

SIXTH EDITION

ORGANIC CHEMISTRY

BROWN • FOOTE • IVERSON • ANSLYN



Online Web
Learning
UMassAmherst

Get a Better Grade in Chemistry!

Log in now to the leading online learning system for chemistry.
Score better on exams, get homework help, and more!

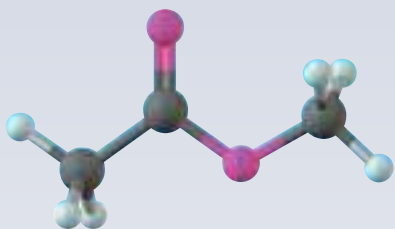
The screenshot shows the OWL interface for a chemistry question. The question asks to determine the geometry of a molecule in a 3D window. The molecule is a central carbon atom bonded to four other atoms, forming a tetrahedral shape. The question includes instructions on how to use the 3D window and a list of possible geometries: Trigonal Planar, Trigonal Bipyramidal, Tetrahedral, and Trigonal Pyramidal. A dropdown menu is provided for the user to select the correct geometry, and a 'CHECK ANSWER' button is visible at the bottom.

- **Master chemistry and improve your grade** using OWL's step-by-step tutorials, and homework questions that provide instant answer-specific feedback. Available 24/7.
- **Learn at your own pace with OWL**, a study smart system that ensures you've mastered each concept before you move on.
- **Access the Cengage Youbook, an e-version of your textbook** enhanced with videos and animations, highlighting, the ability to add notes, and more.

To get started, use the access code that may have been packaged with your text or purchase access online. Check with your instructor to verify that OWL is required for your course before purchasing.

www.cengage.com/OWL

This is an electronic version of the print textbook. Due to electronic rights restrictions, some third party content may be suppressed. Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. The publisher reserves the right to remove content from this title at any time if subsequent rights restrictions require it. For valuable information on pricing, previous editions, changes to current editions, and alternate formats, please visit www.cengage.com/highered to search by ISBN#, author, title, or keyword for materials in your areas of interest.



Organic Chemistry

SIXTH EDITION

William H. Brown

Beloit College

Christopher S. Foote

University of California, Los Angeles

Brent L. Iverson

University of Texas, Austin

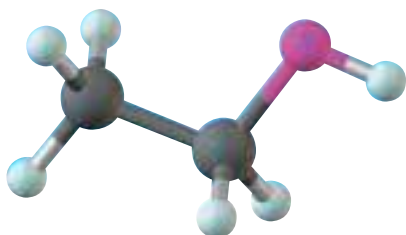
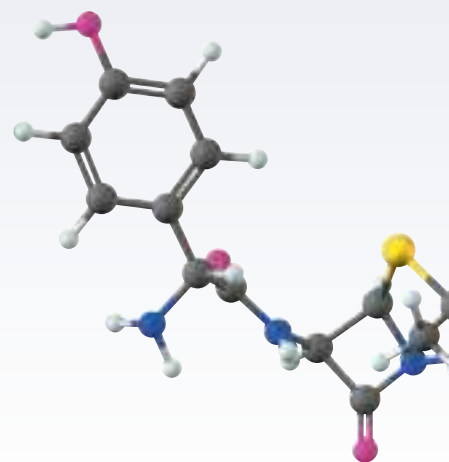
Eric V. Anslyn

University of Texas, Austin

Chapter 29 was originally contributed by

Bruce M. Novak

North Carolina State University



 **BROOKS/COLE**
CENGAGE Learning™

Australia • Brazil • Japan • Korea • Mexico • Singapore • Spain • United Kingdom • United States

Dedication

This Sixth Edition is dedicated to the memory of our dear friend and colleague, Christopher Foote. Chris' insights, encouragement, and dedication to this project can never be replaced. His kind and nurturing spirit lives on in all who are lucky enough to have known him.

About the Authors

WILLIAM H. BROWN is an Emeritus Professor of Chemistry at Beloit College, where he has twice been named Teacher of the Year. His teaching responsibilities included organic chemistry, advanced organic chemistry, and special topics in pharmacology and drug synthesis. He received his Ph.D. from Columbia University under the direction of Gilbert Stork and did postdoctoral work at California Institute of Technology and the University of Arizona.

CHRISTOPHER S. FOOTE received his B.S. from Yale University and his Ph.D. from Harvard University. His scholarly credits include Sloan Fellow; Guggenheim Fellow; ACS Baekland Award; ACS Cope Scholar; Southern California Section ACS Tolman Medal; President, American Society for Photobiology; and Senior Editor, Accounts of Chemical Research. He was a Professor of Chemistry at UCLA.

BRENT L. IVERSON received his B.S. from Stanford University and his Ph.D. from the California Institute of Technology. He is a University Distinguished Teaching Professor at The University of Texas, Austin as well as a respected researcher. Brent's research spans the interface of organic chemistry and molecular biology. His group has developed several patented technologies, including an effective treatment for anthrax.

ERIC V. ANSLYN is a University Distinguished Teaching Professor at The University of Texas at Austin. He earned his bachelor's degree from California State University, Northridge, his Ph.D. from the California Institute of Technology and did postdoctoral work at Columbia University under the direction of Ronald Breslow. Eric has won numerous teaching awards and his research focuses on the physical and bioorganic chemistry of synthetic and natural receptors and catalysts.

