

# **Advanced Organic Chemistry: Reactions, Mechanisms, and Structure**

**JERRY MARCH**

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# Advanced Organic Chemistry: Reactions, Mechanisms, and Structure

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**ADVANCED ORGANIC CHEMISTRY:  
REACTIONS, MECHANISMS, AND STRUCTURE**

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*For* **BEVERLY, GALE, DAVID, and JUNE**

## Preface

This book has grown out of a graduate course in advanced organic chemistry which I have been teaching at Adelphi University for a number of years. It is thus designed for students who have taken the standard one-year undergraduate organic and physical chemistry courses. I have attempted to give equal weight to the three fundamental aspects of the study of organic chemistry: reactions, mechanisms, and structure. A student who has completed a course based on this book should be able to approach the literature directly, with a sound knowledge of modern basic organic chemistry. I have treated lightly, or not at all, the major special areas of organic chemistry: terpenes, carbohydrates, photochemical and electrochemical reactions, steroids, and the like. It is my opinion that these topics are best approached after the first year of graduate study, when the fundamentals have been mastered, either in advanced courses, or directly, by consulting the many excellent books and review articles available on these subjects.

I have organized the material differently from that of most first-year organic textbooks. With a few exceptions, undergraduate organic chemistry is taught on the basis of functional groups: the student is introduced one at a time to the methods of preparation and the reactions of alcohols, ethers, carboxylic acids, etc. Mechanisms are taken up as the reactions are encountered. This is an appropriate way to teach a first course in organic chemistry, since it does not overwhelm the student with too much material too soon. However, for a *second* course, an arrangement based on reaction types is sounder. Since the student has already learned the *language* of organic chemistry, he is prepared to be shown that, despite the large number of organic reactions, a relatively few principles suffice to explain nearly all of them. Accordingly, the reactions-mechanisms section of this book (Part 2) is divided into 10 chapters, each concerned with a different type of reaction. In the first part of each chapter the appropriate basic mechanisms are discussed along with considerations of reactivity and orientation, while the second part consists of numbered sections devoted to individual reactions, where the scope and the mechanism of each reaction are discussed. I have used numbered sections for the reactions, because I have found that students learn better when they are presented with clear outlines (for a further discussion of the arrangement of Part 2, see pp. 247-249). Since the methods for the preparation of individual classes of compounds (e.g., ketones, nitriles, etc.) are not treated all in one place, an index has been provided (Appendix C) by use of which all methods for the preparation of a given type of compound will be found. At first, I had hoped to provide an actual example, from the literature, for each reaction discussed. However, the space required would have been too great. In partial compensation, I have included, for each reaction, a list of all *Organic Syntheses* references. Thus for most reactions the student can consult actual examples in *Organic Syntheses*.

The structure of organic compounds is discussed in the first six chapters



of Part 1. This section provides a necessary background for the understanding of mechanisms, and is also important in its own right. The discussion begins with chemical bonding, proceeds through stereochemistry, and ends with a chapter on instrumental methods used to determine structure. Part 1 concludes with three chapters which give further background to the study of mechanisms.

In addition to reactions, mechanisms, and structure, the student should have some familiarity with organic nomenclature and with the literature of organic chemistry. Chapters devoted to these topics have been placed in the appendix, though many teachers may wish to cover this material at the beginning of the course.

In treating a subject as broad as the basic structures, reactions, and mechanisms of organic chemistry, it is obviously not possible to cover each topic in great depth. Nor would this be desirable even if possible. Nevertheless, students will often wish to pursue individual topics further. An effort has therefore been made to guide the reader to pertinent review articles and books published since about 1950. In this respect, this book is intended to be a guide to the secondary literature (since about 1950) of the field it covers. Furthermore, in a graduate course, students should be encouraged to consult primary sources. To this end I have included about 3,000 references to original papers.

