APPENDIX

D Answers to In-Text Problems

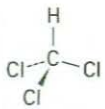
The following answers are meant only as a quick check while you study. Full answers for all problems are provided in the accompanying *Study Guide and Solutions Manual*.

CHAPTER 1

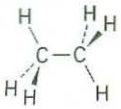
1.1 (a) $1s^2\ 2s^2\ 2p^4$ (b) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$
(c) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

1.2 (a) 2 (b) 2 (c) 6

1.3

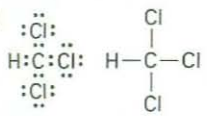


1.4

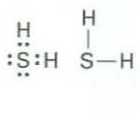


1.5 (a) $GeCl_4$ (b) AlH_3
(c) CH_2Cl_2 (d) SiF_4
(e) CH_3NH_2

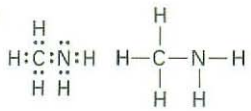
1.6 (a)



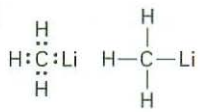
(b)



(c)

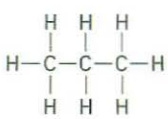


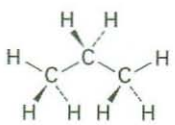
(d)



1.7 C_2H_7 has too many hydrogens for a compound with two carbons.

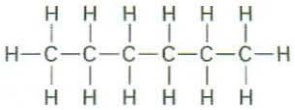
1.8



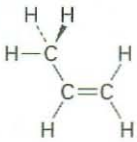


All bond angles are near 109°.

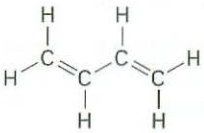
1.9



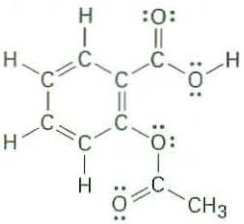
1.10 The CH_3 carbon is sp^3; the double-bond carbons are sp^2; the C=C–C and C=C–H bond angles are approximately 120°; other bond angles are near 109°.



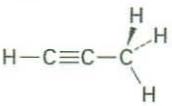
1.11 All carbons are sp^2, and all bond angles are near 120°.



1.12 All carbons except CH_3 are sp^2.

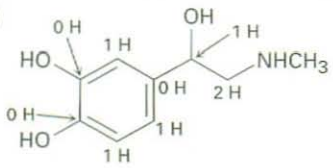


1.13 The CH_3 carbon is sp^3; the triple-bond carbons are sp; the C≡C–C and H–C≡C bond angles are approximately 180°.



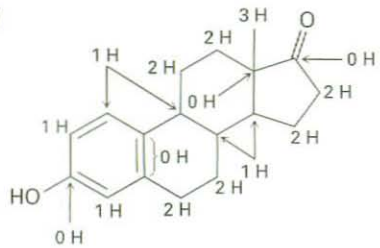
1.14 (a) O has 2 lone pairs and is sp^3-hybridized.
(b) N has 1 lone pair and is sp^3-hybridized.
(c) P has 1 lone pair and is sp^3-hybridized.
(d) S has 2 lone pairs and is sp^3-hybridized.

1.15 (a)



Adrenaline—$C_9H_{13}NO_3$

(b)



Estrone—$C_{18}H_{22}O_2$

1.16 There are numerous possibilities, such as:

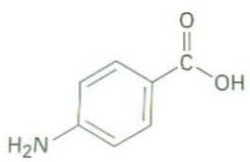
(a) C_5H_{12} $CH_3CH_2CH_2CH_2CH_3$ $CH_3CH_2CH(CH_3)CH_3$ $CH_3C(CH_3)_2CH_3$

(b) C_2H_7N $CH_3CH_2NH_2$ CH_3NHCH_3

(c) C_3H_6O $CH_3CH{=}O$ $H_2C{=}CHCH_2OH$ $H_2C{=}CHOCH_3$

(d) C_4H_9Cl $CH_3CH_2CH_2CH_2Cl$ $CH_3CH_2CH(Cl)CH_3$ $CH_3CH(CH_3)CH_2Cl$

1.17



CHAPTER 2

2.1 (a) H (b) Br (c) Cl (d) C

2.2

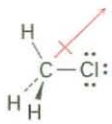
(a) $H_3C^{\delta+}-Cl^{\delta-}$ (b) $H_3C^{\delta+}-NH_2^{\delta-}$ (c) $H_2N^{\delta-}-H^{\delta+}$

(d) H_3C-SH (e) $H_3C^{\delta-}-MgBr^{\delta+}$ (f) $H_3C^{\delta+}-F^{\delta-}$

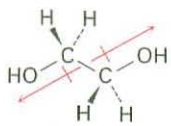
Carbon and sulfur have identical electronegativities.

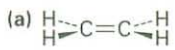
2.3 $H_3C-OH < H_3C-MgBr < H_3C-Li = H_3C-F < H_3C-K$

2.4 The chlorine is electron-rich, and the carbon is electron-poor.

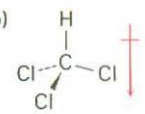


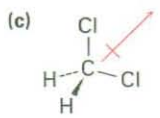
2.5 The two C–O dipoles cancel because of the symmetry of the molecule:

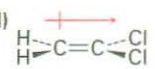


2.6 (a) 

No dipole moment

(b) 

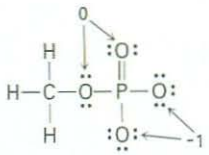
(c) 

(d) 

2.7 For nitrogen: FC = 5 − 8/2 − 0 = +1
For singly bonded oxygen: FC = 6 − 2/2 − 6 = −1

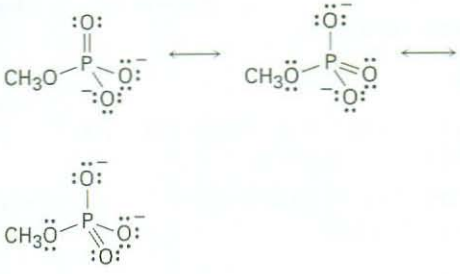
2.8 (a) For carbon: FC = 4 − 8/2 − 0 = 0
For the middle nitrogen: FC = 5 − 8/2 − 0 = +1
For the end nitrogen: FC = 5 − 4/2 − 4 = −1
(b) For nitrogen: FC = 5 − 8/2 − 0 = +1
For oxygen: FC = 6 − 2/2 − 6 = −1
(c) For nitrogen: FC = 5 − 8/2 − 0 = +1
For the end carbon: FC = 4 − 6/2 − 2 = −1

2.9

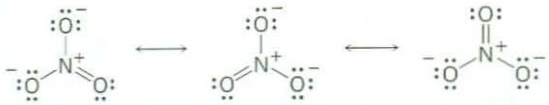


2.10

(a)

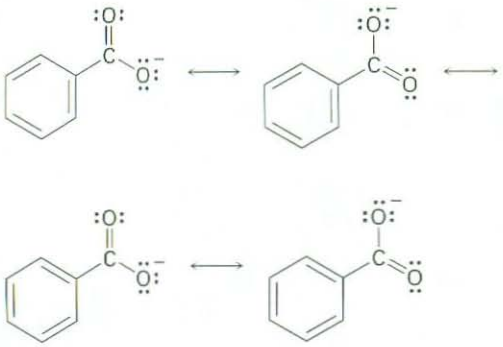


(b)



(c) $H_2C{=}CH{-}CH_2^+ \longleftrightarrow H_2\overset{+}{C}{-}CH{=}CH_2$

(d)



2.11

HNO_3	+	NH_3	⟶	NH_4^+	NO_3^-
Acid		Base		Conjugate acid	Conjugate base

2.12 Phenylalanine is stronger.

2.13 Water is a stronger acid.

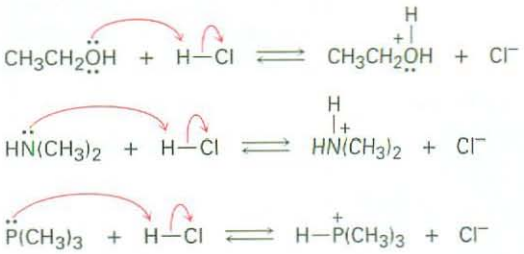
2.14 Neither reaction will take place.

2.15 Reaction will take place.

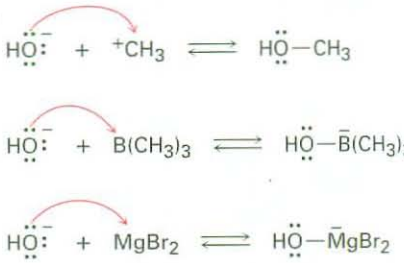
2.16 $K_a = 4.9 \times 10^{-10}$

2.17

(a)

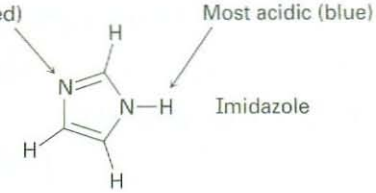


(b)

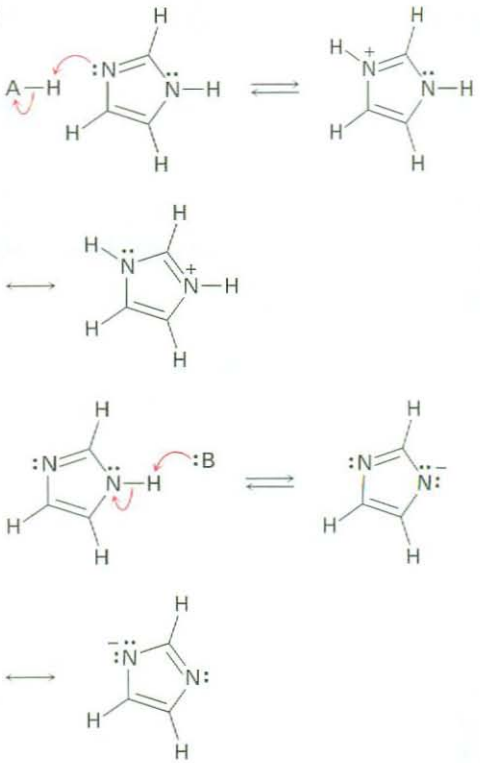


2.18

(a) More basic (red) Most acidic (blue)



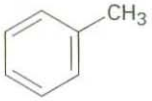
(b)

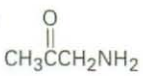


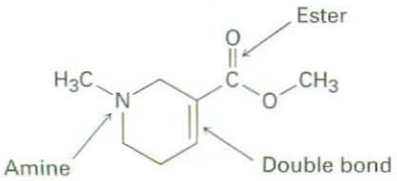
2.19 Vitamin C is water-soluble (hydrophilic); vitamin A is fat-soluble (hydrophilic).

CHAPTER 3

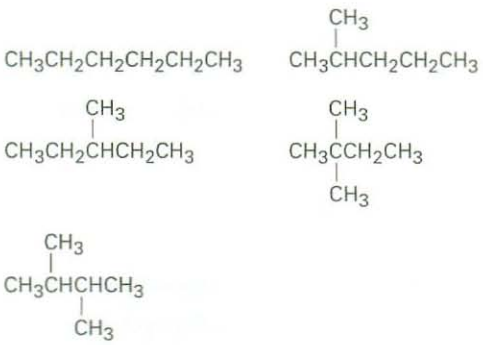
3.1 (a) Sulfide, carboxylic acid, amine
(b) Aromatic ring, carboxylic acid
(c) Ether, alcohol, aromatic ring, amide, C=C bond

3.2 (a) CH_3OH (b)  (c) 

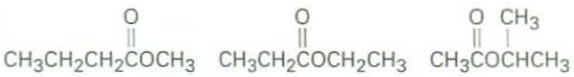
(d) CH_3NH_2 (e)  (f) 

3.3 

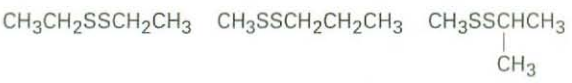
$C_8H_{13}NO_2$

3.4 

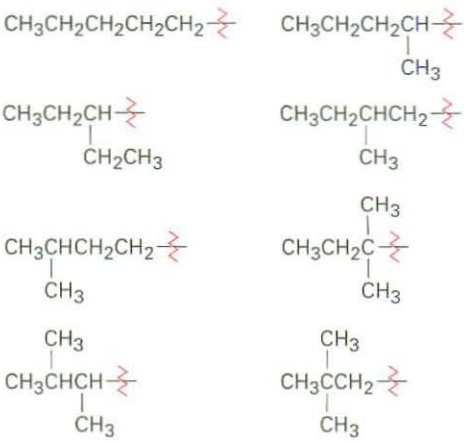
3.5 Part (a) has nine possible answers.

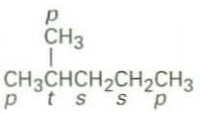
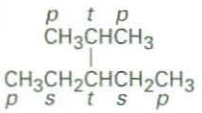
(a) 

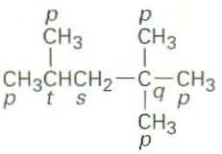
(b) 

(c) 

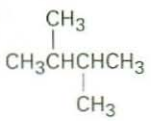
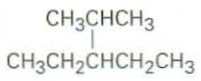
3.6 (a) Two (b) Four

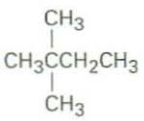
3.7 

3.8 (a)  (b) 

(c) 

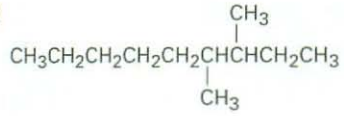
3.9 Primary carbons have primary hydrogens, secondary carbons have secondary hydrogens, and tertiary carbons have tertiary hydrogens.

