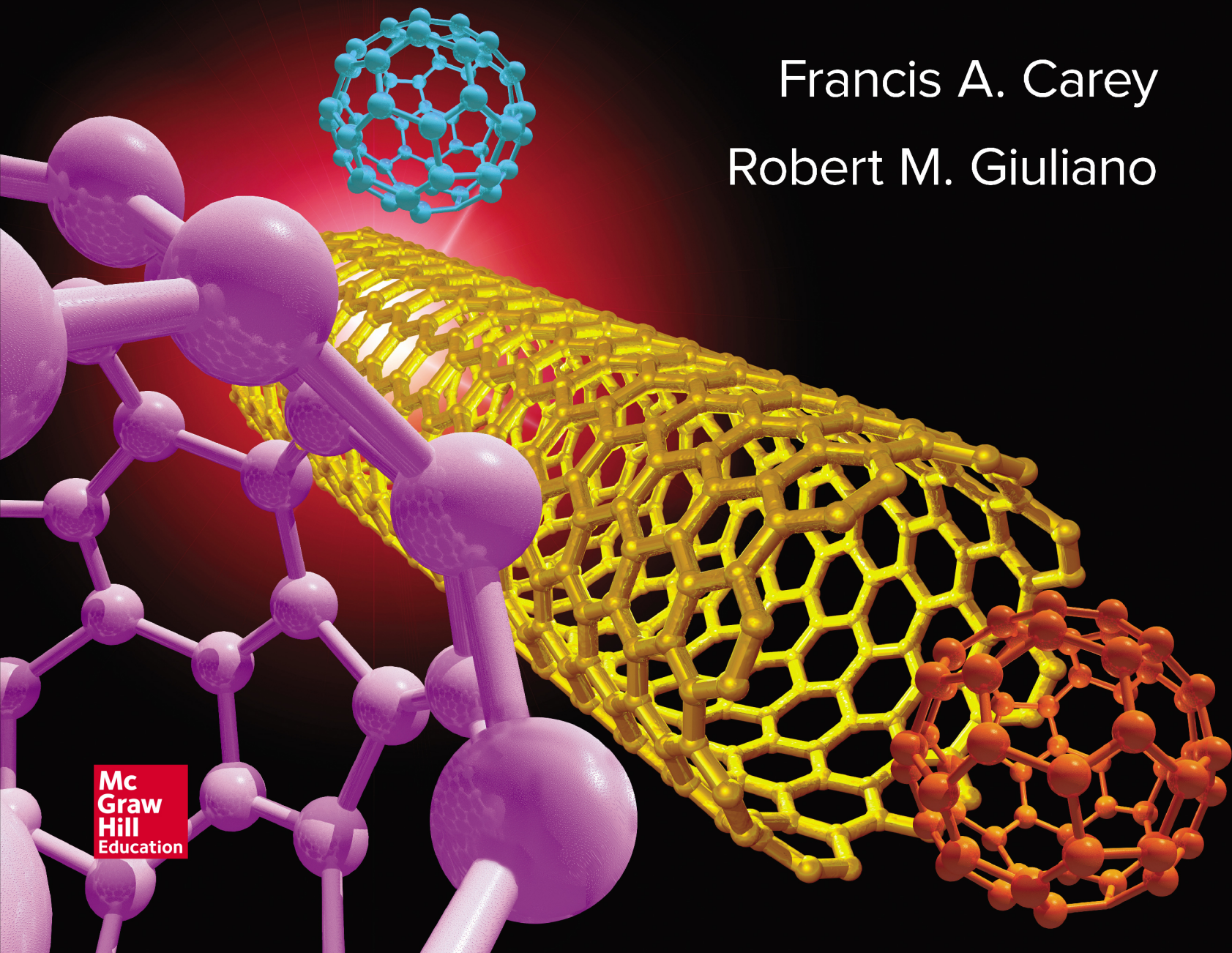


# ORGANIC Chemistry

Tenth Edition

Francis A. Carey  
Robert M. Giuliano



Mc  
Graw  
Hill  
Education

# Organic Chemistry

TENTH EDITION

**Francis A. Carey**

University of Virginia

**Robert M. Giuliano**

Villanova University

**Mc  
Graw  
Hill**  
Education



ORGANIC CHEMISTRY, TENTH EDITION

Published by McGraw-Hill Education, 2 Penn Plaza, New York, NY 10121. Copyright © 2017 by McGraw-Hill Education. All rights reserved. Printed in the United States of America. Previous editions © 2014, 2011, and 2008. No part of this publication may be reproduced or distributed in any form or by any means, or stored in a database or retrieval system, without the prior written consent of McGraw-Hill Education, including, but not limited to, in any network or other electronic storage or transmission, or broadcast for distance learning.

Some ancillaries, including electronic and print components, may not be available to customers outside the United States.

This book is printed on acid-free paper.

1 2 3 4 5 6 7 8 9 0 DOW/DOW 1 0 9 8 7 6

ISBN 978-0-07-351121-4

MHID 0-07-351121-8

Senior Vice President, Products & Markets: *Kurt L. Strand*  
Vice President, General Manager, Products & Markets: *Marty Lange*  
Vice President, Content Design & Delivery: *Kimberly Meriwether David*  
Managing Director: *Thomas Timp*  
Director: *David Spurgeon, Ph.D.*  
Brand Manager: *Andrea M. Pellerito, Ph.D.*  
Director, Product Development: *Rose Koos*  
Product Developer: *Michael R. Ivanov, Ph.D.*  
Marketing Director: *Tammy Hodge*  
Marketing Manager: *Matthew Garcia*  
Director, Content Design & Delivery: *Linda Avenarius*  
Program Manager: *Lora Neyens*  
Content Project Managers: *Laura Bies, Tammy Juran, & Sandy Schnee*  
Buyer: *Sandy Ludovissy*  
Design: *David Hash*  
Content Licensing Specialists: *Ann Marie Jannette & DeAnna Dausener*  
Cover Image: *Fullerene technology* © *Victor Habbick Visions / Science Source*  
Compositor: *Lumina Datamatics, Inc.*  
Printer: *R. R. Donnelley*

All credits appearing on page or at the end of the book are considered to be an extension of the copyright page.

Library of Congress Cataloging-in-Publication Data

Carey, Francis A., 1937-

Organic chemistry / Francis A. Carey, University of Virginia, Robert M. Giuliano, Villanova University. -- Tenth edition.

pages cm

Includes index.

ISBN 978-0-07-351121-4 (alk. paper)

1. Chemistry, Organic. I. Giuliano, Robert M., 1954- II. Title.

QD251.3.C37 2016

547--dc23

2015027007

The Internet addresses listed in the text were accurate at the time of publication. The inclusion of a website does not indicate an endorsement by the authors or McGraw-Hill Education, and McGraw-Hill Education does not guarantee the accuracy of the information presented at these sites.

Each of the ten editions of this text has benefited from the individual and collective contributions of the staff at McGraw-Hill. They are the ones who make it all possible. We appreciate their professionalism and thank them for their continuing support.

This page intentionally left blank

# About the Authors

Before **Frank Carey** retired in 2000, his career teaching chemistry was spent entirely at the University of Virginia.

In addition to this text, he is coauthor (with Robert C. Atkins) of *Organic Chemistry: A Brief Course* and (with Richard J. Sundberg) of *Advanced Organic Chemistry*, a two-volume treatment designed for graduate students and advanced undergraduates.

Frank and his wife Jill are the parents of Andy, Bob, and Bill and the grandparents of Riyad, Ava, Juliana, Miles, Wynne, and Michael.

**Robert M. Giuliano** was born in Altoona, Pennsylvania, and attended Penn State (B.S. in chemistry) and the University of Virginia (Ph.D., under the direction of Francis Carey). Following postdoctoral studies with Bert Fraser-Reid at the University of Maryland, he joined the chemistry department faculty of Villanova University in 1982, where he is currently Professor. His research interests are in synthetic organic and carbohydrate chemistry, and in functionalized carbon nanomaterials.

Bob and his wife Margot, an elementary and preschool teacher he met while attending UVa, are the parents of Michael, Ellen, and Christopher and grandparents of Carina, Aurelia, and Serafina.

# Brief Contents

List of Important Features	xvi
Preface	xx
Acknowledgements	xxix
<b>1</b> Structure Determines Properties	2
<b>2</b> Alkanes and Cycloalkanes: Introduction to Hydrocarbons	52
<b>3</b> Alkanes and Cycloalkanes: Conformations and cis–trans Stereoisomers	94
<b>4</b> Chirality	130
<b>5</b> Alcohols and Alkyl Halides: Introduction to Reaction Mechanisms	168
<b>6</b> Nucleophilic Substitution	206
<b>7</b> Structure and Preparation of Alkenes: Elimination Reactions	238
<b>8</b> Addition Reactions of Alkenes	280
<b>9</b> Alkynes	322
<b>10</b> Introduction to Free Radicals	348
<b>11</b> Conjugation in Alkadienes and Allylic Systems	376
<b>12</b> Arenes and Aromaticity	414
<b>13</b> Electrophilic and Nucleophilic Aromatic Substitution	464
<b>14</b> Spectroscopy	518
<b>15</b> Organometallic Compounds	584
<b>16</b> Alcohols, Diols, and Thiols	620
<b>17</b> Ethers, Epoxides, and Sulfides	656
<b>18</b> Aldehydes and Ketones: Nucleophilic Addition to the Carbonyl Group	692
<b>19</b> Carboxylic Acids	742
<b>20</b> Carboxylic Acid Derivatives: Nucleophilic Acyl Substitution	776
<b>21</b> Enols and Enolates	826
<b>22</b> Amines	864
<b>23</b> Phenols	920
<b>24</b> Carbohydrates	950
<b>25</b> Lipids	996
<b>26</b> Amino Acids, Peptides, and Proteins	1034
<b>27</b> Nucleosides, Nucleotides, and Nucleic Acids	1088
<b>28</b> Synthetic Polymers	1126
<b>Glossary</b>	<b>G-1</b>
<b>Credits</b>	<b>C-1</b>
<b>Index</b>	<b>I-1</b>



# Contents

List of Important Features	xvi
Preface	xx
Acknowledgements	xxix

## CHAPTER 1

### Structure Determines Properties 2

1.1	Atoms, Electrons, and Orbitals	2
	<b>Organic Chemistry: The Early Days</b>	<b>3</b>
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
	<b>Electrostatic Potential Maps</b>	<b>13</b>
1.5	Formal Charge	13
1.6	Structural Formulas of Organic Molecules: Isomers	15
1.7	Resonance and Curved Arrows	19
1.8	Sulfur and Phosphorus-Containing Organic Compounds and the Octet Rule	23
1.9	Molecular Geometries	24
	<b>Molecular Models and Modeling</b>	<b>26</b>
1.10	Molecular Dipole Moments	27
1.11	Curved Arrows, Arrow Pushing, and Chemical Reactions	28
1.12	Acids and Bases: The Brønsted–Lowry View	30
1.13	How Structure Affects Acid Strength	35
1.14	Acid–Base Equilibria	39
1.15	Acids and Bases: The Lewis View	42
1.16	Summary	43
	Problems	46
	Descriptive Passage and Interpretive Problems 1: Amide Lewis Structural Formulas	51

## CHAPTER 2

### Alkanes and Cycloalkanes: Introduction to Hydrocarbons 52

2.1	Classes of Hydrocarbons	53
2.2	Electron Waves and Chemical Bonds	53
2.3	Bonding in H <sub>2</sub> : The Valence Bond Model	54
2.4	Bonding in H <sub>2</sub> : The Molecular Orbital Model	56
2.5	Introduction to Alkanes: Methane, Ethane, and Propane	57
2.6	<i>sp</i> <sup>3</sup> Hybridization and Bonding in Methane	58
	<b>Methane and the Biosphere</b>	<b>59</b>
2.7	Bonding in Ethane	60

2.8	<i>sp</i> <sup>2</sup> Hybridization and Bonding in Ethylene	61
2.9	<i>sp</i> Hybridization and Bonding in Acetylene	62
2.10	Molecular Orbitals and Bonding in Methane	64
2.11	Isomeric Alkanes: The Butanes	65
2.12	Higher <i>n</i> -Alkanes	66
2.13	The C <sub>5</sub> H <sub>12</sub> Isomers	66
2.14	IUPAC Nomenclature of Unbranched Alkanes	68
2.15	Applying the IUPAC Rules: The Names of the C <sub>6</sub> H <sub>14</sub> Isomers	69
	<b>What's in a Name? Organic Nomenclature</b>	<b>70</b>
2.16	Alkyl Groups	72
2.17	IUPAC Names of Highly Branched Alkanes	73
2.18	Cycloalkane Nomenclature	75
2.19	Introduction to Functional Groups	76
2.20	Sources of Alkanes and Cycloalkanes	76
2.21	Physical Properties of Alkanes and Cycloalkanes	78
2.22	Chemical Properties: Combustion of Alkanes	80
	<b>Thermochemistry</b>	<b>82</b>
2.23	Oxidation–Reduction in Organic Chemistry	83
2.24	Summary	85
	Problems	89
	Descriptive Passage and Interpretive Problems 2: Some Biochemical Reactions of Alkanes	93

## CHAPTER 3

### Alkanes and Cycloalkanes: Conformations and *cis*–*trans* Stereoisomers 94

3.1	Conformational Analysis of Ethane	95
3.2	Conformational Analysis of Butane	99
3.3	Conformations of Higher Alkanes	100
	<b>Computational Chemistry: Molecular Mechanics and Quantum Mechanics</b>	<b>101</b>
3.4	The Shapes of Cycloalkanes: Planar or Nonplanar?	102
3.5	Small Rings: Cyclopropane and Cyclobutane	103
3.6	Cyclopentane	104
3.7	Conformations of Cyclohexane	105
3.8	Axial and Equatorial Bonds in Cyclohexane	106
3.9	Conformational Inversion in Cyclohexane	107
3.10	Conformational Analysis of Monosubstituted Cyclohexanes	108
	<b>Enthalpy, Free Energy, and Equilibrium Constant</b>	<b>111</b>
3.11	Disubstituted Cycloalkanes: <i>cis</i> – <i>trans</i> Stereoisomers	112
3.12	Conformational Analysis of Disubstituted Cyclohexanes	113
3.13	Medium and Large Rings	117
3.14	Polycyclic Ring Systems	117



