Ottomic Chemistry

Alas S. Wiegrove

Report L. Caret

Organic Chemistry

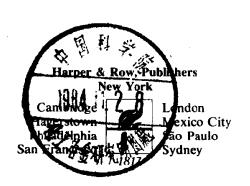
Alan S. Wingrove

Towson State University

Robert L. Caret

Towson State University





Sponsoring Editor: Malvina Wasserman

Project Editors: Eva Marie Strock and Penelope Schmukler

Text and Cover Designer: Nancy B. Benedict Senior Production Manager: Kewal K. Sharma Assistant Production Manager: Marian Hartsough Compositor Syntax International Pte. Ltd.

Printer and Binder: R. R. Donnelley & Sons, Co.

Art Studio: J & R Services; Syntax International Pte. Ltd.

ORGANIC CHEMISTRY

Copyright © 1981 by Alan S. Wingrove and Robert L. Caret

All rights reserved. Printed in the United States of America. No part of this book may be used or reproduced in any manner whatsoever without written permission except in the case of brief quotations embodied in critical articles and reviews. For information address Harper & Row, Publishers, Inc., 10 East 53rd Street, New York, N.Y. 10022.

Library of Congress Cataloging in Publication Data

Wingrove, Alan S., 1939-Organic chemistry.

Includes bibliographical references and index.

1. Chemistry, Organic. I. Caret, Robert L.,

1947-II. Title.

QD251.2.W55 547

ISBN 0-06-163400-X

81-845 AACR2

Permission for the publication herein of Sadtler Standard Spectra® has been granted, and all rights are reserved, by Sadtler Research Laboratories, division of Bio-Rad Laboratories, Inc.

Brief Contents

	Preface xxi
1	Organic Chemistry 1
2	Atomic and Molecular Structure; Molecular Orbital Theory 17
3	Alkanes and Cycloalkanes: Structure, Properties, and Nomenclature 64
4	Alkanes and Cycloalkanes: Preparation and Reactions 121
5	Reaction Mechanisms 145
6	Stereochemistry and Stereoisomerism 184
7	Alkenes and Alkadienes: Structure and Properties 243
8	Alkenes and Alkadienes: Reactions; Natural and Synthetic Polymers 289
9	Alkyl Halides: Substitution and Elimination Reactions 365
10	Alcohols 409
11	Alkynes: Structure, Properties Nomenclature, Preparations, and Reactions 46
12	Spectroscopy 1—Spectroscopic Methods: Infrared and Ultraviolet Spectroscopy 491
13	An Introduction to Benzene, Resonance Structures, and Aromaticity 522
14	Reactions of Aromatic Compounds: Electrophilic Aromatic Substitution 556
15	Spectroscopy 2—Spectroscopic Methods: Nuclear Magnetic Resonance Spectroscopy 623
16	Aryl and Vinyl Halides 670
17	Phenois 695
18	Spectroscopy 3-Spectroscopic Methods: Mass Spectrometry 721
19	Ethers, Epoxides, and Glycols 733
20	Aldehydes and Ketones: Preparation of the Carbon-Oxygen Double Bond 786
21	Aldehydes and Ketones: Reactions of the Carbon-Oxygen Double Bond 818
22	Carboxylic Acids and Dicarboxylic Acids 890
23	Derivatives of Carboxylic and Dicarboxylic Acids 939
24	Reactions of α Hydrogens in Carbonyl and β -Dicarbonyl Compounds: Condensation Reactions 1017
25	Lipids: Fats and Oils 1090
26	Amines 1104
27	Cycloaddition Reactions: Woodward-Hoffmann Rules 1178
28	Amino Acids, Peptides, and Proteins 1210
29	Carbohydrates 1260

Appendix: Reading References 1321

Index 1335

Preface

The inception, formulation, and eventual birth of a new textbook is an evolutionary process, beginning with a need by the author, a need for something better for the students. Upon beginning this project we felt that such a need existed, a text that was better organized and more coherent than currently available texts and written in a style students could both understand and find pleasant. This book is a result of our efforts to attain that goal.

Organic Chemistry is designed and written to be a comprehensive one-year text that can be used with equal facility in courses for chemistry majors, biological science students, and preprofessional students in the medical, dental, and pharmaceutical fields. The text provides a solid background in classical organic chemistry, and the numerous examples of organic compounds of current interest, concern, and/or biochemical importance provide special appeal to the students in the various disciplines.

