ANSWERS TO THE SELF-TESTS

CHAPTER 1

A-1. (a) P;
$$1s^2 2s^2 2p^6 3s^2 3p^3$$

(b)
$$S^{2-}$$
; $1s^22s^22p^63s^23p^6$

Formal charge:
$$-1$$
 0 0 Net charge: -1

$$C$$
) -1 : \ddot{O} :

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(b)
$$O \equiv N - \ddot{O}$$
:

Formal charge: $+1 + 1 - 1$ Net charge: $+1$

Formal charge: 0 0 -1 Net charge: -1

(b)
$$\ddot{O}=N=\ddot{O}$$
:

Formal 0 +1 0 Net charge: +1 charge:

The more stable Lewis structures are

(a)
$$\ddot{\ddot{}}$$
 $\ddot{\ddot{}}$ $\ddot{\ddot{}$

A-4. (a)
$$H - \ddot{C} - \ddot{N} - H$$
 (b) $H - \ddot{C} - \ddot{C} = \dot{C}$



775

A-5. (a)
$$C_{12}H_{20}O$$
 :QH

(b)
$$C_{10}H_{22}$$

A-6. (a) has only
$$sp^3$$
-hybridized carbon atoms

has only sp^2 -hybridized carbon atoms

has only one sp^2 -hybridized carbon atom

A-7.
$$\begin{array}{c} :O: \\ \parallel \\ S^{2+} \\ \bigcirc :O: \\$$

Formal Net charge: -1 charge: -1 0 0

(*d*)

- **A-13.** (a) 11 σ ; 1 π
- (b) 9σ ; 2π
- (c) 12σ ; 4π
- (d) 13σ ; 4π

- **A-14.** (a) H_3C —CH=CH—CH \int_{sp^3} \int_{sp^2} \int_{sp^2}
- (c) All carbons are sp^2 .

- (b) $H \underbrace{C = C}_{SP} \underbrace{CH_2 CH_2}_{SP^3}$
- $(d) \qquad Sp^{2} \qquad C = N$ $Sp^{2} \qquad Sp^{3}$
- B-1. (*b*) B-2. (*b*) B-3. (*d*) (c) B-4. B-5. (*a*) B-6. (*b*) B-7. (*a*) B-8. (*d*) B-9. **B-10.** (*d*) **B-11.** (*b*) (*b*) **B-12.** (*e*)
- **B-13.** (*d*) **B-14.** (*b*) **B-15.** (*d*)

CHAPTER 2

A-1. CH₃CH₂CH₂CH₂— CH₃CH₂CHCH₃

Common:n-Butylsec-ButylSystematic:Butyl1-Methylpropyl

$$\begin{array}{ccc} CH_3 & CH_2 \\ | & | & | \\ CH_3CHCH_2 - & CH_3C - \\ & & CH_3 - \\ & CH_3 - \\$$

Common:Isobutyltert-ButylSystematic:2-Methylpropyl1,1-Dimethylethyl

- **A-2.** (*a*) 28 (8 C—C; 20 C—H)
- (*b*) 27(9 C—C; 18 C—H)

- **A-3.** (a) Oxidized
- (b) Neither
- (c) Neither
- (d) Reduced

- $\begin{array}{ccc} & & \text{CH}_3\text{CHCH}_3\\ \textbf{A-4.} & \textit{(a)} & \text{CH}_3\text{CHCHCHCH}_3\\ & & \text{CH}_3 & \text{CH}_3 \end{array}$
- (b) Six methyl groups, three isopropyl groups
- **A-5.** (*a*) 3,4-Dimethylheptane
- (b) (1,2-Dimethylpropyl)cyclohexane
- **A-6.** Primary Secondary Tertiary
 (a) 4 3 2
 - (a) 4 3 (b) 3 5
- **A-7.** (a) 1,3-Dimethylbutyl; secondary
 - (b) 1,1-Diethylpropyl; tertiary
 - (c) 2,2-Diethylbutyl; primary

3

A-8.
$$CH_3$$
 $CH_3CHCHCH_2CH_3 \equiv C_7H_{16}$ CH_3

$$C_7H_{16} + 11O_2 \longrightarrow 7CO_2 + 8H_2O$$

A-9.



Cyclopentane



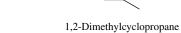
1,1-Dimethylcyclopropane



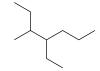
Methylcyclobutane



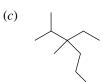
Ethylcyclopropane



A-10. (a)



4-Ethyl-3-methylheptane



3-Ethyl-2,3dimethylhexane

 $(2\hbox{-}Methylbutyl) cyclohexane$

A-11. (a) CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₃

(c) (CH₃)₂CHCHCH(CH₃)₂ | | CH₃

(b) $(CH_3)_3CC(CH_3)_3$

(d) $(CH_3)_3CC(CH_3)_3$

A-12.



2,2-Dimethylpentane



2,4-Dimethylpentane

3-Ethylpentane

(c)

2,3-Dimethylpentane



3,3-Dimethylpentane

A-13. Alcohol, alkene, ester, ketone

A-14. 10,049 kJ/mol

B-1. (a) **B-2.** (d) **B-3.** (d) **B-4.**

B-5. (*b*) **B-6.** (*a*) **B-7.** (*c*) **B-8.** (*c*)

B-9. (a) **B-10.** (a) **B-11.** (b) **B-12.** (e)

B-13. (*d*) **B-14.** (*d*)

CHAPTER 3

A-3. $(CH_3)_3CCH_2C(CH_3)_3 = 2,2,4,4$ -tetramethylpentane

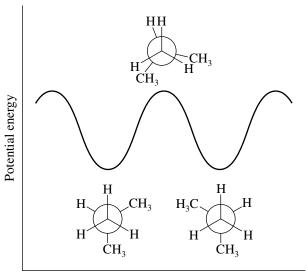
A-7. (a) C (b) A and B (c) D (d) A

A-8.
$$H_3C$$
 H
 $CH(CH_3)_2$
 CH_3
 H
 $CH(CH_3)_2$
 $CH(CH_3)_3$
 $CH(CH_3)_3$
 $CH(CH_3)_3$
 $CH(CH_3)_3$
 $CH(CH_3)_3$
 $CH(CH_3)_3$
 CH

A-9. *cis*-1-Ethyl-3-methylcyclohexane has the lower heat of combustion.

A-10. Tricyclic; C₁₀H₁₆

A-11. The form of the curve more closely resembles ethane than butane.



Torsion angle

- B-1. (*d*)
- B-2. (*b*)
- B-3. (c)
- B-4. (*a*)

- B-5. (c)
- B-6. (*a*)
- B-7. (*d*)
- B-8. (*e*)

- B-9. (c)
- **B-10.** (*e*)
- **B-11.** (*b*)
- **B-12.** (*a*)

- **B-13.** (*d*) **B-14.** (*b*)

CHAPTER 4

- A-1. trans-1-Bromo-3-methylcyclopentane (*a*)
 - 2-Ethyl-4-methyl-1-hexanol

A-2. (a)
$$ICH_2CCH_2CH_2CH_2CH_2CH_3$$

Cl

(b)
$$CH(CH_3)_2$$

- A-3. **Functional class:** 1-ethyl-3-methylbutyl alcohol (*a*)
 - **Substitutive:** 5-methyl-3-hexanol
 - **Functional class:** 1,1,2-trimethylbutyl chloride (*b*) **Substitutive:** 2-chloro-2,3-dimethylpentane
- Conjugate acid CH₃OH₂; conjugate base CH₃O:

OH

- **A-5.** (*a*) CH₃CH₂CH₂Cl
- (b) $CH_3CH_2\dot{C}(CH_3)$

A-6. (a)
$$CH_3CH_2O^- + NH_3 \rightleftharpoons CH_3CH_2OH + NH_2^- (K < 1)$$

$$\begin{array}{cccccc} Conjugate & Conjugate & Stronger & Stronger & base & acid & base & b$$

A-7. (*a*) Three

A-8.
$$CH_3$$
 CH_3 CH_3 CH_3 CH_3 CH_3 CH_2 CI + HCI CH_3

A-9.
$$Br \cdot + \bigcirc \longrightarrow HBr + \bigcirc \longrightarrow Br + Br \cdot$$

A-10.
$$\Delta H^{\circ} = -57 \text{ kJ } (-13.5 \text{ kcal})$$

A-11. (a)
$$(CH_3)_3C - \ddot{O}H + H - Br \longrightarrow (CH_3)_3C - \ddot{O}H_2 + Br^-$$

 $(CH_3)_3C - \ddot{O}H_2 \longrightarrow H_2O + (CH_3)_3C^+$
 $(CH_3)_3C^+ + : \ddot{B}\ddot{r}:^- \longrightarrow (CH_3)_3C - Br$

$$(b) \quad \begin{array}{c} \text{H}_{3}\text{C} \overset{\text{CH}_{3}}{\underset{\delta \wedge +}{\sum}} \text{H} \\ \overset{\text{C}}{\underset{\delta \wedge ----}{\sum}} \\ \text{H}_{3}\text{C} \end{array}$$

(c) Water is displaced directly from the oxonium ion of 1-butanol by bromide ion. A primary carbocation is not involved.