- 3.15** Heterocyclic Compounds 120  
**3.16** Summary 121  
 Problems 124  
 Descriptive Passage and Interpretive Problems 3:  
 Cyclic Forms of Carbohydrates 128

## 4

### CHAPTER

#### Chirality 130

- 4.1** Introduction to Chirality: Enantiomers 130  
**4.2** The Chirality Center 133  
**4.3** Symmetry in Achiral Structures 135  
**4.4** Optical Activity 136  
**4.5** Absolute and Relative Configuration 138  
**4.6** Cahn–Ingold Prelog *R*–*S* Notation 139  
 Homochirality and Symmetry Breaking 142  
**4.7** Fischer Projections 143  
**4.8** Properties of Enantiomers 145  
**4.9** The Chirality Axis 146  
 Chiral Drugs 147  
**4.10** Chiral Molecules with Two Chirality Centers 148  
**4.11** Achiral Molecules with Two Chirality Centers 151  
 Chirality of Disubstituted Cyclohexanes 153  
**4.12** Molecules with Multiple Chirality Centers 153  
**4.13** Resolution of Enantiomers 155  
**4.14** Chirality Centers Other Than Carbon 157  
**4.15** Summary 158  
 Problems 161  
 Descriptive Passage and Interpretive Problems 4:  
 Prochirality 165

## 5

### CHAPTER

#### Alcohols and Alkyl Halides: Introduction to Reaction Mechanisms 168

- 5.1** Functional Groups 169  
**5.2** IUPAC Nomenclature of Alkyl Halides 170  
**5.3** IUPAC Nomenclature of Alcohols 171  
**5.4** Classes of Alcohols and Alkyl Halides 172  
**5.5** Bonding in Alcohols and Alkyl Halides 172  
**5.6** Physical Properties of Alcohols and Alkyl Halides:  
 Intermolecular Forces 173  
**5.7** Preparation of Alkyl Halides from Alcohols and Hydrogen  
 Halides 177  
**5.8** Reaction of Alcohols with Hydrogen Halides: The  $S_N1$   
 Mechanism 179  
 Mechanism 5.1 Formation of *tert*-Butyl Chloride from  
*tert*-Butyl Alcohol and Hydrogen Chloride 180  
**5.9** Structure, Bonding, and Stability of Carbocations 185  
**5.10** Effect of Alcohol Structure on Reaction Rate 188  
**5.11** Stereochemistry and the  $S_N1$  Mechanism 189  
**5.12** Carbocation Rearrangements 191

Mechanism 5.2 Carbocation Rearrangement in the  
 Reaction of 3,3-Dimethyl-2-butanol with Hydrogen  
 Chloride 191

- 5.13** Reaction of Methyl and Primary Alcohols with Hydrogen  
 Halides: The  $S_N2$  Mechanism 193  
 Mechanism 5.3 Formation of 1-Bromoheptane from  
 1-Heptanol and Hydrogen Bromide 194  
**5.14** Other Methods for Converting Alcohols to Alkyl  
 Halides 195  
**5.15** Sulfonates as Alkyl Halide Surrogates 197  
**5.16** Summary 198  
 Problems 200  
 Descriptive Passage and Interpretive Problems 5:  
 More About Potential Energy Diagrams 204

## 6

### CHAPTER

#### Nucleophilic Substitution 206

- 6.1** Functional-Group Transformation by Nucleophilic  
 Substitution 206  
**6.2** Relative Reactivity of Halide Leaving Groups 209  
**6.3** The  $S_N2$  Mechanism of Nucleophilic Substitution 210  
 Mechanism 6.1 The  $S_N2$  Mechanism of Nucleophilic  
 Substitution 211  
**6.4** Steric Effects and  $S_N2$  Reaction Rates 213  
**6.5** Nucleophiles and Nucleophilicity 215  
 Enzyme-Catalyzed Nucleophilic Substitutions of Alkyl  
 Halides 217  
**6.6** The  $S_N1$  Mechanism of Nucleophilic Substitution 217  
 Mechanism 6.2 The  $S_N1$  Mechanism of Nucleophilic  
 Substitution 218  
**6.7** Stereochemistry of  $S_N1$  Reactions 220  
**6.8** Carbocation Rearrangements in  $S_N1$  Reactions 221  
 Mechanism 6.3 Carbocation Rearrangement in the  $S_N1$   
 Hydrolysis of 2-Bromo-3-methylbutane 222  
**6.9** Effect of Solvent on the Rate of Nucleophilic  
 Substitution 223  
**6.10** Nucleophilic Substitution of Alkyl Sulfonates 226  
**6.11** Introduction to Organic Synthesis: Retrosynthetic  
 Analysis 229  
**6.12** Substitution versus Elimination: A Look Ahead 230  
**6.13** Summary 230  
 Problems 232  
 Descriptive Passage and Interpretive Problems 6:  
 Nucleophilic Substitution 236

## 7

### CHAPTER

#### Structure and Preparation of Alkenes: Elimination Reactions 238

- 7.1** Alkene Nomenclature 238  
**7.2** Structure and Bonding in Alkenes 240  
 Ethylene 241

- 7.3** Isomerism in Alkenes 242
- 7.4** Naming Stereoisomeric Alkenes by the *E–Z* Notational System 243
- 7.5** Physical Properties of Alkenes 244
- 7.6** Relative Stabilities of Alkenes 246
- 7.7** Cycloalkenes 248
- 7.8** Preparation of Alkenes: Elimination Reactions 249
- 7.9** Dehydration of Alcohols 250
- 7.10** Regioselectivity in Alcohol Dehydration: The Zaitsev Rule 251
- 7.11** Stereoselectivity in Alcohol Dehydration 252
- 7.12** The E1 and E2 Mechanisms of Alcohol Dehydration 253  
**Mechanism 7.1** The E1 Mechanism for Acid-Catalyzed Dehydration of *tert*-Butyl Alcohol 253
- 7.13** Rearrangements in Alcohol Dehydration 255  
**Mechanism 7.2** Carbocation Rearrangement in Dehydration of 3,3-Dimethyl-2-butanol 256  
**Mechanism 7.3** Hydride Shift in Dehydration of 1-Butanol 257
- 7.14** Dehydrohalogenation of Alkyl Halides 258
- 7.15** The E2 Mechanism of Dehydrohalogenation of Alkyl Halides 259  
**Mechanism 7.4** E2 Elimination of 1-Chlorooctadecane 260
- 7.16** Anti Elimination in E2 Reactions: Stereoelectronic Effects 262
- 7.17** Isotope Effects and the E2 Mechanism 264
- 7.18** The E1 Mechanism of Dehydrohalogenation of Alkyl Halides 265  
**Mechanism 7.5** The E1 Mechanism for Dehydrohalogenation of 2-Bromo-2-methylbutane 266
- 7.19** Substitution and Elimination as Competing Reactions 267
- 7.20** Elimination Reactions of Sulfonates 270
- 7.21** Summary 271  
 Problems 274  
 Descriptive Passage and Interpretive Problems 7:  
 A Mechanistic Preview of Addition Reactions 279

## 8

### CHAPTER

#### Addition Reactions of Alkenes 280

- 8.1** Hydrogenation of Alkenes 280
- 8.2** Stereochemistry of Alkene Hydrogenation 281  
**Mechanism 8.1** Hydrogenation of Alkenes 282
- 8.3** Heats of Hydrogenation 283
- 8.4** Electrophilic Addition of Hydrogen Halides to Alkenes 285  
**Mechanism 8.2** Electrophilic Addition of Hydrogen Bromide to 2-Methylpropene 287  
 Rules, Laws, Theories, and the Scientific Method 289
- 8.5** Carbocation Rearrangements in Hydrogen Halide Addition to Alkenes 290
- 8.6** Acid-Catalyzed Hydration of Alkenes 290  
**Mechanism 8.3** Acid-Catalyzed Hydration of 2-Methylpropene 291

- 8.7** Thermodynamics of Addition–Elimination Equilibria 292
- 8.8** Hydroboration–Oxidation of Alkenes 295
- 8.9** Mechanism of Hydroboration–Oxidation 297  
**Mechanism 8.4** Hydroboration of 1-Methylcyclopentene 297
- 8.10** Addition of Halogens to Alkenes 298  
**Mechanism 8.5** Oxidation of an Organoborane 299  
**Mechanism 8.6** Bromine Addition to Cyclopentene 301
- 8.11** Epoxidation of Alkenes 303  
**Mechanism 8.7** Epoxidation of Bicyclo[2.2.1]-2-heptene 305
- 8.12** Ozonolysis of Alkenes 305
- 8.13** Enantioselective Addition to Alkenes 306
- 8.14** Retrosynthetic Analysis and Alkene Intermediates 308
- 8.15** Summary 309  
 Problems 312  
 Descriptive Passage and Interpretive Problems 8:  
 Oxymercuration 319

## 9

### CHAPTER

#### Alkynes 322

- 9.1** Sources of Alkynes 322
- 9.2** Nomenclature 324
- 9.3** Physical Properties of Alkynes 324
- 9.4** Structure and Bonding in Alkynes: *sp* Hybridization 325
- 9.5** Acidity of Acetylene and Terminal Alkynes 327
- 9.6** Preparation of Alkynes by Alkylation of Acetylene and Terminal Alkynes 329
- 9.7** Preparation of Alkynes by Elimination Reactions 330
- 9.8** Reactions of Alkynes 331
- 9.9** Hydrogenation of Alkynes 332
- 9.10** Addition of Hydrogen Halides to Alkynes 334
- 9.11** Hydration of Alkynes 335  
**Mechanism 9.1** Conversion of an Enol to a Ketone 336
- 9.12** Addition of Halogens to Alkynes 337  
 Some Things That Can Be Made from Acetylene . . .  
 But Aren't 338
- 9.13** Ozonolysis of Alkynes 338
- 9.14** Alkynes in Synthesis and Retrosynthesis 339
- 9.15** Summary 339  
 Problems 342  
 Descriptive Passage and Interpretive Problems 9:  
 Thinking Mechanistically About Alkynes 346

## 10

### CHAPTER

#### Introduction to Free Radicals 348

- 10.1** Structure, Bonding, and Stability of Alkyl Radicals 349
- 10.2** Halogenation of Alkanes 353  
 From Bond Enthalpies to Heats of Reaction 353
- 10.3** Mechanism of Methane Chlorination 354

**Mechanism 10.1** Free-Radical Chlorination of Methane 355

**10.4** Halogenation of Higher Alkanes 356

**10.5** Free-Radical Addition of Hydrogen Bromide to Alkenes and Alkynes 360

**Mechanism 10.2** Free-Radical Addition of Hydrogen Bromide to 1-Butene 361

**10.6** Metal-Ammonia Reduction of Alkynes 363

**Mechanism 10.3** Sodium–Ammonia Reduction of an Alkyne 364

**10.7** Free Radicals and Retrosynthesis of Alkyl Halides 364

**10.8** Free-Radical Polymerization of Alkenes 365

**Mechanism 10.4** Free-Radical Polymerization of Ethylene 366

**Ethylene and Propene: The Most Important Industrial Organic Chemicals** 367

**10.9** Summary 369

Problems 370

Descriptive Passage and Interpretive Problems 10:  
Free-Radical Reduction of Alkyl Halides 373

## 11

### CHAPTER

#### Conjugation in Alkadienes and Allylic Systems 376

**11.1** The Allyl Group 377

**11.2**  $S_N1$  and  $S_N2$  Reactions of Allylic Halides 380

**Mechanism 11.1**  $S_N1$  Hydrolysis of an Allylic Halide 381

**11.3** Allylic Free-Radical Halogenation 383

**Mechanism 11.2** Allylic Chlorination of Propene 385

**11.4** Allylic Anions 386

**11.5** Classes of Dienes: Conjugated and Otherwise 387

**11.6** Relative Stabilities of Dienes 388

**11.7** Bonding in Conjugated Dienes 389

**11.8** Bonding in Allenes 391

**11.9** Preparation of Dienes 392

**Diene Polymers** 393

**11.10** Addition of Hydrogen Halides to Conjugated Dienes 394

**Mechanism 11.3** Addition of Hydrogen Chloride to 1,3-Cyclopentadiene 394

**11.11** Halogen Addition to Dienes 396

**11.12** The Diels–Alder Reaction 397

**11.13** Intramolecular Diels–Alder Reactions 400

**11.14** Retrosynthetic Analysis and the Diels–Alder Reaction 401

**11.15** Molecular Orbital Analysis of the Diels–Alder Reaction 402

**11.16** The Cope and Claisen Rearrangements 403

**11.17** Summary 404

Problems 407

Descriptive Passage and Interpretive Problems 11:  
1,3-Dipolar Cycloaddition 411

## 12

### CHAPTER

#### Arenes and Aromaticity 414

**12.1** Benzene 415

**12.2** The Structure of Benzene 415

**12.3** The Stability of Benzene 417

**12.4** Bonding in Benzene 418

**12.5** Substituted Derivatives of Benzene and Their Nomenclature 420

**12.6** Polycyclic Aromatic Hydrocarbons 422

**Fullerenes, Nanotubes, and Graphene** 424

**12.7** Physical Properties of Arenes 425

**12.8** The Benzyl Group 426

**12.9** Nucleophilic Substitution in Benzylic Halides 427

**Triphenylmethyl Radical Yes, Hexaphenylethane No** 430

**12.10** Benzylic Free-Radical Halogenation 431

**12.11** Benzylic Anions 431

**12.12** Oxidation of Alkylbenzenes 432

**12.13** Alkenylbenzenes 434

**12.14** Polymerization of Styrene 436

**Mechanism 12.1** Free-Radical Polymerization of Styrene 436

**12.15** The Birch Reduction 437

**Mechanism 12.2** The Birch Reduction 438

**12.16** Benzylic Side Chains and Retrosynthetic Analysis 439

**12.17** Cyclobutadiene and Cyclooctatetraene 440

**12.18** Hückel's Rule 441

**12.19** Annulenes 443

**12.20** Aromatic Ions 445

**12.21** Heterocyclic Aromatic Compounds 448

**12.22** Heterocyclic Aromatic Compounds and Hückel's Rule 450

**12.23** Summary 452

Problems 456

Descriptive Passage and Interpretive Problems 12:

