

# ORGANIC CHEMISTRY

Graham Solomons

Craig Fryhle

Scott Snyder

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**TABLE 3.1 RELATIVE STRENGTH OF SELECTED ACIDS AND THEIR CONJUGATE BASES**

	Acid	Approximate $pK_a$	Conjugate Base	
Strongest acid	HSbF <sub>6</sub>	< -12	SbF <sub>6</sub> <sup>-</sup>	Weakest base
	HI	-10	I <sup>-</sup>	
	H <sub>2</sub> SO <sub>4</sub>	-9	HSO <sub>4</sub> <sup>-</sup>	
	HBr	-9	Br <sup>-</sup>	
	HCl	-7	Cl <sup>-</sup>	
	C <sub>6</sub> H <sub>5</sub> SO <sub>3</sub> H	-6.5	C <sub>6</sub> H <sub>5</sub> SO <sub>3</sub> <sup>-</sup>	
	(CH <sub>3</sub> ) <sub>2</sub> OH <sup>+</sup>	-3.8	(CH <sub>3</sub> ) <sub>2</sub> O	
	(CH <sub>3</sub> ) <sub>2</sub> C=OH <sup>+</sup>	-2.9	(CH <sub>3</sub> ) <sub>2</sub> C=O	
	CH <sub>3</sub> OH <sub>2</sub> <sup>+</sup>	-2.5	CH <sub>3</sub> OH	
	H <sub>3</sub> O <sup>+</sup>	-1.74	H <sub>2</sub> O	
	HNO <sub>3</sub>	-1.4	NO <sub>3</sub> <sup>-</sup>	
	CF <sub>3</sub> CO <sub>2</sub> H	0.18	CF <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	
	HF	3.2	F <sup>-</sup>	
	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> H	4.21	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> <sup>-</sup>	
	C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup>	4.63	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	
	CH <sub>3</sub> CO <sub>2</sub> H	4.75	CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	
	H <sub>2</sub> CO <sub>3</sub>	6.35	HCO <sub>3</sub> <sup>-</sup>	
	CH <sub>3</sub> COCH <sub>2</sub> COCH <sub>3</sub>	9.0	CH <sub>3</sub> COCHCOCH <sub>3</sub> <sup>-</sup>	
	NH <sub>4</sub> <sup>+</sup>	9.2	NH <sub>3</sub>	
	C <sub>6</sub> H <sub>5</sub> OH	9.9	C <sub>6</sub> H <sub>5</sub> O <sup>-</sup>	
	HCO <sub>3</sub> <sup>-</sup>	10.2	CO <sub>3</sub> <sup>2-</sup>	
	CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup>	10.6	CH <sub>3</sub> NH <sub>2</sub>	
	H <sub>2</sub> O	15.7	HO <sup>-</sup>	
	CH <sub>3</sub> CH <sub>2</sub> OH	16	CH <sub>3</sub> CH <sub>2</sub> O <sup>-</sup>	
	(CH <sub>3</sub> ) <sub>3</sub> COH	18	(CH <sub>3</sub> ) <sub>3</sub> CO <sup>-</sup>	
	CH <sub>3</sub> COCH <sub>3</sub>	19.2	<sup>-</sup> CH <sub>2</sub> COCH <sub>3</sub>	
	HC≡CH	25	HC≡C <sup>-</sup>	
	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	31	C <sub>6</sub> H <sub>5</sub> NH <sup>-</sup>	
	H <sub>2</sub>	35	H <sup>-</sup>	
	(i-Pr) <sub>2</sub> NH	36	(i-Pr) <sub>2</sub> N <sup>-</sup>	
	NH <sub>3</sub>	38	<sup>-</sup> NH <sub>2</sub>	
	CH <sub>2</sub> =CH <sub>2</sub>	44	CH <sub>2</sub> =CH <sup>-</sup>	
Weakest acid	CH <sub>3</sub> CH <sub>3</sub>	50	CH <sub>3</sub> CH <sub>2</sub> <sup>-</sup>	Strongest base

Increasing acid strength

Increasing base strength



**ORGANIC CHEMISTRY** 11E

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# ORGANIC CHEMISTRY

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**11E**

**WILEY**



**In memory of my beloved son, John Allen Solomons. TWGS**

**For my family. CBF**

**For Cathy, who has always inspired me. SAS**

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# [ BRIEF CONTENTS ]



- 1 The Basics** Bonding and Molecular Structure 1
- 2 Families of Carbon Compounds** Functional Groups, Intermolecular Forces, and Infrared (IR) Spectroscopy 55
- 3 Acids and Bases** An Introduction to Organic Reactions and Their Mechanisms 104
- 4 Nomenclature and Conformations of Alkanes and Cycloalkanes** 142
- 5 Stereochemistry** Chiral Molecules 191
- 6 Ionic Reactions** Nucleophilic Substitution and Elimination Reactions of Alkyl Halides 239
- 7 Alkenes and Alkynes I** Properties and Synthesis. Elimination Reactions of Alkyl Halides 291
- 8 Alkenes and Alkynes II** Addition Reactions 337
- 9 Nuclear Magnetic Resonance and Mass Spectrometry** Tools for Structure Determination 391
- 10 Radical Reactions** 457
- 11 Alcohols and Ethers** Synthesis and Reactions 498
- 12 Alcohols from Carbonyl Compounds** Oxidation–Reduction and Organometallic Compounds 542
- 13 Conjugated Unsaturated Systems** 581
- 14 Aromatic Compounds** 626
- 15 Reactions of Aromatic Compounds** 669
- 16 Aldehydes and Ketones** Nucleophilic Addition to the Carbonyl Group 720
- 17 Carboxylic Acids and Their Derivatives** Nucleophilic Addition–Elimination at the Acyl Carbon 771
- 18 Reactions at the  $\alpha$  Carbon of Carbonyl Compounds** Enols and Enolates 821
- 19 Condensation and Conjugate Addition Reactions of Carbonyl Compounds** More Chemistry of Enolates 858
- 20 Amines** 897
- 21 Phenols and Aryl Halides** Nucleophilic Aromatic Substitution 944
- SPECIAL TOPIC G Carbon–Carbon Bond-Forming and Other Reactions of Transition Metal Organometallic Compounds** G1
- 22 Carbohydrates** 979
- 23 Lipids** 1027
- 24 Amino Acids and Proteins** 1060
- 25 Nucleic Acids and Protein Synthesis** 1105

ANSWERS TO SELECTED PROBLEMS A-1

GLOSSARY GL-1

INDEX I-1

# [ CONTENTS ]

## 1 The Basics

### BONDING AND MOLECULAR STRUCTURE 1



1.1 Life and the Chemistry of Carbon Compounds—We are Stardust 2

**THE CHEMISTRY OF...** Natural Products 3

1.2 Atomic Structure 3

1.3 Chemical Bonds: The Octet Rule 5

1.4 **HOW TO** Write Lewis Structures 7

1.5 Formal Charges and **HOW TO** Calculate Them 12

1.6 Isomers: Different Compounds that Have the Same Molecular Formula 14

1.7 **HOW TO** Write and Interpret Structural Formulas 15

1.8 Resonance Theory 22

1.9 Quantum Mechanics and Atomic Structure 27

1.10 Atomic Orbitals and Electron Configuration 28

1.11 Molecular Orbitals 30

1.12 The Structure of Methane and Ethane:  $sp^3$  Hybridization 32

**THE CHEMISTRY OF...** Calculated Molecular Models: Electron Density Surfaces 36

1.13 The Structure of Ethene (Ethylene):  $sp^2$  Hybridization 36

1.14 The Structure of Ethyne (Acetylene):  $sp$  Hybridization 40

1.15 A Summary of Important Concepts That Come from Quantum Mechanics 43

1.16 **HOW TO** Predict Molecular Geometry: The Valence Shell Electron Pair Repulsion Model 44

1.17 Applications of Basic Principles 47

**[ WHY DO THESE TOPICS MATTER? ]** 48

## 2 Families of Carbon Compounds

### FUNCTIONAL GROUPS, INTERMOLECULAR FORCES, AND INFRARED (IR) SPECTROSCOPY 55



2.1 Hydrocarbons: Representative Alkanes, Alkenes, Alkynes, and Aromatic Compounds 56

2.2 Polar Covalent Bonds 59

2.3 Polar and Nonpolar Molecules 61

2.4 Functional Groups 64

2.5 Alkyl Halides or Haloalkanes 65

2.6 Alcohols and Phenols 67

2.7 Ethers 69

**THE CHEMISTRY OF...** Ethers as General Anesthetics 69

2.8 Amines 70

2.9 Aldehydes and Ketones 71

2.10 Carboxylic Acids, Esters, and Amides 73

2.11 Nitriles 75

2.12 Summary of Important Families of Organic Compounds 76

2.13 Physical Properties and Molecular Structure 77

**THE CHEMISTRY OF...** Fluorocarbons and Teflon 82

2.14 Summary of Attractive Electric Forces 85

**THE CHEMISTRY OF...** Organic Templates Engineered to Mimic Bone Growth 86

2.15 Infrared Spectroscopy: An Instrumental Method for Detecting Functional Groups 86

2.16 Interpreting IR Spectra 90

2.17 Applications of Basic Principles 97

**[ WHY DO THESE TOPICS MATTER? ]** 97

## 3 Acids and Bases

AN INTRODUCTION  
TO ORGANIC  
REACTIONS AND THEIR  
MECHANISMS 104



- 3.1 Acid–Base Reactions 105
- 3.2 **HOW TO** Use Curved Arrows in Illustrating Reactions 107
- [ A MECHANISM FOR THE REACTION ]** Reaction of Water with Hydrogen Chloride: The Use of Curved Arrows 107
- 3.3 Lewis Acids and Bases 109
- 3.4 Heterolysis of Bonds to Carbon: Carbocations and Carbanions 111
- 3.5 The Strength of Brønsted–Lowry Acids and Bases:  $K_a$  and  $pK_a$  113
- 3.6 **HOW TO** Predict the Outcome of Acid–Base Reactions 118
- 3.7 Relationships Between Structure and Acidity 120
- 3.8 Energy Changes 123
- 3.9 The Relationship Between the Equilibrium Constant and the Standard Free–Energy Change,  $\Delta G^\circ$  125
- 3.10 Acidity: Carboxylic Acids versus Alcohols 126
- 3.11 The Effect of the Solvent on Acidity 130
- 3.12 Organic Compounds as Bases 130
- 3.13 A Mechanism for an Organic Reaction 132
- [ A MECHANISM FOR THE REACTION ]** Reaction of *tert*-Butyl Alcohol with Concentrated Aqueous HCl 132
- 3.14 Acids and Bases in Nonaqueous Solutions 133
- 3.15 Acid–Base Reactions and the Synthesis of Deuterium- and Tritium-Labeled Compounds 134
- 3.16 Applications of Basic Principles 135
- [ WHY DO THESE TOPICS MATTER? ]** 136

## 4 Nomenclature and Conformations of Alkanes and Cycloalkanes 142



- 4.1 Introduction to Alkanes and Cycloalkanes 143
- THE CHEMISTRY OF...** Petroleum Refining 143
- 4.2 Shapes of Alkanes 144
- 4.3 **HOW TO** Name Alkanes, Alkyl Halides, and Alcohols: The IUPAC System 146

- 4.4 **HOW TO** Name Cycloalkanes 153
- 4.5 **HOW TO** Name Alkenes and Cycloalkenes 156
- 4.6 **HOW TO** Name Alkynes 158
- 4.7 Physical Properties of Alkanes and Cycloalkanes 159
- THE CHEMISTRY OF...** Pheromones: Communication by Means of Chemicals 161
- 4.8 Sigma Bonds and Bond Rotation 162
- 4.9 Conformational Analysis of Butane 164
- THE CHEMISTRY OF...** Muscle Action 166
- 4.10 The Relative Stabilities of Cycloalkanes: Ring Strain 167
- 4.11 Conformations of Cyclohexane: The Chair and the Boat 168
- THE CHEMISTRY OF...** Nanoscale Motors and Molecular Switches 170
- 4.12 Substituted Cyclohexanes: Axial and Equatorial Hydrogen Groups 171
- 4.13 Disubstituted Cycloalkanes: Cis–Trans Isomerism 175
- 4.14 Bicyclic and Polycyclic Alkanes 179
- 4.15 Chemical Reactions of Alkanes 180
- 4.16 Synthesis of Alkanes and Cycloalkanes 180
- 4.17 **HOW TO** Gain Structural Information from Molecular Formulas and the Index of Hydrogen Deficiency 182
- 4.18 Applications of Basic Principles 184
- [ WHY DO THESE TOPICS MATTER? ]** 185

See **SPECIAL TOPIC A:  $^{13}\text{C}$  NMR Spectroscopy—A Practical Introduction in WileyPLUS**

## 5 Stereochemistry



CHIRAL MOLECULES 191

- 5.1 Chirality and Stereochemistry 192
- 5.2 Isomerism: Constitutional Isomers and Stereoisomers 193
- 5.3 Enantiomers and Chiral Molecules 195
- 5.4 Molecules Having One Chirality Center are Chiral 196
- 5.5 More about the Biological Importance of Chirality 199
- 5.6 **HOW TO** Test for Chirality: Planes of Symmetry 201
- 5.7 Naming Enantiomers: The *R,S*-System 202
- 5.8 Properties of Enantiomers: Optical Activity 206
- 5.9 The Origin of Optical Activity 211

- 5.10 The Synthesis of Chiral Molecules 213
- 5.11 Chiral Drugs 215
- THE CHEMISTRY OF...** Selective Binding of Drug Enantiomers to Left- and Right-Handed Coiled DNA 217
- 5.12 Molecules with More than One Chirality Center 217
- 5.13 Fischer Projection Formulas 223
- 5.14 Stereoisomerism of Cyclic Compounds 225
- 5.15 Relating Configurations through Reactions in which No Bonds to the Chirality Center Are Broken 227
- 5.16 Separation of Enantiomers: Resolution 231
- 5.17 Compounds with Chirality Centers Other than Carbon 232
- 5.18 Chiral Molecules That Do Not Possess a Chirality Center 232
- [ WHY DO THESE TOPICS MATTER? ]** 233

## 6 Ionic Reactions

NUCLEOPHILIC  
SUBSTITUTION  
AND ELIMINATION  
REACTIONS OF ALKYL  
HALIDES **239**



- 6.1 Alkyl Halides 240
- 6.2 Nucleophilic Substitution Reactions 241
- 6.3 Nucleophiles 243
- 6.4 Leaving Groups 245
- 6.5 Kinetics of a Nucleophilic Substitution Reaction: An  $S_N2$  Reaction 245
- 6.6 A Mechanism for the  $S_N2$  Reaction 246
- [ A MECHANISM FOR THE REACTION ]** Mechanism for the  $S_N2$  Reaction 247
- 6.7 Transition State Theory: Free-Energy Diagrams 248
- 6.8 The Stereochemistry of  $S_N2$  Reactions 251
- [ A MECHANISM FOR THE REACTION ]** The Stereochemistry of an  $S_N2$  Reaction 253
- 6.9 The Reaction of *Tert*-Butyl Chloride with Water: An  $S_N1$  Reaction 253
- 6.10 A Mechanism for the  $S_N1$  Reaction 254
- [ A MECHANISM FOR THE REACTION ]** Mechanism for the  $S_N1$  Reaction 255
- 6.11 Carbocations 256
- 6.12 The Stereochemistry of  $S_N1$  Reactions 258
- [ A MECHANISM FOR THE REACTION ]** The Stereochemistry of an  $S_N1$  Reaction 259
- 6.13 Factors Affecting the Rates of  $S_N1$  and  $S_N2$  Reactions 261

- 6.14 Organic Synthesis: Functional Group Transformations Using  $S_N2$  Reactions 271
- THE CHEMISTRY OF...** Biological Methylation: A Biological Nucleophilic Substitution Reaction 273
- 6.15 Elimination Reactions of Alkyl Halides 275
- 6.16 The E2 Reaction 276
- [ A MECHANISM FOR THE REACTION ]** Mechanism for the E2 Reaction 277
- 6.17 The E1 Reaction 278
- [ A MECHANISM FOR THE REACTION ]** Mechanism for the E1 Reaction 279
- 6.18 **HOW TO** Determine Whether Substitution or Elimination Is Favored 280
- 6.19 Overall Summary 282
- [ WHY DO THESE TOPICS MATTER? ]** 283

