



# ORGANIC CHEMISTRY

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## PREFACE

This book is the result of an attempt on the part of the authors to record the substance of Chemistry 34 and Chemistry 36 as they are given at the University of Illinois. Chemistry 34 is for beginners and embraces the entire field, being designed primarily to familiarize the student with the principal types of organic compounds. Part I (Chapters I to XVIII, inclusive) presents the subject matter of this course. Chemistry 36 covers much the same ground as Chemistry 34, but from a more mature viewpoint and with particular emphasis on the use of organic reactions in synthesis. Part II (Chapters XIX to XXXIV) contains the material offered in this course. Together, these courses constitute a year of work in organic chemistry for beginners. Part II has also been used extensively here and elsewhere by graduate students in connection with survey courses and in preparation for Ph.D. examinations. Probably the chief advantage gained by covering the entire subject in each course is due to the repetition which this method involves. In this book the amount of repetition is, for obvious reasons, considerably less than that employed in the classroom. Such details of presentation are left to the teacher.

The general arrangement of the material and the style of presentation are traditional in the department. The only features that are in any sense new and hence not amply tested in the classroom relate to the reports of new developments in the field.

The authors recognize that any credit for the present version belongs in a large degree to their colleagues who have contributed to the development of the courses, the contents of which it purports to reproduce. Foremost among these is Professor C. S. Marvel who was in charge of these courses for many years.

REYNOLD C. FUSON  
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## PART I

### CHAPTER I

#### INTRODUCTION

In the early development of the science of chemistry attention was devoted largely to the acids, bases, and salts. These substances probably were selected because they are soluble in water and most of their reactions are rapid. From the study of these and other compounds the laws governing the combination of the elements were gradually elucidated. However, during this period a very large group of compounds, those present in or obtained from living organisms, was set apart. It was believed that the formation of these so-called *organic* substances could be brought about only in the living plant or animal, and that organic materials could not be treated according to the concepts employed with *inorganic* compounds.

The first of these beliefs was shattered in 1824 when the German chemist Wöhler found that the typical inorganic salt, ammonium cyanate, could be converted easily to the typical organic compound, urea. This demonstration that an organic compound could be synthesized apart from any complex life process thus destroyed the major distinction between inorganic and organic chemistry. Further investigations of organic compounds soon showed that these materials are governed by the same fundamental laws which apply to inorganic substances, and that the real distinction between the two types is that organic materials usually contain both carbon and hydrogen whereas inorganic substances usually do not. The separation of the two fields has been maintained because of the tremendous number of organic compounds, there being several times as many known compounds of carbon as there are of all other elements.

The picture called to the mind of the well-informed man by the words organic chemistry is not one focused on a vast array of carbon compounds. Rather it is a practical, everyday picture of the innumerable articles which he manufactures, buys, sells, and uses. The mere mention of synthetic fabrics, the treatment of leathers, the manufacture of dyes, soaps, and new detergents, the production of better gasolines, oils, and

automobile tires, more enduring paints, new medicines, or cosmetics, brings to mind the extensive fields which organic chemistry has entered. It is no longer news that organic chemistry is an inseparable part of the industries and arts of present-day life.

## SUGGESTED READING

WARREN, "Contemporary Reception of Wöhler's Discovery of the Synthesis of Urea," *J. Chem. Education*, **5**, 1539 (1928).

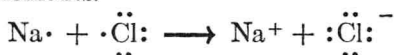


## CHAPTER II

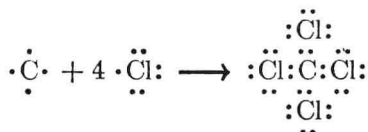
### THE STRUCTURE OF MOLECULES

The property of carbon which distinguishes it most conspicuously is its tendency to form non-ionizing links, both with other carbon atoms and with atoms of different elements. In other words, the type of union most frequently encountered in the carbon compounds is the covalent bond, whereas the polar or electrovalent bond may be considered typical of the inorganic compounds. The differences between these two kinds of valence may be seen by examination of examples.

