

Organic Chemistry

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Page 2

Alkanes

Free-Radical Substitution

3.1 Classification by structure: the family

The basis of organic chemistry, we have said, is the structural theory. We separate all organic compounds into a number of families on the basis of structure. Having done this, we find that we have at the same time classified the compounds as to their physical and chemical properties. A particular set of properties is thus characteristic of a particular kind of structure.

Within a family there are variations in properties. All members of the family may, for example, react with a particular reagent, but some may react more readily than others. Within a single compound there may be variations in properties, one part of a molecule being more reactive than another part. These variations in properties correspond to variations in structure.

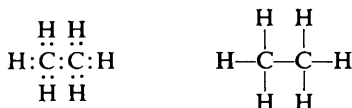
As we take up each family of organic compounds, we shall first see what structure and properties are characteristic of the family. Next we shall see how structure and properties vary within the family. We shall not simply memorize these facts, but, whenever possible, shall try to understand properties in terms of structure, and to understand variations in properties in terms of variations in structure.

Having studied methane in some detail, let us now look at the more complicated members of the alkane family. These hydrocarbons have been assigned to the same family as methane on the basis of their structure, and on the whole their properties follow the pattern laid down by methane. However, certain new points will arise simply because of the greater size and complexity of these compounds.

3.2 Structure of ethane

Next in size after methane is **ethane**, C_2H_6 . If we connect the atoms of this molecule by covalent bonds, following the rule of one bond (one pair of electrons)

for each hydrogen and four bonds (four pairs of electrons) for each carbon, we arrive at the structure



Ethane

Each carbon is bonded to three hydrogens and to the other carbon.

Since each carbon atom is bonded to four other atoms, its bonding orbitals (sp^3 orbitals) are directed toward the corners of a tetrahedron. As in the case of methane, the carbon-hydrogen bonds result from overlap of these sp^3 orbitals with the s orbitals of the hydrogens. The carbon-carbon bond arises from overlap of two sp^3 orbitals.

The carbon-hydrogen and carbon-carbon bonds have the same general electron distribution, being cylindrically symmetrical about a line joining the atomic nuclei (see Fig. 3.1); because of this similarity in shape, the bonds are given the same name, σ bonds (*sigma bonds*).

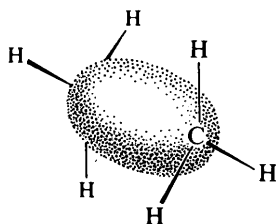


Figure 3.1. Ethane molecule. Carbon-carbon single bond: σ bond.

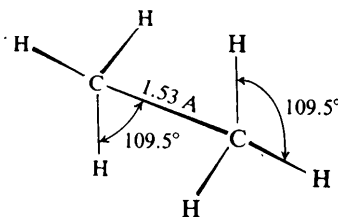


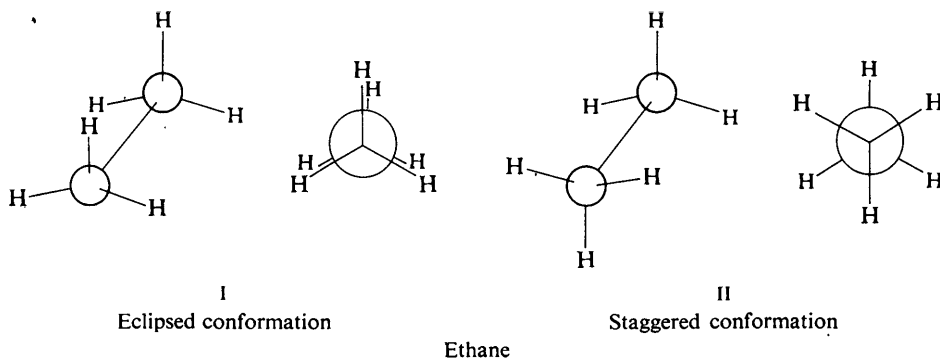
Figure 3.2. Ethane molecule: shape and size.

In ethane, then, the bond angles and carbon-hydrogen bond lengths should be very much the same as in methane, that is, about 109.5° and about 1.10 Å, respectively. Electron diffraction and spectroscopic studies have verified this structure in all respects, giving (Fig. 3.2) the following measurements for the molecule: bond angles, 109.5° ; C-H length, 1.10 Å; C-C length, 1.53 Å. Similar studies have shown that, with only slight variations, these values are quite characteristic of carbon-hydrogen and carbon-carbon bonds and of carbon bond angles in alkanes.

3.3 Free rotation about the carbon-carbon single bond. Conformations. Torsional strain

This particular set of bond angles and bond lengths still does not limit us to a single arrangement of atoms for the ethane molecule, since the relationship between the hydrogens of one carbon and the hydrogens of the other carbon is not specified. We could have an arrangement like I in which the hydrogens exactly oppose each other, an arrangement like II in which the hydrogens are perfectly staggered, or an infinity of intermediate arrangements. Which of these is the actual structure of ethane? The answer is: *all of them*.

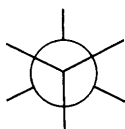
We have seen that the σ bond joining the carbon atoms is cylindrically symmetrical about a line joining the two carbon nuclei; overlap and hence bond



strength should be the same for all these possible arrangements. If the various arrangements do not differ in energy, then the molecule is not restricted to any one of them, but can change freely from one to another. Since the change from one to another involves rotation about the carbon-carbon bond, we describe this freedom to change by saying that *there is free rotation about the carbon-carbon single bond*.

Different arrangements of atoms that can be converted into one another by rotation about single bonds are called conformations. I is called the *eclipsed conformation*; II is called the *staggered conformation*. (The infinity of intermediate conformations are called *skew conformations*.)

The highly useful representations of the kind



are called *Newman projections*, after M. S. Newman, of The Ohio State University, who first proposed their use.

The picture is not yet complete. Certain physical properties show that rotation is *not quite free*: there is an energy barrier of about 3 kcal/mol. The potential energy of the molecule is at a minimum for the staggered conformation, increases with rotation, and reaches a maximum at the eclipsed conformation (Fig. 3.3). Most ethane molecules, naturally, exist in the most stable, staggered conformation; or, put differently, any molecule spends most of its time in the most stable conformation.

How free are ethane molecules to rotate from one staggered arrangement to another? The 3-kcal barrier is not a very high one; even at room temperature the fraction of collisions with sufficient energy is large enough that a rapid inter-conversion between staggered arrangements occurs. For most practical purposes, we may still consider that the carbon-carbon single bond permits free rotation.

The nature of the rotational barrier in ethane is not understood or—what is not exactly the same thing—is not readily explained. It is too high to be due merely to van der Waals forces (Sec. 1.19): although thrown closer together in the eclipsed conformation than in the staggered conformation, the hydrogens on opposite carbons are not big enough for this to

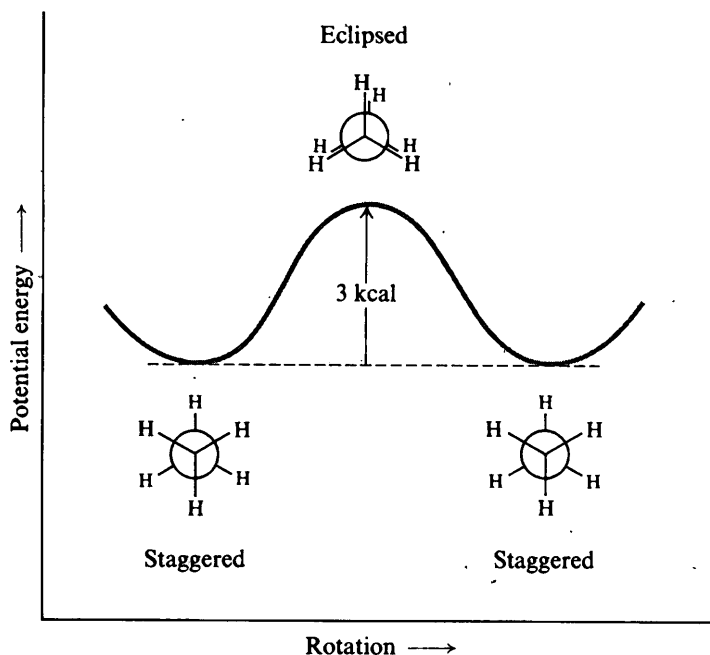


Figure 3.3. Potential energy changes during rotation about carbon-carbon single bond of ethane.

cause appreciable crowding. The barrier is considered to arise in some way from interaction among the electron clouds of the carbon-hydrogen bonds. Quantum mechanical calculations show that the barrier should exist, and so perhaps "lack of understanding" amounts to difficulty in paraphrasing the mathematics in physical terms. Like the bond orbitals in methane, the two sets of orbitals in ethane tend to be as far apart as possible—to be *staggered*.

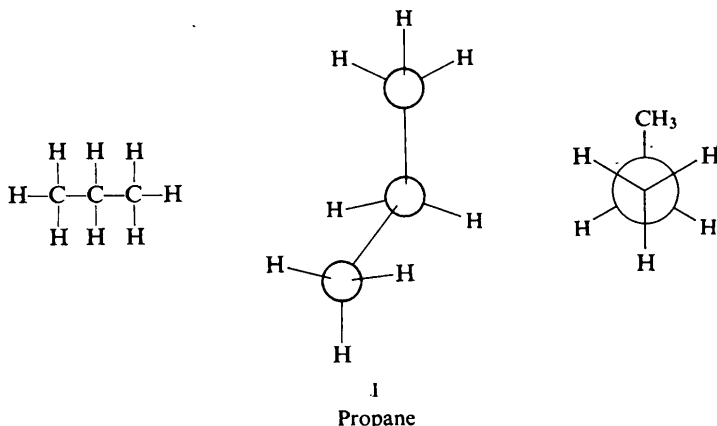
The energy required to rotate the ethane molecule about the carbon-carbon bond is called *torsional energy*. We speak of the relative instability of the eclipsed conformation—or any of the intermediate skew conformations—as being due to *torsional strain*.

As the hydrogens of ethane are replaced by other atoms or groups of atoms, other factors affecting the relative stability of conformations appear: van der Waals forces, dipole-dipole interactions, hydrogen bonding. But the tendency for the bond orbitals on adjacent carbons to be staggered remains, and any rotation away from the staggered conformation is accompanied by torsional strain.

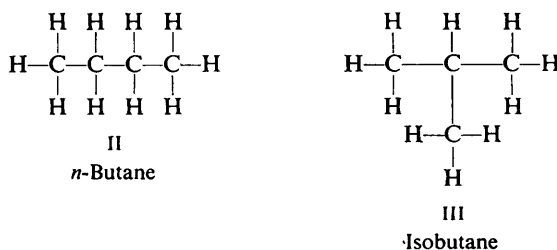
3.4 Propane and the butanes

The next member of the alkane family is **propane**, C_3H_8 . Again following the rule of one bond per hydrogen and four bonds per carbon, we arrive at structure I.

Here, rotation can occur about two carbon-carbon bonds, and again is essentially free. Although the methyl group is considerably larger than hydrogen, the rotational barrier (3.3 kcal/mol) is only a little higher than for ethane. Evidently there is still not significant crowding in the eclipsed conformation, and the rotational barrier is due chiefly to the same factor as the barrier in ethane: *torsional strain*.



When we consider **butane**, C_4H_{10} , we find that there are two possible structures, II and III. II has a four-carbon chain and III has a three-carbon chain with a one-carbon branch. There can be no doubt that these represent different



structures, since no amount of moving, twisting, or rotating about carbon-carbon bonds will cause these structures to coincide. We can see that in the *straight-chain* structure (II) each carbon possesses at least two hydrogens, whereas in the *branched-chain* structure (III) one carbon possesses only a single hydrogen; or we may notice that in the branched-chain structure (III) one carbon is bonded to three other carbons, whereas in the straight-chain structure (II) no carbon is bonded to more than two other carbons.

In agreement with this prediction, we find that two compounds of the same formula, C_4H_{10} , have been isolated. There can be no doubt that these two substances are different compounds, since they show definite differences in their physical and chemical properties (see Table 3.1); for example one boils at 0° and the other at -12° . By definition, they are *isomers* (Sec. 1.24).

Table 3.1 PHYSICAL CONSTANTS OF THE ISOMERIC BUTANES

	<i>n</i> -Butane	Isobutane
b.p.	0°	-12°
m.p.	-138°	-159°
sp.gr. at -20°	0.622	0.604
solub. in 100 mL alcohol	1813 mL	1320 mL

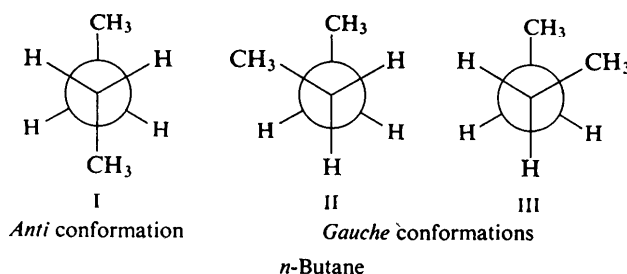
Two compounds of formula C_4H_{10} are known and we have drawn two structures to represent them. The next question is: which structure represents which compound? For the answer we turn to the evidence of **isomer number**. Like methane, the butanes can be chlorinated; the chlorination can be allowed to proceed until there are two chlorine atoms per molecule. From the butane of b.p. 0° , six isomeric products of formula $C_4H_8Cl_2$ are obtained, from the butane of b.p. -12° , only three. We find that we can draw just six dichlorobutanes containing a straight chain of carbon atoms, and just three containing a branched chain. Therefore, the butane of b.p. 0° must have the straight chain, and the butane of b.p. -12° must have the branched chain. To distinguish between these two isomers, the straight-chain structure is called ***n*-butane** (spoken "normal butane") and the branched-chain structure is called **isobutane**.

Problem 3.1 Draw the structures of all possible dichloro derivatives of: (a) *n*-butane; (b) isobutane.

Problem 3.2 Could we assign structures to the isomeric butanes on the basis of the number of isomeric monochloro derivatives?

3.5 Conformations of *n*-butane. Van der Waals repulsion

Let us look more closely at the *n*-butane molecule and the conformations in which it exists. Focusing our attention on the middle C—C bond, we see a molecule similar to ethane, but with a methyl group replacing one hydrogen on each carbon. As with ethane, staggered conformations have lower torsional energies and hence are more stable than eclipsed conformations. But, due to the presence of the methyl groups, two new points are encountered here: first, there are several *different* staggered conformations; and second, a factor besides torsional strain comes into play to affect conformational stabilities.



There is the *anti* conformation, I, in which the methyl groups are as far apart as they can be (dihedral angle 180°). There are two *gauche* conformations, II and III, in which the methyl groups are only 60° apart. (Conformations II and III are mirror images of each other, and are of the same stability; nevertheless, they are different. Make models and convince yourself that this is so.)

