a quattro termini ha angoli di legame a 90° che originano tensione angolare, e quindi è più reattiva.

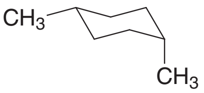
penicillin G



4.62



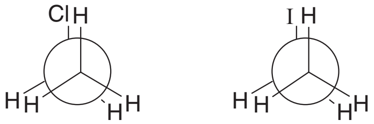
trans-1,4-dimethylcyclohexane
more symmetrical
better packing
higher melting point



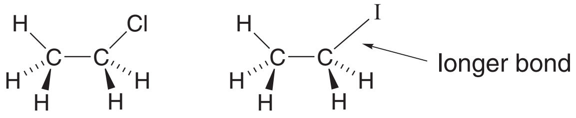
cis-1,4-dimethylcyclohexane

4.63

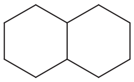
Example:



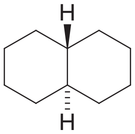
Although I is a much bigger atom than Cl, the C–I bond is also much longer than the C–Cl bond. As a result the eclipsing interaction of the H and I atoms is not very much different from the H,Cl eclipsing interaction in magnitude.



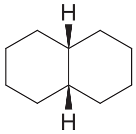
4.64



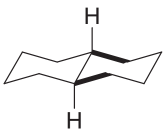
decalin



trans-decalin

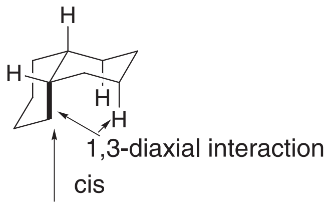


cis-decalin



trans

The trans isomer is more stable since the carbon groups at the ring junction are both in the favorable equatorial position.

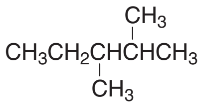


This bond is axial, creating unfavorable 1,3-diaxial interactions.

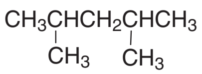
Capitolo 5

5.1

5.2 **Gli isomeri costituzionali** hanno atomi legati d atomi diversi.
Gli stereoisomeri differiscono nella disposizione tridimensionale degli atomi.

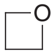
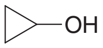
a.

$CH_3CH_2\underset{CH_3}{C}H\overset{CH_3}{C}HCH_3$

and


$CH_3\underset{CH_3}{C}HCH_2\underset{CH_3}{C}HCH_3$

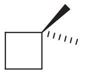
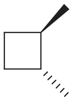
2,3-dimethylpentane 2,4-dimethylpentane

different connectivity of atoms
different names
constitutional isomers

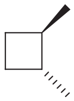
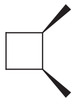
b.

and


4 membered ring 3 membered ring

different connectivity of atoms
constitutional isomers

c.

and


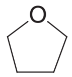
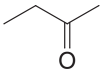
different connectivity of atoms
constitutional isomers

d.

and


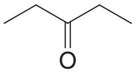
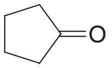
trans isomer cis isomer

Both are 1,2-dimethylcyclobutane,
but the CH_3 groups are oriented differently.
stereoisomers

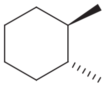
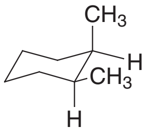
5.3 Usare le definizioni della risposta 5.1.

a.

and


same molecular formula C_4H_8O
different connectivity
constitutional isomers

b.

and


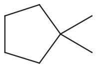
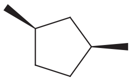
$C_5H_{10}O$ C_5H_8O
different molecular formulas
not isomers

c.

and


one up, one down
trans

both up
cis

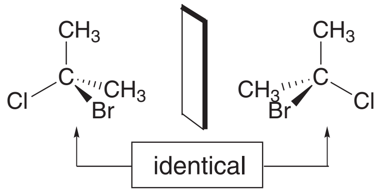
Both compounds are
1,2-dimethylcyclohexane.
one cis, one trans = **stereoisomers**

d.

and


same molecular formula C_7H_{14}
different connectivity
constitutional isomers

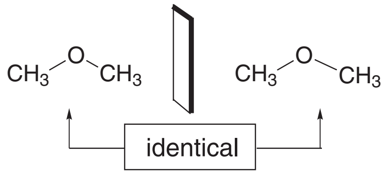
5.4 Disegnare l’immagine speculare di ogni molecola disegnando un piano di simmetria e disegnare la molecola riflessa. **Una molecola chirale è una molecola che non è sovrapponibile alla sua immagine speculare**. Una molecola con un centro stereogenico è sempre chirale. Una molecola con nessun centro stereogenico non è chirale (in generale).

a.



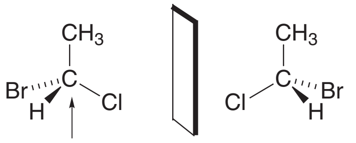
achiral molecule

c.



achiral molecule

b.

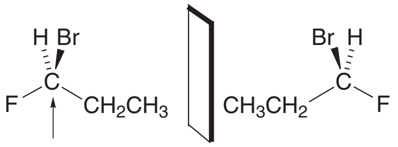


stereogenic center

nonsuperimposable mirror images

chiral molecules

d.



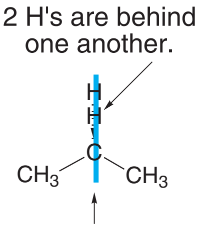
stereogenic center

nonsuperimposable mirror images

chiral molecules

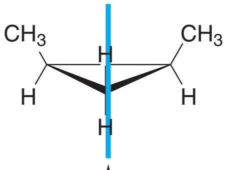
5.5 Il piano di simmetria divide la molecola in due metà identiche.

a.



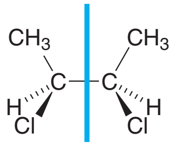
one possible plane of symmetry

b.



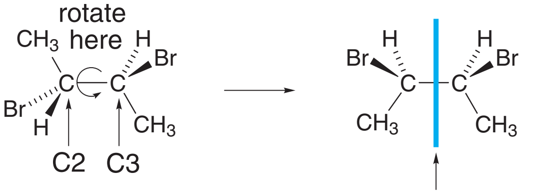
plane of symmetry

c.



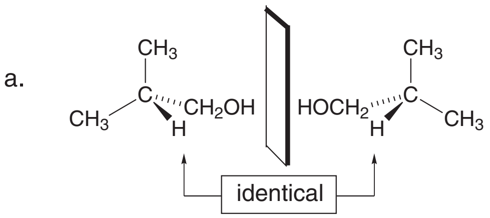
plane of symmetry

5.6 Ruotare attorno al legame C–C centrale così che i gruppi Br siano eclissati.



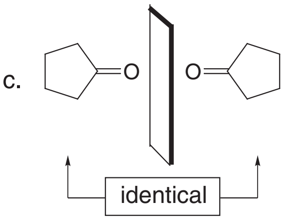
plane of symmetry

5.6 Usare le definizioni della risposta 5.3.



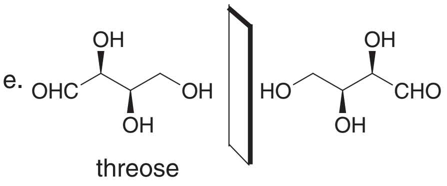
identical

achiral



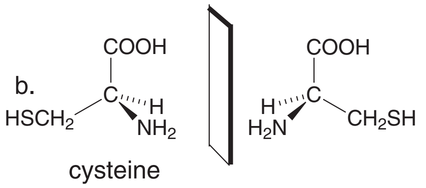
identical

achiral



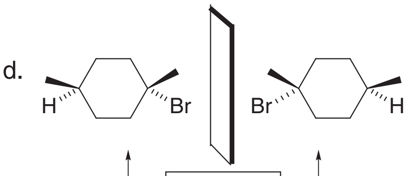
threose

chiral



cysteine

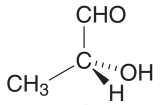
chiral



identical

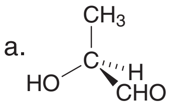
achiral

5.7



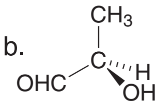
A

R isomer



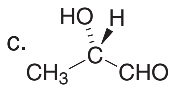
S

enantiomer



R

identical

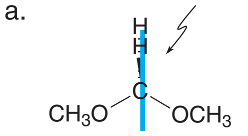


S

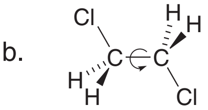
enantiomer

5.8 Il piano di simmetria divide la molecola in **due metà identiche**.

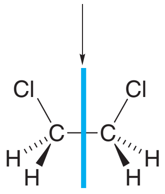
2 H's are aligned.

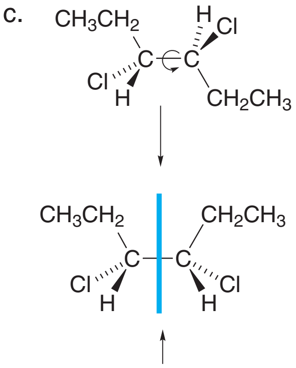


The plane of symmetry is drawn through the hydrogen atoms.

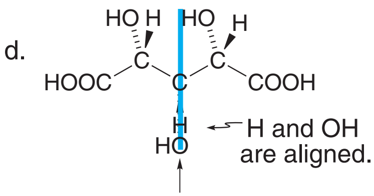


A plane of symmetry is present in the plane of the page; or



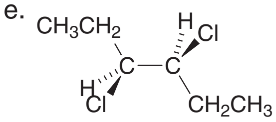


plane of symmetry

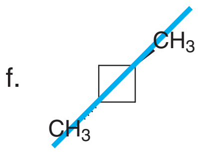


H and OH are aligned.

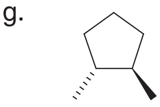
plane of symmetry



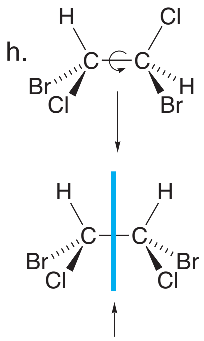
no plane of symmetry



The plane of symmetry bisects the molecule.

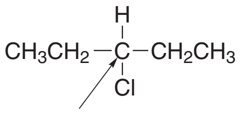


no plane of symmetry



plane of symmetry

5.9 Per individuare un centro stereogenico, non considerare:
Tutti i carboni con 2 o più H, tutti gli atomi ibridi *sp* e *sp*^{2}, e tutti gli eteroatomi.
Successivamente valutare tutti gli atomi rimanenti: uno stereocentro tetraedrico presenta un carbonio legato a **quattro gruppi differenti**.

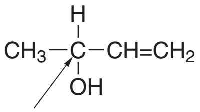
a.


$CH_3CH_2-\overset{H}{\underset{Cl}{C}}-CH_2CH_3$

bonded to 2 identical ethyl groups
0 stereogenic centers

b. $(CH_3)_3CH$

0 stereogenic centers

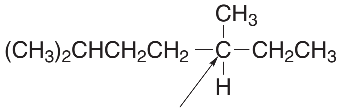
c.


$CH_3-\overset{H}{\underset{OH}{C}}-CH{=}CH_2$

This C is bonded to 4 different groups.
1 stereogenic center

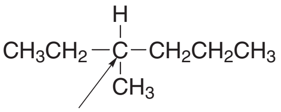
d. $CH_3CH_2CH_2OH$

0 stereogenic centers

e.


$(CH_3)_2CHCH_2CH_2-\overset{CH_3}{\underset{H}{C}}-CH_2CH_3$

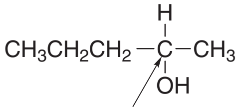
This C is bonded to 4 different groups.
1 stereogenic center

f.


$CH_3CH_2-\overset{H}{\underset{CH_3}{C}}-CH_2CH_2CH_3$

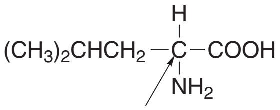
This C is bonded to 4 different groups.
1 stereogenic center

5.10 Usare i suggerimenti della risposta 5.6 per individuare i centri stereogenici.

a.


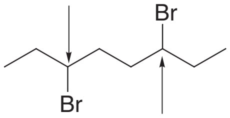
$CH_3CH_2CH_2-\overset{H}{\underset{OH}{C}}-CH_3$

stereogenic center

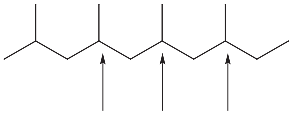
b.


$(CH_3)_2CHCH_2-\overset{H}{\underset{NH_2}{C}}-COOH$

stereogenic center

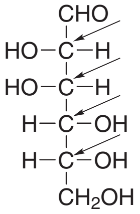
c.


Both C's bonded to 4 different groups.
2 stereogenic centers

d.


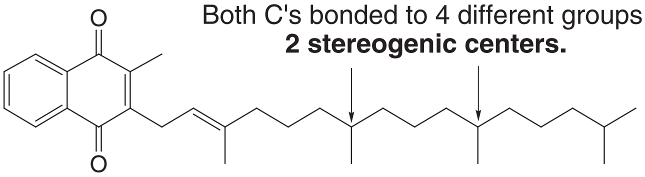
3 C's bonded to 4 different groups.
3 stereogenic centers

5.11 Usare i suggerimenti della risposta 5.6 per individuare i centri stereogenici.

a.


mannose

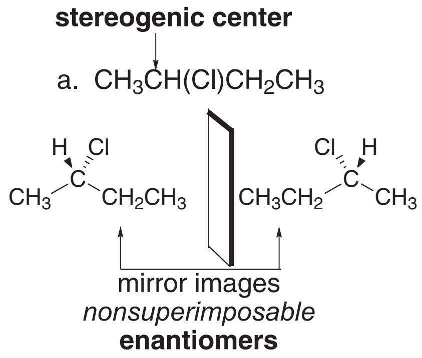
4 C's bonded to 4 different groups:
4 stereogenic centers.

b.


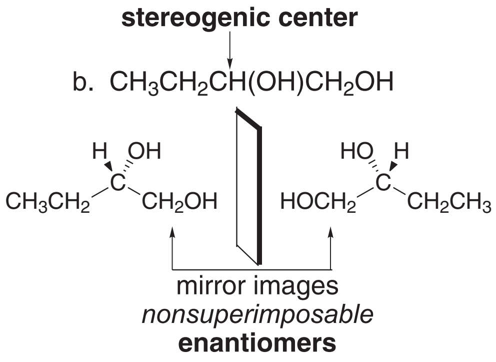
vitamin K_1

Both C's bonded to 4 different groups:
2 stereogenic centers.

5.12 Individuare il C legato a 4 gruppi differenti in ogni molecola. Al centro stereogenico, disegnare due legami nel piano della pagina, uno verso l'osservatore (un cuneo) ed uno dietro (tratteggiato). Successivamente disegnare l'immagine speculare (enantiomero).

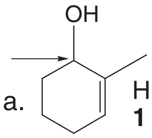


mirror images
nonsuperimposable
enantiomers

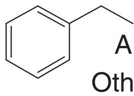


mirror images
nonsuperimposable
enantiomers

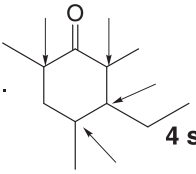
5.13 Usare i suggerimenti della risposta 5.6 per individuare i centri stereogenici..

a.


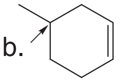
C bonded to
H, OH, 2 different C's:
1 stereogenic center

c.


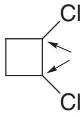
All ring C's are *sp*^{2}.
Other C's have ≥ 2 H's.
no stereogenic centers

e.


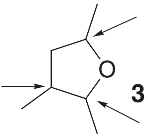
4 C's bonded to 4
different groups:
4 stereogenic centers

b.


C bonded to
H and 3 different C's:
1 stereogenic center

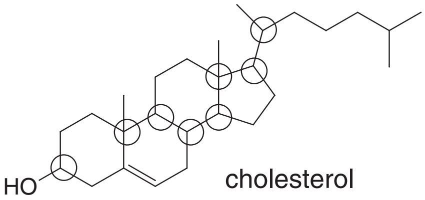
d.


Each labeled C
is bonded to:
H, Cl, CH_2, CHCl:
2 stereogenic centers

f.


3 C's bonded to 4
different groups:
3 stereogenic centers

5.14



cholesterol

All stereogenic C's are circled. Each C is *sp*^{3} hybridized and bonded to 4 different groups.

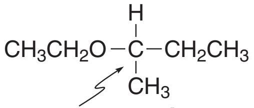
5.15 Usare i suggerimenti della risposta 5.9 per assegnare i centri stereogenici.

a. $CH_3CH_2CH_2CH_2CH_2CH_3$

All C's have 2 or more H's.

0 stereogenic centers

b.



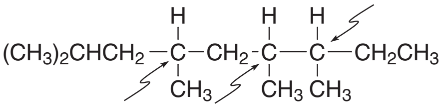
$\mathrm{CH_3CH_2O{-}\overset{H}{\underset{CH_3}{C}}{-}CH_2CH_3}$

1 stereogenic center

c. $(CH_3)_2CHCH(OH)CH(CH_3)_2$

0 stereogenic centers

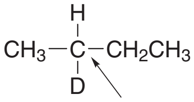
d.



$\mathrm{(CH_3)_2CHCH_2{-}\overset{H}{\underset{CH_3}{C}}{-}CH_2{-}\overset{H}{\underset{CH_3}{C}}{-}\overset{H}{\underset{CH_3}{C}}{-}CH_2CH_3}$

3 stereogenic centers.

e.

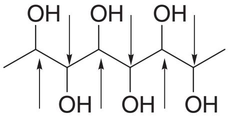


$\mathrm{CH_3{-}\overset{H}{\underset{D}{C}}{-}CH_2CH_3}$

bonded to 4 different groups

1 stereogenic center

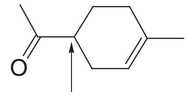
f.



Each labeled C bonded to 4 different groups =

6 stereogenic centers.

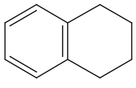
g.



bonded to 4 different groups

1 stereogenic center

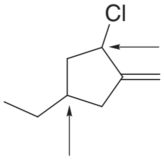
h.



All C's have 2 or more H's, or are sp^2 hybridized.

0 stereogenic centers

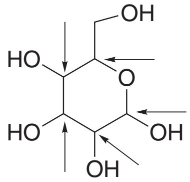
i.



Each bonded to 4 different groups =

2 stereogenic centers.

j.

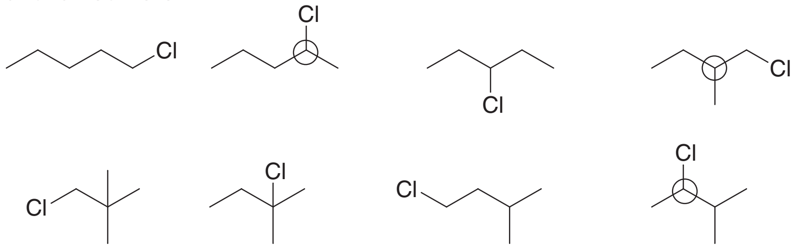


Each labeled C bonded to 4 different groups =

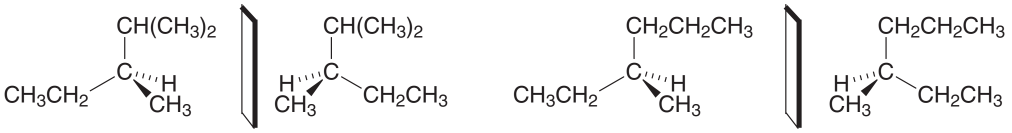
5 stereogenic centers.

5.16 I centri stereogenici sono cerchiati.

Eight constitutional isomers:

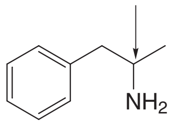


5.17

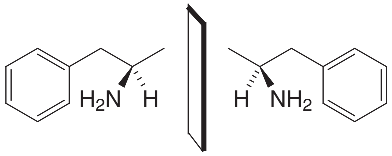


5.18

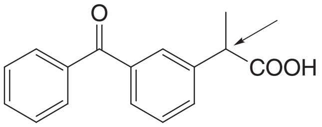
a.



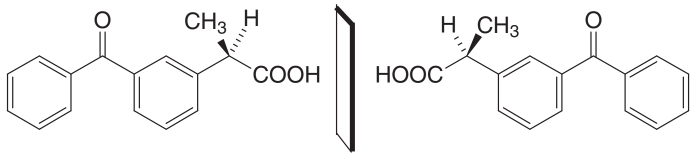
amphetamine



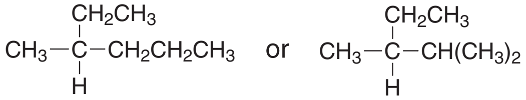
b.



ketoprofen



5.19



$$CH_3-\underset{H}{\overset{CH_2CH_3}{C}}-CH_2CH_2CH_3 \quad \text{or} \quad CH_3-\underset{H}{\overset{CH_2CH_3}{C}}-CH(CH_3)_2$$

5.20 Assegnare la priorità attraverso i numeri atomici: atomi con maggior numero atomico hanno priorità maggiore. Se due atomi sono uguali, osservare gli atomi a cui sono legati ed assegnare la priorità in base al numero atomico di questi atomi.

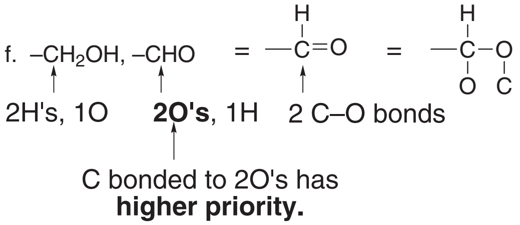
a. $-CH_3$, $-CH_2CH_3$
↑
higher priority

b. –I, –Br
↑
higher priority

c. –H, –D
↑
higher mass
higher priority

d. $-CH_2Br$, $-CH_2CH_2Br$
↑
higher priority

e. $-CH_2CH_2Cl$, $-CH_2CH(CH_3)_2$
↑
higher priority



$$\text{f. } -CH_2OH,\ -CHO \quad = \quad -\overset{H}{\overset{|}{C}}{=}O \quad = \quad -\underset{O}{\overset{H}{C}}-\underset{C}{O}$$

2H's, 1O ↑ **2O's**, 1H ↑ 2 C–O bonds ↑

C bonded to 2O's has **higher priority.**

5.21 Ordinare secondo la priorità decrescente. Minor numero atomico = minore priorità.

Lowest priority = 4, Highest priority = 1

a.

		priority
$-COOH$	C = second lowest atomic number	**3**
$-H$,	H = lowest atomic number	**4**
$-NH_2$,	N = second highest atomic number	**2**
$-OH$	O = highest atomic number	**1**

decreasing priority: $-OH$, $-NH_2$, $-COOH$, $-H$

b.

		priority
$-H$,	H = lowest atomic number	**4**
$-CH_3$,	C bonded to 3H's	**3**
$-Cl$,	Cl = highest atomic number	**1**
$-CH_2Cl$	C bonded to 2H's + **1 Cl**	**2**

decreasing priority: $-Cl$, $-CH_2Cl$, $-CH_3$, $-H$

c.

		priority
$-CH_2CH_3$,	C bonded to 2H's + **1C**	**2**
$-CH_3$,	C bonded to 3H's	**3**
$-H$,	H = lowest atomic number	**4**
$-CH(CH_3)_2$	C bonded to 1H + **2C's**	**1**

decreasing priority: $-CH(CH_3)_2$, $-CH_2CH_3$, $-CH_3$, $-H$

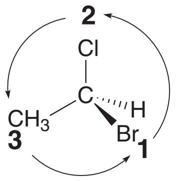
d.

		priority
$-CH=CH_2$,	C bonded to 1H + **2C's**	**2**
$-CH_3$,	C bonded to 3H's	**3**
$-C\equiv CH$,	C bonded to **3C's**	**1**
$-H$	H = lowest atomic number	**4**

decreasing priority: $-C\equiv CH$, $-CH=CH_2$, $-CH_3$, $-H$

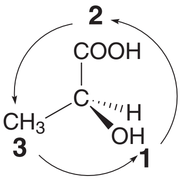
5.22 Per assegnare *R* o *S* ad una molecola, prima ordinare i gruppi. Il gruppo a priorità più bassa deve essere orientato dietro la pagina. Se tracciando un cerchio da (1) → (2) → (3), si procede in direzione oraria, il centro stereogenico sarà chiamato *R*; se il cerchio è in direzione antioraria, è chiamato *S*.

a.



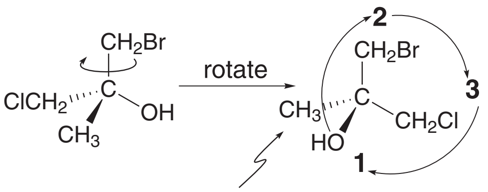
counterclockwise
***S* isomer**

b.



counterclockwise
***S* isomer**

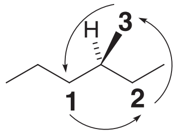
c.



lowest priority group now back

clockwise
***R* isomer**

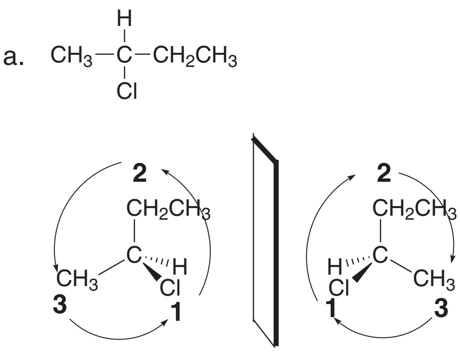
d.



counterclockwise
***S* isomer**

5.23

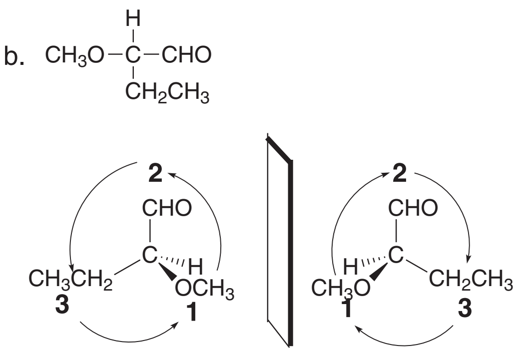
a.



counterclockwise
***S* isomer**

clockwise
***R* isomer**

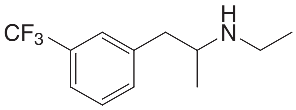
b.



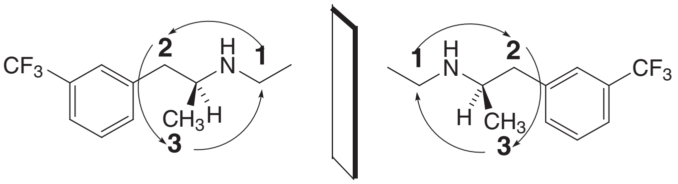
counterclockwise
***S* isomer**

clockwise
***R* isomer**

5.24



fenfluramine



counterclockwise
S isomer
dexfenfluramine

counterclockwise
R isomer

5.25 Assegnare la priorità in base alle regole della risposta 5.20.

a. –OH, –NH$_2$
↑
higher atomic number
higher priority

b. –CD$_3$, –CH$_3$
↑
D higher mass than H
higher priority

c. –CH(CH$_3$)$_2$, –CH$_2$OH
↑
C bonded to O
higher priority

d. –CH$_2$Cl, –CH$_2$CH$_2$CH$_2$Br
↑
C bonded to Cl
higher priority

e. –CHO, –COOH
↑
C has 3 bonds to O
higher priority

f. –CH$_2$NH$_2$, –NHCH$_3$
↑
higher atomic number
higher priority

5.26 Assegnare la priorità in base alle regole della risposta 5.20.

a. –F > –OH > –NH$_2$ > –CH$_3$

b. –(CH$_2$)$_3$CH$_3$ > –CH$_2$CH$_2$CH$_3$ > –CH$_2$CH$_3$ > –CH$_3$

c. –NH$_2$ > –CH$_2$NHCH$_3$ > –CH$_2$NH$_2$ > –CH$_3$

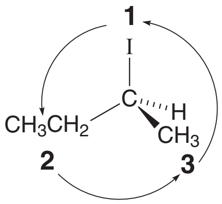
d. –COOH > –CHO > –CH$_2$OH > –H

e. –Cl > –SH > –OH > –CH$_3$

f. –C≡CH > –CH=CH$_2$ > –CH(CH$_3$)$_2$ > –CH$_2$CH$_3$

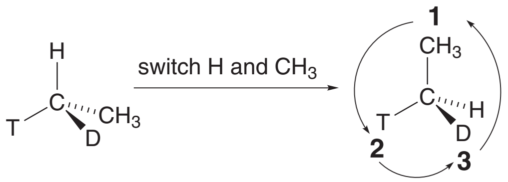
5.27 Usare le regole della risposta 5.22 per assegnare *R* o *S* ad ogni centro stereogenico.

a.



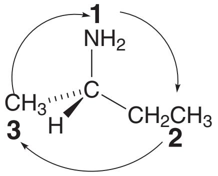
counterclockwise
S isomer

c.



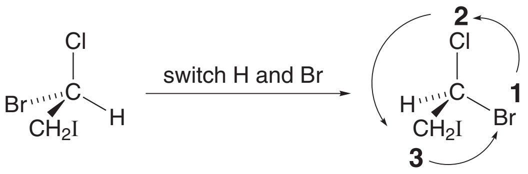
counterclockwise
It looks like an *S* isomer, but we must reverse the answer, *S* to *R*.
***R* isomer**

b.



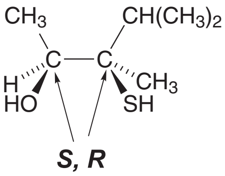
clockwise, but H in front
***S* isomer**

d.

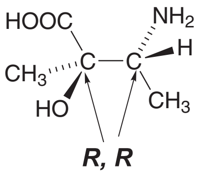


counterclockwise
It looks like an *S* isomer, but we must reverse the answer, *S* to *R*.
***R* isomer**

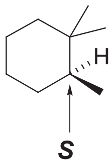
e.



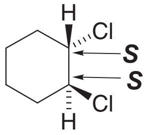
f.



g.

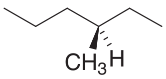


h.

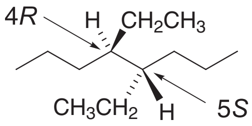


5.28

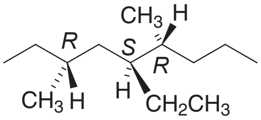
a. (3*R*)-3-methylhexane



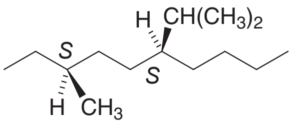
b. (4*R*,5*S*)-4,5-diethyloctane



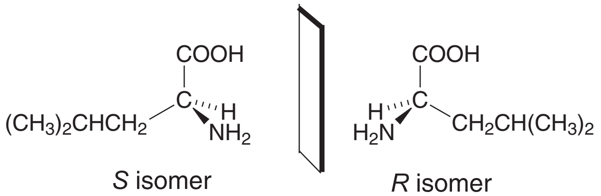
c. (3*R*,5*S*,6*R*)-5-ethyl-3,6-dimethylnonane



d. (3*S*,6*S*)-6-isopropyl-3-methyldecane



5.29 I due enantiomeri dell’ammino acido leucina.

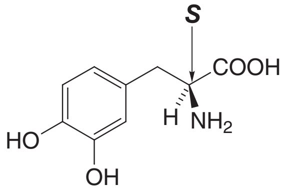


S isomer
naturally occurring

R isomer

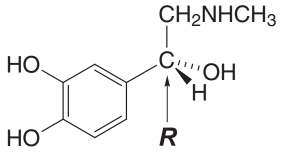
5.30

a.



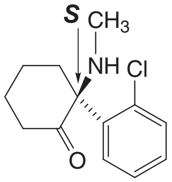
L-dopa

b.



adrenaline

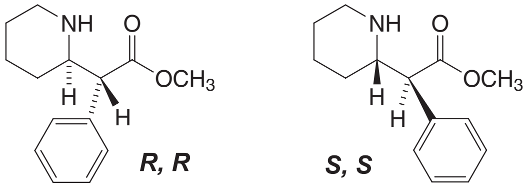
c.



ketamine

5.31

methylphenidate



5.32

Massimo numero di stereoisomeri = 2^n dove n = numero di centri stereogenici.

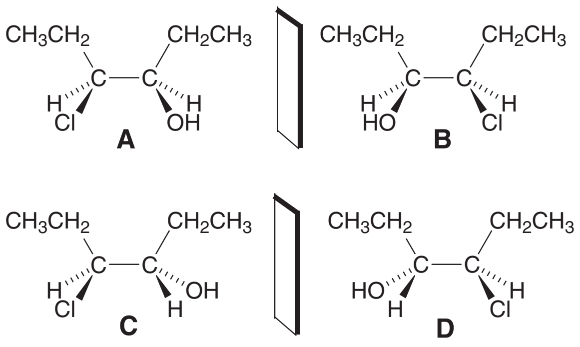
3 stereogenic centers
$2^3 = 8$ stereoisomers

8 stereogenic centers
$2^8 = 256$ stereoisomers

5.33

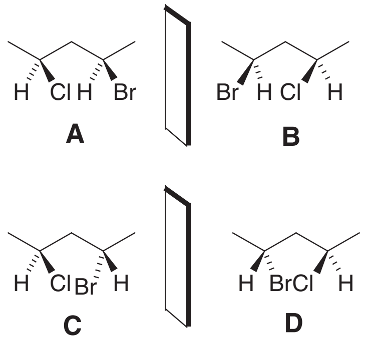
a. $CH_3CH_2CH(Cl)CH(OH)CH_2CH_3$

2 stereogenic centers = 4 stereoisomers



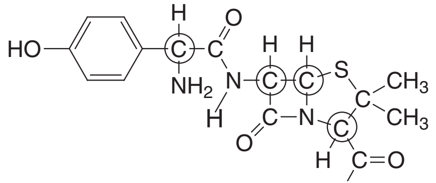
b. $CH_3CH(Br)CH_2CH(Cl)CH_3$.

2 stereogenic centers = 4 stereoisomers



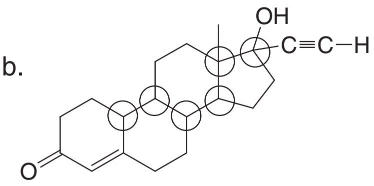
5.34

a.



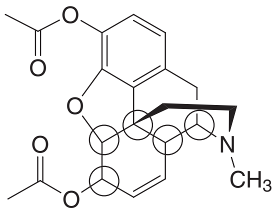
amoxicillin

b.



norethindrone

c.



heroin

5.35

a. $CH_3CH(OH)CH(OH)CH_2CH_3$

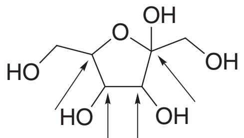
2 stereogenic centers

2^2 = 4 possible stereoisomers

b. $CH_3CH_2CH_2CH(CH_3)_2$

0 stereogenic centers

c.

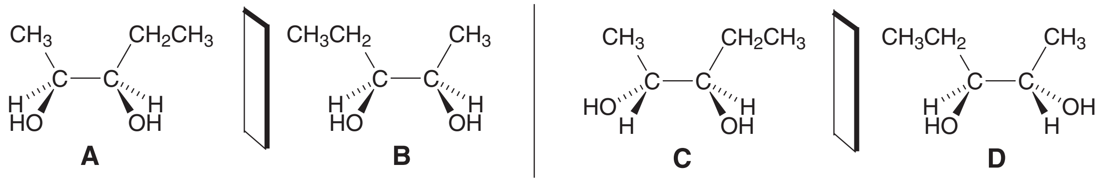


4 stereogenic centers

2^4 = 16 possible stereoisomers

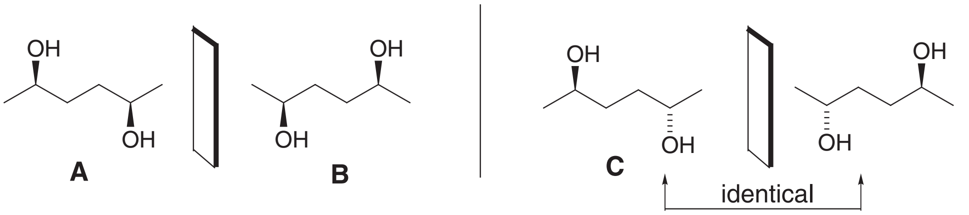
5.36

a. $CH_3CH(OH)CH(OH)CH_2CH_3$



Pairs of enantiomers: **A** and **B**, **C** and **D**.
Pairs of diastereomers: **A** and **C**, **A** and **D**, **B** and **C**, **B** and **D**.

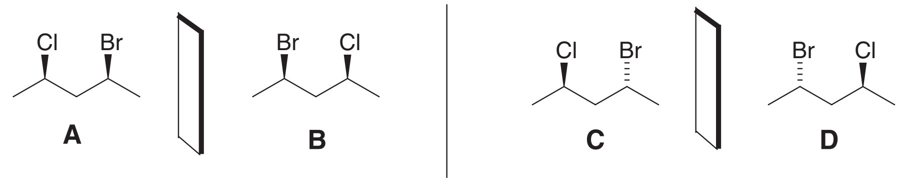
b. $CH_3CH(OH)CH_2CH_2CH(OH)CH_3$



meso compound

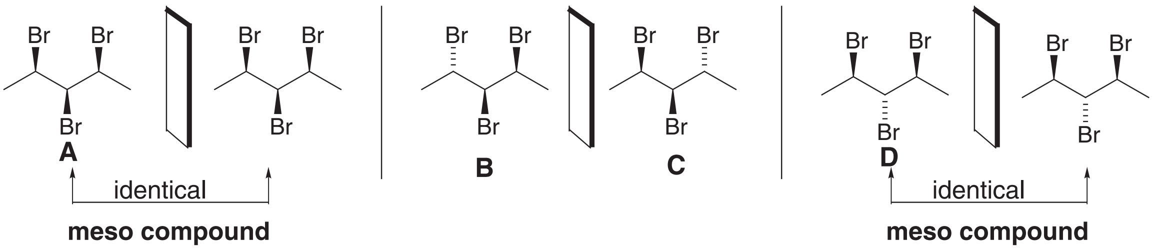
Pair of enantiomers: **A** and **B**.
Pairs of diastereomers: **A** and **C**, **B** and **C**.

c. $CH_3CH(Cl)CH_2CH(Br)CH_3$



Pairs of enantiomers: **A** and **B**, **C** and **D**.
Pairs of diastereomers: **A** and **C**, **A** and **D**, **B** and **C**, **B** and **D**.

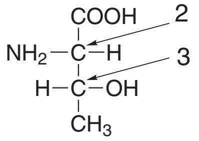
d. $CH_3CH(Br)CH(Br)CH(Br)CH_3$



Pair of enantiomers: **B** and **C**.
Pairs of diastereomers: **A** and **B**, **A** and **C**, **A** and **D**, **B** and **D**, **C** and **D**

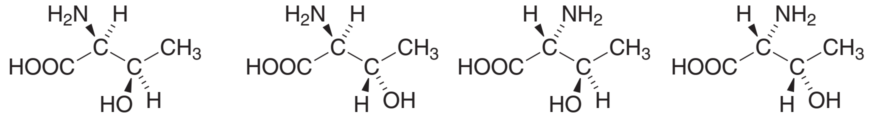
5.37

a.



threonine

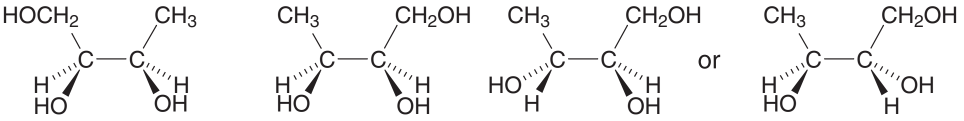
b. and c.



2*S*,3*R* naturally occurring   2*S*,3*S*   2*R*,3*R*   2*R*,3*S*

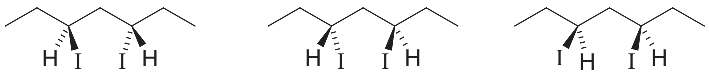
5.38

a.



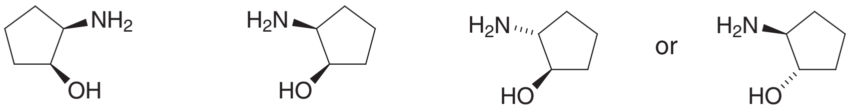
enantiomer   diastereomer   or   diastereomer

b.



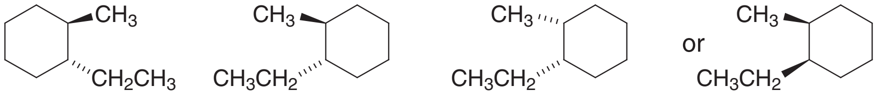
enantiomer   diastereomer

c.



enantiomer   diastereomer   or   diastereomer

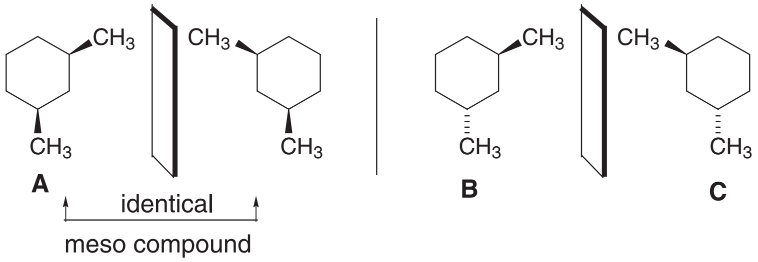
d.



enantiomer   diastereomer   or   diastereomer

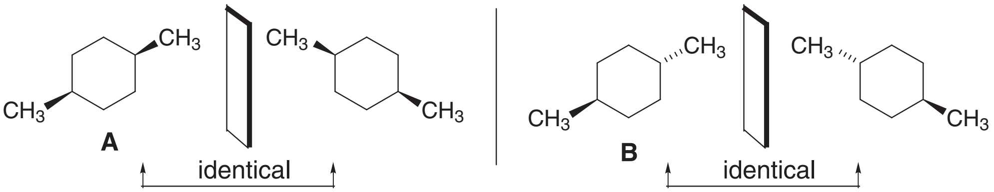
5.39

a.



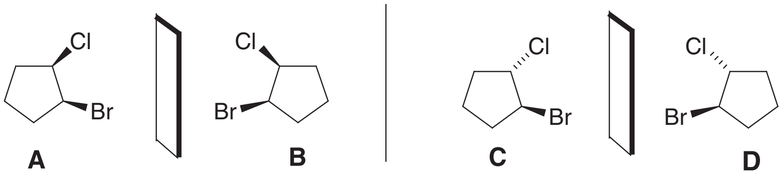
Pair of enantiomers: **B** and **C**.
Pairs of diastereomers: **A** and **B**, **A** and **C**.

b.



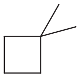
Pair of diastereomers: **A** and **B**.

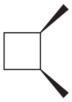
c.

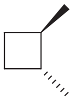


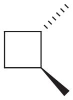
Pairs of enantiomers: **A** and **B**, **C** and **D**.
Pairs of diastereomers: **A** and **C**, **A** and **D**, **B** and **C**, **B** and **D**.

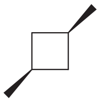
5.40

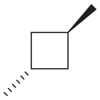

achiral


achiral


chiral


chiral

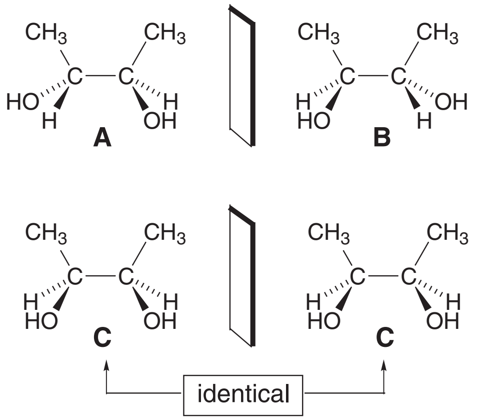

achiral


achiral

5.41

a. $CH_3CH(OH)CH(OH)CH_3$

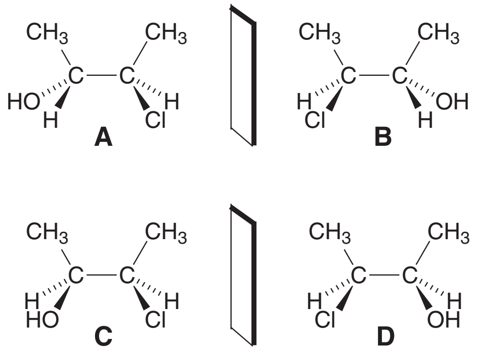
2 stereogenic centers = 4 possible stereoisomers



C is a meso compound.
A and **B** are enantiomers.
Pairs of diastereomers: **A** and **C**, **B** and **C**.

b. $CH_3CH(OH)CH(Cl)CH_3$.

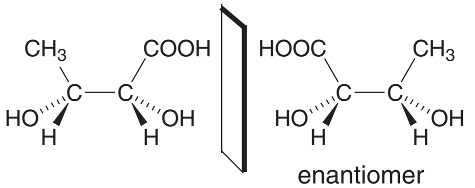
2 stereogenic centers = 4 possible stereoisomers



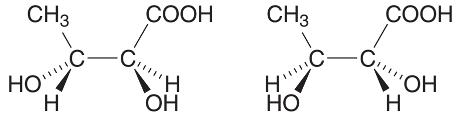
Pairs of enantiomers: **A** and **B**, **C** and **D**.
Pairs of diastereomers: **A** and **C**, **A** and **D**,
B and **C**, **B** and **D**.

5.42 Un **enantiomero** è uno stereoisomero che non è sovrapponibile alla sua immagine speculare. Un **diastereomero** è uno stereoisomero che non è un immagine speculare.

a.

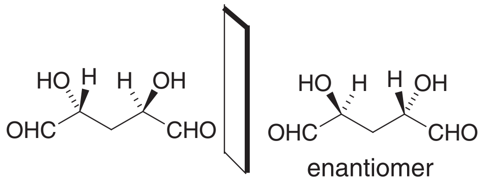


enantiomer

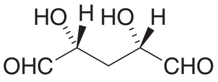


two diastereomers

b.



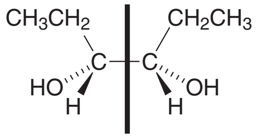
enantiomer



diastereomer

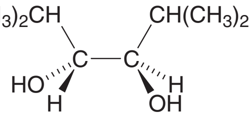
5.43 Un composto meso deve avere almeno 2 centri stereogenici ed un piano di simmetria. E' possibile che si debba fare una rotazione attorno al legame C–C per individuare il piano di simmetria chiaramente.

a.



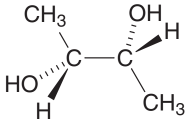
2 stereogenic centers
plane of symmetry
meso compound

b.



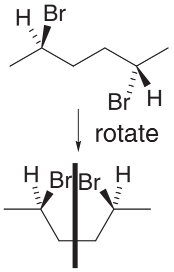
2 stereogenic centers
no plane of symmetry
not a meso compound

c.



2 stereogenic centers
no plane of symmetry
not a meso compound

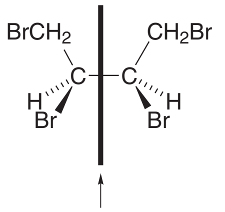
d.



2 stereogenic centers
plane of symmetry
meso compound

5.44 **A** presenta due centri stereogenici ed un piano di simmetria, che lo rende un composto meso achirale. Poiché è sovrapponibile alla sua immagine speculare, non presenta enantiomeri. **B** presenta un solo centro stereogenico. I suoi due possibili stereoisomeri sono una coppia di enantiomeri, ma non diastereomeri.

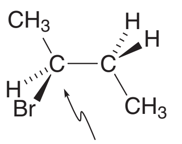
A



plane of symmetry

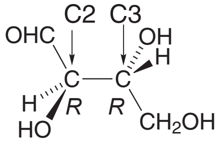
an achiral compound

B



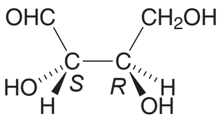
only one stereogenic center
no diastereomer

5.45



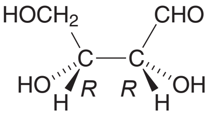
D-erythrose
2*R*,3*R*

a.



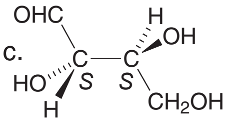
2*S*,3*R*
diastereomer

b.



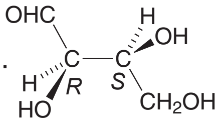
2*R*,3*R*
identical

c.



2*S*,3*S*
enantiomer

d.

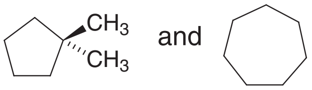


2*R*,3*S*
diastereomer

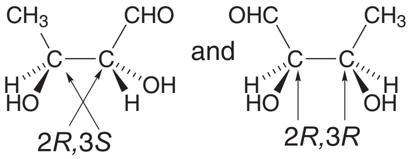
5.46

a.

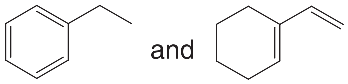

enantiomers

b.


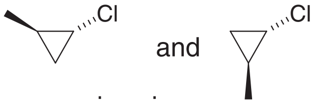
same molecular formula
different connectivity
constitutional isomers

c.


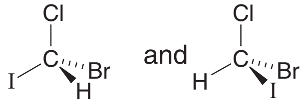
one different configuration
diastereomers

d.


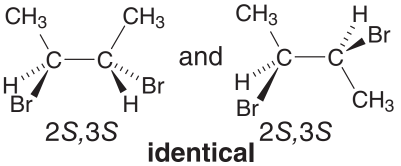
different molecular formulas
not isomers

e.


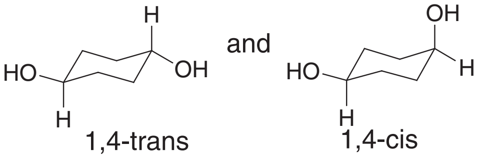
mirror images
not superimposable
enantiomers

f.


enantiomers

g.


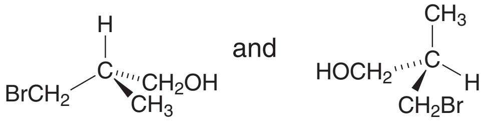
identical

h.


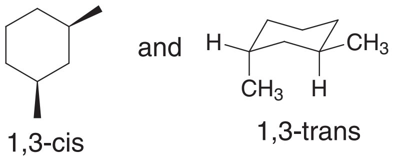
diastereomers

i.

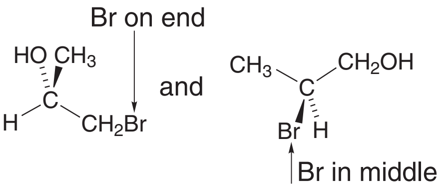

6 H's 12 H's
different molecular formulas
not isomers

j.


enantiomers

k.


diastereomers

l.


different connectivity
constitutional isomers

5.47 L' enantiomero deve avere configurazioni *R,S* esattamente opposte. Diastereomeri con due centri stereogenici hanno un centro con configurazione uguale ed uno diverso.

If a compound is ***R,S:***

Its enantiomer is: ***S,R*** ← Exact opposite: *R* and *S* interchanged.

Its diastereomers are: ***R,R* and *S,S*** ← One designation remains the same, the other changes.

5.48 L' enantiomero deve avere le configurazioni *R,S* esattamente opposte. Per i diastereomeri, almeno una delle configurazioni *R,S* è la stessa, ma non tutte.

a. (2*R*,3*S*)-2,3-hexanediol and (2*R*,3*R*)-2,3-hexanediol

One changes; one remains the same:
diastereomers

b. (2*R*,3*R*)-2,3-hexanediol and (2*S*,3*S*)-2,3-hexanediol

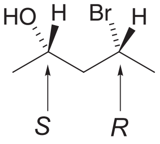
Both *R*'s change to *S*'s:
enantiomers

c. (2*R*,3*S*,4*R*)-2,3,4-hexanetriol and (2*S*,3*R*,4*R*)-2,3,4-hexanetriol

Two change; one remains the same:
diastereomers

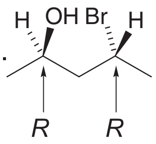
5.49 Per decidere la relazione fra i composti, indicare tutti i centri stereogenici.

- Molecole **identiche** avranno le stesse configurazioni *R,S* .
- Gli **enantiomeri** avranno configurazioni *R,S* opposte.
- I **diastereomeri** avranno almeno una configurazione *R,S* uguale, ma non tutte.



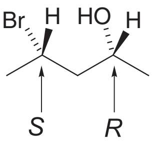
A: 1*S*, 2*R*

a.



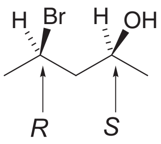
diastereomer

b.



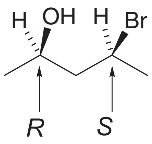
enantiomer

c.



identical

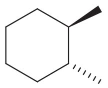
d.



enantiomer

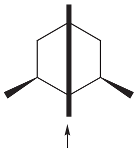
5.50 Tutti i composti meso avranno un piano di simmetria. Essi non possono avere un solo centro stereogenico.

a.



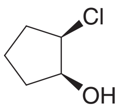
no plane of symmetry
not a meso compound

b.



plane of symmetry
meso compound

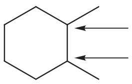
c.



no plane of symmetry
not a meso compound

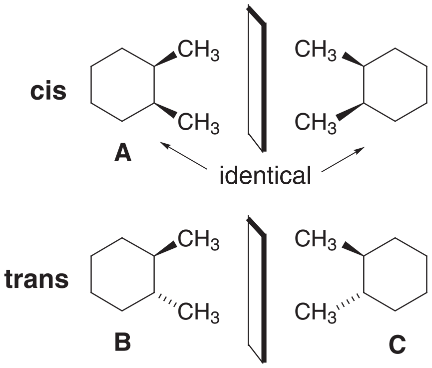
5.51

a.



2 stereogenic centers =
4 stereoisomers maximum

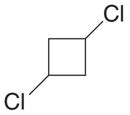
Draw the cis and trans isomers:



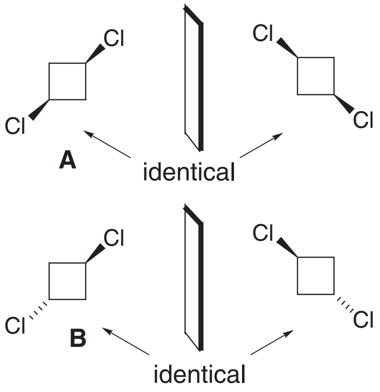
Pair of enantiomers: **B** and **C**.
Pairs of diastereomers: **A** and **B**, **A** and **C**.

Only 3 stereoisomers exist.

c.



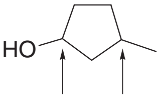
Draw the cis and trans isomers:



Pair of diastereomers: **A** and **B.**

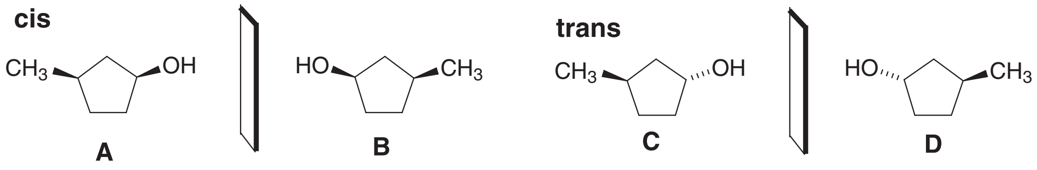
Only 2 stereoisomers exist.

b.



2 stereogenic centers =
4 stereoisomers maximum

Draw the cis and trans isomers:



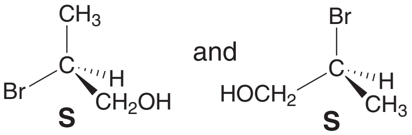
Pairs of enantiomers: **A** and **B, C** and **D.**
Pairs of diastereomers: **A** and **C**, **A** and **D**,
B and **C**, **B** and **D**.

All 4 stereoisomers exist.

5.52 Quattro concetti:

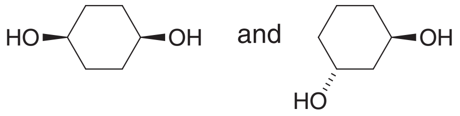
- Gli **enantiomeri** sono isomeri che sono immagini speculari.
- I **diastereomeri** sono stereoisomeri che non sono immagini speculari.
- Gli **isomeri costituzionali** hanno la stessa formula molecolare ma gli atomi legati in maniera diversa.
- Gli **isomeri cis e trans** sono sempre diastereomeri.

a.



same molecular formula
same *R,S* designation:
identical

c.

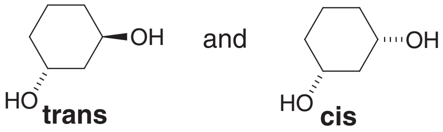


1,4- isomer 1,3-isomer
constitutional isomers

b.

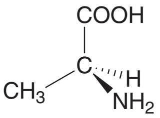
same molecular formula,
opposite configuration at one
stereogenic center
enantiomers

d.



Both 1,3 isomers,
cis and trans:
diastereomers

5.53



(*S*)-alanine
$[\alpha] = +8.5^{o}$
mp = 297 °C

a. Mp = same as the *S* isomer
b. The mp of a racemic mixture is often different from the melting point of the enantiomers.
c. –8.5°, same as *S* but opposite sign
d. 0°
e. Solution of pure (*S*)-alanine: **optically active**
Equal mixture of (*R*) and (*S*)-alanine: **optically inactive**
75% (*S*) and 25% (*R*)-alanine: **optically active**

5.54

$$\boxed{[\alpha] = \frac{\alpha}{l \times c}}$$

α = observed rotation
l = length of tube (dm)
c = concentration (g/mL)

$$[\alpha] = \frac{10^\circ}{1\text{dm} \times (1\text{g}/10\text{mL})} = +100^\circ = \textbf{specific rotation}$$

5.55 Eccesso enantiomerico = ee = % di un enantiomero – % dell'altro enantiomero.

a. 95 – 5 = **90% ee** b. 85 – 15 = **70% ee**

5.56

a. 90% ee means 90% excess of **A**, and 10% racemic mixture of **A** and **B** (5% each).
Therefore, **95% A and 5% B**

b. 99% ee means 99% excess of **A**, and 1% racemic mixture of **A** and **B** (0.5% each).
Therefore, **99.5% A and 0.5% B.**

c. 60% ee means 60% excess of **A**, and 40% racemic mixture of **A** and **B** (20%each).
Therefore, **80% A and 20% B**

5.57

$$\boxed{\text{ee} = \frac{[\alpha]\ \text{mixture}}{[\alpha]\ \text{pure enantiomer}} \times 100\%}$$

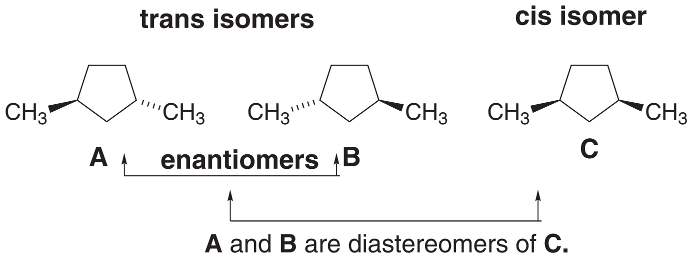
a. $\frac{15}{25} \times 100\% = 60\%$ ee

b. $80\% = \frac{[\alpha]}{25} \times 100\%$ $[\alpha] = +20°$

5.58 • Gli enantiomeri hanno le stesse proprietà fisiche (pf, pe, solubilità), e ruotano il piano della luce polarizzata della stesso angolo ma di verso opposto.

• I diastereomeri hanno proprietà fisiche diverse.

• Una miscela racemica è otticamente inattiva.



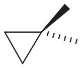
three stereoisomers of 1,3-dimethylcyclopentane

a. The bp's of **A** and **B** are the same. The bp's of **A** and **C** are different.
b. Pure **A**: optically active
Pure **B**: optically active
Pure **C**: optically inactive
Equal mixture of **A** and **B**: optically inactive
Equal mixture of **A** and **C**: optically active
c. There would be two fractions: one containing **A** and **B** (optically inactive), and one containing **C** (optically inactive).

5.59

a. **A** and **B** are constitutional isomers.
A and **C** are constitutional isomers.
B and **C** are diastereomers (cis and trans).
C and **D** are enantiomers.

b.

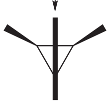


A

A plane of symmetry in the plane of the page

achiral

plane of symmetry



B

achiral

C

chiral

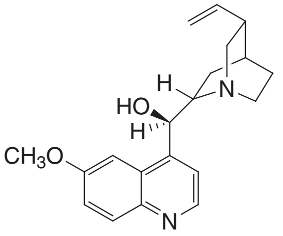
D

chiral

mirror images and not superimposable
enantiomers

c. Alone, **C** and **D** would be optically active.
d. **A** and **B** have a plane of symmetry.
e. **A** and **B** have different boiling points.
B and **C** have different boiling points.
C and **D** have the same boiling point.
f. **B** is a meso compound.
g. An equal mixture of **C** and **D** is optically inactive because it is a racemic mixture.
An equal mixture of **B** and **C** would be optically active.

5.60



quinine

$$\boxed{\text{ee} = \frac{[\alpha]\text{ mixture}}{[\alpha]\text{ pure enantiomer}} \times 100\%}$$

quinine = **A**
quinine's enantiomer = **B**

a.

$$\frac{-50}{-165} \times 100\% = 30\%\text{ ee}$$

$$\frac{-83}{-165} \times 100\% = 50\%\text{ ee}$$

$$\frac{-120}{-165} \times 100\% = 73\%\text{ ee}$$

b. 30% ee = 30% excess one compound (**A**)
remaining 70% = mixture of 2 compounds (35% each **A** and **B)**
Amount of **A** = 30 + 35 = **65%**
Amount of **B** = **35%**

50% ee = 50% the excess one compound (**A**)
remaining 50% = mixture of 2 compounds (25% each **A** and **B)**
Amount of **A** = 50 + 25 = **75%**
Amount of **B = 25%**

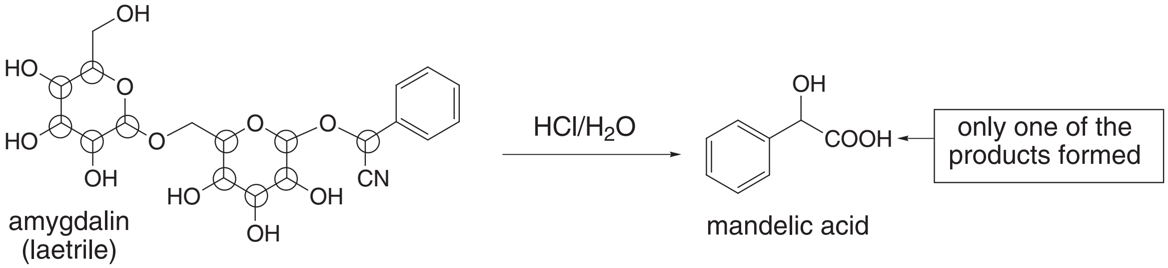
73% ee = 73% excess of one compound (**A**)
remaining 27% = mixture of 2 compounds (13.5% each **A** and **B**)
Amount of **A** 73 + 13.5 = **86.5%**
Amount of **B** = **13.5%**

c. $[\alpha] = +165^{o}$
d. 80% – 20% = 60% ee

e. $$60\% = \frac{[\alpha]\text{ mixture}}{-165^{o}} \times 100\%$$

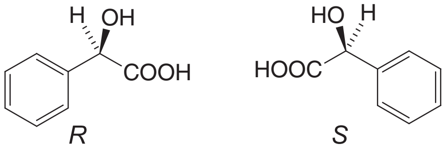
$[\alpha]$ mixture = $-99°$

5.61



a. The 11 stereogenic centers are circled. Maximum number of stereoisomers = 2^{11} = 2048

b. Enantiomers of mandelic acid:



c. 60% – 40% = 20% ee
20% = [α] mixture/–154° x 100%
[α] mixture = –31°

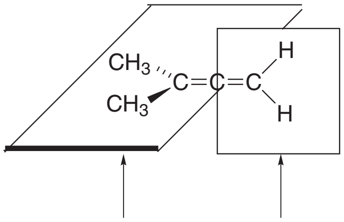
d. $$\text{ee} = \frac{+50^{\circ}}{+154^{\circ}} \times 100\% = 32\%\ \text{ee}$$

[α] for (*S*)-mandelic acid = +154°

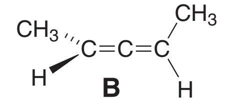
32% excess of the *S* enantiomer
68% of racemic *R* and *S* = 34% *S* and 34% *R*

S enantiomer: 32% + 34% = 66%
R enantiomer = 34%

5.62 Gli alleni contengono un carbonio ibrido *sp* legato doppiamente a due altri carboni. Questo rende i doppi legami dell'allene perpendicolari fra loro. Quando ogni carbonio terminale dell'allene ha due sostituenti uguali, l'allene presenta due piani di simmetria ed è achirale. Quando ogni carbonio terminale dell'allene ha due gruppi diversi, l'allene non ha piani di simmetria e diventa chirale.

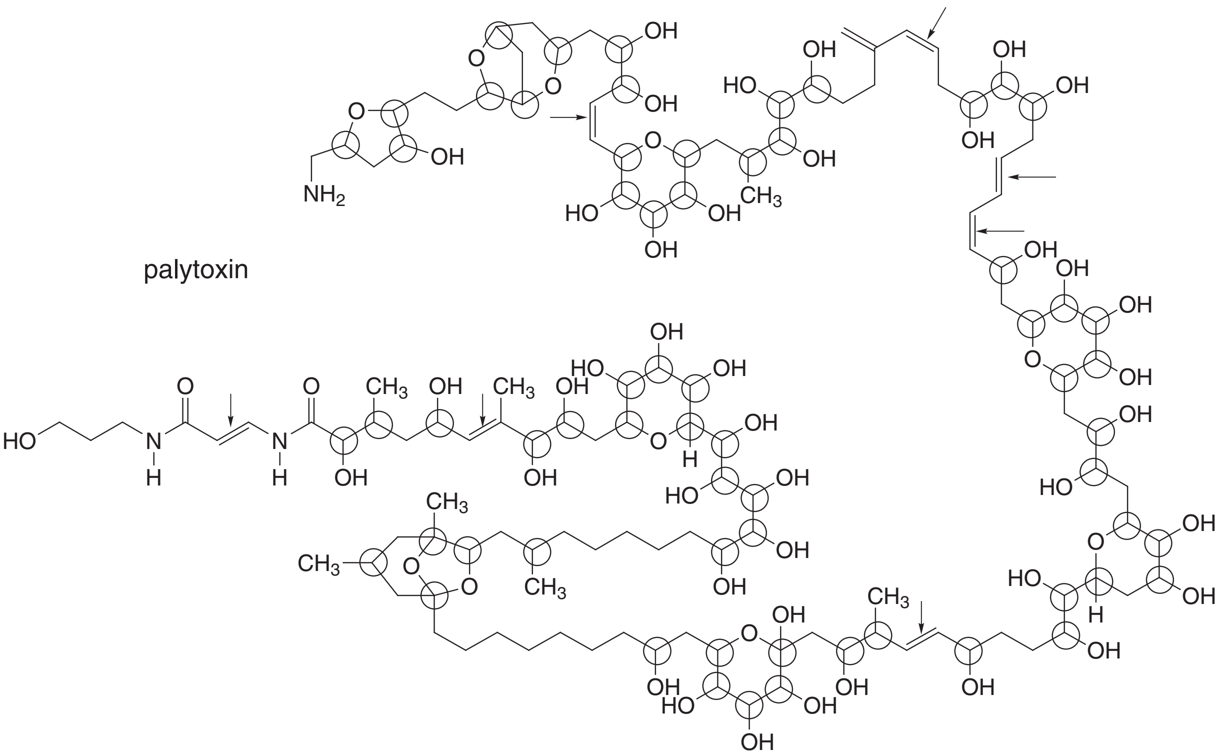


These two substituents are at 90° to these two substituents.
Allene **A** contains two planes of symmetry, making it **achiral.**



B
no plane of symmetry
chiral

5.63



a. I 64 centri stereogenici tetraedrici sono cerchiati.

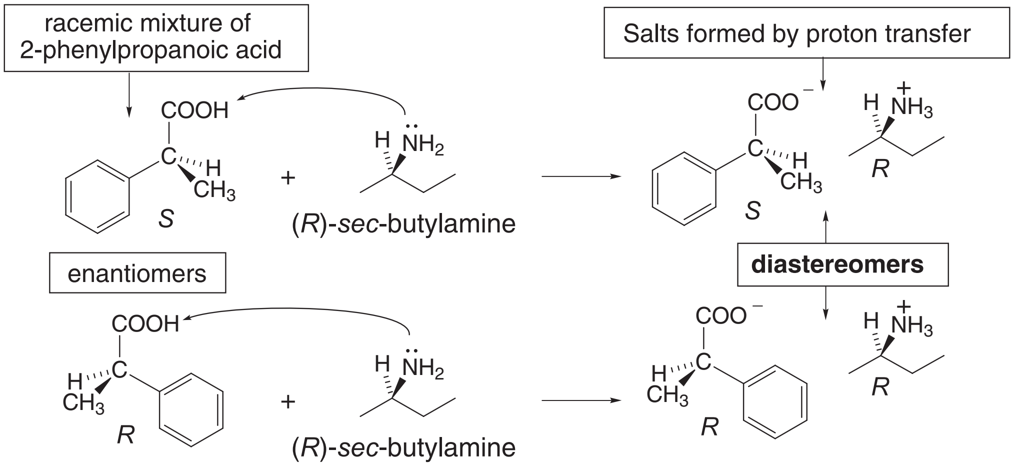
b. A causa della rotazione ristretta attorno ad un doppio legame C–C, i gruppi sul doppio legame non possono interconvertirsi. Tutte le volt che i sostituenti su ciascun carbonio terminale di un doppio legame sono diversi l'uno dall'altro, il doppio legame è un sito stereogenico. Conseguentemente, i seguenti composti con un doppio legame sono isomeri:

These compounds are isomers.

I doppi legami nella palitossina che sono sostituiti da un atomo di carbonio da entrambi i lati sono stereogenici. Ci sono sette doppi legami stereogenici nella palitossina, individuati con le frecce.

c. Il massimo numero di stereoisomeri della palitossina deve includere i 64 centri stereogenici tetraedrici ed i sette doppi legami. Massimo numero di stereoisomeri = $2^{71} = 2.4 \times 10^{21}$.

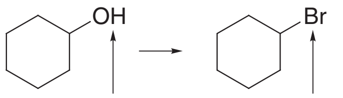
5.64



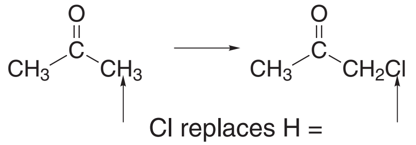
These salts are now **diastereomers,**
and they are now separable by physical methods
since they have different physical properties.

Capitolo 6

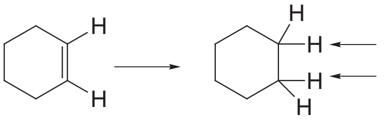
6.1 [1] In una **reazione di sostituzione**, un gruppo sostituisce un altro.
[2] In una **reazione di eliminazione**, elementi del materiale di partenza vengono perduti e si forma un legame π.
[3] In una **reazione di addizione**, elementi vengono aggiunti al materiale di partenza.

a.


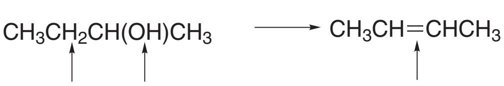
Br replaces OH =
substitution reaction

c.


Cl replaces H =
substitution reaction

b.


addition of 2 H's
addition reaction

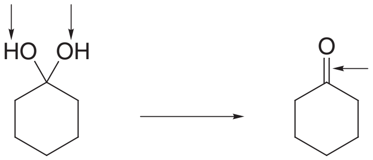
d.


elements lost
(H + OH)

π bond formed

elimination reaction

6.2 Usare i suggerimenti della risposta 6.1.

a.


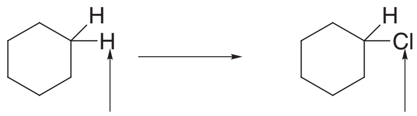
elements lost
(H + OH)

π bond formed

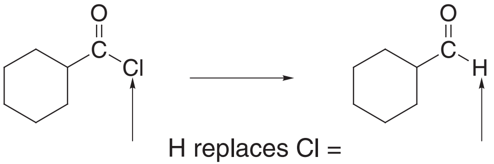
elimination reaction

c.


addition of 2 H's
addition reaction

b.


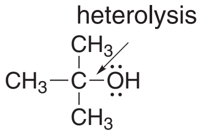
Cl replaces H =
substitution reaction

d.


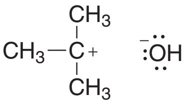
H replaces Cl =
substitution reaction

6.3 **Eterolisi** significa che quando si rompe un legame un atomo prende entrambi gli elettroni. Un carbocatione è un C con una carica positiva, ed un carbanione è un C con una carica negativa.

a.

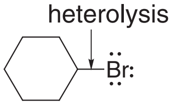


Electrons go to the more electronegative atom, O.

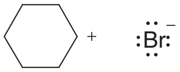


carbocation

b.

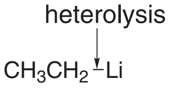


Electrons go to the more electronegative atom, Br.

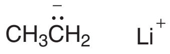


carbocation

c.



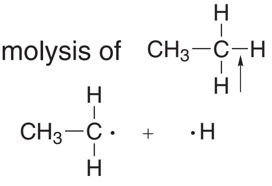
Electrons go to the more electronegative atom, C.



carbanion

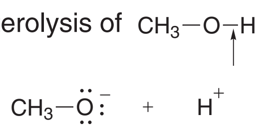
6.4

a. homolysis of

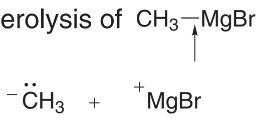


radical

b. heterolysis of



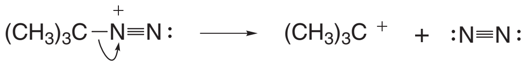
c. heterolysis of



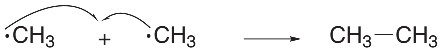
carbanion

6.5 Usare **frecce a punta intera** per mostrare il movimento di coppie elettroniche, e **frecce a semi punta** per mostrare il movimento di singoli elettroni.

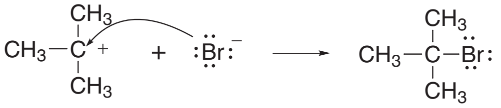
a.



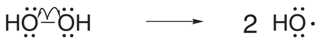
b.



c.

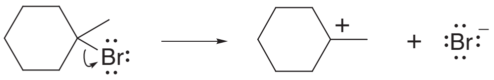


d.

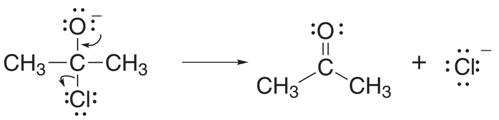


6.6 Usare le regole della risposta 6.5 per disegnare le frecce.

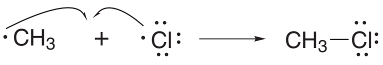
a.



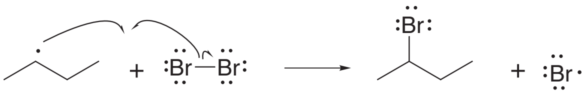
b.



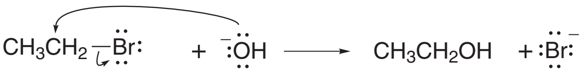
c.



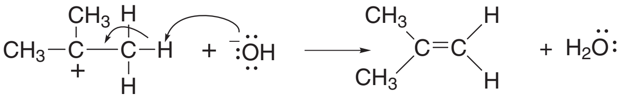
d.



e.

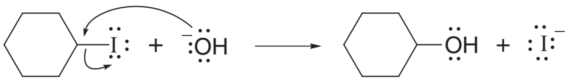


f.

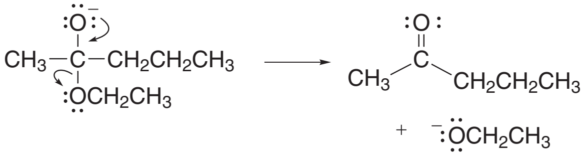


6.7

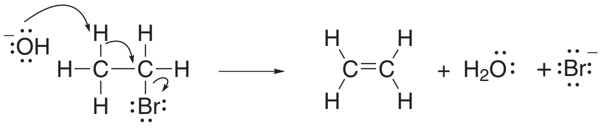
a.



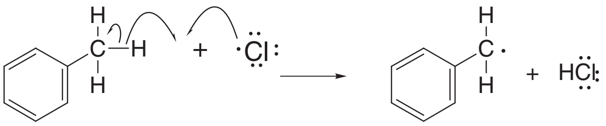
b.



c.



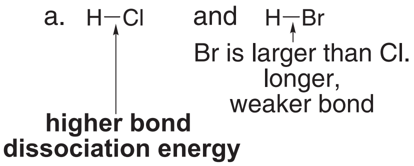
d.



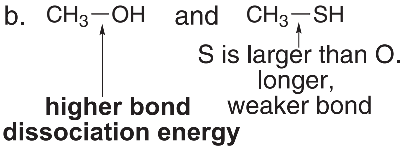
6.8 Aumento del numero di elettroni tra atomi = aumento della forza di legame = aumento dell'energia di dissociazione = diminuzione della lunghezza di legame.

Aumento della grandezza di un atomo = aumento della lunghezza di legame = diminuzione della forza di legame.

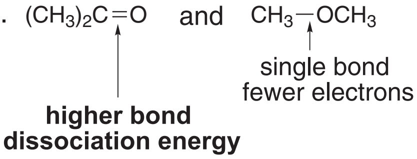
a.



b.

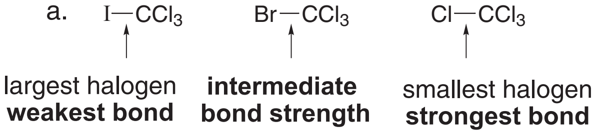


c.

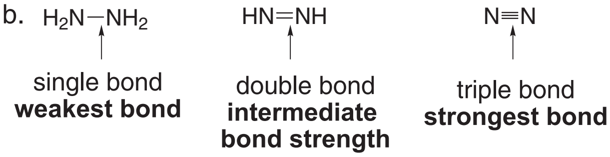


6.9 Usare le regole della risposta 6.8.

a.



b.



6.10 Per determinare il ΔH^o di una reazione (usare i valori in Tabella 6.2):

[1] Sommare le energie di dissociazione di tutti i legami scissi nell'equazione (valori +).

[2] Sommare le energie di dissociazione per tutti i legami formati nell'equazione (valori –).

[3] *Sommare le energie insieme* per ottenere il ΔH^o della reazione.

Un ΔH^o positivo significa che la reazione è ***endotermica***. Un **ΔH^o negativo** significa che la reazione è ***esotermica***.

a. $CH_3CH_2{-}H + Br_2 \longrightarrow CH_3CH_2{-}Br + HBr$

[1] Bonds broken

	ΔH° (kcal/mol)
$CH_3CH_2{-}H$	+ 98
$Br{-}Br$	+ 46
Total	+ 144 kcal/mol

[2] Bonds formed

	ΔH° (kcal/mol)
$CH_3CH_2{-}Br$	– 68
$H{-}Br$	– 88
Total	– 156 kcal/mol

[3] Overall ΔH° =

+ 144 kcal/mol
– 156 kcal/mol
ANSWER: – 12 kcal/mol

b. $\cdot OH + CH_4 \longrightarrow \cdot CH_3 + H_2O$

[1] Bonds broken

	ΔH° (kcal/mol)
$CH_3{-}H$	+ 104 kcal/mol

[2] Bonds formed

	ΔH° (kcal/mol)
$H{-}OH$	– 119 kcal/mol

[3] Overall ΔH° =

+ 104 kcal/mol
– 119 kcal/mol
ANSWER: – 15 kcal/mol

c. $CH_3{-}OH + HBr \longrightarrow CH_3{-}Br + H_2O$

[1] Bonds broken

	ΔH° (kcal/mol)
$CH_3{-}OH$	+ 91
$H{-}Br$	+ 88
Total	+ 179 kcal/mol

[2] Bonds formed

	ΔH° (kcal/mol)
$CH_3{-}Br$	– 70
$H{-}OH$	– 119
Total	– 189 kcal/mol

[3] Overall ΔH° =

+ 179 kcal/mol
– 189 kcal/mol
ANSWER: – 10 kcal/mol

d. $\cdot Br + CH_4 \longrightarrow \cdot H + CH_3Br$

[1] Bonds broken

	ΔH° (kcal/mol)
$CH_3{-}H$	+ 104 kcal/mol

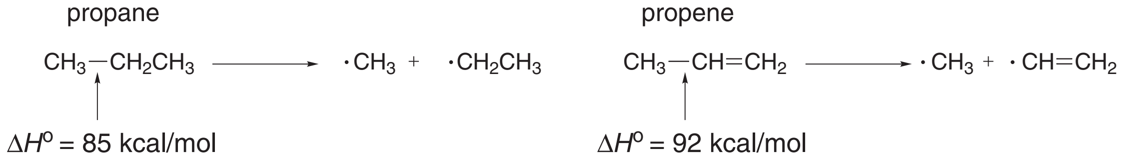
[2] Bonds formed

	ΔH° (kcal/mol)
$CH_3{-}Br$	– 70 kcal/mol

[3] Overall ΔH° =

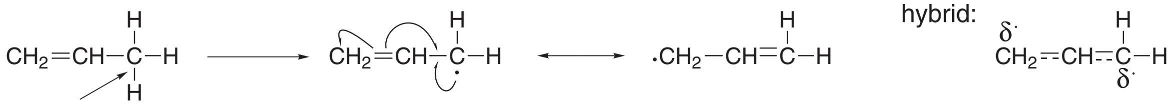
+ 104 kcal/mol
– 70 kcal/mol
ANSWER: + 34 kcal/mol

6.11



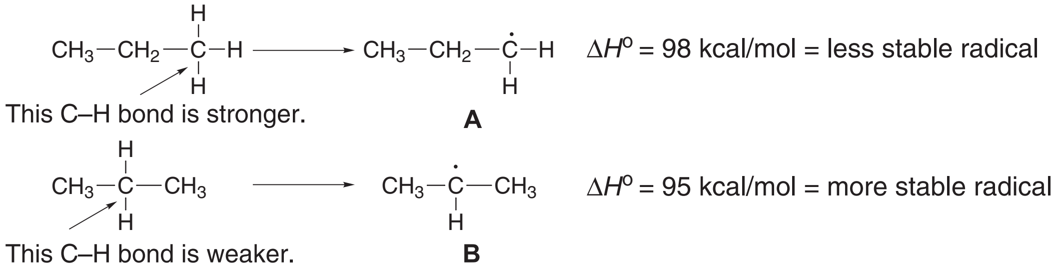
$CH_2{=}CH\bullet$ ha un elettrone spaiato su un C che è parte di un doppio legame. Questo C deve avere una maggior percentuale di carattere *s* nei suoi orbitali ibridi rispetto al C con un elettrone spaiato in $\bullet CH_2CH_3$, e conseguentemente l'elettrone spaiato è trattenuto più vicino al nucleo in $\bullet CH{=}CH_2$, rendendolo meno stabile. [Notare: l'ibridizzazione dei radicali viene discussa nel Capitolo 13. Ma poiché •CH_2CH_3 presenta l'elettrone spaiato su un carbonio legato a tre altri atomi, e •$CH{=}CH_2$ ha l'elettrone spaiato su un carbonio legato solo a due altri atomi, quest'ultimo C deve avere una maggior percentuale di carattere *s* nei suoi orbitali ibridi.]

6.12



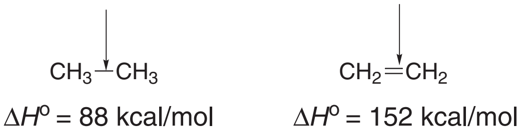
6.13

The more stable radical is formed by a reaction with a smaller ΔH^o.



Since the bond dissociation for cleavage of the C–H bond to form radical **A** is higher, more energy must be added to form it. This makes **A** higher in energy and therefore less stable than **B**.

6.14 Usare l'energia di dissociazione del legame σ C–C dell'etano come stima della forza del legame σ nell'etilene. Successivamente si può anche stimare la forza del legame π.



152 – 88 = 64 kcal/mol = π bond

6.15 Usare le seguenti relazioni per rispondere alle domande:

$\boldsymbol{K_{eq} = 1}$ **quindi** $\boldsymbol{\Delta G^\circ = 0}$**;** $\boldsymbol{K_{eq} > 1}$ **quindi** $\boldsymbol{\Delta G^\circ < 0}$**;** $\boldsymbol{K_{eq} < 1}$ **quindi** $\boldsymbol{\Delta G^\circ > 0}$

a. Un valore negativo di ΔG° significa che l'equilibrio favorisce il prodotto e K_{eq} è > 1. Quindi la risposta è $K_{eq} = 1000$.

b. Un valore minore di ΔG° significa un maggior valore di K_{eq}, e i prodotti sono favoriti $K_{eq} = 10^{-2}$ è più grande di $K_{eq} = 10^{-5}$, e quindi ΔG° è minore.

6.16 Usare le relazioni della risposta 6.15.

a. $K_{eq} = 5.5$. $K_{eq} > 1$ significa che l'equilibrio favorisce i **prodotti**.

b. $\Delta G^\circ = 10.3$ kcal. Un valore positivo di ΔG° signifia che l'equilibro favorisce il **materiale di partenza.**

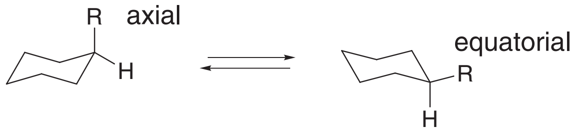
6.17 Quando il prodotto è a minore energia rispetto al materiale di partenza, l'equilibrio favorisce il prodotto.

Quando il materiale di partenza è a minore energia rispetto al prodotto, l'equilibrio favorisce il materiale di partenza.

a. Se **$\Delta G°$ è positivo** l'equilibrio favorisce il materiale di partenza. Quindi il *materiale di partenza ha energia minore del prodotto.*
b. Se **K_{eq} è > 1** l'equilibrio favorisce il prodotto. Perciò il *prodotto ha energia minore dei reagenti.*
c. Se **$\Delta G°$ è negative** l'equilibrio favorisce i prodotti. Quindi i *prodotti hanno energia minore del materiale di partenza.*
d. Se **K_{eq} è < 1** l'equilibrio favorisce il materiale di partenza. Perciò i *reagenti hanno energia minore dei prodotti*.

6.18 a. **falso**. La reazione è endotermica.
b. **vero**. Questo assume che $\Delta G°$ è approssimativamente uguale a $\Delta H°$.
c. **falso**. $K_{eq} < 1$
d. **vero**
e. **falso**. Il materiale di partenza è favorito all'equilibrio.

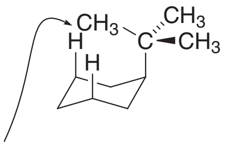
6.19



R	K_{eq}
$-CH_3$	18
$-CH_2CH_3$	23
$-CH(CH_3)_2$	38
$-C(CH_3)_3$	4000

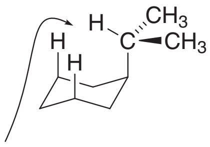
a. Il conformero equatoriale è sempre presente in quantità maggioritaria all'equilibrio poiché la K_{eq} per tutti i gruppi R è maggiore di 1.
b. Il cicloesano con il gruppo $-C(CH_3)_3$ avrà la maggior presenza di conformero equatoriale all'equilibrio poiché questo gruppo presenta la maggior K_{eq}.
c. Il cicloesano con il gruppo $-CH_3$ avrà la maggior presenza di conformero assiale all'equilibrio poiché questo gruppo presenta la minor K_{eq}.
d. Il cicloesano con il gruppo $-C(CH_3)_3$ avrà il $\Delta G°$ più negativo poichè ha la maggior K_{eq}.
e. Più è grande il gruppo R, più è favorito il conformero equatoriale.
f. La K_{eq} per il *tert*-butilcicloesano è più grande perché è più ingombrante degli altri gruppi. Con un gruppo *tert*-butile, un gruppo CH_3 è sempre orientato sopra l'anello quando il gruppo è assiale, originando forti interazioni 1,3-diassiali. Con tutti gli altri sostituenti, il gruppo CH_3 più grande può essere orientato lontano dall'anello, mettendo un H sopra l'anello, rendendo le interazioni 1,3-diassiali meno intense. Confrontare:

tert-butylcyclohexane



severe 1,3-diaxial interactions with the CH_3 groups and the axial H

isopropylcyclohexane



less severe 1,3-diaxial interactions

6.20 Usare le regole della risposta 6.17.

a. $K_{eq} = 0.5$. K_{eq} è minore di uno così i prodotti di partenza sono favoriti.
b. $\Delta G^o = -25$ kcal/mol. ΔG^o è minore di 0 così i prodotti sono favoriti.
c. $\Delta H^o = 2.0$ kcal/mol. ΔH^o è positivo, così i prodotti di partenza sono favoriti .
d. $K_{eq} = 16$. K_{eq} è maggiore di uno così i prodotti sono favoriti.
e. $\Delta G^o = 0.5$ kcal/mol. ΔG^o è maggiore di zero così i prodotti di partenza sono favoriti .
f. $\Delta H^o = 100$ kcal/mol. ΔH^o è positivo così i prodotti di partenza sono favoriti.
g. $\Delta S^o = 2$ cal/K•mol. ΔS^o è maggiore di zero, e così i prodotti sono più disordinati e favoriti.
h. $\Delta S^o = -2$ cal/K•mol. ΔS^o è minore di zero così i materiali di partenza sono più disordinati e favoriti.

6.21 a. Un $\Delta G°$ negativo deve avere $K_{eq} > 1$. $K_{eq} = 10^2$.
b. K_{eq} = [prodotti]/[reagenti] = [1]/[5] = 0.2 = K_{eq}. $\Delta G°$ è positivo.
c. Un $\Delta G°$ negativo ha $K_{eq} > 1$, ed un $\Delta G°$ positivo ha $K_{eq} < 1$. $\Delta G° = -2$ kcal/mol avrà una maggior K_{eq}.

6.22 Reazioni che presentano un aumento di entropia sono favorite. Quando una molecola singola forma due molecole, c'è un aumento di entropia.

a.

increased number of molecules
$\Delta S°$ is positive.
products favored.

b. $CH_3\cdot + CH_3\cdot \longrightarrow CH_3CH_3$

decreased number of molecules
$\Delta S°$ is negative.
starting material favored.

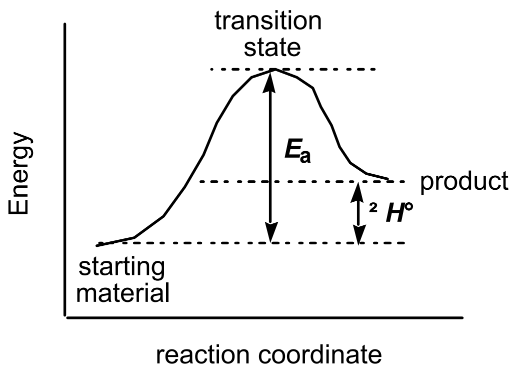
c. $(CH_3)_2C(OH)_2 \longrightarrow (CH_3)_2C{=}O + H_2O$

increased number of molecules
$\Delta S°$ is positive.
products favored.

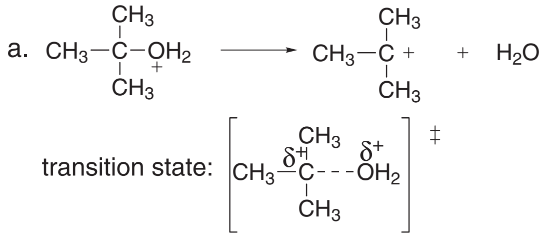
d. $CH_3COOCH_3 + H_2O \longrightarrow CH_3COOH + CH_3OH$

no change in the number of molecules
neither favored

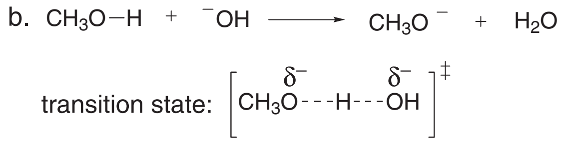
6.23



6.24 Uno stato di transizione è disegnato con linee tratteggiate per indicare i legami parzialmente rotti e parzialmente formati. Ogni atomo che guadagna o perde una carica contiene una carica parziale nello stato di transizione.

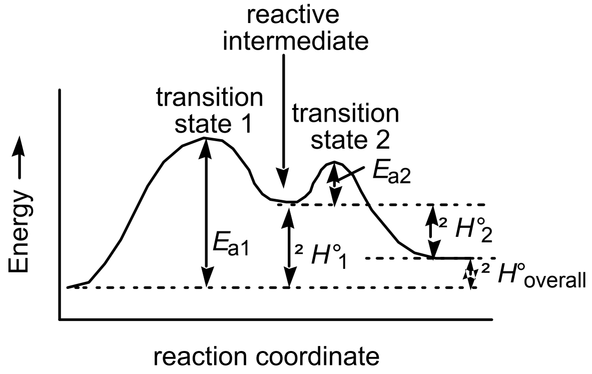

a. $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{+}{O}H_2 \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}{}^+ + H_2O$

transition state: $\left[CH_3-\underset{CH_3}{\overset{CH_3}{\overset{\delta+}{C}}}---\overset{\delta+}{O}H_2 \right]^{\ddagger}$


b. $CH_3O-H + {}^-OH \longrightarrow CH_3O^- + H_2O$

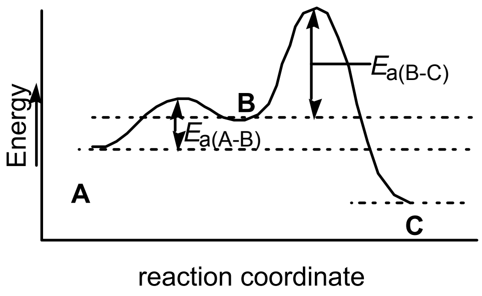
transition state: $\left[CH_3\overset{\delta-}{O}---H---\overset{\delta-}{O}H \right]^{\ddagger}$

6.25



a. Due stadi, perché ci sono due barriere di energia.
b. Vedi le annotazioni sul diagramma.
c. Vedi le annotazioni sul diagramma.
d. E' formato un intermedio reattivo (vedi annotazioni).
e. Il primo stadio è lo stadio lento dal momento che il suo stato di transizione è a più alta energia.
f. La reazione complessiva è endotermica poiché l'energia dei prodotti è maggiore dell'energia dei reagenti.

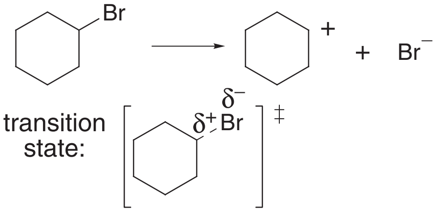
6.26



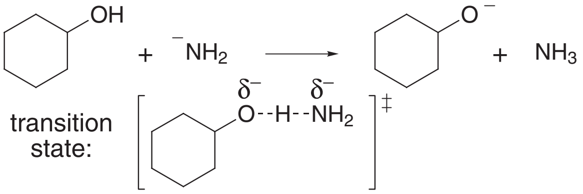
relative energies: C < A < B
B → C is rate limiting.

6.27 Usare i suggerimenti della risposta 6.24 per disegnare lo stato di transizione.

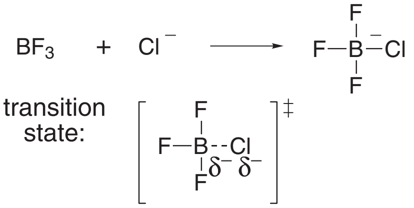
a.



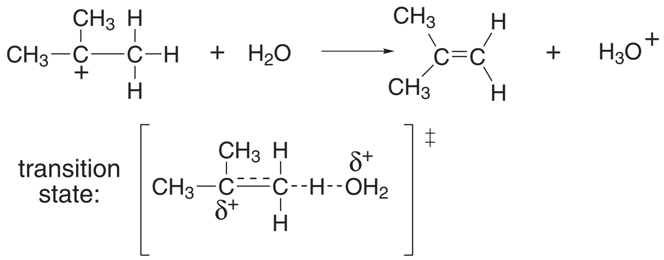
c.



b.

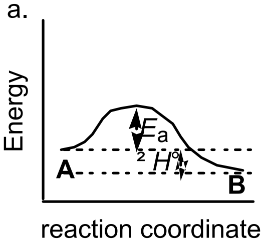


d.



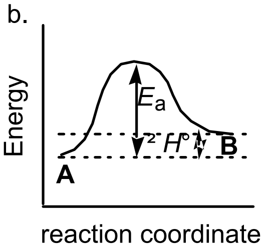
6.28

a.



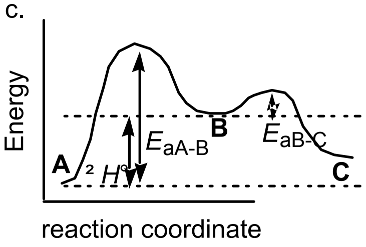
- one step
- exothermic since **B** lower than **A**
- low energy of activation (small energy barrier)

b.



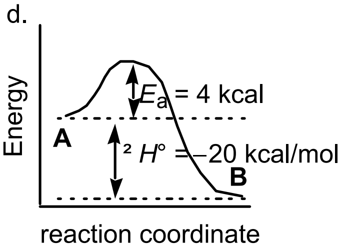
- one step
- endothermic since **B** higher than **A**
- high energy of activation (large energy barrier)

c.



- two steps
- **A** lowest energy
- **B** highest energy
- $E_{a(A\text{-}B)}$ larger than $E_{a(B\text{-}C)}$; $\boldsymbol{E_{a(A\text{-}B)}}$ **is rate-determining**

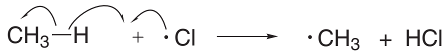
d.



- one step
- exothermic since **B** lower than **A**

6.29

a.



$CH_3{-}H + \cdot Cl \longrightarrow \cdot CH_3 + HCl$

b. $\cdot Cl + CH_4 \longrightarrow \cdot CH_3 + HCl$

[1] Bonds broken

	ΔH^o (kcal/mol)
$CH_3{-}H$	+ 104 kcal/mol

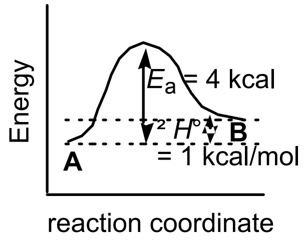
[2] Bonds formed

	ΔH^o (kcal/mol)
H–Cl	– 103 kcal/mol

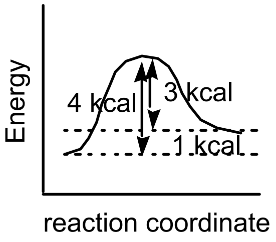
[3] Overall ΔH^o =

	+ 104 kcal/mol
	– 103 kcal/mol
ANSWER:	+ 1 kcal/mol

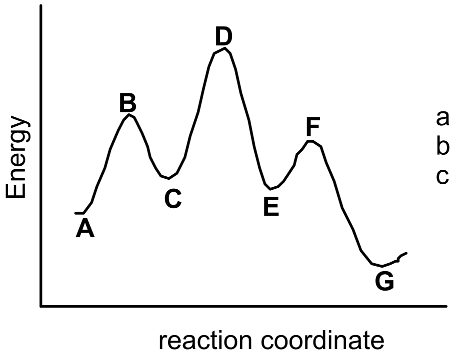
c.



d. La E_a per la reazione inversa è la differenza di energia tra i prodotti e lo stato di transizione, 3 kcal.

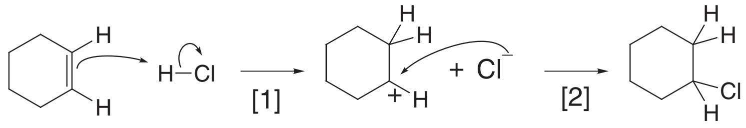


6.30

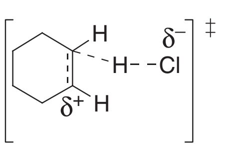


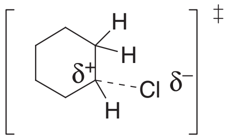
a. **B, D** and **F** are transition states.
b. **C** and **E** are reactive intermediates.
c. The overall reaction has **3 steps.**

6.31

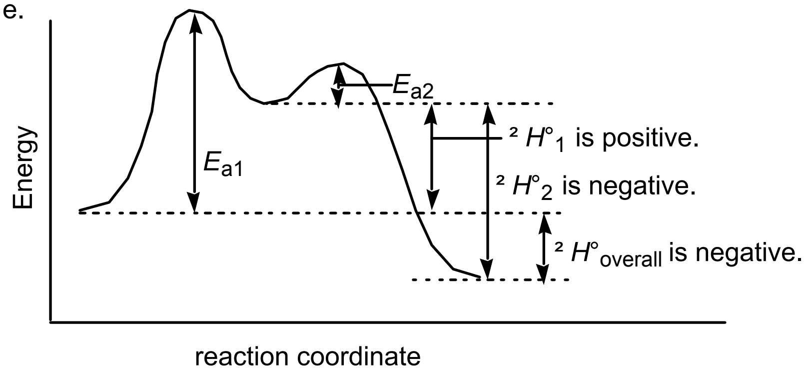


a. Nello stadio [1] si scinde un legame π e il legame H–Cl, e si forma un legame C–H. Il $\Delta H°$ per questo stadio dovrebbe essere positivo poiché sono scissi più legami di quanti se ne formano.
b. Nello stadio [2] si forma un legame. Il $\Delta H°$ per questo passaggio dovrebbe essere negativo poiché si forma un legame e non se ne scinde nessuno.
c. Lo stadio [1] è lo stadio lento poiché è il più difficile.
d. Stato di transizione per lo Stadio [1]: Stato di transizione per lo Stadio [2]:

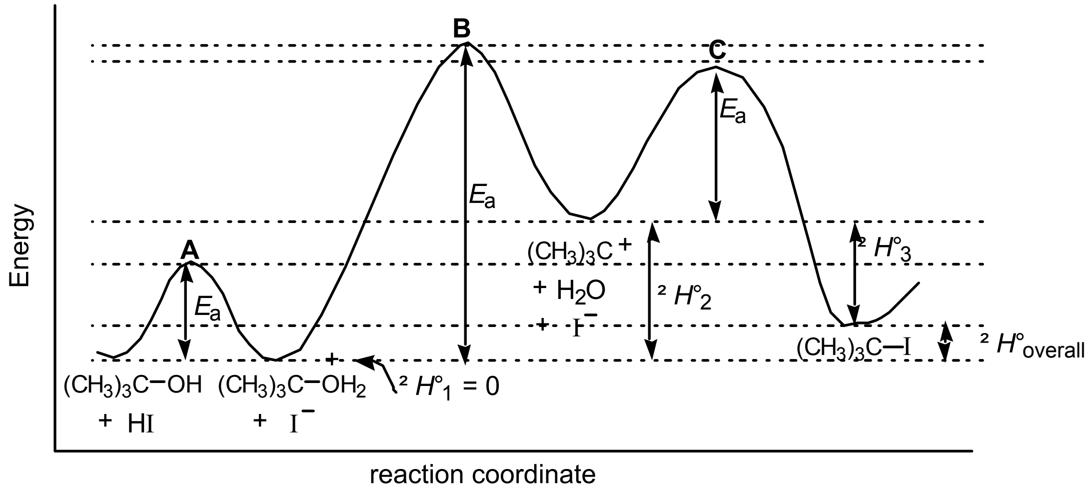




e.



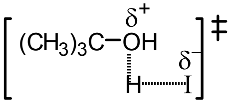
6.32



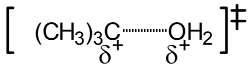
a. La reazione presenta tre stadi, poiché ci sono tre barriere di energia.

b. Vedi sopra.

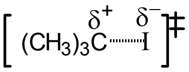
c. Stato di transizione **A** (vedi diagramma per la collocazione):



Stato di transizione **B:**



Stato di transizione **C:**



e. Lo stadio 2 è lo stadio lento poiché questo stadio presenta lo stato di transizione a maggior energia.

6.33 E_a, concentrazione e temperatura influiscono sulla velocità di reazione. $\Delta H°$, $\Delta G°$, e K_{eq} non influiscono sulla velocità di reazione.

a. $\boldsymbol{E_a}$ **= 1 kcal** corrisponde a una reazione più veloce.
b. Una temperatura di **25 °C** avrà una maggior velocità di reazione poiché un'alta temperatura corrisponde a una reazione più veloce.
c. **Nessun cambiamento**: K_{eq} non influisce sulla velocità di reazione.
d. **Nessun cambiamento**: $\Delta H°$ non influisce sulla velocità di reazione.

6.34 Tutti i reagenti nell'equazione di velocità determinano la velocità della reazione.

(1) velocità = $k[CH_3CH_2Br][^-OH]$
a. Triplicando la concentrazione del solo CH_3CH_2Br → **La velocità è triplicata.**
b. Triplicando la concentrazione del solo ^-OH → **La velocità è triplicata.**

(2) velocità = $k[(CH_3)_3COH]$
a. Raddoppiando la concentrazione di $(CH_3)_3COH$ → **La velocità è raddoppiata.**
b. Aumentando la concentrazione di $(CH_3)_3COH$ di un fattore 10 → **La velocità**

c. Triplicando la concentrazione di entrambi $CH_3CH_2CH_2Br$ e ^{-}OH → **La velocità è aumentata di un fattore 9 (3 x 3 = 9).**

è aumentata di un fattore 10.

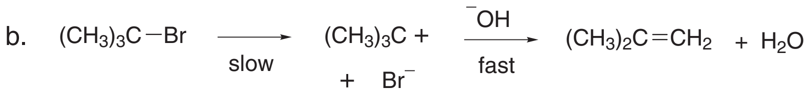
6.35 L'equazione di velocità è determinata dallo stadio lento.

a. $CH_3CH_2{-}Br + {}^{-}OH \longrightarrow CH_2{=}CH_2 + H_2O + Br^{-}$

one step

rate = *k*[CH_3CH_2Br][^{-}OH]

b.



$$(CH_3)_3C{-}Br \xrightarrow[\text{slow}]{} (CH_3)_3C^{+} + Br^{-} \xrightarrow[\text{fast}]{^{-}OH} (CH_3)_2C{=}CH_2 + H_2O$$

two steps

The slow step determines the rate equation.

rate = *k*[$(CH_3)_3CBr$]

6.36 L'E_a, la concentrazione, i catalizzatori, la costante di velocità e la temperatura influenzano la velocità di reazione e così c, d, e, g ed h influenzano la velocità.

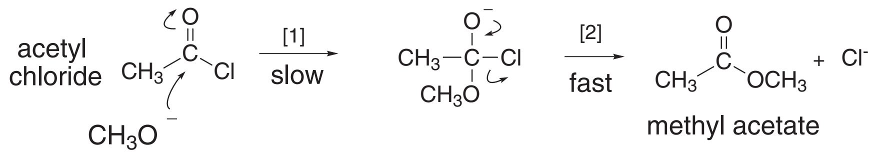
6.37 a. **velocità = *k*[CH_3Br][NaCN]**

b. Raddoppiare [CH_3Br] = **raddoppia la velocità.**

c. Dimezzare [NaCN] = **dimezza la velocità.**

d. Aumentare sia [CH_3Br] che [NaCN] di un fattore 5 = [5][5] = **la velocità aumenta di un fattore 25.**

6.38



a. Solo lo stadio lento è incluso nell'equazione della velocità di reazione: **Velocità = *k*[CH_3O^{-}][CH_3COCl]**

b. CH_3O^{-} è presente nell'espressione della velocità. Aumentare la sua concentrazione di 10 volte aumenterà l velocità di **10 volte.**

c. Quando entrambe le concentrazioni dei reagenti sono aumentate di 10 volte, la velocità aumenta di **100 volte (10 x 10 = 100).**

d. Questa è una reazione di sostituzione (OCH_3 sostituisce Cl).

6.39 a. **Vero**: l'aumento della temperatura aumenta la velocità di reazione.

b. **Vero**: se una reazione è veloce, ha un costante di velocità grande.

c. **Falso: Corretto –** Non c'è nessuna relazione tra $\Delta G°$ e la velocità di reazione.

d. **Falso: Corretto –** Quando E_a è grande, *la costante di velocità è piccola.*

e. **Falso: Corretto -** Non c'è nessuna relazione tra K_{eq} e la velocità di reazione.

f. **Falso: Corretto –** L'aumento della concentrazione di un reagente aumenta la velocità di reazione *solo se il reagente appare nell'equazione della velocità.*

6.40 a. Il primo meccanismo è a singolo stadio: **velocità =** $\boldsymbol{k[(CH_3)_3CI][^-OH]}$

b. Il secondo meccanismo è a due stadi, ma solo il primo stadio sarà presente nell'espressione della velocità poiché è quello lento e conseguentemente quello che determina la velocità: **velocità =** $\boldsymbol{k[(CH_3)_3CI]}$

c. La possibilità [1] è del secondo ordine; la possibilità [2] è di primo ordine.

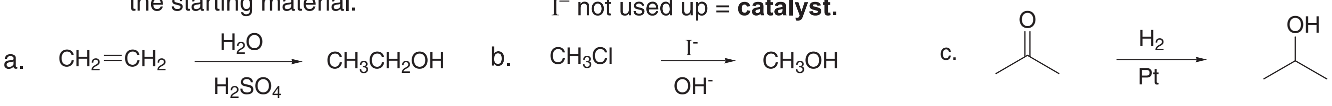
d. Queste espressioni di velocità possono essere usate per mostrare quale meccanismo è corretto attraverso il cambiamento della concentrazione di $[^-OH]$. Se ciò influenza la velocità, la possibilità [1] è corretta. Se non influenza la velocità, la possibilità [2] è corretta.

6.41 Un catalizzatore non è consumato né cambiato alla fine della reazione. Serve solo per aumentare la velocità della reazione.

OH and H are added to the starting material.

I^- not used up = **catalyst.**

H_2 adds to the starting material.



H_2SO_4 is not used up = **catalyst.**

^-OH substitutes for Cl^-.

Pt not used up = **catalyst.**

6.42 La differenza sia nell' acidità che nella dissociazione del legame di CH_3CH_3 nei confronti di HC≡CH è dovuta allo stesso fattore: percento di carattere *s*. La differenza si origina nel fatto che un processo è omolitico e l'altro eterolitico

Energia di dissociazione del legame:

sp^3 hybridized
25% *s*-character

sp hybridized
50% *s*-character
Higher percenter *s*-character makes this bond shorter and stronger.

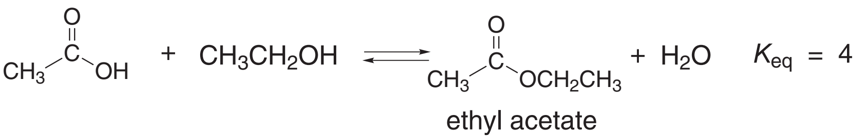
Acidità. Per confrontare l'acidità, si deve confrontare la stabilità delle basi coniugate:

sp^3 hybridized
25% *s*-character

sp hybridized
50% *s*-character
Now a higher percenter *s*-character stabilizes the conjugate base making the starting acid more acidic.

6.43 Nella reazione [1], il numero di molecole dei reagenti e dei prodotti resta costante, così l'entropia non è un fattore. Nella reazione [2], una singola molecola di materiale di partenza forma due molecole di prodotto, con conseguente aumento di entropia. Questo rende il $\Delta G°$ più favorevole, aumentando così la K_{eq}.

6.44



To increase the yield of ethyl acetate, H_2O can be removed from the reaction mixture, or there can be a large excess of one of the starting materials.

6.45 Dal momento che gli atomi di ossigeno sono più elettronegativi di tutti gli altri atomi ad eccezione di F, ogni O nel legame O–O sposta la densità elettronica verso sé stesso. Gli atomi di O sono meno “proni” a condividere densità elettronica in un legame a due elettroni, e ciò indebolisce il legame.

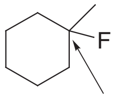
Capitolo 7

7.1 Classificare l'alogenuro alchilico come 1°, 2° o 3° **contando il numero di carboni direttamente legati al carbonio legato all'alogeno.**

C bonded to 1 C
1° alkyl halide

a. $CH_3CH_2CH_2CH_2CH_2{-}Br$

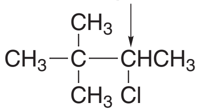
b.



C bonded to 3 C's
3° alkyl halide

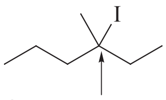
C bonded to 2 C's
2° alkyl halide

c.



$$CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}\underset{\displaystyle Cl}{C}HCH_3$$

d.



C bonded to 3 C's
3° alkyl halide

7.2 Per assegnare il nome ad un composto secondo il sistema IUPAC:

[1] **Nominare la catena principale** individuando la catena carboniosa più lunga.

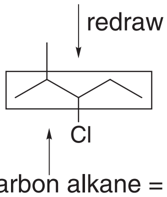
[2] **Numerare la catena** in modo che il primo sostituente abbia il numero più basso. Successivamente **nominare e numerare tutti i sostituenti**, assegnando a sostituenti simili un prefisso (di, tri, ecc.). **Per nominare il sostituente alogeno, cambiare il suffisso *–uro* in *–o*.**

[3] **Combinare tutte le parti**, ordinando in ordine alfabetico, ed ignorando tutti i prefissi ad eccezione di iso.

a. $(CH_3)_2CHCH(Cl)CH_2CH_3$

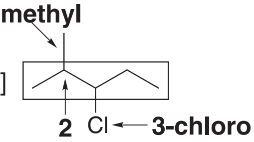
redraw

[1]



5 carbon alkane = **pentane**

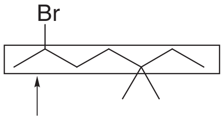
[2]



[3] **3-chloro-2-methylpentane**

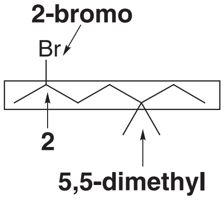
b.

[1]



7 carbon alkane = **heptane**

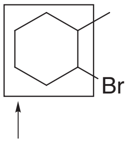
[2]



[3] **2-bromo-5,5-dimethylheptane**

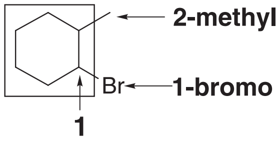
c.

[1]



6 carbon cycloalkane =
cyclohexane

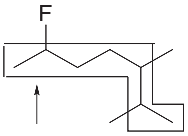
[2]



[3] **1-bromo-2-methylcyclohexane**

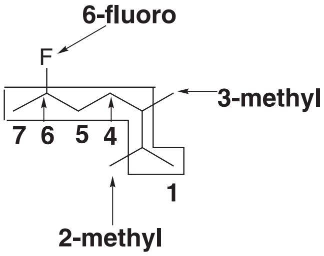
d.

[1]



7 carbon alkane = **heptane**

[2]



[3] **6-fluoro-2,3-dimethylheptane**

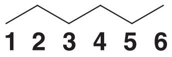
7.3 Per individuare la struttura dal nome:

[1] Trovare il nome della catena principale e disegnare quel numero di carboni. Usare il suffisso per identificare il gruppo funzionale. **(–ano = alcano)**

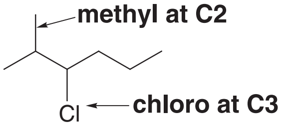
[2] Numerare arbitrariamente i carboni della catena. Aggiungere i sostituenti sul carbonio appropriato.

a. 3-chloro-2-methyl**hexane**

[1] 6 carbon alkane

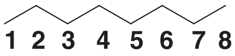


[2]

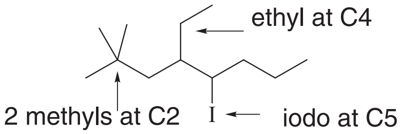


b. 4-ethyl-5-iodo-2,2-dimethyl**octane**

[1] 8 carbon alkane

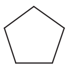


[2]

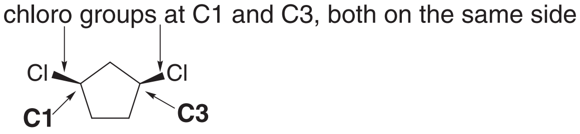


c. *cis*-1,3-dichloro**cyclopentane**

[1] 5 carbon cycloalkane

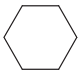


[2]

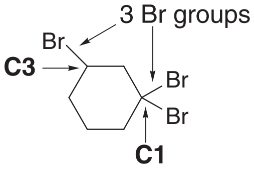


d. 1,1,3-tribromo**cyclohexane**

[1] 6 carbon cycloalkane



[2]



e. **propyl** chloride

[1] 3 carbon alkyl group

$CH_3CH_2CH_2-$

[2] **chloride on end**

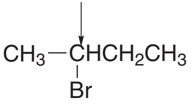
$CH_3CH_2CH_2-Cl$

f. ***sec*-butyl** bromide

[1] 4 carbon alkyl group

$CH_3-\underset{|}{C}HCH_2CH_3$

[2] **bromide**

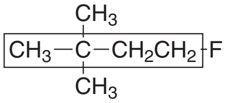


$CH_3-\underset{Br}{\underset{|}{C}}HCH_2CH_3$

7.4 Usare i suggerimenti della risposta 7.2 per assegnare il nome ai composti.

7.4 Usare i suggerimenti della risposta 7.2 per assegnare il nome ai composti.

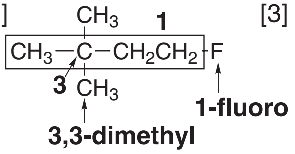
a. [1]



$CH_3-C(CH_3)_2-CH_2CH_2-F$

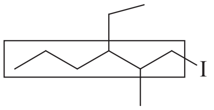
4 carbon alkane = **butane**

[2]



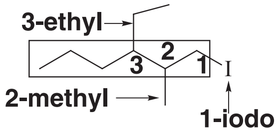
[3] **1-fluoro-3,3-dimethylbutane**

b. [1]



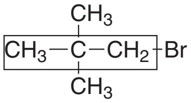
6 carbon alkane = **hexane**

[2]



[3] **3-ethyl-1-iodo-2-methylhexane**

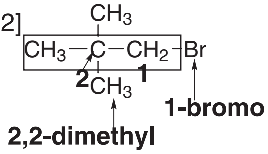
c. [1] $(CH_3)_3CCH_2Br$



$CH_3-C(CH_3)_2-CH_2-Br$

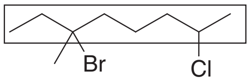
3 carbon alkane = **propane**

[2]



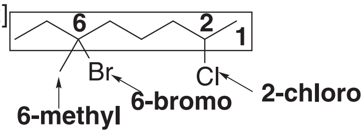
[3] **1-bromo-2,2-dimethylpropane**

d. [1]



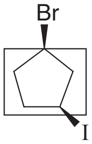
8 carbon alkane = **octane**

[2]



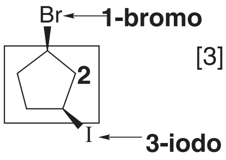
[3] **6-bromo-2-choro-6-methyloctane**

e. [1]



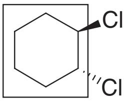
5 carbon cycloalkane = **cyclopentane**

[2]



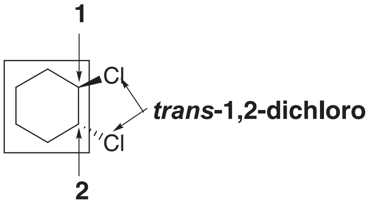
[3] ***cis*-1-bromo-3-iodocyclopentane**

f. [1]



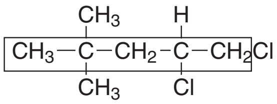
6 carbon cycloalkane = **cyclohexane**

[2]



[3] ***trans*-1,2-dichlorocyclohexane**

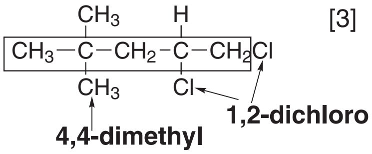
g. [1] $(CH_3)_3CCH_2CH(Cl)CH_2Cl$



$CH_3-C(CH_3)_2-CH_2-CH(Cl)-CH_2Cl$

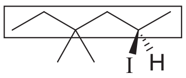
5 carbon alkane = **pentane**

[2]



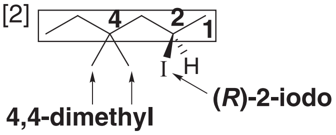
[3] **1,2-dichloro-4,4-dimethylpentane**

h. [1]

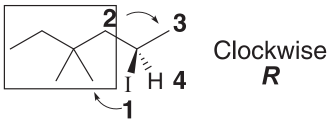


6 carbon alkane = **hexane**
(Indicate the *R*/*S* designation also)

[2]

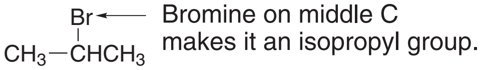


[3] ***(R)*-2-iodo-4,4-dimethylhexane**

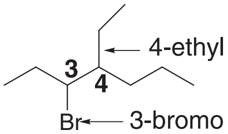


7.5 Per disegnare la struttura, usare i suggerimenti della risposta 7.3.

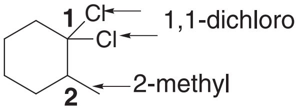
a. **isopropyl** bromide


$$\overset{Br}{\overset{|}{CH_3{-}CHCH_3}}$$

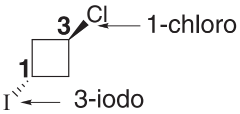
b. 3-bromo-4-ethyl**heptane**



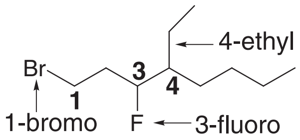
c. 1,1-dichloro-2-methyl**cyclohexane**



d. *trans*-1-chloro-3-iodo**cyclobutane**

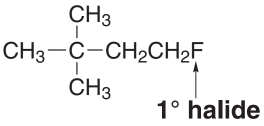


e. 1-bromo-4-ethyl-3-fluoro**octane**

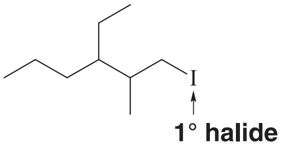


7.6

a.


$$CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2CH_2F$$

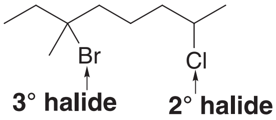
b.



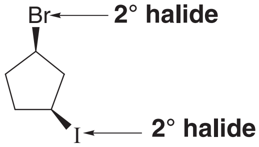
c. $(CH_3)_3CCH_2Br$

1° halide

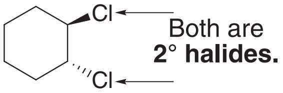
d.



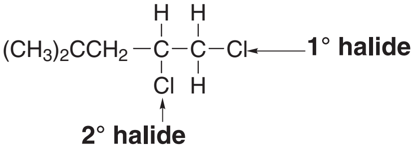
e.



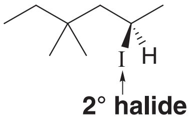
f.



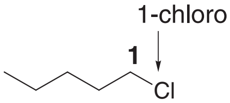
g.


$$(CH_3)_2CCH_2{-}\overset{H}{\underset{Cl}{C}}{-}\overset{H}{\underset{H}{C}}{-}Cl$$

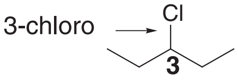
h.



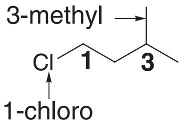
7.7



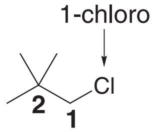
1-chloropentane



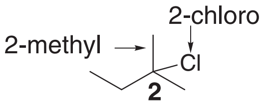
3-chloropentane



1-chloro-3-methylbutane

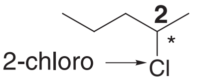


1-chloro-2,2-dimethylpropane

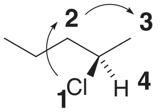


2-chloro-2-methylbutane

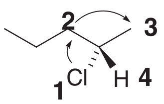
Two stereoisomers



2-chloropentane
[* denotes stereogenic center]

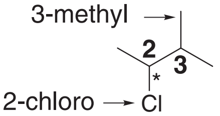


Clockwise
"4" in back =
R

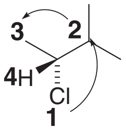


Clockwise
"4" in *front* =
S

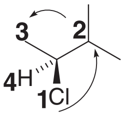
Two stereoisomers



2-chloro-3-methylbutane
[* denotes stereogenic center]

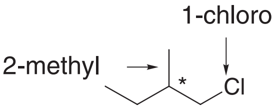


Counterclockwise
"4" in front =
R

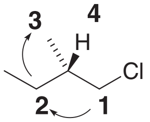


Counterclockwise
"4" in *back* =
S

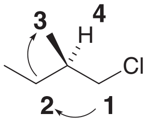
Two stereoisomers



1-chloro-2-methylbutane
[* denotes stereogenic center]



Clockwise
"4" in *front* =
S



Clockwise
"4" in *back* =
R

7.8 I punti di ebollizione degli alogenuri alchilici aumentano all'aumentare del volume (e della polarizzabilità) di X. Ricordare: **forze intermolecolari maggiori = maggior punto di ebollizione.**

a.

$CH_3CH_2CH_2F$ ↑	$CH_3CH_3CH_2Cl$ ↑	$CH_3CH_2CH_2I$ ↑
smallest halogen least polarizable **lowest boiling point**	middle size halogen **intermediate boiling point**	largest halogen most polarizable **highest boiling point**

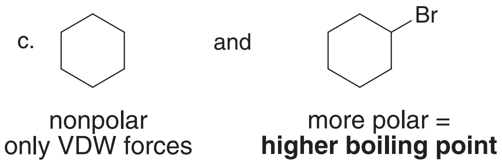
b.

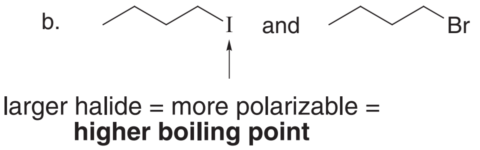
$CH_3(CH_2)_4CH_3$ ↑	$CH_3(CH_2)_5Br$ ↑	$CH_3(CH_2)_5OH$ ↑
weakest forces nonpolar **lowest boiling point**	VDW, DD forces **intermediate boiling point**	OH is capable of hydrogen bonding. strong forces **highest boiling point**

7.9 Usare i suggerimenti della risposta 7.8.

a. $(CH_3)_3CBr$ and $CH_3CH_2CH_2CH_2Br$

larger surface area =
stronger intermolecular forces =
higher boiling point



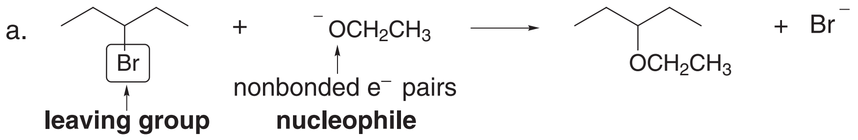


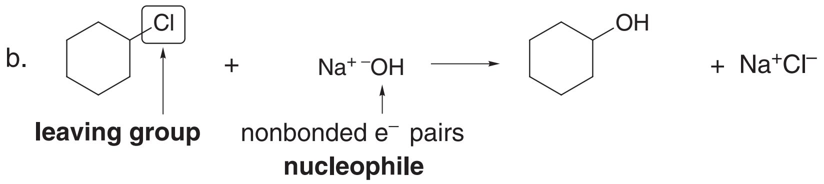
7.10 Per disegnare i prodotti di una reazione i sostituzione nucleofila:

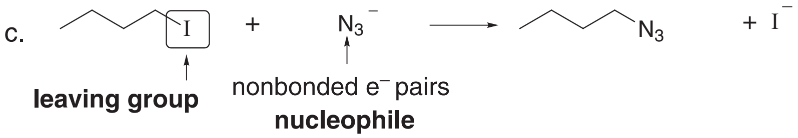
[1] **Trovare il carbonio elettrofilo ibrido *sp*^{3}** con un gruppo uscente.

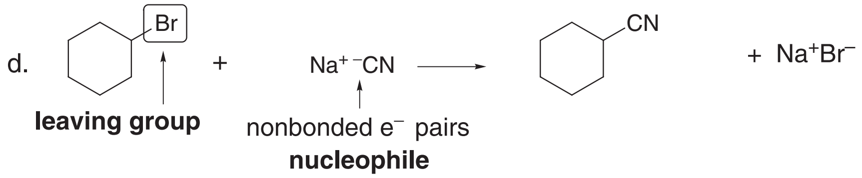
[2] **Trovare il nucleofilo** con coppie elettroniche solitarie o legami π.

[3] **Sostituire il nucleofilo al posto del gruppo uscente** sul carbonio elettrofilo.



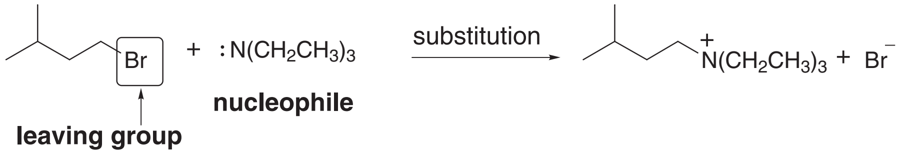




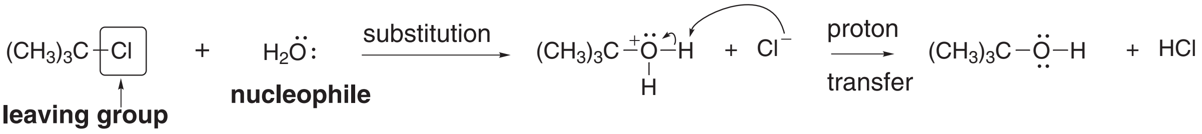


7.11 Usare i passaggi della risposta 7.10 e successivamente disegnare il trasferimento del protone.

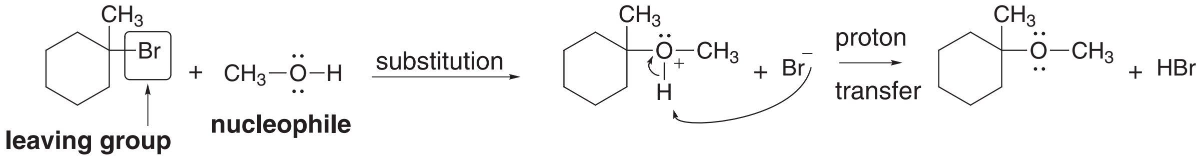
a.



b.

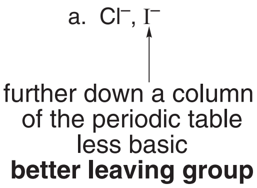


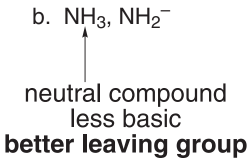
c.

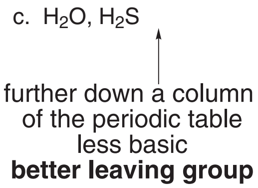


7.12 Confrontare i composti in base alla tendenza di questi gruppi ad agire da gruppi uscenti:

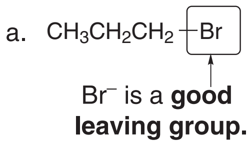
- I migliori gruppi uscenti sono le basi più deboli.
- Un gruppo uscente neutro è sempre migliore della sua base coniugata.

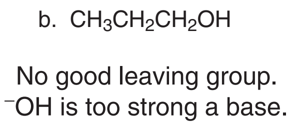


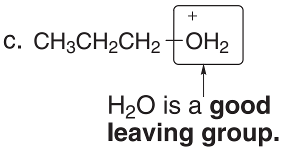


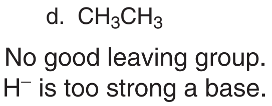


7.13 Buoni gruppi uscenti sono Cl^-, Br^-, I^-, H_2O.



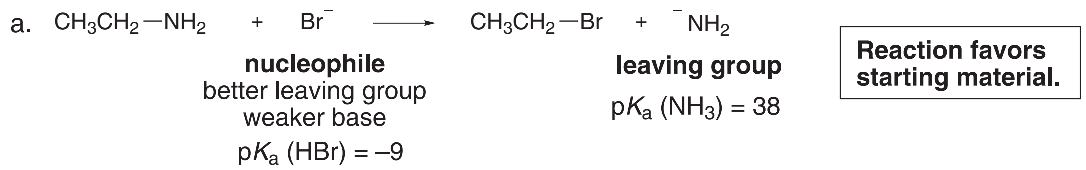




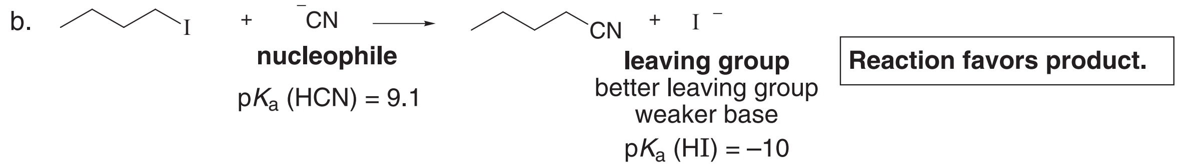


7.14 Per decidere se l'equilibrio favorisce i materiali di partenza o i prodotti, **confrontare il nucleofilo ed il gruppo uscente.** La reazione procede verso la formazione della base più debole.

a. $CH_3CH_2—NH_2 + Br^- \longrightarrow CH_3CH_2—Br + {}^-NH_2$



b.



7.15 Usare queste tre regole per trovare in ogni coppia il nucleofilo più forte:

[1] Confrontare due nucleofili che hanno lo stesso atomo che attacca: **la base più forte è il nucleofilo più forte**.

[2] **I nucleofili carichi negativamente** sono sempre **più forti dei loro acidi coniugati**.

[3] **Attraverso una riga della tavola periodica**, **la nucleofilicità decresce** confrontando specie di carica simile.

a. NH_3, NH_2^-

A negatively charged nucleophile is stronger than its conjugate acid.
stronger nucleophile

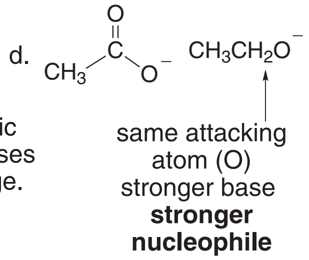
b. CH_3^-, HO^-

Across a row of the periodic table, nucleophilicity decreases with species of same charge.
stronger nucleophile

c. CH_3NH_2, CH_3OH

Across a row of the periodic table, nucleophilicity decreases with species of same charge.
stronger nucleophile

d.



7.16 ***Solventi polari protici*** **possono dare legami idrogeno**, e perciò devono contenere un **H legato ad un O o N elettronegativo**. ***Solventi aprotici polari*** **non possono dare legami idrogeno**, e perciò non contengono nessun legame O–H o N–H.

a. $HOCH_2CH_2OH$
contains 2 O–H bonds
polar protic

b. $CH_3CH_2OCH_2CH_3$
no O–H bonds
polar aprotic

c. $CH_3COOCH_2CH_3$
no O–H bonds
polar aprotic

7.17 • Nei ***solventi polari protici*****, l'andamento della nucleofilicità è opposto a quello della basicità** lungo una colonna della tavola periodica, così la nucleofilicità aumenta.

• Nei ***solventi polari aprotici*****, l'andamento è identico alla basicità** così la nucleofilicità decresce lungo una colonna.

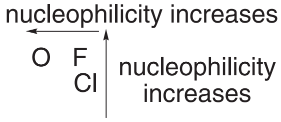
a. Br^- and Cl^- in polar protic solvent

further down the column
more nucleophilic
in protic solvent

b. ^-OH and Cl^- in polar aprotic solvent

further up the column
and to the left in the row
more basic
more nucleophilic

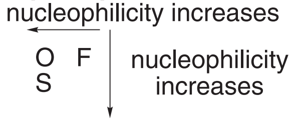
In polar aprotic solvents:



c. HS^- and F^- in polar protic solvent

further down the column
and left in the row
more nucleophilic
in protic solvent

In polar protic solvents:



7.18 Più forte è una base più forte è il nucleofilo eccetto che in solventi polari protici dove la nucleofilicità aumenta lungo una colonna. Per altre regole vedere le risposte 7.11 e 7.13.

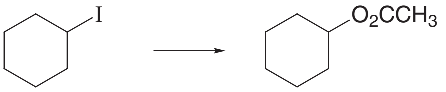
a.	H_2O no charge **weakest nucleophile**	^-OH negatively charged **intermediate nucleophile**	$^-NH_2$ negatively charged further left on periodic table **strongest nucleophile**
b.	Br^- Basicity decreases down a column in polar aprotic solvents. **weakest nucleophile**	F^- Basicity decreases across a row. **intermediate nucleophile**	^-OH **strongest nucleophile**
c.	H_2O **weakest nucleophile**	CH_3COO^- weaker base than ^-OH **intermediate nucleophile**	^-OH **strongest nucleophile**

7.19 Per determinare quale nucleofilo è necessario per condurre ciascuna reazione, osservare il prodotto per vedere che cosa ha rimpiazzato il gruppo uscente.

a. $CH_3CH_2CH_2{-}Br \longrightarrow CH_3CH_2CH_2{-}SH$

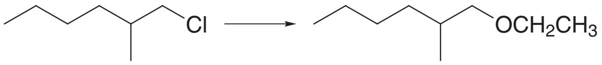
SH replaces Br.
HS^- is needed.

b.



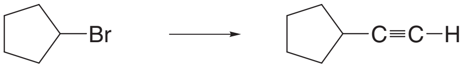
CH_3COO replaces I.
CH_3COO^- is needed.

c.



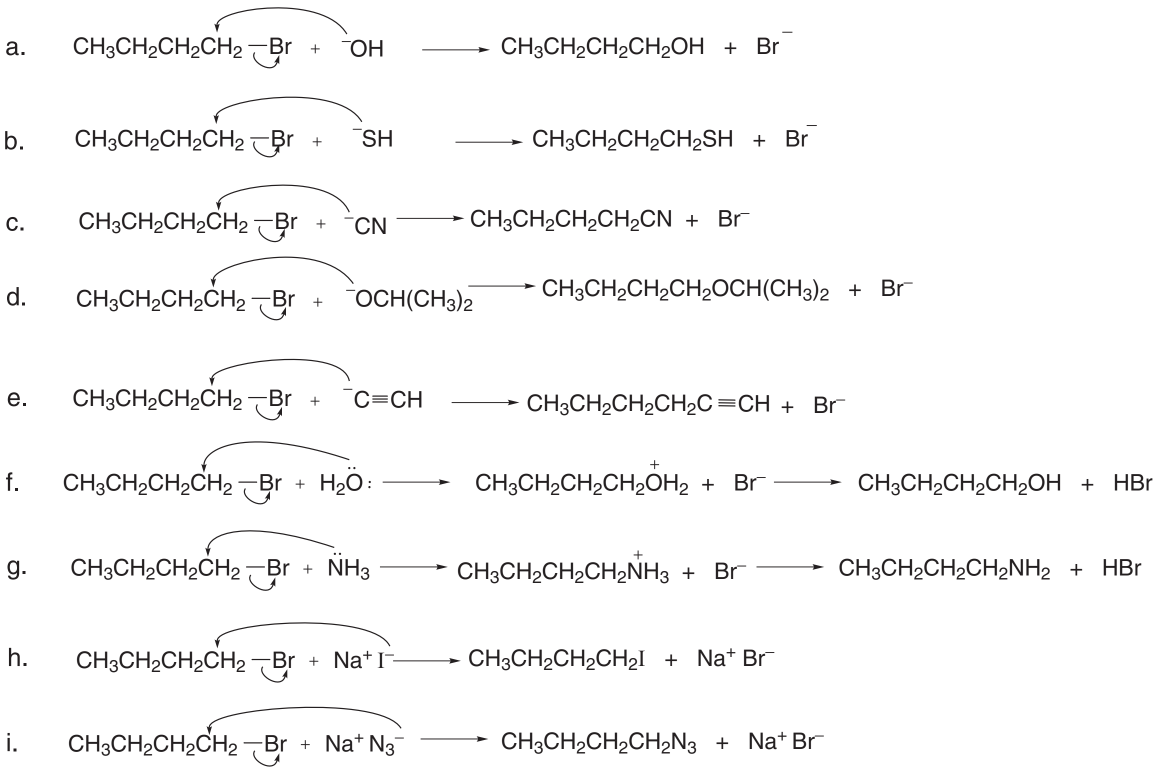
CH_3CH_2O replaces Cl.
$CH_3CH_2O^-$ is needed.

d.



HC≡C replaces Br.
HC≡C^- **is needed.**

7.20



a. $CH_3CH_2CH_2CH_2{-}Br + {}^{-}OH \longrightarrow CH_3CH_2CH_2CH_2OH + Br^{-}$

b. $CH_3CH_2CH_2CH_2{-}Br + {}^{-}SH \longrightarrow CH_3CH_2CH_2CH_2SH + Br^{-}$

c. $CH_3CH_2CH_2CH_2{-}Br + {}^{-}CN \longrightarrow CH_3CH_2CH_2CH_2CN + Br^{-}$

d. $CH_3CH_2CH_2CH_2{-}Br + {}^{-}OCH(CH_3)_2 \longrightarrow CH_3CH_2CH_2CH_2OCH(CH_3)_2 + Br^{-}$

e. $CH_3CH_2CH_2CH_2{-}Br + {}^{-}C{\equiv}CH \longrightarrow CH_3CH_2CH_2CH_2C{\equiv}CH + Br^{-}$

f. $CH_3CH_2CH_2CH_2{-}Br + H_2\ddot{O}: \longrightarrow CH_3CH_2CH_2CH_2\overset{+}{O}H_2 + Br^{-} \longrightarrow CH_3CH_2CH_2CH_2OH + HBr$

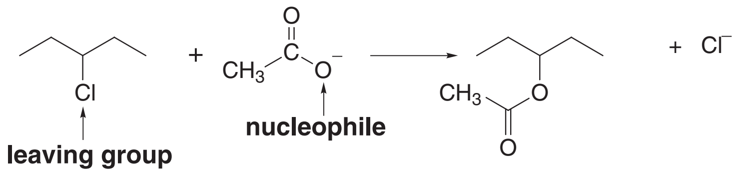
g. $CH_3CH_2CH_2CH_2{-}Br + \ddot{N}H_3 \longrightarrow CH_3CH_2CH_2CH_2\overset{+}{N}H_3 + Br^{-} \longrightarrow CH_3CH_2CH_2CH_2NH_2 + HBr$

h. $CH_3CH_2CH_2CH_2{-}Br + Na^{+}\,I^{-} \longrightarrow CH_3CH_2CH_2CH_2I + Na^{+}\,Br^{-}$

i. $CH_3CH_2CH_2CH_2{-}Br + Na^{+}\,N_3^{-} \longrightarrow CH_3CH_2CH_2CH_2N_3 + Na^{+}\,Br^{-}$

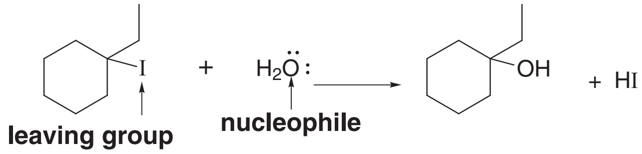
7.21 Usare i passaggi della risposta 7.10 e successivamente disegnare la reazione di trasferimento protonico, quando necessario.

a.

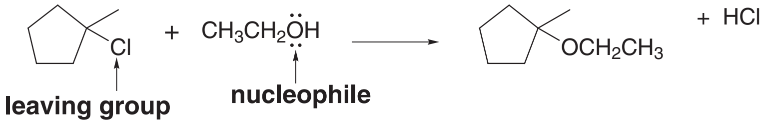


b.

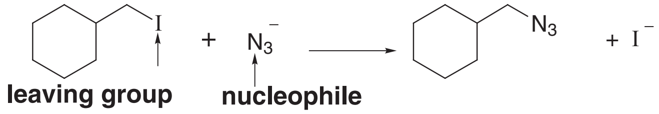
c.



d.



e.

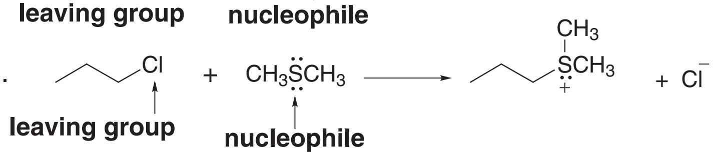


f.

g.

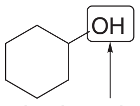
$(CH_3)_3CBr + CH_3COOH \longrightarrow (CH_3)_3COOCCH_3 + HBr$

h.



7.22 Un buon gruppo uscente è una base debole.

a.

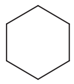


bad leaving group
⁻OH is a strong base.

b. $CH_3CH_2CH_2CH_2\text{—}\boxed{Cl}$

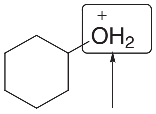
Cl⁻ good leaving group
weak base

c.



This only has C–C
and C–H bonds.
No good leaving group.

d.



good leaving group
H_2O is a weak base.

e. $CH_3CH_2\boxed{NH_2}$

bad leaving group
⁻NH₂ is a strong base.

f. $CH_3CH_2CH_2\text{—}\boxed{I}$

I⁻ good leaving group
weak base

7.23 Usare le regole della risposta 7.12.

a. increasing leaving group ability: $^-NH_2 < {}^-OH < F^-$

$^-NH_2$: most basic **worst leaving group**; F^-: least basic **best leaving group**

b. increasing leaving group ability: $^-NH_2 < {}^-OH < H_2O$

$^-NH_2$: most basic **worst leaving group**; H_2O: least basic **best leaving group**

c. increasing leaving group ability: $Cl^- < Br^- < I^-$

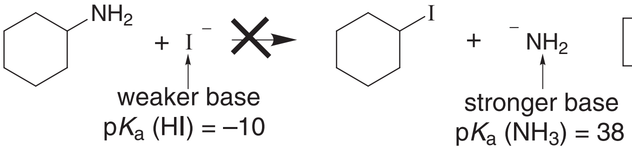
Cl^-: most basic **worst leaving group**; I^-: least basic **best leaving group**

d. increasing leaving group ability: $NH_3 < H_2O < H_2S$

NH_3: most basic **worst leaving group**; H_2S: least basic **best leaving group**

7.24 Confrontare il nucleofilo ed il gruppo uscente in ognuna delle seguenti reazioni. La reazione avverrà se procede verso la formazione della base più debole. Ricordare che più forte è l'acido (minore pK_a), più debole è la base coniugata.

a.



I^-: weaker base, pK_a (HI) = –10

$^-NH_2$: stronger base, pK_a (NH_3) = 38

Reaction will not occur.

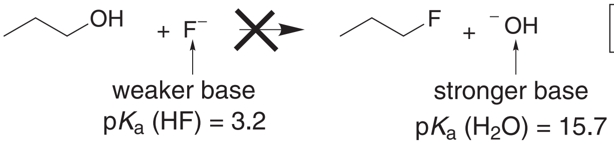
b. $CH_3CH_2I + CH_3O^- \longrightarrow CH_3CH_2OCH_3 + I^-$

CH_3O^-: stronger base, pK_a (CH_3OH) = 15.5

I^-: weaker base, pK_a (HI) = –10

Reaction will occur.

c.

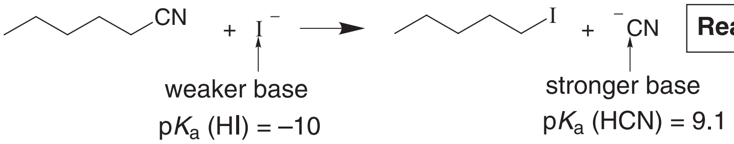


F^-: weaker base, pK_a (HF) = 3.2

^-OH: stronger base, pK_a (H_2O) = 15.7

Reaction will not occur.

d.



I^-: weaker base, pK_a (HI) = –10

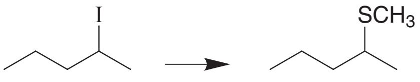
^-CN: stronger base, pK_a (HCN) = 9.1

Reaction will not occur.

7.25

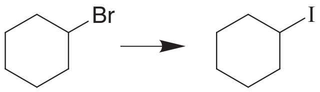
a. $CH_3CH_2CH_2CH_2Br \longrightarrow CH_3CH_2CH_2CH_2OH$ OH replaces Br. **$^-$OH is needed.**

b.



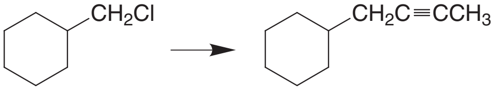
SCH$_3$ replaces I. **$^-$SCH$_3$ is needed.**

c.



I replaces Br. **I$^-$ is needed.**

d. $CH_3CH_2Cl \longrightarrow CH_3CH_2OCH_2CH_3$ OCH_2CH_3 replaces Cl.
$^-OCH_2CH_3$ is needed.

e.


$C{\equiv}CCH_3$ replaces Cl.
$^-C{\equiv}CCH_3$ is needed.

f. $CH_3CH_2Br \longrightarrow CH_3CH_2\overset{+}{N}(CH_3)_3\ Br^-$ $N(CH_3)_3$ replaces Br.
$N(CH_3)_3$ is needed.

7.26 Usare i suggerimenti della risposta 7.18.

a. Across a row of the periodic table nucleophilicity decreases.

$^-OH < {}^-NH_2 < CH_3^-$

b. • In a **polar protic solvent** (CH_3OH), nucleophilicity *increases down a column* of the periodic table, so: ^-SH is more nucleophilic than ^-OH.
• *Negatively charged species* are more nucleophilic than neutral species so ^-OH is more nucleophilic than H_2O.

$H_2O < {}^-OH < {}^-SH$

c. • In a **polar protic solvent** (CH_3OH), nucleophilicity *increases down a column* of the periodic table, so: $CH_3CH_2S^-$ is more nucleophilic than $CH_3CH_2O^-$.
• For two species with same attacking atom the more basic is more nucleophilic so $CH_3CH_2O^-$ is more nucleophilic than CH_3COO^-.

$CH_3COO^- < CH_3CH_2O^- < CH_3CH_2S^-$

d. Compare the nucleophilicity of N, S and O. In a polar aprotic solvent (acetone), nucleophilicity parallels basicity.

$CH_3SH < CH_3OH < CH_3NH_2$

e. In a **polar aprotic solvent** (acetone), nucleophilicity parallels basicity. Across a row and down a column of the periodic table nucleophilicity decreases.

$Cl^- < F^- < {}^-OH$

f. Nucleophilicity decreases across a row so ^-SH is more nucleophilic than Cl^-. In a **polar protic solvent** (CH_3OH), nucleophilicity increases down a column so Cl^- is more nucleophilic than F^-.

$F^- < Cl^- < {}^-SH$

7.27 Gli ioni alogenuro in fase gassosa non risentono di effetto solvente. Conseguentemente, l'andamento sarà lo stesso di quello della basicità – una base più forte è un nucleofilo più forte. Così **$F^- > Cl^- > Br^- > I^-$.**

7.28 ***Solventi polari protici* sono capaci i legami idrogeno**, e perciò devono contenere un H legato ad un atomo elettronegativo di O o N. ***Solventi polari aprotici* sono incapaci di legami idrogeno**, e perciò non contengono nessun legame O–H o N–H.

a. $(CH_3)_2CHOH$
contains O–H bond
protic

b. CH_3NO_2
no O–H or N–H bond
aprotic

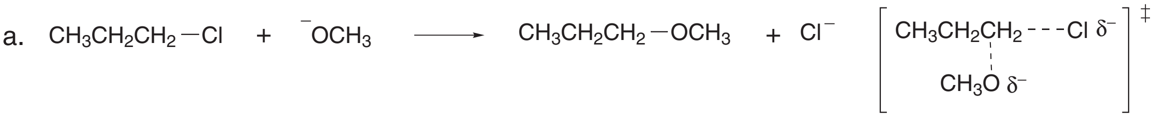
c. CH_2Cl_2
no O–H or N–H bond
aprotic

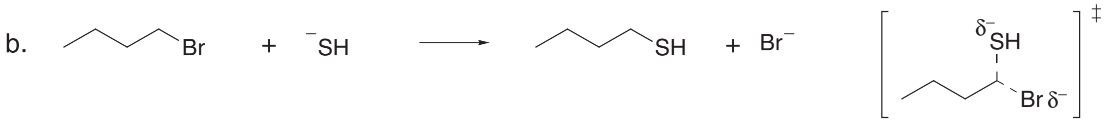
d. NH_3
contains N–H bond
protic

e. $N(CH_3)_3$
no O–H or N–H bond
aprotic

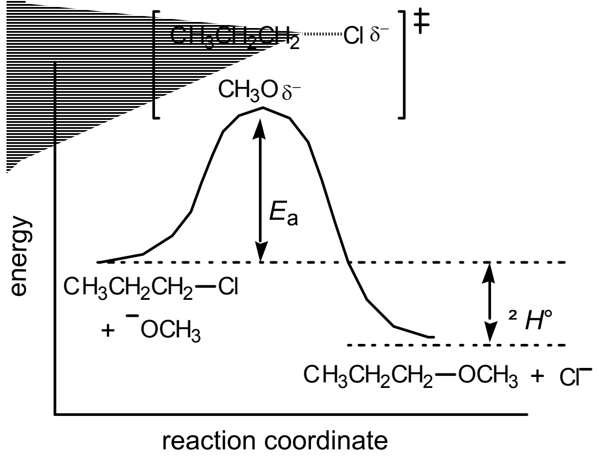
f. $HCONH_2$
contains an N–H bond
protic

7.29 Lo stato di transizione di una reazione S_N2 che presenta **legami tratteggiati sia con il nucleofilo che con il gruppo uscente**, deve contenere cariche parziali.

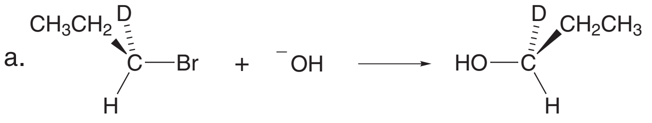


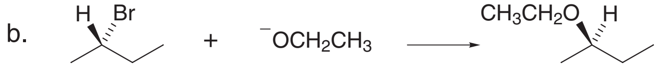


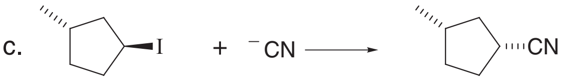
7.30 Tutte le razioni S_N2 sono ad un solo stadio.



7.31 Per disegnare i prodotti di una reazione S_N2, **sostituire il gruppo uscente con il nucleofilo, e poi disegnare la stereochimica con inversione di configurazione al centro stereogenico**.



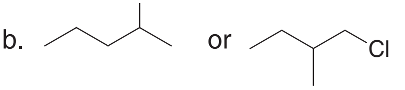




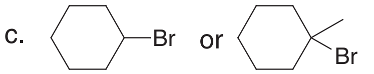
7.32 *L'aumento* del numero di gruppi R *aumenta* l'affollamento dello stato di transizione e *decresce* la velocità di una reazione S_N2.

a. CH_3CH_2-Cl or CH_3-Cl

1° alkyl halide methyl halide **faster reaction**



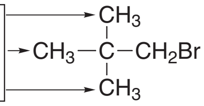
2° alkyl halide 1° alkyl halide **faster reaction**



2° alkyl halide **faster reaction** 3° alkyl halide

7.33

These 3 methyl groups make the alkyl halide sterically hindered.
This slows the rate of an S_N2 reaction even though it is a 1° alkyl halide.



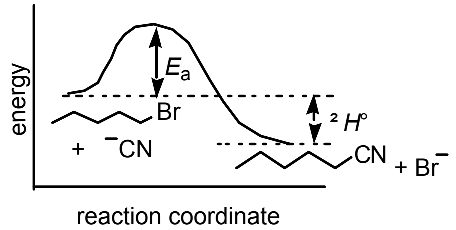
$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2Br$$

7.34

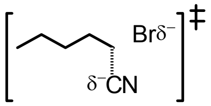
1° alkyl halide
S_N2 reaction

a. Mechanism:

b. Energy diagram:



c. Transition state:



d. Rate equation**:** one step reaction with both nucleophile and alkyl halide in the only step:

rate = k[R-Br][$^-$CN]

e. [1] The leaving group is changed from Br^- to I^-:

Leaving group becomes less basic → a better leaving group → faster reaction.

[2] The solvent is changed from acetone to CH_3CH_2OH:

Solvent changed to polar protic → decreases reaction rate.

[3] The alkyl halide is changed from $CH_3(CH_2)_4Br$ to $CH_3CH_2CH_2CH(Br)CH_3$:

Changed from 1° to 2° alkyl halide → the alkyl halide gets more crowded and the reaction rate decreases.

[4] The concentration of $^-$CN is increased by a factor of 5.

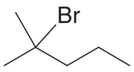
Reaction rate will increase by a factor of five.

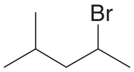
[5] The concentration of both the alkyl halide and $^-$CN are increased by a factor of 5:

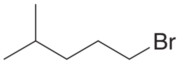
Reaction rate will increase by a factor of 25 (5 x 5 = 25).

7.35 Usare i suggerimenti della risposta 7.32.

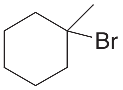
a.

