Answers to Selected Problems

Chapter 1

1.18 (a), (c), (f), (g) are tetrahedral; (e) is trigonal planar; (b) is linear; (d) is angular; (h) is trigonal pyramidal.

1.23 (a) and (d); (b) and (e); and (c) and (f).

1.31 (a), (g), (i), (l), represent different compounds that are not isomeric; (c–e), (h), (j), (m), (n), (o) represent the same compound; (b), (f), (k), (p) represent constitutional isomers.

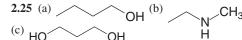
1.38 (a) The structures differ in the positions of the nuclei.

1.46 (a) A negative charge; (b) a negative charge; (c) trigonal pyramidal.

Chapter 2

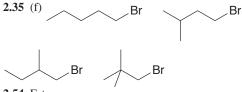
2.11 (c) Propyl bromide; (d) isopropyl fluoride; (e) phenyl iodide.

(e) diisopropyl ether.



2.29 (a) ketone; (c) 2° alcohol; (e) 2° alcohol.

2.30 (a) 3 alkene, and a 2° alcohol; (c) phenyl and 1° amine; (e) phenyl, ester and 3° amine; (g) alkene and 2 ester groups.





Chapter 3

3.2 (a), (c), (d), and (f) are Lewis bases; (b) and (e) are Lewis acids.

3.4 (a) $[H_3O^+] = [HCO_2^-] = .0042 M$; (b) Ionization = 4.2%.

3.5 (a) $pK_a = 7$; (b) $pK_a = -0.7$; (c) Because the acid with a $pK_a = 5$ has a larger K_a , it is the stronger acid.

3.8 The pK_a of the methylaminium ion is equal to 10.6 (Section 3.6B). Because the pK_a of the anilinium ion is equal to 4.6, the anilinium ion is a stronger acid than the methylaminium ion, and aniline (C₆H₅NH₂) is a weaker base than methylamine (CH₃NH₂).

3.14 (a) $CHCl_2CO_2H$ would be the stronger acid because the electron-withdrawing inductive effect of two chlorine atoms would make its hydroxyl proton more positive. (c) CH_2FCO_2H would be the stronger acid because a fluorine atom is more electronegative than a bromine atom and would be more electron withdrawing.

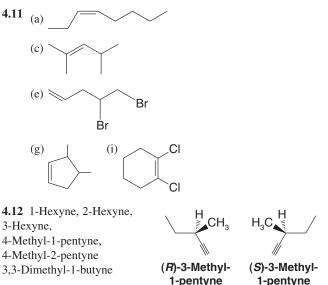
3.28 (a)
$$pK_a = 3.752$$
; (b) $K_a = 10^{-13}$.

Chapter 4

4.8 (a) (1,1-dimethylethyl)cyclopentane or *tert*-butyl-cyclopentane; (c) butylcyclohexane; (e) 2-chlorocyclopentanol.

4.9 (a) 2-Chlorobicyclo[1.1.0]butane; (c) bicyclo[2.1.1]hexane; (e) 2-methylbicyclo[2.2.2]octane.

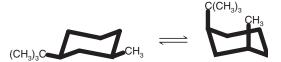
4.10 (a) trans-3-Heptene; (c) 4-ethyl-2-methyl-1-hexene



4.24 (a) 3,3,4-Trimethylhexane; (c) 3,5,7-Trimethylnonane; (e) 2-Bromobicyclo[3.3.1]nonane; (g) Cyclobutylcyclopentane.

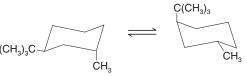
4.39 (a) Pentane would boil higher because its chain is unbranched. (c) 2-Chloropropane because it is more polar and has a higher molecular weight. (e) CH_3COCH_3 because its molecules are more polar.





More stable conformation because both alkyl groups are equatorial

(b)



More stable because larger group is equatorial

ĊH,

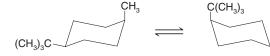
CH.

(c)



More stable conformation because both alkyl groups are equatorial

(d)



More stable because larger group is equatorial

Chapter 5

5.1 (a) achiral; (c) chiral; (e) chiral.

5.2 (a) Yes; (c) no.

5.3 (a) They are the same. (b) They are enantiomers.

5.7 The following possess a plane of symmetry and are, therefore, achiral: screwdriver, baseball bat, hammer.

5.13 (a) enantiomers; (c) enantiomers.

