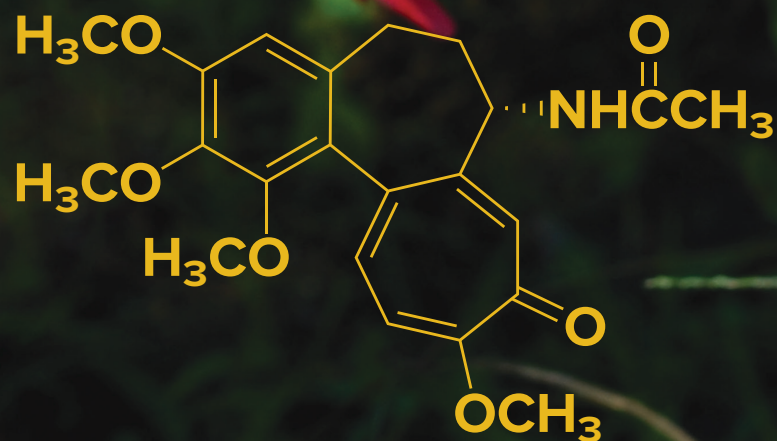


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# Organic CHEMISTRY


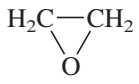
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FRANCIS A. CAREY | ROBERT M. GIULIANO  
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## THE PRINCIPAL FUNCTIONAL GROUPS OF ORGANIC CHEMISTRY

	<i>Example</i>	<i>Acceptable Name(s) of Example</i>	<i>Characteristic Reaction Type</i>
<b>Hydrocarbons</b>			
Alkanes	$\text{CH}_3\text{CH}_3$	Ethane	Free-radical substitution of hydrogen by halogen
Alkenes	$\text{H}_2\text{C}=\text{CH}_2$	Ethene or ethylene	Electrophilic addition to double bond
Alkynes	$\text{HC}\equiv\text{CH}$	Ethyne or acetylene	Electrophilic addition to triple bond
Dienes	$\text{H}_2\text{C}=\text{CHCH}=\text{CH}_2$	1,3-Butadiene	Electrophilic addition to double bonds
Arenes		Benzene	Electrophilic aromatic substitution
<b>Halogen-substituted derivatives of hydrocarbons</b>			
Alkyl halides	$\text{CH}_3\text{CH}_2\text{Cl}$	Chloroethane or ethyl chloride	Nucleophilic substitution; elimination
Alkenyl halides	$\text{H}_2\text{C}=\text{CHCl}$	Chloroethene or vinyl chloride	Electrophilic addition to double bond; elimination
Aryl halides	$\text{C}_6\text{H}_5\text{Cl}$	Chlorobenzene	Electrophilic aromatic substitution; nucleophilic aromatic substitution
<b>Oxygen-containing organic compounds</b>			
Alcohols	$\text{CH}_3\text{CH}_2\text{OH}$	Ethanol or ethyl alcohol	Dehydration; conversion to alkyl halides; esterification
Phenols	$\text{C}_6\text{H}_5\text{OH}$	Phenol	Electrophilic aromatic substitution
Ethers	$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$	Ethoxyethane or diethyl ether	Cleavage by hydrogen halides
Epoxides		Epoxyethane or ethylene oxide or oxirane	Nucleophilic ring opening
Aldehydes	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CH}$	Ethanal or acetaldehyde	Nucleophilic addition to carbonyl group
Ketones	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_3$	2-Propanone or acetone	Nucleophilic addition to carbonyl group
Carboxylic acids	$\text{CH}_3\overset{\text{O}}{\parallel}\text{COH}$	Ethanoic acid or acetic acid	Ionization of carboxyl; esterification

## THE PRINCIPAL FUNCTIONAL GROUPS OF ORGANIC CHEMISTRY

	<i>Example</i>	<i>Acceptable Name(s) of Example</i>	<i>Characteristic Reaction Type</i>
<b>Carboxylic acid derivatives</b>			
Acyl halides	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CCl} \end{array}$	Ethanoyl chloride or acetyl chloride	Nucleophilic acyl substitution
Acid anhydrides	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{CH}_3\text{COCCH}_3 \end{array}$	Ethanoic anhydride or acetic anhydride	Nucleophilic acyl substitution
Esters	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{COCH}_2\text{CH}_3 \end{array}$	Ethyl ethanoate or ethyl acetate	Nucleophilic acyl substitution
Amides	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CNHCH}_3 \end{array}$	<i>N</i> -Methylethanamide or <i>N</i> -methylacetamide	Nucleophilic acyl substitution
<b>Nitrogen-containing organic compounds</b>			
Amines	$\text{CH}_3\text{CH}_2\text{NH}_2$	Ethanamine or ethylamine	Nitrogen acts as a base or as a nucleophile
Nitriles	$\text{CH}_3\text{C}\equiv\text{N}$	Ethanenitrile or acetonitrile	Nucleophilic addition to carbon–nitrogen triple bond
Nitro compounds	$\text{C}_6\text{H}_5\text{NO}_2$	Nitrobenzene	Reduction of nitro group to amine
<b>Sulfur-containing organic compounds</b>			
Thiols	$\text{CH}_3\text{CH}_2\text{SH}$	Ethanethiol	Oxidation to a sulfenic, sulfinic, or sulfonic acid or to a disulfide
Sulfides	$\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3$	Diethyl sulfide	Alkylation to a sulfonium salt; oxidation to a sulfoxide or sulfone



# Organic Chemistry

TWELFTH EDITION

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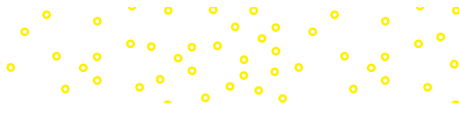
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# Brief Contents

List of Important Features xix

Preface xxiii

Acknowledgements xxx

- 1** Structure Determines Properties 2
- 2** Alkanes and Cycloalkanes: Introduction to Hydrocarbons 56
- 3** Alkanes and Cycloalkanes: Conformations and cis–trans Stereoisomers 100
- 4** Chirality 136
- 5** Alcohols and Alkyl Halides: Introduction to Reaction Mechanisms 174
- 6** Nucleophilic Substitution 212
- 7** Structure and Preparation of Alkenes: Elimination Reactions 246
- 8** Addition Reactions of Alkenes 290
- 9** Alkynes 332
- 10** Introduction to Free Radicals 358
- 11** Conjugation in Alkadienes and Allylic Systems 386
- 12** Arenes and Aromaticity 428
- 13** Electrophilic and Nucleophilic Aromatic Substitution 478
- 14** Spectroscopy 534
- 15** Organometallic Compounds 602
- 16** Alcohols, Diols, and Thiols 640
- 17** Ethers, Epoxides, and Sulfides 678
- 18** Aldehydes and Ketones: Nucleophilic Addition to the Carbonyl Group 716
- 19** Carboxylic Acids 766
- 20** Carboxylic Acid Derivatives: Nucleophilic Acyl Substitution 802
- 21** Enols and Enolates 854
- 22** Amines 894
- 23** Carbohydrates 950
- 24** Lipids 1000
- 25** Amino Acids, Peptides, and Proteins 1040
- 26** Nucleosides, Nucleotides, and Nucleic Acids 1102
- 27** Synthetic Polymers 1138

**Appendix:** Summary of Methods Used to Synthesize a Particular Functional Group **A-1**

**Glossary** **G-1**

**Index** **I-1**

# Contents

List of Important Features xix  
Preface xxiii  
Acknowledgements xxx

## CHAPTER 1

### Structure Determines Properties 2

- 1.1 Atoms, Electrons, and Orbitals 3
  - Organic Chemistry: The Early Days 5**
- 1.2 Ionic Bonds 6
- 1.3 Covalent Bonds, Lewis Formulas, and the Octet Rule 8
- 1.4 Polar Covalent Bonds, Electronegativity, and Bond Dipoles 10
  - Electrostatic Potential Maps 12**
- 1.5 Formal Charge 13
- 1.6 Structural Formulas of Organic Molecules: Isomers 16
  - Curved Arrows and “Electron Pushing” 20**
- 1.7 Resonance and Arrows 21
- 1.8 Sulfur and Phosphorus-Containing Organic Compounds and the Octet Rule 25
- 1.9 Molecular Geometries 26
  - Molecular Models and Modeling 28**
- 1.10 Molecular Dipole Moments 29
- 1.11 Curved Arrows, Arrow Pushing, and Chemical Reactions 30
- 1.12 Acids and Bases: The Brønsted–Lowry View 32
- 1.13 How Structure Affects Acid Strength 37
- 1.14 Acid–Base Equilibria 42
- 1.15 Acids and Bases: The Lewis View 45
- 1.16 Summary 46
  - Problems 49
  - Descriptive Passage and Interpretive Problems 1: Amide Lewis Structural Formulas 54

## CHAPTER 2

### Alkanes and Cycloalkanes: Introduction to Hydrocarbons 56

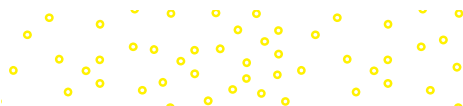
- 2.1 Classes of Hydrocarbons 57
- 2.2 Electron Waves and Chemical Bonds 57
- 2.3 Bonding in H<sub>2</sub>: The Valence Bond Model 58
- 2.4 Bonding in H<sub>2</sub>: The Molecular Orbital Model 59

- 2.5 Introduction to Alkanes: Methane, Ethane, and Propane 61
- 2.6 sp<sup>3</sup> Hybridization and Bonding in Methane 62
  - Methane and the Biosphere 62**
- 2.7 Bonding in Ethane 64
- 2.8 sp<sup>2</sup> Hybridization and Bonding in Ethylene 65
- 2.9 sp Hybridization and Bonding in Acetylene 67
- 2.10 Bonding in Water and Ammonia: Hybridization of Oxygen and Nitrogen 68
- 2.11 Molecular Orbitals and Bonding in Methane 70
- 2.12 Isomeric Alkanes: The Butanes 70
- 2.13 Higher *n*-Alkanes 71
- 2.14 The C<sub>5</sub>H<sub>12</sub> Isomers 72
- 2.15 IUPAC Nomenclature of Unbranched Alkanes 74
- 2.16 Applying the IUPAC Rules: The Names of the C<sub>6</sub>H<sub>14</sub> Isomers 75
  - What’s in a Name? Organic Nomenclature 76**
- 2.17 Alkyl Groups 77
- 2.18 IUPAC Names of Highly Branched Alkanes 79
- 2.19 Cycloalkane Nomenclature 80
- 2.20 Introduction to Functional Groups 81
- 2.21 Sources of Alkanes and Cycloalkanes 81
- 2.22 Physical Properties of Alkanes and Cycloalkanes 83
- 2.23 Chemical Properties: Combustion of Alkanes 85
  - Thermochemistry 88**
- 2.24 Oxidation–Reduction in Organic Chemistry 88
- 2.25 Summary 91
  - Problems 95
  - Descriptive Passage and Interpretive Problems 2: Some Biochemical Reactions of Alkanes 98

## CHAPTER 3

### Alkanes and Cycloalkanes: Conformations and cis–trans Stereoisomers 100

- 3.1 Conformational Analysis of Ethane 101
- 3.2 Conformational Analysis of Butane 105
- 3.3 Conformations of Higher Alkanes 106
  - Computational Chemistry: Molecular Mechanics and Quantum Mechanics 107**
- 3.4 The Shapes of Cycloalkanes: Planar or Nonplanar? 108
- 3.5 Small Rings: Cyclopropane and Cyclobutane 109
- 3.6 Cyclopentane 110
- 3.7 Conformations of Cyclohexane 111
- 3.8 Axial and Equatorial Bonds in Cyclohexane 112
- 3.9 Conformational Inversion in Cyclohexane 114



- 3.10** Conformational Analysis of Monosubstituted Cyclohexanes 115  
**Enthalpy, Free Energy, and Equilibrium Constant** 117
- 3.11** Disubstituted Cycloalkanes: *cis*–*trans* Stereoisomers 118
- 3.12** Conformational Analysis of Disubstituted Cyclohexanes 119
- 3.13** Medium and Large Rings 124
- 3.14** Polycyclic Ring Systems 124
- 3.15** Heterocyclic Compounds 126
- 3.16** **Summary** 127  
**Problems** 130  
**Descriptive Passage and Interpretive Problems 3: Cyclic Forms of Carbohydrates** 135

## 4

### CHAPTER

## Chirality 136

- 4.1** Introduction to Chirality: Enantiomers 136
- 4.2** The Chirality Center 139
- 4.3** Symmetry in Achiral Structures 141
- 4.4** Optical Activity 142
- 4.5** Absolute and Relative Configuration 144
- 4.6** Cahn–Ingold–Prelog *R,S* Notation 145  
**Homochirality and Symmetry Breaking** 148
- 4.7** Fischer Projections 149
- 4.8** Properties of Enantiomers 151  
**Chiral Drugs** 152
- 4.9** Chiral Molecules with Two Chirality Centers 153
- 4.10** Achiral Molecules with Two Chirality Centers 155  
**Chirality of Disubstituted Cyclohexanes** 157
- 4.11** Molecules with Multiple Chirality Centers 158
- 4.12** Resolution of Enantiomers 159
- 4.13** The Chirality Axis 161
- 4.14** Chirality Centers Other Than Carbon 163
- 4.15** **Summary** 164  
**Problems** 167  
**Descriptive Passage and Interpretive Problems 4: Prochirality** 171

## 5

### CHAPTER

## Alcohols and Alkyl Halides: Introduction to Reaction Mechanisms 174

- 5.1** Functional Groups 175
- 5.2** IUPAC Nomenclature of Alkyl Halides 176
- 5.3** IUPAC Nomenclature of Alcohols 177
- 5.4** Classes of Alcohols and Alkyl Halides 178
- 5.5** Bonding in Alcohols and Alkyl Halides 178
- 5.6** Physical Properties of Alcohols and Alkyl Halides: Intermolecular Forces 179

