College of education - First Year 2021 - 2022

Organic Chemistry

Chapter 1

General Introduction

Organic Chemistry

Organic chemistry is the chemistry of the compounds of carbon. Inorganic compounds are those obtained from minerals, while organic compounds are those obtained from vegetable or animal sources, that is, from material produced by living organisms. Until about 1850 many chemists believed that organic compounds must have their origin in living organisms, and consequently could never be synthesized from inorganic materials, these compounds from organic sources had this in common; they all contain the element carbon. Even after it had become clear that these compounds did not have to come from living sources but could be made in the laboratory, it was convenient to keep the name organic to describe them and compounds like them. The division between inorganic and organic compounds has been retained to this day.

Today, although many compounds of carbon are still most conveniently isolated from plant and animal sources, most of them are synthesized. They are sometimes synthesized from inorganic substances like carbonates or cyanides, but more often from other compounds. There are two large reservoirs of organic materials from which simple organic compounds can be obtained; petroleum and coal. Both of these are organic in the old sense, being products of the decay of plants and animals. These simple compounds are used as building blocks from which larger and more complicated compounds can be made.

There are many ways in which these complicated molecules can break apart, or rearrange themselves, to form new molecules; there are many ways in which atoms can be added to these molecules, or new atoms substituted for old ones.

Carbon atoms can attach themselves to one another to an extant not possible for atoms of any other element. Carbon atoms can form chains thousands of atoms long, or rings of all sizes; the chains and rings can have branches and cross-links. To the carbon atoms of these chains and rings there are attached other atoms, chiefly hydrogen, but also fluorine, chlorine, bromine, iodine, oxygen, nitrogen, sulfur, phosphorus, and many others.

Organic chemistry is a field of immense importance to technology: it is the chemistry of dyes and drugs, paper and ink, paint and plastics, gasoline and rubber tires, it is the chemistry of the food we eat and the clothing we wear.

Organic chemistry is fundamental to biology and medicine. A side from water, living organisms are made up chiefly of organic compounds; the molecules of molecular biology are organic molecules. Ultimately, biological processes are a matter of organic chemistry.

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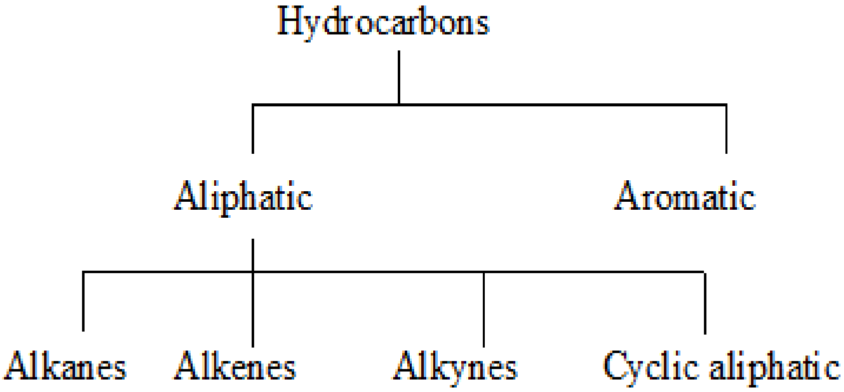
Organic Chemistry

Chapter 2

Alkanes

2.1 Introduction

Hydrocarbons are organic compounds contain only two elements, hydrogen and carbon, and hence are known as hydrocarbons. On the basis of structure, hydrocarbons are divided into two main classes, aliphatic and aromatic. Aliphatic hydrocarbons are further divided into families: alkanes, alkenes, alkynes, and their cyclic analogs (cycloalkanes, etc.).



The simplest member of the alkane family and one of the simplest of all organic compounds is methane, CH_4.

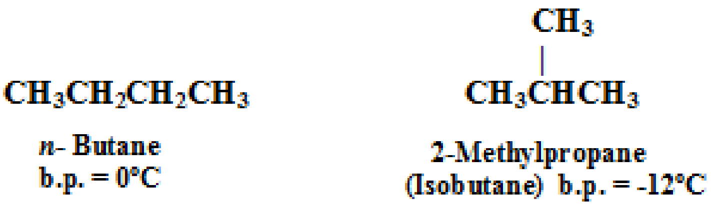
The atoms of the alkane hydrocarbons are joined to one another only through single bonds. The carbon-carbon single bond is of low reactivity. The general formula is $\mathbf{C_{\mathit{n}}H_{\mathit{2n+2}}}$, where n is the number of carbon atoms. For example, if the molecule contains three carbon atoms, $n = 3$ and $(2n + 2) = 8$, the formula is C_3H_8. If the molecule contains ten carbon atoms, $n = 10$ and $(2n + 2) = 22$, the formula is $C_{10}H_{22}$. Each member of the alkanes series differ from the preceding and the succeeding members by CH_2 atoms, and each carbon atom of an alkane molecule is covalently bonded to for other atoms. The first ten members of this series are listed in Table 2.1.

Table 2.1 The first ten member of the alkanes

General formula	Structure	Name
CH_4	CH_4	Methane
C_2H_6	CH_3CH_3	Ethane
C_3H_8	$CH_3CH_2CH_3$	Propane
C_4H_{10}	$CH_3(CH_2)_2CH_3$	Butane
C_5H_{12}	$CH_3(CH_2)_3CH_3$	Pentane
C_6H_{14}	$CH_3(CH_2)_4CH_3$	Hexane
C_7H_{16}	$CH_3(CH_2)_5CH_3$	Heptane
C_8H_{18}	$CH_3(CH_2)_6CH_3$	Octane
C_9H_{20}	$CH_3(CH_2)_7CH_3$	Nonane
$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	Decane

2.2 *Isomerism in Alkanes*

Compounds that have the same molecular formula but different structural formulas were defined as isomers. Isomeric compounds are not possible in the alkanes series until we reach the molecular formula C_4H_{10}. There are two arrangements for the formula C_4H_{10}, and two isomers are known as shown:

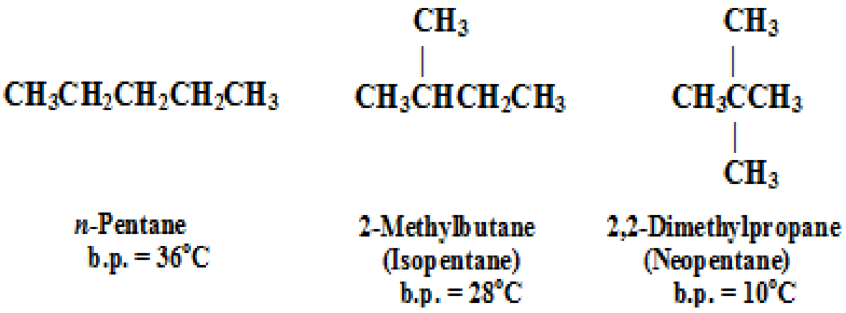


$CH_3CH_2CH_2CH_3$ $\quad$ $CH_3\overset{\overset{CH_3}{|}}{C}HCH_3$

(C_4H_{10} isomers)

They differ both chemically and physically from one another. Experimentally, they can be identified by differences in their melting points, boiling points, densities, solubilities and some other features.

For the formula C_5H_{12}, three isomers have been found, as shown:



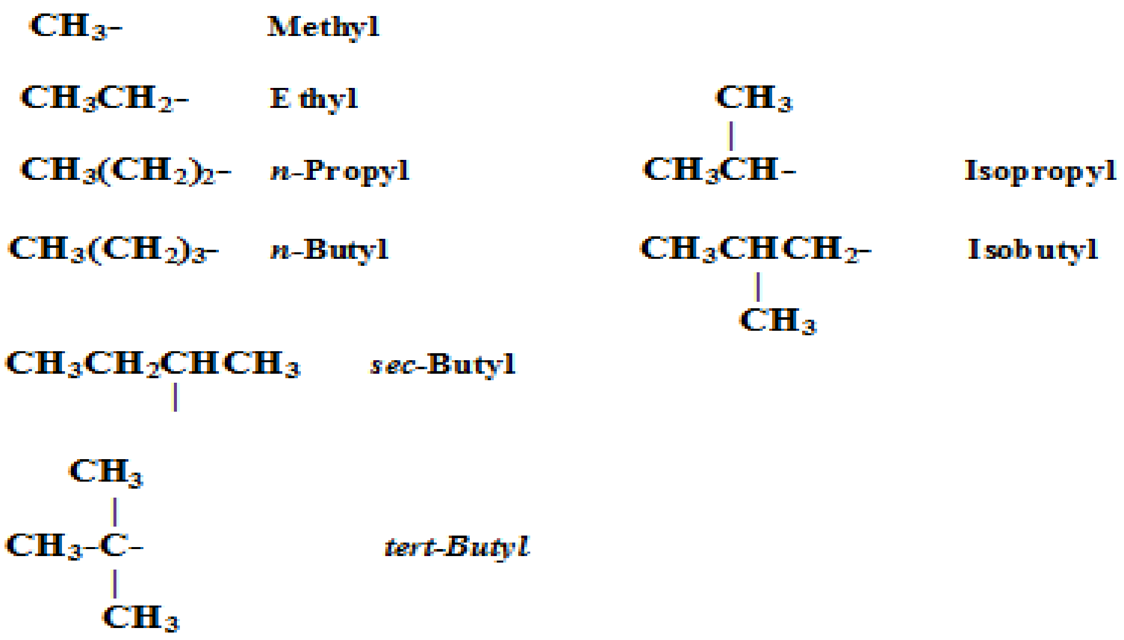
$CH_3CH_2CH_2CH_2CH_3$ $\quad$ $CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_3$ $\quad$ $CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_3$

(C_5H_{12} isomers)

The difference in the structure is due to different arrangements of the carbon atoms.

2.3 Alkyl Groups

Any branch consisting of only carbon and hydrogen and only single bond is called **alkyl group**. The general formula for an alkyl group is C_nH_{2n+1}, since it contains one less hydrogen than the parent alkane, C_nH_{2n+2}.



CH_3-	**Methyl**
CH_3CH_2-	**Ethyl**
$CH_3(CH_2)_2-$	***n*-Propyl**
$CH_3(CH_2)_3-$	***n*-Butyl**
$\overset{\overset{CH_3}{\vert}}{CH_3CH}-$	**Isopropyl**
$CH_3\underset{\underset{CH_3}{\vert}}{CH}CH_2-$	**Isobutyl**
$CH_3CH_2\underset{\vert}{CH}CH_3$	***sec*-Butyl**
$CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-$	***tert*-Butyl**

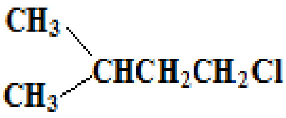
Beyond butyl the number of groups becomes so great that it is impracticable to designate them all by various prefixes. Even though limited, this system is so useful for the small groups just described.

However large the group concerned, the prefix *n*- is used to designate any alkyl group in which all carbons form a single continuous chain and in which the point of attachment is the very end carbon.

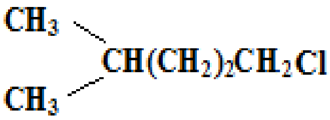
$CH_3CH_2CH_2CH_2CH_2Cl$ $\qquad$ $CH_3(CH_2)_4CH_2Cl$

n-Pentyl chloride $\qquad$ *n*-Hexyl chloride

The prefix *iso*- is used to designate any alkyl group (of six carbons or fewer) that has a single one-carbon branch on the next-to-last carbon of a chain and has the point of attachment at the opposite end of the chain.



Isopentyl chloride



Isohexyl chloride

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

2.4 Nomenclature

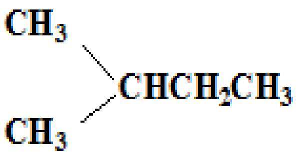
Common names:

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

$CH_3CH_2CH_2CH_2CH_3$ $\qquad$ $CH_3(CH_2)_4CH_3$

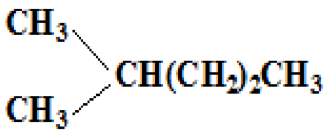
n-Pentane $\qquad$ *n*-Hexane

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



$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!\!>CHCH_2CH_3$

Isopentane



$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!\!>CH(CH_2)_2CH_3$

Isohexane

In naming any other of the higher alkanes, we make use of the IUPAC system.

IUPAC system:

Essentially the rules of the IUPAC system (International Union of Pure and Applied Chemistry) are:

1- Use the ending **(–*ane*)** for all alkanes.

2- Attach a prefix to this, to specify the number of carbon atoms in the longest continuous chain in the molecule. The prefixes through C-10 are:

Meth-	1C	Hex-	6C
Eth-	2C	Hept-	7C
Prop-	3C	Oct-	8C
But-	4C	Non-	9C
Pent-	5C	Dec-	10C

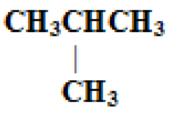
3- Pick the longest continuous chain in a branched chain alkane as the basis for the name.

4- To specify which carbon atom of the parent chain holds a branch, number the parent chain from whichever end of its chain reaches the first branch with the lower number.

5- Determine the correct name for each branch or any other group or atom such as a halogen atom.

6- If the same group occurs more than ones as a side chain, indicate this by the prefix di-, tri-, tetra-, etc., to show how many of these groups are, and indicate by various numbers the positions of each group.

7- If there are several different groups attached to the parent chain, name them in alphabetical order.

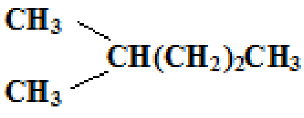


$$CH_3\underset{\substack{|\\ CH_3}}{C}HCH_3$$

Methylpropane
(Isobutane)

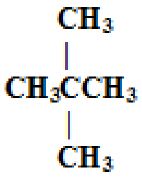
$CH_3(CH_2)_3CH_3$

Pentane
(*n*-Pentane)



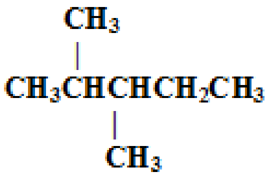
2-Methylpentane
(Isohexane)

(Isopentane)



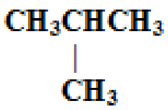
$$\begin{array}{c} CH_3 \\ | \\ CH_3CCH_3 \\ | \\ CH_3 \end{array}$$

Dimethylpropane
(Neopentane)



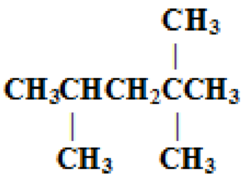
$$\begin{array}{ccccc} & CH_3 & & & \\ & | & & & \\ CH_3 & CH & CH & CH_2 & CH_3 \\ & & | & & \\ & & CH_3 & & \end{array}$$

2,3-Dimethylpentane



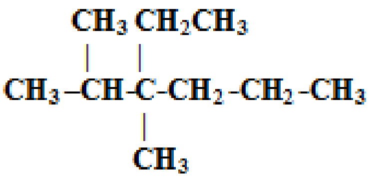
$$\begin{array}{ccc} CH_3 & CH & CH_3 \\ & | & \\ & CH_3 & \end{array}$$

Methylpropane
(Isobutane)



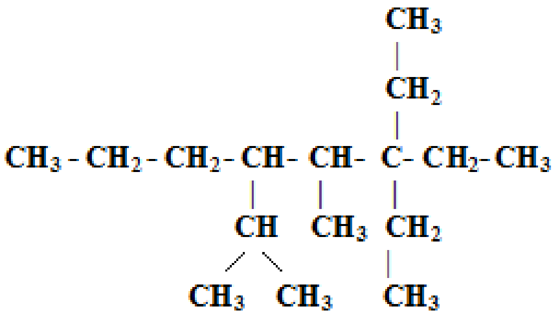
$$\begin{array}{ccccc} & & & CH_3 & \\ & & & | & \\ CH_3 & CH & CH_2 & C & CH_3 \\ & | & & | & \\ & CH_3 & & CH_3 & \end{array}$$

2,2,4-Trimethylpentane



$$\begin{array}{cccccc} & CH_3 & CH_2CH_3 & & & \\ & | & | & & & \\ CH_3- & CH- & C- & CH_2- & CH_2- & CH_3 \\ & & | & & & \\ & & CH_3 & & & \end{array}$$

3-Ethyl-2,3-dimethylhexane



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

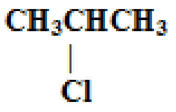
The alkyl halides which appear so often in the alkane chemistry are named *haloalkanes*; that is, halogen is simply treated as a side chain. We first name the alkane as though no halogen were present, and then add *fluoro, chloro, bromo,* or *iodo*, together with any needed number and prefixes.

CH_3Cl

Chloromethane
(Methyl chloride)

CH_3CH_2Br

Bromoethane
(Ethyl bromide)

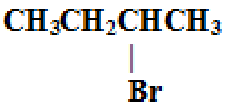


$CH_3\underset{\underset{Cl}{|}}{C}HCH_3$

2-Chloropropane
(Isopropyl chloride)

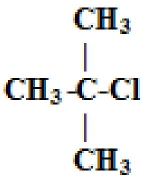
$CH_3CH_2CH_2CH_2Cl$

1-Chlorobutane
(Butyl chloride)



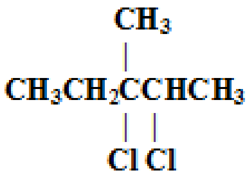
$CH_3CH_2\underset{\underset{Br}{|}}{C}HCH_3$

2-Bromobutane



$CH_3\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{-}Cl$

2-Chloro-2-methylpropane

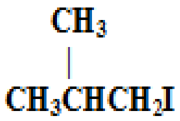


$CH_3CH_2\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}\underset{\underset{Cl}{|}}{C}HCH_3$

2,3-Dichloro-3-methylpentane

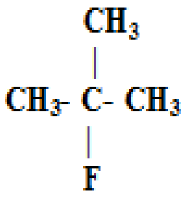
$Cl_2CH - CHCl_2$

1,1,2,2-Tetrachloroethane



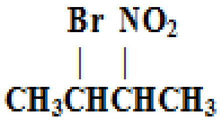
$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2I$

1-Iodo-2-methylpropane



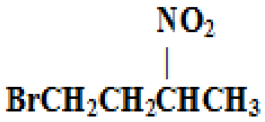
$CH_3\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{F}{|}}{C}}\text{-}CH_3$

2-Fluro-2-methylpropane



$CH_3\overset{\overset{Br}{|}}{C}H\overset{\overset{NO_2}{|}}{C}HCH_3$

2-Bromo-3-nitrobutane



$BrCH_2CH_2\overset{\overset{NO_2}{|}}{C}HCH_3$

1-Bromo-3-nitrobutane

The names shown beneath the structural formulas are systematic names. Those shown in parentheses are common names.

2.5 Physical Properties of Alkanes

The alkane molecule is held together entirely by covalent bonds, which either join two atoms of the same kind and hence are non-polar, or join atoms that differ very little in electronegativity and hence are only slightly polar. Furthermore, these bonds are directed in a very symmetrical way, so that the slight bond polarities tend to cancel out. As a result an alkane molecule is either non-polar or very weakly polar. The forces holding non-polar molecules are limited to van der Waals forces, they are weak and of very short range. They act only between the portions of different molecules that are in close contact, that is, between the surfaces of molecules. Within a family, therefore, we would expect that the larger the molecule and hence the larger its surface area the stronger the intermolecular forces.

The boiling points and the melting points of the alkanes rise as the number of the carbons increases. That is because boiling and melting require overcoming the intermolecular forces of liquid and a solid; the boiling point and melting points rise because these intermolecular forces increase as the molecules get larger.

The branching, lower the boiling points because with branching the shape of the molecule tends to approach that of a sphere; and as this happens the surface area decreases, with the result that the intermolecular forces become weaker and are overcome at a lower temperature.

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

The relative density increases with size of the alkanes, and all alkanes are less dense than water. In general, to be denser than water a compound must contain a heavy atom like Br or I, or several atoms like Cl.