- **A-12.** (*a*) 3-Methyl-3-pentanol
- (c) Fluorine (F_2)
- (*e*) Cl₂

- (b) $KOC(CH_3)_3$
- (d) Ethyl radical, $CH_3\dot{C}H_2$ **B-4.** (c)
- **B-1.** (*e*) **B-2.** (*c*) **B-3.** (*b*) **B-4.**
- **B-5.** (*e*) **B-6.** (*c*) **B-7.** (*d*) **B-8.** (*a*)
- **B-9.** (c) **B-10.** (d) **B-11.** (c) **B-12.** (e)
- **B-13.** (a) **B-14.** (c) **B-15.** (c) **B-16.** (c)

CHAPTER 5

- **A-1.** (*a*) 2,4,4-Trimethyl-2-pentene
- (c) (E)-2,7-Dibromo-3-(2-methylpropyl)-2-heptene
- (b) (E)-3,5-Dimethyl-4-octene
- (d) 5-Methyl-4-hexen-3-ol

- **A-2.** (a)
 - 2,3-Dimethyl-2-pentene

(c)

1,6-Dimethylcyclohexene

- (b) Cl
 - 5-Chloro-2-methyl-1-hexene
- (d) OH

4-Methyl-4-penten-2-ol

- - (b) Isomer 5
- (c) Isomers 1 and 4
- (d) Isomers 2 and 3

5

- **A-4.** Two sp^2 C atoms; four sp^3 C atoms; three sp^2 — sp^3 σ bonds
- **A-5.** (a)
- (c) OH
- (b) Cl
- A-6.

- (Z)-3-Methyl-3-hexene
- (E)-3-Methyl-3-hexene
- **A-7.** (a) $H_2C = CCH_2CH_2CH_3 + (CH_3)_2C = CHCH_2CH_3$ (major) CH_3

$$(b) \qquad \begin{array}{c} \operatorname{CH}_2 & \operatorname{CH}_3 \\ + & \end{array} \qquad \text{(major)}$$

- (c) $(CH_3)_2CHCHCH(CH_3)_2$ (X = CI, Br, I)
- $(d) \quad \begin{array}{c} \text{CH}_3 \\ | \\ \text{CCC(CH}_3)_3 \end{array}$

A-9. Step 1: Protonation

Step 2: Dissociation

Step 3: Deprotonation

$$+$$
 \ddot{O} H_{3} O^{+}

A-11.
$$CH_3 \ddot{O} : \ CH_3 \ Br$$
 $CH_3 + Br^-$

A-12. Cis isomer:

$$(CH_3)_2CH$$
 CI CI

Trans isomer:

$$(CH_3)_2CH$$
 CI
 $CH(CH_3)_2$
 CI

The trans isomer will react faster because its most stable conformation (with the isopropyl group equatorial) has an axial Cl able to undergo E2 elimination.

A-13. Rearrangement (hydride migration) occurs to form a more stable carbocation.

$$OH \xrightarrow{H_3PO_4} OH_2 \xrightarrow{-H^+} H_2O$$

A-14.

3-Ethyl-4,4-dimethyl-2-pentene

B-1. (*c*)

B-2. (*c*)

B-3. (*d*)

B-4. (*c*)

B-5. (*a*)

B-6. (*b*)

B-7. (a)

B-8. (*a*)

B-9. (*a*)

B-10. (*d*)

B-11. (*b*)

B-12. (*c*)

B-13. (*a*)

B-14. (*c*)

B-15. (a)

CHAPTER 6

A-1. Five;

3,4-Dimethyl-1-pentene



2,3-Dimethyl-2-pentene

(*E*)-3,4-Dimethyl-2-pentene



2,3-Dimethyl-1-pentene

(Z)-3,4-Dimethyl-2-pentene

$$\begin{array}{ccc} & & \text{OH} \\ | & \\ \text{A-2.} & (a) & (\text{CH}_3)_2\text{CCH}_2\text{CH}_3 \end{array}$$

(c)

(b) HBr, peroxides

A-3. (a)
$$(B_3 \cap CH_3 \cap CH_3$$

$$(CH_{3}CH_{2}CHCH(CH_{3})_{2} \xrightarrow{NaOCH_{3} \atop CH_{3}OH} CH_{3}CH_{2}CH = C(CH_{3})_{2} \xrightarrow{CH_{3}COOH} CH_{3}CH_{2}CH_{2}CH_{2}CH_{3}CCH_{2}CH_{2}CH_{3}CH_{2}$$

A-4. Initiation: ROOR
$$\xrightarrow{\text{light}}$$
 2RO·
RO· + HBr \longrightarrow ROH + Br·

Propagation: Br· + CH₃CH₂CH=CH₂
$$\longrightarrow$$
 CH₃CH₂ĊHCH₂Br CH₃CH₂CHCH₂Br + Br· CH₃CH₂CH₂CH₂CH₂Br + Br·

A-5.

A-6.
$$CH_3CH_2$$
 $C=C$
 CH_2CH_3
 CH_3COOH
 CH_3CH_2
 CH_3CH_2
 CH_3CH_2
 CH_3CH_2
 CH_3CH_2
 CH_3CH_2
 CH_3CH_3

A-7. Step 1: Protonation to form a carbocation

Step 2: Nucleophilic addition of chloride ion

A-8.
$$H_2C = CCH_2CH_3$$
 or $(CH_3)_2C = CHCH_3$ \xrightarrow{HCl} $CH_3CCH_2CH_2CH_3$

2-Methyl-1-butene 2-Methyl-2-butene 2-Chloro-2-methylbutane

A-10.
$$+$$
 HCl $\xrightarrow{\text{hydride}}$ $\xrightarrow{\text{shift}}$ \downarrow : $\ddot{\text{Cl}}$: $\ddot{\text{Cl}}$

A-11.
$$(CH_3)_2CHC = CH_2$$
 $(CH_3)_2CHCCH_3$
 $(C$

$$C \xrightarrow{1. O_3} (CH_3)_2 C = O (2 \text{ mol})$$

- B-1. (c) B-2. (a) B-3. (c) B-4. (*d*)
- B-5. B-6. B-7. (b) B-8. (b) (*d*) (*e*)
- B-9. **B-10.** (*b*) (b) **B-11.** (*a*) **B-12.** (*e*)
- **B-13.** (*e*)

CHAPTER 7

- 1 and 2, both achiral; identical A-1. (a)
 - (b) 3 and 4, both chiral; enantiomers
 - 5 chiral, 6 achiral (meso); diastereomers (c)
 - 7 and 8, both chiral; diastereomers (*d*)
 - 9 and 10, both chiral; diastereomers (*e*)
- 3: (R)-2-Chlorobutane; A-2.

(S)-2-Chlorobutane

- (2S,3R)-2,3-Dibromopentane;
- (2R,3R)-2,3-Dibromopentane 8:
- (2E,5R)-5-Chloro-2-hexene;
- (2Z,5S)-5-Chloro-2-hexene 10:
- **A-3.** (a) Three; meso form is possible.
- (c) Four; no meso form possible.
- (b) Eight; no meso form possible.



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A-5. Chiral stereoisomers:

ĊH₃

$$\begin{array}{ccccc} CH_3 & CH_3 \\ H - Cl & Cl - H \\ Cl - H & And & Cl - H \\ CH_3 & CH_3 & CH_3 \\ (2S,3S)-2,3- & (2R,3R)-2,3- \\ Dichlorobutane & Dichlorobutane \\ \end{array}$$

CH₃

Meso stereoisomer (achiral); plane of symmetry indicated with dashed line

$$\begin{array}{c} CH_3 \\ H \longrightarrow Cl \\ \hline H \longrightarrow Cl \\ CH_3 \end{array}$$

meso-2,3-Dichlorobutane

A-6. (a)
$$[\alpha] = -31.2^{\circ}$$
 (b) 30% S

A-7. (a)
$$CH_3$$
 CH_3 CH_3

(b)
$$H_3C$$
 H $C=C$ H CI_2 H_3C H CI H_3C H CI

Meso form (only stereoisomer)

$$C) \qquad \underbrace{CH_3COOH}_{CH_3COOH} \qquad \underbrace{H_3C}_{CH_2CH_3} \qquad \underbrace{H_3C}_{CH_2CH_3} \qquad \underbrace{H_3C}_{H} \qquad \underbrace{H_3C}_{H}$$

- **A-8.** (a) (2S,3S)-1,3-Dibromo-2-chlorobutane
 - (b) (R)-1-Ethylcyclohex-2-en-1-ol

A-9. Two: (2R,3S)-2-bromo-3-chlorobutane and (2S,3S)-2-bromo-3-chlorobutane; they are diastereomers.

