Second Edition

The Basis of
Organic Chemistry

International Student Edition

Ralph J. Fessenden
Joan S. Fessenden

Ralph J. Fessenden and Joan S. Fessenden
University of Montana

The Basis of Organic Chemistry

Second Edition

Preface

In revision, we have not changed the philosophy or overall organization of this book. We have corrected errors, tightened things up, and eliminated a few of the more obscure reactions to make room for more problems and chapter summaries.

There have been a few changes in organization. Chapter 1 has been expanded to give a more detailed review on bonding. Optical isomerism has been moved from Chapter 2 to Chapter 11 because it is not used until after this point. The discussion of physical properties in Chapter 18 has been deleted to accommodate a slight expansion of spectroscopy, NMR in particular. Our thanks to Varian Associates for permission to reproduce the nuclear magnetic resonance spectrum of ethyl chloride.

A few additional topics have been added. The E-Z and (R) (S) systems of nomenclature are introduced briefly, as are the subjects of prostaglandins, insect pheromones, and photosynthesis.

We are indebted to our typist, Mrs. Susan Pirrong, whose help has been invaluable.

Ralph J. Fessenden

Joan S. Fessenden

Preface to the First Edition

Organic chemistry is a vigorous field. Modern technology relies heavily upon this field in the production of plastics, textiles, dyes, and fuels; research and its applications in the fields of medicine, pharmacology, nutrition, and agriculture are largely based upon organic chemistry.

Because of the vitality of the field of organic chemistry, an ever-increasing body of knowledge must be presented to the student. Today's student does not require the ability to regurgitate a string of memorized equations. Instead, he needs to be able to grasp organic chemistry as a whole. The student who understands how and why reactions occur develops a "feel" for organic chemistry. This feel cannot be developed by memorization alone.

Therefore, instead of using the traditional approach—that of presenting the reactions of each functional group—we have emphasized the reactions of types of bonds and how these reactions occur. Because the book is directed toward students with varying backgrounds and interests, we have treated reaction mechanisms from a visual standpoint and not a mathematical one.

Like elementary algebra, organic chemistry is a discipline to be applied to other fields. It would be impossible to introduce all the applications of organic chemistry in one book. Since most of us have an interest in biologically oriented fields such as genetics or the study of drugs, the emphasis in the latter chapters is on some of the biological applications of organic chemistry.

This book is directed toward the student who has had a background in general chemistry. Although we assume a knowledge of basic chemistry, material that may be a review for many students is included in the first three chapters. This has been done intentionally. A firm foundation in bonding and structure is necessary for an understanding of why reactions occur.

Study questions have been included at the end of Chapters 1 through 9. These questions are not intended to cover all that the student should know. Rather, they are intended to serve as a study guide. Chapter 10 is a review of important organic reactions. The student may find this chapter useful as a reference, as well as a review.

In the course of preparing this book, we have sought and have received advice from many of our friends and colleagues. In particular, we are indebted to Drs. Donald Canham, James Cox, Walter Hill, Galen Mell, Frank Pettinato, Fred Shafizadeh, and William Waters. The book is intended for students and we are grateful to the students, too numerous to name individually, who have reviewed and criticized portions of the manuscript. In addition, we must praise

our ever-patient typists, Mrs. Patricia Hodge and Mrs. Marjorie Caldwell, and last of all, our sons, Douglas and Bruce, who were forced to fix their own breakfasts and lunches for the duration of the writing. Our thanks to Sadtler Research Laboratories for the ultraviolent, infrared, and nuclear magnetic resonance spectra that are reproduced in this book.

Ralph J. Fessenden

Joan S. Fessenden

Contents

CHAPTER

1

The Covalent Bond

Organic chemistry is usually defined as the chemistry of compounds containing carbon. This definition is as good as any, but how dull! Organic chemistry is the tool that has been used to produce synthetic fabrics and wonder drugs. It is the tool being used to solve the secrets of insect communication. It is the area of study that leads directly to biochemistry, the chemistry of plants and animals. The early chemists defined organic chemistry as the chemistry of compounds derived from living systems. Although many present-day organic compounds never were connected with anything alive, the definition of the early chemists at least has an aura of romance about it.

You will find that, to you, organic chemistry is also the study of a symbolic language. It is a language that is used to describe nature. The symbols that we call formulas represent molecules that form our world. The combination of symbols that form equations represent what the molecules do. By learning the symbolism, you will be able to glean information about the physical and biological properties of the molecules they represent.

Where do we start? All organic molecules have their atoms joined together by covalent bonds. The covalent bond then is a logical point of departure. Let us first look at atoms, then at how atoms are joined together to form organic molecules and at the symbolism that is used to represent the organic molecules. Then we will turn to the molecules themselves and study how these molecules behave in flasks in the laboratory or in living systems.

