## ■ What is Organic Chemistry?

→ Organic chemistry is the study of carbon compounds. The word "organic" was originally used by eighteenth-century chemists to describe substances obtained from living sources—plants and animals. These chemists believed that nature possessed a certain vital force and that only living things could produce organic compounds. This romantic notion was disproved in 1828 by Friedrich Wohler, a German chemist who prepared urea, an organic compound, from the reaction between inorganic compounds lead cyanate and aqueous ammonia:

$$Pb(OCN)_2 + 2NH_3 + 2H_2O \rightarrow 2(NH_2)_2CO + Pb(OH)_2$$

→ Today, well over 20 million synthetic and natural organic compounds are known.

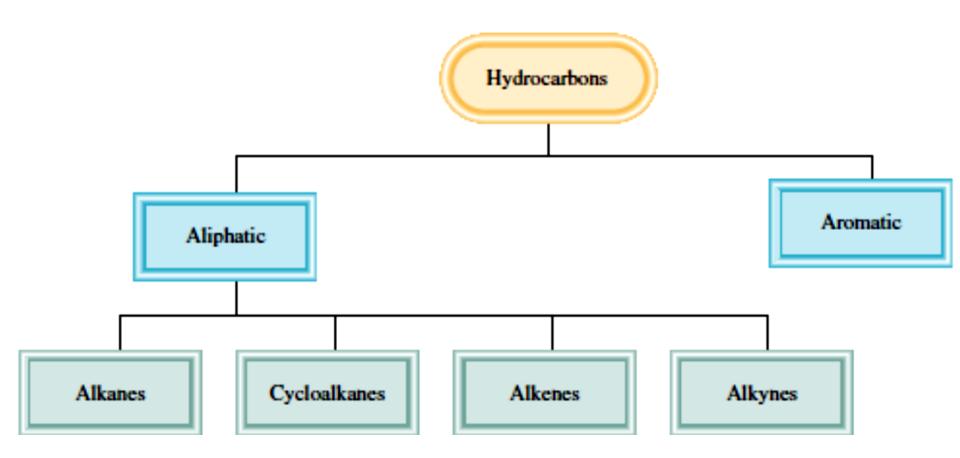
## ■ Classes of Organic Compounds:

- → Carbon can form more compounds than any other element because carbon atoms are able not only to form single, double, and triple carbon-carbon bonds, but also to link up with each other in chains and ring structures.
- → The branch of chemistry that deals with carbon compounds is organic chemistry.
- → Classes of organic compounds can be distinguished according to functional groups they contain.
- → A functional group is a group of atoms that is largely responsible for the chemical behavior of the parent molecule.Different molecules containing the same kind of functional group or

### Classes of Organic Compounds:

- → Different molecules containing the same kind of functional group or groups undergo similar reactions. Thus, by learning the characteristic properties of a few functional groups, we can study and understand the properties of many organic compounds.
- → The functional groups known as **alcohols**, **ethers**, **aldehydes** and **ketones**, **carboxylic acids**, and **amines**, **ester**.
- → Most organic compounds are derived from a group of compounds known as **hydrocarbons** because they are made up of only hydrogen and carbon. On the basis of structure, hydrocarbons are divided into **two main classes—aliphatic and aromatic**. Aliphatic hydrocarbons do not contain the benzene group, or the benzene ring, whereas aromatic hydrocarbons contain one or more benzene rings.

**■ Classes of Organic Compounds:** 



## ■ Aliphatic Hydrocarbons:

#### → Alkanes:

 $\rightarrow$  Alkanes have the general formula  $C_nH_{2n}+2$ , where  $n=1,2,\ldots$  The essential characteristic of alkane hydrocarbon molecules is that only single covalent bonds are present. The alkanes are known as saturated hydrocarbons because they contain the maximum number of hydrogen atoms that can bond with the number of carbon atoms present.

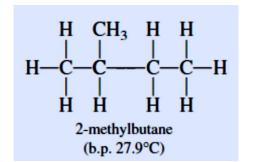
#### → Alkanes:

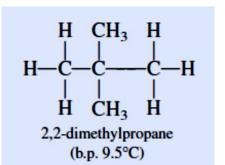
- → The carbon atoms in all the alkanes can be assumed to be sp³-hybridized. The structures of ethane and propane are straightforward, for there is only one way to join the carbon atoms in these molecules. Butane, however, has two possible bonding schemes resulting in the structural isomers n-butane (n stands for normal) and isobutane, molecules that have the same molecular formula, but different structures.
- → In the alkane series, as the number of carbon atoms increases, the number of structural isomers increases rapidly.