3.10 (a)  (b) 

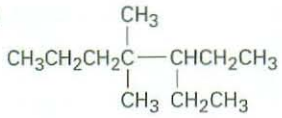
(c) 

3.11 (a) Pentane, 2-methylbutane, 2,2-dimethylpropane
(b) 3,4-Dimethylhexane
(c) 2,4-Dimethylpentane
(d) 2,2,5-Trimethylheptane

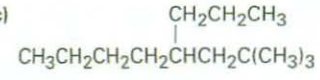
3.12 (a)



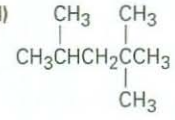
(b)



(c)



(d)

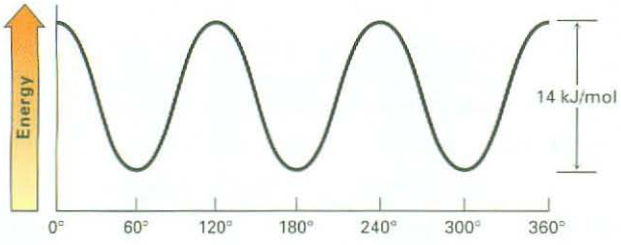


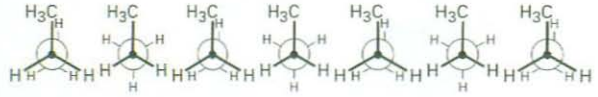
3.13 Pentyl, 1-methylbutyl, 1-ethylpropyl, 3-methylbutyl, 2-methylbutyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl

3.14

3,3,4,5-Tetramethylheptane

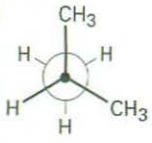
3.15





3.16

(a)



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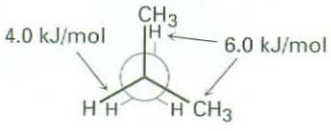
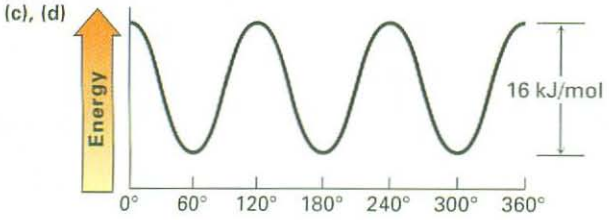


(c), (d)



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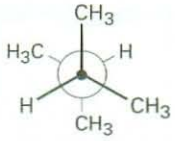

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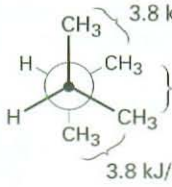
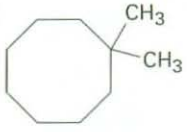


Total: 11.4 kJ/mol

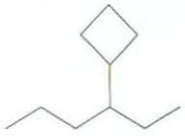
CHAPTER 4

4.1 (a) 1,4-Dimethylcyclohexane
(b) 1-Methyl-3-propylcyclopentane
(c) 3-Cyclobutylpentane
(d) 1-Bromo-4-ethylcyclodecane
(e) 1-Isopropyl-2-methylcyclohexane
(f) 4-Bromo-1-*tert*-butyl-2-methylcycloheptane

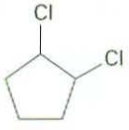
4.2 (a)



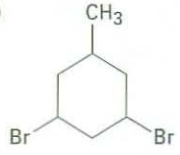
(b)



(c)



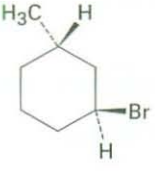
(d)



4.3 3-Ethyl-1,1-dimethylcyclopentane

4.4 (a) *trans*-1-Chloro-4-methylcyclohexane
(b) *cis*-1-Ethyl-3-methylcycloheptane

4.5 (a)



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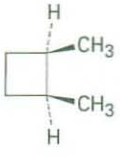
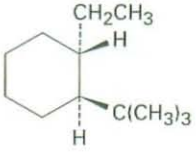


(c)



4.6 The two hydroxyl groups are cis. The two side chains are trans.

4.7 (a) *cis*-1,2-Dimethylcyclopentane
(b) *cis*-1-Bromo-3-methylcyclobutane

4.8 Six interactions; 21% of strain

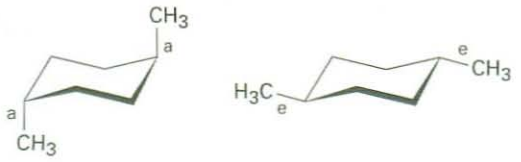
4.9 The cis isomer is less stable because the methyl groups eclipse each other.

4.10 Ten eclipsing interactions; 40 kJ/mol; 35% is relieved.

4.11 Conformation **(a)** is more stable because the methyl groups are farther apart.

4.12

4.13



4.14 Before ring-flip, red and blue are equatorial and green is axial. After ring-flip, red and blue are axial and green is equatorial.

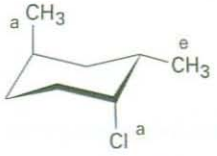
4.15 4.2 kJ/mol

4.16 Cyano group points straight up.

4.17 Equatorial = 70%; axial = 30%

4.18 **(a)** 2.0 kJ/mol **(b)** 11.4 kJ/mol
(c) 2.0 kJ/mol **(d)** 8.0 kJ/mol

4.19



1-Chloro-2,4-dimethylcyclohexane
(less stable chair form)

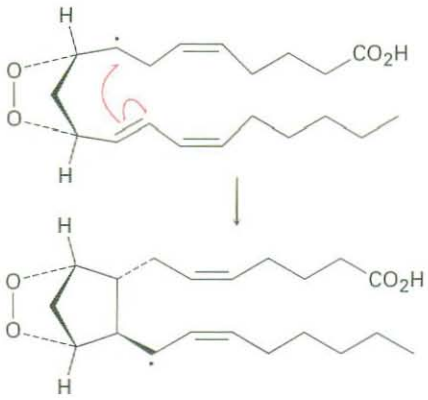
4.20 *trans*-Decalin is more stable because it has no 1,3-diaxial interactions.

CHAPTER 5

5.1 **(a)** Substitution **(b)** Elimination
(c) Addition

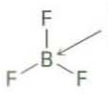
5.2 1-Chloro-2-methylpentane
2-Chloro-2-methylpentane
3-Chloro-2-methylpentane
2-Chloro-4-methylpentane
1-Chloro-4-methylpentane

5.3 A radical addition reaction



5.4 **(a)** Carbon is electrophilic.
(b) Sulfur is nucleophilic.
(c) Nitrogens are nucleophilic.
(d) Oxygen is nucleophilic; carbon is electrophilic.

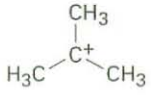
5.5



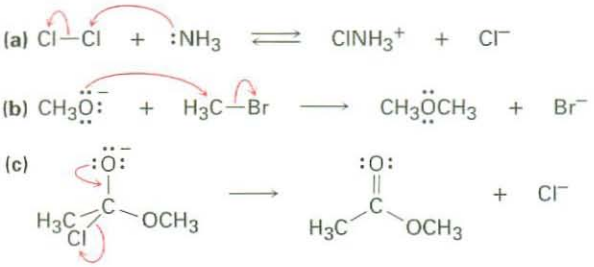
Electrophilic;
vacant *p* orbital

5.6 Bromocyclohexane; chlorocyclohexane

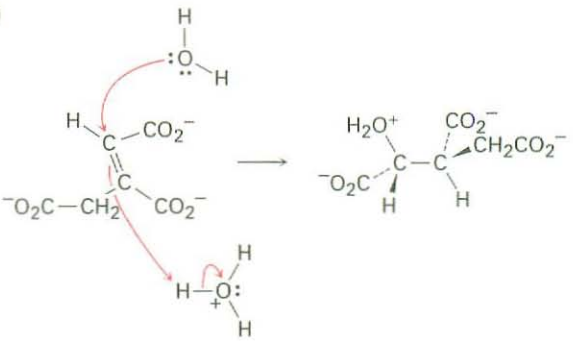
5.7



5.8



5.9

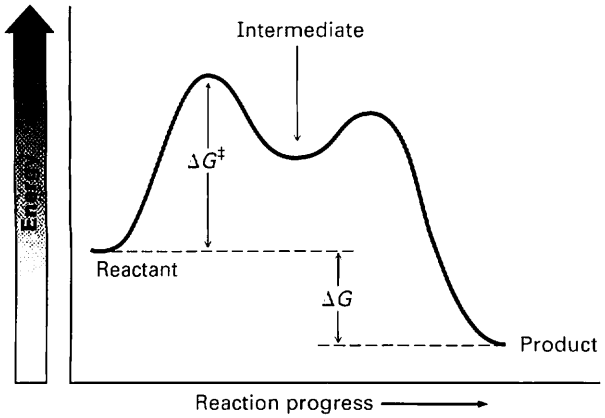


5.10 Negative $\Delta G°$ is more favored.

5.11 Larger K_{eq} is more exergonic.

5.12 Lower $\Delta G^{\ddagger}$ is faster.

5.13



CHAPTER 6

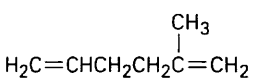
6.1 (a) 1 (b) 2 (c) 2

6.2 (a) 5 (b) 5 (c) 3
(d) 1 (e) 6 (f) 5

6.3 $C_{16}H_{13}ClN_2O$

6.4 (a) 3,4,4-Trimethyl-1-pentene
(b) 3-Methyl-3-hexene
(c) 4,7-Dimethyl-2,5-octadiene
(d) 6-Ethyl-7-methyl-4-nonene

6.5 (a)



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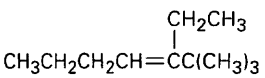

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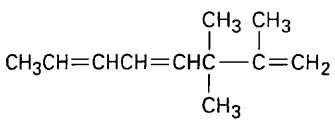
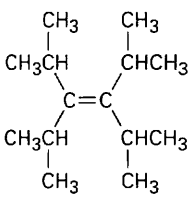


(d)



6.6 (a) 1,2-Dimethylcyclohexene
(b) 4,4-Dimethylcycloheptene
(c) 3-Isopropylcyclopentene

6.7 Compounds (c), (e), and (f) have cis–trans isomers.

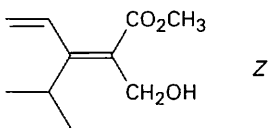
6.8 (a) *cis*-4,5-Dimethyl-2-hexene
(b) *trans*-6-Methyl-3-heptene

6.9 (a) $-Br$ (b) $-Br$ (c) $-CH_2CH_3$
(d) $-OH$ (e) $-CH_2OH$ (f) $-CH{=}O$

6.10 (a) $-Cl$, $-OH$, $-CH_3$, $-H$
(b) $-CH_2OH$, $-CH{=}CH_2$, $-CH_2CH_3$, $-CH_3$
(c) $-CO_2H$, $-CH_2OH$, $-C{\equiv}N$, $-CH_2NH_2$
(d) $-CH_2OCH_3$, $-C{\equiv}N$, $-C{\equiv}CH$, $-CH_2CH_3$

6.11 (a) *Z* (b) *E* (c) *Z* (d) *E*

6.12



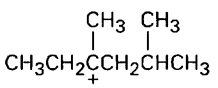
Z

6.13 (a) 2-Methylpropene more stable than 1-butene
(b) *trans*-2-Hexene more stable than *cis*-2-hexene
(c) 1-Methylcyclohexene more stable than 3-methylcyclohexene

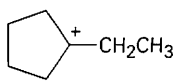
6.14 (a) Chlorocyclohexane
(b) 2-Bromo-2-methylpentane
(c) 4-Methyl-2-pentanol
(d) 1-Bromo-1-methylcyclohexane

6.15 (a) Cyclopentene
(b) 1-Ethylcyclohexene or ethylidenecyclohexane
(c) 3-Hexene
(d) Vinylcyclohexane (cyclohexylethylene)

6.16 (a)



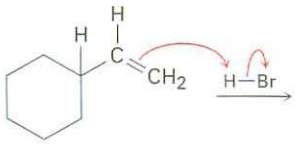
(b)

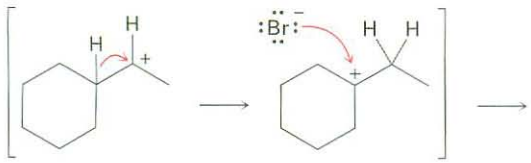


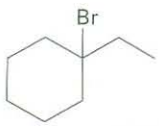
6.17 In the conformation shown, only the methyl-group C–H that is parallel to the carbocation *p* orbital can show hyperconjugation.

