



SECOND EDITION

Organic Chemistry

PRINCIPLES AND
MECHANISMS

Joel Karty

Organic Chemistry

Principles and Mechanisms

SECOND EDITION

Joel M. Karty
Elon University



W. W. NORTON
NEW YORK • LONDON

To Pnut, Fafa, and Jakers

W. W. Norton & Company has been independent since its founding in 1923, when William Warder Norton and Mary D. Herter Norton first published lectures delivered at the People's Institute, the adult education division of New York City's Cooper Union. The firm soon expanded its program beyond the Institute, publishing books by celebrated academics from America and abroad. By midcentury, the two major pillars of Norton's publishing program—trade books and college texts—were firmly established. In the 1950s, the Norton family transferred control of the company to its employees, and today—with a staff of four hundred and a comparable number of trade, college, and professional titles published each year—W. W. Norton & Company stands as the largest and oldest publishing house owned wholly by its employees.

Copyright © 2018, 2014 by W. W. Norton & Company, Inc.
All rights reserved
Printed in Canada

Editor: Erik Fahlgren
Associate Managing Editor, College: Carla L. Talmadge
Editorial Assistant: Sara Bonacum
Managing Editor, College: Marian Johnson
Managing Editor, College Digital Media: Kim Yi
Production Manager: Eric Pier-Hocking
Media Editor: Chris Rapp
Associate Media Editor: Arielle Holstein
Media Project Editor: Jesse Newkirk
Assistant Media Editor: Doris Chiu
Ebook Production Manager: Mateus Manço Teixeira
Ebook Production Coordinator: Lizz Thabet
Marketing Manager, Chemistry: Stacy Loyal
Design Director: Jillian Burr
Photo Editor: Travis Carr
Permissions Manager: Megan Schindel
Composition: Graphic World
Illustrations: Imagineering
Manufacturing: Transcontinental

Permission to use copyrighted material is included at the back of the book.

Library of Congress Cataloging-in-Publication Data

Names: Karty, Joel, author.

Title: Organic chemistry : principles and mechanisms / Joel M. Karty, Elon University.

Description: Second edition. | New York : W.W. Norton & Company, [2018] | Includes index.

Identifiers: LCCN 2017042262 | **ISBN 9780393630756 (hardcover)**

Subjects: LCSH: Chemistry, Organic—Textbooks.

Classification: LCC QD253.2 .K375 2018 | DDC 547—c23 LC record available at <https://lccn.loc.gov/2017042262>

W. W. Norton & Company, Inc., 500 Fifth Avenue, New York, NY 10110

wnorton.com

W. W. Norton & Company Ltd., 15 Carlisle Street, London W1D 3BS

1 2 3 4 5 6 7 8 9 0

About the Author

JOEL KARTY earned his B.S. in chemistry at the University of Puget Sound and his Ph.D. at Stanford University. He joined the faculty of Elon University in 2001, where he currently holds the rank of full professor. He teaches primarily the organic chemistry sequence and also teaches general chemistry. In the summer, Joel teaches at the Summer Biomedical Sciences Institute through the Duke University Medical Center. His research interests include investigating the roles of resonance and inductive effects in fundamental chemical systems and studying the mechanism of pattern formation in Liesegang reactions. He has written a very successful student supplement, *Get Ready for Organic Chemistry*, Second Edition (formerly called *The Nuts and Bolts of Organic Chemistry*).



Brief Contents

1 Atomic and Molecular Structure 1

Interchapter A Nomenclature: The Basic System for Naming Organic Compounds: Alkanes, Haloalkanes, Nitroalkanes, Cycloalkanes, and Ethers 52

2 Three-Dimensional Geometry, Intermolecular Interactions, and Physical Properties 70

3 Orbital Interactions 1: Hybridization and Two-Center Molecular Orbitals 119

Interchapter B Naming Alkenes, Alkynes, and Benzene Derivatives 152

4 Isomerism 1: Conformers and Constitutional Isomers 165

5 Isomerism 2: Chirality, Enantiomers, and Diastereomers 208

Interchapter C Stereochemistry in Nomenclature: *R* and *S* Configurations about Asymmetric Carbons and *Z* and *E* Configurations about Double Bonds 258

6 The Proton Transfer Reaction: An Introduction to Mechanisms, Thermodynamics, and Charge Stability 274

7 An Overview of the Most Common Elementary Steps 328

Interchapter D Molecular Orbital Theory, Hyperconjugation, and Chemical Reactions 364

Interchapter E Naming Compounds with a Functional Group That Calls for a Suffix 1: Alcohols, Amines, Ketones, and Aldehydes 377

8 An Introduction to Multistep Mechanisms: S_N1 and $E1$ Reactions and Their Comparisons to S_N2 and $E2$ Reactions 393

9 Nucleophilic Substitution and Elimination Reactions 1: Competition among S_N2 , S_N1 , $E2$, and $E1$ Reactions 442

Interchapter F Naming Compounds with a Functional Group That Calls for a Suffix 2: Carboxylic Acids and Their Derivatives 503

10 Nucleophilic Substitution and Elimination Reactions 2: Reactions That Are Useful for Synthesis 515

11 Electrophilic Addition to Nonpolar π Bonds 1: Addition of a Brønsted Acid 563

12 Electrophilic Addition to Nonpolar π Bonds 2: Reactions Involving Cyclic Transition States 601

13 Organic Synthesis 1: Beginning Concepts in Designing Multistep Synthesis 641

14 Orbital Interactions 2: Extended π Systems, Conjugation, and Aromaticity 682

15 Structure Determination 1: Ultraviolet–Visible and Infrared Spectroscopies 723

16 Structure Determination 2: Nuclear Magnetic Resonance Spectroscopy and Mass Spectrometry 771

17 Nucleophilic Addition to Polar π Bonds 1: Addition of Strong Nucleophiles 839

18 Nucleophilic Addition to Polar π Bonds 2: Weak Nucleophiles and Acid and Base Catalysis 888

19 Organic Synthesis 2: Intermediate Topics in Synthesis Design, and Useful Redox and Carbon–Carbon Bond-Forming Reactions 946

20 Nucleophilic Addition–Elimination Reactions 1: The General Mechanism Involving Strong Nucleophiles 1000

21 Nucleophilic Addition–Elimination Reactions 2: Weak Nucleophiles 1045

22 Aromatic Substitution 1: Electrophilic Aromatic Substitution on Benzene; Useful Accompanying Reactions 1104

23 Aromatic Substitution 2: Reactions of Substituted Benzenes and Other Rings 1144

24 The Diels–Alder Reaction and Other Pericyclic Reactions 1198

25 Reactions Involving Free Radicals 1247

Interchapter G Fragmentation Pathways in Mass Spectrometry 1295

26 Polymers 1307

Contents

List of Biochemistry Topics xxiii
List of Interest Boxes xxv
List of Connections Boxes xxvi
List of Green Chemistry Boxes xxix
List of Mechanisms xxx
Preface xxxiii

1 Atomic and Molecular Structure 1

1.1 What Is Organic Chemistry? 1
1.2 Why Carbon? 3
1.3 Atomic Structure and Ground State Electron Configurations 4
1.4 The Covalent Bond: Bond Energy and Bond Length 8
1.5 Lewis Dot Structures and the Octet Rule 12
1.6 Strategies for Success: Drawing Lewis Dot Structures Quickly 14
1.7 Electronegativity, Polar Covalent Bonds, and Bond Dipoles 16
1.8 Ionic Bonds 18
1.9 Assigning Electrons to Atoms in Molecules: Formal Charge 19
1.10 Resonance Theory 21
1.11 Strategies for Success: Drawing All Resonance Structures 25
1.12 Shorthand Notations 30
1.13 An Overview of Organic Compounds: Functional Groups 34

THE ORGANIC CHEMISTRY OF BIOMOLECULES

1.14 An Introduction to Proteins, Carbohydrates, and Nucleic Acids:
Fundamental Building Blocks and Functional Groups 37

Chapter Summary and Key Terms 45

Problems 45

INTERCHAPTER

A

Nomenclature: The Basic System for Naming Organic Compounds

Alkanes, Haloalkanes, Nitroalkanes, Cycloalkanes,
and Ethers 52

A.1 The Need for Systematic Nomenclature: An Introduction to
the IUPAC System 52



- A.2** Alkanes and Substituted Alkanes 53
 - A.3** Haloalkanes and Nitroalkanes: Roots, Prefixes, and Locator Numbers 54
 - A.4** Alkyl Substituents: Branched Alkanes and Substituted Branched Alkanes 58
 - A.5** Cyclic Alkanes and Cyclic Alkyl Groups 60
 - A.6** Ethers and Alkoxy Groups 62
 - A.7** Trivial Names or Common Names 63
- Problems 67

2 Three-Dimensional Geometry, Intermolecular Interactions, and Physical Properties 70

- 2.1** Valence Shell Electron Pair Repulsion (VSEPR) Theory: Three-Dimensional Geometry 71
- 2.2** Dash–Wedge Notation 75
- 2.3** Strategies for Success: The Molecular Modeling Kit 77
- 2.4** Net Molecular Dipoles and Dipole Moments 78
- 2.5** Physical Properties, Functional Groups, and Intermolecular Interactions 80
- 2.6** Melting Points, Boiling Points, and Intermolecular Interactions 82
- 2.7** Solubility 91
- 2.8** Strategies for Success: Ranking Boiling Points and Solubilities of Structurally Similar Compounds 96
- 2.9** Protic and Aprotic Solvents 99
- 2.10** Soaps and Detergents 101

THE ORGANIC CHEMISTRY OF BIOMOLECULES

- 2.11** An Introduction to Lipids 105

Chapter Summary and Key Terms 112

Problems 113

3 Orbital Interactions 1 Hybridization and Two-Center Molecular Orbitals 119

- 3.1** Atomic Orbitals and the Wave Nature of Electrons 120
- 3.2** Interaction between Orbitals: Constructive and Destructive Interference 122
- 3.3** An Introduction to Molecular Orbital Theory and σ Bonds: An Example with H_2 124
- 3.4** Hybrid Atomic Orbitals and Geometry 128
- 3.5** Valence Bond Theory and Other Orbitals of σ Symmetry: An Example with Ethane (H_3C-CH_3) 133
- 3.6** An Introduction to π Bonds: An Example with Ethene ($H_2C=CH_2$) 136

- 3.7** Nonbonding Orbitals: An Example with Formaldehyde ($\text{H}_2\text{C}=\text{O}$) 139
 - 3.8** Triple Bonds: An Example with Ethyne ($\text{HC}\equiv\text{CH}$) 140
 - 3.9** Bond Rotation about Single and Double Bonds: Cis and Trans Configurations 141
 - 3.10** Strategies for Success: Molecular Models and Extended Geometry about Single and Double Bonds 144
 - 3.11** Hybridization, Bond Characteristics, and Effective Electronegativity 145
- Chapter Summary and Key Terms 148
- Problems 149

INTERCHAPTER

B

Naming Alkenes, Alkynes, and Benzene Derivatives 152

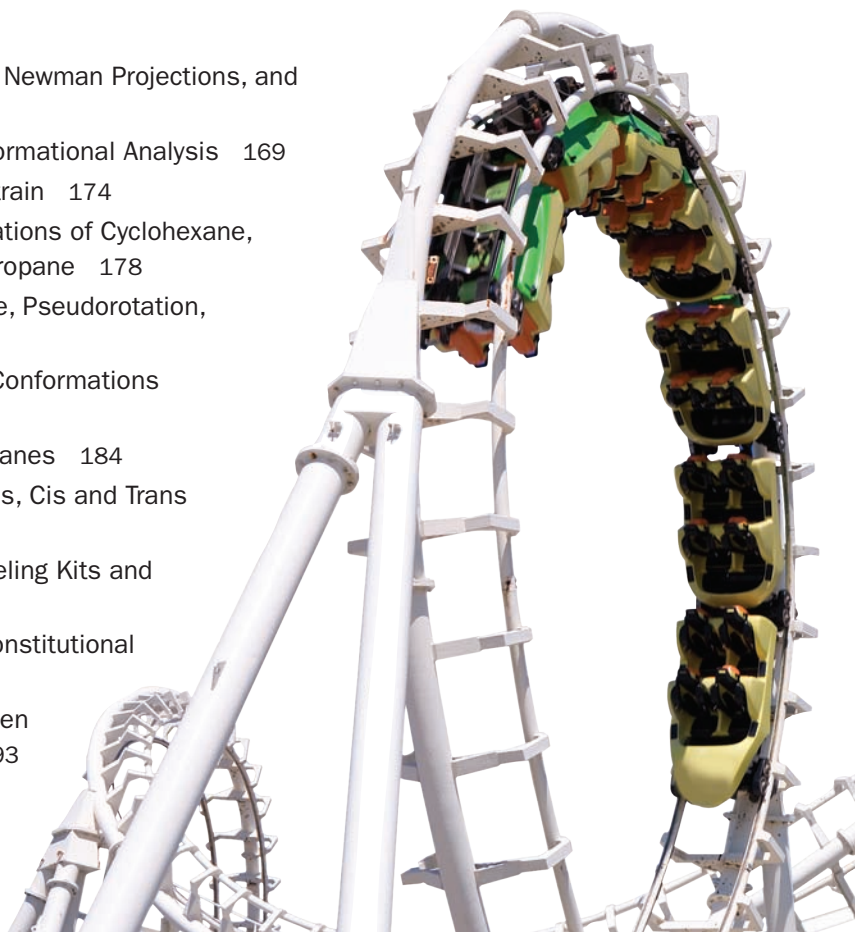
- B.1** Alkenes, Alkynes, Cycloalkenes, and Cycloalkynes: Molecules with One $\text{C}=\text{C}$ or $\text{C}\equiv\text{C}$ 152
 - B.2** Molecules with Multiple $\text{C}=\text{C}$ or $\text{C}\equiv\text{C}$ Bonds 155
 - B.3** Benzene and Benzene Derivatives 157
 - B.4** Trivial Names Involving Alkenes, Alkynes, and Benzene Derivatives 159
- Problems 162

4

Isomerism 1

Conformers and Constitutional Isomers 165

- 4.1** Isomerism: A Relationship 165
- 4.2** Conformers: Rotational Conformations, Newman Projections, and Dihedral Angles 166
- 4.3** Conformers: Energy Changes and Conformational Analysis 169
- 4.4** Conformers: Cyclic Alkanes and Ring Strain 174
- 4.5** Conformers: The Most Stable Conformations of Cyclohexane, Cyclopentane, Cyclobutane, and Cyclopropane 178
- 4.6** Conformers: Cyclopentane, Cyclohexane, Pseudorotation, and Chair Flips 179
- 4.7** Strategies for Success: Drawing Chair Conformations of Cyclohexane 182
- 4.8** Conformers: Monosubstituted Cyclohexanes 184
- 4.9** Conformers: Disubstituted Cyclohexanes, Cis and Trans Isomers, and Haworth Projections 188
- 4.10** Strategies for Success: Molecular Modeling Kits and Chair Flips 189
- 4.11** Constitutional Isomerism: Identifying Constitutional Isomers 190
- 4.12** Constitutional Isomers: Index of Hydrogen Deficiency (Degree of Unsaturation) 193



- 4.13** Strategies for Success: Drawing All Constitutional Isomers of a Given Formula 195

THE ORGANIC CHEMISTRY OF BIOMOLECULES

- 4.14** Constitutional Isomers and Biomolecules: Amino Acids and Monosaccharides 198
- 4.15** Saturation and Unsaturation in Fats and Oils 199

Chapter Summary and Key Terms 201

Problems 202

5 Isomerism 2

Chirality, Enantiomers, and Diastereomers 208

- 5.1** Defining Configurational Isomers, Enantiomers, and Diastereomers 208
- 5.2** Enantiomers, Mirror Images, and Superimposability 210
- 5.3** Strategies for Success: Drawing Mirror Images 212
- 5.4** Chirality 214
- 5.5** Diastereomers 224
- 5.6** Fischer Projections and Stereochemistry 229
- 5.7** Strategies for Success: Converting between Fischer Projections and Zigzag Conformations 231
- 5.8** Physical and Chemical Properties of Isomers 234
- 5.9** Stability of Double Bonds and Chemical Properties of Isomers 238
- 5.10** Separating Configurational Isomers 240
- 5.11** Optical Activity 241

THE ORGANIC CHEMISTRY OF BIOMOLECULES

- 5.12** The Chirality of Biomolecules 245
- 5.13** The D/L System for Classifying Monosaccharides and Amino Acids 247
- 5.14** The D Family of Aldoses 248

Chapter Summary and Key Terms 250

Problems 251

INTERCHAPTER

C

Stereochemistry in Nomenclature

R and *S* Configurations about Asymmetric Carbons and *Z* and *E* Configurations about Double Bonds 258

- C.1** Priority of Substituents and Stereochemical Configurations at Asymmetric Carbons: *R/S* Designations 258
- C.2** Stereochemical Configurations of Alkenes: *Z/E* Designations 268
- Problems 272

6 The Proton Transfer Reaction

An Introduction to Mechanisms, Thermodynamics, and Charge Stability 274

- 6.1** An Introduction to Reaction Mechanisms: The Proton Transfer Reaction and Curved Arrow Notation 275
- 6.2** Chemical Equilibrium and the Equilibrium Constant, K_{eq} 277
- 6.3** Thermodynamics and Gibbs Free Energy 287
- 6.4** Strategies for Success: Functional Groups and Acidity 289
- 6.5** Relative Strengths of Charged and Uncharged Acids: The Reactivity of Charged Species 291
- 6.6** Relative Acidities of Protons on Atoms with Like Charges 293
- 6.7** Strategies for Success: Ranking Acid and Base Strengths—The Relative Importance of Effects on Charge 308
- 6.8** Strategies for Success: Determining Relative Contributions by Resonance Structures 312

THE ORGANIC CHEMISTRY OF BIOMOLECULES

- 6.9** The Structure of Amino Acids in Solution as a Function of pH 314
- 6.10** Electrophoresis and Isoelectric Focusing 317

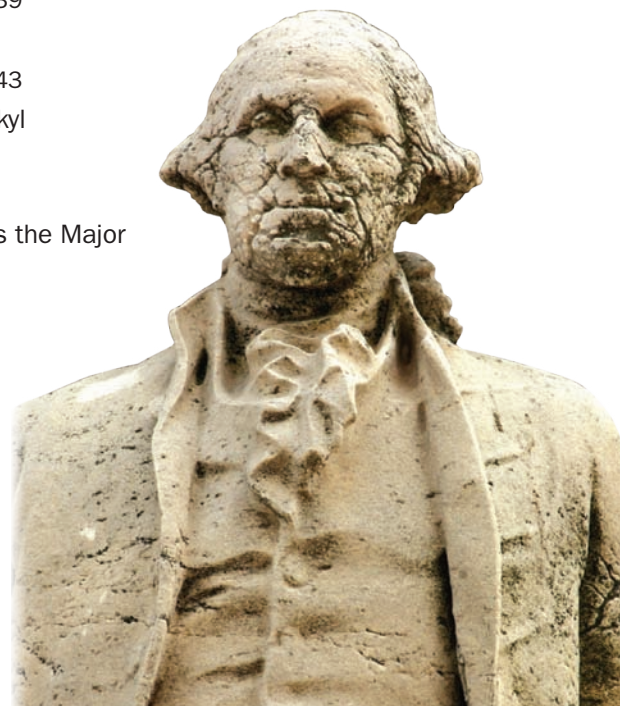
Chapter Summary and Key Terms 320

Problems 321

7 An Overview of the Most Common Elementary Steps

328

- 7.1** Mechanisms as Predictive Tools: The Proton Transfer Step Revisited 329
 - 7.2** Bimolecular Nucleophilic Substitution (S_N2) Steps 334
 - 7.3** Bond-Forming (Coordination) and Bond-Breaking (Heterolysis) Steps 337
 - 7.4** Nucleophilic Addition and Nucleophile Elimination Steps 339
 - 7.5** Bimolecular Elimination ($E2$) Steps 341
 - 7.6** Electrophilic Addition and Electrophile Elimination Steps 343
 - 7.7** Carbocation Rearrangements: 1,2-Hydride Shifts and 1,2-Alkyl Shifts 345
 - 7.8** The Driving Force for Chemical Reactions 347
 - 7.9** Keto–Enol Tautomerization: An Example of Bond Energies as the Major Driving Force 350
- Chapter Summary and Key Terms 355
- Problems 356