Substituent Effects on Reaction Rates and Equilibria 461

## 13

### CHAPTER

#### Electrophilic and Nucleophilic Aromatic Substitution 464

**13.1** Representative Electrophilic Aromatic Substitution Reactions of Benzene 465

**13.2** Mechanistic Principles of Electrophilic Aromatic Substitution 466

**13.3** Nitration of Benzene 467

**Mechanism 13.1** Nitration of Benzene 468

**13.4** Sulfonation of Benzene 469

**Mechanism 13.2** Sulfonation of Benzene 469

**13.5** Halogenation of Benzene 470

**Mechanism 13.3** Bromination of Benzene 471

**Biosynthetic Halogenation** 472

**13.6** Friedel–Crafts Alkylation of Benzene 473

**Mechanism 13.4** Friedel–Crafts Alkylation 473

- 13.7** Friedel–Crafts Acylation of Benzene 475  
**Mechanism 13.5** Friedel–Crafts Acylation 476
- 13.8** Synthesis of Alkylbenzenes by Acylation–Reduction 477
- 13.9** Rate and Regioselectivity in Electrophilic Aromatic Substitution 478
- 13.10** Rate and Regioselectivity in the Nitration of Toluene 480
- 13.11** Rate and Regioselectivity in the Nitration of (Trifluoromethyl)benzene 482
- 13.12** Substituent Effects in Electrophilic Aromatic Substitution: Activating Substituents 484
- 13.13** Substituent Effects in Electrophilic Aromatic Substitution: Strongly Deactivating Substituents 488
- 13.14** Substituent Effects in Electrophilic Aromatic Substitution: Halogens 490
- 13.15** Multiple Substituent Effects 492
- 13.16** Retrosynthetic Analysis and the Synthesis of Substituted Benzenes 494
- 13.17** Substitution in Naphthalene 496
- 13.18** Substitution in Heterocyclic Aromatic Compounds 497
- 13.19** Nucleophilic Aromatic Substitution 498
- 13.20** The Addition–Elimination Mechanism of Nucleophilic Aromatic Substitution 500  
**Mechanism 13.6** Nucleophilic Aromatic Substitution in *p*-Fluoronitrobenzene by the Addition–Elimination Mechanism 501
- 13.21** Related Nucleophilic Aromatic Substitutions 502
- 13.22** Summary 504  
 Problems 508  
 Descriptive Passage and Interpretive Problems 13: Benzyne 515

# 14

## CHAPTER

### Spectroscopy 518

- 14.1** Principles of Molecular Spectroscopy: Electromagnetic Radiation 519
- 14.2** Principles of Molecular Spectroscopy: Quantized Energy States 520
- 14.3** Introduction to <sup>1</sup>H NMR Spectroscopy 520
- 14.4** Nuclear Shielding and <sup>1</sup>H Chemical Shifts 522
- 14.5** Effects of Molecular Structure on <sup>1</sup>H Chemical Shifts 525  
**Ring Currents: Aromatic and Antiaromatic** 530
- 14.6** Interpreting <sup>1</sup>H NMR Spectra 531
- 14.7** Spin–Spin Splitting and <sup>1</sup>H NMR 533
- 14.8** Splitting Patterns: The Ethyl Group 536
- 14.9** Splitting Patterns: The Isopropyl Group 537
- 14.10** Splitting Patterns: Pairs of Doublets 538
- 14.11** Complex Splitting Patterns 539
- 14.12** <sup>1</sup>H NMR Spectra of Alcohols 542  
**Magnetic Resonance Imaging (MRI)** 543
- 14.13** NMR and Conformations 543
- 14.14** <sup>13</sup>C NMR Spectroscopy 544
- 14.15** <sup>13</sup>C Chemical Shifts 545
- 14.16** <sup>13</sup>C NMR and Peak Intensities 548
- 14.17** <sup>13</sup>C–<sup>1</sup>H Coupling 549

- 14.18** Using DEPT to Count Hydrogens 549
- 14.19** 2D NMR: COSY and HETCOR 551
- 14.20** Introduction to Infrared Spectroscopy 553  
**Spectra by the Thousands** 554
- 14.21** Infrared Spectra 555
- 14.22** Characteristic Absorption Frequencies 557
- 14.23** Ultraviolet-Visible Spectroscopy 561
- 14.24** Mass Spectrometry 563
- 14.25** Molecular Formula as a Clue to Structure 568
- 14.26** Summary 569  
 Problems 572  
 Descriptive Passage and Interpretive Problems 14: More on Coupling Constants 581

# 15

## CHAPTER

### Organometallic Compounds 584

- 15.1** Organometallic Nomenclature 585
- 15.2** Carbon–Metal Bonds 585
- 15.3** Preparation of Organolithium and Organomagnesium Compounds 587
- 15.4** Organolithium and Organomagnesium Compounds as Brønsted Bases 588
- 15.5** Synthesis of Alcohols Using Grignard and Organolithium Reagents 589
- 15.6** Synthesis of Acetylenic Alcohols 592
- 15.7** Retrosynthetic Analysis and Grignard and Organolithium Reagents 592
- 15.8** An Organozinc Reagent for Cyclopropane Synthesis 593
- 15.9** Transition-Metal Organometallic Compounds 595  
**An Organometallic Compound That Occurs Naturally: Coenzyme B<sub>12</sub>** 597
- 15.10** Organocopper Reagents 598
- 15.11** Palladium-Catalyzed Cross-Coupling Reactions 601
- 15.12** Homogeneous Catalytic Hydrogenation 603  
**Mechanism 15.1** Homogeneous Catalysis of Alkene Hydrogenation 605
- 15.13** Olefin Metathesis 606  
**Mechanism 15.2** Olefin Cross-Metathesis 608
- 15.14** Ziegler–Natta Catalysis of Alkene Polymerization 609  
**Mechanism 15.3** Polymerization of Ethylene in the Presence of Ziegler–Natta Catalyst 611
- 15.15** Summary 612  
 Problems 614  
 Descriptive Passage and Interpretive Problems 15: Cyclobutadiene and (Cyclobutadiene)tricarbonyliron 618

# 16

## CHAPTER

### Alcohols, Diols, and Thiols 620

- 16.1** Sources of Alcohols 621
- 16.2** Preparation of Alcohols by Reduction of Aldehydes and Ketones 623

- 16.3** Preparation of Alcohols by Reduction of Carboxylic Acids 626
- 16.4** Preparation of Alcohols from Epoxides 626
- 16.5** Preparation of Diols 627
- 16.6** Reactions of Alcohols: A Review and a Preview 629
- 16.7** Conversion of Alcohols to Ethers 630  
**Mechanism 16.1** Acid-Catalyzed Formation of Diethyl Ether from Ethyl Alcohol 630
- 16.8** Esterification 631
- 16.9** Oxidation of Alcohols 633  
**Sustainability and Organic Chemistry** 636
- 16.10** Biological Oxidation of Alcohols 637
- 16.11** Oxidative Cleavage of Vicinal Diols 639
- 16.12** Thiols 640
- 16.13** Spectroscopic Analysis of Alcohols and Thiols 643
- 16.14** **Summary** 645  
**Problems** 648  
**Descriptive Passage and Interpretive Problems 16: The Pinacol Rearrangement** 653

# 17

## CHAPTER

### Ethers, Epoxides, and Sulfides 656

- 17.1** Nomenclature of Ethers, Epoxides, and Sulfides 656
- 17.2** Structure and Bonding in Ethers and Epoxides 658
- 17.3** Physical Properties of Ethers 658
- 17.4** Crown Ethers 660
- 17.5** Preparation of Ethers 661  
**Polyether Antibiotics** 662
- 17.6** The Williamson Ether Synthesis 663
- 17.7** Reactions of Ethers: A Review and a Preview 664
- 17.8** Acid-Catalyzed Cleavage of Ethers 665  
**Mechanism 17.1** Cleavage of Ethers by Hydrogen Halides 666
- 17.9** Preparation of Epoxides 666
- 17.10** Conversion of Vicinal Halohydrins to Epoxides 667
- 17.11** Reactions of Epoxides with Anionic Nucleophiles 668  
**Mechanism 17.2** Nucleophilic Ring Opening of an Epoxide 670
- 17.12** Acid-Catalyzed Ring Opening of Epoxides 671  
**Mechanism 17.3** Acid-Catalyzed Ring Opening of an Epoxide 672
- 17.13** Epoxides in Biological Processes 673
- 17.14** Preparation of Sulfides 673
- 17.15** Oxidation of Sulfides: Sulfoxides and Sulfones 674
- 17.16** Alkylation of Sulfides: Sulfonium Salts 675
- 17.17** Spectroscopic Analysis of Ethers, Epoxides, and Sulfides 676
- 17.18** **Summary** 678  
**Problems** 681  
**Descriptive Passage and Interpretive Problems 17: Epoxide Rearrangements and the NIH Shift** 688

# 18

## CHAPTER

### Aldehydes and Ketones: Nucleophilic Addition to the Carbonyl Group 692

- 18.1** Nomenclature 693
- 18.2** Structure and Bonding: The Carbonyl Group 695
- 18.3** Physical Properties 697
- 18.4** Sources of Aldehydes and Ketones 697
- 18.5** Reactions of Aldehydes and Ketones: A Review and a Preview 701
- 18.6** Principles of Nucleophilic Addition: Hydration of Aldehydes and Ketones 702  
**Mechanism 18.1** Hydration of an Aldehyde or Ketone in Basic Solution 705  
**Mechanism 18.2** Hydration of an Aldehyde or Ketone in Acid Solution 706
- 18.7** Cyanohydrin Formation 706  
**Mechanism 18.3** Cyanohydrin Formation 707
- 18.8** Reaction with Alcohols: Acetals and Ketals 709  
**Mechanism 18.4** Acetal Formation from Benzaldehyde and Ethanol 711
- 18.9** Acetals and Ketals as Protecting Groups 712
- 18.10** Reaction with Primary Amines: Imines 713  
**Mechanism 18.5** Imine Formation from Benzaldehyde and Methylamine 715
- 18.11** Reaction with Secondary Amines: Enamines 716  
**Imines in Biological Chemistry** 717  
**Mechanism 18.6** Enamine Formation 719
- 18.12** The Wittig Reaction 720
- 18.13** Stereoselective Addition to Carbonyl Groups 722
- 18.14** Oxidation of Aldehydes 724
- 18.15** Spectroscopic Analysis of Aldehydes and Ketones 724
- 18.16** **Summary** 727  
**Problems** 730  
**Descriptive Passage and Interpretive Problems 18: The Baeyer–Villiger Oxidation** 738

# 19

## CHAPTER

### Carboxylic Acids 742

- 19.1** Carboxylic Acid Nomenclature 743
- 19.2** Structure and Bonding 745
- 19.3** Physical Properties 745
- 19.4** Acidity of Carboxylic Acids 746
- 19.5** Substituents and Acid Strength 748
- 19.6** Ionization of Substituted Benzoic Acids 750
- 19.7** Salts of Carboxylic Acids 751
- 19.8** Dicarboxylic Acids 753
- 19.9** Carbonic Acid 754
- 19.10** Sources of Carboxylic Acids 755
- 19.11** Synthesis of Carboxylic Acids by the Carboxylation of Grignard Reagents 757



- 19.12** Synthesis of Carboxylic Acids by the Preparation and Hydrolysis of Nitriles 758
- 19.13** Reactions of Carboxylic Acids: A Review and a Preview 759
- 19.14** Mechanism of Acid-Catalyzed Esterification 760  
**Mechanism 19.1** Acid-Catalyzed Esterification of Benzoic Acid with Methanol 760
- 19.15** Intramolecular Ester Formation: Lactones 763
- 19.16** Decarboxylation of Malonic Acid and Related Compounds 764
- 19.17** Spectroscopic Analysis of Carboxylic Acids 766
- 19.18** Summary 767  
Problems 769  
Descriptive Passage and Interpretive Problems 19: Lactonization Methods 774

## 20

### CHAPTER

#### Carboxylic Acid Derivatives: Nucleophilic Acyl Substitution 776

- 20.1** Nomenclature of Carboxylic Acid Derivatives 777
- 20.2** Structure and Reactivity of Carboxylic Acid Derivatives 778
- 20.3** Nucleophilic Acyl Substitution Mechanisms 781
- 20.4** Nucleophilic Acyl Substitution in Acyl Chlorides 782
- 20.5** Nucleophilic Acyl Substitution in Acid Anhydrides 784  
**Mechanism 20.1** Nucleophilic Acyl Substitution in an Anhydride 786
- 20.6** Physical Properties and Sources of Esters 786
- 20.7** Reactions of Esters: A Preview 787
- 20.8** Acid-Catalyzed Ester Hydrolysis 789  
**Mechanism 20.2** Acid-Catalyzed Ester Hydrolysis 790
- 20.9** Ester Hydrolysis in Base: Saponification 792  
**Mechanism 20.3** Ester Hydrolysis in Basic Solution 795
- 20.10** Reaction of Esters with Ammonia and Amines 796
- 20.11** Reaction of Esters with Grignard and Organolithium Reagents and Lithium Aluminum Hydride 797
- 20.12** Amides 798
- 20.13** Hydrolysis of Amides 802  
**Mechanism 20.4** Amide Hydrolysis in Acid Solution 803  
**Mechanism 20.5** Amide Hydrolysis in Basic Solution 805
- 20.14** Lactams 806  
 **$\beta$ -Lactam Antibiotics 806**
- 20.15** Preparation of Nitriles 808
- 20.16** Hydrolysis of Nitriles 809  
**Mechanism 20.6** Nitrile Hydrolysis in Basic Solution 810
- 20.17** Addition of Grignard Reagents to Nitriles 811
- 20.18** Spectroscopic Analysis of Carboxylic Acid Derivatives 811
- 20.19** Summary 813  
Problems 816  
Descriptive Passage and Interpretive Problems 20: Thioesters 822

## 21

### CHAPTER

#### Enols and Enolates 826

- 21.1** Enol Content and Enolization 827  
**Mechanism 21.1** Acid-Catalyzed Enolization of 2-Methylpropanal 829
- 21.2** Enolates 830  
**Mechanism 21.2** Base-Catalyzed Enolization of 2-Methylpropanal 832
- 21.3** The Aldol Condensation 834  
**Mechanism 21.3** Aldol Addition of Butanal 834
- 21.4** Mixed and Directed Aldol Reactions 837  
**From the Mulberry Tree to Cancer Chemotherapy 838**
- 21.5** Acylation of Enolates: The Claisen and Related Condensations 839  
**Mechanism 21.4** Claisen Condensation of Ethyl Propanoate 840
- 21.6** Alkylation of Enolates: The Acetoacetic Ester and Malonic Ester Syntheses 843
- 21.7** The Haloform Reaction 846  
**The Haloform Reaction and the Biosynthesis of Trihalomethanes 847**  
**Mechanism 21.5** The Haloform Reaction 848
- 21.8** Conjugation Effects in  $\alpha,\beta$ -Unsaturated Aldehydes and Ketones 849
- 21.9** Summary 853  
Problems 855  
Descriptive Passage and Interpretive Problems 21: The Enolate Chemistry of Dianions 861