For example, butane,  $C_4H_{10}$ , has two isomers; decane,  $C_{10}H_{22}$ , has 75 isomers; and the alkane  $C_{30}H_{62}$  has over 400 million, or  $4\times10^8$ , possible isomers!

- $\rightarrow$  How many structural isomers can be identified for pentane,  $C_5H_{12}$ ?
- → For small hydrocarbon molecules (eight or fewer C atoms), it is relatively easy to determine the number of structural isomers by trial and error.
- → The first step is to write the straight-chain structure.

The second structure, by necessity, must be a branched chain:





#### Alkane Nomenclature:

**1.** The parent name of the hydrocarbon is that given to the longest continuous chain of carbon atoms in the molecule. Thus, the parent name of the following compound is heptane because there are seven carbon atoms in the longest chain.

$$\begin{array}{c|c}
 & CH_3 \\
 & \downarrow \\
 & CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3
\end{array}$$

**2.** An alkane less one hydrogen atom is an alkyl group. For example, when a hydrogen atom is removed from methane, we are left with the  $CH_3$  fragment, which is called a methyl group. Similarly, removing a hydrogen atom from the ethane molecule gives an ethyl group, or  $C_2H_5$ . Any chain branching off the longest chain is named as an alkyl group.

**3.** When one or more hydrogen atoms are replaced by other groups, the name of the compound must indicate the locations of carbon atoms where replacements are made. The procedure is to number each carbon atom on the longest chain in the direction that gives the smaller numbers for the locations of all branches.

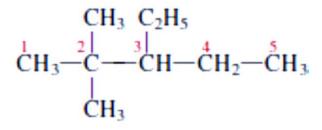
**4.** When there is more than one alkyl branch of the same kind present, we use a prefix such as di-, tri-, or tetra- with the name of the alkyl group. Consider the following examples:

When there are two or more different alkyl groups, the names of the groups are listed alphabetically. For example,

$$CH_3$$
  $C_2H_5$ 
 $CH_3$   $C_2H_5$ 
 $CH_3$   $CH_2$   $CH_2$   $CH_3$ 
 $CH_3$   $CH_2$   $CH_3$ 
 $CH_3$   $CH_3$   $CH_4$   $CH_5$ 
 $CH_4$   $CH_5$   $CH_5$   $CH_5$ 
 $CH_5$   $CH_$ 

**5.** Of course, alkanes can have many different types of substituents. The names of some substituents, including nitro and bromo. Thus, the compound is called 3-bromo-2-nitrohexane. Note that the substituent groups are listed alphabetically in the name, and the chain is numbered in the direction that gives the lowest number to the first substituted carbon atom.

■ Give the IUPAC name of the following compound:



■ Write the structural formula of 5-ethyl-2,4,6-trimethyloctane.

## Optical Isomerism of Substituted Alkanes:

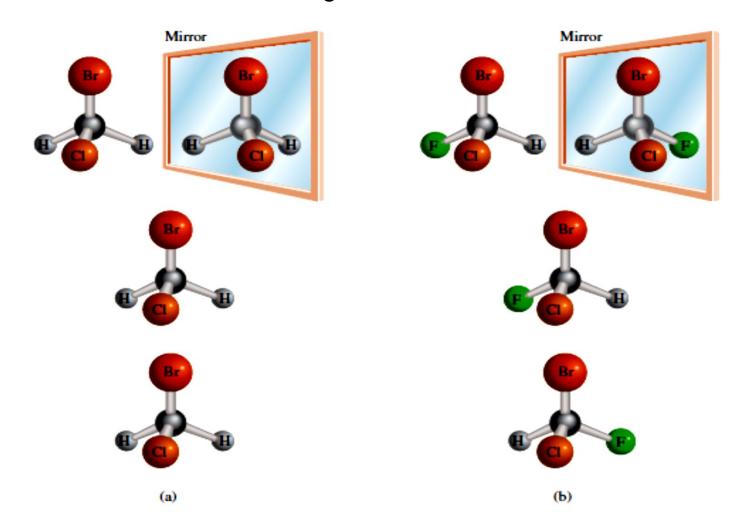
Optical isomers are compounds that are non-superimposable mirror images of each other.

