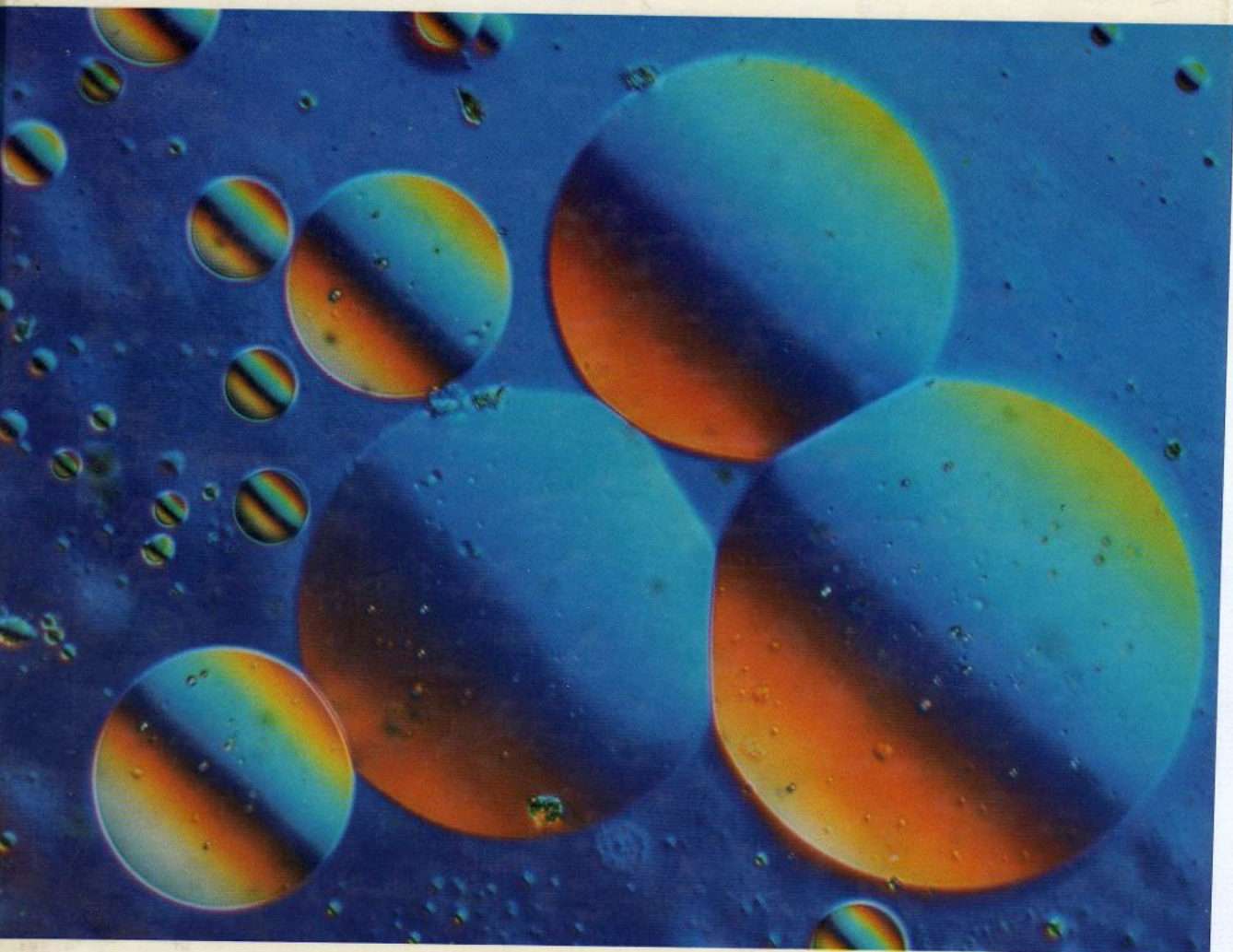


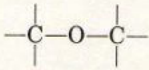




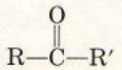
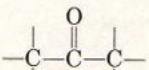
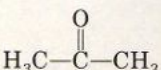
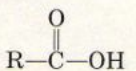
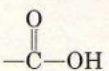

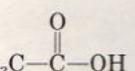
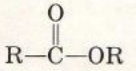
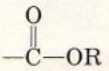

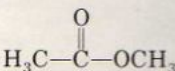
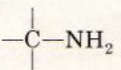
***Second Edition***

# ***Elements of Organic Chemistry***



***Isaak Zimmerman  
Henry Zimmerman***

## Functional Groups and Classes of Organic Compounds

Class	General formula	Functional group	Specific examples
Alkane	RH	C—C (single bond)	H <sub>3</sub> C—CH <sub>3</sub>
Alkene	R—CH=CH <sub>2</sub>	C=C (double bond)	H <sub>2</sub> C=CH <sub>2</sub>
Alkyne	R—C≡CH	C≡C (triple bond)	HC≡CH
Alkyl halide	RX	—X (X = F, Cl, Br, I)	H <sub>3</sub> C—Cl
Alcohol	R—OH	—OH	H <sub>3</sub> C—OH
Ether	R—O—R'		H <sub>3</sub> C—O—CH <sub>3</sub>
Aldehyde			 , 
Ketone			
Carboxylic acid			 , 
Ester			 , 
Amine	R—NH <sub>2</sub>		H <sub>3</sub> C—NH <sub>2</sub>



**2**<sup>nd</sup>  
edition

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# *Elements of Organic Chemistry*

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***Isaak Zimmerman***

Bronx Community College of the City University of New York





***Henry Zimmerman***

New York City Technical College of the City University of New York

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## Characteristic Infrared Absorption Frequencies for Some Common Groups

Frequency range (cm <sup>-1</sup> )	Group	Class of compounds
<b>Stretching vibrations</b>		
3700-3200	O—H	alcohols, phenols
3500-3100	 N—H	1° and 2° amines, amides
3320-3000	≡C—H	terminal alkynes
3100-3000	=C—H	alkenes
	 C—H	aromatics
3000-2800	 C—H	alkanes
3000-2500	O—H---O	carboxylic acids (H bonded)
2260-2240	C≡N	nitriles
2260-2100	C≡C	alkynes
1820-1600	 C=O	aldehydes, ketones, carboxylic acids, and derivatives
1680-1500	C=C	alkenes, aromatics
1560-1490; 1360-1320	—NO <sub>2</sub>	nitro compounds
1200-1000	C—O	alcohols, ethers, carboxylic acids, esters
<b>Bending vibrations</b>		
1470-1430	—CH <sub>2</sub> —; C—H	
1470-1375	CH <sub>3</sub>	
960-900	C=C—H	
1600-1500	aromatic ring (often weak)	
900-700	Ar—H	



## *To our dear parents*

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# Preface

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This revision of *Elements of Organic Chemistry*, like its predecessor, is intended for a first course in organic chemistry. It is especially suited to the needs of students specializing in the life sciences, allied health fields, agricultural sciences, and other related curricula.

We have retained the basic philosophy of the first edition. Foremost, we wish this book to be a teaching text; one that students find readable, and can study and learn from with little dependence on the teacher. To this end, we have taken the same systematic, but *more selective*, approach to our material as in the earlier edition, keeping constantly in mind the student to whom this book is addressed. As in the first edition, the discussion of topics is organized around functional groups. In the selection of our material, we have stressed those aspects of organic chemistry pertinent to health, the environment, and biochemistry, areas of special interest to the career objectives of the students enrolled in the course. The practical uses of organic compounds as drugs, food additives, pesticides, plastics, and other products, as well as their occurrence in nature, are discussed throughout the text.

Nevertheless, a number of changes have been made in this second edition, with the hope to improve on the earlier one.

- The number of preparative methods and reactions presented has been purposely reduced. Some reactions, such as the Wurtz reaction for preparing alkanes, have been omitted because of their obsolescence or lack of practical applications. Others, such as the Gabriel synthesis of amines, have been deleted because of the time limitations inherent in a brief course and because we did not feel that they were important enough for nonchemistry majors.



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# Bonding, Structural Formulas, and Molecular Shapes

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The subject of organic chemistry is unique in that it deals with vast numbers of substances, both natural and synthetic, that directly influence our welfare and standard of living. Organic chemistry is crucial to our economy as the source of countless manufactured products that are essential to our comfort and well-being. The clothes we wear; the petroleum products we use to run our machines; the paper, rubber, wood, plastics, paint, cosmetics, insecticides, and vitamins and drugs that we use every day—all are examples of organic compounds. The chemical substances that make up the organs of our bodies, the food we eat for nourishment, and the chemical reactions that take place inside our bodies are also organic in nature. Organic chemistry is a subject that is fundamental to medicine, biology, and other related disciplines such as nursing, dental hygiene, and medical laboratory technology. Because it is almost impossible to think of an aspect of our daily lives that is not somehow influenced by organic chemistry, the relevance in your study of this exciting and dynamic subject should be quite apparent.

## Organic Chemistry: A Modern Definition 1.1

From observation of the chemical makeup of many organic compounds it was recognized that one constituent common to all was the element **carbon**. Today **organic chemistry** is defined as the *study of carbon/hydrogen-contain-*

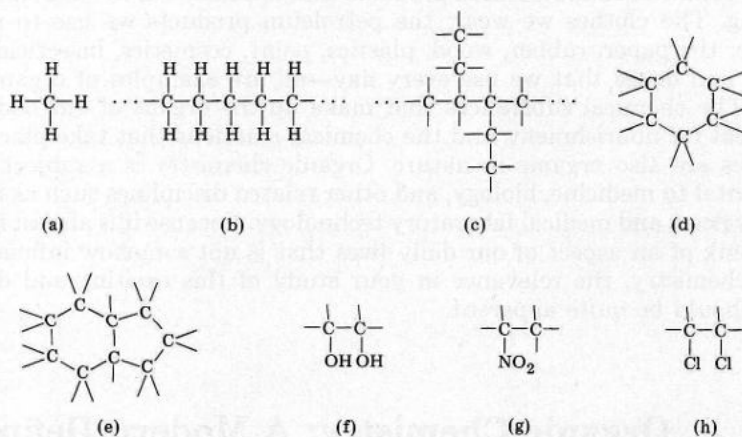
ing compounds and their derivatives. Petroleum and coal are two vast natural reservoirs from which many organic materials are extracted. Both were formed, over long periods of time, from the decay of plants and animals.

## 1.2 The Uniqueness of Carbon

Although carbon ranks only twelfth in abundance among the elements and constitutes less than 0.1% of the earth's crust, oceans, and atmosphere, the number of its compounds far exceeds that of all known inorganic compounds. Inorganic compounds are compounds formed from elements other than carbon. There are only about 90,000 known inorganic compounds, whereas the number of known organic compounds is several million, and thousands of new ones are synthesized and described each year. Thus, it is not surprising that a special branch of chemistry is entirely devoted to the study of the compounds of carbon.

What is unique about the element carbon? Why does it form so many compounds? The answers to these questions lie in the structure of the carbon atom and the position of carbon in the periodic table. These factors enable it to form strong bonds with other carbon atoms and with other elements—most commonly hydrogen, oxygen, nitrogen, and the halogens. As a result, there exist numerous stable carbon-containing substances of various sizes and shapes (see Fig. 1.1).

Each organic compound has its own characteristic set of physical and chemical properties, which depend on the *structure* of the molecule. The structure of a molecule, in turn, depends on how the atoms composing it are bonded to each other. Because this relationship between properties and structure is fundamental to a good understanding of organic chemistry, it is appropriate that we review the topics of atomic structure and chemical bonding.



**Figure 1.1** (a) A representation of methane, the simplest organic molecule. (b) The combination of many carbons with hydrogen in a straight-chain arrangement. (c) The combination of carbons in branched chains. (d, e) The combinations of carbons in rings of different shapes and sizes. (f-h) The combination of carbon with elements other than hydrogen.



## Atomic Structure 1.3

### A Electrons and Energy Levels

Atoms consist essentially of three fundamental particles: **neutrons, protons, and electrons**. Neutrons and protons are found in the nucleus; electrons are outside the nucleus. Neutrons are particles that have no charge, and protons are positively charged particles. The **atomic number** of an element indicates the number of protons. Since an atom is electrically neutral, this means that electrons are negatively charged and that the number of electrons must be equal to the number of protons.

Electrons are distributed around the nucleus in successive **shells**, or principal **energy levels**, of increasing radius. The electrons in levels close to the nucleus have lower energy than do electrons in levels farther from the nucleus.

The various energy levels are designated by capital letters or whole numbers ( $n$ ). The first energy level, the one closest to the nucleus and therefore the one having the lowest energy, is called the *K* level and corresponds to  $n = 1$ . The second energy level, somewhat farther from the nucleus and with a somewhat higher energy content than the *K* level, is called the *L* level and corresponds to  $n = 2$ . The third energy level, the *M* level, corresponds to  $n = 3$ ; the fourth energy level, the *N* level, corresponds to  $n = 4$ —and so on.

Each energy level has a given capacity for electrons. The *K* level may contain a maximum of 2 electrons and never more. The *L* energy level has a maximum capacity for 8 electrons, the *M* level for 18 electrons, and the *N* level for 32 electrons. (The maximum capacity of a shell is equal to  $2n^2$  electrons, where  $n$  is the number of the energy level.)

### B Arrangement of Electrons in Energy Levels

Having learned how many electrons are needed to fill a particular shell, let us consider the order in which electrons enter the various energy levels.

As expected, the first 2 electrons enter the *K* shell and the next 8, the *L* shell. After the *L* energy level is filled, electrons do *not* fill the third energy level (*M* level) to capacity (18 electrons) before the fourth energy level (*N* level) is started. In fact, there are *never more than 8 electrons in the outermost energy level of an atom*. The reason is that 8 electrons in the outermost shell give atoms their greatest stability (noble gas configuration). For example, the element potassium (atomic number 19) has its 19 electrons distributed about the nucleus as

Shell	<i>K</i>	<i>L</i>	<i>M</i>	<i>N</i>
Number of electrons	2	8	8	1
Rather than	2	8	9	0

and the electron distribution (electronic configuration) for calcium (atomic number 20) is

Shell	<i>K</i>	<i>L</i>	<i>M</i>	<i>N</i>
Number of electrons	2	8	8	2
Rather than	2	8	10	0



Table 1.1 Electron Distribution for the First Twenty Elements

Atomic number	Element	Energy level			
		K	L	M	N
1	H	1			
2	He	2			
3	Li	2	1		
4	Be	2	2		
5	B	2	3		
6	C	2	4		
7	N	2	5		
8	O	2	6		
9	F	2	7		
10	Ne	2	8		
11	Na	2	8	1	
12	Mg	2	8	2	
13	Al	2	8	3	
14	Si	2	8	4	
15	P	2	8	5	
16	S	2	8	6	
17	Cl	2	8	7	
18	Ar	2	8	8	
19	K	2	8	8	1
20	Ca	2	8	8	2

The distribution of electrons in the various energy levels for the first twenty elements is shown in Table 1.1.

### C Valence Electrons: Electron-Dot Structures

**Valence electrons** are those electrons located in the outermost energy level, the valence shell. In general, the chemical properties of an element depend on its valence electrons. For this reason, atoms are often depicted by **electron-dot structures**. In such structures the symbol of the element represents the *core* of the atom (the nucleus and all electrons *except* the valence electrons), and the valence electrons are shown as dots, crosses, or small circles around the symbol. To place the electrons around the symbol in the correct manner, follow these simple rules.

1. Imagine that the element's symbol has four sides around it, each with room for two electrons.
2. Pair the first two valence electrons on one side of the symbol.
3. Place the third, fourth, and fifth valence electrons, one at a time, on the remaining three sides.
4. For elements that have more than five valence electrons, the three sides are filled up to a maximum of eight.



For example,

Elements with one valence electron	H ·	Li ·	etc.
Elements with two valence electrons	He :	Be :	etc.
Elements with three valence electrons	B :	Al :	etc.
Elements with four valence electrons	·C :	·Si :	etc.
Elements with five valence electrons	·N :	·P :	etc.
Elements with six valence electrons	·O :	·S :	etc.
Elements with seven valence electrons	·F :	·Cl :	etc.
Elements with eight valence electrons	·Ne :	·Ar :	etc.

## 1.4 Chemical Bonding

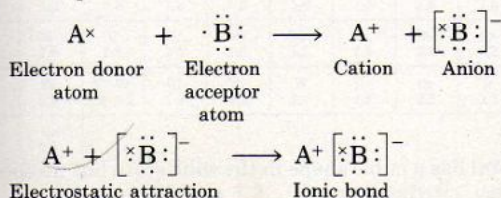
# Chemical Bonding 1.4

In 1916 G. N. Lewis proposed a theory of chemical bonding that accounted for many of the facts regarding the reactivity, or the lack of reactivity, of many elements. Lewis pointed out that the noble gases were particularly stable elements, and he ascribed their lack of reactivity to their having their valence shells filled with electrons: two in the case of helium and eight for the other noble gases. All other elements *do* enter into chemical reactions, and they do so because their valence shells are only partially filled. According to Lewis, in interacting with one another atoms can achieve a greater degree of stability by rearrangement of the valence electrons to acquire the outer-shell structure of the closest noble gas in the periodic table. This can be achieved in either of two ways: (1) through transfer of electrons between atoms (ionic bonding) or (2) through sharing of electrons between atoms (covalent bonding).

## A Ionic Bonding

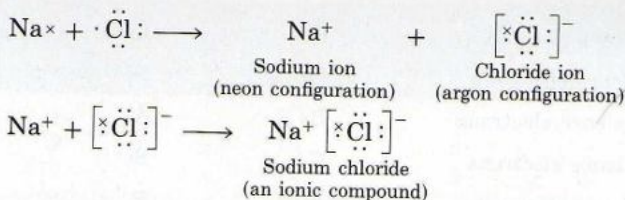
Elements at opposite ends of the periodic table attain the noble gas configuration by *transferring* electrons to one another. In the electron-transfer process, elements at the left of the periodic table give up their valence electrons and become positively charged ions, or *cations*, and those at the right gain the electrons, thus becoming negatively charged ions, or *anions*. The electrostatic force of attraction between oppositely charged ions constitutes the **ionic bond**.

### General equation





## Specific example

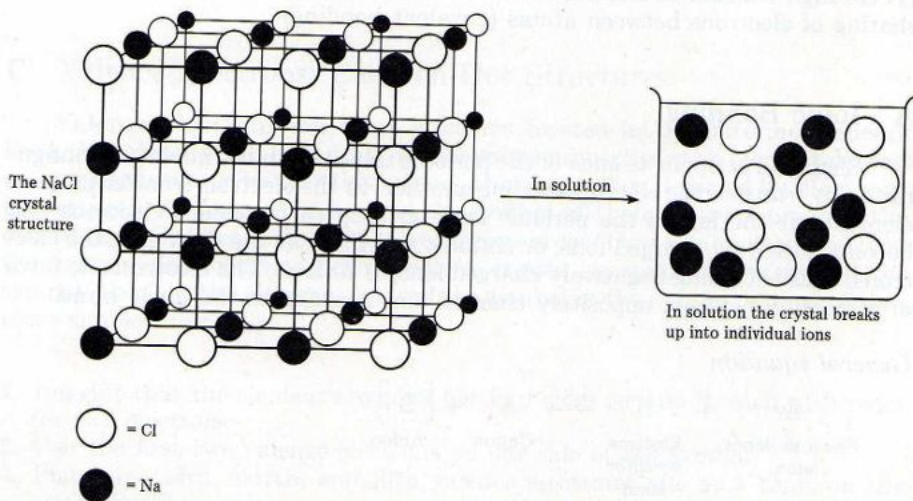


The vast majority of ionic compounds are inorganic substances. In the solid state they exist as high-melting-point crystals owing to the strong electrostatic forces that hold ions together. When the crystals are dissolved or melted, these interionic forces are overcome, and the result is a liquid in which individual ions move randomly about (Fig. 1.2). In contrast, when crystals of a covalent compound such as sucrose (table sugar) are dissolved, we find distributed throughout the solution individual molecules of sugar with definite size and shape.

**Problem 1.1** Write the electron-dot formula showing the combination of magnesium and oxygen to form magnesium oxide, MgO. Clearly indicate the charges on the cation and on the anion.

## B Covalent Bonding

Elements that are close to each other in the periodic table attain the stable noble gas configuration, not through a transfer of electrons but by sharing valence electrons between them. The chemical bond formed when two atoms share

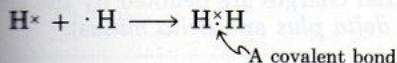


**Figure 1.2** A sodium chloride crystal has a cubic shape in the solid state but no specific shape in solution.

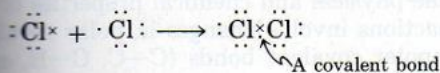


one pair of electrons is called a **covalent bond**. Atoms in most substances are held together by bonds of this type.

The simplest example of a molecule with a covalent bond is hydrogen gas,  $H_2$ . In hydrogen gas each hydrogen atom fills the first energy level (which can hold no more than two electrons) by sharing the combined valence electrons.



Chlorine gas,  $Cl_2$ , is another molecule in which a covalent bond is formed between two like atoms.



In  $Cl_2$  each chlorine atom is surrounded by eight valence electrons, as is argon, its closest noble gas.

Because it is often tedious to write electron-dot diagrams of molecules, we shall introduce a simplified notation. A shared electron pair between two atoms, or single covalent bond, will be represented by a dash (—), and the electrons not involved in bonding (the nonbonding electrons) will be omitted unless needed to make a point. Thus, hydrogen gas is represented as  $H-H$  and chlorine gas as  $Cl-Cl$ .

In molecules that consist of two like atoms, such as elemental hydrogen and elemental chlorine, the bonding electrons are shared equally. This is because both atoms have the same **electronegativity**. The electronegativity is a measure of the attraction the nucleus of an atom has for electrons in its outer shell. Figure 1.3 shows the electronegativity values for the elements proposed by Linus Pauling. You see that from left to right, within a period, the electronegativity values increase, and from top to bottom, within a group, the electronegativity values decrease. Fluorine, with a value of 4.0, is the most electronegative element.

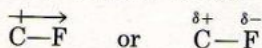
When two unlike atoms form a covalent bond, the bonding electrons are no longer shared equally. In the  $C-F$  bond, for example, the electron pair is shared unequally between the carbon and fluorine atoms. The greater electronegativity of fluorine (4.0) causes the electron pair to be closer to the fluorine atom than to the carbon atom. Such a bond, in which an electron pair is shared unequally, is

H 2.1																	He —						
Li 0.9	Be 1.5																B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne —	
Na 0.9	Mg 1.2																Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar —	
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.8	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr —						
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe —						
Cs 0.7	Ba 0.9	57-71 1.1-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn —						
Fr 0.7	Ra 0.9																						

Figure 1.3 Electronegativity values of the elements (Pauling's scale).

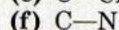
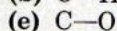
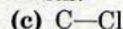
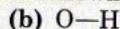
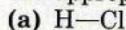


called a **polar covalent bond**. In a polar covalent bond the more electronegative atom assumes a partial negative charge and the less electronegative atom assumes a partial positive charge. The polarity of a bond may be indicated by the symbol  $\rightarrow$ . The head of the arrow points in the direction of the more electronegative atom. The tail, marked with a plus sign, is located at the less electronegative atom. More frequently, the partial charges are denoted by the Greek letter symbols  $\delta+$  and  $\delta-$  (pronounced *delta plus* and *delta minus*).



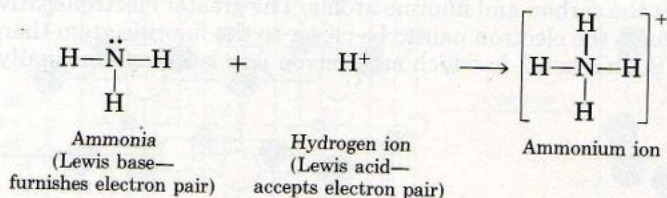
As we proceed through our study of organic chemistry, we will find that polar bonds exert special effects on the physical and chemical properties of organic molecules. In general, most reactions involve changes in polar covalent bonds (C—O, C—Cl, etc.) while nonpolar covalent bonds (C—C, C—H, etc.) remain unaltered.

**Problem 1.2** Show the partial charges by placing the  $\delta+$  and  $\delta-$  symbols on the appropriate atoms in the following polar covalent bonds.



## C Coordinate Covalent Bonding

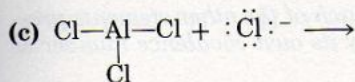
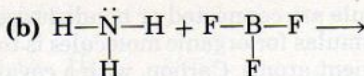
In the covalent bonding discussed so far each of the two atoms contributed one electron to the electron pair shared between them. There are molecules in which one atom supplies *both* electrons to another atom in the formation of a covalent bond. A covalent bond thus formed is called a **coordinate covalent bond**. For example, when ammonia,  $\text{:NH}_3$ , reacts with a proton,  $\text{H}^+$ , to form an ammonium ion,  $\text{NH}_4^+$ , the nitrogen atom in ammonia supplies both electrons to the new bond.



The species that furnishes the electron pair to form a coordinate covalent bond is called a **Lewis base**. The species that accepts the electron pair to complete its valence shell is called a **Lewis acid**. In subsequent chapters we shall have numerous occasions to refer to the concept of Lewis acids and Lewis bases to explain how chemical reactions occur.

**Problem 1.3** Each of the following interactions involves the formation of a coordinate covalent bond. Indicate (1) the structure of the product formed and (2) which species acts as a Lewis acid and which acts as a Lewis base.





## How Many Bonds to an Atom? Covalence Number

## 1.5

The number of covalent bonds an atom can form with other atoms is called its **covalence number**. The covalence numbers of atoms commonly found in organic compounds are listed in Table 1.2.

**Table 1.2** Covalence Numbers for Typical Elements in Organic Compounds

Element	Number of valence electrons	Number of electrons in filled valence shell	Covalence number
H	1	2	1
C	4	8	4
N	5	8	3
O	6	8	2
F, Cl, Br, I (halogens)	7	8	1

Note that the covalence number for an element is equal to the number of electrons needed to fill its valence shell. For example, hydrogen, which has one valence electron, needs one more electron to fill its outermost shell. The covalence number for hydrogen is therefore one. Carbon, which needs four electrons to fill its valence shell, has a covalence number of four, and so on down the list.

**Problem 1.4** Assuming that the method of assigning covalence numbers described is valid, write the covalence numbers for (a) S; (b) P; and (c) Ne.

## Covalence Number and Structural Formula

## 1.6

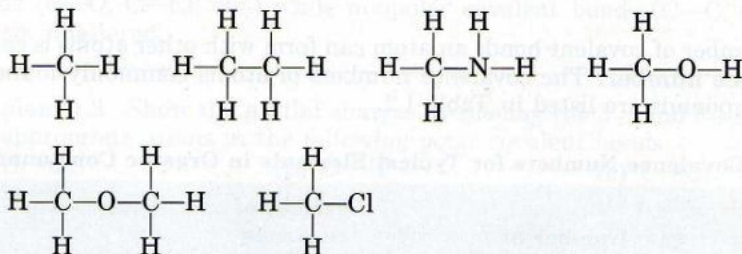
A molecular formula tells us what *kind* of atoms and how *many* of each kind of atom are present in a particular molecule. The molecular formula for ethanol (the drinkable alcohol),  $\text{C}_2\text{H}_6\text{O}$ , tells us that each molecule of ethanol contains two carbon atoms, six hydrogen atoms, and one oxygen atom. A **structural formula**, also called a **constitutional formula**, shows how the atoms in a par-



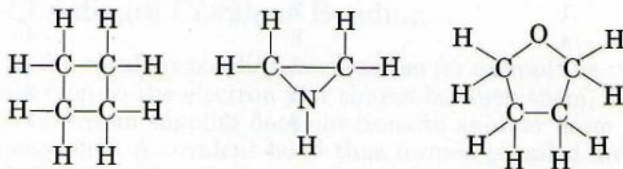
ticular molecule are connected or bonded together. The secret of writing correct structural formulas for organic molecules is to remember the covalence numbers of the component atoms. Carbon, with a covalence number of four, must *always have four bonds in any organic compound, and each of the other elements present must share the number of bonds indicated by its own covalence number* as listed in Table 1.2.

Following are examples of organic molecules in which each element satisfies its covalence number by sharing one electron pair—forming a **single bond**—with another atom connected to it. Carbon has four single bonds, hydrogen and chlorine one each, oxygen two, and nitrogen three.

#### Open-chain (acyclic) compounds

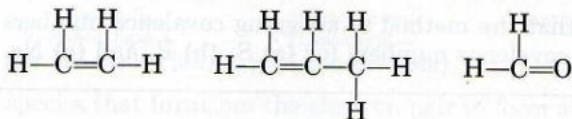


#### Ring (cyclic) compounds

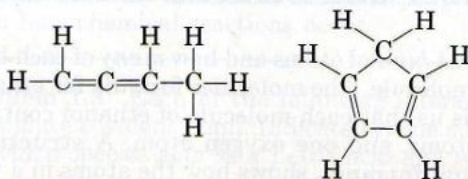


A carbon atom may also share more than one pair of electrons with another carbon atom or with other elements, such as oxygen and nitrogen, to form *multiple bonds*. If two pairs of electrons are shared, a **double bond** is formed; if three pairs of electrons are shared, a **triple bond** is formed. A double bond is represented by two dashes (=) and a triple bond by three dashes (≡).

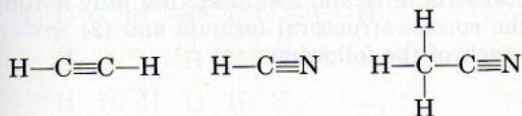
#### Organic molecules with one double bond



#### Organic molecules with two double bonds





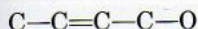


To summarize,

1. Structural formulas show how atoms are connected to one another in a molecule.
2. The structural formula of a compound is correct only if each element satisfies its covalence number.
3. The covalence number may be satisfied by forming single or multiple bonds.

Now consider a specific example.

**Example 1.1** Given the skeletal structure

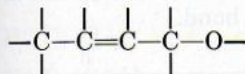


and assuming that only hydrogen atoms are missing, **(a)** draw the correct structural formula and **(b)** write the molecular formula of the completed structure.

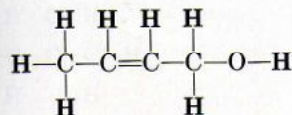
**Solution (a)** (1) Starting from the left, count how many bonds each atom already has. The first carbon has only one bond (a single bond); the second carbon has three bonds (one single and one double bond); the third carbon also has three bonds (one double and one single bond); the fourth carbon has two bonds (two single bonds); and the oxygen atom has one bond.

(2) Determine how many extra bonds each atom needs to fulfill its covalence number. Since carbon has a covalence number of four and oxygen of two (Table 1.2), it means that the first carbon needs three more bonds; the second carbon needs one more bond, as does the third; the fourth carbon atom needs two extra bonds; and the oxygen needs one extra bond.

(3) Place the missing bonds.



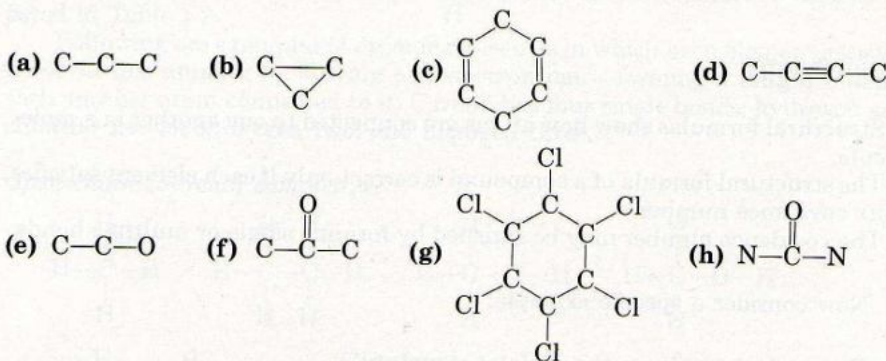
(4) Put in the missing hydrogens to obtain the correct structural formula.



**(b)** Counting the number of atoms of each kind, the molecular formula of the structure in **(a)** is



**Problem 1.5** Given the skeletal structures and assuming that only hydrogen atoms are missing, (1) draw the correct structural formula and (2) write the correct molecular formula for each of the following.

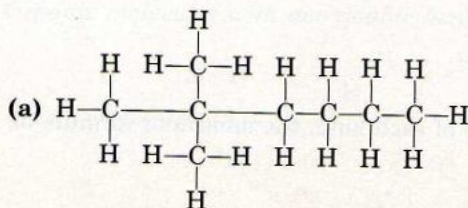


## 1.7 Condensed Structural Formulas

Up to this point we have used expanded structural formulas, in which all bonds are shown, to represent organic molecules. Although very useful in visualizing structures, this method of representation is time-consuming and requires much space. One way to simplify the writing of organic structures is to include only the bonds of multivalent atoms and leave out the bonds of monovalent elements (hydrogen and halogens). The resulting structures are called *partially condensed formulas*. If we omit all bonds except carbon-carbon multiple bonds, we have *fully condensed formulas*. Examples are given in Table 1.3.

Cyclic compounds can also be represented by partially condensed and fully condensed structural formulas, as shown in Table 1.4. In the fully condensed formulas each corner represents a  $\text{CH}_2$  for singly bonded carbon atoms and a  $\text{CH}$  when carbon is linked to another carbon by a double bond.

**Problem 1.6** Write a partially and a fully condensed structural formula for each of these structures.





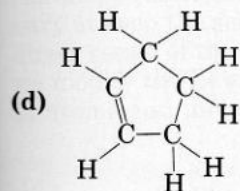
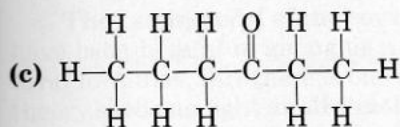
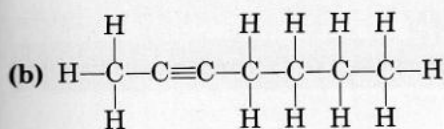


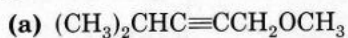
Table 1.3 Examples of Condensed Formulas

Expanded structural formula	Partially condensed formula	Fully condensed formula
$\begin{array}{c} \text{H} & \text{H} \\   &   \\ \text{H}-\text{C}-\text{C}-\text{O}-\text{H} \\   &   \\ \text{H} & \text{H} \end{array}$	$\text{CH}_3-\text{CH}_2-\text{OH}$	$\text{CH}_3\text{CH}_2\text{OH}$
$\begin{array}{c} \text{H} & \text{H} & \text{H} & \text{H} \\   &   &   &   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\   &   &   &   \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ or $\text{CH}_3(\text{CH}_2)_2\text{CH}_3$
$\begin{array}{c} & \text{H} & & \\ &   & & \\ \text{H} & - & \text{C} & - & \text{H} & & \text{H} \\ &   & &   & &   \\ & \text{H} & & \text{H} & & \text{H} \end{array}$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{CH}-\text{CH}_3 \end{array}$	$(\text{CH}_3)_2\text{CHCH}_3$ or $(\text{CH}_3)_3\text{CH}$
$\begin{array}{c} \text{H} & \text{H} & \text{O} \\   &   &    \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\   &   & \\ \text{H} & \text{H} & \end{array}$	$\begin{array}{c} \text{O} \\    \\ \text{CH}_3-\text{CH}_2-\text{CH} \end{array}$	$\text{CH}_3\text{CH}_2\text{CHO}$
$\begin{array}{c} \text{H} & \text{O} & \text{H} \\   &    &   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\   & &   \\ \text{H} & & \text{H} \end{array}$	$\begin{array}{c} \text{O} \\    \\ \text{CH}_3-\text{C}-\text{CH}_3 \end{array}$	$\text{CH}_3\text{COCH}_3$ or $(\text{CH}_3)_2\text{CO}$
$\begin{array}{c} \text{H} & \text{O} \\   &    \\ \text{H}-\text{C}-\text{C}-\text{O}-\text{H} \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{O} \\    \\ \text{CH}_3-\text{C}-\text{OH} \end{array}$	$\text{CH}_3\text{COOH}$

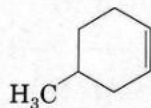
Table 1.4 Some Condensed Cyclic Formulas

Expanded formula	Partially condensed formula	Fully condensed formula
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**Problem 1.7** Given the following condensed structural formulas, write the expanded structures.



(b)





## Shapes of Organic Molecules: 1.8

### Orbital Picture of Covalent Bonds

The Lewis model of the covalent bond and the concept of covalence number have been helpful in giving us a clearer picture of chemical bonding and structural formulas. But there is one aspect of organic chemistry on which the Lewis theory sheds no light at all—molecular geometry—and without also considering the shapes and sizes of organic molecules we cannot begin to discuss their chemistry at even the simplest level. The distinct geometry of organic compounds is a direct result of the covalent bonds involved. For this reason, it is necessary that we modify the Lewis theory of bonding and describe the electronic arrangement in atoms and molecules in terms of orbitals.

#### A Atomic Orbitals

In Section 1.3 we considered the arrangement of electrons within various energy levels, but did not discuss the regions in space occupied by the electrons. Calculations based on spectroscopic studies of atoms have shown that electrons within each energy level are located in orbitals. An **atomic orbital** represents a specific region in space in which an electron is most likely to be found. Atomic orbitals are designated in the order in which they are filled by the letters *s*, *p*, *d*, and *f*. The first energy level (*K* shell) has only one orbital, the *1s*. The second energy level (*L* shell) has four orbitals, one *2s* and three *2p* orbitals. The third energy level (*M* shell) has nine orbitals: one *3s*, three *3p*, and five *3d* orbitals. The atoms we will encounter in most organic compounds have only *s* and *p* orbitals. An *s* orbital is a spherically shaped electron cloud with the atom's nucleus at its center; a *p* orbital is a dumbbell-shaped electron cloud with the nucleus between the two lobes. Each *p* orbital is oriented along one of three perpendicular coordinate axes, that is, in the *x*, *y*, or *z* direction. The *p* orbitals are designated as *2p<sub>x</sub>*, *2p<sub>y</sub>*, and *2p<sub>z</sub>* if they are located in the *L* shell, and as *3p<sub>x</sub>*, *3p<sub>y</sub>*, and *3p<sub>z</sub>* if located in the *M* shell. The shapes of *s* and *p* orbitals are illustrated in Figure 1.4.

The energies of the electrons in orbitals increase in the order shown in Figure 1.5. Note that the three *2p* orbitals are of equal energy, and so are the three *3p* orbitals.

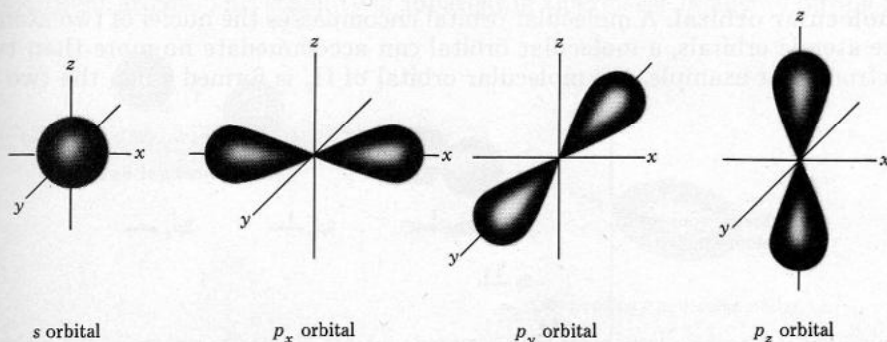
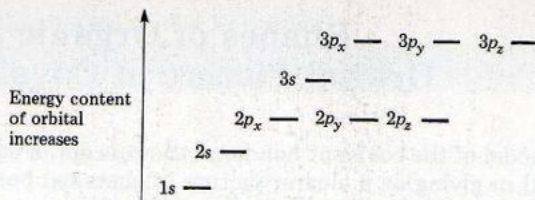


Figure 1.4 Shapes of *s* and *p* orbitals.

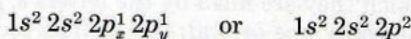


**Figure 1.5** An energy level diagram of atomic orbitals showing the order in which they become filled with electrons.

When filling the atomic orbitals, keep in mind that

1. An atomic orbital can contain no more than two electrons (shown by  $\uparrow$  and  $\downarrow$ ).
2. Electrons fill orbitals of lower energy first (a  $1s$  orbital before a  $2s$  orbital, a  $2s$  orbital before any of the three equivalent  $2p$  orbitals, and so on).
3. No orbital is filled by two electrons until all the orbitals of equal energy have at least one electron.

The electronic configuration of carbon (atomic number 6) can be represented as shown in Figure 1.6. More simply, this distribution is shown by the notation

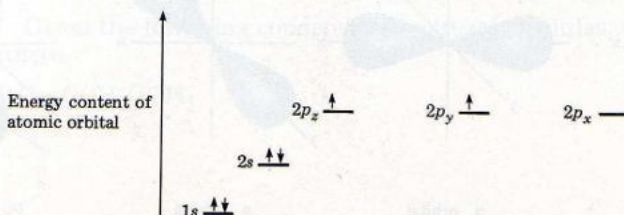


The superscripts indicate the numbers of electrons in the atomic orbitals. Table 1.5 shows the electronic configurations of the first ten elements in the periodic table.

**Problem 1.8** Using  $s$  and  $p$  notation, write the electronic configurations for (a) Na (atomic number 11) and (b) Cl (atomic number 17).

## B Molecular Orbitals

A covalent bond consists of the overlap between two atomic orbitals to form a **molecular orbital**. A molecular orbital encompasses the nuclei of two atoms. Like atomic orbitals, a molecular orbital can accommodate no more than two electrons. For example, the molecular orbital of  $H_2$  is formed when the two  $1s$



**Figure 1.6** Energy level diagram for carbon.



Table 1.5 Electronic Configuration of the First- and Second-Row Elements in the Periodic Table

Atomic number	Symbol	Electronic configuration	1s	2s	2p <sub>x</sub>	2p <sub>y</sub>	2p <sub>z</sub>
			$\uparrow$				
1	H	1s <sup>1</sup>	$\uparrow$				
2	He	1s <sup>2</sup>	$\uparrow\downarrow$				
3	Li	1s <sup>2</sup> 2s <sup>1</sup>	$\uparrow\downarrow$	$\uparrow$			
4	Be	1s <sup>2</sup> 2s <sup>2</sup>	$\uparrow\downarrow$	$\uparrow\downarrow$			
5	B	1s <sup>2</sup> 2s <sup>2</sup> 2p <sub>x</sub> <sup>1</sup>	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$		
6	C	1s <sup>2</sup> 2s <sup>2</sup> 2p <sub>x</sub> <sup>1</sup> 2p <sub>y</sub> <sup>1</sup>	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	
7	N	1s <sup>2</sup> 2s <sup>2</sup> 2p <sub>x</sub> <sup>1</sup> 2p <sub>y</sub> <sup>1</sup> 2p <sub>z</sub> <sup>1</sup>	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$
8	O	1s <sup>2</sup> 2s <sup>2</sup> 2p <sub>x</sub> <sup>2</sup> 2p <sub>y</sub> <sup>1</sup> 2p <sub>z</sub> <sup>1</sup>	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$
9	F	1s <sup>2</sup> 2s <sup>2</sup> 2p <sub>x</sub> <sup>2</sup> 2p <sub>y</sub> <sup>2</sup> 2p <sub>z</sub> <sup>1</sup>	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$
10	Ne	1s <sup>2</sup> 2s <sup>2</sup> 2p <sub>x</sub> <sup>2</sup> 2p <sub>y</sub> <sup>2</sup> 2p <sub>z</sub> <sup>2</sup>	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$

## 1.9 Bond Energy and Bond Length

orbitals from each hydrogen atom overlap. This molecular orbital is cylindrically symmetrical about the axis that joins the two nuclei. Molecular orbitals that have this cylindrical or sausage shape are called **sigma ( $\sigma$ ) orbitals**, and the bond between the two atoms is called a **sigma bond ( $\sigma$  bond)** (Fig. 1.7).

Sigma bonds can be formed not only from a combination of two *s* atomic orbitals, as in H<sub>2</sub>, but also from the end-on overlap of two *p* atomic orbitals or from the overlap of an *s* atomic orbital with a *p* atomic orbital. (Another type of bond, called the pi ( $\pi$ ) bond, which involves the side-side overlap between two *p* atomic orbitals, will be discussed in Chapter 3.)

## Bond Energy and Bond Length 1.9

Since atoms achieve a stable noble gas configuration when they combine to form molecules, we conclude that a molecule is more stable than the isolated constituent atoms. This stability is apparent in the release of energy during the

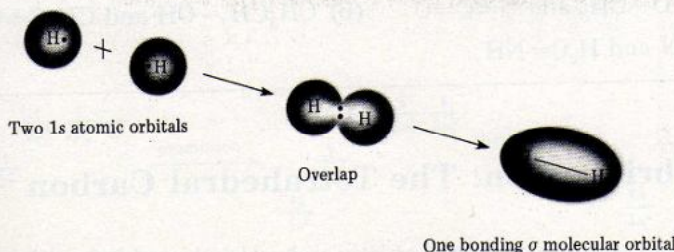


Figure 1.7 Overlap of atomic orbitals between two hydrogen atoms to form a sigma molecular orbital (= sigma bond).

Table 1.6 Bond Dissociation Energies  
of Some Simple Molecules

Molecule	Bond dissociation energy (kcal/mole)
H—H	104
Cl—Cl	58
H—OH	111
H—CH <sub>3</sub>	101
H <sub>3</sub> C—CH <sub>3</sub>	83
H <sub>2</sub> C=CH <sub>2</sub>	146
HC≡CH	200
H <sub>3</sub> C—OH	89
H <sub>2</sub> C=O	166

Table 1.7 Bond Length of  
Some Covalently Bonded  
Atoms

Bond	Bond length (Å)
H—H	0.72
C—H	1.09
O—H	0.96
C—C	1.54
C=C	1.34
C≡C	1.20
C—O	1.43
C=O	1.22

formation of the molecular bond. The amount of energy released when a bond is formed is called the **heat of formation** or the **bond energy**. Conversely, the same amount of energy would have to be supplied to break the bond. The amount of energy that must be absorbed to break a bond is called the **bond dissociation energy**. For a given pair of atoms, the greater the overlap of the atomic orbitals, the stronger the bond and the greater the amount of bond dissociation energy. In the case of H<sub>2</sub>, the bond dissociation energy is 104 kcal/mole. Table 1.6 shows the dissociation energies of certain bonds in some simple molecules. Note that when two atoms are held together by a single bond, the bond dissociation energy is lower than when they are held together by more than one bond.

The distance between nuclei in the molecular structure is called the **bond length**. For a given pair of atoms, the bond length depends upon the extent of overlap of their atomic orbitals. For H<sub>2</sub>, the bond length is 0.72 Å (1 Å = 10<sup>-8</sup> cm). Table 1.7 shows the bond lengths between some covalently bonded atoms. Note that when atoms are held together by more than one bond, the bond lengths become shorter.

**Problem 1.9** Predict which of the carbon-oxygen or carbon-nitrogen bonds in each pair of structures has (1) the greater bond dissociation energy and (2) the longer bond length.

