ORGANIC CHEMISTRY

A BRIEF INTRODUCTORY COURSE

BY

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New York
THE MACMILLAN COMPANY

1928

PREFACE

It is generally conceded that in order to teach any subject effectively it is first necessary to arouse an interest in it. This is not always easy in an elementary course in organic chemistry because of the bewildering array of facts and formulas which confront the beginner. A certain facility in using structural formulas must be acquired and a not inconsiderable body of information must be assimilated as a first step in understanding the subject. Hence, finding a stimulating approach to organic chemistry is often the instructor's most difficult problem. This is particularly true if his classes are largely composed of students who do not intend to continue the study of chemistry. This book is the author's attempt to present an interesting and at the same time adequate account of the chemistry of the compounds of carbon.

The formal classification of compounds which is so valuable to the specialist may be barren to the uninitiated. For this reason, the author has unhesitatingly departed from the traditional arrangement of the subject-matter whenever such departure seemed to promise a more interesting grouping of topics or an easier road to a mastery of the principles of the science. The usual introductory chapter dealing with the purification of compounds, methods of analysis and the calculation of formulas has been omitted. Such dreary reading seems an inauspicious beginning of an attempt to make organic chemistry inviting. Furthermore, much of the material usually included in such a chapter is either a review of fundamentals adequately considered in a first course in general chemistry or a description of laboratory methods, which are best brought to the student's attention in connection with the laboratory work.

The author's experience in presenting organic chemistry to a variety of classes has led him to believe that the alcohols have certain advantages over the hydrocarbons as a point of departure. The necessity for structural formulas can be convincingly demonstrated by the consideration of the isomerism of ethyl alcohol and methyl ether, and attention can be centered on a relatively few accessible compounds with characteristic reactions. From many

points of view the relationship of alcohol and ether to water is much more important than the relationship of these substances to ethane. The value of the paraffin hydrocarbons to the systematist has, in the author's opinion, led to an over-emphasis of their pedagogic importance.

In order to minimize the amount of memory work, only a few examples of each homologous series have been treated and many classes of compounds have been omitted altogether. To warrant consideration in a brief elementary course, a compound must have either scientific or industrial importance. Such topics as industrial alcohol, petroleum, rubber, cellulose nitrate, dyes, coal tar medicinals and the synthesis of compounds from ethylene and acetylene have been treated at some length with a view to showing some interesting practical applications of the science. The ever-increasing number of pre-medical students in courses in organic chemistry requires the inclusion of considerable material dealing with substances of pharmacological and physiological importance.

Problems dealing with the synthesis and structure of simple organic compounds seem to be an effective method of stimulating interest and affording an opportunity for the student to think for himself. For this reason considerable space has been devoted to this aspect of the subject (in particular, Chapter IX). In this connection the recent industrial developments in aliphatic chemistry provide splendid material to illustrate the actual importance of some of the simplest reactions.

This book is designed to be used either in a year course, or, by omitting Chapter XIV and parts of Chapters XXII and XXIII, in a semester course. It is assumed that either of these introductory courses will be followed by a second full year's course in organic chemistry in the case of students who are specializing in chemistry. For the pre-medical and general student the material presented in the following pages should provide sufficient knowledge of the carbon compounds.

The manuscript has been read by a number of kind friends and has been greatly improved by their comments and suggestions. The author takes this opportunity of acknowledging his indebtedness in this connection to his colleagues Professor E. P. Kohler, Dr. W. H. Carothers, Professor E. J. Cohn, and Dr. G. A. Alles,

to Professors Roger Adams and C. S. Marvel of the University of
Illinois and to Professor J. R. Johnson of Cornell University.
Mr. A. R. Davis has been of the greatest assistance in the prepara-
tion of the manuscript and the critical reading of the proof. The
drawings have been prepared by Mr. S. F. Darling. To all these
gentlemen, the author expresses his sincere gratitude.

JAMES B. CONANT.

CAMBRIDGE, MASSACHUSETTS,
May, 1928

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ORGANIC CHEMISTRY

FOREWORD

Organic chemistry is the chemistry of the compounds of carbon. At first sight, it seems strange that one element should be singled out for special attention, and stranger still, perhaps, that this branch of chemistry should be considered important enough to be one of the two major divisions of the subject. No other element shares this honor with carbon; all the rest of chemistry is classed together under the one heading,—inorganic chemistry.

