

Answers to Selected Problems

These short answers are sometimes incomplete, but they should put you on the right track. Complete answers to all problems are found in the *Solutions Manual*.

CHAPTER 1

- 1.5. (a) $\overset{\rightarrow}{\text{C}}-\overset{\leftarrow}{\text{Cl}}$; (b) $\overset{\rightarrow}{\text{C}}-\overset{\leftarrow}{\text{O}}$; (c) $\overset{\rightarrow}{\text{C}}-\overset{\leftarrow}{\text{N}}$; (d) $\overset{\rightarrow}{\text{C}}-\overset{\leftarrow}{\text{S}}$; (e) $\overset{\leftarrow}{\text{C}}-\overset{\rightarrow}{\text{B}}$;
(f) $\overset{\rightarrow}{\text{N}}-\overset{\leftarrow}{\text{Cl}}$; (g) $\overset{\rightarrow}{\text{N}}-\overset{\leftarrow}{\text{O}}$; (h) $\overset{\rightarrow}{\text{N}}-\overset{\leftarrow}{\text{S}}$; (i) $\overset{\rightarrow}{\text{N}}-\overset{\leftarrow}{\text{B}}$; (j) $\overset{\rightarrow}{\text{B}}-\overset{\leftarrow}{\text{Cl}}$.
- 1.6. (a) +1 on O; (b) +1 on N, -1 on Cl; (c) +1 on N, -1 on Cl;
(d) +1 on Na, -1 on O; (e) +1 on C; (f) -1 on C; (g) +1 on Na, -1
on B; (h) +1 on Na, -1 on B; (i) +1 on O, -1 on B; (j) +1 on N;
(k) +1 on K, -1 on O; (l) +1 on O. 1.12. (a) CH_2O , $\text{C}_3\text{H}_6\text{O}_3$;
(b) $\text{C}_2\text{H}_5\text{NO}_2$, same; (c) $\text{C}_2\text{H}_4\text{ClNO}$, same; (d) $\text{C}_2\text{H}_3\text{Cl}$, $\text{C}_4\text{H}_6\text{Cl}_2$.
- 1.13. (a) 0.209; (b) 13.88. 1.15. (a) favors products; (b) favors reactants;
(c) favors products; (d) favors products; (e) favors products; (f) favors
products. 1.16. There is no resonance stabilization of the positive
charge when the other oxygen atom is protonated. 1.17. (a) acetic
acid, ethanol, methylamine; (b) ethoxide, methylamine, ethanol.
- 1.21. (a) carbon; (b) oxygen; (c) phosphorus; (d) chlorine. 1.28. The
following are condensed structures that you should convert to Lewis
structures. (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}(\text{CH}_3)_2$; (c) $\text{CH}_3\text{CH}_2\text{NH}_2$
and CH_3NHCH_3 ; (e) $\text{CH}_2(\text{CH}_2\text{OH})_2$ and $\text{CH}_3\text{CHOHCH}_2\text{OH}$ and
 $\text{CH}_3\text{OCH}_2\text{OCH}_3$ and others; (f) $\text{CH}_2=\text{CHOH}$ and CH_3CHO .
- 1.32. (a) $\text{C}_3\text{H}_5\text{N}$; (b) $\text{C}_4\text{H}_9\text{N}$; (c) $\text{C}_4\text{H}_4\text{O}$; (d) $\text{C}_4\text{H}_9\text{NO}_2$; (e) $\text{C}_{11}\text{H}_{19}\text{NO}$;
(f) $\text{C}_6\text{H}_{12}\text{O}$; (g) $\text{C}_7\text{H}_8\text{O}_3\text{S}$; (h) $\text{C}_7\text{H}_8\text{O}_3$. 1.33. Empirical formula $\text{C}_3\text{H}_6\text{O}$;
molecular formula $\text{C}_6\text{H}_{12}\text{O}_2$. 1.36. (a) different compounds; (b) reso-
nance forms; (c) different compounds; (d) resonance forms; (e) different
compounds; (f) resonance forms; (g) resonance forms; (h) different com-
pounds; (i) resonance forms; (j) resonance forms. 1.39. (b) The =NH
nitrogen atom is the most basic. 1.41. (a) second; (b) first; (c) second;
(d) first; (e) first. 1.49. (a) $\text{CH}_3\text{CH}_2\text{O}^- \text{Li}^+ + \text{CH}_4$; (b) methane;
 CH_3Li is a very strong base. 1.54. (a) $\text{C}_9\text{H}_{12}\text{O}$; (b) $\text{C}_{18}\text{H}_{24}\text{O}_2$.

CHAPTER 2

- 2.2. sp^3 ; Two lone pairs compress the bond angle to 104.5° . 2.4. Methyl
carbon; sp^3 , about 109.5° . Nitrile carbon sp , 180° . Nitrile nitrogen sp , no
bond angle. 2.6. The central carbon is sp , with two unhybridized
 p orbitals at right angles. Each terminal =CH₂ group must be aligned
with one of these p orbitals. 2.9. $\text{CH}_3-\text{CH}=\text{N}-\text{CH}_3$ shows cis-
trans isomerism about the C=N double bond, but $(\text{CH}_3)_2\text{C}=\text{N}-\text{CH}_3$
has two identical substituents on the C=N carbon atom, and there are
no cis-trans isomers. 2.11. (a) constitutional isomers; (b) cis-trans
isomers; (c) constitutional isomers; (d) same compound; (e) same com-
pound; (f) same compound; (g) not isomers; (h) constitutional isomers;
(i) same compound; (j) constitutional isomers; (k) constitutional isomers.
- 2.13. The N—F dipole moments oppose the dipole moment of the lone
pair. 2.15. *trans* has zero dipole moment because the bond dipole
moments cancel. 2.18. (a) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ (c) $\text{CH}_3\text{CH}_2\text{NHCH}_3$;
(d) $\text{CH}_3\text{CH}_2\text{OH}$; (e) CH_3COCH_3 . 2.19. (a) alkane; (b) alkene;
(c) alkyne; (d) cycloalkyne and cycloalkene; (e) cycloalkane and alkene;
(f) aromatic hydrocarbon and alkyne; (g) cycloalkene and alkene;
(h) cycloalkane and alkane; (i) aromatic hydrocarbon and cycloalkene.
- 2.20. (a) aldehyde and alkene; (b) alcohol; (c) ketone; (d) ether and
alkene; (e) carboxylic acid; (f) ether and alkene; (g) ketone and alkene;
(h) aldehyde; (i) alcohol. 2.21. (a) amide; (b) amine; (c) ester; (d) acid
chloride and alkene; (e) ether; (f) nitrile; (g) carboxylic acid; (h) cyclic
ester and alkene; (i) ketone, cyclic ether; (j) cyclic amine; (k) cyclic
amide; (l) amide; (m) cyclic ester; (n) aldehyde, cyclic amine; (o) ketone,
cyclic alkene. 2.25. No stereoisomers. 2.26. Cyclopropane has bond
angles of 60° , compared with the 109.5° bond angle of an unstrained
alkane. 2.29. Urea must have two sp^2 -hybridized nitrogen atoms

- because they are involved in pi-bonding in the other resonance forms.
- 2.34. (a), (e), and (f). 2.35. (a) constitutional isomers; (b) constitutional
isomers; (c) cis-trans isomers; (d) constitutional isomers; (e) cis-trans iso-
mers; (f) same compound; (g) cis-trans isomers; (h) constitutional isomers.
- 2.36. CO_2 is sp -hybridized and linear; the bond dipole moments cancel.
The sulfur atom in SO_2 is sp^2 -hybridized and bent; the bond dipole
moments do not cancel. 2.38. Both can form H-bonds with water, but
only the alcohol can form H-bonds with itself. 2.40. (a), (c), (h), and (l)
can form hydrogen bonds in the pure state. These four plus (b), (d),
(g), (i), (j), and (k) can form hydrogen bonds with water. 2.42. (a) cyclic
ether; (b) cyclic alkene, carboxylic acid; (c) alkene, aldehyde; (d) aromatic,
ketone; (e) alkene, cyclic ester; (f) cyclic amide; (g) aromatic nitrile, ether;
(h) amine, ester; (i) amine, alcohol, carboxylic acid.