Although basically designed for a one-year course on the graduate level, this book can also be used in advanced undergraduate courses, as long as they are preceded by one-year courses in organic and physical chemistry. It can also be adapted, by the omission of a large part of its contents, to a one-semester course. Indeed, even for a one-year course, more is included than can be conveniently covered. Many individual sections can be easily omitted without disturbing continuity.

The reader will observe that this text contains much material which is included in first-year organic and physical chemistry courses, though in most cases it goes more deeply into each subject and, of course, provides references which first-year texts do not. It has been my experience that students who have completed the first-year courses often have a hazy recollection of the material, and greatly profit from a re-presentation of the material, if it is organized in a different way. It is hoped that the organization of the material on reactions and mechanisms will greatly aid the memory and the understanding. In any given course the teacher may want to omit some chapters because his students already have an adequate knowledge of the material, or because there are other graduate courses which cover the areas more thoroughly. Chapters 1, 4, and 6 especially may fall into one of these categories.

Although this is a textbook, it has been designed to have reference value also. Students who are preparing for qualifying examinations and practicing organic chemists will find that Part 2 contains a survey of what is known about the mechanism and scope of about 475 reactions, arranged in an orderly manner based on reaction type and on which bonds are broken and formed. Also valuable for reference purposes are the previously mentioned lists of reactions classified by type of compound prepared (Appendix C) and of all of the *Organic Syntheses* references to each reaction.



It is a pleasure to acknowledge the assistance of a number of chemists who have been kind enough to read portions of the manuscript and to send me their comments, which were exceedingly helpful. I wish to thank Professors J. F. Bunnett, A. W. Burgstahler, D. J. Cram, P. de Mayo, E. L. Eliel, R. W. Griffin, Jr., G. S. Hammond, M. Kreevoy, S. Moon, G. A. Olah, G. C. Pimentel, W. H. Saunders, Jr., C. G. Swain, R. W. Taft, Jr., W. S. Trahanovsky, C. Walling, and R. Wistar, each of whom read one or more chapters, and Professor C. A. Bunton, who read the entire manuscript. In addition, I wish to thank many of my colleagues at Adelphi University who have rendered assistance in various ways, among them: F. Bettelheim, W. P. Gallagher, J. Landesberg, S. Moon, A. J. Sisti, and S. Windwer. Of course, the responsibility for all errors is mine alone.

**Jerry March**

## Bibliographical Note

*In this book the practices used in citing references are slightly different from those prevailing elsewhere. The reader should note:*

- 1 For review articles, both the first and last page numbers are given, so that the reader may form an idea of the length of the article. If reference is made to only a portion of the article, these page numbers are also given.
- 2 Author's initials are omitted in references. They may be found, however, in the author index.
- 3 When a journal is available both in a foreign language and in English, the page numbers of each article are, of course, different. The language of the journal title indicates whether the page number cited is to be found in the original or in the English version.
- 4 Certain hardbound serial publications (see p. 946) are here cited as journals rather than as books.

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# Part One

*This book contains 19 chapters. Chapters 10 through 19, which make up Part 2, are directly concerned with organic reactions and their mechanisms. Chapters 1 through 9 may be thought of as an introduction to Part 2. The first six chapters constitute a unit dealing with the structure of organic compounds. In this unit we shall discuss the kinds of bonding important in organic chemistry, the three-dimensional structure of organic molecules, and the structure of species in which the valence of carbon is less than four. To conclude this section, we shall treat in Chapter 6 some of the methods by means of which structure is determined. Chapters 7 to 9 are concerned with other topics which help to form a background to Part 2: acids and bases, the relationship between structure and reactivity, and a general discussion of mechanisms and of the means by which they are determined.*

## Part One

This book contains 19 chapters. Chapters 1 through 19, which make up Part I, are directly concerned with organic reactions and their mechanisms. Chapters 1 through 8 may be thought of as an introduction to Part I. The first six chapters constitute a unit dealing with the structure of organic compounds. In this unit we shall discuss the kinds of bonding important in organic chemistry, the three-dimensional structure of organic molecules, and the structure of species in which the valence of carbon is less than four. To conclude this section, we shall treat in Chapter 9 some of the methods by means of which structure is determined. Chapters 7 to 9 are concerned with other topics which help to form a background to Part I: acids and bases, the relationship between structure and reactivity, and a general discussion of mechanisms and of the means by which they are determined.