The origin of the name suggests one of the reasons for the importance of organic chemistry: originally the science dealt with the products of plant and animal life. It was long believed that these were in some mysterious way different from the lifeless rocks and minerals with which inorganic chemistry dealt. The distinction was shown to be false by the synthesis from inorganic materials of several natural products. This barrier between the two chemistries was thus broken down and it was recognized that the fundamental laws and principles of both were identical. Since almost all the important substances produced by animate nature contain carbon, the name organic chemistry was transferred to the study of the compounds of this element.

Thus, from its earliest beginnings to the present, organic chemistry has been closely associated with the study of life itself. In many cases it is impossible to mark off organic chemistry from biochemistry, and this, in turn, from physiology. For this reason, a knowledge of organic chemistry has been indispensable to progress in many branches of biology. The connection with medicine has been twofold: on the one hand, through physiology and physiological chemistry, on the other, through pharmacology. The organic chemist's study of such natural drugs as cocaine has led to the synthesis of simpler substances with similar or superior pharmacological action. Today in many medical schools, hospitals and research institutes, the doctor, the phys-

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iologist and the organic chemist are coöperating in a study of the varied problems confronting the medical profession.

From an industrial point of view, the chemistry of plant and animal products is also important. The production of automobile tires from rubber, a complex plant product, is an enormous chemical industry in itself. The manufacture of many common substances, such as vinegar, soap, corn syrup and "vegetable fats" (hydrogenated oils) are examples of applied organic chemistry. So also is the transformation of cotton into artificial silk, automobile varnish, moving picture films and smokeless powder.

From physiology to the coal tar dye industry seems a far cry, but it is not so in reality. Coal tar is a mixture of carbon compounds; from them the chemist has prepared a multitude of new substances of scientific and practical importance. At his bidding, the new coal tar dye industry sprang up. It now supplies practically all the dyes in use and, in addition, many drugs, perfumes, flavors, photographic developers and high explosives. The study of these synthetic coal tar products has gone hand in hand with the investigation of plant and animal substances. Knowledge gained in the one field has been applied to the other, often by the same man. The most distinguished organic chemist of the last generation, Emil Fischer, was able to make rapid progress in the study of the sugars largely because of a discovery made in an investigation of certain compounds prepared from coal tar. He will be remembered for the investigation of varied natural products and also as a pioneer in the study of coal tar dyes.

In listing the important aspects of organic chemistry, petroleum must not be overlooked. This complex mixture of organic compounds has yielded primarily fuel, at first for lamps, and now for the internal combustion engine and the oil-burning steam engine. The organic chemistry of this raw material has been slow in developing. This situation, however, is now beginning to change; already, a number of new and useful compounds are being prepared from petroleum and natural gas.

Many of those who make the acquaintance of organic chemistry on their way to other callings will be impressed chiefly by the applications of the science to medicine or to technology. The success and importance of these applications loom large in the public eye, and the organic chemist has reason to be proud

of them. He knows, however, that they would have been impossible if the science itself had not developed in a rather remarkable and spectacular way in the last part of the nineteenth century, and continued to expand on the sure foundations which were then laid. This science seems to many a more remarkable achievement of the human brain than its technical applications. The two cannot really be separated, however, as even an elementary study of the subject will demonstrate. Both have been kept in mind in the writing of this book in order to give a true picture of the varied and fascinating ramifications of organic chemistry.

CHAPTER I

THE ALCOHOLS

Composition of Ethyl Alcohol. Ethyl alcohol is a substance of such great practical importance that we may well choose it as the starting point in a study of organic chemistry. Later, we shall consider its industrial significance and the commercial methods of preparation. For the present, let us center our attention on a chemical investigation of its constitution. The first step in such a study involves the careful purification of the compound, and the second, the qualitative and quantitative analysis. A discussion of these fundamental methods will be found in a laboratory manual of organic chemistry and we may therefore turn directly to the results. Pure ethyl alcohol is a liquid boiling at 78°; a quantitative analysis shows that it contains carbon, hydrogen and oxygen in such amounts as correspond to the existence of two carbon atoms, six hydrogen atoms and one oxygen atom.