- (a) H<sub>3</sub>C—O—CH<sub>3</sub> and O=C=O      (b) CH<sub>3</sub>CH<sub>2</sub>—OH and  $\begin{array}{c} \text{H} \\ | \\ \text{CH}_3\text{C}=\text{O} \end{array}$
- (c) HC≡N and H<sub>2</sub>C=NH

## 1.10 sp<sup>3</sup> Hybridization: The Tetrahedral Carbon

Now that we have examined atomic and molecular orbitals, we can address ourselves to our main topic of interest, namely, shapes of organic molecules. Let us consider first the simplest organic molecule, methane.



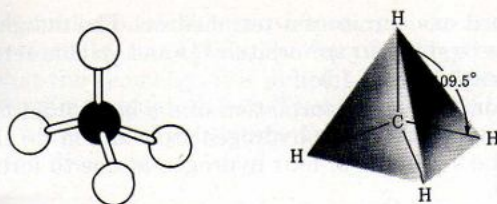
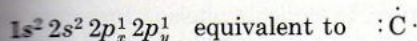


Figure 1.8 The tetrahedral structure of methane.

Based on experimental evidence, methane is known to consist of a carbon atom bonded covalently to four hydrogen atoms, thus having the molecular formula  $\text{CH}_4$ . Each of the four carbon-hydrogen bonds is identical: each has the same strength, 101 kcal/mole, and length, 1.09 Å. We also know that the four bonds are directed toward the corners of a regular **tetrahedron** with all  $\text{H}-\text{C}-\text{H}$  bond angles equal to  $109.5^\circ$  (Fig. 1.8). The tetrahedron is a pyramid-like structure with the carbon atom at the center and each of the four attached atoms or groups of atoms located at a corner.

The picture of the bonded carbon atom we have described is inconsistent with the one predicted from the electronic configuration of the isolated or ground-state carbon, which is



As you can see, there are only two half-filled  $p$  orbitals in the ground-state carbon. We should therefore expect carbon to form not *four* but only *two* covalent bonds, as in  $\text{C}-\text{H}$ , with a bond angle of  $90^\circ$ .

To explain this discrepancy, Linus Pauling proposed that it is possible, by providing the required amount of energy to the ground-state carbon (Fig. 1.9a), to promote one electron from the  $2s$  orbital to the empty  $2p_z$  orbital. The resulting carbon is said to be in an excited or activated state. In this state the carbon atom has four unpaired electrons (Fig. 1.9b), which should account for the formation of four covalent bonds. However, the four bonds would not all be the same; three would be formed from  $2p$  electrons, and the fourth from a  $2s$  electron. But we know from experimentation that the four bonds are identical. Pauling therefore further proposed that the four excited-state orbitals mix together, or **hybridize**, to create four equivalent  $2s2p^3$  ( $sp^3$  for short) hybrid orbitals,

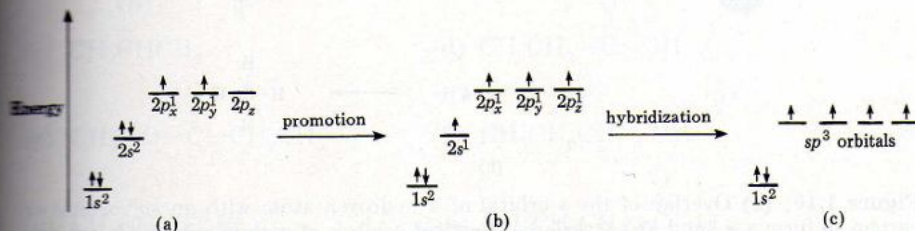
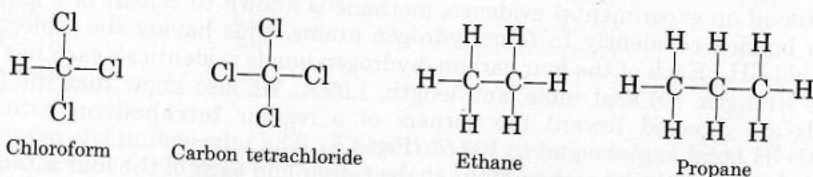


Figure 1.9 (a) The electronic ground state. (b) The activated state. (c) The  $sp^3$ -hybridized state of carbon.

each directed toward one corner of a tetrahedron. The merging of an  $s$  orbital and three  $p$  orbitals to give four  $sp^3$  orbitals ( $\frac{1}{4}s$  and  $\frac{3}{4}p$  characteristic) is referred to as  **$sp^3$  hybridization** (Fig. 1.9c).

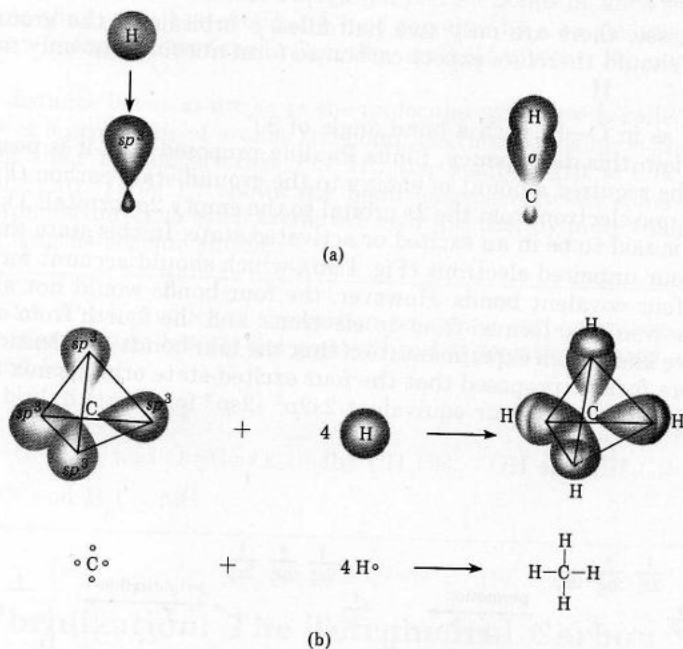
Figure 1.10 shows in (a) the formation of a  $\sigma$  bond from the overlap of one  $sp^3$  orbital with the  $s$  orbital of one hydrogen atom and in (b) the overlap of four  $sp^3$  orbitals with the  $s$  orbitals of four hydrogen atoms to form the tetrahedral methane molecule.

The tetrahedral shape allows for the most effective overlap between the orbitals, thus forming strong bonds. Whenever carbon is singly bonded to other atoms, it utilizes  $sp^3$ -hybridized orbitals and assumes a tetrahedral shape. For example,



all represent molecules in which each carbon atom is  $sp^3$  hybridized. Chloroform and carbon tetrachloride, like methane, consist of a single tetrahedron. Ethane is made up of two tetrahedra, and propane consists of three tetrahedra.

In molecules where the carbon atom is doubly or triply bonded, it utilizes a



**Figure 1.10** (a) Overlap of the  $s$  orbital of a hydrogen atom with an  $sp^3$  orbital of carbon to form a  $\sigma$  bond. (b) Overlap of four  $sp^3$  orbitals of carbon with the  $s$  orbitals of four hydrogen atoms to form the tetrahedral methane molecule.



different kind of hybrid orbital. For this reason, such molecules are no longer tetrahedral, and we shall discuss their geometry in Chapter 3.

No matter what the geometry, it is difficult to represent three-dimensional structures on a two-dimensional surface. Therefore, as a matter of convenience, we will continue to use planar structures unless three-dimensional structures are necessary to the discussion.

## Functional Groups 1.11

There are several million organic compounds. The study of their chemistry is made possible only because we are able to classify them into a limited number of families depending on the **functional groups** present. A functional group is a reactive portion of an organic molecule, an atom, or a group of atoms that confers on the whole molecule its characteristic properties. All compounds with the same functional group belong to one family. Members of a given organic family react in a similar and predictable manner. An example of a functional group, indicating an *alcohol*, is the hydroxyl group, OH, attached to a singly bonded carbon atom, as in  $\text{—}\overset{\text{OH}}{\underset{|}{\text{C}}}\text{—}$ . Thus, the first three of the following structures represent specific alcohols of increasing carbon chain length. The fourth structure,  $\text{R—OH}$ , indicates the general formula for all alcohols; R stands for a carbon chain of any length attached to the functional group.

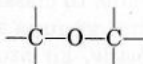





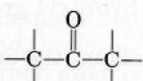


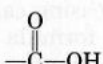



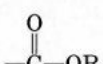


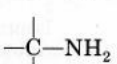
$\text{CH}_3\text{—OH}$	$\text{CH}_3\text{CH}_2\text{—OH}$	$\begin{array}{c} \text{OH} \\   \\ \text{CH}_3\text{CHCH}_3 \end{array}$	$\text{R—OH}$
Methyl alcohol (wood alcohol, toxic)	Ethyl alcohol (beverage alcohol)	Isopropyl alcohol (rubbing alcohol)	General formula for alcohols

Table 1.8 lists some of the functional groups and corresponding classes of compounds. In Chapter 2 we will discuss the chemistry of alkanes, the first class of compounds listed.

**Problem 1.10** Identify the class of compound represented by each structure.

- |   |   |
|---|---|
| (a) $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$   | (b) $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{CH—O—CH}_3 \end{array}$                  |
| (c) $\begin{array}{c} \text{OH} \\   \\ \text{CH}_3\text{CHCH}_3 \end{array}$                 | (d) $\text{CH}_3\text{CH}_2\text{—}\overset{\text{O}}{\underset{  }{\text{C}}}\text{—OH}$           |
| (e) $\text{CH}_3\text{—O—}\overset{\text{O}}{\underset{  }{\text{C}}}\text{—CH}_2\text{CH}_3$ | (f) $\text{CH}_3\text{CH}_2\text{CH}_2\text{—NH}_2$   |
| (g) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$  | (h) $\text{CH}_3\text{CH}_2\text{CH}_2\text{—}\overset{\text{O}}{\underset{  }{\text{C}}}\text{—H}$ |

Table 1.8 Functional Groups and Classes of Organic Compounds

Class	General formula	Functional group	Specific examples
Alkane	RH	C—C (single bond)	H <sub>3</sub> C—CH <sub>3</sub>
Alkene	<sup>a</sup> R—CH=CH <sub>2</sub>	C=C (double bond)	H <sub>2</sub> C=CH <sub>2</sub>
Alkyne	<sup>a</sup> R—C≡CH	C≡C (triple bond)	HC≡CH
Alkyl halide	RX	—X (X = F, Cl, Br, I)	H <sub>3</sub> C—Cl
Alcohol	R—OH	—OH	H <sub>3</sub> C—OH
Ether	R—O—R'		H <sub>3</sub> C—O—CH <sub>3</sub>
Aldehyde	<sup>a</sup> R— 		H—  , H <sub>3</sub> C— 
Ketone	R—  —R'		H <sub>3</sub> C—  —CH <sub>3</sub>
Carboxylic acid	<sup>a</sup> R—  —OH		H—  , H <sub>3</sub> C— 
Ester	<sup>a</sup> R—  —OR		H—  , H <sub>3</sub> C— 
Amine	R—NH <sub>2</sub>		H <sub>3</sub> C—NH <sub>2</sub>

<sup>a</sup>In these classes of compounds R can also be H.

**Problem 1.11** There are three compounds with the molecular formula C<sub>3</sub>H<sub>8</sub>O. Two are alcohols, and one is an ether. Draw their expanded structural formulas and identify the family to which each belongs.

## Summary of Concepts and Reactions

Organic chemistry is the study of carbon/hydrogen-containing compounds and their derivatives. [Sec. 1.1]

Carbon is unique among the elements for its ability to bond infinitely with itself to form compounds of various sizes and shapes as well as to bond with many other elements. [Sec. 1.2]



Atoms consist essentially of three fundamental particles: neutrons, protons, and electrons. The atomic number of an element indicates the number of protons.

[Sec. 1.3A]

Electrons are distributed around the nucleus in shells or energy levels.

[Sec. 1.3A]

There are never more than 8 electrons in the outermost energy level of an atom.

[Sec. 1.3B]

The outer-shell electrons are called valence electrons, and they are depicted by dots around the symbol of the element (electron-dot structures).

[Sec. 1.3C]

Atoms can achieve a noble gas configuration by forming ionic bonds or covalent bonds.

[Sec. 1.4A, B]

Electronegativity is a measure of the attraction the nucleus of an atom has for its valence electrons.

[Sec. 1.4B]

A coordinate covalent bond is formed when one atom supplies 2 electrons to form a bond.

[Sec. 1.4C]

A Lewis base is a species that has 2 electrons available for bonding.

[Sec. 1.4C]

A Lewis acid is a species that can accept an electron pair to complete its valence shell.

[Sec. 1.4C]

Covalence number indicates the number of covalent bonds an atom can form with other atoms.

[Sec. 1.5]

A structural or constitutional formula shows how the atoms in a particular molecule are connected or bonded together.

[Sec. 1.6]

Expanded structural formulas can be simplified by condensing them.

[Sec. 1.7]

An atomic orbital represents a specific region in space where an electron is most likely to be found.

[Sec. 1.8A]

Overlap of two atomic orbitals forms a molecular orbital.

[Sec. 1.8B]

Molecular orbitals with a cylindrical or sausage shape are called sigma ( $\sigma$ ) orbitals, and the covalent bond between the two atoms is called a  $\sigma$  bond.

[Sec. 1.8B]

Bond formation is an energy-releasing process. The amount of energy released when a bond is formed is called the heat of formation or the bond energy.

[Sec. 1.9]

The amount of energy that must be absorbed to break a bond is called the bond dissociation energy. (Bond dissociation energy is numerically equal to heat of formation.)

[Sec. 1.9]

When carbon is bonded to four other atoms, it makes use of  $sp^3$  hybridization and will be at the center of a regular tetrahedron.

[Sec. 1.10]

A functional group is a reactive portion of an organic molecule that confers on the whole molecule its characteristic properties.

[Sec. 1.11]

## Key Terms

carbon  
organic chemistry  
neutron  
proton  
electron  
atomic number  
shell  
energy level  
valence electron  
electron-dot structure  
ionic bond  
covalent bond

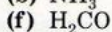
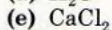
electronegativity  
polar covalent bond  
coordinate covalent bond  
Lewis base  
Lewis acid  
covalence number  
structural formula  
constitutional formula  
single bond  
double bond  
triple bond  
atomic orbital

molecular orbital  
sigma ( $\sigma$ ) orbital  
sigma bond  
heat of formation  
bond energy  
bond dissociation energy  
bond length  
tetrahedron  
hybridize  
 $sp^3$  hybridization  
functional group

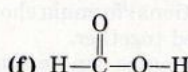
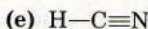
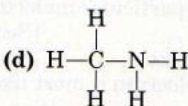
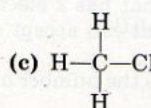
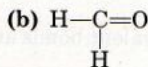
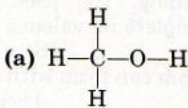
## Exercises

**Valence Electrons and Electron-Dot Structures** [Sec. 1.3]

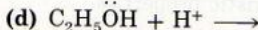
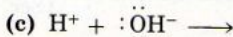
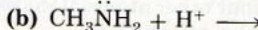
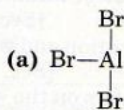
1.1 Write an electron-dot structure for each compound.

**Ionic, Covalent, and Polar Covalent Bonding** [Sec. 1.4A, B]

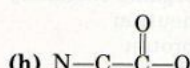
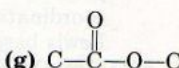
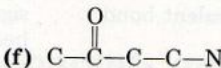
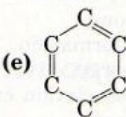
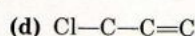
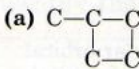
1.2 List which compound(s) in Exercise 1.1 contain(s) (a) only ionic bonds, (b) only nonpolar covalent bonds, (c) only polar covalent bonds, and (d) both nonpolar and polar covalent bonds.

1.3 Show the partial charges by placing  $\delta+$  and  $\delta-$  symbols on the atoms involved in a polar covalent bond.1.4 Arrange the hydrogen halides ( $\text{HI}$ ,  $\text{HBr}$ ,  $\text{HCl}$ ,  $\text{HF}$ ) in order of polarity, from the most polar to the least polar.**Coordinate Covalent Bonding; Lewis Acid and Lewis Base** [Sec. 1.4C]

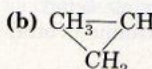
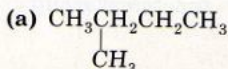
1.5 For each of the following Lewis acid-base interactions (1) indicate the structure of the product formed and (2) identify the Lewis acid and the Lewis base.

**Covalence Number and Structural Formula** [Secs. 1.5, 1.6]

1.6 Given the skeletal structure, and assuming that only hydrogen atoms are missing, draw the correct structural formula for each of the following.



1.7 Check the following structures to see whether or not they represent possible compounds within the rules of covalence. State either "possible" or "impossible" for each.





- (c)  $\text{CH}_3\text{CH}_2\text{—O—CH}_2\text{—O—CH}_3$       (d)  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\overset{\text{O}}{\parallel}\text{C—OH}$
- (e)  $\text{CH}_3\text{CH}_2\underset{\text{Cl}}{\text{CH}_2}\text{Cl}$       (f)  $\text{CH}_3\text{CH}_2=\text{CH}_2$
- (g)  $\text{CH}_3\text{—NH}_2\text{—CH}_3$       (h)  $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{CH}_3$

1.8 Draw a correct structural formula for each “impossible” representation in Exercise 1.7 by either adding or removing hydrogen atoms.

1.9 Draw an expanded structural formula corresponding to each molecular formula.

- (a)  $\text{CHCl}_3$       (b)  $\text{CH}_2\text{F}_2$       (c)  $\text{CH}_4\text{O}$       (d)  $\text{CH}_5\text{N}$       (e)  $\text{C}_2\text{H}_2$   
 (f)  $\text{C}_2\text{H}_4$       (g)  $\text{C}_2\text{H}_6$       (h)  $\text{C}_2\text{H}_5\text{Cl}$       (i)  $\text{CH}_3\text{N}$       (j)  $\text{H}_3\text{NO}$

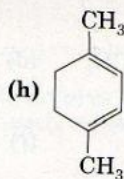
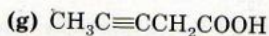
**Condensed and Expanded Structural Formulas** [Sec. 1.7]

1.10 Convert each of the following expanded structural formulas into (1) a partially condensed and (2) a fully condensed formula.

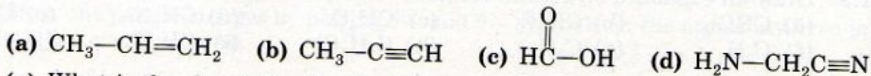
- (a)
- (b)
- (c)
- (d)
- (e)
- (f)
- (g)
- (h)

1.11 Draw the fully expanded structures corresponding to the partially condensed formulas (a-d) and fully condensed formulas (e-h).

- (a)  $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_3$       (b)  $\text{CH}_3\text{—CHF—CH(CH}_3\text{)—CH=CH}_2$
- (c)
- (d)
- (e)  $(\text{CH}_3)_2\text{CH}(\text{CH}_2)_4\text{CH}_3$       (f)  $\text{CH}_3\text{CH=CHCHO}$

**Bond Length, Bond Strength, and Bond Angle** [Secs. 1.9, 1.10]

1.12 For each structure, predict which of the two bonds shown has (1) the greater bond dissociation energy and (2) the longer bond length.

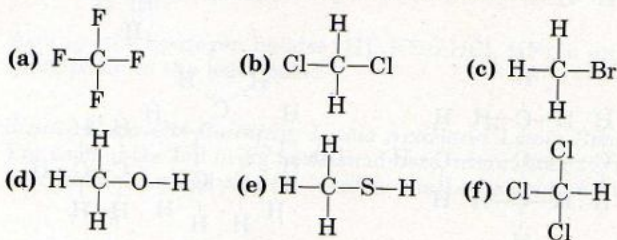


1.13 (a) What is the size of the  $\text{H}-\text{C}-\text{H}$  bond angle in methane,  $\text{CH}_4$ ?

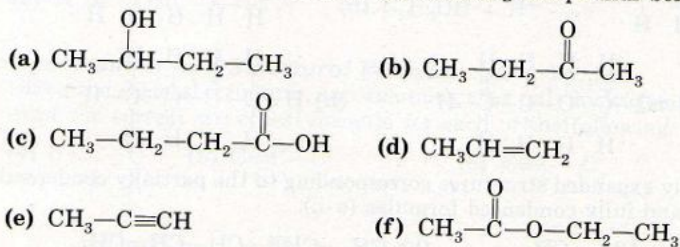
(b) What would you expect the size of the  $\text{F}-\text{C}-\text{F}$  bond angle in carbon tetrafluoride,  $\text{CF}_4$ , to be?

**Hybridization and Shape of Molecules** [Sec. 1.10]

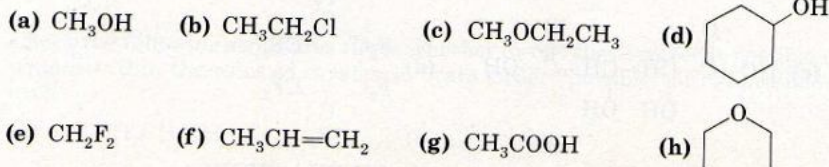
1.14 Indicate (1) the type of hybridized orbital utilized by carbon in each of the following structures and (2) the shape of each molecule.

**Functional Groups and Classification of Compounds** [Sec. 1.11]

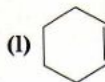
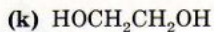
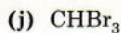
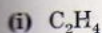
1.15 Name the class to which each of the following compounds belongs.



1.16 Group together those compounds that you expect to behave chemically in a similar manner.





**Cocleance Number, Structural Formula, and Functional Group**

[Secs. 1.5, 1.6, 1.11]

- 1.17 (a)** One alcohol and one ether correspond to  $C_2H_6O$ . Draw their structures.  
**(b)** One aldehyde and one ketone correspond to  $C_3H_6O$ . Draw their structures.  
**(c)** One carboxylic acid and one ester correspond to  $C_2H_4O_2$ . Draw their structures.

# Saturated Hydrocarbons: Alkanes

A large group of organic compounds, known as **hydrocarbons**, contain only the two elements carbon and hydrogen. Based on their structural features, the hydrocarbons are divided into two main classes, the *aliphatics* and *aromatics*.

Aliphatic hydrocarbons are subdivided into three families: *alkanes*, *alkenes*, and *alkynes*. Each family is characterized by a different functional group. **Alkanes**, the topic of this chapter, are characterized by the *carbon-carbon single bond*. Alkanes are also known as *saturated hydrocarbons* because each carbon is bonded to four other atoms, the maximum number of atoms to which any carbon can be attached.

Alkanes show a general lack of chemical reactivity, although they are extremely flammable. The high combustibility of alkanes is one reason for their importance; alkanes constitute the fuels we use in heating our homes and in running our machines.

## 2.1 The Three Simplest Alkanes: Methane, Ethane, Propane

The simplest member of the alkane family is *methane*,  $\text{CH}_4$ , a molecule introduced in Section 1.10. Methane has the shape of a tetrahedron with an *sp*<sup>3</sup>-hybridized carbon at the center. All four C—H bonds in the molecule are equivalent. Figure 2.1 shows different representations of the methane molecule.

The second member of the alkane series, *ethane*,  $\text{C}_2\text{H}_6$ , is shown in Figure



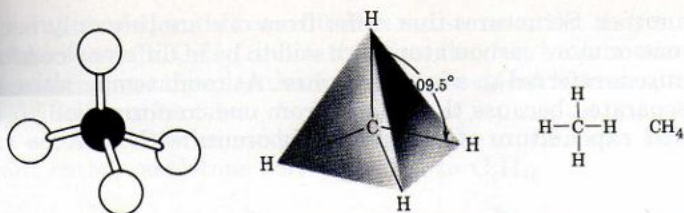
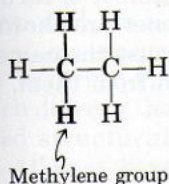


Figure 2.1 Tetrahedral and planar representations of methane.

2.2. Each carbon in ethane is  $sp^3$  hybridized, and the bond joining the two carbons is called an  $sp^3-sp^3$  molecular orbital. In fact, every carbon atom in any alkane makes use of  $sp^3$ -hybridized orbitals, since each is always linked via single bonds to four other atoms.

Note that ethane is larger than methane by a  $\text{CH}_2$ , or methylene group.



This is not to say that ethane is prepared in such a way from methane, but simply to illustrate the structural relation between the two compounds.

Next in the series, with three carbons, is *propane*,  $\text{C}_3\text{H}_8$  (Fig. 2.3). Again, note that propane is larger than ethane by a methylene group. The bent representation of propane in Figure 2.3 indicates that carbon-carbon single bonds are free to rotate in any direction. Because of free rotation, an alkane can assume many different forms depending on the amount of twist or turn of a carbon with

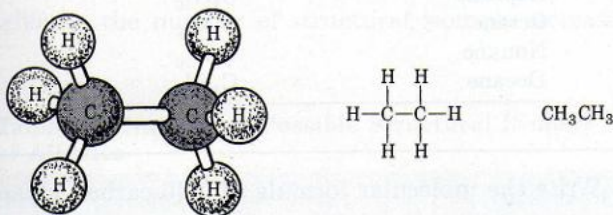


Figure 2.2 Representations of ethane.

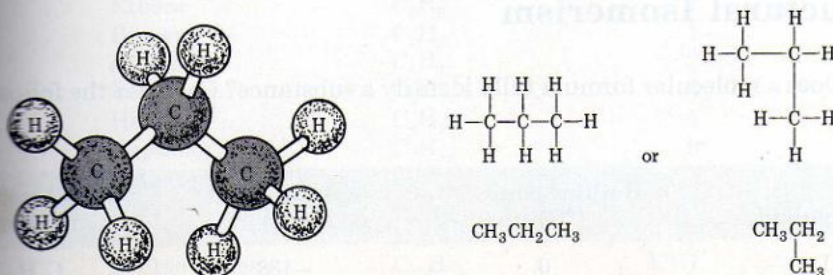


Figure 2.3 Representations of propane.

respect to another. Structures that differ from one another only because of the rotation of one or more carbon atoms are said to be in different **conformations**. Each structure is referred to as a **conformer**. At room temperature conformers cannot be separated because the change from one conformation to another requires so little expenditure of energy that it occurs with extreme rapidity.

## 2.2 Other Alkanes: Homologous Series $C_nH_{2n+2}$

If we keep adding  $CH_2$  groups, one at a time, it is possible to build an infinite series of compounds, called a **homologous series**. In a homologous series each individual member differs from its next neighbor by a constant value, a  $CH_2$  in this case. Each member of a homologous series is called a **homolog**. Methane, ethane, and propane are the first three homologs of the alkane family, whose general formula is  $C_nH_{2n+2}$ . In this general formula  $n$  is the number of carbons. The names and the molecular formulas of the first ten alkanes are shown in Table 2.1. It is important that you memorize these names because the names of many other organic compounds of various classes are derived from them.

Table 2.1 Names and Molecular Formulas of the First Ten Alkanes

Name	Molecular formula
Methane	$CH_4$
Ethane	$C_2H_6$
Propane	$C_3H_8$
Butane	$C_4H_{10}$
Pentane	$C_5H_{12}$
Hexane	$C_6H_{14}$
Heptane	$C_7H_{16}$
Octane	$C_8H_{18}$
Nonane	$C_9H_{20}$
Decane	$C_{10}H_{22}$

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**Problem 2.1** Write the molecular formula of a 40-carbon alkane.

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## 2.3 Structural Isomerism

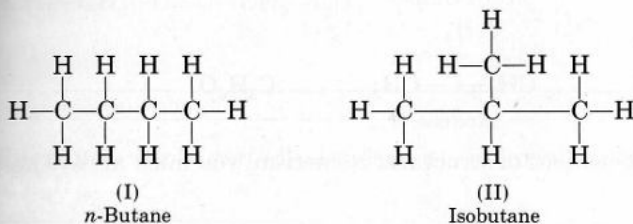
Does a molecular formula fully identify a substance? Consider the following data.

Compound	Boiling point (°C)	Melting point (°C)	Molecular formula
I	0	-138	$C_4H_{10}$
II	-12	-145	$C_4H_{10}$



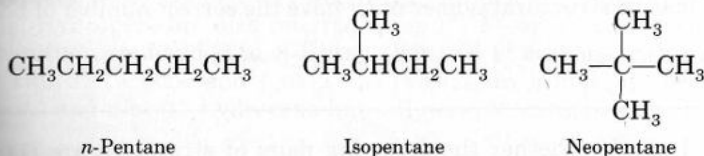
Obviously, compounds I and II are different substances. Yet they both have the same molecular formula,  $C_4H_{10}$ , indicating that they are both butanes. Different compounds with identical molecular formulas are called **isomers**, and the phenomenon is called **isomerism**.

Given a set of molecular models, it is possible to construct two structures with different carbon skeletons corresponding to  $C_4H_{10}$ .



Compound I is called *normal* or *n*-butane. The prefix *n*- indicates that the carbon atoms are arranged in a continuous chain. Compound II, named isobutane, is a branched-chain hydrocarbon. Isomers such as *n*-butane and isobutane, which differ in the sequence of atoms bonded to each other, are more specifically called **structural** or **constitutional isomers**.

Alkanes beyond butane are all capable of structural isomerism. Thus, there are three isomeric pentanes,  $C_5H_{12}$ : *n*-pentane, isopentane, and neopentane.



With higher alkanes the number of structural isomers increases rapidly (see Table 2.2).

Table 2.2 Number of Possible Structural Isomers of Alkanes

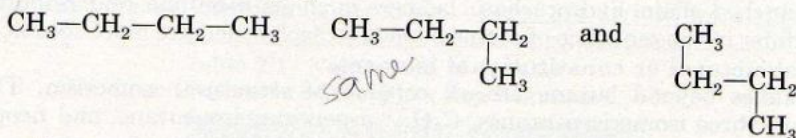
Name	Molecular formula	Number of isomers
Methane	$CH_4$	1
Ethane	$C_2H_6$	1
Propane	$C_3H_8$	1
Butanes	$C_4H_{10}$	2
Pentanes	$C_5H_{12}$	3
Hexanes	$C_6H_{14}$	5
Heptanes	$C_7H_{16}$	9
Octanes	$C_8H_{18}$	18
Nonanes	$C_9H_{20}$	35
Decanes	$C_{10}H_{22}$	75
Pentadecanes	$C_{15}H_{32}$	4,347
Eicosanes	$C_{20}H_{42}$	366,319

Structural isomerism is not confined to alkanes only. In fact, the phenomenon exists among all classes of organic compounds. For example,

		Molecular formula
$\text{CH}_3\text{CH}_2\text{—OH}$ Ethyl alcohol	$\text{CH}_3\text{—O—CH}_3$ Methyl ether	$\text{C}_2\text{H}_6\text{O}$
$\text{CH}_3\text{CH}_2\text{—}\overset{\text{O}}{\parallel}\text{C—H}$ Propionaldehyde	$\text{CH}_3\text{—}\overset{\text{O}}{\parallel}\text{C—CH}_3$ Acetone	$\text{C}_3\text{H}_6\text{O}$

In dealing with questions of structural isomerism, you must always keep in mind that

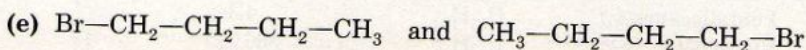
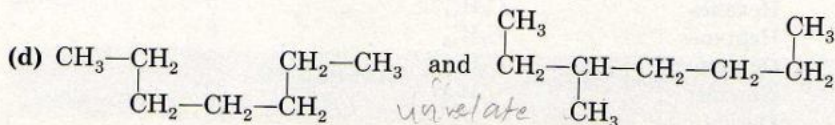
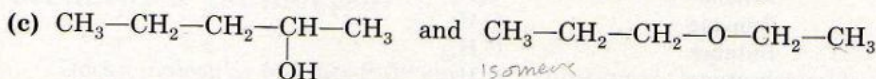
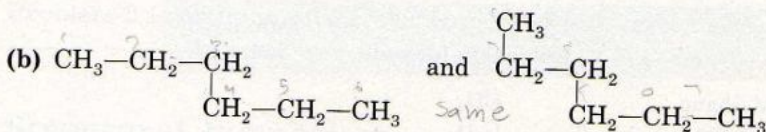
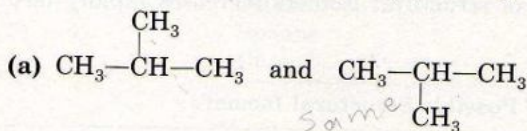
- Structures may be drawn in different conformations (Sec. 2.1). In such cases the various conformers represent the *same* molecule and not separate structural isomers. For example,



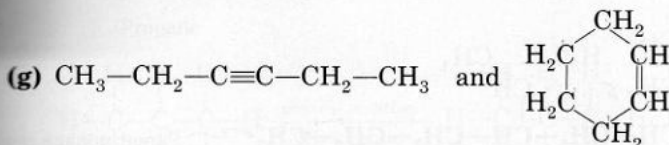
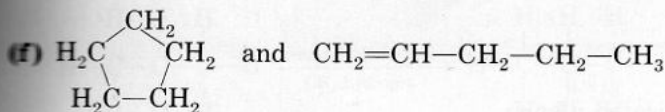
are the same molecule, *n*-butane.

- Every atom in each structural isomer must have the correct number of bonds (Sec. 1.5).

**Problem 2.2** Indicate whether the following pairs of structures are (1) the same, (2) structural isomers, or (3) entirely unrelated.



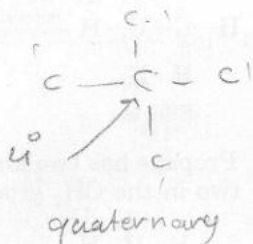
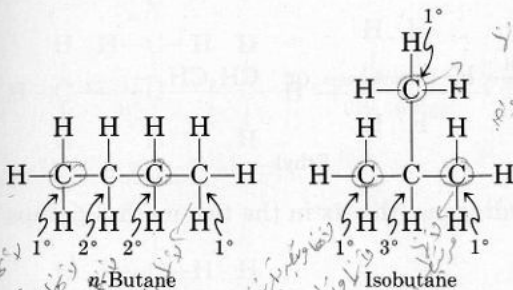




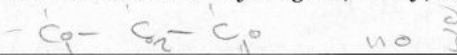
**Problem 2.3** Write partially condensed structures for the five isomeric hexanes,  $\text{C}_6\text{H}_{14}$ .

## Classes of Carbons and Hydrogens 2.4

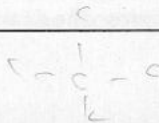
The two isomeric butanes contain three different classes of carbons and hydrogens. A **primary ( $1^\circ$ ) carbon** is one that is bonded to only one other carbon. Carbons bonded to two other carbons are called **secondary ( $2^\circ$ ) carbons**, and those bonded to three other carbons are called **tertiary ( $3^\circ$ ) carbons**. Hydrogens are also referred to as  $1^\circ$ ,  $2^\circ$ , or  $3^\circ$  according to the type of carbon they are bonded to. *n*-Butane has two  $1^\circ$  carbons with six  $1^\circ$  hydrogens and two  $2^\circ$  carbons and four  $2^\circ$  hydrogens. In isobutane there are three  $1^\circ$  carbons and nine  $1^\circ$  hydrogens but only one  $3^\circ$  carbon with one  $3^\circ$  hydrogen.



**Problem 2.4** How many  $1^\circ$ ,  $2^\circ$ , and  $3^\circ$  carbons and hydrogens, if any, are there in propane?

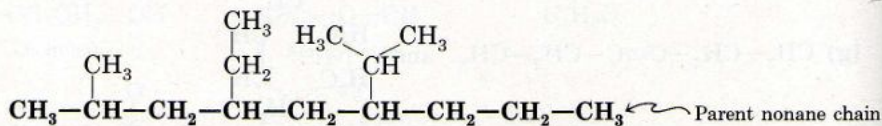


**Problem 2.5** When a carbon is bonded to four other carbon atoms, it is called a **quaternary ( $4^\circ$ ) carbon**. Look at the structure of neopentane (page 31) and determine how many  $1^\circ$ ,  $2^\circ$ ,  $3^\circ$ , and  $4^\circ$  carbons and hydrogens, if any, there are in this molecule.



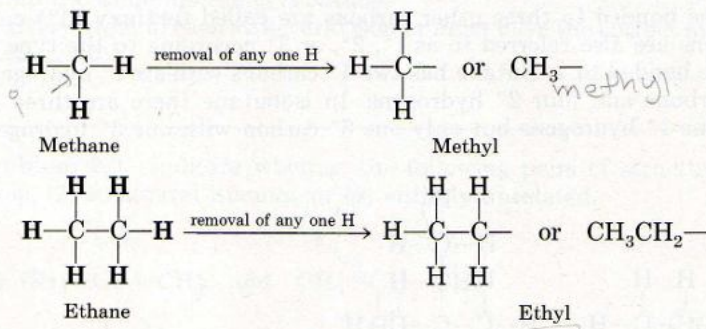
## 2.5 Alkyl Groups

Consider the complicated alkane

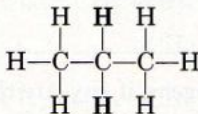


Its molecular formula is  $\text{C}_{15}\text{H}_{32}$ , and Table 2.2 indicates that there are 4347 possible isomers. Therefore 4347 names are needed to identify each one unambiguously. This seemingly impossible task can be accomplished by identifying and naming first the longest continuous carbon chain\* and then the branches that are attached to it. In our example the longest continuous chain has nine carbons and is therefore a nonane. The branches, or alkyl substituents, have names of their own. An **alkyl group** is an alkane from which a hydrogen has been removed. The symbol **R** is used to represent an alkyl group, as in  $\text{R}-\text{OH}$ , the general formula for alcohols (Sec. 1.11).

Individual alkyl groups are named by replacing the suffix -ane of the parent alkane by -yl. Thus the alkyl group  $\text{CH}_3-$ , derived from methane, is called the *methyl* group. Similarly, *ethyl*,  $\text{CH}_3\text{CH}_2-$ , is the alkyl group derived from ethane.



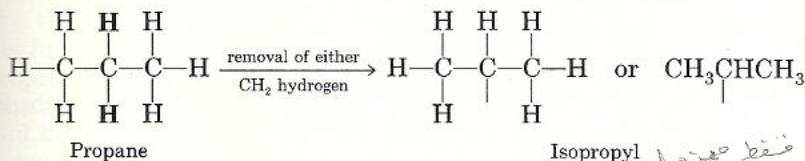
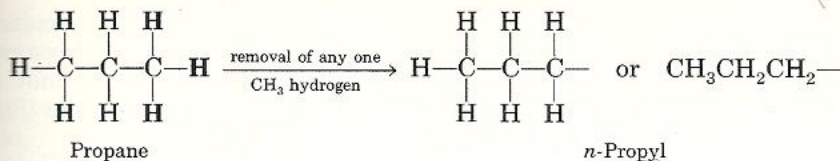
Propane has two kinds of hydrogens: the six in the two methyl groups and the two in the  $\text{CH}_2$  group.



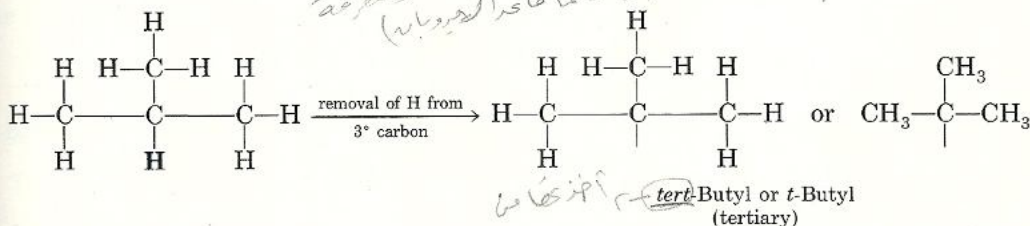
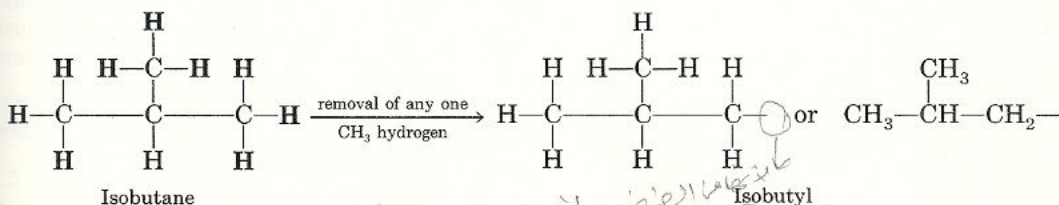
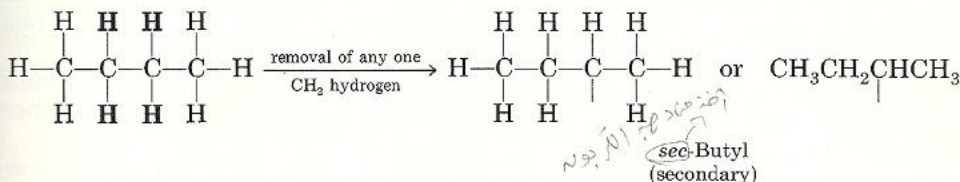
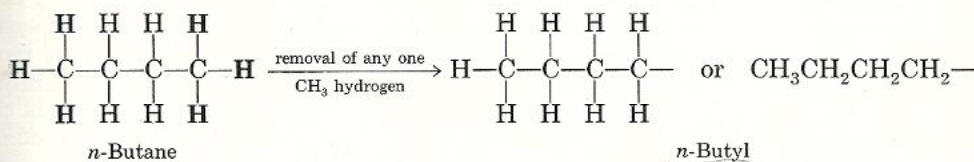
Removal of a hydrogen from either one of the two end carbons gives the *n*-propyl group, while removal of a hydrogen from the middle carbon yields the *isopropyl* group.

\* The longest continuous chain may be determined by following, with one's finger, the sequence of carbon-carbon bonds that includes the maximum number of carbon atoms without ever doubling back over the same bond.





There are four alkyl groups that can be derived from the butanes, two from butane and two from isobutane, because each isomer has two kinds of hydrogens.



Having identified the most common alkyl groups, let us go back to our complicated alkane (page 34) and see if we can now give it an unambiguous name. The alkyl branches on the parent nonane chain are methyl, ethyl, and isopropyl; the compound could therefore be named methylethylisopropylnonane. Although this name does give us much information about the compound, it is still ambiguous: we do not know the locations of the branches on the parent

chain. Thus, you can see that naming a complicated compound is difficult. We need a systematic set of rules. Fortunately, a set of rules, the IUPAC system of nomenclature, is available.

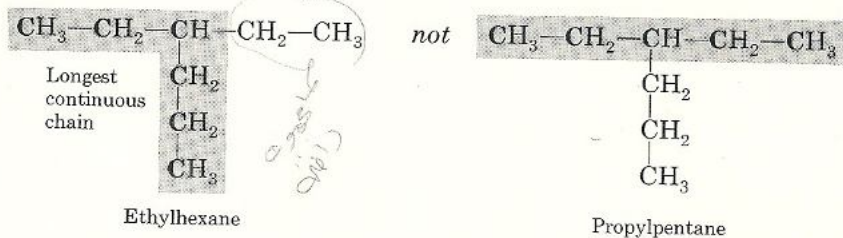
## 2.6 The IUPAC System of Nomenclature

As the number and complexity of organic compounds increased, it became obvious that the early names used to describe them were confusing and inadequate. This problem led eventually to the development of systematic nomenclature rules by the International Chemical Congress, which met in Geneva in 1892. These rules and their subsequent revisions are known today as the **IUPAC system of nomenclature** (International Union of Pure and Applied Chemistry). Although the IUPAC name of a compound makes much more sense, many of the unsystematic names that existed prior to the development of the IUPAC system are still in use today. As a result most organic compounds are known by two or more names: the older unsystematic names, which are referred to as **common** or **trivial**, and the IUPAC names. Isobutane and neopentane are examples of common names. Usually, for compounds of five carbons or less, the common nomenclature is employed. Larger compounds are identified by their IUPAC names.

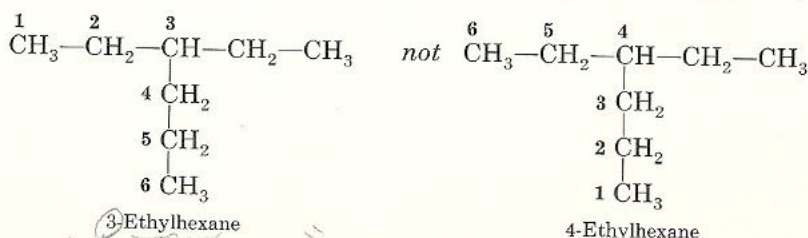
The IUPAC rules that apply to alkanes also form the basis for the nomenclature of all other organic families.

1. Select as the parent structure the longest continuous chain, and consider the compound to have been derived from this structure by the replacement of hydrogens by various alkyl substituents.

In the following example the longest continuous chain contains six carbons; it is therefore a hexane. The substituent is an alkyl branch. Note again that the longest continuous chain is not necessarily straight. It may be bent in various directions because of the free rotation between single-bonded carbon atoms.



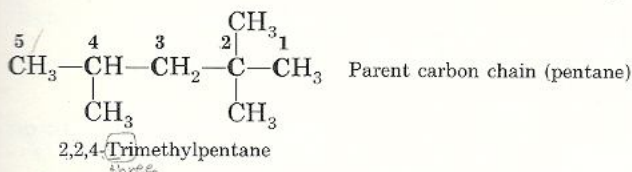
2. Number the carbons in the parent chain starting from whichever end will give the lowest number for the point of attachment of the substituent.



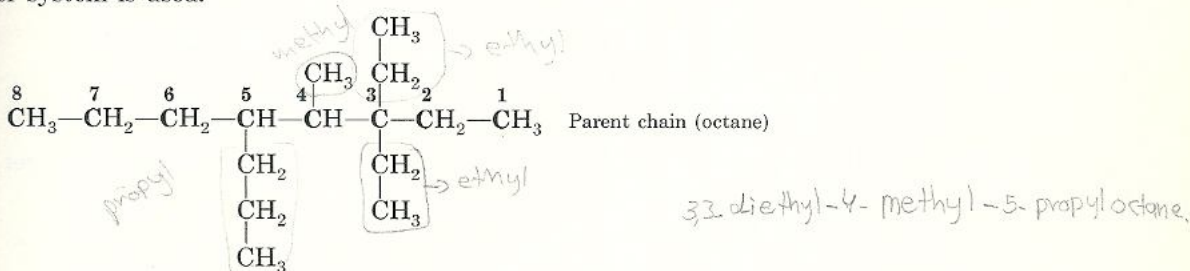


To name the compound, first indicate the position of the substituent on the parent carbon chain by a number (in this example the position number is "3"). The number is followed by a hyphen and the combined name of the substituent (ethyl) and the parent carbon chain (hexane), giving 3-ethylhexane as the full name.

3. If the same alkyl substituent occurs more than once on the parent carbon chain, the prefixes *di-*, *tri-*, *tetra-*, *penta-* and so on, are used to indicate two, three, four, five, and so on. The positions of these substituents are indicated by appropriate numbers separated by commas. If the same substituent occurs twice on the same carbon, the number is repeated. For example,



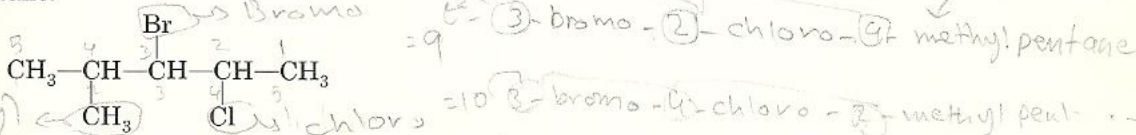
4. If different alkyl substituents are attached on the parent carbon chain, they are named either in order of increasing complexity or in alphabetical order. (It does not matter which method is chosen, as long as the compounds are named consistently.) The chain is numbered from the direction that gives the lowest possible number to one substituent group. For example, the following molecule is named 4-methyl-3,3-diethyl-5-*n*-propyloctane if the order of complexity is used, and 3,3-diethyl-4-methyl-5-*n*-propyloctane if the alphabetical order system is used.



