PRINCIPLES

OF

ORGANIC

CHEMISTRY

Principles of
Organic Chemistry

An Introductory Text in Organic Chemistry

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Preface

This text has been designed for use in a full-year course in organic chemistry—a course designed to stress the fundamental principles of the science for students planning to go on to advanced scientific work in medicine, chemistry, chemical engineering, and allied fields.

It is the authors' conviction that the object of a first course in organic chemistry should be to present to the student a selected body of factual and theoretical material and show how this carefully chosen material, the result of experiment, is used in the development and practice of the science. To this end we have chosen those reactions and concepts which seem to us to be of fundamental significance and applicable to a variety of different situations. We have left out of our discussion a great many reactions and compounds often found in organic chemistry texts, recognizing that only a reasonably restricted amount of material can be *fully* mastered by the student in the time available.

In consonance with this conviction, we have omitted the customary "special topics" chapters that adorn the later pages of many textbooks. Such chapters on dyes, alkaloids, drugs, etc., although they furnish useful reference material, have not been found by us to be of importance or value in the elementary course. With the increasing development of organic theory, the existence of specialists in organic chemistry—the alkaloid chemist, the terpene chemist, etc.—is threatened with extinction. With a thorough grounding in the principal reactions and theories of the subject, the student today can safely venture into the literature of these special fields without fear of encountering mysterious new kinds of behavior of carbon compounds. Those who are for one reason or another interested in examining the structures and reactions of specific examples in these fields find it necessary in any event to consult more specialized articles than can properly be included in an elementary text.

This policy of including only selected reactions implies a more detailed study of the underlying principles involved than is usually found in elementary texts. This we have attempted to accomplish by introducing modern ideas on the mechanism of reactions in all cases where they have served to unify the treatment. An attempt has been made to describe in some detail, in terms of electronic theory, the course of events on a molec-

ular scale in the principal reactions discussed.   The added interest in the classroom which results from these discussions seems to justify this procedure.

A rather large number of exercises and problems are included, and these are assigned liberally.   It has been our experience that only from the working of problems such as those found at the end of each chapter can a student acquire facility in handling the reactions discussed.   The application of memorized facts and theories to the solution of actual problems has been found to be of great importance to student understanding and appreciation of organic chemistry.   The exercises have been so devised that the answers are seldom given by direct quotations from the text; compounds used in the exercises are varied so as to emphasize the essential principles rather than specific isolated facts.   Answers to selected exercises (marked with an asterisk) are included as an aid to study.

A course based on this text may be varied from a one-term course for nonscience students to a full-year course for chemistry majors, depending on the extent to which the exercises are used.   The instructor may introduce additional material at his discretion, and, indeed, is urged to do so.

Aromatic and aliphatic compounds are treated together after Chap. 5. Since the differences in reactions of these two classes are often of a quantitative rather than a qualitative nature, where they exist at all, it is felt that the advantages of this treatment are very real.   This order of presentation has been used before by other authors, and the writers have used it for a number of years in their own courses with gratifying results.

We have not reintroduced the references that were given at the ends of the chapters in the first edition.   We have retained at the ends of the chapters, particularly the earlier ones, historical notes to help the student learn something of the earlier history of organic chemistry.

A new feature is the inclusion, particularly in the earlier chapters, of Industrial Notes.   The rationale of this feature is stated in Chap. 1.   We have also increased the number of exercises.

The prevalence of heterocyclic ring systems in biochemically important compounds and the increasing interest in their synthesis and degradation in the processes of metabolism make some introduction to their chemistry very desirable for chemists and biochemists, and particularly for premedical students, for whom this may be their only formal course in organic chemistry.   For these reasons, we have included a short chapter on the chemistry of heterocycles.   In this chapter we have stressed the relationship of the chemistry of these compounds to simpler aliphatic and aromatic chemistry.   We have shown that the principles which operate are the same fundamental ones that have been studied all along in the course.

This book owes a great deal to influences exerted by teachers, students, and the "literature"—influences which it would be most difficult to acknowledge in detail, but which we do recognize and acknowledge as best we

can. Many of the exercises are, we think, our own. Many others were devised by Drs. R. D. Coghill and J. M. Sturtevant. We must acknowledge the contributions of R. A. Hardy, Jr., who executed some of the line drawings, and we are indebted to Prof. Carl R. Noller and the editor of the *Journal of Chemical Education* for permission to use Figs. 1-4, 3-1, 3-2, 5-1, 6-1, and 12-1.