CHAPTER 3

- 3.1. (a) $\text{C}_{28}\text{H}_{58}$; (b) $\text{C}_{44}\text{H}_{90}$; 3.2. (a) 3-methylpentane; (b) 2-bromo-3-
methylpentane; (c) 5-ethyl-2-methyl-4-propylheptane; (d) 4-isopropyl-2-
methyldecane. 3.4. (a) 2-methylbutane; (b) 2,2-dimethylpropane;
(c) 3-ethyl-2-methylhexane; (d) 2,4-dimethylhexane; (e) 3-ethyl-2,2,4,5-
tetramethylhexane; (f) 4-*tert*-butyl-3-methylheptane. 3.9. (a) $\text{C}_{12}\text{H}_{26}$;
(b) $\text{C}_{15}\text{H}_{32}$. 3.10. (a) hexane < octane < decane; (b) $(\text{CH}_3)_3\text{C}-$
 $\text{C}(\text{CH}_3)_3$ < $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_3$ < octane.
- 3.14. (a) 1,1-dimethyl-3-(1-methylpropyl) cyclopentane or 3-*sec*-butyl-1,1-
dimethylcyclopentane; (b) 3-cyclopropyl-1,1-dimethylcyclohexane;
(c) 4-cyclobutylnonane. 3.16. (b), (c), and (d). 3.17. (a) *cis*-1-methyl-3-
propylcyclobutane; (b) *trans*-1-*tert*-butyl-3-ethylcyclohexane; (c) *trans*-1,2-
dimethylcyclopropane. 3.18. *Trans* is more stable. In the *cis* isomer the
methyl groups are nearly eclipsed. 3.28. (a) *cis*-1,3-dimethylcyclohexane;
(b) *cis*-1,4-dimethylcyclohexane; (c) *trans*-1,2-dimethylcyclohexane;
(d) *cis*-1,3-dimethylcyclohexane; (e) *cis*-1,3-dimethylcyclohexane;
(f) *trans*-1,4-dimethylcyclohexane. 3.30. (a) bicyclo[3.1.0]hexane;
(b) bicyclo[3.3.1]nonane; (c) bicyclo[2.2.2]octane; (d) bicyclo[3.1.1]hep-
tane. 3.33. (a) All except the third (isobutane) are *n*-butane. (b) The first
and fourth structures are *cis*-but-2-ene. The second and fifth structures are
but-1-ene. The third structure is *trans*-but-2-ene, and the last structure is
2-methylpropene. (c) The first and second are *cis*-1,2-dimethylcyclopentane.
The third and fourth are *trans*-1,2-dimethylcyclopentane. The fifth is *cis*-
1,3-dimethylcyclopentane. (f) The first, second, and fourth structures are
2,3-dimethylbutane. The third and fifth structures are 2,2-dimethylbutane.
- 3.37. (a) 3-ethyl-2,2,6-trimethylheptane; (b) 3-ethyl-2,6,7-trimethyloctane;
(c) 3,7-diethyl-2,2,8-trimethyldecane; (d) 1,1-diethyl-2-methylcyclobutane;
(e) bicyclo[4.1.0]heptane; (f) *cis*-1-ethyl-3-propylcyclopentane;
(g) (1,1-diethylpropyl)cyclohexane; (h) *cis*-1-ethyl-4-isopropylcyclodecane.
- 3.39. (a) should be 3-methylhexane; (b) 3-ethyl-2-methylhexane;
(c) 2-chloro-3-methylhexane; (d) 2,2-dimethylbutane; (e) *sec*-butylcyclo-
hexane or (1-methylpropyl)cyclohexane; (f) should be *cis* or *trans*-1,2-
diethylcyclopentane. 3.40. (a) octane; (b) nonane; (c) nonane.
- 3.45. The *trans* isomer is more stable, because both of the bonds to the
second cyclohexane ring are in equatorial positions.

CHAPTER 4

- 4.3. (a) One photon of light would be needed for every molecule of prod-
uct formed (the quantum yield would be 1); (b) Methane does not absorb the
visible light that initiates the reaction, and the quantum yield would
be 1. 4.4. (a) Hexane has three different kinds of hydrogen atoms,
but cyclohexane has only one type. (b) Large excess of cyclohexane.
- 4.5. (a) $K_{\text{eq}} = 2.3$; (b) $[\text{CH}_3\text{Br}] = [\text{H}_2\text{S}] = 0.40 \text{ M}$, $[\text{CH}_3\text{SH}] =$
 $[\text{HBr}] = 0.60 \text{ M}$. 4.8. (a) positive; (b) negative; (c) not easy to predict.
- 4.10. (a) initiation +192 kJ/mole; propagation +67 kJ/mole and
-101 kJ/mole; (b) overall -34 kJ/mole. 4.11. (a) first order; (b) zeroth

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order; (c) first order overall. **4.13.** (a) zero, zero, zeroth order overall; (b) rate = k_r ; (c) increase the surface area of the platinum catalyst. **4.14.** (b) +13 kJ/mole; (c) -4 kJ/mole. **4.15.** (c) +113 kJ/mole. **4.17.** (a) initiation +151 kJ/mole; propagation +138 kJ/mole and -83 kJ/mole; (b) overall +55 kJ/mole; (c) low rate and very unfavorable equilibrium constant. **4.18.** 1°:2° ratio of 6:2, product ratio of 75% 1° and 25% 2°. **4.22.** (a) The combustion of isooctane involves highly branched, more stable tertiary free radicals that react less explosively. (b) *tert*-butyl alcohol forms relatively stable alkoxy radicals that react less explosively. **4.29.** Stability: (d) res 3° > (c) 3° > (b) 2° > (a) 1°. **4.30.** Stability: (d) res 3° > (c) 3° > (b) 2° > (a) 1°. **4.38.** rate = $k_r[H^+][(\text{CH}_3)_3\text{C}-\text{OH}]$; second order overall. **4.41.** $\text{PhCH}_2\cdot > \text{CH}_2=\text{CHCH}_2\cdot > (\text{CH}_3)_3\text{C}\cdot > (\text{CH}_3)_2\text{CH}\cdot > \text{CH}_3\text{CH}_2\cdot > \text{CH}_3\cdot$.

CHAPTER 5

5.1. chiral; corkscrew, desk, screw-cap bottle, rifle, knot, left-handed can opener. **5.2.** (b), (d), (e), and (f) are chiral. **5.3.** (a) chiral, one C*; (b) achiral, no C*; (c) chiral, one C*; (d) chiral, one C*; (e) achiral, no C*; (f) achiral, two C*; (g) chiral, one C*; (h) chiral, two C*; (i) chiral, two C*. **5.5.** (a) mirror, achiral; (b) mirror, achiral; (c) chiral, no mirror; (d) chiral, no mirror; (e) chiral, no mirror; (f) chiral, no mirror; (g) mirror, achiral; (h) mirror, achiral. **5.6.** (a) (*R*); (b) (*S*); (c) (*R*); (d) (*S*), (*S*); (e) (*R*), (*S*); (f) (*R*), (*S*); (g) (*R*), (*R*); (h) (*R*); (i) (*S*). **5.8.** +8.7°. **5.10.** Dilute the sample. If clockwise, will make less clockwise, and vice-versa. **5.12.** e.e. = 33.3%. Specific rotation = 33.3% of +13.5° = +4.5°. **5.15.** (a), (b), (e), and (f) are chiral. Only (e) has asymmetric carbons. **5.16.** (a) enantiomer, enantiomer, same; (b) same, enantiomer, enantiomer; (c) enantiomer, same, same. **5.18.** (a), (d), and (f) are chiral. The others have internal mirror planes. **5.19.** (from 5-18) (a) (*R*); (b) none; (c) none; (d) (*2R*), (*3R*); (e) (*2S*), (*3R*); (f) (*2R*), (*3R*); (new ones) (g) (*R*); (h) (*S*); (i) (*S*). **5.20.** (a) enantiomers; (b) diastereomers; (c) diastereomers; (d) constitutional isomers; (e) enantiomers; (f) diastereomers; (g) enantiomers; (h) enantiomers; (i) diastereomers. **5.23.** (a), (b), and (d) are pairs of diastereomers and could theoretically be separated by their physical properties. **5.30.** (a) same compound; (b) enantiomers; (c) enantiomers; (d) enantiomers; (e) diastereomers; (f) diastereomers; (g) enantiomers; (h) same compound; (i) enantiomers. **5.34.** (b) -15.90°; (c) 7.95°/15.90° = 50% e.e. Composition is 75% (*R*) and 25% (*S*).

CHAPTER 6

6.1. (a) vinyl halide; (b) alkyl halide; (c) alkyl halide; (d) alkyl halide; (e) vinyl halide; (f) aryl halide. **6.5.** (a) ethyl chloride; (b) 1-bromopropane; (c) *cis*-2,3-dibromobut-2-ene; (d) *cis*-1,2-dichlorocyclobutane. **6.7.** Water is denser than hexane, so water forms the lower layer. Chloroform is denser than water, so chloroform forms the lower layer. Water and ethanol are miscible, so they form only one phase. **6.11.** (a) substitution; (b) elimination; (c) elimination, also a reduction. **6.13.** (a) 0.02 mol/L per second. **6.14.** (a) $(\text{CH}_3)_3\text{COCH}_2\text{CH}_3$; (b) $\text{HC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$; (c) $(\text{CH}_3)_2\text{CHCH}_2\text{NH}_2$; (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{N}$; (e) 1-iodopentane; (f) 1-fluoropentane. **6.16.** (a) $(\text{CH}_3\text{CH}_2)_2\text{NH}$, less hindered; (b) $(\text{CH}_3)_2\text{S}$, S more polarizable; (c) PH_3 , P more polarizable; (d) CH_3S^- , neg. charged; (e) $(\text{CH}_3)_3\text{N}$, N less electronegative; (f) acetate is better: more basic, no inductive effect from F; (g) $\text{CH}_3\text{CH}_2\text{CH}_2\text{O}^-$, less hindered; (h) I^- , more polarizable. **6.18.** methyl iodide > methyl chloride > ethyl chloride > isopropyl bromide >> neopentyl bromide, *tert*-butyl iodide. **6.19.** (a) 2-methyl-1-iodopropane; (b) cyclohexyl bromide; (c) isopropyl bromide; (d) 2-chlorobutane; (e) 1-iodobutane. **6.23.** (a) 2-bromopropane; (b) 2-bromo-2-methylbutane; (c) allyl bromide; (d) 2-bromopropane; (e) 2-iodo-2-methylbutane; (f) 2-bromo-2-methylbutane. **6.27.** (a) $(\text{CH}_3)_2\text{C}(\text{OCOCH}_3)\text{CH}_2\text{CH}_3$, first order; (b) 1-methoxy-2-methylpropane, second order; (c) 1-ethoxy-1-methylcyclohexane, first order; (d) methoxycyclohexane, first order; (e) ethoxycyclohexane, second order. **6.36.** 3-methylbut-1-ene by E2 (minor); 2-methylbut-2-ene by E2 (major); and 2-ethoxy-3-methylbutane (trace) by $\text{S}_{\text{N}}2$.