The mirror images of CH<sub>2</sub>ClBr are superimposable but those of CHFClBr are not, no matter how we rotate the molecules. Thus, the CHFClBr molecule is chiral.

Most simple chiral molecules contain at least one asymmetric carbon atom—that is, *a carbon atom bonded to four different atoms or groups of atoms*.

### **■ Optical Isomerism of Substituted Alkanes:**

Perspective drawings of the substituted methanes CH<sub>2</sub>ClBr and CHFClBr and their mirror images.



### Cycloalkanes:

Alkanes whose carbon atoms are joined in rings are known as cycloalkanes. They have the general formula  $C_nH_{2n}$ , where n=3,4,... The simplest cycloalkane is cyclopropane,  $C_3H_6$ .

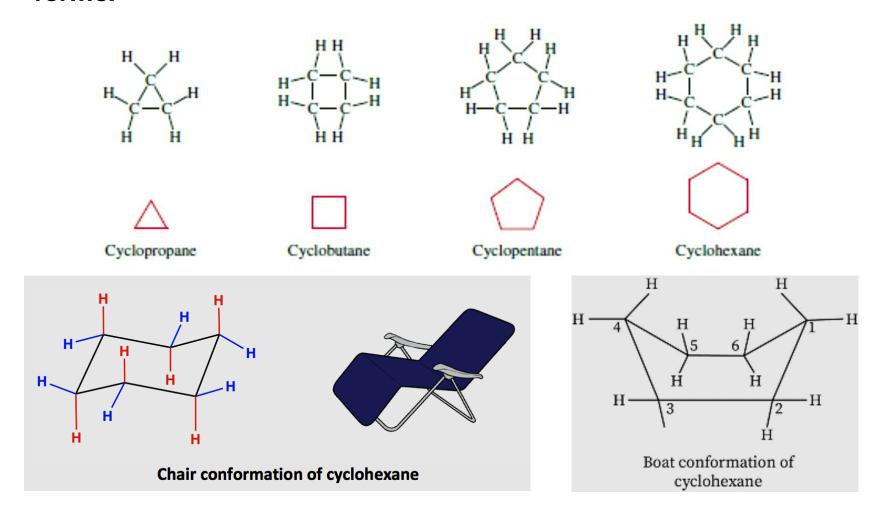
Many biologically significant substances such as cholesterol, testosterone, and progesterone contain one or more such ring systems.

Theoretical analysis shows that cyclohexane can assume two different geometries that are relatively free of strain. By "strain" we mean that bonds are compressed, stretched, or twisted out of normal geometric shapes as predicted by sp<sup>3</sup> hybridization.

The most stable geometry is the chair form.

### Cycloalkanes:

Structures of the first four cycloalkanes and their simplified forms.



#### Alkenes:

The alkenes (also called olefins) contain at least one carbon-carbon double bond.

Alkenes have the general formula  $C_nH_{2n}$ , where  $n=2,3,\ldots$  The simplest alkene is  $C_2H_4$ , ethylene, in which both carbon atoms are sp<sup>2</sup>-hybridized and the double bond is made up of a sigma bond and a pi bond.

#### Alkenes Nomenclature:

In naming alkenes we indicate the positions of the carbon-carbon double bonds. The names of compounds containing C=C bonds end with *-ene*. As with the alkanes, the name of the parent compound is determined by the number of carbon atoms in the longest chain.

#### Alkenes Nomenclature:

- → The numbers in the names of alkenes refer to the lowest numbered carbon atom in the chain that is part of the C=C bond of the alkene. The name "butene" means that there are four carbon atoms in the longest chain.
- → Alkene nomenclature must specify whether a given molecule is cis or trans if it is a geometric isomer.
- → In the *cis isomer*, the two H atoms are on the same side of the C=C bond; in the *trans isomer*, the two H atoms are across from each other.