This revision has profited very greatly from critical reviews obtained for us by the publishers. We wish to thank these reviewers—many of them unknown to us—for the care they gave to the task of analyzing the previous text.

James English, Jr.
Harold G. Cassidy

Remarks for the Student

It is usually taken for granted that the student who takes up the study of organic chemistry has a thorough knowledge of first-year college chemistry. This means that he is familiar with the symbols for atoms and with simple formulas; that he knows enough about the electronic structures of atoms and the ways that bonds are formed between atoms to be able to write down the structures of simple molecules; that he has a general notion of the properties of solids, liquids, and gases; that he knows how valence numbers and molecular weights are determined; that he knows what ions are, and how their presence is recognized; that he is able to use the concepts embodied in the principle of Le Châtelier; and that he can look at the periodic table with an educated eye. It is quite likely, of course, that many of the finer details of first-year chemistry have been forgotten, and the student of organic chemistry will do well to refer to his first-year text immediately if he feels vague about some point. Every attempt will be made to relate the new materials in this course to the earlier work which the student has had and to suggest its relation to work which he will take in other courses, for example, to work in physical, biological, or technical chemistry.

But there will be a great deal of material which will be quite new to the student. This will be made up partly of familiar materials which will be brought together in new ways, for example, in the use of familiar symbols which are constructed into two- or three-dimensional molecular formulas, and partly of new concepts and ideas which will have to be embodied in additional symbols and special language. The student must therefore be prepared for memory work. Since this is the only convenient way to master some of the materials of the course, he might just as well resign himself to it and get on with it. However, he should find that the amount of memory work is no greater than that involved in learning a foreign language, or in learning comparative anatomy. Premedical students regularly pass, and even enjoy, organic chemistry.

Experience has shown that the first half of the first term of the organic chemistry course (about the first eight weeks) is the most crucial part. If the student masters this first work, the rest of the course becomes relatively easy. This is because the subject matter of organic chemistry is very

closely bound together internally. The material learned at the beginning of the course will be used at least implicitly, and usually explicitly, throughout it. The course develops by a process of continual enrichment; it is not a journey in which the road is traveled only once. Much of this early material in the course looks easy, and so the student may have a tendency to slight it. In our experience this is one of the chief causes of the difficulty which some students have with organic chemistry.

One of the objectives of science is to gain understanding of the perceptual world through the manipulation of symbols and concepts. In the branch of science called organic chemistry, not only are the methods of manipulating symbols and concepts very clearly illustrated, but the gains in understanding natural phenomena which have resulted are set forth on every hand to be seen. Almost from the very beginning of the course, the student will be able to appreciate the unfolding methods of this science. It is an important quality of this course that throughout it are illustrated in action the elements of scientific philosophy—the elements of part of the culture of the modern educated individual.

ON SOLVING PROBLEMS

A few words need to be said about the exercises at the ends of the chapters and their solution. These problems vary: A few ask purely routine questions. Others ask for the use of something more than memory. In most cases we have tried to provide problems which probe below the surface of the text material. The student should try to approach these problems in a friendly spirit. They are the best means he has for gauging how well he is mastering the textual material.

Although there is no substitute for actual thinking, there is a technique for dealing with and solving most problems—not only the types of problems found in this book, but all problems. This technique (which is an old one) can only be sketched here, but the student who is interested can find a more complete treatment in a book by Polya.[1] This technique consists in an orderly approach to the problem, using a scheme like the following:

First step: State the problem. This means to write down briefly but clearly and in your own words what you want to do and any related information which clarifies your objectives.

Second step: Look for similarities. See if there is any feature of the problem which is like that of a problem you solved once before. If so, perhaps this is like that other problem, only with a different twist. This step is a kind of partial diagnosis. If you find a similarity, go ahead and solve the problem. Analogy is one of your most powerful tools, and is, in fact, used by most investigators to suggest directions for research. If

[1] G. Polya, "How to Solve It. A New Aspect of Mathematical Method," Princeton University Press, Princeton, N.J., 1945.

you suspect a similarity but can't think of it, go back through the text and check for the elusive resemblance. Always use the index freely. It is there to be used. Remember that these problems all have solutions. If there is no similarity to a problem you have seen or worked out before, take the third step.