INTERCHAPTER

D Molecular Orbital Theory,
Hyperconjugation, and Chemical
Reactions 364

- D.1** Relative Stabilities of Carbocations and Alkenes: Hyperconjugation 364
- D.2** MO Theory and Chemical Reactions 366
Problems 376

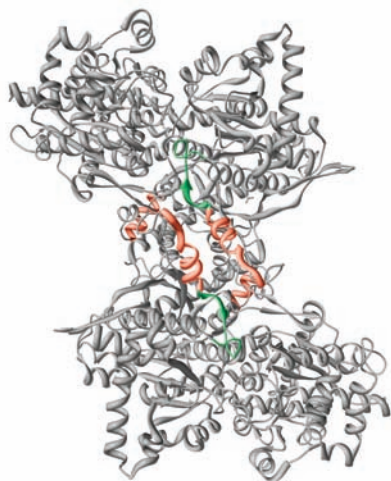
INTERCHAPTER

E Naming Compounds with a Functional
Group That Calls for a Suffix 1
Alcohols, Amines, Ketones, and Aldehydes 377

- E.1** The Basic System for Naming Compounds Having a Functional Group That Calls for a Suffix: Alcohols and Amines 378
- E.2** Naming Ketones and Aldehydes 384
- E.3** Trivial Names of Alcohols, Amines, Ketones, and Aldehydes 386
Problems 390

8 An Introduction to Multistep Mechanisms
 S_N1 and E1 Reactions and Their Comparisons to S_N2
and E2 Reactions 393

- 8.1** The Unimolecular Nucleophilic Substitution (S_N1) Reaction 394
- 8.2** The Unimolecular Elimination (E1) Reaction 398
- 8.3** Direct Experimental Evidence for Reaction Mechanisms 400
- 8.4** The Kinetics of S_N2 , S_N1 , E2, and E1 Reactions 400
- 8.5** Stereochemistry of Nucleophilic Substitution and Elimination Reactions 406
- 8.6** The Reasonableness of a Mechanism: Proton Transfers and Carbocation Rearrangements 421
- 8.7** Resonance-Delocalized Intermediates in Mechanisms 432
Chapter Summary and Key Terms 434
Problems 434



9 Nucleophilic Substitution and Elimination
Reactions 1
Competition among S_N2 , S_N1 , E2, and E1
Reactions 442

- 9.1** The Competition among S_N2 , S_N1 , E2, and E1 Reactions 443
- 9.2** Rate-Determining Steps Revisited: Simplified Pictures of the S_N2 , S_N1 , E2, and E1 Reactions 445

- 9.3** Factor 1: Strength of the Attacking Species 447
- 9.4** Factor 2: Concentration of the Attacking Species 456
- 9.5** Factor 3: Leaving Group Ability 458
- 9.6** Factor 4: Type of Carbon Bonded to the Leaving Group 464
- 9.7** Factor 5: Solvent Effects 470
- 9.8** Factor 6: Heat 476
- 9.9** Predicting the Outcome of an $S_N2/S_N1/E2/E1$ Competition 477
- 9.10** Regioselectivity in Elimination Reactions: Zaitsev's Rule 482
- 9.11** Intermolecular Reactions versus Intramolecular Cyclizations 485
- 9.12** Kinetic Control, Thermodynamic Control, and Reversibility 487

THE ORGANIC CHEMISTRY OF BIOMOLECULES

- 9.13** Nucleophilic Substitution Reactions and Monosaccharides: The Formation and Hydrolysis of Glycosides 490

Chapter Summary and Key Terms 493
Reaction Tables 494
Problems 495

INTERCHAPTER

F

Naming Compounds with a Functional Group That Calls for a Suffix 2

Carboxylic Acids and Their Derivatives 503

- F.1** Naming Carboxylic Acids, Acid Chlorides, Amides, and Nitriles 503
 - F.2** Naming Esters and Acid Anhydrides 507
 - F.3** Trivial Names of Carboxylic Acids and Their Derivatives 510
- Problems 513

10 Nucleophilic Substitution and Elimination Reactions 2

Reactions That Are Useful for Synthesis 515

- 10.1** Nucleophilic Substitution: Converting Alcohols into Alkyl Halides Using PBr_3 and PCl_3 516
- 10.2** Nucleophilic Substitution: Alkylation of Ammonia and Amines 520
- 10.3** Nucleophilic Substitution: Alkylation of α Carbons 523
- 10.4** Nucleophilic Substitution: Halogenation of α Carbons 528
- 10.5** Nucleophilic Substitution: Diazomethane Formation of Methyl Esters 533
- 10.6** Nucleophilic Substitution: Formation of Ethers and Epoxides 535
- 10.7** Nucleophilic Substitution: Epoxides and Oxetanes as Substrates 540
- 10.8** Elimination: Generating Alkynes via Elimination Reactions 548

- 10.9** Elimination: Hofmann Elimination 551
Chapter Summary and Key Terms 554
Reaction Tables 555
Problems 557

11 Electrophilic Addition to Nonpolar π Bonds 1

Addition of a Brønsted Acid 563

- 11.1** The General Electrophilic Addition Mechanism: Addition of a Strong Brønsted Acid to an Alkene 565
11.2 Benzene Rings Do Not Readily Undergo Electrophilic Addition of Brønsted Acids 568
11.3 Regiochemistry: Production of the More Stable Carbocation and Markovnikov's Rule 569
11.4 Carbocation Rearrangements 573
11.5 Stereochemistry 574
11.6 Addition of a Weak Acid: Acid Catalysis 576
11.7 Electrophilic Addition of a Strong Brønsted Acid to an Alkyne 578
11.8 Acid-Catalyzed Hydration of an Alkyne: Synthesis of a Ketone 581
11.9 Electrophilic Addition of a Brønsted Acid to a Conjugated Diene: 1,2-Addition and 1,4-Addition 583
11.10 Kinetic versus Thermodynamic Control in Electrophilic Addition to a Conjugated Diene 586

THE ORGANIC CHEMISTRY OF BIOMOLECULES

- 11.11** Terpene Biosynthesis: Carbocation Chemistry in Nature 589

Chapter Summary and Key Terms 594
Reaction Table 595
Problems 596

12 Electrophilic Addition to Nonpolar π Bonds 2

Reactions Involving Cyclic Transition States 601

- 12.1** Electrophilic Addition via a Three-Membered Ring: The General Mechanism 602
12.2 Electrophilic Addition of Carbenes: Formation of Cyclopropane Rings 604
12.3 Electrophilic Addition Involving Molecular Halogens: Synthesis of 1,2-Dihalides and Halohydrins 607
12.4 Oxymercuration–Reduction: Addition of Water 614
12.5 Epoxide Formation Using Peroxyacids 620
12.6 Hydroboration–Oxidation: Anti-Markovnikov Syn Addition of Water to an Alkene 623



- 12.7** Hydroboration–Oxidation of Alkynes 631
- Chapter Summary and Key Terms 632
- Reaction Tables 633
- Problems 635

13 Organic Synthesis 1

Beginning Concepts in Designing Multistep Synthesis 641

- 13.1** Writing the Reactions of an Organic Synthesis 642
- 13.2** Cataloging Reactions: Functional Group Transformations and Carbon–Carbon Bond-Forming/Breaking Reactions 647
- 13.3** Retrosynthetic Analysis: Thinking Backward to Go Forward 649
- 13.4** Synthetic Traps 654
- 13.5** Choice of the Solvent 662
- 13.6** Considerations of Stereochemistry in Synthesis 664
- 13.7** Strategies for Success: Improving Your Proficiency with Solving Multistep Syntheses 668
- 13.8** Choosing the Best Synthesis Scheme 671
- Chapter Summary and Key Terms 676
- Problems 677

14 Orbital Interactions 2

Extended π Systems, Conjugation, and Aromaticity 682

- 14.1** The Shortcomings of VB Theory 683
- 14.2** Multiple-Center MOs 686
- 14.3** Aromaticity and Hückel's Rules 695
- 14.4** The MO Picture of Benzene: Why It's Aromatic 700
- 14.5** The MO Picture of Cyclobutadiene: Why It's Antiaromatic 702
- 14.6** Aromaticity in Larger Rings: $[n]$ Annulenes 705
- 14.7** Aromaticity and Multiple Rings 706
- 14.8** Heterocyclic Aromatic Compounds 707
- 14.9** Aromatic Ions 710
- 14.10** Strategies for Success: Counting π Systems and π Electrons Using the Lewis Structure 710

THE ORGANIC CHEMISTRY OF BIOMOLECULES

- 14.11** Aromaticity and DNA 714

Chapter Summary and Key Terms 718
Problems 718

15 Structure Determination 1

Ultraviolet–Visible and Infrared Spectroscopies 723

- 15.1** An Overview of Ultraviolet–Visible Spectroscopy 724
- 15.2** The UV–Vis Spectrum: Photon Absorption and Electron Transitions 726
- 15.3** Effects of Structure on λ_{max} 730
- 15.4** IR Spectroscopy 736
- 15.5** A Closer Look at Some Important IR Absorption Bands 745
- 15.6** Structure Elucidation Using IR Spectroscopy 756
- Chapter Summary and Key Terms 762
- Problems 763

16 Structure Determination 2

Nuclear Magnetic Resonance Spectroscopy and Mass Spectrometry 771

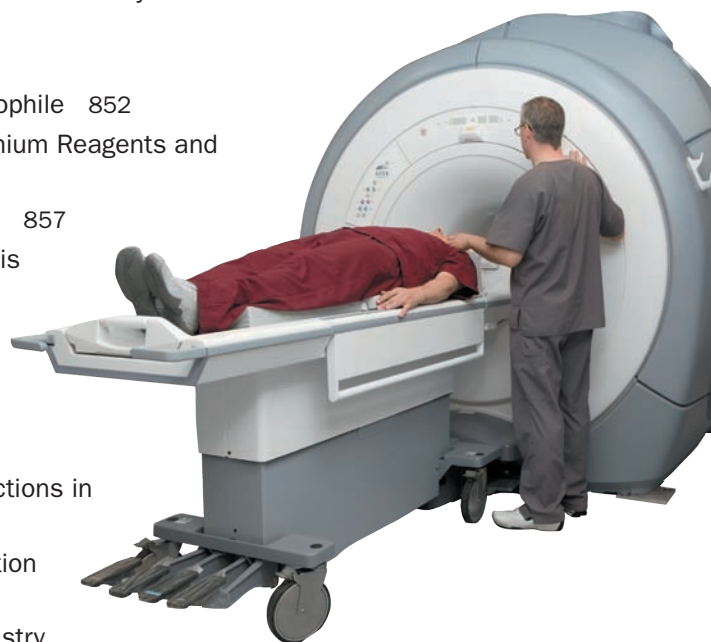
- 16.1** NMR Spectroscopy: An Overview 772
- 16.2** Nuclear Spin and the NMR Signal 773
- 16.3** Chemical Distinction and the Number of NMR Signals 776
- 16.4** Strategies for Success: The Chemical Distinction Test and Molecular Symmetry 778
- 16.5** The Time Scale of NMR Spectroscopy 781
- 16.6** Chemical Shift 783
- 16.7** Characteristic Chemical Shifts, Inductive Effects, and Magnetic Anisotropy 784
- 16.8** Trends in Chemical Shift 789
- 16.9** Integration of Signals 790
- 16.10** Splitting of the Signal by Spin–Spin Coupling: The $N + 1$ Rule 792
- 16.11** Coupling Constants and Signal Resolution 797
- 16.12** Complex Signal Splitting 801
- 16.13** ^{13}C NMR Spectroscopy 804
- 16.14** DEPT ^{13}C NMR Spectroscopy 809
- 16.15** Structure Elucidation Using NMR Spectroscopy 811
- 16.16** Mass Spectrometry: An Overview 818
- 16.17** Features of a Mass Spectrum, the Nitrogen Rule, and Fragmentation 820
- 16.18** Isotope Effects: $M + 1$ and $M + 2$ Peaks 823
- 16.19** Determining a Molecular Formula of an Organic Compound from the Mass Spectrum 826
- Chapter Summary and Key Terms 829
- Problems 830



17 Nucleophilic Addition to Polar π Bonds 1

Addition of Strong Nucleophiles 839

- 17.1** An Overview of the General Mechanism: Addition of Strong Nucleophiles 841
 - 17.2** Substituent Effects: Relative Reactivity of Ketones and Aldehydes in Nucleophilic Addition 842
 - 17.3** Reactions of LiAlH_4 and NaBH_4 844
 - 17.4** Sodium Hydride: A Strong Base but a Poor Nucleophile 852
 - 17.5** Reactions of Organometallic Compounds: Alkyl lithium Reagents and Grignard Reagents 854
 - 17.6** Limitations of Alkyl lithium and Grignard Reagents 857
 - 17.7** Wittig Reagents and the Wittig Reaction: Synthesis of Alkenes 858
 - 17.8** Generating Wittig Reagents 861
 - 17.9** Direct Addition versus Conjugate Addition 863
 - 17.10** Lithium Dialkylcuprates and the Selectivity of Organometallic Reagents 869
 - 17.11** Organic Synthesis: Grignard and Alkyl lithium Reactions in Synthesis 872
 - 17.12** Organic Synthesis: Considerations of Direct Addition versus Conjugate Addition 874
 - 17.13** Organic Synthesis: Considerations of Regiochemistry in the Formation of Alkenes 877
- Chapter Summary and Key Terms 878
- Reaction Tables 879
- Problems 880



18 Nucleophilic Addition to Polar π Bonds 2

Weak Nucleophiles and Acid and Base Catalysis 888

- 18.1** Weak Nucleophiles as Reagents: Acid and Base Catalysis 888
- 18.2** Formation and Hydrolysis Reactions Involving Acetals, Imines, Enamines, and Nitriles 897
- 18.3** The Wolff–Kishner Reduction 906
- 18.4** Enolate Nucleophiles: Aldol and Aldol-Type Additions 908
- 18.5** Aldol Condensations 911
- 18.6** Aldol Reactions Involving Ketones 913
- 18.7** Crossed Aldol Reactions 914
- 18.8** Intramolecular Aldol Reactions 919
- 18.9** Aldol Additions Involving Nitriles and Nitroalkanes 922
- 18.10** The Robinson Annulation 924
- 18.11** Organic Synthesis: Aldol Reactions in Synthesis 925

18.12 Organic Synthesis: Synthesizing Amines via Reductive Amination 927

THE ORGANIC CHEMISTRY OF BIOMOLECULES

18.13 Ring Opening and Closing of Monosaccharides; Mutarotation 929

Chapter Summary and Key Terms 933

Reaction Tables 934

Problems 937

19 Organic Synthesis 2

Intermediate Topics in Synthesis Design, and Useful Redox and Carbon–Carbon Bond-Forming Reactions 946

19.1 Umpolung in Organic Synthesis: Forming Bonds between Carbon Atoms Initially Bearing Like Charge; Making Organometallic Reagents 947

19.2 Relative Positioning of Heteroatoms in Carbon–Carbon Bond-Forming Reactions 951

19.3 Reactions That Remove a Functional Group Entirely from a Molecule: Reductions of C=O to CH₂ 955

19.4 Avoiding Synthetic Traps: Selective Reagents and Protecting Groups 960

19.5 Catalytic Hydrogenation 969

19.6 Oxidations of Alcohols and Aldehydes 976

19.7 Useful Reactions That Form Carbon–Carbon Bonds: Coupling and Alkene Metathesis Reactions 982

Chapter Summary and Key Terms 988

Reaction Tables 989

Problems 991

20 Nucleophilic Addition–Elimination Reactions 1

The General Mechanism Involving Strong Nucleophiles 1000

20.1 An Introduction to Nucleophilic Addition–Elimination Reactions: Transesterification 1001

20.2 Acyl Substitution Involving Other Carboxylic Acid Derivatives: The Thermodynamics of Acyl Substitution 1006

20.3 Reaction of an Ester with Hydroxide (Saponification) and the Reverse Reaction 1009

20.4 Carboxylic Acids from Amides; the Gabriel Synthesis of Primary Amines 1013

20.5 Haloform Reactions 1017

- 20.6** Hydride Reducing Agents: Sodium Borohydride (NaBH_4) and Lithium Aluminum Hydride (LiAlH_4) 1021
- 20.7** Specialized Reducing Agents: Diisobutylaluminum Hydride (DIBAL) and Lithium Tri-*tert*-butoxyaluminum Hydride (LTBA) 1029
- 20.8** Organometallic Reagents 1032
Chapter Summary and Key Terms 1035
Reaction Tables 1036
Problems 1039

21 Nucleophilic Addition–Elimination Reactions 2

Weak Nucleophiles 1045

- 21.1** The General Nucleophilic Addition–Elimination Mechanism Involving Weak Nucleophiles: Alcoholysis and Hydrolysis of Acid Chlorides 1046
- 21.2** Relative Reactivities of Acid Derivatives: Rates of Hydrolysis 1049
- 21.3** Aminolysis of Acid Derivatives 1052
- 21.4** Synthesis of Acid Halides: Getting to the Top of the Stability Ladder 1054
- 21.5** The Hell–Vollhard–Zelinsky Reaction: Synthesizing α -Bromo Carboxylic Acids 1057
- 21.6** Sulfonyl Chlorides: Synthesis of Mesylates, Tosylates, and Triflates 1059
- 21.7** Base and Acid Catalysis in Nucleophilic Addition–Elimination Reactions 1061
- 21.8** Baeyer–Villiger Oxidations 1067
- 21.9** Claisen Condensations 1069
- 21.10** Organic Synthesis: Decarboxylation, the Malonic Ester Synthesis, and the Acetoacetic Ester Synthesis 1078
- 21.11** Organic Synthesis: Protecting Carboxylic Acids and Amines 1082

THE ORGANIC CHEMISTRY OF BIOMOLECULES

- 21.12** Determining a Protein's Primary Structure via Amino Acid Sequencing: Edman Degradation 1084
- 21.13** Synthesis of Peptides 1087

Chapter Summary and Key Terms 1090
Reaction Tables 1091
Problems 1093

22 Aromatic Substitution 1

Electrophilic Aromatic Substitution on Benzene;
Useful Accompanying Reactions 1104

- 22.1** The General Mechanism of Electrophilic Aromatic Substitutions 1106
- 22.2** Halogenation 1109



- 22.3** Friedel–Crafts Alkylation 1111
- 22.4** Limitations of Friedel–Crafts Alkylations 1114
- 22.5** Friedel–Crafts Acylation 1118
- 22.6** Nitration 1121
- 22.7** Sulfonation 1122
- 22.8** Organic Synthesis: Considerations of Carbocation Rearrangements and the Synthesis of Primary Alkylbenzenes 1125
- 22.9** Organic Synthesis: Common Reactions Used in Conjunction with Electrophilic Aromatic Substitution Reactions 1126
- Chapter Summary and Key Terms 1134
- Reaction Tables 1135
- Problems 1137

