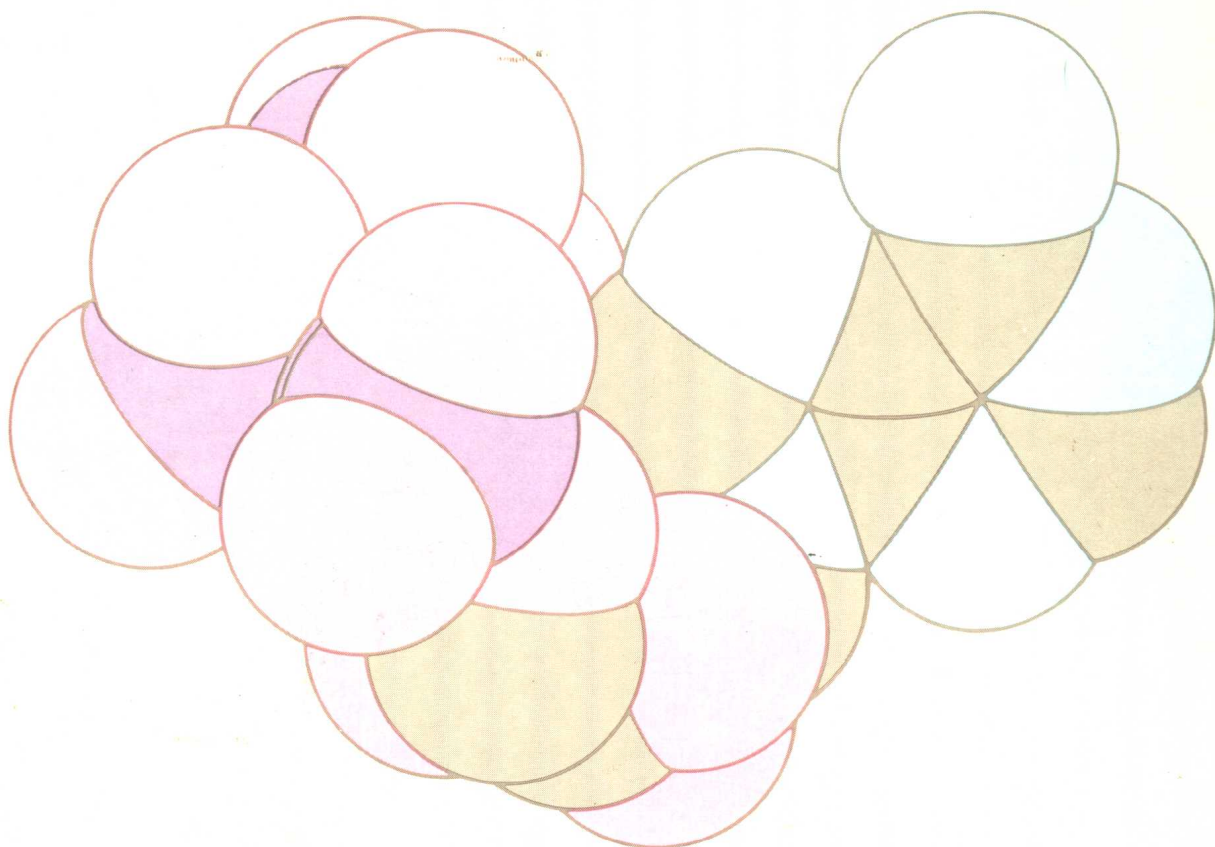


M. K. SCHUMM

# Understanding Organic Chemistry



**M. K. SCHUMM**

MONTGOMERY COLLEGE, ROCKVILLE, MARYLAND

# Understanding Organic Chemistry

**MACMILLAN PUBLISHING COMPANY** NEW YORK

Collier Macmillan Publishers LONDON

Copyright © 1987 by Margot K. Schumm.

PRINTED IN THE UNITED STATES OF AMERICA

All rights reserved. No part of this book may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher.

Macmillan Publishing Company  
866 Third Avenue, New York, New York 10022

Collier Macmillan Canada, Inc.

LIBRARY OF CONGRESS CATALOGING IN PUBLICATION DATA

Schumm, Margot K.  
Understanding organic chemistry.

Includes index.