5.19 (a) diastereomers; (c) no; (e) no.

5.21 (a) represents A; (b) represents C; (c) represents B.

5.23 B (2*S*,3*S*)-2,3-Dibromobutane; C (2*R*,3*S*)-2,3-Dibromobutane.

5.39 (a) same; (c) diastereomers; (e) same; (g) diastereomers; (i) same; (k) diastereomers; (m) diastereomers; (o) diastereomers; (q) same.

Chapter 6

6.6 (a) The reaction is $S_N 2$ and, therefore, occurs with inversion of configuration. Consequently, the configuration of (+)-2-chlorobutane is opposite [i.e., (*S*)] to that of (-)-2-butanol [i.e., (*R*)]. (b) The configuration of (-)-2-iodobutane is (*R*).

6.14 Protic solvents are formic acid, formamide, ammonia, and ethylene glycol. The others are aprotic.

6.16 (a) CH_3O^- ; (c) $(CH_3)_3P$.

6.20 (a) 1-Bromopropane would react more rapidly, because, being a primary halide, it is less hindered. (c) 1-Chlorobutane, because the carbon bearing the leaving group is less hindered than in 1-chloro-2-methylpropane. (e) 1-Chlorohexane because it is a primary halide. Phenyl halides are unreactive in S_N2 reactions.

6.21 (a) Reaction (1) because ethoxide ion is a stronger nucleophile than ethanol; (c) reaction (2) because triphenylphosphine, $(C_6H_5)_3P$, is a stronger nucleophile than triphenylamine. (Phosphorus atoms are larger than nitrogen atoms.)

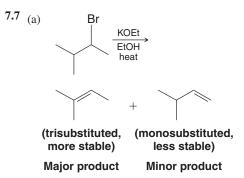
6.22 (a) Reaction (2) because bromide ion is a better leaving group than chloride ion; (c) reaction (2) because the concentration of the substrate is twice that of reaction (1).

6.26 The better yield is obtained by using the secondary halide, 1-bromo-1-phenylethane, because the desired reaction is E2. Using the primary halide will result in substantial S_N^2 reaction as well, producing the alcohol instead of the desired alkene.

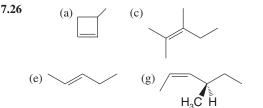
6.38 (a) You should use a strong base, such as RO^- , at a higher temperature to bring about an E2 reaction. (b) Here we want an $S_N I$ reaction. We use ethanol as the solvent *and as the nucleophile*, and we carry out the reaction at a low temperature so that elimination is minimized.

Chapter 7

7.4 (a) 2,3-Dimethyl-2-butene would be the more stable because the double bond is tetrasubstituted. (c) *cis*-3-Hexene would be more stable because its double bond is disubstituted.

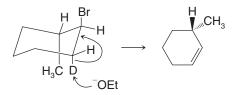


7.25 (a) We designate the position of the double bond by using the *lower* of the two numbers of the doubly bonded carbon atoms, and the chain is numbered from the end nearer the double bond. The correct name is *trans*-2-pentene. (c) We use the lower number of the two doubly bonded carbon atoms to designate the position of the double bond. The correct name is 1-methylcyclohexene.



7.28 (a) (E)-3,5-Dimethyl-2-hexene; (c) 6-methyl-3-heptyne; (e) (3Z,5R)-5-chloro-3-hepten-6-yne.

7.43 Only the deuterium atom can assume the anti coplanar orientation necessary for an E2 reaction to occur.

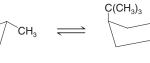


Chapter 8

8.1 2-Bromo-1-iodopropane.

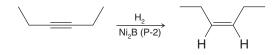
8.7 The order reflects the relative ease with which these alkenes accept a proton and form a carbocation. 2-Methylpropene reacts



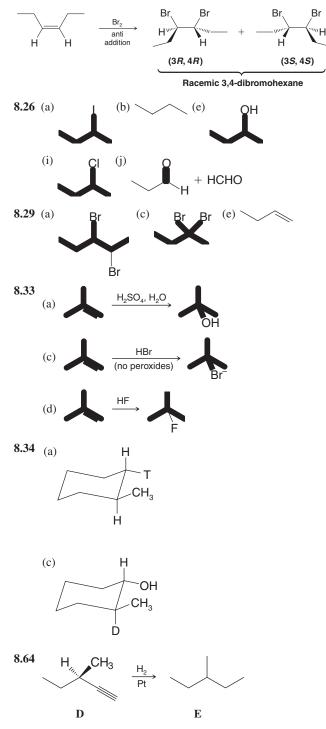


fastest because it leads to a 3° cation; ethene reacts slowest because it leads to a 1° cation.