THE DETERMINATION OF THE EMPIRICAL FORMULA OF ETHYL ALCOHOL
Results of Quantitative Analysis

ELEMENT	PER CENT	ATOMIC WEIGHT	ATOMIC RATIO	RATIO OF ATOMS
Carbon	52.18	$\div$ 12	$=$ 4.35	$4.35 \div 2.17 = 2$
Hydrogen	13.04	$\div$ 1	$=$ 13.04	$13.04 \div 2.17 = 6$
Oxygen	34.78	$\div$ 16	$=$ 2.17	$2.17 \div 2.17 = 1$

The **empirical formula** is therefore C_2H_6O. Such a formula tells us only the relative number of atoms in the molecule. To establish the **molecular formula** of a compound it is necessary to have information in regard to the molecular weight. A determination of the molecular weight (the third step in the investigation) is readily accomplished by finding the density of the vapor.[1]

[1] The molecular weight may also be determined by noting the depression in the freezing point (or elevation in the boiling point) of a suitable solvent in which a weighed amount of the substance has been dissolved. The principle of this method is explained in textbooks of elementary general chemistry. (See, for example, Alexander Smith's *Intermediate Chemistry*, p. 117.)

The results of many such experiments have shown that the molecular weight of ethyl alcohol is 46. The molecular formula of ethyl alcohol is therefore C_2H_6O ($2 \times 12 + 6 + 16 = 46$).

Isomerism. In an elementary study of inorganic chemistry we should hail this result with satisfaction, since the determination of the kind and number of atoms in the molecule is usually sufficient to establish an adequate formula; for example NH_3, HCl, H_2O_2. These are called molecular formulas. Quite the contrary is the case in organic chemistry: such formulas are inadequate in dealing with the compounds of carbon. This may be illustrated by a simple example. Methyl ether, a gas, has exactly the same percentage composition and the same molecular weight as ethyl alcohol. Therefore it must be also represented by the formula C_2H_6O. There can be no doubt about the difference between these compounds, since one is a liquid boiling at 78° and is soluble in water, while the other is a gas at room temperature and is insoluble in water. Their chemical reactions are also entirely different. *Two compounds which have the same molecular formula are said to be isomers;* the phenomenon is known as isomerism.
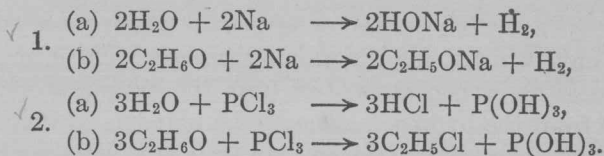
The Necessity for Structural Formulas. Isomerism is very common in organic chemistry. For example, twenty-six isomers with the formula $C_6H_{14}O$ have been prepared and their properties recorded. It is obvious that unless the organic chemist is able to write formulas which represent the differences between isomers, he is in a hopeless position. It was not until about the middle of the last century that a satisfactory method of formulating organic compounds was developed; before this time the chemistry of the carbon compounds was in a confused state. After the invention of structural formulas, organic chemistry advanced by leaps and bounds. The chief name associated with the remarkable advancement in this field of chemistry is that of Kekulé.[1]

The Theory of Linkages. The theory which was advanced to explain the differences between the various isomers may be called the theory of atomic linkages. This assumes that isomerism is due to the different ways in which the same atoms are joined

[1] Friedrich August Kekulé (1829–1896). Professor of Chemistry at the University of Bonn.

together in the molecule. The organic chemist, thus, seeks to express in his structural formulas not only the number and kinds of atoms in the molecule but *the way in which they are linked together*. In other words he must represent the structure of the compound. Let us see how this may be done in the case of ethyl alcohol.

Hydroxyl Group in Alcohols. Ethyl alcohol is very similar to water in many of its chemical properties, as is illustrated by the following reactions with metallic sodium and phosphorus trichloride:

1. (a) $2H_2O + 2Na \longrightarrow 2HONa + H_2$,
   (b) $2C_2H_6O + 2Na \longrightarrow 2C_2H_5ONa + H_2$,

2. (a) $3H_2O + PCl_3 \longrightarrow 3HCl + P(OH)_3$,
   (b) $3C_2H_6O + PCl_3 \longrightarrow 3C_2H_5Cl + P(OH)_3$.

