

ORGANIC CHEMISTRY
SECOND EDITION



SEYHAN EGE

*ORGANIC
CHEMISTRY
SECOND EDITION*

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THE UNIVERSITY OF MICHIGAN*

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To my teachers and my students

Preface

The pedagogical aim of *Organic Chemistry*, Second Edition is to educate students to think independently about organic chemistry. The first edition and now, the second edition, have the same philosophy of teaching: Students can truly learn organic chemistry only if they are actively involved in developing a practical understanding of the causes of chemical change, rather than trying to master organic chemistry through memorization. In both editions, I have presented organic chemistry by consistently emphasizing important themes and by returning to fundamentals again and again. In this way I have helped students to think as practicing chemists do in predicting reactivity from structure. Students have told me that they have learned an entirely new way of thinking—of analyzing problems, sorting facts, reasoning by analogy, looking for patterns—and that consequently their approach to all of their other work has changed.

Like the first edition, the second edition of *Organic Chemistry* has been designed to lead students quickly to the concept that structures of organic compounds determine their chemical reactivity. This theme is apparent immediately, even within the first two chapters of the book that introduce students to structure and bonding. Chapter 3, the first chapter devoted to chemical reactivity, uses the reactions of organic compounds as acids and bases to focus the student's attention on two simple reactions, protonation and deprotonation of organic compounds. Through the practice of solving problems on acidity and basicity, students gain confidence in their ability to predict reactivity as chemists do: by looking at structures of organic compounds and applying fundamental concepts such as atomic and ionic sizes, resonance stabilization of species, and pK_a values. In addition, students learn reactions that are important steps in many of the organic transformations they will study later.

Chapter 3 also introduces mechanisms of organic reactions and the convention of using curved arrows for symbolizing the motion of electrons. Coverage of the concepts of nucleophile and electrophile in Chapter 4 is built on the chemistry, and the language and symbolism of chemistry, learned in Chapter 3. In Chapter 4, the reactions of chloromethane with hydroxide ion and hydrogen bromide with propene are used to introduce thermodynamics and kinetics and the idea of reaction pathways.

Chapter 5 presents the nomenclature and conformation of both alkanes and cycloalkanes. Stereoisomerism is discussed in Chapter 6. With these first six chapters, students have most of the concepts they will need to understand the chemistry presented to them in the rest of the book. Extensive cross-referencing allows instructors considerable flexibility in choosing the order of subjects to follow.

NEW IN THE SECOND EDITION

Features

True mastery of organic chemistry requires that students learn to make discriminating use of their eyes and minds. To this end, several new features have been introduced in the second edition.

Visualizing the Reaction

As in the first edition, complete mechanisms are given for each type of reaction. These mechanisms are now highlighted in "Visualizing the Reaction" boxes set apart from the text. Students must practice developing their powers of imagination and following a process with the "inner eye," and these complete mechanisms, which feature the

judicious use of four colors, enhance the process of visualizing. Acidic or electrophilic sites are highlighted as red atoms, blue shading signifies basic or nucleophilic species, and grey shading emphasizes leaving groups. Color is used to indicate whether the reactive species on one side of an equation are converted into new reactive species after reaction, in order to show students the reversibility of many reactions, especially acid-base reactions.

Four Colors

While four-color printing appears primarily in the “Visualizing the Reaction” boxes, color is also used to enhance figures and to stress, with consistency, various important structural features. For example, in sections where students are just learning to see stereochemistry, green and red shading highlights stereochemical relationships.

Problem-Solving Skills Sections

In working with my students, I have become convinced that encouraging them to analyze problems systematically is the single most important factor in increasing their overall intellectual skills. These new Problem-Solving Skills sections, unique among organic chemistry texts, offer students a systematic, questioning approach to solving organic chemistry problems. These sections do not simply provide a way for students to learn to plug data into a prelearned formula; rather, students learn to reason their way to a solution.

- In Chapter 1, students are introduced to the idea that the solution to a problem in chemistry requires a step-by-step analysis of the problem. This analysis takes the form of questions that students pose to themselves in a systematic way.
- In Chapter 4, students are shown how to reason backwards in solving problems involving simple syntheses.
- In Chapter 7, students are led through the types of questions that help them to predict the product of a reaction and to transform a given starting material into a desired product. These are complex questions with many types of answers, depending on the particular problem being solved. Not all of the questions are directly applicable to the problem under consideration, but represent steps in the processes of deciding how to use the data given in the problem.
- The same method of questioning is applied in Chapter 9 to writing mechanisms. To reinforce this practice for students, in most chapters through Chapter 23, one or two problems are worked out using the same set of questions.
- The *Study Guide* further reinforces the questioning approach used in the book by applying it to solving some of the problems in and at the end of each chapter.

Concept Maps

Concept maps, which appear in the *Study Guide*, are a fourth innovation in this edition of *Organic Chemistry*. Conceived as a practical way to organize and summarize the material presented in the book, these concept maps present major ideas in outline form. Notes in the margin of the textbook alert students that the concept maps are available. While the concept maps provided can be quite helpful to students, students are encouraged to examine the maps and then create their own, because the process of creating a concept map requires them to give up a purely linear way of thinking about a subject and to explore interrelationships. My students who have used this method to organize their lecture notes and to outline related subjects have found the concept maps not only useful, but fun. Encouraging students to work in this way promotes an actively thinking approach to organic chemistry.

A package of transparency masters containing the complete set of concept maps that appear in the *Study Guide* is available to instructors.

In-Text Summaries

Besides the concept maps in the *Study Guide*, two other forms of summary appear in the textbook itself.

- An end-of-chapter *Summary* offers a concise review of the major concepts covered in the chapter.
- End-of-chapter *Tables* summarize the reactions that appear in the chapter. Organized so as to remind students of how the reactions proceed, they are not made up of general reactions to be memorized, but take students briefly through the stages of the reaction again, reminding them of the types of reagents needed, reactive intermediates involved, and the stereochemistry of the reaction. These tables are particularly helpful to students when they are used together with the concept maps in the *Study Guide*.

Easy-to-Use Cross-Referencing

The second edition is cross-referenced with page numbers to enable both students and teachers to locate related topics quickly.

Reorganization

This revision of *Organic Chemistry* has resulted in considerable rearrangement of topics. Important changes include:

- Early and separate chapters on infrared spectroscopy (Chapter 10) and nuclear magnetic spectroscopy (Chapter 11).
- The introduction to stereochemistry concentrated in a separate chapter (Chapter 6).
- Free radicals in a separate chapter. While free radicals are mentioned briefly in Chapter 5 in connection with the reactivity of alkanes, the separate chapter allows a fuller treatment of their use in synthesis and their biological significance.
- Separation of the contents of each of the longer chapters in the first edition into two shorter chapters. The first chapter in each pair contains the material on that topic commonly covered in most courses; the second chapter may either be omitted or taught in a different order. (Note that this edition retains the integration of biologically interesting examples of chemistry throughout the text.) For example, Chapter 14 concentrates on nucleophilic substitution reactions at the carbonyl group of carboxylic acids and their derivatives. Chapter 15 contains the reactions of carboxylic acids and their derivatives with metal hydrides and organometallic reagents. Chapter 16, which covers the chemistry of enolate anions, follows directly after the chemistry of carboxylic acid derivatives and emphasizes aldol and Claisen condensations. Chapter 18, the second chapter in the pair, involves the chemistry of α, β -unsaturated carbonyl compounds and ylides, and follows a chapter on polyenes (Chapter 17). Chapter 19 covers electrophilic aromatic substitution reactions, and the rest of aromatic chemistry comes in Chapter 23, after students have learned about free radicals (Chapter 20), mass spectrometry (Chapter 21), and diazotization reactions (Chapter 22). Aromatic chemistry is further reinforced by a study of heterocyclic compounds in Chapter 24.

The second edition is unchanged from the first edition in its emphasis on an understanding of reactivity rather than on an encyclopedic knowledge of reactions. Students suffer from an overload of different things to remember, and from not learning to think their way toward predicting the outcome of a reaction they have never seen before. Thinking for themselves is a skill that will be valuable to them as graduate students in chemistry, in other sciences with a strong chemical component, and in

medicine. A thorough understanding, with an emphasis on mechanism of a few major reactions, enables students to apply the principles they have learned and gives them the confidence to tackle new situations. I would rather teach students who are confident about their abilities than students who are overwhelmed by a mass of undigested material. Once the fundamental thought processes of chemistry have been learned, teachers find that they can introduce their own favorite reactions to their students.

The length of this book, thus, comes from meticulous explanations and fully detailed mechanisms for selected reactions, mechanisms that were chosen to represent many other reactions of the same type. My experience convinces me that only such an explicit, consistent approach gives students the reinforcement they need to learn a subject they perceive as being difficult.

Does this approach work? Feedback from students has been so positive that it has encouraged me to keep the same approach in this edition as I used in the first edition. I particularly cherish reports from faculty at various schools that students using the book receive better scores than before on the standardized ACS examinations at the end of the year and even complain that the examination was too easy! If the book is used as it is intended, students come to enjoy and be challenged by their intellectual competence. To watch this happen, is, of course, the ultimate satisfaction for a teacher.

SUPPLEMENTS

Study Guide

Roberta W. Kleinman of Lock Haven University, Pennsylvania, and Marjorie L. C. Carter of the University of Michigan are my coauthors for the first and second editions of the *Study Guide*. Both of them have given me invaluable help—especially Roberta Kleinman, who, with her skill at the computer, is responsible for transforming the material into camera-ready copy. As in the first edition, the second edition contains detailed solutions to every problem in the text as well as explanations of the reasoning processes behind the answers for many problems. Some problems in this edition are worked out using the questions developed in the Problem-Solving Skills sections of the text to reinforce students' understanding of this approach.

New concept maps, charts summarizing relationships between key ideas in a section or portion of a section, provide an innovative tool for practice and review. Notes in the margin of the text refer students to relevant concept maps in the *Study Guide*.

Transparency Masters

For classroom use by the instructor, a package of *Transparency Masters* contains the complete set of concept maps that appear in the *Study Guide*.

Transparencies

A complete set of *Transparencies* ($8\frac{1}{2} \times 11$ "), many of them full color, is available free to college adopters of the textbook. Reproduced from selected figures and chemical structures in the text, the transparencies include spectra, molecular orbitals, space-filling models, stereochemistry, and reaction mechanisms.

Software

A variety of quality *software* programs are offered by arrangement with COMPress, a division of Queue, Inc. For information and demonstration disks, contact the Marketing Department at D. C. Heath at 1-(800)-235-3565.

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Many people have contributed to converting the first edition of *Organic Chemistry* into the second edition. Suggestions and corrections from colleagues and students who have used the book are particularly valuable. I owe special thanks to Brian Coppola, Richard Lawton, and John Wiseman of the University of Michigan; Sally Weersing, Muskegon Community College; Dorothy Goldish, Edwin Harris, and Tom Maricich, California State University, Long Beach; David Reingold, Juniata College; Hans Cerfontain, Henk Hiemstra, and Gerrit-Jan Koomen, University of Amsterdam; and Clarisse Habraken, University of Leiden.

Dr. Alex Aisen of the Department of Radiology at the University of Michigan supplied me with information on magnetic resonance imaging and the photograph that appears on page 416 of the text. Torin Dewey, a student of mine who is now doing graduate work at the University of California, Berkeley, took most of the proton magnetic resonance spectra. Frank Parker and James Windak helped with the spectra illustrating Fourier transform nuclear magnetic resonance and infrared methods.

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No amount of thanks will repay my debt to Marjorie Carter and Roberta Kleinman. Not only have they contributed substantially to the *Study Guide*, but they have helped with the text itself too. All of the three-dimensional figures in the text originated with Roberta Kleinman, who combines artistic talent with an interest in how students visualize and learn. She joins me in struggling to see things as the student sees them and not as we, with years of experience, know them to be. I owe a great deal to her critical eye. Marjorie Carter also brings the viewpoint of the students and a questioning mind to the thankless task of proofreading. Many times she has insisted that Roberta and I try again in drawing structures or explaining our reasoning for greater clarity for the student. I value the help of both of these good friends.

Mary Le Quesne, Senior Acquisitions Editor at D. C. Heath, saw the book through revision with an openness toward my ideas, even when they were unconventional, for which I am grateful. Her knowledge of chemistry and her insight contributed greatly to this edition. Cathy Brooks, Senior Production Editor, has guided me patiently and with endless good humor through the traumatic process of the publication of a technical book in four colors. I am grateful for her expertise and her meticulous attention to detail.

Finally, none of this would have been possible without the encouragement of my family and friends. I thank them for their understanding during all of the times when I could not be with them and for their steady love that supports me.

Seyhan N. Ege

Contents

1

An Introduction to Structure and Bonding in Organic Compounds

1

- A LOOK AHEAD **1**
- 1.1** HOW TO STUDY ORGANIC CHEMISTRY **2**
- 1.2** IONIC AND COVALENT COMPOUNDS **4**
- 1.3** IONIC BONDING **4**
- 1.4** COVALENT BONDING **5**
A. Lewis Structures / 5 B. Formal Charges / 7 C. Molecules with Open Shells / 8
D. Multiple Bonds / 9 E. Resonance / 10 F. Problem-Solving Skills / 13
- 1.5** ISOMERS **15**
- 1.6** SHAPES OF COVALENT MOLECULES **18**
A. Tetrahedral Molecules / 18 B. Planar Molecules / 20 C. Linear Molecules / 20
- 1.7** THE POLARITY OF COVALENT MOLECULES **21**
A. Polar Covalent Bonds / 21 B. Dipole Moments of Covalent Molecules / 22
- 1.8** NONBONDING INTERACTIONS BETWEEN MOLECULES **24**
A. Dipole-Dipole Interactions / 24 B. Hydrogen Bonding / 24 C. Van der Waals Forces / 28
- SUMMARY **30**
- ADDITIONAL PROBLEMS **30**

2

Covalent Bonding and Chemical Reactivity

34

- A LOOK AHEAD **34**
- 2.1** INTRODUCTION **35**
- 2.2** ATOMIC ORBITALS **35**
A. The Atomic Orbitals of Hydrogen. A Review / 35 B. Orbitals of Atoms in the Second Row of the Periodic Table / 37
- 2.3** OVERLAP OF ATOMIC ORBITALS. THE FORMATION OF MOLECULAR ORBITALS **38**
A. The Hydrogen Molecule / 38 B. Sigma Bonds Involving *p* Orbitals / 40
- 2.4** HYBRID ORBITALS **41**
A. Tetrahedral Carbon Atoms / 41 B. *sp*³-Hybridized Atoms Other than Carbon / 44
- 2.5** THE ORBITAL PICTURE FOR COMPOUNDS CONTAINING TRIGONAL CARBON ATOMS **48**
A. Covalent Bonding in Alkenes / 48 B. Covalent Bonding in Carbonyl Compounds. Aldehydes and Ketones / 50 C. Carboxylic Acids and Esters / 51

2.6	THE ORBITAL PICTURE FOR LINEAR MOLECULES	53
	A. Bonding in Alkynes / 53	B. Bonding in Nitriles / 54
2.7	COVALENT BOND LENGTHS AND THEIR RELATION TO ORBITAL HYBRIDIZATION	56
	A. Bond Lengths in Hydrocarbons / 56	B. Orbital Hybridization and the Electronegativities of Carbon Atoms / 56
	C. Bond Lengths in Organic Compounds Containing Oxygen and Nitrogen / 57	
2.8	COVALENT BOND STRENGTHS	59
	A. Bond Dissociation Energies / 59	B. Average Bond Energies / 60
2.9	EFFECTS OF BONDING ON CHEMICAL REACTIVITY	62
2.10	THE STRUCTURE OF BENZENE	64
	SUMMARY	67
	ADDITIONAL PROBLEMS	70

3

Reactions of Organic Compounds as Acids and Bases 74

	A LOOK AHEAD	74
3.1	BRØNSTED AND LEWIS ACIDS AND BASES	75
	A. Brønsted-Lowry Theory of Acids and Bases / 75	B. Lewis Theory of Acids and Bases / 76
3.2	REACTIONS OF ORGANIC COMPOUNDS AS BASES	77
3.3	THE USE OF CURVED ARROWS IN WRITING MECHANISMS	81
3.4	CARBON, NITROGEN, OXYGEN, SULFUR, AND HALOGEN ACIDS	84
	A. Relative Acidities and Basicities Within Groups in the Periodic Table / 84	
	B. Relative Acidities and Basicities Across a Period in the Periodic Table / 86	
	C. Organic Cations as Acids / 87	
3.5	EQUILIBRIA IN ACID-BASE REACTIONS	89
	A. Acidity Constants and pK_a / 89	B. Using the Table of pK_a Values to Predict Acid-Base Reactions / 90
	C. The Importance of Solvation in Acidity / 92	D. Equilibrium, Free Energy, Enthalpy, and Entropy / 93
3.6	THE EFFECTS OF STRUCTURAL CHANGES ON ACIDITY	94
	A. The Resonance Effect / 94	B. Inductive and Field Effects / 96
3.7	THE EFFECTS OF STRUCTURAL CHANGES ON BASICITY	100
	A. Carbanions / 100	B. Amines / 102
	SUMMARY	104
	ADDITIONAL PROBLEMS	105

4

Reaction Pathways 109

	A LOOK AHEAD	109
4.1	INTRODUCTION. ELECTROPHILES AND NUCLEOPHILES	110
4.2	THE REACTION OF CHLOROMETHANE WITH HYDROXIDE ION	111
	A. A Nucleophilic Substitution Reaction / 111	B. Energy Changes in the Reaction. Equilibrium / 112
	C. The Rate of the Reaction. Kinetics / 113	D. The Transition State / 114
	E. Free Energy of Activation / 115	F. The Effect of Temperature on the Rate of the Reaction / 116
4.3	ADDITION OF HYDROGEN BROMIDE TO PROPENE	118
	A. An Electrophilic Addition Reaction / 118	B. Markovnikov's Rule. Regioselectivity in a Reaction / 120
	C. Relative Stabilities of Carbocations / 121	D. Equilibria in the Addition of Hydrogen Bromide to Propene / 122
	E. The Energy Diagram for the Addition of Hydrogen Bromide to Propene / 123	F. The Basis for Markovnikov's Rule / 125
	G. Kinetics of a Reaction with Two Steps. The Rate-Determining Step / 126	

4.4	CHEMICAL TRANSFORMATIONS	127
	A. Writing Equations for Organic Reactions / 127	B. Choosing Reagents for Simple Syntheses / 128
	SUMMARY	131
	ADDITIONAL PROBLEMS	132

5 *Alkanes and Cycloalkanes*

137

	A LOOK AHEAD	137
5.1	ISOMERISM AND PHYSICAL PROPERTIES	137
5.2	METHANE	139
5.3	ETHANE	141
	A. The Ethyl Group / 141	B. Isomerism in Disubstituted Ethanes / 142
5.4	PROPANE	143
5.5	BUTANES	145
5.6	CONFORMATION	148
	A. Conformations of Ethane / 148	B. Conformations of Butane / 150
5.7	LINE STRUCTURES FOR ORGANIC COMPOUNDS	153
5.8	NOMENCLATURE	156
	A. Introduction / 156	B. Nomenclature of Alkanes / 157
	C. Nomenclature of Alkyl Halides and Alcohols / 160	D. The Phenyl Group / 162
5.9	CYCLOALKANES	163
	A. Cyclopropane and Cyclobutane. Ring Strain / 163	B. Cyclopentane / 165
	C. Cyclohexane. Conformation in Cyclohexane and in Cyclohexanes with One Substituent / 166	
5.10	THE CHEMICAL PROPERTIES OF ALKANES	170
5.11	STRUCTURAL INFORMATION FROM MOLECULAR FORMULAS	172
	SUMMARY	175
	ADDITIONAL PROBLEMS	176

6 *Stereochemistry*

180

	A LOOK AHEAD	180
6.1	ENANTIOMERS	180
6.2	CHIRALITY	182
6.3	STEREOCENTERS	186
6.4	PLANE-POLARIZED LIGHT AND OPTICAL ACTIVITY	187
	A. Plane-Polarized Light / 187	B. The Experimental Determination of Optical Activity / 187
6.5	THE FORMATION OF STEREOISOMERS IN CHEMICAL REACTIONS. RACEMIC MIXTURES	191
	A. The Addition of Hydrogen Bromide to 1-Butene / 191	B. Racemic Mixtures and Enantiomeric Excess / 192
6.6	THE DISCOVERY OF MOLECULAR DISSYMMETRY	193
6.7	CONFIGURATION, REPRESENTATION AND NOMENCLATURE OF STEREOISOMERS	195
	A. Configuration of Stereoisomers / 195	B. Nomenclature of Stereoisomers / 196
	C. Relative and Absolute Configuration / 200	
6.8	DIASTEREOMERS	201
	A. Compounds with More Than One Stereocenter / 201	B. Compounds Containing Two Stereocenters with Identical Substituents. Meso Forms / 202
6.9	STEREOISOMERISM IN CYCLIC COMPOUNDS	204
	A. Cis and Trans Compounds / 204	B. Configuration and Conformation of Disubstituted Cyclohexanes / 206

6.10	STEREISOMERISM IN ALKENES	211
	A. The Origin of Stereoisomerism in Alkenes / 211	B. Nomenclature of Stereoisomeric Alkenes / 212
6.11	THE RESOLUTION OF A RACEMIC MIXTURE	214
	A. Separation of Mixtures / 214	B. Resolution of Racemic Mixtures / 215
	C. Resolution of Amphetamine / 215	
	SUMMARY	218
	ADDITIONAL PROBLEMS	219

7	<i>Nucleophilic Substitution and Elimination Reactions</i>	223
----------	---	------------

	A LOOK AHEAD	223
7.1	A COMPARISON OF SUBSTITUTION AND ELIMINATION REACTIONS	224
7.2	NUCLEOPHILICITY. SOLVENT EFFECTS	226
	A. A Comparison of Basicity and Nucleophilicity / 226	B. Solvent Effects / 229
7.3	LEAVING GROUPS	231
	A. Experimental Evidence for the Ionization of Alkyl Halides / 231	B. Leaving Groups and Basicity / 232
	C. Making Leaving Groups Better / 233	
7.4	SUBSTITUTION REACTIONS OF PRIMARY AND SECONDARY ALKYL HALIDES	237
	A. Experimental Evidence for Substitution Without Carbocation Intermediates / 237	
	B. The Kinetics of Substitution Reactions of Primary Alkyl Halides. The S_N2 Reaction / 238	
	C. Steric Effects in S_N2 Reactions / 239	D. Stereochemical Evidence for S_N2 Reactions / 242
7.5	KINETICS AND STEREOCHEMISTRY FOR SUBSTITUTION REACTIONS WITH CARBOCATIONS AS INTERMEDIATES	245
	A. The Kinetics of Substitution Reactions of <i>tert</i> -Butyl Chloride. The S_N1 Reaction / 245	
	B. Stereochemistry of the S_N1 Reaction / 248	
7.6	A UNIFIED VIEW OF NUCLEOPHILIC SUBSTITUTION REACTIONS	251
7.7	ELIMINATION REACTIONS	253
	A. The E_1 Reaction in Competition with the S_N1 Reaction. Orientation in the E_1 Reaction / 253	
	B. Competition Between S_N2 and E_2 Reactions / 255	C. Mechanism and Stereochemistry for the E_2 Reaction / 257
7.8	SYNTHESES. NUCLEOPHILIC SUBSTITUTION REACTIONS IN CHEMICAL TRANSFORMATIONS	260
7.9	PROBLEM-SOLVING SKILLS	262
	SUMMARY	267
	ADDITIONAL PROBLEMS	267

8	<i>Alkenes</i>	274
----------	-----------------------	------------

	A LOOK AHEAD	274
8.1	STRUCTURE AND ISOMERISM IN ALKENES	275
8.2	NOMENCLATURE OF ALKENES	275
	A. IUPAC Names for Alkenes / 275	B. Vinyl and Allyl Groups / 277
8.3	RELATIVE STABILITIES OF ALKENES	278
8.4	ELECTROPHILIC ADDITION OF ACIDS TO ALKENES	280
	A. Addition of Water to Alkenes / 280	B. Reaction of Carbocations with Alkenes / 283
8.5	REARRANGEMENTS OF CARBOCATIONS	285
	A. Shifts of Hydrogen Atoms / 285	B. Shifts of Carbon Atoms / 287
8.6	ADDITION OF BROMINE TO ALKENES	289
	A. Bromine as an Electrophile / 289	B. The Bromonium Ion / 290
	C. Stereoselective Reactions. Stereochemistry of the Addition of Bromine to Alkenes / 292	D. The Bromonium Ion and Nucleophiles. Halohydrins / 294

- 8.7 ADDITION OF DIBORANE TO ALKENES 297**
A. Diborane as an Electrophile / 297 B. The Hydroboration Reaction / 299
C. Regioselectivity in Hydroboration Reactions / 300 D. Stereochemistry of Hydroboration Reactions / 301 E. Oxidation of Organoboranes / 302
- 8.8 ADDITION OF HYDROGEN TO ALKENES. CATALYTIC HYDROGENATION REACTIONS 304**
A. Heterogeneous Catalysis / 304 B. Some Hydrogenation Reactions of Alkenes / 306
C. Homogeneous Catalysis. Organometallic Compounds as Hydrogenation Catalysts / 307
- 8.9 OXIDATION REACTIONS OF ALKENES 310**
A. Reaction with Ozone. Ozonolysis / 310 B. Oxidation of Alkenes with Permanganate and Osmium Tetroxide / 314 C. Oxidation of Alkenes with Peroxyacids / 317
D. Problem-Solving Skills / 320
- SUMMARY 322**
ADDITIONAL PROBLEMS 322

9*Alkynes*

330

- A LOOK AHEAD 330**
- 9.1 STRUCTURE AND ISOMERISM OF ALKYNES 331**
- 9.2 NOMENCLATURE OF ALKYNES 331**
- 9.3 ALKYNES AS ACIDS 332**
A. The Preparation of Sodium Acetylide, a Source of Nucleophilic Carbon / 332 B. Reaction of Nucleophilic Acetylide Anions with Alkyl Halides / 333
- 9.4 ELECTROPHILIC ADDITION REACTIONS OF ALKYNES 334**
A. Addition of Hydrogen Halides / 334 B. Addition of Water to Alkynes / 336
C. Problem-Solving Skills / 337 D. Tautomerism / 341
- 9.5 REDUCTION OF ALKYNES 341**
A. Catalytic Hydrogenation of Alkynes / 341 B. Reduction of Alkynes to Alkenes by Dissolving Metals / 343
- 9.6 OZONOLYSIS OF ALKYNES 344**
- 9.7 PLANNING SYNTHESSES 345**
- SUMMARY 350**
ADDITIONAL PROBLEMS 350

10*Infrared Spectroscopy*

355

- A LOOK AHEAD 355**
- 10.1 THE ELECTROMAGNETIC SPECTRUM AND ABSORPTION SPECTROSCOPY 356**
- 10.2 MOLECULAR VIBRATIONS AND ABSORPTION FREQUENCIES IN THE INFRARED REGION 357**
- 10.3 USING INFRARED SPECTROSCOPY TO STUDY CHEMICAL TRANSFORMATIONS. INFRARED SPECTRA OF ALKYNES, ALKENES, AND ALCOHOLS 361**
- 10.4 INFRARED SPECTRA OF COMPOUNDS CONTAINING CARBONYL GROUPS 364**
A. Infrared Spectra of Aldehydes and Ketones / 364 B. Infrared Spectra of Conjugated Carbonyl Compounds / 366 C. Infrared Spectra of Carboxylic Acids and Esters / 366
- SUMMARY 371**
ADDITIONAL PROBLEMS 372

11*Nuclear Magnetic Resonance Spectroscopy*

376

- A LOOK AHEAD 376**
- 11.1 THE EXPERIMENTAL OBSERVATIONS 376**

11.2	THE ORIGIN OF NUCLEAR MAGNETIC RESONANCE SPECTRA	381
11.3	CHEMICAL SHIFT	384
	A. The Origin of the Chemical Shift. Chemical Shift Values for Hydrogen Atoms on Tetrahedral Carbon Atoms / 384	
	B. Special Effects Seen in Proton Magnetic Resonance Spectra of Compounds with π Bonds / 386	
	C. Chemical Shifts of Hydrogen Atoms of Hydroxyl Groups / 389	
	D. Typical Chemical Shifts in Proton Magnetic Resonance Spectra / 391	
11.4	SPIN-SPIN COUPLING	393
	A. The Origin of Spin-Spin Coupling / 393	
	B. Spin-Spin Coupling in Compounds with Multiple Bonds / 399	
	C. More Complex Splitting Patterns / 402	
	D. The Effect of Chemical Exchange on Spin-Spin Coupling / 406	
11.5	CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY	409
11.6	MEDICAL APPLICATIONS OF NUCLEAR MAGNETIC RESONANCE	416
	SUMMARY	418
	ADDITIONAL PROBLEMS	419

12 *Alcohols, Diols, and Ethers*

426

	A LOOK AHEAD	426
12.1	STRUCTURE AND NOMENCLATURE OF ALCOHOLS AND ETHERS	427
	A. Some Typical Alcohols and Ethers and Their Properties / 427	
	B. Nomenclature of Alcohols / 428	
	C. Nomenclature of Ethers / 429	
12.2	PREPARATION OF ALCOHOLS	431
12.3	CONVERTING ALCOHOLS TO ALKYL HALIDES	432
	A. Reactions of Alcohols with Hydrogen Halides / 432	
	B. Reactions with Thionyl Chloride and Phosphorus Halides / 434	
12.4	OXIDATION REACTIONS OF ALCOHOLS	436
	A. Oxidation-Reduction of Organic Compounds / 436	
	B. Oxidation with Sodium Dichromate / 439	
	C. Selective Oxidations. Pyridinium Chlorochromate / 441	
	D. Problem-Solving Skills / 443	
12.5	REACTIONS OF ALKOXIDE ANIONS	445
	A. Preparation of Alkoxide Anions / 445	
	B. Reactions of Alkoxide Anions with Alkyl Halides. The Williamson Synthesis of Ethers / 446	
	C. Intramolecular Reactions of Alkoxide Anions. The Preparation of Cyclic Ethers / 448	
12.6	CLEAVAGE REACTIONS OF ETHERS	450
	A. Reaction with Hydriodic Acid / 450	
	B. Acid-Catalyzed Ring-Opening Reactions of Oxiranes / 451	
	C. Ring-Opening Reactions of Oxiranes with Nucleophiles / 454	
	D. Stereoselective Formation of <i>trans</i> -1,2-Diols from Oxiranes / 455	
	E. Problem-Solving Skills / 457	
12.7	CLEAVAGE OF CARBON-CARBON BONDS IN DIOLS WITH PERIODIC ACID	459
	SUMMARY	461
	ADDITIONAL PROBLEMS	464

13 *Aldehydes and Ketones. Reactions at Electrophilic Carbon Atoms*

473

	A LOOK AHEAD	473
13.1	INTRODUCTION TO CARBONYL COMPOUNDS	474
	A. The Carbonyl Group / 474	
	B. Carbonyl Compounds as Acids and Bases / 475	
	C. The Occurrence of Aldehydes and Ketones in Nature / 477	
13.2	NOMENCLATURE OF CARBONYL COMPOUNDS	478
	A. Nomenclature of Aldehydes and Ketones / 478	
	B. Nomenclature of Polyfunctional Compounds / 480	

- 13.3** PREPARATION OF ALDEHYDE AND KETONES **483**
- 13.4** ADDITION OF THE NUCLEOPHILE HYDRIDE ION. REDUCTION OF ALDEHYDES AND KETONES TO ALCOHOLS **484**
- 13.5** ADDITION OF THE NUCLEOPHILE CYANIDE ION TO THE CARBONYL GROUP. CYANOHYDRIN FORMATION **487**
- 13.6** ADDITION OF OTHER CARBON NUCLEOPHILES TO THE CARBONYL GROUP **488**
 A. Preparation of Organometallic Reagents / 488 B. Reactions of Organometallic Reagents with Aldehydes or Ketones as Electrophiles / 491 C. Reaction of Organometallic Reagents with Oxirane as an Electrophile / 494 D. Problem-Solving Skills / 494
- 13.7** REACTIONS OF ALDEHYDES AND KETONES WITH THE NUCLEOPHILES WATER AND ALCOHOLS **497**
 A. Hydrates / 497 B. Acetals and Ketals / 499 C. Mechanism of Acetal or Ketal Formation and Hydrolysis / 501 D. Cyclic Acetals or Ketals / 502
- 13.8** ADDITION REACTIONS OF NUCLEOPHILES RELATED TO AMMONIA **503**
 A. Compounds Related to Ammonia and Their Use in the Characterization of Aldehydes and Ketones / 503 B. A Mechanism for the Reaction of Compounds Related to Ammonia with Aldehydes and Ketones / 504 C. Reactions of Carbonyl Compounds with Amines / 506 D. Reactions of Carbonyl Compounds with Hydrazines / 506
- 13.9** REDUCTION OF CARBONYL GROUPS TO METHYLENE GROUPS **509**
 A. The Clemmensen Reduction / 509 B. The Wolff-Kishner Reduction / 509 C. Raney Nickel Reduction of Thioacetals and Thioketals / 511
- 13.10** PROTECTING GROUPS IN SYNTHESIS **513**
 A. Acetals and Ketals / 513 B. Ethers / 517
- 13.11** DESIGNING SYNTHESSES **518**
- SUMMARY **523**
- ADDITIONAL PROBLEMS **527**

Carboxylic Acids and Their Derivatives I. Nucleophilic Substitution Reactions at the Carbonyl Group

