

Fundamentals of Organic Chemistry

John McMurry CORNELL UNIVERSITY



Brooks/Cole Publishing Company A Division of Wadsworth, Inc.

© 1990 by Wadsworth, Inc., Belmont, California 94002. All rights reserved. No part of this book may be reproduced, stored in a retrieval system, or transcribed, in any form or by any means—electronic, mechanical, photocopying, recording, or otherwise—without the prior written permission of the publisher, Brooks/Cole Publishing Company, Pacific Grove, California 93950, a division of Wadsworth, Inc.

Printed in the United States of America

10 9 8 7 6 5 4 3 2

Library of Congress Cataloging-in-Publication Data

McMurry, John. Fundamenta

Fundamentals of organic chemistry/John McMurry. — 2nd ed.

p. cm. ISBN 0-534-12300-7

1. Chemistry, Organic. I. Title.

QD251.2.M4 19

547—dc20

89-27419

CIP

Sponsoring Editor: Harvey C. Pantzis

Editorial Assistant: Gerry Del Ré, Jennifer Kehr Production Editor: Joan Marsh/Mary Douglas

Manuscript Editor: Yvonne Howell

Interior Design: Sharon L. Kinghan/Vernon T. Boes

Cover Design: Vernon T. Boes Cover Photo: Courtesy Westlight

Interior Illustration: Vantage Art, Inc., Victor Royer

Typesetting: Syntax International Cover Printing: The Lehigh Press

Printing and Binding: R. R. Donnelley & Sons Company, Crawfordsville

Preface

As I stated in the first edition of this text, my goal has been to write a readable and effective teaching text that presents only those subjects needed for a one-semester or two-quarter course in organic chemistry but that keeps the important pedagogical tools commonly found in larger books. I have taken particular care to incorporate clear explanations of difficult subjects, effective artwork, repetition of important points, and varied end-of-chapter learning tools. The result, I believe, is a book that is easier to learn from than other short organic chemistry texts.

All of the features that made the first edition a success have been improved, and many new ones have been added.

The writing, already clear and accessible, has been further refined at the sentence level on every page.

The artwork has been redone with the use of computer-generated structures to ensure accuracy.

Text and reaction summaries have been added at the end of each chapter, and problem sets have been expanded.

Other changes include expanded treatments of resonance, isomerism, and enzyme structure and function.

Organization

The primary organization of this book is by functional group, beginning in Chapter 2 with alkanes and going on to more complex compounds. Within this primary organization, more emphasis is placed on explaining the fundamental mechanistic similarities of organic reactions than is common in other short texts. Chapter 11, "Carbonyl Alpha-Substitution and Condensation Reactions," for example, helps to remove the artificial lines between ketones and esters by showing how all carbonyl compounds undergo similar reactions.

Organic molecules and organic reactions are presented as early as possible. After a brief review of structure and bonding in Chapter 1, organic molecules and functional groups are introduced in Chapter 2, followed by an initial discussion of organic reactions in Chapter 3.

The Lead-off Reaction: Addition of HCI to Ethylene

An important yet simple polar reaction—the addition of HCl to ethylene—is used as the lead-off to illustrate general principles of organic reactions. This choice has the advantage of relative simplicity (no prior knowledge of stereochemistry and kinetics is required), yet it is also a broadly applicable reaction of a common functional group. Many students attach great importance to a text's lead-off reaction, and I believe that the choice of an important polar reaction serves to introduce students to functional-group chemistry better than a lead-off such as free-radical alkane chlorination.

Spectroscopy

Spectroscopy is treated as a tool, not as a specialized field of study. Infrared, ultraviolet, ¹³C NMR, and ¹H NMR spectroscopies are all covered by showing the kind of information that can be derived from each and how each can be used to answer specific structural questions.