6.43. (a) 2-bromo-2-methylpentane; (b) 1-chloro-1-methylcyclohexane; (c) 1,1-dichloro-3-fluorocycloheptane; (d) 4-(2-bromoethyl)-3-(fluoromethyl)-2-methylheptane; (e) 4,4-dichloro-5-cyclopropyl-1-iodoheptane; (f) *cis*-1,2-dichloro-1-methylcyclohexane. **6.44.** (a) 1-chlorobutane; (b) 1-iodobutane; (c) 4-chloro-2,2-dimethylpentane; (d) 1-bromo-2,2-dimethylpentane; (e) chloromethylcyclohexane; (f) 2-methyl-1-bromopropane. **6.45.** (a) *tert*-butyl chloride; (b) 2-chlorobutane; (c) bromocyclohexane; (d) iodycyclohexane; (e) PhCHBrCH_3 ; (f) 3-bromocyclohexene. **6.48.** (a) rate doubles; (b) rate multiplied by six; (c) rate increases. **6.55.** (a) (*R*)-2-cyanobutane (inversion); (b) (*2S,3R*)-3-methylpentan-2-ol (inversion); (c) racemic mixture of 3-ethoxy-2,3-dimethylpentanes (racemization). **6.56.** (a) diethyl ether; (b) $\text{PhCH}_2\text{CH}_2\text{CN}$; (c) $\text{PhSCH}_2\text{CH}_3$; (d) 1-dodecane; (e) *N*-methylpyridinium iodide; (f) $(\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{NH}_2$; (g) tetrahydrofuran; (h) *cis*-4-methylcyclohexanol. **6.58.** (a) o.p. = e.e. = 15.58/15.90 = 98% (99% (*S*) and 1% (*R*)); (b) The e.e. of (*S*) decreases twice as fast as radioactive iodide substitutes, thus gives the (*R*) enantiomer; implies the $\text{S}_{\text{N}}2$ mechanism. **6.64.** NBS provides low conc. Br_2 for free-radical bromination. Abstraction of one of the CH_2 hydrogens gives a resonance-stabilized free radical; product PhCHBrCH_3 .

CHAPTER 7

7.4. (a) two; (b) one; (c) three; (d) four; (e) five. **7.5.** (a) 4-methylpent-1-ene; (b) 2-ethylhex-1-ene; (c) penta-1,4-diene; (d) penta-1,2,4-triene; (e) 2,5-dimethylcyclopenta-1,3-diene; (f) 4-vinylcyclohexene; (g) allylbenzene or 3-phenylpropene; (h) *trans*-3,4-dimethylcyclopentene; (i) 7-methylenecyclohepta-1,3,5-triene; (j) (*2E,4Z*)-5,6-dimethylhepta-2,4-diene. **7.6.** (1) (a), (c), (d), and (f) show geometric isomerism. **7.7.** (a) 2,3-dimethylpent-2-ene; (b) 3-ethylhexa-1,4-diene; (c) 1-methylcyclopentene; (d) give positions of double bonds; (e) specify *cis* or *trans*; (f) (*E*) or (*Z*), not *cis*. **7.9.** 2,3-dimethylbut-2-ene is more stable by 6.0 kJ/mole. **7.11.** (a) stable; (b) unstable; (c) stable; (d) stable; (e) unstable (maybe stable cold); (f) stable; (g) unstable; (h) stable (i) unstable (maybe stable cold). **7.12.** (a) *cis*-1,2-dibromoethene; (b) *cis* (*trans* has zero dipole moment); (c) 1,2-dichlorocyclohexene. **7.17.** There is no hydrogen *trans* to the bromide leaving group. **7.23.** In the first example the bromines are axial; in the second, equatorial. **7.26.** (a) $\Delta G > 0$, disfavored; (b) $\Delta G < 0$, favored; **7.27.** (a) strong bases and nucleophiles; (b) strong acids and electrophiles; (c) free-radical chain reaction; (d) strong acids and electrophiles. **7.32.** (a) 2-ethylpent-1-ene; (b) 3-ethylpent-2-ene; (c) (*3E,5E*)-2,6-dimethylocta-1,3,5-triene; (d) (*E*)-4-ethylhept-3-ene; (e) 1-cyclohexylcyclohexa-1,3-diene; (f) (*3Z,5Z*)-6-chloro-3-(chloromethyl)octa-1,3,5-triene. **7.36.** (b), (c), (e) and (f) show geometric isomerism. **7.38.** (a) cyclopentene; (b) 2-methylbut-2-ene (major) and 2-methylbut-1-ene (minor); (c) 1-methylcyclohexene (major) and methylenecyclohexane (minor); (d) 1-methylcyclopentene (major), methylenecyclopentane (minor), possibly 3-methylcyclopentene (minor). **7.42.** (a) a 1-haloheptane; (b) a *tert*-butyl halide; (c) a 3-halopentane; (d) a halomethylcyclohexane; (e) a 4-halocyclohexane (preferably *cis*). **7.44.** (a) pent-2-ene; (b) 1-methylcyclopentene; (c) 1-methylcyclohexene; (d) 2-methylbut-2-ene; (rearrangement). **7.56.** E1 with rearrangement by an alkyl shift. The Zaitsev product violates Bredt's rule.

CHAPTER 8

8.1. (a) 2-bromopentane; (b) 2-chloro-2-methylpropane; (c) 1-iodo-1-methylcyclohexane; (d) mixture of *cis*- and *trans*-1-bromo-3-methyl- and 1-bromo-4-methylcyclohexane. **8.3.** (a) 1-bromo-2-methylcyclopentane; (b) 2-bromo-1-phenylpropane. **8.6.** (a) 1-methylcyclopentanol; (b) 2-phenylpropan-2-ol; (c) 1-phenylcyclohexanol. **8.10.** (b) propan-1-ol; (d) 2-methylpentan-3-ol; (f) *trans*-2-methylcyclohexanol. **8.13.** (a) *trans*-2-methylcycloheptanol; (b) mostly 4,4-dimethylpentan-2-ol; (c) -OH *exo* order; (d) the less substituted carbon. **8.16.** (a) The carbocation can be attacked from either face. **8.22.** (a) $\text{Cl}_2/\text{H}_2\text{O}$; (b) KOH/heat , then $\text{Cl}_2/\text{H}_2\text{O}$; (c) $\text{H}_2\text{SO}_4/\text{heat}$, then $\text{Cl}_2/\text{H}_2\text{O}$.

8.28. (a) $\text{CH}_2\text{I}_2 + \text{Zn}(\text{Cu})$; (b) CH_2Br_2 , NaOH , H_2O ; (c) dehydrate (H_2SO_4), then CHCl_3 , $\text{NaOH}/\text{H}_2\text{O}$. **8.34.** (a) *cis*-cyclohexane-1,2-diol; (b) *trans*-cyclohexane-1,2-diol; (c) and (f) (*R,S*)-pentane-2,3-diol (+ enantiomer); (d) and (e) (*R,R*)-pentane-2,3-diol (+ enantiomer). **8.35.** (a) $\text{OsO}_4/\text{H}_2\text{O}_2$; (b) $\text{CH}_3\text{CO}_3\text{H}/\text{H}_3\text{O}^+$; (c) $\text{CH}_3\text{CO}_3\text{H}/\text{H}_3\text{O}^+$; (d) $\text{OsO}_4/\text{H}_2\text{O}_2$. **8.59.** (a) 1-methylcyclohexene, $\text{RCO}_3\text{H}/\text{H}_3\text{O}^+$; (b) cyclooctene, $\text{OsO}_4/\text{H}_2\text{O}_2$; (c) *trans*-cyclodecene, Br_2 ; (d) cyclohexene, $\text{Cl}_2/\text{H}_2\text{O}$. **8.62.** $\text{CH}_3(\text{CH}_2)_{12}\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_3$, *cis* or *trans* unknown.

CHAPTER 9

9.3. decomposition to its elements, C and H_2 . **9.4.** Treat the mixture with NaNH_2 to remove the hex-1-yne. **9.5.** (a) $\text{Na}^+ \text{C}\equiv\text{CH}$ and NH_3 ; (b) $\text{Li}^+ \text{C}\equiv\text{CH}$ and CH_4 ; (c) no reaction; (d) no reaction; (e) acetylene + NaOCH_3 ; (f) acetylene + NaOH ; (g) no reaction; (h) no reaction; (i) $\text{NH}_3 + \text{NaOCH}_3$. **9.7.** (a) NaNH_2 ; butyl halide; (b) NaNH_2 ; propyl halide; NaNH_2 ; methyl halide. (c) NaNH_2 ; ethyl halide; repeat; (d) $\text{S}_\text{N}2$ on *sec*-butyl halide is unfavorable; (e) NaNH_2 ; isobutyl halide (low yield); NaNH_2 ; methyl halide; (f) NaNH_2 added for second substitution on 1,8-dibromooctane might attack the halide. **9.8.** (a) sodium acetylide + formaldehyde; (b) sodium acetylide + CH_3I , then NaNH_2 , then $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$; (c) sodium acetylide + PhCOCH_3 ; (d) sodium acetylide + CH_3I , then NaNH_2 , then $\text{CH}_3\text{CH}_2\text{COCH}_3$. **9.12.** (a) H_2 , Lindlar; (b) Na , NH_3 ; (c) Add halogen, dehydrohalogenate to the alkyne, Na , NH_3 ; (d) NaNH_2 , then EtBr , then H_2 with Lindlar. **9.18.** (a) Cl_2 ; (b) HBr , peroxides; (c) HBr , no peroxides; (d) excess Br_2 ; (e) reduce to hex-1-ene, add HBr ; (f) excess HBr . **9.20.** (a) The two ends of the triple bond are equivalent; (b) The two ends of the triple bond are not equivalent, yet not sufficiently different for good selectivity. **9.21.** (a) hexan-2-one; hexanal; (b) mixtures of hexan-2-one and hexan-3-one; (c) hexan-3-one for both; (d) cyclodecanone for both. **9.24.** (a) $\text{CH}_3\text{C}\equiv\text{C}(\text{CH}_2)_4\text{C}\equiv\text{CCH}_3$. **9.28.** (a) ethylmethylacetylene; (b) phenylacetylene; (c) *sec*-butyl-*n*-propylacetylene; (d) *sec*-butyl-*tert*-butylacetylene. **9.38.** cyclohexa-1,3-diene with ($\text{HC}\equiv\text{C}-\text{CH}=\text{CH}-$) at the 1 position (*cis* or *trans*).