#### **Geometric isomerism:**

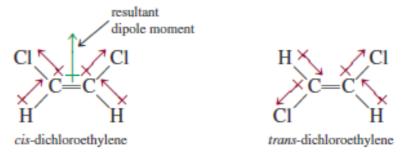
$$H_3C$$
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_4$ 
 $CH_2$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_4$ 
 $CH_5$ 
 $CH_3$ 
 $CH_3$ 

- → The numbers in the names of alkenes refer to the lowest numbered carbon atom in the chain that is part of the C=C bond of the alkene. The name "butene" means that there are four carbon atoms in the longest chain.
- → Alkene nomenclature must specify whether a given molecule is cis or trans if it is a geometric isomer.
- → The term cis means that two particular atoms (or groups of atoms) are adjacent to each other, and trans means that the two atoms (or groups of atoms) are across from each other.

#### ■ Geometric isomerism:

Geometric isomers, which cannot be interconverted without breaking a chemical bond.

■ The molecule dichloroethylene, CIHC=CHCI, can exist as one of the two geometric isomers called cis-dichloroethylene and trans-dichloroethylene:



Generally, cis and trans isomers have distinctly different physical and chemical properties. Heat or irradiation with light is commonly used to bring about the conversion of one geometric isomer to another, a process called cis-trans isomerization, or geometric isomerization. As the above data show, dipole moment measurements can be used to distinguish between geometric isomers. In general, cis isomers possess a dipole moment, whereas trans isomers do not.

#### Alkynes:

Alkynes contain at least one carbon-carbon triple bond. They have the general formula  $C_nH_{2n-2}$ , where  $n=2,3,\ldots$ 

#### ■ Alkyne Nomenclature:

Names of compounds containing carbon-carbon triple bonds end with -yne. Again, the name of the parent compound is determined by the number of carbon atoms in the longest chain for names of alkane counterparts. As in the case of alkenes, the names of alkynes indicate the position of the carbon-carbon triple bond, as, for example,

$$HC = C - CH_2 - CH_3$$
  $H_3C - C = C - CH_3$ 
1-butyne 2-butyne

### ■ Preparation of Alkanes:

## 1) Hydrogenation of unsaturated hydrocarbons.

Alkanes are formed by passing a mixture of an unsaturated hydrocarbon and hydrogen over finely divided nickel ((or platinum) at 250° to 300° C. (Sabatier and Senderens Reaction).

$$CH_2=CH_2 + H_2 \longrightarrow CH_3 - CH_3$$
  
Ethylene Ethane

 $CH \equiv CH + 2H_2 \longrightarrow CH_3 - CH_3$   
Acetylene Ethane

## 2) From Grignard Reagents:

Alkylmagnesium halides (Grignard reagents) when decomposed with water yield pure alkanes.

$$CH_3MgI + HOH \longrightarrow CH_4 + MgI(OH)$$
  
Methylmagneaium Methane  
iodide

## ■ The general reactions of alkanes:

- → Alkanes are generally not considered to be very reactive substances.
- → However, under suitable conditions they do react. For example, natural gas, gasoline, and fuel oil are alkanes that undergo highly exothermic combustion reactions:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$
  $\Delta H^\circ = -890.4 \text{ kJ/mol}$   $2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l)$   $\Delta H^\circ = -3119 \text{ kJ/mol}$ 

#### (1) Halogenation:

Chlorine and bromine can substitute the hydrogen atoms of alkanes with considerable ease, chlorine being more reactive than bromine. Thus by the action of chlorine at ordinary temperature in diffused daylight all the four hydrogen atoms of methane can be successively replaced by chlorine atoms.

$$CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g)$$
  
methyl chloride

→ If an excess of chlorine gas is present, the reaction can proceed further:

$$\operatorname{CH_3Cl}(g) + \operatorname{Cl_2}(g) \longrightarrow \operatorname{CH_2Cl_2}(l) + \operatorname{HCl}(g)$$
 $\operatorname{methylene\ chloride}$ 
 $\operatorname{CH_2Cl_2}(l) + \operatorname{Cl_2}(g) \longrightarrow \operatorname{CHCl_3}(l) + \operatorname{HCl}(g)$ 
 $\operatorname{chloroform}$ 
 $\operatorname{CHCl_3}(l) + \operatorname{Cl_2}(g) \longrightarrow \operatorname{CCl_4}(l) + \operatorname{HCl}(g)$ 
 $\operatorname{carbon\ tetrachloride}$ 