The text is written for the student, in a clear and understandable style, and we made every effort to incorporate detailed explanations of the material so students can use the book on their own. Many published texts assume that students can read between the lines and understand the concepts being put forth; but this is not always true. The real key to studying and learning organic chemistry is a clear and coherent organization. The highlights of the organizational features of this text include:

Functional Group Approach

Organic Chemistry uses the functional group approach, which eliminates the needless repetition and discontinuity of thought that often arises in other texts. For example, we grouped alkanes and cycloalkanes (Chapters 3 and 4), alkenes and alkadienes (Chapters 7 and 8), and atomic and molecular structure (Chapter 2). Also, because the coverage of hydrocarbon chemistry has been reduced, other functional groups (alkyl halides in Chapter 9 and alcohols in Chapter 10) can be easily presented in the first semester. This provides a much more equitable distribution of the material between the two semesters than other texts.

Study Hints

Study hints and other suggestions for study methods that may be potentially useful in helping students succeed and avoid common pitfalls are presented throughout the text. Examples of these highlights, set off by color, include "How To Approach Organic Synthesis," "How To Study Organic Chemistry," "Flash Cards in Organic Chemistry," "How To Draw Resonance Structures," Oxida-

tion and Reduction in Organic Chemistry," "Reactive Intermediates," and "Electrophiles and Nucleophiles." A complete list appears in the Contents of the Study Guide.

Atomic and Molecular Structure

Atomic and molecular structure and molecular orbital theory are presented together in Chapter 2, and the various hybridizations of carbon are developed simultaneously in that chapter. The similarities and differences among these topics can thus be contrasted more readily, to avoid repetition and review in future chapters. For those instructors who choose not to discuss molecular orbital theory, we have separated the theory from the more qualitative discussions of bonding in Chapter 2. Thus, either the qualitative or/and the more theoretical approach to bonding can be taught since they appear in separate sections in the chapter.

Hydrocarbon Chemistry

Numerous modern texts dwell on hydrocarbon chemistry, often to the extent that the first-semester course seldom covers much beyond aromatic chemistry. We reduced the coverage of alkane chemistry, but we still hit the important highlights and introduce the basic concepts that evolve from them. This allows for the coverage of other functional groups, such as alkyl halides (Chapter 9) and alcohols (Chapter 10) in the first semester, permits greater flexibility in the second semester, and gives a better foundation for the laboratory portion of the course.

Mechanisms and Reactive Intermediates

Reaction theory and reaction mechanisms are first introduced and discussed together in Chapter 5, Reaction Mechanisms; nucleophilic aliphatic substitution is also introduced there. Product distribution, the effect of temperature and concentration, the use of stereochemistry, kinetics and isotope labels, and other experimental tools are discussed from the standpoint of explaining how reaction mechanisms are elucidated. The structure of carbocations, carbanions, carbon radicals, and carbenes are all presented in Chapter 2, and in Chapter 5 their relative stabilities, methods of formation, and reactions are contrasted. This material provides a strong foundation for the use of reaction mechanisms throughout the remainder of the text.

Spectroscopy

The spectroscopy material is presented in three separate chapters. Chapter 12 covers infrared and ultraviolet spectroscopy and follows the chapters on alkanes, alkenes, and alkynes; Chapter 15 covers nuclear magnetic resonance and follows aromatic chemistry; and Chapter 18 covers mass spectrometry and follows the aryl halides and phenols. This spreads out the material and gives students time to think about and use their newly gained knowledge of spectral techniques before delving into another technique. Once introduced, spectroscopy is integrated throughout all the subsequent chapters. This building-block ap-

Preface xxiii

proach provides a sound background in both the understanding and use of spectral methods.

Relevant Examples

Numerous relevant examples of organic compounds of bioorganic, medicinal, industrial, and environmental interest abound throughout the text, including sections on sweeteners, smog, soaps and detergents, natural products, prostaglandins, paints, and polymers. Complete chapters dealing with proteins (Chapter 28) and carbohydrates (Chapter 29) are also included. All these examples are grouped by area and listed in the Contents of the Study Guide.

