# ORGANIC CHEMISTRY

Francis A. Carey Robert M. Giuliano

**EIGHTH EDITION** 

McGRAW-HILL INTERNATIONAL EDITION

# Contents

List of Important Features xvii Preface xxii Acknowledgments xxx

# CHAPTER ]

Structure	<b>Determines</b>	<b>Properties</b>	2
Judelaic	Determines	i roperties	_

- 1.1 Atoms, Electrons, and Orbitals 3
- 1.2 Ionic Bonds 6
- 1.3 Covalent Bonds, Lewis Structures, and the Octet Rule 8
- 1.4 Double Bonds and Triple Bonds 10
- 1.5 Polar Covalent Bonds, Electronegativity, and Bond Dipoles 11

#### **Electrostatic Potential Maps 13**

- 1.6 Formal Charge 13
- 1.7 Structural Formulas of Organic Molecules 16
- 1.8 Resonance 19
- 1.9 Writing Organic Structures 23
- 1.10 The Shapes of Some Simple Molecules 26

  Molecular Modeling 26
- 1.11 Molecular Dipole Moments 28
- 1.12 Curved Arrows and Chemical Reactions 29
- 1.13 Acids and Bases: The Arrhenius View 32
- 1.14 Acids and Bases: The Brønsted-Lowry View 33
- 1.15 What Happened to  $pK_b$ ? 37
- 1.16 How Structure Affects Acid Strength 38
- 1.17 Acid-Base Equilibria 42
- 1.18 Lewis Acids and Lewis Bases 45
- 1.19 Summary 46
  Problems 49

Descriptive Passage and Interpretive Problems 1: Amide Lewis Structures 55

# HAPTER 2

# Alkanes and Cycloalkanes: Introduction to Hydrocarbons 56

- 2.1 Classes of Hydrocarbons 57
- 2.2 Electron Waves and Chemical Bonds 58
- 2.3 Bonding in H<sub>2</sub>: The Valence Bond Model 59
- **2.4** Bonding in H<sub>2</sub>: The Molecular Orbital Model 60

2.5	Introduction to	o Alkanes:	Methane,	Ethane,
	and Propane	62		

#### Methane and the Biosphere 63

- 2.6 sp<sup>3</sup> Hybridization and Bonding in Methane 63
- 2.7 Bonding in Ethane 65
- 2.8 Isomeric Alkanes: The Butanes 65
- 2.9 Higher n-Alkanes 66
- **2.10** The  $C_5H_{12}$  Isomers 67
- 2.11 IUPAC Nomenclature of Unbranched Alkanes 69What's in a Name? Organic Nomenclature 70
- **2.12** Applying the IUPAC Rules: The Names of the  $C_6H_{14}$  Isomers 71
- 2.13 Alkyl Groups 72
- 2.14 IUPAC Names of Highly Branched Alkanes 74
- 2.15 Cycloalkane Nomenclature 75
- 2.16 Sources of Alkanes and Cycloalkanes 76
- 2.17 Physical Properties of Alkanes and Cycloalkanes 78
- 2.18 Chemical Properties: Combustion of Alkanes 80
  Thermochemistry 82
- 2.19 Oxidation-Reduction in Organic Chemistry 83
- 2.20 sp<sup>2</sup> Hybridization and Bonding in Ethylene 85
- 2.21 sp Hybridization and Bonding in Acetylene 87
- **2.22** Bonding in Water and Ammonia: Hybridization of Oxygen and Nitrogen 89
- 2.23 Which Theory of Chemical Bonding Is Best? 90
- 2.24 Summary 91 Problems 95

Descriptive Passage and Interpretive Problems 2: Some Biochemical Reactions of Alkanes 99

# CHAPTER 3

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

- 3.1 Conformational Analysis of Ethane 102
- 3.2 Conformational Analysis of Butane 105

  Molecular Mechanics Applied to Alkanes
  and Cycloalkanes 107
- 3.3 Conformations of Higher Alkanes 108
- 3.4 The Shapes of Cycloalkanes: Planar or Nonplanar? 108
- 3.5 Small Rings: Cyclopropane and Cyclobutane 109
- 3.6 Cyclopentane 110
- **3.7** Conformations of Cyclohexane 111
- 3.8 Axial and Equatorial Bonds in Cyclohexane 112
- 3.9 Conformational Inversion in Cyclohexane 114

viii	Contents
3.10	Conformational Analysis of Monosubstituted Cyclohexanes 115
	Enthalpy, Free Energy, and Equilibrium
	Constant 118
3,11	Disubstituted Cyclohexanes: cis-trans Stereoisomers 119
3.12	Conformational Analysis of Disubstituted
3.13	Cyclohexanes 120 Medium and Large Rings 124
3.14	Polycyclic Ring Systems 124
3.15	Heterocyclic Compounds 127
3.16	Summary 128
3.10	Problems 131
	Descriptive Passage and Interpretive Problems 3:
	Cyclic Forms of Carbohydrates 136
	Λ
	4
CH	APTER
Alco	ohols and Alkyl Halides 137
4.1	Functional Groups 138
4.2	IUPAC Nomenclature of Alkyl Halides 140
4.3	IUPAC Nomenclature of Alcohols 141
4.4	Classes of Alcohols and Alkyl Halides 141
4.5	Bonding in Alcohols and Alkyl Halides 142
4.6	Physical Properties of Alcohols and Alkyl Halides:
	Intermolecular Forces 143
4.7	Preparation of Alkyl Halides from Alcohols
	and Hydrogen Halides 147
4.8	Mechanism of the Reaction of Alcohols with Hydroger
	Halides: Hammond's Postulate 148
	Mechanism 4.1 Formation of tert-Butyl Chloride from tert-Butyl Alcohol and Hydrogen Chloride 149
4.0	Potential Energy Diagrams for Multistep Reactions: The
4.9	S <sub>N</sub> 1 Mechanism 153
4.10	Structure, Bonding, and Stability of
4.10	Carbocations 154
4.11	- 157
4.12	
,,	Halides: The S <sub>N</sub> 2 Mechanism 158

Mechanism 4.2 Formation of 1-Bromoheptane from

Mechanism 4.3 Conversion of an Alcohol to an Alkyl

Other Methods for Converting Alcohols to Alkyl

Structure and Stability of Free Radicals 163 From Bond Energies to Heats of Reaction 167