Contents in Brief

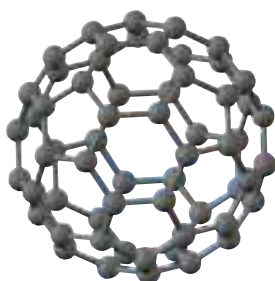
Appendices:

1. Thermodynamics and the Equilibrium Constant
2. Major Classes of Organic Acids
3. Bond Dissociation Enthalpies
4. Characteristic ^1H -NMR Chemical Shifts
5. Characteristic ^{13}C -NMR Chemical Shifts
6. Characteristic Infrared Absorption Frequencies
7. Electrostatic Potential Maps
8. Summary of Stereochemical Terms
9. Summary of the Rules of Nomenclature
10. Common Mistakes in Arrow Pushing
11. Organic Chemistry Road Maps

Glossary

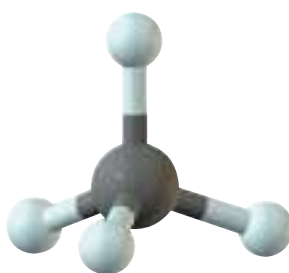
Index

Contents



Chapter 1 Covalent Bonding and Shapes of Molecules 1

- 1.1 Electronic Structure of Atoms 1
- 1.2 Lewis Model of Bonding 6
 - HOW TO Draw Lewis Structures from Condensed Structural Formulas 15
- 1.3 Functional Groups 16
- 1.4 Bond Angles and Shapes of Molecules 21
- 1.5 Polar and Nonpolar Molecules 24
 - CHEMICAL CONNECTIONS Fullerene—A New Form of Carbon 25
- 1.6 Quantum or Wave Mechanics 26
- 1.7 A Combined Valence Bond and Molecular Orbital Theory Approach to Covalent Bonding 30
 - CONNECTIONS TO BIOLOGICAL CHEMISTRY Phosphoesters 37
- 1.8 Resonance 42
 - HOW TO Draw Curved Arrows and Push Electrons in Creating Contributing Structures 43
- 1.9 Molecular Orbitals for Delocalized Systems 48
- 1.10 Bond Lengths and Bond Strengths in Alkanes, Alkenes, and Alkynes 51
 - Summary 52 • Problems 54



Chapter 2 Alkanes and Cycloalkanes 63

- 2.1 The Structure of Alkanes 63
- 2.2 Constitutional Isomerism in Alkanes 65
- 2.3 Nomenclature of Alkanes and the IUPAC System 67
- 2.4 Cycloalkanes 72
- 2.5 Conformations of Alkanes and Cycloalkanes 75
 - HOW TO Draw Alternative Chair Conformations of Cyclohexanes 86
- 2.6 *Cis, Trans* Isomerism in Cycloalkanes and Bicycloalkanes 88
 - HOW TO Convert Planar Cyclohexanes to Chair Cyclohexanes 90
 - CHEMICAL CONNECTIONS The Poisonous Puffer Fish 95
- 2.7 Physical Properties of Alkanes and Cycloalkanes 96
- 2.8 Reactions of Alkanes 99
- 2.9 Sources and Importance of Alkanes 101

Chapter 3 Stereoisomerism and Chirality 114

3.1 Chirality—The Handedness of Molecules 114

3.2 Stereoisomerism 116

HOW TO Draw Chiral Molecules 117

3.3 Naming Chiral Centers—The *R,S* System 120

HOW TO Assign *R* or *S* Configuration to a Chiral Center 122

3.4 Acyclic Molecules with Two or More Stereocenters 123

3.5 Cyclic Molecules with Two or More Stereocenters 129

3.6 Tying All the Terminology Together 132

3.7 Optical Activity—How Chirality Is Detected in the Laboratory 134

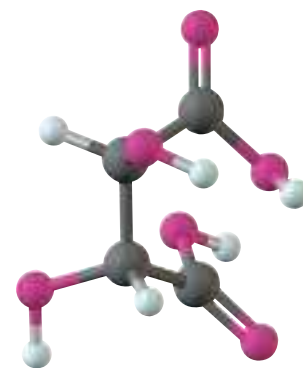
3.8 The Significance of Chirality in the Biological World 137

CONNECTIONS TO BIOLOGICAL CHEMISTRY Chiral Drugs 139

CONNECTIONS TO BIOLOGICAL CHEMISTRY Amino Acids 140

3.9 Separation of Enantiomers—Resolution 140

Summary 144 • Problems 146



Chapter 4 Acids and Bases 153

4.1 Arrhenius Acids and Bases 153

4.2 Brønsted-Lowry Acids and Bases 154

4.3 Acid Dissociation Constants, pK_a , and the Relative Strengths of Acids and Bases 160

4.4 The Position of Equilibrium in Acid-Base Reactions 162

HOW TO Calculate Equilibrium Constants for Acid-Base Reactions 163

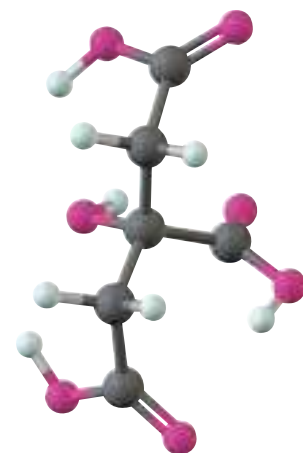
CONNECTIONS TO BIOLOGICAL CHEMISTRY The Ionization of Functional Groups at Physiological pH 164