5. If substituents other than alkyl groups are also present on the parent carbon chain, then all substituents are named alphabetically. The names for some of the more common nonalkyl substituents are

—F	fluoro	—NO <sub>2</sub>	nitro	—CN	cyano
—Cl	chloro				
—Br	bromo	—NH <sub>2</sub>	amino		
—I	iodo				

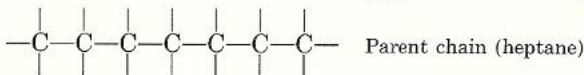
The following compound is therefore named 3-bromo-2-chloro-4-methylpentane.



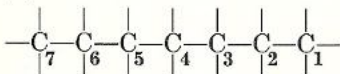
The following examples will help you to understand and apply the IUPAC rules of nomenclature.

**Example 2.1** Write the structural formula of the compound whose IUPAC name is 2,5,5-trimethyl-4-ethylheptane.

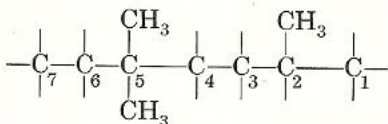
**Solution** (1) Because the parent chain is always indicated by the last part of the compound's name, the chain in this case is a heptane. Write a seven-carbon chain without bothering yet about the hydrogen atoms.



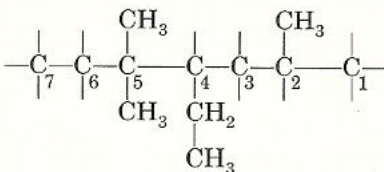
(2) Number the carbons starting from either end.



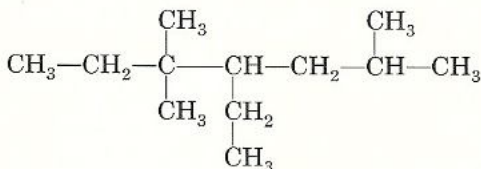
(3) There are three methyl substituents, one on carbon 2 and two on carbon 5.



(4) There is one ethyl substituent on carbon 4.

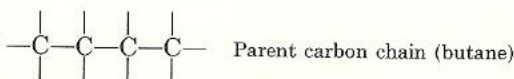


(5) Now add the missing hydrogen atoms on the parent chain to get the correct structure of the compound.

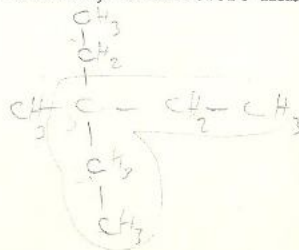
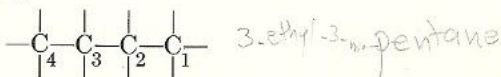


**Example 2.2** The incorrect IUPAC name of a compound is 2,2-diethylbutane. Write the structural formula and correct name of the compound.

**Solution** (1) The parent carbon chain is called butane; it therefore has four carbons.

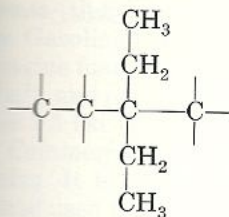


(2) Number the chain.

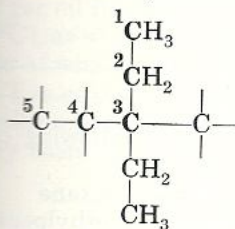




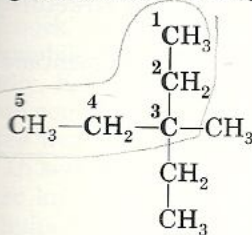
- (3) There are two ethyl substituents on carbon 2.



- (4) The longest continuous chain is not four carbons but five carbons. It is therefore a pentane.

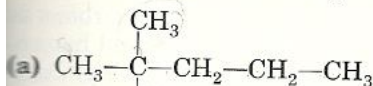


- (5) When the parent chain is renumbered, we find a methyl substituent and an ethyl substituent on carbon 3. Named according to alphabetical order, the compound is 3-ethyl-3-methylpentane. Writing the missing hydrogens gives the correct structural formula.

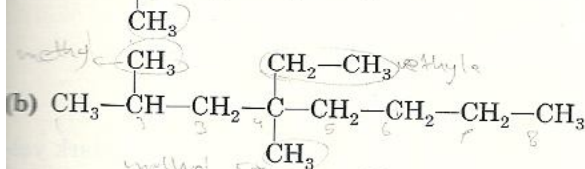


3-Ethyl-3-methylpentane

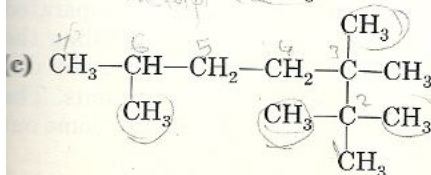
**Problem 2.6** Give the IUPAC name for each of the following compounds. List the alkyl substituents in alphabetical order.



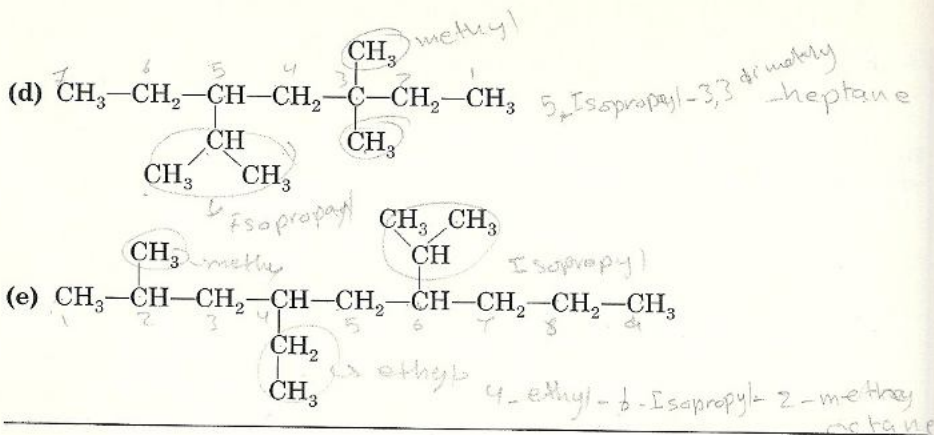
2,2-dimethyl pentane



4-ethyl-3,4-dimethyloctane



2,2,3,6-pentamethyl heptane



**Problem 2.7** Write the structural formula for each of the following compounds.

- |  |                             |
|--|-----------------------------|
| (a) 2-Methylpentane (isohexane)                    | (b) 2,2-Dichlorobutane      |
| (c) 3,4-Dimethyl-5-ethyl-6-isopropylnonane         | (d) 2-Bromo-3-methylpentane |
| (e) 2,4-Dimethyl-5-ethyl-4- <i>t</i> -butylheptane |                             |

**Problem 2.8** These compounds are incorrectly named. Write the structure and correct name for each compound.

- |                                |  |
|--------------------------------|--|
| (a) 4,4-Dimethylpentane        | (b) 2-Methyl-2- <i>sec</i> -butylpentane |
| (c) 2-Ethylpropane             | (d) 2- <i>t</i> -Butylbutane             |
| (e) 3-Methyl-5-isopropylhexane |  |

## 2.7 Sources of Alkanes

The two principal sources of alkanes are petroleum and natural gas, both of which are products of the decay of animal, vegetable, and marine matter. Petroleum and natural gas constitute the chief sources of alkanes up to 40 carbons as well as of many aromatic, alicyclic (cyclic aliphatic hydrocarbons), and heterocyclic (cyclic molecules with more than one kind of atom in the ring) compounds.

### A Petroleum Refining

Petroleum is a viscous oil liquid that varies in appearance from a dark yellow to a brown to a greenish black color. Its various components are separated and purified by a process called *refining*. This is usually done by distilling the petroleum into fractions of different boiling ranges and then treating the distilled petroleum in various ways to remove the undesirable components. The most volatile components (that is, those with the lowest boiling points) come out



first. The less volatile components come out next, and the highest boiling components (those that boil at temperatures above  $400^{\circ}\text{C}$ ) remain behind as residues. Gasoline boils at temperatures between  $40$  and  $200^{\circ}\text{C}$ . Kerosene (used as jet engine fuel) boils at temperatures ranging from  $175$  to  $325^{\circ}\text{C}$ . Lubricating oil, asphalt, and petroleum coke are the highest boiling residues that remain behind. Table 2.3 lists the useful components of refined petroleum.

Commercially, gasoline is by far the most important fraction of petroleum refining. It is not, however, a major fraction of the distillate. One industrial method used to increase the quantity of gasoline is a process known as cracking or *pyrolysis* (from the Greek *pyro*, fire; *lysis*, breaking) (see Fig. 2.4). In this process the higher-molecular-weight alkanes in petroleum, usually the kerosene and gas oil fractions, are heated in a chamber to very high temperatures ( $400$ – $700^{\circ}\text{C}$ ), at which point they are broken into a mixture of smaller hydrocarbons, some of which have molecular sizes in the range of gasoline constituents.

The refined products of petroleum, known as *petrochemicals*, have great industrial importance. They are used as raw materials in the manufacture of many useful finished products, as Figure 2.5 indicates.

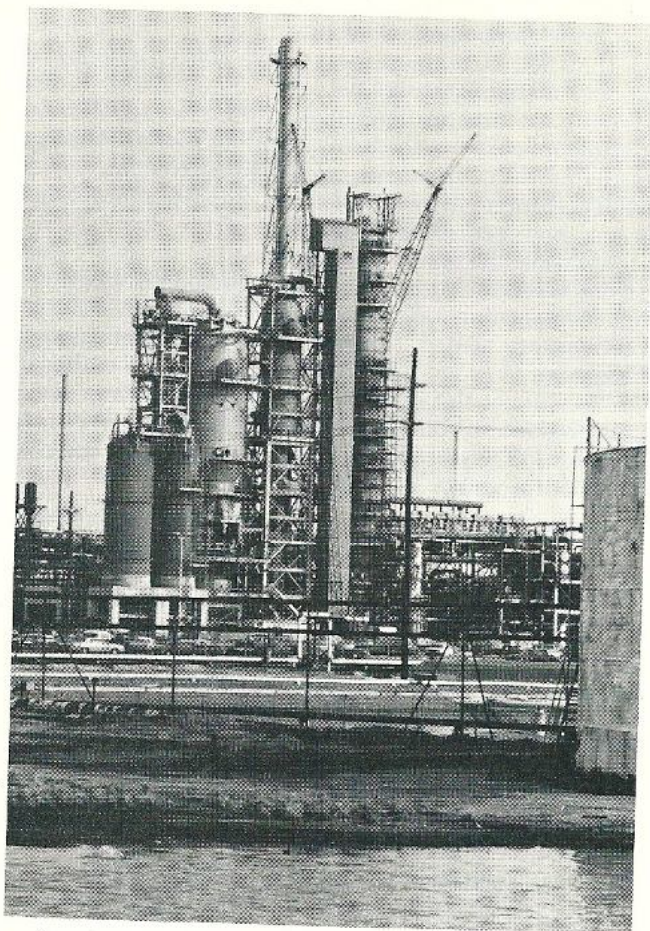
## B Octane Number

Gasoline performance in internal combustion engines has for many years been rated on the basis of the **octane number** scale. The higher the octane number assigned to a fuel, the better its performance and the lower the incidence of “knock” in the engine. *Knocking* is the familiar sharp “ping” that occurs in an automobile engine when driving up a steep grade or attempting to accelerate too rapidly. Knocking is caused by the premature ignition of the fuel–air mixture before completion of the compression stroke, resulting in reduced power and in engine wear.

In setting up the octane number scale, *n*-heptane, a poor fuel that causes severe knocking, was arbitrarily assigned an octane rating of zero. 2,2,4-Trimethylpentane (known as isooctane by the petroleum industry), an excellent fuel with no knocking tendency, was assigned an octane rating of 100. The octane ratings of other fuels are determined by comparing their knocking tendency with that of a synthetic blend of 2,2,4-trimethylpentane and *n*-heptane. The familiar “regular” gasoline with an octane rating of 90 has a knocking character-

Table 2.3 Some Components of Refined Petroleum

Fraction	Boiling range ( $^{\circ}\text{C}$ )	Carbon content
Gas	Below 20	$\text{C}_1$ – $\text{C}_4$
Petroleum ether	20–60	$\text{C}_5$ – $\text{C}_6$
Naphtha	60–100	$\text{C}_6$ – $\text{C}_7$
Gasoline	40–200	$\text{C}_5$ – $\text{C}_{10}$
Kerosene	175–325	$\text{C}_{11}$ – $\text{C}_{18}$
Gas oil	300–500	$\text{C}_{15}$ – $\text{C}_{40}$
Lubricating oil, asphalt, petroleum coke, and paraffins	Above 400	$\text{C}_{15}$ – $\text{C}_{40}$



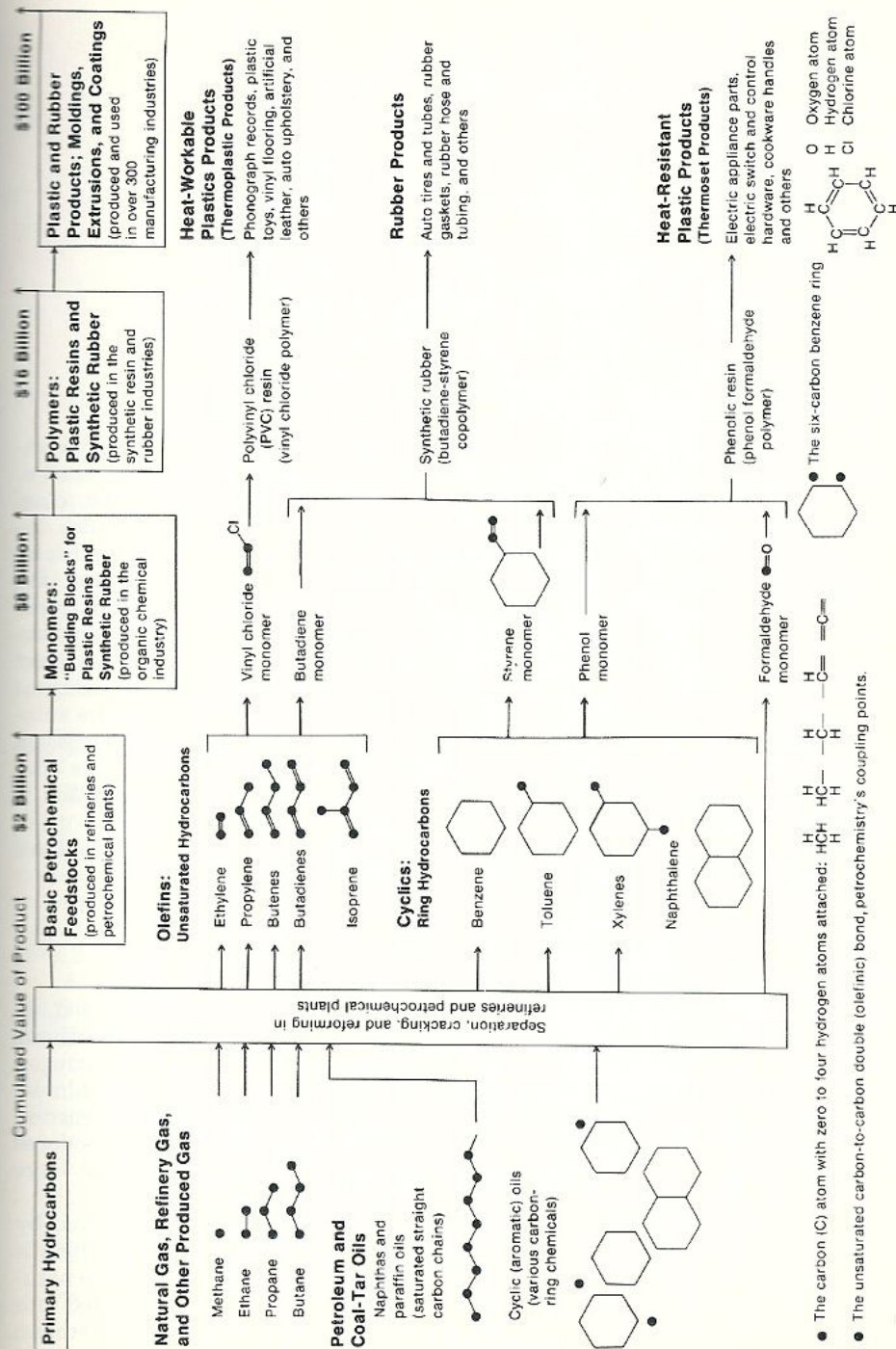
**Figure 2.4** A fluid catalytic cracking unit used in the production of gasoline. [Courtesy Mobil Oil Corp.]

istic equivalent to that of a mixture of 10% *n*-heptane and 90% 2,2,4-trimethylpentane.

When the system of rating a fuel was first established, no other known hydrocarbons gave better engine performance than 2,2,4-trimethylpentane. Since then, however, new hydrocarbons that are superior fuels have been discovered and given an octane rating higher than 100. Hydrocarbons that surpass 2,2,4-trimethylpentane in knock performance are rated not by their knocking tendency but by their *power output* as compared with the power developed by the standard octane. Thus, octane numbers over 100 are based differently than those under 100. Table 2.4 lists octane numbers of some hydrocarbons. Note that octane numbers decrease with increasing chain length and increase with increasing branching.

The octane number of a poor fuel can also be improved by blending it with small amounts of additives. Commercial Ethyl Fluid, which is added to gasolines to improve their octane ratings, consists of approximately 59% tetraethyllead,





**Figure 2.5** Manufactured products made from petrochemicals. [From The New York Times, Jan. 6, 1974. © 1974 by The New York Times Company. Reprinted by permission.]

Table 2.4 Octane Number of Some Hydrocarbons

Hydrocarbon	Octane number
<i>n</i> -Hexane	26
<i>n</i> -Heptane	0
<i>n</i> -Octane	-20
<i>n</i> -Nonane	-35
2-Methylpentane	73
2-Methylhexane	45
2-Methylheptane	24
2,2-Dimethylhexane	77
2,3-Dimethylbutane	93
2,2,4-Trimethylpentane	100
2,2,3-Trimethylpentane	116

13% ethylene bromide, 24% ethylene chloride, and 4% kerosene and dye. Tetraethyllead,  $(C_2H_5)_4Pb$ , is an efficient antiknock agent but has one disadvantage: its combustion product, lead oxide, is reduced to metallic lead that clogs the cylinder valves of an engine. Some lead, a dangerous pollutant, is also discharged into the air through the exhaust pipe. To remove the deposited lead, ethylene bromide and ethylene chloride are added with the tetraethyllead into the gasoline. Each additive reacts with the lead in the engine and transforms it into gaseous lead bromide and lead chloride at the combustion temperature. These gases are then discharged through the exhaust pipe. The net effect is to clean the engine but also to pollute the air even more. Although stringent federal emission standards were passed to combat pollution caused by the automobile, they have of late been relaxed because of the energy crisis. The emission control equipment put in automobiles since 1973 has increased gasoline consumption, and their effect in actually lessening the amount of pollution is questionable.

Other additives such as TCP (tricresyl phosphate) and boron hydrides have also enhanced the performance of many gasolines.

## C Natural Gas

Natural gas consists of the low-molecular-weight alkanes from  $C_1$  to  $C_8$ . It is composed primarily of methane (80%); the other constituents are ethane (13%), propane (3%), butane (1%),  $C_5$  through  $C_8$  alkanes (0.5%), and nitrogen (2.5%). Natural gas is a cleaner fuel than petroleum because it contains almost none of the sulfur compounds usually found in petroleum. The combustion of natural gas, unlike the combustion of many petroleum products, produces very little sulfur dioxide,  $SO_2$ , a troublesome air pollutant in many large cities.

The propane and butane components of natural gas can be removed by liquefaction and compressed into cylinders to be sold as bottled gas, which is used for fuel in many rural areas. In heavily populated urban centers, the natural gas is distributed by means of pipelines. Natural gas is also converted into many other important organic compounds, such as alcohols, aldehydes, ketones, carboxylic acids, and alkyl halides.



Methane is also called marsh gas because it rises as bubbles on the surface of marshes and peat bogs. Like propane, butane, and other alkanes, methane is highly flammable, and its spontaneous ignition in marshes is responsible for the ghostly looking blue flames called will-o'-the-wisps.

## Physical Properties of Alkanes 2.8

By physical properties we mean those properties that can be observed without the compound undergoing a chemical reaction.

### A Physical States and Solubilities

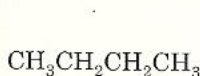
Alkanes occur at room temperature as gases, liquids, and solids. Alkanes from  $C_1$  to  $C_4$  are gases; most  $C_5$  to  $C_{17}$  alkanes are liquids; and the  $C_{18}$  and larger alkanes are wax-like solids.

Alkanes are nonpolar compounds. Their solubility characteristic may be predicted by what is commonly known as the "like dissolves like" rule. What this rule means is that nonpolar compounds are soluble in other nonpolar solvents and that polar compounds are generally soluble in other polar solvents. Thus, alkanes are soluble in the nonpolar solvents carbon tetrachloride,  $CCl_4$ , and benzene,  $C_6H_6$ , but they are insoluble in polar solvents such as water.

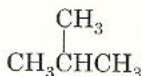
### B Boiling Points

When a substance boils, it changes from a liquid to a gas, a process requiring energy. The boiling points of normal hydrocarbons increase with increasing molecular weight. One explanation for this trend is that as molecules become larger there are more forces of attraction between them, and more energy is needed to go from the liquid to the gaseous state. Except for the very small alkanes, the boiling point rises  $20\text{--}30^\circ\text{C}$  for each addition of a carbon atom to the chain (Fig. 2.6).

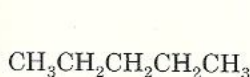
Among isomeric alkanes, the straight-chain compound has the highest boiling point. For the other isomers, the greater the number of branches, the lower the boiling point. For example,



*n*-Butane  
(bp =  $0^\circ\text{C}$ )



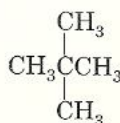
Isobutane  
(bp =  $-12^\circ\text{C}$ )



*n*-Pentane  
(bp =  $36^\circ\text{C}$ )



Isopentane  
(bp =  $28^\circ\text{C}$ )



Neopentane  
(bp =  $9.5^\circ\text{C}$ )

$C_1$  to  $C_4$  are gases  
 $C_5$  to  $C_{17}$  are liquid  
 $C_{18}$  and larger are wax-like solids

① nonpolar  
② they are soluble in nonpolar solvents like  $CCl_4$ , tetra chloride, and Benzene

highest B.P.  
straight chain

the greater the number of branches  
lower B.P.

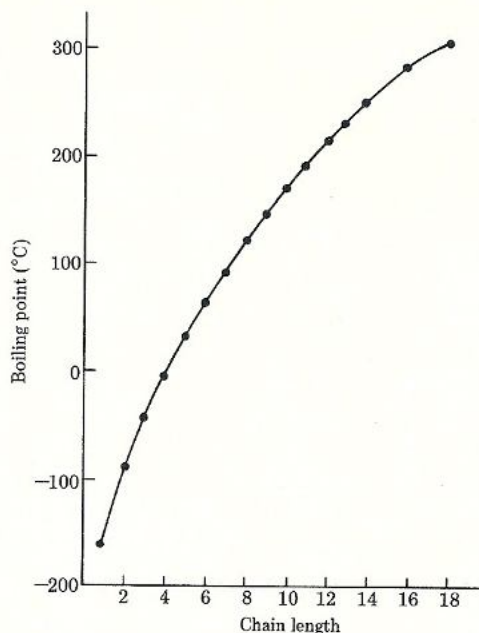


Figure 2.6 Boiling points of normal alkanes.

The decrease in boiling points with increased branching can be explained as follows: as branching increases, the molecule becomes more compact, decreasing its surface area. With a smaller surface area, the intermolecular forces of attraction are diminished, requiring less energy to go from the liquid state to the gaseous state.

---

**Problem 2.9** Arrange the following compounds in order of increasing boiling points: *n*-hexane; 2,2-dimethylbutane; 2-methylpentane.

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### C Melting Points

The melting points of alkanes also increase with increasing molecular weight. However, unlike the change in boiling point, there is no regularity in the change in melting point with the number of carbon atoms in a molecule. Also, differences in melting points between straight-chain and branched-chain compounds follow no regular pattern.

## 2.9 Preparation of Alkanes

A great number of alkanes can be obtained in pure form most economically by fractional distillation of crude petroleum. In some cases it is necessary to synthesize an alkane that cannot be obtained from natural sources, and labora-



ary methods of preparation are available. These consist of converting another class of compounds into alkanes. For this reason, we shall not discuss the preparations of alkanes until we encounter other classes of organic compounds.

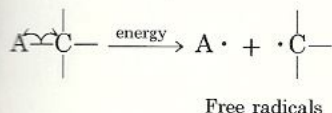
Before proceeding to the reactions of alkanes, which involve the breaking and making of bonds, we shall first look into the various ways a bond can be broken and the notations used to indicate the movement of electrons.

## Notations for Bond Breaking and Bond Making 2.10

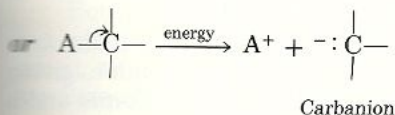
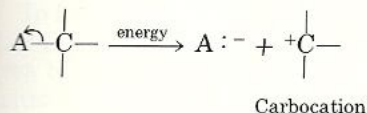
A covalent bond can be broken in either of two ways, *homolytically* or *heterolytically*. Homolytic cleavage occurs when a bond splits evenly into two neutral fragments, each with one odd electron. A fishhook arrow  $\curvearrowright$  indicates the movement of a single electron. Heterolytic cleavage occurs when a bond breaks unevenly, forming two oppositely charged fragments. A full-headed curved arrow  $\curvearrowright$  denotes the movement of an electron pair. Both homolytic and

heterolytic cleavages are illustrated with the hypothetical molecule  $A-\overset{\overset{|}{|}}{\underset{\underset{|}{|}}{C}}-$ .

### Homolytic cleavage



### Heterolytic cleavage



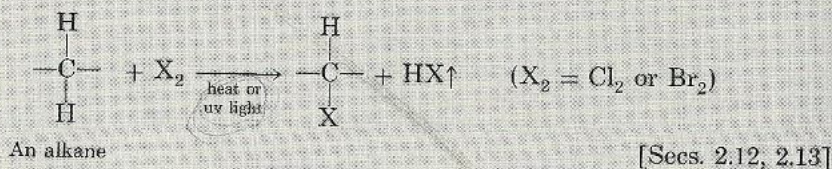
Each species produced by homolytic cleavage has an odd electron and is called a **free radical**. In the case of heterolytic cleavage, depending on how cleavage has occurred, the carbon is either a positively charged ion called a **carbocation**,  $^+\overset{\overset{|}{|}}{\underset{\underset{|}{|}}{C}}-$ , or a negatively charged ion called a **carbanion**,  $^-\overset{\overset{|}{|}}{\underset{\underset{|}{|}}{C}}-$ . Free radicals, carbocations, and carbanions are reactive species that appear only as short-lived intermediates in organic reactions. We will encounter free radicals in halogenation, the first reaction of alkanes.

## 2.11 Reactions of Alkanes

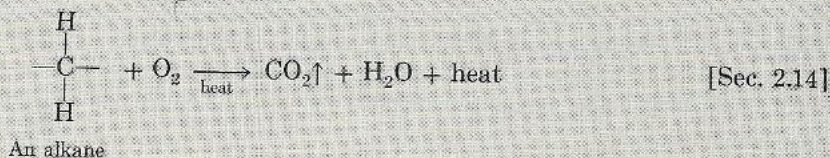
Compared with most other classes of compounds, saturated hydrocarbons undergo very few reactions, and this is why they were originally called *paraffinic* hydrocarbons (from the Latin *parum*, little; *affinis*, affinity). We shall consider two important reactions that alkanes do undergo, namely, **halogenation** and **combustion**. In the former reaction only carbon-hydrogen bonds are broken; in the latter both carbon-hydrogen and carbon-carbon bonds are ruptured.

These reactions are presented here in a general form. They are discussed in greater detail in the next three sections.

### 1. Halogenation



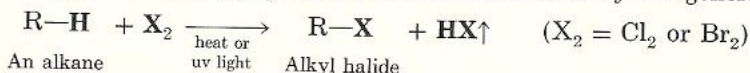
### 2. Combustion



## 2.12 Halogenation

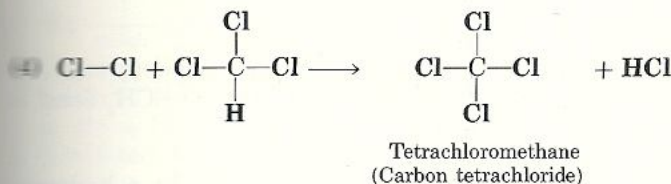
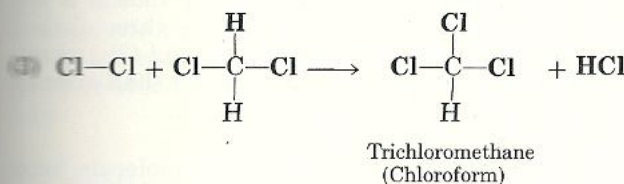
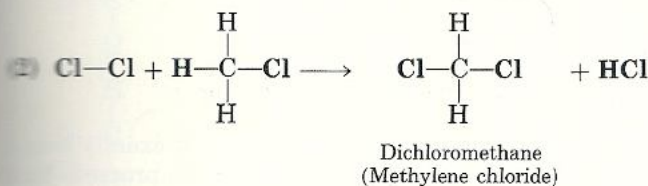
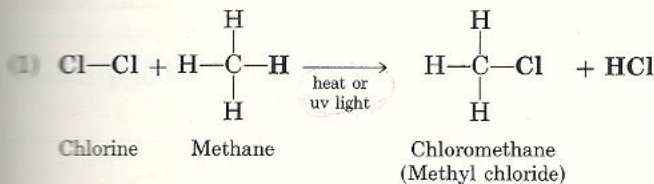
Halogenation is the typical **substitution reaction** of alkanes. It involves the replacement of hydrogen by halogen, usually chlorine or bromine, giving alkyl chlorides or alkyl bromides. Fluorine reacts explosively with alkanes and is thus an unsuitable reagent for the preparation of alkyl fluorides. Iodine is too unreactive and is not used in the halogenation of alkanes. Only chlorine and bromine react readily with alkanes under easily controllable conditions and are therefore used in the reaction.

Halogenation of alkanes takes place at high temperatures or under the influence of ultraviolet light. The reaction is illustrated by the general equation





Chlorination of an alkane usually gives a mixture of products because more than one hydrogen may be substituted by chlorine atoms. For example, the chlorination of methane yields a mixture of four different products.

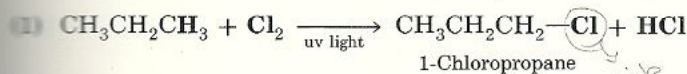


substitution =  
substitute =

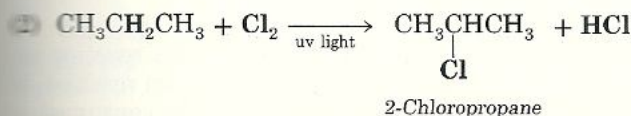
To form a *monohalogenated* product, where only one H atom is replaced by either Cl or Br, the reaction is conducted with a small amount of halogen and an excess of hydrocarbon. Under these conditions, the supply of halogen is exhausted as the first hydrogen of the hydrocarbon is replaced so there is practically no possibility for substitution of the remaining hydrogen atoms.

Both methane and ethane give only one monochlorinated product because in each compound all hydrogen atoms are equivalent. When propane is chlorinated, two monochlorinated products, 1-chloropropane and 2-chloropropane, are formed.

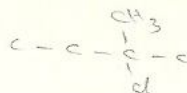
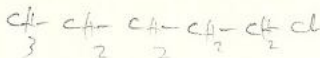
The form monohalogenated where only one H atom is replaced by



either Cl or Br



(b)

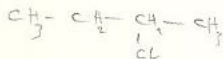
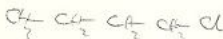


50

Saturated  
Hydrocarbons:  
Alkanes

**Problem 2.10** Name and give the structures of all the products of the monochlorination of (a) butane and (b) pentane.

(a)



**Problem 2.11** Name and give the structures of all the products of the monobromination of (a) isobutane and (b) 2,2-dimethylbutane.

## 2.13 Mechanism of Halogenation of Alkanes

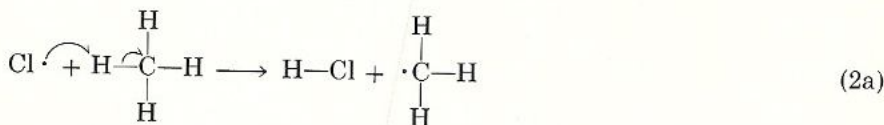
A **reaction mechanism** is a detailed step-by-step model of exactly how a given reaction is believed to take place. Halogenation of alkanes proceeds by a **free-radical chain mechanism**. Recall (Sec. 2.10) that a free radical is any reactive species with an odd electron. The mechanism involves three distinct steps: (1) a chain-initiation step, (2) a chain-propagating step, and (3) a chain-terminating step. Using chlorine and methane as our reactants, we shall examine these steps and see how they contribute to the overall reaction.

**1. Chain-initiation step.** Homolytic cleavage of a chlorine molecule forms two highly reactive chlorine free radicals.

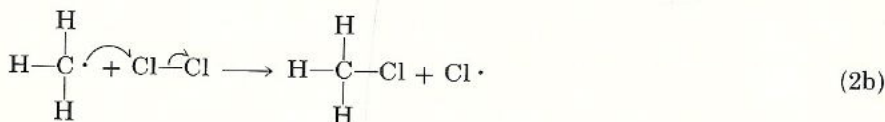


(Note that the weaker Cl—Cl bond, rather than the stronger H—CH<sub>3</sub> bond, is broken in the initial step. See Table 1.4.)

**2. Chain-propagating step.** The chlorine free radical attacks a hydrogen atom from methane, forming a methyl free radical and HCl.



The reactive methyl free radical quickly reacts with another molecule of chlorine to give methyl chloride and another chlorine free radical.

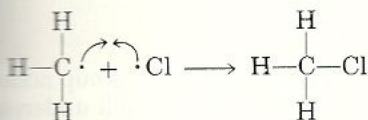
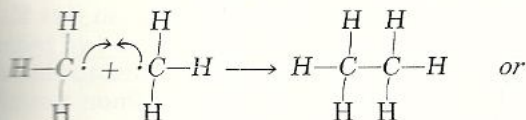


Back to (2a)

The chlorine free radical can go on to repeat reaction (2a). The reaction sequence (2a) to (2b) to (2a) to (2b) and so on is referred to as a chain reaction. It will continue indefinitely until one of the reactants is completely consumed or until two reactive intermediates react together.



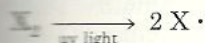
**3. Chain-terminating step.** The termination of the chain reaction sequence by reaction of two reactive intermediates may occur when two chlorine atoms react together to form a chlorine molecule, when two methyl free radicals react together to produce a new alkane, which is a dimer of the parent alkane, or when an alkyl free radical reacts with a chlorine atom to give an alkyl halide. The three reactions are



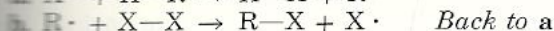
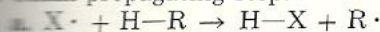
The net effect of each of the possible occurrences is to remove from circulation one of the reactive species.

The overall general mechanism of free-radical halogenation is summarized here.

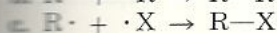
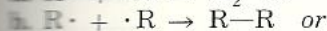
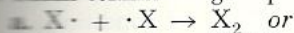
**1. Chain-initiation step:**



**2. Chain-propagating step:**



**3. Chain-terminating step:**

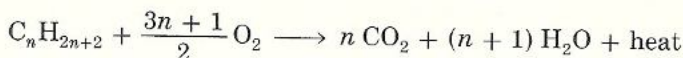


**Problem 2.12** Monochlorination of ethane follows the same course as the chlorination of methane. Write the mechanism for the chlorination of ethane.

## Combustion of Alkanes 2.14

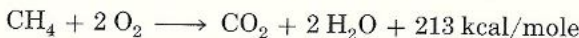
When ignited in the presence of excess oxygen, alkanes are oxidized to carbon dioxide and water. A large quantity of heat (the heat of combustion) is liberated in the process. In fact, the heat is the most important product of this reaction because it is the source of power used to warm our homes and run our machines.

## General equation

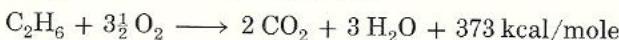


## Specific examples

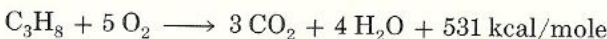
## Complete combustion of methane



## Complete combustion of ethane

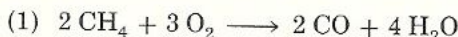


## Complete combustion of propane



Note that about 160 kcal of heat is liberated for each methylene group added to the hydrocarbon chain. The mechanism of this reaction is not well understood, but is believed to involve a complex series of free-radical reactions.

The incomplete combustion of alkanes liberates poisonous carbon monoxide (CO) or carbon in the form of soot; both are major contributors to air pollution. Incomplete combustion of fuels frequently occurs in automobile engines, where it results in carbon deposit in the pistons and in expulsion of toxic carbon monoxide in the exhaust fumes. This is why it is dangerous to drive an automobile with all the windows closed, or to warm up the car in a closed garage. The incomplete combustion of methane is illustrated in the following equations.



Although soot is a nuisance when it forms in automobile engines, large quantities are used industrially, mainly in the manufacture of tires. This soot is produced by conducting the second reaction under controlled conditions.

**Problem 2.13** Write the equation for the complete combustion of *n*-butane, and estimate the value of its heat of combustion.

## 2.15 Cycloalkanes: Nomenclature

Cycloalkanes are saturated hydrocarbons that exist in the form of a ring. Except for the three- and four-membered cyclic alkanes, which are very reactive, cyclic alkanes are as unreactive as their open-chain analogs. For this reason they are also called *cycloparaffins*. In the petroleum industry they are known as *naphthenes* because they are isolated from the naphtha fraction of petroleum.

Cycloalkanes are named by adding the prefix *cyclo-* to the name of the open-chain hydrocarbon that has the same number of carbon atoms as in the ring. For example, the three-carbon cycloalkane is called *cyclopropane*, and the four-carbon cycloalkane is called *cyclobutane*. Expanded and partially condensed structural formula representations of cyclic alkanes are given in Section 1.7.

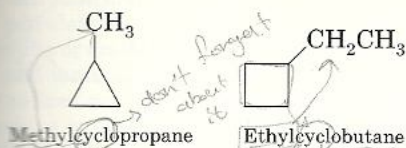


green chain

مشتقات البترول  
التي تحتوي على  
الهيدروجين والكربون  
والمشبعة

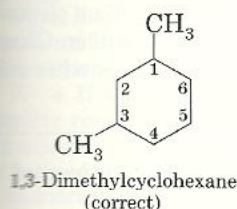


When only one substituent is attached to the ring, we name the substituent first and then name the ring. For example,

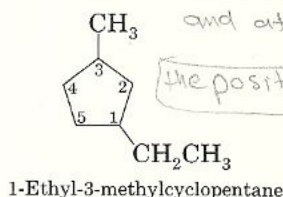
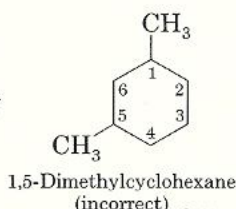


when only one substituent is attached don't we name the substituent first and

If two or more substituents are attached to the ring, their positions are specified by numbers. The number 1 is assigned to one of the ring carbons bearing a substituent; then the rest of the ring is numbered in a way that will give the lowest number(s) for the position of the other substituent(s).



not



when 2 or more substituent and attached to ring the positions and specified by number

**Problem 2.14** Write the condensed structural formula for each of the incorrectly named compounds, and give the correct name for each.

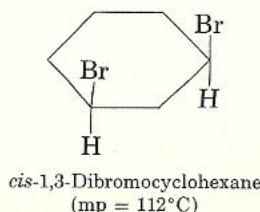
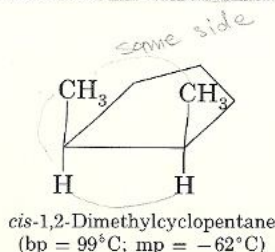
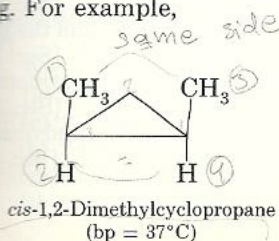
- (a) 1,3-Dichlorocyclopropane      (b) 1,4-Dimethylcyclobutane  
 (c) 3,5-Dibromocyclopentane      (d) 6,6-Dibromocyclohexane  
 (e) 1,5-Dimethylcyclohexane      (f) 2,2-Dichloro-5-methylcyclohexane

الاسماء الخاطئة التي تحتوي على عيوب في تسمية المركبات الدائرية

## Geometric Isomerism in Cycloalkanes

## 2.16

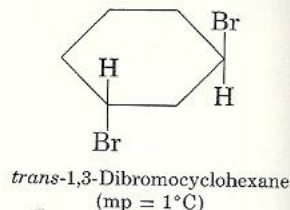
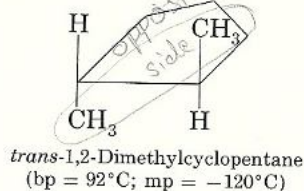
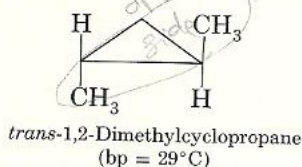
In open-chain alkanes very little energy is needed to twist around the carbon-carbon bond, and we say there is *free rotation* (Sec. 2.1). In contrast, in cycloalkanes the carbons are held together in a ring, and so much energy is needed for carbon-carbon bonds to rotate that the ring would break before complete rotation takes place. Therefore, we say that there is *no free rotation* in cycloalkanes. The lack of free rotation of single-bonded carbons in a ring produces a kind of isomerism called **geometric isomerism**. A cycloalkane with two substituents on different carbons of the ring can exist as a *cis* isomer or as a *trans* isomer. In the *cis* isomer the two substituents are on the same side of the ring. For example,



Geometric isomerism

① ≠ ②      ③ ≠ ④

In the *trans* isomer the two substituents are on opposite sides of the ring.



Note that *cis* and *trans* isomers have the same sequence of atoms bonded to each other and are therefore *not* structural isomers. *Cis-trans* isomers differ only in their **configurations**, that is, the orientation in space of the substituents around a carbon. For this reason geometric isomers are referred to as *stereoisomers*. (The subject of stereoisomerism is dealt with in greater detail in Chapter 6.) Nevertheless, *cis* and *trans* isomers represent distinct molecules with different physical properties.

**Problem 2.15** Draw a condensed structural formula for each compound.

- cis*-1-Chloro-2-methylcyclopentane
- trans*-1,3-Difluorocyclohexane
- 1,1-Dimethylcyclohexane
- 1,1-Dibromo-3-methylcyclopentane (Note: There are no *cis* or *trans* in this case. Why?)

**Problem 2.16** Which compounds can exist as geometric isomers?

- 1,2-Dibromocyclobutane
- 1,1-Dimethylcyclohexane
- 1,2-Dimethylcyclohexane
- 1,1-Dichloro-2-methylcyclohexane

## Summary of Concepts and Reactions

Alkanes are saturated hydrocarbons consisting only of C—C and C—H single bonds.

They have the general formula  $C_nH_{2n+2}$ .

[Secs. 2.1, 2.2]

Alkanes form a homologous series.

[Sec. 2.2]

All carbon atoms in alkanes are  $sp^3$  hybridized and have a tetrahedral shape.

[Sec. 2.1]

There is free rotation about the C—C single bond in open-chain alkanes.

[Sec. 2.1]

Conformations are structures that differ by rotation about a C—C single bond. At room temperature individual conformers cannot be separated.

[Sec. 2.1]

Different compounds with identical molecular formulas are called isomers, and the phenomenon is called isomerism.

[Sec. 2.3]

Isomers that differ in the sequence of atoms bonded to each other are called structural or constitutional isomers.

[Sec. 2.3]

There are four classes of carbons: primary ( $1^\circ$ ), secondary ( $2^\circ$ ), tertiary ( $3^\circ$ ), and quaternary ( $4^\circ$ ).

[Sec. 2.4]

An alkyl group (R) is an alkane from which a hydrogen has been removed.