Nomenclature

The IUPAC system of nomenclature is used throughout. For the most part, this involves the use of systematic names, although a few IUPAC-approved nonsystematic names such as acetic acid, acetone, ethylene, and phenol are also employed. Since it's unlikely that these few common names will disappear from everyday use in the near future, it's probably best for students to learn them.

Coverage

The coverage in this book is up to date, reflecting important advances of the past decade. For example, ¹³C NMR is introduced as a routine spectroscopic tool, equal in importance to ¹H NMR. Similarly, the chemistry of nucleic acids is covered, including a section on DNA sequencing by the Maxam-Gilbert method.

Interludes

Brief "interludes" are included at the end of each chapter. Meant to serve as short breathers between chapters, these interludes show interesting applications of organic chemistry to industrial and biological systems. They can be covered by the instructor or left for student reading.

Practice Problems

Each chapter contains many worked-out examples that illustrate how problems can be solved. Each practice problem and solution is then followed by a similar problem for the reader to solve. These worked-out examples are valuable because of their appearance in the text, but they are not meant to serve as a replacement for the accompanying *Study Guide and Solutions Manual*.

The state of the s

Pedagogy

In addition to the features mentioned above, every effort has been made to make this book as effective, clear, and readable as possible—in short, to make it easy to learn from.

Paragraphs usually start with summary sentences.

Transitions between paragraphs and between topics are smooth.

Extensive use is made of computer-generated, airbrushed art and carefully rendered stereochemical formulas.

Extensive cross-referencing to earlier material is used.

A second color is used to indicate the changes that occur during reactions.

More than 800 problems are included, both within the text and at the end of every chapter. These include both drill and thought problems.

Key terms are defined in the margin next to where they are first used.

An innovative vertical format is used to explain reaction mechanisms. The mechanisms are printed vertically, while explanations of the changes taking place in each step are printed next to the reaction arrow. This format allows the reader to see easily what is occurring at each step in a reaction without having to jump back and forth between the text and structures.

Study Guide and Solutions Manual

A carefully prepared Study Guide and Solutions Manual accompanies this text. Written by Susan McMurry, this companion volume answers all in-text and end-of-chapter problems and explains in detail how answers are obtained. In addition, many valuable supplemental materials are given, including: a list of study goals for each chapter, a glossary, a summary of name reactions, a summary of organic reaction mechanisms, a summary of the uses of important reagents, tables of spectroscopic information, a list of suggested readings, and a discussion on the rules of nomenclature for polyfunctional molecules.

Acknowledgments

I sincerely thank the many people whose help and suggestions were so valuable in the creation of this book. Foremost is my wife Susan who read, criticized, and improved all aspects of the text, and who authored the accompanying *Study Guide and Solutions Manual*. Among the reviewers providing thoughtful comments were R. A. Abramovitch, Clemson University; Orville L. Boge, Mesa State College; Gerald Caple, Northern Arizona University; George B. Clemans, Bowling Green State University; Donald Grant, University of Saskatchewan; George Kraus, Iowa State University; Gordon L. Lange, University of Guelph, Ontario, Canada; Anne G. Lenhert, Kansas State University; Barbara J. Mayer, California State University at Fresno; and Daniel O'Brien, Texas A & M University.

Special thanks are due Mary Douglas, Harvey Pantzis, Joan Marsh, and others of the Brooks/Cole staff for their usual fine work.

A Note for Students

We have similar goals. Yours is to learn organic chemistry; mine is to do everything possible to help you learn. It's going to require work on your part, but the following suggestions should prove helpful:

Don't read the text immediately. As you begin each new chapter, look it over first. Read the introductory paragraphs, find out what topics will be covered, and then turn to the end of the chapter and read the summary. You'll be in a much better position to understand new material if you first have a general idea of where you're heading. Once you've begun a chapter, read it several times. First read the chapter rapidly, making checks or comments in the margin next to important or difficult points; then return for an in-depth study.

