

INTRODUCTION.

WHAT IS ORGANIC CHEMISTRY ALL ABOUT?

You now are starting the study of organic chemistry, which is the chemistry of compounds of carbon. In this introductory chapter, we will tell you something of the background and history of organic chemistry, something of the problems and the rewards involved, and something of our philosophy of what is important for you to learn so that you will have a reasonable working knowledge of the subject, whether you are just interested in chemistry or plan for a career as a chemist, an engineer, a physician, a biologist, and so on. The subject is very large; more than two million organic compounds have been isolated or prepared and characterized, yet the number of guiding principles is relatively small. You certainly will not learn everything about organic chemistry from this book, but with a good knowledge of the guiding principles, you will be able later to find out what you need to know either from the chemical literature, or directly by experiment in the laboratory.

Unfortunately, learning about and learning how to use organic chemistry is not a straightforward process, wherein one step leads to another in a simple, logical way like Euclidean geometry. A more realistic analogy would be to consider yourself thrust into and required to deal successfully with a sizable group of strangers speaking a new and complex language. In such a situation, one has to make many decisions—how much of the language to learn at the

outset? Which people are the best to interact with first? Which will be the most important to know in the long run? How well does one have to know each person? How much does one have to know about the history of the group to understand their interactions? These are difficult questions, and a period of confusion, if not anxiety, is expected in any attempt to complete a task of this kind in a set, brief period of time. Clearly, it would be difficult to learn all at once the language, the people, and the interactions between them. Nonetheless, this is pretty much what is expected of you in learning organic chemistry.

A number of approaches have been devised to help you become familiar with and use organic chemistry. In terms of our analogy, one way is to learn the language, then the relationships between the people, and finally, well prepared, to proceed to interact with the people singly and then in groups. Such an approach may be logical in concept, but is not to everyone's taste as a way to learn. Many of us do better with an interactive approach, where language, relationships, and people are worked out more or less in concert, with attendant misunderstandings and ambiguities.

What we will try to do is to introduce some of the important basic concepts and the elements of the language of organic chemistry, then show how these are used in connection with various classes of compounds. The initial round will be a fairly extensive one and you should not expect to be able to master everything at once. This will take practice and we will provide opportunity for practice.

One of the appealing yet bothersome features of modern organic chemistry is its extraordinary vitality. Unlike Euclidean geometry or classical mechanics, it is evolving rapidly and many of the concepts introduced in this book are either new or have been drastically modified in the past ten years. Every issue of the current chemical journals has material of such basic interest that one would like to include it in an introductory course. Truly, those who write organic textbooks write on water, with no hope of producing *the* definitive book. Things just change too fast. Despite this, one of the great ideas of modern civilization, namely that organic compounds can be described in terms of more or less simple three-dimensional molecular structures with atoms held together by chemical bonds, has persisted for more than one hundred years and seems unlikely to be superseded, no matter how much it is refined and modified.

1-1 A BIT OF HISTORY

You may not be much interested in the way that organic chemistry developed, but if you skip to the next section without reading further, you will miss some of the flavor of a truly great achievement—of how a few highly creative chemists were able, with the aid of a few simple tools, to determine the structures of molecules, far too small and too elusive to be seen individually with the finest optical microscope, manifesting themselves only by the collective behavior of at least millions of millions at once.

Try to visualize the problems confronting the organic chemist of 100 years ago. You will have no more than reasonably pure samples of organic compounds, the common laboratory chemicals of today, glassware, balances, thermometers, means of measuring densities, and a few optical instruments. You also will have a relatively embryonic theory that there are molecules in those bottles and that one compound differs from another because its molecules have different members or kinds of atoms and different arrangements of bonds. Your task will be to determine what kinds and what numbers of atoms they contain, that is, to determine their *molecular formulas*. Obviously, a compound with formula C_2H_6O and one with $C_2H_6O_2$ are not the same compound. But suppose two compounds from different sources both are C_2H_6O . To decide whether these are the *same or different* you could smell them (far better to *sniff* than to inhale), taste them (emphatically not recommended), see if they have the same appearance and viscosity (if liquids), or use more sophisticated criteria: boiling point, melting point, density, or refractive index. Other possibilities would be to see if they both have the same solubility in water or other solvents and whether they give the same reaction products with various reagents. Of course, all this gets a bit tough when the compounds are not pure and no good ways are available to purify them, but that is part of the job. Think about how you might proceed.

In retrospect it is surprising that in less than fifty years an enormous, even if incomplete, edifice of structural organic chemistry was constructed on the basis of the results of chemical reactions without determination of a single bond distance, and with no electronic theory as a guide. Interestingly, all of the subsequent developments of the quantum mechanical theory of chemical bonds has not altered this edifice in significant ways. Indeed, for a long time, a goal of molecular quantum mechanics was simply to be able to corroborate that when an organic chemist draws a single line between two carbon atoms to show that they are bonded, he in fact knows what he is doing. And that when he draws two (or three) bonds between the carbons to indicate a double (or triple) bond, quantum mechanics supports this also as a valid idea.

Furthermore, when modern tools for determining organic structures that involve actually measuring the distances between the atoms became available, these provided great convenience, but no great surprises. To be sure, a few structures turned out to be incorrect because they were based on faulty or inadequate experimental evidence. But, on the whole, the modern three-dimensional representations of molecules that accord with actual measurements of bond distances and angles are in no important respect different from the widely used three-dimensional ball-and-stick models of organic molecules, and these, in essentially their present form, date from at least as far back as E. Paterno, in 1869.

How was all of this achieved? Not by any very simple process. The essence of some of the important ideas follow, but it should be clear that what actually took place was far from straightforward. A diverse group of people was involved; many firmly committed to, if not having a vested interest in, earlier working hypotheses or *paradigms* that had served as useful bases for earlier experimentation, but were coming apart at the seams because they could

not accommodate the new facts that kept emerging. As is usual in human endeavors, espousal of new and better ideas did not come equally quickly to all those used to thinking in particular ways. To illustrate, at least one famous chemist, Berthelot, still used HO as the formula for water twenty-five years after it seemed clear that H₂O was a better choice.

1-1A Determination of Molecular Formulas

Before structures of molecules could be established, there had to be a means of establishing molecular formulas and for this purpose the key concept was Avogadro's hypothesis, which can be stated in the form "equal volumes of gases at the same temperature and pressure contain the same number of molecules." Avogadro's hypothesis allowed assignment of *relative* molecular weights from measurements of gas densities. Then, with analytical techniques that permit determination of the weight percentages of the various elements in a compound, it became possible to set up a self-consistent set of relative atomic weights.¹ From these and the relative molecular weights, one can assign molecular formulas. For example, if one finds that a compound contains 22.0% carbon (atomic weight = 12.00), 4.6% hydrogen (atomic weight = 1.008), and 73.4% bromine (atomic weight = 79.90), then the ratios of the numbers of atoms are $(22.0/12.00):(4.6/1.008):(73.4/79.90) = 1.83:4.56:0.92$. Dividing each of the last set of numbers by the smallest (0.92) gives 1.99:4.96:1 \cong 2:5:1, which suggests a molecular formula of C₂H₅Br, or a multiple thereof. If we know that hydrogen gas is H₂ and has a molecular weight of $2 \times 1.008 = 2.016$, we can compare the weight of a given volume of hydrogen with the weight of the same volume of our unknown in the gas phase at the same temperature and pressure. If the experimental ratio of these weights turns out to be 54, then the molecular weight of the unknown would be $2.016 \times 54 = 109$ and the formula C₂H₅Br would be correct (see Exercise 1-15).

1-1B Valence

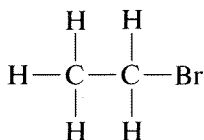
If we assume that the molecule is held together by chemical bonds, without knowing more, we could write numerous structures such as H—H—H—H—H—C—C—Br, H—C—Br—H—H—C—H—H, and so on. However, if we also know of the existence of stable H₂, but not H₃; of stable Br₂, but not of Br₃; and of stable CH₃Br, CH₂Br₂, CHBr₃, and CBr₄, but not of CH₄Br, CHBr, CBr, and so on, a pattern of what is called *valence* emerges.

¹We will fess up here the long and important struggle of getting a truly self-consistent table of atomic weights. If you are interested in the complex history of this problem and the clear solution to it proposed by S. Cannizzaro in 1860, there are many accounts available in books on the history of chemistry. One example is J. R. Partington, *A History of Chemistry*, Vol. IV, Macmillan, London, 1964. Relative atomic weights now are based on ¹²C = 12 (exactly).