## 7 Alkenes and Alkynes I

PROPERTIES  
AND SYNTHESIS.  
ELIMINATION  
REACTIONS OF  
ALKYL HALIDES **291**



- 7.1 Introduction 292
- 7.2 The (*E*)-(*Z*) System for Designating Alkene Diastereomers 292
- 7.3 Relative Stabilities of Alkenes 293
- 7.4 Cycloalkenes 296
- 7.5 Synthesis of Alkenes via Elimination Reactions 296
- 7.6 Dehydrohalogenation of Alkyl Halides 297
- [ A MECHANISM FOR THE REACTION ]** E2 Elimination Where There Are Two Axial  $\beta$  Hydrogens 302
- [ A MECHANISM FOR THE REACTION ]** E2 Elimination Where the Only Axial  $\beta$  Hydrogen Is from a Less Stable Conformer 302
- 7.7 Acid-Catalyzed Dehydration of Alcohols 303
- [ A MECHANISM FOR THE REACTION ]** Acid-Catalyzed Dehydration of Secondary or Tertiary Alcohols: An E1 Reaction 307
- [ A MECHANISM FOR THE REACTION ]** Dehydration of a Primary Alcohol: An E2 Reaction 308
- 7.8 Carbocation Stability and the Occurrence of Molecular Rearrangements 309
- [ A MECHANISM FOR THE REACTION ]** Formation of a Rearranged Alkene During Dehydration of a Primary Alcohol 312

- 7.9 The Acidity of Terminal Alkynes 313  
7.10 Synthesis of Alkynes by Elimination Reactions 314

**[ A MECHANISM FOR THE REACTION ]**

Dehydrohalogenation of *vic*-Dibromides to Form Alkynes 315

- 7.11 Terminal Alkynes Can Be Converted to Nucleophiles for Carbon–Carbon Bond Formation 316

- 7.12 Hydrogenation of Alkenes 318

**THE CHEMISTRY OF...** Hydrogenation in the Food Industry 319

- 7.13 Hydrogenation: The Function of the Catalyst 320

- 7.14 Hydrogenation of Alkynes 321

**[ A MECHANISM FOR THE REACTION ]** The Dissolving Metal Reduction of an Alkyne 322

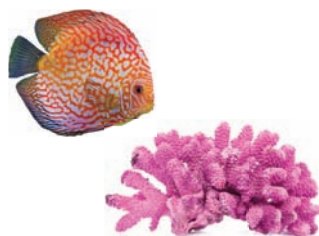
- 7.15 An Introduction to Organic Synthesis 323

**THE CHEMISTRY OF...** From the Inorganic to the Organic 325

**[ WHY DO THESE TOPICS MATTER? ]** 327

## 8 Alkenes and Alkynes II

### ADDITION REACTIONS 337



- 8.1 Addition Reactions of Alkenes 338  
8.2 Electrophilic Addition of Hydrogen Halides to Alkenes: Mechanism and Markovnikov's Rule 340

**[ A MECHANISM FOR THE REACTION ]** Addition of a Hydrogen Halide to an Alkene 341

**[ A MECHANISM FOR THE REACTION ]** Addition of HBr to 2-Methylpropene 343

- 8.3 Stereochemistry of the Ionic Addition to an Alkene 345

**[ THE STEREOCHEMISTRY OF THE REACTION... ]** Ionic Addition to an Alkene 345

- 8.4 Addition of Water to Alkenes: Acid-Catalyzed Hydration 346

**[ A MECHANISM FOR THE REACTION ]** Acid-Catalyzed Hydration of an Alkene 346

- 8.5 Alcohols from Alkenes through Oxymercuration–Demercuration: Markovnikov Addition 349

**[ A MECHANISM FOR THE REACTION ]** Oxymercuration 351

- 8.6 Alcohols from Alkenes through Hydroboration–Oxidation: Anti-Markovnikov Syn Hydration 352

- 8.7 Hydroboration: Synthesis of Alkylboranes 353

**[ A MECHANISM FOR THE REACTION ]** Hydroboration 354

- 8.8 Oxidation and Hydrolysis of Alkylboranes 355

**[ A MECHANISM FOR THE REACTION ]** Oxidation of Trialkylboranes 356

- 8.9 Summary of Alkene Hydration Methods 358

- 8.10 Protonolysis of Alkylboranes 359

- 8.11 Electrophilic Addition of Bromine and Chlorine to Alkenes 359

**[ A MECHANISM FOR THE REACTION ]** Addition of Bromine to an Alkene 361

**THE CHEMISTRY OF...** The Sea: A Treasury of Biologically Active Natural Products 362

- 8.12 Stereospecific Reactions 363

**[ THE STEREOCHEMISTRY OF THE REACTION... ]**

Addition of Bromine to *cis*- and *trans*-2-Butene 364

- 8.13 Halohydrin Formation 364

**[ A MECHANISM FOR THE REACTION ]** Halohydrin Formation from an Alkene 365

**THE CHEMISTRY OF...** Citrus-Flavored Soft Drinks 366

- 8.14 Divalent Carbon Compounds: Carbenes 366

- 8.15 Oxidation of Alkenes: Syn 1,2-Dihydroxylation 368

**THE CHEMISTRY OF...** Catalytic Asymmetric Dihydroxylation 370

- 8.16 Oxidative Cleavage of Alkenes 371

**[ A MECHANISM FOR THE REACTION ]** Ozonolysis of an Alkene 373

- 8.17 Electrophilic Addition of Bromine and Chlorine to Alkynes 374

- 8.18 Addition of Hydrogen Halides to Alkynes 374

- 8.19 Oxidative Cleavage of Alkynes 375

- 8.20 **HOW TO** Plan a Synthesis: Some Approaches and Examples 376

**[ WHY DO THESE TOPICS MATTER? ]** 381

## 9 Nuclear Magnetic Resonance and Mass Spectrometry

### TOOLS FOR STRUCTURE DETERMINATION 391



- 9.1 Introduction 392

- 9.2 Nuclear Magnetic Resonance (NMR) Spectroscopy 392

- 9.3 **HOW TO** Interpret Proton NMR Spectra 398

- 9.4 Nuclear Spin: The Origin of the Signal 401

- 9.5 Detecting the Signal: Fourier Transform NMR Spectrometers 403

- 9.6 The Chemical Shift 405

- 9.7 Shielding and Deshielding of Protons 406
- 9.8 Chemical Shift Equivalent and Nonequivalent Protons 408
- 9.9 Signal Splitting: Spin–Spin Coupling 411
- 9.10 Proton NMR Spectra and Rate Processes 420
- 9.11 Carbon-13 NMR Spectroscopy 422
- 9.12 Two-Dimensional (2D) NMR Techniques 428
- THE CHEMISTRY OF...** Magnetic Resonance Imaging in Medicine 431
- 9.13 An Introduction to Mass Spectrometry 431
- 9.14 Formation of Ions: Electron Impact Ionization 432
- 9.15 Depicting the Molecular Ion 432
- 9.16 Fragmentation 433
- 9.17 Isotopes in Mass Spectra 440
- 9.18 GC/MS Analysis 443
- 9.19 Mass Spectrometry of Biomolecules 444
- [ WHY DO THESE TOPICS MATTER? ]** 444

## 10 Radical Reactions 457



- 10.1 Introduction: How Radicals Form and How They React 458
- [ A MECHANISM FOR THE REACTION ]** Hydrogen Atom Abstraction 459
- [ A MECHANISM FOR THE REACTION ]** Radical Addition to a  $\pi$  Bond 459
- THE CHEMISTRY OF...** Acne Medications 459
- 10.2 Homolytic Bond Dissociation Energies ( $DH^\circ$ ) 460
- 10.3 Reactions of Alkanes with Halogens 463
- 10.4 Chlorination of Methane: Mechanism of Reaction 465
- [ A MECHANISM FOR THE REACTION ]** Radical Chlorination of Methane 465
- 10.5 Halogenation of Higher Alkanes 468
- [ A MECHANISM FOR THE REACTION ]** Radical Halogenation of Ethane 468
- 10.6 The Geometry of Alkyl Radicals 471
- 10.7 Reactions That Generate Tetrahedral Chirality Centers 471
- [ A MECHANISM FOR THE REACTION ]** The Stereochemistry of Chlorination at C2 of Pentane 472
- [ A MECHANISM FOR THE REACTION ]** The Stereochemistry of Chlorination at C3 of (S)-2-Chloropentane 473
- 10.8 Allylic Substitution and Allylic Radicals 475
- 10.9 Benzylic Substitution and Benzylic Radicals 478

- 10.10 Radical Addition to Alkenes: The Anti-Markovnikov Addition of Hydrogen Bromide 481
- [ A MECHANISM FOR THE REACTION ]** Anti-Markovnikov Addition of HBr 481
- 10.11 Radical Polymerization of Alkenes: Chain-Growth Polymers 483

- [ A MECHANISM FOR THE REACTION ]** Radical Polymerization of Ethene (Ethylene) 484
- 10.12 Other Important Radical Reactions 487

- THE CHEMISTRY OF...** Antioxidants 489
- THE CHEMISTRY OF...** Ozone Depletion and Chlorofluorocarbons (CFCs) 490
- [ WHY DO THESE TOPICS MATTER? ]** 491

See **SPECIAL TOPIC B**: Chain-Growth Polymers in *WileyPLUS*

## 11 Alcohols and Ethers

### SYNTHESIS AND REACTIONS 498



- 11.1 Structure and Nomenclature 499
- 11.2 Physical Properties of Alcohols and Ethers 501
- 11.3 Important Alcohols and Ethers 503
- THE CHEMISTRY OF...** Ethanol as a Biofuel 504
- THE CHEMISTRY OF...** Cholesterol and Heart Disease 505
- 11.4 Synthesis of Alcohols from Alkenes 505
- 11.5 Reactions of Alcohols 507
- 11.6 Alcohols as Acids 509
- 11.7 Conversion of Alcohols into Alkyl Halides 510
- 11.8 Alkyl Halides from the Reaction of Alcohols with Hydrogen Halides 510
- 11.9 Alkyl Halides from the Reaction of Alcohols with  $PBr_3$  or  $SOCl_2$  513
- 11.10 Tosylates, Mesylates, and Triflates: Leaving Group Derivatives of Alcohols 514
- [ A MECHANISM FOR THE REACTION ]** Conversion of an Alcohol into a Mesylate (an Alkyl Methanesulfonate) 516
- 11.11 Synthesis of Ethers 517
- [ A MECHANISM FOR THE REACTION ]** Intermolecular Dehydration of Alcohols to Form an Ether 517
- [ A MECHANISM FOR THE REACTION ]** The Williamson Ether Synthesis 518
- 11.12 Reactions of Ethers 522
- [ A MECHANISM FOR THE REACTION ]** Ether Cleavage by Strong Acids 522

11.13 Epoxides 523

[ A MECHANISM FOR THE REACTION ] Alkene Epoxidation 524

**THE CHEMISTRY OF...** The Sharpless Asymmetric Epoxidation 524

11.14 Reactions of Epoxides 525

[ A MECHANISM FOR THE REACTION ] Acid-Catalyzed Ring Opening of an Epoxide 525

[ A MECHANISM FOR THE REACTION ] Base-Catalyzed Ring Opening of an Epoxide 526

11.15 Anti 1,2-Dihydroxylation of Alkenes via Epoxides 528

**THE CHEMISTRY OF...** Environmentally Friendly Alkene Oxidation Methods 530

11.16 Crown Ethers 531

**THE CHEMISTRY OF...** Transport Antibiotics and Crown Ethers 532

11.17 Summary of Reactions of Alkenes, Alcohols, and Ethers 532

[ WHY DO THESE TOPICS MATTER? ] 534

## 12 Alcohols from Carbonyl Compounds

OXIDATION–  
REDUCTION AND  
ORGANOMETALLIC  
COMPOUNDS 542



12.1 Structure of the Carbonyl Group 543

12.2 Oxidation–Reduction Reactions in Organic Chemistry 544

12.3 Alcohols by Reduction of Carbonyl Compounds 546

[ A MECHANISM FOR THE REACTION ] Reduction of Aldehydes and Ketones by Hydride Transfer 548

**THE CHEMISTRY OF...** Alcohol Dehydrogenase—A Biochemical Hydride Reagent 548

**THE CHEMISTRY OF...** Stereoselective Reductions of Carbonyl Groups 550

12.4 Oxidation of Alcohols 551

[ A MECHANISM FOR THE REACTION ] The Swern Oxidation 552

[ A MECHANISM FOR THE REACTION ] Chromic Acid Oxidation 554

12.5 Organometallic Compounds 556

12.6 Preparation of Organolithium and Organomagnesium Compounds 557

12.7 Reactions of Organolithium and Organomagnesium Compounds 558

[ A MECHANISM FOR THE REACTION ] The Grignard Reaction 561

12.8 Alcohols from Grignard Reagents 561

12.9 Protecting Groups 570

[ WHY DO THESE TOPICS MATTER? ] 571

See **First Review Problem Set** in *WileyPLUS*

## 13 Conjugated Unsaturated Systems 581



13.1 Introduction 582

13.2 The Stability of the Allyl Radical 582

13.3 The Allyl Cation 586

13.4 Resonance Theory Revisited 587

13.5 Alkadienes and Polyunsaturated Hydrocarbons 591

13.6 1,3-Butadiene: Electron Delocalization 592

13.7 The Stability of Conjugated Dienes 595

13.8 Ultraviolet–Visible Spectroscopy 596

13.9 Electrophilic Attack on Conjugated Dienes: 1,4-Addition 604

13.10 The Diels–Alder Reaction: A 1,4-Cycloaddition Reaction of Dienes 608

**THE CHEMISTRY OF...** Molecules with the Nobel Prize in Their Synthetic Lineage 617

[ WHY DO THESE TOPICS MATTER? ] 617

## 14 Aromatic Compounds 626



14.1 The Discovery of Benzene 627

14.2 Nomenclature of Benzene Derivatives 628

14.3 Reactions of Benzene 630

14.4 The Kekulé Structure for Benzene 631

14.5 The Thermodynamic Stability of Benzene 632

14.6 Modern Theories of the Structure of Benzene 634

14.7 Hückel's Rule: The  $4n + 2 \pi$  Electron Rule 637

14.8 Other Aromatic Compounds 645

- THE CHEMISTRY OF...** Nanotubes 648
- 14.9 Heterocyclic Aromatic Compounds 648
- 14.10 Aromatic Compounds in Biochemistry 650
- 14.11 Spectroscopy of Aromatic Compounds 652
- THE CHEMISTRY OF...** Sunscreens (Catching the Sun's Rays and What Happens to Them) 656
- [ WHY DO THESE TOPICS MATTER? ]** 657

## 15 Reactions of Aromatic Compounds 669



- 15.1 Electrophilic Aromatic Substitution Reactions 670
- 15.2 A General Mechanism for Electrophilic Aromatic Substitution 671
- 15.3 Halogenation of Benzene 673
- [ A MECHANISM FOR THE REACTION ]** Electrophilic Aromatic Bromination 673
- 15.4 Nitration of Benzene 674
- [ A MECHANISM FOR THE REACTION ]** Nitration of Benzene 675
- 15.5 Sulfonation of Benzene 675
- [ A MECHANISM FOR THE REACTION ]** Sulfonation of Benzene 676
- 15.6 Friedel–Crafts Alkylation 676
- [ A MECHANISM FOR THE REACTION ]** Friedel–Crafts Alkylation 677
- 15.7 Friedel–Crafts Acylation 678
- [ A MECHANISM FOR THE REACTION ]** Friedel–Crafts Acylation 680
- 15.8 Limitations of Friedel–Crafts Reactions 680
- 15.9 Synthetic Applications of Friedel–Crafts Acylations: The Clemmensen and Wolff–Kishner Reductions 683
- 15.10 Substituents Can Affect Both the Reactivity of the Ring and the Orientation of the Incoming Group 685
- 15.11 How Substituents Affect Electrophilic Aromatic Substitution: A Closer Look 690
- 15.12 Reactions of the Side Chain of Alkylbenzenes 699
- THE CHEMISTRY OF...** Industrial Styrene Synthesis 701
- [ A MECHANISM FOR THE REACTION ]** Benzylic Halogenation 701

- 15.13 Alkenylbenzenes 702
- 15.14 Synthetic Applications 704
- 15.15 Allylic and Benzylic Halides in Nucleophilic Substitution Reactions 708
- 15.16 Reduction of Aromatic Compounds 710
- [ A MECHANISM FOR THE REACTION ]** Birch Reduction 710
- [ WHY DO THESE TOPICS MATTER? ]** 711