Keep up with the material. Who's likely to do a better job—the runner who trains five miles per day for weeks before a race, or the one who suddenly trains twenty miles the day before the race? Organic chemistry is a subject that builds on previous knowledge. You have to keep up with the material on a daily basis.

Work the problems. There are no shortcuts here. Working problems is the only way to learn organic chemistry. The practice problems show you how to approach the material, the in-text problems provide immediate practice, and the end-of-chapter problems provide additional drill and some real challenges. Answers and explanations for all problems are given in the accompanying *Study Guide and Solutions Manual*.

Ask questions. Faculty members and teaching assistants are there to help you. Most of them will turn out to be extremely helpful and genuinely interested in seeing you learn.

Use molecular models. Organic chemistry is a three-dimensional science. Although this book uses many careful drawings to help you visualize molecules, there's no substitute for building a molecular model, turning it in your hands, and looking at it from different views.

Use the study guide. The Study Guide and Solutions Manual that accompanies this text gives complete solutions to all problems and provides a wealth of

v 1 m sta ska ak Spail i k sa ka ka l

supplementary material. Included are a list of study goals for each chapter, outlines of each chapter, a large glossary, a summary of name reactions, a summary of methods for preparing functional groups, a summary of the uses of important reagents, tables of spectroscopic information, a list of suggested readings, and a discussion on the naming of polyfunctional compounds. Find out ahead of time what's there so that you'll know where to go when you need help.

Good luck. I sincerely hope you enjoy learning organic chemistry and that you come to see the logic and beauty of its structure. I would be glad to receive comments and suggestions from any who have learned from this book.

a de la companya del companya de la companya del companya de la co

Brief Contents

1	Structure and Bonding 1
2	The Nature of Organic Compounds: Alkanes 26
3	Alkenes: The Nature of Organic Reactions 60
4	Alkenes and Alkynes 88
	Aromatic Compounds 124
5	
6	Stereochemistry 158
7	Alkyl Halides 186
8	Alcohols, Ethers, and Phenols 219
9	Aldehydes and Ketones: Nucleophilic Addition
	Reactions 252
10	Carboxylic Acids and Derivatives 279
11	Carbonyl Alpha-Substitution Reactions and Condensation
	Reactions 318
12	Amines 345
13	Structure Determination 372
14	Biomolecules: Carbohydrates 403
15	Biomolecules: Amino Acids, Peptides, and Proteins 433
	Biomolecules: Lipids and Nucleic Acids 462
16	Biofficiecules. Lipids and Masiero Meras
	APPENDIX Nomenclature of Polyfunctional Organic Compounds A1
	Nomenclature of Polyfunctional Organic Compounds A1

INDEX 11

Contents

1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 1.10 1.11 1.12	STRUCTURE AND BONDING Atomic Structure 2 Electronic Configuration of Atoms 4 Development of Chemical Bonding Theory 6 The Nature of Chemical Bonds: lonic Bonds 6 The Nature of Chemical Bonds: Covalent Bonds 8 Formation of Covalent Bonds 10 Hybridization: The Formation of sp³ Orbitals 11 The Structure of Methane 13 The Structure of Ethane 14 Hybridization: sp² Orbitals and the Structure of Ethylene 15 Hybridization: sp Orbitals and the Structure of Acetylene 18 Bond Polarity and Electronegativity 19 Summary and Key Words 22 Working Problems 22 Additional Problems 23	1
2.1 2.2 2.3 2.4	THE NATURE OF ORGANIC COMPOUNDS: ALKANES Functional Groups 26 Alkanes and Alkyl Groups: Isomers 30 Naming Branched-Chain Alkanes 35 Properties of Alkanes 38	26