It will be noticed that in the first two reactions, sodium hydroxide and a compound, C_2H_5ONa (sodium ethylate), are formed by the replacement of one hydrogen of the molecule. In the second two reactions, the phosphorus atom becomes attached to an hydroxyl group which in one case has been removed from water and in the other must come from the alcohol. The facts of inorganic chemistry show that atoms in water must be arranged $H-O-H$; the existence of the hydroxyl group (OH) in water, therefore, is evident. Since phosphorous acid is formed in Equation 2b also, we may conclude with considerable assurance that *ethyl alcohol has an hydroxyl group.*
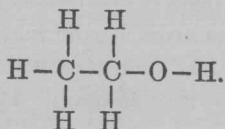
These two reactions are also characteristic of another well-known substance,—**methyl alcohol.** This compound (also known as *methanol*) has the molecular formula CH_4O as determined by the analysis and vapor density of a carefully purified sample. Since it reacts with sodium evolving hydrogen, and with phosphorus trichloride forming phosphorous acid $P(OH)_3$, we conclude that it also contains an hydroxyl group. We may, therefore, write the formulas CH_3OH for methyl alcohol and C_2H_5OH for ethyl alcohol. These formulas, however, are still not perfectly clear. How are the carbon and hydrogen atoms arranged in the groups CH_3 and C_2H_5?

Structure of Methyl and Ethyl Alcohols. In the case of methyl alcohol, the question raised in the last paragraph is

easily answered. There is only one possible arrangement of the atoms in CH_3OH if hydrogen has the valence of one. The three hydrogen atoms must be attached to the lone carbon and this, in turn, must be bound to the hydroxyl group. Thus we have a complete structural formula:

$$H-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-O-H.$$
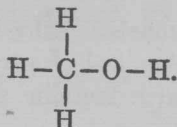
The dash (−) whether vertical or horizontal stands for a valence bond, a link, which joins the atoms together. There are four bonds from the carbon atom, two from the oxygen atom, and only one from the hydrogen atom. The founders of the structural theory assumed that carbon always has a valence of *four* in organic compounds, oxygen of two, and hydrogen of one. If this is true, the complete structural formula of ethyl alcohol is:

$$H-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-O-H.$$

By attempting to write a variety of structural formulas for ethyl alcohol it is easy to convince oneself that there is only one way of writing C_2H_5OH, *provided* that the valence of hydrogen is one, oxygen two, and carbon four. It is, of course, immaterial whether the formula be written from right to left or left to right or at what angle the various atoms are connected. The structural formula simply says that the two carbon atoms in ethyl alcohol are joined to each other, and that one is attached to three hydrogens, the other to two hydrogen atoms and the hydroxyl group.

Writing Structural Formulas. A study of a great variety of organic compounds has made certain the original assumption in regard to the valence of carbon, oxygen and hydrogen. Carbon always has a valence of four, except in a few unusual substances (p. 255). Therefore, in writing structural formulas we must arrange the atoms in such a way that each carbon atom always is connected with four linkages, oxygen with two, and hydrogen

with one. *Every formula should be tested by noting the valence of each atom.*

Structure of Methyl Ether. Methyl ether, spoken of above as the isomer of ethyl alcohol, reacts neither with phosphorus trichloride nor with sodium; therefore, it has *no* hydroxyl group. It has the following formula, which, it is easy to see, represents a molecule of an entirely different nature from that of ethyl alcohol. This case of isomerism is thus explained satisfactorily by the structural theory:
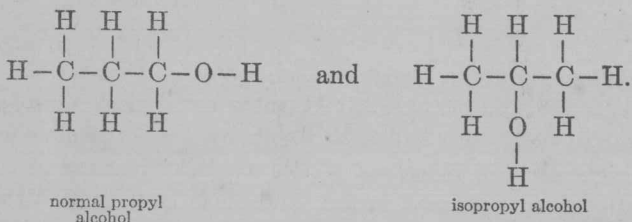
$$\begin{array}{ccc} H & & H \\ | & & | \\ H-C-O-C-H. \\ | & & | \\ H & & H \end{array}$$

methyl ether
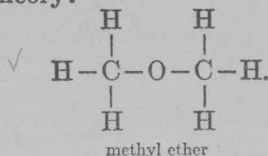
The Alcohols are a Class of Compounds. Besides the well-known methyl and ethyl alcohols, there are a great many other substances which are called alcohols by the organic chemist. They all show the reactions which we have learned are characteristic of an hydroxyl group, and their structural formulas, therefore, must show the linkage $-O-H$. They form a graded series with an increasing number of carbon atoms. Such a series of compounds is called an *homologous series* and is illustrated below.