8.25 By converting the 3-hexyne to cis-3-hexene using H₂/Ni₂B (P-2).

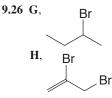


Then, addition of bromine to cis-3-hexene will yield (3R,4R), and (3S,4S)-3,4-dibromohexane as a racemic form.



Chapter 9

- **9.4** (a) One; (b) two; (c) two; (d) one; (e) two; (f) two.
- 9.8 A doublet (3H) downfield; a quartet (1H) upfield.
- 9.9 A, CH₃CHICH₃; B, CH₃CHCl₂; C, CH₂CICH₂CH₂Cl
- 9.40 Phenylacetylene.

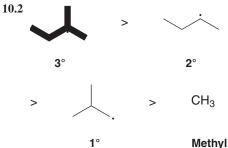


9.24 Q is bicyclo[2.2.1]hepta-2,5-diene.

R is bicyclo[2.2.1]heptane.

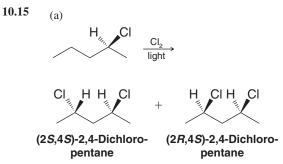
Chapter 10

10.1 (a) $\Delta H^{\circ} = -545 \text{ kJ mol}^{-1}$; (c) $\Delta H^{\circ} = -101 \text{ kJ mol}^{-1}$; (e) $\Delta H^{\circ} = +53 \text{ kJ mol}^{-1}$; (g) $\Delta H^{\circ} = -132 \text{ kJ mol}^{-1}$.





10.14 (a) Cyclopentane; (b) 2,2-dimethylpropane.

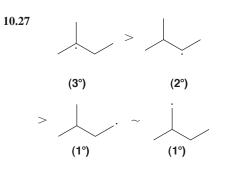


(c) No, (2R,4S)-2,4-dichloropentane is achiral because it is a meso compound. (It has a plane of symmetry passing through C3.)

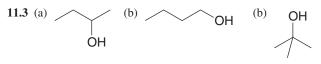
(e) Yes, by fractional distillation or by gas-liquid chromatography. (Diastereomers have different physical properties. Therefore, the two isomers would have different vapor pressures.)

10.16 (a) The only fractions that would contain chiral molecules (as enantiomers) would be those containing 1-chloro-2-methylbutane and the two diastereomers of 2-chloro-3-methylbutane. These fractions would not show optical activity, however, because they would contain racemic forms of the enantiomers.

(b) Yes, the fractions containing 1-chloro-2-methylbutane and the two containing the 2-chloro-3-methylbutane diastereomers.

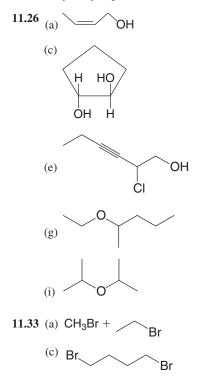


Chapter 11



11.10 Use an alcohol containing labeled oxygen. If all of the labeled oxygen appears in the sulfonate ester, then it can be concluded that the alcohol C-O bond does not break during the reaction.

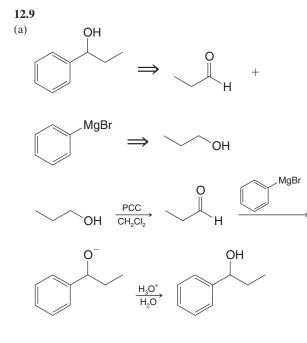
11.25 (a) 3,3-Dimethyl-1-butanol; (c) 2-methyl-1,4-butanediol; (e) 1-methyl-2-cyclopenten-1-ol.