A part of the second discontinuous and the se

COMIENIS	
2.5 2.6 2.7 2.8 2.9 2.10 2.11	Conformations of Ethane 39 Drawing Chemical Structures 42 Cycloalkanes: Cis—Trans Isomerism 43 Naming Cycloalkanes 44 Conformations of Some Common Cycloalkanes 45 Axial and Equatorial Bonds in Cyclohexane 49 Conformational Mobility of Cyclohexane 49 INTERLUDE: Petroleum 53 Summary and Key Words 54
2	Additional Problems 55 ALKENES: THE NATURE OF ORGANIC
3	REACTIONS 60
3.1	Naming Alkenes 60
3.2	Electronic Structure of Alkenes 63
3.3	Cis-Trans Isomers 64
3.4	Sequence Rules: The E,Z Designation 66
3.5	Kinds of Organic Reactions 69
3.6	How Reactions Occur: Mechanisms 71
3.7	An Example of a Polar Reaction: Addition of HCI to Ethylene 74
3.8	The Mechanism of an Organic Reaction: Addition of HCI to Ethylene 75
3.9	Describing a Reaction: Rates and Equilibria 76
3.10	Describing a Reaction: Reaction Energy Diagrams and Transition States 78
3.11	Describing a Reaction: Intermediates 80
	INTERLUDE: Carrots, Alkenes, and the Chemistry of Vision 82
	Summary and Key Words 84
	Additional Problems 85
4	ALKENES AND ALKYNES 88
4.1	Addition of HX to Alkenes 88
	Orientation of Alkene Addition Reactions: Markovnikov's
	Rule 90

4.3 4.4 4.5 4.6 4.7 4.8	Carbocation Structure and Stability 92 Hydration of Alkenes 93 Addition of Halogens to Alkenes 95 Hydrogenation of Alkenes 98 Oxidation of Alkenes 98 Alkene Polymers 101
4.9	Preparation of Alkenes: Elimination Reactions 104
4.10	Conjugated Dienes 106
4.11	Stability of Allylic Carbocations: Resonance 108
4.12 4.13	Drawing and Interpreting Resonance Forms 110 Alkynes 112
4.14 4.15	Reactions of Alkynes: Addition of H_2 , HX, and X_2 113 Addition of Water to Alkynes 115
	INTERLUDE: Natural Rubber 117
	Summary and Key Words 118
	Summary of Reactions 119 Additional Problems 121
5	AROMATIC COMPOUNDS 124
5.1 5.2 5.3	Naming Aromatic Compounds 124 Structure of Benzene: The Kekulé Proposal 127 Stability of Benzene 127
5.4 5.5 5.6	Structure of Benzene: The Resonance Proposal 128 Chemistry of Benzene: Electrophilic Aromatic Substitution 130 Bromination of Benzene 131
5.7	Other Electrophilic Aromatic Substitution Reactions 133
5.8	The Friedel-Crafts Alkylation and Acylation Reactions 135
5.9	Reactivity in Electrophilic Aromatic Substitution 137
5.10	Orientation of Reactions on Substituted Aromatic Rings 140
5.11	Trisubstituted Benzenes: Additivity of Effects 145
5.12	Oxidation and Reduction of Aromatic Compounds 146
5.13	Polycyclic Aromatic Hydrocarbons 147
5.14	Organic Synthesis 148
	INTERLUDE: Polycyclic Aromatic Hydrocarbons and Cancer 151
	Summary and Key Words 152