6.18 The second step is exergonic; the transition state resembles the carbocation.

6.19







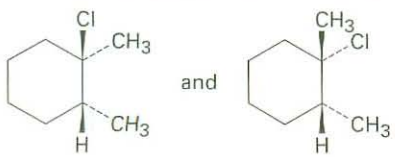
CHAPTER 7

7.1 2-Methyl-2-butene and 2-methyl-1-butene

7.2 Five

7.3 *trans*-1,2-Dichloro-1,2-dimethylcyclohexane

7.4



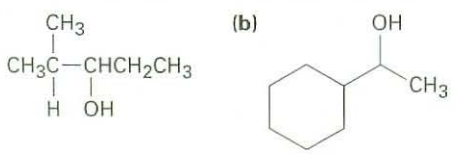
7.5 *trans*-2-Bromocyclopentanol

7.6 Markovnikov

7.7 (a) 2-Pentanol (b) 2-Methyl-2-pentanol

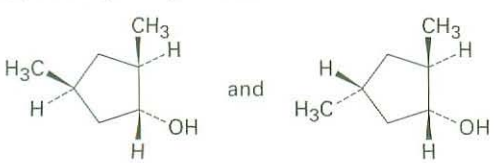
7.8 (a) Oxymercuration of 2-methyl-1-hexene or 2-methyl-2-hexene
(b) Oxymercuration of cyclohexylethylene or hydroboration of ethylidenecyclohexane

7.9

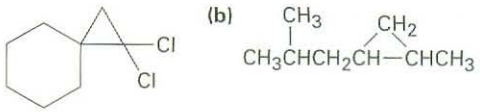


7.10 (a) 3-Methyl-1-butene
(b) 2-Methyl-2-butene
(c) Methylenecyclohexane

7.11

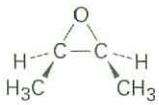


7.12



7.13 (a) 2-Methylpentane
(b) 1,1-Dimethylcyclopentane

7.14



cis-2,3-Epoxybutane

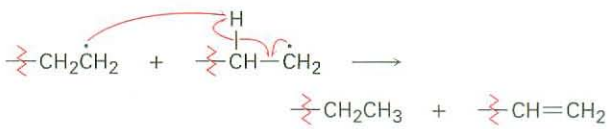
7.15 (a) 1-Methylcyclohexene
(b) 2-Methyl-2-pentene
(c) 1,3-Butadiene

7.16 (a) $CH_3COCH_2CH_2CH_2CH_2CO_2H$
(b) $CH_3COCH_2CH_2CH_2CH_2CHO$

7.17 (a) 2-Methylpropene (b) 3-Hexene

7.18 (a) $H_2C{=}CHOCH_3$ (b) $ClCH{=}CHCl$

7.19



CHAPTER 8

8.1 (a) 2,5-Dimethyl-3-hexyne
(b) 3,3-Dimethyl-1-butyne
(c) 3,3-Dimethyl-4-octyne
(d) 2,5,5-Trimethyl-3-heptyne
(e) 6-Isopropylcyclodecyne
(f) 2,4-Octadiene-6-yne

8.2 1-Hexyne, 2-hexyne, 3-hexyne, 3-methyl-1-pentyne, 4-methyl-1-pentyne, 4-methyl-2-pentyne, 3,3-dimethyl-1-butyne

8.3 (a) 1,1,2,2-Tetrachloropentane
(b) 1-Bromo-1-cyclopentylethylene
(c) 2-Bromo-2-heptene and 3-bromo-2-heptene

8.4 (a) 4-Octanone
(b) 2-Methyl-4-octanone and 7-methyl-4-octanone

8.5 (a) 1-Pentyne (b) 2-Pentyne

8.6 (a) $C_6H_5C{\equiv}CH$ (b) 2,5-Dimethyl-3-hexyne

8.7 (a) Mercuric sulfate–catalyzed hydration of phenylacetylene
(b) Hydroboration/oxidation of cyclopentylacetylene

8.8 (a) Reduce 2-octyne with Li/NH_3
(b) Reduce 3-heptyne with H_2/Lindlar catalyst
(c) Reduce 3-methyl-1-pentyne

8.9 No: (a), (c), (d); yes: (b)

8.10 (a) 1-Pentyne + CH_3I, or propyne + $CH_3CH_2CH_2I$
(b) 3-Methyl-1-butyne + CH_3CH_2I
(c) Cyclohexylacetylene + CH_3I

8.11 $CH_3C{\equiv}CH \xrightarrow[2.\ CH_3I]{1.\ NaNH_2} CH_3C{\equiv}CCH_3$

$\xrightarrow[\text{Lindlar cat.}]{H_2}$ *cis*-$CH_3CH{=}CHCH_3$

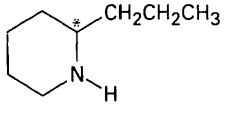
8.12 (a) $KMnO_4$, H_3O^+
(b) H_2/Lindlar
(c) 1. H_2/Lindlar; 2. HBr
(d) 1. H_2/Lindlar; 2. BH_3; 3. NaOH, H_2O_2
(e) 1. H_2/Lindlar; 2. Cl_2
(f) O_3

8.13 (a) 1. $HC{\equiv}CH + NaNH_2$; 2. $CH_3(CH_2)_6CH_2Br$; 3. 2 H_2/Pd
(b) 1. $HC{\equiv}CH + NaNH_2$; 2. $(CH_3)_3CCH_2CH_2I$; 3. 2 H_2/Pd
(c) 1. $HC{\equiv}CH + NaNH_2$; 2. $CH_3CH_2CH_2CH_2I$; 3. BH_3; 4. H_2O_2
(d) 1. $HC{\equiv}CH + NaNH_2$; 2. $CH_3CH_2CH_2CH_2CH_2I$; 3. $HgSO_4$, H_3O^+

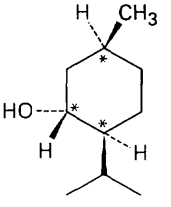
CHAPTER 9

9.1 Chiral: screw, beanstalk, shoe

9.2 (a)



(b)



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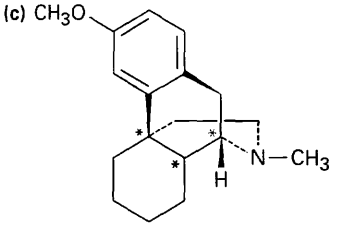

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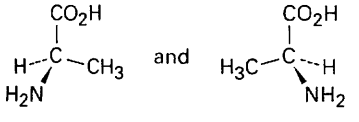
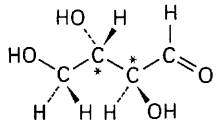


9.4 (a)



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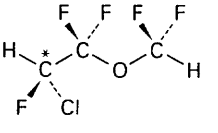


9.5 Levorotatory

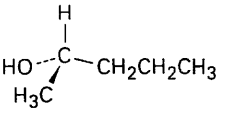
9.6 +16.1°

9.7 (a) $-OH$, $-CH_2CH_2OH$, $-CH_2CH_3$, $-H$
(b) $-OH$, $-CO_2CH_3$, $-CO_2H$, $-CH_2OH$
(c) $-NH_2$, $-CN$, $-CH_2NHCH_3$, $-CH_2NH_2$
(d) $-SSCH_3$, $-SH$, $-CH_2SCH_3$, $-CH_3$

9.8 (a) *S* (b) *R* (c) *S*

9.9 (a) *S* (b) *S* (c) *R*

9.10



9.11 *S*

9.12 (a) *R,R* (b) *S,R* (c) *R,S* (d) *S,S*

Compounds (a) and (d) are enantiomers and are diastereomeric with (b) and (c).

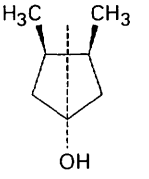
9.13 *R,R*

9.14 *S,S*

9.15 (a), (d)

9.16 Compounds (a) and (c) have meso forms.

9.17



Meso

9.18 The product retains its *S* stereochemistry.

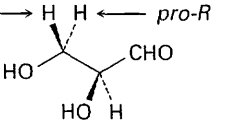
9.19 Two diastereomeric salts: (*R*)-lactic acid plus (*S*)-1-phenylethylamine and (*S*)-lactic acid plus (*S*)-1-phenylethylamine

9.20 (a) Constitutional isomers (b) Diastereomers

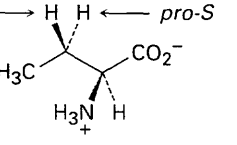
9.21 An optically inactive, non-50:50 mixture of two racemic pairs: (2*R*,4*R*) + (2*S*,4*S*) and (2*R*,4*S*) + (2*S*,4*R*)

9.22 Non-50:50 mixture of two racemic pairs: (1*S*,3*R*) + (1*R*,3*S*) and (1*S*,3*S*) + (1*R*,3*R*)

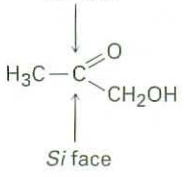
9.23 (a)



(b)

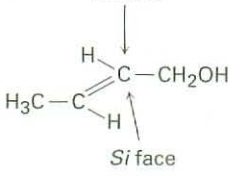


9.24 (a) *Re* face



Si face

(b) *Re* face



Si face

9.25 (*S*)-Lactate

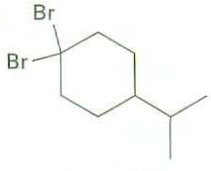
9.26 The —OH adds to the *Re* face of C2, and —H adds to the *Re* face of C3. The overall addition has anti stereochemistry.

CHAPTER 10

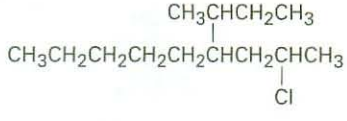
10.1 (a) 1-Iodobutane
(b) 1-Chloro-3-methylbutane
(c) 1,5-Dibromo-2,2-dimethylpentane
(d) 1,3-Dichloro-3-methylbutane
(e) 1-Chloro-3-ethyl-4-iodopentane
(f) 2-Bromo-5-chlorohexane

10.2 (a) $CH_3CH_2CH_2C(CH_3)_2CH(Cl)CH_3$
(b) $CH_3CH_2CH_2C(Cl)_2CH(CH_3)_2$
(c) $CH_3CH_2C(Br)(CH_2CH_3)_2$

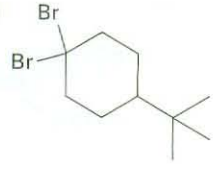
(d)



(e)



(f)



10.3 Chiral: 1-chloro-2-methylpentane, 3-chloro-2-methylpentane, 2-chloro-4-methylpentane

Achiral: 2-chloro-2-methylpentane, 1-chloro-4-methylpentane

10.4 1-Chloro-2-methylbutane (29%), 1-chloro-3-methylbutane (14%), 2-chloro-2-methylbutane (24%), 2-chloro-3-methylbutane (33%)

10.5

10.6 The intermediate allylic radical reacts at the more accessible site and gives the more highly substituted double bond.

10.7 (a) 3-Bromo-5-methylcycloheptene and 3-bromo-6-methylcycloheptene
(b) Four products

10.8 (a) 2-Methyl-2-propanol + HCl
(b) 4-Methyl-2-pentanol + PBr_3
(c) 5-Methyl-1-pentanol + PBr_3
(d) 2,4-Dimethyl-2-hexanol + HCl

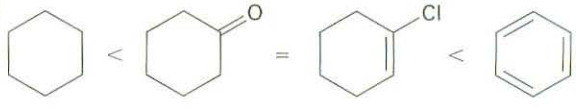
10.9 Both reactions occur.

10.10 React Grignard reagent with D_2O.

10.11 (a) 1. NBS; 2. $(CH_3)_2CuLi$
(b) 1. Li; 2. CuI; 3. $CH_3CH_2CH_2CH_2Br$
(c) 1. BH_3; 2. H_2O_2, NaOH; 3. PBr_3; 4. Li, then CuI; 5. $CH_3(CH_2)_4Br$

10.12

(a)



(b) $CH_3CH_2NH_2 < H_2NCH_2CH_2NH_2 < CH_3C{\equiv}N$

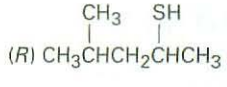
10.13 (a) Reduction (b) Neither

CHAPTER 11

11.1 (*R*)-1-Methylpentyl acetate, $CH_3CO_2CH(CH_3)CH_2CH_2CH_2CH_3$

11.2 (*S*)-2-Butanol

11.3 (*S*)-2-Bromo-4-methylpentane ⟶



11.4 (a) 1-Iodobutane (b) 1-Butanol
(c) 1-Hexyne (d) Butylammonium bromide

11.5 (a) $(CH_3)_2N^-$ (b) $(CH_3)_3N$ (c) H_2S

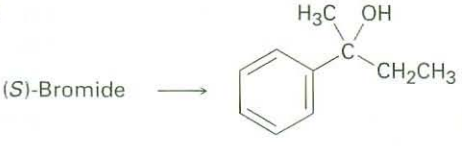
11.6 $CH_3OTos > CH_3Br > (CH_3)_2CHCl > (CH_3)_3CCl$

11.7 Similar to protic solvents

11.8 Racemic 1-ethyl-1-methylhexyl acetate

11.9 90.1% racemization, 9.9% inversion

11.10

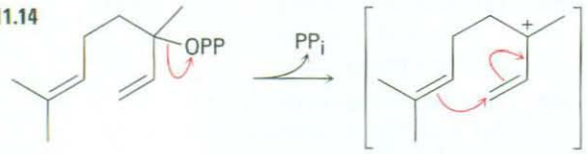


11.11 $H_2C{=}CHCH(Br)CH_3 > CH_3CH(Br)CH_3 > CH_3CH_2Br > H_2C{=}CHBr$

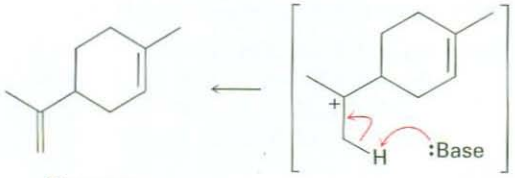
11.12 The same allylic carbocation intermediate is formed.

11.13 (a) S_N1 (b) S_N2

11.14



Linalyl diphosphate



Limonene

11.15 (a) Major: 2-methyl-2-pentene; minor: 4-methyl-2-pentene
(b) Major: 2,3,5-trimethyl-2-hexene; minor: 2,3,5-trimethyl-3-hexene and 2-isopropyl-4-methyl-1-pentene
(c) Major: ethylidenecyclohexane; minor: cyclohexylethylene

11.16 (a) 1-Bromo-3,6-dimethylheptane
(b) 4-Bromo-1,2-dimethylcyclopentane

11.17 (*Z*)-1-Bromo-1,2-diphenylethylene

11.18 (*Z*)-3-Methyl-2-pentene

11.19 Cis isomer reacts faster because the bromine is axial.

11.20 (a) S_N2 (b) E2 (c) S_N1 (d) E1cB

CHAPTER 12

12.1 $C_{19}H_{28}O_2$

12.2 (a) 2-Methyl-2-pentene (b) 2-Hexene

12.3 (a) 43, 71 (b) 82 (c) 58 (d) 86

12.4 102 (M^+), 84 (dehydration), 87 (alpha cleavage), 59 (alpha cleavage)

12.5 X-ray energy is higher; $\lambda = 9.0 \times 10^{-6}$ m is higher in energy.

12.6 (a) 2.4×10^6 kJ/mol (b) 4.0×10^4 kJ/mol
(c) 2.4×10^3 kJ/mol (d) 2.8×10^2 kJ/mol
(e) 6.0 kJ/mol (f) 4.0×10^{-2} kJ/mol

12.7 (a) Ketone or aldehyde (b) Nitro compound
(c) Carboxylic acid

12.8 (a) CH_3CH_2OH has an −OH absorption.
(b) 1-Hexene has a double-bond absorption.
(c) $CH_3CH_2CO_2H$ has a very broad −OH absorption.