## 16 Aldehydes and Ketones



### NUCLEOPHILIC ADDITION TO THE CARBONYL GROUP 720

- 16.1 Introduction 721
- 16.2 Nomenclature of Aldehydes and Ketones 721
- 16.3 Physical Properties 723
- THE CHEMISTRY OF...** Aldehydes and Ketones in Perfumes 724
- 16.4 Synthesis of Aldehydes 724
- [ A MECHANISM FOR THE REACTION ]** Reduction of an Acyl Chloride to an Aldehyde 727
- [ A MECHANISM FOR THE REACTION ]** Reduction of an Ester to an Aldehyde 728
- [ A MECHANISM FOR THE REACTION ]** Reduction of a Nitrile to an Aldehyde 728
- 16.5 Synthesis of Ketones 729
- 16.6 Nucleophilic Addition to the Carbon–Oxygen Double Bond 732
- [ A MECHANISM FOR THE REACTION ]** Addition of a Strong Nucleophile to an Aldehyde or Ketone 733
- [ A MECHANISM FOR THE REACTION ]** Acid-Catalyzed Nucleophilic Addition to an Aldehyde or Ketone 733
- 16.7 The Addition of Alcohols: Hemiacetals and Acetals 735
- [ A MECHANISM FOR THE REACTION ]** Hemiacetal Formation 735
- [ A MECHANISM FOR THE REACTION ]** Acid-Catalyzed Hemiacetal Formation 736
- [ A MECHANISM FOR THE REACTION ]** Base-Catalyzed Hemiacetal Formation 736
- [ A MECHANISM FOR THE REACTION ]** Hydrate Formation 737
- [ A MECHANISM FOR THE REACTION ]** Acid-Catalyzed Acetal Formation 738
- 16.8 The Addition of Primary and Secondary Amines 741



- [ **A MECHANISM FOR THE REACTION** ] Imine Formation 742
- [ **A MECHANISM FOR THE REACTION** ] The Wolff–Kishner Reduction 743
- THE CHEMISTRY OF...** A Very Versatile Vitamin, Pyridoxine (Vitamin B<sub>6</sub>) 744
- [ **A MECHANISM FOR THE REACTION** ] Enamine Formation 745
- 16.9 The Addition of Hydrogen Cyanide: Cyanohydrins 746
- [ **A MECHANISM FOR THE REACTION** ] Cyanohydrin Formation 746
- 16.10 The Addition of Ylides: The Wittig Reaction 747
- [ **A MECHANISM FOR THE REACTION** ] The Wittig Reaction 749
- 16.11 Oxidation of Aldehydes 751
- 16.12 The Baeyer–Villiger Oxidation 751
- [ **A MECHANISM FOR THE REACTION** ] The Baeyer–Villiger Oxidation 752
- 16.13 Chemical Analyses for Aldehydes and Ketones 753
- 16.14 Spectroscopic Properties of Aldehydes and Ketones 753
- 16.15 Summary of Aldehyde and Ketone Addition Reactions 756
- [ **WHY DO THESE TOPICS MATTER?** ] 757

## 17

### Carboxylic Acids and Their Derivatives

#### NUCLEOPHILIC ADDITION–ELIMINATION AT THE ACYL CARBON 771

- 17.1 Introduction 772
- 17.2 Nomenclature and Physical Properties 772
- 17.3 Preparation of Carboxylic Acids 781
- 17.4 Acyl Substitution: Nucleophilic Addition–Elimination at the Acyl Carbon 784
- [ **A MECHANISM FOR THE REACTION** ] Acyl Substitution by Nucleophilic Addition–Elimination 784
- 17.5 Acyl Chlorides 786
- [ **A MECHANISM FOR THE REACTION** ] Synthesis of Acyl Chlorides Using Thionyl Chloride 787
- 17.6 Carboxylic Acid Anhydrides 788
- 17.7 Esters 789
- [ **A MECHANISM FOR THE REACTION** ] Acid-Catalyzed Esterification 790



- [ **A MECHANISM FOR THE REACTION** ] Base-Promoted Hydrolysis of an Ester 793
- 17.8 Amides 796
- [ **A MECHANISM FOR THE REACTION** ] DCC-Promoted Amide Synthesis 798
- [ **A MECHANISM FOR THE REACTION** ] Acidic Hydrolysis of an Amide 799
- [ **A MECHANISM FOR THE REACTION** ] Basic Hydrolysis of an Amide 799
- [ **A MECHANISM FOR THE REACTION** ] Acidic Hydrolysis of a Nitrile 801
- [ **A MECHANISM FOR THE REACTION** ] Basic Hydrolysis of a Nitrile 801
- THE CHEMISTRY OF...** Penicillins 802
- 17.9 Derivatives of Carbonic Acid 802
- 17.10 Decarboxylation of Carboxylic Acids 805
- 17.11 Chemical Tests for Acyl Compounds 807
- 17.12 Polyesters and Polyamides: Step-Growth Polymers 807
- 17.13 Summary of the Reactions of Carboxylic Acids and Their Derivatives 809
- [ **WHY DO THESE TOPICS MATTER?** ] 812

## 18

### Reactions at the $\alpha$ Carbon of Carbonyl Compounds

#### ENOLS AND ENOLATES 821

- 18.1 The Acidity of the  $\alpha$  Hydrogens of Carbonyl Compounds: Enolate Anions 822
- 18.2 Keto and Enol Tautomers 823
- 18.3 Reactions via Enols and Enolates 825
- [ **A MECHANISM FOR THE REACTION** ] Base-Catalyzed Enolization 825
- [ **A MECHANISM FOR THE REACTION** ] Acid-Catalyzed Enolization 826
- [ **A MECHANISM FOR THE REACTION** ] Base-Promoted Halogenation of Aldehydes and Ketones 827
- [ **A MECHANISM FOR THE REACTION** ] Acid-Catalyzed Halogenation of Aldehydes and Ketones 828
- [ **A MECHANISM FOR THE REACTION** ] The Haloform Reaction 829
- THE CHEMISTRY OF...** Chloroform in Drinking Water 829
- 18.4 Lithium Enolates 831
- 18.5 Enolates of  $\beta$ -Dicarbonyl Compounds 834



- 18.6 Synthesis of Methyl Ketones: The Acetoacetic Ester Synthesis 835
- 18.7 Synthesis of Substituted Acetic Acids: The Malonic Ester Synthesis 840
- [ A MECHANISM FOR THE REACTION ]** The Malonic Ester Synthesis of Substituted Acetic Acids 840
- 18.8 Further Reactions of Active Hydrogen Compounds 844
- 18.9 Synthesis of Enamines: Stork Enamine Reactions 844
- 18.10 Summary of Enolate Chemistry 847
- [ WHY DO THESE TOPICS MATTER? ]** 849

See **SPECIAL TOPIC C: Step-Growth Polymers** in *WileyPLUS*

## 19 Condensation and Conjugate Addition Reactions of Carbonyl Compounds



MORE CHEMISTRY OF ENOLATES 858

- 19.1 Introduction 859
- 19.2 The Claisen Condensation: A Synthesis of  $\beta$ -Keto Esters 859
- [ A MECHANISM FOR THE REACTION ]** The Claisen Condensation 860
- [ A MECHANISM FOR THE REACTION ]** The Dieckmann Condensation 862
- 19.3  $\beta$ -Dicarbonyl Compounds by Acylation of Ketone Enolates 864
- 19.4 Aldol Reactions: Addition of Enolates and Enols to Aldehydes and Ketones 865
- [ A MECHANISM FOR THE REACTION ]** The Aldol Addition 866
- [ A MECHANISM FOR THE REACTION ]** Dehydration of the Aldol Addition Product 867
- [ A MECHANISM FOR THE REACTION ]** The Acid-Catalyzed Aldol Reaction 867
- THE CHEMISTRY OF...** A Retro-Aldol Reaction in Glycolysis—Dividing Assets to Double the ATP Yield 870
- 19.5 Crossed Aldol Condensations 871
- [ A MECHANISM FOR THE REACTION ]** A Directed Aldol Synthesis Using a Lithium Enolate 875
- 19.6 Cyclizations via Aldol Condensations 876
- [ A MECHANISM FOR THE REACTION ]** The Aldol Cyclization 877

- 19.7 Additions to  $\alpha,\beta$ -Unsaturated Aldehydes and Ketones 877

**[ A MECHANISM FOR THE REACTION ]** The Conjugate Addition of HCN 879

**[ A MECHANISM FOR THE REACTION ]** The Conjugate Addition of an Amine 879

**[ A MECHANISM FOR THE REACTION ]** The Michael Addition 880

**THE CHEMISTRY OF...** Conjugate Additions to Activate Drugs 881

19.8 The Mannich Reaction 882

**[ A MECHANISM FOR THE REACTION ]** The Mannich Reaction 882

**THE CHEMISTRY OF...** A Suicide Enzyme Substrate 883

19.9 Summary of Important Reactions 884

**[ WHY DO THESE TOPICS MATTER? ]** 885

See **SPECIAL TOPIC D: Thiols, Sulfur Ylides, and Disulfides** in *WileyPLUS*

See **SPECIAL TOPIC E: Thiol Esters and Lipid Biosynthesis** in *WileyPLUS*

## 20 Amines 897



- 20.1 Nomenclature 898
- 20.2 Physical Properties and Structure of Amines 899
- 20.3 Basicity of Amines: Amine Salts 901
- THE CHEMISTRY OF...** Biologically Important Amines 906
- 20.4 Preparation of Amines 908
- [ A MECHANISM FOR THE REACTION ]** Alkylation of  $\text{NH}_3$  909
- [ A MECHANISM FOR THE REACTION ]** Reductive Amination 912
- [ A MECHANISM FOR THE REACTION ]** The Hofmann Rearrangement 915
- 20.5 Reactions of Amines 917
- 20.6 Reactions of Amines with Nitrous Acid 918
- [ A MECHANISM FOR THE REACTION ]** Diazotization 919
- THE CHEMISTRY OF...** *N*-Nitrosoamines 919
- 20.7 Replacement Reactions of Arenediazonium Salts 920
- 20.8 Coupling Reactions of Arenediazonium Salts 924
- 20.9 Reactions of Amines with Sulfonyl Chlorides 926
- THE CHEMISTRY OF...** Essential Nutrients and Antimetabolites 927
- 20.10 Synthesis of Sulfa Drugs 928

- 20.11 Analysis of Amines 929  
20.12 Eliminations Involving Ammonium Compounds 931  
20.13 Summary of Preparations and Reactions of Amines 932

[ **WHY DO THESE TOPICS MATTER?** ] 934

See **SPECIAL TOPIC F:** Alkaloids in *WileyPLUS*

## 21 Phenols and Aryl Halides

NUCLEOPHILIC AROMATIC  
SUBSTITUTION 944



- 21.1 Structure and Nomenclature of Phenols 945  
21.2 Naturally Occurring Phenols 946  
21.3 Physical Properties of Phenols 947  
21.4 Synthesis of Phenols 947  
21.5 Reactions of Phenols as Acids 949  
21.6 Other Reactions of the O—H Group of Phenols 952  
21.7 Cleavage of Alkyl Aryl Ethers 952  
21.8 Reactions of the Benzene Ring of Phenols 953

**THE CHEMISTRY OF...** Polyketide Anticancer Antibiotic Biosynthesis 954

21.9 The Claisen Rearrangement 956

21.10 Quinones 957

**THE CHEMISTRY OF...** The Bombardier Beetle's Noxious Spray 958

21.11 Aryl Halides and Nucleophilic Aromatic Substitution 959

[ **A MECHANISM FOR THE REACTION** ] The  $S_NAr$  Mechanism 960

**THE CHEMISTRY OF...** Bacterial Dehalogenation of a PCB Derivative 961

[ **A MECHANISM FOR THE REACTION** ] The Benzyne Elimination–Addition Mechanism 962

21.12 Spectroscopic Analysis of Phenols and Aryl Halides 966

**THE CHEMISTRY OF...** Aryl Halides: Their Uses and Environmental Concerns 967

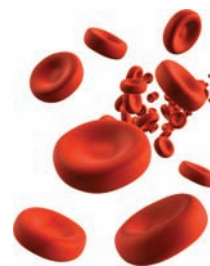
[ **WHY DO THESE TOPICS MATTER?** ] 969

See **Second Review Problem Set** in *WileyPLUS*

**SPECIAL TOPIC G:** Carbon–Carbon Bond–Forming and Other Reactions of Transition Metal Organometallic Compounds G-1

See **SPECIAL TOPIC H:** Electrocyclic and Cycloaddition Reactions in *WileyPLUS*

## 22 Carbohydrates 979



- 22.1 Introduction 980  
22.2 Monosaccharides 982  
22.3 Mutarotation 987  
22.4 Glycoside Formation 988

[ **A MECHANISM FOR THE REACTION** ] Formation of a Glycoside 988

[ **A MECHANISM FOR THE REACTION** ] Hydrolysis of a Glycoside 989

22.5 Other Reactions of Monosaccharides 990

22.6 Oxidation Reactions of Monosaccharides 994

22.7 Reduction of Monosaccharides: Alditols 999

22.8 Reactions of Monosaccharides with Phenylhydrazine: Osazones 999

[ **A MECHANISM FOR THE REACTION** ] Phenyllosazone Formation 1000

22.9 Synthesis and Degradation of Monosaccharides 1000

22.10 The D Family of Aldoses 1002

22.11 Fischer's Proof of the Configuration of D-(+)-Glucose 1003

22.12 Disaccharides 1005

**THE CHEMISTRY OF...** Artificial Sweeteners (How Sweet It Is) 1008

22.13 Polysaccharides 1009

22.14 Other Biologically Important Sugars 1013

22.15 Sugars That Contain Nitrogen 1014

22.16 Glycolipids and Glycoproteins of the Cell Surface: Cell Recognition and the Immune System 1016

**THE CHEMISTRY OF...** Patrolling Leukocytes and Sialyl Lewis<sup>x</sup> Acids 1018

22.17 Carbohydrate Antibiotics 1018

22.18 Summary of Reactions of Carbohydrates 1019

[ **WHY DO THESE TOPICS MATTER?** ] 1020

## 23 Lipids 1027



23.1 Introduction 1028

23.2 Fatty Acids and Triacylglycerols 1028

**THE CHEMISTRY OF...** Olestra and Other Fat Substitutes 1032

**THE CHEMISTRY OF...** Self-Assembled Monolayers—Lipids in Materials Science and Bioengineering 1036

23.3 Terpenes and Terpenoids 1037

- 23.4 Steroids 1040  
**THE CHEMISTRY OF...** The Enzyme Aromatase 1046  
 23.5 Prostaglandins 1049  
 23.6 Phospholipids and Cell Membranes 1050  
**THE CHEMISTRY OF...** STEALTH<sup>®</sup> Liposomes for Drug Delivery 1053  
 23.7 Waxes 1054  
**[ WHY DO THESE TOPICS MATTER? ]** 1054

## 24 Amino Acids and Proteins 1060



- 24.1 Introduction 1061  
 24.2 Amino Acids 1062  
 24.3 Synthesis of  $\alpha$ -Amino Acids 1068  
**[ A MECHANISM FOR THE REACTION ]** Formation of an  $\alpha$ -Aminonitrile during the Strecker Synthesis 1069  
 24.4 Polypeptides and Proteins 1070  
 24.5 Primary Structure of Polypeptides and Proteins 1073  
 24.6 Examples of Polypeptide and Protein Primary Structure 1077  
**THE CHEMISTRY OF...** Sickle-Cell Anemia 1079  
 24.7 Polypeptide and Protein Synthesis 1080  
 24.8 Secondary, Tertiary, and Quaternary Structures of Proteins 1086  
 24.9 Introduction to Enzymes 1090  
 24.10 Lysozyme: Mode of Action of an Enzyme 1092  
**THE CHEMISTRY OF...** Carbonic Anhydrase: Shuttling the Protons 1094

- 24.11 Serine Proteases 1094  
 24.12 Hemoglobin: A Conjugated Protein 1096  
**THE CHEMISTRY OF...** Some Catalytic Antibodies 1096  
 24.13 Purification and Analysis of Polypeptides and Proteins 1098  
 24.14 Proteomics 1100  
**[ WHY DO THESE TOPICS MATTER? ]** 1102

## 25 Nucleic Acids and Protein Synthesis 1105



- 25.1 Introduction 1106  
 25.2 Nucleotides and Nucleosides 1107  
 25.3 Laboratory Synthesis of Nucleosides and Nucleotides 1110  
 25.4 Deoxyribonucleic Acid: DNA 1113  
 25.5 RNA and Protein Synthesis 1120  
 25.6 Determining the Base Sequence of DNA: The Chain-Terminating (Dideoxynucleotide) Method 1128  
 25.7 Laboratory Synthesis of Oligonucleotides 1131  
 25.8 The Polymerase Chain Reaction 1133  
 25.9 Sequencing of the Human Genome: An Instruction Book for the Molecules of Life 1135  
**[ WHY DO THESE TOPICS MATTER? ]** 1136