## 22

### CHAPTER

#### Amines 864

- 22.1** Amine Nomenclature 865
- 22.2** Structure and Bonding 867
- 22.3** Physical Properties 868
- 22.4** Basicity of Amines 869  
**Amines as Natural Products 874**
- 22.5** Tetraalkylammonium Salts as Phase-Transfer Catalysts 875
- 22.6** Reactions That Lead to Amines: A Review and a Preview 876
- 22.7** Preparation of Amines by Alkylation of Ammonia 878
- 22.8** The Gabriel Synthesis of Primary Alkylamines 879
- 22.9** Preparation of Amines by Reduction 880  
**Mechanism 22.1** Lithium Aluminum Hydride Reduction of an Amide 883
- 22.10** Reductive Amination 884
- 22.11** Reactions of Amines: A Review and a Preview 885
- 22.12** Reaction of Amines with Alkyl Halides 887
- 22.13** The Hofmann Elimination 887
- 22.14** Electrophilic Aromatic Substitution in Arylamines 889

- 22.15** Nitrosation of Alkylamines 891  
**22.16** Nitrosation of Arylamines 893  
**22.17** Synthetic Transformations of Aryl Diazonium Salts 894  
**22.18** Azo Coupling 898  
**From Dyes to Sulfa Drugs 899**  
**22.19** Spectroscopic Analysis of Amines 899  
**22.20** Summary 902  
**Problems 908**  
**Descriptive Passage and Interpretive Problems 22:**  
**Synthetic Applications of Enamines 916**

## 23

### CHAPTER

#### Phenols 920

- 23.1** Nomenclature 920  
**23.2** Structure and Bonding 922  
**23.3** Physical Properties 922  
**23.4** Acidity of Phenols 923  
**23.5** Substituent Effects on the Acidity of Phenols 924  
**23.6** Sources of Phenols 925  
**23.7** Naturally Occurring Phenols 926  
**23.8** Reactions of Phenols: Electrophilic Aromatic Substitution 927  
**23.9** Reactions of Phenols: O-Alkylation and O-Acylation 930  
**23.10** Carboxylation of Phenols: Aspirin and the Kolbe–Schmitt Reaction 932  
**James Bond, Oxidative Stress, and Antioxidant Phenols 933**  
**23.11** Cleavage of Aryl Ethers by Hydrogen Halides 935  
**23.12** Claisen Rearrangement of Allyl Aryl Ethers 936  
**23.13** Oxidation of Phenols: Quinones 937  
**23.14** Spectroscopic Analysis of Phenols 938  
**23.15** Summary 939  
**Problems 941**  
**Descriptive Passage and Interpretive Problems 23:**  
**Directed Metalation of Aryl Ethers 947**

## 24

### CHAPTER

#### Carbohydrates 950

- 24.1** Classification of Carbohydrates 951  
**24.2** Fischer Projections and D,L Notation 951  
**24.3** The Aldotetroses 952  
**24.4** Aldopentoses and Aldohexoses 954  
**24.5** A Mnemonic for Carbohydrate Configurations 956  
**24.6** Cyclic Forms of Carbohydrates: Furanose Forms 956  
**24.7** Cyclic Forms of Carbohydrates: Pyranose Forms 960  
**24.8** Mutarotation 962  
**Mechanism 24.1** Acid-Catalyzed Mutarotation of D-Glucopyranose 963  
**24.9** Carbohydrate Conformation: The Anomeric Effect 964  
**24.10** Ketoses 966  
**24.11** Deoxy Sugars 967

- 24.12** Amino Sugars 968  
**24.13** Branched-Chain Carbohydrates 969  
**24.14** Glycosides: The Fischer Glycosidation 969  
**Mechanism 24.2** Preparation of Methyl D-Glucopyranosides by Fischer Glycosidation 971  
**24.15** Disaccharides 973  
**24.16** Polysaccharides 975  
**How Sweet It Is! 976**  
**24.17** Application of Familiar Reactions to Monosaccharides 977  
**24.18** Oxidation of Monosaccharides 980  
**24.19** Glycosides: Synthesis of Oligosaccharides 982  
**Mechanism 24.3** Silver-Assisted Glycosidation 984  
**24.20** Glycobiology 985  
**24.21** Summary 987  
**Problems 988**  
**Descriptive Passage and Interpretive Problems 24:**  
**Emil Fischer and the Structure of (+)-Glucose 993**

## 25

### CHAPTER

#### Lipids 996

- 25.1** Acetyl Coenzyme A 997  
**25.2** Fats, Oils, and Fatty Acids 998  
**25.3** Fatty Acid Biosynthesis 1001  
**25.4** Phospholipids 1003  
**25.5** Waxes 1005  
**25.6** Prostaglandins 1006  
**Nonsteroidal Antiinflammatory Drugs (NSAIDs) and COX-2 Inhibitors 1008**  
**25.7** Terpenes: The Isoprene Rule 1009  
**25.8** Isopentenyl Diphosphate: The Biological Isoprene Unit 1012  
**25.9** Carbon–Carbon Bond Formation in Terpene Biosynthesis 1012  
**25.10** The Pathway from Acetate to Isopentenyl Diphosphate 1015  
**25.11** Steroids: Cholesterol 1017  
**Mechanism 25.1** Biosynthesis of Cholesterol from Squalene 1019  
**25.12** Vitamin D 1020  
**Good Cholesterol? Bad Cholesterol? What's the Difference? 1020**  
**25.13** Bile Acids 1021  
**25.14** Corticosteroids 1021  
**25.15** Sex Hormones 1022  
**25.16** Carotenoids 1023  
**Crocuses Make Saffron from Carotenes 1024**  
**25.17** Summary 1025  
**Problems 1026**  
**Descriptive Passage and Interpretive Problems 25:**  
**Polyketides 1031**



# CHAPTER 26

## Amino Acids, Peptides, and Proteins 1034

- 26.1** Classification of Amino Acids 1035  
**26.2** Stereochemistry of Amino Acids 1039  
**26.3** Acid–Base Behavior of Amino Acids 1040  
**Electrophoresis** 1043  
**26.4** Synthesis of Amino Acids 1044  
**26.5** Reactions of Amino Acids 1045  
**26.6** Some Biochemical Reactions of Amino Acids 1047  
**Mechanism 26.1** Pyridoxal 5'-Phosphate-Mediated Decarboxylation of an  $\alpha$ -Amino Acid 1048  
**Mechanism 26.2** Transamination: Biosynthesis of L-Alanine from L-Glutamic Acid and Pyruvic Acid 1051  
**26.7** Peptides 1053  
**26.8** Introduction to Peptide Structure Determination 1056  
**26.9** Amino Acid Analysis 1056  
**26.10** Partial Hydrolysis and End Group Analysis 1057  
**26.11** Insulin 1059  
**26.12** Edman Degradation and Automated Sequencing of Peptides 1060  
**Mechanism 26.3** The Edman Degradation 1061  
**Peptide Mapping and MALDI Mass Spectrometry** 1062  
**26.13** The Strategy of Peptide Synthesis 1063  
**26.14** Amino and Carboxyl Group Protection and Deprotection 1064  
**26.15** Peptide Bond Formation 1065  
**Mechanism 26.4** Amide Bond Formation Between a Carboxylic Acid and an Amine Using *N,N'*-Dicyclohexylcarbodiimide 1067  
**26.16** Solid-Phase Peptide Synthesis: The Merrifield Method 1068  
**26.17** Secondary Structures of Peptides and Proteins 1070  
**26.18** Tertiary Structure of Polypeptides and Proteins 1073  
**Mechanism 26.5** Carboxypeptidase-Catalyzed Hydrolysis 1076  
**26.19** Coenzymes 1077  
**Oh NO! It's Inorganic!** 1078  
**26.20** Protein Quaternary Structure: Hemoglobin 1078  
**26.21** G-Protein-Coupled Receptors 1079  
**26.22** Summary 1080  
**Problems** 1082  
**Descriptive Passage and Interpretive Problems 26: Amino Acids in Enantioselective Synthesis** 1085

# CHAPTER 27

## Nucleosides, Nucleotides, and Nucleic Acids 1088

- 27.1** Pyrimidines and Purines 1089  
**27.2** Nucleosides 1092  
**27.3** Nucleotides 1094  
**27.4** Bioenergetics 1095  
**27.5** ATP and Bioenergetics 1096

- 27.6** Phosphodiesters, Oligonucleotides, and Polynucleotides 1098  
**27.7** Nucleic Acids 1099  
**27.8** Secondary Structure of DNA: The Double Helix 1100  
**"It Has Not Escaped Our Notice . . ."** 1100  
**27.9** Tertiary Structure of DNA: Supercoils 1102  
**27.10** Replication of DNA 1104  
**27.11** Ribonucleic Acids 1106  
**27.12** Protein Biosynthesis 1108  
**27.13** AIDS 1109  
**27.14** DNA Sequencing 1110  
**27.15** The Human Genome Project 1112  
**27.16** DNA Profiling and the Polymerase Chain Reaction 1112  
**27.17** Recombinant DNA Technology 1115  
**27.18** Summary 1116  
**Problems** 1119  
**Descriptive Passage and Interpretive Problems 27: Oligonucleotide Synthesis** 1121

# CHAPTER 28

## Synthetic Polymers 1126

- 28.1** Some Background 1126  
**28.2** Polymer Nomenclature 1127  
**28.3** Classification of Polymers: Reaction Type 1128  
**28.4** Classification of Polymers: Chain Growth and Step Growth 1130  
**28.5** Classification of Polymers: Structure 1131  
**28.6** Classification of Polymers: Properties 1134  
**28.7** Addition Polymers: A Review and a Preview 1134  
**28.8** Chain Branching in Free-Radical Polymerization 1137  
**Mechanism 28.1** Branching in Polyethylene Caused by Intramolecular Hydrogen Transfer 1138  
**Mechanism 28.2** Branching in Polyethylene Caused by Intermolecular Hydrogen Transfer 1139  
**28.9** Anionic Polymerization: Living Polymers 1139  
**Mechanism 28.3** Anionic Polymerization of Styrene 1140  
**28.10** Cationic Polymerization 1141  
**Mechanism 28.4** Cationic Polymerization of 2-Methylpropene 1142  
**28.11** Polyamides 1143  
**28.12** Polyesters 1144  
**28.13** Polycarbonates 1145  
**28.14** Polyurethanes 1145  
**28.15** Copolymers 1146  
**Conducting Polymers** 1148  
**28.16** Summary 1149  
**Problems** 1152  
**Descriptive Passage and Interpretive Problems 28: Chemically Modified Polymers** 1153

**Glossary G-1**

**Credits C-1**

**Index I-1**

# List of Important Features

## Mechanisms

- 5.1** Formation of *tert*-Butyl Chloride from *tert*-Butyl Alcohol and Hydrogen Chloride 180
- 5.2** Carbocation Rearrangement in the Reaction of 3,3-Dimethyl-2-butanol with Hydrogen Chloride 191
- 5.3** Formation of 1-Bromoheptane from 1-Heptanol and Hydrogen Bromide 194
- 6.1** The  $S_N2$  Mechanism of Nucleophilic Substitution 211
- 6.2** The  $S_N1$  Mechanism of Nucleophilic Substitution 218
- 6.3** Carbocation Rearrangement in the  $S_N1$  Hydrolysis of 2-Bromo-3-methylbutane 222
- 7.1** The E1 Mechanism for Acid-Catalyzed Dehydration of *tert*-Butyl Alcohol 253
- 7.2** Carbocation Rearrangement in Dehydration of 3,3-Dimethyl-2-butanol 256
- 7.3** Hydride Shift in Dehydration of 1-Butanol 257
- 7.4** E2 Elimination of 1-Chlorooctadecane 260
- 7.5** The E1 Mechanism for Dehydrohalogenation of 2-Bromo-2-methylbutane 266
- 8.1** Hydrogenation of Alkenes 282
- 8.2** Electrophilic Addition of Hydrogen Bromide to 2-Methylpropene 287
- 8.3** Acid-Catalyzed Hydration of 2-Methylpropene 291
- 8.4** Hydroboration of 1-Methylcyclopentene 297
- 8.5** Oxidation of an Organoborane 299
- 8.6** Bromine Addition to Cyclopentene 301
- 8.7** Epoxidation of Bicyclo[2.2.1]-2-heptene 305
- 9.1** Conversion of an Enol to a Ketone 336
- 10.1** Free-Radical Chlorination of Methane 355
- 10.2** Free-Radical Addition of Hydrogen Bromide to 1-Butene 361
- 10.3** Sodium–Ammonia Reduction of an Alkyne 364
- 10.4** Free-Radical Polymerization of Ethylene 366
- 11.1**  $S_N1$  Hydrolysis of an Allylic Halide 381
- 11.2** Allylic Chlorination of Propene 385
- 11.3** Addition of Hydrogen Chloride to 1,3-Cyclopentadiene 394
- 12.1** Free-Radical Polymerization of Styrene 436
- 12.2** The Birch Reduction 438
- 13.1** Nitration of Benzene 468
- 13.2** Sulfonation of Benzene 469
- 13.3** Bromination of Benzene 471
- 13.4** Friedel–Crafts Alkylation 473
- 13.5** Friedel–Crafts Acylation 476
- 13.6** Nucleophilic Aromatic Substitution in *p*-Fluoronitrobenzene by the Addition–Elimination Mechanism 501
- 15.1** Homogeneous Catalysis of Alkene Hydrogenation 605
- 15.2** Olefin Cross-Metathesis 608
- 15.3** Polymerization of Ethylene in the Presence of Ziegler–Natta Catalyst 611
- 16.1** Acid-Catalyzed Formation of Diethyl Ether from Ethyl Alcohol 630
- 17.1** Cleavage of Ethers by Hydrogen Halides 666
- 17.2** Nucleophilic Ring Opening of an Epoxide 670
- 17.3** Acid-Catalyzed Ring Opening of an Epoxide 672
- 18.1** Hydration of an Aldehyde or Ketone in Basic Solution 705
- 18.2** Hydration of an Aldehyde or Ketone in Acid Solution 706
- 18.3** Cyanohydrin Formation 707
- 18.4** Acetal Formation from Benzaldehyde and Ethanol 711
- 18.5** Imine Formation from Benzaldehyde and Methylamine 715
- 18.6** Enamine Formation 719
- 19.1** Acid-Catalyzed Esterification of Benzoic Acid with Methanol 760
- 20.1** Nucleophilic Acyl Substitution in an Anhydride 786
- 20.2** Acid-Catalyzed Ester Hydrolysis 790
- 20.3** Ester Hydrolysis in Basic Solution 795
- 20.4** Amide Hydrolysis in Acid Solution 803
- 20.5** Amide Hydrolysis in Basic Solution 805
- 20.6** Nitrile Hydrolysis in Basic Solution 810
- 21.1** Acid-Catalyzed Enolization of 2-Methylpropanal 829
- 21.2** Base-Catalyzed Enolization of 2-Methylpropanal 832
- 21.3** Aldol Addition of Butanal 834
- 21.4** Claisen Condensation of Ethyl Propanoate 840
- 21.5** The Haloform Reaction 848
- 22.1** Lithium Aluminum Hydride Reduction of an Amide 883
- 24.1** Acid-Catalyzed Mutarotation of D-Glucopyranose 963
- 24.2** Preparation of Methyl D-Glucopyranosides by Fischer Glycosidation 971
- 24.3** Silver-Assisted Glycosidation 984
- 25.1** Biosynthesis of Cholesterol from Squalene 1019
- 26.1** Pyridoxal 5'-Phosphate-Mediated Decarboxylation of an  $\alpha$ -Amino Acid 1048
- 26.2** Transamination: Biosynthesis of L-Alanine from L-Glutamic Acid and Pyruvic Acid 1051
- 26.3** The Edman Degradation 1061
- 26.4** Amide Bond Formation Between a Carboxylic Acid and an Amine Using *N,N'*-Dicyclohexylcarbodiimide 1067
- 26.5** Carboxypeptidase-Catalyzed Hydrolysis 1076
- 28.1** Branching in Polyethylene Caused by Intramolecular Hydrogen Transfer 1138
- 28.2** Branching in Polyethylene Caused by Intermolecular Hydrogen Transfer 1139
- 28.3** Anionic Polymerization of Styrene 1140
- 28.4** Cationic Polymerization of 2-Methylpropene 1142