→ A great deal of experimental evidence suggests that the initial step of the first halogenation reaction occurs as follows:

$$Cl_2 + energy \longrightarrow Cl \cdot + Cl \cdot$$

## (2) Reaction with acids (HNO<sub>3</sub> and $H_2SO_4$ ):

- → Nitric acid has no action on lower alkanes but by its long, continued action on higher hydrocarbons one of their hydrogen atoms may be replaced by a nitro-group, NO<sub>2</sub> (Nitration).
- → Alkanes react with fuming sulphuric acid at elevated temperatures to produce alkanesulphonic acids.

The process involves the replacement of one H of the alkane by sulphonic acid group, -SO<sub>3</sub>H and is known as *Sulphonation*.

$$C_6H_{13}H_{13}H_{14} + H_0H_0O_2 \longrightarrow C_6H_{13}NO_2 + H_2O$$
Hexane Nitric acid

 $C_6H_{13}H_{13}H_{14} + H_0H_0O_3$ 

## (3) Pyrolysis:

By the term pyrolysis (Gr., pyr=fire; *lysis*= loosing) is meant the conversion of an organic substance to one or more new substances by the action of heat alone.(In absence of air)

- → chemical decomposition occurs in two ways:
- (i) by fission of C-H linkages to form an unsaturated hydro carbon and hydrogen gas; and (ii) by fission of C-C linkages to give simpler hydrocarbons one alkane and one alkene.
- → Thus propane when pyrolysed at about 600°C, is decomposed as follows:

(i) 
$$CH_3-CH_2-CH_3 \longrightarrow CH_3-CH=CH_2 + H_2$$
  
Propane Propene

(ii)  $CH_3-CH_2-CH_3 \longrightarrow CH_2=CH_2 + CH_4$ 

#### Methods of Formation of Alkene:

→ Most of the methods of preparation of alkenes depend upon the principle that the removal of atoms or groups from adjacent carbon atoms of n-chain, results in the creation of a double bond.

Where X and. Y may be same or different

Ethanol

## 1) By dehydration of alcohols:

When heated with a dehydrating agent; like concentrated sulphuric acid or phosphoric acid, alcohols lose a molecule of water forming alkenes.

Ethene

## (2) By dehydrohalogenation of alkyl halides:

When heated with alcoholic solution of potassium hydroxide (alcoholic potash), alkyl halides eliminate a Hydrogen and halogen atom from adjacent carbon atoms to form an alkene:

(3) By partial hydrogenation of alkynes: The alkyne mixed with hydrogen gas is passed over finely divided platinum or palladium, or heated nickel, when it adds only two H atoms to give alkene.

$$H_3C$$
— $C$ = $C$ — $C$ +  $H_2$   $H_3C$ — $C$ = $C$ +  $H_3C$ — $C$ +  $H_3C$ — $C$ +  $H_3C$ — $C$ +  $H_3C$ — $C$ +  $H_3C$ +  $H_$ 

#### Reactions of Alkene:

→ In general, alkenes give the following types of reactions:

### (i) Addition Reaction:

In these reactions, the reagent adds along the double bond, which is then converted to a single bond.

#### (ii) Polymerisation:

The valenc bonds constituting the double bond are not in a stable condition. They become more labile at high temperature. Thus many molecules of an alkene may join together to form compound of higher molecular weights.

### (i) Addition of Halogens:

Alkenes react readily with halogens by addition, forming dihalogen derivatives:

$$H_2C = CH_2 + CI_2 \longrightarrow CIH_2C - CH_2CI$$
Ethene Ethylenechloride

 $H_3C - HC = CH_2 + CI_2 \longrightarrow H_3C - CIHC - CH_2CI$ 

Propylene Propylenechloride

#### (ili) Addition of Halogen acids:

The addition reactions to the C=C bond includes;

The addition of a hydrogen halide to an unsymmetrical alkene such as propene is more complicated because two products are possible

$$H_2C = CH_2 + HBr \longrightarrow H_3C - CH_2Br$$
Ethene Ethelne bromide
$$H_3C - HC = CH_2 + HBr \longrightarrow H_3C - CH_2 - CH_2Br + H_3C - CH_3$$
Propelene 1-Bromopropane 2-Bromopropane

- In 1871, Vladimir Markovnikov<sup>†</sup> postulated a generalization that enables us to predict the outcome of such an addition reaction.
- This generalization, now known as Markovnikov's rule, states that in the addition of unsymmetrical (that is, polar) reagents to alkenes, the positive portion of the reagent (usually hydrogen) adds to the carbon atom that already has the most hydrogen atoms.
- In the presence of oxygen or peroxides as catalysts, the addition of HBr to propene takes a course opposite to that predicted by Markownikoff's rule. This effect caused by the presence of peroxide is called "peroxide effect".