ANSWERS TO SELECTED PROBLEMS A-1  
 GLOSSARY GL-1  
 INDEX I-1

## [A MECHANISM FOR THE REACTION ]

### CHAPTER 3

Reaction of Water with Hydrogen Chloride: The Use of Curved Arrows 107

Reaction of *tert*-Butyl Alcohol with Concentrated Aqueous HCl 132

### CHAPTER 6

Mechanism for the S<sub>N</sub>2 Reaction 247

The Stereochemistry of an S<sub>N</sub>2 Reaction 253

Mechanism for the S<sub>N</sub>1 Reaction 255

The Stereochemistry of an S<sub>N</sub>1 Reaction 259

Mechanism for the E2 Reaction 277

Mechanism for the E1 Reaction 279

### CHAPTER 7

E2 Elimination Where There Are Two Axial  $\beta$  Hydrogens 302

E2 Elimination Where the Only Axial  $\beta$  Hydrogen Is from a Less Stable Conformer 302

Acid-Catalyzed Dehydration of Secondary or Tertiary Alcohols: An E1 Reaction 307

Dehydration of a Primary Alcohol: An E2 Reaction 308

Formation of a Rearranged Alkene During Dehydration of a Primary Alcohol 312

Dehydrohalogenation of *vic*-Dibromides to Form Alkynes 315

The Dissolving Metal Reduction of an Alkyne 322

### CHAPTER 8

Addition of a Hydrogen Halide to an Alkene 341

Addition of HBr to 2-Methylpropene 343

Ionic Addition to an Alkene 345

Acid-Catalyzed Hydration of an Alkene 346

Oxymercuration 351

Hydroboration 354

Oxidation of Trialkylboranes 356

Addition of Bromine to an Alkene 361

Addition of Bromine to *cis*- and *trans*-2-Butene 364

Halohydrin Formation from an Alkene 365

Ozonolysis of an Alkene 373

### CHAPTER 10

Hydrogen Atom Abstraction 459

Radical Addition to a  $\pi$  Bond 459

Radical Chlorination of Methane 465

Radical Halogenation of Ethane 468

The Stereochemistry of Chlorination at C2 of Pentane 472

The Stereochemistry of Chlorination at C3 of (*S*)-2-Chloropentane 473

Anti-Markovnikov Addition of HBr 481

Radical Polymerization of Ethene (Ethylene) 484

### CHAPTER 11

Conversion of an Alcohol into a Mesylate (an Alkyl Methanesulfonate) 516

Intermolecular Dehydration of Alcohols to Form an Ether 517

The Williamson Ether Synthesis 518

Ether Cleavage by Strong Acids 522

Alkene Epoxidation 524

Acid-Catalyzed Ring Opening of an Epoxide 525

Base-Catalyzed Ring Opening of an Epoxide 526

### CHAPTER 12

Reduction of Aldehydes and Ketones by Hydride Transfer 548

The Swern Oxidation 552

Chromic Acid Oxidation 554

The Grignard Reaction 561

### CHAPTER 15

Electrophilic Aromatic Bromination 673

Nitration of Benzene 675

Sulfonation of Benzene 676

Friedel–Crafts Alkylation 677

Friedel–Crafts Acylation 680

Benzylic Halogenation 701

Birch Reduction 710

### CHAPTER 16

Reduction of an Acyl Chloride to an Aldehyde 727

Reduction of an Ester to an Aldehyde 728

Reduction of a Nitrile to an Aldehyde 728

Addition of a Strong Nucleophile to an Aldehyde or Ketone 733

Acid-Catalyzed Nucleophilic Addition to an Aldehyde or Ketone 733

Hemiacetal Formation 735

Acid-Catalyzed Hemiacetal Formation 736

Base-Catalyzed Hemiacetal Formation 736

Hydrate Formation 737

Acid-Catalyzed Acetal Formation 738

Imine Formation 742

The Wolff–Kishner Reduction 743

Enamine Formation 745

Cyanohydrin Formation 746

The Wittig Reaction 749


The Baeyer–Villiger Oxidation 752

### CHAPTER 17

Acyl Substitution by Nucleophilic Addition–Elimination 784

Synthesis of Acyl Chlorides Using Thionyl Chloride 787





Acid-Catalyzed Esterification 790  
Base-Promoted Hydrolysis of an Ester 793  
DCC-Promoted Amide Synthesis 798  
Acidic Hydrolysis of an Amide 799  
Basic Hydrolysis of an Amide 799  
Acidic Hydrolysis of a Nitrile 801  
Basic Hydrolysis of a Nitrile 801

#### CHAPTER 18

Base-Catalyzed Enolization 825  
Acid-Catalyzed Enolization 826  
Base-Promoted Halogenation of Aldehydes and Ketones 827  
Acid-Catalyzed Halogenation of Aldehydes and Ketones 828  
The Haloform Reaction 829  
The Malonic Ester Synthesis of Substituted Acetic Acids 840

#### CHAPTER 19

The Claisen Condensation 860  
The Dieckmann Condensation 862  
The Aldol Addition 866  
Dehydration of the Aldol Addition Product 867  
The Acid-Catalyzed Aldol Reaction 867

A Directed Aldol Synthesis Using a Lithium Enolate 875  
The Aldol Cyclization 877  
The Conjugate Addition of HCN 879  
The Conjugate Addition of an Amine 879  
The Michael Addition 880  
The Mannich Reaction 882

#### CHAPTER 20

Alkylation of  $\text{NH}_3$  909  
Reductive Amination 912  
The Hofmann Rearrangement 915  
Diazotization 919

#### CHAPTER 21

The  $\text{S}_{\text{N}}\text{Ar}$  Mechanism 960  
The Benzyne Elimination–Addition Mechanism 962

#### CHAPTER 22

Formation of a Glycoside 988  
Hydrolysis of a Glycoside 989  
Phenylosazone Formation 1000

#### CHAPTER 24

Formation of an  $\alpha$ -Aminonitrile during the Strecker Synthesis 1069

---

## THE CHEMISTRY OF...

#### CHAPTER 1

Natural Products 3  
Calculated Molecular Models: Electron Density Surfaces 36

#### CHAPTER 2

Ethers as General Anesthetics 69  
Fluorocarbons and Teflon 82  
Organic Templates Engineered to Mimic Bone Growth 86

#### CHAPTER 4

Petroleum Refining 143  
Pheromones: Communication by Means of Chemicals 161  
Muscle Action 166  
Nanoscale Motors and Molecular Switches 170

#### CHAPTER 5

Selective Binding of Drug Enantiomers to Left- and Right-Handed Coiled DNA 217

#### CHAPTER 6

Biological Methylation: A Biological Nucleophilic Substitution Reaction 273

#### CHAPTER 7

Hydrogenation in the Food Industry 319  
From the Inorganic to the Organic 325

#### CHAPTER 8

The Sea: A Treasury of Biologically Active Natural Products 362  
Citrus-Flavored Soft Drinks 366  
Catalytic Asymmetric Dihydroxylation 370

#### CHAPTER 9

Magnetic Resonance Imaging in Medicine 431

#### CHAPTER 10

Acne Medications 459  
Antioxidants 489  
Ozone Depletion and Chlorofluorocarbons (CFCs) 490

#### CHAPTER 11

Ethanol as a Biofuel 504  
Cholesterol and Heart Disease 505  
The Sharpless Asymmetric Epoxidation 524

Environmentally Friendly Alkene Oxidation Methods 530  
Transport Antibiotics and Crown Ethers 532

#### CHAPTER 12

Alcohol Dehydrogenase—A Biochemical Hydride Reagent 548  
Stereoselective Reductions of Carbonyl Groups 550

#### CHAPTER 13

Molecules with the Nobel Prize in Their Synthetic Lineage 617

#### CHAPTER 14

Nanotubes 648  
Sunscreens (Catching the Sun's Rays and What Happens to Them) 656

#### CHAPTER 15

Industrial Styrene Synthesis 701

#### CHAPTER 16

Aldehydes and Ketones in Perfumes 724  
A Very Versatile Vitamin, Pyridoxine (Vitamin B<sub>6</sub>) 744

#### CHAPTER 17

Penicillins 802

#### CHAPTER 18

Chloroform in Drinking Water 829

#### CHAPTER 19

A Retro-Aldol Reaction in Glycolysis—Dividing Assets to Double the ATP Yield 870

Conjugate Additions to Activate Drugs 881  
A Suicide Enzyme Substrate 883

#### CHAPTER 20

Biologically Important Amines 906  
*N*-Nitrosoamines 919  
Essential Nutrients and Antimetabolites 927

#### CHAPTER 21

Polyketide Anticancer Antibiotic Biosynthesis 954  
The Bombardier Beetle's Noxious Spray 958  
Bacterial Dehalogenation of a PCB Derivative 961  
Aryl Halides: Their Uses and Environmental Concerns 967

#### CHAPTER 22

Artificial Sweeteners (How Sweet It Is) 1008  
Patrolling Leukocytes and Sialyl Lewis<sup>x</sup> Acids 1018

#### CHAPTER 23

Olestra and Other Fat Substitutes 1032  
Self-Assembled Monolayers—Lipids in Materials Science and Bioengineering 1036  
The Enzyme Aromatase 1046  
STEALTH<sup>®</sup> Liposomes for Drug Delivery 1053

#### CHAPTER 24

Sickle-Cell Anemia 1079  
Carbonic Anhydrase: Shuttling the Protons 1094  
Some Catalytic Antibodies 1096

## HOW TO...

#### CHAPTER 1

1.4 How To Write Lewis Structures 7  
1.5 Formal Charges and How To Calculate Them 12  
1.7 How To Write and Interpret Structural Formulas 15  
How To Draw Bond-Line Formulas 18  
1.8A The Use of Curved Arrows: How To Write Resonance Structures 24  
1.16 How To Predict Molecular Geometry: The Valence Shell Electron Pair Repulsion Model 44

#### CHAPTER 2


How To Interpret an IR Spectrum without any Knowledge of the Structure 95

#### CHAPTER 3

3.2 How To Use Curved Arrows in Illustrating Reactions 107  
3.6 How To Predict the Outcome of Acid–Base Reactions 118

#### CHAPTER 4

4.3 How To Name Alkanes, Alkyl Halides, and Alcohols: the IUPAC System 146  
4.3A How To Name Unbranched Alkyl Groups 147  
4.3B How To Name Branched-Chain Alkanes 147  
4.3C How To Name Branched Alkyl Groups 149  
4.3D How To Classify Hydrogen Atoms 151  
4.3E How To Name Alkyl Halides 151  
4.3F How To Name Alcohols 152  
4.4 How To Name Cycloalkanes 153  
4.4A How To Name Monocyclic Cycloalkanes 153  
4.4B How To Name Bicyclic Cycloalkanes 155  
4.5 How To Name Alkenes and Cycloalkenes 156  
4.6 How To Name Alkynes 158  
4.8A Newman Projections and How To Draw Them 162  
4.8B How To Do a Conformational Analysis 163

- 
- 4.12A How To Draw Chair Conformational Structures 172
- 4.17 How To Gain Structural Information from Molecular Formulas and the Index of Hydrogen Deficiency 182

#### CHAPTER 5

- 5.6 How To Test for Chirality: Planes of Symmetry 201
- 5.7A How To Assign (*R*) and (*S*) Configurations 202
- 5.12A How To Draw Stereoisomers for Molecules Having More Than One Chirality Center 218
- 5.12C How To Name Compounds with More Than One Chirality Center 222
- 5.13A How To Draw and Use Fischer Projections 223

#### CHAPTER 6

- 6.18 How To Determine Whether Substitution or Elimination Is Favored 280

#### CHAPTER 7

- 7.2A How To Use the (*E*)-(Z) System 292
- 7.6A How To Favor an E2 Mechanism 297

#### CHAPTER 8

- 8.1A How To Understand Additions to Alkenes 338
- 8.20 How To Plan a Synthesis: Some Approaches and Examples 376
- How To Apply Retrosynthetic Analysis to 2-Bromobutane 377
- How To Apply Stereochemical Considerations in Planning a Synthesis of 2,3-Butanediol Enantiomers 379

#### CHAPTER 9

- 9.3 How To Interpret Proton NMR Spectra 398

#### CHAPTER 10

- 10.2A How To Use Homolytic Bond Dissociation Energies to Determine the Relative Stabilities of Radicals 460

#### CHAPTER 11

- 11.17A How To Use Alkenes in Synthesis 533

#### CHAPTER 12

- 12.8A How To Plan a Grignard Synthesis 564

#### CHAPTER 13

- 13.4A How To Write Proper Resonance Structures 587
- 13.4B How To Estimate the Relative Stability of Contributing Resonance Structures 589
- 13.10C How To Predict the Products of a Diels–Alder Reaction 614
- 13.10D How To Use a Diels–Alder Reaction in a Retrosynthetic Analysis 615

#### CHAPTER 14

- 14.7A How To Diagram the Relative Energies of  $\pi$  Molecular Orbitals in Monocyclic Systems Based on Hückel's Rule 637

#### CHAPTER 16

- 16.10A How To Plan a Wittig Synthesis 749





# [ PREFACE ]

## “IT’S ORGANIC CHEMISTRY!”

That’s what we want students to exclaim after they become acquainted with our subject. Our lives revolve around organic chemistry, whether we all realize it or not. When we understand organic chemistry, we see how life itself would be impossible without it, how the quality of our lives depends upon it, and how examples of organic chemistry leap out at us from every direction. That’s why we can envision students enthusiastically exclaiming “It’s organic chemistry!” when, perhaps, they explain to a friend or family member how one central theme—organic chemistry—pervades our existence. We want to help students experience the excitement of seeing the world through an organic lens, and how the unifying and simplifying nature of organic chemistry helps make many things in nature comprehensible.

Our book makes it possible for students to learn organic chemistry well and to see the marvelous ways that organic chemistry touches our lives on a daily basis. Our book helps students develop their skills in critical thinking, problem solving, and analysis—skills that are so important in today’s world, no matter what career paths they choose. The richness of organic chemistry lends itself to solutions for our time, from the fields of health care, to energy, sustainability, and the environment. After all, it’s organic chemistry!

Guided by these goals, and by wanting to make our book even more **accessible to students** than it has ever been before, we have brought many changes to this edition.

## NEW TO THIS EDITION

With this edition we bring Scott Snyder on board as a co-author. We’re very excited to have Scott join our team. Scott brings a rich resource of new perspectives to the book, particularly in the arena of complex molecule synthesis. Scott has infused new examples and applications of exciting chemistry that help achieve our goals. In addition to adding his perspectives to the presentation of core chemistry throughout the book, Scott’s work is manifest in most of this edition’s chapter openers and in all of the chapter closers, couched in a new feature called “Why do these topics matter?”.

“**Why do these topics matter?**” is a new feature that bookends each chapter with a teaser in the opener and a captivating example of organic chemistry in the closer. The chapter opener seeks to whet the student’s appetite both for the core chemistry in that chapter as well as a prize that comes at the end of the chapter in the form of a “Why do these topics matter?” vignette. These new closers consist of fascinating nuggets of organic chemistry that stem from research relating to medical, environmental, and other aspects of organic chemistry in the world around us, as well as the history of the science. They show the rich relevance of what students have learned to applications that have direct bearing on our lives and wellbeing. For example, in Chapter 6, the opener talks about the some of the benefits and drawbacks of making substitutions in a recipe, and then compares such changes to the nucleophilic displacement reactions that similarly allow chemists to change molecules and their properties. The closer then shows how exactly such reactivity has enabled scientists to convert simple table sugar into the artificial sweetener Splenda which is 600 times as sweet, but has no calories!

**Laying the foundation earlier** Certain tools are absolutely key to success in organic chemistry. Among them is the ability to draw structural formulas quickly and correctly. In this edition, we help students learn these skills even sooner than ever before by moving coverage of structural formulas and the use curved arrows earlier in the text (Section 3.2). We have woven together instruction about Lewis structures, covalent bonds, and dash structural formulas, so that students build their skills in these areas as a coherent unit, using organic examples that include alkanes, alkenes, alkynes, and alkyl halides. One could say that it’s a “use organic to teach organic” approach.