ATOMS AND MOLECULES

The smallest particle of matter is the *atom*. Elements, such as helium, may be composed of just single atoms. However, most elements (such as oxygen) and

1

all compounds are composed of *molecules*, which are groups of two or more atoms bonded together in some fashion or other.

An atom is composed of a small, heavy *nucleus* that is surrounded by lightweight negatively charged *electrons*. The nucleus contains *protons* (positively charged particles) and *neutrons* (neutral particles). Other particles have been discovered in nuclei but to the test-tube chemist protons and neutrons are the principal concern. In order to be electrically neutral, an atom must contain the same number of electrons and protons. In this situation, the electrical charge is balanced; the amount of negative charge equals the amount of positive charge.

SHELLS AND ENERGY LEVELS OF THE ELECTRONS

The electrons of an atom are not scattered at random around the nucleus, nor are the electrons free to wander as they please. Rather, the electrons are restricted to certain general regions of space, or shells, around the nucleus. The electrons in a given shell all have approximately the same energy; therefore, there is an *energy level* associated with each shell. We often refer to these energy levels to indicate their respective shells; when we speak of the "first energy level," we imply "the first shell" and vice versa.

The first energy level is associated with the shell closest to the nucleus. Attractions between oppositely charged particles, like gravitational attractions, are stronger when the particles are closer together and lessen with increasing distance. Therefore, electrons in the first shell are more strongly attracted by the positively charged nucleus than electrons that are farther away; these electrons in the first shell are more difficult to remove from the atom. We say that these closer electrons have *lower energy*. Therefore, the first energy level is the level of electrons of the lowest energy.

The second shell is farther away from the nucleus than the first. The electrons in the second level are easier to pull away from the atom than electrons in the first shell level. This energy level is of slightly higher energy than the first. The third shell is farther out than the second and is of higher energy

TABLE 1-1. Maximum Number of Electrons in the First Four Energy Levels

Energy Level	Number of Electrons
1	2
2	8
3	18
4	32

than the second. Each succeeding energy level through the seventh is of successively higher energy.

Each of the different shells can accommodate a limited number of electrons. The first shell can hold no more than two electrons. The second shell can have no more than eight electrons; the third, 18; and the fourth, 32. (See Table 1-1.) The reasons for these limits will become apparent shortly.

Because the positively charged nucleus attracts the negatively charged electrons as close to themselves as possible, electrons seek the lowest energy level possible. As the number of protons is increased in the nucleus, the lower energy levels fill up with electrons first, then the higher levels fill in succession.

The scheme in Figure 1-1 shows the electronic structures of hydrogen, helium, and the second-period elements of the Periodic Table. The number of electrons in the first and second shells are under the atomic symbols, while the atomic numbers (the numbers of protons in the nucleus) are above the symbols.

In this scheme, we can see that hydrogen has one electron in the first shell and helium has two. Now, the first shell is filled. Lithium, the next element, has its third electron in the second shell. As we work through the row up to neon, we can see the second energy level filling until it holds its maximum of eight electrons.

It is the electrons in the outermost shells that are used for forming bonds between atoms. The number of bonding electrons is a major factor in the chemical reactivity of an element. In compound formation, an atom strives for a complete outermost shell and will accept electrons, lose electrons, or share electrons to achieve this goal. (Because their outer shells are already filled, the gases in Group 0 of the Periodic Table are *inert*, or unreactive.)

PROBLEM

1-1: Sodium is just below lithium in the Periodic Table. How many electrons are in each of the shells of a sodium atom?

FIGURE 1-1. The electronic structures of the elements in the first and second periods of the Periodic Table.

ATOMIC RADII

Atoms of different elements vary in size. The term we use to compare sizes of atoms is the *atomic radius*, which is defined as the distance from the center of the nucleus to the outermost electrons.

The radius of an atom is determined, in part, by the number of shells containing electrons and surrounding the nucleus. The greater the number of shells, the greater the atomic radius. In the Periodic Table, as we go down any group, we are in effect adding an electronic shell, and we observe that the atomic radii increase. The atomic radius of fluorine is 0.72 Angstroms, while that of chlorine is 0.994 Angstroms (see Table 1–2).

Besides the number of shells present, the atomic radius is affected by the attraction of the protons in the nucleus for the electrons around the nucleus. If the attraction is *greater*, the nucleus pulls harder on its electrons and holds them closer; the atomic radius is *smaller*.

A nucleus with a greater positive charge has a greater attraction for electrons than a nucleus with a lesser charge. Therefore, the number of protons in the nucleus is a major factor in the amount of attraction the nucleus has for its electrons. The greater the number of protons, the greater is the pull on all the electrons, including the outermost bonding electrons. As we go from left to right in any period of the Periodic Table, we do not add any more energy levels, but we do add one proton to the nucleus (and one more electron to the outer level), and we observe a *decrease* in the atomic radii. Thus, oxygen with eight protons in its nucleus (and eight electrons) has an atomic radius of 0.74 Angstroms, while fluorine, with nine protons (and nine electrons) has an atomic radius of 0.72 Angstroms. In summary, we can say:

Atomic radii *increase* as we go down any one group in the Periodic Table because of added energy levels.