Mechanism of Methane Chlorination 168

Halogenation of Higher Alkanes 170

Mechanism 4.4 Free-Radical Chlorination of

1-Heptanol and Hydrogen Bromide 159

More on Activation Energy 160

Chloride with Thionyl Chloride 161 Halogenation of Alkanes 162

4.16 Chlorination of Methane 162

Halides 160

Methane 168

4.13

4.14

4.15

4.18

4.19

4.20 Summary 174 Problems 177 Descriptive Passage and Interpretive Problems 4: More About Potential Energy Diagrams 182 CHAPTER Structure and Preparation of Alkenes: **Elimination Reactions** 184 Alkene Nomenclature 185 5.1 Structure and Bonding in Alkenes 187 5.2 Ethylene 188 5.3 Isomerism in Alkenes 189 Naming Stereoisomeric Alkenes by the E-Z Notational 5.4 System 190 Physical Properties of Alkenes 192 5.5 Relative Stabilities of Alkenes 194 5.6 Cycloalkenes 197 5.7 Preparation of Alkenes: Elimination Reactions 198 5.8 Dehydration of Alcohols 199 5.9 Regioselectivity in Alcohol Dehydration: The Zaitsev 5.10 Rule 200 Stereoselectivity in Alcohol Dehydration 202 5.11 5.12 The E1 and E2 Mechanisms of Alcohol Dehydration 202 Mechanism 5.1 The E1 Mechanism for Acid-Catalyzed Dehydration of tert-Butyl Alcohol 203 Rearrangements in Alcohol Dehydration 204 Mechanism 5.2 Carbocation Rearrangement in Dehydration of 3,3-Dimethyl-2-butanol 205 Mechanism 5.3 Hydride Shift in Dehydration of rogen 1-Butanol 207 Dehydrohalogenation of Alkyl Halides 208 5.14 The E2 Mechanism of Dehydrohalogenation of Alkyl Halides 210 s: The Mechanism 5.4 E2 Elimination of an Alkyl Halide 211 Anti Elimination in E2 Reactions: Stereoelectronic 5.16 Effects 212 5.17 Halides 214 Mechanism 5.5 The E1 Mechanism for

Isotope Effects and the E2 Mechanism 213

The E1 Mechanism of Dehydrohalogenation of Alkyl Dehydrohalogenation of 2-Bromo-2-methylbutane in Ethanol 215

5.19 Summary 216 Problems 220 Descriptive Passage and Interpretive Problems 5: A Mechanistic Preview of Addition Reactions 224

# CHAPTER

### Addition Reactions of Alkenes

- Hydrogenation of Alkenes 227 6.1
- Heats of Hydrogenation 228 6.2 Mechanism 6.1 Hydrogenation of Alkenes 229

ix Contents

6.3	Stereochemistry of Alkene Hydrogenation 230	7.3	Sym
6.4	Electrophilic Addition of Hydrogen Halides to	7.4	Opt
	Alkenes 232	7.5	Abso
6.5	Regioselectivity of Hydrogen Halide Addition: Markovnikov's Rule 233	7.6	The Syst
	<b>Mechanism 6.2</b> Electrophilic Addition of a Hydrogen	7.7	Fiscl
	Halide to an Alkene 233	7.7 7.8	Prop
6.6	Mechanistic Basis for Markovnikov's Rule 235	7.9	Chir
0.0	Rules, Laws, Theories, and the Scientific	7.15	Chi
	Method 237	7.10	Rea
6.7	Carbocation Rearrangements in Hydrogen Halide	7.11	Chi
	Addition to Alkenes 237		Cen
6.8	Addition of Sulfuric Acid to Alkenes 239	7.12	Ach
6.9	Acid-Catalyzed Hydration of Alkenes 240	7.13	Mol
	Mechanism 6.3 Acid-Catalyzed Hydration of		Chi
	2-Methylpropene 241	7.14	Rea
6.10	Thermodynamics of Addition-Elimination Equilibria 242	7.15	Res
6.11	Hydroboration-Oxidation of Alkenes 245	7.16	Ster
6.12	Stereochemistry of Hydroboration-Oxidation 247  Mechanism of Hydroboration-Oxidation 247	7.17	Chi
6.13	Mechanism 6.4 Hydroboration of	7.18	Sun
	1-Methylcyclopentene 248		Pro
	Mechanism 6.5 Oxidation of an Organoborane 249		Des
6.14	Addition of Halogens to Alkenes 250		Pro
6.15	Stereochemistry of Halogen Addition 250		
6.16	Mechanism of Halogen Addition to Alkenes:		
	Halonium Ions 251		
	Mechanism 6.6 Electrophilic Addition of Bromine to		
	Ethylene 252	СН	A P T
	Mechanism 6.7 Formation of Bromohydrin 253	<u></u>	
6.17	Conversion of Alkenes to Vicinal Halohydrins 253	Nucleo	
6.18	Free-Radical Addition of Hydrogen Bromide to Alkenes 254		
	Mechanism 6.8 Free-Radical Addition of Hydrogen	8.1	Fun Sub
	Bromide to 1-Butene 256	8.2	Rela
6.19	Epoxidation of Alkenes 257	8.3	The
	Mechanism 6.9 Epoxidation of an Alkene 259	0.5	Suk
6.20	·		Me
6.21	Reactions of Alkenes with Alkenes: Polymerization 261		Sub
	Mechanism 6.10 Acid-Catalyzed Dimerization of	8.4	Ste
	2-Methylpropene 262	8.5	Nu
	Ethylene and Propene: The Most Important	8.6	The
	Industrial Organic Chemicals 263		Sub
	Mechanism 6.11 Free-Radical Polymerization of		En
	Ethylene 264		Alk
6.22			Me
	Problems 269 Descriptive Passage and Interpretive Problems 6:	8.7	Sul Cai
	Oxymercuration 275	8.8	Ste
	Onymerculation are	8.9	Ca
		8.10	Effe
	7	5	Sul

# CHAPTER

### Stereochemistry 278

- Molecular Chirality: Enantiomers 279 7.1
- 7.2 The Chirality Center 281

- metry in Achiral Structures 283
- tical Activity 284
- olute and Relative Configuration 286
- Cahn-Ingold-Prelog R-S Notational tem 288
- her Projections 290
- perties of Enantiomers 292
- rality Axis 293

#### ral Drugs 294

- ctions That Create a Chirality Center 296
- ral Molecules with Two Chirality iters 299
- niral Molecules with Two Chirality Centers 301
- lecules with Multiple Chirality Centers 303 irality of Disubstituted Cyclohexanes 304
- ctions That Produce Diastereomers 305
- olution of Enantiomers 307
- reoregular Polymers 309
- rality Centers Other Than Carbon 310
- nmary 311 blems 314 scriptive Passage and Interpretive Problems 7: chirality 320