12.9 1450–1600 cm^{-1}: aromatic ring; 2100 cm^{-1}: C≡C; 3300 cm^{-1}: C≡C−H

12.10 (a) 1715 cm^{-1} (b) 1730, 2100, 3300 cm^{-1}
(c) 1720, 2500–3100, 3400–3650 cm^{-1}

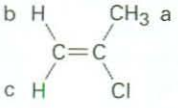
12.11 1690, 1650, 2230 cm^{-1}

CHAPTER 13

13.1 7.5×10^{-5} kJ/mol for ^{19}F; 8.0×10^{-5} kJ/mol for ^1H

13.2 1.2×10^{-4} kJ/mol

13.3 The vinylic C−H protons are nonequivalent.



13.4 (a) 7.27 δ (b) 3.05 δ
(c) 3.46 δ (d) 5.30 δ

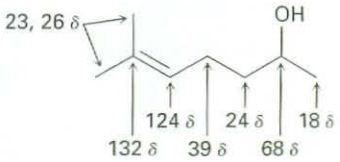
13.5 (a) 420 Hz (b) 2.1 δ (c) 1050 Hz

13.6 (a) 4 (b) 7 (c) 4 (d) 5 (e) 5 (f) 7

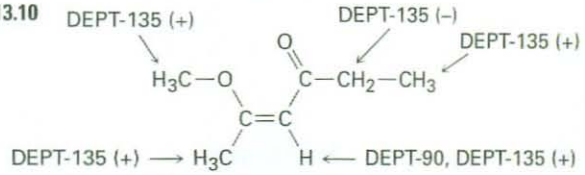
13.7 (a) 1,3-Dimethylcyclopentene
(b) 2-Methylpentane
(c) 1-Chloro-2-methylpropane

13.8 $-CH_3$, 9.3 δ; $-CH_2-$, 27.6 δ; C=O, 174.6 δ; $-OCH_3$, 51.4 δ

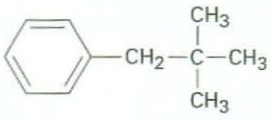
13.9



13.10



13.11



13.12 A DEPT-90 spectrum would show two absorptions for the non-Markovnikov product (RCH=CHBr) but no absorptions for the Markovnikov product ($RBrC{=}CH_2$).

13.13 (a) Enantiotopic (b) Diastereotopic
(c) Diastereotopic (d) Diastereotopic
(e) Diastereotopic (f) Homotopic

13.14 (a) 2 (b) 4 (c) 3 (d) 4 (e) 5 (f) 3

13.15 4

13.16 (a) 1.43 δ (b) 2.17 δ (c) 7.37 δ
(d) 5.30 δ (e) 9.70 δ (f) 2.12 δ

13.17 Seven kinds of protons

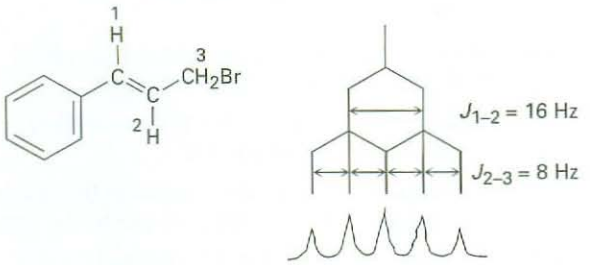
13.18 Two peaks; 3:2 ratio

13.19 (a) $-CHBr_2$, quartet; $-CH_3$, doublet
(b) CH_3O-, singlet; $-OCH_2-$, triplet; $-CH_2Br$, triplet
(c) $ClCH_2-$, triplet; $-CH_2-$, quintet
(d) CH_3-, triplet; $-CH_2-$, quartet; $-CH-$, septet; $(CH_3)_2$, doublet
(e) CH_3-, triplet; $-CH_2-$, quartet; $-CH-$, septet; $(CH_3)_2$, doublet
(f) =CH, triplet, $-CH_2-$, doublet, aromatic C–H, two multiplets

13.20 (a) CH_3OCH_3 (b) $CH_3CH(Cl)CH_3$
(c) $ClCH_2CH_2OCH_2CH_2Cl$
(d) $CH_3CH_2CO_2CH_3$ or $CH_3CO_2CH_2CH_3$

13.21 $CH_3CH_2OCH_2CH_3$

13.22 J_{1-2} = 16 Hz; J_{2-3} = 8 Hz



13.23 1-Chloro-1-methylcyclohexane has a singlet methyl absorption.

CHAPTER 14

14.1 Expected $\Delta H°_{hydrog}$ for allene is −252 kJ/mol. Allene is less stable than a nonconjugated diene, which is less stable than a conjugated diene.

14.2 1-Chloro-2-pentene, 3-chloro-1-pentene, 4-chloro-2-pentene

14.3 4-Chloro-2-pentene predominates in both.

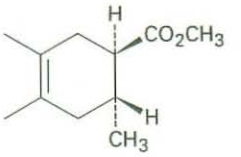
14.4 1,2-Addition: 6-bromo-1,6-dimethylcyclohexene

1,4-Addition: 6-bromo-1,6-dimethylcyclohexene, 3-bromo-1,2-dimethylcyclohexene

14.5 Interconversion occurs by S_N1 dissociation to a common intermediate cation.

14.6 The double bond is more highly substituted.

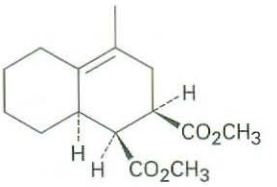
14.7



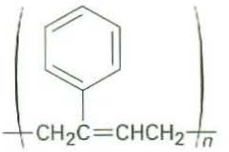
14.8 Good dienophiles: (a), (d)

14.9 Compound (a) is *s*-cis. Compound (c) can rotate to *s*-cis.

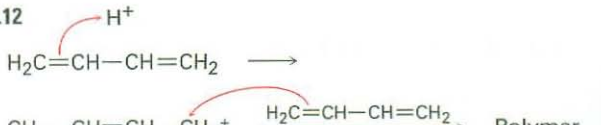
14.10



14.11



14.12



14.13 300–600 kJ/mol; UV energy is greater than IR or NMR energy.

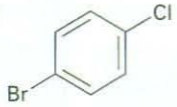
14.14 1.46×10^{-5} M

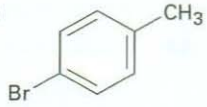
14.15 All except (a) have UV absorptions.

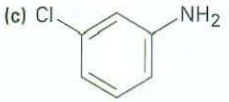
CHAPTER 15

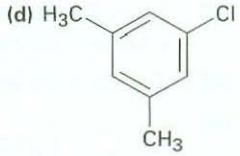
15.1 (a) Meta (b) Para (c) Ortho

15.2 (a) *m*-Bromochlorobenzene
(b) (3-Methylbutyl)benzene
(c) *p*-Bromoaniline
(d) 2,5-Dichlorotoluene
(e) 1-Ethyl-2,4-dinitrobenzene
(f) 1,2,3,5-Tetramethylbenzene

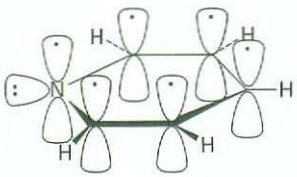
15.3 (a) 

(b) 

(c) 

(d) 

15.4 Pyridine has an aromatic sextet of electrons.



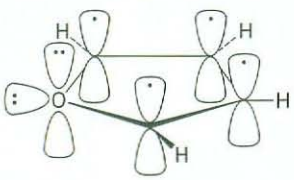
Pyridine

15.5 Cyclodecapentaene is not flat because of steric interactions.

15.6 All C–C bonds are equivalent; one resonance line in both ^{1}H and ^{13}C NMR spectra.

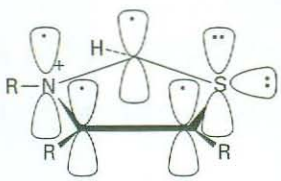
15.7 The cyclooctatetraenyl dianion is aromatic (ten π electrons) and flat.

15.8

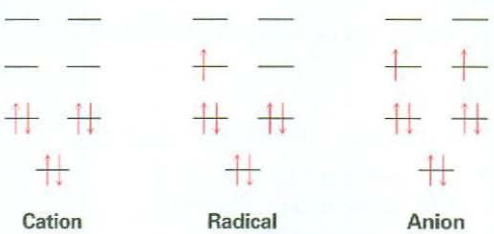


Furan

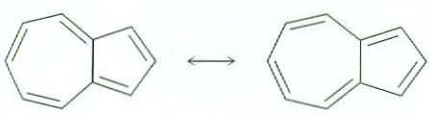
15.9 The thiazolium ring has six π electrons.



15.10


Cation **Radical** **Anion**

15.11



15.12 The three nitrogens in double bonds each contribute one; the remaining nitrogen contributes two.

CHAPTER 16

16.1 *o*-, *m*-, and *p*-Bromotoluene

16.2 *o*-Xylene: 2; *p*-xylene: 1; *m*-xylene: 3

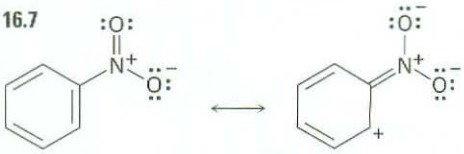
16.3 D^+ does electrophilic substitutions on the ring.

16.4 No rearrangement: (a), (b), (e)

16.5 *tert*-Butylbenzene

16.6 (a) $(CH_3)_2CHCOCl$ (b) PhCOCl

16.7


and others

16.8


and others

16.9 (a) *o*- and *p*-Bromonitrobenzene
(b) *m*-Bromonitrobenzene
(c) *o*- and *p*-Chlorophenol
(d) *o*- and *p*-Bromoaniline

16.10 (a) Phenol > Toluene > Benzene > Nitrobenzene
(b) Phenol > Benzene > Chlorobenzene > Benzoic acid
(c) Aniline > Benzene > Bromobenzene > Benzaldehyde

16.11 Alkylbenzenes are more reactive than benzene itself, but acylbenzenes are less reactive.

16.12 Toluene is more reactive; the trifluoromethyl group is electron-withdrawing.

16.13 The nitrogen electrons are donated to the nearby carbonyl group and are less available to the ring.

16.14 The meta intermediate is most favored.

16.15 (a) Ortho and para to $-OCH_3$
(b) Ortho and para to $-NH_2$
(c) Ortho and para to $-Cl$

16.16 (a) Reaction occurs ortho and para to the $-CH_3$ group.
(b) Reaction occurs ortho and para to the $-OCH_3$ group.

16.17 The phenol is deprotonated by KOH to give an anion that carries out a nucleophilic acyl substitution reaction on the fluoronitrobenzene.

16.18 Only one benzyne intermediate can form from *p*-bromotoluene; two different benzyne intermediates can form from *m*-bromotoluene.

16.19 (a) *m*-Nitrobenzoic acid
(b) *p*-*tert*-Butylbenzoic acid

16.20 A benzyl radical is more stable than a primary alkyl radical by 52 kJ/mol and is similar in stability to an allyl radical.

16.21 1. CH_3CH_2Cl, $AlCl_3$; 2. NBS; 3. KOH, ethanol

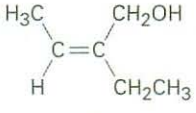
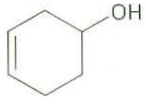
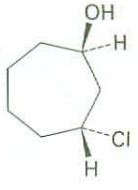
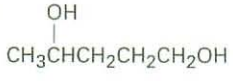
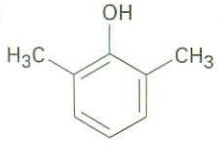
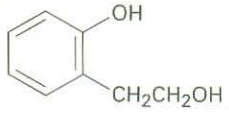
16.22 1. PhCOCl, $AlCl_3$; 2. H_2/Pd

16.23 (a) 1. HNO_3, H_2SO_4; 2. Cl_2, $FeCl_3$
(b) 1. CH_3COCl, $AlCl_3$; 2. Cl_2, $FeCl_3$; 3. H_2/Pd
(c) 1. CH_3CH_2COCl, $AlCl_3$; 2. Cl_2, $FeCl_3$; 3. H_2/Pd; 4. HNO_3, H_2SO_4
(d) 1. CH_3Cl, $AlCl_3$; 2. Br_2, $FeBr_3$; 3. SO_3, H_2SO_4

16.24 (a) Friedel–Crafts acylation does not occur on a deactivated ring.
(b) Rearrangement occurs during Friedel–Crafts alkylation with primary halides; chlorination occurs ortho to the alkyl group.