- A LOOK AHEAD **541**
- 14.1** PROPERTIES OF THE FUNCTIONAL GROUPS IN CARBOXYLIC ACIDS AND THEIR DERIVATIVES **543**
 A. The Functional Groups in Carboxylic Acids and Their Derivatives / 543 B. Physical Properties of Low-Molecular-Weight Acids and Acid Derivatives / 545
- 14.2** NOMENCLATURE OF CARBOXYLIC ACIDS AND THEIR DERIVATIVES **547**
 A. Naming Carboxylic Acids / 547 B. Naming Acyl Groups, Acid Chlorides, and Anhydrides / 550 C. Naming Salts and Esters / 551 D. Naming Amides, Imides, and Nitriles / 552
- 14.3** ACIDITY OF CARBOXYLIC ACIDS **555**
- 14.4** PREPARATION OF CARBOXYLIC ACIDS **557**
 A. Carboxylic Acids as Products of Oxidation Reactions / 557 B. Reactions of Organometallic Reagents with Carbon Dioxide / 558
- 14.5** CONVERTING CARBOXYLIC ACIDS TO ACID CHLORIDES AND ACID ANHYDRIDES **560**
 A. Preparation of Acid Chlorides / 560 B. Preparation of Acid Anhydrides / 560
- 14.6** REACTIONS OF CARBOXYLIC ACID DERIVATIVES WITH WATER AS NUCLEOPHILE **562**
 A. Hydrolysis Reactions / 562 B. Problem-Solving Skills / 565 C. Mechanisms of Hydrolysis Reactions / 568 D. Problem-Solving Skills / 572 E. Relative Reactivities of Acid Derivatives / 575
- 14.7** REACTION OF CARBOXYLIC ACIDS AND ACID DERIVATIVES WITH ALCOHOLS AS NUCLEOPHILES **576**

- A. Preparation of Esters / 576 B. The Mechanism of the Esterification Reaction / 580
 C. Biological Transesterification Reactions / 581
- 14.8 REACTIONS OF CARBOXYLIC ACID DERIVATIVES WITH AMMONIA OR AMINES AS NUCLEOPHILES. PREPARATION OF AMIDES 582**
- SUMMARY 584**
- ADDITIONAL PROBLEMS 586**

15

Carboxylic Acids and Their Derivatives II. Synthetic Transformations and Compounds of Biological Interest **590**

- A LOOK AHEAD 590**
- 15.1 REACTIONS OF ORGANOMETALLIC REAGENTS WITH CARBOXYLIC ACIDS AND THEIR DERIVATIVES 591**
- A. Grignard Reagents / 591 B. Organolithium Reagents / 594
- 15.2 REDUCTION OF CARBOXYLIC ACIDS AND THEIR DERIVATIVES 596**
- A. Lithium Aluminum Hydride / 596 B. Diisobutylaluminum Hydride / 600
 C. Problem-Solving Skills / 602
- 15.3 LACTONES 604**
- 15.4 LIPIDS, FATS, OILS, AND WAXES 609**
- 15.5 SURFACE-ACTIVE COMPOUNDS. SOAPS 612**
- SUMMARY 614**
- ADDITIONAL PROBLEMS 616**

16

Enols and Enolate Anions as Nucleophiles I. Halogenation, Alkylation, and Condensation Reactions **628**

- A LOOK AHEAD 628**
- 16.1 ENOLS 629**
- A. Carbanions as Reactive Intermediates / 629 B. Enols and Enolate Anions / 630
 C. Exchanging α -Hydrogen Atoms for Deuterium Atoms / 635 D. Ambident Nucleophiles / 636
 E. Relative Stabilities of Enolate Anions / 637
- 16.2 REACTIONS OF ENOLS AND ENOLATE ANIONS WITH HALOGENS AS ELECTROPHILES 640**
- A. Halogenation Reactions in Acidic Media / 640 B. Halogenation Reactions in Basic Solution. The Haloform Reaction / 641
- 16.3 REACTIONS OF ENOLATE ANIONS FROM KETONES AND ESTERS WITH ALKYL HALIDES AS ELECTROPHILES 645**
- A. Alkylation of Ketones / 645 B. Alkylation of Esters / 646 C. Problem-Solving Skills / 647
- 16.4 REACTION OF STABILIZED ENOLATE ANIONS WITH ALKYL HALIDES AS ELECTROPHILES 649**
- A. Alkylation of Ethyl Acetoacetate. Decarboxylation of β -Ketoacids / 649 B. Alkylation of Diethyl Malonate / 651
 C. Barbituric Acid Derivatives / 654
- 16.5 REACTIONS OF ENOLATE ANIONS WITH CARBONYL COMPOUNDS 656**
- A. The Aldol Condensation / 656 B. Biological Significance of the Retroaldol Reaction / 660
 C. The Formation of β -Ketoesters. The Claisen Condensation / 662
 D. The Dieckmann Condensation / 665 E. A Unified Look at Condensation Reactions / 665
 F. Problem-Solving Skills / 668
- SUMMARY 671**
- ADDITIONAL PROBLEMS 674**