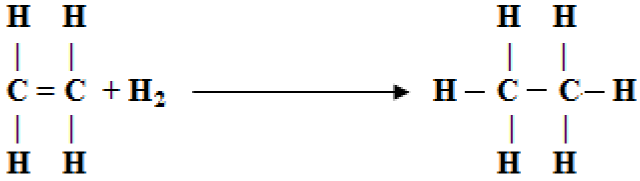
2.6 Preparation of Alkanes

1- Hydrogenation of alkenes

Hydrogenation is the most useful method for preparing alkanes. It is the addition of H_2 to a multiple bond.

$$C_nH_{2n} \xrightarrow{H_2+Pt,Pd\text{ or }Ni} C_nH_{2n+2}$$

Alkene **Alkane**



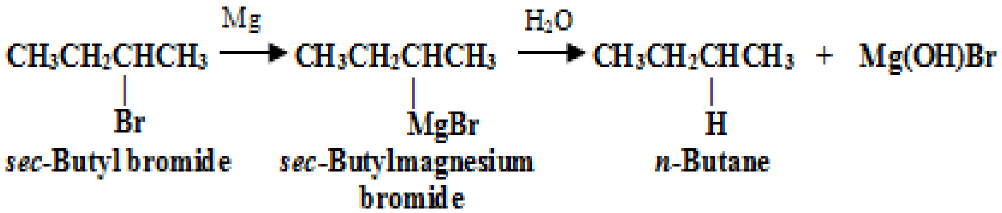
Ethylene **Ethane**

2- Reduction of alkyl halides

(a) Hydrolysis of Grignard reagent

When a solution of an alkyl halide in dry ethyl ether, is allowed to stand over turnings of metallic magnesium, the resulting solution is known as a Grignard reagent. The reaction with water gives an alkane.

$$R-X + Mg \longrightarrow \underset{\text{Grignard Reagent}}{R-MgX} \xrightarrow{H_2O} R-H + Mg(OH)X$$



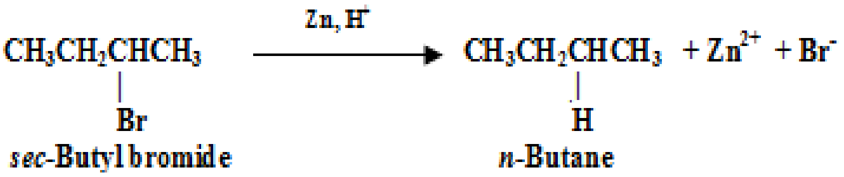
$$\underset{\underset{\textstyle Br}{|}}{CH_3CH_2CHCH_3} \xrightarrow{Mg} \underset{\underset{\textstyle MgBr}{|}}{CH_3CH_2CHCH_3} \xrightarrow{H_2O} \underset{\underset{\textstyle H}{|}}{CH_3CH_2CHCH_3} + Mg(OH)Br$$

sec-Butyl bromide　*sec*-Butylmagnesium bromide　*n*-Butane

(b) Reduction by metal and acid

Reduction of an alkyl halide with metal and acid, involves the replacement of a halogen atom by a hydrogen atom. The product is an alkane.

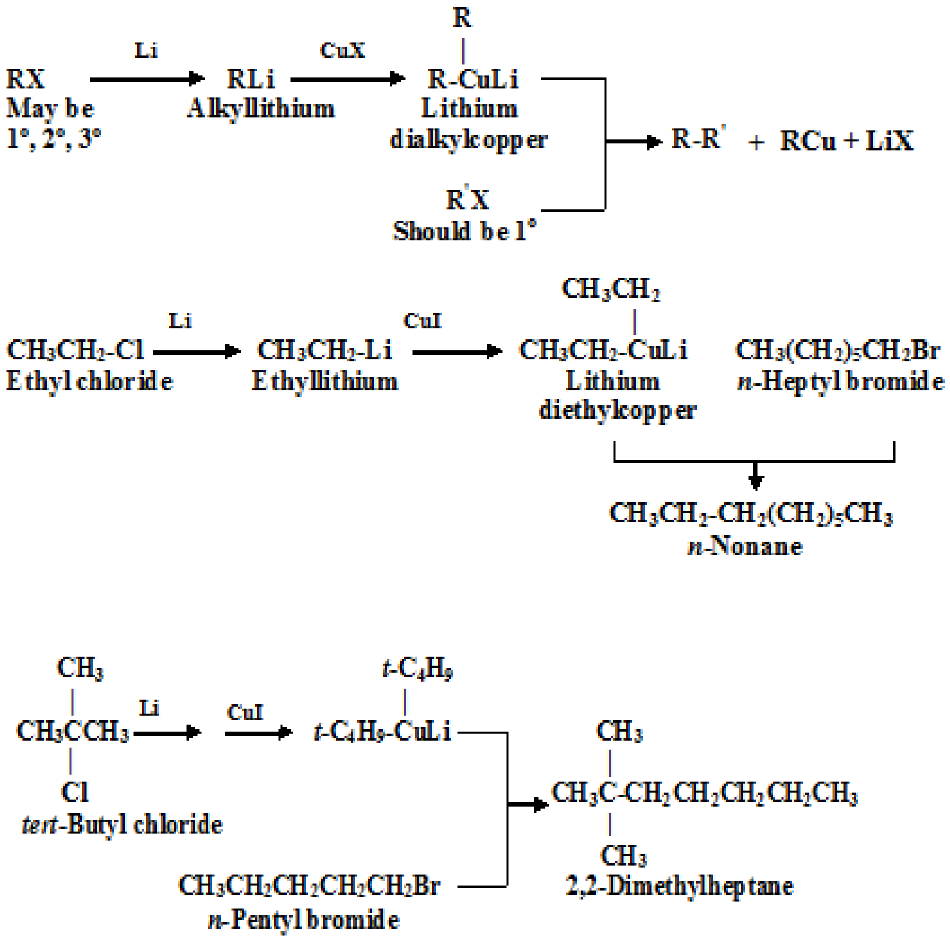
$$R-X + Zn + H^+ \longrightarrow R-H + Zn^{2+} + X^-$$



$$\underset{\underset{\textstyle Br}{|}}{CH_3CH_2CHCH_3} \xrightarrow{Zn,\,H^+} \underset{\underset{\textstyle H}{|}}{CH_3CH_2CHCH_3} + Zn^{2+} + Br^-$$

sec-Butyl bromide　*n*-Butane

3- Coupling of alkyl halides with organometallic compounds

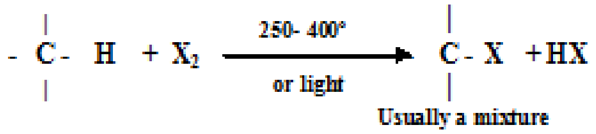


2.7 *Reactions of Alkanes*

Alkanes are generally not considered to be very reactive substance. However, under suitable conditions they are do react.

1- Halogenation

Alkanes react with the halogens (except iodine) to form substitution products.



$$-\overset{|}{\underset{|}{C}}-H + X_2 \xrightarrow[\text{or light}]{250\text{-}400^{\circ}} \overset{|}{\underset{|}{C}}-X + HX$$

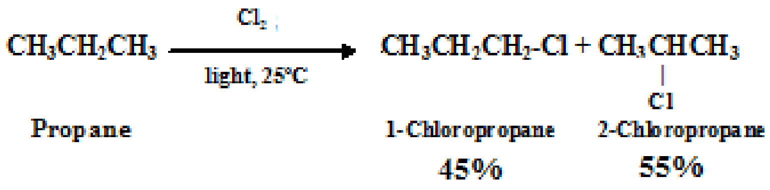
Usually a mixture

Reactivity X_2: $Cl_2 > Br_2$

H_2: $3^{\circ} > 2^{\circ} > 1^{\circ} > 2^{\circ}$ CH_3-H

$$CH_3CH_3 + \xrightarrow[\text{light, 25°C}]{Cl_2} CH_3CH_2\text{-}Cl$$

Ethane Chloroethane

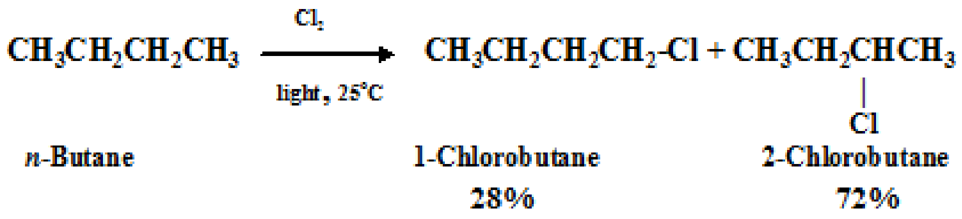


$$CH_3CH_2CH_3 \xrightarrow[\text{light, 25°C}]{Cl_2} CH_3CH_2CH_2\text{-}Cl + CH_3\underset{\underset{Cl}{|}}{C}HCH_3$$

Propane

1-Chloropropane 45%

2-Chloropropane 55%

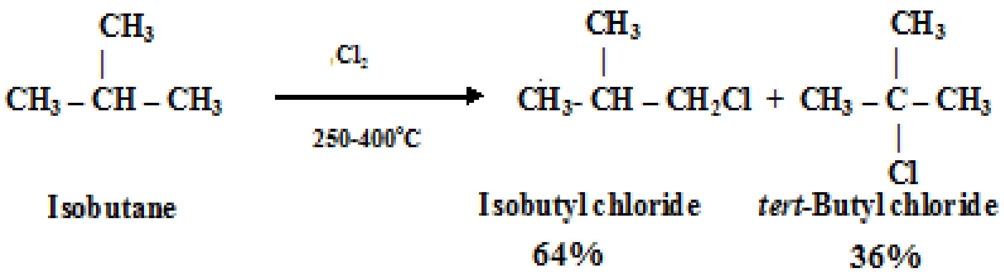


$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{light, 25°C}]{Cl_2} CH_3CH_2CH_2CH_2\text{-}Cl + CH_3CH_2\underset{\underset{Cl}{|}}{C}HCH_3$$

n-Butane

1-Chlorobutane 28%

2-Chlorobutane 72%



$$CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_3 \xrightarrow[250\text{-}400^{\circ}C]{Cl_2} CH_3\text{-}\overset{\overset{CH_3}{|}}{C}H-CH_2Cl + CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_3$$

Isobutane

Isobutyl chloride 64%

tert-Butyl chloride 36%

2- Oxidation (Combustion)

Although alkanes are resistant to attack by oxidizing agents generally, they all undergo combustion in air or oxygen, the products of complete oxidation being carbon dioxide and water.

$$C_nH_{2n+2} + \text{excess } O_2 \xrightarrow{\text{flame}} nCO_2 + (n+1)\, H_2O$$

$$CH_4 + 2O_2 \xrightarrow{\text{flame}} CO_2 + 2H_2O$$

$$C_5H_{12} + 8O_2 \xrightarrow{\text{flame}} 5CO_2 + 6H_2O$$

Organic Chemistry

Chapter 3

Alkenes

3.1 Introduction

Molecules of the alkene (also called olefins) series of hydrocarbons are characterized by having two adjacent carbon atoms joined to one another by a double bond. The carbon-carbon double bond is unsaturated and hence highly reactive toward a wide variety of reagents.

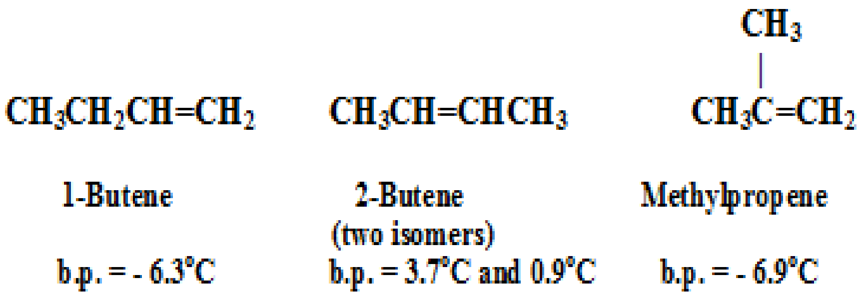
The general formula of alkenes is $\mathbf{C_nH_{2n}}$, where n is the number of carbon atoms. The first nine members of this series are listed in Table 3.1.

Table 3.1 The first nine member of the alkenes

General formula	Structure	Name
C_2H_4	$CH_2 = CH_2$	Ethene
C_3H_6	$CH_2 = CHCH_3$	Propene
C_4H_8	$CH_2 = CHCH_2CH_3$	1-Butene
C_5H_{10}	$CH_2 = CH(CH_2)_2CH_3$	1-Pentene
C_6H_{12}	$CH_2 = CH(CH_2)_3CH_3$	1-Hexene
C_7H_{14}	$CH_2 = CH(CH_2)_4CH_3$	1-Heptene
C_8H_{16}	$CH_2 = CH(CH_2)_5CH_3$	1-Octene
C_9H_{18}	$CH_2 = CH(CH_2)_6CH_3$	1-Nonene
$C_{10}H_{20}$	$CH_2 = CH(CH_2)_7CH_3$	1-Decene

3.2 Isomerism in Alkenes

Isomeric compounds are also possible in the alkenes. For the molecular formula C_4H_8, there are three different ways of organizing the four carbon atoms and the double bond:



$CH_3CH_2CH=CH_2$ $\quad$ $CH_3CH=CHCH_3$ $\quad$ $CH_3\overset{CH_3}{\overset{|}{C}}=CH_2$

1-Butene, b.p. = - 6.3°C

2-Butene (two isomers), b.p. = 3.7°C and 0.9°C

Methylpropene, b.p. = - 6.9°C

(C_4H_8 isomers)

3.3 *Nomenclature*

Common names are seldom used except for three simple alkene; ethylene, propylene, and isobutylene. Most alkene are named by IUPAC system.

1- The longest continuous chain of carbon atoms containing the double bond serves as the parent compound.

2- The ending ***–ane*** of the corresponding alkane hydrocarbon name is replaced by the ending ***–ene***.

3- The position of the double bond is indicated by the lower number of the numbers of the carbon atoms to which it is attached. The number that represents this position is placed before the parent compound name. Alkyl groups attached to the parent compound are designated as is done for the alkane.

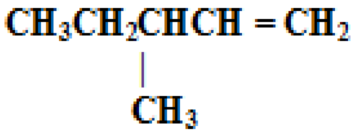
4- If a geometric isomer is designated, the name begins with *cis*- or *trans*-.

$CH_3CH_2CH_2CH_2CH=CH_2$

1- Hexene

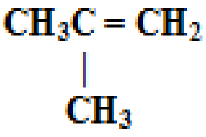
$CH_2=CHCH_2CH_3$

1-Butene



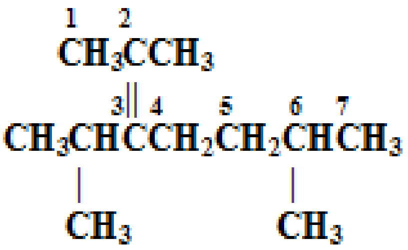
$$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}CH = CH_2$$

3-Methyl-1-pentene



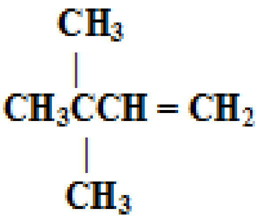
$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}} = CH_2$$

2-Methylpropene



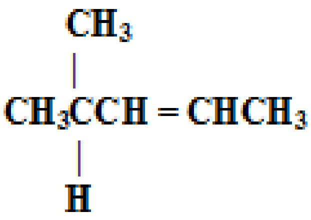
$$CH_3\underset{\displaystyle CH_3}{\underset{|}{CH}}\overset{\displaystyle \overset{1}{CH_3}\overset{2}{C}CH_3}{\overset{\|}{\overset{3}{C}}}\overset{4}{C}H_2\overset{5}{C}H_2\underset{\displaystyle CH_3}{\underset{|}{\overset{6}{C}H}}\overset{7}{C}H_3$$

3-isopropyl-2,6-Dimethyl -2-heptene



$$CH_3\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}CH = CH_2$$

3,3-Dimethyl-1-butene

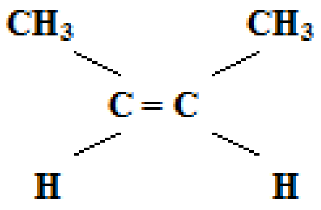


$$CH_3\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}CH = CHCH_3$$

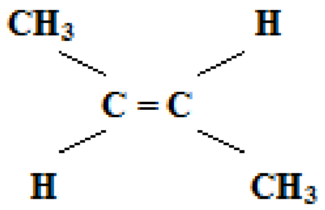
4-Methyl-2-pentene

$Cl_2C = CHCl$

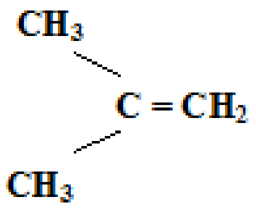
Trichloroethene



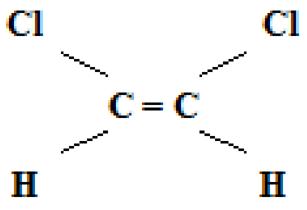
cis-2-Butene



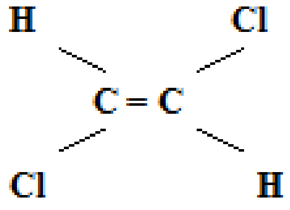
trans-2-Butene



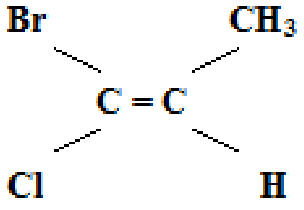
2-Methylpropene



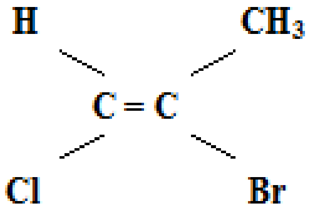
cis-1,2-Dichloroethene



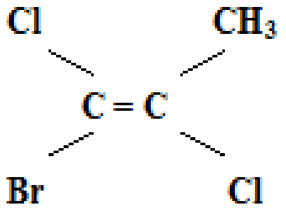
trans-1,2-Dichloroethene



1-Bromo-1-chloropropene



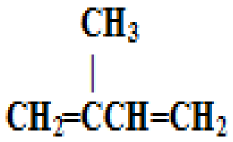
2-Bromo-1-chloropropene



1-Bromo-1,2-dichloropropene

$CH_2{=}CHCH_2CH{=}CH_2$

1,4-Pentadiene



$$CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}CH{=}CH_2$$

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

3.4 *Physical Properties of Alkenes*

The alkenes possess physical properties that are essentially the same as those of the alkanes. They are insoluble in water, but quite soluble in non-polar solvents like benzene, ether, and chloroform. They are less dense than water. The boiling point rises with increasing carbon number; as with alkane, branching lowers the boiling point.

Like alkanes, alkenes are at most only weakly polar. Since the loosely held π electrons of the double bond are easily pulled or pushed, dipole moments are larger than for alkanes.

3.5 *Preparation of Alkenes*

1- Dehydrohalogenation of alkyl halides

Dehydrohalogenation involves loss of the halogen atom and of hydrogen atom from a carbon adjacent to the one losing the halogen.

$$-\underset{\underset{\displaystyle H}{|}}{\overset{|}{C}}-\underset{\underset{\displaystyle X}{|}}{\overset{|}{C}}- + KOH \xrightarrow{\text{alcohol}} -\overset{|}{C}{=}\overset{|}{C}- + KX + H_2O$$

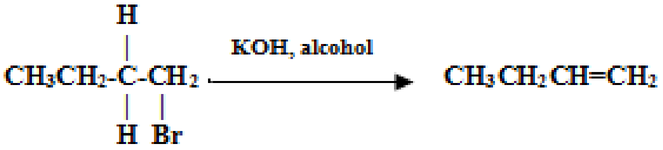
Ease of dehydrohalogenation $3° > 2° > 1°$
of alkyl halides

$$CH_3CH_2CH_2CH_2Cl \xrightarrow{KOH,\ alcohol} CH_3CH_2CH = CH_2 + KCl + H_2O$$

***n*-Butyl chloride** **1-Butene**

$$CH_3CH_2CHClCH_3 \xrightarrow{KOH,\ alcohol} CH_3CH{=}CHCH_3 + CH_3CH_2CH{=}CH_2$$

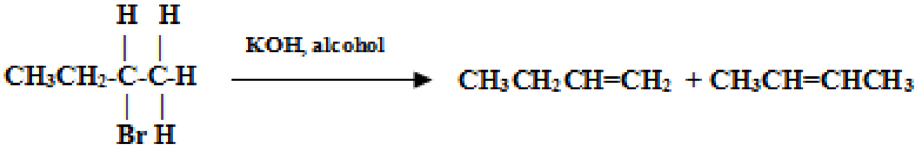
***sec*-Butyl chloride** **2-Butene 80%** **1-Butene 20%**



$$CH_3CH_2-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\underset{\displaystyle Br}{C}H_2 \xrightarrow{KOH,\ alcohol} CH_3CH_2CH{=}CH_2$$

***sec*-Butyl bromide**

1-Butene
Only product

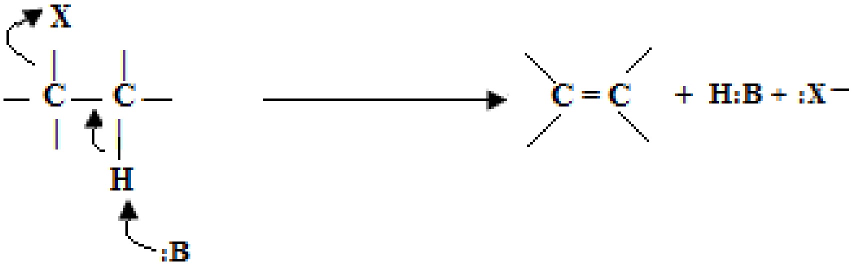


$$CH_3CH_2-\overset{\displaystyle H}{\underset{\displaystyle Br}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H \xrightarrow{KOH,\ alcohol} CH_3CH_2CH{=}CH_2 + CH_3CH{=}CHCH_3$$

***sec*-Butyl bromide**

1-Butene 19% **2-Butene 81%**

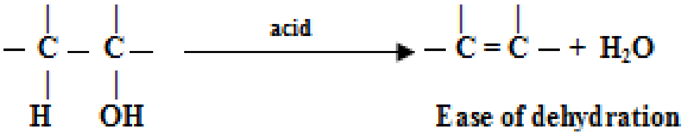
***Mechanism*:**



The base **:**B can be neutral or negatively charged: for example, H_2O or OH^-. The conjugate acid H:B will then be positively charged or neutral: for example, H_3O or H_2O.