1. Chemistry, Organic.	I. Title.	
QD251.2.S374 1986	547	86-16370
ISBN 0-02-408200-7		

Printing: 1 2 3 4 5 6 7 8      Year: 7 8 9 0 1 2 3 4 5 6

ISBN 0-02-408200-7

# Preface

## To the Student

Imagine that you are listening to a recording of a Beethoven piano sonata by the late Artur Rubinstein, one of the greatest pianists of the 20th century, and thoroughly enjoying the experience. If you had studied the piano and perhaps even played the piece, in addition to simply enjoying the music, you would most likely marvel at Mr. Rubinstein's technique and appreciate his unique interpretation of the work. If you were yourself a composer or a student of composition, you would appreciate the performance at yet another level, and that would be the structure and musical development of the composition itself. A similar case can be made for the appreciation of any art form or craft. Viewing a great masterpiece, be it a painting, a sculpture, a porcelain bowl, a cathedral, or the production of a great play, is an entirely different experience if you have ever painted, attempted to create a great sculpture, studied architecture, or written, performed in, directed or produced a play. It is generally true that the more we know about the way things work or are made, the more we can appreciate the product that results.

In the same way, a study of organic chemistry will allow you to gain an understanding of and appreciation for the detailed processes that are involved in the function of even the simplest forms of life. An understanding of the fundamental principles that govern these processes will give you an appreciation and reverence for life that cannot be obtained in any other way. While this study may require considerable effort on your part (and what worthwhile endeavor does not?), that effort will be amply rewarded by a new-found awareness of the beauty embodied in a condition that is so infinitely complex, yet so delicately balanced, that the exchange of but one amino acid in a protein containing hundreds of amino acids can cause a disease as serious as sickle-cell anemia (Chapter 13). As your understanding of organic chemistry develops and you begin to relate this understanding to biochemical systems,

you will more fully comprehend the magnificent order and exquisite organization that evolved as matter was transformed from chaos to LIFE.

The first twelve chapters of this book contain the fundamental principles of organic chemistry, most of the basic reaction types used by cells, and biochemical illustrations of many of these. When you have mastered this material you will have the understanding and appreciation alluded to above and something more, for you will have laid a foundation upon which you can continue to learn and increase your understanding of the chemical behavior of living systems. This knowledge and understanding will be essential to you professionally if you are planning a career in the health field. It will also be useful to you as a member of our present-day society. In an age when scientific research is giving humans a growing ability to gain control over all aspects of the life process, there will be grave moral and ethical decisions to be made. The chemistry you learn here will give you a firm base from which to reach reasoned conclusions.

There are many different ways to use a textbook, and some methods are much more effective than others. The following suggestions are offered to help you to use this book in both an efficient and effective manner.

1. Note the study aids that are provided for you:
  - a. Important terms are printed in the text in **boldface** and their definitions are shown in *italics*. These terms are also listed, by section, under the heading "Key Terms" at the end of each chapter.
  - b. Each chapter has a detailed summary that is extensively cross referenced.
  - c. Questions and problems that test your understanding of the material discussed in a section are listed at the end of the section.
  - d. Answers to the questions or parts of questions whose numbers are printed in color are included in the text.
2. Begin your study of each chapter by first reading it casually just for content.
3. Follow this by rereading the chapter section by section. Make an outline in which you translate all of the major ideas that are presented into your own words. If you cannot complete the chapter at one sitting, check your mastery of the material you have studied by attempting to answer some of the related questions, especially those for which answers have been provided in the text. It is also very helpful to write down any questions you have about the material as these questions arise, so that you will not forget them before you have an opportunity to ask your instructor about them.
4. Use the chapter summaries as a study guide when you are reviewing for an examination.
5. Take your textbook to class with you so that if figures and tables from the text are used you will have them at hand for notes and comments.
6. You may feel the need to see more detailed answers than those provided in the text where only the briefest answers have been provided. In addition, you may also want to work the exercises for which no answers are given in the text. If so, you may want to purchase the Solutions Manual-Study Guide which provides answers, with explanations, to all the questions in the text. The Solutions Manual-Study Guide also includes a variety of additional study aids, several short quizzes for each chapter (with answers), and a comprehensive Dictionary of Terms.