4.5 Thermochemistry and Mechanisms of Acid-Base Reactions 165

4.6 Molecular Structure and Acidity 169

4.7 Lewis Acids and Bases 174

Summary 177 • Problems 179



Chapter 5 Alkenes: Bonding, Nomenclature, and Properties 186

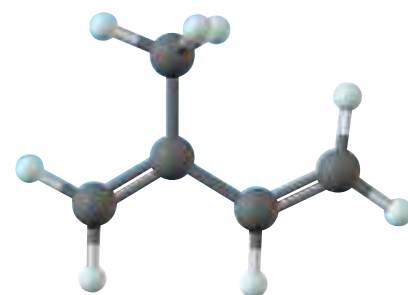
5.1 Structure of Alkenes 187

HOW TO Calculate the Index of Hydrogen Deficiency 188

5.2 Nomenclature of Alkenes 190

5.3 Physical Properties of Alkenes 196

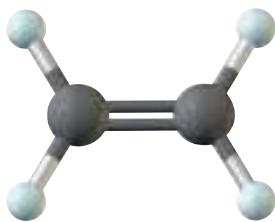
CHEMICAL CONNECTIONS The Case of the Iowa and New York Strains of the European Corn Borer 196



5.4 Naturally Occurring Alkenes—Terpene Hydrocarbons 197

CONNECTIONS TO BIOLOGICAL CHEMISTRY The Importance of *Cis* Double Bonds in Fats Versus Oils 199

Summary 200 • Problems 201



Chapter 6 Reactions of Alkenes 206

6.1 Reactions of Alkenes—An Overview 206

6.2 Organic Reactions Involving Reactive Intermediates 207

6.3 Electrophilic Additions 217

6.4 Hydroboration-Oxidation 236

6.5 Oxidation 240

HOW TO Write a Balanced Half-Reaction 242

6.6 Reduction 244

CONNECTIONS TO BIOLOGICAL CHEMISTRY *Trans* Fatty Acids: What They Are and How To Avoid Them 247

6.7 Molecules Containing Chiral Centers as Reactants or Products 248

Summary 253 • Problems 257



Chapter 7 Alkynes 266

7.1 Structure of Alkynes 266

7.2 Nomenclature of Alkynes 267

7.3 Physical Properties of Alkynes 269

7.4 Acidity of 1-Alkynes 269

7.5 Preparation of Alkynes 270

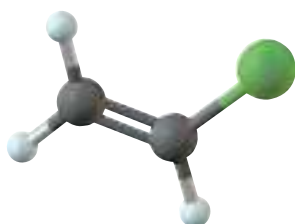
7.6 Electrophilic Addition to Alkynes 273

7.7 Hydration of Alkynes to Aldehydes and Ketones 275

7.8 Reduction of Alkynes 280

7.9 Organic Synthesis 282

Summary 285 • Problems 289



Chapter 8 Haloalkanes, Halogenation, and Radical Reactions 296

8.1 Structure 296

8.2 Nomenclature 297

8.3 Physical Properties of Haloalkanes 298

8.4 Preparation of Haloalkanes by Halogenation of Alkanes 302

8.5 Mechanism of Halogenation of Alkanes 305

CHEMICAL CONNECTIONS Freons 309

8.6 Allylic Halogenation 313

8.7 Radical Autoxidation 317

8.8 Radical Addition of HBr to Alkenes 320

Summary 323 • Problems 326

Chapter 9 Nucleophilic Substitution and β -Elimination 331

9.1 Nucleophilic Substitution in Haloalkanes 332

9.2 Mechanisms of Nucleophilic Aliphatic Substitution 334

9.3 Experimental Evidence for S_N1 and S_N2 Mechanisms 338

9.4 Analysis of Several Nucleophilic Substitution Reactions 353

9.5 β -Elimination 356

9.6 Mechanisms of β -Elimination 357

9.7 Experimental Evidence for E1 and E2 Mechanisms 360

9.8 Substitution Versus Elimination 366

9.9 Analysis of Several Competitions Between Substitutions and Eliminations 370

9.10 Neighboring Group Participation 372

CONNECTIONS TO BIOLOGICAL CHEMISTRY Mustard Gases and the Treatment of Neoplastic Diseases 375

Summary 376 • Problems 380

Chapter 10 Alcohols 390

10.1 Structure and Nomenclature of Alcohols 391

10.2 Physical Properties of Alcohols 393

CONNECTIONS TO BIOLOGICAL CHEMISTRY The Importance of Hydrogen Bonding in Drug-Receptor Interactions 395

10.3 Acidity and Basicity of Alcohols 397

10.4 Reaction of Alcohols with Active Metals 398

10.5 Conversion of Alcohols to Haloalkanes and Sulfonates 399

10.6 Acid-Catalyzed Dehydration of Alcohols 405

10.7 The Pinacol Rearrangement 410

10.8 Oxidation of Alcohols 412

CHEMICAL CONNECTIONS Blood Alcohol Screening 416

CONNECTIONS TO BIOLOGICAL CHEMISTRY The Oxidation of Alcohols by NAD^+ 418

10.9 Thiols 420

Summary 424 • Problems 428

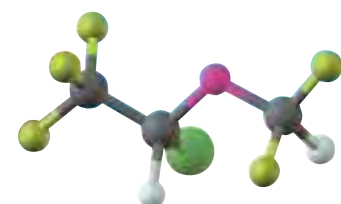
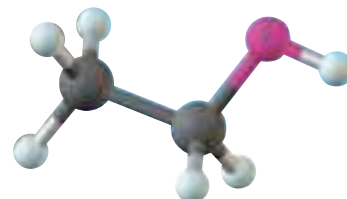
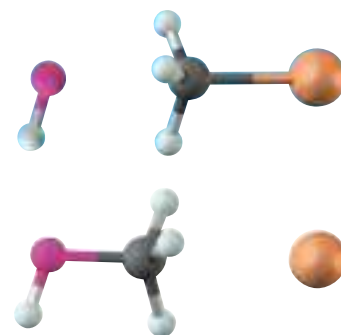
Chapter 11 Ethers, Epoxides, and Sulfides 436