## Tables

- |             |   |             |   |
|-------------|---|-------------|---|
| <b>1.1</b>  | Electron Configurations of the First Twelve Elements of the Periodic Table 5                            | <b>13.2</b> | Classification of Substituents in Electrophilic Aromatic Substitution Reactions 485                   |
| <b>1.2</b>  | Lewis Formulas of Methane, Ammonia, Water, and Hydrogen Fluoride 9                                      | <b>13.3</b> | Representative Electrophilic Aromatic Substitution Reactions 505                                      |
| <b>1.3</b>  | Selected Values from the Pauling Electronegativity Scale 11   | <b>13.4</b> | Limitations on Friedel–Crafts Reactions 506   |
| <b>1.4</b>  | Selected Bond Dipole Moments 12   | <b>14.1</b> | Splitting Patterns of Common Multiplets 537   |
| <b>1.5</b>  | A Systematic Approach to Writing Lewis Formulas 16  | <b>14.2</b> | Chemical Shifts of Representative Carbons 546   |
| <b>1.6</b>  | Introduction to the Rules of Resonance 21   | <b>14.3</b> | Infrared Absorption Frequencies of Some Common Structural Units 560                                   |
| <b>1.7</b>  | VSEPR and Molecular Geometry 24   | <b>14.4</b> | Absorption Maxima of Some Representative Alkenes and Polyenes 562                                     |
| <b>1.8</b>  | Acidity Constants ( $pK_a$ ) of Acids 33  | <b>14.5</b> | Approximate Values of Proton Coupling Constants (in Hz) 581   |
| <b>2.1</b>  | The Number of Constitutionally Isomeric Alkanes of Particular Molecular Formulas 67                     | <b>15.1</b> | Reactions of Grignard Reagents with Aldehydes and Ketones 591   |
| <b>2.2</b>  | IUPAC Names of Unbranched Alkanes 69  | <b>16.1</b> | Reactions Discussed in Earlier Chapters That Yield Alcohols 622                                       |
| <b>2.3</b>  | Heats of Combustion ( $-\Delta H^\circ$ ) of Representative Alkanes 81                                  | <b>16.2</b> | Reactions of Alcohols Discussed in Earlier Chapters 629   |
| <b>2.4</b>  | Summary of IUPAC Nomenclature of Alkanes and Cycloalkanes 87  | <b>16.3</b> | Preparation of Alcohols by Reduction of Carbonyl Functional Groups 645                                |
| <b>2.5</b>  | Summary of IUPAC Nomenclature of Alkyl Groups 89  | <b>16.4</b> | Reactions of Alcohols Presented in This Chapter 647   |
| <b>3.1</b>  | Heats of Combustion ( $-\Delta H^\circ$ ) of Cycloalkanes 103   | <b>16.5</b> | Oxidation of Alcohols 648   |
| <b>3.2</b>  | Heats of Combustion of Isomeric Dimethylcyclohexanes 113  | <b>17.1</b> | Physical Properties of Diethyl Ether, Pentane, and 1-Butanol 659                                      |
| <b>4.1</b>  | The Cahn–Ingold–Prelog Sequence Rules 140   | <b>17.2</b> | Preparation of Ethers and Epoxides 680  |
| <b>4.2</b>  | Classification of Isomers 159   | <b>18.1</b> | Summary of Reactions Discussed in Earlier Chapters That Yield Aldehydes and Ketones 699               |
| <b>5.1</b>  | Functional Groups in Some Important Classes of Organic Compounds 170                                    | <b>18.2</b> | Summary of Reactions of Aldehydes and Ketones Discussed in Earlier Chapters 701                       |
| <b>5.2</b>  | Boiling Points of Some Alkyl Halides and Alcohols 175   | <b>18.3</b> | Equilibrium Constants ( $K_{hyd}$ ) and Relative Rates of Hydration of Some Aldehydes and Ketones 702 |
| <b>5.3</b>  | Conversions of Alcohols to Alkyl Halides and Sulfonates 199   | <b>18.4</b> | Reactions of Aldehydes and Ketones with Derivatives of Ammonia 716                                    |
| <b>6.1</b>  | Functional-Group Transformation via Nucleophilic Substitution 207                                       | <b>18.5</b> | Nucleophilic Addition to Aldehydes and Ketones 728  |
| <b>6.2</b>  | Nucleophilicity of Some Common Nucleophiles 216   | <b>19.1</b> | Systematic and Common Names of Some Carboxylic Acids 744  |
| <b>6.3</b>  | Properties of Some Solvents Used in Nucleophilic Substitution 223                                       | <b>19.2</b> | Effect of Substituents on Acidity of Carboxylic Acids 749   |
| <b>6.4</b>  | Relative Rate of $S_N2$ Displacement of 1-Bromobutane by Azide in Various Solvents 224                  | <b>19.3</b> | Acidity of Some Substituted Benzoic Acids 751   |
| <b>6.5</b>  | Relative Rate of $S_N1$ Solvolysis of <i>tert</i> -Butyl Chloride as a Function of Solvent Polarity 225 | <b>19.4</b> | Summary of Reactions Discussed in Earlier Chapters That Yield Carboxylic Acids 756                    |
| <b>6.6</b>  | Approximate Relative Leaving-Group Abilities 227  | <b>19.5</b> | Summary of Reactions of Carboxylic Acids Discussed in Earlier Chapters 759                            |
| <b>6.7</b>  | Comparison of $S_N1$ and $S_N2$ Mechanisms of Nucleophilic Substitution in Alkyl Halides 231            | <b>20.1</b> | Conversion of Acyl Chlorides to Other Carboxylic Acid Derivatives 783                                 |
| <b>7.1</b>  | Preparation of Alkenes by Elimination Reactions of Alcohols and Alkyl Halides 273                       | <b>20.2</b> | Conversion of Acid Anhydrides to Other Carboxylic Acid Derivatives 785                                |
| <b>8.1</b>  | Heats of Hydrogenation of Some Alkenes 284  | <b>20.3</b> | Preparation of Esters 788   |
| <b>8.2</b>  | Addition Reactions of Alkenes 310   | <b>20.4</b> | Conversion of Esters to Other Carboxylic Acid Derivatives 789   |
| <b>9.1</b>  | Structural Features of Ethane, Ethylene, and Acetylene 326  | <b>20.5</b> | Intermolecular Forces in Amides 799   |
| <b>9.2</b>  | Preparation of Alkynes 341  | <b>20.6</b> | Preparation of Nitriles 808   |
| <b>10.1</b> | Some Bond Dissociation Enthalpies 351   | <b>21.1</b> | Enolization Equilibria (keto $\rightleftharpoons$ enol) of Some Carbonyl Compounds 827                |
| <b>10.2</b> | Some Compounds with Carbon–Carbon Double Bonds Used to Prepare Polymers 368                             | <b>21.2</b> | $pK_a$ Values of Some Aldehydes, Ketones, and Esters 831  |
| <b>12.1</b> | Names of Some Frequently Encountered Derivatives of Benzene 420   | <b>22.1</b> | Basicity of Amines As Measured by the $pK_a$ of Their Conjugate Acids 870                             |
| <b>12.2</b> | Reactions Involving Alkyl and Alkenyl Side Chains in Arenes and Arene Derivatives 454                   | <b>22.2</b> | Effect of <i>para</i> Substituents on the Basicity of Aniline 872                                     |
| <b>13.1</b> | Representative Electrophilic Aromatic Substitution Reactions of Benzene 465                             | <b>22.3</b> | Methods for Carbon–Nitrogen Bond Formation Discussed in Earlier Chapters 877                          |

- 22.4** Reactions of Amines Discussed in Previous Chapters 886
- 22.5** Preparation of Amines 903
- 22.6** Reactions of Amines Discussed in This Chapter 905
- 22.7** Synthetically Useful Transformations Involving Aryl Diazonium Ions (Section 22.17) 906
- 23.1** Comparison of Physical Properties of an Arene, a Phenol, and an Aryl Halide 923
- 23.2** Acidities of Some Phenols 924
- 23.3** Electrophilic Aromatic Substitution Reactions of Phenols 928
- 24.1** Some Classes of Monosaccharides 951
- 24.2** Familiar Reaction Types of Carbohydrates 978
- 25.1** Some Representative Fatty Acids 999
- 25.2** Classification of Terpenes 1010
- 26.1** The Standard Amino Acids 1036
- 26.2** Acid–Base Properties of Amino Acids with Neutral Side Chains 1041
- 26.3** Acid–Base Properties of Amino Acids with Ionizable Side Chains 1042
- 26.4** Covalent and Noncovalent Interactions Between Amino Acid Side Chains in Proteins 1074
- 27.1** Pyrimidines and Purines That Occur in DNA and/or RNA 1091
- 27.2** The Major Pyrimidine and Purine Nucleosides in RNA and DNA 1093
- 27.3**  $\Delta G^\circ$  for the Hydrolysis of Bioenergetically Important Phosphates 1097
- 27.4** The Genetic Code (Messenger RNA Codons) 1107
- 27.5** Distribution of DNAs with Increasing Number of PCR Cycles 1115
- 28.1** Recycling of Plastics 1133
- 28.2** Summary of Alkene Polymerizations Discussed in Earlier Chapters 1135

## Boxed Essays

### Chapter 1

- Organic Chemistry: The Early Days 3
- Electrostatic Potential Maps 13
- Molecular Models and Modeling 26

### Chapter 2

- Methane and the Biosphere 59
- What's in a Name? Organic Nomenclature 70
- Thermochemistry 82

### Chapter 3

- Computational Chemistry: Molecular Mechanics and Quantum Mechanics 101
- Enthalpy, Free Energy, and Equilibrium Constant 111

### Chapter 4

- Homochirality and Symmetry Breaking 142
- Chiral Drugs 147
- Chirality of Disubstituted Cyclohexanes 153

### Chapter 6

- Enzyme-Catalyzed Nucleophilic Substitutions of Alkyl Halides 217

### Chapter 7

- Ethylene 241

### Chapter 8

- Rules, Laws, Theories, and the Scientific Method 289

### Chapter 9

- Some Things That Can Be Made from Acetylene . . . But Aren't 338

### Chapter 10

- From Bond Enthalpies to Heats of Reaction 353
- Ethylene and Propene: The Most Important Industrial Organic Chemicals 367

### Chapter 11

- Diene Polymers 393

### Chapter 12

- Fullerenes, Nanotubes, and Graphene 424
- Triphenylmethyl Radical Yes, Hexaphenylethane No 430

### Chapter 13

- Biosynthetic Halogenation 472

### Chapter 14

- Ring Currents: Aromatic and Antiaromatic 530
- Magnetic Resonance Imaging (MRI) 543
- Spectra by the Thousands 554

### Chapter 15

- An Organometallic Compound That Occurs Naturally: Coenzyme B<sub>12</sub> 597

### Chapter 16

- Sustainability and Organic Chemistry 636

### Chapter 17

- Polyether Antibiotics 662

### Chapter 18

- Imines in Biological Chemistry 717

### Chapter 20

- $\beta$ -Lactam Antibiotics 806

### Chapter 21

- From the Mulberry Tree to Cancer Chemotherapy 838
- The Haloform Reaction and the Biosynthesis of Trihalomethanes 847

### Chapter 22

- Amines as Natural Products 874
- From Dyes to Sulfa Drugs 899

### Chapter 23

- James Bond, Oxidative Stress, and Antioxidant Phenols 933

### Chapter 24

- How Sweet It Is! 976

### Chapter 25

- Nonsteroidal Antiinflammatory Drugs (NSAIDs) and COX-2 Inhibitors 1008
- Good Cholesterol? Bad Cholesterol? What's the Difference? 1020
- Crocuses Make Saffron from Carotenes 1024

### Chapter 26

- Electrophoresis 1043
- Peptide Mapping and MALDI Mass Spectrometry 1062
- Oh NO! It's Inorganic! 1078