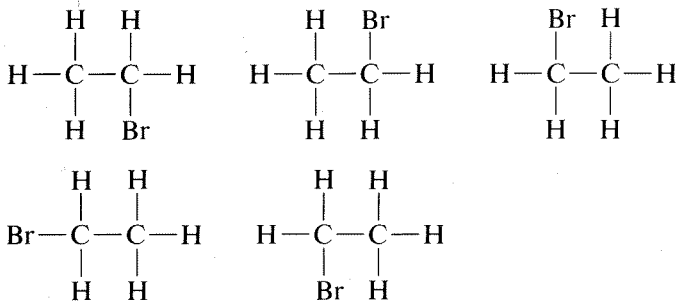
It will be seen that the above formulas all are consistent if hydrogen atoms and bromine atoms form just *one* bond (are univalent) while carbon atoms form *four* bonds (are tetravalent). This may seem almost naively simple today, but a considerable period of doubt and uncertainty preceded the acceptance of the idea of definite valences for the elements that emerged about 1852.

1-1C Structural Formulas

If we accept hydrogen and bromine as being univalent and carbon as tetravalent, we can write



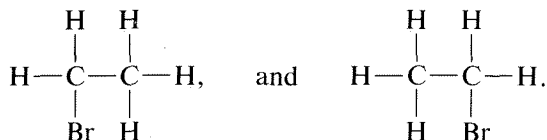
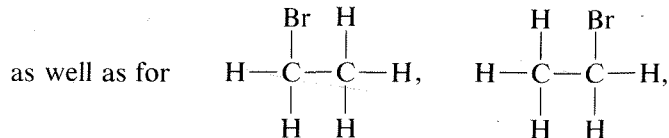
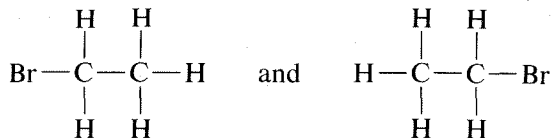
as a structural formula for $\text{C}_2\text{H}_5\text{Br}$.² However, we also might have written



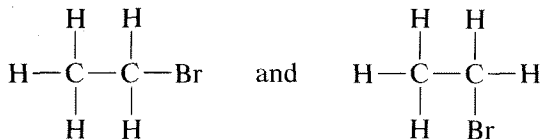
There is a serious problem as to whether these formulas represent the *same* or *different* compounds. All that was known in the early days was that every purified sample of $\text{C}_2\text{H}_5\text{Br}$, no matter how prepared, had a boiling point of 38°C and density of 1.460 g ml^{-1} . Furthermore, all looked the same, all smelled the same, and all underwent the same chemical reactions. There was no evidence that $\text{C}_2\text{H}_5\text{Br}$ was a mixture or that more than one compound of this formula could be prepared. One might conclude, therefore, that all of the structural formulas above represent a single substance even though they superficially, at least, look different. Indeed, because $\text{H}-\text{Br}$ and $\text{Br}-\text{H}$ are two different ways of *writing* a formula for the same substance, we suspect

²Formulas such as this appear to have been used first by Crum Brown, in 1864, after the originators of structural formulas, A. Kekulé and A. Couper (1858), came up with rather awkward, impractical representations. It seems incredible today that even the drawing of these formulas was severely criticized for many years. The pot was kept boiling mainly by H. Kolbe, a productive German chemist with a gift for colorful invective and the advantage of a podium provided by being editor of an influential chemical journal.

that the same is true for



There are, though, two of these structures that could be different from one another, namely

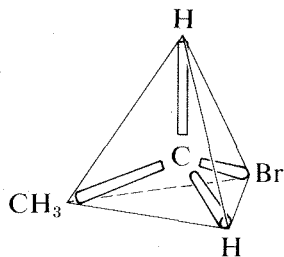


In the first of these, CH_3- is located opposite the $\text{Br}-$ and the $\text{H}-$'s on the carbon with the Br also are opposite one another. In the second formula, CH_3- and $\text{Br}-$ are located *next* to each other as are the $\text{H}-$'s on the same carbon. We therefore have a problem as to whether these two different formulas also represent different compounds.

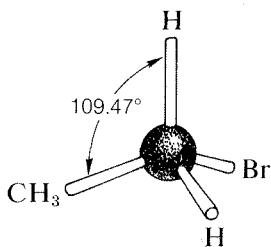
1-1D Tetrahedral Carbon

A brilliant solution to the problem posed in the preceding section came in 1874 when J. H. van't Hoff proposed that all four valences of carbon are equivalent and directed to the corners of a regular tetrahedron.³ If we redraw the structures for $\text{C}_2\text{H}_5\text{Br}$ as **1**, we see that there is only *one* possible arrangement and, contrary to the impression we got from our earlier structural formulas, the bromine is *equivalently* located with respect to each of the hydrogens on the same carbon.

³The name of J. A. Le Bel also is associated with this particular idea, but the record shows that Le Bel actually opposed the tetrahedral formulations, although, simultaneously with van't Hoff, he made a related very important contribution, as will be discussed in Chapter 5.



1

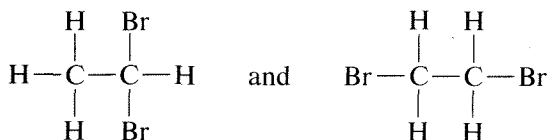


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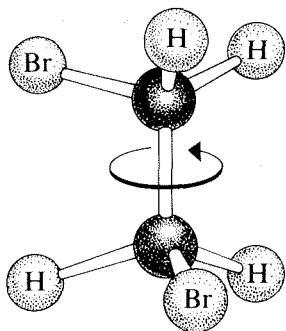
A convenient way of representing organic molecules in three dimensions, which shows the tetrahedral relationships of the atoms very clearly, uses the so-called ball-and-stick models **2**. The sticks that represent the bonds or valences form the tetrahedral angles of 109.47° .

1-1E The Question of Rotational Isomers

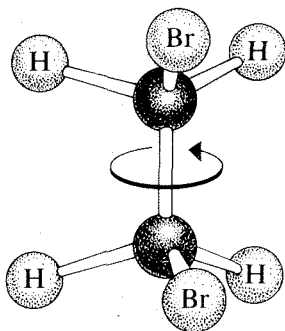
The tetrahedral carbon does not solve all problems without additional postulates. For example, there are two different compounds known with the *same* formula $C_2H_4Br_2$. These substances, which we call **isomers**, can be reasonably written as



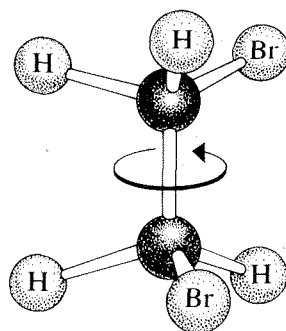
However, ball-and-stick models suggest further possibilities for the second structure, for example **3**, **4**, and **5**:



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4



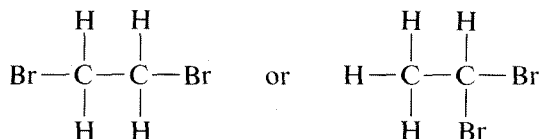
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This is a problem apparently first clearly recognized by Paterno, in 1869. We call these rotational (or conformational) isomers, because one is converted to another by rotation of the halves of the molecule with respect to one another, with the C–C bond acting as an axle. If this is not clear, you should make a ball-and-stick model and see what rotation around the C–C bond does to the relationships between the atoms on the carbons.

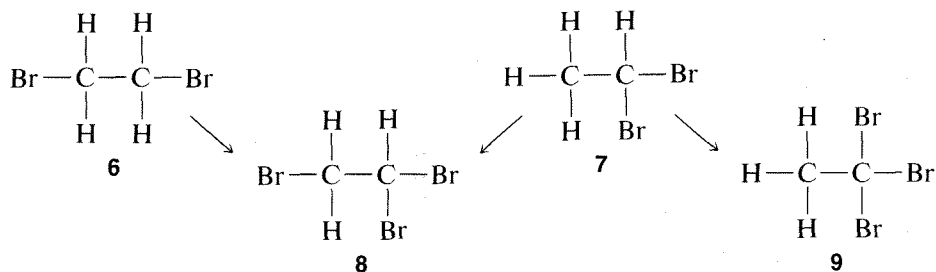
The difficulty presented by these possibilities finally was circumvented by a brilliant suggestion by van't Hoff of "free rotation," which holds that isomers corresponding to different rotational angles, such as **3**, **4**, and **5**, do not have separate stable existence, but are interconverted by rotation around the C–C bond so rapidly that they are indistinguishable from one another. Thus there is only *one* isomer corresponding to the different possible rotational angles and a total of only *two* isomers of formula $C_2H_4Br_2$. As we shall see, the idea of free rotation required extensive modification some 50 years after it was first proposed, but it was an extremely important paradigm, which, as often happens, became so deeply rooted as to become essentially an article of faith for later organic chemists. Free rotation will be discussed in more detail in Chapters 5 and 27.