Third step: Devise an attack on the problem. With organic chemistry problems this almost always means starting to work the problem backwards, in a stepwise manner. This is a reasonable thing to do. For example, suppose you are asked to convert compound Q to compound Z. There are a great many reactions which you can apply to Q, only a few of which can ultimately lead to Z. Why not start with Z and work backwards, keeping Q in mind? If at a given point you are "stuck"—say you can't think of any way of making Z—use the index. Look up ways of making Z-like substances. Also, as you go through the course, keep tables of useful reactions, such as those for shortening and for lengthening carbon chains, etc.

Fourth step: Carry out the plan of attack which you devised. This is usually done along with the third step.

Fifth step: Check your solution. Find out if it meets the conditions set down in the original problem.

Next time you get stuck on a problem try out this systematic technique.

The following references relate to studying and to solving problems:

H. M. Dadourian, "How to Study, How to Solve Arithmetic through Calculus," Addison-Wesley Publishing Company, Reading, Mass., 1951.

W. Jepson, "How to Think Clearly," Longmans, Green & Co., Inc., New York, 1937.

G. Polya, "How to Solve It. A New Aspect of Mathematical Method," Princeton University Press, Princeton, N.J., 1945.

M. Wertheimer, "Productive Thinking," Harper & Brothers, New York, 1945.

C. T. Morgan and J. Deese, "How to Study," McGraw-Hill Book Company, Inc., New York, 1957.

Contents

CHAPTER 1

Introduction

1-1. Definitions. Chemistry is the science that deals with the structures and properties of substances and with the reactions by means of which these structures and properties may be changed. Organic chemistry is the chemistry of those substances containing carbon. Some compounds which, according to this definition, would be called organic have been studied in the inorganic part of first-year chemistry. The carbonates, acetates, cyanides, and complex cyanides may be listed here, together with carbon dioxide, as examples. Some of these compounds, for example, calcium carbonate and potassium cyanide, are easily thought of as being inorganic, because their chemistry is so much like that of inorganic substances of various kinds and because substances like marble are, after all, minerals. But coal and petroleum are minerals, and no one would argue that they are not organic substances. Besides, many inorganic substances display properties which are like those of organic substances, so that the difference between organic and inorganic chemistry (which has to be made for very practical reasons, apart from any historical justification) cannot rest on degree of likeness of reactions but is much better made, arbitrarily, sharply dependent on the presence of carbon. It must then be pointed out that since such compounds of carbon as the carbonates, ferro- and ferricyanides, thiocyanates, etc., have already been dealt with in first-year chemistry, little attention will be paid to them here.

1-2. The Carbon Atom. Since all organic molecules contain carbon, it is important to know certain facts about the atom itself and the substances formed from it. Carbon has an atomic weight of 12 and an atomic number of 6, and is classified in group IV of the second period of the periodic classification of the elements.

The first shell of electrons outside the nucleus of the carbon atom comprises two electrons and is therefore a complete shell; the second, and valence, shell comprises four electrons. These electrons appear to be arranged in subshells, such that the electrons of any given shell are not all the same "average distance" from the nucleus and are not of the same energy. The structure of the valence-electron shell will be referred to later. Since the valence shell is completed only when eight electrons are available

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to it, it is apparent that the carbon atom requires an additional number of electrons equal to that in the valence shell for completion of this shell. These electrons may be obtained, as shown below, through a process of compound-formation.

Table 1-1.   Periodic Classification of Some of the Elements
of Low Atomic Number

Period	Group							
	I	II	III	IV	V	VI	VII	0
1				H^a				He
2	Li	Be	B	C	N	O	F	Ne
3	Na	Mg	Al	Si	P	S	Cl	A

^{a} Hydrogen (not properly in group IV) is placed above carbon because it also has its valence shell half filled and its bond formation with other elements resembles that of carbon.