#### philic Substitution 322

- nctional Group Transformation by Nucleophilic ostitution 323
- ative Reactivity of Halide Leaving Groups 326
- e S<sub>N</sub>2 Mechanism of Nucleophilic bstitution 327
  - chanism 8.1 The S<sub>N</sub>2 Mechanism of Nucleophilic bstitution 327
- eric Effects in S<sub>N</sub>2 Reaction Rates 330
- icleophiles and Nucleophilicity 332
- e S<sub>N</sub>1 Mechanism of Nucleophilic bstitution 334

#### zyme-Catalyzed Nucleophilic Substitutions of kyl Halides 335

- echanism 8.2 The S<sub>N</sub>1 Mechanism of Nucleophilic bstitution 336
- rbocation Stability and S<sub>N</sub>1 Reaction Rates 337
- ereochemistry of S<sub>N</sub>1 Reactions 338
- rbocation Rearrangements in S<sub>N</sub>1 Reactions 339
- ect of Solvent on the Rate of Nucleophilic bstitution 340
  - Mechanism 8.3 Carbocation Rearrangement in the S<sub>N</sub>1 Hydrolysis of 2-Bromo-3-methylbutane 340
- Substitution and Elimination as Competing 8.11 Reactions 344
- 8.12 Nucleophilic Substitution and Elimination of Alkyl Sulfonates 347

8.13 Summary 350
Problems 351
Descriptive Passage and Interpretive Problems 8:
Nucleophilic Substitution 356

# CHAPTER 9

### Alkynes 359

9.1	Sources	of	Alkynes	360

- 9.2 Nomenclature 362
- 9.3 Physical Properties of Alkynes 362
- **9.4** Structure and Bonding in Alkynes: *sp* Hybridization 362
- 9.5 Acidity of Acetylene and Terminal Alkynes 365
- **9.6** Preparation of Alkynes by Alkyation of Acetylene and Terminal Alkynes 367
- 9.7 Preparation of Alkynes by Elimination Reactions 368
- 9.8 Reactions of Alkynes 370
- 9.9 Hydrogenation of Alkynes 370
- 9.10 Metal-Ammonia Reduction of Alkynes 372
- 9.11 Addition of Hydrogen Halides to Alkynes 373Mechanism 9.1 Sodium–Ammonia Reduction of an Alkyne 373
- 9.12 Hydration of Alkynes 375

**Mechanism 9.2** Conversion of an Enol to a Ketone 376

Ketone 3/6

9.13 Addition of Halogens to Alkynes 377

Some Things Can Be Made from Acetylene . . .
But Aren't 378

- 9.14 Ozonolysis of Alkynes 378
- 9.15 Summary 379 Problems 382

Descriptive Passage and Interpretive Problems 9: Thinking Mechanistically About Alkynes 386

# CHAPTER 10

# Conjugation in Alkadienes and Allylic Systems 388

- 10.1 The Allyl Group 389
- 10.2 Allylic Carbocations 390
- 10.3 S<sub>N</sub>1 Reactions of Allylic Halides 392
   Mechanism 10.1 Hydrolysis of an Allylic Halide 393
- 10.4 S<sub>N</sub>2 Reactions of Allylic Halides 394
- 10.5 Allylic Free Radicals 395
- **10.6** Allylic Halogenation 396

Mechanism 10.2 Allylic Chlorination of Propene 397

- 10.7 Allylic Anions 399
- 10.8 Classes of Dienes 400
- 10.9 Relative Stabilities of Dienes 401

- 10.10 Bonding in Conjugated Dienes 402
- 10.11 Bonding in Allenes 404
- **10.12** Preparation of Dienes 405

#### Diene Polymers 406

- 10.13 Addition of Hydrogen Halides to Conjugated Dienes 407
  - **Mechanism 10.3** Addition of Hydrogen Chloride to 1,3 Cyclopentadiene 408
- 10.14 Halogen Addition to Dienes 409
- 10.15 The Diels-Alder Reaction 410
- 10.16 The  $\pi$  Molecular Orbitals of Ethylene and 1,3-Butadiene 415
- 10.17 A π Molecular Orbital Analysis of the Diels-Alder Reaction 417
   Mechanism 10.4 Orbital Interaction in the Diels-Alder Reaction 417
- 10.18 Summary 418

Problems 421

Descriptive Passage and Interpretive Problems 10: Intramolecular and Retro Diels-Alder Reactions 425

# CHAPTER 11

# Arenes and Aromaticity 428

- 11.1 Benzene 429
- 11.2 The Structure of Benzene 430
- 11.3 The Stability of Benzene 432
- **11.4** An Orbital Hybridization View of Bonding in Benzene 433
- 11.5 The  $\alpha$  Molecular Orbitals of Benzene 434
- 11.6 Substituted Derivatives of Benzene and Their Nomenclature 435
- 11.7 Polycyclic Aromatic Hydrocarbons 438
- **11.8** Physical Properties of Arenes 439

#### Carbon Clusters, Fullerenes, and Nanotubes 440

- 11.9 Reactions of Arenes: A Preview 440
- 11.10 The Birch Reduction 442
- 11.11 Free-Radical Halogenation of Alkylbenzenes 442Mechanism 11.1 The Birch Reduction 443
- 11.12 Oxidation of Alkylbenzenes 446
- 11.13 S<sub>N</sub>1 Reactions of Benzylic Halides 448
- 11.14 S<sub>N</sub>2 Reactions of Benzylic Halides 449
- 11.15 Preparation of Alkenylbenzenes 450
- 11.16 Addition Reactions of Alkenylbenzenes 451
- 11.17 Polymerization of Styrene 453
  - **Mechanism 11.2** Free-Radical Polymerization of Styrene 453
- 11.18 Cyclobutadiene and Cyclooctatetraene 454
- 11.19 Hückel's Rule 456
- 11.20 Annulenes 458
- 11.21 Aromatic Ions 460
- 11.22 Heterocyclic Aromatic Compounds 463
- **11.23** Heterocyclic Aromatic Compounds and Hückel's Rule 465
- 11.24 Summary 467

Problems 470 Descriptive Passage and Interpretive Problems 11: The Hammett Equation 474