1-1F The Substitution Method for Proof of Structure

The problem of determining whether a particular isomer of $C_2H_4Br_2$ is



could be solved today in a few minutes by spectroscopic means, as will be explained in Chapter 9. However, at the time structure theory was being developed, the structure had to be deduced on the basis of chemical reactions, which could include either how the compound was formed or what it could be converted to. A virtually unassailable proof of structure, where it is applicable, is to determine how many different *substitution* products each of a given group of isomers can give. For the $C_2H_4Br_2$ pair of isomers, *substitution of a bromine for a hydrogen* will be seen to give only *one* possibility with one compound and *two* with the other:

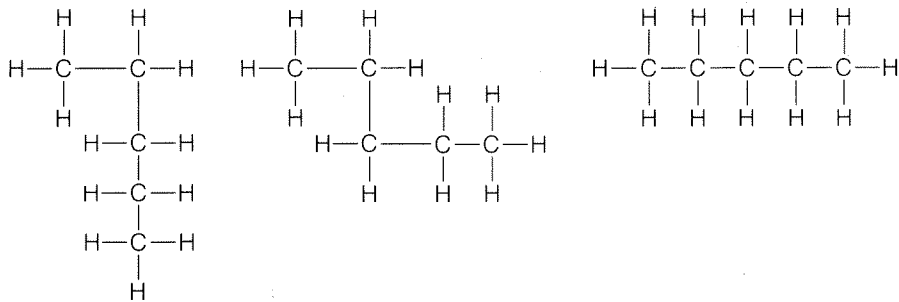


Therefore, if we have two bottles, one containing one $C_2H_4Br_2$ isomer and one the other and run the substitution test, the compound that gives only one product is **6** and the one that gives a mixture of two products is **7**. Further, it will be seen that the test, besides telling which isomer is **6** and which is **7**, establishes the structures of the two possible $C_2H_3Br_3$ isomers, **8** and **9**. Thus only **8** can be formed from both of the different $C_2H_4Br_2$ isomers whereas **9** is formed from only one of them.

Exercise 1-1 How many *different* isomers are there of $C_2H_2Br_4$? (Assume free-rotating tetrahedral carbon and univalent hydrogen and bromine.) How could one determine which of these isomers is which by the substitution method?

Exercise 1-2 A compound of formula $C_3H_6Br_2$ is found to give only a *single* substance, $C_3H_5Br_3$, on further substitution. What is the structure of the $C_3H_6Br_2$ isomer and of its substitution product?

Exercise 1-3 A compound of formula C_5H_{12} gives only a *single* monobromo substitution product of formula $C_5H_{11}Br$. What is the structure of this C_5H_{12} isomer? (Notice that carbon can form both continuous chains and branched chains. Also notice that structures such as the following represent the *same* isomer because the bonds to carbon are tetrahedral and are free to rotate.)

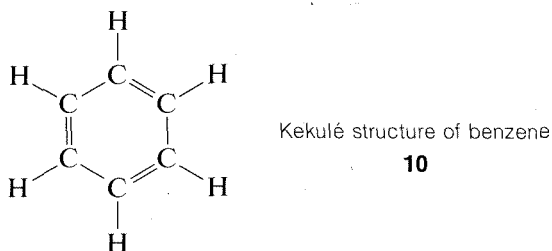


Exercise 1-4 A gaseous compound of formula C_2H_4 reacts with liquid bromine (Br_2) to give a single $C_2H_4Br_2$ compound. The $C_2H_4Br_2$ so formed gives only *one* $C_2H_3Br_3$ substitution product. Deduce the structure of C_2H_4 and the bromo compounds derived from it. (This was a key problem for the early organic chemists.)

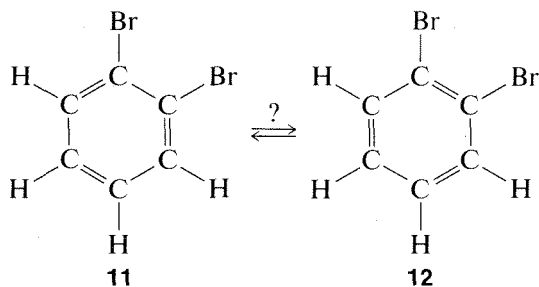
1-1G The Benzene Problem

There were already many interconversion reactions of organic compounds known at the time that valence theory, structural formulas, and the concept of the tetrahedral carbon came into general use. As a result, it did not take long before much of organic chemistry could be fitted into a concordant whole. One difficult problem was posed by the structures of a group of substitution

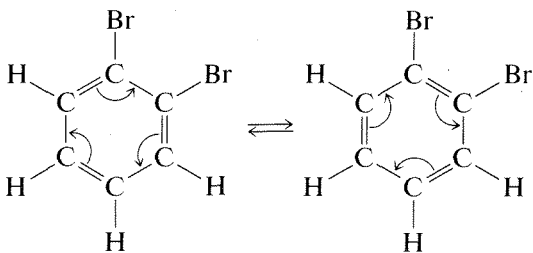
products of benzene, C_6H_6 , called "aromatic compounds," which for a long time defied explanation. Benzene itself had been prepared first by Michael Faraday, in 1825. An ingenious solution for the benzene structure was provided by A. Kekulé, in 1866, wherein he suggested (apparently as the result of a hallucinatory perception) that the six carbons were connected in a hexagonal ring with alternating single and double carbon-to-carbon bonds, and with each carbon connected to a single hydrogen, **10**:



This concept was controversial, to say the least, mainly on two counts. Benzene did not behave as expected, as judged by the behavior of other compounds with carbon-to-carbon double bonds and also because there should be two different dibromo substitution products of benzene with the bromine on adjacent carbons (**11** and **12**) but only one such compound could be isolated.

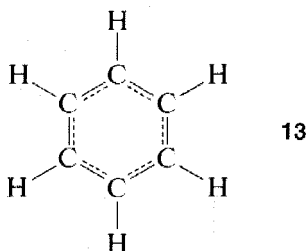


Kekulé explained the second objection away by maintaining that **11** and **12** were in rapid equilibrium through concerted bond shifts, in something like the same manner as the free-rotation hypothesis mentioned previously:



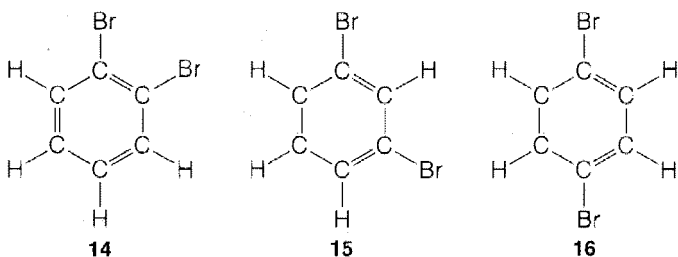
However, the first objection could not be dismissed so easily and quite a number of alternative structures were proposed over the ensuing years. The controversy was not really resolved until it was established that benzene is a

regular planar hexagon, which means that all of its C–C bonds have the same length, in best accord with a structure written not with double, not with single, but with 1.5 bonds between the carbons, as in **13**:



This, in turn, generated a massive further theoretical controversy over just how **13** should be interpreted, which, for a time, even became a part of “Cold-War” politics!⁴ We shall examine experimental and theoretical aspects of the benzene structure in some detail later. It is interesting that more than 100 years after Kekulé’s proposal the final story on the benzene structure is yet to be told.⁵

Exercise 1-5 Three different dibromobenzenes are known, here represented by just one of the Kekulé structures, **14**, **15**, and **16**:

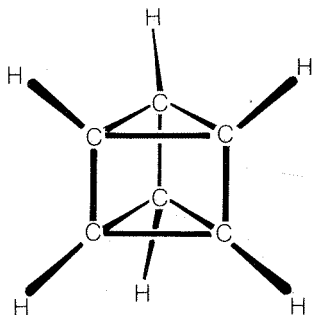
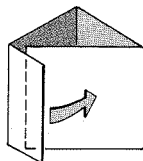


Show how the substitution method described in Section 1-1F could be used to determine which isomer is which and, in addition, establish the structures of the various possible tribromobenzenes of formula $C_6H_3Br_3$.