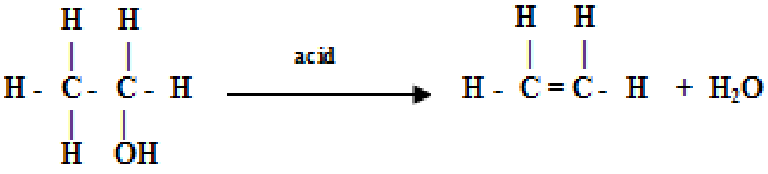
2- Dehydration of alcohols

In the dehydration of alcohols, the H and OH are lost from adjacent carbons. An acid catalyst is necessary and application of heat.



$$-\underset{\mathrm{H}}{\overset{|}{\underset{|}{C}}}-\underset{\mathrm{OH}}{\overset{|}{\underset{|}{C}}}- \xrightarrow{\text{acid}} -\overset{|}{C}=\overset{|}{C}- + H_2O$$

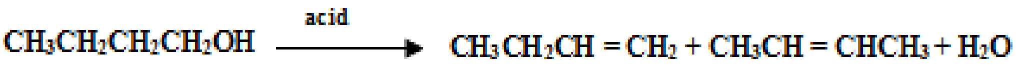
Ease of dehydration of alcohols
3° > 2° > 1°



$$H-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\underset{|}{\overset{|}{C}}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\underset{|}{\overset{|}{C}}}}-H \xrightarrow{\text{acid}} H-\overset{\mathrm{H}}{\overset{|}{C}}=\overset{\mathrm{H}}{\overset{|}{C}}-H + H_2O$$

Ethyl alcohol

Ethylene

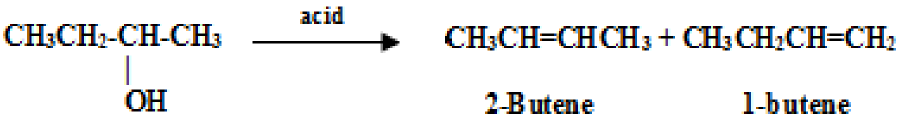


$$CH_3CH_2CH_2CH_2OH \xrightarrow{\text{acid}} CH_3CH_2CH=CH_2 + CH_3CH=CHCH_3 + H_2O$$

n-Butyl alcohol

1-Butene

2-Butene
Chief product



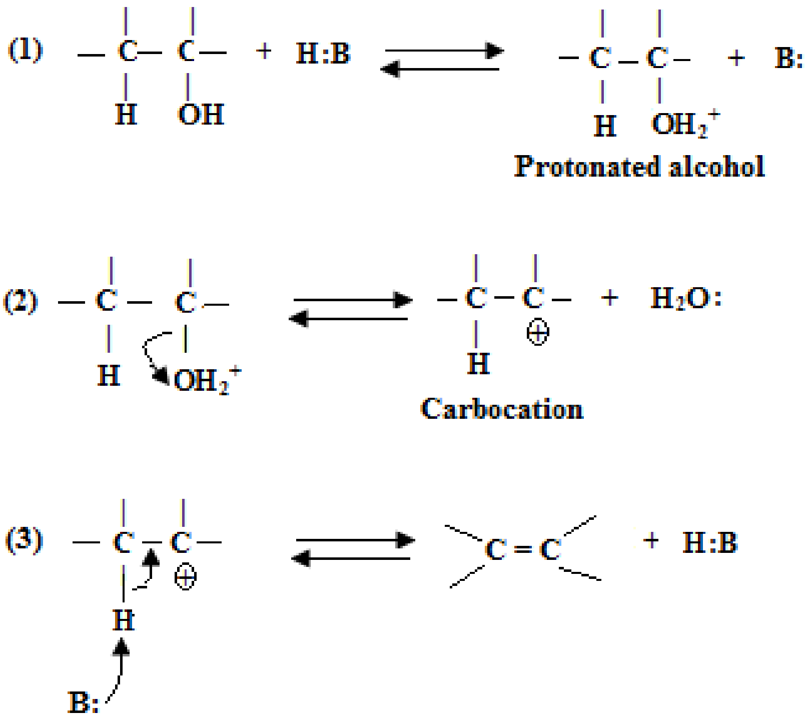
$$CH_3CH_2\text{-}\underset{\mathrm{OH}}{\underset{|}{CH}}\text{-}CH_3 \xrightarrow{\text{acid}} CH_3CH=CHCH_3 + CH_3CH_2CH=CH_2$$

sec-Butyl alcohol

2-Butene
Chief product

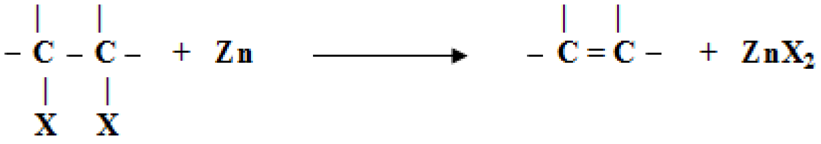
1-butene

***Mechanism*:**



3- Dehalogenation of vicinal dihalides

Alkenes can be prepared by elimination of two halide atoms from a vicinal (neighboring) dihalides.



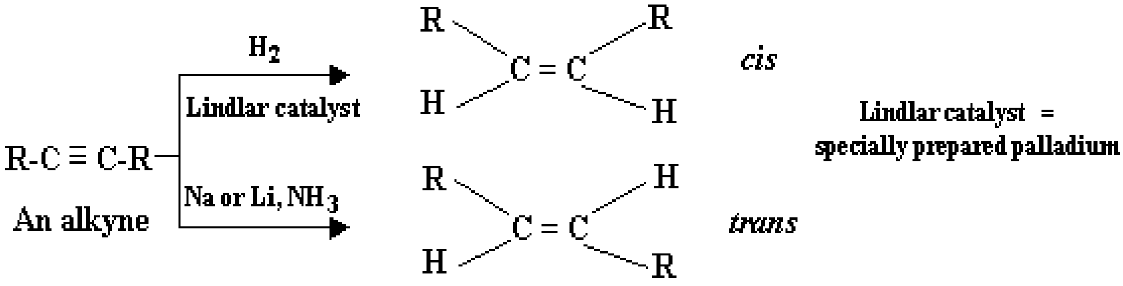
$$-\underset{X}{\overset{|}{C}}-\underset{X}{\overset{|}{C}}- + Zn \longrightarrow -\overset{|}{C}=\overset{|}{C}- + ZnX_2$$

$CH_3CHBrCHBrCH_3 \xrightarrow{Zn} CH_3CH = CHCH_3 + ZnBr_2$

2,3-Dibromobutane **2-Butene**

4- Reduction of alkynes

Trans alkene can be obtained by reduction of alkynes with sodium or lithium in liquid ammonia. Cis alkene is obtained by hydrogenation of alkynes with a specially prepared palladium called Lindlar catalyst.



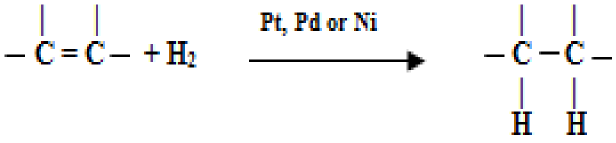
3.6 *Reactions of alkenes*

The presences of the carbon-carbon double bond confers very considerable chemical activity on the alkenes and consequently they react with a much wider variety of reagents than do the alkanes. The π-bond component of the double bond is weaker than the σ-bond component and the π-electrons are more easily accessible to attacking reagents.

(Addition Reactions)

1- Addition of hydrogen

When an alkene is mixed with hydrogen, there is no appreciable reaction, but in the presence of certain metal catalysts such as nickel, platinum or palladium, a fairly rapid reaction occurs leading to the uptake of hydrogen.



$$-\overset{|}{C}=\overset{|}{C}- + H_2 \xrightarrow{\text{Pt, Pd or Ni}} -\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\underset{H}{|}}{\overset{|}{C}}-$$

$$\mathbf{CH_3CH = CH_2 \xrightarrow{H_2,\ Ni} CH_3CH_2CH_3}$$

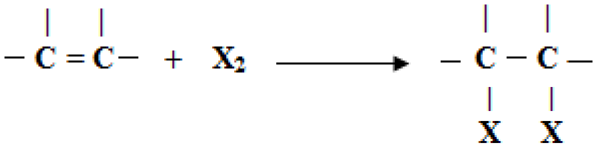
Propene **Propane**
(Propylene)

$$\mathbf{CH_2 = CH_2 \xrightarrow{H_2,\ Ni} CH_3CH_3}$$

Ethylene **Ethane**

2- Addition of halogen

Chlorine and bromine react readily with alkenes, in the liquid or vapour states, to form dihalogeno addition products, the two halogen atoms are attached to adjacent carbons. Iodine generally fails to react.



$$-\overset{|}{C}=\overset{|}{C}- + X_2 \longrightarrow -\underset{\underset{X}{|}}{\overset{|}{C}}-\underset{\underset{X}{|}}{\overset{|}{C}}-$$

$\mathbf{X_2 = Cl_2, Br_2}$

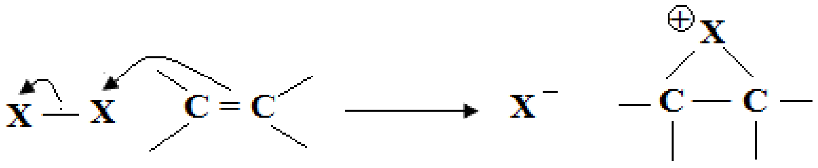
$$CH_3CH = CH_2 \xrightarrow{Br_2 \text{ in } CCl_4} CH_3CHBrCH_2Br$$

Propene
(Propylene)

1,2-Dibromopropane
(Propylene bromide)

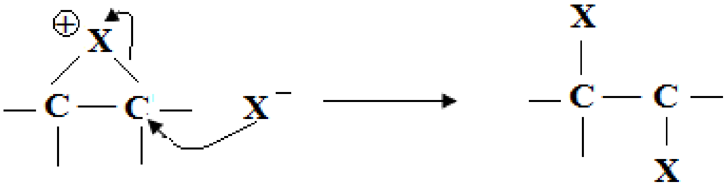
Mechanism:

(1)



A halonium ion

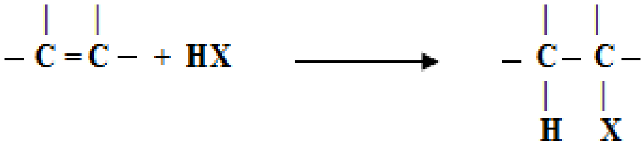
(2)



In step (1) a halogen is transferred, without a pair of electrons, from a halogen molecule to the carbon-carbon double bond; there is formed a halide ion and organic cation. In step (2) this cation reacts with a halide ion to yield the addition product.

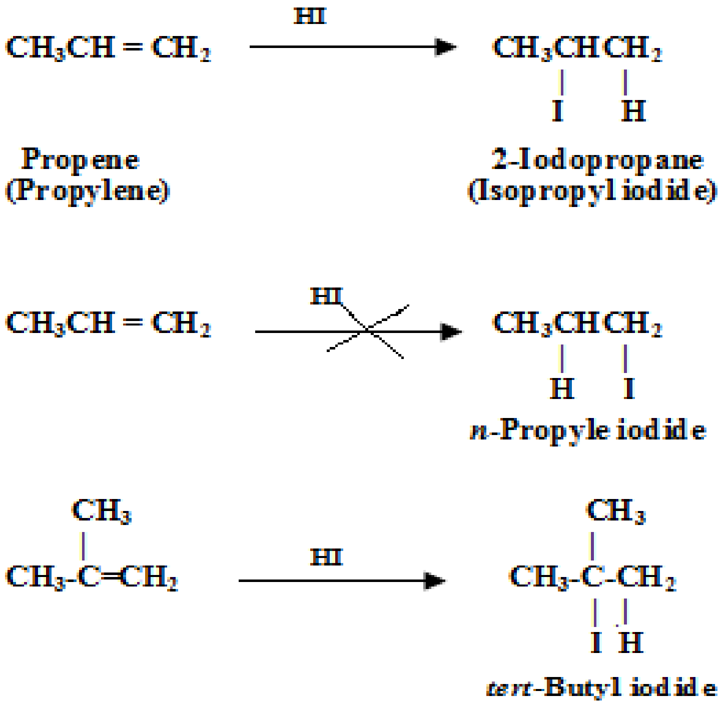
3- Addition of hydrogen halides

Alkenes react, usually on heating, with hydrogen halides (either gaseous or in concentrated solution) to form an addition product.

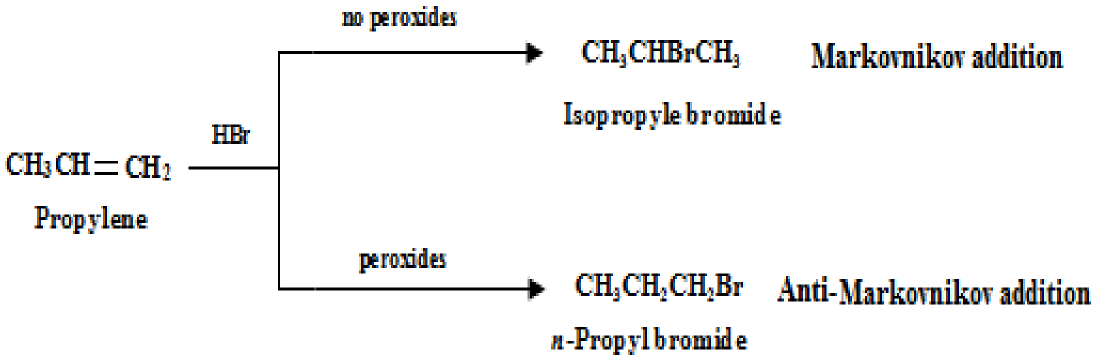


HX = HCl, HBr, HI

The hydrogen attaches itself to the carbon that already holds the greater number of hydrogens. This statement is called ***Markovnikov's rule***.

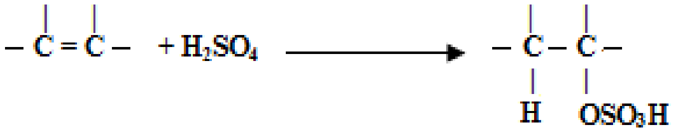


If the reaction take place in the absence of peroxide, the addition of HBr, to alkenes follows Markovnikov's rule. On the other hand, if the reaction take place in the presence of peroxide, HBr adds to alkenes in the reverse direction.

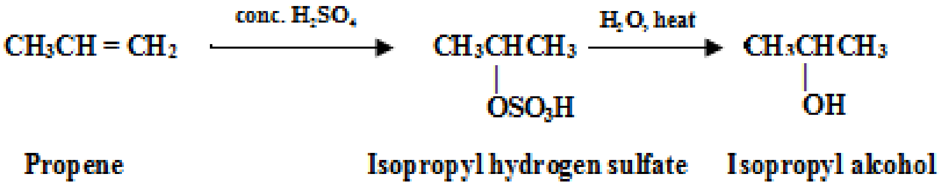


4- Addition of sulfuric acid

Alkenes are slowly absorbed when they are bubbled through, or shaken with, cold concentrated sulphuric acid. The reaction involves the addition of H and HSO_4 groups across the double bond, to form alkyl hydrogen sulfates, which is on dilution with water and heating yield alcohol.

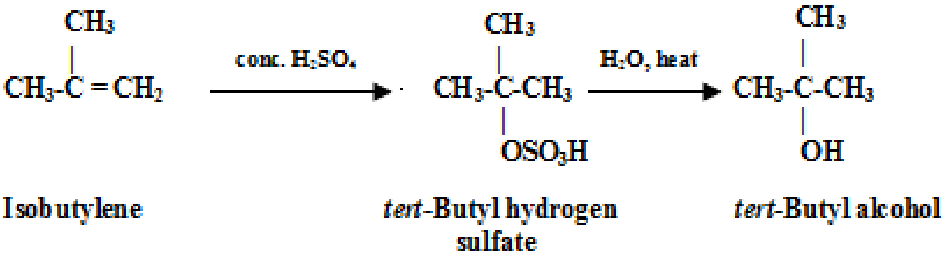


$$-\overset{|}{C}=\overset{|}{C}- \; + H_2SO_4 \longrightarrow -\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\underset{OSO_3H}{|}}{\overset{|}{C}}-$$



$$CH_3CH=CH_2 \xrightarrow{\text{conc. } H_2SO_4} CH_3\underset{\underset{OSO_3H}{|}}{C}HCH_3 \xrightarrow{H_2O,\ \text{heat}} CH_3\underset{\underset{OH}{|}}{C}HCH_3$$

Propene — Isopropyl hydrogen sulfate — Isopropyl alcohol

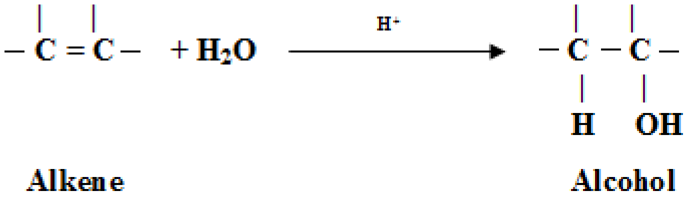


$$CH_3\text{-}\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow{\text{conc. } H_2SO_4} CH_3\text{-}\underset{\underset{OSO_3H}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH_3 \xrightarrow{H_2O,\ \text{heat}} CH_3\text{-}\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH_3$$

Isobutylene — *tert*-Butyl hydrogen sulfate — *tert*-Butyl alcohol

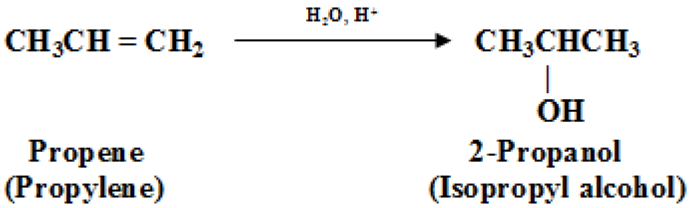
5- Addition of water. Hydration

Alkenes are also react with water, and this reaction is carried out in a dilute acid medium. The reaction follows Markovnikov's rule.



$$-\overset{|}{C}=\overset{|}{C}- \; + H_2O \xrightarrow{H^+} -\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\underset{OH}{|}}{\overset{|}{C}}-$$

Alkene — Alcohol

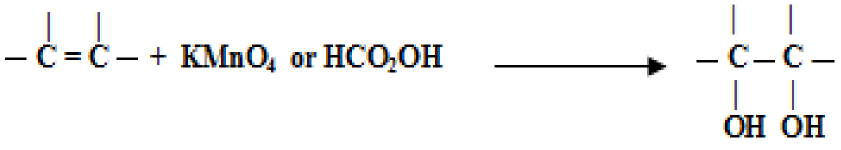


$$CH_3CH=CH_2 \xrightarrow{H_2O,\ H^+} CH_3\underset{\displaystyle OH}{\underset{|}{CH}}CH_3$$

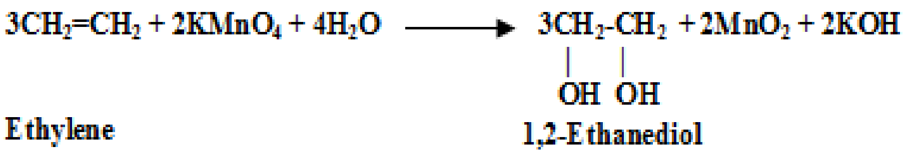
Propene (Propylene) — 2-Propanol (Isopropyl alcohol)

6- Hydroxylation – glycol formation

Alkanes are highly resistant to chemical oxidizing agents under normal conditions. In contrast, alkenes are quite sensitive to oxidation by several oxidizing agent. If an alkene is shaken with a few drops of a dilute acidified solution of $KMnO_4$, the purple solution is rapidly decolorized. The alkene is oxidized to an addition product, in which two hydroxyl groups have been added across the carbon-carbon double bond; the product is a di-alcohol or diol.