The *anti* conformation, it has been found, is more stable (by 0.8 kcal/mol) than the *gauche* (Fig. 3.4). Both are free of torsional strain. But in a *gauche* conformation, the methyl groups are crowded together, that is, are thrown together closer than the sum of their van der Waals radii; under these conditions, van der Waals forces are *repulsive* (Sec. 1.19) and raise the energy of the conformation. We say that there

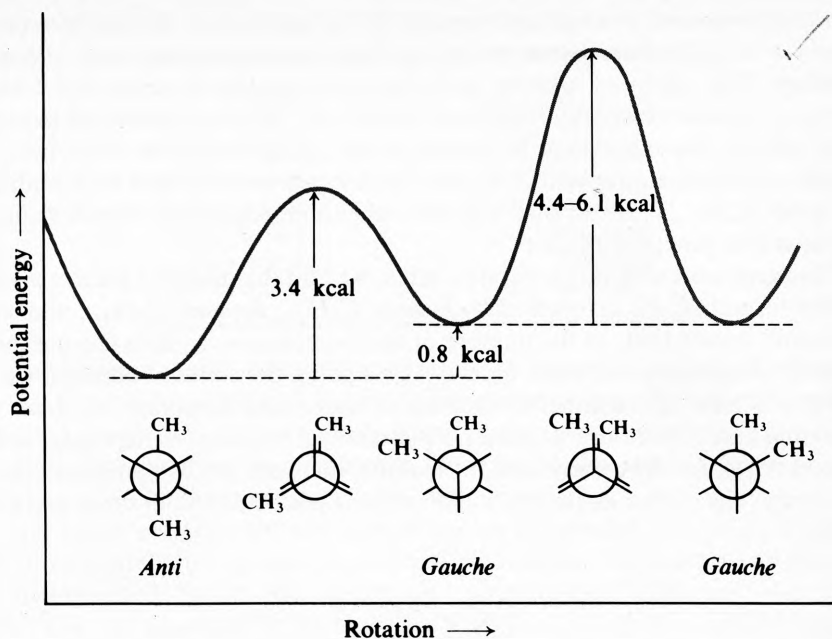


Figure 3.4. Potential energy changes during rotation about C_2-C_3 bond of *n*-butane.

is *van der Waals repulsion* (or *steric repulsion*) between the methyl groups, and that the molecule is less stable because of *van der Waals strain* (or *steric strain*).

Van der Waals strain can affect not only the relative stabilities of various staggered conformations, but also the heights of the barriers between them. The energy maximum reached when two methyl groups swing past each other—rather than past hydrogens—is the highest rotational barrier of all, and has been estimated at 4.4–6.1 kcal/mol. Even so, it is low enough that—at ordinary temperatures, at least—the energy of molecular collisions causes rapid rotation; a given molecule exists now in a *gauche* conformation, and the next instant in the *anti* conformation.

We shall return to the relationships among conformations like these of *n*-butane in Sec. 4.20.

Problem 3.3 Both calculations and experimental evidence indicate that the dihedral angle between the methyl groups in the *gauche* conformation of *n*-butane is actually somewhat *larger* than 60° . How would you account for this?

Problem 3.4 Considering only rotation about the bond shown, draw a potential energy *vs.* rotation curve like Fig. 3.4 for:

(a) $(CH_3)_2CH-CH(CH_3)_2$; (b) $(CH_3)_2CH-CH_2CH_3$; (c) $(CH_3)_3C-C(CH_3)_3$.

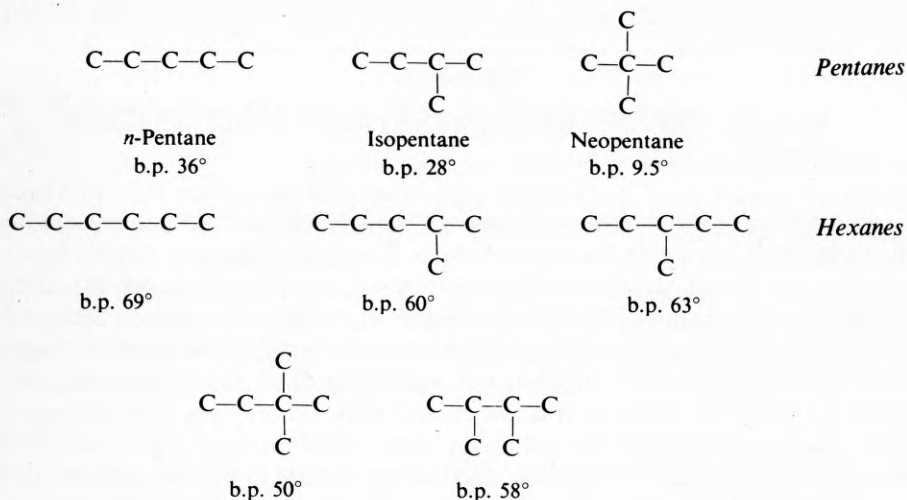
(d) Compare the heights of the various energy barriers with each other and with those in Fig. 3.4.

3.6 Higher alkanes. The homologous series

If we examine the molecular formulas of the alkanes we have so far considered, we see that butane contains one carbon and two hydrogens more than propane, which in turn contains one carbon and two hydrogens more than ethane, and so on.

A series of compounds in which each member differs from the next member by a constant amount is called a **homologous series**, and the members of the series are called **homologs**. The family of alkanes forms such a homologous series, the constant difference between successive members being CH_2 . We also notice that in each of these alkanes the number of hydrogen atoms equals two more than twice the number of carbon atoms, so that we may write as a *general formula* for members of this series, $\text{C}_n\text{H}_{2n+2}$. As we shall see later, other homologous series have their own characteristic general formulas.

In agreement with this general formula, we find that the next alkane, *pentane*, has the formula C_5H_{12} , followed by *hexane*, C_6H_{14} , *heptane*, C_7H_{16} , and so on. We would expect that, as the number of atoms increases, so does the number of possible arrangements of those atoms. As we go up the series of alkanes, we find that this is true: the number of isomers of successive homologs increases at a surprising rate. There are 3 isomeric pentanes, 5 hexanes, 9 heptanes, and 75 decanes (C_{10}); for the twenty-carbon eicosane, there are 366,319 possible isomeric structures! The carbon skeletons of the isomeric pentanes and hexanes are shown below.



It is important to practice drawing the possible isomeric structures that correspond to a single molecular formula. In doing this, a set of molecular models is especially helpful since it will show that many structures which appear to be different when drawn on paper are actually identical.

Problem 3.5 Draw the structures of: (a) the nine isomeric heptanes (C_7H_{16}); (b) the eight chloropentanes ($\text{C}_5\text{H}_{11}\text{Cl}$); (c) the nine dibromobutanes ($\text{C}_4\text{H}_8\text{Br}_2$).

3.7 Nomenclature

We have seen that the names *methane*, *ethane*, *propane*, *butane*, and *pentane* are used for alkanes containing respectively one, two, three, four, and five carbon atoms. Table 3.2 gives the names of many larger alkanes. Except for the first four members of the family, the name is simply derived from the Greek (or Latin) prefix for the particular number of carbons in the alkane; thus **pentane** for five, **hexane** for six, **heptane** for seven, **octane** for eight, and so on.

Table 3.2 NAMES OF ALKANES

CH_4	methane	C_9H_{20}	nonane
C_2H_6	ethane	$\text{C}_{10}\text{H}_{22}$	decane
C_3H_8	propane	$\text{C}_{11}\text{H}_{24}$	undecane
C_4H_{10}	butane	$\text{C}_{12}\text{H}_{26}$	dodecane
C_5H_{12}	pentane	$\text{C}_{14}\text{H}_{30}$	tetradecane
C_6H_{14}	hexane	$\text{C}_{16}\text{H}_{34}$	hexadecane
C_7H_{16}	heptane	$\text{C}_{18}\text{H}_{38}$	octadecane
C_8H_{18}	octane	$\text{C}_{20}\text{H}_{42}$	eicosane

The student should certainly memorize the names of at least the first ten alkanes. Having done this, one has at the same time essentially learned the names of the first ten alkenes, alkynes, alcohols, etc., since the names of many families of compounds are closely related. Compare, for example, the names *propane*, *propene*, and *propyne* for the three-carbon alkane, alkene, and alkyne.

But nearly every alkane can have a number of isomeric structures, and there must be an unambiguous name for each of these isomers. The butanes and pentanes are distinguished by the use of prefixes: *n*-butane and *isobutane*; *n*-pentane, *isopentane*, and *neopentane*. But there are 5 hexanes, 9 heptanes, and 75 decanes; it would be difficult to devise, and even more difficult to remember, a different prefix for each of these isomers. It is obvious that some systematic method of naming is needed.

As organic chemistry has developed, several different methods have been devised to name the members of nearly every class of organic compounds; each method was devised when the previously used system had been found inadequate for the growing number of increasingly complex organic compounds. Unfortunately for the student, perhaps, several systems have survived and are in current use. Even if we are content ourselves to use only one system, we still have to understand the names used by other chemists; hence it is necessary for us to learn more than one system of nomenclature. But before we can do this, we must first learn the names of certain organic groups.

3.8 Alkyl groups

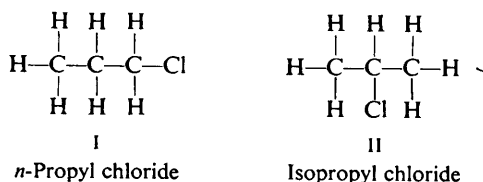
In our study of inorganic chemistry, we found it useful to have names for certain groups of atoms that compose only part of a molecule and yet appear many times as a unit. For example, NH_4^+ is called *ammonium*; NO_3^- , *nitrate*; SO_3^{2-} , *sulfite*; and so on.

In a similar way names are given to certain groups that constantly appear as structural units of organic molecules. We have seen that chloromethane, CH_3Cl , is also known as *methyl chloride*. The CH_3 group is called **methyl** wherever it appears, CH_3Br being *methyl bromide*; CH_3I , *methyl iodide*; and CH_3OH , *methyl alcohol*. In an analogous way, the C_2H_5 group is **ethyl**; C_3H_7 , **propyl**; C_4H_9 , **butyl**; and so on.

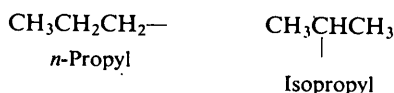
These groups are named simply by dropping *-ane* from the name of the corresponding alkane and replacing it by *-yl*. They are known collectively as **alkyl groups**. The general formula for an alkyl group is $\text{C}_n\text{H}_{2n+1}$, since it contains one less hydrogen than the parent alkane, $\text{C}_n\text{H}_{2n+2}$.

Among the alkyl groups we again encounter the problem of isomerism. There

is only one methyl chloride or ethyl chloride, and correspondingly only one methyl group or ethyl group. We can see, however, that there are two propyl chlorides, I and II, and hence that there must be two propyl groups. These groups both contain

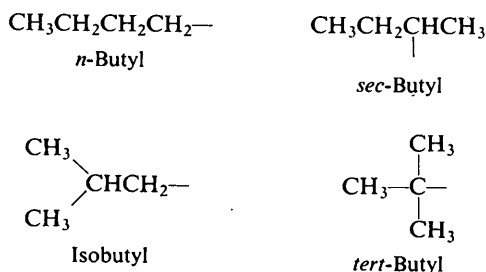


the propane chain, but differ in the point of attachment of the chlorine; they are called ***n*-propyl** and **isopropyl**. We can distinguish the two chlorides by the names



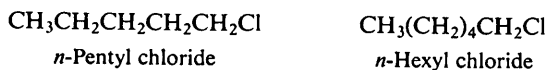
n-propyl chloride and isopropyl chloride; we distinguish the two propyl bromides, iodides, alcohols, and so on in the same way.

We find that there are four butyl groups, two derived from the straight-chain *n*-butane, and two derived from the branched-chain isobutane. These are given the designations ***n*-** (*normal*), ***sec*-** (*secondary*), ***iso*-**, and ***tert*-** (*tertiary*), as shown below. Again the difference between *n*-butyl and *sec*-butyl and between isobutyl and *tert*-butyl lies in the point of attachment of the alkyl group to the rest of the molecule.



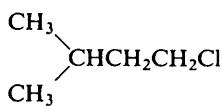
Beyond butyl the number of isomeric groups derived from each alkane becomes so great that it is impracticable to designate them all by various prefixes. Even though limited, this system is so useful for the small groups just described that it is widely used; a student must therefore memorize these names and learn to recognize these groups at a glance in whatever way they happen to be represented.

However large the group concerned, one of its many possible arrangements can still be designated by this simple system. The prefix ***n*-** is used to designate any alkyl group in which all carbons form a single continuous chain and in which the point of attachment is the very end carbon. For example:

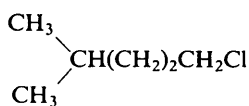


The prefix ***iso*-** is used to designate any alkyl group (of six carbons or fewer)

that has a single one-carbon branch on the next-to-last carbon of a chain and has the point of attachment at the opposite end of the chain. For example:



Isopentyl chloride



Isohexyl chloride

If the branching occurs at any other position, or if the point of attachment is at any other position, this name does not apply.

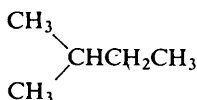
Now that we have learned the names of certain alkyl groups, let us return to the original problem: the naming of alkanes.

3.9 Common names of alkanes

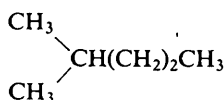
As we have seen, the prefixes *n*-, *iso*-, and *neo*- are adequate to differentiate the various butanes and pentanes, but beyond this point an impracticable number of prefixes would be required. However, the prefix *n*- has been retained for any alkane, no matter how large, in which all carbons form a continuous chain with no branching:

*n*-Pentane*n*-Hexane

An *isoalkane* is a compound of six carbons or fewer in which all carbons except one form a continuous chain and that one carbon is attached to the next-to-end carbon:



Isopentane



Isohexane

In naming any other of the higher alkanes, we make use of the IUPAC system, outlined in the following section.

(It is sometimes convenient to name alkanes as derivatives of methane; see, for example, I at the top of p. 137.)

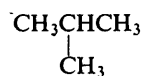
3.10 IUPAC names of alkanes

To devise a system of nomenclature that could be used for even the most complicated compounds, various committees and commissions representing the chemists of the world have met periodically since 1892. In its present modification, the system so devised is known as the **IUPAC system** (International Union of Pure and Applied Chemistry). Since this system follows much the same pattern for all families of organic compounds, we shall consider it in some detail as applied to the alkanes.

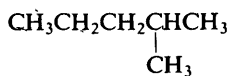
Essentially the rules of the IUPAC system are:

1. Select as the parent structure the longest continuous chain, and then consider the compound to have been derived from this structure by the replacement

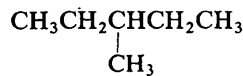
of hydrogen by various alkyl groups. Isobutane (I) can be considered to arise from propane by the replacement of a hydrogen atom by a methyl group, and thus may be named *methylpropane*.