⁴The “resonance theory,” to be discussed in detail in Chapters 6 and 21, was characterized in 1949 as a physically and ideologically inadmissible theory formulated by “decadent bourgeois scientists.” See L. R. Graham, *Science and Philosophy in the Soviet Union*, Vintage Books, New York, 1974, Chapter VIII, for an interesting account of this controversy.

⁵Modern organic chemistry should not be regarded at all as a settled science, free of controversy. To be sure, personal attacks of the kind indulged in by Kolbe and others often are not published, but profound and indeed acrimonious differences of scientific interpretation exist and can persist for many years.

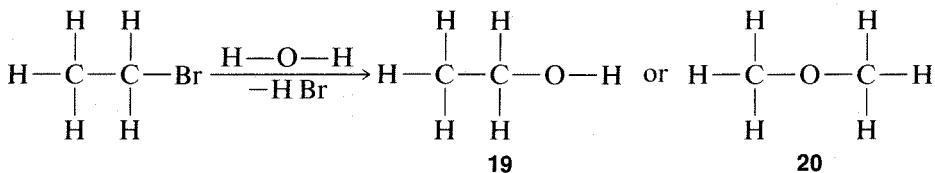
Exercise 1-6 The German chemist Ladenburg, in 1868, suggested the prismatic formula **17** for benzene:

**17****18**

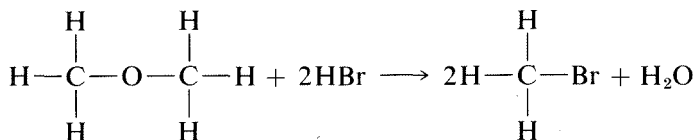
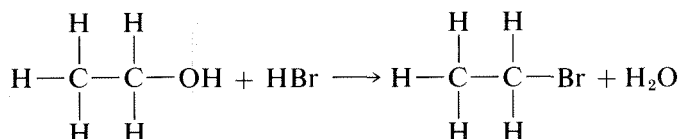
Assuming the C–C bonds of the prism all are the same length, determine how many mono-, di-, and tribromine-substituted isomers are possible for **17**. Compare the results with those expected for benzene with structure **13**. If you have molecular models of the ball-and-stick type, these will be very helpful. A simple alternative model for **17** would be a piece of stiff paper folded and fastened as in **18** to give a prism with three equal square faces.

1-1H Proof of Structure through Reactions

The combination of valence theory and the substitution method as described in Section 1-1F gives, for many compounds, quite unequivocal proofs of structure. Use of chemical transformations for proofs of structure depends on the applicability of a simple guiding principle, often called the “**principle of least structural change.**” As we shall see later, many exceptions are known and care is required to keep from making serious errors. With this caution, let us see how the principle may be applied. The compound C_2H_5Br discussed in Section 1-1A reacts slowly with water to give a product of formula C_2H_6O . The normal valence of oxygen is two, and we can write two, and only two, different structures, **19** and **20**, for C_2H_6O :

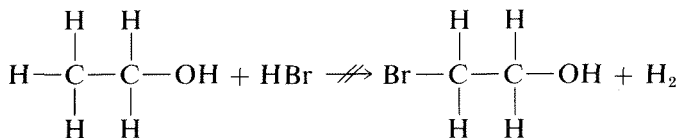


The principle of least structural change favors **19** as the product, because the reaction to form it is a simple replacement of bromine bonded to carbon by —OH, whereas formation of **20** would entail a much more drastic rearrangement of bonds. The argument is really a subtle one, involving an assessment of the reasonableness of various possible reactions. On the whole, however, it works rather well and, in the specific case of the C_2H_6O isomers, is strongly supported by the fact that treatment of **19** with strong hydrobromic acid (HBr) converts it back to C_2H_5Br . In contrast, the isomer of structure **20** reacts with HBr to form two molecules of CH_3Br :



In each case, C—O bonds are broken and C—Br bonds are formed.

We could conceive of many other possible reactions of C_2H_6O with HBr, for example

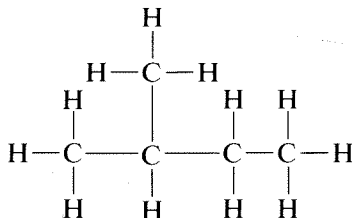


which, as indicated by $\not\Rightarrow$, does *not* occur, but hardly can be ruled out by the principle of least structural change itself. Showing how the probability of such alternative reactions can be evaluated will be a very large part of our later discussions.

Exercise 1-7 The compound C_2H_5Br reacts slowly with the compound CH_4O to yield a single substance of formula C_3H_8O . Assuming normal valences throughout, write structural formulas for CH_4O and the *three different* possible structural (not rotational) isomers of C_3H_8O and show how the principle of least structural change favors one of them as the reaction product. What would you expect to be formed from each of these three C_3H_8O isomers with strong hydrobromic acid?

1-1I Reactivity, Saturation, Unsaturation, and Reaction Mechanisms

The substitution method and the interconversion reactions discussed for proof of structure possibly may give you erroneous ideas about the reactions and reactivity of organic compounds. We certainly do not wish to imply that it is a simple, straightforward process to make all of the possible substitution products of a compound such as



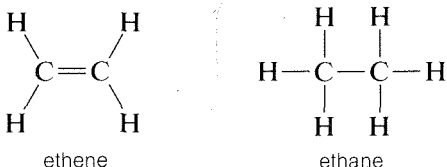
In fact, as will be shown later, direct substitution of bromine for hydrogen with compounds such as this does not occur readily, and when it does occur, the four possible substitution products indeed are formed, but in far from equal amounts because there are *differences in reactivity* for substitution at the different positions. Actually, some of the substitution products are formed only in very small quantities. Fortunately, this does not destroy the validity of the substitution method but does make it more difficult to apply. If direct substitution fails, some (or all) of the possible substitution products may have to be produced by indirect means. Nonetheless, you must understand that the success of the substitution method depends on determination of the total number of possible isomers—it does *not* depend on how the isomers are prepared.

Later, you will hear a lot about compounds or reagents being “reactive” and “unreactive.” You may be exasperated by the loose way that these terms are used by organic chemists to characterize how fast various chemical changes occur. Many familiar inorganic reactions, such as the neutralization of hydrochloric acid with sodium hydroxide solution, are extremely fast at ordinary temperatures. But the same is not often true of reactions of organic compounds. For example, $\text{C}_2\text{H}_5\text{Br}$ treated in two different ways is converted to gaseous compounds, one having the formula C_2H_6 and the other C_2H_4 . The C_2H_4 compound, **ethene**, reacts *very quickly* with bromine to give $\text{C}_2\text{H}_4\text{Br}_2$, but the C_2H_6 compound, **ethane**, does not react with bromine except at high temperatures or when exposed to sunlight (or similar intense light). The reaction products then are HBr and $\text{C}_2\text{H}_5\text{Br}$, and later, HBr and $\text{C}_2\text{H}_4\text{Br}_2$, $\text{C}_2\text{H}_3\text{Br}_3$, and so on.

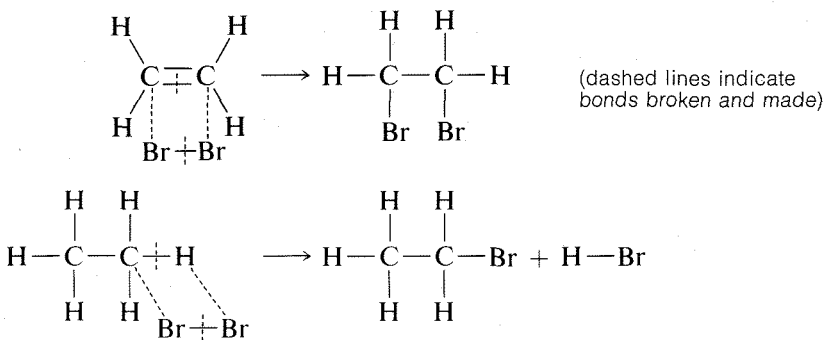
We clearly can characterize C_2H_4 as “reactive” and C_2H_6 as “unreactive” toward bromine. The early organic chemists also used the terms “unsaturated” and “saturated” for this behavior, and these terms are still in wide use today. But we need to distinguish between “unsaturated” and “reactive,” and between “saturated” and “unreactive,” because these pairs of terms are not synonymous. The equations for the reactions of ethene and ethane with

bromine are different in that ethene *adds* bromine, $C_2H_4 + Br_2 \longrightarrow C_2H_4Br_2$, whereas ethane *substitutes* bromine, $C_2H_6 + Br_2 \longrightarrow C_2H_5Br + HBr$.