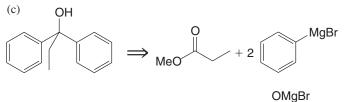


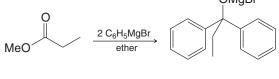
Chapter 12

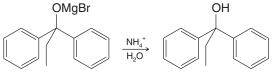
12.3 (a) LiAlH₄; (c) NaBH₄

12.4 (a)
$$^+$$
NHCrO₃Cl⁻(PCC)/CH₂Cl₂
(c) H₂CrO₄/acetone

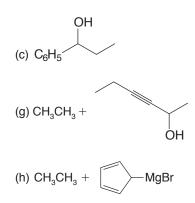




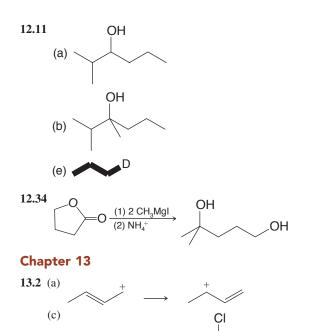




$12.10 \ \ (a) \ CH_3CH_3; \ (b) \ CH_3CH_2D;$



A-4



13.6 (b) 1,4-Cyclohexadiene and 1,4-pentadiene are isolated dienes.

and

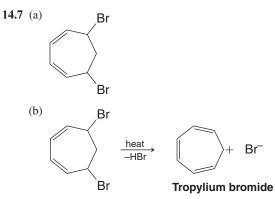
13.15 (a) 1,4-Dibromobutane + t-BuOK, and heat; (g) HC \equiv CCH=CH₂ + H₂, Ni₂B (P-2).

13.19 (a) 1-Butene + *N*-bromosuccinimide, then *t*-BuOK and heat; (e) cyclopentane + Br_2 , hv, then *t*-BuOK and heat, then *N*-bromosuccinimide.

13.42 The endo adduct is less stable than the exo, but is produced at a faster rate at 25° C. At 90° C the Diels-Alder reaction becomes reversible; an equilibrium is established, and the more stable exo adduct predominates.

Chapter 14

- **14.1** (a) 4-Bromobenzoic acid (or *p*-bromobenzoic acid)
 - (b) 2-Benzyl-1.3-cyclohexadiene
 - (c) (2-chloro-2-pentyl) benzene
 - (d) Phenyl propyl ether



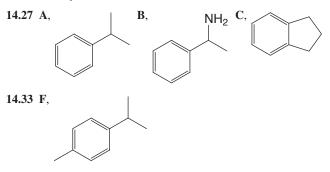
These results suggest that the bonding in tropylium bromide is ionic; that is, it consists of a positive tropylium ion and a negative bromide ion. **14.9** The cyclopropenyl cation.

14.15 A, *o*-bromotoluene; **B**, *p*-bromotoluene; **C**, *m*-bromotoluene; **D**, benzyl bromide.

14.23 Hückel's rule should apply to both pentalene and heptalene. Pentalene's antiaromaticity can be attributed to its having 8 π electrons. Heptalene's lack of aromaticity can be attributed to its having 12 π electrons. Neither 8 nor 12 is a Hückel number.

14.25 The bridging $-CH_2$ group causes the 10 π electron ring system (below) to become planar. This allows the ring to become aromatic.

14.28 (a) The cycloheptatrienyl anion has 8 π electrons, and does not obey Hückel's rule; the cyclononatetraenyl anion with 10 π electrons obeys Hückel's rule.

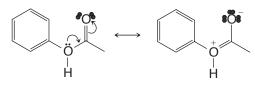


Chapter 15

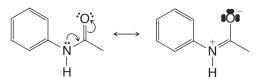
(racemic)

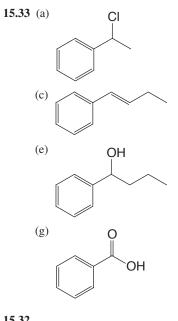
15.6 If the methyl group had no directive effect on the incoming electrophile, we would expect to obtain the products in purely statistical amounts. Since there are two ortho hydrogen atoms, two meta hydrogen atoms, and one para hydrogen, we would expect to get 40% ortho (2/5), 40% meta (2/5), and 20% para (1/5). Thus, we would expect that only 60% of the mixture of mononitrotoluenes would have the nitro group in the ortho or para position. And, we would expect to obtain 40% of *m*-nitrotoluene. In actuality, we get 96% of combined *o*- and *p*-nitrotoluene and only 4% *m*-nitrotoluene. This result shows the ortho–para directive effect of the methyl group.