Attention is called to the central position of carbon in the periodic classification. It would appear equally easy for such an atom to lose or to gain four electrons to achieve a stable configuration; actually neither complete gain nor loss takes place but instead a different kind of behavior, which will be described in due course.

In chemical combination, carbon may exhibit a valence of two, three, or four. Recall that the valence is a pure number, representing a combining ratio. A valence of two is shown in carbon monoxide. A few compounds in which a valence of three is exhibited will be discussed later and are not of much importance to this course. By far the majority of organic compounds (over a million) contain carbon in the tetravalent form. The terms *tetravalent*, *divalent*, etc., as applied to carbon compounds refer to the number of bonds formed by the carbon atoms in the various compounds under·consideration; for example, carbon is tetravalent in CH_4, with no implications about the sign which may be given to the atom.

1-3. Chemical Bonds. Four types of chemical bonds are usually distinguished: electrovalent, covalent, coordinate, and metallic. Metallic bonds will not be of interest here. *Electrovalent*, or *ionic*, bonds are bonds in which the bonded atoms carry explicit charges. The familiar case is $Na^+ Cl^-$. Here the two atoms are held together by the electrostatic (Coulomb) attraction between the + and the − charges. The charge originates in the structure of the ion: Na^+ has lost its outer valence electron and so shows the effect of an extra, uncompensated nuclear proton; the ion

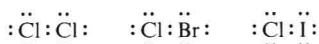$$:\overset{..}{\underset{..}{Cl}}:^-$$

has one more electron than needed to compensate its nuclear charge, and thus is a negative ion of charge −1. An electron has been *transferred*, in

effect, from the valence shell of one atom to that of the other. Note that the bond is not directed in space. In solid sodium chloride, each Na⁺ is surrounded by six Cl⁻ ions and these in turn by six Na⁺ ions, so that the whole mass of the substance is bound together into a giant polymeric[1] molecule. These substances usually have high melting and boiling points. Electrovalent linkages are more often found in inorganic than in organic compounds. This is often used as a convenient distinction between inorganic and organic compounds but is not sufficiently reliable or fundamental.

A *covalent bond* is formed by the sharing of two electrons by the bonded atoms, one electron being in effect (no matter how the bond is actually produced) contributed by each of the bonded atoms. There is no permanent transfer of electrons; the bond electrons contribute to the valence shells of both bonded atoms; they are *shared*. The sharing is equal when the two atoms are alike; thus in

$$\text{H:H} \quad \text{and} \quad :\overset{..}{\underset{..}{Cl}}:\overset{..}{\underset{..}{Cl}}:$$
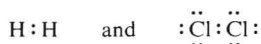
the shared pair may be expected to contribute as much to the valence shell of one atom as to that of the other. If the two atoms are not alike, then the sharing is not equal; for example, it becomes progressively more unequal in the bonds

$$:\overset{..}{\underset{..}{Cl}}:\overset{..}{\underset{..}{Cl}}: \quad :\overset{..}{\underset{..}{Cl}}:\overset{..}{\underset{..}{Br}}: \quad :\overset{..}{\underset{..}{Cl}}:\overset{..}{\underset{..}{I}}:$$

The electrons tend to spend a larger part of the time with Cl than with Br, or I, that is, to contribute more to the valence shell of the Cl.[2] The Cl is said to be *electronegative* with respect to the Br or I *in the final structure*; it is an *electron acceptor* in the bond in which the Br or I acts the part of *electron donor*. However, it must be remembered always that these terms are relative. That an atom is an electron acceptor in a given bond does not mean that an actual transfer of an electron necessarily occurs; it merely means that the atom enjoys the use of the electron, so to speak, more than does the other atom of the bond. Also the terms can be used correctly only of the atom when bonded to another and relative to the other. Thus in the bond Cl—Br, Br is the donor; in the bond Br—I, Br is the acceptor. This is a very important point. Which of two atoms in a bond is the acceptor and which the donor (that is, which is more electronegative and

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[1] *Polymeric* is derived from the Greek words meaning "abounding in parts." The prefix *poly-* is often used in scientific literature meaning "abounding in," thus "polyhalide," having many halogen atoms.