You should reserve the term “unsaturated” for compounds that can, at least potentially, react by *addition*, and “saturated” for compounds that can only be expected to react by *substitution*. The difference between addition and substitution became much clearer with the development of the structure theory that called for carbon to be tetravalent and hydrogen univalent. Ethene then was assigned a structure with a carbon-carbon *double* bond, and ethane a structure with a carbon-to-carbon *single* bond:



Addition of bromine to ethene subsequently was formulated as breaking one of the carbon-carbon bonds of the double bond and attaching bromine to these valences. Substitution was written similarly but here bromine and a C-H bond are involved:

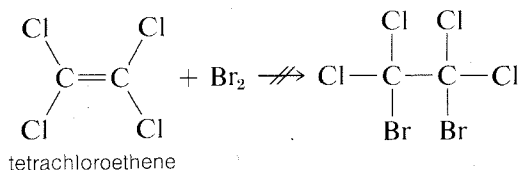


We will see later that the way in which these reactions actually occur is much more complicated than these simple equations indicate. In fact, such equations are regarded best as chemical accounting operations. The number of bonds is shown correctly for both the reactants and the products, and there is an indication of which bonds break and which bonds are formed in the overall process. However, do not make the mistake of assuming that no other bonds are broken or made in intermediate stages of the reaction.

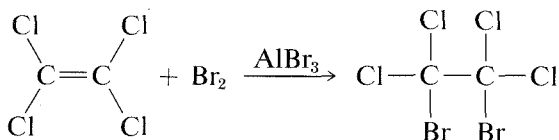
Much of what comes later in this book will be concerned with what we know, or can find out, about the **mechanisms** of such reactions—a reaction mechanism being the actual sequence of events by which the reactants become converted to the products. Such information is of extraordinary value in defining and understanding the range of applicability of given reactions for practical preparations of desired compounds.

The distinction we have made between “unsaturated” and “reactive” is best illustrated by a definite example. Ethene is “unsaturated” (and “reactive”)

toward bromine, but tetrachloroethene, C_2Cl_4 , will not add bromine at all under the same conditions and is clearly “unreactive.” But is it also “saturated”?



The answer is definitely no, because if we add a small amount of aluminum bromide, $AlBr_3$, to a mixture of tetrachloroethene and bromine, addition does occur, although sluggishly:



Obviously, tetrachloroethene is “unsaturated” in the sense it can undergo addition, even if it is unreactive to bromine in the absence of aluminum bromide.

The aluminum bromide functions in the addition of bromine to tetrachloroethene as a **catalyst**, which is something that facilitates the conversion of reactants to products. The study of the nature and uses of catalysts will concern us throughout this book. Catalysis is our principal means of controlling organic reactions to help form the product we want in the shortest possible time.

Exercise 1-8 There are a large number of known isomers of C_5H_{10} , and some of these are typically unsaturated, like ethene, while others are saturated, like ethane. One of the saturated isomers on bromine substitution gives only *one* compound of formula C_5H_9Br . Work out a structure for this isomer of C_5H_{10} and its monobromo substitution product.

1-2 WHAT PREPARATION SHOULD YOU HAVE?

We have tried to give you a taste of the beginnings of organic chemistry and a few of the important principles that brought order out of the confusion that existed as to the nature of organic compounds. Before moving on to other matters, it may be well to give you some ideas of what kind of preparation will be helpful to you in learning about organic chemistry from this textbook.

The most important thing you can bring is a strong desire to master the subject. We hope you already have some knowledge of general chemistry and

that you already will have had experience with simple inorganic compounds. That you will know, for example, that elemental bromine is Br_2 and a noxious, dark red-brown, corrosive liquid; that sulfuric acid is H_2SO_4 , a syrupy colorless liquid that reacts with water with the evolution of considerable heat and is a strong acid; that sodium hydroxide is NaOH , a colorless solid that dissolves in water to give a strongly alkaline solution. It is important to know the characteristics of acids and bases, how to write simple, balanced chemical reactions, such as $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$, and $2\text{NaOH} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$, what the concept of a mole of a chemical substance is, and to be somewhat familiar with the periodic table of the elements as well as with the metric system, at least insofar as grams, liters, and degrees centigrade are concerned. Among other things, you also should understand the basic ideas of the differences between salts and covalent compounds, as well as between gases, liquids, and solids; what a solution is; the laws of conservation of mass and energy; the elements of how to derive the Lewis electron structures of simple molecules such as $\text{H}:\ddot{\text{O}}:\text{H} = \text{water}$; that $PV = nRT$; and how to calculate molecular formulas from percentage compositions and molecular weights. We shall use no mathematics more advanced than simple algebra but we do expect that you can use logarithms and are able to carry through the following conversions forward and backward:

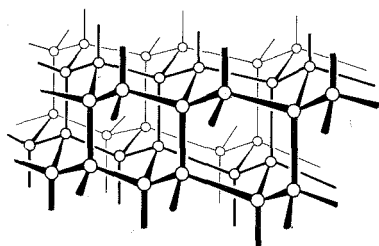
$$\log_{10} 510,000 = \log_{10} (5.1 \times 10^5) = 5.708$$

The above is an incomplete list, given to illustrate the level of preparation we are presuming in this text. If you find very much of this list partly or wholly unfamiliar, you don't have to give up, but have a good general chemistry textbook available for study and reference—and use it! Some useful general chemistry books are listed at the end of the chapter. A four-place table of logarithms will be necessary; a set of ball-and-stick models and a chemical handbook will be very helpful, as would be a small electronic calculator or slide rule to carry out the simple arithmetic required for many of the exercises.

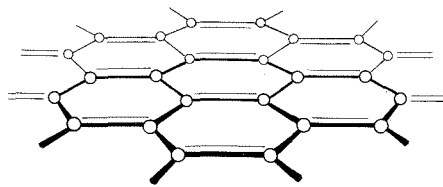
In the next section, we review some general chemistry regarding salt-like and covalent compounds that will be of special relevance to our later discussions.

1-3 WHY IS ORGANIC CHEMISTRY SPECIAL?

Let us consider some of the factors that make so much of chemistry center on a single element, carbon. One very important feature is that carbon-carbon bonds are strong, so long chains or rings of carbon atoms bonded to one another are possible. Diamond and graphite are two familiar examples, the diamond lattice being a three-dimensional network of carbon atoms, whereas graphite more closely resembles a planar network. The lubricating properties of graphite actually are related to its structure, which permits the planes to slide one past the other.



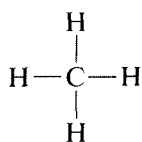
diamond lattice



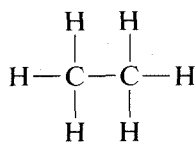
graphite

(O carbon atom)

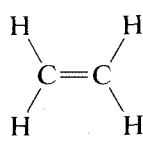
But carbon is not unique in forming bonds to itself because other elements such as boron, silicon, and phosphorus form strong bonds *in the elementary state*. The uniqueness of carbon stems more from the fact that it forms strong carbon-carbon bonds that also are strong when in combination with other elements. For example, the combination of hydrogen with carbon affords a remarkable variety of carbon hydrides, or **hydrocarbons** as they usually are called. In contrast, none of the other second-row elements except boron gives a very extensive system of stable hydrides, and most of the boron hydrides are much more reactive than hydrocarbons, especially to water and air.



methane



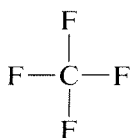
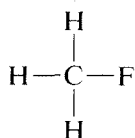
ethane



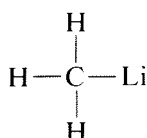
ethene

(typical hydrocarbons)

Carbon forms bonds not only with itself and with hydrogen but also with many other elements, including strongly electron-attracting elements such as fluorine and strongly electropositive metals such as lithium:

tetrafluoromethane
(carbon tetrafluoride)

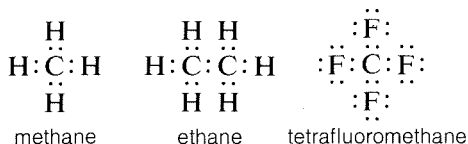
methyl fluoride



methyl lithium

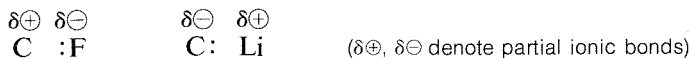
Why is carbon so versatile in its ability to bond to very different kinds of elements? The special properties of carbon can be attributed to its being a relatively small atom with four valence electrons. To form simple saltlike compounds such as sodium chloride, $\text{Na}^{\oplus}\text{Cl}^{\ominus}$, carbon would have to either lose the four valence electrons to an element such as fluorine and be converted to a quadripositive ion, $\text{C}^{4\oplus}$, or acquire four electrons from an element such as lithium and form a quadrinegative ion, $\text{C}^{4\ominus}$. Gain of four electrons would be energetically very unfavorable because of mutual repulsion between the electrons.