[Sec. 2.5]



- Alkanes are known by two or more names, common names and IUPAC names. [Sec. 2.6]
- The two principal sources of alkanes are petroleum and natural gas. The components of petroleum are separated by a process called refining. [Sec. 2.7A]
- Pyrolysis or cracking is an industrial method used to break large molecules into smaller and more useful molecules. [Sec. 2.7A]
- The refined products of petroleum are called petrochemicals. [Sec. 2.7A]
- Knocking is produced by a fuel with a low octane number rating. [Sec. 2.7B]
- Methane is the major constituent of natural gas. [Sec. 2.7C]
- The solubility of alkanes may be predicted by means of the "like dissolves like" rule. [Sec. 2.8A]
- The physical properties of alkanes depend on chain length and degree of branching. [Sec. 2.8B]
- A covalent bond can be broken during the course of an alkane reaction in either of two ways, homolytically or heterolytically. [Sec. 2.10]
- Alkanes undergo two types of reactions, halogenation and combustion. [Sec. 2.11]
- Halogenation proceeds via a free-radical chain mechanism: (a)  $R-H + X\cdot \rightarrow R\cdot + HX$ ; (b)  $R\cdot + X_2 \rightarrow RX + X\cdot$ ; back to (a). [Sec. 2.13]
- Complete combustion of alkanes yields  $CO_2$ ,  $H_2O$ , and heat. [Sec. 2.14]
- Cycloalkanes are saturated hydrocarbons that exist in the form of a ring. [Sec. 2.15]
- The lack of free rotation of singly bonded carbons in a ring gives rise to a kind of isomerism called geometric isomerism. [Sec. 2.16]
- Geometric isomers in cycloalkanes can be formed by two substituents on the same side (*cis*) or opposite sides (*trans*) of the ring. [Sec. 2.16]

## Key Terms

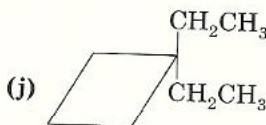
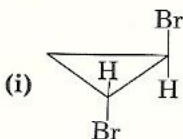
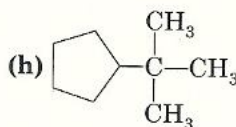
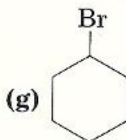
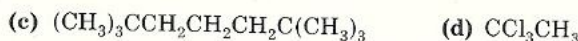
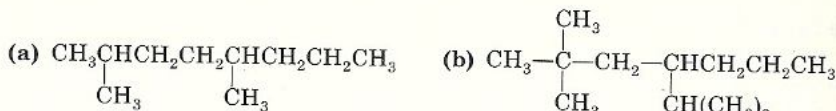
hydrocarbons	primary ( $1^\circ$ ) carbons	carbocation
alkanes	secondary ( $2^\circ$ ) carbons	carbanion
conformation	tertiary ( $3^\circ$ ) carbons	halogenation
conformer	quaternary ( $4^\circ$ ) carbon	combustion
homologous series	alkyl group, R	substitution reaction
homolog	IUPAC system of nomenclature	reaction mechanism
isomers	common (trivial) names	free-radical chain mechanism
isomerism	octane number	geometric isomerism
structural (constitutional) isomers	free radical	configuration

## Exercises

### Structure and Nomenclature of Alkanes and Cycloalkanes [Secs. 2.5, 2.6, 2.15, 2.16]

- 2.1 Write structural formulas for the following compounds.
- |   |  |
|---|--|
| (a) 3-Methylheptane                       | (b) 2,3-Dimethylpentane                      |
| (c) 2,3-Dimethyl-4-ethylhexane            | (d) 2,3,5-Trimethylhexane                    |
| (e) 2-Chloro-3-methylpentane              | (f) 2-Bromo-2,3-dichlorobutane               |
| (g) 1,1,2,2-Tetrabromopropane             | (h) Methylcyclobutane                        |
| (i) <i>trans</i> -1,2-Dibromocyclopentane | (j) <i>cis</i> -1-Chloro-2-ethylcyclopropane |

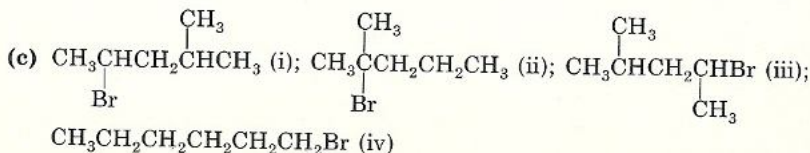
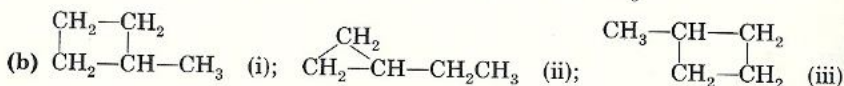
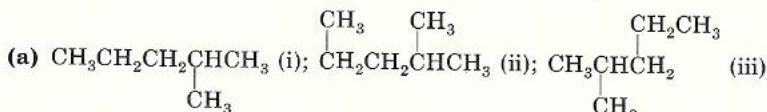
2.2 Give IUPAC names for the following compounds.



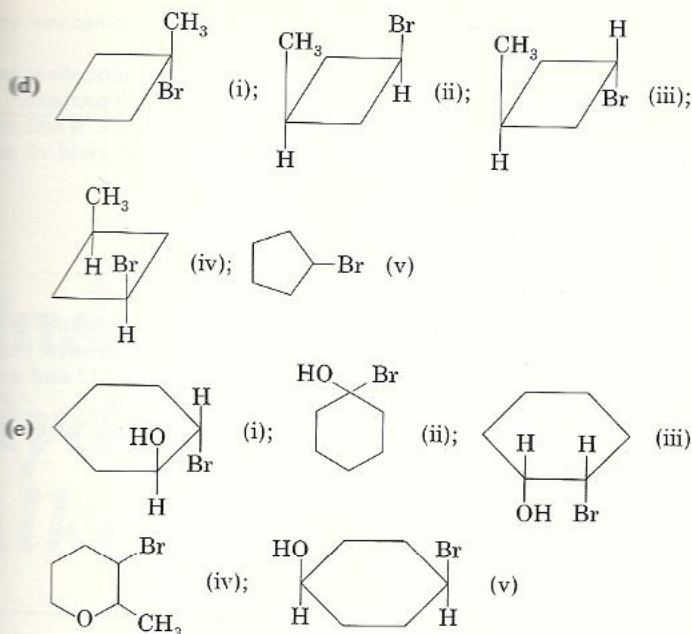
- 2.3 Write the structure for each of the incorrectly named compounds listed below. Explain why the given name is incorrect and give a correct name in each case.
- (a) 3-Methylbutane      (b) 2-Ethylpropane  
(c) 2,3-Dibromopropane      (d) *cis*-1,3-Dimethylcyclopropane  
(e) 3,4-Dichloropentane      (f) 1,1,3-Trimethylbutane  
(g) 2-Bromo-3-ethylbutane      (h) *trans*-1,6-Dimethylcyclohexane

**Structural Isomerism and Geometric Isomerism** [Secs. 2.3, 2.16]

- 2.4 Draw the indicated number of structural isomers of compounds for each molecular formula.
- (a)  $\text{C}_3\text{H}_7\text{Cl}$  (two isomers)      (b)  $\text{C}_2\text{H}_7\text{N}$  (two isomers)  
(c)  $\text{C}_3\text{H}_8\text{O}$  (three isomers)      (d)  $\text{C}_3\text{H}_9\text{N}$  (four isomers)  
(e)  $\text{C}_4\text{H}_9\text{Cl}$  (four isomers)      (f)  $\text{C}_3\text{H}_6\text{BrCl}$  (five isomers)
- 2.5 There are seven isomeric dibromocyclohexanes, including *cis-trans* isomers, having molecular formula  $\text{C}_6\text{H}_{10}\text{Br}_2$ . Draw the structures of the seven compounds, using condensed formulas for the rings.
- 2.6 For each group of structures, identify the structural isomers, the geometric isomers, and the structures that represent the same compound.







- 2.7 Four possible isomers can be obtained upon monochlorination of 2,2,4-trimethylpentane. Draw partially condensed formulas for each of these compounds and name each isomer according to the IUPAC system.

**Classes of Carbons and Hydrogens** [Sec. 2.4]

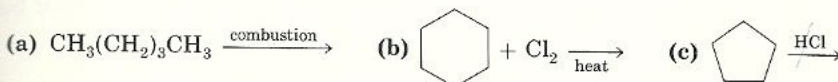
- 2.8 How many 1°, 2°, 3°, and 4° carbons and hydrogens (if any) are there in 2,2,4-trimethylpentane (the alkane with an octane rating of 100)?

**Physical Properties of Alkanes** [Sec. 2.8]

- 2.9 Without referring to tables, arrange each series of compounds in order of increasing boiling point.
- n*-Pentane; *n*-hexane, *n*-butane
  - n*-Hexane; *n*-pentane, 2-methylpentane
  - n*-Octane; 2,2,3-trimethylpentane, 2-methylheptane

**Reactions of Alkanes and Cycloalkanes** [Secs. 2.11–2.16]

- 2.10 Complete each of the following reactions by writing the structure of the product. If no reaction occurs, state so.



- 2.11 Draw structures for all possible monochlorinated and polychlorinated compounds that can be formed upon chlorination of ethane.
- 2.12 Bromination of ethane proceeds by the same mechanism as chlorination of ethane. Give the complete mechanism for the reaction, showing the initiation, propagation, and termination steps.
- 2.13 Isomeric compounds can sometimes be distinguished by observing the number of monochlorinated compounds that each one forms.
- If a compound forms three monochloro compounds, is it *n*-pentane or 2-methylbutane?

- (b) If a compound forms three monochloro compounds, is it *n*-hexane or 2,3-dimethylbutane?
- 2.14 Draw structures, including *cis-trans* isomers, for all possible monobrominated compounds that can be formed upon bromination of methylcyclopentane.
- 2.15 In the chlorination of ethane,  $C_2H_6$ , the product we want is  $C_2H_5Cl$ . Which one of the following experimental conditions is likely to give the best yield of monochlorinated product? Explain why.
- (a)  $C_2H_6 + Cl_2 \xrightarrow{\text{uv light}}$       (b)  $C_2H_6 + Cl_2 \xrightarrow{\text{dark, room temp}}$
- (c)  $C_2H_6 + Cl_2(\text{excess}) \xrightarrow{\text{uv light}}$       (d)  $C_2H_6(\text{excess}) + Cl_2 \xrightarrow{\text{uv light}}$
- 2.16 In the monochlorination of ethane, trace amounts of chlorinated butanes are also found, suggesting that at some point in the reaction *n*-butane was formed. Refer to the mechanism of free-radical halogenation of alkanes in Section 2.13 and explain how *n*-butane could be formed during the chlorination of ethane.
- 2.17 The heat of combustion of a straight-chain alkane is  $850 (\pm 5)$  kcal/mole. Which alkane has undergone complete combustion?



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# Unsaturated Hydrocarbons I: Alkenes

---

In Chapter 2 we discussed the chemistry of alkanes, the saturated hydrocarbons. Many hydrocarbons contain fewer hydrogens than do alkanes having the same number of carbon atoms. Because these compounds are deficient in hydrogen, we say that they are **unsaturated**. Unsaturated hydrocarbons *must* contain *multiple* bonds between carbon atoms. One family, distinguished by the presence of a carbon-carbon *double bond*, is called the **alkenes** or **olefins** and has the general formula  $C_nH_{2n}$ . A second class of compounds, the **alkynes**, is characterized by the presence of a carbon-carbon *triple bond*. The general formula of alkynes is  $C_nH_{2n-2}$ . **Dienes** are unsaturated hydrocarbons that contain *two* carbon-carbon double bonds. **Polyenes** are unsaturated hydrocarbons that contain more than two carbon-carbon double bonds.

This chapter treats the alkenes. The alkynes, dienes, and polyenes are discussed in Chapter 4.

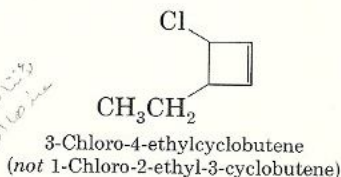
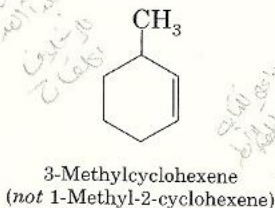
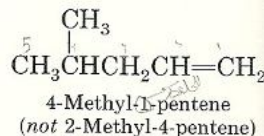
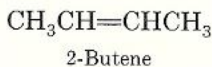
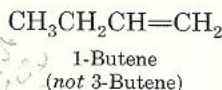
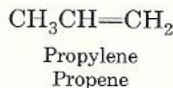
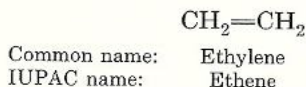
## Nomenclature of Alkenes 3.1

The simplest members of the alkene series ( $C_2$  and  $C_3$ ) are usually called by their common names, which are derived from the corresponding alkanes by replacing the *-ane* ending by *-ylene*. Larger alkenes are usually called by their IUPAC names. Except for a few additions, the IUPAC rules for naming alkenes

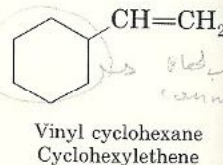
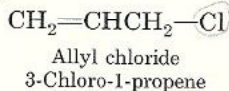
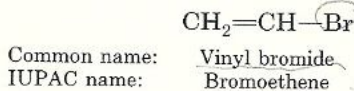
are similar to those used for naming alkanes. Briefly, the rules are

1. The longest continuous carbon chain containing the double bond is selected as the parent chain.
2. The name of the parent carbon chain is obtained by replacing the -ane ending of the corresponding alkane by -ene.
3. The parent carbon chain is numbered in a manner that will give the doubly bonded carbon atoms the lowest numbers even if it results in the substituents getting higher numbers.
4. The position of the double bond is indicated by the number of the lower-numbered doubly bonded carbon.
5. In cycloalkenes, the double bond is always found between carbon 1 and carbon 2. It is therefore not necessary to specify the position of the double bond with a number. If substituents are present, the ring must be numbered, starting from the double bond, in the direction that gives the substituents the lowest number(s).

Thus,



Compounds derived from ethylene and propylene are occasionally given special names. The  $\text{CH}_2=\text{CH}-$  group is called the **vinyl group**, and  $\text{CH}_2=\text{CHCH}_2-$  is called the **allyl group**.

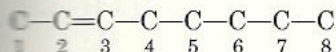


To reinforce the rules of nomenclature let us work out a simple example.

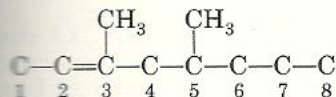
**Example 3.1** Write the structural formula of 3,5-dimethyl-4-isopropyl-2-octene.



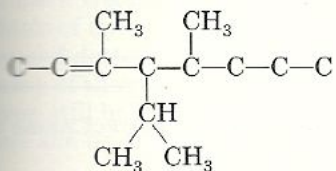
**Solution** (1) The parent carbon chain is an octene, and the double bond is located between the second and third carbons. Write the parent carbon chain without bothering yet with the hydrogen atoms.



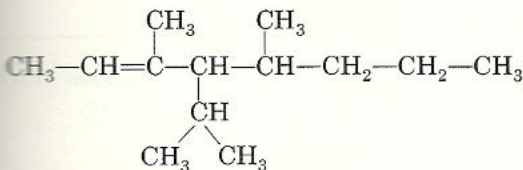
(2) Two methyl groups are attached on the parent carbon chain, one on carbon 3 and the other on carbon 5.



(3) An isopropyl group is attached on carbon 4.



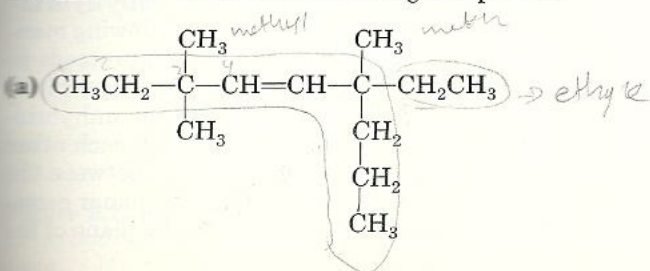
(4) Put in the missing hydrogens to get the correct structure.

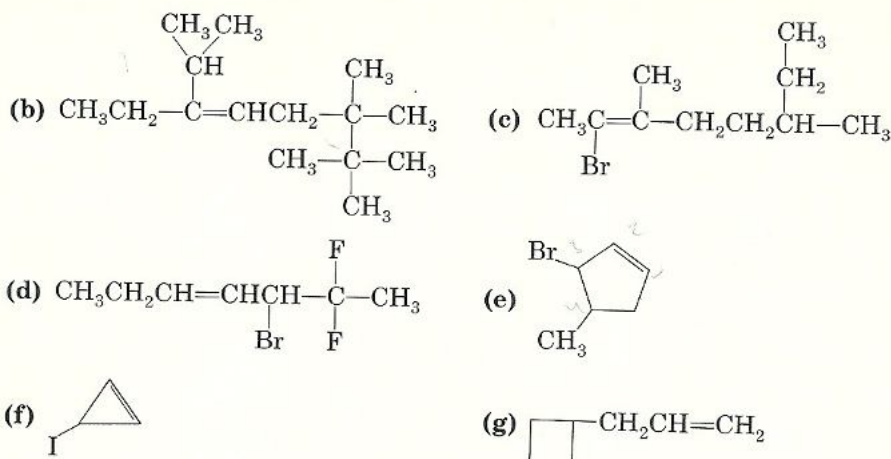


**Problem 3.1** Write the structural formulas for these compounds.

- 2-Methyl-2-butene
- 4,5-Dimethyl-3-isopropyl-2-hexene
- 2-Chloro-4-methyl-2-pentene
- 3-Bromo-2-chloro-3-methyl-1-pentene
- 1,3-Dimethylcyclohexene
- 1-Bromo-3-chlorocyclobutene

**Problem 3.2** Name the following compounds.





**Problem 3.3** The names in this list are incorrect. Give the correct name and structure for each compound listed.

- |                                 |                                       |
|---------------------------------|---------------------------------------|
| (a) 2,2-Dimethyl-4-pentene      | (b) 4,5-Dimethyl-2-isopropyl-2-hexene |
| (c) 4- <i>n</i> -Butyl-5-hexene | (d) 2-Chloro-6-methylcyclohexene      |
| (e) 1,2-Dimethyl-3-cyclopentene |                                       |

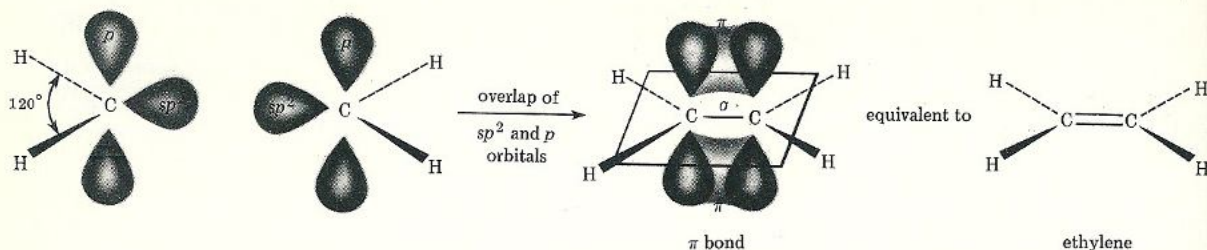
Now that we know how to recognize and name alkenes, let us look into how a carbon-carbon double bond is formed, and also into its geometry.

## 3.2 Geometry of the Carbon-Carbon Double Bond: *sp*<sup>2</sup> Hybridization

In alkanes carbon is always bonded to four atoms. As a consequence, the singly bonded carbon uses *sp*<sup>3</sup>-hybridized orbitals that are directed toward the corners of a regular tetrahedron. In alkenes, on the other hand, the doubly bonded carbon is always attached to only three other atoms. As a consequence, the doubly bonded carbon *must* use a different kind of hybridization and *must* assume a different shape. Let us look at the type of hybrid orbitals in and the shape of the simplest alkene, ethylene. In ethylene the carbons are *sp*<sup>2</sup> hybridized ( $\frac{1}{3}s$  and  $\frac{2}{3}p$  characteristics). These orbitals are formed in the following manner: As with *sp*<sup>3</sup> hybridization (Sec. 1.10), the ground-state carbon proceeds to its excited state, but this time the 2*s* orbital and only two of the three 2*p* orbitals hybridize. The result is three equivalent *sp*<sup>2</sup> hybrid orbitals and one unhybridized 2*p*<sub>z</sub> orbital (Fig. 3.1). The three *sp*<sup>2</sup> orbitals get as far away from each other as possible by assuming a *planar* arrangement with an angle of 120° between the hybrid orbitals. This type of arrangement is also known as trigonal planar geometry. The remaining unhybridized 2*p*<sub>z</sub> orbital is perpendicular to the plane of the *sp*<sup>2</sup> orbitals (Fig. 3.2).



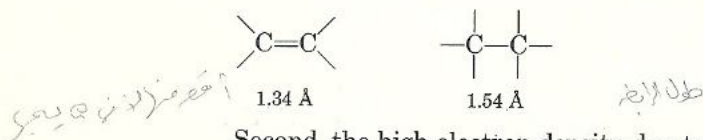




**Figure 3.3** End-on overlap of two  $sp^2$  orbitals to form a  $\sigma$  bond between the two carbons of ethylene and side-side overlap of the  $2p_z$  orbitals to form a  $\pi$  bond.

called *side-side* overlap. The bond formed in this sidewise overlap is called a  $\pi$  (**pi**) bond. Thus the two carbons of ethylene are attached together by an  $sp^2$ - $sp^2$   $\sigma$  bond and a  $\pi$  bond (from  $2p_z$ - $2p_z$  overlap) resulting in a carbon-carbon double bond ( $C=C$ ). The  $\pi$  bond, a weaker bond than the  $\sigma$  bond (65 kcal/mole vs 83 kcal/mole), is the one that breaks in the course of a chemical reaction. The formation of these bonds is illustrated in Figure 3.3.

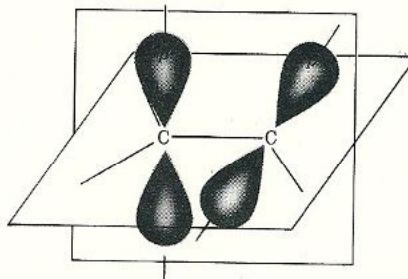
The carbon-carbon double bond, shown in Figure 3.3, accounts for several properties of alkenes. First, the carbon-carbon double bond is shorter by about 0.2 Å than the carbon-carbon single bond because two pairs of electrons pull the two nuclei closer together than does only one pair.



Second, the high electron density due to the pair of electrons in the  $\pi$  bond explains the reactivity of alkenes (Sec. 3.12).

Third, rotation about a carbon-carbon double bond is restricted because rotation of one carbon with respect to the other requires that the  $\pi$  bond be broken (see Fig. 3.4). Ordinarily this does not occur unless sufficient energy (about 65 kcal/mole) is supplied to the molecule in the form of heat or ultraviolet radiation.

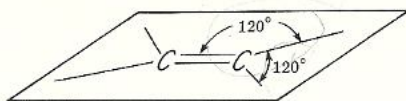
Fourth, restricted rotation about the carbon-carbon double bond requires



**Figure 3.4** Rotation of one carbon with respect to the other diminishes the overlap of their  $2p_z$  orbitals to the extent that if rotation is allowed to proceed to a full 90° the  $\pi$  bond would break.



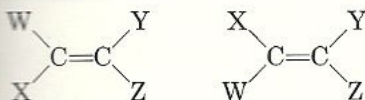
that the two carbon atoms and the four other atoms attached to them lie in the same plane.



Finally, the restricted rotation about the carbon-carbon double bond and the planar geometry that results from it give rise to a type of isomerism, geometric isomerism, which is discussed in the next section.

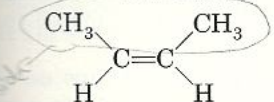
## Geometric Isomerism in Alkenes 3.3

Alkenes of the type  $WXC=CYZ$ , where W differs from X and Y from Z, can exist as **geometric isomers**. This type of isomerism was encountered earlier in connection with cycloalkanes (Sec. 2.16). In cycloalkanes geometric isomerism is due to restricted rotation about the carbon-carbon single bond in a ring. In alkenes geometric isomerism is due to hindered rotation about the carbon-carbon double bond.



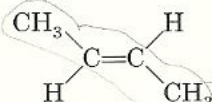
Geometric isomers

When two similar groups are on the same side of the double bond, the compound is called the *cis* isomer; when they are on the opposite sides of the double bond, the compound is called the *trans* isomer. For example,



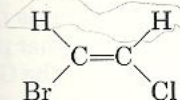
*cis*-2-Butene

(mp =  $-139^{\circ}\text{C}$ ; bp =  $3.7^{\circ}\text{C}$ )

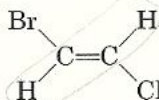


*trans*-2-Butene

(mp =  $-106^{\circ}\text{C}$ ; bp =  $0.9^{\circ}\text{C}$ )



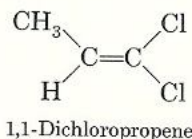
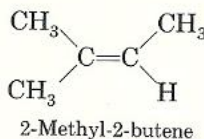
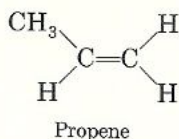
*cis*-1-Bromo-2-chloroethene



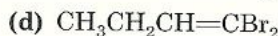
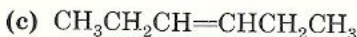
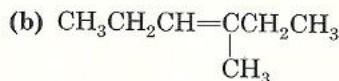
*trans*-1-Bromo-2-chloroethene

Geometric isomers differ from one another only in the way in which the substituents are arranged in space relative to the plane of the  $\text{C}=\text{C}$  bond. Since they can be interconverted only by the breaking and making of bonds, *cis* and *trans* isomers are stable molecules capable of independent existence. They have different physical properties and can be separated by fractional crystallization or distillation. Geometric isomers have similar chemical properties, since they are members of the same class of organic compounds. If two identical groups are attached to any one of the doubly bonded carbons ( $W = X$  or  $Y = Z$ ), geometric

isomerism is not possible. For example, the following compounds have no geometric isomers.



**Problem 3.4** Which of the following compounds can exist as *cis-trans* isomers? Draw the structures of the geometric isomers.



**Problem 3.5** Draw the structures of the following compounds.

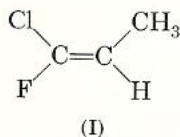
(a) *trans*-4-Octene

(b) *cis*-1,2-Dichloropropene

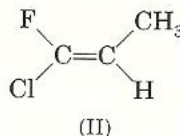
(c) *trans*-3-Methyl-2-pentene

(d) *cis*-3,4-Dibromocyclopentene

For alkenes with four different substituents such as



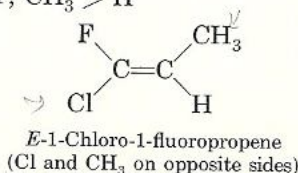
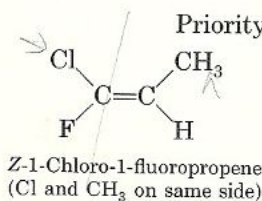
or



the terms *cis* and *trans* are ambiguous for distinguishing the two geometric isomers. As a result, another system, the *E,Z* system, has been devised to describe such compounds unambiguously.

Basically, the *E,Z* system works as follows. Arrange the groups on *each* carbon of the  $\text{C}=\text{C}$  bond in order of priority. The priority depends on atomic number: the higher the atomic number of the atom directly attached to the double-bonded carbon, the higher the priority.

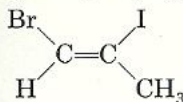
Thus, in structure (I), the priority at one end of the  $\text{C}=\text{C}$  bond is  $\text{Cl} > \text{F}$ , and at the other end the priority is  $\text{CH}_3 > \text{H}$ . If the two groups of higher priority are on the same side of the  $\text{C}=\text{C}$  plane, the isomer is labeled *Z* (from the German *zusammen*, together). If the two groups of higher priority are on opposite sides of the  $\text{C}=\text{C}$  plane, the isomer is labeled *E* (from the German *entgegen*, opposite). Thus, for I and II we have





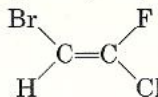
Further examples are

Priority: Br > H, I > CH<sub>3</sub>



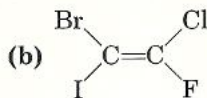
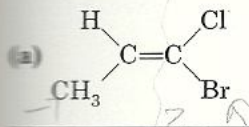
Z-1-Bromo-2-iodopropene

Priority: Br > H, Cl > F



E-1-Bromo-2-chloro-2-fluoroethene

**Problem 3.6** Name the following compounds using the *E,Z* nomenclature.



The *E,Z* system is less ambiguous and more versatile than the *cis-trans* system and is being used more and more in the literature. Nevertheless, *cis* and *trans* have been in common use for so many years that they are unlikely to disappear.

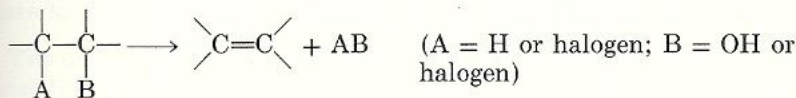
## Physical Properties of Alkenes 3.4

In general, the physical properties of alkenes are much the same as those of corresponding alkanes. At room temperature the C<sub>2</sub> to C<sub>4</sub> alkenes are gases; the C<sub>5</sub> to C<sub>18</sub> alkenes are liquids, and those above C<sub>18</sub> are solids.

Like alkanes, alkenes are insoluble in water and soluble in nonpolar organic solvents such as benzene or in carbon tetrachloride.

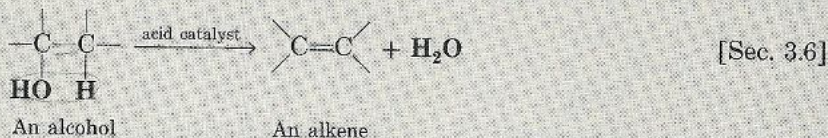
## Preparation of Alkenes 3.5

Alkenes are prepared in the laboratory by one of two general methods, each of which involves the **elimination** of an atom or group of atoms from adjacent carbons and the subsequent formation of a carbon-carbon double bond.

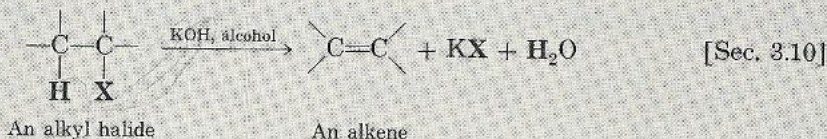


The two preparative methods are briefly illustrated here and discussed in greater detail in the sections that follow.

## 1. Dehydration of alcohols (ROH)

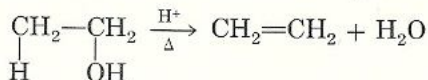


## 2. Dehydrohalogenation of alkyl halides (RX)

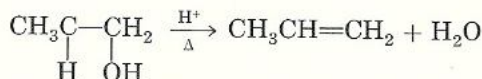


## 3.6 Dehydration of Alcohols

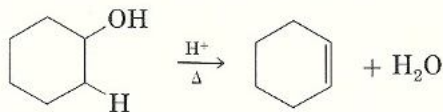
When an alcohol is heated in the presence of a mineral acid catalyst, it readily loses a molecule of water to give an alkene. The acid catalysts most commonly used are sulfuric acid,  $H_2SO_4$ , and phosphoric acid,  $H_3PO_4$ . In these equations  $H^+$  represents the acid catalyst and  $\Delta$  represents the heat applied.



IUPAC name: Ethanol                      Ethene  
Common name: Ethyl alcohol          Ethylene

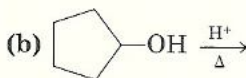
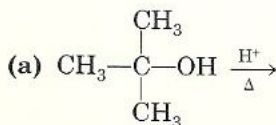


IUPAC name: 1-Propanol                      Propene  
Common name: *n*-Propyl alcohol          Propylene



IUPAC name: Cyclohexanol                      Cyclohexene  
Common name: Cyclohexyl alcohol

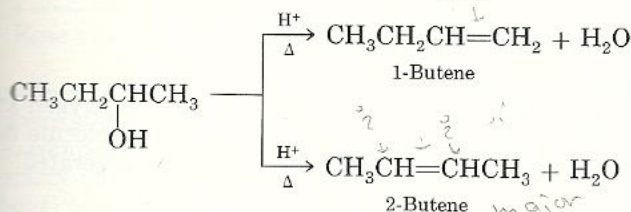
**Problem 3.7** Write the structure of the product of the dehydration of each of the following alcohols.





## Which Alkene Predominates? Saytzeff's Rule 3.7

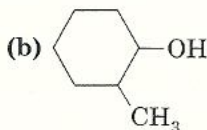
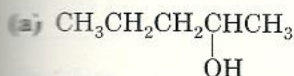
The examples of dehydration of alcohols discussed in the previous section produced a single alkene as the possible product. Suppose, however, that the loss of water from adjacent carbon atoms can give rise to more than one alkene, as in the dehydration of 2-butanol.



Which alkene predominates, 1-butene or 2-butene? A generalization known as **Saytzeff's rule** applies: *In every instance in which more than one alkene can be formed, the major product is always the alkene with the most alkyl substituents attached on the double-bonded carbons.*

Applying Saytzeff's rule to the dehydration of 2-butanol enables us to predict that 2-butene, with two alkyl substituents attached to  $\text{C}=\text{C}$ , is the **major** product, and 1-butene, with only one alkyl group, is the **minor** product. (Bear in mind that application of Saytzeff's rule requires you to count the number of alkyl groups bonded to  $\text{C}=\text{C}$ ; the size of the alkyl group is immaterial.)

**Problem 3.8** Give the major and minor products of the dehydration of



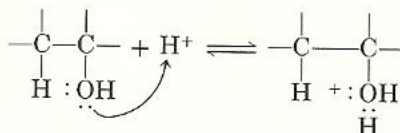
Now that you have seen examples of the dehydration of some specific alcohols, let us look into the mechanism of the reaction.

## Mechanism of Dehydration of Alcohols 3.8

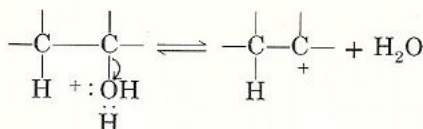
The dehydration of alcohols involves a **carbocation**, a reaction intermediate mentioned earlier in Section 2.10. A carbocation is a highly reactive, unstable intermediate in which the carbon carries a positive charge. Once formed, carbocations do not persist for any length of time. Their lack of stability causes them to quickly react further to form uncharged products. When the reaction is the dehydration of an alcohol, the uncharged product is an alkene.

The mechanism of dehydration basically involves the following steps.\*

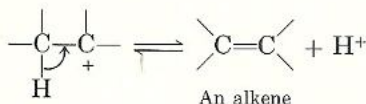
**Step 1.** Protonation of the alcohol: The proton of the acid catalyst is transferred to the oxygen atom, which functions as a Lewis base. This step is identical to the protonation of water to form hydronium ions.



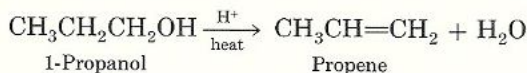
**Step 2.** Formation of a carbocation: The highly electronegative oxygen atom pulls electrons away from carbon, breaking the bond. A water molecule is released, and a carbocation with its positively charged carbon is generated.



**Step 3.** Loss of a proton from the carbocation regenerates the acid catalyst and simultaneously forms the alkene.



**Problem 3.9** Write the mechanism for the dehydration of 1-propanol to propene.

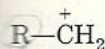


### 3.9 Classes of Carbocations and Ease of Dehydration of Alcohols

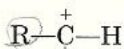
In the previous section it was established that the dehydration of alcohols involves a carbocation intermediate. Carbocations are classified as primary (1°), secondary (2°), or tertiary (3°) according to the number of carbon atoms attached to the positively charged carbon.

\*To be consistent with the convention adopted in Section 2.10, a curved double-headed arrow  $\curvearrowright$  is used to indicate the making or breaking of a bond involving a pair of electrons. In writing mechanisms that involve movements of a pair of electrons, the curved arrow *always* goes from the electron-rich to the electron-deficient atom.

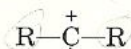




1° carbocation

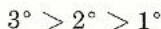


2° carbocation



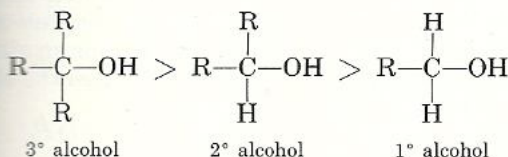
3° carbocation

The ease of formation and the stabilities of carbocations follow the order



Ease of formation and stabilities of carbocations

Thus, in a reaction that involves the formation of a carbocation intermediate, the more stable tertiary carbocation is the more easily formed. This means that when comparing the relative rates of dehydration among alcohols, we can expect a tertiary alcohol (one in which the C—OH group is directly attached to three carbons) to react faster than a secondary alcohol (one in which the C—OH is bonded to two carbons), and the latter faster than a primary alcohol (one in which the C—OH is attached to one carbon).



3° alcohol

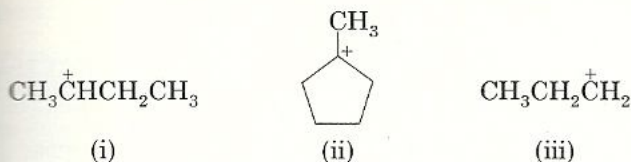
2° alcohol

1° alcohol

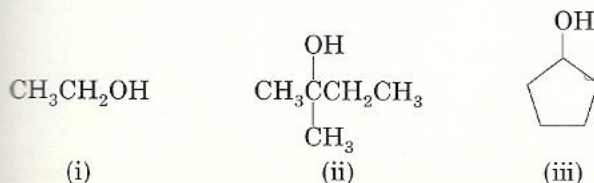
Ease of dehydration or rate of dehydration

The expectation is borne out by the fact that tertiary alcohols often undergo dehydration upon treatment with dilute acid at room temperature, whereas concentrated acid and elevated temperatures are usually required to convert primary alcohols into alkenes.

**Problem 3.10** Arrange these carbocations in order of increasing stabilities.



**Problem 3.11** Arrange these alcohols in order of ease of dehydration.

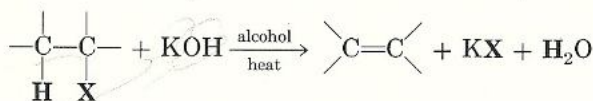


Before discussing the second method of preparing alkenes, let us summarize what you have learned thus far in the first method of preparation, the dehydration of alcohols.

1. The dehydration of alcohols requires an acid catalyst.
2. The predominant alkene formed follows Saytzeff's rule, which states that the major product is the alkene with the most alkyl substituents attached on the double-bonded carbons.
3. The reaction proceeds via a carbocation intermediate.
4. The stabilities of carbocations and the ease of dehydration of alcohols follows the order  $3^\circ > 2^\circ > 1^\circ$ .

### 3.10 Dehydrohalogenation of Alkyl Halides

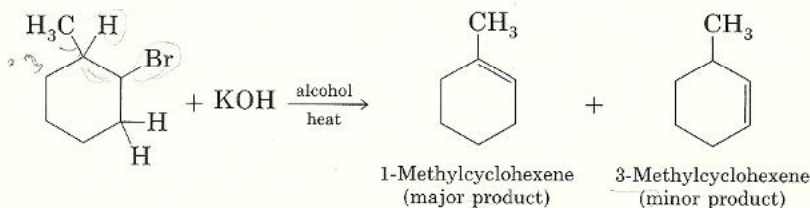
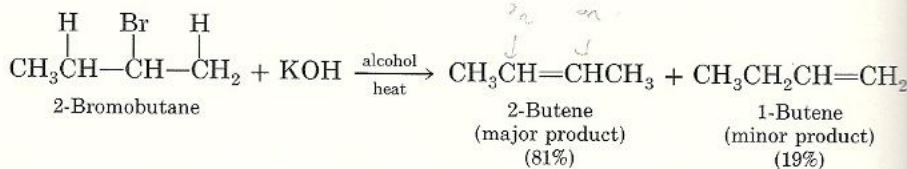
Alkenes can also be prepared under alkaline conditions, in which case an alkyl halide,  $RX$ , is required as the starting material. Thus, heating an alkyl halide with a solution of potassium hydroxide,  $KOH$ , in alcohol, yields an alkene. This reaction is known as **dehydrohalogenation** because it involves the elimination of  $H$  and of  $X$  from adjacent carbon atoms.



An alkyl halide

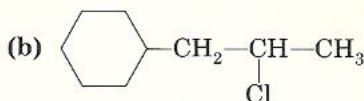
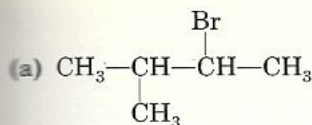
An alkene

As with the dehydration of an alcohol, the dehydrohalogenation of an alkyl halide may form more than one alkene. In such case Saytzeff's rule again applies; that is, the alkene with the most alkyl substituents on the double-bonded carbons predominates. For example,



**Problem 3.12** Give the structure of the major and minor products of the dehydrohalogenation of





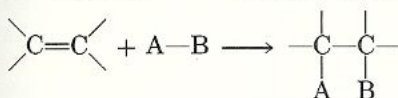
The mechanisms of dehydrohalogenation depend on the type of alkyl halide used (whether 1°, 2°, or 3° alkyl halide). They are discussed in Chapter 8.

## Reactions of Alkenes 3.11

All alkenes contain a carbon-carbon double bond, and all except ethylene also contain a saturated alkyl chain as part of the molecule. The chemistry of alkenes can therefore be divided into two general types of reactions: (1) addition reactions that involve the carbon-carbon double bond and (2) substitution reactions that usually involve the saturated alkyl chain. Let us first examine the various kinds of addition reactions.

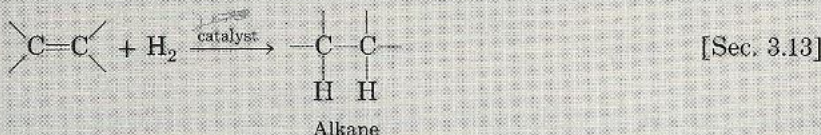
## Additions to the Carbon-Carbon Double Bond 3.12

The typical reaction of alkenes is addition to the C=C group. An addition reaction is one in which a reagent, A—B, adds across the double bond to give a saturated product that contains all the atoms of both reactants.

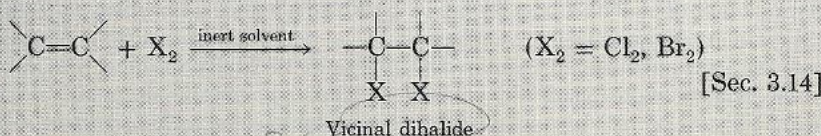


The addition reactions we will encounter in this chapter are summarized as follows.

### 1. Addition of hydrogen: catalytic hydrogenation

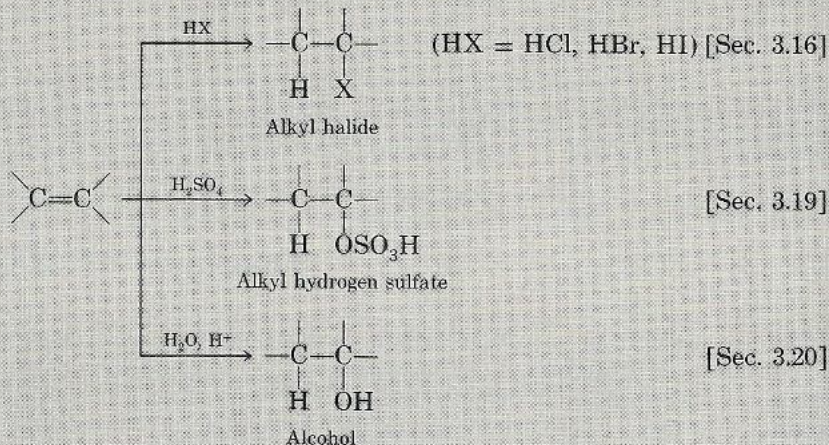


### 2. Addition of halogens: halogenation

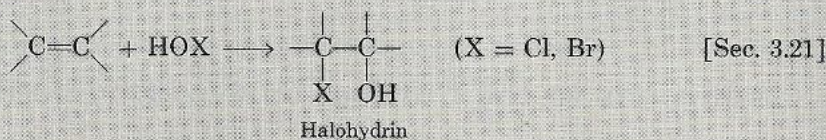




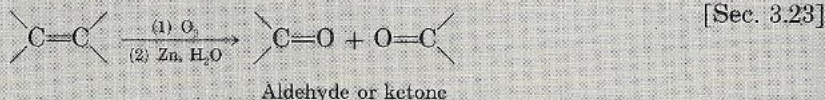
## 3. Electrophilic addition to alkenes: addition of acids (H—A)



## 4. Addition of HOX: halohydrin formation



## 5. Ozonolysis



## 6. Polymerization (addition of &gt;C=C&lt; to another &gt;C=C&lt;)

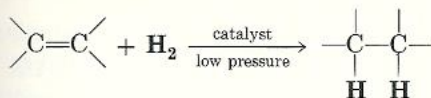


## 3.13 Addition of Hydrogen: Catalytic Hydrogenation

The carbon-carbon double bond of alkenes can add a mole of hydrogen in the presence of suitable catalysts to give an alkane. This method, called the **catalytic hydrogenation** of alkenes, is carried out as follows. The alkene is dissolved in a suitable solvent in the presence of finely divided platinum (Pt), nickel (Ni), or palladium (Pd) catalyst. Hydrogen gas is then bubbled at low pressure into the reaction vessel with constant stirring. The yield of alkane by this method is quite good.



## General equation

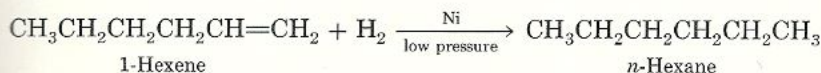
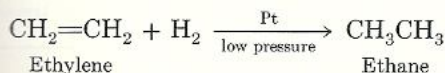


An alkene

An alkane

## 3.14 Addition of Halogens: Halogenation

## Specific examples

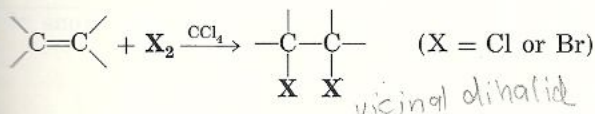


Hydrogenation has important industrial applications in the manufacture of high-octane automobile and aviation fuels and in the preparation of synthetic detergents. The reaction can also be used to analyze the extent of unsaturation in a molecule.

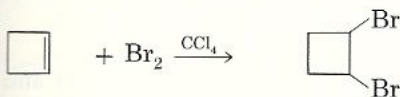
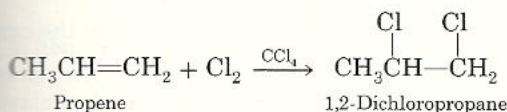
## Addition of Halogens: Halogenation 3.14

When an alkene is treated at room temperature with a solution of bromine or chlorine in carbon tetrachloride or some other inert solvent, the halogen adds rapidly to the double bond of the alkene to give the corresponding vicinal dihalide (two halogens attached to adjacent carbons).

## General equation



## Specific examples



Cyclobutene

1,2-Dibromocyclobutane

Iodine is too unreactive and will not add to the double bond of an alkene. Fluorine is too reactive and reacts explosively with an alkene, making it an unsuitable reactant.

The addition of bromine to an alkene is useful as a practical test for detecting unsaturation (see Sec. 3.22).

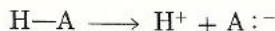
The addition of halogens to an alkene proceeds by a mechanism similar to (but somewhat more complicated than) the addition of acids discussed in the next sections.

**Problem 3.13** Write the structure of the product expected from the reaction at room temperature of (a) 2-butene with  $\text{Br}_2$  in  $\text{CCl}_4$  and (b) cyclohexene with  $\text{Cl}_2$  in  $\text{CCl}_4$ .

## 3.15 Electrophilic Addition to Alkenes: Addition of Acids

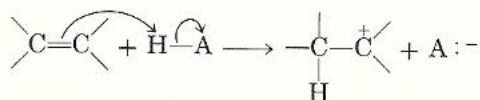
The next few reactions of alkenes to be discussed involve the addition to the double bond of reagents whose general formulas are represented by the symbol  $\text{H}-\text{A}$ . These may be hydrogen halides ( $\text{H}-\text{Cl}$ ,  $\text{H}-\text{Br}$ ,  $\text{H}-\text{I}$ ), sulfuric acid ( $\text{H}-\text{OSO}_3\text{H}$ ), or water ( $\text{H}-\text{OH}$ ). The addition of all these reagents to the double bond follows the same mechanism. For this reason, the general mechanism of their addition will be discussed before their specific reactions are given.

Hydrogen halides, sulfuric acid, and water all contain an ionizable hydrogen.

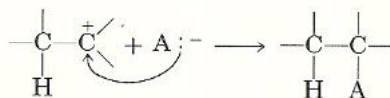


The positively charged hydrogen ion is an electron-deficient species. Any electron-deficient species is called an **electrophile**, and any electron-rich species is called a **nucleophile**. The addition of  $\text{H}-\text{A}$  to an alkene is believed to be a two-step process.

**Step 1.** The hydrogen ion (the electrophile) attacks the  $\pi$  electrons of the alkene, forming a  $\text{C}-\text{H}$  bond and a carbocation.



**Step 2.** The negatively charged species  $\text{A}^-$  (a nucleophile) attacks the carbocation and forms a new  $\text{C}-\text{A}$  bond.