CHAPTER 10

10.1. (a) 2-phenylbutan-2-ol; (b) (*E*)-5-bromohept-3-en-2-ol; (c) 4-methylcyclohex-3-en-1-ol; (d) *trans*-2-methylcyclohexanol; (e) (*E*)-2-chloro-3-methylpent-2-en-1-ol; (f) (2*R*,3*S*)-2-bromohexan-3-ol. **10.4.** (a) 8,8-dimethylnonane-2,7-diol; (b) octane-1,8-diol; (c) *cis*-cyclohex-2-ene-1,4-diol; (d) 3-cyclopentylheptane-2,4-diol; (e) *trans*-cyclobutane-1,3-diol. **10.5.** (a) cyclohexanol; more compact; (b) 4-methylphenol; more compact, stronger H-bonds; (c) 3-ethylhexan-3-ol; more spherical; (d) cyclooctane-1,4-diol; more OH groups per carbon; (e) enantiomers; equal solubility. **10.7.** (a) methanol; less substituted; (b) 2-chloropropan-1-ol; chlorine closer to the OH group; (c) 2,2-dichloroethanol; two chlorines to stabilize the alkoxide; (d) 2,2-difluoropropan-1-ol; F is more electronegative than Cl, stabilizing the alkoxide. **10.9.** The anions of 2-nitrophenol and 4-nitrophenol (but not 3-nitrophenol) are stabilized by resonance with the nitro group. **10.10.** (a) The phenol (left) is deprotonated by sodium hydroxide; it dissolves; (b) In a separatory funnel, the alcohol (right) will go into an ether layer and the phenolic compound will go into an aqueous sodium hydroxide layer. **10.11.** (b), (f), (g), (h). **10.15.** (a) three ways: (i) $\text{CH}_3\text{CH}_2\text{MgBr} + \text{PhCOCH}_2\text{CH}_2\text{CH}_3$; (ii) $\text{PhMgBr} + \text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_2\text{CH}_3$; (iii) $\text{CH}_3\text{CH}_2\text{CH}_2\text{MgBr} + \text{PhCOCH}_2\text{CH}_3$; (b) $\text{PhMgBr} + \text{PhCOPh}$. (c) $\text{EtMgBr} + \text{cyclopentanone}$; (d) $c\text{-C}_5\text{H}_9\text{MgBr} + \text{pentan-2-one}$. **10.17.** (a) 2 $\text{PhMgBr} + \text{PhCOCl}$; (b) 2 $\text{CH}_3\text{CH}_2\text{MgBr} + (\text{CH}_3)_2\text{CHCOCl}$; (c) 2 $c\text{-HxMgBr} + \text{PhCOCl}$. **10.19.** (a) $\text{PhMgBr} + \text{ethylene oxide}$; (b) $(\text{CH}_3)_2\text{CHCH}_2\text{MgBr} + \text{ethylene oxide}$; (c) 2-methylcyclohexylmagnesium bromide + ethylene oxide. **10.23.** (a) Grignard removes NH proton; (b) Grignard attacks ester; (c) Water will destroy Grignard; (d) Grignard removes OH proton. **10.26.** (a) heptanoic acid + LiAlH_4 ; or heptanal + NaBH_4 ; (b) heptan-2-one + NaBH_4 ; (c) 2-methylhexan-3-one + NaBH_4 ; (d) ketoester + NaBH_4 . **10.34.** (a) hexan-1-ol, larger surface

area; (b) hexan-2-ol, hydrogen-bonded; (c) hexane-1,5-diol, two OH groups; (d) hexan-2-ol. **10.38.** (a) cyclohexylmethanol; (b) 2-cyclopentylpentan-2-ol; (c) 2-methyl-1-phenylpropan-1-ol; (d) methane + 3-hydroxycyclohexanone; (e) cyclopentylmethanol; (f) triphenylmethanol; (g) $\text{Ph}_2\text{C}(\text{OH})(\text{CH}_2)_4\text{OH}$; (h) 5-phenylnonan-5-ol; (i) reduction of just the ketone, but not the ester; (j) 3-(2-hydroxyethyl)cyclohexanol from reduction of ketone and ester; (k) the tertiary alcohol from Markovnikov orientation of addition of $\text{H}-\text{OH}$; (l) the secondary alcohol from anti-Markovnikov orientation of addition of $\text{H}-\text{OH}$; (m) (2*S*,3*S*)-hexane-2,3-diol (+ enantiomer); (n) (2*S*,3*R*)-hexane-2,3-diol (+ enantiomer); (o) hepta-1,4-diene. **10.39.** (a) EtMgBr ; (b) Grignard with formaldehyde; (c) $c\text{-HxMgBr}$; (d) cyclohexylmagnesium bromide with ethylene oxide; (e) PhMgBr with formaldehyde; (f) 2 CH_3MgI ; (g) cyclopentylmagnesium bromide.

CHAPTER 11

11.1. (a) oxidation, oxidation; (b) oxidation, oxidation, reduction, oxidation; (c) neither (C2 is oxidation, C3 reduction); (d) reduction; (e) oxidation; (f) neither; (g) neither; (h) neither; then reduction; (i) oxidation; (j) oxidation then neither; (k) oxidation; (l) reduction then oxidation, no net change. **11.6.** Cr reagents: (a) PCC; (b) chromic acid; (c) chromic acid or Jones reagent; (d) oxidize, add Grignard; (f) dehydrate, hydroborate, oxidize (chromic acid or Jones reagent). **11.7.** An alcoholic has more alcohol dehydrogenase. More ethanol is needed to tie up this larger amount of enzyme. **11.8.** CH_3COCHO (pyruvaldehyde) and CH_3COCOOH (pyruvic acid). **11.10.** Treat the tosylate with (a) bromide; (b) ammonia; (c) ethoxide; (d) cyanide. **11.14.** (a) chromic acid or Lucas reagent; (b) chromic acid or Lucas reagent; (c) Lucas reagent only; (d) Lucas reagent only; allyl alcohol forms a resonance-stabilized carbocation. (e) Lucas reagent only. **11.19.** (a) thionyl chloride (retention); (b) tosylate (retention), then $\text{S}_\text{N}2$ using chloride ion (inversion). **11.20.** resonance-delocalized cation, positive charge spread over two carbons. **11.22.** (a) 2-methylbut-2-ene (+ 2-methylbut-1-ene); (b) pent-2-ene (+ pent-1-ene); (c) pent-2-ene (+ pent-1-ene); (d) $c\text{-Hx}=\text{C}(\text{CH}_3)_2$ (+ 1-isopropylcyclohexene); (e) 1-methylcyclohexene (+ 3-methylcyclohexene). **11.25.** Using $\text{R}-\text{OH}$ and $\text{R}'-\text{OH}$ will form $\text{R}-\text{O}-\text{R}$, $\text{R}'-\text{O}-\text{R}'$, and $\text{R}-\text{O}-\text{R}'$. **11.31.** (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCl} + \text{propan-1-ol}$; (b) $\text{CH}_3\text{CH}_2\text{COCl} + \text{butan-1-ol}$; (c) $(\text{CH}_3)_2\text{CHCOCl} + p\text{-methylphenol}$; (d) $\text{PhCOCl} + \text{cyclopropanol}$. **11.33.** An acidic solution (to protonate the alcohol) would protonate methoxide ion. **11.34.** (a) the alkoxide of cyclohexanol and an ethyl halide or tosylate; (b) dehydration of cyclohexanol. **11.42.** (a) Na , then ethyl bromide; (b) NaOH , then PCC to aldehyde; Grignard, then dehydrate; (c) Mg in ether, then $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$, then oxidize; (d) PCC, then EtMgBr . **11.46.** (a) thionyl chloride; (b) make tosylate, displace with bromide; (c) make tosylate, displace with hydroxide. **11.52.** Compound A is butan-2-ol. **11.59.** X is but-3-en-1-ol; Y is tetrahydrofuran (5-membered cyclic ether).

CHAPTER 12

12.3. (a) alkene; (b) alkane; (c) terminal alkyne. **12.4.** (a) amine (secondary); (b) acid; (c) alcohol. **12.5.** (a) conjugated ketone; (b) ester; (c) primary amide. **12.6.** (a) 3070 $\text{C}-\text{H}$; 1642 $\text{C}=\text{C}$ alkene; (b) 2712, 2814 $-\text{CHO}$; 1691 carbonyl-aldehyde; (c) over-inflated $\text{C}-\text{H}$ region $-\text{COOH}$; 1703 carbonyl (maybe conjugated); 1650 $\text{C}=\text{C}$ (maybe conjugated)-conjugated acid; (d) 1742 ester (or strained ketone)-ester. **12.7.** (a) bromine ($\text{C}_6\text{H}_5\text{Br}$); (b) iodine ($\text{C}_2\text{H}_5\text{I}$); (c) chlorine ($\text{C}_4\text{H}_7\text{Cl}$); (d) nitrogen ($\text{C}_7\text{H}_{17}\text{N}$). **12.8.** the isobutyl cation, $(\text{CH}_3)_2\text{CHCH}_2^+$. **12.11.** 126: loss of water; 111: allylic cleavage; 87: cleavage next to alcohol. **12.14.** (a) about 1660 and 1710; the carbonyl is much stronger; (b) about 1660 for both; the ether is much stronger; (c) about 1660 for both; the imine is much stronger; (d) about 1660 for both; the terminal alkene is stronger. **12.16.** (a) $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOH}$; (b) $(\text{CH}_3)_2\text{CHCOCH}_3$; (c) $\text{PhCH}_2\text{C}\equiv\text{N}$; (d) $\text{PhCH}_2\text{CH}_2\text{OH}$. **12.17.** (a) 86, 71, 43; (b) 98, 69; (c) 84, 87, 45. **12.20.** (a) 1-bromobutane. **12.23.** (c) oct-1-yne.