15.9 (b) Structures such as the following compete with the benzene ring for the oxygen electrons, making them less available to the benzene ring.

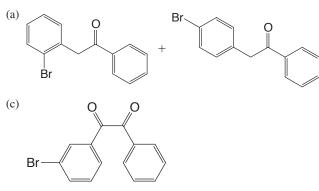


(d) Structures such as the following compete with the benzene ring for the nitrogen electrons, making them less available to the benzene ring.





15.32



Chapter 16

16.2 (a) 1-Pentanol; (c) pentanal; (e) benzyl alcohol.

16.6 A hydride ion.

16.17 (b) $CH_3CH_2Br + (C_6H_5)_3P$, then strong base, then $C_6H_5COCH_3$; (d) $CH_3I + (C_6H_5)_3P$, then strong base, then cyclopentanone; (f) $CH_2 = CHCH_2Br + (C_6H_5)_3P$, then strong base, then C₆H₅CHO.

16.20 (a) $CH_3CH_2CH_2OH$; (c) $CH_3CH_2CH_2OH$ (h) $CH_3CH_2CH = CHCH_3$; (j) $CH_3CH_2CO_2^{-}NH_4^{+} + Ag_{\downarrow}$ (l) CH₃CH₂CH=NNHCONH₂; (n) CH₃CH₂CO₂

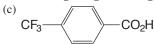
16.46 X is

С

16.47 Y is 1-phenyl-2-butanone; Z is 4-phenyl-2-butanone.

Chapter 17

17.3 (a) CH_2FCO_2H ; (c) CH_2CICO_2H ; (e) $CH_3CH_2CHFCO_2H$;

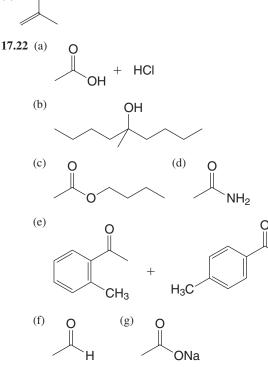


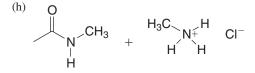
17.6 (a) $C_6H_5CH_2Br + Mg$ in diethyl ether, then CO_2 , then H_3O^+ ; (c) $CH_2 = CHCH_2Br + Mg$ in diethyl ether, then CO_2 , then H_3O^+ .

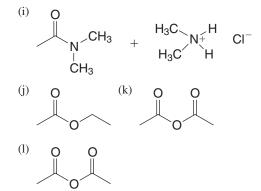
17.7 (a), (c), and (e).

17.9 In the carboxyl of benzoic acid.

17.14 (a) $(CH_3)_3CCO_2H + SOCI_2$, then NH₃, then P₄O₁₀, heat; (b)







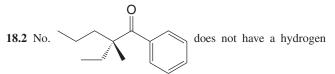
17.46 (a) Diethyl succinate; (c) ethyl phenylacetate; (e) ethyl chloroacetate.

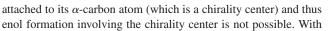
17.47 X is diethyl malonate.

Chapter 18

18.1 The enol form is phenol. It is especially stable because it is aromatic.

19.17





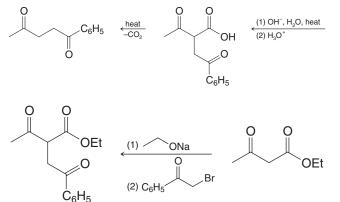
the chirality center is a
$$\beta$$
 carbon and

thus enol formation does not affect it.

18.5 Base is consumed as the reaction takes place. A catalyst, by definition, is not consumed.

18.8 (a) Reactivity is the same as with any $S_N 2$ reaction. With primary halides substitution is highly favored, with secondary halides elimination competes with substitution, and with tertiary halides elimination is the exclusive course of the reaction. (b) Acetoacetic ester and 2-methylpropene. (c) Bromobenzene is unreactive toward nucleophilic substitution.

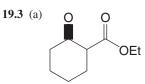
18.10 Working backward



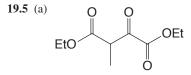
18.17 In a polar solvent, such as water, the keto form is stabilized by solvation. When the interaction with the solvent becomes minimal, the enol form achieves stability by internal hydrogen bonding.