[2] Whenever a dot is used to represent an electron in a definite position with respect to two atoms, it is implied that there is a region of maximum electron density at this point, in other words, that the probability of finding the electron at this point is greater than that of finding it anywhere else about the atom at any given time. One might say that the electron spends more time in the region indicated by the dot than in any other region. This is why the bonds act as though they are in fixed positions relative to each other.

which less) can be judged from the numbers of electrons in the outer shells and from the positions in the periodic table. As would be expected, the order of increasing electronegativity is

$$C < N < O < F$$
$$I < Br < Cl < F$$
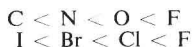
It is directly related to the ease with which the outer shell of the atom is completed and to the closeness of this outer shell to the nucleus of the atom.[1] The covalent bond differs from the electrovalent in this respect: that the bonding electrons are shared by the bonded atoms. But there is another exceedingly important difference: *the covalent bond is directed in space*. Thus the bond can be localized and drawn with a directed line; it can be treated as a vector quantity, if desired.[2]

Simple compounds with none but covalent bonds usually have relatively low melting and boiling points. This suggests that these electrically more symmetrical molecules are held to one another less firmly than oppositely charged ions. An exception to this statement is found when the covalently bound molecule is very large, or is polymeric. Graphite and diamond are covalently bonded polymer-like combinations of carbon, and they have very high melting points.

The *coordinate* (coordinate covalent) bond is also a two-electron bond, and the electrons are shared by the two bonded atoms, but in effect (no matter how the bond may actually be formed) both electrons are provided by one of the atoms, as can be confirmed by counting the valence electrons and the nuclear charges. These bonds are found widely in inorganic and organic molecules, and several examples are given below. The molecules are written with bonding electrons showing, and with simple bonds, where $\rightarrow$ designates a coordinate bond and the arrow points from the atom where the electron pair originated. With coordinate bonds the concept of electronegativity is no longer useful. Other factors, such as the drive to fill the valence shell with a *pair* of electrons, become more important.
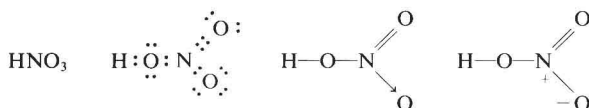

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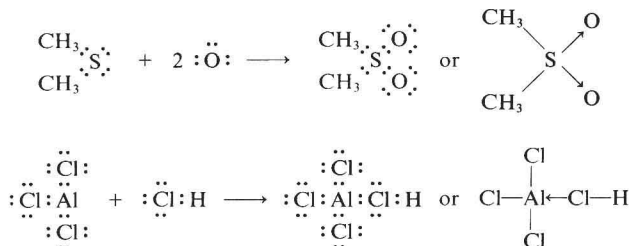
[1] Other factors such as type of groups attached to an atom may affect its relative electronegativity and have to be taken into account in predicting this.

[2] A vector quantity has magnitude and direction. It is indicated by an arrow, the length of which is related to quantity, and the direction of which indicates the direction of the vector.

The coordinate bond differs from the ionic one in that it is directed in space; it differs from the covalent in that the sharing is not well balanced, and indeed, coordinate bonds are often written to show this; the arrow implies it. Sometimes the bond is written with a line to show sharing and a $+$ and $-$ to show the electrical dissymmetry of the bond:

$$HNO_3 \qquad H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:N\overset{:O:}{\underset{:\overset{\cdot\cdot}{O}:}{\cdot}} \qquad H-O-N\overset{O}{\underset{O}{\diagdown}} \qquad H-O-\overset{+}{N}\overset{O}{\underset{-O}{\diagdown}}$$

The $+$ and $-$ charges shown are known as *formal charges*. The formal charge on an atom in a molecule or ion is calculated by balancing the excess protons in the kernel of the atom concerned (the atomic number less the number of electrons in the completed shells) against the number of electrons in its valence shell. One assumes that each atom is entitled to one of each shared pair and all of any unshared pairs of electrons. Thus N in HNO_3 has a kernel excess charge of 5^+. Four shared pairs of electrons around it correspond to a charge of -4 for a net formal charge of $+1$. This formal charge is symbolized by the small $+$ in the structural formula above. This calculation may be expressed in equation form: formal charge = kernel charge less (number of unshared electrons plus $\frac{1}{2}$ number of shared electrons).

