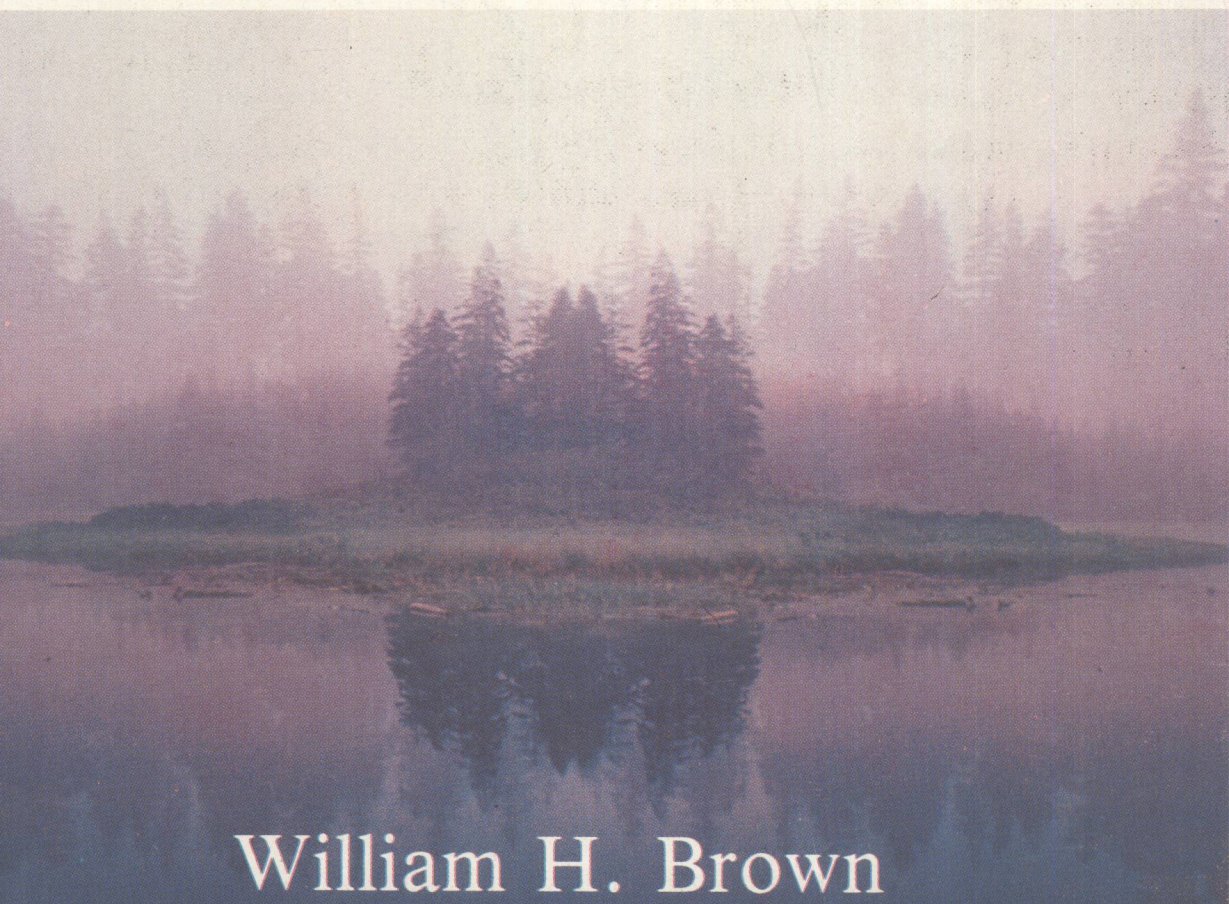


INTRODUCTION TO ORGANIC CHEMISTRY

SECOND EDITION

Wadsworth International Student Edition



William H. Brown

INTRODUCTION TO ORGANIC CHEMISTRY

SECOND EDITION

William H. Brown
Beloit College

Willard Grant Press
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Preface

This second edition provides an introduction to organic chemistry and assumes as background a course in general chemistry. Although students take a short organic course for different reasons, most have one thing in common. They are aiming toward careers in science, but few if any intend to become professional chemists. Rather, they are preparing for careers in areas that require a grounding in the fundamentals of organic chemistry. Here is the place to examine the structure, properties, and reactions of rather simple organic molecules. The student can then build on this knowledge in later course work and in professional life.