12

# CHAPTER

### Reactions of Arenes: Electrophilic and Nucleophilic Aromatic Substitution 478

12.1	Representative Electrophilic Aromatic Substitut	ion
	Reactions of Benzene 479	

- 12.2 Mechanistic Principles of Electrophilic Aromatic Substitution 480
- Nitration of Benzene 482 12.3 Mechanism 12.1 Nitration of Benzene 483
- 12.4 Sulfonation of Benzene 484
- 12.5 Halogenation of Benzene 484 Mechanism 12.2 Sulfonation of Benzene 485 Biosynthetic Halogenation 486 Mechanism 12.3 Bromination of Benzene 486
- 12.6 Friedel-Crafts Alkylation of Benzene 488 Mechanism 12.4 Friedel-Crafts Alkylation 489
- 12.7 Friedel-Crafts Acylation of Benzene 490 Mechanism 12.5 Friedel-Crafts Acylation 491
- 12.8 Synthesis of Alkylbenzenes by Acylation-Reduction 492
- 12.9 Rate and Regioselectivity in Electrophilic Aromatic Substitution 494
- 12.10 Rate and Regioselectivity in the Nitration of Toluene 495
- 12.11 Rate and Regioselectivity in the Nitration of (Trifluoromethyl) Benzene 497
- 12.12 Substituent Effects in Electrophilic Aromatic Substitution: Activating Substituents 499
- 12.13 Substituent Effects in Electrophilic Aromatic Substitution: Strongly Deactivating Substituents 503
- 12.14 Substituent Effects in Electrophilic Aromatic Substitution: Halogens 506
- 12.15 Multiple Substituent Effects 507
- 12.16 Regioselective Synthesis of Disubstituted Aromatic Compounds 510
- 12.17 Substitution in Naphthalene 512
- 12.18 Substitution in Heterocyclic Aromatic Compounds 513
- 12.19 Nucleophilic Aromatic Substitution 514
- 12.20 Nucleophilic Substitution in Nitro-Substituted Aryl Halides 515
- 12.21 The Addition-Elimination Mechanism of Nucleophilic Aromatic Substitution 516 Mechanism 12.6 Nucleophilic Aromatic Substitution in p-Fluoronitrobenzene by the Addition-Elimination Mechanism 518
- 12.22 Related Nucleophilic Aromatic Substitutions 520
- 12.23 Summary 521 Problems 525 Descriptive Passage and Interpretive Problems 12: Benzyne 534

# CHAPTER

#### Spectroscopy 538

- Principles of Molecular Spectroscopy: Electromagnetic Radiation 539
- Principles of Molecular Spectroscopy: Quantized 13.2 Energy States 541
- 13.3 Introduction to <sup>1</sup>H NMR Spectroscopy 541
- 13.4 Nuclear Shielding and <sup>1</sup>H Chemical Shifts 543
- 13.5 Effects of Molecular Structure on <sup>1</sup>H Chemical Shifts 546

#### Ring Currents—Aromatic and Antiaromatic 551

- 13.6 Interpreting <sup>1</sup>H NMR Spectra 552
- Spin-Spin Splitting in <sup>1</sup>H NMR Spectroscopy 555 13.7
- 13.8 Splitting Patterns: The Ethyl Group 557
- 13.9 Splitting Patterns: The Isopropyl Group 559
- 13.10 Splitting Patterns: Pairs of Doublets 559
- 13.11 Complex Splitting Patterns 561
- 13.12 <sup>1</sup>H NMR Spectra of Alcohols 563 Magnetic Resonance Imaging (MRI) 564
- 13.13 NMR and Conformations 564
- 13.14 13C NMR Spectroscopy 565
- 13.15 <sup>13</sup>C Chemical Shifts 567
- 13.16 <sup>13</sup>C NMR and Peak Intensities 569
- **13.17** <sup>13</sup>C–<sup>1</sup>H Coupling 570
- 13.18 Using DEPT to Count Hydrogens Attached to <sup>13</sup>C 570
- 13.19 2D NMR: COSY and HETCOR 572
- 13.20 Introduction to Infrared Spectroscopy 574

#### Spectra by the Thousands 575

- 13.21 Infrared Spectra 576
- 13.22 Characteristic Absorption Frequencies 578
- 13.23 Ultraviolet-Visible (UV-VIS) Spectroscopy 582
- 13.24 Mass Spectrometry 584
- 13.25 Molecular Formula as a Clue to Structure 589
- 13.26 Summary 590

Problems 593

Descriptive Passage and Interpretive Problems 13: Calculating Aromatic <sup>13</sup>C Chemical Shifts 603

# CHAPTER

### Organometallic Compounds 606

- 14.1 Organometallic Nomenclature 607
- 14.2 Carbon-Metal Bonds in Organometallic Compounds 608
- 14.3 Preparation of Organolithium Compounds 609
- 14.4 Preparation of Organomagnesium Compounds: Grignard Reagents 610
- 14.5 Organolithium and Organomagnesium Compounds as Brønsted Bases 612
- 14.6 Synthesis of Alcohols Using Grignard Reagents 614

4.7	Synthesis of Alcohols Using Organolithium Reagents 616
4.8	Synthesis of Acetylenic Alcohols 616
4.9	Retrosynthetic Analysis 617
4 10	Alkana Synthosis Using Organosannas Dos

14.10 Alkane Synthesis Using Organocopper Reagents 620 Mechanism 14.1 Formation of a Lithium Diaklycuprate (Gilman Reagent) 621

14.11 An Organozinc Reagent for Cyclopropane Synthesis 622

14.12 Carbenes and Carbenoids 623 Mechanism 14.2 Similarities Between the Mechanisms of Reaction of an Alkene with Iodomethylzinc Iodide and a Peroxy Acid 624

14.13 Transition-Metal Organometallic Compounds 625 An Organometallic That Occurs Naturally: Coenzyme B<sub>12</sub> 627

14.14 Homogeneous Catalytic Hydrogenation 628 Mechanism 14.3 Homogeneous Hydrogenation of Propene in the Presence of Wilkinson's Catalyst 629

14.15 Olefin Metathesis 631

Mechanism 14.4 Olefin Cross-Metathesis 632

14.16 Ziegler-Natta Catalysis of Alkene Polymerization 634 Mechanism 14.5 Polymerization of Ethylene in the Presence of a Ziegler-Natta Catalyst 635

14.17 Summary 636 Problems 639

Descriptive Passage and Interpretive Problems 14: The Heck Reaction 643

# CHAPTER

# Alcohols, Diols, and Thiols 646

Sources of Alcohols 647 15.1

15.2 Preparation of Alcohols by Reduction of Aldehydes and Ketones 648 Mechanism 15.1 Sodium Borohydride Reduction of an Aldehyde or Ketone 653

15.3 Preparation of Alcohols by Reduction of Carboxylic Acids 654

Preparation of Alcohols from Epoxides 654 15.4

15.5 Preparation of Diols 656

Reactions of Alcohols: A Review and a Preview 658 15.6

15.7 Conversion of Alcohols to Ethers 658

Esterification 660 Mechanism 15.2 Acid-Catalyzed Formation of Dietyl Ether from Ethyl Alcohol 660