# CHAPTER ONE

## Localized Chemical Bonding

*Localized chemical bonding*, which is treated in this chapter, may be defined as bonding in which the electrons are shared by two and only two nuclei. In Chapter 2 we shall consider *delocalized bonding*, in which electrons are shared by more than two nuclei. But before we can intelligently discuss bonding at all, we must consider the electronic structure of atoms, in which the electrons surround only one nucleus.

**Atomic Orbitals.**<sup>1</sup> The fundamental principle upon which wave mechanics is based is that electrons behave as waves (for example, they may be diffracted) and that consequently a wave equation may be written for them, in the same sense that light waves, sound waves, etc., can be described by wave equations. The equation which serves as a mathematical model for electrons is known as the *Schrödinger equation*, and for a one-electron system is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad (1)$$

where  $m$  is the mass of the electron,  $E$  is its total energy,  $V$  is its potential energy, and  $h$  is Planck's constant. In physical terms, the function  $\psi$  expresses the square root of the probability of finding the electron at any position defined by the coordinates  $x$ ,  $y$ , and  $z$ , where the origin is at the nucleus. For systems containing more than one electron the equation is similar, but more complicated.

The solutions to the Schrödinger equation are themselves equations. Solutions exist only for certain values of  $E$ . These are called *eigenvalues*, and the solutions are called *eigenfunctions*. This is another way of saying that the energy possessed by electrons is quantized. For the hydrogen atom, which is spherically symmetrical, the natural coordinate system is the system of spherical polar coordinates ( $r$ ,  $\theta$ , and  $\phi$ ), and solutions to (1) for the hydrogen atom are generally expressed in these coordinates. The spherical coordinates are related to the rectangular coordinates as follows (see Figure 1):

$$x = r \sin \theta \cos \phi \quad (2)$$

$$y = r \sin \theta \sin \phi \quad (3)$$

$$z = r \cos \theta \quad (4)$$

$$r = (x^2 + y^2 + z^2)^{1/2} \quad (5)$$

<sup>1</sup>The treatment of atomic and molecular orbitals given here is necessarily simplified. For much fuller treatments of orbital theory as applied to organic chemistry, see Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, 1961; Coulson, "Valence," 2d ed., Oxford University Press, New York, 1961; Coulson and Stewart, in Patai, "The Chemistry of Alkenes," pp. 1-147, Interscience Publishers, Inc., New York, 1964; and Higasi, Baba, and Rembaum, "Quantum Organic Chemistry," Interscience Publishers, Inc., New York, 1965.



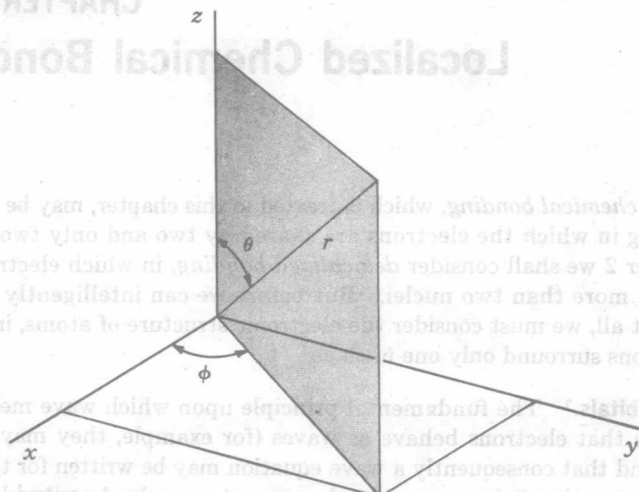


Figure 1. The spherical coordinates.