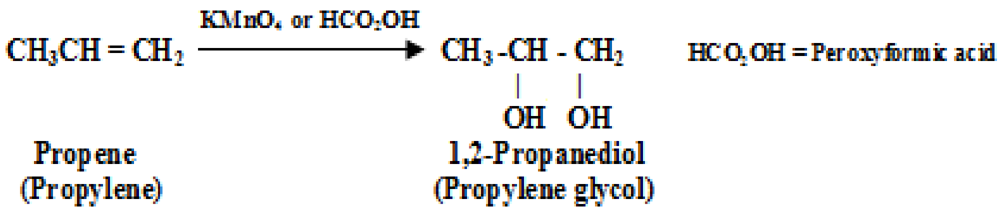


$$-\overset{|}{C}=\overset{|}{C}- + KMnO_4 \text{ or } HCO_2OH \longrightarrow -\underset{\displaystyle OH}{\underset{|}{\overset{|}{C}}}-\underset{\displaystyle OH}{\underset{|}{\overset{|}{C}}}-$$



$$3CH_2{=}CH_2 + 2KMnO_4 + 4H_2O \longrightarrow 3\underset{\displaystyle OH}{\underset{|}{CH_2}}-\underset{\displaystyle OH}{\underset{|}{CH_2}} + 2MnO_2 + 2KOH$$

Ethylene — 1,2-Ethanediol



$$CH_3CH=CH_2 \xrightarrow{KMnO_4 \text{ or } HCO_2OH} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH_2}}$$

HCO_2OH = Peroxyformic acid

Propene (Propylene) — 1,2-Propanediol (Propylene glycol)

7- Polymerization

In the presence of a certain catalyst, alkene molecule can add on to each other in a head-to-tail fashion to form long-chain molecules of a very high relative molecular mass.

$$n\ CH_2 = CH_2 \xrightarrow[\text{pressure}]{O_2,\ \text{heat}} -CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$$

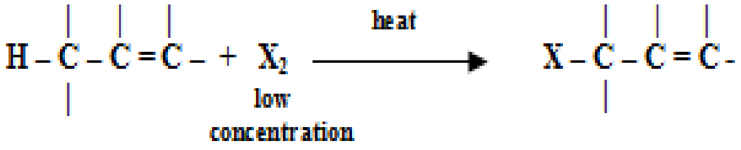
$$\text{or}\quad (-CH_2-CH_2-)_n$$

Ethylene **Polyethylene**

(Substitution Reactions)

Halogenation. Allylic substitution

Alkenes react with halogens, substitution reaction. The reaction carried out as follow:

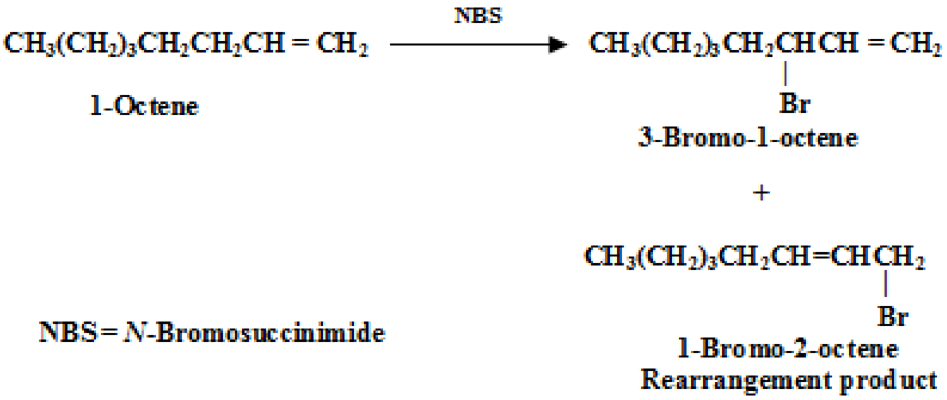


$$H-C-C=C- + X_2 \xrightarrow[\text{low concentration}]{\text{heat}} X-C-C=C-$$

$X_2 = Cl_2, Br_2$

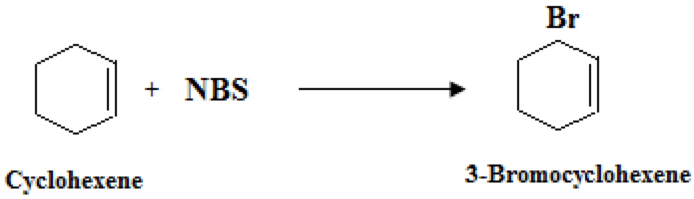
$$CH_3CH = CH_2 \xrightarrow[600°C]{Cl_2} ClCH_2CH = CH_2$$

Propene (Propylene) 3-Chloro-1-propene (Allyl chloride)



$$CH_3(CH_2)_3CH_2CH_2CH=CH_2 \xrightarrow{NBS} CH_3(CH_2)_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH=CH_2 + CH_3(CH_2)_3CH_2CH=CH\underset{\displaystyle Br}{\underset{|}{C}}H_2$$

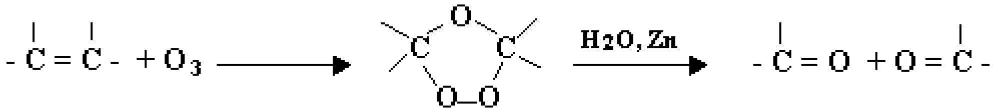
NBS = *N*-Bromosuccinimide

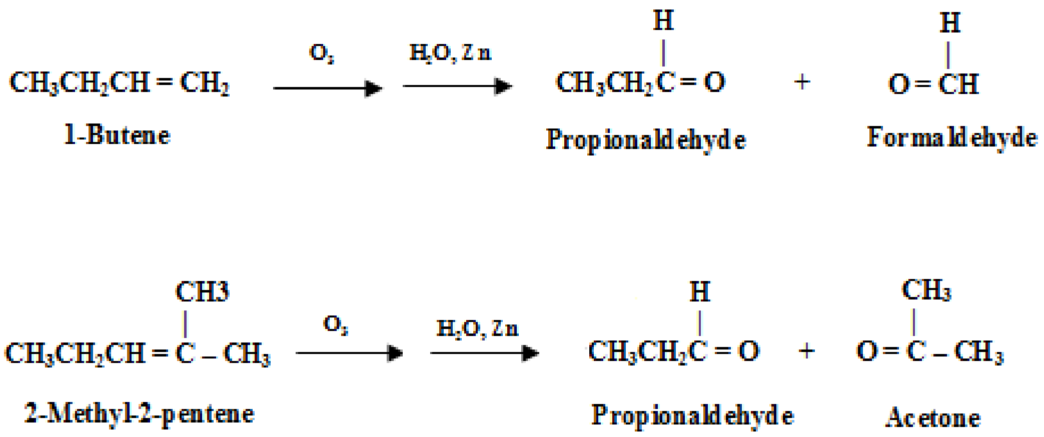


(Cleavage Reactions)

Ozonolysis

O_3 (ozone) is produced by passage of an electric discharge through oxygen O_2. If the mixture of gases is bubbled through a solution of an alkene at low temperature, an unstable product known as an ozonide is formed. Ozonides are unstable and are readily hydrolysed to form aldehydes or ketones.





$$CH_3CH_2CH=CH_2 \xrightarrow{O_3} \xrightarrow{H_2O,\ Zn} CH_3CH_2\overset{\overset{H}{|}}{C}=O \ + \ O=\overset{\overset{H}{|}}{C}H$$

$$CH_3CH_2CH=\overset{\overset{CH3}{|}}{C}-CH_3 \xrightarrow{O_3} \xrightarrow{H_2O,\ Zn} CH_3CH_2\overset{\overset{H}{|}}{C}=O \ + \ O=\overset{\overset{CH_3}{|}}{C}-CH_3$$

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Organic Chemistry

Chapter 4

Alkynes

4.1 Introduction

Molecules of alkyne series of hydrocarbon are characterized by having two adjacent carbon atoms joined to one another by a triple bond. The carbon-carbon triple bond is unsaturated and highly reactive toward the reagents that double bonds react with.

The general formula is **C_nH_{2n-2}**.

$HC \equiv CH$	Ethyne (acetylene)
$HC \equiv CCH_3$	Propyne
$HC \equiv CCH_2CH_3$	1-Butyne
$HC \equiv C(CH_2)_2CH_3$	1-Pentyne
$HC \equiv C(CH_2)_3CH_3$	1-Hexyne
$HC \equiv C(CH_2)_4CH_3$	1-Heptyne
$HC \equiv C(CH_2)_5CH_3$	1-Octyne
$HC \equiv C(CH_2)_6CH_3$	1-Nonyne
$HC \equiv C(CH_2)_7CH_3$	1-Decyne

4.2 Nomenclature

The alkynes are named according to two systems. In one, they are considered to be derived from acetylene by replacement of one or both hydrogen atoms by alkyl group.

$H - C \equiv C - C_2H_5$	**(Ethylacetylene)**	**1-Butyne**
$CH_3 - C \equiv C - CH_3$	**(Dimethylacetylene)**	**2-Butyne**

$CH_3 - C \equiv C - CH(CH_3)_2$ (Isopropylmethylacetylene) 4-Methyl-2-pentyne

For more complicated alkyne the IUPAC names are used. The rules are exactly as for the alkenes, except that the ending **-yne** is used in place of **–ene**.

$HC = CCH_2CH_3$

1-Butyne

$CH_3C = CCH_3$

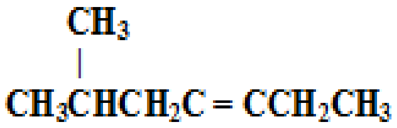
2-Butyne

$CH_3C = CCH_2CH_3$

2-Pentyne

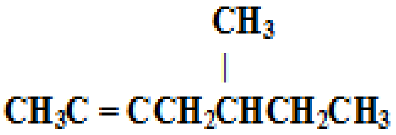
$CH_3CH = CHCH_2C = CH$

4-Hexen-1-yne



$$CH_3\underset{}{\overset{\overset{\displaystyle CH_3}{|}}{C}}HCH_2C = CCH_2CH_3$$

6-Methyl-3-heptyne



$$CH_3C = CCH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2CH_3$$

5-Methyl-2-heptyne

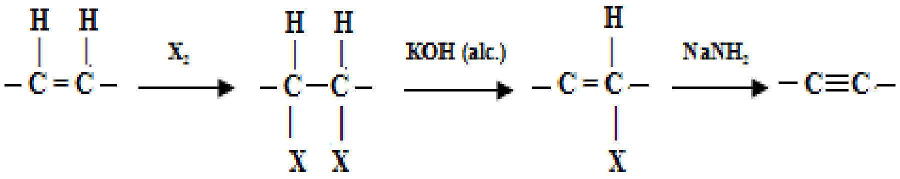
4.3 Physical Properties of Alkynes

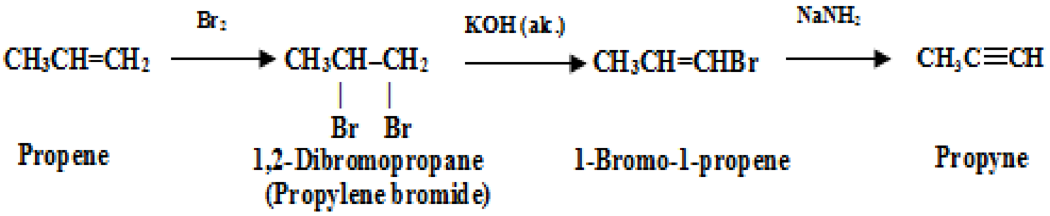
Being compounds of low polarity, the alkynes have physical properties that are essentially the same as those of the alkanes and alkenes. They are insoluble in water but quite soluble in the usual organic solvents of low polarity: ether, benzene, and carbon tetrachloride. They are less dense than water. Their boiling points show the usual increase with increasing carbon number, and the usual effects of chain branching; they are very nearly the same as the boiling points of alkanes and alkenes with the same carbon skeletons.

4.4 Preparation of Alkynes

1- Dehydrohalogenation of alkyl halides

Alkynes is formed by elimination of atoms or groups from two adjacent carbons (double dehydrohalogenation).





Propene — 1,2-Dibromopropane (Propylene bromide) — 1-Bromo-1-propene — Propyne

2- Reaction of metal acetylides with alkyl halides

Lithium or sodium acetylides can react with primary alkyl halides. The alkyl group becomes attached to the triply bonded carbon, and a new, larger alkyne has been generated.

$$-C\equiv C-H \xrightarrow{LiNH_2} -C\equiv C\!:^{-}Li^{+} + \underset{\text{R must be }1^{o}}{RX} \longrightarrow -C\equiv C-R + LiX$$

$$HC\equiv C\!:^{-}Li^{+} + CH_3CH_2CH_2CH_2Br \longrightarrow HC\equiv C-CH_2CH_2CH_2CH_3 + LiBr$$

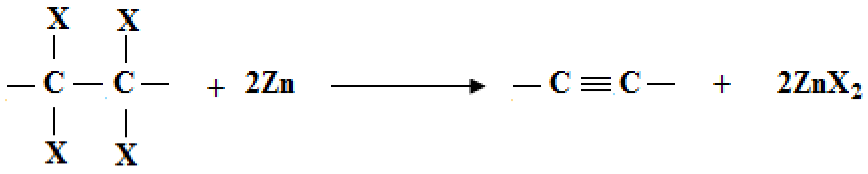
Lithium acetylide   ***n*-Butyl bromide**   **1-Hexyne (*n*-Butylacetylene)**

$$CH_3(CH_2)_4C\equiv C\text{-}Li + CH_3(CH_2)_3CH_2Cl \longrightarrow CH_3(CH_2)_4C\equiv C-CH_2(CH_2)_3CH_3$$

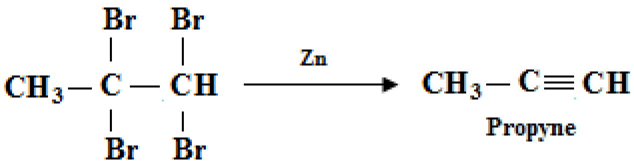
Lithium *n*-pentylacetylide   ***n*-Pentyl chloride**   **6-Dodecyne**

3- Dehalogenation of tetrahalides

Alkynes can be prepared by dehalogenation of trtrahalides.



$$-\overset{X}{\underset{X}{C}}-\overset{X}{\underset{X}{C}}- + 2Zn \longrightarrow -C\equiv C- + 2ZnX_2$$



$$CH_3-\overset{Br}{\underset{Br}{C}}-\overset{Br}{\underset{Br}{CH}} \xrightarrow{Zn} \underset{\text{Propyne}}{CH_3-C\equiv CH}$$

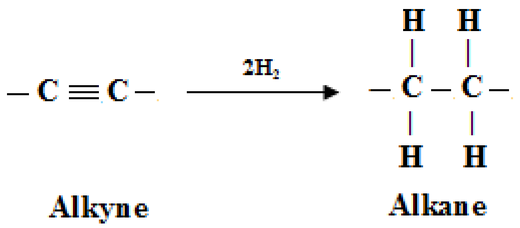
6.5 *Reactions of Alkynes*

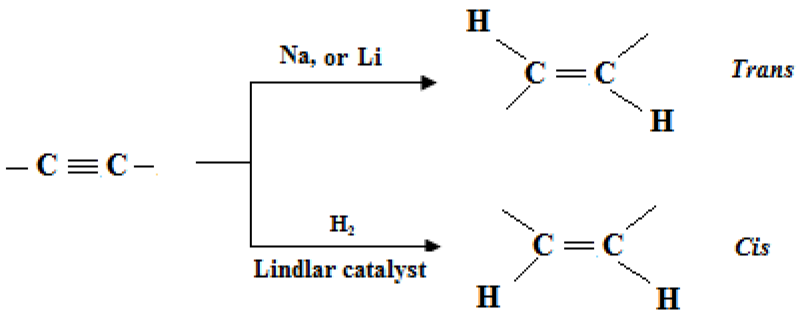
The carbon-carbon triple bond –C≡C– consists of one σ-bond and two weaker π-bonds, so it is not surprising that addition reactions are a characteristic feature of this functional group. Despite its high formal unsaturation, the triple bond dose not usually react so vigorously as a carbon-carbon double bond, as in alkenes, and it is therefore sometimes possible to stop the addition reaction after the uptake of 1 mol of reactant, rather than 2 mol which would be possible in principle.

(Addition Reactions)

1- Addition of hydrogen

As would be expected, alkynes can be hydrogenated catalytically, taking up 2 mol of hydrogen per mol of alkyne to form the corresponding saturated molecule. Careful control of the hydrogenation can stop the reaction at the alkene stage.

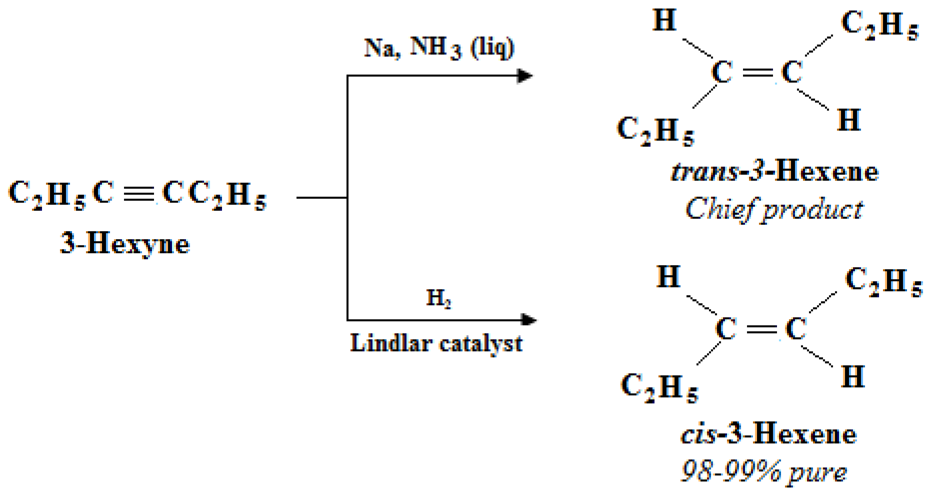




$$CH_3\text{-}C\equiv C\text{-}CH_3 \xrightarrow{2H_2,\ Ni} CH_3CH_2CH_2CH_3$$

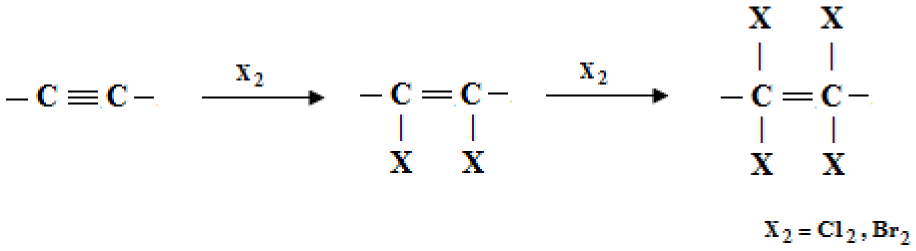
2-Butyne

n-Butane



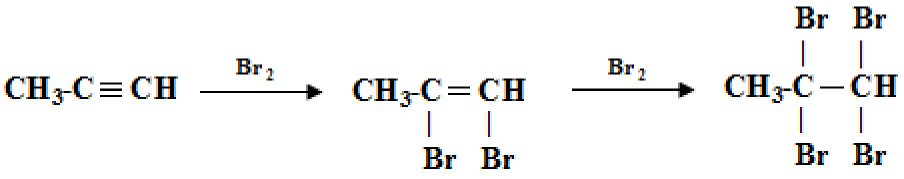
2- Addition of halogen

Alkynes can react with chlorine and bromine to yield tetrahaloalkanes. A dihaloalkene is an intermediate.



$$-C\equiv C- \xrightarrow{X_2} -\underset{X}{C}=\underset{X}{C}- \xrightarrow{X_2} -\overset{X}{\underset{X}{C}}=\overset{X}{\underset{X}{C}}-$$

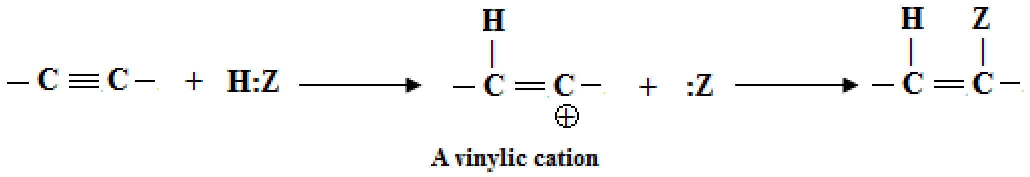
$X_2 = Cl_2, Br_2$

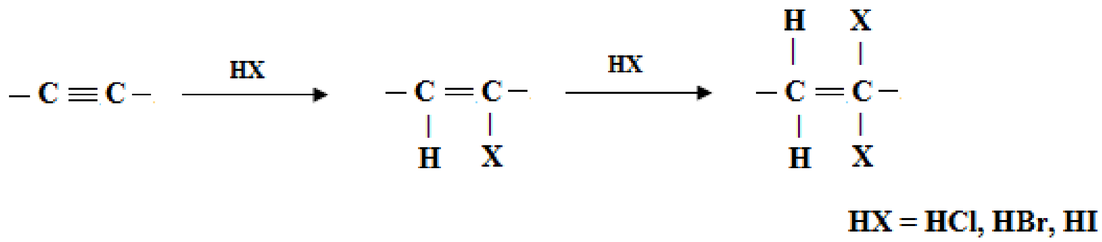


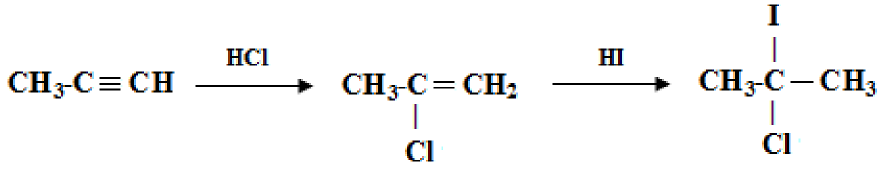
$$CH_3\text{-}C\equiv CH \xrightarrow{Br_2} CH_3\text{-}\underset{Br}{C}=\underset{Br}{CH} \xrightarrow{Br_2} CH_3\text{-}\overset{Br}{\underset{Br}{C}}-\overset{Br}{\underset{Br}{CH}}$$

3- Addition of hydrogen halides

Alkynes also react with hydrogen halides to form alkyl halides. Addition of acids like hydrogen halides is electrophilic addition, and it appears to follow the same mechanism with alkynes as with alkenes: via an intermediate carbocation. The difference is that here the intermediate is a *vinylic cation*.