CHAPTER 17

17.1 (a) 5-Methyl-2,4-hexanediol
(b) 2-Methyl-4-phenyl-2-butanol
(c) 4,4-Dimethylcyclohexanol
(d) *trans*-2-Bromocyclopentanol
(e) 4-Bromo-3-methylphenol
(f) 2-Cyclopenten-1-ol

17.2 (a) 
(b) 
(c) 
(d) 
(e) 
(f) 

17.3 Hydrogen-bonding is more difficult in hindered alcohols.

17.4 (a) $HC{\equiv}CH < (CH_3)_2CHOH < CH_3OH < (CF_3)_2CHOH$
(b) *p*-Methylphenol < Phenol < *p*-(Trifluoromethyl)phenol
(c) Benzyl alcohol < Phenol < *p*-Hydroxybenzoic acid

17.5 The electron-withdrawing nitro group stabilizes an alkoxide ion, but the electron-donating methoxyl group destabilizes the anion.

17.6 (a) 2-Methyl-3-pentanol
(b) 2-Methyl-4-phenyl-2-butanol
(c) *meso*-5,6-Decanediol

17.7 (a) $NaBH_4$ (b) $LiAlH_4$ (c) $LiAlH_4$

17.8 (a) Benzaldehyde or benzoic acid (or ester)
(b) Acetophenone
(c) Cyclohexanone
(d) 2-Methylpropanal or 2-methylpropanoic acid (or ester)

17.9 (a) 1-Methylcyclopentanol
(b) 1,1-Diphenylethanol
(c) 3-Methyl-3-hexanol

17.10 (a) Acetone + CH_3MgBr, or ethyl acetate + 2 CH_3MgBr
(b) Cyclohexanone + CH_3MgBr
(c) 3-Pentanone + CH_3MgBr, or 2-butanone + CH_3CH_2MgBr, or ethyl acetate + 2 CH_3CH_2MgBr
(d) 2-Butanone + PhMgBr, or ethyl phenyl ketone + CH_3MgBr, or acetophenone + CH_3CH_2MgBr
(e) Formaldehyde + PhMgBr
(f) Formaldehyde + $(CH_3)_2CHCH_2MgBr$

17.11 Cyclohexanone + CH_3CH_2MgBr

17.12 1. *p*-TosCl, pyridine; 2. NaCN

17.13 (a) 2-Methyl-2-pentene
(b) 3-Methylcyclohexene
(c) 1-Methylcyclohexene
(d) 2,3-Dimethyl-2-pentene
(e) 2-Methyl-2-pentene

17.14 (a) 1-Phenylethanol (b) 2-Methyl-1-propanol
(c) Cyclopentanol

17.15 (a) Hexanoic acid, hexanal (b) 2-Hexanone
(c) Hexanoic acid, no reaction

17.16 S_N2 reaction of F^- on silicon with displacement of alkoxide ion.

17.17 Protonation of 2-methylpropene gives the *tert*-butyl cation, which carries out an electrophilic aromatic substitution reaction.

17.18 Disappearance of −OH absorption; appearance of C=O

17.19 (a) Singlet (b) Doublet (c) Triplet
(d) Doublet (e) Doublet (f) Singlet

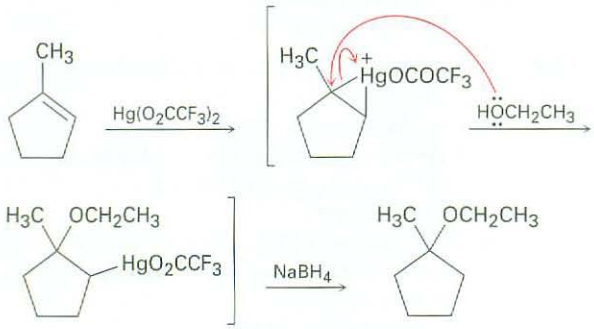
CHAPTER 18

18.1 (a) Diisopropyl ether
(b) Cyclopentyl propyl ether
(c) *p*-Bromoanisole or 4-bromo-1-methoxybenzene
(d) 1-Methoxycyclohexene
(e) Ethyl isobutyl ether
(f) Allyl vinyl ether

18.2 A mixture of diethyl ether, dipropyl ether, and ethyl propyl ether is formed in a 1:1:2 ratio.

18.3 (a) $CH_3CH_2CH_2O^- + CH_3Br$
(b) $PhO^- + CH_3Br$
(c) $(CH_3)_2CHO^- + PhCH_2Br$
(d) $(CH_3)_3CCH_2O^- + CH_3CH_2Br$

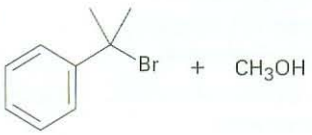
18.4



18.5 (a) Either method (b) Williamson
(c) Alkoxymercuration (d) Williamson

18.6 (a) Bromoethane > 2-Bromopropane > Bromobenzene
(b) Bromoethane > Chloroethane > 1-Iodopropene

18.7 (a)



(b)

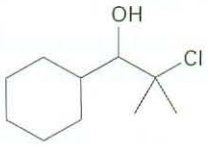
18.8 Protonation of the oxygen atom, followed by E1 reaction

18.9 Br^- and I^- are better nucleophiles than Cl^-.

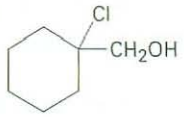
18.10 *o*-(1-Methylallyl)phenol

18.11 Epoxidation of *cis*-2-butene yields *cis*-2,3-epoxybutane, while epoxidation of *trans*-2-butene yields *trans*-2,3-epoxybutane.

18.12 (a)

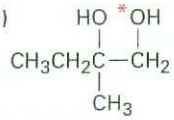


(b)



18.13 (a) 1-Methylcyclohexene + OsO_4; then $NaHSO_3$
(b) 1-Methylcyclohexene + *m*-chloroperoxybenzoic acid, then H_3O^+

18.14 (a)



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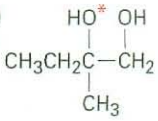

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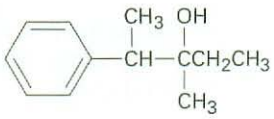


18.16 (a) 2-Butanethiol
(b) 2,2,6-Trimethyl-4-heptanethiol
(c) 2-Cyclopentene-1-thiol
(d) Ethyl isopropyl sulfide
(e) *o*-Di(methylthio)benzene
(f) 3-(Ethylthio)cyclohexanone

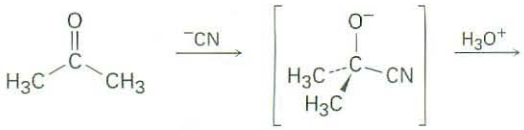
18.17 (a) 1. $LiAlH_4$; 2. PBr_3; 3. $(H_2N)_2C{=}S$; 4. H_2O, NaOH
(b) 1. HBr; 2. $(H_2N)_2C{=}S$; 3. H_2O, NaOH

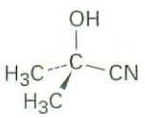
18.18 1,2-Epoxybutane

PREVIEW OF CARBONYL CHEMISTRY

1. Acetyl chloride is more electrophilic than acetone.

2.





3. (a) Nucleophilic acyl substitution
(b) Nucleophilic addition
(c) Carbonyl condensation

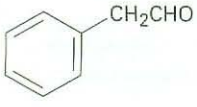
CHAPTER 19

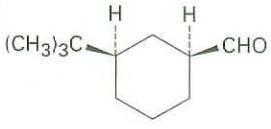
19.1 (a) 2-Methyl-3-pentanone
(b) 3-Phenylpropanal
(c) 2,6-Octanedione
(d) *trans*-2-Methylcyclohexanecarbaldehyde
(e) Pentanedial
(f) *cis*-2,5-Dimethylcyclohexanone

19.2

(a) CH_3CHCH_2CHO (with CH_3 branch)

(b) $CH_3CHCH_2CCH_3$ (with Cl and O)

(c) 

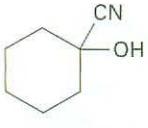
(d) 

(e) $H_2C{=}CCH_2CHO$ (with CH_3 branch)

(f) $CH_3CH_2CHCH_2CH_2CHCHO$ (with CH_3 and CH_3CHCl branches)

19.3 (a) PCC (b) 1. O_3; 2. Zn (c) DIBAH

19.4 (a) $Hg(OAc)_2$, H_3O^+
(b) 1. CH_3COCl, $AlCl_3$; 2. Br_2, $FeBr_3$
(c) 1. Mg; 2. CH_3CHO; 3. H_3O^+; 4. PCC
(d) 1. BH_3; 2. H_2O_2, NaOH; 3. PCC

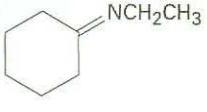
19.5 

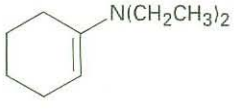
19.6 The electron-withdrawing nitro group in *p*-nitrobenzaldehyde polarizes the carbonyl group.

19.7 $CCl_3CH(OH)_2$

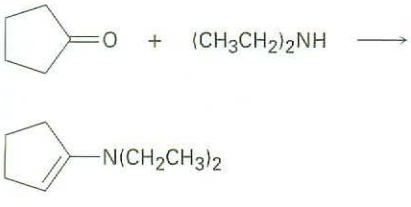
19.8 Labeled water adds reversibly to the carbonyl group.

19.9 The equilibrium is unfavorable for sterically hindered ketones.

19.10 

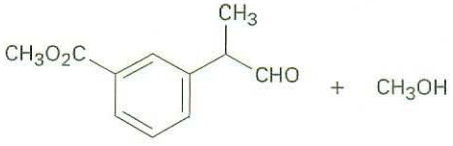
and 

19.11 The steps are the exact reverse of the forward reaction.

19.12 

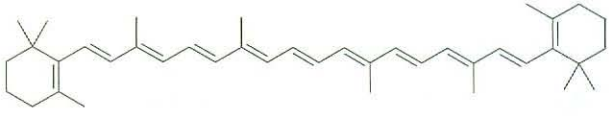
19.13 (a) H_2/Pd (b) N_2H_4, KOH
(c) 1. H_2/Pd; 2. N_2H_4, KOH

19.14 The mechanism is identical to that between a ketone and 2 equivalents of a monoalcohol (text Figure 19.12).

19.15 

19.16 (a) Cyclohexanone + $(Ph)_3P{=}CHCH_3$
(b) 2-Cyclohexenone + $(Ph)_3P{=}CH_2$
(c) Acetone + $(Ph)_3P{=}CHCH_2CH_2CH_3$
(d) Acetone + $(Ph)_3P{=}CHPh$
(e) $PhCOCH_3$ + $(Ph)_3P{=}CHPh$
(f) 2-Cyclohexenone + $(Ph)_3P{=}CH_2$

19.17



***β*-Carotene**

19.18 Intramolecular Cannizzaro reaction

19.19 Addition of the *pro-R* hydrogen of NADH takes place on the *Re* face of pyruvate.

19.20 The −OH group adds to the *Re* face at C2, and −H adds to the *Re* face at C3, to yield (2*R*,3*S*)-isocitrate.

19.21 

19.22 (a) 3-Buten-2-one + $(CH_3CH_2CH_2)_2CuLi$
(b) 3-Methyl-2-cyclohexenone + $(CH_3)_2CuLi$
(c) 4-*tert*-Butyl-2-cyclohexenone + $(CH_3CH_2)_2CuLi$
(d) Unsaturated ketone + $(H_2C{=}CH)_2CuLi$

19.23 Look for appearance of either an alcohol or a saturated ketone in the product.

19.24 (a) 1715 cm^{-1} (b) 1685 cm^{-1}
(c) 1750 cm^{-1} (d) 1705 cm^{-1}
(e) 1715 cm^{-1} (f) 1705 cm^{-1}

19.25 (a) Different peaks due to McLafferty rearrangement
(b) Different peaks due to α cleavage and McLafferty rearrangement
(c) Different peaks due to McLafferty rearrangement

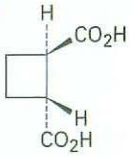
19.26 IR: 1750 cm^{-1}; MS: 140, 84

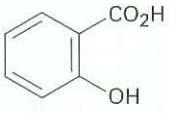
CHAPTER 20

20.1 (a) 3-Methylbutanoic acid
(b) 4-Bromopentanoic acid
(c) 2-Ethylpentanoic acid
(d) *cis*-4-Hexenoic acid
(e) 2,4-Dimethylpentanenitrile
(f) *cis*-1,3-Cyclopentanedicarboxylic acid

20.2

(a) $CH_3CH_2CH_2CH(CH_3)CHCO_2H$ (b) $CH_3CH(CH_3)CH_2CH_2CO_2H$

(c) 

(d) 

(e) 

(f) $CH_3CH_2CH{=}CHCN$

20.3 Dissolve the mixture in ether, extract with aqueous NaOH, separate and acidify the aqueous layer, and extract with ether.

20.4 43%

20.5 (a) 82% dissociation (b) 73% dissociation

20.6 Lactic acid is stronger because of the inductive effect of the −OH group.

20.7 The dianion is destabilized by repulsion between charges.

20.8 More reactive

20.9 (a) *p*-Methylbenzoic acid < Benzoic acid < *p*-Chlorobenzoic acid
(b) Acetic acid < Benzoic acid < *p*-Nitrobenzoic acid

20.10 (a) 1. Mg; 2. CO_2; 3. H_3O^+
(b) 1. Mg; 2. CO_2; 3. H_3O^+ or 1. NaCN; 2. H_3O^+

20.11 1. NaCN; 2. H_3O^+; 3. $LiAlH_4$

20.12 1. PBr_3; 2. NaCN; 3. H_3O^+; 4. $LiAlH_4$

20.13 (a) Propanenitrile + CH_3CH_2MgBr, then H_3O^+
(b) *p*-Nitrobenzonitrile + CH_3MgBr, then H_3O^+

20.14 1. NaCN; 2. CH_3CH_2MgBr, then H_3O^+

20.15 A carboxylic acid has a very broad −OH absorption at 2500–3300 cm^{-1}.

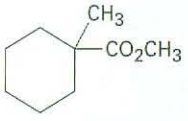
20.16 4-Hydroxycyclohexanone: H−C−O absorption near 4 δ in ^1H spectrum and C=O absorption near 210 δ in ^{13}C spectrum. Cyclopentanecarboxylic acid: $-CO_2H$ absorption near 12 δ in ^1H spectrum and $-CO_2H$ absorption near 170 δ in ^{13}C spectrum.