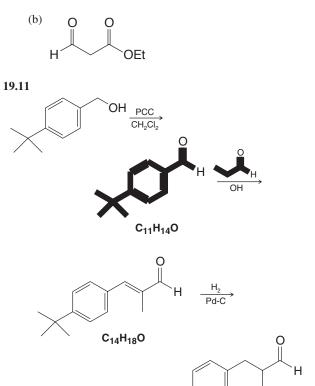
18.25 (b) **D** is racemic *trans*-1,2-cyclopentanedicarboxylic acid, **E** is *cis*-1,2-cyclopentanedicarboxylic acid, a meso compound.

Chapter 19

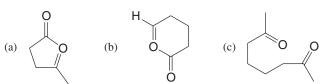


(b) To undergo a Dieckmann condensation, diethyl 1,5-pentanedioatc would have to form a highly strained four-membered ring.

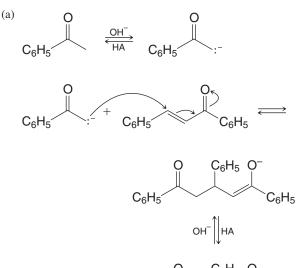


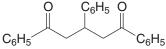


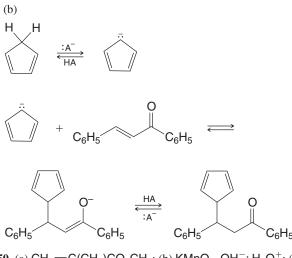
Lily aldehyde (C₁₄H₂₀O)



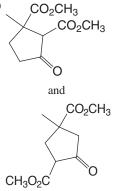
Notice that starting compounds are drawn so as to indicate which atoms are involved in the cyclization reaction. **19.19**







19.50 (a) $CH_2 = C(CH_3)CO_2CH_3$; (b) $KMnO_4$, OH^- ; H_3O^+ ; (c) CH_3OH , HA; (d) CH_3ONa , then H_3O^+ (e) and (f) CO_2CH_2



(g) OH⁻, H₂O, then H₃O⁺; (h) heat (-CO₂); (i) CH₃OH, HA; (j) CO_2CH_3

CHCO₂CH₃

(k) H_2 , Pt; (m) CH₃ONa, then H_3O^+ ; (n) 2 NaNH₂ + 2 CH₃I

Chapter 20

20.5 (a) $CH_3(CH_2)_3CHO + NH_3 \xrightarrow{H_2, Ni} CH_3(CH_2)_3CH_2NH_2$ (c) $CH_3(CH_2)_4CHO + C_6H_5NH_2 \xrightarrow{\text{LiBH}_3CN}$

CH₃(CH₂)₄CH₂NHC₆H₅

20.6 The reaction of a secondary halide with ammonia is almost always accompanied by some elimination.

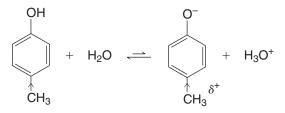
20.7 (a) Methoxybenzene + HNO₃ + H₂SO₄, then Fe + HCl; (b) Methoxybenzene + CH₃COCl + AlCl₃, then NH₃ + H₂ + Ni; (c) toluene + Cl₂ and light, then (CH₃)₃N; (d) *p*-nitrotoluene + KMnO₄ + OH⁻, then H₃O⁺, then SOCl₂ followed by NH₃, then NaOBr (Br₂ in NaOH); (e) toluene + *N*-bromosuccinimide in CCl₄, then KCN, then LiAlH₄.

20.12 *p*-Nitroaniline + Br_2 + Fe, followed by $H_2SO_4/NaNO_2$ followed by CuBr, then H_2/Pt , then $H_2SO_4/NaNO_2$ followed by H_3PO_2 .

20.45 W is N-benzyl-N-ethylaniline.

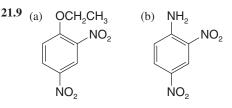
Chapter 21

21.1 The electron-releasing group (i.e., $-CH_3$) changes the charge distribution in the molecule so as to make the hydroxyl oxygen less positive, causing the proton to be held more strongly; it also destabilizes the phenoxide anion by intensifying its negative charge. These effects make the substituted phenol less acidic than phenol itself.



Electron-releasing — CH_3 destabilizes the anion more than the acid. pK_a is larger than for phenol.

21.4 (a) The para-sulfonated phenol. (b) For ortho sulfonation.