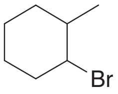

3° alkyl halide
least reactive

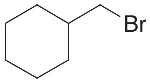

2° alkyl halide
intermediate reactivity


1° alkyl halide
most reactive

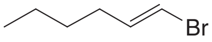
b.

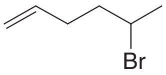

3° alkyl halide
least reactive

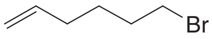

2° alkyl halide
intermediate reactivity


1° alkyl halide
most reactive

c.


vinyl halide
least reactivity


2° alkyl halide
intermediate reactivity


1° alkyl halide
most reactive

7.36

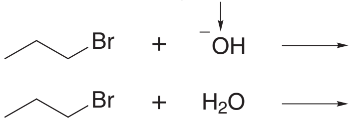
better leaving group

a. $CH_3CH_2Br + {}^-OH \longrightarrow$ **faster reaction**

$CH_3CH_2Cl + {}^-OH \longrightarrow$

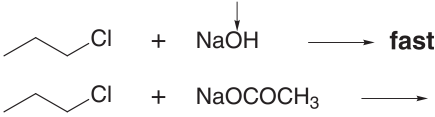
stronger nucleophile

b.

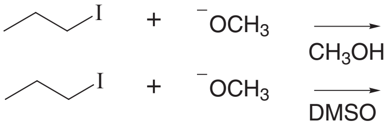

faster reaction

stronger nucleophile

c.


faster reaction

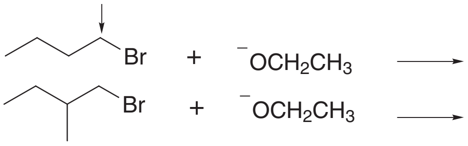
d.


faster reaction

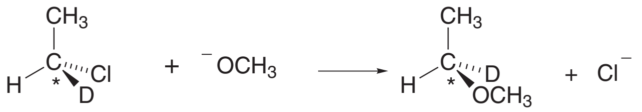
polar aprotic solvent

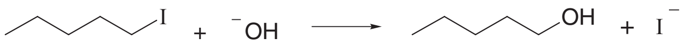
less steric hinderance

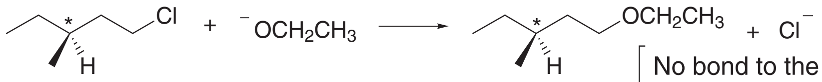
e.

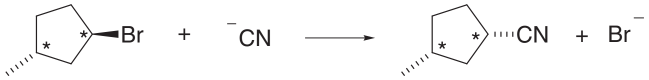

faster reaction

7.37 Tutte le reazioni S_N2 procedono attraverso attacco da retro del nucleofilo. Quando l'attacco nucleofilo avviene su un centro stereogenico, si ha inversione di configurazione.

a.

inversion of configuration

b.


c.

No bond to the stereogenic center is broken, since the leaving group is not bonded to the stereogenic center.

d.

inversion of configuration

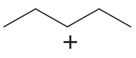
[* denotes a stereogenic center]

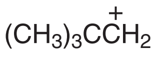
7.38 **I carbocationi sono classificati attraverso il numero dei gruppi R legati al carbonio**: 0 gruppi R = metile, 1 gruppo R = 1°, 2 gruppi R = 2°, e 3 gruppi R = 3°.

a.

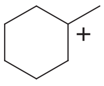
$CH_3\overset{+}{C}HCH_2CH_3$

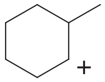
2 R groups
2° carbocation

b.

2 R groups
2° carbocation

c.

$(CH_3)_3C\overset{+}{C}H_2$

1 R group
1° carbocation

d.

3 R groups
3° carbocation

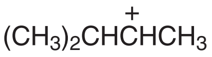
e.

2 R groups
2° carbocation

7.39 Per i carbocationi: **Aumento del numero di gruppi R = Aumento della stabilità**.

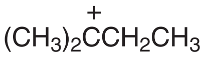
a.

$(CH_3)_2CHCH_2\overset{+}{C}H_2$

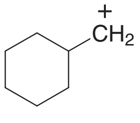
1° carbocation
least stable

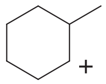

$(CH_3)_2CH\overset{+}{C}HCH_3$

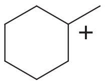
2° carbocation
intermediate stability


$(CH_3)_2\overset{+}{C}CH_2CH_3$

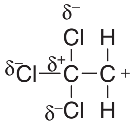
3° carbocation
most stable

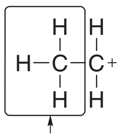
b.

1° carbocation
least stable


2° carbocation
intermediate stability


3° carbocation
most stable

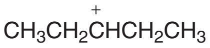
7.40


3 Cl groups -
electron *withdrawing*
destabilizing
less stable

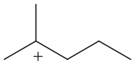

methyl group
without added Cl's
more stable

In $Cl_3CCH_2^+$, i tre atomi di Cl elettron attrattori posizionano una parziale carica positiva sul carbonio adiacente al carbocatione, destabilizzandolo.

7.41 Seguire le definizioni della risposta 7.38.

a.

$CH_3CH_2\overset{+}{C}HCH_2CH_3$

2° carbocation

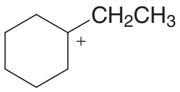
b.


3° carbocation

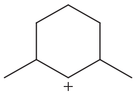
c.

$(CH_3)_2CHCH_2\overset{+}{C}H_2$

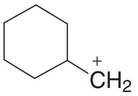
1° carbocation

d.


3° carbocation

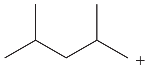
e.


2° carbocation

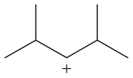
f.


1° carbocation

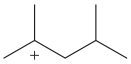
7.42 Per i carbocationi: **Aumento del numero di gruppi R = Aumento della stabilità**.

a.


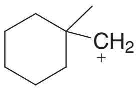
1° carbocation
least stable



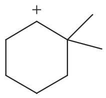
2° carbocation
intermediate stablity



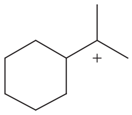
3° carbocation
most stable

b.


1° carbocation
least stable



2° carbocation
intermediate stablity

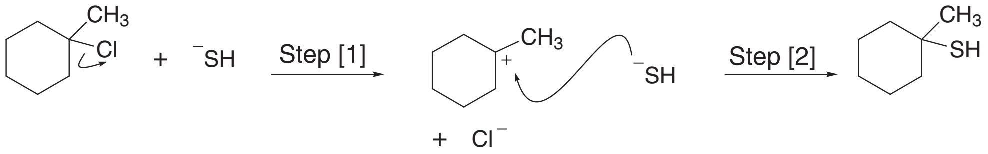


3° carbocation
most stable

7.43 In una reazione del primo ordine, **la velocità cambia con ogni cambiamento di [RX]**. La velocità è indipendente da ogni cambiamento di [nucleofilo].

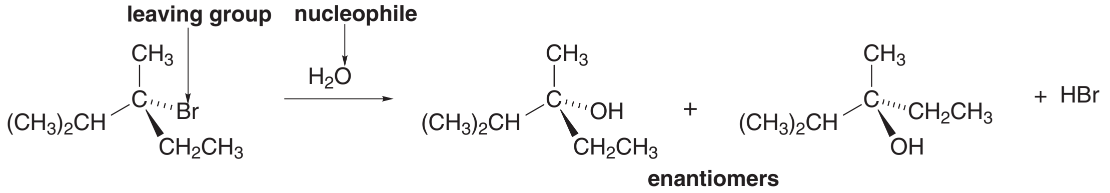
a. Se [RX] viene triplicata, e [:Nu$^-$] resta uguale: **la velocità triplica.**
b. Se sia [RX] che [:Nu$^-$] vengono triplicate: **la velocità triplica.**
c. Se [RX] viene dimezzata, e [:Nu$^-$] resta uguale: **la velocità si dimezza.**
d. Se [RX] viene dimezzata, e [:Nu$^-$] viene raddoppiata: **la velocità si dimezza.**

7.44 I due passaggi di una reazione S_N1 sono:
[1] **Rottura del legame C–Z per formare un carbocatione (Z = gruppo uscente).**
[2] **Formazione del legame C–Nu.**

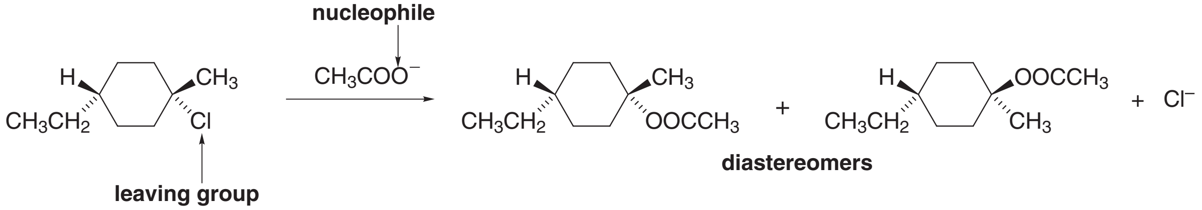


7.45 In reazioni S_N1, avviene sempre racemizzazione di un centro stereogenico. Disegnare i due prodotti, con le due possibili configurazioni del centro stereogenico.

a.



b.



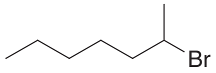
7.46 La velocità di reazione aumenta all'aumentare della sostituzione alchilica.

a. $(CH_3)_3CBr$ and $(CH_3)_3CCH_2Br$

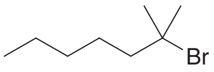
3° alkyl halide **faster $S_N1$reaction**

1° alkyl halide **slower $S_N1$reaction**

b.



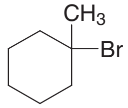
and



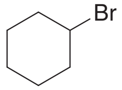
2° alkyl halide **slower $S_N1$reaction**

3° alkyl halide **faster $S_N1$reaction**

c.



and

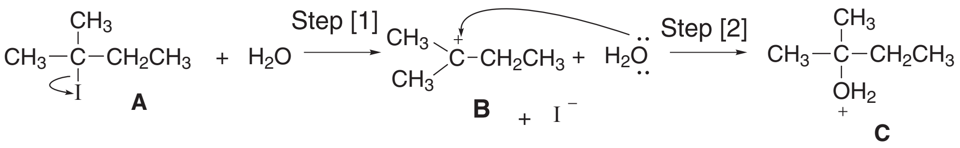


3° alkyl halide **faster $S_N1$reaction**

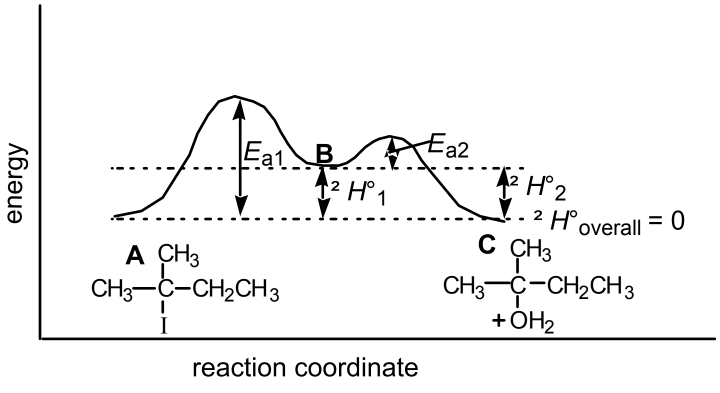
2° alkyl halide **slower $S_N1$reaction**

7.47

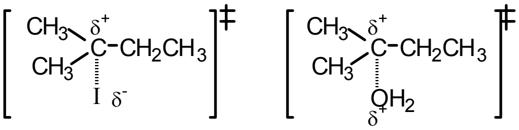
a. Mechanism: **S_N1 only**



b. Energy diagram:



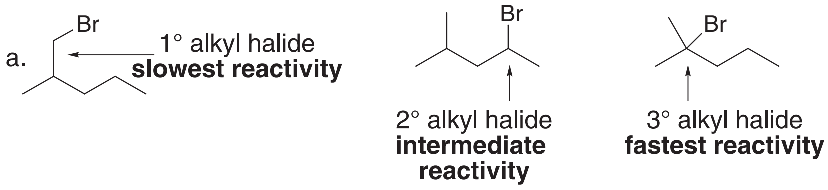
c. Transition states:

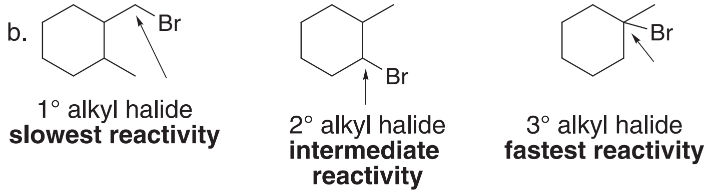


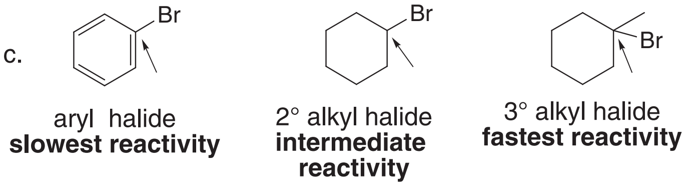
d. rate equation: **rate = $k[(CH_3)_2CICH_2CH_3]$**

e. [1] Leaving group changed from I^- to Cl^-: **rate decreases** since I^- is a better leaving group.
[2] Solvent changed from H_2O (polar protic) to DMF(polar aprotic):
rate decreases since polar protic solvent favors S_N1.
[3] Alkyl halide changed from 3° to 2°: **rate decreases** since 2° carbocations are less stable.
[4] $[H_2O]$ increased by factor of five: **no change in rate** since H_2O is not in rate equation.
[5] [R-X] and $[H_2O]$ increased by factor of five: **rate increases** by a factor of five. (Only the concentration of R-X affects the rate.)

7.48 La velocità della reazione S_N1 aumenta con l'aumentare della sostituzione alchilica.



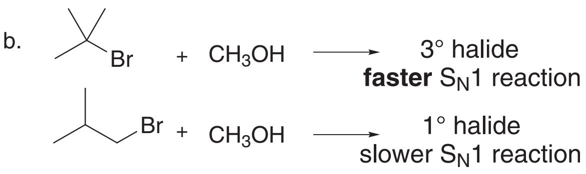


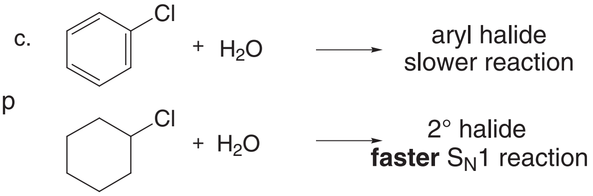


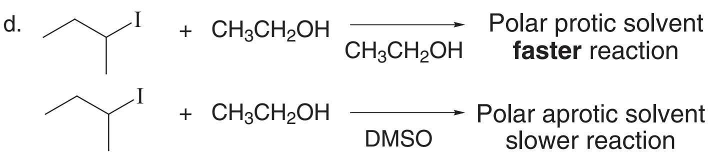
7.49 La velocità della reazione S_N1 aumenta con l'aumentare della sostituzione alchilica, solventi polari protici, e migliori gruppi uscenti.

a. $(CH_3)_3CCl + H_2O \longrightarrow$

$(CH_3)_3CI + H_2O \longrightarrow$ better leaving group **faster** reaction

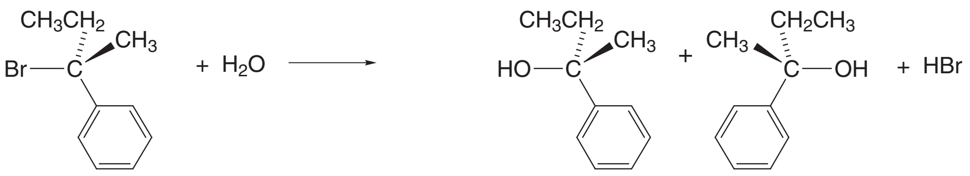




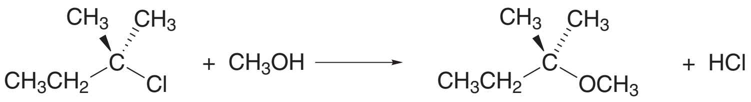


7.50

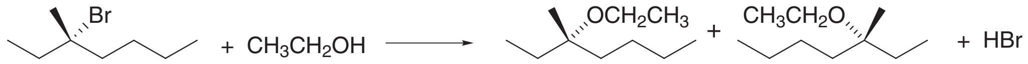
a.



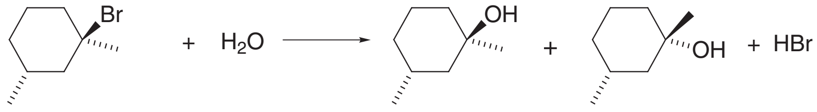
b.



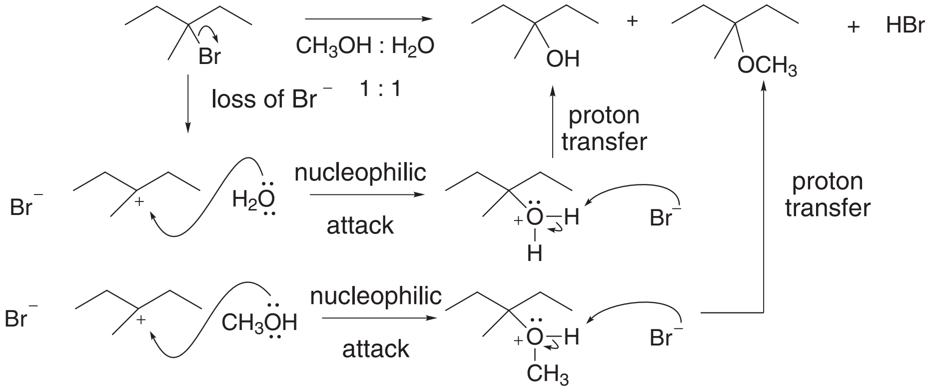
c.



d.



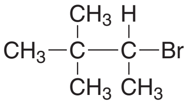
7.51



7.52 Solventi più polari favoriscono le reazioni $\mathrm{S_N}1$ attraverso la stabilizzazione del carbocatione intermedio. Diminuzione della polarità del solvente diminuisce la velocità della reazione $\mathrm{S_N}1$ rendendo l' E_a più elevata.

7.53
- Per **alogenuri alchilici metilici e 1°**, si avrà solo $\mathrm{S_N}2$.
- Per **alogenuri alchilici 2°**, si avrà $\mathrm{S_N}1$ e $\mathrm{S_N}2$.
- Per **alogenuri alchilici 3°**, si avrà solo $\mathrm{S_N}1$.

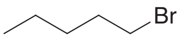
a.



$CH_3-C(CH_3)_2-CH(CH_3)-Br$

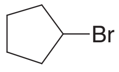
2° alkyl halide
$\mathrm{S_N}1$ and $\mathrm{S_N}2$

b.



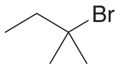
1° alkyl halide
$\mathrm{S_N}2$

c.



2° alkyl halide
$\mathrm{S_N}1$ and $\mathrm{S_N}2$

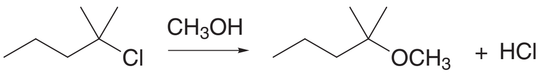
d.



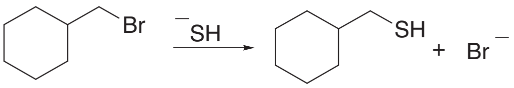
3° alkyl halide
$\mathrm{S_N}1$

7.54
- Per **alogenuri alchilici metilici e 1°**, si avrà solo $\mathrm{S_N}2$.

- Per **alogenuri alchilici 2°**, si avrà S_N1 e S_N2 ed altri fattori determineranno quale meccanismo sarà operante.
- Per **alogenuri alchilici 3°**, si avrà solo S_N1.

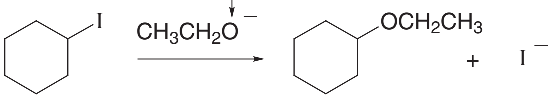
a.


3° alkyl halide
only S_N1

b.


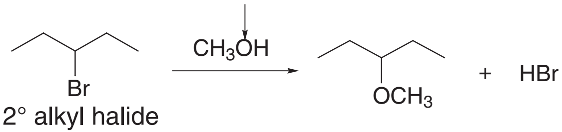
1° alkyl halide
only S_N2

Strong nucleophile
favors S_N2.

c.


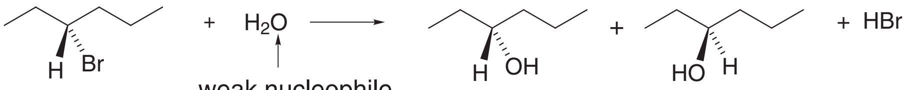
2° alkyl halide
Both $S_N1$and S_N2 are possible.

Weak nucleophile
favors S_N1.

d.


2° alkyl halide
Both $S_N1$and S_N2 are possible.

7.55 Prima decidere se la reazione procede *via* un meccanismo S_N1 o S_N2. Quindi disegnare il prodotto, con la stereochimica.

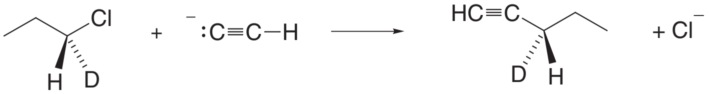
a.


2° alkyl halide
S_N1 and S_N2

weak nucleophile
favors S_N1

enantiomers

S_N1 = racemization at the stereogenic C

b.


1° alkyl halide
S_N2 only

S_N2 = inversion at the stereogenic C

7.56 I composti con gruppi uscenti migliori reagiscono più velocemente. Basi più deboli sono gruppi uscenti migliori.

a. $CH_3CH_2CH_2Cl$ and $CH_3CH_2CH_2I$
↑
weaker base
better leaving group

b. $(CH_3)_3CBr$ and $(CH_3)_3CI$
↑
weaker base
better leaving group

c. $(CH_3)_3C-OH$ and $(CH_3)_3C-\boxed{\overset{+}{O}H_2}$
↑
weaker base
better leaving group

d. $CH_3CH_2CH_2OH$ and $CH_3CH_2CH_2-\boxed{OCOCH_3}$
↑
weaker base
better leaving group

7.57 • **Solventi polari protici** favoriscono il meccanismo S_N1 attraverso la solvatazione del carbocatione intermedio e dell'alogenuro.
• **Solventi polari aprotici** favoriscono il meccanismo S_N2 rendendo il nucleofilo più forte.

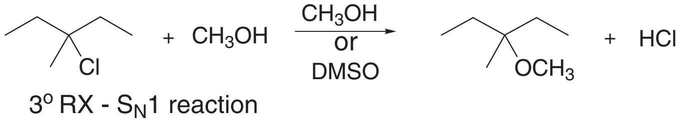
a. CH_3CH_2OH	b. CH_3CN	c. CH_3COOH	d. $CH_3CH_2OCH_2CH_3$
polar protic solvent	*polar aprotic solvent*	*polar protic solvent*	*polar aprotic solvent*
contains an O–H bond	no O–H or N–H bond	contains an O–H bond	no O–H or N–H bond
favors S_N1	**favors S_N2**	**favors S_N1**	**favors S_N2**

7.58 Confrontare i solventi nelle reazioni seguenti. **Perchè un solvente aumenti la velocità di reazione di una reazione S_N1, il solvente deve essere *polare protico*.**

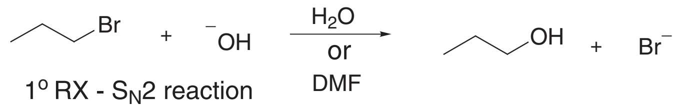
a. $(CH_3)_3CBr + H_2O \xrightarrow[(CH_3)_2C=O]{H_2O \text{ or}} (CH_3)_3COH + HBr$

3° RX - S_N1 reaction

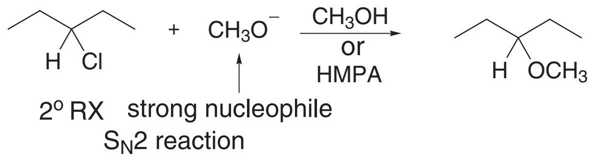
H_2O
Polar protic solvent
increases the rate of an S_N1 reaction.

b.


CH_3OH
Polar protic solvent
increases the rate of an S_N1 reaction.

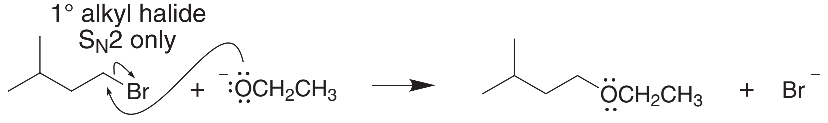
c.


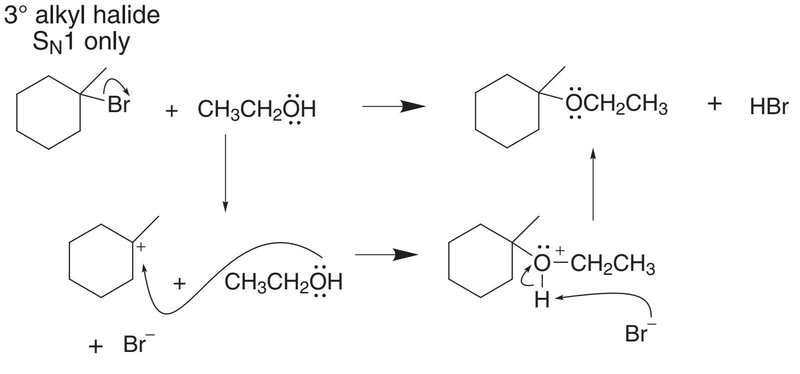
DMF $[HCON(CH_3)_2]$
Polar aprotic solvent
increases the rate of an S_N2 reaction.

d.


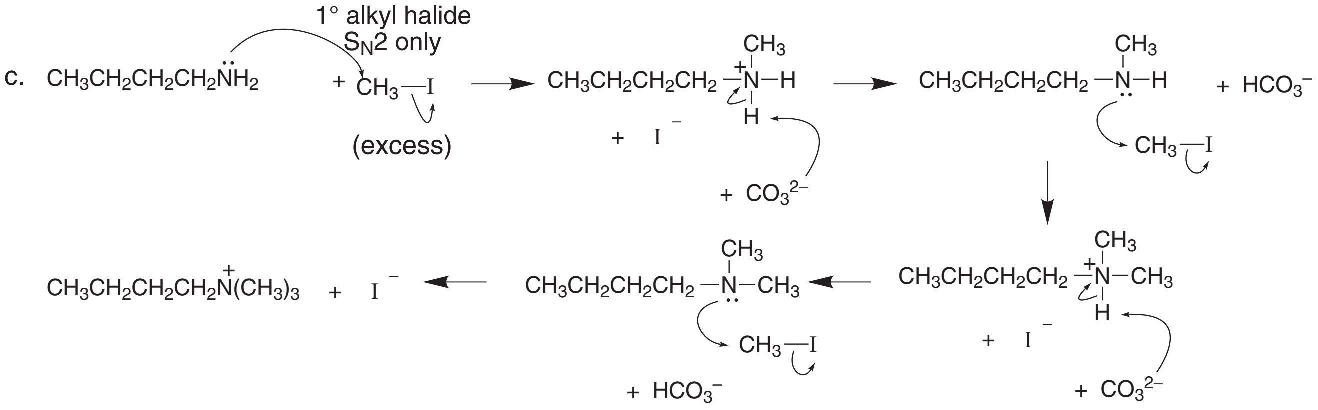
HMPA $[(CH_3)_2N]_3P=O$
Polar aprotic solvent
increases the rate of an S_N2 reaction.

7.59 Prima decidere se la reazione procederà con meccanismo S_N1 o S_N2 (Risposta 7.36), e successivamente disegnare il meccanismo.

a.


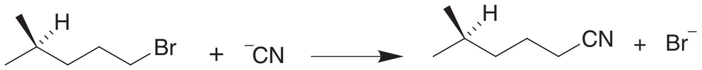
b.


c.



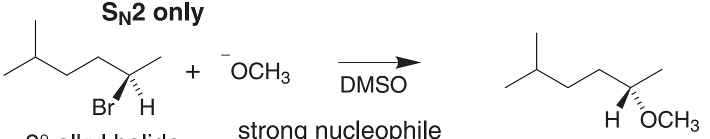
7.60

a.



1° alkyl halide
S_N2 only

b.

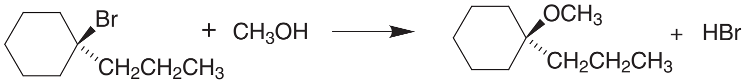


2° alkyl halide
S_N1 and S_N2

strong nucleophile
polar aprotic solvent
Both favor S_N2.

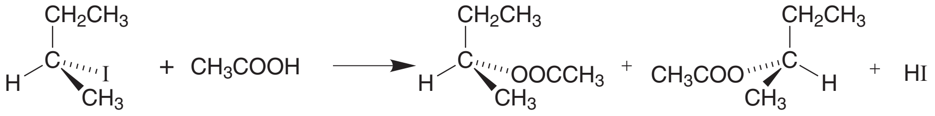
reaction at a stereogenic center
inversion of configuration

c.



3° alkyl halide
S_N1 only

d.



2° alkyl halide
S_N1 and S_N2

Weak nucleophile
favors S_N1.

reaction at a stereogenic center
racemization of product

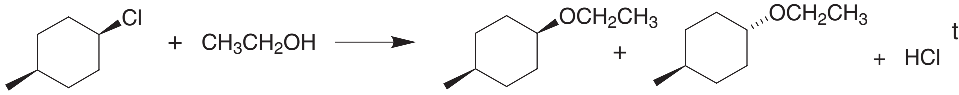
e.

2° alkyl halide
S_N1 and S_N2

strong nucleophile
polar aprotic solvent
Both favor S_N2.

reaction at a stereogenic center
inversion of configuration

f.



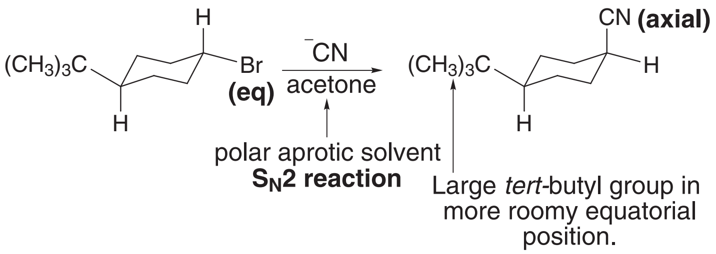
2° alkyl halide
S_N1 and S_N2

Weak nucleophile
favors S_N1.

two products - **diastereomers**
Nucleophile attacks
from above and below.

7.61

a.

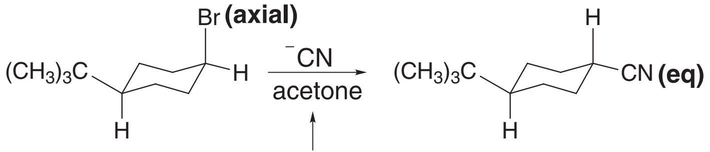


polar aprotic solvent
S_N2 reaction

Large *tert*-butyl group in more roomy equatorial position.

inversion (equatorial to axial)

b.



polar aprotic solvent
S_N2 reaction

inversion (axial to equatorial)

7.62

$$CH_3{-}I \xrightarrow[CH_3OH]{NaOCH_3 \; + \; NaSCH_3} CH_3{-}OCH_3 + \underset{\textbf{major product}}{CH_3{-}SCH_3}$$

polar protic solvent
Nucleophilicity increases
down a column as anion size increases.
$^-SCH_3$ is the better nucleophile.

$$CH_3{-}I \xrightarrow[(CH_3)_2S{=}O]{NaOCH_3 \; + \; NaSCH_3} \underset{\textbf{major product}}{CH_3{-}OCH_3} + CH_3{-}SCH_3$$

polar aprotic solvent
Nucleophilicity decreases
down a column as anion size increases.
$^-OCH_3$ is the better nucleophile.

7.63

a. Hexane is nonpolar and therefore few nucleophiles will dissolve in it.

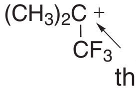
b. $(CH_3)_3CO^-$ is a stronger base than $CH_3CH_2O^-$:

The three electron donating CH_3 groups add electron density to the negative charge of the conjugate base, destabilizing it and making it a stronger base.

c. By the Hammond postulate, the S_N1 reaction is faster with RX that form more stable carbocations.

$(CH_3)_3C^+$

3° Carbocation is stabilized by three electron donor CH_3 groups.



$$(CH_3)_2\underset{CF_3}{\underset{|}{C}}{}^+$$

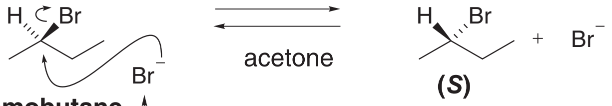
Although this carbocation is also 3°, the three electron withdrawing F atoms destabilize the positive charge. Since the carbocation is less stable, the reaction to form it is slower.

d. The identifty of the nucleophile does not affect the rate of S_N1 reactions since the nucleophile does not appear in the rate-determining step.

e.

Polar aprotic solvent
favors S_N2 reaction.

2° alkyl halide
S_N1 or S_N2



(*R*)-2-bromobutane
optically active

strong nucleophile
favors S_N2 reaction

This compound reacts with Br^- until a 50:50
mixture results, making the mixture optically inactive.
Then either compound can react with Br^- and the
mixture remains optically inactive.

7.64

1° alkyl halides react by
S_N2 reactions.
H_2O is a weak nucleophile
and favors **S_N1** reactions.
This makes the reactions slow.

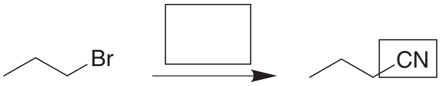
$$CH_3Cl \xrightarrow[\text{slow}]{H_2O} CH_3OH$$

$$CH_2Cl_2 \xrightarrow[\text{extremely slow}]{H_2O} CH_3OH$$

H_2O is a weak nucleophile. Since CH_3Cl must react by S_N2, the weak nucleophile means a slower reaction. Adding more Cl's adds steric hindrance, decreasing the rate even more.

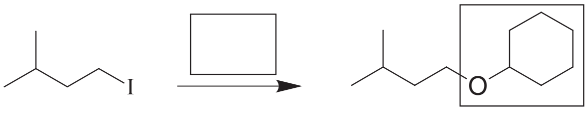
7.65

a.

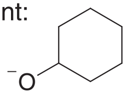


The nucleophile has replaced the leaving group.
Missing reagent: **^-CN**

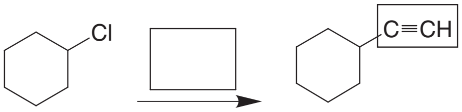
b.



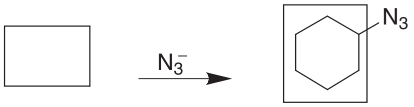
The nucleophile has replaced the leaving group.
Missing reagent:



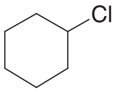
c.

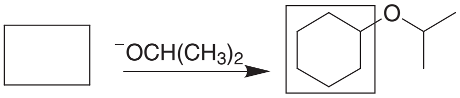


The nucleophile has replaced the leaving group.
Missing reagent: $^-C{\equiv}CH$

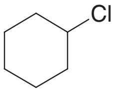
d.


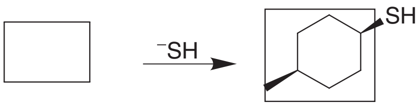
The nucleophile has replaced the halide.
Starting material:



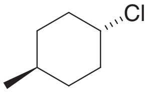
e.


The nucleophile has replaced the halide.
Starting material:



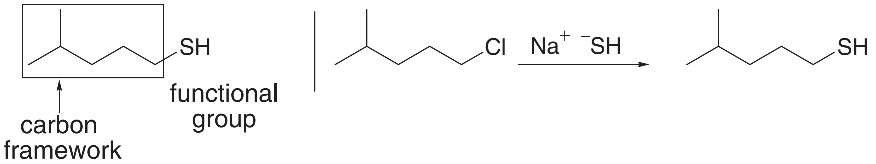
f.


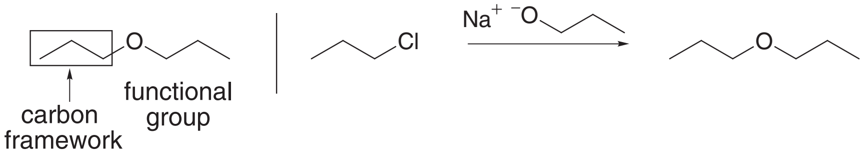
The nucleophile has replaced the halide.
Starting material:

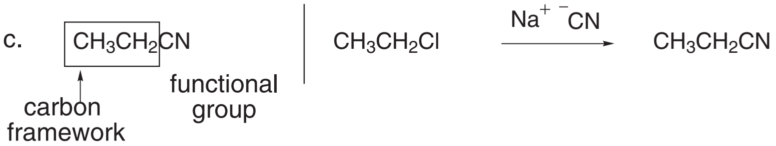


The leaving must have the opposite orientation to the position of the nucleophile in the product.

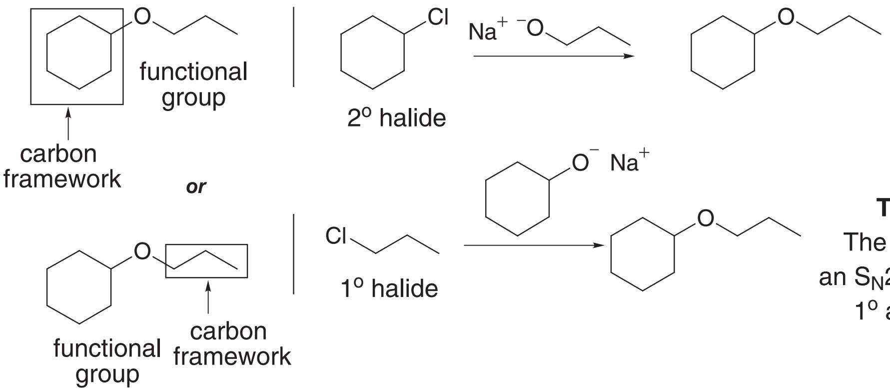
7.66 Per individuare una sintesi, individuare la frazione carboniosa ed il gruppo funzionale del prodotto. **La frazione carboniosa deriva dall'alogenuro alchilico ed il gruppo funzionale da nucleofilo.**

a.


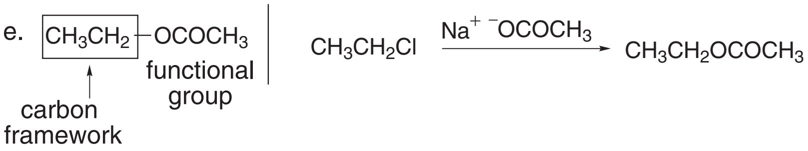
b.


c.


$\boxed{CH_3CH_2}CN$ | $CH_3CH_2Cl \xrightarrow{Na^+ \ ^-CN} CH_3CH_2CN$

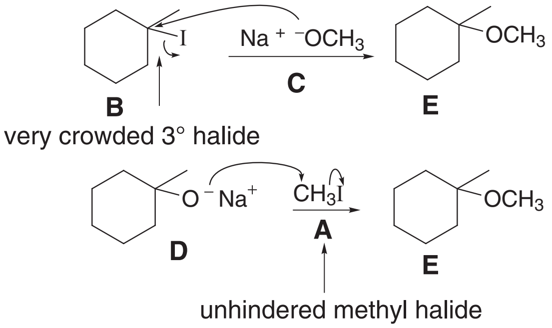
d.


This path is preferred.
The strong nucleophile favors an S_N2 reaction so an unhindered 1° alkyl halide reacts faster.

e.


$\boxed{CH_3CH_2}-OCOCH_3$ | $CH_3CH_2Cl \xrightarrow{Na^+ \ ^-OCOCH_3} CH_3CH_2OCOCH_3$

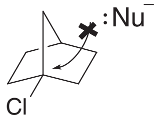
7.67



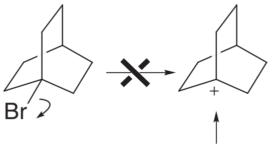
preferred method
The strong nucleophile favors S_N2 reaction so the alkyl halide should be unhindered for a faster reaction.

7.68

A and **B** can't react by an S_N2 mechanism because the backside attack of the nucleophile is blocked:



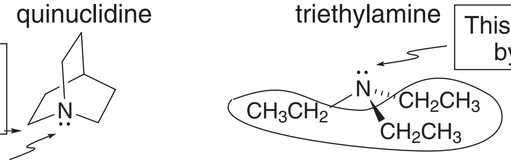
The S_N1 reaction would require a planar carbocation, and geometry doesn't allow this to occur. The resulting carbocation cannot adopt the needed trigonal planar geometry and thus it does not form.



This carbocation cannot adopt a trigonal planar geometry.

7.69 L'ingombro sterico diminuisce la nucleofilicità.

The three alkyl groups are "tied back" in a ring, making the electron pair more available.



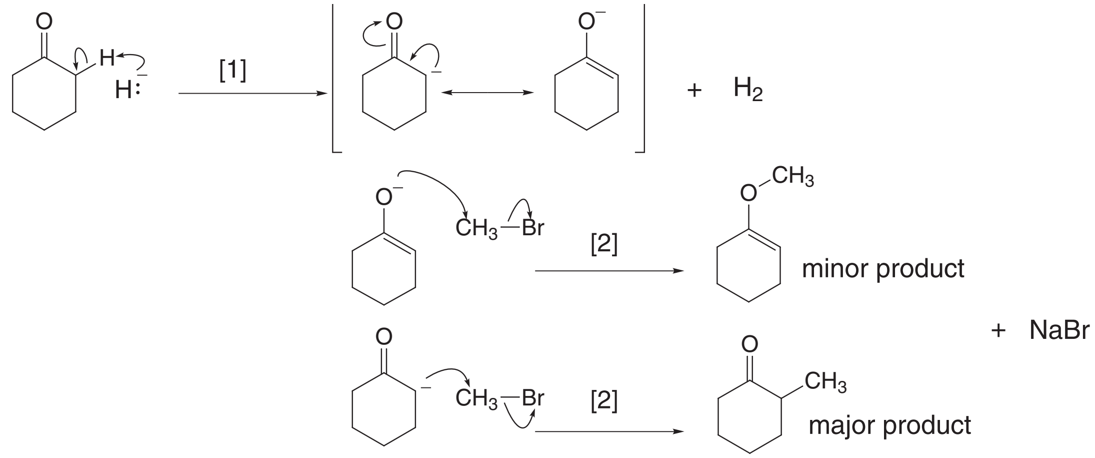
This electron pair is more hindered by the three CH_2CH_3 groups.

These bulky groups around the N cause steric hindrance and this decreases nucleophilicity.

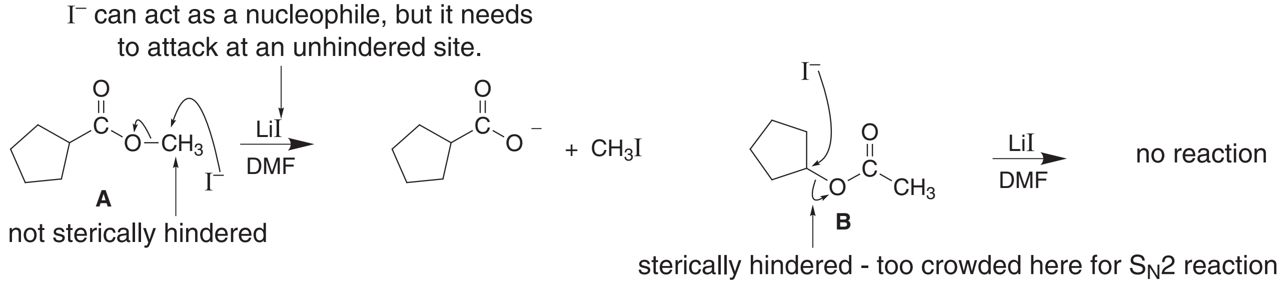
This electron pair on quinuclidine is much more available than the one on triethylamine.

less steric hindrance
more nucleophilic

7.70



7.71



I^- can act as a nucleophile, but it needs to attack at an unhindered site.

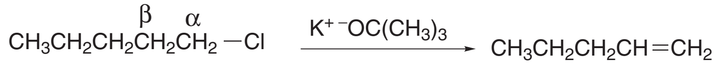
not sterically hindered

sterically hindered - too crowded here for S_N2 reaction

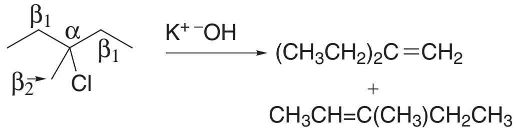
Capitolo 8

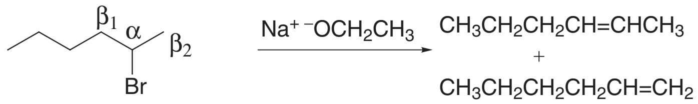
8.1 • Il carbonio legato al gruppo uscente è il **carbonio α**. Ogni carbonio legato ad esso è un **carbonio β**.

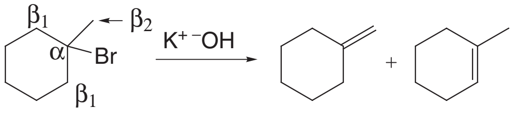
- **Per disegnare i prodotti di una reazione di eliminazione:** Rimuovere il gruppo uscente dal carbonio α ed un H dal carbonio β e formare un legame π.

a.


$CH_3CH_2CH_2\overset{\beta}{C}H_2\overset{\alpha}{C}H_2{-}Cl \xrightarrow{K^+\,^-OC(CH_3)_3} CH_3CH_2CH_2CH{=}CH_2$

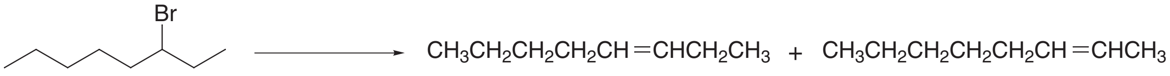
c.


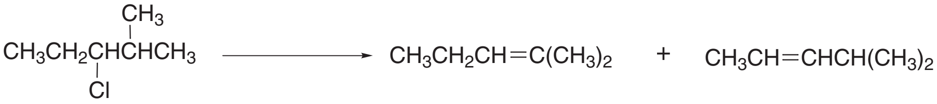
b.


d.


8.2

a. $CH_3CH_2CH_2CH_2CH_2CH_2Br \longrightarrow CH_3CH_2CH_2CH_2CH{=}CH_2$

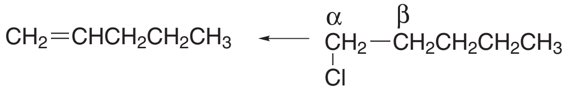
b.


c.


$CH_3CH_2\underset{Cl}{\underset{|}{C}}H\overset{CH_3}{\overset{|}{C}}HCH_3 \longrightarrow CH_3CH_2CH{=}C(CH_3)_2 + CH_3CH{=}CHCH(CH_3)_2$

d.

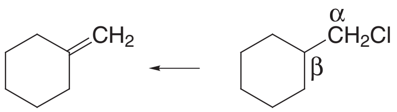

8.3 Per dare un solo prodotto in una reazione di eliminazione, **l'alogenuro di partenza deve avere un solo tipo di carboni β.**

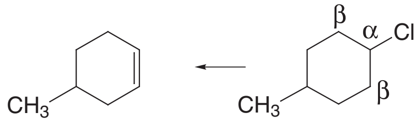
a.


$CH_2{=}CHCH_2CH_2CH_3 \longleftarrow \underset{Cl}{\overset{\alpha}{C}H_2}{-}\overset{\beta}{C}H_2CH_2CH_2CH_3$

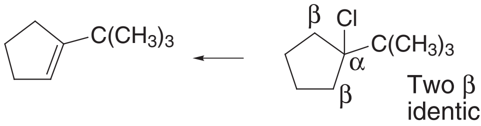
b.


$(CH_3)_2CHCH{=}CH_2 \longleftarrow (CH_3)_2CH\overset{\beta}{C}H_2{-}\overset{\alpha}{C}H_2Cl$

c.


d.


Two β carbons are identical.

e.


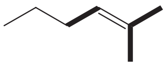
Two β carbons are identical.

8.4 Gli alcheni sono classificati attraverso il numero di atomi legati al doppio legame. Un alchene monosostituito presenta un atomo di carbonio legato al doppio legame, un alchene disostituito presenta due atomi di carbonio legati al doppio legame, ecc. (Gli atomi o i legami in grassetto sono legati al C=C.)

a. $\mathbf{C}H_3CH{=}CH\mathbf{C}H_2CH_3$

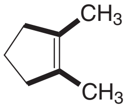
2 C's bonded to C=C
disubstituted

b.



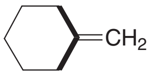
3 C's bonded to C=C
trisubstituted

c.



4 C's bonded to C=C
tetrasubstituted

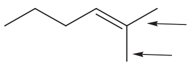
d.



2 C's bonded to C=C
disubstituted

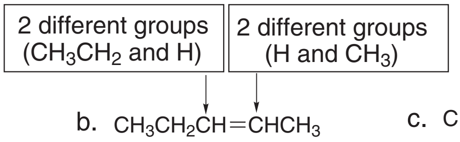
8.5 Perchè esistano isomeri cis e trans, i due gruppi su ciascun carbonio terminale del doppio legame devono essere diversi tra loro.

a.



two CH_3 groups
no cis or
trans isomers

b.

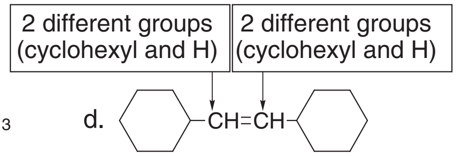


cis and trans isomers possible

c. $CH_2{=}CHCH_2CH_2CH_3$

two H's
no cis or
trans isomers

d.

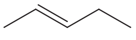


cis and trans isomers possible

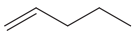
8.6 Due definizioni:

- **Gli isomeri costituzionali** differiscono nell'ordine in cui gli atomi sono legati fra loro.
- **Gli stereoisomeri** differiscono solo nella disposizione 3-D degli atomi nello spazio.

a.

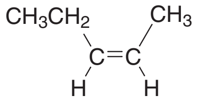


and



different connectivity of atoms
constitutional isomers

c.



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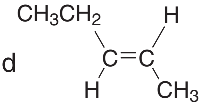
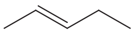


cis trans
different arrangement of atoms in space
stereoisomers

b.



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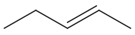
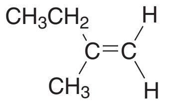
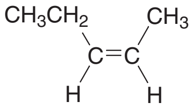


trans trans
identical

d.



and

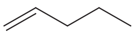


different connectivity of atoms
constitutional isomers

8.7 Due regole per predire la stabilità relativa degli alcheni:

[1] Gli alcheni trans sono più stabili di quelli cis.
[2] La stabilità di un alchene aumenta all'aumentare dei gruppi R sul doppio legame C=C.

a.



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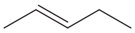
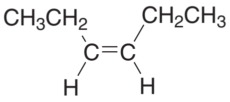
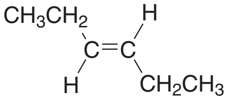


monosubstituted disubstituted
more stable

b.

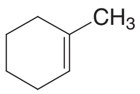


and

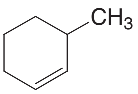


cis trans
more stable

c.



and



trisubstituted
more stable

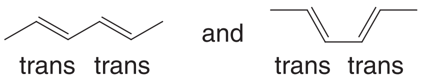
disubstituted

8.8 Usare le definizioni della risposta 8.6.

a.

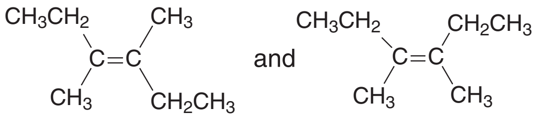
different connectivity
constitutional isomers

c.



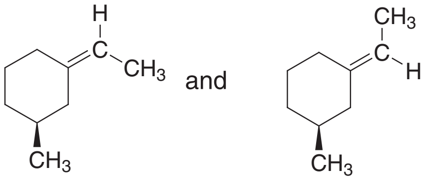
identical

b.



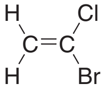
stereoisomers

d.



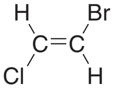
stereoisomers

8.9 Ci sono tre isomeri diversi. Gli isomeri cis e trans sono diastereomeri.

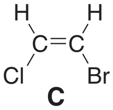


A

constitutional isomer
of **B** and **C**



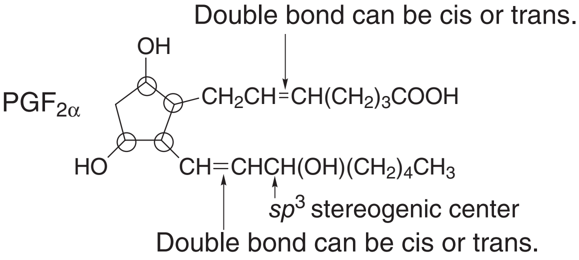
B



C

diastereomers

8.10



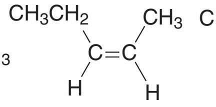
a. 5 sp^3 stereogenic centers (4 circled, one labeled)
b. 2 double bonds can both be cis or trans.
c. 2^7 = 128 stereoisomers possible

8.11 Usare le regole delle risposta 8.5 per ordinare gli alcheni.

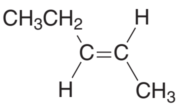
a. $CH_2{=}CHCH_2CH_2CH_3$

monosubstituted

least stable



disubstituted
cis
intermediate stability

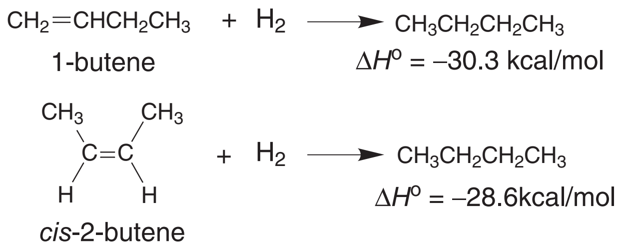


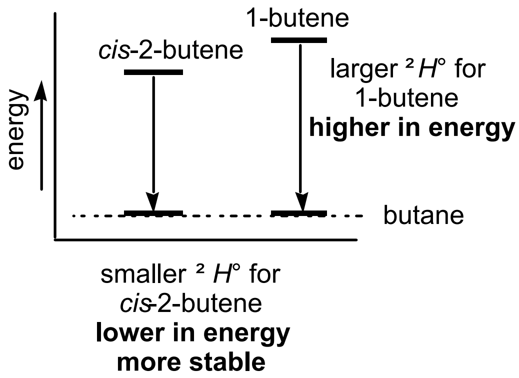
disubstituted
trans
most stable

b. $CH_2{=}CHCH(CH_3)_2$ $CH_2{=}C(CH_3)CH_2CH_3$ $(CH_3)_2C{=}CHCH_3$

$CH_2{=}CHCH(CH_3)_2$	$CH_2{=}C(CH_3)CH_2CH_3$	$(CH_3)_2C{=}CHCH_3$
monosubstituted	disubstituted	trisubstituted
least stable	**intermediate stability**	**most stable**

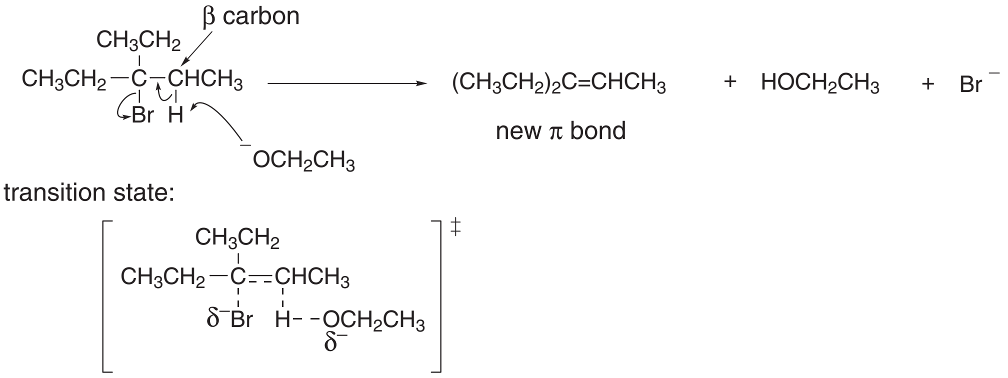
8.12 **Un valore più negativo di Δ*H*° significa che la reazione è più esotermica**. Poichè sia l'1-butene che il *cis*-2-butene formano lo stesso prodotto (butano) questo dato mostra che l' 1-butene presenta un'energia più elevata, **dal momento che viene rilasciata più energia nella reazione di idrogenazione**.



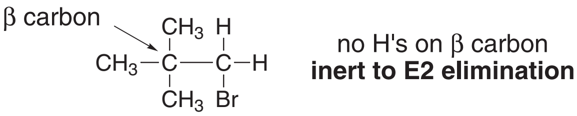


8.13 In un meccanismo E2, quattro legami sono coinvolti in un singolo passaggio. Usare le frecce curve per mostrare queste azioni simultanee:

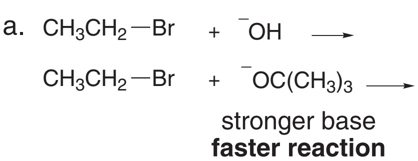
[1] La base attacca un idrogeno su un carbonio β.
[2] Si forma un legame π.
[3] Il gruppo uscente viene allontanato.

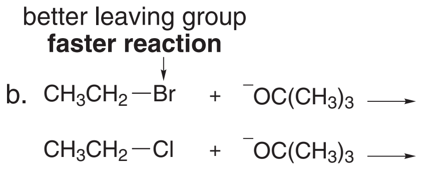


8.14 Perchè possa avvenire una eliminazione E2 è necessaria la presenza di almeno un idrogeno su un carbonio β.



8.15





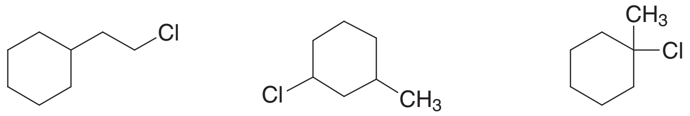
8.16 All'aumentare dei gruppi R sul carbonio che porta il gruppo uscente, la velocità di una reazione E2 aumenta.

a. $(CH_3)_2CHCH_2CH_2CH_2Br$ — 1° alkyl halide **least reactive**

$(CH_3)_2CHCH_2CH(Br)CH_3$ — 2° alkyl halide **intermediate reactivity**

$(CH_3)_2C(Br)CH_2CH_2CH_3$ — 3° alkyl halide **most reactive**

b.



1° alkyl halide **least reactive** — 2° alkyl halide **intermediate reactivity** — 3° alkyl halide **most reactive**

8.17 Usare le seguenti caratteristiche di una reazione E2 per rispondere alle domande:

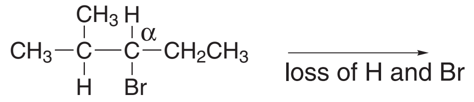
[1] Le reazioni E2 sono del secondo ordine ed ad un singolo stadio.
[2] Gli alogenuri più sostituiti reagiscono più velocemente.
[3] Le reazioni con basi forti o gruppi uscenti migliori sono più veloci.
[4] Le reazioni con solventi polari aprotici sono più veloci.

Equazione della velocità: velocità = *k*[RX][Base]

a. triplicare la concentrazione dell'alogenuro alchilico = **la velocità triplica**
b. dimezzare la concentrazione della base = **la velocità dimezza**
c. cambiare il solvente da CH_3OH a DMSO = **la velocità aumenta** (Un solvente polare aprotico è migliore per l'E2.)
d. cambiare il gruppo uscente da I^- a Br^- = **la velocità decresce** (I^- è un gruppo uscente migliore.)
e. cambiare la base da ^-OH a H_2O = **la velocità decresce** (base più debole)
f. cambiare l'alogenuro alchilico da CH_3CH_2Br a $(CH_3)_2CHBr$ = **la velocità aumenta** (Gli alogenuri più sostituiti reagiscono più velocemente).

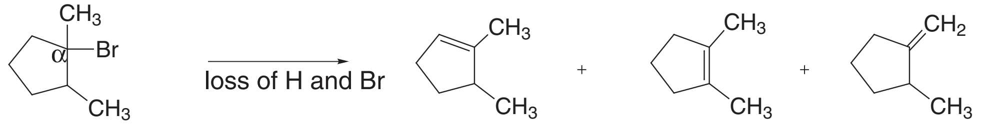
8.18 La regola di Zaitsev stabilisce: In una reazione di β-eliminazione, il prodotto maggioritario ha il doppio legame più sostituito.

a.



$(CH_3)_2C{=}CHCH_2CH_3$ trisubstituted **major product** + $(CH_3)_2CHCH{=}CHCH_3$ disubstituted **minor product**

b.



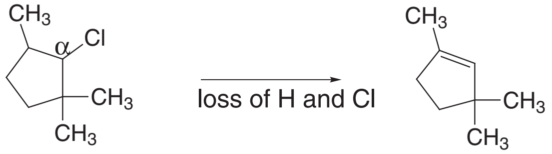
trisubstituted **minor product** — tetrasubstituted **major product** — disubstituted **minor product**

c.

\+ $CH_3CH_2CH_2CH_2CH{=}CHCH_3$

monosubstituted **minor product** — disubstituted **major product**

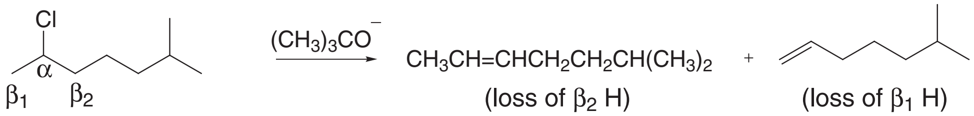
d.



trisubstituted **ONLY product**

8.19

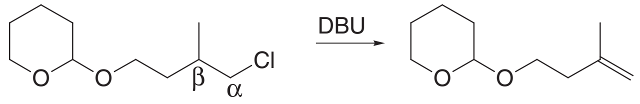
a.



(loss of β_2 H) **major product** disubstituted

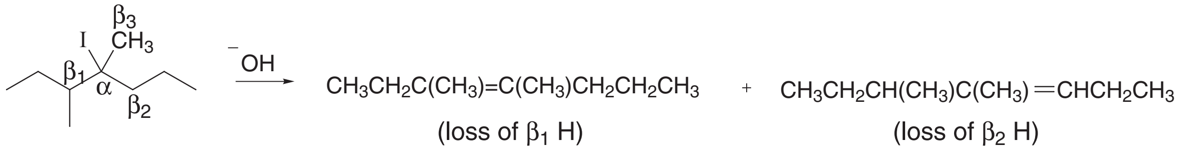
(loss of β_1 H) monosubstituted

b.



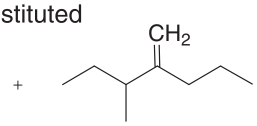
only product

c.



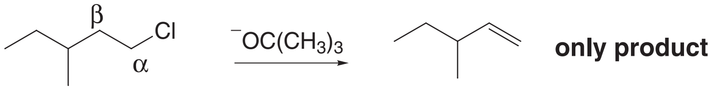
(loss of β_1 H) **major product** tetrasubstituted

(loss of β_2 H) trisubstituted



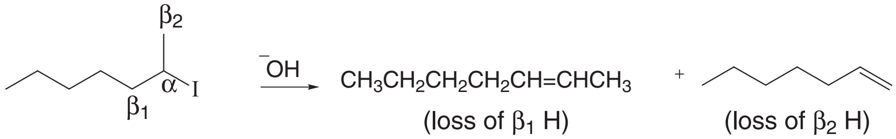
(loss of β_3 H) disubstituted

d.



only product

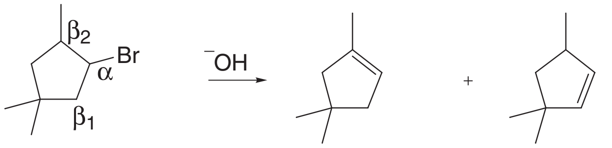
e.



(loss of β_1 H) **major product** disubstituted

(loss of β_2 H) monosubstituted

f.

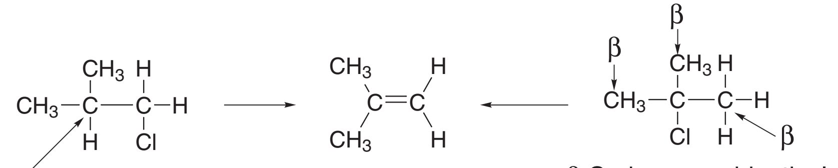


(loss of β_2 H) **major product** trisubstituted

(loss of β_1 H) disubstituted

8.20 Per dare un alchene solo come prodotto dell'eliminazione, l'alogenuro alchilico deve avere alternativamente:

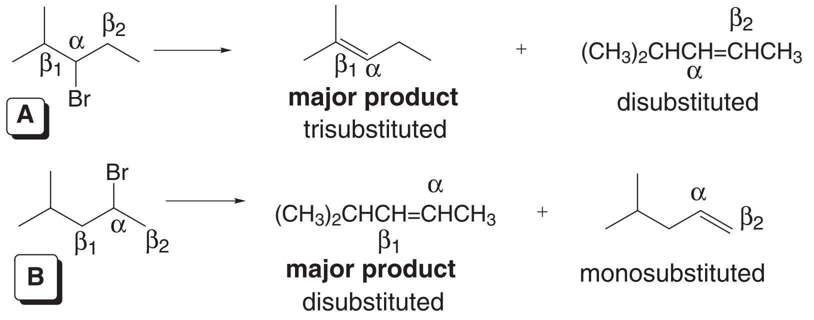
- Solo un carbonio β con un atomo di idrogeno.
- Tutti i carboni β identici così che i prodotti dell'eliminazione risultano identici.



only one β carbon

β Carbons are identical.

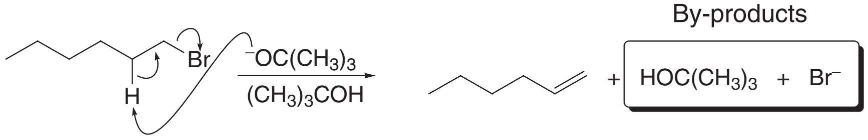
8.21 Disegnare i prodotti della reazione E2 e confrontare il numero dei carboni legati al C=C.



A fornisce un alchene trisostituito come prodotto maggioritario ed un alchene disostituito come prodotto secondario. **B** fornisce un alchene disostituito come prodotto maggioritario ed un alchene monosostituito come prodotto secondario. Poiché sia il prodotto maggioritario che quello secondario formati da **A** hanno più gruppi alchilici (e sono quindi più stabili) di quelli formati da **B**, **A** reagisce più velocemente in una reazione di eliminazione.

8.22

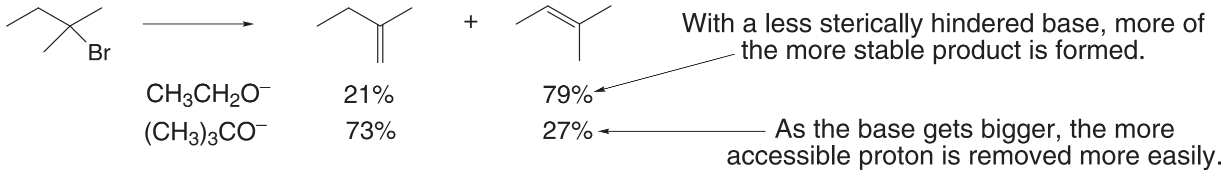
a. Mechanism:



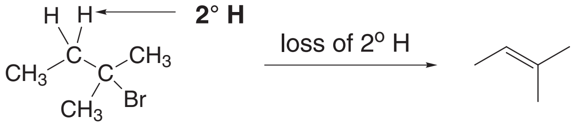
b. **Rate = k[R-Br][$^-$OC(CH$_3$)$_3$]**

1. Solvent changed to DMF (polar aprotic) = **rate increases**
2. [$^-$OC(CH$_3$)$_3$] decreased = **rate decreases**
3. Base changed to $^-$OH = **rate decreases** (weaker base)
4. Halide changed to 2° = **rate increases** (More substituted RX reacts faster.)
5. Leaving group changed to I$^-$ = **rate increases** (better leaving group)

8.23

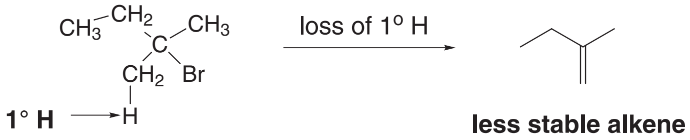


Removal of the less accessible 2^o H gives the more substituted, more stable alkene.



This pathway is usually **favored**, as is the case with CH$_3$CH$_2$O$^-$ as base.

Removal of the more accessible 1° H gives the less substituted, less stable alkene.



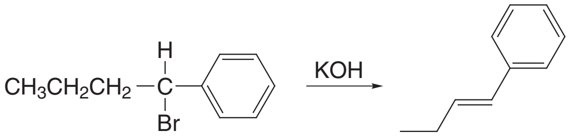
The 1° H is more accessible,
less sterically hindered.
With a bulkier base,
this proton is more readily removed.

As the base gets **bulkier**, the more accessible proton is removed faster; thus, the 1° H reacts faster than the 2° H, and the less stable alkene predominates.

Explanation: 1° H's are more easily removed than 2° H's with sterically hindered bases.

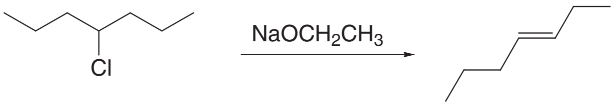
8.24

a.



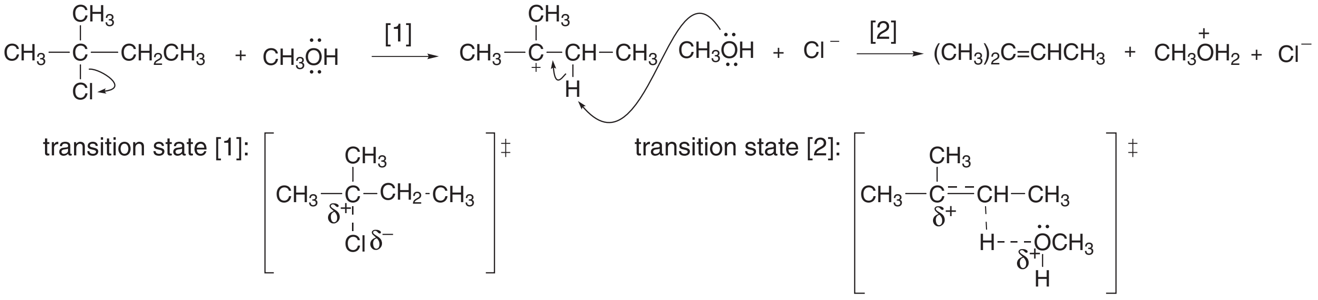
trans isomer more stable
major product

b.

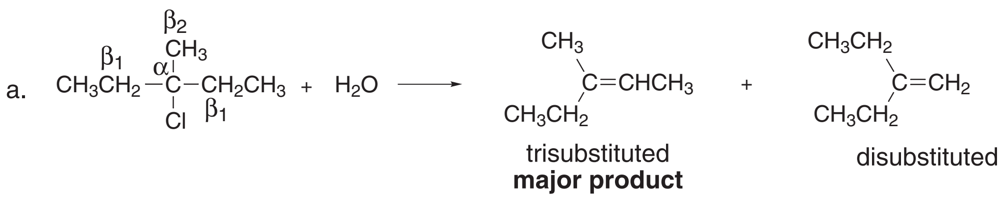


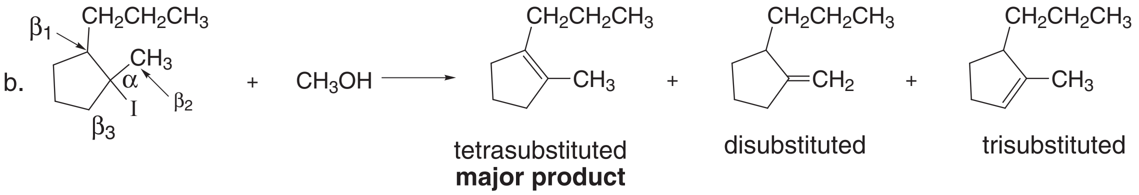
trans isomer more stable
major product

8.25 Un meccanismo E1 presenta due stadi:
[1] Il gruppo uscente si distacca, originando un carbocatione.
[2] Una base estrae un protone da un carbonio β, e si forma un legame π.



8.26 La regola di Zaitsev stabilisce: In una reazione di β-eliminazione, il prodotto maggioritario ha il doppio legame più sostituito.





8.27 Usare le seguenti caratteristiche di una reazione **E1** per rispondere alle domande:

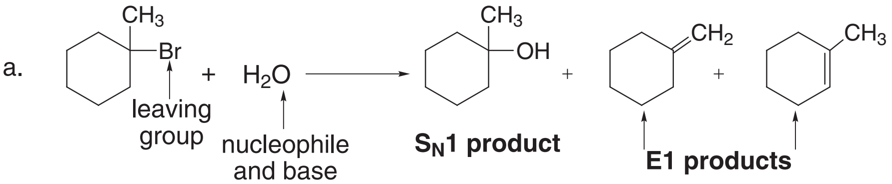
[1] Le razioni E1 sono del primo ordine ed a due stadi.
[2] Alogenuri più sostituiti reagiscono più velocemente.
[3] Sono preferite basi più deboli.
[4] Le reazioni con migliori gruppi uscenti sono più veloci.
[5] Le reazioni in solventi polari protici sono più veloci.

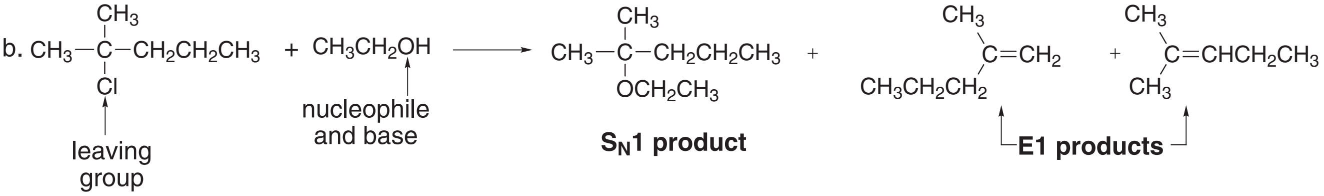
Equazione della velocità: velocità = *k*[RX] La base non influenza la velocità.

a. Raddoppio della concentrazione dell'alogenuro alchilico = **la velocità raddoppia**
b. Raddoppio della concentrazione della = **nessun cambiamento** (La base non è presente nell'equazione della velocità.)
c. cambiare l'alogenuro alchilico da $(CH_3)_3CBr$ a $CH_3CH_2CH_2Br$ = **la velocità decresce** (Alogenuri più sostituiti reagiscono più velocemente.)

8.28 Sia la reazione S_N1 che quella E1 procedono attraverso la formazione di un carbocatione. Per disegnare i prodotti:

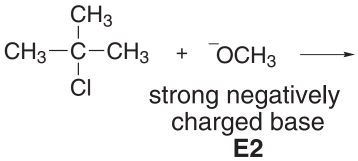
[1] **Per la reazione S_N1,** sostituire il nucleofilo al gruppo uscente.
[2] **Per la reazione E1**, rimuovere un protone da un carbonio β e creare un nuovo legame π.





8.29 Le reazioni E2 sono favorite da basi con una forte carica negativa ed avvengono con alogenuri 1°, 2° e 3°, essendo i 3° i più reattivi.

Le reazioni E1 sono favorite da basi neutre più deboli e non avvengono con alogenuri 1° poiché essi formano carbocationi molto instabili.

a.


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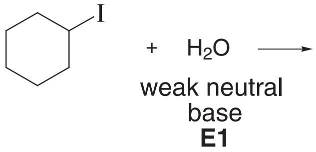

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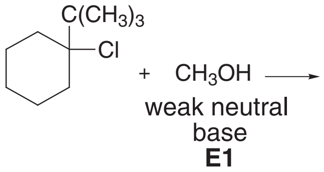

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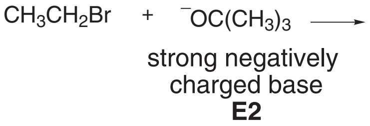
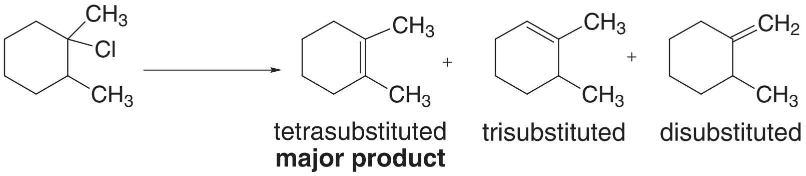


8.30

a.


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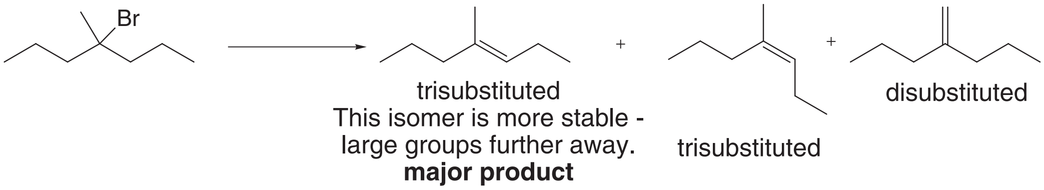
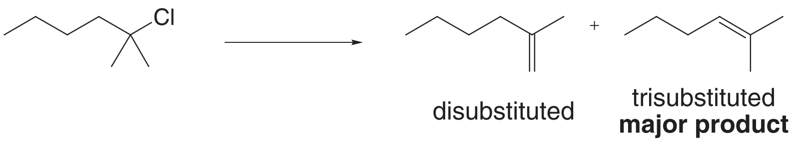
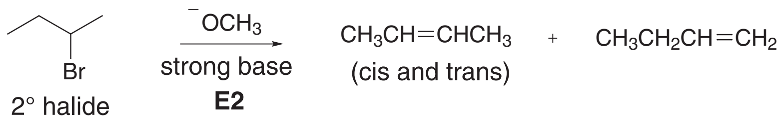


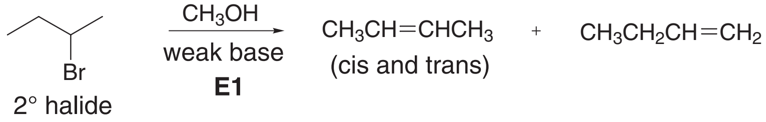
c.


8.31 Usare le regole della risposta 8.29.

a.



b.



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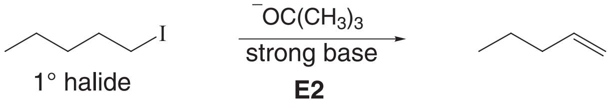
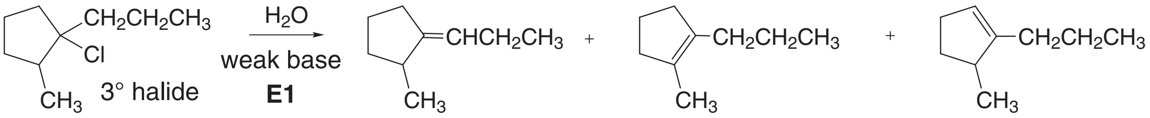
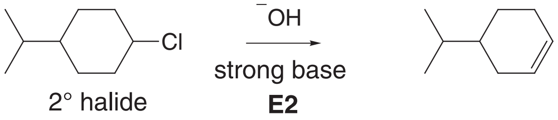


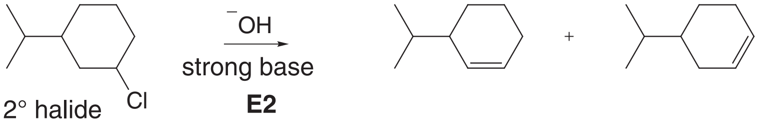
d.



e.

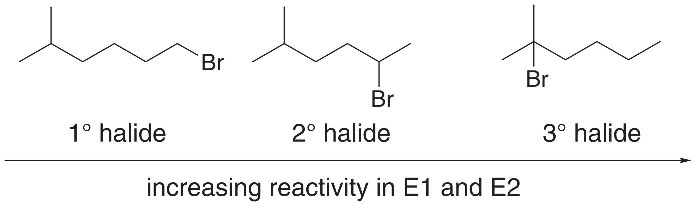


f.

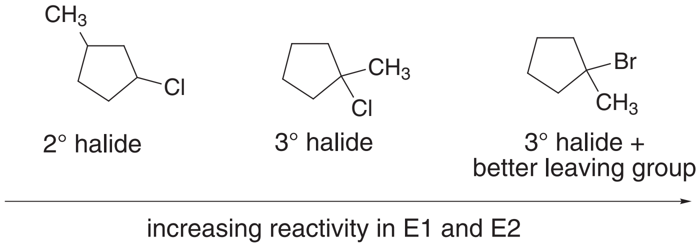


8.32 L'ordine di reattività è lo stesso sia per E2 che E1: 1° < 2° < 3°

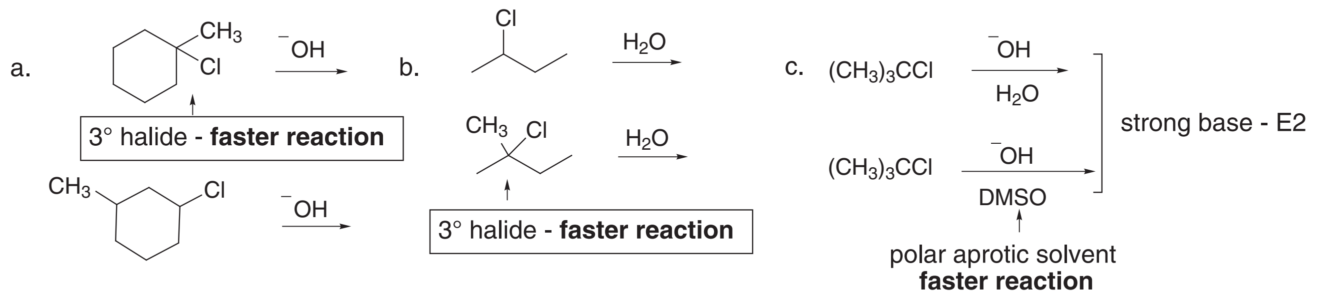
a.



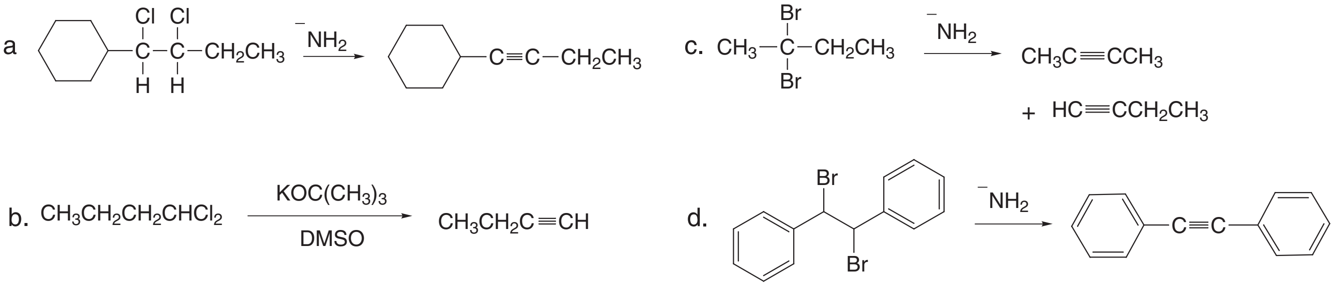
b.



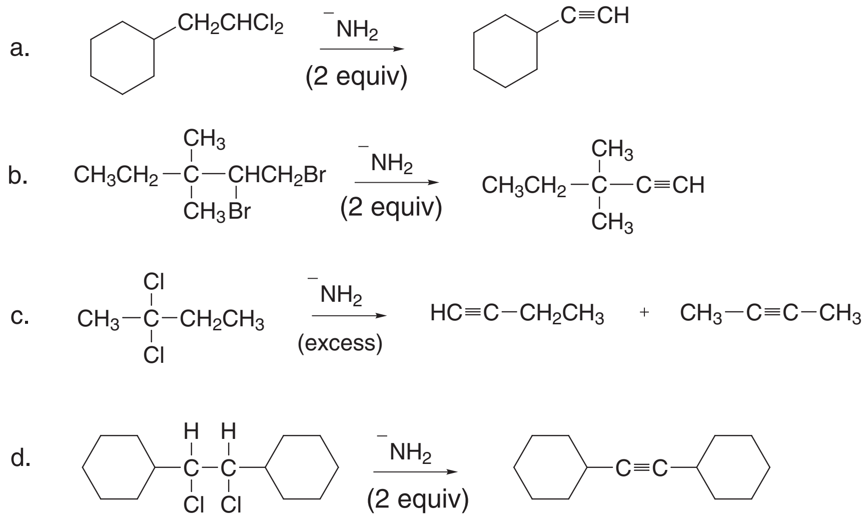
8.33



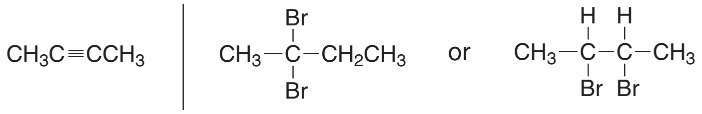
8.34 Disegnare gli alchini che si formano per eliminazione di due equivalenti di HX.

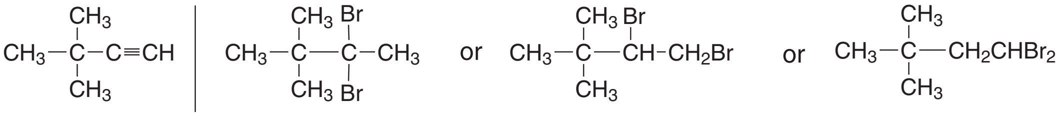


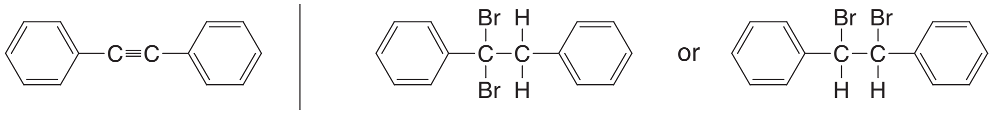
8.35



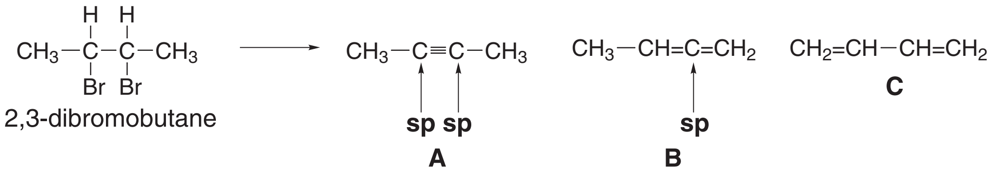
8.36

a.


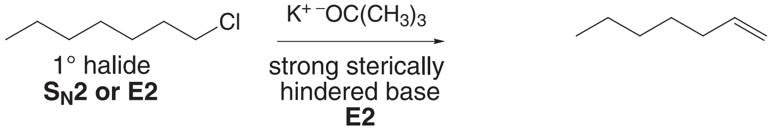
b.


c.


8.37



8.38

a.


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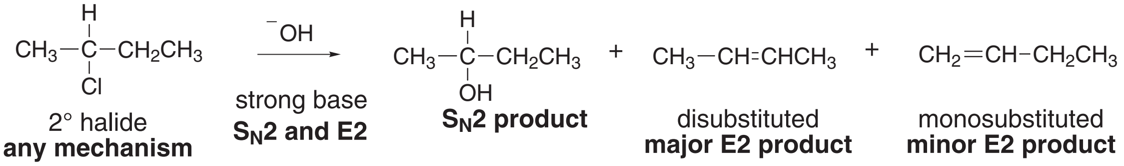

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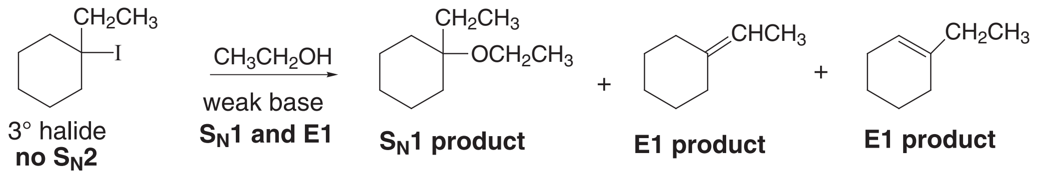
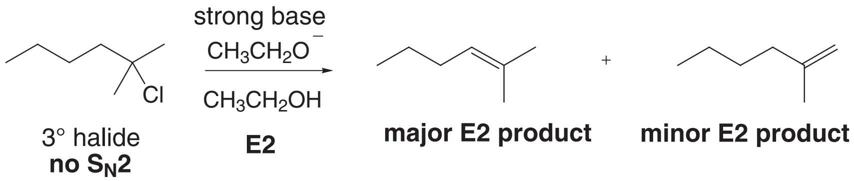
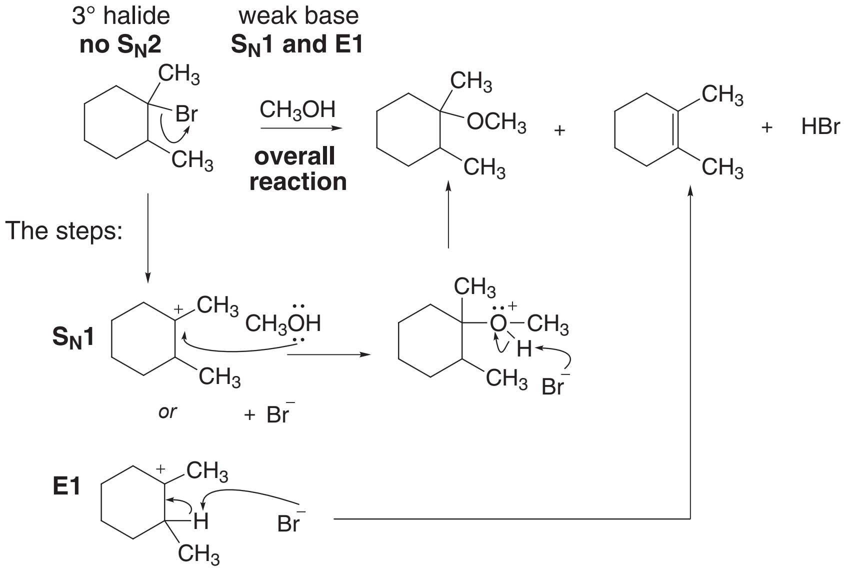


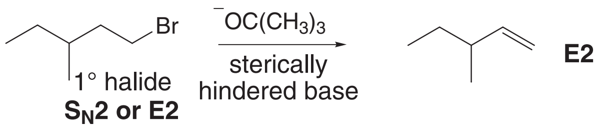
d.


8.39

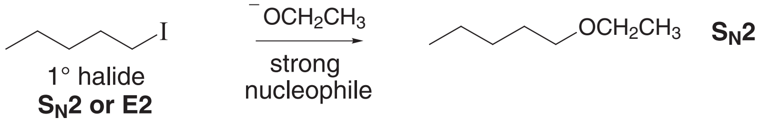


8.40

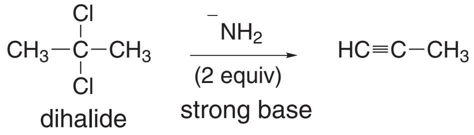
a.



b.

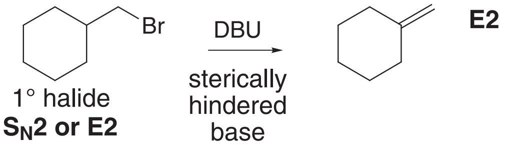


c.

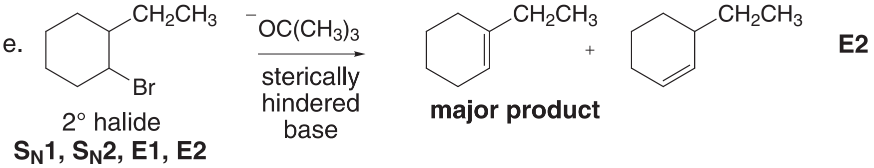


$$CH_3-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}-CH_3 \xrightarrow[\text{(2 equiv)}]{^{-}NH_2} HC\equiv C-CH_3$$

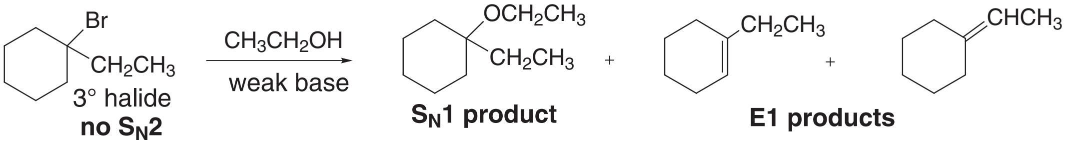
d.


Br
1° halide
S_N2 or E2
DBU
sterically hindered base
E2

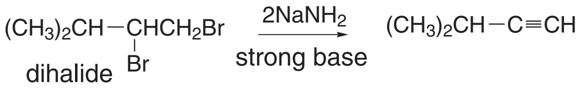
e.


CH_2CH_3
Br
2° halide
S_N1, S_N2, E1, E2
$^-OC(CH_3)_3$
sterically hindered base
CH_2CH_3
major product
+
CH_2CH_3
E2

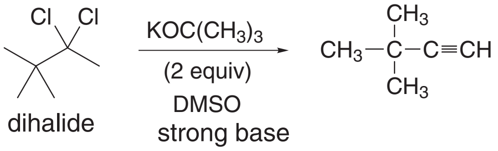
f.


Br
CH_2CH_3
3° halide
no S_N2
CH_3CH_2OH
weak base
OCH_2CH_3
CH_2CH_3
S_N1 product
+
CH_2CH_3
+
$CHCH_3$
E1 products

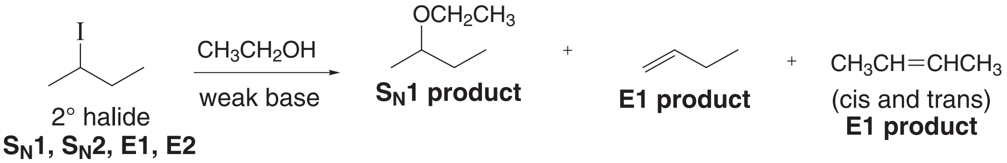
g.


$(CH_3)_2CH-CHCH_2Br$
Br
dihalide
$2NaNH_2$
strong base
$(CH_3)_2CH-C\equiv CH$

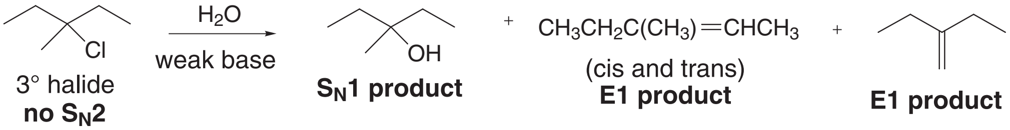
h.


Cl
Cl
dihalide
$KOC(CH_3)_3$
(2 equiv)
DMSO
strong base
CH_3
$CH_3-C-C\equiv CH$
CH_3

i.

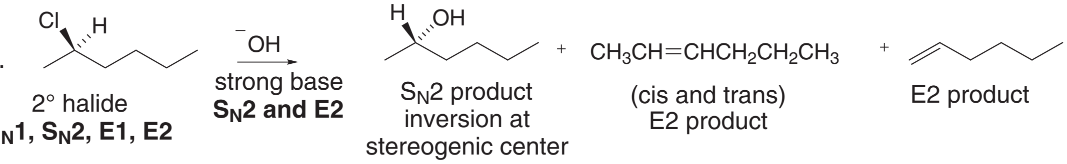

I
2° halide
S_N1, S_N2, E1, E2
CH_3CH_2OH
weak base
OCH_2CH_3
S_N1 product
+
E1 product
+
$CH_3CH=CHCH_3$
(cis and trans)
E1 product

j.

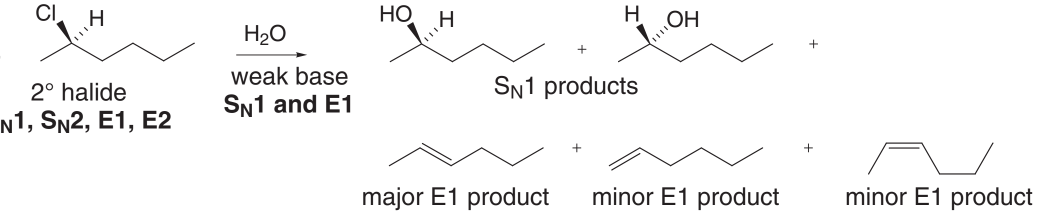

Cl
3° halide
no S_N2
H_2O
weak base
OH
S_N1 product
+
$CH_3CH_2C(CH_3)=CHCH_3$
(cis and trans)
E1 product
+
E1 product

8.41

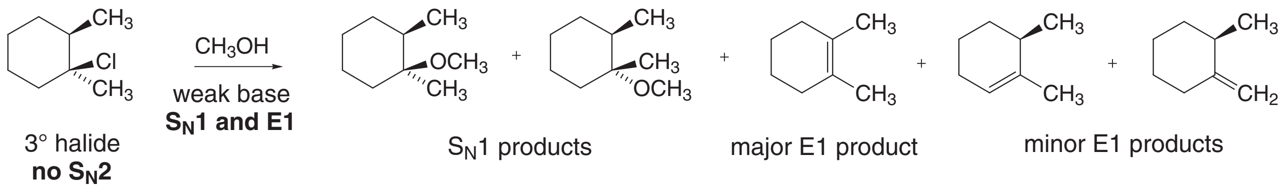
a.



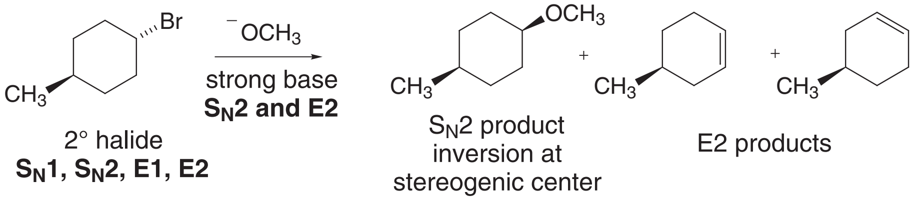
b.



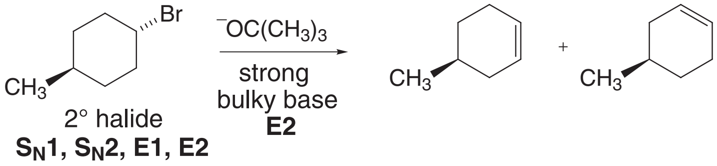
c.



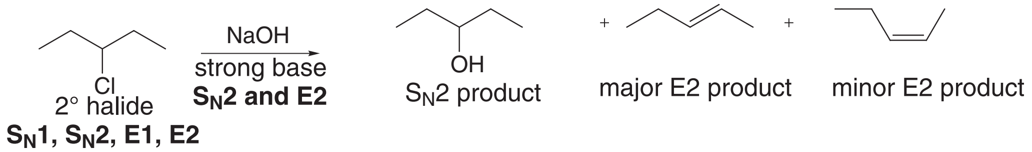
d.



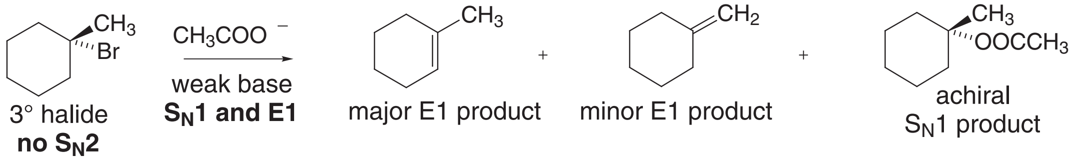
e.



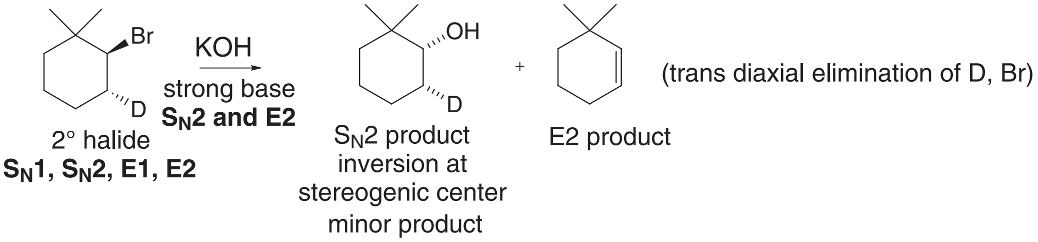
f.



g.

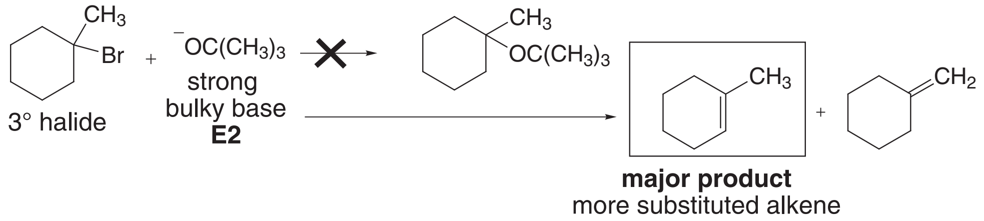


h.



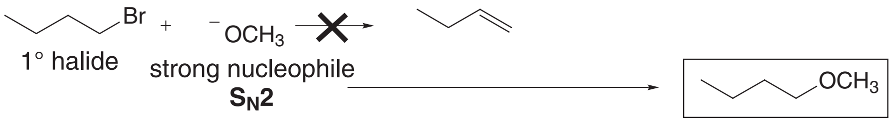
8.42

a.



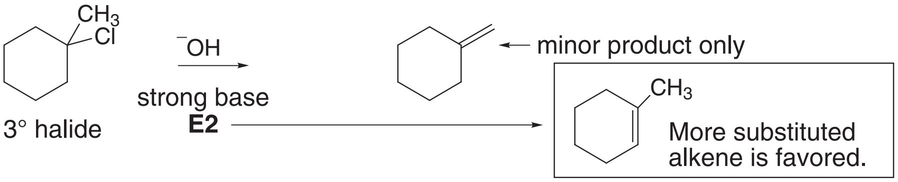
No substitution occurs with a strong bulky base and a 3^{o} RX. The C with the leaving group is too crowded for an S_N2 substitution to occur. Elimination occurs instead by an E2 mechanism.

b.

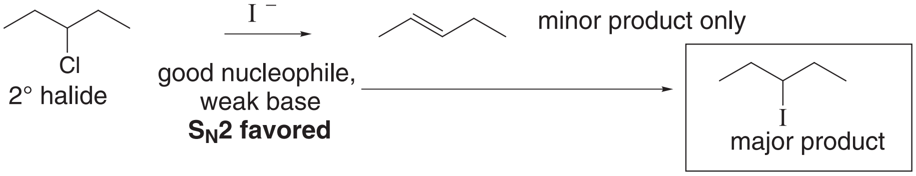


All elimination reactions are slow with 1° halides.
The strong nucleophile reacts by an S_N2 mechanism instead.

c.

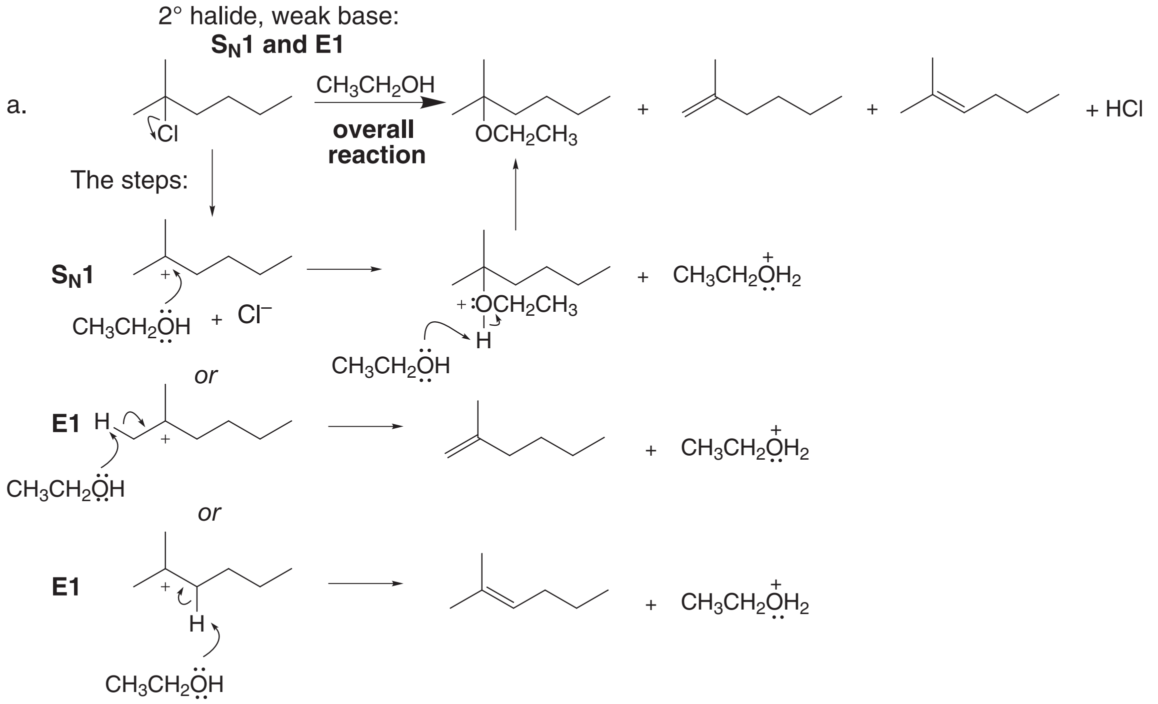


d.

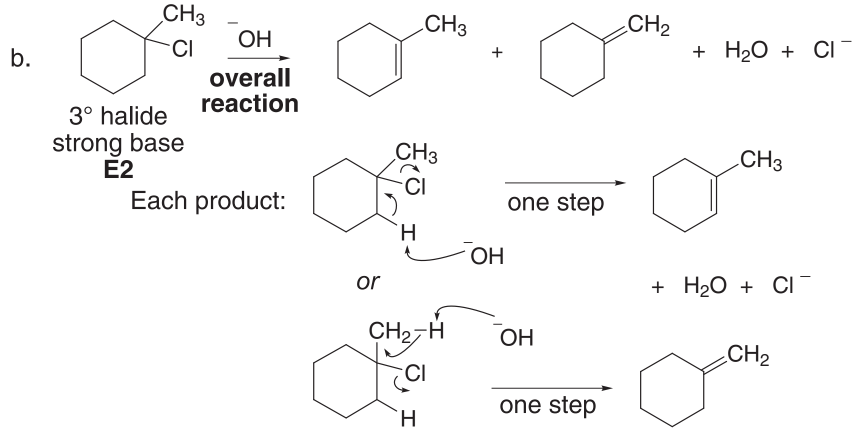


The 2^{o} halide can react by an E2 or S_N2 reaction with a negatively charged nucleophile or base. Since I^- is a weak base, substitution by an S_N2 mechanism is favored.

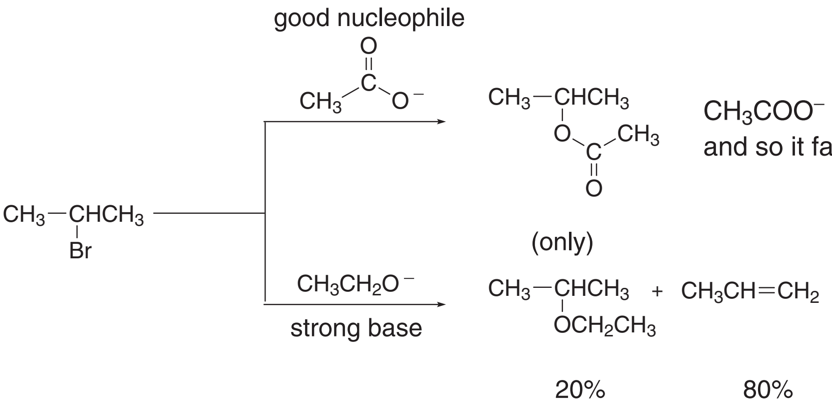
8.43



Any base (such as CH_3CH_2OH or Cl^-) can be used to remove a proton to form an alkene. If Cl^- is used, HCl is formed as a reaction by-product. If CH_3CH_2OH is used, $(CH_3CH_2OH_2)^+$ is formed instead.



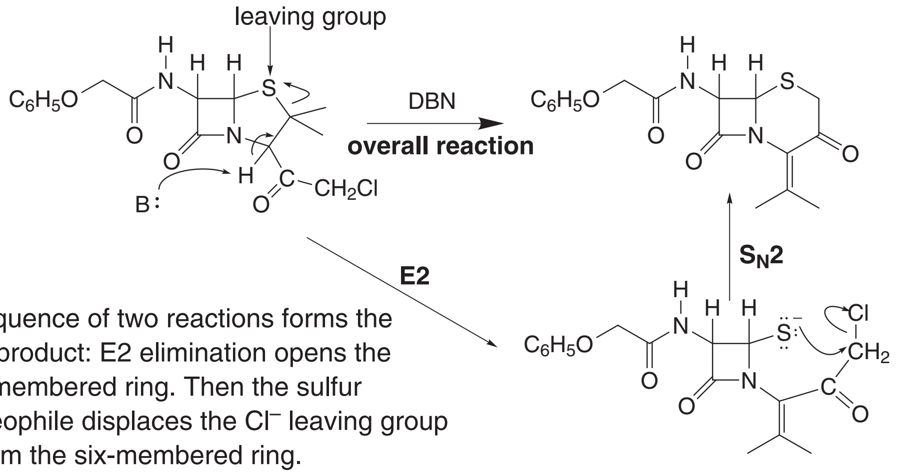
8.44



CH_3COO^- is a good nucleophile and a weak base and so it favors substitution by S_N2.

The strong base gives both S_N2 and E2 products, but since the 2° RX is somewhat hindered to substitution, the E2 product is favored.

8.45

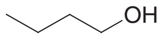


A sequence of two reactions forms the final product: E2 elimination opens the five-membered ring. Then the sulfur nucleophile displaces the Cl^- leaving group to form the six-membered ring.

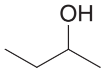
Capitolo 9

9.1 • **Gli alcoli** sono classificati come 1°, 2° or 3°, dipendentemente dal numero degli atomi di carbonio legati al carbonio con il gruppo OH.

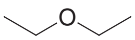
- **Gli eteri simmetrici** hanno due gruppi R identici, e gli **eteri asimmetrici** hanno gruppi R che sono diversi.



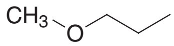
1° alcohol



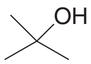
2° alcohol



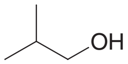
symmetrical ether



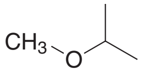
unsymmetrical ether



3° alcohol



1° alcohol



unsymmetrical ether

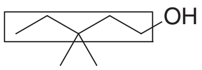
9.2 Per dare il nome all'alcol:

[1] **Individuare la catena più lunga che porta il gruppo OH come sostituente**. Assegnare il nome alla molecola come derivato di quel numero di carboni cambiando il suffisso **–e** dell'alcano con il suffisso **–ol**.

[2] **Numerare la catena carboniosa assegnando al carbonio con il gruppo OH il numero più basso**. Quando il gruppo OH è legato ad un ciclo, l'anello viene numerato cominciando dal carbonio con il gruppo OH, e il numero "1" viene generalmente omesso.

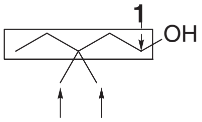
[3] Applicare le altre regole di nomenclatura per completare il nome.

a. [1]



5 carbons = **pentanol**

[2]



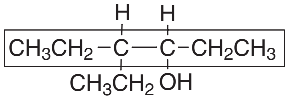
3,3-dimethyl

[3] **3,3-dimethyl-1-pentanol**

b. $(CH_3CH_2)_2CHCH(OH)CH_2CH_3$

$\downarrow$ redraw

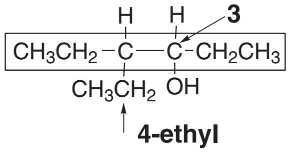
[1]



$\boxed{CH_3CH_2-\underset{CH_3CH_2}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-CH_2CH_3}$

6 carbons = **hexanol**

[2]

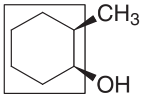


$\boxed{CH_3CH_2-\underset{CH_3CH_2}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-CH_2CH_3}$

4-ethyl

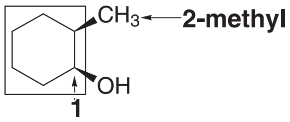
[3] **4-ethyl-3-hexanol**

c. [1]



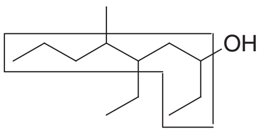
6 carbon ring = **cyclohexanol**

[2]



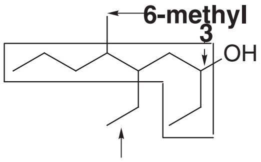
[3] ***cis*-2-methylcyclohexanol**

d. [1]



9 carbons = **nonanol**

[2]



5-ethyl

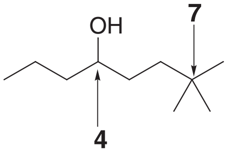
[3] **5-ethyl-6-methyl-3-nonanol**

9.3 Per scrivere il nome dalla struttura:

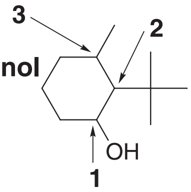
[1] Trovare il nome della catena più lunga e disegnare la struttura.

[2] Aggiungere i sostituenti alla catena principale.

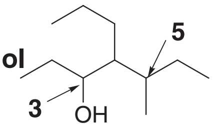
a. 7,7-dimethyl-4-**octanol**



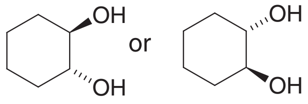
c. 2-*tert*-butyl-3-methyl**cyclohexanol**



b. 5-methyl-4-propyl-3-**heptanol**



d. *trans*-1,2-**cyclohexanediol**



9.4 Per assegnare il nome ad eteri semplici:

[1] Assegnare il nome ad entrambi i gruppi alchilici legati all'ossigeno.

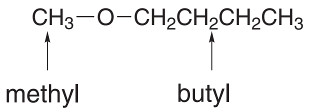
[2] Ordinare questi nomi in ordine alfabetico e poi aggiungere la parola ***etere***. Per eteri simmetrici, assegnare il nome al gruppo alchilico ed aggiungere il prefisso ***di***.

Per assegnare il nome agli eteri con il sistema IUPAC:

[1] Individuare i due gruppi alchilici legati all'ossigeno dell'etere. La catena più corta diventa il sostituente, nominato come gruppo alcossi.

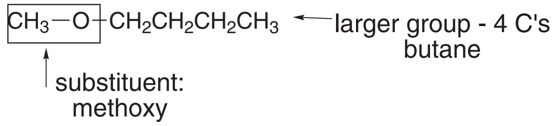
[2] Numerare la catena per assegnare il numero più basso al primo sostituente.

a. **common name:**



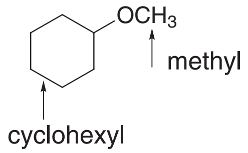
butyl methyl ether

IUPAC name:



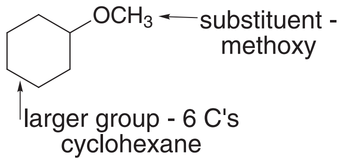
1-methoxybutane

b. **common name:**



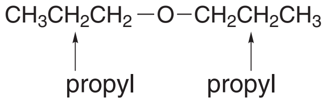
cyclohexyl methyl ether

IUPAC name:



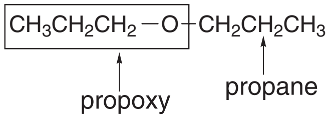
methoxycyclohexane

c. **common name:**



dipropyl ether

IUPAC name:



1-propoxypropane

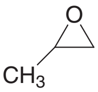
9.5 Tre modi di assegnare il nome agli epossidi:

[1] Gli epossidi sono nominati come derivati dell'ossirano, l'epossido più semplice.

[2] Gli epossidi possono essere nominati considerando l'ossigeno un sostituente chiamato gruppo **epossi**, legato ad una catena idrocarburica. Usare due numeri per indicare a quali atomi l'ossigeno è legato.

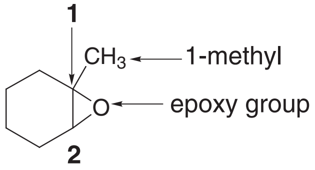
[3] Gli epossidi possono essere nominati come **alchene ossidi** rimpiazzando mentalmente l'ossigeno epossidico con un doppio legame. Assegnare il nome all'alchene (Capitolo 10) ed aggiungere la parola ***ossido***.

a.



Three possibilities:
[1] **methyloxirane**
[2] **1,2-epoxypropane**
[3] **propene oxide**

b.

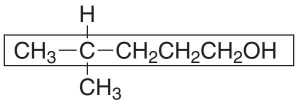


One possibility:
6 carbons = cyclohexane
1,2-epoxy-1-methylcyclohexane

9.6 Usare i suggerimenti della risposta 9.2.

a. $(CH_3)_2CHCH_2CH_2CH_2OH$

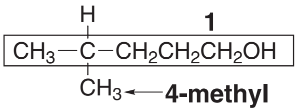
[1]



$\boxed{CH_3-\overset{H}{\underset{CH_3}{C}}-CH_2CH_2CH_2OH}$

5 carbons = **pentanol**

[2]

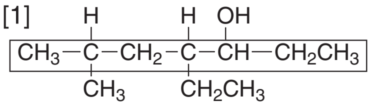


$\boxed{CH_3-\overset{H}{\underset{CH_3}{C}}-CH_2CH_2\overset{1}{C}H_2OH}$

[3] **4-methyl-1-pentanol**

b. $(CH_3)_2CHCH_2CH(CH_2CH_3)CH(OH)CH_2CH_3$

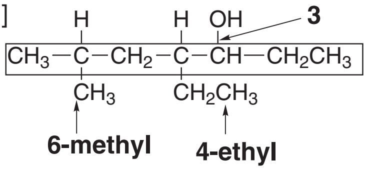
[1]



$\boxed{CH_3-\overset{H}{\underset{CH_3}{C}}-CH_2-\overset{H}{\underset{CH_2CH_3}{C}}-\overset{OH}{C}H-CH_2CH_3}$

7 carbons = **heptanol**

[2]

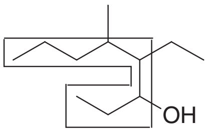


$\boxed{CH_3-\overset{H}{\underset{CH_3}{C}}-CH_2-\overset{H}{\underset{CH_2CH_3}{C}}-\overset{OH}{C}H-CH_2CH_3}$

[3] **4-ethyl-6-methyl-3-heptanol**

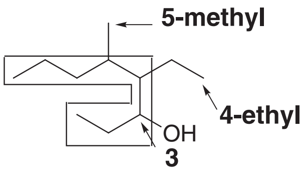
c.

[1]



8 carbons = **octanol**

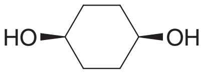
[2]



[3] **4-ethyl-5-methyl-3-octanol**

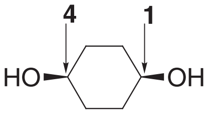
d.

[1]



cyclohexanediol

[2]

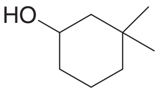


cis

[3] ***cis*-1,4-cyclohexanediol**

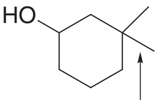
e.

[1]



6 carbons = **cyclohexanol**

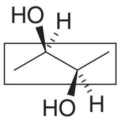
[2]



[3] **3,3-dimethylcyclohexanol**

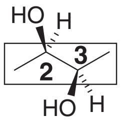
f.

[1]



4 carbons = **butanediol**

[2]

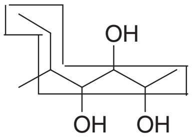


2*R*, 3*R*

[3] **(2*R*,3*R*)-2,3-butanediol**

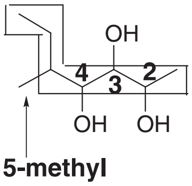
g.

[1]



7 carbons = **heptanetriol**

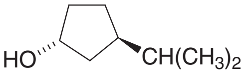
[2]



[3] **5-methyl-2,3,4-heptanetriol**

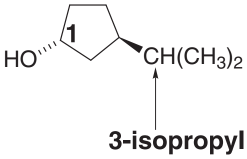
h.

[1]



5 carbons = **cyclopentanol**

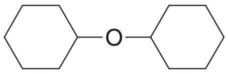
[2]



[3] **3-isopropylcyclopentanol**

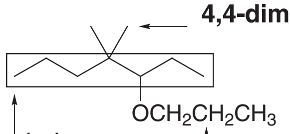
9.7 Usare le regole delle risposte 9.4 e 9.5.

a.



common name: **dicyclohexyl ether**

b.



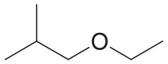
4,4-dimethyl

longest chain = **heptane**

substituent = **3-propoxy**

IUPAC name: **4,4-dimethyl-3-propoxyheptane**

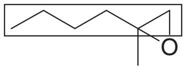
c.



common name: **ethyl isobutyl ether**

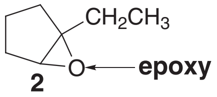
IUPAC name: **1-ethoxy-2-methylpropane**

d.



1,2-epoxy-2-methylhexane
or **1-butyl-1-methyloxirane**
or **2-methylhexene oxide**

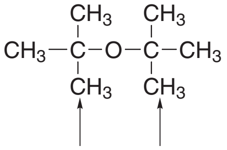
e.



5 carbons = **cyclopentane**

IUPAC name: **1,2-epoxy-1-ethylcyclopentane**

f.



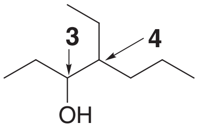
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

***tert*-butyl** ***tert*-butyl**

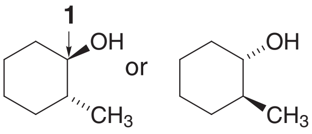
common name: **di-*tert*-butyl ether**

9.8 Usare i suggerimenti della risposta 9.3.

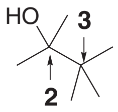
a. 4-ethyl-3-**heptanol**



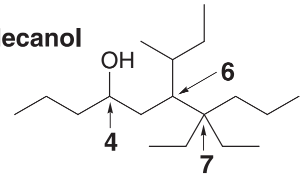
b. *trans*-2-methyl**cyclohexanol**



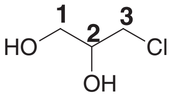
c. 2,3,3-trimethyl-2-**butanol**



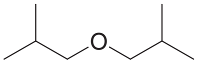
d. 6-*sec*-butyl-7,7-diethyl-4-**decanol**



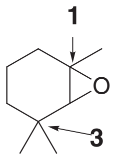
e. 3-chloro-1,2-**propanediol**



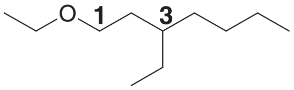
f. diisobutyl ether



g. 1,2-epoxy-1,3,3-trimethy**lcyclohexane**

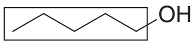


h. 1-ethoxy-3-ethyl**heptane**

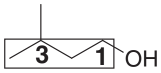


9.9

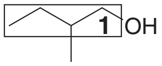
Eight constitutional isomers of molecular formula $C_5H_{12}O$ containing an OH group:



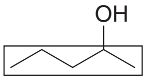
1-pentanol



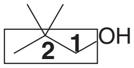
3-methyl-1-butanol



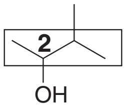
2-methyl-1-butanol



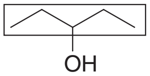
2-pentanol



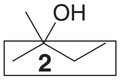
2,2-dimethyl-1-propanol



3-methyl-2-butanol



3-pentanol



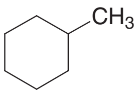
2-methyl-2-butanol

9.10 Due regole per i punti di ebollizione:

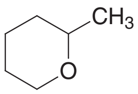
[1] **Più intense le forze più alto il p.e.**

[2] **Il p.e. aumenta all'aumentare dei legami idrogeno.** Per gli alcoli con lo stesso numero di atomi di carbonio: legami idrogeno e p.e. aumentano: 3° ROH < 2° ROH < 1° ROH.

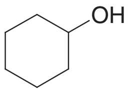
a.



VDW
lowest bp

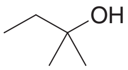


VDW
DD
intermediate bp

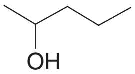


VDW
DD
hydrogen
bonding
highest bp

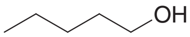
b.



3° ROH
lowest bp



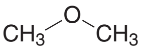
2° ROH
intermediate bp



1° ROH
highest bp

9.11 Disegnare il dimetil etere e l'etanolo ed analizzare le loro forze intermolecolari per spiegare la tendenza osservata.

dimethyl ether



CH_3OCH_3

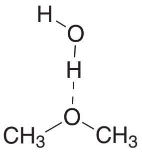
VDW
DD
no HB
much lower bp

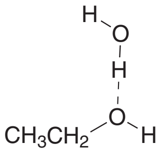
ethanol

CH_3CH_2OH

VDW
DD
HB
Two molecules of CH_3CH_2OH can hydrogen bond to each other.
stronger forces = much higher bp

Both molecules contain an O atom and can hydrogen bond with water. They have fewer than 5 C's and are therefore **water soluble**.



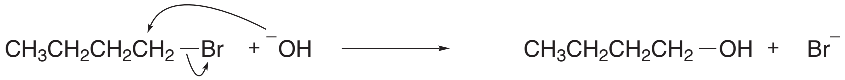


9.12 Usare le regole dei punti di ebollizione della risposta 9.10.

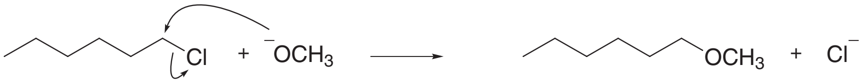
a.	$CH_3CH_2OCH_3$	$(CH_3)_2CHOH$	$CH_3CH_2CH_2OH$
	↑	↑	↑
	ether	2° alcohol	1° alcohol
	no hydrogen bonding	hydrogen bonding	hydrogen bonding
	lowest bp	**intermediate bp**	**highest bp**

b.	$CH_3CH_2CH_2CH_2CH_2CH_3$	$CH_3CH_2CH_2CH_2CH_2CH_2OH$	$HOCH_2CH_2CH_2CH_2CH_2CH_2OH$
	no OH group	one OH group	two OH groups
	lowest water solubility	**intermediate water solubility**	**highest water solubility**

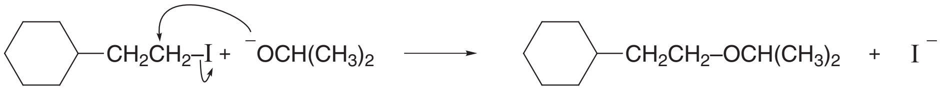
9.13 Disegnare i prodotti della sostituzione nella seguente reazione sostituendo l' ^{-}OH o ^{-}OR al posto di X nei prodotti di partenza.

a.


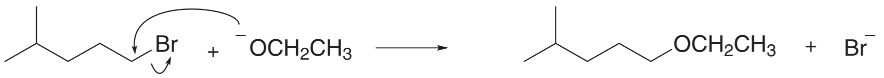
alcohol

b.


unsymmetrical ether

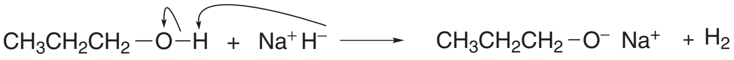
c.


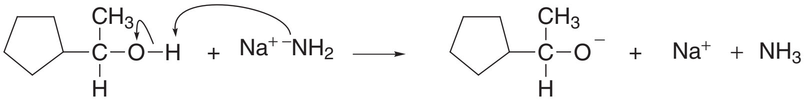
unsymmetrical ether

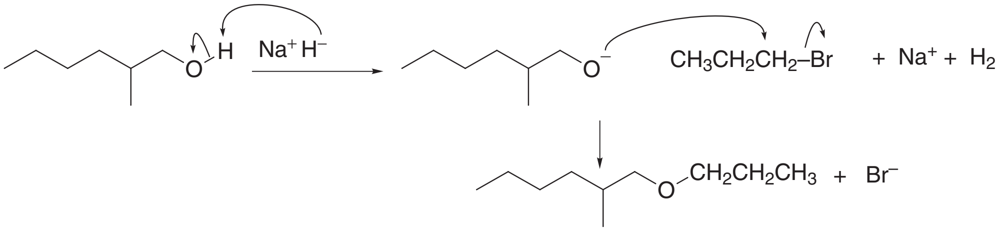
d.


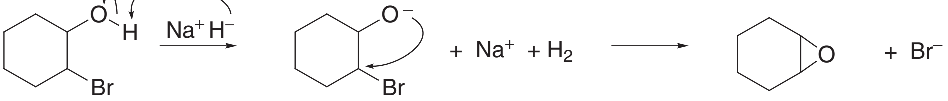
unsymmetrical ether

9.14 NaH e $NaNH_2$ sono basi forti che possono rimuovere un protone da un alcol, creando un nucleofilo.

a.


b.


c.


d.


$C_6H_{10}O$

9.15 Solo gli acidi che hanno pK_a inferiore a –2 sono abbastanza forti per protonare un alcol.

a. HF (pK_a = 3) = above –2; **not strong enough**

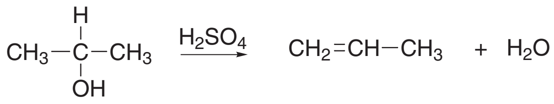
b. $HClO_4$ (pK_a = –10) = below –2; **strong enough to protonate an alcohol.**

c. $C_6H_5SO_3H$ (pK_a = –7) = below –2; **strong enough to protonate an alcohol.**

d. CH_3COOH (pK_a = 5) = above –2; **not strong enough**

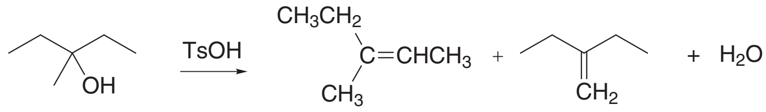
9.16 La disidratazione segue la regola di Zaitsev, così l'alchene più stabile, e più sostituito è il prodotto maggioritario.

a.



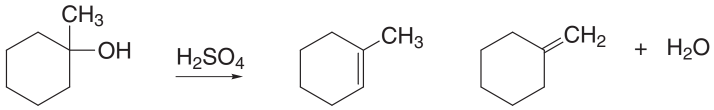
$$CH_3-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-CH_3 \xrightarrow{H_2SO_4} CH_2{=}CH-CH_3 + H_2O$$

b.



trisubstituted **major product** disubstituted **minor product**

c.



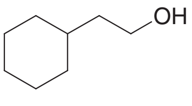
trisubstituted **major product** disubstituted **minor product**

9.17 La velocità della disidratazione aumenta all'aumentare del numero dei gruppi R.

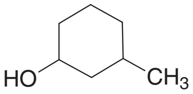
a.

$(CH_3)_2CHCH_2CH_2CH_2OH$	$(CH_3)_2CHCH_2CH(OH)CH_3$	$(CH_3)_2C(OH)CH_2CH_2CH_3$
1° alcohol **slowest reaction**	2° alcohol **intermediate reactivity**	3° alcohol **fastest reaction**

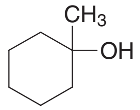
b.



1° alcohol
slowest reaction



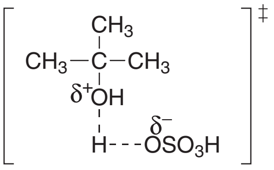
2° alcohol
intermediate reactivity



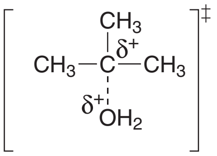
3° alcohol
fastest reaction

9.18 Ci sono tre stadi nel meccanismo E1 per la disidratazione degli alcoli, e tre stati di transizione.

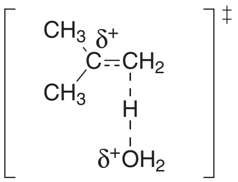
transition state [1]:



transition state [2]:

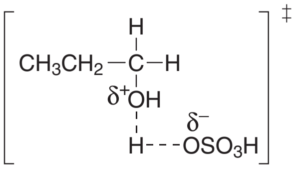


transition state [3]:

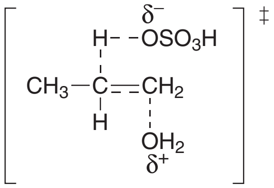


9.19

transition state [1]:



transition state [2]:



9.20

a. $CH_3CH_2CH_2OH \xrightarrow{H_2SO_4} CH_3CH{=}CH_2 + H_2O$

b. $CH_3CH_2CH_2OH \xrightarrow{NaH} CH_3CH_2CH_2O^- \ Na^+ + H_2$

c. $CH_3CH_2CH_2OH \xrightarrow[ZnCl_2]{HCl} CH_3CH_2CH_2Cl + H_2O$

d. $CH_3CH_2CH_2OH \xrightarrow{HBr} CH_3CH_2CH_2Br + H_2O$

e. $CH_3CH_2CH_2OH \xrightarrow[\text{pyridine}]{SOCl_2} CH_3CH_2CH_2Cl$

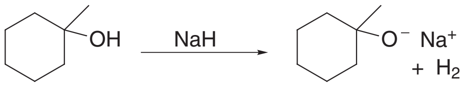
f. $CH_3CH_2CH_2OH \xrightarrow{PBr_3} CH_3CH_2CH_2Br$

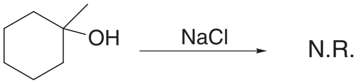
g. $CH_3CH_2CH_2OH \xrightarrow[\text{pyridine}]{TsCl} CH_3CH_2CH_2OTs$

h. $CH_3CH_2CH_2OH \xrightarrow{[1]\ NaH} CH_3CH_2CH_2O^- \ Na^+ \xrightarrow{[2]\ CH_3CH_2Br} CH_3CH_2CH_2OCH_2CH_3$

i. $CH_3CH_2CH_2OH \xrightarrow{[1]\ TsCl} CH_3CH_2CH_2OTs \xrightarrow{[2]\ NaSH} CH_3CH_2CH_2SH$

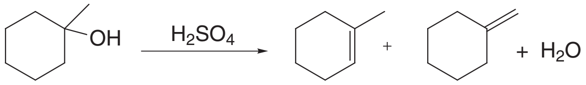
9.21

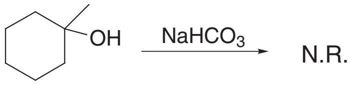
a.


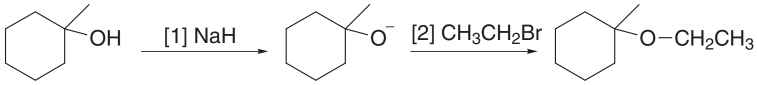
b.


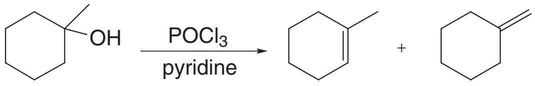
c.


d.

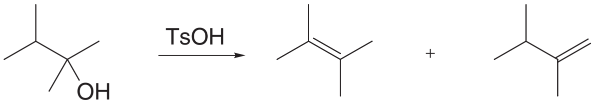

e.


f.


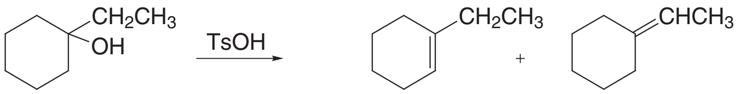
g.


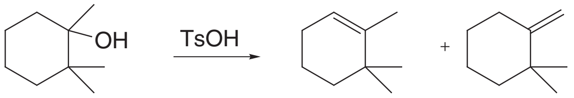
h.


9.22 La disidratazione segue la regola di Zaitsev, e l'alchene più stabile e più sostituito è il prodotto maggioritario.

a.


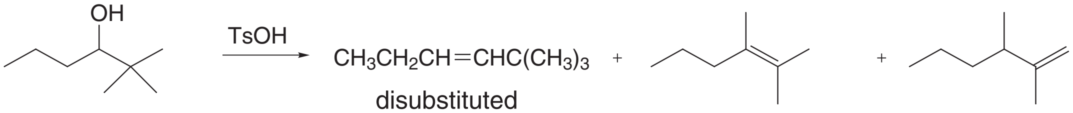
tetrasubstituted **major product** disubstituted

b.


c.


trisubstituted **major product** disubstituted

d. $CH_3CH_2CH_2CH_2OH \xrightarrow{TsOH} CH_3CH_2CH{=}CH_2$

e.


disubstituted

tetrasubstituted **major product** disubstituted

Two products formed by carbocation rearrangement

L'alchene più stabile è il prodotto principale.

9.23

trans and disubstituted **major product** monosubstituted cis and disubstituted

9.24 OTs è un buon gruppo uscente e sarà sostituito da un nucleofilo facilmente. Disegnare i prodotti sostituendo il nucleofilo al posto dell' OTs nel materiale di partenza.

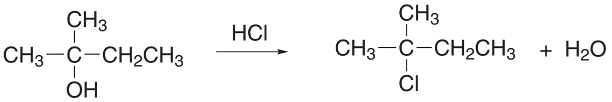
a. $CH_3CH_2CH_2CH_2-OTs \xrightarrow[\textbf{S}_\textbf{N}\textbf{2}]{CH_3SH} CH_3CH_2CH_2CH_2-SCH_3 + HOTs$

b. $CH_3CH_2CH_2CH_2-OTs \xrightarrow[\textbf{S}_\textbf{N}\textbf{2}]{NaOCH_2CH_3} CH_3CH_2CH_2CH_2-OCH_2CH_3 + Na^+ \ ^-OTs$

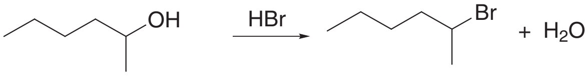
c. $CH_3CH_2CH_2CH_2-OTs \xrightarrow[\textbf{S}_\textbf{N}\textbf{2}]{NaOH} CH_3CH_2CH_2CH_2-OH + Na^+ \ ^-OTs$

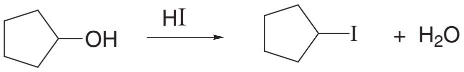
d. $CH_3CH_2CH_2CH_2-OTs \xrightarrow[\textbf{E2}]{K^+ \ ^-OC(CH_3)_3} CH_3CH_2CH{=}CH_2 + (CH_3)_3COH + K^+ \ ^-OTs$

9.25

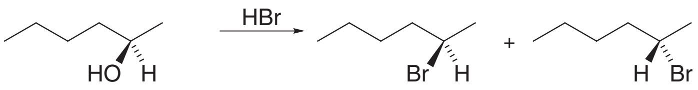
a. 

$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}-CH_2CH_3 \xrightarrow{HCl} CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle Cl}{C}}-CH_2CH_3 + H_2O$$

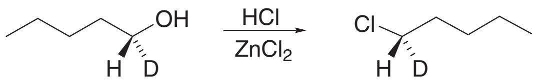
c. 

b. 

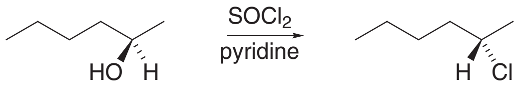
9.26

a. 

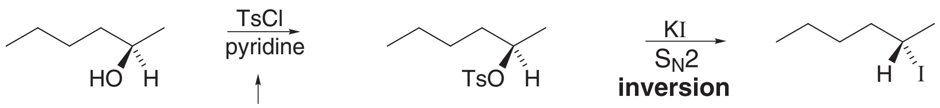
2° Alcohol will undergo S_N1.
racemization

b. 

1° Alcohol will undergo S_N2.
inversion

c. 

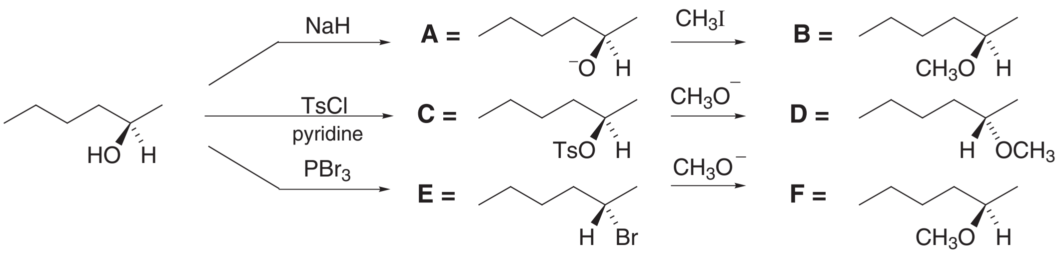
$SOCl_2$ always implies S_N2.
inversion

d. 

Configuration is maintained.
C–O bond is not broken.

9.27

a.



b. **B** and **D** are enantiomers.

c. **B** and **F** are identical.

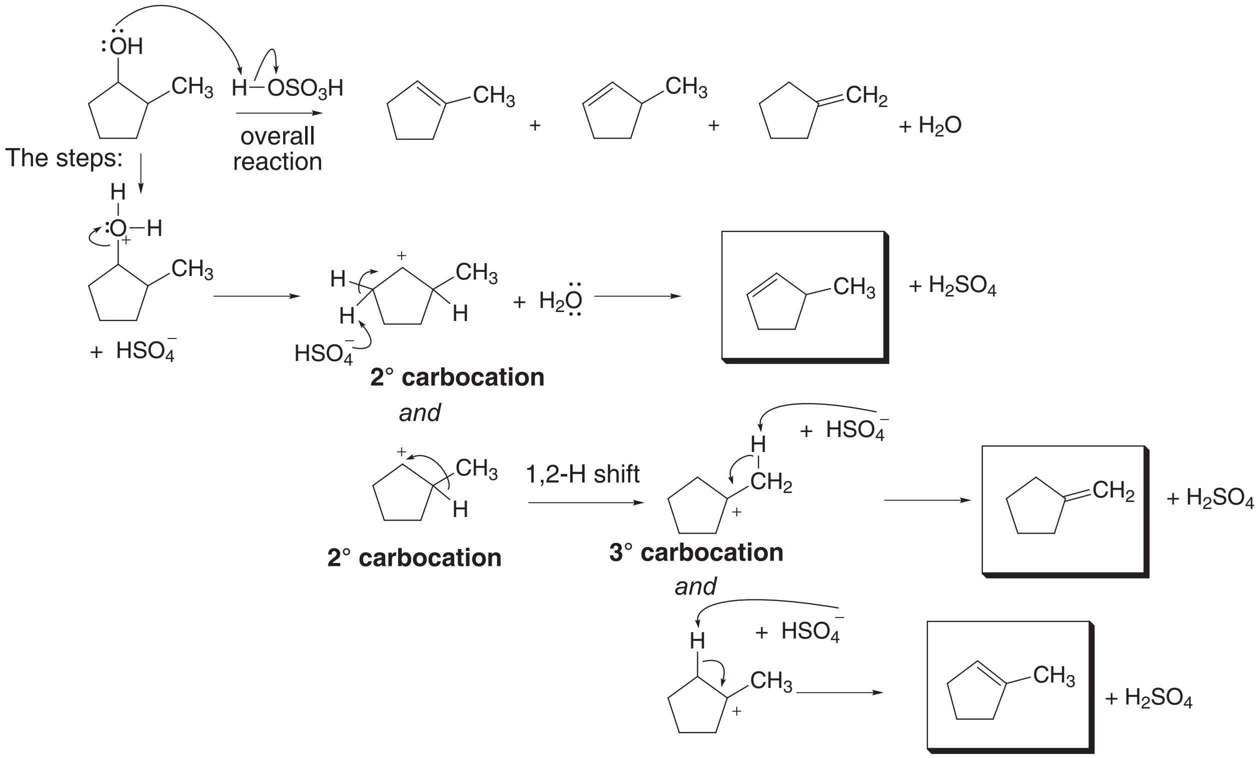
9.28 La disidratazione acido catalizzata segue un meccanismo E1 per ROH 2° e 3° con uno stadio aggiuntivo per creare un buon gruppo uscente. I tre passaggi sono:

[1] Protonare l'ossigeno per creare un buon gruppo uscente.

[2] Rompere il legame C–O per formare un carbocatione.

[3] Rimuovere un idrogeno β per formare un legame π.

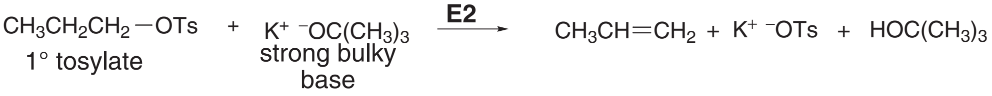
a.



9.29

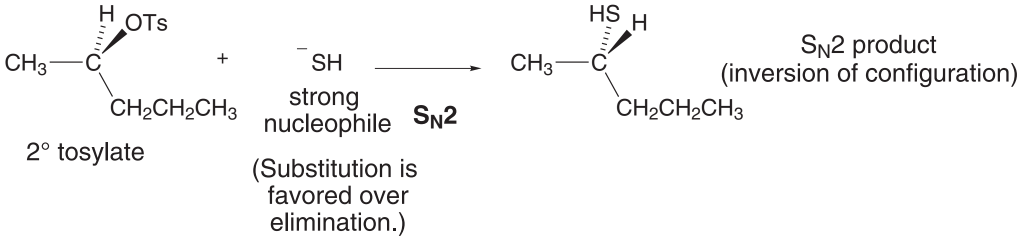
a.

b.



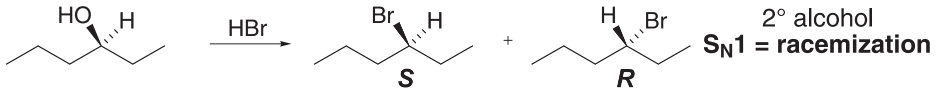
$$CH_3CH_2CH_2{-}OTs + K^+\ {}^-OC(CH_3)_3 \xrightarrow{E2} CH_3CH{=}CH_2 + K^+\ {}^-OTs + HOC(CH_3)_3$$

c.

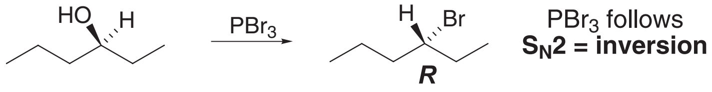


9.30

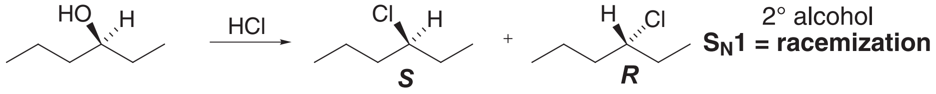
a.



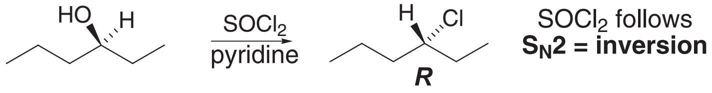
b.



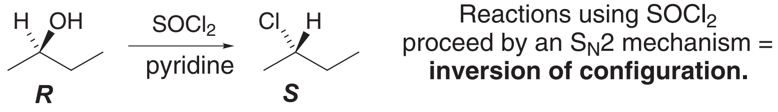
c.



d.



9.31 Le reazioni di sostituzione degli alcoli usando $SOCl_2$ procedono attraverso un meccanismo S_N2. Di conseguenza,c'è **inversione di configurazione** al centro stereogenico.



9.32 Le reazioni di sostituzione degli alcoli usando PBr_3 procede attraverso un meccanismo S_N2. Di conseguenza, c'è inversione di configurazione al centro stereogenico.

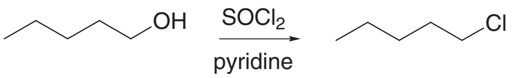
9.33 Stereochimica della conversione di ROH a RX per reagente:

[1] **HX**– con 1°, S_N2, inversione di configurazione; con 2° e 3°, S_N1, racemizzazione.

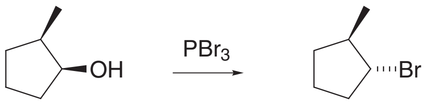
[2] **$SOCl_2$** – S_N2, inversione di configurazione.

[3] **PBr_3** – S_N2, inversione di configurazione.

a.

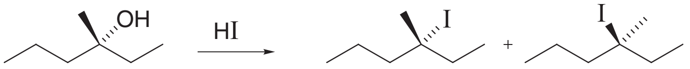


c.



S_N2 =
inversion

b.

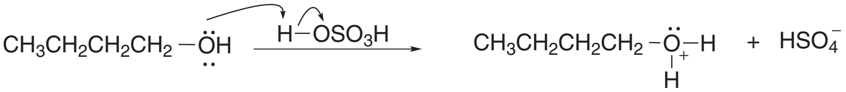


3° alcohol, S_N1 =
racemization

9.34

$$CH_3CH_2CH_2CH_2OH \xrightarrow[\text{overall reaction}]{H_2SO_4\text{ , NaBr}} CH_3CH_2CH_2CH_2Br + CH_3CH_2CH{=}CH_2 + CH_3CH_2CH_2CH_2OCH_2CH_2CH_2CH_3$$

Step [1] for all products: Formation a good leaving group



$$CH_3CH_2CH_2CH_2-\ddot{O}H \xrightarrow{H-OSO_3H} CH_3CH_2CH_2CH_2-\overset{+}{\ddot{O}}(H)-H + HSO_4^-$$

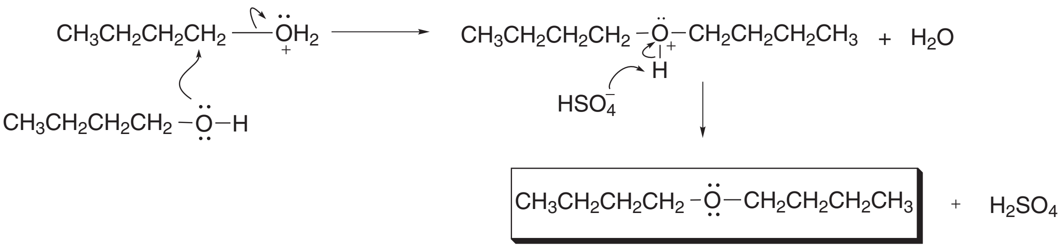
Formation of $CH_3CH_2CH_2CH_2Br$:

$$CH_3CH_2CH_2CH_2-\overset{+}{\ddot{O}}(H)-H \quad Na^+\ Br^- \longrightarrow \boxed{CH_3CH_2CH_2CH_2Br} + H_2\ddot{O}$$

Formation of $CH_3CH_2CH{=}CH_2$:

$$CH_3CH_2CH(H)-CH_2-\overset{+}{\ddot{O}}(H)-H \quad HSO_4^- \longrightarrow \boxed{CH_3CH_2CH{=}CH_2} + H_2\ddot{O}$$

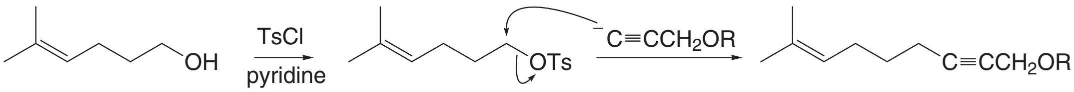
Ether forms (from the protonated alcohol):



$$CH_3CH_2CH_2CH_2-\overset{+}{\ddot{O}}H_2 + CH_3CH_2CH_2CH_2-\ddot{O}-H \longrightarrow CH_3CH_2CH_2CH_2-\overset{+}{\ddot{O}}(H)-CH_2CH_2CH_2CH_3 + H_2O$$

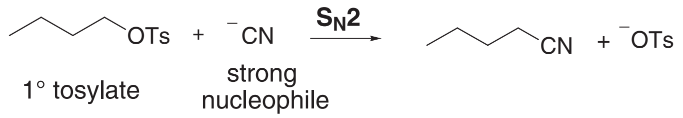
$$\xrightarrow{HSO_4^-} \boxed{CH_3CH_2CH_2CH_2-\ddot{O}-CH_2CH_2CH_2CH_3} + H_2SO_4$$

9.35



9.36

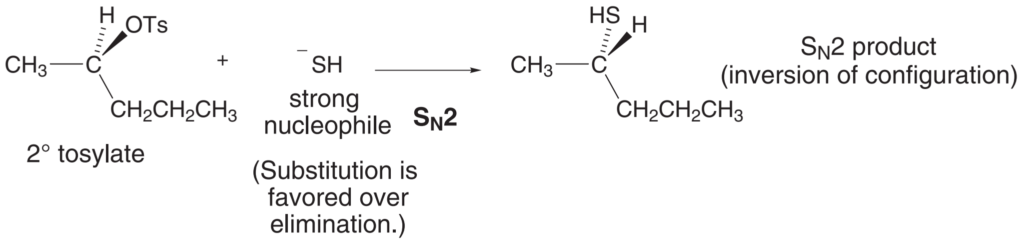
a.



b. $CH_3CH_2CH_2-OTs + K^+\ ^-OC(CH_3)_3 \xrightarrow{E2} CH_3CH{=}CH_2 + K^+\ ^-OTs + HOC(CH_3)_3$

1° tosylate — strong bulky base

c.



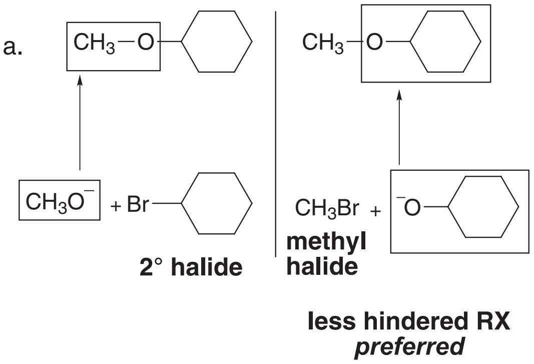
9.37 Per sintetizzare un etere usando la sintesi degli eteri di Williamson:

[1] Prima trovare i due possibili alcossidi ed e gli alogenuri alchilici necessari per la sostituzione nucleofila.

[2] Classificare gli alogenuri alchilici come 1°, 2°, or 3°. Il meccanismo favorito è quello che prevede l'alchene meno ingombrato.

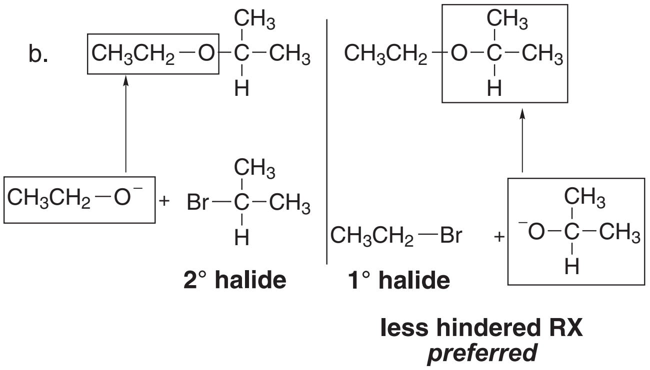
Two possibilities:

a.



Two possibilities:

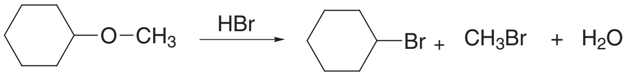
b.



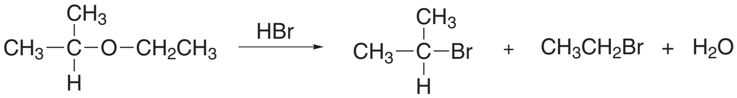
9.38

a. $CH_3CH_2-O-CH_2CH_3 \xrightarrow{HBr} 2\ CH_3CH_2-Br + H_2O$

c.



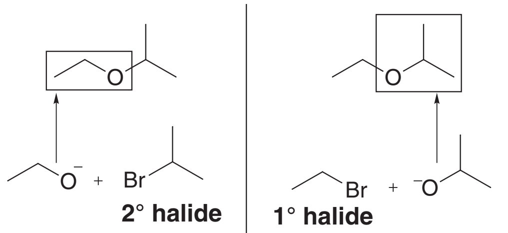
b.



$$CH_3-\underset{H}{\overset{CH_3}{C}}-O-CH_2CH_3 \xrightarrow{HBr} CH_3-\underset{H}{\overset{CH_3}{C}}-Br + CH_3CH_2Br + H_2O$$

9.39

a.

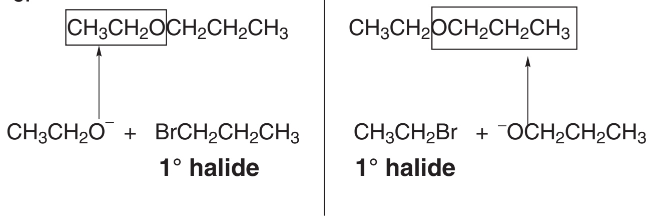


2° halide

1° halide

less hindered RX
preferred path

c.