23 Aromatic Substitution 2

Reactions of Substituted Benzenes and Other Rings 1144

- 23.1** Regiochemistry of Electrophilic Aromatic Substitution: Defining Ortho/Para and Meta Directors 1145
- 23.2** What Characterizes Ortho/Para and Meta Directors and Why? 1147
- 23.3** The Activation and Deactivation of Benzene toward Electrophilic Aromatic Substitution 1155
- 23.4** The Impacts of Substituent Effects on the Outcomes of Electrophilic Aromatic Substitution Reactions 1159
- 23.5** The Impact of Reaction Conditions on Substituent Effects 1162
- 23.6** Electrophilic Aromatic Substitution on Disubstituted Benzenes 1164
- 23.7** Electrophilic Aromatic Substitution Involving Aromatic Rings Other than Benzene 1168
- 23.8** Azo Coupling and Azo Dyes 1172
- 23.9** Nucleophilic Aromatic Substitution Mechanisms 1173
- 23.10** Organic Synthesis: Considerations of Regiochemistry; Attaching Groups in the Correct Order 1179
- 23.11** Organic Synthesis: Interconverting Ortho/Para and Meta Directors 1180
- 23.12** Organic Synthesis: Considerations of Protecting Groups 1183
- Chapter Summary and Key Terms 1186
- Reaction Table 1187
- Problems 1188

24 The Diels–Alder Reaction and Other Pericyclic Reactions 1198

- 24.1** Curved Arrow Notation and Examples 1199
- 24.2** Conformation of the Diene 1203
- 24.3** Substituent Effects on the Reaction 1206

- 24.4** Stereochemistry of Diels–Alder Reactions 1208
- 24.5** Regiochemistry of Diels–Alder Reactions 1213
- 24.6** The Reversibility of Diels–Alder Reactions; the Retro Diels–Alder Reaction 1216
- 24.7** Syn Dihydroxylation of Alkenes and Alkynes Using OsO₄ or KMnO₄ 1218
- 24.8** Oxidative Cleavage of Alkenes and Alkynes 1220
- 24.9** Organic Synthesis: The Diels–Alder Reaction in Synthesis 1226
- 24.10** A Molecular Orbital Picture of the Diels–Alder Reaction 1228
 - Chapter Summary and Key Terms 1235
 - Reaction Tables 1235
 - Problems 1237



25 Reactions Involving Free Radicals 1247

- 25.1** Homolysis: Curved Arrow Notation and Radical Initiators 1248
- 25.2** Structure and Stability of Alkyl Radicals 1252
- 25.3** Common Elementary Steps That Free Radicals Undergo 1257
- 25.4** Radical Halogenation of Alkanes: Synthesis of Alkyl Halides 1260
- 25.5** Radical Addition of HBr: Anti-Markovnikov Addition 1275
- 25.6** Stereochemistry of Free Radical Halogenation and HBr Addition 1278
- 25.7** Dissolving Metal Reductions: Hydrogenation of Alkenes and Alkynes 1279
- 25.8** Organic Synthesis: Radical Reactions in Synthesis 1283
 - Chapter Summary and Key Terms 1286
 - Reaction Table 1287
 - Problems 1287

INTERCHAPTER

G Fragmentation Pathways in Mass Spectrometry 1295

- G.1** Alkanes 1296
- G.2** Alkenes and Aromatic Compounds 1298
- G.3** Alkyl Halides, Amines, Ethers, and Alcohols 1300
- G.4** Carbonyl-Containing Compounds 1304
 - Problems 1306

26 Polymers 1307

- 26.1** Free Radical Polymerization: Polystyrene as a Model 1308
- 26.2** Anionic and Cationic Polymerization Reactions 1320

26.3	Ring-Opening Polymerization Reactions	1323
26.4	Step-Growth Polymerization	1325
26.5	Linear, Branched, and Network Polymers	1330
26.6	Chemical Reactions after Polymerization	1332
26.7	General Aspects of Polymer Structure	1338
26.8	Properties of Polymers	1344
26.9	Uses of Polymers: The Relationship between Structure and Function in Materials for Food Storage	1351
26.10	Degradation and Depolymerization	1353

THE ORGANIC CHEMISTRY OF BIOMOLECULES

26.11	Biological Macromolecules	1355
--------------	---------------------------	------

Chapter Summary and Key Terms 1362

Problems 1363

Appendix A: Values of K_a and pK_a for Various Acids APP-1

Appendix B: Characteristic Reactivities of Particular Compound Classes APP-4

Appendix C: Reactions That Alter the Carbon Skeleton APP-9

Appendix D: Synthesizing Particular Compound Classes via Functional Group Transformations APP-15

Glossary G-1

Answers to Your Turns ANS-1

Credits C-1

Index I-1

Biochemistry Topics

Proteins and Amino Acids Organic Chemistry of Biomolecules

- An introduction to proteins 37
- Amino acid structure and polypeptides 38
- Constitutional isomers of amino acids 198
- The D/L system for classifying amino acids 247
- The structure of amino acids in solution as a function of pH 314
- Electrophoresis and isoelectric focusing 317
- Determining a protein's primary structure via amino acid sequencing: Edman degradation 1084
- Synthesis of peptides 1087
- Polypeptides: Primary, secondary, tertiary, and quaternary structures 1355
- α -Helix; β -sheet 1357
- Planarity of a peptide 1358
- Ribbon structures 1359
- Hydrophobic effect 1359

Interest Boxes

- Enzyme active sites 103
- Phosphorylation of an enzyme's active site 420
- Using proton transfer reactions to discover new drugs 427
- How an enzyme can manipulate the reactivity of a nucleophile and substrate 475
- Kinetic control, thermodynamic control, and mad cow disease 589
- Aromaticity helping us breathe: A look at hemoglobin 709
- Imine formation and hydrolysis in biochemical reactions 903

Nucleic Acids Organic Chemistry of Biomolecules

- An introduction to nucleic acids 37
- Nucleotide structure, RNA and DNA 42
- Aromaticity and DNA 714
- The structure of DNA; complementarity of DNA base pairs 715
- Pi stacking 716
- The story of Watson and Crick 717

Interest Boxes

- DNA alkylation: Cancer causing and cancer curing 547
- Benzo[a]pyrene: Smoking, epoxidation, and cancer 623
- UV-Vis spectroscopy and DNA melting points 735
- Michael addition in the fight against cancer 869
- Protecting groups in DNA synthesis 969
- Biological cycloaddition reactions 1202

Carbohydrates Organic Chemistry of Biomolecules

- An introduction to carbohydrates 37
- Monosaccharide structure and polysaccharides 40
- Constitutional isomers of monosaccharides 198
- Acyclic and cyclic structures of monosaccharides 198
- Structures of aldoses, ketoses, pentoses, and hexoses 199
- The D/L system for classifying monosaccharides 247
- The D family of aldoses 248
- The formation and hydrolysis of glycosides 490
- α - and β -glycosidic linkages; 1,4- and 1,6-glycosidic linkages 491

Ring opening and closing of monosaccharides;
mutarotation 929
Nomenclature involving pyranoses and furanoses 930
Anomers and the anomeric carbon 931
Polysaccharides 1355
Amylose, amylopectin 1360

Interest Boxes

Sugar transformers 354

Lipids

Organic Chemistry of Biomolecules

An introduction to lipids 105
Structures of fats, oils, and fatty acids 105
Phospholipids and cell membranes 106

Steroids, terpenes, and terpenoids 109
Classifications of terpenes (mono, sesqui, di, tri) 110
Waxes 111
Saturation and unsaturation in fats and oils 199
Effect of unsaturation on boiling point and melting
point 200
Terpene biosynthesis: Carbocation chemistry in
nature 589
Biosynthesis of cholesterol and other
terpenes/terpenoids 592

Interest Boxes

Conjugated linoleic acids 697
Biodiesel and transesterification 1005
Biological Claisen condensations 1077
Free radicals in the body: Lipid peroxidation and
vitamin E 1274

Interest Boxes

- Chemistry with Chicken Wire 5
- Turning an Inorganic Surface into an Organic Surface 11
- Climbing Like Geckos 89
- Enzyme Active Sites: The Lock-and-Key Model 103
- Quantum Teleportation 123
- Carbyne: The World's Strongest Material 147
- An All-Gauche Alkane 177
- Cubane: A Useful "Impossible" Compound? 183
- Nanocars 225
- Mapping the Earth with Polarimetry 245
- pK_a and the Absorption and Secretion of Drugs 286
- Superacids: How Strong Can an Acid Be? 307
- "Watching" a Bond Break 347
- Sugar Transformers: Tautomerization in the Body 354
- Phosphorylation: An Enzyme's On/Off Switch 420
- Using Proton Transfer Reactions to Discover New Drugs 427
- Rotaxanes: Exploiting Steric Hindrance 470
- How an Enzyme Can Manipulate the Reactivity of a Nucleophile and Substrate 475
- DNA Alkylation: Cancer Causing and Cancer Curing 547
- Mechanically Generated Acid and Self-Healing Polymers 553
- Electrophilic Addition and Laser Printers 572
- Kinetic Control, Thermodynamic Control, and Mad Cow Disease 589
- Halogenated Metabolites: True Sea Treasures 615
- Benzo[a]pyrene: Smoking, Epoxidation, and Cancer 623
- Manipulating Atoms One at a Time: Single-Molecule Engineering 661
- Conjugated Linoleic Acids 697
- Aromaticity Helping Us Breathe: A Look at Hemoglobin 709
- UV-Vis Spectroscopy and DNA Melting Points 735
- IR Spectroscopy and the Search for Extraterrestrial Life 758
- Magnetic Resonance Imaging 803
- Mass Spectrometry, *CSI*, and *Grey's Anatomy* 828
- NADH as a Biological Hydride Reducing Agent 852
- Michael Addition in the Fight against Cancer 869
- Imine Formation and Hydrolysis in Biochemical Reactions 903
- Protecting Groups in DNA Synthesis 969
- Chromic Acid Oxidation and the Breathalyzer Test 981
- Biodiesel and Transesterification 1005
- The Stability Ladder in Biochemical Systems 1010
- Biological Claisen Condensations 1077
- Aromatic Sulfonation: Antibiotics and Detergents 1124
- Sodium Nitrite and Foods: Preventing Botulism but Causing Cancer? 1132
- Iodized Salt and Electrophilic Aromatic Substitution 1152
- 2,4,6-Trinitrotoluene (TNT) 1160
- Biological Cycloaddition Reactions 1202
- Ethene, $KMnO_4$, and Fruit Ripening 1225
- Halogenated Alkanes and the Ozone Layer 1265
- Free Radicals in the Body: Lipid Peroxidation and Vitamin E 1274
- Supramolecular Polymers: Polymers That Can Heal Themselves 1333
- Plastic Made from Corn?  1354

Connections Boxes

- Molecular hydrogen and the *Hindenburg* 8
- Bonds as springs; greenhouse gases 9
- Chlorine radicals in the stratosphere breaking down ozone 12
- Methanol and the production of plastics, paints, explosives, and fuel 13
- Borane and thionyl chloride as reagents in organic synthesis 14
- The formate anion and the mitochondria of cells 20
- Oximes: nylon-6, nerve-agent antidotes, and artificial sweeteners 21
- Cationic species as reactive intermediates in organic reactions 24
- Benzene and crude oil 25
- Acetic acid, vinegar, and organic chemistry 25
- Naphthalene and mothballs 29
- Acetamide as a plasticizer or solvent 30
- Crotonaldehyde in foodstuffs 31
- Pyrrrole and the heme group; benzoic acid and skin ointments 33
- Cyclohexanone and nylon 36
- δ -Valerolactone and polyesters; pentanoic acid and fragrant esters 36
- Bromomethane as a pesticide 56
- Freon 142b as a refrigerant 57
- Diethyl ether as a common organic solvent and an anesthetic 67
- Acetonitrile and acetone as organic solvents; ethane in the petrochemical industry 73
- 2-Aminoethanol in the production of shampoos and detergents 73
- Butan-2-ol as a precursor to butan-2-one 76
- The pros and cons of carbon tetrachloride 79
- Methylene chloride: industrial uses and the drinking bird 80
- Chloromethane as a refrigerant, local anesthetic, and herbicide 80
- Sodium methanoate with fabric dye and as a flavor enhancer 81
- Formic acid in ant venom and its uses 81
- Ethanol as more than an alcoholic beverage 84
- Elemental iodine as a disinfectant and its use in analytical chemistry 89
- Toluene: an organic solvent, a precursor to TNT, and its use in extracting hemoglobin 92
- 2-Naphthol as a precursor in dye production 96
- DMSO and its medicinal uses 99
- H₂ and its wide variety of uses 125
- Ethane in the industrial production of ethene 133
- Methane and natural gas 135
- Ethene: a precursor to polyethylene, and its importance in the laboratory 136
- The high temperature of burning acetylene 140
- HCN: industrial uses and eucalyptus leaf beetles 141
- Fluoroethene, Tedlar, and the Goodyear blimp 143
- α -Linolenic acid as a dietary supplement 144
- 1,2,3-Trimethylbenzene as a fuel stabilizer 158
- Propylene as a precursor of polypropylene, a plastic with many applications 159
- Isobutylene as a fuel additive and a precursor to butyl rubber 159
- The sweetness of anisole 160
- Styrene in Styrofoam, coffee beans, and cinnamon 161
- Xylene: crude oil, industrial uses, and root canals 161
- 1,2-Dibromoethane to control insect infestation 172
- Cooling cyclohexane to slow chair flips 181
- Methylcyclohexane as a solvent for cellulose ethers 185
- But-1-ene and plastic plumbing pipes 191
- Cyclobutane and the thymine dimer 191
- Acetaldehyde as an intermediate in the metabolism of ethanol 194
- Oxirane: production of antifreeze and the sterilization of medical devices 194
- Butanediol fermentation 220
- 1-Bromopropane: from asphalt production to dry cleaning 222
- Tetrahydrofuran and Spandex 235
- Ammonia, window cleaners, and the Haber–Bosch process 277
- 4-Methylphenol: pig odor and the production of antioxidants 279
- Phenol, from plastics to antiseptics 281
- Methanamine: industrial uses and putrefaction 282

Isopropyl alcohol: an antiseptic, a solvent, and a gasoline additive 290

Trichloroacetic acid in biochemistry and cosmetics 291

Aniline: Tylenol and blue jeans 310

Trimethylamine and the freshness of fish 331

Nitrobenzene: a fragrance and a precursor to explosives, dyes, and drugs 344

Cyclohexanol as a nylon precursor 378

5-Aminopentan-1-ol in the synthesis of antitumor manzamines 381

Propane-1,2-diol in antifreeze 383

Butanal in natural oils and as a feedstock in industrial synthesis 386

tert-Butyl alcohol in the synthesis of fuel additives 386

Benzyl alcohol: uses in industry and as a food and perfume additive 387

Ethylamine: solvated electrons and the production of herbicides 388

Dimethylamine: rubber vulcanization and allergy medicines 388

Formaldehyde: uses in industry, medicine, and embalming 389

Benzaldehyde in the synthesis of dyes and pharmaceuticals and as a flavoring agent 389

Butanone as an industrial solvent and in dry-erase markers 389

Acetophenone in the production of inks, coatings, and pharmaceuticals 390

Benzyl chloride in synthesis, from flavoring agents to cleaning products 401

Methoxyphenylmethane as a fragrance 422

Cyclohexene and synthetic fibers 425

β -Propiolactone in medicine: blood plasma, tissue grafts, and flu vaccines 426

2-Methylbutan-2-ol once used as an anesthetic 429

2-Methylbut-3-en-2-ol and the bark beetle 432

HCN: cherries, apples, and mining precious metals 452

Bromocyclohexane and confocal microscopy 454

2-Methoxyphenol and swarming locusts 462

Allyl halides, from pharmaceuticals to boats 469

Styrene and your take-out meal 477

Hex-1-ene and plastics 483

Tetrahydropyran: organic synthesis and sugars 485

(*E*)-9-Oxodec-2-enoic acid and bees 504

Natural compounds from watercress and fungi 506

Shikimic acid and antiviral medication 507

Ethyl butanoate as a flavoring agent 508

Acetic anhydride in the synthesis of aspirin and other compounds 510

Phosphorus tribromide in the synthesis of the anesthetic Brevital 517

Tetraethylammonium bromide and the treatment of hypertension 522

Methyl acetate as a nail polish remover 534

The oxetane ring in the treatment of cancer 540

2-Methoxyethanol and safety in air travel 541

2-Phenylethanol in flowers and perfumes 542

3-Hydroxypropanenitrile and knitted clothing 542

Indene as a protective fruit coating 571

1,2-Diphenylethene and keeping your color laundry bright 575

Propyne as a rocket fuel 580

Buta-1,3-diene and the making of car tires 584

Heptan-2-one: insect bites and gorgonzola cheese 619

Cyclohexane-1,2-diol and the North American beaver 622

Heptan-1-ol and understanding the heart 624

Borane and fuel cells in automobiles 625

Hexanal and the flavor of cooked meats 631

Butanoic acid and rancid butter 646

(Bromomethyl)benzene and chemical warfare 654

Overcoming synthetic traps in biochemical reactions 656

Methylenecyclopentane in the synthesis of an antiviral and antitumor agent 656

(*S*)-Naproxen as the painkiller Aleve 664

Using diisopinocampheylborane to carry out an enantioselective hydroboration–oxidation 668

Cyclooctene as trans and cis isomers 674

Buta-1,3-diene and 3-D printers 685

Cycloocta-1,3,5,7-tetraene from fungus in the *Eucryphia cordifolia* tree 700

Biphenyl as a citrus fruit preservative 706

Anthracene: insecticidal and fungicidal properties and the Sistine Chapel 707

Pyridine: numerous chemical applications; found in marshmallow plants 707

Furan and your morning coffee 708

trans-Penta-1,3-diene and soft drinks 732

Methanimine and extraterrestrial life 733

4-Methylpentan-2-one and mining silver and gold 749

1-Phenylpropan-2-one and the manufacture of amphetamine and methamphetamine 750

Heptanal as a flavoring agent and in cosmetics 752

Benzophenone and plastic packaging 754

Dichloroacetic acid, from tattoo removal to cancer treatment 778

Chloroethene in the production of pipes for plumbing 780

- Ethylbenzene to make styrene and to recover natural gas 790
- 1,4-Dimethylbenzene and plastic water bottles 791
- Propanal in the manufacture of alkyd resins 803
- Benzyl chloride and pharmaceuticals 808
- Dodecane as a substitute for jet fuel 823
- 3-Methylbutanal in cheese, beer, chicken, and fish 841
- Butyllithium and the production of some types of rubber 854
- Benzonitrile, resins and pharmaceuticals 855
- Propenal, from herbicides to fried food 863
- Cyclohex-2-en-1-one and the total synthesis of morphine 865
- Pentanal as a fruity flavor additive and in the vulcanization of rubber 897
- 3-Hydroxybutanal as a hypnotic 908
- 4-Hydroxy-4-methylpentanone in gravure printing inks 913
- Cinnamaldehyde in cinnamon 916
- Bromobenzene as an additive to motor oils 948
- 3-Methylpentan-3-ol and anxiety and tension 951
- 1-Phenylpropan-1-one in the synthesis of ephedrine 955
- 3-Hydroxypropanal and the health benefits of probiotic bacteria 966
- Benzene-1,2-diol and the synthesis of vanilla flavoring 968
- Limonene in the rinds of citrus fruits 975
- Ethyl indole-2-carboxylate in the synthesis of intracellular signaling compounds 1002
- Benzoyl chloride and the synthesis of acne medicine 1006
- Ethyl acetate and decaffeinated coffee 1011
- The monopotassium salt of phthalic acid and analytical chemistry 1049
- Phenylalanine as an essential dietary amino acid 1059
- Hexyl acetate in hard candy 1063
- 1,3-Diphenylpropane-1,3-dione in licorice and as an anticancer agent 1074
- Diethyl malonate in the synthesis of barbiturates 1078
- Cyclohexylbenzene and lithium ion batteries 1113
- (1-Methylethyl)benzene and polycarbonate plastics 1115
- 1-Phenylbutan-1-one in the synthesis of the antipsychotic haloperidol 1121
- Benzenesulfonic acid and the treatment of angina 1122
- N-Phenylbenzamide to counter effects of hardening arteries 1129
- p-Nitrophenol in the synthesis of fever and pain relievers 1146
- m-Dinitrobenzene, from an explosive to the synthesis of dyes 1146
- o-Nitrotoluene in the manufacture of herbicides 1151
- 2,4,6-Tribromophenol as a wood preservative and fungicide and in the manufacture of flame retardants 1162
- Prontosil, the first sulfa drug discovered 1173
- p-Nitrobenzoic acid and Novocain dental anesthetic 1181
- 4-Vinylcyclohexene in the manufacture of soaps and cosmetics 1203
- Bicyclo[2.2.1]hept-2-ene and motorcycle riders 1206
- The cyclopentadienyl anion as a valuable ligand for organometallic complexes 1217
- Dicyclopentadiene and fiberglass/polyester composites in heavy vehicles 1218
- (2R,3S)-2,3-Dihydroxybutanoic acid as a naturally occurring metabolite in humans 1218
- Diphenylethanedione and the breakdown of neurotransmitters 1220
- Chlorine and clean water 1249
- Ethers and the hazards on exposure to air in the laboratory 1251
- A solvated electron and the absorption of visible light 1279
- Polyacrylonitrile and safe drinking water 1314
- Polypropylenes: roofing adhesives and Rubbermaid containers 1318
- Bakelite, from kitchenware to billiard balls 1332

