



## PREFACE

This book is a complete revision of the 1939 edition of *The Chemistry of Organic Compounds*; it is the joint product of two authors. We have felt that the time has come in teaching organic chemistry to alter in certain respects the conventional approach to reaction rates and equilibria. Practicing organic chemists will agree that these two subjects lie at the root of any realistic discussion of the behavior of the carbon compounds in the laboratory or in industry. Today when so many industrial processes depend on the ability of the chemist to operate at high temperatures, the relation between temperature and equilibrium constant is particularly important. We have therefore introduced gradually the basic physicochemical principles underlying chemical equilibria. We have done this without introducing those considerations in physical chemistry which are associated with the terms free energy and entropy. We believe that with the aid of certain rules and principles carefully stated in the text it is possible for even a beginning student to understand in a general way how energy relations control equilibria. Of course underlying such a presentation as we have just described there must be constant emphasis on the difference between rates and equilibria. This is a theme recurring throughout the book.

The introduction of new physicochemical concepts and data (including an expansion of the earlier treatment of the electronic theory of valence and of resonance) has been accomplished, we believe, without interfering with the arrangement of material which characterized the earlier editions. We have retained the basic idea that new material should be introduced on a sound pedagogical rather than a formal basis. In bringing the whole treatment up to date much new material from industrial chemistry has been introduced. Recent developments connected with the aliphatic hydrocarbons in particular have been included because these developments are of such importance in the preparation of liquid fuels and synthetic rubber. In spite of all the new material, the book is not materially larger than the previous edition. We have condensed the treatment of certain less important topics and have eliminated a few minor topics.

Throughout the book small changes in the presentation have been made in order to gain effectiveness.

The rapid expansion of the fields of biochemistry and pharmacology in the last decade poses a serious problem to the authors of a book of this type. It is impossible to include all the compounds which are of interest to the general public in connection with medicine and public health. Furthermore we doubt the educational value of the mere inclusion of structural formulas of a great variety of complex substances. We have tried to cover the major topics and to relate the chemistry of the compounds considered to the principles expounded in this book. Considerable space has been devoted to a few basic biological processes which have been elucidated sufficiently to enable a fairly complete account of the mechanism to be presented. Other processes where our ignorance is still very great have only been mentioned. Even for students who are going on to specialize in biology or medicine we think this choice of material provides the soundest basis.

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## 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.

While organic chemistry, today, is still concerned with compounds produced by plants and animals and is thus closely allied with biochemistry, it also deals with many other substances. Many of these are derived from petroleum and coal tar and are of great industrial importance. Thus the work of the organic chemist touches that of the biologist and the doctor on the one hand, and that of the chemical engineer in such industries as petroleum, rubber, and the coal-tar dyes and drugs on the other.

Many of those who make the acquaintance of organic chemistry on their way to other callings will be impressed chiefly by its applications to medicine and technology. These applications are possible, however, only as a result of the remarkable development of the science of organic chemistry in the last hundred years. This scientific development is to many as remarkable an achievement as are the technical applications. The two cannot be separated, however, and both have been kept in mind in writing this book.

## Chapter 1

### 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. Let us center our attention first 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  $78^{\circ}$ ; 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

<i>Element</i>	<i>Per Cent</i>	<i>Atomic Weight</i>	<i>Atomic Ratio</i>	<i>Ratio of Atoms</i>
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 we must determine its molecular weight. This is readily done by finding the density of the vapor or by noting the depression of the freezing point (or elevation of the boiling point) of a suitable solvent in which a weighed amount of the substance has been dissolved. 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  $\text{NH}_3$ ,  $\text{HCl}$ ,  $\text{H}_2\text{O}_2$ . These are called *molecular formulas*. Quite the reverse is true 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 related to the ether used in anesthesia, has exactly the same percentage composition and the same molecular weight as ethyl alcohol. Therefore it must be also represented by the formula  $\text{C}_2\text{H}_6\text{O}$ . There can be no doubt about the difference between these compounds, since one is a liquid boiling at  $78^\circ$  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.*<sup>1</sup>