Atomic radii *decrease* as we go across any one row in the Periodic Table because of the increasing number of protons.

TABLE 1–2. Atomic Radii for Some Elements

Group	IA	IIA	IIIA	IVA	VA	VIA	VIIA
Element	Li	Be	B	C	N	O	F
Atomic radius[a]	1.225	0.889	0.80	0.771	0.74	0.74	0.72
Element	Na	Mg	Al	Si	P	S	Cl
Atomic radius	1.572	1.364	1.248	1.173	1.10	1.04	0.994

[a] Atomic radius in Angstroms (Å), where 1 Å = 10^{-8} cm. Values from Therald Moeller, *Inorganic Chemistry* (New York: John Wiley and Sons, 1952). Reprinted by permission.

increasing atomic radii →

The Periodic Table

decreasing atomic radii ———→
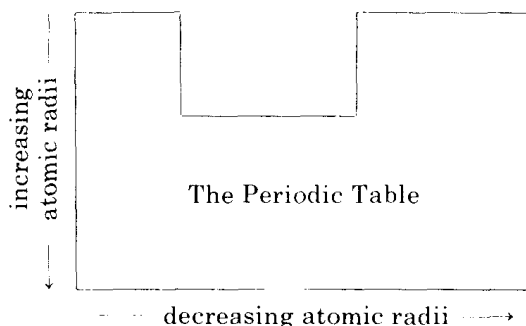
ELECTRONEGATIVITY

Electrons are held by their respective nuclei because of the electrical attraction between the protons and the electrons. However, electrical attraction decreases with increasing distance between the positive and negative charges. Thus, atoms in the same row or group with smaller atomic radii have a greater hold on the outer electrons. Because bonds between atoms are formed by the interactions of these outer electrons, the importance of the "tightness" or "looseness" of the electrons in the outer energy level becomes apparent.

In order to discuss the covalent bonds between atoms with different pulls on the bonding electrons, we need a *measure* of the ability of an atom to attract the bonding electrons. This measure is called the *electronegativity* of the element. An element with atoms that have a greater ability to attract bonding electrons is said to have a greater electronegativity. The smaller fluorine atom has a greater electronegativity than the larger chlorine atom.

fluorine
smaller atomic radius;
greater electronegativity

chlorine
larger atomic radius;
lesser electronegativity
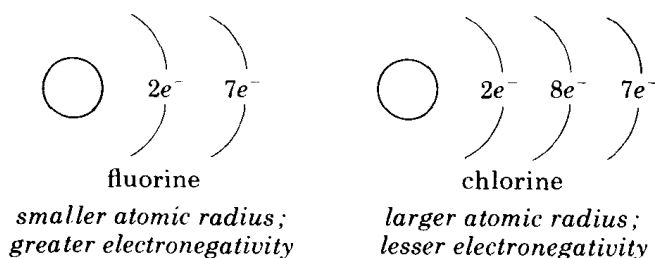
The elements have been rated according to their electronegativities. Figure 1–2 shows the elements in the Periodic Table with numerical values (under the atomic symbols) given for their relative electronegativities. These electronegativity values are based upon a scale with lithium as 1.0 (low electronegativity) and fluorine as 4.0 (high electronegativity). The other elements are rated in comparison with these two.

The elements on the left side of the Periodic Table have low electronegativities compared to those on the right side. An atom of one of these left-side

1 **H** 2·1																	2 **He**
3 **Li** 1·0	4 **Be** 1·5											5 **B** 2·0	6 **C** 2·5	7 **N** 3·0	8 **O** 3·5	9 **F** 4·0	10 **Ne**
11 **Na** 0·9	12 **Mg** 1·2											13 **Al** 1·5	14 **Si** 1·8	15 **P** 2·3	16 **S** 2·5	17 **Cl** 3·0	18 **Ar**
19 **K** 0·8	20 **Ca** 1·0	21 **Sc** 1·3	22 **Ti** 1·5	23 **V** 1·6	24 **Cr** 1·6	25 **Mn** 1·5	26 **Fe** 1·8	27 **Co** 1·8	28 **Ni** 1·8	29 **Cu** 1·9	30 **Zn** 1·6	31 **Ga** 1·6	32 **Ge** 1·8	33 **As** 2·0	34 **Se** 2·4	35 **Br** 2·8	36 **Kr**
37 **Rb** 0·8	38 **Sr** 1·0	39 **Y** 1·3	40 **Zr** 1·4	41 **Nb** 1·6	42 **Mo** 1·8	43 **Tc** 1·9	44 **Ru** 2·2	45 **Rh** 2·2	46 **Pd** 2·2	47 **Ag** 1·9	48 **Cd** 1·7	49 **In** 1·7	50 **Sn** 1·8	51 **Sb** 1·9	52 **Te** 2·1	53 **I** 2·5	54 **Xe**
55 **Cs** 0·7	56 **Ba** 0·9	57 **La** 1·1	58 71 **Ce→Lu**	72 **Hf** 1·3	73 **Ta** 1·5	74 **W** 1·7	75 **Re** 1·9	76 **Os** 2·2	77 **Ir** 2·2	78 **Pt** 2·2	79 **Au** 2·4	80 **Hg** 1·9	81 **Tl** 1·8	82 **Pb** 1·8	83 **Bi** 1·9	84 **Po** 2·0	85 **At** 2·2	86 **Rn**
87 **Fr** 0·7	88 **Ra** 0·9	89 **Ac** 1·1	90 103 **Th→Lr**	104 **Ku**	105 **Ha**