The formation of the carbocation in step 1 is the more difficult and consequently the slower step in the mechanism. The slowest step in any reaction mechanism is called the **rate-determining step**. The type of reaction just described, which involves the attack by an electrophilic reagent on the  $\pi$  electrons, falls in a general category called **electrophilic addition reactions**.

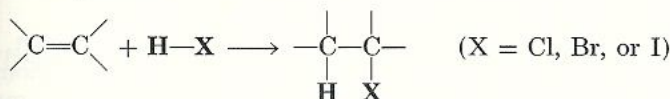
Now that you have seen the general mechanism of electrophilic addition, some specific examples will be discussed.



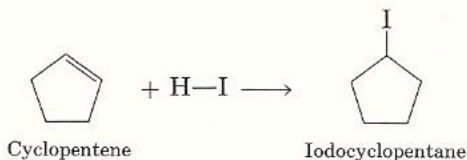
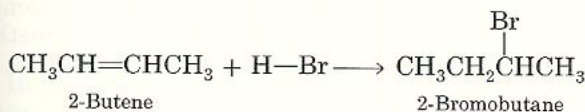
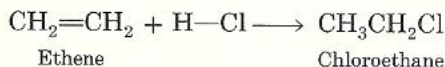
## Addition of Hydrogen Halides 3.16

Alkenes react with hydrogen chloride, HCl, hydrogen bromide, HBr, and hydrogen iodide, HI, to form alkyl halides, RX. This reaction is also known as **hydrohalogenation** (in contrast to dehydrohalogenation) because H and X are added to the double-bonded carbons.

*General equation*



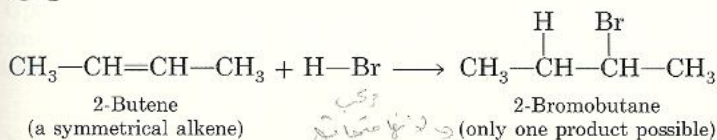
*Specific examples*



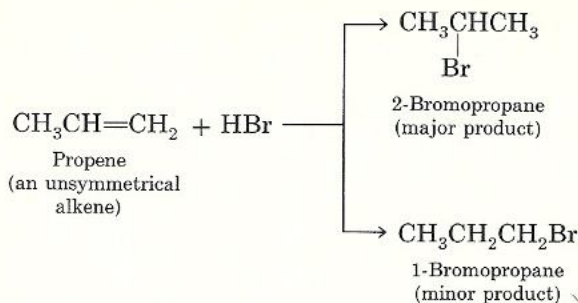
**Problem 3.14** Write the mechanism of the addition of HCl to ethene.

## Markovnikov's Rule 3.17

When hydrogen halide is added to a symmetrical alkene such as  $\text{RCH}=\text{CHR}$ , there is only one possible product because the two double-bonded carbons are equivalent. This is illustrated by the reaction of 2-butene with HBr.

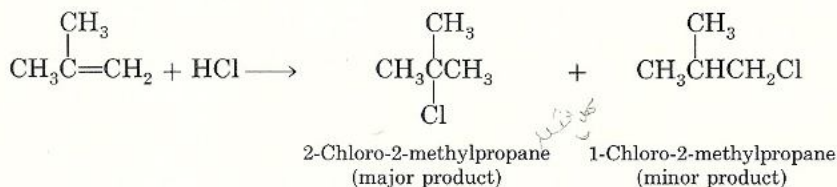


With unsymmetrical alkenes, however, such as those of the type  $\text{RCH}=\text{CHR}'$  ( $\text{R}' \neq \text{R}$ ), the possibility exists for the hydrogen halide to add in two ways and thus give two isomeric products. The addition of HBr to propene, for example, could yield 1-bromopropane, 2-bromopropane, or both.

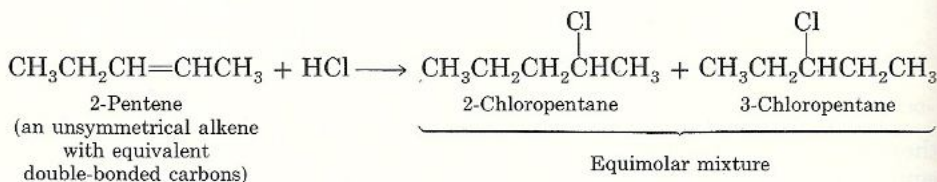


Statistically, the two products should be formed in equal amounts. In fact, the major product is 2-bromopropane. Based on the results of many observations of alkene reactions, the Russian chemist Vladimir Markovnikov in 1869 summarized his findings in a statement now known as **Markovnikov's rule**: *In electrophilic addition of H—X to unsymmetrical alkenes the hydrogen of the hydrogen halide adds to the double-bonded carbon that bears the greater number of hydrogen atoms and the negative halide ion adds to the other double-bonded carbon.*

According to this rule, the addition of HCl to 2-methylpropene, for example, yields 2-chloro-2-methylpropane as the major product and 1-chloro-2-methylpropane as the minor product.



In some unsymmetrical alkenes the two double-bonded carbons may be equivalent (may contain the same number of hydrogen atoms), but the addition of H—X still gives two possible products. In such cases an approximately equimolar mixture of the two possible addition products is obtained. For example, the addition of HCl to 2-pentene yields an equal mixture of 2-chloropentane and 3-chloropentane.



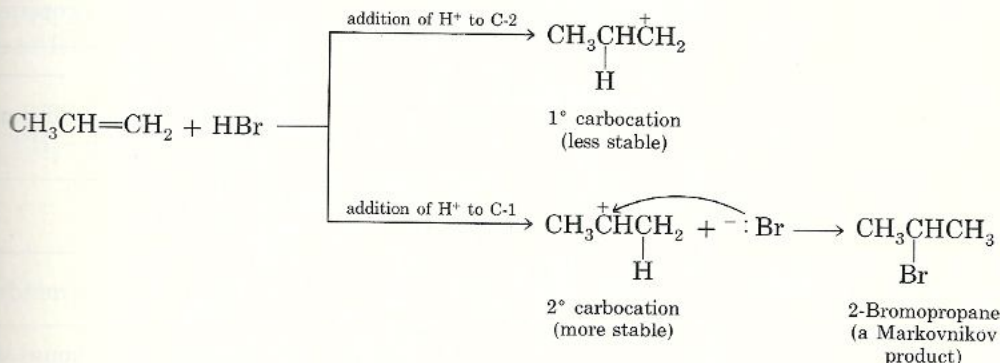
### 3.18 Explanation for Markovnikov's Rule

The explanation for Markovnikov's rule may be given in light of the general mechanism of electrophilic addition. The addition of HX to an alkene involves the formation of a carbocation intermediate. We should expect the more stable



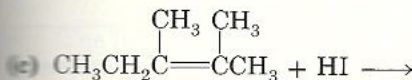
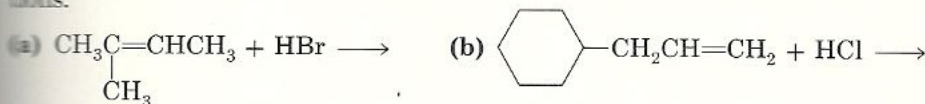
carbocation to be preferentially formed. Recall from Section 3.9 that the stability of a carbocation follows the order  $3^\circ > 2^\circ > 1^\circ$ .

Returning to the previous example of the addition of HBr to propene, we can see that two different carbocation intermediates are possible. The formation of each depends on which double-bonded carbon the hydrogen ion of HBr adds to. Addition of the hydrogen to C-2 gives a primary carbocation, and addition at C-1 gives the more stable secondary carbocation.



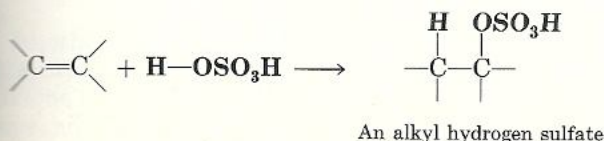
In modern terms Markovnikov's rule can be restated: *The addition of an unsymmetrical reagent HX to an unsymmetrical alkene proceeds in such a direction as to produce the more stable carbocation.*

**Problem 3.15** Write the structures of the major products of the following reactions.

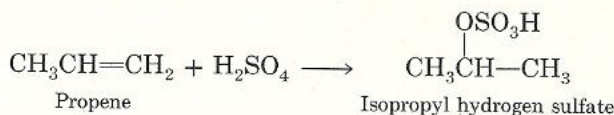


## Addition of Sulfuric Acid 3.19

Upon thorough mixing, cold concentrated sulfuric acid adds across the double bond of alkenes to give alkyl hydrogen sulfate. The general equation for this reaction is



Addition of sulfuric acid to alkenes also follows Markovnikov's rule, as illustrated in the reaction with propene.



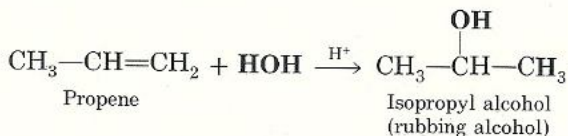
**Problem 3.16** Write the mechanism of the addition of  $\text{H}_2\text{SO}_4$  to propene.

**Problem 3.17** Write the structure of the major product of the addition of  $\text{H}_2\text{SO}_4$  to (a) 1-butene; (b) 2-butene; and (c) 1-methylcyclohexene.

### 3.20 Addition of Water: Hydration

When heated with water in the presence of an acid catalyst, alkenes yield alcohols (ROH). The process is called **hydration** of alkenes because it involves the addition of water across the double bond.

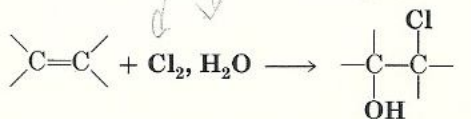
The addition of HOH across the double bond is in accordance with Markovnikov's rule: The hydrogen goes to the double-bonded carbon that bears the greater number of hydrogen atoms and the hydroxyl group goes to the other double-bonded carbon.



**Problem 3.18** Write the structure of the major product of the hydration of (a) ethylene; (b) 1-butene; and (c) 1-methylcyclopentene.

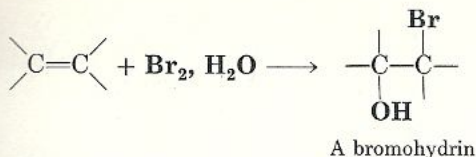
### 3.21 Addition of HOX: Halohydrin Formation

When an alkene is treated with aqueous chlorine or aqueous bromine, the addition product is a **halohydrin**. (When  $\text{Cl}_2$  is used, the product is a chlorohydrin; when  $\text{Br}_2$  is used, the product is a bromohydrin.)

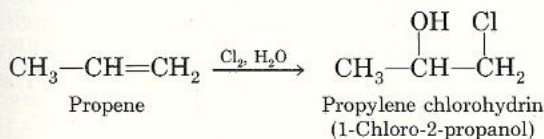


A chlorohydrin





The reaction proceeds as if hypochlorous acid,  $\text{HO}-\text{Cl}$ , or hypobromous acid,  $\text{HO}-\text{Br}$ , were the adding reagent. The chloronium ion,  $\text{Cl}^+$ , or bromonium ion,  $\text{Br}^+$ , is the electrophile, and the hydroxide ion,  $\text{OH}^-$ , the nucleophile. Addition of  $\text{HOX}$  also follows Markovnikov's rule, as illustrated with propene.

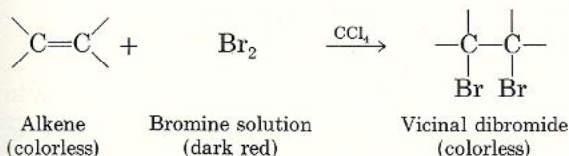


**Problem 3.19** Write the mechanism for the addition of  $\text{HOCl}$  to propene.

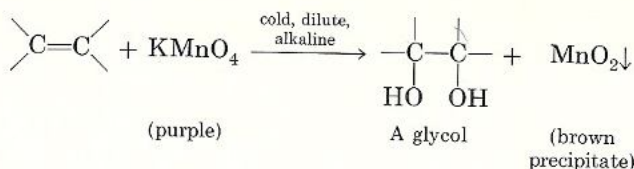
**Problem 3.20** Write the structure of the major product expected on reaction of (a) ethylene with aqueous chlorine; (b) 1-butene with aqueous chlorine; (c) 2-methylpropene with aqueous bromine; and (d) 1-methylcyclopentene with aqueous bromine.

## Visual Tests for Unsaturation 3.22

The functional group of alkenes is the  $\text{C}=\text{C}$  bond. What simple visual test can we use to detect unsaturation? Of the reactions discussed so far the addition of bromine is frequently used. Bromine itself is a dark red liquid, whereas both the alkene and the addition product are colorless. Thus, to test whether a substance is an alkene, we add to it a solution of bromine in an inert solvent ( $\text{CCl}_4$ ). If the substance is an alkene (or an alkyne), the bromine solution will be rapidly decolorized.



Another visual test for unsaturation is the **Baeyer test**. In this test, a dilute, alkaline solution of purple potassium permanganate,  $\text{KMnO}_4$ , is added to an alkene (or alkyne) at room temperature. A *glycol*, a compound with two  $\text{OH}$  groups, and a brown precipitate of manganese dioxide,  $\text{MnO}_2$ , are formed.



Replacement of a purple-colored solution by a brown precipitate indicates positive Baeyer test.

The addition of  $\text{H}_2\text{SO}_4$  to alkenes (or alkynes) is yet another visual test for unsaturation. Alkenes will dissolve in concentrated  $\text{H}_2\text{SO}_4$ , with evolution of heat and form homogeneous mixtures. Alkanes do not react with concentrated  $\text{H}_2\text{SO}_4$  and will separate from the acid; two distinct layers form. *A word of caution:* Other types of compounds also react with and dissolve in  $\text{H}_2\text{SO}_4$  (or oxygen-containing compounds, many nitrogen-containing compounds, and some aromatic compounds).

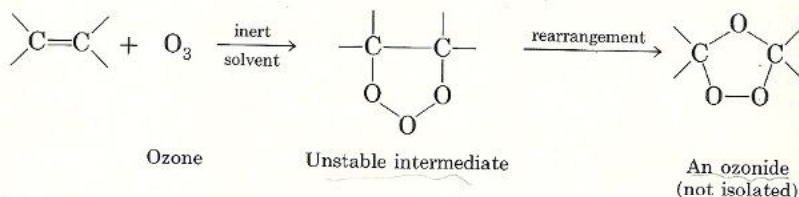
**Problem 3.21** Compound A,  $\text{C}_6\text{H}_{12}$ , gave the following results.

- (1)  $\text{A} + \text{Br}_2 \xrightarrow{\text{CCl}_4}$  solution remains dark red
- (2)  $\text{A} + \text{cold, concentrated } \text{H}_2\text{SO}_4 \longrightarrow$  two distinct layers
- (3)  $\text{A} + \text{dilute } \text{KMnO}_4 \longrightarrow$  solution remains purple
- (4)  $\text{A} + \text{Br}_2 \xrightarrow{\text{heat}} \text{C}_6\text{H}_{11}\text{Br}$  (a single isomer)

What is the structure of A?

## 3.23 Ozonolysis

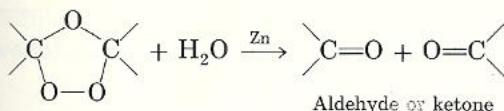
When ozone-rich oxygen gas is passed through a solution of an alkene dissolved in an inert solvent, the carbon-carbon double bond is broken and an ozonide is produced. Ozonides, like other compounds containing the peroxid group,  $-\text{O}-\text{O}-$ , are quite unstable and may explode violently and unpredictably. Consequently, they are not isolated.



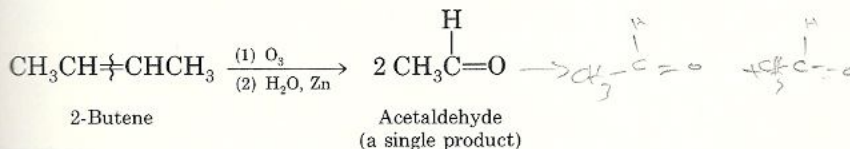
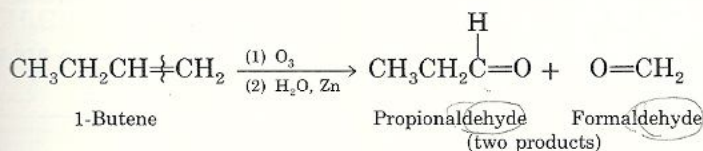
Further addition of water in the presence of a zinc catalyst results in the formation of two smaller products, each of which contains a carbonyl group  $\text{C}=\text{O}$ , at the position where the carbon-carbon double bond was. These products

may be aldehydes,  $\text{R}-\overset{\text{H}}{\text{C}}=\text{O}$ , or ketones,  $\text{R}-\overset{\text{R}}{\text{C}}=\text{O}$ , depending on the structure of the starting alkene.





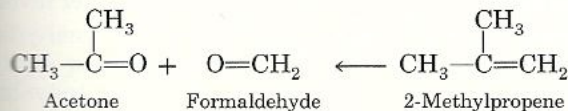
Ozonolysis is a valuable degradative reaction, for it can be used to locate the position of a double bond on the parent alkene chain. This is done by identifying the structure(s) of the product(s) obtained on treatment of an alkene with ozone. For example, suppose we wanted to know whether a given compound is 1-butene or its isomer, 2-butene. Both compounds have the same molecular formula,  $\text{C}_4\text{H}_8$ ; both decolorize bromine in carbon tetrachloride; and both give a positive Baeyer test. One way we can distinguish between them is by ozonolysis, because they both yield different identifiable products. The ozonolysis of 1-butene yields formaldehyde,  $\text{H}_2\text{C}=\text{O}$ , and propionaldehyde,  $\text{CH}_3\text{CH}_2\text{CH}=\text{O}$ , whereas the ozonolysis of 2-butene yields only one product, acetaldehyde,  $\text{CH}_3\text{CH}=\text{O}$ .



To be sure that you understand the value of ozonolysis in determining the structure of an alkene, you should work through Example 3.2.

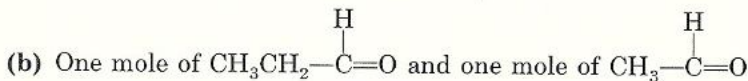
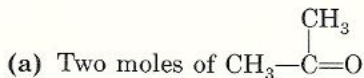
**Example 3.2** The products of the ozonolysis of an alkene were identified as acetone,  $(\text{CH}_3)_2\text{C}=\text{O}$ , and formaldehyde,  $\text{CH}_2=\text{O}$ . What is the structure of the parent alkene?

**Solution** If you recall, the carbonyl carbons were originally double-bonded carbons. The structure of the parent alkene can therefore be determined by eliminating the oxygen atoms from the two carbonyl carbons and joining them by a double bond. Thus, the parent alkene is 2-methylpropene.



**Problem 3.22** Write the structure of the product expected from the ozonolysis of (a) 2-methyl-2-pentene; (b) cyclopentene; and (c) 2-hexene.

**Problem 3.23** Write the structure of the parent alkene given the following products of ozonolysis.



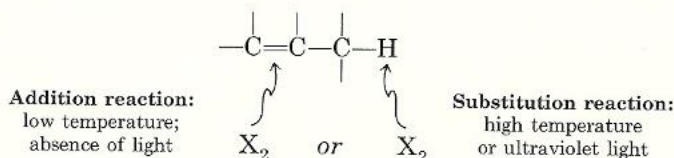
**Problem 3.24** Compound B,  $\text{C}_6\text{H}_{12}$ , gave the following results.

- (1)  $\text{B} + \text{Br}_2 \xrightarrow{\text{CCl}_4}$  colorless solution
- (2)  $\text{B} + \text{dilute KMnO}_4 \longrightarrow$  brown precipitate
- (3)  $\text{B} + \text{O}_3$  followed by treatment with  $\text{Zn}$ ,  $\text{H}_2\text{O}$  yielded  $\text{CH}_3\text{CH}_2\text{CHO}$  as the only product.

What are the two possible structures for B? (*Hint: The two structures are geometric isomers.*)

## 3.24 Substitution Reactions: Halogenation at High Temperatures

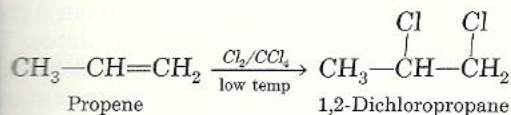
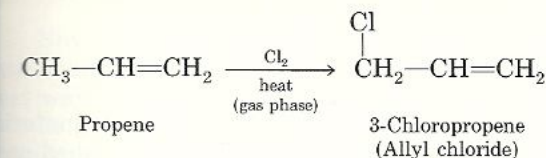
So far discussion has focused on addition reactions that take place exclusively at the carbon-carbon double bond. With the exception of ethylene, all alkenes contain saturated alkyl groups as part of their structures. What kind of reactions can we expect to occur there? Since these alkyl groups are saturated, we can expect them to undergo the typical alkane reaction, which is free-radical substitution. Let us use halogenation as an example of a substitution reaction. We already know that halogen can attack the double bond as well as the saturated alkyl site (Sec. 2.12). Can we control the experimental conditions so that the halogen attacks only one of these sites? The answer is yes. Alkenes are more reactive than alkanes. Their reactions therefore take place under milder experimental conditions. Alkenes undergo addition of halogen at low temperature, even in the dark, and generally in the liquid phase. On the other hand, alkanes undergo substitution by halogen only at elevated temperatures or under the influence of ultraviolet light (Sec. 2.12) and generally in the gas phase. The latter conditions favor a free-radical substitution reaction, whereas the former favor an addition reaction.



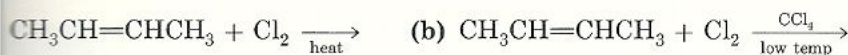
For example, the treatment of propene with chlorine at high temperatures yields chiefly the substitution product 3-chloropropene (allyl chloride). Reaction



chlorine with propene in the liquid phase at low temperature, in the dark, yields only 1,2-dichloropropane, an addition product.

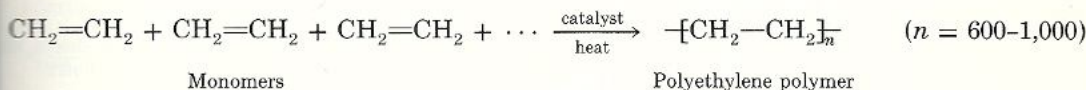


**Problem 3.25** Write the structure of the major product expected in each reaction.



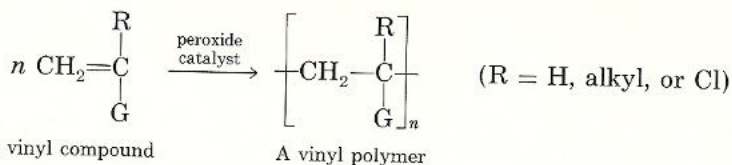
## Polymerization 3.25

One important property of alkenes is their ability to form giant molecules called **polymers**. Polymers are prepared by the polymerization process, which involves the reaction of alkene units with themselves (from the Greek *poly*, many; *meros*, unit). The basic alkene unit is referred to as a **monomer**. Under the influence of various catalysts alkene monomers add to one another indefinitely in a process called **addition polymerization**. Alkene polymers form useful products such as plastics and rubber. For example, the polymerization of ethylene, which takes place when ethylene is heated in the presence of a suitable catalyst, produces a waxy polymer called polyethylene. The overall reaction




Polyethylene is widely used for the manufacture of plastic bottles, wire insulation, toys, packaging, and wearing apparel. Ethylene is one of the most important alkenes produced in the United States. In 1980 the United States production of ethylene was 28.3 billion pounds.

The substitution of one of the hydrogens of ethylene by some other group produces a vinyl compound ( $\text{CH}_2=\text{CH—}$ , a vinyl group;  $\text{CH}_2=\text{CH—G}$ , a vinyl compound). These polymerize in much the same manner as ethylene, and produce **vinyl polymers**. The general equation for the polymerization of vinyl compounds is



Vinyl polymers are important because they constitute the raw materials used by the plastics industry for the manufacture of many useful finished products. For example, the polymerization of vinyl chloride produces polyvinyl chloride, which is used as a rubber substitute, for pipes, and as an insulator. The polymerization of tetrafluoroethylene produces the tough plastic known as Teflon. Teflon is a chemically inert substance widely used in insulation materials and as a coating in "nonstick" cooking utensils. Table 3.1 lists some important vinyl polymers and their uses in the plastic industry.

Table 3.1 Some Important Vinyl Polymers and Their Uses in the Plastics Industry

R	G	Monomer	Polymer	Name	Uses
-H	-Cl	$\text{CH}_2=\overset{\text{H}}{\underset{\text{Cl}}{\text{C}}}$	$\left[ \text{CH}_2-\overset{\text{H}}{\underset{\text{Cl}}{\text{C}}} \right]_n$	polyvinyl chloride	electrical insulators; pipes
-H	-C≡N	$\text{CH}_2=\overset{\text{H}}{\underset{\text{C}\equiv\text{N}}{\text{C}}}$	$\left[ \text{CH}_2-\overset{\text{H}}{\underset{\text{C}\equiv\text{N}}{\text{C}}} \right]_n$	polyacrylonitrile (Orlon)	fibers for clothing
-H		$\text{CH}_2=\overset{\text{H}}{\underset{\text{C}_6\text{H}_5}{\text{C}}}$	$\left[ \text{CH}_2-\overset{\text{H}}{\underset{\text{C}_6\text{H}_5}{\text{C}}} \right]_n$	polystyrene	electrical insulators; foamed plastic fabrication
-H	$-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	$\text{CH}_2=\overset{\text{H}}{\underset{\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3}{\text{C}}}$	$\left[ \text{CH}_2-\overset{\text{H}}{\underset{\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3}{\text{C}}} \right]_n$	polyvinyl acetate	plastic sheets, films, and fibers
-Cl	-Cl	$\text{CH}_2=\overset{\text{Cl}}{\underset{\text{Cl}}{\text{C}}}$	$\left[ \text{CH}_2-\overset{\text{Cl}}{\underset{\text{Cl}}{\text{C}}} \right]_n$	polyvinylidene chloride (Saran)	seat covers; self- adhering food wrappers
-CH <sub>3</sub>	$-\overset{\text{O}}{\parallel}{\text{C}}-\text{OCH}_3$	$\text{CH}_2=\overset{\text{CH}_3}{\underset{\text{C}=\text{O}-\text{OCH}_3}{\text{C}}}$	$\left[ \text{CH}_2-\overset{\text{CH}_3}{\underset{\text{C}=\text{O}-\text{OCH}_3}{\text{C}}} \right]_n$	polymethyl methacrylate (Plexiglas; Lucite)	transparent sheets; unbreakable substitute for glass; paints



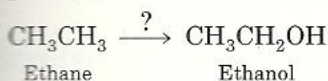
## Planning a Synthesis 3.26

Now that you have learned the chemistry of alkanes and alkenes, let us see how that knowledge can be put to practice in synthesizing a compound in the best way possible.

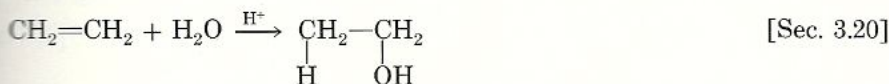
In general, the best approach to a problem involving the synthesis of a compound is working *backward*, that is, from the product to the starting material. To illustrate, let us work out the following example.

**Example 3.3** Suppose you wish to prepare ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ , starting from ethane. (You may use any inorganic reagent and any reaction conditions).

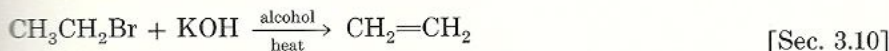
**Solution** First draw the structures of the starting material and of the product.



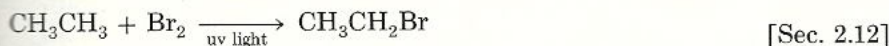
Working backward, ethanol can be obtained via hydration of an alkene, ethylene.



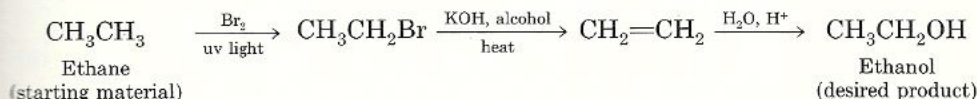
Ethylene, in turn, can be obtained via dehydrohalogenation of an ethyl halide, for example, bromoethane.



Bromoethane, in turn, is obtained from ethane via free-radical bromination.



The overall series of reactions is therefore



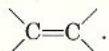
Now work out the following synthesis problem.

### Problem 3.26

Starting from	Synthesize
(a) $\text{CH}_3\text{CH}_2\text{OH}$	$\text{CH}_3\text{CH}_3$
(b) $\text{CH}_3\text{CH}_2\text{Br}$	$\text{HOCH}_2\text{CH}_2\text{Cl}$
(c) $\text{CH}_3\text{CH}_2\text{Cl}$	$\text{HOCH}_2\text{CH}_2\text{OH}$
(d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	$\text{CH}_3\text{CHBrCH}_3$
(e) $\text{CH}_3\text{CH}=\text{CH}_2$	$\text{BrCH}_2\text{CHBrCH}_2\text{Br}$
(Hint: First do a reaction at the saturated carbon.)	

## Summary of Concepts and Reactions

Alkenes are unsaturated hydrocarbons that contain a carbon-carbon double bond,



[Sec. 3.1]

Alkenes are named in the IUPAC system by replacement of the ending -ane of alkanes by -ene. The position of the double bond is indicated by the lowest possible number.

[Sec. 3.1]

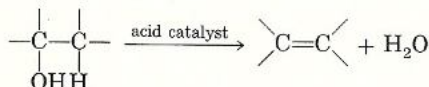
The groups attached to the  $sp^2$ -hybridized carbons in an alkene lie in the same plane.

[Sec. 3.2]

Because of the lack of rotation about the carbon-carbon double bond, geometric isomers can exist when different groups are attached to both carbons.

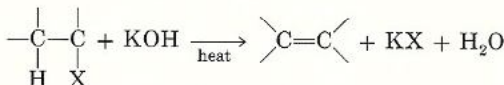
[Sec. 3.3]

Alkenes may be prepared by the dehydration of alcohols



[Sec. 3.6]

or by the dehydrohalogenation of alkyl halides

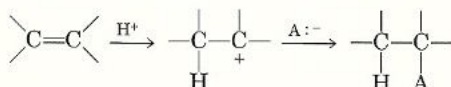


[Sec. 3.10]

The typical reaction of alkenes is addition to  $\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \end{array}$ .

[Sec. 3.12]

Most reactions of alkenes are electrophilic additions

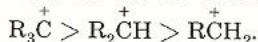


[Sec. 3.15]

All additions of H—A to unsymmetrical alkenes follow Markovnikov's rule.

[Sec. 3.17]

Addition of H—A involves the formation of the most stable carbocation;

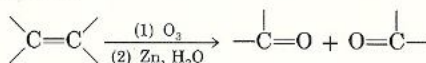


[Sec. 3.18]

Alkenes decolorize (a)  $\text{Br}_2$  in  $\text{CCl}_4$  and (b) dilute solution of  $\text{KMnO}_4$  (Baeyer's test).

[Sec. 3.22]

Ozonolysis



is a reaction used to locate the position of the double bond.

[Sec. 3.23]

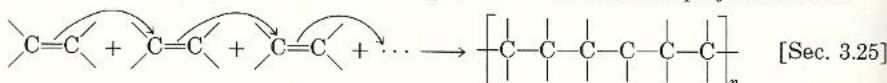
The saturated part of an alkene reacts like an alkane.

[Sec. 3.24]

Alkenes can form giant molecules called polymers. The basic unit of a polymer is called a monomer.

[Sec. 3.25]

Alkene monomers add to one another in a process called addition polymerization.



[Sec. 3.25]

The substitution of one hydrogen of a doubly bonded carbon by another group produces a vinyl compound ( $\text{CH}_2=\text{CH}-\text{G}$ ). Polymerization of a vinyl compound produces a vinyl polymer.

[Sec. 3.25]

The best approach to a problem involving the synthesis of a compound is to work backward, that is, from the product back to the starting material.

[Sec. 3.26]



unsaturated  
alkenes (olefins) $C_nH_{2n}$ 

alkynes

 $C_nH_{2n-2}$ 

dienes

polyenes

vinyl group

allyl group

 $sp^2$  hybridized $\pi$  (pi) bond

geometric isomers

*E*, *Z* system

elimination

Saytzeff's rule

carbocation

dehydrohalogenation

addition reaction

catalytic hydrogenation

electrophile

nucleophile

rate-determining step

electrophilic addition

hydrohalogenation

Markovnikov's rule

hydration

vicinal dihalide

halohydrin

Baeyer test

polymers

monomer

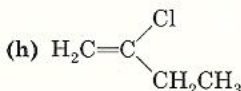
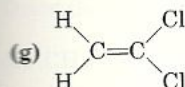
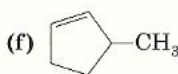
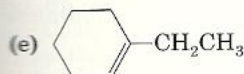
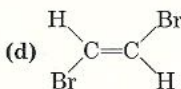
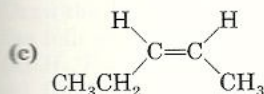
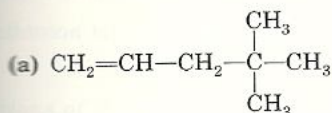
addition polymerization

vinyl polymers

## Exercises

## Structure, Nomenclature, and Geometric Isomerism [Secs. 3.1, 3.3]

3.1 Give the IUPAC names for the following structures. Use *cis* and *trans* designations where pertinent for geometric isomers.



3.2 Write formulas for the following named compounds.

(a) 3-Methyl-1-butene

(b) 5-Bromo-2-methyl-2-hexene

(c) 4-Chlorocyclohexene

(d) Vinylcyclopropane

(e) Allylcyclopentane

(f) *cis*-3-Hexene(g) *trans*-2-Heptene(h) *trans*-1,2-Dicyclopropylethene(i) *Z*-2-Bromo-1-chloropropene(j) *E*-1-Bromo-1-chloro-2-fluoroethene

3.3 State what is wrong with the following names and give the correct name for each molecule.

(a) 2-Ethyl-2-pentene

(b) 2-*n*-Propyl-2-butene

(c) 3-Methyl-2-butene

(d) 3-*n*-Butyl-1-hexene

(e) 1-Methyl-2-cyclobutene

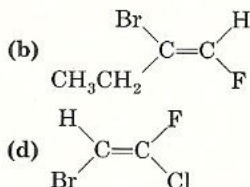
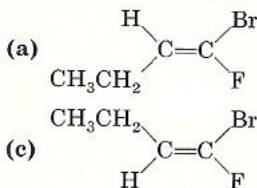
(f) 2,5-Dimethylcyclohexene

3.4 Which of the following compounds can exist as *cis* and *trans* isomers? Draw the structures of the geometric isomers.

(a) 1-Butene

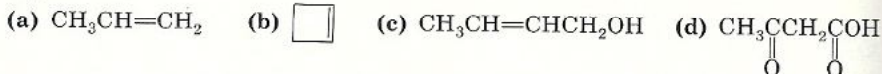
(b) 2-Pentene

- (c) 1-Bromo-3-hexene  
(e) 1,1-Dichloroethene  
(d) 1-Chloro-2-methylpropene  
(f) 2-Methyl-2-pentene
- 3.5 There are three compounds with molecular formula  $C_2H_2Cl_2$ . Draw the structure of each compound and indicate which isomer(s) is (are) structural (constitutional) and which is (are) geometric (*cis-trans*).
- 3.6 Including geometric isomers, there are sixteen alkenes of formula  $C_6H_{12}$ . Draw and name each structure, and indicate which are geometric isomers.
- 3.7 Name the following structures using the *E,Z* system of nomenclature.



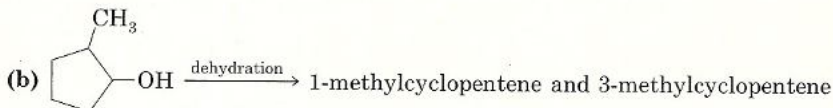
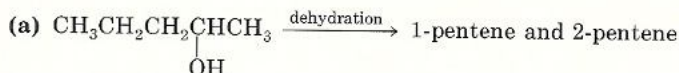
### Hybridization and Shapes of Molecules [Secs. 1.10, 3.2]

- 3.8 Indicate the type of hybridization and the shape about each carbon in the following structures.

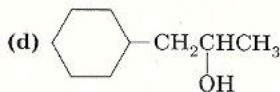
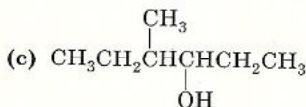
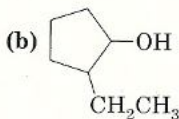
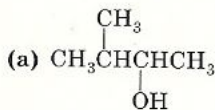


### Preparation of Alkenes [Secs. 3.6-3.9]

- 3.9 Which of the products named for each reaction is the major product according to Saytzeff's rule?

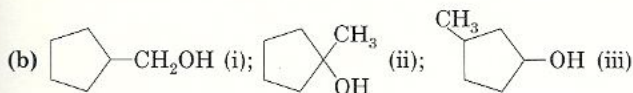
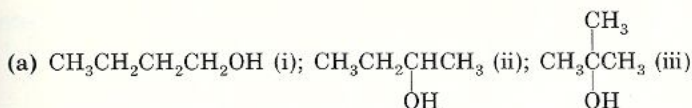


- 3.10 Using Saytzeff's rule write the structure of the *main* product obtained on dehydration of each of the following alcohols.

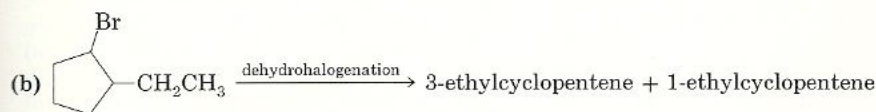
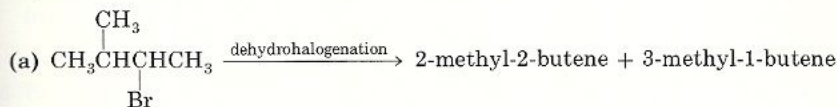


- 3.11 Dehydration of 2-butanol,  $CH_3CH(OH)CH_2CH_3$ , yields 2-butene (major product) and 1-butene (minor product). Write a mechanism that accounts for the formation of these two products.
- 3.12 Arrange the alcohols in each group in order of ease of dehydration.





3.13 Which of the products named for each reaction is the major product according to Saytzeff's rule?



3.14 Using Saytzeff's rule write the structure of the *main* product obtained on dehydrohalogenation of each of the following compounds.

- (a) 2-Bromopentane                      (b) 2-Bromo-2-methylpentane  
(c) 3-Bromo-2-methylpentane        (d) 3-Bromo-2,3-dimethylpentane

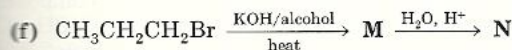
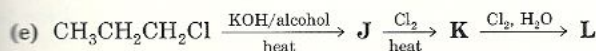
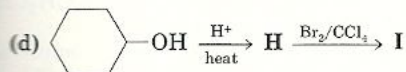
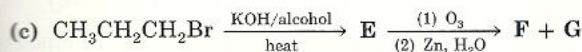
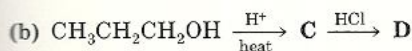
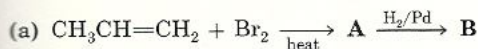
### Reactions of Alkenes [Secs. 3.11-3.24]

3.15 Draw the structure of the product expected on treatment of 2-butene with each of the following.

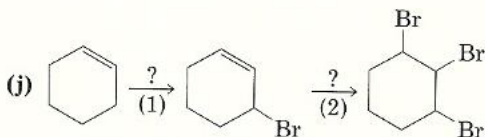
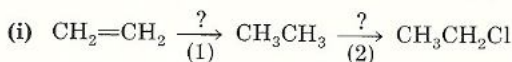
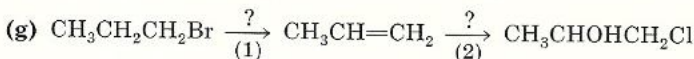
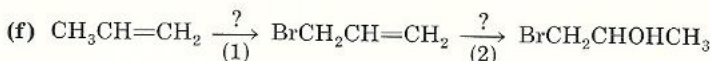
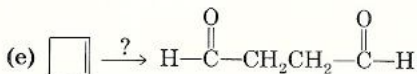
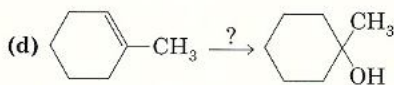
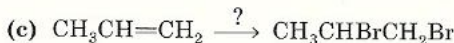
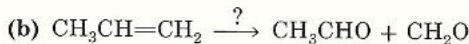
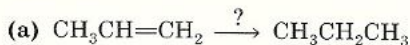
- (a)  $\text{H}_2/\text{Pd}$                                       (b)  $\text{HCl}$   
(c) Cold, concentrated  $\text{H}_2\text{SO}_4$               (d)  $\text{H}_2\text{O}, \text{H}^+$   
(e)  $\text{Br}_2, \text{H}_2\text{O}$                                   (f)  $\text{Br}_2$  in  $\text{CCl}_4$   
(g) Cold, dilute  $\text{KMnO}_4$                       (h)  $\text{O}_3$  followed by  $\text{Zn}, \text{H}_2\text{O}$

3.16 Draw the structures of the major product(s) expected on treatment of 1-butene with the reagents listed in Exercise 3.15.

3.17 Draw the structures of the products, A through N.



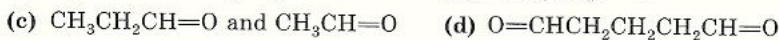
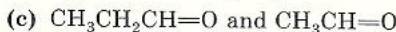
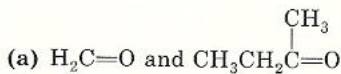
3.18 For each reaction, fill in the missing reagent(s) and, where pertinent, the reaction conditions.



**Identification and Structural Determination** [Secs. 3.22, 3.23]

3.19 *n*-Hexane and 1-hexene are both colorless liquids with similar boiling points. What three simple tests would distinguish the two compounds? Indicate what you would see.

3.20 Give the structure of an alkene that would give each of the following product(s) on ozonolysis.



3.21 Compound **A**,  $\text{C}_4\text{H}_9\text{Br}$ , on treatment with alcoholic KOH, gave compound **B**,  $\text{C}_4\text{H}_8$ . Treatment of **B** with ozone followed by zinc and water yields  $\text{CH}_3\text{CH}_2\text{CH}=\text{O}$  and  $\text{O}=\text{CH}_2$ . What are the structures of **A** and **B**?

3.22 A compound  $\text{C}_4\text{H}_9\text{Br}$  (**A**), on treatment with alcoholic KOH, gave compound **B**,  $\text{C}_4\text{H}_8$ . Treatment of **B** with ozone followed by zinc and water yielded  $\text{CH}_3\text{CH}=\text{O}$  as the only product. What two possible structures for **B** account for these facts? What is the structure for **A**?

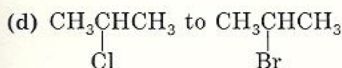
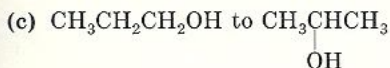
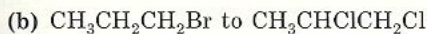
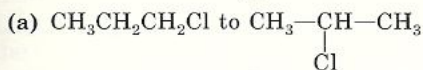
3.23 A compound **A**,  $\text{C}_4\text{H}_9\text{Br}$ , on treatment with alcoholic KOH, gave compound **B**,  $\text{C}_4\text{H}_8$ . Treatment of **B** with ozone followed by zinc and water yielded  $(\text{CH}_3)_2\text{C}=\text{O}$  and  $\text{O}=\text{CH}_2$ . What two possible structures for **B** account for these facts? What is the structure for **A**?



**Synthesis Problems** [Sec. 3.26]

**3.24** By means of equations show how you would carry out the synthetic conversion indicated. For each step, indicate the reagents needed and the reaction conditions.

Exercises



**3.25** Beginning with ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ , as your only organic starting material, show how you would prepare each of the compounds listed. (You may use any other needed reagent.) Where more than one step is required, show each reaction clearly.

(a) Ethene

(b) Bromoethane

(c) Ethane

(d) 1,2-Dichloroethane

(e) 2-Chloroethanol,  $\text{HOCH}_2\text{CH}_2\text{Cl}$

(f) Ethylene glycol,  $\text{HOCH}_2\text{CH}_2\text{OH}$

# 4

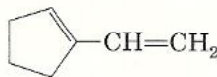
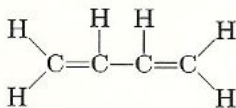
## Unsaturated Hydrocarbons II: Dienes, Polyenes, and Alkynes

In Chapter 3 we discussed the chemistry of alkenes. In this chapter we will study the chemistry of hydrocarbons that are even more unsaturated than simple alkenes. These include compounds that contain two or more double bonds as well as those that contain triple bonds.

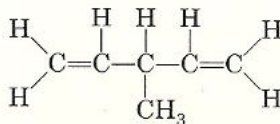
### 4.1 Structure and Nomenclature of Dienes

Alkenes that contain two double bonds are called **dienes** (that is, they have two *ene* functions). If the double bonds are separated by only *one* single bond,

$\text{—C=C—C=C—}$ , the diene is said to be **conjugated**.



If the double bonds are separated by *more* than one single bond, the diene is called a **nonconjugated** diene, and the double bonds are said to be **isolated**.





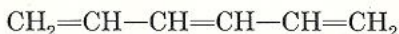
Dienes are named by the IUPAC system in essentially the same way as alkenes except that the suffix *-adiene* replaces the ending *-ene* of the alkene. Also, two numbers are needed to indicate the locations of the double bonds in the chain. In cyclic dienes one of the double bonds is always assigned the number 1, and the other is given the lowest possible number. This system can be extended to compounds that contain three double bonds (**trienes**), four double bonds (**tetraenes**), or many double bonds (**polyenes**).



1,4-Pentadiene  
(nonconjugated)



1,3-Cyclohexadiene  
(conjugated)



1,3,5-Hexatriene  
(conjugated)



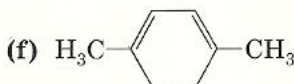
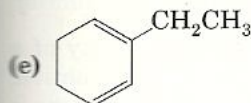
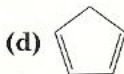
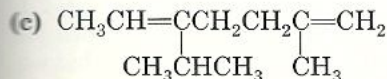
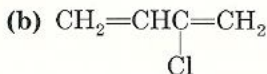
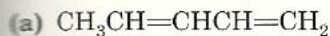
1,3,5,7-Cyclooctatetraene  
(conjugated)

**Problem 4.1** Write the structures of the following compounds.

- |                             |                                  |
|-----------------------------|----------------------------------|
| (a) 1,3-Butadiene           | (b) 1,4-Cyclohexadiene           |
| (c) 2-Methyl-2,5-heptadiene | (d) 2-Methyl-1,3-cyclopentadiene |
| (e) 1-Vinylcyclobutene      | (f) 1-Allylcyclopentene          |

**Problem 4.2** Indicate which dienes in Problem 4.1 are conjugated and which contain isolated double bonds.

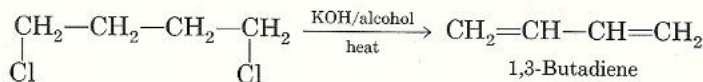
**Problem 4.3** Name the following compounds.