11.1 Structure of Ethers 436

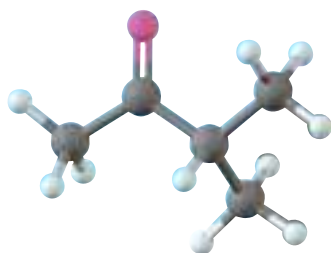
11.2 Nomenclature of Ethers 437

11.3 Physical Properties of Ethers 438

11.4 Preparation of Ethers 439

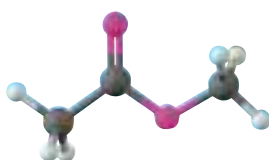


- 11.5 Reactions of Ethers 443
- 11.6 Silyl Ethers as Protecting Groups 445
- 11.7 Epoxides: Structure and Nomenclature 447
- 11.8 Synthesis of Epoxides 448
- 11.9 Reactions of Epoxides 452
- 11.10 Ethylene Oxide and Epichlorohydrin: Building Blocks in Organic Synthesis 455
- 11.11 Crown Ethers 458
- 11.12 Sulfides 459
- Summary 460 • Problems 465



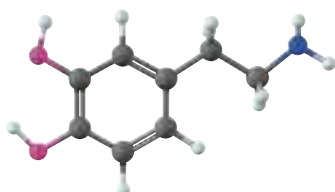
Chapter 12 Infrared Spectroscopy 474

- 12.1 Electromagnetic Radiation 474
- 12.2 Molecular Spectroscopy 475
- 12.3 Infrared Spectroscopy 476
- 12.4 Interpreting Infrared Spectra 481
- 12.5 Solving Infrared Spectral Problems 490
- Summary 490 • Problems 492



Chapter 13 Nuclear Magnetic Resonance Spectroscopy 495

- 13.1 Nuclear Spin States 495
- 13.2 Orientation of Nuclear Spins in an Applied Magnetic Field 496
- 13.3 Nuclear Magnetic "Resonance" 498
- 13.4 An NMR Spectrometer 500
- 13.5 Equivalent Hydrogens 501
- 13.6 Signal Areas 503
- 13.7 Chemical Shift 504
- 13.8 Signal Splitting and the ($n + 1$) Rule 508
- 13.9 The Origins of Signal Splitting 510
- 13.10 Stereochemistry and Topicity 517
- CHEMICAL CONNECTIONS Magnetic Resonance Imaging 520
- 13.11 ^{13}C -NMR 521
- 13.12 Interpretation of NMR Spectra 523
- HOW TO Solve NMR Spectral Problems 526
- Summary 528 • Problems 531



Chapter 14 Mass Spectrometry 539

- 14.1 A Mass Spectrometer 539
- 14.2 Features of a Mass Spectrum 542
- 14.3 Interpreting Mass Spectra 546

14.4 Mass Spectrometry in the Organic Synthesis Laboratory and
Other Applications 554

Summary 555 • Problems 556

Chapter 15 An Introduction to Organometallic Compounds 561

15.1 Organomagnesium and Organolithium Compounds 561

15.2 Lithium Diorganocopper (Gilman) Reagents 566

15.3 Carbenes and Carbenoids 569

Summary 573 • Problems 575

Chapter 16 Aldehydes and Ketones 581

16.1 Structure and Bonding 581

16.2 Nomenclature 582

16.3 Physical Properties 585

16.4 Reactions 586

16.5 Addition of Carbon Nucleophiles 588

16.6 The Wittig Reaction 594

16.7 Addition of Oxygen Nucleophiles 598

16.8 Addition of Nitrogen Nucleophiles 606

CONNECTIONS TO BIOLOGICAL CHEMISTRY Pyridoxine (Vitamin B₆): A Carrier
of Amino Groups 610

16.9 Keto-Enol Tautomerism 612

16.10 Oxidation 616

16.11 Reduction 617

CONNECTIONS TO BIOLOGICAL CHEMISTRY NADH: The Biological Equivalent
of a Hydride Reducing Agent 621

16.12 Reactions at an α -Carbon 624

Summary 627 • Problems 633

Chapter 17 Carboxylic Acids 649

17.1 Structure 649

17.2 Nomenclature 650

17.3 Physical Properties 653

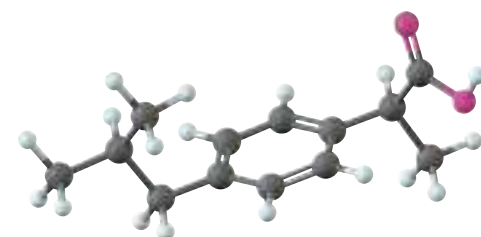
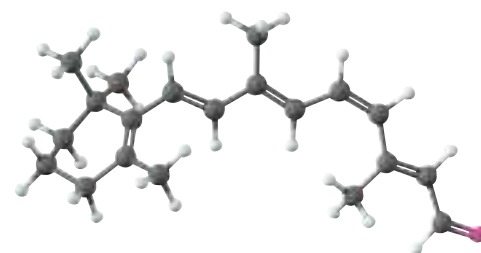
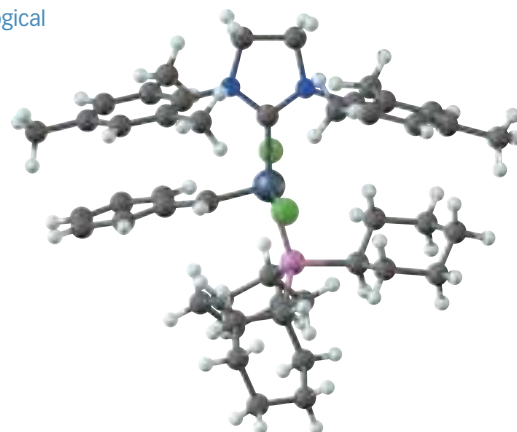
CHEMICAL CONNECTIONS From Willow Bark to Aspirin and Beyond 654