  Peroxides

  H<sub>3</sub>C—CH<sub>2</sub>—CH<sub>2</sub>Br

### (iii) Addition of oxygen:

Lower alkenes react with oxygen by addition in the presence of If special catalyst to form epoxides.

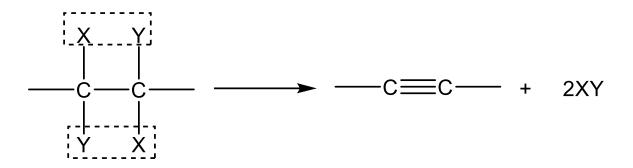
$$H_2C = CH_2 + 1/2 O_2$$
 Ag Catalyst  $H_2C = CH_2$  Ethene Ethylene oxide (Epoxides)

### (iv) Polymerisation:

At high temperature and in the presence of acid catalyst alkene molecules add to one another to form *polymers*.

## Methods of Formation of Alkyne:

- → The methods of formation of alkynes are essentially of two types:
- (i) Those in which a triple bond is created in a 'more saturated molecule by the elimination of sufficient atoms from adjacent carbon atoms.
- (if) Those in which a compound already containing a triple bond is taken as the starting material from which is built the length of the carbon chain.



Where X and. Y may be same or different

### ■ Methods of Formation of Alkyne:

## (1) Dehydrohalogenation of dihaloalkanes:

Dihalogen substituted alkanes with alcoholic potash eliminate two atoms of hydrogen and two atoms of halogen from the adjacent carbon atoms resulting in the formation of alkynes.

$$H_3C$$
  $C$   $C$   $H$   $H_3C$   $H_$ 

#### I, 2-Dibromopropane

$$H_3C$$
 $H_2$ 
 $H_3C$ 
 $H_4$ 
 $H_5$ 
 $H_5$ 
 $H_6$ 
 $H_7$ 
 $H_8$ 
 $H_8$ 
 $H_8$ 
 $H_8$ 
 $H_8$ 
 $H_8$ 
 $H_9$ 
 $H_$ 

1,1, 2,2-Tetraibromopropane

## Reactions of Alkyne:

## (i) Addition of hydrogen:

In the presence of suitable catalyst alkynes add two molecule of hydrogen first forming corresponding alkenes and finally the alkanes.

$$H_3C$$
— $C$ = $CH$   $\xrightarrow{+ H_2}$   $H_3C$ — $C$ = $CH_2$   $\xrightarrow{+ H_2}$   $H_3C$ — $C$   $\xrightarrow{- C}$   $H_3$   $H_3C$ — $C$   $H_3$   $H_3C$ — $C$   $H_3$   $H_3C$ — $C$   $H_3$   $H_3$ 

#### (ii) Polymerisation:

Alkyne which passed through a red hot quartz or iron tube polymerize to give benzene.

#### Alcohols:

→ All alcohols contain the hydroxyl functional group, -OH. The common alcohol is ethyl alcohol, or ethanol, is by far the best known. It is produced biologically by the fermentation of sugar or starch. In the absence of oxygen, the enzymes present in bacterial cultures or yeast catalyse the reaction.

$$C_6H_{12}O_6(aq) \xrightarrow{\text{enzymes}} 2CH_3CH_2OH(aq) + 2CO_2(g)$$

→ Commercially, ethanol is prepared by an addition reaction in which water is combined with ethylene at about 280 °C and 300 atm:

$$CH_2 = CH_2(g) + H_2O(g) \xrightarrow{H_2SO_4} CH_3CH_2OH(g)$$

#### Reactions of Alcohols:

→ Ethanol can also be oxidized by inorganic oxidizing agents, such as acidified dichromate, to acetaldehyde and acetic acid:

$$CH_3CH_2OH \xrightarrow{Cr_2O_7^{2-}} CH_3CHO \xrightarrow{Cr_2O_7^{2-}} CH_3COOH$$