Racemic mixture

B-1. (*c*)

B-2. (*c*)

B-3. (*b*)

(b)

B-4. (*d*)

B-5. (*b*)

B-6. (*c*)

B-7. (*d*)

B-8. (*d*)

B-9. (*b*)

B-10. (*c*)

B-11. (*d*)

B-12. (*d*)

B-13. (*e*)

B-14. (*b*)

CHAPTER 8

A-1. (a) CH₃CH₂CH₂CH₂OCH₂CH₃

(e) N_3

$$(X = OTs, Br, I)$$

$$(g) \begin{array}{c} CH_3 \\ HS \longrightarrow H \\ F \\ CH_2CF \end{array}$$

A-2. $(CH_3)_2CHO^-Na^+ + CH_3CH_2CH_2Br$

$$\textbf{A-3.} \quad (a) \quad \textbf{H} \xrightarrow{\begin{array}{c} \textbf{CH}_3 \\ \textbf{OTs} \\ \textbf{CH}_2\textbf{CH}_3 \end{array}} \xrightarrow{\begin{array}{c} \textbf{NaBr} \\ \textbf{DMSO} \end{array}} \quad \textbf{Br} \xrightarrow{\begin{array}{c} \textbf{CH}_3 \\ \textbf{H} \\ \textbf{CH}_2\textbf{CH}_3 \end{array}} \xrightarrow{\begin{array}{c} \textbf{NaCN} \\ \textbf{CH}_2\textbf{CH}_3 \end{array}} \quad \textbf{H} \xrightarrow{\begin{array}{c} \textbf{CH}_3 \\ \textbf{CH}_2\textbf{CH}_3 \end{array}}$$

(b)

A-4. Step 1: Ionization to form a secondary carbocation



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Step 2: Rearrangement by methyl migration to form a more stable tertiary carbocation

$$\begin{array}{cccc} CH_3 & CH_3 \\ \hline CH_3C - CHCH_3 & \longrightarrow & CH_3C - CHCH_3 \\ \hline CH_3 & CH_3 & CH_3 \end{array}$$

Step 3: Capture of the carbocation by water, followed by deprotonation

A-5. (a) $(CH_3)_3CBr \xrightarrow{CH_3OH} (CH_3)_3COCH_3$

 S_N1 , unimolecular substitution; rate = $k[(CH_3)_3CBr]$

 S_N 2, bimolecular substitution; rate = $k[C_6H_{11}Cl][NaN_3]$

- **A-6.** (a) Sodium iodide is soluble in acetone, whereas the byproduct of the reaction, sodium bromide, is not. According to Le Chatelier's principle, the reaction will shift in the direction that will replace the component removed from solution, in this case toward product.
 - (b) Protic solvents such as water form hydrogen bonds to anionic nucleophiles, thus stabilizing them and decreasing their nucleophilic strength. Aprotic solvents such as DMSO do not solvate anions very strongly, leaving them more able to express their nucleophilic character.

A-7.
$$OH O^- Na^+$$

$$CH_3CH_2OH CH_3CH_2Br$$

$$A B C D$$

A-9. Dissociation to give a secondary carbocation

$$\begin{array}{cccc} CH_3CH_2CH_2CHCH(CH_3)_2 & \longrightarrow & CH_3CH_2CH_2\overset{\dagger}{C}HCH(CH_3)_2 \\ & & \\ Br \end{array}$$

Rearrangement by hydride migration to give a tertiary carbocation

$$\begin{array}{cccc} CH_3CH_2CH_2\overset{\dagger}{\underset{H}{\overset{}}}HC(CH_3)_2 & \longrightarrow & CH_3CH_2CH_2\overset{\dagger}{C}(CH_3)_2 \\ & H \end{array}$$

Capture of the carbocation by water to give product

$$CH_{3}CH_{2}CH_{2}CH_{2}\overset{\dagger}{C}(CH_{3})_{2} + : \ddot{O}H_{2} \xrightarrow{(-H^{+})} CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}C(CH_{3})_{2}$$

- **B-1.** (*b*) **B-2.** (*c*) **B-3.** (*d*) **B-4.** (*c*)
- **B-5.** (*d*) **B-6.** (*a*) **B-7.** (*c*) **B-8.** (*d*)
- **B-9.** (c) **B-10.** (a) **B-11.** (a) **B-12.** (c)
- **B-13.** (*c*) **B-14.** (*c*)

CHAPTER 9

- **A-1.** (*a*) 4,5-Dimethyl-2-hexyne
- (c) 6,6-Dimethylcyclodecyne
- (b) 4-Ethyl-3-propyl-1-heptyne
- A-2. (a) C1 (e) $(CH_3)_2CHC \equiv CH$ $CH_3CH_2CH_2C = CH_2$
 - (b) $CH_3CH_2CH_2CCH_3$ (f) $Na, NH_3(l)$
 - (c) H_2O , H_2SO_4 , $HgSO_4$ (g) H_3C C=C CH_2CH_3
 - $(d) \qquad \begin{matrix} \text{CH}_3 \\ \text{C=C} \end{matrix} \qquad \qquad \begin{matrix} \text{CH}_3 \\ \text{(h)} \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CHCO}_2\text{H} + \text{CH}_3\text{CH}_2\text{CO}_2\text{H}} \\ \text{H} \end{matrix}$
- **A-3.** Reaction (2) is effective; the desired product is formed by an S_N^2 reaction.

Reaction (1) is not effective, owing to E2 elimination from the secondary bromide.

Br
$$CH_3CH_2CHCH_3 + CH_3C \equiv CNa \longrightarrow CH_3CH = CHCH_3 + CH_3C \equiv CH + NaBr$$

A-4. (a)
$$CH_3CH_2Br \xrightarrow{KOC(CH_3)_3} H_2C = CH_2 \xrightarrow{Br_2} BrCH_2CH_2Br$$

$$BrCH_2CH_2Br \xrightarrow{1. NaNH_2, NH_3} HC = CH \xrightarrow{1. NaNH_2} HC = CCH_2CH_3$$

(b)
$$\text{HC} = \text{CCH}_2\text{CH}_3 \xrightarrow{\text{NaNH}_2} \text{NaC} = \text{CCH}_2\text{CH}_3 \xrightarrow{\text{CH}_3\text{CH}_2\text{Br}} \text{CH}_3\text{CH}_2\text{C} = \text{CCH}_2\text{CH}_3$$

(d)
$$HC \equiv CH \xrightarrow{NaNH_2} HC \equiv CNa \xrightarrow{(CH_3)_2CHCH_2Br} HC \equiv CCH_2CH(CH_3)_2$$

$$HC \equiv CCH_2CH(CH_3)_2 \xrightarrow{H_2O, H_2SO_4} CH_3CCH_2CH(CH_3)_2$$

A-5.
$$H_3C$$
 H $C=C$ H $CH_2CH_2CH_2CH_3$ (E) -2-Heptene

A-6.
$$(CH_3)_3CC \equiv CH$$
 $(CH_3)_3CC \equiv C$: Na^+

$$\mathrm{CH_3CH_2CH_2OH}$$
 $\mathrm{CH_3CH_2CH_2Br}$ C D

A-7. E:
$$HC \equiv CCH_2CH_3$$
 F: $CH_3CH_2C \equiv CCH_2CH_3$

A-8.
$$\bigcirc$$
 C=CH $\xrightarrow{\text{H}_2}$ \bigcirc CH=CH₂ $\xrightarrow{\text{1. B}_2\text{H}_6}$ \bigcirc CH₂CH₂OH

CHAPTER 10

A-1.
$$H_2C$$
= $CHCH_2CH$ = CH_2 H_2C = $CHCH$ = $CHCH_3$ (Conjugated)

$$\begin{array}{cccc} H_2C = CHC = CH_2 & H_2C = C = CHCH_2CH_3 \\ & & H_2C = C = C(CH_3)_2 \\ & & CH_3 & CH_3CH = C = CHCH_3 \end{array} \right\} Allenes$$

A-2.
$$H_2C=CH$$
 CH_3 $H_2C=CH$ H $H_2C=CHC=CH_2$ CH_3 CH_3 CH_3 CH_3 CH_3 CH_3

A-3.

(c)
$$+$$
 \bigcirc O \bigcirc (d) \bigcirc N—Br (NBS), hear

A-6.
$$CH_3$$

- **B-1.** (b) **B-2.** (c) **B-3.** (a) **B-4.** (c)
- **B-5.** (a) **B-6.** (d) **B-7.** (a) **B-8.** (a)
- **B-9.** (a) **B-10.** (d)

CHAPTER 11

- **A-1.** (a) m-Bromotoluene
- (c) o-Chloroacetophenone
- (b) 2-Chloro-3-phenylbutane
- (d) 2,4-Dinitrophenol

A-3. (a)
$$(10 \pi \text{ electrons})$$
 (b) $(14 \pi \text{ electrons})$

- **A-4.** (a) Eight π electrons. No, the substance is not aromatic.
 - (b) 6 π electrons. Yes, it is aromatic.
 - (c) 14 π electrons. Yes, it is aromatic.