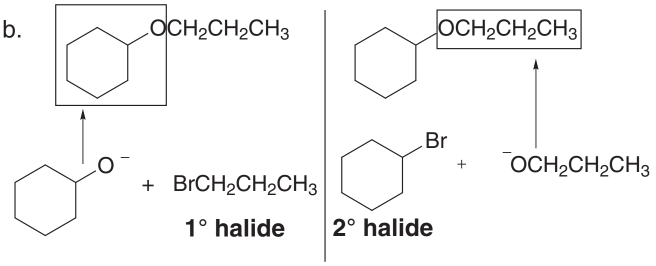


1° halide

1° halide

Neither path preferred.

b.



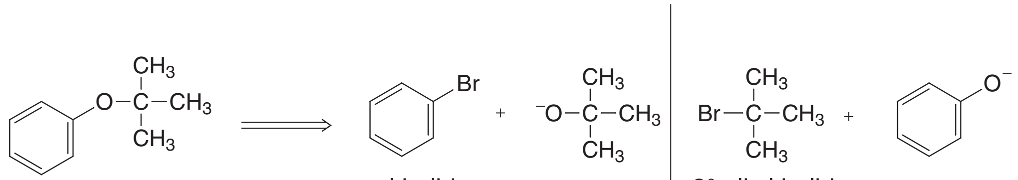
1° halide

2° halide

less hindered RX
preferred path

9.40 Un alogenuro terziario è troppo ingombrato ed un alogeuro arilico è troppo poco reattivo per dare la sintesi degli eteri di Williamson.

Two possible starting materials:



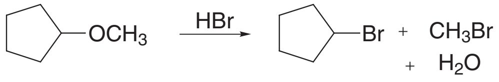
aryl halide
unreactive in S_N2

3° alkyl halide
too sterically hindered for S_N2

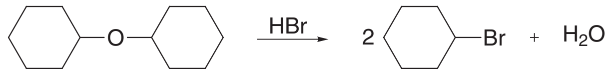
9.41

a. $(CH_3)_3COCH_2CH_2CH_3 \xrightarrow{HBr} (CH_3)_3CBr + BrCH_2CH_2CH_3 + H_2O$

c.

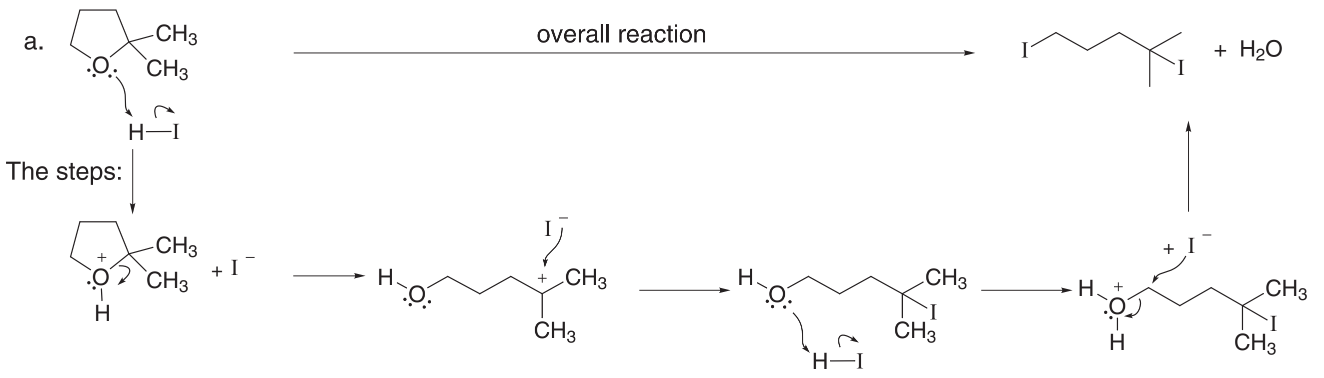


b.

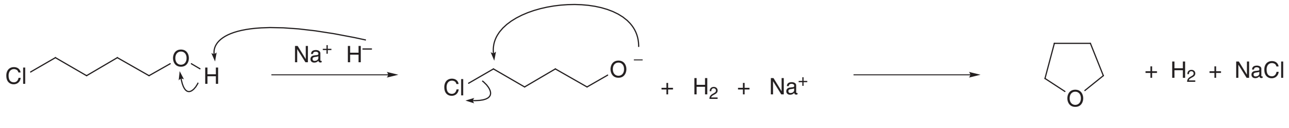


9.42

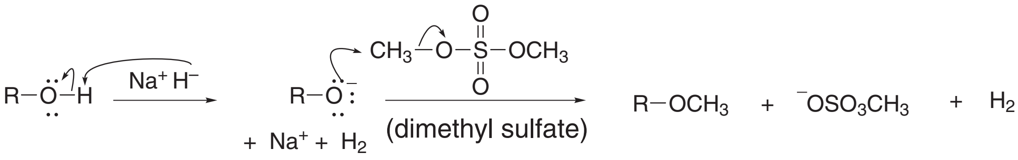
a.



b.

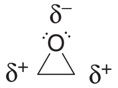


9.43



Dimethyl sulfate is a reactive methylating agent because $^-OSO_3CH_3$ is a very good leaving group; it is a resonance-stabilized, weak conjugate base. The conjugate acid of $^-OSO_3CH_3$ is $HOSO_3CH_3$, which is a strong acid, similar in acidity to H_2SO_4.

9.44 Confrontare gli epossidi ed il ciclopropano. Perchè un composto sia reattivo nei confronti dei nucleofili, deve essere elettrofilo.



epoxide

cyclopropane

O is electronegative and pulls electron density away from C's. This makes them electrophilic and reactive with nucleophiles.

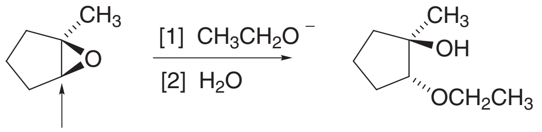
Cyclopropane has all C's and H's, so all nonpolar bonds. There are no electrophilic C's so it will not react with nucleophiles.

9.45 Due regole per la reazione di un epossido:

[1] I nucleofili attaccano dal retro dell'epossido.

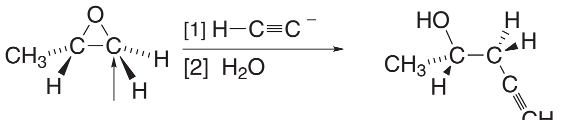
[2] I nucleofili carichi negativamente attaccano al carbonio meno sostituito.

a.



Attack here:
less substituted C
backside attack

b.

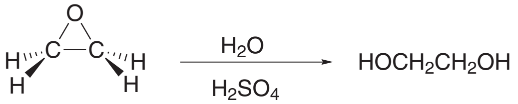


Attack here:
less substituted C
backside attack

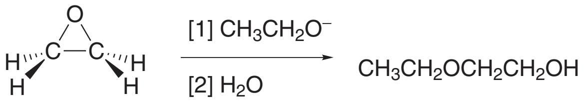
9.46

a.

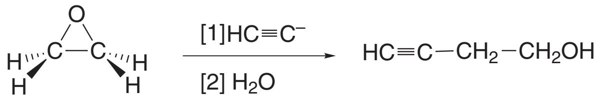
b.



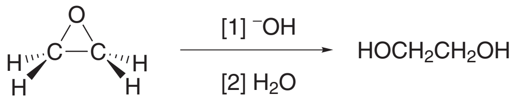
c.



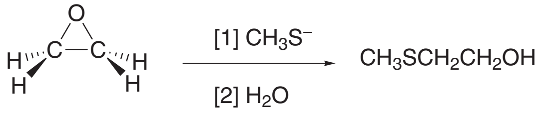
d.



e.

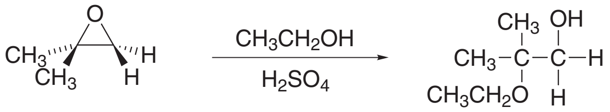


f.

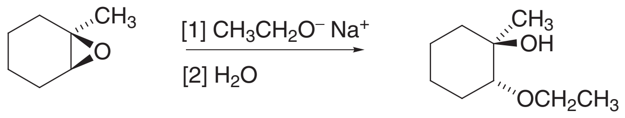


9.47

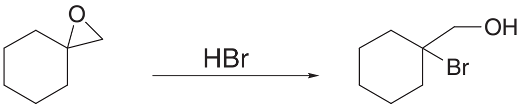
a.



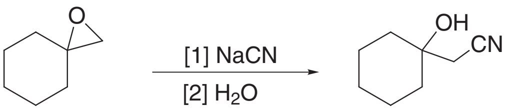
b.



c.

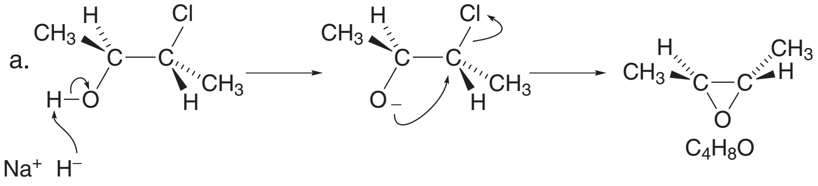


d.



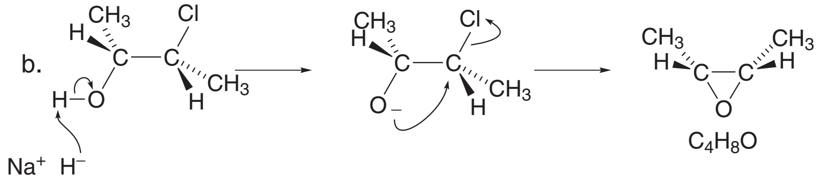
9.48

a.



The 2 CH_3 groups are anti in the starting material, making them trans in the product.

b.



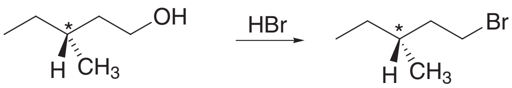
The 2 CH_3 groups are gauche in the starting material, making them cis in the product.

9.49

a.

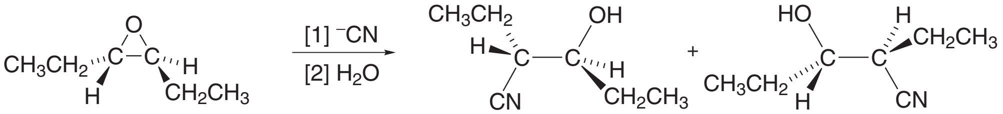
Bulky base favors E2.

b.



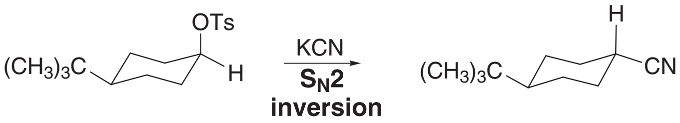
Keep the stereochemistry at the stereogenic center [*] the same here since no bond is broken to it.

c.

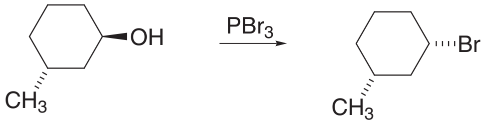


identical

d.

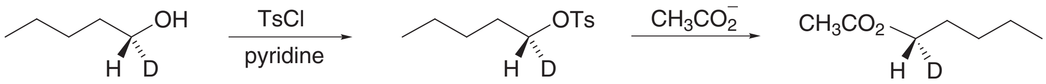


e.

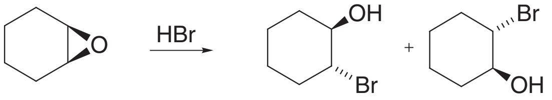


S_N2 inversion

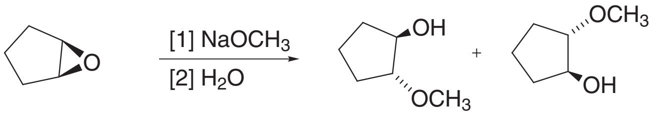
f.



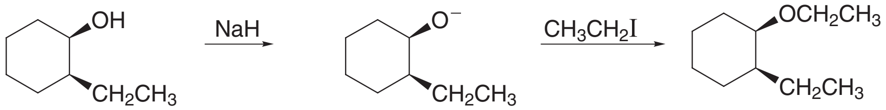
g.



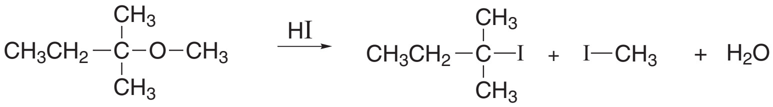
h.



i.



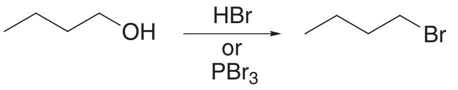
j.



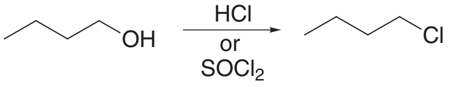
$$CH_3CH_2-\overset{CH_3}{\underset{CH_3}{C}}-O-CH_3 \xrightarrow{HI} CH_3CH_2-\overset{CH_3}{\underset{CH_3}{C}}-I + I-CH_3 + H_2O$$

9.50

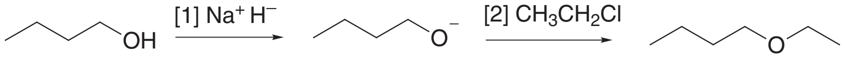
a.



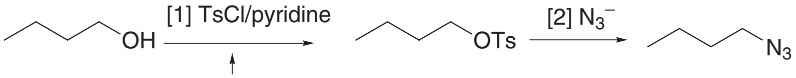
b.



c.



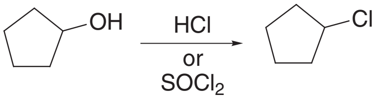
d.



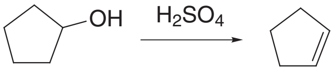
Make OH a good leaving group (use TsCl), then add N_3^-.

9.51

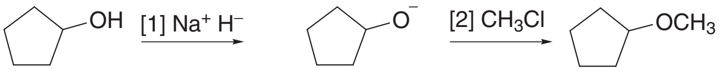
a.



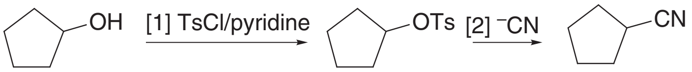
b.



c.

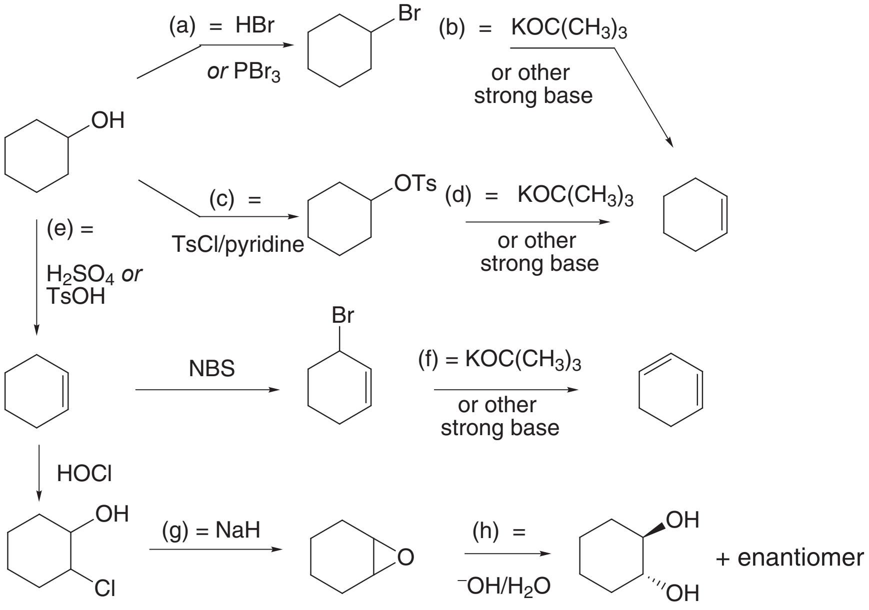


d.

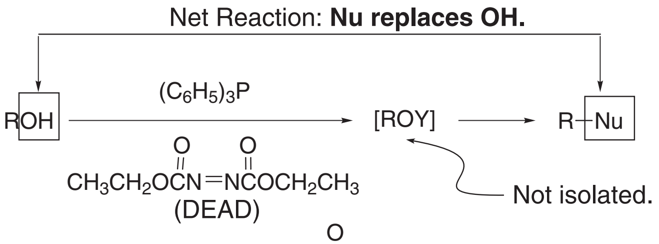


Make OH a good leaving group (use TsCl), then add ^-CN.

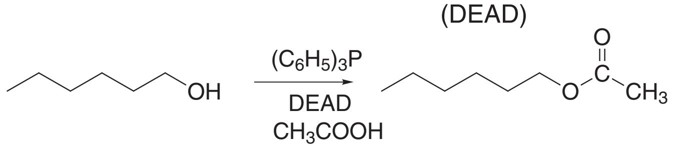
9.52


OH
(a) = HBr
or PBr3
Br
(b) = KOC(CH3)3
or other strong base
(c) =
TsCl/pyridine
OTs
(d) = KOC(CH3)3
or other strong base
(e) =
H2SO4 or TsOH
NBS
Br
(f) = KOC(CH3)3
or other strong base
HOCl
OH
Cl
(g) = NaH
O
(h) =
−OH/H2O
OH
OH
+ enantiomer

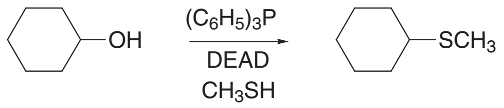
9.53


Net Reaction: Nu replaces OH.
ROH
(C6H5)3P
CH3CH2OCN=NCOCH2CH3
(DEAD)
[ROY]
R–Nu
Not isolated.

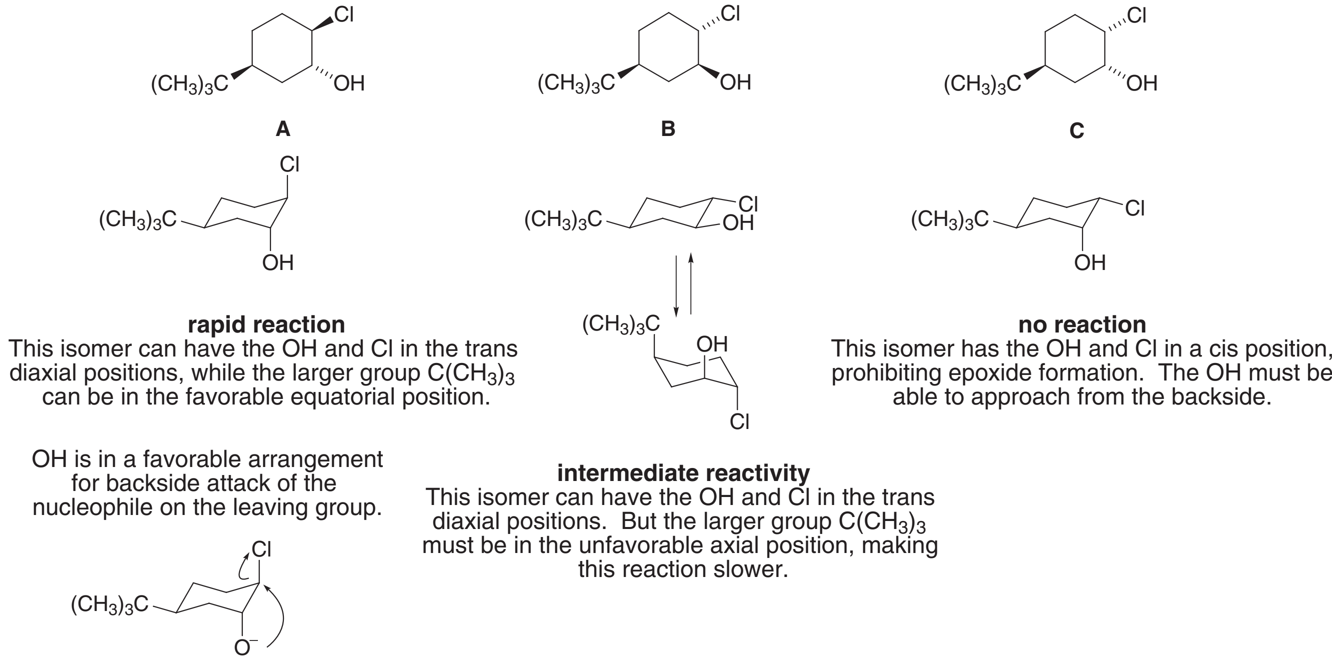
a.


OH
(C6H5)3P
DEAD
CH3COOH
O
C
CH3

b.


OH
(C6H5)3P
DEAD
CH3SH
SCH3

9.54



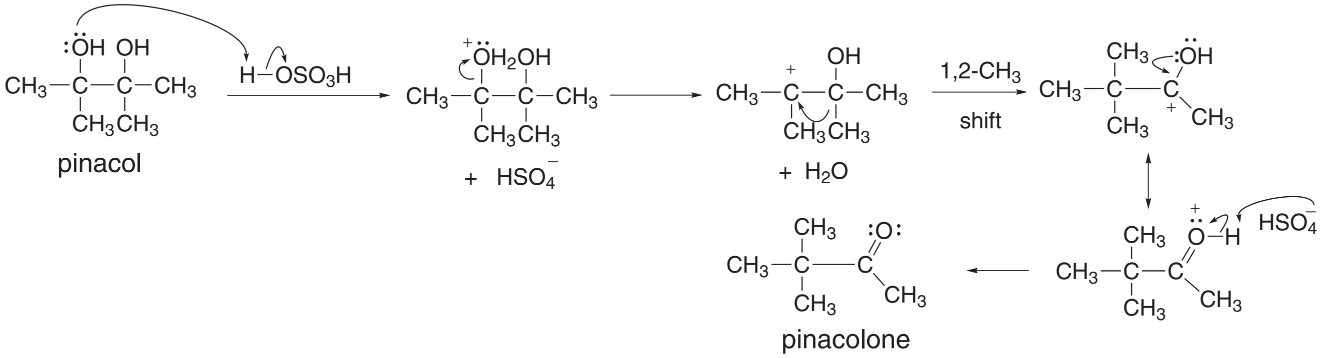
rapid reaction
This isomer can have the OH and Cl in the trans diaxial positions, while the larger group $C(CH_3)_3$ can be in the favorable equatorial position.

OH is in a favorable arrangement for backside attack of the nucleophile on the leaving group.

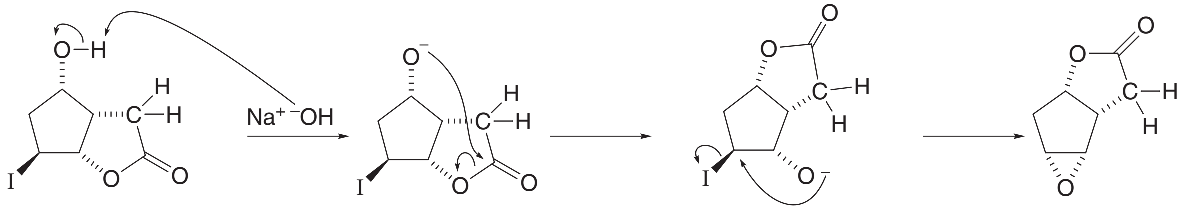
intermediate reactivity
This isomer can have the OH and Cl in the trans diaxial positions. But the larger group $C(CH_3)_3$ must be in the unfavorable axial position, making this reaction slower.

no reaction
This isomer has the OH and Cl in a cis position, prohibiting epoxide formation. The OH must be able to approach from the backside.

9.55

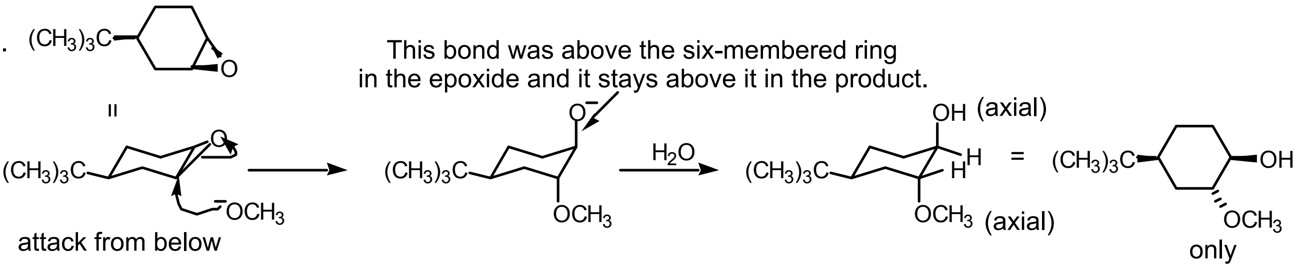


9.56



9.57 Bisogna disegnare il prodotto che mette il nucleofilo ed il gruppo uscente (O^-) trans e diassiali.

a.



This bond was above the six-membered ring in the epoxide and it stays above it in the product.

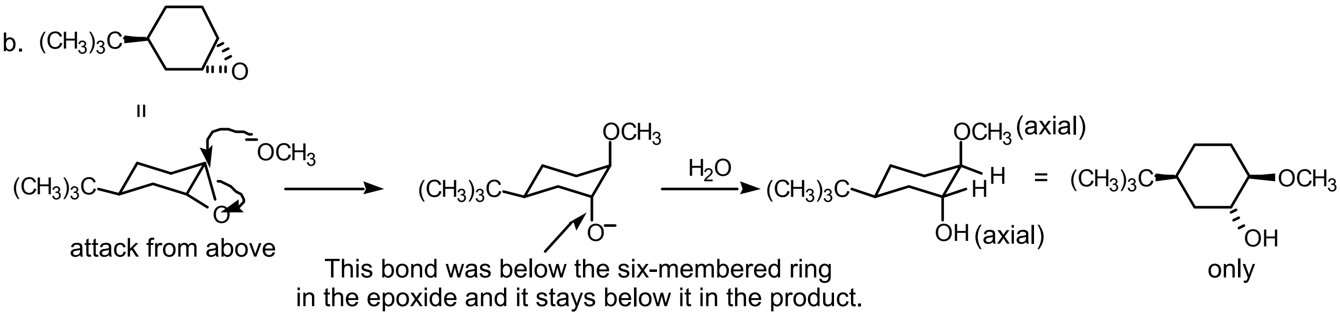
attack from below

(axial)

(axial)

only

b.



attack from above

This bond was below the six-membered ring in the epoxide and it stays below it in the product.

(axial)

(axial)

only

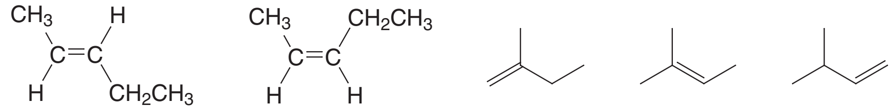
The nucleophile must always approach by backside attack; i.e. if the epoxide is drawn "up" it must attack from below. Even though both ends of the epoxide are equally substituted, nucleophilic attack occurs at only one C–O bond, the one that gives trans diaxial products, as drawn.

Capitolo 10

10.1

Six alkenes of molecular formula C_5H_{10}.

$CH_2{=}CHCH_2CH_2CH_3$



trans cis

diastereomers

10.2 Per assegnare il nome ad un alchene:

[1] Trovare la catena più lunga che contiene il doppo legame. Cambiare la desinenza –***ano*** in –***ene***.
[2] Numerare la catena dando al doppio legame il numero più basso. Il nome dell'alchene è assegnato dal primo numero.
[3] Applicare tutte le altre regole di nomenclatura.

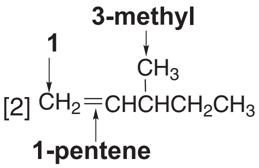
Per assegnare il nome ad un cicloalchene:

[1] Quando il doppio legame è contenuto in un ciclo, è sempre posizionato tra il C1 e il C2. Omettere il numero "1" nel nome. Cambiare la desinenza –***ano*** in –***ene***.
[2] Numerare l'anello in senso orario o antiorario in modo da assegnare al primo sostituente il numero più basso.
[3] Applicare tutte le altre regole di nomenclatura.

a. [1] $CH_2{=}CHCHCH(CH_3)CH_2CH_3$

5 C chain with double bond
pentene

[2]



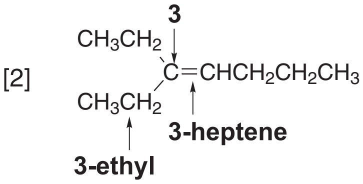
$$\overset{\displaystyle CH_3}{\underset{}{CH_2{=}CH\overset{|}{C}HCH_2CH_3}}$$

[3] **3-methyl-1-pentene**

b. [1] $(CH_3CH_2)_2C{=}CHCH_2CH_2CH_3$

7 C chain with double bond
heptene

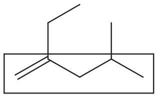
[2]



$$(CH_3CH_2)(CH_3CH_2)C{=}CHCH_2CH_2CH_3$$

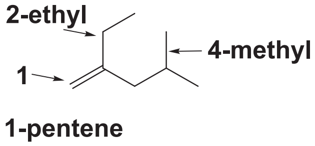
[3] **3-ethyl-3-heptene**

c. [1]



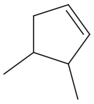
5 C chain with double bond
pentene

[2]



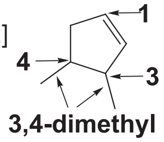
[3] **2-ethyl-4-methyl-1-pentene**

d. [1]



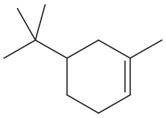
5 C ring with a double bond
cyclopentene

[2]



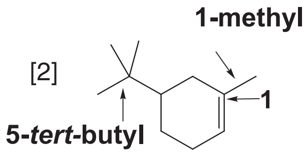
[3] **3,4-dimethylcyclopentene**

e. [1]



6 C ring with a double bond
cyclohexene

[2]



[3] **5-*tert*-butyl-1-methylcyclohexene**

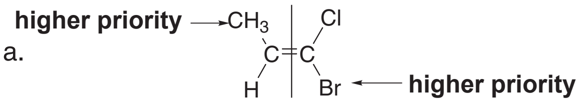
10.3 Per definire un alchene come *E* o *Z*:

[1] **Assegnare le priorità** ai due sostituenti ***su ognuna delle estremità*** usando le regole per la nomenclatura *R*,*S*.

[2] **Assegnare *E* o *Z*** in funzione della posizione dei due gruppi a priorità più alta.

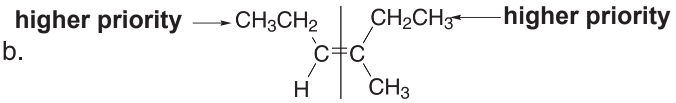
- Il prefisso ***E*** è usato quando i due gruppi con priorità più alta sono su **lati opposti.**
- Il prefisso ***Z*** è usato quando i due gruppi con priorità più alta sono **sullo stesso lato** del doppio legame.

a.



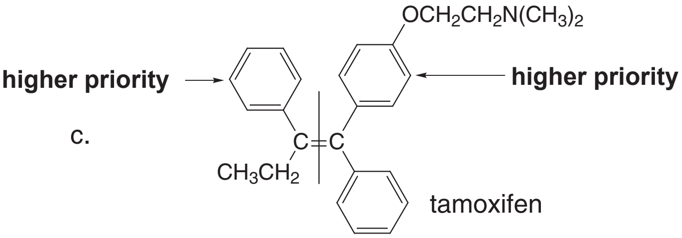
Two higher priority groups are on opposite sides: ***E* isomer**

b.



Two higher priority groups are on the same side: ***Z* isomer**

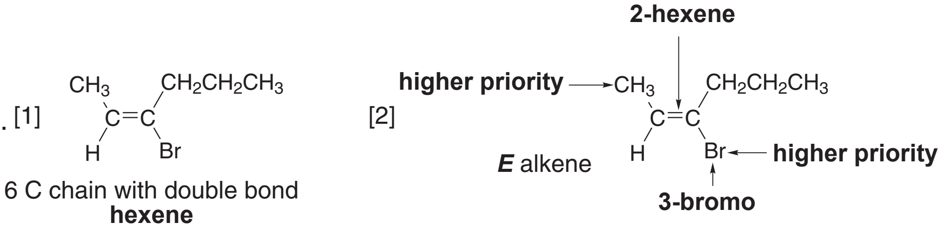
c.



Two higher priority groups are on the same side: ***Z* isomer**

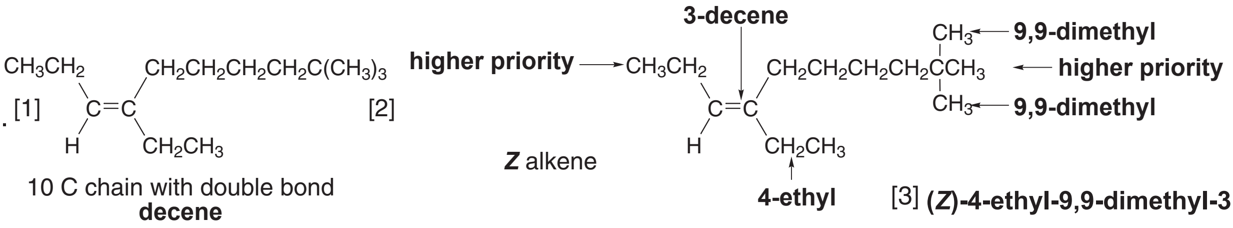
10.4 Per assegnare il nome ad un alchene: Prima seguire le regole della risposta 10.4. Poi, quando necessario, assegnare un prefisso *E* o *Z* sulla base della priorità, come nella risposta 10.5.

a.



[3] **(*E*)-3-bromo-2-hexene**

b.



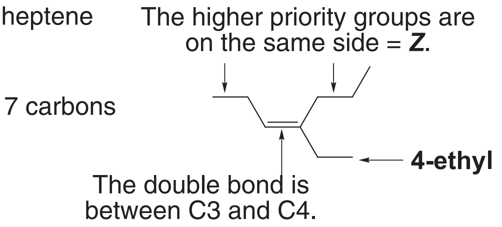
[3] **(*Z*)-4-ethyl-9,9-dimethyl-3-decene**

10.5 Operare a ritroso per disegnare la struttura dal nome:

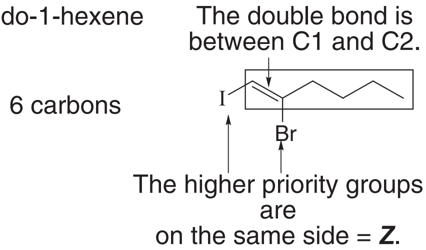
[1] Individuare la radice corrispondente e il gruppo funzionale e disegnare la struttura, ricordando che il doppio legame si trova fra il C1 e il C2 per i cicloalcheni.

[2] Legare i sostituenti sul carbonio opportuno.

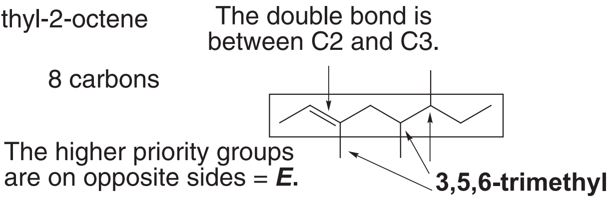
a. (*Z*)-4-ethyl-3-heptene



c. (*Z*)-2-bromo-1-iodo-1-hexene



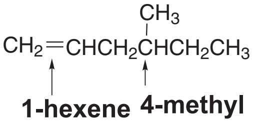
b. (*E*)-3,5,6-trimethyl-2-octene



10.6 Assegnare il nome agli alcheni seguendo le regole delle risposte 10.2 e 10.3.

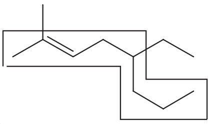
a. $CH_2{=}CHCH_2CH(CH_3)CH_2CH_3$

6 C chain with a double bond = **hexene**

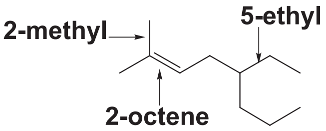


4-methyl-1-hexene

b.

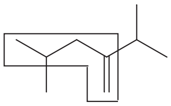


8 C chain with a double bond = **octene**

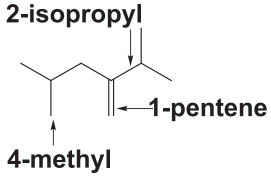


5-ethyl-2-methyl-2-octene

c.

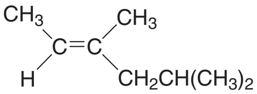


5 C chain with a double bond = **pentene**

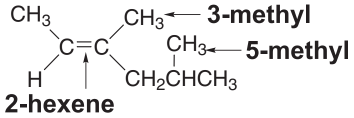


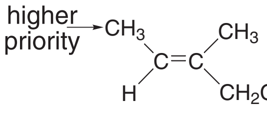
2-isopropyl-4-methyl-1-pentene

d.



6 C chain with a double bond = **hexene**

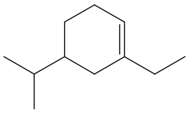




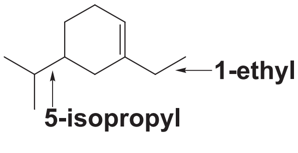
(*E*)-3,5-dimethyl-2-hexene

Higher priority groups are on opposite sides = ***E* alkene.**

e.

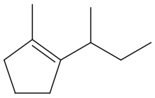


6 C ring with a double bond = **cyclohexene**

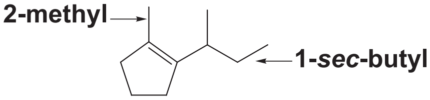


1-ethyl-5-isopropylcyclohexene

f.



5 C ring with a double bond = **cyclopentene**

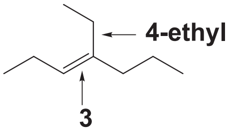


1-*sec*-butyl-2-methylcyclopentene

10.7 Usare le regole della risposta 10.5.

a. (*E*)-4-ethyl-3-**heptene**

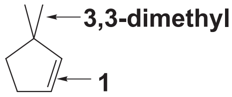
7 carbons



Higher priority groups on opposite sides = *E*.

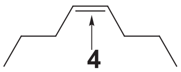
b. 3,3-dimethyl**cyclopentene**

5 carbon ring



c. *cis*-4-**octene**

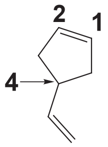
8 carbons



Higher priority groups on the same side = cis.

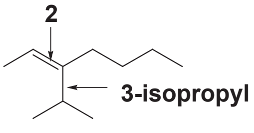
d. 4-vinyl**cyclopentene**

5 carbon ring



e. (*Z*)-3-isopropyl-2-**heptene**

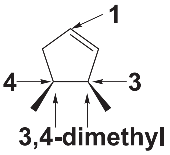
7 carbons



Higher priority groups on the same side = *Z*.

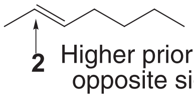
f. *cis*-3,4-dimethyl**cyclopentene**

5 carbon ring



g. *trans*-2-**heptene**

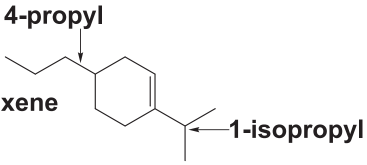
7 carbons



Higher priority groups on opposite sides = trans.

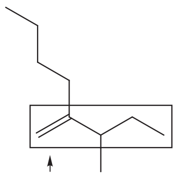
h. 1-isopropyl-4-propyl**cyclohexene**

6 carbon ring

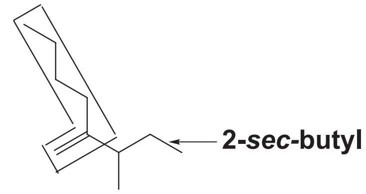


10.8

a. 2-butyl-3-methyl-1-pentene

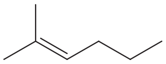


As written, this is the parent chain, but there is another longer chain containing the double bond.



new name:
2-*sec*-butyl-1-hexene

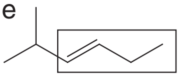
b. (*Z*)-2-methyl-2-hexene



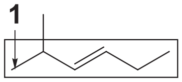
new name:
2-methyl-2-hexene

Two groups on one end of the C=C are the same (2 CH_3's), so no *E* and *Z* isomers are possible.

c. (*E*)-1-isopropyl-1-butene

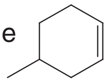


As written, this is the parent chain, but there is another longer chain containing the double bond.

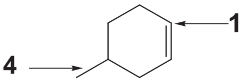


new name:
(*E*)-2-methyl-3-hexene

d. 5-methylcyclohexene

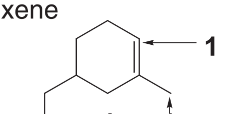


As written the methyl
is at C5. Renumber
to put it at C4.

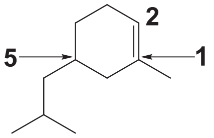


new name:
4-methylcyclohexene

e. 4-isobutyl-2-methylcylohexene

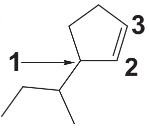


As written this methyl
is at C2. Renumber
to put it at C1.

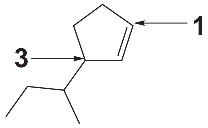


new name:
5-isobutyl-1-methylcyclohexene

f. 1-*sec*-butyl-2-cyclopentene



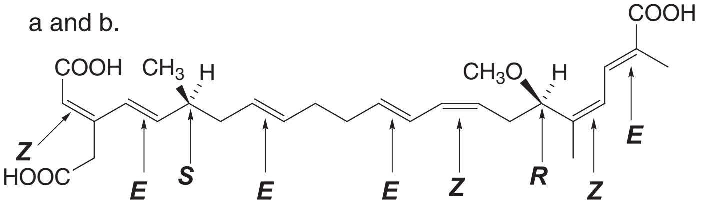
This has the double bond between
C2 and C3. Cycloalkenes must
have the double bond between
C1 and C2. Renumber.



new name:
3-*sec*-butylcyclopentene

10.9

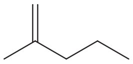
a and b.



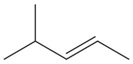
bongkrekic acid

c. Since there are 7 double bonds
and 2 tetrahedral stereogenic
centers, $2^9 = 512$ possible stereoisomers.

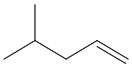
10.10



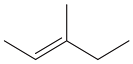
2-methyl-1-pentene



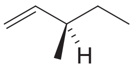
(*E*)-4-methyl-2-pentene



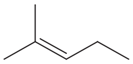
4-methyl-1-pentene



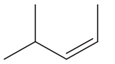
(*E*)-3-methyl-2-pentene



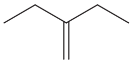
(*R*)-3-methyl-1-pentene



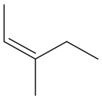
2-methyl-2-pentene



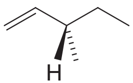
(*Z*)-4-methyl-2-pentene



2-ethyl-1-butene



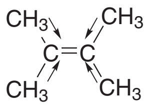
(*Z*)-3-methyl-2-pentene



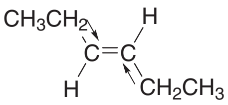
(*S*)-3-methyl-1-pentene

10.11 Per ordinare gli isomeri in base al punto di ebollizione crescente:

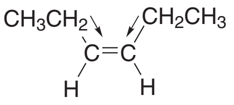
Considerare le differenze di polarità: *un piccolo dipolo netto* rende un alchene più polare, e di conseguenza possiede un punto di ebollizione più elevato rispetto ad un alchene che non ha *nessun dipolo netto*. Gli isomeri cis hanno punti di ebollizione maggiori rispetto ai trans.



All dipoles cancel.
smallest surface area
no net dipole
lowest bp



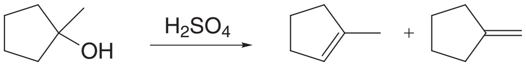
Two dipoles cancel.
no net dipole
trans isomer
intermediate bp



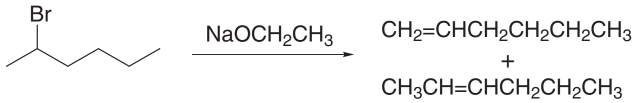
Two dipoles reinforce.
net dipole
cis isomer
highest bp

10.12

a.



b.

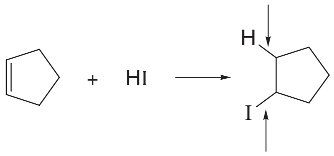


10.13 Per disegnare i prodotti di una reazione di addizione:

[1] Identificare i due legami che saranno rotti nella reazione. Si rompe sempre il legame π.

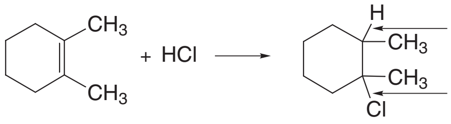
[2] Disegnare il prodotto formando i due nuovi legami σ.

a.



two new σ bonds

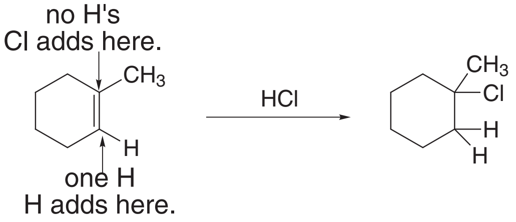
b.



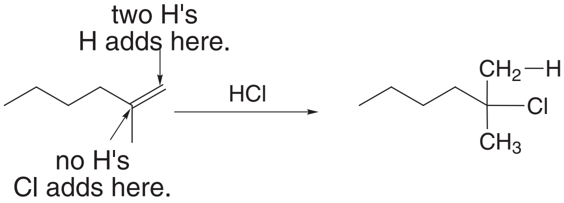
two new σ bonds

10.14 L'addizione agli alcheni segue la regola di Markovnikov: quando HX si addiziona ad un alchene asimmetrico, l'atomo di H si lega al C che ha il maggior numero di atomi di H.

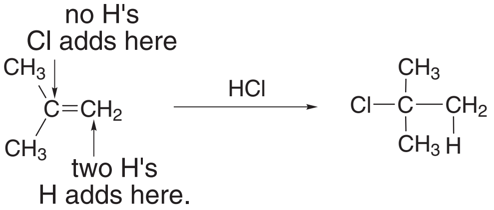
a.



c.

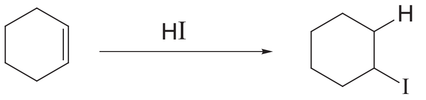


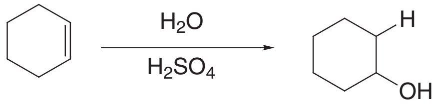
b.

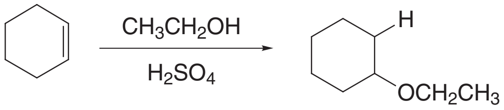


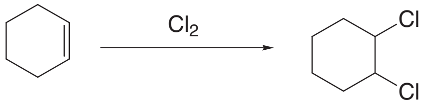
10.15

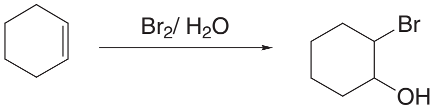
a.

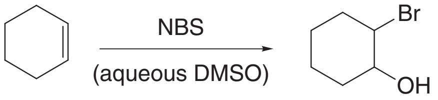

b.


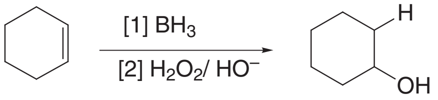
c.


d.


e.


f.


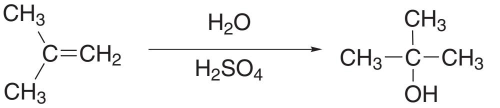
g.


h.


10.16

a.


b.


c.


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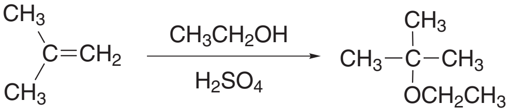

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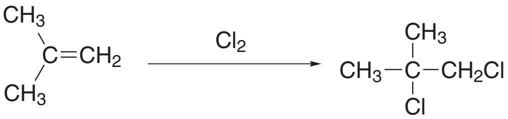

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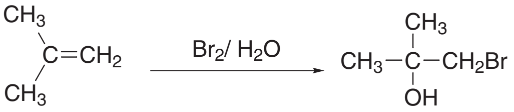
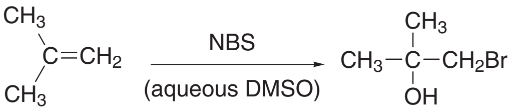


g.


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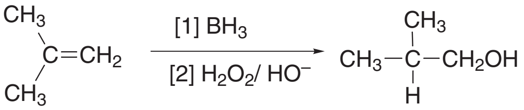
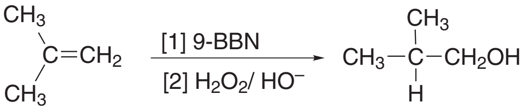
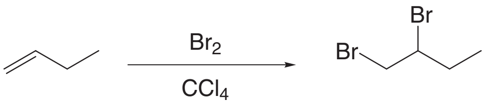
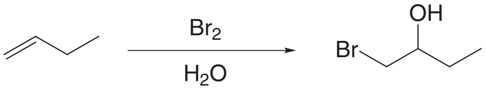


i.


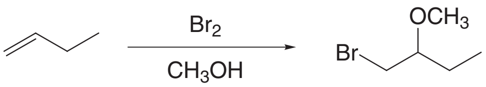
10.17

a.


Halogenation

b.


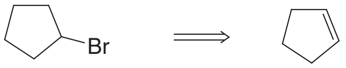
Halohydrin formation: Br adds to the C that had more H's to begin with.

c.


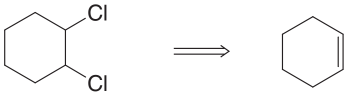
Same as halohydrin formation, except CH_3OH in place of H_2O.

10.18

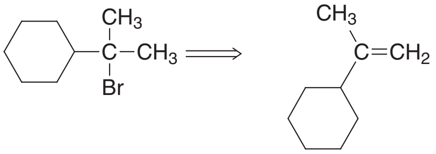
a.



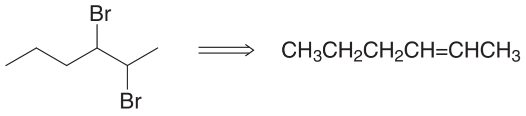
b.



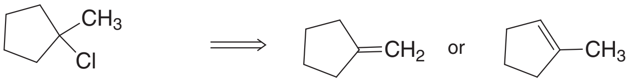
c.



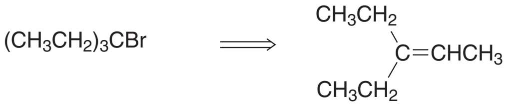
d.



e.

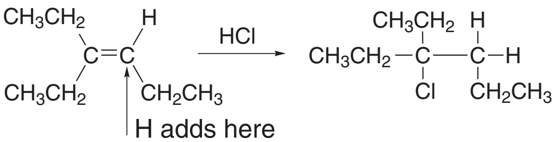


f.



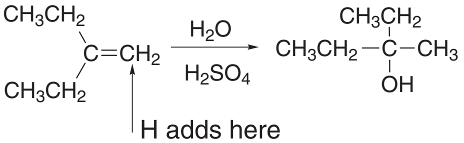
10.19

a. $(CH_3CH_2)_2C{=}CHCH_2CH_3$



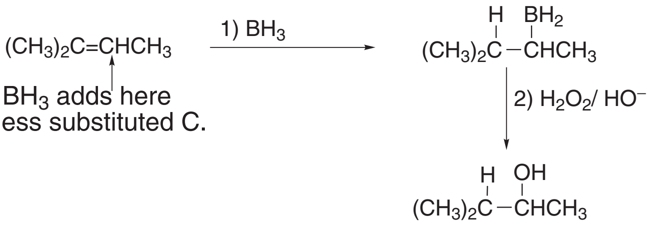
H adds here
to less substituted C.

b. $(CH_3CH_2)_2C{=}CH_2$



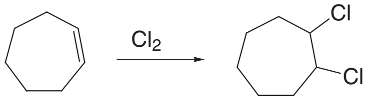
H adds here
to less substituted C.

c.

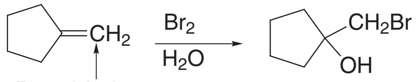


BH3 adds here
to less substituted C.

d.

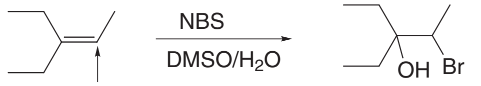


e.



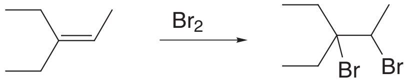
Br adds here
to less substituted C.

f.

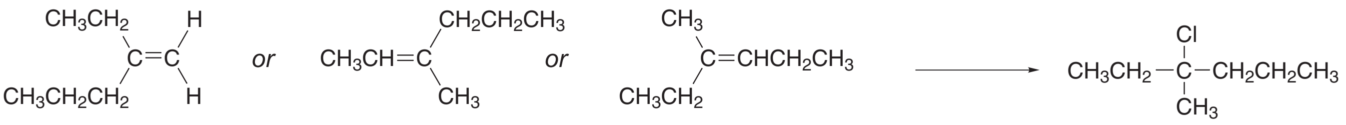


Br adds here
to less substituted C.

g.

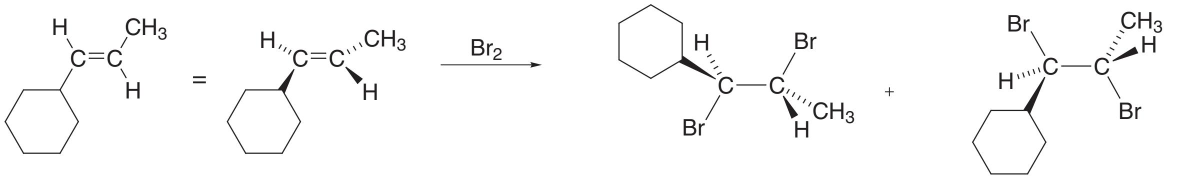


10.20

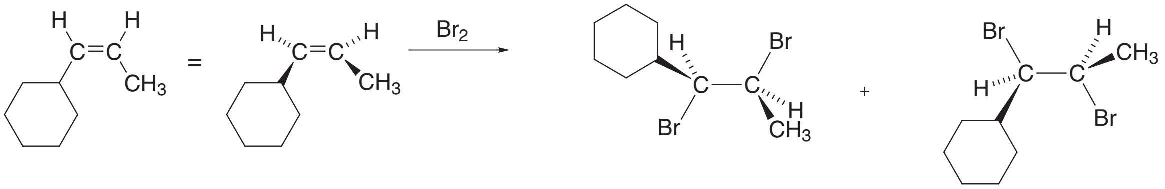


10.21

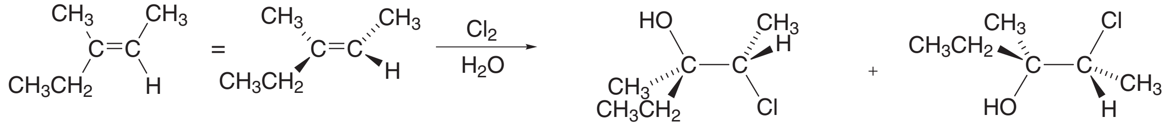
a.



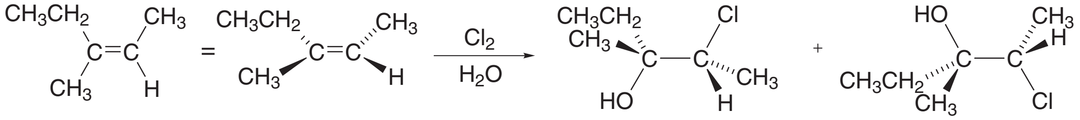
b.



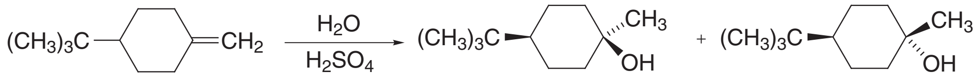
c.

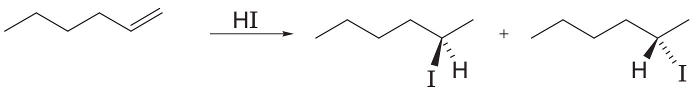


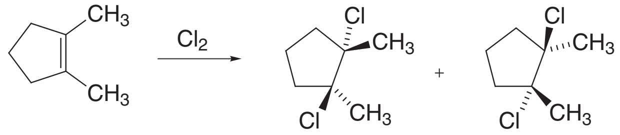
d.



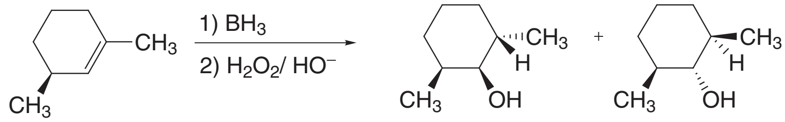
10.22

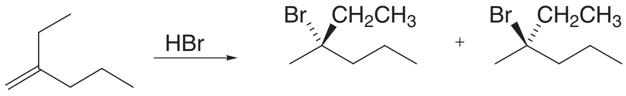
a. 

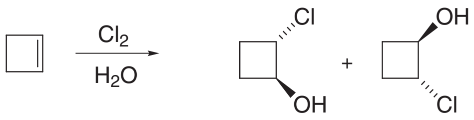
b. 

c. 

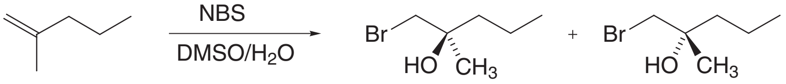
Only anti addition.

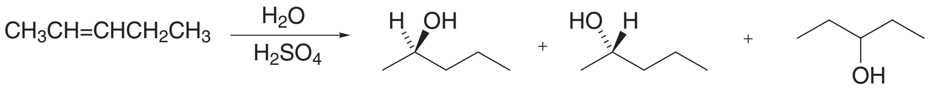
d. 

e. 

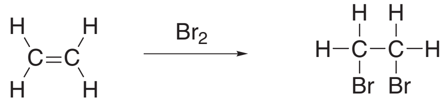
f. 

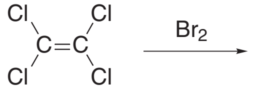
Only anti addition.

g. 

h. 

10.23

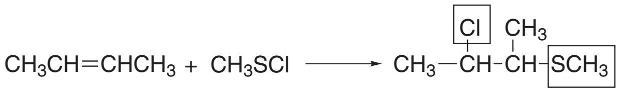
ethylene 

tetrachloroethylene 

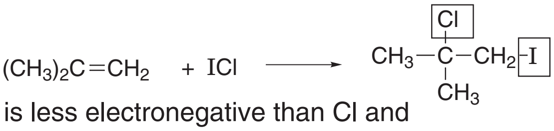
No reaction

In addition of Br_2, the alkene must act as an electron rich nucleophile. With four electronegative Cl atoms withdrawing electron density from the C=C, tetrachloroethylene is much less electon rich, and therefore it is a poorer nucleophile. This makes it less reactive with Br_2.

10.24

a. 

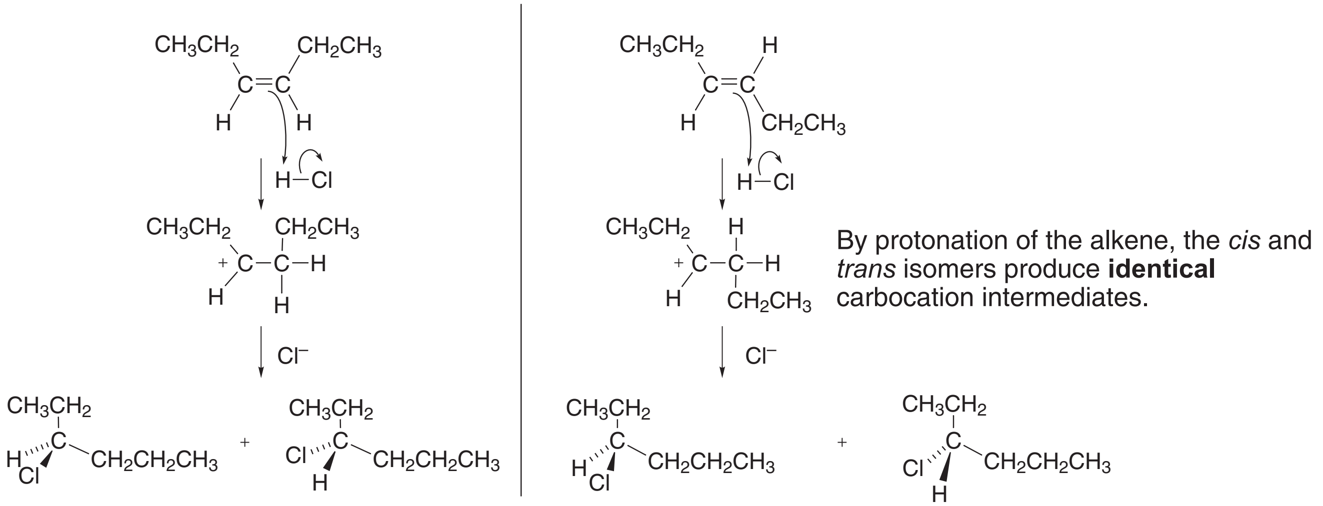
$CH_3CH{=}CHCH_3 + CH_3SCl \longrightarrow CH_3{-}\underset{}{\overset{\boxed{Cl}}{CH}}{-}\overset{CH_3}{CH}{-}\boxed{SCH_3}$

b. 

$(CH_3)_2C{=}CH_2 + ICl \longrightarrow CH_3{-}\overset{\boxed{Cl}}{\underset{CH_3}{C}}{-}CH_2{-}\boxed{I}$

I is less electronegative than Cl and therefore it is the electrophile in this reaction. It ends up on the less substituted C.

10.25

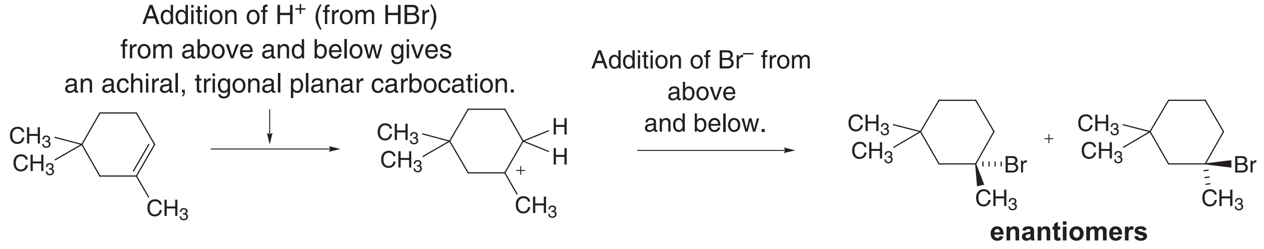


By protonation of the alkene, the *cis* and *trans* isomers produce **identical** carbocation intermediates.

Both *cis*- and *trans*-3-hexene give the same racemic mixture of products, so the reaction is not stereospecific.

10.26 Per disegnare i prodotti, ricordare che l'addizione di HBr avviene attraverso la formazione di un carbocatione intermedio.

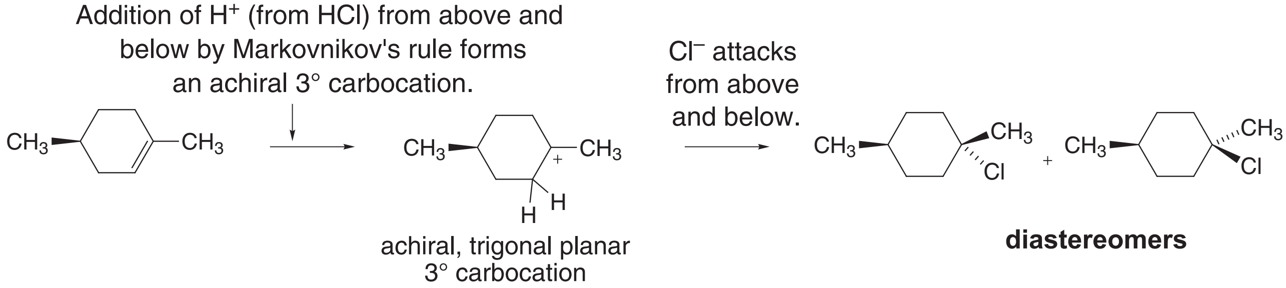
a.


Addition of H^+ (from HBr) from above and below gives an achiral, trigonal planar carbocation.

Addition of Br^- from above and below.

enantiomers

b.


Addition of H^+ (from HCl) from above and below by Markovnikov's rule forms an achiral 3° carbocation.

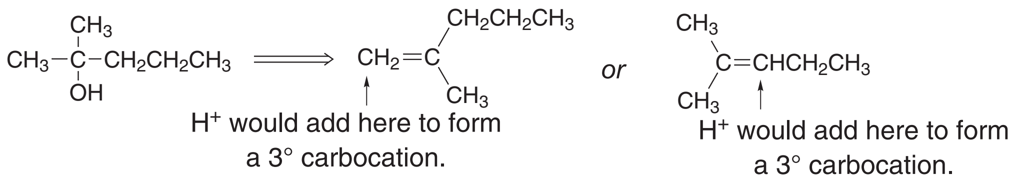
Cl^- attacks from above and below.

achiral, trigonal planar 3° carbocation

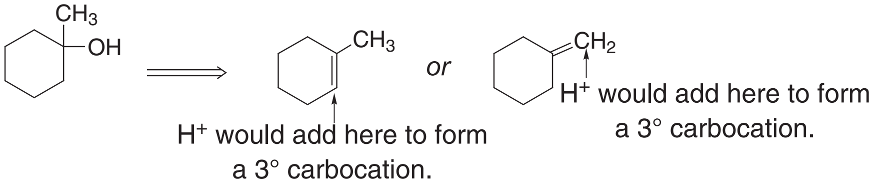
diastereomers

10.27

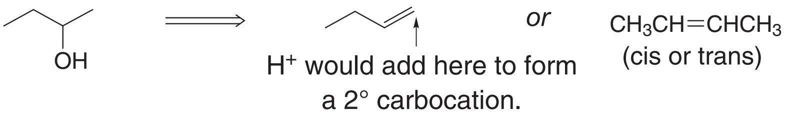
a.



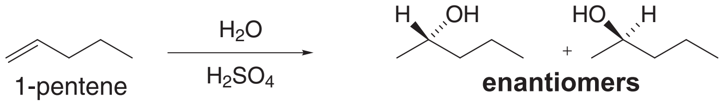
b.



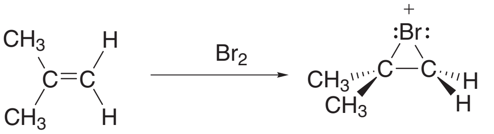
c.



10.28

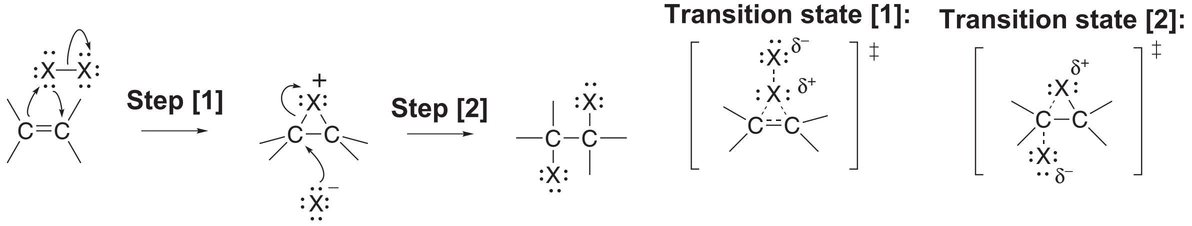


10.29



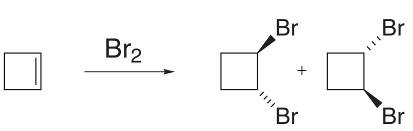
10.30 I due stadi del meccanismo di alogenazione di un alchene sono:

[1] Addizione di X^+ all'alchene per formare uno ione alonio ciclico.
[2] Attacco nucleofilo di X^-.

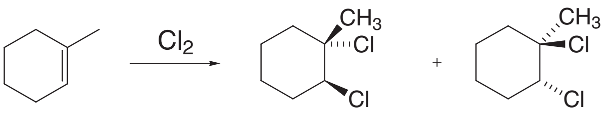


10.31 L'alogenazione di un alchene addiziona due elementi X con modalità anti.

a.

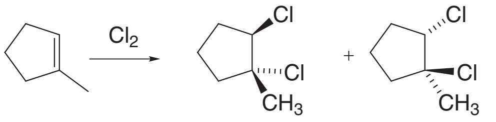


b.



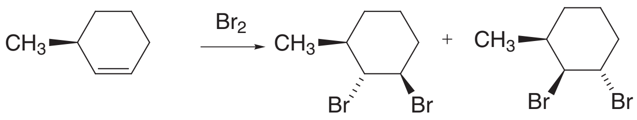
10.32 Per disegnare i prodotti di alogenazione di un alchene, ricordare che l'alogeno si addiziona alle due estremità del doppio legame esclusivamente in modo anti.

a.



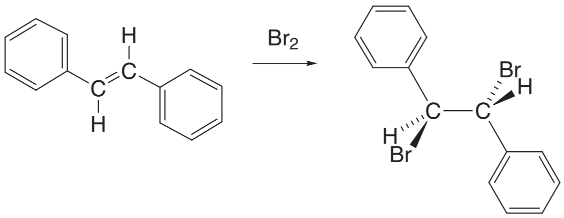
enantiomers

c.



diastereomers

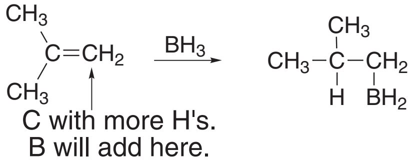
b.



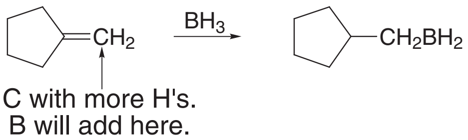
achiral meso compound

10.33 Nell'idroborazione l'atomo di boro è l'elettrofilo e si lega all'atomo di carbonio che ha il maggior numero di atomi di H.

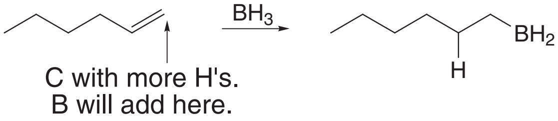
a.



c.



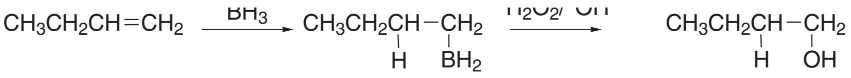
b.



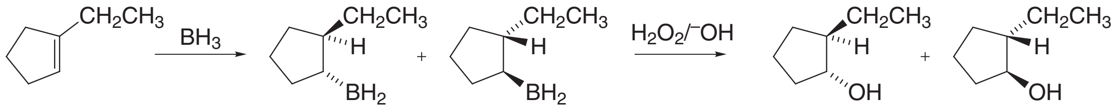
10.34 La reazione di idroborazione–ossidazione avviene in due stadi:

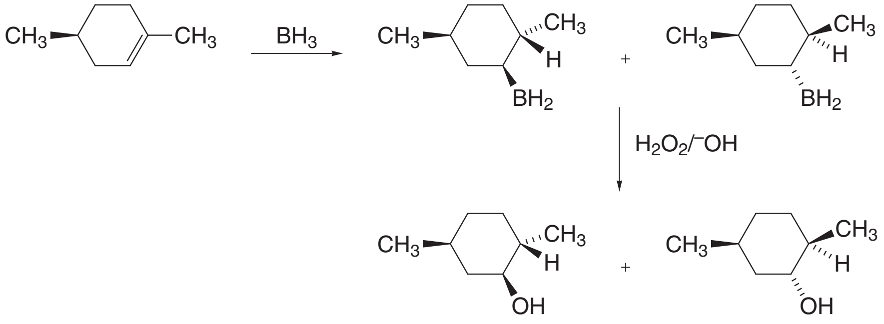
[1] Addizione syn di BH_3, con il borano sul carbonio meno sostituito.

[2] OH sostituisce BH_2 con ritenzione di configurazione.

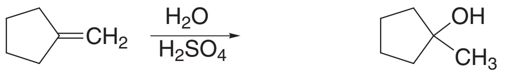
a. 

$$CH_3CH_2CH{=}CH_2 \xrightarrow{BH_3} CH_3CH_2\underset{H}{\underset{|}{C}}H{-}\underset{BH_2}{\underset{|}{C}}H_2 \xrightarrow{H_2O_2/^-OH} CH_3CH_2\underset{H}{\underset{|}{C}}H{-}\underset{OH}{\underset{|}{C}}H_2$$

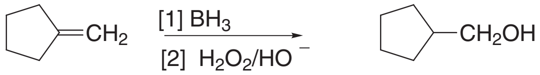
b. 

c. 

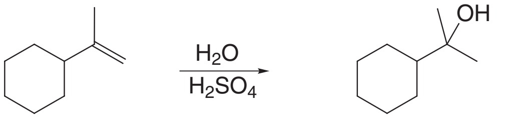
10.35

a. 

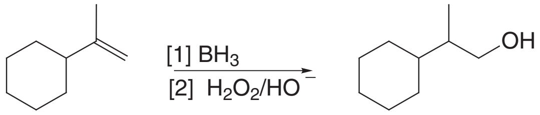
Hydration places the OH
on the more substituted carbon.

b. 

Hydroboration–oxidation places the OH
on the less substituted carbon.

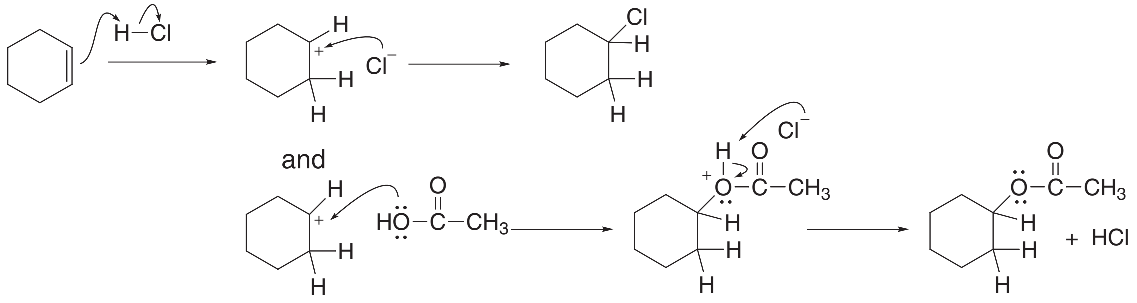
c. 

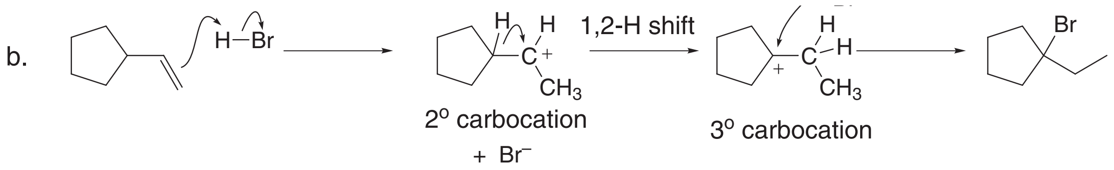
Hydration places the OH
on the more substituted carbon.

d. 

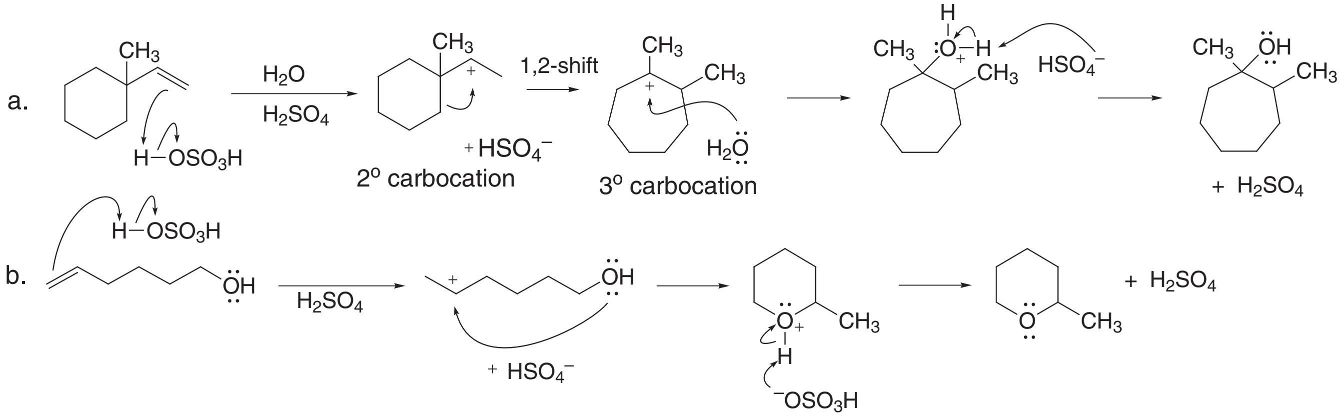
Hydroboration–oxidation places the OH
on the less substituted carbon.

10.36

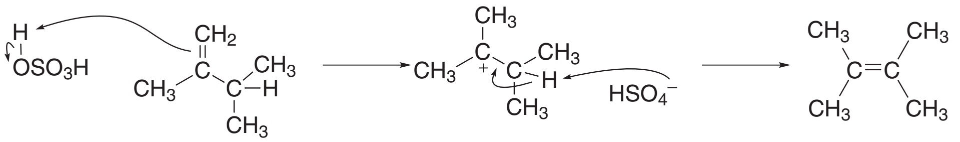
a. 



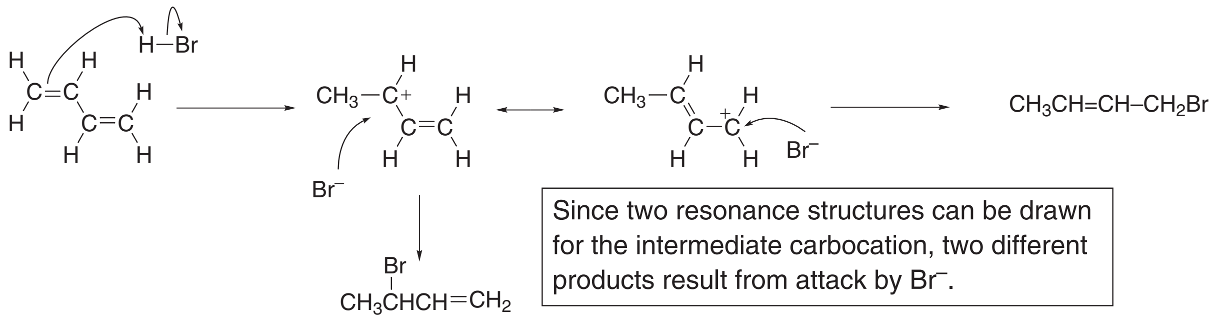
10.37



10.38 La reazione di isomerizzazione avviene per protonazione e deprotonazione.

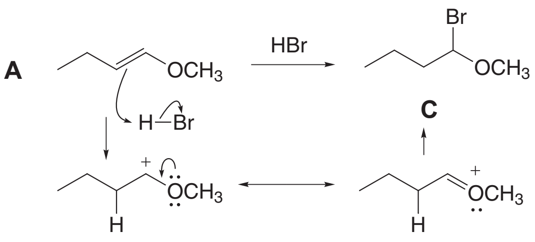


10.39

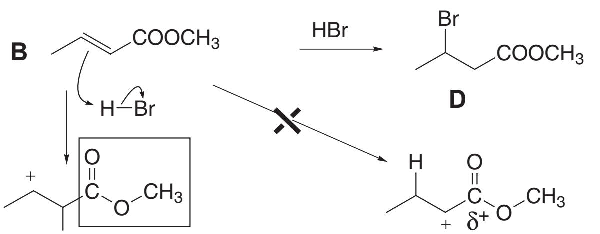


Since two resonance structures can be drawn for the intermediate carbocation, two different products result from attack by Br⁻.

10.40



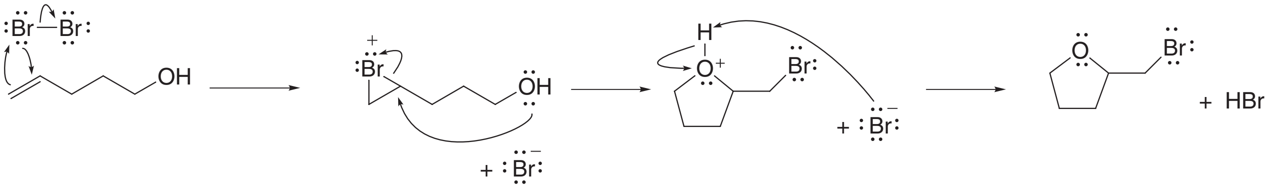
This carbocation is resonance stabilized by the O atom, and therefore preferentially forms and results in **C**.



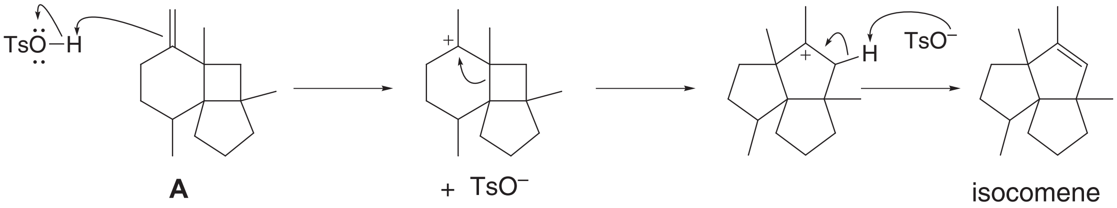
This carbocation is formed preferentially and results in product **D**. It is not destabilized by an adjacent electron withdrawing $COOCH_3$ group.

This carbocation is destabilized by the δ^+ on the adjacent C, so it does not form.

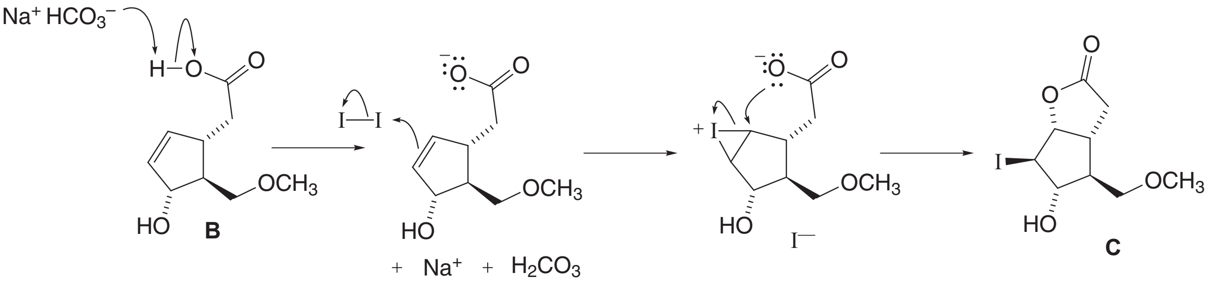
10.41



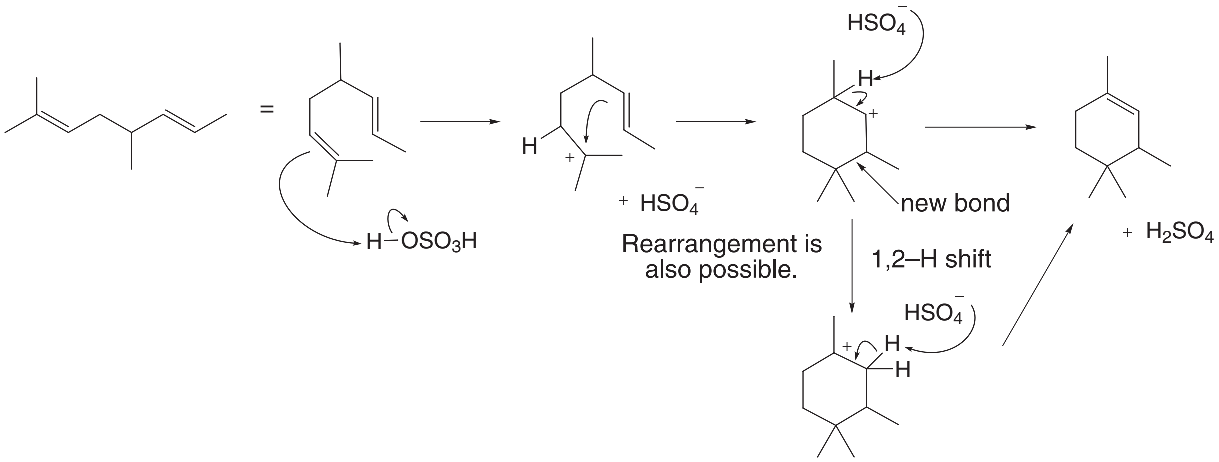
10.42



10.43



10.44


=
H
H–OSO₃H
+ HSO₄⁻
HSO₄⁻
H
new bond
Rearrangement is also possible.
1,2–H shift
HSO₄⁻
H
H
+ H₂SO₄

Capitolo 11

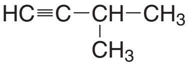
11.1 • Un ***alchino interno*** ha il triplo legame in *mezzo* alla catena carboniosa.
• Un ***alchino terminale*** ha il triplo legame all'*estremità* della catena carboniosa.

$HC\equiv C-CH_2CH_2CH_3$

terminal alkyne

$CH_3-C\equiv C-CH_2CH_3$

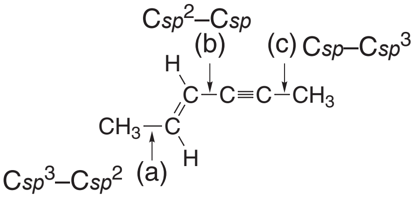
internal alkyne



$HC\equiv C-\underset{CH_3}{CH}-CH_3$

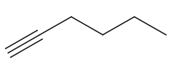
terminal alkyne

11.2

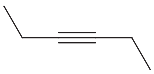


11.3 Come per gli alcheni, maggiore è il numero di gruppi alchilici legati al C ibridato *sp*, più stabile è l'alchino. Questo rende gli alchini interni più stabili degli alchini terminali.

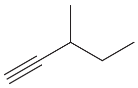
11.4 Per assegnare il nome a un alchino:
[1] Individuare la catena più lunga che contiene entrambi gli atomi del triplo legame, e numerare la catena in modo da assegnare al primo carbonio del triplo legame il numero più basso
[2] Indicare il nome di tutti i sostituenti seguendo le altre regole della nomenclatura.



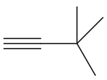
1-hexyne



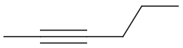
3-hexyne



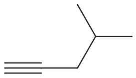
3-methyl-1-pentyne



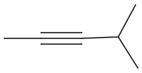
3,3-dimethyl-1-butyne



2-hexyne



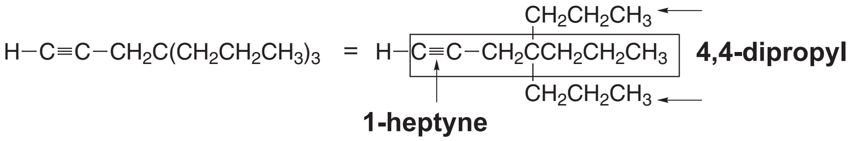
4-methyl-1-pentyne



4-methyl-2-pentyne

11.5 Usare le indicazioni della risposta 11.4 per attribuire il nome a ciascun alchino.

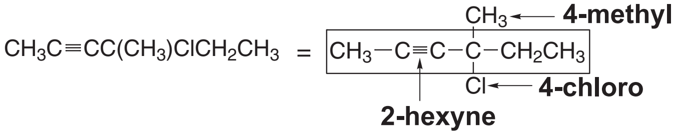
a.



$H-C\equiv C-CH_2C(CH_2CH_2CH_3)_3 = H-\boxed{C\equiv C-CH_2\overset{CH_2CH_2CH_3}{\underset{CH_2CH_2CH_3}{C}}CH_2CH_2CH_3}$

4,4-dipropyl-1-heptyne

b.

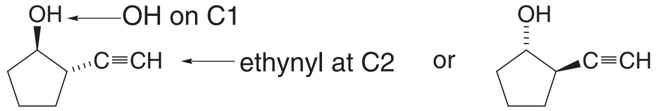


$CH_3C\equiv CC(CH_3)ClCH_2CH_3 = \boxed{CH_3-C\equiv C-\overset{CH_3}{\underset{Cl}{C}}-CH_2CH_3}$

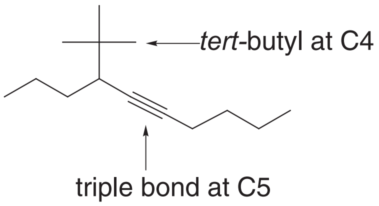
4-chloro-4-methyl-2-hexyne

11.6 Operare a ritroso per scrivere la struttura dal nome:
[1] Individuare la radice corrispondente e il gruppo funzionale.
[2] Legare i sostituenti sul carbonio opportuno.

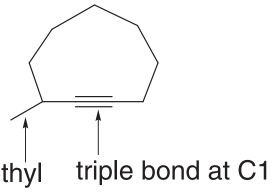
a. *trans*-2-ethynyl**cyclopentanol**
5 C ring with OH at C1



b. 4-*tert*-butyl-5-**decyne**
10 C chain with
a triple bond



c. 3-methyl**cyclononyne**
9 C ring with a
triple bond at C1



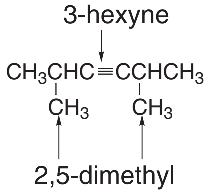
11.7 Usare le regole della risposta 11.4 per attribuire il nome agli alchini.

5 3

a. $CH_3CH_2CH(CH_3)C{\equiv}CCH_2CH_3$ **5-methyl-3-heptyne**

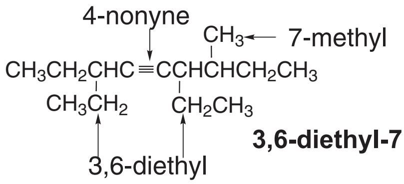
5-methyl 3-heptyne

b.



$CH_3\underset{CH_3}{C}HC{\equiv}C\underset{CH_3}{C}HCH_3$ **2,5-dimethyl-3-hexyne**

c.



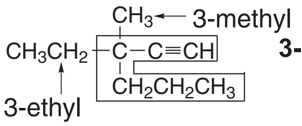
$CH_3CH_2\underset{CH_3CH_2}{C}HC{\equiv}C\underset{CH_2CH_3}{C}H\overset{CH_3}{C}HCH_2CH_3$

3,6-diethyl-7-methyl-4-nonyne

d. $HC{\equiv}C-CH(CH_2CH_3)CH_2CH_2CH_3$ **3-ethyl-1-hexyne**

1-hexyne 3-ethyl

e.



$CH_3CH_2-\overset{CH_3}{\underset{CH_2CH_2CH_3}{C}}-C{\equiv}CH$ **3-ethyl-3-methyl-1-hexyne**

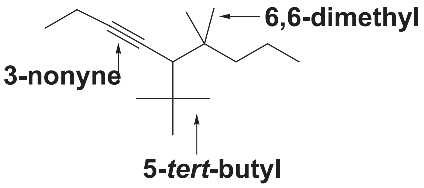
f. $CH_3CH_2C{\equiv}CCH_2C{\equiv}CCH_3$ **2,5-octadiyne**

5 2

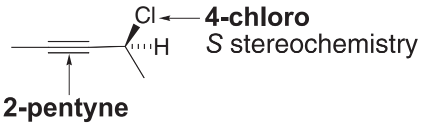
11.8 Usare le regole della risposta 11.6 per disegnare la struttura.

a. 5,6-dimethyl-2-**heptyne**

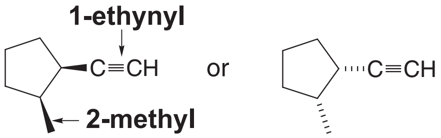
b. 5-*tert*-butyl-6,6-dimethyl-3-**nonyne**



c. (*S*)-4-chloro-2-**pentyne**



d. *cis*-1-ethynyl-2-methyl**cyclopentane**



11.9 Sono due i fattori che determinano un aumento del punto di ebollizione. I carboni di un alchino ibridati *sp* permettono una maggiore attrazione dovuta alle forze di van der Waals fra le molecole dell'alchino. Inoltre, poiché un triplo legame è più polarizzabile di un doppio legame, questo aumenta anche le forze di van der Waals tra due molecole.

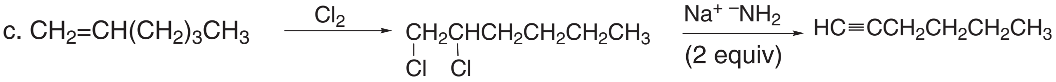
11.10 Per convertire un alchene in un alchino:

[1] Formare dall'alchene un dialogenuro vicinale per addizione di X_2.

[2] Addizionare una base per rimuovere due equivalenti di HX e formare l'alchino.

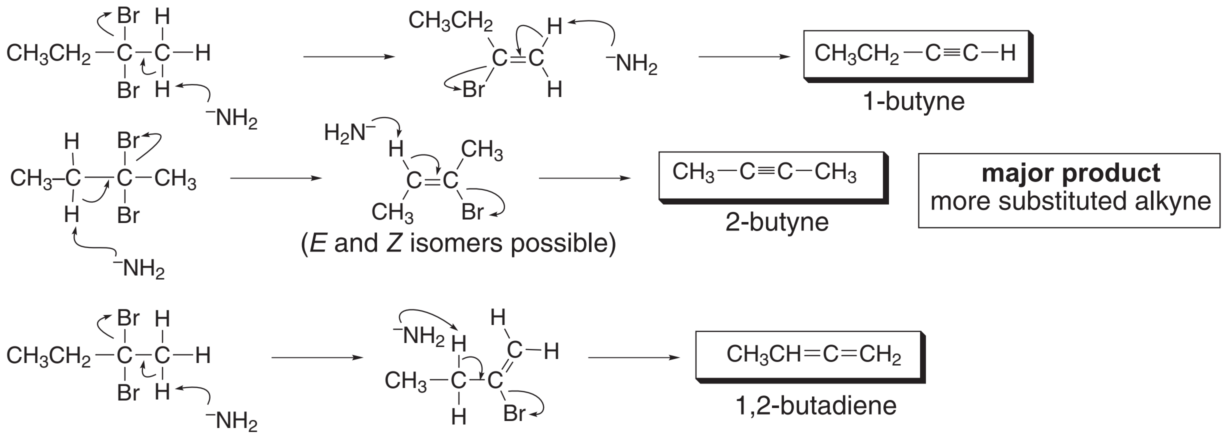
a. $Br_2CH(CH_2)_4CH_3 \xrightarrow{Na^+ \ ^-NH_2} \underset{\text{not isolated}}{\left[BrCH{=}CHCH_2CH_2CH_2CH_3 \right]} \xrightarrow{Na^+ \ ^-NH_2} HC{\equiv}CCH_2CH_2CH_2CH_3$

b. $CH_2{=}CCl(CH_2)_3CH_3 \xrightarrow{Na^+ \ ^-NH_2} HC{\equiv}CCH_2CH_2CH_2CH_3$



c. $CH_2{=}CH(CH_2)_3CH_3 \xrightarrow{Cl_2} \underset{Cl}{CH_2}\underset{Cl}{C}HCH_2CH_2CH_2CH_3 \xrightarrow[\text{(2 equiv)}]{Na^+ \ ^-NH_2} HC{\equiv}CCH_2CH_2CH_2CH_3$

11.11



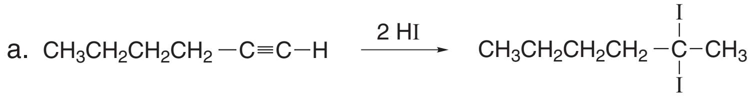
11.12 L'acetilene ha un pK_a di 25, quindi le **basi che hanno un acido coniugato con un pK_a *maggiore di* 25** sono in grado di deprotonarlo.

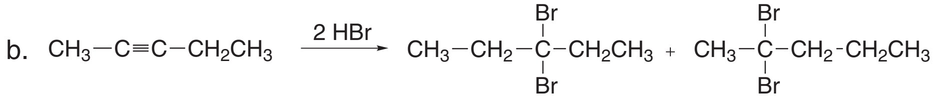
a. CO_3^{2-} [pK_a (HCO_3^-)= 10.2]
pK_a < 25 = **Cannot deprotonate acetylene.**

b. CH_2=CH^- [pK_a (CH_2=CH_2) = 44]
pK_a > 25 = **Can deprotonate acetylene.**

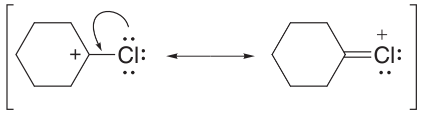
c. $(CH_3)_3CO^-$ {pK_a [$(CH_3)_3COH$]= 18}
pK_a < 25 = **Cannot deprotonate acetylene.**

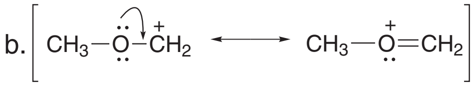
11.13 Per disegnare i prodotti della reazione con HX:
- Addizionare due moli di HX al triplo legame, seguendo la regola di Markovnikov.
- Entrambi gli atomi di X si legano al C più sostituito.

a.

$$CH_3CH_2CH_2CH_2-C\equiv C-H \xrightarrow{2\ HI} CH_3CH_2CH_2CH_2-\overset{I}{\underset{I}{C}}-CH_3$$

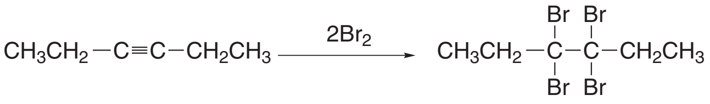
b.

$$CH_3-C\equiv C-CH_2CH_3 \xrightarrow{2\ HBr} CH_3-CH_2-\overset{Br}{\underset{Br}{C}}-CH_2CH_3 + CH_3-\overset{Br}{\underset{Br}{C}}-CH_2\text{-}CH_2CH_3$$

11.14

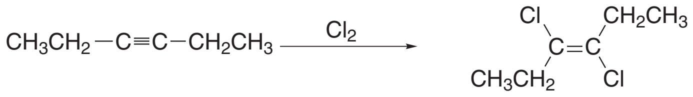
a.


b.


11.15 L'addizione di un equivalente di X_2 agli alchini forma un dialogenuro trans.
L'addizione di due equivalenti di X_2 agli alchini forma tetralogenuri.

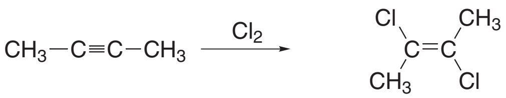


$$CH_3CH_2-C\equiv C-CH_2CH_3 \xrightarrow{2Br_2} CH_3CH_2-\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{Br}{C}}-CH_2CH_3$$



***trans* dihalide**

11.16

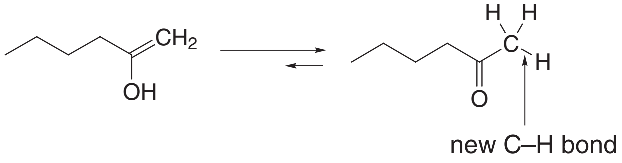


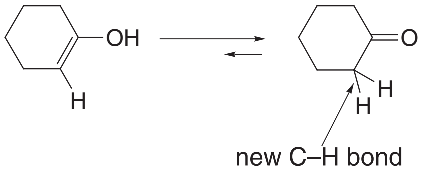
The two Cl atoms are electron withdrawing, making the π bond less electron rich and therefore less reactive with an electrophile.

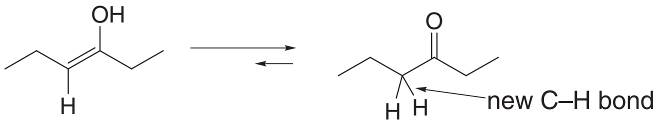
11.17 Per disegnare la forma chetonica di ciascun enolo:

[1] Convertire il gruppo C–OH in C=O su una estremità del doppio legame.

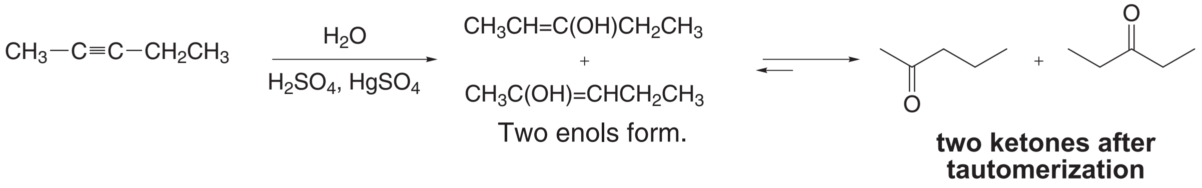
[2] Sull'altra estremità addizionare un protone.

a. 

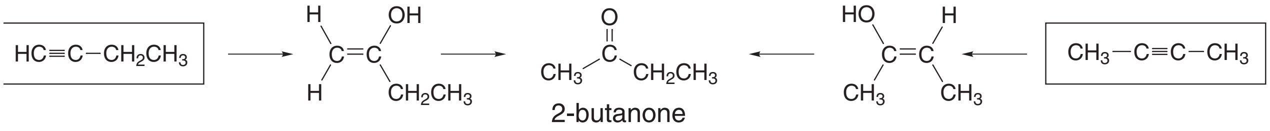
c. 

b. 

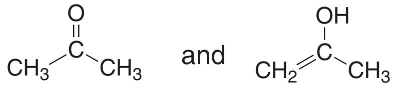
1.18 Il trattamento degli alchini con H_2O, H_2SO_4, e $HgSO_4$ forma chetoni.



1.19 Per determinare quali sono i due alchini che danno il chetone, operare a ritroso disegnando gli enoli e quindi gli alchini.



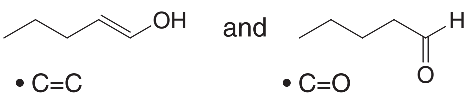
1.20 I tautomeri cheto-enolici sono isomeri costituzionali in equilibrio che differiscono per la posizione del doppio legame e di un idrogeno. L'OH nell'enolo deve essere legato al C=C.

a. 

- C=O
- one more CH bond

- C=C
- OH on C=C

keto-enol tautomers

c. 

- C=C
- OH on C=C

- C=O
- one more CH bond

keto-enol tautomers

b. 

OH is not bonded to the C=C.

NOT keto-enol tautomers

d. 

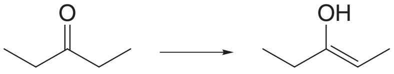
OH is not bonded to the C=C.

NOT keto-enol tautomers

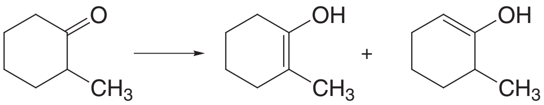
11.21 Per scrivere la forma enolica di ogni tautomero chetonico:

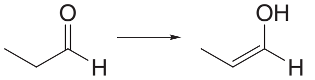
[1] Cambiare il C=O in C–OH.

[2] Cambiare un singolo legame C–C in un doppio legame, accertando che il gruppo OH sia legato al C=C.

a. 

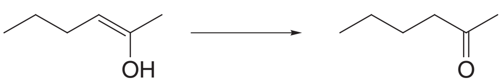
[*E/Z* isomers possible]

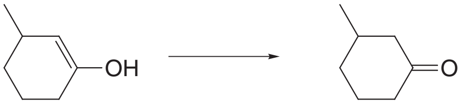
c. 

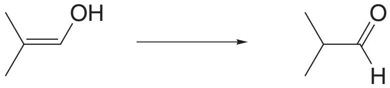
b. CH_3CH_2CHO = 

[*E/Z* isomers possible]

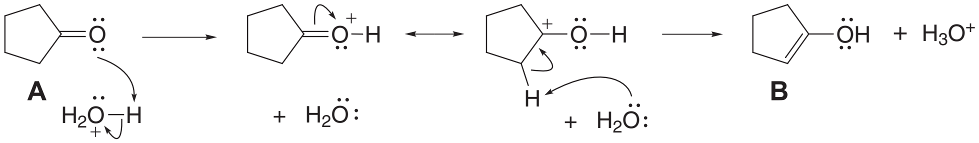
11.22 Usare le regole della risposta 11.17 per disegnare ogni forma chetonica.

a. 

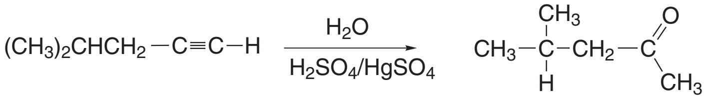
c. 

b. 

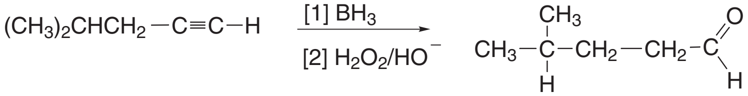
11.23



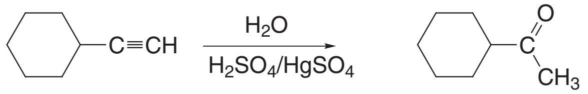
11.24 La reazione con H_2O, H_2SO_4, e $HgSO_4$ addiziona l'ossigeno al carbonio *più* sostituito.
La reazione con [1] BH_3, [2] $H_2O_2/^{-}OH$ addiziona l'ossigeno al carbonio *meno* sostituito.

a. 

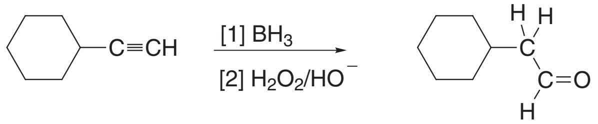
Forms a **ketone.** H_2O is added with the O atom on the *more* substituted carbon.

b. 

Forms an **aldehyde**. H_2O is added with the O atom on the *less* substituted carbon.

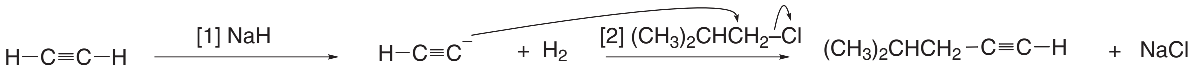
c. 

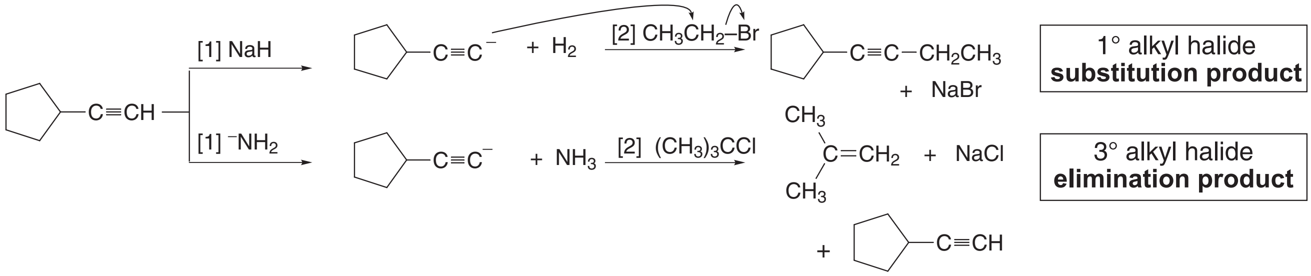
Forms a **ketone.** H_2O is added with the O atom on the *more* substituted carbon.

d. 

Forms an **aldehyde**. H_2O is added with the O atom on the *less* substituted carbon.

11.25

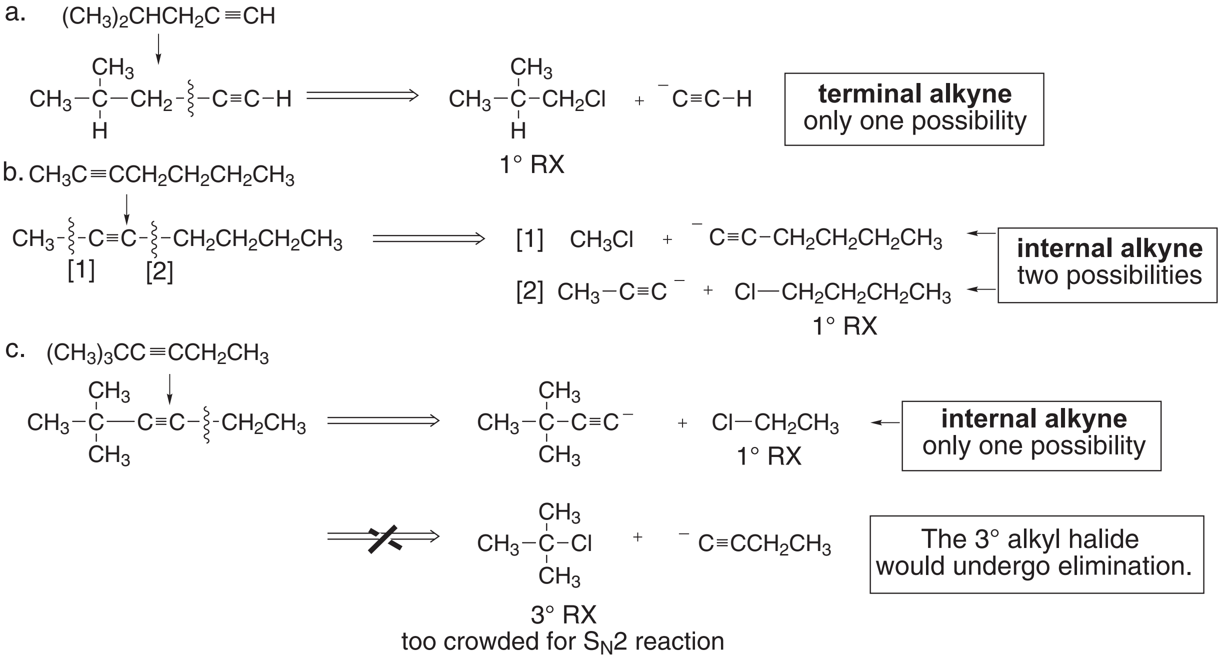
a. 

b. 

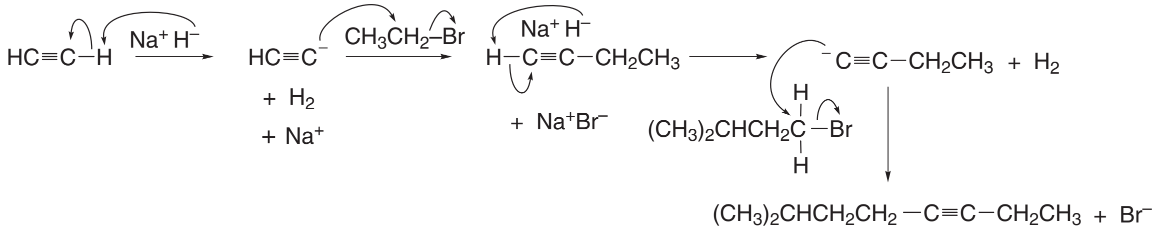
1° alkyl halide **substitution product**

3° alkyl halide **elimination product**

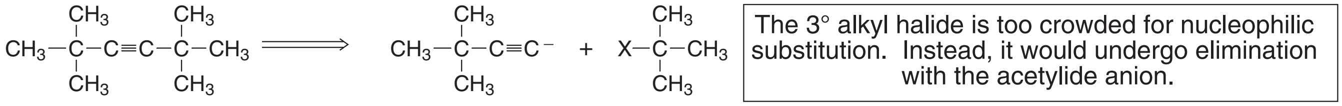
11.26



11.27



11.28



2,2,5,5-tetramethyl-3-hexyne

11.29 L'equilibrio favorisce sempre la formazione dell'acido più debole e della base più debole.

a. $HC\equiv C^- + CH_3OH \rightleftharpoons HC\equiv CH + CH_3O^-$

$pK_a = 15.5$ $pK_a = 25$

weaker acid

Equilibrium favors products.

c. $HC\equiv CH + Na^+Br^- \rightleftharpoons HC\equiv C^- Na^+ + HBr$

$pK_a = 25$ $pK_a = -9$

weaker acid

Equilibrium favors starting materials.

b. $CH_3C\equiv CH + CH_3^- \rightleftharpoons CH_3C\equiv C^- + CH_4$

$pK_a = 25$ $pK_a = 50$

weaker acid

Equilibrium favors products.

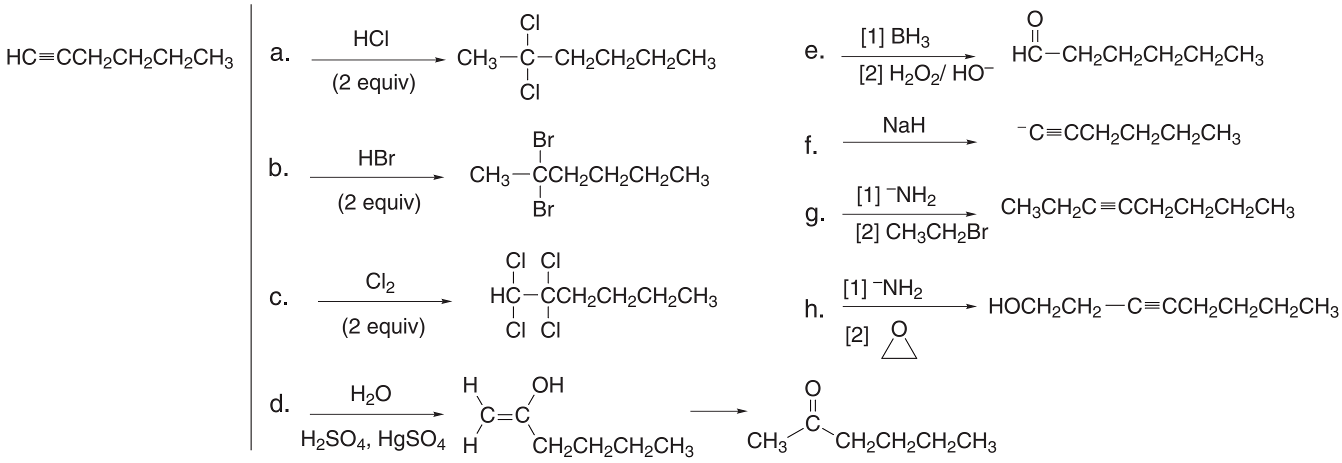
d. $CH_3CH_2C\equiv C^- + CH_3COOH \rightleftharpoons CH_3CH_2C\equiv CH + CH_3COO^-$

$pK_a = 4.8$ $pK_a = 25$

weaker acid

Equilibrium favors products.

11.30



$HC\equiv CCH_2CH_2CH_2CH_3$

a. $\xrightarrow[\text{(2 equiv)}]{HCl} CH_3-\underset{Cl}{\overset{Cl}{C}}-CH_2CH_2CH_2CH_3$

b. $\xrightarrow[\text{(2 equiv)}]{HBr} CH_3-\underset{Br}{\overset{Br}{C}}CH_2CH_2CH_2CH_3$

c. $\xrightarrow[\text{(2 equiv)}]{Cl_2} H\underset{Cl}{\overset{Cl}{C}}-\underset{Cl}{\overset{Cl}{C}}CH_2CH_2CH_2CH_3$

d. $\xrightarrow[H_2SO_4,\ HgSO_4]{H_2O}$ (H)(H)C=C(OH)(CH₂CH₂CH₂CH₃) $\longrightarrow CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_3$

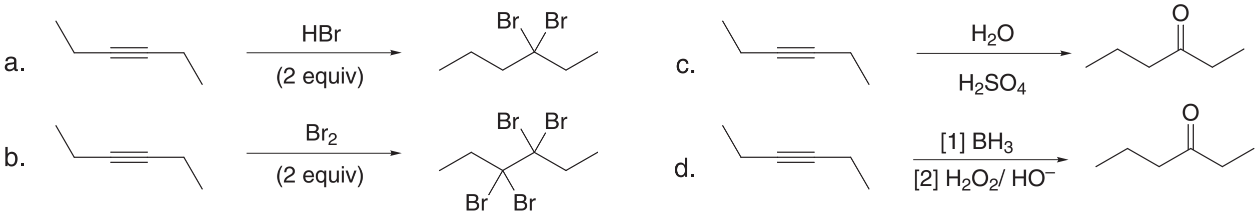
e. $\xrightarrow[\text{[2] } H_2O_2/\ HO^-]{\text{[1] } BH_3} H\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_2CH_2CH_3$

f. $\xrightarrow{NaH} {}^-C\equiv CCH_2CH_2CH_2CH_3$

g. $\xrightarrow[\text{[2] } CH_3CH_2Br]{\text{[1] } ^-NH_2} CH_3CH_2C\equiv CCH_2CH_2CH_2CH_3$

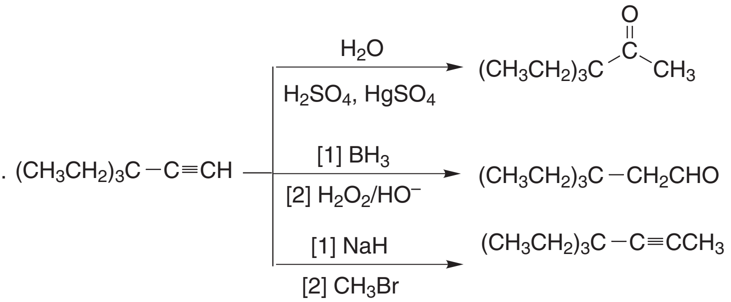
h. $\xrightarrow[\text{[2]}]{\text{[1] } ^-NH_2} HOCH_2CH_2-C\equiv CCH_2CH_2CH_2CH_3$

11.31



11.32

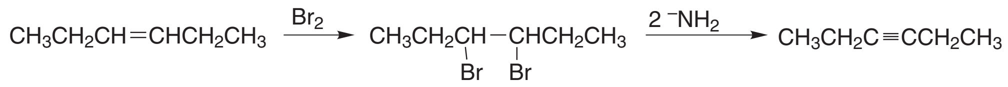
a.



b.

$$CH_3CH_2CH_2CH(CH_3)CH_2CHBr_2 \xrightarrow{2\ {}^-NH_2} CH_3CH_2CH_2CH(CH_3)C{\equiv}CH$$

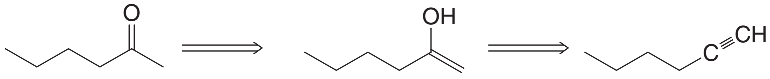
c.



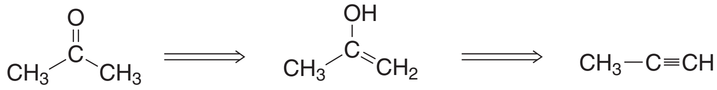
$$CH_3CH_2CH{=}CHCH_2CH_3 \xrightarrow{Br_2} CH_3CH_2\underset{Br}{C}H-\underset{Br}{C}HCH_2CH_3 \xrightarrow{2\ {}^-NH_2} CH_3CH_2C{\equiv}CCH_2CH_3$$

11.33

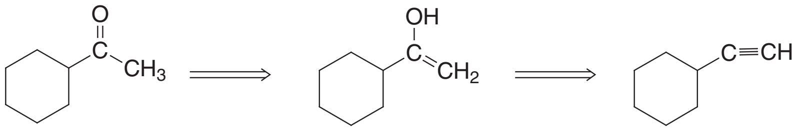
a.



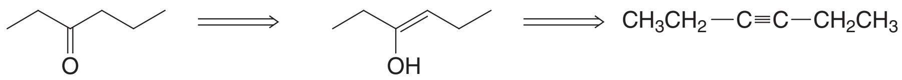
b.



c.

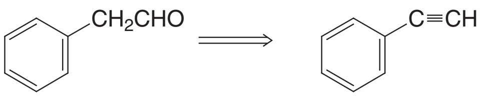


d.

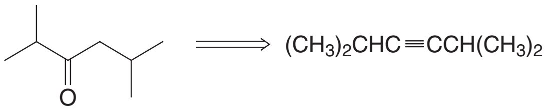


11.34

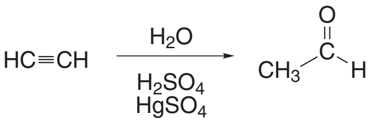
a.

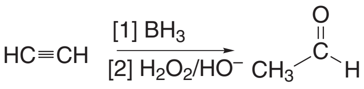


b.



11.35 L'alchino che fornisce la stessa aldeide per trattamento con H_2O, H_2SO_4, $HgSO_4$ e BH_3, seguito da H_2O_2/ HO^- non deve avere atomi di carbonio interni. E' quindi HC≡CH.

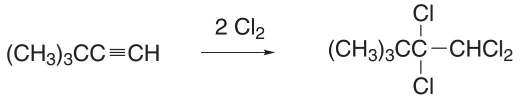




11.36

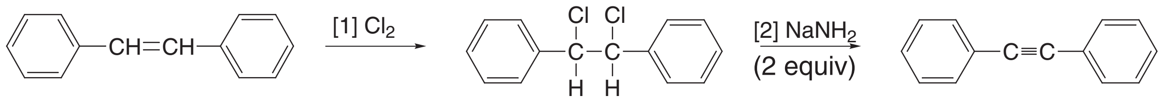
a.

b.

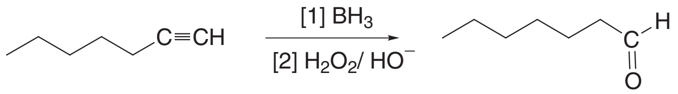


$$(CH_3)_3CC{\equiv}CH \xrightarrow{2\ Cl_2} (CH_3)_3C\overset{Cl}{\underset{Cl}{C}}{-}CHCl_2$$

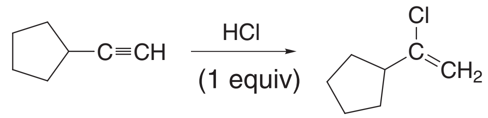
c.



d.

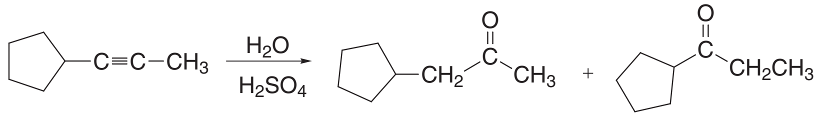


e.

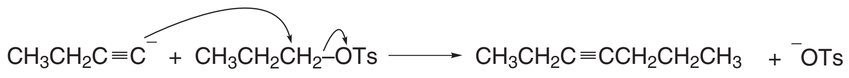


f. $HC{\equiv}C^{-} + D_2O \longrightarrow HC{\equiv}CD + DO^{-}$

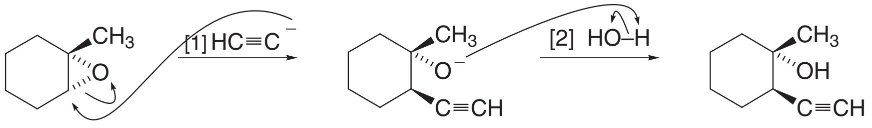
g.



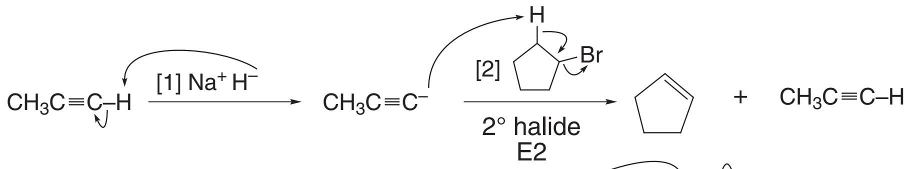
h.



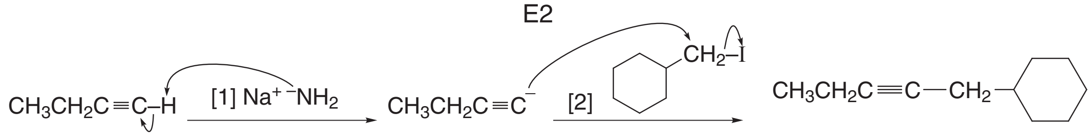
i.



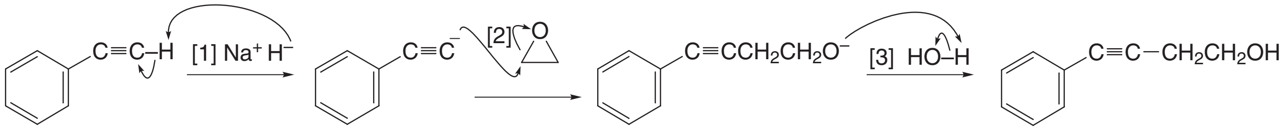
j.



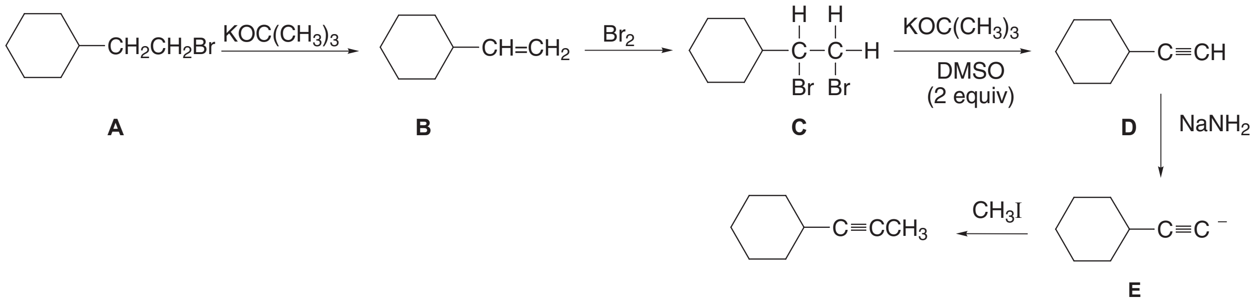
k.



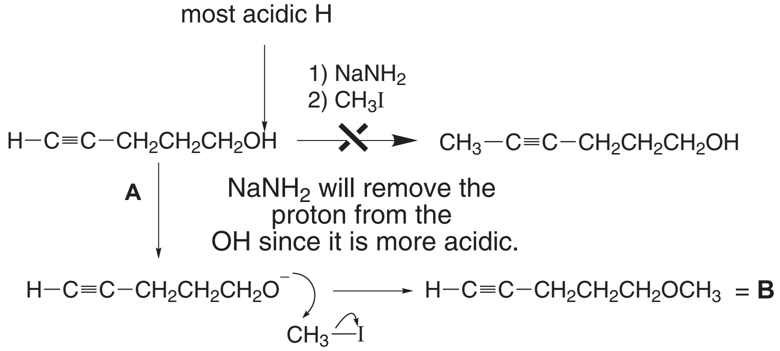
l.



11.37



11.38

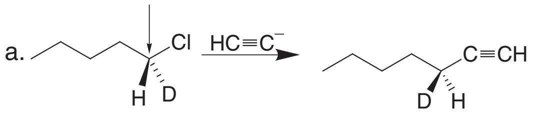


most acidic H

NaNH$_2$ will remove the proton from the OH since it is more acidic.

11.39

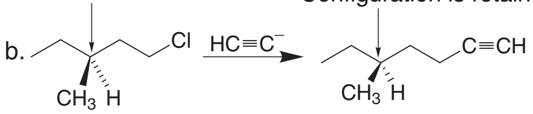
Stereogenic center at the site of reaction.

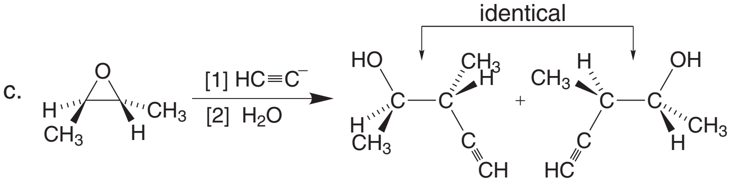


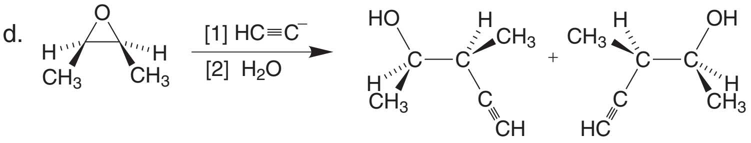
inversion

Stereogenic center NOT at the site of reaction.

Configuration is retained.



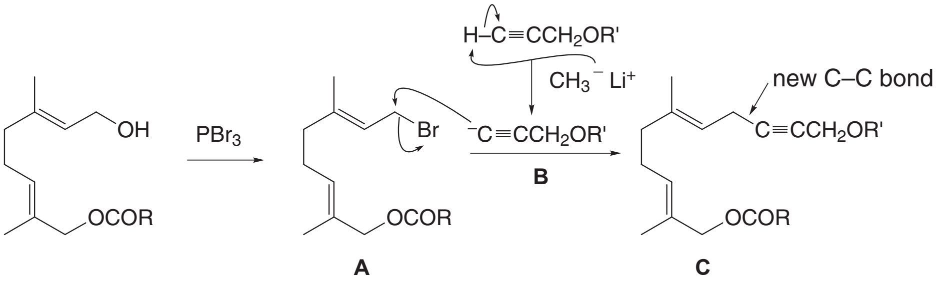




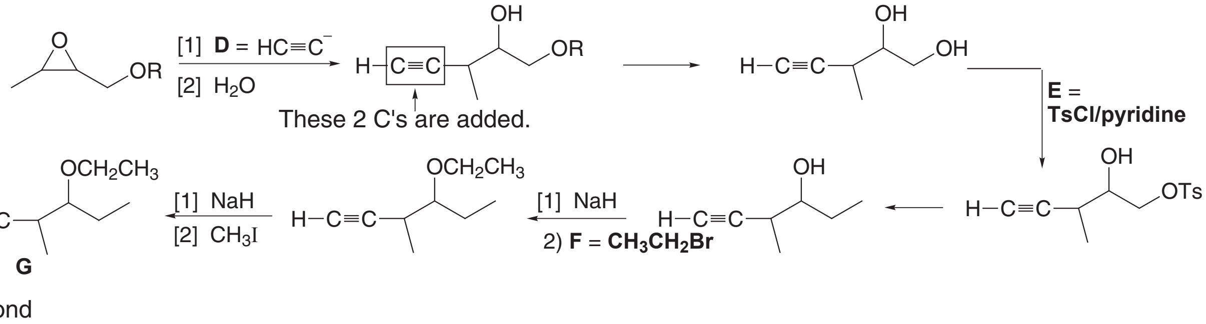
enantiomers

11.40

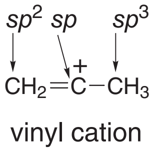
a.

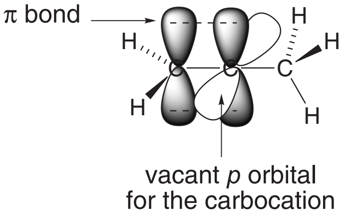


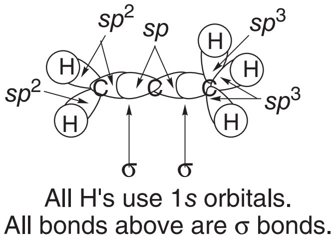
b.



11.41 Disegnare due diagrammi per mostrare i legami σ e π.

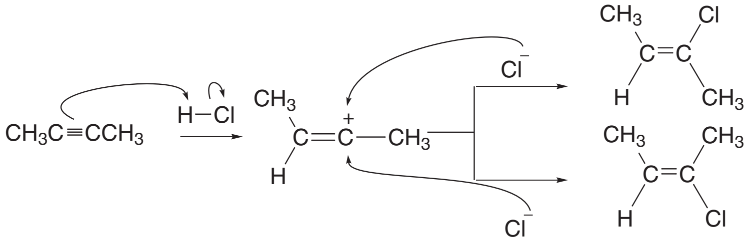






La carica positiva in un carbocatione vinilico è posizionata su un carbonio che è ibridato *sp*, mentre nel $(CH_3)_2CH^+$, la carica positiva si trova su un atomo di carbonio ibridato sp^2. Il maggior carattere *s* sul carbonio destabilizza la carica positiva sul catione vinilico. Inoltre, il carbocatione carico positivamente è legato ad un carbonio ibridato sp^2, che dona elettroni meno facilmente di un carbonio ibridato sp^3.

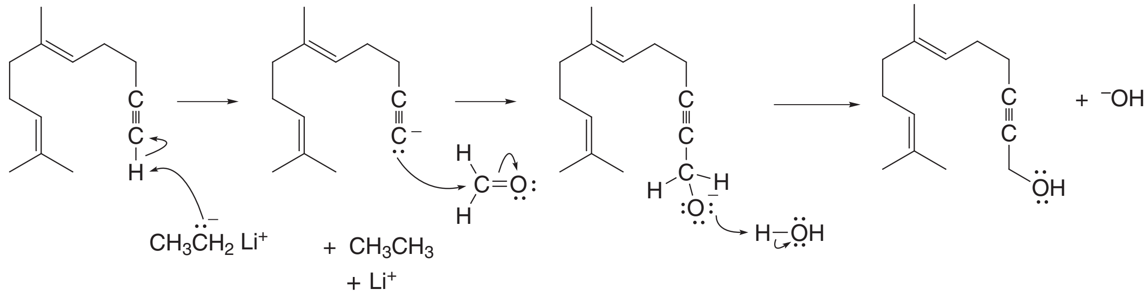
11.42



Cl$^-$ attack on the opposite side to the H yields the ***Z*** isomer.

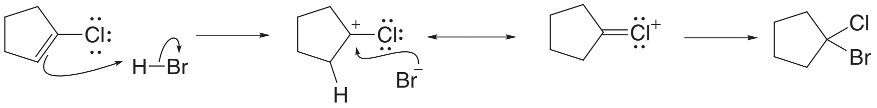
Cl$^-$ attack on the same side as the H yields the ***E*** isomer.

11.43

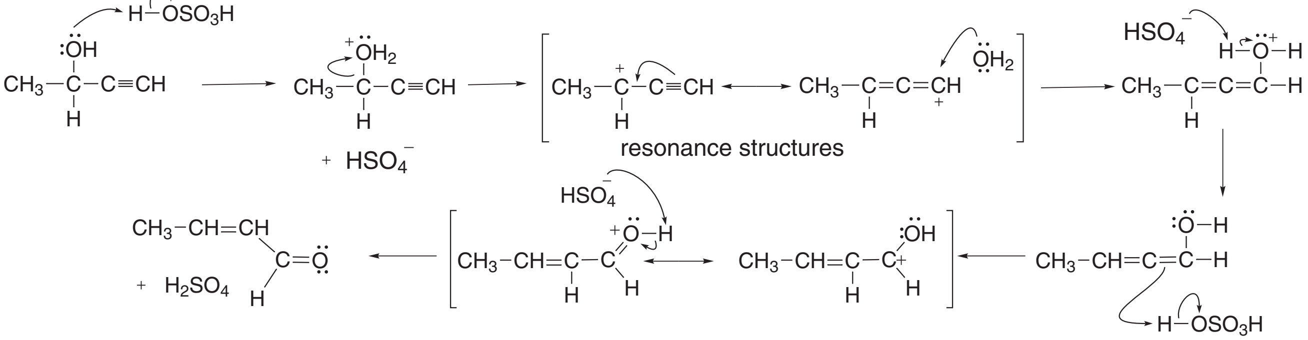


11.44

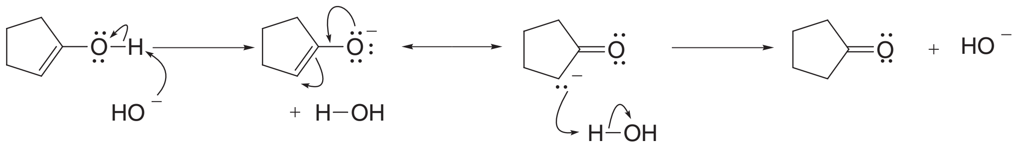
a.



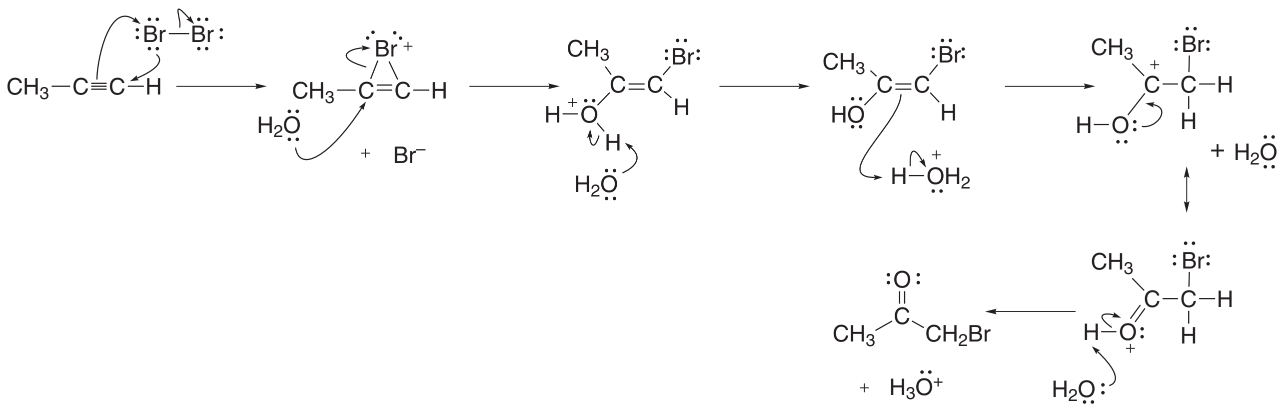
b.



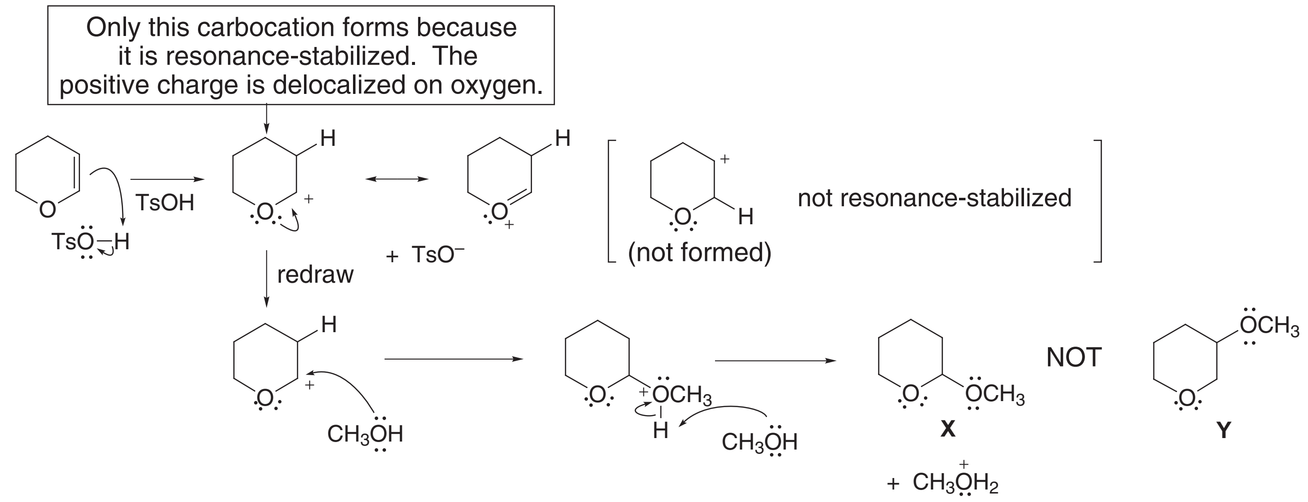
11.45



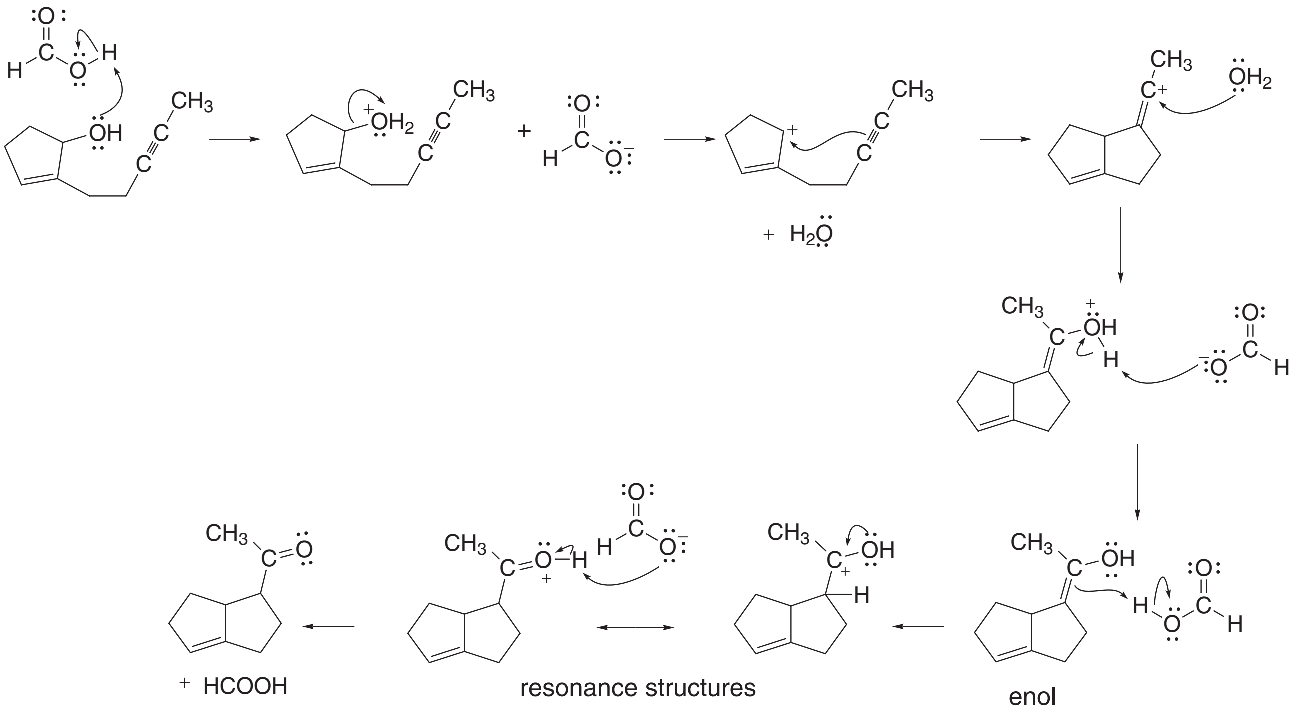
11.46



11.47


Only this carbocation forms because it is resonance-stabilized. The positive charge is delocalized on oxygen.

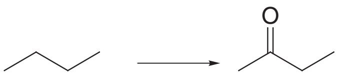
11.48



Capitolo 12

12.1 L'*ossidazione* consiste in un *aumento* del numero di legami C–Z (di solito legami C–O) *oppure* in una *diminuzione* del numero di legami C–H.

La *riduzione* consiste in una *diminuzione* del numero di legami C–Z (di solito legami C–O) *oppure* in un *aumento* del numero di legami C–H.

a.

oxidation

b.

reduction

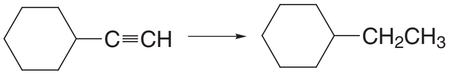
c.

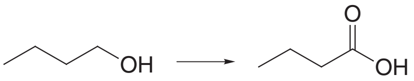
oxidation

d. $CH_2{=}CH_2 \longrightarrow CH_3CH_2Cl$ **neither**

1 new C–H bond
and 1 new C–Cl bond

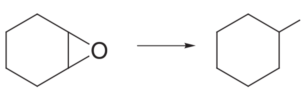
12.2 Usare le indicazioni della risposta 12.1.

a.

reduction

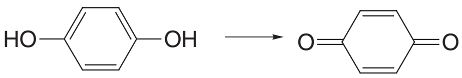
b.

oxidation

c. $CH_3CH_2Br \longrightarrow CH_2{=}CH_2$ **neither**

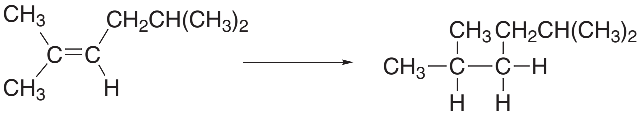
1 C–H and 1 C–Br
bond are removed.

d.

reduction

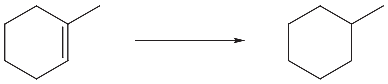
e. $CH_2{=}CH_2 \longrightarrow ClCH_2CH_2Cl$ **oxidation**
(2 new C–Cl bonds)

f.

oxidation

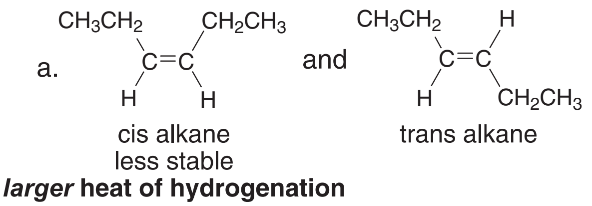
12.3 L'**idrogenazione** è l'addizione di idrogeno. Quando gli alcheni sono idrogenati, sono *ridotti* per addizione di H_2 al legame π. Per disegnare l'alcano, addizionare un H a ciascun C del doppio legame.

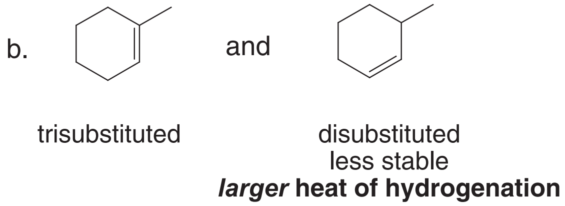
a.


b.

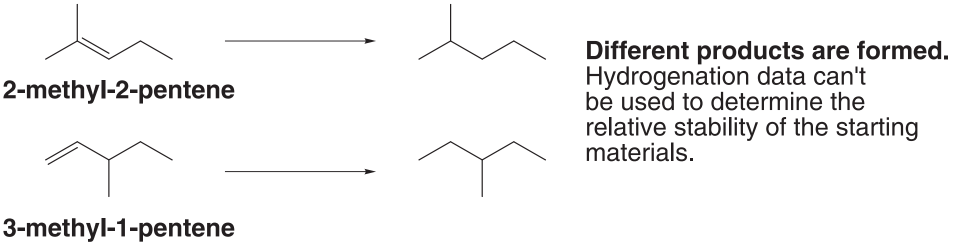

c.


12.4 Gli alcheni cis sono meno stabili degli alcheni trans, quindi hanno un calore di idrogenazione più elevato. All'aumentare della sostituzione con gruppi alchilici, aumenta la stabilità di un C=C, diminuendo il calore di idrogenazione.

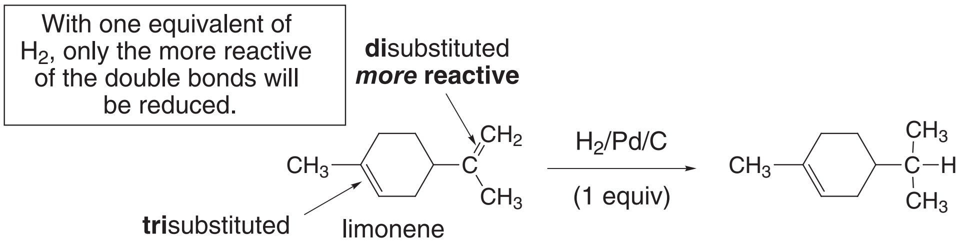




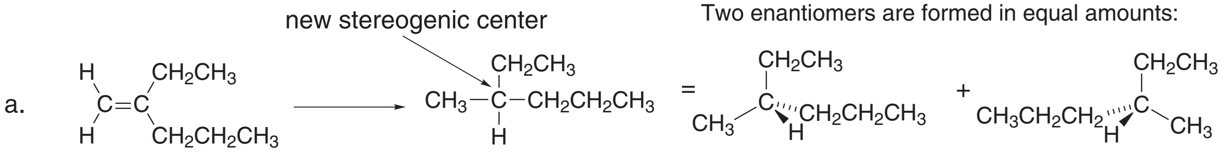
12.5 Per usare i calori di idrogenazione per determinare la stabilità relativa dei composti di partenza, devono essere identici i prodotti di idrogenazione.

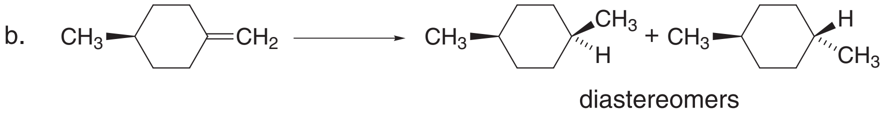


12.6 All'aumentare della sostituzione alchilica sul C=C, diminuisce la velocità di idrogenazione.



12.7

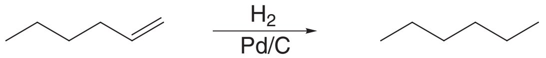




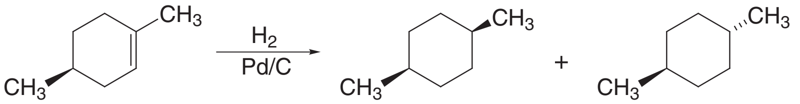
diastereomers

12.8 Usare le regole della risposta 12.3 e disegnare i prodotti di addizione sin di H_2 sopra e sotto al C=C.

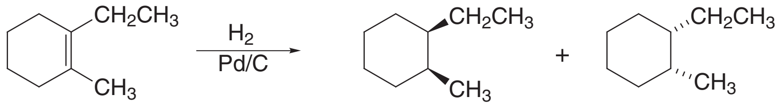
a.



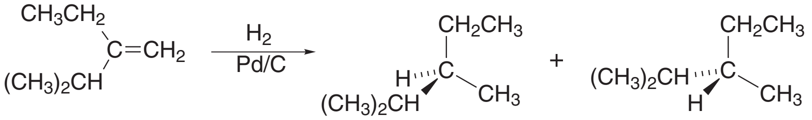
b.



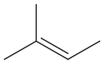
c.



d.



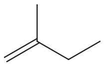
12.9 All'aumentare della sostituzione alchilica aumenta la stabilità dell'alchene, e diminuisce il calore di idrogenazione.



2-methyl-2-butene

trisubstituted

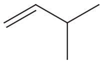
smallest ΔH^o = –26.9 kcal/mol



2-methyl-1-butene

disubstituted

intermediate ΔH^o = –28.5 kcal/mol



3-methyl-1-butene

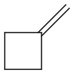
monosubstituted

largest ΔH^o = –30.3 kcal/mol

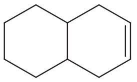
12.10

A possible structure:

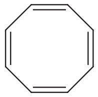
a. Compound **A**: molecular formula C_5H_8: hydrogenated to C_5H_{10}.
2 degrees of unsaturation, 1 is hydrogenated.
1 ring and 1 π bond →



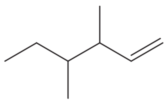
b. Compound **B**: molecular formula $C_{10}H_{16}$: hydrogenated to $C_{10}H_{18}$.
3 degrees of unsaturation, 1 is hydrogenated.
2 rings and 1 π bond →



c. Compound **C**: molecular formula C_8H_8: hydrogenated to C_8H_{16}.
5 degrees of unsaturation, 4 are hydrogenated.
1 ring and 4 π bonds →



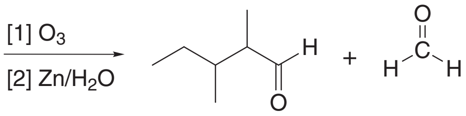
12.11

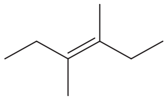


A

a. **mono**substituted
largest heat of hydrogenation
b. **fastest** reaction rate

c.

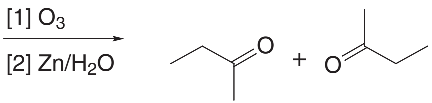




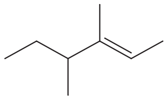
B

a. **tetra**substituted
smallest heat of hydrogenation
b. **slowest** reaction rate

c.



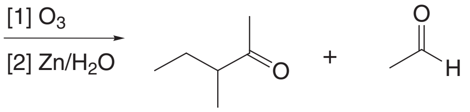
identical



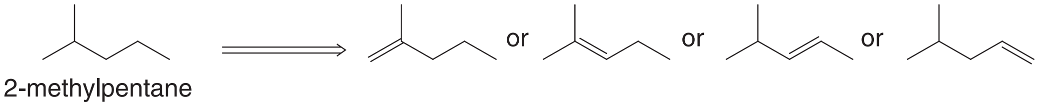
C

a. **tri**substituted
intermediate heat of hydrogenation
b. **intermediate** reaction rate

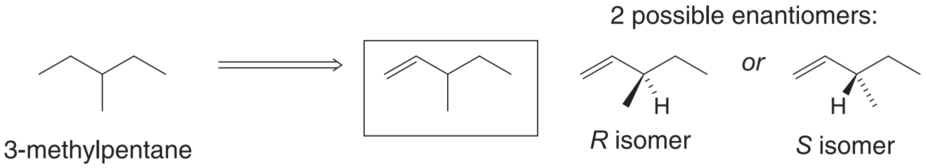
c.



12.12 Operare a ritroso per trovare l'alchene che viene idrogenato a 2-metilpentano.



12.13 Operare a ritroso per trovare l'alchene che viene idrogenato a 3-metilpentano.



12.14 L'idrogenazione in assenza di catalizzatore ha una elevata E_a, rendendola una reazione cineticamente lenta, così l'idrogenazione avviene solo in presenza di un catalizzatore. Il meccanismo con catalisi è multistadio, ma nessun stadio ha uno stato di transizione con energia così elevata come la reazione non catalizzata. E' termodinamicamente favorito perchè l'energia viene liberata durante l'idrogenazione: i composti di partenza si trovano ad una energia maggiore dei prodotti, fornendo all'idrogenazione un $\Delta H°$ negativo.

12.15

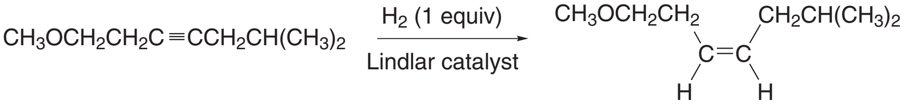
$$\begin{array}{c} HC\equiv CCH_2CH_2CH_3 \\ \textit{or} \\ CH_3C\equiv CCH_2CH_3 \end{array} \xrightarrow[Pd]{H_2} CH_3CH_2CH_2CH_2CH_3$$

12.16 Per disegnare i prodotti dell'idrogenazione catalitica ricordare:

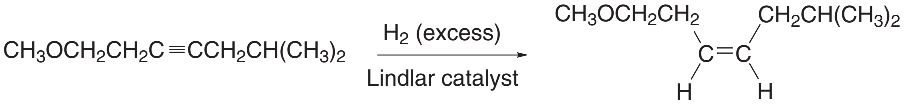
- H_2 (eccesso)/Pd riduce **alcheni ed alchini ad alcani**.
- H_2 (eccesso)/catalizzatore di Lindlar riduce ***solo*** **gli alchini a cis alcheni**.

a. $CH_3OCH_2CH_2C{\equiv}CCH_2CH(CH_3)_2 \xrightarrow[\text{Pd/C}]{H_2\text{ (excess)}} CH_3OCH_2CH_2CH_2CH_2CH_2CH(CH_3)_2$

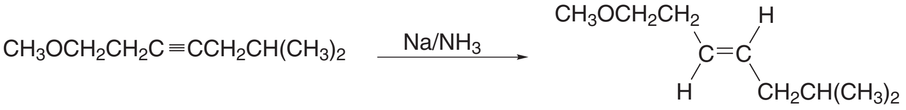
b.



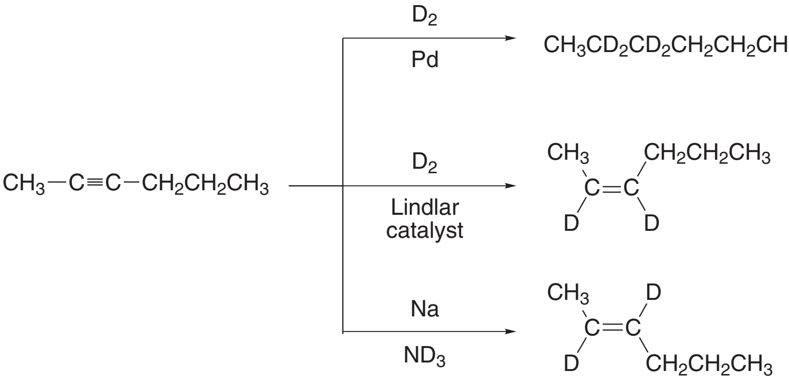
c.



d.



12.17

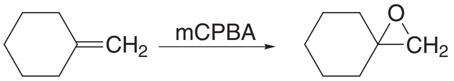


12.18 Per disegnare il prodotto, addizionare un atomo di O sul legame π de gruppo C=C.

a.

$(CH_3)_2C{=}CH_2 \xrightarrow{\text{mCPBA}} (CH_3)_2\overset{O}{C{-}CH_2}$

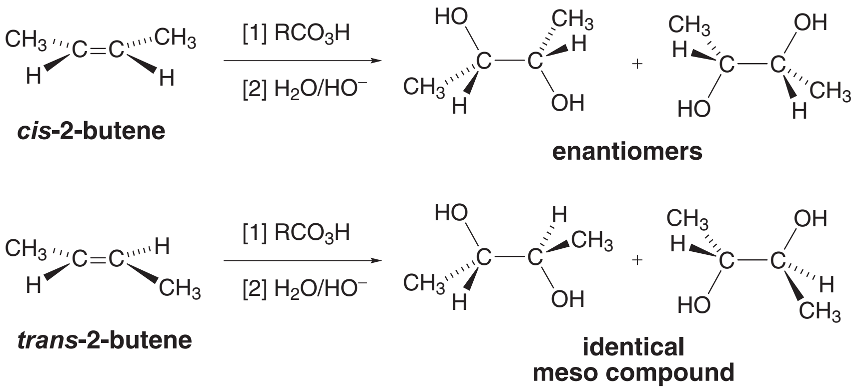
c.