→ The alcohols are very weakly acidic; they do not react with strong bases, such as NaOH. The alkali metals react with alcohols to produce hydrogen:

### ■ Aldehydes and Ketones :

- → The functional group in these compounds is the carbonyl group C=O. In an aldehyde at least one hydrogen atom is bonded to the carbon in the carbonyl group. In a ketone, the carbon atom in the carbonyl group is bonded to two hydrocarbon groups.
  - → Ketones generally are less reactive than aldehydes. The simplest ketone is acetone, a pleasant-smelling liquid that is used mainly as a solvent for organic compounds and nail polish remover.
  - → Under mild oxidation conditions, it is possible to convert alcohols to aldehydes and ketones:

$$C_2H_5OH + 1/2O_2 \longrightarrow CH_3CHO$$
 $CH_3CH(OH)CH_3 + 1/2O_2 \longrightarrow CH_3COCH_3$ 

#### Aldehydes and Ketones :

→ **Aldol Condensation:** In the presence of a mild alkali, two molecules of aldehyde unit to produce a molecule of aldol, which is both an aldehyde and an alcohol. Thus,

This special type of condensation encountered in aldehydes is called Aldol condensation. If heated with a dehydrating agent the aldol molecule loses a molecule of water yielding an alkene.

$$H_3C$$
 —  $C$  —  $C$ 

### ■ Carboxylic Acids:

- → Carboxylic acids are widely distributed in nature; they are found in both the plant and animal kingdoms. All protein molecules are made of **amino acids**, a special kind of carboxylic acid containing an amino group (-NH<sub>2</sub>) and a carboxyl group (-COOH).
- → Under appropriate conditions both alcohols and aldehydes can be oxidized to carboxylic acids,

$$C_2H_5OH + O_2 \longrightarrow CH_3COOH + H_2O$$
 $CH_3CHO + 1/2O_2 \longrightarrow CH_3COOH$ 

Unlike the inorganic acids HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>, carboxylic acids are usually weak. They react with alcohols to form pleasant-smelling esters:  $\bigcirc$ 

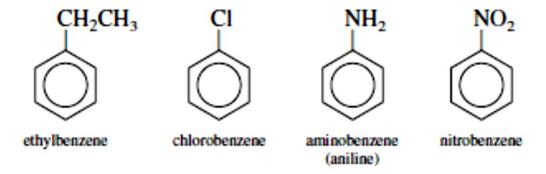
$$H_{2}$$
 CH<sub>3</sub>COOH + C<sub>2</sub>H<sub>5</sub>OH  $\longrightarrow$  H<sub>3</sub>C—C—O—C —CH

#### ■ Aromatic Hydrocarbons:

Benzene, the parent compound of this large family of organic substances, was discovered by Michael Faraday in 1826. Over the next 40 years, chemists were preoccupied with determining its molecular structure. Finally, in 1865, August Kekulé† deduced that the benzene molecule could be best represented by a ring structure—a cyclic compound consisting of six carbon atoms:

#### ■ Nomenclature of Aromatic Compounds:

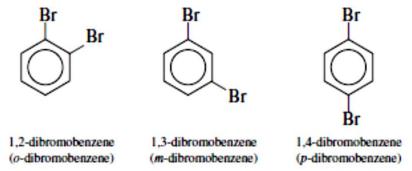
The naming of monosubstituted benzenes, that is, benzenes in which one H atom has been replaced by another atom or a group of atoms, is quite straightforward, as shown here:



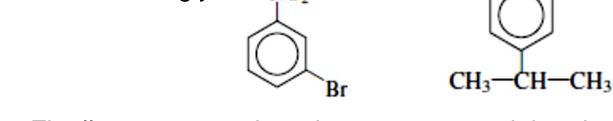
→ If more than one substituent is present, we must indicate the location of the second group relative to the fi rst. The systematic way to accomplish this is to number the carbon atoms as follows:



Three different dibromobenzenes are possible:



- $\rightarrow$  The prefixes o- (ortho-), m- (meta-), and p- (para-) are also used to denote the relative positions of the two substituted groups.
- $\rightarrow$  Compounds in which the two substituted groups are different are named accordingly.  $NO_2$



 $\rightarrow$  Finally, we note that the group containing benzene minus a hydrogen atom ( $C_6H_5$ ) is called the *phenyl* group. Thus, the following molecule is called 2-phenylpropane:

### ■ Reactions of Aromatic Compounds:

- → Benzene is a colourless, flammable liquid obtained chiefly from petroleum and coal tar.
- → The most remarkable chemical property of benzene is its relative inertness. Although it has the high degree of unsaturation, it is much less reactive than either ethylene or acetylene. The stability of benzene is the result of electron delocalization.
- → Benzene can be hydrogenated, but only with difficulty. The following reaction is carried out at significantly higher temperatures and pressures than are similar reactions for the alkenes.

#### ■ Reactions of Aromatic Compounds:

→ Alkenes react readily with halogens to form addition products, because the pi bond in C=C can be broken easily. The most common reaction of halogens with benzene is the substitution reaction, in which an atom or group of atoms replaces an atom or groups of atoms in another molecule. For example,

bromobenzene

#### **Substitution reaction**

#### **Addition reaction**

→ Note that if the reaction were an addition reaction, electron delocalization would be destroyed in the product and the molecule would not have the aromatic characteristic of chemical unreactivity.

### ■ Reactions of Aromatic Compounds:

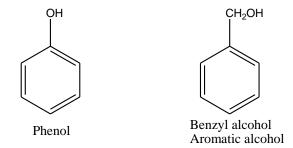
→ Alkyl groups can be introduced into the ring system by allowing benzene to react with an alkyl halide using AlCl<sub>3</sub> as the catalyst:

$$+ CH_3CH_2Cl \xrightarrow[\text{catalyst}]{AlCl_3} + HCl Friedel-Crafts alkylation}$$

$$+ CH_3CH_2Cl \xrightarrow[\text{catalyst}]{AlCl_3} + HCl Friedel-Crafts alkylation$$

#### Aromatic Hydroxy Deri va t i ves:

Aromatic hydroxy derivatives are of two types: (I) phenols, in which the OH group is attached to the nucleus; and (2) aromatic alcohols, in which the OH group is attached to the side-chain.



### ■ Preparation of phenol:

→ Hydrolysis of diazonium salts: Phenols are conveniently prepared by boiling a diazonium sulphate with water.

$$N_2SO_3$$
 OH +  $Na_2SO_4$ 

→ Hydrolysis of aryl halides: Phenols may be formed by heating aryl chlorides with aqueous sodium hydroxide under Pressure.

### Properties of phenol:

- → Phenols are acidic because of two reasons:
- Oxygen atom of the hydroxyl group linked with the benzene ring has a pronounced tendency to share its lone pair of electrons with the benzene ring.
- 1) Greater stability of the phenolate ion by resonance, got after the proton release.

#### Reactions of the OH Group:

→ Reduction with Zinc dust: When distilled with zinc dust, phenols yield the parent hydrocarbons.

### Reactions of the Phenyl group:

(1) **Substitution reactions:** Phenol readily undergoes nitration, sulphonation and halogenation in the *ortho* and *para* positions to OH group.

### ■ Reactions of the Phenyl group:

(2) Reimer-Tiemann reaction: When heated with chloroform and alkali, phenol is converted into salicyl aldehyde. Some p-isomer is also produced.

(3) Friedel-Crafts reaction: Phenol undergoes the Friedel Crafts reaction to form mainly the *p*-derivatives.

### ■ Aromatic Nitro-Compounds:

→ They are the derivatives of aromatic hydrocarbons in which one or more H-atoms of the nucleus have been replaced by nitro groups, NO₂.

### → Reduction of Nitro-compounds:

The reduction of nitrobenzene with a metal and acid (Sn+HCl; Fe+HCl) gives aniline.

#### ■ Preparation of 2, 4, 6-Trinirotoluene (TNT):

Trinitrotoluene is extensively employed as a high explosive (TNT). It may be prepared by nitrating toluene with a mixture of fuming nitric acid and fuming sulphuric acid, but generally it is prepared by carrying the reaction in three- independent steps.