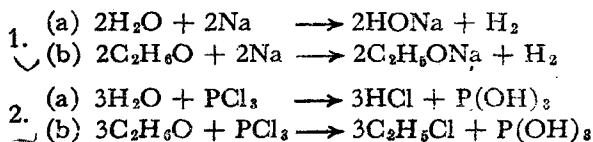
**The Necessity for Structural Formulas.** Isomerism is very common in organic chemistry. For example, twenty-six isomers with the formula  $\text{C}_6\text{H}_{14}\text{O}$  have been prepared and their properties recorded. It is obvious that unless the organic chemist is able to write formulas which 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 introduction 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.<sup>1</sup>

**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 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 his formulation must represent the structure of the compound. Let us see how this may be done for ethyl alcohol.

<sup>1</sup> Friedrich August Kekulé (1829-1896). Professor of Chemistry at the University of Bonn.



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



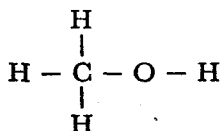
It will be noticed that in the first two reactions, sodium hydroxide and a compound,  $\text{C}_2\text{H}_5\text{ONa}$  (sodium ethoxide), are formed by the replacement of one hydrogen atom of the molecule. In the second set of reactions, the phosphorus atom becomes attached to an hydroxyl group which in one case has been removed from water and in the other must come from the alcohol. The facts of inorganic chemistry show that the atoms in the water molecule must be arranged  $\text{H} - \text{O} - \text{H}$ ; the existence of the hydroxyl group ( $\text{OH}$ ) is evident. Since the phosphorous acid is formed from alcohol as well as from water (equations 2a, 2b), 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 (commonly called *wood alcohol*) has the molecular formula  $\text{CH}_4\text{O}$  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,  $\text{P(OH)}_3$ , we conclude that it also contains an hydroxyl group. We may, therefore, write the formulas  $\text{CH}_3\text{OH}$  for methyl alcohol and  $\text{C}_2\text{H}_5\text{OH}$  for ethyl alcohol. These formulas, however, are still not perfectly clear. How are the carbon and hydrogen atoms arranged in the groups  $\text{CH}_3$  and  $\text{C}_2\text{H}_5$ ?

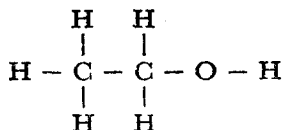
**Structure of Methyl and Ethyl Alcohols.** The founders of the structural theory assumed that in organic compounds carbon always has a valence of four, oxygen of two, and hydrogen of one. With this as a basis the question just raised concerning the structure of methyl alcohol is easily answered. *There is only one possible arrangement of the atoms in  $\text{CH}_3\text{OH}$* , and that is, 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** or **graphical formula**.

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



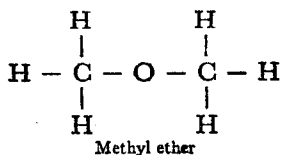
each hydrogen atom. Applying the same principles, the complete structural formula of ethyl alcohol is



By attempting to write a variety of structural arrangements for ethyl alcohol it is easy to convince oneself that there is only one way of writing  $\text{C}_2\text{H}_5\text{OH}$ , *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 hydrogen atoms, 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 very unusual substances. 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.



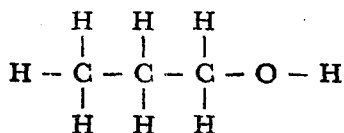
**The Alcohols as a Class of Compounds.** Besides the well-known methyl and ethyl alcohols, there are a great many other substances which are called *alcohols* by the organic chemist. They all show the reactions which we have learned are characteristic of an hydroxyl group, and their structural formulas, therefore, must show the linkage  $-\text{O}-\text{H}$ . 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	$\text{CH}_3\text{OH}$		One substance
Ethyl alcohol	$\text{C}_2\text{H}_5\text{OH}$	$\text{>CH}_2$	One substance
Propyl alcohols	$\text{C}_3\text{H}_7\text{OH}$	$\text{>CH}_2$	Two substances
Butyl alcohols	$\text{C}_4\text{H}_9\text{OH}$	$\text{>CH}_2$	Four substances
Amyl alcohols	$\text{C}_5\text{H}_{11}\text{OH}$	$\text{>CH}_2$	Eight substances