Summaries

Many summaries of important material are included to help the student, such as summaries of K_a 's, K_b 's, spectral data, nomenclature, and bond energies. A summary of reactions follows each chapter; a complete reaction summary is compiled in the Study Guide.

Study Problems and Reading References

The text contains more than 900 problems of varying difficulty with over 3000 parts. About 50 percent of these problems are incorporated into the text as questions; about 50 percent are end-of-chapter study questions. Unlike most of the other texts in this field, this text's problems are written for the students—they are the type of problems instructors write for their own exams—and will provide a great deal of needed and useful practice. Reading references are presented in the appendix. Most of these references are from the *Journal of Chemical Education* and can be read and understood by the beginning student; selected textbooks are also listed whenever appropriate.

Study Guide and Answer Book

The Study Guide contains (1) a detailed answer for each problem, (2) a complete summary of nomenclature, (3) a complete summary of all reactions in the text, and (4) lists of relevant sections from the text by area (for example, industrial chemistry, bioorganic chemistry, medicinal chemistry, and environmental chemistry). The Study Guide will be very useful and invaluable to students as an aid in understanding and mastering organic chemistry.

Acknowledgments

A project of this magnitude is the result of the efforts of many individuals. We would like to thank the reviewers who read and criticized all or portions of the manuscript at the various stages of its development: Paul Barks (North Hennepin Community College, Minnesota), Paula Bruice (University of California, Santa Barbara), Robert Coley (Montgomery Community College, Maryland), Rasma Derrums (Miami-Dade Community College, Florida), Lloyd Dolby (University of Oregon, Eugene), Robert Gilman (Rochester Institute of Technology, New York), Kenneth Kemp (University of Nevada, Reno), Axtell Kramer, Jr.

(Meramec Community College, Missouri), Ronald Magid (University of Tennessee), John Mangravite (West Chester State College, Pennsylvania), Kenneth Marsi (California State University, Long Beach), James Mulvaney (University of Arizona, Tucson), Michael Ogliaruso (Virginia Polytechnic Institute), J. David Rawn (Towson State University, Maryland), Lanny Replogle (San Jose State University, California), Paul Robbins (Armstrong State College, Georgia), Richard Schowen (University of Kansas, Lawrence), Jan Simek (California Polytechnic Institute, California), Lawrence Singer (University of Southern California), Carl Snyder (University of Miami, Coral Gables), J. J. Topping (Towson State University, Maryland), and Gary Yost (Towson State University, Maryland).

We are also grateful to Leroy (Skip) Wade (Colorado State University) for twice reviewing the entire manuscript, for proofreading the galleys, for checking all the problems, and for his many helpful suggestions.

Thanks are due to the staff of Harper & Row who took a dream and made it a reality; in particular, Malvina (Mal) Wasserman, Chemistry Editor, Penny Schmukler and Eve Strock, Project Editors, and Lois Lombardo and Karen Judd, Managing Editors.

Our typists, Betty Caret, Kathy Mulqueen, Sharon Osenburg, and Nancy Scales, who made it all possible, deserve much credit.

And finally, we express our indebtedness to our students who gave us the reason for beginning, the courage to continue, and the fortitude to complete the project.

We are sincerely grateful to them all.