The formation of sodium chloride from the elements illustrates the simplest mode of formation of an electrovalent bond. The sodium atom has one electron (Group I of the periodic table) in its valence shell. Beneath this valence electron lies a complete shell of eight electrons. The chlorine atom has an outer shell of seven electrons (Group VII of the periodic table). When these two atoms react, the electron simply passes from the sodium atom to the chlorine atom so that both resulting particles have outer shells of eight electrons. The sodium atom, by losing the negatively charged electron, becomes the positive sodium ion. The chlorine atom, by gaining the electron, becomes the negative chloride ion. There is actually no bond between the two ions. They attract each other, by virtue of their opposite charges, but an individual sodium ion will be attracted by any negative ion which happens to be near it, and not solely by the particular chloride ion to which it originally yielded its electron. The following equation represents the formation of sodium chloride from the elements.



The formation of carbon tetrachloride from carbon and chlorine involves a process of a different type. The carbon atom (Group IV of the periodic table) has four electrons in its valence shell. When it reacts with a chlorine atom it contributes one electron, and the chlorine contributes one, to the formation of a pair held jointly by the two atoms. By combining with four chlorine atoms, the carbon atom acquires a shell of eight electrons, as follows:

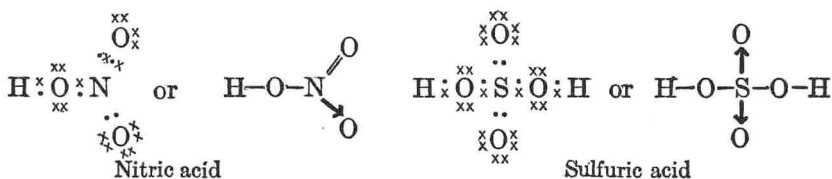


As indicated in the formula there is no actual transfer of electrons here, but rather a sharing in such a way that each atom is able to complete its octet. The result is a *fixed* bond between the carbon atom and the chlorine atom.

A comparison of the properties of sodium chloride and carbon tetrachloride illustrates the differences between ionic compounds and covalent compounds. For instance, sodium chloride is high-melting and non-volatile. It is soluble in water. Its reactions, being the reactions of the sodium ion and the chloride ion, are extremely rapid. Carbon tetrachloride, on the other hand, is a volatile liquid. It is insoluble in water. Most of its reactions are extremely slow in comparison with those of sodium chloride. Thus, sodium chloride reacts instantly with silver nitrate to give a precipitate of silver chloride, but under ordinary conditions carbon tetrachloride does not react at all with silver nitrate. This shows that each chlorine atom is firmly attached to the carbon atom and that no chloride ions are present.

It is not to be concluded from the foregoing discussion that inorganic compounds contain only ionic or electrovalent bonds, nor that all links in all organic compounds are covalent bonds. Actually, many inorganic compounds contain covalent bonds, and many organic substances have one or more electrovalent linkages.

A third type of valence, known as the *coordinate covalence*, also occurs in both organic and inorganic materials. It consists of a shared pair of electrons, both of which are contributed by one of the atoms. It is present in such common reagents as sulfuric acid and nitric acid. In the formulas below the electrons originally belonging to the nitrogen, sulfur, and hydrogen atoms are indicated by dots, while those of the oxygen atoms are represented by crosses.



It will be noted that in these formulas the nitrogen and sulfur atoms have complete octets. One of the oxygen atoms in nitric acid has achieved this state by sharing the pair furnished by the nitrogen atom. In sulfuric acid two oxygen atoms are held in this manner. Formulas of this kind are usually abbreviated as shown, an arrow indicating the coordinate covalent link. The arrow points from the donor to the acceptor of the electron pair. The coordinate covalent link is sometimes called the

semipolar bond. The origin of this term becomes clear from a consideration of the nitrogen-oxygen coordination bond in nitric acid. Since it still has all its original six electrons plus an interest in the pair which holds it to the nitrogen, the oxygen must have a negative charge. The nitrogen, on the other hand, since it has given up a share of the pair to the oxygen atom without gaining any interest in the latter's electrons, must bear a positive charge.