For a given point  $P$ , the coordinate  $r$  is the distance between the origin ( $O$ ) and the point, while  $\theta$  represents the angle between the line  $OP$  and the  $z$  axis, and  $\phi$  is the angle between the  $xz$  plane and the plane containing  $OP$  and the  $z$  axis.

For the hydrogen atom, the potential energy is

$$V = -\frac{Ze^2}{r} \quad (6)$$

where  $r$  is the distance between the nucleus and the electron,  $e$  the charge on the electron, and  $Z$  the nuclear charge (in this case, 1). The solution of the Schrödinger equation which corresponds to the lowest possible energy for the electron is

$$\psi = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0} \quad (7)$$

where

$$a_0 = \frac{h^2}{4\pi^2 m e^2} \quad (8)$$

The energy corresponding to this solution is

$$E = -\frac{2\pi m Z^2 e^4}{h^2} \quad (9)$$

which turns out to be  $-13.60$  electron volts. The distance  $a_0$ , which is equal to  $0.529 \text{ \AA}$ , is called the *Bohr radius*.

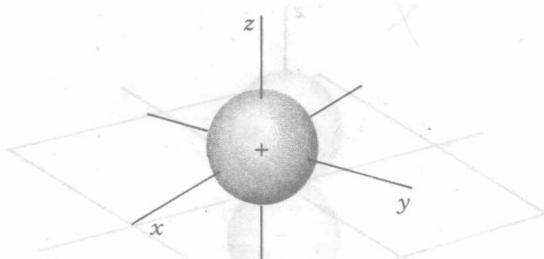


Figure 2. The wave function for the lowest energy level (ground state) of the hydrogen atom.

Three of the higher solutions are

$$\psi = \frac{1}{\sqrt{32\pi}} \left( \frac{Z}{a_0} \right)^{5/2} r e^{-Zr/2a_0} \cos \theta \quad (10)$$

$$\psi = \frac{1}{\sqrt{64\pi}} \left( \frac{Z}{a_0} \right)^{5/2} r e^{-Zr/2a_0} \sin \theta \cos \phi \quad (11)$$

$$\psi = \frac{1}{\sqrt{64\pi}} \left( \frac{Z}{a_0} \right)^{5/2} r e^{-Zr/2a_0} \sin \theta \sin \phi \quad (12)$$

Since the energies corresponding to these three eigenfunctions are equal, the energy levels are said to be degenerate. There are an infinite number of other solutions, each with its corresponding energy, but there are no solutions with an energy between those of any two successive solutions.

Since these eigenfunctions are equations, we may graph them. The graphs are three-dimensional pictures of the density of the electron. The graph corresponding to Eq. (7) shows that the electron density is distributed symmetrically about the nucleus. The density increases along a line beginning at the nucleus and proceeding in any direction until a maximum is reached, after which it rapidly drops off. This maximum is at  $r = 0.529 \text{ \AA}$ ; that is, it is at the Bohr radius. Although in theory there is still some density at an infinite distance from the nucleus, it is possible to draw a sphere with a radius of about four or five times that of the Bohr radius and enclose nearly all the electron density in it. Such a sphere is shown in Figure 2.

A wave function like that depicted in Figure 2 is called an *orbital*, or an electron cloud. Some are spherical, like that in Figure 2. These are called *s* orbitals. The orbital corresponding to Eq. (10), shown in Figure 3, is called a *p* orbital. Unlike *s* orbitals, *p* orbitals are not spherically symmetrical but are directed along one of the axes. Note that there is no probability of finding the electron at any point on the *xy* plane. Any such region in space is called a *node*. In Figure 3 one lobe of the orbital is labeled + and the other -. These signs do not refer to positive or negative *charges*, since both lobes of an electron cloud must be negatively charged. They are the signs of the function  $\psi$ . When two parts of any orbital are separated by a node, then  $\psi$  always has opposite signs on the two sides of the node.