CHAPTER 13

13.1. (a) δ 2.17; (b) δ 2.17; (c) 130 Hz. **13.3.** (a) three; (b) two; (c) three; (d) two; (e) three; (f) five. **13.6.** (a) 2-methylbut-3-yn-2-ol; (b) dimethoxybenzene; (c) 1,2-dibromo-2-methylpropane. **13.10.** *trans* $\text{CHCl}=\text{CHCN}$. **13.11.** (a) 1-chloropropane; (b) methyl *p*-methylbenzoate, $\text{CH}_3\text{C}_6\text{H}_4\text{COOCH}_3$. **13.14.** (a) H^a , δ 9.7 (doublet); H^b , δ 6.6 (multiplet); H^c , δ 7.4 (doublet); (b) $J_{ab} = 8$ Hz, $J_{bc} = 18$ Hz (approx). **13.18.** (a) Five; the two hydrogens on C3 are diastereotopic. (b) Six; all the CH_2 groups have diastereotopic hydrogens. (c) Six; three on the Ph, and the CH_2 hydrogens are diastereotopic. (d) Three; the hydrogens *cis* and *trans* to the Cl are diastereotopic. **13.21.** (a) butane-1,3-diol; (b) $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$. **13.24.** (a) $(\text{CH}_3)_2\text{CHCOOH}$; (b) $\text{PhCH}_2\text{CH}_2\text{CHO}$; (c) $\text{CH}_3\text{COCOCH}_2\text{CH}_3$; (d) $\text{CH}_2=\text{CHCH}(\text{OH})\text{CH}_3$; (e) $\text{CH}_3\text{CH}_2\text{C}(\text{OH})(\text{CH}_3)\text{CH}(\text{CH}_3)_2$. **13.29.** (a) allyl alcohol, $\text{H}_2\text{C}=\text{CHCH}_2\text{OH}$. **13.30.** (a) 4-hydroxybutanoic acid lactone (cyclic ester). **13.31.** (a) cyclohexene. **13.32.** isobutyl bromide. **13.36.** (a) isopropyl alcohol. **13.38.** (a) $\text{PhCH}_2\text{CH}_2\text{OCOCH}_3$. **13.42.** 1,1,2-trichloropropane. **13.45.** **A** is 2-methylbut-2-ene (Zaitsev product); **B** is 2-methylbut-1-ene. **13.47.** PhCH_2CN .

CHAPTER 14

14.2. $(\text{CH}_3\text{CH}_2)_2\text{O}^+ \text{AlCl}_3^-$ **14.4.** (a) methoxyethene; methyl vinyl ether; (b) ethyl isopropyl ether; 2-ethoxypropane; (c) 2-chloroethyl methyl ether; 1-chloro-2-methoxyethane; (d) 2-ethoxy-2,3-dimethylpentane; (e) 1,1-dimethoxycyclopentane; (f) *trans*-2-methoxycyclohexanol; (g) cyclopropyl methyl ether; methoxycyclopropane. **14.6.** (a) dihydropyran; (b) 2-chloro-1,4-dioxane; (c) 3-isopropylpyran; (d) *trans*-2,3-diethyloxirane or *trans*-3,4-epoxyhexane; (e) 3-bromo-2-ethoxyfuran; (f) 3-bromo-2,2-dimethyloxetane. **14.11.** Intermolecular condensation of a mixture of methanol and ethanol would produce a mixture of diethyl ether, dimethyl ether, and ethyl methyl ether. **14.13.** Intermolecular condensation might work for (a). Use the Williamson for (b). Alkymercuration is best for (c). **14.15.** (a) bromocyclohexane and ethyl bromide; (b) 1,5-diiodopentane; (c) phenol and methyl bromide; (e) phenol, ethyl bromide, and 1,4-dibromo-2-methylbutane. **14.23.** Epoxidation of ethylene gives ethylene oxide, and catalytic hydration of ethylene gives ethanol. Acid-catalyzed opening of the epoxide in ethanol gives cello-solve. **14.26.** (a) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}^- \text{Na}^+$; (b) $\text{H}_2\text{NCH}_2\text{CH}_2\text{O}^- \text{Na}^+$; (c) $\text{Ph}-\text{SCH}_2\text{CH}_2\text{O}^- \text{Na}^+$; (d) $\text{PhNHCH}_2\text{CH}_2\text{OH}$; (e) $\text{N}\equiv\text{C}-\text{CH}_2\text{CH}_2\text{O}^- \text{Na}^+$; (f) $\text{N}_3\text{CH}_2\text{CH}_2\text{O}^- \text{Na}^+$. **14.27.** (a) 2-methylpropane-1,2-diol, ^{18}O at the C2 hydroxyl group; (b) 2-methylpropane-1,2-diol, ^{18}O at the C1 hydroxyl group; (c) (2*S*,3*S*)-2-methoxy-3-methylpentan-3-ol; (d) (2*R*,3*R*)-3-methoxy-3-methylpentan-2-ol. **14.34.** (a) The old ether had autoxidized to form peroxides. On distillation, the peroxides were heated and concentrated, and they detonated; (b) Discard the old ether or treat it to reduce the peroxides. **14.38.** (c) epoxide + NaOCH_3 in methanol; (d) epoxide + methanol, H^+ . **14.42.** Sodium then ethyl iodide gives retention of configuration. Tosylation gives retention, then the Williamson gives inversion. Second product +15.6°. **14.46.** $(\text{CH}_3\text{OCH}_2\text{CH}_2)_2\text{O}$. **14.47.** phenyloxirane.

CHAPTER 15

15.1. (a) hexa-2,4-diene < hexa-1,3-diene < hexa-1,4-diene < hexa-1,5-diene < hexa-1,2-diene < hexa-1,3,5-triene; (b) third < fifth < fourth < second < first. **15.8.** (a) **A** is 3,4-dibromobut-1-ene; **B** is 1,4-dibromobut-2-ene; (c) Hint: **A** is the kinetic product, **B** is the thermodynamic product; (d) Isomerization to an equilibrium mixture. 10% **A** and 90% **B**. **15.9.** (a) 1-(bromomethyl)cyclohexene and 2-bromo-1-methylenecyclohexane. **15.11.** (a) 3-bromocyclopentene; (c) PhCH_2Br . **15.12.** Both generate the same allylic carbanion. **15.13.** In this reaction, alkylolithiums or Grignard reagents can be used interchangeably. (a) allyl bromide + phenyllithium; (b) isopropyllithium + 1-bromobut-2-ene; (c) 1,4-dibromobut-2-ene + two equivalents of propyllithium. **15.20.** (b) $[4 + 2]$ cycloaddition of one butadiene with just one of the double bonds of another butadiene. **15.21.** 800. **15.22.** (a) 353 nm;

(b) 313 nm; (c) 232 nm; (d) 292 nm. **15.24.** (a) isolated; (b) conjugated; (c) cumulated; (d) conjugated; (e) conjugated; (f) cumulated and conjugated. **15.25.** (a) allylcyclohexane; (b) 3-chlorocyclopentene; (c) 3-bromo-2-methylpropene; (e) 4-bromobut-2-en-1-ol and 1-bromobut-3-en-2-ol; (f) 5,6-dibromohexa-1,3-diene, 1,6-dibromohexa-2,4-diene, and 3,6-dibromohexa-1,4-diene (minor); (g) 1-(methoxymethyl)-2-methylcyclopentene and 1-methoxy-1-methyl-2-methylenecyclopentane; (h) and (i) Diels–Alder adducts. **15.26.** (a) allyl bromide + isobutyl Grignard; (b) 1-bromo-3-methylbut-2-ene + $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{MgBr}$; (c) cyclopentyl-MgBr + 1-bromopent-2-ene. **15.28.** (a) 19,000; (b) second structure. **15.32.** (a) The product isomerized, 1630 suggests conjugated; the UV spectrum supports conjugation; (b) 2-propylcyclohexa-1,3-diene.

CHAPTER 16

16.2. (a) +31.8 kJ/mole; (b) –88.6 kJ/mole; (c) –112.0 kJ/mole. **16.5.** Two of the eight pi electrons are unpaired in two non-bonding orbitals, an unstable configuration. **16.7.** (a) nonaromatic (internal H's prevent planarity); (b) nonaromatic (one ring atom has no *p* orbital); (c) aromatic, [14]annulene; (d) aromatic (in the outer system). **16.8.** Azulene is aromatic, but the other two are antiaromatic. **16.10.** The cation (cyclopropenium ion) is aromatic; the anion is antiaromatic. **16.12.** (a) antiaromatic if planar; (b) aromatic if planar; (c) aromatic if planar; (d) antiaromatic if planar; (e) nonaromatic; (f) aromatic if planar. **16.14.** cyclopropenium fluoroborate. **16.19.** (a) aromatic; (b) aromatic; (c) nonaromatic; (d) aromatic; (e) aromatic; (f) nonaromatic; (g) aromatic; (h) not aromatic. **16.24.** (a) fluorobenzene; (b) 4-phenylbut-1-yne; (c) 3-methylphenol or *m*-cresol; (d) *o*-nitrostyrene; (e) *p*-bromobenzoic acid; (f) isopropyl phenyl ether; (g) 3,4-dinitrophenol; (h) benzyl ethyl ether. **16.25.** 3-phenylprop-2-en-1-ol. **16.27.** (a) *o*-dichlorobenzene; (b) *p*-nitroanisole; (c) 2,3-dibromobenzoic acid; (d) 2,7-dimethoxynaphthalene; (e) *m*-chlorobenzoic acid; (f) 2,4,6-trichlorophenol; (g) 2-*sec*-butylbenzaldehyde; (h) cyclopropenium tetrafluoroborate. **16.30.** The second is deprotonated to an aromatic cyclopentadienyl anion. **16.31.** (d), (e) The fourth structure, with two three-membered rings, was considered the most likely and was called Ladenburg benzene. **16.37.** (a) three; (b) one; (c) *meta*-dibromobenzene. **16.38.** (a) α -chloroacetophenone; (b) 4-bromo-1-ethylbenzene. **16.45.** 2-isopropyl-5-methylphenol.