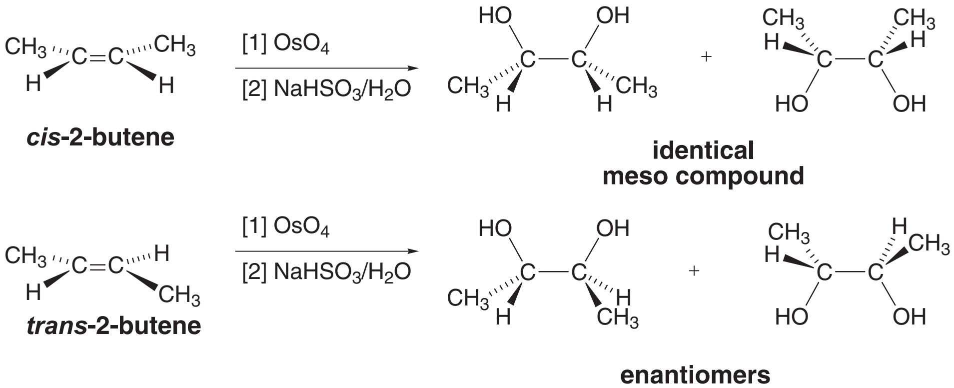
b.

$(CH_3)_2C{=}C(CH_3)_2 \xrightarrow{\text{mCPBA}} (CH_3)_2\overset{O}{C{-}C}(CH_3)_2$

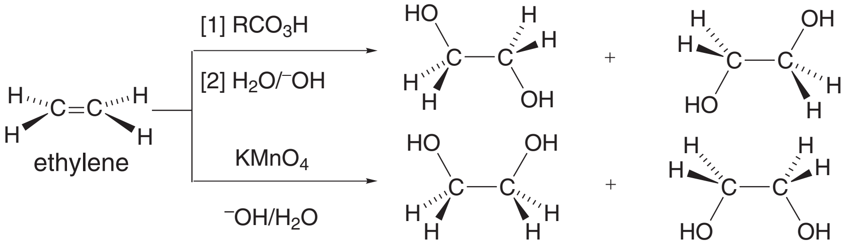
12.19 Il trattamento di un alchene con un perossiacido, seguito da H_2O/HO^- addiziona due gruppi ossidrilci con modalità **anti**. Il *cis*-2-butene e il *trans*-2-butene forniscono prodotti diversi di diidrossilazione. Il *cis*-2-butene dà una miscela di due enantiomeri e il *trans*-2-butene fornisce un composto meso. La reazione è stereospecifica, perchè due reagenti stereoisomerici forniscono prodotti diversi, che sono anche stereoisomeri fra loro.



12.20 Il trattamento di un alchene con OsO_4 addiziona due gruppi ossidrilici in maniera **sin**. Il *cis*-2-butene e il *trans*-2-butene forniscono diversi stereoisomeri in questa diidrossilazione, quindi la reazione è stereospecifica.



12.21

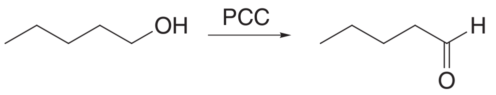


There are no stereogenic centers, so all the products are identical ($HOCH_2CH_2OH$).

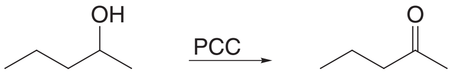
12.22 Per l'**ossidazione degli alcoli,** ricordare:

- **gli alcoli 1°** sono ossidati ad aldeidi con PCC.
- **gli alcoli 1°** sono ossidati ad acidi carbossilici con agenti ossidanti come CrO_3 o $Na_2Cr_2O_7$.
- **gli alcoli 2°** sono ossidati a chetoni con tutti gli ossidanti al Cr^{6+}.

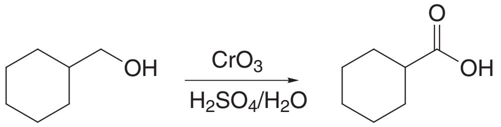
a.



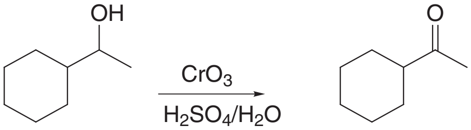
b.



c.

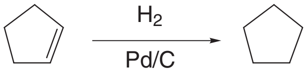


d.

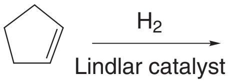


12.23

a.

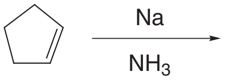


b.



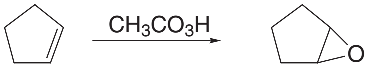
no reaction

c.

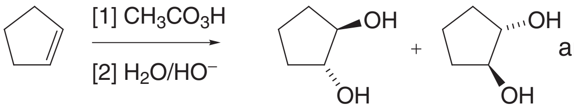


no reaction

d.

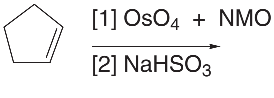


e.



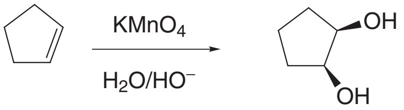
anti addition

f.



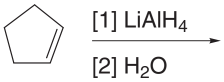
syn addition

g.



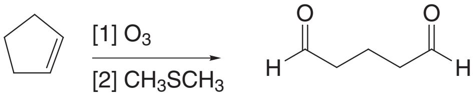
syn addition

h.

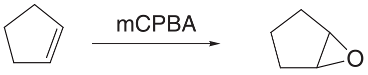


no reaction

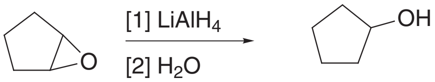
i.



j.

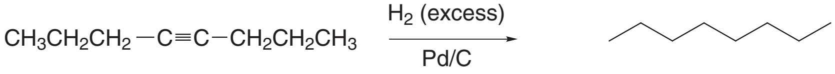


k.

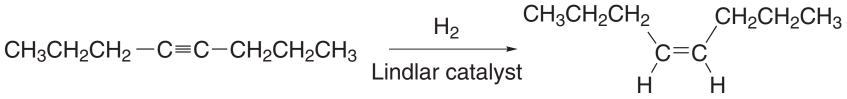


12.24

a.

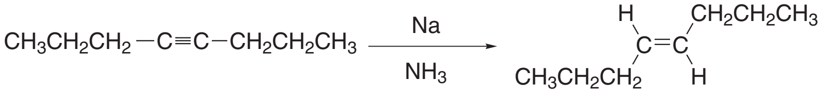


b.



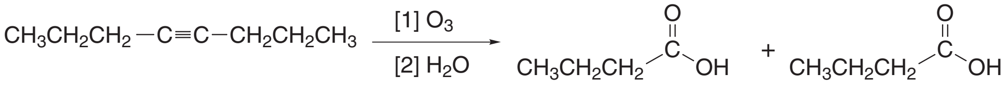
cis alkene

c.



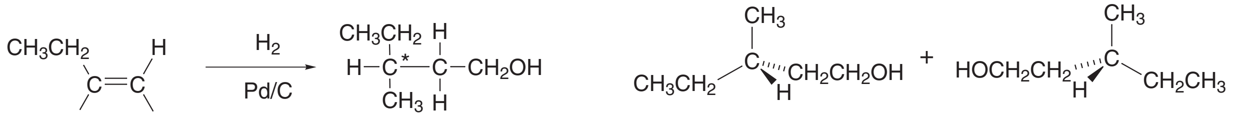
trans alkene

d.



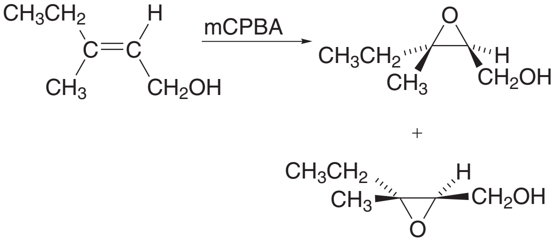
identical

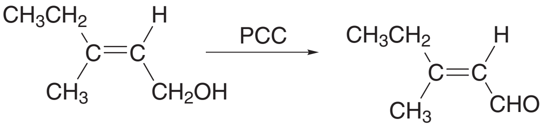
12.25

a.


[* = new stereogenic center.]

Two enantiomers are formed.

b.


c.


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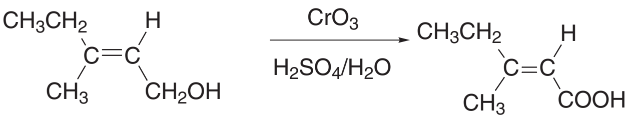
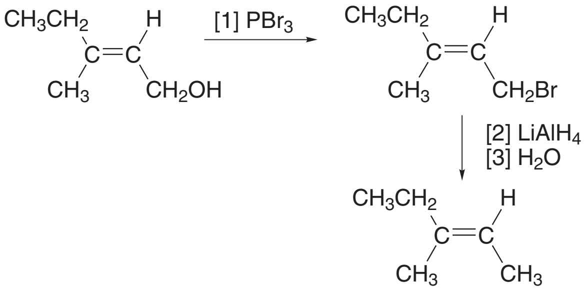
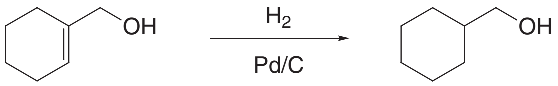
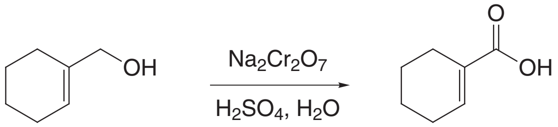
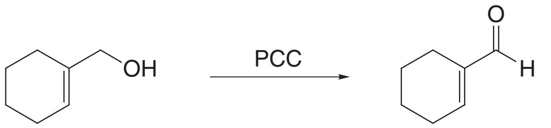


e.


12.26

a.


b.


c.


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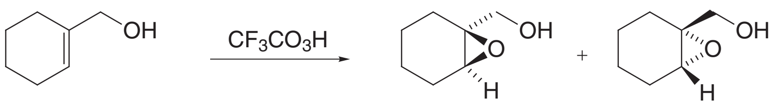

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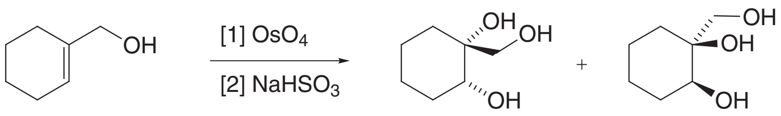
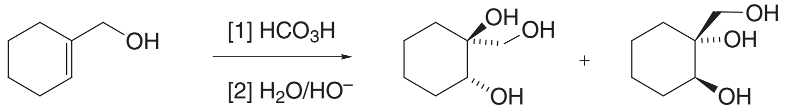
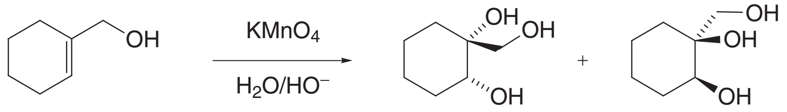


f.

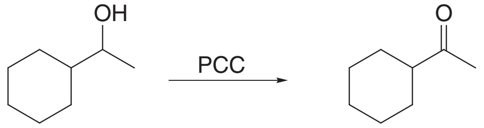


g.



12.27

a.



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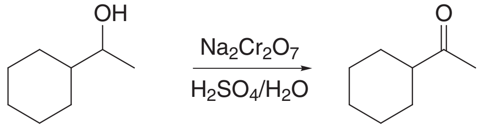

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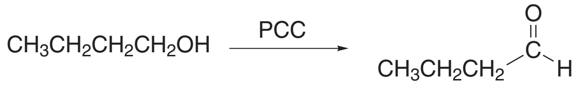

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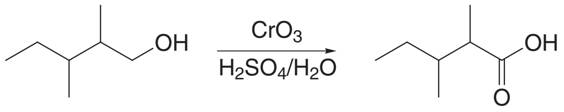
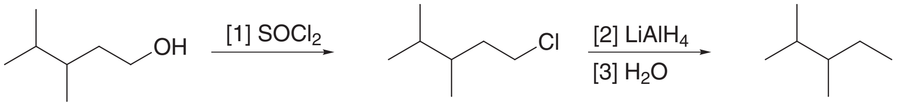


12.28

a.



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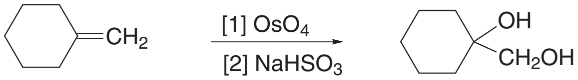

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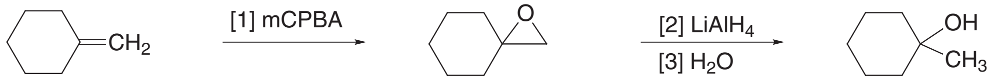
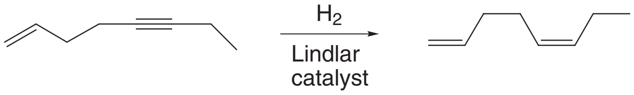
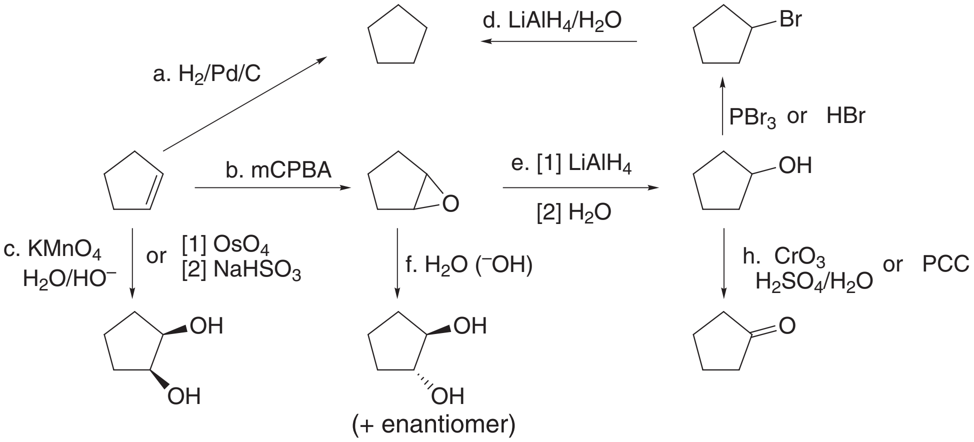


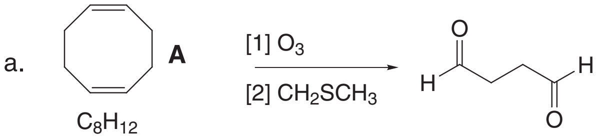
d.

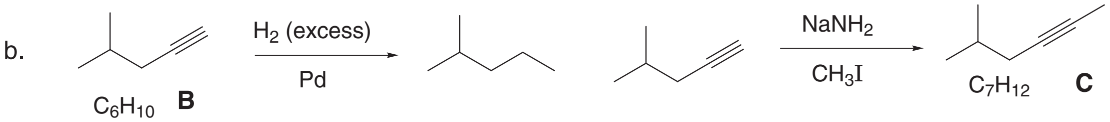


12.29



12.30

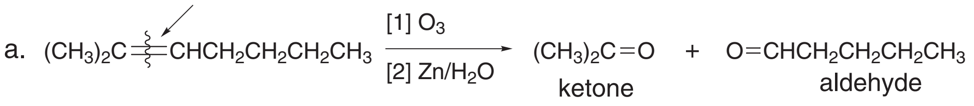




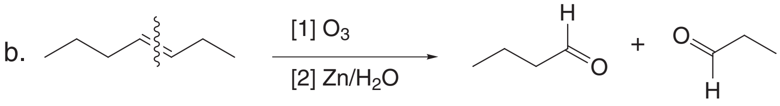
12.31 Per disegnare i prodotti della scissione ossidativa:

- **Individuare tutti i legami π** nella molecola.
- **Sostituire ciascun C=C con *due* C=O**.

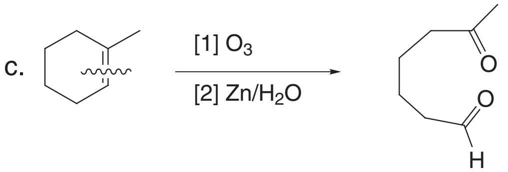
Replace this π bond with two C=O's.



One **ketone** and one **aldehyde** are formed.



Two **aldehydes** are formed.



A **dicarbonyl** compound is formed.

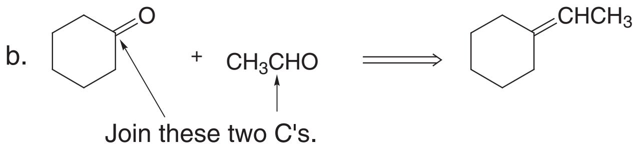
12.32 Per trovare l'alchene che fornisce i prodotti di scissione ossidativa:

- **Individuare i due gruppi carbonilici** nei prodotti.
- **Unire i due carboni carbonilici** con un doppio legame. Questo è il doppio legame che si rompe durante l'ozonolisi.

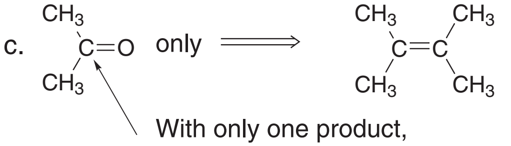
a. $(CH_3)_2C{=}O + (CH_3CH_2)_2C{=}O \Longrightarrow (CH_3)_2C{=}C(CH_2CH_3)_2$

Join these two C's.

b.



c.

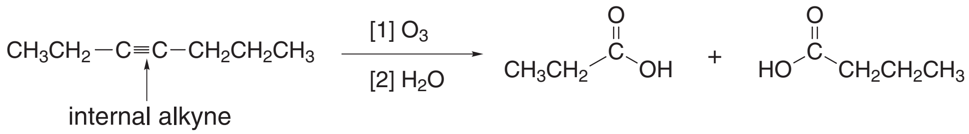


With only one product,
the alkene must be symmetrical
around the double bond. Join
this C to the same C in another
identical molecule.

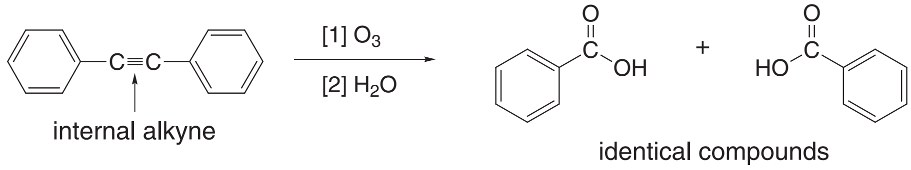
12.33 Per scrivere i prodotti della scissione ossidativa degli alchini:

- **Individuare il triplo legame**.
- Per gli alchini interni, **convertire il C ibridato *sp* in COOH.**
- Per gli alchini terminali, il **C ibridato *sp* diventa CO_2**.

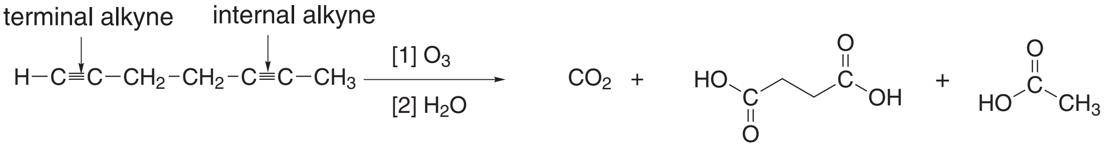
a.



b.



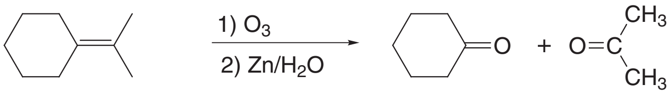
c.



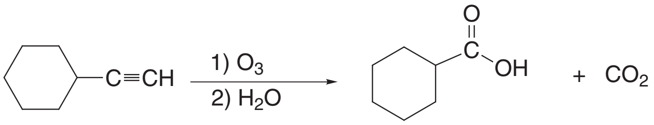
12.34 Usare le indicazioni della risposta 12.31.

a. $(CH_3CH_2)_2C{=}CHCH_2CH_3 \xrightarrow[\text{2) } CH_3SCH_3]{\text{1) } O_3} (CH_3CH_2)_2C{=}O + O{=}CHCH_2CH_3$

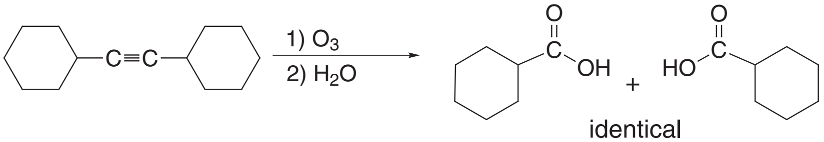
b.



c.



d.

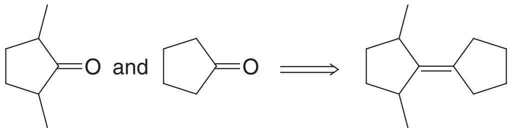


identical

12.35

a. $(CH_3)_2C{=}O$ and $CH_2{=}O$ $\Longrightarrow$ $(CH_3)_2C{=}CH_2$

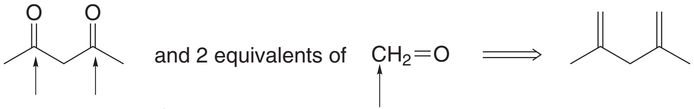
b.



c. $CH_3CH_2CH_2CHO$ only $\Longrightarrow$ $CH_3CH_2CH_2CH{=}CHCH_2CH_2CH_3$

Join this C to the same C
in another identical molecule.

d.

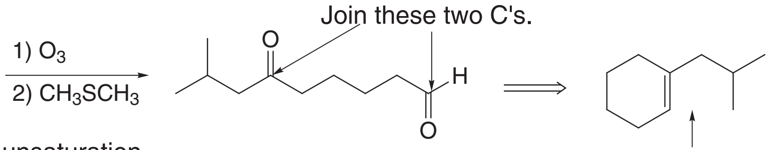


Join both of these C's
to a C from formaldehyde.

formaldehyde C

12.36 Usare le indicazioni della risposta 12.32.

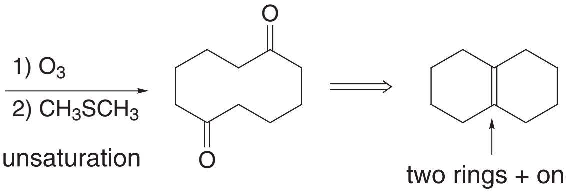
a. $C_{10}H_{18}$



2 degrees of unsaturation

one ring + one π bond

b. $C_{10}H_{16}$



3 degrees of unsaturation

two rings + one π bond

12.37

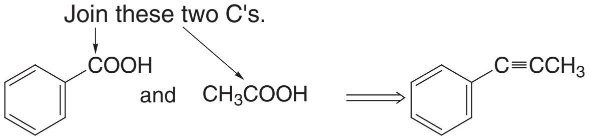
Join these two C's.

a. $CH_3CH_2CH_2CH_2COOH$ and CO_2 $\Longrightarrow$ $CH_3CH_2CH_2CH_2C{\equiv}CH$

Join these two C's.

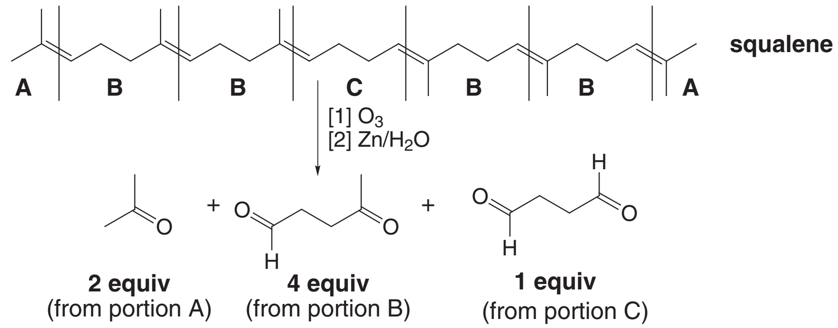
b. CH_3CH_2COOH and $CH_3CH_2CH_2COOH$ $\Longrightarrow$ $CH_3CH_2C{\equiv}CCH_2CH_2CH_3$

c.

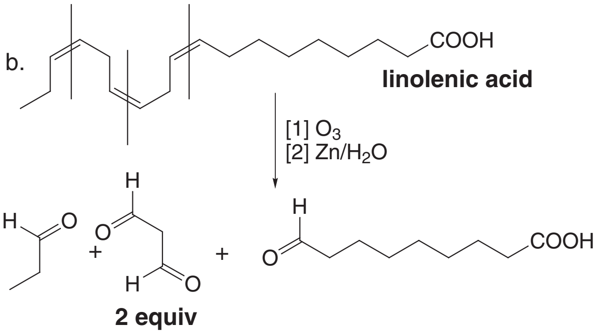


12.38

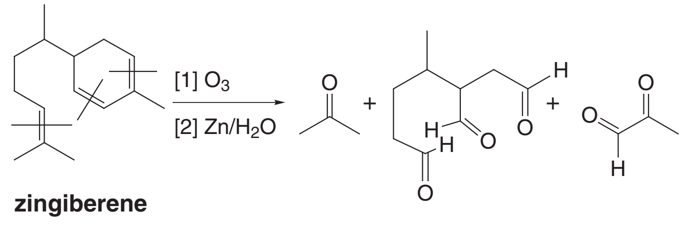
a.



b.

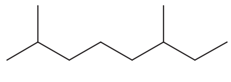


c.



12.39

$C_{10}H_{16} \xrightarrow[Pd/C]{H_2}$

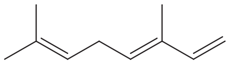


2,6-dimethyloctane

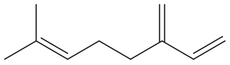
3 degrees of unsaturation

The hydrogenation reaction tells you that both oximene and myrcene have 3 π bonds (and no rings). Use this carbon backbone and add in the double bonds based on the oxidative cleavage products.

Oximene: $(CH_3)_2C{=}O$ $CH_2{=}O$ $CH_2(CHO)_2$ $CH_3-\overset{\overset{O}{\|}}{C}-CHO$ $\Longrightarrow$



Myrcene: $(CH_3)_2C{=}O$ $CH_2{=}O$ (2 equiv) $H-\overset{\overset{O}{\|}}{C}-CH_2CH_2-\overset{\overset{O}{\|}}{C}-CHO$ $\Longrightarrow$

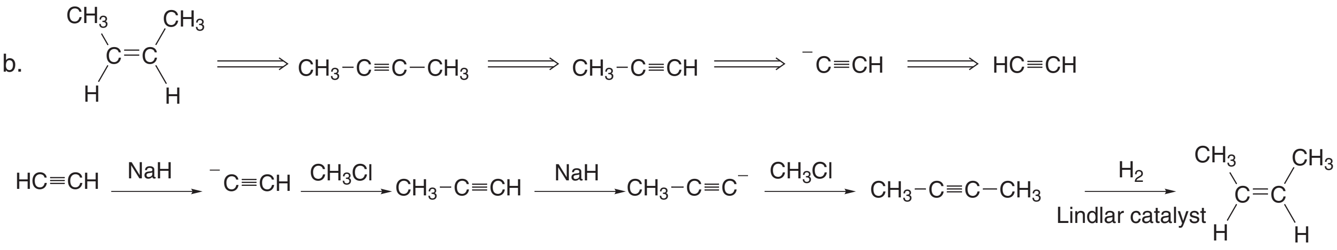


12.40 Usare l'analisi retrosintetica per progettare una sintesi per ciascun idrocarburo a partire dall'acetilene.

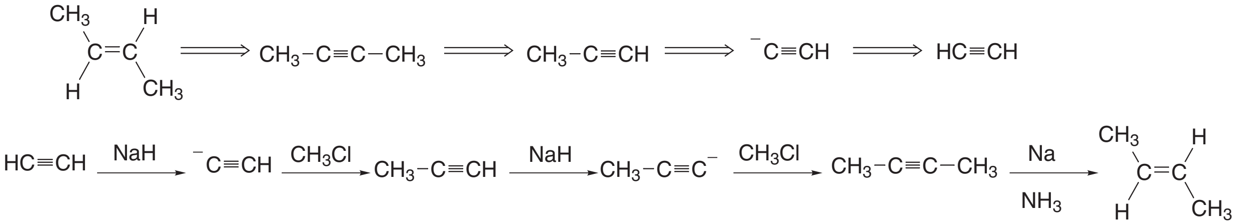
a. $CH_3CH_2CH{=}CH_2 \Longrightarrow CH_3CH_2CH{\equiv}CH \Longrightarrow {}^{-}C{\equiv}CH \Longrightarrow HC{\equiv}CH$

$$HC{\equiv}CH \xrightarrow{NaH} {}^{-}C{\equiv}CH \xrightarrow{CH_3CH_2Cl} CH_3CH_2C{\equiv}CH \xrightarrow[\text{Lindlar catalyst}]{H_2} CH_3CH_2CH{=}CH_2$$

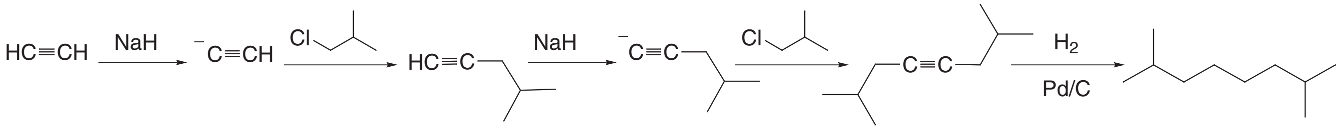
b.



c.

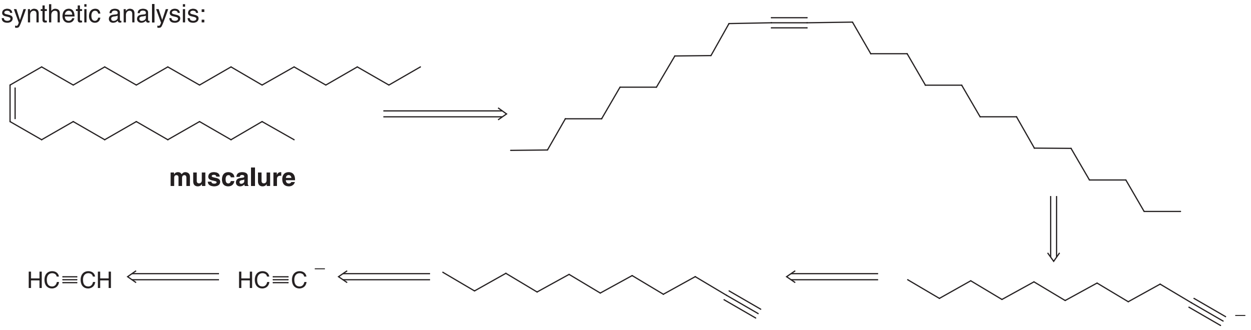


d. $(CH_3)_2CHCH_2CH_2CH_2CH_2CH(CH_3)_2 \Longrightarrow HC{\equiv}CCH_2CH(CH_3)_2 \Longrightarrow {}^{-}C{\equiv}CH \Longrightarrow HC{\equiv}CH$

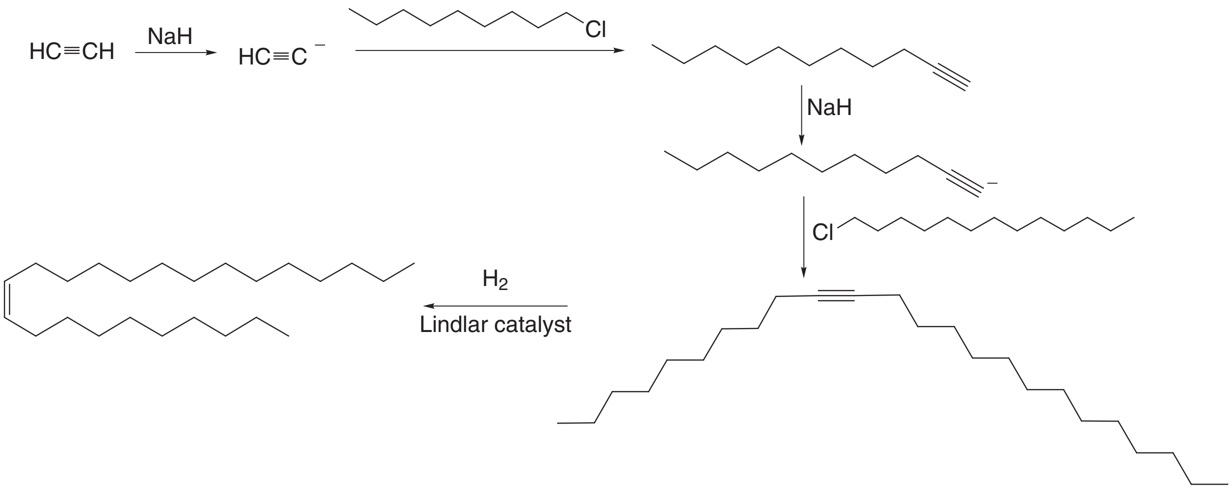


12.41

Retrosynthetic analysis:

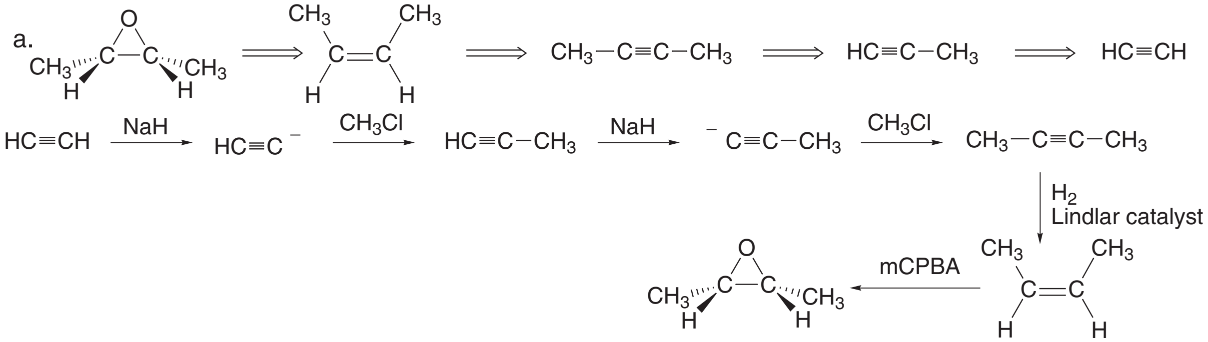


Synthetic direction:

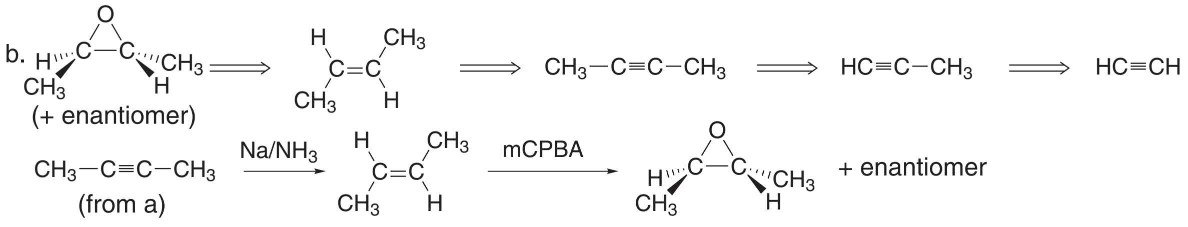


12.42

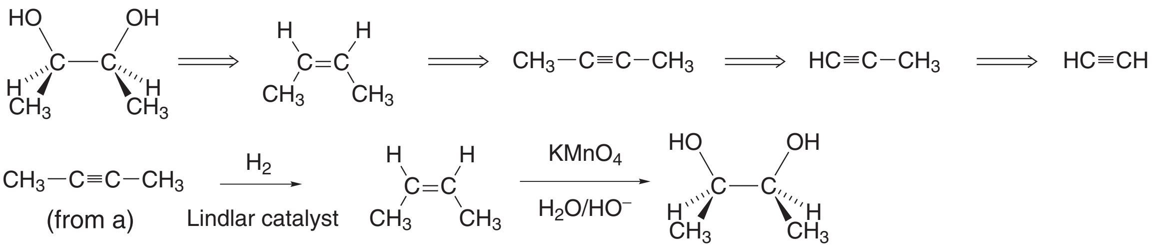
a.



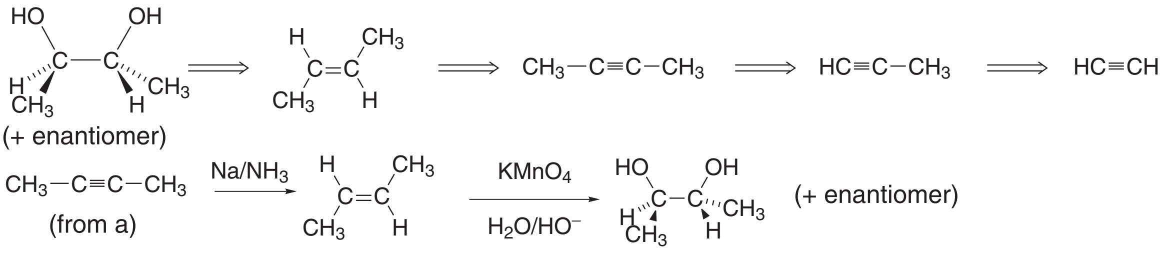
b.



c.

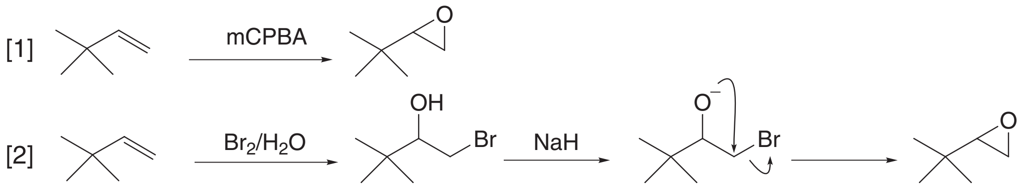


d.



12.43

Two methods:



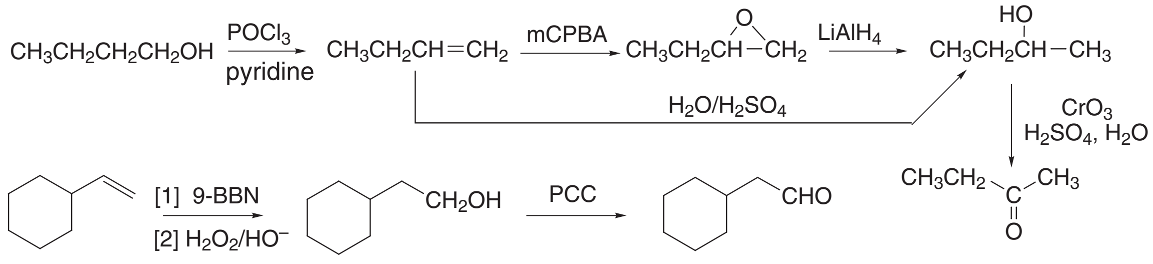
12.44

a.

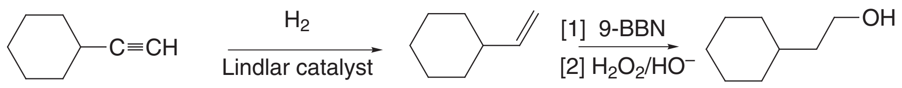
$$\mathrm{CH_3CH_2CH{=}CH_2} \xrightarrow[\text{[2] } \mathrm{H_2O_2/HO^-}]{\text{[1] 9-BBN}} \mathrm{CH_3CH_2CH_2CH_2OH} \xrightarrow[\mathrm{H_2SO_4,\ H_2O}]{\mathrm{CrO_3}} \mathrm{CH_3CH_2CH_2COOH}$$

b.

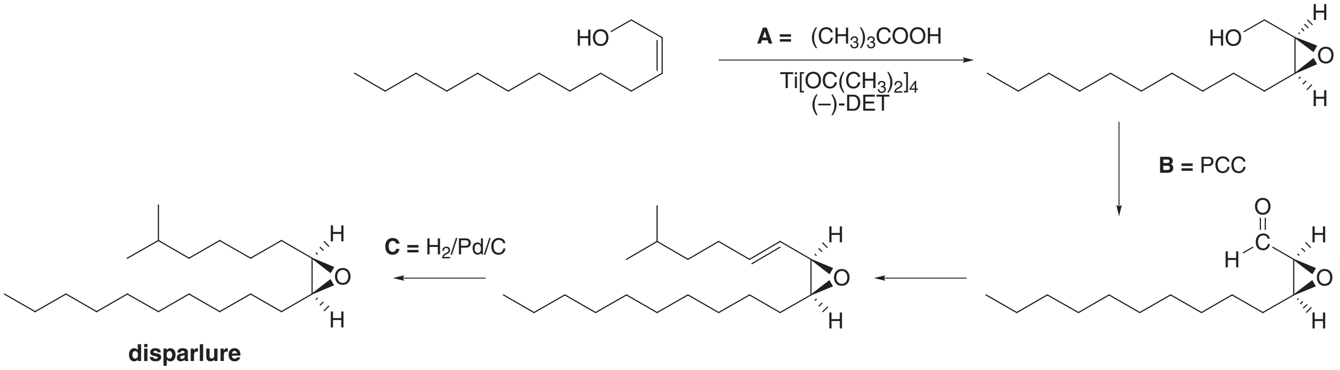
c.



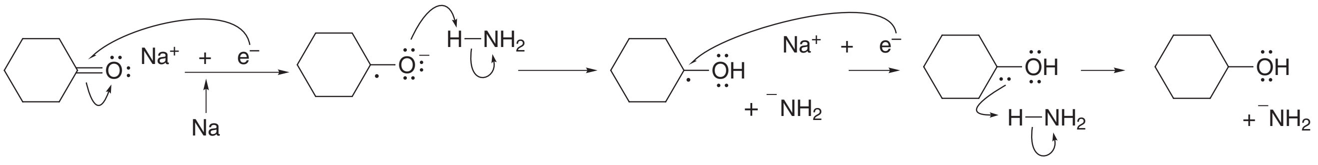
d.



12.45

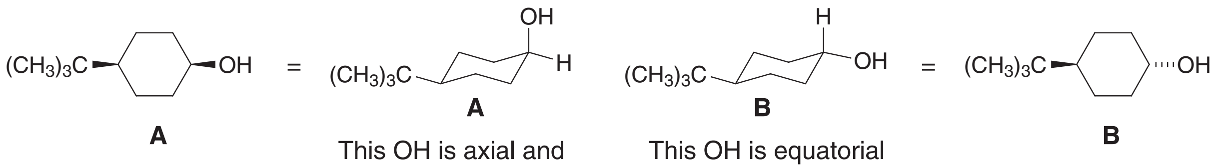


12.46



12.47

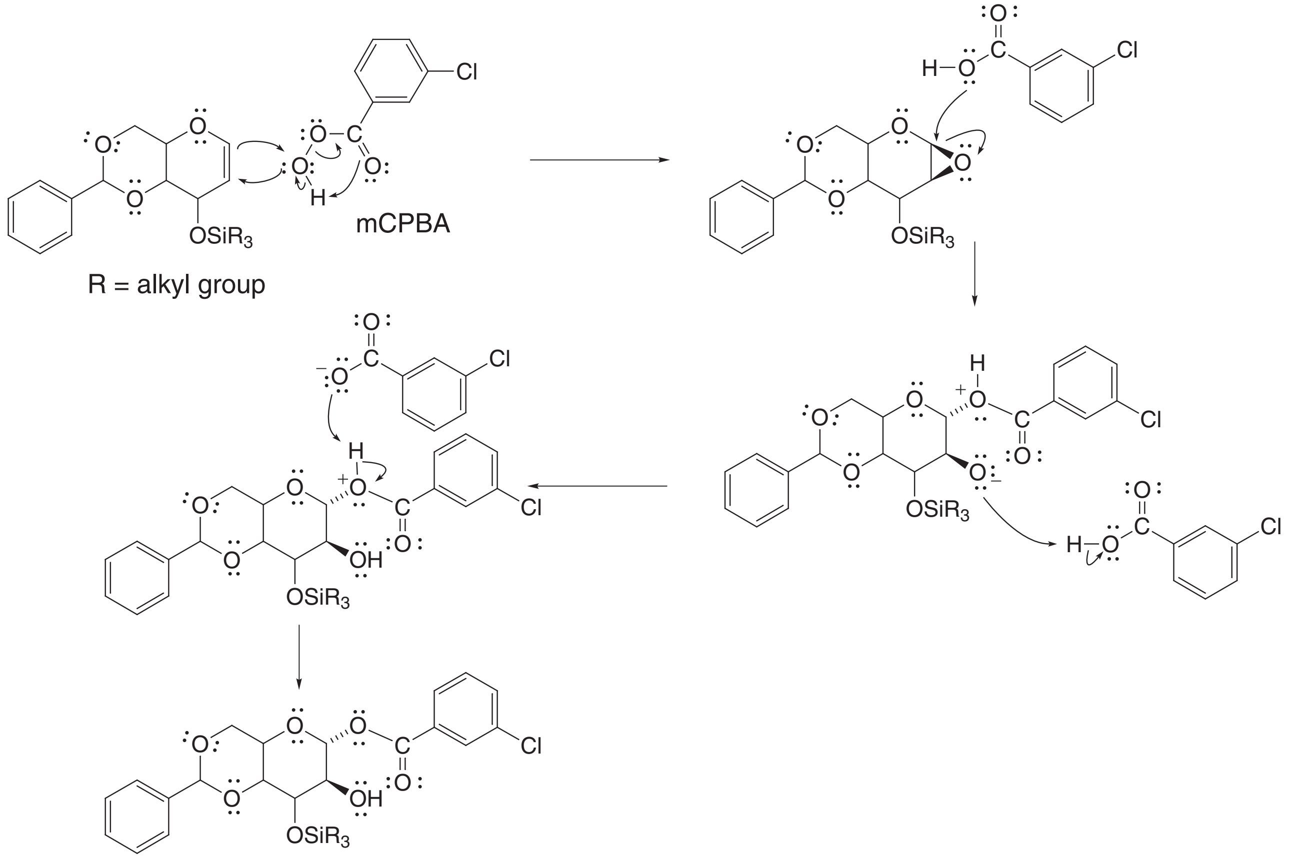
The favored conformation
for both molecules places
the *tert*-butyl group equatorial.



This OH is axial and
will react **faster**.

This OH is equatorial
and will react **more slowly**.

12.48

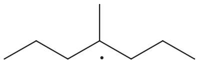


Capitolo 13

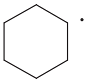
13.1 I radicali 1° sono su carboni legati solo ad un altro carbonio; i radicali 2° sono su carboni legati a due altri carboni; i radicali 3° sono su carboni legati ad altri tre carboni.

a. $CH_3CH_2-\underset{\cdot}{C}HCH_2CH_3$

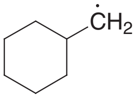
2° radical

b.


3° radical

c.


2° radical

d.


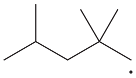
1° radical

13.2 La stabilità di un radicale aumenta al'aumentare dei gruppi alchilici legati al carbonio radicalico.

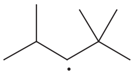
a. $(CH_3)_2CH\dot{C}H_2$ — 1° radical **least stable**

$CH_3CH_2\dot{C}HCH_3$ — 2° radical **intermediate stability**

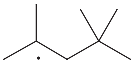
$(CH_3)_3C\cdot$ — 3° radical **most stable**

b.


1° radical **least stable**



2° radical **intermediate stability**

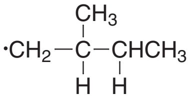


3° radical **most stable**

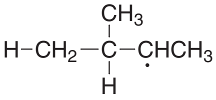
13.3

a. increasing bond strength: b < c < a

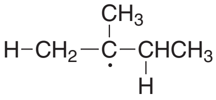
b and c.


$\cdot CH_2-\overset{CH_3}{\underset{H}{C}}-\underset{H}{C}HCH_3$

1° radical **least stable**


$H-CH_2-\overset{CH_3}{\underset{H}{C}}-\underset{\cdot}{C}HCH_3$

2° radical **intermediate stablity**


$H-CH_2-\overset{CH_3}{\underset{\cdot}{C}}-\underset{H}{C}HCH_3$

3° radical **most stable**

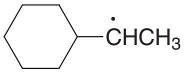
d. increasing H abstraction: a < c < b

13.4 Usare i suggerimenti della risposta 13.2 per ordinare i radicali.

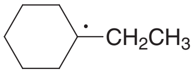
a. $(CH_3)_2CHCH_2CH(CH_3)\dot{C}H_2$ — 1° radical **least stable**

$(CH_3)_2CH\dot{C}HCH(CH_3)_2$ — 2° radical **intermediate stablity**

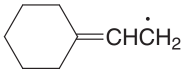
$(CH_3)_2\dot{C}CH_2CH(CH_3)_2$ — 3° radical **most stable**

b.


2° radical **least stable**

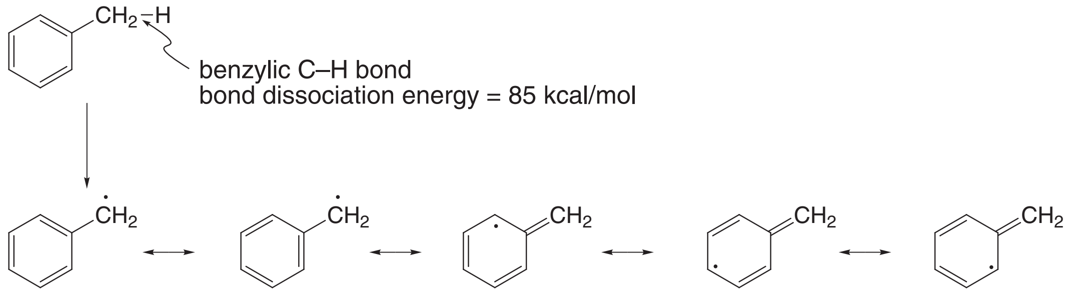


3° radical **intermediate stablity**



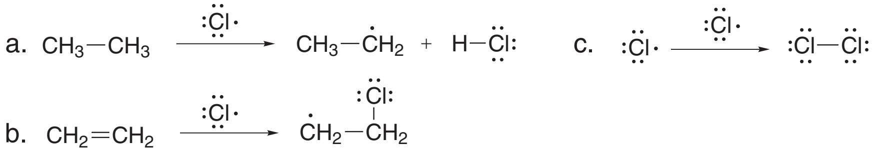
allylic radical **most stable**

13.5 Disegnare il radicale formato per scissione del legame C–H benzilico. Successivamente disenare le strutture di risonanza. La presenza di più strutture di risonanza (cinque in questo caso) rende il radicale più stabile, ed il legame C–H benzilico più debole.



13.6 Reazione di un radicale con:

- un alcano cattura un atomo di idrogeno e crea un nuovo radicale al carbonio.
- un alchene genera un nuovo legame ad un carbonio, ed un nuovo radicale al carbonio.
- Un altro radicale forma un legame.

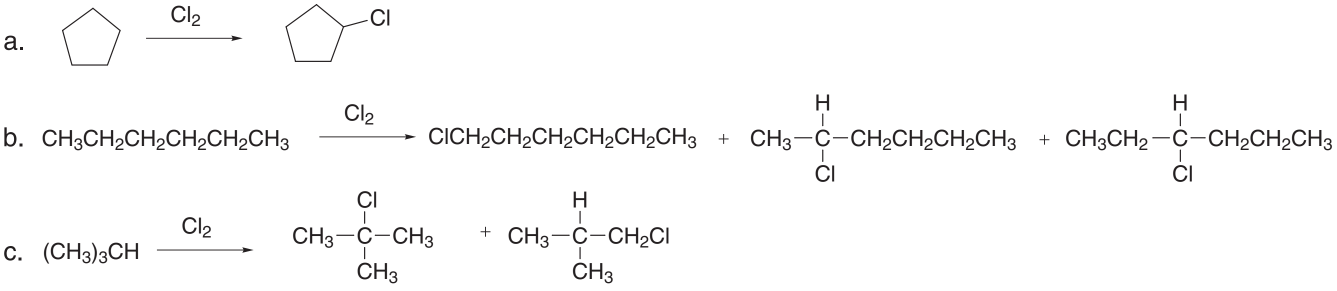


a. $CH_3{-}CH_3 \xrightarrow{:\ddot{Cl}\cdot} CH_3{-}\dot{C}H_2 + H{-}\ddot{Cl}:$

b. $CH_2{=}CH_2 \xrightarrow{:\ddot{Cl}\cdot} \dot{C}H_2{-}\overset{:\ddot{Cl}:}{\overset{|}{C}H_2}$

c. $:\ddot{Cl}\cdot \xrightarrow{:\ddot{Cl}\cdot} :\ddot{Cl}{-}\ddot{Cl}:$

13.7 **La monoclorurazione** è una reazione di sostituzione radicalica in cui un Cl sostituisce un H generando un alogenuro alchilico.

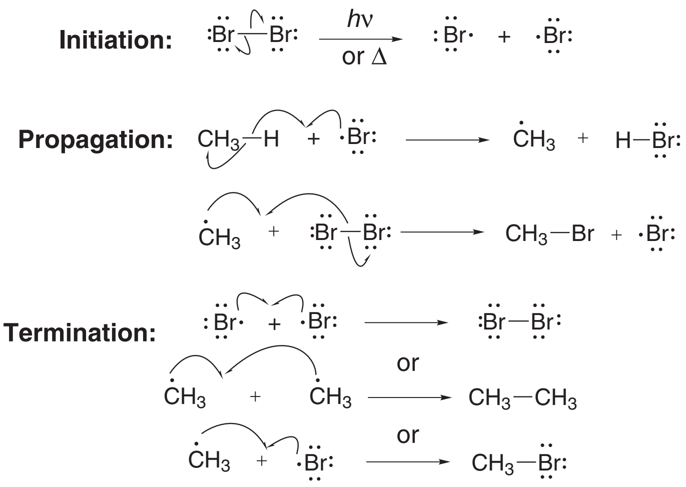


b. $CH_3CH_2CH_2CH_2CH_2CH_3 \xrightarrow{Cl_2} ClCH_2CH_2CH_2CH_2CH_2CH_3 + CH_3{-}\underset{Cl}{\overset{H}{C}}{-}CH_2CH_2CH_2CH_3 + CH_3CH_2{-}\underset{Cl}{\overset{H}{C}}{-}CH_2CH_2CH_3$

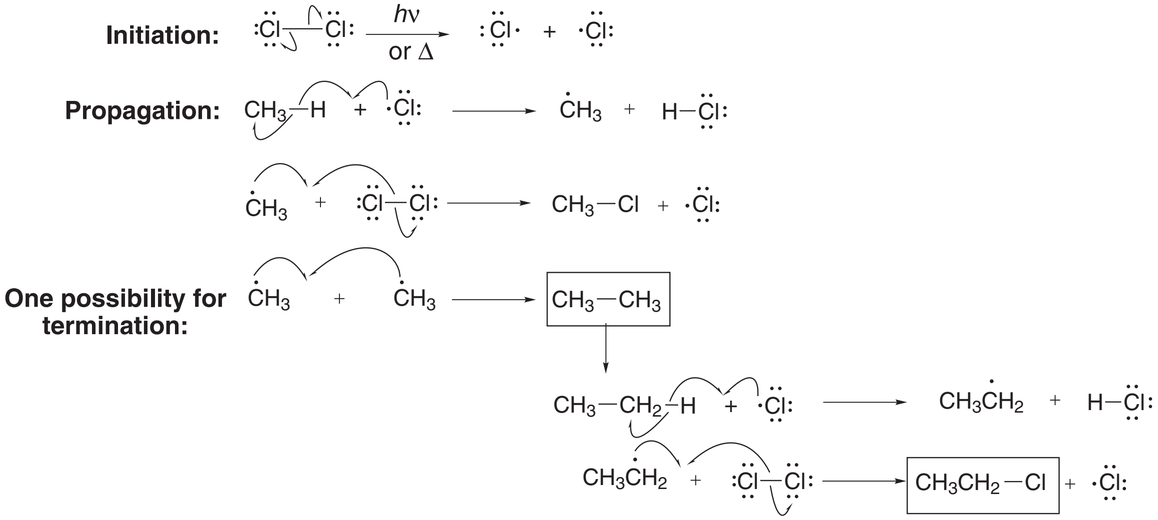
c. $(CH_3)_3CH \xrightarrow{Cl_2} CH_3{-}\underset{CH_3}{\overset{Cl}{C}}{-}CH_3 + CH_3{-}\underset{CH_3}{\overset{H}{C}}{-}CH_2Cl$

13.8 Se un alcano fornisce un prodotto di monoalogenazione con Cl_2, tutti gli idrogeni del prodotto di partenza devono essere identici. Un solo composto di formula molecolare C_5H_{12} ha tutti gli idrogeni identici: $(CH_3)_4C$.

13.9

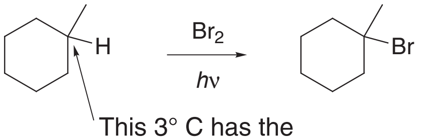


13.10



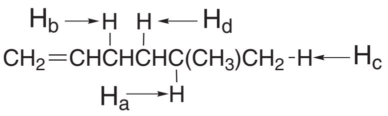
13.11 Per disegnare il prodotto della bromurazione:

- Disegnare il prodotto di partenza e trovare il legame C–H più reattivo (sul carbonio più sostituito).
- Il prodotto maggioritario si forma per **scissione del legame C–H più debole**.



This 3° C has the most reactive C–H bond.

13.12



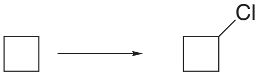
$$\mathrm{CH_2{=}\overset{H_b\rightarrow H}{C}H\overset{H\leftarrow H_d}{C}H\underset{H_a\rightarrow H}{C}HC(CH_3)CH_2{-}H \leftarrow H_c}$$

H_a = bonded to an *sp*^{3} 3° carbon
H_b = bonded to an allylic carbon
H_c = bonded to an *sp*^{3} 1° carbon
H_d = bonded to an *sp*^{3} 2° carbon

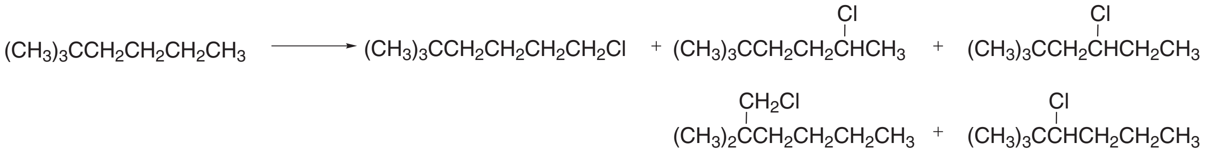
Increasing ease of abstraction:
$\mathbf{H_c < H_d < H_a < H_b}$

13.13 Usare i suggerimenti della risposta 13.7.

a.

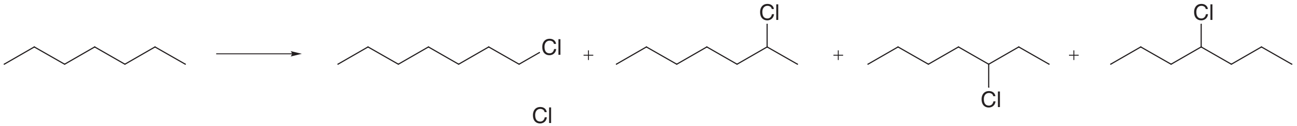


b.

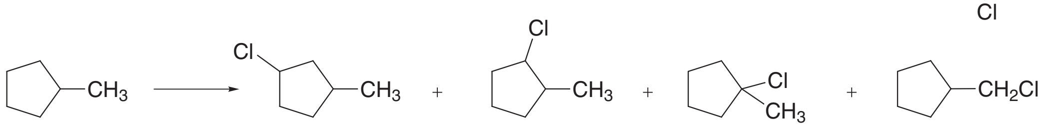


$$\mathrm{(CH_3)_3CCH_2CH_2CH_2CH_3 \longrightarrow (CH_3)_3CCH_2CH_2CH_2CH_2Cl + (CH_3)_3CCH_2CH_2\overset{Cl}{C}HCH_3 + (CH_3)_3CCH_2\overset{Cl}{C}HCH_2CH_3}$$
$$\mathrm{(CH_3)_2\overset{CH_2Cl}{C}CH_2CH_2CH_2CH_3 + (CH_3)_3C\overset{Cl}{C}HCH_2CH_2CH_3}$$

c.



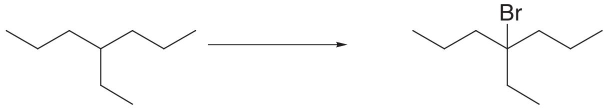
d.



13.14 Per disegnare il prodotto della bromurazione:

- Disegnare il materiale di partenza e trovare il legame C–H più reattivo (sul carbonio più sostituito).
- Il prodotto maggioritario si forma per scissione del legame **C–H più debole**.

l.



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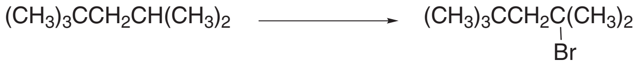
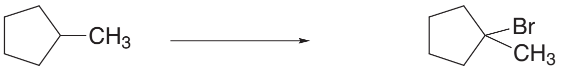


$$\mathrm{(CH_3)_3CCH_2CH(CH_3)_2 \longrightarrow (CH_3)_3CCH_2\underset{Br}{C}(CH_3)_2}$$

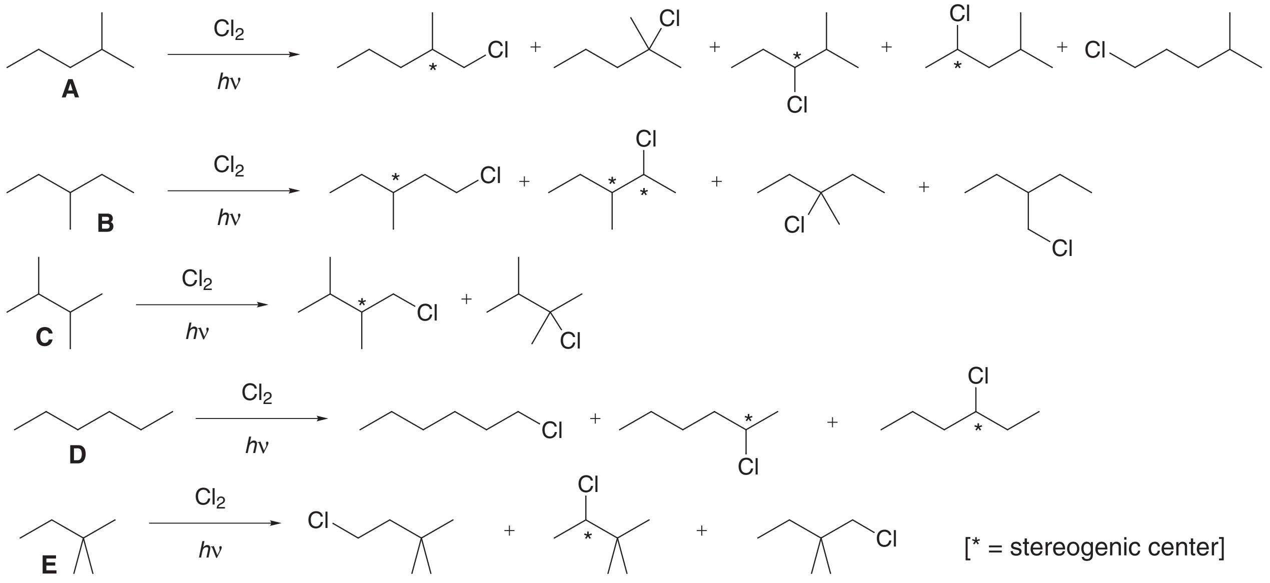
c.



d.

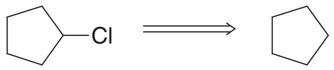
$$\mathrm{(CH_3)_3CCH_2CH_3 \longrightarrow (CH_3)_3C\overset{Br}{C}HCH_3}$$

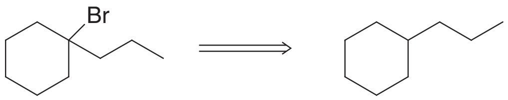
13.15 Disegnare tutti gli alcani isomeri di C_6H_{14} e i loro prodotti di clorurazione. Successivamente determinare quale lettera corrisponde a quale alcano.

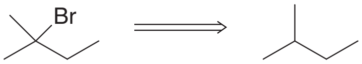


[* = stereogenic center]

13.16 L'alogenazione sostituisce un legame C–H con un legame C–X. Per trovare l'alcano necessario per ottenere ciascuno degli alogenuri alchilici, sostituire X con H.

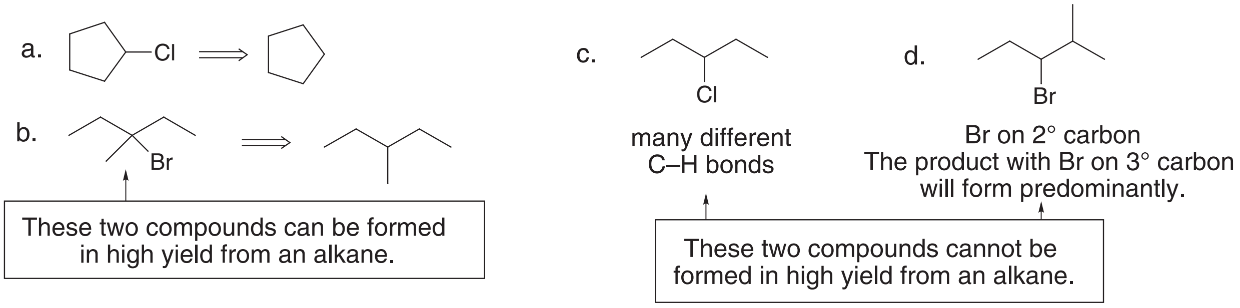
a. 

c. 

b. 

d. $(CH_3)_3CCH_2Cl \Longrightarrow (CH_3)_3CCH_3$

13.17 Perché un alcano fornisca un prodotto di monoalogenzaione principale per reazione con Cl_2, tutti gli idrogeni devono essere identici nel prodotto di partenza. Perché un alcano fornisca un prodotto principale per bromurazione, deve avere un carbonio più sostituitone prodotto di partenza.



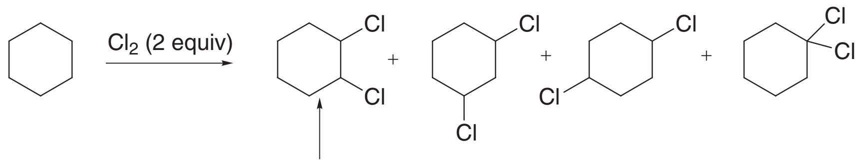
many different C–H bonds

Br on 2° carbon
The product with Br on 3° carbon will form predominantly.

These two compounds can be formed in high yield from an alkane.

These two compounds cannot be formed in high yield from an alkane.

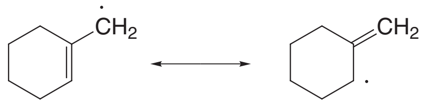
13.18 Clorurazione con due equivalenti di Cl_2 produce una varietà di prodotti.



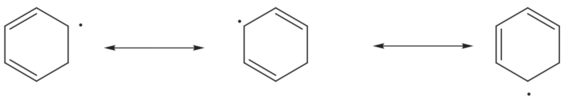
The desired product is only one of four products formed.

13.19 Disegnare le strutture di risonanza muovendo i legami π ed il radicale.

a.



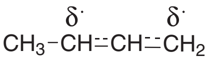
b.



13.20 Disegnare la strutture di risonanza muovendo il legame π e gli elettroni spaiati. L'ibrido viene disegnato con linee tratteggiate per i legami che sono in una struttura di risonanza ma non nell'altra. Il simbolo δ• è usato su ogni atomo che presenta un elettrone spaiato in ciascuna struttura di risonanza.

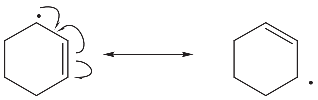
a.

hybrid:

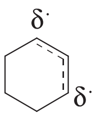


$\overset{\delta\cdot}{CH}$ … $CH_3-\overset{\delta\cdot}{C}H\text{=-}CH\text{=-}\overset{\delta\cdot}{C}H_2$

b.

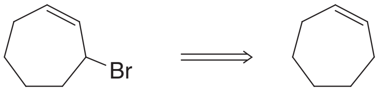


hybrid:



13.21 Reazione di un alchene con NBS + *hν* produce prodotti di sostituzione allilica

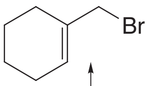
a.



one possible product: **high yield**

b. $CH_3CH_2CH{=}CHCH_2Br$

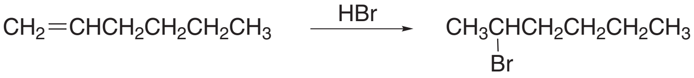
c.



Cannot be made in high yield by allylic halogenation.
Any alkene starting material would yield a mixture of allylic halides.

13.22

a.



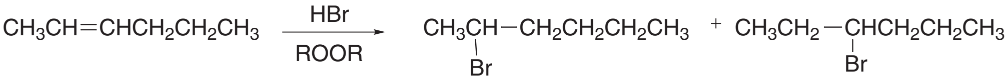
$$CH_2{=}CHCH_2CH_2CH_2CH_3 \xrightarrow{HBr} \underset{\displaystyle Br}{CH_3CH}CH_2CH_2CH_2CH_3$$

b.

c.

$$(CH_3)_2C{=}CHCH_3 \xrightarrow{HBr} (CH_3)_2\overset{\displaystyle Br}{C}-CH_2CH_3$$

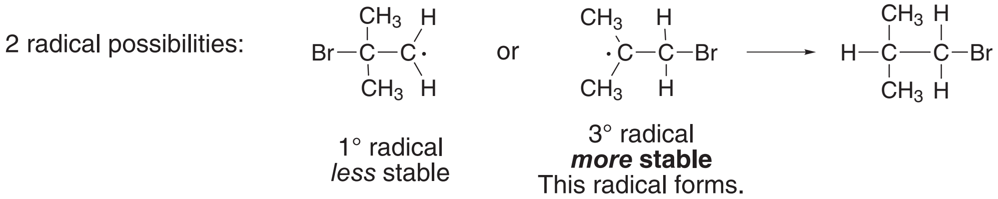
d.



$$CH_3CH{=}CHCH_2CH_2CH_3 \xrightarrow[ROOR]{HBr} CH_3\underset{\displaystyle Br}{CH}-CH_2CH_2CH_2CH_3 + CH_3CH_2-\underset{\displaystyle Br}{CH}CH_2CH_2CH_3$$

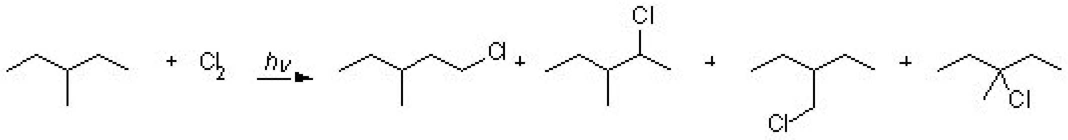
13.23 Nell’addizione di HBr in condizioni radicaliche:

- Br• si addiziona in modo da formare il radicale più stabile.
- Successivamente H• si addizione al carbonio radicalico.

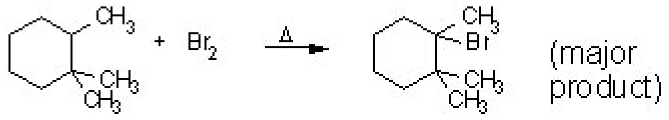


13.24

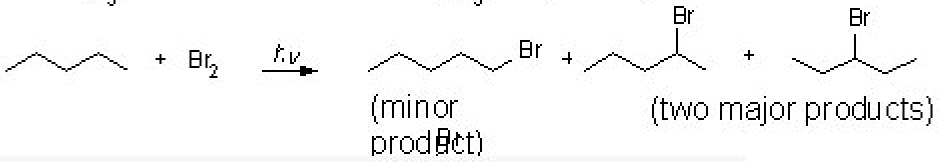
a.



b.



c.



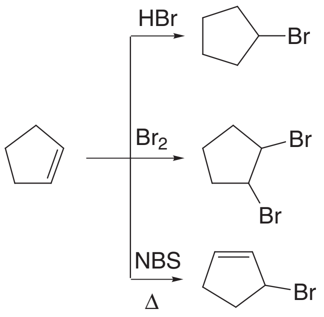
e.

f.

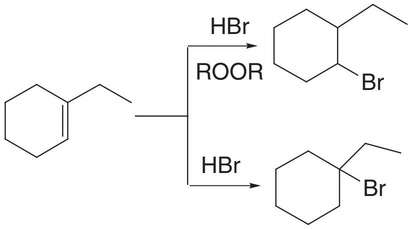
g.

13.25

a.

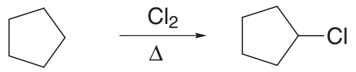


b.

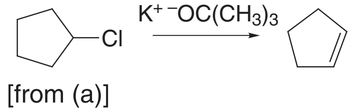


13.26

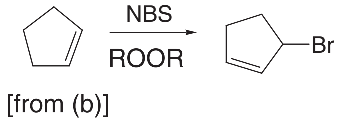
a.



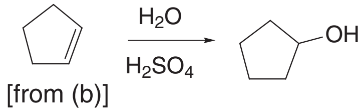
b.



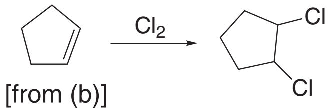
c.



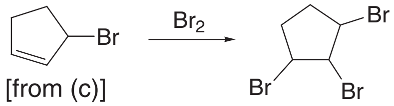
d.



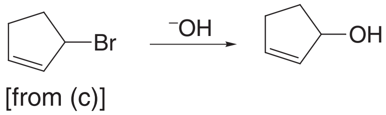
e.



f.

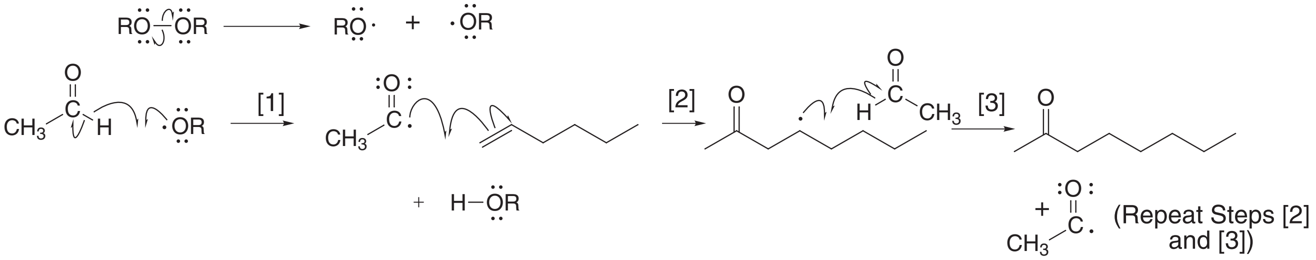


g.

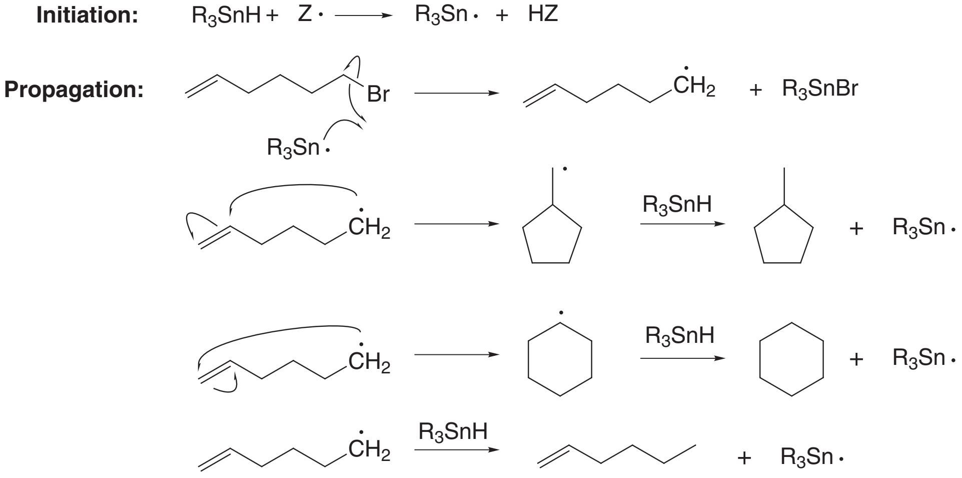


h.

13.27



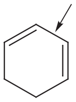
13.28



Capitolo 1 4

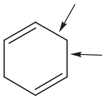
14.1 **I dieni isolati** hanno due doppi legami separati da due o più legami σ.
I dieni coniugati hanno due doppi legami separati solo da un legame σ.

a.



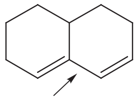
one σ bond separates
two double bonds =
conjugated diene

b.



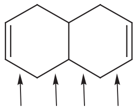
two σ bonds separate
two double bonds =
isolated diene

c.



one σ bond separates
two double bonds =
conjugated diene

d.



four σ bonds separate
two double bonds =
isolated diene

14.2 La **coniugazione** avviene quando ci sono orbitali *p* su tre o più atomi adiacenti. I doppi legami separati da 2 legami σ non sono coniugati.

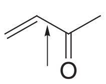
a. $CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$

All of the carbon atoms are sp^2 hybridized. Each π bond is separated by only 1 σ bond.
conjugated

b.

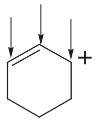
The two π bonds are separated by three σ bonds.
NOT conjugated

c.



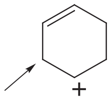
The two π bonds are separated by only 1 σ bond.
conjugated

d.



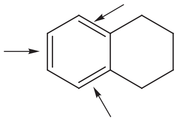
Three adjacent carbon atoms are sp^2 hybridized and have an unhybridized *p* orbital.
conjugated

e.



This carbon is not sp^2 hybridized.
NOT conjugated

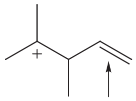
14.3 Usare le indicazioni della risposta 14.1.



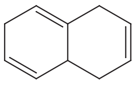
3 π bonds with only
1 σ bond between
conjugated

$CH_2{=}CHC{\equiv}N$

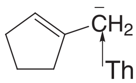
2 multiple bonds with only
1 σ bond between
conjugated



1 π bond with
no adjacent sp^2 hybridized atoms
NOT conjugated

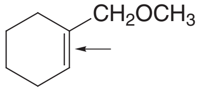


3 π bonds with 2 or
more σ bonds between
NOT conjugated



This C is sp^2.

1 π bond with
an adjacent sp^2 hybridized atom
The lone pair occupies a *p* orbital,
so there are *p* orbitals on
three adjacent atoms.
conjugated



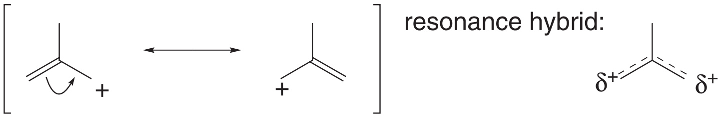
1 π bond with
no adjacent sp^2 hybridized atoms
NOT conjugated

14.4 Due strutture di risonanza differiscono solo per la disposizione degli elettroni. Tutti i legami σ rimangono nella stessa disposizione. Possono essere spostati gli elettroni di non legame ed i legami π. Per disegnare un ibrido:

Usare una linea tratteggiata tra gli atomi che hanno un legame π in una struttura di risonanza e non nell'altra.

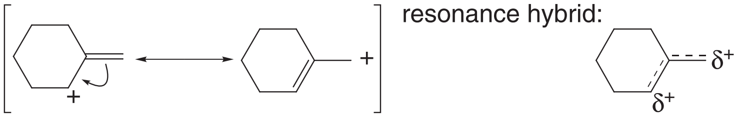
- Usare ul simbolo δ per gli atomi con una carica o radicale in una struttura e non nell'altra.

a.



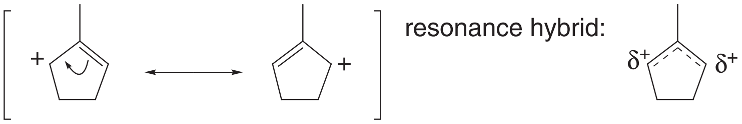
The + charge is delocalized on two carbons.

b.



The + charge is delocalized on two carbons.

c.



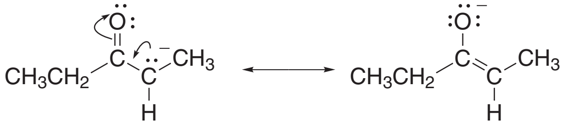
The + charge is delocalized on two carbons.

14.5

a.

Move the charge and the double bond.

b.



Move the charge and the double bond.

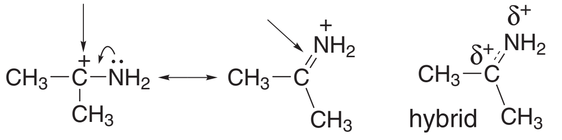
c.

Move the lone pair.

14.6 Per paragonare le strutture di risonanza:

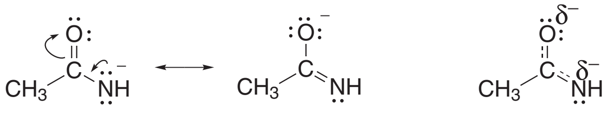
- Strutture di risonanza con **più legami** sono più stabili.
- Strutture di risonanza in cui **ogni atomo ha un ottetto sono più stabili**.
- Strutture di risonanza con **atomi neutri** sono più stabili di quelle con separazione di carica.
- Strutture di risonanza in cui la **carica negativa è posizionata sull'atomo più elettronegativo** sono più stabili.

a.



least stable one more bond all atoms have an octet better resonance structure **intermediate stability** **most stable**

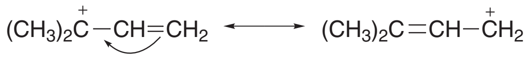
b.



least stable negative charge on the more electronegative atom better resonance structure **intermediate stability** **most stable**

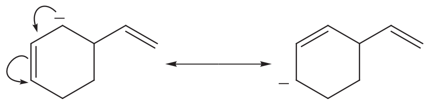
14.7

a.

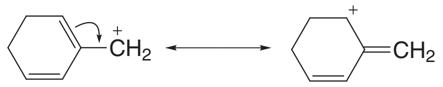


$(CH_3)_2\overset{+}{C}-CH=CH_2 \longleftrightarrow (CH_3)_2C=CH-\overset{+}{C}H_2$

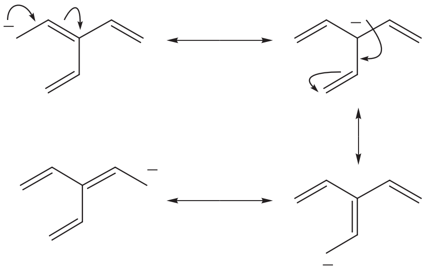
b.



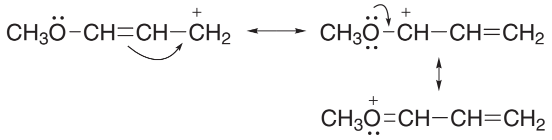
c.



d.

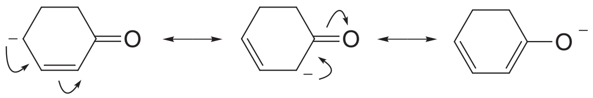


e.

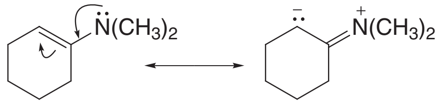


$CH_3\ddot{O}-CH=CH-\overset{+}{C}H_2 \longleftrightarrow CH_3\ddot{O}-\overset{+}{C}H-CH=CH_2 \longleftrightarrow CH_3\overset{+}{O}=CH-CH=CH_2$

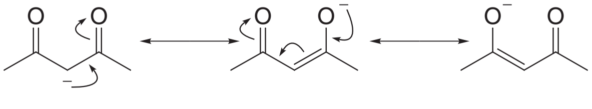
f.



g.

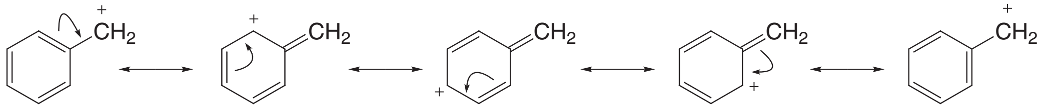


h.

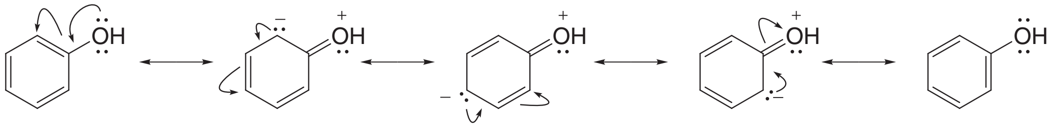


14.8

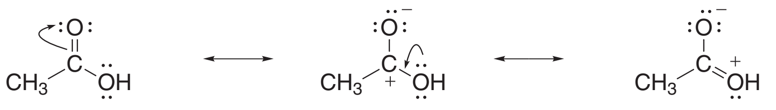
a.

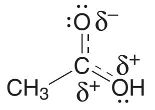


b.



14.9 Usare le regole della risposta 14.4.

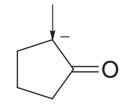




A	B	C	D
no charges all atoms have an octet 4 bonds (C–C + C–O) **most stable**	2 charges C does not have an octet 3 bonds (C–C + C–O) **least stable**	2 charges all atoms have an octet 4 bonds (C–C + C–O) **intermediate stability**	resonance hybrid

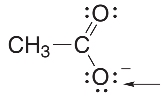
14.10 In ogni sistema allilico devono essere presenti orbitali *p* per delocalizzare il doppietto elettronico.

a.



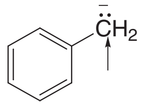
sp^2 hybridized
trigonal planar geometry

b.



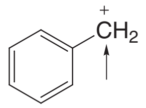
sp^2 hybridized
trigonal planar geometry

c.

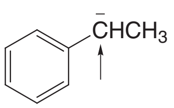


sp^2 hybridized
trigonal planar geometry

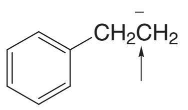
14.11

a. 

The benzylic C is *sp*^{2} hybridized.
trigonal planar

b. 

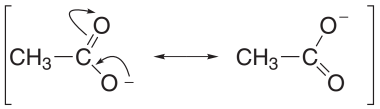
The benzylic C is *sp*^{2} hybridized.
trigonal planar

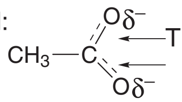
c. 

This carbon is NOT part of
a conjugated system.
4 groups = *sp*^{3} hybridized
tetrahedral

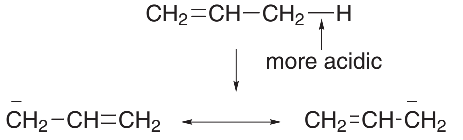
14.12

a. Two equivalent resonance structures delocalize the π bond and the negative charge.



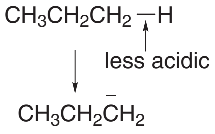
hybrid: 

These bond lengths are equal
because they are identical.

b. 

$$CH_2{=}CH{-}CH_2{-}H \rightarrow \overset{-}{C}H_2{-}CH{=}CH_2 \longleftrightarrow CH_2{=}CH{-}\overset{-}{C}H_2$$

Resonance stabilization delocalizes the
negative charge on 2 C's after loss of a proton.
This makes propene more acidic than propane.

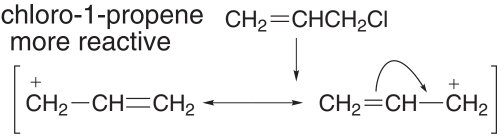


$$CH_3CH_2CH_2{-}H \rightarrow CH_3CH_2\overset{-}{C}H_2$$

only one Lewis structure

c. S_N1 reactions proceed via a carbocation intermediate. Draw the carbocation formed on loss of Cl and compare.

3-chloro-1-propene
more reactive



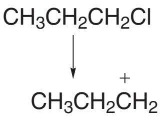
$$CH_2{=}CHCH_2Cl \rightarrow \left[\overset{+}{C}H_2{-}CH{=}CH_2 \longleftrightarrow CH_2{=}CH{-}\overset{+}{C}H_2\right]$$

resonance-stabilized carbocation

Two resonance structures delocalize
the positive charge on 2 C's making the
3-chloro-1-propene more reactive.

$CH_3CH_2CH_2Cl$ is a 1° halide, which does not react by an S_N1 reaction because cleavage of the C–Cl bond forms a highly unstable 1° carbocation.

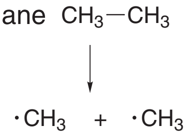
1-chloropropane
less reactive



$$CH_3CH_2CH_2Cl \rightarrow CH_3CH_2\overset{+}{C}H_2$$

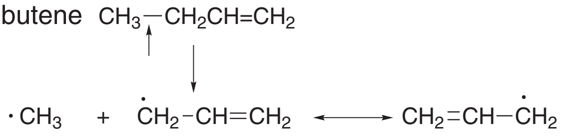
only one Lewis structure
very unstable

d. Draw the products of cleavage of the bond.

ethane 

$$CH_3{-}CH_3 \rightarrow \cdot CH_3 + \cdot CH_3$$

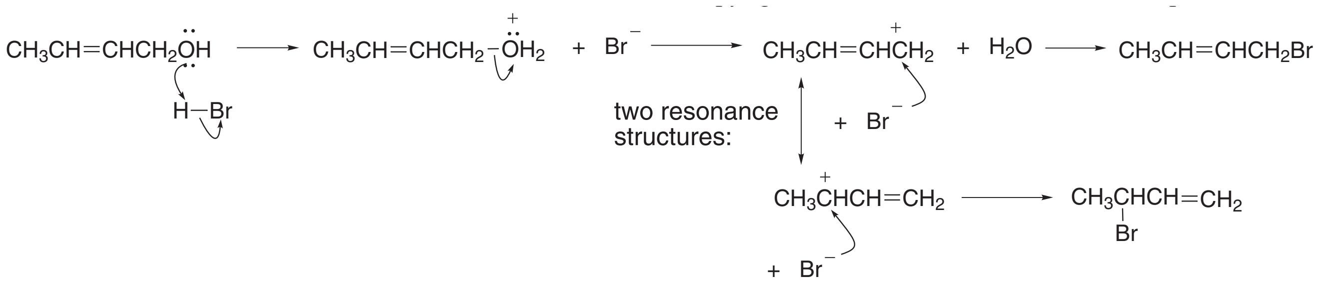
Two unstable radicals form.

1-butene 

$$CH_3{-}CH_2CH{=}CH_2 \rightarrow \cdot CH_3 + \dot{C}H_2{-}CH{=}CH_2 \longleftrightarrow CH_2{=}CH{-}\dot{C}H_2$$

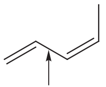
One resonance-stabilized radical forms.
This makes the bond dissociation
energy lower because a more stable radical is formed.

14.13

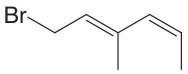


14.14 Usare le indicazioni della risposta 14.15.

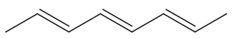
a. (3*Z*)-1,3-pentadiene in the *s*-trans conformation



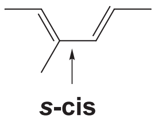
b. (2*E*,4*Z*)-1-bromo-3-methyl-2,4-hexadiene



c. (2*E*,4*E*,6*E*)-2,4,6-octatriene

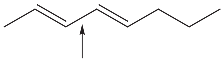


d. (*E*,*E*)-3-methyl-2,4-hexadiene in the *s*-cis conformation

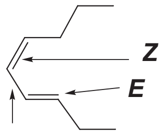


14.15 Il conformero ***s*-cis** ha i due doppi legami **dalla stessa parte** rispetto al legame singolo. Il conformero ***s*-trans** ha i due doppi legami **da parti opposte** rispetto al legame singolo.

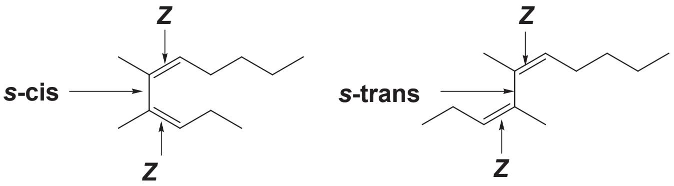
a. (2*E*,4*E*)-2,4-**octadiene** in the *s*-trans conformation



b. (3*E*,5*Z*)- 3,5-**nonadiene** in the *s*-cis conformation



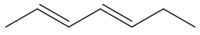
c. (3*Z*,5*Z*)-4,5-dimethyl-3,5-**decadiene** in both the *s*-cis and *s*-trans conformers.

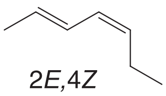


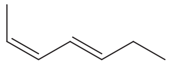
14.16 La lunghezza di legame dipende dall'ibridazione e dalla percentuale di carattere *s*. I legami con maggiore percentuale di carattere *s* hanno orbitali più piccoli e più corti. Confrontare l'ibridazione degli atomi di carbonio nei legami per ordinare i legami secondo la lunghezza crescente.

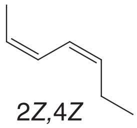
$CH_3CH_2-CH_3$	$CH_2=CH-CH_3$	$CH_2=CH-CH=CH_2$
two *sp*^{3} hybridized carbons 25% *s*-character **longest bond**	one *sp*^{2} hybridized carbon one *sp*^{3} hybridized carbon **intermediate length bond**	two *sp*^{2} hybridized carbons 33% *s*-character **shortest bond**

14.17


2E,4E

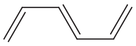

2E,4Z


2Z,4E

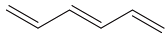

2Z,4Z

14.18

a.

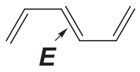

(3*E*)-1,3,5-hexatriene
both *s*-cis

and


(3*E*)-1,3,5-hexatriene
both *s*-trans

different conformers

c.



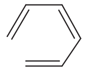
(3*E*)-1,3,5-hexatriene

and

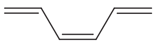
(3*Z*)-1,3,5-hexatriene

different stereoisomers

b.


(3*Z*)-1,3,5-hexatriene
both *s*-cis

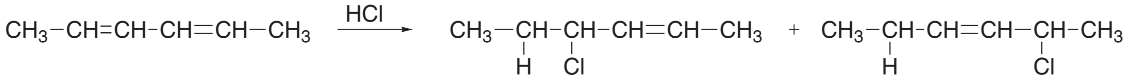
and


(3*Z*)-1,3,5-hexatriene
both *s*-trans

different conformers

14.19 I dieni coniugati reagiscono con HX per formare prodotti 1,2- e 1,4-.

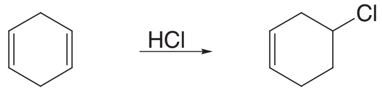
a.



$$CH_3-CH=CH-CH=CH-CH_3 \xrightarrow{HCl} CH_3-\underset{H}{CH}-\underset{Cl}{CH}-CH=CH-CH_3 + CH_3-\underset{H}{CH}-CH=CH-\underset{Cl}{CH}-CH_3$$

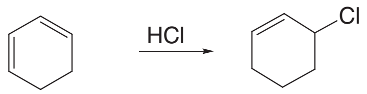
1,2-product **1,4-product**

b.

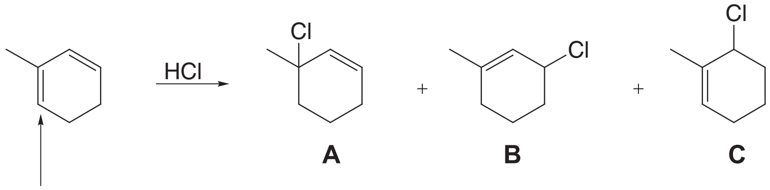


isolated diene

c.



d.

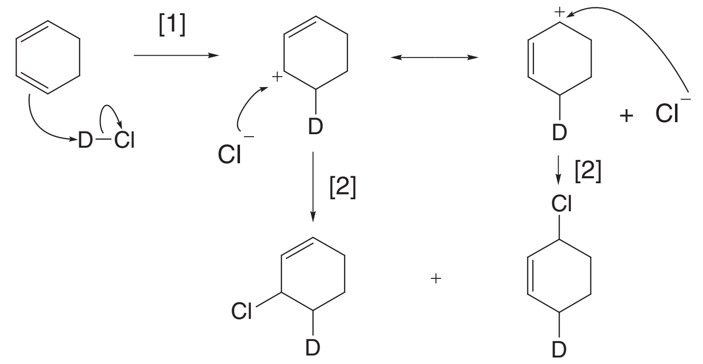


This double bond is more reactive, so **C** is probably a minor product because it results from HCl addition to the less reactive double bond.

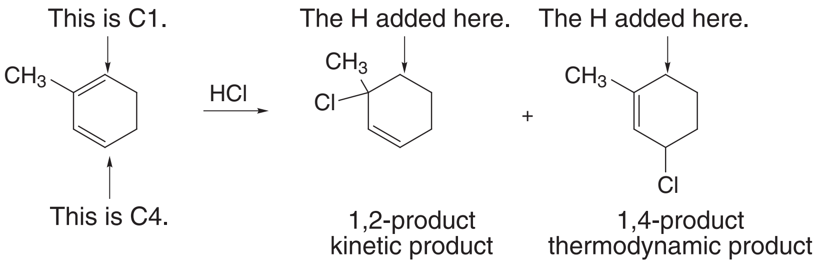
14.20 Il meccanismo di addizione di DCl prevede due stadi:

[1] L'**addizione di D^+** forma un carbocatione stabilizzato per risonanza.

[2] L'**attacco nucleofilo di $Cl^–$** forma prodotti 1,2- e 1,4-.



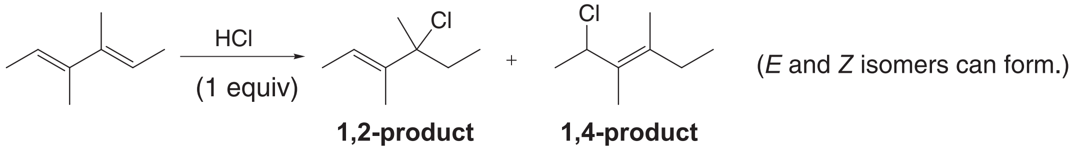
14.21 Classificare i prodotti come prodotti 1,2- o 1,4-. Il prodotto 1,2- è il prodotto cinetico, e il prodotto 1,4-, che ha i doppi legami più sostituiti, è quello termodinamico.



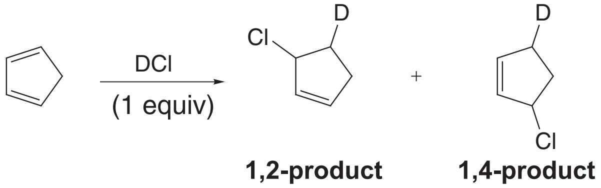
14.22 I dieni coniugati reagiscono con HX per formare prodotti 1,2- e 1,4-.

a.

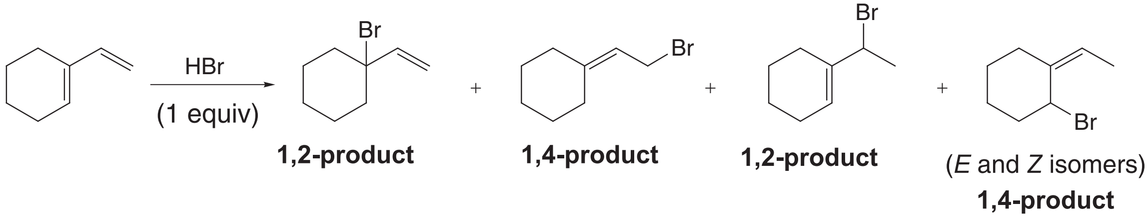
b.



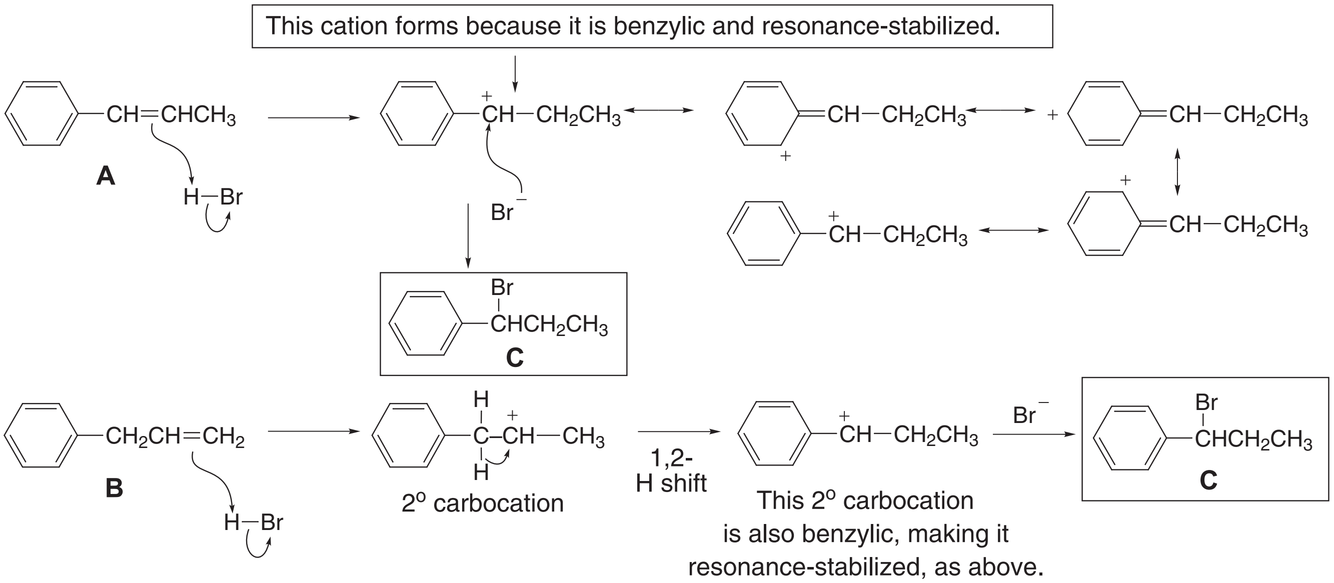
c.



d.



14.23

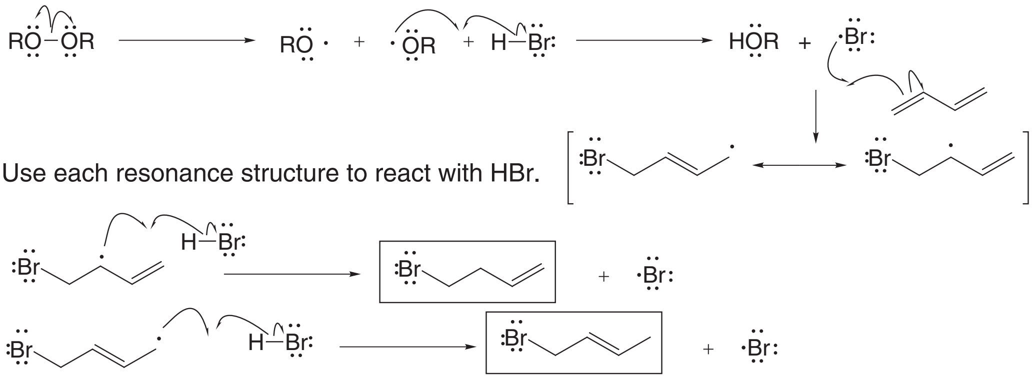

This cation forms because it is benzylic and resonance-stabilized.

2° carbocation

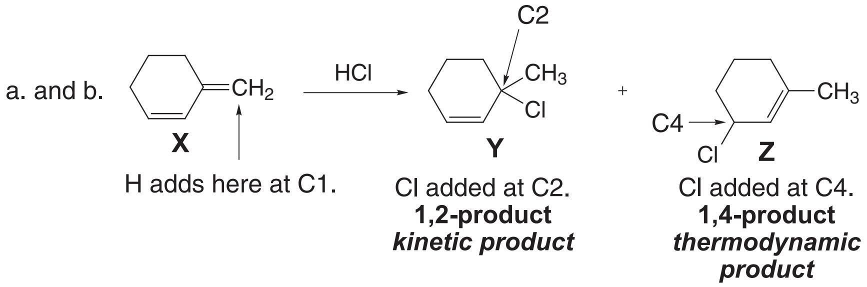
1,2-H shift

This 2° carbocation is also benzylic, making it resonance-stabilized, as above.

14.24 Per disegnare il meccanismo della reazione di un diene con HBr/ROOR, ricordare dal Capitolo 13 che quando un alchene è trattato con HBr in condizioni radicaliche, il Br va sul carbonio con più atomi di idrogeno.


Use each resonance structure to react with HBr.

14.25



H adds here at C1.

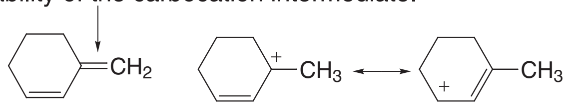
Cl added at C2.
1,2-product
kinetic product

Cl added at C4.
1,4-product
thermodynamic product

Y is the kinetic product because of the proximity effect. H and Cl add across two adjacent atoms.
Z is the thermodynamic product because it has a more stable trisubstituted double bond.

Addition occurs at the labeled double bond due to the stability of the carbocation intermediate.

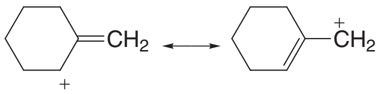
c.



The two resonance structures for this allylic cation are 3° and 2° carbocations.

more stable intermediate
Addition occurs here.

If addition occurred at the other C=C, the following allylic carbocation would form:

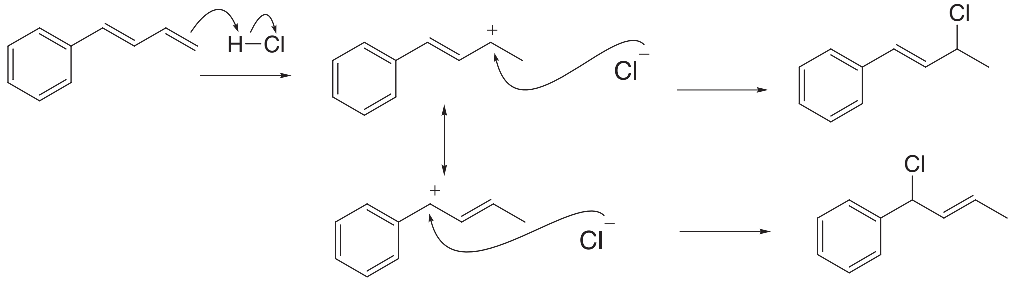


The two resonance structures for this allylic cation are 1° and 2° carbocations.

less stable

14.26

Addition of HCl at the terminal double bond forms a carbocation that is highly resonance-stabilized since it is both allylic and benzylic. Such stabilization does not occur when HCl is added to the other double bond. This gives rise to two products of electrophilic addtion.



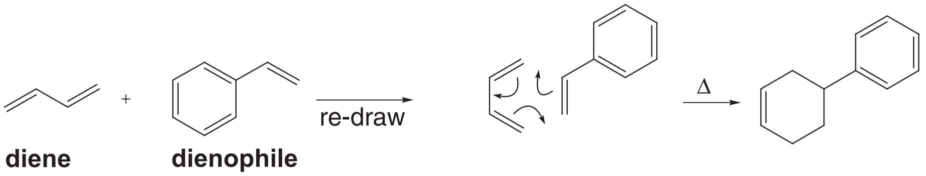
1,2-product

1,4-product

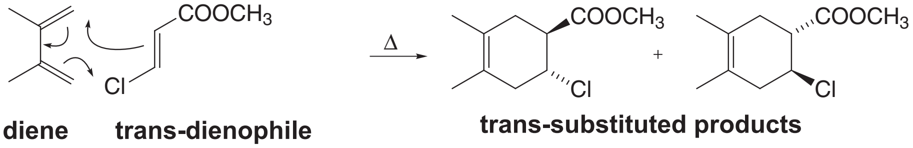
(+ four more resonance structures that delocalize the positive charge onto the benzene ring)

14.27 Usare le indicazioni della risposta 16.16.

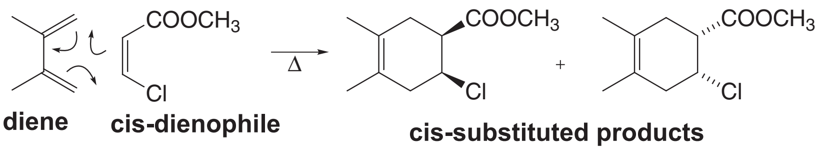
a.



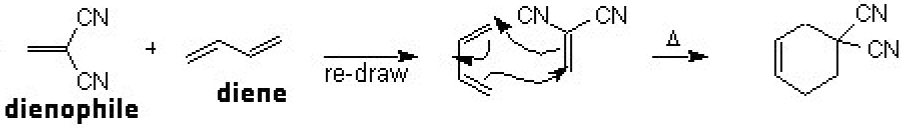
b.



c.

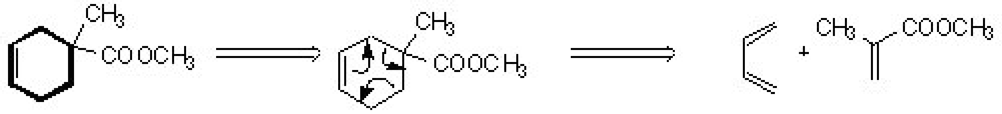


e.

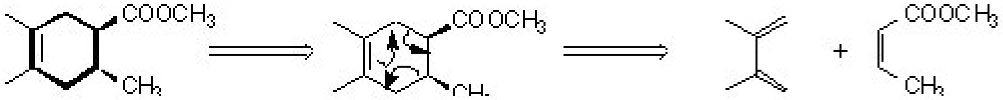


14.28 Usare le indicazioni della risposta 16.22.

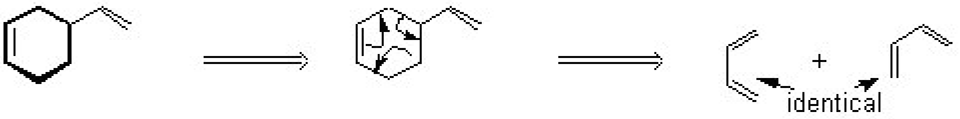
a.



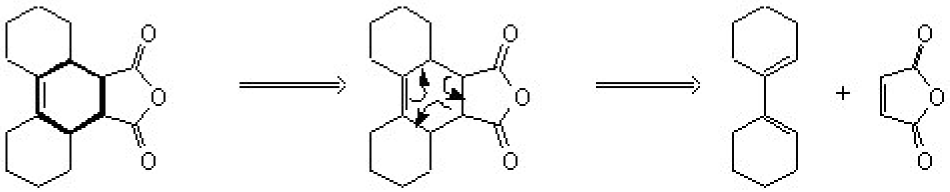
b.



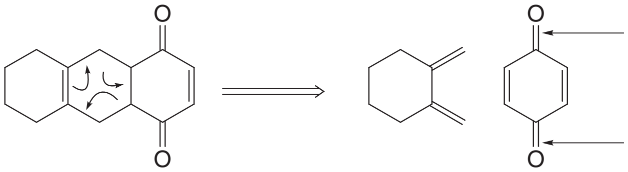
d.



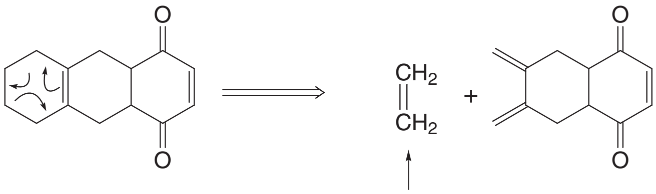
f.



14.29



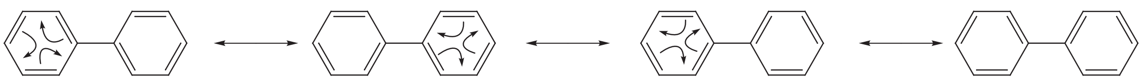
This pathway is **prefered** because the dienophile has electron-withdrawing C=O groups which make it more reactive.



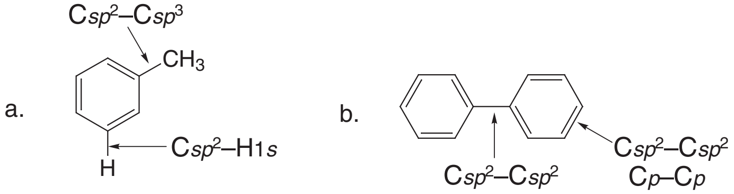
no electron-withdrawing groups
less reactive

Capitolo 1 5

15.1 Muovere gli elettroni nei legami π per disegnare tutte la principali strutture risonanti.

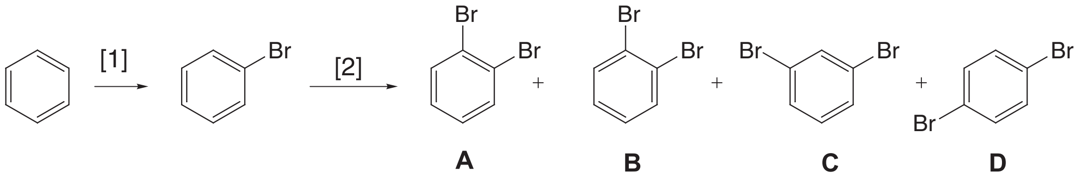


15.2 Considerare l'ibridazione degli atomi coinvolti in ciascun legame. Gli atomi di carbonio nell'anello del benzene sono circondati da tre gruppi e sono ibridati sp^2.



15.3 a. Se il benzene potesse essere descritto da una singola struttura di Kekulé, nella Reazione [1] si formerebbe un solo prodotto, ma ci sarebbero quattro (non tre) dibromobenzeni (**A**–**D**), perché i legami adiacenti C–C sono diversi—uno è singolo ed uno è doppio. Quindi, i composti **A** e **B** *non* sarebbero identici. **A** ha due atomi di Br legati allo stesso doppio legame, ma **B** ha due atomi di Br su doppi legami diversi.

b. Nella descrizione che tiene conto della risonanza, si formerebbe un solo prodotto nella Reazione [1], dal momento che tutti gli atomi di C sono identici, ma sono possibili solo tre dibromobenzeni (isomeri orto, meta, e para). **A** e **B** sono identici, perché ogni legame C–C è identico e con lunghezza di legame intermedia fra un legame C–C singolo e un legame C–C doppio.



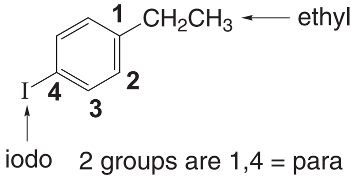
15.4 Per denominare un anello **benzenico monosostituito**, si denomina il sostituente e si aggiunge la parola *benzene*.

- Per denominare un **anello disostituito**, scegliere il prefisso corretto (orto = 1,2; meta = 1,3; para = 1,4) e mettere in ordine alfabetico i sostituenti. Usare un nome comune se è un derivato di un benzene monosostituito.
- Per denominare un **anello polisostituito**, numerare l'anello in modo da dare i numeri più piccoli possibile e quindi seguire le altre regole della nomenclatura.

a. isopropyl group ↓ $PhCH(CH_3)_2$

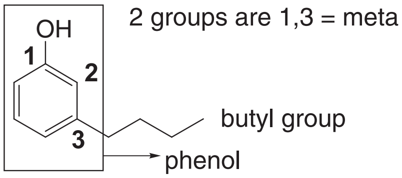
isopropylbenzene

b.



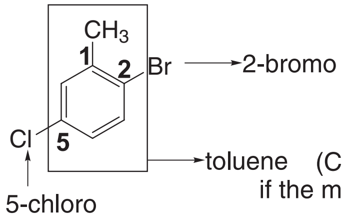
***p*-ethyliodobenzene**

c.



***m*-butylphenol**

d.

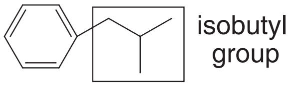


(CH$_3$ group must be at the "1" position, if the molecule is named as a toluene derivative.)

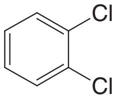
2-bromo-5-chlorotoluene

15.5 Operare a ritroso per disegnare la struttura dai nomi.

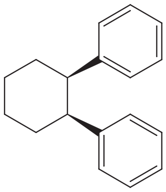
a. isobutylbenzene



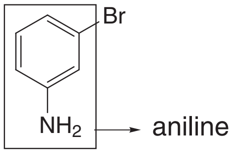
b. *o*-dichlorobenzene



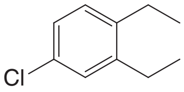
c. *cis*-1,2-diphenylcyclohexane



d. *m*-bromoaniline

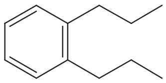


e. 4-chloro-1,2-diethylbenzene



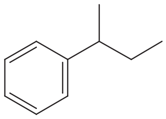
15.6 Per denominare i composti usare le indicazioni della risposta 15.4.

a.



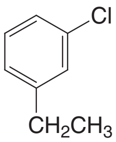
o-dipropylbenzene

b.



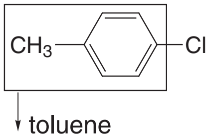
sec-butylbenzene

c.



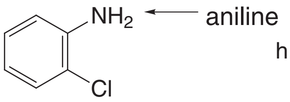
m-chloroethylbenzene

d.



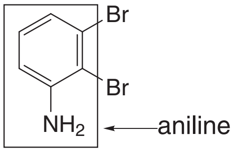
p-chlorotoluene

e.



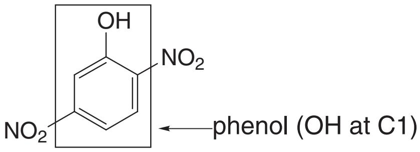
o-chloroaniline

f.



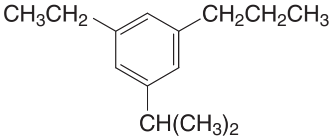
2,3-dibromoaniline

g.



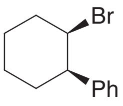
2,5-dinitrophenol

h.



1-ethyl-3-isopropyl-5-propylbenzene

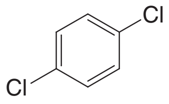
i.



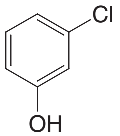
cis-1-bromo-2-phenylcyclohexane

15.7

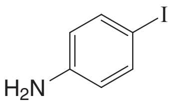
a. *p*-dichlorobenzene



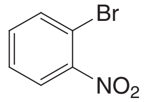
b. *m*-chlorophenol



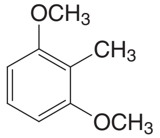
c. *p*-iodoaniline



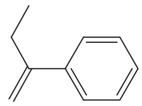
d. *o*-bromonitrobenzene



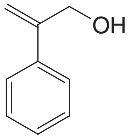
e. 2,6-dimethoxytoluene



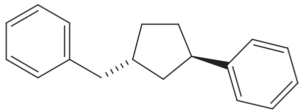
f. 2-phenyl-1-butene



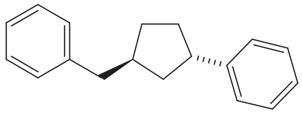
g. 2-phenyl-2-propen-1-ol



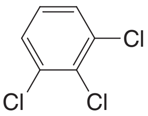
h. *trans*-1-benzyl-3-phenylcyclopentane



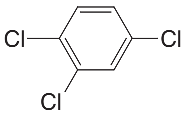
or



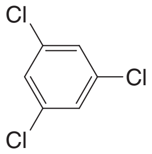
15.8



1,2,3-trichlorobenzene

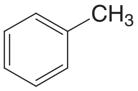


1,2,4-trichlorobenzene



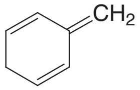
1,3,5-trichlorobenzene

15.9 Il composto meno stabile ha il più alto calore di idrogenazione.



A

benzene ring, more stable
lower Δ$H°$



B

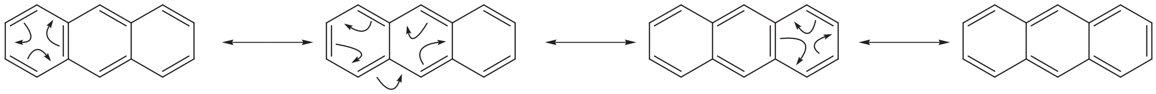
no benzene ring, less stable
higher Δ$H°$

15.10 Per essere aromatico, un anello deve avere $4n + 2$ elettroni π.

16 π e^-	20 π e^-	22 π e^-
$4n$	$4n$	$4n + 2$
4(4) = 16	4(5) = 20	4(5) + 2 = 22
antiaromatic	**antiaromatic**	**aromatic**

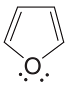
15.11 Gli annuleni hanno legami alternati doppi e singoli. Un numero dispari di atomi di carbonio nell'anello significa che possono esserci due legami singoli adiacenti. Quindi un annulene che ha un numero dispari di atomi di carbonio non esiste.

15.12



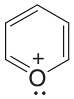
15.13 Per stabilire se un eterociclo è aromatico, contare se un doppietto elettronico di non legame rende l'anello aromatico nel calcolo 4*n* +2.

a.



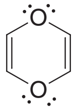
count 2 of O's
nonbonded electrons
$4n + 2 = 4(1) + 2 = 6$
aromatic

b.



no lone pair from O
$4n + 2 = 4(1) + 2 = 6$
aromatic

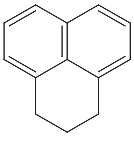
c.



with one lone
pair from each O
there are 8 electrons
not aromatic

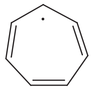
15.14 Contare gli elettroni nei legami π. Ogni legame π ha due elettroni.

a.



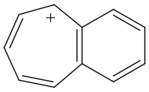
10 π electrons

b.



7 π electrons

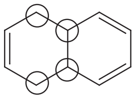
c.



10 π electrons

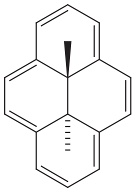
15.15 Per essere aromatici, i composti devono essere ciclici, planari, completamente coniugati, ed avere $4n + 2$ elettroni π.

a.



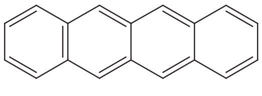
circled C's are not sp^2
not completely conjugated
not aromatic

b.



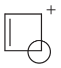
14 π electrons in outer ring
aromatic

c.



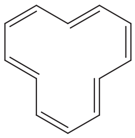
4 benzene rings
joined together
aromatic

d.



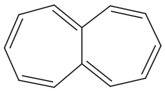
circled C's are not sp^2
not completely conjugated
not aromatic

e.



12 π electrons
does **not** have $4n + 2$
π electrons

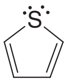
f.



12 π electrons
does **not** have $4n + 2$
π electrons

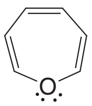
15.16 Per stabilire se un eterociclo è aromatico, contare se un doppietto elettronico di non legame rende l'anello aromatico nel calcolo 4*n* +2

a.



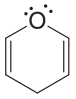
6 π electrons
counting a lone pair from S
4(1) + 2 = 6
aromatic

c.



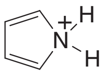
not aromatic

e.



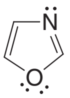
not aromatic

g.



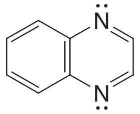
N is not sp^2 (no *p* orbital)
not aromatic

b.



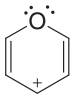
6 π electrons
counting a lone pair from O
4(1) + 2 = 6
aromatic

d.



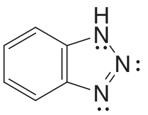
10 π electrons
4(2) + 2 = 10
aromatic

f.



6 π electrons,
counting a lone pair from O
4(1) + 2 = 6
aromatic

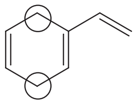
h.



10 π electrons
4(2) + 2 = 10
aromatic

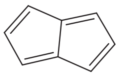
15.17

a.



circled C's are
not sp^2
not aromatic

c.

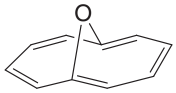


8 π electrons
4(2) = 8
antiaromatic

e.

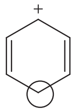
4 π electrons
4(1) = 4
antiaromatic

b.



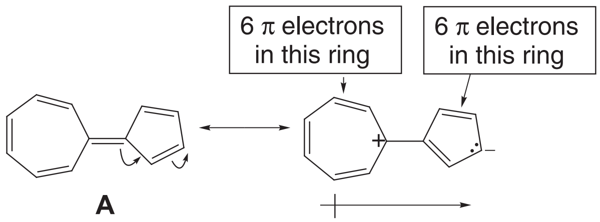
10 π electrons
in 10-membered ring
4(2) + 2 = 10
aromatic

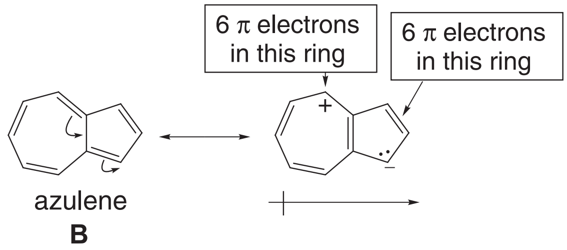
d.



circled C is
not sp^2
not aromatic

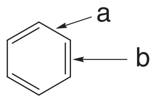
15.18





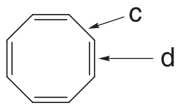
In entrambi i composti **A** e **B**, possono essere disegnate strutture risonanti con una carica negativa sull'anello a cinque termini e una carica positiva sull'anello a sette. Queste strutture risonanti mostrano che ciascun anello ha 6 elettroni π, rendendolo così aromatico. Ogni molecola ha un dipolo tale che l'anello a sette termini è elettron-deficiente e l'anello a cinque termini è elettron-ricco.

15.19 Il benzene ha legami C–C di uguale lunghezza, intermedia fra un legame C–C doppio ed uno singolo. Il cicloottatetraene non è planare ed è non aromatico, così i suoi doppi legami sono localizzati.



6 electrons: aromatic
all bonds of equal length
intermediate

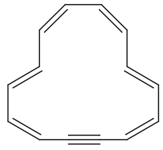
cyclooctatetraene



not aromatic
longer single bond
localized double bond: **shorter**

d < a = b < c

15.20

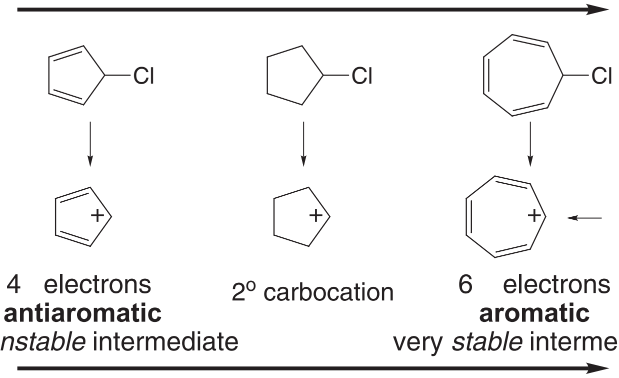


C

a. 16 total electrons
b. 14 electrons delocalized in the ring. [Note: Two of the electrons in the triple bond are localized between two C's, perpendicular to the π electrons delocalized in the ring.]
c. By having 2 of the *p* orbitals of the C–C triple bond co-planar with the *p* orbitals of all the C=C's, the total number of electrons delocalized in the ring is 14. 4(3) + 2 = 14, giving it the right number of electrons to be **aromatic.**

15.21 La velocità di una reazione S_N1 aumenta all'aumentare della stabilità dell'intermedio carbocationico.

increasing reactivity



4 electrons
antiaromatic
very *unstable* intermediate

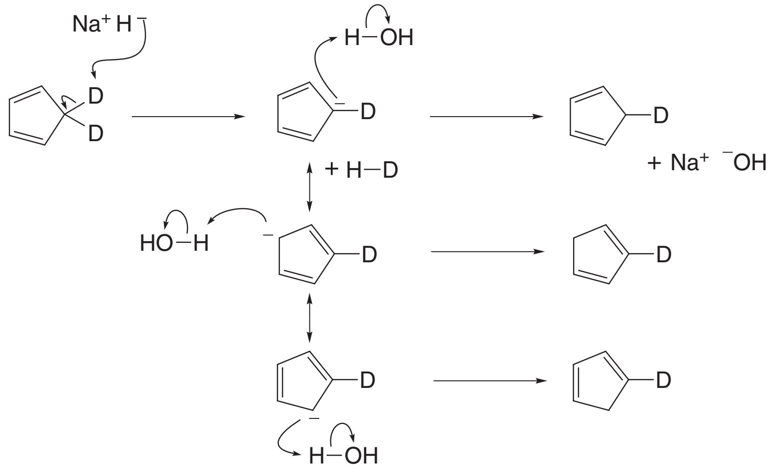
2° carbocation

6 electrons
aromatic
very *stable* intermediate

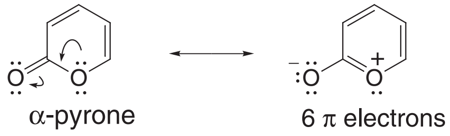
increasing stability

The aromatic carbocation is delocalized over the whole ring making it a very stable intermediate and most easily formed in an S_N1 reaction.

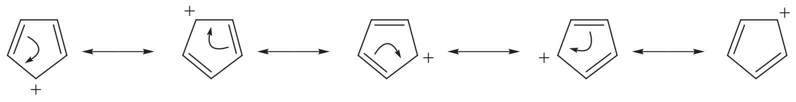
15.22



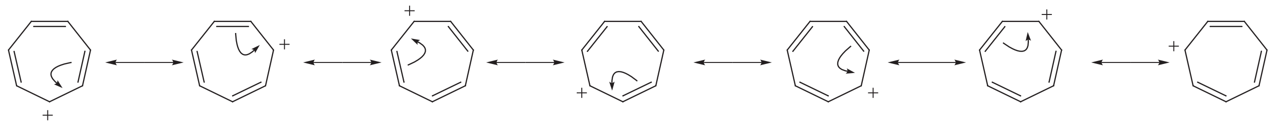
15.23 L'α-pirone reagisce come il benzene perché è aromatico. Può essere disegnata una seconda struttura di risonanza, che mostra come l'anello possieda sei elettroni π. Perciò, l'α-pirone dà le reazioni caratteristiche dei composti aromatici, cioè di sostituzione e non di addizione.



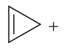
15.24



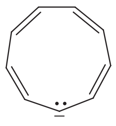
15.25



15.26 Per essere aromatici, gli ioni devono avere, gli ioni devono avere $4n + 2$ eletroni π.

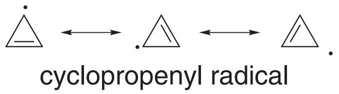
a. 

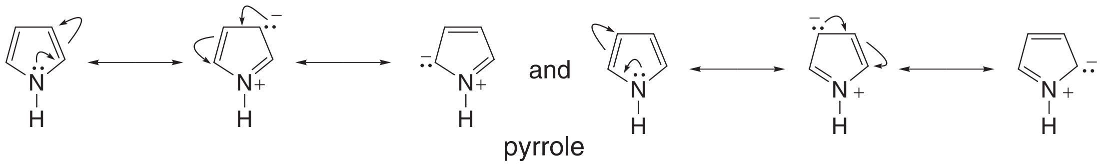
2 π electrons
$4(0) + 2 = 2$
aromatic

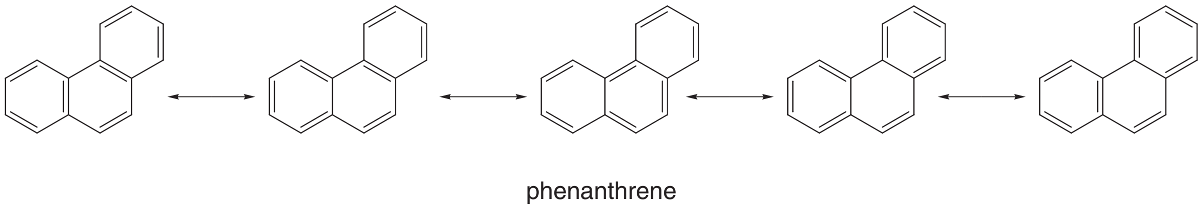
d. 

10 π electrons
$4(2) + 2 = 10$
aromatic

15.27

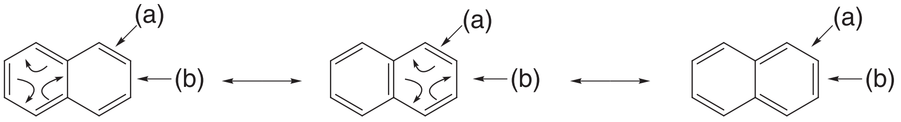
a. 

b. 

c. 

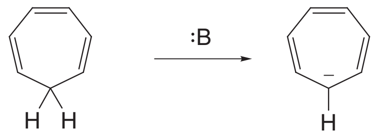
15.28

Naphthalene can be drawn as three resonance structures:



In two of the resonance structures bond (a) is a double bond, and bond (b) is a single bond. Therefore, bond (b) has more single bond character, making it longer.

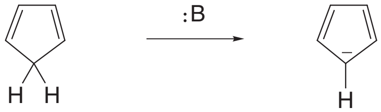
15.29 Confrontare la reazione dell'1,3,5-cicloeptatriene con una base, con quella del ciclopentadiene con una base. Ricordare che il composto con la base coniugata più stabile ha il pK_a più basso.



1,3,5-cycloheptatriene
pK_a = 39

8 π Electrons make this conjugate base especially unstable (**antiaromatic**).

Since the conjugate base is unstable, the pK_a of 1,3,5-cycloheptatriene is **high**.

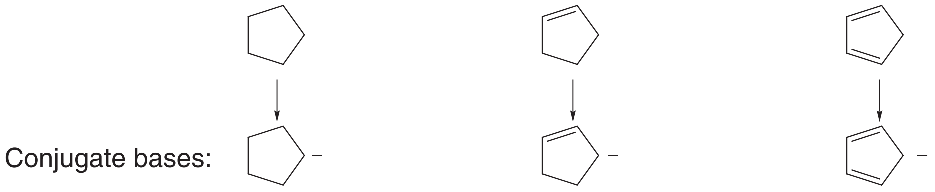


cyclopentadiene

6 π electrons
aromatic conjugate base
very stable anion

Since the conjugate base is very stable, the pK_a of cyclopentadiene is much **lower**.

15.30 Il composto con la base coniugata più stabile è il più acido.



no resonance delocalization

Most unstable base so **least acidic acid.**

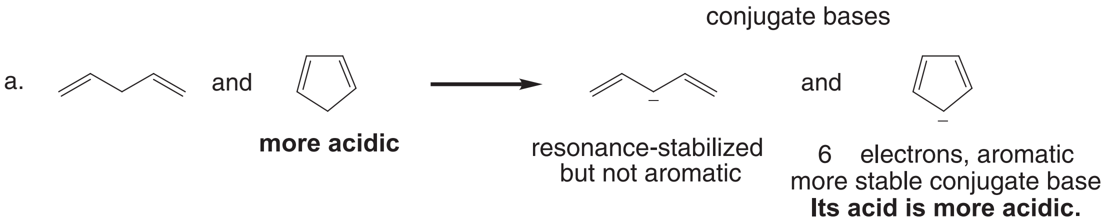
2 resonance structures

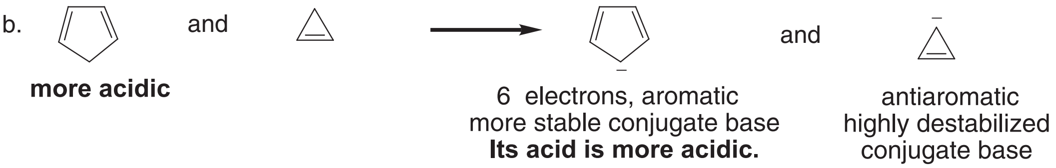
The acid is **intermediate in acidity.**

aromatic conjugate base
most stable

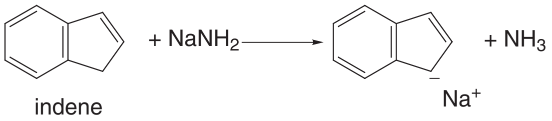
The acid is the **most acidic.**

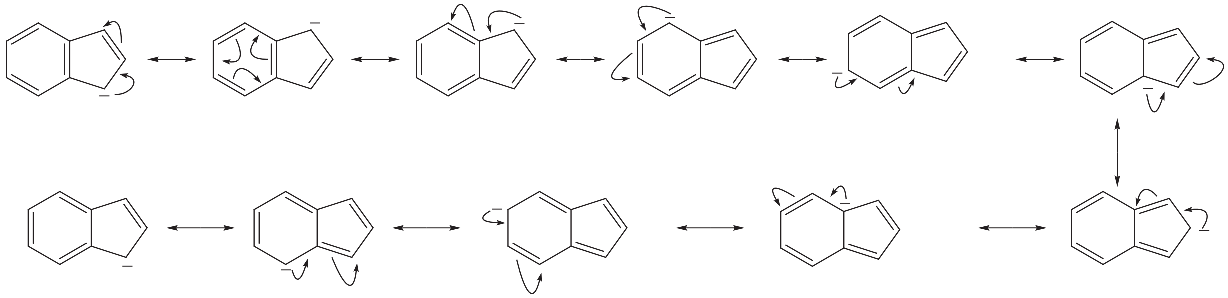
15.31 Il composto con la base coniugata più stabile è un acido più forte. Disegnare e confrontare le basi coniugate di ciascuna coppia di composti.





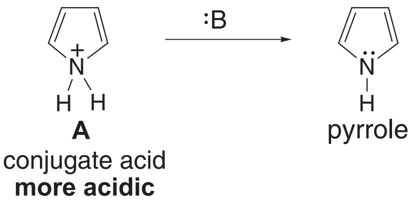
15.32

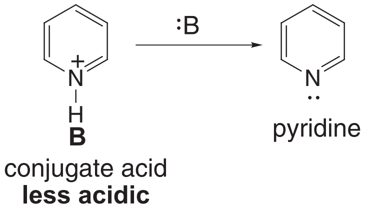




The conjugate base of indene has 10 electrons making it aromatic and very stable. Therefore, indene is more acidic than many hydrocarbons.

15.33

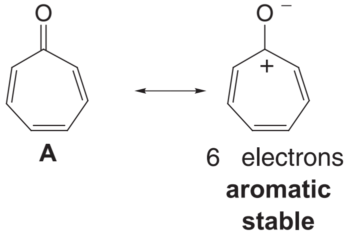


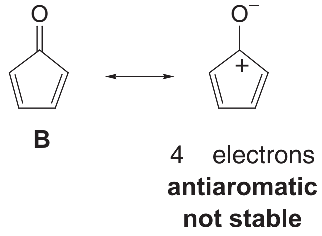


La perdita di un protone da **A** (che non è aromatico) dà due elettroni ad N, così il pirrolo ha sei elettroni π che possono essere delocalizzati nell'anello a cinque termini, rendendolo aromatico. Questo fa sì che la deprotonazione sia un processo altamente favorito.

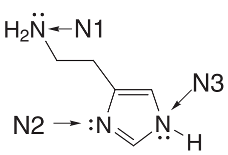
Sia **B** che la sua base coniugata (piridina) sono aromatici. Poiché **B** ha sei elettroni π, è già aromatico, così c'è meno da guadagnare nella deprotonazione, e quindi **B** è meno acido di **A**.

15.34 Una seconda struttura di risonanza per **A** mostra che l'anello è completamente coniugato ed ha 6 elettroni π, e quindi è aromatico e particolarmente stabile. Una simile struttura risonante a separazione di carica per **B** rende l'anello completamente coniugato, ma dà all'anello 4 elettroni π, rendendolo antiaromatico ed instabile.





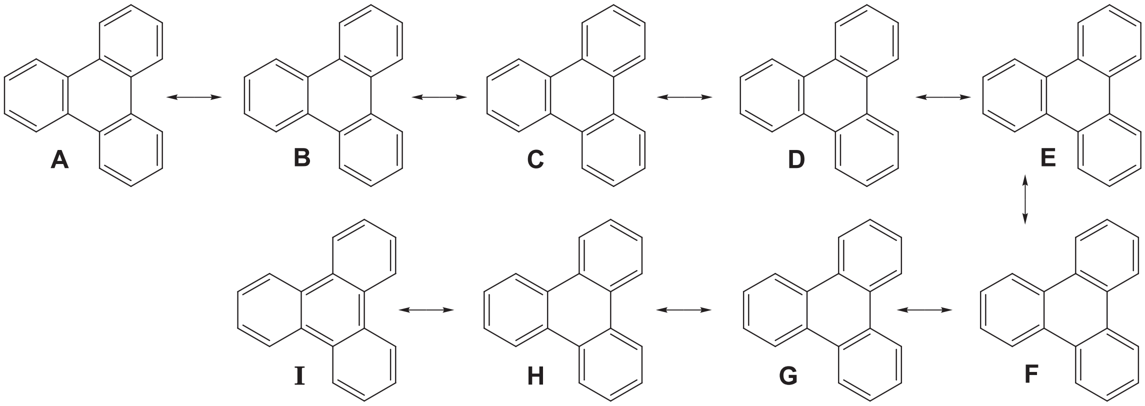
15.35



N1: La coppia elettronica occupa un orbitale ibrido sp^3 su un atomo di N.
N2: La coppia elettronica si trova in un orbitale ibrido sp^2 e non è delocalizzata sull'anello a cinque termini.
N3: La coppia elettronica è in un orbitale *p*, delocalizzata sull'anello a cinque termini, rendendolo aromatico.

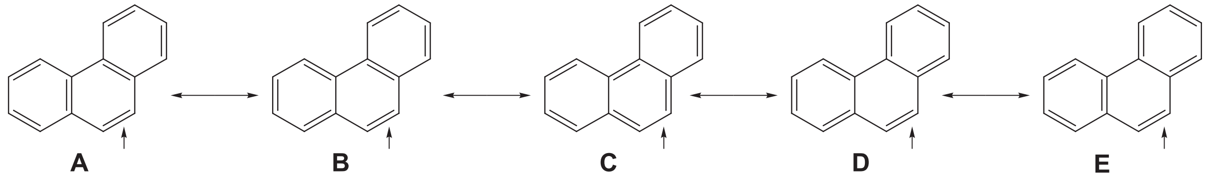
La basicità dipende dalla capacità di un atomo a donare una coppia elettronica. Le coppie elettroniche che sono delocalizzate in un sistema π rendendolo aromatico, sono meno disponibili per la donazione elettronica, e quindi risulta meno basico. La basicità dipende anche dalla percentuale di carattere *s*. Più alta è la percentuale di carattere di *s,* più debole è la base. Gli elettroni sono trattenuti più vicini al nucleo e quindi sono meno disponibili per la donazione elettronica. Perciò, la basicità in ordine crescente è: N3 < N2 < N1.

15.36 Strutture risonanti per il trifenilene:



Tutte le strutture risonanti **A–H** hanno tre legami doppi e tre singoli nei tre anelli esterni a sei termini. Ciò significa che ogni anello si comporta come un benzene isolato, dando sostituzione piuttosto che addizione perché la densità degli elettroni π è delocalizzata in ogni anello a sei termini. Solo la struttura di risonanza **I** non ha questa forma. Ogni legame C–C del trifenilene ha quattro (o cinque) strutture risonanti in cui è un legame singolo e quattro (o cinque) strutture risonanti in cui è un legame doppio.

Strutture risonanti per il il fenantrene:

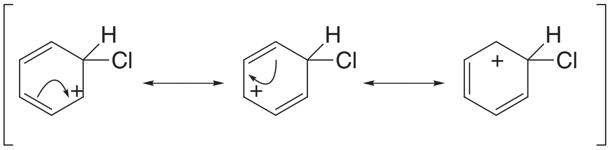


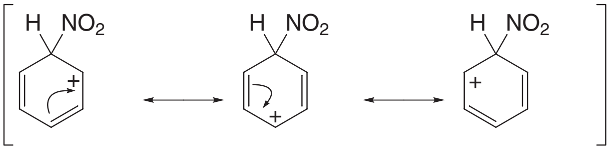
Con il fenantrene, quattro delle cinque strutture risonanti hanno un doppio legame sui carboni indicati (Solo **C** non ne ha). Questo significa che questi due atomi di C hanno un maggior carattere di doppio legame degli altri legami C–C nel fenantrene, rendendoli più soggetti alla reazione di addizione che alla sostituzione.

Capitolo 1 6

16.1 Gli elettroni π del benzene sono delocalizzati sui sei atomi dell'anello, aumentando la stabilità del benzene e risultando meno disponibili per la donazione elettronica. In un alchene, i due elettroni π sono localizzati tra i due atomi di C, che risultano più nucleofili e quindi più reattivi con un elettrofilo rispetto agli elettroni delocalizzati nel benzene.

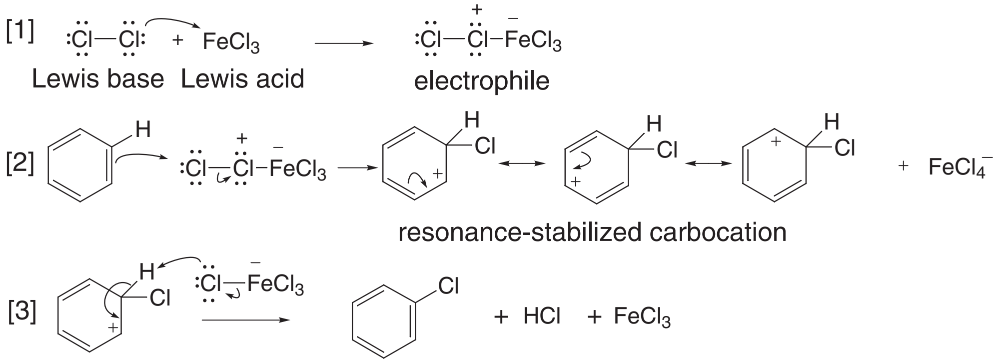
16.2 Quando si disegnano le strutture di risonanza, la carica è sempre posizionata in orto o para ad uno degli atomi dell'anello ibridati *sp*^{3}.

a. 

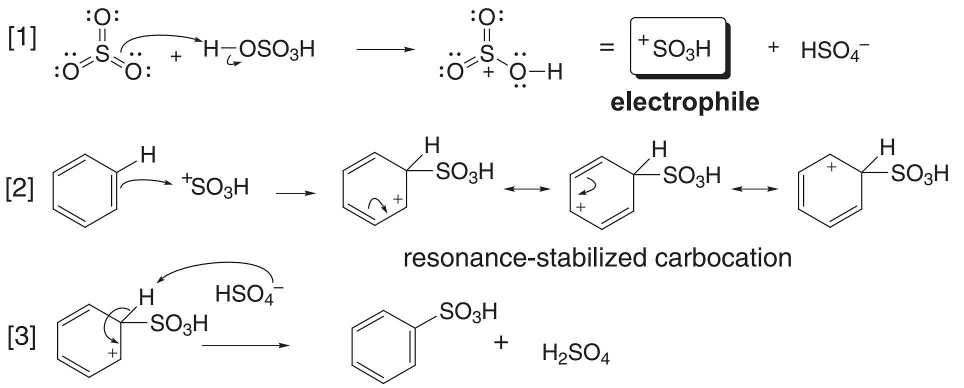
b. 

16.4

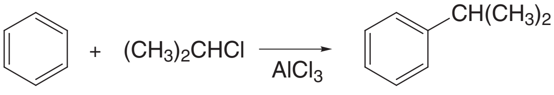
16.5 L'addizione di Cl_2 con $FeCl_3$ come catalizzatore avviene in due parti. La prima è la formazione di un elettrofilo, seguita da una reazione di sostituzione in due stadi.



16.6 Nel meccanismo ci sono due parti. La prima parte è la formazione di un elettrofilo. La seconda parte è una reazione di sostituzione in due stadi.



16.7 L'alchilazione di Friedel–Crafts consiste nel trasferimento di un gruppo alchilico da un alogeno all'anello benzenico. Nell'acilazione di Friedel–Crafts un gruppo acilico è trasferito da un alogeno all'anello benzenico.

a.


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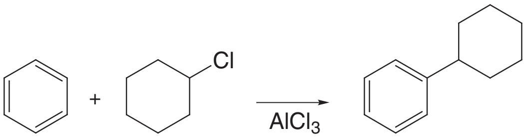

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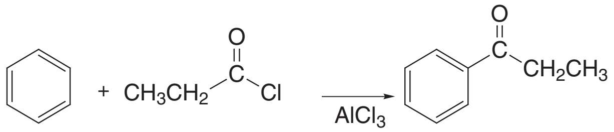
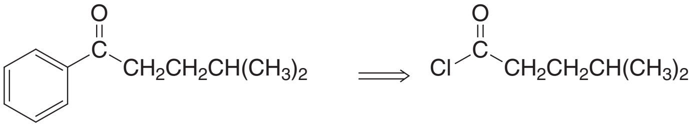


16.8 Ricordare che un gruppo acilico è trasferito da un atomo di Cl all'anello benzenico. Per disegnare il cloruro acilico, sostituire un Cl all'anello del benzene.

a.


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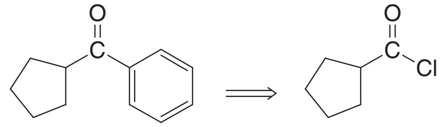

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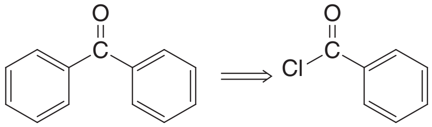
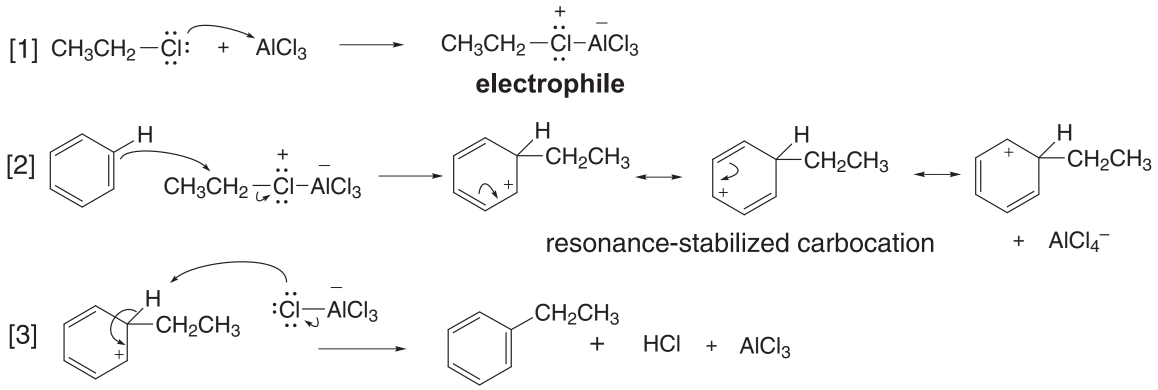
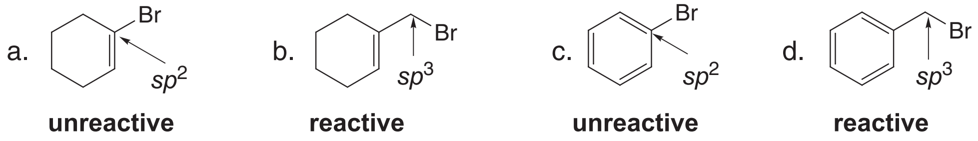


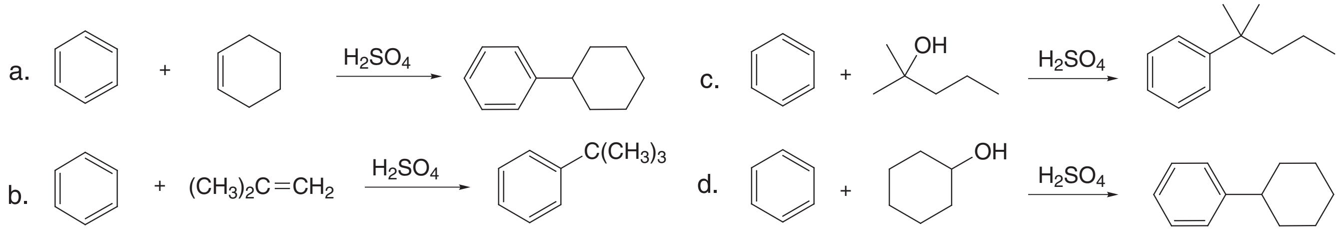
16.9



16.10 Per reagire in una reazione di alchilazione di Friedel–Crafts, X deve essere legato ad un atomo di carbonio ibridato *sp*^{3}.



16.11 Sia gli alcheni che gli alcoli possono formare carbocationi per le reazioni di alchilazione di Friedel–Crafts.



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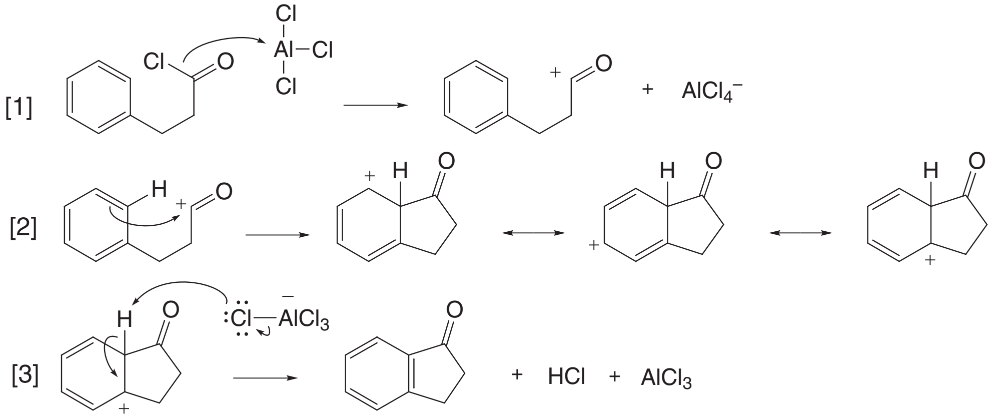
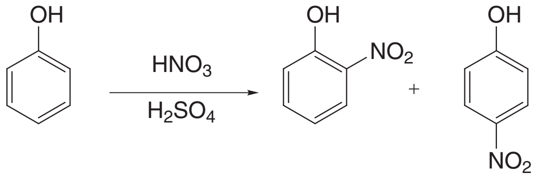


16.13 L'OH è orto, para orientante.

a.


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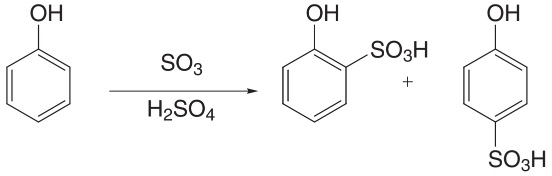

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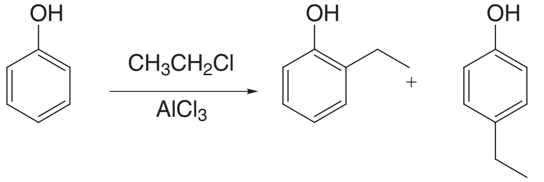

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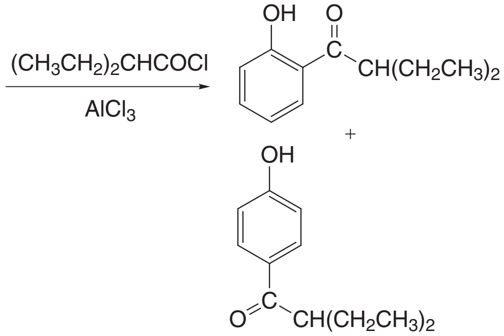

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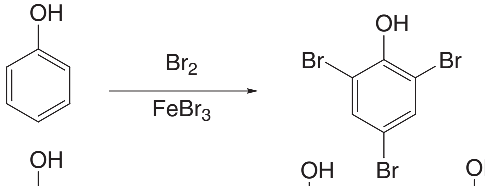

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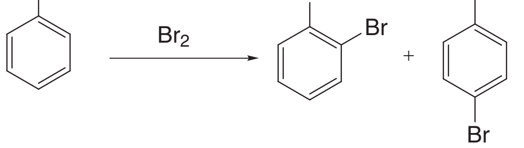

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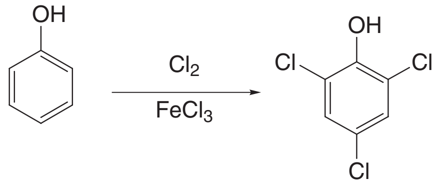

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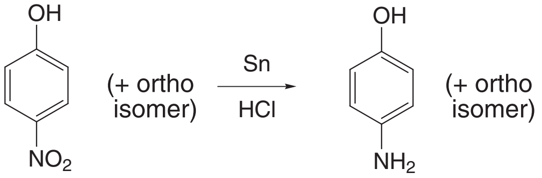

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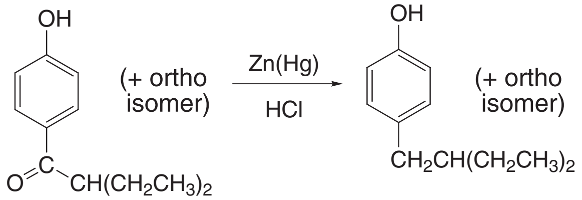

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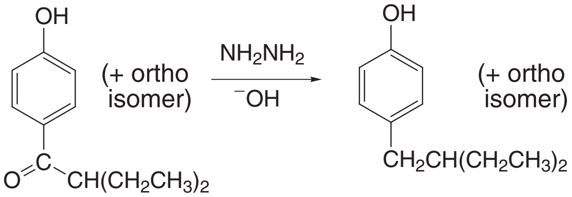

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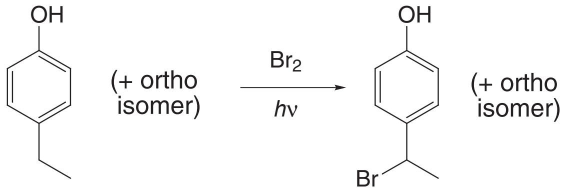
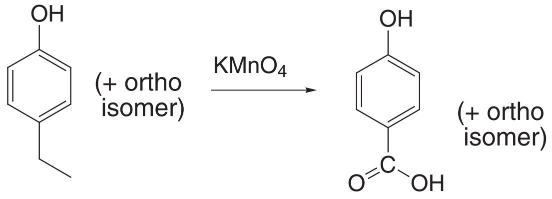
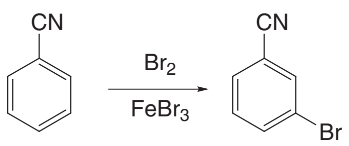


l.