## Preparation and Properties of Dienes 4.2

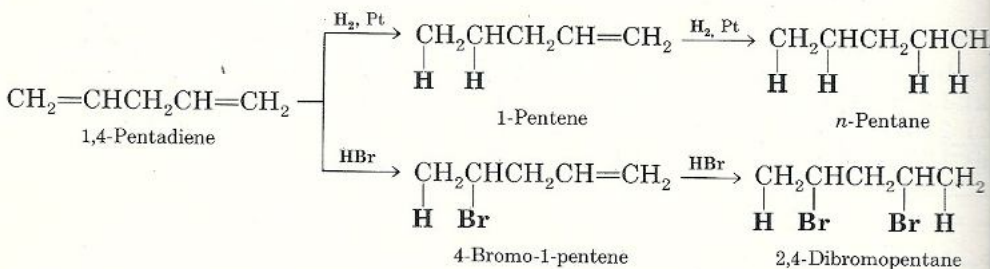
Dienes may be prepared by applying any of the appropriate methods used to prepare simple alkenes (Sec. 3.5). Of course, the starting molecule must have the right kind of functional groups in the proper positions. For example, a conven-

ient method for preparing 1,3-butadiene in the laboratory is to heat 1,4-dichlorobutane with an alcoholic solution of potassium hydroxide, a dehydrohalogenation reaction (Sec. 3.10).



1,3-Butadiene is a raw material used in the manufacture of synthetic rubber (Sec. 4.6A).

As far as the chemical properties are concerned, dienes undergo the typical reactions of unsaturated hydrocarbons—addition reactions. In nonconjugated dienes the isolated double bonds have little effect on each other, and they therefore behave as if they were two separate alkenes. Consequently, the chemical properties of nonconjugated dienes are the same as those of simple alkenes except for the fact that they consume twice as much reagent.



In conjugated dienes, on the other hand, the proximity of the double bonds affects their chemical properties in ways that make them different from nonconjugated dienes. This difference is evidenced by the fact that conjugated dienes are *more stable* than nonconjugated dienes and that they undergo an unexpected reaction, *1,4-addition*.

## 4.3 Stability of Conjugated Dienes: Heat of Hydrogenation

Experimentally, one of the methods used to determine the stability of a diene is to measure the **heat of hydrogenation**. The heat of hydrogenation,  $\Delta H$ , is the amount of energy released (in kilocalories per mole) when the diene is reduced to an alkane.

For example, if we compare the amounts of heat released when 1,4-pentadiene and 1,3-pentadiene are converted to pentane, we find that hydrogenation of the nonconjugated diene releases 60.8 kcal/mole, whereas the heat of hydrogenation of 1,3-pentadiene (a conjugated diene) is 54.1 kcal/mole (Fig. 4.1). The product, pentane, has the same energy regardless of the starting diene. The fact that 1,3-pentadiene releases less energy on hydrogenation than 1,4-pentadiene means that the conjugated diene contains less energy, or is more stable, than the nonconjugated diene.



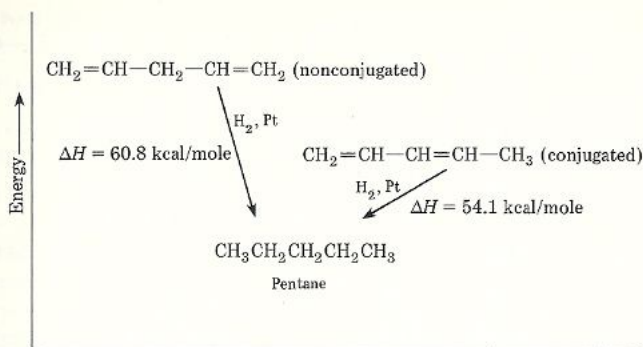


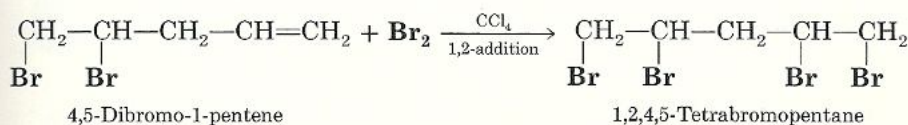
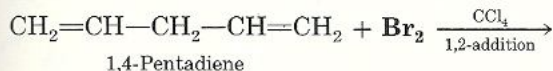
Figure 4.1 Conversion of two dienes to the same alkane releases different amounts of energy; 1,3-pentadiene (conjugated) is more stable than 1,4-pentadiene (nonconjugated).

Numerous experiments, similar to the one just described, have established that whenever two dienes, one conjugated and the other isolated, are converted to the same alkane, *invariably* the conjugated diene is more stable than the diene with the isolated double bonds.

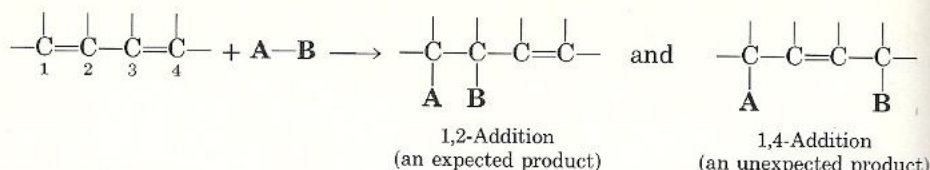
Before we discuss *why* conjugated dienes are more stable, let us point out how they also differ from nonconjugated dienes in their addition reactions.

## Electrophilic Addition to Conjugated Dienes: 4.4 1,4-Addition

When a mole of a reagent capable of adding to an alkene reacts with a nonconjugated diene, the expected addition to *adjacent* double-bonded carbons is obtained. The addition of a reagent to a pair of adjacent carbons is called **1,2-addition**. For example, treatment of 1,4-pentadiene with just enough of a solution of bromine in carbon tetrachloride to form the dihalide gives the expected 1,2-addition product, 4,5-dibromo-1-pentene. Addition of another mole of bromine gives another 1,2-addition product, 1,2,4,5-tetrabromopentane.



Treatment of a conjugated diene with bromine under similar conditions gives, in addition to the expected 1,2-addition product, an unexpected **1,4-addition** product.



*1,4-Addition occurs when a reagent attaches itself to the carbons at the two ends of a conjugated system.*

Thus, treatment of 1,3-butadiene with bromine yields not only the expected 3,4-dibromo-1-butene (1,2-addition product) but also the unexpected 1,4-dibromo-2-butene (1,4-addition product). Treatment with hydrogen bromide, HBr, yields not only the expected product 3-bromo-1-butene (1,2-addition) but also an unexpected product, 1-bromo-2-butene (1,4-addition). Treatment with hydrogen in the presence of a suitable catalyst yields not only the expected 1-butene (1,2-addition) but also 2-butene (1,4-addition). These reactions are represented in Figure 4.2. *Frequently, the unexpected 1,4-addition product is the major one* (especially when reactions are conducted at 25°C and above).

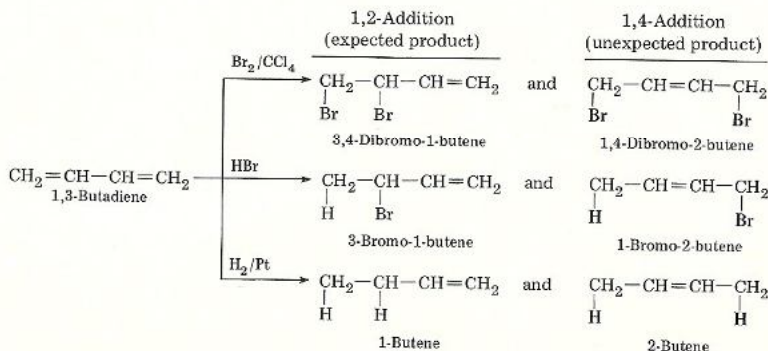
We have just seen that conjugated dienes undergo an unexpected reaction, 1,4-addition. We have also observed that they are more stable than their nonconjugated isomers (Sec. 4.3). How do we account for these facts? The explanation is provided by a concept in structural theory called resonance.

**Problem 4.4** Draw the structures of the product(s) that can result from the addition of 1 mole each of

- |   |  |
|---|--|
| (a) HBr to 2,4-hexadiene                              | (b) Br <sub>2</sub> in CCl <sub>4</sub> to 2,4-hexadiene |
| (c) H <sub>2</sub> O, H <sup>+</sup> to 2,4-hexadiene | (d) HCl to 1,3-cyclohexadiene                            |
| (e) H <sub>2</sub> /Pt to 1,4-pentadiene              | (f) HBr to 1,4-cyclohexadiene                            |

## 4.5 Resonance

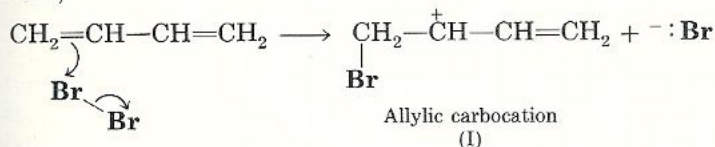
To account for 1,4-addition, we must examine the mechanism of the reaction. As with simple alkenes, addition occurs by a two-step process. The first step involves the attack on the  $\pi$  bond by an electrophile to form a carbocation. Thus,



**Figure 4.2** Addition of one mole of a reagent to a conjugated diene gives rise to an expected 1,2-addition product and an unexpected 1,4-addition product.

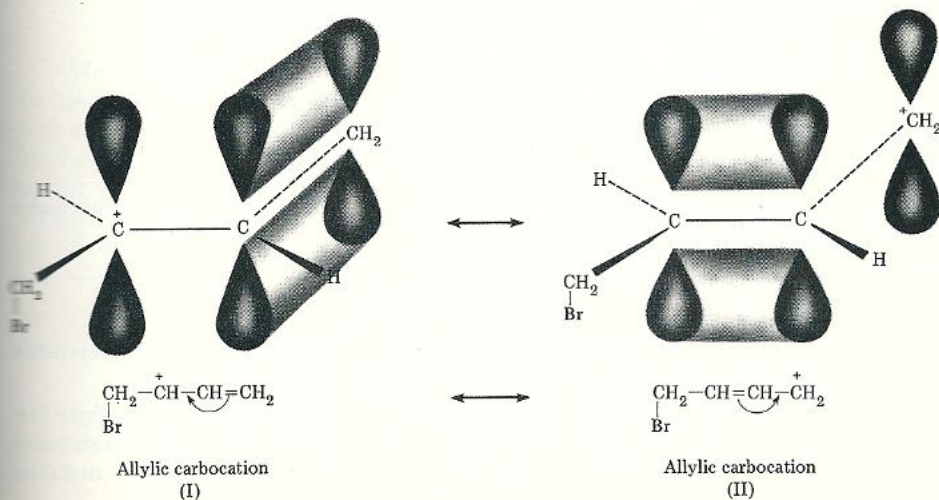


addition of bromine to 1,3-butadiene results in a secondary carbocation. This carbocation is also called an **allylic carbocation** because it is part of an allylic structure ( $-\text{CH}_2-\text{CH}=\text{CH}_2$ , the allyl group;  $-\overset{+}{\text{C}}\text{H}-\text{CH}=\text{CH}_2$ , the allylic carbocation).

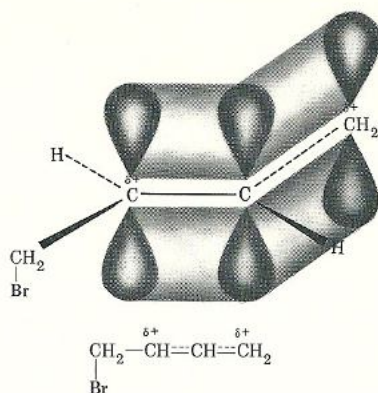


Actually, our representation of the allylic carbocation is inadequate. Figure 4.3 illustrates why this is so. As can be seen, the representation of the allylic carbocation (I) shows that the positive charge is on a carbon having a vacant  $p$  orbital. This  $p$  orbital is next to a  $\pi$  bond. The proximity of  $\pi$  electrons to the positive charge will cause them to be attracted to it, resulting in structure II, also an allylic carbocation. In II, as in I, there is a positively charged carbon with a vacant  $p$  orbital, and next to it there is a  $\pi$  bond. The  $\pi$  electrons in II are also attracted to the positive charge, resulting in allylic carbocation (I). In effect the  $\pi$  electrons are not bonded specifically to two atoms but are dispersed over three atoms. The term **delocalization** is used whenever  $\pi$  electrons *simultaneously* form a bond between more than a single pair of atoms. The phenomenon of delocalization of electrons is called **resonance**.

Note that neither structure I nor II truly represents the allylic carbocation. The allylic carbocation is actually a new type of species called a **resonance hybrid**. A resonance hybrid is a *single* species that combines the characteristics of two or more structures that differ only in their electronic arrangements. The individual structures are called **contributing structures** that have no real existence. The symbol  $\longleftrightarrow$  is used to represent resonance between contributing structures of a resonance hybrid. The double-headed arrow should not be confused with  $\rightleftharpoons$ , which indicates an equilibrium between real structures. The resonance hybrid is illustrated in Figure 4.4.



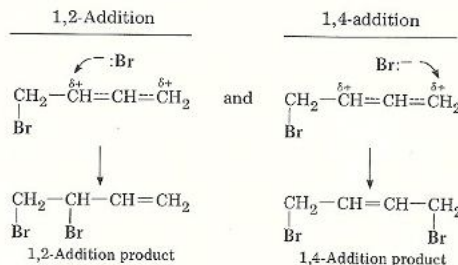
**Figure 4.3** Two contributing structures of an allylic carbocation, neither of which exists in reality.



**Figure 4.4** Two representations of an allylic carbocation resonance hybrid. Below the orbital picture is a single structure containing broken bond lines to indicate the distribution of the positive charge between the C-2 and C-4 positions.

Because of the delocalization of the positive charge over two atoms, C-2 and C-4, the resonance hybrid is more stable (i.e., contains less energy) than any of the contributing structures where the positive charge is localized on one carbon atom only. The extra stability of the resonance hybrid is called the **resonance energy**.

With this more accurate picture of the allylic carbocation we can now account for the formation of the unexpected 1,4-addition product. The attack by  $^-:\text{Br}$ , the nucleophile, in the second step of the addition mechanism can take place at either C-2 or C-4. Attack at C-2 gives the 1,2-addition product, and attack at C-4 gives the 1,4-addition product (Fig. 4.5).



**Figure 4.5** Addition of the bromide ion to C-2 and C-4 giving a 1,2-addition and a 1,4-addition product, respectively.

**Problem 4.5** The carboxylate anion,  $\text{R}-\text{C} \begin{array}{l} \text{O} \\ // \\ \text{O}^- \end{array}$ , is stabilized by resonance

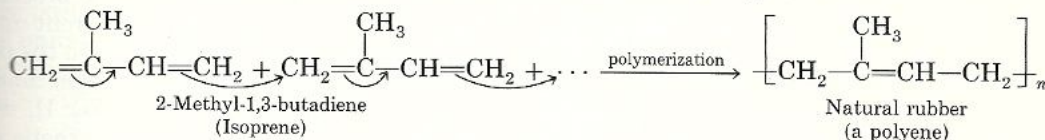
since the negative charge can be delocalized over both oxygen atoms. Write formulas for (a) the two contributing resonance structures and (b) the resonance hybrid using dashed bond lines to indicate the distribution of the negative charge over the two oxygen atoms.



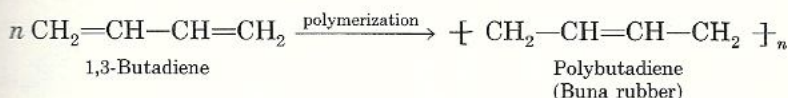
## Polymerization of Conjugated Dienes: Polyenes 4.6

### A Natural and Synthetic Rubber

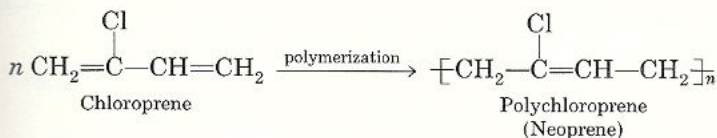
Like ethylene or substituted ethylenes (Sec. 3.25), conjugated dienes may polymerize into compounds that still contain many double bonds. Compounds that contain several double bonds are generally referred to as polyenes. The polymerization of conjugated dienes is commercially important because both natural and synthetic rubber are polymers of conjugated dienes. Natural rubber is a polymer of the conjugated diene 2-methyl-1,3-butadiene or **isoprene**.



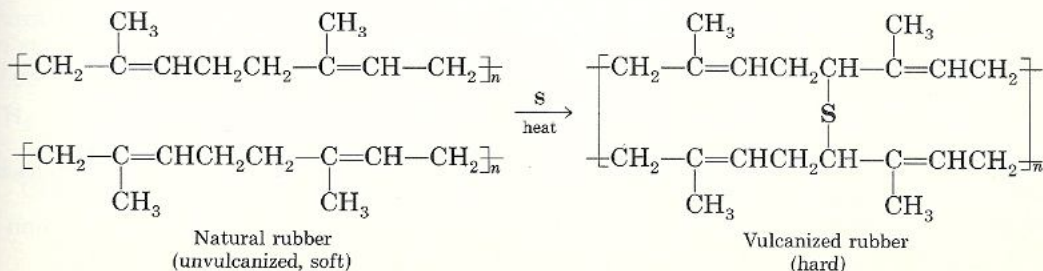
Synthetic rubbers are made through polymerization of different conjugated dienes. For example, the polymerization of 1,3-butadiene produces a soft rubbery polymer manufactured since 1927 under the trade name of **Buna rubber**.



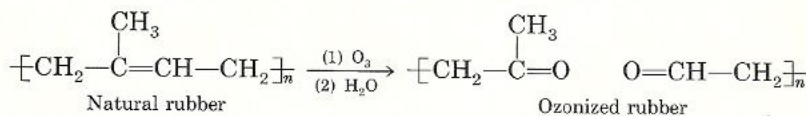
The similar polymerization of its derivative 2-chloro-1,3-butadiene, or **chloroprene**, forms a rubber substitute called **neoprene**. Neoprene is superior to natural rubber in its resistance to oil, gasoline, and other organic solvents.



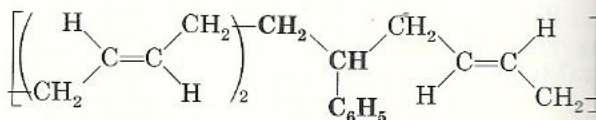
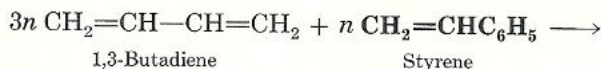
Natural or synthetic rubber is too soft to be of much use in industry. Its hardness and durability can be improved by **vulcanization**, a technique that was discovered accidentally in 1834 by Charles Goodyear. He found that when rubber is treated with sulfur (vulcanized) a tougher polymer is produced. The sulfur atoms form bridges between different chains in the rubber molecule. These cross-links make the rubber harder and stronger than the original unvulcanized rubber.



The process of vulcanization made possible the manufacture of tough rubber tires for the automobile industry. We frequently observe that old tires lose their flexibility, become stiff and brittle, and develop small cracks. This is because, like simple alkenes, the rubber undergoes ozonolysis with the ozone and moisture present in the atmosphere, resulting in the cleavage of the long polymer chain into smaller chains.



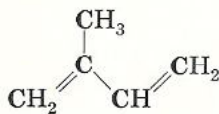
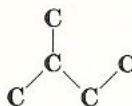
Other synthetic rubber polymers may also be prepared by the process of copolymerization. **Copolymerization** occurs when two or more different unsaturated monomers are mixed together and are allowed to polymerize. In the polymer thus formed the monomeric units may be distributed in a random manner or they may alternate along the polymer chain. During World War II, when natural rubber became unavailable to this country, an excellent synthetic substitute called SBR (styrene-butadiene rubber) was developed from the copolymerization of 1,3-butadiene and styrene,  $\text{CH}_2=\text{CHC}_6\text{H}_5$ . SBR, which has since been used extensively in the automobile industry, consists of about three parts butadiene and one part styrene.



Styrene-butadiene rubber (SBR)

## B Natural Polyenes

Some natural polyenes, called **terpenes**, are found in many plants. Terpenes may be viewed as consisting of **isoprene units** joined together in groups of two, three, four, six, or eight. An isoprene unit is a sequence of five carbon atoms that resembles isoprene.

2-Methyl-1,3-butadiene  
(Isoprene)

An isoprene unit

Terpenes are classified according to the number of isoprene units, as indicated in Table 4.1.

Geraniol, which has a sweet rose odor, and limonene, which gives lemon and

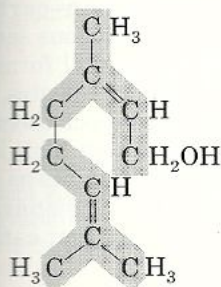
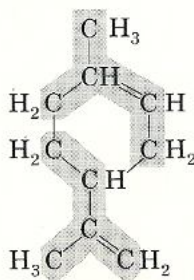


Table 4.1 Classes of Terpenes

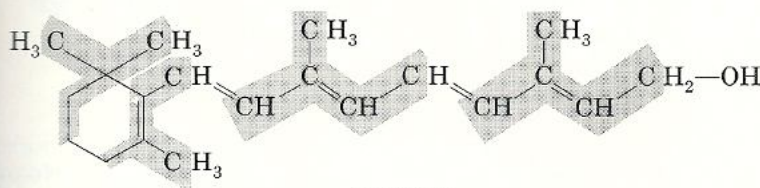
	Number of carbon atoms	Number of isoprene units
Monoterpenes	10	2
Sesquiterpenes	15	3
Diterpenes	20	4
Triterpenes	30	6
Tetraterpenes	40	8

4.6 Polymerization  
of Conjugated  
Dienes: Polyenes

Orange peels their characteristic odors, are examples of monoterpenes. The isoprene units are shaded.

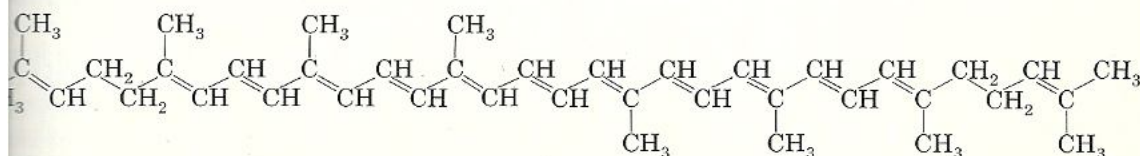
Geraniol  
(rose)Limonene  
(lemon, orange)

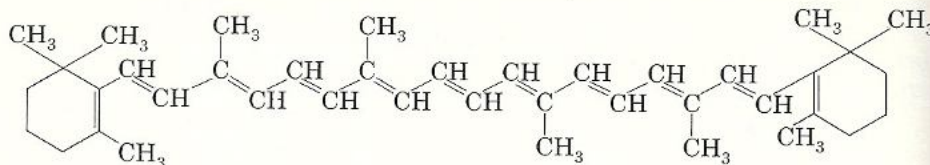
Vitamin A, a fat-soluble vitamin essential for resisting infections and for good vision, is an example of a diterpene.

Vitamin A  
(Retinol)

**Problem 4.6** The reddish yellow pigments found in tomatoes, carrots, and other fruits and vegetables are terpenes. Lycopene occurs in ripe tomatoes and watermelon, and  $\beta$ -carotene is found in carrots, tomatoes, and spinach. From the structures determine how many isoprene units each has.

**Lycopene**



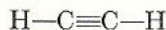
(b)  $\beta$ -Carotene

## 4.7 Alkynes

An **alkyne** is an unsaturated hydrocarbon that contains a **carbon-carbon triple bond**. Like alkanes and alkenes, alkynes also form a homologous series, the increment again being  $-\text{CH}_2-$ , a methylene group. The general formula that characterizes the alkyne series is  $\text{C}_n\text{H}_{2n-2}$ . As the formula indicates, alkynes are even more unsaturated than alkenes, and we would expect them to undergo the same reactions as alkenes; namely, electrophilic addition. This is in fact the case, except that twice as much reagent can be added to alkynes as can be added to alkenes. Alkynes are also synthesized in much the same manner as alkenes, except that twice as many atoms are eliminated from adjacent carbon atoms.

## 4.8 Geometry of the Carbon-Carbon Triple Bond: sp Hybridization

The simplest member of the alkyne series is acetylene,  $\text{C}_2\text{H}_2$ .



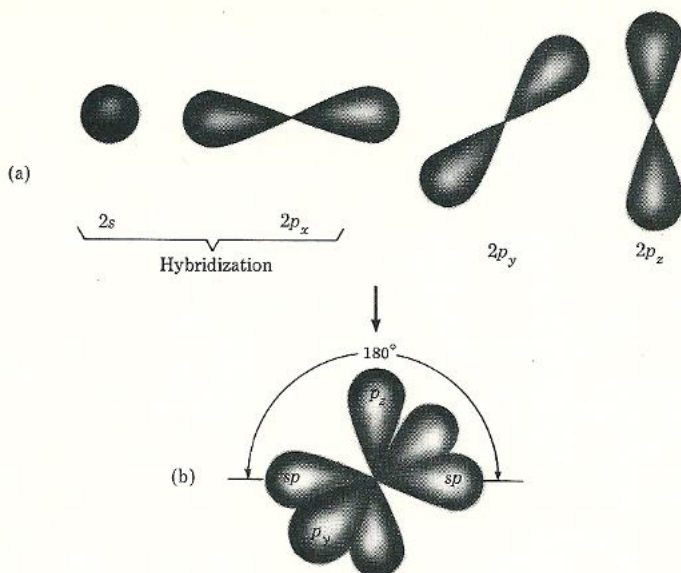
Acetylene

From the structure of acetylene we see that each carbon is bonded to two other atoms. Acetylene is also a linear molecule with a bond angle of  $180^\circ$ . This geometry can be explained by a third type of hybridization called sp hybridization ( $\frac{1}{2}s$  and  $\frac{1}{2}p$  characteristics). As with alkanes and alkenes, carbon proceeds first to its excited state, but in the hybridization step only one  $s$  and one  $p$  orbital mix together to form two equivalent sp orbitals. This leaves two unhybridized  $p$  orbitals, which are perpendicularly oriented to each other and to the plane of the hybrid  $sp$  orbitals (Fig. 4.6).

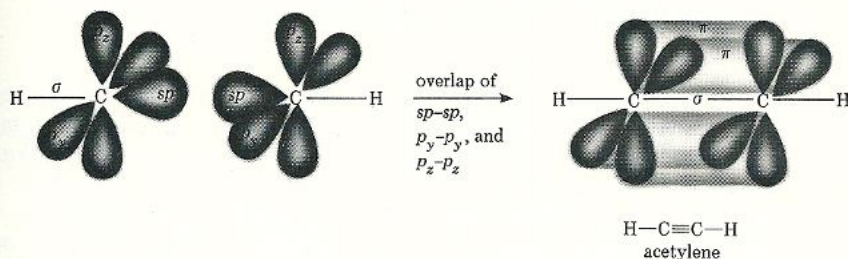
The union of the two carbons in acetylene occurs by the end-on overlap of their  $sp$  orbitals to form a  $\sigma$  bond. The remaining  $sp$  orbitals bond with the  $s$  orbital of hydrogen and also form  $\sigma$  bonds. The two unhybridized  $p$  orbitals overlap in a sidewise fashion to form two  $\pi$  bonds. Both carbons thus are joined by one  $\sigma$  bond and two  $\pi$  bonds, which together form a triple bond (Fig. 4.7).

Not only is acetylene a linear molecule, but substituted acetylenes  $\text{R}-\text{C}\equiv\text{C}-\text{H}$  or  $\text{R}-\text{C}\equiv\text{C}-\text{R}$  are also linear, and for this reason *cis-trans* isomerism is impossible in this class of compounds. The carbon-carbon triple bond is





**Figure 4.6** (a) Hybridization of a  $2s$  orbital and a  $2p$  orbital to form (b) two linear  $sp$ -hybridized orbitals with bond angle of  $180^\circ$  and two unhybridized  $p$  orbitals perpendicularly oriented to each other and to the plane of the hybrid  $sp$  orbitals.

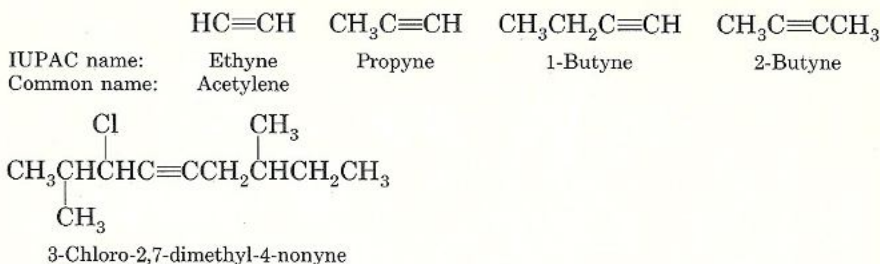


**Figure 4.7** End-on overlap of two  $sp$  orbitals to form a  $\sigma$  bond between the two carbons of acetylene and side-side overlap of the  $p_y$  orbitals and the  $p_z$  orbitals to form two  $\pi$  bonds.

made up of a strong  $\sigma$  bond and two weaker  $\pi$  bonds. Consequently, it is both shorter ( $1.20 \text{ \AA}$ ) and stronger ( $200 \text{ kcal/mole}$ ) than the carbon-carbon double bond of alkenes ( $1.34 \text{ \AA}$  and  $83 \text{ kcal/mole}$ ).

## Nomenclature of Alkynes 4.9

Although alkynes can be named by both common and IUPAC nomenclatures, all alkynes except acetylene are generally named by the IUPAC nomenclature. The IUPAC rules for alkynes are the same as those used for alkenes, except that the ending *-yne* replaces *-ene*.



**Problem 4.7** Write the condensed structural formula for

- |                           |                           |
|---------------------------|---------------------------|
| (a) 1-Pentyne             | (b) 3-Hexyne              |
| (c) 3,3-Dimethyl-1-butyne | (d) 1-Cyclohexyl-2-butyne |

**Problem 4.8** The names given for the compounds listed here are incorrect. Draw their structures and give their correct name.

- |                                    |   |
|------------------------------------|---|
| (a) 4-Pentyne                      | (b) 2-Chloro-2- <i>n</i> -propyl-3-butyne |
| (c) 2,2-Dibromo-5-methyl-3-pentyne | (d) 4,4-Dimethyl-2-butyne                 |

## 4.10 Physical Properties of Alkynes

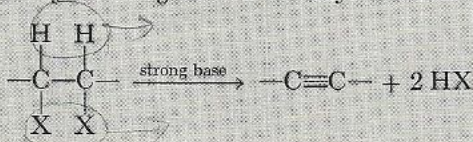
Alkynes have physical properties that are essentially the same as those of alkanes and alkenes. They are insoluble in water but quite soluble in the usual organic solvents such as benzene, ether, and carbon tetrachloride. Like alkanes and alkenes, alkynes are less dense than water; their boiling points show the usual increase with increasing molecular weight; and their boiling points are close to those of alkanes or alkenes with the same carbon skeleton. Like alkanes or alkenes the  $\text{C}_2$ - $\text{C}_4$  alkynes are gases, the  $\text{C}_5$ - $\text{C}_{18}$  alkynes are liquids, and those with more than eighteen carbons are solids.

$\text{C}_2 - \text{C}_4 \rightarrow \text{gases}$   
 $\text{C}_5 - \text{C}_{18} \rightarrow \text{liquid}$   
 $\text{C}_{18} \leftarrow \text{solid}$

## 4.11 Preparation of Alkynes

Basically, alkynes are synthesized by two methods.

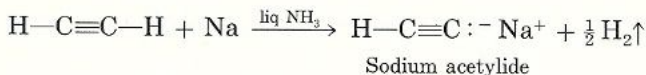
1. Dehydrohalogenation of alkyl dihalides using a strong base





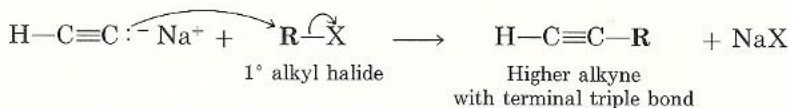


as **metal acetylides**. For example, sodium in liquid ammonia reacts with acetylene to form a sodium acetylide salt and hydrogen.

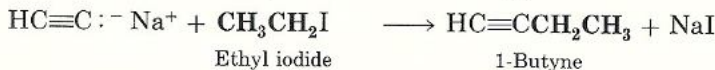


This sodium salt can react with primary alkyl halides to form higher alkynes with the triple bond at the end of the chain (that is, terminal alkynes).

*General equation*

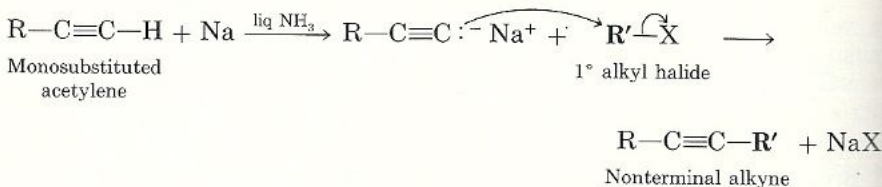


*Specific examples*

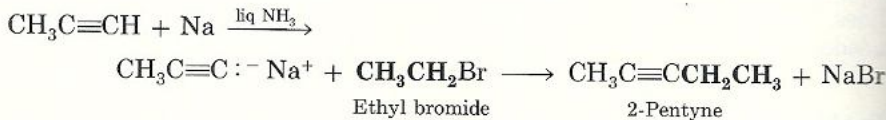


Monosubstituted acetylenes can react in a similar fashion, but give higher alkynes with nonterminal triple bonds.

*General equation*



*Specific example*



With secondary and tertiary alkyl halides, sodium acetylides generally bring about dehydrohalogenation to give alkenes rather than the desired alkylation product.

**Problem 4.10** Starting with acetylene, show how you would synthesize the following compounds (you may use any other needed reagents).

(a) 2-Butyne

(b) 1-Pentyne

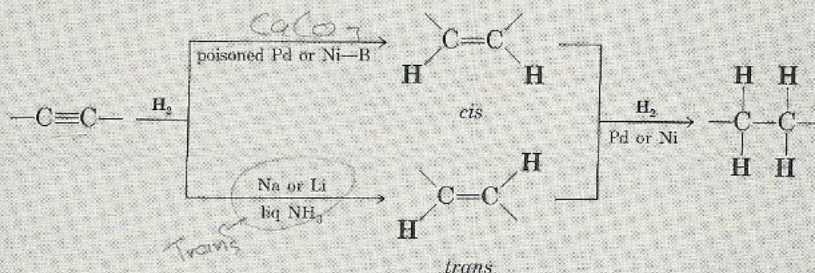
(c) 2-Pentyne



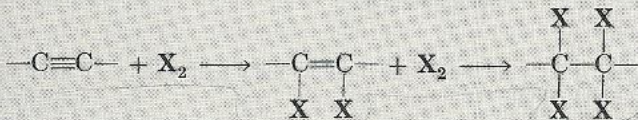
## Reactions of Alkynes 4.12

Alkynes undergo reactions that are similar to those of alkenes, except that they are capable of adding two molecules of a reagent for each triple bond present. Addition of reagents occurs in two stages, producing first an alkene and, upon further addition, a saturated compound. By proper selection of experimental conditions, it is possible to stop the reaction at the alkene stage, but it is usually difficult to do so. We shall focus our attention on the following reactions.

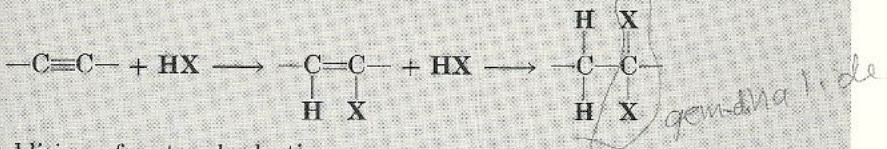
### 1. Addition of hydrogen



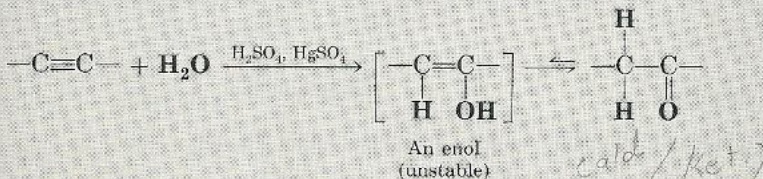
### 2. Addition of halogen



### 3. Addition of hydrogen halide

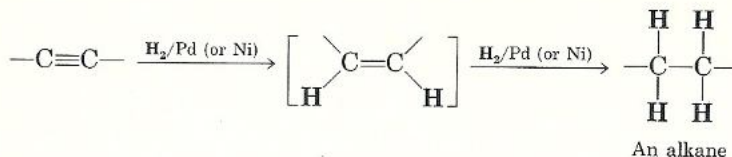


### 4. Addition of water: hydration

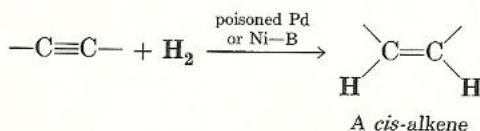


## A Addition of Hydrogen

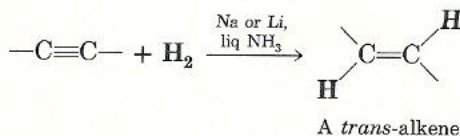
Like alkenes, alkynes may add hydrogen in the presence of suitable catalysts, such as platinum, palladium, or nickel. Under these conditions, however, the hydrogenation cannot be stopped at the alkene stage, and the final product is always an alkane.



Conversion of alkynes to the alkene stage can be accomplished only by using special catalysts. Depending on the choice of catalyst, the product may be a *cis*-alkene or a *trans*-alkene, where such isomerism is possible. Addition of a controlled amount of hydrogen either in the presence of deactivated or *poisoned* palladium (which is prepared by adding lead acetate to palladium) or using a nickel boride catalyst, Ni-B, gives almost entirely a *cis*-alkene.



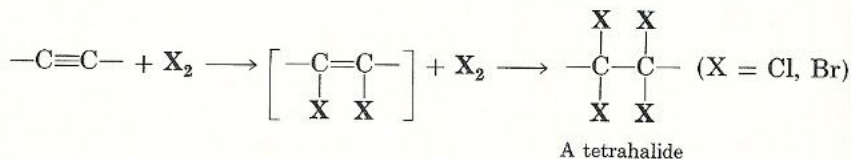
Treatment of alkynes with sodium or lithium in liquid ammonia yields predominantly *trans*-alkenes.



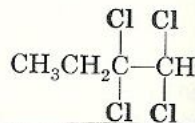
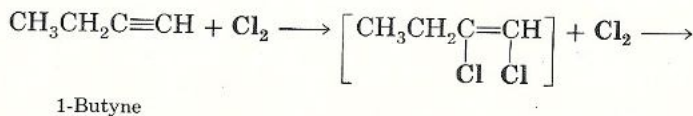
## B Addition of Halogen

Alkynes react with equivalents of halogen to give tetrahalides. As with alkenes, this reaction is restricted to chlorine and bromine.

*General equation*



*Specific example*



1,1,2,2-Tetrachlorobutane



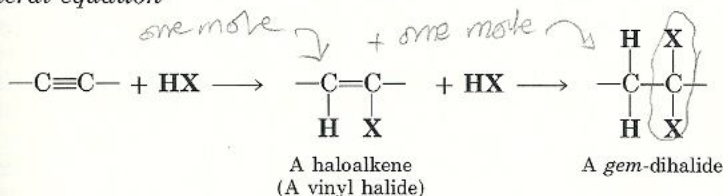
## C Addition of Hydrogen Halide

111

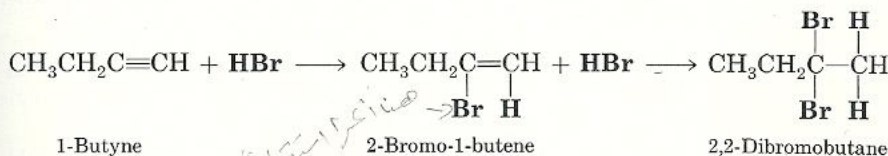
4.12 Reactions of Alkynes

The addition of hydrogen chloride, bromide, or iodide to alkynes follows Markovnikov's rule (Sec. 3.17). The reaction proceeds in two steps and may be stopped at the haloalkene (or vinyl halide) stage or, if allowed to react further with another mole of HX, to the *gem*-dihalide stage. The term *gem*-dihalide (from the Latin *geminus*, twin) signifies that both halogens are on the same carbon atom.

### General equation



### Specific example

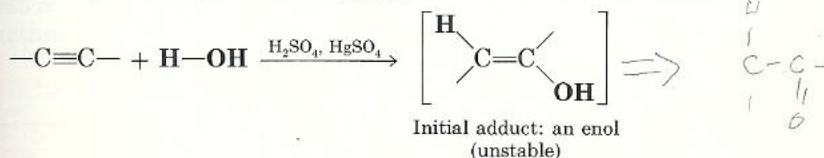


**Problem 4.11** Starting with acetylene, show how you would synthesize these compounds.

- (a) 1,1-Dibromoethane                      (b) 1,2-Dibromoethane  
(c) 2,2-Dibromobutane                      (d) 2,3-Dibromobutane

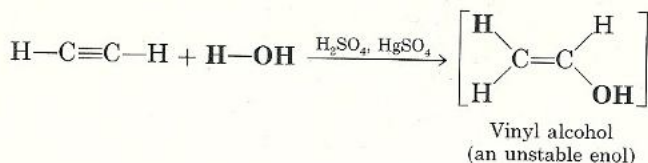
## D Addition of Water: Hydration

Water adds to alkynes in the presence of dilute sulfuric acid and mercuric sulfate catalyst. The addition of water follows Markovnikov's rule (Sec. 3.17) to give initially an adduct called an enol.

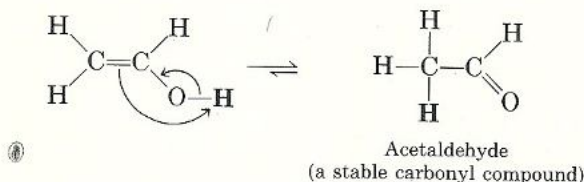


The term **enol** is derived from the combination of the suffixes *-ene*, characteristic of alkenes, and *-ol*, characteristic of alcohols. Structurally, an enol is any compound that contains a carbon-carbon double bond (alkenes) to which is attached a hydroxyl group (alcohols). Enols are unstable compounds and are converted immediately to more stable products that contain a C=O or carbonyl

group. For example, the addition of water to acetylene gives first vinyl alcohol, an unstable enol,



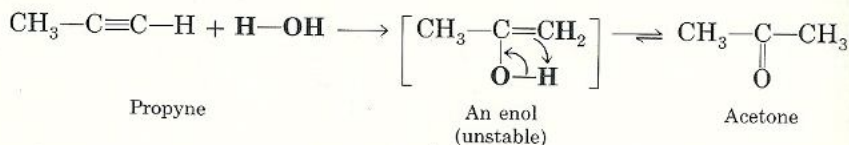
which rearranges to a carbonyl compound, acetaldehyde.



Acetaldehyde is but a single member of a larger class of compounds known as

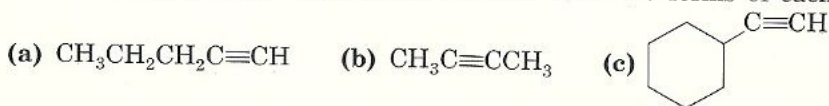
aldehydes ( $\text{R}-\overset{\text{H}}{\underset{|}{\text{C}}}=\text{O}$ ), which will be discussed in Chapter 10. Acetylene is the only alkyne that will give an aldehyde upon hydration. Substituted acetylenes

also undergo hydration, but yield only ketones ( $\text{R}-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{R}'$ ). For example, the hydration of propyne yields the ketone acetone.



Because all enols, except vinyl alcohol, are converted to ketones, the spontaneous conversion of the unstable enol into a carbonyl, or **keto**, form is referred to as **enol-keto tautomerism**, an isomerization reaction. Note that the enol and keto forms of a compound, also called **tautomers**, are *distinct molecules*. They should not be confused with the resonance forms (Sec. 4.5), which have no real independent existence. Enol-keto tautomerism is an *equilibrium reaction* that involves the shift of a proton and of an electron pair. In the hydration of alkynes, this equilibrium strongly favors the keto side.

**Problem 4.12** Draw the structures of the product formed from the hydration of the following compounds. Draw the enol and keto forms of each product.



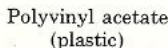


## 4.13

is produced industrially by the pyrolysis of methane.

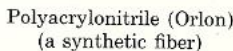


mixed with the proper amount of air, it burns with a bright, intense white flame. "Carbide" lamps, as they were called at the time, were widely used as a source of light prior to the invention of electric bulbs. Today, about half of the acetylene consumed in the United States is used for welding, cutting, and cleaning iron and steel by means of the oxyacetylene torch. Because of its low cost and high chemical reactivity, acetylene is also used as the starting material for a wide variety of important organic compounds, such as acetaldehyde, acetic acid, plastics, and rubber compounds. For example, catalytic addition of acetic acid to acetylene yields vinyl acetate, which is used to manufacture plastics such as polyvinyl acetate and polyvinyl alcohol (PVA), from which floor coverings, upholstery materials, and shoe soles are made.

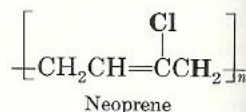
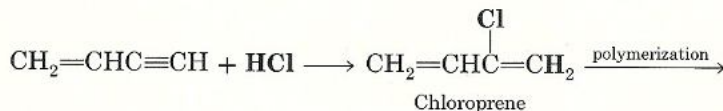
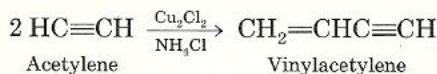


Polyvinyl alcohol (PVA)

acrylonitrile, used in the production of the synthetic fiber polyacrylonitrile, or *Orlon*, and the synthetic rubber *Buna N rubber* (a copolymer of 1,3-butadiene and acrylonitrile).



Under the influence of cuprous chloride,  $\text{Cu}_2\text{Cl}_2$ , and ammonium chloride,  $\text{NH}_4\text{Cl}$ , acetylene can be made to dimerize into vinylacetylene,  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$ . Careful addition of hydrogen chloride to vinylacetylene gives the important conjugated diene 2-chloro-1,3-butadiene, or *chloroprene*. Recall from Section 4.6 that polymerization of this conjugated diene monomer gives the commercially important synthetic rubber *Neoprene*. This valuable synthesis was discovered by J. A. Nieuwand in 1929.

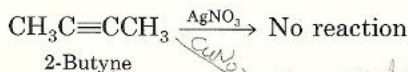
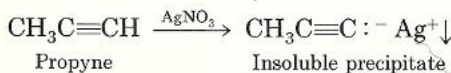


Acetylene is a reactive substance. When being liquefied under pressure, it is liable to explode violently if subjected to heat or shock. At atmospheric pressure, however, acetylene is soluble in acetone (25 volumes of acetylene for each volume of acetone) and forms a stable mixture. Therefore, for commercial purposes acetylene can be safely transported in pressure cylinders saturated with acetone. At higher pressure, acetylene can be stored safely in the presence of an inert gas such as nitrogen.

#### 4.14 Visual Tests for Alkynes

Alkynes, like alkenes, are unsaturated hydrocarbons. Therefore, the same tests that were used to distinguish between alkenes and alkanes apply to alkynes. Alkynes give positive tests with  $\text{Br}_2$  in carbon tetrachloride, with dilute  $\text{KMnO}_4$  (Baeyer test) and with  $\text{H}_2\text{SO}_4$ .