Name	General Formula	Difference	Number of Isomers
Methyl alcohol	CH_3OH		one substance
		$>CH_2$	
Ethyl alcohol	C_2H_5OH		one substance
		$>CH_2$	
Propyl alcohols	C_3H_7OH		two substances
		$>CH_2$	
Butyl alcohols	C_4H_9OH		four substances
		$>CH_2$	
Amyl alcohols	$C_5H_{11}OH$		eight substances

We may define an homologous series as a series of similar compounds in which *each member differs from the one below it and the one above it by CH_2.* It will be noted that all the compounds of this series correspond to a general formula $C_nH_{2n+1}OH$.

That is, the number of hydrogen atoms (not including that of the OH group) is one more than twice the carbon atoms.

Isomeric Propyl and Butyl Alcohols. When we come to the substance C_3H_7OH in the homologous series of alcohols, we find that *more than one substance is represented by the formula*. In other words, a still more subtle type of isomerism is now at hand. The reason for this is evident from a consideration of the complete structural formulas of such substances. Bearing in mind the rules in regard to the valence of the different atoms and the fact that the substances all contain one hydroxyl group, we find that there are two and *only two* ways of arranging the atoms in C_3H_7OH; these are:
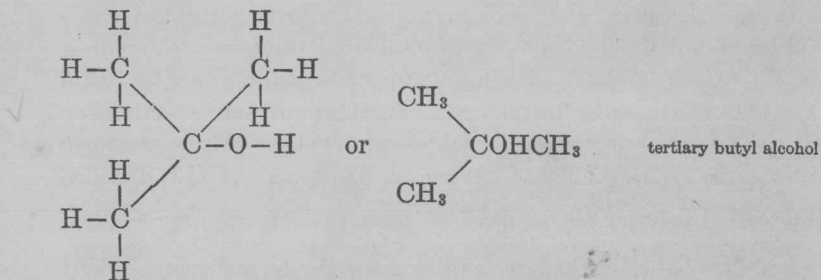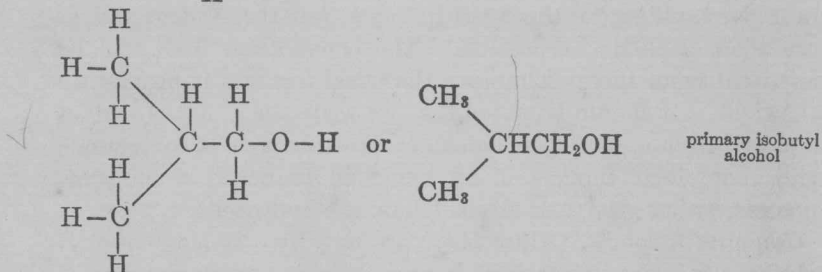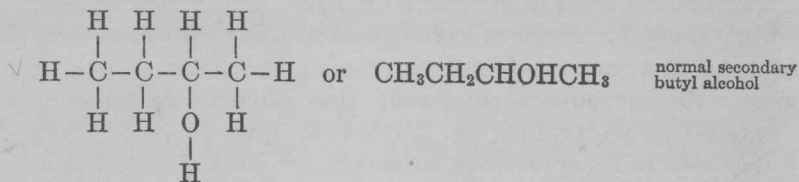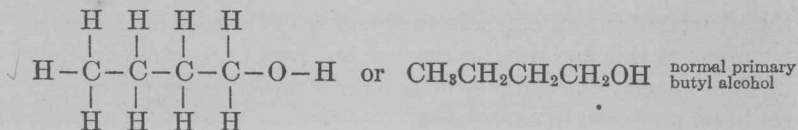
$$
\begin{array}{ccc}
\text{H} & \text{H} & \text{H} \\
| & | & | \\
\text{H}-\text{C}-\text{C}-\text{C}-\text{O}-\text{H} \\
| & | & | \\
\text{H} & \text{H} & \text{H}
\end{array}
\quad \text{and} \quad
\begin{array}{ccc}
\text{H} & \text{H} & \text{H} \\
| & | & | \\
\text{H}-\text{C}-\text{C}-\text{C}-\text{H}. \\
| & | & | \\
\text{H} & \text{O} & \text{H} \\
& | \\
& \text{H}
\end{array}
$$

<center>normal propyl alcohol   isopropyl alcohol</center>

These formulas are usually written as $CH_3CH_2CH_2OH$ and $CH_3CHOHCH_3$. There are actually two and *only* two substances C_3H_7OH; one is normal propyl alcohol boiling at 98°, the other is isopropyl alcohol which boils at 82°.