FIGURE 1–2. Electronegativities of the elements. The elements in the more highly shaded areas are more electronegative. Adapted with permission. From Garth L. Lee, Harry O. Van Orden, and Ronald O. Ragsdale, *General and Organic Chemistry* **(Philadelphia: W. B. Saunders Co., 1971), p. 71.**

elements (sodium, for example) tends to lose its outer electrons in compound formation and become a cation, or positively charged ion: $Na \rightarrow Na^+ + e^-$. In this way, the atom (now an ion) has gained a complete outer shell. On the right side of the Periodic Table (disregarding the inert gases) are the elements with high electronegativities. An atom with a high electronegativity tends *not* to lose its outer electrons. For example, a halogen atom, with a high electronegativity and a high affinity for electrons, tends to *gain* an electron to fill its outermost shell and to form an anion, a negatively charged ion: $Cl + e^- \rightarrow Cl^-$.

PROBLEM

1–2: Rank the following in terms of increasing electronegativity (lowest to highest): carbon, nitrogen, oxygen, chlorine, hydrogen.

But what of carbon, the element that gave birth to organic chemistry? With four electrons in its outer energy level and with an intermediate electronegativity, carbon must compromise. Instead of gaining four more electrons or losing four electrons, a carbon atom has a tendency to *share* electrons with other atoms. Not only carbon, but many elements that can form ions are also capable of sharing electrons.

IONIC BONDS

An ionic bond is formed when there is a complete transfer of an electron from one atom to another. A classic case of a compound that has an ionic bond is sodium chloride (NaCl, or $Na^+ Cl^-$), common table salt. There are several ways we may represent the transfer of an electron from a neutral sodium atom to a neutral chlorine atom to give sodium chloride:

$$Na + Cl \longrightarrow Na^+ + Cl^-$$
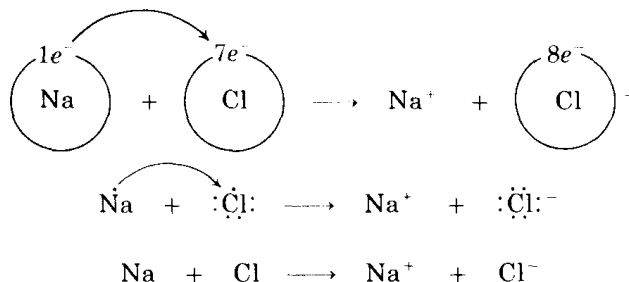
All three equations mean the same thing. An atom of sodium gives up an electron to an atom of chlorine to yield a positively charged sodium cation (Na^+) and a negatively charged chloride anion (Cl^-). The positively charged sodium ion is attracted to the negatively charged chloride ion by the attraction between opposite electrical charges. This attraction between a positive ion and a negative ion is called an *ionic bond*.

PROBLEM

1–3: Give the equation (using dots for electrons) for the formation of the ionic compound $CaCl_2$.

Most ionic compounds are crystalline solids at room temperature. A crystal of sodium chloride large enough to see, of course, must contain more than one pair of ions; there must be trillions of ions present for us to see a crystal. An ionic crystal is formed from positive and negative ions alternating in a three-dimensional crystal lattice (see Figure 1–3). In the crystal lattice of sodium chloride, each sodium ion is surrounded by chloride ions, and each chloride ion is surrounded by sodium ions. Each charged ion exerts an attraction toward all the oppositely charged ions surrounding it. Because of these large-scale mutual attractions, ionic compounds tend to have very high melting points. Also, because the ions are attracted but not actually attached to each other, the ions become separated from each other when the crystal is dissolved in water.

COVALENT BONDS

A covalent bond is the sharing of two electrons by two atoms. Atoms joined by ionic bonds are free to leave each other when they are in solution. Atoms