**Chapter 27**

"It Has Not Escaped Our Notice . . ." 1100

**Chapter 28**

Conducting Polymers 1148

**Descriptive Passage and Interpretive Problems****Chapter 1**

Amide Lewis Structural Formulas 51

**Chapter 2**

Some Biochemical Reactions of Alkanes 93

**Chapter 3**

Cyclic Forms of Carbohydrates 128

**Chapter 4**

Prochirality 165

**Chapter 5**

More About Potential Energy Diagrams 204

**Chapter 6**

Nucleophilic Substitution 236

**Chapter 7**

A Mechanistic Preview of Addition Reactions 279

**Chapter 8**

Oxymercuration 319

**Chapter 9**

Thinking Mechanistically About Alkynes 346

**Chapter 10**

Free-Radical Reduction of Alkyl Halides 373

**Chapter 11**

1,3-Dipolar Cycloaddition 411

**Chapter 12**

Substituent Effects on Reaction Rates and Equilibria 461

**Chapter 13**

Benzyne 515

**Chapter 14**

More on Coupling Constants 581

**Chapter 15**

Cyclobutadiene and (Cyclobutadiene)tricarbonyliron 618

**Chapter 16**

The Pinacol Rearrangement 653

**Chapter 17**

Epoxide Rearrangements and the NIH Shift 688

**Chapter 18**

The Baeyer–Villiger Oxidation 738

**Chapter 19**

Lactonization Methods 774

**Chapter 20**

Thioesters 822

**Chapter 21**

The Enolate Chemistry of Dianions 861

**Chapter 22**

Synthetic Applications of Enamines 916

**Chapter 23**

Directed Metalation of Aryl Ethers 947

**Chapter 24**

Emil Fischer and the Structure of (+)-Glucose 992

**Chapter 25**

Polyketides 1031

**Chapter 26**

Amino Acids in Enantioselective Synthesis 1085

**Chapter 27**

Oligonucleotide Synthesis 1121

**Chapter 28**

Chemically Modified Polymers 1153



# Preface

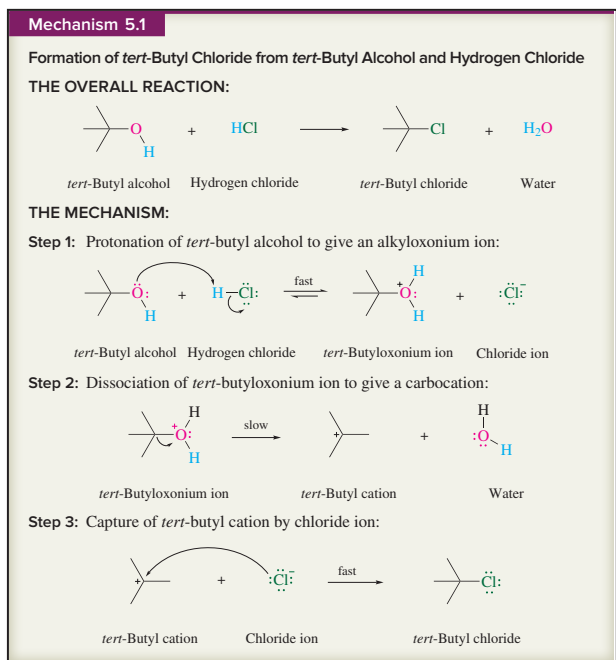
## Overview

The power of X-ray crystallographic analysis was cited in Dorothy Crowfoot Hodgkin's 1964 Chemistry Nobel Prize Lecture:

A great advantage of X-ray analysis as a method of chemical structure analysis is its power to show some totally unexpected and surprising structure with, at the same time, complete certainty.

From Linus Pauling's 1954 Nobel Prize for research on the chemical bond, to Dorothy Crowfoot Hodgkin's in 1964 for solving the structure of vitamin B<sub>12</sub> and other biochemical substances, to Robert Lefkowitz and Brian Kobilka's in 2012 for solving the structure of G protein-coupled receptors, chemists of all persuasions have shared a common interest in the structure of molecules. It is this common interest in structure that has guided the shaping of this edition. Its most significant change is the relocation of chirality, previously a Chapter 7 topic, to Chapter 4 where it now is closer to the other fundamental structural concepts such as molecular shape, constitution, and conformation. A broader background in structure, acquired earlier in this new presentation, is designed to provide students the conceptual tools they need to understand and apply the relationship between the structures of organic compounds and their properties.

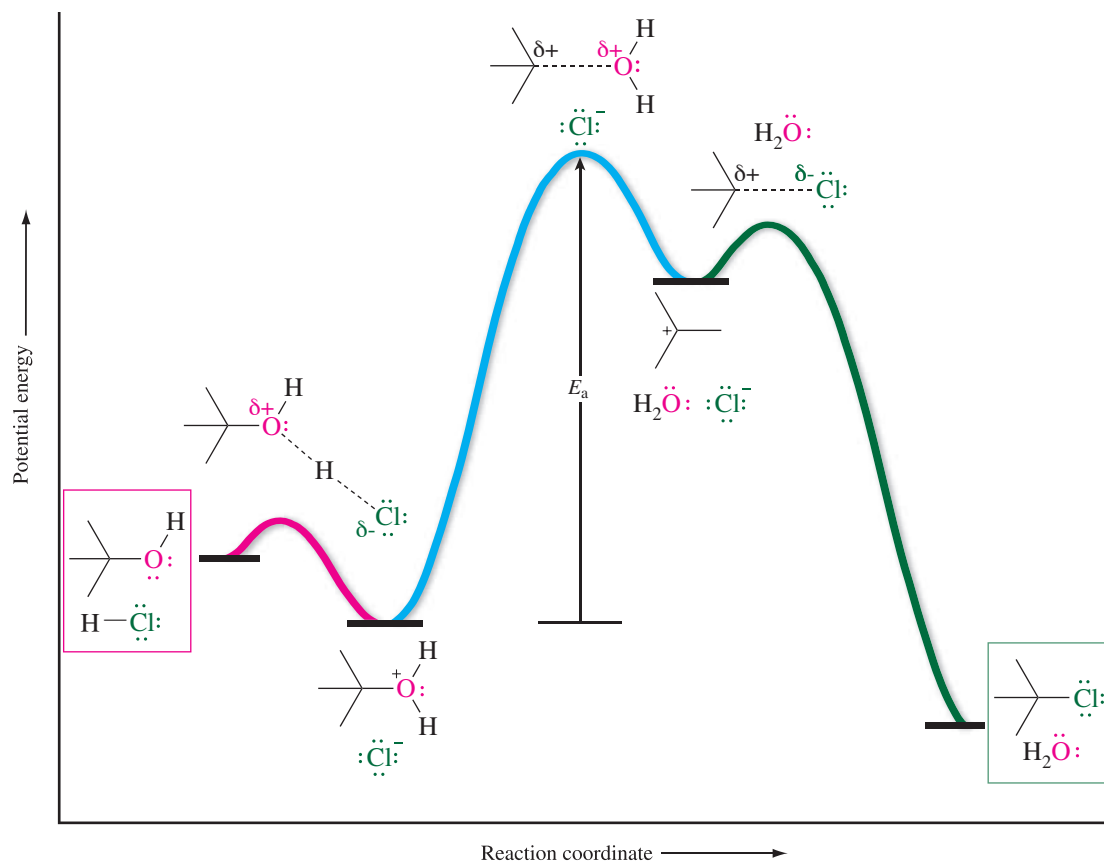
## Mechanism



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<sub>N</sub>1 Mechanism” shows how the potential energy diagrams for three elementary steps are combined to give the diagram for the overall reaction.



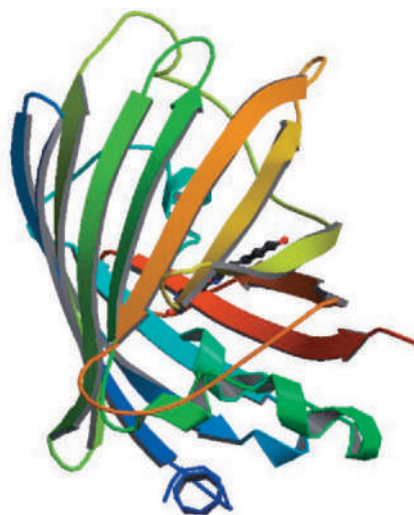
## Enhanced Graphics

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 24 Carbohydrates
- ▶ Chapter 25 Lipids
- ▶ Chapter 26 Amino Acids, Peptides, and Proteins
- ▶ Chapter 27 Nucleosides, Nucleotides, and Nucleic Acids



**Figure 26.16**

Barrel-shaped green fluorescent protein (GFP) has an outer  $\beta$ -sheet structure and an  $\alpha$  helix in the inner region.



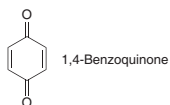
## Generous and Effective Use of Tables

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.

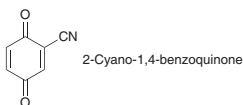
### Problem 11.18

Dicarbonyl compounds such as quinones are reactive dienophiles.

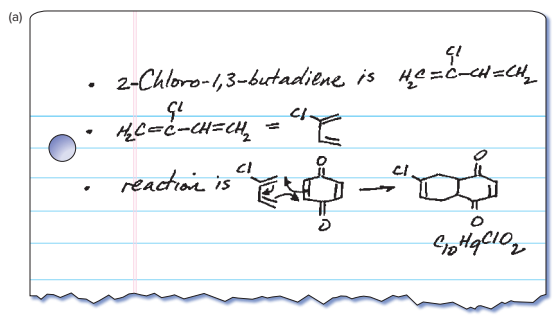
(a) 1,4-Benzoquinone reacts with 2-chloro-1,3-butadiene to give a single product  $C_{10}H_9ClO_2$  in 95% yield. Write a structural formula for this product.



(b) 2-Cyano-1,4-benzoquinone undergoes a Diels-Alder reaction with 1,3-butadiene to give a single product  $C_{11}H_9NO_2$  in 84% yield. What is its structure?

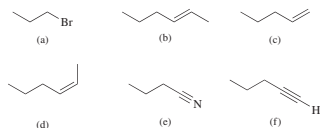


### Sample Solution



### Synthesis

10.29 Outline a synthesis of each of the following compounds from isopropyl alcohol. A compound prepared in one part can be used as a reactant in another. (*Hint:* Which of the compounds shown can serve as a starting material to all the others?)



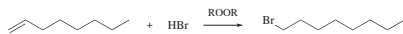
10.30 Guiding your reasoning by retrosynthetic analysis, show how you could prepare each of the following compounds from the given starting material and any necessary organic or inorganic reagents. All require more than one synthetic step.

- Cyclopentyl iodide from cyclopentane
- 1-Bromo-2-methylpropane from 2-bromo-2-methylpropane
- meso*-2,3-Dibromobutane from 2-butyne
- 1-Heptene from 1-bromopentane
- cis*-2-Hexene from 1,2-dibromopentane
- Butyl methyl ether ( $CH_3CH_2CH_2CH_2OCH_3$ ) from 1-butene
- from

10.31 (*Z*)-9-Tricosene [ $(Z)$ - $CH_3(CH_2)_7CH=CH(CH_2)_{14}CH_3$ ] is the sex pheromone of the female housefly. Synthetic (*Z*)-9-tricosene is used as bait to lure male flies to traps that contain insecticide. Using acetylene and alcohols of your choice as starting materials, along with any necessary inorganic reagents, show how you could prepare (*Z*)-9-tricosene.

### Mechanism

10.32 Suggest a reasonable mechanism for the following reaction. Use curved arrows to show electron flow.



10.33 Cyclopropyl chloride has been prepared by the free-radical chlorination of cyclopropane. Write a stepwise mechanism for this reaction.

TABLE 24.2 Familiar Reaction Types of Carbohydrates

Reaction and comments	Example
1. <b>Reduction:</b> Carbonyl groups in carbohydrates are reduced by the same methods used for aldehydes and ketones: reduction with sodium borohydride or lithium aluminum hydride or by catalytic hydrogenation.	
2. <b>Cyanohydrin formation:</b> Reaction of an aldose with HCN gives a mixture of two diastereomeric cyanohydrins.	
3. <b>Acylation:</b> All available hydroxyl groups of carbohydrates are capable of undergoing acylation to form esters.	
4. <b>Alkylation:</b> Carbohydrate hydroxyl groups react with alkyl halides, especially methyl and benzyl halides, to give ethers.	
5. <b>Acetal formation:</b> Carbohydrates can serve as the diol component in the formation of cyclic acetals on reaction with aldehydes and ketones in the presence of an acid catalyst. In the example shown, the catalyst is a Lewis acid.	
6. <b>Pyranose-furanose isomerization:</b> The furanose and pyranose forms of a carbohydrate are cyclic hemiacetals and equilibrate by way of their open-chain isomer.	
7. <b>Enolization:</b> Enolization of the open-chain form of a carbohydrate gives an enediol. Carbohydrates that are epimeric at C-2 give the same enediol.	

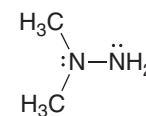
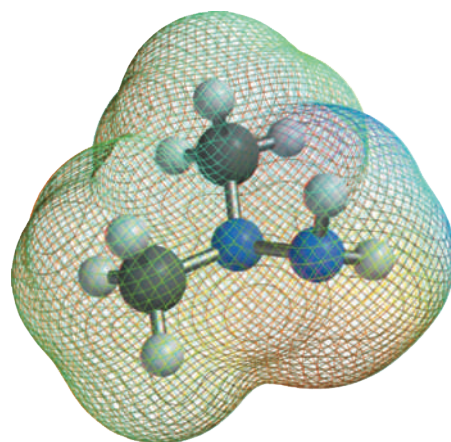
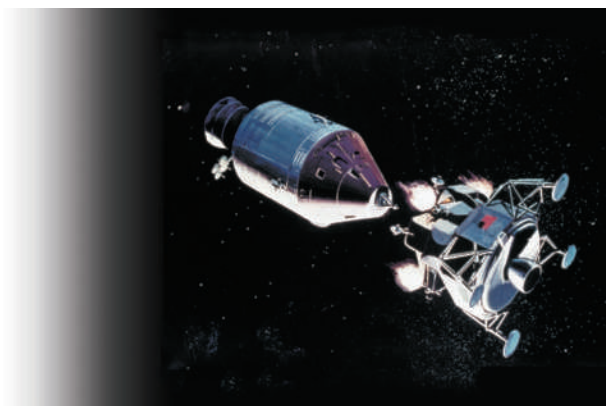
## Problems

- 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 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.