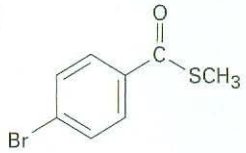
CHAPTER 21

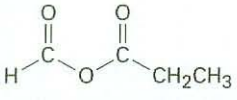
21.1 (a) 4-Methylpentanoyl chloride
(b) Cyclohexylacetamide
(c) Isopropyl 2-methylpropanoate
(d) Benzoic anhydride
(e) Isopropyl cyclopentanecarboxylate
(f) Cyclopentyl 2-methylpropanoate
(g) *N*-Methyl-4-pentenamide
(h) (*R*)-2-Hydroxypropanoyl phosphate
(i) Ethyl 2,3-Dimethyl-2-butenethioate

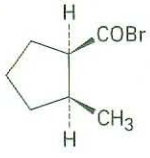
21.2

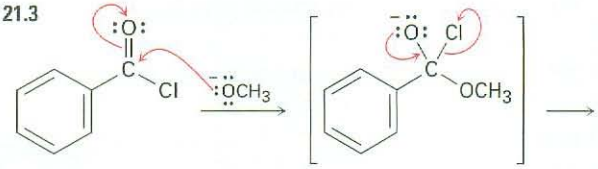
(a) $C_6H_5CO_2C_6H_5$ (b) $CH_3CH_2CH_2CON(CH_3)CH_2CH_3$

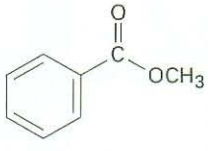
(c) $(CH_3)_2CHCH_2CH(CH_3)COCl$ (d) 

(e) $CH_3CH_2CCH_2COCH_2CH_3$ (f) 

(g) 

(h) 

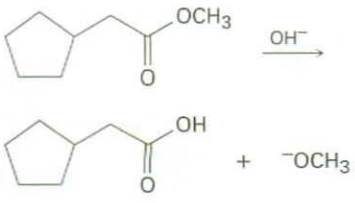
21.3 



21.4 (a) Acetyl chloride > Methyl acetate > Acetamide
(b) Hexafluoroisopropyl acetate > 2,2,2-Trichloroethyl acetate > Methyl acetate

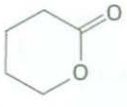
21.5 (a) $CH_3CO_2^-\ Na^+$ (b) CH_3CONH_2
(c) $CH_3CO_2CH_3 + CH_3CO_2^-\ Na^+$
(d) $CH_3CONHCH_3$

21.6



21.7 (a) Acetic acid + 1-butanol
(b) Butanoic acid + methanol
(c) Cyclopentanecarboxylic acid + isopropyl alcohol

21.8



21.9 (a) Propanoyl chloride + methanol
(b) Acetyl chloride + ethanol
(c) Benzoyl chloride + ethanol

21.10 Benzoyl chloride + cyclohexanol

21.11 This is a typical nucleophilic acyl substitution reaction, with morpholine as the nucleophile and chloride as the leaving group.

21.12 (a) Propanoyl chloride + methylamine
(b) Benzoyl chloride + diethylamine
(c) Propanoyl chloride + ammonia

21.13 (a) Benzoyl chloride + $[(CH_3)_2CH]_2CuLi$, or 2-methylpropanoyl chloride + Ph_2CuLi
(b) 2-Propenoyl chloride + $(CH_3CH_2CH_2)_2CuLi$, or butanoyl chloride + $(H_2C{=}CH)_2CuLi$

21.14 This is a typical nucleophilic acyl substitution reaction, with *p*-hydroxyaniline as the nucleophile and acetate ion as the leaving group.

21.15 Monomethyl ester of benzene-1,2-dicarboxylic acid

21.16 Reaction of a carboxylic acid with an alkoxide ion gives the carboxylate ion.

21.17 $HOCH_2CH_2CH_2CHO$

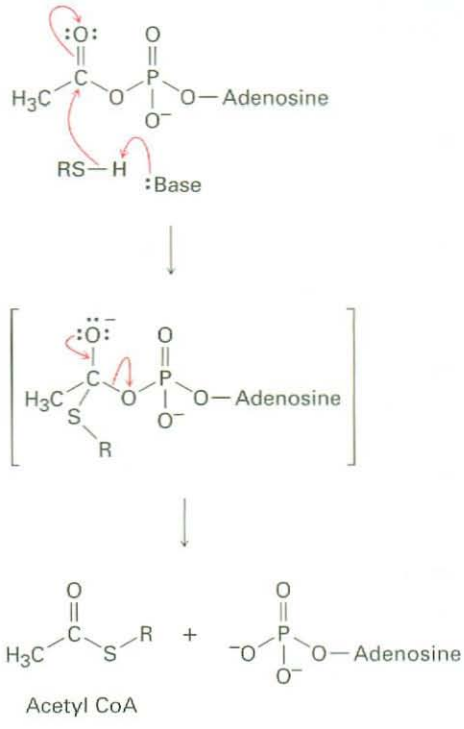
21.18 (a) $CH_3CH_2CH_2CH(CH_3)CH_2OH$
(b) $PhOH + PhCH_2OH$

21.19 (a) Ethyl benzoate + 2 CH_3MgBr
(b) Ethyl acetate + 2 PhMgBr
(c) Ethyl pentanoate + 2 CH_3CH_2MgBr

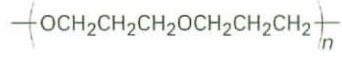
21.20 (a) H_2O, NaOH
(b) Benzoic acid + BH_3
(c) $LiAlH_4$

21.21 1. Mg; 2. CO_2, then H_3O^+; 3. $SOCl_2$; 4. $(CH_3)_2NH$; 5. $LiAlH_4$

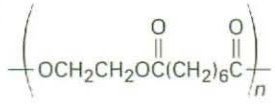
21.22



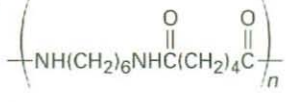
21.23 (a)



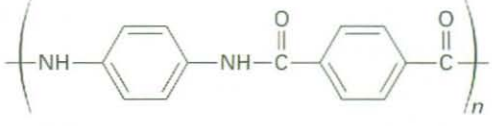
(b)



(c)



21.24

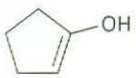
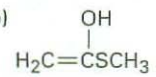
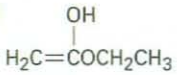
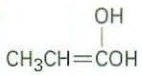


21.25 The product has a large amount of cross-linking.

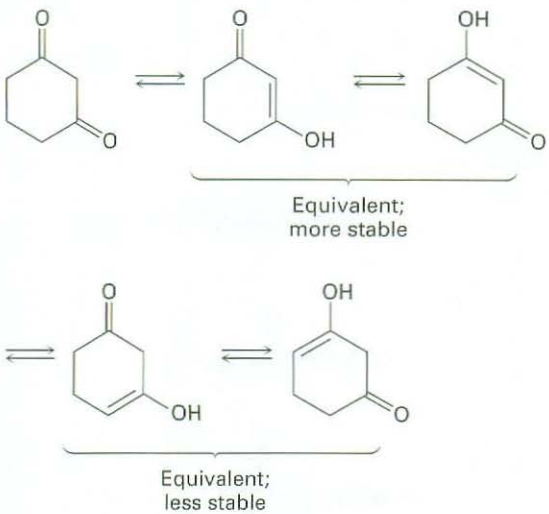
21.26 (a) Ester (b) Acid chloride
(c) Carboxylic acid
(d) Aliphatic ketone or cyclohexanone

21.27 (a) $CH_3CH_2CH_2CO_2CH_2CH_3$ and other possibilities
(b) $CH_3CON(CH_3)_2$
(c) $CH_3CH{=}CHCOCl$ or $H_2C{=}C(CH_3)COCl$

CHAPTER 22

22.1 (a) 
(b) 
(c) 
(d) $CH_3CH{=}CHOH$
(e) 
(f) 

22.2 (a) 4 (b) 3 (c) 3 (d) 2 (e) 4 (f) 5

22.3 

22.4 Acid-catalyzed formation of an enol is followed by deuteronation of the enol double bond and dedeuteronation of oxygen.

22.5 1. Br_2; 2. Pyridine, heat

22.6 The intermediate α-bromo acid bromide undergoes a nucleophilic acyl substitution reaction with methanol to give an α-bromo ester.

22.7 (a) $CH_3C\underline{H}_2CHO$ (b) $(CH_3)_3CCOC\underline{H}_3$
(c) $CH_3CO_2\underline{H}$ (d) $PhCON\underline{H}_2$
(e) $CH_3CH_2C\underline{H}_2CN$ (f) $C\underline{H}_3CON(CH_3)_2$

22.8 $^{-}{:}CH_2C{\equiv}N{:} \longleftrightarrow H_2C{=}C{=}\ddot{N}{:}^{-}$

22.9 Acid is regenerated, but base is used stoichiometrically.

22.10 (a) 1. $Na^+\ ^-OEt$; 2. $PhCH_2Br$; 3. H_3O^+
(b) 1. $Na^+\ ^-OEt$; 2. $CH_3CH_2CH_2Br$; 3. $Na^+\ ^-OEt$; 4. CH_3Br; 5. H_3O^+
(c) 1. $Na^+\ ^-OEt$; 2. $(CH_3)_2CHCH_2Br$; 3. H_3O^+

22.11 Malonic ester has only two acidic hydrogens to be replaced.

22.12 1. $Na^+\ ^-OEt$; 2. $(CH_3)_2CHCH_2Br$; 3. $Na^+\ ^-OEt$; 4. CH_3Br; 5. H_3O^+

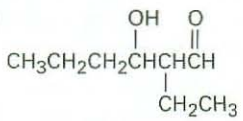
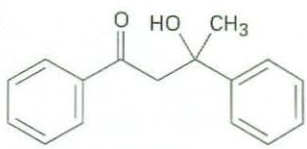
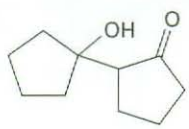
22.13 (a) $(CH_3)_2CHCH_2Br$ (b) $PhCH_2CH_2Br$

22.14 None can be prepared.

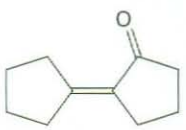
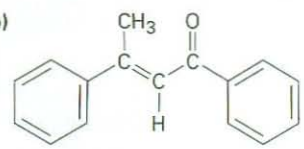
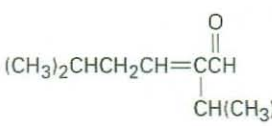
22.15 1. 2 $Na^+\ ^-OEt$; 2. $BrCH_2CH_2CH_2CH_2Br$; 3. H_3O^+

22.16 (a) Alkylate phenylacetone with CH_3I
(b) Alkylate pentanenitrile with CH_3CH_2I
(c) Alkylate cyclohexanone with $H_2C{=}CHCH_2Br$
(d) Alkylate cyclohexanone with excess CH_3I
(e) Alkylate $C_6H_5COCH_2CH_3$ with CH_3I
(f) Alkylate methyl 3-methylbutanoate with CH_3CH_2I

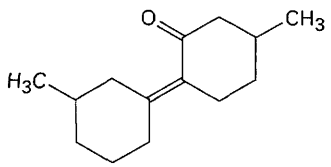
CHAPTER 23

23.1 (a) 
(b) 
(c) 

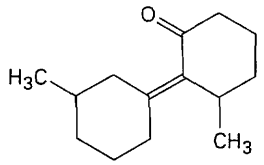
23.2 The reverse reaction is the exact opposite of the forward reaction.

23.3 (a) 
(b) 
(c) 

23.4



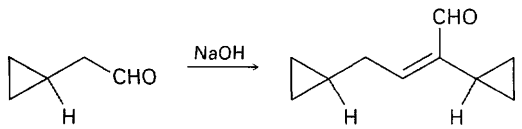
and



23.5 (a) Not an aldol product (b) 3-Pentanone

23.6 1. NaOH; 2. $LiAlH_4$; 3. H_2/Pd

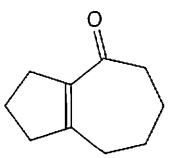
23.7



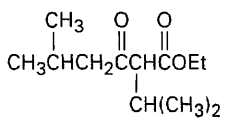
23.8 (a) $C_6H_5CHO + CH_3COCH_3$
(b), (c) Not easily prepared

23.9 The CH_2 position between the two carbonyl groups is so acidic that it is completely deprotonated to give a stable enolate ion.