CHAPTER 17

17.3. The sigma complex for *p*-xylene has the + charge on two 2° carbons and one 3° carbon, compared with three 2° carbons in benzene. **17.9.** Bromine *adds* to the alkene but *substitutes* on the aryl ether, evolving gaseous HBr. **17.10.** Strong acid is used for nitration, and the amino group of aniline is protonated to a deactivating $-\text{NH}_3^+$ group. **17.12.** (a) 2,4- and 2,6-dinitrotoluene; (b) 3-chloro-4-nitrotoluene and 5-chloro-2-nitrotoluene; (c) 3- and 5-nitro-2-bromobenzoic acid; (d) 4-methoxy-3-nitrobenzoic acid; (e) 5-methyl-2-nitrophenol and 3-methyl-4-nitrophenol. **17.15.** (a) phenylcyclohexane; (b) *o*- and *p*-methylanisole, with overalkylation products; (c) 1-isopropyl-4-(1,1,2-trimethylpropyl)benzene. **17.16.** (a) phenylcyclohexane; (b) *tert*-butylbenzene; (c) *p*-di-*tert*-butylbenzene; (d) *o*- and *p*-isopropyltoluene. **17.17.** (a) *tert*-butylbenzene; (b) 2- and 4-*sec*-butyltoluene; (c) no reaction; (d) (1,1,2-trimethylpropyl)benzene. **17.18.** (a) *sec*-butylbenzene and others; (b) OK; (c) +disub, trisub; (d) No, deactivated; (e) OK. **17.20.** (a) $(\text{CH}_3)_2\text{CHCH}_2\text{COCl}$, benzene, AlCl_3 ; (b) $(\text{CH}_3)_3\text{CCOCl}$, benzene, AlCl_3 ; (c) PhCOCl , benzene, AlCl_3 ; (d) CO/HCl , $\text{AlCl}_3/\text{CuCl}$, anisole; (f) Clemmensen on (b); (g) $\text{CH}_3(\text{CH}_2)_2\text{COCl}$, benzene, AlCl_3 then Clemmensen. **17.21.** Fluoride leaves in a fast exothermic step; the C–F bond is only slightly weakened in the reactant-like transition state (Hammond postulate). **17.23.** (a) 2,4-dinitroanisole; (b) 2,4- and 3,5-dimethylphenol; (c) *N*-methyl-4-nitroaniline; (d) 2,4-dinitrophenylhydrazine. **17.33.** (a) (trichloromethyl)hexachlorocyclohexane; (c) *cis*- and *trans*-1,2-dimethylcyclohexane; (d) 1,4-dimethylcyclohexa-1,4-diene. **17.34.** (a) benzoic acid; (b) terephthalic acid

(benzene-1,4-dicarboxylic acid); (c) phthalic acid (benzene-1,2-dicarboxylic acid). **17.36.** 60% beta, 40% alpha; reactivity ratio = 1.9 to 1. **17.39.** (a) 1-bromo-1-phenylpropane. **17.40.** (a) HBr, then Grignard with ethylene oxide; (b) CH_3COCl and AlCl_3 , then Clemmensen, Br_2 and light, then $^-\text{OCH}_3$; (c) nitrate, then Br_2 and light, then NaCN. **17.42.** (a) 3-ethoxytoluene; (b) *m*-tolyl acetate; (c) 2,4,6-tribromo-3-methylphenol; (d) 2,4,6-tribromo-3-(tribromomethyl)phenol; (e) 2-methyl-1,4-benzoquinone; (f) 2,4-di-*tert*-butyl-5-methylphenol. **17.50.** indanone. **17.60.** kinetic control at 0 °C, thermodynamic control at 100 °C.

CHAPTER 18

18.1. (a) 5-hydroxyhexan-3-one; ethyl β -hydroxypropyl ketone; (b) 3-phenylbutanal; β -phenylbutylaldehyde; (c) *trans*-2-methoxycyclohexanecarbaldehyde; (d) 6,6-dimethylcyclohexa-2,4-dienone. **18.2.** (a) 2-phenylpropanal; (b) acetophenone. **18.3.** No γ -hydrogens. **18.8.** (a) heptan-3-one; (b) pentanal; (c) phenylacetone; (d) benzyl cyclopentyl ketone; (e) phenylacetaldehyde. **18.10.** (a) benzyl alcohol; (b) benzaldehyde; (c) hept-1-en-3-one; (d) pent-3-enal; (e) 3-propylpenta-1,4-dien-3-ol; (f) 5-hydroxypentanal. **18.13.** $[(\text{CH}_3)_3\text{P}-\text{R}]^+$ could lose a proton from a CH_3 . **18.16.** (a) Wittig of $\text{PhCH}_2\text{Br} + \text{acetone}$; (b) Wittig of $\text{CH}_3\text{I} + \text{PhCOCH}_3$; (c) Wittig of $\text{PhCH}_2\text{Br} + \text{PhCH}=\text{CHCHO}$; (d) Wittig of $\text{EtBr} + \text{cyclohexanone}$. **18.18.** second < fourth < first < third. **18.22.** *Z* and *E* isomers. **18.23.** (a) cyclohexanone and methylamine; (b) butan-2-one and ammonia; (c) acetaldehyde and aniline; (d) 6-aminoheptan-2-one. **18.27.** (a) benzaldehyde and semicarbazide; (b) camphor and hydroxylamine; (c) tetralone and phenylhydrazine; (d) cyclohexanone and 2,4-DNP; (e) 4-(*o*-aminophenyl)butan-2-one. **18.30.** (a) tetralone and ethanol; (b) acetaldehyde and propan-2-ol; (c) hexane-2,4-dione and ethanediol; (d) cyclohexanone and propane-1,3-diol; (e) 5-hydroxypentanal and cyclohexanol; (f) $(\text{HOCH}_2\text{CH}_2\text{CH}_2)_2\text{CHCHO}$. **18.34.** (a) 4-hydroxycyclohexanecarboxylic acid; (b) 4-oxocyclohexanecarboxylic acid; (c) 3-oxocyclohexanecarboxylic acid; (d) *cis*-3,4-dihydroxycyclohexanecarboxylic acid. **18.36.** (a) indane; (b) hexane; (c) ethylene ketal of 2-propylcyclohexanone; (d) propylcyclohexane. **18.43.** hexane-2,5-dione. **18.44.** 1-phenylbutan-2-one (benzyl ethyl ketone). **18.46.** cyclobutanone. **18.52.** (all H^+ cat.) (a) cyclobutanone and hydroxylamine; (b) benzaldehyde and cyclopentylamine; (c) benzylamine and cyclopentanone; (d) β -tetralone and ethylene glycol; (e) cyclohexylamine and acetone; (f) cyclopentanone and methanol. **18.57.** (a) NaBD_4 , then H_2O ; (b) NaBD_4 , then D_2O ; (c) NaBH_4 , then D_2O . **18.60.** (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCl}$ and AlCl_3 , then Clemmensen; (b) EtMgBr , then H_3O^+ ; (c) $\text{Cl}_2/\text{FeCl}_3$, then Dow process to phenol; NaOH, CH_3I , then Gatterman; (d) oxidize to the acid, SOCl_2 , then AlCl_3 . **18.64.** (a) hexan-3-one; (b) hexan-2-one and hexan-3-one; (c) hexan-2-one; (d) cyclodecanone; (e) 2- and 3-methylcyclodecanone. **18.66.** A heptan-2-one. **18.69.** A is the ethylene acetal of butan-2-one; B is butan-2-one. **18.70.** *trans*-but-2-enal (crotonaldehyde).

CHAPTER 19

19.1. Pyridine, 2-methylpyridine, pyrimidine, pyrrole, imidazole, indole, and purine are aromatic. **19.3.** (a) pentan-2-amine; (b) *N*-methylbutan-2-amine; (c) *m*-aminophenol; (d) 3-methylpyrrole; (e) *trans*-cyclopentane-1,2-diamine; (f) *cis*-3-aminocyclohexanecarbaldehyde. **19.4.** (a) resolvable (chiral carbons); (b) not resolvable (N inverts); (c) symmetric; (d) not resolvable; proton on N is removable; (e) resolvable (chiral quat. salt). **19.6.** (a) aniline < ammonia < methylamine < NaOH; (b) *p*-nitroaniline < aniline < *p*-methylaniline; (c) pyrrole < aniline < pyridine < piperidine; (d) 3-nitropyrrole < pyrrole < imidazole. **19.7.** (a) secondary amine; (b) primary amine; (c) alcohol. **19.8.** isobutylamine. **19.9.** (a) piperidine; (b) diethylmethylamine; (c) propanal; (d) propan-1-ol. **19.16.** (a) benzylamine + excess CH_3I ; (b) 1-bromopentane + excess NH_3 ; (c) benzyl bromide + excess NH_3 . **19.17.** (a) $\text{CH}_3\text{CONHCH}_2\text{CH}_3$; (b) $\text{PhCON}(\text{CH}_3)_2$; (c) *N*-hexanoyl-piperidine. **19.23.** (a) cyclohexanediazonium chloride (then cyclohexanol and cyclohexene); (b) *N*-nitroso-*N*-ethylhexan-2-amine;

(c) *N*-nitrosopiperidine; (d) benzenediazonium chloride. **19.25.** (a) diazotize, then HBF_4 , heat; (b) diazotize, then CuCl ; (c) protect (CH_3COCl), then 3 $\text{CH}_3\text{I}/\text{AlCl}_3$, H_3O^+ , diazotize, H_3PO_2 ; (d) diazotize, then CuBr ; (e) diazotize, then KI ; (f) diazotize, then CuCN ; (g) diazotize, then H_2SO_4 , H_2O , heat; (h) diazotize, then couple with resorcinol. **19.26.** (a) CH_3NH_2 , $\text{NaBH}(\text{OAc})_3$; (b) PhCHO , $\text{NaBH}(\text{OAc})_3$; (c) aniline/ H^+ , then LiAlH_4 ; (d) $\text{H}_2\text{NOH}/\text{H}^+$, then LiAlH_4 ; (e) $\text{H}_2\text{NOH}/\text{H}^+$ then LiAlH_4 ; (f) piperidine + cyclopentanone + $\text{NaBH}(\text{OAc})_3$. **19.31.** (a) nitrate, reduce; (b) brominate, then nitrate and reduce; (c) nitrate, then brominate and reduce; (d) oxidize toluene, then nitrate and reduce. **19.34.** only (b), (d), (f), and (h). **19.48.** (a) triethylamine; (b) An acid converts it to a solid ammonium salt. (c) Rinse the clothes with diluted vinegar (acetic acid). **19.51.** A is butan-2-amine; B is diethylamine. **19.53.** 2,2-dimethylpropan-1-amine.