## Opener for Chapter 1



The Apollo lunar module is powered by a liquid fuel containing a mixture of substances, each with its own ignition characteristics and energy properties. One of the fuels is called UDMH, which stands for “unsymmetrical dimethylhydrazine.” Its chemical name is *N,N*-dimethylhydrazine.

- End-of-Chapter Summaries highlight and consolidate all of the important concepts and reactions within a chapter.

**TABLE 8.2** Addition Reactions of Alkenes

Reaction (section) and Comments	General Equation and Specific Example
<p><b>Catalytic hydrogenation (Sections 8.1–8.3)</b> Alkenes react with hydrogen in the presence of a platinum, palladium, rhodium, or nickel catalyst to form the corresponding alkane. Both hydrogens add to the same face of the double bond (syn addition). Heats of hydrogenation can be used to compare the relative stability of various double-bond types.</p>	$\text{R}_2\text{C}=\text{CR}_2 + \text{H}_2 \xrightarrow{\text{Pt, Pd, Rh, or Ni}} \text{R}_2\text{CHCHR}_2$ <p>Alkene                      Hydrogen                      Alkane</p> <p><i>cis</i>-Cyclododecene                      Cyclododecane (100%)</p>
<p><b>Addition of hydrogen halides (Sections 8.4–8.5)</b> A proton and a halogen add to the double bond of an alkene to yield an alkyl halide. Addition proceeds in accordance with Markovnikov's rule: hydrogen adds to the carbon that has the greater number of hydrogens, halide to the carbon that has the fewer hydrogens. The regioselectivity is controlled by the relative stability of the two possible carbocation intermediates. Because the reaction involves carbocations, rearrangement is possible.</p>	$\text{RCH}=\text{CR}'_2 + \text{HX} \longrightarrow \text{RCH}_2-\underset{\text{X}}{\text{CR}'_2}$ <p>Alkene                      Hydrogen halide                      Alkyl halide</p> <p>Methylene-cyclohexane                      Hydrogen chloride                      1-Chloro-1-methylcyclohexane (75–80%)</p>
<p><b>Acid-catalyzed hydration (Section 8.6)</b> Addition of water to the double bond of an alkene takes place according to Markovnikov's rule in aqueous acid. A carbocation is an intermediate and is captured by a molecule of water acting as a nucleophile. Rearrangements are possible.</p>	$\text{RCH}=\text{CR}'_2 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{RCH}_2-\underset{\text{OH}}{\text{CR}'_2}$ <p>Alkene                      Water                      Alcohol</p> <p>2-Methylpropene                      50% H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O                      <i>tert</i>-Butyl alcohol (55–58%)</p>
<p><b>Hydroboration–oxidation (Sections 8.8–8.9)</b> This two-step sequence converts alkenes to alcohols with a regioselectivity opposite to Markovnikov's rule. Addition of H and OH is stereospecific and syn. The reaction involves electrophilic addition of a boron hydride to the double bond, followed by oxidation of the intermediate organoborane with hydrogen peroxides. Carbocations are not intermediates and rearrangements do not occur.</p>	$\text{RCH}=\text{CR}'_2 \xrightarrow[2. \text{H}_2\text{O}_2, \text{HO}^-]{1. \text{B}_2\text{H}_6, \text{diglyme}} \text{RCH}(\text{OH})-\text{CHR}'_2$ <p>Alkene                      Alcohol</p> <p>4-Methyl-1-pentene                      4-Methyl-1-pentanol (80%)</p>
<p><b>Addition of Halogens (Section 8.10)</b> Reactions with Br<sub>2</sub> or Cl<sub>2</sub> are the most common and yield vicinal dihalides except when the reaction is carried out in water. In water, the product is a vicinal halohydrin. The reactions involve a cyclic halonium ion intermediate and are stereospecific (anti addition). Halohydrin formation is regioselective; the halogen bonds to the carbon of C=C that has the greater number of hydrogens.</p>	$\text{R}_2\text{C}=\text{CR}'_2 + \text{X}_2 \longrightarrow \text{R}_2\text{C}(\text{X})-\text{CR}'_2(\text{X})$ <p>Alkene                      Halogen                      Vicinal dihalide</p> $\text{RCH}=\text{CR}'_2 + \text{X}_2 + \text{H}_2\text{O} \longrightarrow \text{RCH}(\text{X})-\underset{\text{OH}}{\text{CR}'_2} + \text{HX}$ <p>Alkene                      Halogen                      Water                      Vicinal halohydrin                      Hydrogen halide</p>

## 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

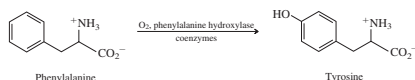
### Descriptive Passage and Interpretive Problems 17

#### Epoxide Rearrangements and the NIH Shift

This passage is about two seemingly unrelated aspects of epoxides:

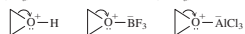
1. epoxide rearrangements
2. arene oxides

These two topics merge in an important biological transformation in which neither the reactant nor the product is an epoxide—the conversion of the amino acid phenylalanine to tyrosine.



#### Epoxide rearrangements

In some epoxide ring-opening reactions C—O bond cleavage is accompanied by the development of enough carbocation character at carbon ( $\delta^+$  C—O) to allow rearrangement to occur. These reactions are typically promoted by protonation of the epoxide oxygen or by its coordination to Lewis acids such as boron trifluoride ( $\text{BF}_3$ ) and aluminum chloride ( $\text{AlCl}_3$ ).



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.

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 28 passages—listed on page xix—are accompanied by more than 100 total multiple-choice problems.

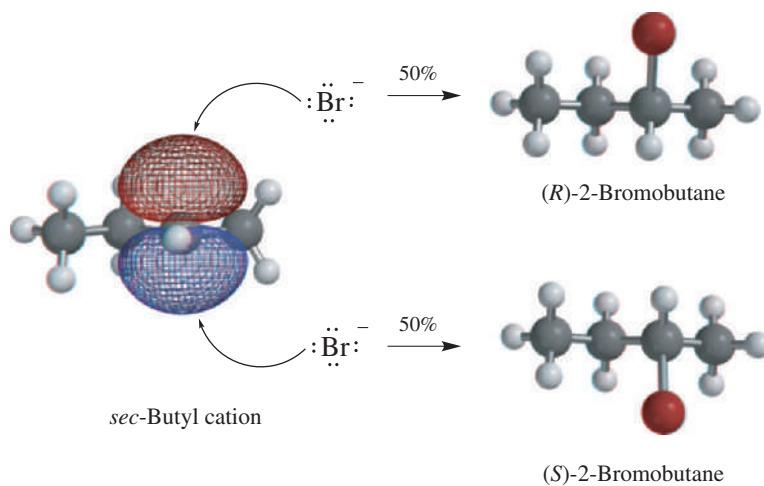
The passages focus on a wide range of topics—

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.

## What's New

- Chirality has been moved from its place as Chapter 7 in previous editions to Chapter 4 here and required major changes in this chapter and in the chapters on nucleophilic substitution and alkenes as well. For example, electrophilic additions to alkenes are not revisited to cover their stereochemical aspects. These additions now appear in the appropriate alkene chapter along with their mechanism and stereochemical details. An example is the addition of HB to 1-butene.



Spiraling through topics is reduced with the earlier placement of chirality and chapter reorganization, allowing some topics to be explained in greater detail. Stereoelectronic effects in E2 eliminations, for example, are now presented as another example of a stereospecific process.

- ▶ Nucleophilic substitution, previously Chapters 4 and 8, is now covered back-to-back in Chapters 5 and 6. This change makes for a tighter presentation in the early part of the book where mechanisms are first introduced.
- ▶ A new chapter on the chemistry of free radicals, Chapter 10 has been added. This change improves topic flow in the first chapter on nucleophilic substitution and allows a more unified approach to free-radical chemistry.
- ▶ A new Descriptive Passage and Interpretive Problems “Free-Radical Reduction of Alkyl Halides” has been added to the new chapter on free radicals. Likewise, a new Descriptive Passage “1,3-Dipolar Cycloaddition” has been added to Chapter 11.
- ▶ The revision of **structural drawings** to bond-line format, begun in previous editions, continues. These drawings not only reflect common usage in organic chemistry as it is practiced and taught, but also foster a closer connection between what the student reads in the text, what the instructor presents in the class, what is used throughout the electronic resources in Connect and SmartBook, and what appears on examinations.
- ▶ All end-of-chapter problems are now grouped according to topic. This should allow students to identify and focus more readily on specific areas where they need more practice.
- ▶ Several new chapter openers have been created for this edition.



# connect<sup>®</sup>

## Required=Results

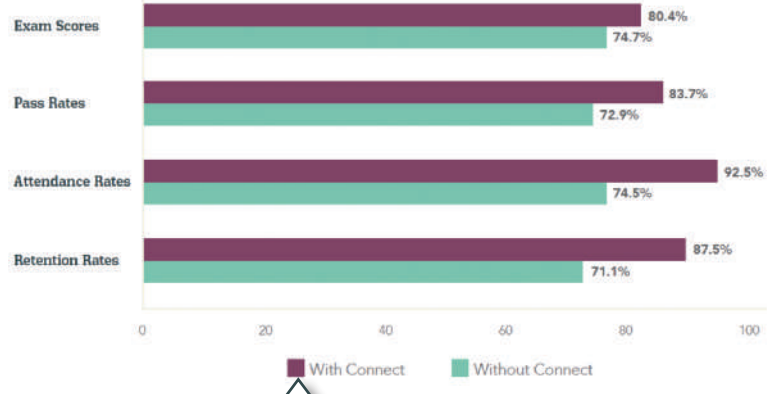


### McGraw-Hill Connect<sup>®</sup> Learn Without Limits

Connect is a teaching and learning platform that is proven to deliver better results for students and instructors.

Connect empowers students by continually adapting to deliver precisely what they need, when they need it, and how they need it, so your class time is more engaging and effective.

Course outcomes improve with Connect.



Using **Connect** improves passing rates by **10.8%** and retention by **16.4%**.

88% of instructors who use **Connect** require it; instructor satisfaction increases by 38% when **Connect** is required.

## Analytics

### Connect Insight<sup>®</sup>

Connect Insight is Connect's new one-of-a-kind visual analytics dashboard—now available for both instructors and students—that provides at-a-glance information regarding student performance, which is immediately actionable. By presenting assignment, assessment, and topical performance results together with a time metric that is easily visible for aggregate or individual results, Connect Insight gives the user the ability to take a just-in-time approach to teaching and learning, which was never before available. Connect Insight presents data that empowers students and helps instructors improve class performance in a way that is efficient and effective.

Connect helps students achieve better grades



Based on McGraw-Hill Education Connect Effectiveness Study 2013

Students can view their results for any **Connect** course.

## Mobile

Connect's new, intuitive mobile interface gives students and instructors flexible and convenient, anytime-anywhere access to all components of the Connect platform.





# Adaptive



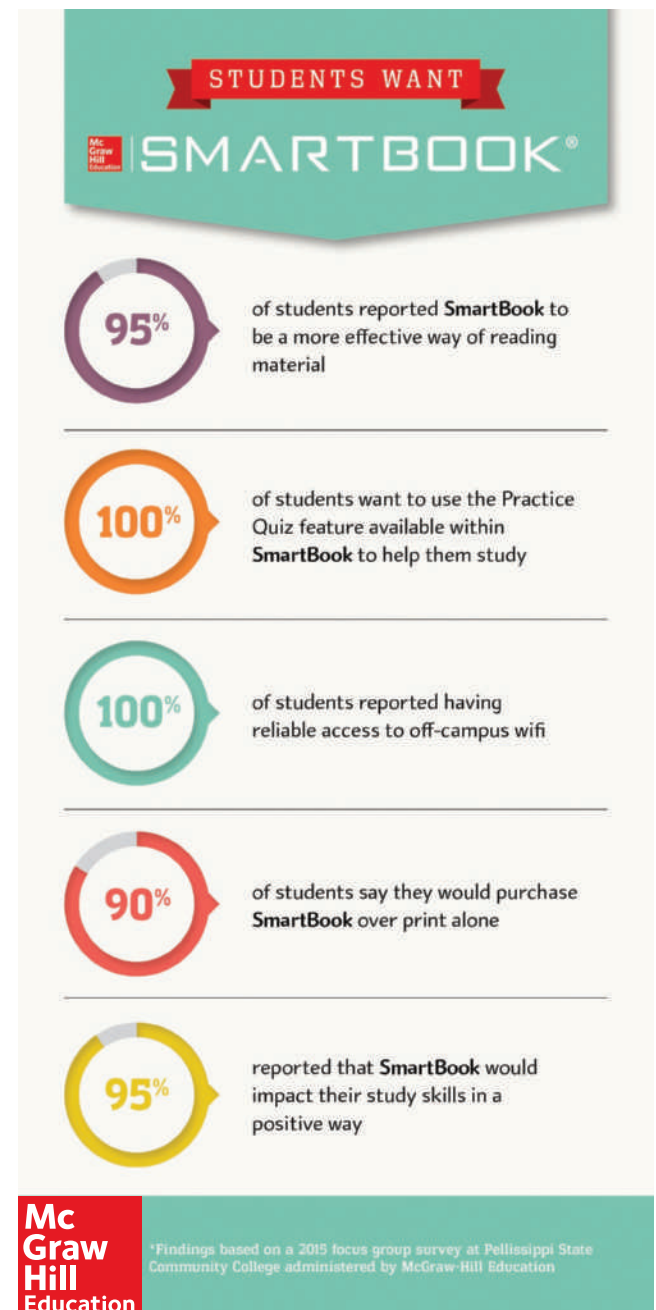
More students earn **A's** and **B's** when they use McGraw-Hill Education **Adaptive** products.

## SmartBook<sup>®</sup>

Proven to help students improve grades and study more efficiently, SmartBook contains the same content within the print book, but actively tailors that content to the needs of the individual. SmartBook's adaptive technology provides precise, personalized instruction on what the student should do next, guiding the student to master and remember key concepts, targeting gaps in knowledge and offering customized feedback, and driving the student toward comprehension and retention of the subject matter. Available on smartphones and tablets, SmartBook puts learning at the student's fingertips—anywhere, anytime.

Over **4 billion questions** have been answered, making McGraw-Hill Education products more intelligent, reliable, and precise.