- 5.7** Preparation of Alkyl Halides from Alcohols and Hydrogen Halides 183
- 5.8** Reaction of Alcohols with Hydrogen Halides: The  $S_N1$  Mechanism 185  
**Mechanism 5.1** Formation of *tert*-Butyl Chloride from *tert*-Butyl Alcohol and Hydrogen Chloride 186
- 5.9** Structure, Bonding, and Stability of Carbocations 191
- 5.10** Effect of Alcohol Structure on Reaction Rate 194
- 5.11** Stereochemistry and the  $S_N1$  Mechanism 195
- 5.12** Carbocation Rearrangements 197  
**Mechanism 5.2** Carbocation Rearrangement in the Reaction of 3,3-Dimethyl-2-butanol with Hydrogen Chloride 197
- 5.13** Reaction of Methyl and Primary Alcohols with Hydrogen Halides: The  $S_N2$  Mechanism 199  
**Mechanism 5.3** Formation of 1-Bromoheptane from 1-Heptanol and Hydrogen Bromide 200
- 5.14** Other Methods for Converting Alcohols to Alkyl Halides 201
- 5.15** Sulfonates as Alkyl Halide Surrogates 203
- 5.16** **Summary** 204  
**Problems** 206  
**Descriptive Passage and Interpretive Problems 5: More About Potential Energy Diagrams** 210

## 6

### CHAPTER

## Nucleophilic Substitution 212

- 6.1** Functional-Group Transformation by Nucleophilic Substitution 212
- 6.2** Relative Reactivity of Halide Leaving Groups 215
- 6.3** The  $S_N2$  Mechanism of Nucleophilic Substitution 216  
**Mechanism 6.1** The  $S_N2$  Mechanism of Nucleophilic Substitution 217
- 6.4** Steric Effects and  $S_N2$  Reaction Rates 219
- 6.5** Nucleophiles and Nucleophilicity 221  
**Enzyme-Catalyzed Nucleophilic Substitutions of Alkyl Halides** 223
- 6.6** The  $S_N1$  Mechanism of Nucleophilic Substitution 224  
**Mechanism 6.2** The  $S_N1$  Mechanism of Nucleophilic Substitution 225
- 6.7** Stereochemistry of  $S_N1$  Reactions 226
- 6.8** Carbocation Rearrangements in  $S_N1$  Reactions 228  
**Mechanism 6.3** Carbocation Rearrangement in the  $S_N1$  Hydrolysis of 2-Bromo-3-methylbutane 228
- 6.9** Effect of Solvent on the Rate of Nucleophilic Substitution 229
- 6.10** Nucleophilic Substitution of Alkyl Sulfonates 232
- 6.11** Introduction to Organic Synthesis: Retrosynthetic Analysis 235
- 6.12** Substitution versus Elimination: A Look Ahead 236
- 6.13** **Summary** 237  
**Problems** 238  
**Descriptive Passage and Interpretive Problems 6: Nucleophilic Substitution** 243

# CHAPTER 7

## Structure and Preparation of Alkenes: Elimination Reactions 246

- 7.1 Alkene Nomenclature 246
- 7.2 Structure and Bonding in Alkenes 248  
**Ethylene** 249
- 7.3 Isomerism in Alkenes 250
- 7.4 Naming Stereoisomeric Alkenes by the *E–Z* Notational System 252
- 7.5 Physical Properties of Alkenes 253
- 7.6 Relative Stabilities of Alkenes 254
- 7.7 Cycloalkenes 256
- 7.8 Preparation of Alkenes: Elimination Reactions 258
- 7.9 Dehydration of Alcohols 258
- 7.10 Regioselectivity in Alcohol Dehydration: The Zaitsev Rule 259
- 7.11 Stereoselectivity in Alcohol Dehydration 261
- 7.12 The E1 and E2 Mechanisms of Alcohol Dehydration 261  
**Mechanism 7.1** The E1 Mechanism for Acid-Catalyzed Dehydration of *tert*-Butyl Alcohol 262
- 7.13 Rearrangements in Alcohol Dehydration 263  
**Mechanism 7.2** Carbocation Rearrangement in Dehydration of 3,3-Dimethyl-2-butanol 264  
**Mechanism 7.3** Hydride Shift in Dehydration of 1-Butanol 265
- 7.14 Dehydrohalogenation of Alkyl Halides 266
- 7.15 The E2 Mechanism of Dehydrohalogenation of Alkyl Halides 268  
**Mechanism 7.4** The E2 Mechanism of 1-Chlorooctadecane 269
- 7.16 Anti Elimination in E2 Reactions: Stereoelectronic Effects 271
- 7.17 Isotope Effects and the E2 Mechanism 273
- 7.18 The E1 Mechanism of Dehydrohalogenation of Alkyl Halides 274  
**Mechanism 7.5** The E1 Mechanism for Dehydrohalogenation of 2-Bromo-2-methylbutane 275
- 7.19 Substitution and Elimination as Competing Reactions 276
- 7.20 Elimination Reactions of Sulfonates 279
- 7.21 **Summary** 280  
**Problems** 283  
**Descriptive Passage and Interpretive Problems 7: A Mechanistic Preview of Addition Reactions** 288

# CHAPTER 8

## Addition Reactions of Alkenes 290

- 8.1 Hydrogenation of Alkenes 290
- 8.2 Stereochemistry of Alkene Hydrogenation 291

- Mechanism 8.1** Hydrogenation of Alkenes 292
- 8.3 Heats of Hydrogenation 293
- 8.4 Electrophilic Addition of Hydrogen Halides to Alkenes 295  
**Mechanism 8.2** Electrophilic Addition of Hydrogen Bromide to 2-Methylpropene 297  
**Rules, Laws, Theories, and the Scientific Method** 299
- 8.5 Carbocation Rearrangements in Hydrogen Halide Addition to Alkenes 300
- 8.6 Acid-Catalyzed Hydration of Alkenes 301  
**Mechanism 8.3** Acid-Catalyzed Hydration of 2-Methylpropene 301
- 8.7 Thermodynamics of Addition–Elimination Equilibria 303
- 8.8 Hydroboration–Oxidation of Alkenes 305
- 8.9 Mechanism of Hydroboration–Oxidation 307  
**Mechanism 8.4** Hydroboration of 1-Methylcyclopentene 308  
**Mechanism 8.5** Oxidation of an Organoborane 309
- 8.10 Addition of Halogens to Alkenes 310  
**Mechanism 8.6** Bromine Addition to Cyclopentene 311
- 8.11 Epoxidation of Alkenes 314  
**Mechanism 8.7** Epoxidation of Bicyclo[2.2.1]-2-heptene 315
- 8.12 Ozonolysis of Alkenes 316
- 8.13 Enantioselective Addition to Alkenes 317
- 8.14 Retrosynthetic Analysis and Alkene Intermediates 318
- 8.15 **Summary** 320  
**Problems** 323  
**Descriptive Passage and Interpretive Problems 8: Oxymercuration** 329

# CHAPTER 9

## Alkynes 332

- 9.1 Sources of Alkynes 332
- 9.2 Nomenclature 334
- 9.3 Physical Properties of Alkynes 334
- 9.4 Structure and Bonding in Alkynes: *sp* Hybridization 335
- 9.5 Acidity of Acetylene and Terminal Alkynes 337
- 9.6 Preparation of Alkynes by Alkylation of Acetylene and Terminal Alkynes 339
- 9.7 Preparation of Alkynes by Elimination Reactions 341
- 9.8 Reactions of Alkynes 342
- 9.9 Hydrogenation of Alkynes 342
- 9.10 Addition of Hydrogen Halides to Alkynes 344
- 9.11 Hydration of Alkynes 345  
**Mechanism 9.1** Conversion of an Enol to a Ketone 346
- 9.12 Addition of Halogens to Alkynes 347  
**Some Things That Can Be Made from Acetylene . . . But Aren't** 348
- 9.13 Ozonolysis of Alkynes 348

- 9.14** Alkynes in Synthesis and Retrosynthesis 349  
**9.15** Summary 349  
 Problems 352  
 Descriptive Passage and Interpretive Problems 9:  
 Thinking Mechanistically About Alkynes 356

# 10

## CHAPTER

### Introduction to Free Radicals 358

- 10.1** Structure, Bonding, and Stability of Alkyl Radicals 359  
**10.2** Halogenation of Alkanes 362  
 From Bond Enthalpies to Heats of Reaction 363  
**10.3** Mechanism of Methane Chlorination 364  
 Mechanism 10.1 Free-Radical Chlorination of Methane 365  
**10.4** Halogenation of Higher Alkanes 366  
**10.5** Free-Radical Addition of Hydrogen Bromide to Alkenes and Alkynes 370  
 Mechanism 10.2 Free-Radical Addition of Hydrogen Bromide to 1-Butene 371  
**10.6** Metal–Ammonia Reduction of Alkynes 373  
 Mechanism 10.3 Sodium–Ammonia Reduction of an Alkyne 374  
**10.7** Free Radicals and Retrosynthesis of Alkyl Halides 374  
**10.8** Free-Radical Polymerization of Alkenes 375  
 Mechanism 10.4 Free-Radical Polymerization of Ethylene 376  
 Ethylene and Propene: The Most Important Industrial Organic Chemicals 377  
**10.9** Summary 379  
 Problems 380  
 Descriptive Passage and Interpretive Problems 10: Free-Radical Reduction of Alkyl Halides 383

# 11

## CHAPTER

### Conjugation in Alkadienes and Allylic Systems 386

- 11.1** The Allyl Group 387  
**11.2** S<sub>N</sub>1 and S<sub>N</sub>2 Reactions of Allylic Halides 390  
 Mechanism 11.1 S<sub>N</sub>1 Hydrolysis of an Allylic Halide 391  
**11.3** Allylic Free-Radical Halogenation 394  
 Mechanism 11.2 Allylic Chlorination of Propene 396  
**11.4** Allylic Anions 397  
**11.5** Classes of Dienes: Conjugated and Otherwise 398  
**11.6** Relative Stabilities of Dienes 399  
**11.7** Bonding in Conjugated Dienes 400  
**11.8** Bonding in Allenes 402  
**11.9** Preparation of Dienes 403  
 Diene Polymers 404

- 11.10** Addition of Hydrogen Halides to Conjugated Dienes 405  
 Mechanism 11.3 Addition of Hydrogen Chloride to 1,3-Cyclopentadiene 405  
**11.11** Halogen Addition to Dienes 407  
**11.12** The Diels–Alder Reaction 408  
**11.13** Intramolecular Diels–Alder Reactions 411  
**11.14** Retrosynthetic Analysis and the Diels–Alder Reaction 412  
**11.15** Molecular Orbital Analysis of the Diels–Alder Reaction 413  
 Pericyclic Reactions in Chemical Biology 414  
**11.16** The Cope and Claisen Rearrangements 415  
**11.17** Summary 416  
 Problems 419  
 Descriptive Passage and Interpretive Problems 11:  
 1,3-Dipolar Cycloaddition 425

# 12

## CHAPTER

### Arenes and Aromaticity 428

- 12.1** Benzene 429  
**12.2** The Structure of Benzene 429  
**12.3** The Stability of Benzene 431  
**12.4** Bonding in Benzene 432  
**12.5** Substituted Derivatives of Benzene and Their Nomenclature 434  
**12.6** Polycyclic Aromatic Hydrocarbons 436  
 Fullerenes, Nanotubes, and Graphene 438  
**12.7** Physical Properties of Arenes 439  
**12.8** The Benzyl Group 440  
**12.9** Nucleophilic Substitution in Benzylic Halides 441  
 Triphenylmethyl Radical Yes, Hexaphenylethane No 444  
**12.10** Benzylic Free-Radical Halogenation 445  
**12.11** Benzylic Anions 446  
**12.12** Oxidation of Alkylbenzenes 447  
**12.13** Alkenylbenzenes 448  
**12.14** Polymerization of Styrene 450  
 Mechanism 12.1 Free-Radical Polymerization of Styrene 451  
**12.15** The Birch Reduction 451  
 Mechanism 12.2 The Birch Reduction 452  
**12.16** Benzylic Side Chains and Retrosynthetic Analysis 453  
**12.17** Cyclobutadiene and Cyclooctatetraene 454  
**12.18** Hückel's Rule 455  
**12.19** Annulenes 457  
**12.20** Aromatic Ions 459  
**12.21** Heterocyclic Aromatic Compounds 463  
**12.22** Heterocyclic Aromatic Compounds and Hückel's Rule 464

- 12.23** Summary 466  
 Problems 470  
 Descriptive Passage and Interpretive Problems 12:  
 Substituent Effects on Reaction Rates and  
 Equilibria 475

# 13

## CHAPTER

### Electrophilic and Nucleophilic Aromatic Substitution 478

- 13.1** Representative Electrophilic Aromatic Substitution Reactions of Benzene 479  
**13.2** Mechanistic Principles of Electrophilic Aromatic Substitution 480  
**13.3** Nitration of Benzene 481  
**Mechanism 13.1** Nitration of Benzene 482  
**13.4** Sulfonation of Benzene 483  
**Mechanism 13.2** Sulfonation of Benzene 483  
**13.5** Halogenation of Benzene 484  
**Mechanism 13.3** Bromination of Benzene 485  
**Biosynthetic Halogenation 486**  
**13.6** Friedel–Crafts Alkylation of Benzene 487  
**Mechanism 13.4** Friedel–Crafts Alkylation 487  
**13.7** Friedel–Crafts Acylation of Benzene 489  
**Mechanism 13.5** Friedel–Crafts Acylation 490  
**13.8** Synthesis of Alkylbenzenes by Acylation–Reduction 491  
**13.9** Rate and Regioselectivity in Electrophilic Aromatic Substitution 492  
**13.10** Rate and Regioselectivity in the Nitration of Toluene 494  
**13.11** Rate and Regioselectivity in the Nitration of (Trifluoromethyl)benzene 496  
**13.12** Substituent Effects in Electrophilic Aromatic Substitution: Activating Substituents 498  
**13.13** Substituent Effects in Electrophilic Aromatic Substitution: Strongly Deactivating Substituents 502  
**13.14** Substituent Effects in Electrophilic Aromatic Substitution: Halogens 505  
**13.15** Multiple Substituent Effects 506  
**13.16** Retrosynthetic Analysis and the Synthesis of Substituted Benzenes 508  
**13.17** Substitution in Naphthalene 510  
**13.18** Substitution in Heterocyclic Aromatic Compounds 511  
**13.19** Nucleophilic Aromatic Substitution 512  
**13.20** The Addition–Elimination Mechanism of Nucleophilic Aromatic Substitution 514  
**Mechanism 13.6** Nucleophilic Aromatic Substitution in *p*-Fluoronitrobenzene by the Addition–Elimination Mechanism 516  
**13.21** Related Nucleophilic Aromatic Substitutions 517  
**13.22** Summary 518  
 Problems 522  
 Descriptive Passage and Interpretive Problems 13:  
 Benzyne 530

# 14

## CHAPTER

### Spectroscopy 534

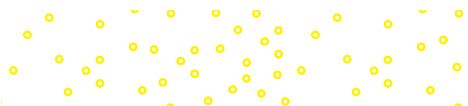
- 14.1** Principles of Molecular Spectroscopy: Electromagnetic Radiation 535  
**14.2** Principles of Molecular Spectroscopy: Quantized Energy States 536  
**14.3** Introduction to <sup>1</sup>H NMR Spectroscopy 536  
**14.4** Nuclear Shielding and <sup>1</sup>H Chemical Shifts 538  
**14.5** Effects of Molecular Structure on <sup>1</sup>H Chemical Shifts 541  
**Ring Currents: Aromatic and Antiaromatic 546**  
**14.6** Interpreting <sup>1</sup>H NMR Spectra 547  
**14.7** Spin–Spin Splitting and <sup>1</sup>H NMR 549  
**14.8** Splitting Patterns: The Ethyl Group 552  
**14.9** Splitting Patterns: The Isopropyl Group 553  
**14.10** Splitting Patterns: Pairs of Doublets 554  
**14.11** Complex Splitting Patterns 555  
**14.12** <sup>1</sup>H NMR Spectra of Alcohols 558  
**Magnetic Resonance Imaging (MRI) 559**  
**14.13** NMR and Conformations 559  
**14.14** <sup>13</sup>C NMR Spectroscopy 560  
**14.15** <sup>13</sup>C Chemical Shifts 561  
**14.16** <sup>13</sup>C NMR and Peak Intensities 564  
**14.17** <sup>13</sup>C–<sup>1</sup>H Coupling 565  
**14.18** Using DEPT to Count Hydrogens 565  
**14.19** 2D NMR: COSY and HETCOR 567  
**14.20** Introduction to Infrared Spectroscopy 569  
**Spectra by the Thousands 570**  
**14.21** Infrared Spectra 571  
**14.22** Characteristic Absorption Frequencies 573  
**14.23** Ultraviolet-Visible Spectroscopy 577  
**14.24** Mass Spectrometry 579  
**14.25** Molecular Formula as a Clue to Structure 584  
**14.26** Summary 585  
 Problems 588  
 Descriptive Passage and Interpretive Problems 14:  
 More on Coupling Constants 598

# 15

## CHAPTER

### Organometallic Compounds 602

- 15.1** Organometallic Nomenclature 603  
**15.2** Carbon–Metal Bonds 603  
**15.3** Preparation of Organolithium and Organomagnesium Compounds 605  
**15.4** Organolithium and Organomagnesium Compounds as Brønsted Bases 606  
**15.5** Synthesis of Alcohols Using Grignard and Organolithium Reagents 607  
**15.6** Synthesis of Acetylenic Alcohols 610



- 15.7** Retrosynthetic Analysis and Grignard and Organolithium Reagents 610
- 15.8** An Organozinc Reagent for Cyclopropane Synthesis 611  
**Mechanism 15.1** Similarities Between the Mechanisms of Reaction of an Alkene with Iodomethylzinc Iodide and a Peroxy Acid 612
- 15.9** Carbenes and Carbenoids 613
- 15.10** Transition-Metal Organometallic Compounds 614  
**An Organometallic Compound That Occurs Naturally: Coenzyme B<sub>12</sub>** 617
- 15.11** Organocopper Reagents 618
- 15.12** Palladium-Catalyzed Cross-Coupling 620
- 15.13** Homogeneous Catalytic Hydrogenation 623  
**Mechanism 15.2** Homogeneous Catalysis of Alkene Hydrogenation 625
- 15.14** Olefin Metathesis 626  
**Mechanism 15.3** Olefin Cross-Metathesis 628
- 15.15** Ziegler–Natta Catalysis of Alkene Polymerization 629  
**Mechanism 15.4** Polymerization of Ethylene in the Presence of Ziegler–Natta Catalyst 631
- 15.16** Summary 632  
 Problems 634  
 Descriptive Passage and Interpretive Problems 15: Allylindium Reagents 638

# 16

## CHAPTER

### Alcohols, Diols, and Thiols 640

- 16.1** Sources of Alcohols 641
- 16.2** Preparation of Alcohols by Reduction of Aldehydes and Ketones 643
- 16.3** Preparation of Alcohols by Reduction of Carboxylic Acids 646
- 16.4** Preparation of Alcohols from Epoxides 646
- 16.5** Preparation of Diols 647
- 16.6** Reactions of Alcohols: A Review and a Preview 649
- 16.7** Conversion of Alcohols to Ethers 650  
**Mechanism 16.1** Acid-Catalyzed Formation of Diethyl Ether from Ethyl Alcohol 650
- 16.8** Esterification 651
- 16.9** Oxidation of Alcohols 653  
**Sustainability and Organic Chemistry** 656
- 16.10** Biological Oxidation of Alcohols 658
- 16.11** Oxidative Cleavage of Vicinal Diols 659
- 16.12** Thiols 660
- 16.13** Spectroscopic Analysis of Alcohols and Thiols 663
- 16.14** Summary 665  
 Problems 668  
 Descriptive Passage and Interpretive Problems 16: The Pinacol Rearrangement 674

# 17

## CHAPTER

### Ethers, Epoxides, and Sulfides 678

- 17.1** Nomenclature of Ethers, Epoxides, and Sulfides 678
- 17.2** Structure and Bonding in Ethers and Epoxides 680
- 17.3** Physical Properties of Ethers 680
- 17.4** Crown Ethers 682
- 17.5** Preparation of Ethers 683  
**Polyether Antibiotics** 684
- 17.6** The Williamson Ether Synthesis 685
- 17.7** Reactions of Ethers: A Review and a Preview 687
- 17.8** Acid-Catalyzed Cleavage of Ethers 688  
**Mechanism 17.1** Cleavage of Ethers by Hydrogen Halides 689
- 17.9** Preparation of Epoxides 690
- 17.10** Conversion of Vicinal Halohydrins to Epoxides 691
- 17.11** Reactions of Epoxides with Anionic Nucleophiles 692  
**Mechanism 17.2** Nucleophilic Ring Opening of an Epoxide 694
- 17.12** Acid-Catalyzed Ring Opening of Epoxides 694  
**Mechanism 17.3** Acid-Catalyzed Ring Opening of an Epoxide 696
- 17.13** Epoxides in Biological Processes 697
- 17.14** Preparation of Sulfides 697
- 17.15** Oxidation of Sulfides: Sulfoxides and Sulfones 698
- 17.16** Alkylation of Sulfides: Sulfonium Salts 699
- 17.17** Spectroscopic Analysis of Ethers, Epoxides, and Sulfides 700
- 17.18** Summary 702  
 Problems 705  
 Descriptive Passage and Interpretive Problems 17: Epoxide Rearrangements and the NIH Shift 713

# 18

## CHAPTER

### Aldehydes and Ketones: Nucleophilic Addition to the Carbonyl Group 716

- 18.1** Nomenclature 717
- 18.2** Structure and Bonding: The Carbonyl Group 719
- 18.3** Physical Properties 722
- 18.4** Sources of Aldehydes and Ketones 722
- 18.5** Reactions of Aldehydes and Ketones: A Review and a Preview 726
- 18.6** Principles of Nucleophilic Addition: Hydration of Aldehydes and Ketones 727  
**Mechanism 18.1** Hydration of an Aldehyde or Ketone in Basic Solution 730  
**Mechanism 18.2** Hydration of an Aldehyde or Ketone in Acid Solution 731

- 18.7** Cyanohydrin Formation 731  
**Mechanism 18.3** Cyanohydrin Formation 732
- 18.8** Reaction with Alcohols: Acetals and Ketals 734  
**Mechanism 18.4** Acetal Formation from Benzaldehyde and Ethanol 736
- 18.9** Acetals and Ketals as Protecting Groups 737
- 18.10** Reaction with Primary Amines: Imines 738  
**Mechanism 18.5** Imine Formation from Benzaldehyde and Methylamine 740
- 18.11** Reaction with Secondary Amines: Enamines 741  
**Imines in Biological Chemistry** 742  
**Mechanism 18.6** Enamine Formation 744
- 18.12** The Wittig Reaction 745
- 18.13** Stereoselective Addition to Carbonyl Groups 748
- 18.14** Oxidation of Aldehydes 749
- 18.15** Spectroscopic Analysis of Aldehydes and Ketones 750
- 18.16** Summary 752  
 Problems 755  
**Descriptive Passage and Interpretive Problems 18:**  
**The Baeyer–Villiger Oxidation** 763

# 19

## CHAPTER

### Carboxylic Acids 766

- 19.1** Carboxylic Acid Nomenclature 767
- 19.2** Structure and Bonding 769
- 19.3** Physical Properties 769
- 19.4** Acidity of Carboxylic Acids 770
- 19.5** Substituents and Acid Strength 772
- 19.6** Ionization of Substituted Benzoic Acids 774
- 19.7** Salts of Carboxylic Acids 775
- 19.8** Dicarboxylic Acids 777
- 19.9** Carbonic Acid 778
- 19.10** Sources of Carboxylic Acids 779
- 19.11** Synthesis of Carboxylic Acids by the Carboxylation of Grignard Reagents 781
- 19.12** Synthesis of Carboxylic Acids by the Preparation and Hydrolysis of Nitriles 782
- 19.13** Reactions of Carboxylic Acids: A Review and a Preview 783
- 19.14** Mechanism of Acid-Catalyzed Esterification 784  
**Mechanism 19.1** Acid-Catalyzed Esterification of Benzoic Acid with Methanol 784
- 19.15** Intramolecular Ester Formation: Lactones 787
- 19.16** Decarboxylation of Malonic Acid and Related Compounds 788  
**Enzymatic Decarboxylation of a  $\beta$ -Keto Acid** 790
- 19.17** Spectroscopic Analysis of Carboxylic Acids 791
- 19.18** Summary 792  
 Problems 794  
**Descriptive Passage and Interpretive Problems 19:**  
**Lactonization Methods** 799

# 20

## CHAPTER

### Carboxylic Acid Derivatives: Nucleophilic Acyl Substitution 802

- 20.1** Nomenclature of Carboxylic Acid Derivatives 803
- 20.2** Structure and Reactivity of Carboxylic Acid Derivatives 804  
**Reaction Trends: Aldehydes and Ketones vs. Carboxylic Acid Derivatives** 805
- 20.3** Nucleophilic Acyl Substitution Mechanisms 808
- 20.4** Nucleophilic Acyl Substitution in Acyl Chlorides 809
- 20.5** Nucleophilic Acyl Substitution in Acid Anhydrides 811  
**Mechanism 20.1** Nucleophilic Acyl Substitution in an Anhydride 813
- 20.6** Physical Properties and Sources of Esters 813
- 20.7** Reactions of Esters: A Preview 814
- 20.8** Acid-Catalyzed Ester Hydrolysis 816  
**Mechanism 20.2** Acid-Catalyzed Ester Hydrolysis 817
- 20.9** Ester Hydrolysis in Base: Saponification 819  
**The Ball Method** 821  
**Mechanism 20.3** Ester Hydrolysis in Basic Solution 823
- 20.10** Reaction of Esters with Ammonia and Amines 824
- 20.11** Reaction of Esters with Grignard and Organolithium Reagents and Lithium Aluminum Hydride 825
- 20.12** Amides 826
- 20.13** Hydrolysis of Amides 830  
**Mechanism 20.4** Amide Hydrolysis in Acid Solution 831  
**Mechanism 20.5** Amide Hydrolysis in Basic Solution 833
- 20.14** Lactams 834  
 **$\beta$ -Lactam Antibiotics** 834
- 20.15** Preparation of Nitriles 836
- 20.16** Hydrolysis of Nitriles 837  
**Mechanism 20.6** Nitrile Hydrolysis in Basic Solution 838
- 20.17** Addition of Grignard Reagents to Nitriles 839
- 20.18** Spectroscopic Analysis of Carboxylic Acid Derivatives 839
- 20.19** Summary 841  
 Problems 844  
**Descriptive Passage and Interpretive Problems 20:**  
**Thioesters** 851

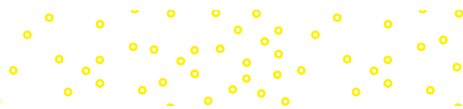
# 21

## CHAPTER

### Enols and Enolates 854

- 21.1** Aldehyde, Ketone, and Ester Enolates 855
- 21.2** The Aldol Condensation 858  
**Mechanism 21.1** Aldol Addition of Butanal 859
- 21.3** Mixed and Directed Aldol Reactions 862  
**From the Mulberry Tree to Cancer Chemotherapy** 863





- 21.4** Acylation of Enolates: The Claisen and Related Condensations 864  
**Mechanism 21.2** Claisen Condensation of Ethyl Propanoate 865
- 21.5** Alkylation of Enolates: The Acetoacetic Ester and Malonic Ester Syntheses 868
- 21.6** Enol Content and Enolization 871  
**Mechanism 21.3** Acid-Catalyzed Enolization of 2-Methylpropanal 873
- 21.7** The Haloform Reaction 875  
**Mechanism 21.4** The Haloform Reaction 876
- 21.8** Some Chemical and Stereochemical Consequences of Enolization 877
- 21.9** Conjugation Effects in  $\alpha,\beta$ -Unsaturated Aldehydes and Ketones 878
- 21.10** Summary 882  
 Problems 884  
 Descriptive Passage and Interpretive Problems 21: The Knoevenagel Reaction 891