## Ionic Reactions

NUCLEOPHILIC SUBSTITUTION AND  
ELIMINATION REACTIONS OF ALKYL HALIDES

Not all substitutions are a good thing; for instance, we wouldn't want to accidentally use salt in place of the needed amount of sugar in a batch of chocolate chip cookies. But with some substitutions, we get something even better: organic chemistry that is often the case, since nucleophilic substitution reactions (which we will learn about in this chapter) allow the conversion of functional groups within a given molecule into entirely different functional groups, leading to new compounds with distinct properties. Moreover, nature utilizes a number of specific substitution reactions that are required for life.

## IN THIS CHAPTER WE WILL CONSIDER:

- what groups can be replaced (i.e., substituted) or eliminated
- the various mechanisms by which such processes occur
- the conditions that can promote such reactions

**[ WHY DO THESE TOPICS MATTER? ]** At the end of the chapter, we will show an example where just a few substitution reactions can convert table sugar into a sweetener that has no calories—a sugar substitute that is not salty but is in fact 600 times sweeter than sugar itself!

photo credit: (sugar bowl) Sylvie Slezak Photography/Getty Images (salt pouring) Tom Gill/Getty Images (sugar pouring) Tom Gill/Getty Images

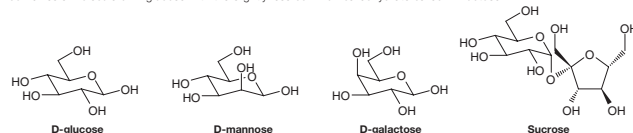
**WHY DO THESE TOPICS MATTER?**

New opening vignettes prepare the students and foreshadow the relevance of chapter content, asking the question “Why do these topics matter?” Closing vignettes answer the question by relating real world or historical aspects of organic chemistry.

**[ WHY Do These Topics Matter? ]**

## SUBSTITUTING THE CALORIES OF TABLE SUGAR

As we shall see in more detail in Chapter 24, simple carbohydrates, or monosaccharides, can exist in the form of a six-membered ring system with a chair conformation. The name carbohydrate derives from “hydrated carbon” since most carbon atoms have an H and OH attached. In the examples below, the structural differences of the monosaccharides glucose, mannose, and galactose are based on the change of one or more chirality centers through what we could formally consider to be an inversion reaction. As such, all of these carbohydrates are diastereomers of each other. Based on what you already know about torsional strain from Chapter 4, it should come as no surprise that D-glucose is the most common monosaccharide; D-glucose has the least strain because all of its substituents are in equatorial positions. All other six-carbon sugars have at least one axial group, and thus possess some 1,3-diaxial strain. Standard table sugar, or sucrose, is a disaccharide, since it combines a molecule of D-glucose with the slightly less common carbohydrate called D-fructose.



All carbohydrates taste sweet, though not equally so. D-Fructose, for example, tastes approximately 1.5 times sweeter than the same amount of simple table sugar, while D-glucose is only about 0.75 times as sweet. Irrespective of their individual degrees of sweetness, however, it is the fact that they are all sweet that lets us perceive their presence in foods whether they are found naturally or have been added (often from corn syrup or cane sugar) to create a more unique flavor profile. Either way, their

239

**Getting to the heart of the matter quicker** Acid-base chemistry, and electrophiles and nucleophiles are at the heart of organic chemistry. Students cannot master the subject if they do not have a firm and early grasp of these topics. In this edition, we cut to the chase with these topics earlier in Chapter 3 than ever before, providing a streamlined and highly efficient route to student mastery of these critical concepts.

**Improving a core area: substitution reactions** All organic instructors know how important it is for their students to have a solid understanding of substitution reactions. This is one reason our text has proven its lasting value. In this edition we have even further enhanced the presentation of substitution reactions in several ways, including a revised introduction of  $S_N1$  reactions (Section 6.10) through the classic hydrolysis experiments of Hughes, and a newly organized presentation of solvent effects on the rate of substitution reactions.

**Striking a strong balance of synthetic methods** Students need to learn methods of organic synthesis that are useful, as environmentally friendly as possible, and that are placed in the best overall contextual framework. In this edition we incorporate the Swern oxidation (Section 12.4), long held as a useful oxidation method and one that provides a less toxic alternative to chromate oxidations in some cases. We also restore coverage of the Wolff-Kishner reduction (Section 16.8C) and the Baeyer-Villiger oxidation (Section 16.12), two methods whose importance has been proven by the test of time. The chemistry of radical reactions has also been refocused and streamlined by reducing thermochemistry content and by centralizing the coverage of allylic and benzylic radical substitutions (including NBS reactions) in one chapter (Sections 10.8 and 10.9), instead of distributing it between two, as before. The addition of sulfuric acid to alkenes and the Kolbe reaction have been deleted from the text, since these have little practical use in the laboratory. Toward the inclusion of modern, though mechanistically complex, methods of organic synthesis, we introduce catalytic oxidation methods (e.g., Sharpless and others) in special boxes, and provide coverage of transition metal organometallic reactions (Heck, Suzuki, and others) in Special Topic G.

**Maintaining an eye for clarity** With every edition we improve the presentation of topics, reactions, and diagrams where the opportunity arises. In this edition some examples include improved discussion and diagrams regarding endo and exo Diels-Alder transition states, the effect of diene stereochemistry in Diels-Alder reactions (Section 13.10B), and improved mechanism depictions for aromatic sulfonation and thionyl chloride substitution.

**Resonating with topics in spectroscopy** The authors have incorporated new figures to depict shielding and deshielding of alkenyl and alkynyl hydrogens by magnetic anisotropy, and clarified the discussion of shielding and deshielding in NMR chemical shifts (no longer invoking the terms upfield and downfield). The discussion of chlorine and bromine isotopic signatures in mass spectra has been enhanced, and presentation of mass spectrometer designs has been refocused.

**Showing how things work** A mechanistic understanding of organic chemistry is key to student success in organic chemistry. Mechanisms have always been central to the book, and in this edition the authors have added a mechanistic framework for the Swern and chromate alcohol oxidations (Section 12.4) by presenting elimination of the carbinol hydrogen and a leaving group from oxygen as the common theme.

## TRADITIONAL PEDAGOGICAL STRENGTHS

**Solved Problems** Knowing “where to begin” to solve organic chemistry problems is one of the greatest challenges faced by today’s students. By modeling problem solving strategies, students begin to understand the patterns inherent in organic chemistry and learn to apply that knowledge to new situations. In this edition we have added even more Solved Problems. Now over 165 Solved Problems guide students in their strategies for problem solving. Solved Problems are **usually paired with a related Practice Problem**.

**Practice Problems** Students need ample opportunities to practice and apply their new found strategies for solving organic chemistry problems. We’ve added to our rich array of in-text Practice Problems to provide students with even more opportunities to check their progress as they study. If they can work the practice problem, they should move on. If not, they should review the preceding presentation.

### SOLVED PROBLEMS

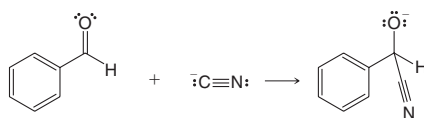
model problem solving strategies.

### PRACTICE PROBLEMS

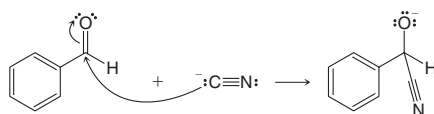
provides opportunities to check progress.

#### SOLVED PROBLEM 3.3

Identify the electrophile and the nucleophile in the following reaction, and add curved arrows to indicate the flow of electrons for the bond-forming and bond-breaking steps.



**STRATEGY AND ANSWER:** The aldehyde carbon is electrophilic due to the electronegativity of the carbonyl oxygen. The cyanide anion acts as a Lewis base and is the nucleophile, donating an electron pair to the carbonyl carbon, and causing an electron pair to shift to the oxygen so that no atom has more than an octet of electrons.

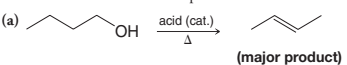


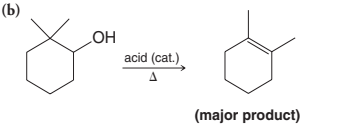
#### PRACTICE PROBLEM 3.4

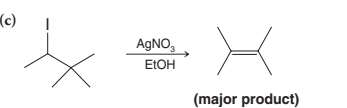
Use the curved-arrow notation to write the reaction that would take place between dimethylamine ( $\text{CH}_3$ )<sub>2</sub>NH and boron trifluoride. Identify the Lewis acid, Lewis base, nucleophile, and electrophile and assign appropriate formal charges.

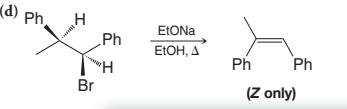
**End-of-Chapter Problems** As athletes and musicians know, practice makes perfect. The same is true with organic chemistry. The End of Chapter problems, categorized by topic, provide essential practice for students and help them build mastery of both concepts and skills presented throughout the chapter. Many of the End of Chapter problems are cast in a visual format using structures, equations, and schemes. In addition, we still provide **Challenge Problems** and **Learning Group Problems** to address myriad teaching goals and styles. Learning Group Problems engage students in synthesizing information and concepts from throughout a chapter. They can be used to facilitate collaborative learning in small groups, and can serve as a culminating activity that demonstrates student mastery over an integrated set of principles. Supplementary material provided to instructors includes suggestions about how to orchestrate the use of learning groups.

**7.44** Provide a mechanistic explanation for each of the following reactions:

(a)  (major product)

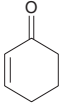
(b)  (major product)

(c)  (major product)

(d)  (Z only)

**INDEX OF HYDROGEN DEFICIENCY**

**7.45** What is the index of hydrogen deficiency (IHD) (degree of unsaturation) for each of the following?

(a)  (b)  $C_6H_8Br_4$

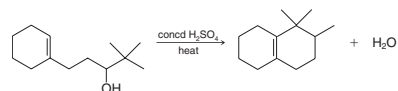
**7.46** Caryophyllene, a compound found in oil of cloves, has the molecular formula  $C_{15}H_{24}$ . When caryophyllene is hydrogenated with an excess of hydrogen in the presence of a platinum catalyst produces a compound with the molecular formula  $C_{15}H_{28}$ . How many (a) double bonds and (b) rings does a molecule of caryophyllene have?

### END-OF-CHAPTER

**PROBLEMS** are grouped and labeled by topic. Students and instructors can more easily select problems for specific purposes.

### LEARNING GROUP PROBLEMS

- (a) Synthesize (3*S*,4*R*)-3,4-dibromo-1-cyclohexylpentane (and its enantiomer, since a racemic mixture will be formed) from ethyne, 1-chloro-2-cyclohexylethane, bromomethane, and any other reagents necessary. (Use ethyne, 1-chloro-2-cyclohexylethane, and bromomethane as the sole sources of carbon atoms.) Start the problem by showing a retrosynthetic analysis. In the process, decide which atoms of the target molecule will come from which atoms of the starting reagents. Also, bear in mind how the stereospecificity of the reactions you employ can be used to achieve the required stereochemical form of the final product.
  - Explain why a racemic mixture of products results from this synthesis.
  - How could the synthesis be modified to produce a racemic mixture of the (3*R*,4*R*) and (3*S*,4*S*) isomers instead?
- Write a reasonable and detailed mechanism for the following transformation:



**A Mechanism for the Reaction** Understanding mechanisms and the ability to recognize patterns among them is a key component in determining student success in organic chemistry. We provide A Mechanism for the Reaction boxes that show step-by-step details about how reactions take place so that students have the tools to understand rather than memorize organic reactions.

### A MECHANISM FOR THE REACTION

Stepped out reactions with just the right amount of detail provides the tools for students to understand rather than memorize reaction mechanisms

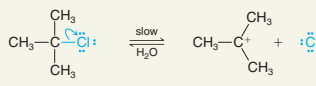
**[ A MECHANISM FOR THE REACTION — Mechanism for the  $S_N1$  Reaction ]**

**Reaction**

$$CH_3-C(CH_3)_2-Cl + 2 H_2O \longrightarrow CH_3-C(CH_3)_2-OH + H_3O^+ + :Cl^-$$

**Mechanism**

**Step 1**

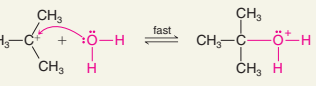


Aided by the polar solvent, a chlorine departs with the electron pair that bonded it to the carbon.

This slow step produces the 3° carbocation intermediate and a chloride ion. Although not shown here, the ions are solvated (and stabilized) by water molecules.

**Free energy diagram for Step 1:** The energy profile shows a single high energy barrier (Transition state 1) leading to a local minimum (the carbocation intermediate). The activation energy is  $\Delta G^\ddagger_{(1)}$ , which is much larger than  $\Delta G^\ddagger_{(2)}$  or  $\Delta G^\ddagger_{(3)}$ , hence this is the slowest step.

**Step 2**

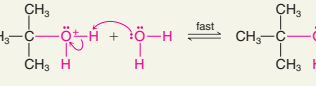


A water molecule acting as a Lewis base donates an electron pair to the carbocation (a Lewis acid). This gives the cationic carbon eight electrons.

The product is a tert-butyl oxonium ion (or protonated tert-butyl alcohol).

**Free energy diagram for Step 2:** The energy profile shows a lower energy barrier (Transition state 2) leading to a local minimum (the oxonium ion intermediate).

**Step 3**



A water molecule acting as a Brønsted base accepts a proton from the tert-butyl oxonium ion.

The products are tert-butyl alcohol and a hydronium ion.

**Free energy diagram for Step 3:** The energy profile shows a very low energy barrier (Transition state 3) leading to the final products.

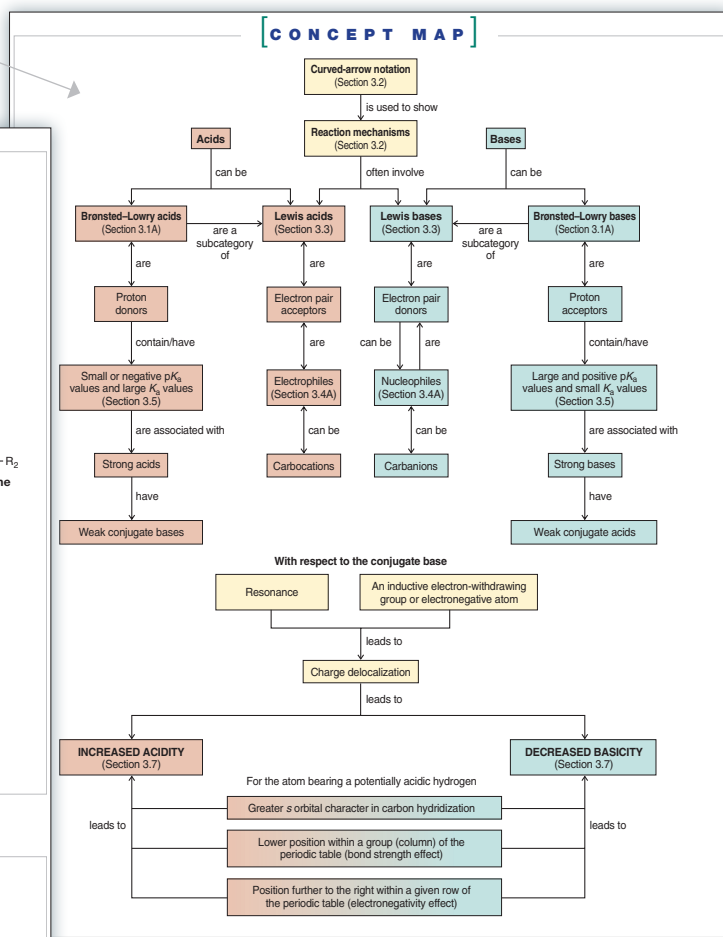
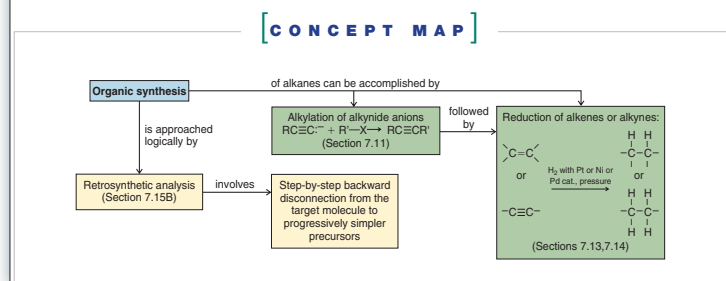
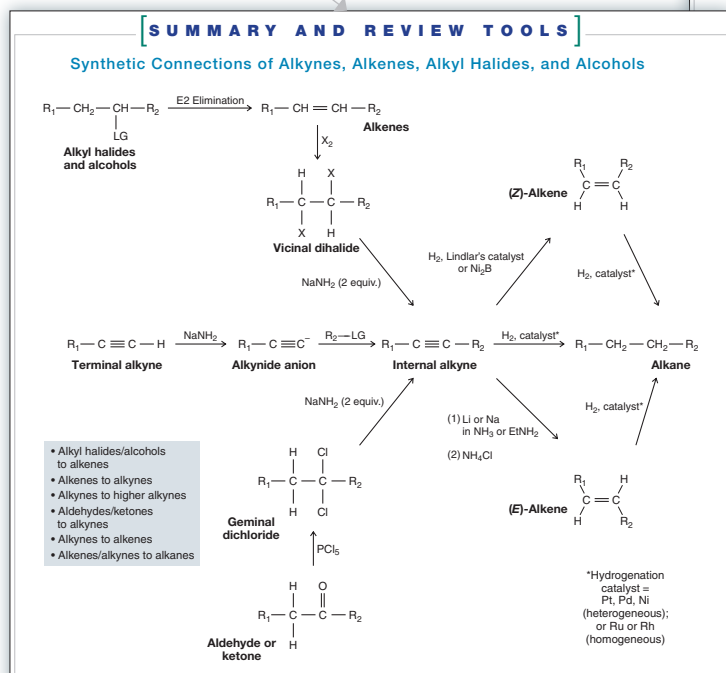
**Key Ideas as Bullet Points** The amount of content covered in organic chemistry can be overwhelming to students. To help students focus on the most essential topics, key ideas are emphasized as bullet points in every section. In preparing bullet points, we have distilled appropriate concepts into simple declarative statements that convey core ideas accurately and clearly. No topic is ever presented as a bullet point if its integrity would be diminished by oversimplification, however.