16.14 CN è meta orientante che disattiva l'anello del benzene.

a.


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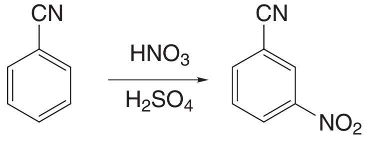
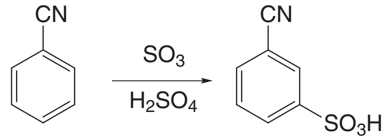


c.


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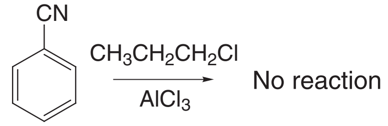

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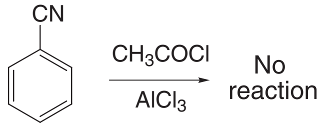
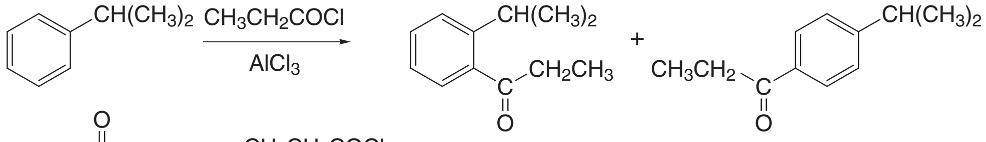
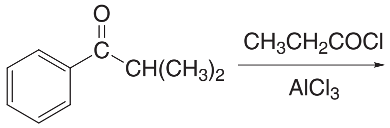


16.15

a.

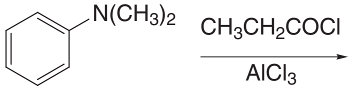


b.



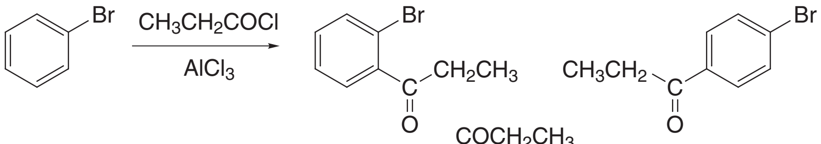
no reaction

c.



no reaction

d.



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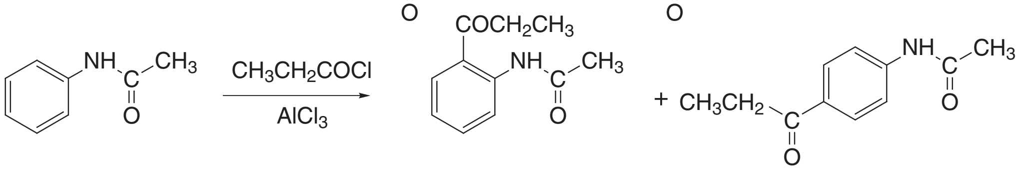
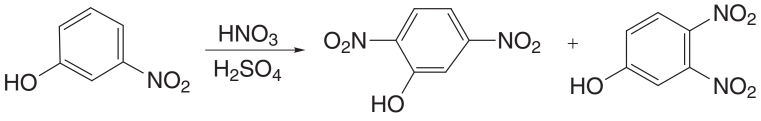


16.16

a.



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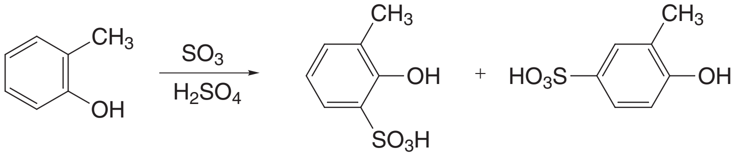

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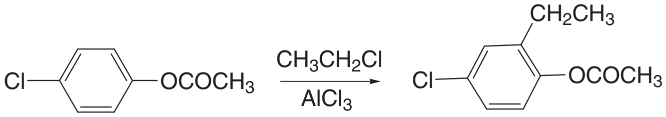

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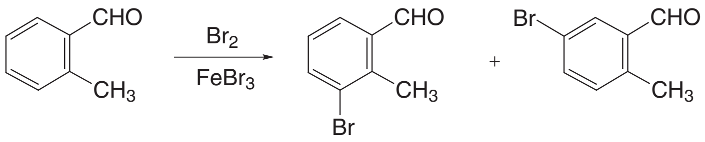

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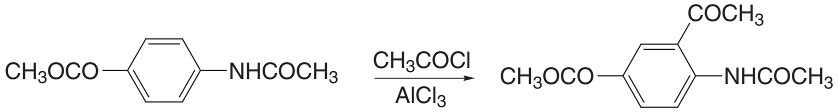

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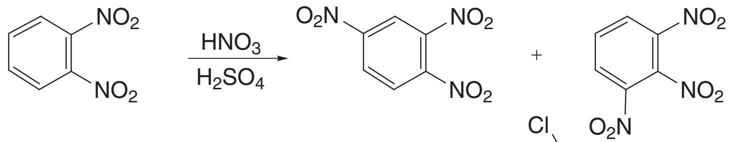
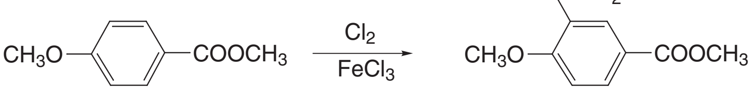


g.



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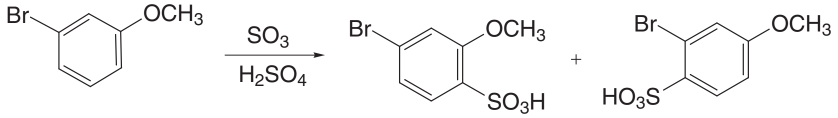
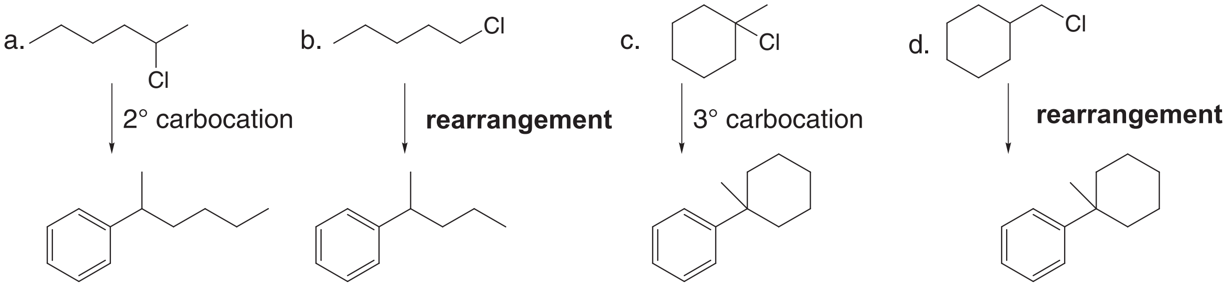


16.17 Tenere conto dei riarrangiamenti.



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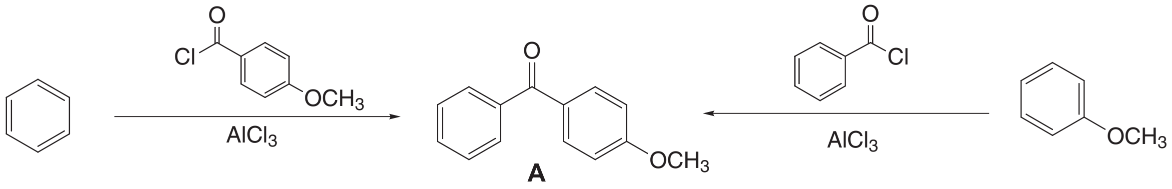
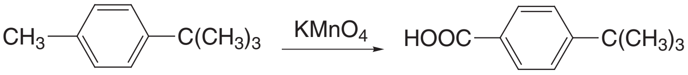


16.19

a.



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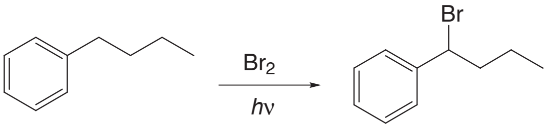

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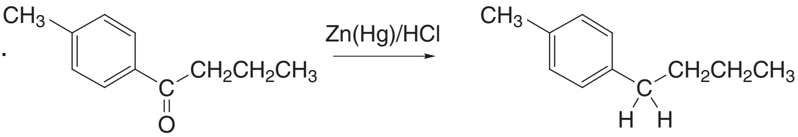

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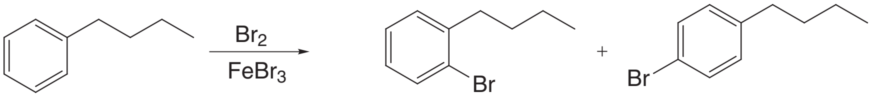

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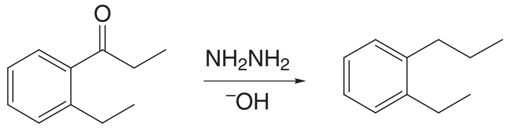

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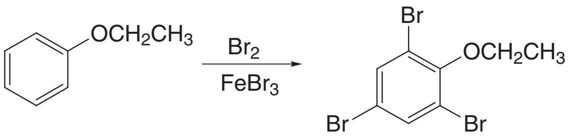
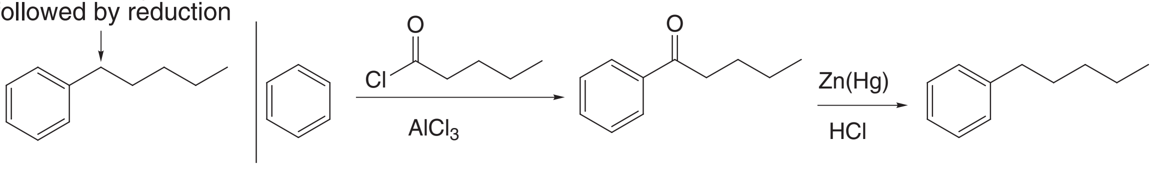


16.20

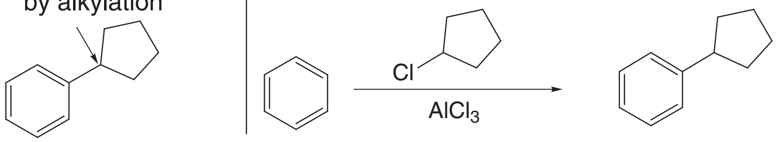
C bonded to 2 H's must use acylation followed by reduction

a.

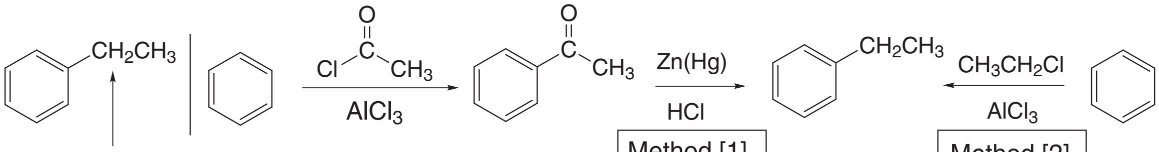


C bonded to 1H can be added directly by alkylation

b.



c.



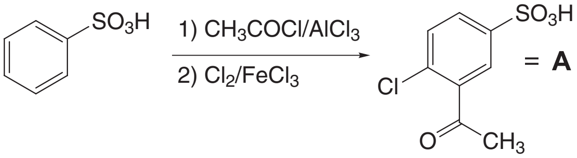
Method [1]

Method [2]

Ethyl group can be introduced by two methods.

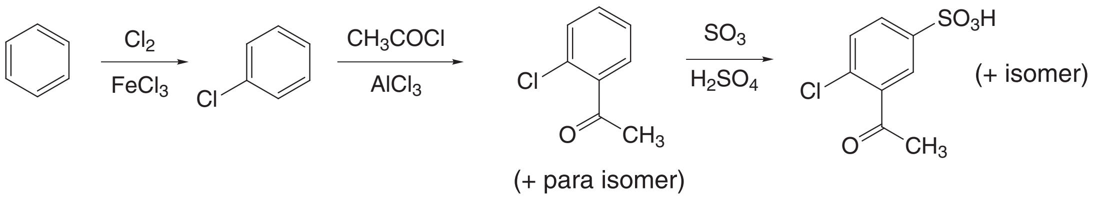
16.21

a.



Step [1] won't work because a Friedel–Crafts reaction can't be done on a deactivated benzene ring, as is the case with the SO_3H substituent. Even if Step [1] did work, the second step would introduce Cl meta to SO_3H, not para as drawn.

Alternate synthesis:



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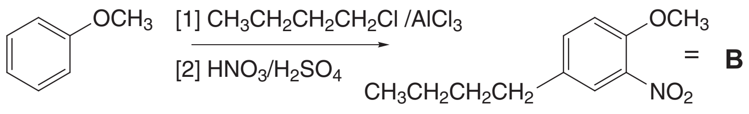
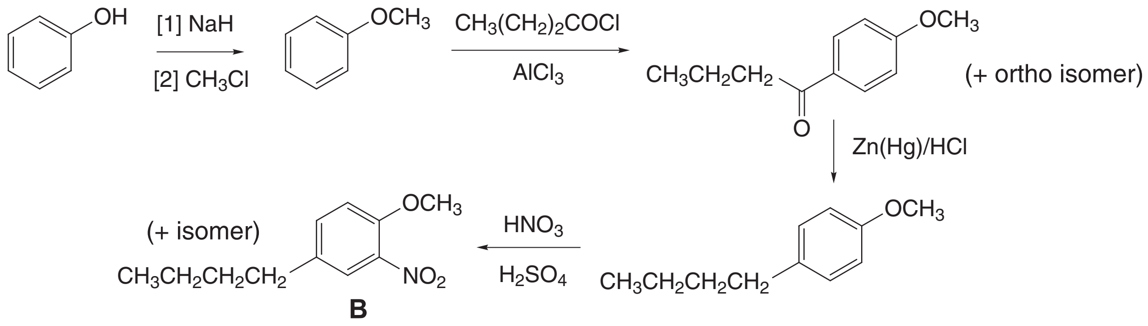


Step [1] involves a Friedel–Crafts alkylation using a 1^o alkyl halide that will undergo rearrangement, so that a butyl group will not be introduced as a side chain.

Alternate synthesis:



16.22

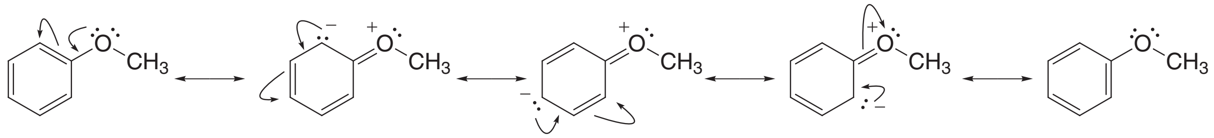
a. $-CH_2CH_2CH_2CH_3$
alkyl group
electron donating

b. $-Br$
halide
electron withdrawing

c. $-OCH_2CH_3$
electronegative O
electron withdrawing

16.23 I gruppi elettron donatori posizionano una carica negativa sull'anello del benzene. Disegnare le strutture di risonanza per mostrare come $-OCH_3$ posiziona una carica negativa sull'anello. I gruppi elettron attrattori collocano una carica positiva sul benzene. Disegnare le strutture di risonanza per mostrare come $-COCH_3$ posiziona una carica positiva sull'anello.

a.



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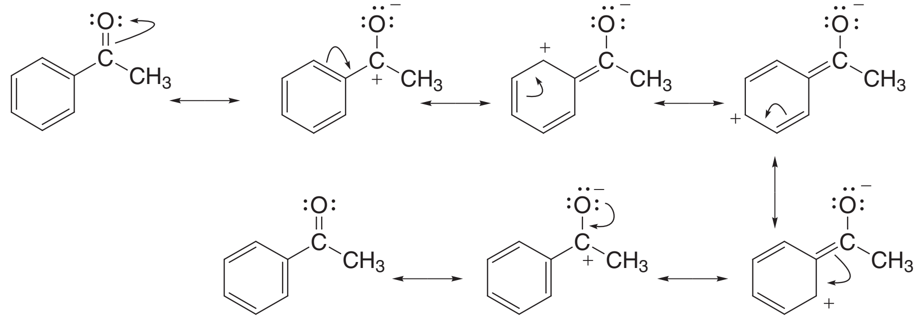
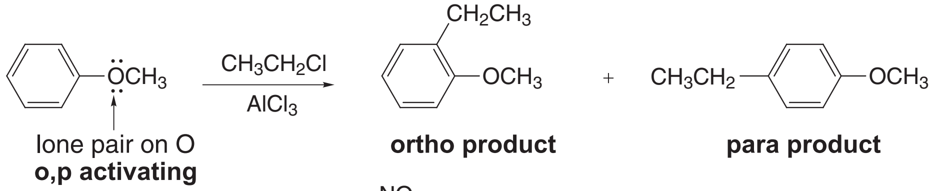


16.24 Prima classificare i composti di partenza come: orto, para attivanti, orto, para disattivanti, o meta disattivanti. Quindi disegnare i prodotti.

a.



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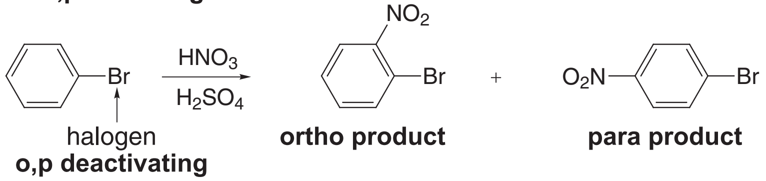
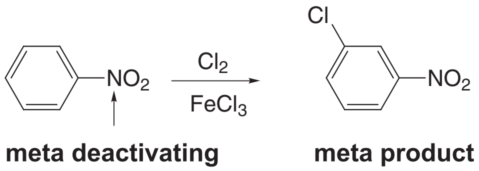
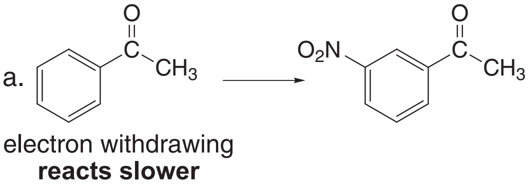


c.

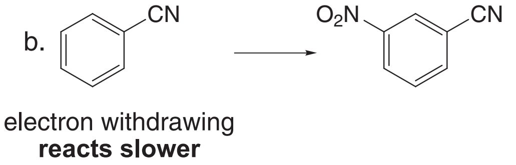


16.25 **I gruppi elettron-donatori** fanno reagire il composto ***più velocemente*** del benzene nelle reazioni di sostituzione elettrofila aromatica. **I gruppi elettron-attrattori** fanno reagire il composto ***più lentamente*** del benzene nelle reazioni di sostituzione elettrofila aromatica.

a.



b.



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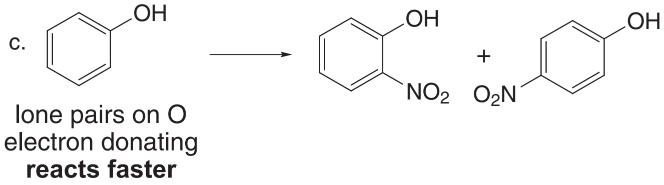
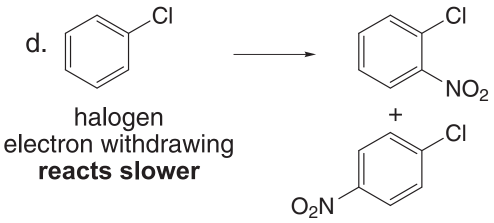


d.



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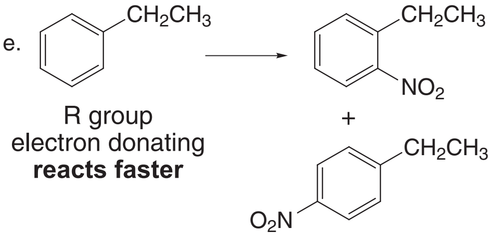
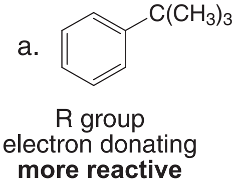
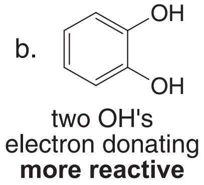


16.26 **I gruppi elettron-donatori** rendono il composto ***più reattivo*** del benzene nelle reazioni di sostituzione elettrofila aromatica. **I gruppi elettron-attrattori** rendono il composto ***meno reattivo*** del benzene nelle reazioni di sostituzione elettrofila aromatica.

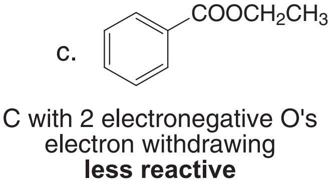
a.



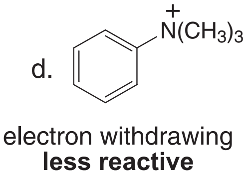
b.



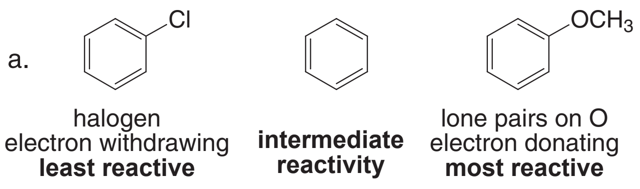
c.



d.



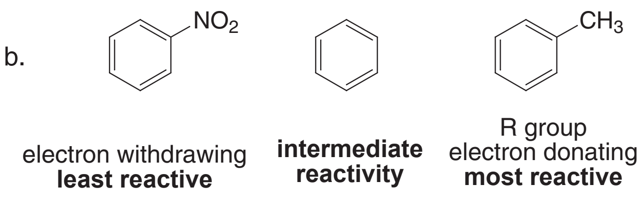
16.27



halogen
electron withdrawing
least reactive

intermediate reactivity

lone pairs on O
electron donating
most reactive

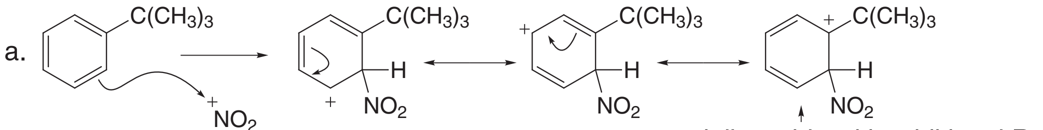


electron withdrawing
least reactive

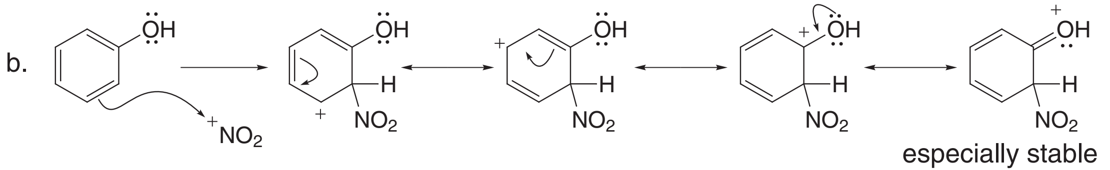
intermediate reactivity

R group
electron donating
most reactive

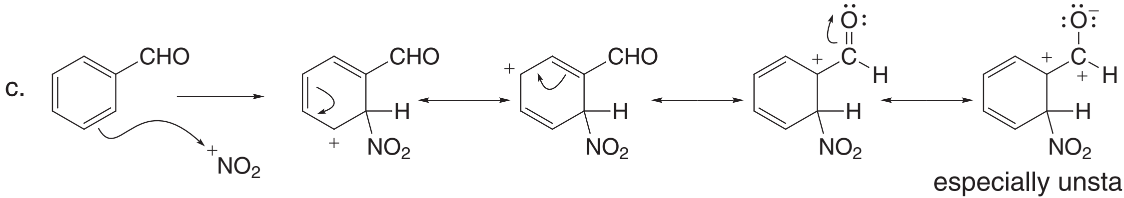
16.28 Strutture risonanti particolarmente stabili hanno tutti gli atomi con un ottetto. I carbocationi con più gruppi R elettron-donatori sono anche strutture più stabili. Strutture risonanti particolarmente instabili hanno cariche adiacenti uguali.



especially stable with additional R group
stabilized carbocation

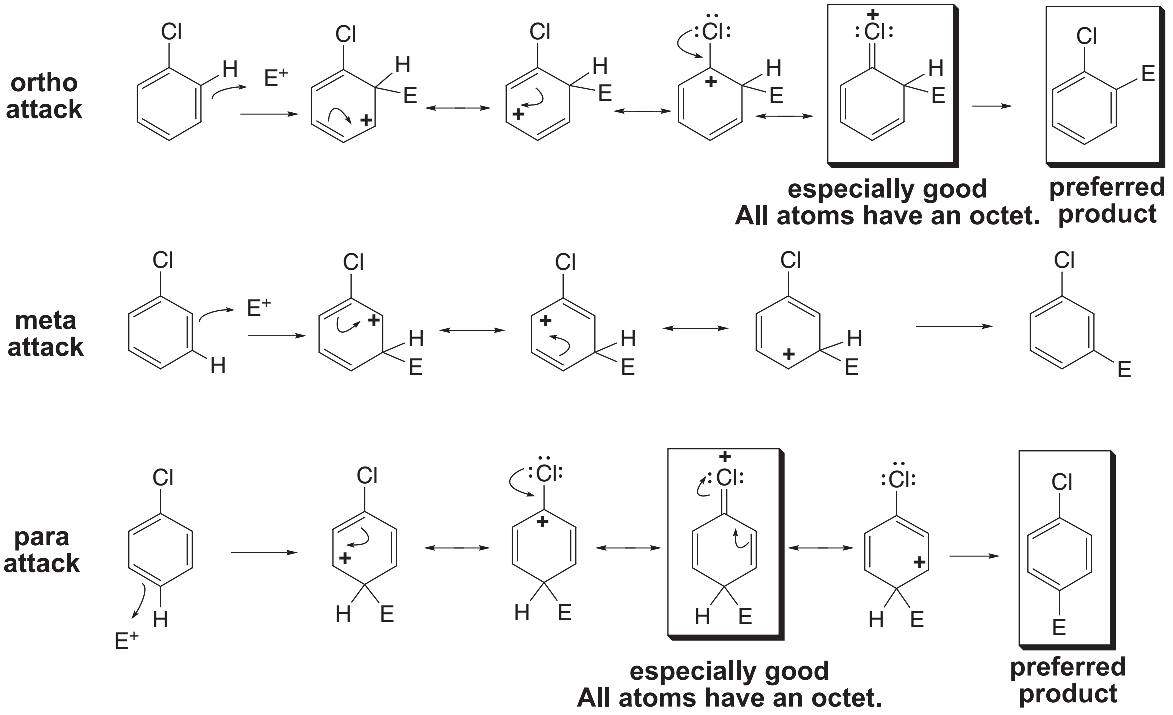


especially stable
all atoms have an octet



especially unstable
2 adjacent + charges

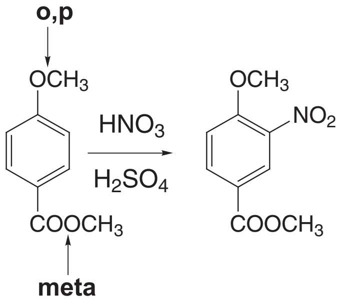
16.29



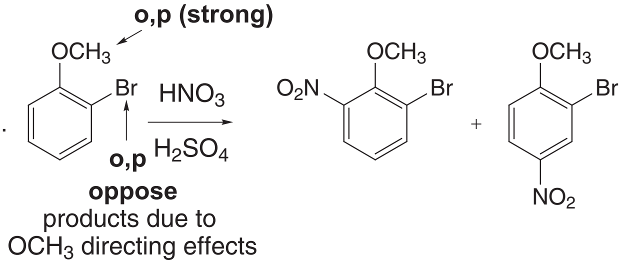
16.30 Per disegnare il prodotto di reazione con HNO_3/H_2SO_4 ed i derivati benzenici disostituiti ricordare:

- Se i due effetti orientanti si rinforzano a vicenda, il nuovo sostituente sarà collocato nella posizione attivata da entrambi.
- Se gli effetti orientanti sono opposti, predomina l'effetto del gruppo attivante più forte.
- Non avviene nessuna sostituzione tra due sostituenti in meta.

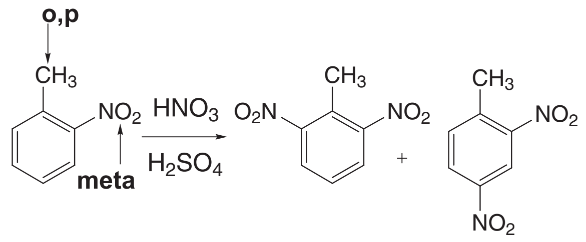
a.



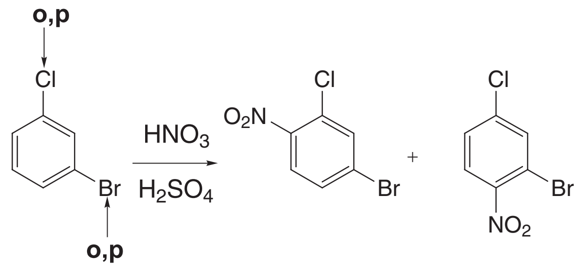
b.



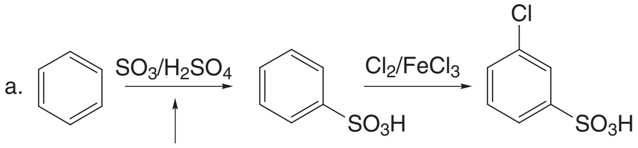
c.



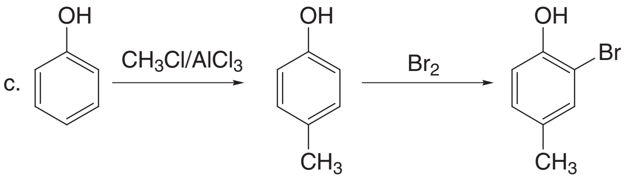
d.



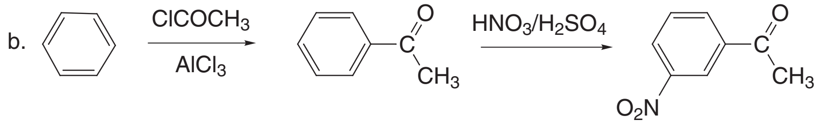
16.31



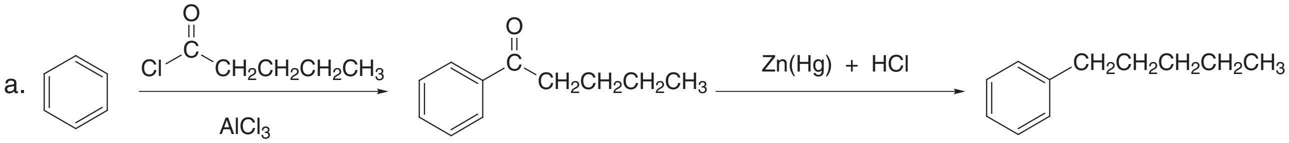
Put meta director on first.

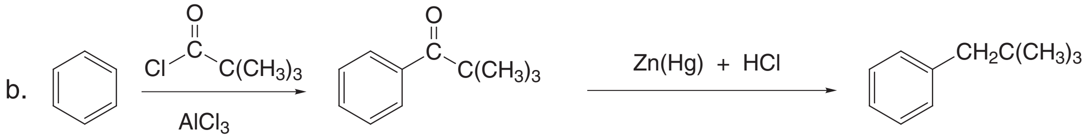


(+ ortho isomer) Br goes ortho to the stronger activator.



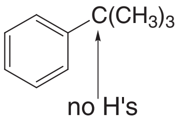
16.32 Prima usare una reazione di acilazione, e quindi ridurre il gruppo carbonilico per formare l'alchil benzene.



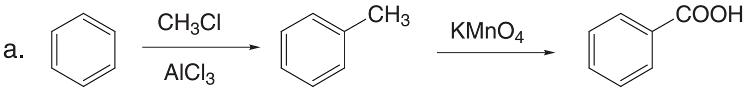


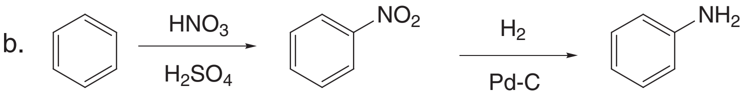
16.33

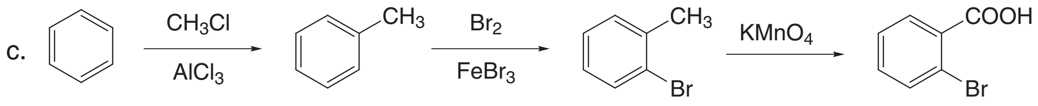
$C_6H_5C(CH_3)_3$ cannot be made by Friedel–Crafts acylation because there are no benzylic hydrogens. All products of Friedel–Crafts acylation followed by reduction have two benzylic hydrogens where the C=O was reduced. $C_6H_5C(CH_3)_3$ can be made by Friedel–Crafts alkylation using $(CH_3)_3CCl$ and $AlCl_3$.



16.34



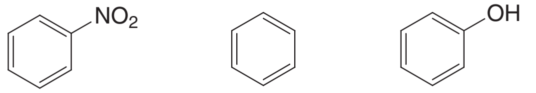




(+ para isomer)

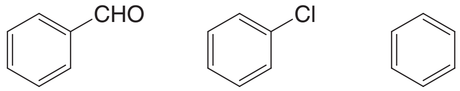
16.35 Usare le indicazioni della risposta 16.26 per mettere in ordine i composti.

a.



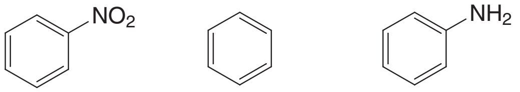
least reactive **intermediate reactivity** **most reactive**

b.



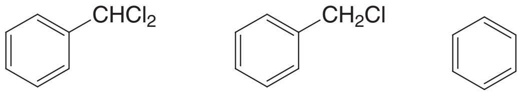
least reactive **intermediate reactivity** **most reactive**

c.



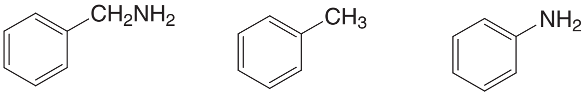
least reactive **intermediate reactivity** **most reactive**

d.



least reactive **intermediate reactivity** **most reactive**

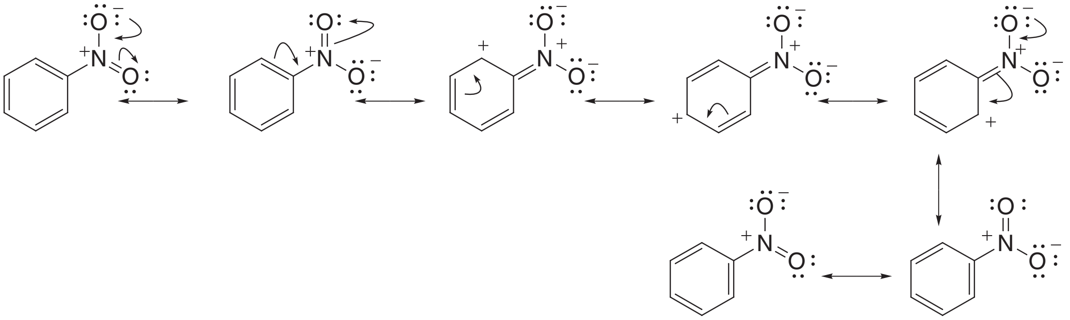
e.



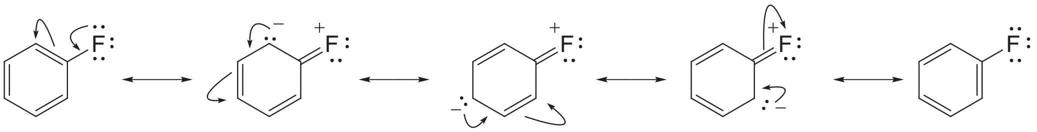
least reactive **intermediate reactivity** **most reactive**

16.36 Gruppi elettron-attrattori delocalizzano una carica positiva sull'anello benzenico. Disegnare le strutture di risonanza per mostrare come NO_2 colloca una carica positiva nell'anello, generando un effetto di risonanza elettron-attrattore. Gruppi elettron-donatori delocalizzano una carica negativa sull'anello benzenico. Disegnare le strutture di risonanza per mostrare come F colloca una carica negativa nell'anello, generando un effetto di risonanza elettron-donatore.

a.

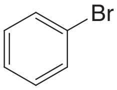


b.

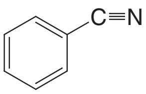


16.37

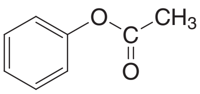
[1]



[2]



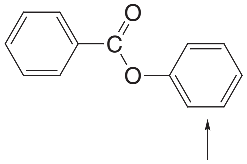
[3]



[1]	[2]	[3]
a. withdraw	a. withdraw	a. withdraw
b. donate	b. wtihdraw	b. donate
c. less	c. less	c. more
d. deactivate	d. deactivate	d. activate

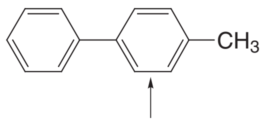
16.38

a.



more electron rich
due to O atom
more reactive

b.

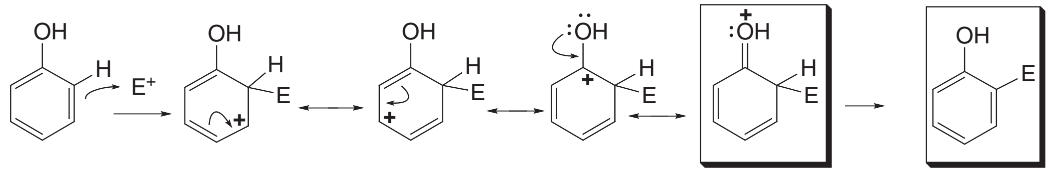


more electron rich
due to CH_3 group
more reactive

16.39

a.

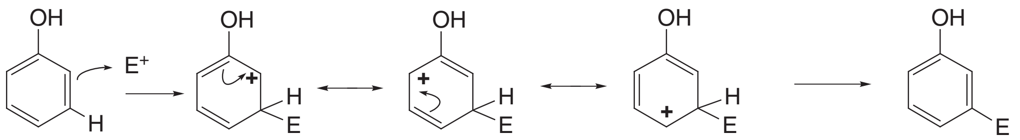
ortho attack



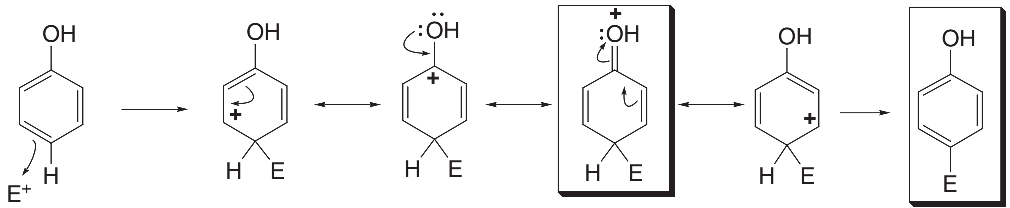
especially good
All atoms have an octet.

preferred product

meta attack



para attack

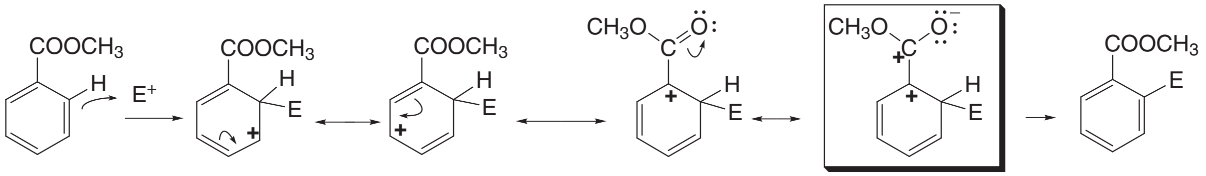


especially good
All atoms have an octet.

preferred product

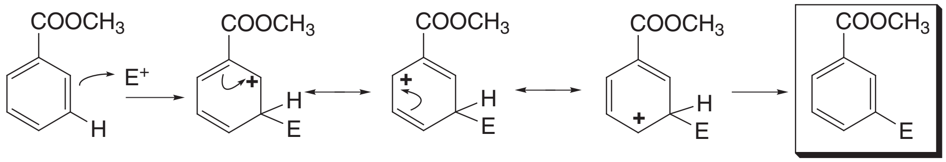
b.

ortho attack



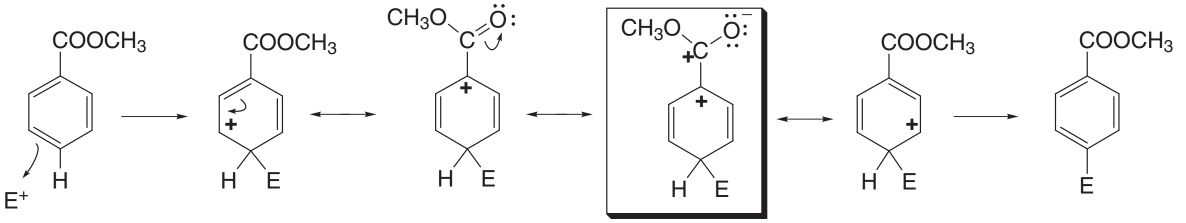
destabilized
two adjacent like charges

meta attack



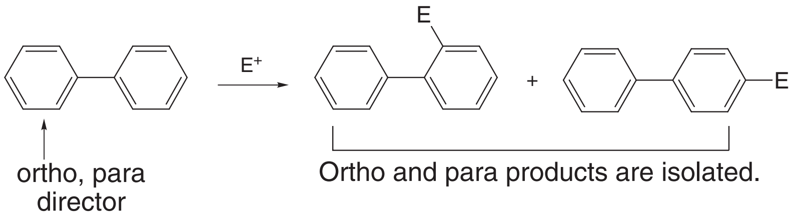
preferred product

para attack



destabilized
two adjacent like charges

16.40



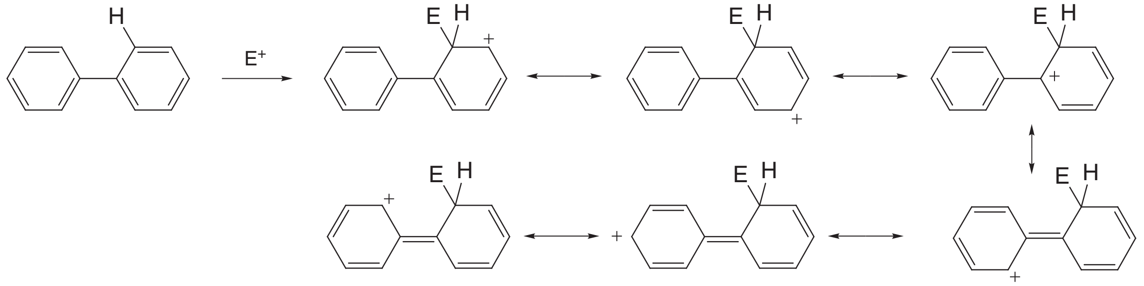
ortho, para director

Ortho and para products are isolated.

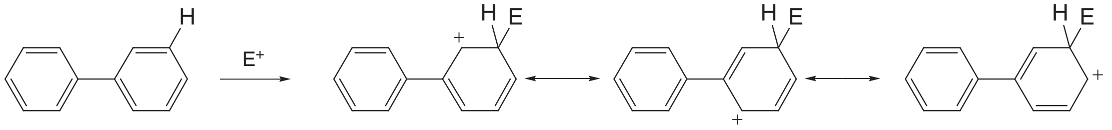
A benzene ring is an electron rich substituent that stabilizes an intermediate positive charge by an electron donating resonance effect. As a result, it activates a benzene ring toward reaction with electrophiles.

With ortho and para attack there is additional resonance stabilization that delocalizes the positive charge onto the second benzene ring. Such additional stabilization is not possible with meta attack.

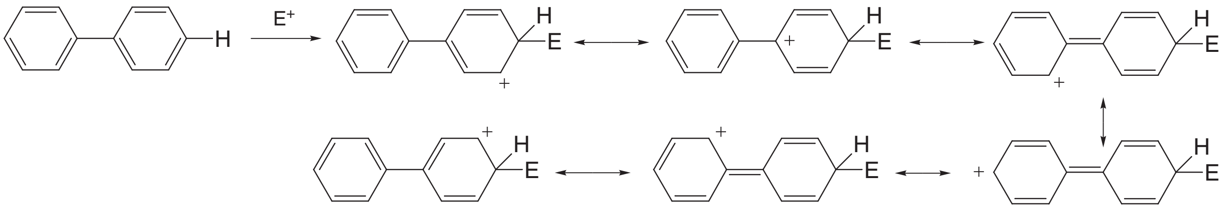
Ortho attack:



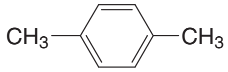
Meta attack:



Para attack:

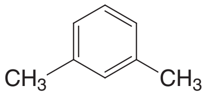


16.41



p-xylene

slower

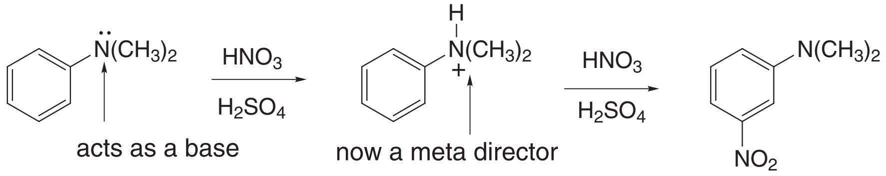


m-xylene

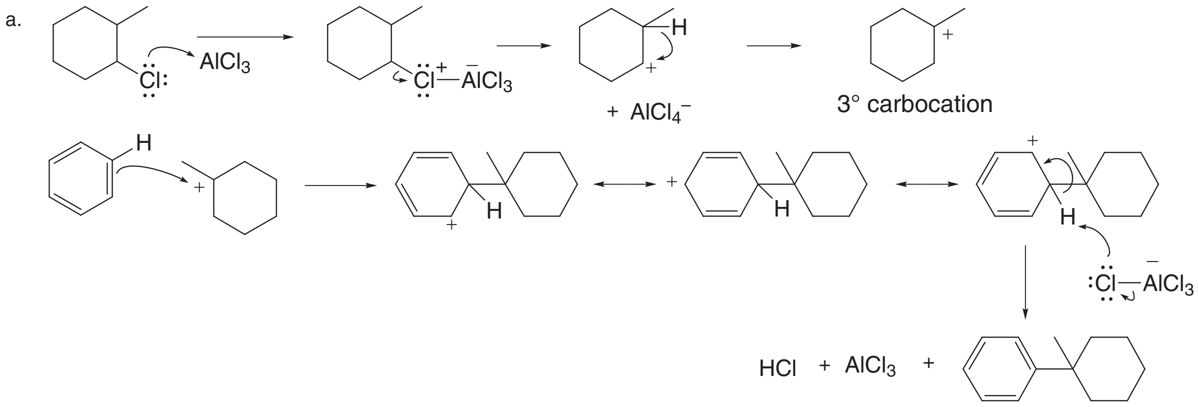
faster

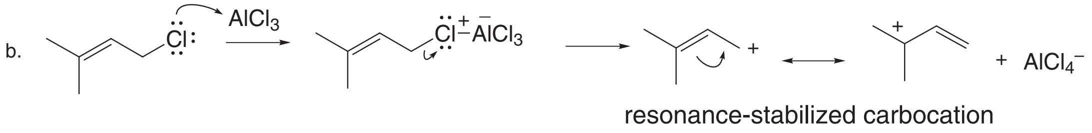
CH_3 is an ortho, para director. In *m*-xylene, the directing effects of the two CH_3 groups reinforce each other, making it react faster. In *p*-xylene, the two groups activate different C's, so the reaction is slower.

16.42 Nelle condizioni acide della nitrazione, l'atomo di N del composto di partenza risulta protonato, così l'atomo direttamente legato all'anello del benzene ha una carica (+). Questo lo rende meta orientante, e perciò il gruppo NO_2 attacca in posizione meta.

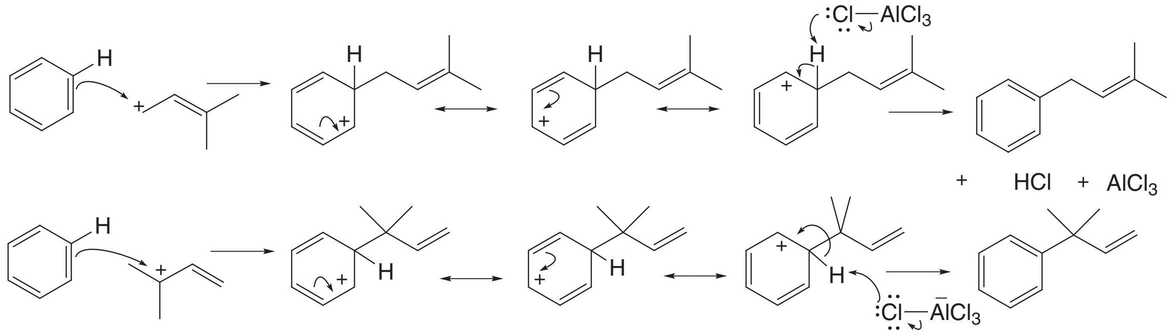


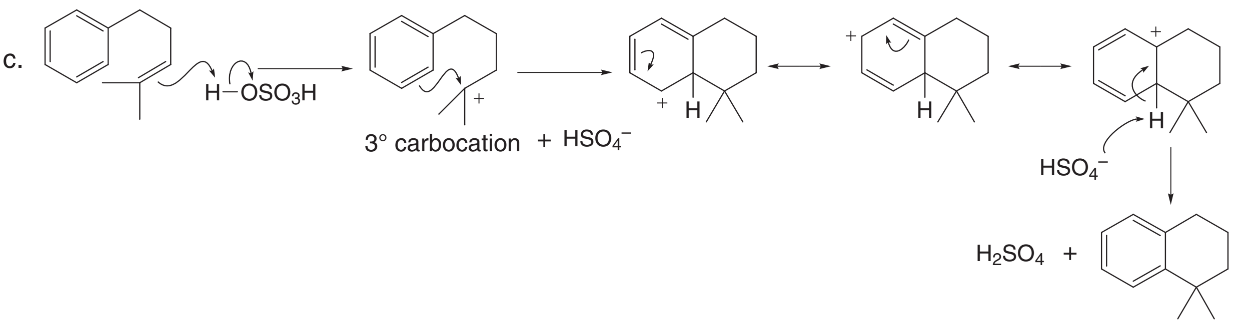
16.43





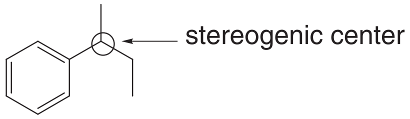
Use both resonance forms to show how two products are formed.



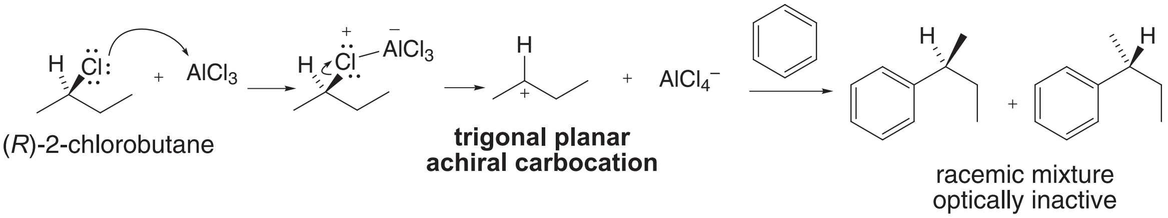


16.44

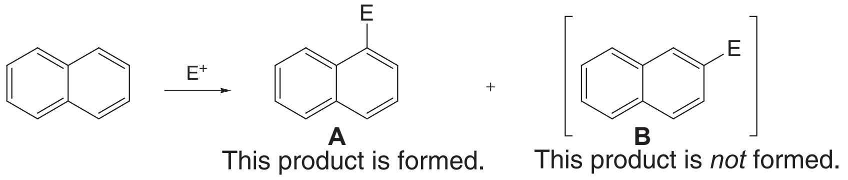
a. The product has one stereogenic center.

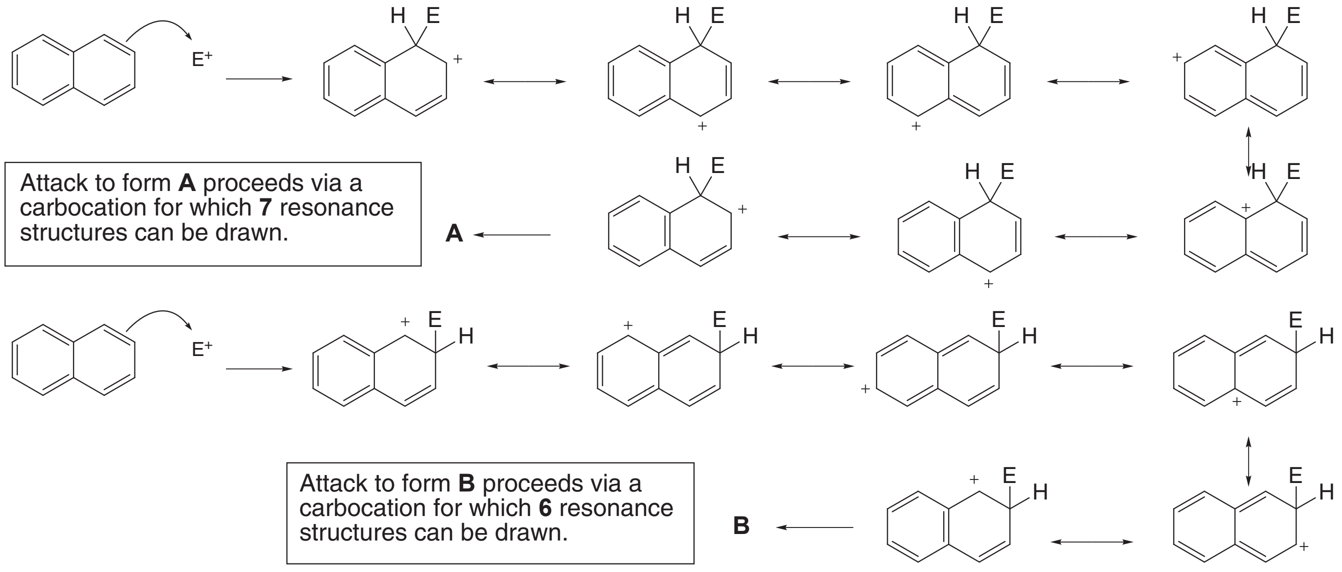


b. The mechanism for Friedel–Crafts alkylation with this 2° halide involves formation of a trigonal planar carbocation. Since the carbocation is achiral, it reacts with benzene with equal probability from two possible directions (above and below) to afford an optically inactive, racemic mixture of two products.



16.45



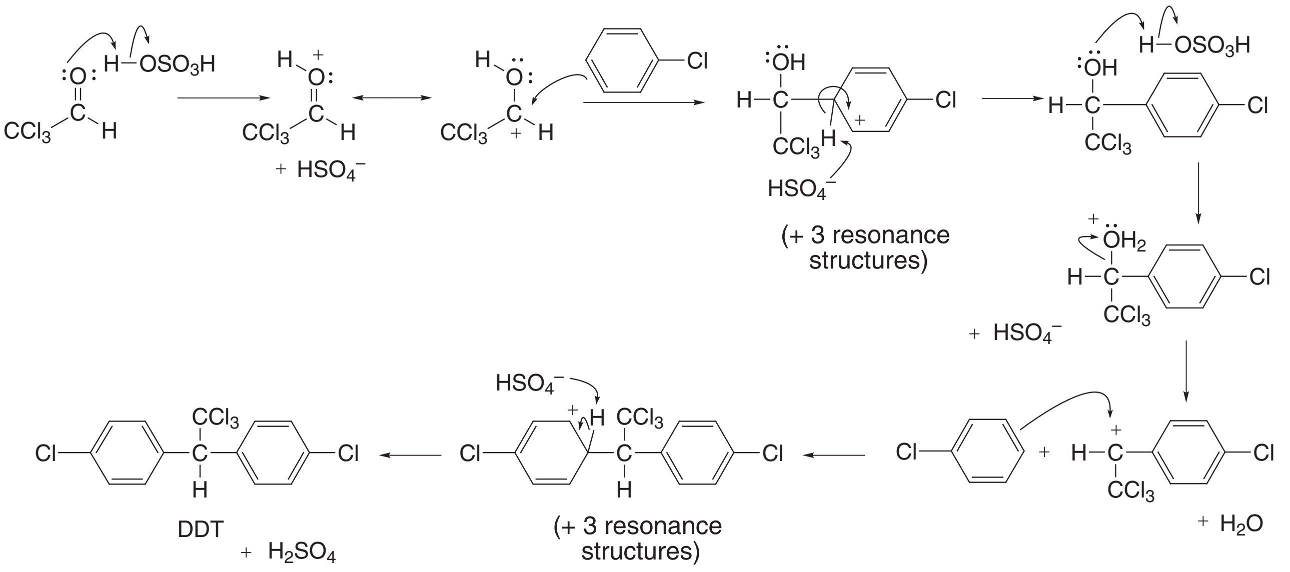


Attack to form **A** proceeds via a carbocation for which **7** resonance structures can be drawn.

Attack to form **B** proceeds via a carbocation for which **6** resonance structures can be drawn.

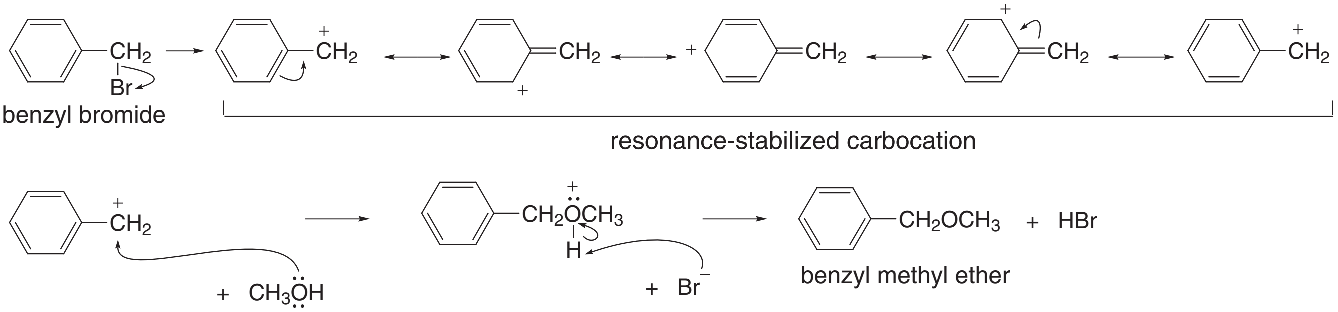
A reaction that occurs by way of the more stable carbocation is preferred so product **A** is formed.

16.46

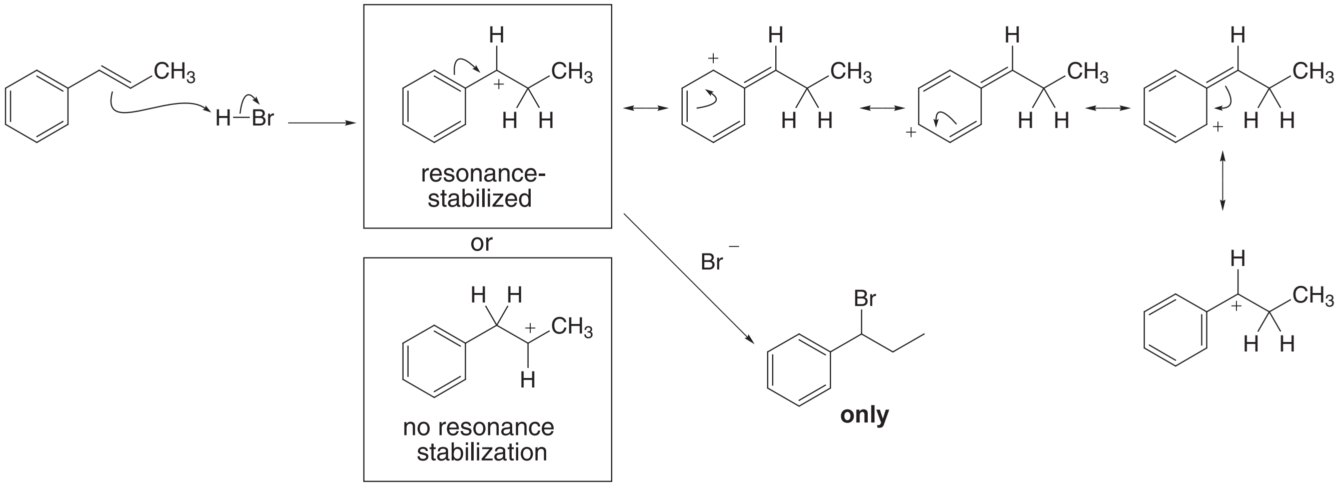


16.47 Il bromuro di benzile forma un intermedio stabilizzato per risonanza, che gli permette di reagire rapidamente in condizioni che favoriscono la S_N1.

Formation of a resonance-stabilized carbocation:

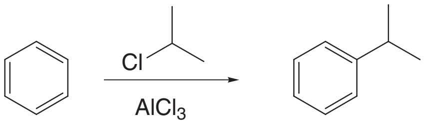


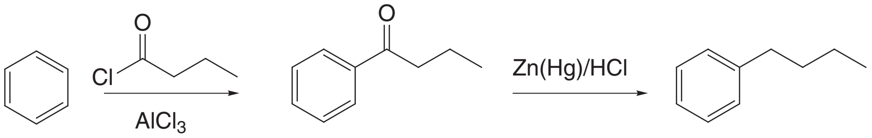
16.48 L'addizione di HBr forma soltanto un bromuro alchilico, perché l'intermedio carbocationico che porta alla sua formazione è stabilizzato per risonanza.

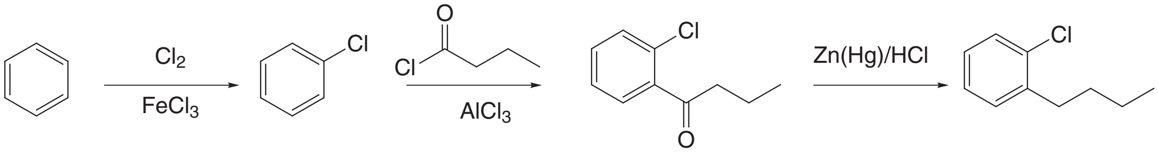


As a result, this carbocation does not form.

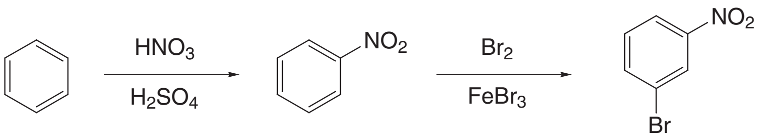
16.49

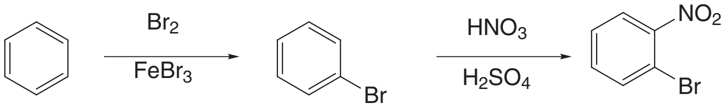
a.


b.


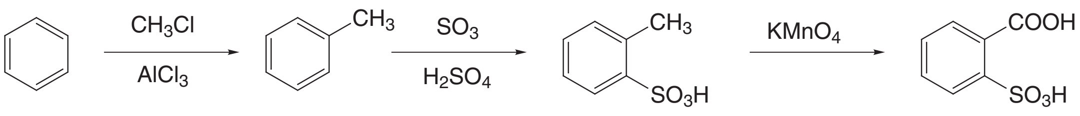
c.


(+ para isomer)

d.


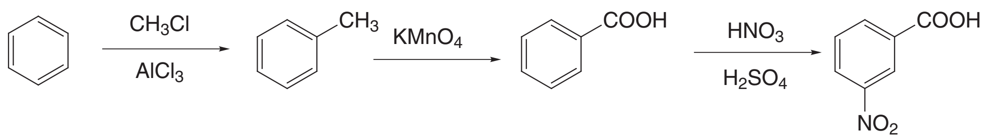
e.


(+ para isomer)

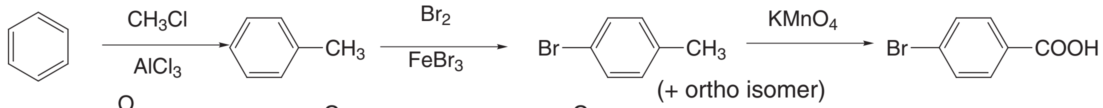
f.


(+ para isomer)

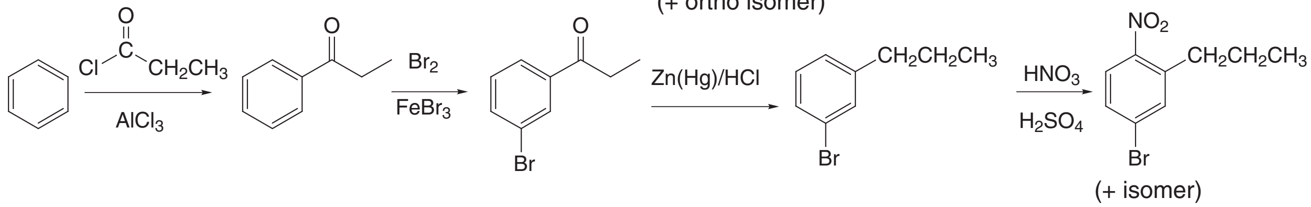
g.



h.

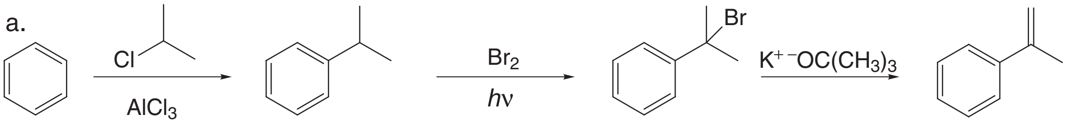


i.

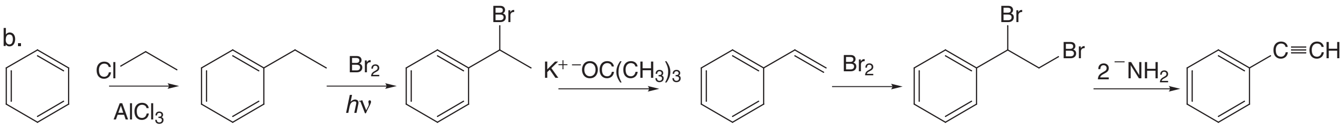


16.50

a.

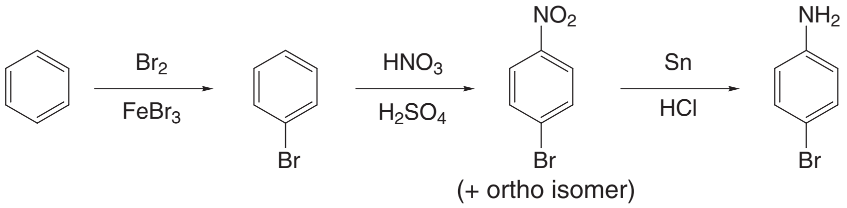


b.

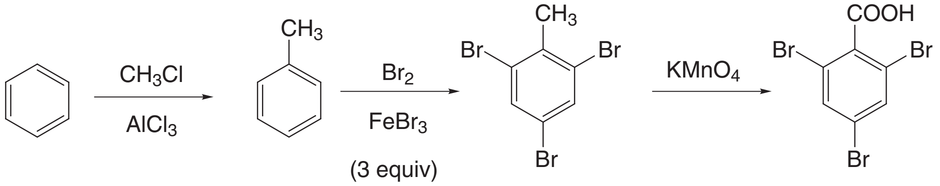


16.51

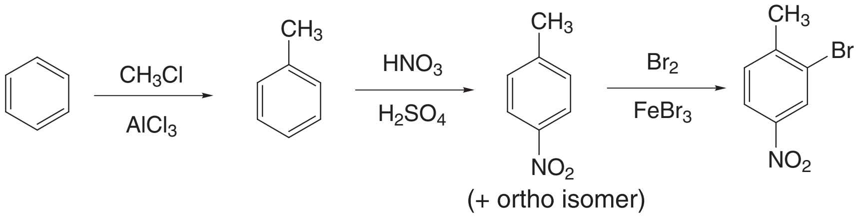
a.



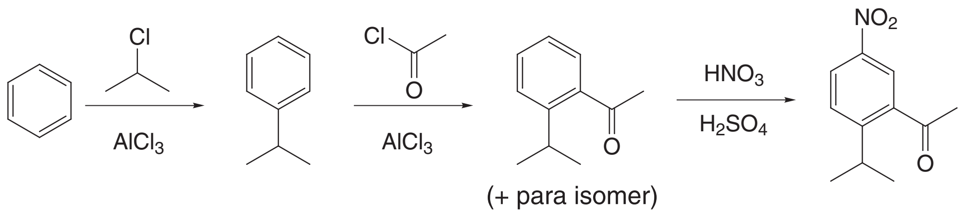
b.



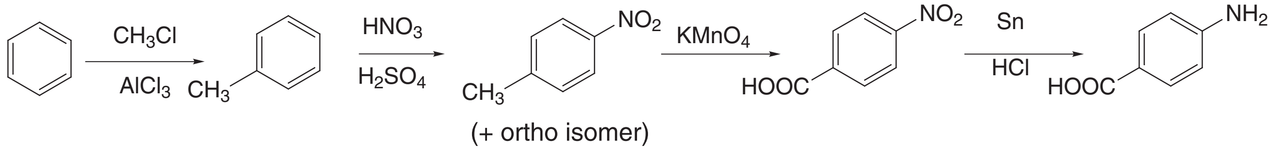
c.



d.

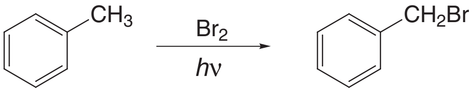


e.

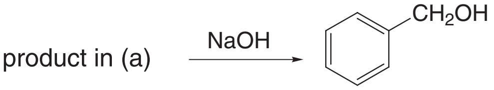


16.52

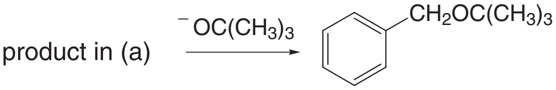
a.



b.



c.



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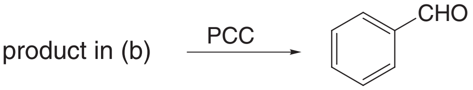
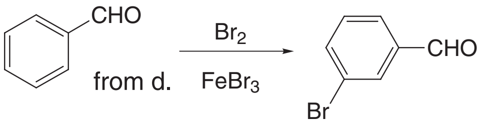
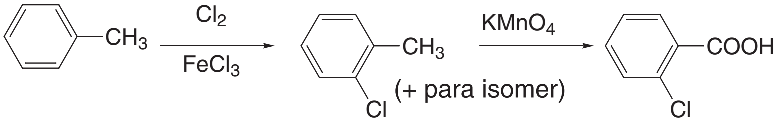


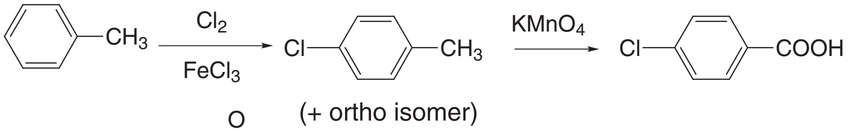
e.



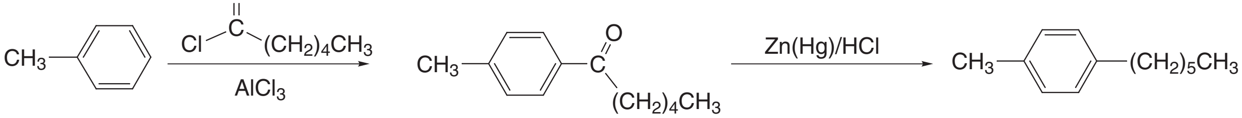
f.



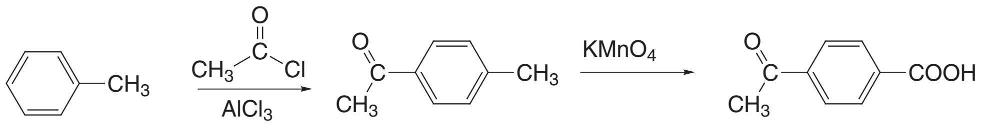
g.



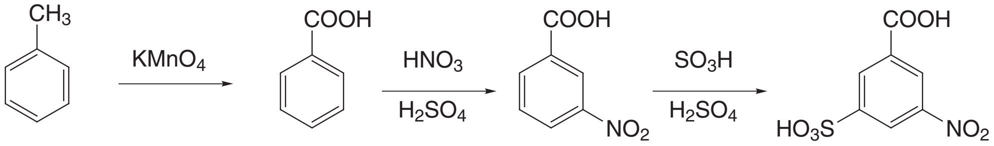
h.



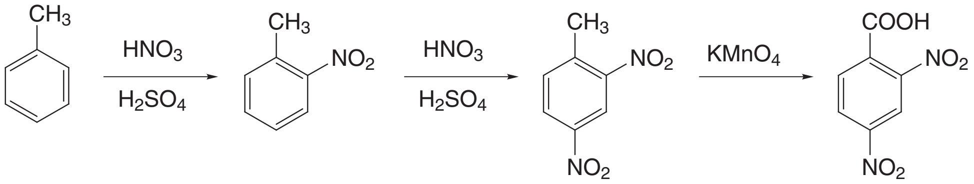
i.



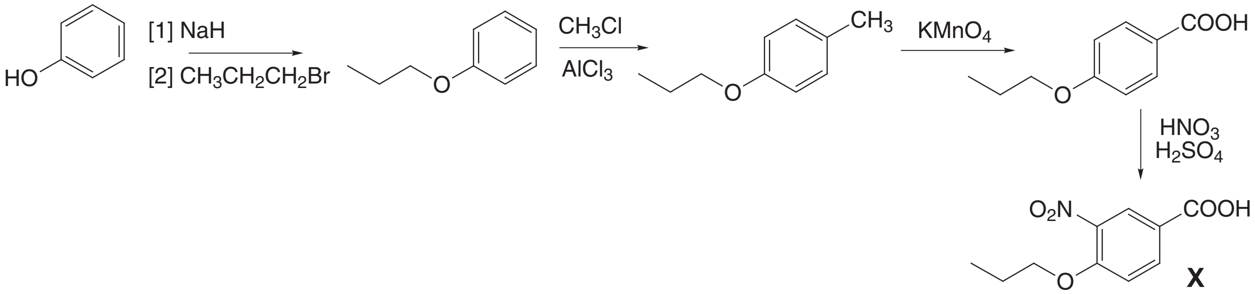
j.



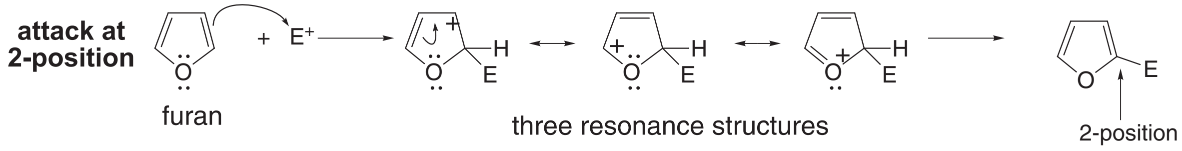
k.

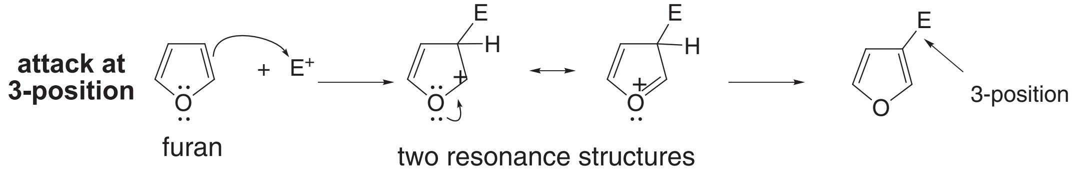


16.53

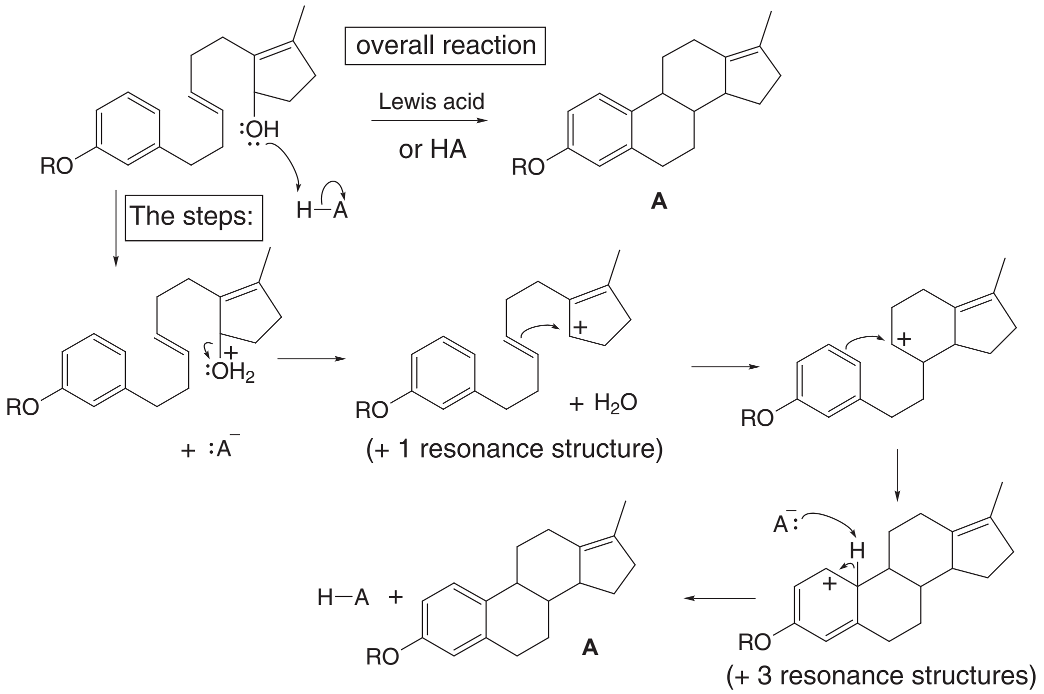


16.54 L'attacco sulla posizione 2 è favorito perché il carbocatione risultante è maggiormente stabilizzato per risonanza rispetto al carbocatione che si forma dall'attacco sulla posizione 3.





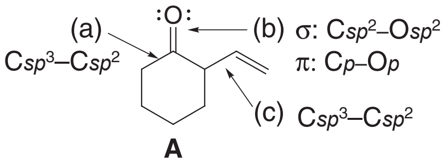
16.55 Disegnare un meccanismo a stadi per la seguente reazione intramolecolare, che è stata usata per la sintesi dell'ormone sessuale femminile estrone.


overall reaction
Lewis acid
or HA
RO
:OH
H—A
A
The steps:
+ :A⁻
+ H₂O
(+ 1 resonance structure)
A:
H
(+ 3 resonance structures)
H—A +
A

Capitolo 17

17.1

a.

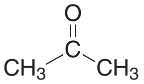


A

b. The O is sp^2 hybridized.
Both lone pairs occupy sp^2 hybrid orbitals.

17.2 Un composto carbonilico con un buon gruppo uscente dà luogo a reazioni di sostituzione. Quelli senza un buon gruppo uscente danno addizione.

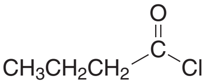
a.



$CH_3\overset{\overset{O}{\|}}{C}CH_3$

no good leaving group
addition reactions

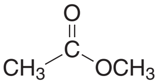
b.



$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}Cl$

Cl–good leaving group
substitution reactions

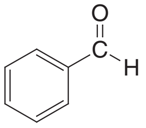
c.



$CH_3\overset{\overset{O}{\|}}{C}OCH_3$

OCH_3–reasonable leaving group
substitution reactions

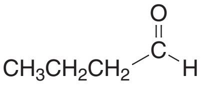
d.



no good leaving group
addition reactions

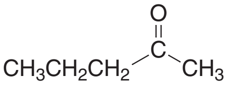
17.3 Le aldeidi sono più reattive dei chetoni. In composti carbonilici con gruppi uscenti, tanto migliore è il gruppo uscente, tanto più reattivo è il composto carbonilico.

a.



$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}H$

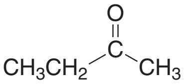
and



$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3$

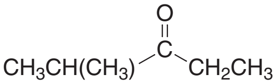
less hindered carbonyl
more reactive

b.



$CH_3CH_2\overset{\overset{O}{\|}}{C}CH_3$

and

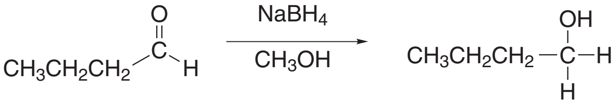


$CH_3CH(CH_3)\overset{\overset{O}{\|}}{C}CH_2CH_3$

less hindered carbonyl
more reactive

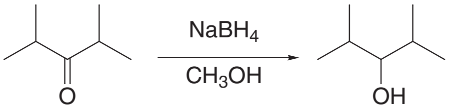
17.4 $NaBH_4$ riduce le aldeidi ad alcoli 1° ed i chetoni ad alcoli 2°.

a.

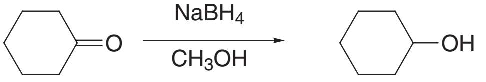


$$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}H \xrightarrow[CH_3OH]{NaBH_4} CH_3CH_2CH_2-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-H$$

c.

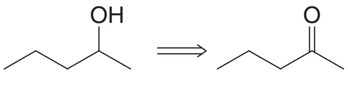


b.

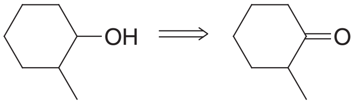


17.5 Gli alcoli 1° sono preparati dalle aldeidi, ed i secondari dai cheoni.

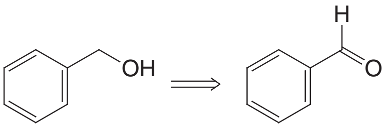
a.



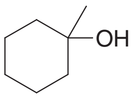
b.



c.



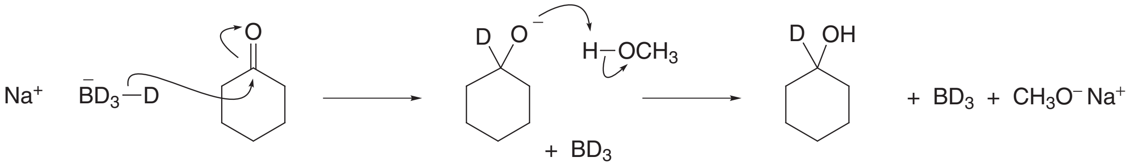
17.6



3° Alcohols cannot be made by reduction of a carbonyl group,
because they do not contain a H on the C with the OH.

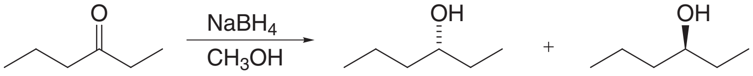
1-methylcyclohexanol

17.7

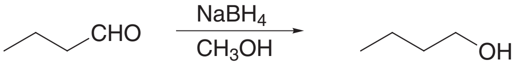


17.8

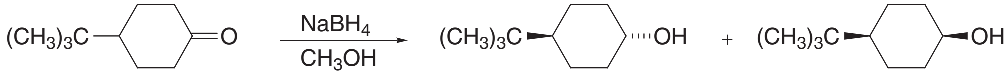
a.



b.

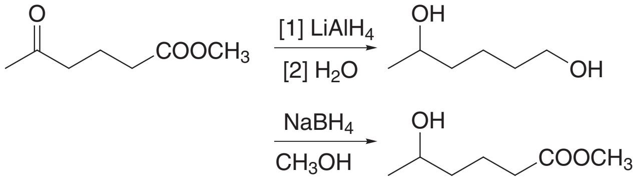


c.

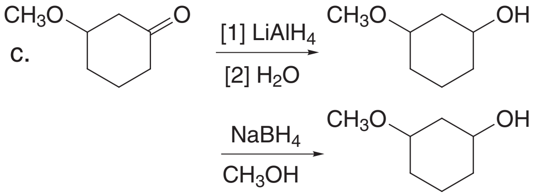


17.9

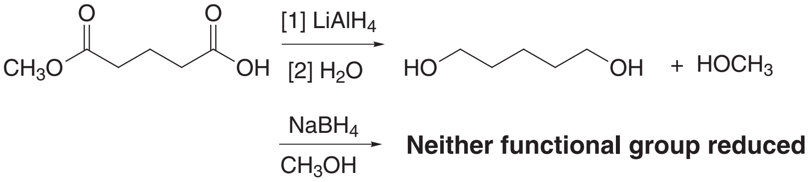
a.



c.

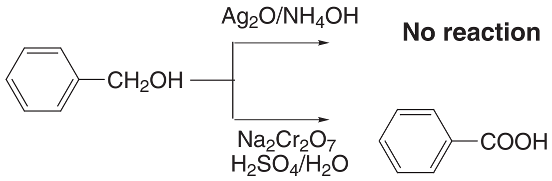


b.

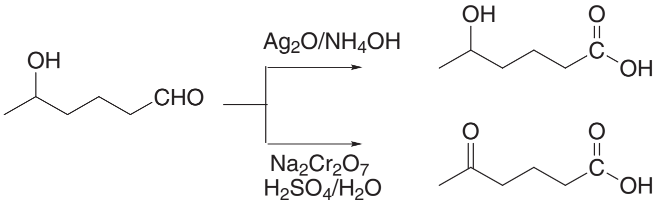


17.10 Il reagente di Tollens reagisce solo con aldeidi.

a.



b.

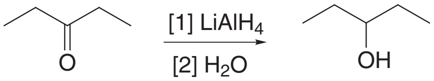


17.11 Viene indicato un possibile reagente:

a. $CH_3CH_2CHO \xrightarrow[\text{[2] } H_2O]{\text{[1] } LiAlH_4} CH_3CH_2CH_2OH$

reduction

b.

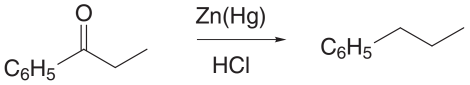


reduction

c. $CH_3CH_2CHO \xrightarrow[H_2SO_4/H_2O]{CrO_3} CH_3CH_2COOH$

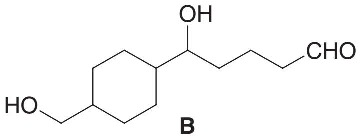
oxidation

d.

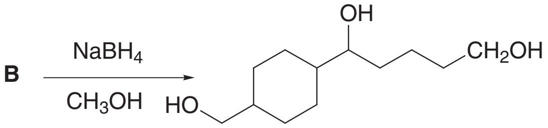


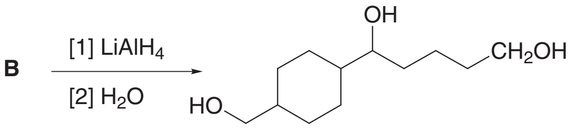
reduction

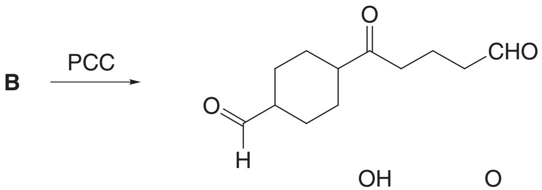
17.12

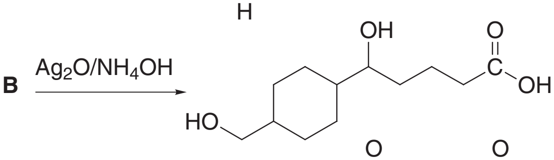


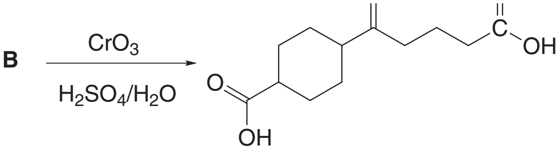
B

a.


b.


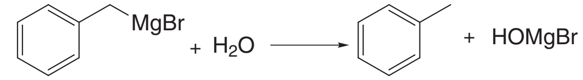
c.


d.


e.


17.13

a.


c.


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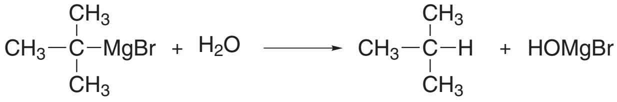
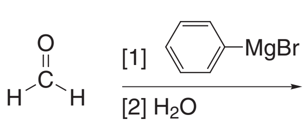


$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-MgBr + H_2O \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-H + HOMgBr$$

d. $CH_3CH_2C{\equiv}C{-}Li + H_2O \longrightarrow CH_3CH_2C{\equiv}CH + LiOH$

17.14 Per disegnare il prodotto, addizionare l'anello del benzene al composto carbonilico e protonare l'ossigeno.

a.


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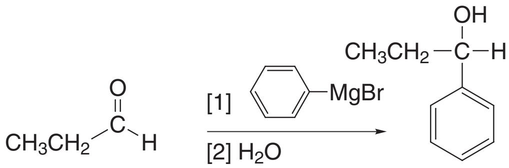

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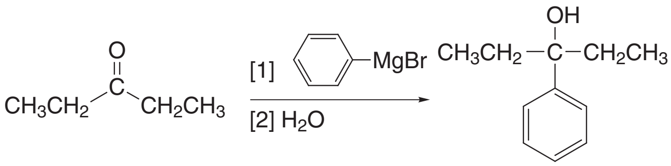

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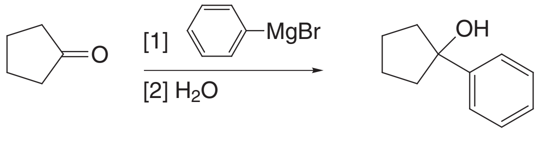
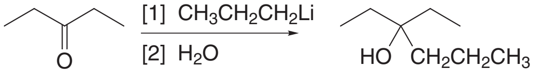


17.15 Per disegnare i prodotti, addizionare il gruppo alchilico al composto carbonilico e protonare l'ossigeno.

a.


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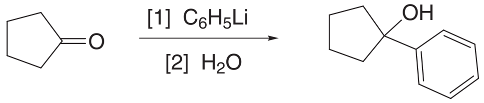

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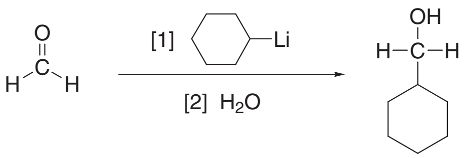

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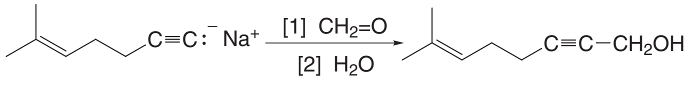
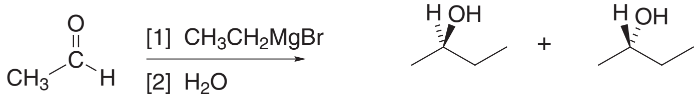


17.16 L'addizione di RM avviene sempre sopra e sotto il piano della molecola, perciò se si forma un nuovo centro stereogenico, si ha una miscela di enantiomeri.

a.


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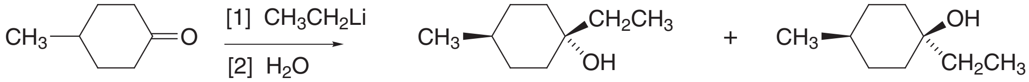
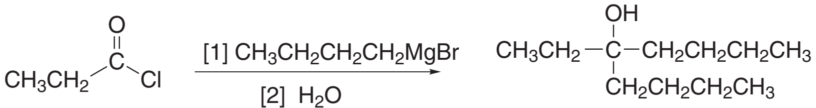


17.17

a.


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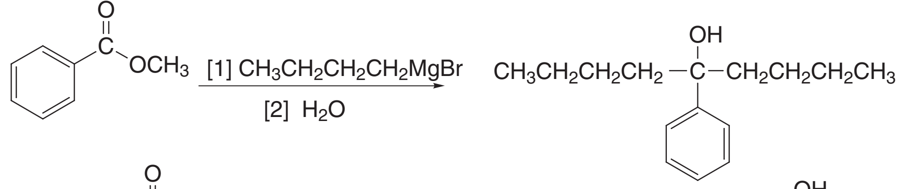

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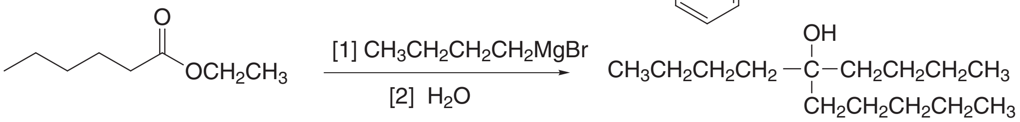
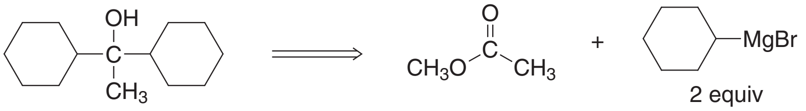


17.18

a.


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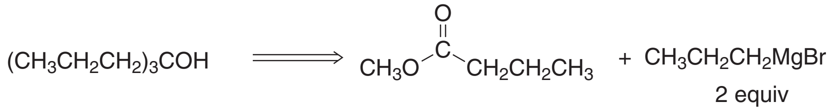

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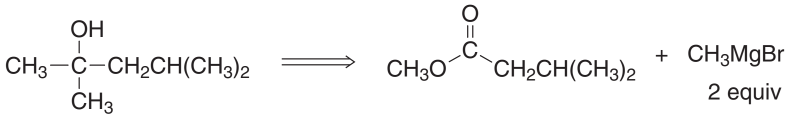
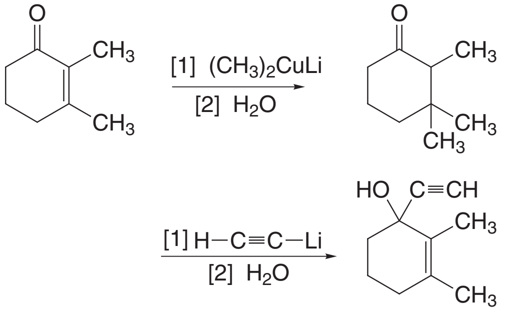


17.19 La reazione caratteristica dei composti carbonilici α,β-insaturi è l'addizione nucleofila. I reagenti di Grignard e gli organolitio danno luogo ad addizione 1,2 e i reagenti organocuprati danno addizione 1,4.

a.


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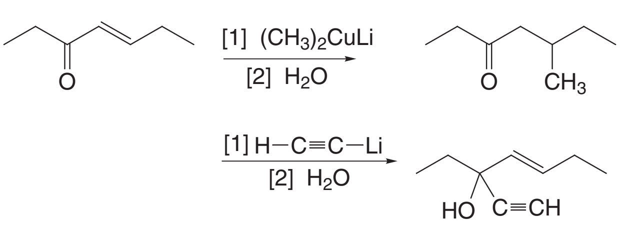
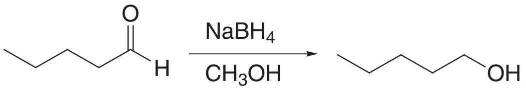


17.20

a.



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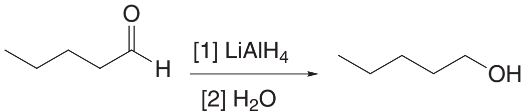

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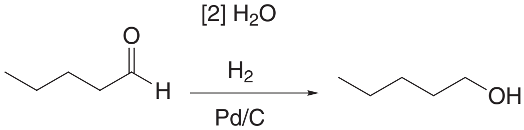

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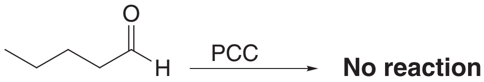

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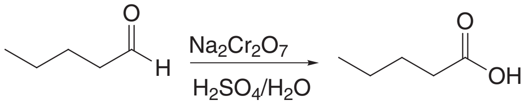

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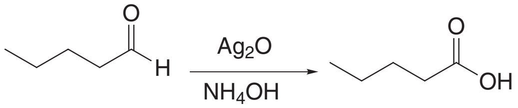
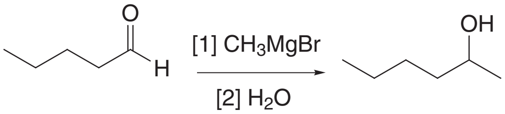


g.



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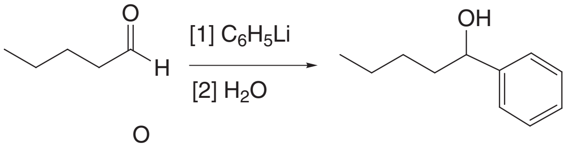

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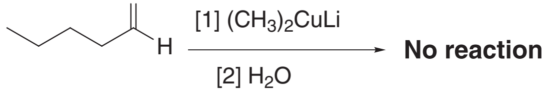

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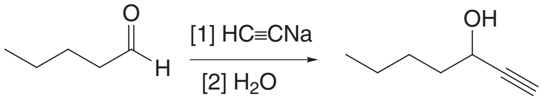
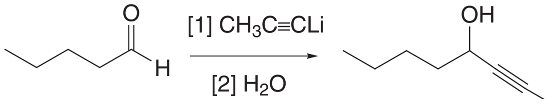
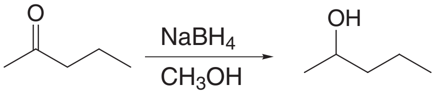


k.



17.21

a.



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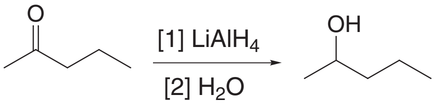

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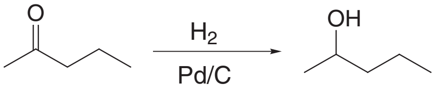

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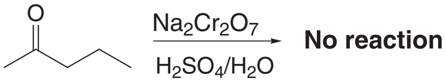

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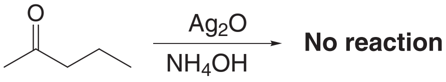

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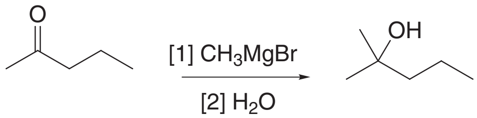

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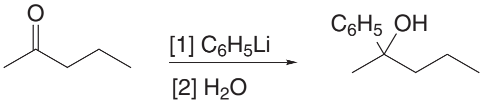

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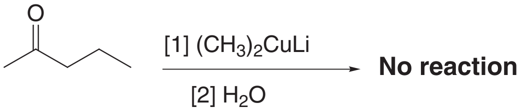

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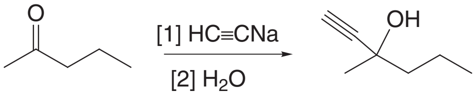

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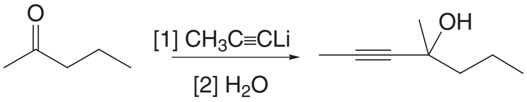

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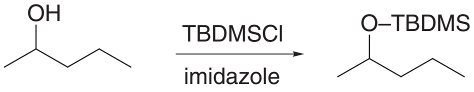

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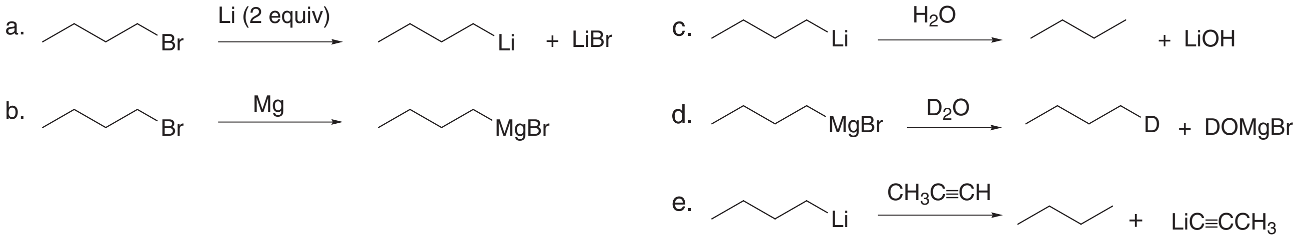

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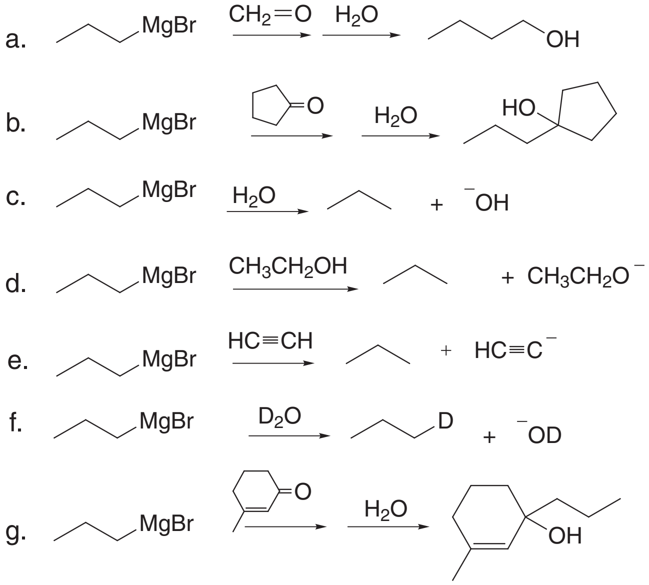

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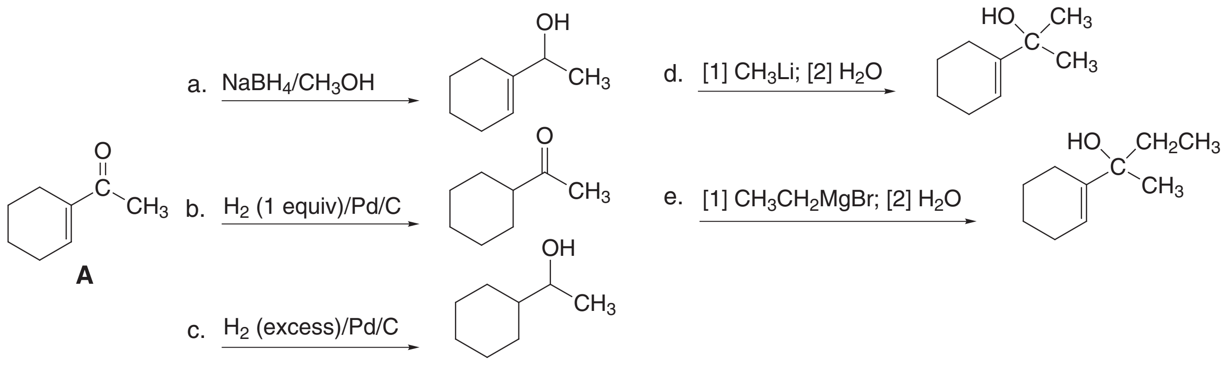

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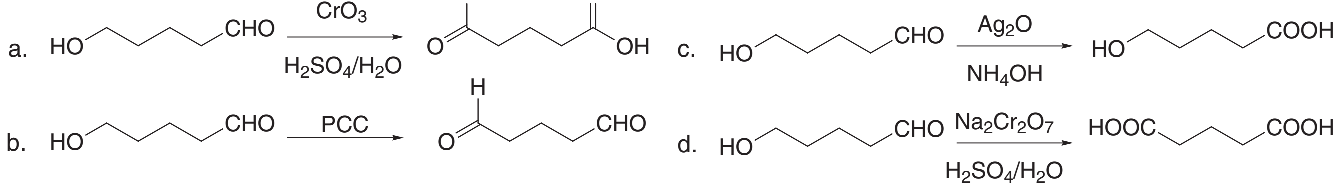
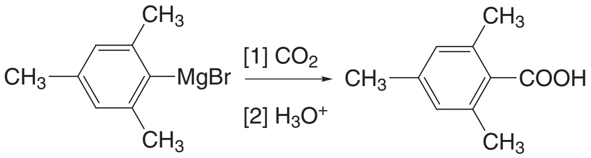


17.26

a.


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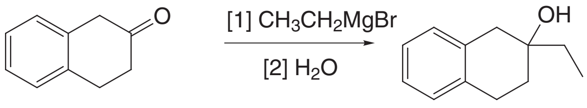

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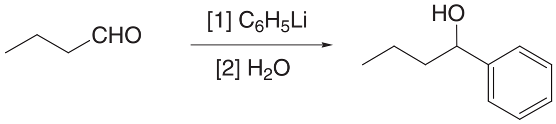

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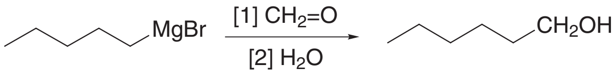

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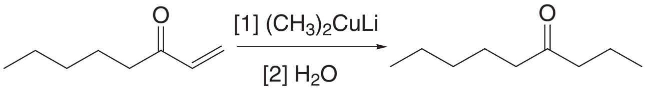

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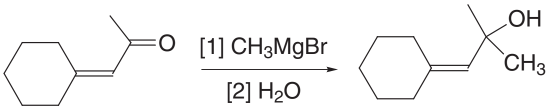

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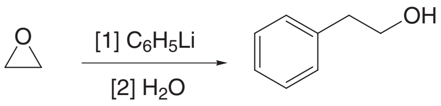

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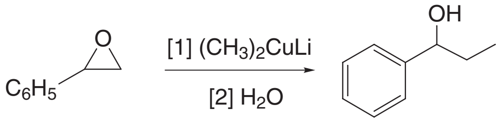
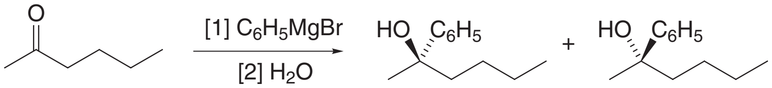


17.27

a.


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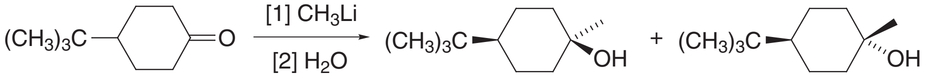

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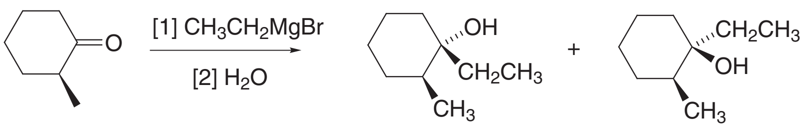

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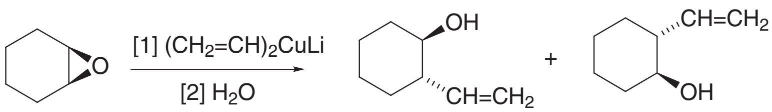
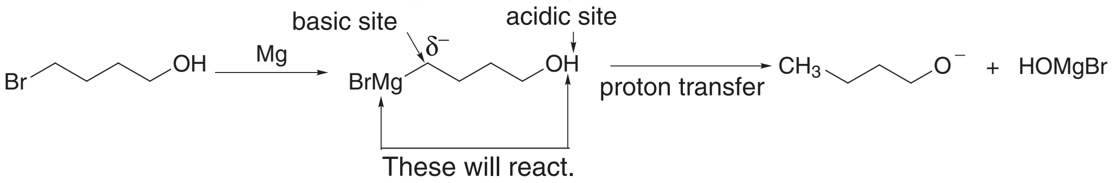
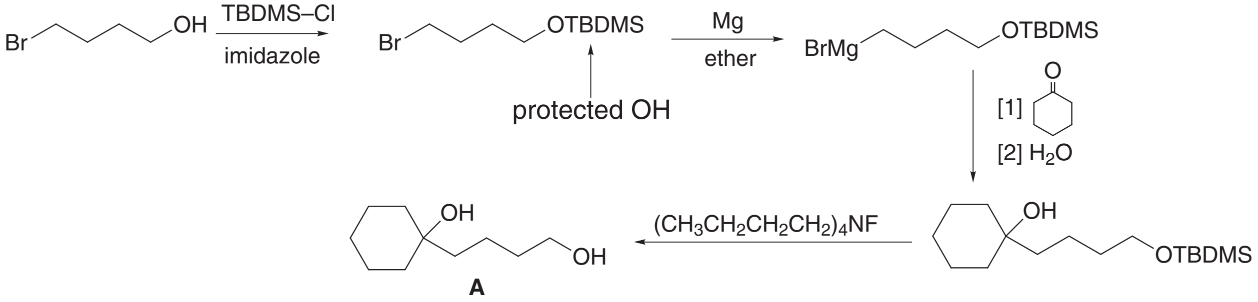


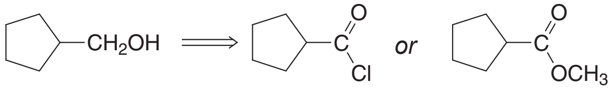
17.28 Poiché un reagente di Grignard contiene un atomo di carbonio con una parziale carica negativa, agisce come base e reagisce con l'OH dell'alogenuro di partenza, $BrCH_2CH_2CH_2CH_2OH$. Questa reazione acido–base decompone il reagente di Grignard cosicché l'addizione non può avvenire. Per aggirare il problema, il gruppo OH può essere protetto come *tert*-butildimetilsilil etere, da cui può essere preparato un reagente di Grignard.



INSTEAD: Use a protecting group.



17.29 I cloruri acilici e gli esteri possono essere ridotti ad alcoli 1°. Mantenere lo stesso scheletro molecolare disegnando l'estere e il cloruro acilico precursori.

a.


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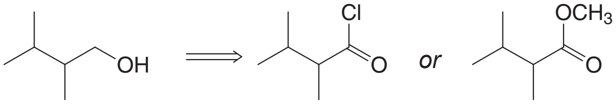
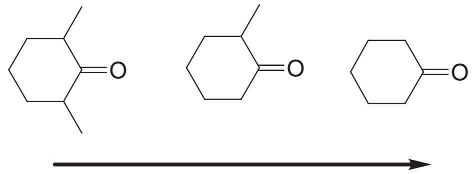


17.30 All'aumentare del numero di gruppi R legati al C carbonilico, diminuisce la reattività verso l'attacco nucleofilo.

a. $(CH_3)_2C{=}O$ $CH_3CH{=}O$ $CH_2{=}O$

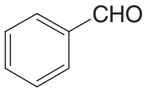
2 R groups 1 R group 0 R groups

increasing reactivity
decreasing alkyl substitution

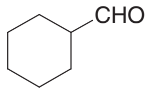
b. 

increasing reactivity
decreasing steric hindrance

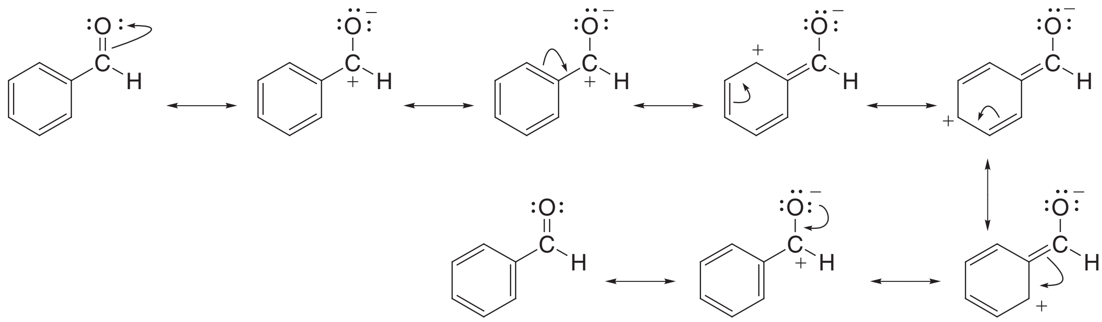
17.31 Le aldeidi più stabili sono meno reattive verso l'attacco nucleofilo.



benzaldehyde
Several resonance structures delocalize the partial positive charge on the carbonyl carbon making it more stable, and less reactive towards nucleophilic attack.



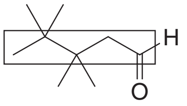
cyclohexanecarbaldehyde
This aldehyde has no added resonance stabilization.



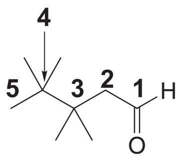
17.32 • Per nominare un'aldeide legata ad una catena di atomi di carbonio: [1] Trovare la catena più lunga contenente il gruppo CHO e sostituire la *–o* finale con *-ale*. [2] Numerare la catena carboniosa in modo da assegnare al CHO il C1, ma omettere questo numero dal nome. Applicare tutte le altre regole della nomenclatura.

• Per nominare un'aldeide con il CHO legato ad un anello: [1] Nominare l'anello ed aggiungere il suffisso *–carbaldehyde*. [2] Numerare l'anello in modo da porre il CHO sul C1, ma omettere questo numero dal nome. Applicare tutte le altre regole della nomenclatura.

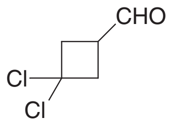
a. $(CH_3)_3CC(CH_3)_2CH_2CHO$



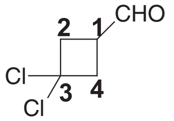
5 C chain = pentanal



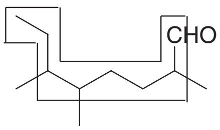
3,3,4,4-tetramethylpentanal

c. 

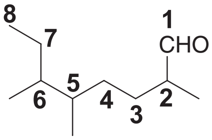
4 C ring = cyclobutanecarbaldehyde



3,3-dichlorocyclobutane-carbaldehyde

b. 

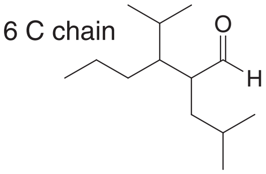
8 C chain = octanal



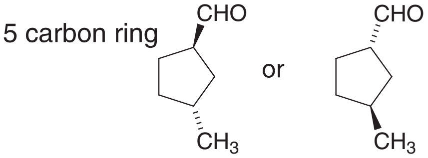
2,5,6-trimethyloctanal

17.33 Lavorare all'indietro, dal nome alla struttura, usando le regole della nomenclatura della risposta 21.3.

a. 2-isobutyl-3-isopropyl**hexanal**

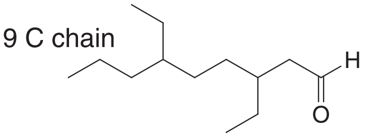


b. *trans*-3-methyl**cyclopentanecarbaldehyde**



c. 1-methyl**cyclopropanecarbaldehyde**

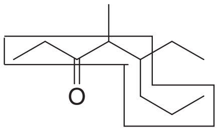
d. 3,6-diethyl**nonanal**



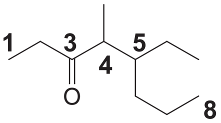
17.34 • Per nominare un chetone aciclico: [1] Trovare la catena più lunga contenente il gruppo carbonilico e sostituire la *–o* finale in *–one*. [2] Numerare la catena di atomi di carbonio in modo da assegnare al C carbonilico il numero più basso. Applicare tutte le altre regole della nomenclatura.

• Per nominare un chetone ciclico: [1] Nominare l'anello e sostituire la *–o* finale in *–one*. [2] Numerare gli atomi di C in modo da porre il C carbonilico sul C1 ed assegnare il numero più basso al primo sostituente incontrato. Applicare tutte le altre regole della nomenclatura.

a.

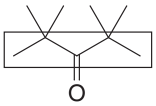


8 C chain = octanone

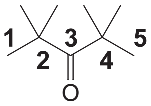


5-ethyl-4-methyl-3-octanone

c. $(CH_3)_3CCOC(CH_3)_3$

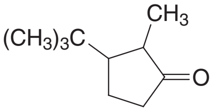


5 C chain = pentanone

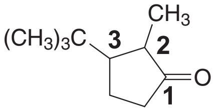


2,2,4,4-tetramethyl-3-pentanone

b.



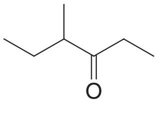
5 C ring = cyclopentanone



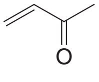
3-*tert*-butyl-2-methylcyclopentanone

17.35 La maggior parte dei nomi comuni sono formati assegnando il nome ad entrambi i gruppi alchilici sul C carbonilico, ordinandoli in ordine alfabetico, ed aggiungendo la parola chetone.

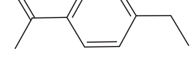
a. *sec*-butyl ethyl ketone



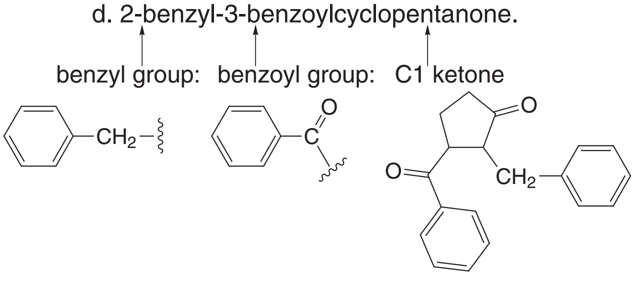
b. methyl vinyl ketone



c. *p*-ethylacetophenone

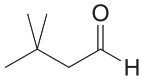


d. 2-benzyl-3-benzoylcyclopentanone.



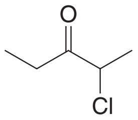
17.36 Usare le regole delle risposte 19.3 e 19.5 per assegnare il nome ad aldeidi e chetoni.

a. $(CH_3)_3CCH_2CHO$ $\xrightarrow{\text{redraw}}$



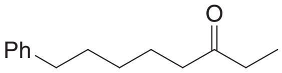
4 C = butanal
3,3-dimethybutanal

b.



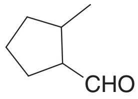
5 C = pentanone
2-chloro-3-pentanone

c.



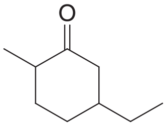
8 C = octanone
8-phenyl-3-octanone

d.



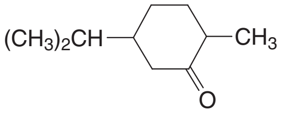
5 C ring
2-methyl-cyclopentanecarbaldehyde

e.



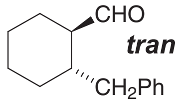
6 C ring = cyclohexanone
5-ethyl-2-methyl-cyclohexanone

f.



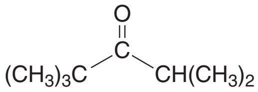
6 C ring = cyclohexanone
5-isopropyl-2-methyl-cyclohexanone

g.

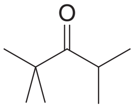


***trans*-2-benzylcyclohexanecarbaldehyde**

h.

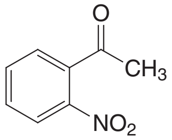


$(CH_3)_3C-C(=O)-CH(CH_3)_2$ $\xrightarrow{\text{redraw}}$



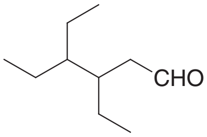
5 C = pentanone
2,2,4-trimethyl-3-pentanone
(common name:
***tert*-butyl isopropyl ketone)**

i.



***o*-nitroacetophenone**

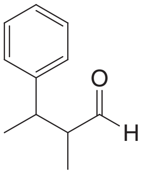
j.



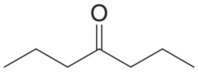
6 C = hexanal
3,4-diethylhexanal

17.37

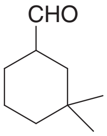
a. 2-methyl-3-phenylbutanal



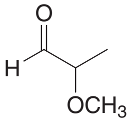
b. dipropyl ketone



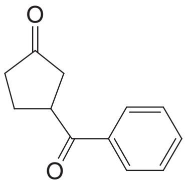
c. 3,3-dimethylcyclohexanecarbaldehyde



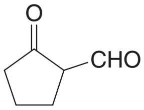
d. α-methoxypropionaldehyde



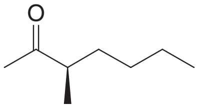
e. 3-benzoylcyclopentanone



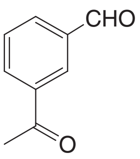
f. 2-formylcyclopentanone



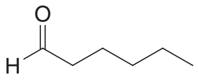
g. (*R*)-3-methyl-2-heptanone



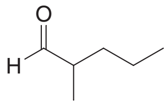
h. *m*-acetylbenzaldehyde



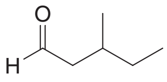
17.38



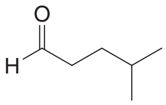
hexanal



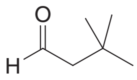
2-methylpentanal



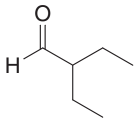
3-methylpentanal



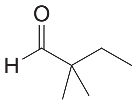
4-methylpentanal



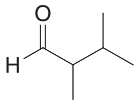
3,3-dimethylbutanal



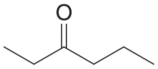
2-ethylbutanal



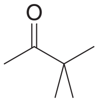
2,2-dimethylbutanal



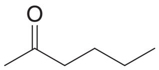
2,3-dimethylbutanal



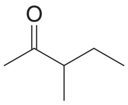
3-hexanone



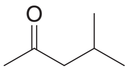
3,3-dimethyl-2-butanone



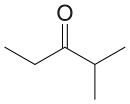
2-hexanone



3-methyl-2-pentanone



4-methyl-2-pentanone



2-methyl-3-pentanone

17.39

a. $CH_3CH_2CH_2COOCH_3 \xrightarrow[\text{[2] } H_2O]{\text{[1] DIBAL–H}} CH_3CH_2CH_2CHO$

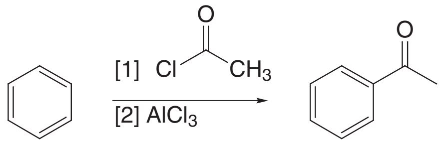
b. $CH_3CH_2CH_2CH_2OH \xrightarrow{\text{PCC}} CH_3CH_2CH_2CHO$

c. $HC{\equiv}CCH_2CH_3 \xrightarrow[\text{[2] } H_2O_2/HO^-]{\text{[1] } BH_3} CH_3CH_2CH_2CHO$

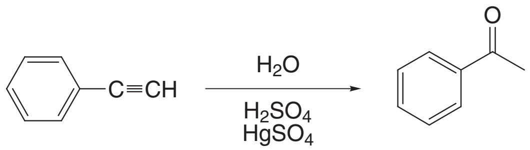
d. $CH_3CH_2CH_2CH{=}CHCH_2CH_2CH_3 \xrightarrow[\text{[2] } Zn/H_2O]{\text{[1] } O_3} CH_3CH_2CH_2CHO$

17.40

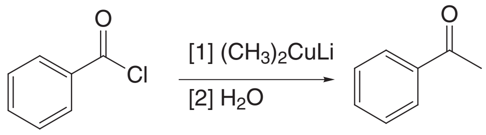
a.



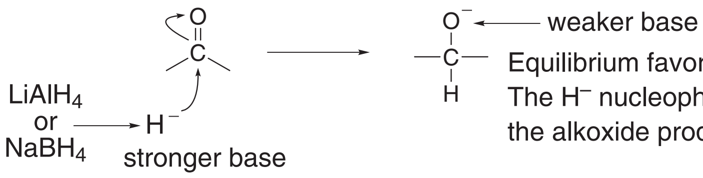
c.



b.

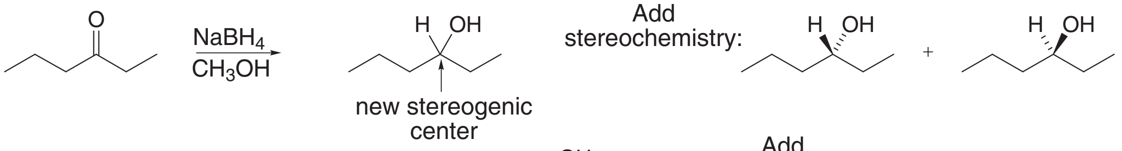


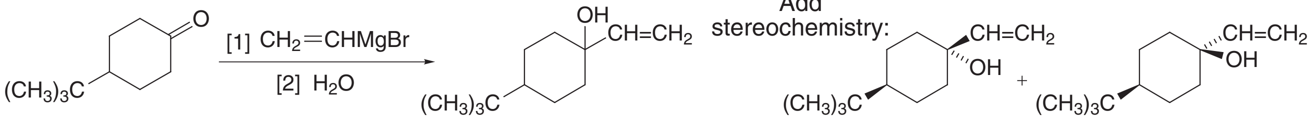
17.41

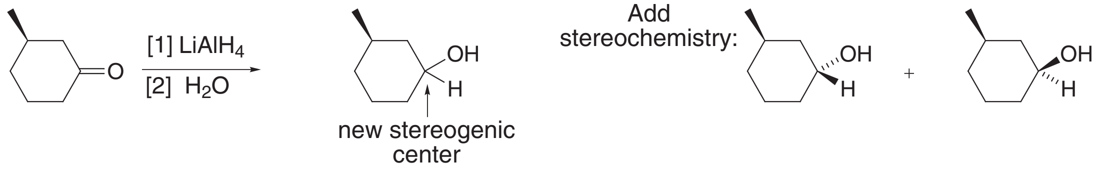


Equilibrium favors the weaker base.
The H⁻ nucleophile is a much stronger base than the alkoxide product.

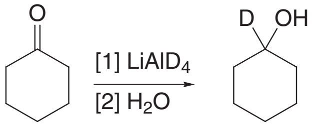
17.42 L'addizione di un idruro avviene sul C carbonilico planare, cosicché sono possibili due differenti configurazioni al nuovo centro stereogenico.

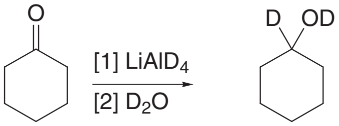
a.


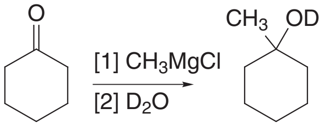
b.


c.


17.43

a.


c.


e.


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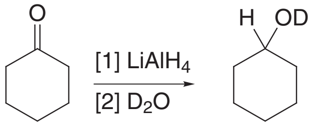
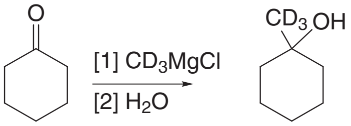
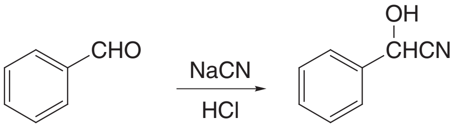
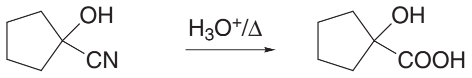


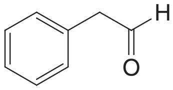
d.


17.44 Il trattamento di un'aldeide o di un chetone con NaCN/HCl addiziona HCN al doppio legame. I gruppi ciano sono idrolizzati da H_3O^+ per sostituire i 3 legami C–N con 3 legami C–O.

a.


b.


17.45



= $C_6H_5CH_2CHO$ phenylacetaldehyde

a. $\xrightarrow{NaBH_4/CH_3OH}$ $C_6H_5CH_2CH_2OH$

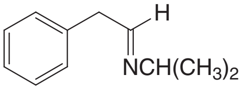
b. $\xrightarrow{[1]\ LiAlH_4;\ [2]\ H_2O}$ $C_6H_5CH_2CH_2OH$

c. $\xrightarrow{[1]\ CH_3MgBr;\ [2]\ H_2O}$ $C_6H_5CH_2CH(OH)CH_3$

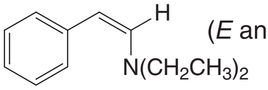
d. $\xrightarrow{NaCN/HCl}$ $C_6H_5CH_2CH(OH)CN$

e. $\xrightarrow{Ph_3P{=}CHCH_3}$ $C_6H_5CH_2CH{=}CHCH_3$ (E and Z isomers)

f. $\xrightarrow[\text{mild acid}]{(CH_3)_2CHNH_2}$

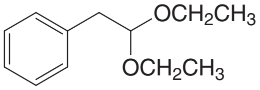


g. $\xrightarrow{(CH_3CH_2)_2NH/\text{mild acid}}$

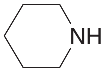


(*E* and *Z* isomers)

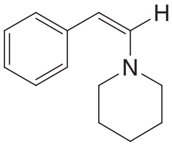
h. $\xrightarrow{CH_3CH_2OH\ (\text{excess})/H^+}$



i.

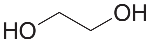


+ mild acid $\longrightarrow$

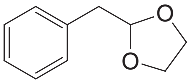


(*E* and *Z* isomers)

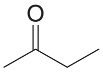
j.



$\xrightarrow{/H^+}$

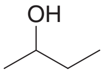


17.46

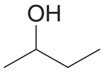


2-butanone

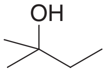
a. $\xrightarrow{NaBH_4/CH_3OH}$



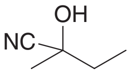
b. $\xrightarrow{[1]\ LiAlH_4;\ [2]\ H_2O}$



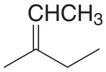
c. $\xrightarrow{[1]\ CH_3MgBr;\ [2]\ H_2O}$



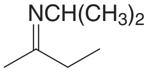
d. $\xrightarrow{NaCN/HCl}$



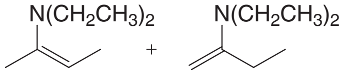
e. $\xrightarrow{Ph_3P{=}CHCH_3}$



f. $\xrightarrow{(CH_3)_2CHNH_2/\text{mild }H^+}$

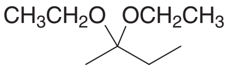


g. $\xrightarrow{(CH_3CH_2)_2NH/\text{mild }H^+}$

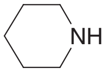


(*E* and *Z* isomers)

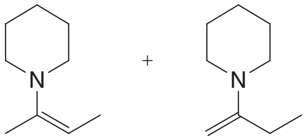
h. $\xrightarrow{CH_3CH_2OH\ (\text{excess})/H^+}$



i.

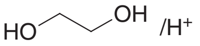


+ mild H^+ $\longrightarrow$

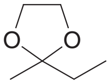


(*E* and *Z* isomers)

j.

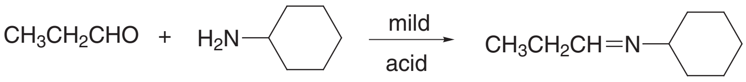


$\xrightarrow{/H^+}$

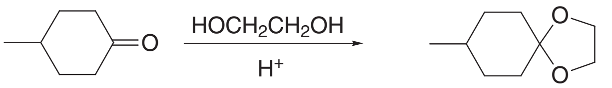


17.47

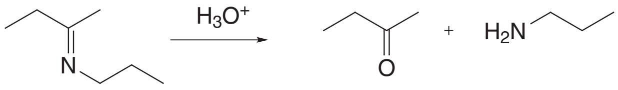
a.



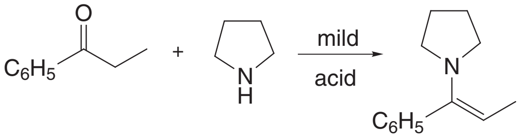
b.



c.

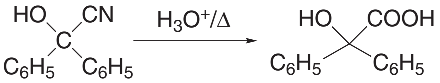


d.

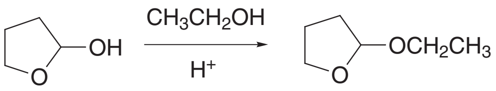


(*E* and *Z* isomers)

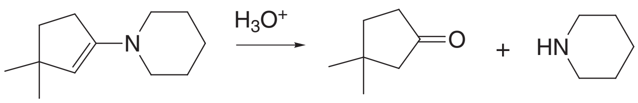
e.



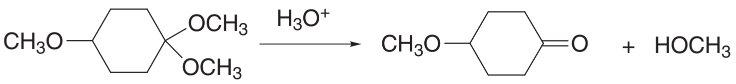
f.



g.

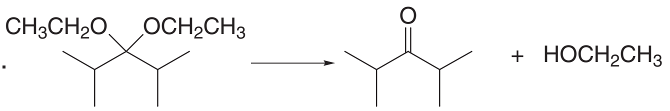


h.

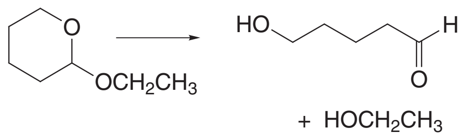


17.48

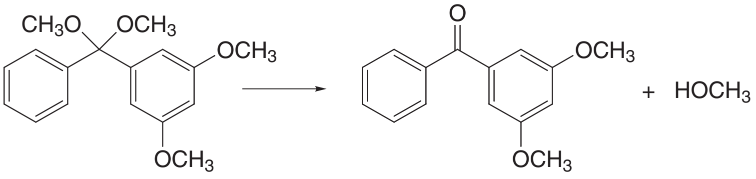
a.



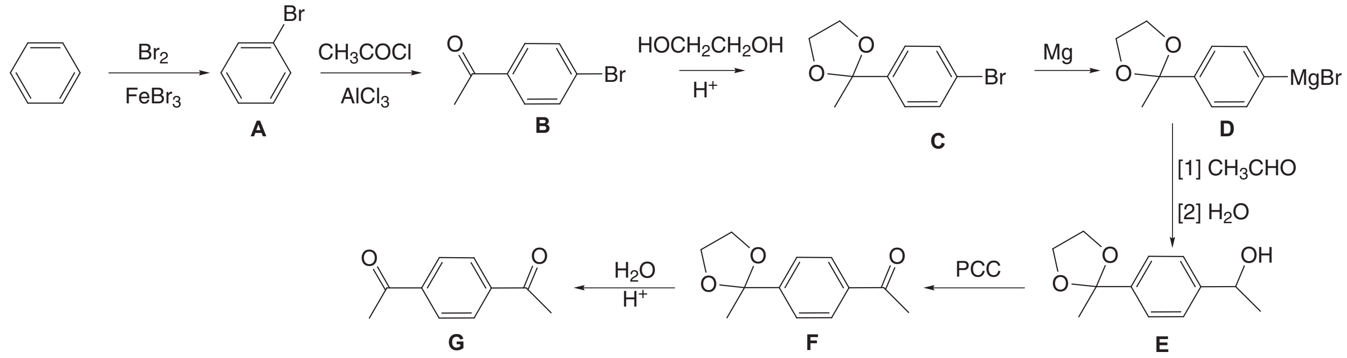
c.



b.

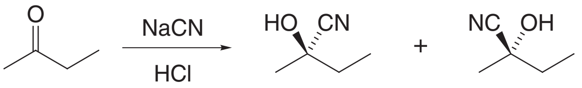


17.49 Considerare solo il prodotto para, quando è possibile la formazione di una miscela orto, para.

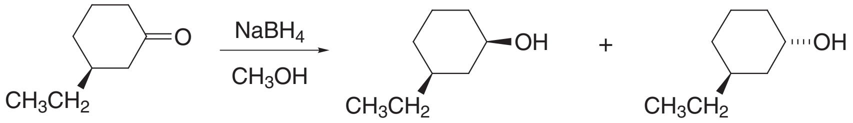


17.50

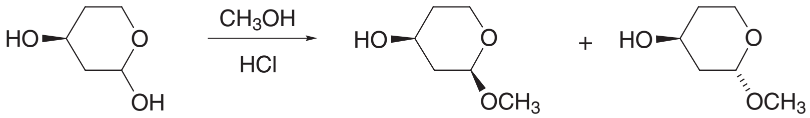
a.



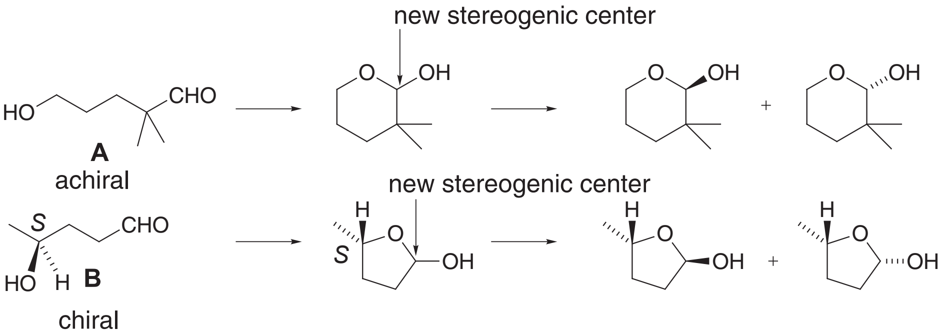
b.



c.



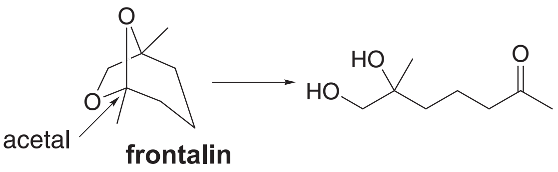
17.51

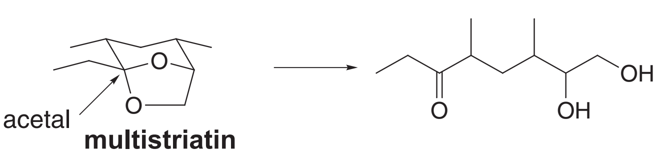


An equal mixture of enantiomers results, so the product is optically inactive.

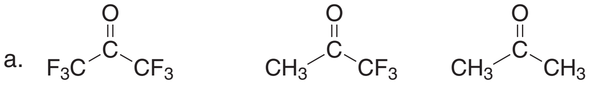
A mixture of diastereomers results. Both compounds are chiral and they are not enantiomers, so the mixture is optically active.

17.52





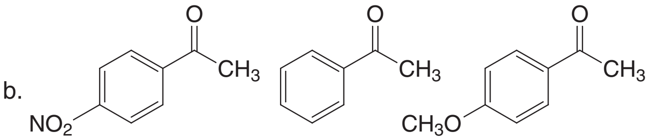
17.53 All'aumentare del numero di gruppi R legati al C carbonilico, aumenta anche la stabilità dovuta ad effetti elettron donatori.



2 electron withdrawing groups **least stable highest percentage of hydrate**

1 electron withdrawing group

2 electron donating groups **most stable lowest percentage of hydrate**

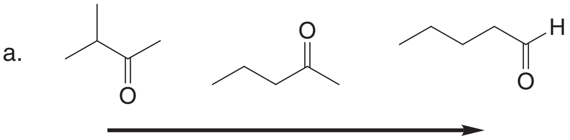


NO$_2$ group - electron withdrawing **least stable highest percentage of hydrate**

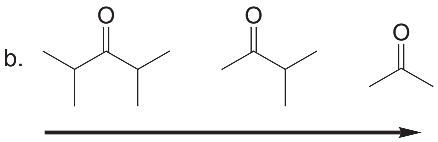
no groups on benzene

CH$_3$O group - electron donating **most stable lowest percentage of hydrate**

17.54 Usare le regole della risposta 19.1.

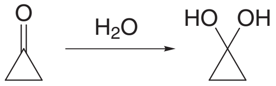


increasing reactivity
decreasing steric hindrance



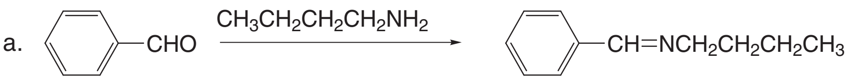
increasing reactivity
decreasing steric hindrance

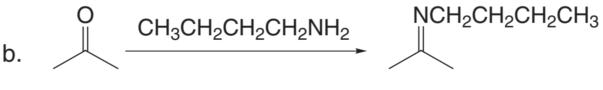
17.55

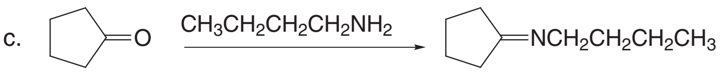


Less stable carbonyl compounds give a higher percentage of hydrate. Cyclopropanone is an unstable carbonyl compound because the bond angles around the carbonyl carbon deviate considerably from the desired angle. Since the carbonyl carbon is *sp*^{2} hybridized, the optimum bond angle is 120°, but the three-membered ring makes the C–C–C bond angles only 60°. This destabilizes the ketone, giving a high concentration of hydrate when dissolved in H$_2$O.

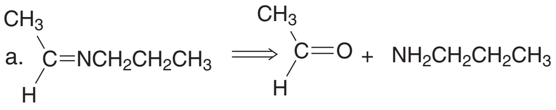
17.56 Quando un'ammina 1° reagisce con una aldeide o un chetone, il C=O è sostituito con il C=NR.

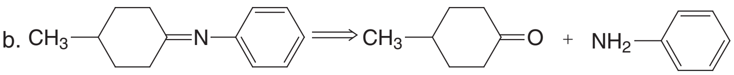




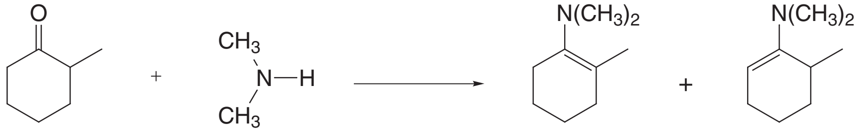


17.57 Ricordare che il C=NR si forma da un C=O ed un gruppo NH$_2$ di un'ammina 1°.

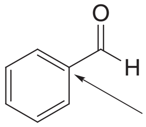




17.58

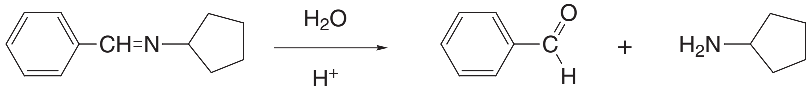


17.59

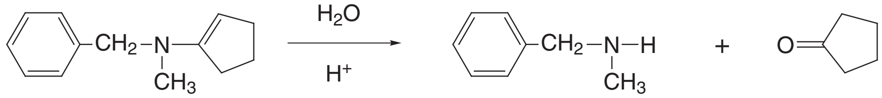


This carbon has 4 bonds to C's. To make an enamine, it needs a H atom, which is lost as H_2O when the enamine is formed.

17.60
- Le immine sono idrolizzate ad ammine 1° e composti carbonilici.
- Le enammine sono idrolizzate ad ammine 2° e composti carbonilici.

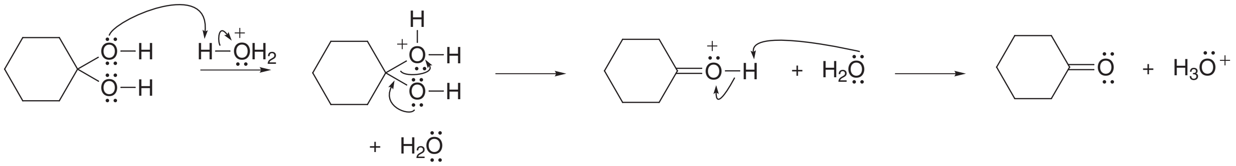
a. 

imine 1° amine

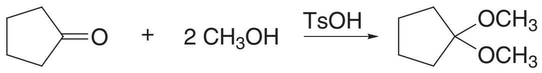
b. 

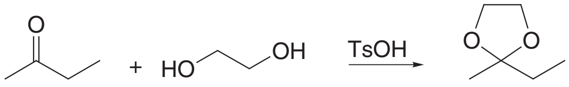
enamine 2° amine

17.61

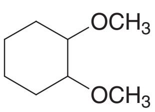


17.62 Il trattamento di un'aldeide o chetone con due equivalenti di un alcol porta alla formazione di acetali (un C legato a 2 gruppi OR).

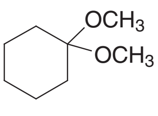
a. 

b. 

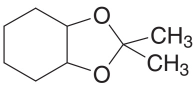
17.63

a. 

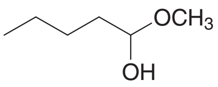
2 OR groups
on different C's.
2 ethers

b. 

2 OR groups
on same C.
acetal

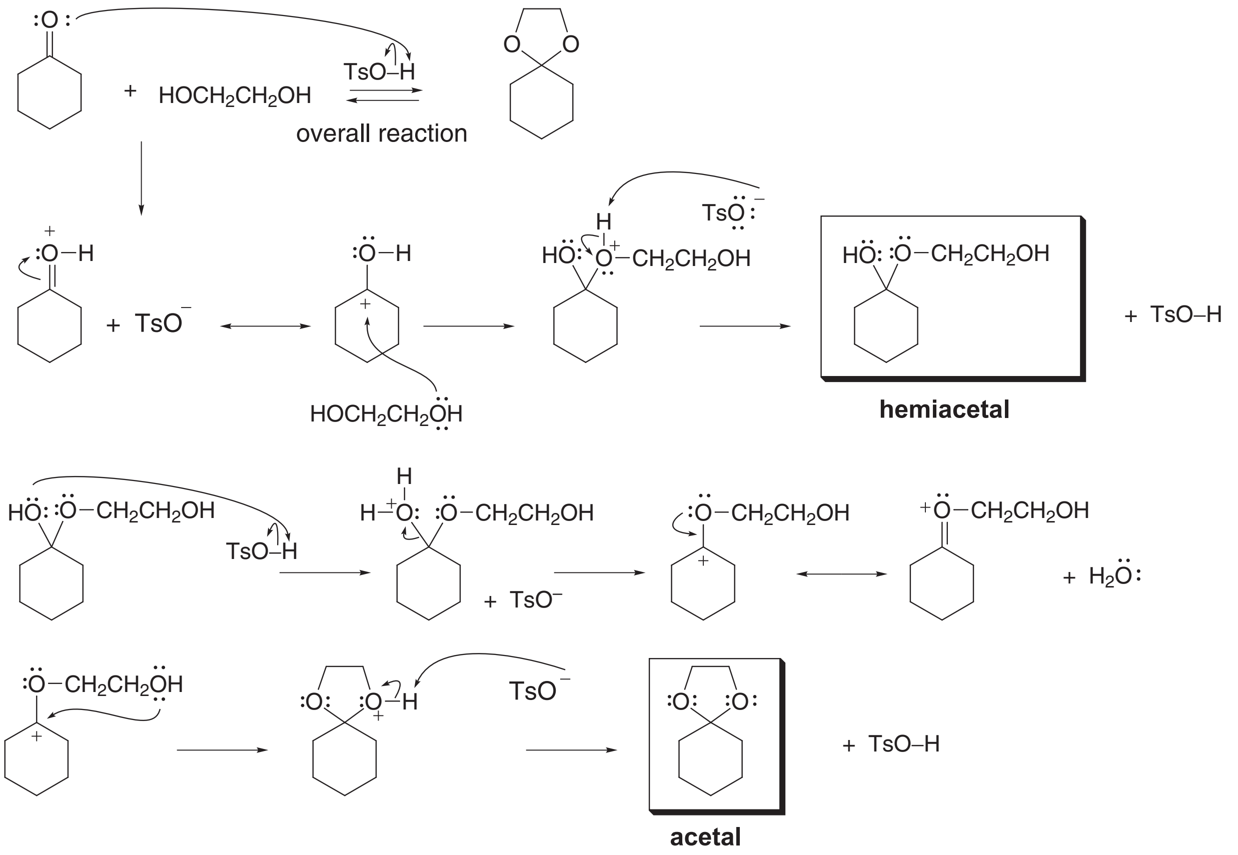
c. 

2 OR groups
on same C.
acetal

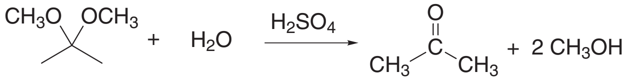
d. 

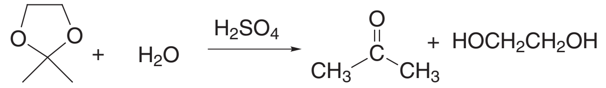
1 OR group and
1 OH group
on same C.
hemiacetal

17.64 Il meccanismo consiste in due parti: [1] Addizione nucleofila di ROH per formare un emiacetale; [2] Conversione dell'emiacetale in un acetale.

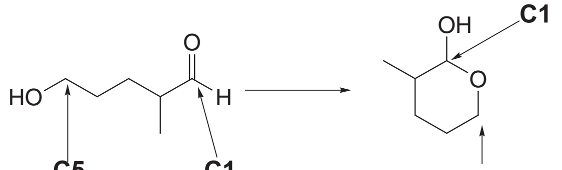


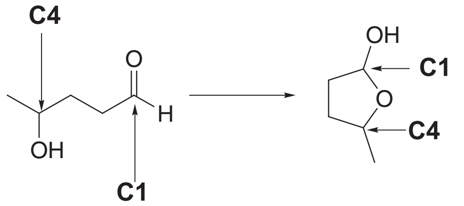
17.65

a.


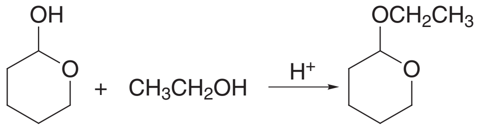
b.


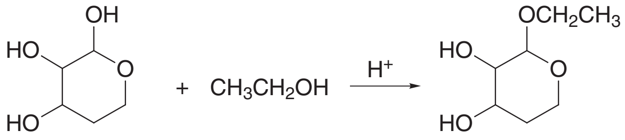
17.66

a.


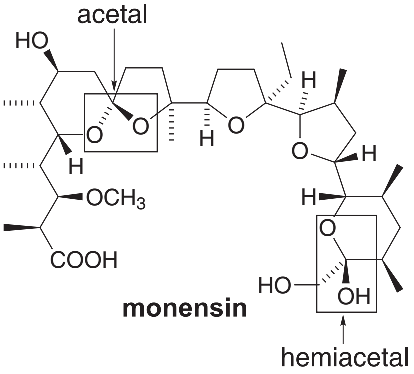
b.


17.67 L'OH emiacetalico è sostituito da un gruppo OR per formare un acetale.

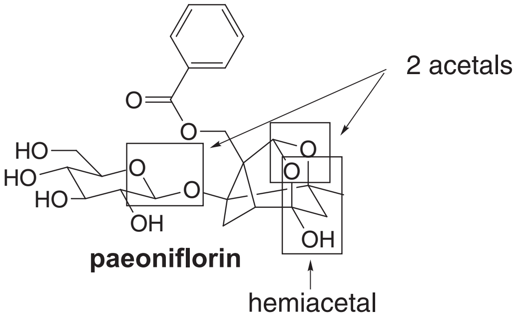
a.


b.


17.68



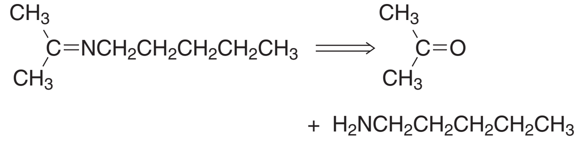
monensin



paeoniflorin

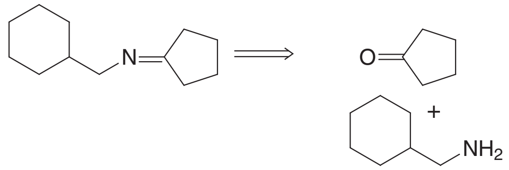
17.69

a.

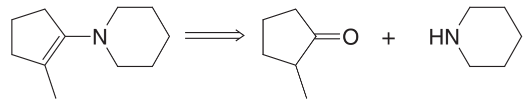


$$(CH_3)_2C{=}NCH_2CH_2CH_2CH_2CH_3 \Longrightarrow (CH_3)_2C{=}O + H_2NCH_2CH_2CH_2CH_2CH_3$$

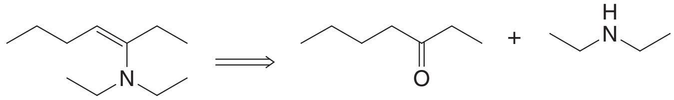
b.



c.



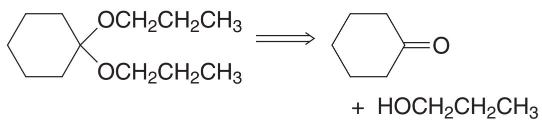
d.



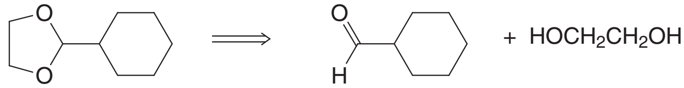
17.70

a. $(CH_3CH_2)_2C(OCH_2CH_3)_2 \Longrightarrow (CH_3CH_2)_2C{=}O + HOCH_2CH_3$

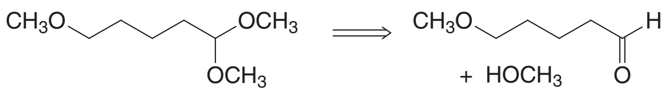
b.



c.



d.



17.71

a. $C_6H_5{-}CH_2OH \xrightarrow{\text{PCC}} C_6H_5{-}CHO$

b. $C_6H_5{-}COCl \xrightarrow[\text{[2] } H_2O]{\text{[1] LiAlH[OC(CH}_3)_3]_3} C_6H_5{-}CHO$

c. $C_6H_5{-}COOCH_3 \xrightarrow[\text{[2] } H_2O]{\text{[1] DIBAL-H}} C_6H_5{-}CHO$

d. $C_6H_5{-}COOH \xrightarrow[\text{[2] } H_2O]{\text{[1] LiAlH}_4} C_6H_5{-}CH_2OH \xrightarrow{\text{PCC}} C_6H_5{-}CHO$

e. $C_6H_5{-}CH_3 \xrightarrow{\text{KMnO}_4} C_6H_5{-}COOH \xrightarrow[\text{[2] } H_2O]{\text{[1] LiAlH}_4} C_6H_5{-}CH_2OH \xrightarrow{\text{PCC}} C_6H_5{-}CHO$

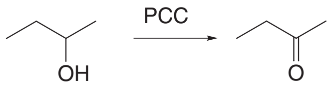
f. $C_6H_5{-}CH{=}CH_2 \xrightarrow[\text{[2] Zn/}H_2O]{\text{[1] } O_3} C_6H_5{-}CHO$

g. $C_6H_5{-}CH{=}NCH_2CH_2CH_3 \xrightarrow[H^+]{H_2O} C_6H_5{-}CHO$

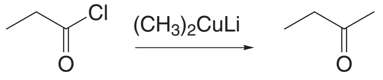
h. $C_6H_5{-}CH(OCH_2CH_3)_2 \xrightarrow[H^+]{H_2O} C_6H_5{-}CHO$

17.72

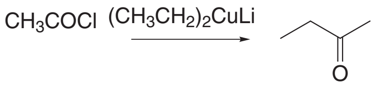
a.



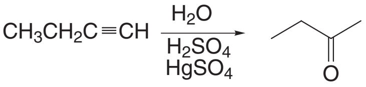
b.



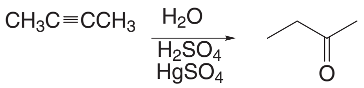
c.



d.

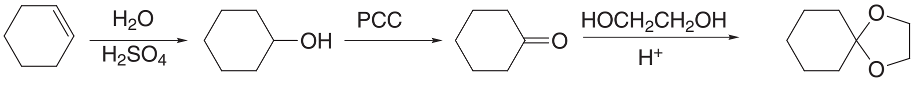


e.