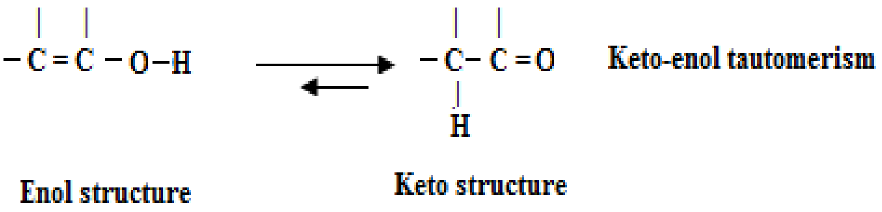






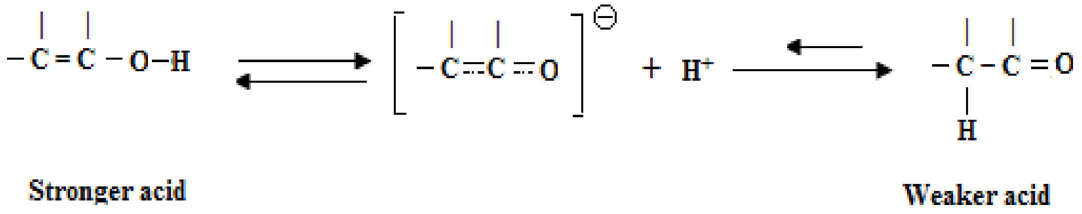
4- Addition of water (hydration)

In the presence of dilute sulphuric acid and a mercury(II) sulphate catalyst at about 60°C, water adds across a triple bond and alkyne is said to be hydrated. If hydration of acetylene followed the same pattern as hydration of alkenes, we would expect addition of H- and –OH to the triple bond to yield *vinyl alcohol*. But all attempts to prepare vinyl alcohol result-like hydration of acetylene, in the formation of acetaldehyde.

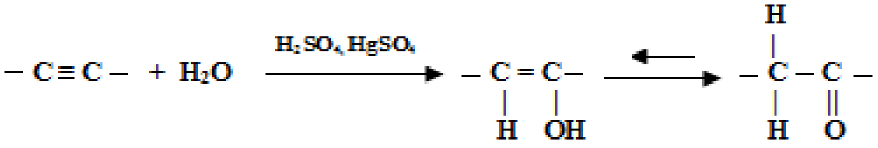


$$-C=C-O-H \rightleftharpoons -\underset{H}{C}-C=O$$

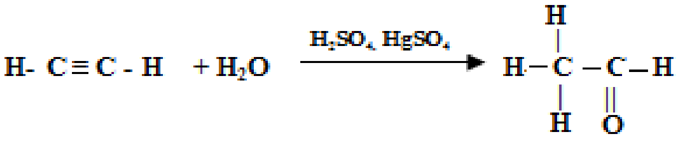
Rearrangement of this enol-keto kind take place particularly easily because of the polarity of the –O-H bond. A hydrogen ion separates readily from oxygen to form a hybrid anion; but when a hydrogen ion (most likely a *different* one) returns, to oxygen, it may readily come off again; but when it attaches itself to carbon, it tends to stay there. This is actually an example of the tendency of a stronger acid to displace a weaker acid from its salt.



$$-C=C-O-H \rightleftharpoons \left[-C\cdots C\cdots O\right]^{\ominus} + H^{+} \rightleftharpoons -\underset{H}{C}-C=O$$

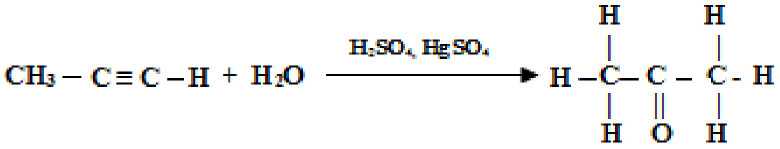


$$-C\equiv C- + H_2O \xrightarrow{H_2SO_4,\ HgSO_4} -\underset{H}{C}=\underset{OH}{C}- \rightleftharpoons -\overset{H}{\underset{H}{C}}-\underset{O}{\overset{\|}{C}}-$$



Acetaldehyde

$$H-C\equiv C-H + H_2O \xrightarrow{H_2SO_4,\ HgSO_4} H-\overset{H}{\underset{H}{C}}-\underset{O}{\overset{\|}{C}}-H$$



Acetone

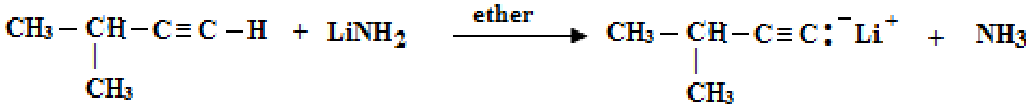
$$CH_3-C\equiv C-H + H_2O \xrightarrow{H_2SO_4,\ HgSO_4} H-\overset{H}{\underset{H}{C}}-\underset{O}{\overset{\|}{C}}-\overset{H}{\underset{H}{C}}-H$$

(Reaction as Acid)

$$-C\equiv C-H + \text{base} \longrightarrow -C\equiv C:^{-}$$

Formation of metal acetylides

Hydrogen attached to triply bonded carbon, as in acetylene or any alkyne with the triple bond at the end of the chain (RC≡C-H), shows appreciable acidity. So when a terminal triple bond is treated with an alkylmagnesium halide or an alkyllithium, the alkane is displaced from its salt, and the metal acetylide is obtained.



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C\equiv C-H + LiNH_2 \xrightarrow{\text{ether}} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C\equiv C:^{-}Li^{+} + NH_3$$

Lithium isopropylacetylide

$$CH_3-C\equiv C-H + n\text{-BuLi} \longrightarrow CH_3C\equiv C^{-}Li^{+} + n\text{-BuH}$$

Lithium methyacetylide

$$HC\equiv CH + C_2H_5MgBr \longrightarrow HC=CMgBr + C_2H_6$$

Ethynylmagnesium bromide

Organic Chemistry

Chapter 5

Alcohols

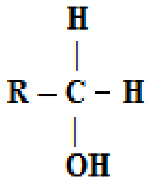
5.1 Introduction

All alcohols contain the hydroxyl group **(-OH)** attached to a saturated carbon. These have the general formula **R-OH**, where **R** is an alkyl or substituted alkyl group. The group may be primary, secondary, or tertiary; it may be open chain or cyclic; it may contain a double bond, a halogen atom, an aromatic ring, or additional hydroxyl group. The **-OH** group is the functional group, determines the properties characteristic of this family. Variations in structure of the **R** group may affect the rate at which the alcohol undergoes certain reactions, and even, in a few cases, may affect the kind of reaction.

Compound in which the hydroxyl group is attached directly to an aromatic ring are not alcohols; they are phenols.

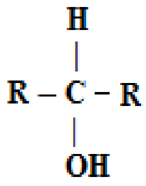
5.2 Classification of alcohols

Alcohols other than methanol, are classified as, primary, secondary, or tertiary, depending on the number of carbons bonded to the carbon atom bearing the **–OH** group. If one carbon is bonded to this carbon atom, the alcohol is primary, if two carbons are bonded, it is secondary, and if three carbons are bonded, it is tertiary.



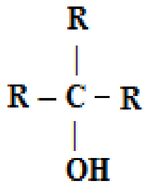
$$\mathrm{R-\underset{\displaystyle OH}{\overset{\displaystyle H}{C}}-H}$$

Primary (1°)



$$\mathrm{R-\underset{\displaystyle OH}{\overset{\displaystyle H}{C}}-R}$$

Secondary (2°)

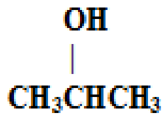


$$\mathrm{R-\underset{\displaystyle OH}{\overset{\displaystyle R}{C}}-R}$$

Tertiary (3°)

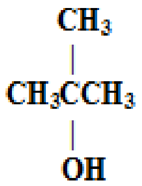
CH_3CH_2OH

Ethanol (1°)



$$\mathrm{CH_3\overset{\displaystyle OH}{C}HCH_3}$$

2-Propanol (2°)



$$\mathrm{CH_3\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{C}}CH_3}$$

2-Methyl-2-propanol (3°)

5.3 Nomenclature

Among the simple alcohols the common names are very commonly used. To write these names, simply put the name of its alkyl group and follow it by the word alcohol. For example; CH_3OH methyl alcohol.

The IUPAC rules for naming the alcohols are very similar to those for naming alkanes, and the following principle are followed:

1- The longest carbon chain that contains the hydroxyl group is considered the parent compound.

2- The **–e** ending of the name of this carbon chain is replaced by **–ol**.

3- The location of the hydroxyl and any other groups are shown by the smallest possible numbers, with the position of the hydroxyl group having the highest priority.

CH_3OH

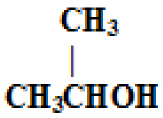
Methanol (Methyl alcohol)

CH_3CH_2OH

Ethanol (Ethyl alcohol)

$CH_3CH_2CH_2OH$

1-Propanol

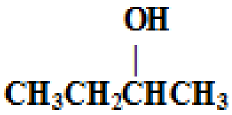


$\overset{CH_3}{\overset{|}{CH_3C}}HOH$

2-Propanol (Isopropyl alcohol)

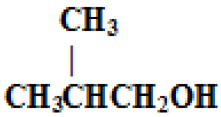
$CH_3CH_2CH_2CH_2OH$

1- Butanol



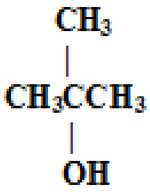
$CH_3CH_2\overset{OH}{\overset{|}{C}}HCH_3$

2-Butanol (*sec*-Butyl alcohol)



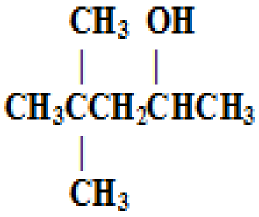
$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2OH$

2-Methyl-1-propanol
(Isobutyl alcohol)



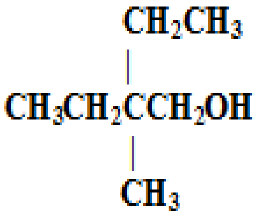
$CH_3\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_3$

2-Methyl-2-propanol
(*tert*-Butyl alcohol)



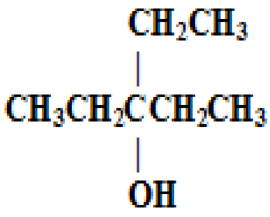
$CH_3\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_2\overset{\overset{OH}{|}}{C}HCH_3$

4,4-Dimethyl-2-pentanol



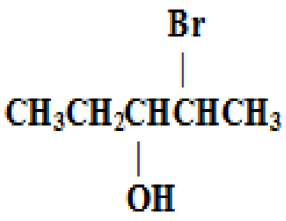
$CH_3CH_2\underset{\underset{CH_3}{|}}{\overset{\overset{CH_2CH_3}{|}}{C}}CH_2OH$

2-Ethyl-2-methyl-1-butanol



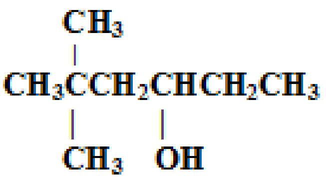
$CH_3CH_2\underset{\underset{OH}{|}}{\overset{\overset{CH_2CH_3}{|}}{C}}CH_2CH_3$

3-Ethyl-3-pentanol



$CH_3CH_2\underset{\underset{OH}{|}}{C}H\overset{\overset{Br}{|}}{C}HCH_3$

2-Bromo-3-pentanol

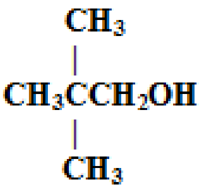


$$\begin{array}{l} \quad CH_3 \\ \quad\ | \\ CH_3CCH_2CHCH_2CH_3 \\ \quad\ |\qquad\ \ | \\ \quad CH_3\quad OH \end{array}$$

5,5-Dimethyl-3-hexanol

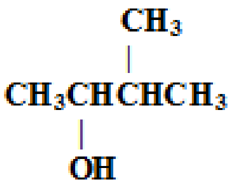
$ClCH_2CH_2OH$

2-Chloroethanol



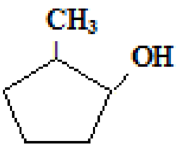
$$\begin{array}{l} \quad CH_3 \\ \quad\ | \\ CH_3CCH_2OH \\ \quad\ | \\ \quad CH_3 \end{array}$$

2,2-Dimethyl-1-propanol

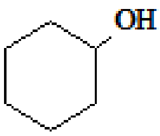


$$\begin{array}{l} \qquad\quad CH_3 \\ \qquad\quad\ | \\ CH_3CHCHCH_3 \\ \qquad\ | \\ \qquad OH \end{array}$$

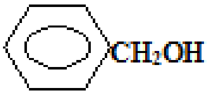
3-Methyl-2-butanol



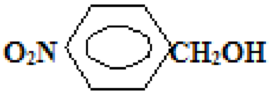
2-Methylcyclopentanol



Cyclohexanol

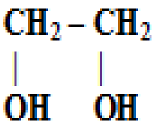


(Benzyl alcohol)



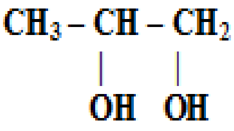
(*p*-Nitrobenzyl alcohol)

In the IUPAC system, a compound containing two hydroxyl groups is named as a diol, one containing three hydroxyl groups is named as a triol, and so on.



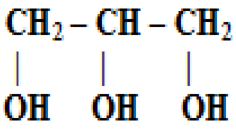
$$\begin{array}{l} CH_2 - CH_2 \\ \ | \qquad\ \ | \\ OH \quad OH \end{array}$$

1,2-Ethanediol
(Ethylene glycol)



$$\begin{array}{l} CH_3 - CH - CH_2 \\ \qquad\quad\ | \qquad\ | \\ \qquad\ \ OH \quad OH \end{array}$$

1,2-Propanediol
(Propylene glycol)



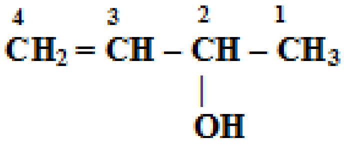
$$\begin{array}{l} CH_2 - CH - CH_2 \\ \ | \qquad\ \ | \qquad\ | \\ OH \quad OH \quad OH \end{array}$$

1,2,3-Propanetriol
(Glycerol, Glycerin)

An alcohol containing a double bond is named as an alkenol, with number to indicate the position of the double bond and the hydroxyl group.

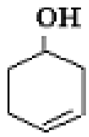
$$\overset{3}{C}H_2 = \overset{2}{C}H - \overset{1}{C}H_2OH$$

2-Propen-1-ol



$$\overset{4}{C}H_2 = \overset{3}{C}H - \underset{\displaystyle OH}{\overset{2}{C}H} - \overset{1}{C}H_3$$

3-Buten-2-ol



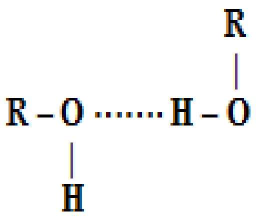
4-Cyclohexenol

5.4 Physical Properties of Alcohols

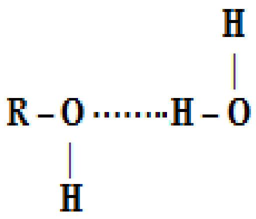
Alcohol molecules are polar, because the **–OH** group is highly polar. To show this, only compare boiling of ethane for example (formula weight 30 , b.p. –89), with methyl alcohol (formula weight 32 , b.p. 65).

Force of attraction between alcohol molecules obviously must be greater than between molecules of alkanes. Hydrogen bonding account for this.

The presence of an alcohol group sharply increases the tendency to dissolve in water. Methane, for example, is insoluble in water, but methyl alcohol is completely soluble, because of the hydrogen bonding with water as illustrated:



Intermolecular bonding

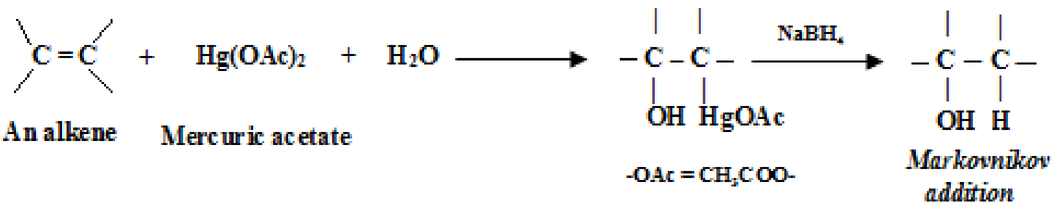


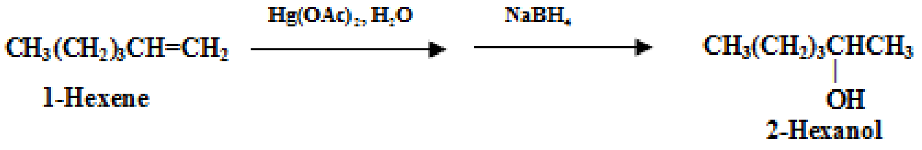
Hydrogen bonding with water

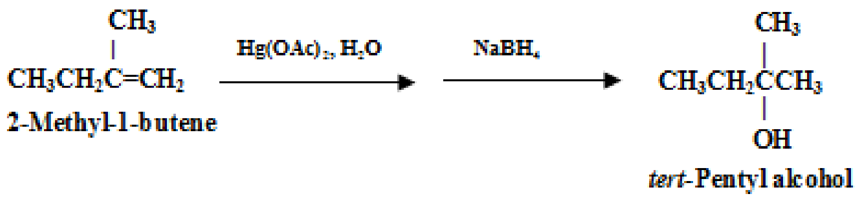
5.5 *Preparation of Alcohols*

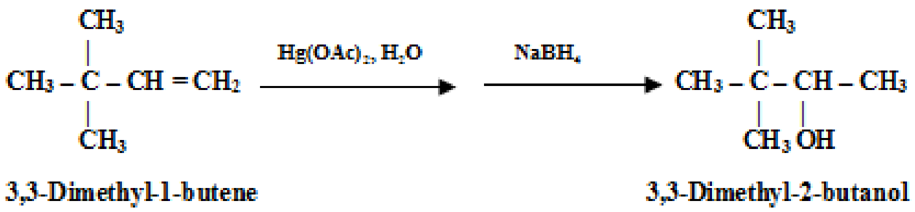
1- Oxymercuration – demercuration

Alkenes react with mercuric acetate in the presence of water to give hydroxymercurial compounds which on reduction yield alcohols.



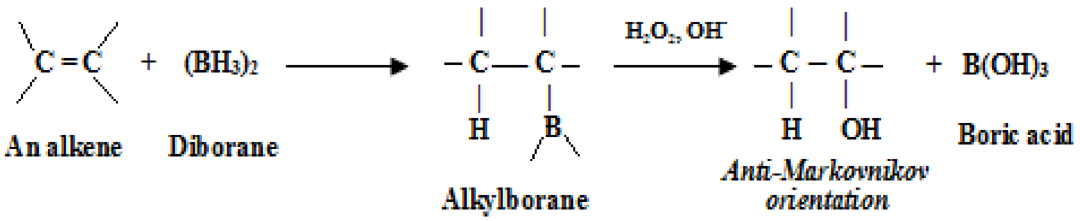


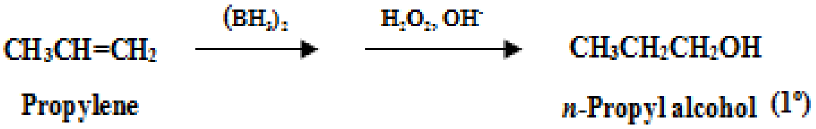




2- Hydroboration - oxidation

With the reagent diborane, $(BH_3)_2$, alkene undergo hydroboration to yield alkylboranes, which on oxidation give alcohols. Hydroboration involves addition of BH_3 to the double bond, with hydrogen becoming attached to one doubly bonded carbon, and boron to the other. The alkylborane can then undergo oxidation, in which the boron is replaced by -OH.

