

ORGANIC CHEMISTRY

Concepts and Applications

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To Pat Molly Tim, Dan Marilyn, Elizabeth, Art, and Della

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PREFACE

Organic Chemistry: Concepts and Applications is an introduction to the theory and practical applications of organic chemistry. The text is intended to provide background information for students in such fields as the health sciences, biology, agriculture, law, ecology, home economics, and technology. In addition to providing the essential and most important organic reactions, we have included theoretical concepts such as reaction mechanisms in order to illustrate the molecular nature of complex organic reactions and to emphasize their structural implications. The material is presented so that the student is frequently exposed to related applications of the principles under discussion. For example, discussions of such topics as carcinogens, chemistry of eyesight, vitamins, hormones, alkaloids, prostaglandins, and antibiotics are integrated within the text to provide a background for students aiming for a career in the health sciences as well as to serve as interest sustainers for others.

In the initial chapters we give special emphasis to the essential foundation of molecular orbital hybrids and nomenclature. Many texts treat these topics superficially, failing to realize that students, while they are actively engaged in the body of organic chemistry, are still struggling with recognition of the compound structures and especially the naming of the molecules. Consequently, we felt it important to give special and extensive coverage of the naming and identification of organic compounds. As an additional aid we have provided a chart on the inside cover for the easy identification of the functional groups and classes of organic compounds. We have also included an extensive glossary at the end of the text as a reference for definitions of technical terms used in the text.

Our presentation of material is structured around two important features designed to reinforce the material being taught. Following the introduction to each chapter is a list of expectations that identifies the most important information and concepts that the student is expected to learn by the end of the chapter. Section titles then appear in the form of questions, thereby providing additional guidance and motivation. A set of problems and questions at the end of each chapter corresponds to the expectations stated at the beginning, thus providing the students with a means of testing themselves as they proceed.

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John A. Miller
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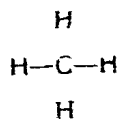
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1

Fundamentals for the Study of Organic Chemistry

WHY STUDY ORGANIC CHEMISTRY?

Twentieth-century man floats on a sea of technology that is largely a result of the giant steps taken in the world of organic chemistry. The term "organic chemistry" was originally used to denote the chemistry of carbon-containing compounds of living systems. The eighteenth-century chemist, who was well on his way to understanding the world of inert or nonliving substances of inorganic chemistry, found these "organic" compounds beyond his ability to synthesize. The compound sodium chloride (NaCl) could be created easily from the combination of the inorganic elements sodium and chlorine, but compounds such as ethyl alcohol, whose formula was known to

be $\text{C}_2\text{H}_5\text{O}$, could not be formed by the simple combination of the elements carbon, hydrogen, and oxygen. Such compounds were thought to be creatable by nature only and all compounds containing carbon were called organic. But in 1828 the German chemist Wöhler synthesized uræa, an organic compound, by accident when he evaporated by heating inorganic ammonium cyanate (NH_4CNO). From that day on, organic chemistry was no longer in a distinct class by itself, although its name did not change.

The study of organic chemistry began with and continues with the most involved and complicated forms of chemistry, the

chemistry of living systems. The study of **organic chemistry** ensures progress and understanding in biology and other related fields. For example, anyone studying the chemistry of life very quickly learns how drugs, antibiotics, and other organic compounds cause striking changes in the human body and mind.

Not quite so complicated but still important is the technological application of organic chemistry in the twentieth century. This chemical technology has created a

seemingly endless flood of new materials, ranging from pesticides to plastics. But in the wake of these new materials has come pollution and its sometimes deadly effect on the living world. Thus we have gained both benefits and corresponding problems from the application of organic chemistry.

An awareness of the fundamental aspects of organic chemistry promotes an awareness of its application to the physical and natural sciences.

EXPECTATIONS

This first chapter will review some essential material that you have already studied in previous courses in general chemistry, but more concisely and pragmatically. At the conclusion of this chapter, you will be expected to be able to do the following:

1. State the primary element present in all organic compounds and which other elements are frequently found in organic compounds.
2. Draw pictorial representations of the electronic structure of the first ten elements of the periodic chart using the atomic orbital method.
3. Describe the nature and some of the manifestations of covalent and ionic bonding.
4. Draw a pictorial representation of the sp^3 hybrid orbital configuration of carbon

and describe how it is assumed to be formed.

5. Draw pictorial representations of the compounds methane and ethane using the sp^3 hybridized orbital of carbon.
6. Draw diagrams of methane and ethane using Lewis structures and the ball-and-stick model of molecules.
7. Extend the concept of the carbon sp^3 hybrid orbitals to show how the carbon-to-carbon single-bond linkages are formed. Also show this with Lewis structures.
8. Describe the geometric shape of molecules created by the sp^3 hybrid orbital bonding of carbon.
9. Extend the hybrid orbital bonding model to explain bonding with elements other than carbon.

1.1 What are the important atomic elements normally associated with organic chemistry?

Figure 1.1 shows the periodic table of the elements. The listing of the elements in order of increasing atomic weight results in the periodic repetition of elements with similar chemical and physical properties. The vertical columns of elements in the periodic chart, which have similar properties, are called families or groups. Specifically, the electronic arrangements of the active outer electrons are similar in all the elements in a particular column. Above each atomic symbol is the atomic number (z), which indicates the number of electrons orbiting the central nucleus of the atom. The nucleus contains a sum of protons equal to the atomic number, and additional neutrons to yield the atomic mass of the element. For all practical purposes, the atomic mass is the sum of the masses of the protons and neutrons; electrons add very little mass to the atom. The atomic mass or weight stated under each elemental symbol is the weighted average of all the isotopes of that element. Isotopes are atoms with the same number of protons but varying numbers of neutrons in the nucleus. For example, the normal collection of chlorine atoms consists of two isotopes. One has an atomic weight of 34.9688 atomic mass units (amu) and makes up 75.774 percent of any collection of chlorine atoms. The other isotope constitutes 24.23

FIGURE 1.1 Periodic table of the elements (Some of the more important elements have electronegativity values listed after their symbols)

GROUP	I	II											III	IV	V	VI	VII	0
PERIOD																		
1	1 H(2 1) 1.0																	2 He 4.0
2	3 Li(1 0) 6.9	4 Be(1 5) 9.0											5 B(2.0) 10.8	6 C(2 5) 12.0	7 N(3 0) 14.0	8 O(3 5) 16.0	9 F(4 0) 19.0	10 Ne 20.2
3	11 Na(0 9) 23.0	12 Mg(1 2) 24.3	Transition elements										13 Al(1 5) 27.0	14 Si(1.8) 28.1	15 P(2 1) 31.0	16 S(2 5) 32.1	17 Cl(3 0) 35.5	18 Ar 39.9
4	19 K 39.1	20 Ca 40.1											21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.8
5	37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I(2 5) 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57-71 * †	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra 226	89-103 †															

*	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 147	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
†	89 Ac (227)	90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lw (257)