**“How to” Sections** Students need to master important skills to support their conceptual learning. “How to” Sections throughout the text give step-by-step instructions to guide students in performing important tasks, such as using curved arrows, drawing chair conformations, planning a Grignard synthesis, determining formal charges, writing Lewis structures, and using  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra to determine structure.

**The Chemistry of . . .** Virtually every instructor has the goal of showing students how organic chemistry relates to their field of study and to their everyday life experience. The authors assist their colleagues in this goal by providing boxes titled “The Chemistry of . . .” that provide interesting and targeted examples that engage the student with chapter content.

**Summary and Review Tools** At the end of each chapter, Summary and Review Tools provide visually oriented roadmaps and frameworks that students can use to help organize and assimilate concepts as they study and review chapter content. Intended to accommodate diverse learning styles, these include Synthetic Connections, Concept Maps, Thematic Mechanism Review Summaries, and the detailed Mechanism for the Reaction boxes already mentioned. We also provide Helpful Hints and richly annotated illustrations throughout the text.

**SUMMARY AND REVIEW TOOLS** Visually oriented study tools accommodate diverse learning styles.





## COVERAGE

Throughout the book, we have streamlined or reduced content to match the modern practice of organic chemistry, and we have provided new coverage of current reactions, while maintaining our commitment to an appropriate level and breadth of coverage.

- Chapters on carbonyl chemistry that are organized to emphasize mechanistic themes of nucleophilic addition, acyl substitution, and reactivity at the  $\alpha$ -carbon.
- Presentation of the important modern synthetic methods of the Grubbs, Heck, Sonogashira, Stille, and Suzuki transition metal catalyzed carbon-carbon bond-forming reactions in a practical and student-oriented way that includes review problems and mechanistic context (Special Topic G).

## ORGANIZATION — An Emphasis on the Fundamentals

So much of organic chemistry makes sense and can be generalized if students master and apply a few fundamental concepts. Therein lays the beauty of organic chemistry. If students learn the essential principles, they will see that memorization is not needed to succeed.

Most important is for students to have a solid understanding of structure—of hybridization and geometry, steric hindrance, electronegativity, polarity, formal charges, and resonance—so that they can make intuitive sense of mechanisms. It is with these topics that we begin in Chapter 1. In Chapter 2 we introduce the families of functional groups—so that students have a platform on which to apply these concepts. We also introduce intermolecular forces, and infrared (IR) spectroscopy—a key tool for identifying functional groups. Throughout the book we include calculated models of molecular orbitals, electron density surfaces, and maps of electrostatic potential. These models enhance students' appreciation for the role of structure in properties and reactivity.

We begin our study of mechanisms in the context of acid-base chemistry in Chapter 3. Acid-base reactions are fundamental to organic reactions, and they lend themselves to introducing several important topics that students need early in the course: (1) curved arrow notation for illustrating mechanisms, (2) the relationship between free-energy changes and equilibrium constants, and (3) the importance of inductive and resonance effects and of solvent effects.

In Chapter 3 we present the first of many “A Mechanism for the Reaction” boxes, using an example that embodies both Brønsted-Lowry and Lewis acid-base principles. All throughout the book, we use boxes like these to show the details of key reaction mechanisms. All of the Mechanism for the Reaction boxes are listed in the Table of Contents so that students can easily refer to them when desired.

A central theme of our approach is to emphasize the relationship between structure and reactivity. This is why we choose an organization that combines the most useful features of a functional group approach with one based on reaction mechanisms. Our philosophy is to emphasize mechanisms and fundamental principles, while giving students the anchor points of functional groups to apply their mechanistic knowledge and intuition. The structural aspects of our approach show students what organic chemistry is. Mechanistic aspects of our approach show students how it works. And wherever an opportunity arises, we show them what it does in living systems and the physical world around us.

In summary, our writing reflects the commitment we have as teachers to do the best we can to help students learn organic chemistry and to see how they can apply their knowledge to improve our world. The enduring features of our book have proven over the years to help students learn organic chemistry. The changes in our 11th edition make organic chemistry even more accessible and relevant. Students who use the in-text learning aids, work the problems, and take advantage of the resources and practice available in *WileyPLUS* (our online teaching and learning solution) will be assured of success in organic chemistry.

# TEACHING AND LEARNING RESOURCES

## WILEYPLUS FOR ORGANIC CHEMISTRY— A Powerful Teaching and Learning Solution



*WileyPLUS* is an innovative, research-based online environment for effective teaching and learning. *WileyPLUS* builds student confidence because it takes the guesswork out of studying by providing students with a clear roadmap: what to do, how to do it, if they did it right. Students will take more initiative so instructors will have greater impact on their achievement in the classroom and beyond.

**Breadth of Depth of Assessment:** Four unique silos of assessment are available to instructors for creating online homework and quizzes and are designed to enable and support problem-solving skill development and conceptual understanding

### WILEYPLUS ASSESSMENT FOR ORGANIC CHEMISTRY

REACTION EXPLORER	MEANINGFUL PRACTICE OF MECHANISMS AND SYNTHESIS PROBLEMS (A DATABASE OF OVER 100,000 QUESTIONS)
IN CHAPTER/EOC ASSESSMENT	90-100% OF REVIEW PROBLEMS AND END OF CHAPTER (EOC) QUESTIONS ARE CODED FOR ONLINE ASSESSMENT
CONCEPT MASTERY	PRE-BUILT CONCEPT MASTERY ASSIGNMENTS ( FROM DATABASE OF OVER 25,000 QUESTIONS)
TEST BANK	RICH TESTBANK CONSISTING OF OVER 3,000 QUESTIONS

**Reaction Explorer** Students ability to understand mechanisms and predict synthesis reactions greatly impacts their level of success in the course. Reaction Explorer is an interactive system for **learning and practicing reactions, syntheses** and **mechanisms** in organic chemistry with advanced support for the automatic generation of random problems and curved arrow mechanism diagrams.

### MECHANISM EXPLORER:

valuable practice with reactions and mechanisms

### SYNTHESIS EXPLORER:

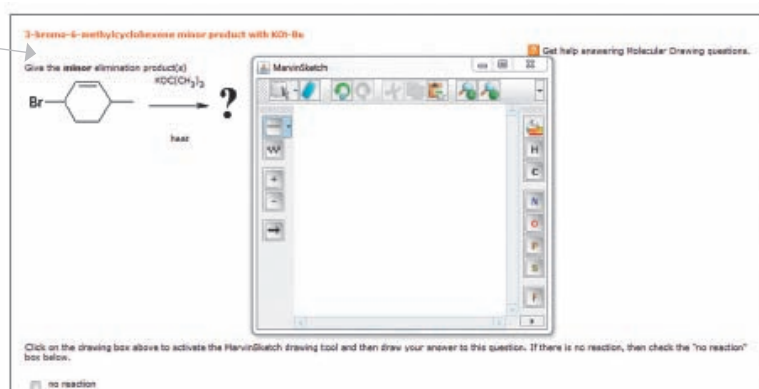
meaningful practice with single and multi-step synthesis

The image displays two screenshots from the WileyPLUS interface. The left screenshot, titled "Mechanism Step Sketch and Submission", shows a chemical reaction step where a methyl bromide cation ( $\text{H}_3\text{C}-\text{Br}^+$ ) reacts with a cyanide ion ( $:\text{N}\equiv\text{C}^-$ ). Below the reaction is a "Submitted Mechanism Steps" table with columns for "Reactant / Intermediate" and "Product / Intermediate". The "Overall Reaction" section shows the full reaction:  $\text{H}_3\text{C}-\text{Br} + \text{N}\equiv\text{C}^- + \text{Na}^+ \xrightarrow{\text{Mix Reactants, Aprotic}} \text{N}\equiv\text{C}-\text{CH}_3$ . The right screenshot, titled "Synthesis Explorer", shows a multi-step synthesis problem. It includes a "Reactants" section with  $\text{Br}-\text{CH}_3$  and  $\text{H}_3\text{C}-\text{CH}_2-\text{Br}$ , a "Reagents" section with instructions: "1. Mix Reactants in DMF or THF (solvent) (2.  $\text{H}_2\text{O}$  (Aqueous workup))" and "Mix Reactants in Alcohol (solvent)", and a "Target Product" section with a nitrile structure. A "Pathway" section at the bottom shows a sequence of boxes for "Select a Reactant", "Select a Reagent", and "Apply Reaction to Generate Product(s)".

**End of Chapter Problems.** Approximately 90% of the end of chapter problems are included in *WileyPLUS*. Many of the problems are algorithmic and feature structure drawing/assessment functionality using MarvinSketch, with immediate answer feedback and video question assistance. A subset of these end of chapter problems is linked to **Guided Online tutorials** which are stepped-out problem-solving tutorials that walk the student through the problem, offering individualized feedback at each step.

**Prebuilt concept mastery assignments** Students must continuously practice and work organic chemistry in order to master the concepts and skills presented in the course. Prebuilt concept mastery assignments offer students ample opportunities for practice, covering all the major topics and concepts within an organic chemistry course. Each assignment is organized by topic and features **feedback for incorrect answers**. These assignments are drawn from a unique database of over 25,000 questions, over half of which require students to draw a structure using MarvinSketch.

### PREBUILT CONCEPT MASTERY ASSIGNMENTS



## WHAT DO STUDENTS RECEIVE WITH WILEYPLUS?

- The complete digital textbook, saving students up to 60% off the cost of a printed text.
- Question assistance, including links to relevant sections in the online digital textbook.
- Immediate feedback and proof of progress, 24/7.
- Integrated, multi-media resources that address students' unique learning styles, levels of proficiency, and levels of preparation by providing multiple study paths and encourage more active learning.

## WILEYPLUS STUDENT RESOURCES

**NEW Chapter 0 General Chemistry Refresher.** To ensure students have mastered the necessary prerequisite content from general chemistry, and to eliminate the burden on instructors to review this material in lecture, *WileyPLUS* now includes a complete chapter of core general chemistry topics with corresponding assignments. Chapter 0 is available to students and can be assigned in *WileyPLUS* to ensure and gauge understanding of the core topics required to succeed in organic chemistry.

**NEW Prelecture Assignments.** Preloaded and ready to use, these assignments have been carefully designed to assess students prior to their coming to class. Instructors can assign these pre-created quizzes to gauge student preparedness prior to lecture and tailor class time based on the scores and participation of their students.

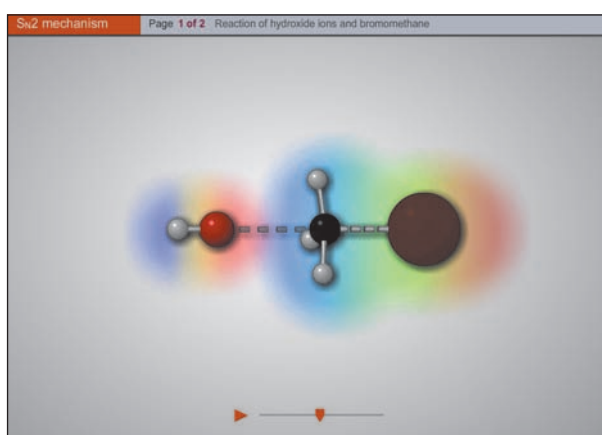




**Video Mini-Lectures, Office Hour Videos, and Solved Problem Videos** In each chapter, several types of video assistance are included to help students with conceptual understanding and problem solving strategies. The video mini-lectures focus on challenging concepts; the office hours videos take these concepts and apply them to example problems, emulating the experience that a student would get if she or he were to attend office hours and ask for assistance in working a problem. The Solved Problem videos demonstrate good problem solving strategies for the student by walking through in text solved problems using audio and a whiteboard. The goal is to illustrate good problem solving strategies.

**Skill Building Exercises** are animated exercises with instant feedback to reinforce the key skills required to succeed in organic chemistry.

**3D Molecular Visualizations** use the latest visualization technologies to help students visualize concepts with audio. Instructors can assign quizzes based on these visualizations in *WileyPLUS*.




## WHAT DO INSTRUCTORS RECEIVE WITH WILEYPLUS?

- Reliable resources that reinforce course goals inside and outside of the classroom.
- The ability to easily identify students who are falling behind by tracking their progress and offering assistance easily, even before they come to office hours. *WileyPLUS* simplifies and automates such tasks as student performance assessment, creating assignments, scoring student work, keeping grades, and more.
- Media-rich course materials and assessment content that allow you to customize your classroom presentation with a wealth of resources and functionality from PowerPoint slides to a database of rich visuals. You can even add your own materials to your *WileyPLUS* course.

## ADDITIONAL INSTRUCTOR RESOURCES

All Instructor Resources are available within *WileyPLUS* or they can be accessed by contacting your local Wiley Sales Representative. Many of the assets are located on the book companion site, [www.wiley.com/college/solomons](http://www.wiley.com/college/solomons)

**Test Bank** Authored by Robert Rossi, of Gloucester County College, Jeffrey Allison, of Austin Community College, and Gloria Silva, of Carnegie Mellon University, the Test Bank for this edition has been completely revised and updated to include over 3,000 short answer, multiple choice, and essay/drawing questions. The Test Bank files, along with a software tool for managing and creating exams, are available online.



**PowerPoint Lecture Slides** PowerPoint Lecture Slides have been prepared by Professor William Tam, of the University of Guelph, Dr. Phillis Chang, and Gary Porter, of Bergen Community College. The PowerPoint slides include additional examples, illustrations, and presentations that help reinforce and test students' grasp of organic chemistry concepts. An additional set of PowerPoint slides features the illustrations, figures, and tables from the text. All PowerPoint slide presentations are customizable to fit your course.

**Personal Response System (“Clicker”) Questions** A bank of questions is available for anyone using personal response system technology in their classroom. The clicker questions are also available in a separate set of PowerPoint slides.

**Digital Image Library** Images from the text are available online in JPEG format. Instructors may use these images to customize their presentations and to provide additional visual support for quizzes and exams.

## ADDITIONAL STUDENT RESOURCES

### Study Guide and Solutions Manual (978-1-118-14790-0)

The Study Guide and Solutions Manual for *Organic Chemistry, Eleventh Edition*, authored by Jon Antilla, of the University of South Florida, Robert Johnson, of Xavier University, Craig Fryhle, Graham Solomons, and Scott Snyder **contains explained solutions to all of the problems in the text.** The Study Guide also contains:

- An introductory essay “Solving the Puzzle—or—Structure is Everything” that serves as a bridge from general to organic chemistry
- Summary tables of reactions by mechanistic type and functional group
- A review quiz for each chapter
- A set of hands-on molecular model exercises
- Solutions to the problems in the Special Topics sections (many of the Special Topics are only available within *WileyPLUS*)

## MOLECULAR VISIONS™ MODEL KITS

We believe that the tactile and visual experience of manipulating physical models is key to students' understanding that organic molecules have shape and occupy space. To support our pedagogy, we have arranged with the Darling Company to bundle a special ensemble of Molecular Visions™ model kits with our book (for those who choose that option). We use Helpful Hint icons and margin notes to frequently encourage students to use hand-held models to investigate the three-dimensional shape of molecules we are discussing in the book.

## CUSTOMIZATION AND FLEXIBLE OPTIONS TO MEET YOUR NEEDS

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SCOTT A. SNYDER



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**T. W. GRAHAM SOLOMONS** did his undergraduate work at The Citadel and received his doctorate in organic chemistry in 1959 from Duke University where he worked with C. K. Bradsher. Following this he was a Sloan Foundation Postdoctoral Fellow at the University of Rochester where he worked with V. Boekelheide. In 1960 he became a charter member of the faculty of the University of South Florida and became Professor of Chemistry in 1973. In 1992 he was made Professor Emeritus. In 1994 he was a visiting professor with the Faculté des Sciences Pharmaceutiques et Biologiques, Université René Descartes (Paris V). He is a member of Sigma Xi, Phi Lambda Upsilon, and Sigma Pi Sigma. He has received research grants from the Research Corporation and the American Chemical Society Petroleum Research Fund. For several years he was director of an NSF-sponsored Undergraduate Research Participation Program at USF. His research interests have been in the areas of heterocyclic chemistry and unusual aromatic compounds. He has published papers in the *Journal of the American Chemical Society*, the *Journal of Organic Chemistry*, and the *Journal of Heterocyclic Chemistry*. He has received several awards for distinguished teaching. His organic chemistry textbooks have been widely used for 30 years and have been translated into French, Japanese, Chinese, Korean, Malaysian, Arabic, Portuguese, Spanish, Turkish, and Italian. He and his wife Judith have a daughter who is a building conservator and a son who is a research biochemist.

**CRAIG BARTON FRYHLE** is Chair and Professor of Chemistry at Pacific Lutheran University. He earned his B.A. degree from Gettysburg College and Ph.D. from Brown University. His experiences at these institutions shaped his dedication to mentoring undergraduate students in chemistry and the liberal arts, which is a passion that burns strongly for him. His research interests have been in areas relating to the shikimic acid pathway, including molecular modeling and NMR spectrometry of substrates and analogues, as well as structure and reactivity studies of shikimate pathway enzymes using isotopic labeling and mass spectrometry. He has mentored many students in undergraduate research, a number of who have later earned their Ph.D. degrees and gone on to academic or industrial positions. He has participated in workshops on fostering undergraduate participation in research, and has been an invited participant in efforts by the National Science Foundation to enhance undergraduate research in chemistry. He has received research and instrumentation grants from the National Science Foundation, the M J. Murdock Charitable Trust, and other private foundations. His work in chemical education, in addition to textbook coauthorship, involves incorporation of student-led teaching in the classroom and technology-based strategies in organic chemistry. He has also developed experiments for undergraduate students in organic laboratory and instrumental analysis courses. He has been a volunteer with the hands-on science program in Seattle public schools, and Chair of the Puget Sound Section of the American Chemical Society. His passion for climbing has led to ascents of high peaks in several parts of the world. He resides in Seattle with his wife, where both enjoy following the lives of their two daughters as they unfold in new places.

**SCOTT A. SNYDER** is Associate Professor of Chemistry at Columbia University. He grew up in the suburbs of Buffalo NY and was an undergraduate at Williams College, where he graduated summa cum laude in 1999, before pursuing his doctoral studies at The Scripps Research Institute under the tutelage of K. C. Nicolaou as an NSF, Pfizer, and Bristol-Myers-Squibb predoctoral fellow. While there, he co-authored the graduate textbook *Classics in Total Synthesis II* with his doctoral mentor. Scott was then an NIH postdoctoral fellow in the laboratories of E. J. Corey at Harvard University before assuming his current position in 2006. His research interests lie in the arena of natural products total synthesis, especially in the realm of unique polyphenols and halogenated materials, and to date he has trained more than 60 students at the high school, undergraduate, graduate, and postdoctoral levels and co-authored more than 40 research and review articles. Scott has received a number of awards and honors, including a Camille and Henry Dreyfus New Faculty Award, Amgen New Faculty and Young Investigator Awards, Eli Lilly New Faculty and Grantee Awards, a Bristol-Myers Squibb Unrestricted Grant Award, an NSF CAREER Award, an Alfred P. Sloan Foundation Fellowship, a DuPont Young Professor Award, and an Arthur C. Cope Scholar Award from the American Chemical Society. He has also received recognition for his teaching through a Cottrell Scholar Award from the Research Corporation for Science Advancement and a Columbia Presidential Teaching Award. He is a member of the international advisory board for *The Chemical Record* and the editorial board of *Chirality*. He lives north of New York City with his wife Cathy where he enjoys gardening, cooking, and watching movies.



# [ TO THE STUDENT ]

Contrary to what you may have heard, organic chemistry does not have to be a difficult course. It will be a rigorous course, and it will offer a challenge. But you will learn more in it than in almost any course you will take—and what you learn will have a special relevance to life and the world around you. However, because organic chemistry can be approached in a logical and systematic way, you will find that with the right study habits, mastering organic chemistry can be a deeply satisfying experience. Here, then, are some suggestions about how to study:

**1. Keep up with your work from day to day—never let yourself get behind.**

Organic chemistry is a course in which one idea almost always builds on another that has gone before. It is essential, therefore, that you keep up with, or better yet, be a little ahead of your instructor. Ideally, you should try to stay one day ahead of your instructor's lectures in your own class preparations. The lecture, then, will be much more helpful because you will already have some understanding of the assigned material. Your time in class will clarify and expand ideas that are already familiar ones.

**2. Study material in small units, and be sure that you understand each new section before you go on to the next.**

Again, because of the cumulative nature of organic chemistry, your studying will be much more effective if you take each new idea as it comes and try to understand it completely before you move on to the next concept.

**3. Work all of the in-chapter and assigned problems.**

One way to check your progress is to work each of the in-chapter problems when you come to it. These problems have been written just for this purpose and are designed to help you decide whether or not you understand the material that has just been explained. You should also carefully study the Solved Problems. If you understand a Solved Problem and can work the related in-chapter problem, then you should go on; if you cannot, then you should go back and study the preceding material again. Work all of the problems assigned by your instructor from the end of the chapter, as well. Do all of your problems in a notebook and bring this book with you when you go to see your instructor for extra help.

**4. Write when you study.**

Write the reactions, mechanisms, structures, and so on, over and over again. Organic chemistry is best assimilated through the fingertips by writing, and not through the eyes by simply looking, or by highlighting material in the text, or by referring to flash cards. There is a good reason for this. Organic structures, mechanisms, and reactions

are complex. If you simply examine them, you may think you understand them thoroughly, but that will be a misperception. The reaction mechanism may make sense to you in a certain way, but you need a deeper understanding than this. You need to know the material so thoroughly that you can explain it to someone else. This level of understanding comes to most of us (those of us without photographic memories) through writing. Only by writing the reaction mechanisms do we pay sufficient attention to their details, such as which atoms are connected to which atoms, which bonds break in a reaction and which bonds form, and the three-dimensional aspects of the structures. When we write reactions and mechanisms, connections are made in our brains that provide the long-term memory needed for success in organic chemistry. We virtually guarantee that your grade in the course will be directly proportional to the number of pages of paper that you fill with your own writing in studying during the term.

**5. Learn by teaching and explaining.**

Study with your student peers and practice explaining concepts and mechanisms to each other. Use the Learning Group Problems and other exercises your instructor may assign as vehicles for teaching and learning interactively with your peers.

**6. Use the answers to the problems in the Study Guide in the proper way.**

Refer to the answers only in two circumstances: (1) When you have finished a problem, use the Study Guide to check your answer. (2) When, after making a real effort to solve the problem, you find that you are completely stuck, then look at the answer for a clue and go back to work out the problem on your own. The value of a problem is in solving it. If you simply read the problem and look up the answer, you will deprive yourself of an important way to learn.

**7. Use molecular models when you study.**

Because of the three-dimensional nature of most organic molecules, molecular models can be an invaluable aid to your understanding of them. When you need to see the three-dimensional aspect of a particular topic, use the Molecular Visions™ model set that may have been packaged with your textbook, or buy a set of models separately. An appendix to the *Study Guide* that accompanies this text provides a set of highly useful molecular model exercises.

**8. Make use of the rich online teaching resources in WileyPLUS**

and do any online exercises that may be assigned by your instructor.



CHAPTER

# 1



## The Basics

### BONDING AND MOLECULAR STRUCTURE

**O**rganic chemistry plays a role in all aspects of our lives, from the clothing we wear, to the pixels of our television and computer screens, to preservatives in food, to the inks that color the pages of this book. If you take the time to understand organic chemistry, to learn its overall logic, then you will truly have the power to change society. Indeed, organic chemistry provides the power to synthesize new drugs, to engineer molecules that can make computer processors run more quickly, to understand why grilled meat can cause cancer and how its effects can be combated, and to design ways to knock the calories out of sugar while still making food taste deliciously sweet. It can explain biochemical processes like aging, neural functioning, and cardiac arrest, and show how we can prolong and improve life. It can do almost anything.

#### IN THIS CHAPTER WE WILL CONSIDER:

- what kinds of atoms make up organic molecules
- the principles that determine how the atoms in organic molecules are bound together
- how best to depict organic molecules

**[ WHY DO THESE TOPICS MATTER? ]** At the end of the chapter, we will see how some of the unique organic structures that nature has woven together possess amazing properties that we can harness to aid human health.

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## 1.1 LIFE AND THE CHEMISTRY OF CARBON COMPOUNDS—WE ARE STARDUST



NASA/Photo Researchers, Inc.

Supernovae were the crucibles in which the heavy elements were formed.

**Organic chemistry is the chemistry of compounds that contain the element carbon.** If a compound does not contain the element carbon, it is said to be *inorganic*.

Look for a moment at the periodic table inside the front cover of this book. More than a hundred elements are listed there. The question that comes to mind is this: why should an entire field of chemistry be based on the chemistry of compounds that contain this one element, carbon? There are several reasons, the primary one being this: **carbon compounds are central to the structure of living organisms and therefore to the existence of life on Earth. We exist because of carbon compounds.**

What is it about carbon that makes it the element that nature has chosen for living organisms? There are two important reasons: carbon atoms can form strong bonds to other carbon atoms to form rings and chains of carbon atoms, and carbon atoms can also form strong bonds to elements such as hydrogen, nitrogen, oxygen, and sulfur. Because of these bond-forming properties, carbon can be the basis for the huge diversity of compounds necessary for the emergence of living organisms.

From time to time, writers of science fiction have speculated about the possibility of life on other planets being based on the compounds of another element—for example, silicon, the element most like carbon. However, the bonds that silicon atoms form to each other are not nearly as strong as those formed by carbon, and therefore it is very unlikely that silicon could be the basis for anything equivalent to life as we know it.

### 1.1A What Is the Origin of the Element Carbon?

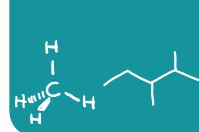
Through the efforts of physicists and cosmologists, we now understand much of how the elements came into being. The light elements hydrogen and helium were formed at the beginning, in the Big Bang. Lithium, beryllium, and boron, the next three elements, were formed shortly thereafter when the universe had cooled somewhat. All of the heavier elements were formed millions of years later in the interiors of stars through reactions in which the nuclei of lighter elements fuse to form heavier elements.

The energy of stars comes primarily from the fusion of hydrogen nuclei to produce helium nuclei. This nuclear reaction explains why stars shine. Eventually some stars begin to run out of hydrogen, collapse, and explode—they become supernovae. Supernovae explosions scatter heavy elements throughout space. Eventually, some of these heavy elements drawn by the force of gravity became part of the mass of planets like the Earth.

### 1.1B How Did Living Organisms Arise?

This question is one for which an adequate answer cannot be given now because there are many things about the emergence of life that we do not understand. However, we do know this. Organic compounds, some of considerable complexity, are detected in outer space, and meteorites containing organic compounds have rained down on Earth since it was formed. A meteorite that fell near Murchison, Victoria, Australia, in 1969 was found to contain over 90 different amino acids, 19 of which are found in living organisms on Earth. While this does not mean that life arose in outer space, it does suggest that events in outer space may have contributed to the emergence of life on Earth.

In 1924 Alexander Oparin, a biochemist at the Moscow State University, postulated that life on Earth may have developed through the gradual evolution of carbon-based molecules in a “primordial soup” of the compounds that were thought to exist on a prebiotic Earth: methane, hydrogen, water, and ammonia. This idea was tested by experiments carried out at the University of Chicago in 1952 by Stanley Miller and Harold Urey. They showed that amino acids and other complex organic compounds are synthesized when an electric spark (think of lightning) passes through a flask containing a mixture of these four compounds (think of the early atmosphere). Miller and Urey in their 1953 publication reported that five amino acids (essential constituents of proteins) were formed. In 2008, examination of archived solutions from Miller and Urey’s original



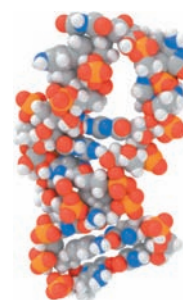
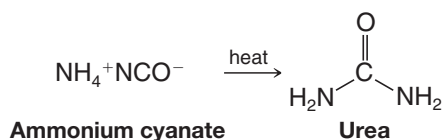
experiments have shown that 22 amino acids, rather than the 5 amino acids originally reported, were actually formed.

Similar experiments have shown that other precursors of biomolecules can also arise in this way—compounds such as ribose and adenine, two components of RNA. Some RNA molecules can not only store genetic information as DNA does, they can also act as catalysts, as enzymes do.

There is much to be discovered to explain exactly how the compounds in this soup became living organisms, but one thing seems certain. The carbon atoms that make up our bodies were formed in stars, so, in a sense, we are stardust.

### 1.1C Development of the Science of Organic Chemistry

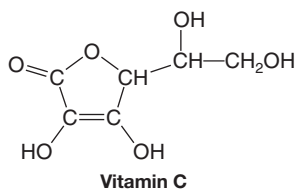
The science of organic chemistry began to flower with the demise of a nineteenth century theory called vitalism. According to vitalism, organic compounds were only those that came from living organisms, and only living things could synthesize organic compounds through intervention of a vital force. Inorganic compounds were considered those compounds that came from nonliving sources. Friedrich Wöhler, however, discovered in 1828 that an organic compound called urea (a constituent of urine) could be made by evaporating an aqueous solution of the inorganic compound ammonium cyanate. With this discovery, the synthesis of an organic compound, began the evolution of organic chemistry as a scientific discipline.



An RNA molecule

## THE CHEMISTRY OF... Natural Products

Despite the demise of vitalism in science, the word “organic” is still used today by some people to mean “coming from living organisms” as in the terms “organic vitamins” and “organic fertilizers.” The commonly used term “organic food” means that the food was grown without the use of synthetic fertilizers and pesticides. An “organic vitamin” means to these people that the vitamin was isolated from a natural source and not synthesized by a chemist. While there are sound arguments to be made against using food contaminated with certain pesticides, while there may be environmental benefits to be obtained from organic farming, and while “natural” vitamins may contain beneficial substances not present in synthetic vitamins, it is impossible to argue that pure “natural” vitamin C, for example, is healthier than pure “synthetic” vitamin C, since the two substances are identical in all respects. In science today, the study of compounds from living organisms is called natural products chemistry. In the closer to this chapter we will consider more about why natural products chemistry is important.



Vitamin C is found in various citrus fruits.

FOODCOLLECTION/Image Source

## 1.2 ATOMIC STRUCTURE

Before we begin our study of the compounds of carbon we need to review some basic but familiar ideas about the chemical elements and their structure.

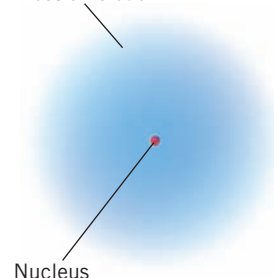
- The **compounds** we encounter in chemistry are made up of **elements** combined in different proportions.
- **Elements** are made up of **atoms**. An atom (Fig. 1.1) consists of a dense, positively charged *nucleus* containing **protons** and **neutrons** and a surrounding cloud of **electrons**.

Each proton of the nucleus bears one positive charge; electrons bear one negative charge. Neutrons are electrically neutral; they bear no charge. Protons and neutrons have

Electron cloud

Nucleus

**FIGURE 1.1** An atom is composed of a tiny nucleus containing protons and neutrons and a large surrounding volume containing electrons. The diameter of a typical atom is about 10,000 times the diameter of its nucleus.



nearly equal masses (approximately 1 atomic mass unit each) and are about 1800 times as heavy as electrons. Most of the **mass** of an atom, therefore, comes from the mass of the nucleus; the atomic mass contributed by the electrons is negligible. Most of the **volume** of an atom, however, comes from the electrons; the volume of an atom occupied by the electrons is about 10,000 times larger than that of the nucleus.