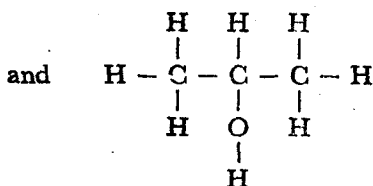
We may define an homologous series as <sup>a</sup>a series of similar compounds in which *each member differs from the one below it and the one above it by  $\text{CH}_2$* . It will be noted that all the compounds of this series correspond to a **general formula**  $\text{C}_n\text{H}_{2n+1}\text{OH}$ . 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  $\text{C}_3\text{H}_7\text{OH}$  in the homologous series of alcohols, we find that *more than one substance is represented by the formula*. In other words, a 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



Normal propyl alcohol

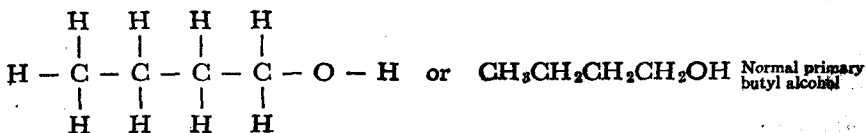


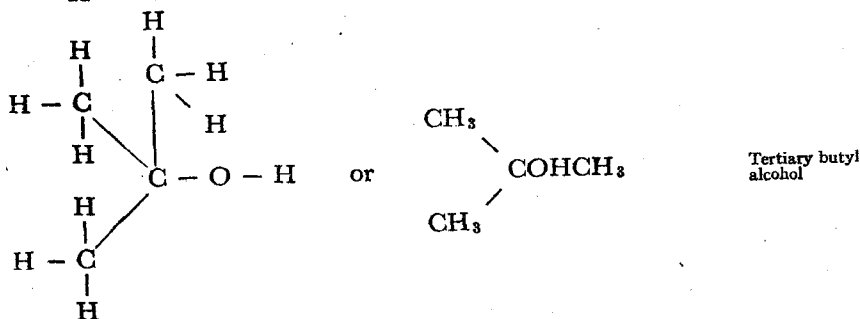
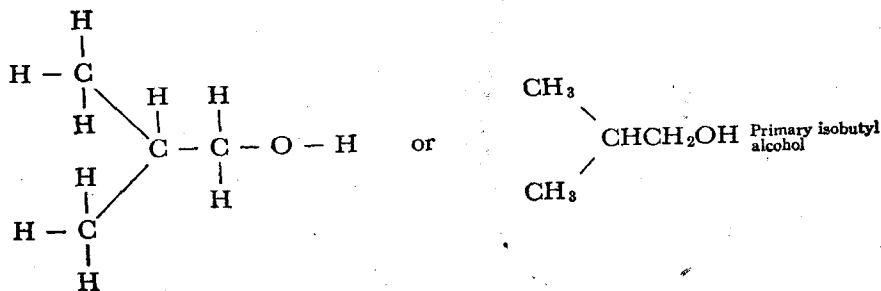
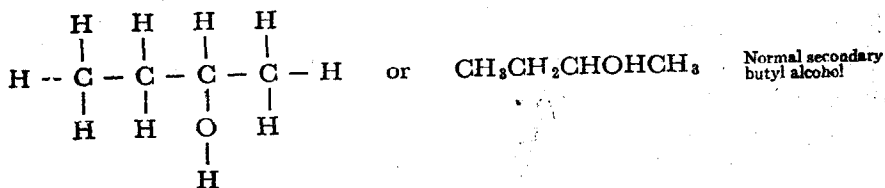
Isopropyl alcohol

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  $98^\circ$ , the other is isopropyl alcohol which boils at  $82^\circ$ .