## 22

### CHAPTER

## Amines 894

- 22.1** Amine Nomenclature 895
- 22.2** Structure and Bonding 897
- 22.3** Physical Properties 899
- 22.4** Basicity of Amines 899  
**Amines as Natural Products** 904
- 22.5** Tetraalkylammonium Salts as Phase-Transfer Catalysts 905
- 22.6** Reactions That Lead to Amines: A Review and a Preview 906
- 22.7** Preparation of Amines by Alkylation of Ammonia 908
- 22.8** The Gabriel Synthesis of Primary Alkylamines 909
- 22.9** Preparation of Amines by Reduction 910  
**Mechanism 22.1** Lithium Aluminum Hydride Reduction of an Amide 913
- 22.10** Reductive Amination 914
- 22.11** Reactions of Amines: A Review and a Preview 915
- 22.12** Reaction of Amines with Alkyl Halides 917
- 22.13** The Hofmann Elimination 917
- 22.14** Electrophilic Aromatic Substitution in Arylamines 919
- 22.15** Nitrosation of Alkylamines 921
- 22.16** Nitrosation of Arylamines 923
- 22.17** Synthetic Transformations of Aryl Diazonium Salts 924
- 22.18** Azo Coupling 928  
**From Dyes to Sulfa Drugs** 928
- 22.19** Spectroscopic Analysis of Amines 930
- 22.20** Summary 932  
 Problems 938  
 Descriptive Passage and Interpretive Problems 22: Synthetic Applications of Enamines 947

## 23

### CHAPTER

## Carbohydrates 950

- 23.1** Classification of Carbohydrates 951
- 23.2** Fischer Projections and D,L Notation 951
- 23.3** The Aldotetroses 952
- 23.4** Aldopentoses and Aldohexoses 954
- 23.5** A Mnemonic for Carbohydrate Configurations 956
- 23.6** Cyclic Forms of Carbohydrates: Furanose Forms 956
- 23.7** Cyclic Forms of Carbohydrates: Pyranose Forms 960
- 23.8** Mutarotation 962  
**Mechanism 23.1** Acid-Catalyzed Mutarotation of D-Glucopyranose 963
- 23.9** Carbohydrate Conformation: The Anomeric Effect 964
- 23.10** Ketoses 966
- 23.11** Deoxy Sugars 967
- 23.12** Amino Sugars 968
- 23.13** Branched-Chain Carbohydrates 969
- 23.14** Glycosides: The Fischer Glycosidation 969  
**Mechanism 23.2** Preparation of Methyl D-Glucopyranosides by Fischer Glycosidation 971
- 23.15** Disaccharides 973
- 23.16** Polysaccharides 975  
**How Sweet It Is!** 977
- 23.17** Application of Familiar Reactions to Monosaccharides 978
- 23.18** Oxidation of Carbohydrates 981
- 23.19** Glycosides: Synthesis of Oligosaccharides 984  
**Mechanism 23.3** Silver-Assisted Glycosidation 985
- 23.20** Glycobiology 986  
**Oligosaccharides in Infectious Disease** 989
- 23.21** Summary 990  
 Problems 991  
 Descriptive Passage and Interpretive Problems 23: Emil Fischer and the Structure of (+)-Glucose 996

## 24

### CHAPTER

## Lipids 1000

- 24.1** Acetyl Coenzyme A 1001
- 24.2** Fats, Oils, and Fatty Acids 1002
- 24.3** Fatty Acid Biosynthesis 1005
- 24.4** Phospholipids 1007
- 24.5** Waxes 1010
- 24.6** Prostaglandins 1011  
**Nonsteroidal Antiinflammatory Drugs (NSAIDs) and COX-2 Inhibitors** 1013
- 24.7** Terpenes: The Isoprene Rule 1014

- 24.8** Isopentenyl Diphosphate: The Biological Isoprene Unit 1017
- 24.9** Carbon–Carbon Bond Formation in Terpene Biosynthesis 1017
- 24.10** The Pathway from Acetate to Isopentenyl Diphosphate 1020
- 24.11** Steroids: Cholesterol 1022  
**Mechanism 24.1** Biosynthesis of Cholesterol from Squalene 1024
- 24.12** Vitamin D 1025  
**Good Cholesterol? Bad Cholesterol? What's the Difference?** 1025
- 24.13** Bile Acids 1026
- 24.14** Corticosteroids 1026
- 24.15** Sex Hormones 1027
- 24.16** Carotenoids 1028  
**Crocuses Make Saffron from Carotenes** 1028
- 24.17** Summary 1030  
 Problems 1032  
 Descriptive Passage and Interpretive Problems 24: Polyketides 1036

## CHAPTER 25

### Amino Acids, Peptides, and Proteins 1040

- 25.1** Classification of Amino Acids 1041
- 25.2** Stereochemistry of Amino Acids 1046
- 25.3** Acid–Base Behavior of Amino Acids 1048  
**Electrophoresis** 1051
- 25.4** Synthesis of Amino Acids 1052
- 25.5** Reactions of Amino Acids 1053
- 25.6** Peptides 1055
- 25.7** Introduction to Peptide Structure Determination 1058
- 25.8** Amino Acid Analysis 1058
- 25.9** Partial Hydrolysis and End Group Analysis 1058
- 25.10** Insulin 1060
- 25.11** Edman Degradation and Automated Sequencing of Peptides 1062  
**Mechanism 25.1** The Edman Degradation 1062
- 25.12** Mass Spectrometry of Peptides and Proteins 1064  
**Peptide Mapping and MALDI Mass Spectrometry** 1065
- 25.13** The Strategy of Peptide Synthesis 1066
- 25.14** Amino and Carboxyl Group Protection and Deprotection 1068
- 25.15** Peptide Bond Formation 1070  
**Mechanism 25.2** Amide Bond Formation Between a Carboxylic Acid and an Amine Using *N,N'*-Dicyclohexylcarbodiimide 1071
- 25.16** Solid-Phase Peptide Synthesis: The Merrifield Method 1072
- 25.17** Secondary Structures of Peptides and Proteins 1074
- 25.18** Tertiary Structure of Polypeptides and Proteins 1077
- 25.19** Protein Quaternary Structure: Hemoglobin 1079
- 25.20** Enzymes 1081

- Mechanism 25.3** Carboxypeptidase-Catalyzed Hydrolysis 1082
- 25.21** Coenzymes in Reactions of Amino Acids 1083  
**Mechanism 25.4** Pyridoxal 5'-Phosphate-Mediated Decarboxylation of an  $\alpha$ -Amino Acid 1084  
**Mechanism 25.5** Transamination: Biosynthesis of L-Alanine from L-Glutamic Acid and Pyruvic Acid 1088  
**Oh NO! It's Inorganic!** 1090
- 25.22** G-Protein-Coupled Receptors 1090
- 25.23** Summary 1091  
 Problems 1093  
 Descriptive Passage and Interpretive Problems 25: Amino Acids in Enantioselective Synthesis 1098

## CHAPTER 26

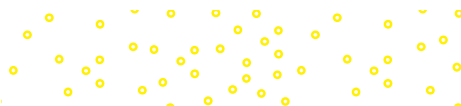
### Nucleosides, Nucleotides, and Nucleic Acids 1102

- 26.1** Pyrimidines and Purines 1103
- 26.2** Nucleosides 1105
- 26.3** Nucleotides 1107
- 26.4** Bioenergetics 1109
- 26.5** ATP and Bioenergetics 1110
- 26.6** Phosphodiester, Oligonucleotides, and Polynucleotides 1112
- 26.7** Phosphoric Acid Esters 1113
- 26.8** Deoxyribonucleic Acids 1115  
**"It Has Not Escaped Our Notice . . ."** 1116
- 26.9** Secondary Structure of DNA: The Double Helix 1117
- 26.10** Replication of DNA 1118
- 26.11** Ribonucleic Acids 1120  
**mRNA Therapeutics** 1125
- 26.12** Protein Biosynthesis 1125
- 26.13** DNA Sequencing 1126
- 26.14** Summary 1128  
 Problems 1130  
 Descriptive Passage and Interpretive Problems 26: Oligonucleotide Synthesis 1133

## CHAPTER 27

### Synthetic Polymers 1138

- 27.1** Some Background 1138  
**From Bakelite to Nylon** 1139
- 27.2** Polymer Nomenclature 1140
- 27.3** Classification of Polymers: Reaction Type 1141
- 27.4** Classification of Polymers: Chain Growth and Step Growth 1143



<b>27.5</b>	Classification of Polymers: Structure	1144	<b>27.13</b>	Polycarbonates	1158
<b>27.6</b>	Classification of Polymers: Properties	1147	<b>27.14</b>	Polyurethanes	1158
<b>27.7</b>	Addition Polymers: A Review and a Preview	1147	<b>27.15</b>	Copolymers	1159
<b>27.8</b>	Chain Branching in Free-Radical Polymerization	1150		<b>Conducting Polymers</b>	<b>1161</b>
	<b>Mechanism 27.1</b> Branching in Polyethylene Caused by Intramolecular Hydrogen Transfer	1151	<b>27.16</b>	Summary	1162
	<b>Mechanism 27.2</b> Branching in Polyethylene Caused by Intermolecular Hydrogen Transfer	1152		Problems	1165
<b>27.9</b>	Anionic Polymerization: Living Polymers	1152		Descriptive Passage and Interpretive Problems 27:	
	<b>Mechanism 27.3</b> Anionic Polymerization of Styrene	1153		Chemically Modified Polymers	1166
<b>27.10</b>	Cationic Polymerization	1154	<b>Appendix:</b>	Summary of Methods Used to Synthesize a Particular Functional Group	<b>A-1</b>
	<b>Mechanism 27.4</b> Cationic Polymerization of 2-Methylpropene	1155	<b>Glossary</b>	<b>G-1</b>	
<b>27.11</b>	Polyamides	1156	<b>Index</b>	<b>I-1</b>	
<b>27.12</b>	Polyesters	1157			

# List of Important Features

## Mechanisms

- 5.1** Formation of *tert*-Butyl Chloride from *tert*-Butyl Alcohol and Hydrogen Chloride 186
- 5.2** Carbocation Rearrangement in the Reaction of 3,3-Dimethyl-2-butanol with Hydrogen Chloride 197
- 5.3** Formation of 1-Bromoheptane from 1-Heptanol and Hydrogen Bromide 200
- 6.1** The S<sub>N</sub>2 Mechanism of Nucleophilic Substitution 217
- 6.2** The S<sub>N</sub>1 Mechanism of Nucleophilic Substitution 225
- 6.3** Carbocation Rearrangement in the S<sub>N</sub>1 Hydrolysis of 2-Bromo-3-methylbutane 228
- 7.1** The E1 Mechanism for Acid-Catalyzed Dehydration of *tert*-Butyl Alcohol 262
- 7.2** Carbocation Rearrangement in Dehydration of 3,3-Dimethyl-2-butanol 264
- 7.3** Hydride Shift in Dehydration of 1-Butanol 265
- 7.4** The E2 Mechanism of 1-Chlorooctadecane 269
- 7.5** The E1 Mechanism for Dehydrohalogenation of 2-Bromo-2-methylbutane 275
- 8.1** Hydrogenation of Alkenes 292
- 8.2** Electrophilic Addition of Hydrogen Bromide to 2-Methylpropene 297
- 8.3** Acid-Catalyzed Hydration of 2-Methylpropene 301
- 8.4** Hydroboration of 1-Methylcyclopentene 308
- 8.5** Oxidation of an Organoborane 309
- 8.6** Bromine Addition to Cyclopentene 311
- 8.7** Epoxidation of Bicyclo[2.2.1]-2-heptene 315
- 9.1** Conversion of an Enol to a Ketone 346
- 10.1** Free-Radical Chlorination of Methane 365
- 10.2** Free-Radical Addition of Hydrogen Bromide to 1-Butene 371
- 10.3** Sodium–Ammonia Reduction of an Alkyne 374
- 10.4** Free-Radical Polymerization of Ethylene 376
- 11.1** S<sub>N</sub>1 Hydrolysis of an Allylic Halide 391
- 11.2** Allylic Chlorination of Propene 396
- 11.3** Addition of Hydrogen Chloride to 1,3-Cyclopentadiene 405
- 12.1** Free-Radical Polymerization of Styrene 451
- 12.2** The Birch Reduction 452
- 13.1** Nitration of Benzene 482
- 13.2** Sulfonation of Benzene 483
- 13.3** Bromination of Benzene 485
- 13.4** Friedel–Crafts Alkylation 487
- 13.5** Friedel–Crafts Acylation 490
- 13.6** Nucleophilic Aromatic Substitution in *p*-Fluoronitrobenzene by the Addition–Elimination Mechanism 516
- 15.1** Similarities Between the Mechanisms of Reaction of an Alkene with Iodomethylzinc Iodide and a Peroxy Acid 612
- 15.2** Homogeneous Catalysis of Alkene Hydrogenation 625
- 15.3** Olefin Cross-Metathesis 628
- 15.4** Polymerization of Ethylene in the Presence of Ziegler–Natta Catalyst 631
- 16.1** Acid-Catalyzed Formation of Diethyl Ether from Ethyl Alcohol 650
- 17.1** Cleavage of Ethers by Hydrogen Halides 689
- 17.2** Nucleophilic Ring Opening of an Epoxide 694
- 17.3** Acid-Catalyzed Ring Opening of an Epoxide 696
- 18.1** Hydration of an Aldehyde or Ketone in Basic Solution 730
- 18.2** Hydration of an Aldehyde or Ketone in Acid Solution 731
- 18.3** Cyanohydrin Formation 732
- 18.4** Acetal Formation from Benzaldehyde and Ethanol 736
- 18.5** Imine Formation from Benzaldehyde and Methylamine 740
- 18.6** Enamine Formation 744
- 19.1** Acid-Catalyzed Esterification of Benzoic Acid with Methanol 784
- 20.1** Nucleophilic Acyl Substitution in an Anhydride 813
- 20.2** Acid-Catalyzed Ester Hydrolysis 817
- 20.3** Ester Hydrolysis in Basic Solution 823
- 20.4** Amide Hydrolysis in Acid Solution 831
- 20.5** Amide Hydrolysis in Basic Solution 833
- 20.6** Nitrile Hydrolysis in Basic Solution 838
- 21.1** Aldol Addition of Butanal 859
- 21.2** Claisen Condensation of Ethyl Propanoate 865
- 21.3** Acid-Catalyzed Enolization of 2-Methylpropanal 873
- 21.4** The Haloform Reaction 876
- 22.1** Lithium Aluminum Hydride Reduction of an Amide 913
- 23.1** Acid-Catalyzed Mutarotation of D-Glucopyranose 963
- 23.2** Preparation of Methyl D-Glucopyranosides by Fischer Glycosidation 971
- 23.3** Silver-Assisted Glycosidation 985
- 24.1** Biosynthesis of Cholesterol from Squalene 1024
- 25.1** The Edman Degradation 1062
- 25.2** Amide Bond Formation Between a Carboxylic Acid and an Amine Using *N,N'*-Dicyclohexylcarbodiimide 1071
- 25.3** Carboxypeptidase-Catalyzed Hydrolysis 1082
- 25.4** Pyridoxal 5'-Phosphate-Mediated Decarboxylation of an  $\alpha$ -Amino Acid 1084
- 25.5** Transamination: Biosynthesis of L-Alanine from L-Glutamic Acid and Pyruvic Acid 1088
- 27.1** Branching in Polyethylene Caused by Intramolecular Hydrogen Transfer 1151
- 27.2** Branching in Polyethylene Caused by Intermolecular Hydrogen Transfer 1152
- 27.3** Anionic Polymerization of Styrene 1153
- 27.4** Cationic Polymerization of 2-Methylpropene 1155