Green Chemistry Boxes

- NaBH₄ as a greener alternative to LiAlH₄ 847
- Green alternatives to Grignard reactions 855
- Weighing E1 and E2 reactions against Wittig reactions 877
- Aldol addition reactions as highly atom efficient 908
- Avoiding the use of solvents in crossed aldol reactions 914
- Weighing Raney-nickel reductions against Wolff–Kishner and Clemmensen reductions 958
- Selective reactions versus the use of protecting groups 962
- KMnO₄ as a less toxic but less selective oxidizing agent than H₂CrO₄ 982
- Hydrogen peroxide as a green oxidizing agent in Baeyer–Villiger reactions 1068
- Graphite as a green catalyst in Friedel–Crafts alkylations 1112
- Using a room temperature ionic liquid as the solvent in nucleophilic aromatic substitution reactions 1176
- Diels–Alder reactions minimizing waste 1200
- Zeolite catalysts, a green alternative to OsO₄ in syn dihydroxylation 1219
- Weighing KMnO₄ against OsO₄ in syn dihydroxylation 1219
- Reducing waste in dissolving metal reductions 1280

Mechanisms

- General S_N2 mechanism (Equation 8-1) 394
- General S_N1 mechanism (Equation 8-2) 394
- General E2 mechanism (Equation 8-4) 398
- General E1 mechanism (Equation 8-5) 398
- S_N1 mechanism and stereochemistry (Equation 8-18) 407
- S_N2 mechanism under basic conditions (Equation 8-28) 423
- S_N1 mechanism under acidic conditions (Equation 8-31) 424
- Solvent-mediated proton transfer in S_N2 (Equations 8-34 and 8-35) 426
- S_N1 mechanism with a carbocation rearrangement (Equation 8-38) 430
- S_N1 mechanism proceeding through a resonance-delocalized carbocation intermediate (Equation 8-42) 433
- Competition among S_N2 , S_N1 , E2, and E1 mechanisms (Equations 9-1 through 9-4) 443
- Rate-determining steps in S_N2 , S_N1 , E2, and E1 mechanisms (Equations 9-5 through 9-8) 445
- S_N2 conversion of a 1° alcohol to an alkyl bromide using HBr (Equation 9-21) 462
- S_N2 conversion of a phenyl methyl ether to a phenol and bromomethane using HBr (Equation 9-24) 463
- Acid-catalyzed dehydration of an alcohol (Equation 9-26) 463
- S_N2 conversion of an alkyl chloride to an alkyl bromide (Equation 9-36) 479
- Solvolysis of an alkyl halide (Equations 9-38 and 9-39) 480
- E2 conversion of a substituted cyclohexyl tosylate to a substituted cyclohexene (Equation 9-41) 481
- Acid-catalyzed glycoside formation of a sugar (Equation 9-54) 491
- S_N2 conversion of a 1° alcohol to an alkyl bromide using HBr (Equation 10-2) 516
- PBr_3 conversion of an alcohol to an alkyl bromide (Equation 10-8) 518
- S_N2 alkylation of an amine (Equation 10-13) 521
- Alkylation of an α carbon of a ketone or aldehyde (Equation 10-19) 524
- Regioselective alkylation of an α carbon of a ketone using LDA (Equation 10-22) 526
- Regioselective alkylation of an α carbon of a ketone using a bulky alkoxide base (Equation 10-25) 527
- Halogenation of an α carbon of a ketone or aldehyde under basic conditions (Equation 10-27) 529
- Polyhalogenation of an α carbon of a ketone or aldehyde under basic conditions (Equation 10-29) 530
- Halogenation of an α carbon of a ketone or aldehyde under acidic conditions (Equation 10-31) 532
- Diazomethane formation of a methyl ester (Equation 10-33) 534
- Williamson ether synthesis (Equation 10-36) 536
- Formation of a cyclic ether from a haloalcohol under basic conditions (Equation 10-39) 537
- Formation of a symmetric ether from an alcohol under acidic conditions (Equation 10-42) 538
- Ring opening of an epoxide under basic conditions (Equation 10-48) 541
- Alkylation and ring opening of an epoxide using alkyllithium or Grignard reagents (Equation 10-51) 542
- Ring opening of an unsymmetric epoxide under basic conditions (Equation 10-56) 543
- Ring opening of an unsymmetric epoxide under acidic conditions (Equation 10-58) 545
- Formation of a terminal alkyne from a vinylic halide (Equation 10-66) 549
- Hofmann elimination (Equation 10-70) 551
- Addition of a Brønsted acid to an alkene (Equation 11-3) 565
- Addition of a Brønsted acid to an alkene, with carbocation rearrangement (Equation 11-9) 573
- Acid-catalyzed hydration of an alkene (Equation 11-15) 577
- Addition of a Brønsted acid to an alkyne to produce a geminal dihalide (Equation 11-17) 579
- Addition of a Brønsted acid to an alkyne to produce a vinylic halide (Equation 11-19) 581
- Acid-catalyzed hydration of an alkyne (Equation 11-21) 582
- Addition of a Brønsted acid to a conjugated diene (Equation 11-25) 584
- Addition of carbene to an alkene (Equation 12-5) 605
- Addition of dichlorocarbene to an alkene (Equation 12-8) 606

- Addition of a molecular halogen to an alkene, including stereochemistry (Equations 12-10 and 12-11) 608
- Addition of HOX to a symmetric alkene (Equation 12-18) 612
- Addition of HOX to an unsymmetric alkene (Equation 12-20) 614
- Oxymercuration–reduction of an alkene (Equation 12-23) 616
- Epoxidation of an alkene using a peroxyacid (Equation 12-33) 621
- Hydroboration of an alkene (Equation 12-36) 625
- Oxidation of a trialkylborane (Equation 12-40) 629
- Generic addition of a strong nucleophile to a π polar bond (Equation 17-1) 841
- Simplified picture of the NaBH_4 reduction of a ketone (Equation 17-7) 846
- Simplified picture of the LiAlH_4 reduction of an aldehyde (Equation 17-8) 846
- More accurate picture of the NaBH_4 reduction of a ketone (Equation 17-9) 846
- Proton transfer involving alkyllithium reagents (Equation 17-18) 854
- Alkyllithium reaction involving a ketone (Equation 17-21) 856
- Grignard reaction involving a nitrile (Equation 17-22) 856
- Wittig reaction (Equation 17-26) 860
- Generating a Wittig reagent (Equation 17-29) 861
- Direct addition of a nucleophile to a conjugated aldehyde (Equation 17-31) 864
- Conjugate addition of a nucleophile to a conjugated aldehyde (Equation 17-32) 864
- Uncatalyzed nucleophilic addition of a weak nucleophile to a ketone (Equation 18-3) 890
- Base-catalyzed nucleophilic addition of a weak nucleophile to a ketone (Equation 18-4) 890
- Acid-catalyzed nucleophilic addition of a weak nucleophile to a ketone (Equation 18-5) 891
- Addition of HCN to a ketone (Equation 18-7) 893
- Conjugate addition of a weak nucleophile to a conjugated ketone (Equation 18-10) 895
- Acid-catalyzed formation of an acetal (Equation 18-13) 898
- Acid-catalyzed formation of an imine (Equation 18-19) 900
- Acid-catalyzed formation of an enamine (Equation 18-22) 902
- Acid-catalyzed hydrolysis of a nitrile to form an amide (Equation 18-25) 905
- Base-catalyzed hydrolysis of a nitrile to form an amide (Equation 18-26) 905
- Wolff–Kishner reduction of a ketone (Equation 18-28) 907
- Self-aldol addition involving an aldehyde (Equation 18-31) 909
- Dehydration of an aldol product under basic conditions: An E1cb mechanism (Equation 18-33) 911
- Dehydration of an aldol product under acidic conditions (Equation 18-35) 912
- Self-aldol addition involving a ketone (Equation 18-38) 914
- Aldol condensation forming a ring (Equation 18-48) 920
- Reductive amination of an aldehyde (Equation 18-63) 928
- Ring formation in a monosaccharide (Equation 18-66) 930
- Catalytic hydrogenation of an alkene (Figure 19-2) 971
- Chromic acid oxidation of a 2° alcohol (Equation 19-33) 978
- Suzuki coupling reaction (Equation 19-44) 985
- Heck coupling reaction (Equation 19-46) 986
- General mechanism for alkene metathesis reactions (Equation 19-50) 988
- Transesterification under basic conditions (Equation 20-2) 1002
- Esterification of an acid chloride under basic conditions (Equation 20-4) 1006
- Saponification: Conversion of an ester into a carboxylate anion (Equation 20-9) 1012
- Hydrolysis of an amide under basic conditions (Equation 20-11) 1014
- Gabriel synthesis of a 1° amine (Equation 20-13) 1016
- Haloform reaction (Equation 20-16) 1018
- NaBH_4 reduction of an acid chloride to a 1° alcohol (Equation 20-20) 1021
- LiAlH_4 reduction of a carboxylic acid to a 1° alcohol (Equation 20-24) 1026
- LiAlH_4 reduction of an amide to an amine (Equation 20-26) 1027
- Reduction of an acid chloride to an aldehyde using $\text{LiAlH}(\text{O}-t\text{-Bu})_3$ (Equation 20-29) 1030
- Reduction of an ester to an aldehyde using DIBAL (Equation 20-31) 1031
- Conversion of an acid chloride to a 3° alcohol (Equation 20-35) 1033
- Hydrolysis of an acid chloride under neutral conditions (Equation 21-4) 1047
- Aminolysis of an acid chloride (Equation 21-9) 1053
- SOCl_2 conversion of a carboxylic acid to an acid chloride (Equation 21-14) 1055
- Hell–Volhard–Zelinsky reaction to form an α -bromo acid (Equation 21-18) 1058
- Sulfonation of an alcohol (Equation 21-21) 1060
- Base-catalyzed transesterification (Equation 21-25) 1062

Acid-catalyzed transesterification
 (Equation 21-29) 1063
 Amide hydrolysis under acidic conditions
 (Equation 21-33) 1066
 Baeyer–Villiger oxidation (Equation 21-35) 1067
 Claisen condensation (Equation 21-37) 1069
 Decarboxylation of a β -keto ester
 (Equation 21-49) 1079
 Amide formation via dicyclohexylcarbodiimide coupling
 (Equation 21-56) 1087
 General mechanism of electrophilic aromatic
 substitution on benzene (Equation 22-4) 1106
 Bromination of benzene (Equation 22-8) 1109
 Friedel–Crafts alkylation of benzene
 (Equation 22-12) 1112
 Friedel–Crafts alkylation of benzene involving a
 carbocation rearrangement (Equation 22-16) 1115
 Friedel–Crafts alkylation involving a 1° alkyl halide
 (Equation 22-18) 1116
 Friedel–Crafts acylation of benzene
 (Equation 22-22) 1118
 Nitration of benzene (Equation 22-24) 1121
 Sulfonation of benzene (Equation 22-26) 1123
 Diazotization of benzene (Equation 22-35) 1131
 Nucleophilic aromatic substitution on benzene, via
 nucleophilic addition–elimination
 (Equation 23-35) 1174
 Nucleophilic aromatic substitution on benzene, via a
 benzyne intermediate (Equation 23-40) 1177
 Diels–Alder reaction (Equation 24-2) 1199
 Syn dihydroxylation of an alkene involving OsO_4
 (Equation 24-31) 1219
 Oxidative cleavage of an alkene involving KMnO_4
 (Equation 24-37) 1221
 Oxidative cleavage of a *cis*-1,2-diol involving periodate
 (Equation 24-41) 1223
 Ozonolysis of an alkene (Equation 24-45) 1225
 Radical chlorination of an alkane (Equations 25-18
 through 25-20) 1261
 Production of Br_2 from *N*-bromosuccinimide
 (Equation 25-28) 1272
 Radical addition of HBr to an alkene
 (Equation 25-33) 1275
 Radical hydrogenation of an alkyne via dissolving metal
 reduction (Equation 25-41) 1281
 Birch reduction of benzene (Equation 25-45) 1282
 Free-radical polymerization (Equations 26-3 through
 26-8) 1311

Preface

Focused on the Student, Organized by Mechanism

When an organic reaction is presented to a novice, only the structural differences between the reactants and products are immediately apparent. Students tend to see only *what* happens, such as the transformation of one functional group into another, changes in connectivity, and aspects of stereochemistry. It should therefore not be surprising that students, when presented reactions, are tempted to commit the reactions to memory. But there are far too many reactions and accompanying details for memorization to work in organic chemistry.

This is where mechanisms come into play. Mechanisms allow us to understand the sequences of elementary steps—the step-by-step pathways—that convert the reactants to products, so we can see *how* and *why* reactions take place as they do. Moreover, the mechanisms that describe the large number of reactions in the course are constructed from just a handful of elementary steps, so mechanisms allow us to see *similarities* among reactions that are not otherwise apparent. In other words, mechanisms actually *simplify* organic chemistry. Thus, teaching students mechanisms—enabling students to understand and simplify organic chemistry—is an enormous key to success in the course.

At the outset of my teaching career, I fully appreciated the importance of mechanisms, so during my first couple years of teaching, I emphasized mechanisms *very* heavily. I did so under a functional group organization where reactions are pulled together according to the functional groups that react. That is the organization under which I learned organic chemistry, and it is also the way that most organic chemistry textbooks are organized. Despite my best efforts, the majority of my students struggled with even the basics of mechanisms and, consequently, turned to flash cards as their primary study tool. They tried to memorize their way through the course, which made matters worse.

I began to wonder what impact the *organization*—an organization according to functional group—had on deterring my students from mechanisms. I had good reason to be concerned because, as I alluded to earlier, functional groups tend to convey *what*, whereas mechanisms convey *how* and *why*. What kinds of mixed messages were my students receiving when I was heavily emphasizing mechanisms, while the organization of the material was giving priority to functional groups? To probe that question, I made a big change to my teaching.

The third year I taught organic chemistry, I rearranged the material to pull together reactions that had the same or similar mechanisms—that is, I taught under a *mechanistic organization*. I made no other changes that year; the course content, course structure, and my teaching style all remained the same. I even taught out of the same textbook. But that year I saw dramatic improvements in my students' mastery of mechanisms.¹ Students had *control* over the material, which proved to be a tremendous motivator. They were better able to solve different kinds of problems with confidence. Ultimately, I saw significant

¹Bowman, B. G.; Karty, J. M.; Gooch, G. Teaching a Modified Hendrickson, Cram and Hammond Curriculum in Organic Chemistry. *J. Chem. Educ.* **2007**, *84*, 1209.

improvements in student performance, morale, and retention. I was convinced that students benefit remarkably from learning under a mechanistic organization.

My goal in writing this book is to support instructors who are seeking what I was seeking: getting students to use mechanisms to learn organic chemistry in order to achieve better performances and to have better experiences in their organic courses. Using a functional group organization to achieve these outcomes can be an uphill battle because of the high priority that it inherently places on functional groups. This textbook, on the other hand, allows students to receive the same message from both their instructor and their textbook—a clear and consistent message that mechanisms are vital to success in the course.

A Closer Look: Why Is a Mechanistic Organization Better?

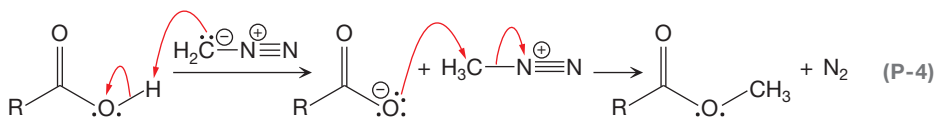
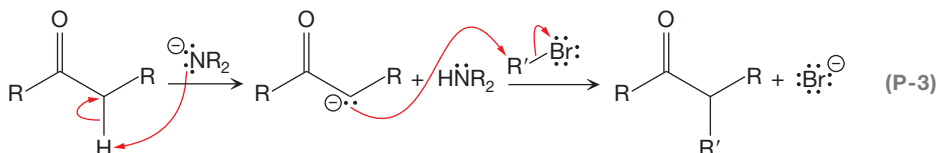
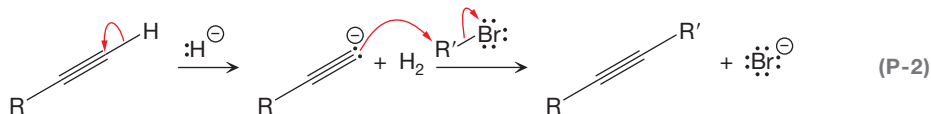
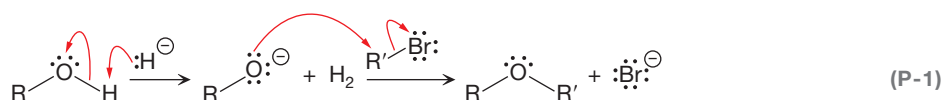
Consider what the novice sees when they begin a new *functional group chapter*. In an alcohols chapter, for example, students first learn how to recognize and name alcohols, then they study the physical properties of alcohols. Next, students might spend time on special spectroscopic characteristics of alcohols, after which they learn various routes that can be used to synthesize alcohols from other species. Finally, students move into the heart of the chapter: new reactions that alcohols undergo and the mechanisms that describe them. Within a particular functional group chapter, students find themselves bouncing among *several themes*.

Even within the discussion of new reactions and mechanisms that a particular functional group can undergo, students are typically faced with widely varying reaction types and mechanisms. Take again the example of alcohols. Students learn that alcohols can act as an acid or as a base; alcohols can act as nucleophiles to attack a saturated carbon in a substitution reaction, or to attack the carbon atom of a polar π bond in a nucleophilic addition reaction; protonated alcohols can act as electrophiles in an elimination reaction; and alcohols can undergo oxidation, too.