Alan S. Wingrove Robert L. Caret

PERIODIC TABLE OF THE ELEMENTS

1100000000000000000000000000000000000	•	_		- 9	T		3	T		+	Т			Τ		0	T			7		
HA HA HA HA HA HA HA HA	VIII.	٦	'n	4.002	1_			<u> </u>			<u> </u>			↓_			┸	3 2	(222)			
HA HA HA HA HA HA HA HA				VIIA	0	\ [I	18,9984	17	ひ	35.453	35	R	79.916	53	-	126,904	85	Δt	(210)			
HA				MA	~	· C	15.9994	16	S	32.064	*	8	78.96	52	Ę.	127.60	2	<u>م</u>	(210)			
HA				VA	7	·Z	14.0067	15	٦	30.9738	33	As	74.922	51	Sp	121.75	83	ä	208.980			
HA				IVA	4	ۍ د	12.011	14		28.086	32	છ	72.60	20	Sn	118.69	82	숩	207.19			
HA				IIIA		~	10.811	13	V	26.9815	31	g	69.72	63	- I	114.82	81	F	204.37			
11A Pa Pa Pa Pa Pa Pa Pa P							,	4	- · -	811							1	Hø	200.59			
11A Pa Pa Pa Pa Pa Pa Pa P										18	29	రె	63.54	47	Ag	107.870	79	Au	196.961			
IIA													58.71	\$	Pd	106.4	78] . } !		
IIA								1	VIII B)]			58.933	45	Rh	102.905	77	1	192.2			
IIA											26	F.	55.847	\$	Ru	0.	9,	SO	190.2			
11A 12 Mg 24.312 12 Ca Sc Ti VB 40.08 44.956 41.956 72 72 73 87.62 88.905 91.22 73 74.19 75 71 72 73 88.89 104 118.91 118.91 118.91 118.91 118.91 128.91 23 24.31										VIIB						(98)	75	Re	186.20			
11A Be 9.0122 12 Mg 24.312 IIIB 11B 1VB 22 Ca Sc Ti 40.08 38 39 40 Sr Y Sr Y Sr Sr Y Sr Sr Sr Y Sr										VIB	24	ن	51.996	42	Mo	95.94	74	≥	183.85			
11A Be 9.0122 Mg 24.312 Mg 24.312 Mg 24.312 Mg 24.312 Mg 38 39 Sc 40.08 44.956 38 39 Sr Y 87.62 88.905 56 57 Ba 137.34 138.91 88 89 Ra †Ac (226) (227)									!	VB	23	>	50.942	1+	N _P	92.906	73	Ta	180.948	105	Ha	(260)
11.A Be 9.0122 Mg 24.312 Ca 40.08 87.62 88 137.34 Ra (226)									<u> </u>	IVB	22	Ξ	47.90	2	Zr	91.22	72	Hť	178.49	10	Ku	(261)
										IIIB	77	ઝ	44.956	39	>	88.905	57	# *	138.91	68	†Ac	(227)
1A 1 H 1.00797 1.0077				IIA	4	8	9.0122	12	Mg	24.312	2	ථ	40.08	38	ઢ	87.62	98	쿏	137.34	æ ,	2	(226)
	٧I	-	H	1.00797	3	<u>'</u>	6.939	= ;	Z	22.9898	61	¥	39.102	37	3	85.47	55	ర	132,905	78	F	(223)

	71	2	174.97	
	02	S	173.04	
	69	Tm	168.934	
	89	Ē	167.26	
	29	Ho	164.930	
[;	9	D\	162.50	
	2	Tp	158.924	
	40	3	157.25	
5	6	Eu	151.96	
5	7 ,	EX	150.35	
17	5 1	E	(147)	
2	3	2	144.24	
60) (t	140.907	
8.5	3 (ب ئ	140.12	

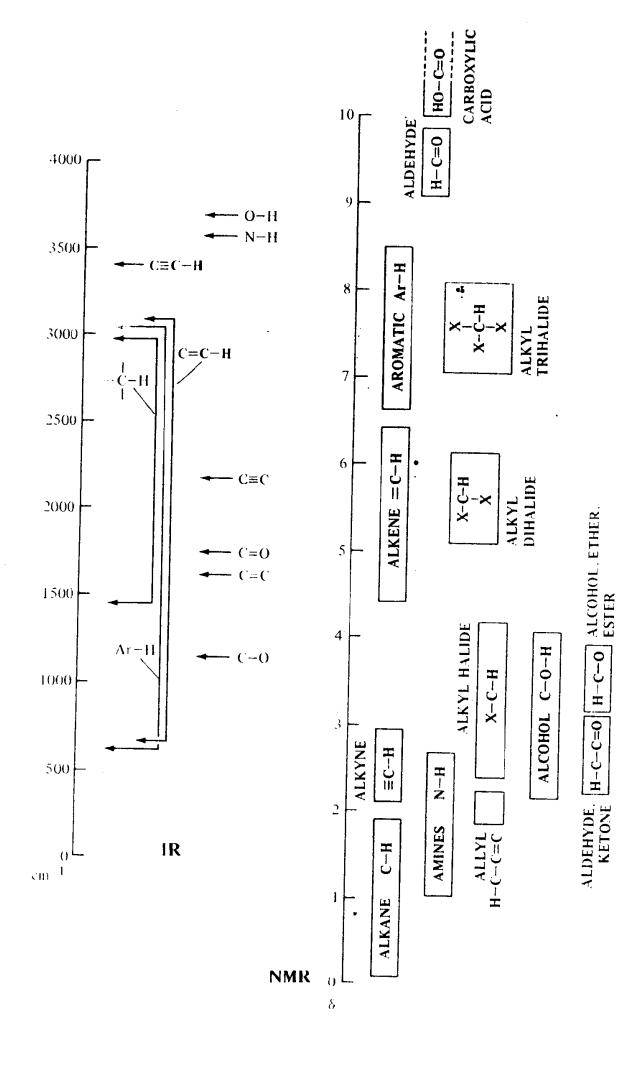
	103 Lw (257)
	102 No (253)
	101 Md (256)
	100 Fm (253)
	99 Es (254)
	98 Cf (251)
	97 Bk (249)
	96 Cm (247)
;	95 • Am (243)
	94 Pu (242)
	93 Np (237)
	92 U 238.03
	91 Pa (231)
	90 † T.h 232.038