**Tables**

- 1.1** Electron Configurations of the First Twelve Elements of the Periodic Table 6
- 1.2** Lewis Formulas of Methane, Ammonia, Water, and Hydrogen Fluoride 9
- 1.3** Selected Values from the Pauling Electronegativity Scale 12
- 1.4** Selected Bond Dipole Moments 13
- 1.5** A Systematic Approach to Writing Lewis Formulas 16
- 1.6** Introduction to the Rules of Resonance 23
- 1.7** VSEPR and Molecular Geometry 26
- 1.8** Acidity Constants ( $pK_a$ ) of Acids 35
- 2.1** The Number of Constitutionally Isomeric Alkanes of Particular Molecular Formulas 72
- 2.2** IUPAC Names of Unbranched Alkanes 74
- 2.3** Heats of Combustion ( $-\Delta H^\circ$ ) of Representative Alkanes 86
- 2.4** Summary of IUPAC Nomenclature of Alkanes and Cycloalkanes 93
- 2.5** Summary of IUPAC Nomenclature of Alkyl Groups 94
- 3.1** Heats of Combustion ( $-\Delta H^\circ$ ) of Cycloalkanes 109
- 3.2** Heats of Combustion of Isomeric Dimethylcyclohexanes 120
- 4.1** The Cahn–Ingold–Prelog Sequence Rules 146
- 4.2** Classification of Isomers 165
- 5.1** Functional Groups in Some Important Classes of Organic Compounds 176
- 5.2** Boiling Points of Some Alkyl Halides and Alcohols 181
- 5.3** Conversions of Alcohols to Alkyl Halides and Sulfonates 205
- 6.1** Functional-Group Transformation via Nucleophilic Substitution 213
- 6.2** Nucleophilicity of Some Common Nucleophiles 222
- 6.3** Properties of Some Solvents Used in Nucleophilic Substitution 230
- 6.4** Relative Rate of  $S_N1$  Solvolysis of *tert*-Butyl Chloride as a Function of Protic Solvent Polarity 230
- 6.5** Relative Rate of  $S_N2$  Displacement of 1-Bromobutane by Azide in Various Solvents 232
- 6.6** Approximate Relative Leaving-Group Abilities 233
- 6.7** Comparison of  $S_N1$  and  $S_N2$  Mechanisms of Nucleophilic Substitution in Alkyl Halides 237
- 7.1** Preparation of Alkenes by Elimination Reactions of Alcohols and Alkyl Halides 282
- 8.1** Heats of Hydrogenation of Some Alkenes 294
- 8.2** Addition Reactions of Alkenes 320
- 9.1** Structural Features of Ethane, Ethylene, and Acetylene 336
- 9.2** Preparation of Alkynes 351
- 10.1** Some Bond Dissociation Enthalpies 361
- 10.2** Some Compounds with Carbon–Carbon Double Bonds Used to Prepare Polymers 378
- 12.1** Names of Some Frequently Encountered Derivatives of Benzene 434
- 12.2** Reactions Involving Alkyl and Alkenyl Side Chains in Arenes and Arene Derivatives 468
- 13.1** Representative Electrophilic Aromatic Substitution Reactions of Benzene 479
- 13.2** Classification of Substituents in Electrophilic Aromatic Substitution Reactions 499
- 13.3** Representative Electrophilic Aromatic Substitution Reactions 519
- 13.4** Limitations on Friedel–Crafts Reactions 520
- 14.1** Splitting Patterns of Common Multiplets 553
- 14.2** Chemical Shifts of Representative Carbons 562
- 14.3** Infrared Absorption Frequencies of Some Common Structural Units 576
- 14.4** Absorption Maxima of Some Representative Alkenes and Polyenes 578
- 14.5** Approximate Values of Proton Coupling Constants (in Hz) 598
- 15.1** Reactions of Grignard Reagents with Aldehydes and Ketones 609
- 16.1** Reactions Discussed in Earlier Chapters That Yield Alcohols 642
- 16.2** Reactions of Alcohols Discussed in Earlier Chapters 649
- 16.3** Preparation of Alcohols by Reduction of Carbonyl Functional Groups 665
- 16.4** Reactions of Alcohols Presented in This Chapter 667
- 16.5** Oxidation of Alcohols 668
- 17.1** Physical Properties of Diethyl Ether, Pentane, and 1-Butanol 681
- 17.2** Preparation of Ethers and Epoxides 704
- 18.1** Summary of Reactions Discussed in Earlier Chapters That Yield Aldehydes and Ketones 723
- 18.2** Summary of Reactions of Aldehydes and Ketones Discussed in Earlier Chapters 726
- 18.3** Equilibrium Constants ( $K_{\text{hydr}}$ ) and Relative Rates of Hydration of Some Aldehydes and Ketones 727
- 18.4** Reactions of Aldehydes and Ketones with Derivatives of Ammonia 741
- 18.5** Nucleophilic Addition to Aldehydes and Ketones 753
- 19.1** Systematic and Common Names of Some Carboxylic Acids 768
- 19.2** Effect of Substituents on Acidity of Carboxylic Acids 773
- 19.3** Acidity of Some Substituted Benzoic Acids 775
- 19.4** Summary of Reactions Discussed in Earlier Chapters That Yield Carboxylic Acids 780
- 19.5** Summary of Reactions of Carboxylic Acids Discussed in Earlier Chapters 783
- 20.1** Conversion of Acyl Chlorides to Other Carboxylic Acid Derivatives 810
- 20.2** Conversion of Acid Anhydrides to Other Carboxylic Acid Derivatives 812
- 20.3** Preparation of Esters 815
- 20.4** Conversion of Esters to Other Carboxylic Acid Derivatives 816
- 20.5** Intermolecular Forces in Amides 827
- 20.6** Preparation of Nitriles 836
- 21.1**  $pK_a$  Values of Some Aldehydes, Ketones, and Esters 855
- 21.2** Enolization Equilibria (keto  $\rightleftharpoons$  enol) of Some Carbonyl Compounds 872
- 22.1** Basicity of Amines as Measured by the  $pK_a$  of Their Conjugate Acids 900
- 22.2** Effect of *para* Substituents on the Basicity of Aniline 902
- 22.3** Methods for Carbon–Nitrogen Bond Formation Discussed in Earlier Chapters 907

- 22.4** Reactions of Amines Discussed in Previous Chapters 916
- 22.5** Preparation of Amines 933
- 22.6** Reactions of Amines Discussed in This Chapter 935
- 22.7** Synthetically Useful Transformations Involving Aryl Diazonium Ions (Section 22.17) 936
- 23.1** Some Classes of Monosaccharides 951
- 23.2** Familiar Reaction Types of Carbohydrates 979
- 24.1** Some Representative Fatty Acids 1003
- 24.2** Classification of Terpenes 1015
- 25.1** The Standard Amino Acids 1042
- 25.2** Acid–Base Properties of Amino Acids with Neutral Side Chains 1049
- 25.3** Acid–Base Properties of Amino Acids with Ionizable Side Chains 1049
- 25.4** Covalent and Noncovalent Interactions Between Amino Acid Side Chains in Proteins 1079
- 26.1** Pyrimidines and Purines That Occur in DNA and/or RNA 1104
- 26.2** The Major Pyrimidine and Purine Nucleosides in RNA and DNA 1106
- 26.3**  $\Delta G^\circ$  for the Hydrolysis of Bioenergetically Important Phosphates 1112
- 27.1** Recycling of Plastics 1146
- 27.2** Summary of Alkene Polymerizations Discussed in Earlier Chapters 1148

## Boxed Essays

### Chapter 1

- Organic Chemistry: The Early Days 5
- Electrostatic Potential Maps 12
- Curved Arrows and “Electron Pushing” 20
- Molecular Models and Modeling 28

### Chapter 2

- Methane and the Biosphere 62
- What’s in a Name? Organic Nomenclature 76
- Thermochemistry 88

### Chapter 3

- Computational Chemistry: Molecular Mechanics and Quantum Mechanics 107
- Enthalpy, Free Energy, and Equilibrium Constant 117

### Chapter 4

- Homochirality and Symmetry Breaking 148
- Chiral Drugs 152
- Chirality of Disubstituted Cyclohexanes 157

### Chapter 6

- Enzyme-Catalyzed Nucleophilic Substitutions of Alkyl Halides 223

### Chapter 7

- Ethylene 249

### Chapter 8

- Rules, Laws, Theories, and the Scientific Method 299

### Chapter 9

- Some Things That Can Be Made from Acetylene . . . But Aren’t 348

### Chapter 10

- From Bond Enthalpies to Heats of Reaction 363
- Ethylene and Propene: The Most Important Industrial Organic Chemicals 377

### Chapter 11

- Diene Polymers 404
- Pericyclic Reactions in Chemical Biology 414

### Chapter 12

- Fullerenes, Nanotubes, and Graphene 438
- Triphenylmethyl Radical Yes, Hexaphenylethane No 444

### Chapter 13

- Biosynthetic Halogenation 486

### Chapter 14

- Ring Currents: Aromatic and Antiaromatic 546
- Magnetic Resonance Imaging (MRI) 559
- Spectra by the Thousands 570

### Chapter 15

- An Organometallic Compound That Occurs Naturally: Coenzyme B<sub>12</sub> 617

### Chapter 16

- Sustainability and Organic Chemistry 656

### Chapter 17

- Polyether Antibiotics 684

### Chapter 18

- Imines in Biological Chemistry 742

### Chapter 19

- Enzymatic Decarboxylation of a  $\beta$ -Keto Acid 790

### Chapter 20

- Reaction Trends: Aldehydes and Ketones vs. Carboxylic Acid Derivatives 805
- The Ball Method 821
- $\beta$ -Lactam Antibiotics 834

### Chapter 21

- From the Mulberry Tree to Cancer Chemotherapy 863

### Chapter 22

- Amines as Natural Products 904
- From Dyes to Sulfa Drugs 928

### Chapter 23

- How Sweet It Is! 977
- Oligosaccharides in Infectious Disease 989

### Chapter 24

- Nonsteroidal Antiinflammatory Drugs (NSAIDs) and COX-2 Inhibitors 1013
- Good Cholesterol? Bad Cholesterol? What’s the Difference? 1025
- Crocuses Make Saffron from Carotenes 1028

### Chapter 25

- Electrophoresis 1051
- Peptide Mapping and MALDI Mass Spectrometry 1065
- Oh NO! It’s Inorganic! 1090

### Chapter 26

- “It Has Not Escaped Our Notice . . .” 1116
- mRNA Therapeutics 1125

### Chapter 27

- From Bakelite to Nylon 1139
- Conducting Polymers 1161

## Descriptive Passage and Interpretive Problems

### Chapter 1

Amide Lewis Structural Formulas 54

### Chapter 2

Some Biochemical Reactions of Alkanes 98

### Chapter 3

Cyclic Forms of Carbohydrates 135

### Chapter 4

Prochirality 171

### Chapter 5

More About Potential Energy Diagrams 210

### Chapter 6

Nucleophilic Substitution 243

### Chapter 7

A Mechanistic Preview of Addition Reactions 288

### Chapter 8

Oxymercuration 329

### Chapter 9

Thinking Mechanistically About Alkynes 356

### Chapter 10

Free-Radical Reduction of Alkyl Halides 383

### Chapter 11

1,3-Dipolar Cycloaddition 425

### Chapter 12

Substituent Effects on Reaction Rates and Equilibria 475

### Chapter 13

Benzyne 530

### Chapter 14

More on Coupling Constants 598

### Chapter 15

Allylindium Reagents 638

### Chapter 16

The Pinacol Rearrangement 674

### Chapter 17

Epoxide Rearrangements and the NIH Shift 713

### Chapter 18

The Baeyer–Villiger Oxidation 763

### Chapter 19

Lactonization Methods 799

### Chapter 20

Thioesters 851

### Chapter 21

The Knoevenagel Reaction 891

### Chapter 22

Synthetic Applications of Enamines 947

### Chapter 23

Emil Fischer and the Structure of (+)-Glucose 996

### Chapter 24

Polyketides 1036

### Chapter 25

Amino Acids in Enantioselective Synthesis 1098

### Chapter 26

Oligonucleotide Synthesis 1133

### Chapter 27

Chemically Modified Polymers 1166

# Preface

## Overview

*“There is a close analogy between organic chemistry in its relation to biochemistry and pure mathematics in its relation to physics.”*

Sir Robert Robinson

This quote from Sir Robert Robinson exemplifies two broad goals in the creation of the twelfth edition of Francis Carey’s organic chemistry textbook. We want our students to have a deeper understanding of the physical concepts that underlie organic chemistry, and we want them to have a broader knowledge of the role of organic chemistry in biological systems. The Carey team includes two new coauthors starting with the eleventh edition, Neil Allison, and Susan Bane, who have expertise in physical organic chemistry and in biochemistry. Significant changes in the areas of structure and mechanism and in bioorganic chemistry have been incorporated into the twelfth edition. These and other changes are highlighted below.