With the substantial jumping around that takes place within a particular functional group chapter, it is easy to see how students can become overwhelmed. Under a functional group organization, students don't receive intrinsic and clear guidance as to what they should focus on, not only within a particular functional group chapter, but also from one chapter to the next. Without clear guidance, and without substantial time for focus, students often see no choice but to memorize. And they will memorize what they perceive to be most important—predicting products of reactions, typically ignoring, or giving short shrift to, fundamental concepts and mechanisms.

Under the mechanistic organization in this book, students experience a *coherent story* of chemical reactivity. The story begins with molecular structure and energetics, and then guides students into reaction mechanisms through a few transitional chapters. Thereafter, students study how and why reactions take place as they do, focusing on one type of mechanism at a time. Ultimately, students learn how to intuitively use reactions in synthesis. In this manner, students have clear and consistent guidance as to what their focus should be on, both within a single chapter and throughout the entire book.

The *patterns* we, as experts, see become clear to students when they learn under this mechanistic organization. Consider the following four mechanisms:



The mechanism in Equation P-1 is for a Williamson synthesis of an ether; the one in Equation P-2 is for an alkylation of a terminal alkyne; the one in Equation P-3 is for an alkylation of a ketone; and the one in Equation P-4 is for the conversion of a carboxylic acid to a methyl ester. In these four reactions, the reactants are an alcohol, an alkyne, a ketone, and a carboxylic acid. In a functional group organization, these reactions will be taught in *four separate chapters*. Because all four reaction mechanisms are identical—a deprotonation followed by an $\text{S}_{\text{N}}2$ step—all four reactions are taught in the *same* chapter in this book: Chapter 10.

Seeing these patterns early, students more naturally embrace mechanisms and use them when solving problems. Moreover, as students begin to see such patterns unfold in one chapter, they develop a better toolbox of mechanisms to draw on in subsequent chapters. Ultimately, students gain *confidence* in using mechanisms to predict what will happen and why. I believe this is vital to their success throughout the course and later on admission exams such as the MCAT.

Details about the Organization

Continuing with the success of the first edition, the book remains divided into three major parts:

Part I: Atomic and molecular structure

- Chapter 1: Atomic structure, Lewis structures and the covalent bond, and resonance theory, culminating in an introduction to functional groups
- Chapter 2: Aspects of three-dimensional geometry and its impacts on intermolecular forces
- Chapter 3: Structure in terms of hybridization and molecular orbital (MO) theory
- Chapters 4 and 5: Isomerism in its entirety, including constitutional isomerism, conformational isomerism, and stereoisomerism

Much of the material in Chapters 1–5 will be new to students, such as organic functional groups, protic and aprotic solvents, effective electronegativity, conformers and cyclohexane chair structures, and stereoisomers. Chapters 1–5 also contain a significant amount of material that students will recognize from general chemistry, such as electronic configurations, Lewis structures and resonance, intermolecular forces, VSEPR theory and hybridization, and constitutional isomers. Because most students do not retain everything they should from general chemistry, I have made the general chemistry topics in this textbook more extensive than in other textbooks. Knowing that this extended coverage is in the book, instructors should feel comfortable covering as much or as little of it as they see fit for their students.

Part II: Developing a toolbox for working with mechanisms

- Chapters 6 and 7: Ten common elementary steps of mechanisms
- Chapter 8: Beginnings of multistep mechanisms using S_N1 and E1 reactions as examples

Mechanisms are vital to succeeding in organic chemistry, but before tackling mechanisms, students must have the proper tools. Chapters 6–8 give students those tools, dealing with aspects of elementary steps in Chapters 6 and 7 before dealing with aspects of multistep mechanisms in Chapter 8. Therefore, the chapters in Part II act a transition from Part I to Part III, which deals more intently with reactions.

Chapter 7 is a particularly important part of this transition. Students learn how to work with elementary steps in Chapter 7 in a low-risk environment, where there are no demands to predict products. Thus, there is no pressure to memorize overall reactions. Furthermore, the fact that Chapter 7 brings together the 10 most common elementary steps—making up the mechanisms of the many hundreds of reactions students will encounter through Chapter 23—sends a strong message to students that mechanisms *simplify* organic chemistry. In turn, students take to heart from the outset that mechanisms are worthwhile to learn.

Part III: Major reaction types

- Chapters 9 and 10: Nucleophilic substitution and elimination
- Chapters 11 and 12: Electrophilic addition
- Chapters 17 and 18: Nucleophilic addition
- Chapters 20 and 21: Nucleophilic addition–elimination
- Chapters 22 and 23: Aromatic substitution
- Chapter 24: Diels–Alder reactions and other pericyclic reactions
- Chapter 25: Radical reactions
- Chapter 26: Polymerization

Several of these chapters come in pairs, where the first chapter is used to introduce key ideas about the reaction or mechanism and the second chapter explores the reaction or mechanism to greater depth and breadth.

Pairing the chapters this way provides flexibility. An instructor could teach all of the chapters in order. Alternatively, following the guidelines set by the American Chemical Society, an instructor could teach the first of each paired chapter in the first semester as part of “foundational” coursework. Then, the remaining chapters would represent “in-depth” coursework for the second semester. Teaching the chapters in this order would also allow an instructor to teach carbonyl chemistry in the first semester.

Interspersed in Part III are chapters dealing with multistep synthesis (Chapters 13 and 19), conjugation and aromaticity (Chapter 14), and spectroscopy (Chapters 15 and 16). The spectroscopy chapters are self-contained and can be taught earlier, at the instructor’s discretion. They can even be taught separately in the laboratory. The spectroscopy chapters are movable like this because, with the mechanistic organization of the book, important aspects of spectroscopy are not integrated in reaction chapters like they typically are in a functional group text.

The two chapters devoted to multistep synthesis (Chapters 13 and 19), on the other hand, are strategically located. Chapter 13 appears after students have spent several chapters working with reactions. Having quite a few reactions under their belts, students can appreciate retrosynthetic analysis, as well as cataloging reactions as functional group transformations or reactions that alter the carbon skeleton. Moreover, Chapter 13 appears early enough so students can practice their skills devising multistep syntheses throughout the entire second half of the book; each subsequent chapter has multiple synthesis problems. Additionally, Chapter 13 is an excellent review of reactions students learned to that point in the book, so it could be taught at the end of the first semester as a capstone, or it could be taught at the beginning of the second semester to help jog students' memories in preparation for second semester.

Chapter 19 is delayed a few more chapters because it deals with content related to reactions from Chapter 18, including protecting groups and choosing carbon-carbon bond-forming reactions that result in the desired relative positioning of functional groups. The multistep synthesis topics in Chapter 19 are somewhat more challenging than the ones in Chapter 13, so whereas Chapter 13 should be covered in most mainstream courses, instructors can choose to cover only certain sections of Chapter 19.

I have found that treating multisynthesis in dedicated chapters makes it more meaningful to students. When I taught synthesis under a functional group organization, it became a distraction to the reactions that students were simultaneously learning. I also found that students often associated a synthetic strategy only with the functional group for which it was introduced. For example, when the idea of protecting groups is introduced in the ketones/aldehydes chapter of a textbook organized by functional group, students tended to associate protecting groups with ketones and aldehydes *only*. My dedicated synthesis chapters help students focus on synthesis without compromising their focus on reactions. Furthermore, synthesis strategies are discussed more holistically, so students can appreciate them in a much broader context rather than being applicable to just a single functional group.

Another major organizational feature of the book pertains to nomenclature. Nomenclature is separated out from the main chapters, in five relatively short interchapters—Interchapters A, B, C, E, and F. Separating nomenclature from the main chapters in this way removes distractions. It also allows students to focus on specific rules of nomenclature instead of specific compound classes. With each new nomenclature interchapter, the complexity of the material increases by applying the new rules to the ones introduced earlier.

The instructor has flexibility as to how to work with these nomenclature interchapters. They can be covered in lecture or easily assigned for self-study. They can be split over two semesters or could all be covered in the first semester. The locations of the interchapters in the book (i.e., immediately after Chapters 1, 3, 5, 7, and 9), however, should be taken as indicators as to the earliest that each interchapter should be assigned or taught. Covering a nomenclature interchapter substantially earlier than it appears in the book would expose students to compound classes well before those types of compounds are dealt with in the main chapters.

Finally, the application of MOs toward chemical reactions is separated from the main reaction chapters, and is presented, instead, as an optional, self-contained unit—Interchapter D. This interchapter appears just after Chapter 7, the overview of the 10 most common elementary steps. Each elementary step from Chapter 7 is revisited from the perspective of frontier MO theory. Because this interchapter is optional, chapters later in the book do not rely on coverage of this material.

Presenting this frontier MO theory material together in an optional unit, as I have done in Interchapter D in this book, offers two main advantages to students. First, it removes a potential distraction from the main reaction chapters and, being optional, instructors have the choice of not covering it at all. Another advantage comes from the fact that the MO pictures of all 10 common elementary steps appear together in the interchapter. Therefore, instructors who wish to cover this interchapter can expect their students to come away with a better understanding of the bigger picture of MO theory as it pertains to chemical reactions.

Focused on the Student

While the organization provides a coherent story, I've included pedagogy that promotes active learning and makes this book a better tool for students.

Strategies for Success. I wrote these sections to help students build specialized skills they need in this course. For example, Chapter 1 provides strategies for drawing all resonance structures of a given species, and sections in Chapters 2 and 3 are devoted to the importance of molecular modeling kits in working with the three-dimensional aspects of molecules and also with the different rotational characteristics of single and double bonds. In Chapter 4, students are shown step by step how to draw chair conformations of cyclohexane and how to draw all constitutional isomers of a given formula. Chapter 5 provides help with drawing mirror images of molecules. One Strategies for Success section in Chapter 6 helps students estimate pK_a values and another helps students rank acid

4.7 Strategies for Success: Drawing Chair Conformations of Cyclohexane

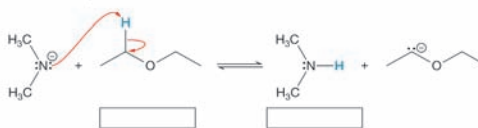
Given the abundance of cyclohexane rings, it would soon become cumbersome if we always had to represent chair conformations three-dimensionally as ball-and-stick models (Fig. 4-23a) or in dash-wedge notation (Fig. 4-23b). Chemists, therefore, have devised the shorthand notation for drawing chair conformations shown in Figure 4-23c.

and base strengths based only on their Lewis structures. In Chapter 14, I include a section that shows students how to use the Lewis structure to assess conjugation and aromaticity, and Chapter 16 has a section that teaches students the chemical distinction test for nuclear magnetic resonance.

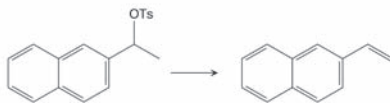
Your Turn exercises. Getting students to read *actively* can be challenging, so I wrote the Your Turns in each chapter to motivate this type of behavior. Your Turns are basic exercises that ask students to either answer a question, look something up in a table, construct a molecule using a model kit, or interact with art in a figure or data in a plot. These exercises are also intended to be “reality checks” for students as they read. If a student cannot solve or answer a Your Turn exercise easily, then that student should interpret this as a signal to either reread the previous section(s) or seek help. Short answers to all Your Turns are provided in the back of the book and complete solutions to these exercises are provided in the *Study Guide and Solutions Manual*.

YOUR TURN 6.5

Verify the preceding statement that diethyl ether would be a suitable solvent for $(\text{CH}_3)_2\text{N}^-$. To do so, use Table 6-1 to fill in the boxes below with the appropriate pK_a values and label which one is the stronger acid. Indicate which side of the reaction is favored at equilibrium. Is this the same side that is favored in Equation 6-11?



Complete the following synthetic step by indicating that water is used as the solvent and that the reaction is carried out at 70 °C.



YOUR TURN 13.2

Consistent and effective problem-solving approach. Helping students become expert problem solvers, in this course and beyond, is one of my major goals. I have developed the Solved Problems in the book to train students how to approach a problem. Each Solved Problem is broken down into two parts: *Think* and *Solve*. In the Think part, students are provided a handful of guiding *questions* that I want them to be asking as they approach the problem. In the Solve part, those questions are answered and the problem is solved. This

mirrors the strategy I use to help students during office hours, and we have used these same steps for *every* problem in the *Study Guide and Solutions Manual* that accompanies the book.

Biochemistry and the MCAT. Most students taking organic chemistry are biology majors or are seeking a career in a health profession. They appreciate seeing how organic chemistry relates to their interests and look for ways in which this course will prepare them for the admissions exams (such as the MCAT) that may have a large impact on their future.

Rather than relegating biochemistry to the end of the book, I have placed self-contained Organic Chemistry of Biomolecules sections at the ends of several chapters, beginning with Chapter 1. The topics chosen for these sections cover many of the topics dealt with on the MCAT, which means that the Organic Chemistry of Biomolecules sections are not *in addition to* what students are expected to know for the MCAT; they are topics that students *should know* for the test. In even the earliest of chapters, students have the tools to start learning aspects of this traditional biochemistry coverage. More importantly, these sections provide reinforcement of topics. In each biomolecules section, the material is linked directly back to concepts encountered earlier in the chapter.

These Organic Chemistry of Biomolecules sections are both optional and flexible. Instructors can decide to cover only a few of these topics or none at all, and can do so either as they appear in the book or as special topics at the end of the second semester.

A range of interesting applications. In addition to the Organic Chemistry of Biomolecules sections, most chapters have two special interest boxes. These boxes apply a concept in the chapter to some depth toward a discovery or process that can have significant appeal to students, perhaps delving into a biochemical process or examining new and novel materials. In addition to reinforcing concepts from the chapter, these boxes are intended to provide *meaning* to what students are learning, and to motivate students to dig deeper.

In addition to these special interest boxes, several Connections boxes in each chapter provide glimpses into the everyday utility of molecules that students have just seen.

New to the Second Edition

Organization of end-of-chapter problems. At the end of each chapter, problems are grouped by concept or section so students can easily identify the types of problems they need to work on. A set of Integrated Problems follows those sets of focused problems. These Integrated Problems require students to bring together major concepts from multiple sections within the chapter, or from multiple chapters, as they would on an exam. These problems also help students stay familiar with material from earlier in the book, thus reducing the time that students would need to spend separately for review. In addition to organizing problems this way, problems that relate to aspects of synthesis are labeled (SYN), so students and instructors can find those types of problem quickly.

More than 300 new problems. Based on user and reviewer feedback, several new problems have been added to each chapter to provide students even more opportunities to hone their problem-solving skills and to assess their mastery of the material. Some of these new problems are specifically geared toward material from the Organic Chemistry of Biomolecules sections from within the chapter, and are grouped together among the end-of-chapter problems to make them easily identifiable.

More Solved Problems. The first edition provided students with about seven Solved Problems per chapter on average. Several new Solved Problems have been added, bringing the average to about eight per chapter. This gives students more opportunities to receive guidance on the strategies they should use when solving a problem. In addition, Solved Problems have been added to each nomenclature interchapter. Nomenclature builds in complexity as new rules are introduced, and each Solved Problem is designed to help students navigate those new rules.

SOLVED PROBLEM 11.3

Predict the major product when indene is treated with HCl.

Think Which C=C double bond will undergo electrophilic addition? What are the possible products and the corresponding carbocation intermediates from which they are produced? Which carbocation intermediate is more stable?

Solve The rightmost C=C double bond is the one that will undergo electrophilic addition. The others make up a benzene ring and are much too stable to react under these conditions. The two possible products of HCl addition differ by which C atom gains the H⁺ and which gains the Cl⁻:

THE ORGANIC CHEMISTRY OF BIOMOLECULES

1.14 An Introduction to Proteins, Carbohydrates, and Nucleic Acids: Fundamental Building Blocks and Functional Groups

CONNECTIONS

4-Methylphenol, also called *para*-cresol, is one of the compounds responsible for the odor of pigs and is also found in human sweat. One of the main uses of 4-methylphenol is in the production of antioxidants.



Nomenclature presented in five interchapters rather than four. In the first edition, nomenclature was presented in four interchapters. The fourth nomenclature interchapter dealt with all compound classes that call for the addition of a suffix, including amines, alcohols, ketones, aldehydes, and carboxylic acids and their derivatives. Users found this to be too much material for one chapter, so in the second edition, that interchapter has been split into two: Interchapters E and F. Interchapter E deals with alcohols, amines, ketones, and aldehydes; Interchapter F deals with carboxylic acids and their derivatives.

Addition of green chemistry. Based on user feedback, I have added a new section on green chemistry to Chapter 13, the first devoted chapter on multistep synthesis. Section 13.8b provides an overview of green chemistry and its importance, and then delves into three of the 12 main principles of green chemistry outlined by the American Chemical Society: less toxic reagents and solvents; safer synthesis routes; and minimizing by-products and other waste. In subsequent reaction chapters, students will find Green Chemistry boxes in the margin notes, which highlight green aspects of some reactions and provide green alternatives to others. For students planning on a career in chemistry, the goal is to instill in them the importance of considering green chemistry when designing and carrying out a synthesis. All students should know what green chemistry is, and should come to appreciate the fact that chemists in the 21st century are increasingly prioritizing the well-being of our planet.

New strategies to help students analyze IR, NMR, and mass spectra. Even with a strong foundation in the principles that underlie IR and NMR spectroscopy and mass spectrometry, it can still be quite a challenge for students to analyze a spectrum in a way that brings the individual pieces of information together. To help students along these lines in the first edition, I presented spectra of unknowns and then brought students through the analysis methodically, although somewhat passively. New to the second edition, I now present separate strategies up front to analyze IR, NMR, and mass spectra, with sequential steps that students can follow. Then I show students how to apply these strategies toward the analysis of spectra of unknowns. Students are encouraged to develop other strategies that might work better for them, but until then, students have an effective strategy that they can use and rely on.

Oxidation states moved to Chapter 17. In the first edition, calculating oxidation states of atoms was presented in Chapter 1 alongside the calculation of formal charges. Although grouping those two topics together makes sense because of the similarities between the two methods, users reported that students weren't sufficiently applying the ideas of oxidation states toward redox reactions until Chapter 17. Therefore, in the second edition, I moved the calculation of oxidation states to Section 17.3b, where hydride reductions are discussed.

Nobel Prize-winning coupling and metathesis reactions. Because of their importance to organic chemistry, transition metal coupling reactions and alkene metathesis reactions have been added to the second edition. These include: coupling reactions involving dialkylcuprates; the Suzuki reaction; the Heck reaction; and the Grubbs reaction. The utility of these reactions is primarily in organic synthesis, specifically in the formation of new carbon-carbon bonds, so these reactions have been added to Chapter 19, the second chapter devoted to organic synthesis.

Azo coupling and azo dyes. The presentation of azo coupling and a short discussion on azo dyes have been added to Chapter 23, the second chapter on aromatic substitution reactions. The benefits of this section are twofold. First, it is an application of diazotization (Chapter 22) and substituent effects in aromatic substitution (Chapter 23), so it provides reinforcement of newly learned concepts. Second, students can easily relate to dyes, so it is an excellent example of the daily impacts organic chemistry has on students' lives.

Connections boxes. Students often ask, "How does organic chemistry apply to me?" or, "Why should I care about organic chemistry?" For the chemistry major or the student going on to medical school or another health profession, the long-term answer might be apparent. Connections boxes, which are new to the second edition, are designed to help answer that question as it relates to the immediate. In the margins of each chapter, students will find several Connections boxes that highlight the importance or application of

a molecule that was just encountered. Students might see that the molecule is integral in the synthesis of a pharmaceutical drug, or that the molecule is important in the manufacture of a material that students use daily. More than just helping provide an answer to the above questions, these Connections boxes also help keep students *interested* in the material, and an interested student is a more successful student.