This text can be divided roughly into two parts. The first, Chapters 1 to 10, lays the foundation in organic chemistry by discussing the structures and typical reactions of the important functional groups with which the student must be familiar. Although the basic approach and content of these chapters is retained from the first edition, many suggestions and comments from users have been incorporated into the second. One of the most obvious changes is the redistribution of material from the former Chapter 2, "Chemical and Physical Properties," to appropriate places in subsequent chapters. For example, polarity of bonds and molecules is now treated in Chapter 1 along with the discussions of covalent bonding. Intermolecular forces, hydrogen bonding, and the solubility of organic molecules in polar solvents now appear in Chapter 5, along with the discussion of physical properties of alcohols and ethers. Acidity and basicity of organic substances has been integrated into the sections dealing with chemical and physical properties.

Regrouping material in this way has two distinct advantages. First, students will move quickly from the discussion of structure and bonding in Chapter 1 to what is for them the substance of organic chemistry—alkanes,

alkenes, alcohols, etc. Second, students can master better the relationships between structure and physical and chemical properties now that these important concepts are placed within the context of appropriate chapters.

Added to Chapter 3 on the chemistry of alkenes is a discussion of the free radical polymerization of ethylene and substituted ethylenes. In Chapter 5 greater emphasis is placed on the fact that conversions of alcohols to aldehydes, ketones, and carboxylic acids are oxidations, rather than dwelling on how such oxidations are carried out in the laboratory. The discussion of the Williamson ether synthesis in the same chapter has been expanded to show how substitution can be maximized and elimination minimized by the proper choice of starting materials.

The discussion of fatty acids, soaps, and detergents appears now in Chapter 8, "Carboxylic Acids." Students find this material very interesting, and it is easily presented at this point. The structure and important reactions of acyl halides are presented in Chapter 9, "Functional Derivatives of Carboxylic Acids."

Chapters 11 to 14, comprising the second part of the book, provide a comprehensive coverage of the structure and function of four key classes of biomolecules: carbohydrates, lipids, amino acids and proteins, and nucleic acids. A number of changes have been made in these chapters in the second edition.

A section on the structure of ascorbic acid and its role in the cross-linking of collagen fibers has been added to the carbohydrates chapter. Chapter 12 now contains: expanded discussions of fats, oils, waxes, and phospholipids; a new section treating the organization of phospholipids in cell membranes; a fuller discussion of the structure and function of the fat-soluble vitamins, steroid hormones, and bile acids.


Chapter 13 offers a more balanced introduction to the structure and physical properties of amino acids and proteins. Discussion has been expanded on the acid-base properties of amino acids, the zwitterion structure, isoelectric points and the physical basis for electrophoresis. Reference to the Sanger method for end group determination has been deleted in favor of the newer and more versatile Edman degradation. Finally, the discussion of quaternary structure of proteins and the physical basis for protein denaturation has been enlarged.

Throughout the book problems have been revised, and their number has been increased substantially. One new type of exercise emphasizes transformations—how to convert one substance to another. Most require no more than two or three steps. The intent of these problems is to provide one more way for students to practice using the important reactions discussed within the chapters. In my experience the investment of time and effort in doing them leads to a better understanding of organic chemistry.

All of the mini-essays retained from the first edition have been revised and updated. Two new ones, entitled "Ethylene" and "Clinical Chemistry—The Search for Specificity," have been added. The purpose of these short, optional articles is to reveal to students the role of the organic chemistry just learned in areas of concern and interest to them. Offering a glimpse of the human involvement in research and discovery, the essays demonstrate that organic chemistry is an exciting and creative field.