15.9 Oxidation of Alcohols 663 Mechanism 15.3 Chromic Acid Oxidation of 2-Propanol 665

15.10 Biological Oxidation of Alcohols 666 Mechanism 15.4 Dimethyl Sulfoxide Oxidation of an Alcohol 666 Economic and Environmental Factors in Organic

Synthesis 667 15.11 Oxidative Cleavage of Vicinal Diols 669 Mechanism 15.5 Oxidation of Ethanol by NAD+ 669

15.12 Thiols 670

15.13 Spectroscopic Analysis of Alcohols and Thiols 674

15.14 Summary 675 Problems 679 Descriptive Passage and Interpretive Problems 15: The Pinacol Rearrangement 684

# CHAPTER

### Ethers, Epoxides, and Sulfides 686

Nomenclature of Ethers, Epoxides, and Sulfides 687

16.2 Structure and Bonding in Ethers and Epoxides 688

16.3 Physical Properties of Ethers 689

16.4 Crown Ethers 690

16.5 Preparation of Ethers 692 Polyether Antibiotics 693

16.6 The Williamson Ether Synthesis 694

16.7 Reactions of Ethers: A Review and a Preview 695

16.8 Acid-Catalyzed Cleavage of Ethers 696 Mechanism 16.1 Cleavage of Ethers by Hydrogen Halides 697

Preparation of Epoxides: A Review and a Preview 698

16.10 Conversion of Vicinal Halohydrins to Epoxides 699

16.11 Reactions of Epoxides: A Review and a Preview 700

16.12 Nucleophilic Ring Opening of Epoxides 701 Mechanism 16.2 Nucleophilic Ring Opening of an Epoxide 703

16.13 Acid-Catalyzed Ring Opening of Epoxides 703 Mechanism 16.3 Acid-Catalyzed Ring Opening of Ethylene Oxide 704

16.14 Epoxides in Biological Processes 706

16.15 Preparation of Sulfides 706

16.16 Oxidation of Sulfides: Sulfoxides and Sulfones 707

16.17 Alkylation of Sulfides: Sulfonium Salts 708 Mechanism 16.4 Nucleophilic Substitution of Adenosine Triphosphate (ATP) by Methionine 709

16.18 Spectroscopic Analysis of Ethers, Epoxides, and Sulfides 709

16.19 Summary 711 Problems 715

Descriptive Passage and Interpretive Problems 16: Epoxide Rearrangements and the NIH Shift 721

## CHAPTER

### Aldehydes and Ketones: Nucleophilic Addition to the Carbonyl Group 724

17.1 Nomenclature 725

17.2 Structure and Bonding: The Carbonyl Group 728

17.3 Physical Properties 730

17.4 Sources of Aldehydes and Ketones 730

4.7	Synthesis of Alcohols Using Organ Reagents 616	nolithium
4.8 4.9	Synthesis of Acetylenic Alcohols Retrosynthetic Analysis 617	616

14.10 Alkane Synthesis Using Organocopper Reagents 620Mechanism 14.1 Formation of a Lithium Diaklycuprate (Gilman Reagent) 621

**14.11** An Organozinc Reagent for Cyclopropane Synthesis 622

14.12 Carbenes and Carbenoids 623
 Mechanism 14.2 Similarities Between the Mechanisms of Reaction of an Alkene with Iodomethylzinc Iodide and a Peroxy Acid 624

14.13 Transition-Metal Organometallic Compounds 625
An Organometallic That Occurs Naturally:
Coenzyme B<sub>12</sub> 627

14.14 Homogeneous Catalytic Hydrogenation 628
 Mechanism 14.3 Homogeneous Hydrogenation of Propene in the Presence of Wilkinson's Catalyst 629

14.15 Olefin Metathesis 631

Mechanism 14.4 Olefin Cross-Metathesis 632

**14.16** Ziegler-Natta Catalysis of Alkene Polymerization 634 **Mechanism 14.5** Polymerization of Ethylene in the Presence of a Ziegler-Natta Catalyst 635

14.17 Summary 636 Problems 639

Descriptive Passage and Interpretive Problems 14: The Heck Reaction 643

# CHAPTER L

# Alcohols, Diols, and Thiols 646

15.1 Sources of Alcohols 647

15.2 Preparation of Alcohols by Reduction of Aldehydes and Ketones 648
 Mechanism 15.1 Sodium Borohydride Reduction of an Aldehyde or Ketone 653

15.3 Preparation of Alcohols by Reduction of Carboxylic Acids 654

15.4 Preparation of Alcohols from Epoxides 654

15.5 Preparation of Diols 656

15.6 Reactions of Alcohols: A Review and a Preview 658

15.7 Conversion of Alcohols to Ethers 658

15.8 Esterification 660Mechanism 15.2 Acid-Catalyzed Formation of Dietyl Ether from Ethyl Alcohol 660

15.9 Oxidation of Alcohols 663

Mechanism 15.3 Chromic Acid Oxidation of 2-Propanol 665

15.10 Biological Oxidation of Alcohols 666Mechanism 15.4 Dimethyl Sulfoxide Oxidation of an Alcohol 666Economic and Environmental Factors in Organic

Synthesis 667
15.11 Oxidative Cleavage of Vicinal Diols 669

Mechanism 15.5 Oxidation of Ethanol by NAD+ 669

15.12 Thiols 670

15.13 Spectroscopic Analysis of Alcohols and Thiols 674

15.14 Summary 675
Problems 679
Descriptive Passage and Interpretive Problems 15:
The Pinacol Rearrangement 684

# CHAPTER

#### Ethers, Epoxides, and Sulfides 686

16.1 Nomenclature of Ethers, Epoxides, and Sulfides 687

16.2 Structure and Bonding in Ethers and Epoxides 688

**16.3** Physical Properties of Ethers 689

**16.4** Crown Ethers 690

16.5 Preparation of Ethers 692Polyether Antibiotics 693

16.6 The Williamson Ether Synthesis 694

16.7 Reactions of Ethers: A Review and a Preview 695

16.8 Acid-Catalyzed Cleavage of Ethers 696Mechanism 16.1 Cleavage of Ethers by Hydrogen Halides 697

16.9 Preparation of Epoxides: A Review and a Preview 698

16.10 Conversion of Vicinal Halohydrins to Epoxides 699

16.11 Reactions of Epoxides: A Review and a Preview 700

16.12 Nucleophilic Ring Opening of Epoxides 701Mechanism 16.2 Nucleophilic Ring Opening of an Epoxide 703

16.13 Acid-Catalyzed Ring Opening of Epoxides 703Mechanism 16.3 Acid-Catalyzed Ring Opening of Ethylene Oxide 704

16.14 Epoxides in Biological Processes 706

16.15 Preparation of Sulfides 706

16.16 Oxidation of Sulfides: Sulfoxides and Sulfones 707

16.17 Alkylation of Sulfides: Sulfonium Salts 708
 Mechanism 16.4 Nucleophilic Substitution of Adenosine Triphosphate (ATP) by Methionine 709