MULTIPLE ATOMIC WEIGHTS OF THE ELEMENTS

	······································	T		T"		
C_1	12.01	H ₁	1.01	O_1	16.00	
C_2	24.02	H ₂	2.02	O_2	32.00	
C ₃	36.03	H ₃	3.02	O_3	48.00	
C ₄	48.04	H ₄	4.03	04	64.00	
Cs	60.06	H ₅	5.04	O ₅	79.99	
C ₆	72.07	H ₆	6.05	06	95.99	
C_7	84.08	H ₇	7.06	0,	111.99	
C ₈	96.08	H ₈	8.06	08	127.99	
C ₉	108.10	H ₉	9.07	09	143.99	
C ₁₀	120.11	H ₁₀	10.08	O ₁₀	159.98	

N_1	14.01	\mathbf{F}_1	19.00	Cl ₁	35.45
N ₂	28.01	. F ₂	38.00	Cl ₂	70.91
N ₃	42.02	F_3	57.00	Cl ₃	106.36
N ₄	56.03	F ₄	75.99	Cl ₄	141.81
N ₅	70.03	F ₅	94.99	Cl ₅	177.27
	,				

Br ₁	79.91 159.83	I ₁ I ₂	126.90 253.81
Br ₃	239.75	I ₃	380.71
Br ₄	319.66	14	507.62
Br ₅	399.58	I ₅	634.52
	, , , , , , , , , , , , , , , , , , ,		



QUICK REFERENCES

NOMENCLATURE

Alkanes	Sec. 3.10
Alkenes	7.5
Alkynes	11.2
Aromatics	13.9
Alcohols	10.1
Alkyl Halides	3.10
Ethers	19.1
Carboxylic Acids	22.1
Acid Derivatives	23.1
Aldehydes	20.2
Ketones	20.2
Phenols	17.1
Aryl Halides	16.1
Amines	26.1, 26.5

SPECTROSCOPY

IR	Table	12-3	
UV	Table	12-4	
NMR		15-1	
MS		18-1	

K_a's, **K**_b's

General Review	Sec. 5.7C
Alkanes, Alkenes and Alkynes	11.7
Alcohols	10.9
Phenols	17.4, 17.5
Carboxylic Acids	22.9
Amines	26.3, 26.5B
Ethers	19.9