Acknowledgments

Special thanks to my wife Valerie and my boys Joshua and Jacob for being my biggest fans. Their love and immense support throughout my work on the second edition not only helped push me to the finish line, but they continue to make my achievements worthwhile.

Many thanks to my colleagues in the chemistry department at Elon for your understanding, especially Dan Wright and Karl Sienerth, who served as my department chairs during this endeavor. And a tremendous thank-you to Kathy Matera for the real-time feedback you have given me over the years, and for all the times I barged into your office to pick your brain when I was in the midst of working through a quandary with the book.

I remain indebted to my students. Thank you for bringing such great energy to learning organic chemistry year in and year out, and thank you for allowing me to learn from you.

I continue to be amazed with the members of the Norton team. Erik Fahlgren, thank you for your continued belief in me and in the potential this book has to help teachers teach and to help students learn. John Murdzek, your insights in the developmental process have truly enabled me to reach students more effectively and meaningfully. Arielle Holstein and Sara Bonacum, thank you for being the glue that has held this entire project together. And a further congratulations to Arielle for your new position as Associate Media Editor; thank you for the great work you have done on the book's ancillaries. To Carla Talmadge and Connie Parks, many thanks for holding me to a high standard in the copyediting and page proofing stages. Travis Carr and Elyse Rieder, I admire your patience and persistence when I need just the right photo. Christopher Rapp and Christine Pruis, thank you for your work on the online resources for the book, which not only add value to the book but also make the book more effective. Lisa Buckley, what a fantastic job on the interior design, giving the book a warm and inviting feel. And Stacy Loyal, you continue to amaze me with your vision and the creativity you bring to marketing the book.

A special thanks, once again, to Marie Melzer. With the energy and the insight that you have continued to bring, I could not imagine a better coauthor on the *Study Guide and Solutions Manual*. And to Steve Pruett, I truly value your work on the polymers chapter in the first edition.

Finally, I am indebted to the many reviewers, whose feedback has been instrumental in making several significant improvements over the first edition. I am especially grateful to Joachim Schantl, who accuracy-checked nearly the *entire* book! I am in awe of your breadth and depth of knowledge, as well as your attention to detail. Many, many thanks.

Reviewers of Second Edition

Aron Anderson, Gustavus Adolphus College
Niels Andersen, University of Washington
Amelia Anderson-Wile, Ohio Northern University
Christina Bagwill, Saint Louis University
Joshua Beaver, University of North Carolina, Chapel Hill
David Bergbreiter, Texas A & M University
Shannon Biros, Grand Valley State University
Dan Blanchard, Kutztown University

Elizabeth Blue, Campbell University
Luc Boisvert, University of Puget Sound
Michelle Boucher, Utica College
Rick Bunt, Middlebury College
Nancy Carpenter, University of Minnesota, Morris
Timothy Clark, University of San Diego
Kimberly Cousins, California State University, San Bernardino
Ashton Cropp, Virginia Commonwealth University

Anna Drotor, Metropolitan State University of Denver
Nathan Duncan, Maryville College
Brendan Dutmer, Highland Community College
Todd Eckroat, Penn State, Behrend
Daniel Esterline, Thomas More College
Amanda Evans, California State University, Fullerton
Christoph Fahrni, Georgia State Institute of Technology

Suzanne Fernandez, Lehigh University
Michael Findlater, Texas Tech University
Abbey Fischer, University of Wisconsin–
Barron County
Stephen Foley, University of Saskatchewan
Malcolm Forbes, Bowling Green State
University
Denis Fourches, North Carolina State
University
Andrew Frazer, University of Central Florida
Gregory Friestad, University of Iowa
Brian Frink, Lakeland College
Brian Ganley, University of Missouri
Kevin Glaeske, Wisconsin Lutheran College
Sarah Goforth, Campbell University
Harold Goldston Jr., Des Moines Area
Community College
Anne Gorden, Auburn University
Dustin Gross, Sam Houston State University
Matthew Hart, Grand Valley State University
Allan Headley, Texas A & M University
Ian Hill, Gustavus Adolphus College
Daniel Holley, Columbus State University
Robert Hughes, East Carolina State
University
Philip Hultin, University of Manitoba
William Jenks, Iowa State University
Bob Kane, Baylor University
Kristopher Keuseman, Mount Mercy
University
Brett Kite, Shenandoah University
Jeremy Klosterman, University of California,
San Diego
Kazunori Koide, University of Pittsburgh
Shane Lamos, St. Michael's College
Nicholas Leadbeater, University of
Connecticut
Carl Lecher, Marian University
Larry Lee, Camosun College

Diana Leung, University of Alabama,
Tuscaloosa
Nicholas Llewellyn, Emory University
Carl Lovely, University of Texas, Arlington
Breyawn Lybbert, University of Wisconsin
Helena Malinakova, University of Kansas
Richard Manderville, University of Guelph
Kristen Mascall, Brandeis University
Eugene Mash, University of Arizona
Daniell Mattern, University of Mississippi
Jimmy Mays, University of Tennessee,
Knoxville
Vanessa McCaffrey, Albion College
Justin Mohr, University of Illinois, Chicago
Suazette Mooring, Georgia State University
Jesse More, Loyola University
Andrew Morehead, East Carolina University
Cheryl Moy, University of North Carolina,
Chapel Hill
R. Scott Murphy, Regina University
Joan Mutanyatta-Comar, Georgia State
University
David Nagib, Ohio State University
Felix Ngassa, Grand Valley State University
Taeboem Oh, California State University,
Northridge
Joshua Osbourn, West Virginia University
Keith Pascoe, Georgia State University
Gitendra Paul, Malcolm X College
Michael Pelter, Purdue University Northwest
Angela Perkins, University of Minnesota
Joanna Petridou-Fischer, Spokane Falls
Community College
Tarakeshwar Pilarsetty, Arizona State
University
Smitha Pillai, Arizona State University
Kyle Plunkett, Southern Illinois University
Pamela Pollet, Georgia Institute of Technology

Brian Popp, West Virginia University
Walda Powell, Meredith College
Stephen Pruett, Jefferson Community and
Technical College
Frank Rossi, State University of New York,
Cortland
Nicholas Salzameda, California State
University, Fullerton
Robert Sammelson, Ball State University
Joachim Schantl, University of Florida
Jacob Schroeder, Clemson University
Reza Sedaghat-Herati, Missouri State
University
Jia Sheng, University of Albany
Abbas Shilabin, East Tennessee State
University
Matthew Siebert, Missouri State University
Chatu Sirimanne, California State University,
Los Angeles
Heather Sklenicka, Rochester Community and
Technical College
Mike Slade, University of Evansville
Greg Slough, Kalamazoo College
Gary Spessard, University of Arizona
Nicholas Stephanopoulos, Arizona State
University
Robert Ternansky, University of California,
San Diego
Sadanandan Velu, University of Alabama,
Birmingham
Martin Walker, The State University of New
York, Potsdam
Don Warner, Boise State University
Michael Weaver, University of Florida
Lyndon West, Florida Atlantic University
Anne Wilson, Butler University
Kai Ylijoki, Saint Mary's University
Yimin Zhu, Pennsylvania State University,
Altoona

Reviewers of the First Edition

Robert Allen, Arkansas Tech University
Herman Ammon, University of Maryland
Carolyn Anderson, Calvin College
Aaron Aponick, University of Florida
Phyllis Arthasery, Ohio University
Jared Ashcroft, Pasadena City College
Athar Ata, University of Winnipeg
Jovica Badjic, Ohio State University
John Bellizzi, University of Toledo
Daniel Berger, Bluffton University
Anthony Bishop, Amherst College
Rebecca Broyer, University of Southern
California

Larry Calhoun, University of New Brunswick
Shawn Campagna, University of Tennessee,
Knoxville
Nancy Carpenter, University of Minnesota,
Morris
Brad Chamberlain, Luther College
Robert Coleman, Ohio State University
Tammy Davidson, University of Florida
Lorraine Deck, University of New Mexico
Sergei Dzyuba, Texas Christian University
Jeff Elbert, University of Northern Iowa
Seth Elsheimer, University of Central Florida
Eric Finney, University of Washington

Andrew Frazer, University of Central Florida
Larry French, St. Lawrence University
Gregory Friestad, University of Iowa
Brian Frink, Lakeland University
Anne Gorden, Auburn University
Christopher Gorman, North Carolina State
University
Oliver Graudejus, Arizona State University
Robert Grossman, University of Kentucky
Daniel Gurnon, DePauw University
Jeffrey Hansen, DePauw University
Bryan Hanson, DePauw University
Andrew Harned, University of Minnesota

Stewart Hart, Arkansas Tech University
John Hershberger, Arkansas State University
Gail Horowitz, Brooklyn College
Roger House, Auburn University
Philip Hultin, University of Manitoba
Kevin Jantzi, Valparaiso University
Amanda Jones, Wake Forest University
Jeff Jones, Washington State University
Paul Jones, Wake Forest University
Robert Kane, Baylor University
Arif Karim, Austin Community College
Steven Kass, University of Minnesota
Stephen Kawai, Concordia University
Valerie Keller, University of Chicago
Mark Keranen, University of Tennessee at Martin
Kristopher Keuseman, Mount Mercy College
Angela King, Wake Forest University
Jesudoss Kingston, Iowa State University
Francis Klein, Creighton University
Jeremy Klosterman, Bowling Green State University
Dalila Kovacs, Grand Valley State University
Jason Locklin, University of Georgia
Brian Long, University of Tennessee, Knoxville
Claudia Lucero, California State University, Sacramento
David Madar, Arizona State University Polytechnic
Kirk Manfredi, University of Northern Iowa

Eric Masson, Ohio University
Anita Mattson, Ohio State University
Gerald Mattson, University of Central Florida
Jimmy Mays, University of Tennessee, Knoxville
Alison McCurdy, California State University, Los Angeles
Dominic McGrath, University of Arizona
Mark McMills, Ohio University
Marie Melzer, Old Dominion University
Ognjen Miljanic, University of Houston
Justin Miller, Hobart and William Smith Colleges
Stephen Miller, University of Florida
Barbora Morra, University of Toronto
Joseph O'Connor, University of California, San Diego
James Parise, University of Notre Dame
Gitendra Paul, Malcolm X Community College
Noel Paul, Ohio State University
James Poole, Ball State University
Christine Pruis, Arizona State University
Harold Rogers, California State University, Fullerton
Sheryl Rummel, Pennsylvania State University
Nicholas Salzameda, California State University, Fullerton
Adrian Schwan, University of Guelph
Colleen Scott, Southern Illinois University, Carbondale

Alan Shusterman, Reed College
Joseph Simard, University of New England
Chad Snyder, Western Kentucky University
John Sorensen, University of Manitoba
Levi Stanley, Iowa State University
Laurie Starkey, California State University, Pomona
Tracy Thompson, Alverno College
Nathan Tice, Butler University
John Tomlinson, Wake Forest University
Melissa VanAlstine-Parris, Adelphi University
Nanine Van Draanen, California Polytechnic State University
Qian Wang, University of South Carolina
Don Warner, Boise State University
Haim Weizman, University of California, San Diego
Lisa Whalen, University of New Mexico
James Wilson, University of Miami
Laurie Witucki, Grand Valley State University
James Wollack, St. Catherine University
Andrei Yudin, University of Toronto
Michael Zagorski, Case Western Reserve University
Rui Zhang, Western Kentucky University
Regina Zibuck, Wayne State University
Eugene Zubarev, Rice University
James Zubricky, University of Toledo

Additional Resources For Students

Study Guide and Solutions Manual

by Joel Karty, Elon University, and Marie Melzer

Written by two dedicated teachers, this guide provides students with fully worked solutions to all unworked problems in the text. Every solution follows the Think and Solve format used in the textbook, so the approach to problem solving is modeled consistently.

Smartwork5 (digital.wwnorton.com/karty2)

Smartwork5 is the most intuitive online tutorial and homework system available for organic chemistry. A powerful engine supports and grades a wide variety of problems written for the text, including numerous arrow-pushing problems. *Every* problem in Smartwork5 has hints and answer-specific feedback to coach students and provide the help they need, when they need it. Problems in Smartwork5 link directly to the appropriate page in the ebook so students have an instant reference and are prompted to read.

Assigning, editing, and administering homework within Smartwork5 is easy. Instructors can select from Norton's bank of more than 3200 high-quality, class-tested problems. Using the sort and search features, instructors can identify problems by chapter section, learning objective, question type, and more. Instructors can use premade assignments provided by Norton authors, modify those assignments, or create their own. Instructors

also have access to intuitive question authoring tools—the same ones Norton authors use. These tools make it easy to customize the question content to fit the course needs. Smartwork5 integrates seamlessly with most campus learning management systems and can be used on computers and tablets.

The Smartwork5 course features:

- **An expert author team.** The Smartwork5 course was authored by instructors who teach at a diverse group of schools: Arizona State University, Florida State University, Brigham Young University, Butler University, and Mesa Community College. The authors have translated their experience in teaching a diverse student population by creating a library of problems that will appeal to instructors at all schools.
- **An upgraded drawing tool.** Smartwork5 contains an upgraded 2-D drawing tool that mimics drawing on paper, reduces frustration, and helps students focus on the problem at hand. This intuitive drawing tool supports multistep mechanism and multistep synthesis problems and provides students with answer-specific feedback for every problem.
- **Ease of use for students.** The 2-D drawing tool has a variety of features that make drawing easy and efficient. Students are provided with templates including a variety of common rings and a carbon chain drawing tool. In addition, Smartwork5 presents students with commonly used elements, a simple click to add lone pairs option, and ease-of-use features such as undo, redo, simple-click erase, and zoom-in/zoom-out.
- **Question variety.** The Smartwork5 course offers a diverse set of problems including:
 - Nomenclature problems
 - Multistep Mechanism problems
 - Multistep Synthesis problems
 - Reaction problems
 - Spectroscopy problems
- **Conceptual question types include:**
 - Multiple-choice/multiple select
 - Ranking
 - Sorting
 - Labeling
 - Numeric entry
 - Short answer
- **Pooled problems.** Smartwork5 features sets of pooled problems for multistep mechanisms and nomenclature to promote independent work. Groups of similar problems are “pooled” into one problem so different students receive different problems from the pool. Instructors can choose our preset pools or create their own.

Ebook (digital.wwnorton.com/karty2)

An affordable and convenient alternative to the print text, the Norton Ebook lets students access the entire book and much more: They can search, highlight, and take notes with ease. The Norton Ebook allows instructors to share their notes with students. The ebook can be viewed on computers and tablets and will stay synced between devices. The online ebook is available at no extra cost with the purchase of a new print text or it may be purchased stand-alone with Smartwork5.

Molecular Model Kits

Norton partners with two model kits and can package either with the textbook for an additional cost.

Darling Molecular Model Kit. Atoms with their valences already attached are constructed by snapping together V-shaped pieces in a jigsaw style, emphasizing bond angles and symmetry elements of the atoms. Double bonds are independent, rectangular units to emphasize the planarity of sp^2 -hybridized atoms. Large substituents can be represented by various colored marker balls.

This kit includes 120 pieces:

- 57 sp^3 pieces (black, red, blue, silver black, turquoise, gray)
- 16 sp^2 pieces (gray)
- 18 marker balls (white, red, green, blue)
- 7 double bonds (gray)
- 6 half double bonds (gray, red)
- 2 trigonal atoms (gray)
- 2 linear bonds (gray)
- 2 linear triple bonds (gray)
- 4 bond extenders
- 4 octahedral pieces (pink)
- 2 Atom Visions™ balls

HGS Molecular Structure Model Kit. The HGS kit reflects the traditional ball-and-stick model for constructing molecules. Conjugation can be illustrated using trigonal planar atoms that have five holes to accommodate three bonds and the two lobes of a p orbital. Double bonds can be constructed using curved sticks to occupy two valences of a tetrahedral atom.

This kit includes 210 pieces:

- 30 tetrahedral carbon atoms (black)
- 14 trigonal planar carbon atoms (black)
- 30 hydrogen atoms (light blue)
- 4 oxygen atoms (red)
- 6 nitrogen atoms (blue)
- 4 chlorine atoms (green)
- 2 metal atoms (grey)
- 12 orbital plates (green, blue)
- 108 bond pieces, 5 types (light blue, orange, green, yellow, white)

Please contact your Norton representative about ordering and pricing options for packaging model kits.

For Instructors

Instructor's Guide

by Michelle Boucher, Utica College, and Cliff Coss, Northern Arizona University

Written by users of the first edition, the *Instructor's Guide* is an invaluable resource for instructors organizing their course by mechanism for the first time. Based on their experience, Michelle and Cliff provide a brief overview of every chapter followed by a section-by-section summary that illustrates how easy and rewarding it is to teach a mechanistically organized course. In addition to providing an easy transition, the authors offer other resources, such as class-tested clicker questions that instructors may choose to incorporate into their course. While this guide is an excellent resource for adopters, it may also answer questions for instructors who are interested in a mechanistic organization but are concerned about the transition. The *Instructor's Guide* includes a chapter for each of the 26 chapters in the textbook, plus a chapter for the molecular orbital theory interchapter and a chapter for each of the nomenclature interchapters.

Clickers in Action: Active Learning in Organic Chemistry

by Suzanne M. Ruder, Virginia Commonwealth University

This instructor-oriented resource provides information on implementing clickers in organic chemistry courses. Part I gives instructors information on how to choose and manage a classroom response system, develop effective questions, and integrate the questions into their courses. Part II contains 140 class-tested, lecture-ready questions. Most

questions include histograms that show actual student response, generated in large classes with 200–300 students over multiple semesters. Each question also includes insights and suggestions for implementation. The 140 questions from the book are sorted to correspond to the chapters in the textbook.

Test Bank

by James Wollack, St. Catherine University, Jennifer Griffith, Western Washington University, and Chris Markworth, Western Washington University

After teaching with the first edition, our authors have written problems that will make assessing your students easy. Whether your exams are multiple choice, short answer and require drawing, or both, the variety and quality of the problems in the test bank will exceed your needs. The test bank contains approximately 1600 multiple-choice and short-answer questions classified by section and difficulty level. It is available with Exam-View Test Generator software, allowing instructors to effortlessly create, administer, and manage assessments. The convenient and intuitive test-making wizard makes it easy to create customized exams with no software learning curve. Other key features include the ability to create paper exams with algorithmically generated variables and export files directly to Blackboard, Canvas, Desire2Learn, and Moodle.

Instructor's Resources: Flash Drive

This helpful classroom presentation tool features:

- Select photographs and every piece of line art in JPEG format
- Select photographs and every piece of line art in PowerPoint
- Lecture PowerPoint slides with integrated figures from the book
- *Instructor's Guide* in PDF format
- Test bank in PDF, Word, and ExamView formats
- Approximately 500 lecture-ready questions, in PowerPoint, from *Clickers in Action* as well as Joel Karty's course

Downloadable Instructor's Resources (www.norton.com/instructors)

This instructor-only, password-protected site features instructional content for use in lecture and distance education, including test-item files, PowerPoint lecture slides, images, figures, and more. The instructor's website includes:

- Select photographs and every piece of line art in JPEG format
- Select photographs and every piece of line art in PowerPoint
- Lecture PowerPoint slides with integrated figures from the book
- *Instructor's Guide* in PDF format
- Test bank in PDF, Word, and ExamView formats
- Approximately 500 lecture-ready questions, in PowerPoint, from *Clickers in Action* as well as Joel Karty's course

Author Blog: www.teachthemechanism.com

In July 2012, Joel Karty started a blog about his approach and his experience teaching a course organized by mechanism. Now there are more than 120 guest blog posts written by professors who use Joel's book, garnering nearly 60,000 views and 20+ active conversations. What once was an informational blog has now grown into a platform for a community of instructors to share their experiences and insights, have open-forum discussions, view sample materials, and watch videos of Joel as he discusses a number of topics, including how he believes a mechanistic organization allows users of his book to have increased expectations about student understanding. You are encouraged to visit the blog and join the community.