A-6. (a)

(d) $Na_2Cr_2O_7$, H_2SO_4 , H_2O , heat

(b) $C_6H_5CH_2X$ (X = Cl, Br, I, OTs)

(e) 0

 $(f) \quad \begin{array}{c} \text{OH} \\ \mid \\ \text{C}_{6}\text{H}_{5}\text{CHCHCH}_{3} \\ \mid \\ \text{Br} \end{array}$

A-7. (I)
$$C_6H_5CH$$
=CHCH₃ \xrightarrow{HBr} $C_6H_5CHCH_2CH_3$

(II)
$$C_6H_5CH_2CH_2CH_3 \xrightarrow[light]{Br_2} C_6H_5CHCH_2CH_3$$

$$\mathbf{A-8.} \quad \stackrel{^{+}\mathrm{CH-CH_{3}}}{\longleftarrow} \quad \stackrel{\mathrm{CH-CH_{3}}}{\longleftarrow} \quad \stackrel{\mathrm{CH-CH_{3}}}{\longleftarrow} \quad \stackrel{^{+}\mathrm{CH-CH_{3}}}{\longleftarrow} \quad \stackrel{^{+}\mathrm{CH-CH_{3}$$

A-10.
$$(CH_3)_3C$$
 — CH_2CH_3

B-1. (c) **B-2.** (c) **B-3.** (a) **B-4.** (b)

B-5. (a) **B-6.** (d) **B-7.** (b) **B-8.** (d)

B-9. (*b*) **B-10.** (*d*) **B-11.** (*a*) **B-12.** (*b*)

B-13. (c) **B-14.** (d) **B-15.** (c)

CHAPTER 12

A-1.
$$CH_3H$$
 CH_3H Br Br



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A-2. (a)
$$NO_2$$

Slower

Slower

CH2CH3 CH2CH3

Faster

A-3. (a)
$$NO_2^+$$
 (b) $Br - \bar{Br} - \bar{Fe}Br_3$ (c) SO_3

$$(c)$$
 SO₃

A-4. (a)
$$CCH(CH_3)_2$$

$$C(CH_3)_3$$

$$(d) \qquad \qquad \bigvee^{\text{O}} \text{NO}_2$$

A-5. (a)
$$\begin{array}{c} NO_2 \\ CI \\ CH_3 \end{array}$$

$$(c) \qquad Cl \qquad + Cl$$

(b)
$$CI$$
 CN $+$ CI CN CN OCH_3

$$(b) \qquad \qquad \overset{\text{O}}{\underset{\text{AlCl}_{3}}{\text{C}_{6}\text{H}_{5}\text{CH}_{2}\text{C}_{6}\text{H}_{5}}} \qquad \overset{\text{O}}{\underset{\text{Cl}_{2}, \text{FeCl}_{3}}{\text{Cl}}} \qquad \overset{\text{O}}{\underset{\text{Cl}_{2}, \text{Cl}_{2}}{\text{Cl}}} \qquad \overset{\text{O}}{\underset{\text{Cl}_{2}, \text{Cl}_{2}}{\text{Cl}_{2}}} \qquad \overset{\text{O}}{\underset{\text{Cl}_{2}, \text{Cl}_{2}}{\text{Cl}}} \qquad \overset{\text{O}}{\underset{\text{Cl}_{2}, \text{Cl}_{2}}{\text{Cl}_{2}}} \qquad \overset{\text{O}}{\underset{\text{Cl}_{2}, \text{Cl}_{2}}{\text{Cl}_{2}, \text{Cl}_{2}}} \qquad \overset{\text{O}}{\underset{\text{Cl}_{2}, \text{Cl}_{2}}{\text{Cl}_{2}}} \qquad \overset{\text{O}}{\underset{\text{Cl}_{2}, \text{Cl}_{2}}{\text{Cl}_{2}}} \qquad \overset{\text{O}}{\underset{\text{Cl}_{2}, \text{Cl}_{2}}} \qquad \overset{\text{O}}{\underset{\text{Cl}_{2}, \text{Cl}_{2}}} \qquad \overset{\text{Cl}_{2}, \text{Cl}_{2}}} \qquad \overset{\text{O}}{\underset{\text{Cl}_{2}, \text{Cl}_{2}}} \qquad \overset{\text{O}}{$$

(c)
$$CH$$

$$N_2H_4, KOH, heat \text{ or } Zn(Hg), HCl$$

$$CH_3$$

$$CH_3C)_2O$$

$$AlCl_3$$

$$CH_3C$$

A-7. (a)
$$(a)$$
 (a) $($

$$(CH_3)_2CH \xrightarrow{\qquad \qquad Br_2 \qquad \qquad } (CH_3)_2C \xrightarrow{\qquad \qquad NO_2 \qquad NO_2 \qquad NO_2 \qquad NO_2} \qquad H_2C = C \xrightarrow{\qquad \qquad NO_2 \qquad NO_2} (CH_3)_2CH \xrightarrow{\qquad \qquad NO_2} (CH_3$$

[Prepared from benzene as in Problem A-6(e)]

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A-8.

B-1. (c) **B-2.** (b) **B-3.** (c) **B-4.** (b)

B-5. (a) **B-6.** (b) **B-7.** (c) **B-8.** (b)

B-9. (c) **B-10.** (a) **B-11.** (e) **B-12.** (c)

B-13. (c) **B-14.** (c) **B-15.** (c)

CHAPTER 13

A-1. 1: 6.10 ppm 3: 200 MHz

2: 1305 Hz 4: 0.00 ppm

A-2. (a) Two signals $BrCH_2CH_2CH_2Br$

a b a a: triplet b: pentet

(b) Two signals $CH_3CH_2CCH_2CH_3$ A B B B B B

a: triplet *b*: quartet

(c) Three signals, all singlets

 \mathbf{A} -3. **A**: $\mathbf{CH}_3\mathbf{COC}(\mathbf{CH}_3)_3$ **B**: $\mathbf{CH}_3\mathbf{OCC}(\mathbf{CH}_3)_3$

A-5. Seven signals:

a: $\delta 10-30 \text{ ppm}$

b: δ 20–40 ppm

c: δ 190–220 ppm

d–g: δ 110–175 ppm

$$\begin{array}{c|c}
g & & & \\
& & & \\
f & e & & \\
f & e & & \\
\end{array}$$

$$\begin{array}{c|c}
GCH_2CH_3$$

A-6. Pentane: three signals; 2-methylbutane: four signals; 2,2-dimethylpropane: two signals

A-7. 2,3-Dimethylbutane: $(CH_3)_2CHCH(CH_3)_2$

B-1. (*d*) **B-2.** (*a*) **B-3.** (*b*) **B-4.** (*b*)

B-5. (*b*) **B-6.** (*a*) **B-7.** (*b*) **B-8.** (*a*) **B-9.** (*c*) **B-10.** (*a*) **B-11.** (*c*) **B-12.** (*c*)

B-13. (a) **B-14.** (a) **B-15.** (d)

CHAPTER 14

A-1. (a)
$$X$$
 Li $+ 2Li$ $+ LiX$ $(X = Cl, Br, I)$

(b)
$$(CH_3)_3CBr + Mg \longrightarrow (CH_3)_3CMgBr$$

(c)
$$2C_6H_5CH_2Li + CuX \longrightarrow (C_6H_5CH_2)_2CuLi + LiX$$

(X = Cl, Br, I)

OH HO
$$CH_2CH_3$$

A-2. (a) $(C_6H_5)_2CCH_3 + CH_3CH_2OH$ (d)

(b)
$$(CH_3)_2CHCH_2D$$
 (e) H_3C

$$(c)$$
 H_3C CH_2OH

A-3. (a)
$$C_6H_5CH + (CH_3)_3CMgX$$
 and $C_6H_5MgX + (CH_3)_3CCH$
 $(X = Cl, Br, I)$ $(X = Cl, Br, I)$

(b) O O
$$\parallel$$
 CH₃CH₂CH₂CH + CH₃CH₂CH₂MgX and CH₃CH₂CH₂CH₂CH + CH₃CH₂CH₂MgX (X = Cl, Br, I) (X = Cl, Br, I)

A-4. (a)
$$(CH_3CH_2CH_2)_2CuLi$$
 (c) CH_2I_2 , $Zn(Cu)$ (b) $(CH_3)_2CHMgX$ (X = Cl, Br, I)

A-5. Solvents A, B, and E are suitable; they are all ethers. Solvents C and F have acidic hydrogens and will react with a Grignard reagent. Solvent D is an ester which will react with a Grignard reagent.

$$\textbf{A-6.} \quad CH_3(CH_2)_3OH \quad \xrightarrow{PBr_3} \quad CH_3(CH_2)_3Br \quad \xrightarrow{2Li} \quad CH_3(CH_2)_3Li \; + \; LiBr$$

$$2CH_3(CH_2)_3Li \; + \; CuBr \quad \longrightarrow \quad (C_4H_9)_2CuLi \quad \xrightarrow{CH_3(CH_2)_3Br} \quad CH_3(CH_2)_6CH_3$$

A-7. (I)
$$(CH_3)_2CHCCH_3 + CH_3MgBr$$

O
(II) $CH_3CCH_3 + (CH_3)_2CHMgBr$

(III) $(CH_3)_2CHCO_2CH_3 + 2CH_3MgBr$

A-8.
$$C_6H_5CH_2CH_3$$
 $\xrightarrow{NBS}_{peroxides, heat}$ $C_6H_5CHCH_3$ $\xrightarrow{Mg}_{diethyl \ ether}$ $C_6H_5CHMgBr$

$$C_6H_5CHMgBr \xrightarrow{1. CH_3CH}_{2. H_3O^+}$$
 $C_6H_5CHCHCH_3$

$$C_6H_5CHCHCH_3$$

$$C_6H_5CHMgBr \xrightarrow{0. CH_3CHCHCHCH_3}_{0H}$$

A-9. (a)
$$OH$$

$$CCH_2CH_3$$

$$CH_3$$
(c) $C=CCH_3$
(b) OH

CHAPTER 15

A-1. (a)
$$OSO_4$$
, $(CH_3)_3COOH$, $(CH_3)_3CO$

A-2. (a) $C_6H_5CH_2CH$

(c) $(C_6H_5CH_2CH_2)_2O$

(b) O \parallel (b) CH₃CCl, pyridine; or

(d) $K_2Cr_2O_7$, H^+ , H_2O , heat

 $\begin{matrix} O \\ \parallel \\ (CH_3C)_2O; \text{ or } CH_3CO_2H, H^+ \end{matrix}$