**16.18** Spectroscopic Analysis of Ethers, Epoxides, and Sulfides 709

16.19 Summary 711 Problems 715

Descriptive Passage and Interpretive Problems 16: Epoxide Rearrangements and the NIH Shift 721

# CHAPTER 17

# Aldehydes and Ketones: Nucleophilic Addition to the Carbonyl Group 724

17.1 Nomenclature 725

17.2 Structure and Bonding: The Carbonyl Group 728

17.3 Physical Properties 730

17.4 Sources of Aldehydes and Ketones 730

Contents xiii

17.5	Reactions of Aldehydes and Ketones: A Review
17.5	and a Preview 734
17.6	Principles of Nucleophilic Addition: Hydration of
	Aldehydes and Ketones 735
	Mechanism 17.1 Hydration of an Aldehyde or Ketone
	in Basic Solution 738
17.7	Cyanohydrin Formation 739
	<b>Mechanism 17.2</b> Hydration of an Aldehyde or Ketone in Acid Solution 739
	Mechanism 17.3 Cyanohydrin Formation 740
17.8	Acetal Formation 742
,,,,	Mechanism 17.4 Acetal Formation from Benzaldehyde
	and Ethanol 743
17.9	Acetals as Protecting Groups 745
17.10	Reaction with Primary Amines: Imines 746
	Mechanism 17.5 Imine Formation from Benzaldehyde
	and Methylamine 747
	Imines in Biological Chemistry 749
17.11	Reaction with Secondary Amines: Enamines 751
	Mechanism 17.6 Enamine Formation from Cyclopentanone and Pyrrolidine 752
17 <b>1</b> 2	The Wittig Reaction 752
17,14	Mechanism 17.7 The Witting Reaction 754
17.13	Planning an Alkene Synthesis via the Wittig
	Reaction 755
17.14	, ,
17.15	,
17.16	Spectroscopic Analysis of Aldehydes and Ketones 759
17.17	Summary 761
	Problems 764  Descriptive Passage and Interpretive Problems 17:
	The Baeyer-Villiger Oxidation 772
	40
	IX
CHA	APTER IO
Carl	poxylic Acids 776
18.1	Carboxylic Acid Nomenclature 777
18.2	Structure and Bonding 779
18.3	Physical Properties 780
18.4	Acidity of Carboxylic Acids 780
18.5	Substituents and Acid Strength 783
18.6	Ionization of Substituted Benzoic Acids 785
18.7	Salts of Carboxylic Acids 786
18.8 18.9	Dicarboxylic Acids 788
	Carbonic Acid 789 Sources of Carboxylic Acids 790
18.11	Synthesis of Carboxylic Acids by the Carboxylation
.0.11	of Grignard Reagents 792
18.12	Synthesis of Carboxylic Acids by the Preparation
	and Hydrolysis of Nitriles 793
18.13	Reactions of Carboxylic Acids: A Review
1011	and a Preview 794
18.14	Mechanism of Acid-Catalyzed Esterification 794

Mechanism 18.1 Acid-Catalyzed Esterification of

Benzoic Acid with Methanol 796

18.15	Intramolecular Ester Formation: Lactones 798
18.16	Decarboxylation of Malonic Acid and Related
	Compounds 799
	Spectroscopic Properties of Carboxylic Acids 802
18.18	Summary 803 Problems 805
	Descriptive Passage and Interpretive Problems 18:
	Lactonization Methods 809
	10
<b>с</b> ц ,	$_{\text{APTER}}$ $19$
Спи	APTER 1
Carl	poxylic Acid Derivatives: Nucleophilic
	•
ACY	Substitution 812
19.1	Nomenclature of Carboxylic Acid Derivatives 814
19.2	Structure and Reactivity of Carboxylic Acid
19.3	Derivatives 815
17.5	General Mechanism for Nucleophilic Acyl Substitution 818
19.4	Nucleophilic Acyl Substitution in Acyl Chlorides 820
	Mechanism 19.1 Acid-Catalyzed Hydrolysis of an Acyl
	Chloride via a Tetrahedral Intermediate 822
19.5	Nucleophilic Acyl Substitution in Acid Anhydrides 823
	Mechanism 19.2 Nucleophilic Acyl Substitution in an
19.6	Anhydride 824 Sources of Esters 825
19.7	Physical Properties of Esters 827
19.8	Reactions of Esters: A Preview 827
19.9	Acid-Catalyzed Ester Hydrolysis 829
	Mechanism 19.3 Acid-Catalyzed Ester Hydrolysis 830
19.10	, , , , , , , , , , , , , , , , , , , ,
	Mechanism 19.4 Ester Hydrolysis in Basic
10 11	Solution 834 Reaction of Esters with Ammonia and Amines 835
	Reaction of Esters with Grignard Reagents: Synthesis
	of Tertiary Alcohols 836
	Mechanism 19.5 Reaction of an Ester with a Grignard
	Reagent 837
19.13	······································
19 14	Hydride 838 Amides 839
	Hydrolysis of Amides 843
	Mechanism 19.6 Amide Hydrolysis in Acid
	Solution 844
	Mechanism 19.7 Amide Hydrolysis in Basic
10.17	Solution 846
19.16	Lactams 847
10 17	β- <b>Lactam Antibiotics 847</b> Preparation of Nitriles 848
	Hydrolysis of Nitriles 849
	Addition of Grignard Reagents to Nitriles 850
	J J

Mechanism 19.8 Nitrile Hydrolysis in Basic

19.20 Spectroscopic Analysis of Carboxylic Acid Derivatives 852

Solution 851

19.21 Summary 853 Problems 856 Descriptive Passage and Interpretive Problems 20: Thioesters 863

CHAPTER

#### **Enols and Enolates 866**

- 20.1 Aldehyde, Ketone, and Ester Enolates 867
- 20.2 Enolate Regiochemistry 872
- 20.3 The Aldol Condensation 873 Mechanism 20.1 Aldol Addition of Butanal 874 Mechanism 20.2 Dehydration in a Base-Catalyzed Aldol Condensation 876
- Mixed Aldol Condensations 878 Chalcones: From the Mulberry Tree to Cancer Chemotherapy 880
- 20.5 The Claisen Condensation 882 Mechanism 20.3 The Claisen Condensation of Ethyl Acetate 883
- 20.6 Intramolecular Claisen Condensation: The Dieckmann Cyclization 884
- Mixed Claisen Condensations 885
- 20.8 Acylation of Ketones with Esters 886
- 20.9 Alkylation of Enolates 887
- 20.10 The Acetoacetic Ester Synthesis 889
- **20.11** The Malonic Ester Synthesis 891
- 20.12 Alkyation of Chiral Enolates 893
- 20.13 Enolization and Enol Content 895 Mechanism 20.4 Base-Catalyzed Enolization of an Aldehyde or Ketone in Aqueous Solution 899