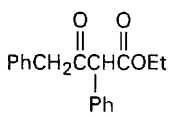
23.10



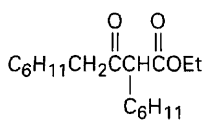
23.11 (a)



(b)

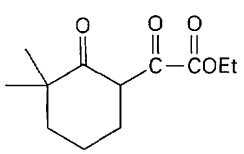


(c)

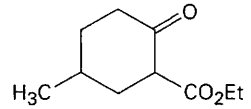


23.12 The cleavage reaction is the exact reverse of the forward reaction.

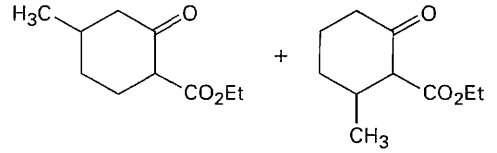
23.13



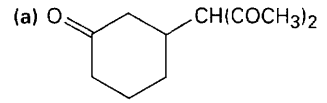
23.14



23.15

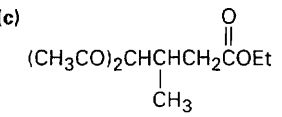


23.16 (a)



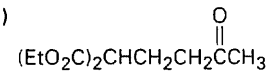
(b) $(CH_3CO)_2CHCH_2CH_2CN$

(c)



23.17

(a)



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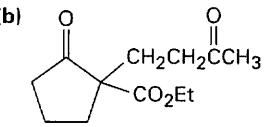
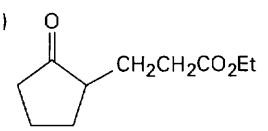


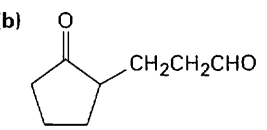
23.18 $CH_3CH_2COCH{=}CH_2 + CH_3CH_2NO_2$

23.19

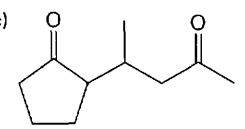
(a)



(b)

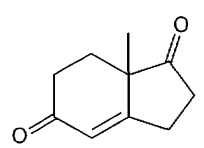


(c)



23.20 (a) Cyclopentanone enamine + propenenitrile
(b) Cyclohexanone enamine + methyl propenoate

23.21



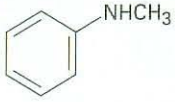
23.22 2,5,5-Trimethyl-1,3-cyclohexanedione + 1-penten-3-one

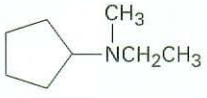
CHAPTER 24

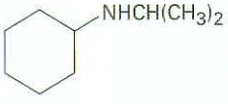
24.1 (a) *N*-Methylethylamine
(b) Tricyclohexylamine
(c) *N*-Methyl-*N*-propylcyclohexylamine
(d) *N*-Methylpyrrolidine
(e) Diisopropylamine
(f) 1,3-Butanediamine

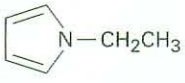
24.2

(a) $[(CH_3)_2CH]_3N$ (b) $(H_2C{=}CHCH_2)_2NH$

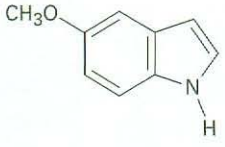
(c) 

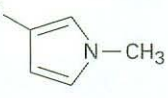
(d) 

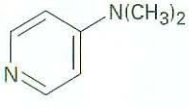
(e) 

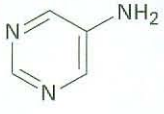
(f) 

24.3

(a) 

(b) 

(c) 

(d) 

24.4 (a) $CH_3CH_2NH_2$ (b) NaOH
(c) CH_3NHCH_3

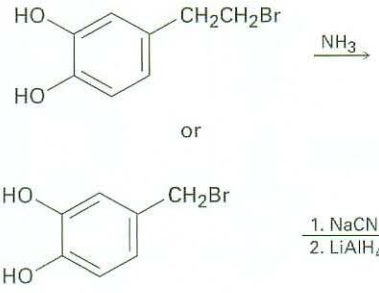
24.5 Propylamine is stronger; benzylamine $pK_b = 4.67$; propylamine $pK_b = 3.29$

24.6 (a) *p*-Nitroaniline < *p*-Aminobenzaldehyde < *p*-Bromoaniline
(b) *p*-Aminoacetophenone < *p*-Chloroaniline < *p*-Methylaniline
(c) *p*-(Trifluoromethyl)aniline < *p*-(Fluoromethyl)aniline < *p*-Methylaniline

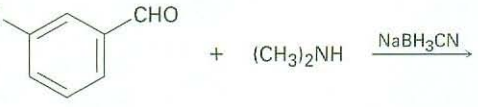
24.7 Pyrimidine is essentially 100% neutral (unprotonated).

24.8 (a) Propanenitrile or propanamide
(b) *N*-Propylpropanamide
(c) Benzonitrile or benzamide
(d) *N*-Phenylacetamide

24.9 The reaction takes place by two nucleophilic acyl substitution reactions.

24.10 

24.11 (a) Ethylamine + acetone, or isopropylamine + acetaldehyde
(b) Aniline + acetaldehyde
(c) Cyclopentylamine + formaldehyde, or methylamine + cyclopentanone

24.12 

24.13 (a) 4,4-Dimethylpentanamide or 4,4-dimethylpentanoyl azide
(b) *p*-Methylbenzamide or *p*-methylbenzoyl azide

24.14 (a) 3-Octene and 4-octene
(b) Cyclohexene
(c) 3-Heptene
(d) Ethylene and cyclohexene

24.15 $H_2C{=}CHCH_2CH_2CH_2N(CH_3)_2$

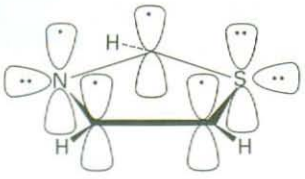
24.16 1. HNO_3, H_2SO_4; 2. H_2/PtO_2; 3. $(CH_3CO)_2O$; 4. $HOSO_2Cl$; 5. aminothiazole; 6. H_2O, NaOH

24.17 (a) 1. HNO_3, H_2SO_4; 2. H_2/PtO_2; 3. 2 CH_3Br
(b) 1. HNO_3, H_2SO_4; 2. H_2/PtO_2; 3. $(CH_3CO)_2O$; 4. Cl_2; 5. H_2O, NaOH
(c) 1. HNO_3, H_2SO_4; 2. Cl_2, $FeCl_3$; 3. $SnCl_2$
(d) 1. HNO_3, H_2SO_4; 2. H_2/PtO_2; 3. $(CH_3CO)_2O$; 4. 2 CH_3Cl, $AlCl_3$; 5. H_2O, NaOH

24.18 (a) 1. CH_3Cl, $AlCl_3$; 2. HNO_3, H_2SO_4; 3. $SnCl_2$; 4. $NaNO_2$, H_2SO_4; 5. CuBr; 6. $KMnO_4$, H_2O
(b) 1. HNO_3, H_2SO_4; 2. Br_2, $FeBr_3$; 3. $SnCl_2$, H_3O^+; 4. $NaNO_2$, H_2SO_4; 5. CuCN; 6. H_3O^+
(c) 1. HNO_3, H_2SO_4; 2. Cl_2, $FeCl_3$; 3. $SnCl_2$; 4. $NaNO_2$, H_2SO_4; 5. CuBr
(d) 1. CH_3Cl, $AlCl_3$; 2. HNO_3, H_2SO_4; 3. $SnCl_2$; 4. $NaNO_2$, H_2SO_4; 5. CuCN; 6. H_3O^+
(e) 1. HNO_3, H_2SO_4; 2. H_2/PtO_2; 3. $(CH_3CO)_2O$; 4. 2 Br_2; 5. H_2O, NaOH; 6. $NaNO_2$, H_2SO_4; 7. CuBr

24.19 1. HNO_3, H_2SO_4; 2. $SnCl_2$; 3a. 2 equiv. CH_3I; 3b. $NaNO_2$, H_2SO_4; 4. product of 3a + product of 3b

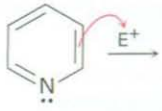
24.20

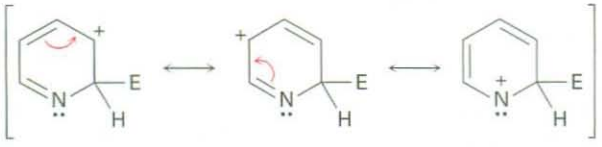


24.21 4.1% protonated

24.22

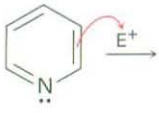
Attack at C2:

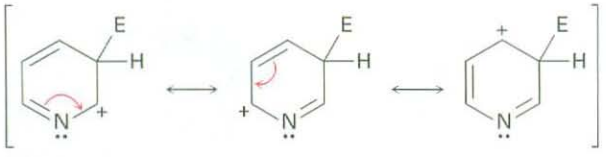




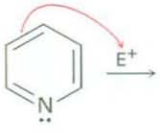
Unfavorable

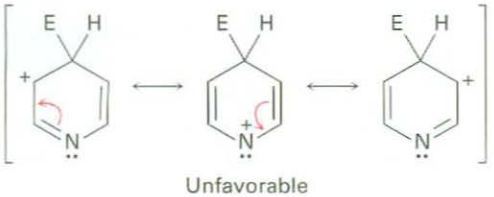
Attack at C3:





Attack at C4:

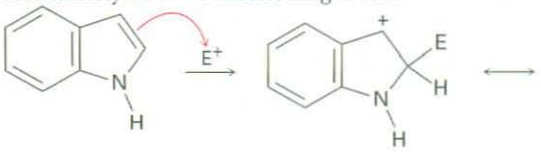


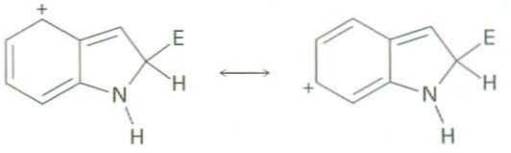


Unfavorable

24.23 The side-chain nitrogen is more basic than the ring nitrogen.

24.24 Reaction at C2 is disfavored because the aromaticity of the benzene ring is lost.





24.25 $(CH_3)_3CCOCH_3 \longrightarrow (CH_3)_3CCH(NH_2)CH_3$

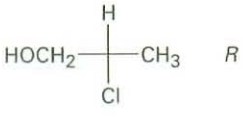
CHAPTER 25

25.1 (a) Aldotetrose
(b) Ketopentose
(c) Ketohexose
(d) Aldopentose

25.2 (a) *S* (b) *R* (c) *S*

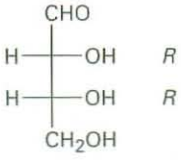
25.3 A, B, and C are the same.

25.4



R

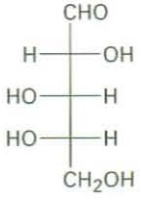
25.5



R, *R*

25.6 (a) L-Erythrose; 2*S*,3*S*
(b) D-Xylose; 2*R*,3*S*,4*R*
(c) D-Xylulose; 3*S*,4*R*

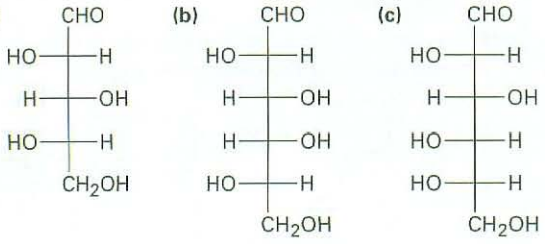
25.7



L-(+)-Arabinose

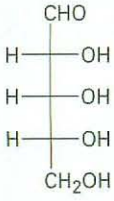
25.8

(a) (b) (c)



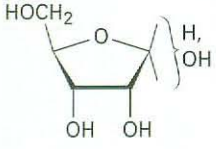
25.9 16 D and 16 L aldoheptoses

25.10

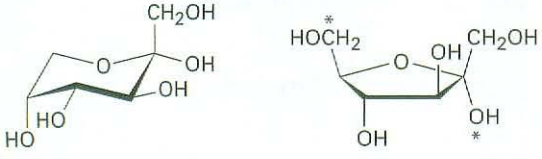


D-Ribose

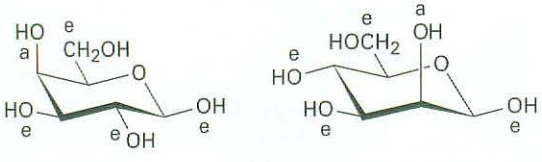
25.11



25.12

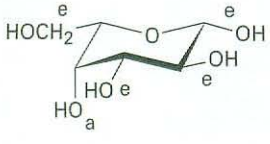


25.13



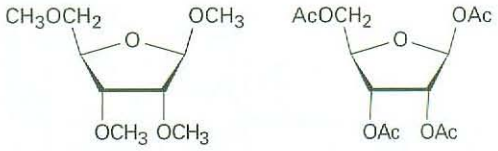
β-D-Galactopyranose β-D-Mannopyranose

25.14



25.15 α-D-Allopyranose

25.16



25.17 D-Galactitol has a plane of symmetry and is a meso compound, whereas D-glucitol is chiral.

25.18 The −CHO end of L-gulose corresponds to the $-CH_2OH$ end of D-glucose after reduction.

25.19 D-Allaric acid has a symmetry plane and is a meso compound, but D-glucaric acid is chiral.

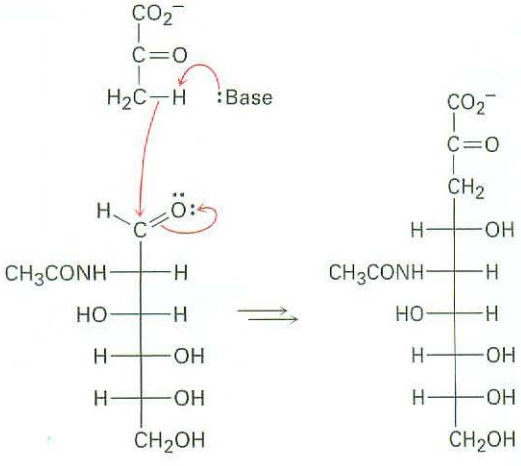
25.20 D-Allose and D-galactose yield meso aldaric acids; the other six D-hexoses yield optically active aldaric acids.

25.21 D-Allose + D-altrose

25.22 L-Xylose

25.23 D-Xylose and D-lyxose

25.24



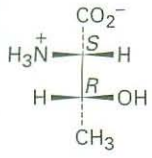
25.25 (a) The hemiacetal ring is reduced.
(b) The hemiacetal ring is oxidized.
(c) All hydroxyl groups are acetylated.