A-3. (a) $(CH_3)_2CHO^-Na^+$

(b) $(CH_3)_2C=O$

(f) CH_3CH_2 COCH(CH_3)

(c) $(CH_3)_2C=O$

O || (g) CH₃COCH(CH₃)₂

 $(d) \quad \begin{matrix} \mathsf{O} \\ \parallel \\ \mathsf{CH}_3\mathsf{COCH}(\mathsf{CH}_3)_2 \end{matrix}$

A-4. (I)

$$(CH_3)_2CHBr + Mg \longrightarrow (CH_3)_2CHMgBr \xrightarrow{1. H_2C-CH_2} (CH_3)_2CHCH_2CH_2OH$$

 $(II) \quad (CH_3)_2 CHCH_2 Br \ + \ Mg \quad \longrightarrow \quad (CH_3)_2 CHCH_2 MgBr$

$$(CH_3)_2CHCH_2MgBr$$
 $\xrightarrow{1. H_2C=O}$ $(CH_3)_2CHCH_2CH_2OH$

A-5. (a)

$$(c) \qquad \begin{array}{c} H_3C \\ C = C \\ H \end{array} CH_3$$

$$(b)$$
 HO OH

A-6. (a) PCC or PDC in CH_2Cl_2

- (b) $Na_2Cr_2O_7$, H^+ , H_2O , heat
- (c) 1. LiAlH₄; 2. H₂O
- (d) OsO_4 , $(CH_3)_3COOH$, $(CH_3)_3COH$, HO^-

A-7. OH OH CO_2H CO_2CH

A-8. (*a*)

$$(CH_3)_2C = CHCH_3 \xrightarrow{\begin{array}{ccc} 1. \ B_2H_6 \\ \hline 2. \ H_2O_2, \ HO \end{array}} (CH_3)_2CHCHCH_3 \xrightarrow{\begin{array}{ccc} PDC \\ \hline CH_2Cl_2 \end{array}} (CH_3)_2CHCCH_3$$

$$(b) \quad \begin{array}{c|c} O & OH & O\\ \parallel & 1. \operatorname{CH_3CH_2MgBr} \\ \hline CH & \frac{1. \operatorname{CH_3CH_2MgBr}}{2. \operatorname{H_3O^+}} & \begin{array}{c} OH & O\\ \parallel & \\ \hline \end{array} \\ \begin{array}{c} CHCH_2CH_3 & \xrightarrow{\operatorname{Na_2Cr_2O_7}} \\ \hline \end{array} \\ \begin{array}{c} H^+, H_2O \end{array} \\ \end{array}$$

$$C_6H_5CH_3 \xrightarrow{\text{NBS}} C_6H_5CH_2Br \xrightarrow{\text{Mg}} C_6H_5CH_2MgBr \xrightarrow{\text{1.H}_2C \xrightarrow{\text{CH}_2}} C_6H_5CH_2CH_2CH_2OH$$

$$\downarrow K_2Cr_2O_7 \\ H^+, H_2O \\ \text{heat}$$

$$C_6H_5CH_2CH_2CO_2CH_2CH_3 \quad {\overset{CH_3CH_2OH}{\longleftarrow}} \quad C_6H_5CH_2CH_2CO_2H$$

- B-1. (*e*) B-2. (*d*) B-3. (*c*) B-4. (c) B-5. (*b*) B-6. (*b*) B-7. (*a*) B-8. (*a*) B-9. (*d*) **B-11.** (b) **B-12.** (*d*) **B-10.** (*a*)
- **B-13.** (*e*) **B-14.** (*a*) **B-15.** (*c*)

CHAPTER 16

A-1. CH₃OCH₂CH₂CH₃
Methyl propyl ether
CH₃OCH(CH₃)₂
Isopropyl methyl ether
CH₃CH₂OCH₂CH₃
Diethyl ether

A-2. (a)
$$CH_3CH_2$$
 CH_3

(b)
$$H_3C$$
 H OH

$$(c)$$
 $C_6H_5CHCH_2OH$

$$(f)$$
 $C_6H_5SCH_2CH_3$

A-3. (a)
$$OH \longrightarrow Na \longrightarrow O^- Na^+ \longrightarrow CH_3CH_2I \longrightarrow OCH_2CH_3$$

A-4.
$$CH_3CH_2OH \xrightarrow{H_2SO_4} H_2C = CH_2 \xrightarrow{CH_3COOH} H_2C \xrightarrow{CH_2}$$

$$CH_{3}CH_{2}OH \xrightarrow{Na} CH_{3}CH_{2}O^{-}Na^{+} \xrightarrow{H_{2}C-CH_{2} \atop CH_{3}CH_{2}OH} CH_{3}CH_{2}OCH_{2}CH_{2}OH$$

A-5. (a)
$$\stackrel{\text{HO}}{\longrightarrow}$$
 $\stackrel{\text{Br}}{\longrightarrow}$ $\stackrel{\text{NaOH}}{\longrightarrow}$ $\stackrel{\text{NaSCH}_3}{\longrightarrow}$ $\stackrel{\text{NaSCH}_3}{\longrightarrow}$ $\stackrel{\text{NaSCH}_3}{\longrightarrow}$ $\stackrel{\text{NaSCH}_3}{\longrightarrow}$ $\stackrel{\text{NaSCH}_3}{\longrightarrow}$ $\stackrel{\text{NaSCH}_3}{\longrightarrow}$ $\stackrel{\text{NaSCH}_3}{\longrightarrow}$ $\stackrel{\text{CH}_3}{\longrightarrow}$ $\stackrel{\text{CH}_3}{\longrightarrow}$ $\stackrel{\text{CH}_4}{\longrightarrow}$ $\stackrel{\text{CH}_4}{\longrightarrow}$ $\stackrel{\text{CH}_5}{\longrightarrow}$ $\stackrel{\text{CH}_4}{\longrightarrow}$ $\stackrel{\text{CH}_5}{\longrightarrow}$ $\stackrel{\text{CH}_4}{\longrightarrow}$ $\stackrel{\text{CH}_5}{\longrightarrow}$ $\stackrel{$

A-6. A:
$$\bigcirc$$
 CH₂OH **B:** \bigcirc CH₂OCH₂CH₃

A-7.
$$\begin{array}{c} O \\ \hline \\ 1. \text{ CH}_3\text{MgBr} \\ \hline \\ 2. \text{ H}_3\text{O}^+ \\ \hline \\ \end{array} \begin{array}{c} H_3\text{C} \\ \hline \\ \text{heat} \\ \end{array} \begin{array}{c} \text{CH}_3 \\ \hline \\ \text{heat} \\ \end{array}$$

$$\begin{array}{c} CH_3 \\ \hline \\ CH_3 \\ \hline \\ \end{array} \begin{array}{c} OH \\ \hline \\ \end{array} \begin{array}{c} OH \\ \hline \\ \end{array} \begin{array}{c} OH \\ \hline \\ \end{array}$$

A-8.
$$H_2N$$
 HO

CHAPTER 17

- **A-1.** (a) 3,4-Dimethylhexanal
 - (b) 2,2,5-Trimethylhexan-3-one
 - (c) trans-4-Bromo-2-methylcyclohexanone
 - (d) 5-Methyl-4-hexen-3-one

A-2.
$$CH_3C$$
 CH_3C CH_3 CH_3 CH_3 CH_3 CH_3 CH_3 CH_4 CH_5 CH_5



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(e)
$$\sim$$
 NNHC₆H₅ CH₃

$$(f)\quad \mathsf{CH_3CH_2CH_2CH}(\mathsf{OCH_2CH_3})_2$$

$$(c)$$
 $(CH_3)_2CHCH + HOCH_2CH_2CH_2OH$

$$(g)$$
 $C_6H_5CCH_2CH_3 + (CH_3)_2NH$

(d)
$$(C_6H_5)_3\overset{+}{P} - \ddot{C}HCH_2CH_3$$

A-4. (a)
$$(C_6H_5)_3\dot{P}$$
— $CH_2CH(CH_3)_2$ $Br^ (C_6H_5)_3\dot{P}$ — $\ddot{C}HCH(CH_3)_2$ B C_6H_5CH = $CHCH(CH_3)_2$

C

A-5. (a) (1) CH_3MgI ; (2) H_3O^+ ; (3) H_2SO_4 , heat

$$(b) \quad \left(\mathsf{C}_{6}\mathsf{H}_{5}\right)_{3}^{+} - \ddot{\bar{\mathsf{C}}}\mathsf{H}_{2} \quad [\mathsf{from} \; \left(\mathsf{C}_{6}\mathsf{H}_{5}\right)_{3}\mathsf{P} \; + \; \mathsf{C}\mathsf{H}_{3}\mathsf{I} \quad \longrightarrow \quad \overset{\mathsf{C}_{4}\mathsf{H}_{9}\mathsf{L}\mathsf{i}}{-} \\ \end{array}$$