17.4 Acidity 655

17.5 Preparation of Carboxylic Acids 659

17.6 Reduction 659

CHEMICAL CONNECTIONS Industrial Synthesis of Acetic Acid—Transition Metal
Catalysis 660



17.7 Esterification 661

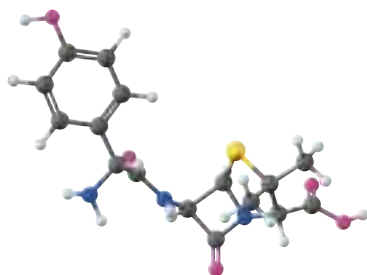
CHEMICAL CONNECTIONS The Pyrethrins: Natural Ester-containing Insecticides of Plant Origin 663

17.8 Conversion to Acid Chlorides 664

CHEMICAL CONNECTIONS Esters as Flavoring Agents 664

17.9 Decarboxylation 665

CONNECTIONS TO BIOLOGICAL CHEMISTRY Ketone Bodies and Diabetes Mellitus 667
Summary 668 • Problems 671



Chapter 18 Functional Derivatives of Carboxylic Acids 680

18.1 Structure and Nomenclature 681

CHEMICAL CONNECTIONS From Cocaine to Procaine and Beyond 683

CHEMICAL CONNECTIONS From Moldy Clover to a Blood Thinner 684

CHEMICAL CONNECTIONS The Penicillins and Cephalosporins: β -Lactam Antibiotics 686

18.2 Acidity of Amides, Imides, and Sulfonamides 687

CONNECTIONS TO BIOLOGICAL CHEMISTRY The Unique Structure of Amide Bonds 688

18.3 Characteristic Reactions 689

18.4 Reaction with Water: Hydrolysis 694

HOW TO Write Mechanisms for Interconversions of Carboxylic Acid Derivatives 696

CHEMICAL CONNECTIONS Mechanistic Alternatives For Ester Hydrolysis: S_N2 and S_N1 Possibilities 702

18.5 Reaction with Alcohols 708

18.6 Reactions with Ammonia and Amines 710

18.7 Reaction of Acid Chlorides with Salts of Carboxylic Acids 712

18.8 Interconversion of Functional Derivatives 712

18.9 Reactions with Organometallic Compounds 713

18.10 Reduction 716

Summary 721 • Problems 727

Chapter 19 Enolate Anions and Enamines 742

19.1 Formation and Reactions of Enolate Anions: An Overview 742

19.2 Aldol Reaction 744

19.3 Claisen and Dieckmann Condensations 751

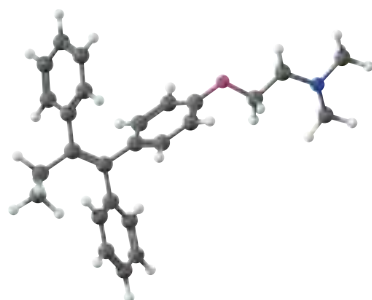
19.4 Claisen and Aldol Condensations in the Biological World 757

CHEMICAL CONNECTIONS Drugs That Lower Plasma Levels of Cholesterol 758

19.5 Enamines 760

19.6 Acetoacetic Ester Synthesis 763

19.7 Malonic Ester Synthesis 768



19.8 Conjugate Addition to α,β -Unsaturated Carbonyl Compounds 771

19.9 Crossed Enolate Reactions Using LDA 780

Summary 784 • Problems 790

Chapter 20 Dienes, Conjugated Systems, and Pericyclic Reactions 810

20.1 Stability of Conjugated Dienes 810

20.2 Electrophilic Addition to Conjugated Dienes 814

20.3 UV-Visible Spectroscopy 820

20.4 Pericyclic Reaction Theory 824

CHEMICAL CONNECTIONS Curry and Cancer 825

20.5 The Diels-Alder Reaction 827

20.6 Sigmatropic Shifts 836

Summary 841 • Problems 845



Chapter 21 Benzene and the Concept of Aromaticity 853

21.1 The Structure of Benzene 854

21.2 The Concept of Aromaticity 858

21.3 Nomenclature 867

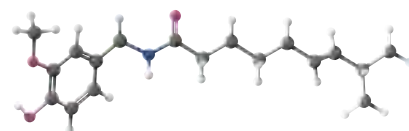
CHEMICAL CONNECTIONS Carcinogenic Polynuclear Aromatic Hydrocarbons and Smoking 870