Mechanism 20.5 Acid-Catalyzed Enolization of an Aldehyde or Ketone in Aqueous Solution 899

- **20.14**  $\alpha$  Halogenation of Aldehydes and Ketones 900 Mechanism 20.6 Acid-Catalyzed Bromination of Acetone 901 Mechanism 20.7 Cleavage of a Tribromomethyl Ketone 903
- **20.15**  $\alpha$  Halogenation of Carboxylic Acids: The Hell-Volhard-Zelinsky Reaction 904 The Haloform Reaction and the Biosynthesis of Trihalomethanes 904
- 20.16 Some Chemical and Stereochemical Consequences of Enolization 906
- **20.17** Effects of Conjugation in  $\alpha,\beta$ -Unsaturated Aldehydes and Ketones 907
- **20.18** Conjugate Addition to  $\alpha, \beta$ -Unsaturated Carbonyl Compounds 908
- **20.19** Addition of Carbanions to  $\alpha,\beta$ -Unsaturated Ketones: The Michael Reaction 910
- 20.20 Conjugate Addition of Organocopper Reagents to α,β-Unsaturated Carbonyl Compounds 912

20.21 Summary 913 Problems 917 Descriptive Passage and Interpretive Problems 20: The Enolate Chemistry of Dianions 926

#### Amines 930

- 21.1 Amine Nomenclature 931
- 21.2 Structure and Bonding 933
- 21.3 Physical Properties 935
- 21.4 Basicity of Amines 936

#### Amines as Natural Products 941

- 21.5 Tetraalkylammonium Salts as Phase-Transfer Catalysts 942
- 21.6 Reactions That Lead to Amines: A Review and a Preview 943
- 21.7 Preparation of Amines by Alkylation of Ammonia 945
- 21.8 The Gabriel Synthesis of Primary Alkylamines 946
- 21.9 Preparation of Amines by Reduction 947 Mechanism 21.1 Lithium Aluminum Hydride Reduction of an Amide 950
- 21.10 Reductive Amination 951
- 21.11 Reactions of Amines: A Review and a Preview 952
- 21.12 Reaction of Amines with Alkyl Halides 954
- 21.13 The Hofmann Elimination 954
- 21.14 Electrophilic Aromatic Substitution in Arylamines 956
- 21.15 Nitrosation of Alkylamines 958
- 21.16 Nitrosation of Arylamines 960 Mechanism 21.2 Reactions of an Alkyl Diazonium Ion 960
- 21.17 Synthetic Transformations of Aryl Diazonium Salts 961
- 21.18 Azo Coupling 965

#### From Dyes to Sulfa Drugs 966

- 21.19 Spectroscopic Analysis of Amines 967
- 21.20 Summary 970

Problems 976

Descriptive Passage and Interpretive Problems 21: Synthetic Applications of Enamines 984

CHAPTER

#### Phenols 988

- 22.1 Nomenclature 989
- 22.2 Structure and Bonding 990
- 22.3 Physical Properties 991
- 22.4 Acidity of Phenols 992
- 22.5 Substituent Effects on the Acidity of Phenols 993
- 22.6 Sources of Phenols 995
- 22.7 Naturally Occurring Phenols 996
- 22.8 Reactions of Phenols: Electrophilic Aromatic Substitution 997

Contents

	Spectroscopic Analysis of Phenols 1009
	Summary 1011
	Problems 1013
	Descriptive Passage and Interpretive Problems 22: Directed Metalation of Aryl Ethers 1019
	Directed Metalation of Allyl Letters 1015
	77
	PTER $23$
CHA	PTER 4
Carb	ohydrates 1022
	Classification of Carbohydrates 1023
23.2	Fischer Projections and D,L Notation 1024
23.3	The Aldotetroses 1025
	Aldopentoses and Aldohexoses 1026
	A Mnemonic for Carbohydrate Configurations 1028
	Cyclic Forms of Carbohydrates: Furanose Forms 1029
	Cyclic forms of Carbohydrates: Pyranose Forms 1032
23.8	Mutarotation 1035
	Mechanism 23.1 Acid-Catalyzed Mutarotation of
22.0	p-Glucopyranose 1037 Carbohydrate Conformation: The Anomeric Effect 1038
	Carbohydrate Conformation: The Anomeric Effect 1038 Ketoses 1039
	Deoxy Sugars 1040
22.11	Amino Sugars 1041
23.12	Branched-Chain Carbohydrates 1042
	Glycosides: The Fischer Glycosidation 1043
23.17	Mechanism 23.2 Preparation of Methyl
	p-Glucopyranisides by Fischer Glycosidation 1044
23.15	Disaccharides 1046
23.16	Polysaccharides 1048
	How Sweet It Is! 1049
23.17	Reactions of Carbohydrates 1050
	Reduction of Monosaccharides 1050
23.19	Oxidation of Monosaccharides 1051
23.20	Periodic Acid Oxidation 1053
23.21	Cyanohydrin Formation and Chain Extension 1054
23.22	Epimerization, Isomerization, and Retro-Aldol Cleavage 1055
23.23	Acylation and Alkylation of Carbohydrate Hydroxyl
	Groups 1056
23.24	Glycosides: Synthesis of Oliosaccharides 1058
	Mechanism 23.3 Silver-Assisted Glycosidation 1060
	Glycobiology 1062
23.26	Summary 1064
	Problems 1067
	Descriptive Passage and Interpretive Problems 23: Emil Fischer and the Structure of (+)-Glucose 1072
	e de la companya de La companya de la co

22.9 Acylation of Phenols 999

Phenols 1004

22.11 Preparation of Aryl Ethers 1002

**22.10** Carboxylation of Phenols: Aspirin and the Kolbe-Schmitt Reaction 1001

22 14 Oxidation of Phenols: Ouinones 1008

James Bond, Oxidative Stress, and Antioxidant

22.12 Cleavage of Aryl Ethers by Hydrogen Halides 1006

22.13 Claisen Rearrangement of Allyl Aryl Ethers 1007

# CHAPTER 24

Lipids	1	0	7	4
--------	---	---	---	---

241	Acetyl	Coenzyme	Δ	1075
Z4.I	Acetvi	COGLIZALIE	$\sim$	10/3

- 24.2 Fats, Oils, and Fatty Acids 1077
- 24.3 Fatty Acid Biosynthesis 1080
- 24.4 Phospholipids 1082
   Mechanism 24.1 Biosynthesis of a Butanoyl Group from Acetyl and Malonyl Building Blocks 1082
- **24.5** Waxes 1085
- 24.6 Prostaglandins 1086