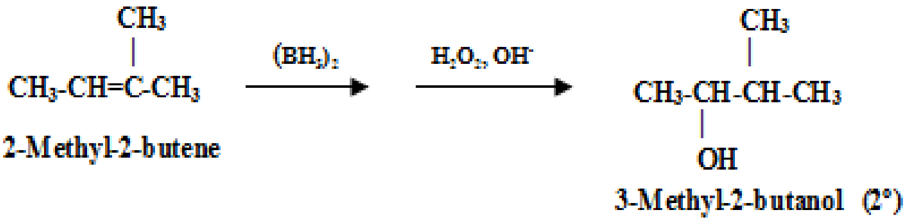




$$CH_3CH{=}CH_2 \xrightarrow{(BH_3)_2} \xrightarrow{H_2O_2,\ OH^-} CH_3CH_2CH_2OH$$

Propylene

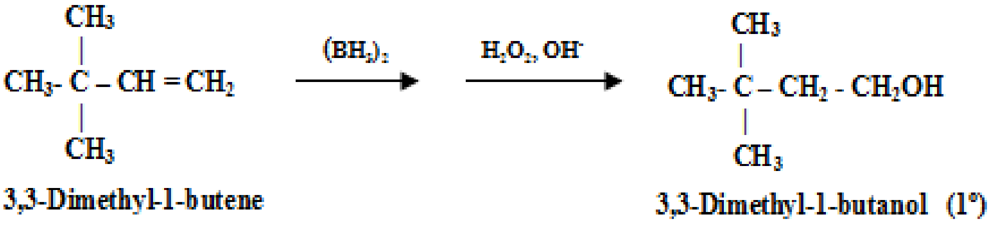
n-Propyl alcohol (1°)



$$CH_3\text{-}CH{=}\overset{\displaystyle CH_3}{\overset{|}{C}}\text{-}CH_3 \xrightarrow{(BH_3)_2} \xrightarrow{H_2O_2,\ OH^-} CH_3\text{-}\underset{\underset{\displaystyle OH}{|}}{CH}\text{-}\overset{\displaystyle CH_3}{\overset{|}{CH}}\text{-}CH_3$$

2-Methyl-2-butene

3-Methyl-2-butanol (2°)



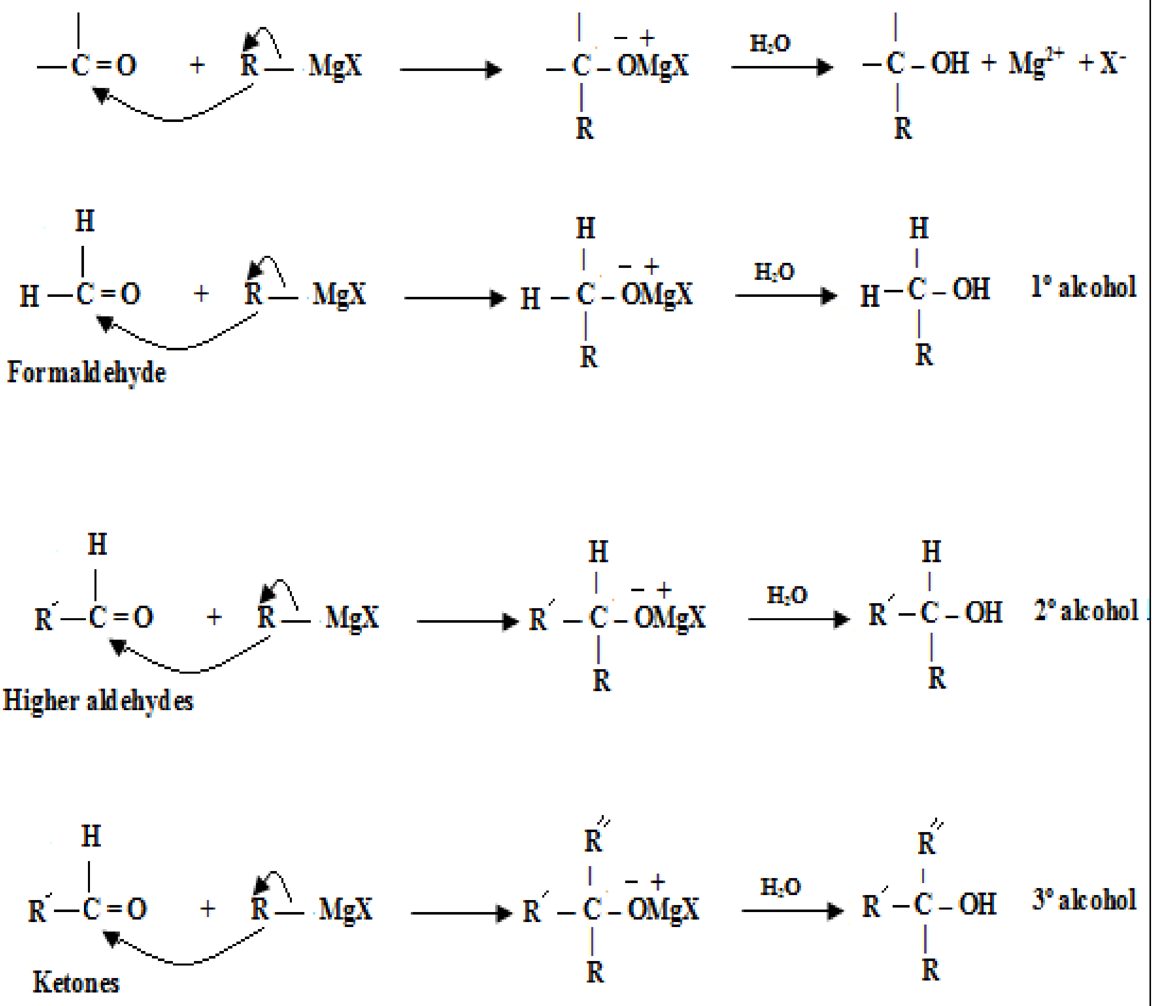
$$CH_3\text{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\displaystyle CH_3}{\overset{|}{C}}}-CH=CH_2 \xrightarrow{(BH_3)_2} \xrightarrow{H_2O_2,\ OH^-} CH_3\text{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\displaystyle CH_3}{\overset{|}{C}}}-CH_2\text{-}CH_2OH$$

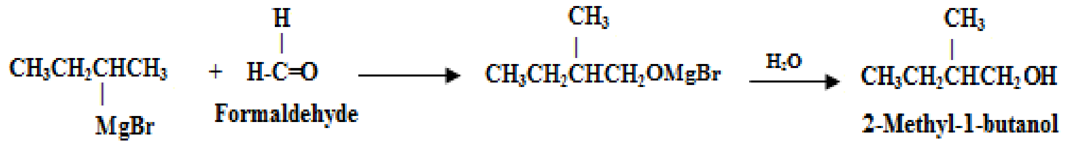
3,3-Dimethyl-1-butene

3,3-Dimethyl-1-butanol (1°)

3- Grignard reaction

One of the most important uses of the Grignard reagent lies in its reaction with aldehydes and ketones. The product is the magnesium salt of the weakly acidic alcohol and is easily converted into alcohol itself by the addition of the stronger acid, water.



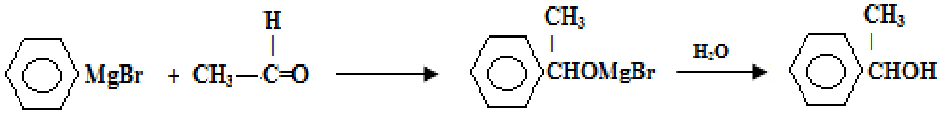


sec-Butylmagnesium bromide

Formaldehyde

2-Methyl-1-butanol 1°

(*sec*-Butylcarbinol)

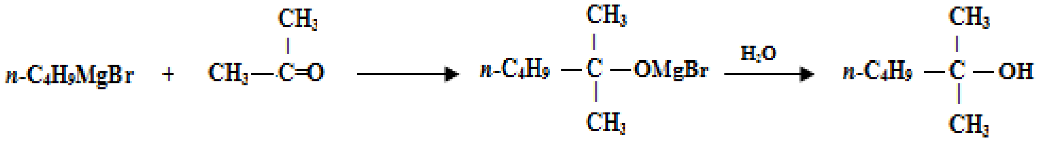


Phenylmagnesium bromide

Acetaldehyde

1- Phenylethanol 2°

(Phenylmethylcarbinol)



n-Butylmagnesium bromide

Acetone

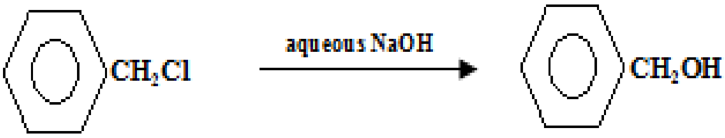
2-Methyl-2-hexanol 3°

(*n*-Butyldimethylcarbinol)

4- Hydrolysis of alkyl halides

Alcohols can be prepared by the hydrolysis of alkyl halides.

$$R\text{-}X + OH^- \text{ (or } H_2O) \longrightarrow R\text{-}OH + X^- \text{ (or HX)}$$

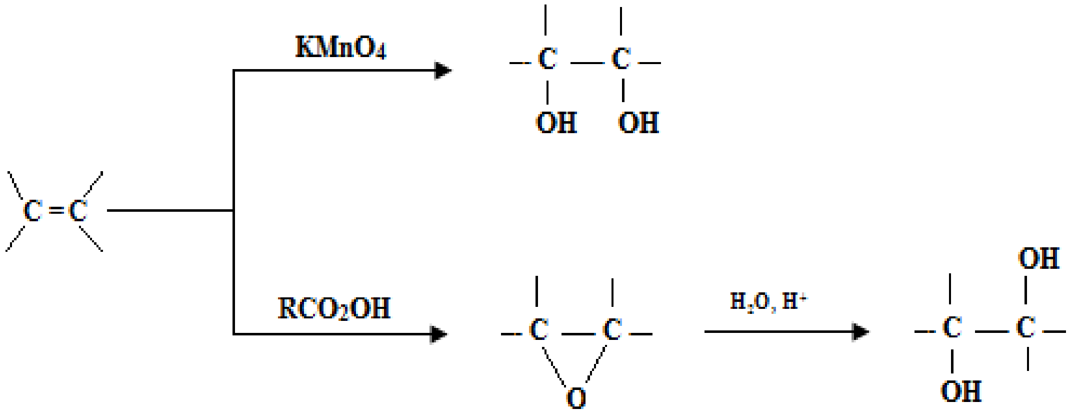


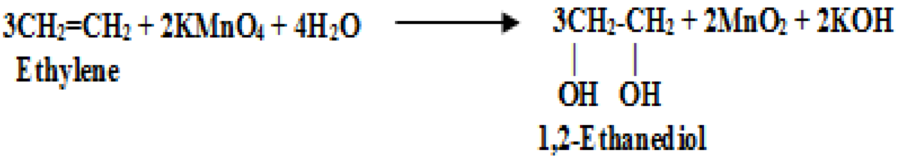
Benzyl chloride

Benzyl alcohol

5- Hydroxylation of alkenes

Certain oxidizing agents convert alkenes into **1,2-diols**: dihydroxy alcohols containing the two –OH groups on adjacent carbons. (They are also known as *glycols*).





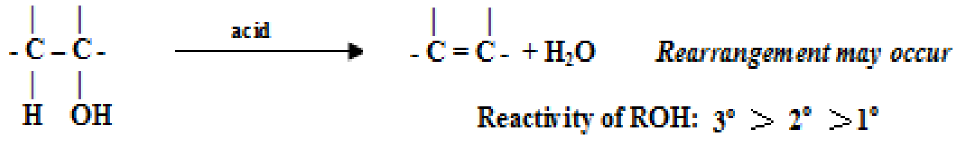
$$\underset{\text{Ethylene}}{3CH_2{=}CH_2} + 2KMnO_4 + 4H_2O \longrightarrow \underset{\text{1,2-Ethanediol}}{3\underset{OH}{\underset{|}{C}}H_2\text{-}\underset{OH}{\underset{|}{C}}H_2} + 2MnO_2 + 2KOH$$

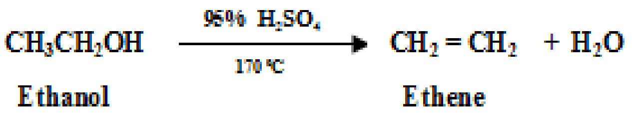
5.6 *Reactions of Alcohols*

Alcohols are saturated compounds containing the functional group –OH. They can undergo nucleophilic substitution reactions, in which the hydroxyl group is displaced by other groups, or they can undergo elimination reactions, involving the loss of the elements of water when reacted with a dehydrating agent. Primary and secondary alcohols also undergo oxidation and the hydroxyl group shows acidic properties when treated with reactive metals.

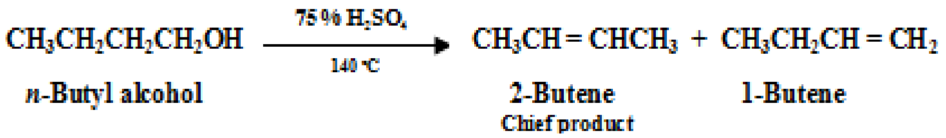
1- Dehydration

As alcohols contain the hydroxyl group –OH, they may undergo the elimination of the elements of water. Concentrated sulphuric acid has a very strong affinity for water and behaves as a dehydrating agent towards alcohols. When heated with sulphuric acid, alcohols can be dehydrated to alkenes.



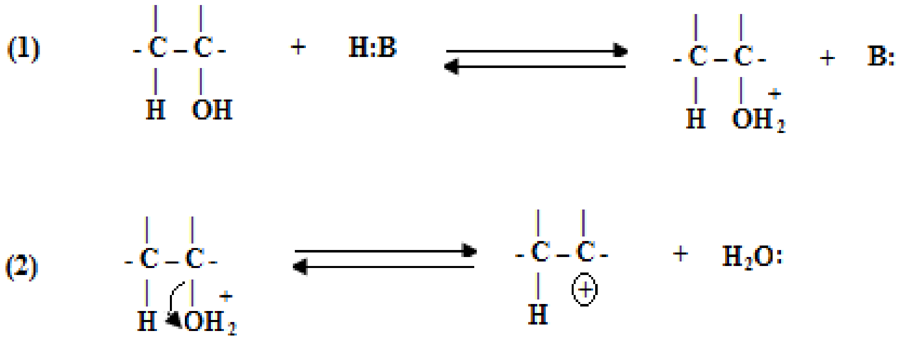


$$CH_3CH_2OH \xrightarrow[170\,°C]{96\%\ H_2SO_4} CH_2=CH_2 + H_2O$$

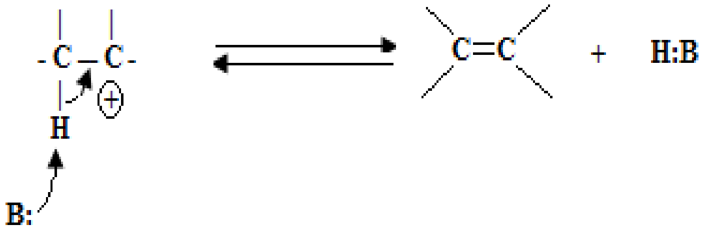


$$CH_3CH_2CH_2CH_2OH \xrightarrow[140\,°C]{75\%\ H_2SO_4} CH_3CH=CHCH_3 + CH_3CH_2CH=CH_2$$

Mechanism:



(3)



2- Reaction with hydrogen halides

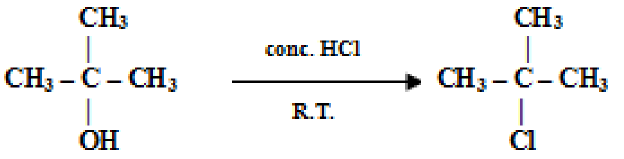
Under a variety of conditions, and using a variety of reagents, alcohols may be converted into alkyl halides. The reaction is catalyzed by acids, and rearrangement of the alkyl group occurs, except with most 1° alcohols.

$$R-OH + HX \longrightarrow R-X + H_2O \quad R\ \textit{may rearrange}$$

Reactivity of HX: HI > HBr > HCl

Reactivity of ROH: allyl, benzyl > 3° > 2° > 1°

$$\underset{n\text{-Pentyl alcohol}}{CH_3CH_2CH_2CH_2CH_2OH} \xrightarrow[\text{heat}]{HCl,\ ZnCl_2} \underset{n\text{-Pentyl chloride}}{CH_3CH_2CH_2CH_2CH_2Cl}$$



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3 \xrightarrow[\text{R.T.}]{\text{conc. HCl}} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_3$$

tert-Butyl alcohol *tert*-Butyl chloride

Mechanism:

(1) $R\text{-}OH + HX \rightleftharpoons R\text{-}OH_2^+ + :X^-$ *all except methanol and most 1° alcohols*

(2) $R\text{-}OH_2^+ \rightleftharpoons R^+ + H_2O:$

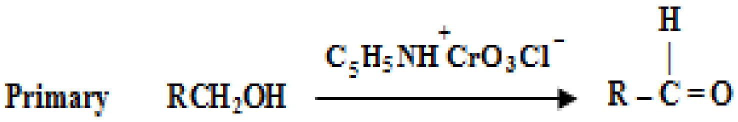
(3) $R^+ + :X^- \rightleftharpoons R\text{-}X$

$:X^- + R\text{-}OH_2^+ \longrightarrow [\overset{\delta-}{X}\ldots\ldots R\ldots\ldots\overset{\delta+}{OH_2}] \longrightarrow X\text{-}R + H_2O:$

most 1° alcohols
and methanol

3- Oxidation

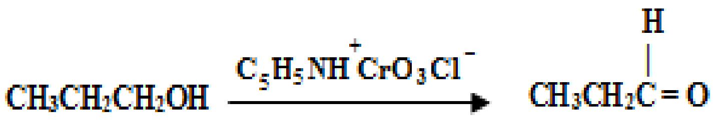
Alcohols react with strong oxidizing agents, to give products which depend on the structure of the alcohol. The reaction involves the loss of one or more hydrogens (α-hydrogen) from the carbon bearing the –OH group.



$$\text{Primary} \quad RCH_2OH \xrightarrow{C_5H_5\overset{+}{N}HCrO_3Cl^-} R-\overset{\overset{\displaystyle H}{|}}{C}=O$$

Aldehyde

$C_5H_5\overset{+}{N}HCrO_3Cl^-$ = Pyridinium chlorochromate

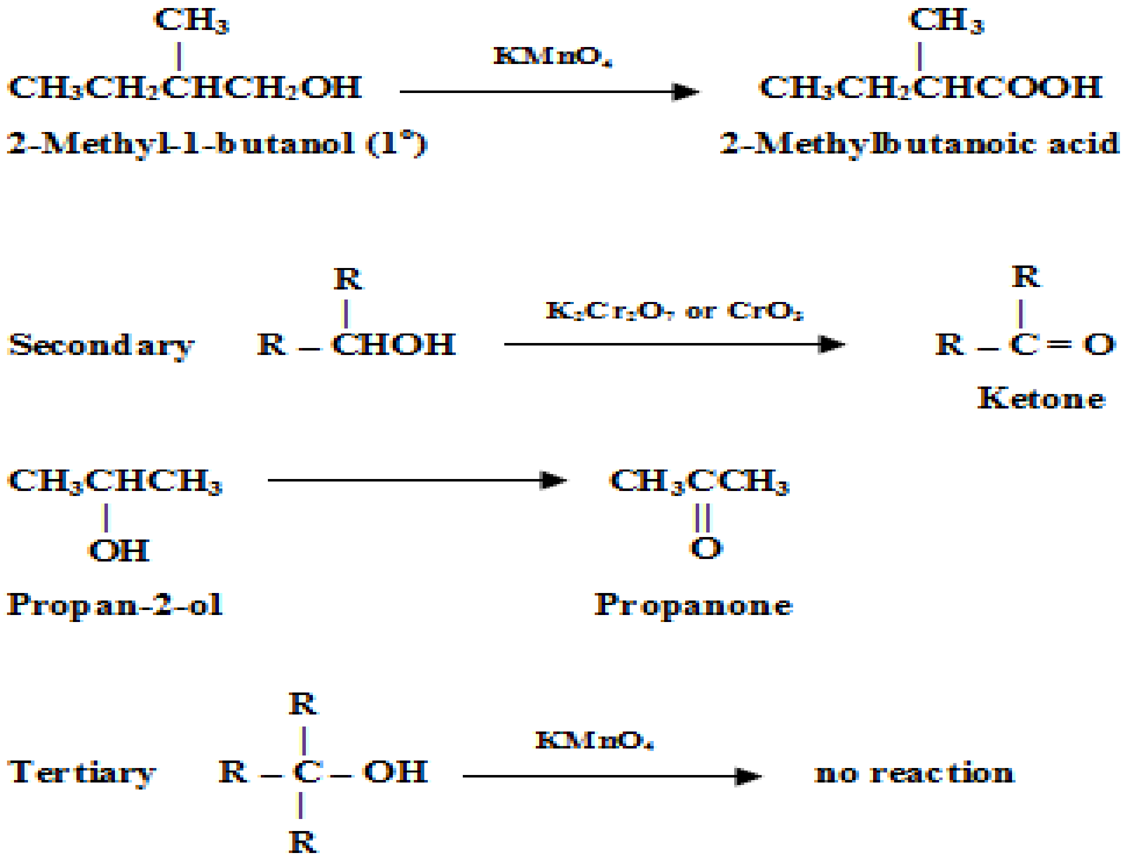


$$CH_3CH_2CH_2OH \xrightarrow{C_5H_5\overset{+}{N}HCrO_3Cl^-} CH_3CH_2\overset{\overset{\displaystyle H}{|}}{C}=O$$

n-Propyl alcohol (1°) Propionaldehyde

$$\text{Primary} \quad RCH_2OH \xrightarrow{KMnO_4} R-COOH$$

Carboxylic acid



$$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2OH \xrightarrow{KMnO_4} CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCOOH$$

2-Methyl-1-butanol (1°) 2-Methylbutanoic acid

Secondary $$R-\overset{\overset{R}{|}}{C}HOH \xrightarrow{K_2Cr_2O_7 \text{ or } CrO_3} R-\overset{\overset{R}{|}}{C}=O$$

Ketone

$$CH_3\underset{\underset{OH}{|}}{C}HCH_3 \longrightarrow CH_3\underset{\underset{O}{\|}}{C}CH_3$$

Propan-2-ol Propanone

Tertiary $$R-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}-OH \xrightarrow{KMnO_4} \text{no reaction}$$

4- Reaction as acids: reaction with active metals

The alcohols react with metals like sodium and potassium to form ionic compounds called alkoxides.