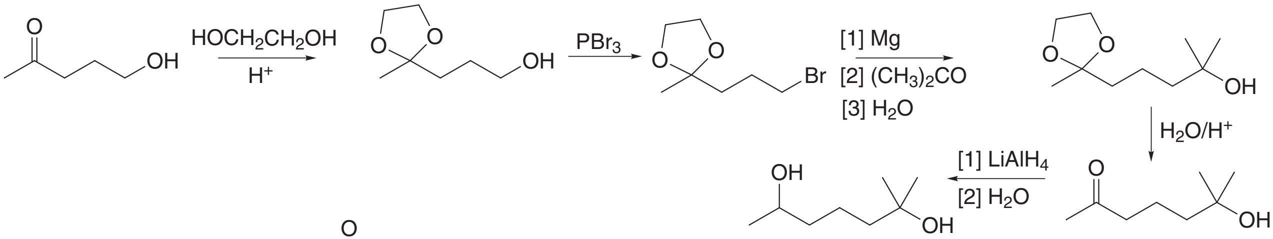


17.73

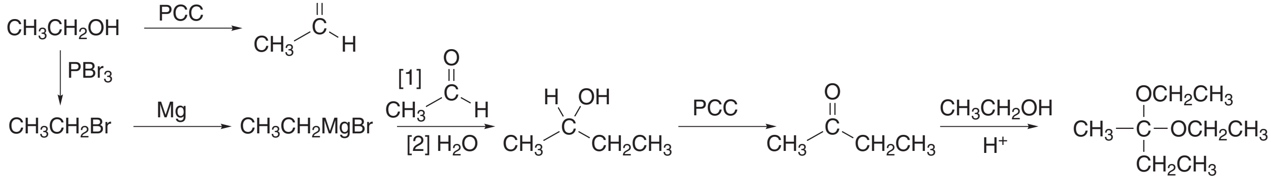
a.



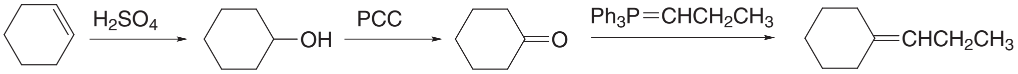
b.



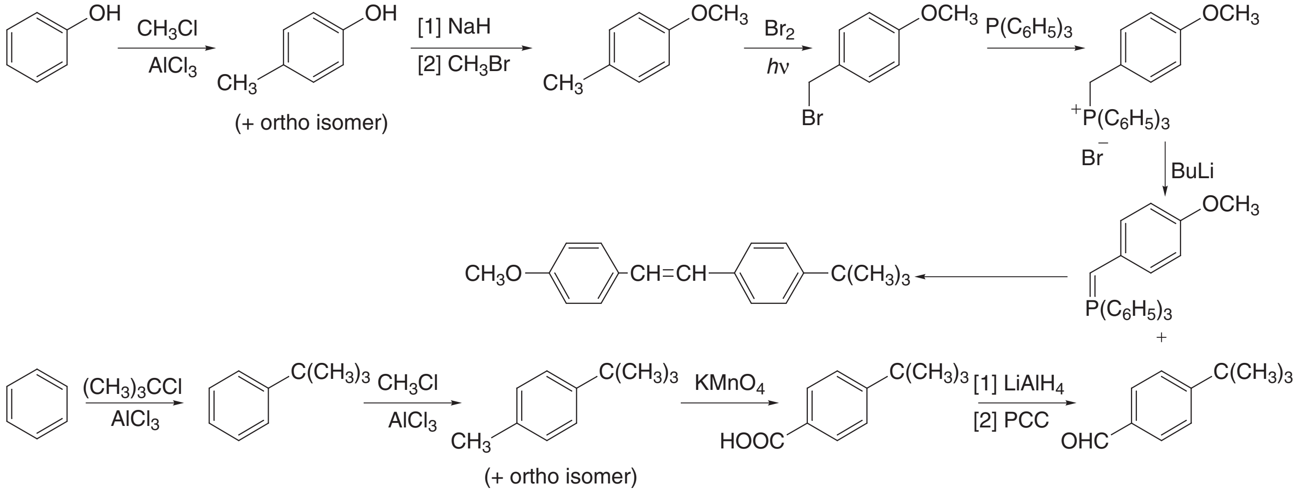
c.



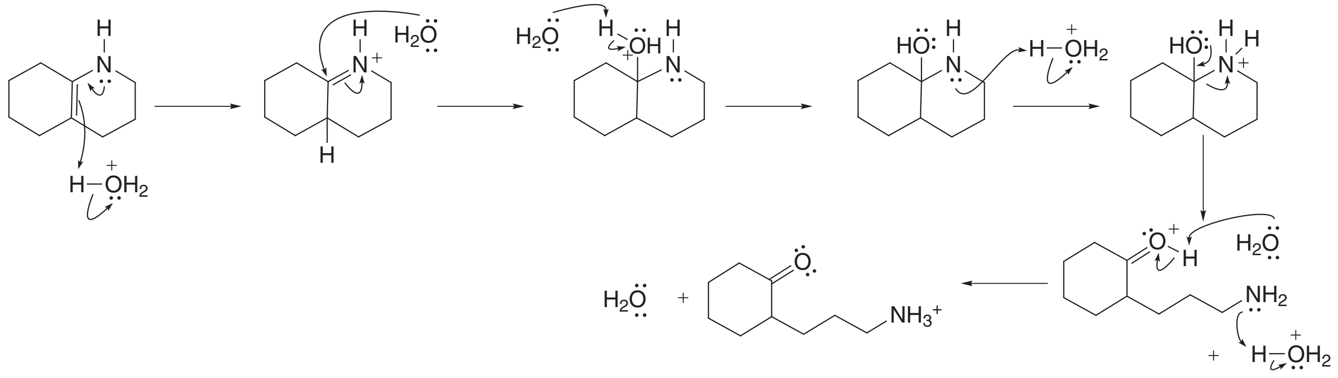
d.



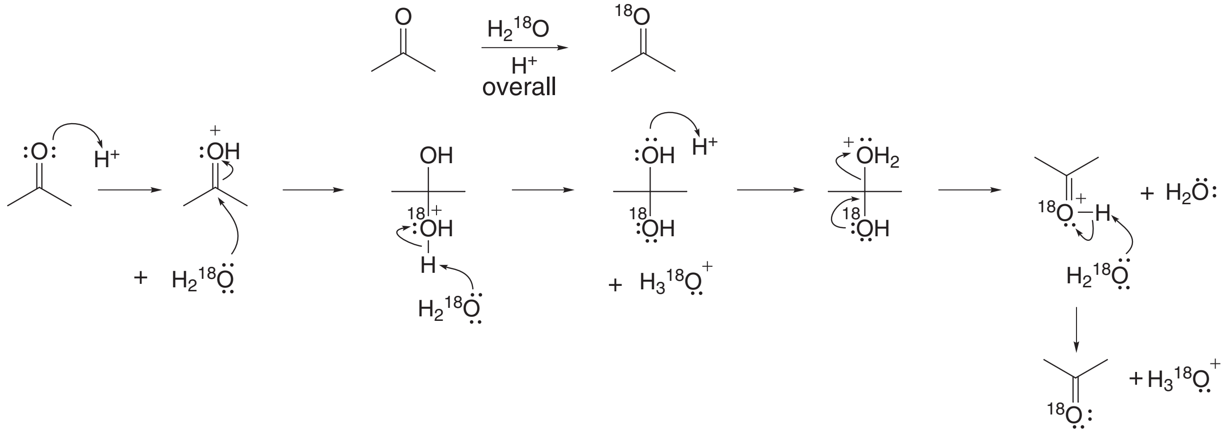
e.



17.74

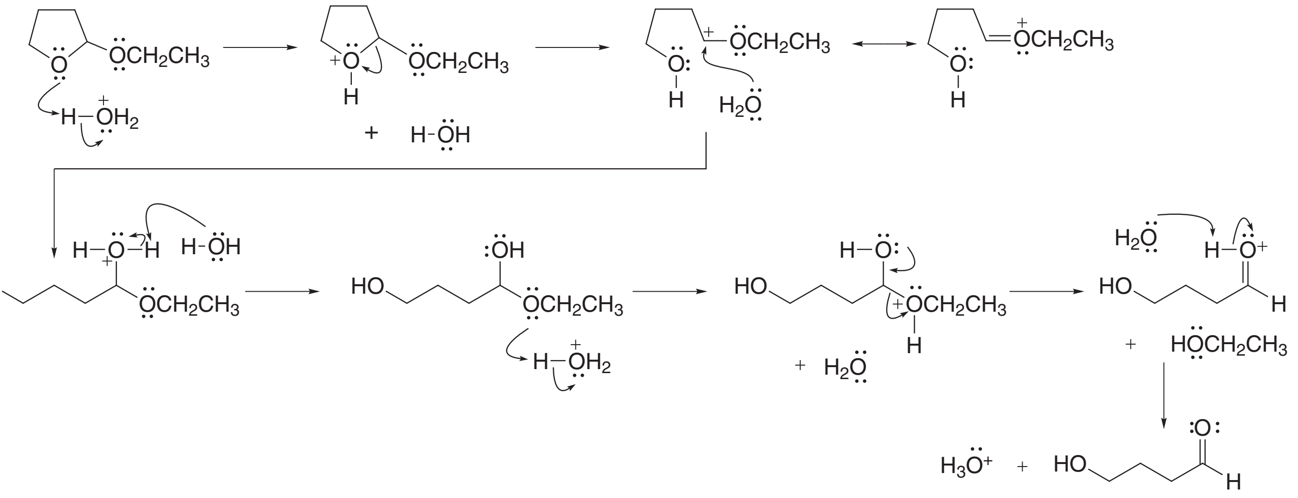


17.75

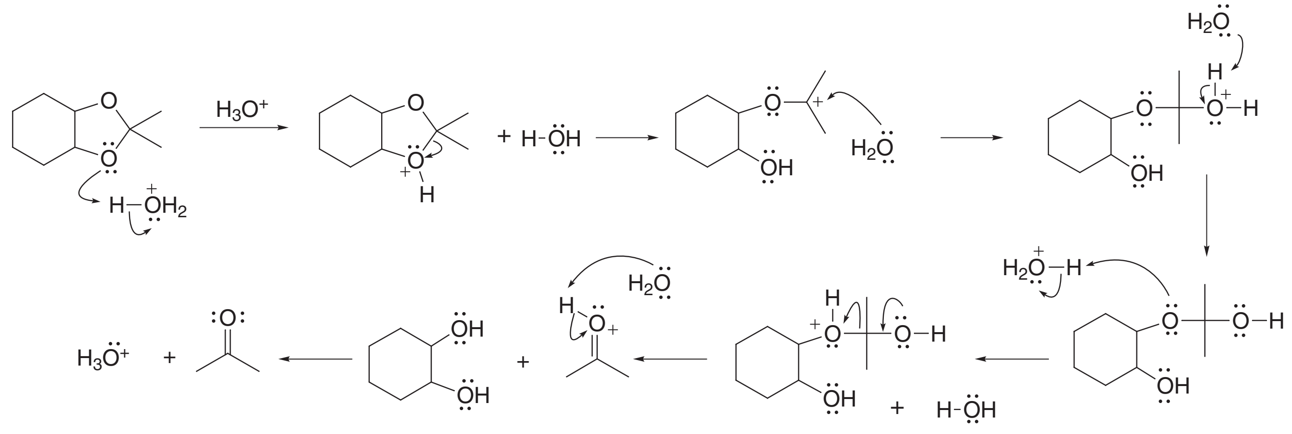


17.76

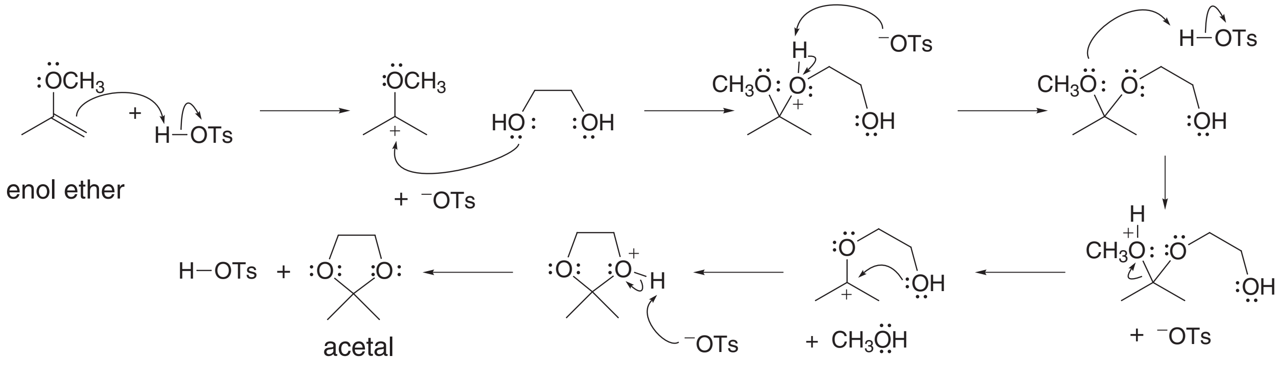
a.



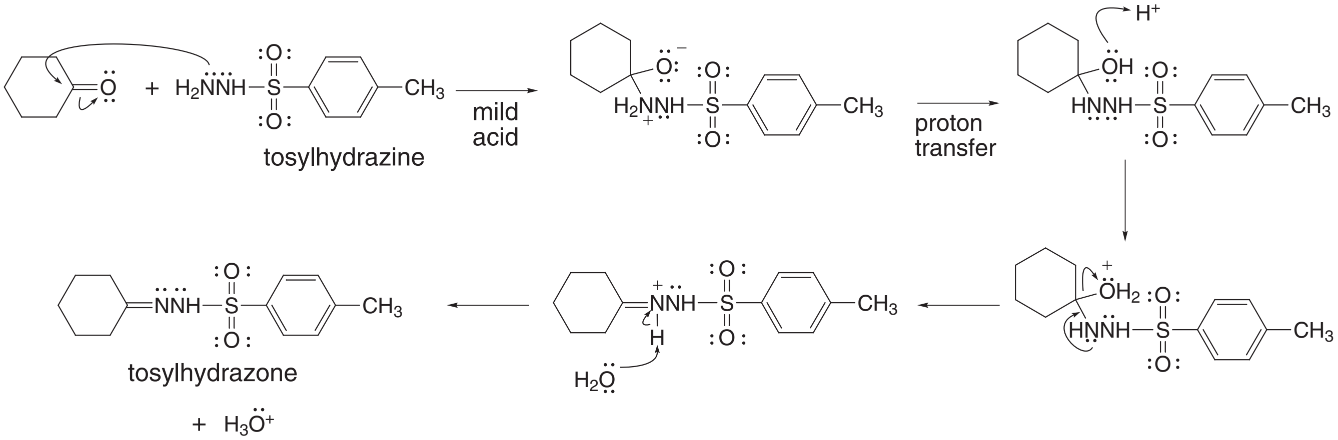
b.



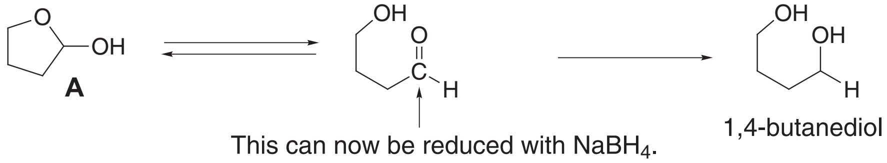
17.77



17.78



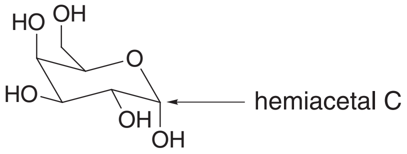
17.79 L'emiacetale **A** è in equilibrio con la sua idrossialdeide ciclica. L'aldeide può essere ridotta dall'idruro e questo porta alla formazione di 1,4-butandiolo.



17.80 Il β-D-glucosio ha cinque centri stereogenici. L'α- e il β-D-glucosio sono stereoisomeri (diastereomeri). **A** e il β-D-glucosio sono isomeri costituzionali.

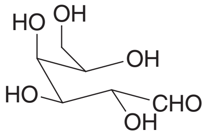
17.81

a.

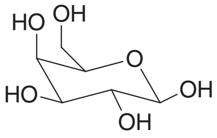


α-D-galactose

c.

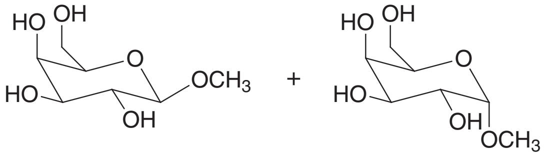


b.



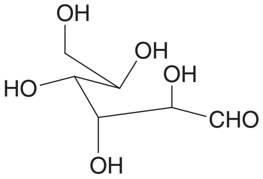
β-D-galactose

d.

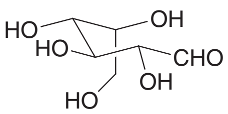


17.82

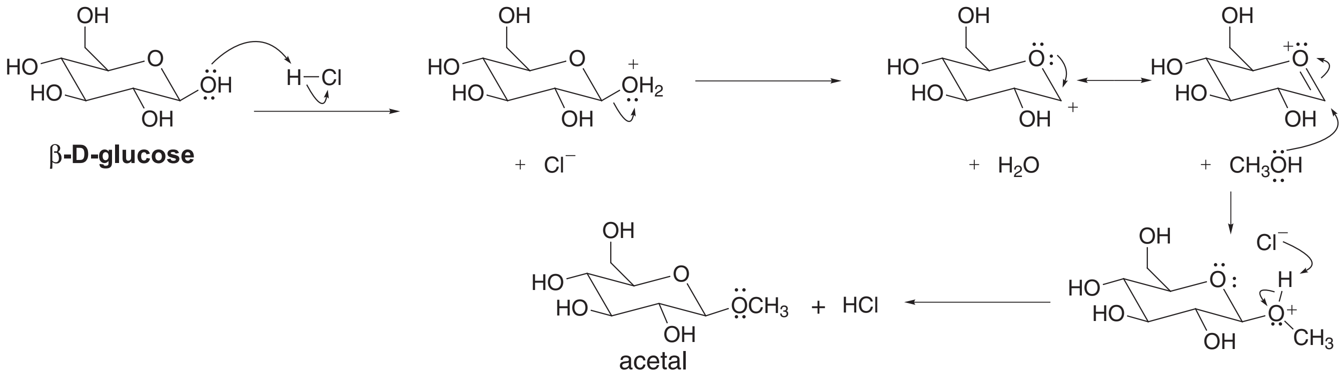
a.



b.



17.83

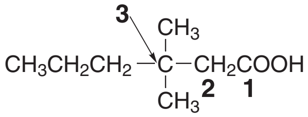


Captolo 18

18.1 Per denominare un acido carbossilico:

[1] Trovare la catena più lunga che contiene il gruppo COOH e cambiare la desinenza *–o* in *–oico*.
[2] Numerare la catena in modo che il COOH sia il C1, ma omettere questo numero dal nome.
[3] Seguire tutte le altre regole della nomenclatura.

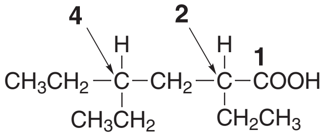
a.



$\mathrm{CH_3CH_2CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2COOH}$

Number the chain to put COOH at C1.
6 carbon chain = **hexanoic acid**
3,3-dimethylhexanoic acid

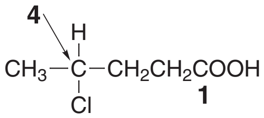
c.



$\mathrm{CH_3CH_2{-}\overset{H}{\underset{CH_3CH_2}{C}}{-}CH_2{-}\overset{H}{\underset{CH_2CH_3}{C}}{-}COOH}$

Number the chain to put COOH at C1.
6 carbon chain = **hexanoic acid**
2,4-diethylhexanoic acid

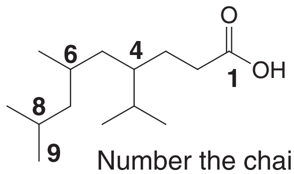
b.



$\mathrm{CH_3{-}\overset{H}{\underset{Cl}{C}}{-}CH_2CH_2COOH}$

Number the chain to put COOH at C1.
5 carbon chain = **pentanoic acid**
4-chloropentanoic acid

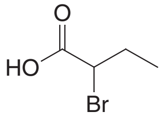
d.



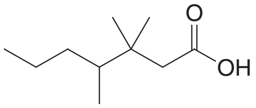
Number the chain to put COOH at C1.
9 carbon chain = **nonanoic acid**
4-isopropyl-6,8-dimethylnonanoic acid

18.2

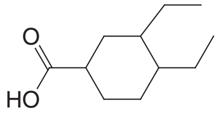
a. 2-bromo**butanoic acid**



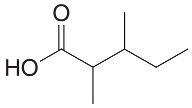
c. 3,3,4-trimethyl**heptanoic acid**



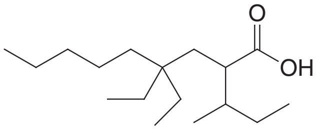
e. 3,4-diethyl**cyclohexanecarboxylic acid**



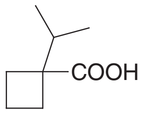
b. 2,3-dimethyl**pentanoic acid**



d. 2-*sec*-butyl-4,4-diethyl**nonanoic acid**

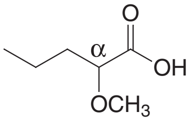


f. 1-isopropyl**cyclobutane-carboxylic acid**

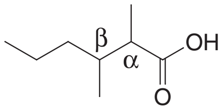


18.3

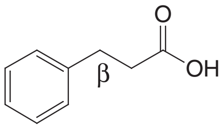
a. α-methoxy**valeric acid**



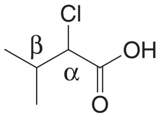
c. α,β-dimethyl**caproic acid**



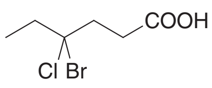
b. β-phenyl**propionic acid**



d. α-chloro-β-methyl**butyric acid**

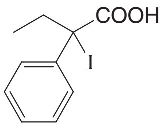


18.4

a. 

6 carbon chain = **hexanoic acid** *or* **caproic acid**

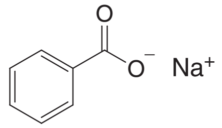
4-bromo-4-chlorohexanoic acid
or
γ-bromo-γ-chlorocaproic acid

b. 

4 carbon chain = **butanoic acid** *or* **butyric acid**

2-iodo-2-phenylbutanoic acid
or
α-iodo-α-phenylbutyric acid

18.5

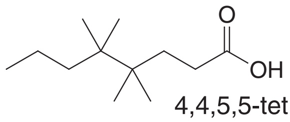


sodium benzoate

18.6 Usare le regole della risposta 19.1 per denominare i composti.

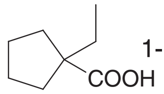
a. $(CH_3)_2CHCH_2CH_2CO_2H$ 4-methylpentanoic acid

b. $BrCH_2COOH$ 2-bromoacetic acid

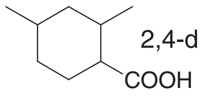
c. 

4,4,5,5-tetramethyloctanoic acid

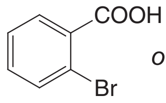
d. $CH_3CH_2CH_2COO^{-}Li^{+}$ lithium butanoate

e. 

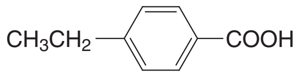
1-ethylcyclopentanecarboxylic acid

f. 

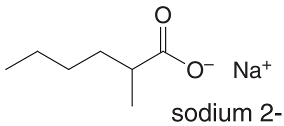
2,4-dimethylcyclohexanecarboxylic acid

g. 

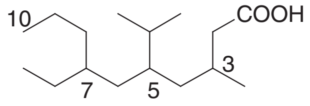
o-bromobenzoic acid

h. 

p-ethylbenzoic acid

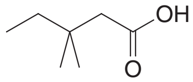
i. 

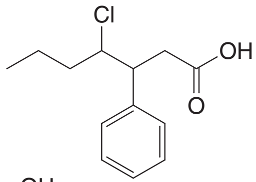
sodium 2-methylhexanoate

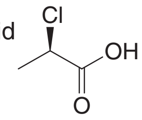
j. 

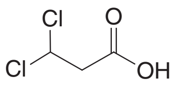
7-ethyl-5-isopropyl-3-methyldecanoic acid

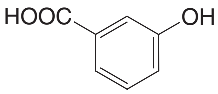
18.7

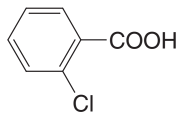
a. 3,3-dimethylpentanoic acid 

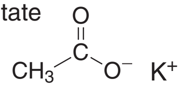
b. 4-chloro-3-phenylheptanoic acid 

c. (*R*)-2-chloropropanoic acid 

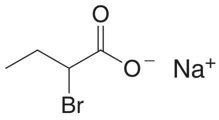
d. β,β-dichloropropionic acid 

e. *m*-hydroxybenzoic acid 

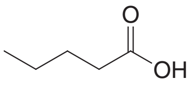
f. *o*-chlorobenzoic acid 

g. potassium acetate 

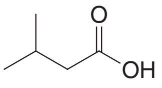
$CH_3COO^{-}\ K^{+}$

h. sodium α-bromobutyrate 

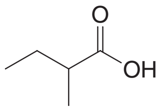
18.8



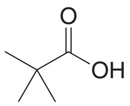
pentanoic acid



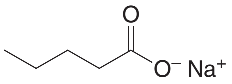
3-methylbutanoic acid



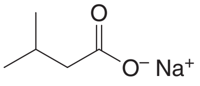
2-methylbutanoic acid



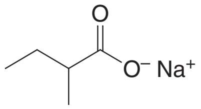
2,2-dimethylpropanoic acid



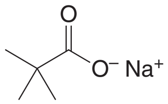
sodium pentanoate



sodium 3-methylbutanoate



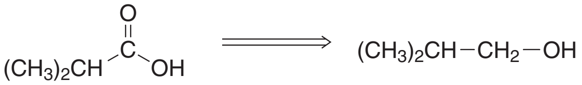
sodium 2-methylbutanoate



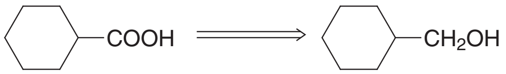
sodium
2,2-dimethylpropanoate

18.9 Gli alcoli 1° sono convertiti in acidi carbossilici da reazioni di ossidazione.

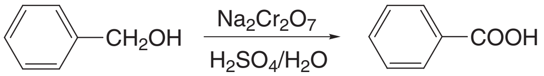
a. 

b. 

$(CH_3)_2CH\text{–}\overset{\overset{O}{\|}}{C}\text{–}OH \Longrightarrow (CH_3)_2CH\text{–}CH_2\text{–}OH$

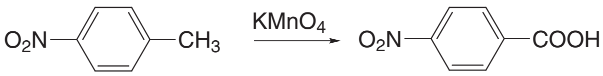
c. 

18.10

a. 

A

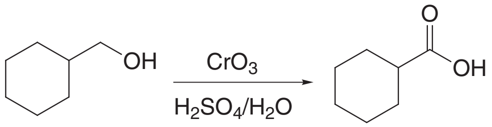
b. $\underset{\mathbf{B}}{CH_3C\equiv CCH_3} \xrightarrow[\text{[2] } H_2O]{\text{[1] } O_3} CH_3COOH$ (2 equiv)

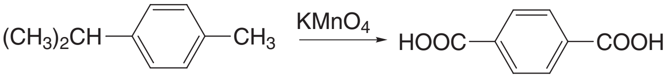
c. 

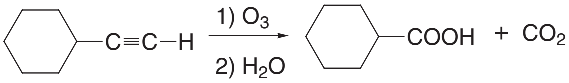
C

(Any R group with benzylic H's
can be present para to NO_2.)

18.11

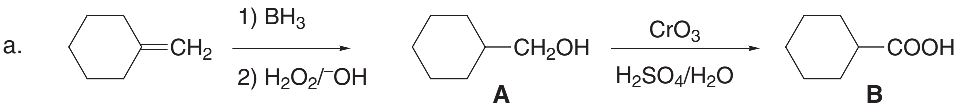
a. 

b. 

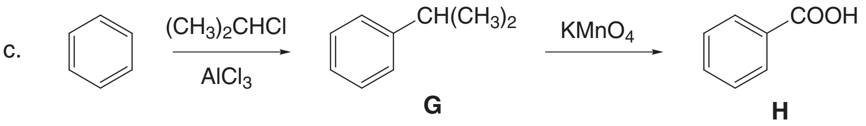
c. 

d. $CH_3(CH_2)_6CH_2OH \xrightarrow[H_2SO_4/H_2O]{Na_2Cr_2O_7} CH_3(CH_2)_6COOH$

18.12



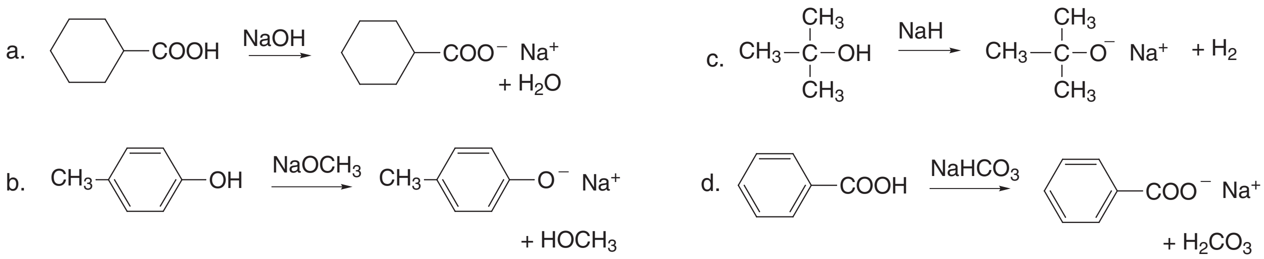
b. $HC{\equiv}CH \xrightarrow[2)\ CH_3I]{1)\ NaNH_2} \underset{\textbf{C}}{HC{\equiv}CCH_3} \xrightarrow[2)\ CH_3CH_2I]{1)\ NaNH_2} \underset{\textbf{D}}{CH_3CH_2C{\equiv}CCH_3} \xrightarrow[2)\ H_2O]{1)\ O_3} \underset{\textbf{E}}{CH_3CH_2COOH} \ \mathbf{+}\ \underset{\textbf{F}}{CH_3COOH}$



18.13 Gli acidi carbossilici reagiscono con tutti i reagenti elencati, eccetto CrO_3. Essi sono infatti al massimo grado di ossidazione, così non possono essere facilmente ossidati ad altri composti con agenti ossidanti come CrO_3.

a. NaOH b. HCl c. $LiAlH_4$ d. CrO_3 **NO REACTION** e. $NaOCH_3$

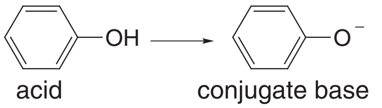
18.14



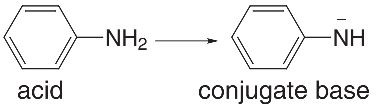
18.15 CH_3COOH ha un pK_a di 4.8. Ciascuna base con un acido coniugato con pK_a maggiore di 4.8 può deprotonarlo.

a. F^- pK_a (HF) = 3.2 **not strong enough**
b. $(CH_3)_3CO^-$ pK_a $[(CH_3)_3COH]$= 18 **strong enough**
c. CH_3^- pK_a (CH_4) = 50 **strong enough**
d. $^-NH_2$ pK_a (NH_3) = 38 **strong enough**
e. Cl^- pK_a (HCl) = –7.0 **not strong enough**

18.16 L'acido più forte ha la base coniugata più debole. Ricordare l'andamento periodico che determina l'acidità.



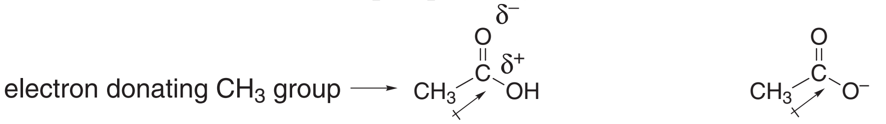
weaker, more stable conjugate base
O is further right in the periodic table
O is more electronegative.
stronger acid



stronger, less stable conjugate base
N is further left in the periodic table
weaker acid

18.17 I gruppi elettron-attrattori rendono un acido più acido, abbassando il suo valore di pK_a.

18.18 L'acido acetico ha un gruppo metile elettron donatore adiacente al gruppo carbossilico. Il gruppo CH_3 stabilizza l'acido e destabilizza la vicina carica negativa sulla base coniugata, rendendo il CH_3COOH meno acido (con pK_a più alto) di HCOOH.



acetic acid
CH_3 stabilizes the partial positive charge.

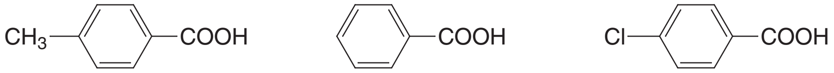
conjugate base
CH_3 destabilizes the negative charge.
a less stable conjugate base

18.19

a. CH_3COOH	$HSCH_2COOH$	$HOCH_2COOH$	b. ICH_2CH_2COOH	ICH_2COOH	$I_2CHCOOH$
least acidic	**intermediate acidity**	**most acidic**	**least acidic**	**intermediate acidity**	**most acidic**

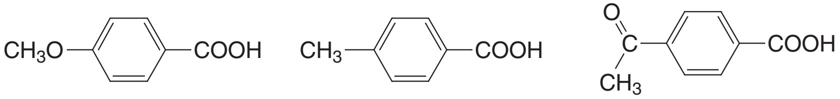
18.20

a.



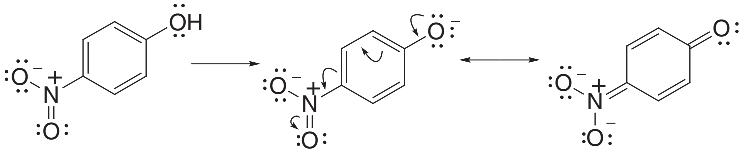
least acidic **intermediate acidity** **most acidic**

b.



least acidic **intermediate acidity** **most acidic**

18.21



p-nitrophenol
pK_a = 7.2

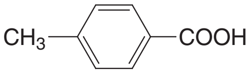
two of the possible resonance structures

The (–) charge is delocalized on the NO_2 group, stabilizing the conjugate base, making *p*-nitrophenol more acidic than phenol.

18.22

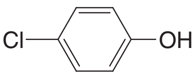
Bases: [1] ^{-}OH pK_a (H_2O) = 15.7; [2] $CH_3CH_2^{-}$ pK_a (CH_3CH_3) = 50; [3] $^{-}NH_2$ pK_a (NH_3) = 38; [4] NH_3 pK_a (NH_4^{+}) = 9.4; [5] $HC{\equiv}C^{-}$ pK_a ($HC{\equiv}CH$) = 25.

a.



pK_a = 4.3
All of the bases
can deprotonate this.

b.



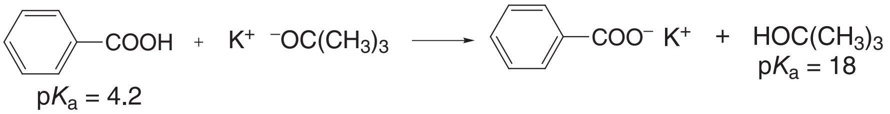
pK_a = 9.4
^{-}OH, $CH_3CH_2^{-}$, $^{-}NH_2$ and $HC{\equiv}C^{-}$
can deprotonate this.

c. $(CH_3)_3COH$

pK_a = 18
$CH_3CH_2^{-}$, $^{-}NH_2$ and $HC{\equiv}C^{-}$
can deprotonate this.

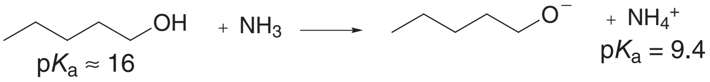
18.23

a.



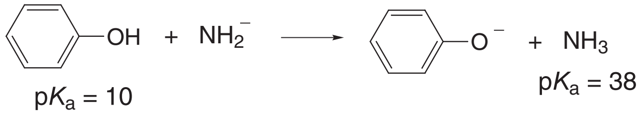
Reaction favors products.

b.



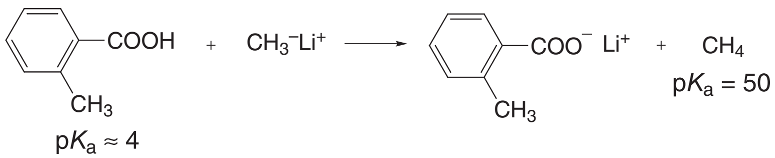
Reaction favors reactants.

c.



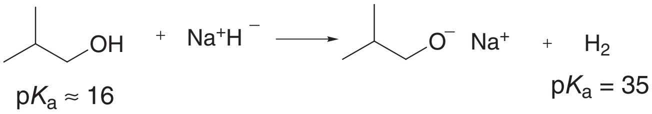
Reaction favors products.

d.



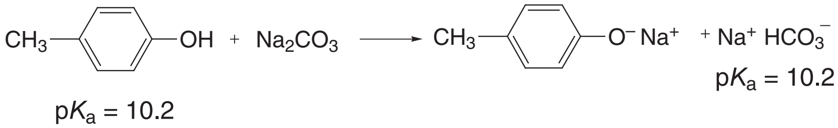
Reaction favors products.

e.



Reaction favors products.

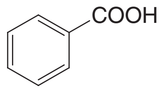
f.



With the same pK_a for the starting acid and the conjugate acid, an equal amount of starting materials and products is present.

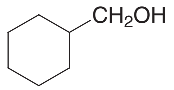
18.24 L'acido più forte ha il più basso pK_a e la base coniugata più debole.

a.



carboxylic acid
stronger acid
lower pK_a
weaker conjugate base

and



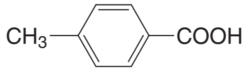
alcohol
weaker acid
higher pK_a
stronger conjugate base

b. $ClCH_2COOH$
weaker acid
higher pK_a
stronger conjugate base

and

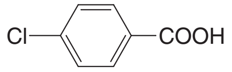
FCH_2COOH
F is more electronegative
stronger acid
lower pK_a
weaker conjugate base

c.



CH_3 is electron donating
weaker acid
higher pK_a
stronger conjugate base

and



Cl is electron withdrawing
stronger acid
lower pK_a
weaker conjugate base

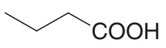
d. $NCCH_2COOH$
CN is electron withdrawing
stronger acid
lower pK_a
weaker conjugate base

and

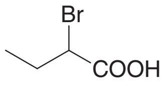
CH_3COOH
weaker acid
higher pK_a
stronger conjugate base

18.25

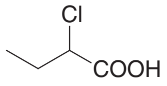
a.



least acidic

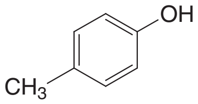


Br is electronegative
intermediate acidity

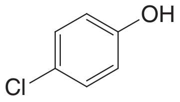


Cl more electronegative
most acidic

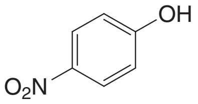
b.



least acidic

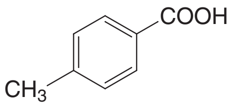


intermediate acidity

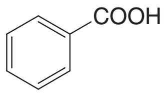


most acidic

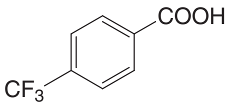
c.



least acidic

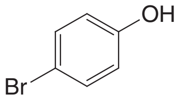


intermediate acidity

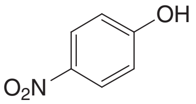


most acidic

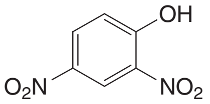
d.



least acidic



intermediate acidity



most acidic

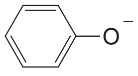
18.26

a. $BrCH_2COO^-$
weakest base

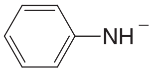
$BrCH_2CH_2COO^-$
intermediate basicity

$(CH_3)_3CCOO^-$
strongest base

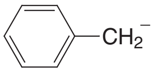
b.



weakest base

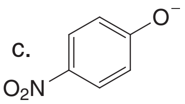


intermediate basicity

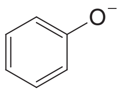


strongest base

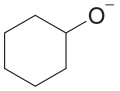
c.



weakest base



intermediate basicity



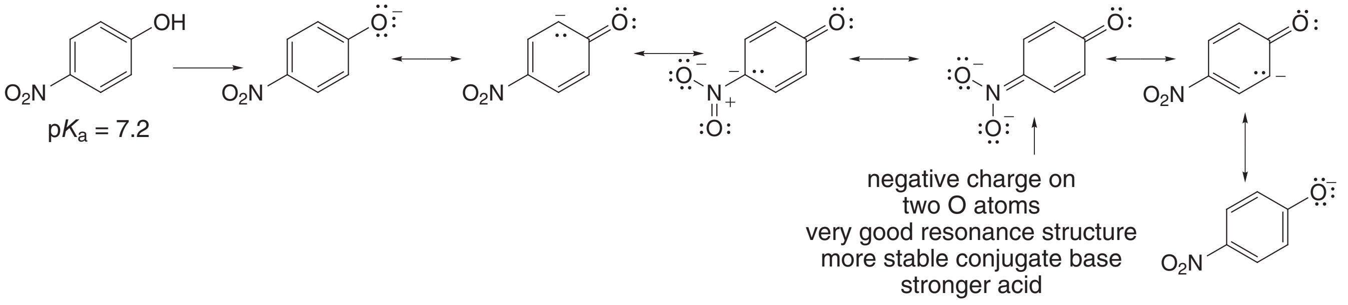
strongest base

18.27

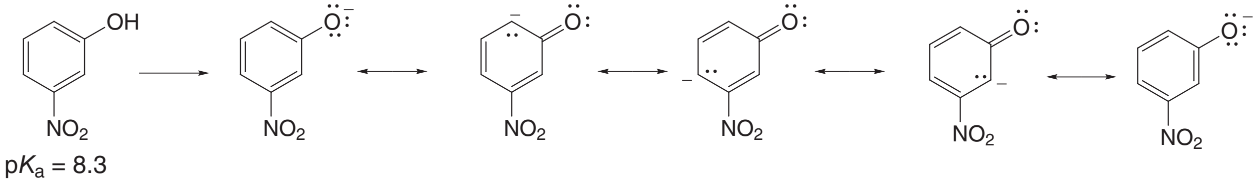
increasing acidity →

	ICH_2COOH	$BrCH_2COOH$	FCH_2COOH	$F_2CHCOOH$	F_3CCOOH
pK_a values	least acidic 3.12	2.86	2.66	1.24	most acidic 0.28

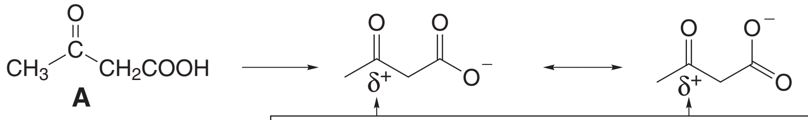
18.28 Nell'isomero para, la carica negativa della base coniugata è delocalizzata sia sull'anello benzenico che sul gruppo NO_2, mentre nell'isomero meta non può essere delocalizzata sul gruppo NO_2. Questo rende la base coniugata dell'isomero para maggiormente stabilizzata per risonanza, e il fenolo para sostituito più acido del suo isomero meta.



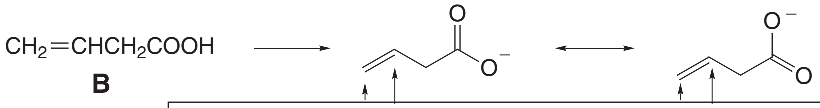
negative charge on two O atoms
very good resonance structure
more stable conjugate base
stronger acid



18.29 Sia **A** che **B** hanno gruppi stabilizzanti per la base coniugata, rendendoli più acidi di CH_3CH_2COOH.

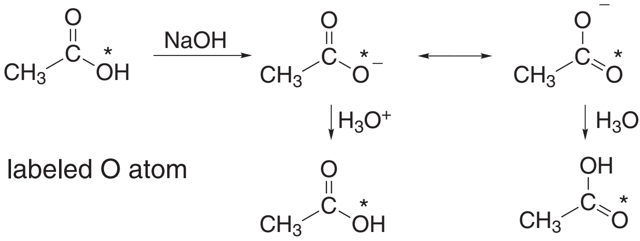


The nearby partial positive charge on the C=O group stabilizes the conjugate base, so the starting acid is more acidic.



The sp^2 hybridized C's of the double bond have a higher percent *s*-character than an sp^3 hybridized C, so they pull more electron density toward them, stabilizing the conjugate base. This makes **B** more acidic than CH_3CH_2COOH.

18.30

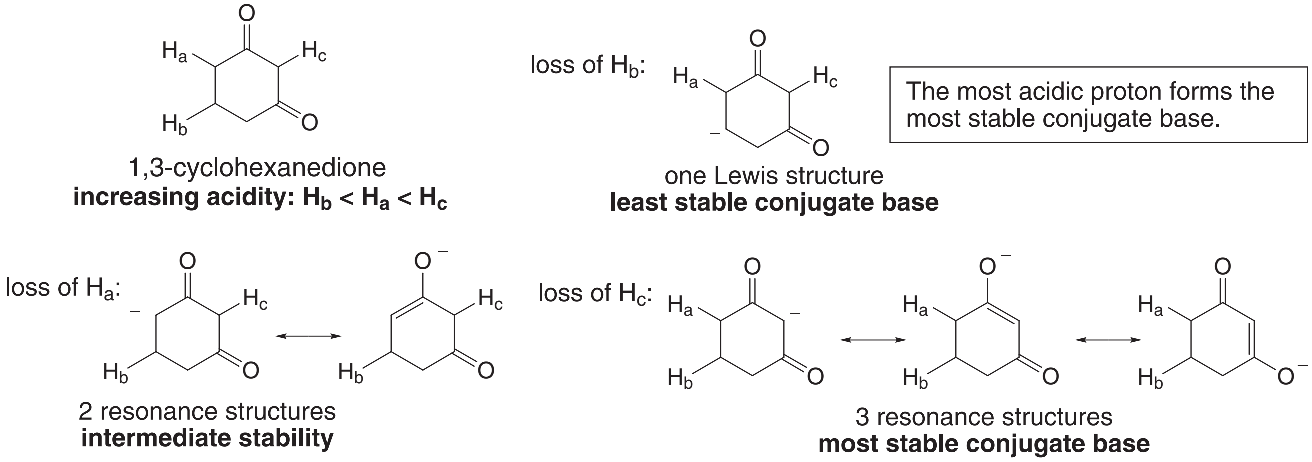


labeled O atom

The resonance-stabilized carboxylate anion can now be protonated on either O atom, the one with the label and the one without the label.

The label is now in two different locations.

18.31



1,3-cyclohexanedione
increasing acidity: $H_b < H_a < H_c$

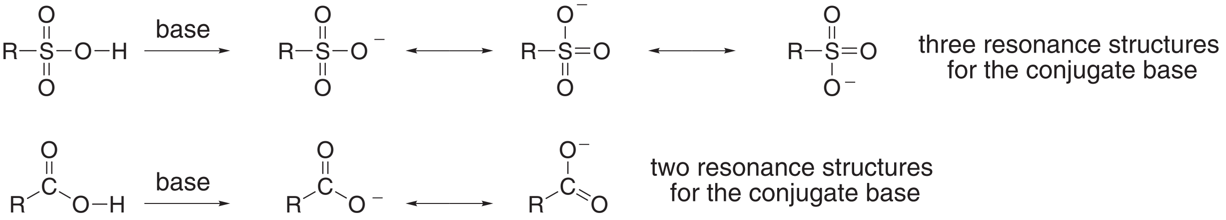
one Lewis structure
least stable conjugate base

The most acidic proton forms the most stable conjugate base.

2 resonance structures
intermediate stability

3 resonance structures
most stable conjugate base

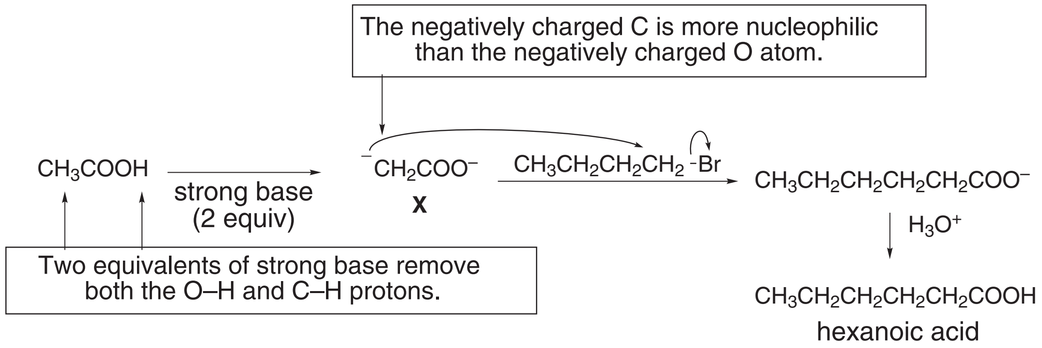
18.32 Come al solito, confrontare la stabilità delle basi coniugate. Con RSO_3H, la perdita di un protone forma una base coniugata che ha tre strutture di risonanza, tutte equivalenti, e posiziona una carica negativa sull'atomo di O più elettronegativo. Con la base coniugata di RCOOH, ci sono solo due di queste strutture risonanti. Quindi la base coniugata RSO_3^- è maggiormente stabilizzata per risonanza di $RCOO^-$, così RSO_3H è un acido più forte di RCOOH.



three resonance structures for the conjugate base

two resonance structures for the conjugate base

18.33

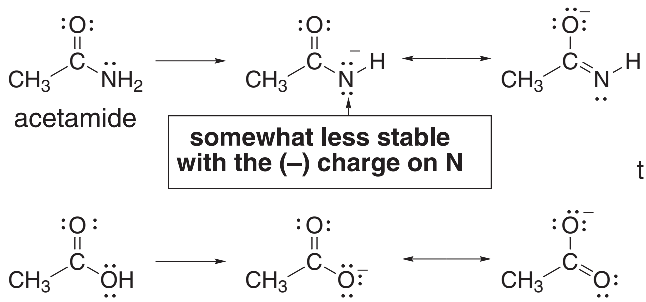


The negatively charged C is more nucleophilic than the negatively charged O atom.

Two equivalents of strong base remove both the O–H and C–H protons.

hexanoic acid

18.34



O is more electronegative than N, making the conjugate base of CH_3COOH more stable than the conjugate base of acetamide. Therefore, acetamide is less acidic.

18.35

weaker conjugate base
better leaving group

$CF_3SO_3H \longrightarrow CF_3SO_3^-$

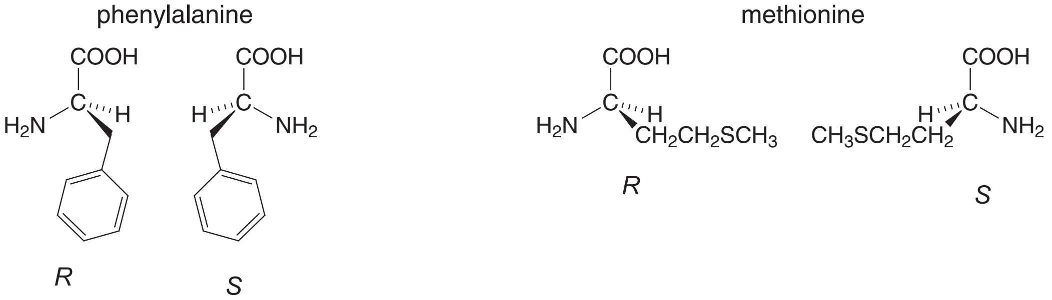
CF_3 is electron *withdrawing*
stronger acid
lower pK_a

stronger conjugate base
worse leaving group

$CH_3SO_3H \longrightarrow CH_3SO_3^-$

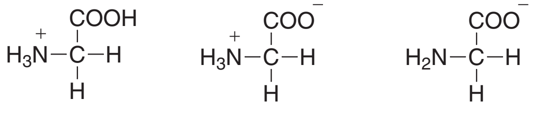
CH_3 is electron *donating*
weaker acid
higher pK_a

18.36



18.37 Poiché gli amminoacidi esistono come zwitterioni (cioè sali), sono troppo polari per essere solubili nei solventi organici come l'etere dietilico. Sono perciò solubili in acqua.

18.38



$$\overset{+}{H_3N}-CH_2-COOH \qquad \overset{+}{H_3N}-CH_2-COO^- \qquad H_2N-CH_2-COO^-$$

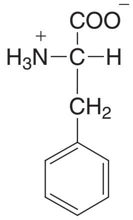
pH = 1

glycine
neutral form

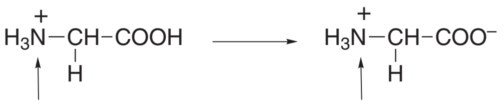
pH = 11

18.39

$$\mathrm{p}I = \frac{\mathrm{p}K_a(\mathrm{COOH}) + \mathrm{p}K_a(\mathrm{NH_3^+})}{2} = \frac{(2.58) + (9.24)}{2} = 5.91$$



18.40



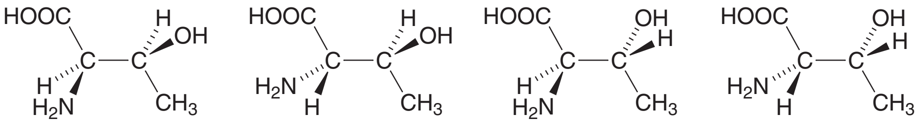
$$H_3\overset{+}{N}-\underset{H}{CH}-COOH \longrightarrow H_3\overset{+}{N}-\underset{H}{CH}-COO^-$$

electron withdrawing group

The nearby (+) stabilizes the conjugate base by an electron withdrawing inductive effect, thus making the starting acid more acidic.

18.41

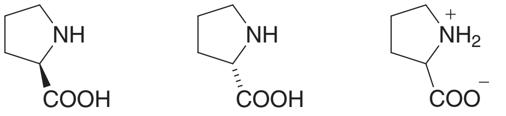
threonine



2*R*,3*S* 2*S*,3*S* 2*R*,3*R* 2*S*,3*R*

naturally occurring

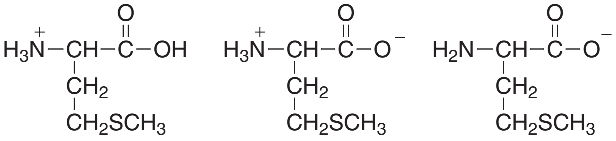
18.42



proline enantiomer zwitterion

18.43

a. methionine

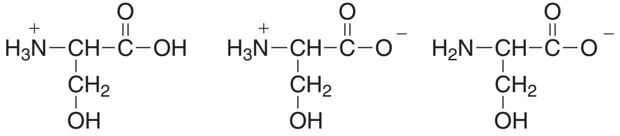


$$H_3\overset{+}{N}-\underset{\underset{CH_2SCH_3}{|}}{\underset{CH_2}{|}}{CH}-\overset{O}{\overset{||}{C}}-OH \quad H_3\overset{+}{N}-CH(CH_2CH_2SCH_3)-\overset{O}{\overset{||}{C}}-O^- \quad H_2N-CH(CH_2CH_2SCH_3)-\overset{O}{\overset{||}{C}}-O^-$$

pH = 1 pH = 7 pH = 11

form at isoelectric point

b. serine



$$H_3\overset{+}{N}-CH(CH_2OH)-\overset{O}{\overset{||}{C}}-OH \quad H_3\overset{+}{N}-CH(CH_2OH)-\overset{O}{\overset{||}{C}}-O^- \quad H_2N-CH(CH_2OH)-\overset{O}{\overset{||}{C}}-O^-$$

pH = 1 pH = 7 pH = 11

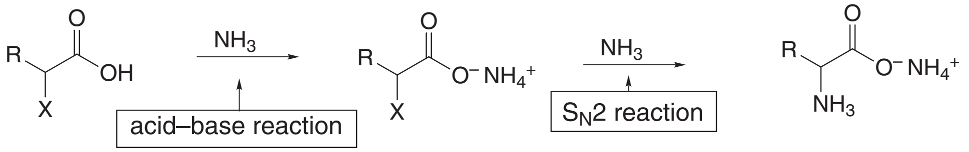
form at isoelectric point

18.44

a. cysteine $$pI = \frac{pK_a(COOH) + pK_a(NH_3^+)}{2} = (2.05) + (10.25) / 2 = \mathbf{6.15}$$

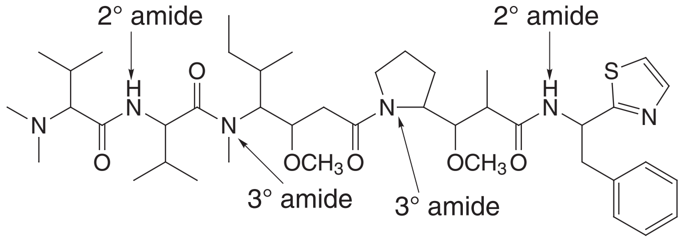
b. methionine $$pI = \frac{pK_a(COOH) + pK_a(NH_3^+)}{2} = (2.28) + (9.21) / 2 = \mathbf{5.75}$$

18.45

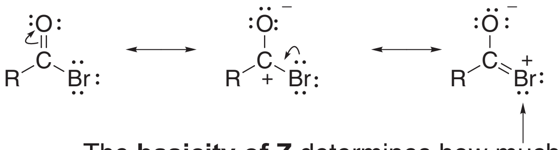


The first equivalent of NH_3 acts as a base to remove a proton from the carboxylic acid. A second equivalent then acts as a nucleophile to displace X to form the ammonium salt of the amino acid.

18.46 Il numero di legami C–N determina la classificazione come ammidi 1°, 2°, o 3°.

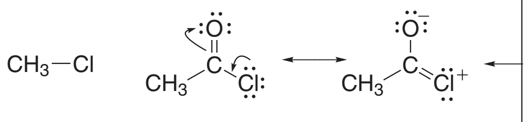


18.47 All'aumentare della basicità di Z, aumenta la stabilità di RCOZ, a causa dell'aumento della stabilizzazione che deriva dalla risonanza.

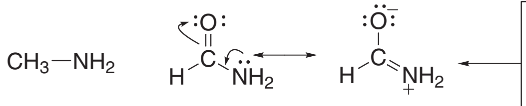


The **basicity of Z** determines how much this structure contributes to the hybrid. Br^- is less basic than ^-OH, so RCOBr is less stable than RCOOH.

18.48



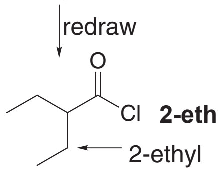
This resonance structure contributes little to the hybrid since Cl^- is a weak base. Thus, the C–Cl bond has little double bond character, making it similar in length to the C–Cl bond in CH_3Cl.



This resonance structure contributes more to the hybrid since $^-NH_2$ is more basic. Thus, the C–N bond in $HCONH_2$ has more double bond character, making it shorter than the C–N bond in CH_3NH_2.

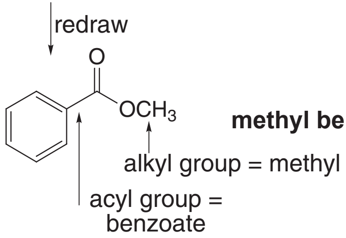
18.49

a. $(CH_3CH_2)_2CH-COCl$



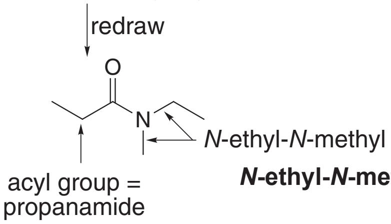
2-ethylbutanoyl chloride

b. $C_6H_5COOCH_3$



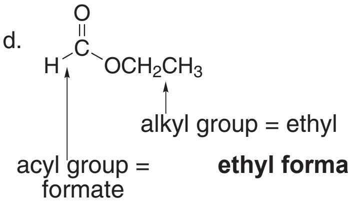
methyl benzoate

c. $CH_3CH_2CON(CH_3)CH_2CH_3$



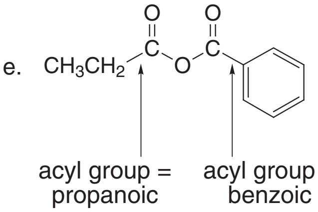
_N_-ethyl-_N_-methylpropanamide

d.



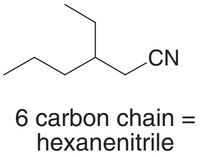
ethyl formate

e.



benzoic propanoic anhydride

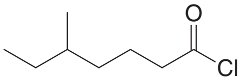
f.



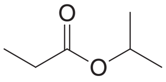
3-ethylhexanenitrile

18.50

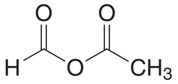
a. 5-methylheptanoyl chloride



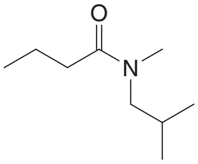
b. isopropyl propanoate



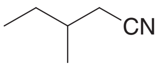
c. acetic formic anhydride



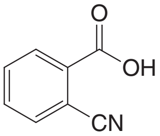
d. *N*-isobutyl-*N*-methylbutanamide



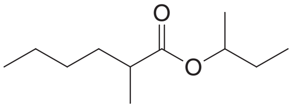
e. 3-methylpentanenitrile



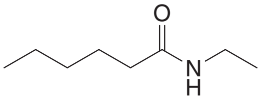
f. *o*-cyanobenzoic acid



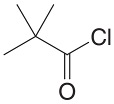
g. *sec*-butyl 2-methylhexanoate



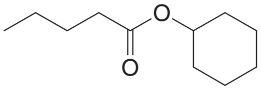
h. *N*-ethylhexanamide



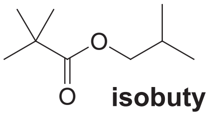
18.51

a.


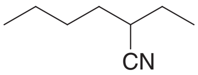
2,2-dimethylpropanoyl chloride

b.


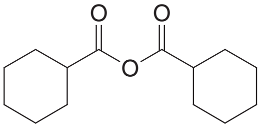
cyclohexyl pentanoate

c.


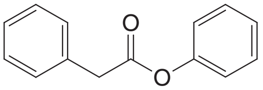
isobutyl 2,2-dimethylpropanoate

d.


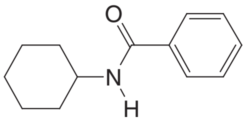
2-ethylhexanenitrile

e.


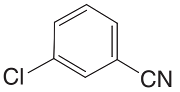
cyclohexanecarboxylic anhydride

f.


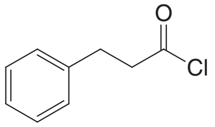
phenyl phenylacetate

g.


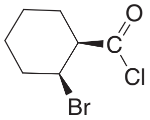
***N*-cyclohexylbenzamide**

h.


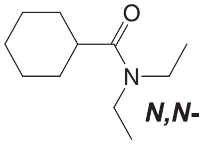
***m*-chlorobenzonitrile**

i.


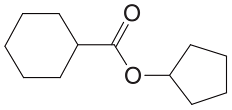
3-phenylpropanoyl chloride

j.


***cis*-2-bromocyclohexanecarbonyl chloride**

k.


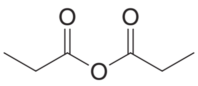
***N,N*-diethylcyclohexanecarboxamide**

l.


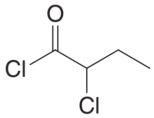
cyclopentyl cyclohexanecarboxylate

18.52

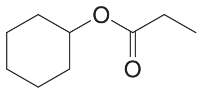
a. propanoic anhydride



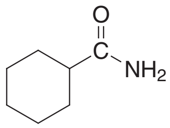
b. α-chlorobutyryl chloride



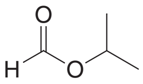
c. cyclohexyl propanoate



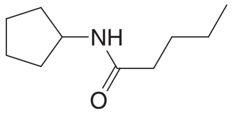
d. cyclohexanecarboxamide



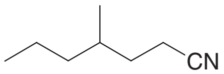
e. isopropyl formate



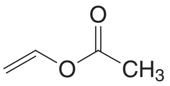
f. *N*-cyclopentylpentanamide



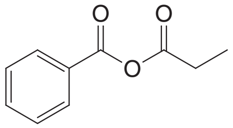
g. 4-methylheptanenitrile



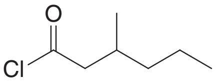
h. vinyl acetate



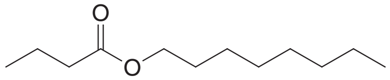
i. benzoic propanoic anhydride



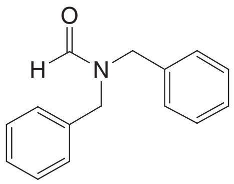
j. 3-methylhexanoyl chloride



k. octyl butanoate

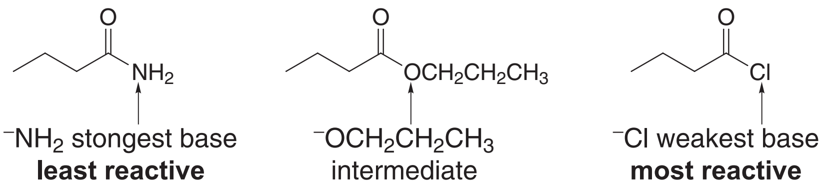


l. *N,N*-dibenzylformamide

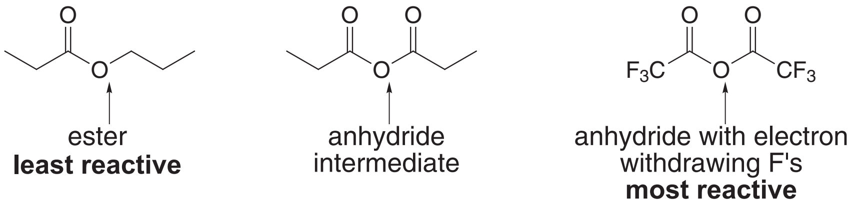


18.53 Classificare i composti usando le regole della risposta 20.13.

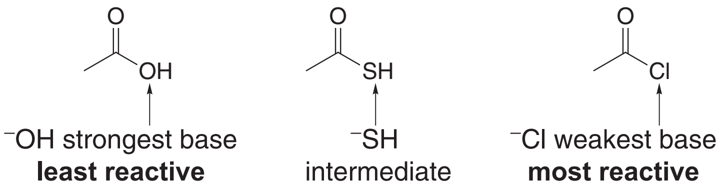
a.



b.

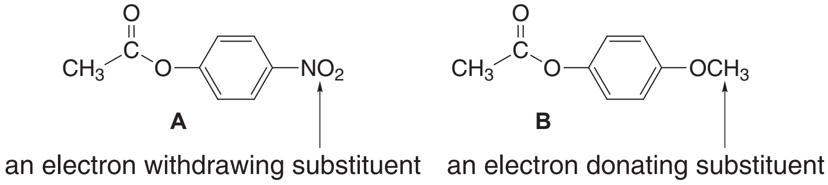


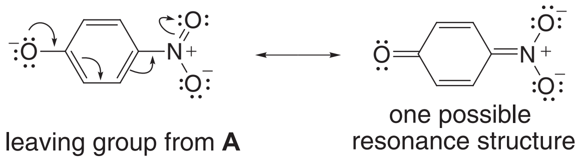
c.



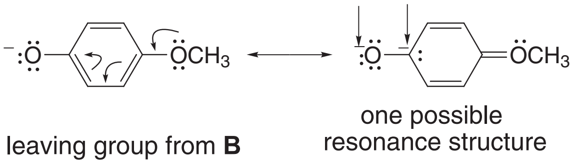
18.54

Better leaving groups make acyl compounds more reactive. **A** has an electron withdrawing NO_2 group, which stabilizes the negative charge of the leaving group, whereas **B** has an electron donating OCH_3 group, which destabilizes the leaving group.



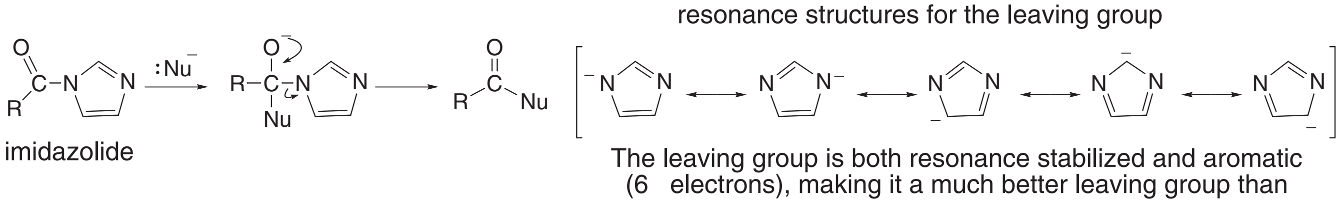


Delocalizing the negative charge on the NO_2 stabilizes the leaving group making **A** more reactive than **B**.



Adjacent negative charges destabilize the leaving group.

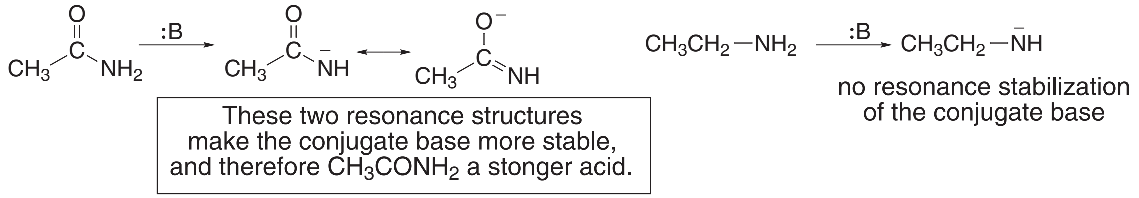
18.55



The leaving group is both resonance stabilized and aromatic (6 electrons), making it a much better leaving group than exists in a regular amide.

18.56

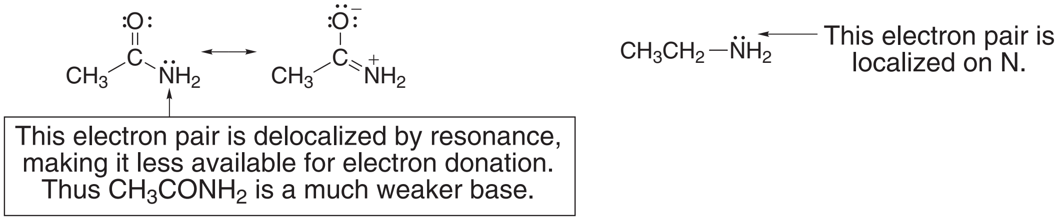
Reaction as an acid:



These two resonance structures make the conjugate base more stable, and therefore CH_3CONH_2 a stonger acid.

no resonance stabilization of the conjugate base

Reaction as a base:

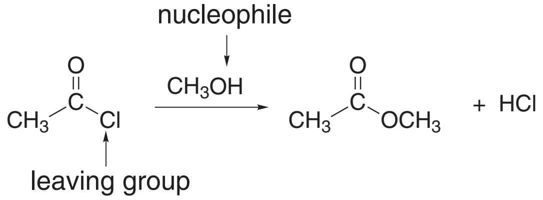


This electron pair is localized on N.

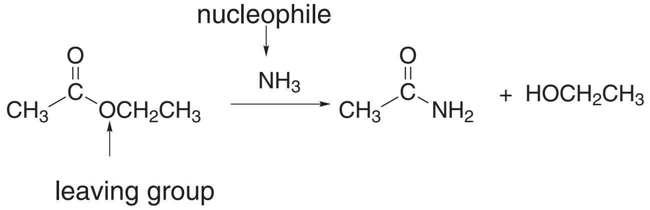
This electron pair is delocalized by resonance, making it less available for electron donation. Thus CH_3CONH_2 is a much weaker base.

18.57 Per disegnare i prodotti di queste reazioni di sostituzione nucleofila acilica, individuare il nucleofilo ed il gruppo uscente. Poi sostituire il gruppo uscente con il nucleofilo e disegnare un prodotto neutro.

a.

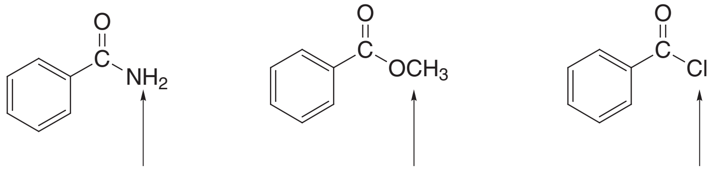


b.



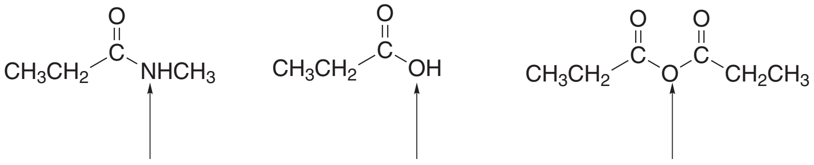
18.58 Migliore è il gruppo uscente, più reattivo risulta il derivato dell'acido carbossilico. La base più debole è il miglior gruppo uscente.

a.



$^-NH_2$ stongest base **least reactive** $^-OCH_3$ intermediate ^-Cl weakest base **most reactive**

b.



$^-NHCH_3$ stongest base **least reactive** ^-OH intermediate $^-OOCCH_2CH_3$ weakest base **most reactive**

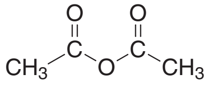
18.59 I composti acilici più reattivi possono essere convertiti nei composti acilici meno reattivi.

a. CH_3COCl more reactive $\xrightarrow[\textbf{YES}]{}$ CH_3COOH less reactive

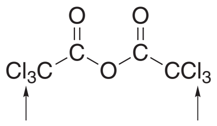
c. CH_3COOCH_3 less reactive $\xrightarrow[\textbf{NO}]{}$ CH_3COCl more reactive

b. $CH_3CONHCH_3$ less reactive $\xrightarrow[\textbf{NO}]{}$ CH_3COOCH_3 more reactive

18.60



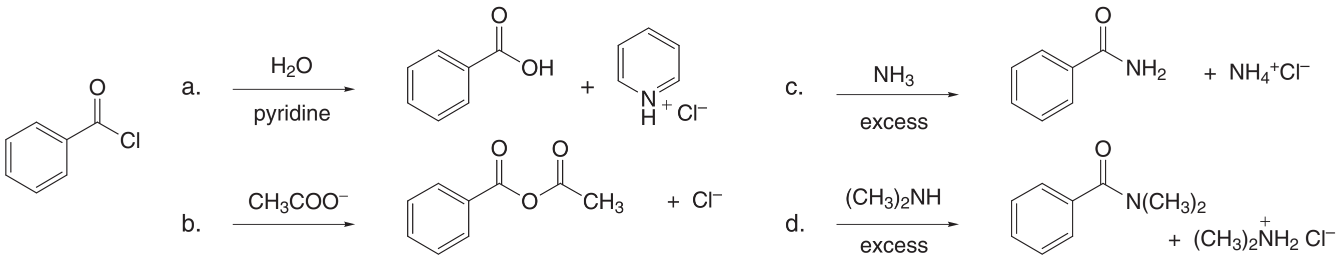
acetic anhydride



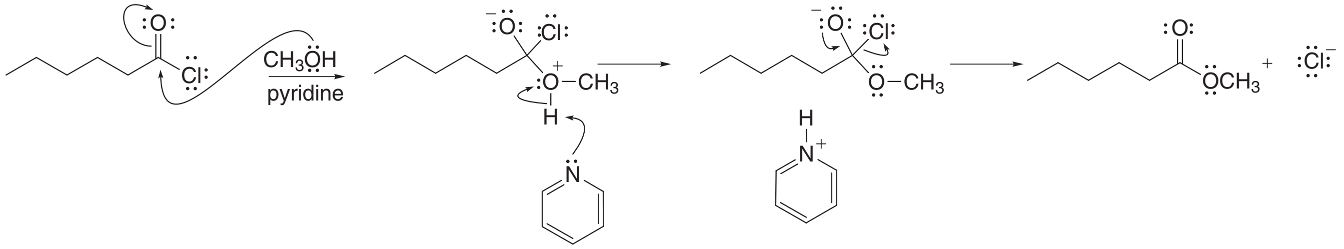
trichloroacetic anhydride

The Cl atoms are electron withdrawing, which makes the conjugate base (the leaving group, CCl_3COO^-) weaker and more stable.

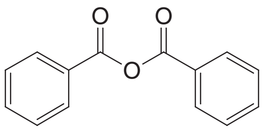
18.61

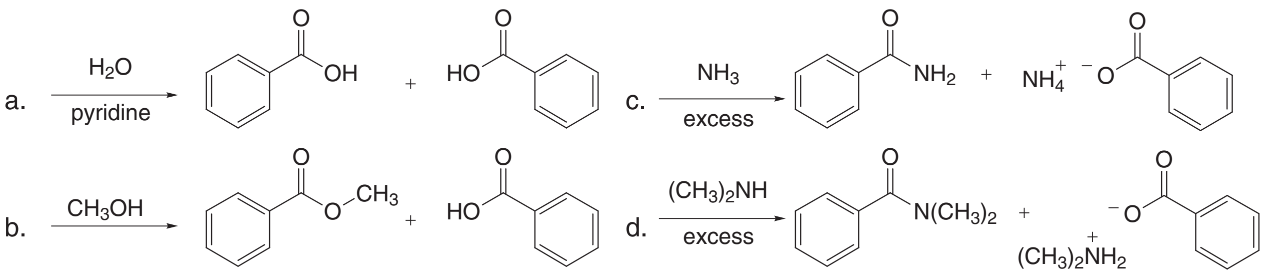


18.62 Il meccanismo ha 3 stadi: [1] attacco nucleofilo dell'O; [2] trasferimento di un protone; [3] eliminazione del gruppo uscente Cl^- per formare il prodotto.



18.63

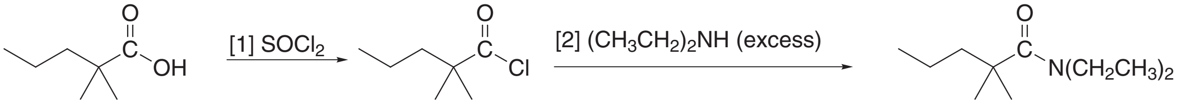




18.64 La reazione di un acido carbossilico con cloruro di tionile lo converte in un cloruro dell'acido.

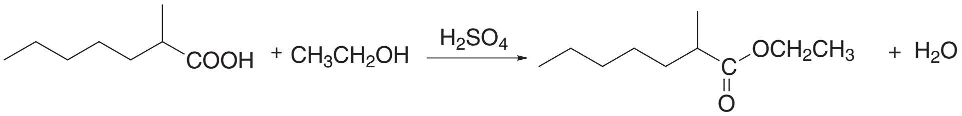
a.

b.

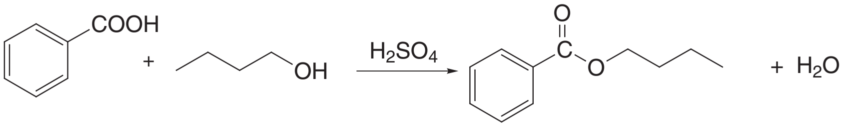


18.65

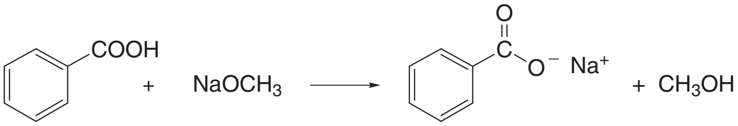
a.



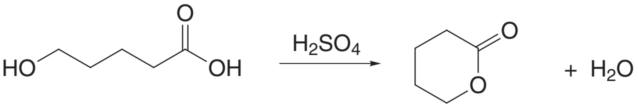
b.



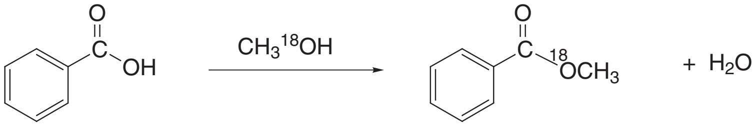
c.



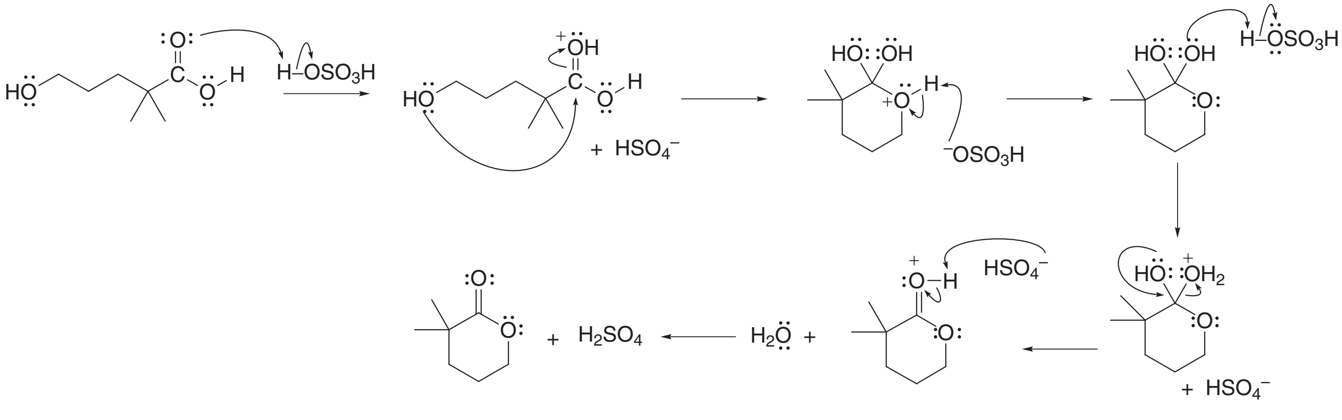
d.



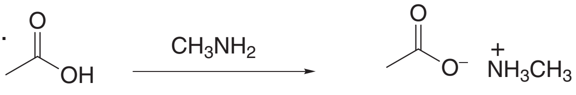
18.66

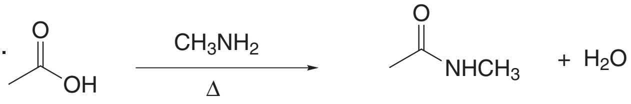


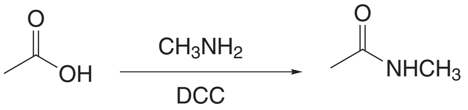
18.67



18.68

a.


b.


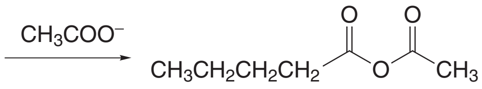
c.


18.69

$CH_3CH_2CH_2CH_2COCl$

a. $\xrightarrow[\text{pyridine}]{H_2O}$ $CH_3CH_2CH_2CH_2COOH$

b. $\xrightarrow[\text{pyridine}]{CH_3CH_2OH}$ $CH_3CH_2CH_2CH_2COOCH_2CH_3$

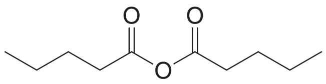
c.


d. $\xrightarrow[\text{excess}]{NH_3}$ $CH_3CH_2CH_2CH_2CONH_2$

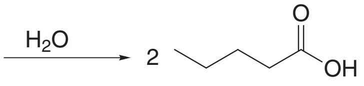
e. $\xrightarrow[\text{excess}]{(CH_3CH_2)_2NH}$ $CH_3CH_2CH_2CH_2CON(CH_2CH_3)_2$

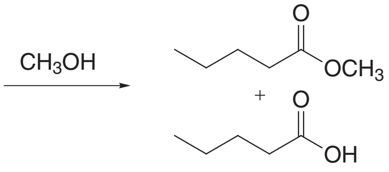
f. $\xrightarrow[\text{excess}]{C_6H_5NH_2}$ $CH_3CH_2CH_2CH_2CONHC_6H_5$

18.70

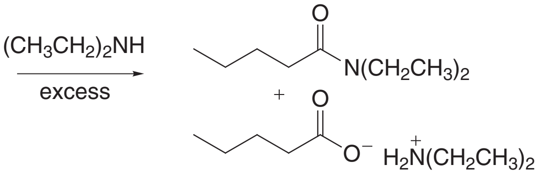


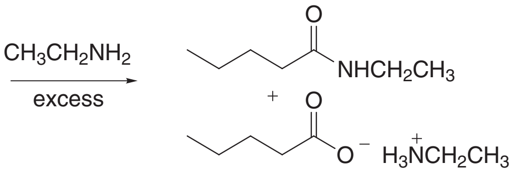
a. $\xrightarrow{SOCl_2}$ no reaction

b.


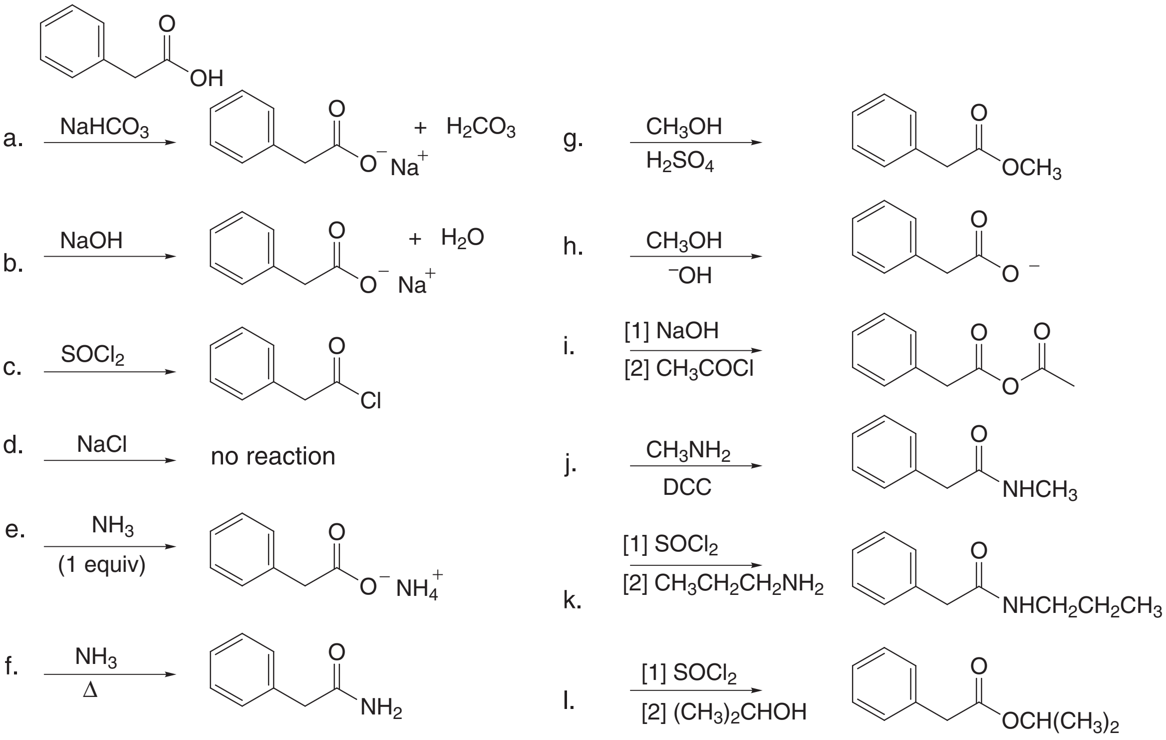
c.


d. $\xrightarrow{NaCl}$ no reaction

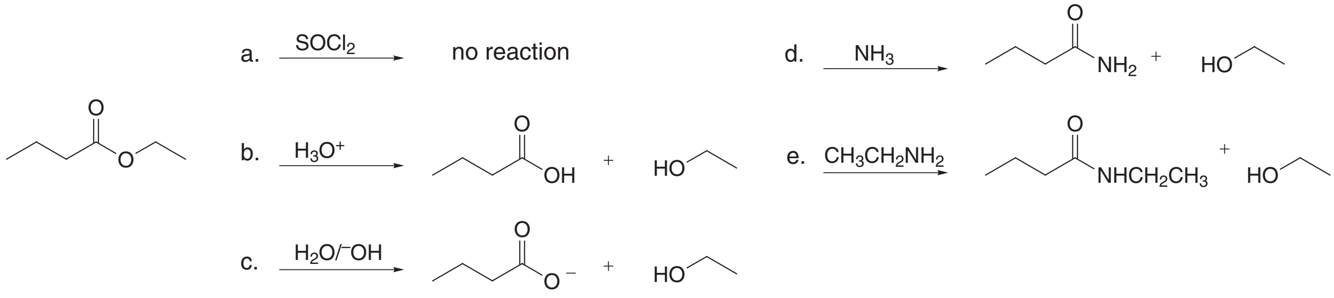
e.


f.


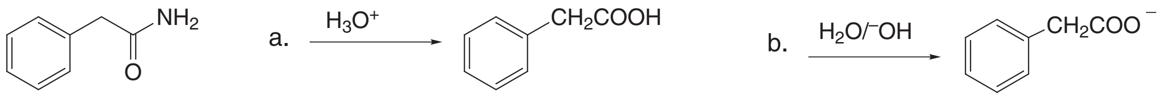
18.71



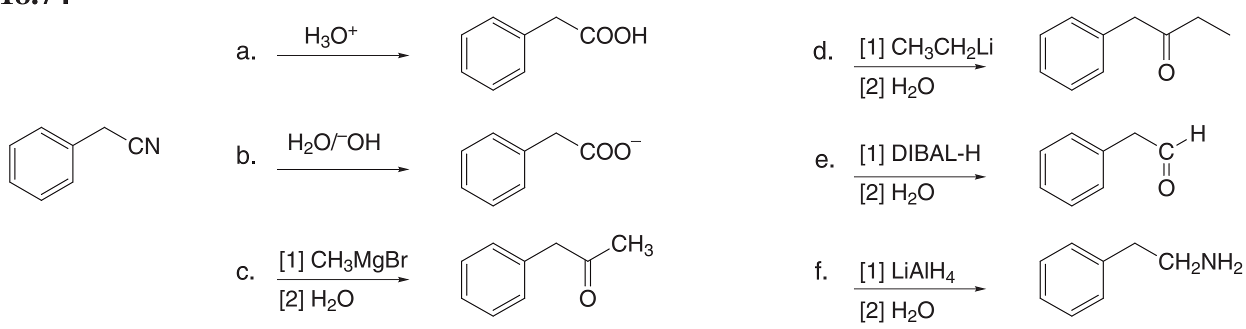
18.72



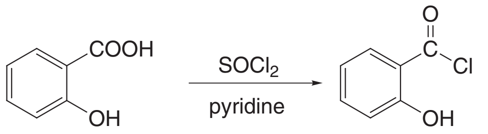
18.73

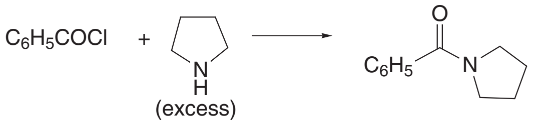


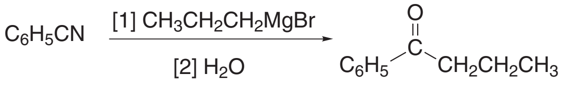
18.74

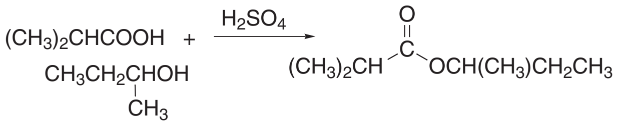


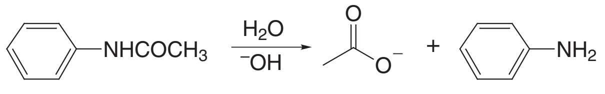
18.75

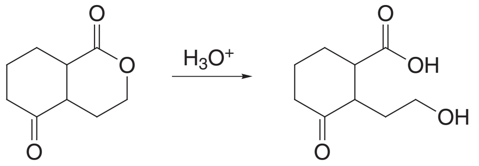
a.


b.


c.


d.


e.


f.


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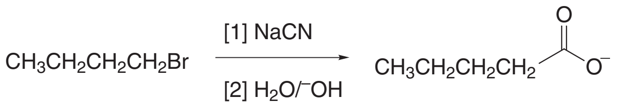
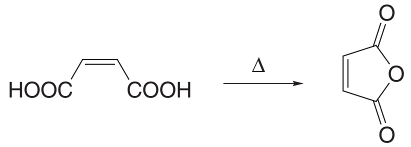
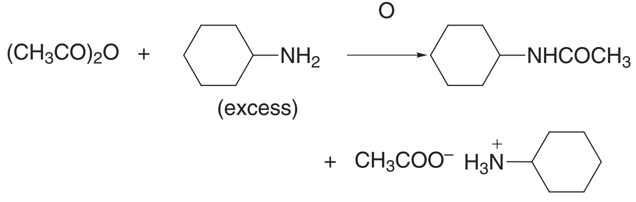


h. $C_6H_5CH_2COOH \xrightarrow[\text{[2] } CH_3CH_2CH_2CH_2NH_2 \text{ [3] } LiAlH_4 \text{ [4] } H_2O]{\text{[1] } SOCl_2} C_6H_5CH_2CH_2NHCH_2CH_2CH_2CH_3$

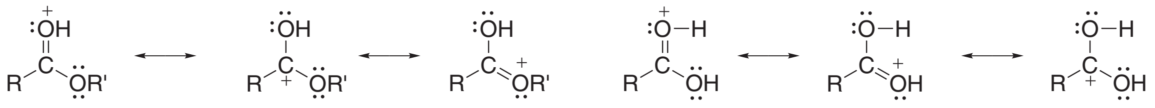
i. $C_6H_5CH_2CH_2CH_2CN \xrightarrow{H_3O^+} C_6H_5CH_2CH_2CH_2COOH$

j.


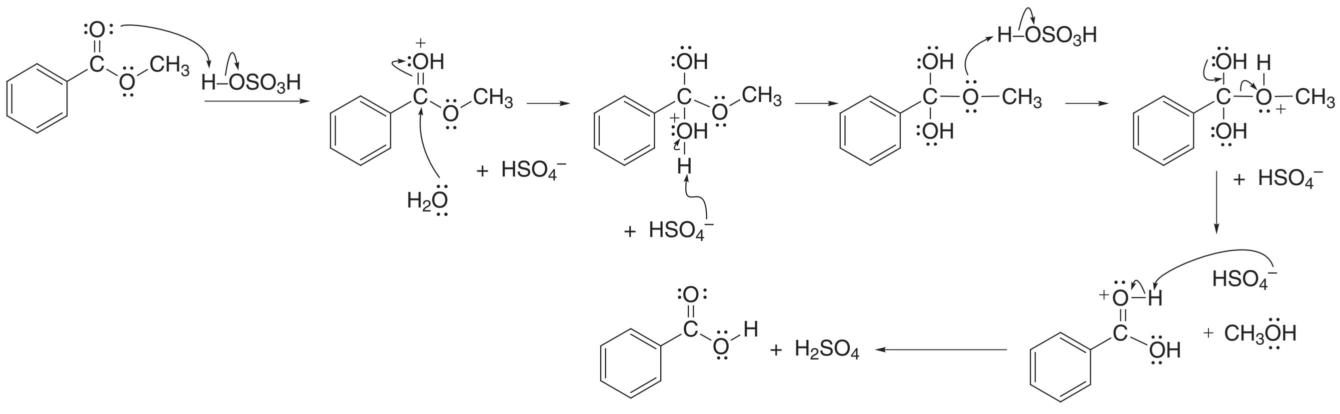
k.


l. $C_6H_5CH_2CH_2COOCH_2CH_3 \xrightarrow[^-OH]{H_2O} C_6H_5CH_2CH_2COO^- + HOCH_2CH_3$

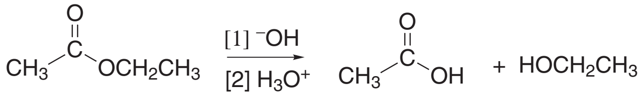
18.76



18.77



18.78 In queste condizioni l'estere è idrolizzato per formare un acido carbossilico e un alcol.

a.


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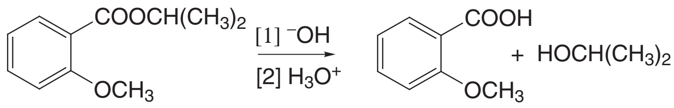

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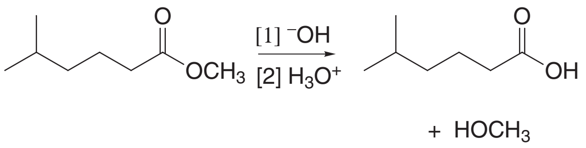
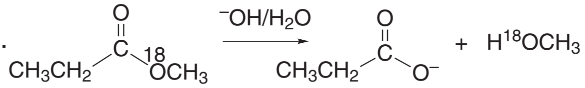


18.79

a.


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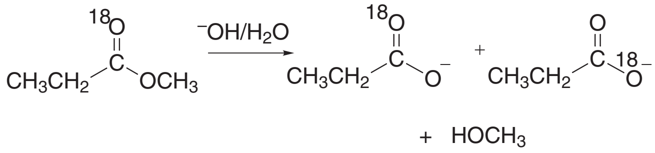
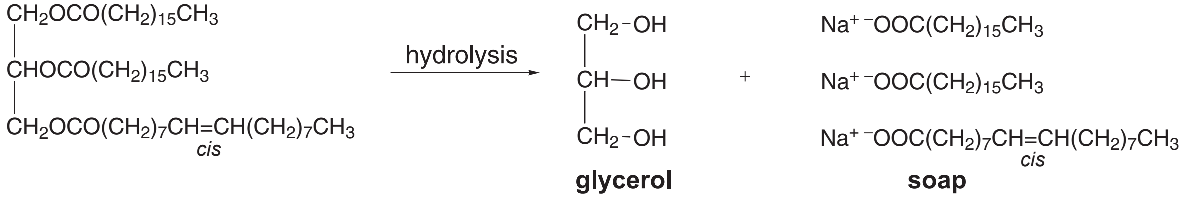
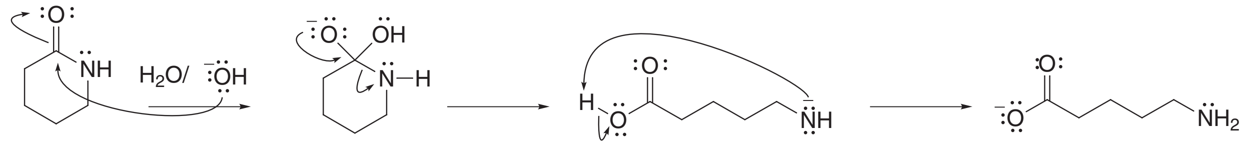


18.80



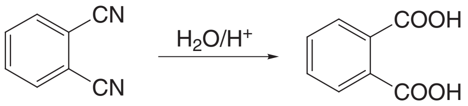
glycerol **soap**

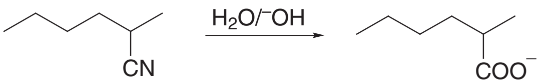
18.81



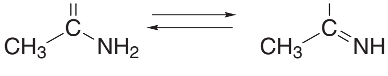
18.82

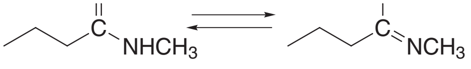
a. $CH_3CH_2CH_2{-}Br \xrightarrow{NaCN} CH_3CH_2CH_2{-}CN$

b.


c.


18.83

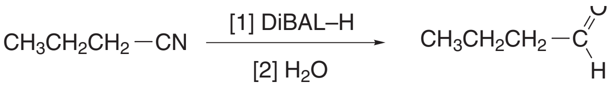
a.


b.


c.

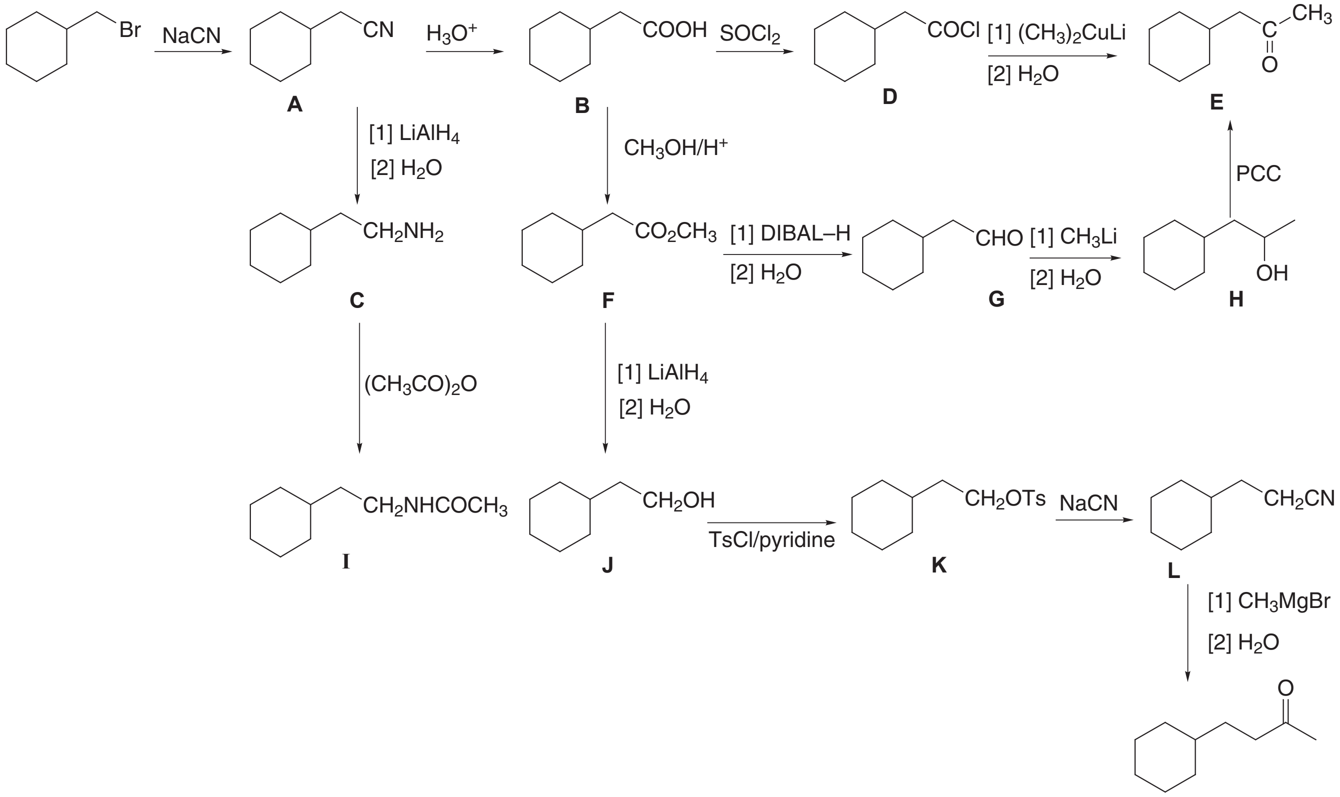

18.84

a. $CH_3CH_2-Br \xrightarrow[\text{[2] } LiAlH_4 \text{ [3] } H_2O]{\text{[1] } NaCN} CH_3CH_2-CH_2NH_2$

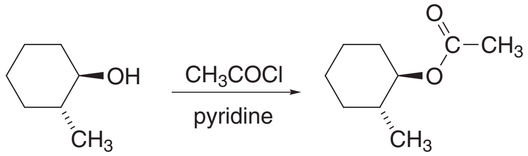
b. 

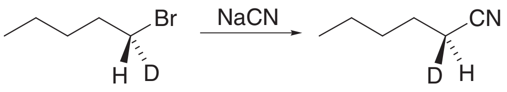
$CH_3CH_2CH_2-CN \xrightarrow[\text{[2] } H_2O]{\text{[1] DiBAL–H}} CH_3CH_2CH_2-\overset{O}{\underset{H}{C}}$

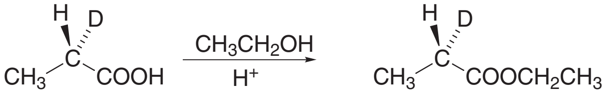
18.85

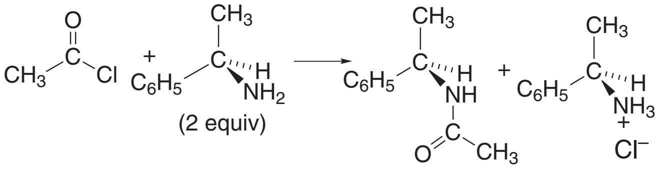


18.86

a. 

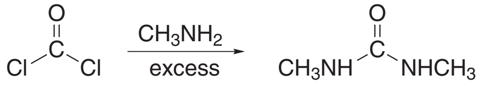
b. 

c. 

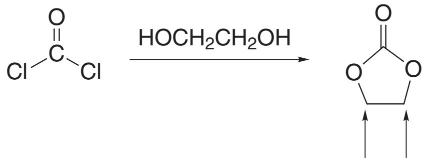
d. 

18.87

a.

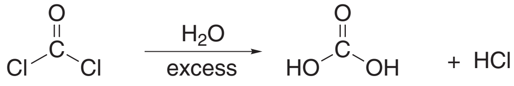


b.



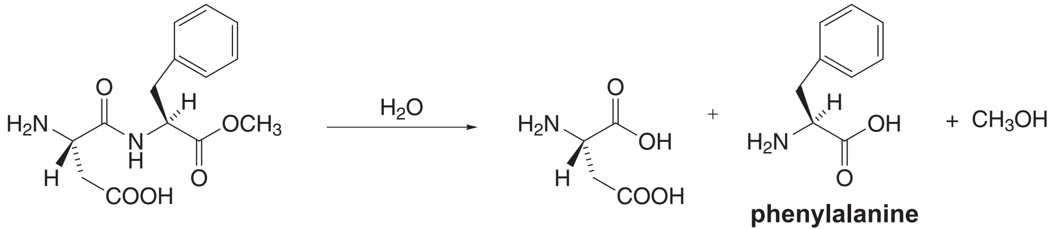
All H's on these C's are identical.

c.



Reaction with H_2O vapor in the lungs results in the formation of HCl, increasing the acidity of the lungs.

18.88

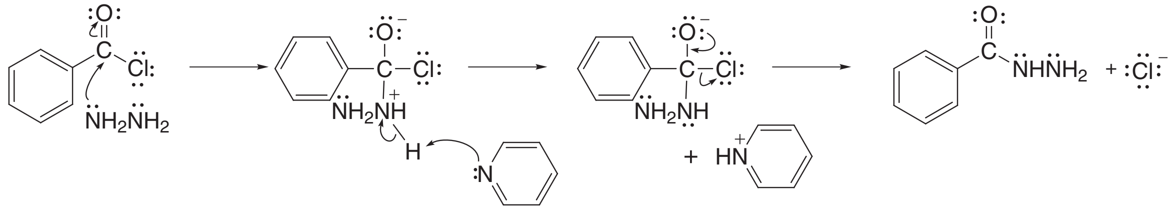


aspartame

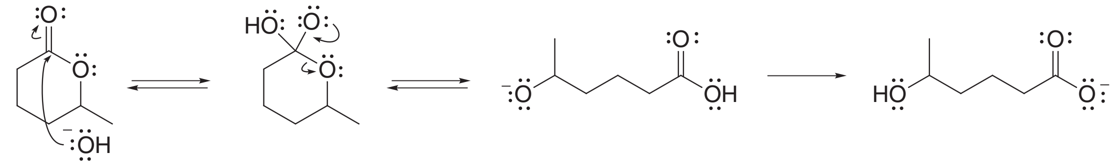
phenylalanine

18.89

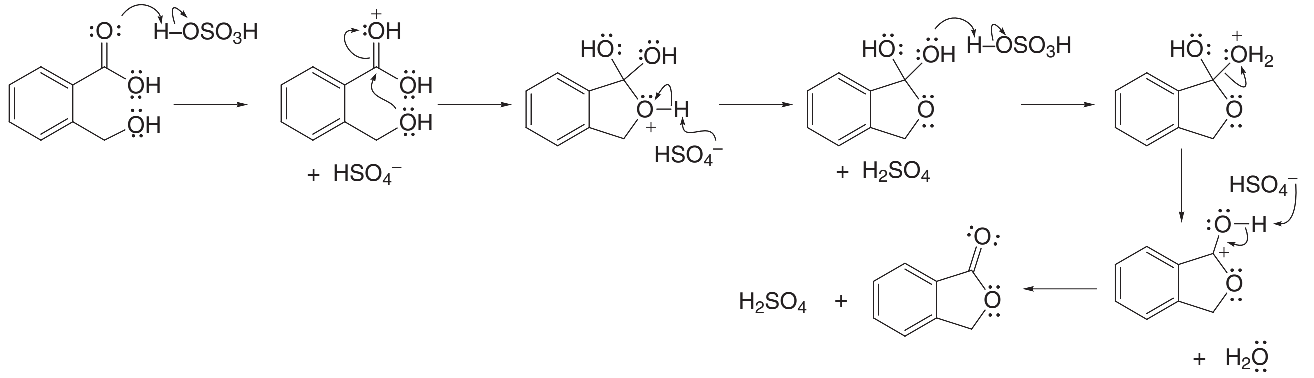
a.



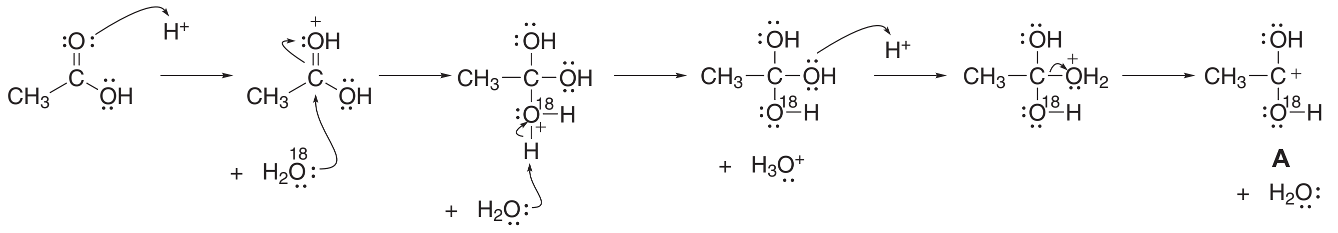
b.



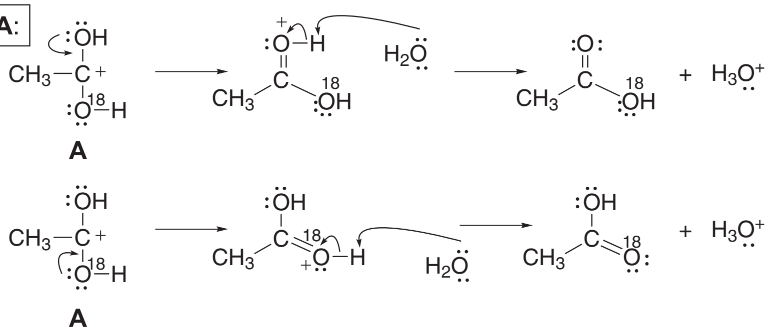
c.



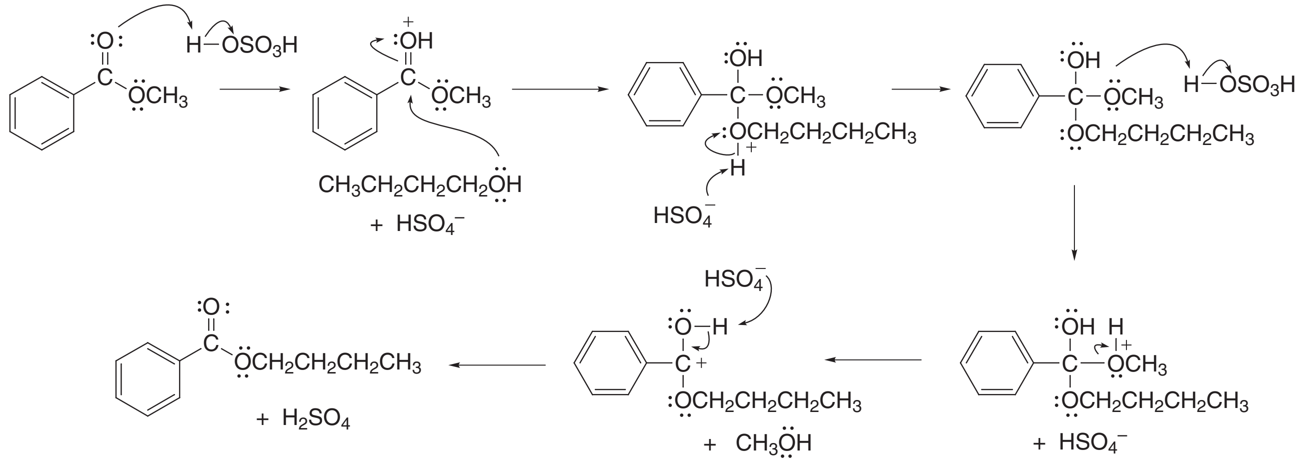
18.90



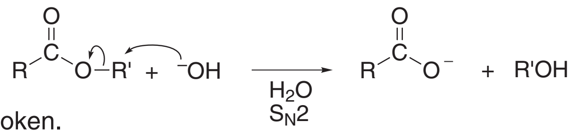
Two possibilities for **A**:

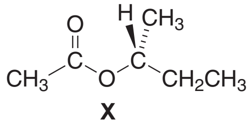


18.91

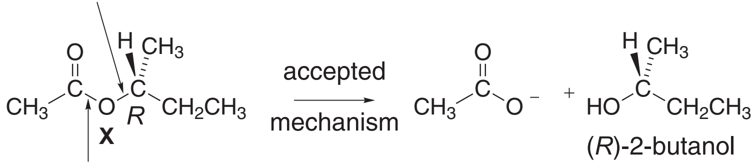


18.92



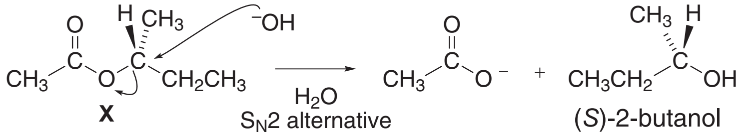


This bond is not broken.



This bond is cleaved.

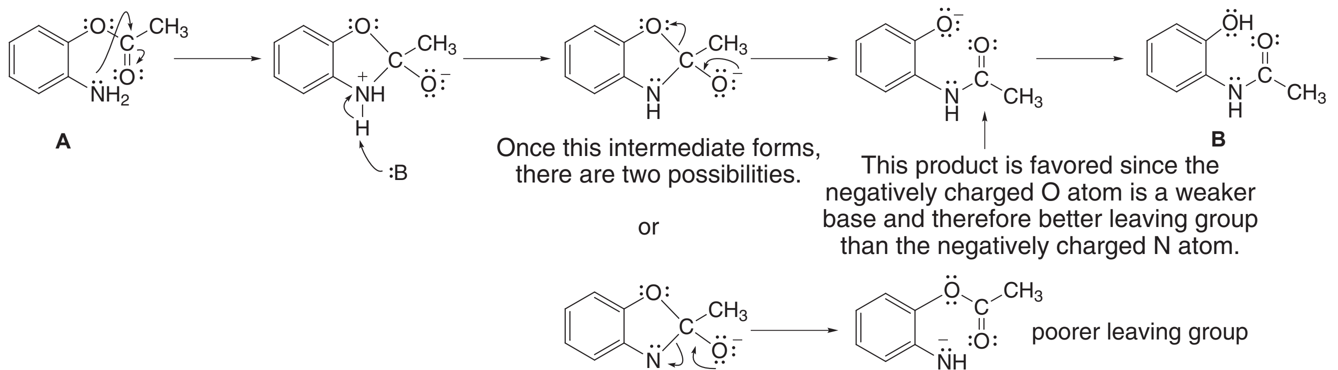
According to the accepted mechanism, the stereochemistry around the stereogenic center is retained in the product.



This S_N2 mechanism would form the product of inversion leading to (*S*)-2-butanol. Since (*R*)-2-butanol is the only product formed, the S_N2 mechanism does not occur during ester hydrolysis.

18.93

Reaction in base:

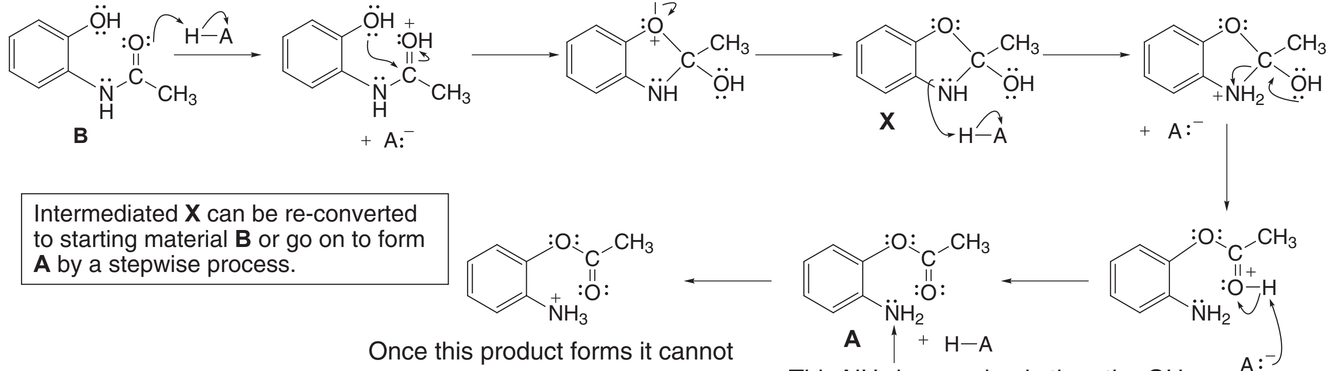


Once this intermediate forms, there are two possibilities.

This product is favored since the negatively charged O atom is a weaker base and therefore better leaving group than the negatively charged N atom.

poorer leaving group

Reaction in acid:

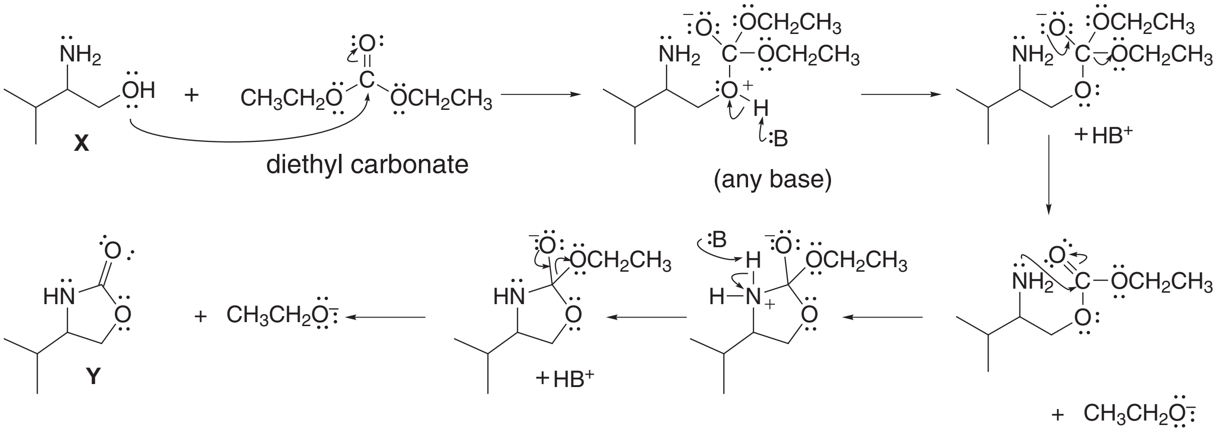


Intermediated **X** can be re-converted to starting material **B** or go on to form **A** by a stepwise process.

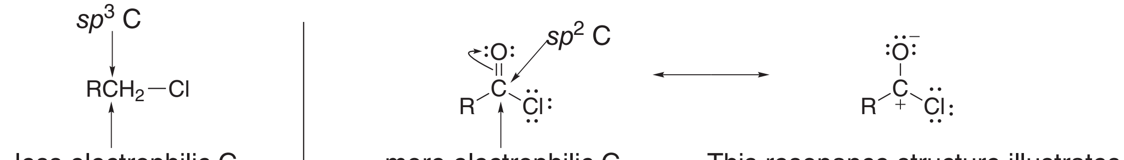
Once this product forms it cannot revert to **B** since RNH_3^+ no longer has a lone pair so it is not a nucleophile.

This NH_2 is more basic than the OH group in **B**, so it is protonated in acid.

18.94



18.95



less electrophilic C
more crowded C since it is
surrounded by four atoms

more electrophilic C
due to electron withdrawing O
more reactive

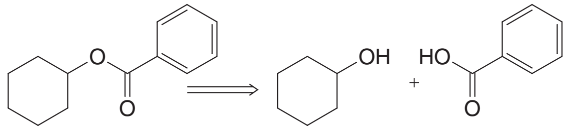
This resonance structure illustrates
how the electronegative O atom
withdraws more electron density
from C.

The *sp*^{2} hybridized C of RCOCl is much less crowded,
and this makes nucleophilic attack easier as well.

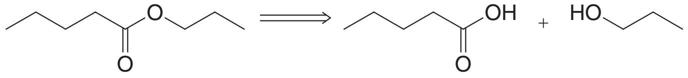
18.96 L'esterificazione di Fischer è il trattamento di un acido carbossilico con un alcol in presenza di un catalizzatore acido per formare un estere.

a. $(CH_3)_3CCO_2CH_2CH_3 \Longrightarrow (CH_3)_3CCOOH + HOCH_2CH_3$

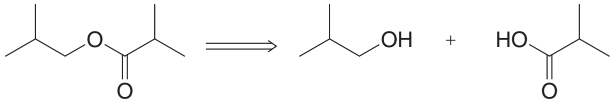
b.



c.

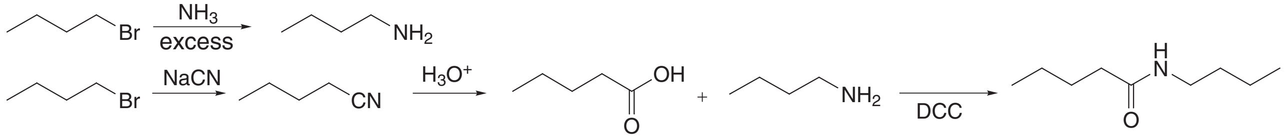


d.

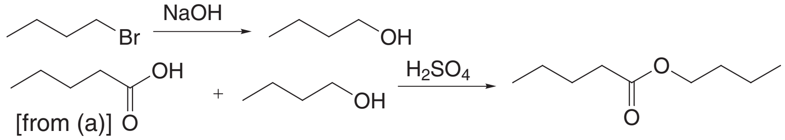


18.97

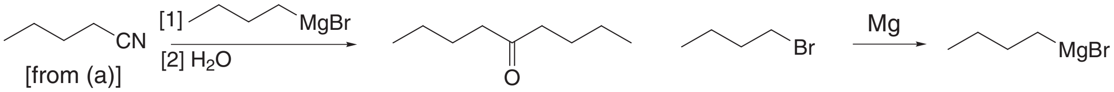
a.



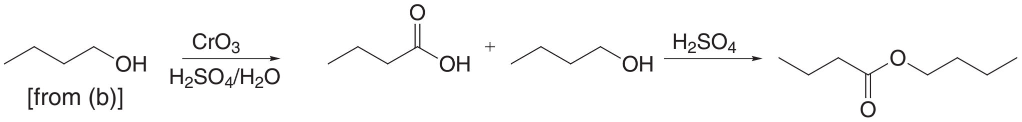
b.



c.



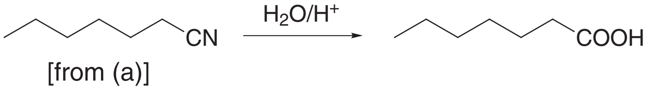
d.



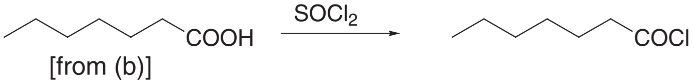
18.98

a.

b.



c.



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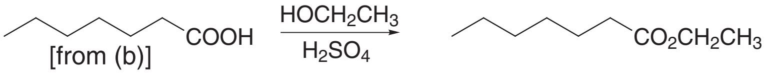

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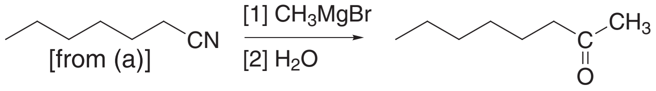
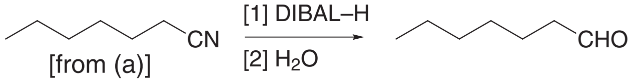
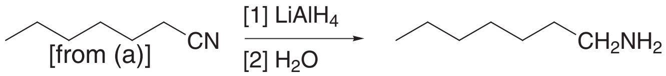


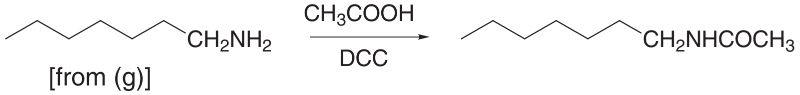
f.



g.



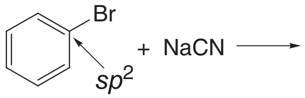
h.



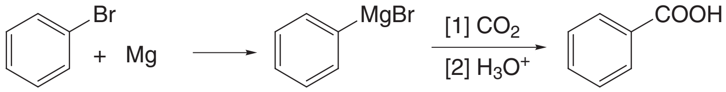
18.99

a. $$CH_3Cl + NaCN \longrightarrow CH_3{-}CN \xrightarrow{H_3O^+} CH_3{-}COOH$$

$$CH_3{-}Cl + Mg \longrightarrow CH_3{-}MgCl \xrightarrow[\text{[2] } H_3O^+]{\text{[1] } CO_2} CH_3{-}COOH$$

b. 

This method can't be used because an S_N2 reaction can't be done on an *sp*^{2} hybridized C.



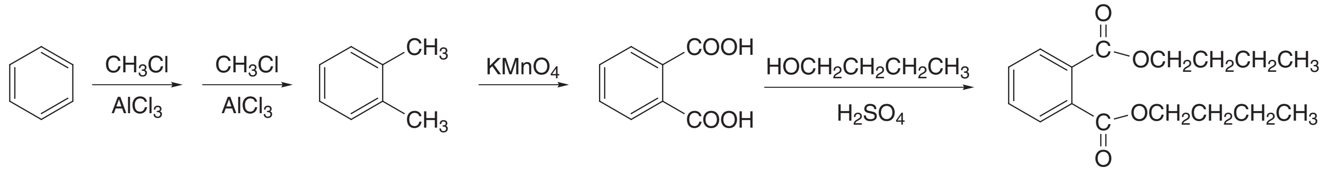
c. $$(CH_3)_3CCl + NaCN \longrightarrow$$ This method can't be used because an S_N2 reaction can't be done on a 3° C.

$$(CH_3)_3C{-}Cl + Mg \longrightarrow (CH_3)_3C{-}MgCl \xrightarrow[\text{[2] } H_3O^+]{\text{[1] } CO_2} (CH_3)_3C{-}COOH$$

d. $$HOCH_2CH_2CH_2CH_2Br + NaCN \longrightarrow HOCH_2CH_2CH_2CH_2{-}CN \xrightarrow{H_3O^+} HOCH_2CH_2CH_2CH_2{-}COOH$$

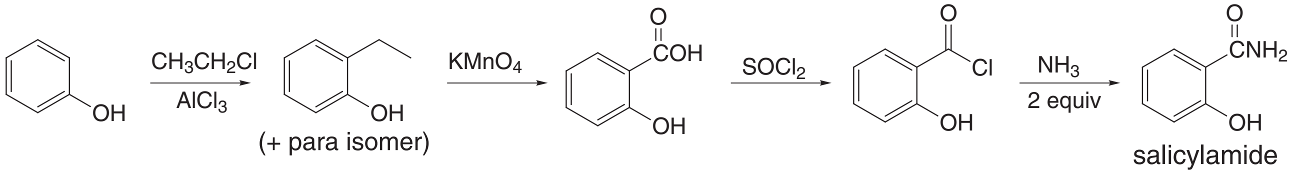
$$HOCH_2CH_2CH_2CH_2{-}Br + Mg \longrightarrow$$ This method can't be used because you can't make a Grignard reagent with an acidic OH group.

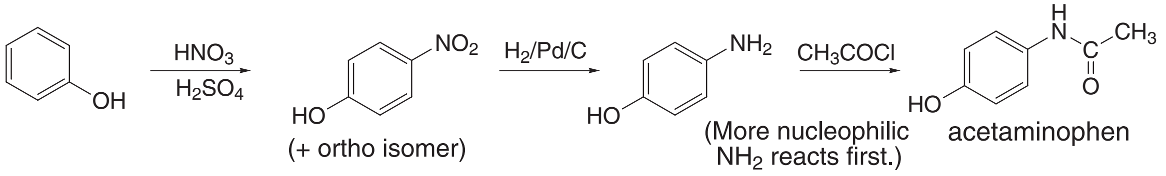
18.100

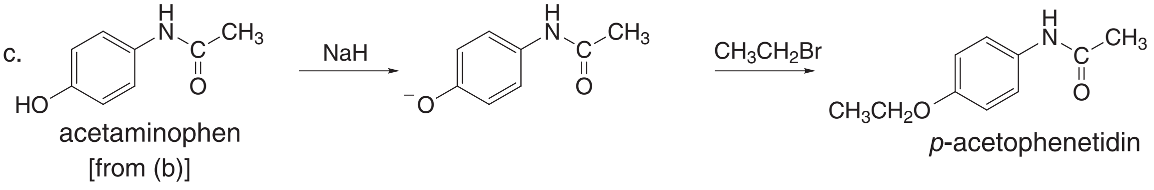


dibutyl phthalate

18.101

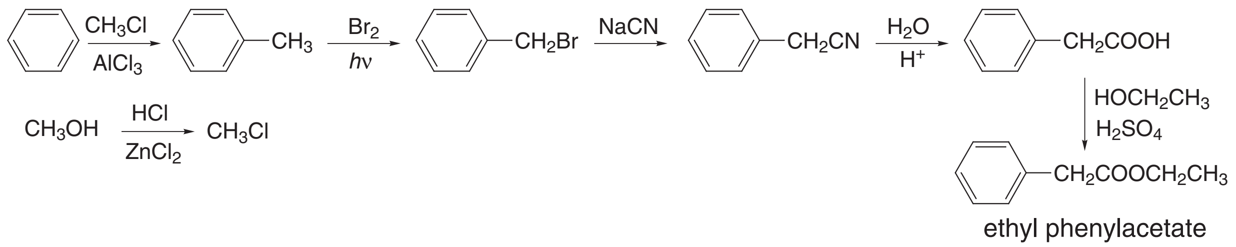
a. 

b. 

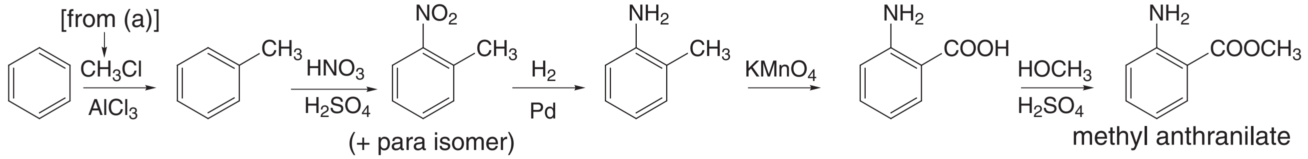
c. 

18.102

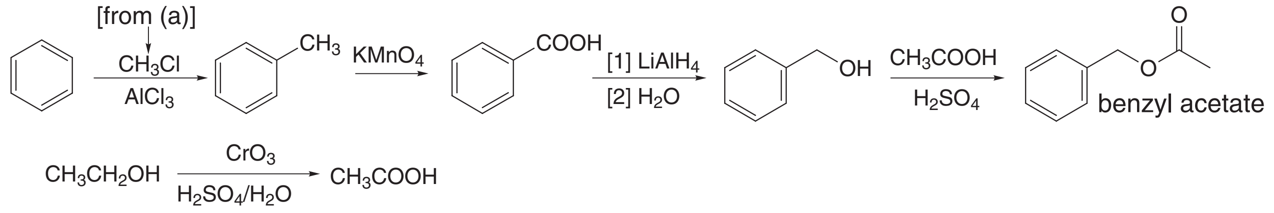
a.



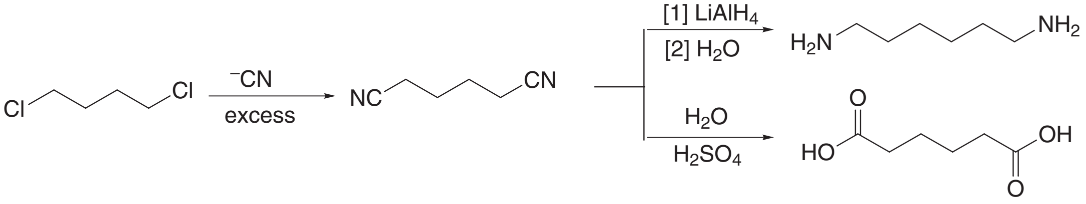
b.



c.

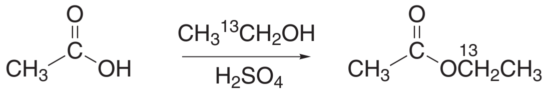


18.103



18.104

a.



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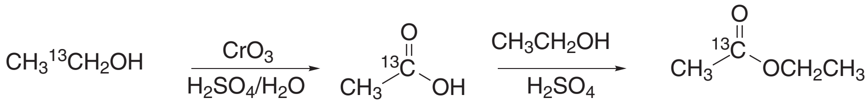

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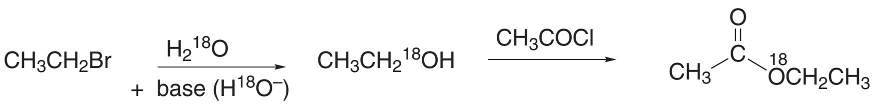

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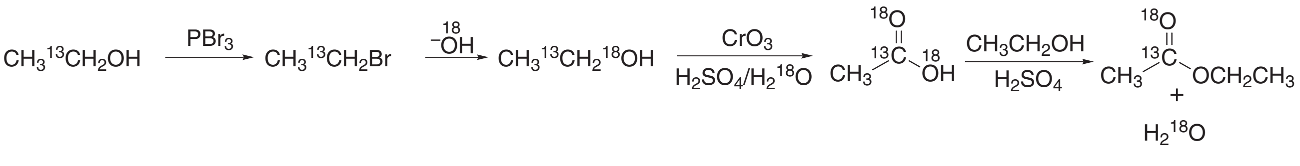
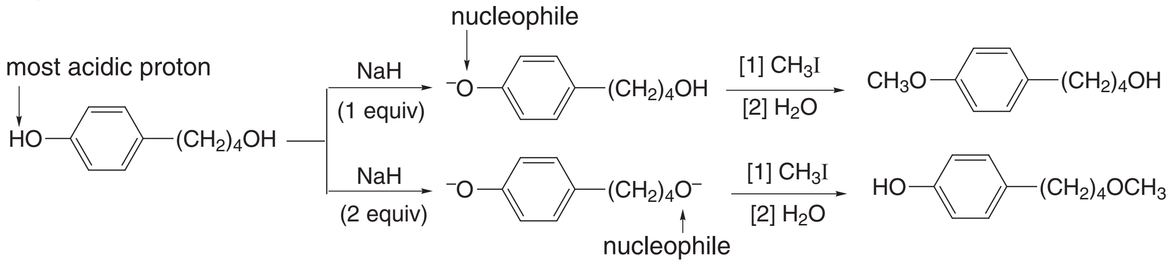
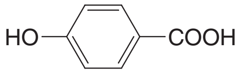


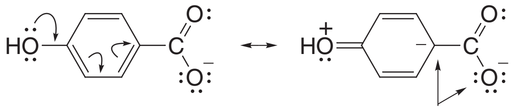
18.105 Il primo equivalente di NaH rimuove il protone più acido, cioè il protone dell'OH del fenolo. Il fenossido risultante può quindi reagire come nucleofilo per sostituire lo I, e formare il prodotto di sostituzione. Con due equivalenti, vengono rimossi entrambi i protoni sui gruppi OH. In questo caso l'atomo di O più nucleofilo è la base più forte; cioè l'alcossido formato dall'alcol (non il fenossido) reagisce prima in una reazione di sostituzione nucleofila attraverso l'O carico negativamente.



18.106

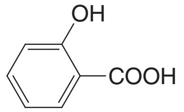


p-hydroxybenzoic acid
less acidic than benzoic acid

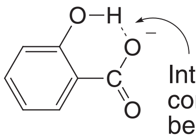


like charges on nearby atoms
destabilizing

The OH group donates electron density by its resonance effect and this destabilizes the conjugate base, making the acid less acidic than benzoic acid.

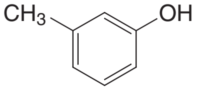


o-hydroxybenzoic acid
more acidic than benzoic acid

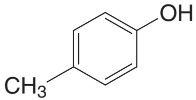


Intramolecular hydrogen bonding stabilizes the conjugate base, making the acid more acidic than benzoic acid.

18.107 In base all'andamento periodico, H_d è il meno acido poiché è legato all'N (non all'O). H_c è il meno acido dei protoni su OH perché non è legato all'anello benzenico, e quindi la sua base coniugata non è stabilizzata per risonanza. H_a e H_b sono allora i protoni più acidi, sebbene la loro acidità relativa sia difficile da determinare. Generalmente i gruppi alchilici sul benzene diminuiscono l'acidità dell'OH fenolico più nella posizione para che in meta. Ad esempio, il *p*-cresolo è piuttosto meno acido del *m*-cresolo:

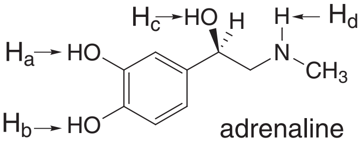


m-cresol
pK_a = 10.01
more acidic



p-cresol
pK_a = 10.17
less acidic

Se il gruppo alchilico sul benzene ha un simile effetto elettron donatore, questo rende l'H_a più acido di H_b. L'ordine di acidità crescente è: $H_d < H_c < H_b < H_a$.



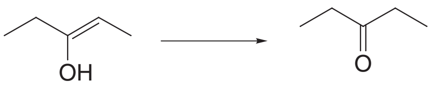
adrenaline

Capitolo 19

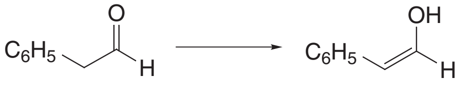
19.1
- Per convertire un chetone nel suo tautomero enolico, cambiare il gruppo C=O in C–OH, disegnare un nuovo doppio legame con il carbonio in posizione α, e rimuovere un protone dall'altro termine del doppio legame C=C.
- Per convertire un enolo nella sua forma chetonica, individuare il C=C legato a un OH. Cambiare il C–OH in C=O, aggiungere un protone all'altro termine del doppio legame C=C, ed eliminare il doppio legame.

[Nei casi in cui sono possibili isomeri *E* e *Z*, viene disegnato un solo stereoisomero.]

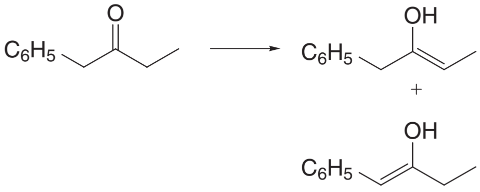
a.



b.

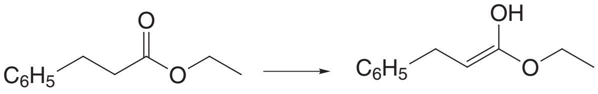


c.

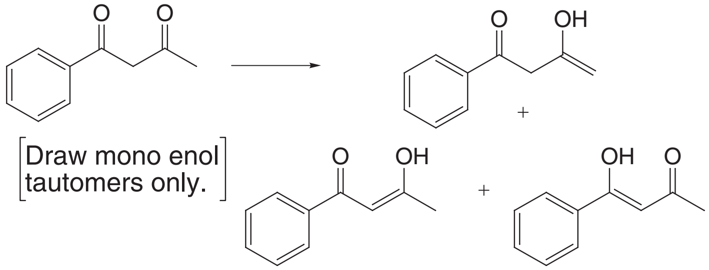


d.

e.

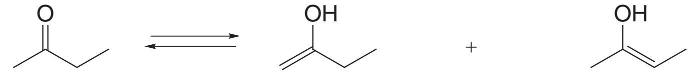


f.



[Draw mono enol tautomers only.]

19.2

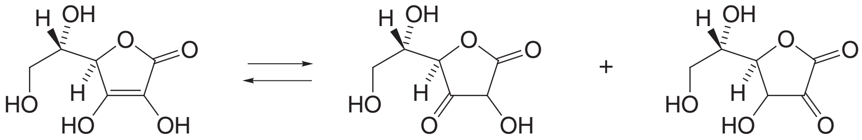


2-butanone

C=C has one C bonded to it.

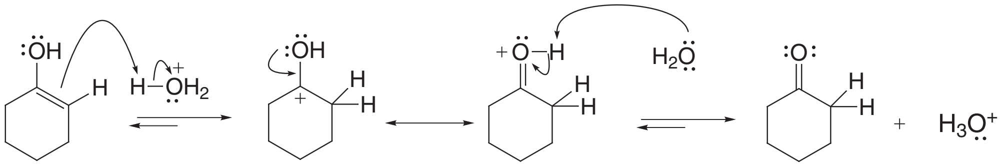
C=C has 2 C's bonded to it. The more substituted double bond is **more stable.**

19.3

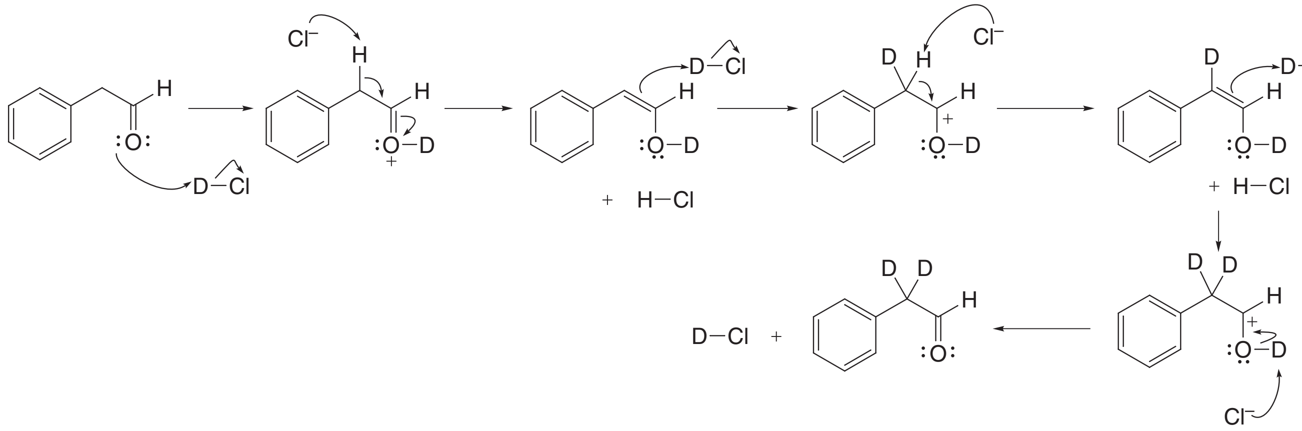


vitamin C

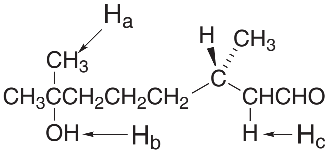
19.4 Il meccanismo ha due stadi: protonazione seguita da deprotonazione.



19.5



19.6 Considerare a cosa è legato ogni protone per determinare l'ordine di acidità.



$H_a < H_c < H_b$

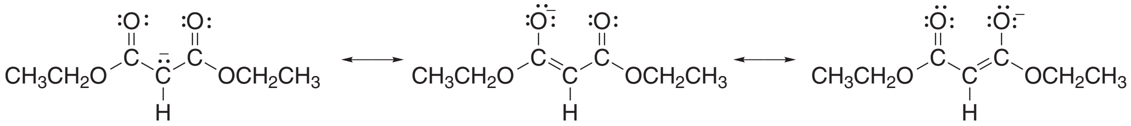
H_a is bonded to a CH_3 group = **least acidic**.

H_c is bonded to an α C = **intermediate acidity**.

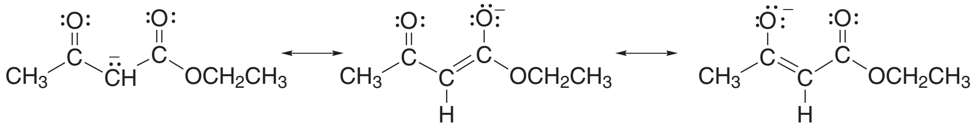
H_b is bonded to an O = **most acidic**.

19.7

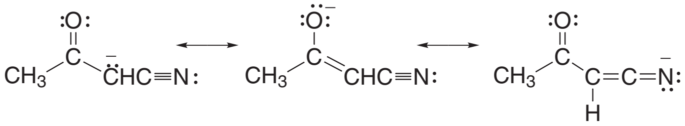
a.



b.

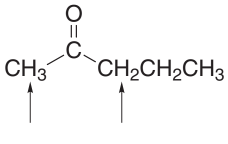


c.

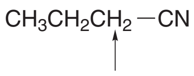


19.8

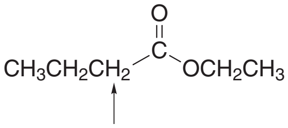
a.



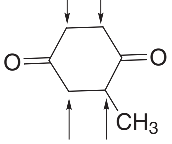
b.



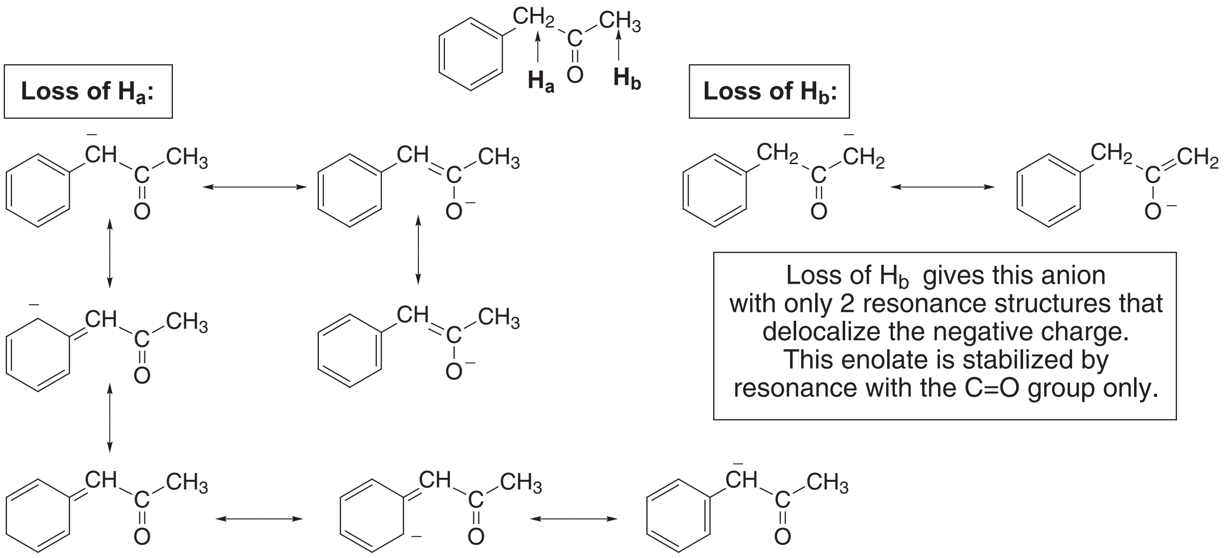
c.



d.



19.9

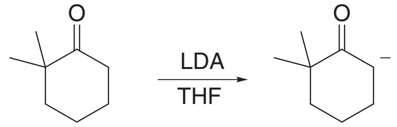


Loss of H_b gives this anion with only 2 resonance structures that delocalize the negative charge. This enolate is stabilized by resonance with the C=O group only.

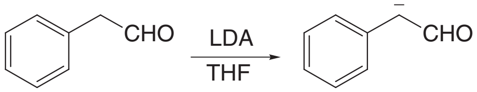
Loss of H_a gives this anion, which is highly resonance stabilized, making H_a more acidic than H_b. This enolate is stabilized by resonance with both the C=O group and the benzene ring.

19.10 In ciascuna reazione, l'LDA rimuove il protone più acido.

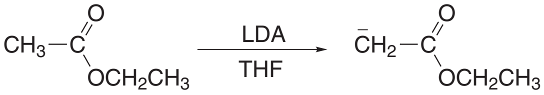
a.



b.



c.

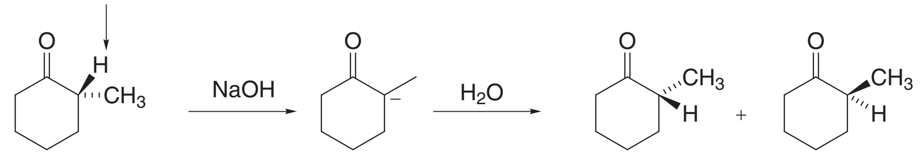


$$CH_3-C(=O)OCH_2CH_3 \xrightarrow[THF]{LDA} \overset{-}{C}H_2-C(=O)OCH_2CH_3$$

d.

19.11

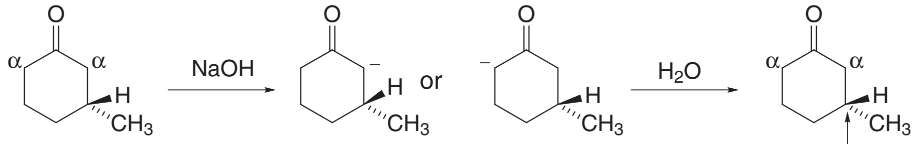
This acidic H is removed with base to form an achiral enolate.



(*R*)-2-methylcyclohexanone

achiral

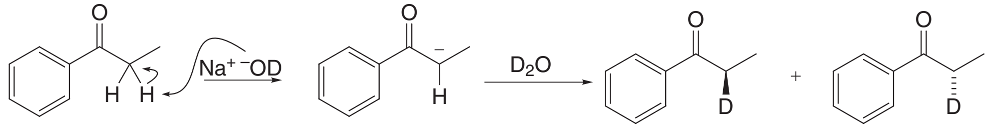
Protonation of the planar achiral enolate occurs with equal probability from two sides so a racemic mixture is formed. The racemic mixture is optically inactive.



(*R*)-3-methylcyclohexanone

This stereogenic center is not located at the α carbon, so it is not deprotonated with base. Its configuration is retained in the product, and the product remains optically active.

19.12

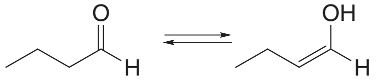


Removal of a proton from the α carbon forms an enolate, which can be protonated from either face to form two enantiomers in equal amounts.

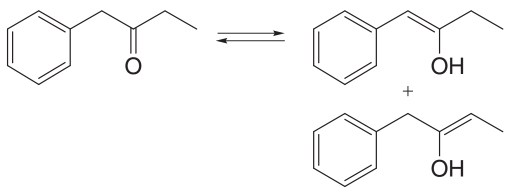
19.13

Usare le regole della risposta 21.1 per disegnare il tautomero (o i tautomeri) enolici. Nei casi in cui possono formarsi isomeri *E* e *Z*, viene disegnato un solo stereoisomero.

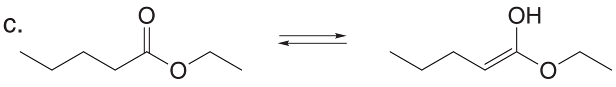
a.



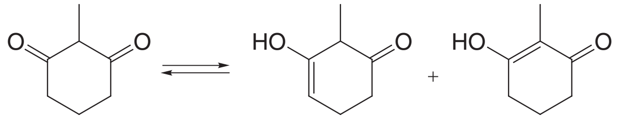
b.



c.

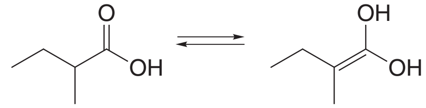


d.

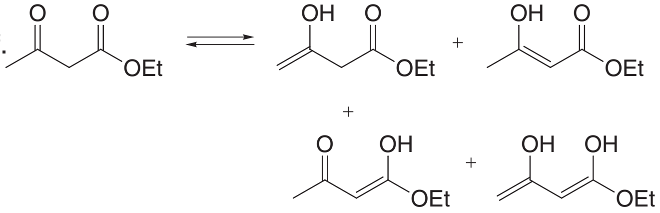


(mono enol form)

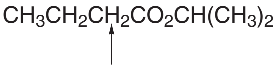
e.

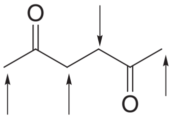


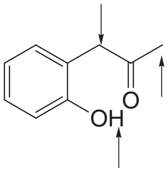
f.

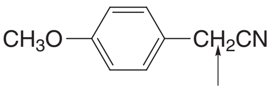


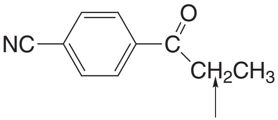
19.14

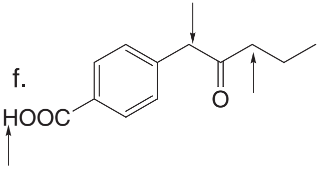
a.

$CH_3CH_2CH_2CO_2CH(CH_3)_2$

b.


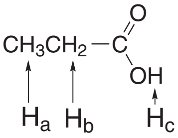
c.


d.


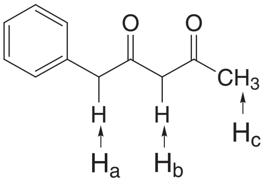
e.


f.


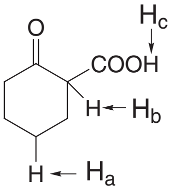
19.15

a.


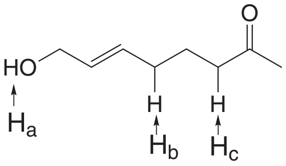
H_a is bonded to a CH_3 group = **least acidic**.
H_b is bonded to an α C = **intermediate acidity**.
H_c is bonded to O = **most acidic**.

b.


H_c is bonded to an α C = **least acidic**.
H_a is bonded to an α C , and is adjacent to a benzene ring = **intermediate acidity**.
H_b is bonded to an α C, between two C=O groups = **most acidic**.

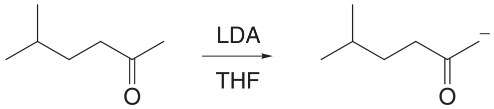
c.


H_a is bonded to a CH_2 group = **least acidic**.
H_b is bonded to an α C = **intermediate acidity**.
H_c is bonded to O = **most acidic**.

d.


H_b is bonded to a CH_2 group = **least acidic**.
H_c is bonded to an α C = **intermediate acidity**.
H_a is bonded to O = **most acidic**.

19.16

a.


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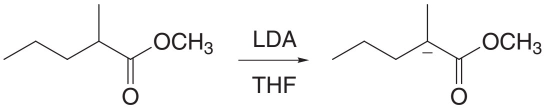
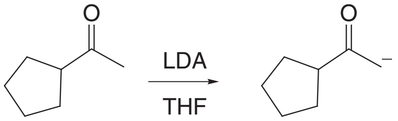
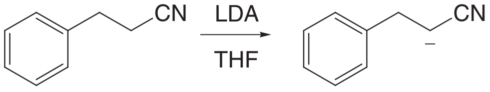


c.


d.


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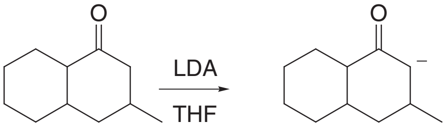

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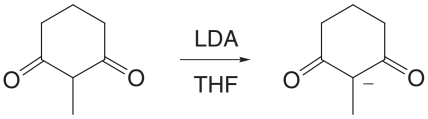
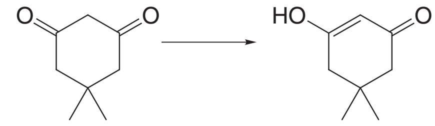


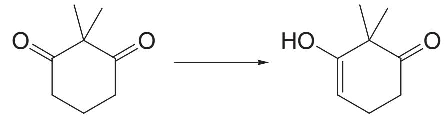
19.17 I tautomeri enolici hanno gruppi OH che danno una banda slargata a 3600–3200 cm^{-1}, che può essere facilmente individuata attraverso l' IR.

19.18



5,5-dimethyl-1,3-cyclohexanedione

5,5-Dimethyl-1,3-cyclohexanedione exists predominantly in its enol form because the C=C of the enol is conjugated with the other C=O of the dicarbonyl compound. Conjugation stabilizes this enol.

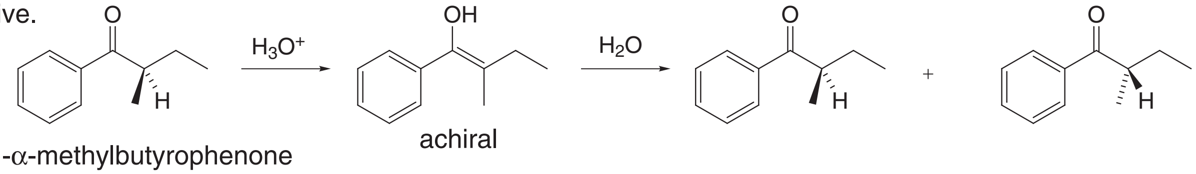


2,2-dimethyl-1,3-cyclohexanedione

The enol of 2,2-dimethyl-1,3-cyclohexanedione is not conjugated with the other carbonyl group. In this way it resembles the enol of any other carbonyl compound, and thus it is present in low concentration.