THE FIRST AND ONLY  
**ADAPTIVE READING  
EXPERIENCE DESIGNED  
TO TRANSFORM THE  
WAY STUDENTS READ**



## Instructor Resources

### Presentation Tools

Accessed from the Instructor Resources in the Connect Library, Presentation Tools contains photos, artwork, and 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.
- **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 in the Connect Library are:

- **Classroom Response System Questions** bring interactivity into the classroom or lecture hall. These wireless response systems, which are essentially remotes that are easy to use and engage students, give the instructor and students immediate feedback from the entire class. Wireless response systems allow instructors to motivate student preparation, interactivity, and active learning. 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.
- **Animations** cover the most important mechanisms for *Organic Chemistry* are provided.

### Test Bank

A test bank with over 1300 questions is available with the tenth edition. The Test Bank is available as both Word and PDF files and is assignable through Connect 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.



# ACKNOWLEDGEMENTS

Special thanks to the author of the Student Solutions Manual, Neil Allison, University of Arkansas, who had a monumental task in updating the manual for this edition. The authors also acknowledge the generosity of Sigma-Aldrich for providing almost all of the 300-MHz NMR spectra.

## Reviewers

Hundreds of teachers of organic chemistry have reviewed this text in its various editions. Our thanks to all of them.

The addition of LearnSmart to the McGraw-Hill digital offerings has been invaluable. Thank you to the individuals who gave their time and talent to develop LearnSmart for *Organic Chemistry*.

Margaret R. Asirvatham, *University of Colorado, Boulder*

Peter de Lijser, *California State University, Fullerton*

*Organic Chemistry* is also complemented by the exemplary digital products in Connect. We are extremely appreciative for the talents of the following individuals who played important roles in the authoring and content development for our digital products.

Neil Allison, *University of Arkansas*

Ned B. Bowden, *University of Iowa*

Philip A. Brown, *North Carolina State*

William E. Crowe, *Louisiana State University*

Kimi Hatton, *George Mason University*

Ed Hilinski, *Florida State University*

T. Keith Hollis, *Mississippi State University*

Jennifer A. Irvin, *Texas State University*

Phil Janowicz, *California State University – Fullerton*

Michael Lewis, *Saint Louis University*

James M. Salvador, *University of Texas at El Paso*

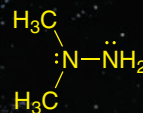
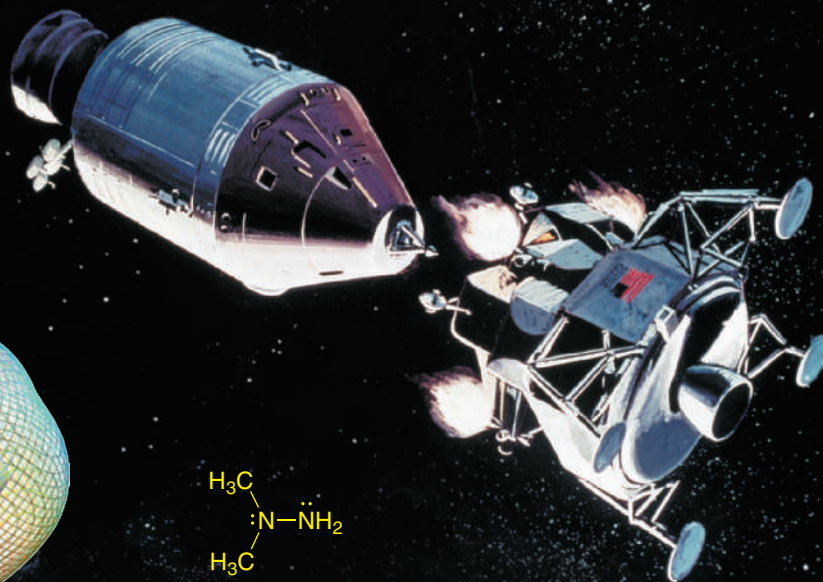
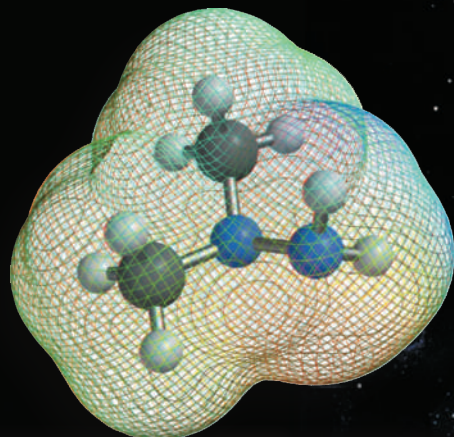
Buchang Shi, *Eastern Kentucky University*

Brooke A. Van Horn, *College of Charleston*

This page intentionally left blank

# Organic Chemistry

# 1



## CHAPTER OUTLINE

- 1.1 Atoms, Electrons, and Orbitals 2
  - Organic Chemistry: The Early Days 3
- 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 13
- 1.5 Formal Charge 13
- 1.6 Structural Formulas of Organic Molecules: Isomers 15
- 1.7 Resonance and Curved Arrows 19
- 1.8 Sulfur and Phosphorus-Containing Organic Compounds and the Octet Rule 23
- 1.9 Molecular Geometries 24
  - Molecular Models and Modeling 26
- 1.10 Molecular Dipole Moments 27
- 1.11 Curved Arrows, Arrow Pushing, and Chemical Reactions 28
- 1.12 Acids and Bases: The Brønsted–Lowry View 30
- 1.13 How Structure Affects Acid Strength 35
- 1.14 Acid–Base Equilibria 39
- 1.15 Acids and Bases: The Lewis View 42
- 1.16 Summary 43
- Problems 46
- Descriptive Passage and Interpretive Problems 1: Amide Lewis Structural Formulas 51

The Apollo lunar module is powered by a liquid fuel containing a mixture of substances, each with its own ignition characteristics and energy properties. One of the fuels is called UDMH, which stands for “unsymmetrical dimethylhydrazine.” Its formula is  $(\text{CH}_3)_2\text{NHNH}_2$  and its chemical name is *N,N*-dimethylhydrazine.

## Structure Determines Properties

**Structure\*** is the key to everything in chemistry. The properties of a substance depend on the atoms it contains and the way these atoms are connected. What is less obvious, but very powerful, is the idea that someone who is trained in chemistry can look at the structural formula of a substance and tell you a lot about its properties. This chapter begins your training toward understanding the relationship between structure and properties in organic compounds. It reviews some fundamental principles of the Lewis approach to molecular structure and bonding. By applying these principles, you will learn to recognize structural patterns that are more stable than others and develop skills in communicating structural information that will be used throughout your study of organic chemistry. A key relationship between structure and properties will be introduced by examining the fundamentals of acid–base chemistry from a structural perspective.

### 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

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

## 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. He is best remembered for a brief paper he published in 1828 in which he 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.



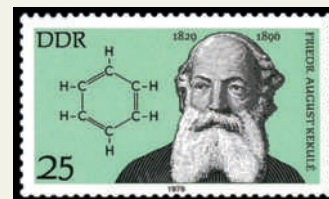
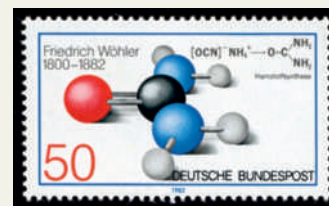
This transformation was remarkable at the time because an *inorganic* salt, ammonium cyanate, was converted to urea, a known *organic* substance earlier isolated from urine. It is now recognized as a significant early step toward overturning the philosophy of vitalism. Although Wöhler himself made no 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 he 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.

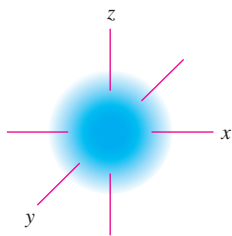
Three mid-nineteenth-century scientists, August Kekulé, Archibald S. Couper, and Alexander M. Butlerov, stand out for separately proposing the elements of the structural theory. The essential features of Kekulé’s theory, developed and presented while he taught at Heidelberg in 1858, were that carbon normally formed four bonds and had the capacity to bond to other carbons so as 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 thereafter, 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.



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).



**Figure 1.1**

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

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



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



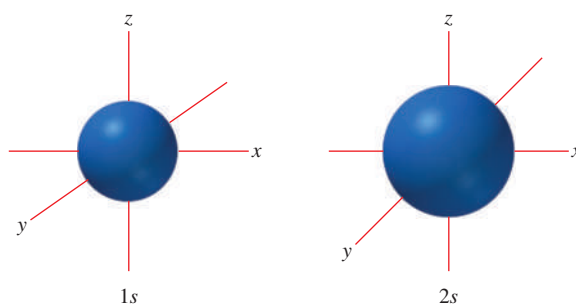
The **period** (or **row**) of the periodic table in which an element appears corresponds to the principal quantum number of the highest numbered occupied orbital ( $n = 1$  in the case of hydrogen and helium). Hydrogen and helium are first-row elements; lithium ( $n = 2$ ) is a second-row element.

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

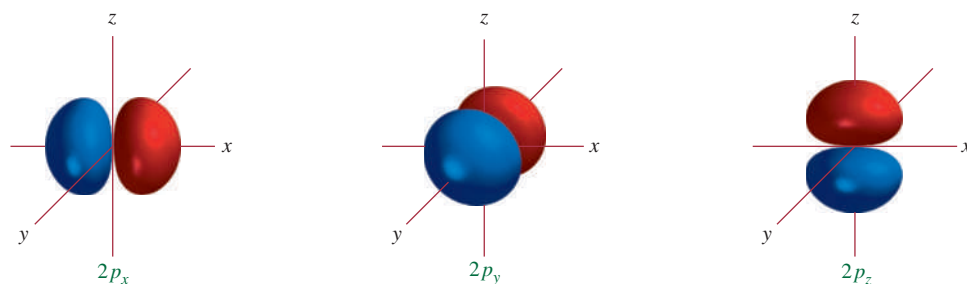
A complete periodic table of the elements is presented at the back of the book.

**Figure 1.2**

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







**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.

“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

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.

**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	$2p_x$	$2p_y$	$2p_z$	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

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.

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

### Problem 1.1

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

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.

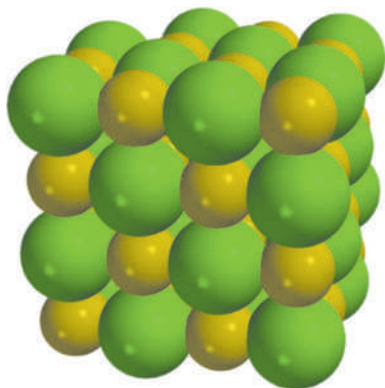
### Problem 1.2

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  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^1$ .

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. The next section illustrates this with a brief review of ionic bonding.



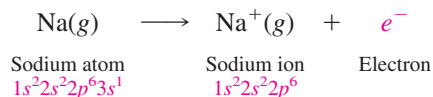
**Figure 1.4**

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 balls are  $\text{Na}^+$  and the larger balls 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.



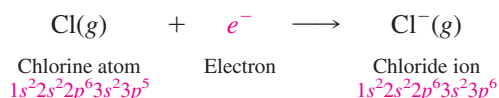
[The symbol (g) indicates that the species is present in the gas phase.]

### Problem 1.3

Species that have the same number of electrons are described as *isoelectronic*. What +2 ion is isoelectronic with  $\text{Na}^+$ ? 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  $\text{Cl}^-$ , 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

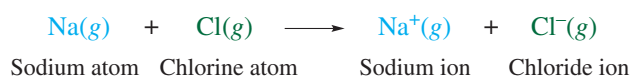
Which of the following ions possess a noble gas electron configuration?

- (a)  $\text{K}^+$                       (c)  $\text{H}^-$                       (e)  $\text{F}^-$   
 (b)  $\text{He}^+$                       (d)  $\text{O}^-$                       (f)  $\text{Ca}^{2+}$

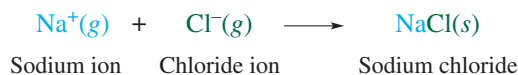
**Sample Solution** (a) Potassium has atomic number 19, and so a potassium atom has 19 electrons. The ion  $\text{K}^+$ , therefore, has 18 electrons, the same as the noble gas argon. The electron configurations of both  $\text{K}^+$  and Ar are  $1s^2 2s^2 2p^6 3s^2 3p^6$ .

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 sodium (496 kJ/mol) and the electron affinity of chlorine ( $-349$  kJ/mol), we would conclude that the overall process is endothermic by  $+147$  kJ/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  $\text{Na}^+$  and  $\text{Cl}^-$ , 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 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.

### Problem 1.5

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

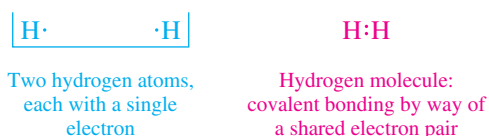
Ionic bonding was proposed by the German physicist Walther Kossel in 1916 in order to explain the ability of substances such as molten sodium chloride to conduct an electric current. He was the son of Albrecht Kossel, winner of the 1910 Nobel Prize in Physiology or Medicine for early studies of nucleic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

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.

Gilbert Newton Lewis has been called the greatest American chemist.

### 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 helium.



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.



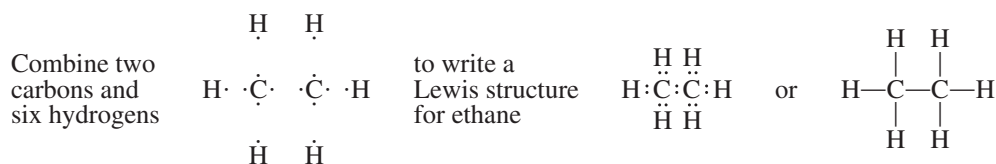
Unshared pairs are also called *lone pairs*.

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 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.

With four valence electrons, carbon normally forms four covalent bonds as shown in Table 1.2 for  $CH_4$ . In addition to C—H bonds, most organic compounds contain covalent C—C bonds. Ethane ( $C_2H_6$ ) is an example.



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

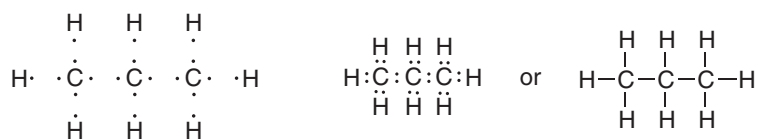
Compound	Atom	Number of valence electrons in atom	Atom and sufficient number of hydrogen atoms to complete octet	Lewis formula	
				Dot	Line
Methane	Carbon	4	$\begin{array}{c} \text{H} \\   \\ \text{H} \cdot \text{C} \cdot \text{H} \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\   \\ \text{H}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

**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:

