ADVANCED ORGANIC CHEMISTRY

★ BY E. EARL ROYALS ★

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ORGANIC CHEMISTRY

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New York
PRENTICE-HALL, INC.
1954

PREFACE

This book is intended to present a practically useful integration of descriptive fact and unifying theory for the advanced student of organic chemistry in such manner that he may attain a mature grasp of the subject. Every effort has been made that *Advanced Organic Chemistry* be a usable textbook; it is not intended to be a one-volume reference work. The subject matter and arrangement of this book have developed from my experiences during the past six years in offering to beginning graduate students at Emory University a one-year course in organic chemistry. *Advanced Organic Chemistry* is suggested as a suitable textbook for similar first-year graduate courses, or for any second course in organic chemistry following a thorough elementary course. It is intended that this book be useful to graduate students throughout their graduate training, for example, in preparing for comprehensive examinations. It is also hoped that practicing organic chemists desirous of maintaining contact with the broad field of organic chemistry and the more modern developments therein will find it useful.

The emphasis in this book is on transformations of organic matter, presented in such manner as to reveal fundamental behavior patterns in terms of the unifying principles of electronic theory. The criticism sometimes heard that organic electronic theory has contributed little or nothing toward the prediction and discovery of new organic reactions, and is therefore unworthy of attention, leaves me unimpressed. Electronic theory is here presented as a practically useful aid to the understanding and memory, not as a predictive tool. Discussions of theory and the applications of organic reactions to synthesis and degradation are not separated; every effort is made to relate theoretical and mechanistic considerations to the practical problems of synthesis and analysis.

The selection of material for inclusion in this book and the order or presentation have been dictated by the desire to present the advanced student with essential basic principles. This book does not contain everything that the graduate student is expected to know about organic chemistry; it is my hope that mastery of its contents will provide the graduate student with that fundamental knowledge necessary to attainment of maturity in the fascinating art of organic chemistry. The order of presentation of material corresponds neither to the classical aliphatic-aromatic division nor to a complete scrambling of the two. I believe that the order chosen serves best my aims as stated above. The general topics treated, in the order of their presentation are: (1) certain basic theory, (2) the fundamental types of carbon skeleton, namely, the acyclic and cyclic, (3) the chemistry of the alkene and alkyne linkages, including aromatics, as the prototypes of the unsaturated linkage between similar atoms, and (4) the chemistry of the carbonyl linkage, as the prototype of the unsaturated linkage between dissimilar atoms. This arrangement covers in orderly fashion essentially the entire field of basic organic chemistry. Explicit consideration of organic nitrogen and sulfur compounds as classes is not included, partly because these subjects are adequately treated elsewhere, and mostly because I feel that mastery of such specialized topics follows easily from the basic topics here considered.

Because of the great emphasis on mechanistic interpretations in current organic chemical research, it is inevitable that certain portions of this book dealing with mechanisms will soon be woefully incomplete. I recognize that even at this writing several subjects here treated have received much additional study. Consequently, I have endeavored to so present mechanistic considerations that future research will require that what is here given be extended and elaborated rather than discarded. The reader will recognize that this is high endeavor indeed, foredoomed to incomplete fulfillment. I will appreciate corrections and constructive criticisms from readers.

A number of persons have contributed directly and indirectly to the successful completion of this work, and to them I am grateful. Drs. J. Sam Guy and Osborne R. Quayle, past and present chairmen of the Department of Chemistry of Emory University, have encouraged and aided this understanding from the beginning. My colleague, Dr. Charles T. Lester, has read the entire book in manuscript, and portions have been read and most helpfully criticized by Dr. Richard T. Arnold, Dr. James Cason, Dr. Carl Niemann and Dr. Donald Noyce. The staff of Prentice-Hall, Inc., and Dr. Wendell Latimer, Editor of the Chemistry Series, have been most helpful and cooperative. The burden of typing the manuscript fell to Mrs. Frieda Aman, Mrs. Virginia Hartsfield, Mrs. Betsy Stritch, and Mrs. Dorothy Covington. The author index was prepared by Mrs. Martha Bartholomew. Mr. K. C. Brannock, Mr. Arthur H. Neal, Mr. A. G. Robinson, III, and Mr. Charles E. Savage assisted in the awesome task of sorting the approximately eleven thousand index cards and locating initials for the author index. I wish that I might express my appreciation individually to the many graduate students at Emory University who have encouraged this work, critically read sections and chapters, and variously aided me in achieving whatever qualities of a good textbook are found herein. I express gratitude to my wife, Edith, who has borne this which even the marriage vows did not anticipate with love and understanding. Finally, I must thank my very good friend, "Mike" Salmoides, who has afforded me periods of genuine release when the game seemed hardly worth the candle.

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PART TWO

THE CHEMISTRY OF CARBONYL COMPOUNDS

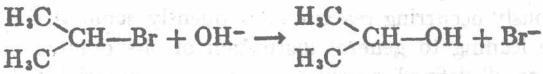
PART ONE:

THE CHEMISTRY OF THE HYDROCARBONS AND CERTAIN OF THEIR UNIVALENT DERIVATIVES

CHAPTER 1

THE STRUCTURE AND REACTIVITY OF ORGANIC COMPOUNDS

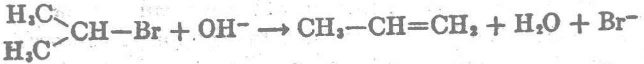
CHEMISTRY is the study of the transformations of matter. If we accept this dangerously precise definition, organic chemistry is the study of the transformations undergone by that class of matter which we call organic. The graduate student is thoroughly familiar with the fact that no longer can organic chemistry be defined and differentiated from inorganic chemistry on the basis of a relation to living versus nonliving matter. Organic chemistry might best be defined simply as the chemistry of the hydrocarbons and their derivatives. Organic chemistry, then, is concerned with such transformations of matter as that exemplified by the following equation.



We begin with a particular species of organic matter, isopropyl bromide, and treat it with a source of hydroxide ions, say sodium hydroxide. The result is a transformation of the organic matter, isopropyl bromide, into the entirely different organic matter, isopropyl alcohol. The chemical union of bromine to carbon, whatever its nature, has been disrupted, and a new chemical union of carbon to hydroxyl has been established. To express the result differently, a certain functional group has disappeared and a new functional group has been formed. A functional group in organic chemistry is simply a group of atoms which is capable of functioning chemically. Several important characteristics distinguish such organic reactions as this from such typical inorganic transformations as, say, the interaction of silver nitrate with sodium chloride.

We may note first that the transformation of organic matter is characteristically slow; thus, while the reaction between silver nitrate and sodium chloride is immeasurably fast, the reaction of isopropyl bromide with hydroxide ion requires hours at room temperature. Consequently, the apparatus and techniques used in organic chemistry differ from those used in the inorganic field; elevated temperatures and long reaction periods are the rule in organic chemistry, necessitating the use of reflux condensers, autoclaves, stirring devices, and similar equipment not ordinarily required in inorganic practice.

Second, many inorganic reactions proceed in quantitative fashion, so that the quantity of silver chloride obtainable from a given weight of silver nitrate may be accurately calculated from the stoichiometric equation for the reaction, and this quantity can be actually obtained in practice. Indeed, the procedures of inorganic analysis are based on this quantitative nature of the reactions involved. In distinct contrast, the quantitative reaction is exceptionally rare among organic reactions. Yields of 80–90% of the theoretical are excellent, yields of the order of 50% are often considered acceptable, and frequently the organic chemist must be satisfied with yields of 20–30%. We are, of course, speaking of yields based on any one particular stoichiometric equation. There are two principal reasons for the nonquantitative nature of organic reactions. First, very few species of organic matter are capable of undergoing only one reaction under a given set of experimental conditions; side reactions almost invariably occur. Thus, on treatment of isopropyl bromide with hydroxide ion, not only does the reaction according to the equation above occur, but there is a side reaction leading to the elimination of hydrogen bromide from the organic molecule with formation of propene.



$$\begin{matrix}H_3C\\ H_3C\end{matrix}\!>CH{-}Br + OH^- \longrightarrow CH_3{-}CH{=}CH_2 + H_2O + Br^-$$

To the extent that this second reaction occurs, the yield of isopropyl alcohol calculated on the basis of the first equation is made smaller. Since these two reactions are the only important ones characteristic of isopropyl bromide under the action of hydroxide ion, the combined yields of isopropyl alcohol and propene total approximately 100% of the theoretical. In other cases, there are more simultaneously occurring reactions; frequently some of these side reactions are of the type leading to general disruption of the organic molecule or to a polymerization to ill-defined products so that a material balance of organic matter involved in the reaction can be obtained only by taking into account the miserable tars, or "gunks," all too familiar to the practicing organic chemist. It should be emphasized at this point, however, that the organic chemist is not completely at the mercy of a natural perversity of inanimate matter; by judiciously picking reaction paths and reaction conditions much can be accomplished toward directing the over-all result into the desired path. This is the art of organic chemistry. A second factor limiting the yields obtainable from organic reactions is reversibility of reaction. Thus acetic acid reacts with ethyl alcohol to form ethyl acetate and water.

$$CH_3{-}CO_2H + CH_3CH_2OH \rightleftarrows CH_3{-}CO{-}OCH_2CH_3 + H_2O$$

Ethyl acetate, however, is capable of reacting with water to form acetic acid and ethyl alcohol. If one brings together equimolar quantities of acetic acid and ethyl alcohol, reaction will proceed as indicated by the above equation in the forward direction. Regardless of how long one waits, however, only about ⅔ of the quantity of ethyl acetate calculated from the above equation will be obtained. Reaction apparently stops at this point. However, if one brings together equimolar quantities of water and ethyl acetate, reaction according to the reverse of the above equation occurs, and this reverse reaction apparently stops when about ⅓ of the ethyl acetate has reacted. It appears, then, that in neither case does reaction actually stop, but that we are dealing with a reversible reaction leading to a dynamic equilibrium. Such equilibria will be treated in more detail in a subsequent section of this chapter. The point being emphasized here is that the reversibility of such reactions places a definite limit on the yield of product obtainable under any given set of experimental conditions. Again, the organic chemist may choose conditions which favor the desired direction of the equilibrium transformation. In this case, the well-known laws of chemical equilibrium are the guide rather than a specialized organic chemical art.

A third characterizing feature of organic reactions may be noted in connection with the reaction of acetic acid with ethyl alcohol. Catalysts are frequently necessary. Thus the speeds of the forward and reverse directions of this reaction are markedly accelerated by the presence of acids or bases, so that the normal equilibrium state of the reaction is established more rapidly in the presence of these substances than in their absence. Indeed, many such reactions of organic substances are impractically slow in the absence of catalysts. Much will be said in this book concerning catalysts and catalysis, but it will suffice here to point out the frequent necessity of catalysis of organic reactions and to emphasize that a catalyst does not exert its accelerating effect on reaction velocity merely by its presence in the reaction mixture, but that the catalyst actually enters into the reaction. Its failure to disappear during reaction is the result of regeneration in a subsequent reaction step. For example, the general course of a catalyzed reaction may be indicated as follows. The reaction being catalyzed is

$$A + B \rightarrow C$$

A catalyst, X, might function according to some such scheme as

(1) $A + X \rightarrow AX$

(2) $AX + B \rightarrow C + X$

In the first reaction step, a complex is formed between the catalyst and one reactant (the substrate) which may subsequently react with the second reactant to form the final product with regeneration of the catalyst, simultaneously or in still a third reaction step. The acceleration of reaction speed results from the fact that the complex AX is of such nature that it is more reactive toward B than is A alone. Catalysts may be employed in both reversible and nonreversible reactions; in the case of reversible reactions, the speeds of forward and reverse reactions are influenced similarly, so that the composition of the equilibrium mixture is not affected.

A fourth general characteristic of organic transformations is that the reactants and products involved are of complex structure. Indeed, it has long been recognized that the possession of definite molecular structure is a distinguishing characteristic of the compounds of carbon. The significance of molecular structure is well illustrated from consideration of the development of the classical concept of valence. The idea of valence, or combining capacity, of the inorganic elements is really quite simple. If one assigns to hydrogen the arbitrary valence of 1, chlorine must also have a valence of 1, since it forms the compound HCl. Similarly, calcium must have a valence of 2 since it forms with chlorine the compound $CaCl_2$. And so on for the other common inorganic elements. Inherent in the concept of valence is the idea that valence may not be fractional and that the integral values may not vary except within well-defined limits. Now consider the series of perfectly well-characterized compounds of carbon: CH_4, C_2H_4, C_2H_2, C_2H_6, C_3H_8, C_4H_{10}, etc. Apparently, carbon may exhibit the classical valences 4, 2, 1, 3, 8/3, 5/2, etc. This difficulty was resolved by Kekulé[1] in 1858 with his invention of the structural formula. The student is thoroughly familiar with this fundamental concept; the assumptions are that carbon has a valence of 4, hydrogen 1, etc., and that carbon may join to carbon. On the framework of this concept of the structural formula the entire edifice of organic chemistry has been constructed. It is a fitting tribute to Kekulé and many other organic chemists of comparable stature that even in our modern day of wave mechanics and similar concepts, the structural formula is taken as the indispensable point of departure for discussion and calculation. It is highly improbable that a graduate student of organic chemistry on hearing the word "acetone" thinks first of a colorless, mobile liquid boiling at about 56°C; the first mental image is the structural formula, $CH_3{-}CO{-}CH_3$, or perhaps even the "spider web" variation.

Returning to the question of the influence of structural complexity on the general nature of the transformations of organic matter, we may note the development of the ideas of organic functionality and homology. A homologous series of compounds is customarily defined as a group of structurally similar compounds, each member of which differs from the preceding member by the unit $-CH_2-$. The concept of homology embraces the idea that the members of a homologous series exhibit similar reactions and a regular gradation of physical properties through the series. A general formula may be assigned to a homologous series. Thus the general formula $C_nH_{2n+1}OH$ represents a homologous series of alcohols. In many of the reactions of alcohols, the unit of structure $-OH$ undergoes some transformation, the remainder of the structure, however large or complex, remaining unchanged. Hence we say that the group $-OH$ is the functional group. It is almost universal teaching practice to allay the fears of the beginning student of organic chemistry with the comforting thought that he may master the reactions of thousands of organic compounds by learning the characteristic reactions of a few "representative" members of a homologous series or by learning the characteristic reactions of certain functional groups. The author wishes in no wise to censure this practice, recognizing that the general truth of these rules raises organic chemistry to the status of an orderly, logical science. The student does not progress far beyond the beginning stages of the mastery of organic chemistry, however, before he realizes that he must begin to reinterpret the meaning of the term "structurally similar compounds" so glibly mouthed in the definition of homology. Consider, for example, the series of homologous carboxylic acids:

$H{-}CO_2H$	formic acid
$CH_3{-}CO_2H$	acetic acid
$CH_3{-}CH_2{-}CO_2H$	propionic acid

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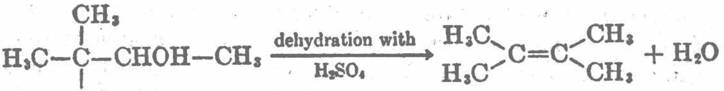
[1] Kekulé, *Ann.*, *106*, 154 (1858).

In some respects the reactions of these three carboxylic acids are quite similar. All three, for example, react with ethyl alcohol to form the corresponding esters; the speeds of these reactions, however, are vastly different. The difficulty of transferring knowledge of chemical behavior down the series does not stop with the recognition that the velocities of similar reactions will differ. This is for the simple reason that acetic acid possesses functional groups not present in formic acid; i.e., the second member of the series has an α-CH_3 unit. Similarly, propionic acid possesses an α-CH_2 unit and a β-CH_3, neither of which is present in formic acid. Fortunately, as the homologous series is ascended, the newly introduced functional groups become less important to the behavior of the structure. To take a more obvious example of the limitations which must be imposed on application of the homology and functionality concepts, the series of compounds $CH_3{-}CH_2{-}Cl$, $(CH_3)_2CH{-}Cl$, $(CH_3)_3C{-}Cl$ satisfies a part of the definition of homology in that each member differs from the preceding member by the unit of structure $-CH_2-$, and each member possesses the functional group C—Cl, but the compounds are not "structurally similar." The three compounds, then, are not members of a homologous series. The reactions of the first and third members of the above series are not even qualitatively similar; for example, ethyl chloride reacts with potassium cyanide to give ethyl cyanide, while *t*-butyl chloride reacts with the same reagent under the same conditions to give isobutene with elimination of hydrogen chloride. Obviously, the β-hydrogen acts as functional group in the case of *t*-butyl chloride, but not in the case of ethyl chloride. It is important to realize that the carbon skeleton itself, usually considered as inert, may assume the role of functional group under rather mild reaction conditions. For example,



$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CHOH-CH_3 \xrightarrow[H_2SO_4]{\text{dehydration with}} (H_3C)_2C{=}C(CH_3)_2 + H_2O$$

(major product)

Examination of the structures of reactant and product shows clearly that the carbon skeleton has functioned in this transformation.

These few illustrations of the limitations which must be placed on applications of the concepts of homology and functionality serve to emphasize the most important aspect of a mature consideration of the transformations of organic matter. The valence bond is to the organic chemist a shorthand symbol for a particular mode of chemical behavior. The structural formula, then, which is an assembly of valence bonds, should be a symbol for the complete chemical behavior of the substance which it represents. It is apparent, however, from the examples considered above that the C—Cl and C—H linkages in ethyl chloride and in *t*-butyl chloride do not behave similarly even under identical experimental conditions; i.e., our symbol for a valence bond does not represent an invariable mode of chemical behavior. We are faced with two alternatives: if our symbols are accurately to express chemical behavior, we must either invent a multitude of symbols, admitting explicitly that a C—H bond is not always "just a C—H bond," or we must assume that the chemical behavior of a given valence bond, represented by a single symbol, may vary with its structural environment. The inconvenience of the first alternative is apparent; its adoption would be comparable to abandoning our present alphabet to adopt the Chinese symbolism. The second alternative is much the more convenient, and as we shall see later, a closer approximation to the truth. We are thus led to the concept of the mutual interaction of groups within organic structures and are faced with the necessity of interpreting the nature of the chemical valence bond and the mechanisms by which valence bonds may mutually interact to produce the fascinating variety of modes of chemical behavior exhibited by organic matter.

The demonstration, principally within the last fifty years, of the electrical nature of matter has provided us with a precise and highly useful picture of chemical structure and chemical interaction which enables us to predict in many cases the behavior of organic substances and almost invariably enables us to rationalize in a most satisfying manner already observed behavior. The remainder of this chapter will be devoted to a presentation of certain general principles and theories which the author feels are most helpful in rationalizing the behavior of organic matter in the process of transformation. It is not within the purpose of this text to attempt to present all the evidence on which these fundamental principles are based; their utility, however, will be evident from their application throughout the remainder of this text.

The nature of chemical bonding.[2] The atom is composed of a dense central nucleus and a surrounding complement of electrons. The nucleus is composed of neutrons (neutral particles of zero charge and mass equal to that of the proton) and protons (the unit of positive charge and atomic mass) in such numbers that the sum of neutrons and protons is the mass number of the atom and the number of protons is the atomic number (or nuclear charge). The number of electrons (units of negative charge and of negligible mass) in the external complement is equal to the atomic number (or nuclear charge), so that the entire atom is electrically neutral. The compact nucleus contributes the entire mass of the atom, is the locus of positive charge, and remains unchanged during chemical transformation. Its most significant property for purposes of our chemical discussion is its positive charge, given numerically by the atomic number. The extranuclear electrons are distributed about the nucleus in various energy levels. According to earlier theories of atomic structure, the extranuclear electrons revolved about the nucleus in perfectly definite orbits very much as the planets revolve about the sun. More recently, this idea of definite orbits has been abandoned in favor of a less precise but considerably more accurate and useful picture of atomic structure. This picture has emerged from the application of quantum mechanics (perhaps better, wave mechanics) to the problem of atomic structure. The quantum mechanics is a body of mathematical theory based upon the premises that energy is not continuous but composed of discrete particles, called quanta, and that the mechanical behavior of electrons is describable in terms of the mathematical equations for a wave motion. The application

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[2] Pauling, *The Nature of the Chemical Bond*, 2d ed., Ithaca: Cornell University Press, 1944; Gilman, *Organic Chemistry*, 2d ed., Vol. 2, New York: John Wiley & Sons, Inc., 1943, Chaps. 25, 26.

of this method results in description of electron behavior as a probability phenomenon; i.e., we may specify the most probable position or the most probable energy of an electron, but we may not assign a precise and invariable value. Thus, in the case of the hydrogen atom, we may say that the single extranuclear electron moves about the nucleus at a varying speed and at a varying distance from the nucleus, but that the most probable speed is a certain v_0 and the most probable distance from the nucleus is a certain a_0. The earlier Bohr theory assumed that the single electron of the hydrogen atom revolved about the nucleus in a perfectly definite circular orbit of radius 0.529 A and at a constant velocity of 2.182×10^8 cm per sec; these values correspond to the values of a_0 and v_0 of the newer theory. According to the newer theory, a picture of the physical structure of the hydrogen atom at any particular instant of time is meaningless; as a time average, however, it is convenient to picture the nucleus as being surrounded by a cloud of electron stuff of varying density, the maximum electron density being at the distance a_0 from the nucleus. For atoms more complicated than hydrogen, the general picture is the same; there are more extranuclear electrons, however, contributing to the time-average electron cloud about the nucleus, and instead of there being a single maximum in electron density at one most probable distance from the nucleus, there are several regions of electron concentration. In other words, the extranuclear electrons arrange themselves in energy levels about the nucleus. In addition to its motion about a nucleus an electron spins about its own axis, and this spin may be positive or negative relative to a certain direction; this electron spin generates an electromagnetic field which can be neutralized by the spin of an oppositely oriented electron. Two electrons of opposite spin may pair and occupy an energy level referred to as an orbital. The various possible atomic orbitals differ in energy, and these relative energies may be conveniently represented by a diagram of the type shown in Fig. 1. It will be noted that the energy levels arrange themselves into shells, designated K, L, M, and N, and subshells designated s, p, d, and f.

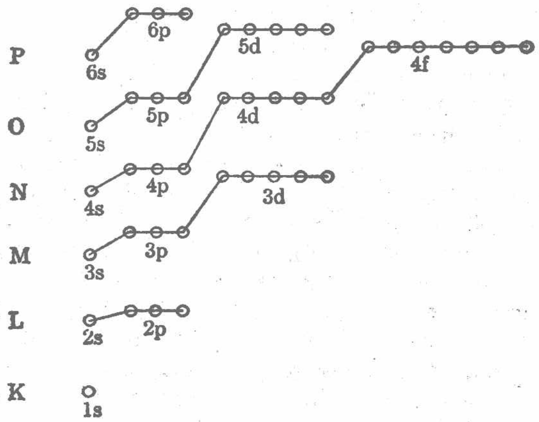

FIGURE 1