I
Methylpropane
(Isobutane)



II
2-Methylpentane

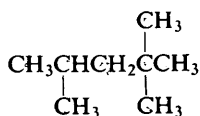


III
3-Methylpentane

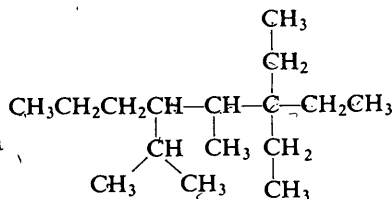
2. Where necessary, as in the isomeric methylpentanes (II and III), indicate by a number the carbon to which the alkyl group is attached.

3. In numbering the parent carbon chain, start at whichever end results in the use of the lowest numbers; thus II is called *2-methylpentane* rather than 4-methylpentane.

4. If the same alkyl group occurs more than once as a side chain, indicate this by the prefix *di-*, *tri-*, *tetra-*, etc., to show how many of these alkyl groups there are, and indicate by various numbers the positions of *each* group, as in *2,2,4-trimethylpentane* (IV).



IV
2,2,4-Trimethylpentane

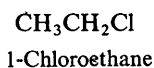


V
3,3-Diethyl-5-isopropyl-4-methyloctane

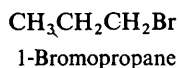
5. If there are several different alkyl groups attached to the parent chain, name them in order of increasing size or in alphabetical order; as in *3,3-diethyl-5-isopropyl-4-methyloctane* (V).

There are additional rules and conventions used in naming very complicated alkanes, but the five fundamental rules mentioned here will suffice for the compounds we are likely to encounter.

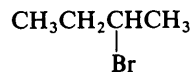
The alkyl halides which appear so often in alkane chemistry are named as *haloalkanes*; that is, halogen is simply treated as a side chain. We first name the alkane as though no halogen were present, and then add *fluoro*, *chloro*, *bromo*, or *iodo*, together with any needed numbers and prefixes.



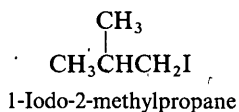
1-Chloroethane



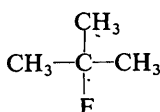
1-Bromopropane



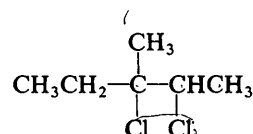
2-Bromobutane



1-Iodo-2-methylpropane



2-Fluoro-2-methylpropane



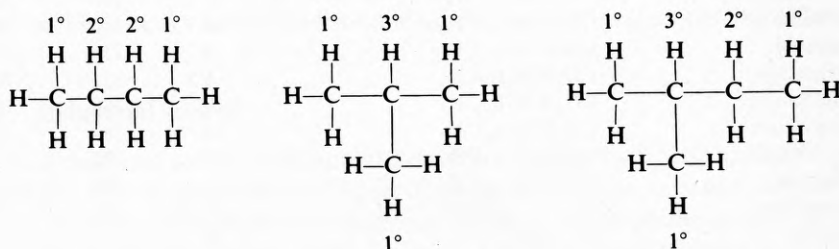
2,3-Dichloro-3-methylpentane

Problem 3.6 Give the IUPAC names for: (a) the isomeric hexanes shown on page 86; (b) the nine isomeric heptanes (see Problem 3.5, p. 86).

Problem 3.7 Give the IUPAC names for: (a) the eight isomeric chloropentanes; (b) the nine isomeric dibromobutanes (see Problem 3.5, p. 86).

3.11 Classes of carbon atoms and hydrogen atoms

It has been found extremely useful to classify each carbon atom of an alkane with respect to the number of other carbon atoms to which it is attached. A **primary** (1°) carbon atom is attached to only one other carbon atom; a **secondary** (2°) is attached to two others; and a **tertiary** (3°) to three others. For example:



Each hydrogen atom is similarly classified, being given the same designation of *primary*, *secondary*, or *tertiary* as the carbon atom to which it is attached.

We shall make constant use of these designations in our consideration of the relative reactivities of various parts of an alkane molecule.

3.12 Physical properties

The physical properties of the alkanes follow the pattern laid down by methane, and are consistent with the alkane structure. An alkane molecule is held together entirely by covalent bonds. These bonds either join two atoms of the same kind and hence are non-polar, or join two atoms that differ very little in electronegativity and hence are only slightly polar. Furthermore, these bonds are directed in a very symmetrical way, so that the slight bond polarities tend to cancel out. As a result an alkane molecule is either non-polar or very weakly polar.

As we have seen (Sec. 1.19), the forces holding non-polar molecules together (van der Waals forces) are weak and of very short range; they act only between the portions of different molecules that are in close contact, that is, between the surfaces of molecules. Within a family, therefore, we would expect that the larger the molecule—and hence the larger its surface area—the stronger the intermolecular forces.

Table 3.3 lists certain physical constants for a number of the *n*-alkanes. As we can see, the boiling points and melting points rise as the number of carbons increases. The processes of boiling and melting require overcoming the intermolecular forces of a liquid and a solid; the boiling points and melting points rise because these intermolecular forces increase as the molecules get larger.

Except for the very small alkanes, the boiling point rises 20 to 30 degrees for each carbon that is added to the chain; we shall find that this increment of 20–30° per

Table 3.3 ALKANES

Name	Formula	M.p., °C	B.p., °C	Density (at 20°)
Methane	CH ₄	- 183	- 162	
Ethane	CH ₃ CH ₃	- 172	- 88.5	
Propane	CH ₃ CH ₂ CH ₃	- 187	- 42	
<i>n</i> -Butane	CH ₃ (CH ₂) ₂ CH ₃	- 138	0	
<i>n</i> -Pentane	CH ₃ (CH ₂) ₃ CH ₃	- 130	36	0.626
<i>n</i> -Hexane	CH ₃ (CH ₂) ₄ CH ₃	- 95	69	.659
<i>n</i> -Heptane	CH ₃ (CH ₂) ₅ CH ₃	- 90.5	98	.684
<i>n</i> -Octane	CH ₃ (CH ₂) ₆ CH ₃	- 57	126	.703
<i>n</i> -Nonane	CH ₃ (CH ₂) ₇ CH ₃	- 54	151	.718
<i>n</i> -Decane	CH ₃ (CH ₂) ₈ CH ₃	- 30	174	.730
<i>n</i> -Undecane	CH ₃ (CH ₂) ₉ CH ₃	- 26	196	.740
<i>n</i> -Dodecane	CH ₃ (CH ₂) ₁₀ CH ₃	- 10	216	.749
<i>n</i> -Tridecane	CH ₃ (CH ₂) ₁₁ CH ₃	- 6	234	.757
<i>n</i> -Tetradecane	CH ₃ (CH ₂) ₁₂ CH ₃	5.5	252	.764
<i>n</i> -Pentadecane	CH ₃ (CH ₂) ₁₃ CH ₃	10	266	.769
<i>n</i> -Hexadecane	CH ₃ (CH ₂) ₁₄ CH ₃	18	280	.775
<i>n</i> -Heptadecane	CH ₃ (CH ₂) ₁₅ CH ₃	22	292	
<i>n</i> -Octadecane	CH ₃ (CH ₂) ₁₆ CH ₃	28	308	
<i>n</i> -Nonadecane	CH ₃ (CH ₂) ₁₇ CH ₃	32	320	
<i>n</i> -Eicosane	CH ₃ (CH ₂) ₁₈ CH ₃	36		
Isobutane	(CH ₃) ₂ CHCH ₃	- 159	- 12	
Isopentane	(CH ₃) ₂ CHCH ₂ CH ₃	- 160	28	.620
Neopentane	(CH ₃) ₄ C	- 17	9.5	
Isohexane	(CH ₃) ₂ CH(CH ₂) ₂ CH ₃	- 154	60	.654
3-Methylpentane	CH ₃ CH ₂ CH(CH ₃)CH ₂ CH ₃	- 118	63	.676
2,2-Dimethylbutane	(CH ₃) ₃ CCH ₂ CH ₃	- 98	50	.649
2,3-Dimethylbutane	(CH ₃) ₂ CHCH(CH ₃) ₂	- 129	58	.668

carbon holds not only for the alkanes but also for each of the homologous series that we shall study.

The increase in melting point is not quite so regular, since the intermolecular forces in a crystal depend not only upon the size of the molecules but also upon how well they fit into a crystal lattice.

The first four *n*-alkanes are gases, but, as a result of the rise in boiling point and melting point with increasing chain length, the next 13 (C₅-C₁₇) are liquids, and those containing 18 carbons or more are solids.

Problem 3.8 Using the data of Table 3.3, make a graph of: (a) b.p. *vs.* carbon number for the *n*-alkanes; (b) m.p. *vs.* carbon number; (c) density *vs.* carbon number.

There are somewhat smaller differences among the boiling points of alkanes that have the same carbon number but different structures. On pages 83 and 86 the boiling points of the isomeric butanes, pentanes, and hexanes are given. We see that in every case a *branched-chain isomer has a lower boiling point than a straight-chain isomer*, and further, that the more numerous the branches, the lower the boiling point. Thus *n*-butane has a boiling point of 0° and isobutane - 12°. *n*-Pentane has a boiling point of 36°, isopentane with a single branch 28°, and neopentane with two branches 9.5°. This effect of branching on boiling point is

observed within all families of organic compounds. That branching should lower the boiling point is understandable: with branching the shape of the molecule tends to approach that of a sphere; and as this happens the surface area decreases, with the result that the intermolecular forces become weaker and are overcome at a lower temperature (Sec. 1.20).

In agreement with the rule of thumb, "like dissolves like," the alkanes are soluble in non-polar solvents such as benzene, ether, and chloroform, and are insoluble in water and other highly polar solvents. Considered themselves as solvents, the liquid alkanes dissolve compounds of low polarity and do not dissolve compounds of high polarity.

The density increases with size of the alkanes, but tends to level off at about 0.8; thus all alkanes are less dense than water. It is not surprising that nearly all organic compounds are less dense than water since, like the alkanes, they consist chiefly of carbon and hydrogen. In general, to be denser than water a compound must contain a heavy atom like bromine or iodine, or several atoms like chlorine.

3.13 Industrial source

The principal source of alkanes is **petroleum**, together with the accompanying **natural gas**. Decay and millions of years of geological stresses have transformed the complicated organic compounds that once made up living plants or animals into a mixture of alkanes ranging in size from one carbon to 30 or 40 carbons. Formed along with the alkanes, and particularly abundant in California petroleum, are *cycloalkanes* (Chap. 5), known to the petroleum industry as *naphthenes*.

The other fossil fuel, coal, is a potential second source of alkanes: processes are being developed to convert coal, through hydrogenation, into gasoline and fuel oil, and into synthetic gas to offset anticipated shortages of natural gas.

Natural gas contains, of course, only the more volatile alkanes, that is, those of low molecular weight; it consists chiefly of methane and progressively smaller amounts of ethane, propane, and higher alkanes. For example, a sample taken from a pipeline supplied by a large number of Pennsylvania wells contained methane, ethane, and propane in the ratio of 12:2:1, with higher alkanes making up only 3% of the total. The propane-butane fraction is separated from the more volatile components by liquefaction, compressed into cylinders, and sold as *bottled gas* in areas not served by a gas utility.

Petroleum is separated by distillation into the various fractions listed in Table 3.4; because of the relationship between boiling point and molecular weight, this amounts to a rough separation according to carbon number. Each fraction is still a very complicated mixture, however, since it contains alkanes of a range of carbon numbers, and since each carbon number is represented by numerous isomers. The use that each fraction is put to depends chiefly upon its volatility or viscosity, and it matters very little whether it is a complicated mixture or a single pure compound. (In gasoline, as we shall see in Sec. 3.30, the structures of the components are of key importance.)

The chief use of all but the non-volatile fractions is as fuel. The gas fraction, like natural gas, is used chiefly for heating. Gasoline is used in those internal combustion engines that require a fairly volatile fuel, kerosine is used in tractor and jet engines, and gas oil is used in Diesel engines. Kerosine and gas oil are also used for heating purposes, the latter being the familiar "furnace oil."

Table 3.4 PETROLEUM CONSTITUENTS

Fraction	Distillation Temperature, °C	Carbon Number
Gas	Below 20°	C ₁ -C ₄
Petroleum ether	20-60°	C ₅ -C ₆
Ligroin (light naphtha)	60-100°	C ₆ -C ₇
Natural gasoline	40-205°	C ₅ -C ₁₀ , and cycloalkanes
Kerosine	175-325°	C ₁₂ -C ₁₈ , and aromatics
Gas oil	Above 275°	C ₁₂ and higher
Lubricating oil	Non-volatile liquids	Probably long chains attached to cyclic structures
Asphalt or petroleum coke	Non-volatile solids	Polycyclic structures

The lubricating oil fraction, especially that from Pennsylvania crude oil (*paraffin-base petroleum*), often contains large amounts of long-chain alkanes (C₂₀-C₃₄) that have fairly high melting points. If these remained in the oil, they might crystallize to waxy solids in an oil line in cold weather. To prevent this, the oil is chilled and the wax is removed by filtration. After purification this is sold as solid *paraffin wax* (m.p. 50-55°) or used in *petrolatum jelly* (Vaseline). Asphalt is used in roofing and road building. The coke that is obtained from paraffin-base crude oil consists of complex hydrocarbons having a high carbon-to-hydrogen ratio; it is used as a fuel or in the manufacture of carbon electrodes for the electrochemical industries. Petroleum ether and ligroin are useful solvents for many organic materials of low polarity.

In addition to being used directly as just described, certain petroleum fractions are converted into other kinds of chemical compounds. Catalytic **isomerization** changes straight-chain alkanes into branched-chain ones. The **cracking** process (Sec. 3.31) converts higher alkanes into smaller alkanes and alkenes, and thus increases the gasoline yield; it can even be used for the production of "natural" gas. In addition, the alkenes thus formed are the most important raw materials for the large-scale synthesis of organic compounds. The process of **catalytic reforming** (Sec. 16.5) converts alkanes and cycloalkanes into aromatic hydrocarbons and thus provides the chief raw material for the large-scale synthesis of another broad class of compounds.

3.14 Industrial source vs. laboratory preparation

We shall generally divide the methods of obtaining a particular kind of organic compound into two categories: *industrial source* and *laboratory preparation*. We may contrast the two in the following way, although it must be realized that there are many exceptions to these generalizations.

An industrial source must provide large amounts of the desired material at the lowest possible cost. A laboratory preparation may be required to produce only a few hundred grams or even a few grams; cost is usually of less importance than the time of the investigator.

For many industrial purposes a mixture may be just as suitable as a pure compound; even when a single compound is required, it might be economically feasible to separate it from a mixture, particularly when the other components may also be marketed. In the laboratory a chemist nearly always wants a single pure

compound. Separation of a single compound from a mixture of related substances is very time-consuming and frequently does not yield material of the required purity. Furthermore, the raw material for a particular preparation may well be the hard-won product of a previous preparation or even series of preparations, and hence one wishes to convert it as completely as possible into the desired compound. On an industrial scale, if a compound cannot be isolated from naturally occurring material, it may be synthesized along with a number of related compounds by some inexpensive reaction. In the laboratory, whenever possible, a reaction is selected that forms a single compound in high yield.

In industry it is frequently worthwhile to work out a procedure and design apparatus that may be used in the synthesis of only one member of a chemical family. In the laboratory a chemist is seldom interested in preparing the same compound over and over again, and hence makes use of methods that are applicable to many or all members of a particular family.

In our study of organic chemistry, we shall concentrate our attention on versatile laboratory preparations rather than on limited industrial methods. In learning these we may, for the sake of simplicity, use as examples the preparation of compounds that may actually never be made by the method shown. We may discuss the synthesis of ethane by the hydrogenation of ethylene, even though we can buy all the ethane we need from the petroleum industry. However, if we know how to convert ethylene into ethane, then, when the need arises, we also know how to convert 2-methyl-1-hexene into 2-methylhexane, or cholesterol into cholestanol, or, for that matter, cottonseed oil into oleomargarine.

3.15 Preparation

Each of the smaller alkanes, from methane through *n*-pentane and isopentane, can be obtained in pure form by fractional distillation of petroleum and natural gas; neopentane does not occur naturally. Above the pentanes the number of isomers of each homolog becomes so large and the boiling point differences become so small that it is no longer feasible to isolate individual, pure compounds; these alkanes must be synthesized by one of the methods outlined below.

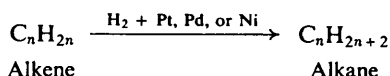
In some of these equations, the symbol **R** is used to represent **any alkyl group**. This convenient device helps to summarize reactions that are typical of an entire family, and emphasizes the essential similarity of the various members.

In writing these generalized equations, however, we must not lose sight of one important point. An equation involving RCl, to take a specific example, has meaning only in terms of a reaction that we can carry out in the laboratory using a real compound, like methyl chloride or *tert*-butyl chloride. Although *typical* of alkyl halides, a reaction may differ widely in rate or yield depending upon the particular alkyl group actually concerned. We may use quite different experimental conditions for methyl chloride than for *tert*-butyl chloride; in an extreme case, a reaction that goes well for methyl chloride might go so slowly or give so many side products as to be completely useless for *tert*-butyl chloride.

By far the most important of these methods is the hydrogenation of alkenes. When shaken under a slight pressure of hydrogen gas in the presence of a small amount of catalyst, alkenes are converted smoothly and quantitatively into alkanes of the same carbon skeleton. The method is limited only by the availability of the proper alkene. This is not a very serious limitation; as we shall see (Sec. 7.11),

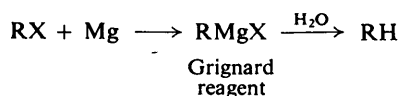
PREPARATION OF ALKANES

1. Hydrogenation of alkenes. Discussed in Sec. 8.3.

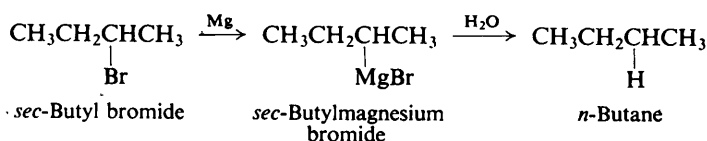


2. Reduction of alkyl halides

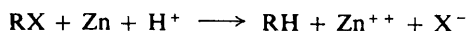
(a) Hydrolysis of Grignard reagent. Discussed in Sec. 3.16.



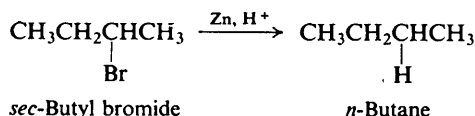
Example:



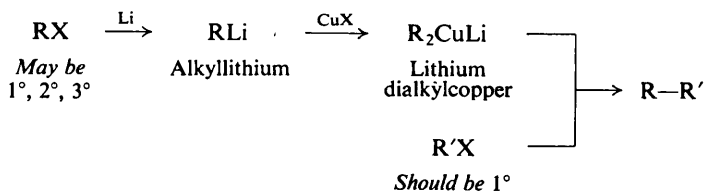
(b) Reduction by metal and acid. Discussed in Sec. 3.15.



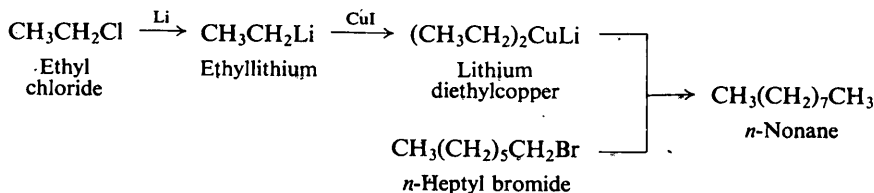
Example:



3. Coupling of alkyl halides with organometallic compounds. Discussed in Sec. 3.17.

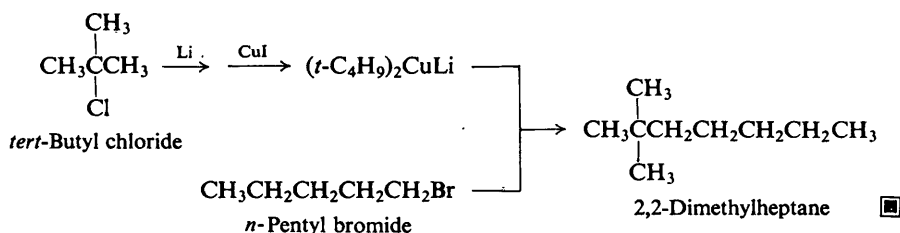


Examples:



CONT.

CONT.



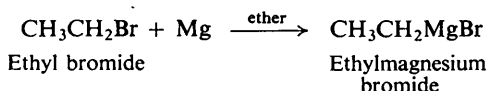
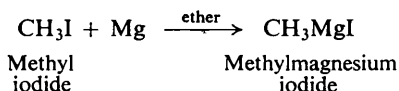
alkenes are readily prepared, chiefly from alcohols, which in turn can be readily synthesized (Sec. 10.6) in a wide variety of sizes and shapes.

Reduction of an alkyl halide, either via the Grignard reagent or directly with metal and acid, involves simply the replacement of a halogen atom by a hydrogen atom; the carbon skeleton remains intact. This method has about the same applicability as the previous method, since, like alkenes, alkyl halides are generally prepared from alcohols. Where either method could be used, the hydrogenation of alkenes would probably be preferred because of its simplicity and higher yield.

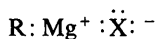
The coupling of alkyl halides with organometallic compounds is the only one of these methods in which carbon-carbon bonds are formed and a new, bigger carbon skeleton is generated.

3.16 The Grignard reagent: an organometallic compound

When a solution of an alkyl halide in dry ethyl ether, $(\text{C}_2\text{H}_5)_2\text{O}$, is allowed to stand over turnings of metallic magnesium, a vigorous reaction takes place: the solution turns cloudy, begins to boil, and the magnesium metal gradually disappears. The resulting solution is known as a **Grignard reagent**, after Victor Grignard (of the University of Lyons) who received the Nobel prize in 1912 for its discovery. It is one of the most useful and versatile reagents known to the organic chemist.

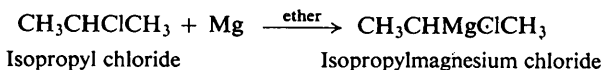
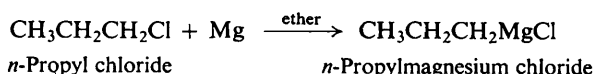


The Grignard reagent has the general formula RMgX , and the general name **alkylmagnesium halide**. The carbon-magnesium bond is covalent but highly polar, with carbon pulling electrons from electropositive magnesium; the magnesium-halogen bond is essentially ionic.



Since magnesium becomes bonded to the same carbon that previously held

halogen, the alkyl group remains intact during the preparation of the reagent. Thus *n*-propyl chloride yields *n*-propylmagnesium chloride, and isopropyl chloride yields isopropylmagnesium chloride.

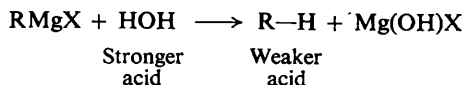


The Grignard reagent is the best-known member of a broad class of substances, called **organometallic** compounds, in which carbon is bonded to a metal: lithium, potassium, sodium, zinc, mercury, lead, thallium—almost any metal known. Each kind of organometallic compound has, of course, its own set of properties, and its particular uses depend on these. But, whatever the metal, it is less electronegative than carbon, and the carbon-metal bond—like the one in the Grignard reagent—is highly polar. Although the organic group is not a full-fledged *carbanion*—an anion in which carbon carries negative charge (Sec. 7.16)—it nevertheless has considerable carbanion character. As we shall see, organometallic compounds owe their enormous usefulness chiefly to one common quality: they can serve as a source from which carbon is readily transferred *with its electrons*.



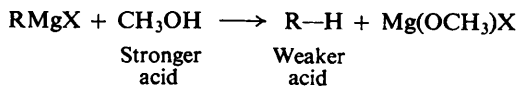
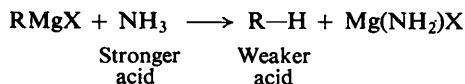
The Grignard reagent is highly reactive. It reacts with numerous inorganic compounds including water, carbon dioxide, and oxygen, and with most kinds of organic compounds; in many of these cases the reaction provides the best way to make a particular class of organic compound.

The reaction with water to form an alkane is typical of the behavior of the Grignard reagent—and many of the more reactive organometallic compounds—toward acids. In view of the marked carbanion character of the alkyl group, we may consider the Grignard reagent to be the magnesium salt, RMgX , of the extremely weak acid, R-H . The reaction



is simply the displacement of the weaker acid, R-H , from its salt by the stronger acid, HOH .

An alkane is such a weak acid that it is displaced from the Grignard reagent by compounds that we might ordinarily consider to be very weak acids themselves,



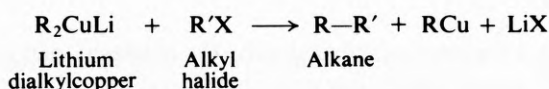
or possibly not acids at all. Any compound containing hydrogen attached to oxygen or nitrogen is tremendously more acidic than an alkane, and therefore can decompose the Grignard reagent: for example, ammonia or methyl alcohol. For the preparation of an alkane, one acid is as good as another, so we naturally choose water as the most available and convenient.

Problem 3.9 (a) Which alkane would you expect to get by the action of water on *n*-propylmagnesium chloride? (b) On isopropylmagnesium chloride? (c) Answer (a) and (b) for the action of deuterium oxide ("heavy water," D₂O).

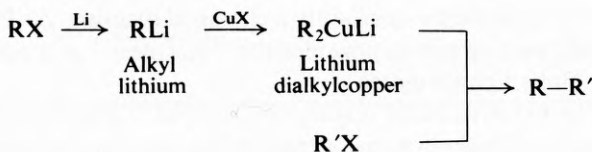
Problem 3.10 On conversion into the Grignard reagent followed by treatment with water, how many alkyl bromides would yield: (a) *n*-pentane; (b) 2-methylbutane; (c) 2,3-dimethylbutane; (d) neopentane? Draw the structures in each case.

3.17 Coupling of alkyl halides with organometallic compounds

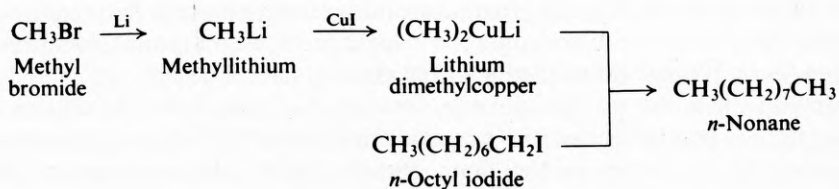
To make an alkane of higher carbon number than the starting material requires formation of carbon-carbon bonds, most directly by the coupling together of two alkyl groups. The most versatile method of doing this is through a synthesis developed during the late 1960's by E. J. Corey and Herbert House, working independently at Harvard University and Massachusetts Institute of Technology. Coupling takes place in the reaction between a *lithium dialkylcopper*, R₂CuLi, and an alkyl halide, R'X. (R' stands for an alkyl group that may be the same as, or different from, R.)

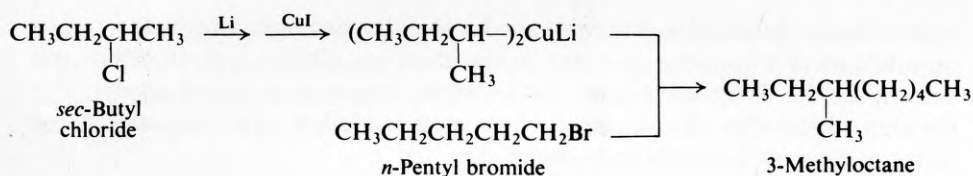


An alkyl lithium, RLi, is prepared from an alkyl halide, RX, in much the same way as a Grignard reagent. To it is added cuprous halide, CuX, and then, finally, the second alkyl halide, R'X. Ultimately, the alkane is synthesized from the two alkyl halides, RX and R'X.



For good yields, R'X should be a *primary* halide; the alkyl group R in the organometallic may be primary, secondary, or tertiary. For example:





The choice of organometallic reagent is crucial. Grignard reagents or organolithium compounds, for example, couple with only a few unusually reactive organic halides. Organosodium compounds couple, but are so reactive that they couple, as they are being formed, with their parent alkyl halide; the reaction of sodium with alkyl halides (*Wurtz reaction*) is thus limited to the synthesis of symmetrical alkanes, R—R.

Organocopper compounds were long known to be particularly good at the formation of carbon-carbon bonds, but are unstable. Here, they are generated *in situ* from the organolithium, and then combine with more of it to form these relatively stable organometallics. They exist as complex aggregates but are believed to correspond roughly to $\text{R}_2\text{Cu}^- \text{Li}^+$. The anion here is an example of an *ate* complex, the negative counterpart of an *onium* complex (ammonium, oxonium).

Although the mechanism is not understood, this much is clear: the alkyl group R is transferred from copper, taking a pair of electrons with it, and becomes attached to the alkyl group R' in place of halide ion (*nucleophilic aliphatic substitution*, Sec. 6.10).

Problem 3.11 (a) Outline two conceivable syntheses of 2-methylpentane from three-carbon compounds. (b) Which of the two would you actually use? Why?

3.18 Reactions

The alkanes are sometimes referred to by the old-fashioned name of *paraffins*. This name (Latin: *parum affinis*, not enough affinity) was given to describe what appeared to be the low reactivity of these hydrocarbons.

But reactivity depends upon the choice of reagent. If alkanes are inert toward hydrochloric and sulfuric acids, they react readily with acids like HF-SbF_5 and $\text{FSO}_3\text{H-SbF}_5$ ("magic acid") to yield a variety of products. If alkanes are inert toward oxidizing agents like potassium permanganate or sodium dichromate, most of this chapter is devoted to their oxidation by halogens. Certain yeasts feed happily on alkanes to produce proteins—certainly a chemical reaction. As Professor M. S. Kharasch (p. 348) used to put it, consider the "inertness" of a room containing natural gas, air, and a lighted match.

Still, on a comparative basis, reactivity *is* limited. "Magic acid" is, after all, one of the strongest acids known; halogenation requires heat or light; combustion needs a flame or spark to get it started.

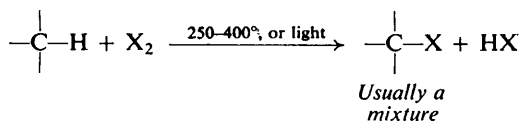
Much of the chemistry of alkanes involves free-radical chain reactions, which take place under vigorous conditions and usually yield mixtures of products. A reactive particle—typically an atom or free radical—is needed to begin the attack on an alkane molecule. It is the generation of this reactive particle that requires the vigorous conditions: the dissociation of a halogen molecule into atoms, for example, or even (as in pyrolysis) dissociation of the alkane molecule itself.

In its attack, the reactive particle abstracts hydrogen from the alkane; the alkane itself is thus converted into a reactive particle which continues the reaction sequence, that is, carries on the chain. But an alkane molecule contains many

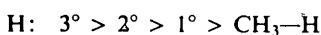
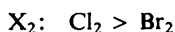
hydrogen atoms and the particular product eventually obtained depends upon which of these hydrogen atoms is abstracted. Although an attacking particle may show a certain selectivity, it can abstract a hydrogen from any part of the molecule, and thus bring about the formation of many isomeric products.

REACTIONS OF ALKANES

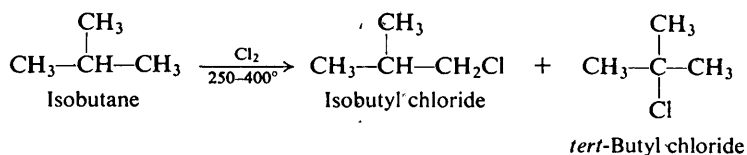
1. Halogenation. Discussed in Secs. 3.19–3.22.



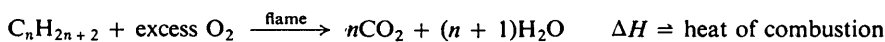
Reactivity



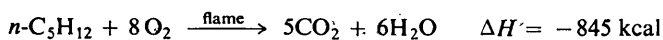
Example:



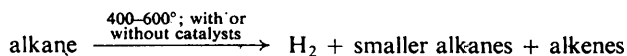
2. Combustion. Discussed in Sec. 3.30.



Example:



3. Pyrolysis (cracking). Discussed in Sec. 3.31.



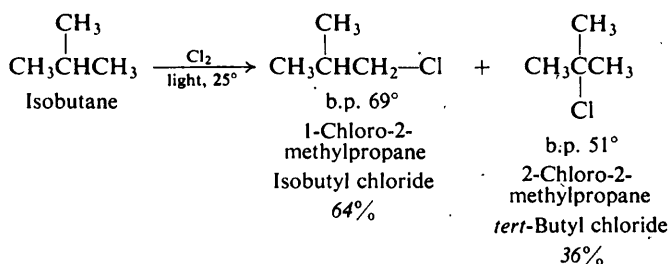
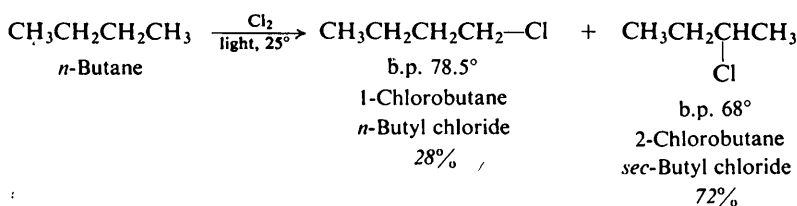
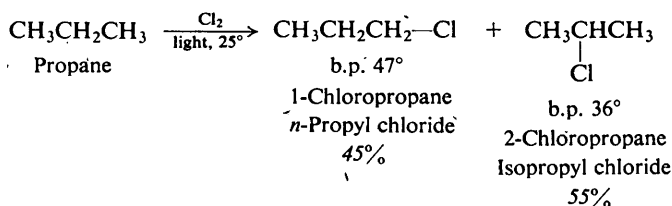
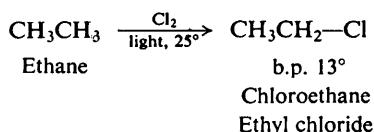
3.19 Halogenation

As we might expect, halogenation of the higher alkanes is essentially the same as the halogenation of methane. It can be complicated, however, by the formation of mixtures of isomers.

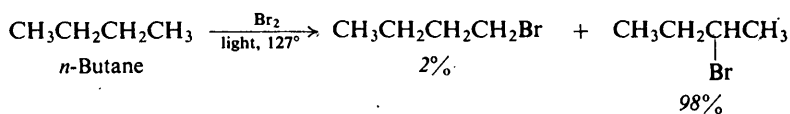
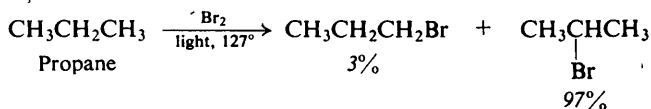
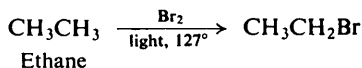
Under the influence of ultraviolet light, or at 250–400°, chlorine or bromine converts alkanes into chloroalkanes (alkyl chlorides) or bromoalkanes (alkyl bromides); an equivalent amount of hydrogen chloride or hydrogen bromide is formed at the same time. When diluted with an inert gas, and in an apparatus

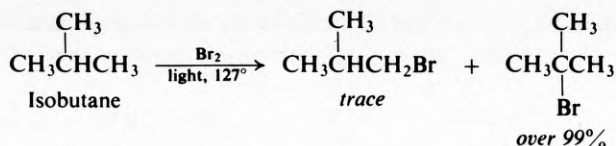
designed to carry away the heat produced, fluorine has recently been found to give analogous results. As with methane, iodination does not take place at all.

Depending upon which hydrogen atom is replaced, any of a number of isomeric products can be formed from a single alkane. Ethane can yield only one haloethane; propane, *n*-butane, and isobutane can yield two isomers each; *n*-pentane can yield three isomers, and isopentane, four isomers. Experiment has shown that on halogenation an alkane yields a mixture of all possible isomeric products, indicating that all hydrogen atoms are susceptible to replacement. For example, for chlorination:



Bromination gives the corresponding bromides but in different proportions:





Problem 3.12 Draw the structures of: (a) the three monochloro derivatives of *n*-pentane; (b) the four monochloro derivatives of isopentane.

Although both chlorination and bromination yield mixtures of isomers, the results given above show that the *relative amounts* of the various isomers differ markedly depending upon the halogen used. Chlorination gives mixtures in which no isomer greatly predominates; in bromination, by contrast, one isomer may predominate to such an extent as to be almost the only product, making up 97–99% of the total mixture. In bromination, there is a high degree of *selectivity* as to which hydrogen atoms are to be replaced. (As we shall see in Sec. 3.28, this characteristic of bromination is due to the relatively low reactivity of bromine atoms, and is an example of a general relationship between *reactivity* and *selectivity*.)

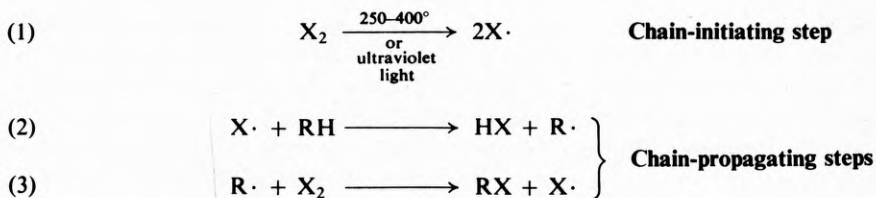
Chlorination of an alkane is not usually suitable for the laboratory preparation of an alkyl chloride; any one product is necessarily formed in low yield, and is difficult to separate from its isomers, whose boiling points are seldom far from its own. Bromination, on the other hand, often gives a nearly pure alkyl bromide in high yield. As we shall see, it is possible to predict just which isomer will predominate; if this product is the one desired, direct bromination could be a feasible synthetic route.

On an industrial scale, chlorination of alkanes is important. For many purposes—for example, use as a solvent—a mixture of isomers is just as suitable as, and much cheaper than, a pure compound. It may be even worthwhile, when necessary, to separate a mixture of isomers if each isomer can then be marketed.

Problem 3.13 How do you account for the fact that not only bromination but also chlorination is a feasible laboratory route to a neopentyl halide, $(\text{CH}_3)_3\text{CCH}_2\text{X}$?

3.20 Mechanism of halogenation

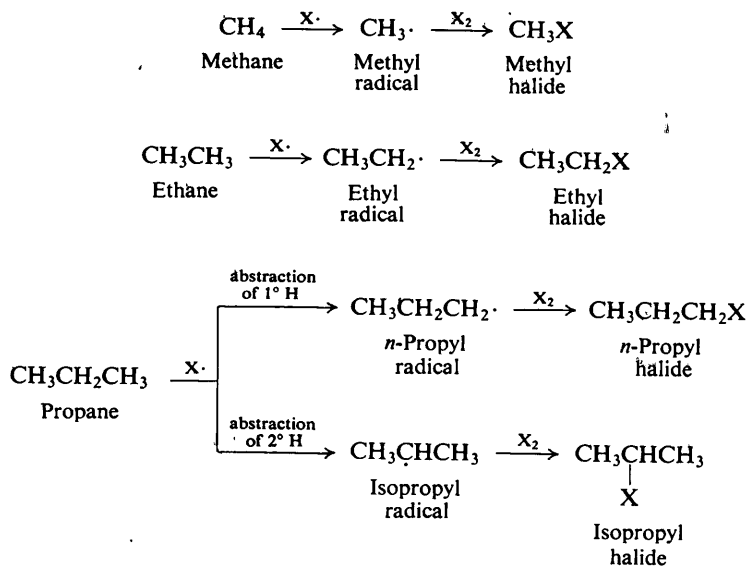
Halogenation of alkanes proceeds by the same mechanism as halogenation of methane:



then (2), (3), (2), (3), etc., until finally a chain is terminated (Sec. 2.13)

A halogen atom abstracts hydrogen from the alkane (RH) to form an alkyl radical (R·). The radical in turn abstracts a halogen atom from a halogen molecule to yield the alkyl halide (RX).

Which alkyl halide is obtained depends upon which alkyl radical is formed.



This in turn depends upon the alkane and which hydrogen atom is abstracted from it. For example, *n*-propyl halide is obtained from a *n*-propyl radical, formed from propane by abstraction of a primary hydrogen; isopropyl halide is obtained from an isopropyl radical, formed by abstraction of a secondary hydrogen.

How fast an alkyl halide is formed depends upon how fast the alkyl radical is formed. Here also, as was the case with methane (Sec. 2.20), of the two chain-propagating steps, step (2) is more difficult than step (3), and hence controls the

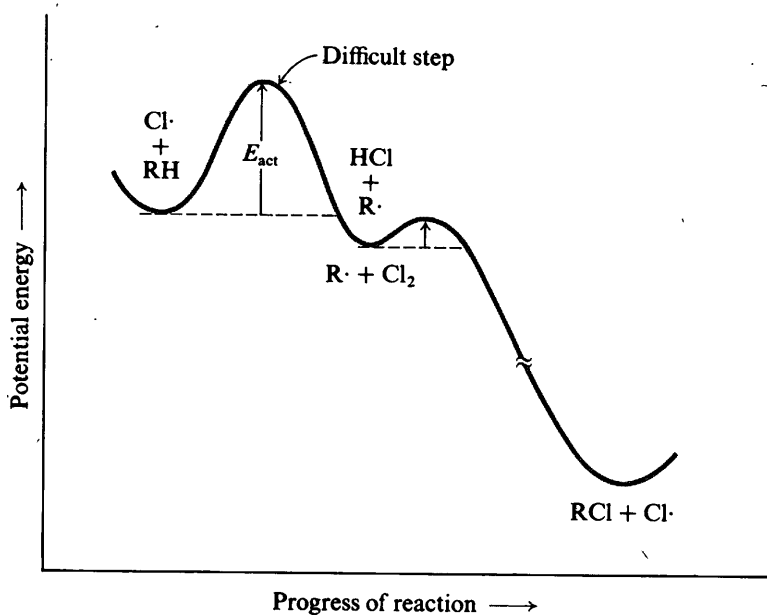


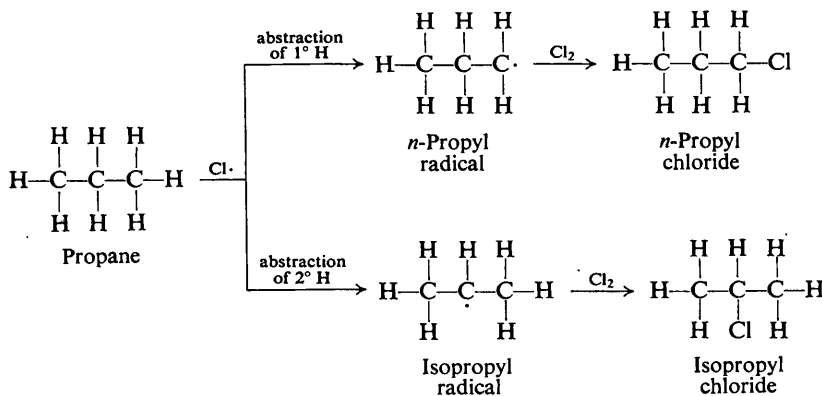
Figure 3.5. Potential energy changes during progress of reaction: chlorination of an alkane. Formation of radical is rate-controlling step.

rate of overall reaction. Formation of the alkyl radical is difficult, but once formed the radical is readily converted into the alkyl halide (see Fig. 3.5).

3.21 Orientation of halogenation

With this background let us turn to the problem of **orientation**; that is, let us examine the factors that determine *where* in a molecule reaction is most likely to occur. It is a problem that we shall encounter again and again, whenever we study a compound that offers more than one reactive site to attack by a reagent. It is an important problem, because orientation determines what product we obtain.

As an example let us take chlorination of propane. The relative amounts of *n*-propyl chloride and isopropyl chloride obtained depend upon the relative rates at which *n*-propyl radicals and isopropyl radicals are formed. If, say, isopropyl radicals are formed faster, then isopropyl chloride will be formed faster, and will make up a larger fraction of the product. As we can see, *n*-propyl radicals are formed by abstraction of primary hydrogens, and isopropyl radicals by abstraction of secondary hydrogens.



Thus *orientation is determined by the relative rates of competing reactions*. In this case we are comparing the rate of abstraction of primary hydrogens with the rate of abstraction of secondary hydrogens. What are the factors that determine the rates of these two reactions, and in which of these factors may the two reactions differ?

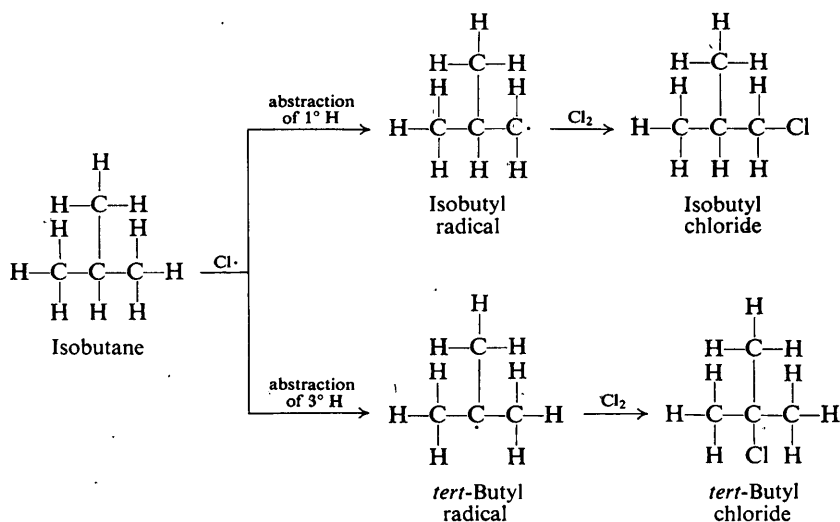
First of all, there is the collision frequency. This must be the same for the two reactions, since both involve collisions of the same particles: a propane molecule and a chlorine atom.

Next, there is the probability factor. If a primary hydrogen is to be abstracted, the propane molecule must be so oriented at the time of collision that the chlorine atom strikes a primary hydrogen; if a secondary hydrogen is to be abstracted, the propane must be so oriented that the chlorine collides with a secondary hydrogen. Since there are six primary hydrogens and only two secondary hydrogens in each molecule, we might estimate that the probability factor favors abstraction of primary hydrogens by the ratio of 6:2, or 3:1.

Considering only collision frequency and our guess about probability factors, we predict that chlorination of propane would yield *n*-propyl chloride and isopropyl chloride in the ratio of 3:1. As shown on page 102, however, the two chlorides are formed in roughly equal amounts, that is, in the ratio of about 1:1, or 3:3. The

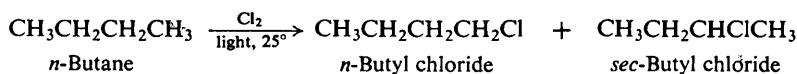
proportion of isopropyl chloride is about three times as great as predicted. Evidently, about three times as many collisions with secondary hydrogens are successful as collisions with primary hydrogens. If our assumption about the probability factor is correct, this means that E_{act} is less for abstraction of a secondary hydrogen than for abstraction of a primary hydrogen.

Chlorination of isobutane presents a similar problem. In this case, abstraction of one of the nine primary hydrogens leads to the formation of isobutyl chloride, whereas abstraction of a single tertiary hydrogen leads to the formation of *tert*-butylchloride. We would estimate, then, that the probability factor favors formation



of isobutyl chloride by the ratio of 9:1. The experimental results given on page 102 show that the ratio is roughly 2:1, or 9:4.5. Evidently, about 4.5 times as many collisions with the tertiary hydrogen are successful as collisions with the primary hydrogens. This, in turn, probably means that E_{act} is less for abstraction of a tertiary hydrogen than for abstraction of a primary hydrogen, and, in fact, even less than for abstraction of a secondary hydrogen.

Study of the chlorination of a great many alkanes has shown that these are typical results. After allowance is made for differences in the probability factor, the rate of abstraction of hydrogen atoms is always found to follow the sequence $3^\circ > 2^\circ > 1^\circ$. At room temperature, for example, the relative rates *per hydrogen atom* are 5.0:3.8:1.0. Using these values we can predict quite well the ratio of isomeric chlorination products from a given alkane. For example:



$$\begin{aligned} \frac{\textit{n-butyl chloride}}{\textit{sec-butyl chloride}} &= \frac{\text{no. of } 1^\circ \text{ H}}{\text{no. of } 2^\circ \text{ H}} \times \frac{\text{reactivity of } 1^\circ \text{ H}}{\text{reactivity of } 2^\circ \text{ H}} \\ &= \frac{6}{4} \times \frac{1.0}{3.8} \\ &= \frac{6}{15.2} \text{ equivalent to } \frac{28\%}{72\%} \end{aligned}$$

In spite of these differences in reactivity, chlorination rarely yields a great preponderance of any single isomer. In nearly every alkane, as in the examples we have studied, the less reactive hydrogens are the more numerous; their lower reactivity is compensated for by a higher probability factor, with the result that appreciable amounts of every isomer are obtained.

Problem 3.14 Predict the proportions of isomeric products from chlorination at room temperature of: (a) propane; (b) isobutane; (c) 2,3-dimethylbutane; (d) *n*-pentane (Note: There are *three* isomeric products); (e) isopentane; (f) 2,2,3-trimethylbutane; (g) 2,2,4-trimethylpentane. For (a) and (b) check your calculations against the experimental values given on page 102.

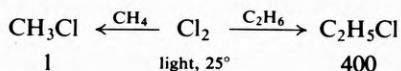
The same sequence of reactivity, $3^\circ > 2^\circ > 1^\circ$, is found in bromination, but with enormously larger reactivity ratios. At 127° , for example, the relative rates per hydrogen atom are 1600:82:1. Here, differences in reactivity are so marked as vastly to outweigh probability factors.

Problem 3.15 Answer Problem 3.14 for bromination at 127° .

3.22 Relative reactivities of alkanes toward halogenation

The best way to measure the relative reactivities of different compounds toward the same reagent is by the **method of competition**, since this permits an exact quantitative comparison under identical reaction conditions. Equimolar amounts of two compounds to be compared are mixed together and allowed to react with a limited amount of a particular reagent. Since there is not enough reagent for both compounds, the two compete with each other. Analysis of the reaction products shows which compound has consumed more of the reagent and hence is more reactive.

For example, if equimolar amounts of methane and ethane are allowed to react with a small amount of chlorine, about 400 times as much ethyl chloride as methyl chloride is obtained, showing that ethane is 400 times as reactive as methane. When allowance is made for the relative numbers of hydrogens in the two kinds of molecules, we see that each hydrogen of ethane is about 270 times as reactive as each hydrogen of methane.



Problem 3.16 Because of the rather large difference in reactivity between ethane and methane, competition experiments have actually used mixtures containing more methane than ethane. If the molar ratio of methane to ethane were 10:1, what ratio of ethyl chloride to methyl chloride would you expect to obtain? What practical advantage would this experiment have over one involving a 1:1 ratio?

Data obtained from similar studies of other compounds are consistent with this simple generalization: *the reactivity of a hydrogen depends chiefly upon its class, and not upon the alkane to which it is attached*. Each primary hydrogen of propane, for example, is about as easily abstracted as each primary hydrogen in *n*-butane or isobutane; each secondary hydrogen of propane, about as easily as each secondary hydrogen of *n*-butane or *n*-pentane; and so on.

The hydrogen atoms of methane, which fall into a special class, are even less reactive than primary hydrogens, as shown by the above competition with ethane.

Problem 3.17 On chlorination, an equimolar mixture of ethane and neopentane yields neopentyl chloride and ethyl chloride in the ratio of 2.3:1. How does the reactivity of a primary hydrogen in neopentane compare with that of a primary hydrogen in ethane?

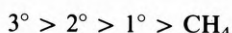
3.23 Ease of abstraction of hydrogen atoms. Energy of activation

At this stage we can summarize the effect of structure on halogenation of alkanes in the following way. The controlling step in halogenation is abstraction of hydrogen by a halogen atom:



The relative ease with which the different classes of hydrogen atoms are abstracted is:

Ease of abstraction
of hydrogen atoms



This sequence applies (a) to the various hydrogens within a single alkane and hence governs **orientation** of reaction, and (b) to the hydrogens of different alkanes and hence governs **relative reactivities**.

Earlier, we concluded that these differences in ease of abstraction—like most differences in rate between closely related reactions (Sec. 2.19)—are probably due to differences in E_{act} . By study of halogenation at a series of temperatures (Sec. 2.18), the values of E_{act} listed in Table 3.5 were measured. In agreement with our tentative conclusions, the increasing rate of reaction along the series, methyl, 1° , 2° , 3° , is paralleled by a decreasing E_{act} . In chlorination the differences in E_{act} , like the differences in rate, are small; in bromination both differences are large.

Table 3.5 ENERGIES OF ACTIVATION, KCAL/MOL

$\text{R-H} + \text{X}\cdot \longrightarrow \text{R}\cdot + \text{H-X}$		
R	X = Cl	X = Br
CH_3	4	18
1°	1	13
2°	0.5	10
3°	0.1	7.5

We have seen (Sec. 2.18) that the larger the E_{act} of a reaction, the larger the increase in rate brought about by a given rise in temperature. We have just found that the differences in rate of abstraction among primary, secondary, and tertiary hydrogens are due to differences in E_{act} . We predict, therefore, that a rise in temperature should speed up abstraction of primary hydrogens (with the largest E_{act}) most, and abstraction of tertiary hydrogens (with the smallest E_{act}) least; the three classes of hydrogen should then display more nearly the same reactivity.

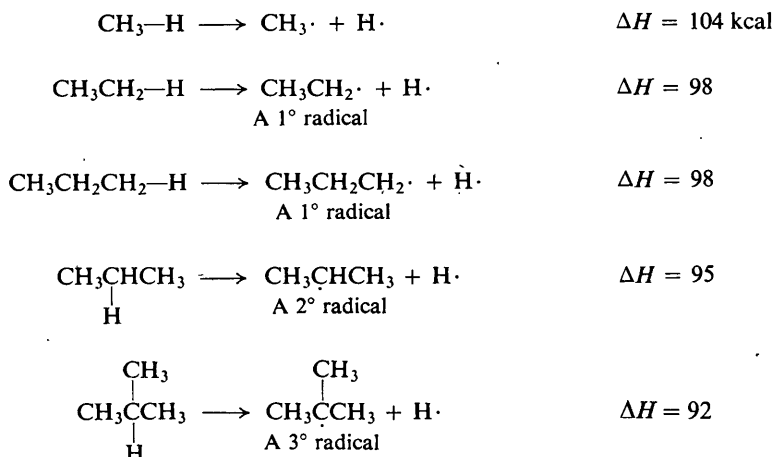
This leveling-out effect has indeed been observed: as the temperature is raised, the relative rates per hydrogen atom change from 5.0:3.8:1.0 toward 1:1:1. At very high temperatures virtually every collision has enough energy for abstraction of even primary

hydrogens. It is generally true that *as the temperature is raised a given reagent becomes less selective in the position of its attack*; conversely, as the temperature is lowered it becomes more selective.

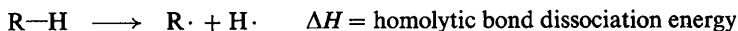
How can we account for the effect of structure on ease of abstraction of hydrogen atoms? Since this is a matter of E_{act} , we must look for our answer, as always, in the transition state. To do this, however, we must first shift our focus from the hydrogen atom being abstracted to the radical being formed.

3.24 Stability of free radicals

In Table 1.2 (p. 20) we find the homolytic dissociation energies of the bonds that hold hydrogen atoms to a number of groups. These values are the ΔH 's of the following reactions:



By definition, this bond dissociation energy is the amount of energy that must be supplied to convert a mole of alkane into radicals and hydrogen atoms. As we can see, the amount of energy needed to form the various classes of radicals decreases in the order: $\text{CH}_3\cdot > 1^\circ > 2^\circ > 3^\circ$.

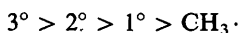


If less energy is needed to form one radical than another, it can only mean that, *relative to the alkane from which it is formed*, the one radical contains less energy than the other, this is to say, is *more stable* (see Fig. 3.6).

We are not attempting to compare the absolute energy contents of, say, methyl and ethyl radicals; we are simply saying that the difference in energy between methane and methyl radicals is greater than the difference between ethane and ethyl radicals. *When we compare stabilities of free radicals, it must be understood that our standard for each radical is the alkane from which it is formed.* As we shall see, this is precisely the kind of stability that we are interested in.

Relative to the alkane from which each is formed, then, the order of stability of free radicals is:

Stability of
free radicals



at the same time listed them in order of their stability. **The more stable the free radical, the more easily it is formed.**

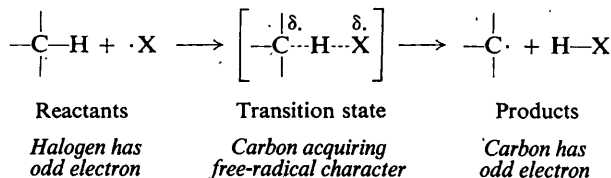
This is an extremely useful generalization. *Radical stability seems to govern orientation and reactivity in many reactions where radicals are formed.* The addition of bromine atoms to alkenes (Sec. 8.23), for example, is a quite different sort of reaction from the one we have just studied; yet, there too, orientation and reactivity can be governed by radical stability. (Even in those cases where other factors—steric hindrance, polar effects—are significant or even dominant, it is convenient to use radical stability as a point of departure.)

3.26 Transition state for halogenation

Is it reasonable that the more stable radical should be formed more easily?

We have already seen that the differences in reactivity toward halogen atoms are due chiefly to differences in E_{act} : the more stable the radical, then, the lower the E_{act} for its formation. This, in turn, means that the more stable the radical, the more stable the transition state leading to its formation—both stabilities being measured, as they must be, against the same standard, the reactants. (*Remember: E_{act} is the difference in energy content between reactants and transition state.*)

Examination of the transition state shows that this is exactly what we would expect. As we saw before (Sec. 2.23), the hydrogen-halogen bond is partly formed and the carbon-hydrogen bond is partly broken. To the extent that the bond is



broken, the alkyl group possesses character of the free radical it will become. *Factors that tend to stabilize the free radical tend to stabilize the incipient free radical in the transition state.*

We have seen that the stabilities of free radicals follow the sequence $3^\circ > 2^\circ > 1^\circ > \text{CH}_3 \cdot$. A certain factor (*delocalization of the odd electron*, Sec. 9.11) causes the energy difference between isobutane and the *tert*-butyl radical, for example, to be smaller than between propane and the isopropyl radical. It is not unreasonable that this same factor should cause the energy difference between isobutane and the *incipient tert*-butyl radical in the transition state to be smaller than between propane and the *incipient* isopropyl radical in its transition state (Fig. 3.7, following page).

3.27 Orientation and reactivity

Throughout our study of organic chemistry, we shall approach the problems of orientation and reactivity in the following way.