(c) $HOCH_2CH_2OH$, $H^+(cat)$, heat

$$(d)$$
 CH_3COOH

A-6. (a)
$$H_3C$$
 OH CH_3

(b)
$$H_3C$$
 OH $=$ $CH_3CCH_2CH_2CH_2CCH_2OH$ CH_3

A-7. (*a*)

$$CH_{3}CH_{2}I + (C_{6}H_{5})_{3}P \longrightarrow (C_{6}H_{5})_{3}\overset{\dagger}{P} - CH_{2}CH_{3} I^{-} \xrightarrow{C_{4}H_{9}Li} (C_{6}H_{5})_{3}\overset{\dagger}{P} - \ddot{C}HCH_{3}$$

$$(CH_{3})_{2}C = O + (C_{6}H_{5})_{3}\overset{\dagger}{P} - \ddot{C}HCH_{3} \longrightarrow (CH_{3})_{2}C = CHCH_{3} \xrightarrow{CH_{3}COOH} (CH_{3})_{2}C - CHCH_{3}$$

$$(b)$$

$$CH_{3} \xrightarrow{HOCH_{2}CH_{2}OH} CH_{3} \xrightarrow{PCC} CH_{3} \xrightarrow{L.CH_{3}Mgl} CH_{3}$$

$$(c) \xrightarrow{HOCH_{2}CH_{2}OH} CO_{2}H \xrightarrow{H^{+}} CH_{2}OH CH_{2}OH$$

$$CH_{2}OH \xrightarrow{H^{+}} CH_{3}OH CH_{3}OH CH_{2}OH$$

$$A-8. CH_{3}CH \xrightarrow{H^{+}} CH_{3}CH \xrightarrow{CH_{3}CH} CH_{3}OH CH_{3}OH$$

$$CH_{3}CH \xrightarrow{H^{+}} CH_{3}CH \xrightarrow{CH_{3}CH} CH_{3}OH CH_{3}OH$$

$$CH_{3}CH \xrightarrow{H^{+}} CH_{3}CH \xrightarrow{CH_{3}CH} CH_{3}OH CH_{3}OH$$

$$CH_{3}CH \xrightarrow{H^{+}} CH_{3}CH \xrightarrow{CH_{3}CH} CH_{3}OH \xrightarrow{CH_{3}CH} CH_{3}OH$$

$$CH_{3}CH \xrightarrow{H^{+}} CH_{3}CH \xrightarrow{CH_{3}CH} CH_{3}OH$$

$$CH_{3}CH \xrightarrow{H^{+}} CH_{3}CH \xrightarrow{CH_{3}CH} CH_{3}OH$$

$$CH_{3}CH \xrightarrow{H^{+}} CH_{3}CH \xrightarrow{CH_{3}CH} CH_{3}OH$$

$$CH_{3}CH \xrightarrow{CH_{3}CH} CH_{3}CH \xrightarrow{CH_{3}CH} CH_{3}CH$$

$$CH_{3}CH \xrightarrow{CH_{3}CH} CH_$$

B-1. (*c*) **B-2.** (*d*) **B-3.** (*a*) **B-4.** (*c*) B-5. (*b*) **B-6.** (*b*) **B-7.** (*a*) **B-8.** (*b*) B-9. (*e*) **B-10.** (*c*) **B-11.** (*c*) **B-12.** (*c*) **B-13.** (*d*) **B-14.** (*e*) **B-15.** (*a*) **B-16.** (*c*)

CHAPTER 18

A-1. (a)
$$H_2C = CCH_2CH_3$$
 and $CH_3C = CHCH_3$ (c) H

(b) OH
 OH



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A-2.
$$C_6H_5CH_2CH = CCH CH_3CH_2)_2CHCH_2CCH_2CH_3$$

$$C_6H_5$$
A
B

A-3.
$$CH_3CH_2CHCHCH CH_3CHCHC(CH_3)_2$$

 $CH_3 CH_3 HC=O$

$$\begin{array}{cccc} OH & OH & O\\ & & & & \\ CH_3CH_2CHC(CH_3)_2 & CH_3CHCHCHCH\\ & & & & \\ HC=O & CH_3 & CH_3 \end{array}$$

A-4.
$$CH_3CH_2OH \xrightarrow{PCC} CH_3CH$$

A-5.

$$\begin{array}{ccc} & \text{OH} & \text{O} \\ & \parallel & \parallel \\ \text{(b)} & \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHCHCH} \\ & \parallel & \text{CH}_2\text{CH}_2\text{CH}_3 \end{array}$$

(c)
$$CH_3$$
 CH_3

$$d) \qquad \begin{array}{c} O \\ \parallel \\ -\text{CHCH}_2\text{C} - \\ \parallel \\ \text{SCH}_3 \end{array}$$

A-7.

$$CH_{3}CHCH + -\ddot{O}CH_{3}CHCH \xrightarrow{H_{2}C=O}CH_{3}CHCH \xrightarrow{H_{0}CHCH}CH_{2}CH_{2}CHCH$$

- B-1. (*a*)
- B-2. (c)
- B-3. (b)
- **B-4.** (*b*)

- B-5. (a)
- B-6.
- B-7. (c)
- B-8. (*e*)

- B-9. (c)
- (c) **B-10.** (*b*)
- **B-11.** (*a*)
- **B-12.** (a)

CHAPTER 19

- A-1. 4-Methyl-5-phenylhexanoic acid (a)
 - (*b*) Cyclohexanecarboxylic acid
 - 3-Bromo-2-ethylbutanoic acid (c)
- 4-Phenylbutanoic acid is C₆H₅CH₂CH₂CH₂CO₂H. A-2.

$$C_{6}H_{5}CH_{2}CH_{2}CH(CO_{2}H)_{2} \xrightarrow{\text{heat}}$$

$$C_{6}H_{5}CH_{2}CH_{2}CH_{2}Br \xrightarrow{1. CN^{-}} \xrightarrow{2. H^{+}, H_{2}O, \text{heat}}$$

$$C_{6}H_{5}CH_{2}CH_{2}CH_{2}Br \xrightarrow{1. Mg} \xrightarrow{2. CO_{2}}$$

A-3.
$$C_6H_5CH_2CO_2H + CH_3CH_2OH \xrightarrow{H^+(cat)} C_6H_5CH_2COCH_2CH_3 + H_2O$$

A-4.
$$(CH_3)_2CHCH_2CHCO_2H$$
 $(CH_3)_2CHCH_2CHCO_2H$ $C_6H_5CC(CH_3)_2$ CO_2H

A-5. (a)
$$\xrightarrow{\text{Mg}}$$
 MgBi

(b)
$$\xrightarrow{1. \text{LiAlH}_4}$$
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

$$(c) \xrightarrow{\text{Br}_2, P} \text{CH}_3\text{CH}_2\text{CHCOH}$$

$$(d) \quad \text{CH}_{3}\text{CH}_{2}\text{CH} \quad \xrightarrow{\text{H}^{+}, \text{H}_{2}\text{O}} \\ \text{OH}$$

A-8.
$$CH_3COH \xrightarrow{H^+} CH_3COH + H\ddot{O}CH_3 \longrightarrow CH_3COH \xrightarrow{-H^+} CH_3COH + HOCH_3 \longrightarrow CH_3COH +$$

- B-1. (b) B-2. B-3. B-4. (*d*) (*a*) (*c*)
- B-5. B-8. (*d*) (c) B-6. (*d*) B-7. (c)
- B-9. **B-10.** (*c*) **B-11.** (*e*) (*e*)

CHAPTER 20

- **A-1.** (a) Propyl butanoate
 - (c) 4-Methylpentanoyl chloride (b) N-Methylbenzamide
- (b) CH₃CNHCHCH₂CH₃ ĊH₃

- **A-3.** (*a*) SOCl₂
 - (b) Br_2 , NaOH, H_2O
- **A-4.** (a) $CH_3CO_2H +$
- (d) $CH_3CH_2CN(CH_3)_2 + CH_3CH_2OH$
- (e) H_3C $-CO_2H + CH_3NH_3 HSO_4^-$

$$(c) \qquad \begin{array}{c} O \\ \\ \\ COCH_2CH_3 \\ \\ COH \\ \\ O \end{array}$$

A-5.
$$C_0H_5$$
 C_0H_5 C_0H_5

A-10. The compound is 2-chloropropanamide.

 $\hbox{$2$-Chloropropanamide}$

The compound may be prepared from propanoic acid as shown.