# Nonsteroidal Anti-Inflammatory Drugs (NSAIDS) and COX-2 Inhibitors 1088

- 24.7 Terpenes: The Isoprene Rule 1090
- 24.8 Isopentenyl Pyrophosphate: The Biological Isoprene Unit 1093
- **24.9** Carbon-Carbon Bond Formation in Terpene Biosynthesis 1093
- **24.10** The Pathway from Acetate to Isopentenyl Diphosphate 1096
- 24.11 Steroids: Cholesterol 1098

  Mechanism 24.2 Biosynthesis of Cholesterol from Squalene 1100
- **24.12** Vitamin D 1101

# Good Cholesterol? Bad Cholesterol? What's the Difference? 1102

- **24.13** Bile Acids 1103
- 24.14 Corticosteroids 1103
- **24.15** Sex Hormones 1103
- **24.16** Carotenoids 1104

#### Crocuses Make Saffron from Carotenes 1105

24.17 Summary 1106
Problems 1108
Descriptive Passage and Interpretive Problems 24:
Polyketides 1112

# CHAPTER 25

### Amino Acids, Peptides, and Proteins 1116

- 25.1 Classification of Amino Acids 1118
- 25.2 Stereochemistry of Amino Acids 1123
- 25.3 Acid-Base Behavior of Amino Acids 1124

#### Electrophoresis 1127

- 25.4 Synthesis of Amino Acids 1128
- 25.5 Reactions of Amino Acids 1130
- 25.6 Some Biochemical Reactions of Amino Acids 1130
   Mechanism 25.1 Pyridoxal 5'-Phosphate-Mediated
   Decarboxylation of an α-Amino Acid 1131
   Mechanism 25.2 Transamination: Biosynthesis of
   L-Alanaine from L-Glutamic Acid and Pyruvic Acid 1135
- **25.7** Peptides 1137
- 25.8 Introduction to Peptide Structure Determination 1140

xvi Contents

**26.9** Tertiary Structure of DNA: Supercoils 1190

26.10 Replication of DNA 1191

25.9 Amino Acid Analysis 1140	<b>26.11</b> Ribonucleic Acids 1193
<b>25.10</b> Partial Hydrolysis of Peptides 1141	26.12 Protein Biosynthesis 1196
25.11 End Group Analysis 1141	<b>26.13</b> AIDS 1197
<b>25.12</b> Insulin 1143	26.14 DNA Sequencing 1198
25.13 The Edman Degradation and Automated Sequencing	26.15 The Human Genome Project 1200
of Peptides 1144	26.16 DNA Profiling and the Polymerase Chain
Mechanism 25.3 The Edman Degradation 1145	Reaction 1201
Peptide Mapping and MALDI Mass	<b>26.17</b> Recombinant DNA Technology 1204
Spectrometry 1146	26.18 Summary 1205
<b>25.14</b> The Strategy of Peptide Synthesis 1147	Problems 1208
25.15 Amino Group Protection 1148	Descriptive Passage and Interpretive Problems 26:
25.16 Carboxyl Group Protection 1151	Oligonucleotide Synthesis 1210
25.17 Peptide Bond Formation 1151	·
Mechanism 25.4 Amide Bond Formation Between	77
a Carboxylic Acid and Amine Using N,N'-	$_{\text{CHAPTER}}$ 27
Dicyclohexylcarboiimide 1152  25.18 Solid-Phase Peptide Synthesis: The Merrifield	CHAPTER
Method 1153	C.,
25.19 Secondary Structures of Polypeptides and	Synthetic Polymers 1216
Proteins 1155	27.1 Some Background 1217
25.20 Tertiary Structure of Peptides and Proteins 1159	27.2 Polymer Nomenclature 1218
Mechanism 25.5 Carboxypeptidase-Catalyzed	27.3 Classification of Polymers: Reaction Type 1219
Hydrolysis 1162	27.4 Classification of Polymers: Chain Growth
<b>25.21</b> Coenzymes 1163	and Step Growth 1220
Oh NO! It's Inorganic! 1164	27.5 Classification of Polymers: Structure 1221
25.22 Protein Quaternary Structure: Hemoglobin 1164	27.6 Classification of Polymers: Properties 1223
25.23 G-Coupled Protein Receptors 1165	27.7 Addition Polymers: A Review and a Preview 1225
25.24 Summary 1166	<b>27.8</b> Chain Branching in Free-Radical Polymerization 1227
Problems 1168	Mechanism 27.1 Branching in Polyethylene Caused by
Descriptive Passage and Interpretive Problems 25:	Intramolecular Hydrogen Transfer 1228
Amino Acids in Enatioselective Synthesis 1171	Mechanism 27.2 Branching in Polyethylene Caused by
	Intermolecular Hydrogen Transfer 1229  27.9 Anionic Polymerization: Living Polymers 1230
	Mechanism 27.3 Anionic Polymerization of Styrene 1230
CHAPTER $26$	<b>27.10</b> Cationic Polymerization 1232
CHAPTER <b>20</b>	<b>27.11</b> Polyamides 1233
	Mechanism 27.4 Cationic Polymerization of
Nucleosides, Nucleotides,	2-Methylpropene 1233
and Nucleic Acids 1174	<b>27.12</b> Polyesters 1234
	27.13 Polycarbonates 1236
<b>26.1</b> Pyrimidines and Purines 1175	27.14 Polyurethanes 1236
26.2 Nucleosides 1178	<b>27.15</b> Copolymers 1237
26.3 Nucleotides 1180	Conducting Polymers 1239
26.4 Bioenergetics 1182	27.16 Summary 1241
26.5 ATP and Bioenergetics 1182	Problems 1243
26.6 Phosphodiesters, Oligonucleotides,	Descriptive Passage and Interpretive Problems 27:
and Polynucleotides 1184	Chemical Modification of Polymers 1245
26.7 Nucleic Acids 1185	
26.8 Secondary Structure of DNA: The Double Helix 1186	Glossary G-1
"It has not escaped our notice " 1188	Credits C-1
AN M. LOCKISTO STRUCTURE OF LINEAU SUPERCORE 1100	

Index I-1