BOND DISSOCIATION ENERGIES

Table 5-1

Detailed Contents

Preface xxi

 1.1 Introduction to Organic Chemistry 1 1.2 Organic Versus Inorganic Chemistry 2 1.3 Identification of Organic Compounds 6 1.4 Classification of Organic Compounds; The Study of Organic Chemistry 10 1.5 Study of Organic Chemistry 13 2 Atomic and Molecular Structure; Molecular Orbital Theory 17 2.1 Atomic and Molecular Structure: An Historical Overview 2.2 The Quantum Mechanical Atom: The Beginnings 18 2.3 The Quantum Mechanical Atom: Wave Mechanics 20 	
 1.3 Identification of Organic Compounds 6 1.4 Classification of Organic Compounds; The Study of Organic Chemistry 10 1.5 Study of Organic Chemistry 13 2 Atomic and Molecular Structure; Molecular Orbital Theory 17 2.1 Atomic and Molecular Structure: An Historical Overview 2.2 The Quantum Mechanical Atom: The Beginnings 18 2.3 The Quantum Mechanical Atom: Wave Mechanics 20 	
 Classification of Organic Compounds; The Study of Organic Chemistry 10 Study of Organic Chemistry 13 Atomic and Molecular Structure; Molecular Orbital Theory 17 Atomic and Molecular Structure: An Historical Overview The Quantum Mechanical Atom: The Beginnings 18 The Quantum Mechanical Atom: Wave Mechanics 20 	
Chemistry 10 1.5 Study of Organic Chemistry 13 2 Atomic and Molecular Structure; Molecular Orbital Theory 17 2.1 Atomic and Molecular Structure: An Historical Overview 2.2 The Quantum Mechanical Atom: The Beginnings 18 2.3 The Quantum Mechanical Atom: Wave Mechanics 20	
 1.5 Study of Organic Chemistry 13 Atomic and Molecular Structure; Molecular Orbital Theory 17 2.1 Atomic and Molecular Structure: An Historical Overview 2.2 The Quantum Mechanical Atom: The Beginnings 18 2.3 The Quantum Mechanical Atom: Wave Mechanics 20 	2
Atomic and Molecular Structure; Molecular Orbital Theory 17 2.1 Atomic and Molecular Structure: An Historical Overview 2.2 The Quantum Mechanical Atom: The Beginnings 18 2.3 The Quantum Mechanical Atom: Wave Mechanics 20	
 2.1 Atomic and Molecular Structure: An Historical Overview 2.2 The Quantum Mechanical Atom: The Beginnings 18 2.3 The Quantum Mechanical Atom: Wave Mechanics 20 	
 2.2 The Quantum Mechanical Atom: The Beginnings 18 2.3 The Quantum Mechanical Atom: Wave Mechanics 20 	
2.3 The Quantum Mechanical Atom: Wave Mechanics 20	17
2.3 The Quantum Mechanical Atom: Wave Mechanics 20	
2.4 Molecular Companya, Malacular (David) Oublish D. 1.7	
2.4 Molecular Structure; Molecular (Bond) Orbitals; Bond Leng	gth 24
2.5 Covalent Bonds in Simple Molecules; The Sigma (σ) Bond	26
2.6 Structure of Carbon and Methane; Hybridization 28	
2.7 Formation of More Complex Organic Molecules 33	
2.8 Structure of Reactive Intermediates in Organic Chemistry	41
2.9 Hybridization in Boron, Nitrogen, and Oxygen 46	
2.10 Polarity and Electronegativity 50	
2.11 Atomic Orbitals: A More Detailed View 54	
2.12 Molecular Orbitals (MO's) 56	
2.13 Linear Combination of Atomic Orbitals (LCAO's) 56	
2.14 Molecular Orbitals and Bonding 57	
2.15 σ Versus π Molecular Orbitals 59	
2.16 Alkanes 60	
2.17 Alkenes and Alkynes 61	
3 Alkanes and Cycloalkanes: Structure, Properties, and Nomenclature	64
3.1 Methane 64	
3.2 Ethane 65	
3.3 Ethane and the Carbon-Carbon Single Bond; Conformations and Free Rotation 66	al Analysis
3.4 Propane 71	
3.5 Butane; Structural Isomers 71	
3.6 Conformations of Butane 72	
3.7 Pentane 76	
3.8 Isomers of Higher Hydrocarbons; The Homologous Series	78
3.9 System for Writing Structural Isomers 79	
3.10 Nomenclature: Common Names; IUPAC System 81	