---

## To the Instructor

This text is designed to introduce students to the science of organic chemistry by means of a gradual and logical development of the powerful underlying generalizations that are the necessary foundation for an understanding of both organic chemistry and biochemistry. The title, *Understanding Organic Chemistry*, is the key to the choice of topics and examples, and to the order in which these are presented. Each new chapter builds on the foundation laid in the preceding chapter or chapters. Extensive cross-referencing helps the process by giving students ready access to the connecting ideas. In this way, as students progress through the text they begin to see that there are concepts, such as the relative stabilities of intermediate carbocations, that can be used to explain many facts that on the surface do not appear to be related at all.

Such understanding can only be achieved by *teaching mechanism*—not just by laying out the elementary steps in a given mechanism but by an in-depth discussion. As a result, students can understand why knowing the mechanism through which a given reaction proceeds is the key that allows chemists to predict the differences in behavior of specific compounds within a given class of compounds and thereby to control the outcome of a reaction.

Some instructors consider the study of reaction mechanism both unnecessary and too advanced to be included in a course for nonscience majors. In many instances this is because these individuals were fortunate enough not to have studied organic chemistry before the nineteen fifties. In those days almost all organic reactions were identified by the name of the chemist or chemists who developed them; empirical rules were memorized along with an extensive list of exceptions. Also there was little or no emphasis on the teaching of systematic nomenclature, so that the connection between the name of a compound and its structure was not always obvious. Organic chemistry was mysterious, magical, feared by most of the students who had to take it, and looked down upon by other chemists as being more of an “art” than a science. While no one would claim that by teaching mechanism we can eliminate memorization, it can be claimed that there is less to memorize and what is memorized will be retained longer, if we teach the unifying theories, the reaction mechanisms, and show how they explain the varying behavior of individual compounds.

Systematic IUPAC nomenclature is emphasized, not because the students are expected to become experts in the naming of organic compounds, but because it is an effective way to train students to recognize the major structural features that must be identified before they can predict the chemical behavior of the compound, because it imposes a mental discipline that is necessary for an understanding of the subject, and because it gives students a tool for understanding the nature of the chemicals with which they come in daily contact. The *Solutions Manual-Study Guide* includes succinct outlines of the rules governing the nomenclature of the classes of compounds studied, designed for easy review.

Chapter 1 contains selected topics in inorganic chemistry, serves as an introduction to the course, and provides the background material necessary for success in the course. The material contained in this chapter is especially needed by students returning to the classroom after a number of years away from school, or by those students who may have had some chemistry, but not the traditional first semester college chemistry course which is the usual prerequisite.

Systematic nomenclature based on the rules contained in *Nomenclature of Organic Compounds*, number 126 in the *Advances in Chemistry* series published by the American Chemical Society is introduced in Chapter 2 and used throughout the text. All compounds known mainly by their common names are also identified by their IUPAC names.

Organic reaction mechanisms are introduced in Chapter 2 by means of the free radical substitution mechanism. This mechanism was selected because it provides a review of covalent bonding that is essential to an understanding of what is to follow. (Remember that many students have had only one semester of general chemistry.) Discussion of the free radical chain mechanism in this chapter is limited. Only the basic steps are outlined. No attempt is made to discuss the difference in reactivity of hydrocarbons, or of the halogens. (Some additional refinements are made after the discussion of the relative stabilities of carbocations.) However, the discussion is developed sufficiently to show that in this reaction many products can be formed, and that it is an understanding of the reaction mechanism that allows the chemist to adjust the conditions of specific reactions in order to maximize the production of one desired product. This early introduction to reaction mechanism is the first step in a succession of ideas that should ultimately give students an appreciation of the magnificence of enzymes as catalysts. Through this process students will come to see that a study of organic chemistry provides a path to the understanding and appreciation of life that can be attained in no other way. Such an approach is also more likely to provide students with a background in organic chemistry that will enable them to understand the inevitable changes in chemical theory and practice that will occur throughout their lives.

While there is much in the sequence of topics that is traditional, there are several important variants. Cycloalkanes and alkenes are treated together in Chapter 3 as a way of introducing functional group isomerism and also geometric isomerism. Optical isomerism is introduced in Chapter 5, long before the chapter on carbohydrates. The early treatment of chirality not only permits a more complete discussion of nucleophilic substitution, one that includes the stereochemical differences between the  $S_N1$  and  $S_N2$  mechanisms, but also provides opportunity for reinforcement in subsequent chapters. Then when Chapter 9, on carbohydrates, is reached the leap from the discussion of simple monofunctional organic compounds to the much more complex multifunctional aldoses and ketoses, which is usually quite a shock to students, is not quite as difficult.