The question of whether or not to include material on spectroscopy in a short introductory book is a difficult one to answer. While more and more instructors are introducing this topic, others, for very good reasons, choose not to do so. Spectroscopy is clearly a part of the workday life of almost

everyone in the health and biological sciences. For this reason I have chosen to include spectroscopy, and I have tried to do this in a way that will be useful to those who want to use it but easily omitted by those who do not want to use it.

All discussions are qualitative in nature and require no more background than what students have from general chemistry. Any section or problem containing spectral information is marked with the symbol  so that it can be easily identified.

A chapter at the end of the book introduces infrared, ultraviolet-visible, and nuclear magnetic resonance spectroscopy. This chapter may be taken up at any time once Chapter 2 has been completed. Free-standing sections on the major spectral characteristics of each functional group have been added to appropriate chapters.

Problems requiring the use of spectral information are included at the ends of problem sets. Most ask the student to list the characteristics that will allow him or her to identify the functional group or distinguish between pairs of substances. Frequently these problems are presented with ones asking the student for a chemical means for making the same determination.

A second edition of the *Study Guide* is also available. Its purpose is to guide students in their approach to solving organic chemistry problems and to provide complete and detailed solutions to all problems in the text.

Acknowledgments

The second edition of this text has been shaped by the suggestions and opinions expressed by users of the first, particularly: Kenneth Andersen, University of New Hampshire; Warren Biggerstaff, California State University, Fresno; Robert Caret, Towson State University; George Clemans, Bowling Green State University; William Dolbier, University of Florida; John Gilje, University of Hawaii; Robert Ingham, Ohio University; Ronald Johns, Spokane Falls Community College; George Levy, Florida State University; Robert Nagler, Western Michigan University; Roy Pointer, Bloomsburg State University; James Rudesill, North Dakota State University; Robert Smalley, Emporia Kansas State College; L.G. Wade, Colorado State University; George Wahl, North Carolina State University.

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1

The Covalent Bond and the Geometry of Molecules

1.1 Introduction

An introduction to organic chemistry must begin with a review of atomic structure and bonding. Much of organic chemistry is the chemistry of carbon and only a few other elements: hydrogen, nitrogen, oxygen, and the halogens. Therefore, in this chapter we will describe how atoms of these elements combine to form molecules by sharing electron pairs, and then we will examine the three-dimensional shapes of some simple organic molecules. Finally we will develop the concept of constitutional isomerism and functional groups. In subsequent chapters we will turn to the reactions organic molecules undergo, the conditions under which certain bonds can be broken and new ones formed, and the ways to convert one molecule into another.

Although discussions of this type can become quite sophisticated, we must not lose sight of the fact that they are based on the application of a few fundamental and logical principles. By the time you finish this course, you should have a good working knowledge of these principles.

1.2 Electronic Structure of Atoms

You should already know certain fundamental principles about the electronic structure of atoms and ionic and covalent bonding from a previous course in chemistry. Let us review some of these briefly.

TABLE 1.1 The electronic configuration of the first 18 elements.

Element	Atomic Number	Orbital							
		1s	2s	2p _x	2p _y	2p _z	3s	3p _x	3p _y 3p _z
H	1	1							
He	2	2							
Li	3	2	1						
Be	4	2	2						
B	5	2	2	1					
C	6	2	2	1	1				
N	7	2	2	1	1	1			
O	8	2	2	2	1	1			
F	9	2	2	2	2	1			
Ne	10	2	2	2	2	2			
Na	11	2	2	2	2	2	1		
Mg	12	2	2	2	2	2	2		
Al	13	2	2	2	2	2	2	1	
Si	14	2	2	2	2	2	2	1	1
P	15	2	2	2	2	2	2	1	1
S	16	2	2	2	2	2	2	2	1
Cl	17	2	2	2	2	2	2	2	1
Ar	18	2	2	2	2	2	2	2	2

An atom of an element consists of a dense nucleus surrounded by electrons. The nucleus bears a positive charge that is numerically equal to the number of electrons that surround it. The mass of an atom is concentrated in the nucleus and is equal to the sum of the masses of the protons and neutrons in the nucleus.