## Mechanism

The text is organized according to functional groups—structural units within a molecule that are most closely identified with characteristic properties. Reaction mechanisms are emphasized early and often in an effort to develop the student’s ability to see similarities in reactivity across the diverse range of functional groups encountered in organic chemistry. Mechanisms are developed from observations; thus, reactions are normally presented first, followed by their mechanism.

In order to maintain consistency with what our students have already learned, this text presents multistep mechanisms in the same way as most general chemistry textbooks—that is, as a series of *elementary steps*. Additionally, we provide a brief comment about how each step contributes to the overall mechanism. Section 1.11 “Curved Arrows, Arrow Pushing, and Chemical Reactions” provides the student with an early introduction to the notational system employed in all of the mechanistic discussions in the text.

Numerous reaction mechanisms are accompanied by potential energy diagrams. Section 5.8 “Reaction of Alcohols with Hydrogen Halides: The  $S_N1$  Mechanism” shows how the potential energy diagrams for three elementary steps are combined to give the diagram for the overall reaction.

## Enhanced Graphics

The teaching of organic chemistry has especially benefited as powerful modeling and graphics software has become routinely available. Computer-generated molecular models and electrostatic potential maps were integrated into the third edition of this text and their number has increased in succeeding editions; also seeing increasing use are molecular orbital theory and the role of orbital interactions in chemical reactivity.

## Coverage of Biochemical Topics

From its earliest editions, four chapters have been included on biochemical topics and updated to cover topics of recent interest.

- ▶ Chapter 23 Carbohydrates
- ▶ Chapter 24 Lipids
- ▶ Chapter 25 Amino Acids, Peptides, and Proteins
- ▶ Chapter 26 Nucleosides, Nucleotides, and Nucleic Acids



## Generous and Effective Use of Tables

Annotated summary tables have been a staple of *Organic Chemistry* since the first edition. Some tables review reactions from earlier chapters, others the reactions or concepts of a current chapter. Still other tables walk the reader step-by-step through skill builders and concepts unique to organic chemistry. Well received by students and faculty alike, these summary tables remain one of the text's strengths.

## Problems

- ▶ Problem-solving strategies and skills are emphasized throughout. Understanding is progressively reinforced by problems that appear within topic sections.
- ▶ For many problems, sample solutions are given, including examples of handwritten solutions from the authors.
- ▶ The text now contains more than 1400 problems, many of which contain multiple parts. End-of-chapter problems are now organized to conform to the primary topic areas of each chapter.

## Pedagogy

- ▶ A list of tables, mechanisms, boxed features, and Descriptive Passages and Interpretive Questions is included in the front matter as a quick reference to these important learning tools in each chapter.
- ▶ Each chapter begins with an opener that is meant to capture the reader's attention. Chemistry that is highlighted in the opener is relevant to chemistry that is included in the chapter.
- ▶ End-of-Chapter Summaries highlight and consolidate all of the important concepts and reactions within a chapter.

## Audience

*Organic Chemistry* is designed to meet the needs of the “mainstream,” two-semester undergraduate organic chemistry course. From the beginning and with each new edition, we have remained grounded in some fundamental notions. These include important issues concerning the intended audience. Is the topic appropriate for them with respect to their interests, aspirations, and experience? Just as important is the need to present an accurate picture of the present state of organic chemistry. How do we know what we know? What makes organic chemistry worth knowing? Where are we now? Where are we headed?

## Descriptive Passages and Interpretive Problems

Many organic chemistry students later take standardized pre-professional examinations composed of problems derived from a descriptive passage; this text includes comparable passages and problems to familiarize students with this testing style.

Thus, every chapter concludes with a self-contained *Descriptive Passage and Interpretive Problems* unit that complements the chapter's content while emulating the “MCAT style.” These 27 passages—listed on page xxii—are accompanied by more than 100 total multiple-choice problems.

The passages focus on a wide range of topics—from structure, synthesis, mechanism, and natural products. They provide instructors with numerous opportunities to customize their own organic chemistry course, while giving students practice in combining new information with what they have already learned.

## A Student-Focused Revision

Many updates have been made according to changing scientific data and are based on current events and reviewer feedback. The following “What's New” summary lists the more major additions and refinements.

## What's New

### General Revisions

#### Reflecting the Diverse World Around Us

McGraw Hill believes in unlocking the potential of every learner at every stage of life. To accomplish that, we are dedicated to creating products that reflect, and are accessible to, all the diverse, global customers we serve. Within McGraw Hill, we foster a culture of belonging, and we work with partners who share our commitment to equity, inclusion, and diversity in all forms. In McGraw Hill Higher Education, this includes, but is not limited to, the following:

- ▶ Refreshing and implementing inclusive content guidelines around topics including generalizations and stereotypes, gender, abilities/disabilities, race/ethnicity, sexual orientation, diversity of names, and age.
- ▶ Enhancing best practices in assessment creation to eliminate cultural, cognitive, and affective bias.
- ▶ Maintaining and continually updating a robust photo library of diverse images that reflect our student populations.
- ▶ Including more diverse voices in the development and review of our content.

Strengthening art guidelines to improve accessibility by ensuring meaningful text and images are distinguishable and perceivable by users with limited color vision and moderately low vision.

- ▶ Each trend is now set in a shadowbox with a clear title to highlight the importance of the trend and aid in student understanding. The description of the trend is placed at the bottom.
- ▶ Color has been revised for consistency in many areas to help students better understand three-dimensional structure, stereochemistry, and reactions. Reaction coordinate diagrams' rate-determining steps, as well as their protonation and deprotonation steps, have their own consistent color. Similarly, any other reaction mechanistic steps are color consistent.
- ▶ New illustrations have also been added throughout the new edition to clarify topics and enhance the student learning experience. All  $pK_a$  values were evaluated and updated.
- ▶ Integration values are now included in all proton NMR spectra starting with the Chapter 14 (Spectroscopy).

### Chapter-Specific Revisions

- ▶ In Chapter 1, Rosalind Franklin's important work that was critical in the discovery of the DNA double helix is included in the boxes essay entitled *Molecular Models and Modeling*. A new boxed essay, *Curved Arrows and "Electron Pushing,"* is included to aid in student understanding of the concept.
- ▶ In Chapter 3, new art was added, reinforcing the relative hydrogen positions in chair cyclohexane. Hydrogen and bromine values to the chair-chair interconversion table were added.
- ▶ In Chapter 4, the chirality axis section was moved to the penultimate section position. The discussion of molecules with two chirality centers now follows the discussion on enantiomers.
- ▶ In Chapter 12, the spin density of the benzyl radical has been added. Electron pushing was added into the Birch reduction (Mechanism 12.2). Lawrence Knox, a prominent African-American chemist who first reported tropylium bromide, was added.
- ▶ The orientation of art to bond-line structures was improved in Chapters 7 (*cis*-2-butene) and 13 (acylium ion).
- ▶ An improved discussion of peak integration in  $^1\text{H}$  NMR in Chapter 14 was added.
- ▶ In Chapter 17, the discussion of the stereochemistry of the reaction of epoxides with nucleophiles was improved.

- ▶ Chapter 18 reinforces molecular orbital descriptions in Chapters 7 and 11 by a discussion of the  $\pi$  molecular orbitals of the carbonyl group, while introducing the concept that a more electronegative oxygen's  $2p$  orbital is lower in energy than carbon's  $2p$  orbital.
- ▶ Chapter 20 begins with a new boxed essay emphasizing the structural reasons why reactions of nucleophiles with carboxylic acid derivatives yield substitution products compared to the addition products formed with aldehydes and ketones (Chapter 18). A second boxed essay recounts how Alice Ball, the first female and first African-American graduate and faculty member at the University of Hawai'i, converted an oily plant extract into a form that was effectively used in the treatment of Hansen's disease (leprosy).
- ▶ Lipid nanoparticles are described in the context of liposomes in Chapter 24. Lipid nanoparticles are critical to the success of mRNA vaccines.
- ▶ The importance of using relative stereochemical descriptors (D,L) rather than absolute stereochemistry descriptors (*R,S*) for amino acids is explained and emphasized early in Chapter 25.
- ▶ In Chapter 26, the recent success of oligonucleotide-based drugs is highlighted in a new boxed essay entitled *mRNA Therapeutics*. Discussion of topics such as DNA sequencing has been updated to encompass next-generation sequencing, and outdated material was removed.

## Instructor Resources



**ALEKS (Assessment and Learning in Knowledge Spaces)** is a web-based system for individualized assessment and learning available 24/7 over the Internet. ALEKS uses artificial intelligence to accurately determine a student's knowledge and then guides them to the material that they are most ready to learn. ALEKS offers immediate feedback and access to ALEKSPedia—an interactive text that contains concise entries on chemistry topics. ALEKS is also a full-featured course management system with rich reporting features that allow instructors to monitor individual and class performance, set student goals, assign/grade online quizzes, and more. ALEKS allows instructors to spend more time on concepts while ALEKS teaches students practical problem-solving skills. And with ALEKS 360, your student also has access to this text's eBook. Learn more at [www.aleks.com/highered/science](http://www.aleks.com/highered/science)



**McGraw Hill Virtual Labs** is a must-see, outcomes-based lab simulation. It assesses a student's knowledge and adaptively corrects deficiencies, allowing the student to learn faster and retain more knowledge with greater success. First, a student's knowledge is adaptively leveled on core learning outcomes: Questioning reveals knowledge deficiencies that are corrected by the delivery of content that is conditional on a student's response. Then, a simulated lab experience requires the student to think and act like a scientist:

recording, interpreting, and analyzing data using simulated equipment found in labs and clinics. The student is allowed to make mistakes—a powerful part of the learning experience! A virtual coach provides subtle hints when needed, asks questions about the student's choices, and allows the student to reflect on and correct those mistakes. Whether your need is to overcome the logistical challenges of a traditional lab, provide better lab prep, improve student performance, or make your online experience one that rivals the real world, McGraw Hill Virtual Labs accomplishes it all.

Instructors have access to the following instructor resources:

## Presentation Tools

Accessed from the Instructor Resources, Presentation Tools contains photos, artwork, and accessible Lecture PowerPoints that can be used to create customized lectures, visually enhanced tests and quizzes, compelling course websites, or attractive printed support materials. All assets are copyrighted by McGraw Hill Higher Education, but can be used by instructors for classroom purposes. The visual resources in this collection include:

- ▶ **Art** Full-color digital files of all illustrations in the book can be readily incorporated into lecture presentations, exams, or custom-made classroom materials. In addition, all files are pre-inserted into PowerPoint slides for ease of lecture preparation.
- ▶ **Photos** The photo collection contains digital files of photographs from the text, which can be reproduced for multiple classroom uses.
- ▶ **Accessible PowerPoint® Lecture Outlines** Ready-made presentations that combine art and lecture notes are provided for each chapter of the text.

Also accessed through your textbook's Instructor Resources are:

- ▶ **Classroom Response System Questions** (Clicker Questions) Nearly 600 questions covering the content of the *Organic Chemistry* text are available on the *Organic Chemistry* site for use with any classroom response system.
- ▶ **Captioned Videos** Closed-captioned videos covering the most important topics for *Organic Chemistry* are provided.

## Test Bank

A test bank with over 1300 questions is available with the twelfth edition. The Test Bank is available in the TestGen test-generating software to quickly create customized exams.

## Student Resources

### Solutions Manual

The Student Solutions Manual provides step-by-step solutions guiding the student through the reasoning behind each problem in the text. There is also a self-test section at the end of each chapter that is designed to assess the student's mastery of the material.

### Schaum's Outline of Organic Chemistry

This helpful study aid provides students with hundreds of solved and supplementary problems for the organic chemistry course.

## Create

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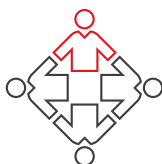


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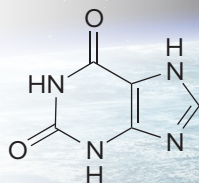
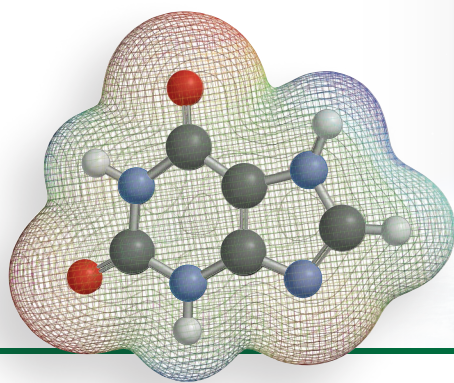
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# Organic Chemistry





## CHAPTER OUTLINE

- 1.1 Atoms, Electrons, and Orbitals 3
  - Organic Chemistry: The Early Days 5
- 1.2 Ionic Bonds 6
- 1.3 Covalent Bonds, Lewis Formulas, and the Octet Rule 8
- 1.4 Polar Covalent Bonds, Electronegativity, and Bond Dipoles 10
  - Electrostatic Potential Maps 12
- 1.5 Formal Charge 13
- 1.6 Structural Formulas of Organic Molecules: Isomers 16
  - Curved Arrows and “Electron Pushing” 20
- 1.7 Resonance and Arrows 21
- 1.8 Sulfur and Phosphorus-Containing Organic Compounds and the Octet Rule 25
- 1.9 Molecular Geometries 26
  - Molecular Models and Modeling 28
- 1.10 Molecular Dipole Moments 29
- 1.11 Curved Arrows, Arrow Pushing, and Chemical Reactions 30
- 1.12 Acids and Bases: The Brønsted–Lowry View 32
- 1.13 How Structure Affects Acid Strength 37
- 1.14 Acid–Base Equilibria 42
- 1.15 Acids and Bases: The Lewis View 45
- 1.16 Summary 46
- Problems 49
- Descriptive Passage and Interpretive Problems 1: Amide Lewis Structural Formulas 54

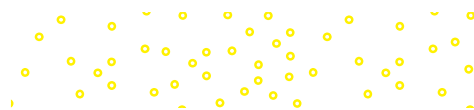
A class of meteors that strikes our planet is classified as “carbonaceous.” They bring organic compounds with them—even compounds as complicated as the DNA base xanthine.