21.4 Phenols 870

CHEMICAL CONNECTIONS Capsaicin, for Those Who Like It Hot 872

21.5 Reactions at a Benzylic Position 879

Summary 883 • Problems 888



Chapter 22 Reactions of Benzene and Its Derivatives 906

22.1 Electrophilic Aromatic Substitution 907

22.2 Disubstitution and Polysubstitution 917

22.3 Nucleophilic Aromatic Substitution 924

Summary 928 • Problems 932



Chapter 23 Amines 947

23.1 Structure and Classification 947

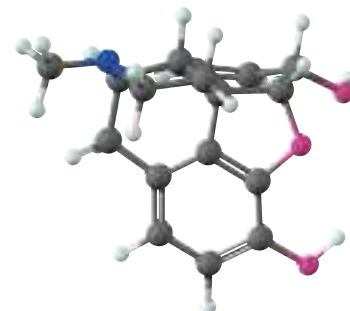
23.2 Nomenclature 948

23.3 Chirality of Amines and Quaternary Ammonium Ions 951

23.4 Physical Properties 952

CHEMICAL CONNECTIONS The Poison Dart Frogs of South America 953

23.5 Basicity 954



23.6 Reactions with Acids 961

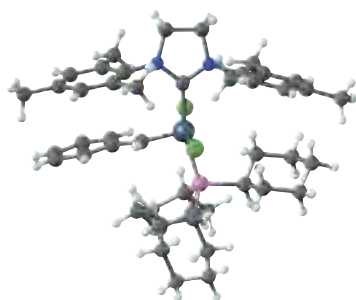
23.7 Preparation 964

23.8 Reaction with Nitrous Acid 966

23.9 Hofmann Elimination 974

23.10 Cope Elimination 976

Summary 977 • Problems 983



Chapter 24 Catalytic Carbon-Carbon Bond Formation 1000

24.1 Carbon-Carbon Bond-Forming Reactions from
Earlier Chapters 1001

24.2 Organometallic Compounds and Catalysis 1002

24.3 The Heck Reaction 1002

24.4 Catalytic Allylic Alkylation 1008

24.5 Palladium-Catalyzed Cross-Coupling Reactions 1012

24.6 Alkene Metathesis 1017

Summary 1019 • Problems 1023



Chapter 25 Carbohydrates 1037

25.1 Monosaccharides 1038

25.2 The Cyclic Structure of Monosaccharides 1042

CHEMICAL CONNECTIONS L-Ascorbic Acid (Vitamin C) 1044

25.3 Reactions of Monosaccharides 1046

CHEMICAL CONNECTIONS Testing for Glucose 1051

25.4 Disaccharides and Oligosaccharides 1052

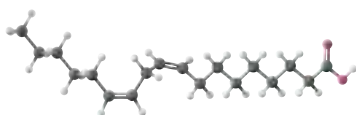
CHEMICAL CONNECTIONS A, B, AB, and O Blood Group Substances 1055

25.5 Polysaccharides 1055

CHEMICAL CONNECTIONS High-Fructose Corn Syrup 1057

25.6 Glucosaminoglycans 1058

Summary 1059 • Problems 1063



Chapter 26 Lipids 1071

26.1 Triglycerides 1071

26.2 Soaps and Detergents 1074

CONNECTIONS TO BIOLOGICAL CHEMISTRY FAD/FADH₂: Agents for Electron
Transfer in Biological Oxidation-Reductions: Fatty Acid Oxidation 1077

26.3 Prostaglandins 1078

26.4 Steroids 1081

26.5 Phospholipids 1085

CHEMICAL CONNECTIONS Snake Venom Phospholipases 1087

26.6 Fat-Soluble Vitamins 1088

CHEMICAL CONNECTIONS Vitamin K, Blood Clotting, and Basicity 1090

Summary 1091 • Problems 1093

Chapter 27 Amino Acids and Proteins 1098

27.1 Amino Acids 1098

27.2 Acid-Base Properties of Amino Acids 1101

27.3 Polypeptides and Proteins 1106

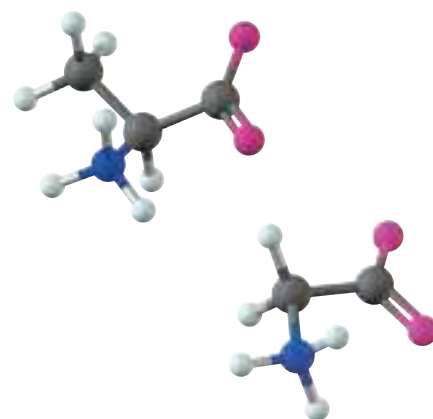
27.4 Primary Structure of Polypeptides and Proteins 1107

27.5 Synthesis of Polypeptides 1113

27.6 Three-Dimensional Shapes of Polypeptides and Proteins 1117

CHEMICAL CONNECTIONS Spider Silk 1123

Summary 1124 • Problems 1128



Chapter 28 Nucleic Acids 1134

28.1 Nucleosides and Nucleotides 1135

28.2 The Structure of DNA 1137

CHEMICAL CONNECTIONS The Search for Antiviral Drugs 1140

28.3 Ribonucleic Acids 1143

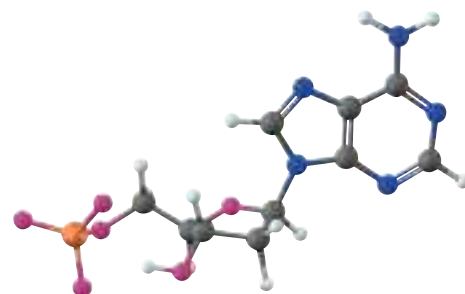
CHEMICAL CONNECTIONS The Fountain of Youth 1144

28.4 The Genetic Code 1146

28.5 Sequencing Nucleic Acids 1148

CHEMICAL CONNECTIONS DNA Fingerprinting 1152

Summary 1153 • Problems 1155



Chapter 29 Organic Polymer Chemistry 1158

29.1 The Architecture of Polymers 1159

29.2 Polymer Notation and Nomenclature 1159

29.3 Molecular Weights of Polymers 1160

29.4 Polymer Morphology—Crystalline Versus Amorphous Materials 1161

29.5 Step-Growth Polymerizations 1162

CHEMICAL CONNECTIONS Stitches That Dissolve 1168

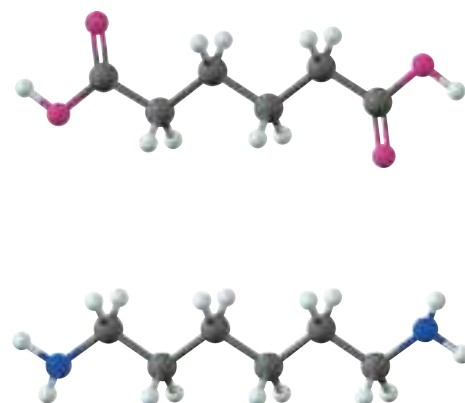
29.6 Chain-Growth Polymerizations 1169

CHEMICAL CONNECTIONS Organic Polymers That Conduct Electricity 1172

CHEMICAL CONNECTIONS The Chemistry of Superglue 1179

CHEMICAL CONNECTIONS Recycling of Plastics 1184

Summary 1186 • Problems 1189



Appendices:

1. Thermodynamics and the Equilibrium Constant A-1
2. Major Classes of Organic Acids A-2
3. Bond Dissociation Enthalpies A-3
4. Characteristic ^1H -NMR Chemical Shifts A-4
5. Characteristic ^{13}C -NMR Chemical Shifts A-5
6. Characteristic Infrared Absorption Frequencies A-6
7. Electrostatic Potential Maps A-7
8. Summary of Stereochemical Terms A-8
9. Summary of the Rules of Nomenclature A-12
10. Common Mistakes in Arrow Pushing A-20
11. Organic Chemistry Road Maps A-25

Glossary G-1

Index I-1

List of Mechanisms

Chapter 6 Reactions of Alkenes

- Electrophilic Addition of HBr to 2-Butene (Section 6.3A)
- Acid-Catalyzed Hydration of Propene (Section 6.3B)
- Carbocation Rearrangement in the Addition of HCl to an Alkene (Section 6.3C)
- Addition of Bromine with Anti Stereoselectivity (Section 6.3D)
- Halohydrin Formation and Its Anti Stereoselectivity (Section 6.3E)
- Oxymercuration-Reduction of an Alkene (Section 6.3F)
- Hydroboration (Section 6.4)
- Oxidation of a Trialkylborane by Alkaline Hydrogen Peroxide (Section 6.4)
- Formation of an Ozonide (Section 6.5B)

Chapter 7 Alkynes

- Addition of HBr to an Alkyne (Section 7.6B)
- HgSO₄/H₂SO₄ Catalyzed Hydration of an Alkyne (Section 7.7B)
- Reduction of an Alkyne by Sodium in Liquid Ammonia (Section 7.8C)

Chapter 8 Haloalkanes, Halogenation, and Radical Reactions

- Radical Chlorination of Ethane (Section 8.5B)
- Allylic Bromination of Propene Using NBS (Section 8.6A)
- Radical-Initiated Non-Markovnikov Addition of HBr to Alkenes (Section 8.8)

Chapter 9 Nucleophilic Substitution and β -Elimination

- An S_N2 Reaction (Section 9.2A)
- An S_N1 Reaction (Section 9.2B)
- Rearrangement During Solvolysis of 2-Chloro-3-phenylbutane (Section 9.3F)
- E1 Reaction of 2-Bromo-2-methylpropane (Section 9.6A)
- E2 Reaction of 2-Bromopropane (Section 9.6B)
- E2 Reaction of meso-1,2-Dibromo-1,2-diphenylethane (Section 9.7C)
- E2 Reaction of the Enantiomers of 1,2-Dibromo-1,2-diphenylethane (Section 9.7C)
- E2 Reaction of *cis*-1-Chloro-2-isopropylcyclohexane (Section 9.7C)
- Hydrolysis of a Sulfur Mustard—Participation by a Neighboring Group (Section 9.10)

Chapter 10 Alcohols

- Reaction of a 3° Alcohol with HBr—An S_N1 Reaction (Section 10.5A)
- Reaction of a 1° Alcohol with HBr—An S_N2 Reaction (Section 10.5A)
- Rearrangement upon Treatment of Neopentyl Alcohol with HCl (Section 10.5A)

Chapter 11 Ethers, Epoxides, and Sulfides

Acid-Catalysed Intermolecular Dehydration of a Primary Alcohol (Section 11.4B)

Acid-Catalyzed Addition of an Alcohol to an Alkene (Section 11.4C)

Acid-Catalyzed Cleavage of a Dialkyl Ether (Section 11.5A)

Epoxidation of an Alkene by RCO_3H (Section 11.8C)

Acid-Catalyzed Hydrolysis of an Epoxide (Section 11.9A)

Nucleophilic Opening of an Epoxide Ring (Section 11.9B)

Chapter 14 Mass Spectrometry

McLafferty Rearrangement of a Ketone (Section 14.3E)

McLafferty Rearrangement of a Carboxylic Acid (Section 14.3F)

Chapter 15 An Introduction to Organometallic Compounds

Formation of Dichlorocarbene and Its Reaction with Cyclohexene (Section 15.3B)

The Simmons-Smith Reaction with an Alkene (Section 15.3C)

Chapter 16 Aldehydes and Ketones

Grignard Reagent Reacting with Formaldehyde (Section 16.5A)

Organolithium Reagent Reacting with a Ketone (Section 16.5B)

Alkyne Anion Reacting with a Ketone (Section 16.5C)

Formation of a Cyanohydrin (Section 16.5D)

The Wittig Reaction (Section 16.6)

Base-Catalyzed Formation of a Hemiacetal (Section 16.7B)

Acid-Catalyzed Formation of a Hemiacetal (Section 16.7B)

Acid-Catalyzed Formation of an Acetal (Section 16.7B)

Formation of an Imine from an Aldehyde or Ketone (Section 16.8A)

Base-Catalyzed Equilibration of Keto and Enol Tautomers (Section 16.9)

Acid-Catalyzed Equilibration of Keto and Enol Tautomers (Section 16.9A)