Preface for the Student

Organic Chemistry and You

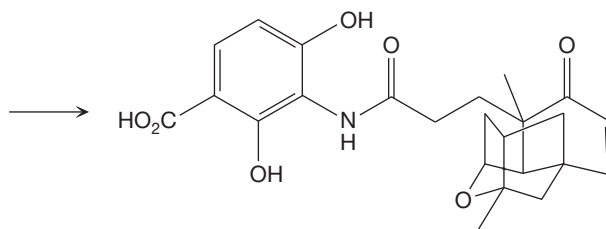
You are taking organic chemistry for a reason—you might be pursuing a career in which an understanding of organic chemistry is crucial, or the course might be required for your particular field of study, or both. You might even be taking the course simply out of interest. Regardless of the reason, organic chemistry impacts your life in significant ways.

Consider, for example, the growing concern about the increasing resistance of bacteria to antibiotics over the past several decades. Perhaps no germ has caused more alarm than methicillin-resistant *Staphylococcus aureus* (MRSA), a type of bacteria responsible for staph infections. Methicillin is a member of the penicillin family of antibiotics, and resistance to methicillin in these bacteria was first observed in 1961. Today MRSA, which has been called a *superbug*, is resistant to most antibiotics, including *all* penicillin-derived antibiotics.

A breakthrough in the fight against MRSA occurred in 2006 with the discovery of a compound called platensimycin, isolated from *Streptomyces* spores. The way that platensimycin targets bacteria is different from that of any other antibiotic in use and, therefore, it is not currently susceptible to bacterial resistance.



Streptomyces spores



Platensimycin

Platensimycin is found in a type of South African mushroom, *Streptomyces platensis*, and was discovered by screening 250,000 natural product extracts for antibacterial activity. Sheo B. Singh (Merck Research Laboratories) and coworkers determined the structure of platensimycin using a technique called nuclear magnetic resonance (NMR) spectroscopy, which we discuss in Chapter 16. Not long after, K. C. Nicolaou and coworkers from the Scripps Research Institute (La Jolla, California) and the University of California, San Diego, were the first to devise a synthesis of platensimycin from other readily available chemicals.

The story of platensimycin, from discovery to synthesis, involves several of the subdisciplines that make up the field of organic chemistry.

- **Biological chemistry (biochemistry):** The study of the behavior of biomolecules and the nature of chemical reactions that occur in living systems.
- **Structure determination:** The use of established experimental techniques to determine the structure of newly discovered compounds.
- **Organic synthesis:** The design of pathways for making new compounds from existing, readily available compounds by means of known organic reactions.

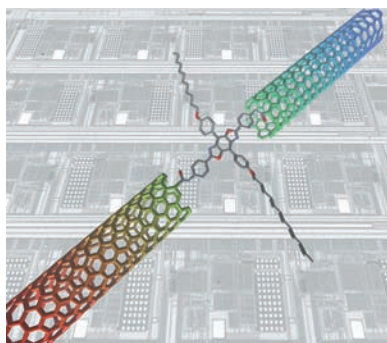
Because each of these areas typically focuses on solving existing and practical problems, they are considered to be *applied* areas of organic chemistry. However, other areas of organic chemistry, considered to be *theoretical* in nature, provide the foundations on which such applications rest. They focus on answering questions about the *how* and *why* of chemical processes. For example, an understanding of the basic principles of NMR spectroscopy (an analytical technique discussed in Chapter 16) underlies our ability to determine molecular structure. Understanding the principles that govern organic reactions (such as those involved in the synthesis of platensimycin) may allow us to enhance yields, not only by altering reaction conditions, but also perhaps by devising



FIGURE P.1 Some uses of plastics Plastics, which are designed and created in the laboratories of organic chemists, are found in a wide range of products, such as (a) food packaging, (b) an artificial heart, (c) body armor made from Kevlar, and (d) a Boeing 787, a commercial jet whose body consists largely of composite materials made from plastics and carbon fibers.



(a)



(b)

FIGURE P.2 Organic chemistry in the electronics industry (a) A smartphone whose display is made from organic light-emitting diodes. (b) A molecular switch in which an organic molecule joins together two carbon nanotubes—sheets of carbon in the form of cylinders with a diameter on the order of 10^{-9} meter.

entirely new synthesis schemes. And understanding platensimycin's specific mode of attack on bacteria will likely guide us in modifying its chemical structure to make it even more effective.

The story of platensimycin showcases the importance of organic chemistry in the pharmaceutical industry, but organic chemistry is at the center of other high-profile areas as well, including the fabrication of new materials such as plastics (the topic of Chapter 26). The durability and chemical stability of plastics have made them excellent choices for use in food packaging (Fig. P.1a) and the fabrication of the artificial heart (Fig. P.1b). Plastics are the source of synthetic fibers such as nylon and polyester, which are often used in the clothing industry, as well as Kevlar, which is used to make body armor (Fig. P.1c). Composite materials made from plastic and carbon fibers are so strong that some commercial jets are now constructed with a body made largely from plastics (Fig. P.1d).

Organic chemistry has also been at the forefront of generating new materials for electronic devices. Organic light-emitting diodes (OLEDs) are the main components of electronic displays for many high-end smartphones (Fig. P.2a), and single organic molecules can be used to make electronic switches tens of thousands of times smaller than those used in today's integrated circuits (Fig. P.2b).

Perhaps even more important to our lives is the impact that organic chemistry can have on our ability to understand, and solve, environmental problems, such as overflowing landfills (Fig. P.3a), the destruction of the stratospheric ozone layer (Fig. P.3b), and global warming (Fig. P.3c). Organic chemistry, for example, is helping provide new ways to recycle waste materials. Additionally, organic chemistry has been used to engineer new coolants that are safer for the environment than the chlorofluorocarbons (CFCs) used in the late 20th century in refrigerators and air conditioners. Finally, organic chemistry may lead us to economically feasible processes by which we can synthesize hydrogen gas, a fuel whose combustion product is only water. This could be a welcome alternative to coal and oil, whose combustion products not only cause air and water pollution, but also generate carbon dioxide, one of several greenhouse gases responsible for global warming.

Because organic chemistry is important in so many ways, you will find two special interest boxes in the main part of each chapter, which show how the material in the chapter directly connects to issues that you might find more relevant or more interesting. Take the time to read those boxes, and consider researching them even further. In addition to those special interest boxes, you will find several Connections boxes in the margins of each chapter, each of which provides a glimpse into how a molecule you just encountered relates to an aspect of everyday life.

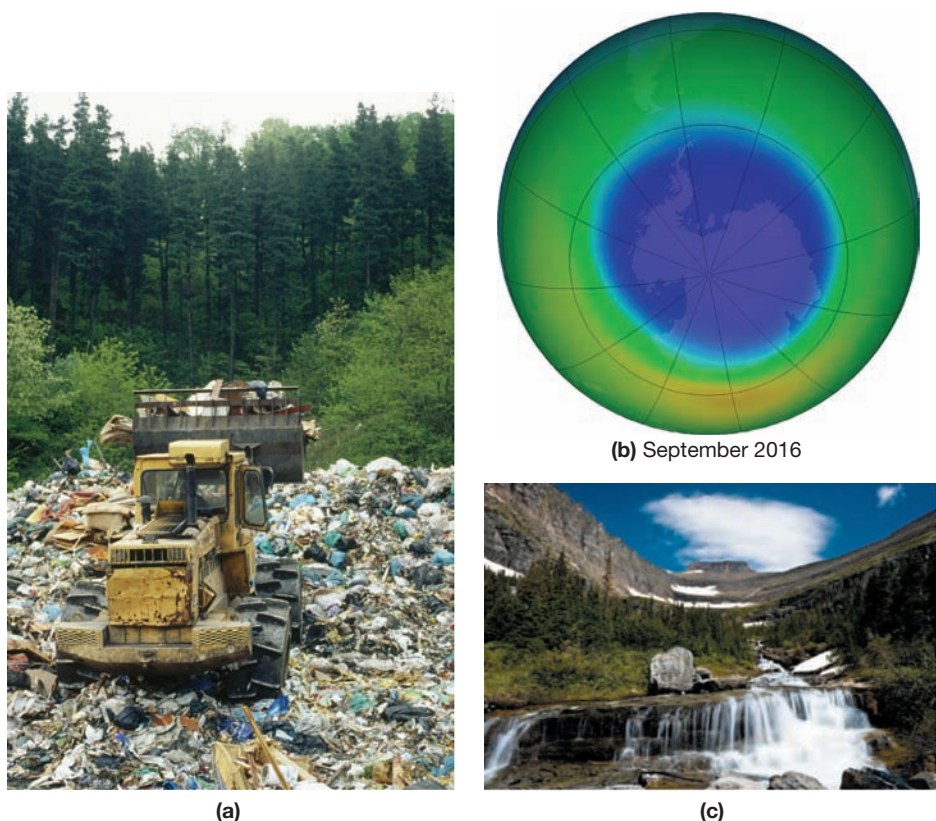


FIGURE P.3 Organic chemistry and the environment Organic chemistry continues to play a significant role in solving environmental problems, such as (a) overflowing landfills, (b) ozone depletion (the area in blue represents the ozone hole over Antarctica), and (c) global warming (the ice sheets in Montana's Glacier National Park have been melting at a dramatically accelerating rate over the past 90 years).

Some Suggestions for Studying

Perhaps you have heard that organic chemistry is difficult. Perhaps you have heard that it requires an enormous amount of memorization. Are these statements true? It depends on how you approach the course. What is true is that this book contains a lot of information — *much more than you can memorize*. There is a better way.

Organic chemistry can be *understood* through models and theories that are built on *fundamental concepts*. Consider, for example, that when two compounds react under a given set of conditions, the outcome of that reaction is precisely the same each and every time. Is this because the reactant molecules have memorized what products they are supposed to make? No—they are obeying certain chemical laws, and those laws can be learned.

You will spend considerable effort throughout this course developing those models and theories. *Reaction mechanisms*—detailed steps that show how reactions take place—are among the most important ideas to develop. If you devote your time and energy to understanding them and learning how they are applied toward solving problems, you will find that much of organic chemistry can be conquered without rote memorization, and you will find the course to be quite rewarding and enjoyable. Moreover, the skills you develop in organic chemistry will apply to complex situations you will face beyond this course.

If you are planning on a career in a health profession, it is particularly important for you to focus on understanding and applying concepts as opposed to memorizing. On standardized exams like the MCAT, you will often need to choose between answers that look equally good to students who have memorized the material. To a student who is well versed in applying concepts and mechanisms toward solving problems, on the other hand, those choices are more easily discernible.

In light of how important it is to understand concepts and mechanisms, your success in this course will demand a lot of time and devotion. Therefore, you should consider the following suggestions for using that time, and this book, most efficiently:

- **Read actively and diligently.** You should try to read the assigned sections before class if possible. Reading prior to class means that you will see the material for the second time in class. This will allow you to better process information and give you ample opportunity to ask pertinent questions. When you read, you should have a pen or pencil in hand so you can underline or highlight what you feel is important, and take notes about what you find enlightening or confusing. When the text refers to a figure or reaction mechanism, take that as a cue to study that figure now. Be sure that what the text is describing makes sense to you before you move on. If you are referred to a previous chapter, flip to the appropriate page to refresh your memory.
- **Your Turns.** The Your Turn exercises are relatively short activities that ask you to complete a task based on what you have just read. These exercises were developed to help you remain *actively engaged* while you read. They should also help you quickly evaluate whether you understand the topic at hand. I encourage you to *work through all Your Turn exercises in each chapter* and quickly check the answers in the back of the book. Feedback from students who have used this book supports this advice.
- **Problems.** As with anything new you attempt, mastery requires practice. Most of your practice should come from solving problems. I have included more than 2000 problems throughout this book. Many are integrated into the chapters, but most are gathered at the end of each chapter. Take the time to work through as many problems as possible, and use them to assess areas of strength and weakness.

That said, it's time to get started. Keep your focus on concepts and mechanisms, work hard, and ask questions!

Organic chemistry is often referred to as the chemistry of life because biological compounds such as DNA, proteins, and carbohydrates are themselves organic molecules. In this chapter, we examine some of the bonding characteristics of these and other organic molecules, which are constructed primarily from carbon, hydrogen, nitrogen, and oxygen.



1

Atomic and Molecular Structure

Organic chemistry is often called “the chemistry of life” because certain types of compounds, and the reactions they undergo, are suitable to sustain life, while others are not. What are the characteristics of such compounds and what advantages do those compounds afford living organisms? Here in Chapter 1 we begin to answer these questions.

We review several aspects of atomic and molecular structure typically covered in a general chemistry course, including ionic and covalent bonding, the basics of Lewis dot structures, and resonance theory. We then begin to tighten our focus on organic molecules, presenting various types of shorthand notation that organic chemists often use and introducing you to functional groups commonly encountered in organic chemistry.

Toward the end of this chapter, we shift our focus to examining specific classes of biomolecules: amino acids, monosaccharides, and nucleotides. Not only does such a discussion provide insight into the relevance of organic chemistry to biological systems, but it also reinforces specific topics covered in the chapter, such as functional groups.

1.1 What Is Organic Chemistry?

Organic chemistry is the branch of chemistry involving *organic compounds*. What, then, is an organic compound?

In the late 1700s, scientists defined an **organic compound** as one that could be obtained from a *living* organism, whereas **inorganic compounds** encompassed

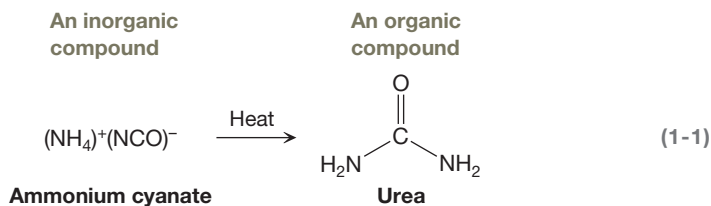
Chapter Objectives

On completing Chapter 1 you should be able to:

1. Distinguish organic compounds from inorganic ones.
2. Explain the advantages that come from carbon being the basis of organic molecules.
3. Describe the basic structure of an atom and understand that the vast majority of its volume is taken up by electrons.
4. Determine the ground state electron configuration of any atom in the first three rows of the periodic table and distinguish valence electrons from core electrons.
5. Define bond length and bond energy and understand how these two quantities depend on the number of bonds between a given pair of atoms.
6. Draw the Lewis structure of a species, given only its connectivity and total charge.
7. Differentiate between a nonpolar covalent bond, a polar covalent bond, and an ionic bond, and distinguish a covalent compound from an ionic compound.
8. Assign the formal charge to any atom in a molecular species, given only its Lewis structure.
9. Describe what a resonance structure is and explain the effect that resonance has on a species' stability.
10. Draw all resonance structures of a given species, as well as its resonance hybrid, and determine the relative stabilities of resonance structures.
11. Draw and interpret Lewis structures, condensed formulas, and line structures.
12. Explain why functional groups are important and identify functional groups that are common in organic chemistry.

everything else. It was believed that organic compounds could *not* be made in the laboratory; instead, only living systems could summon up a mysterious “vital force” needed to synthesize them. This belief was called **vitalism**. By this definition, many familiar compounds, such as glucose (a sugar), testosterone (a hormone), and deoxyribonucleic acid (DNA), are *organic* (Fig. 1-1).

This definition of organic compounds broke down in 1828, when Friedrich Wöhler (1800–1882), a German physician and chemist, synthesized urea (an organic compound known to be a major component of mammalian urine) by heating a solution of ammonium cyanate (an inorganic compound; Equation 1-1).



If vitalism couldn't account for the distinction between organic and inorganic compounds, what could? Gradually, chemists arrived at our modern definition:

An **organic compound** contains a substantial amount of carbon and hydrogen.

This definition, however, is still imperfect, because it leaves considerable room for interpretation. For example, many chemists would classify carbon dioxide (CO_2) as *inorganic* because it does not contain any hydrogen atoms, whereas others would argue that it is *organic* because it contains carbon and is critical in living systems. In plants, it is a starting material in photosynthesis, and in animals, it is a by-product of respiration. Similarly, tetrachloromethane (carbon tetrachloride, CCl_4) contains no hydrogen, but many would classify it as an organic compound. Butyllithium ($\text{C}_4\text{H}_9\text{Li}$), on the other hand, is considered by many to be inorganic, despite the fact that 13 of its 14 atoms are carbon or hydrogen. Although this definition of an organic compound has its inadequacies, it does allow chemists to classify most molecules.

Consequently, carbon atoms can link together in chains of almost any length and rings of various sizes, allowing for an enormous range in molecular size and shape. Moreover, the ability to form four bonds means there is potential for *branching* at each carbon in the chain. And each carbon atom is capable of forming not only single bonds, but double and triple bonds as well. These characteristics make possible a tremendous number of compounds, even with a relatively small number of carbon atoms. Indeed, to date, tens of millions of organic compounds are known, and the list is growing rapidly as we continue to discover or synthesize new compounds.

Far less diversity would be possible in compounds based on another element, such as oxygen. Oxygen atoms tend to form two covalent bonds, which would allow for a linear chain only (as shown in the hypothetical example on p. 3). No branching could occur, nor could other groups or atoms be attached to the chain except at the ends. Furthermore, the atoms along the chain could not participate in either double or triple bonds.

If carbon works so well, then why *not* silicon, which appears just below carbon in the periodic table? Elements in the same group (column) of the periodic table tend to exhibit similar chemical properties, so silicon, too, can form four covalent bonds, giving it the same potential for diversity as carbon.

The answer is *stability*. As we see in Section 1.4, the carbon atom forms rather strong bonds with a variety of atoms, including other carbon atoms. For example, it takes 339 kJ/mol (81 kcal/mol) to break an average C—C single bond, and 418 kJ/mol (100 kcal/mol) to break an average C—H bond. By contrast, it takes only 223 kJ/mol (53 kcal/mol) to break a typical Si—Si bond. The strength of typical bonds involving carbon atoms goes a long way toward keeping biomolecules intact—an essential characteristic for molecules whose job is to store information or provide cellular structure.

Even though organic molecules are based on the carbon atom, what would life be like, hypothetically, if silicon atoms were to replace carbon atoms in biomolecules such as glucose (C₆H₁₂O₆)? Glucose is broken down by our bodies through respiration to extract energy, according to the overall reaction in Equation 1-2. One of the by-products is carbon dioxide, a gas, which is exhaled from the lungs. In a world in which life is based on silicon, glucose would be Si₆H₁₂O₆, and its by-product would be silicon dioxide (SiO₂), as shown in Equation 1-3. Silicon dioxide, a solid, is the main component of sand; in its crystalline form, it is known as quartz (Fig. 1-3).



FIGURE 1-3 Quartz crystal Quartz (silicon dioxide) is the silicon analog of carbon dioxide. Whereas carbon dioxide is gaseous, silicon dioxide is a solid.