At first sight it might appear that there were many different ways of arranging the atoms in the molecule C_3H_7OH, all of which conformed to the rules of valence. That this is not the case, perhaps becomes convincingly demonstrated only by actual trial with a pencil and paper. It will be remembered that the linkage of two carbon atoms through oxygen is excluded from the possibilities by the fact that the compound has an hydroxyl group (it is an alcohol). Hydrogen has only one valence bond and therefore can not serve to join two other atoms together. Therefore the three carbon atoms must be joined in a chain. The position of the hydroxyl group is the only variable left. This group may be placed at the right end, in the center or at the left end. The seven hydrogen atoms of C_3H_7OH now will be found sufficient to occupy the seven remaining bonds of the three carbon atoms. A moment's consideration will convince one that there is no difference between the two ends of this symmetrical chain of carbon atoms. Whether the hydroxyl group is written at the left end or the right end is without significance. Both arrangements represent the same linkage,—they could be cut out and superimposed on each other by merely turning through 180°. The arrangement with the hydroxyl group in the center is different. This can not be superimposed on the other

formula because the hydroxyl group is attached to a carbon atom in the middle of the chain. This carbon atom has only one hydrogen: the terminal atoms have two. Thus, in one formula we have the group $>$CHOH, in the other $-CH_2OH$.

The isomerism of the butyl alcohols, C_4H_9OH, is represented by the following structural formulas:

$$\begin{array}{ccccc} H & H & H & H \\ | & | & | & | \\ H-C-C-C-C-O-H \\ | & | & | & | \\ H & H & H & H \end{array} \quad \text{or} \quad CH_3CH_2CH_2CH_2OH \quad \begin{array}{l}\text{normal primary}\\ \text{butyl alcohol}\end{array}$$

$$\begin{array}{ccccc} H & H & H & H \\ | & | & | & | \\ H-C-C-C-C-H \\ | & | & | & | \\ H & H & O & H \\ & & | \\ & & H \end{array} \quad \text{or} \quad CH_3CH_2CHOHCH_3 \quad \begin{array}{l}\text{normal secondary}\\ \text{butyl alcohol}\end{array}$$

primary isobutyl alcohol

or

$$\begin{array}{c}CH_3\\ \diagdown\\ CHCH_2OH\\ \diagup\\ CH_3\end{array}$$

tertiary butyl alcohol

or

$$\begin{array}{c}CH_3\\ \diagdown\\ COHCH_3\\ \diagup\\ CH_3\end{array}$$

Thus, with the aid of the structural theory, we can predict the number of isomers which are possible in the case of the propyl alcohols and butyl alcohols, and test the prediction by experiment. Repeated trials in many laboratories have shown that such pre-

dictions of the structural theory are always verified. By working long enough and hard enough, it is always possible to make the number of isomers required by the theory, but more than this number have never been found. Since the number of isomers increases very rapidly as one goes up an homologous series, many isomers of the higher members have not yet been prepared. However, since our experimental facts and the predictions of the structural theory coincide so precisely in the case of the lower members of this and other series, we feel perfectly confident that in time exactly the number of isomers demanded by the theory could be prepared in each case.

Conventions Used in Writing Formulas. As a matter of convenience, organic chemists have agreed to write their structural formulas in a condensed form, and the student would do well to master the conventions employed. The extended formulas of the butyl alcohols which are printed on page 10 on the left (sometimes called spider web formulas) are often useful at first in understanding the theory of linkages, but the student should use them as little as possible. The conventions used will be apparent from these examples; the usual formula is printed on the right. It should be noted that we write the group of carbon and hydrogen atoms after each other, in straight chain compounds and show their connection by bonds in branched chain compounds; other groups or atoms follow the hydrogen.

Naming Alcohols. Since there are only two isomeric propyl alcohols, it is possible to refer to them by using the terms *normal* and *iso*. By using the word normal to indicate a straight chain (abbreviated by *n-*, thus *n*-propyl alcohol) and *iso* to denote a forked chain, a fairly satisfactory method of naming the butyl alcohols can also be developed. Furthermore, an examination of the various butyl alcohols will show that they can be arranged into three groups. Those having the grouping $-CH_2OH$ which are called primary alcohols, those having the grouping $>CHOH$ which are called secondary, and those with the grouping $\searrow COH$ which are designated as tertiary alcohols. We shall postpone any considerations of a more complete system of nomenclature until the next chapter.

The names of the first five normal straight chain alcohols are