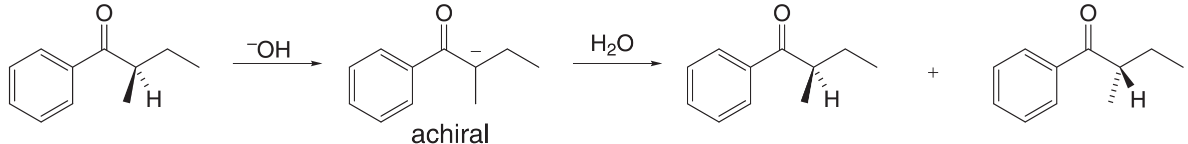
19.19

In the presence of acid, (*R*)-α-methylbutyrophenone enolizes to form an achiral enol. Protonation of the enol from either face forms an equal mixture of two enantiomers, making the solution optically inactive.



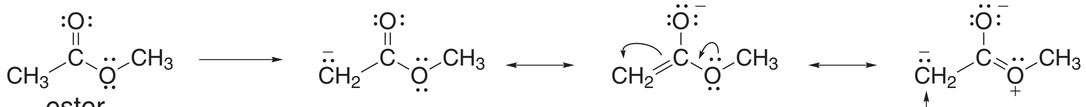
(*R*)-α-methylbutyrophenone

In the presence of base, (*R*)-α-methylbutyrophenone is deprotonated to form an achiral enolate, which can then be protonated from either face to form an optically inactive mixture of two enantiomers.



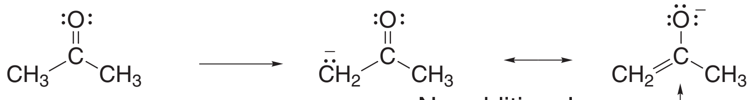
(*R*)-α-methylbutyrophenone

19.20



ester

The O atom of the ester OR group donates electron density by a resonance effect. The resulting resonance structure keeps a negative charge on the less electronegative C end of the enolate. This destabilizes the resonance hybrid of the conjugate base, and makes the α H's of the ester less acidic.



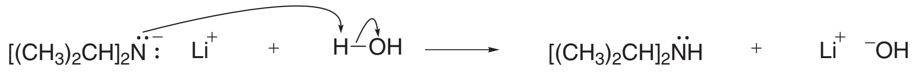
ketone

No additional resonance structures.

This structure, which places a negative charge on the O atom, is the major contributor to the hybrid, stabilizing it, and making the α H's of the ketone more acidic.

19.21

LDA reacts with the most acidic proton. If there is any H_2O present, it would immediately react with the base:

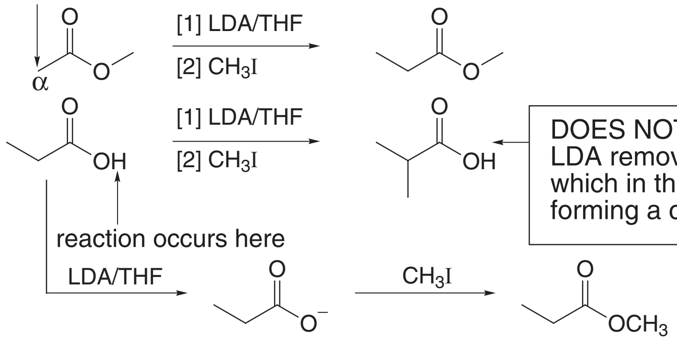


$[(CH_3)_2CH]_2N^-\ Li^+ + H{-}OH \longrightarrow [(CH_3)_2CH]_2NH + Li^+\ {}^-OH$

LDA

19.22

The most acidic proton in methyl acetate is on the α carbon. LDA removes this proton to form an enolate, which goes on to react with CH_3I to form $CH_3CH_2COOCH_3$.

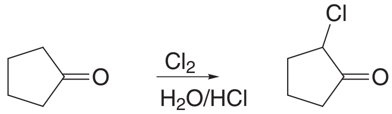


carboxylate anion

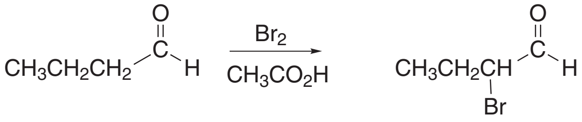
DOES NOT FORM
LDA removes the most acidic proton in propanoic acid, which in this case is the OH proton of the carboxylic acid, forming a carboxylate anion.

19.23

a.

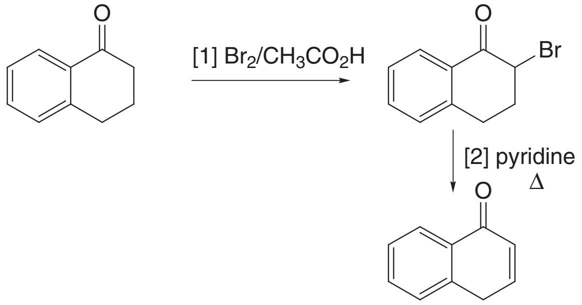


b.



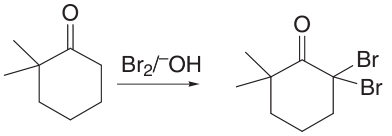
$CH_3CH_2CH_2CHO \xrightarrow[CH_3CO_2H]{Br_2} CH_3CH_2CH(Br)CHO$

c.

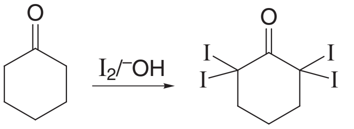


19.24

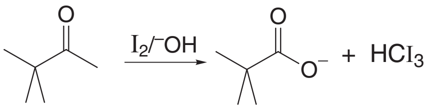
a.



b.

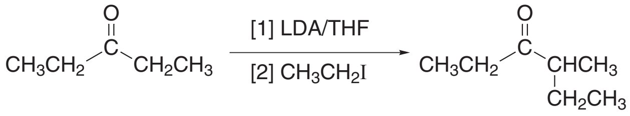


c.



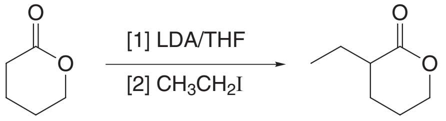
19.25

a.

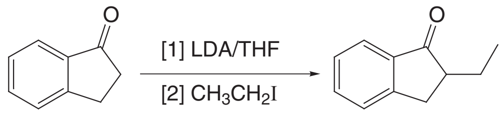


$CH_3CH_2COCH_2CH_3 \xrightarrow[\text{[2] } CH_3CH_2I]{\text{[1] LDA/THF}} CH_3CH_2COCH(CH_3)CH_2CH_3$

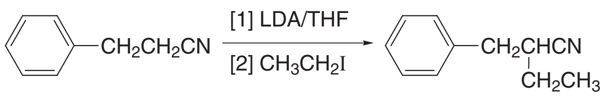
c.



b.



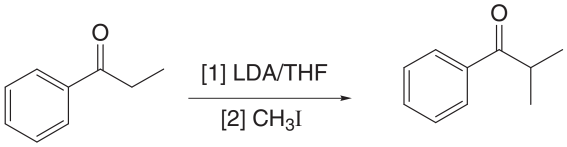
d.



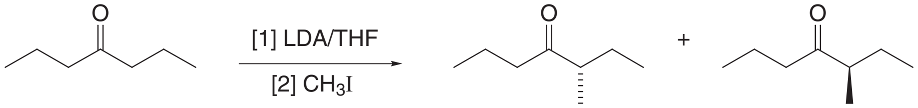
$C_6H_5CH_2CH_2CN \xrightarrow[\text{[2] } CH_3CH_2I]{\text{[1] LDA/THF}} C_6H_5CH_2CH(CN)CH_2CH_3$

19.26

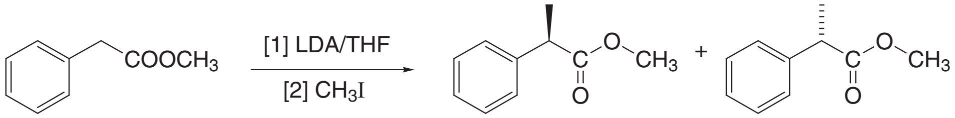
a.



b.

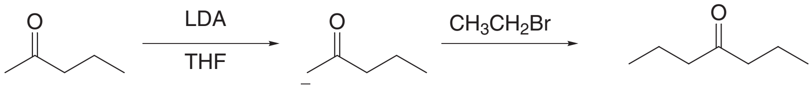


c.



19.27

a.



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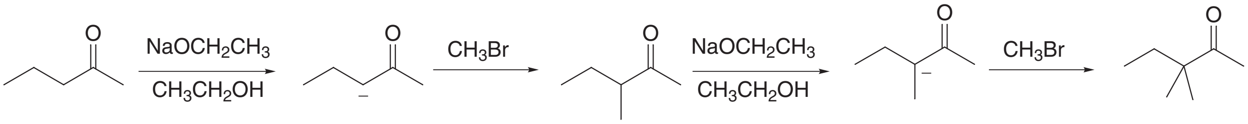
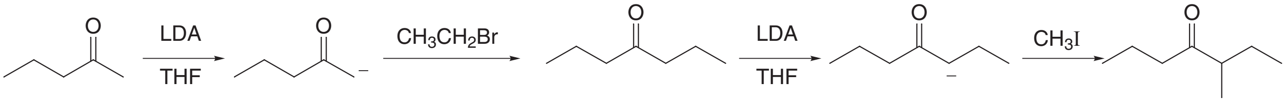
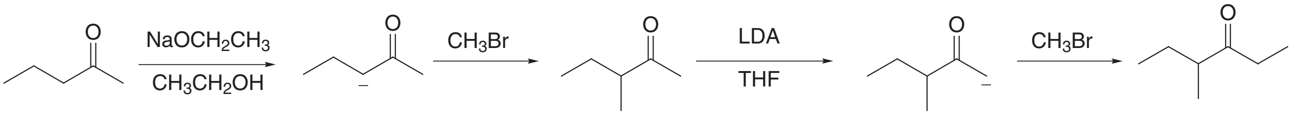


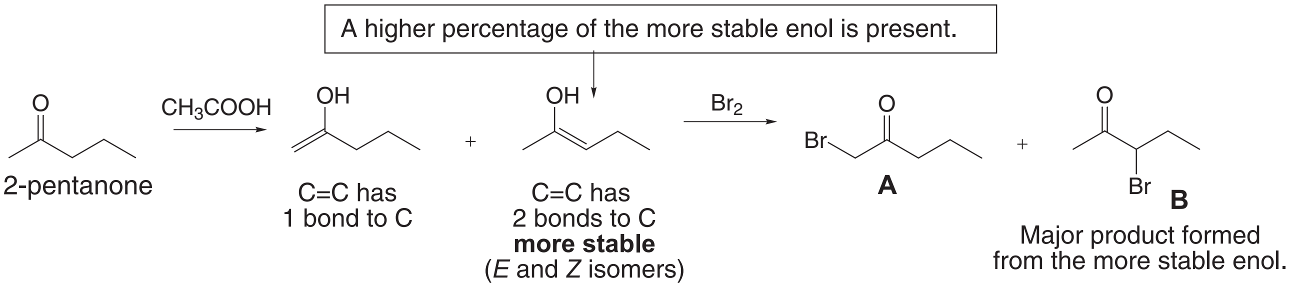
c.



d.



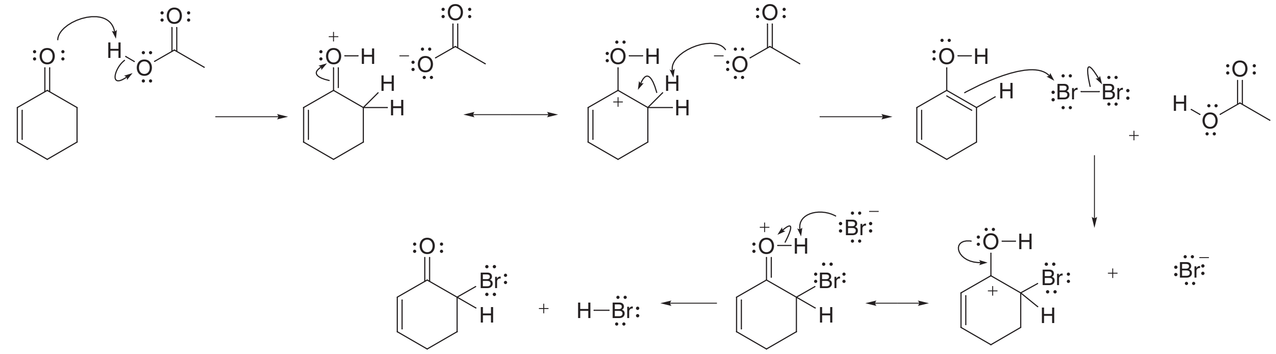
19.28 Il meccanismo dell'alogenazione acido-catalizzata consiste di due parti: **tautomerizzazione** del composto carbonilico nella forma enolica, e **reazione dell'enolo con l'alogeno.**



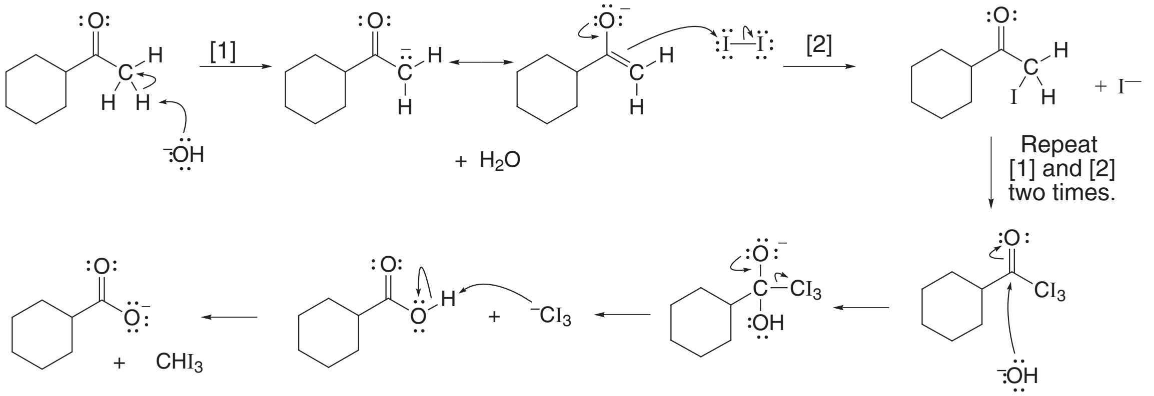
19.29 • Il meccanismo dell'alogenazione acido-catalizzata (Parte a) consiste di due parti: **tautomerizzazione** del composto carbonilico nella forma enolica, e **reazione dell'enolo con l'alogeno.**

- Nella reazione dell'aloformio (Parte b), i tre atomi H del gruppo CH_3 sono successivamente sostituiti da X, per formare un intermedio che viene rotto in maniera ossidativa da basi.

a.

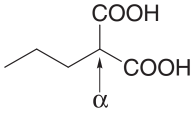


b.



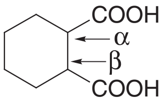
19.29 La decarbossilazione avviene solo quando un gruppo carbossilico è legato al carbonio in α di un altro gruppo carbonilico.

a.



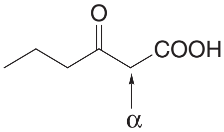
YES

b.



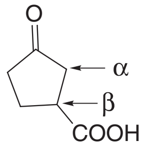
NO

c.



YES

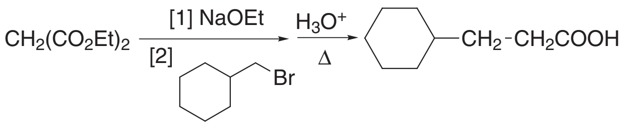
d.



NO

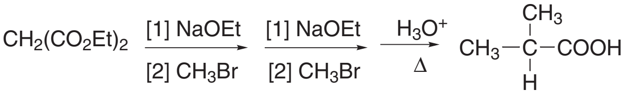
19.30

a.



$CH_2(CO_2Et)_2 \xrightarrow[\text{[2]}]{\text{[1] NaOEt}} \xrightarrow[\Delta]{H_3O^+}$ —CH_2-CH_2COOH

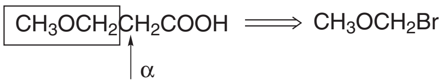
b.



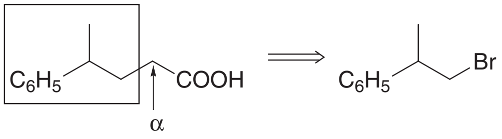
$CH_2(CO_2Et)_2 \xrightarrow[\text{[2] }CH_3Br]{\text{[1] NaOEt}} \xrightarrow[\text{[2] }CH_3Br]{\text{[1] NaOEt}} \xrightarrow[\Delta]{H_3O^+} CH_3-\overset{CH_3}{\underset{H}{C}}-COOH$

19.31 Individuare il C in α al gruppo COOH, e identificare tutti i gruppi alchilici ad esso legati. Questi gruppi provengono da altri alogenuri, e il resto della molecola proviene dal dietil malonato.

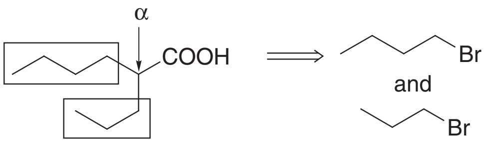
a.



b.

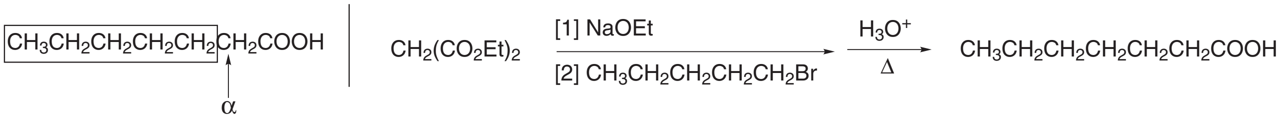


c.

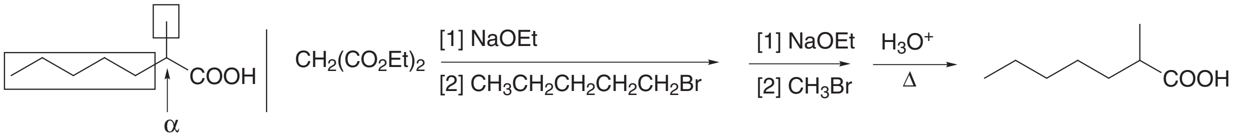


19.32

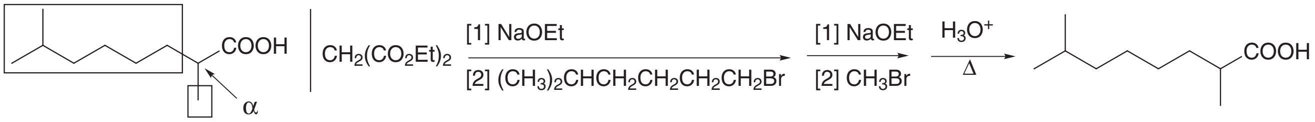
a.



b.

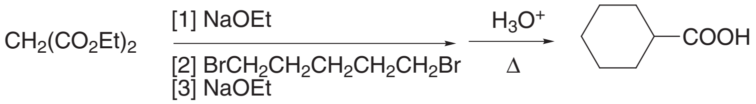


c.

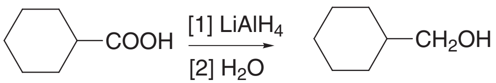


19.33

a.

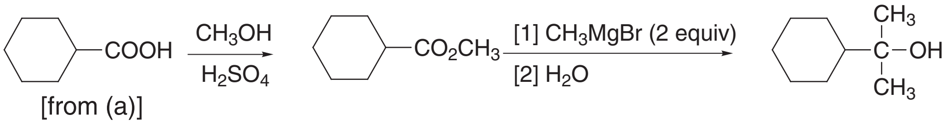


b.



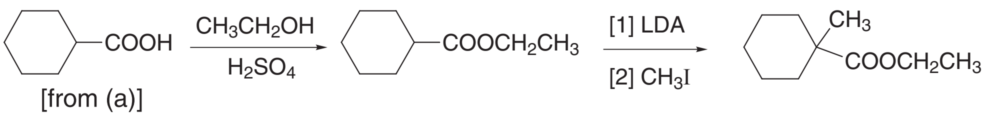
[from (a)]

c.



[from (a)]

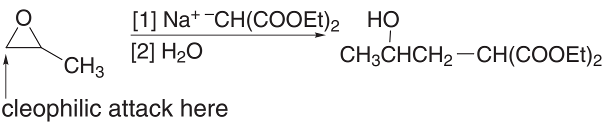
d.



[from (a)]

19.34

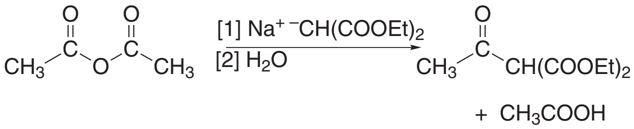
a.



b. $CH_2{=}O \xrightarrow[\text{[2] } H_2O]{\text{[1] } Na^{+}\,{}^{-}CH(COOEt)_2} HOCH_2CH(COOEt)_2$

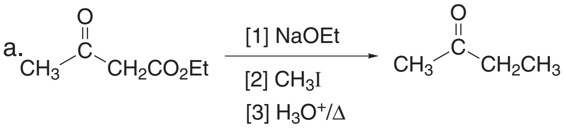
c.

d.

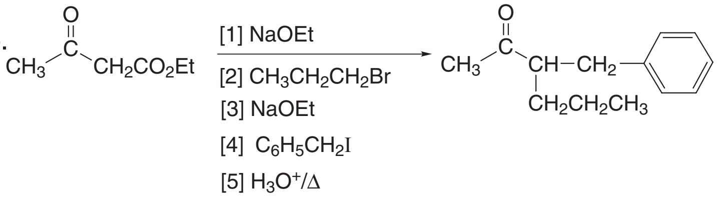


19.35

a.

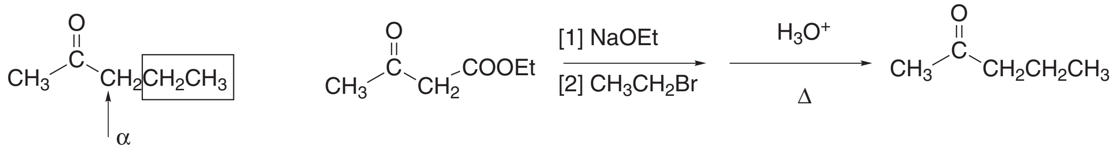


b.

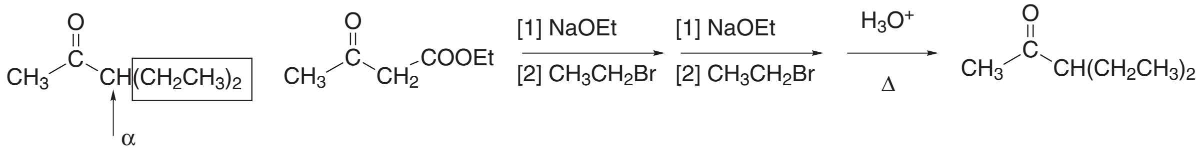


19.36 Individuare il C in α. Tutti i gruppi alchilici sul carbonio in α derivano da altri alogenuri, e il resto della molecola proviene dall'etil acetoacetato.

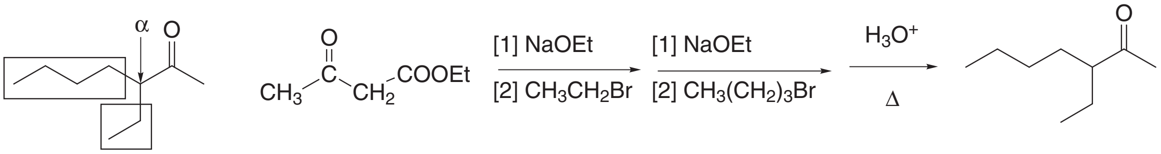
a.



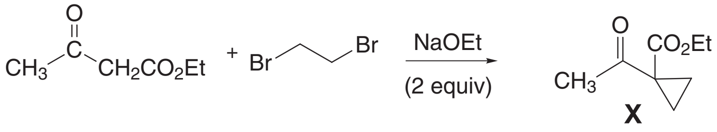
b.



c.

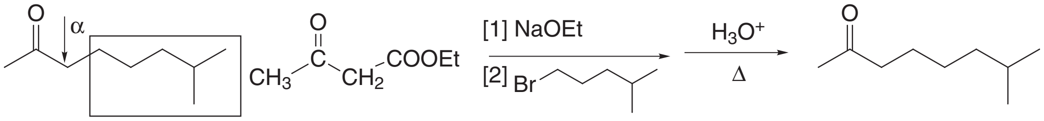


19.37

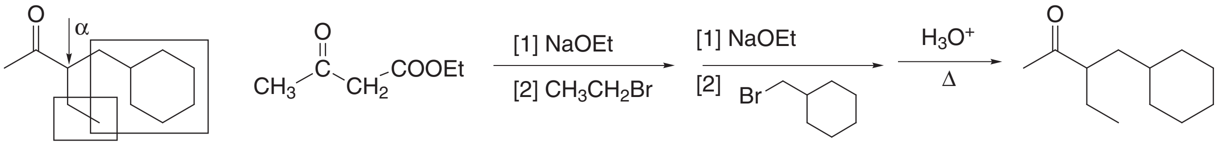


19.38 Usare le indicazioni della risposta 21.37.

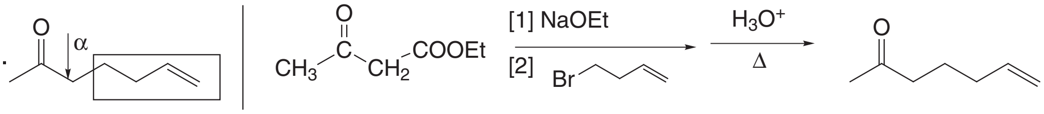
a.



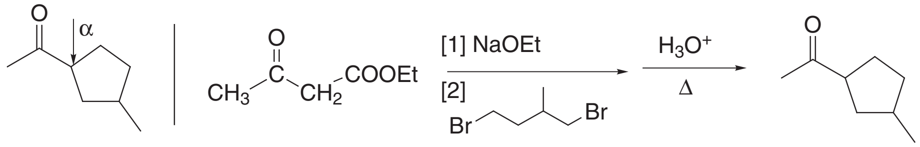
b.



c.

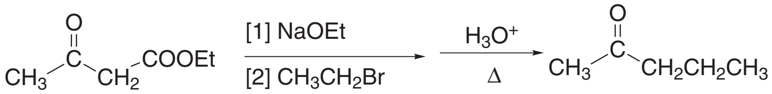


d.



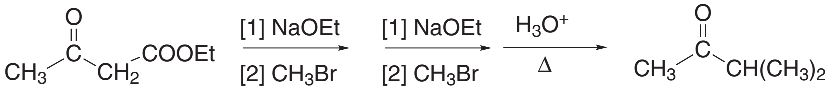
19.39

a.



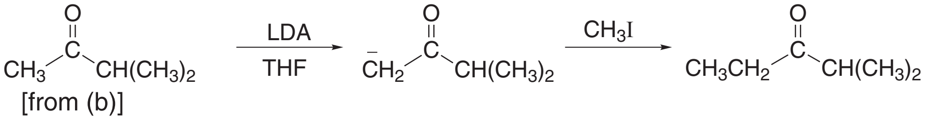
$$CH_3\overset{O}{\overset{\|}{C}}CH_2COOEt \xrightarrow[\text{[2] } CH_3CH_2Br]{\text{[1] NaOEt}} \xrightarrow[\Delta]{H_3O^+} CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3$$

b.



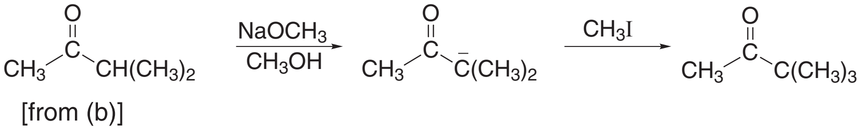
$$CH_3\overset{O}{\overset{\|}{C}}CH_2COOEt \xrightarrow[\text{[2] } CH_3Br]{\text{[1] NaOEt}} \xrightarrow[\text{[2] } CH_3Br]{\text{[1] NaOEt}} \xrightarrow[\Delta]{H_3O^+} CH_3\overset{O}{\overset{\|}{C}}CH(CH_3)_2$$

c.



$$\underset{\text{[from (b)]}}{CH_3\overset{O}{\overset{\|}{C}}CH(CH_3)_2} \xrightarrow[\text{THF}]{\text{LDA}} \overset{-}{C}H_2\overset{O}{\overset{\|}{C}}CH(CH_3)_2 \xrightarrow{CH_3I} CH_3CH_2\overset{O}{\overset{\|}{C}}CH(CH_3)_2$$

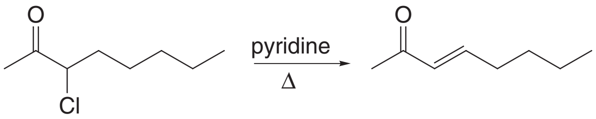
d.



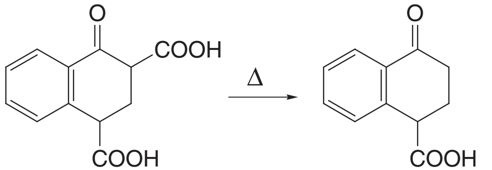
$$\underset{\text{[from (b)]}}{CH_3\overset{O}{\overset{\|}{C}}CH(CH_3)_2} \xrightarrow[CH_3OH]{NaOCH_3} CH_3\overset{O}{\overset{\|}{C}}\overset{-}{C}(CH_3)_2 \xrightarrow{CH_3I} CH_3\overset{O}{\overset{\|}{C}}C(CH_3)_3$$

19.40

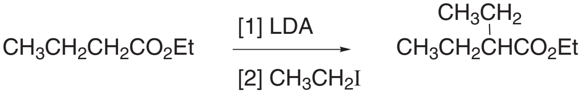
a.



b.

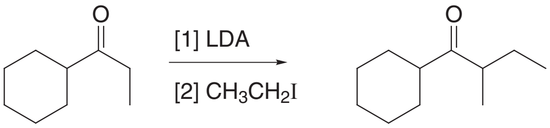


c.

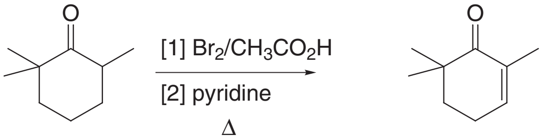


$$CH_3CH_2CH_2CO_2Et \xrightarrow[\text{[2] } CH_3CH_2I]{\text{[1] LDA}} CH_3CH_2\overset{CH_3CH_2}{\overset{|}{C}H}CO_2Et$$

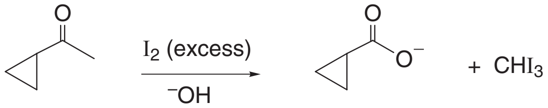
d.



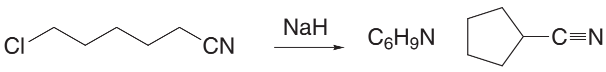
e.



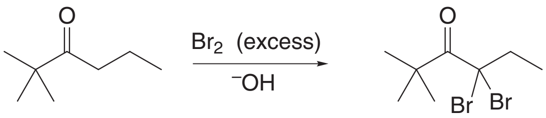
f.



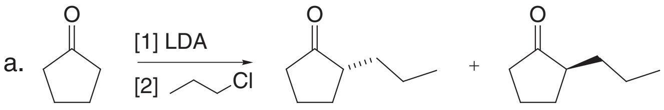
g.

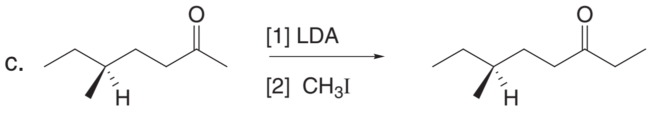


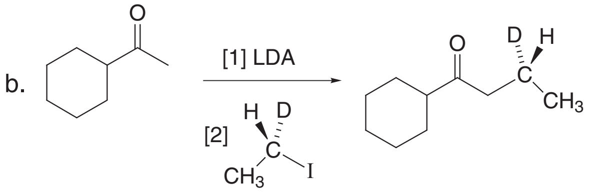
h.



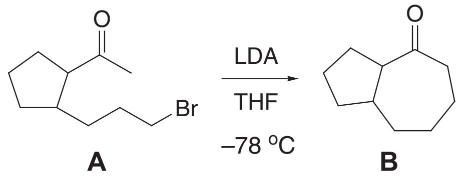
19.41

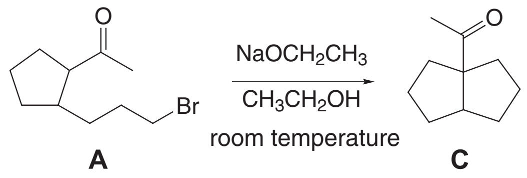




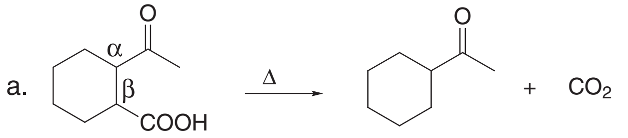


19.42





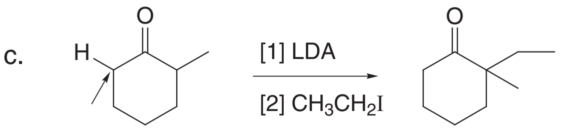
19.43



In order for decarboxylation to occur readily, the COOH group must be bonded to the α C of another carbonyl group. In this case, it is bonded to the β carbon.

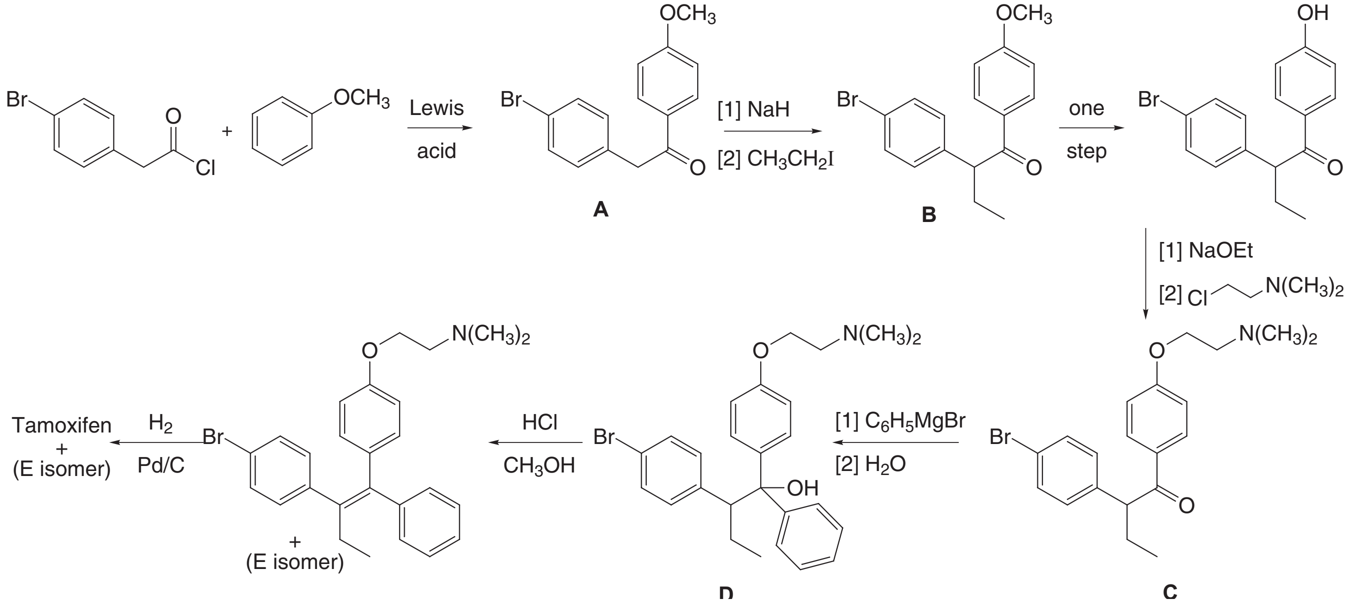
b. $CH_2(CO_2Et)_2 \xrightarrow[\text{[2] }(CH_3CH_2)_3CBr]{\text{[1] NaOEt}} (CH_3CH_2)_3CCH(CO_2Et)_2$

The 3° alkyl halide is too crowded to react with the strong nucleophile by an S_N2 mechanism.

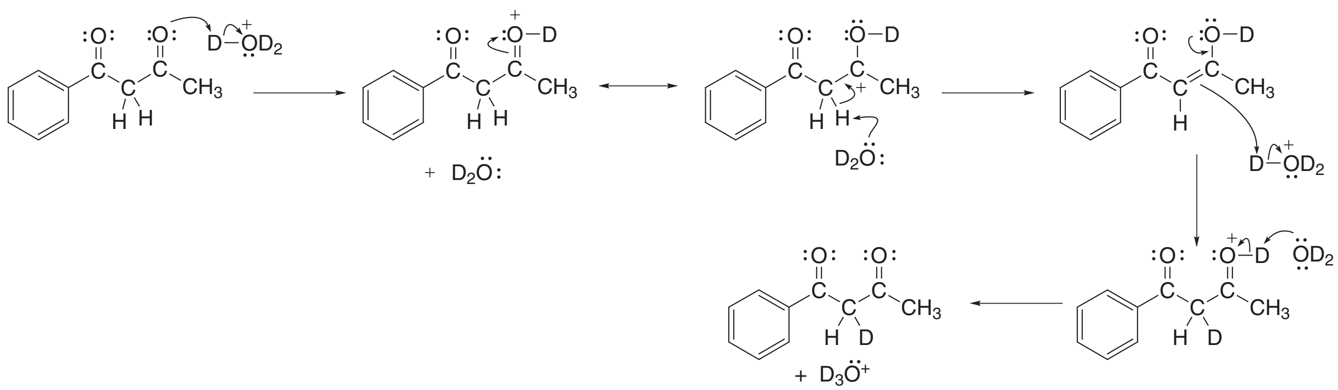


LDA removes a H from the less substituted C, forming the kinetic enolate. This product is from the thermodynamic enolate, which gives substitution on the more substituted α C.

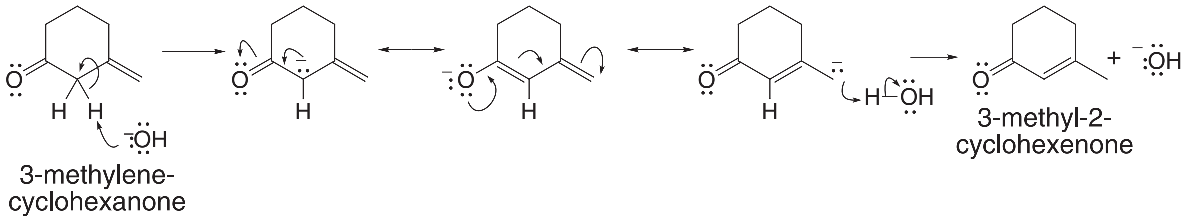
19.44



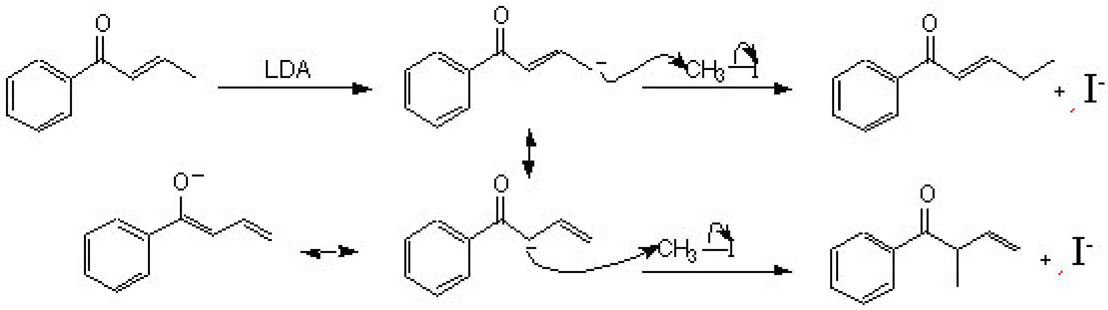
19.45



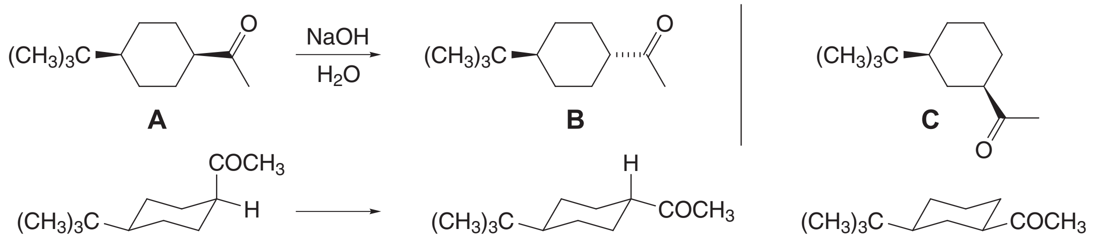
19.46



19.47



19.48



One axial and one equatorial group, **less stable**

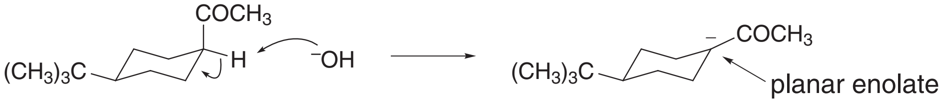
Both groups are equatorial. **more stable**

This isomerization will occur since it makes a more stable compound.

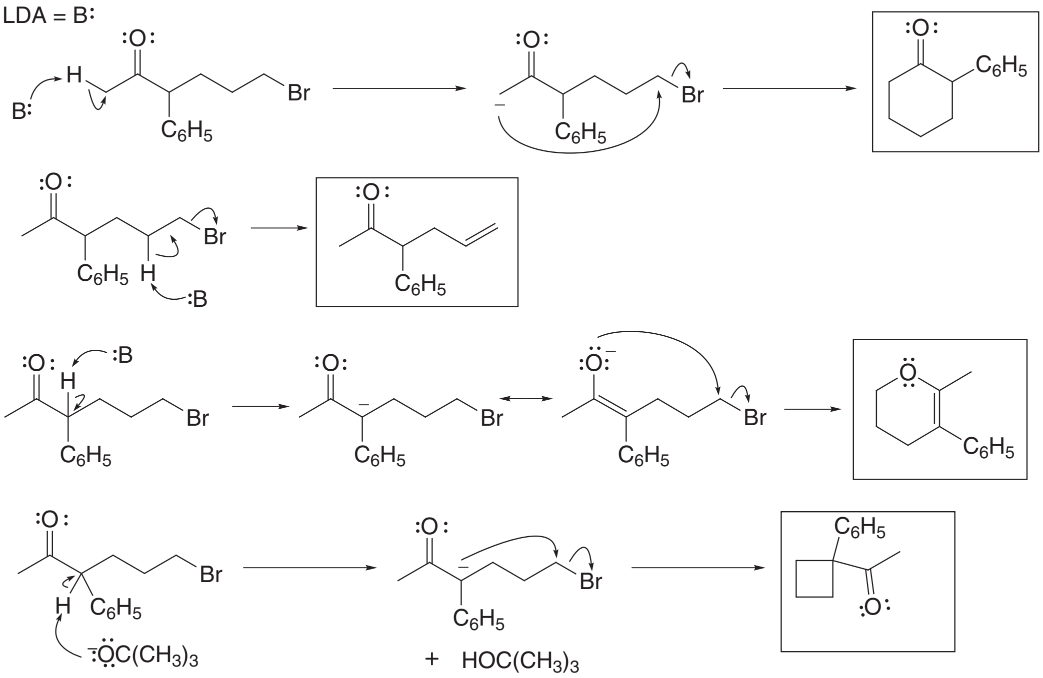
Both groups are equatorial.

Compound **C** will not isomerize since it already has the more stable arrangement of substituents.

Isomerization occurs by way of an intermediate enolate, which can be protonated to either re-form **A**, or give **B**. Since **B** has two large groups equatorial, it is favored at equilibrium.



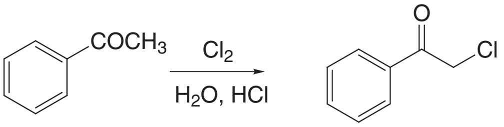
19.49



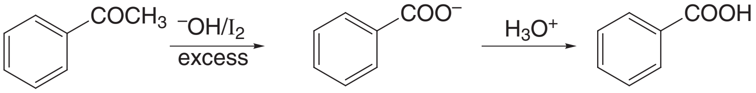
This reaction occurs with both bases [LDA or KOC(CH$_3$)$_3$].

19.50

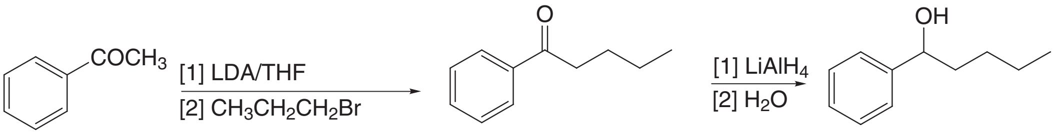
a.



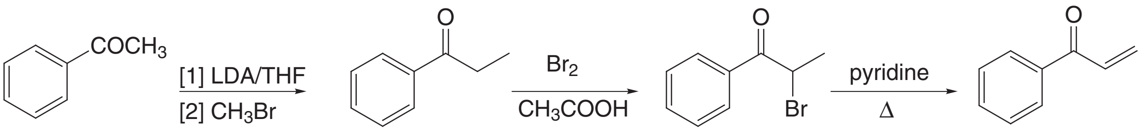
b.



c.

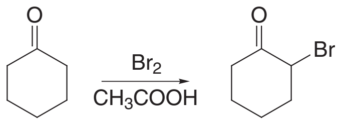


d.

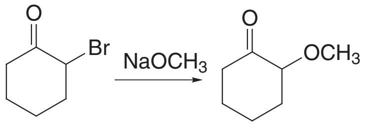


19.51

a.

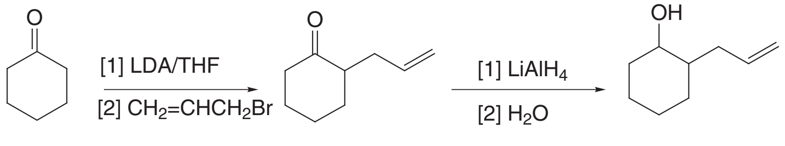


b.

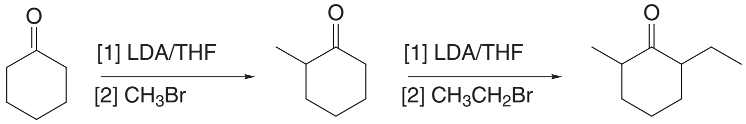


[from (a)]

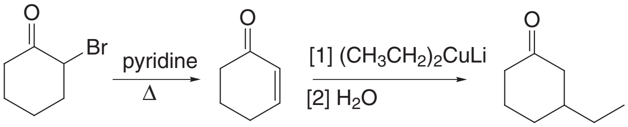
c.



d.

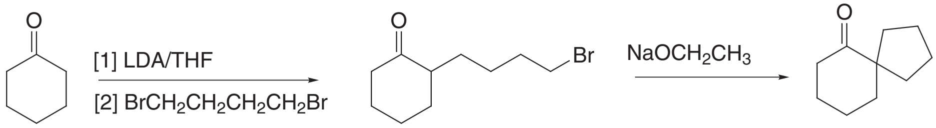


e.

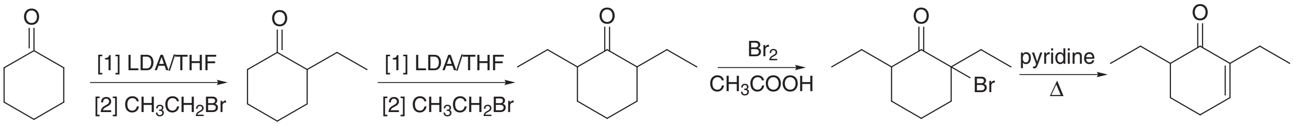


[from (a)]

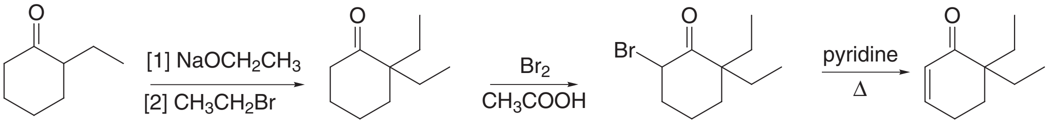
f.



g.



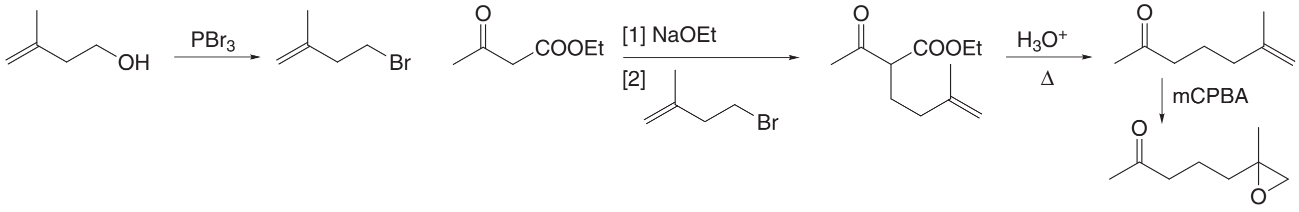
h.



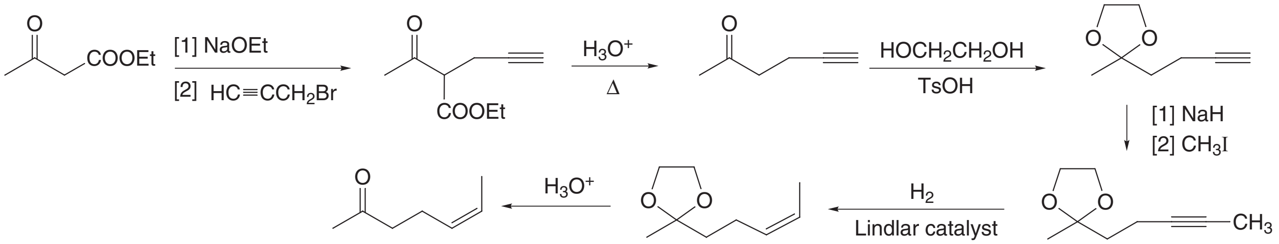
[from (g)]

19.52

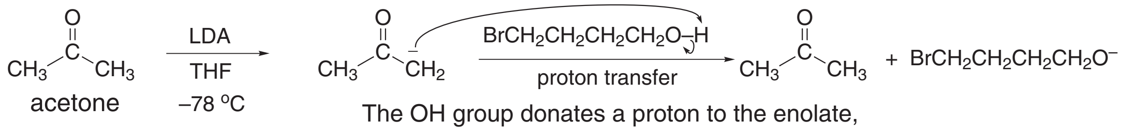
a.



b.

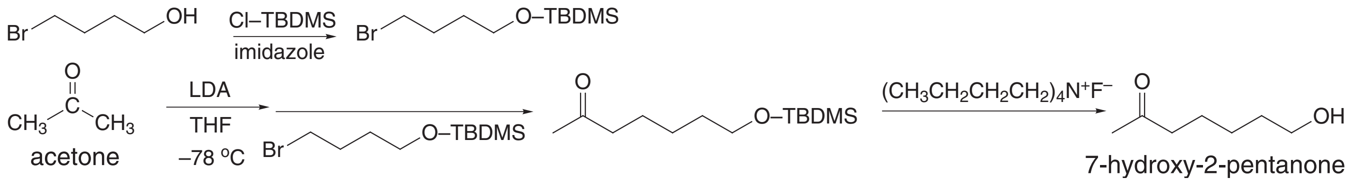


19.53



The OH group donates a proton to the enolate, which acts as a base.

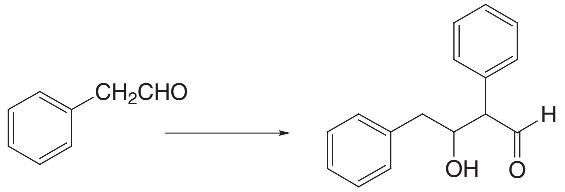
To synthesize the desired product, a protecting group is needed:



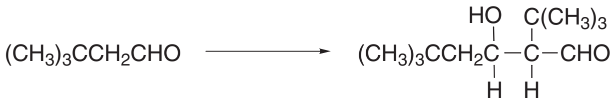
7-hydroxy-2-pentanone

19.54

a.

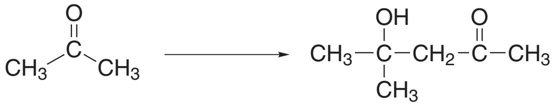


b.



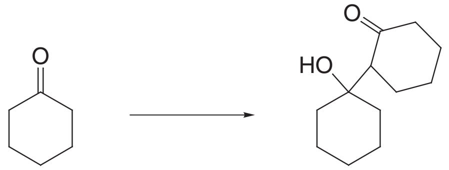
$$(CH_3)_3CCH_2CHO \longrightarrow (CH_3)_3CCH_2\overset{HO}{\underset{H}{C}}-\overset{C(CH_3)_3}{\underset{H}{C}}-CHO$$

c.



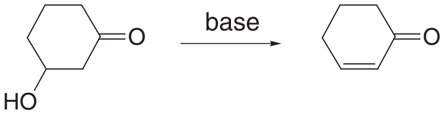
$$CH_3\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

d.

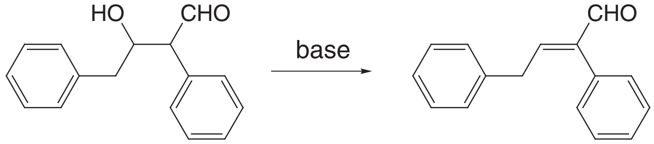


19.55

a.



b.



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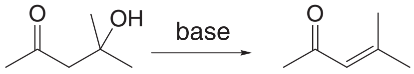
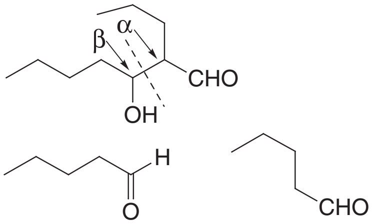
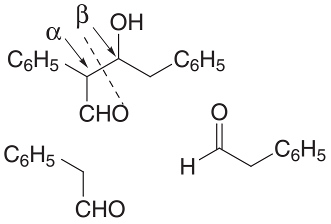


19.56 Individuare i carboni in α e β rispetto al gruppo carbonilico, e dividere la molecola in due frammenti attraverso questo legame. Il C in α e tutti gli atomi legati ad esso appartengono a un componente carbonilico. Il C in β e tutti gli atomi legati ad esso appartengono all'altro componente carbonilico.

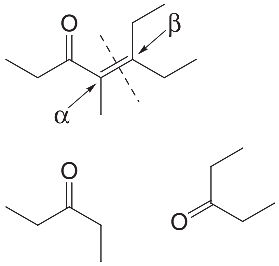
a.



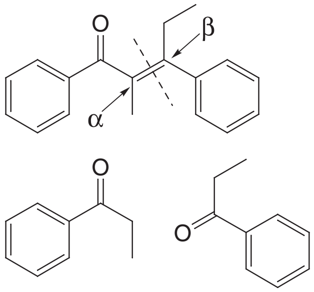
c.



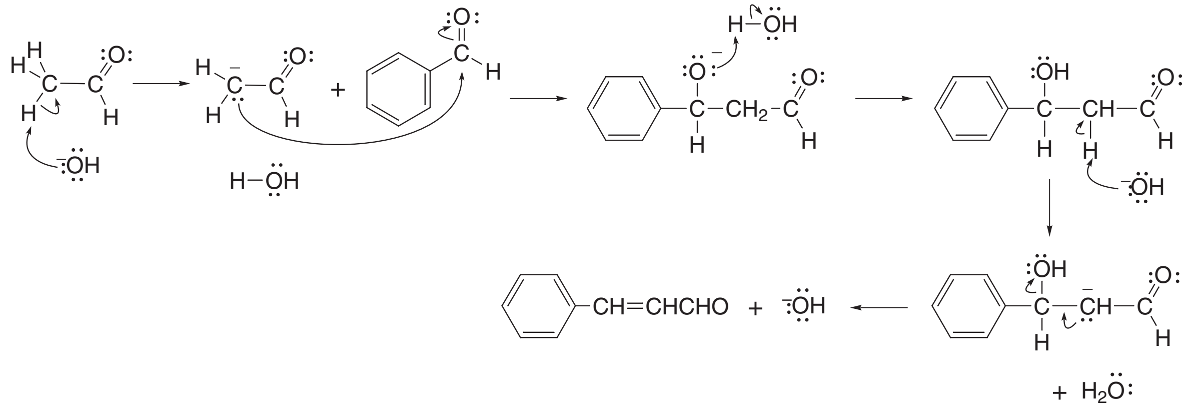
b.



d.

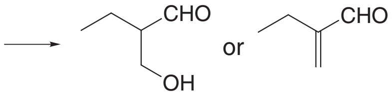


19.57

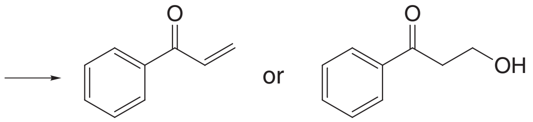


19.58

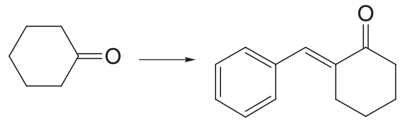
a. $CH_3CH_2CH_2CHO$ and $CH_2{=}O$



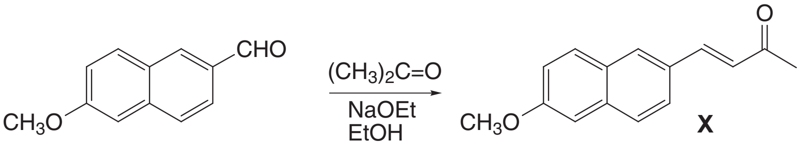
b. $C_6H_5COCH_3$ and $CH_2{=}O$



c. C_6H_5CHO and

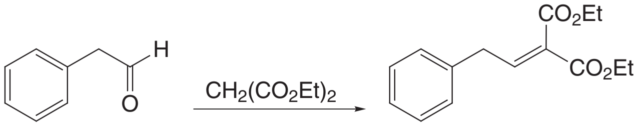


19.59

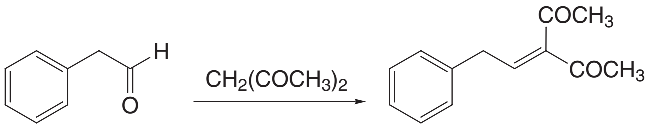


19.60

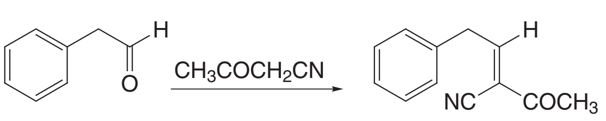
a.



b.

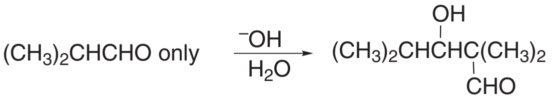


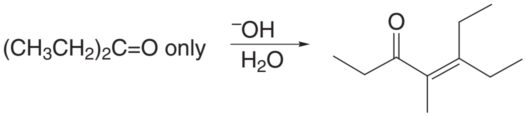
c.

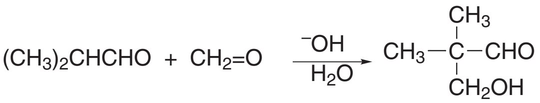


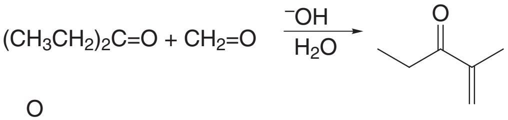
(*E* and *Z* isomers)

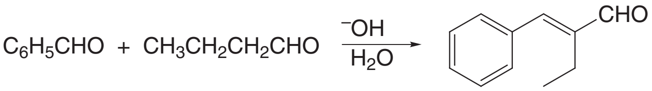
19.61 Il prodotto di una reazione aldolica è un composto β-idrossi carbonilico o un composto carbonilico α,β-insaturo. Quest'ultimo tipo di composto si ottiene come prodotto, a meno che l'eliminazione di H_2O non possa formare un sistema coniugato.

a.

$(CH_3)_2CHCHO$ only $\xrightarrow[H_2O]{^-OH}$ $(CH_3)_2CH\overset{OH}{C}H\underset{CHO}{C}(CH_3)_2$

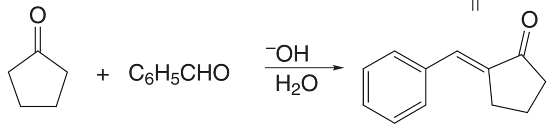
d.


b.

$(CH_3)_2CHCHO + CH_2{=}O \xrightarrow[H_2O]{^-OH} CH_3-\overset{CH_3}{\underset{CH_2OH}{C}}-CHO$

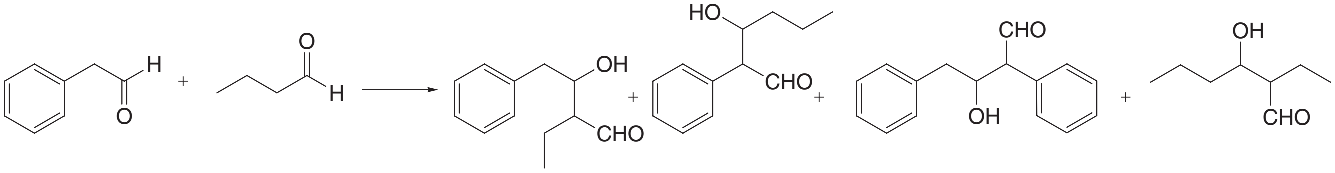
e.


c.


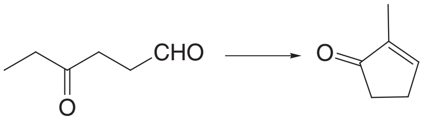
(*E* and *Z* isomers)

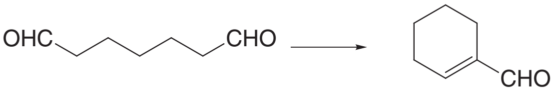
f.


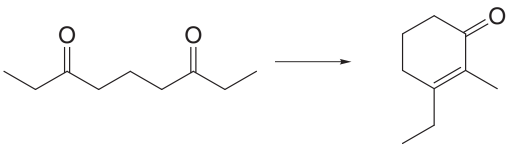
19.62



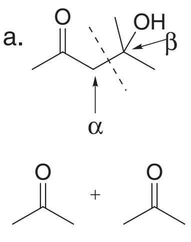
19.63

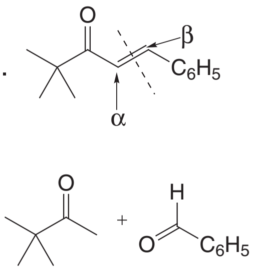
a.


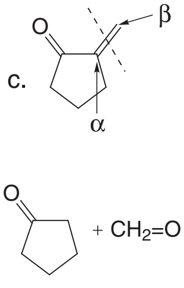
c.


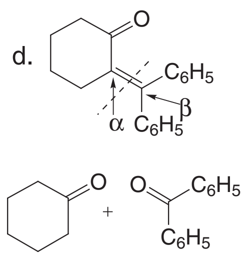
b.


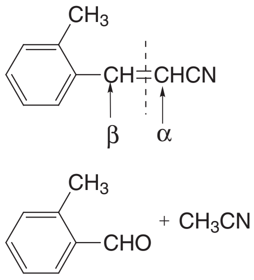
19.64 Individuare i carboni in α e β rispetto al gruppo carbonilico, e dividere la molecola in due frammenti attraverso questo legame. Il C in α e tutti gli atomi legati ad esso appartengono a un componente carbonilico. Il C in β e tutti gli atomi legati ad esso appartengono all'altro componente carbonilico.

a.


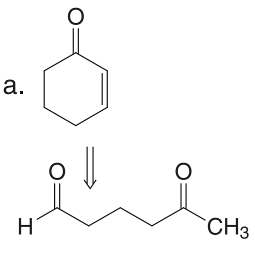
b.


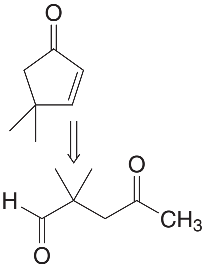
c.


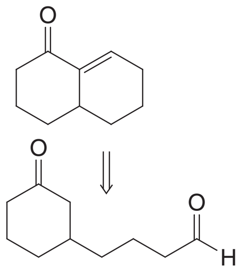
d.


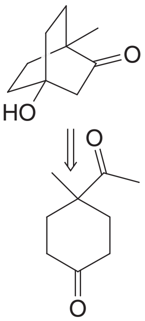
e.


19.65

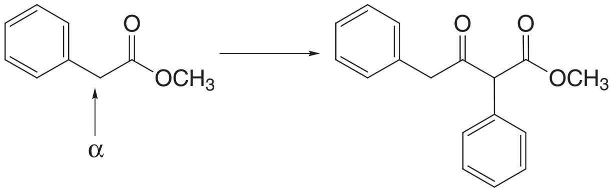
a.


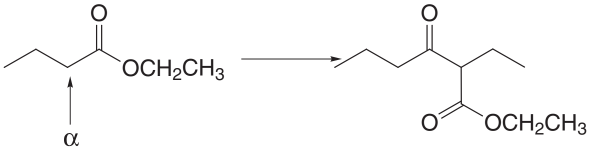
b.


c.


d.


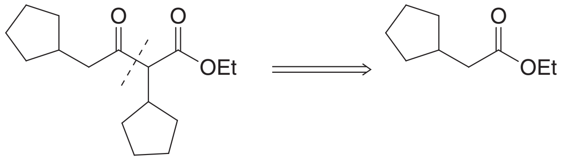
19.66 Per formare il β–cheto estere unire il C in α di un estere al C carbonilico dell'altro estere.

a.


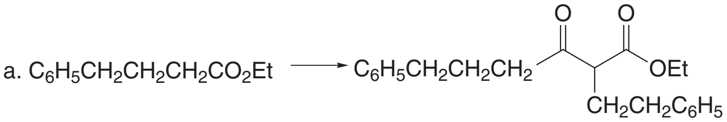
b.


19.67

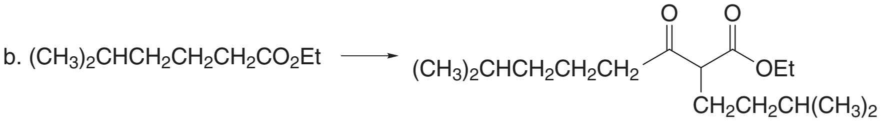
a.


b.


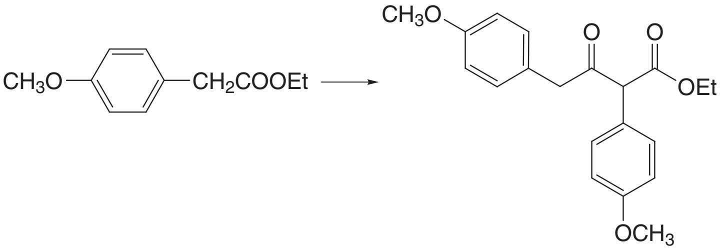
19.68



a. $C_6H_5CH_2CH_2CH_2CO_2Et \longrightarrow C_6H_5CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}\underset{CH_2CH_2C_6H_5}{CH}\overset{O}{\overset{\|}{C}}OEt$

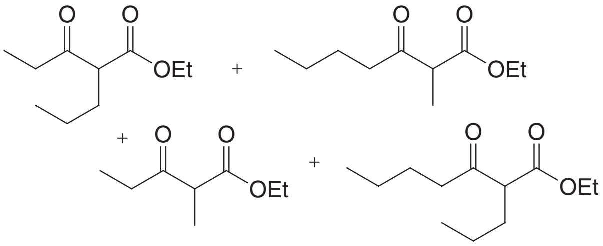


b. $(CH_3)_2CHCH_2CH_2CH_2CO_2Et \longrightarrow (CH_3)_2CHCH_2CH_2CH_2\overset{O}{\overset{\|}{C}}\underset{CH_2CH_2CH(CH_3)_2}{CH}\overset{O}{\overset{\|}{C}}OEt$

c.


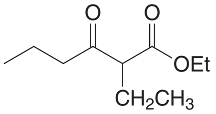
19.69

$CH_3CH_2CH_2CH_2CO_2Et + CH_3CH_2CO_2Et \longrightarrow$

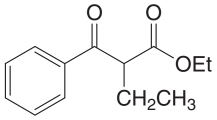


19.70

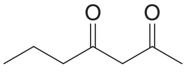
a. $CH_3CH_2CH_2CO_2Et$ only $\longrightarrow$



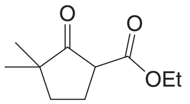
b. $CH_3CH_2CH_2CO_2Et + C_6H_5CO_2Et \longrightarrow$



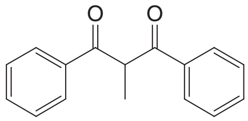
c. $CH_3CH_2CH_2CO_2Et + (CH_3)_2C{=}O \longrightarrow$



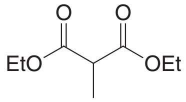
d. $EtO_2CC(CH_3)_2CH_2CH_2CH_2CO_2Et \longrightarrow$



e. $C_6H_5COCH_2CH_3 + C_6H_5CO_2Et \longrightarrow$



f. $CH_3CH_2CH_2CO_2Et + (EtO)_2C{=}O \longrightarrow$

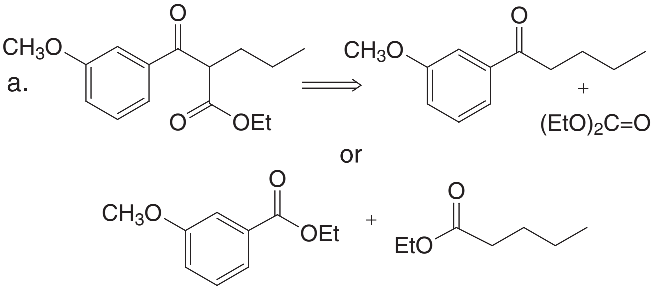


g.

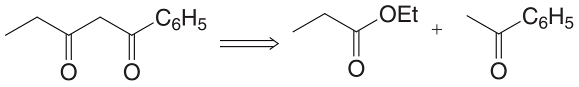
h.

19.71

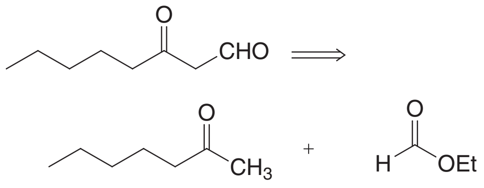
a.



b.

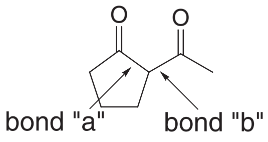


c.

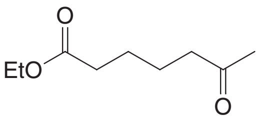


d. $C_6H_5CH(COOEt)_2 \Longrightarrow$

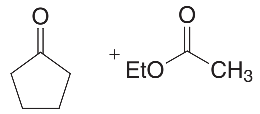
19.72



To form bond a:

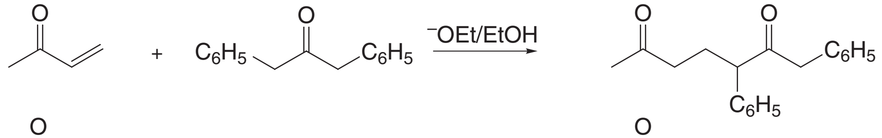


To form bond b:

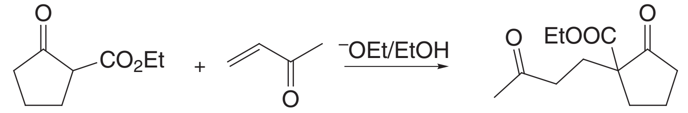


19.73

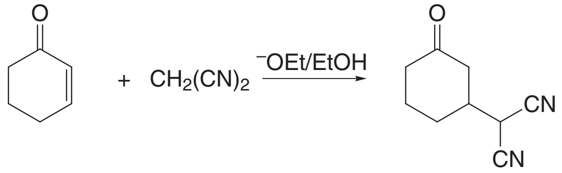
a.



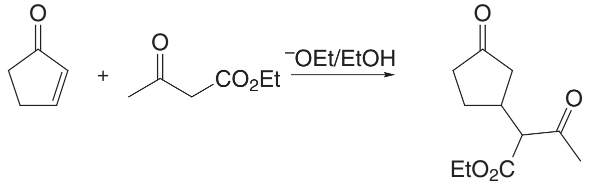
b.



c.

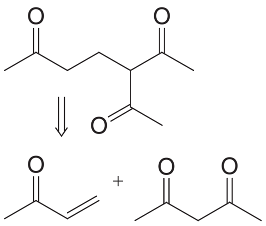


d.

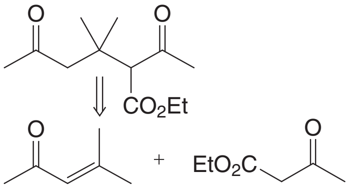


19.74

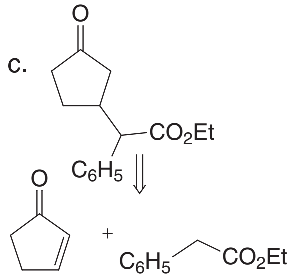
a.



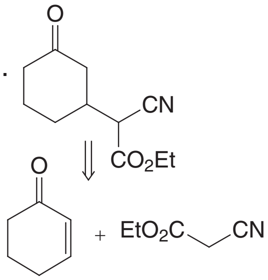
b.



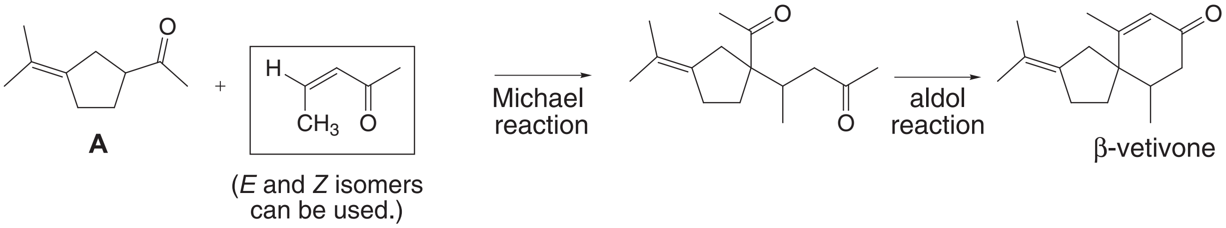
c.



d.



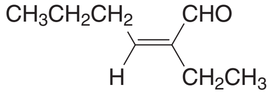
19.75



19.76

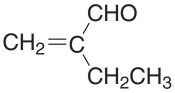
$CH_3CH_2CH_2CHO$

a. $\xrightarrow{^-OH/H_2O}$

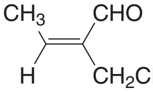


(*E* and *Z*)

b. $\xrightarrow{^-OH\ /CH_2=O/H_2O}$

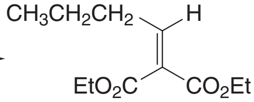


c. $\xrightarrow{[1]\ LDA;\ [2]\ CH_3CHO;\ [3]\ H_2O}$

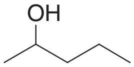


(*E* and *Z*)

d. $\xrightarrow{CH_2(CO_2Et)_2/NaOEt/EtOH}$



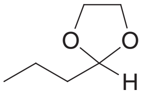
e. $\xrightarrow{[1]\ CH_3Li;\ [2]\ H_2O}$



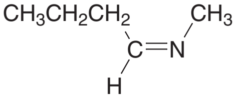
f. $\xrightarrow{NaBH_4/CH_3OH}$ $CH_3CH_2CH_2CH_2OH$

g. $\xrightarrow{H_2/Pd}$ $CH_3CH_2CH_2CH_2OH$

h. $\xrightarrow{HOCH_2CH_2OH/TsOH}$



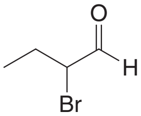
i. $\xrightarrow{CH_3NH_2,\text{ mild acid}}$



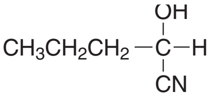
j. $\xrightarrow{(CH_3)_2NH,\text{ mild acid}}$ $CH_3CH_2CH=CHN(CH_3)_2$ (*E* and *Z*)

k. $\xrightarrow{CrO_3/H_2SO_4}$ $CH_3CH_2CH_2COOH$

l. $\xrightarrow{Br_2/CH_3COOH}$

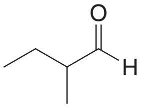


m. $\xrightarrow{NaCN/HCl}$

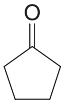
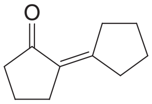


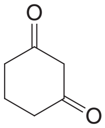
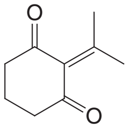
$CH_3CH_2CH_2-\overset{OH}{\underset{CN}{C}}-H$

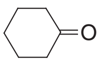
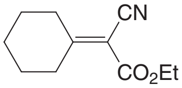
n. $\xrightarrow{[1]\ LDA;\ [2]\ CH_3I}$

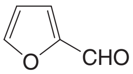
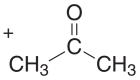
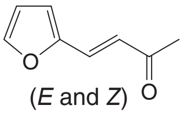


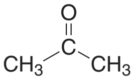
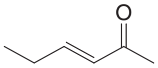
19.77.

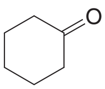
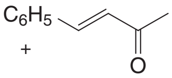
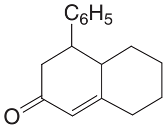
a.  $\xrightarrow[H_2O]{^-OH}$ 

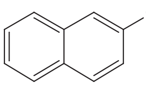
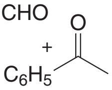
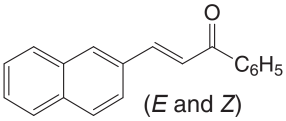
b.  $\xrightarrow[(CH_3)_2C=O]{NaOEt/EtOH}$ 

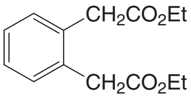
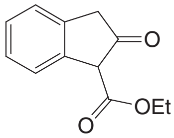
c. $NCCH_2CO_2Et$ $\xrightarrow{NaOEt/EtOH}$  

d.  +  $CH_3\overset{O}{\overset{\|}{C}}CH_3$ $\xrightarrow[H_2O]{^-OH}$  (*E* and *Z*)

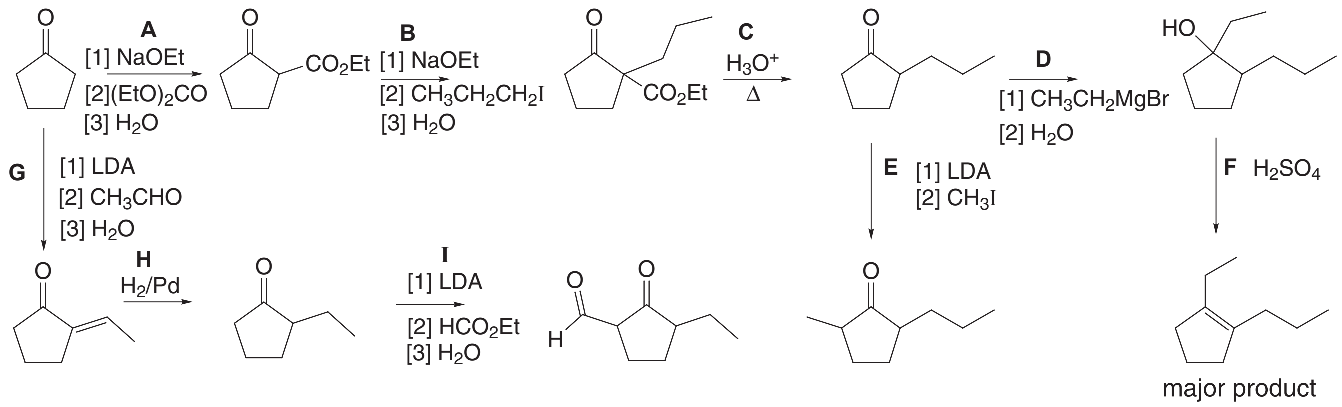
e.  $CH_3\overset{O}{\overset{\|}{C}}CH_3$ $\xrightarrow[[2]\ CH_3CH_2CHO\ [3]\ H_2O]{[1]\ LDA}$  (*E* and *Z*)

f.  +  $\xrightarrow[CH_3OH]{NaOCH_3}$ 

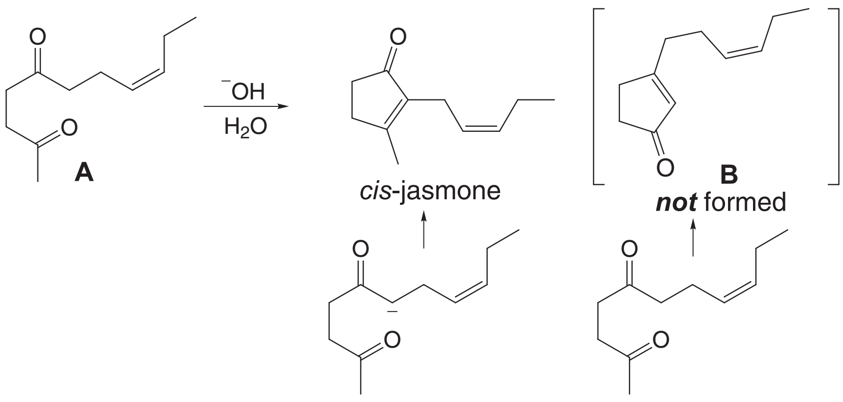
g.  +  $\xrightarrow[H_2O]{^-OH}$  (*E* and *Z*)

h.  $\xrightarrow[[2]\ H_3O^+]{[1]\ NaOEt/EtOH}$ 

19.78



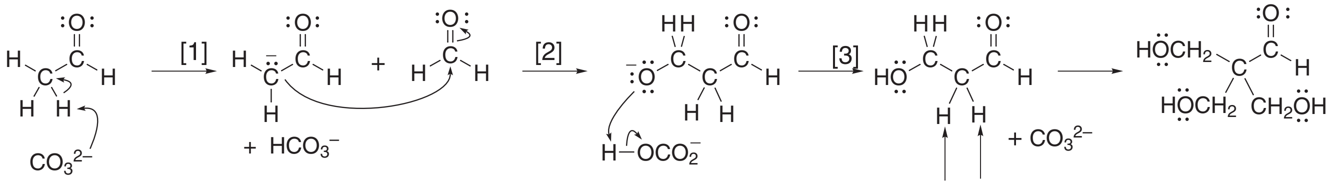
19.79



cis-Jasmone is formed from this more substituted and therefore more stable enolate. Under equilibrium conditions ($^-$OH, H$_2$O) this thermodynamic enolate predominates.

This less substituted enolate is not favored by the base/solvent conditions chosen.

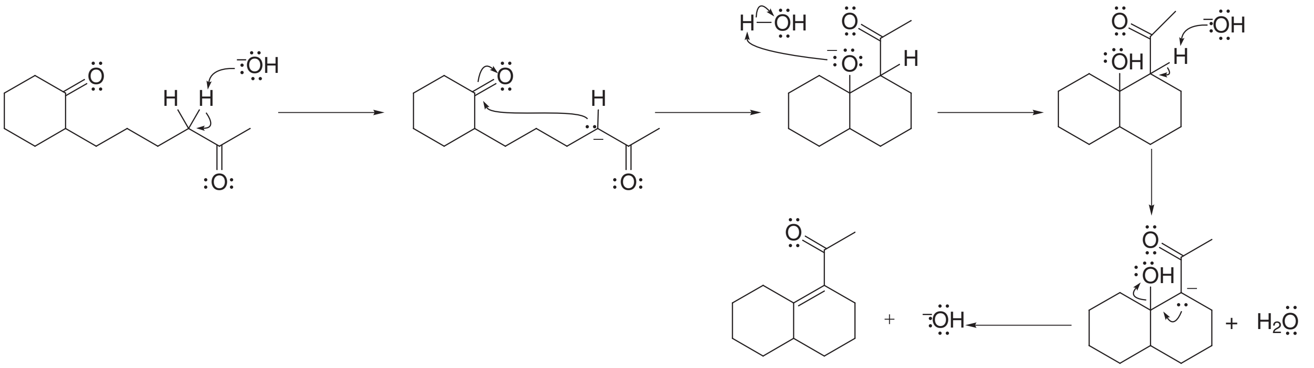
19.80



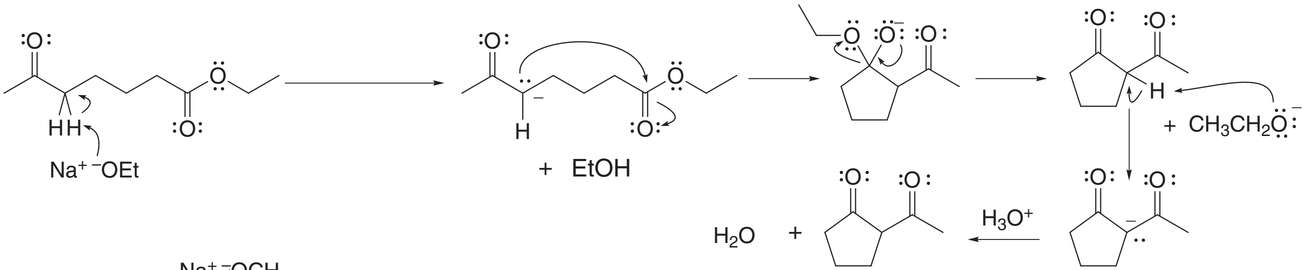
Repeat steps [1]–[3] with these two H's and CO$_3^{2-}$.

19.81

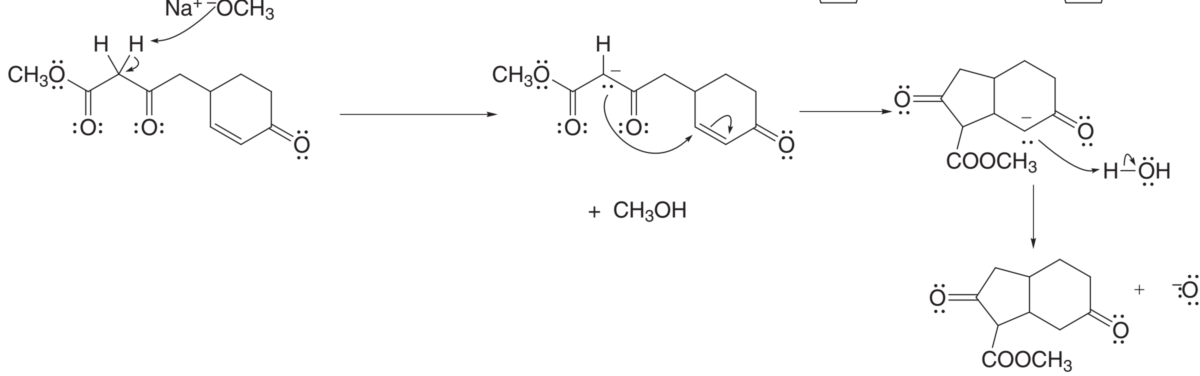
a.



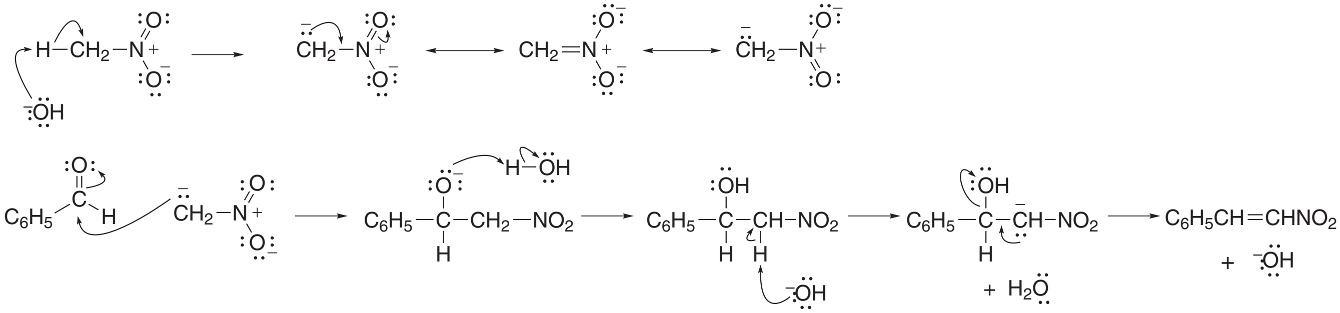
b.



c.

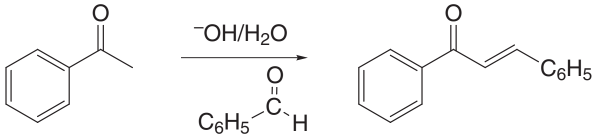


19.82

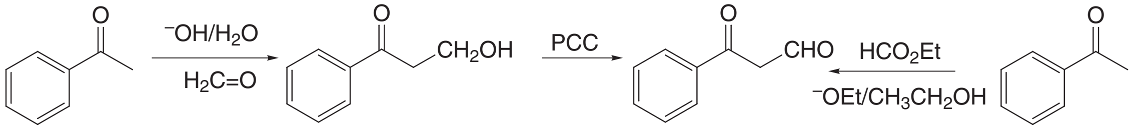


19.83

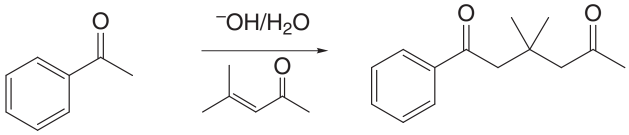
a.



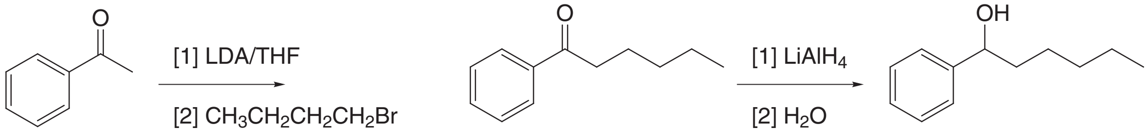
b.



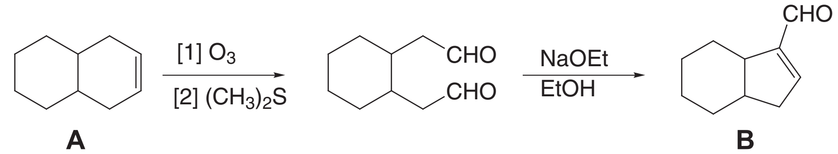
c.



d.

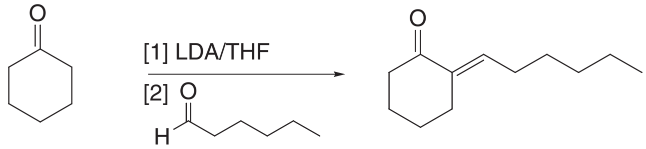


19.84

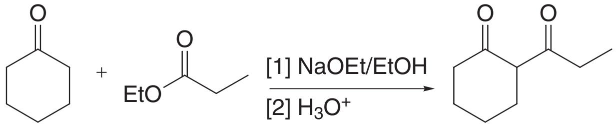


19.85

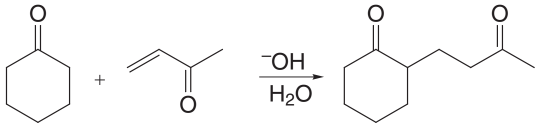
a.



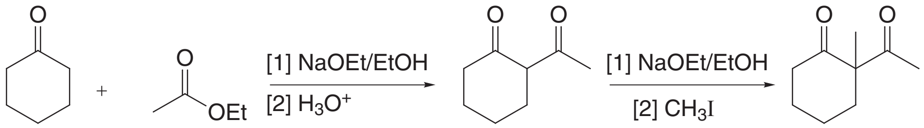
b.



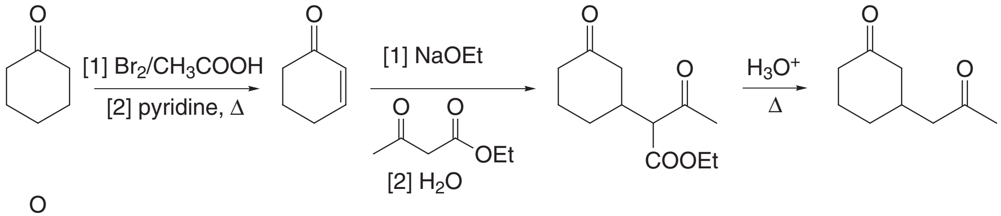
c.



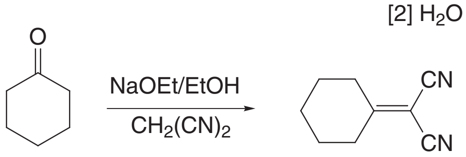
d.



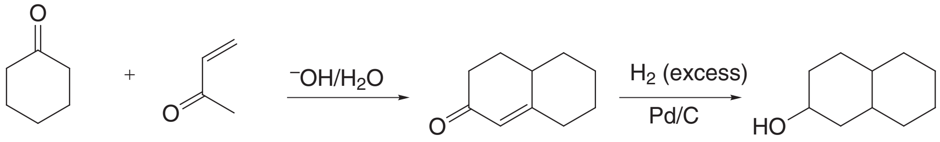
e.



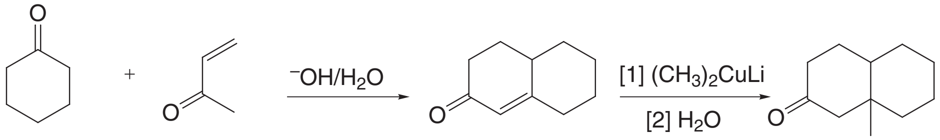
f.



g.

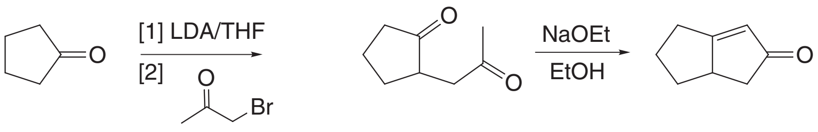


h.

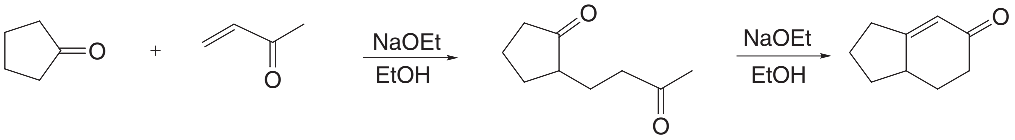


19.86

a.

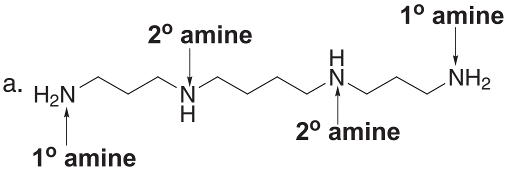


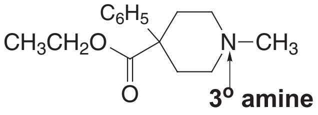
b.

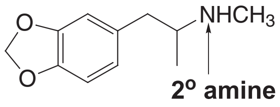


Capitolo 20

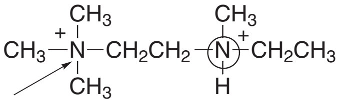
20.1 Le ammine sono classificate come 1°, 2°, o 3° secondo il numero di gruppi alchilici legati all'atomo di azoto.

a.


b.


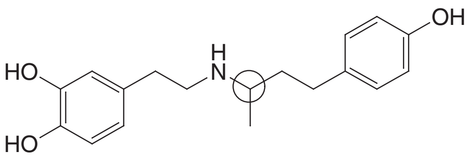
c.


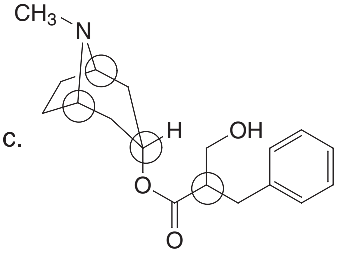
20.2 L'atomo di N di un sale di ammonio quaternario è un centro stereogenico quando l'N è circondato da quattro gruppi diversi. Tutti i centri stereogenici sono cerchiati.

a.


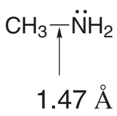
$CH_3-\overset{+}{N}(CH_3)_2-CH_2CH_2-\overset{+}{N}(CH_3)(H)-CH_2CH_3$

N has 3 similar groups.

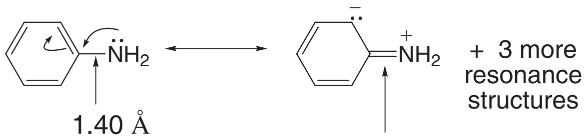
b.


c.


20.3



The C–N bond is formed from two sp^3 hybridized atoms and the lone pair is localized on N.



Because the lone pair on N can be delocalized on the benzene ring, the C–N bond has partial double bond character, making it shorter. Both the C and N atoms must be sp^2 hybridized (+ have a *p* orbital) for delocalization to occur. The higher percent *s*-character in both C and N shortens the bond as well.

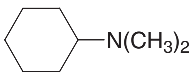
20.4

a. $CH_3CH_2CH(NH_2)CH_3$

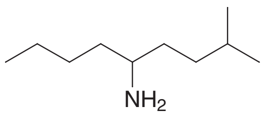
2-butanamine
or
sec-butylamine

b. $(CH_3CH_2CH_2CH_2)_2NH$

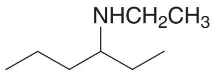
dibutylamine

c.


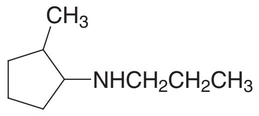
N,N-dimethylcyclohexanamine

d.


2-methyl-5-nonanamine

e.


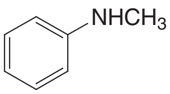
N-ethyl-3-hexanamine

f.


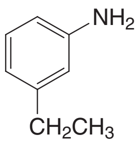
N-propyl-2-methylcyclopentanamine

20.5 Le ammine aromatiche sono definite come derivati dell'anilina.

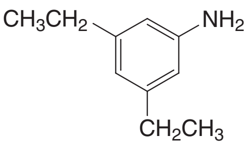
a. *N*-methylaniline



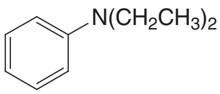
b. *m*-ethylaniline



c. 3,5-diethylaniline

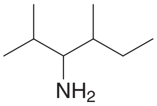


d. *N,N*-diethylaniline

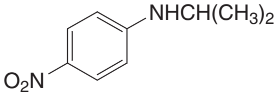


20.6 Un gruppo NH_2 se è considerato un sostituente è detto **gruppo amminico**.

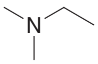
a. 2,4-dimethyl-3-hexanamine



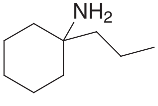
c. *N*-isopropyl-*p*-nitroaniline



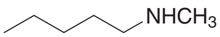
e. *N,N*-dimethylethylamine



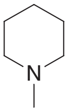
g. 1-propylcyclohexylamine



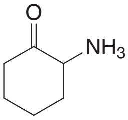
b. *N*-methylpentylamine



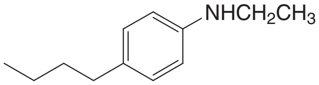
d. *N*-methylpiperidine



f. 2-aminocyclohexanone



h. *p*-butyl-*N*-ethylaniline

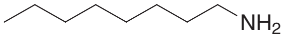


20.7

a. $CH_3NHCH_2CH_2CH_2CH_3$

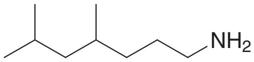
N-methyl-1-butanamine
(*N*-methylbutylamine)

b.



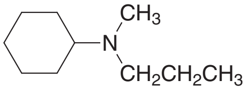
1-octanamine
(octylamine)

c.



4,6-dimethyl-1-heptanamine

d.



*N-m*ethyl-*N*-propylcyclohexanamine

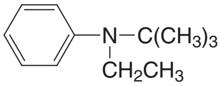
e. $(CH_3CH_2CH_2)_3N$

tripropylamine

f. $(C_6H_5)_2NH$

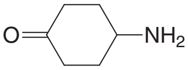
diphenylamine

g.



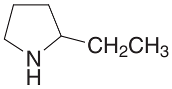
N-tert-butyl-*N*-ethylaniline

h.



4-aminocyclohexanone

i.

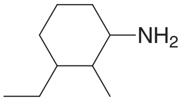


2-ethylpyrrolidine

j. $CH_3CH_2CH_2CH(NH_2)CH(CH_3)_2$

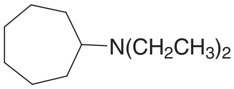
2-methyl-3-hexanamine

k.



3-ethyl-2-methylcyclohexanamine

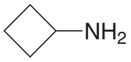
l.



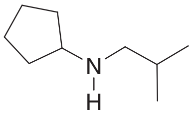
N,N-diethylcycloheptanamine

20.8

a. cyclobutylamine



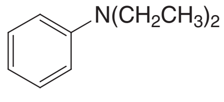
b. *N*-isobutylcyclopentylamine



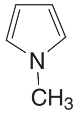
c. tri-*tert*-butylamine

$N[C(CH_3)_3]_3$

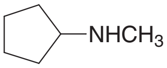
d. *N,N*-diethylaniline



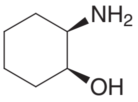
e. *N*-methylpyrrole



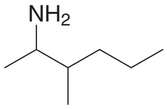
f. *N*-methylcyclopentylamine



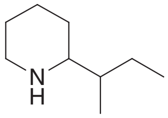
g. *cis*-2-aminocyclohexanol



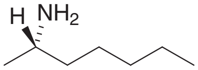
h. 3-methyl-2-hexanamine



i. 2-*sec*-butylpiperidine

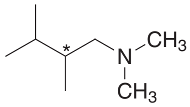


j. (*S*)-2-heptanamine



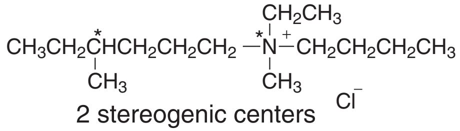
20.9 [* indica un centro stereogenico]

a.



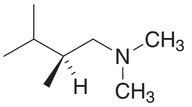
1 stereogenic center
2 stereoisomers

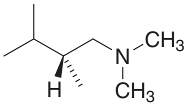
b.

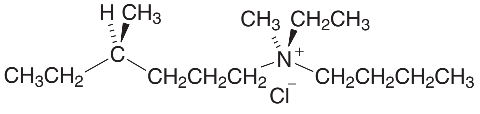


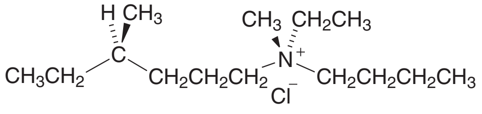
$CH_3CH_2\underset{CH_3}{\overset{*}{C}}HCH_2CH_2CH_2-\underset{CH_3}{\overset{CH_2CH_3}{\overset{*}{N^+}}}-CH_2CH_2CH_2CH_3 \quad Cl^-$

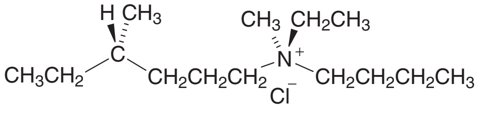
2 stereogenic centers
4 stereoisomers

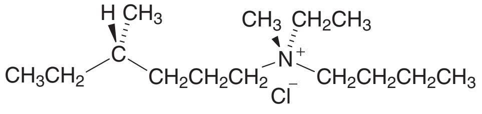












20.10 Il pK_a di molte ammine protonate è 10–11, il pK_a dell'acido di partenza deve essere **minore di 10** perché l'equilibrio favorisca i prodotti. Le ammine pertanto vengono prontamente protonate da acidi inorganici forti come HCl e H_2SO_4, ed anche da acidi carbossilici.

a. $CH_3CH_2CH_2CH_2-NH_2 + HCl \rightleftharpoons CH_3CH_2CH_2CH_2-\overset{+}{N}H_3 + Cl^-$

pK_a = –7

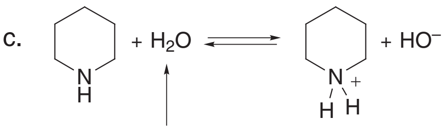
pK_a ≈ 10
weaker acid
products favored

b. $C_6H_5COOH + (CH_3)_2NH \rightleftharpoons (CH_3)_2\overset{+}{N}H_2 + C_6H_5COO^-$

pK_a = 4.2

pK_a = 10.7
weaker acid
products favored

c.



pK_a = 15.7
weaker acid
reactants favored

pK_a ≈ 10

20.11 Più debole è l'acido coniugato, maggiore è il suo pK_a e più forte è la base. (I valori di pK_a sono dell'acido coniugato di una data ammina).

a. CH_3NH_2 (pK_a = 10.7) and $CH_3CH_2NH_2$ (pK_a = 10.8)

stronger conjugate acid
weaker base

weaker conjugate acid
stronger base

b. $(CH_3CH_2)_3N$ (pK_a = 11.0) and $(CH_3)_3N$ (pK_a = 9.8)

weaker conjugate acid
stronger base

stronger conjugate acid
weaker base

20.12 Le alchilammine 1°, 2°, e 3° sono più basiche di NH_3 per l'effetto induttivo elettron donatore dei gruppi R.

a. $(CH_3)_2NH$ and NH_3

2° alkylamine
CH_3 groups are electron donating.
stronger base

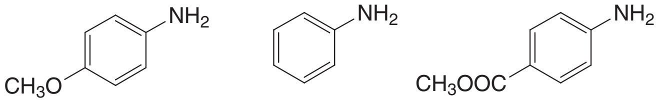
b. $CH_3CH_2NH_2$ and $ClCH_2CH_2NH_2$

1° alkylamine
stronger base

1° alkylamine
Cl is electron withdrawing.
weaker base

20.13 Le arilammine sono meno basiche delle alchilammine perché la coppia elettronica sull'N è delocalizzato. Gruppi elettron donatori aumentano la densità elettronica del benzene, rendendo le arilammine più basiche dell'anilina. Gruppi elettron attrattori sottraggono densità elettronica dal benzene, rendendo le arilammine meno basiche dell'anilina.

a.

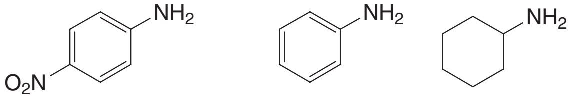


electron
donating group
most basic

arylamine
intermediate
basicity

electron
withdrawing group
least basic

b.

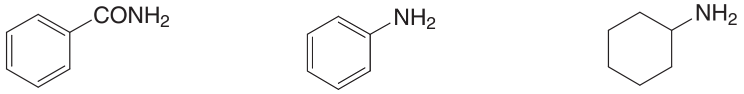


electron
withdrawing group
least basic

arylamine
intermediate
basicity

alkylamine
most basic

20.14 Le ammidi sono molto meno basiche delle ammine perché la coppia elettronica sull'N è altamente delocalizzata.



amide
least basic

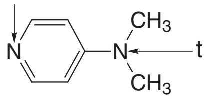
arylamine
intermediate basicity

alkylamine
most basic

20.15

a.

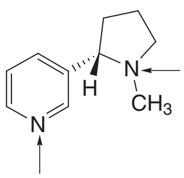
sp² hybridized
more basic



This N is also sp² hybridized so the electron pair can delocalize onto the aromatic ring. Delocalization makes this N less basic.

DMAP
4-(dimethylamino)pyridine

b.



sp³ hybridized N
stronger base

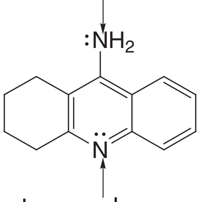
nicotine

sp² hybridized N
higher percent s-character
weaker base

20.16

a.

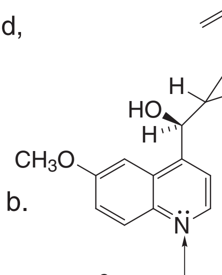
This electron pair is delocalized, making it a weaker base.



stronger base

This compound is similar to DMAP in Problem 25.27a.

b.

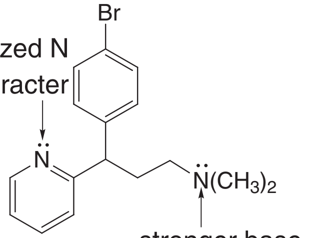


stronger base
sp^3 hybridized N
25% *s*-character

sp^2 hybridized N
33% s-character

c.

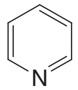
sp^2 hybridized N
33% *s*-character



stronger base
sp^3 hybridized N
25% *s*-character

20.17

a. $(CH_3CH_2)_2NH$ or



sp^3 hybridized N **stronger base** — *sp*^{2} hybridized N **weaker base**

b. $C_6H_5NHCH_3$ or $C_6H_5CH_2NH_2$

arylamine **weaker base** — alkylamine **stronger base**

c. $HCON(CH_3)_2$ or $(CH_3)_3N$

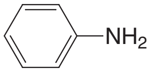
amide **weaker base** — alkylamine **stronger base**

d. $(CH_3CH_2)_2NH$ or $(ClCH_2CH_2)_2NH$

2° alkylamine **stronger base** — 2° alkylamine Cl is electron withdrawing. **weaker base**

20.18

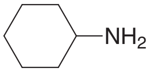
a.



arylamine
least basic

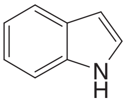
NH_3

intermediate basicity

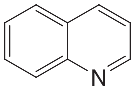


alkylamine
most basic

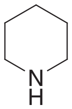
b.



delocalized electron pair on N
least basic

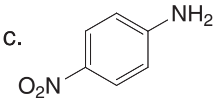


sp^2 hybridized N
intermediate basicity

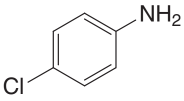


sp^3 hybridized N
most basic

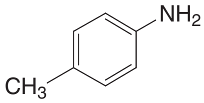
c.



electron withdrawing group
least basic

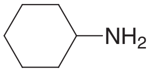


intermediate basicity



electron donating group
most basic

d. $(C_6H_5)_2NH$ — $C_6H_5NH_2$

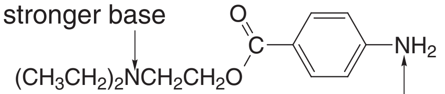


diarylamine **least basic** — arylamine **intermediate basicity** — alkylamine **most basic**

20.19

a.

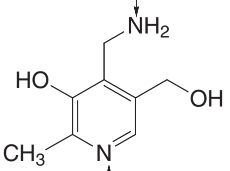
sp^3 hybridized N
stronger base



delocalized electron pair

b.

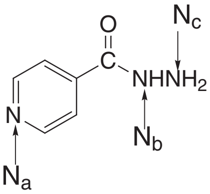
sp^3 hybridized N
stronger base



sp^2 hybridized N

20.20

a.



$N_b < N_a < N_c$

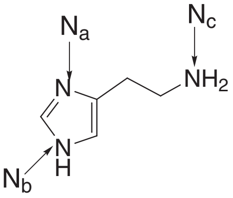
Order of basicity: $N_b < N_a < N_c$

N_b – The electron pair on this N atom is delocalized on the O atom; least basic.

N_a – The electron pair on this N atom is not delocalized, but is on an *sp*^{2} hybridized atom.

N_c – The electron pair on this N atom is on an *sp*^{3} hybridized N; most basic.

b.



$N_b < N_a < N_c$

Order of basicity: $N_b < N_a < N_c$

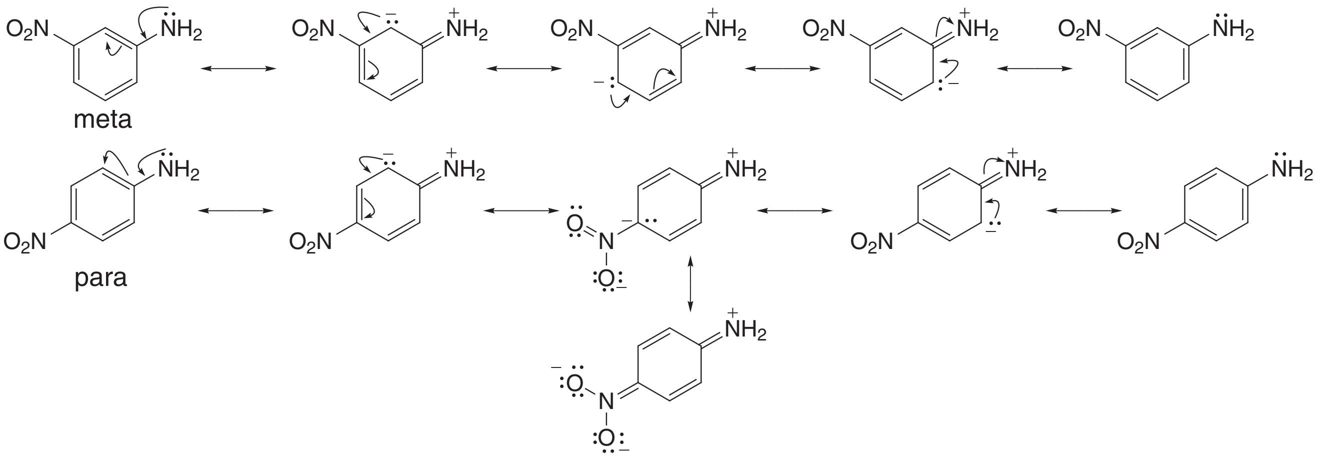
N_b – The electron pair on this N atom is delocalized on the aromatic five-membered ring; least basic.

N_a – The electron pair on this N atom is not delocalized, but is on an *sp*^{2} hybridized atom.

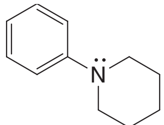
N_c – The electron pair on this N atom is on an *sp*^{3} hybridized N; most basic.

20.21

The para isomer is the weaker base because the electron pair on its NH_2 group can be delocalized onto the NO_2 group. In the meta isomer, no resonance structure places the electron pair on the NO_2 group, and fewer resonance structures can be drawn:

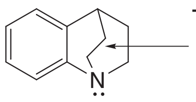


20.22



A

pK_a of the conjugate acid = 5.2
stronger conjugate acid
weaker base
The electron pair of this arylamine is delocalized on the benzene ring, decreasing its basicity.

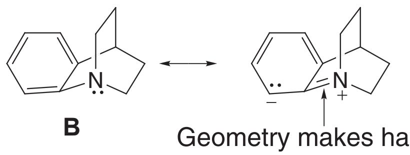


This two-carbon bridge makes it difficult for the lone pair on N to delocalize on the aromatic ring.

B

pK_a of the conjugate acid = 7.29
weaker conjugate acid
stronger base

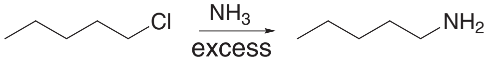
Resonance structures that place a double bond between the N atom and the benzene ring are destabilized. Since the electron pair is more localized on N, compound **B** is more basic.



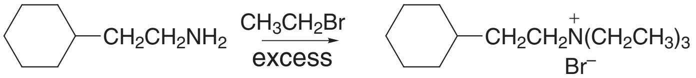
Geometry makes having a double bond here difficult.

20.23 La reazione $S_N2$di un alogenuro alchilico con NH_3 o un'ammina forma un ammina.

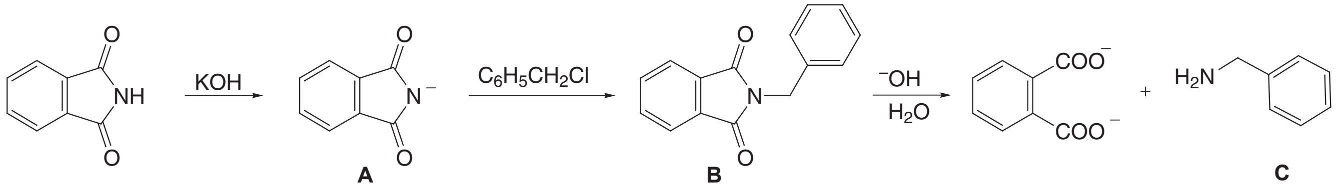
a.



b.

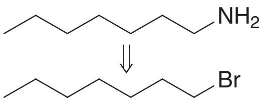


20.24



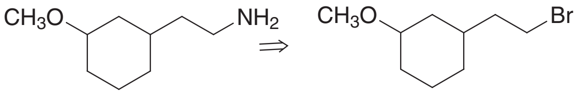
20.25 La sintesi di Gabriel converte un alogenuro alchilico in un'ammina 1° attraverso un processo a due stadi: sostituzione nucleofila seguita da idrolisi.

a.



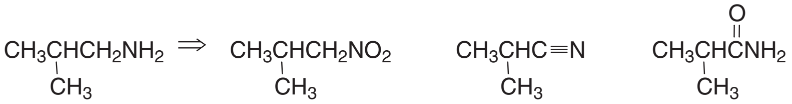
b. $(CH_3)_2CHCH_2CH_2NH_2$
$\Downarrow$
$(CH_3)_2CHCH_2CH_2Br$

c.



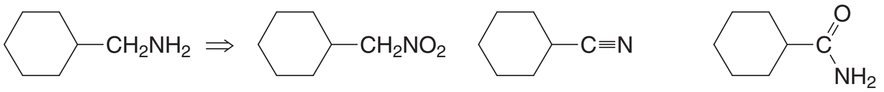
20.26 I nitrili sono ridotti ad ammine 1° LiAlH$_4$. I gruppi nitro sono ridotti ad ammine 1° per azione di una varietà di agenti riducenti. **Le ammidi 1°, 2°, e 3° sono ridotte ad ammine 1°, 2°, e 3°** rispettivamente, con LiAlH$_4$.

a.

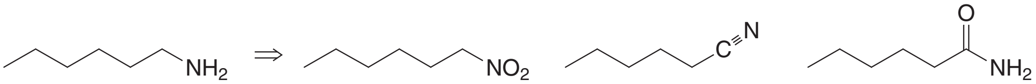


$CH_3\underset{CH_3}{CH}CH_2NH_2 \Rightarrow CH_3\underset{CH_3}{CH}CH_2NO_2 \quad CH_3\underset{CH_3}{CH}C{\equiv}N \quad CH_3\underset{CH_3}{CH}\overset{O}{\overset{\|}{C}}NH_2$

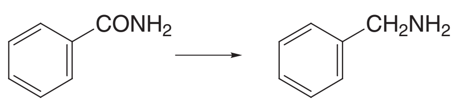
b.

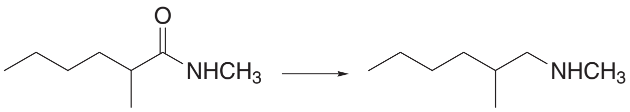


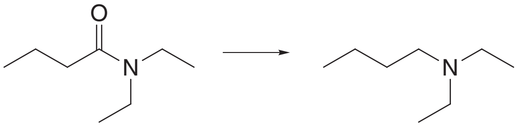
c.



20.27 Le ammidi 1°, 2°, e 3° sono ridotte ad ammine 1°, 2°, e 3° rispettivamente, con LiAlH$_4$.

a.


c.


b.


20.28

(CH$_3$)$_2$CHNH$_2$

isopropylamine

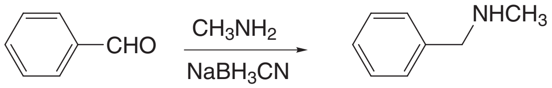
General reaction:

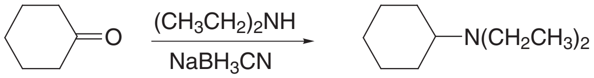
$$R{-}C{\equiv}N \xrightarrow{[H]} RCH_2NH_2$$

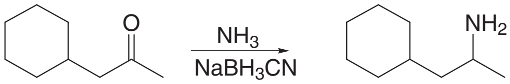
The amine needs 2 H's here.

The C bonded to the N must have 2 H's to be formed by reduction of a nitrile.

20.29 L'amminazione riduttiva è un metodo a due stadi che converte aldeidi e chetoni in ammine 1^o, 2^o, and 3^o. L'amminazione riduttiva sostituisce un C=O con un legame C–H ed uno C–N .

a.


c.


b.


20.30

a. $C_6H_5CH_2CH_2CH_2Br \xrightarrow[\text{excess}]{NH_3} C_6H_5CH_2CH_2CH_2NH_2$

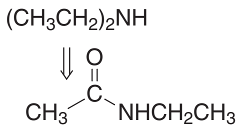
b. $C_6H_5CH_2CH_2Br \xrightarrow{NaCN} C_6H_5CH_2CH_2CN \xrightarrow[\text{[2] } H_2O]{\text{[1] } LiAlH_4} C_6H_5CH_2CH_2CH_2NH_2$

c. $C_6H_5CH_2CH_2CH_2NO_2 \xrightarrow[Pd/C]{H_2} C_6H_5CH_2CH_2CH_2NH_2$

d. $C_6H_5CH_2CH_2CONH_2 \xrightarrow[\text{[2] } H_2O]{\text{[1] } LiAlH_4} C_6H_5CH_2CH_2CH_2NH_2$

e. $C_6H_5CH_2CH_2CHO \xrightarrow[NaBH_3CN]{NH_3} C_6H_5CH_2CH_2CH_2NH_2$

20.31

a.


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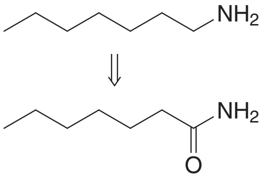
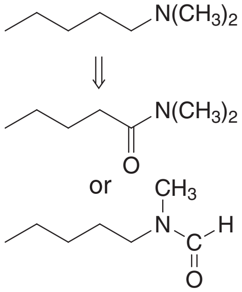
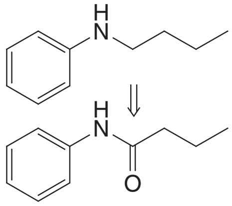
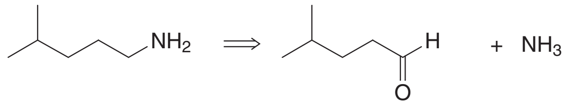
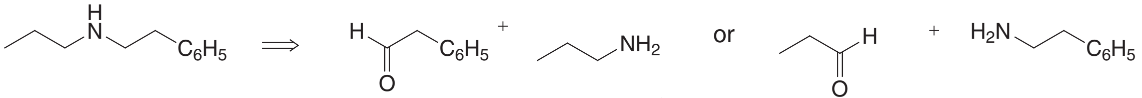


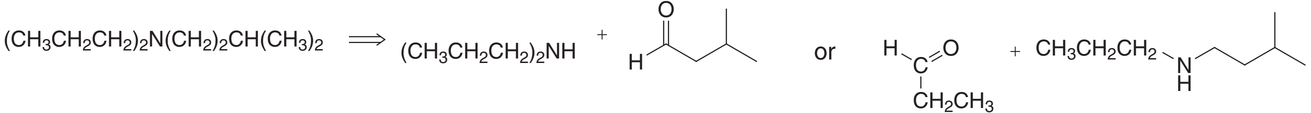
c.


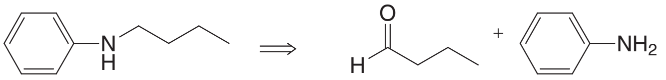
d.


20.32 In una amminazione riduttiva, un gruppo alchilico sull'N deriva dal composto carbonilico. Il resto della molecola deriva dall'NH$_3$ o dall'ammina.

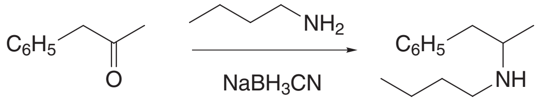
a.


b.


c.


d.


20.33

a.


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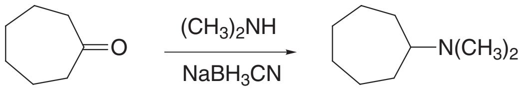
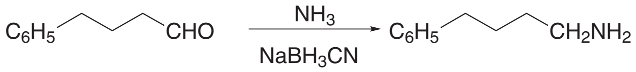
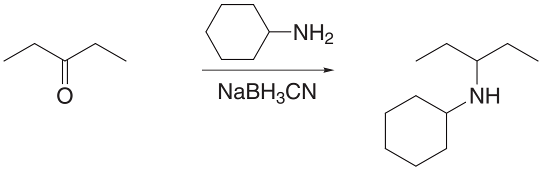
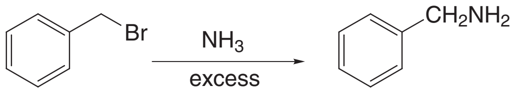


c.


d.


20.34

a.


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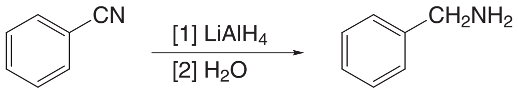
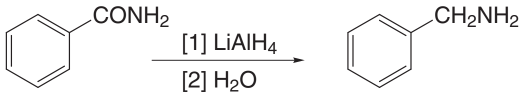
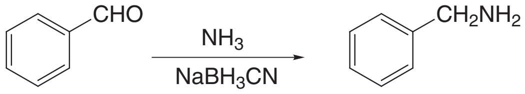
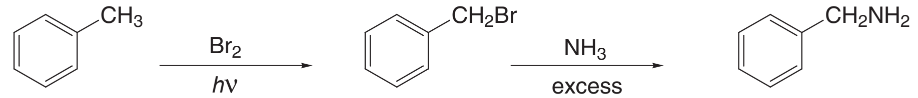
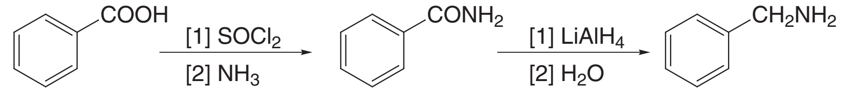
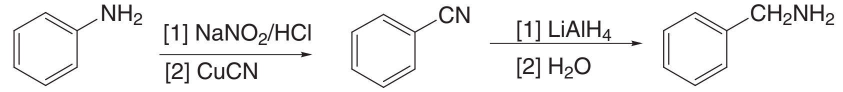


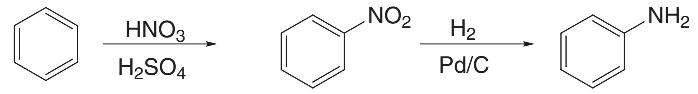
c.


d.


e.


f.


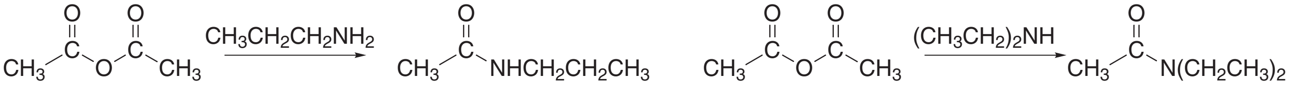
g.


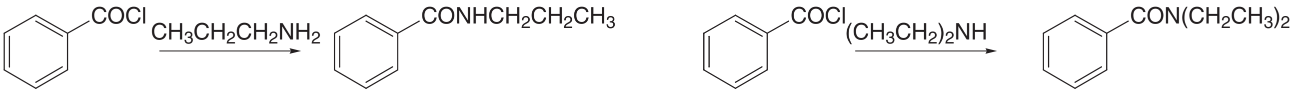
h.


then as in (g).

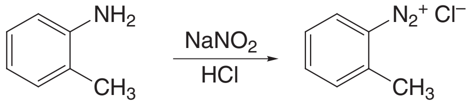
20.35 Le ammine attaccano i gruppi carbonilici per formare prodotti di addizione nucleofila o di sostituzione.

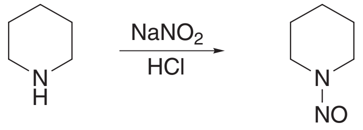
a.

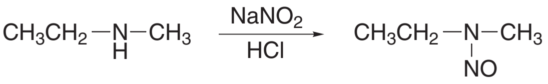

b.


c.


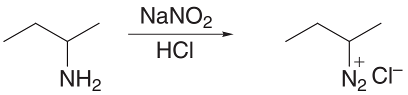
20.36

a.


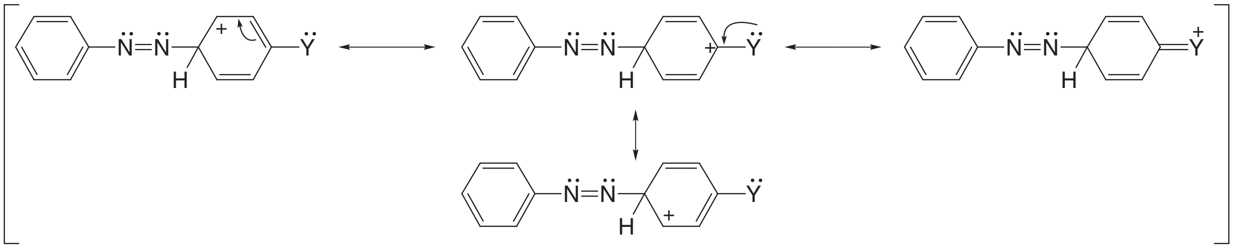
c.


b.


$$CH_3CH_2-\underset{H}{N}-CH_3 \xrightarrow[HCl]{NaNO_2} CH_3CH_2-\underset{NO}{N}-CH_3$$

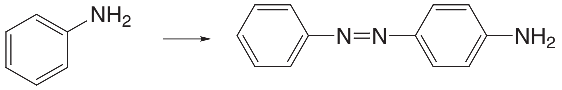
d.


20.37

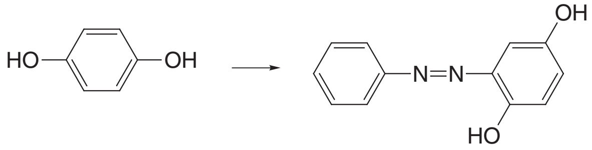


20.38

a.



c.



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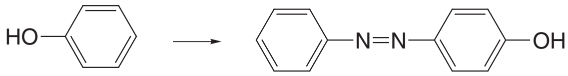
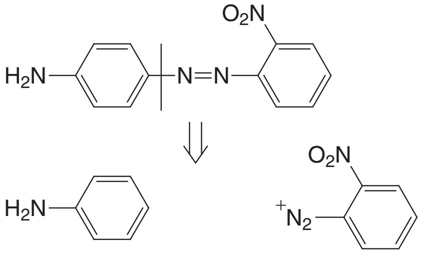
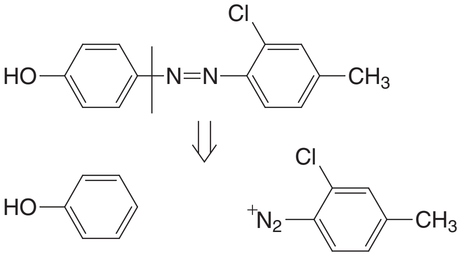


20.39 Per determinare quali reagenti sono necessari per sintetizzare un particolare azo composto, dividere sempre la molecola in due componenti: **uno ha un anello benzenico con lo ione diazonio, e l'altro ha un anello benzenico con un gruppo fortemente elettron donatore.**

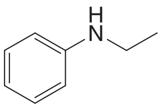
a.



b.

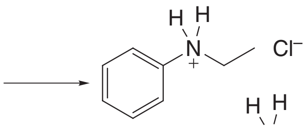


20.40

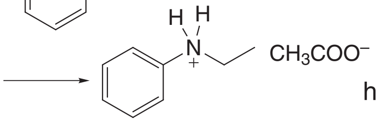


N-ethylaniline

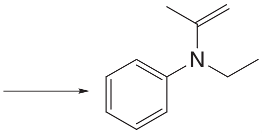
a. HCl



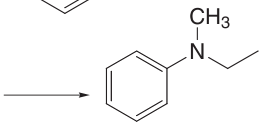
b. CH_3COOH



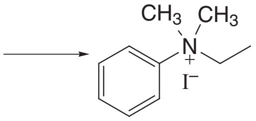
c. $(CH_3)_2C{=}O$



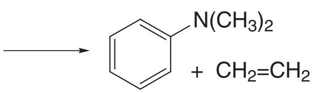
d. $CH_2O/NaBH_3CN$



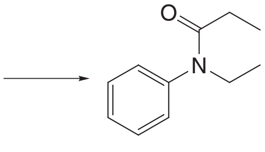
e. CH_3I (excess)



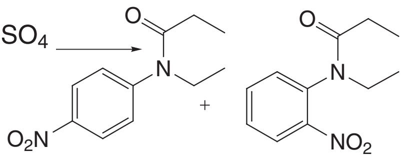
f. CH_3I (excess), followed by Ag_2O and Δ



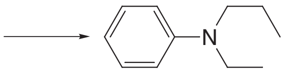
g. CH_3CH_2COCl



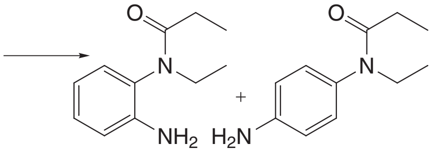
h. The product in (g), then HNO_3/H_2SO_4



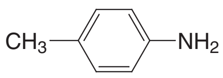
i. The product in (g), then [1] $LiAlH_4$; [2] H_2O



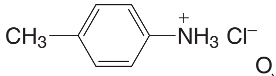
j. The product in (h), then H_2/Pd



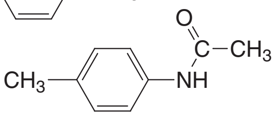
20.41


p-methylaniline

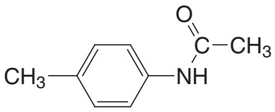
a. HCl $\longrightarrow$



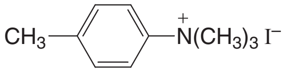
b. CH_3COCl $\longrightarrow$



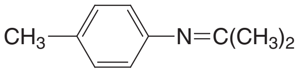
c. $(CH_3CO)_2O$ $\longrightarrow$



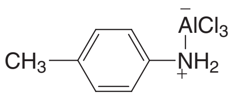
d. excess CH_3I $\longrightarrow$



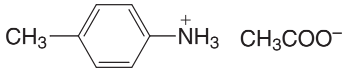
e. $(CH_3)_2C=O$ $\longrightarrow$



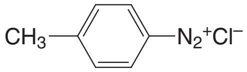
f. $CH_3COCl/AlCl_3$ $\longrightarrow$



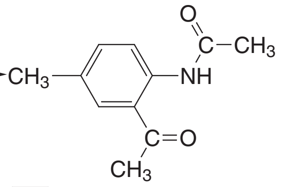
g. CH_3COOH $\longrightarrow$



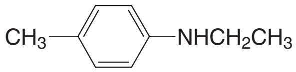
h. $NaNO_2/HCl$ $\longrightarrow$



i. step (b), then $CH_3COCl/AlCl_3$ $\longrightarrow$



j. $CH_3CHO/NaBH_3CN$ $\longrightarrow$



20.42

a. $CH_3CH_2CH_2CH_2NH_2 \xrightarrow{ClCOC_6H_5} CH_3CH_2CH_2CH_2NHCOC_6H_5$

b. $CH_3CH_2CH_2CH_2NH_2 \xrightarrow{O=C(CH_2CH_3)_2} CH_3CH_2CH_2CH_2N=C(CH_2CH_3)_2$

c. $CH_3CH_2CH_2CH_2NH_2 \xrightarrow[\substack{\text{[2] } Ag_2O \\ \text{[3] } \Delta}]{\text{[1] } CH_3I \text{ (excess)}} CH_3CH_2CH=CH_2$

d. $CH_3CH_2CH_2CH_2NH_2 \xrightarrow{C_6H_5CH_2Br} CH_3CH_2CH_2CH_2NHCH_2C_6H_5$

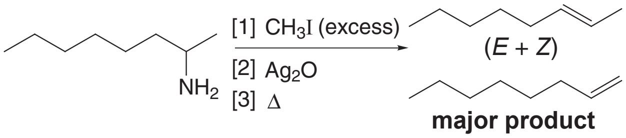
e. $CH_3CH_2CH_2CH_2NH_2 \xrightarrow{CH_3CH_2Br} CH_3CH_2CH_2CH_2NHCH_2CH_3$

f. $CH_3CH_2CH_2CH_2NH_2 \xrightarrow[\text{excess}]{CH_3I} [CH_3CH_2CH_2CH_2N(CH_3)_3]^+I^-$

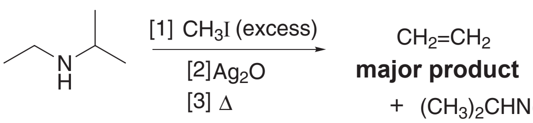
20.43

a. $CH_3(CH_2)_6NH_2 \xrightarrow[\text{[2] } Ag_2O \text{ [3] } \Delta]{\text{[1] } CH_3I \text{ (excess)}} CH_3(CH_2)_4CH{=}CH_2$

b.



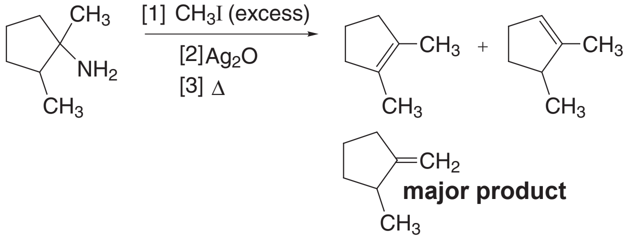
c.



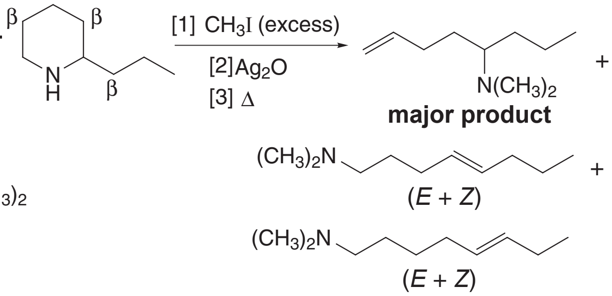
$+ \ (CH_3)_2CHN(CH_3)_2$

$CH_2{=}CHCH_3 \ + \ CH_3CH_2N(CH_3)_2$

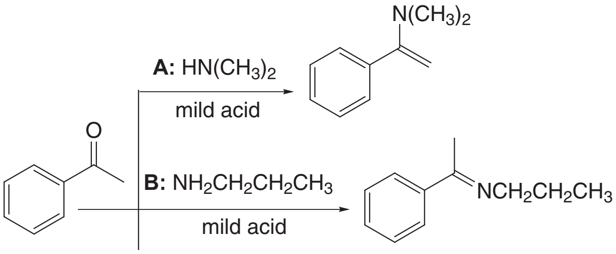
d.

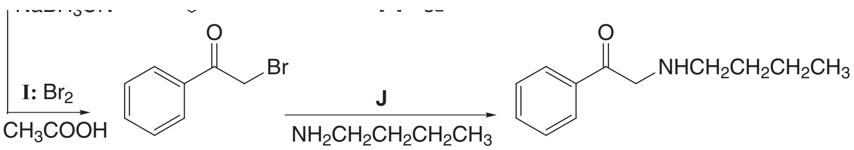


e.

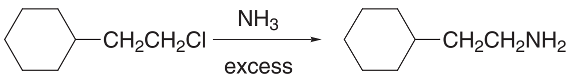


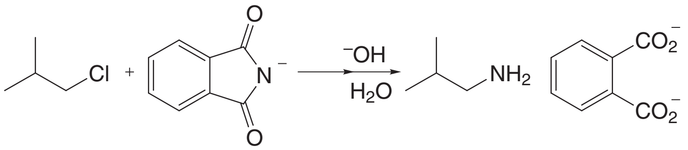
20.44

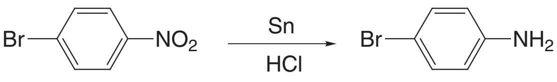


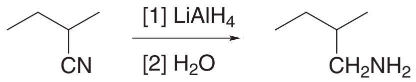


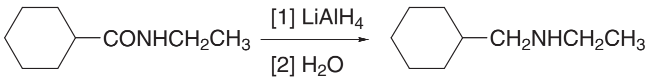
20.45

a.


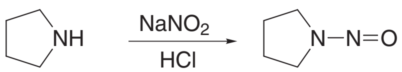
b.


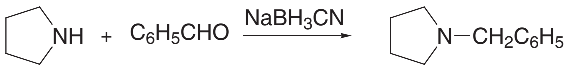
c.


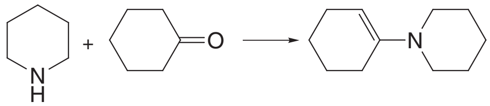
d.


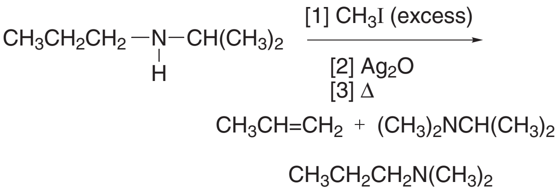
e.


f. $C_6H_5CH_2CH_2NH_2 + (C_6H_5CO)_2O \longrightarrow C_6H_5CH_2CH_2NHCOC_6H_5$

g.


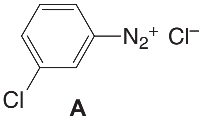
h.


i.


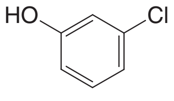
j.

$CH_3CH_2CH_2-\underset{H}{\underset{|}{N}}-CH(CH_3)_2 \xrightarrow[\text{[2] }Ag_2O \text{ [3] }\Delta]{\text{[1] }CH_3I\text{ (excess)}} CH_3CH{=}CH_2 + (CH_3)_2NCH(CH_3)_2$

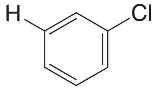
$CH_3CH_2CH_2N(CH_3)_2$

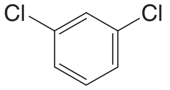
20.46

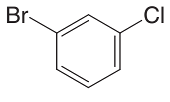


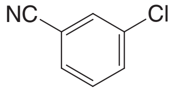
A

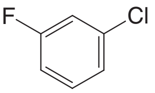
a. H_2O


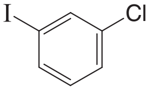
b. H_3PO_2


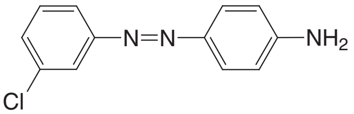
c. CuCl


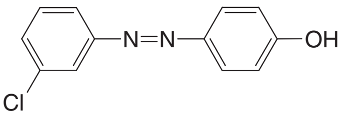
d. CuBr


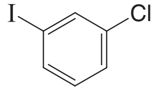
e. CuCN


f. HBF_4


g. NaI


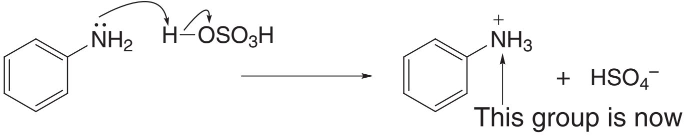
h. $C_6H_5NH_2$


i. C_6H_5OH


j. KI


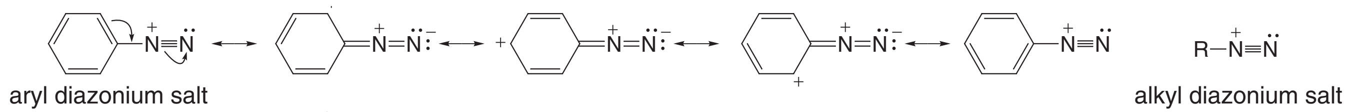
20.47

Under the acidic conditions of the reaction, aniline is first protonated to form an ammonium salt that has a positive charge on the atom bonded to the benzene ring. The $-NH_3^+$ is now an electron withdrawing meta director, so significant amounts of meta substitution occurs.



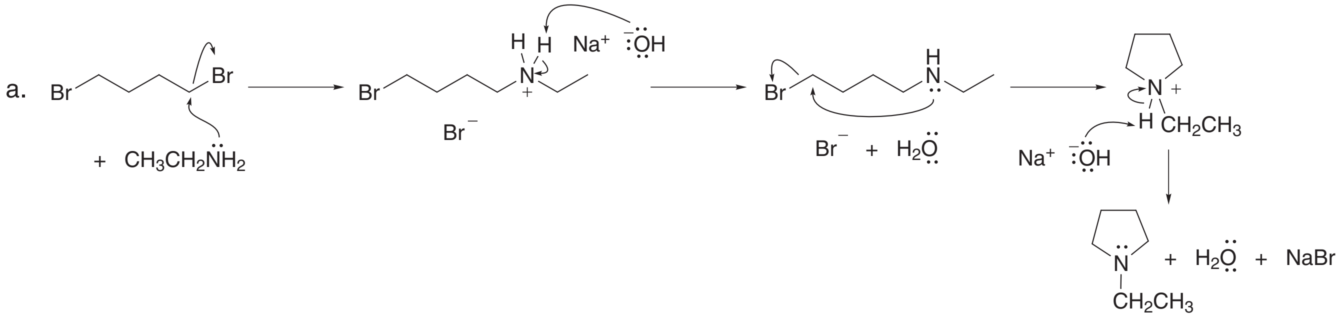
This group is now a *meta* director.

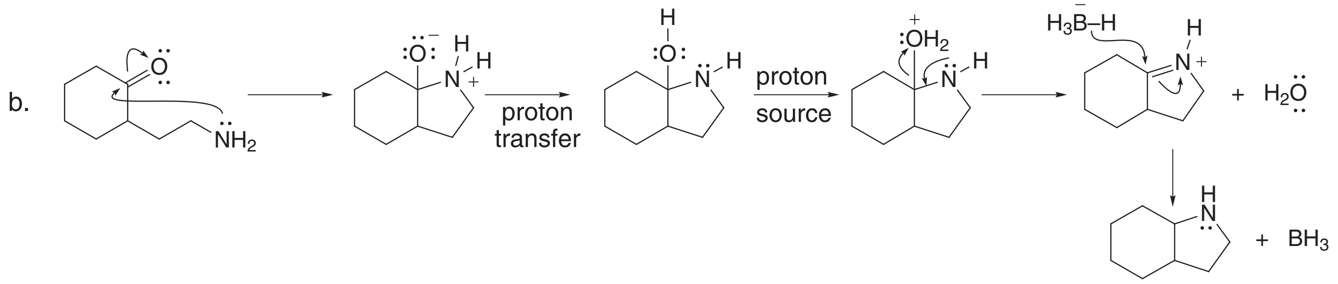
20.48



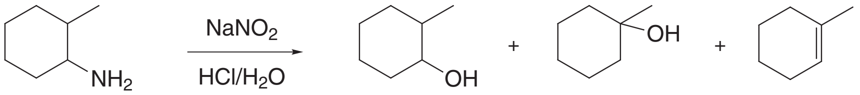
The N_2^+ group on an aromatic ring is stabilized by resonance, whereas the alkyl diazonium salt is not.

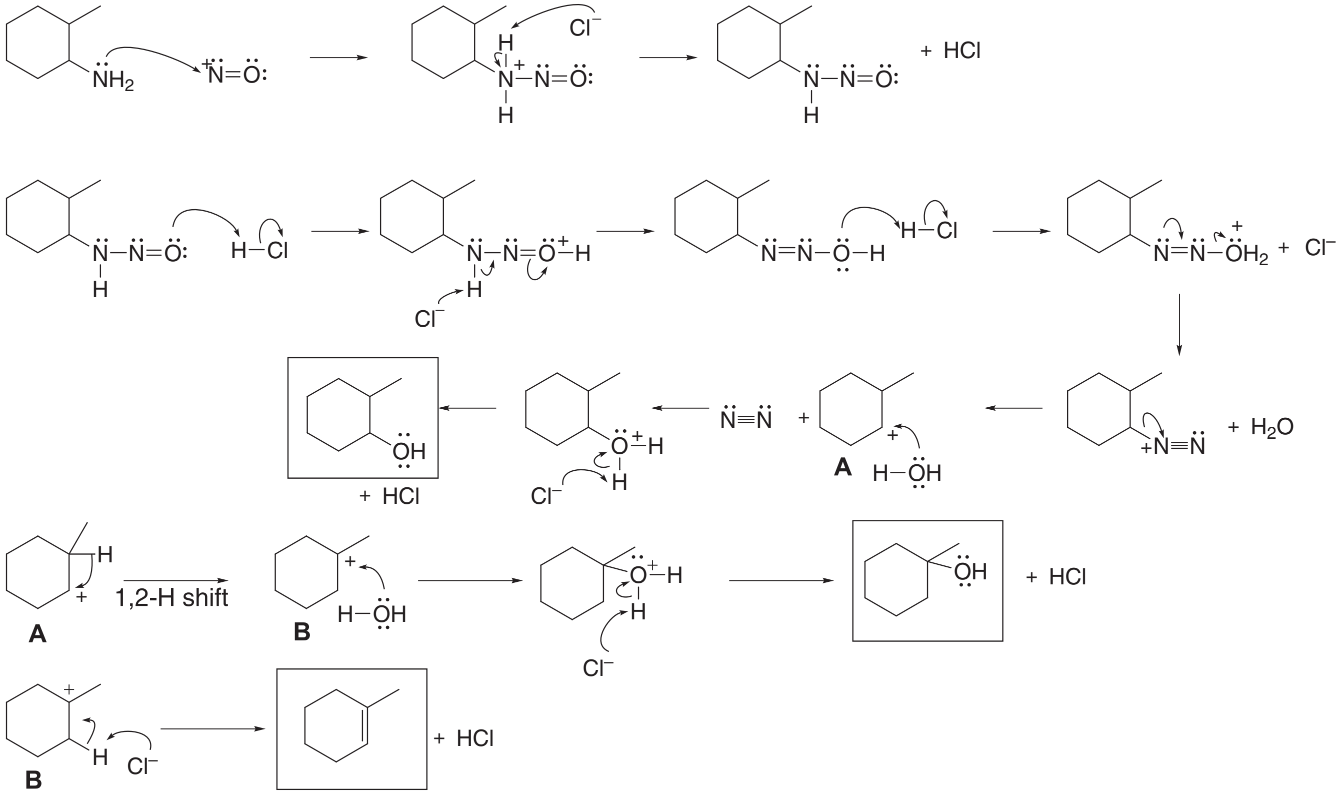
20.49





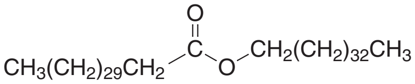
20.50


NH2
NaNO2
HCl/H2O
OH
+
OH
+


NH2
N=O
Cl−
H
+ HCl
H–Cl
Cl−
A
H–OH
+ H2O
N≡N
+ HCl
1,2-H shift
B
+ HCl
B
Cl−
+ HCl

Capitolo 21

21.1 Le cere sono esteri (RCOOR′) formati da alcol ad alto peso molecolare (R′OH) ed acidi grassi (RCOOH).

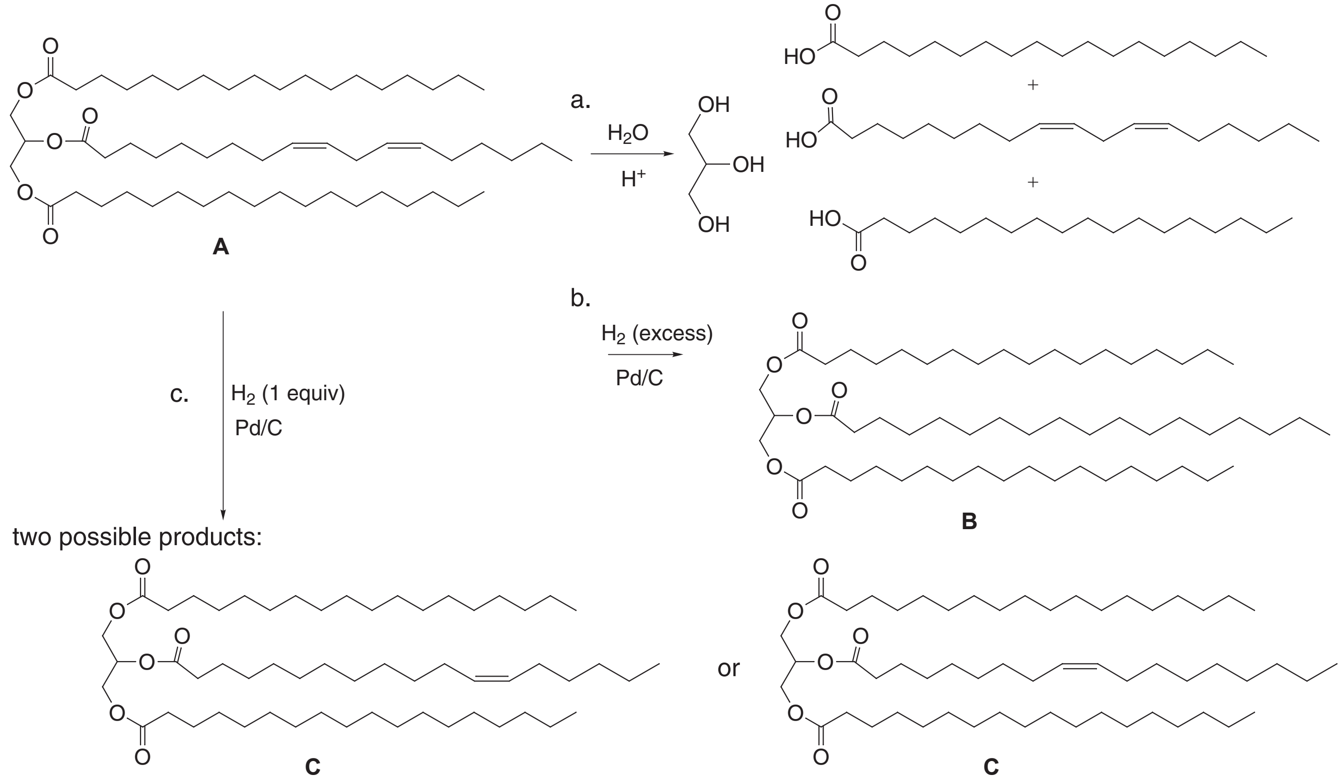


$CH_3(CH_2)_{29}CH_2C(=O)OCH_2(CH_2)_{32}CH_3$

carnauba wax component

21.2 L'acido eicosapentenoico ha 20 carboni e 5 doppi legami C=C. Poiché all'aumentare del numero dei doppi legami diminuisce il punto di fusione, l'acido eicosapentenoico dovrebbe avere un punto di fusione più basso dell'acido arachidonico, cioè < –49°C.

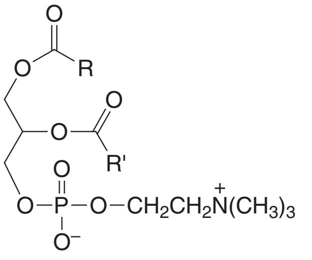
21.3



21.4

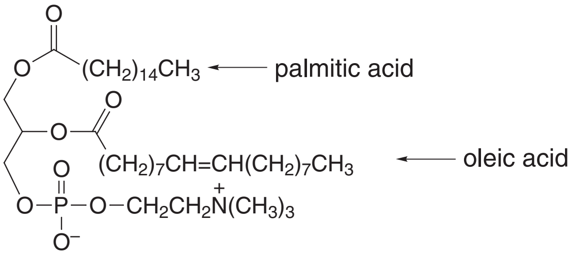
A	<	**C**	<	**B**
2 double bonds		1 double bond		0 double bonds
lowest melting point		**intermediate melting point**		**highest melting point**

21.5 Una lecitina è un tipo di fosfoacilglicerolo. Due dei gruppi ossidrilici del glicerolo sono esterificati con acidi grassi. Il terzo gruppo OH è parte di un fosfodiestere, che è ulteriormente legato ad un altro alcol a basso peso molecolare.

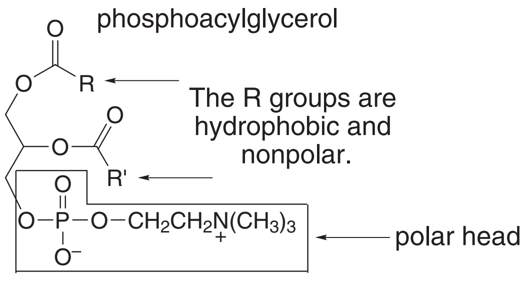


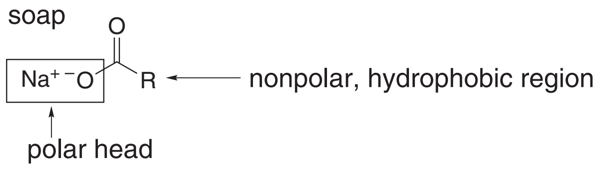
general structure of a lecithin

one possibility:



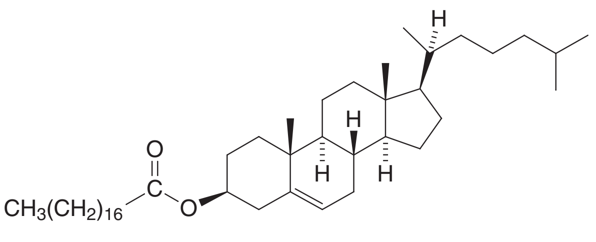
21.6 I saponi ed i fosfoacilgliceroli hanno componenti idrofile ed idrofobe. Entrambi i composti hanno una "testa" ionica che è attratta da solventi polari come l' H_2O. Questa testa è di piccole dimensioni in confronto con la regione idrofoba, che consiste di una o due lunghe catene idrocarburiche. Queste catene non polari consistono solamente di legami C–C e C–H ed esibiscono solo forze di van der Waals.