PaulFleet/iStock/Getty Images

## Structure Determines Properties

Chemists like to call their discipline “The Central Science” because of its relationship to physics on one side and biology on the other. In the same way, among the various subdisciplines of chemistry, organic chemistry can be said to be central. It adapts the physical principles that underlie the content of general chemistry courses to the relationships between structure and properties of compounds based on carbon—the most versatile of all the elements.

This chapter begins your training toward understanding the relationship between structure and properties by reviewing the fundamentals of the Lewis approach to molecular structure and bonding and describes the various graphical ways molecular structures are presented. Principles of acid–base chemistry—emphasized in a quantitative way in introductory chemistry courses—are revisited qualitatively as a tool for introducing the effect of structure on properties. This structure/property relationship is what makes organic chemistry important. The same atom (carbon) is common to many structural types, countless compounds with different properties, and much variation in the degree to which a particular property is expressed. What is equally remarkable is the degree to which a relatively small group of principles suffice to connect the structure of a substance to its properties.



## 1.1 Atoms, Electrons, and Orbitals

Before discussing structure and bonding in *molecules*, let's first review some fundamentals of *atomic* structure. Each element is characterized by a unique **atomic number  $Z$** ,\* which is equal to the number of protons in its nucleus. A neutral atom has equal numbers of protons, which are positively charged, and electrons, which are negatively charged.

Electrons were believed to be particles from the time of their discovery in 1897 until 1924, when the French physicist Louis de Broglie suggested that they have wavelike properties as well. Two years later Erwin Schrödinger took the next step and calculated the energy of an electron in a hydrogen atom by using equations that treated the electron as if it were a wave. Instead of a single energy, Schrödinger obtained a series of energies, each of which corresponded to a different mathematical description of the electron wave. These mathematical descriptions are called **wave functions** and are symbolized by the Greek letter  $\psi$  (psi).

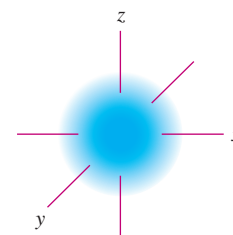
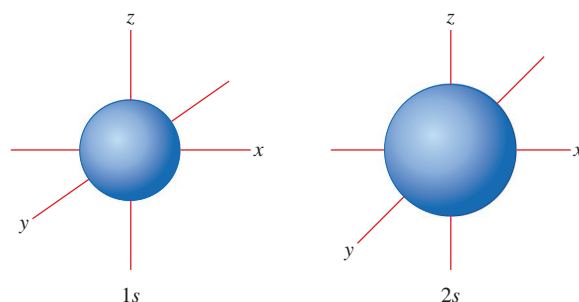
According to the Heisenberg uncertainty principle, we can't tell exactly where an electron is, but we can tell where it is most likely to be. The probability of finding an electron at a particular spot relative to an atom's nucleus is given by the square of the wave function ( $\psi^2$ ) at that point. Figure 1.1 illustrates the probability of finding an electron at various points in the lowest energy (most stable) state of a hydrogen atom. The darker the color in a region, the higher the probability. The probability of finding an electron at a particular point is greatest near the nucleus and decreases with increasing distance from the nucleus but never becomes zero.

Wave functions are also called **orbitals**. For convenience, chemists use the term "orbital" in several different ways. A drawing such as Figure 1.1 is often said to represent an orbital. We will see other kinds of drawings in this chapter, and use the word "orbital" to describe them too.

Orbitals are described by specifying their size, shape, and directional properties. Spherically symmetrical ones such as shown in Figure 1.1 are called *s orbitals*. The letter *s* is preceded by the **principal quantum number  $n$**  ( $n = 1, 2, 3$ , etc.), which specifies the **shell** and is related to the energy of the orbital. An electron in a *1s* orbital is likely to be found closer to the nucleus, is lower in energy, and is more strongly held than an electron in a *2s* orbital.

Instead of probability distributions, it is more common to represent orbitals by their **boundary surfaces**, as shown in Figure 1.2 for the *1s* and *2s* orbitals. The region enclosed by a boundary surface is arbitrary but is customarily the volume where the probability of finding an electron is high—on the order of 90–95%. Like the probability distribution plot from which it is derived, a picture of a boundary surface is usually described as a drawing of an orbital.

A hydrogen atom ( $Z = 1$ ) has one electron; a helium atom ( $Z = 2$ ) has two. The single electron of hydrogen occupies a *1s* orbital, as do the two electrons of helium. We write their electron configurations as



**Figure 1.1**

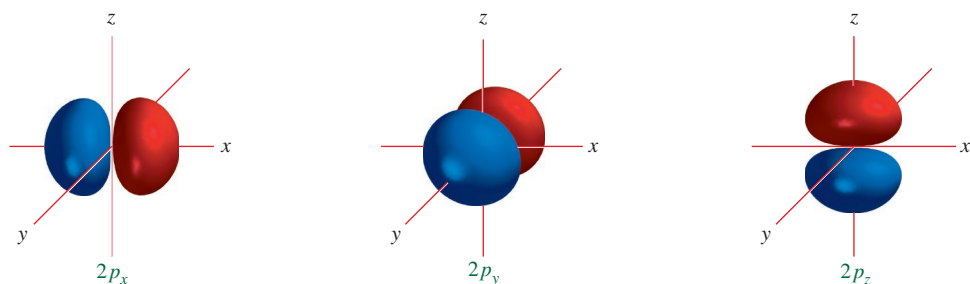
Probability distribution ( $\psi^2$ ) for an electron in a *1s* orbital.

**Figure 1.2**

Boundary surfaces of a *1s* orbital and a *2s* orbital.

\*A glossary of the terms shown in boldface may be found immediately before the index at the back of the book.

Other methods are also used to contrast the regions of an orbital where the signs of the wave function are different. Some mark one lobe of a  $p$  orbital + and the other -. Others shade one lobe and leave the other blank. When this level of detail isn't necessary, no differentiation is made between the two lobes.



**Figure 1.3**

Boundary surfaces of the  $2p$  orbitals. The wave function changes sign at the nucleus. The two halves of each orbital are indicated by different colors. The  $yz$ -plane is a nodal surface for the  $2p_x$  orbital. The probability of finding a  $2p_x$  electron in the  $yz$ -plane is zero. Analogously, the  $xz$ -plane is a nodal surface for the  $2p_y$  orbital, and the  $xy$ -plane is a nodal surface for the  $2p_z$  orbital.

In addition to being negatively charged, electrons possess the property of **spin**. The **spin quantum number** of an electron can have a value of either  $+\frac{1}{2}$  or  $-\frac{1}{2}$ . According to the **Pauli exclusion principle**, two electrons may occupy the same orbital only when they have opposite, or “paired,” spins. For this reason, no orbital can contain more than two electrons. Because two electrons fill the  $1s$  orbital, the third electron in lithium ( $Z = 3$ ) must occupy an orbital of higher energy. After  $1s$ , the next higher energy orbital is  $2s$ . The third electron in lithium therefore occupies the  $2s$  orbital, and the electron configuration of lithium is



A complete periodic table of the elements is presented at the back of the book.

The **period** (or **row**) of the periodic table in which an element appears corresponds to the principal quantum number of the highest numbered occupied orbital ( $n = 1$  in the case of hydrogen and helium). Hydrogen and helium are first-row elements; lithium ( $n = 2$ ) is a second-row element.

With beryllium ( $Z = 4$ ), the  $2s$  level becomes filled and, beginning with boron ( $Z = 5$ ), the next orbitals to be occupied are  $2p_x$ ,  $2p_y$ , and  $2p_z$ . These three orbitals (Figure 1.3) are of equal energy and are characterized by boundary surfaces that are usually described as “dumbbell-shaped.” The axes of the three  $2p$  orbitals are at right angles to one another. Each orbital consists of two “lobes,” represented in Figure 1.3 by regions of different colors. Regions of a single orbital, in this case, each  $2p$  orbital, may be separated by **nodal surfaces** where the wave function changes sign and the probability of finding an electron is zero.

The electron configurations of the first 12 elements, hydrogen through magnesium, are given in Table 1.1. In filling the  $2p$  orbitals, notice that each is singly occupied before any one is doubly occupied. This general principle for orbitals of equal energy is known as **Hund’s rule**. Of particular importance in Table 1.1 are *hydrogen*, *carbon*, *nitrogen*, and *oxygen*. Countless organic compounds contain nitrogen, oxygen, or both in addition to carbon, the essential element of organic chemistry. Most of them also contain hydrogen.

It is often convenient to speak of the **valence electrons** of an atom. These are the outermost electrons, the ones most likely to be involved in chemical bonding and reactions. For second-row elements these are the  $2s$  and  $2p$  electrons. Because four orbitals ( $2s$ ,  $2p_x$ ,  $2p_y$ ,  $2p_z$ ) are involved, the maximum number of electrons in the **valence shell** of any second-row element is 8. Neon, with all its  $2s$  and  $2p$  orbitals doubly occupied, has eight valence electrons and completes the second row of the periodic table. For **main-group elements**, the number of valence electrons is equal to its group number in the periodic table.

Detailed solutions to all of the problems are found in the *Student Solutions Manual* along with a brief discussion and advice on how to do problems of the same type.

### Problem 11

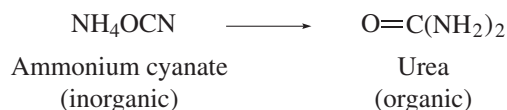
How many electrons does carbon have? How many are valence electrons? What third-row element has the same number of valence electrons as carbon?

## Organic Chemistry: The Early Days

**E**ighteenth-century chemists regarded their science as being composed of two branches. One dealt with substances obtained from natural or living sources and was called *organic chemistry*; the other dealt with materials from nonliving matter—minerals and the like—and was called *inorganic chemistry*. Over time, combustion analysis established that the compounds derived from natural sources contained carbon, and a new definition of organic chemistry emerged: *Organic chemistry is the study of carbon compounds*. This is the definition we still use today.

As the eighteenth century gave way to the nineteenth, many scientists still subscribed to a doctrine known as *vitalism*, which held that living systems possessed a “vital force” that was absent in nonliving systems. Substances derived from natural sources (*organic*) were thought to be fundamentally different from *inorganic* ones. It was believed that *inorganic* compounds could be synthesized in the laboratory, but *organic* compounds could not—at least not from *inorganic* materials.

In 1823, Friedrich Wöhler, after completing medical studies in Germany, spent a year in Stockholm studying under one of the world’s foremost chemists of the time, Jöns Jacob Berzelius. Wöhler subsequently went on to have a distinguished independent career, spending most of it at the University of Göttingen. Wöhler is best remembered for a brief paper published in 1828 in which it was noted that, on evaporating an aqueous solution of ammonium cyanate, he obtained “colorless, clear crystals often more than an inch long,” which were not ammonium cyanate but were instead urea.



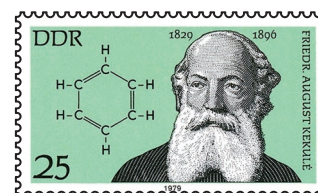
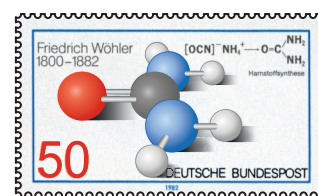
This transformation was remarkable at the time because an *inorganic* salt, ammonium cyanate, was converted to urea, a known *organic* substance earlier isolated from urine. It is now recognized as a significant early step toward overturning the philosophy of vitalism. Although Wöhler made no extravagant claims concerning the relationship of his discovery to vitalist theory, the die was cast, and over the next generation organic chemistry outgrew vitalism. What particularly seemed to excite Wöhler and Berzelius had very little to do with vitalism. Berzelius was interested in cases in which two clearly different materials had the same elemental composition, and thus invented the word *isomers* to apply to them. Wöhler’s observation that an

*inorganic* compound (ammonium cyanate) of molecular formula  $\text{CH}_4\text{N}_2\text{O}$  could be transformed into an *organic* compound (urea) of the same molecular formula had an important bearing on the concept of isomerism.

From the concept of isomerism, we can trace the origins of the *structural theory*—the idea that a specific arrangement of atoms uniquely defines a substance. Ammonium cyanate and urea are different compounds because they have different structures.

Three mid-nineteenth-century scientists, August Kekulé, Archibald S. Couper, and Alexander M. Butlerov, stand out for separately proposing the elements of the structural theory. The essential features of Kekulé’s theory, developed and presented while he taught at Heidelberg in 1858, were that carbon normally formed four bonds and had the capacity to bond to other carbons to form long chains. Isomers were possible because the same elemental composition (say, the  $\text{CH}_4\text{N}_2\text{O}$  molecular formula common to both ammonium cyanate and urea) accommodates more than one pattern of atoms and bonds. Shortly after that, Couper, a Scot working at the École de Médecine in Paris, and Butlerov, a Russian chemist at the University of Kazan, proposed similar theories.

In the late nineteenth and early twentieth centuries, major discoveries about atoms and electrons placed theories of molecular structure and bonding on a more secure, physics-based foundation. Several of these are described at the beginning of this section.



(Left & top right): David Tietz/Editorial Image, LLC; (bottom right): PjrStamps/Alamy Stock Photo

Once the  $2s$  and  $2p$  orbitals are filled, the next level is the  $3s$ , followed by the  $3p_x$ ,  $3p_y$ , and  $3p_z$  orbitals. Electrons in these orbitals are farther from the nucleus than those in the  $2s$  and  $2p$  orbitals and are of higher energy.