Sodium Borohydride Reduction of an Aldehyde or Ketone (Section 16.11A)

Wolff-Kishner Reduction (Section 16.11E)

Acid-Catalyzed α -Halogenation of a Ketone (Section 16.12C)

Base-Promoted α -Halogenation of a Ketone (Section 16.12C)

Chapter 17 Carboxylic Acids

Formation of a Methyl Ester Using Diazomethane (Section 17.7B)

Decarboxylation of a β -Ketocarboxylic Acid (Section 17.9A)

Decarboxylation of a β -Dicarboxylic Acid (Section 17.9B)

Chapter 18 Functional Derivatives of Carboxylic Acids

Fischer Esterification (Section 18.3E)

Hydrolysis of an Acid Chloride (Section 18.4A)

Hydrolysis of an Ester in Aqueous Base (Saponification) (Section 18.4C)

Hydrolysis of an Amide in Aqueous Acid (Section 18.4D)

Hydrolysis of an Amide in Aqueous Base (Section 18.4D)

Hydrolysis of a Cyano Group to an Amide in Aqueous Base (Section 18.4E)

Reaction of an Acid Chloride and Ammonia (Section 18.6A)

Reaction of an Ester with a Grignard Reagent (Section 18.9A)

Reduction of an Ester by Lithium Aluminum Hydride (Section 18.10A)

Reduction of an Amide by Lithium Aluminum Hydride (Section 18.10B)

Chapter 19 Enolate Anions and Enamines

Base-Catalyzed Aldol Reaction (Section 19.2A)

Acid-Catalyzed Aldol Reaction (Section 19.2A)

Acid-Catalyzed Dehydration of an Aldol Product (Section 19.2A)

Claisen Condensation (Section 19.3A)

Alkylation of an Enamine (Section 19.5A)

Michael Reaction—Conjugate Addition of Enolate Anions (Section 19.8A)

Chapter 20 Dienes, Conjugated Systems, and Pericyclic Reactions

1,2- and 1,4-Addition to a Conjugated Diene (Section 20.2A)

The Claisen Rearrangement (Section 20.6A)

The Cope Rearrangement (Section 20.6B)

Chapter 21 Benzene and the Concept of Aromaticity

Kolbe Carboxylation of Phenol (Section 21.4E)

Chapter 22 Reactions of Benzene and its Derivatives

Electrophilic Aromatic Substitution—Chlorination (Section 22.1A)

Formation of the Nitronium Ion (Section 22.1B)

Friedel-Crafts Alkylation (Section 22.1C)

Friedel-Crafts Acylation—Generation of an Acylium Ion (Section 22.1C)

Nucleophilic Aromatic Substitution via a Benzyne Intermediate (Section 22.3A)

Nucleophilic Aromatic Substitution by Addition-Elimination (Section 22.3B)

Chapter 23 Amines

Formation of the Nitrosyl Cation (Section 23.8)

Reaction of a 2° Amine with the Nitrosyl Cation to Give an *N*-Nitrosamine (Section 23.8C)

Reaction of a 1° Amine with Nitrous Acid (Section 23.8D)

The Tiffeneau-Demjanov Reaction (Section 23.8D)

The Hofmann Elimination (Section 23.9)

The Cope Elimination (Section 23.10)

Chapter 24 Catalytic Carbon-Carbon Bond Formation

The Heck Reaction (Section 24.3B)

The Catalytic Cycle for Allylic Alkylation (Section 24.4A)

The Catalytic Cycle of Cross-Coupling (Section 24.4A)

Chapter 26 Lipids

Oxidation of a Fatty Acid $\text{—CH}_2\text{—CH}_2\text{—}$ to —CH=CH— by FAD (Section 26.2C)

Chapter 27 Amino Acids and Proteins

Cleavage of a Peptide Bond at Methionine by Cyanogen Bromide (Section 27.4B)

Edman Degradation—Cleavage of an *N*-Terminal Amino Acid (Section 27.4B)

Chapter 29 Organic Polymer Chemistry

Radical Polymerization of a Substituted Ethylene (Section 29.6A)

Ziegler-Natta Catalysis of Ethylene Polymerization (Section 29.6B)

Homogeneous Catalysis for Ziegler-Natta Coordination Polymerization (Section 29.6B)

Initiation of Anionic Polymerization of Alkenes (Section 29.6D)

Initiation of Anionic Polymerization of Butadiene (Section 29.6D)

Initiation of Cationic Polymerization of an Alkene by $\text{HF} \cdot \text{BF}_3$ (Section 29.6D)

Initiation of Cationic Polymerization of an Alkene by a Lewis Acid (Section 29.6D)

- [click Dark & Dangerous: A Collection of Paranormal Treats here](#)
- [download Kirchner here](#)
- **[Midnight Robber pdf, azw \(kindle\), epub](#)**
- **[read online Poland \(DK Eyewitness Travel Guide\) here](#)**
- [read Fiasco RPG Companion](#)
- [click Reasons of State \(Neversink\)](#)

- <http://unpluggedtv.com/lib/Dark---Dangerous--A-Collection-of-Paranormal-Treats.pdf>
- <http://hasanetmekci.com/ebooks/Kirchner.pdf>
- <http://serazard.com/lib/Midnight-Robber.pdf>
- <http://test1.batsinbelfries.com/ebooks/The-Power-of-Focus--How-to-Hit-Your-Business--Personal-and-Financial-Targets-with-Absolute-Confidence-and-Certai>
- <http://www.satilik-kopek.com/library/Why-I-Built-my-Solar-Home-Off-the-Grid.pdf>
- <http://reseauplatoparis.com/library/Discovering-Us--True-Love--Book-1-.pdf>