Both problems involve comparing the rates of closely related reactions: in the case of orientation, reactions at different sites in the same compound; in the case of reactivity, reactions with different compounds. For such closely related reactions,

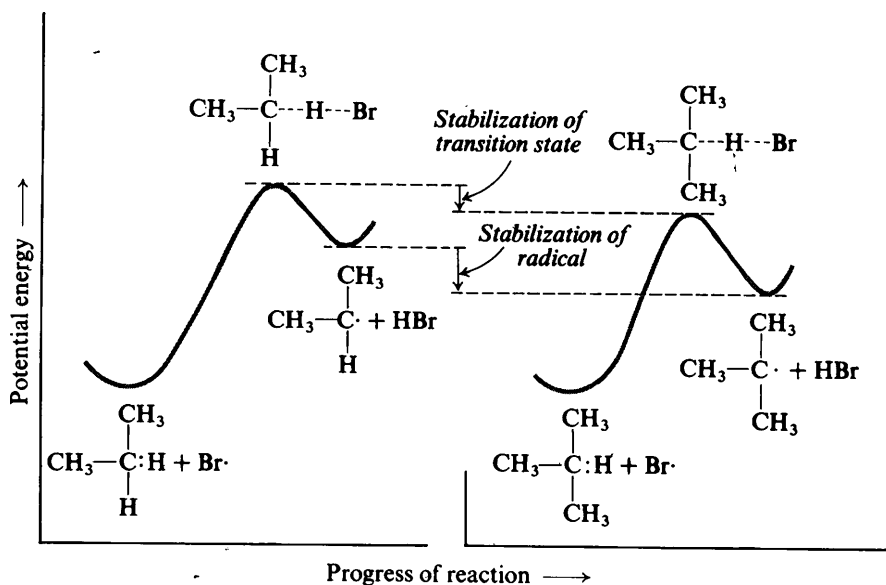


Figure 3.7. Molecular structure and rate of reaction. Stability of transition state parallels stability of radical: more stable radical formed faster. (Plots aligned with each other for easy comparison.)

variations in rate are due mostly to differences in E_{act} ; by definition, E_{act} is the difference in energy content between reactants and transition state.

We shall examine the most likely structure for the transition state, then, to see what structural features affect its stability without at the same time affecting by an equal amount the stability of the reactants; that is, we shall look for factors that tend to increase or decrease the energy difference between reactants and transition state. Having decided what structural features affect the E_{act} , we shall compare the transition states for the reactions whose rates we wish to compare: the more stable the transition state, the faster the reaction.

In many, if not most, reactions where a free radical is formed, as in the present case, the transition state differs from the reactants chiefly in being like the product. It is reasonable, then, that the factor most affecting the E_{act} should be the *radical character* of the transition state. Hence we find that the more stable the radical the more stable the transition state leading to its formation, and the faster the radical is formed.

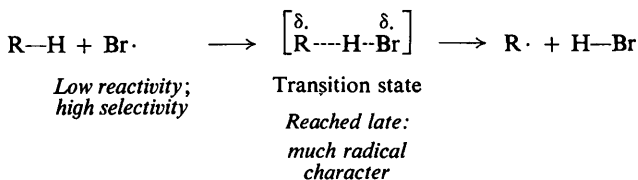
3.28 Reactivity and selectivity

In its attack on alkanes, the bromine atom is much more selective than the chlorine atom (with relative rate factors of 1600:82:1 as compared with 5.0:3.8:1). It is also much less reactive than the chlorine atom (only 1/375,000 as reactive toward methane, for example, as we saw in Sec. 2.19). This is just one example of a general relationship: in a set of similar reactions, the *less reactive* the reagent, the *more selective* it is in its attack.

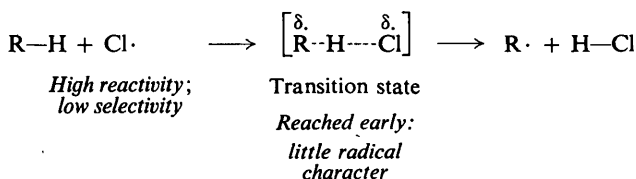
To account for this relationship, we must recall what we learned in Sec. 2.24. In the attack by the comparatively unreactive bromine atom, the transition state is reached late in the reaction process, after the alkyl group has developed

considerable radical character. In the attack by the highly reactive chlorine atom, the transition state is reached early, when the alkyl group has gained very little radical character.

Bromination



Chlorination



Now, by "selectivity" we mean here the differences in rate at which the various classes of free radicals are formed; a more stable free radical is formed faster, we said, because the factor that stabilizes it—delocalization of the odd electron (Sec. 9.11)—also stabilizes the incipient radical in the transition state. If this is so, then the more fully developed the radical character in the transition state, the more effective delocalization will be in stabilizing the transition state. The isopropyl radical, for example, is 3 kcal more stable than the *n*-propyl radical; if the radicals were *completely* formed in the transition state, the difference in E_{act} would be 3 kcal. Actually, in bromination the difference in E_{act} is 3 kcal: equal, within the limits of experimental error, to the maximum potential stabilization, indicating as we expected, a great deal of radical character. In chlorination, by contrast, the difference in E_{act} is only 0.5 kcal, indicating only very slight radical character.

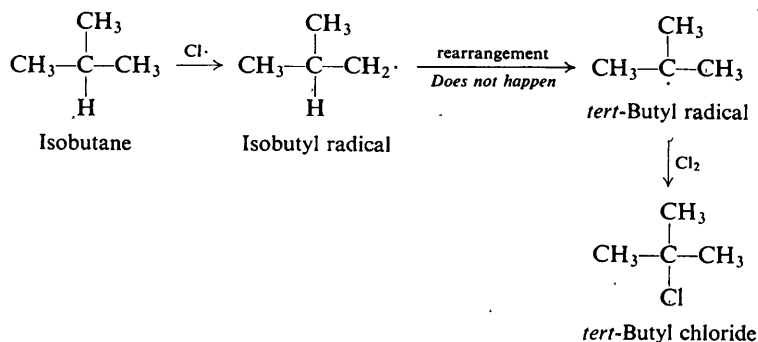
A similar situation exists for reactions of other kinds. Whatever the factor responsible for differences in stability among a set of transition states—whether it is delocalization of an odd electron, or accommodation of a positive or negative charge, or perhaps a change in crowding of the atoms—the factor will operate more effectively when the transition state is more fully developed, that is, when the reagent is less reactive.

3.29 Non-rearrangement of free radicals. Isotopic tracers

Our interpretation of orientation (Sec. 3.21) was based on an assumption that we have not yet justified: that the relative amounts of isomeric halides we find in the product reflect the relative rates at which various free radicals were formed from the alkane. From isobutane, for example, we obtain twice as much isobutyl chloride as *tert*-butyl chloride, and we assume from this that, by abstraction of hydrogen, isobutyl radicals are formed twice as fast as *tert*-butyl radicals.

Yet how do we know, in this case, that every isobutyl radical that is formed

ultimately yields a molecule of isobutyl chloride? Suppose some isobutyl radicals were to change—by *rearrangement* of atoms—into *tert*-butyl radicals, which then react with chlorine to yield *tert*-butyl chloride. This supposition is not so far-fetched

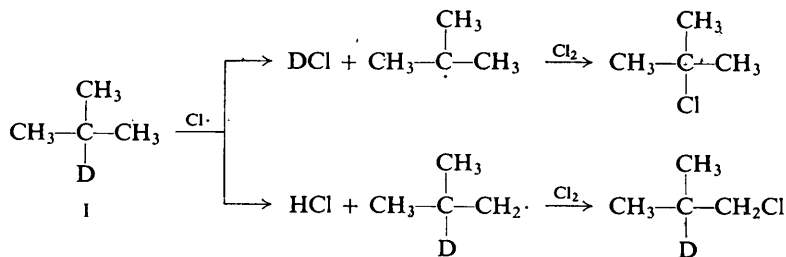


as we, in our present innocence, might think; the doubt it raises is a very real one. We shall shortly see that another kind of reactive intermediate particle, the carbocation, is very prone to rearrange, with less stable ions readily changing into more stable ones (Sec. 6.26).

H. C. Brown (p. 471) and Glen Russell (now of Iowa State University) decided to test the possibility that free radicals, like carbocations, might rearrange, and chose the chlorination of isobutane as a good test case, because of the large difference in stability between *tert*-butyl and isobutyl radicals. If rearrangement of alkyl radicals can indeed take place, it should certainly happen here.

What the problem comes down to is this: does every abstraction of primary hydrogen lead to isobutyl chloride, and every abstraction of tertiary hydrogen lead to *tert*-butyl chloride? This, we might say, we could never know, because all hydrogen atoms are exactly alike. But are they? Actually, three isotopes of hydrogen exist: ^1H , *protium*, ordinary hydrogen; ^2H or D, *deuterium*, heavy hydrogen; and ^3H or T, *tritium*. Protium and deuterium are distributed in nature in the ratio of 5000:1. (Tritium, the unstable, radioactive isotope, is present in traces, but can be made by neutron bombardment of ^6Li .) Modern methods of separation of isotopes have made very pure deuterium available, at moderate prices, in the form of deuterium oxide, D_2O , heavy water.

Brown and Russell prepared the deuterium-labeled isobutane I,

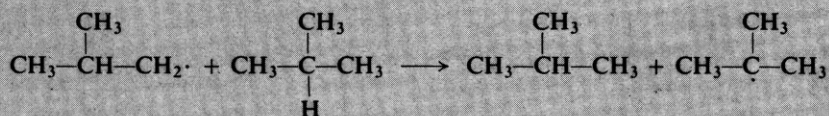


photochemically chlorinated it, and analyzed the products. The DCl:HCl ratio (determined by the mass spectrometer) was found to be equal (within experimental error) to the *tert*-butyl chloride: isobutyl chloride ratio. Clearly, every abstraction of a tertiary hydrogen (*deuterium*) gave a molecule of *tert*-butyl chloride, and every

abstraction of a primary hydrogen (*protium*) gave a molecule of isobutyl chloride. *Rearrangement of the intermediate free radicals did not occur.*

All the existing evidence indicates quite strongly that, although rearrangement of free radicals occasionally happens, it is not very common and does not involve simple alkyl radicals.

Problem 3.18 (a) What results would have been obtained if some isobutyl radicals had rearranged to *tert*-butyl radicals? (b) Suppose that, instead of rearranging, isobutyl radicals were, in effect, converted into *tert*-butyl radicals by the reaction



What results would Brown and Russell have obtained?

Problem 3.19 Keeping in mind the availability of D_2O , suggest a way to make I from *tert*-butyl chloride. (*Hint*: See Sec. 3.16.)

The work of Brown and Russell is just one example of the way in which we can gain insight into a chemical reaction by using isotopically labeled compounds. We shall encounter many other examples in which isotopes, used either as *tracers*, as in this case, or for the detection of *isotope effects* (Sec. 7.18), give us information about reaction mechanisms that we could not get in any other way.

Besides deuterium and tritium, isotopes commonly used in organic chemistry include: ^{14}C , available as $^{14}\text{CH}_3\text{OH}$ and $\text{Ba}^{14}\text{CO}_3$; ^{18}O , as H_2^{18}O ; ^{15}N , as $^{15}\text{NH}_3$, $^{15}\text{NO}_3^-$, and $^{15}\text{NO}_2^-$; ^{36}Cl , as chlorine or chloride; ^{131}I , as iodide.

Problem 3.20 Bromination of methane is slowed down by the addition of HBr (Problem 13, p. 77); this is attributed to the reaction



which, as the reverse of one of the chain-carrying steps, slows down bromination. How might you test whether or not this reaction actually occurs in the bromination mixture?

Problem 3.21 In Sec. 2.12 the reaction



was listed as probable but unproductive. Given ordinary chlorine (made up of ^{35}Cl and ^{37}Cl) and $^{36}\text{Cl}_2$, and a mass spectrometer, how would you go about finding out whether or not the reaction actually occurs?

3.30 Combustion

The reaction of alkanes with oxygen to form carbon dioxide, water, and—most important of all—*heat*, is the chief reaction occurring in the internal combustion engine; its tremendous practical importance is obvious.

The mechanism of this reaction is extremely complicated and is not yet fully understood. There seems to be no doubt, however, that it is a free-radical chain reaction. The reaction is extremely exothermic and yet requires a very high temperature, that of a flame, for its initiation. As in the case of chlorination, a great deal of energy is required for the bond-breaking that generates the initial

reactive particles; once this energy barrier is surmounted, the subsequent chain-carrying steps proceed readily and with the evolution of energy.

A higher compression ratio has made the modern gasoline engine more efficient than earlier ones, but has at the same time created a new problem. Under certain conditions the smooth explosion of the fuel-air mixture in the cylinder is replaced by **knocking**, which greatly reduces the power of the engine.

The problem of knocking has been successfully met in two general ways: (a) proper selection of the hydrocarbons to be used as fuel, and (b) addition of tetraethyllead.

Experiments with pure compounds have shown that hydrocarbons of differing structures differ widely in knocking tendency. The relative antiknock tendency of a fuel is generally indicated by its **octane number**. An arbitrary scale has been set up, with *n*-heptane, which knocks very badly, being given an octane number of zero, and 2,2,4-trimethylpentane ("iso-octane") being given the octane number of 100. There are available today fuels with better antiknock qualities than "iso-octane."

The gasoline fraction obtained by direct distillation of petroleum (*straight-run gasoline*) is improved by addition of compounds of higher octane number; it is sometimes entirely replaced by these better fuels. Branched-chain alkanes and alkenes, and aromatic hydrocarbons generally have excellent antiknock qualities; these are produced from petroleum hydrocarbons by *catalytic cracking* (Sec. 3.31) and *catalytic reforming* (Sec. 16.5). Highly branched alkanes are synthesized from alkenes and alkanes by *alkylation* (Sec. 8.21).

In 1922 T. C. Midgley, Jr., and T. A. Boyd (of the General Motors Research Laboratory) found that the octane number of a fuel is greatly improved by addition of a small amount of tetraethyllead, $(C_2H_5)_4Pb$. Gasoline so treated is called *ethyl gasoline* or *leaded gasoline*. Nearly 50 years of research finally showed that tetraethyllead probably works by producing tiny particles of lead oxides, on whose surface certain reaction chains are broken.

In addition to carbon dioxide and water, however, the gasoline engine discharges other substances into the atmosphere, substances that are either smog-producing or downright poisonous: unburned hydrocarbons, carbon monoxide, nitrogen oxides, and, from leaded gasoline, various compounds of lead—in the United States, hundreds of tons of lead a day. Growing public concern about these pollutants has caused a minor revolution in the petroleum and auto industries. *Converters* are being developed to clean up exhaust emissions: by catalytic oxidation of hydrocarbons and carbon monoxide, and by the breaking down of nitrogen oxides into nitrogen and oxygen. But most of these oxidation catalysts contain platinum, which is poisoned by lead; there has been a move to get the lead out of gasoline—not, initially, to cut down on lead pollution, but to permit converters to function. This has, in turn, brought back the problem of knocking, which is being met in two ways: (a) by lowering the compression ratio of the new automobiles being built; and (b) by increasing the octane number of gasoline through changes in hydrocarbon composition—through addition of aromatics and through increased use of isomerization (Sec. 3.13).