The presence of the electrical dissymmetry suggests that there are some residual Coulomb forces in the neighborhood of these bonds. This is in fact the case and may account in part for hydration effects and associations between molecules, as described below, Sec. 1-8.
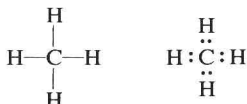
The covalent bond is not itself completely free from these residual forces. Even a bond between identical atoms shows some ionic character. This is because of the "motion" of the bond electrons.

For example, in $H:H$ one could imagine that the electrons are situated some of the time in the position shown, that for some of the time one electron is with each atom $H\cdot \quad \cdot H$, $H\cdot \quad \cdot H$, and $\cdot H \ H\cdot$, and even that both electrons are with one or the other $H^+:H^-$, $H:^- H^+$, of the atoms. These latter are ionically bonded. In fact none of these "forms" has any real existence, but the molecule may be regarded as a "hybrid" of them (Sec. 1-6). It has been computed that the bond $H—H$ has about 5 per cent ionic character; this means that the "unevenness" of the electron distribution corresponds to this figure, not that five out of every hundred molecules are completely ionized. Where the sharing is less perfect, the ionic character will constitute a greater percentage of the total bond character; thus the bonds in HI, HBr, HCl, and HF show respectively 4, 11, 19, and 60 per cent ionic character.

The electrons which form the covalent bond are thought to be paired

because they differ in, as it is sometimes said, direction of spin. They are thought to complement each other in forming the bond.

1-4. Structure of Carbon in Compounds. The carbon atom is three-dimensional, but since it is difficult, and indeed quite impractical, always to picture the three-dimensionality of carbon, the atom is usually pictured by means of a somewhat distorted projection as a two-dimensional figure. The symbolization goes still further. The carbon kernel (nucleus and first shell of electrons) is written C, and the bonds are written as lines or as pairs of electrons,

$$
\begin{array}{c}
\text{H} \\
| \\
\text{H—C—H} \\
| \\
\text{H}
\end{array}
\qquad
\begin{array}{c}
\text{H} \\
\cdot\cdot \\
\text{H:C:H} \\
\cdot\cdot \\
\text{H}
\end{array}
$$

or if the resulthis unequivocal, omitted entirely, CH_4. This kind of symbonsm is employed throughout organic chemistry, and the student will find himself slipping easily into it.
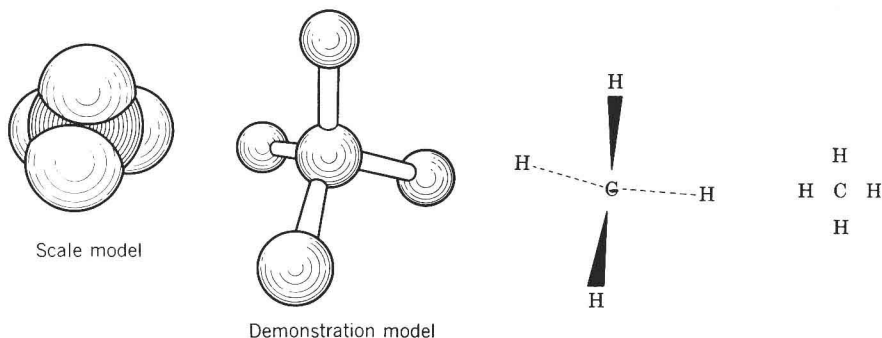

Scale model

Demonstration model

FIG. 1-1. Models of the methane molecule, CH_4.

It should not be forgotten, however, that the molecules formed with carbon are three-dimensional objects, even though we may write them as though they were flat and virtually two-dimensional (see Fig. 1-1).

A great deal of evidence exists that the four bonds of carbon are identical, and that under normal conditions they reside equidistant from each other around the atom. Some of the most convincing evidence will remain until later in the course, but sufficient evidence can be described here to support the point.

If one or more of the bonds of tetravalent carbon were different from the rest, then it would be expected that there might be more than one compound with the formula CH_3Cl (see, for example, Fig. 1-2a). However, all pure samples of CH_3Cl, no matter by what different reactions they have been made, have been found identical. There is no evidence that one