Not all aspects of electrophilic aromatic substitution are discussed in Chapter 4, the chapter that deals with aromatic chemistry. Here only the basics of the reaction are treated. Activation and deactivation are explained in a general way and the functional groups that serve as activators or deactivators are identified. The explanations for the reactivity and orientation of substitution of different classes of aromatic compounds are then explained in detail in the sections on aryl halides, phenols, and the aromatic aldehydes, ketones, acids, and amines. This provides both reinforcement of the fundamental principles and an opportunity to point out the ways in which the presence of one functional group effects the chemical properties of another.

Even though there is usually not enough time to cover it in depth, the chapter on biochemistry, Chapter 15, is included for a number of reasons. First, it provides students with a means of testing just how much they have learned in the course by using their newly acquired understanding to learn new material, and *this after all is why they have taken or have had to take the course*. If they have learned enough to pass the course, they should be able to understand, at least in part, the discussion on me-

tabolism, especially since most of them have already been exposed to these systems in biology courses. Second, wherever possible, the biochemical transformations that are shown are related to the organic reactions of the same type that were taught earlier. One of the greatest satisfactions for an organic chemistry teacher comes when a student suddenly realizes that biology has become much more comprehensible now that she/he has learned organic chemistry. Both teacher and student are rewarded when the student, often with a flash of insight, finally comprehends some aspect of molecular biology which he/she has previously been taught but not *really* understood.

The brief discussion of spectroscopy in Chapter 16 is included to acquaint the student with some of the tools that enable chemists either to identify known compounds or to determine the structure of new compounds. This material is often best covered in the laboratory section of the course.

At the end of each chapter there is a list of key words organized in chronological order by section. In the chapter, each key word is printed in boldface and its definition and/or explanation is printed in italics. In addition, each key word is printed in boldface in the index and more fully defined in the Dictionary that is included in the *Solutions Manual-Study Guide*. There is also a detailed and extensively cross-referenced summary at the end of each chapter that can be used as a study guide when the student reviews for examinations.

Each chapter has 15 or more questions and problems, some designed to develop skills and others to test for understanding. Instead of interrupting the flow of ideas and giving the pages of the text a cluttered appearance, the objective of giving students quick access to questions that are related to the topic being discussed is met by listing the related questions at the end of the section. Additional questions organized into "end of chapter" quizzes that cover only one or two concepts are provided in the *Solutions Manual-Study Guide*. Brief answers to selected questions, indicated by numbers and/or letters printed in color, are provided in the appendix. The answers to all of the questions in the text, with accompanying explanations where appropriate, are provided in the *Solutions Manual-Study Guide*.

---

## Acknowledgments

The skills I have acquired in the art of teaching, especially the art of teaching chemistry, I attribute first to my own chemistry teachers who inspired me to become a chemist and served as role models: Steven Marion, Milton Rosen, David Davidson, and most of all my mentor Henry Linschitz and second to my students. To Waters Ross I owe thanks for giving me the opportunity to return to the classroom and for the support and encouragement he gave me as I was learning my craft.

Many people have been involved either directly or indirectly in the preparation of this manuscript. Without their help this project could never have been successfully completed. They are Sister Mary Reyfus whose positive reaction to the first rough draft encouraged me to keep going, Rose Marie Flynn and David Cross who reviewed and edited the second draft, Barbara Silsby, Barbara Enagonio, and Richard and Bruce Schumm who did proofreading and gave technical advice, Heather Murcheson and Elizabeth Rouse who checked the answers to the questions, and all of the students who class-tested the many supplemental handouts that were the foundation for this book and the first draft. Thanks also to the copyeditor Roberta Gellis, and the Macmillan "team," Gregory Payne, Tom Vance, Peter Gordon, Elisabeth Belfer, Marianne Cortissoz, John Travis, and Robert Freese.



## Preface

My special thanks to the more than 20 concerned chemistry educators whose advice at every stage of the manuscript proved invaluable.

My typist, Janice Jones, has earned my everlasting gratitude not only for producing page after page of beautifully typed manuscript but also for the commitment she made to seeing the project through to a successful end and the many hours she spent away from her family so that we could meet "one more deadline."