7.7	C44-
ж.	Contents

3.11	Physical Properties of Alkanes 92	
3.12	General Structure and Nomenclature 95	
3.13	Physical Properties of Cycloalkanes 97	
3.14	Structural Properties of Unsubstituted Cycloalkanes 98	
	Evidence for Cycloalkane Stability: Heats of Combustion 106-	
3.16	Conformational Analysis of Monosubstituted Cyclohexanes 108	
3.17	Disubstituted Cyclic Compounds; cis-trans Isomerism 113	
3.18	Conformational Analysis for Disubstituted Cyclohexane Derivatives	116
	es and Cycloalkanes: Preparation and Reactions 121	
4.1	Industrial Sources 121	•
4.2	124	
4.3	Reactivity of Alkanes and Cycloalkanes 129	
4.4^	Halogenation; A Substitution Reaction 130	
4.5	Examples of Halogenation of Alkanes 131	
4.6	The state of the s	
4.7	The same and transferrence of the same and t	
4.8	Nitration of Alkanes: Another Free-Radical Reaction 137	
4.9	Combustion 138	
4.10	Petroleum, Gasoline, Fuels, and Pollution 139	
4.11	Air Pollution and Its Causes; Mechanism of Photochemical Smog	
	Formation 140	
4.12	Ozone and the Environment 141	
4.13	Summary of Reactions 142	
Reaction Mechanisms 145		
5.1	What Is a Reaction Mechanism? 145	
5.2	Chemical Reactions: A Graphical Representation 146	
5.3	Thermodynamics 147	
5.4	Energy of Activation 148	
5.5	Transition State Versus Reaction Intermediate 149	
5.6	Bond Breaking and Forming; Reversibility of Chemical Reactions	151
5.7	Reactive Intermediates 157	
5.8	Kinetics Versus Thermodynamics 169	
	How To Study a Reaction Mechanism 171	
5.10	Reaction Mechanisms: Product Distribution 171	
	Reaction Mechanisms: Intermediates 172	
5.12	Reaction Mechanisms: Kinetics 173	
5.13	Reaction Mechanisms: Catalysis 175	
	Reaction Mechanisms: Solvent Effects 175	
	Reaction Mechanisms: Substituent Effects 177	
5.16	Nucleophilic Aliphatic Substitution: S _N 2 177	
Stereo	chemistry and Stereoisomerism 184	
6.1	Optical Properties of Molecules; Optical Activity and the	
	Polarimeter 184	
6.2	Molecular Asymmetry and the Discovery of Enantiomers 188	
	Structures of Enantiomers; Requirements for Their Existence 190	
6.4	Further Evidence for the Tetrahedral Carbon Atom; Symmetry and Stereochemistry 192	
	Interaction of Light with Matter; Enantiomers and Optical	
	Activity 195	
	* ************************************	

Contents		
6.6	Properties of Enantiomers 197	
6.7	Optical Purity; Racemic Compounds and Resolution 199	
	Designation of Configuration: R and S System 201	
	Reactions Involving Optically Active Compounds; Evidence for	
	Free-Radical Structure and Nucleophilic Substitution 205	
6.10	Another Way To Depict Structure of Enantiomers: Fischer	
0.10	Projection Formula 211	
6.11	Stereoisomers of Molecules Containing Two Asymmetric Carbon	
0.11	Atoms 215	
6.12	Stereoisomers of Compounds Containing Two Analogous Asymmetric	
•••	Carbon Atoms 219	
6.13	Determination of the Number of Stereoisomers 223	
	Properties of Diastereomers; Compounds That Contain Two	
.,.,	Asymmetric Carbon Atoms 224	
6.15	Examples of Biological Reactions Involving Optically Active	
	Compounds 228	
6.16	Reactions That Generate a Second Asymmetric Center in a	
51.0	Molecule 229	
6 17	Stereoisomerism in Cyclic Compounds 232	
	Stereoisomerism in Cyclohexane Derivatives 235	
	Other Elements That Impart Asymmetry to Molecules 236	
,	2.00.000 1.1	
Alken	es and Alkadienes: Structure and Properties 243	
7.1	Ethene: The Carbon-Carbon Double Bond 243	
7.2	Propene 244	
7.3	The Butenes; Geometric Isomerism 244	
7.4	Criteria for the Existence of Geometric Isomers in Alkenes 246	
7.5	Nomenclature of Alkenes 247	
7.6	Cycloalkenes and Exocyclic Double Bonds: Nomenclature 251	
7.7	Properties of Alkenes 252	
7.8	Alkadienes: Nomenclature and Classification 254	
7.9	Structure of Conjugated and Nonconjugated Dienes 256	
7.10	Dehydrogenation of Alkanes 259	
7.11	Dehydrohalogenation of Alkyl Halides; E2 Mechanism 261	
7.12	Structure-Reactivity and Structure-Product Distribution Relationships	
	in Dehydrohalogenation 264	
7.13	Stereochemistry of the Dehydrohalogenation Reaction 266	
	Dehydration of Alcohols 270	
7.15	Mechanism for Acid-Catalyzed Dehydration of Alcohols 271	
7.16	Use of Carbocation Stability To Explain Reactivity in Dehydration	
	Reactions 276	
7.17	Product Distribution in Dehydration Reactions 277	
7.18	Carbocation Rearrangements: 1,2-Hydride and 1,2-Alkyl Shifts 278	