Customarily, carbon completes its valence-shell octet by *sharing* electrons with other atoms. In compounds with shared electron bonds (or covalent bonds) such as methane, ethane, or tetrafluoromethane, each of the bonded atoms including carbon has its valence shell filled, as shown in the following electron-pair or Lewis⁶ structures:



In this way, repulsions between electrons associated with completion of the valence shell of carbon are compensated by the electron-attracting powers of the positively charged nuclei of the atoms to which the carbon is bonded.

However, the electrons of a covalent bond are not necessarily shared equally by the bonded atoms, especially when the affinities of the atoms for electrons are very different. Thus, carbon-fluorine and carbon-lithium bonds, although they are not ionic, are polarized such that the electrons are associated more with the atom of higher electron affinity. This is usually the atom with the higher effective nuclear charge.



We see then a gradation from purely ionic to purely covalent bonding in different molecules, and this is manifest in their chemical and physical properties. Consider, for instance, the hydrides of the elements in the second horizontal row of the periodic table. Their melting and boiling points,⁷ where known, are given below.

	LiH	BeH ₂	BH ₃	CH ₄	NH ₃	H ₂ O	HF
mp, °C	680	(decomposes at 125)	—	−182	−78	0	−83.7
bp, °C	—		—	−161	−33	100	+19.7

Lithium hydride can be regarded as a saltlike *ionic* compound, $\text{Li}^{\oplus}:\text{H}^{\ominus}$. Electrostatic attractions between oppositely charged ions in the crystal lattice

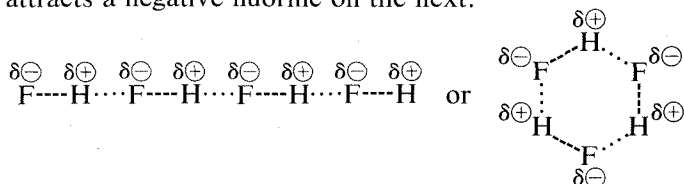
⁶G. N. Lewis (1876–1946), the renowned U.S. chemist, was the first to grasp the significance of the electron-pair in molecular structure. He laid the foundation for modern theory of structure and bonding in his treatise on *Valence and the Structure of Atoms and Molecules* (1923).

⁷Throughout this text all temperatures not otherwise designated should be understood to be in °C; absolute temperatures will be shown as °K.

are strong, thereby causing lithium hydride to be a high-melting, nonvolatile solid like sodium chloride, lithium fluoride, and so on.

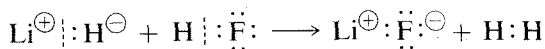
Methane, CH_4 , is at the other extreme. It boils at -161° , which is about 800° lower even than the melting point of lithium hydride. Because carbon and hydrogen have about the same electron-attracting power, C-H bonds have little ionic character, and methane may be characterized as a *nonpolar* substance. As a result, there is relatively little electrostatic attraction between methane molecules and this allows them to "escape" more easily from each other as gaseous molecules—hence the low boiling point.

Hydrogen fluoride has a boiling point some 200° higher than that of methane. The bonding electron pair of HF is drawn more toward fluorine than to hydrogen so the bond may be formulated as $\overset{\delta^+}{\text{H}}\cdots\overset{\delta^-}{\text{F}}$. In liquid hydrogen fluoride, the molecules tend to aggregate through what is called **hydrogen bonding** in chains and rings arranged so the positive hydrogen on one molecule attracts a negative fluorine on the next:

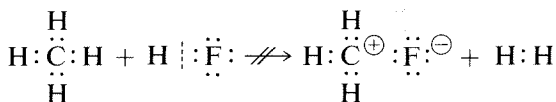


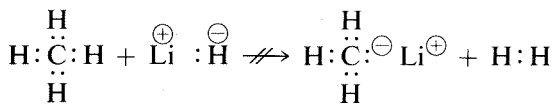
When liquid hydrogen fluoride is vaporized, the temperature must be raised sufficiently to overcome these intermolecular electrostatic attractions; hence the boiling point is high compared to liquid methane. Hydrogen fluoride is best characterized as a *polar*, but not ionic, substance. Although the O-H and N-H bonds of water and ammonia have somewhat less ionic character than the H-F bonds of hydrogen fluoride, these substances also are relatively polar in nature and also associate through hydrogen bonding in the same way as does hydrogen fluoride.

The chemical properties of lithium hydride, methane, and hydrogen fluoride are in accord with the above formulations. Thus, when the bond to the hydrogen is broken, we might expect it to break in the sense $\text{Li}^+ \vdots \text{H}^-$ for lithium hydride, and $\overset{\delta^+}{\text{H}} \vdots \overset{\delta^-}{\text{F}}$ for hydrogen fluoride so that the electron pair goes with the atom of highest electron affinity. This is indeed the case as the following reaction indicates:



Methane, with its relatively nonpolar bonds, is inert to almost all reagents that could remove hydrogen as H^\oplus or H^\ominus except under anything but extreme conditions. As would be expected, methyl cations CH_3^\oplus and methyl anions CH_3^\ominus are very difficult to generate and are extremely reactive. For this reason, the following reactions are not observed:

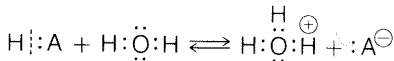




From the foregoing you may anticipate that the chemistry of carbon compounds will be largely the chemistry of covalent compounds and will not at all resemble the chemistry of inorganic salts such as sodium chloride. You also may anticipate that the major differences in chemical and physical properties of organic compounds will arise from the nature of the *other* elements bonded to carbon. Thus methane is not expected to, nor does it have, the same chemistry as other one-carbon compounds such as methyllithium, CH_3Li , or methyl fluoride, CH_3F .

Exercise 1-9 Lithium hydride could be written as either $\text{Li}^{\oplus}:\text{H}^{\ominus}$ or $\text{H}^{\oplus}:\text{Li}^{\ominus}$ depending on whether lithium or hydrogen is more electron-attracting. Explain why hydrogen is actually more electron-attracting, making the correct structure $\text{Li}^{\oplus}:\text{H}^{\ominus}$.

Exercise 1-10 An acid (HA) can be defined as a substance that donates a proton to a base, for example water. The proton-donation reaction usually is an equilibrium reaction and is written as



Predict which member of each of the following pairs of compounds would be the stronger acid. Give your reasons.

- a. LiH , HF c. H_2O_2 , H_2O
 b. NH_3 , H_2O d. CH_4 , CF_3H

1-4 THE BREADTH OF ORGANIC CHEMISTRY

Organic chemistry originally was defined as the chemistry of those substances formed by living matter and, for quite a while, there was a firm belief that it would never be possible to prepare organic compounds in the laboratory outside of a living system. However, after the discovery by Wöhler, in 1828, that a supposedly typical organic compound, urea, could be prepared by heating an inorganic salt, ammonium cyanate, this definition gradually lost significance and organic chemistry now is broadly defined as the chemistry of carbon-containing compounds. Nonetheless, the designation “organic” is still very pertinent because the chemistry of organic compounds is also the chemistry of living organisms.

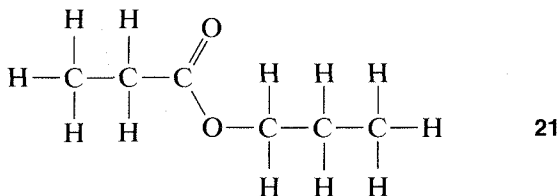
Each of us and every other living organism is comprised of, and endlessly manufactures, organic compounds. Further, all organisms consume organic compounds as raw materials, except for those plants that use photosynthesis or related processes to synthesize their own from carbon dioxide. To understand every important aspect of this chemistry, be it the details of photosynthesis, digestion, reproduction, muscle action, memory or even the thought process itself, is a primary goal of science and it should be recognized that only through application of organic chemistry will this goal be achieved.

Modern civilization consumes vast quantities of organic compounds. Coal, petroleum, and natural gas are primary sources of carbon compounds for use in production of energy and as starting materials for the preparation of plastics, synthetic fibers, dyes, agricultural chemicals, pesticides, fertilizers, detergents, rubbers and other elastomers, paints and other surface coatings, medicines and drugs, perfumes and flavors, antioxidants and other preservatives, as well as asphalts, lubricants, and solvents that are derived from petroleum.

Much has been done and you soon may infer from the breadth of the material that we will cover that most everything worth doing already has been done. However, many unsolved scientific problems remain and others have not even been thought of but, in addition, there are many technical and social problems to which answers are badly needed. Some of these include problems of pollution of the environment, energy sources, overpopulation and food production, insect control, medicine, drug action, and improved utilization of natural resources.