*M. K. Schumm*

ROCKVILLE, MARYLAND

# Contents

## 1 Basic Concepts

1

1.1	The Building Blocks of Life	1
1.2	Ionic Bonding	4
1.3	Covalent Bonding	6
1.4	Sigma and Pi Bonds	12
1.5	Bonding of Carbon	14
1.6	Bond Polarity	14
1.7	Polarity of Molecules	16
1.8	Hydrogen Bonding	18
1.9	Structure, Size, and Physical Properties	19
1.10	Acid–Base Theories	25
1.11	pH and Buffers	30
1.12	Oxidation–Reduction	37
	<i>Chapter Summary</i>	38
	<i>Key Terms</i>	40
	<i>Questions</i>	40

## 2 The Alkanes

44

2.1	The Death of the Vital Force Theory and Birth of Organic Chemistry	44
2.2	Classification of Hydrocarbons: The Backbone or Skeleton of All Organic Compounds	45
2.3	Source and Physical Properties of Hydrocarbons	46
2.4	Structural Isomerism	50
2.5	Classification of Saturated Carbon Atoms	55
2.6	Nomenclature	56
2.7	Rules for Systematic Naming of Organic Compounds: The IUPAC System	57

Contents	2.8	Rotation About the Carbon-to-Carbon Single Bond: Conformation	63
	2.9	Preparation of Alkanes	67
	2.10	Preparation of Alkanes: Hydrolysis of a Grignard Reagent	68
	2.11	Reactions of Alkanes: Combustion	70
	2.12	Reactions of Alkanes: Halogenation	71
		<i>Chapter Summary</i>	77
		<i>Key Terms</i>	78
		<i>Questions</i>	79

### 3 Cycloalkanes, Alkenes, Alkynes, and Functional Group Isomerism 82

3.1	Cycloalkanes and Functional Group Isomerism	82
3.2	Physical Properties of Cycloalkanes	86
3.3	Nomenclature and Structure of Cycloalkanes	86
3.4	Ring Strain and Conformation	87
3.5	Conformations of Cyclohexane	89
3.6	Stereoisomerism of Cycloalkanes: Configuration	90
3.7	Chemistry of the Cycloalkanes	92
3.8	Heterocyclic Compounds	93
3.9	Alkenes: Source and Physical Properties	95
3.10	Naming the Alkenes	95
3.11	Geometry and Hybridization of the Carbon Atoms Forming the Double Bond; the Vinyl Carbons	97
3.12	<i>Cis-Trans</i> Isomerism in Alkenes	99
3.13	<i>Cis-Trans</i> Isomerism in Biochemistry	101
3.14	Preparation of Alkenes	103
3.15	Reactions of Alkenes: Addition Reactions	107
3.16	Electrophilic Addition: Specific Reactions	109
3.17	Orientation of Addition of Unsymmetrical Electrophilic Reagents to Unsymmetrical Alkenes: Markovnikov's Rule and the Relative Stabilities of Carbocations	111
3.18	Rearrangement	115
3.19	Reactions of Alkenes: Free Radical Substitution	117
3.20	Reactions of Alkenes: Polymerization	120
3.21	Analysis of Alkenes	122
3.22	Alkynes: Structure, Geometry, and Hybridization	122
3.23	Alkynes: Source and Physical Properties	124
3.24	Nomenclature of Alkynes	124
3.25	Preparation	124
3.26	Reactions of Alkynes	125
	<i>Chapter Summary</i>	127
	<i>Key Terms</i>	129
	<i>Questions</i>	129

### 4 Benzene and Other Aromatic Hydrocarbons 134

4.1	The Distinction Between Aliphatic and Aromatic Compounds	134
4.2	The Structure of Benzene	134
4.3	Aromatic Character or Aromaticity	141