CHAPTER 20

20.2. (a) 2-iodo-3-methylpentanoic acid; α -iodo- β -methylvaleric acid; (b) (*Z*)-3,4-dimethylhex-3-enoic acid; (c) 2,3-dinitrobenzoic acid; (d) *trans*-1,2-cyclohexanedicarboxylic acid; (e) 2-chlorobenzene-1,4-dicarboxylic acid; 2-chloroterephthalic acid; (f) 3-methylhexanedioic acid; β -methyladipic acid. **20.3.** (a) first, second, third; (b) third, second, first; (c) third, second, fourth, first. **20.7.** Broad acid OH centered around 3000; conjugated carbonyl about 1690; $\text{C}=\text{C}$ about 1650. **20.8.** (a) propanoic acid; (b) $-\text{CHO}$ proton triplet between $\delta 9$ and $\delta 10$. **20.11.** (a) KMnO_4 (b) KMnO_4 ; (c) $\text{PhMgBr} + \text{ethylene oxide}$, oxidize; (d) PBr_3 , Grignard, CO_2 ; (e) conc. KMnO_4 , heat; (f) KCN , then H_3O^+ . **20.15.** (a) methanol and salicylic acid, H^+ ; methanol solvent, dehydrating agent; (b) methanol and formic acid, H^+ , distill product as it forms; (c) ethanol and phenylacetic acid, H^+ , ethanol solvent, dehydrating agent. **20.16.** (a) see Fischer esterification; (b) $\text{C}-^{18}\text{O}-\text{CH}_3$; (c) mass spectrometry. **20.19.** (a) phenylacetic acid and LiAlH_4 ; (b) phenylacetic acid and LiAlH_4 , then PCC; (c) 3-oxocyclopentanecarboxylic acid + B_2H_6 , then H_3O^+ . **20.21.** (a) benzene + $\text{CH}_3\text{CH}_2\text{COCl}$, AlCl_3 ; or propionic acid + 2 PhLi , then H_3O^+ ; (b) Add 2 CH_3Li , then H_3O^+ . **20.36.** (a) Grignard + CO_2 ; or KCN , then H_3O^+ ; (b) conc. KMnO_4 , heat; (c) Ag^+ ; (d) SOCl_2 , then $\text{LiAlH}(\text{O}-i\text{-Bu})_3$; or LiAlH_4 , then PCC; (e) CH_3OH , H^+ ; or CH_2N_2 ; (f) LiAlH_4 or B_2H_6 ; (g) SOCl_2 , then excess CH_3NH_2 . **20.38.** diastereomers. **20.40.** (a) 2-phenylpropanoic acid; (b) 2-methylpropenoic acid; (c) *trans*-hex-2-enoic acid. **20.43.** phenoxyacetic acid. **20.45.** (a) stockroom; heptaldehyde; students; heptanoic acid; (b) air oxidation; (c) prepare fresh samples immediately before using.

CHAPTER 21

21.2. No aldehyde $\text{C}-\text{H}$ at 2700 and 2800; no acid $\text{O}-\text{H}$ centered at 3000. **21.4.** (a) acid chloride $\text{C}=\text{O}$ at 1810; (b) primary amide $\text{H}_2\text{C}=\text{CHCONH}_2$ at 1640, two $\text{N}-\text{H}$ around 3300; (c) anhydride $\text{C}=\text{O}$ double absorption at 1740 and 1810. **21.5.** (a) acrylamide, (b) 5-hydroxyhexanoic acid lactone. **21.8.** (a) ethanol, propionyl chloride; (b) phenol, 3-methylhexanoyl chloride; (c) benzyl alcohol, benzoyl chloride; (d) cyclopropanol, cyclohexanecarbonyl chloride; (e) *tert*-butyl alcohol, acetyl chloride; (f) allyl alcohol, succinoyl chloride. **21.9.** (a) dimethylamine, acetyl chloride; (b) aniline, acetyl chloride; (c) ammonia, cyclohexanecarbonyl chloride; (d) piperidine, benzoyl chloride. **21.10.** (i) PhCH_2OH ; (ii) Et_2NH . **21.25.** (a) butan-1-amine; (b) cyclohexylethylamine; (c) $(\text{CH}_2)_6\text{NH}$ (7-membered ring); (d) morpholine; (e) cyclohexylmethylpropylamine. **21.30.** (a) benzene + acetyl chloride; (b) benzene + benzoyl chloride; (c) benzene + butyryl chloride, then Clemmensen. **21.32.** (a) *n*-octyl alcohol, acetic formic anhydride (formyl chloride is unavailable); (b) *n*-octyl alcohol, acetic anhydride (cheap, easy to use); (c) phthalic anhydride, ammonia (anhydride forms monoamide); (d) succinic anhydride, methanol (anhydride forms monoester). **21.34.** (a) acetic anhydride; (b) methanol, H^+ ; (c) LiAlH_4 , then protonate; (d) PhNH_2 , warm. **21.37.** (a) SOCl_2 , then $\text{HN}(\text{CH}_3)_2$, then LiAlH_4 ; (b) acetic anhydride, then

LiAlH₄. **21.38.** (a) SOCl₂, then NH₃, then POCl₃; (b) LiAlH₄, make tosylate, NaCN; (c) Fe/HCl, diazotize, CuCN. **21.44.** (a) ethyl benzoate; (b) acetic benzoic anhydride; (c) PhCONHPh; (d) 4-methoxybenzophenone; (e) Ph₃COH; (f) benzaldehyde. **21.47.** (after H⁺) (a) HCOOH + PhOH; (b) CH₃CH₂COOH + CH₃CH₂OH; (c) 3-(*o*-hydroxyphenyl)propanoic acid; (d) (CH₂OH)₂ + (COOH)₂. **21.48.** (a) acetic formic anhydride; (b) SOCl₂, then CH₃COONa; (c) oxalyl chloride; (d) H⁺ and heat to form anhydride, then one equivalent of (CH₃)₂CHOH; (e) oxidize aldehyde with Ag⁺, then form lactone with H⁺; (f) NaBH₄ to reduce aldehyde, then H⁺ to form lactone. **21.55.** (a) Ph₃COH; (b) 3 EtMgBr + EtCOOEt, then H₃O⁺. **21.59.** **A** is hexanenitrile; **B** is hexanamide. **21.62.** Acetic anhydride; add water to hydrolyze it to dilute acetic acid. **21.64.** CH₃CH₂OCOCH₂CN. **21.65.** ethyl crotonate. **21.67.** δ-valerolactam.