1-5 SOME PHILOSOPHICAL OBSERVATIONS

As you proceed with your study of organic chemistry, you may well feel confused as to what it is you are actually dealing with. On the one hand, there will be exhortations to remember how organic chemistry pervades our everyday life. And yet, on the other hand, you also will be exhorted to think about organic compounds in terms of abstract structural formulas representing molecules when there is absolutely no way at all to deal with molecules as single entities. Especially if you are not studying organic compounds in the laboratory concurrently, you may come to confuse the abstraction of formulas and ball-and-stick models of the molecules with the reality of organic compounds, and this would be most undesirable. At each stage of the way, you should try to make, or at least visualize, a juncture between a structural formula and an actual substance in a bottle. This will not be easy—it takes time to reach the level of experience that a practicing organic chemist has so that he can tell you with some certainty that the structural formula **21** represents, in actuality, a limpid, colorless liquid with a pleasant odor, slightly soluble in water, boiling somewhere about 100°.



21

A useful method for developing this sort of feeling for the relationship between structures and actual compounds is to check your perception of particular substances with their properties as given in a chemical handbook.

One, perhaps comforting, thought for you at this time is that differences between the chemical behaviors of relatively similar organic compounds usually are ascribed to just three important and different kinds of effects—two of which have root in common experience. One, called *steric hindrance*, is a manifestation of experience that two solid objects cannot occupy the same space at once. Another is the *electrical effect*, which boils down to a familiar catechism that like electrical charges repel each other and unlike charges attract each other. The remaining important effect, the one that has no basis in common experience, derives from quantum mechanics. The *quantum mechanical effect* explains why benzene is unusually stable, how and why many reactions occur in special ways and, probably most important of all, the ways that organic compounds interact with electromagnetic radiation of all kinds—from radio waves to x rays.

We shall try to give as clear explanations as possible of the quantum mechanical effect, but some of it will just have to be accepted as fact that we cannot ourselves experience directly nor understand intuitively. For example, when a grindstone rotates, so far as our experience goes, it can have an infinitely variable rate of rotation and, consequently, infinitely variable rotational (angular) momentum. However, molecules in the gas phase have only *specific* rotation rates and corresponding *specific* rotational momentum values. No measurement technique can detect in-between values of these quantities. Molecules are “quantized rotators.” About all you can do is try to accept this fact, and if you try long enough, you may be able to substitute familiarity for understanding and be happy with that.

All of us have some concepts we use continually (even perhaps unconsciously) about energy and work. Thermodynamics makes these concepts quantitative and provides very useful information about what might be called the potential for any process to occur, be it production of electricity from a battery, water running uphill, photosynthesis, or formation of nitrogen oxides in combustion of gasoline. In the past, most organic chemists seldom tried to apply thermodynamics to the reactions in which they were interested. Much of this was due to the paucity of thermodynamic data for more than a few organic compounds, but some was because organic chemists often liked to think of themselves as artistic types with little use for quantitative data on their reactions (which may have meant that they didn't really know about thermodynamics and were afraid to ask).

Times have changed. Extensive thermochemical data are now available, the procedures are well understood, and the results both useful and interesting. We shall make considerable use of thermodynamics in our exposition of organic chemistry. We believe it will greatly improve your understanding of why some reactions go and others do not.

Finally, you should recognize that you almost surely will have some problems with the following chapters in making decisions as to how much time and emphasis you should put on the various concepts, principles, facts, and so on, that we will present for you. As best we can, we try to help you by pointing out that this idea, fact, and so on, is "especially important," or words to that effect. Also, we have tried to underscore important information by indicating the breadth of its application to other scientific disciplines as well as to technology. In addition, we have caused considerable material to be set in smaller type and indented. Such material includes extensions of basic ideas and departments of fuller explanation. In many places, the exposition is more complete than it needs to be for you at the particular location in the book. However, you will have need for the extra material later and it will be easier to locate and easier to refresh your memory on what came before, if it is in one place. We will try to indicate clearly what you should learn immediately and what you will want to come back for later.

The problem is, no matter what we think is important, you or your professor will have your own judgments about relevance. And because it is quite impossible to write an individual text for your particular interests and needs, we have tried to accommodate a range of interests and needs through providing a rather rich buffet of knowledge about modern organic chemistry. Hopefully, all you will need is here, but there is surely much more, too. So, to avoid intellectual indigestion, we suggest you not try to learn everything as it comes, but rather try hardest to understand the basic ideas and concepts to which we give the greatest emphasis. As you proceed further, the really important facts, nomenclature, and so on (the kind of material that basically requires memorization), will emerge as that which, in your own course of study, you will find you use over and over again. In hope that you may wish either to learn more about particular topics or perhaps gain better understanding through exposure to a different perspective on how they can be presented, we have provided supplementary reading lists at the end of each chapter.

Our text contains many exercises. You will encounter some in the middle of the chapters arranged to be closely allied to the subject at hand. Others will be in the form of supplementary exercises at the end of the chapters. Many of the exercises will be drill; many others will extend and enlarge upon the text. The more difficult problems are marked with a star (*).

Additional Reading

Useful general chemistry textbooks:

R. E. Dickerson, H. B. Gray, and G. P. Haight, Jr., *Chemical Principles*, 2nd ed., W. A. Benjamin, Inc., Menlo Park, Calif., 1974.

M. J. Sienko and R. A. Plane, *Chemical Principles and Properties*, 2nd ed., McGraw-Hill Book Company, New York, 1974.

L. Pauling, *General Chemistry*, 3rd ed., W. H. Freeman and Company, San Francisco, 1970.

B. H. Mahan, *University Chemistry*, 2nd ed., Addison-Wesley Publishing Company, Reading, Mass., 1969.

G. C. Pimentel and R. O. Spratley, *Understanding Chemistry*, Holden-Day, Inc., San Francisco, 1971.

R. H. Eastman, *General Chemistry, Experiment and Theory*, Holt, Rinehart and Winston, New York, 1970.

W. L. Masterton and E. J. Slowinski, *Chemical Principles*, 3rd ed., W. B. Saunders Company, Philadelphia, 1973.

A useful book on quantitative relationships:

S. W. Benson, *Chemical Calculations*, 3rd ed., John Wiley and Sons, Inc., New York, 1971.

A very detailed book on the history of organic chemistry:

J. R. Partington, *A History of Chemistry*, Macmillan, London, 1964.

Supplementary Exercises

1-11 (This problem is in the nature of review of elementary inorganic chemistry and may require reference to a general chemistry book.) Write Lewis structures for each of the following compounds. Use distinct, correctly placed dots for the electrons. Mark all atoms that are not neutral with charges of the proper sign.

a. ammonia, NH_3

f. hydrogen peroxide, HOOH

b. ammonium bromide, NH_4Br

g. hydroxylamine, HONH_2

c. hydrogen cyanide, HCN

h. nitric acid, HNO_3

d. ozone ($\angle \text{O}-\text{O}-\text{O} = 120^\circ$)

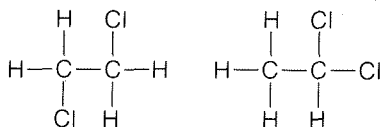
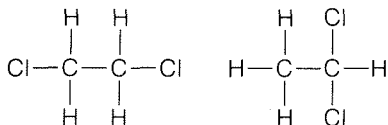
i. hydrogen sulfide, H_2S

e. carbon dioxide, CO_2

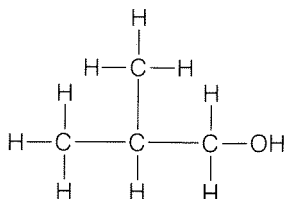
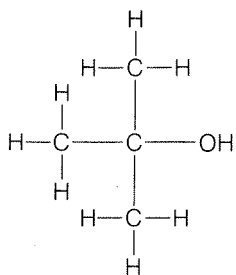
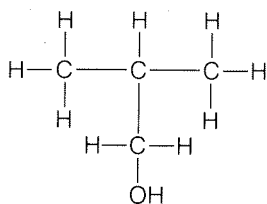
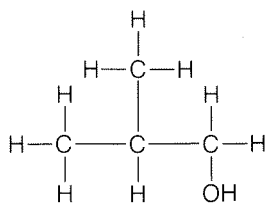
j. boron trifluoride, BF_3

1-12 Use ball-and-stick models or suitable three-dimensional drawings to determine which members of the following sets of formulas represent identical compounds, provided "free rotation" is considered to be possible around all *single* bonds (except when these bonds are present in a cyclic structure):

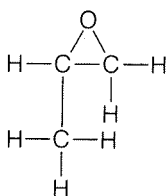
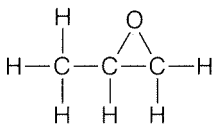
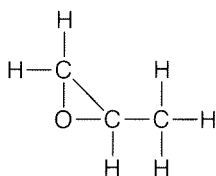
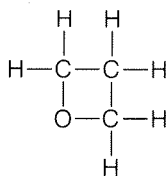
a.



b.