4.4	Source and Physical Properties of Aromatic Hydrocarbons	142
4.5	Nomenclature of Benzene Derivatives	143
4.6	Electrophilic Aromatic Substitution	145
4.7	Electrophilic Aromatic Substitution: Specific Examples	148
4.8	Electrophilic Aromatic Substitution: Activation and Deactivation	152
4.9	Electrophilic Aromatic Substitution: Orientation	154
4.10	The Arenes	156
4.11	Physical Properties and Nomenclature of Arenes	156
4.12	Preparation of Alkylbenzenes	156
4.13	Reactions of Arenes	159
	<i>Chapter Summary</i> 164 <i>Key Terms</i> 166 <i>Questions</i> 166	
<b>5</b>	<b>Optical Activity of Organic Compounds</b>	<b>170</b>
5.1	Optical Activity	170
5.2	Optical Activity and the Tetrahedral Carbon Atom	173
5.3	Generation of a Chiral Carbon from an Achiral Compound: The Racemic Mixture	175
5.4	Representation of the Chiral Center	176
5.5	Differentiating Between Enantiomers: Absolute Configuration	178
5.6	The Chiral Center: <i>R</i> and <i>S</i> Notation	178
5.7	Importance of Optical Isomerism in Biochemistry: <i>D</i> and <i>L</i> Families	182
5.8	Relationship of <i>D</i> and <i>L</i> (or <i>R</i> and <i>S</i> ) to Optical Rotation, (+) and (−)	183
5.9	Compounds with More than One Chiral Center	185
5.10	Chemical Separation of Enantiomers: Resolution	187
	<i>Chapter Summary</i> 188 <i>Key Terms</i> 188 <i>Questions</i> 189	
<b>6</b>	<b>The Organic Halides—Aliphatic and Aromatic</b>	<b>191</b>
6.1	Organic Halogen Compounds: Use, Source, and Nomenclature	191
6.2	Physical Properties of Organic Halogen Compounds	194
6.3	Preparation of Organic Halogen Compounds	194
6.4	Reactions of Alkyl Halides: Nucleophilic Substitution	195
6.5	Reactions of Alkyl Halides: Specific Examples of Nucleophilic Substitution	201
6.6	Reactions of Alkyl Halides: Elimination	204
6.7	Reactions of Alkyl Halides: Preparation of a Grignard Reagent	207
6.8	Reactions of Aryl Halides: Nucleophilic Substitution	208
6.9	Reactions of Aryl Halides: Electrophilic Substitution	208
6.10	Comparison of Alkyl and Aryl Halides	210
6.11	Qualitative Analysis of the Organic Halides	211
6.12	The Stability Conferred by $sp^2$ Hybridization of Benzylic Carbon Atoms	211
	<i>Chapter Summary</i> 213 <i>Key Terms</i> 214 <i>Questions</i> 214	

<b>7</b>	<b>Alcohols, Phenols, Ethers, and Thiols</b>	<b>218</b>
7.1	Introduction	218
7.2	The Alcohols—Methanol and Ethanol	219
7.3	Physical Properties of the Alcohols, Phenols, and Thiols	220
7.4	Naming the Alcohols	222
7.5	Classification of Alcohols	224
7.6	Preparation of Alcohols	224
7.7	Preparation of Alcohols: Electrophilic Addition to Alkenes	224
7.8	Preparation of Alcohols: Substitution of OH for Halogen	227
7.9	Preparation of Alcohols Using the Grignard Reagent	227
7.10	Reactions of Alcohols: Reactions as Acids	229
7.11	Reactions of Alcohols: Reactions as Bases	230
7.12	Reactions of Alcohols: Oxidation	232
7.13	Reactions of Alcohols: Nucleophilic Substitution Reactions with Hydrogen Halides	234
7.14	Reactions of Alcohols: Substitution Using $PX_3$ or $SOCl_2$	237
7.15	Reactions of Alcohols: Dehydration	238
7.16	The Phenols	240
7.17	Reactions of Phenols	243
7.18	The Ethers	248
7.19	Preparation and Reactions of Ethers	249
7.20	Thiols and Disulfides	252
7.21	Qualitative Analysis of Alcohols and Phenols	254
	<i>Chapter Summary</i>	255
	<i>Key Terms</i>	256
	<i>Questions</i>	257
<b>8</b>	<b>Carbonyl Compounds: Aldehydes and Ketones</b>	<b>261</b>
8.1	The Carbonyl Functional Group	261
8.2	Source and Physical Properties	263
8.3	Nomenclature	267
8.4	Order of Precedence of Functional Groups in the Naming of Organic Compounds	268
8.5	Preparation of Aldehydes and Ketones: Oxidation of Alcohols	270
8.6	Preparation of Aldehydes: Reduction of Acid Chlorides	272
8.7	Preparation of Aldehydes: Oxidation of Aryl Methyl Compounds	273
8.8	Preparation of Ketones: Hydration of Alkynes	274
8.9	Preparation of Ketones: Friedel–Crafts Acylation	275
8.10	Reactions of Aldehydes and Ketones: Oxidation	276
8.11	Reactions of Aldehydes and Ketones: Reduction	278
8.12	Reactions of Aldehydes and Ketones: Acyl Nucleophilic Addition	280
8.13	Reactions of Aldehydes and Ketones: Specific Examples of Nucleophilic Addition	281
8.14	Reactions of Aldehydes and Ketones: Addition of Ammonia and Ammonia Derivatives Followed by Elimination of Water	293
8.15	Reactions of Aldehydes and Ketones: Acetal Formation	296