3.31 Pyrolysis: cracking

Decomposition of a compound by the action of heat alone is known as **pyrolysis**. This word is taken from the Greek *pyr*, fire, and *lysis*, a loosing, and

hence to chemists means "cleavage by heat"; compare *hydrolysis*, "cleavage by water."

The pyrolysis of alkanes, particularly when petroleum is concerned, is known as **cracking**. In *thermal cracking* alkanes are simply passed through a chamber heated to a high temperature. Large alkanes are converted into smaller alkanes, alkenes, and some hydrogen. This process yields predominantly ethylene (C_2H_4) together with other small molecules. In a modification called *steam cracking*, the hydrocarbon is diluted with steam, heated for a fraction of a second to 700–900°, and rapidly cooled. Steam cracking is of great importance in the production of hydrocarbons as chemicals, including ethylene, propylene, butadiene, isoprene, and cyclopentadiene. Another source of smaller hydrocarbons is *hydrocracking*, carried out in the presence of a catalyst and hydrogen, at high pressure and at much lower temperatures (250–450°).

The low-molecular-weight alkenes obtained from these cracking processes can be separated and purified, and are the most important raw materials for the large-scale synthesis of aliphatic compounds.

Most cracking, however, is directed toward the production of fuels, not chemicals, and for this *catalytic cracking* is the major process. Higher boiling petroleum fractions (typically, gas oil) are brought into contact with a finely divided silica-alumina catalyst at 450–550° and under slight pressure. Catalytic cracking not only increases the yield of gasoline by breaking large molecules into smaller ones, but also improves the quality of the gasoline: this process involves carbocations (Sec. 6.20), and yields alkanes and alkenes with the highly branched structures desirable in gasoline.

Through the process of *alkylation* (Sec. 8.21) some of the smaller alkanes and alkenes are converted into high-octane synthetic fuels.

Finally, by the process of *catalytic reforming* (Sec. 16.5) enormous quantities of the aliphatic hydrocarbons of petroleum are converted into *aromatic* hydrocarbons which are used not only as superior fuels but as the starting materials in the synthesis of most aromatic compounds (Chap. 14).

3.32 Determination of structure

One of the commonest and most important jobs in organic chemistry is to determine the structural formula of a compound just synthesized or isolated from a natural source.

The compound will fall into one of two groups, although at first we probably shall not know *which* group. It will be either (a) a previously reported compound, which we must identify, or (b) a new compound, whose structure we must prove.

If the compound has previously been encountered by some other chemist who determined its structure, then a description of its properties will be found somewhere in the chemical literature, together with the evidence on which its structure was assigned. In that case, we need only to show that our compound is identical with the one previously described.

If, on the other hand, our compound is a new one that has never before been reported, then we must carry out a much more elaborate proof of structure.

Let us see—in a general way now, and in more detail later—just how we would go about this job. We are confronted by a flask filled with gas, or a few milliliters of liquid, or a tiny heap of crystals. We must find the answer to the question: *what is it?*

First, we purify the compound and determine its physical properties: melting point, boiling point, density, refractive index, and solubility in various solvents. In the laboratory today, we would measure various spectra of the compound (Chap. 17), in particular the infrared spectrum and the NMR spectrum; indeed, because of the wealth of information to be gotten in this way, spectroscopic examination might well be the first order of business after purification. From the mass spectrum we would get a very accurate molecular weight. Increasingly, structure is being determined in the most direct way possible: by x-ray analysis, which can show the precise distribution of atoms in a molecule.

We would carry out a qualitative elemental analysis to see what elements are present (Sec. 2.26). We might follow this with a quantitative analysis, and from this and the molecular weight we could calculate a molecular formula (Sec. 2.27); we would certainly do this if the compound is suspected of being a new one.

Next, we study systematically the behavior of the compound toward certain reagents. This behavior, taken with the elemental analysis, solubility properties, and spectra, generally permits us to *characterize* the compound, that is, to decide what family the unknown belongs to. We might find, for example, that the compound is an alkane, or that it is an alkene, or an aldehyde, or an ester.

Now the question is: *which* alkane is it? Or which alkene, or which aldehyde, or which ester? To find the answer, we first go to the chemical literature and look up compounds of the particular family to which our unknown belongs.

If we find one described whose physical properties are identical with those of our unknown, then the chances are good that the two compounds are identical. For confirmation, we generally convert the unknown by a chemical reaction into a new compound called a **derivative**, and show that this derivative is identical with the product derived in the same way from the previously reported compound.

If, on the other hand, we do not find a compound described whose physical properties are identical with those of our unknown, then we have a difficult job on our hands: we have a new compound, and must prove its structure. We may carry out a *degradation*: break the molecule apart, identify the fragments, and deduce what the structure must have been. To clinch any proof of structure, we attempt to *synthesize* the unknown by a method that leaves no doubt about its structure.

Problem 3.22 The final step in the proof of structure of an unknown alkane was its synthesis by the coupling of lithium di(*tert*-butyl)copper with *n*-butyl bromide. What was the alkane?

In Chap. 17, after we have become familiar with more features of organic structure, we shall see how spectroscopy fits into the general procedure outlined above.

3.33 Analysis of alkanes

An unknown compound is characterized as an alkane on the basis of negative evidence.

Upon qualitative elemental analysis, an alkane gives negative tests for all elements except carbon and hydrogen. A quantitative combustion, if one is carried out, shows the absence of oxygen; taken with a molecular weight determination, the combustion gives the molecular formula, C_nH_{2n+2} , which is that of an alkane.

An alkane is insoluble not only in water but also in dilute acid and base and

in concentrated sulfuric acid. (As we shall see, most kinds of organic compounds dissolve in one or more of these solvents.)

An alkane is unreactive toward most chemical reagents. Its infrared spectrum lacks the absorption bands characteristic of groups of atoms present in other families of organic compounds (like OH, C=O, C=C, etc.).

Once the unknown has been characterized as an alkane, there remains the second half of the problem: finding out *which* alkane.

On the basis of its physical properties—boiling point, melting point, density, refractive index, and, most reliable of all, its infrared and mass spectra—it may be identified as a previously studied alkane of known structure.

If it turns out to be a new alkane, the proof of structure can be a difficult job. Combustion and molecular weight determination give its molecular formula. Clues about the arrangement of atoms are given by its infrared and NMR spectra. (For compounds like alkanes, it may be necessary to lean heavily on x-ray diffraction and mass spectrometry.)

Final proof lies in synthesis of the unknown by a method that can lead only to the particular structure assigned.

(The spectroscopic analysis of alkanes will be discussed in Chap. 17.)

PROBLEMS

1. Give the structural formula of: ✓

- | | |
|---------------------------------|---------------------------------|
| (a) 2,2,3,3-tetramethylpentane | (f) 2,5-dimethylhexane |
| (b) 2,3-dimethylbutane | (g) 3-ethyl-2-methylpentane |
| (c) 3,4,4,5-tetramethylheptane | (h) 2,2,4-trimethylpentane |
| (d) 4-ethyl-3,4-dimethylheptane | (i) 3-chloro-2-methylpentane |
| (e) 4-ethyl-2,4-dimethylheptane | (j) 1,2-dibromo-2-methylpropane |

2. Draw out the structural formula and give the IUPAC name of:

- | | |
|--|---|
| (a) $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_3$ | (g) $(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)_3$ |
| (b) $\text{CH}_3\text{CBr}_2\text{CH}_3$ | (h) $(\text{CH}_3)_2\text{CClCH}(\text{CH}_3)_2$ |
| (c) $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_3$ | (i) $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)_2$ |
| (d) $(\text{C}_2\text{H}_5)_2\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3$ | (j) $(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)\text{CH}_2\text{C}(\text{C}_2\text{H}_5)_2\text{CH}_3$ |
| (e) $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)_2$ | (k) $(\text{CH}_3)_2\text{CHC}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{CH}_2\text{CH}_3$ |

- | | |
|---|--|
| (f) $\text{CH}_3\text{CH}_2\underset{\text{CH}_3}{\text{CH}}\text{CH}_2\underset{\text{CH}_2\text{CH}_2\text{CH}_3}{\text{CH}}\text{CH}_2\text{CH}_3$ | (l) $\text{CH}_3\text{CH}_2\underset{\text{CH}_3}{\text{CH}}\text{CH}_2\underset{\text{CH}_2\text{CH}_2\text{CH}_3}{\text{CH}}\text{CHCH}_3$ |
|---|--|

3. Pick out an alkane in Problem 1 or 2 that has: (a) no tertiary hydrogen; (b) one tertiary hydrogen; (c) two tertiary hydrogens; (d) no secondary hydrogen; (e) two secondary hydrogens; (f) half the number of secondary hydrogens as primary hydrogens.

4. Pick out an alkane (if any) in Problem 1 or 2 that contains: ✓

- | | |
|----------------------------------|---|
| (a) one isopropyl group | (g) one <i>tert</i> -butyl group |
| (b) two isopropyl groups | (h) two <i>tert</i> -butyl groups |
| (c) one isobutyl group | (i) an isopropyl group and a <i>sec</i> -butyl group |
| (d) two isobutyl groups | (j) a <i>tert</i> -butyl group and an isobutyl group |
| (e) one <i>sec</i> -butyl group | (k) a methyl, an ethyl, a <i>n</i> -propyl; and a <i>sec</i> -butyl group |
| (f) two <i>sec</i> -butyl groups | |

5. What alkane or alkanes of molecular weight 86 have: (a) two monobromo derivatives? (b) three? (c) four? (d) five? (e) How many dibromo derivatives does the alkane in (a) have? (f) Name the monobromo derivatives in (a).

6. How many mono-, di-, and trichloro derivatives are possible for cyclopentane? (Structure given in Sec. 5.2.)

7. Without referring to tables, list the following hydrocarbons in order of decreasing boiling points (i.e., highest boiling at top, lowest at bottom):

- (a) 3,3-dimethylpentane (c) 2-methylheptane (e) 2-methylhexane
(b) *n*-heptane (d) *n*-pentane

8. Write balanced equations, naming all organic products, for the following reactions:

- (a) isobutyl bromide + Mg/ether (e) product of (a) + D₂O
(b) *tert*-butyl bromide + Mg/ether (f) *sec*-butyl chloride + Li, then CuI
(c) product of (a) + H₂O (g) product of (f) + ethyl bromide
(d) product of (b) + H₂O

9. Write equations for the preparation of *n*-butane from:

- (a) *n*-butyl bromide (d) 1-butene, CH₃CH₂CH=CH₂
(b) *sec*-butyl bromide (e) 2-butene, CH₃CH=CHCH₃
(c) ethyl chloride

10. Draw structures of all products expected from monochlorination at room temperature of:

- (a) *n*-hexane (c) 2,2,4-trimethylpentane
(b) isohexane (d) 2,2-dimethylbutane

11. Predict the proportions of products in the preceding problem.

12. (a) Reaction of an aldehyde with a Grignard reagent is an important way of making alcohols. Why must one scrupulously dry the aldehyde before adding it to the Grignard reagent? (b) Why would one not prepare a Grignard reagent from BrCH₂CH₂OH?

13. On the basis of bond strengths in Table 1.2, page 20, add the following free radicals to the stability sequence of Sec. 3.24:

- (a) *vinyl*, H₂C=CH·
(b) *allyl*, H₂C=CHCH₂·
(c) *benzyl*, C₆H₅CH₂·

Check your answer in Sec. 16.15.

14. On the basis of your answer to Problem 13, predict how the following would fit into the sequence (Sec. 3.23) that shows ease of abstraction of hydrogen atoms:

- (a) *vinyl*ic hydrogen, H₂C=CH—H
(b) *allyl*ic hydrogen, H₂C=CHCH₂—H
(c) *benzyl*ic hydrogen, C₆H₅CH₂—H

Check your answer against the facts in Secs. 9.3 and 16.14.

15. Free-radical chlorination of *either* *n*-propyl or isopropyl bromide gives 1-bromo-2-chloropropane, and of *either* isobutyl or *tert*-butyl bromide gives 1-bromo-2-chloro-2-methylpropane. What appears to be happening? Is there any pattern to this behavior?

16. (a) If a rocket were fueled with kerosine and liquid oxygen, what weight of oxygen would be required for every liter of kerosine? (Assume kerosine to have the average composition of *n*-C₁₄H₃₀.) (b) How much heat would be evolved in the combustion of one liter of kerosine? (Assume 157 kcal/mol for each —CH₂— group and 186 kcal/mol for each —CH₃ group.) (c) If it were to become feasible to fuel a rocket with free hydrogen atoms, what weight of fuel would be required to provide the same heat as a liter of kerosine and the necessary oxygen? (Assume H₂ as the sole product.)

17. By what two quantitative methods could you show that a product isolated from the chlorination of propane was a monochloro or a dichloro derivative of propane? Tell exactly what results you would expect from each of the methods.

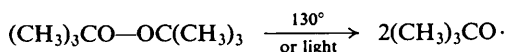
18. On the basis of certain evidence, including its infrared spectrum, an unknown compound of formula $C_{10}H_{22}$ is suspected of being 2,7-dimethyloctane. How could you confirm or disprove this tentatively assigned structure?

19. (a) A solution containing an unknown amount of methyl alcohol (CH_3OH) dissolved in *n*-octane is added to an excess of methylmagnesium iodide dissolved in the high-boiling solvent, *n*-butyl ether. A gas is evolved, and is collected and its volume measured: 1.04 cm^3 (corrected to STP). What is the gas, and how is it formed? What weight of methyl alcohol was added to the Grignard reagent?

(b) A sample of 4.12 mg of an unknown alcohol, ROH, is added to methylmagnesium iodide as above; there is evolved 1.56 cm^3 of gas (corrected to STP). What is the molecular weight of the alcohol? Suggest a possible structure or structures for the alcohol.

(c) A sample of 1.79 mg of a compound of mol. wt. about 90 gave 1.34 cm^3 of the gas (corrected to STP). How many "active (that is, acidic) hydrogens" are there per molecule? Assuming all these to be in $-OH$ groups, suggest a structure for the alcohol. (This is an example of the Zerewitinoff active hydrogen determination.)

20. (a) *tert*-Butyl peroxide is a stable, easy-to-handle liquid that serves as a convenient source of free radicals:



A mixture of isobutane and CCl_4 is quite stable at $130-140^\circ$. If a small amount of *tert*-butyl peroxide is added, a reaction occurs that yields (chiefly) *tert*-butyl chloride and chloroform. A small amount of *tert*-butyl alcohol ($(CH_3)_3COH$, equivalent to the peroxide used) is also isolated. Give all steps in a likely mechanism for this reaction.

(b) When irradiated with ultraviolet light, or in the presence of a small amount of peroxides, *tert*-butyl hypochlorite, $(CH_3)_3C-O-Cl$, reacts with alkanes to form, in equimolar amounts, alkyl chlorides and *tert*-butyl alcohol. Outline all steps in a likely mechanism for this reaction.