CHAPTER 21

Α

В

$$C_{6}H_{5}CCH_{3} + CH_{3}CH_{2}OCOCH_{2}CH_{3} \xrightarrow{NaOCH_{2}CH_{3}} C_{6}H_{5}CCH_{2}COCH_{2}CH_{3} \xrightarrow{1. NaOCH_{2}CH_{3}} C_{6}H_{5}CCH_{2}CCH_{3} \xrightarrow{0} C_{6}H_{5}CCH_{2}CCH_{3} \xrightarrow{0} CH_{2}CCH_{3} \xrightarrow{0} C$$

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A-5. Enolization of the Claisen condensation product is necessary for completion of the reaction. The condensation product of ethyl 3-methylbutanoate can enolize; the product from condensation of ethyl 2-methylpropanoate cannot.

$$\begin{array}{c|cccc} O & H_3CO \\ \parallel & & & \\ 2CH_3CH_2CHCOCH_2CH_3 & & & \\ CH_3 & & & CH_3CH_2CCOCH_2CH_3 \\ CH_3 & & & CH_3CH_2CHC \\ & & & & \\ CH_3 & & & CH_3CH_2CHC \\ & & & & \\ CH_3 & & & \\ \end{array}$$

Ethyl 2-methylbutanoate

Claisen product cannot enolize

B-1. (b) B-2. B-4. (b) (*d*) B-3. (c) B-5. (c) B-6. (c) B-7. (b) B-8. (*d*)

CHAPTER 22

- **A-1.** (a) 1,1-Dimethylpropylamine or 2-methyl-2-butanamine; primary
 - (b) N-Methylcyclopentylamine or N-methylcyclopentanamine; secondary
 - (c) m-Bromo-N-propylaniline; secondary

A-2. (a) NaN₃ (b) KCN (c)
$$N^- K^+$$

A-3. (a)
$$H_3C$$
 \longrightarrow $N_2^+ Cl^-$ (e) O_2N \longrightarrow CH_2CH_3 \longrightarrow CH_2CH_3

(b)
$$H_3C$$
 —Br (f) N — $N(CH_3)_2$ (c) H_3PO_2 (g) — NCH_2CH_3

$$(d)$$
 $(CH_3C)_2O$ or CH_3CCI

A-5. (*a*)

$$(b) \quad \mathsf{C_6H_6} \quad \xrightarrow{\mathsf{HNO_3}} \quad \overset{\mathsf{NO_2}}{\underset{\mathsf{H_2SO_4}}{}} \quad \overset{\mathsf{NNO_2}}{\underbrace{\hspace{1cm}}} \quad \overset{\mathsf{NH_2}}{\underset{\mathsf{Cl}}{}} \quad \overset{\mathsf{1. Sn, HCl}}{\underbrace{\hspace{1cm}}} \quad \overset{\mathsf{Cl_2, FeCl_3}}{\underbrace{\hspace{1cm}}} \quad \overset{\mathsf{Cl_2, FeCl$$

(c)
$$C_6H_5NH_2 \xrightarrow{NaNO_2, HCl} C_6H_5N_2^+ Cl^- \xrightarrow{C_6H_5N(CH_3)_2} C_6H_5N = N - N(CH_3)_2$$

A-6. In the para isomer, resonance delocalization of the electron pair of the amine nitrogen involves the nitro group.

A-7. Strongest base: C, an alkylamine

Weakest base: D, a lactam (cyclic amide)

B-1. (b) **B-2.** (d) **B-3.** (c) **B-4.** (d) **B-5.** (c) **B-6.** (e) **B-7.** (d) **B-8.** (c)

B-5. (*c*) **B-6.** (*e*) **B-7.** (*d*) **B-8.** (*c*) **B-9.** (*d*) **B-10.** (*e*) **B-11.** (*c*) **B-12.** (*b*)

B-13. (c) **B-14.** (c)

CHAPTER 23

A-1. (a)
$$CF_3$$
 CF_3 CF_3 $CCH_3)_3$ CCH_3 CCH_3

 CF_3 $C(CH_3)_3$ C

$$(b) \qquad \begin{array}{c} \text{CH}_3\text{O} \\ \text{Cl} \\ \text{N} \\ \text{O} \end{array}$$

A-3. (a) (

(b)
$$CI$$
 CI NH_2 $NANH_2, NH_3$ $CH(CH_3)_2$ $CH(CH_3)_2$

(+ ortho isomer) (+ meta isomer)

The mechanism for para substitution is similar.

- **B-1.** (*a*)
- B-2.
- B-3.
- (c) **B-4.**

- B-5.
- (*b*)
- **B-6.** (*a*)

(a)

B-7.

(a)

B-8.

(*d*)

(a)

CHAPTER 24

A-1. *p*-Hydroxybenzaldehyde is the stronger acid. The phenoxide anion is stabilized by conjugation with the aldehyde carbonyl.

 $o ext{-}Cresol$

m-Cresol

$$\begin{array}{c|c} OH & OH \\ \hline \\ CH_3 & CH_3 \end{array}$$

p-Cresol



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A-3.
$$OH$$
 OH OH OH CCH_2CH_3 CH_3 CH_3

(Friedel-Crafts acylation)

$$\begin{array}{c|c} OH & O \\ \hline \\ OCCH_2CH_3 \\ \hline \\ CH_3 \end{array} + CH_3CH_2CCl \xrightarrow{\text{(absence of AlCl}_3)} \begin{array}{c} O \\ \hline \\ OCCH_2CH_3 \\ \hline \\ CH_3 \end{array}$$

(Esterification)

A-4. (a)
$$\langle - \rangle$$
 OH + BrCH(CH₃)₂

(c) CO₂, 125°C, 100 atm

$$O^{-}$$
 Na⁺
 CH_3 + BrCH₂CH(CH₃)₂ (d) OH

OCH₂CH=CHCH₂CH₃ OH
$$CH_2CH_3$$
 CHCH=CH₂

A-6.

B-1. (*d*) **B-2.** (*d*) **B-3.** (*b*) **B-4.** (*a*) **B-5.** (*c*) **B-6.** (*b*) **B-7.** (*b*) **B-8.** (*c*)

CHAPTER 25

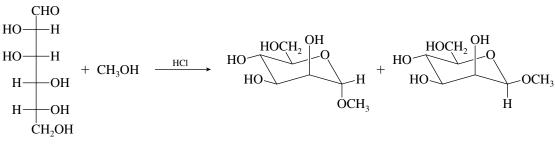
(c)
$$H$$
 H OH (e) R CHO H OH OH CH_2OH

$$(d) \qquad \begin{array}{c} O \\ H \\ OH \end{array} \qquad OH$$

 β -D-Erythrofuranose

3.
$$(a)$$
 HOOH OH (c) HOOH OH HOCH₂ OOH

- **A-4.** β -D-Idopyranose (β -pyranose form of D-idose)
- **A-5.** The products are diastereomers.



D-Mannose Methanol Meth

 $\begin{array}{ccc} \text{Methyl} & \text{Methyl} \\ \alpha\text{-D-mannopyranoside} & \beta\text{-D-mannopyranoside} \end{array}$

- **B-1.** (b) **B-2.** (d) **B-3.** (b) **B-4.** (a) **B-5.** (c)
- **B-6.** (c) **B-7.** (a) **B-8.** (c) **B-9.** (c) **B-10.** (c)

CHAPTER 26

A-1.
$$C_{17}H_{35}COCH O + 3NaOH \longrightarrow CH_2OH CH_2OCC_{17}H_{35}$$

$$CH_2OH CH_2OCC_{17}H_{35} COCH O + 3NaOH CH_2OH$$

$$CH_2OCC_{17}H_{35} COCH CH_2OH$$

$$CH_2OH$$

$$CH_2OH$$

A-2. Fats are triesters of glycerol. A typical example is tristearin, shown in the preceding problem. A wax is usually a mixture of esters in which the alkyl and acyl group each contain 12 or more carbons. An example is hexadecyl hexadecanoate (cetyl palmitate).

$$\begin{array}{c}
O \\
\parallel \\
C_{15}H_{31}COC_{16}H_{33}
\end{array}$$

A-3. (a) Monoterpene;

(b) Sesquiterpene;

(c) Diterpene;

A-4.
$$CH_3(CH_2)_7$$
 $C=C$ $(CH_2)_7CO_2H$ $C=C(CH_2)_6CH_2$ H $C=C(CH_2)_6CH_2$ H $C=C(CH_2)_6CH_2$ $C=C$



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$$HC \equiv C(CH_2)_6 CH_2 \quad H \quad \xrightarrow{NaNH_2} \quad Na^+ \quad : C \equiv C(CH_2)_6 CH_2 \quad H \quad \xrightarrow{CH_3(CH_2)_6 CH_2 Br} \quad CH_3(CH_2)_7 C \equiv C(CH_2)_6 CH_2 \quad H$$

$$CH_{3}(CH_{2})_{7} C = C \underbrace{ (CH_{2})_{7}CO_{2}H }_{H} \underbrace{ H_{2} \atop \text{Lindlar Pd} } CH_{3}(CH_{2})_{7}C \equiv C(CH_{2})_{7}CO_{2}H \underbrace{ Na_{2}Cr_{2}O_{7} \atop \text{H}_{2}SO_{4}, H_{2}O} CH_{3}(CH_{2})_{7}C \equiv C(CH_{2})_{7}CH \underbrace{ Na_{2}Cr_{2}O_{7} \atop \text{H}_{2}SO_{4}, H_{2}O} CH_{3}(CH_{2})_{7}C \equiv C(CH_{2})_{7}CH \underbrace{ Na_{2}Cr_{2}O_{7} \atop \text{H}_{2}SO_{4}, H_{2}O} CH_{3}(CH_{2})_{7}C \equiv C(CH_{2})_{7}CH \underbrace{ Na_{2}Cr_{2}O_{7} \atop \text{H}_{2}SO_{4}, H_{2}O} CH_{3}(CH_{2})_{7}C = C(CH_{2})_{7}CH \underbrace{ Na_{2}Cr_{2}O_{7} \atop \text{H}_{2}SO_{4}, H_{2}O_{7}C = C(CH_{2})_{7}CH \underbrace{ Na_{2}Cr_{2}O_{7} \atop \text{H}_{2}SO_{4}, H_{2}O_{7}C = C(CH_{2})_{7}CH + C(CH_{2})_{7}C = C(CH_{2})_{7}CH + C(CH_{2})_{7}CH + C(CH_{2})_{7}C = C(CH_{2})_{7}CH + C(C$$

(b) **B-2.** (a) **B-3.** (c) **B-4.** (c)

B-5. (a) **B-6.** (a)

B-1.