21.10 That *o*-chlorotoluene leads to the formation of two products (*o*-cresol and *m*-cresol), when submitted to the conditions used in the Dow process, suggests that an elimination-addition mechanism takes place.

21.11 2-Bromo-1,3-dimethylbenzene, because it has no *o*-hydrogen atom, cannot undergo an elimination. Its lack of reactivity toward sodium amide in liquid ammonia suggests that those compounds (e.g., bromobenzene) that do react, react by a mechanism that begins with an elimination.

21.14 (a) 4-Fluorophenol because a fluorine substituent is more electron withdrawing than a methyl group. (e) 4-Fluorophenol because fluorine is more electronegative than bromine.

21.16 (a) 4-Chlorophenol will dissolve in aqueous NaOH; 4-chloro-1-methylbenzene will not. (c) Phenyl vinyl ether will react with bromine in carbon tetrachloride by addition (thus decolorizing the solution); ethyl phenyl ether will not. (e) 4-Ethylphenol will dissolve in aqueous NaOH; ethyl phenyl ether will not.

Chapter 22

22.1 (a) Two; (b) two; (c) four.

22.5 Acid catalyzes hydrolysis of the glycosidic (acetal) group.

22.9 (a) 2 CH₃CHO, one molar equivalent HIO₄; (b) HCHO + $HCO_2H + CH_3CHO$, two molar equivalents HIO₄;

(c) HCHO + OHCCH(OCH₃)₂, one molar equivalent HIO₄; (d) HCHO + HCO₂H + CH₃CO₂H, two molar equivalents HIO₄; (e) 2 CH₃CO₂H + HCO₂H, two molar equivalents HIO₄

22.18 D-(+)-Glucose.

22.23 One anomeric form of D-mannose is dextrorotatory ($[\alpha]_D = + 29.3$), the other is levorotatory ($[\alpha]_D = -17.0$).

22.24 The microorganism selectively oxidizes the —CHOH **24.8** Glutathione is group of D-glucitol that corresponds to C5 of D-glucose.

22.27 A is D-altrose; B is D-talose, C is D-galactose

Chapter 23

23.5 Br_2 in CCl_4 would react with geraniol (discharging the bromine color) but would not react with menthol.

23.12 (a) C₂H₅OH, HA, heat; or SOCl₂, then C₂H₅OH; (d) SOCl₂, then (CH₃)₂NH; (g) SOCl₂, then LiAlH[OC(CH₃)₃]₃

23.15 Elaidic acid is *trans*-9-octadecenoic acid.

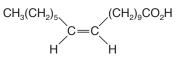
23.19 A is CH₃(CH₂)₅C=CNa

B is $CH_3(CH_2)_5C \equiv CCH_2(CH_2)_7CH_2CI$

C is
$$CH_3(CH_2)_5C \equiv CCH_2(CH_2)_7CH_2CN$$

E is CH₃(CH₂)₅C = CCH₂(CH₂)₇CH₂CO₂H

Vaccenic acid is



23.20 F is FCH₂(CH₂)₆CH₂C=CH

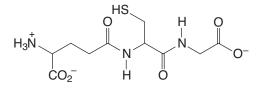
G is $FCH_2(CH_2)_6CH_2C \equiv C(CH_2)_7CI$

H is $FCH_2(CH_2)_6CH_2C \equiv C(CH_2)_7CN$

I is $FCH_2(CH_2)_7C \equiv C(CH_2)_7CO_2H$

Chapter 24

24.5 The labeled amino acid no longer has a basic $-NH_2$ group; it is, therefore, insoluble in aqueous acid.



24.22 Arg·Pro·Pro·Gly·Phe·Ser·Pro·Phe·Arg

 $24.23 \quad Val\cdot Leu\cdot Lys\cdot Phe\cdot Ala\cdot Glu\cdot Ala$

Chapter 25

25.9

25.2 (a) The nucleosides have an *N*-glycosidic linkage that (like an *O*-glycosidic linkage) is rapidly hydrolyzed by aqueous acid, but one that is stable in aqueous base.

25.4 (a) The isopropylidene group is part of a cyclic acetal. (b) By treating the nucleoside with acetone and a trace of acid.

25.7 (b) Thymine would pair with adenine, and, therefore, adenine would be introduced into the complementary strand where guanine should occur.