The electrons of an atom are concentrated in certain three-dimensional regions called orbitals. These electron orbitals are grouped in shells or principal energy levels identified by the principal quantum numbers 1, 2, 3, and so on. These are also sometimes referred to by the letters *K*, *L*, *M*, etc. The principal quantum number 1 shell consists of a single orbital, the 1s orbital; the 2 shell consists of four orbitals, the 2s, 2p_x, 2p_y, and 2p_z; the 3 shell consists of nine orbitals, one 3s orbital, three 3p orbitals, and five 3d orbitals.

In addition to the number and kind of orbitals, we need to remember that an orbital can accommodate a maximum of two electrons. Thus the maximum number of electrons that can occupy the first shell is two; the second shell, eight; and the third shell, eighteen. If we “build” an atom by surrounding the nucleus with just enough electrons to neutralize its positive charge, the first orbital to fill will be the 1s, that is, the orbital of lowest energy (the one closest to the nucleus). Next to fill will be the 2s orbital, then the 2p, etc. Table 1.1 shows the electronic configuration of the first eighteen elements of the periodic table.

We generally focus our attention on the electrons in the outermost or valence shell for it is these electrons that participate in chemical bonding and reaction. The valence electrons are represented by one or more dots surrounding the usual symbol for the atom. Each dot represents one valence electron. In the second-period elements, lithium through neon, we consider the nucleus and the two 1s electrons as a unit called the kernel. In the third-period elements, sodium through argon, we consider the two 1s

H·								He·
Li·	Be:	·B:	·C:	·N:	·O:	·F:	·Ne:	
Na·	Mg:	·Al:	·Si:	·P:	·S:	·Cl:	·Ar:	

TABLE 1.2 Valence electrons for the first 18 elements.

electrons, the two $2s$, and the six $2p$ electrons as the kernel. Thus we would write the valence electrons for the first eighteen elements as shown in Table 1.2.

You should compare these valence electron representations with the electron configurations given in Table 1.1. For example, notice that in Table 1.2 beryllium is shown with two paired valence electrons; these are the two paired $2s$ electrons listed in Table 1.1. Carbon is shown with four valence electrons, two of which are paired and two of which are unpaired; these represent the two paired $2s$ electrons and the single $2p_x$ and $2p_y$ electrons listed in Table 1.1. Notice also that carbon and silicon each have four valence electrons, nitrogen and phosphorus each have five valence electrons, oxygen and sulfur each have six valence electrons, and fluorine and chlorine each have seven valence electrons.

Although the number of valence electrons for each of these pairs of atoms is the same, the shells in which these valence electrons are found are different. For C, N, O, and F, the valence electrons belong to the principal quantum number 2 shell. With eight electrons this shell is completely filled. For Si, P, S, and Cl, the valence electrons belong to the principal quantum number 3 shell. This shell is only partially filled with eight electrons; the $3s$ and $3p$ orbitals are fully occupied but the five $3d$ orbitals can accommodate an additional ten valence electrons. Because of this difference between the number and kind of orbitals in shells 2 and 3, we should expect differences in the covalent bonding of oxygen and sulfur, and of nitrogen and phosphorus. Such differences do exist, as we shall see.

1.3 The Lewis Model of the Covalent Bond

In 1916, Gilbert N. Lewis, Professor of Chemistry at the University of California, came up with a beautifully simple hypothesis that unified many of the apparently disparate facts about reactions of the chemical elements. Lewis pointed out that the chemical inertness of the noble gases indicates a high degree of stability of the electronic complements of these elements: helium with a shell of two electrons, neon with shells of two and eight electrons, and argon with shells of two, eight, and eight electrons.

According to the Lewis model of bonding, elements other than the noble gases can achieve a greater degree of stability by gaining, losing, or sharing electrons, and atoms will tend to undergo reactions to acquire a noble gas electronic configuration in their outer (valence) shell. For example, sodium (which has one too many valence electrons for the electronic configuration of neon) and chlorine (which has one too few valence electrons for the electronic configuration of argon) can achieve a mutually advantageous state by the transfer of one electron from the sodium atom to