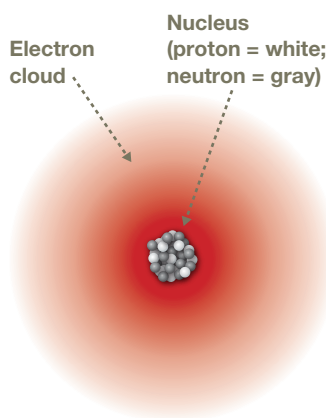
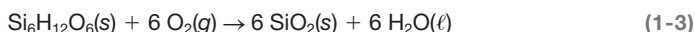
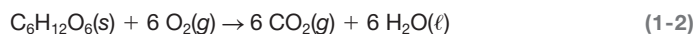


FIGURE 1-4 Basic structure of the atom Atoms are composed of a nucleus surrounded by a cloud of electrons. Protons (white) and neutrons (gray) make up the nucleus. (This figure is not to scale. If it were, the size of the electron cloud, which is much larger than the size of the nucleus, would have a radius on the order of 500 meters!)



1.3 Atomic Structure and Ground State Electron Configurations

In Section 1.2, we saw that carbon's bonding characteristics are what give rise to the large variety of organic molecules. Those bonding characteristics, and the bonding characteristics of all atoms, are governed by the electrons that the atom has.

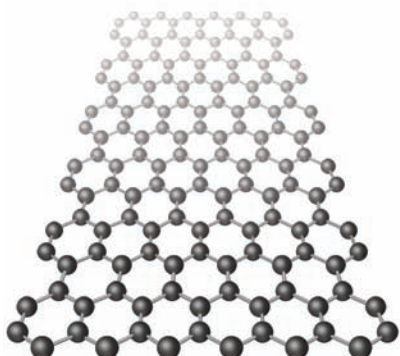
This section, then, is devoted to the nature of electrons in atoms. We first review the basic structure of an atom, followed by a discussion of orbitals and shells. Finally, we review electron configurations, distinguishing between *valence electrons*—electrons that can be used for bonding—and *core electrons*.

1.3a The Structure of the Atom

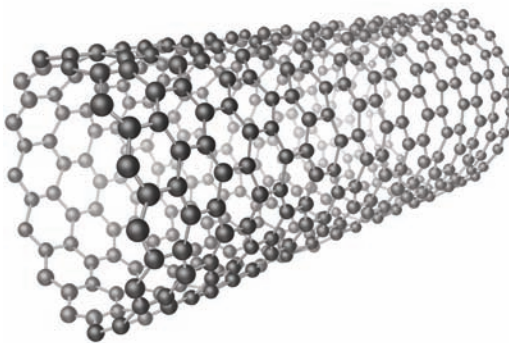
At the center of an atom (Fig. 1-4) is a positively charged nucleus, composed of *protons* and *neutrons*. Surrounding the nucleus is a cloud of negatively charged *electrons*, attracted to the nucleus by simple **electrostatic forces** (the forces by which opposite

Chemistry with Chicken Wire

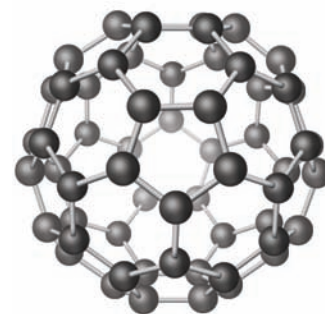
Even though carbon takes center stage in organic chemistry, organic molecules invariably include other atoms as well, such as hydrogen, nitrogen, oxygen, and halogen atoms. Some of the most exciting chemistry today, however, involves extended frameworks of *only* carbon. A single flat sheet of such a framework is called *graphene*, and resembles molecular chicken wire. Wrapped around to form a cylinder, a graphene sheet forms what is called a *carbon nanotube*. Pure carbon can even take the form of a soccer ball—the so-called *buckminsterfullerene*.



A sheet of graphene



A carbon nanotube



Buckminsterfullerene

These structures themselves have quite interesting electronic properties, giving them a bright future in nanoelectronics. Carbon nanotubes and buckminsterfullerenes have high tensile strength, moreover, giving them potential use for structural reinforcement in concrete, sports equipment, and body armor. Chemical modification gives these structures an even wider variety of potential uses. Graphene oxide, for example, has promising antimicrobial activity, and attaching certain molecular groups to the surface of a carbon nanotube or buckminsterfullerene has potential for use as drug carriers for cancer therapeutics.

charges attract one another and like charges repel one another). Individual electrons are incredibly small, even much smaller than the nucleus, but the space that electrons occupy (i.e., the *electron cloud*) is much larger than the nucleus. In other words:

- The size of an atom is essentially defined by the size of its electron cloud.
- The vast majority of an electron cloud (and thus the vast majority of an atom) is empty space.

Table 1-1 lists the mass and charge of each of these elementary particles. Notice that the masses of the proton and neutron are significantly greater than that of the electron, so the mass of an atom is essentially the mass of just the nucleus.

An atom, by definition, has no net charge. Consequently, the number of electrons in an atom must equal the number of protons. The number of protons in the nucleus, called the **atomic number (Z)**, defines the element. For example, a nucleus that has six protons has an atomic number of 6, and can only be a carbon nucleus.

If the number of protons and the number of electrons are unequal, then the entire **species** (that particular combination of protons, neutrons, and electrons) bears a net charge, and is called an **ion**. A negatively charged ion, an **anion** (pronounced AN-eye-on), results from an excess of electrons. A positively charged ion, a **cation** (pronounced CAT-eye-on), results from a deficiency of electrons.

TABLE 1-1 Charges and Masses of Subatomic Particles

Particle	Charge (e) ^a	Mass (u) ^b
Proton	+1	~1
Neutron	0	~1
Electron	-1	~0.0005

^ae = Elementary charge.

^bu = Unified atomic mass unit.

SOLVED PROBLEM 1.1

How many protons and electrons does a cation of the carbon atom have if its net charge is +1?

Think How many protons are there in the nucleus of a carbon atom? Does a cation have more protons than electrons, or vice versa? How many more, given the net charge of the species?

Solve A carbon atom's nucleus has six protons. A cation with a +1 charge should have one more proton than it has electrons, so this species must have five electrons.

PROBLEM 1.2 (a) How many protons and electrons does an anion of the carbon atom have if its net charge is -1 ? **(b)** How many protons and electrons does a cation of the oxygen atom have if its net charge is +1? **(c)** How many protons and electrons does an anion of the oxygen atom have if its net charge is -1 ?

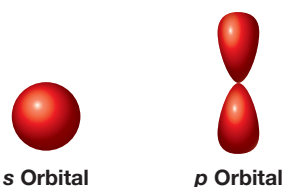


FIGURE 1-5 Orbitals Orbitals represent regions in space where an electron is likely to be. An s orbital is spherical, and a p orbital is a dumbbell.

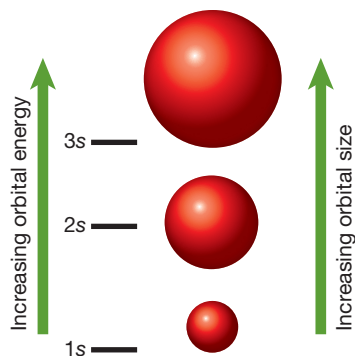


FIGURE 1-6 Relationship between principal quantum number, orbital size, and orbital energy As the shell number of an orbital increases, its size and energy increase, too. The horizontal black lines indicate each orbital's energy.

1.3b Atomic Orbitals and Shells

Electrons in an isolated atom reside in **atomic orbitals**. As we shall see, the exact location of an electron can never be pinpointed. An orbital, however, specifies the region of space where the *probability* of finding a given electron is high. More simplistically, we can view orbitals as “rooms” that house electrons. Atomic orbitals are examined in greater detail in Chapter 3; for now, it will suffice to review some of their more basic concepts.

- Atomic orbitals have different shapes. An s orbital, for example, is a sphere, whereas a p orbital has a dumbbell shape with two lobes (Fig. 1-5). Each orbital is centered on the nucleus of its atom or ion.
- Atomic orbitals are organized in *shells* (also known as *energy levels*). A **shell** is defined by the **principal quantum number, n** . There are an infinite number of shells in an atom, given that n can assume any integer value from 1 to infinity.
 - The first shell ($n = 1$) contains only an s orbital, called 1s.
 - The second shell ($n = 2$) contains one s orbital and three p orbitals, called 2s, $2p_x$, $2p_y$, and $2p_z$.
 - The third shell ($n = 3$) contains one s orbital, three p orbitals, and five d orbitals.
- Up to two electrons are allowed in any orbital.
 - Therefore, the first shell can contain up to two electrons (a **duet**).
 - The second shell can contain up to eight electrons (an **octet**).
 - The third shell can contain up to 18 electrons.
- With increasing shell number, the *size* and *energy* of the atomic orbital increase. For example, comparing s orbitals in the first three shells, the size and energy increase in the order $1s < 2s < 3s$, as shown in Figure 1-6. Similarly, a 2p orbital is smaller in size and lower in energy than a 3p orbital.
- Within a given shell, an atomic orbital's energy increases in the following order: $s < p < d$, etc. In the second shell, for example, the 2s orbital is lower in energy than the 2p.

1.3c Ground State Electron Configurations: Valence Electrons and Core Electrons

The way in which electrons are arranged in atomic orbitals is called the atom's **electron configuration**. The *most stable* (i.e., the lowest energy) electron configuration is called the **ground state** configuration. Knowing an atom's ground state configuration provides insight into the atom's chemical behavior, as we will see.

With the relative energies of atomic orbitals established, an atom's ground state electron configuration can be obtained by applying the following three rules:

1. **Pauli's exclusion principle:** No more than two electrons (i.e., zero, one, or two electrons) can occupy a single orbital; two electrons in the same orbital must have opposite spins.
2. **Aufbau principle:** Each successive electron must fill the lowest energy orbital available.
3. **Hund's rule:** Before a second electron can be paired in the same orbital, all other orbitals *at the same energy* must contain a single electron.

According to these three rules, the first 18 electrons fill orbitals as indicated in Figure 1-7. Each arrow represents an electron, and the direction of the arrow—up or down—represents the electron's spin.

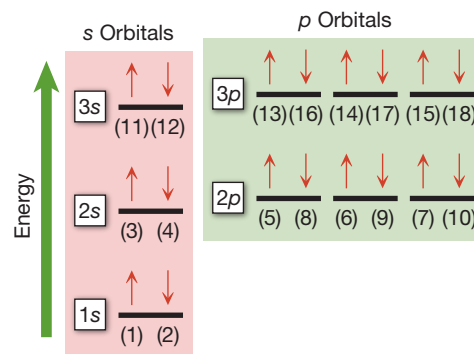


FIGURE 1-7 Energy diagram of atomic orbitals for the first 18 electrons The order of electron filling is indicated in parentheses. Each horizontal black line represents a single orbital. Each successive electron fills the lowest energy orbital available. Notice in the 2p and 3p sets of orbitals that no electrons are paired up until the addition of the fourth electron.

In Figure 1-7, place a box around all of the orbitals in the second shell and label them.

Answers to Your Turns are in the back of the book.

YOUR TURN 1.1

In the ground state, the six electrons found in a carbon atom would fill the orbitals as shown in Figure 1-8, with two electrons in the 1s orbital, two electrons in the 2s orbital, and one electron in each of two different 2p orbitals (it doesn't matter which two). The shorthand notation for this electron configuration is $1s^2 2s^2 2p^2$.

Knowing the ground state electron configuration of an atom, we can distinguish *valence* electrons from *core* electrons.

- **Valence electrons** are those occupying the highest energy (i.e., valence) shell. For the carbon atom, the valence shell is the $n = 2$ shell.
- **Core electrons** occupy the remaining lower energy shells of the atom. For the carbon atom, the core electrons occupy the $n = 1$ shell.

Valence electrons are important because, as we discuss in Section 1.5, they participate in covalent bonds. As we can see in Figure 1-8, for example, carbon has four valence electrons and two core electrons, so bonding involving carbon is governed by those four valence electrons.

In Figure 1-8, place a circle around the valence electrons and label them. Place a box around all of the core electrons and label them.

We can use the periodic table to quickly determine how many valence electrons an atom has (a copy of the periodic table appears inside the book's front cover).

The number of valence electrons in an atom is the same as the atom's *group number*.

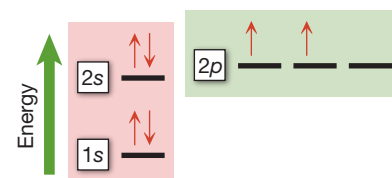


FIGURE 1-8 Energy diagram for the ground state electron configuration of the carbon atom This configuration is abbreviated $1s^2 2s^2 2p^2$.

YOUR TURN 1.2

Carbon is located in group 4A, consistent with its four valence electrons, whereas chlorine (group 7A) has seven. According to its ground state electron configuration ($1s^2 2s^2 2p^6 3s^2 3p^5$), chlorine's valence electrons occupy the third shell.

Atoms are especially stable when they have completely filled valence shells. This is exemplified by the **noble gases** (group 8A), such as helium and neon, because they have completely filled valence shells and they do *not* form bonds to make compounds. Although the specific origin of this “extra” stability is beyond the scope of this book, the consequences are the basis for the octet and duet rules we routinely use when drawing Lewis structures (Section 1.5).

SOLVED PROBLEM 1.3

Write the ground state electron configuration of the nitrogen atom. How many valence electrons does it have? How many core electrons does it have?

Think How many total electrons are there in a nitrogen atom? What is the order in which the atomic orbitals should be filled (see Fig. 1-7)? What is the valence shell and where do the core electrons reside?

Solve There are seven total electrons ($Z = 7$ for N). The first two are placed in the $1s$ orbital and the next two in the $2s$ orbital, leaving one electron for each of the three $2p$ orbitals. The electron configuration is $1s^2 2s^2 2p^3$. The valence shell is the second shell, so there are five valence electrons and two core electrons.

PROBLEM 1.4 Write the ground state electron configuration of the oxygen atom. How many valence electrons and how many core electrons are there?

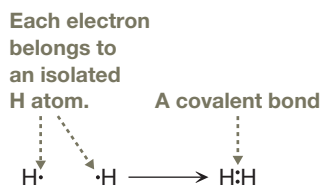


FIGURE 1-9 A covalent bond A covalent bond is the sharing of two electrons between nuclei.

CONNECTIONS Molecular hydrogen (Fig. 1-9) is a very light gas and was used for buoyancy in the *Hindenburg*, a commercial passenger airship in the 1930s. Unfortunately, hydrogen gas is also very highly flammable, and the airship caught fire and was destroyed over New Jersey on May 6, 1937, killing 36 people.



1.4 The Covalent Bond: Bond Energy and Bond Length

In a compound, nuclei are held together by chemical bonds. Two types of fundamental bonds in chemistry are the *covalent bond* and the *ionic bond* (see Section 1.8). A **covalent bond** is characterized by the *sharing of valence electrons* between two or more atoms, as shown for two H atoms in a molecule of H_2 (hydrogen gas) in Figure 1-9.

In Section 1.5, we will explore how various molecules can be constructed from atoms through the formation of covalent bonds, but first let's examine the nature of covalent bonds more closely. Why do they form at all?

We can begin to answer this question by examining Figure 1-10a, which illustrates how the energy of two H atoms changes as a function of the distance between their nuclei. In particular, when two H atoms separated by a large distance are brought together, their total energy begins to decrease.

Lower energy corresponds to greater stability.

At one particular internuclear distance, the energy of the molecule is at a minimum, while at shorter distances the energy rises dramatically.

The internuclear distance at which energy is the lowest is called the **bond length** of the H—H bond. The energy that is required to remove the H atoms from that internuclear distance to infinity (toward the right in the figure) is the **bond strength**, or **bond energy**, of the H—H bond.

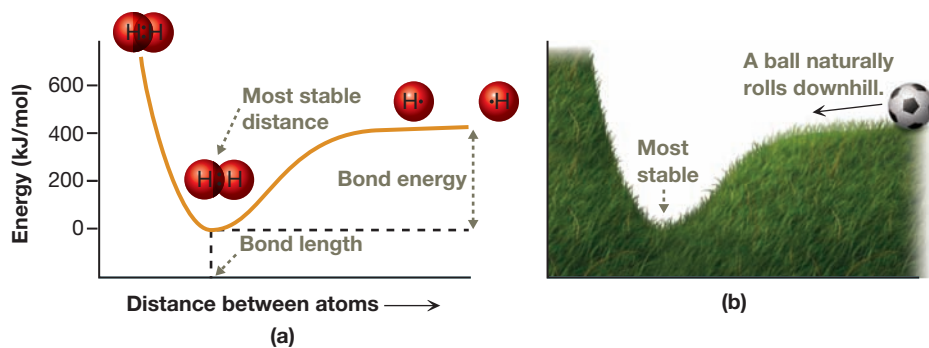


FIGURE 1-10 Formation of a chemical bond (a) Plot of energy as a function of the internuclear distance for two H atoms. The H atoms are most stable at the distance at which energy is a minimum. (b) A ball at the top of a hill becomes more stable at the bottom of the hill, and therefore tends to roll downhill.

This idea is analogous to a ball rolling down a hill (Fig. 1-10b). A ball at the top of a hill has more potential energy than a ball at the bottom, so the ball at the top tends to roll downhill, coming to rest at the bottom. By the same token, it takes energy to roll the ball from the bottom of the hill back to the top.

Estimate the bond energy of the bond represented by Figure 1-10a.

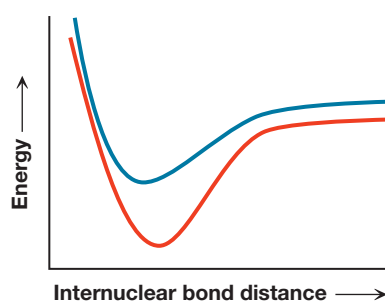
It is often convenient to *think of a covalent bond as a spring that connects two atoms*. Just as it takes energy to lengthen or shorten a covalent bond from its bond length, it takes energy to stretch or compress a spring from its rest position, as shown in Figure 1-11.

SOLVED PROBLEM 1.5

In the diagram shown here, which curve represents a stronger covalent bond?

Think How can bond breaking be represented for each curve? Which of those processes requires more energy?

Solve Bond breaking is represented by climbing from the bottom of the curve toward the right (i.e., the internuclear bond distance increases toward the right). For this process, more energy is required for the red curve, so the red curve represents a stronger bond.



PROBLEM 1.6 Which of the two curves in Solved Problem 1.5 represents a longer bond?

Why are two hydrogen atoms connected by a covalent bond lower in energy than two isolated hydrogen atoms? Largely it is because of the additional electrostatic attraction experienced by electrons when they are *shared* between nuclei. In

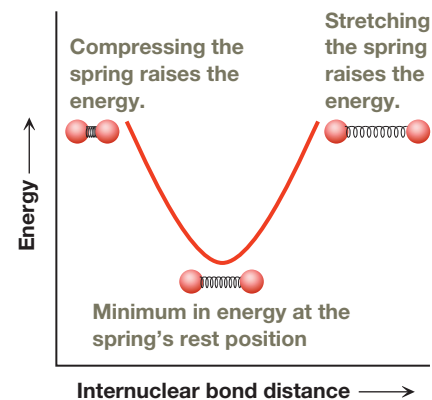


FIGURE 1-11 The spring model of a covalent bond The energy curve of a spring connecting two masses resembles that of the covalent bond shown in Figure 1-10a. Both stretching and compressing the spring from its rest position increase the energy in the spring.

YOUR TURN 1.3

CONNECTIONS The behavior of covalent bonds as springs (Fig. 1-11) is what enables greenhouse gases like carbon dioxide (CO_2) and methane (CH_4) to absorb infrared radiation and warm the atmosphere.