### Problem 1.2

Referring to the periodic table as needed, write electron configurations for all the elements in the third period.

**Sample Solution** The third period begins with sodium and ends with argon. The atomic number  $Z$  of sodium is 11, and so a sodium atom has 11 electrons. The maximum number of electrons in the  $1s$ ,  $2s$ , and  $2p$  orbitals is ten, and so the eleventh electron of sodium occupies a  $3s$  orbital. The electron configuration of sodium is  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^1$ .

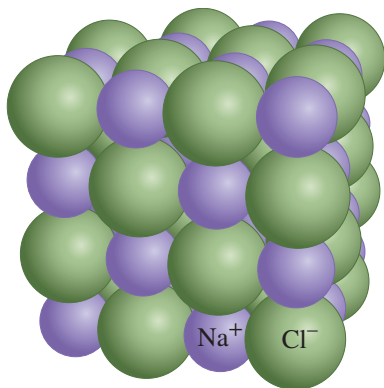
In-chapter problems that contain multiple parts are accompanied by a sample solution to part (a).

**TABLE 1.1** Electron Configurations of the First Twelve Elements of the Periodic Table

Element	Atomic number $Z$	Number of electrons in indicated orbital					
		1s	2s	2p <sub>x</sub>	2p <sub>y</sub>	2p <sub>z</sub>	3s
Hydrogen	1	1					
Helium	2	2					
Lithium	3	2	1				
Beryllium	4	2	2				
Boron	5	2	2	1			
Carbon	6	2	2	1	1		
Nitrogen	7	2	2	1	1	1	
Oxygen	8	2	2	2	1	1	
Fluorine	9	2	2	2	2	1	
Neon	10	2	2	2	2	2	
Sodium	11	2	2	2	2	2	1
Magnesium	12	2	2	2	2	2	2

Neon, in the second period, and argon, in the third, have eight electrons in their valence shell; they are said to have a complete **octet** of electrons. Helium, neon, and argon belong to the class of elements known as **noble gases** or **rare gases**. The noble gases are characterized by an extremely stable “closed-shell” electron configuration and are very unreactive.

*Structure determines properties* and the properties of atoms depend on atomic structure. All of an element’s protons are in its nucleus, but the element’s electrons are distributed among orbitals of various energy and distance from the nucleus. More than anything else, we look at its electron configuration when we wish to understand how an element behaves. Section 1.2 illustrates this with a brief review of ionic bonding.

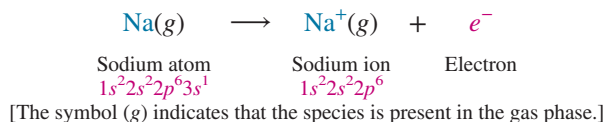
**Figure 1.4**

An ionic bond is the force of attraction between oppositely charged ions. Each  $\text{Na}^+$  ion in the crystal lattice of solid  $\text{NaCl}$  is involved in ionic bonding to each of six surrounding  $\text{Cl}^-$  ions and vice versa. The smaller spheres are  $\text{Na}^+$  and the larger spheres are  $\text{Cl}^-$ .

## 1.2 Ionic Bonds

Atoms combine with one another to give **compounds** having properties different from the atoms they contain. The attractive force between atoms in a compound is a **chemical bond**. One type of chemical bond, called an **ionic bond**, is the force of attraction between oppositely charged species (**ions**) (Figure 1.4). Positively charged ions are referred to as **cations**; negatively charged ions are **anions**.

Whether an element is the source of the cation or anion in an ionic bond depends on several factors, for which the periodic table can serve as a guide. In forming ionic compounds, elements at the left of the periodic table typically lose electrons, giving a cation that has the same electron configuration as the preceding noble gas. Loss of an electron from sodium, for example, yields  $\text{Na}^+$ , which has the same electron configuration as neon.

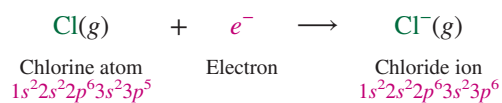


### Problem 1.3

Species that have the same number of electrons are described as *isoelectronic*. What +2 ion is isoelectronic with Na<sup>+</sup>? What -2 ion?

A large amount of energy, called the **ionization energy**, must be transferred to any atom to dislodge an electron. The ionization energy of sodium, for example, is 496 kJ/mol (119 kcal/mol). Processes that absorb energy are said to be **endothermic**. Compared with other elements, sodium and its relatives in group 1A have relatively low ionization energies. In general, ionization energy increases across a row in the periodic table.

Elements at the right of the periodic table tend to gain electrons to reach the electron configuration of the next higher noble gas. Adding an electron to chlorine, for example, gives the anion Cl<sup>-</sup>, which has the same closed-shell electron configuration as the noble gas argon.



The SI (*Système International d'Unités*) unit of energy is the *joule* (J). An older unit is the *calorie* (cal). Many chemists still express energy changes in units of kilocalories per mole (1 kcal/mol = 4.184 kJ/mol).

### Problem 1.4

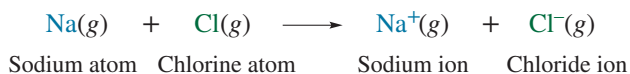
Which of the following ions possess a noble gas electron configuration?

- |                     |                    |                      |
|---------------------|--------------------|----------------------|
| (a) K <sup>+</sup>  | (c) H <sup>-</sup> | (e) F <sup>-</sup>   |
| (b) He <sup>+</sup> | (d) O <sup>-</sup> | (f) Ca <sup>2+</sup> |

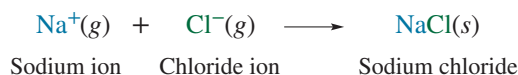
**Sample Solution** (a) Potassium has atomic number 19, and so a potassium atom has 19 electrons. The ion K<sup>+</sup>, therefore, has 18 electrons, the same as the noble gas argon. The electron configurations of both K<sup>+</sup> and Ar are 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>.

Energy is released when a chlorine atom captures an electron. Energy-releasing reactions are described as **exothermic**, and the energy change for an exothermic process has a negative sign. The energy change for addition of an electron to an atom is referred to as its **electron affinity** and is -349 kJ/mol (-83.4 kcal/mol) for chlorine.

We can use the ionization energy of sodium and the electron affinity of chlorine to calculate the energy change for the reaction:



Were we to simply add the ionization energy of 496 kJ/mol (119 kcal/mol) for sodium and the electron affinity of -349 kJ/mol (-83.4 kcal/mol) for chlorine, we would conclude that the overall process is endothermic by +147 kJ/mol (+35 kcal/mol). The energy liberated by adding an electron to chlorine is insufficient to override the energy required to remove an electron from sodium. This analysis, however, fails to consider the force of attraction between the oppositely charged ions Na<sup>+</sup> and Cl<sup>-</sup>, as expressed in terms of the energy released in the formation of solid NaCl from the separated gas-phase ions:



This *lattice energy* is 787 kJ/mol (188 kcal/mol) and is more than sufficient to make the overall process for formation of sodium chloride from the elements exothermic. Forces between charged particles are called **electrostatic**, or **Coulombic**, and constitute an ionic bond when they are attractive.

Ionic bonding was proposed by the German physicist Walther Kossel in 1916 in order to explain the ability of substances such as molten sodium chloride to conduct an electric current. Walther Kossel was the son of Albrecht Kossel, winner of the 1910 Nobel Prize in Physiology or Medicine for early studies of nucleic acids.

### Problem 1.5

What is the electron configuration of  $C^+$ ? Of  $C^-$ ? Does either one of these ions have a noble gas (closed-shell) electron configuration?

Ionic bonds are very common in *inorganic* compounds, but rare in *organic* ones. The ionization energy of carbon is too large and the electron affinity too small for carbon to realistically form a  $C^{4+}$  or  $C^{4-}$  ion. What kinds of bonds, then, link carbon to other elements in millions of organic compounds? Instead of losing or gaining electrons, carbon *shares* electrons with other elements (including other carbon atoms) to give what are called covalent bonds.

## 1.3 Covalent Bonds, Lewis Formulas, and the Octet Rule

The **covalent**, or **shared electron pair**, model of chemical bonding was first suggested by G. N. Lewis of the University of California in 1916. Lewis proposed that a *sharing* of two electrons by two hydrogen atoms permits each one to have a stable closed-shell electron configuration analogous to that of helium.



Two hydrogen atoms,  
each with a single  
electron



Hydrogen molecule:  
covalent bonding by way of  
a shared electron pair

The amount of energy required to dissociate a hydrogen molecule  $H_2$  to two separate hydrogen atoms is its **bond dissociation enthalpy**. For  $H_2$  it is quite large, amounting to +435 kJ/mol (+104 kcal/mol). The main contributor to the strength of the covalent bond in  $H_2$  is the increased Coulombic force exerted on its two electrons. Each electron in  $H_2$  “feels” the attractive force of two nuclei, rather than one as it would in an isolated hydrogen atom.

Only the electrons in an atom’s valence shell are involved in covalent bonding. Fluorine, for example, has nine electrons, but only seven are in its valence shell. Pairing a valence electron of one fluorine atom with one of a second fluorine gives a fluorine molecule ( $F_2$ ) in which each fluorine has eight valence electrons and an electron configuration equivalent to that of the noble gas neon. Shared electrons count toward satisfying the octet of both atoms.



Two fluorine atoms, each  
with seven electrons in  
its valence shell



Fluorine molecule:  
covalent bonding by way of  
a shared electron pair

The six valence electrons of each fluorine that are not involved in bonding comprise three **unshared pairs**.

Structural formulas such as those just shown for  $H_2$  and  $F_2$  where electrons are represented as dots are called **Lewis formulas**, or **Lewis structures**. It is usually more convenient to represent shared electron-pair bonds as lines and to sometimes omit electron pairs.

The Lewis model limits second-row elements (Li, Be, B, C, N, O, F, Ne) to a total of eight electrons (shared plus unshared) in their valence shells. Hydrogen is limited to two. Most of the elements that we’ll encounter in this text obey the **octet rule**: *In forming compounds they gain, lose, or share electrons to achieve a stable electron configuration characterized by eight valence electrons*. When the octet rule is satisfied for carbon, nitrogen, oxygen, and fluorine, each has an electron configuration analogous to that of the noble gas neon. The Lewis formulas of methane ( $CH_4$ ), ammonia ( $NH_3$ ), water ( $H_2O$ ), and hydrogen fluoride (HF) given in Table 1.2 illustrate the octet rule.

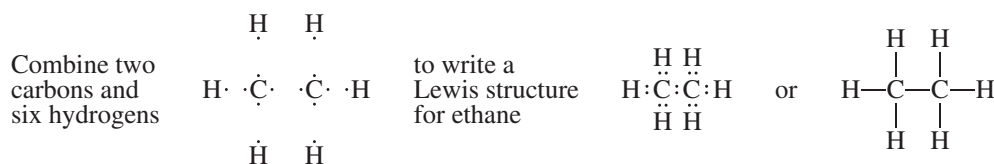
Gilbert Newton Lewis has been called the greatest American chemist.

Unshared pairs are also called *lone pairs*.

**TABLE 1.2** Lewis Formulas of Methane, Ammonia, Water, and Hydrogen Fluoride

Compound	Atom	Number of valence electrons in atom	Atom and sufficient number of hydrogen atoms to complete octet	Lewis formula	
				Dot	Line
Methane	Carbon	4	$\begin{array}{c} \text{H} \\ \cdot \\ \text{H} \cdot \text{C} \cdot \text{H} \\ \cdot \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \vdots \\ \text{H} : \text{C} : \text{H} \\ \vdots \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$
Ammonia	Nitrogen	5	$\begin{array}{c} \text{H} \\ \cdot \\ \text{H} \cdot \text{N} \cdot \text{H} \\ \cdot \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \vdots \\ \text{H} : \text{N} : \text{H} \\ \vdots \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{N}-\text{H} \\   \\ \text{H} \end{array}$
Water	Oxygen	6	$\text{H} \cdot \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} \cdot \text{H}$	$\text{H} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} : \text{H}$	$\text{H}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}-\text{H}$
Hydrogen fluoride	Fluorine	7	$\text{H} \cdot \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}} \cdot$	$\text{H} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}} \cdot$	$\text{H}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}} \cdot$

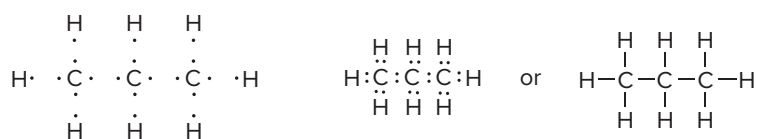
With four valence electrons, carbon normally forms four covalent bonds as shown in Table 1.2 for  $\text{CH}_4$ . In addition to C—H bonds, most organic compounds contain covalent C—C bonds. Ethane ( $\text{C}_2\text{H}_6$ ) is an example.

**Problem 1.6**

Write Lewis formulas, including unshared pairs, for each of the following. Carbon has four bonds in each compound.

- (a) Propane ( $\text{C}_3\text{H}_8$ )                      (c) Methyl fluoride ( $\text{CH}_3\text{F}$ )  
 (b) Methanol ( $\text{CH}_4\text{O}$ )                      (d) Ethyl fluoride ( $\text{C}_2\text{H}_5\text{F}$ )

**Sample Solution** (a) The Lewis formula of propane is analogous to that of ethane but the chain has three carbons instead of two.



Combine three carbons and eight hydrogens

to write a Lewis formula for propane

The ten covalent bonds in the Lewis formula shown account for 20 valence electrons, which is the same as that calculated from the molecular formula ( $\text{C}_3\text{H}_8$ ). The eight hydrogens of  $\text{C}_3\text{H}_8$  contribute 1 electron each and the three carbons 4 each, for a total of 20 (8 from the hydrogens and 12 from the carbons). Therefore, all the valence electrons are in covalent bonds; propane has no unshared pairs.

Lewis's concept of shared electron-pair bonds allows for four-electron double bonds and six-electron triple bonds. Ethylene ( $\text{C}_2\text{H}_4$ ) has 12 valence electrons, which can be distributed as follows: