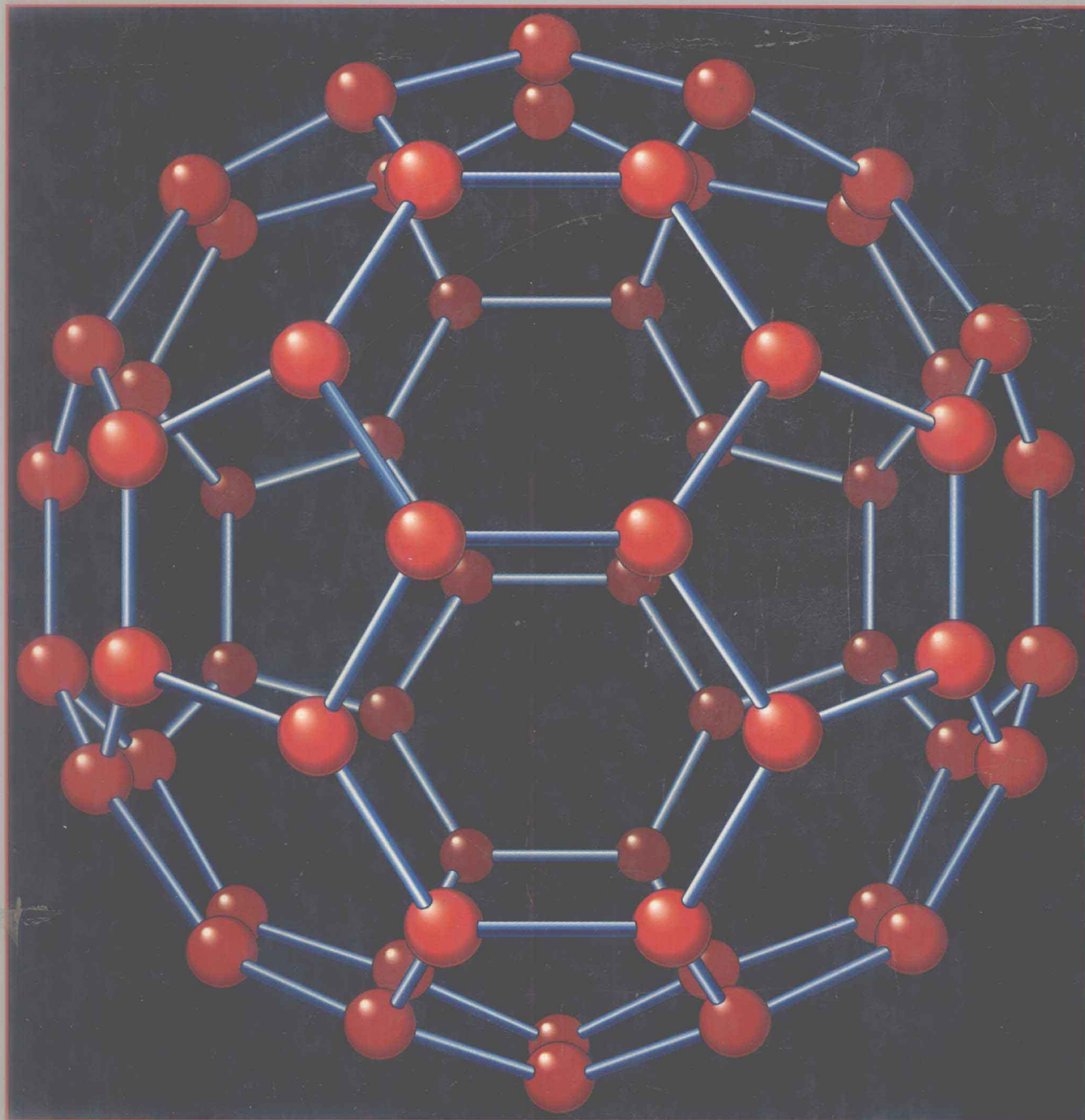


ORGANIC CHEMISTRY

FRANCIS A. CAREY



SECOND EDITION

ORGANIC CHEMISTRY

SECOND EDITION

FRANCIS A. CAREY

Department of Chemistry
University of Virginia

McGRAW-HILL, INC.

| | | | | | |
|----------|-----------|---------------|----------|-----------|-------|
| New York | St. Louis | San Francisco | Auckland | Bogotá | |
| Caracas | Lisbon | London | Madrid | Mexico | Milan |
| Montreal | New Delhi | Paris | San Juan | Singapore | |
| Sydney | Tokyo | Toronto | | | |

ORGANIC CHEMISTRY

Copyright © 1992, 1987 by McGraw-Hill, Inc. All rights reserved.
Printed in the United States of America. Except as permitted under the
United States Copyright Act of 1976, no part of this publication may be
reproduced or distributed in any form or by any means, or stored in a data
base or retrieval system, without the prior written permission of the
publisher.

5 6 7 8 9 0 VNH VNH 9 0 9 8 7 6 5 4

ISBN 0-07-009934-0

This book was set in Times Roman by Progressive Typographers, Inc.
The editors were Kirk Emry and David A. Damstra;
the designer was Rafael Hernandez;
the production supervisor was Annette Mayeski.
The copy editor was Richard A. Mickey.
The photo researcher was Elyse Rieder.
New drawings were done by J & R Services, Inc.
Von Hoffmann Press, Inc., was printer and binder.

The stamps in the introduction (pp. 1–5) are courtesy of James O. Schreck, professor of chemistry,
University of Northern Colorado.

Library of Congress Cataloging-in-Publication Data

Carey, Francis A., (date).

Organic chemistry / Francis A. Carey.—2nd ed.

p. cm.

Includes index.

ISBN 0-07-009934-0

1. Chemistry, Organic. I. Title.

QD251.2.C364 1992

547—dc20

91-19188

The ¹H nuclear magnetic resonance spectra are reproduced with permission from “The Aldrich
Library of NMR Spectra,” first edition, C. J. Pouchert and J. R. Campbell, the Aldrich Chemical
Company, 1975.

Infrared spectra are reproduced with permission from “The Aldrich Library of FT-IR Spectra,” C. J.
Pouchert, the Aldrich Chemical Company, 1985.

The ¹³C nuclear magnetic resonance spectra are reproduced with permission from “Carbon-13 NMR
Spectra: A Collection of Assigned, Coded, and Indexed Spectra,” by LeRoy F. Johnson and William
C. Jankowski, Wiley-Interscience, New York, 1972.

Figure 13.26 is courtesy of the National Institutes of Health.

Mass spectra are reproduced with permission from “EPA/NIH Mass Spectral Data Base,” Supplement
I, S. R. Heller and G. W. A. Milne, National Bureau of Standards, 1980.

Figure 13.34 is adapted from R. Isaksson, J. Roschester, J. Sandstrom, and L.-G. Wistrand, *Journal of
the American Chemical Society*, **1985**, *107*, 4074–4075 with permission of the American Chemical
Society.

Figure 27.19 is adapted with permission from F. A. Quijoco and W. N. Lipscomb in “Advances in
Protein Chemistry,” Volume 25, C. B. Anfinsen, Jr., J. T. Edsall, and F. M. Richards, Editors,
Academic Press, New York, NY, 1971.

Figure 27.22 is adapted with permission from Richard E. Dickerson in “The Proteins,” second edition,
Volume II, H. Neurath, Editor, Academic Press, New York, NY, 1964.

ABOUT THE AUTHOR

Francis A. Carey, a native of Pennsylvania, was educated in the public schools of Philadelphia, at Drexel University (B.S. in chemistry, 1959), and at Penn State (Ph.D. 1963). Following postdoctoral work at Harvard and military service, he was appointed to the chemistry faculty of the University of Virginia in 1966. With his students, he has published over forty research papers in synthetic and mechanistic organic chemistry. He is coauthor (with Richard J. Sundberg) of *Advanced Organic Chemistry*, a two-volume treatment designed for graduate students and advanced undergraduates, and (with Robert C. Atkins) of *Organic Chemistry: A Brief Course*.

*This edition is dedicated to
the memory of George S. Sasin,
professor of chemistry at Drexel University,
who first introduced me to organic chemistry.*

PREFACE

Organic chemistry is an intrinsically interesting subject, one that offers explanations for many of the things that arouse our curiosity. What, for example, is the basis for the belief that eating carrots helps maintain good eyesight? The answer is an organic chemical. Carrots contain β -carotene ($C_{40}H_{56}$), an orange-red pigment that is oxidized in the liver to a compound called *retinal* ($C_{20}H_{28}O$). Retinal combines with a protein in the eye to give a substance which has the property of absorbing visible light and transmitting it as an impulse to the brain where it is interpreted as a visual image.

Organic chemistry has a long tradition of relating the properties of a substance to its molecular structure and, more than anything else, *the relationship between how a substance behaves and the way its atoms are connected is what chemistry is all about.*

Those who teach organic chemistry point out that, unlike the course in general chemistry where topics often appear unrelated, each new topic in organic chemistry builds on what has come before. Experience has shown that students learn organic chemistry best when it is presented in a **functional group format**. Such an approach divides the material into closely related units of manageable size. Students retain their knowledge best when they understand *how* organic reactions occur. The number of fundamental **reaction mechanisms** is far fewer than the number of functional group families and provides the conceptual framework that ties together the transformations that form the body of the course. Rather than being a mass of unconnected facts, organic chemistry is a fabric in which facts and principles support one another.

As in the first edition of this text *reaction mechanisms are stressed, but within a functional group framework.* The mechanistic discussion in the first edition was made more accessible to the student by presenting the individual steps of a reaction as a series of equations with commentary in a stand-alone figure. The number of reaction mechanisms presented in this way has been increased in the second edition.

New to this edition are twenty-five **essays** scattered throughout the text. These boxed essays provide a combination of historical perspective and additional insight into the contemporary relevance of organic chemistry. A few of the topics discussed in these essays include *molecular modeling, anabolic steroids, gas chromatography-mass spectrometry, Kekulé's dreams, and carbon clusters.*

The inclusion of **marginal notes** is also new. Many are biographical and remind us that organic chemistry is a human enterprise, one that becomes more interesting when we know something about the people responsible for the discoveries we read about. Some suggest articles, usually in the *Journal of Chemical Education*, to which readers interested in a fuller account of some topic can refer for additional information. Others offer a one-sentence generalization of a principle, or comments on terminology, applications, etc.

SIGNIFICANT CHANGES IN CONTENT AND ORGANIZATION

- Chapter 1 includes an early introduction to *orbital hybridization* in methane, ethane, ethylene, and acetylene.
- Two chapters that dealt separately with the *structure and preparation of alkenes* in the first edition have been combined into a single chapter (Chapter 5). Similarly, the pair of chapters describing *alkylamines and arylamines* have been rewritten to provide a unified treatment of both amine classes in Chapter 22.
- *Fischer projection formulas* are now introduced along with the principal aspects of stereochemistry in Chapter 7.

The text continues to be **selective** rather than encyclopedic in its scope. One feature of the first edition was the deliberate exclusion of a number of reactions that had been traditionally included in the introductory organic chemistry course but which are rarely used today. The extent to which organic chemistry instructors noticed and agreed with these omissions was encouraging. Accordingly, the pruning process has continued in this edition and has made space available for an expanded treatment of topics of more current interest.

Polymers, both natural and synthetic, receive increased attention. The synthesis and properties of addition polymers are developed in chapters concerned with the reactions of alkenes (Chapter 6), conjugated dienes (Chapter 10), and styrene (Chapter 11). Condensation polymers, especially polyesters and polyamides, are discussed along with carboxylic acid derivatives in Chapter 21.

Some of the new topics introduced in this edition include:

- *Birch reduction*
- *Claisen rearrangement*
- *electrocyclic reactions*
- *Baeyer-Villiger oxidation*
- *DNA sequencing*

The coverage of other topics, most notably *organosulfur chemistry*, *pericyclic reactions*, and *heterocyclic compounds*, has been expanded.

STUDY AND LEARNING AIDS FOR THE STUDENT

The design and placement of **annotated summary tables** were well-received features of the first edition and the number and variety of such tables has been increased. Several of the new tables resemble the earlier ones in being concerned with reactions, while others emphasize skills and concepts such as the *writing of Lewis structures*, the *rules of resonance*, the *IUPAC rules for alkanes and alkyl groups*, and *structural limitations on Friedel-Crafts reactions*.

The number of **problems** has been increased. More importantly, so has their quality and variety. Instructors seemed satisfied with the number and level of drill

problems, but some expressed a wish for more problems involving mechanistic reasoning. Most of the new problems are of that type.

Each **end-of-chapter summary** has been rewritten and expanded.

A **glossary** has been added and appears at the end of the book just before the index.

In general, students seem to grasp the IUPAC rules relatively easily and prefer systematic names to common ones. Consequently, *systematic IUPAC nomenclature receives even greater emphasis than before*.

This edition uses *four colors* throughout the book. By color coding various atoms and groups, the text directs the reader's attention toward the important features of chemical structures and their reacting sites.

SUPPLEMENTS

Study Guide by Francis A. Carey and Robert C. Atkins. This valuable supplement provides solutions to all problems in the text. Each solution is sufficiently detailed to provide the student with the steps leading to the solution. In addition, each chapter includes summaries headed *Important Terms and Concepts* or *Important Reactions*. These are intended to provide brief overviews of the major points and topics presented in each chapter of the text. At the conclusion of each chapter is a Self-Test designed to test the student's mastery of the material.

Overhead Transparencies. These four-color transparencies of illustrations from the text include reproductions of spectra, orbital diagrams, key tables, computer-generated molecular models, and step-by-step reaction mechanisms.

Test Bank. Available to instructors in print and IBM-PC and Macintosh computerized versions.

ACKNOWLEDGMENTS

Special thanks go to Randi Rossignol, David A. Damstra, and Robert C. Atkins. As senior editor at McGraw-Hill, Randi was a continuing source of ideas and a colleague whose judgment could be relied on. It was a pleasure to work with her. David Damstra was the McGraw-Hill editor in charge of production. His "can-do" attitude and his professionalism are both sincerely appreciated. Bob Atkins is my coauthor on the *Study Guide* that accompanies this text. But more than that, Bob is someone to share ideas with. His opinions have helped shape the text to make it more useful to the student.

The first edition of this text was developed in the belief that the students who take organic chemistry are highly motivated and intellectually curious. The second edition reaffirms its commitment to these students. In attempting to make this text more useful than the first, I am pleased to acknowledge the generous assistance of a great many people. Teachers who reviewed the text during the preparation of the second edition include:

Neil T. Allison, Fullbright College
 William F. Bailey, University of Connecticut
 John L. Belletire, University of Cincinnati
 Robert Boschan, University of California—Los Angeles
 Andrej Cieplak, Fordham University
 Leticia J. El-Naggar, Bucks County Community College
 Morris L. Fishman, New York University

CONTENTS IN BRIEF

| | |
|--|-------|
| PREFACE | xxvii |
| INTRODUCTION | 1 |
| 1 CHEMICAL BONDING | 6 |
| 2 ALKANES | 48 |
| 3 CONFORMATIONS OF ALKANES AND CYCLOALKANES | 82 |
| 4 ALCOHOLS AND ALKYL HALIDES | 117 |
| 5 STRUCTURE AND PREPARATION OF ALKENES. ELIMINATION REACTIONS | 161 |
| 6 REACTIONS OF ALKENES: ADDITION REACTIONS | 205 |
| 7 STEREOCHEMISTRY | 258 |
| 8 NUCLEOPHILIC SUBSTITUTION | 303 |
| 9 ALKYNES | 342 |
| 10 CONJUGATION IN ALKADIENES AND ALLYLIC SYSTEMS | 369 |
| 11 ARENES AND AROMATICITY | 407 |
| 12 REACTIONS OF ARENES. ELECTROPHILIC AROMATIC SUBSTITUTION | 452 |
| 13 SPECTROSCOPY | 499 |
| 14 ORGANOMETALLIC COMPOUNDS | 553 |
| 15 ALCOHOLS, DIOLS, AND THIOLS | 593 |
| 16 ETHERS, EPOXIDES, AND SULFIDES | 634 |
| 17 ALDEHYDES AND KETONES. NUCLEOPHILIC ADDITION TO THE CARBONYL GROUP | 673 |
| 18 ENOLS, ENOLATES, AND ENAMINES | 724 |
| 19 CARBOXYLIC ACIDS | 762 |
| 20 CARBOXYLIC ACID DERIVATIVES. NUCLEOPHILIC ACYL SUBSTITUTION | 804 |
| 21 ESTER ENOLATES | 863 |
| 22 AMINES | 895 |

| | | |
|-----------|---|-------------|
| 23 | ARYL HALIDES | 957 |
| 24 | PHENOLS | 978 |
| 25 | CARBOHYDRATES | 1012 |
| 26 | ACETATE-DERIVED NATURAL PRODUCTS | 1058 |
| 27 | AMINO ACIDS, PEPTIDES, AND PROTEINS. NUCLEIC ACIDS | 1094 |
| | APPENDIX 1. PHYSICAL PROPERTIES | 1154 |
| | APPENDIX 2. ANSWERS TO IN-TEXT PROBLEMS | 1163 |
| | GLOSSARY | 1217 |
| | INDEX | 1247 |

CONTENTS

| | |
|--|-------|
| PREFACE | xxvii |
| INTRODUCTION | 1 |
| The Origins of Organic Chemistry | 1 |
| Berzelius, Wöhler, and Vitalism | 1 |
| The Structural Theory | 2 |
| Electronic Theories of Structure and Reactivity | 3 |
| The Impact of Organic Chemistry | 3 |
| Challenges and Opportunities | 4 |
| CHAPTER 1 | |
| CHEMICAL BONDING | 6 |
| 1.1 Atoms, Electrons, and Orbitals | 6 |
| 1.2 Ionic Bonds | 9 |
| 1.3 Covalent Bonds | 11 |
| 1.4 Multiple Bonding in Lewis Structures | 13 |
| 1.5 Polar Covalent Bonds and Electronegativity | 14 |
| 1.6 Formal Charge | 16 |
| 1.7 Writing Structural Formulas of Organic Molecules | 18 |
| 1.8 Constitutional Isomers | 22 |
| 1.9 Resonance | 23 |
| 1.10 The Shapes of Some Simple Molecules | 27 |
| 1.11 Molecular Dipole Moments | 30 |
| 1.12 Molecular Orbitals of the Hydrogen Molecule | 31 |
| 1.13 sp^3 Hybridization and Bonding in Methane | 32 |
| 1.14 sp^3 Hybridization and Bonding in Ethane | 35 |

| | | |
|------|--|----|
| 1.15 | <i>sp</i> ² Hybridization and Bonding in Ethylene | 35 |
| 1.16 | <i>sp</i> Hybridization and Bonding in Acetylene | 38 |
| 1.17 | Which Theory of Chemical Bonding is Best? | 40 |
| 1.18 | Summary | 40 |
| | Problems | 43 |

CHAPTER 2

ALKANES 48

| | | |
|------|---|----|
| 2.1 | Classes of Hydrocarbons | 48 |
| 2.2 | Functional Groups in Hydrocarbons | 49 |
| 2.3 | Functionally Substituted Derivatives of Alkanes | 50 |
| 2.4 | Carbonyl-Containing Functional Groups | 51 |
| 2.5 | Introduction to Alkanes: Methane | 51 |
| 2.6 | Ethane and Propane | 52 |
| 2.7 | Isomeric Alkanes: The Butanes | 53 |
| 2.8 | Higher <i>n</i> -Alkanes | 53 |
| 2.9 | The C ₅ H ₁₂ Isomers | 54 |
| 2.10 | Systematic IUPAC Nomenclature of Unbranched Alkanes | 56 |
| | <i>A Brief History of Systematic Organic Nomenclature</i> | 57 |
| 2.11 | Applying the IUPAC Rules: The Names of the C ₆ H ₁₄ Isomers | 58 |
| 2.12 | Alkyl Groups | 60 |
| 2.13 | IUPAC Names of Highly Branched Alkanes | 62 |
| 2.14 | Cycloalkane Nomenclature | 64 |
| 2.15 | Sources of Alkanes and Cycloalkanes | 65 |
| 2.16 | Physical Properties of Alkanes and Cycloalkanes | 66 |
| 2.17 | Chemical Properties. Combustion of Alkanes | 69 |
| | <i>Thermochemistry</i> | 71 |
| 2.18 | Oxidation-Reduction in Organic Chemistry | 73 |
| 2.19 | Summary | 75 |
| | Problems | 78 |

CHAPTER 3

CONFORMATIONS OF ALKANES
AND CYCLOALKANES 82

| | | |
|------|---|-----|
| 3.1 | Conformational Analysis of Ethane | 83 |
| 3.2 | Internal Rotation in Ethane | 84 |
| 3.3 | Conformational Analysis of Butane | 86 |
| | <i>Molecular Modeling</i> | 88 |
| 3.4 | Conformations of Higher Alkanes | 89 |
| 3.5 | The Shapes of Cycloalkanes: Planar or Nonplanar? | 89 |
| 3.6 | Conformations of Cyclohexane | 91 |
| 3.7 | Axial and Equatorial Bonds in Cyclohexane | 92 |
| 3.8 | Conformational Inversion (Ring Flipping) in Cyclohexane | 93 |
| 3.9 | Conformational Analysis of Monosubstituted Cyclohexanes | 96 |
| | <i>Enthalpy, Free Energy, and Equilibrium Constant</i> | 98 |
| 3.10 | Small Rings: Cyclopropane and Cyclobutane | 99 |
| 3.11 | Cyclopentane | 100 |
| 3.12 | Medium and Large Rings | 100 |

| | | |
|------|---|-----|
| 3.13 | Disubstituted Cycloalkanes. Stereoisomers | 101 |
| 3.14 | Conformational Analysis of Disubstituted Cyclohexanes | 103 |
| 3.15 | Polycyclic Ring Systems | 107 |
| 3.16 | Heterocyclic Compounds | 109 |
| 3.17 | Summary | 110 |
| | Problems | 112 |

CHAPTER 4
ALCOHOLS AND ALKYL HALIDES 117

| | | |
|------|--|------------|
| 4.1 | IUPAC Nomenclature of Alkyl Halides | 118 |
| 4.2 | IUPAC Nomenclature of Alcohols | 118 |
| 4.3 | Classes of Alcohols and Alkyl Halides | 119 |
| 4.4 | Bonding in Alcohols and Alkyl Halides | 120 |
| 4.5 | Physical Properties of Alcohols and Alkyl Halides | 121 |
| 4.6 | Acids and Bases: General Principles | 124 |
| 4.7 | Acid-Base Reactions. A Mechanism for Proton Transfer | 127 |
| 4.8 | Acidity of Alcohols. Alkoxide Ions | 128 |
| 4.9 | Preparation of Alkyl Halides from Alcohols and Hydrogen Halides | 129 |
| 4.10 | Mechanism of the Reaction of Alcohols with Hydrogen Halides | 131 |
| 4.11 | Structure, Bonding, and Stability of Carbocations | 132 |
| 4.12 | Potential Energy Diagrams for Multistep Reactions | 135 |
| 4.13 | Effect of Alcohol Structure on Reaction Rate | 137 |
| 4.14 | Mechanism of the Reaction of Primary Alcohols with Hydrogen Halides | 139 |
| 4.15 | Other Methods for Converting Alcohols to Alkyl Halides | 139 |
| 4.16 | Halogenation of Alkanes | 140 |
| 4.17 | Chlorination of Methane | 141 |
| 4.18 | Structure and Stability of Free Radicals <i>From Bond Energies to Heats of Reaction</i> | 142 146 |
| 4.19 | Mechanism of Methane Chlorination | 147 |
| 4.20 | Halogenation of Higher Alkanes. Regioselectivity | 149 |
| 4.21 | Summary | 152 |
| | Problems | 156 |

CHAPTER 5
STRUCTURE AND PREPARATION OF ALKENES.
ELIMINATION REACTIONS 161

| | | |
|-----|---|-----|
| 5.1 | Alkene Nomenclature | 161 |
| | <i>Ethylene</i> | 163 |
| 5.2 | Structure and Bonding in Alkenes | 164 |
| 5.3 | Isomerism in Alkenes | 166 |
| 5.4 | Naming Stereoisomeric Alkenes by the <i>E-Z</i> Notational System | 167 |
| 5.5 | Physical Properties of Alkenes | 170 |
| 5.6 | Relative Stabilities of Alkenes | 171 |
| 5.7 | Sources of Strain in Cycloalkenes | 174 |
| 5.8 | Preparation of Alkenes: Elimination Reactions | 176 |
| 5.9 | Dehydration of Alcohols | 177 |

| | | |
|------|--|-----|
| 5.10 | Regioselectivity in Alcohol Dehydration: The Zaitsev Rule | 178 |
| 5.11 | The Mechanism of Acid-Catalyzed Dehydration of Alcohols | 180 |
| 5.12 | Rearrangements in Alcohol Dehydration | 182 |
| 5.13 | Dehydrohalogenation of Alkyl Halides | 186 |
| 5.14 | Mechanism of the Dehydrohalogenation of Alkyl Halides: The E2 Mechanism | 188 |
| 5.15 | Anti Elimination in E2 Reactions: Stereoelectronic Effects | 191 |
| 5.16 | Stereoselectivity in E2 Elimination Reactions | 192 |
| 5.17 | A Different Mechanism for Alkyl Halide Elimination: The E1 Mechanism | 194 |
| 5.18 | Summary | 195 |
| | Problems | 199 |

CHAPTER 6

REACTIONS OF ALKENES: ADDITION REACTIONS 205

| | | |
|------|---|-----|
| 6.1 | Hydrogenation of Alkenes | 205 |
| 6.2 | Heats of Hydrogenation | 207 |
| 6.3 | Stereochemistry of Alkene Hydrogenation | 209 |
| 6.4 | Electrophilic Addition of Hydrogen Halides to Alkenes | 211 |
| 6.5 | Regioselectivity of Hydrogen Halide Addition: Markovnikov's Rule | 212 |
| 6.6 | Mechanistic Basis for Markovnikov's Rule | 214 |
| 6.7 | Free-Radical Addition of Hydrogen Bromide to Alkenes | 217 |
| 6.8 | Addition of Sulfuric Acid to Alkenes | 220 |
| 6.9 | Acid-Catalyzed Hydration of Alkenes | 222 |
| 6.10 | Hydroboration-Oxidation of Alkenes | 225 |
| 6.11 | Stereochemistry of Hydroboration-Oxidation | 228 |
| 6.12 | Mechanism of Hydroboration-Oxidation | 228 |
| 6.13 | Addition of Halogens to Alkenes | 231 |
| 6.14 | Stereochemistry of Halogen Addition | 232 |
| 6.15 | Mechanism of Halogen Addition of Alkenes. Halonium Ions | 233 |
| 6.16 | Conversion of Alkenes to Vicinal Halohydrins | 235 |
| 6.17 | Epoxidation of Alkenes | 237 |
| 6.18 | Ozonolysis of Alkenes | 240 |
| 6.19 | Analysis of Alkenes: Molecular Formula as a Clue to Structure | 242 |
| 6.20 | Reactions of Alkenes with Alkenes: Polymerization <i>Ethylene and Propene: The Most Important Industrial Organic Chemicals</i> | 246 |
| 6.21 | Introduction to Organic Chemical Synthesis | 247 |
| 6.22 | Summary | 250 |
| | Problems | 252 |

CHAPTER 7

STEREOCHEMISTRY 258

| | | |
|-----|--|-----|
| 7.1 | Molecular Chirality. Enantiomers | 258 |
| 7.2 | The Stereogenic Center | 260 |
| 7.3 | Symmetry in Achiral Structures | 262 |
| 7.4 | Properties of Chiral Molecules: Optical Activity | 264 |

| | | |
|------|--|------------|
| 7.5 | Absolute and Relative Configuration | 267 |
| 7.6 | The Cahn-Ingold-Prelog <i>R-S</i> Notational System | 268 |
| 7.7 | Fischer Projection Formulas | 272 |
| 7.8 | Physical Properties of Enantiomers | 273 |
| 7.9 | Stereochemistry in Chemical Reactions That Produce Chiral Molecules | 274 |
| 7.10 | Chiral Molecules with Two Stereogenic Centers | 278 |
| 7.11 | Achiral Molecules with Two Stereogenic Centers <i>Chirality of Disubstituted Cyclohexanes</i> | 280 282 |
| 7.12 | Molecules with Multiple Stereogenic Centers | 283 |
| 7.13 | Chemical Reactions That Produce Diastereomers | 285 |
| 7.14 | Resolution of Enantiomers | 288 |
| 7.15 | Stereoregular Polymers | 291 |
| 7.16 | Stereogenic Centers Other Than Carbon | 292 |
| 7.17 | Summary | 293 |
| | Problems | 295 |

CHAPTER 8
NUCLEOPHILIC SUBSTITUTION 303

| | | |
|------|--|-----|
| 8.1 | Functional Group Transformation by Nucleophilic Substitution | 303 |
| 8.2 | Substitution of One Halogen by Another | 306 |
| 8.3 | Relative Reactivity of Halide Leaving Groups | 307 |
| 8.4 | The Bimolecular (S_N2) Mechanism of Nucleophilic Substitution | 308 |
| 8.5 | Stereochemistry of S_N2 Reactions | 309 |
| 8.6 | How S_N2 Reactions Occur | 311 |
| 8.7 | Steric Effects in S_N2 Reactions | 312 |
| 8.8 | Nucleophiles and Nucleophilicity | 314 |
| 8.9 | The Unimolecular (S_N1) Mechanism of Nucleophilic Substitution | 317 |
| 8.10 | Carbocation Stability and the Rate of Substitution by the S_N1 Mechanism | 318 |
| 8.11 | Stereochemistry of S_N1 Reactions | 320 |
| 8.12 | Carbocation Rearrangements in S_N1 Reactions | 322 |
| 8.13 | Solvent Effects | 323 |
| 8.14 | Substitution and Elimination as Competing Reactions | 325 |
| 8.15 | Sulfonate Esters as Substrates in Nucleophilic Substitution Reactions | 328 |
| 8.16 | A Retrospective Look: Reactions of Alcohols with Hydrogen Halides | 331 |
| 8.17 | Summary | 333 |
| | Problems | 333 |

CHAPTER 9
ALKYNES 342

| | | |
|-----|--------------------|-----|
| 9.1 | Sources of Alkynes | 342 |
| 9.2 | Nomenclature | 343 |

| | | |
|------|---|-----|
| 9.3 | Structure and Bonding in Alkynes. <i>sp</i> Hybridization | 344 |
| 9.4 | Cycloalkynes | 345 |
| 9.5 | Physical Properties | 346 |
| 9.6 | Acidity of Acetylene and Terminal Alkynes | 346 |
| 9.7 | Preparation of Alkynes by Alkylation of Acetylene and Terminal Alkynes | 349 |
| 9.8 | Preparation of Alkynes by Elimination Reactions | 351 |
| 9.9 | Reactions of Alkynes | 353 |
| 9.10 | Hydrogenation of Alkynes | 353 |
| 9.11 | Metal-Ammonia Reduction of Alkynes | 355 |
| 9.12 | Addition of Hydrogen Halides to Alkynes | 357 |
| 9.13 | Hydration of Alkynes | 359 |
| 9.14 | Addition of Halogens to Alkynes | 360 |
| 9.15 | Ozonolysis of Alkynes | 361 |
| 9.16 | Summary | 362 |
| | Problems | 363 |