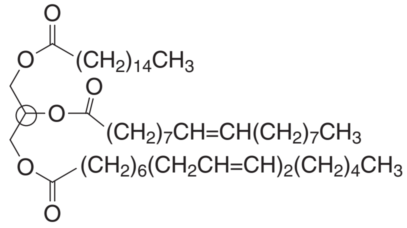
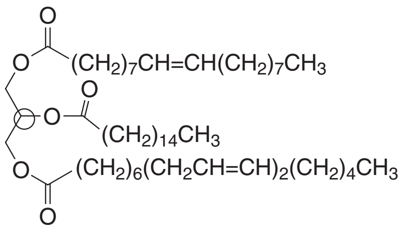
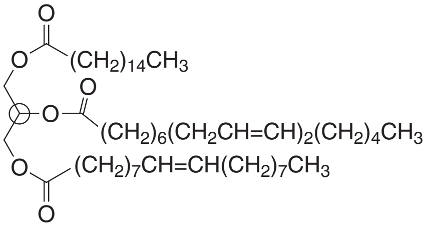


21.7 Le vitamine liposolubili sono idrofobe e perciò sono facilmente immagazzinate nei tessuti adiposi del corpo. Le vitamine idrosolubili, d'altra parte, sono facilmente espulse con le urine e conseguentemente non possono esserne accumulate grandi quantità nel corpo.

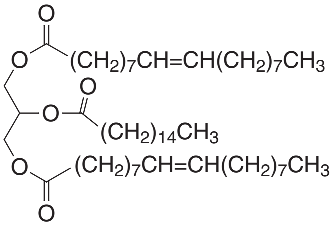
21.8



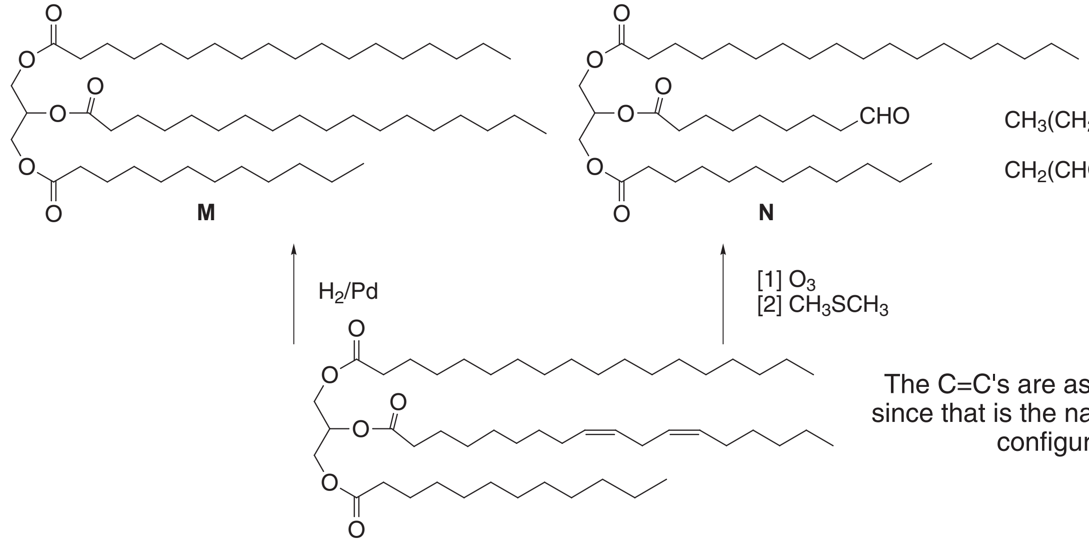
21.9 Ogni composto ha un centro stereogenico tetraedrico, conseguentemente ci sono due stereoisomeri possibili (due enantiomeri).

21.10



21.11



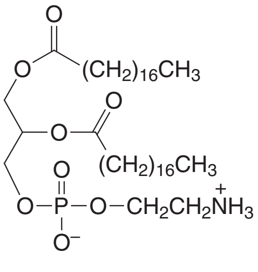
M **N** **L**

$CH_3(CH_2)_4CHO$ = **O**

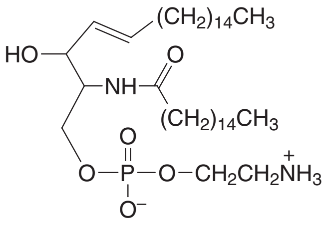
$CH_2(CHO)_2$ = **P**

The C=C's are assumed to be *Z*, since that is the naturally occurring configuration.

21.12 Quando R″ = $CH_2CH_2NH_3^+$, il composto è detto **fosfatidiletanolammina** o **cefalina.**

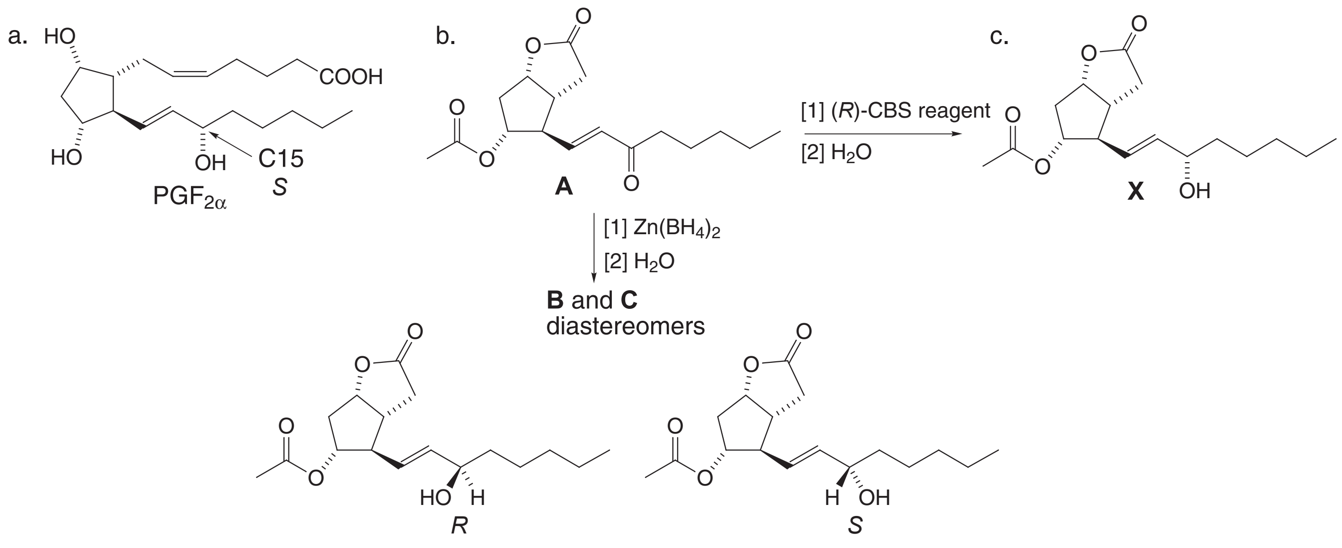


cephalin



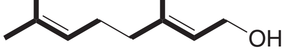
sphingomyelin

21.13



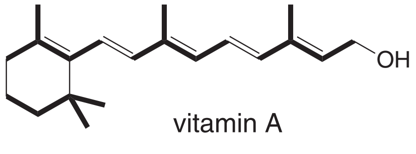
21.14

a.



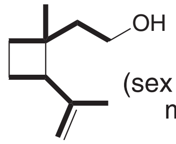
geraniol
(roses and geraniums)

b.



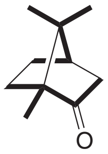
vitamin A

c.



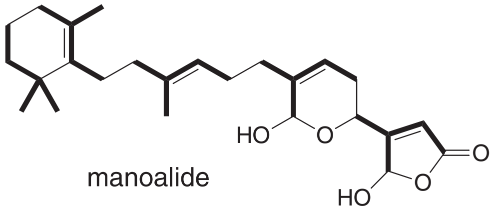
grandisol
(sex phoromone of the
male boll weevil)

d.



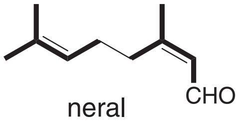
camphor

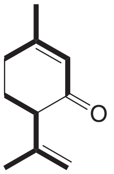
21.15

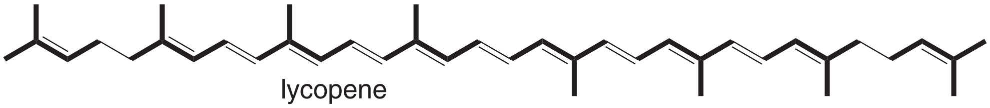


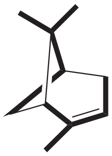
manoalide

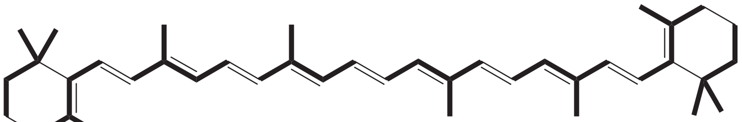
21.16

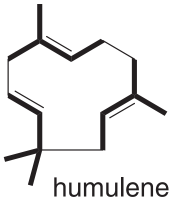
a.

neral

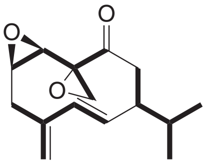
b.

carvone

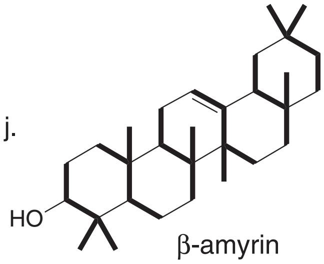
d.

lycopene

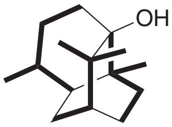
c.

α-pinene

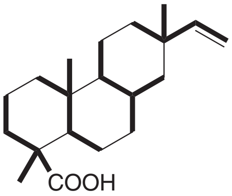
e.

β-carotene

f.

humulene

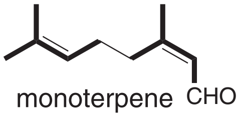
h.

periplanone B

j.

β-amyrin

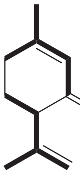
g.

patchouli alcohol

i.

dextropimaric acid

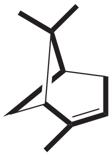
21.17 Un ***monoterpene*** **contiene 10 carboni** e due unità isopreniche; un ***sesquiterpene*** **contiene 15 carboni** e tre unità isopreniche, etc. Vedi la tabella 26.5.

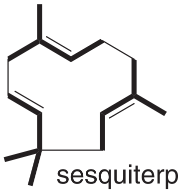
a.


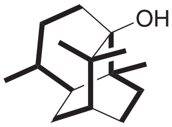
monoterpene

b.


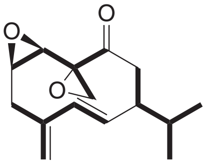
monoterpene

c.

monoterpene

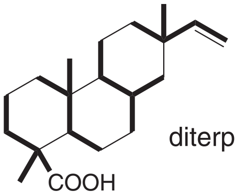
f.

sesquiterpene

g.


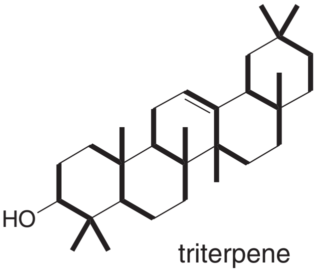
sesquiterpene

h.


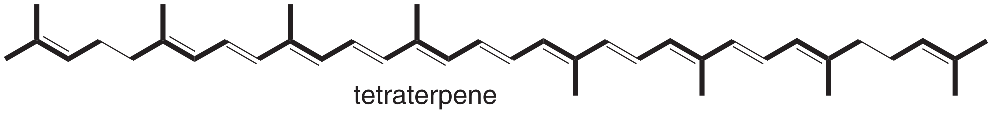
sesquiterpene

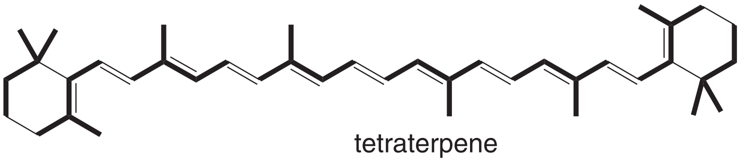
i.


diterpene

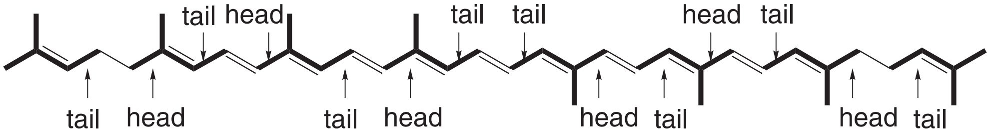
j.


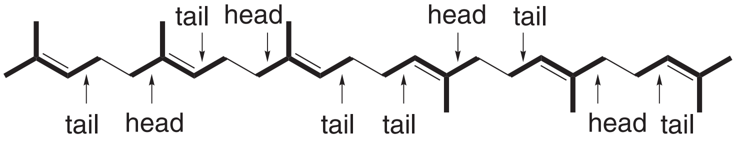
triterpene

d.

tetraterpene

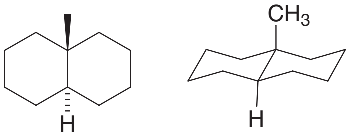
e.

tetraterpene

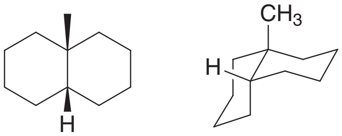
21.18

lycopene


squalene


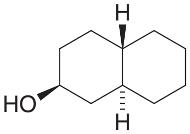
21.19

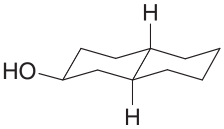
a.


b.


21.20

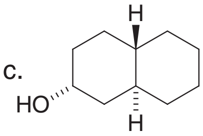
a.

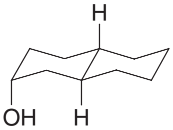




equatorial OH

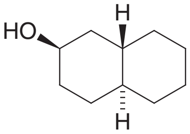
c.

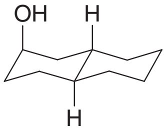




axial OH

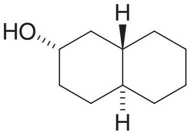
b.

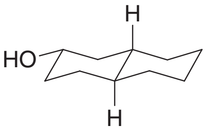




axial OH

d.



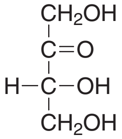


equatorial OH

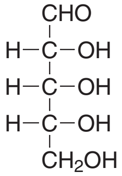
Capitolo 22

22.1 Un *chetoso* è un monosaccaride che contiene un chetone. Un *aldoso* è un monosaccaride che contiene un'aldeide. Un monosaccaride viene chiamato: un *trioso* se ha tre carboni; un *tetroso* se ha quattro carboni; un *pentoso* se ha cinque carboni; un *esoso* se ha sei carboni, e così via.

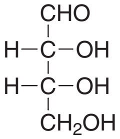
a. a ketotetrose



b. an aldopentose



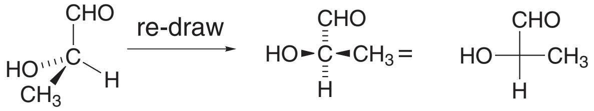
c. an aldotetrose



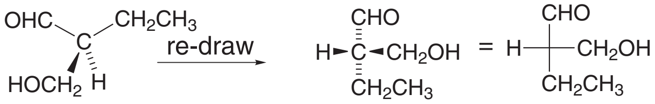
22.2 Ruotare e ridisegnare ogni molecola per posizionare i legami orizzontali davanti al piano e quelli verticali dietro al piano. Successivamente usare una croce per rappresentare il centro stereogenico nella formula di proiezione di Fischer.

a.

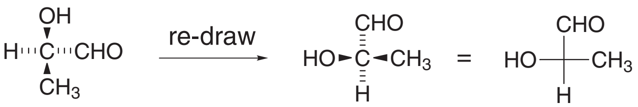
b.



c.



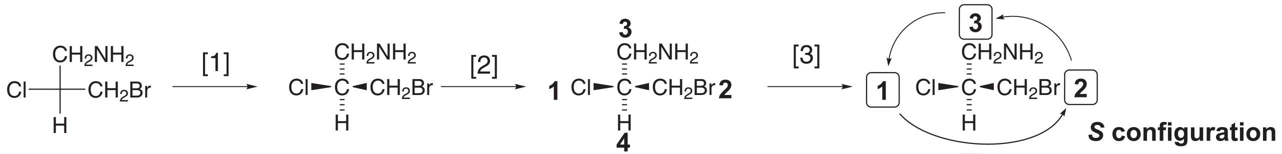
d.



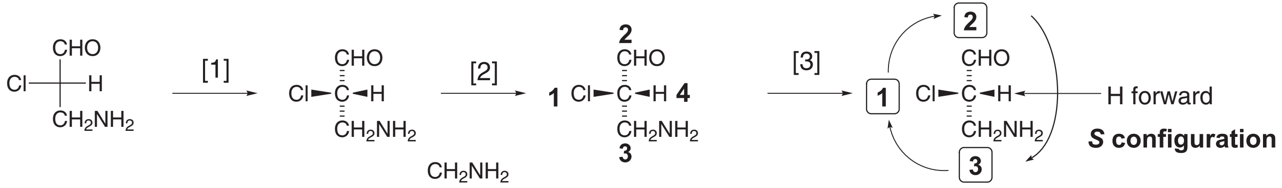
22.3 Per ogni molecola:

[1] Convertire la formula di proiezione di Fischer in una rappresentazione con cunei e tratteggi.
[2] Assegnare le priorità (Sezione 5.6).
[3] Determinare *R* o *S* nella solita maniera. Rovesciare la risposta se il gruppo con priorità [4] è orientato verso l'osservatore (su un cuneo).

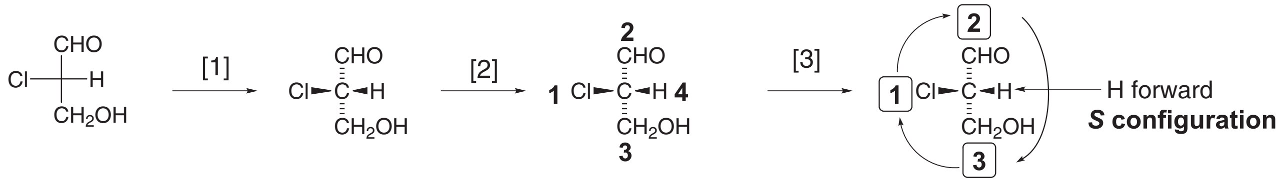
a.



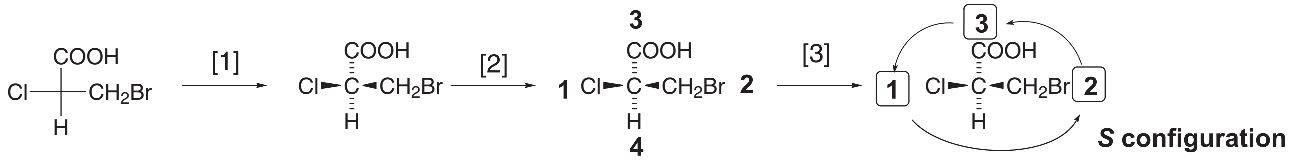
b.



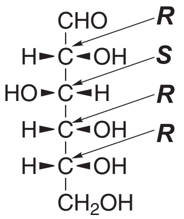
c.



d.

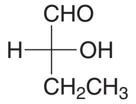


22.4



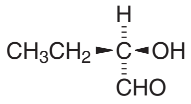
D-glucose

22.5 Indicare i composti con *R* o *S* e quindi classificare.



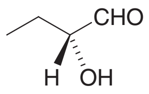
A
R

a.



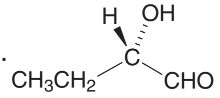
R
identical

b.



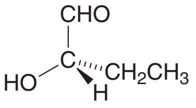
R
identical

c.



S
enantiomer

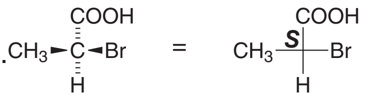
d.



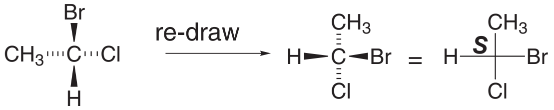
S
enantiomer

22.6 Usare i suggerimenti della risposta 25.2 per disegnare ogni proiezione di Fischer.

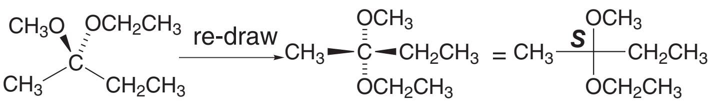
a.



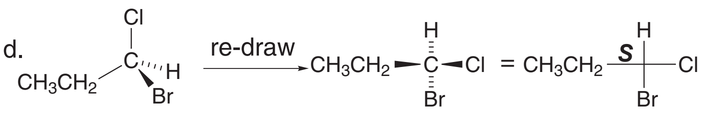
b.



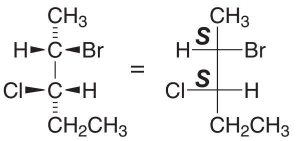
c.



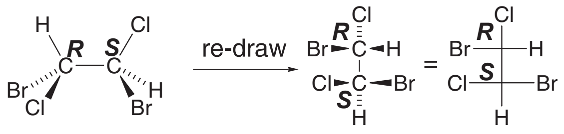
d.



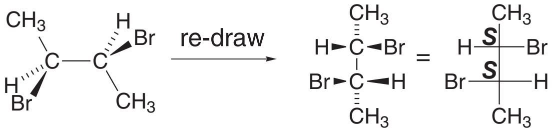
e.



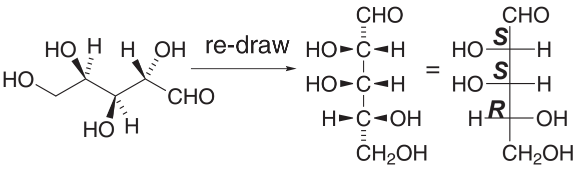
f.



g.

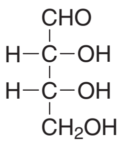


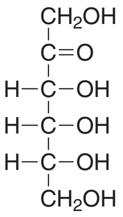
h.



22.7

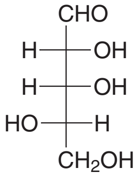
a. aldotetrose: 2 stereogenic centers b. a ketohexose: 3 stereogenic centers





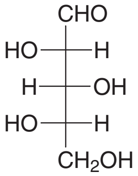
22.8 A Uno zucchero D ha il gruppo OH sul centro stereogenico più lontano dal carbonile sulla destra. Uno zucchero L ha il gruppo OH sul centro stereogenico più lontano dal carbonile sulla sinistra.

a.



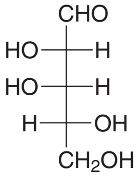
A

OH group on the left: **L sugar**.



B

OH group on the left: **L sugar**.

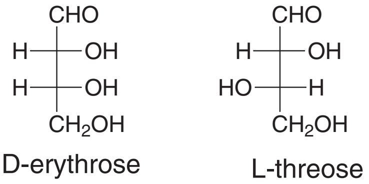


C

OH group on the right: **D sugar**.

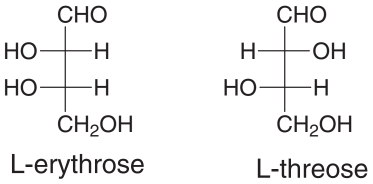
b. A and B are diastereomers.
A and C are enantiomers.
B and C are diastereomers.

22.9



D-erythrose L-threose

diastereomers



L-erythrose L-threose

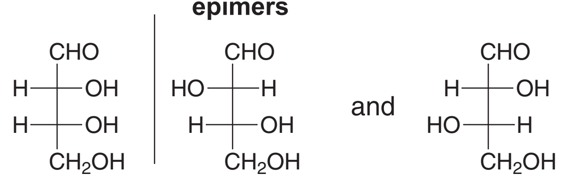
diastereomers

22.10 La notazione D- indica la posizione del gruppo OH sul centro stereogenico più lontano dal carbonile, e non ha nessuna relazione con il fatto che lo zucchero sia destrorotatorio o levorotatorio. Questi termini descrivono un fenomeno fisico, la direzione della rotazione del piano della luce polarizzata.

22.11 Esistono 32 aldoeptosi; 16 sono zuccheri D.

22.12 Gli *epimeri* sono due diastereomeri che differiscono nella configurazione di un solo centro stereogenico.

epimers

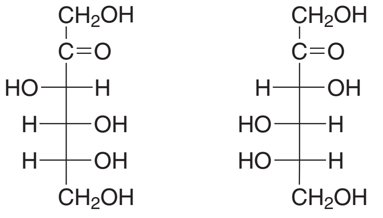


D-erythrose

22.13 a. D-allosio e L-allosio: **enantiomeri**
b. D-altrosio e D-gulosio: **diastereomeri** ma non epimeri
c. D-galattosio e D-talosio: **epimeri**
d. D-mannosio e D-fruttosio: **isomeri costituzionali**
e. D-fruttosio e D-sorbosio: **diastereomeri** ma non epimeri
f. L-sorbosio e L-tagatosio: **epimeri**

22.14

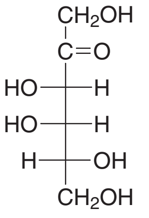
a.



D-fructose L-fructose

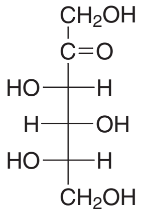
enantiomers

b.



D-tagatose

c.



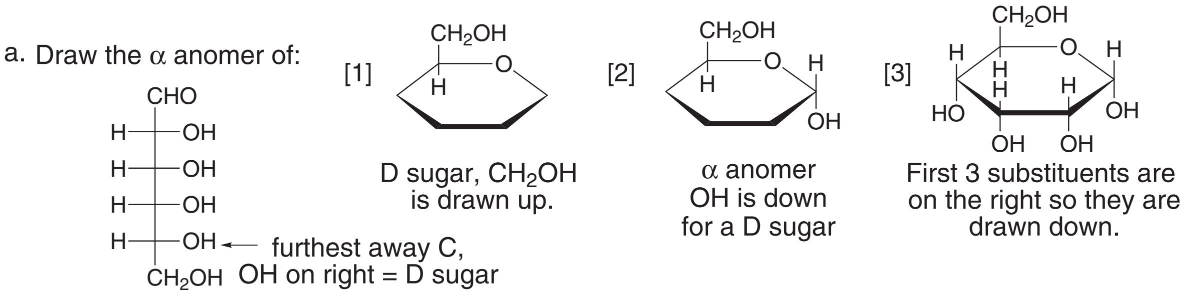
L-sorbose

22.15 Stadio [1]: Mettere l'atomo di O nell'angolo in alto a destra di un esagono, ed aggiungere il gruppo CH_2OH sul primo carbonio ruotando in senso antiorario a partire dall'atomo di O.

Stadio [2]: Metter il carbonio anomerico sul primo carbonio ruotando in senso orario a partire dall’atomo di O.

Stadio [3]: Aggiungere i sostituenti ai rimanenti tre centri stereogenici, in senso orario attorno all’anello.

a. Draw the α anomer of:



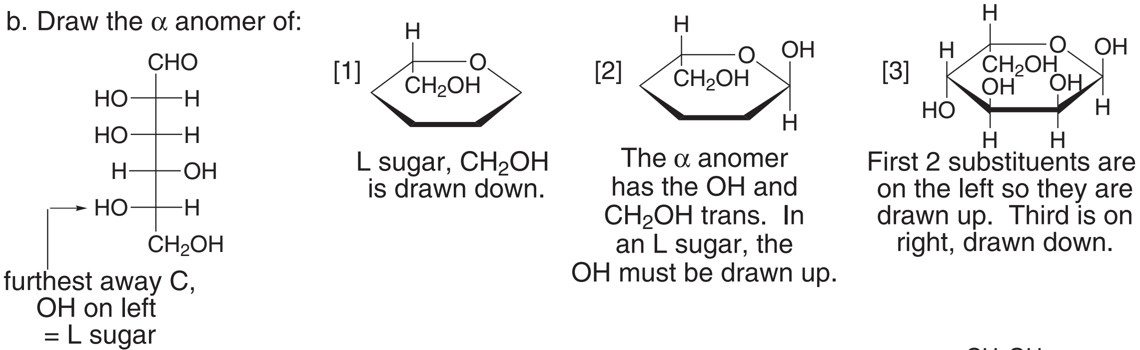
furthest away C, OH on right = D sugar

[1] D sugar, CH_2OH is drawn up.

[2] α anomer OH is down for a D sugar

[3] First 3 substituents are on the right so they are drawn down.

b. Draw the α anomer of:



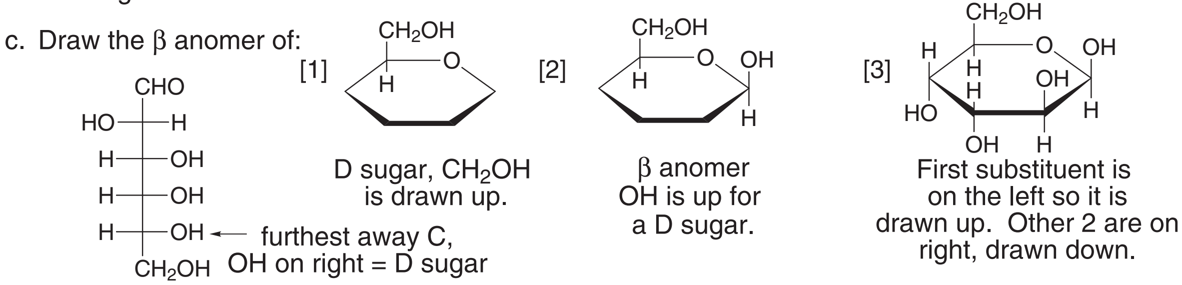
furthest away C, OH on left = L sugar

[1] L sugar, CH_2OH is drawn down.

[2] The α anomer has the OH and CH_2OH trans. In an L sugar, the OH must be drawn up.

[3] First 2 substituents are on the left so they are drawn up. Third is on right, drawn down.

c. Draw the β anomer of:



furthest away C, OH on right = D sugar

[1] D sugar, CH_2OH is drawn up.

[2] β anomer OH is up for a D sugar.

[3] First substituent is on the left so it is drawn up. Other 2 are on right, drawn down.

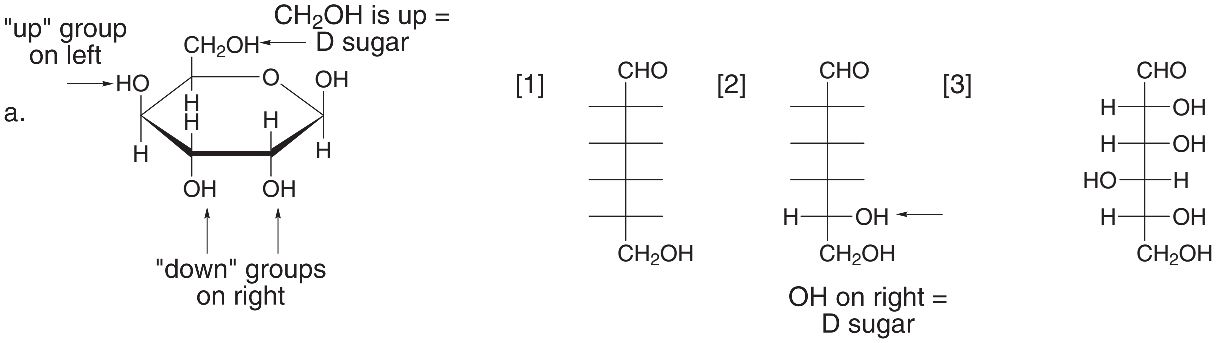
22.16 Per convertire ogni proiezione di Haworth nella sua forma aciclica:

[1] Disegnare lo scheletro carbonioso con il CHO in alto ed il CH_2OH in basso.

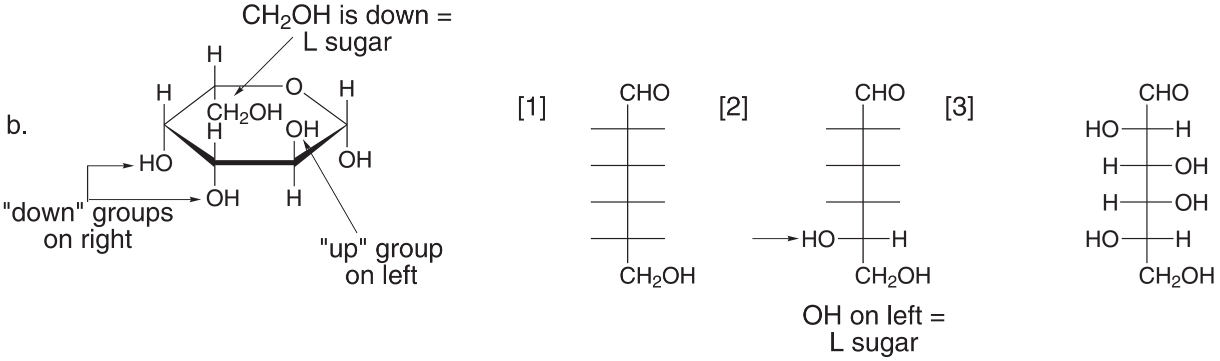
[2] Disegnare il gruppo OH più lontano dal C=O.
Un gruppo CH_2OH disegnato in alto individua uno zucchero D; un gruppo CH_2OH disegnato in basso individua uno zucchero L.

[3] Aggiungere gli altri tre centri stereogenici, in senso antiorario attorno all’anello.
I gruppi “in alto” vanno a sinistra e i gruppi “in basso” vanno sulla destra.

a.



b.

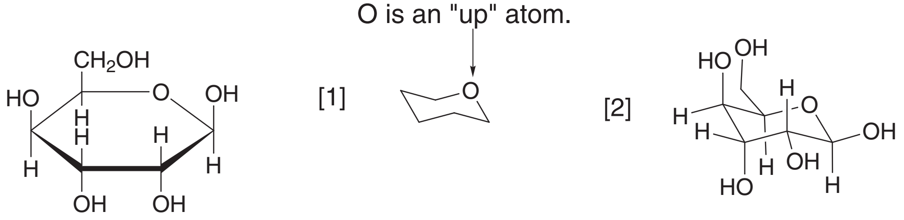


22.17 Per convertire una proiezione di Haworth in una rappresentazione 3-D come cicloesano a sedia:

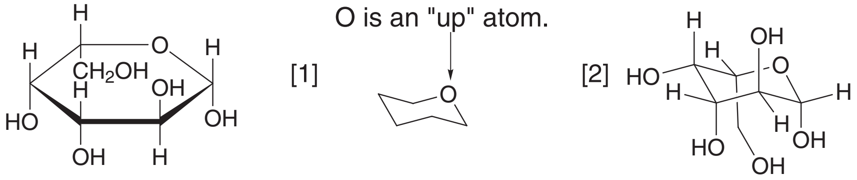
[1] Disegnare l'anello piranosico come sedia con l' O come atomo "in alto".

[2] Aggiungere i sostituenti attorno all'anello.

a.

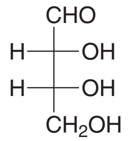


b.



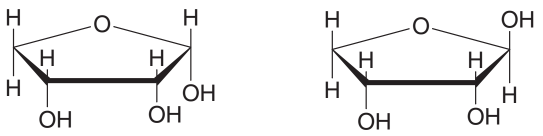
With so many axial groups, this is not the more stable conformer of this sugar.

22.18 La ciclizzazione produce sempre un nuovo centro stereogenico al carbonio anomerico, così sono possibili due diversi anomeri.

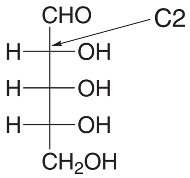


D-erythrose

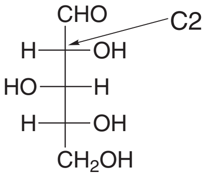
Two anomers of D-erythrose:



22.19



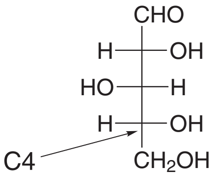
D-ribose



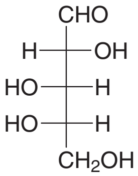
D-xylose

***R* at C2.**

22.20 Gli *epimeri* sono due diastereomeri che differiscono nella configurazione di un solo centro stereogenico.



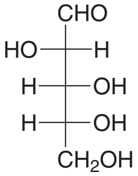
D-xylose



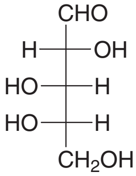
L-arabinose

22.21

a.

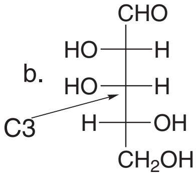


D-arabinose



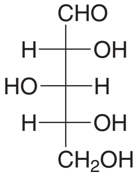
enantiomer

b.



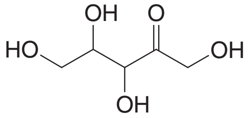
epimer

c.



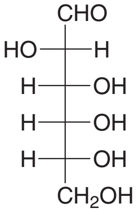
diastereomer
(but not epimer)

d.

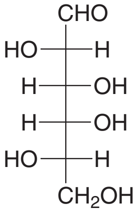


constitutional isomer

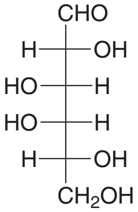
22.22



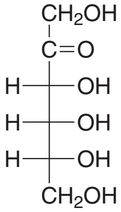
A



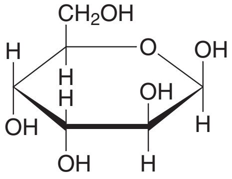
B



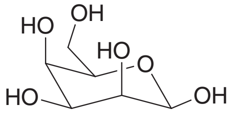
C



D



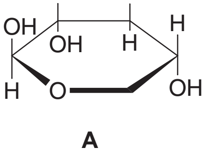
E



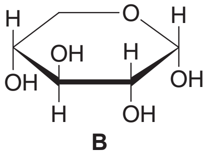
F

a. **A** and **B** **epimers**
b. **A** and **C** **diastereomers**
c. **B** and **C** **enantiomers**
d. **A** and **D** **constitutional isomers**
e**.** **E** and **F** **diastereomers**

22.23

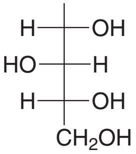


A



B

a. anomers, epimers, diastereomers, reducing sugars
b.

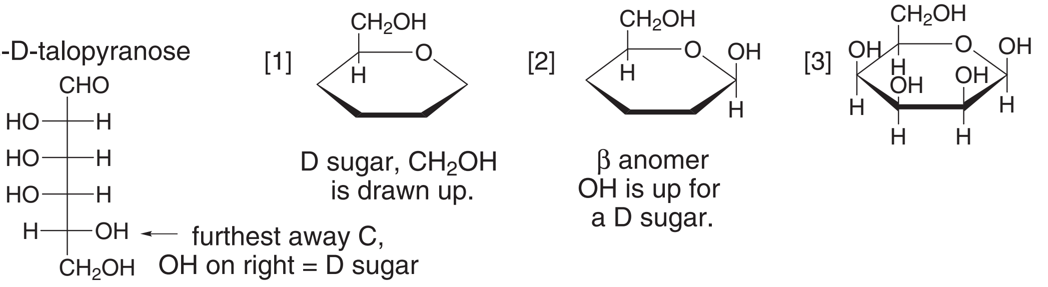


D-xylose

This is the acyclic form of both **A** and **B**.

22.24 Usare i suggerimenti della risposta 25.15.

a. β-D-talopyranose



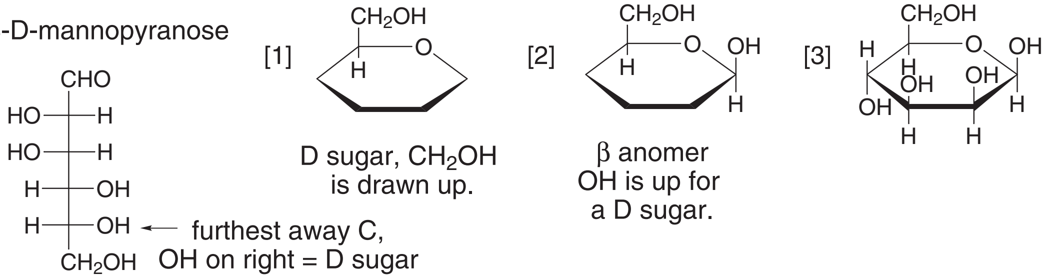
furthest away C, OH on right = D sugar

D sugar, CH_2OH is drawn up.

β anomer OH is up for a D sugar.

D-talose

b. β-D-mannopyranose



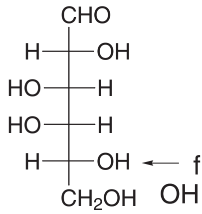
furthest away C, OH on right = D sugar

D sugar, CH_2OH is drawn up.

β anomer OH is up for a D sugar.

D-mannose

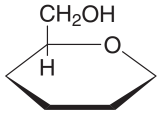
c. α-D-galactopyranose



furthest away C, OH on right = D sugar

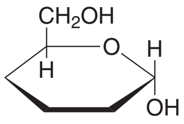
D-galactose

[1]



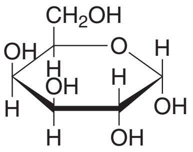
D sugar, CH_2OH is drawn up.

[2]

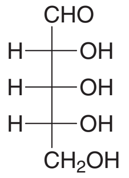


α anomer OH is down.

[3]



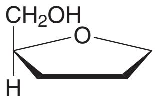
d. α-D-ribofuranose



furthest away C, OH on right = D sugar

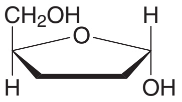
D-ribose

[1]

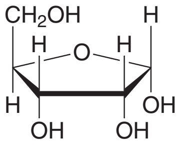


D sugar, CH_2OH is drawn up.

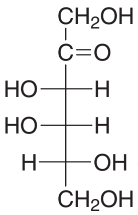
[2]



[3]



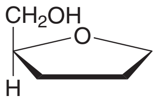
e. α-D-tagatofuranose



furthest away C, OH on right = D sugar

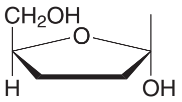
D-tagatose

[1]



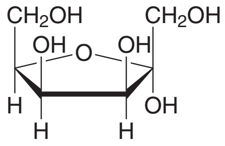
D sugar, CH_2OH is drawn up.

[2]



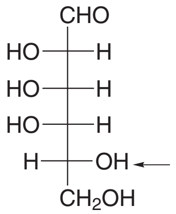
α anomer OH is down.

[3]

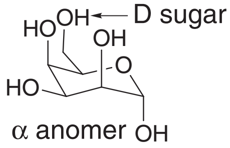


22.25

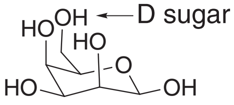
a.



furthest away C, OH on right = D sugar

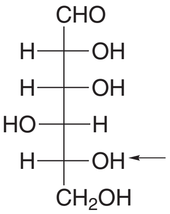


α anomer

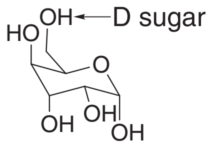


β anomer

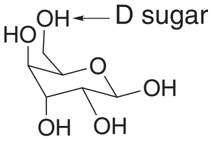
b.



furthest away C, OH on right = D sugar

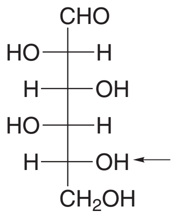


α anomer

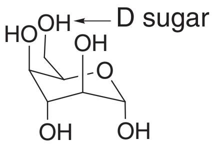


β anomer

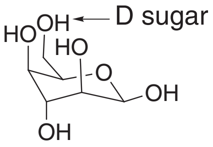
c.



furthest away C,
OH on right = D sugar



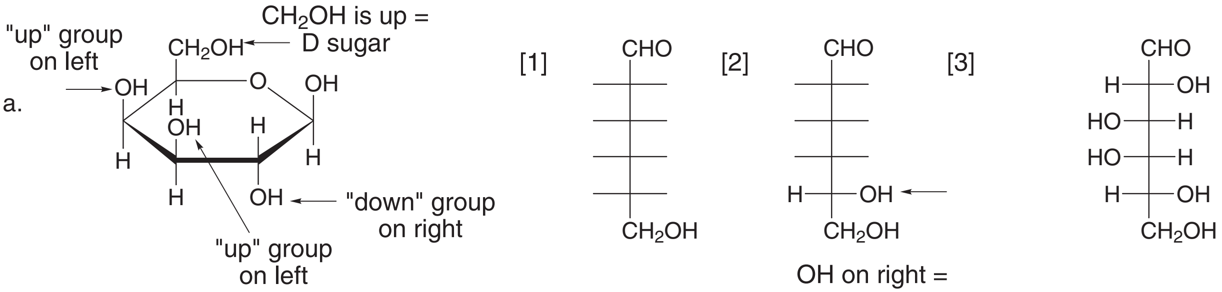
α anomer



β anomer

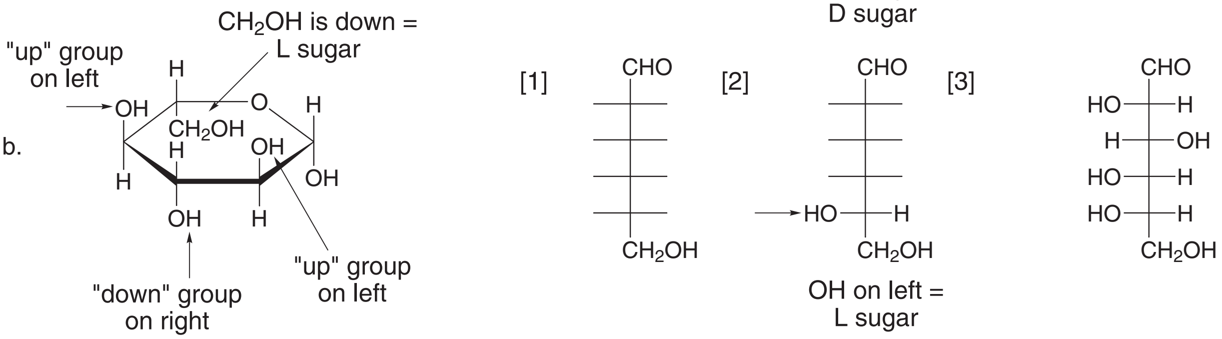
22.26 Usare i suggerimenti della risposta 25.16.

a.



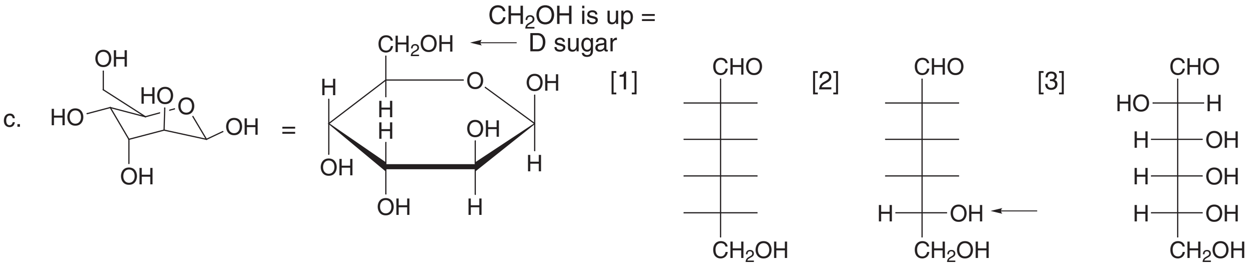
OH on right =
D sugar

b.



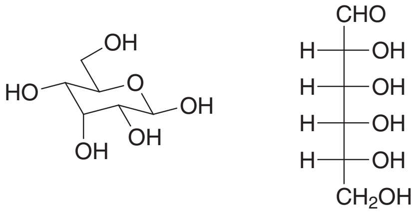
OH on left =
L sugar

c.

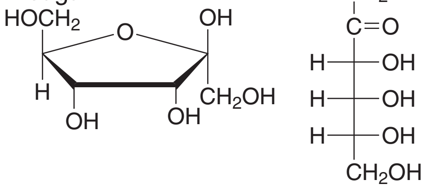


OH on right =
D sugar

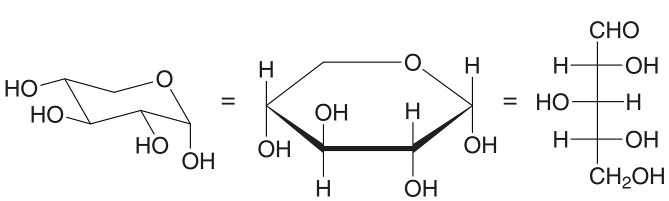
d.



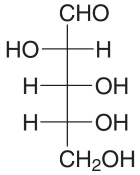
e. D sugar



f.

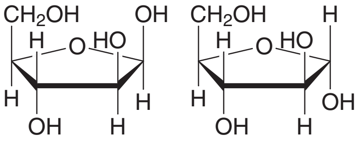


22.27



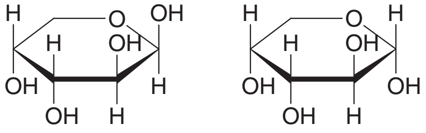
D-arabinose

a.



β anomer α anomer

b.

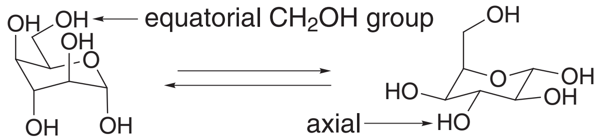


two anomers in the pyranose form

22.28

Two anomers of D-idose, as well as two conformers of each anomer:

α anomer

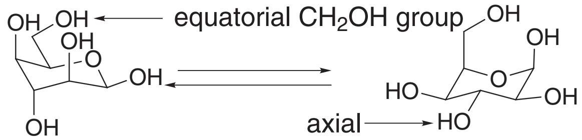


4 axial substituents

4 equatorial OH groups

More stable conformer for the α anomer—the CH_2OH is axial, but all other groups are equatorial.

β anomer



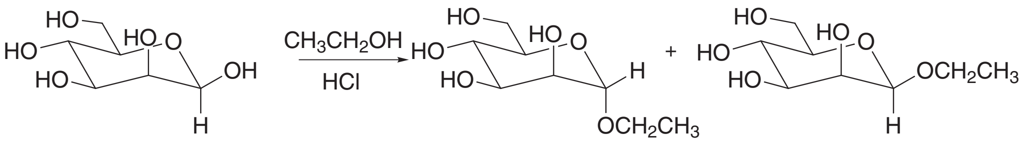
3 axial substituents

3 equatorial OH groups

The more stable conformer for the β anomer—the CH_2OH is axial, as is the anomeric OH, but three other OH groups are equatorial.

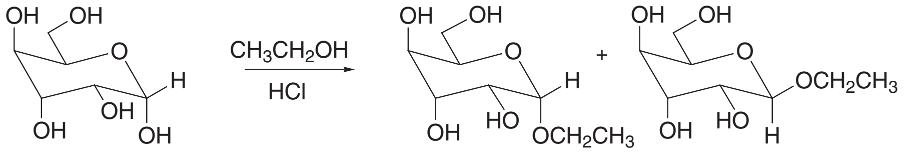
22.29

a.



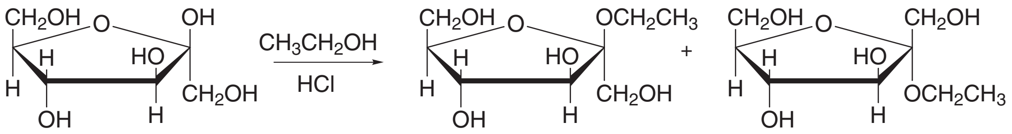
β-D-mannose

b.



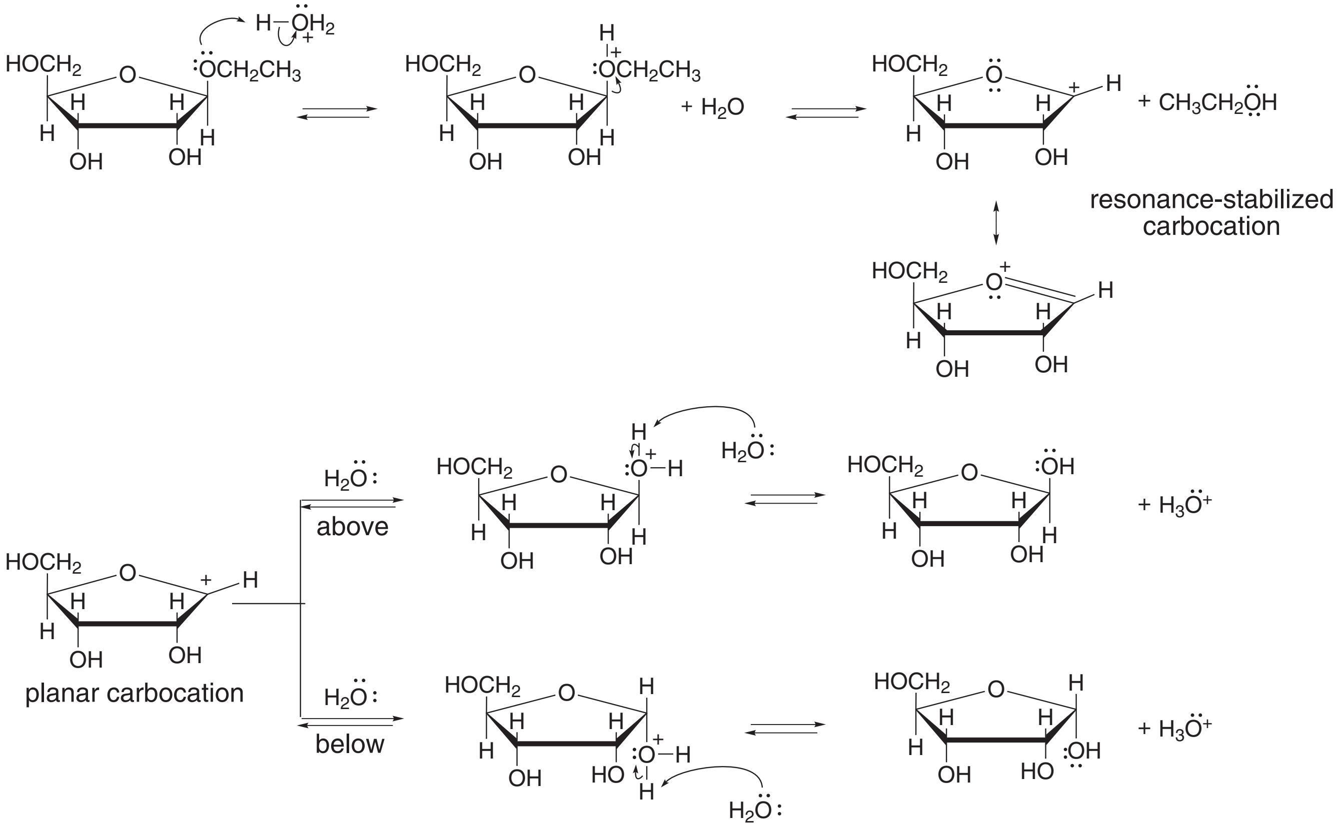
α-D-gulose

c.



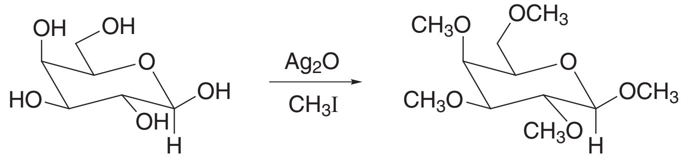
β-D-fructose

22.30

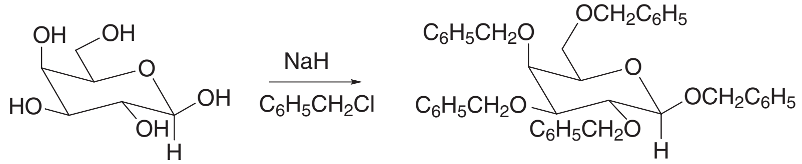


22.31

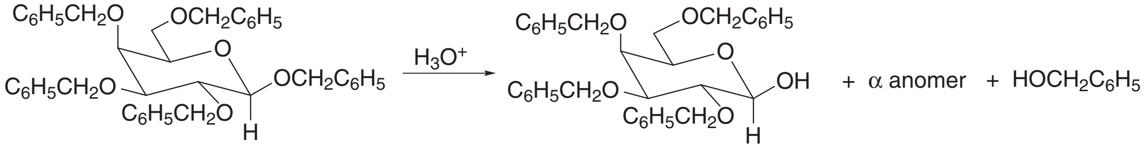
a.



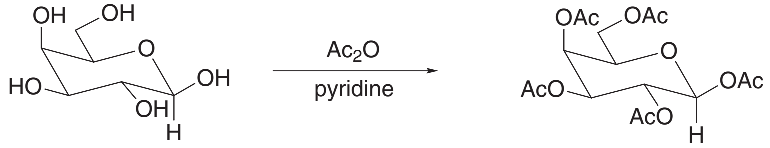
b.



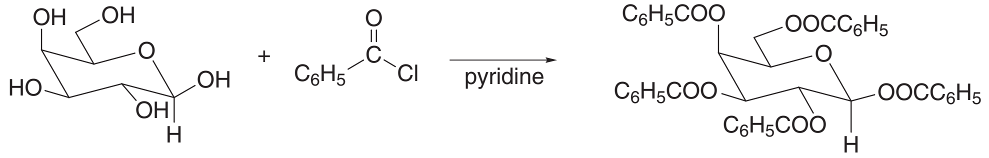
c.



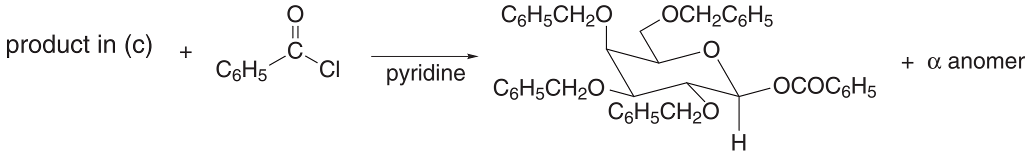
d.



e.

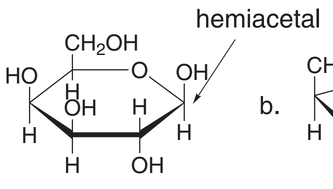


f.



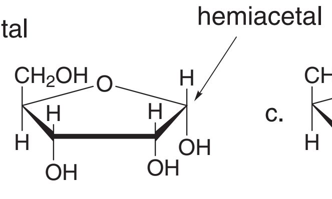
22.32 I carboidrati che contengono un emiacetale sono in equilibrio con un aldeide aciclica, e ciò li rende zuccheri riducenti. I glicosidi sono acetali, e conseguentemente non sono in equilibrio con nessuna aldeide aciclica, e ciò li rende zuccheri non riducenti.

a.



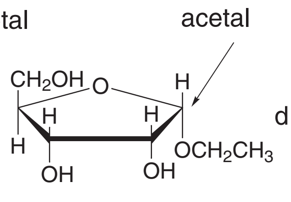
reducing sugar

b.



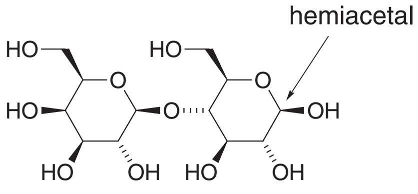
reducing sugar

c.



nonreducing sugar

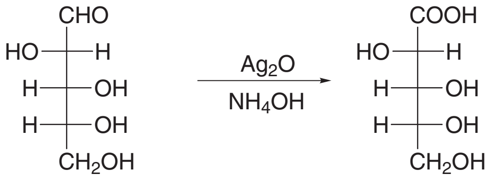
d.



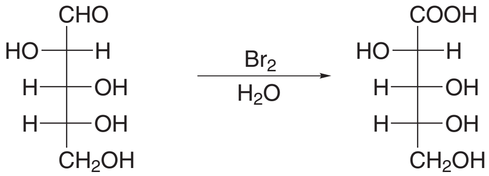
lactose
reducing sugar

22.33

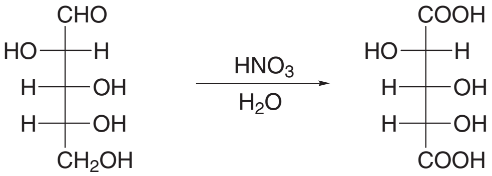
a.



b.

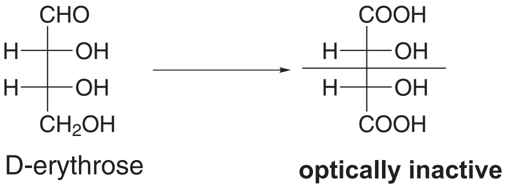


c.

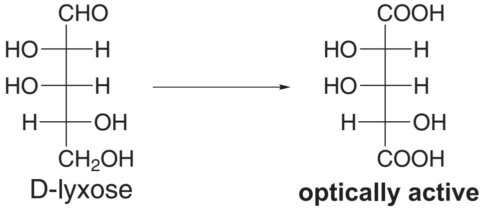


22.34 Molecole con un piano di simmetria sono otticamente inattive.

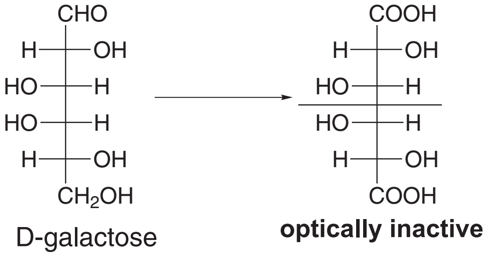
a.



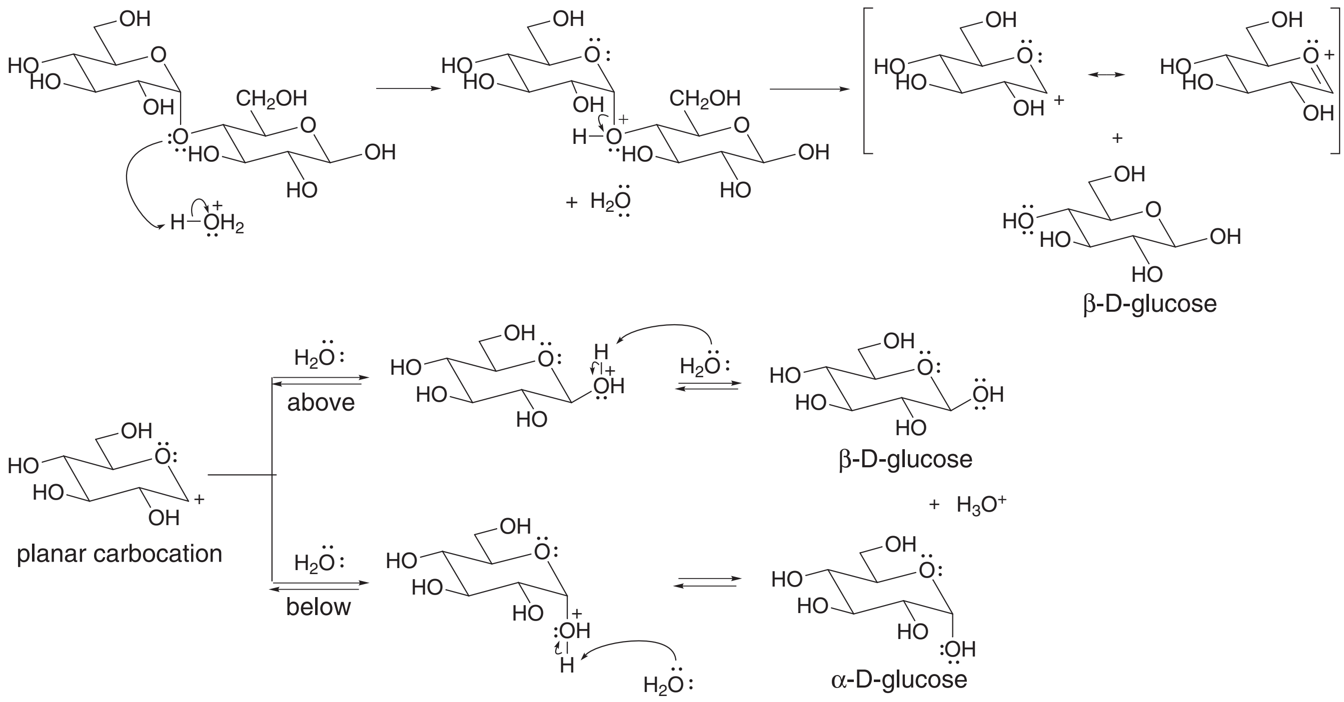
b.



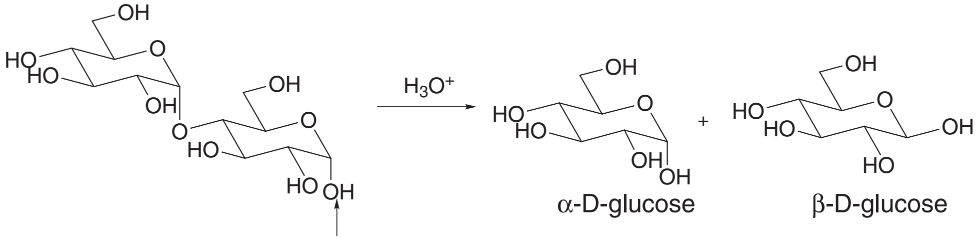
c.



22.35



22.36

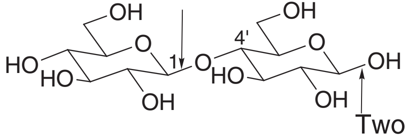


α **anomer**

The same products are formed on hydrolysis of the α and β anomers of maltose.

22.37

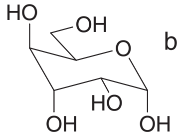
β glycoside bond



Cellobiose

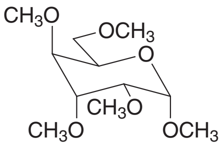
Two possible anomers here. β OH is drawn.

22.38

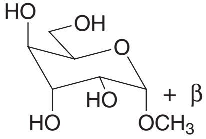


D-gulose

a. CH_3I/Ag_2O

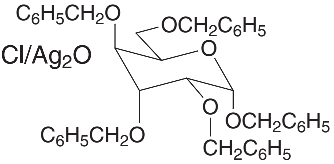


b. CH_3OH/HCl

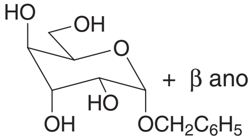


+ β anomer

c. $C_6H_5CH_2Cl/Ag_2O$

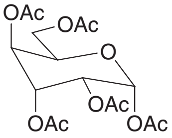


d. $C_6H_5CH_2OH/HCl$

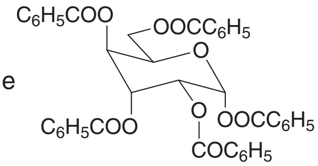


+ β anomer

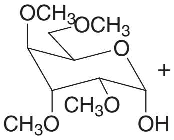
e. Ac_2O/pyridine



f. C_6H_5COCl/pyridine

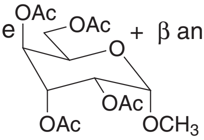


g. The product in (a), then H_3O^+



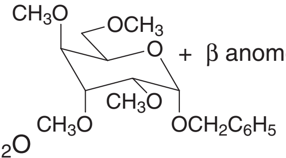
+ β anomer

h. The product in (b), then Ac_2O/pyridine



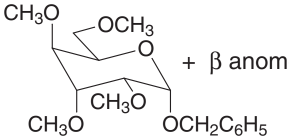
+ β anomer

i. The product in (g), then $C_6H_5CH_2Cl/Ag_2O$



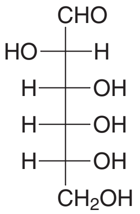
+ β anomer

j. The product in (d), then CH_3I/Ag_2O

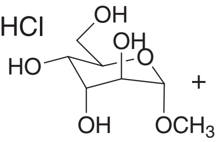


+ β anomer

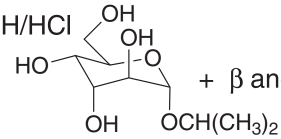
22.39


D-altrose

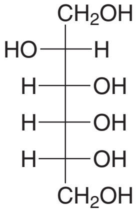
a. CH_3OH/HCl


+ β anomer

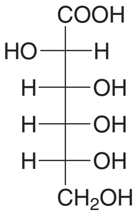
b. $(CH_3)_2CHOH/HCl$


+ β anomer

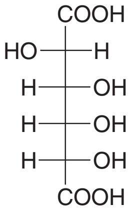
c. $NaBH_4/CH_3OH$



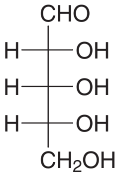
d. Br_2/H_2O



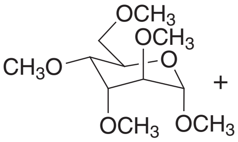
e. HNO_3/H_2O



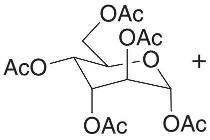
f. [1] NH_2OH
[2] $(CH_3CO)_2O$, $NaOCOCH_3$
[3] $NaOCH_3$



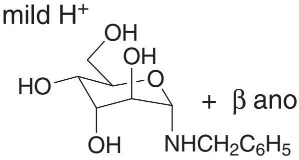
h. CH_3I/Ag_2O


+ β anomer

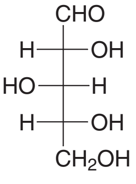
i. Ac_2O/pyridine


+ β anomer

j. $C_6H_5CH_2NH_2$/ mild H^+

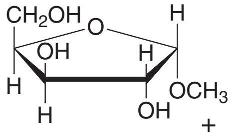

+ β anomer

22.40



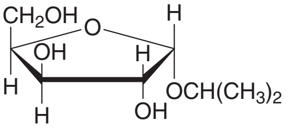
D-xylose

a. CH_3OH/HCl



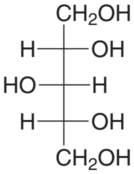
+ β anomer

b. $(CH_3)_2CHOH/HCl$

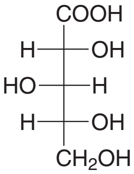


+ β anomer

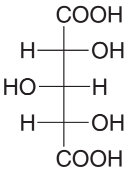
c. $NaBH_4/CH_3OH$



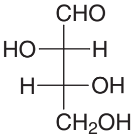
d. Br_2/H_2O



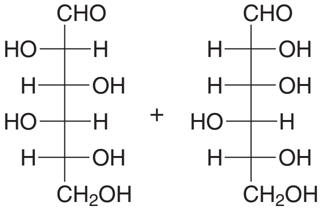
e. HNO_3/H_2O



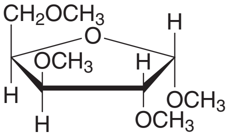
f. [1] NH_2OH
[2] $(CH_3CO)_2O$, $NaOCOCH_3$
[3] $NaOCH_3$



g. [1] NaCN, HCl
[2] $H_2/Pd/BaSO_4$
[3] H_3O^+

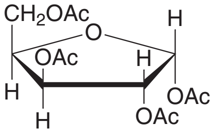


h. CH_3I/Ag_2O



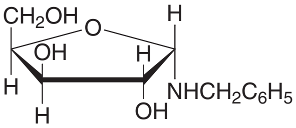
+ β anomer

i. Ac_2O/pyridine



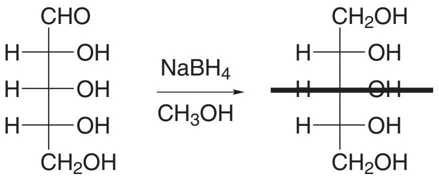
+ β anomer

j. $C_6H_5CH_2NH_2$/ mild H^+

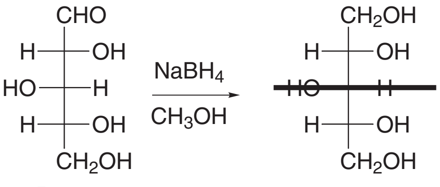


+ β anomer

22.41 Molecole con un piano di simmetria sono otticamente inattive.



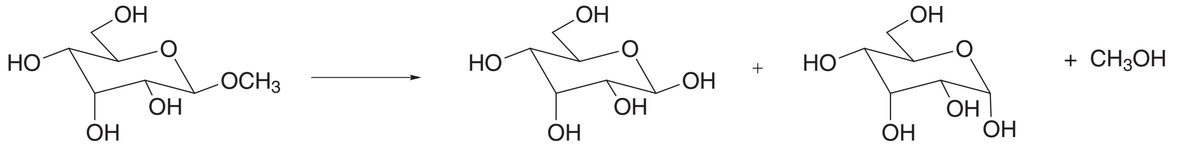
D-ribose



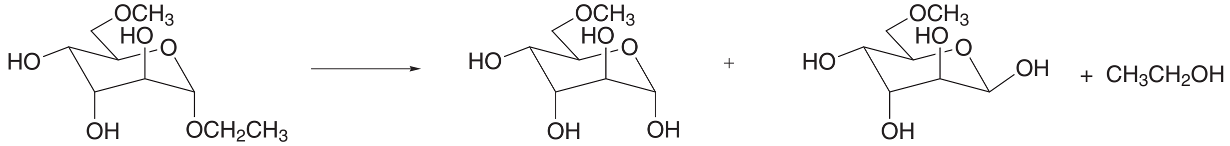
D-xylose

22.42

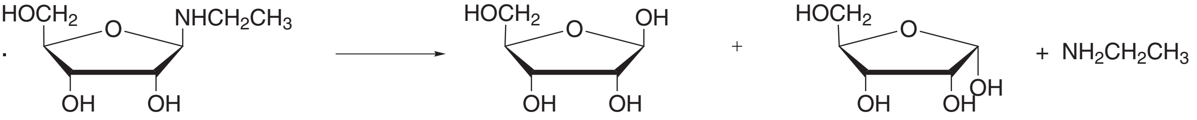
a.



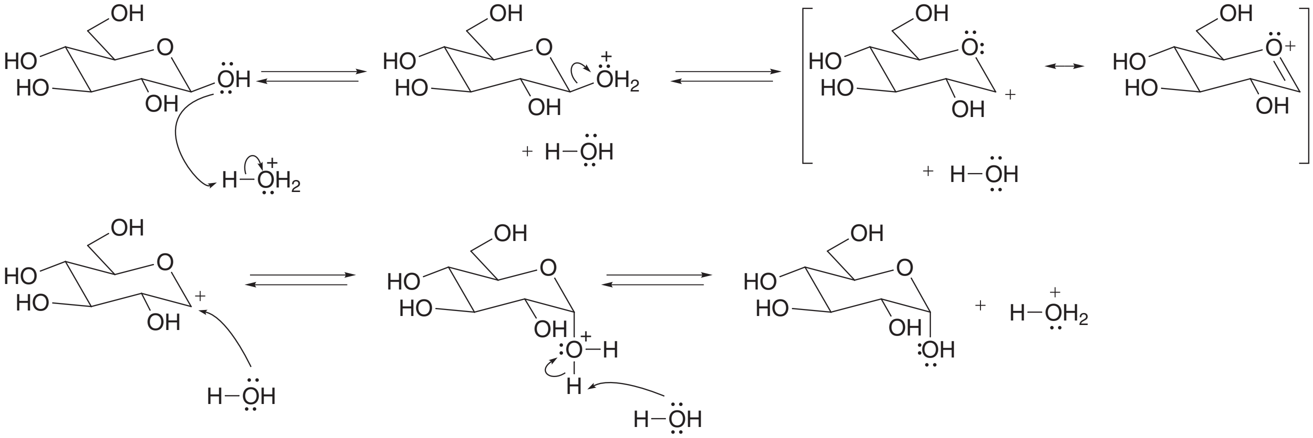
b.



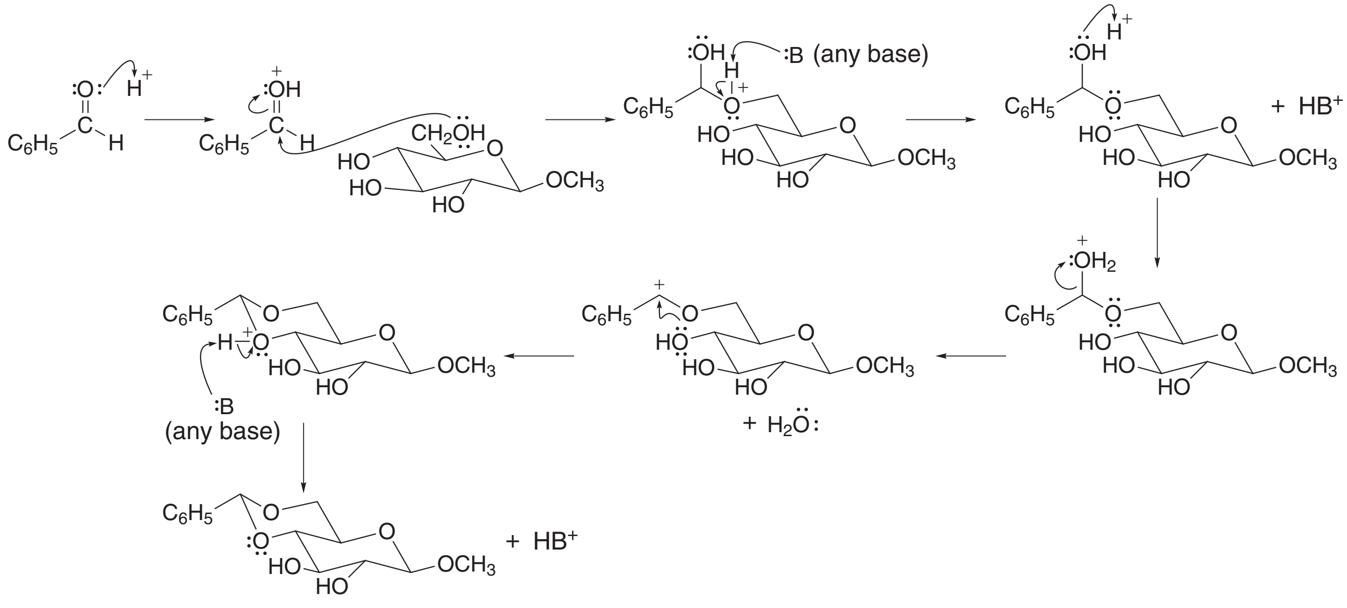
c.



22.43

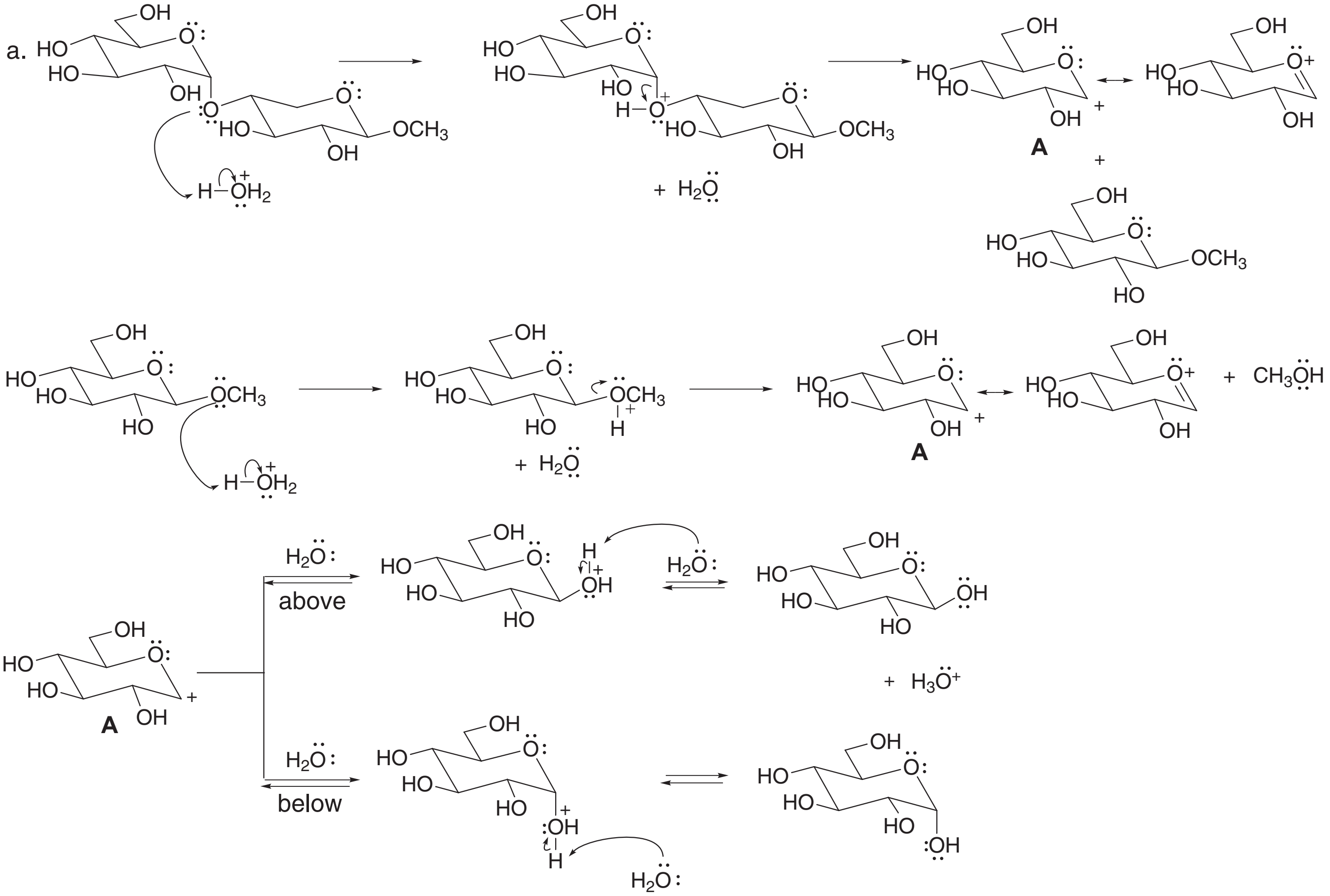


22.44

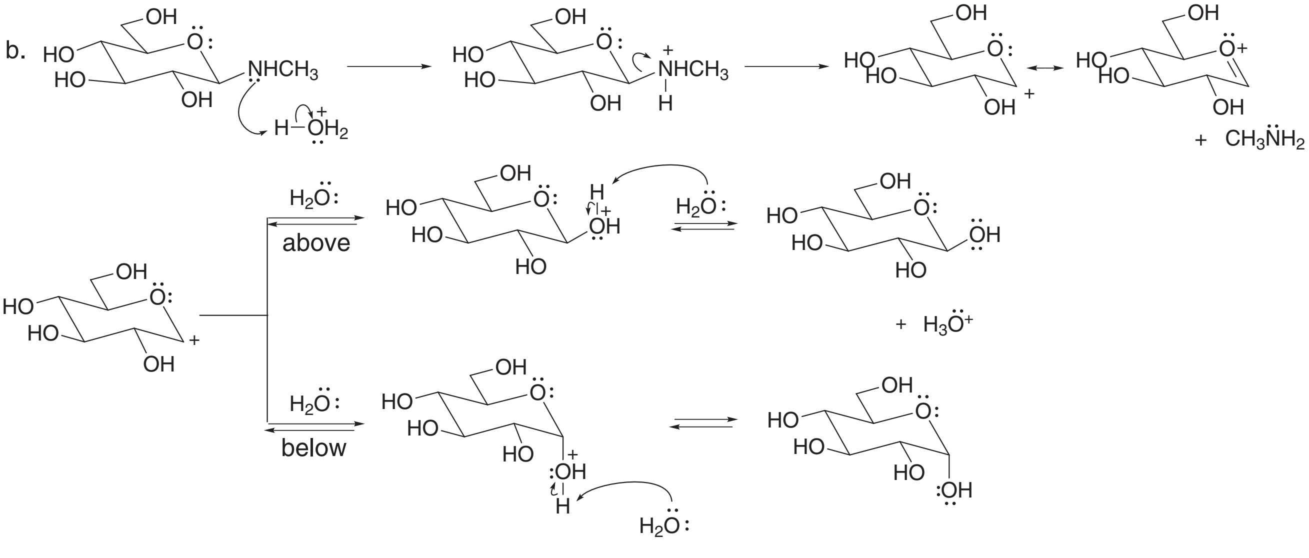


22.45

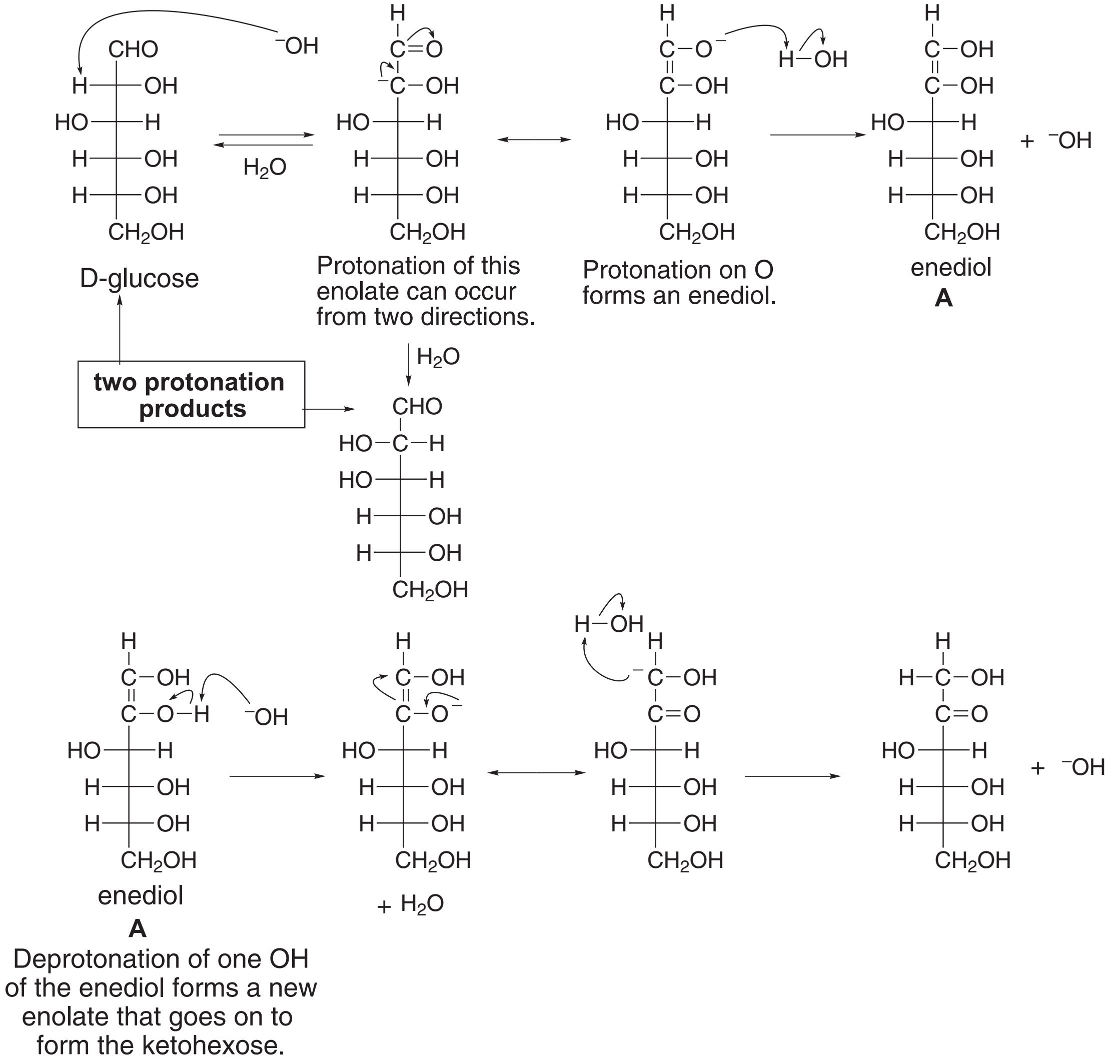
a.



b.

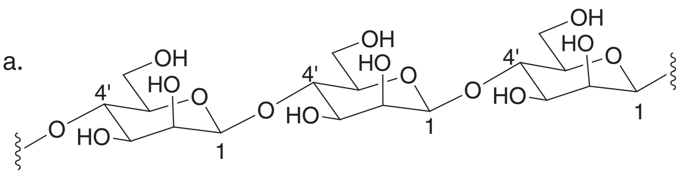


22.46

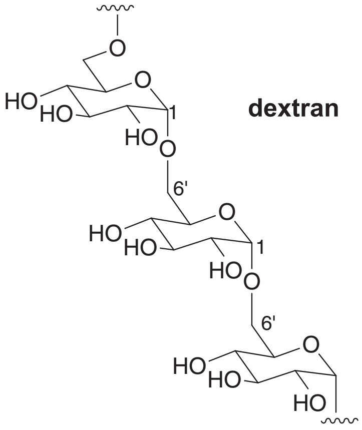


22.47

a.



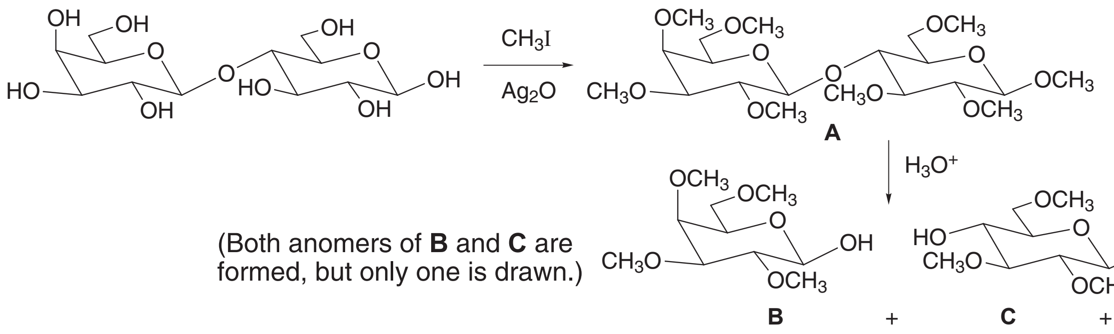
b.



dextran

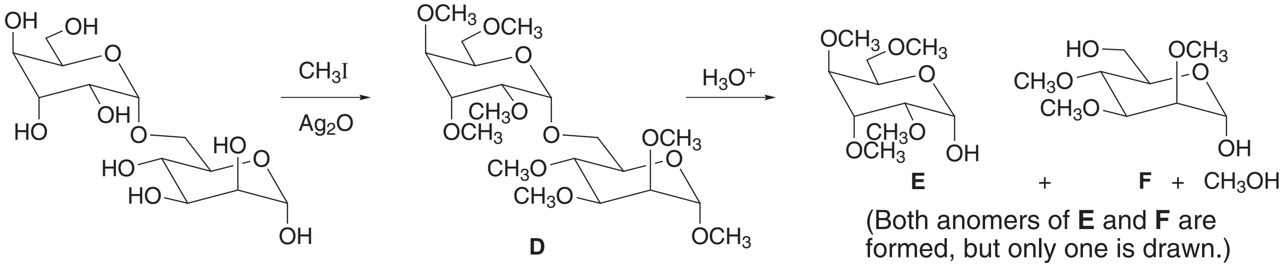
22.48

a.



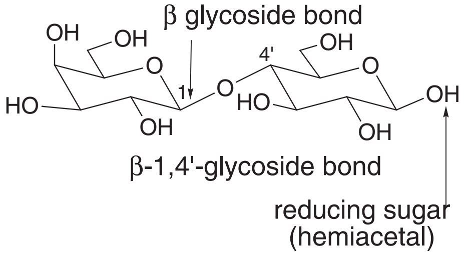
(Both anomers of **B** and **C** are formed, but only one is drawn.)

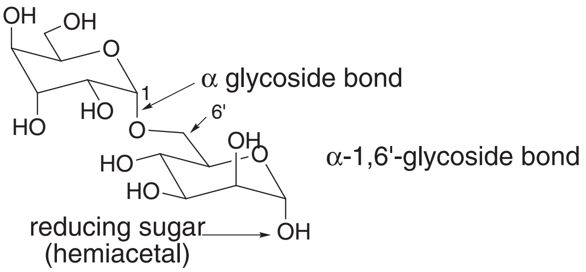
b.



(Both anomers of **E** and **F** are formed, but only one is drawn.)

22.49





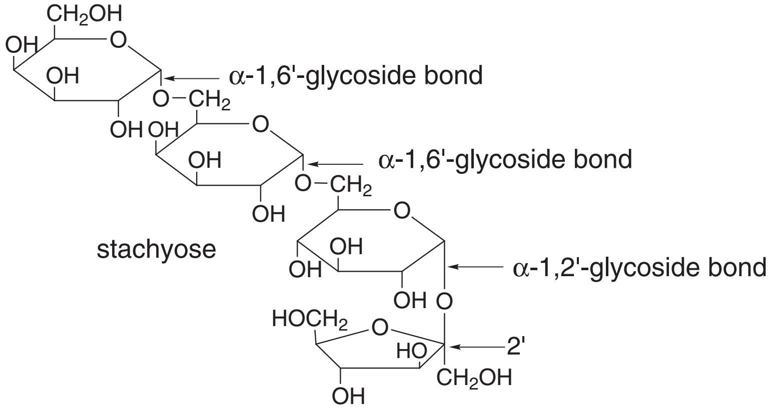
a.

b. β-1,4'-glycoside bond α-1,6'-glycoside bond

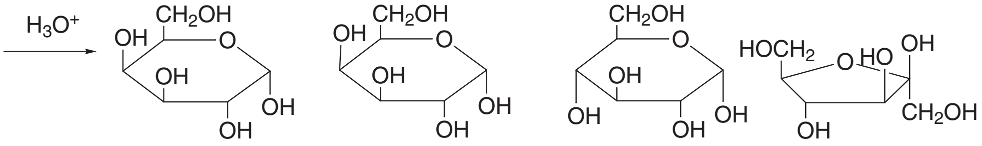
c.

22.50

a and b.



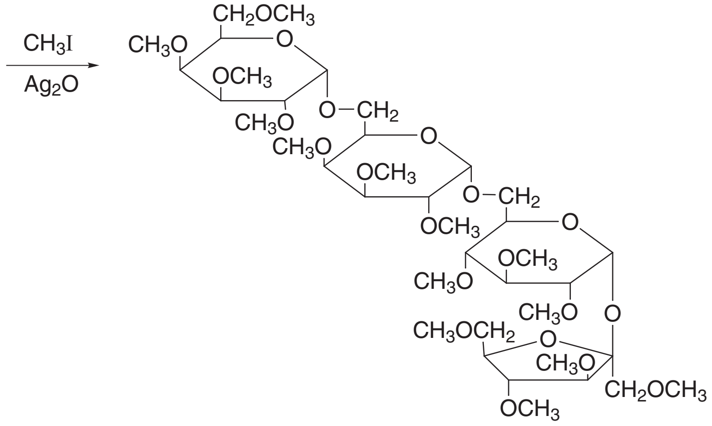
c.



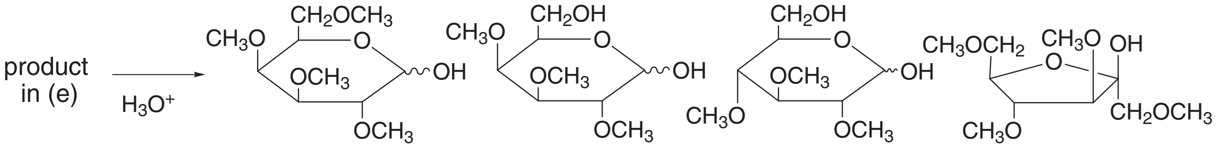
α and β Anomers of each monosaccharide are formed,
but only one anomer is drawn.

d. Stachyose is not a reducing sugar since it contains no hemiacetal.

e.

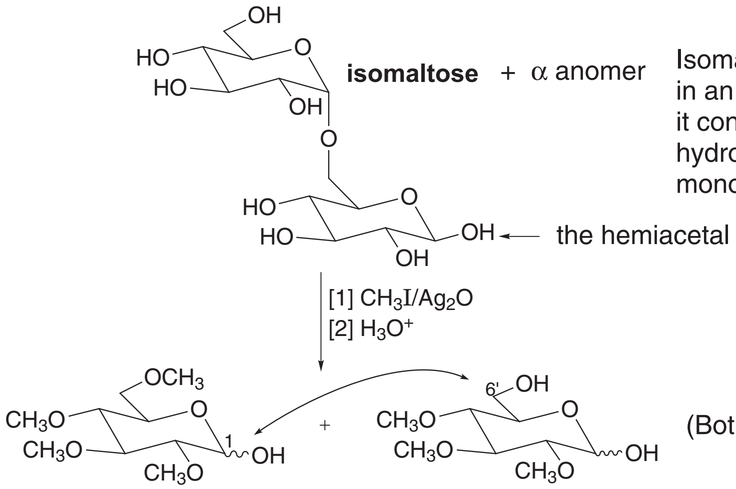


f.



α and β Anomers of each
monosaccharide are formed.

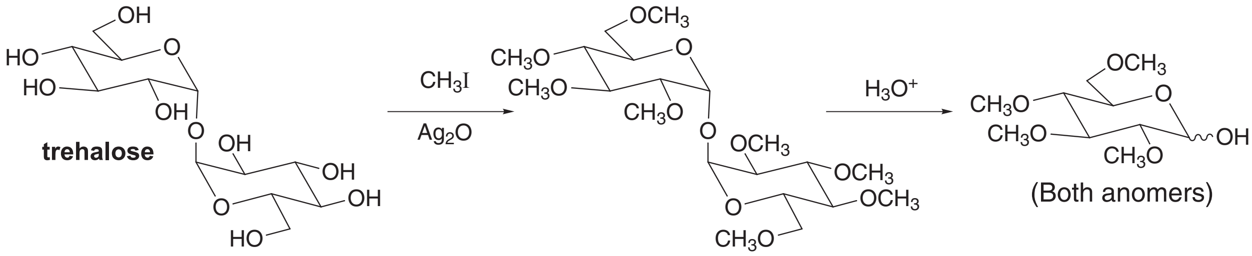
22.51



Isomaltose must be composed of two glucose units in an α glycosidic linkage. Since it is a reducing sugar it contains a hemiacetal. The free OH groups in the hydrolysis products show where the two monosaccharides are joined.

(Both anomers are present.)

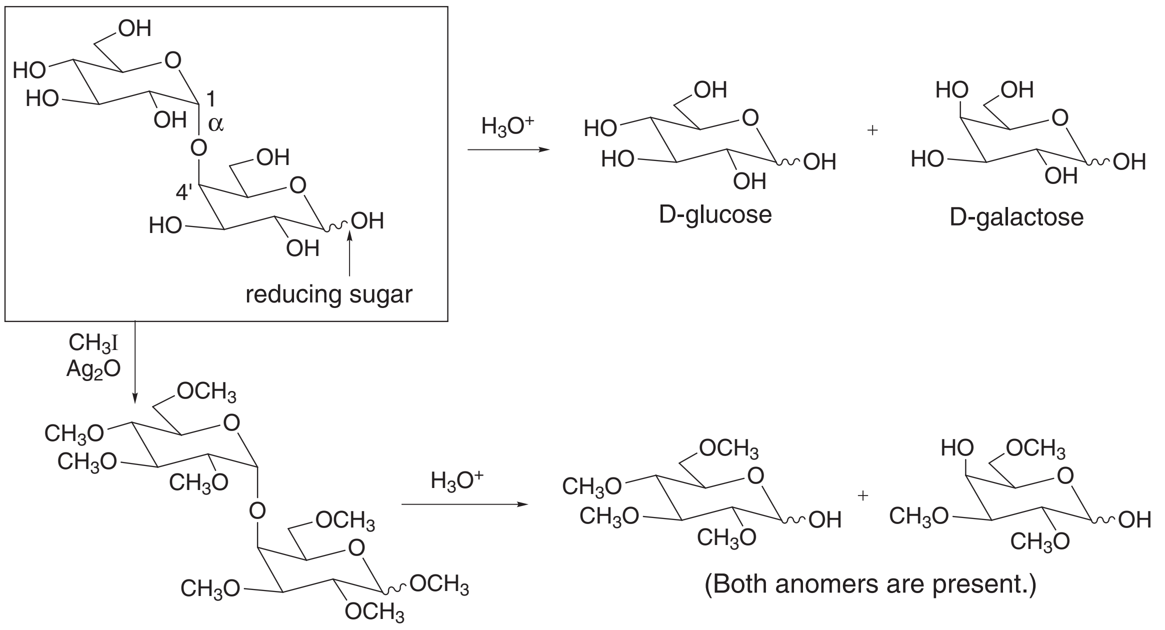
22.52



(Both anomers)

Trehalose must be composed of D-glucose units only, joined in an α glycosidic linkage. Since trehalose is nonreducing it contains no hemiacetal. Since there is only one product formed after methylation and hydrolysis, the two anomeric C's must be joined.

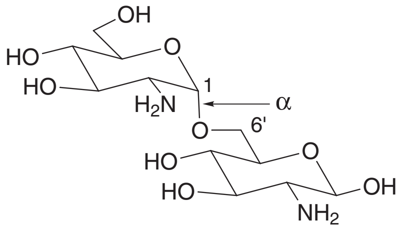
22.53



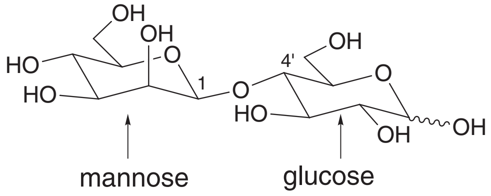
The disaccharide is composed of D-glucose and D-galactose joined in an α-glycosidic linkage. Since it is a reducing sugar it contains a hemiacetal. The free OH's in the two-step reaction show where the two monosaccharides were joined.

22.54

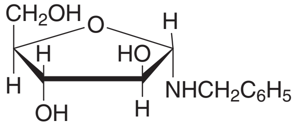
a.



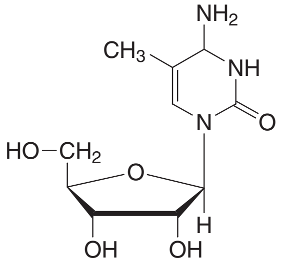
b.



c.

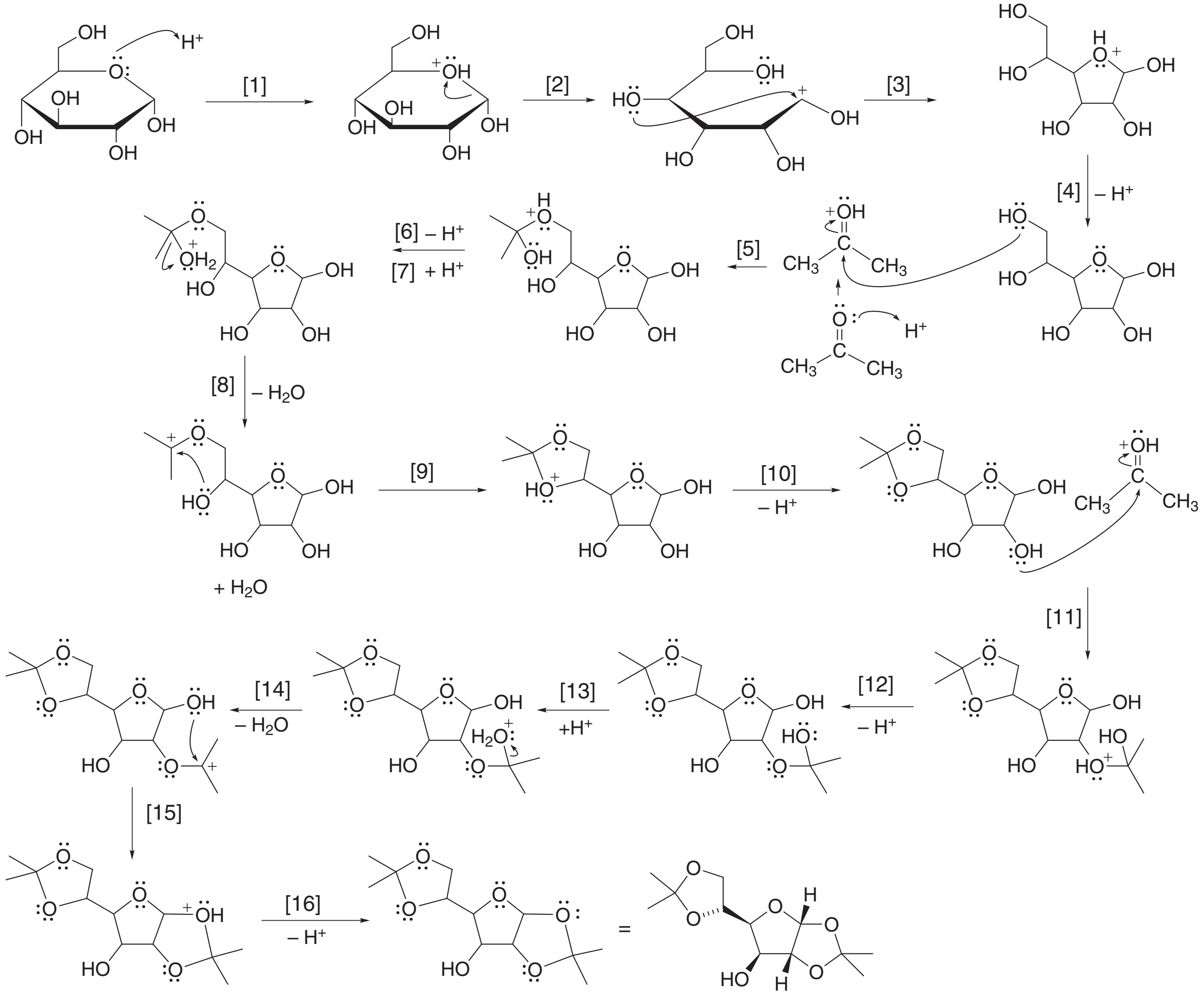


d.



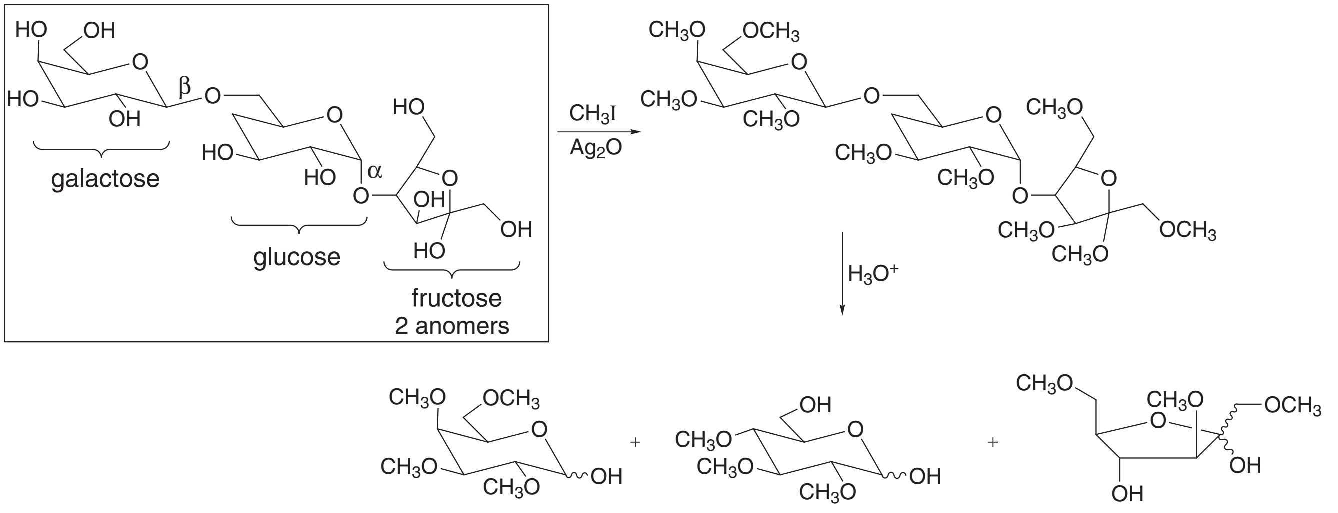
22.55

Ignoring stereochemistry along the way:



22.56

The hydrolysis data suggest that the trisaccharide has D-galactose on one end and D-fructose on the other. D-galactose must be joined to its adjacent sugar by a β glycosidic linkage. D-Fructose must be joined to its adjacent sugar by an α glycosidic linkage.



2,3,4,6-tetra-*O*-methyl-D-galactose

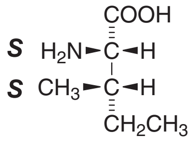
2,3,4-tri-*O*-methyl-D-glucose

1,3,6-tri-*O*-methyl-D-fructose

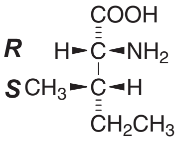
(Both anomers of each compound are formed.)

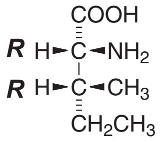
Capitolo 23

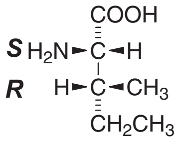
23.1



L-isoleucine

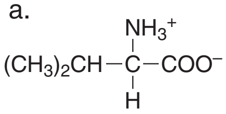






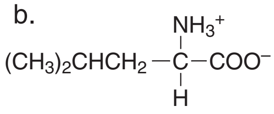
23.2

a.



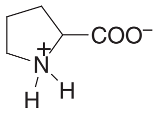
$(CH_3)_2CH-CH(NH_3^+)-COO^-$

b.

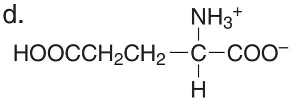


$(CH_3)_2CHCH_2-CH(NH_3^+)-COO^-$

c.



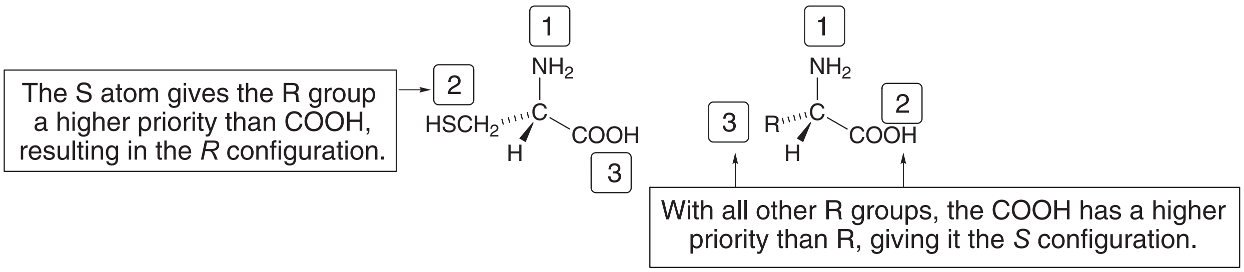
d.



$HOOCCH_2CH_2-CH(NH_3^+)-COO^-$

23.3 In un amminoacido, il gruppo carbossilico elettron attrattore destabilizza lo ione ammonio (–NH_3^+), rendendolo più disponibile a donare un protone; cioè, lo rende un acido più forte. Inoltre, il gruppo carbossilico elettron attrattore sottrae densità elettronica dal gruppo amminico (–NH_2) della base coniugata, rendendola una base più debole di un'ammina 1°, che non ha nessun gruppo elettron attrattore.

23.4 Tutti gli L-amminoacidi, eccetto la cisteina, hanno **configurazione *S***. La L-cisteina ha configurzione *R* perché il gruppo R contiene un atomo di zolfo, che ha priorità maggiore.

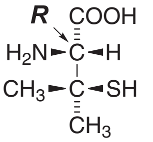


The S atom gives the R group a higher priority than COOH, resulting in the *R* configuration.

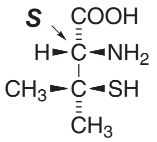
With all other R groups, the COOH has a higher priority than R, giving it the *S* configuration.

23.5

a.

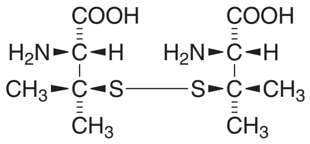


(*R*)-penicillamine
L-penicillamine

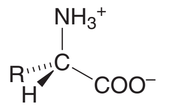


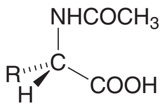
(*S*)-penicillamine
D-penicillamine

b.

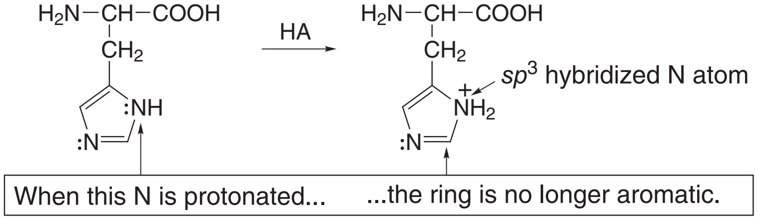


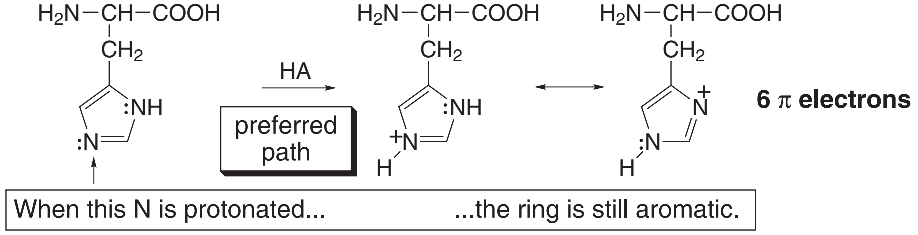
23.6 Gli amminoacidi sono insolubili in dietil etere perché sono molto polari; nella forma neutra, esistono come sali. Il dietil etere è debolmente polare, così gli amminoacidi non sono solubili. Gli *N*-acetil amminoacidi sono solubili perché sono polari ma non sono sotto forma di sale.


amino acid, a salt
H_2O soluble and ether insoluble

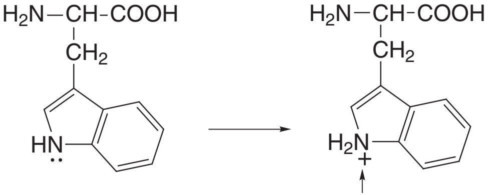

N-acetyl amino acid
Ether soluble

23.7



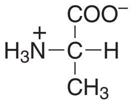


23.8

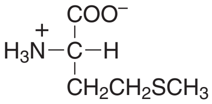

No *p* orbital on N.
The five-membered ring is no longer aromatic.

The ring structure on tryptophan is aromatic since each atom contains a *p* orbital. Protonation of the N atom would disrupt the aromaticity, making this a less favorable reaction.

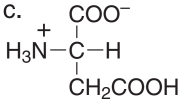
23.9 Al proprio punto isoelettrico, ogni amminoacido è neutro.

a.

$H_3\overset{+}{N}-\underset{CH_3}{\overset{COO^-}{C}}-H$

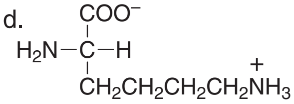
alanine

b.

$H_3\overset{+}{N}-\underset{CH_2CH_2SCH_3}{\overset{COO^-}{C}}-H$

methionine

c.

$H_3\overset{+}{N}-\underset{CH_2COOH}{\overset{COO^-}{C}}-H$

aspartic acid

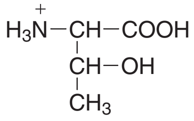
d.

$H_2N-\underset{CH_2CH_2CH_2CH_2\overset{+}{N}H_3}{\overset{COO^-}{C}}-H$

lysine

23.10 a. [1] acido glutammico usare i valori di pK_a 2.10 + 4.07
[2] lisina: usare i valori di pK_a 8.95 + 10.53
[3] arginina: usare i valori di pK_a 9.04 + 12.48
b. In generale il p*I* di un amminoacido acido è minore di quello di un amminoacido neutro.
c. In generale il p*I* di un amminoacido basico è maggiore di quello di un amminoacido neutro.

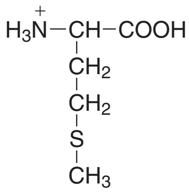
23.11

a. **threonine**
p*I* = 5.06
(+1) charge at pH = 1



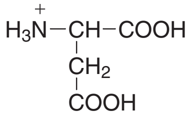
$H_3\overset{+}{N}-\underset{\substack{|\\CH-OH\\|\\CH_3}}{CH}-COOH$

b. **methionine**
p*I* = 5.74
(+1) charge at pH = 1



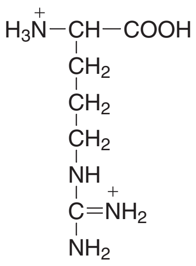
$H_3\overset{+}{N}-\underset{\substack{|\\CH_2\\|\\CH_2\\|\\S\\|\\CH_3}}{CH}-COOH$

c. **aspartic acid**
p*I* = 2.98
(+1) charge at pH = 1



$H_3\overset{+}{N}-\underset{\substack{|\\CH_2\\|\\COOH}}{CH}-COOH$

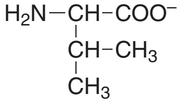
d. **arginine**
p*I* = 5.41
(+2) charge at pH = 1



$H_3\overset{+}{N}-\underset{\substack{|\\CH_2\\|\\CH_2\\|\\CH_2\\|\\NH\\|\\C=\overset{+}{N}H_2\\|\\NH_2}}{CH}-COOH$

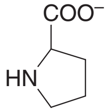
23.12

a. **valine**
p*I* = 6.00
(–1) charge
at pH = 11

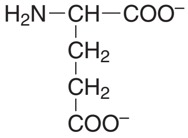


$H_2N-\underset{\substack{|\\CH-CH_3\\|\\CH_3}}{CH}-COO^-$

b. **proline**
p*I*= 6.30
(–1) charge
at pH = 11

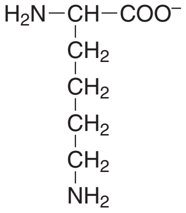


c. **glutamic acid**
p*I*= 3.08
(–2) charge
at pH = 11



$H_2N-\underset{\substack{|\\CH_2\\|\\CH_2\\|\\COO^-}}{CH}-COO^-$

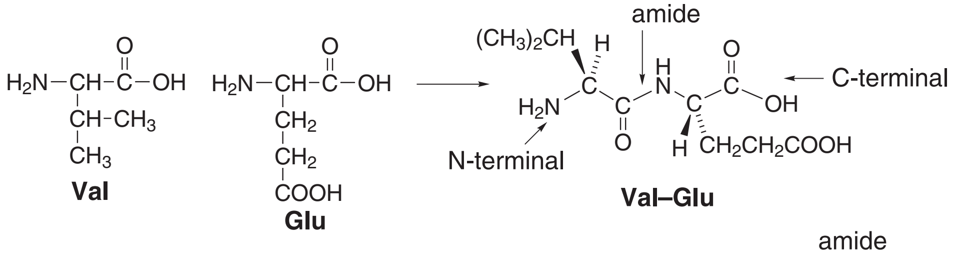
d. **lysine**
p*I* = 9.74
(–1) charge
at pH = 11



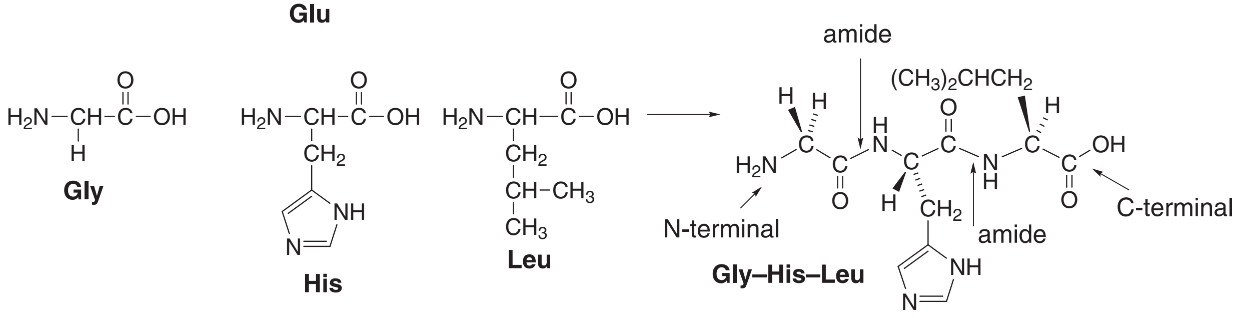
$H_2N-\underset{\substack{|\\CH_2\\|\\CH_2\\|\\CH_2\\|\\CH_2\\|\\NH_2}}{CH}-COO^-$

23.13 Disegnare il peptide legando un gruppo COOH con l'NH_2 seguente.

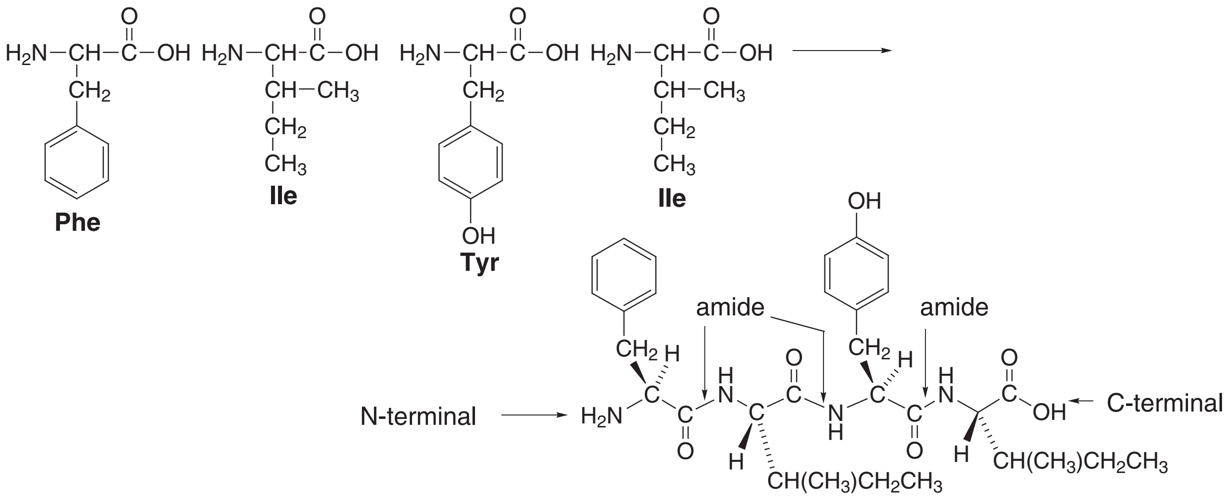
a.



b.



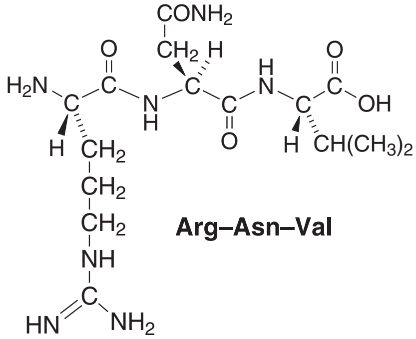
c.



Phe–Ile–Tyr–Ile

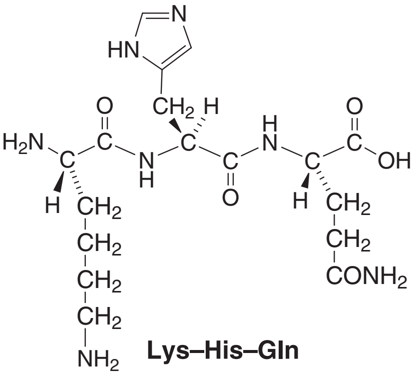
23.14

a.



Arg–Asn–Val

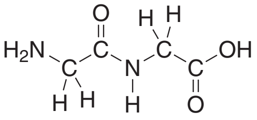
b.



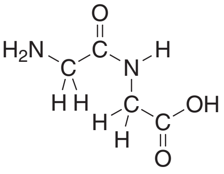
Lys–His–Gln

23.15 Ci sono sei diversi tripeptidi che si possono formare da tre amminoacidi: A–B–C, A–C–B, B–A–C, B–C–A, C–A–B, C–B–A.

23.16 La conformazione *s*-trans ha i due gruppi R orientati da parti *opposte* rispetto al legame C–N. La conformazione *s*-cis ha i due gruppi R orientati dalla *stessa* parte rispetto al legame C–N.



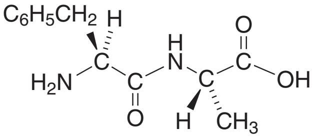
s-trans



s-cis

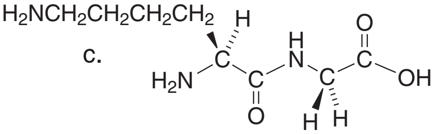
23.17

a.



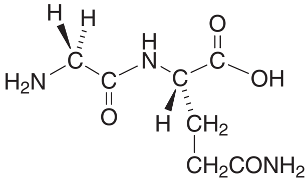
Phe–Ala

c.



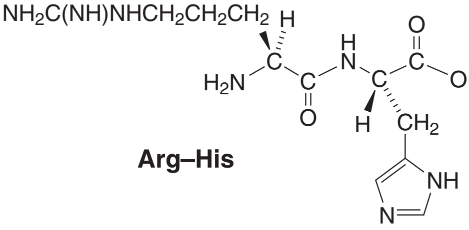
Lys–Gly

b.



Gly–Gln

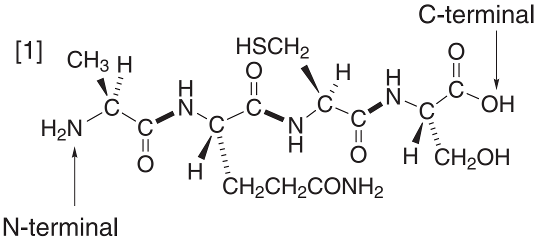
d.



Arg–His

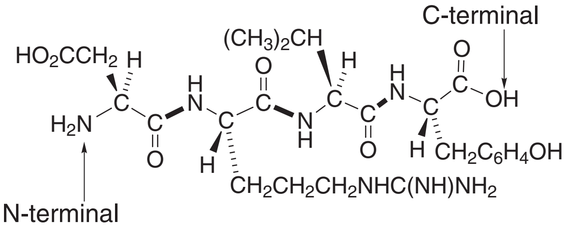
23.18 I legami ammidici sono linee piene, non cunei.

[1]



Ala–Gln–Cys–Ser
A–Q–C–S

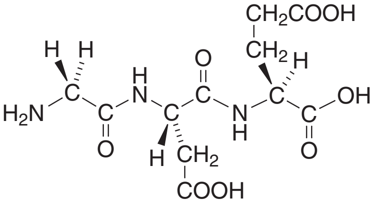
[2]



Asp–Arg–Val–Tyr
D–R–V–Y

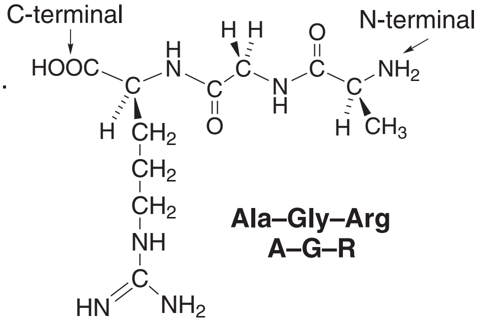
23.19 Attribuire il nome al peptide dall'estremità N-terminale alla C-terminale.

a.



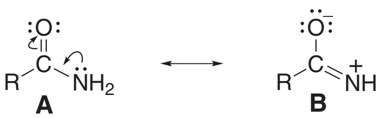
Gly–Asp–Glu
G–D–E

b.



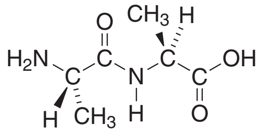
Ala–Gly–Arg
A–G–R

23.20 Un legame peptidico C–N è più forte di un legame estereo C–O perché il legame C–N ha maggior carattere di doppio legame a causa della risonanza. Poiché l'N è più basico dell'O, un legame ammidico C–N è più stabilizzato dalla delocalizzazione del doppietto solitario sull'N.

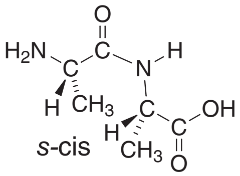


Structure **B** contributes greatly to the resonance hybrid and thus shortens and strengthens the C–N bond.

23.21 Usare le definizioni della risposta 26.16.



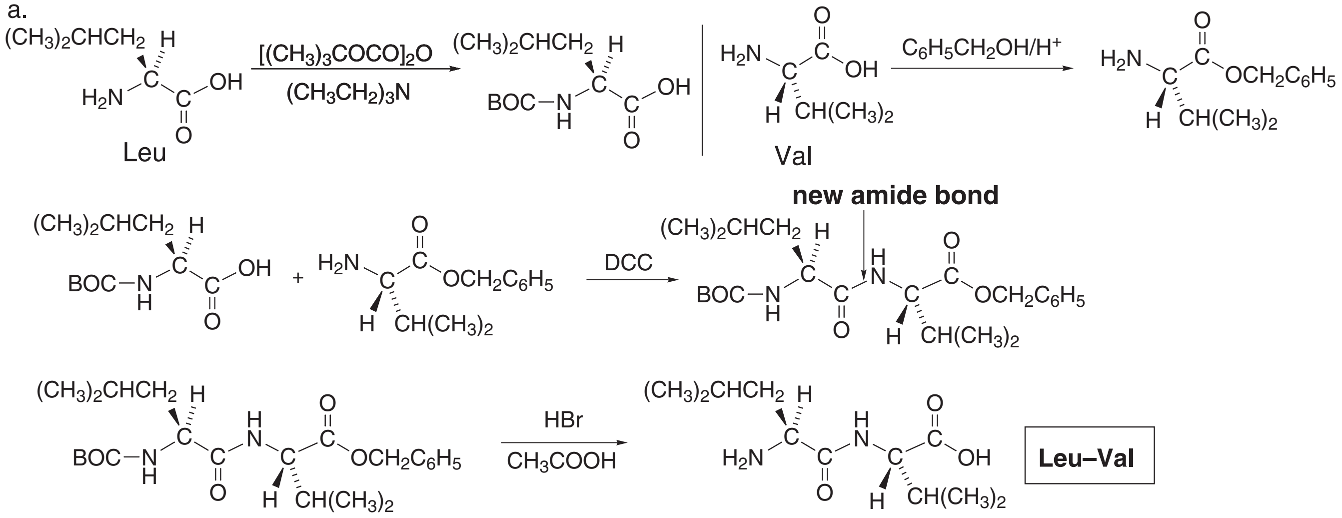
s-trans



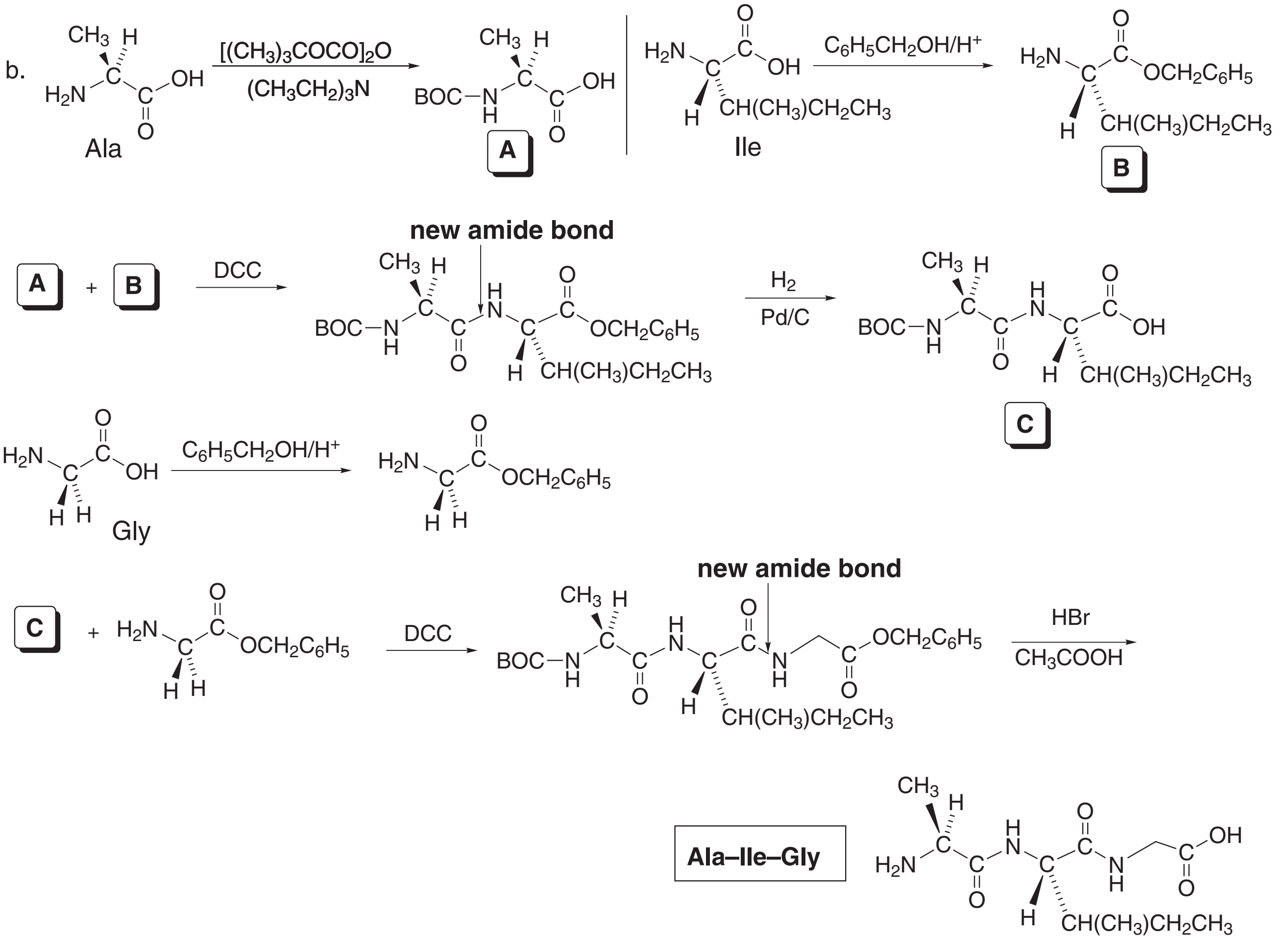
s-cis

23.22

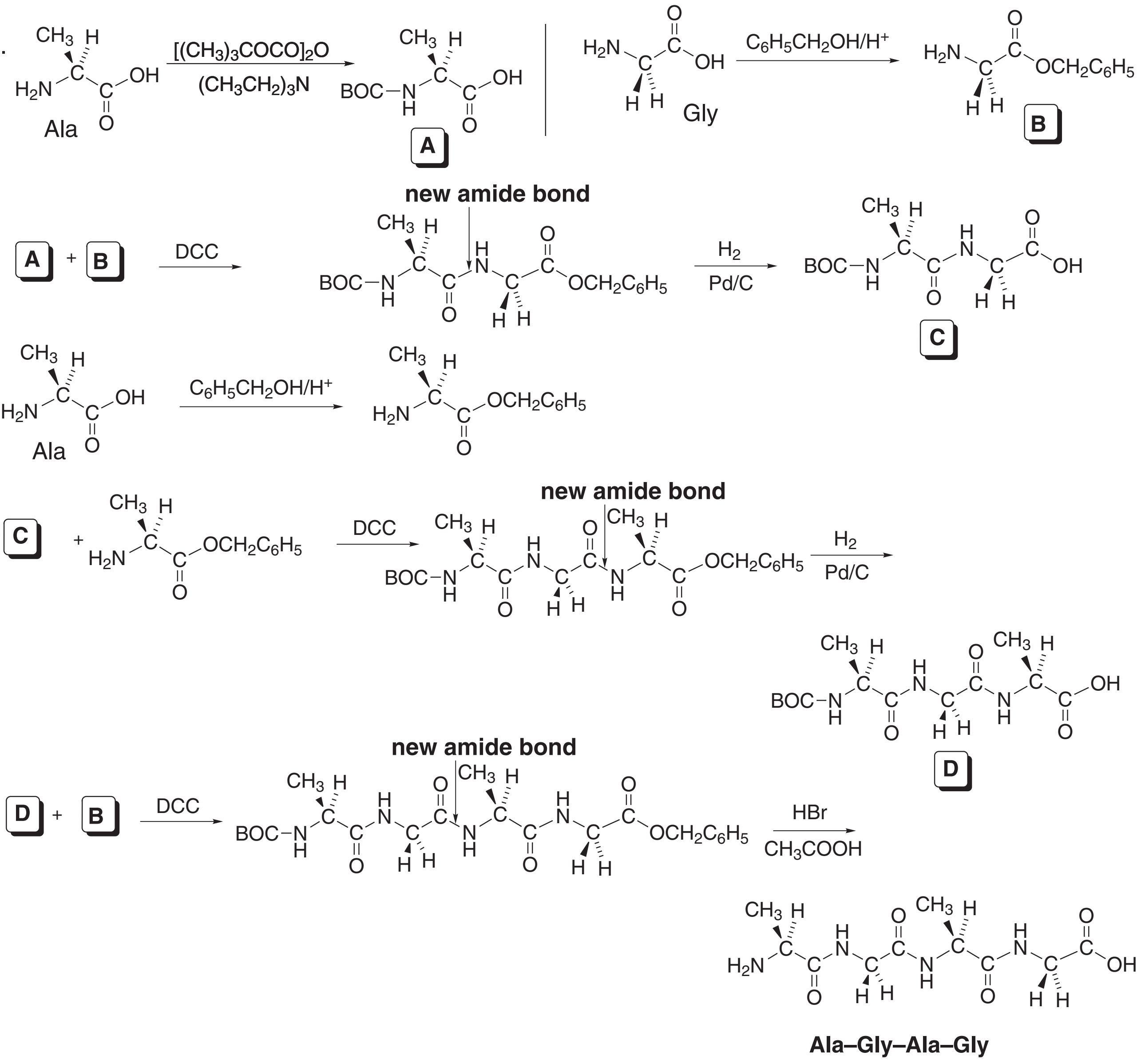
a.



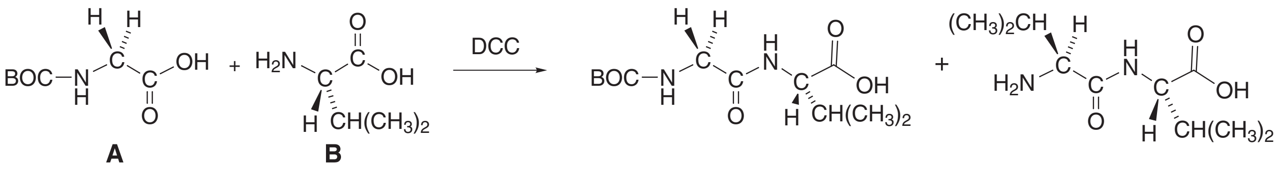
b.



c.

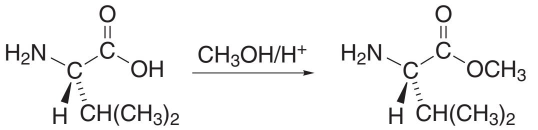


23.23 **A** e **B** possono reagire per formare un'ammide, oppure due moelecole di **B** possono formare un'ammide.

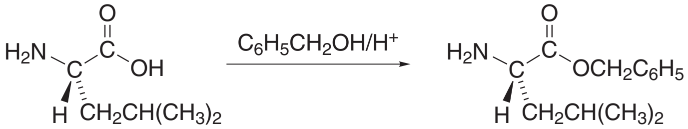


23.24

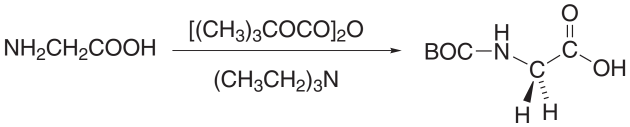
a.



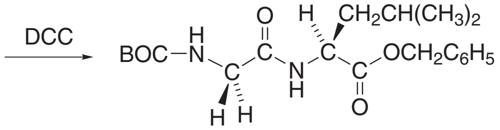
b.



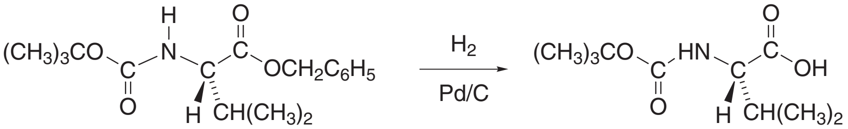
c.



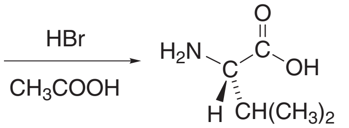
d. product in (b) + product in (c)



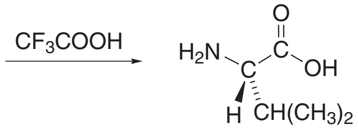
e.



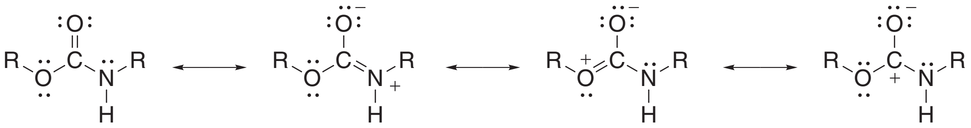
f. starting material in (e)



g. product in (e)



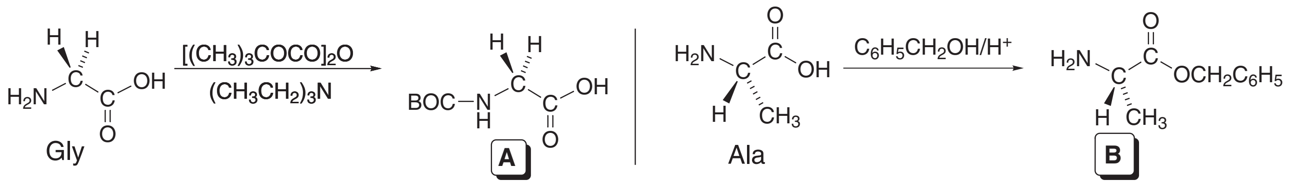
23.25

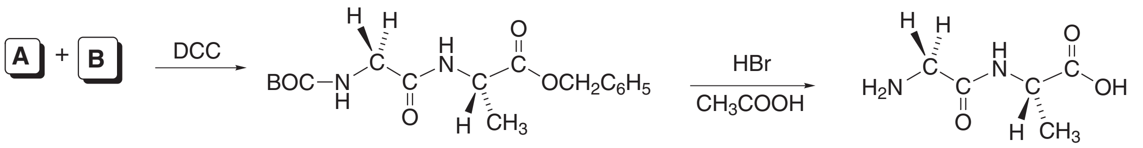


carbamate

23.26

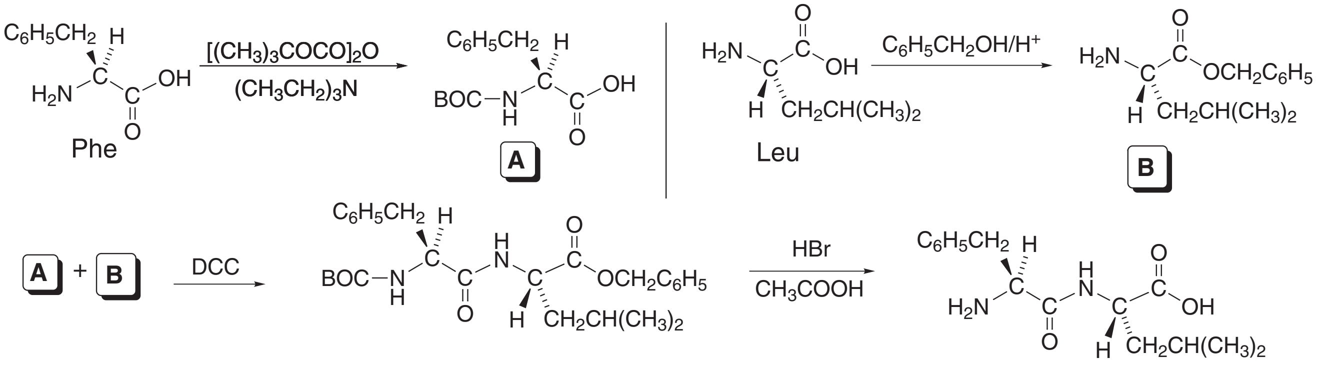
a.





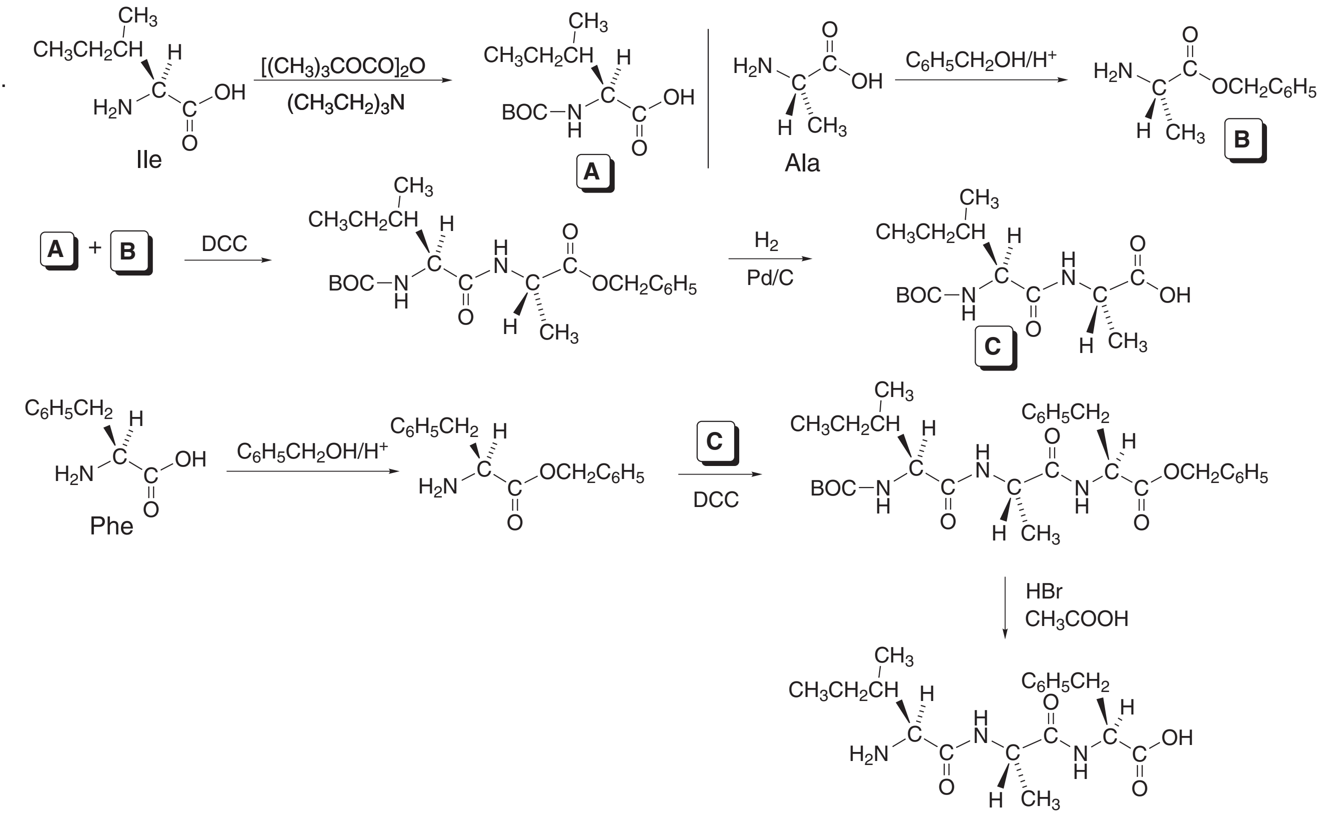
Gly–Ala

b.



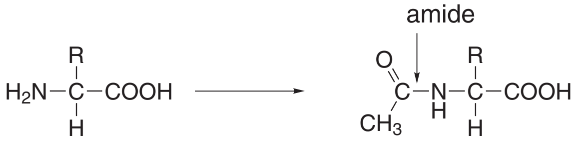
Phe–Leu

c.



Ile–Ala–Phe

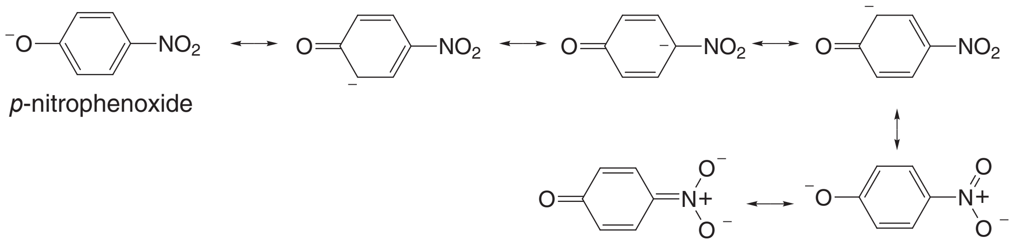
23.27 Un gruppo acetile sull'NH_2 forma un'ammide. Sebbene questa ammide protegga il gruppo amminico durante la reazione, l'ammide non ha una reattività diversa rispetto a ciascun legame ammidico del peptide. Per rimuovere il gruppo acetile dopo la formazione del legame peptidico, sarebbero necessarie forti condizioni di reazione, che potrebbero anche rompere i legami ammidici del peptide.



N-acetyl amino acid

23.28

a. A *p*-nitrophenyl ester activates the carboxyl group of the first amino acid to amide formation by converting the OH group into a good leaving group, the *p*-nitrophenoxide group, which is highly resonance stabilized. In this case the electron withdrawing NO_2 group further stabilizes the leaving group.

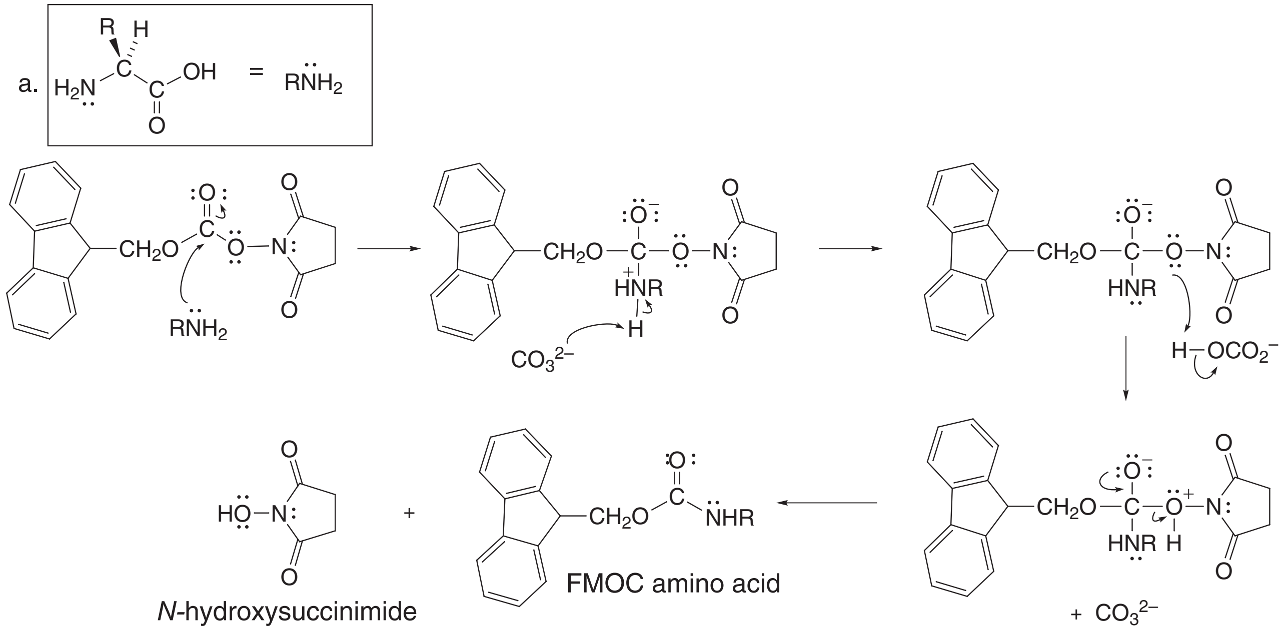


The negative charge is delocalized on the O atom of the NO_2 group.

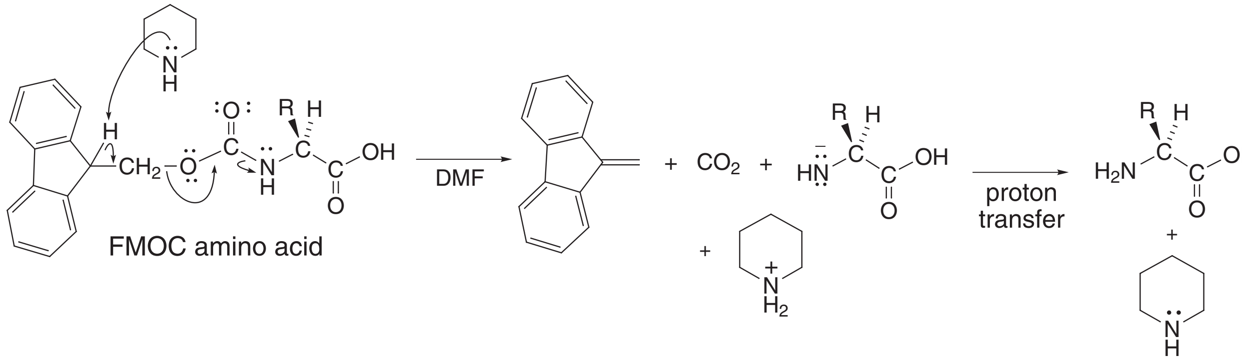
b. The *p*-methoxyphenyl ester contains an electron donating OCH_3 group, making $CH_3OC_6H_4O^-$ a poorer leaving group than $NO_2OC_6H_4O^-$, so this ester does not activate the amino acid to amide formation as much.

23.29

a.

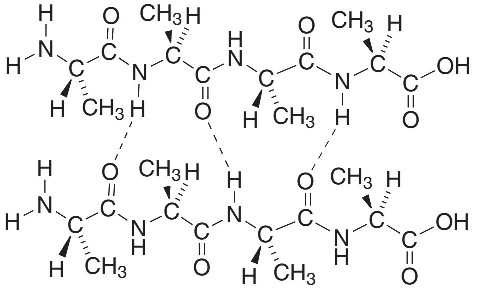


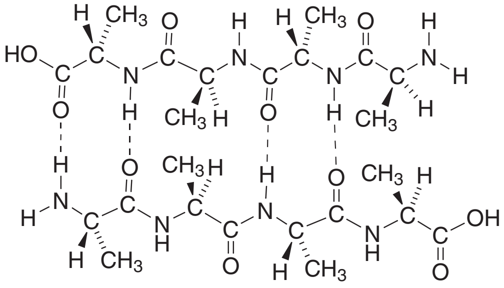
b.



23.30 I foglietti β antiparalleli sono più stabili dei foglietti β paralleli per la geometria. L'N–H e il C=O di una catena sono direttamente allineati con l'N–H e il C=O di una catena adiacente nei foglietti β antiparalleli, mentre non lo sono nei foglietti β paralleli. Ciò rende più debole quest'ultimo gruppo di legami a idrogeno.

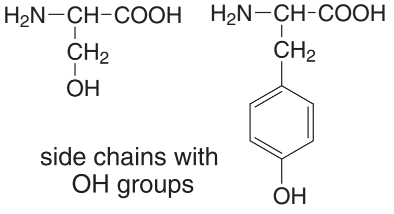
23.31 Nel foglietto β *parallelo*, i filamenti sono allineati nella *stessa* direzione dall'amminoacido N-terminale al C-terminale. Nel foglietto β *antiparallelo*, i filamenti sono allineati in direzioni *opposta*.


parallel


antiparallel

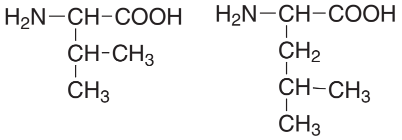
23.32

a. Ser and Tyr


side chains with OH groups

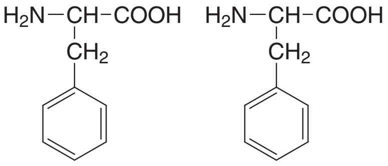
hydrogen bonding

b. Val and Leu


side chains with only C–C and C–H bonds

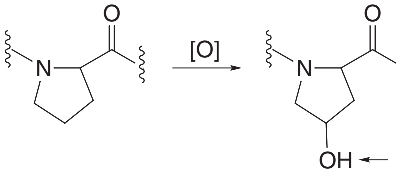
van der Waals forces

c. 2 Phe residues


van der Waals forces

23.33 Gli amminoacidi comunemente presenti all'interno delle proteine globulari hanno catene laterali non polari o debolmente polari: isoleucina e fenilalanina. Gli amminoacidi comunemente presenti sulla superficie hanno COOH, NH_2, e altri gruppi che possono formare legami idrogeno con l'acqua: acido aspartico, lisina, arginina, e acido glutammico.

23.34 I residui di prolina nel collagene sono idrossilati per aumentare le interazioni di legame idrogeno.


The new OH group allows more hydrogen bonding interactions between the chains of the triple helix, thus stabilizing it.