- Alkenes and Alkadienes: Reactions; Natural and Synthetic Polymers 289
 - 8.1 Ionic Addition Reactions 289

7.19 Dehalogenation of Dihalides 282 7.20 Preparation of Alkadienes 283 7.21 Summary of Reactions 283

7

- 8.2 Addition of Hydrogen Halides (Unsymmetrical Reagent) to Alkenes 290
- 8.3 Mechanism of Hydrogen Halide Addition to Alkenes 291
- 8.4 Further Evidence for Electrophilic Addition: Rearrangements 295

0.0	Geometry of Carbocations 298
8.7	Addition of Sulfuric Acid (Unsymmetrical Reagent) to Alkenes 300
8.8	Summary of Electrophilic Addition Reactions of Acidic Reagents;
	Markovnikov's Rule 301
8.9	Addition of Hydrogen Bromide to Alkenes in the Presence of
	Peroxides 302
8.10	Addition of Unsymmetrical Reagents to Alkadienes 304
	Product Distribution in Addition of Unsymmetrical Reagents to
	Conjugated Alkadienes 308
8.12	Hydrogenation; Addition of Hydrogen (Symmetrical Reagent) to
	Alkenes 310
8.13	Hydrogenation of Alkadienes 313
8.14	Use of Catalytic Hydrogenation in Structure Determination 314
8.15	Heats of Hydrogenation; Evidence for Alkene Stability 315
	Halogenation: Addition of Halogens (Symmetrical Reagent) to
	Alkenes 317
8.17	Mechanism and Stereochemistry of Bromine Addition 318
8.18	Stereochemistry of Bromine Addition to Open-Chain Alkenes 322
8.19	Chlorination: Addition of Chlorine to Alkenes 323
	Halogenation of Alkadienes 324
	Relative Reactivities of Alkenes in Addition Reactions 324
8.22	Addition of Hypohalous Acids (Unsymmetrical Reagent) to Alkenes;
	Formation of Halohydrins 326
8.23	Addition of Alkenes to Alkenes; Carbocation Reaction 327
8.24	Addition of Alkanes to Alkenes; Alkylation Reactions 329
8.25	Applications of Carbocation Chemistry to Natural Products 331
8.26	Carbocations: Summary 332
8.27	Reaction of Alkenes with Oxidizing Agents; cis-Hydroxylation and
	the Baeyer Test 332
	Stereochemistry of Hydroxylation of Open-Chain Alkenes 335
	Cycloaddition Reactions 335
8.30	Substitution Reactions of Alkenes; Allyl and Vinyl Radicals 336
8.31	Cleavage of Carbon-Carbon Double Bonds; Ozonolysis 339
8.32	Cleavage of Carbon-Carbon Double Bonds by Permanganate 342
8.33	Qualitative Analysis; Detection of Alkenes 344
	Polymerization of Alkenes 345
8.35	Polymerization of Alkadienes; Rubber 348
8.36	Other Naturally Occurring Products That Contain Double Bonds 350
8.37	Summary of Reactions 355
Alkyl l	Halides: Substitution and Elimination Reactions 365
9.1	Structure, Nomenclature, and Preparation 365
~ ~	The state of the s

8.5 Hydration: Addition of Water (Unsymmetrical Reagent) to Alkenes 296

- 9.2 Physical Properties 366
- 9.3 Nucleophilic Aliphatic Substitution 368
- 9.4 Nucleophilic Aliphatic Substitution; Effect of Alkyl Group Structure on Chemical Kinetics 368
- 9.5 $S_N 2$ Reactions: Mechanism and Evidence 370
- 9.6 Effect of Alkyl Group Structure on S_N2 Reactivity 372
- 9.7 Effect of Nucleophiles on S_N2 Reactivity 375
- 9.8 Effect of Leaving Group on $S_N 2$ Reactivity 378