8.16	Reactions of Aldehydes and Ketones: Electrophilic Aromatic Substitution	298
8.17	Tautomerism	299
8.18	Qualitative Analysis of Aldehydes and Ketones	302
	<i>Chapter Summary</i>	302
	<i>Key Terms</i>	304
	<i>Questions</i>	305

## 9 The Carbohydrates

310

9.1	Introduction	310
9.2	Properties and Structures of Glucose and Fructose	312
9.3	Stereosomerism of Glucose and Fructose	314
9.4	The Cyclic Structure of Glucose: Mutarotation	315
9.5	Structural Formulas Commonly Used to Represent Glucose and other Carbohydrates	318
9.6	Classification of Carbohydrates	320
9.7	The D and L Families of Sugars: Optical Families	321
9.8	Absolute Configuration	325
9.9	Isomeric Relationships Among the Monosaccharides	325
9.10	Reactions of Monosaccharides	326
9.11	Deoxy Sugars	333
9.12	Amino Sugars	334
9.13	Sugar Phosphates	334
9.14	The Disaccharides	335
9.15	The Polysaccharides of Glucose: Cellulose, Starch, and Glycogen	338
	<i>Chapter Summary</i>	342
	<i>Key Terms</i>	344
	<i>Questions</i>	345

## 10 Carboxylic Acids, Their Salts, and Some Derivatives: Esters, Amides, and Anhydrides

348

10.1	Introduction	348
10.2	Sources of the Carboxylic Acids	349
10.3	Physical Properties of the Carboxylic Acids	349
10.4	Nomenclature of the Carboxylic Acids	350
10.5	Acidity of the Carboxylic Acids	352
10.6	Preparation of Carboxylic Acids	357
10.7	Reactions of Carboxylic Acids: Salt Formation	358
10.8	Reactions of Carboxylic Acids: Reactions That Involve Breaking the C—OH Bond	359
10.9	Reactions of Carboxylic Acids: Effect of the Carboxyl Group on the Hydrocarbon Portion of the Molecule	366
10.10	Salts of the Carboxylic Acids	366
10.11	Esters	368
10.12	Amides	380
10.13	Anhydrides	387
	<i>Chapter Summary</i>	388
	<i>Key Terms</i>	390
	<i>Questions</i>	391

<b>11</b>	<b>The Lipids</b>	<b>395</b>
11.1	Introduction	395
11.2	Classifications of Lipids	396
11.3	The Naturally Occurring Fatty Acids	397
11.4	The Naturally Occurring Fats and Oils	399
11.5	Detergent Action of Soaps and Synthetic Detergents	405
11.6	The Waxes	407
11.7	Compound Lipids	407
11.8	The Nonhydrolyzable or Simple Lipids	410
11.9	Biological Membranes	415
	<i>Chapter Summary</i>	418
	<i>Key Terms</i>	418
	<i>Questions</i>	419
<b>12</b>	<b>Amines and Amino Acids</b>	<b>422</b>
12.1	Nitrogen and the Nitrogen Cycle	422
12.2	Classification of Organic Amines	423
12.3	Nomenclature	425
12.4	Physical Properties	426
12.5	Preparation of Amines	426
12.6	Reactions of Amines	432
12.7	Amino Acids	439
	<i>Chapter Summary</i>	448
	<i>Key Terms</i>	449
	<i>Questions</i>	449
	<i>Prologue to Chapters 13–15</i>	453
<b>13</b>	<b>Proteins</b>	<b>456</b>
13.1	Introduction	456
13.2	Classification of Proteins	456
13.3	Peptides	458
13.4	Determination of Amino Acid Sequence in Polypeptides and Proteins	459
13.5	Synthesis of Polypeptides and Proteins	464
13.6	The Structure of Proteins	467
13.7	Denaturation of Proteins	478
13.8	The Effect of Amino Acid Substitutions on Protein Function	481
13.9	Enzymes	483
13.10	Composition of Enzymes	486
13.11	The Mechanism of Enzyme Action	486
	<i>Chapter Summary</i>	487
	<i>Key Terms</i>	488
	<i>Questions</i>	489
<b>14</b>	<b>Nucleic Acids: Structure and Function</b>	<b>492</b>
14.1	Nucleic Acid and the Self-replication of Living Organisms	492
14.2	Types of Nucleic Acids and Their Functions	493
14.3	The Composition of Deoxyribonucleic acid, DNA	493