$R-OH + M \longrightarrow RO^-M^+ + \frac{1}{2}H_2$ M = Na, K, Mg, Al .....etc.

Reactivity of ROH: $CH_3OH > 1° > 2° > 3°$

$CH_3CH_2OH \xrightarrow{Na} CH_3CH_2O^-Na^+ + \frac{1}{2}H_2$

Ethyl alcohol Sodium ethoxide

Organic Chemistry

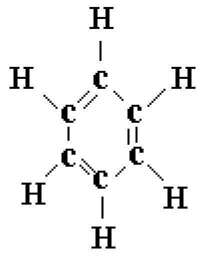
Chapter 6

Aromatic Hydrocarbons

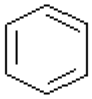
6.1 Introduction

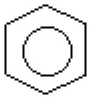
Hydrocarbons containing one or more benzene rings called aromatic hydrocarbons. The word ***aromatic*** was derived from (*aroma*) which describes the odour of these compounds. While ***aliphatic*** means *fatty*, and include open-chain compounds and those cyclic compounds that resemble them.

Benzene, the parent compound of this large family of organic substances, has the general formula $\mathbf{C_nH_{2n-6}}$.



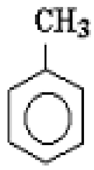
Kekulé structure



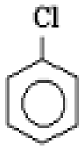


6.2 Nomenclature of Benzene Derivatives

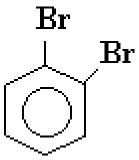
Substituted benzenes are named in a systematic manner by combining the substituent name with the word benzene. If more than one substituent is present, the location of the second group must be indicated relative to the first. Some substituted benzenes have special names like toluene, aniline, phenol and so on. We can use the abbreviation *o*- , *m*- and *p*- to indicate the position of the substituent. The IUPAC system retains certain common names for several of the simpler monosubstituted alkyl benzene.



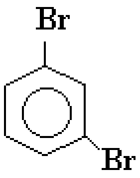
Methylebenzene
(Toluene)



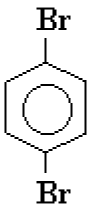
Chlorobenzene



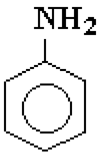
1,2-Dibromobenzene
(*o*-Dibromobenzene)



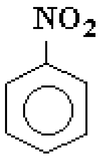
1,3-Dibromobenzene
(*m*-Dibromobenzene)



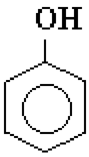
1,4-Dibromobenzene
(*p*-Dibromobenzene)



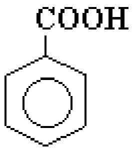
Aminobenzene
(Aniline)



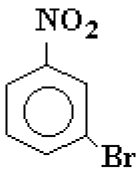
Nitrobenzene



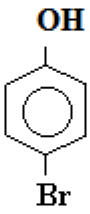
Hydroxybenzene
(Phenol)



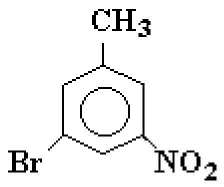
Benzenecarboxylic acid
(Benzoic acid)



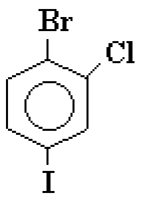
3-Bromonitrobenzene
(*m*-Bromonitrobenzene)



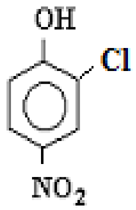
(*p*-Bromophenol)



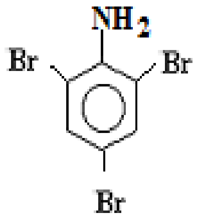
5-Bromo-3-nitrotoluene



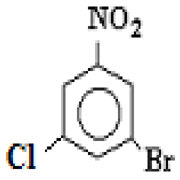
2-Chloro-4-iodobromobenzene



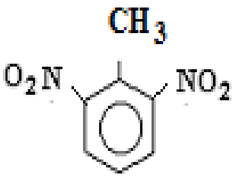
2-Chloro-4-nitrophenol



2,4,6-Tribromoaniline



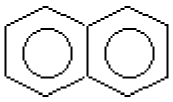
3-Bromo-5-chloronitrobenzene



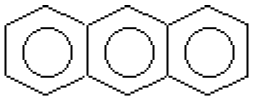
2,6-Dinitrotoluene

6.3 Polynuclear Aromatic Hydrocarbons

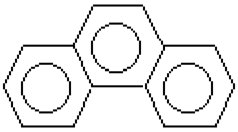
Two aromatic rings that share a pair of carbon atoms are said to be *fused*. The simplest and most important of these fused-ring hydrocarbon is *naphthalene* $C_{10}H_8$.



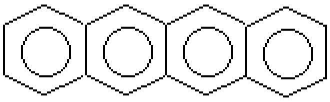
Naphthalene



Anthracene

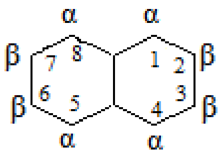


Phenanthrene

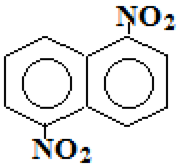


Naphthacene

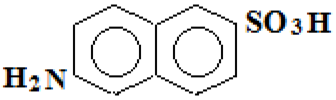
Positions in the naphthalene ring system are designated as shown:



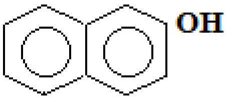
Two isomeric monosubstituted naphthalene are differentiated by the prefixes 1- and 2-, or α- and β-. The arrangement of groups in more highly substituted naphthalenes is indicated by numbers:



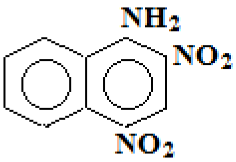
1,5-Dinitronaphthalene



6-Amino-2-naphthalenesulfonic acid



2-Naphthol
β-Naphthol



2,4-Dinitro-1-naphthylamine

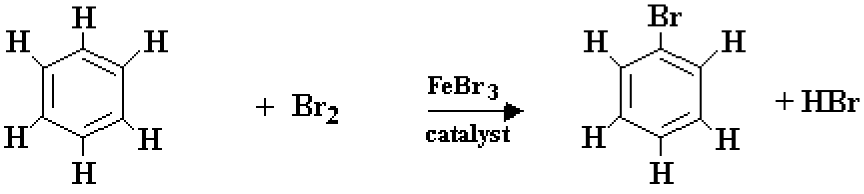
6.4 Properties of Benzene

Benzene is a colorless, flammable liquid obtained chiefly from coal tar. Although it has the same empirical formula as a acetylene (CH) and a high degree of unsaturation (three C=C bonds), it is much less reactive than either ethylene and acetylene.

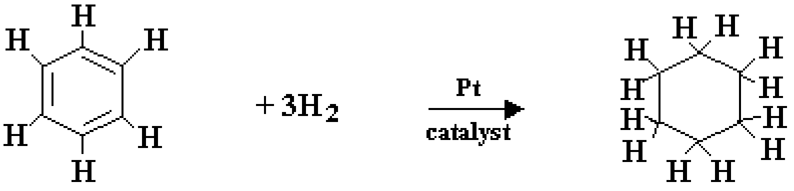
The stability of benzene is the result of electron delocalization, the electrons in the three pairs (pi e^-) circulate around the entire ring.

Having this much room, which the six electrons can move, the benzene molecule strongly resists any chemical event that might disrupt this closed circuit of electrons.

Benzene undergoes substitution rather than addition reactions. Substitution reaction is the replacement of an atom or a group of atoms in a compound by another atom or another group of atoms.

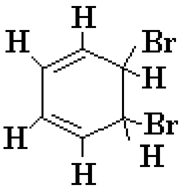


Addition reaction like hydrogenation, very difficult to happen, only with higher temperature and pressure than in the alkanes.



Benzene **Cyclohexane**

Note that if the reaction was addition, electron delocalization would be destroyed in the product:



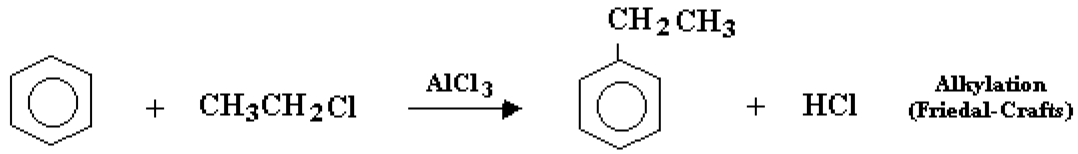
The molecule would not exhibit the usual aromatic characteristic of chemical unreactivity.

6.5 Reactions of Benzene

The particularly characteristic delocalized system of π-electrons within the benzene molecule means that benzene is not easily attacked by acids, alkalis or oxidizing agents, unlike other unsaturated compounds such as alkenes. Like alkenes, however, it does undergo some addition reactions, although substitution reactions are much more characteristic of benzene's chemical behaviour.

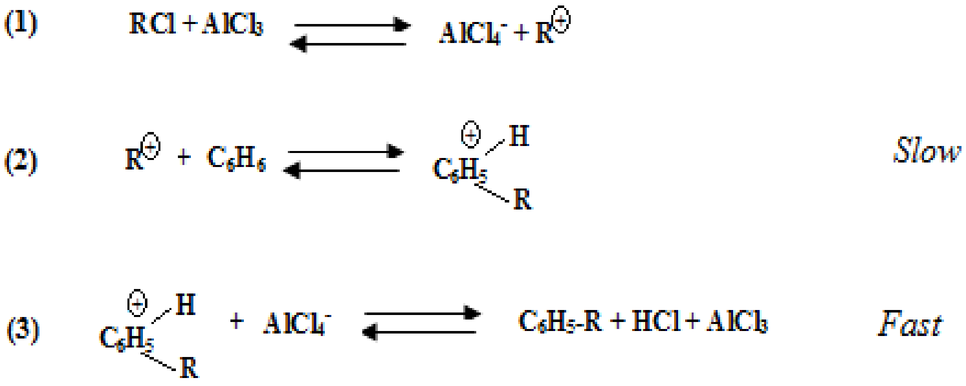
1- Substitution reaction with alkyl halides

Benzene reacts exothermically with alkyl halides, in the presence of powdered, anhydrous aluminum chloride. Hydrogen halide evolved. This type of reaction is called Friedel-Crafts reaction.



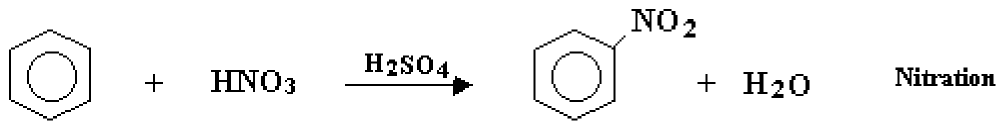
Benzene **Ethyl chloride** **Ethylbenzene**

Mechanism:



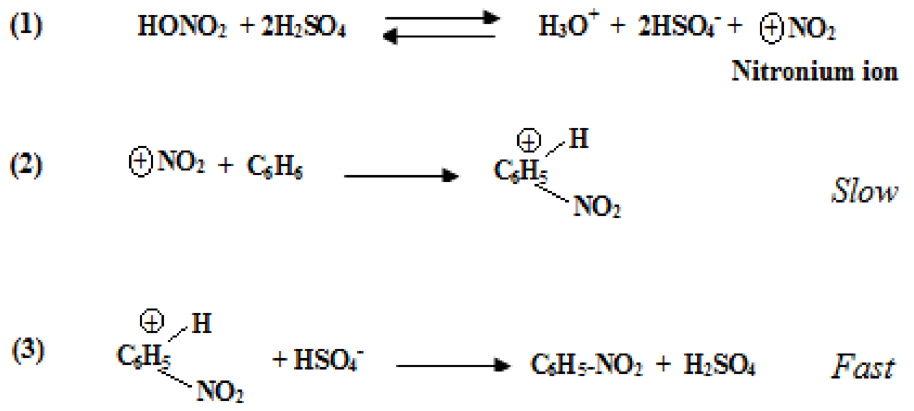
2- Substitution reaction with nitric acid

The substitution of one or more nitro group into the benzene ring is effected by the use of a special nitrating mixture of concentrated nitric and sulphuric acid.



Benzene **Nitric acid** **Nitrobenzene**

***Mechanism*:**



(1) $HONO_2 + 2H_2SO_4 \rightleftharpoons H_3O^+ + 2HSO_4^- + \oplus NO_2$

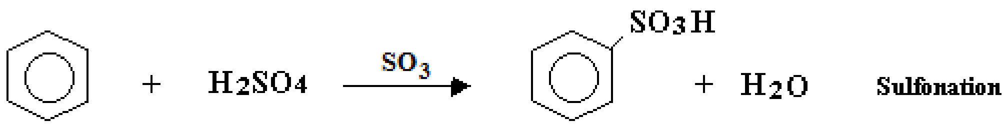
Nitronium ion

(2) $\oplus NO_2 + C_6H_6 \longrightarrow \overset{\oplus}{C_6H_5}{<}^{H}_{NO_2}$ *Slow*

(3) $\overset{\oplus}{C_6H_5}{<}^{H}_{NO_2} + HSO_4^- \longrightarrow C_6H_5\text{-}NO_2 + H_2SO_4$ *Fast*

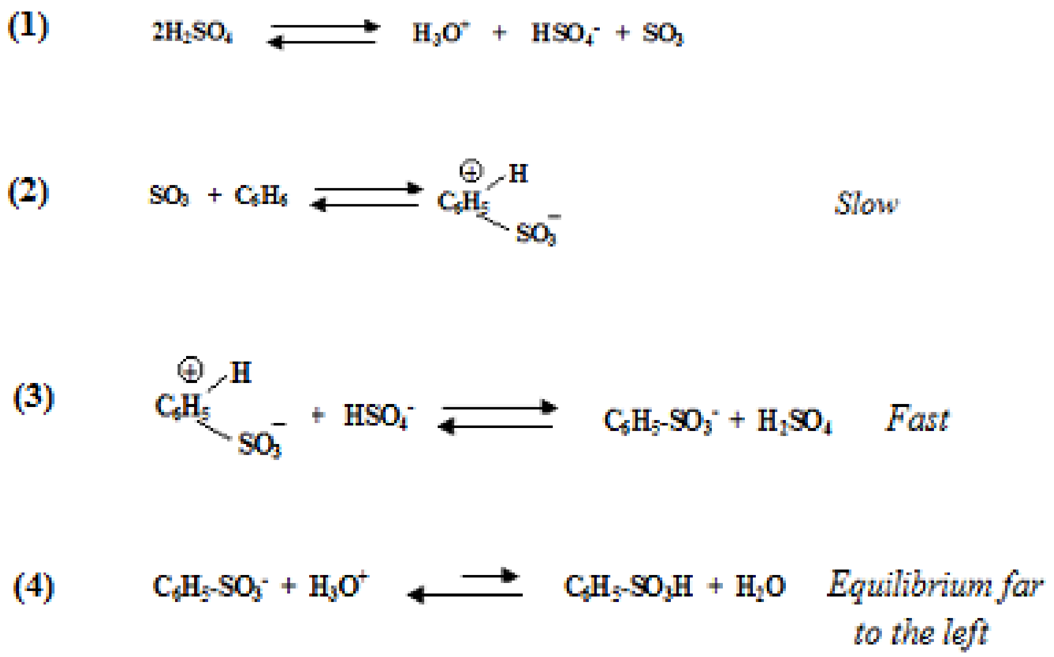
3- Substitution reaction with sulfuric acid

Under the same conditions of nitration, benzene is unattacked by concentrated sulphuric acid, but if it is heated under reflux for about 6 h with the concentrated acid, sulphonation takes place.



Benzene **Sulfuric acid** **Benzenesulfonic acid**

***Mechanism*:**



(1) $$2H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- + SO_3$$

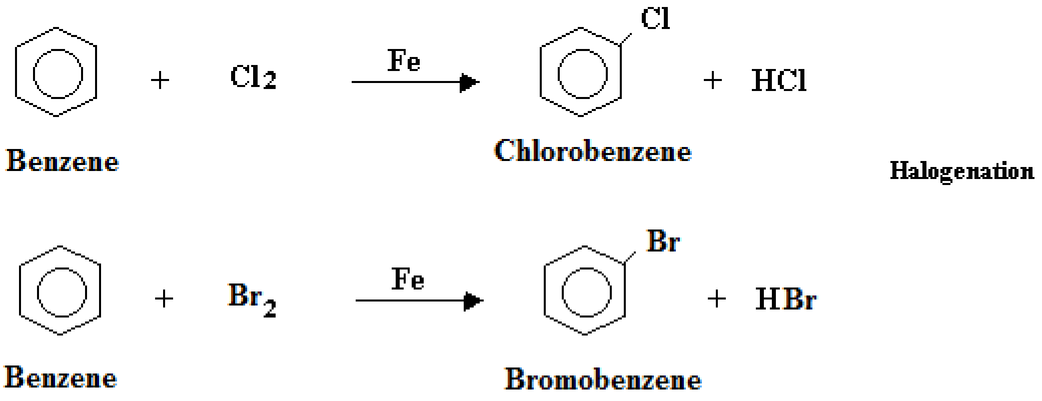
(2) $$SO_3 + C_6H_6 \rightleftharpoons \overset{\oplus\ H}{C_6H_5}\!\!\underset{SO_3^-}{}$$ *Slow*

(3) $$\overset{\oplus\ H}{C_6H_5}\!\!\underset{SO_3^-}{} + HSO_4^- \rightleftharpoons C_6H_5\text{-}SO_3^- + H_2SO_4$$ *Fast*

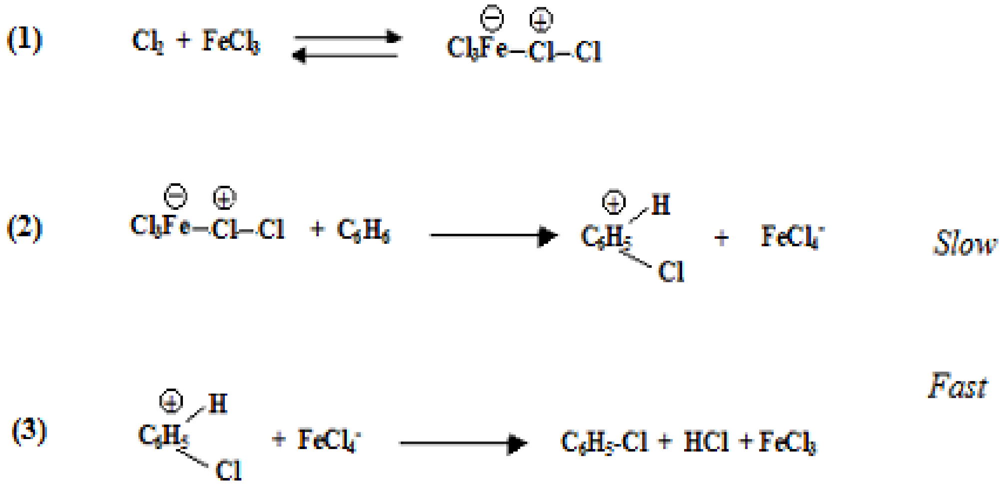
(4) $$C_6H_5\text{-}SO_3^- + H_3O^+ \rightleftharpoons C_6H_5\text{-}SO_3H + H_2O$$ *Equilibrium far to the left*

4- Substitution reaction with halogens

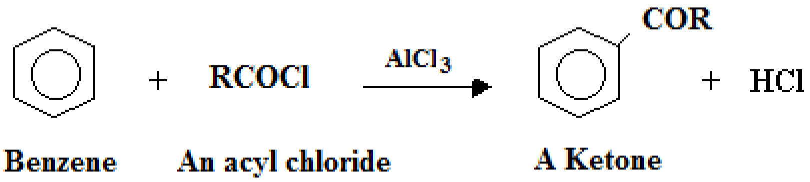
Benzene reacts with halogens in the presence of certain catalyst, such as iron or iron (III) or aluminum chloride, substituted compound being formed.