The elements commonly found in organic molecules are carbon, hydrogen, nitrogen, oxygen, phosphorus, and sulfur, as well as the halogens: fluorine, chlorine, bromine, and iodine.

Each **element** is distinguished by its **atomic number ( $Z$ )**, a **number equal to the number of protons in its nucleus**. Because an atom is electrically neutral, **the atomic number also equals the number of electrons surrounding the nucleus**.

## 1.2A Isotopes

Before we leave the subject of atomic structure and the periodic table, we need to examine one other observation: **the existence of atoms of the same element that have different masses**.

For example, the element carbon has six protons in its nucleus giving it an atomic number of 6. Most carbon atoms also have six neutrons in their nuclei, and because each proton and each neutron contributes one atomic mass unit (1 amu) to the mass of the atom, carbon atoms of this kind have a mass number of 12 and are written as  $^{12}\text{C}$ .

- **Although all the nuclei of all atoms of the same element will have the same number of protons**, some atoms of the same element **may have different masses** because they have **different numbers of neutrons**. Such atoms are called **isotopes**.

For example, about 1% of the atoms of elemental carbon have nuclei containing 7 neutrons, and thus have a mass number of 13. Such atoms are written  $^{13}\text{C}$ . A tiny fraction of carbon atoms have 8 neutrons in their nucleus and a mass number of 14. Unlike atoms of carbon-12 and carbon-13, atoms of carbon-14 are radioactive. The  $^{14}\text{C}$  isotope is used in *carbon dating*. The three forms of carbon,  $^{12}\text{C}$ ,  $^{13}\text{C}$ , and  $^{14}\text{C}$ , are isotopes of one another.

Most atoms of the element hydrogen have one proton in their nucleus and have no neutron. They have a mass number of 1 and are written  $^1\text{H}$ . A very small percentage (0.015%) of the hydrogen atoms that occur naturally, however, have one neutron in their nucleus. These atoms, called *deuterium* atoms, have a mass number of 2 and are written  $^2\text{H}$ . An unstable (and radioactive) isotope of hydrogen, called *tritium* ( $^3\text{H}$ ), has two neutrons in its nucleus.

### PRACTICE PROBLEM 1.1

There are two stable isotopes of nitrogen,  $^{14}\text{N}$  and  $^{15}\text{N}$ . How many protons and neutrons does each isotope have?

## 1.2B Valence Electrons

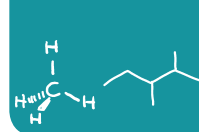
We discuss the electron configurations of atoms in more detail in Section 1.10. For the moment we need only to point out that the electrons that surround the nucleus exist in **shells** of increasing energy and at increasing distances from the nucleus. The most important shell, called the **valence shell**, is the outermost shell because the electrons of this shell are the ones that an atom uses in making chemical bonds with other atoms to form compounds.

- How do we know how many electrons an atom has in its valence shell? We look at the periodic table. The number of electrons in the valence shell (called **valence electrons**) is equal to the group number of the atom. For example, carbon is in group **IVA** and carbon has *four* valence electrons; oxygen is in group **VIA** and oxygen has *six* valence electrons. The halogens of group **VIIA** all have *seven* electrons.

### PRACTICE PROBLEM 1.2

How many valence electrons does each of the following atoms have?

- (a) Na    (b) Cl    (c) Si    (d) B    (e) Ne    (f) N



## 1.3 CHEMICAL BONDS: THE OCTET RULE

The first explanations of the nature of chemical bonds were advanced by G. N. Lewis (of the University of California, Berkeley) and W. Kössel (of the University of Munich) in 1916. Two major types of chemical bonds were proposed:

- 1. Ionic** (or electrovalent) bonds are formed by the transfer of one or more electrons from one atom to another to create ions.
- 2. Covalent** bonds result when atoms share electrons.

The central idea in their work on bonding is that atoms without the electronic configuration of a noble gas generally react to produce such a configuration because these configurations are known to be highly stable. For all of the noble gases except helium, this means achieving an octet of electrons in the valence shell.

- The **valence shell** is the outermost shell of electrons in an atom.
- The tendency for an atom to achieve a configuration where its valence shell contains eight electrons is called the **octet rule**.

The concepts and explanations that arise from the original propositions of Lewis and Kössel are satisfactory for explanations of many of the problems we deal with in organic chemistry today. For this reason we shall review these two types of bonds in more modern terms.

### 1.3A Ionic Bonds

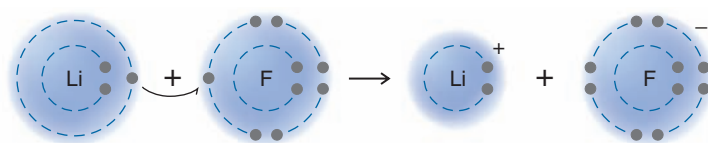
Atoms may gain or lose electrons and form charged particles called **ions**.

- An **ionic bond** is an attractive force between oppositely charged ions.

One source of such ions is a reaction between atoms of widely differing electronegativities (Table 1.1).

- **Electronegativity is a measure of the ability of an atom to attract electrons.**
- Electronegativity increases as we go across a horizontal row of the periodic table from left to right and it increases as we go up a vertical column (Table 1.1).

An example of the formation of an ionic bond is the reaction of lithium and fluorine atoms:



Lithium, a typical metal, has a very low electronegativity; fluorine, a nonmetal, is the most electronegative element of all. The loss of an electron (a negatively charged species)

#### Helpful Hint

Terms and concepts that are fundamentally important to your learning organic chemistry are set in bold blue type. You should learn them as they are introduced. These terms are also defined in the glossary.

#### Helpful Hint

We will use electronegativity frequently as a tool for understanding the properties and reactivity of organic molecules.

TABLE 1.1 ELECTRONEGATIVITIES OF SOME OF THE ELEMENTS

Increasing electronegativity →						
		H				
		2.1				
Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K						Br
0.8						2.8

↑ Increasing electronegativity

by the lithium atom leaves a lithium cation ( $\text{Li}^+$ ); the gain of an electron by the fluorine atom gives a fluoride anion ( $\text{F}^-$ ).

- Ions form because atoms can achieve the electronic configuration of a noble gas by gaining or losing electrons.

The lithium cation with two electrons in its valence shell is like an atom of the noble gas helium, and the fluoride anion with eight electrons in its valence shell is like an atom of the noble gas neon. Moreover, crystalline lithium fluoride forms from the individual lithium and fluoride ions. In this process negative fluoride ions become surrounded by positive lithium ions, and positive lithium ions by negative fluoride ions. In this crystalline state, the ions have substantially lower energies than the atoms from which they have been formed. Lithium and fluorine are thus “stabilized” when they react to form crystalline lithium fluoride.

We represent the formula for lithium fluoride as  $\text{LiF}$ , because that is the simplest formula for this ionic compound.

Ionic substances, because of their strong internal electrostatic forces, are usually very high melting solids, often having melting points above  $1000\text{ }^\circ\text{C}$ . In polar solvents, such as water, the ions are solvated (see Section 2.13D), and such solutions usually conduct an electric current.

- Ionic compounds, often called **salts**, form only when atoms of very different electronegativities transfer electrons to become ions.

### PRACTICE PROBLEM 1.3

Using the periodic table, which element in each pair is more electronegative?

- (a) Si, O      (b) N, C      (c) Cl, Br      (d) S, P

## 1.3B Covalent Bonds and Lewis Structures

When two or more atoms of the same or similar electronegativities react, a complete transfer of electrons does not occur. In these instances the atoms achieve noble gas configurations by *sharing electrons*.

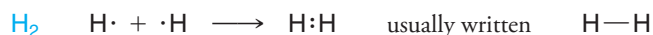
- **Covalent bonds** form by sharing of electrons between atoms of similar electronegativities to achieve the configuration of a noble gas.
- **Molecules** are composed of atoms joined exclusively or predominantly by covalent bonds.

Molecules may be represented by electron-dot formulas or, more conveniently, by formulas where each pair of electrons shared by two atoms is represented by a line.

- A **dash structural formula** has lines that show bonding electron pairs and includes elemental symbols for the atoms in a molecule.

Some examples are shown here:

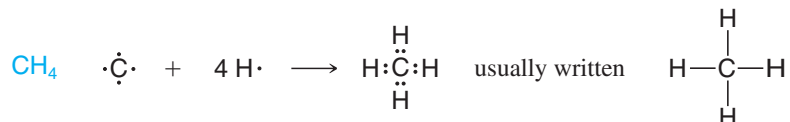
1. Hydrogen, being in group IA of the periodic table, has one valence electron. Two hydrogen atoms share electrons to form a hydrogen molecule,  $\text{H}_2$ .

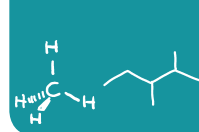


2. Because chlorine is in group VIIA, its atoms have seven valence electrons. Two chlorine atoms can share electrons (one electron from each) to form a molecule of  $\text{Cl}_2$ .

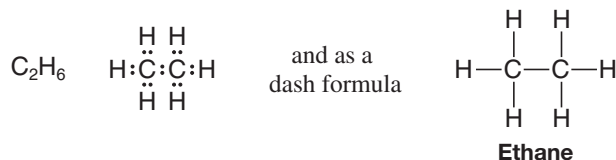


3. And a carbon atom (group IVA) with four valence electrons can share each of these electrons with four hydrogen atoms to form a molecule of methane,  $\text{CH}_4$ .



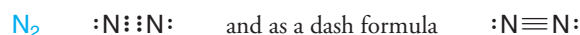


Two carbon atoms can use one electron pair between them to form a **carbon–carbon single bond** while also bonding hydrogen atoms or other groups to achieve an octet of valence electrons. Consider the example of ethane below.

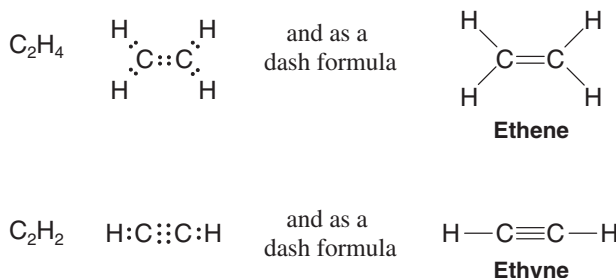


These formulas are often called **Lewis structures**; in writing them we show all of the valence electrons. Unshared electron pairs are shown as dots, and in dash structural formulas, bonding electron pairs are shown as lines.

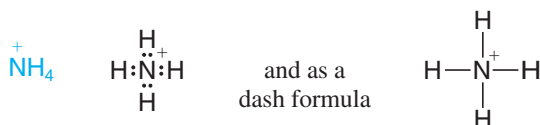
4. Atoms can share *two or more pairs of electrons* to form **multiple covalent bonds**. For example, two nitrogen atoms possessing five valence electrons each (because nitrogen is in group VA) can share electrons to form a **triple bond** between them.



Carbon atoms can also share more than one electron pair with another atom to form a multiple covalent bond. Consider the examples of a **carbon–carbon double bond** in ethene (ethylene) and a **carbon–carbon triple bond** in ethyne (acetylene).



5. Ions, themselves, may contain covalent bonds. Consider, as an example, the ammonium ion.



Consider the following compounds and decide whether the bond in them would be ionic or covalent.

- (a) KCl    (b) F<sub>2</sub>    (c) PH<sub>3</sub>    (d) CBr<sub>4</sub>

### PRACTICE PROBLEM 1.4

## 1.4 HOW TO WRITE LEWIS STRUCTURES

Several simple rules allow us to draw proper Lewis structures:

1. Lewis structures show the connections between atoms in a molecule or ion using **only the valence electrons of the atoms involved**. Valence electrons are those of an atom's outermost shell.
2. For main group elements, the number of valence electrons a neutral atom brings to a Lewis structure is the same as its group number in the periodic table.

### Helpful Hint

The ability to write proper **Lewis structures** is one of the most important tools for learning organic chemistry.

Carbon, for example, is in group IVA and has four valence electrons; the halogens (e.g., fluorine) are in group VIIA and each has seven valence electrons; hydrogen is in group IA and has one valence electron.

3. **If the structure we are drawing is a negative ion (an anion), we add one electron for each negative charge to the original count of valence electrons. If the structure is a positive ion (a cation), we subtract one electron for each positive charge.**
4. **In drawing Lewis structures we try to give each atom the electron configuration of a noble gas.** To do so, we draw structures where atoms share electrons to form covalent bonds or transfer electrons to form ions.
  - a. Hydrogen forms one covalent bond by sharing its electron with an electron of another atom so that it can have two valence electrons, the same number as in the noble gas helium.
  - b. Carbon forms four covalent bonds by sharing its four valence electrons with four valence electrons from other atoms, so that it can have eight electrons (the same as the electron configuration of neon, satisfying the octet rule).
  - c. To achieve an octet of valence electrons, elements such as nitrogen, oxygen, and the halogens typically share only some of their valence electrons through covalent bonding, leaving others as unshared electron pairs.

The following problems illustrate the rules above.

### SOLVED PROBLEM 1.1

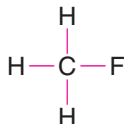
Write the Lewis structure of  $\text{CH}_3\text{F}$ .

#### STRATEGY AND ANSWER:

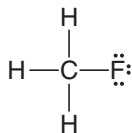
1. We find the total number of valence electrons of all the atoms:

$$\begin{array}{ccccccc}
 & & 4 & + & 3(1) & + & 7 & = & 14 \\
 & & \uparrow & & \uparrow & & \uparrow & & \\
 & & \text{C} & & 3\text{H} & & \text{F} & & 
 \end{array}$$

2. We use pairs of electrons to form bonds between all atoms that are bonded to each other. We represent these bonding pairs with lines. In our example this requires four pairs of electrons (8 of the 14 valence electrons).

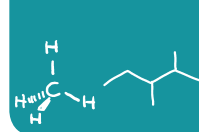


3. We then add the remaining electrons in pairs so as to give each hydrogen 2 electrons (a duet) and every other atom 8 electrons (an octet). In our example, we assign the remaining 6 valence electrons to the fluorine atom in three non-bonding pairs.



**PRACTICE PROBLEM 1.5** Write the Lewis structure of (a)  $\text{CH}_2\text{F}_2$  (difluoromethane) and (b)  $\text{CHCl}_3$  (chloroform).

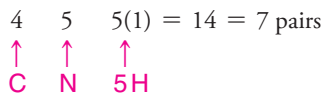



**SOLVED PROBLEM 1.2**

Write a Lewis structure for methylamine ( $\text{CH}_3\text{NH}_2$ ).

**STRATEGY AND ANSWER:**

1. We find the total number of valence electrons for all the atoms.



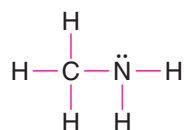
2. We use one electron pair to join the carbon and nitrogen.



3. We use three pairs to form single bonds between the carbon and three hydrogen atoms.

4. We use two pairs to form single bonds between the nitrogen atom and two hydrogen atoms.

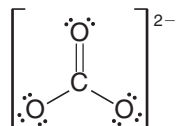
5. This leaves one electron pair, which we use as a lone pair on the nitrogen atom.



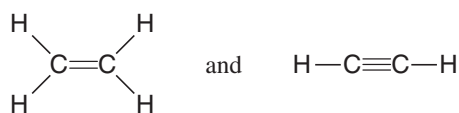
Write the Lewis structure of  $\text{CH}_3\text{OH}$ .

**PRACTICE PROBLEM 1.6**

5. If necessary, we use multiple bonds to satisfy the octet rule (i.e., give atoms the noble gas configuration). The carbonate ion ( $\text{CO}_3^{2-}$ ) illustrates this:



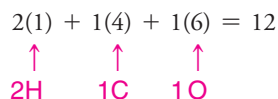
The organic molecules ethene ( $\text{C}_2\text{H}_4$ ) and ethyne ( $\text{C}_2\text{H}_2$ ), as mentioned earlier, have a double and triple bond, respectively:


**SOLVED PROBLEM 1.3**

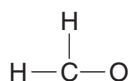
Write the Lewis structure of  $\text{CH}_2\text{O}$  (formaldehyde).

**STRATEGY AND ANSWER:**

1. Find the total number of valence electrons of all the atoms:



2. (a) Use pairs of electrons to form single bonds.



(continues on next page)