The carbon atom forms covalent links not only with chlorine, but with a great variety of elements, including the other halogens, hydrogen, oxygen, nitrogen, sulfur, phosphorus, and occasionally other elements. Most striking of all is the formation of stable covalent bonds with other carbon atoms. Thus, organic compounds may contain carbon atoms in *chains* of two, three, four, or more. In fact, there is no known limit to the number of carbon atoms which may be united in this way. When this is considered, together with the various elements mentioned which may be united with the carbon atoms in these chains, it becomes evident that the number of possible organic compounds is extremely large. In addition, as a consequence of the fixed character of a covalent bond, it is often possible to obtain many different compounds from the same group of atoms by varying the *arrangement* of the atoms within the molecule. Such compounds are said to be *isomers*; the phenomenon, known as *isomerism*, is very common among organic compounds.

Because of the formation of carbon chains and the existence of isomers, there is no mathematical limit to the number of possible carbon compounds. The successful treatment of organic chemistry must, therefore, depend upon the classification of the compounds into broad groups of related substances. A very satisfactory classification is that based on *structure*. By structure is meant the manner of attachment of the various atoms which make up a particular compound. For example, carbon atoms can be joined by one, two, or three bonds, giving rise to three different species of compounds. Carbon forms stable single, double, and triple bonds with nitrogen also. Moreover, it may be joined to sulfur, the halogens, and many other elements.

As a result of the remarkable and varied capacity of carbon for combining with itself and with other elements, many different types of organic compounds are possible. Each type or class is characterized by a particular group known as its *functional group*. A few of the principal functional groups and the classes of compounds to which they give rise are shown in Table I.

Of the dozens of classes of organic compounds, the basic type is that composed of *hydrocarbons*, compounds containing only hydrogen and carbon. Since the hydrocarbons furnish the foundations upon which

all other types of organic compounds are built, it is desirable to consider them first.

TABLE I  
SOME SIMPLE FUNCTIONAL GROUPS

Class of Compound	Functional Group	
	Formula	Name
Alcohols	-OH	Hydroxyl group
Acids	$\begin{array}{c} \text{O} \\ \parallel \\ \text{-C-OH} \end{array}$	Carboxyl group
Aldehydes and ketones	$\begin{array}{c} \text{O} \\ \parallel \\ \text{>C=O} \end{array}$	Carbonyl group
Amines	-NH <sub>2</sub>	Amino group
Mercaptans	-SH	Sulfhydryl group
Nitro compounds	-NO <sub>2</sub>	Nitro group
Sulfonic acids	-SO <sub>3</sub> H	Sulfonic acid group

## CHAPTER III

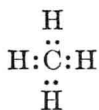
### SATURATED HYDROCARBONS

#### Methane

The hydrocarbons can be grouped into various classes on the basis of their chemical reactions. Those called *saturated* hydrocarbons have been so named because of their relative inertness. The name *paraffin* (too little affinity) carries the same connotation.

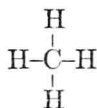
The simplest of the paraffin hydrocarbons is methane,  $\text{CH}_4$ . It is the chief constituent of natural gas, and as such occurs in large quantities. It has been called *marsh gas* because of its formation during the anaerobic fermentation of vegetable matter beneath the stagnant water of swamps. Methane usually occurs along with coal, and because it forms an explosive mixture ("fire damp") with air, its presence constitutes one of the hazards of mining.

Since carbon has a valence of four, it is obvious that each of the hydrogen atoms in the methane molecule must be attached directly to the carbon atom. The bonds are covalent, so the formula may be written as follows:



Electronic formula of methane

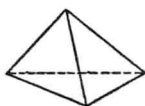
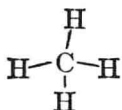
In practice, formulas of this type are used only when it is necessary to call particular attention to the electrons of the bonds. For convenience the links are usually represented by lines. Each line in the formula below is, then, to be considered as an abbreviation indicating a pair of electrons shared between the two atoms which it joins.