Summary of Reactions 153 Additional Problems 154

xviii	CONTENTS

0	STEREOCHEMISTRY	158
6.1	Stereochemistry and the Tetrahedral Carbon 158	
6.2	Chirality 160	
6.3	Optical Activity 164	
6.4 6.5	Specific Rotation 165	
6.6	Pasteur's Discovery of Enantiomers 166 Sequence Rules for Specification of Configuration 167	
6.7	Diastereomers 170	
6.8	Meso Compounds 172	
6.9	Molecules with More Than Two Chiral Centers 174	
6.10	Racemic Mixtures 175	
6.11	Physical Properties of Stereoisomers 176	
6.12	A Brief Review of Isomerism 176	
6.13	Stereochemistry of Reactions: Addition of HBr to Alkenes	178
	INTERLUDE: Chirality in Nature 179	
	Summary and Key Words 180	
	Additional Problems 181	
7		
	ALKYL HALIDES	186
7.1	Naming Alkyl Halides 186	
7.2	Preparation of Alkyl Halides: Radical Chlorination of Alkanes 187	
7.3	Alkyl Halides from Alcohols 190	
7.4	Reactions of Alkyl Halides: Grignard Reagents 191	
7.5	Nucleophilic Substitution Reactions: The Discovery 193	
7.6	Kinds of Nucleophilic Substitution Reactions 194	
7.7	The S _N 2 Reaction 195	
7.8	The S _N 1 Reaction 200	
7.9 7.10		04
7.10 7.11	Elimination Reactions of Alkyl Halides: The E1 Reaction 20)8
7.12	A Summary of Reactivity: S_N1 , S_N2 , E1, E2 209 Biological Substitution Reactions 210	
, <u></u>		
	INTERLUDE: Alkyl Halides and the Ozone Hole 211	
	Summary and Key Words 213 Summary of Reactions 213	
	Additional Problems 215	
	AGENCIAL FORIOTIS ZIO	

The state of the s

8	ALCOHOLS, ETHERS, AND PHENOLS	219
8.1	Naming Alcohols, Phenols, and Ethers 220	
8.2	Properties of Alcohols, Phenols, and Ethers: Hydrogen Bonding 222	
8.3	Acids and Bases: A Review 224	
8.4	Properties of Alcohols and Phenols: Acidity 228	
8.5	Synthesis of Alcohols 230	
8.6	Alcohols from Carbonyl Compounds 230	
8.7	Ethers from Alcohols: The Williamson Ether Synthesis 233	
8.8	Reactions of Alcohols 234	
8.9	Synthesis and Reactions of Phenols 237	
8.10	Reactions of Ethers: Acidic Cleavage 238	
8.11	Cyclic Ethers: Epoxides 240	
8.12	Ring-Opening Reactions of Epoxides 241	
8.13	Thiols and Sulfides 242	
	INTERLUDE: Industrial Uses of Simple Alcohols and PhenoIs	244
	Summary and Key Words 245	
	Summary of Reactions 246	
	Additional Problems 249	

9	ALDEHYDES AND KETONES: NUCLEOPHILIC ADDITION REACTIONS	252
9.1	Kinds of Carbonyl Compounds 252	
9.2	Structure and Properties of Carbonyl Groups 254	
9.3	Naming Aldehydes and Ketones 254	
9.4	Synthesis of Aldehydes 257	
9.5	Synthesis of Ketones 258	
9.6	Oxidation of Aldehydes 259	
9.7	Reactions of Aldehydes and Ketones: Nucleophilic Additions 260	
9.8	Nucleophilic Addition of H ₂ O: Hydration 262	
9.9	Nucleophilic Addition of Grignard Reagents: Alcohol Formation 264	
9.10	Nucleophilic Addition of Amines: Imine Formation 266	

CONTENTS	
9.11 9.12	Nucleophilic Addition of Alcohols: Acetal Formation 267 Nucleophilic Addition of Phosphorus Ylides: The Wittig Reaction 269
9.13	Some Biological Nucleophilic Addition Reactions 271 INTERLUDE: Chemical Warfare in Nature 272
	Summary and Key Words 273 Summary of Reactions 274 Additional Problems 275

XX

$\Lambda \cap$		
IU	CARBOXYLIC ACIDS AND DERIVATIVES	279
10.1	Naming Carboxylic Acids and Derivatives 279	
10.2	Occurrence, Structure, and Properties of Carboxylic Acids	283
10.3	Acidity of Carboxylic Acids 284	
10.4	Synthesis of Carboxylic Acids 286	
10.5	Nucleophilic Acyl Substitution Reactions 288	
10.6	Reactions of Carboxylic Acids 290	
10.7	Chemistry of Acid Halides 294	
10.8	Chemistry of Acid Anhydrides 296	
10.9	Chemistry of Esters 298	
10.10	Chemistry of Amides 302	
10.11	Chemistry of Nitriles 304	
10.12	Nylon and Polyester: Step-Growth Polymers 306	
	INTERLUDE: Thiol Esters: Biological Carboxylic Acid Derivatives 309	
	Summary and Key Words 310	
	Summary of Reactions 311	
	Additional Problems 313	