CHAPTER 10

CONJUGATION IN ALKADIENES AND ALLYLIC
SYSTEMS

369

| | | |
|-------|---|-----|
| 10.1 | The Allyl Group | 369 |
| 10.2 | Allylic Carbocations | 370 |
| 10.3 | Allylic Free Radicals | 373 |
| 10.4 | Allylic Halogenation | 374 |
| 10.5 | Classes of Dienes | 376 |
| 10.6 | Relative Stabilities of Alkadienes | 378 |
| 10.7 | Electron Delocalization in Conjugated Dienes | 379 |
| 10.8 | Bonding in Allenes | 381 |
| 10.9 | Preparation of Dienes | 383 |
| 10.10 | Addition of Hydrogen Halides to Conjugated Dienes | 384 |
| 10.11 | Halogen Addition to Dienes | 386 |
| | <i>Diene Polymers</i> | 387 |
| 10.12 | The Diels-Alder Reaction | 388 |
| 10.13 | Stereoselectivity of Diels-Alder Reactions | 391 |
| 10.14 | Electrocyclic Reactions of Polyenes | 392 |
| 10.15 | The π Molecular Orbitals of Alkenes and Conjugated Polyenes | 394 |
| 10.16 | A π Molecular Orbital Analysis of the Diels-Alder Reaction | 397 |
| 10.17 | A π Molecular Orbital Analysis of Electrocyclic Reactions | 398 |
| 10.18 | Summary | 399 |
| | Problems | 402 |

CHAPTER 11

ARENES AND AROMATICITY

407

| | | |
|------|---|-----|
| 11.1 | Benzene | 407 |
| 11.2 | Benzene Reactivity | 408 |
| 11.3 | Kekule's Formulation of the Benzene Structure | 409 |
| | <i>Benzene, Dreams, and Creative Thinking</i> | 410 |

| | | |
|-------|---|-----|
| 11.4 | Structural Features of Benzene | 411 |
| 11.5 | A Resonance Description of Bonding in Benzene | 411 |
| 11.6 | The Stability of Benzene | 412 |
| 11.7 | An Orbital Hybridization Model of Bonding in Benzene | 414 |
| 11.8 | The π Molecular Orbitals of Benzene | 414 |
| 11.9 | Substituted Derivatives of Benzene and Their Nomenclature | 415 |
| 11.10 | Polycyclic Aromatic Hydrocarbons | 418 |
| 11.11 | Physical Properties of Arenes | 419 |
| 11.12 | Reactions of Arenes: A Preview | 420 |
| 11.13 | The Birch Reduction | 420 |
| 11.14 | Free-Radical Halogenation of Alkylbenzenes | 422 |
| 11.15 | Oxidation of Alkylbenzenes | 425 |
| 11.16 | Nucleophilic Substitution in Benzylic Halides | 426 |
| 11.17 | Preparation of Alkenylbenzenes | 428 |
| 11.18 | Addition Reactions of Alkenylbenzenes | 428 |
| 11.19 | Polymerization of Styrene | 430 |
| 11.20 | Cyclobutadiene and Cyclooctatetraene | 431 |
| 11.21 | Hückel's Rule. Annulenes | 433 |
| 11.22 | Aromatic Ions | 435 |
| 11.23 | Heterocyclic Aromatic Compounds | 439 |
| 11.24 | Heterocyclic Aromatic Compounds and Hückel's Rule | 441 |
| | <i>Carbon Clusters</i> | 442 |
| 11.25 | Summary | 443 |
| | Problems | 446 |

CHAPTER 12

REACTIONS OF ARENES. ELECTROPHILIC
AROMATIC SUBSTITUTION 452

| | | |
|-------|--|-----|
| 12.1 | Representative Electrophilic Aromatic Substitution Reactions of Benzene | 453 |
| 12.2 | Mechanistic Principles of Electrophilic Aromatic Substitution | 454 |
| 12.3 | Nitration of Benzene | 456 |
| 12.4 | Sulfonation of Benzene | 457 |
| 12.5 | Halogenation of Benzene | 458 |
| 12.6 | Friedel-Crafts Alkylation of Benzene | 460 |
| 12.7 | Friedel-Crafts Acylation of Benzene | 463 |
| 12.8 | Synthesis of Alkylbenzenes by Acylation-Reduction | 465 |
| 12.9 | Rate and Orientation in Electrophilic Aromatic Substitution | 467 |
| 12.10 | Rate and Orientation in the Nitration of Toluene | 468 |
| 12.11 | Rate and Orientation in the Nitration of (Trifluoromethyl)benzene | 471 |
| 12.12 | Substituent Effects in Electrophilic Aromatic Substitution: Activating Substituents | 473 |
| 12.13 | Substituent Effects in Electrophilic Aromatic Substitution: Deactivating Substituents | 477 |
| 12.14 | Substituent Effects in Electrophilic Aromatic Substitution: Halogen Substituents | 480 |
| 12.15 | Multiple Substituent Effects | 481 |