Structural formula of methane

This structural formula fails to represent correctly the distribution in space of the atoms in the methane molecule. It is known that the

four pairs of electrons about a carbon atom arrange themselves so that each pair is at the greatest possible distance from each of the other pairs. The result is that the four valences are directed in such a way that the four attached groups bear the same spatial relation to each other as do the four points of a regular tetrahedron. An accurate representation of the methane molecule must, then, involve a three-dimensional drawing.

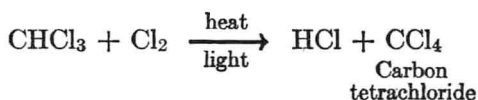
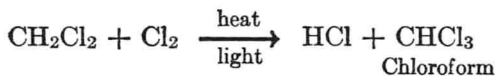
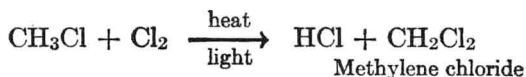
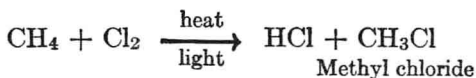


Because of this distribution of valences, carbon is often referred to as a *tetrahedral* atom. It will become apparent later that the spatial relationship of the groups about a carbon atom may have a profound influence on the properties of a compound. However, because they are difficult to draw, the three-dimensional formulas are used only when they are necessary.

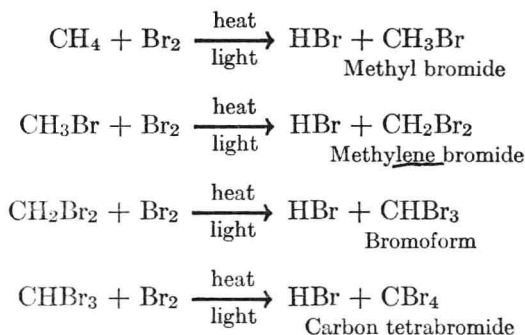
Although the paraffins are the least reactive of the hydrocarbons, they do nevertheless undergo a variety of transformations under the influence of appropriate reagents. Thus, whereas it resists the action of mild oxidizing agents such as aqueous solutions of potassium permanganate, methane is readily oxidized when heated sufficiently with oxygen. This, of course, is the reaction which takes place when natural gas is burned.



Chlorine attacks methane, but only at elevated temperatures or in the presence of ultraviolet light. The reaction involves the removal of hydrogen atoms, their places being taken by chlorine atoms.

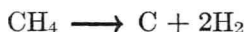


The reaction is of the type known as a *substitution*. By substitution is meant the direct replacement of hydrogen by other atoms. A similar substitution occurs when bromine is used.



Iodine, the least reactive of the halogens, does not react with methane. However, the iodine derivatives of methane, methyl iodide, methylene iodide, iodoform, and carbon tetraiodide, can be obtained by other methods. Fluorine is so extremely reactive that direct fluorination is seldom used. In fact, neither the chlorination nor the bromination of methane is easily controlled. Because the rates of chlorination of methane, methyl chloride, methylene chloride, and chloroform are nearly identical, an attempt to prepare any one of the chlorine derivatives results in a mixture containing all four of them in addition to unchanged methane. Other methods which give the individual derivatives are therefore more convenient for laboratory preparations.

Like nearly all organic compounds, methane decomposes under the influence of extreme heat. The products are carbon and hydrogen.



This reaction is used in the preparation of lampblack from natural gas. A simple way of effecting it is to burn methane with a limited quantity of air. The heat of the flame causes the decomposition of the methane which is in excess of the oxygen present. Thermal decomposition of organic compounds is usually referred to as *pyrolysis*. When a hydrocarbon is concerned, the reaction is sometimes called *cracking*.