CHAPTER 27

A-1. (a)
$$C_6H_5CH_2CH$$
 (b) $C_6H_5CH_2OCNHCHCO_2H$ (c) DCCI $CH(CH_3)_2$

A-2.
$$O_2N$$
 NHCHCO₂H O_2 O_2 O_3 O_4 O_5 O_5

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 $\dot{C}H_2CH(CH_3)$,

(b) Leu-Val =
$$H_3$$
NCHC—NHCHCO₂-
$$CH_2$$
CH(CH₃)₂

N-Protect leucine:
$$C_6H_5CH_2OCC1 + H_3\overset{+}{N}CHCO_2^ \xrightarrow{1. NaOH, H_2O}$$
 $C_6H_5CH_2OCNHCHCO_2H$ $CH_2CH(CH_3)_2$ $C_6H_5CH_2OCNHCHCO_2H$ $CH_2CH(CH_3)_2$ (Z-Leu)

C-Protect valine:
$$C_6H_5CH_2OH + H_3\overset{+}{N}CHCO_2^- \xrightarrow{H^+} H_3\overset{+}{N}CHCOCH_2C_6H_5$$

 $CH(CH_3)_2$

- **A-4.** Leu-Val-Gly-Ala-Phe
- (c) Serine **A-5.** (a) Pentapeptide (e) Ser-Ala-Leu-Phe-Gly
 - (b) Four (d) Glycine

A-6. (a)

DNP-Ala

Leu

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(c) Same as part b; Ala-Gly-Phe + Leu

$$(d) \quad \begin{matrix} \text{O} & \text{O} & \text{O} & \text{CH}_2\text{CH}(\text{CH}_3)_2 \\ \parallel & \parallel & \parallel & \parallel & \parallel \\ \text{CH}_3\text{CH}_2\text{OCNHCHCNHCH}_2\text{CNHCHCNHCHCO}_2\text{H} \\ \parallel & \parallel & \parallel \\ \text{CH}_3 & \text{CH}_2\text{C}_6\text{H}_5 \end{matrix}$$

Z-Ala-Gly-Phe-Leu

B-1. (c) **B-2.** (c) **B-3.** (a) **B-4.** (d)

B-5. (c) **B-6.** (b) **B-7.** (c) **B-8.** (a)

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APPENDIX B

TABLES

Table B-1 Bond Dissociation Energies of Some Representative Compounds*

Bond dissociation energy, kJ/mol		Bond dissociation energy, kJ/mol
(kcal/mol)	Bond	(kcal/mol)
Diatomic	c molecules	
435 (104)	H—F	568 (136)
159 (38)	H—Cl	431 (103)
242 (58)	H—Br	366 (87.5)
192 (46)	H—I	297 (71)
150 (36)		
All	kanes	
435 (104)	CH ₂ —CH ₂	368 (88)
		355 (85)
` '		351 (84)
* *	5 2	334 (80)
380 (91)	\ 3/3 3	· /
Alkyl	halides	
451 (108)	(CH ₃) ₂ CH—F	439 (105)
349 (83.5)	(CH ₃) ₂ CH—Cl	339 (81)
293 (70)	$(CH_3)_2CH$ —Br	284 (68)
234 (56)	$(CH_3)_3C$ —Cl	330 (79)
338 (81)	$(CH_3)_3C$ —Br	263 (63)
343 (82)	5.5	
Water a	nd alcohols	
497 (119)	CH ₃ CH ₂ —OH	380 (91)
426 (102)	(CH ₃) ₂ CH—OH	385 (92)
380 (91)	$(CH_3)_3C$ —OH	380 (91)
	energy, kJ/mol (kcal/mol) Diatomic 435 (104) 159 (38) 242 (58) 192 (46) 150 (36) All 435 (104) 410 (98) 410 (98) 410 (98) 397 (95) 380 (91) Alkyl 451 (108) 349 (83.5) 293 (70) 234 (56) 338 (81) 343 (82) Water and 497 (119) 426 (102)	Diatomic molecules Diatomic molecules 435 (104) H—F 159 (38) H—Cl 242 (58) H—Br 192 (46) H—I 150 (36) Alkanes 435 (104) CH₃—CH₃ 410 (98) CH₃CH₂—CH₃ 410 (98) (CH₃)₂CH—CH₃ 397 (95) (CH₃)₂CH—CH₃ 380 (91) Alkyl halides Alkyl halides (CH₃)₂CH—F 349 (83.5) (CH₃)₂CH—Cl 293 (70) (CH₃)₂CH—Br 234 (56) (CH₃)₂CH—Br 234 (56) (CH₃)₃C—Cl 338 (81) (CH₃)₃C—Br 343 (82) Water and alcohols

^{*}Note: Bond dissociation energies refer to bonds indicated in structural formula for each substance.





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Table B-2 Acid Dissociation Constants*

Acid	Formula	Conjugate base	Dissociation constant	pK_a
Hydrogen fluoride	H —F	F-	3.5×10^{-4}	3.5
Acetic acid	CH_3CO_2 — H	CH ₃ CO ₂	1.8×10^{-5}	4.7
Hydrogen cyanide	H—CN	CN^-	7.2×10^{-10}	9.1
Phenol	C_6H_5O — H	$C_6H_5O^-$	1.3×10^{-10}	9.8
Water	HO— Н	HO^-	1.8×10^{-16}	15.7
Ethanol	CH_3CH_2O — H	$\mathrm{CH_{3}CH_{2}O^{-}}$	10^{-16}	16
Alkyne (terminal; $R = alkyl$)	RC = C - H	$RC = C^-$	10^{-26}	26
Ammonia	NH_2 — H	$\mathrm{NH_2}^-$	10^{-36}	36
Alkene C—H	RCH = CH - H	RCH=CH-	10^{-45}	45
Alkane C—H	$RCH_2CH_2\mathbf{H}$	$RCH_2CH_2^-$	10^{-62}	62

^{*}Note: Acid strength decreases from top to bottom of the table; conjugate base strength increases from top to bottom.

Table B-3 Chemical Shifts of Representative Types of Protons

Type of proton	Chemical shift (δ), ppm*	Type of proton	Chemical shift (δ), ppm*
H— C — R	0.9–1.8	H—C—NR	2.2–2.9
H-C-C=C	1.6–2.6	H—C—Cl	3.1–4.1
$\mathbf{H} - \overset{\mathbf{O}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}}{\overset{\mathbf{C}}}}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}}{\overset{\mathbf{C}}}}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}}{\overset{\mathbf{C}}}}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}}{\overset{\mathbf{C}}}{\overset{\mathbf{C}}}}{\overset{C}}{\overset{\mathbf{C}}}}{\overset{\mathbf{C}}}}}{\overset{\mathbf{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}$	2.1–2.5	H —C— Br	2.7–4.1
Н−С≡С−	2.5	H —C—O	3.3–3.7
$\mathbf{H} - \overset{\mid}{\mathbf{C}} - \mathbf{Ar}$ $\mathbf{H} - \overset{\mid}{\mathbf{C}} = \mathbf{C}$	2.3–2.8	H —NR	$1{-}3^{\dagger}$
H-C=C	4.5–6.5	H—OR	0.55^\dagger
H —Ar	6.5–8.5	H—OAr	$6-8^{\dagger}$
H-C-	9–10	H-oc-	10-13 [†]

^{*}These are approximate values relative to tetramethylsilane; other groups within the molecule can cause a proton signal to appear outside of the range cited.



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 $[\]dagger$ The chemical shifts of protons bonded to nitrogen and oxygen are temperature- and concentration-dependent.

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Table B-4 Chemical Shifts of Representative Carbons

Type of carbon	Chemical shift (δ), ppm*	Type of carbon	Chemical shift (δ), ppm*
RCH ₃	0–35)c=c(100-150
R_2CH_2	15–40		
R_3 CH	25–50		110–175
RCH_2NH_2	35–50		
RCH ₂ OH	50-65		190–220
-C≡C-	65–90		

^{*} Approximate values relative to tetramethylsilane.

Table B-5 Infrared Absorption Frequencies of Some Common Structural Units

Structural unit	Frequency, cm ⁻¹	Structural unit	Frequency, cm ⁻¹
	Strete	ching vibrations	
Single bonds Double bonds			bonds
—O—H (alcohols)	3200-3600	C = C	1620–1680
—O—H (carboxylic acids)	2500–3600	C=O	
N—H	3350-3500	Aldehydes and ketones	1710–1750
sp C—H	3310-3320	Carboxylic acids	1700–1725
<i>sp</i> ² C─H	3000-3100	Acid anhydrides	1800-1850 and 1740-1790
<i>sp</i> ³ C—H	2850-2950	Acyl halides	1770–1815
•		Esters	1730-1750
<i>sp</i> ² C—O	1200	Amides	1680-1700
<i>sp</i> ² C─O <i>sp</i> ³ C─O	1025-1200		
		Triple l	bonds
		—C≡C—	2100-2200
		—C≡N	2240–2280
	Bending vibra	tions of diagnostic value	
Alkenes	Alkenes Substituted derivatives of benzene		ives of benzene
Cis-disubstituted	665–730	Monosubstituted	730-770 and 690-710
Trans-disubstituted	960-980	Ortho-disubstituted	735–770
Trisubstituted	790-840	Meta-disubstituted	750-810 and 680-730
		Para-disubstituted	790–840