Contents	14.4	The Structure of DNA	499	
	14.5	The Ribonucleic Acids: Composition and Structure	503	
	14.6	DNA: Function in Replication and Transcription	507	
	14.7	RNA and the Synthesis of Protein: Gene Translation	510	
	14.8	Inhibition of Protein Synthesis by Antibiotics	516	
	14.9	Recombinant DNA	518	
		<i>Chapter Summary</i>	519	<i>Key Terms</i> 520 <i>Questions</i> 520
<b>15</b>	<b>The Chemistry of the Living State</b>			<b>522</b>
	15.1	Biochemical Cycles and a Definition of Life	522	
	15.2	The Structure and Properties of ATP	525	
	15.3	The Unique Role of the ATP–ADP System	528	
	15.4	Metabolism: An Overview	531	
	15.5	The Generation and Storage of Metabolic Energy: Glycolysis	536	
	15.6	The Generation and Storage of Metabolic Energy: The Tricarboxylic Acid Cycle	543	
	15.7	The Generation and Storage of Metabolic Energy: Oxidative Phosphorylation	548	
	15.8	The Energy Efficiency of Respiration	549	
	15.9	A Glimpse at the Interrelationships Between Respiration and Some of the Major Biosynthetic Pathways	550	
	15.10	Transamination	554	
	15.11	The Biosynthesis of Glucose: Gluconeogenesis	556	
	15.12	Photosynthesis	559	
	15.13	Conclusion	559	
		<i>Chapter Summary</i>	560	<i>Key Terms</i> 561 <i>Questions</i> 561
<b>16</b>	<b>Molecular Spectroscopy—How the Chemist Determines Molecular Structure</b>			<b>564</b>
	16.1	Introduction	564	
	16.2	Electromagnetic Radiation and the Electromagnetic Spectrum	565	
	16.3	The Effect of Radiation on Atoms and Molecules	568	
	16.4	Mass Spectrometry	570	
	16.5	Ultraviolet and Visible Absorption Spectroscopy	573	
	16.6	Infrared Absorption Spectroscopy	575	
	16.7	Nuclear Magnetic Resonance Spectroscopy	583	
		<i>Chapter Summary</i>	591	<i>Key Terms</i> 592 <i>Questions</i> 592
<b>Suggestions for Further Study</b>				<b>595</b>
<b>Answers to Selected Questions</b>				<b>597</b>
<b>Index</b>				<b>615</b>
				<b>xix</b>



# 1

## Basic Concepts

Some of the material covered in this chapter will be a review of topics you have already studied in your introductory chemistry course, and some will be new. These subjects are included here so that you will have ready access to the background material essential to your understanding of the organic chemistry and biochemistry you are about to learn, whether or not they are formally covered in your class discussions.

### 1.1 The Building Blocks of Life

Since it is our aim to understand the structure, organization, and function of matter in living systems, it might be well to look at the levels of organization of matter. These are listed in Figure 1.1 together with the branches of the natural sciences that can be involved in their study.

Figure 1.2, a portion of the periodic chart showing about one third of the known elements, includes nearly all of the elements necessary for life. Of these, only *carbon*, *hydrogen*, *oxygen*, *nitrogen*, *phosphorus*, and *sulfur* (shown in color) are constituents of the basic molecules of which living matter is composed. Other elements (shaded)—Ca, Cl, Co, Cr, Cu, I, Fe, Mg, Mn, Mo, K, Na, and Zn—are also essential to living systems, but with three notable exceptions they are present in much smaller amounts, mainly as ions. Calcium is one exception because it is a major component of exoskeletons (shells), bones, and teeth and is therefore often present in fairly large amounts. Iron and iodine

Figure 1.1  
Levels of Organization of  
Matter—An Overview