11	CARBONYL ALPHA-SUBSTITUTION REACTIONS AND CONDENSATION REACTIONS	318
11.1	Keto-Enol Tautomerism 319	
11.2	Reactivity of Enols: The Mechanism of α -Substitution	

The state of the s

11.3 11.4 11.5 11.6 11.7 11.8	Alpha Halogenation of Ketones and Aldehydes 323 Acidity of α-Hydrogen Atoms: Enolate Ion Formation 324 Reactivity of Enolate Ions 327 Alkylation of Enolate Ions 328 Carbonyl Condensation Reactions 333 Condensations of Aldehydes and Ketones: The Aldol Reaction 334
11.9 11.10	Dehydration of Aldol Products: Synthesis of Enones 336 Condensation of Esters: The Claisen Condensation Reaction 337 INTERLUDE: Biological Carbonyl Condensation Reactions 339 Summary and Key Words 340 Summary of Reactions 341 Additional Problems 342
12.1 12.2 12.3 12.4 12.5 12.6 12.7 12.8	AMINES Naming Amines 346 Structure and Properties of Amines 348 Amine Basicity 349 Resolution of Enantiomers by Use of Amine Salts 352 Synthesis of Amines 354 Reactions of Amines 357 Heterocyclic Amines 360 Naturally Occurring Amines: Morphine Alkaloids 364 INTERLUDE: Organic Dyes and the Chemical Industry 366 Summary and Key Words 367 Summary of Reactions 367 Additional Problems 368
13.1 13.2 13.3 13.4	STRUCTURE DETERMINATION 372 Infrared Spectroscopy and the Electromagnetic Spectrum 372 Infrared Spectroscopy of Organic Molecules 375 Ultraviolet Spectroscopy 379 Interpreting Ultraviolet Spectra: The Effect of Conjugation 380

xxii	CONTENTS	
	13.5	Nuclear Magnetic Resonance Spectroscopy 381
	13.6	The Nature of NMR Absorptions 383
	13.7	Chemical Shifts 385
	13.8	Chemical Shifts in ¹ H NMR Spectra 386
	13.9	Integration of ¹ H NMR Spectra: Proton Counting 388
	13.10	Spin-Spin Splitting in ¹ H NMR Spectra 389
	13.11	Use of ¹ H NMR Spectra 392
	13.12	¹³ C NMR Spectroscopy 393
		INTERLUDE: Colored Organic Compounds 396
		Summary and Key Words 397
		Additional Problems 398

14	BIOMOLECULES: CARBOHYDRATES	403
14.1	Classification of Carbohydrates 404	
14.2	Configurations of Monosaccharides: Fischer Projections	405
14.3	D,L Sugars 407	
14.4	Configurations of Aldoses 409	
14.5	Cyclic Structures of Monosaccharides: Hemiacetal Formation 410	
14.6	Monosaccharide Anomers: Mutarotation 414	
14.7	Conformations of Monosaccharides 415	
14.8	Reactions of Monosaccharides 416	
14.9	Disaccharides 421	
14.10	Polysaccharides 423	
14.11	Other Important Carbohydrates 425	
14.12	Cell-Surface Carbohydrates 426	
	INTERLUDE: Sweetness 427	
	Summary and Key Words 428 Additional Problems 429	

15	BIOMOLECULES: AMINO ACIDS, PEPTIDES, AND PROTEINS	433
15.1 15.2	Structures of Amino Acids 434 Dipolar Structure of Amino Acids 437	