Terminal alkynes,  $\text{RC}\equiv\text{CH}$ , can be differentiated from nonterminal alkynes,  $\text{RC}\equiv\text{CR}$ , by means of reactions involving heavy metal ions ( $\text{Ag}^+$  or  $\text{Cu}^+$ ). Terminal alkynes form insoluble precipitates; nonterminal alkynes do not react and leave a clear solution.



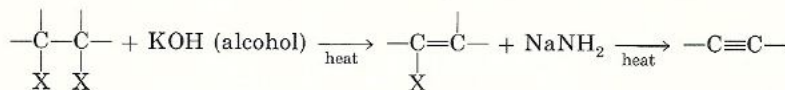
Heavy metal acetylides are unstable and, if allowed to dry, are likely to explode. Consequently, they should be destroyed while still wet by treating them with warm nitric acid. The strong mineral acid regenerates the alkyne.



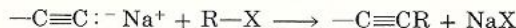


Alkynes have physical properties similar to those of alkenes. [Sec. 4.10]  
 Terminal alkynes react with certain metals to form salts called metal acetylides. [Sec. 4.11B]

Alkynes may be synthesized by dehydrohalogenation of vicinal dihalides



or by reaction of sodium acetylide with a 1° alkyl halide



Alkynes undergo reactions similar to those of alkenes. [Sec. 4.11A, B]

Addition of H<sub>2</sub>O in the presence of dilute H<sub>2</sub>SO<sub>4</sub> and an HgSO<sub>4</sub> catalyst produces first an unstable enol that is converted into a keto group, a process called enol-keto tautomerism. [Sec. 4.12]

Acetylene is the only alkyne of significant industrial importance. [Sec. 4.12D]

Alkynes decolorize Br<sub>2</sub> in CCl<sub>4</sub> and also give a positive Baeyer test. Only terminal alkynes form precipitates with heavy metal ions such as Ag<sup>+</sup> and Cu<sup>+</sup>. [Sec. 4.13]

## Key Terms

dienes	allylic carbocation	isoprene units
conjugated	delocalization	alkyne
nonconjugated	resonance	carbon-carbon triple bond
isolated	resonance hybrid	C <sub>n</sub> H <sub>2n-2</sub>
trienes	contributing structures	metal acetylides
tetraenes	resonance energy	enol
polyenes	isoprene	keto
heat of hydrogenation	vulcanization	enol-keto tautomerism
1,2-addition	copolymerization	tautomers
1,4-addition	terpenes	

## Exercises

### Structure and Nomenclature of Dienes, Polyenes, and Alkynes [Secs. 4.1, 4.9]

4.1 Draw structures for each of the following.

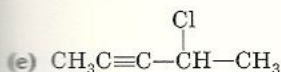
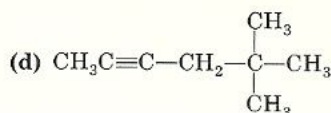
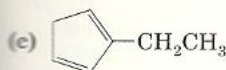
- |                                 |                                |
|---------------------------------|--------------------------------|
| (a) 2,4-Heptadiene              | (b) 3,4-Dimethyl-1,4-octadiene |
| (c) 2-Methyl-1,3-cyclohexadiene | (d) Isoprene                   |
| (e) 1,3,5,7-Cyclooctatetraene   | (f) 2-Heptyne                  |
| (g) 1,4-Heptadiyne              | (h) Cyclooctyne                |
| (i) Vinylacetylene              | (j) Cyclopropylacetylene       |
| (k) 3,3-Dimethyl-1-hexyne       | (l) Allylacetylene             |

4.2 Classify the dienes in Exercise 4.1 as conjugated or isolated.

4.3 Name the following compounds according to the IUPAC rules.

- |   |   |
|---|---|
| (a) (CH <sub>3</sub> ) <sub>2</sub> CHCH=CHCH <sub>2</sub> CH=CH <sub>2</sub> | (b) CH <sub>2</sub> =CBr-CH=CH <sub>2</sub> |
|---|---|





4.4 Write the structural formulas and give the IUPAC names for all dienes with the indicated molecular formulas.

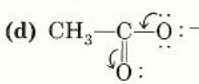
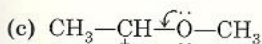
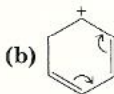
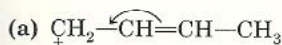
(a)  $\text{C}_5\text{H}_8$  (5 structural isomers)      (b)  $\text{C}_6\text{H}_{10}$  (16 structural isomers)

4.5 Draw the structural formulas and give the IUPAC names for all alkynes with the molecular formulas shown in Exercise 4.4.

**Resonance and Resonance Contributing Structures** [Sec. 4.5]

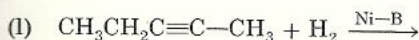
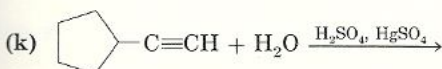
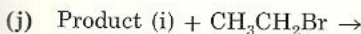
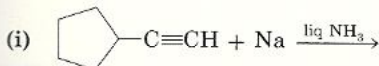
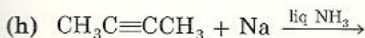
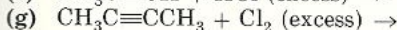
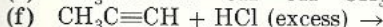
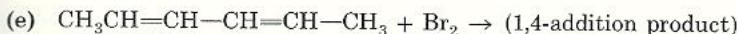
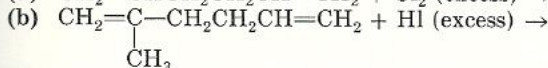
4.6 When an electrophile ( $\text{H}^+$ , for example) attacks 1,3-butadiene, it always does so at C-1 rather than at C-2. How do you account for this fact? (*Hint*: Draw the structures of the carbocations formed in each case.)

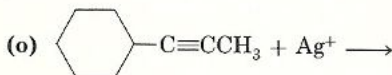
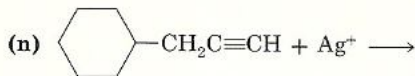
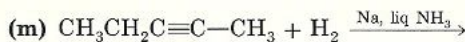
4.7 Write a resonance contributing form for each structure (the delocalization of electrons is indicated by the arrows).



**Preparations and Reactions of Dienes and Alkynes** [Secs. 4.2, 4.4, 4.11, 4.12]

4.8 Draw the structure of the product for each reactions. If no reaction occurs, state so.)





4.9 Starting from acetylene write equations for the preparation of the compounds indicated here. If more than one step is required, show each step clearly.

- (a) Ethane (b) Ethyl chloride (c) 1,1-Dichloroethane  
(d) 1,1,2,2-Tetrabromoethane (e) 1-Butyne (f) 3-Hexyne  
(g) *cis*-3-Hexene (h) *trans*-3-Hexene

4.10 Starting with 1-pentyne in each case, show how you would convert it to the products indicated. You may use any other required organic or inorganic chemicals. If more than one step is necessary, show each step clearly.

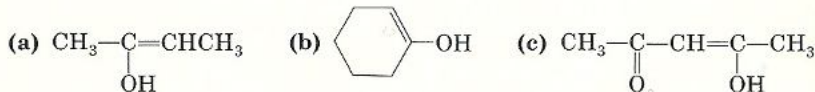
- (a) Pentane (b) 1,1,2,2-Tetrabromopentane  
(c) 2-Pentanone,  $\text{CH}_3-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{CH}_2\text{CH}_2\text{CH}_3$  (d) 1-Pentene

- (e) 2,2-Dichloropentane (f) 3-Heptyne

4.11 How can (a) 1-hexene be converted to 1-hexyne and (b) 1-bromopentane be converted to 1-pentyne?

#### Enol-Keto Tautomerism [Sec. 4.12D]

4.12 Write the structure of the keto tautomer corresponding to each of the following enol forms.



#### Visual Tests and Identification of Structures [Secs. 4.12, 4.13]

4.13 An unknown compound A has the molecular formula  $\text{C}_5\text{H}_8$ . Suggest a possible structure for A from these data.

- (1) One mole of A takes up two moles of bromine.  
(2) A does not react with either sodium metal or heavy metal ions ( $\text{Ag}^+$  or  $\text{Cu}^+$ ).

- (3) Ozonolysis of one mole of A yields two moles of  $\text{H}-\overset{\text{H}}{\underset{|}{\text{C}}}=\text{O}$  and one mole of  $\text{O}=\overset{\text{CH}_3}{\underset{|}{\text{C}}}-\overset{\text{H}}{\underset{|}{\text{C}}}=\text{O}$ .

4.14 An unknown compound B has the molecular formula  $\text{C}_5\text{H}_8$ . Suggest a possible structure for B from these data.

- (1) One mole of B takes up two moles of hydrogen.  
(2) B forms a precipitate with  $\text{Ag}^+$  or  $\text{Cu}^+$ .  
(3) Treatment of B with  $\text{H}_2\text{O}$  in the presence of dilute  $\text{H}_2\text{SO}_4$  and mercuric sulfate catalyst yields  $\text{CH}_3\text{CH}_2\text{CH}_2\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{CH}_3$  as the main product.

4.15 An unknown compound C has the molecular formula  $\text{C}_5\text{H}_8$ . Suggest a possible structure for C from these data.

- (1) One mole of C takes up two moles of chlorine.  
(2) Compound C decolorizes a solution of  $\text{Br}_2$  in  $\text{CCl}_4$ .  
(3) Compound C forms no precipitate with either  $\text{Ag}^+$  or  $\text{Cu}^+$ .



- (4) Treatment of C with  $\text{H}_2\text{O}$  in the presence of dilute sulfuric acid and mercuric sulfate catalyst yields an equimolar mixture of  $\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_3$ .

### Definitions of Terms

- 4.16 Define or give an example of (a) conjugated diene, (b) resonance contributing structures, (c) allyl carbocation, (d) 1,2-addition, (e) 1,4-addition, (f) sesquiterpene, (g) copolymerization, (h) vulcanization, (i) acetylide ion, (j) enol-keto tautomerism.

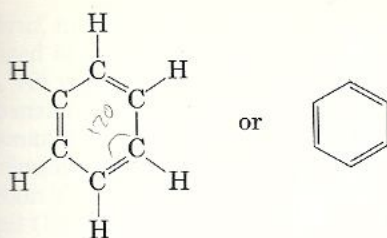
# Benzene and Aromatic Compounds

The term *aromatic* was used originally to designate compounds with spicy or sweet-smelling odors derived from plants. Often these pleasantly fragrant substances contained a variety of groups, such as  $-\text{OCH}_3$ ,  $-\text{CH}=\text{CH}-\text{COOH}$ ,

$$\begin{array}{c} \text{H} \\ | \\ -\text{C}=\text{O} \end{array}$$
 attached to a  $\text{C}_6\text{H}_5$  unit. This same unit was found also among products obtained by distillation of coal tar. One such product, phenol, has the formula  $\text{C}_6\text{H}_5\text{OH}$ , and another, **benzene**, has the formula  $\text{C}_6\text{H}_6$  or  $\text{C}_6\text{H}_5-\text{H}$ . With time, as odorless and vile-smelling substances that contained the  $\text{C}_6\text{H}_5$  unit were discovered, the original meaning of the term aromatic was abandoned. The expression *aromatic compounds* came to mean benzene and derivatives of benzene. Today a compound is said to be **aromatic** if it is *benzene-like in its properties*. This definition includes benzene and benzene derivatives as well as other substances that, although they bear no resemblance to benzene superficially, nevertheless behave like benzene. Obviously, we must begin our study of aromatic compounds with a discussion of benzene itself.

## 5.1 Structure of Benzene: Resonance Description

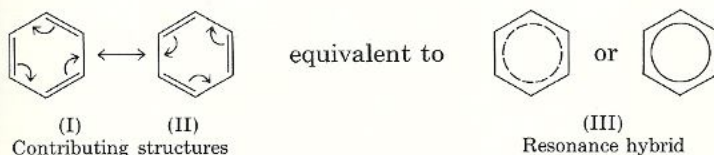




Each carbon in benzene is attached to three atoms and is therefore  $sp^2$  hybridized. As expected, the bond angles in benzene are  $120^\circ$ . For two principal reasons, however, the description just given is unsatisfactory.

1. If the structure we have shown were correct, we would expect benzene to be "1,3,5-cyclohexatriene." If benzene were 1,3,5-cyclohexatriene, we would expect the molecule to have the shape of an irregular hexagon with three C—C bond lengths of 1.54 Å (typical of single bonds) and three C=C bonds of 1.34 Å (typical of double bonds). However, evidence from x-ray diffraction experiments reveals that *all* carbon-carbon bonds in benzene are of equal length, 1.39 Å.
2. If the structure of benzene we have shown were correct, we would expect benzene to undergo addition reactions. In fact, the typical reaction of benzene (and other aromatic compounds) is **substitution**, rather than addition.

The true structure of benzene can be explained by the concept of resonance. Recall that according to the resonance theory (Sec. 4.5), whenever a substance can be represented by two or more equivalent or nearly equivalent structures that differ only in the position of valence electrons, the actual molecule does not correspond to any of the *contributing structures* but is a *resonance hybrid* of all of them. Thus, benzene is actually a resonance hybrid (III) of the two imaginary contributing structures (I and II).



In the resonance hybrid, the broken and solid circles within the hexagon represent the even distribution of the valence electrons over the six carbon atoms.

## Structure of Benzene: 5.2 Molecular Orbital Description

The delocalization of electrons over the six carbons may easily be seen in the molecular orbital picture of benzene. It should be emphasized that the results of the molecular orbital approach are identical to those of the resonance method.

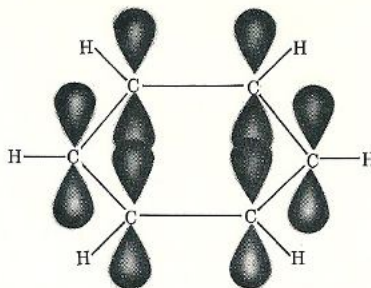


Figure 5.1 Molecular orbital picture of benzene without  $p$  orbital overlap.

Figure 5.1 shows the molecular orbital picture of benzene without  $p$ -orbital overlap.

To complete the picture, it should be remembered that any pair of adjacent  $p$  orbitals is capable of side-side overlap to form a  $\pi$  bond. Three double bonds can be formed by overlap of the  $p$  orbitals of C-1 and C-2, C-3 and C-4, and C-5 and C-6 (Fig. 5.2a) or by overlap of  $p$  orbitals of C-2 and C-3, C-4 and C-5, and C-6 and C-1 (Fig. 5.2b).

Which of these structures is the correct one? Neither. They both are contributing forms that have no physical reality. The true structure of benzene is a

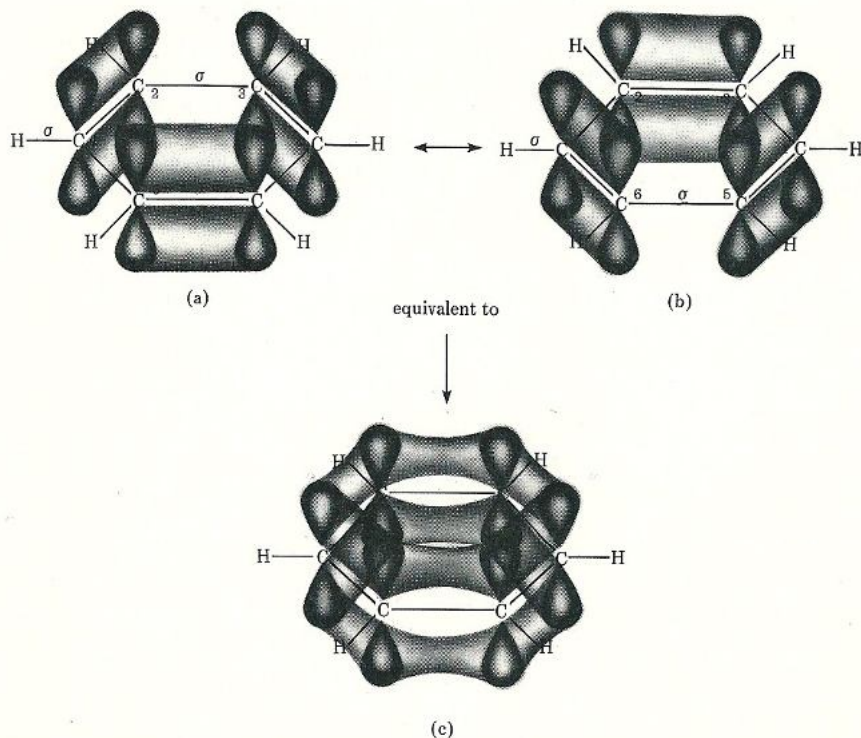


Figure 5.2 (a, b) Imaginary contributing structures of the resonance hybrid (c) that represents the true structure of benzene.



hybrid, not a mixture of (a) and (b). In the hybrid, the  $\pi$ -electron cloud is delocalized all over the ring (Fig. 5.2c).

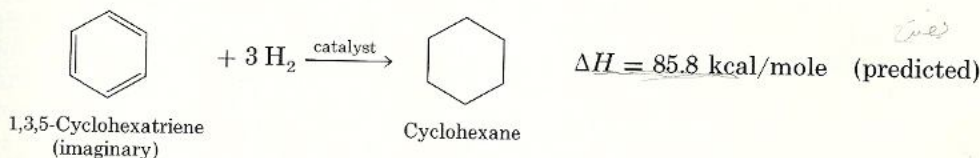
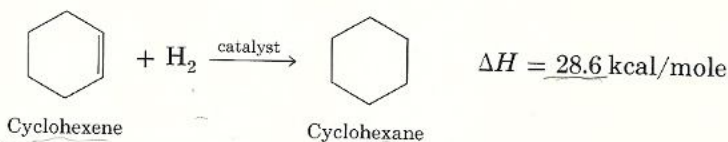
An immediate benefit of the resonance or the molecular orbital description of benzene is that it agrees with the physical measurements of the molecule. As a resonance hybrid, we expect benzene to be a planar molecule having the shape of a regular hexagon, with bond angles of  $120^\circ$ . We also expect *all* the carbon-carbon bond distances to be intermediate ( $1.39 \text{ \AA}$ ) between the usual C—C single bond ( $1.54 \text{ \AA}$ ) and the typical C=C double bond ( $1.34 \text{ \AA}$ ). All the experimental data confirm our expectations.

The resonance picture helps also to explain the lack of reactivity of benzene toward addition. The reasoning is that the delocalization of  $\pi$  electrons confers a great degree of stability on benzene. This degree of stability is so great that the  $\pi$  bonds of the molecule will normally resist breaking. The typical reaction of benzene is substitution, which leaves the  $\pi$ -electron cloud around the ring intact, rather than addition, which disrupts the  $\pi$  cloud around the ring.\*

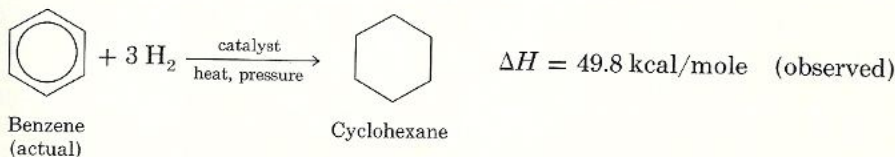
One line of experimental evidence showing that the stability of benzene is due to the  $\pi$  cloud around the ring is discussed in the next section.

## Stability of Benzene: Resonance Energy 5.3

The heat of hydrogenation of cyclohexene is  $28.6 \text{ kcal/mole}$ . If a benzene molecule has three localized double bonds—that is, if it were 1,3,5-cyclohexatriene—we would expect its heat of hydrogenation to be  $3 \times 28.6$  or  $85.8 \text{ kcal/mole}$ .



Actually, when benzene is hydrogenated to cyclohexane, *only 49.8 kcal/mole of energy is liberated.*



\* Addition reactions (hydrogenation, bromination, etc.) can take place, but vigorous conditions, such as high heat or high pressure, are needed.

The amount of energy released on hydrogenation of benzene is 36.0 kcal/mole less ( $85.8 - 49.8 = 36.0$  kcal/mole) than that predicted for the hypothetical 1,3,5-cyclohexatriene. The fact that benzene liberates 36 kcal/mole less energy than predicted can only mean that benzene contains 36 kcal/mole less energy or, in other words, that benzene is more *stable* by 36 kcal/mole than predicted. Obviously, this greater stability of the molecule must come from the fact that the  $\pi$  electrons in benzene are delocalized. We refer to this amount of stabilization between the energy liberated by the actual structure of benzene, with its delocalized  $\pi$  electrons, and the energy liberated by the hypothetical 1,3,5-cyclohexatriene, with its localized  $\pi$  electrons, as the **resonance energy**. It is the preservation of this large resonance energy that is the source of benzene's tendency to undergo substitution rather than addition reactions and gives it its aromatic character.

**Problem 5.1** Hydrogenation of one mole of naphthalene,  $C_{10}H_8$ , with five moles of hydrogen releases 82.0 kcal of heat. Assuming the heat of hydrogenation of a normal double bond to be 28.6 kcal/mole, calculate the resonance energy of naphthalene.

Recall that we defined aromatic compounds as those with benzene-like properties. Like benzene, aromatic compounds tend to undergo substitution rather than addition reactions and, for the same reason, to retain their resonance energy. Can we predict which compound is aromatic? The answer is yes, as will be shown in the next section.

## 5.4 Aromatic Character: The $(4n + 2)$ $\pi$ Rule






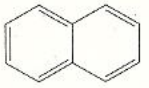
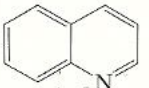
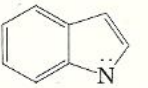
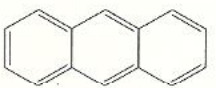
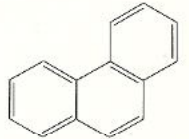
Extensive studies have revealed that aromatic character, or **aromaticity**, is associated with several structural requirements. First, aromatic compounds are *cyclic* structures that contain what *looks like* a continuous system of alternating double and single bonds. Actually, the  $\pi$  electrons are delocalized through overlap of adjacent  $p$  orbitals. To permit such delocalization, a second structural requirement must be met: aromatic compounds must be *planar*. Finally, aromaticity is possible only if the number of  $\pi$  electrons in the compound is  $(4n + 2)$ , where  $n$  is zero or a positive integer ( $n = 0, 1, 2, 3$ , and so on). Examples of aromatic compounds that obey this  $(4n + 2)$   $\pi$  rule, also known as **Hückel's rule**, are shown in Table 5.1.

A glance at the table reveals that some aromatic compounds, such as naphthalene, anthracene, or phenanthrene, resemble benzene structurally: they consist of two or more benzene rings fused together. Others, such as pyrrole, bear no structural resemblance to benzene. Nevertheless, pyrrole and all other compounds listed in Table 5.1 show aromatic properties because they satisfy the  $(4n + 2)$   $\pi$  rule.\*

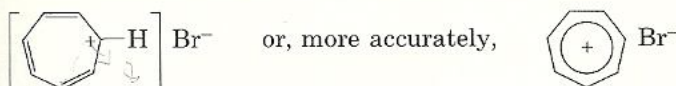
\* The two nonbonded electrons *within* the ring of pyrrole, furan, and other molecules shown in the table are part of the  $\pi$  system and should be counted when applying Hückel's rule.



Table 5.1 Examples of Aromatic Compounds Containing  $(4n + 2) \pi$  Electrons

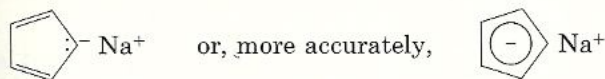
$n$	$4n + 2$	Structure and name of aromatic compound				
1	6					
		Benzene	Pyridine	Pyrrole	Furan	Thiophene
2	10					
		Naphthalene	Quinoline	Indole		
3	14					
		Anthracene	Phenanthrene			

Aromaticity according to the  $(4n + 2) \pi$  rule shows up even more strikingly in certain organic ions. All carbocations encountered up to this point have been very reactive, short-lived intermediates. Tropylium bromide, on the other hand, is a stable, high-melting salt that is soluble in water.



Tropylium bromide

The tropylium ion is a seven-membered ring that contains three double bonds. Since the ring has a total of six  $\pi$  electrons, it is therefore aromatic. Similarly, cyclopentadiene, in contrast to nearly all other hydrocarbons, is quite acidic. It is readily converted to its sodium salt.



Sodium cyclopentadienide

The cyclopentadienide anion,  $\text{C}_5\text{H}_5^-$ , is also aromatic and particularly stable because the five-membered ring has a sextet or  $\pi$  electrons, two double bonds from the ring and a pair of nonbonded electrons.

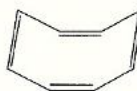
What does it mean if the sum of the  $\pi$  electrons in a cyclic, conjugated system does not follow the  $(4n + 2) \pi$  rule? It means, simply, that the compound is not aromatic. Cyclooctatetraene, for example, contains a  $\pi$  system of electrons. Because no integral value of  $n$  can give the number 8 according to the  $(4n + 2) \pi$  rule, cyclooctatetraene is not aromatic. As predicted, cyclooctatetraene reacts readily with bromine in the dark and with cold dilute permanganate, just as an ordinary alkene does. Furthermore, x-ray diffraction studies have

shown that cyclooctatetraene has a "tub" shape rather than the planar shape required for an aromatic compound.



Eight  $\pi$  electrons

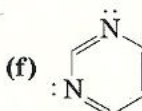
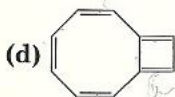
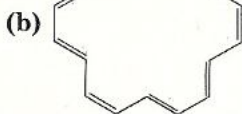
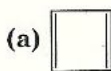
Cyclooctatetraene  
(not aromatic)



"Tub" shape of cyclooctatetraene

In our discussion of aromaticity we have represented benzene and other compounds as having alternating double and single bonds. This was done as a matter of convenience to illustrate the application of the  $(4n + 2) \pi$  rule. Keep in mind that in aromatic compounds such bonds do not really exist; in the actual structure the  $\pi$  bonds are delocalized.

**Problem 5.2** Predict which of the following structures might be expected to possess aromatic character. Explain the basis for your choice.



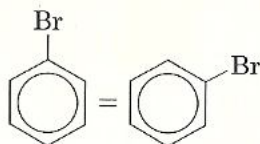
## 5.5 Nomenclature of Aromatic Compounds

Now that we are familiar with the criteria for aromaticity, we should learn how to name members of the various families of aromatic compounds, especially the derivatives of benzene. We will then be ready to study their reactions.

### A Monosubstituted Benzenes

Because all six positions in benzene are equivalent, there is no need to specify by a number the position of a substituent for monosubstituted benzenes. All that is required is to indicate the nature of the substituents present. For example, replacement of one of the hydrogens by bromine yields a single product, bromobenzene.

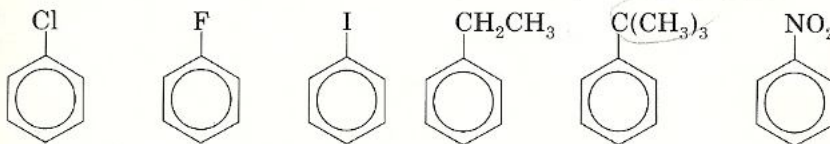




Bromobenzene

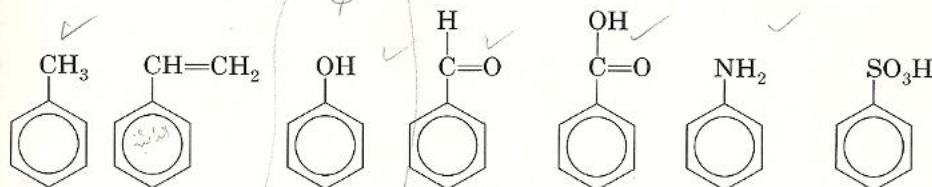
The two structures represent the same molecule because all positions are equivalent.

Other monosubstituted benzenes that can be named in the same manner, by placing the name of the substituent in front of the word "benzene," are



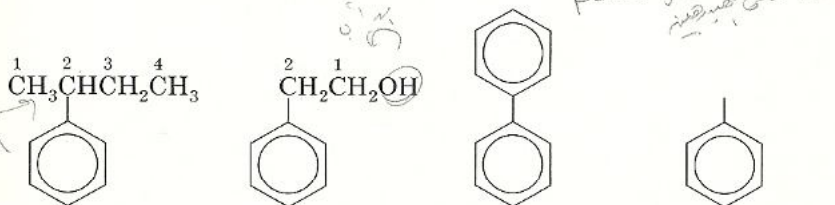
Chlorobenzene Fluorobenzene Iodobenzene Ethylbenzene tert-Butylbenzene Nitrobenzene

Some monosubstituted benzenes are considered parent compounds because they occur so frequently. For that reason they are given common names that you should memorize.



Toluene Styrene Phenol Benzaldehyde Benzoic acid Aniline Benzenesulfonic acid

Sometimes it is more convenient to name the benzene ring as a substituent, as in the following structures.



2-Phenylbutane

2-Phenylethanol

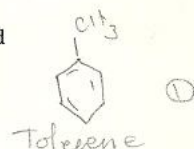
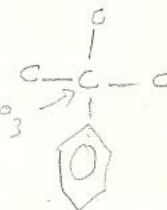
Biphenyl

The phenyl group,  $C_6H_5$   
(Ph or  $\phi$ )

The **phenyl** group, symbolized by Ph or  $\phi$ , is a benzene from which one hydrogen has been removed. Another common aromatic substituent is the **benzyl** group, derived by removing a hydrogen from the  $CH_3$  group in toluene.

phenyl  $\rightarrow$  بنزين منقوص الهيدروجين

benzyl  $\rightarrow$  تولىل منقوص الهيدروجين

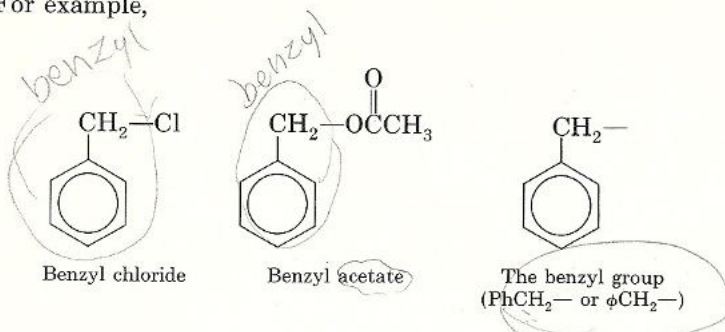


removed H



benzyl

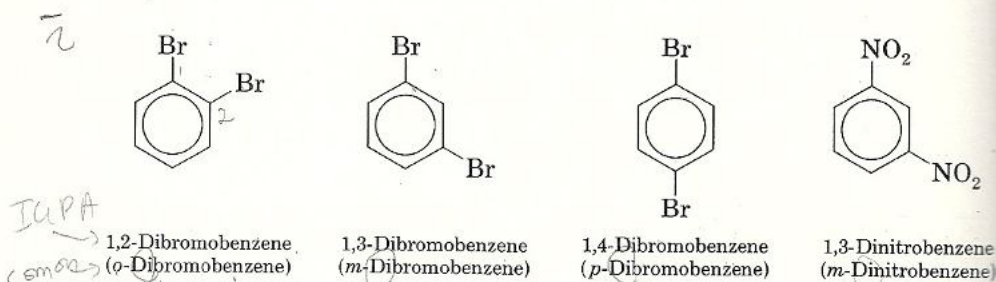
For example,



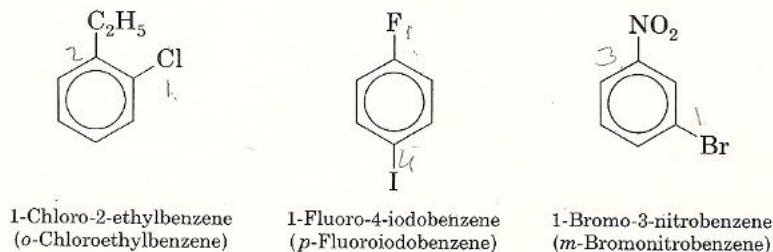
The benzyl group is often abbreviated as  $\text{PhCH}_2-$  or  $\phi\text{CH}_2-$ .

## B Disubstituted Benzenes

All disubstituted benzenes, no matter what the substituents, can give rise to three possible isomers. To differentiate between the isomers, the relative positions of the substituents are designated by numbers or, more commonly, by the prefixes ortho (o-), meta (m-), or para (p-).

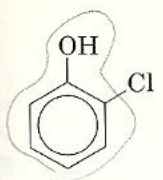
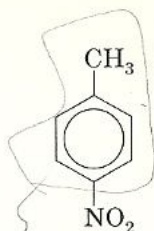
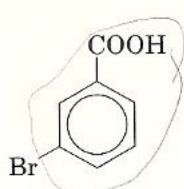
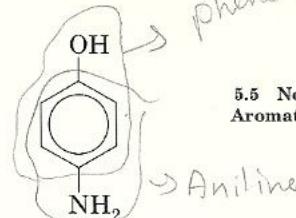


When the substituents are different, they are listed in alphabetical order.  
For example,

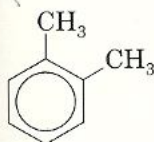


If one of the substituents is part of a parent compound, then the disubstituted benzene is named as a derivative of the parent compound.

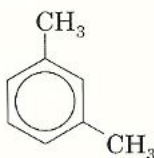


2-Chlorophenol  
(o-Chlorophenol)4-Nitrotoluene  
(p-Nitrotoluene)3-Bromobenzoic acid  
(m-Bromobenzoic acid)4-Aminophenol  
(p-Aminophenol)  
or  
4-Hydroxyaniline  
(p-Hydroxyaniline)

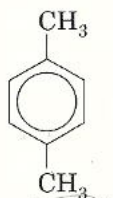
Like monosubstituted benzenes, certain disubstituted benzenes are referred to by their common names. The dimethylbenzenes, for example, are known as xylenes.



o-Xylene

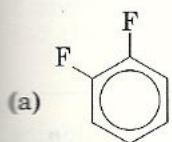


m-Xylene

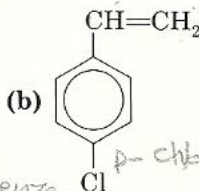


p-Xylene

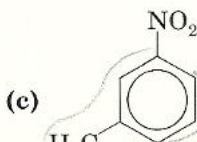
**Problem 5.3** Name each of the following structures using ortho, meta, and para designations for disubstituted compounds.



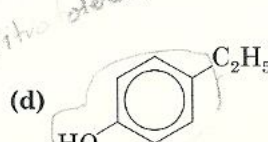
o-Difluorobenzene



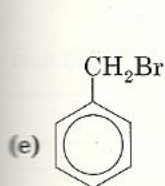
p-chlorostyrene



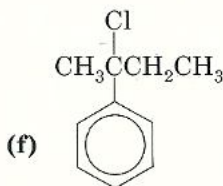
(c)



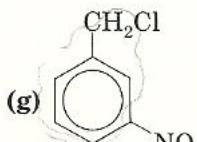
(d)



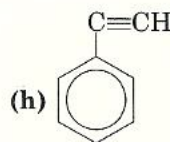
benzyl bromide



(f)



(g)



(h)

**Problem 5.4** Draw the structure of each of the compounds named.

(a) 2-Phenylpentane

(b) p-Nitroethylbenzene

(c) m-Chlorobenzaldehyde

(d) o-Ethylaniline

(e) m-Bromobenzenesulfonic acid

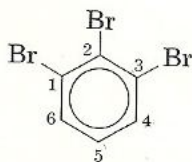
(f) 2,2-Dimethyl-1-phenylbutane

(g) p-Bromotoluene

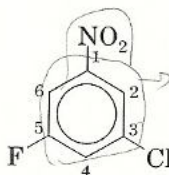
(h) m-Nitrobenzoic acid

## C Polysubstituted Benzenes

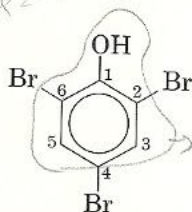
When three or more substituents are present, the ring must be numbered and the positions of the substituents must be specified by numbers. As with other classes of compounds previously encountered, the numbering starts with one substituent and continues around the ring so as to use the lowest possible numbers for the other substituents. When the substituents are different the last one named is understood to be in position 1. As with disubstituted benzenes, if one of the group is part of the parent compound, then the carbon that bears the functional group of the parent compound is assigned the number 1.



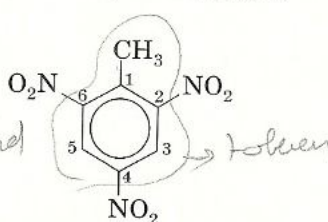
1,2,3-Tribromobenzene  
(not 1,2,6-Tribromobenzene)



3-Chloro-5-fluoronitrobenzene  
(nitro on carbon 1)



2,4,6-Tribromophenol  
(OH on carbon 1)

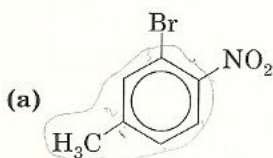


2,4,6-Trinitrotoluene (TNT)  
(CH<sub>3</sub> on carbon 1)

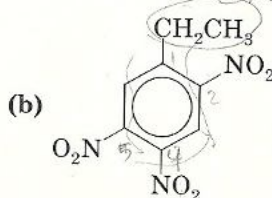
**Problem 5.5** Write the structural formulas that correspond to the following names.

- |                                    |                                     |
|------------------------------------|-------------------------------------|
| (a) 2,6-Dibromotoluene             | (b) 1,2,4,5-Tetrachlorobenzene      |
| (c) 2-Benzyl-3-nitro-5-bromophenol | (d) 2,4,6-Tribromoaniline           |
| (e) 3,5-Dinitrobenzoic acid        | (f) 2,3-Dichlorobenzaldehyde        |
| (g) 2,4-Dinitrofluorobenzene       | (h) 3,5-Dibromobenzenesulfonic acid |

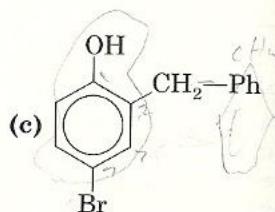
**Problem 5.6** Give names for the following structures.



3-Bromo-4-nitrotoluene

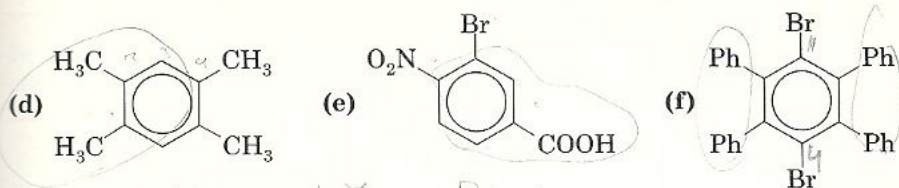


2,4,6-Trinitroethylbenzene



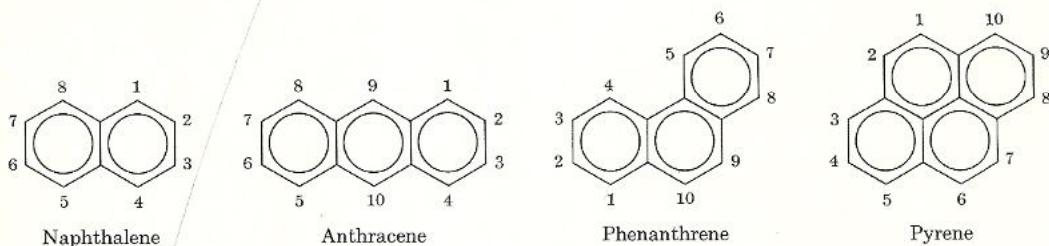
3-Bromo-2-phenylphenol



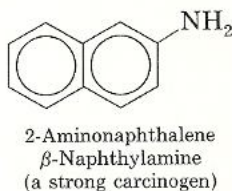
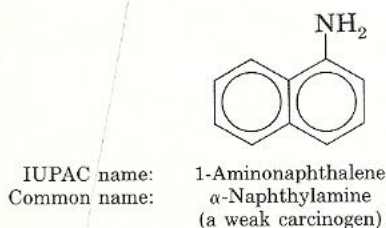


## D Polynuclear Aromatic Hydrocarbons

Benzene rings may be fused together to form *polynuclear aromatic hydrocarbons*. Examples of polynuclear aromatic hydrocarbons containing two, three, and four rings are

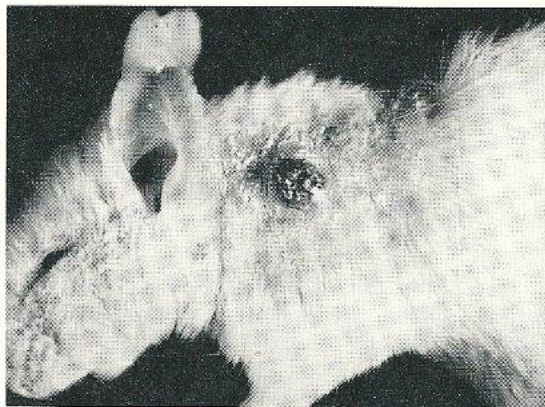
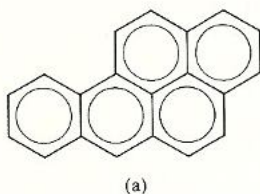
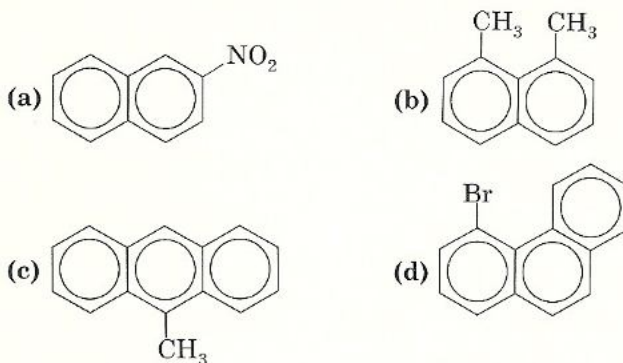


In naphthalene, positions 1, 4, 5, and 8 are equivalent, as are positions 2, 3, 6, and 7. Often, the 1-position in naphthalene is called the *alpha* ( $\alpha$ ) position and C-2 the *beta* ( $\beta$ ) position. Thus,



**Problem 5.7** Write the structures of

- |                                |                                   |
|--------------------------------|-----------------------------------|
| (a) 2-Methylnaphthalene        | (b) 1-Chloronaphthalene           |
| (c) $\alpha$ -Nitronaphthalene | (d) $\beta$ -Fluoronaphthalene    |
| (e) 1,5-Dimethylnaphthalene    | (f) 1,3,6,8-Tetranitronaphthalene |
| (g) 1-Bromoanthracene          | (h) 9-Bromoanthracene             |
| (i) 1,5-Dinitroanthracene      | (j) 1-Bromophenanthrene           |
| (k) 3-Bromophenanthrene        | (l) 4,5-Dimethylphenanthrene      |

**Problem 5.8** Name the following structures.

(b)

**Figure 5.3** (a) 3,4-Benzopyrene, a potent carcinogen. (b) Two stages in the development of a skin tumor induced in the mouse using 3,4-benzopyrene. [From J. C. Arcos, "Cancer: chemical factors in environment," part 1. *American Laboratory*, 10(6), 65 (1978). Reprinted with permission.]

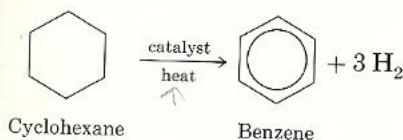


**Problem 5.9** Which other position(s) in monosubstituted anthracenes are equivalent to (a) position 1, (b) position 2, and (c) position 9?

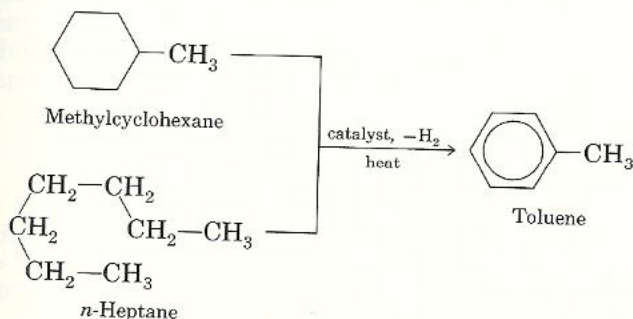
A number of polycyclic aromatic hydrocarbons are carcinogens. 3,4-Benzopyrene (Fig. 5.3a) has the dubious distinction of being the most widely distributed hydrocarbon carcinogen in the environment. The compound is the main hydrocarbon carcinogen in cigarette smoke, auto emissions, and soot.

## Sources of Aromatic Compounds 5.6

Although compounds that contain the benzene ring are widely dispersed in nature, the two major sources of aromatic compounds are coal tar and petroleum. Until about 1940, benzene, toluene, xylenes, naphthalene, anthracene, and various other aromatic compounds were obtained by the distillation of coal tar, a by-product in the manufacture of coke for steel. In the past 40 years, the demand for aromatic compounds has far outstripped the amount available from coal tar, so that the major source of the commercially significant aromatic compounds (benzene, toluene, and xylenes) is now the petroleum industry. Alkanes and cycloalkanes found in petroleum are converted to benzene and alkylbenzenes by catalytic dehydrogenation. Benzene, for example, is synthesized on a large scale by dehydrogenation of cyclohexane.



A cyclic precursor is not always required, since cyclization of an aliphatic chain occurs in the same process. Thus, toluene can be obtained by the dehydrogenation of methylcyclohexane or of *n*-heptane, both of which are found in petroleum.



Xylenes are also made industrially in the same manner from dimethylcyclohexanes or from the appropriate octanes found in petroleum.

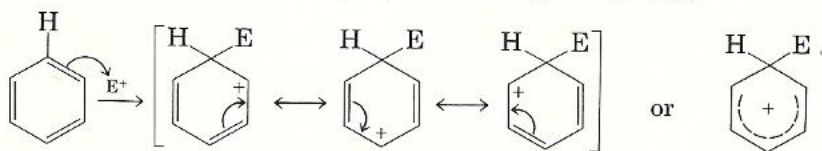
Benzene, toluene, and xylenes are the basic raw materials for most other aromatic compounds. Derivatives are obtained from these hydrocarbons by reactions that are discussed in the sections that follow.

**Problem 5.10** Assuming that no rearrangement occurs during dehydrogenation, predict the products obtained from the dehydrogenation of (a) 1,2-dimethylcyclohexane, (b) 1,3-dimethylcyclohexane, and (c) 1,4-dimethylcyclohexane.

## 5.7 Electrophilic Aromatic Substitution: General Mechanism

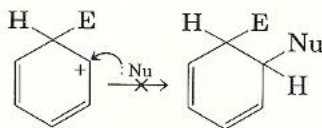
Because the aromatic ring is extremely stable, a highly reactive agent is required to react with the benzene ring. The aromatic ring, with its delocalized  $\pi$  electrons, is also an electron-rich system. We might therefore expect that attack on the ring takes place by means of an electron-deficient species, or an **electrophile**. This is indeed the case. The reaction of benzene with a typical electrophile,  $E^+$ , is similar to the addition of an electrophile to an alkene, and is shown as step (1) of the reaction mechanism.

**Step 1.** The electrophile  $E^+$  approaches the  $\pi$  cloud of the aromatic ring and forms a bond to carbon, creating a positive charge in the ring.



The resulting carbocation has three important contributing structures that spread the positive charge over the other five carbon atoms, although more so on the carbons that are ortho and para to the position attacked by the electrophile.