CHAPTER 22

22.8. (a) PhC(NCH₃)CH₃; (b) CH₂=C(Ph)NMe₂; (c) cyclohexanone phenyl imine; (d) piperidine enamine of cyclohexanone. **22.9.** (a) enamine + allyl bromide; (b) enamine + PhCH₂Br; (c) enamine + PhCOCl. **22.13.** (a), (b) cyclopentanecarboxylate and chloroform/iodoform; (c) PhCOCBr₂CH₃. **22.19.** (a) 3-hydroxy-2-methylpentanal; (b) 3-hydroxy-2,4-diphenylbutanal. **22.20.** retro-aldol, reverse of aldol condensation. **22.24.** (a) 2-ethylhex-2-enal; (b) 1,3-diphenylbut-2-en-1-one; (c) 2-cyclohexylidenecyclohexanone. **22.26.** PhCH=CHCOCH=CHPh, "dibenzalacetone". **22.28.** (a) 2-methyl-3,3-diphenylprop-2-enal; (b) 4,4-dimethyl-1-phenylpent-2-en-1-one. **22.29.** benzaldehyde and acetaldehyde. **22.32.** (a) butanal and pentanal (no); (b) two PhCOCH₂CH₃ (yes); (c) acetone and PhCHO (yes); (d) 6-oxoheptanal (yes, but also attack by enolate of aldehyde); (e) nonane-2,8-dione (yes). **22.34.** (a) transesterification to a mixture of methyl and ethyl esters; (b) saponification. **22.35.** no second alpha proton to form the final enolate to drive the reaction to completion. **22.36.** (a) methyl 2-methyl-3-oxopentanoate; (b) ethyl 2,4-diphenyl-3-oxobutanoate. **22.37.** methyl 2-benzyl-5-phenyl-3-oxopentanoate. **22.38.** (a) ethyl butyrate; (b) methyl phenylacetate; (c) ethyl 3-methylbutanoate, or common name: ethyl isovalerate. **22.42.** (a) PhCO—CH(Ph)COOCH₃; (b) poor choice, four products; (c) EtOCOCO—CH₂COOEt; (d) EtOCOCH(CH₃)COOEt. **22.43.** (a) PhCOOEt + CH₃CH₂COOEt; (b) PhCH₂COOMe + MeOCOCOMe; (c) (EtO)₂C=O + PhCH₂COOEt; (d) (CH₃)₃CCOOMe + CH₃(CH₂)₃COOMe. **22.47.** Alkylate malonic ester with; (a) PhCH₂Br; (b) CH₃I twice; (c) PhCH₂CH₂Br; (d) Br(CH₂)₄Br (twice). **22.49.** (a) 4-phenylbutan-2-one; (b) cyclobutyl methyl ketone; (c) cyclopentanone. **22.50.** Alkylate acetoacetic ester with: (a) PhCH₂Br; (b) Br(CH₂)₄Br (twice); (c) PhCH₂Br, then CH₂=CHCH₂Br. **22.53.** Alkylate the enamine of cyclohexanone with MVK. **22.56.** (a) malonic ester anion + ethyl cinnamate; (b) acetoacetic ester anion + acrylonitrile, then H₃O⁺; (c) enamine of cyclopentanone + acrylonitrile, then H₃O⁺; (d) enamine of 2-methylcyclopentanone + PhCOCH=CH₂, then H₃O⁺; (e) alkylate acetoacetic ester with CH₃I, then MVK, then H₃O⁺; (f) cyclopent-2-enone + (CH₂=CH)₂CuLi. **22.61.** (1) g < b < f < a < e < c < d; (2) a, c, d, e. **22.66.** (a) EtCOPh + MVK; (b) cyclohexanone and ethyl vinyl ketone; (c) cyclohexanone and (CH₃)₂C=CHCOCH₃. **22.70.** Alkylate with: (a) PhCH₂Br; (b) CH₃CH₂Br, then (bromomethyl)cyclopentane; (c) Br(CH₂)₅Br, alkylate on each end to make a cyclohexane ring. **22.71.** Alkylate with: (a) CH₃CH₂Br, then PhCH₂Br; (b) Br(CH₂)₄Br; (c) MVK (hydrolysis, decarboxylation, then aldol gives product). **22.75.** (a) Dieckmann of dimethyl adipate, alkylation by allyl bromide, hydrolysis and decarboxylation; (c) Robinson with CH₃CH=CHCOCH₃, then reduction; (d) form enamine or enolate, acylate with ClCOOEt, methylate with CH₃I, do aldol with benzaldehyde.

CHAPTER 23

23.2. (a) two C*, two pairs of enantiomers; (b) one C*, one pair of enantiomers; (c) four C*, eight pairs of enantiomers; three C*, four pairs of enantiomers. **23.5.** (R) for D series, (S) for L series.

23.15. 28% alpha, 72% beta. **23.19.** Galactitol is symmetrical (meso) and achiral. **23.20.** L-gulose has the same structure as D-glucose, but with the CHO and CH₂OH ends interchanged. **23.21.** (a) D-mannonic acid; (b) D-galactonic acid; (c) Br₂ does not oxidize ketoses. **23.22.** (a) D-mannaric acid; (b) D-galactaric acid. **23.23.** **A** is galactose; **B** is glucose. **23.24.** (a) non-reducing; (b) reducing; (c) reducing; (d) non-reducing; (e) reducing; (f) "sucrose" is nonreducing; should have "-oside" ending. **23.27.** glucose, benzaldehyde, and HCN (toxic). **23.38.** **A** = D-galactose; **B** = D-talose; **C** = D-lyxose; **D** = D-threose. **23.44.** reducing and mutarotating. **23.45.** reducing and mutarotating. **23.46.** Trehalose is α-D-glucopyranosyl-α-D-glucopyranoside. **23.47.** Melibiose is 6-O-(α-D-galactopyranosyl)-D-glucopyranose. **23.54.** (a) D-ribose; (b) D-altrose; (c) L-erythrose; (d) L-galactose; (e) L-idose. **23.65.** (a) D-arabinose and D-lyxose; (b) D-threose; (c) **X** = D-galactose; (d) No; the optically active hexose is degraded to an optically active pentose that is oxidized to an optically active aldaric acid; (e) D-threose gives an optically active aldaric acid. **23.66.** (a) D-tagatose is a ketohexose, the C4 epimer of D-fructose; (b) A pyranose with the anomeric carbon (C2) bonded to the oxygen atom of C6. **23.71.** (a) no; (b) yes; (c) Only applies to double stranded DNA.

CHAPTER 24

24.6. As in pyrrole, the lone pair on the indole N is part of the aromatic sextet. One N in histidine is like that in pyridine, with the lone pair in an sp² hybrid orbital. **24.9.** Reductive amination of (a) CH₃COCOOH; (b) (CH₃)₂CHCH₂COCOOH; (c) HOCH₂COCOOH; (d) H₂NCOCH₂CH₂COCOOH. **24.10.** Start with (a) CH₃COOH; (b) (CH₃)₂CHCH₂CH₂COOH; (c) HOOCCH₂CH₂CH₂COOH. **24.11.** N-phthalimidomalonic ester and (a) (CH₃)₂CHBr; (b) PhCH₂Br; (c) BrCH₂CH₂COO⁻; (d) (CH₃)₂CHCH₂Br. **24.15.** The free amino group of the deacylated L enantiomer should become protonated (and soluble) in dilute acid. **24.23.** (a) nucleophilic aromatic substitution; (b) Edman cleaves only the N-terminal amino acid, leaving the rest of the chain intact for further degradation. **24.25.** Cys-Tyr-Phe-Gln-Asn-Cys-Pro-Arg-Gly·NH₂. **24.27.** Add ethyl chloroformate, then Gly, ethyl chloroformate, then Leu. Deprotect using H₂ and Pd. **24.30.** Add TFA (CF₃COOH), then Boc-Gly and DCC, then TFA, then Boc-Leu and DCC, then HF. **24.34.** (a) Ruhemann's purple; (b) alanine; (c) CH₃CONH(CH₂)₄CH(COOH)NHCOCH₃; (d) L-proline and N-acetyl-D-proline; (e) CH₃CH₂CH(CH₃)CH(NH₂)CN; (f) isoleucine; (g) 2-bromo-4-methylpentanoic acid (after water workup); (h) 2-amino-4-methylpentanoic acid or leucine. **24.35.** (a) NH₃/H₂/Pd; (b) Br₂/PBr₃, H₂O, excess NH₃; (c) NH₃/HCN/H₂O, H₃O⁺; (d) Gabriel-malonic ester synthesis. **24.37.** Convert the alcohol to a tosylate and displace with excess ammonia. **24.42.** aspartylphenylalanine methyl ester. **24.43.** Phe-Ala-Gly-Met-Ala. **24.46.** (a) C-terminal amide (CONH₂), or amide (Gln) of Glu; (b) The N-terminal Glu is a cyclic amide (a "pyroglutamyl" group) that effectively blocks the N-terminus. The C-terminal Pro is an amide; (c) cyclic pentapeptide. **24.49.** Ornithine is H₂N(CH₂)₃CH(NH₂)COOH, a homolog of lysine, with a similar pI. **24.51.** Ala-Lys-Phe-Gln-Gly-Tyr-Arg-Ser-Leu-Ile.

CHAPTER 25

25.2. Hydrogenation of trilinolein (m.p. below -4 °C) gives tristearin (m.p. 72 °C). **25.9.** Estradiol is a phenol, soluble in aqueous sodium hydroxide. **25.13.** (1) sesquiterpene; (2) monoterpene; (3) monoterpene; (4) sesquiterpene. **25.15.** (a) a triglyceride (a fat); (b) an alkyl sulfate detergent; (c) a wax; (d) a sesquiterpene; (e) a prostaglandin; (f) a steroid. **25.17.** (a) H₂/Ni, LiAlH₄; (b) H₂/Ni; (c) stearic acid from (b) add SOCl₂, then octadecan-1-ol (a); (d) O₃, then (CH₃)₂S; (e) KMnO₄, then H⁺; (f) Br₂/PBr₃, then H₂O. **25.19.** reduce (LiAlH₄), esterify with sulfuric acid. **25.21.** (a) Sodium stearate precipitates in dilute acid or Ca²⁺; (b) Paraffin "wax" does not saponify; (c) Myristic acid shows acidic properties when treated with base; (d) Triolein decolorizes Br₂ in CCl₄. **25.28.** Petroselenic acid is *cis*-octadec-6-enoic acid.

CHAPTER 26

26.1. The radical intermediates would not be benzylic if they added with the other orientation. **26.3.** The benzylic hydrogens are more likely to be abstracted. **26.4.** They all add to give the more highly substituted carbocation. **26.5.** (a) is possible; (b) is very good; (c) is terrible. **26.6.** The cation at the end of a chain abstracts hydride from a benzylic position in the middle of a chain. In isobutylene, a tertiary cation would have to abstract a hydride from a secondary position: unlikely. **26.15.** The third hydroxyl group of glycerol allows for profuse cross-linking of the chains (with a terephthalic acid linking two of these hydroxyl groups), giving a very rigid polyester. **26.19.** Glycerol allows

profuse cross-linking, as in Problem 26-15. **26.23.** (a) a polyurethane; (b) condensation polymer; (c) $\text{HO}(\text{CH}_2)_3\text{NH}_2$ and CO_2 . **26.24.** (a) a polyester; (b) condensation polymer; (c) dimethyl terephthalate and butane-1,4-diol; transesterification. **26.25.** (a) a polyurea; (b) condensation polymer; (c) $\text{H}_2\text{N}(\text{CH}_2)_9\text{NH}_2$ and CO_2 . **26.26.** (a) polyether (addition polymer); (b) ethylene oxide; (c) base catalyst. **26.28.** (a) $-\text{CH}_2-\text{O}-[\text{CH}_2-\text{O}]_n-$; (c) addition polymer. **26.31.** (b) and (c) No to both. Poly(vinyl acetate) is an addition polymer. The ester bonds are not in the main polymer chain; (d) Vinyl alcohol (the enol form of acetaldehyde) is not stable.

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