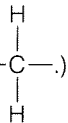


c.

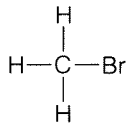


1-13 Write structures for all of the *different* monobromo substitution products (of Br for H) you would expect for each of the following compounds. (Where CH_3- ap-

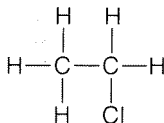
pears in these structures it is an abbreviation for $\text{H}-\text{C}-$.)

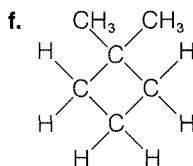
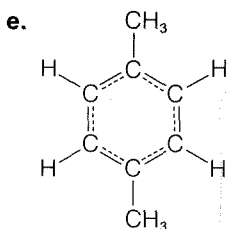
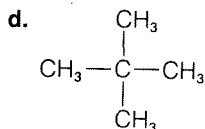
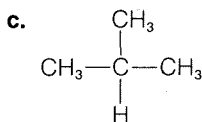


a.



b.





1-14 There are two isomers of C_3H_6 with normal carbon and hydrogen valences. Each adds bromine—one rapidly and the other very sluggishly—to give *different* isomers of $\text{C}_3\text{H}_6\text{Br}_2$. The $\text{C}_3\text{H}_6\text{Br}_2$ derived from the C_3H_6 isomer that reacts sluggishly with bromine can give just *two* different $\text{C}_3\text{H}_5\text{Br}_3$ isomers on further bromine substitution, whereas the other $\text{C}_3\text{H}_6\text{Br}_2$ compound can give *three* different $\text{C}_3\text{H}_5\text{Br}_3$ isomers on further substitution. What are the structures of the C_3H_6 isomers and their $\text{C}_3\text{H}_6\text{Br}_2$ addition products?

1-15* (Remember that here and elsewhere, * denotes a more difficult exercise.) The vast majority of organic substances are compounds of carbon with hydrogen, oxygen, nitrogen, or the halogens. Carbon and hydrogen can be determined in combustible compounds by burning a weighed sample in a stream of oxygen (Figure 1-1) and absorbing the resulting water and carbon dioxide in tubes containing anhydrous magnesium perchlorate and soda lime, respectively. The gain in weight of these tubes corresponds to the weights of the water and the carbon dioxide formed.

The molecular weight of a moderately volatile substance can be determined by the historically important **Victor Meyer procedure**, by which the volume of gas produced by vaporization of a weighed sample of an unknown is measured at a given

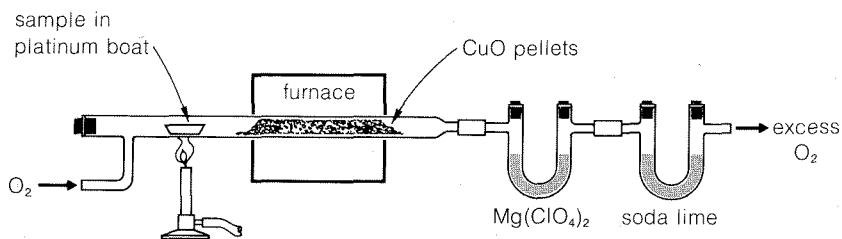


Figure 1-1 Schematic representation of a combustion train for determination of carbon and hydrogen in combustible substances

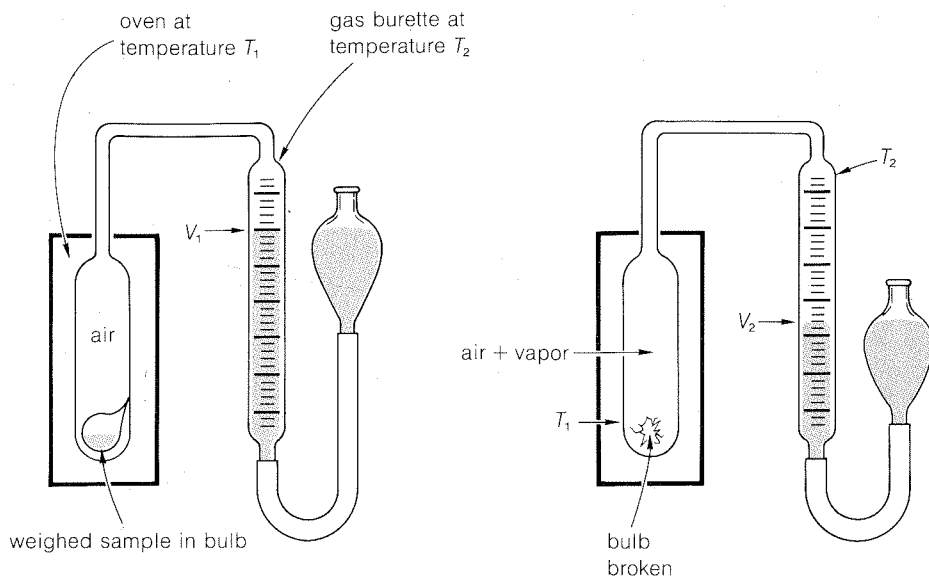


Figure 1-2 Schematic diagram of a Victor Meyer apparatus for determination of the vapor density of a substance that is volatile at the oven temperature T_1 . The air displaced from the heated chamber by the volatilization of the sample in the bulb is measured in the gas burette at temperature T_2 as the difference in the burette readings V_2 and V_1 .

temperature (Figure 1-2). The relationship $PV = nRT$ is used here, in which P is the pressure in mm of mercury, V is the volume in ml, T is the absolute temperature in $^{\circ}\text{K}$ [$= 273.15 + T(^{\circ}\text{C})$], n is the number of moles, and R is the gas constant = 62,400 in units of $(\text{mm Hg} \times \text{ml})/(\text{moles} \times ^{\circ}\text{K})$. The number of moles, n , equals m/M in which m is the weight of the sample and M is the gross molecular weight. An example of the use of the Victor Meyer method follows.

A 0.005372-g sample of a liquid carbon-hydrogen-oxygen compound on combustion gave 0.01222 g of CO_2 and 0.00499 g of H_2O . In the Victor Meyer method, 0.0343 g of the compound expelled a quantity of air at 100° (373°K) which, when collected at 27° (300°K) and 728 mm Hg, amounted to 15.2 ml.

Show how these results lead to the empirical and molecular formula of $\text{C}_3\text{H}_6\text{O}$. Write at least five isomers that correspond to this formula with univalent H, divalent O, and tetravalent C.

1-16 Determine the molecular formula of a compound of molecular weight 80 and elemental percentage composition by weight of C = 45.00, H = 7.50, and F = 47.45. Write structures for all the possible isomers having this formula. (See Exercise 1-15 for a description of how percentage composition is determined by combustion experiments.)

1-17 Why is the boiling point of water (100°) substantially higher than the boiling point of methane (-161°)?

1-18 Dimethylmercury, $\text{CH}_3\text{—Hg—CH}_3$, is a volatile compound of bp 96° , whereas mercuric fluoride F—Hg—F is a high-melting solid having mp 570° . Explain what differences in bonding in the two substances are expected that can account for the great differences in physical properties.

1-19* There are four possible isomers of $\text{C}_4\text{H}_9\text{Br}$. Let us call two of these *A* and *B*. Both *A* and *B* react with water to give the *same* isomer of $\text{C}_4\text{H}_{10}\text{O}$ and this isomer of $\text{C}_4\text{H}_{10}\text{O}$ reacts with strong HBr to give back only *A*. Substitution of *A* with bromine gives only *one* of the possible $\text{C}_4\text{H}_8\text{Br}_2$ isomers. Substitution of *B* with bromine gives three different $\text{C}_4\text{H}_8\text{Br}_2$ isomers, and one of these is identical with the $\text{C}_4\text{H}_8\text{Br}_2$ from the substitution of *A*. Write structural formulas for *A* and *B*, and the isomers of $\text{C}_4\text{H}_8\text{Br}_2$ formed from them with bromine, and for the isomers of $\text{C}_4\text{H}_{10}\text{O}$ expected to be formed from them with water. Indicate in which reaction the principle of least structural change breaks down.