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 so will be most quickly and convincingly demonstrated 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 cannot 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  $180^\circ$ . The arrangement with the hydroxyl group in the center is different. This cannot be superimposed on the other formula because the hydroxyl group is attached to a carbon atom in the middle of the chain. Thus, in one formula we have the group  $\text{>CHOH}$ , in the other  $-\text{CH}_2\text{OH}$ .

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





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 predictions 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 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 8 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.

**Three-Dimensional Models.** The theory of linkages was developed to explain the isomerism of organic compounds. The structures of many substances were deduced from their reactions and transformations very much as we have done for ethyl alcohol and dimethyl ether. In the last twenty years evidence as to the correctness of these conclusions of the organic chemist has accumulated as a result of the labors of physicists. For example, a measurement of the diffraction of X rays by crystals enables physicists to calculate the distances between the centers of the atoms in various compounds. Similarly, a study of the diffraction of an electron beam by gases leads to conclusions as to the interatomic distances in the molecules of which the gas is composed. As a result of all these studies we can construct three-dimensional models of the simple organic molecules with considerable assurance. Such physical measurements have proved a very valuable aid to the organic chemist in interpreting purely chemical evidence. Nowadays one should get used to thinking of formulas in three-dimensional terms early in the course. This can be done best by handling models built to scale. On paper we often depict the carbon atoms in such models as regular tetrahedra since the measurements of the physicists have shown what the chemist long suspected, that the four carbon valences were at angles to each other which corresponded to such an arrangement. The angle of the two valences of oxygen in both alcohol and ether is approximately  $111^\circ$ . The interatomic distances are very nearly constant and those we are interested in here are:

## INTERATOMIC DISTANCE

## SUM OF RADII OF ATOMS

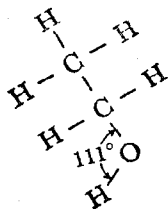
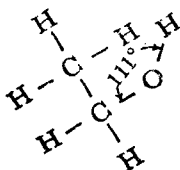
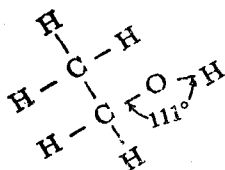
C - C	1.54 Å <sup>1</sup>	0.77 + 0.77 Å
C - H	1.07 Å	0.77 + 0.30 Å
C - O	1.43 Å	0.77 + 0.66 Å
O - H	0.96 Å	0.66 + 0.30 Å

<sup>1</sup> The Ångstrom unit, Å, is one one hundred millionth ( $10^{-8}$ ) of a centimeter.

Such distances would result if the atomic radii were essentially the same in all related compounds and were as follows: carbon 0.77, oxygen 0.66, hydrogen 0.30. We shall see later that these radii are modified in certain types of compounds.

Construction of three-dimensional models will show that in all but the simplest compounds there are many ways in which the atoms in a chain may be placed with regard to each other. In the solid state there is one stable relation which is believed to correspond in most compounds to a zigzag chain. In the liquid form, in solution, or in gases, however, the molecules through thermal agitation take various shapes though certain configurations may be more favored than others. But the different shapes into which the same model can be twisted *do not correspond to different isomers*. This is an important point for the student to understand at the outset in considering the spatial arrangements of the atoms in a molecule.

For example, the different spatial relationships of the atoms in ethyl alcohol indicated below do not correspond to different substances. The energy required to change any one arrangement into another (a change which involves no breaking of bonds, only rotation about bonds) is so slight that all the molecules in a gas or a liquid or solution would never be lined up in this one way; rather they would be distributed at random among the many different spatial relations which would result by twisting the atoms with reference to each other.



These are three of the many spatial relationships of the atoms in a molecule of  $C_2H_5OH$ . They do not correspond to different substances. All the atomic distances and angles are the same, of course.

Because a model may be twisted into so many shapes, it is difficult to depict it on paper without implying that one relationship is more important than another. Therefore, we shall use pictures of three-dimensional models only occasionally and continue to use the two-dimensional formulas to represent the structures of almost all the organic compounds considered in this book. It is essential, however,

for the student to construct three-dimensional models for himself and to learn to visualize organic structures in three dimensions.