CHAPTER 26

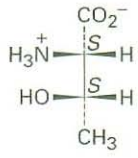
26.1 Aromatic: Phe, Tyr, Trp, His; sulfur-containing: Cys, Met; alcohols: Ser, Thr; hydrocarbon side chains: Ala, Ile, Leu, Val, Phe

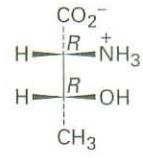
26.2 The sulfur atom in the $-CH_2SH$ group of cysteine makes the side chain higher in priority than the $-CO_2H$ group.

26.3



L-Threonine





Diastereomers of L-threonine

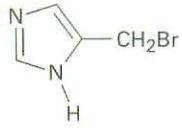
26.4 Net positive at pH = 5.3; net negative at pH = 7.3

26.5 **(a)** Start with 3-phenylpropanoic acid:
1. Br_2, PBr_3; 2. NH_3

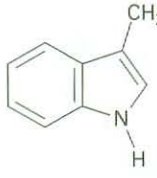
(b) Start with 3-methylbutanoic acid:
1. Br_2, PBr_3; 2. NH_3

26.6 **(a)** $(CH_3)_2CHCH_2Br$

(b)

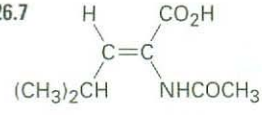


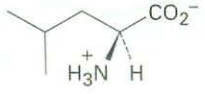
(c)



(d) $CH_3SCH_2CH_2Br$

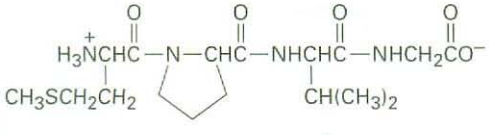
26.7



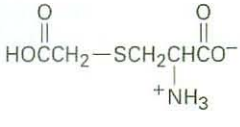


26.8 Val-Tyr-Gly (VYG), Tyr-Gly-Val (YGV), Gly-Val-Tyr (GVY), Val-Gly-Tyr (VGY), Tyr-Val-Gly (YVG), Gly-Tyr-Val (GYV)

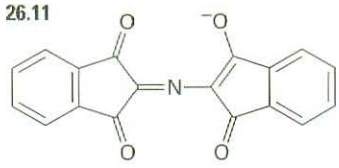
26.9



26.10



26.11

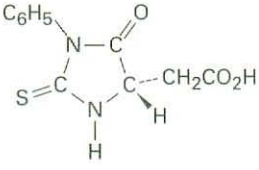


26.12 Trypsin: Asp-Arg + Val-Tyr-Ile-His-Pro-Phe

Chymotrypsin: Asp-Arg-Val-Tyr + Ile-His-Pro-Phe

26.13 Methionine

26.14



26.15 **(a)** Arg-Pro-Leu-Gly-Ile-Val
(b) Val-Met-Trp-Asp-Val-Leu (VMWNVL)

26.16 This is a typical nucleophilic acyl substitution reaction, with the amine of the amino acid as the nucleophile and *tert*-butyl carbonate as the leaving group. The *tert*-butyl carbonate then loses CO_2 and gives *tert*-butoxide, which is protonated.

26.17 (1) Protect the amino group of leucine.
(2) Protect the carboxylic acid group of alanine.
(3) Couple the protected amino acids with DCC.
(4) Remove the leucine protecting group.
(5) Remove the alanine protecting group.

26.18 **(a)** Lyase **(b)** Hydrolase **(c)** Oxidoreductase

CHAPTER 27

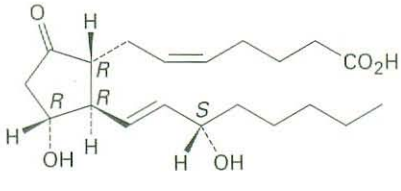
27.1 $CH_3(CH_2)_{18}CO_2CH_2(CH_2)_{30}CH_3$

27.2 Glyceryl tripalmitate is higher melting.

27.3 $[CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2^-]_2\ Mg^{2+}$

27.4 Glyceryl dioleate monopalmitate → glycerol + 2 sodium oleate + sodium palmitate

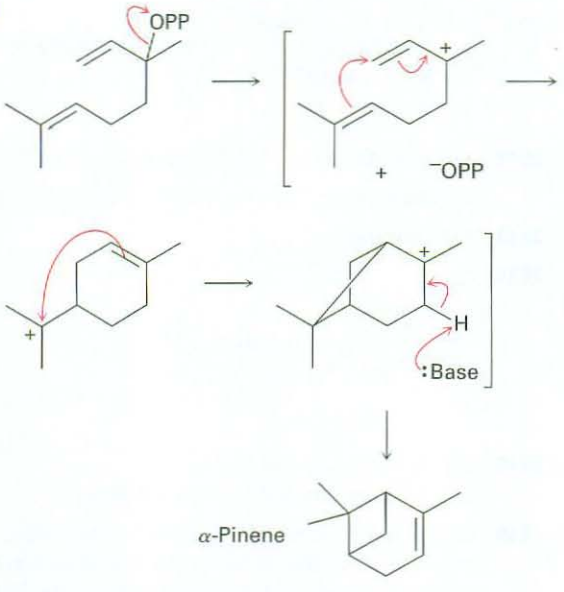
27.5



27.6 The *pro-S* hydrogen is cis to the $-CH_3$ group; the *pro-R* hydrogen is trans.

27.7

(a)



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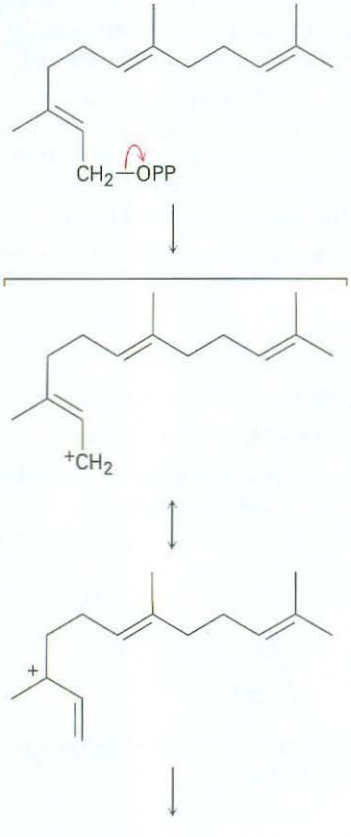
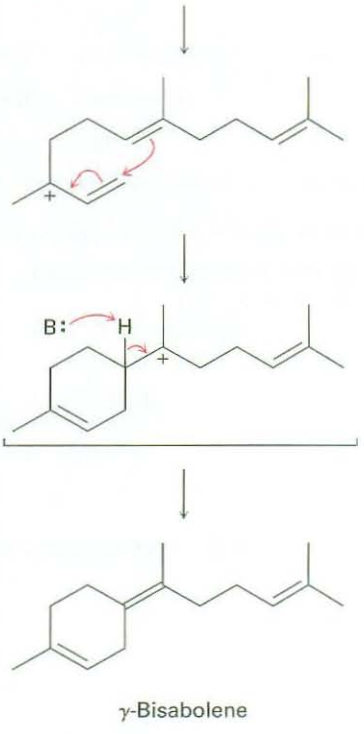
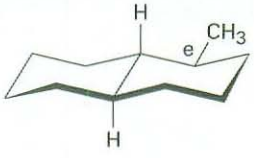




27.8

(a)



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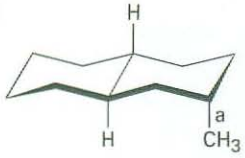

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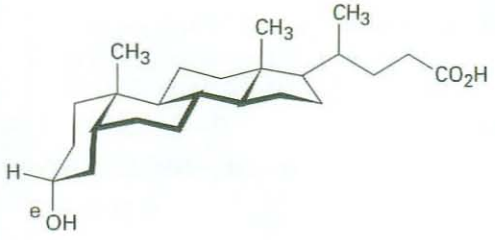
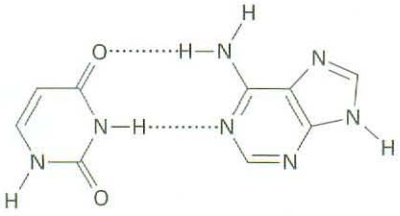


27.10 Three methyl groups are removed, the side-chain double bond is reduced, and the double bond in the B ring is migrated.

CHAPTER 28

28.3 (5′) ACGGATTAGCC (3′)

28.4



28.5 (3′) CUAAUGGCAU (5′)

28.6 (5′) ACTCTGCGAA (3′)

28.7 (a) GCU, GCC, GCA, GCG
(b) UUU, UUC
(c) UUA, UUG, CUU, CUC, CUA, CUG
(d) UAU, UAC

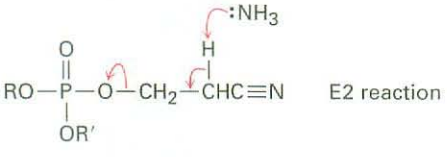
28.8 (a) AGC, GGC, UGC, CGC
(b) AAA, GAA
(c) UAA, CAA, GAA, GAG, UAG, CAG
(d) AUA, GUA

28.9 Leu-Met-Ala-Trp-Pro-Stop

28.10 (5′) TTA-GGG-CCA-AGC-CAT-AAG (3′)

28.11 The cleavage is an S_N1 reaction that occurs by protonation of the oxygen atom followed by loss of the stable triarylmethyl carbocation.

28.12



CHAPTER 29

29.1 $HOCH_2CH(OH)CH_2OH + ATP \longrightarrow HOCH_2CH(OH)CH_2OPO_3^{2-} + ADP$

29.2 Caprylyl CoA ⟶ Hexanoyl CoA ⟶ Butyryl CoA ⟶ 2 Acetyl CoA

29.3 (a) 8 acetyl CoA; 7 passages
(b) 10 acetyl CoA; 9 passages

29.4 The dehydration is an E1cB reaction.

29.5 At C2, C4, C6, C8, and so forth

29.6 The *Si* face

29.7 Steps 7 and 10

29.8 Steps 1, 3: Phosphate transfers; steps 2, 5, 8: isomerizations; step 4: retro-aldol reaction; step 5: oxidation and nucleophilic acyl substitution; steps 7, 10: phosphate transfers; step 9: E2 dehydration

29.9 C1 and C6 of glucose become $-CH_3$ groups; C3 and C4 become CO_2.

29.10 Citrate and isocitrate

29.11 E2 elimination of water, followed by conjugate addition

29.12 *pro-R*; anti geometry

29.13 The reaction occurs by two sequential nucleophilic acyl substitutions, the first by a cysteine residue in the enzyme, with phosphate as leaving group, and the second by hydride donation from NADH, with the cysteine residue as leaving group.

29.14 Initial imine formation between PMP and α-ketoglutarate is followed by double-bond rearrangement to an isomeric imine and hydrolysis.

29.15 $(CH_3)_2CHCH_2COCO_2^-$

29.16 Asparagine

CHAPTER 30

30.1 Ethylene: ψ_1 is the HOMO and ψ_2^* is the LUMO in the ground state; ψ_2^* is the HOMO and there is no LUMO in the excited state. 1,3-Butadiene: ψ_2 is the HOMO and ψ_3^* is the LUMO in the ground state; ψ_3^* is the HOMO and ψ_4^* is the LUMO in the excited state.

30.2 Disrotatory: *cis*-5,6-dimethyl-1,3-cyclohexadiene; conrotatory: *trans*-5,6-dimethyl-1,3-cyclohexadiene. Disrotatory closure occurs.

30.3 The more stable of two allowed products is formed.

30.4 *trans*-5,6-Dimethyl-1,3-cyclohexadiene; *cis*-5,6-dimethyl-1,3-cyclohexadiene

30.5 *cis*-3,6-Dimethylcyclohexene; *trans*-3,6-dimethylcyclohexene

30.6 A [6 + 4] suprafacial cycloaddition

30.7 An antarafacial [1,7] sigmatropic rearrangement

30.8 A series of [1,5] hydrogen shifts occur.

30.9 Claisen rearrangement is followed by a Cope rearrangement.

30.10 (a) Conrotatory (b) Disrotatory
(c) Suprafacial (d) Antarafacial
(e) Suprafacial

CHAPTER 31

31.1 $H_2C{=}CHCO_2CH_3 < H_2C{=}CHCl < H_2C{=}CHCH_3 < H_2C{=}CH{-}C_6H_5$

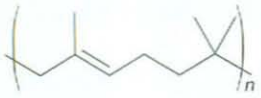
31.2 $H_2C{=}CHCH_3 < H_2C{=}CHC_6H_5 < H_2C{=}CHC{\equiv}N$

31.3 The intermediate is a resonance-stabilized benzylic carbanion, $Ph{-}\ddot{C}HR$.

31.4 The polymer has no chirality centers.

31.5 No, the polymers are racemic.

31.6



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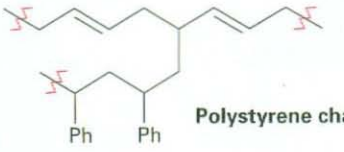

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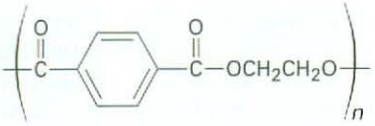

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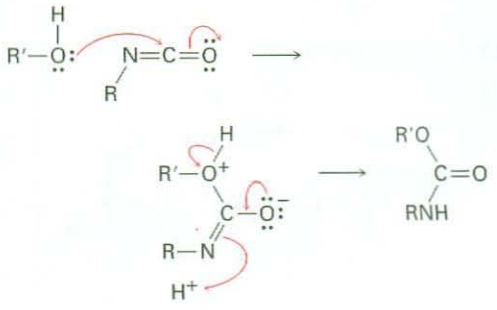

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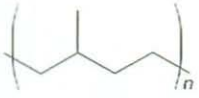

Atactic

31.11