### The Higher Paraffins

Methane is the simplest member of a series of hydrocarbons of very similar chemical characteristics. The next higher member is ethane ( $\text{C}_2\text{H}_6$ ) and following ethane are propane ( $\text{C}_3\text{H}_8$ ) and butane ( $\text{C}_4\text{H}_{10}$ ). These compounds may be represented by the general formula  $\text{C}_n\text{H}_{2n+2}$

in which  $n$  is the number of carbon atoms. The formulas and boiling points of a number of them are given in Table II. It will be seen that the formula of any member can be obtained by adding  $\text{CH}_2$  to that of the preceding member. Such a series of compounds is known as a *homologous series*. A homologous series may be defined as a group of structurally similar compounds, each member of which differs from the preceding member by  $\text{CH}_2$ . The concept of homology is one of the fundamentals of organic chemistry.

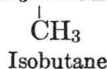
TABLE II  
STRAIGHT-CHAIN SATURATED HYDROCARBONS

Name	Boiling Point	Formula	Structural Formula
Methane	-161°	$\text{CH}_4$	$\text{CH}_4$
Ethane	-88	$\text{C}_2\text{H}_6$	$\text{CH}_3\text{CH}_3$
Propane	-45	$\text{C}_3\text{H}_8$	$\text{CH}_3\text{CH}_2\text{CH}_3$
Butane	0	$\text{C}_4\text{H}_{10}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
Pentane	36	$\text{C}_5\text{H}_{12}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
Hexane	69	$\text{C}_6\text{H}_{14}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
Heptane	98	$\text{C}_7\text{H}_{16}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
Octane	125	$\text{C}_8\text{H}_{18}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
Nonane	151	$\text{C}_9\text{H}_{20}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
Decane	174	$\text{C}_{10}\text{H}_{22}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

Only one carbon skeleton can be written for each of the hydrocarbons up to and including propane. However, in the formula,  $\text{C}_4\text{H}_{10}$ , the carbons may be arranged either in a *straight chain*,  $-\overset{|}{\text{C}}-\overset{|}{\text{C}}-\overset{|}{\text{C}}-\overset{|}{\text{C}}-$ , or in a *branched chain*,  $-\overset{|}{\text{C}}-\overset{|}{\text{C}}-\overset{|}{\text{C}}-$ . Actually two different butanes, called normal butane (*n*-butane) and isobutane, are known:



*n*-Butane

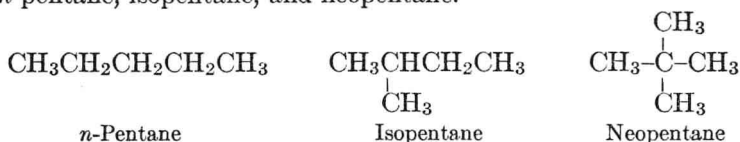


These compounds have entirely different physical properties. For instance, the boiling point of isobutane ( $-10^\circ$ ) differs by ten degrees from that of *n*-butane ( $0^\circ$ ). It will be seen later that there are also differences in their chemical properties.

Butane and isobutane are *isomers* of each other. *Isomerism* may be defined as the existence of two or more compounds of the same molecular formula, but of different structures.



In a similar manner it is possible to write three structures for the formula,  $C_5H_{12}$ , and, in fact, three isomeric pentanes are known. They are *n*-pentane, isopentane, and neopentane.



The number of possible isomers increases rapidly as the number of carbon atoms in the hydrocarbon molecule is increased. Thus, there are five hexanes, nine heptanes, eighteen octanes, and thirty-five nonanes. The method used above for naming the isomeric butanes and pentanes would become extremely cumbersome if an attempt were made to extend it to larger molecules. For this reason a simple system of naming such organic compounds was devised by a group of chemists meeting in Geneva in 1894. The following are the principles of the *Geneva system of nomenclature*.

1. A compound is named as a derivative of the hydrocarbon corresponding to the longest carbon chain present in the molecule. The name of this hydrocarbon serves as the stem of the name of the compound.

2. The type of the compound, that is, the homologous series to which it belongs, is indicated by a suffix. For the paraffins this suffix is *ane*.

3. Groups attached to the carbon chain are indicated by suitable prefixes. In order to specify the location of these groups the carbon chain is numbered in such a way that the numbers used in the name are the smallest possible.

The use of these rules is illustrated by the names of the five hexanes. The  $CH_3$  group is known as the methyl group.