**Classification of 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 the prefix *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 the three following groups: (1) those having the grouping  $-\text{CH}_2\text{OH}$  which are called *primary* alcohols; (2) those having the grouping  $\text{>CHOH}$  which are called *secondary*; (3) those with the grouping  $\text{>COH}$  which are designated as *tertiary* alcohols.

**Naming Primary Alcohols.** The first five normal straight-chain alcohols are named in the table below. The alcohols with six or more carbon atoms are named with a Greek prefix indicating the number of carbon atoms. For example, the normal alcohol  $\text{C}_{10}\text{H}_{21}\text{OH}$  is *n*-decyl alcohol. The general formula for each group of alcohols is easily written by recalling that a general formula for the series is  $\text{C}_n\text{H}_{2n+1}\text{OH}$ .

**Naming Secondary and Tertiary Alcohols.** Where there are only a few isomers, it is possible to find simple names for the different isomeric alcohols as is done with the butyl alcohols given in the table on page 14. There is only one secondary and only one tertiary butyl alcohol. But higher in the series we get into difficulty. There are three secondary alcohols isomeric with *n*-amyl alcohol,  $\text{C}_5\text{H}_{11}\text{OH}$ . How are they to be named?

A convenient method of naming alcohols is to regard them as though they were built up by taking methyl alcohol,  $\text{CH}_3\text{OH}$ , and replacing one or more of the hydrogens of the  $\text{CH}_3$  by groups of carbon and hydrogen atoms called *alkyl groups*. These groups in turn are named from the alcohol to which they are related. Thus the  $\text{CH}_3$  group of methyl alcohol is known as the *methyl group*, the  $\text{CH}_3\text{CH}_2$  or  $\text{C}_2\text{H}_5$  of ethyl alcohol is known as the *ethyl group*, and so on.

The following are the common alkyl groups.

$\text{CH}_3-$

$\text{CH}_3\text{CH}_2-$  or  $\text{C}_2\text{H}_5-$

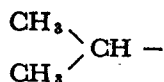
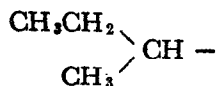
$\text{CH}_3\text{CH}_2\text{CH}_2-$

Methyl group

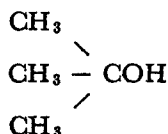
Ethyl group

Normal propyl group

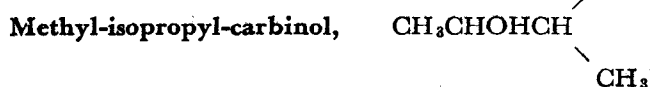


**Isopropyl group****Sec.-butyl group**

When we consider complex alcohols as derivatives of methyl alcohol,  $\text{CH}_3\text{OH}$ , this latter substance is called *carbinol*. We then name the alkyl groups which are attached to the carbon atom which holds the OH group. Such alkyl groups are *substituents* since they may be regarded as having been substituted in place of hydrogen atoms of the parent substance,  $\text{CH}_3\text{OH}$  or carbinol.

**Trimethyl-carbinol is:**This is also written as  $(\text{CH}_3)_3\text{COH}$ .

The three isomeric secondary amyl alcohols are:

which is also written  $\text{CH}_3\text{CHOHCH}(\text{CH}_3)_2$ ; and

For the sake of clarity, where there are a number of different alkyl groups hyphens are often used to separate the prefixes. It is equally correct to write an unhyphenated word, e.g., methylisopropylcarbinol; it is usually considered incorrect, however, to write methyl isopropyl carbinol. In this book we shall use hyphens whenever there are prefixes representing several substituents.

**Physical Properties of Alcohols.** If we compare the boiling points of the normal primary alcohols in the homologous series  $\text{C}_n\text{H}_{2n+1}\text{OH}$ , a very interesting gradual and regular change is noticed. This is illustrated below.