The intermediate carbocation has two possible fates. It could react with an electron-rich species, a nucleophile,  $:Nu$ , to give an addition product. With alkenes, this is the normally observed process. If this were to happen to aromatic compounds, however, the product that would result, a cyclohexadiene, would no longer have the great amount of resonance energy characteristic of the aromatic system.

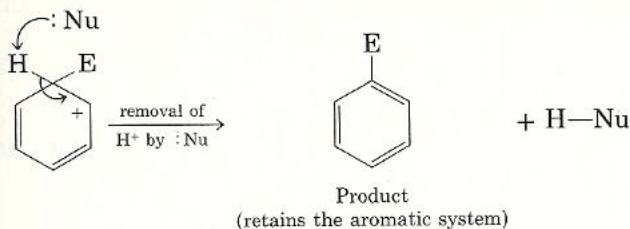


Addition of a nucleophile to the carbocation intermediate would destroy the aromatic system

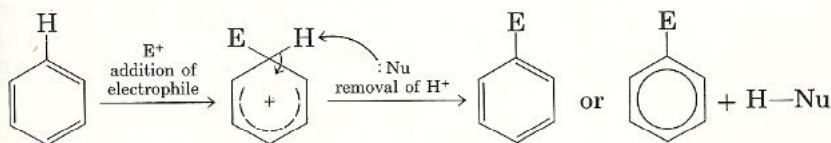
To retain the aromatic system, the carbocation does *not* combine with the nucleophile. Instead, the nucleophile abstracts a proton from the carbocation intermediate. The loss of the proton allows the electrons from the carbon-hydrogen bond to go back into the ring, thus restoring the aromatic system.



**Step 2.** The removal of the proton by the nucleophile, which leads to the restoration of the aromatic ring, is the second step in the reaction mechanism.



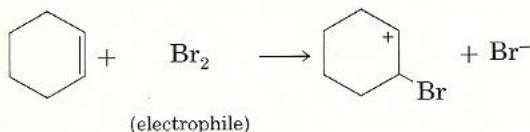
The net overall result of this two-step mechanism is the *substitution of the group  $E^+$  for a proton ( $H^+$ )*. Hence the name given to this mechanism is **electrophilic aromatic substitution**.



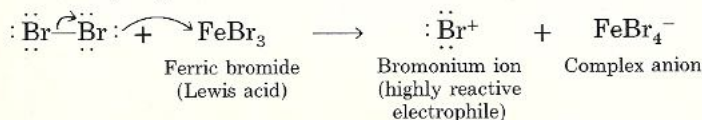
Now that we are familiar with the general aspects of electrophilic aromatic substitution, we are almost ready to study the reactions of specific electrophiles with benzene. Before doing so, however, let us see how electrophiles sufficiently reactive to attack the aromatic ring are generated.

## The Role of Catalysts in Electrophilic Aromatic Substitution 5.8

In almost all electrophilic aromatic substitutions a catalyst is needed for a reaction to take place. The catalysts are usually Lewis acids or a protonic acid. *The purpose of these catalysts is to generate powerful electrophiles.* Contrast, for example, the bromination of cyclohexene with the bromination of benzene. Bromination of cyclohexene (an alkene) takes place rapidly in the presence of molecular bromine,  $Br_2$ , and no catalyst is needed. The attacking electrophile in this case is molecular bromine itself.

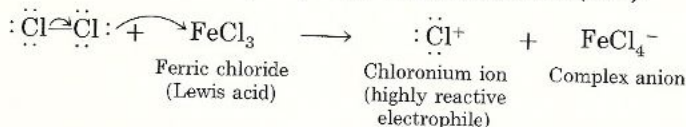


Bromine alone, however, is not a reactive enough electrophile to attack the benzene ring; a catalyst is needed to generate a more powerful electrophile,  $Br^+$ . The positively charged bromine ion, or **bromonium ion**, is formed when molecular bromine,  $Br_2$ , reacts with a Lewis acid, such as ferric bromide.

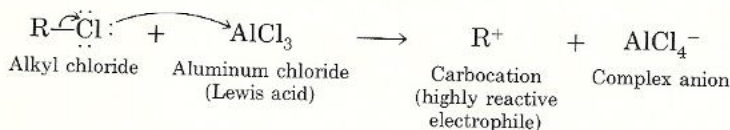


Ferric bromide, the Lewis acid, is by definition deficient in electrons. It will, therefore, combine with any species that is capable of donating an electron pair to it, which in this case is the bromine molecule. In the process, a complex anion,  $\text{FeBr}_4^-$ , and the bromonium ion,  $\text{Br}^+$ , are simultaneously formed. The latter is a more reactive electrophile than  $\text{Br}_2$  and is able to attack the benzene ring to eventually yield bromobenzene.

Similarly, chlorination of benzene requires the presence of a Lewis acid catalyst, usually ferric chloride. Again, the function of ferric chloride is to generate a highly reactive electrophile, the **chloronium ion** ( $\text{Cl}^+$ ).

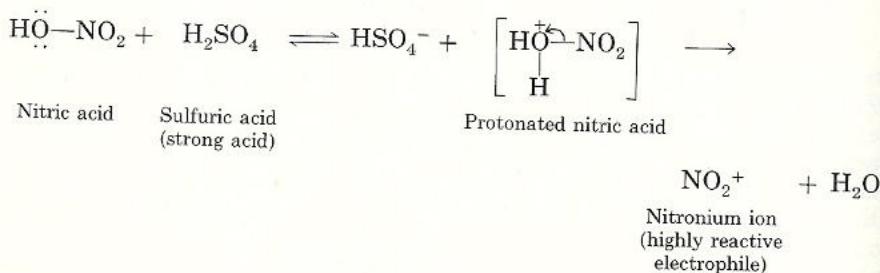


Aluminum chloride,  $\text{AlCl}_3$ , is another Lewis acid catalyst frequently used to generate highly reactive electrophiles. For example, the reaction of an alkyl chloride,  $\text{R}-\text{Cl}$ , with aluminum chloride yields a complex anion,  $\text{AlCl}_4^-$ , and a **carbocation**,  $\text{R}^+$ , a powerful electrophile.



The carbocation, once formed, can attack the aromatic ring, a process known as *alkylation* (see Section 5.9).

*Nitration* of benzene, the substitution of  $\text{NO}_2$  for H, and *sulfonation* of benzene, the substitution of  $\text{SO}_3\text{H}$  for H, usually also require the addition of a catalyst to help produce reactive electrophiles. The attacking electrophile in nitration is the **nitronium ion**,  $\text{NO}_2^+$ , whose formation is facilitated by the presence of sulfuric acid (the catalyst).



Sulfuric acid, the stronger acid, donates a proton to nitric acid, the weaker acid, to yield a protonated nitric acid intermediate and hydrogen sulfate. Upon losing water, the intermediate generates the nitronium ion,  $\text{NO}_2^+$ , a powerful electrophile.

Sulfonation of benzene is usually carried out in fuming sulfuric acid, which is a solution of  $\text{SO}_3$  in  $\text{H}_2\text{SO}_4$ . In sulfonation, an active electrophile is the  **$\text{SO}_3\text{H}^+$  ion** whose formation is brought about according to

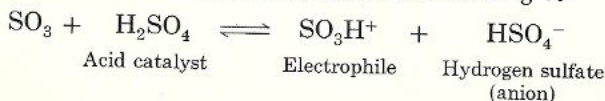




Table 5.2 The Electrophiles in Common Aromatic Substitution Reactions

Electrophile	Name of reaction
$\text{Cl}^+$ or $\text{Br}^+$	halogenation
$\text{R}^+$	alkylation
$\text{NO}_2^+$	nitration
$\text{SO}_3\text{H}^+$	sulfonation

As in nitration, sulfuric acid acts as a catalyst by providing a hydrogen ion to  $\text{SO}_3$ , thus creating the active electrophile  $\text{SO}_3\text{H}^+$ .

To recapitulate, acid catalysts are needed in electrophilic aromatic substitution reactions to generate reactive electrophiles. The electrophiles in common aromatic substitutions are shown in Table 5.2. Each of these electrophilic agents plays the same role as  $\text{E}^+$  does in the general mechanism of electrophilic aromatic substitution shown on page 135.

The common electrophilic aromatic substitutions of benzene are illustrated in the next section.

## Specific Electrophilic Aromatic Substitution Reactions 5.9

Halogenation, alkylation,\* nitration, and sulfonation are the typical electrophilic aromatic substitution reactions. These reactions are shown in Figure 5.4. Note that in each reaction the net result is the replacement of a hydro-

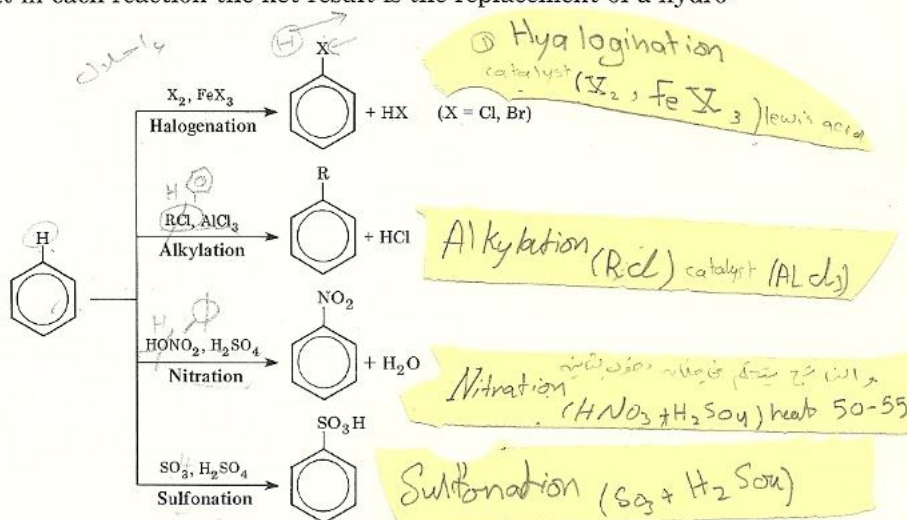


Figure 5.4 Common electrophilic aromatic substitution reactions.

\* The reaction, known as Friedel-Crafts alkylation, was discovered in 1877 by a French chemist, Charles Friedel, and an American, M. Crafts.

gen in benzene by one of the electrophiles listed in Table 5.2. The specific mechanism for each reaction also follows the general pattern described in Section 5.7.

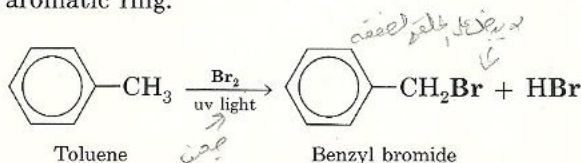
**Problem 5.11** Based on the general mechanism of electrophilic aromatic substitution shown in Section 5.7, and from the discussion in Section 5.8, write the mechanism for (a) the chlorination of benzene and (b) the nitration of benzene.

## 5.10 Side-Chain Reactions of Aromatic Compounds

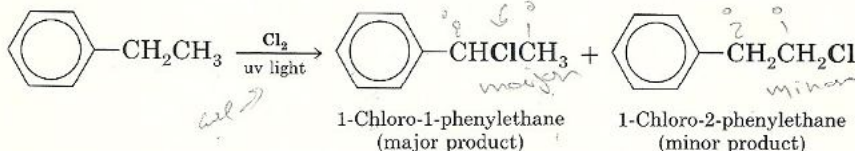
In the previous section methods for introducing a substituent directly into an aromatic ring via electrophilic substitution were examined. In this section we consider reactions involving alkyl side chains.

### A Halogenation of an Alkyl Side Chain

An alkylbenzene contains both an aliphatic and an aromatic portion. We might, therefore, expect the aliphatic portion (the alkyl side chain) to undergo free-radical substitution characteristic of alkanes (see Sec. 2.12) and the ring to undergo electrophilic substitution characteristic of benzene. This is indeed the case. For example, bromination of toluene in the presence of uv light (free-radical conditions) yields exclusively benzyl bromide; there is no substitution in the aromatic ring.

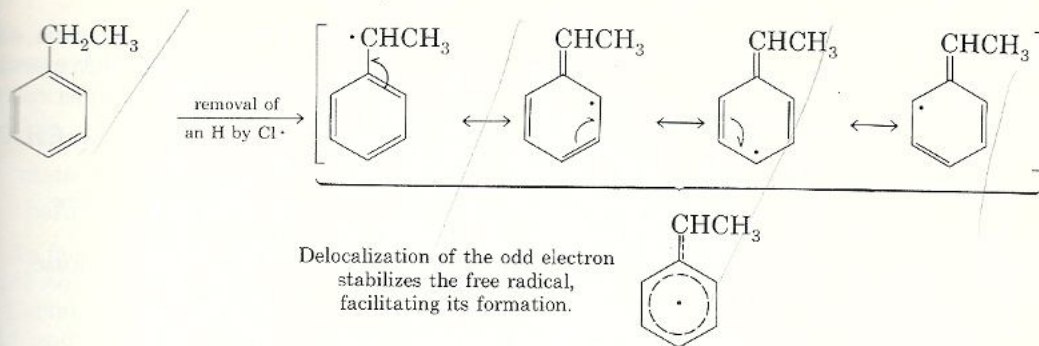


Similarly, when ethylbenzene is chlorinated under free-radical conditions, substitution occurs in the alkyl portion only, and the product formed is almost exclusively 1-chloro-1-phenylethane, with small amounts of 1-chloro-2-phenylethane.

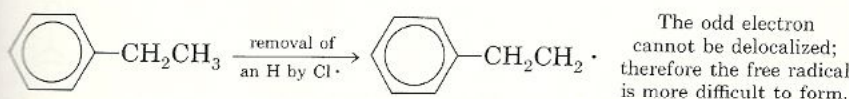


To account for the almost exclusive formation of 1-chloro-1-phenylethane we must look at the free-radical intermediates. Removal of a hydrogen from the carbon adjacent to the aromatic ring gives a benzyl type of free radical that is relatively easy to form because it can be stabilized by resonance.





Removal of a hydrogen from the methyl group of ethylbenzene gives a free radical in which the odd electron cannot be stabilized by resonance, thus minimizing the formation of 1-chloro-2-phenylethane.



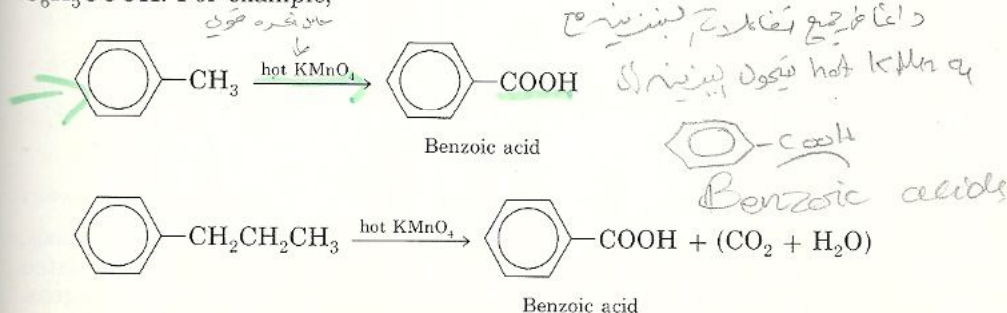
**Problem 5.12** Predict the major organic products formed in these reactions.



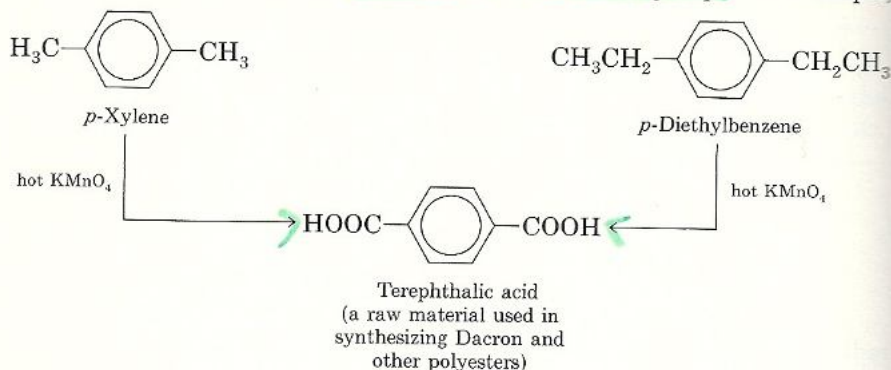
Halogenation of alkylbenzenes under electrophilic conditions (that is, treatment of an alkylbenzene with bromine or chlorine in the presence of ferric halide) leads to substitution in the ring. The exact position(s) of the incoming halogen will be dealt with later (Sec. 5.11).

## B Oxidation of an Alkyl Side Chain

Another reaction of the alkyl side chain is its conversion into a *carboxyl group*,  $\text{COOH}$ , by treatment with hot potassium permanganate. Regardless of the length of the alkyl chain, the product is always the same—benzoic acid,  $\text{C}_6\text{H}_5\text{COOH}$ . For example,

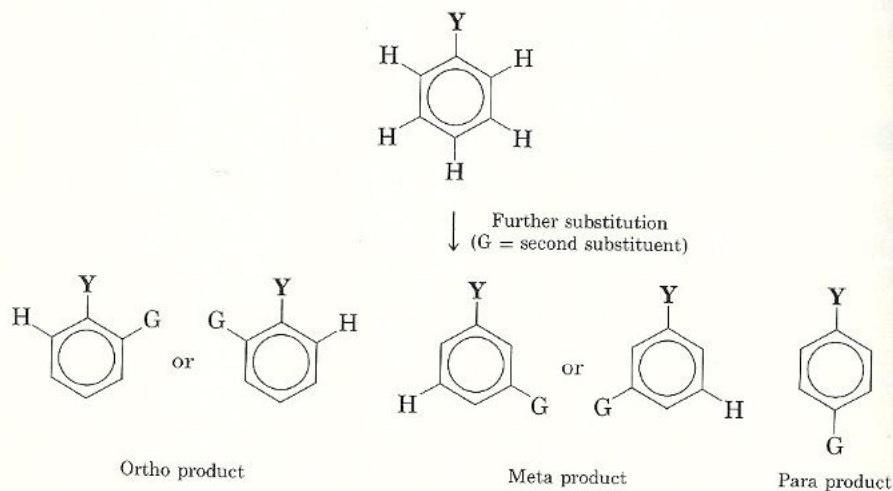


Rings with more than one alkyl chain are similarly oxidized; each alkyl chain, regardless of its length, is converted to a COOH group. For example,



## 5.11 Disubstituted Benzenes: Orientation

In previous sections the discussion centered on methods of introducing one substituent on a benzene ring. As we have noted, certain monosubstituted benzenes are made via direct electrophilic substitution (Sec. 5.9), whereas others are prepared indirectly by converting a substituent already present in the ring into another (Sec. 5.10). Like benzene, monosubstituted benzenes are capable of undergoing further substitution. When a second group, G, is introduced into a monosubstituted benzene,  $\text{C}_6\text{H}_5\text{—Y}$ , three possible isomeric compounds can theoretically be formed.



If the second substituent were to join the ring on a purely statistical basis, the relative proportions of ortho, meta, and para products could be calculated easily. The monosubstituted benzene,  $\text{C}_6\text{H}_5\text{—Y}$ , has five replaceable hydrogens. Among these five hydrogens, the two that are ortho to Y are equivalent to each



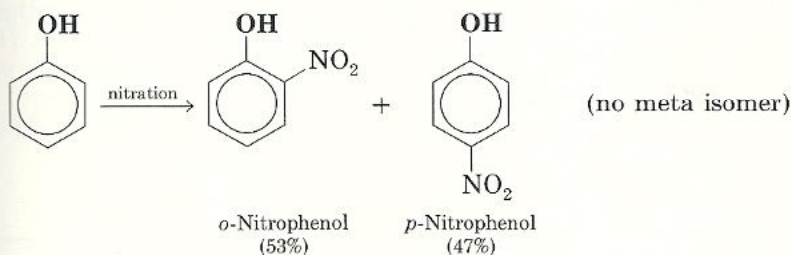
other, as are the two hydrogens in the meta position. Therefore, if the entering substituent G were to join the ring on a purely statistical basis, the proportions of each isomer would be

ortho =  $\frac{2}{3}$  of the total, or 40%

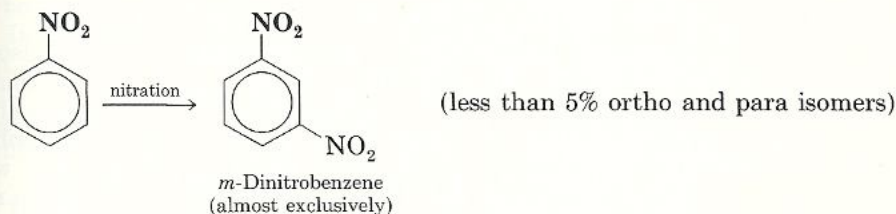
meta =  $\frac{2}{3}$  of the total, or 40%

para =  $\frac{1}{3}$  of the total, or 20%

In fact, such distribution is never observed. *The actual distribution depends on the nature of the first substituent, Y, and falls into two and only two categories.* Certain Ys direct the second substituent G, regardless of what G is, into the ortho and para positions. Other Ys direct the second substituent G, regardless of the nature of G, primarily into the meta position. For example, when phenol is nitrated, the only products formed are *o*-nitrophenol and *p*-nitrophenol; no meta isomer is produced. The OH group (the original substituent) is said to be an **ortho, para director**.



Nitration of nitrobenzene, on the other hand, yields almost exclusively *m*-dinitrobenzene. The NO<sub>2</sub> group (the original substituent) is therefore referred to as a **meta director**.



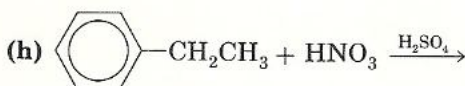
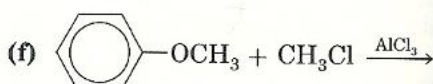
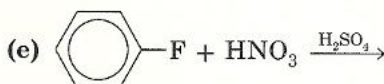
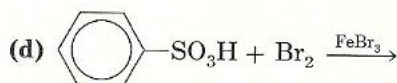
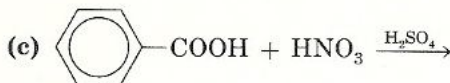
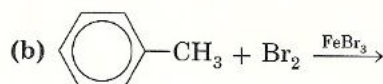
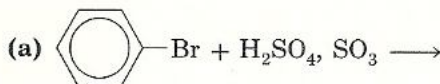
In Table 5.3 you will find a summary of the orienting effects of a number of substituents. Remember, the orientation of the second substituent, regardless of its nature, is dependent on Y only.

**Table 5.3 Orientation Effects of Substituents Y in Electrophilic Aromatic Substitution**

Ortho,para directors	Meta directors
$-\text{OH}, -\text{OR}$ $-\text{NH}_2, -\text{NHR}, -\text{NR}_2$ $-\text{C}_6\text{H}_5$ $-\text{CH}_3, -\text{R}$ (alkyl) $-\text{F}, -\text{Cl}, -\text{Br}, -\text{I}$	$-\text{NO}_2$ $-\text{SO}_3\text{H}$ $-\text{COOH}, -\text{COOR}$ $-\text{CHO}, -\text{COR}$ $-\text{CN}$

meta directors

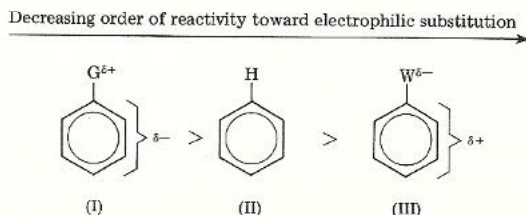
**Problem 5.13** Consult Table 5.3 and predict the major products in the following reactions. If the product is a mixture of ortho and para isomers, show both isomers.



## 5.12 Disubstitution: Reactivity

In addition to the orientation effect, the presence of a substituent also affects the *rate* of electrophilic substitution reactions. Intuitively, it is reasonable to assume that those substituents that release electrons to the ring more effectively than the hydrogen they replace will *activate* the ring toward electrophilic substitution. Such substituents will cause the reaction to go *faster* than with benzene. Conversely, those substituents that withdraw electrons from the ring more effectively than the hydrogen they replace will *deactivate* the ring toward electrophilic substitution. Such substituents will cause the reaction to go *slower* than with benzene.

The order of reactivity predicted for electrophilic substitution is shown in Figure 5.5. Experimental observations confirm these predictions: ortho,para di-



**Figure 5.5** Substituent G donates electrons to the ring, thus activating it, relative to benzene. Substituent W withdraws electrons from the ring, thus deactivating it.



Table 5.4 Orientation and Reactivity Effects of Substituents in Electrophilic Aromatic Substitution

Substituent	Effect on reactivity
<b>Ortho,para directors</b>	
$\text{—OH, —OR, —NH}_2, \text{—NHR, —NR}_2$	strongly activating
$\text{—C}_6\text{H}_5, \text{—CH}_3, \text{—R (alkyl)}$	moderately activating
$\text{—F, —Cl, —Br, —I}$	deactivating
<b>Meta directors</b>	
$\text{—NO}_2, \text{—SO}_3\text{H, —COOH, —COOR}$	strongly deactivating
$\text{—CHO, —COR, —CN}$	deactivating

directors, which donate electrons to a ring, activate the ring toward electrophilic substitution, whereas meta-directing groups, which withdraw electrons from a ring, deactivate the ring toward electrophilic substitution. The only important exception to this generalization occurs in the halobenzenes,  $\text{C}_6\text{H}_5\text{X}$  ( $\text{X} = \text{F, Cl, Br, I}$ ). Although fluorine, chlorine, bromine, and iodine are ortho,para directors, these substituents deactivate an aromatic ring in electrophilic substitutions. The orientation and reactivity effects of substituents are summarized in Table 5.4.

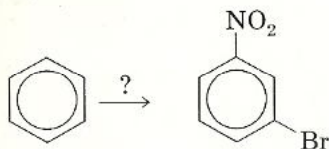
## Planning an Aromatic Synthesis 5.13

Now that you have learned a great deal of aromatic chemistry, let us see how that knowledge can be used to prepare a particular aromatic compound in the best way possible.

In any aromatic synthesis two kinds of information must be kept in mind. First, you must know the different methods by which a given substituent is introduced into the ring. Second, you must be aware of how the group(s) already present will influence the orientation of an incoming substituent. These points are illustrated in the following examples.

**Example 5.1** Starting from benzene, synthesize *m*-bromonitrobenzene.

**Solution** (1) Draw the structure of the starting material and the structure of the product.

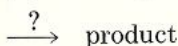


Benzene

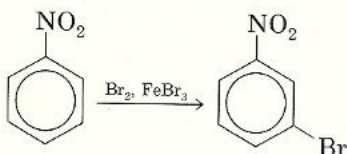
*m*-Bromonitrobenzene

Obviously, two substitutions have taken place. Therefore two steps are required: bromination of the ring and nitration of the ring.

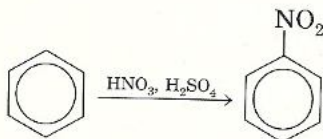
(2) Working backward, decide what reaction leads to the product.



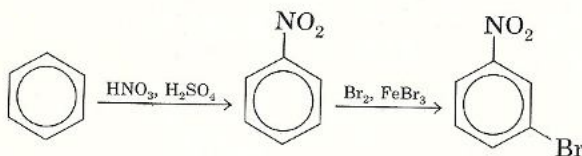
Since the  $-\text{NO}_2$  group is a meta director (whereas  $-\text{Br}$  is an ortho,para-directing group), the last reaction is bromination of nitrobenzene.



(3) The reactants leading to nitrobenzene are



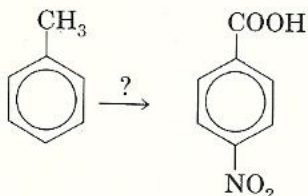
(4) Write the overall synthesis in the right order.



The alternate sequence (bromination followed by nitration) would have given a mixture of *o*-bromonitrobenzene and *p*-bromonitrobenzene, the wrong isomers.

**Example 5.2** Suppose that you wish to synthesize *p*-nitrobenzoic acid, starting from toluene.

**Solution** First, draw the structure of the starting material and the structure of the product.



Toluene

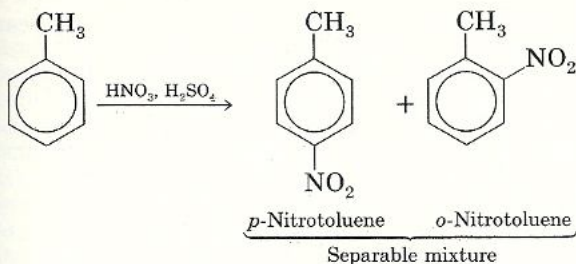
*p*-Nitrobenzoic acid

Obviously, two changes have occurred. The side chain ( $\text{CH}_3$ ) has been oxidized to  $\text{COOH}$ , and a nitro group has been introduced. Therefore two steps are required: a side-chain oxidation and a nitration. Which step should be carried out first?

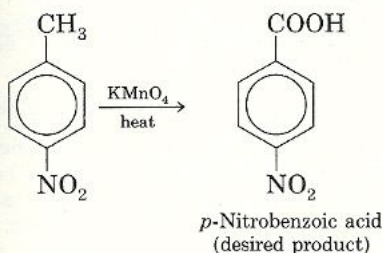
Note that the para isomer of nitrobenzoic acid is required. Toluene *must therefore be nitrated first* because the methyl group is an ortho,para director.



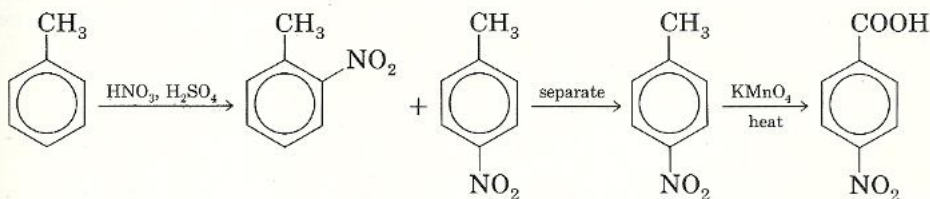
## 1. Nitration of toluene



## 2. Oxidation of the side chain

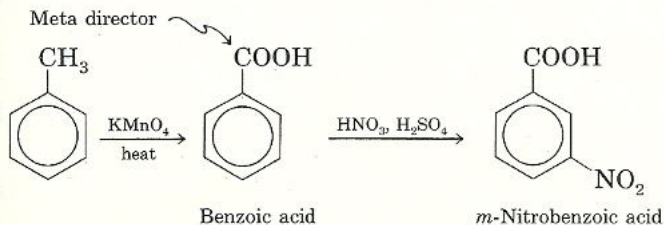


The correct sequence of steps to arrive at the desired product is therefore nitration followed by oxidation.



If the reverse were done (that is, if toluene were oxidized first, followed by the nitration of benzoic acid), the product obtained would be exclusively *m*-nitrobenzoic acid, an unwanted isomer.

## 3. Oxidation followed by nitration yields the wrong isomer.



As you see, it is important to use the correct sequence of steps if the desired product is to be obtained.

**Problem 5.14** Starting from benzene and any other reagents needed, show how you would synthesize these compounds. Assume that ortho,para mixtures can be separated.

- (a) *o*-Nitrotoluene  
(c) Benzoic acid

- (b) *m*-Chlorobenzenesulfonic acid  
(d) Benzyl chloride

## Summary of Concepts and Reactions

Aromatic compounds are compounds that are benzene-like in their properties. Benzene itself is a cyclic, planar structure of formula  $C_6H_6$ . [Sec. 5.1]

In benzene all carbons are  $sp^2$  hybridized and all carbon-carbon bonds are of equal length. [Sec. 5.1]

Benzene is actually a resonance hybrid of two imaginary contributing structures. [Secs. 5.1, 5.2]

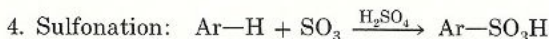
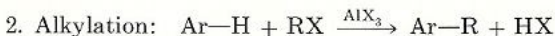
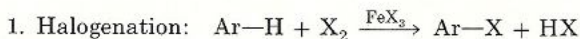
Benzene and other aromatic hydrocarbons are stabilized by large resonance energies. It is the preservation of these large resonance energies (36 kcal/mole for benzene) that is the source of aromatic hydrocarbons' tendency to undergo substitution rather than addition. [Sec. 5.3]

All aromatic compounds must obey the  $(4n + 2) \pi$  rule, also known as Hückel's rule. [Sec. 5.4]

The two major sources of aromatic compounds are coal tar and petroleum. [Sec. 5.6]

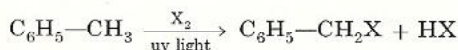
Reactions of aromatic compounds proceed via an electrophilic aromatic substitution mechanism. In almost all electrophilic aromatic substitutions a catalyst is needed for reaction to take place. The purpose of the catalyst is to generate powerful electrophiles. [Secs. 5.7, 5.8]

The most common electrophilic aromatic substitution reactions are



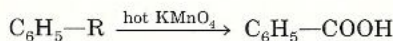
[Sec. 5.9]

The aliphatic portion of an alkylbenzene can undergo two kinds of reactions: (1) free-radical halogenation



and (2) oxidation

[Sec. 5.10A]



[Sec. 5.10B]

When a substituent is already present on the ring, it affects the ring in two ways:

1. It can direct a second substituent to an ortho or para position (ortho,para director) or to a meta position (meta director). [Sec. 5.11]
2. It can activate or deactivate the ring. [Sec. 5.12]



benzene  
aromatic  
substitution  
resonance energy  
aromaticity  
Hückel's rule  
phenyl  
benzyl  
ortho (*o*-)

meta (*m*-)  
para (*p*-)  
electrophile  
electrophilic aromatic  
substitution  
bromonium ion ( $\text{Br}^+$ )  
chloronium ion ( $\text{Cl}^+$ )  
carbocation ( $\text{R}^+$ )

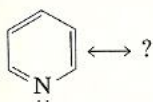
nitronium ion ( $\text{NO}_2^+$ )  
 $\text{SO}_3\text{H}^+$  ion  
halogenation  
Friedel-Crafts alkylation  
nitration  
sulfonation  
ortho,para director  
meta director

## Exercises

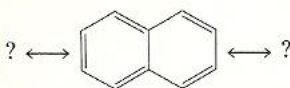
**Resonance, Resonance Energy, Aromaticity** [Secs. 5.1-5.4]

5.1 Refer to the diagram on page 121 and draw

(a) A resonance-contributing structure of pyridine

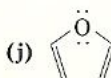
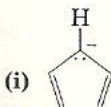
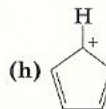
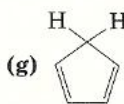
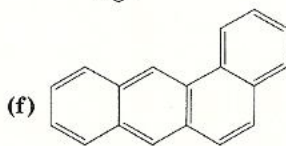
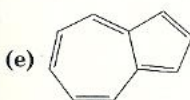
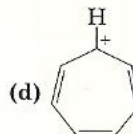
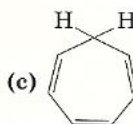
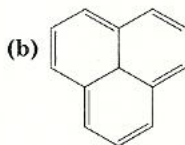


(b) Two resonance-contributing structures of naphthalene



5.2 Hydrogenation of one mole of anthracene,  $\text{C}_{14}\text{H}_{10}$ , with seven moles of hydrogen releases 116.2 kcal of heat. Assuming the heat of hydrogenation of a normal double bond to be 28.6 kcal/mole, calculate the resonance energy of anthracene.

5.3 Which of these structures will be aromatic according to the  $(4n + 2) \pi$  rule?

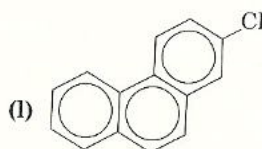
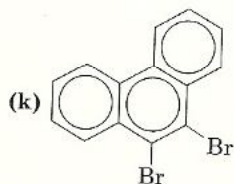
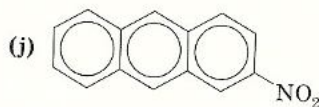
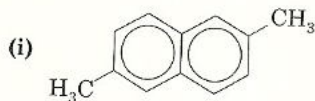
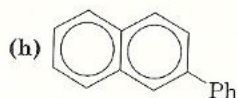
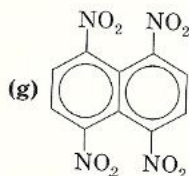
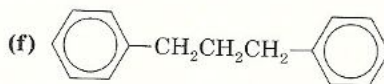
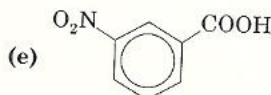
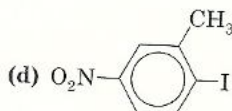
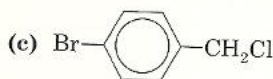
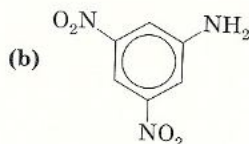
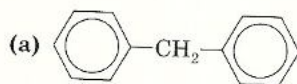


**Structure and Nomenclature** [Sec. 5.5]

5.4 Draw structures for these compounds.

- |                                    |   |
|------------------------------------|---|
| (a) Aniline                        | (b) Toluene                             |
| (c) Benzoic acid                   | (d) Phenol                              |
| (e) Isopropylbenzene (cumene)      | (f) <i>o</i> -Diethylbenzene            |
| (g) Triphenylmethane               | (h) <i>p</i> -Xylene                    |
| (i) <i>p</i> -Chlorobenzyl bromide | (j) <i>m</i> -Nitrobenzenesulfonic acid |
| (k) 3,5-Dibromostyrene             | (l) 1,2-Diphenylethane                  |
| (m) <i>m</i> -Chloroaniline        | (n) Pentachlorophenol                   |
| (o) Hexamethylbenzene              | (p) 2-Aminonaphthalene                  |
| (q) 2,6-Dichloronaphthalene        | (r) 2-Bromoanthracene                   |
| (s) 9,10-Diphenylanthracene        | (t) 1-Nitrophenanthrene                 |
| (u) 3,5-Dimethylphenanthrene       | (v) 2,4,6-Tribromophenanthrene          |

5.5 Name these compounds.

5.6 Write the structures and give names for four aromatic compounds with the formula  $C_7H_7Br$ .

5.7 Write structures and give names for all possible isomeric:

- |                                     |                                       |
|-------------------------------------|---------------------------------------|
| (a) Dichloroanilines (six isomers)  | (b) Chloronitrotoluenes (ten isomers) |
| (c) Bromonitrophenols (ten isomers) | (d) Dibromonaphthalenes (ten isomers) |

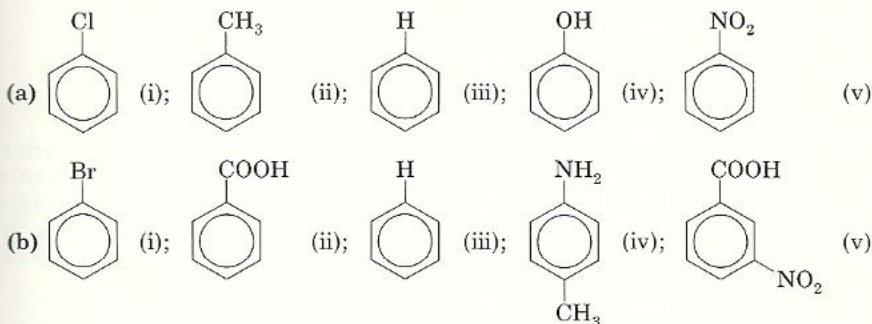


**Mechanisms of Electrophilic Aromatic Substitution Reactions** [Secs. 5.7, 5.8]

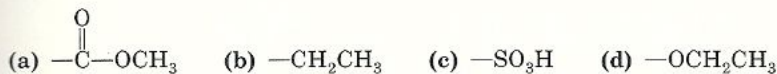
- 5.8 Treatment of benzene with  $\text{CH}_3\text{Cl}$  catalyzed by  $\text{AlCl}_3$  yields toluene. Write the mechanism for the reaction and show all contributing forms in the reaction intermediate.
- 5.9 When a mixture of benzene and 2-methylpropene is heated in the presence of sulfuric acid catalyst, *t*-butylbenzene is formed. Write the complete mechanism to account for the formation of *t*-butylbenzene.

**Orientation and Reactivity** [Secs. 5.11, 5.12]

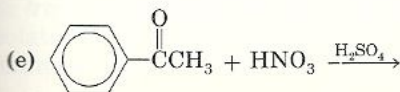
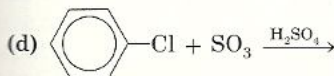
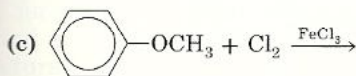
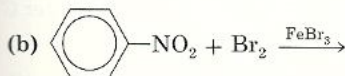
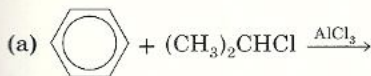
- 5.10 Arrange the following series of compounds in decreasing order of reactivity toward bromination.

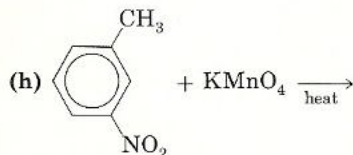
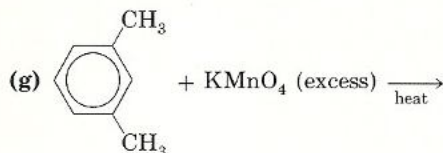
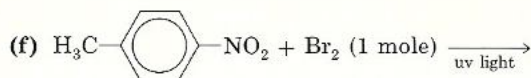


- 5.11 Predict the orientation and reactivity effects of these substituents.

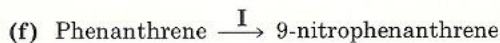
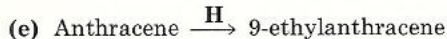
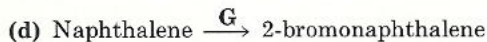
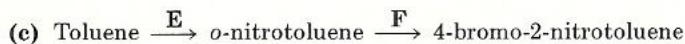
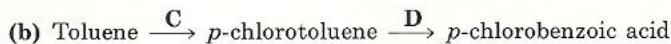
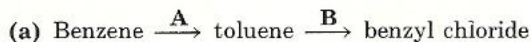
**Reactions and Syntheses** [Secs. 5.9–5.13]

- 5.12 Draw the structures and give the names, using ortho, meta, and para designations, for the major products of the monochlorination when each of these compounds is reacted with chlorine and ferric chloride.
- (a) Ethylbenzene (b) Chlorobenzene (c) Nitrobenzene  
(d) Benzenesulfonic acid (e) Iodobenzene (f) Phenol
- 5.13 Complete the following reactions. When a mixture of ortho and para isomers is expected, show both isomers.

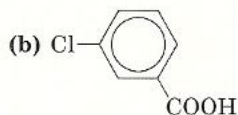
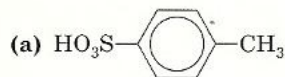




5.14 Draw the structures of the reactant and the product for the transformations shown here and supply the necessary reagents A through I. (Assume that substitutions on naphthalene, anthracene, and phenanthrene require the same reagents as benzene.)



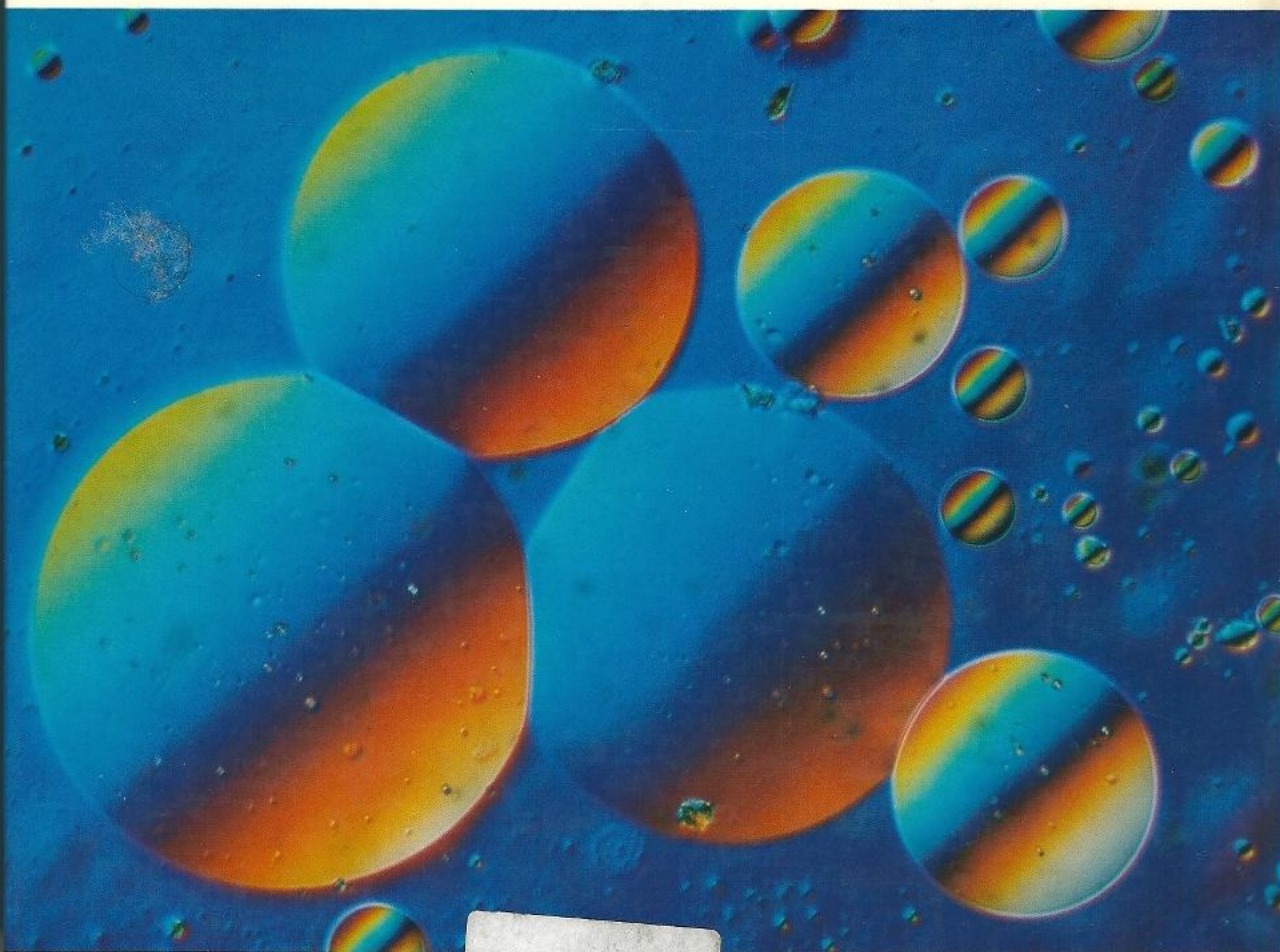
5.15 Starting from benzene and any other reagents needed, show how you would synthesize the following products. Assume that ortho,para mixtures can be separated.



5.16 There are three isomeric diethylbenzenes, A, B, and C. On nitration, isomer A gave *three* mononitro derivatives, isomer B gave *one* nitro compound, and isomer C gave *two* nitro compounds. What are the structures of A, B, and C?



Light Fuel Oil, 400/1. The drop shapes of EL-type mineral oil are produced by careful emulsification in glycerol. The three dimensionality of the photograph is obtained by means of the interference-contrast technique. Photomicrograph by Manfred Kage/Peter Arnold, Inc.



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