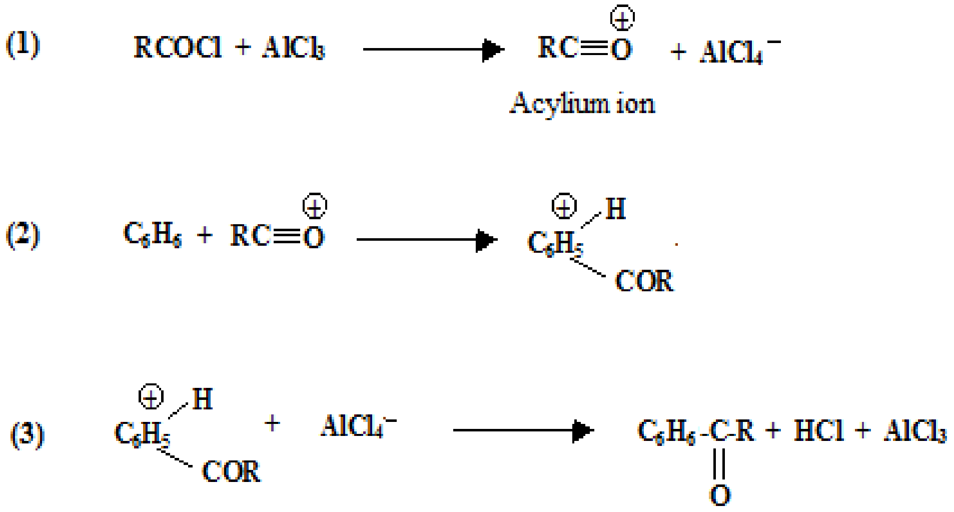
Mechanism:



5- Friedel-Crafts acylation



Mechanism:



6.6 Electrophilic Aromatic Substitution

We have already seen that the characteristic reaction of benzene involve substitution, in which the resonance-stabilized ring system is preserved.

Above and below the plane of the benzene ring is a cloud of π electrons. Because of resonance, these π electrons are more involved in the holding together carbon nuclei than are the π electrons of a carbon-carbon double bond. Still, in comparison with σ electrons, these π electrons are loosely held and are available to a reagent that is seeking electrons.

It is not surprising that in its typical reactions the benzene ring serve as a source of electrons, that is, as a base. The compounds with which it reacts are deficient in electrons, that is, are electrophilic reagent or acids. Just as the typical reactions of the alkenes are electrophilic addition reactions, so the typical reactions of the benzene ring are electrophilic substitution reactions.

These reactions are characteristic not only of benzene itself, but of the benzene ring wherever it is found, and, indeed, of many aromatic rings, benzenoid and non-benzenoid.

Electrophilic aromatic substitution includes a wide variety of reactions: nitration, halogenation, sulfonation, and Friedel-Crafts reactions, undergo by nearly all aromatic rings; reactions like nitrosation and diazo coupling, undergone only by rings of high reactivity.

1- Nitration

$$\mathrm{ArH + HONO_2 \xrightarrow{H_2SO_4} ArNO_2 + H_2O} \qquad \mathrm{Ar = aryl}$$

A nitro compound

2- Sulfonation

$$\mathrm{ArH + HOSO_3H \xrightarrow{SO_3} ArSO_3H + H_2O}$$

A sulfonic acid

3- Halogenation

$$\mathrm{ArH + Cl_2 \xrightarrow{Fe} ArCl + HCl}$$

An aryl chloride

$$\mathrm{ArH + Br_2 \xrightarrow{Fe} ArBr + HBr}$$

An aryl bromide

4- Friedel-Crafts alkylation

$$\mathrm{ArH + RCl \xrightarrow{AlCl_3} ArR + HCl}$$

An alkylbenzene

5- Friedel-Crafts acylation

$$\mathrm{ArH + RCOCl \xrightarrow{AlCl_3} ArCOR + HCl}$$

An acyl chloride **A ketone**

6- Protonation

$$\mathrm{ArSO_3H + H^+ \xrightarrow{H_2O} Ar\text{-}H + H_2SO_4}$$

Desulfonation

7- Nitrosation

$$\mathrm{ArH + HONO \longrightarrow Ar\text{-}N{=}O + H_2O}$$

Only for highly reactive ArH

A nitroso compound

8- Diazo coupling

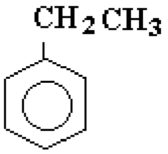
$$\mathrm{ArH + Ar'N_2^+X^- \longrightarrow Ar\text{-}N{=}NAr' + HX}$$

Only for highly reactive ArH

A diazonium salt **An azo compound**

6.7 Arenes

Many important compounds are not just aliphatic or just aromatic, however, but contain both aliphatic and aromatic units; hydrocarbons of this kind are known collectively as **arenes**. Ethylbenzene, for example, contains a benzene ring and an aliphatic side chain.



Ethylbenzene

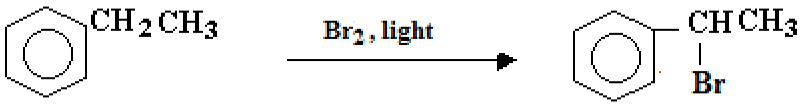
What kind of chemical properties might we expect of one of these mixed aliphatic-aromatic hydrocarbons? First, we might expect it to show two sets of chemical properties. The ring of ethylbenzene should undergo the electrophilic substitution characteristic of benzene, and the side chain should undergo the free radical substitution characteristic of ethane. Second, the properties of each portion of the molecule should be modified by the presence of the other portion. The ethyl group should modify the aromatic properties of the ring., and the ring should modify the aliphatic properties of the side chain.

These predictions are correct. Treatment of ethylbenzene with nitric acid and sulfuric acid, for instance, introduces a nitro group into the ring; treatment with bromine in the presence of light introduce a bromine atom into the side chain.

More readily than for benzene

***o*-Nitroethylbenzen** ***p*-Nitroethylbenzene**

Chief product



More readily than for ethane

1-Bromo-1-phenylethane

(α-Phenylethyl bromide)

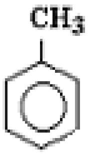
Only product

But because of the ethyl group, nitration take place more readily than with benzene itself, and occurs chiefly at the positions *ortho* and *para* to the ethyl group; and because of the ring, bromination takes place more readily than with ethane, and occurs exclusively on the carbon nearer the ring. Thus each portion of the molecule affects the reactivity of the other portion and determines the orientation of attack.

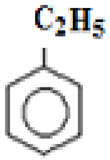
In the same way we may have a molecule that is part aromatic and part alkene, or part aromatic and part alkyne. Again each portion of such a molecule shows the properties characteristic of its particular structure, although these properties are modified by the other portion of the molecule.

6.8 Nomenclature

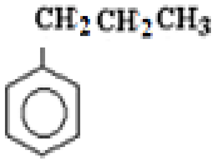
The simplest of the alkylbenzenes, methylbenzene, is given the special name of **toluene**. Compounds containing longer side chains are named by prefixing the name of the alkyl group to the word *–benzene*, as, for example, in *ethylbenzene, n-propylbenzene*, and *isobutylbenzene*.



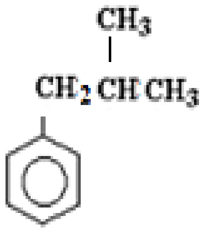
Toluene



Ethylbenzene

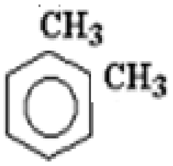


***n*-Propylbenzene**

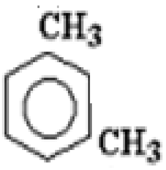


Isobutylbenzene

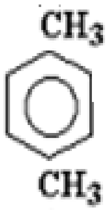
The simplest of the dialkylbenzenes, the dimethylbenzene, are given the special names of **xylenes**, we have, then, *o-xylene*, *m-xylene*, and *p-xylene*.



***o*-Xylene**



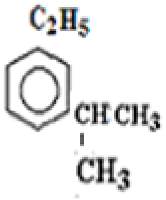
***m*-Xylene**



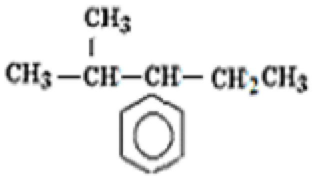
***p*-Xylene**

Dialkylbenzenes containing one methyl group are named as derivatives of toluene, while others are named by prefixing the names of both alkyl groups to the word *–benzene*.

***p*-Ethyltoluene**

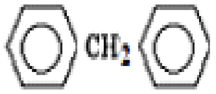


***m*-Ethylisopropylbenzene**



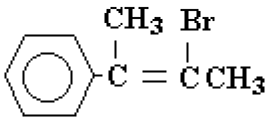
2-Methyl-3-phenylpentane

A compound containing a very complicated side chain might be named as a *phenylalkane* (C_6H_6 = **phenyl**). Compounds containing more than one benzene ring are nearly always named as derivatives of alkanes.

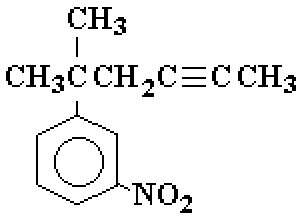


Diphenylmethane

1,2-Diphenylethane

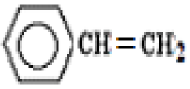


2-Bromo-3-phenyl-2-butene



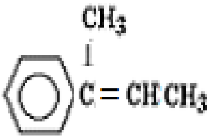
5-Methyl-5-*meta*-nitrophenyl-2-hexyne

The simplest alkenylbenzene has the special name **styrene**. Others are generally named as substituted alkenes, occasionally as substituted benzenes. alkynylbenzenes are named as substituted alkynes.

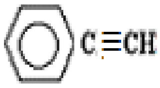


Styrene
(Phenylethylene)

3-Phenylpropene
(Allylbenzene)



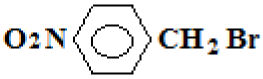
2-Phenyl-2-butene



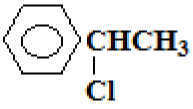
Phenylacetylene

If a halogen is attached directly to the aromatic ring, the compound is an aryl halide; if the halogen is not attached directly to the ring, the compound is an aralkyl halide. The $C_6H_5CH_2$-group is given the special name of **benzyl**.

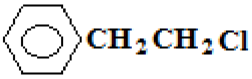
(Benzyl bromide)



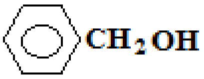
(*p*-Nitrobenzyl bromide)



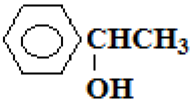
1-Phenyl-1-chloroethane



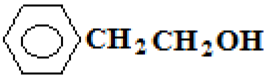
2-Phenyl-1-chloroethane



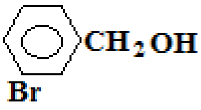
(Benzyl Acohol)



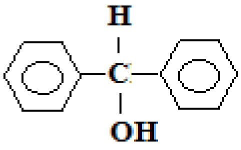
1-Phenylethanol



2-phenylethanol



(*m*-Bromobenzyl alcohol)



Diphenylmethanol

6.9 Physical Properties of Arenes

As a compounds of low polarity, the alkylbenzenes possess physical properties that are essentially the same as those of the hydrocarbons. They are insoluble in water, but quite soluble in non-polar solvent like ether, carbon tetrachloride. They are almost always less dense than water. Boiling points rise with increasing molecular weight, the boiling point increment being the usual 20-30° for each carbon atom.

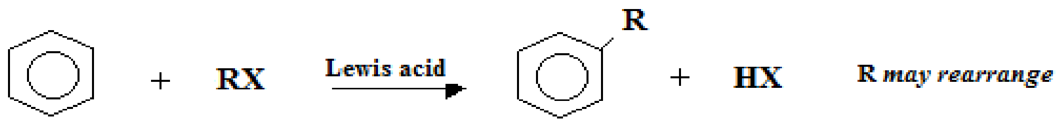
Since melting points depends not only on molecular weight but also on molecular shape, their relationship to structure is a very complicated one. One important general relationship does exist, however, between melting point and structure of aromatic compound: among isomeric disubstituted benzenes, the *para* isomer generally melts considerably higher than the other two. The xylenes, for example, boil within six degrees of one another; yet they differ widely in melting point, the *o*- and *m*-isomers melting at -25° and -48°, and the *p*-isomer melting at +13°. Since dissolution, like melting, involves overcoming the intermolecular forces of the crystal, it is not surprising to find that generally the *para* isomer is also the least soluble in a given solvent.

The higher melting point and lower solubility of a *para* isomer is only a special example of the general effect of molecular symmetry on intracrystalline forces. The more symmetrical a compound, the better it fits into a crystal lattice and hence the higher the melting point and lower the solubility. *Para* isomers are simply the most symmetrical of disubstituted benzenes.

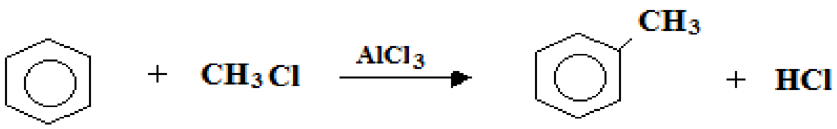
6-10 Preparation of Alkylbenzenes

1- Attachment of alkyl group: Friedel-Crafts alkylation

If a small amount of anhydrous aluminum chloride is added to a mixture of benzene and methyl chloride. A vigorous reaction occurs, hydrogen chloride gas is evolved, and toluene can be isolated from the reaction mixture.



Lewis acid: $AlCl_3$, BF_3, HF, etc.
Ar-X cannot be used in place of R-X

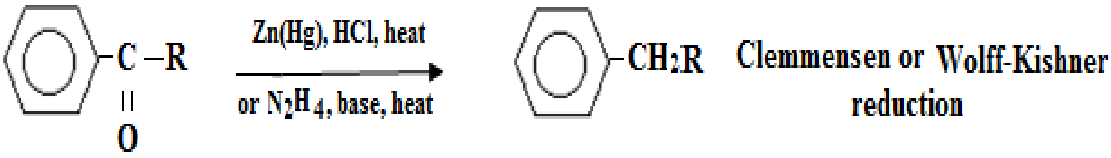


From polyhalogenated alkanes it is possible to prepare compounds containing more than one aromatic ring.

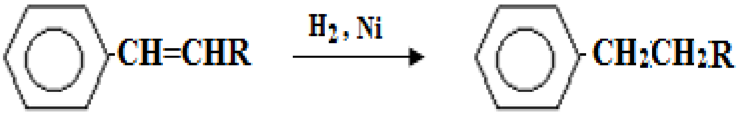
$$2C_6H_6 + CH_2Cl_2 \xrightarrow{AlCl_3} \underset{\text{Diphenylmethane}}{C_6H_5CH_2C_6H_5} + 2HCl$$

2- Conversion of side chain

Aldehydes and ketones can be reduced to hydrocarbons by the action (a) of amalgamated zinc and concentrated hydrochloric acid, the Clemmensen reduction; or (b) of hydrazine, NH_2NH_2, and a strong base like KOH or potassium tetrabutoxide, the Wolff-Kishner reduction.

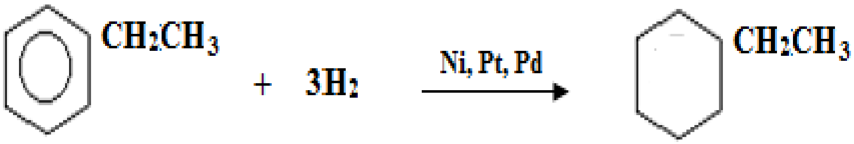


A ketone



6-11 Reactions of Alkylbenzenes

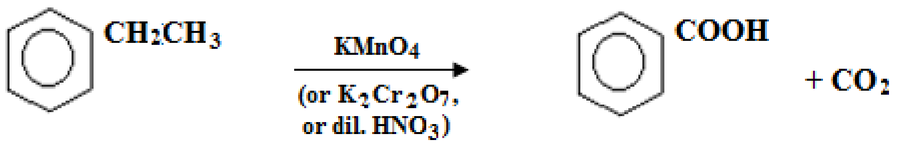
1- Hydrogenation



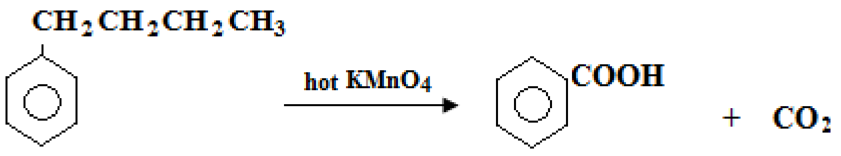
Ethylbenzene **Ethylcyclohexane**

2- Oxidation

Although benzene and alkanes are quite unreactive toward the usual oxidizing agents ($KMnO_4$, $K_2Cr_2O_7$, etc.), the benzene ring renders an aliphatic side chain quite susceptible to oxidation. The side chain oxidized down to the ring, only a carboxyl group (-COOH) remaining to indicate the position of the original side chain. Potassium permanganate is generally used for this purpose, although potassium dichromate or dilute nitric acid also can be used. (Oxidation of a side chain is more difficult, however, than oxidation of an alkene, and requires prolonged treatment with hot $KMnO_4$).



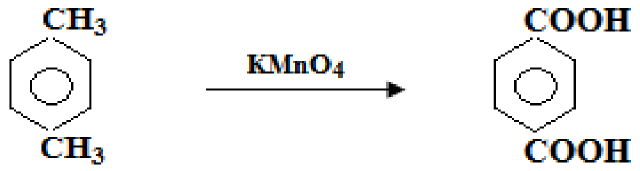
Ethylbenzene **Benzoic acid**



***n*-Butylbenzene** **Benzoic acid**

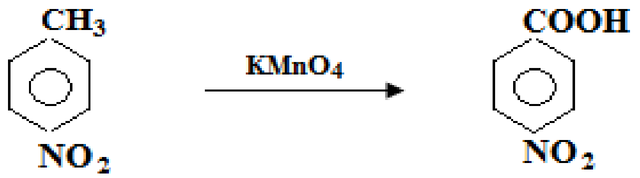
This reaction is used for two purposes: (a) synthesis of carboxylic acid, and (b) identification of alkylbenzenes.

(a) Synthesis of carboxylic acids. One of the most useful methods of preparing an aromatic carboxylic acid involves oxidation of the proper alkylbenzene.



p-Xylene

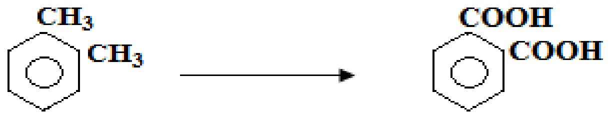
Terephthalic acid
1,4-Benzenedicarboxylic acid



p-Nitrotoluene

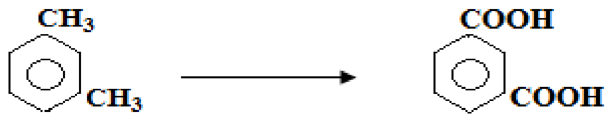
p-Nitrobenzoic acid

(b) Identification of alkylbenzenes



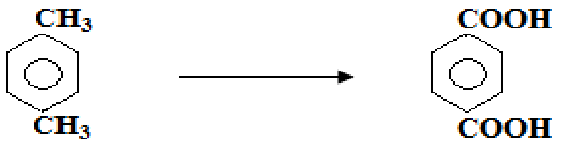
o-Xylene
b.p. 144 °C

Phthalic acid
m.p. 231 °C



m-Xylene
b.p. 139 °C

Isophthalic acid
m.p. 348 °C

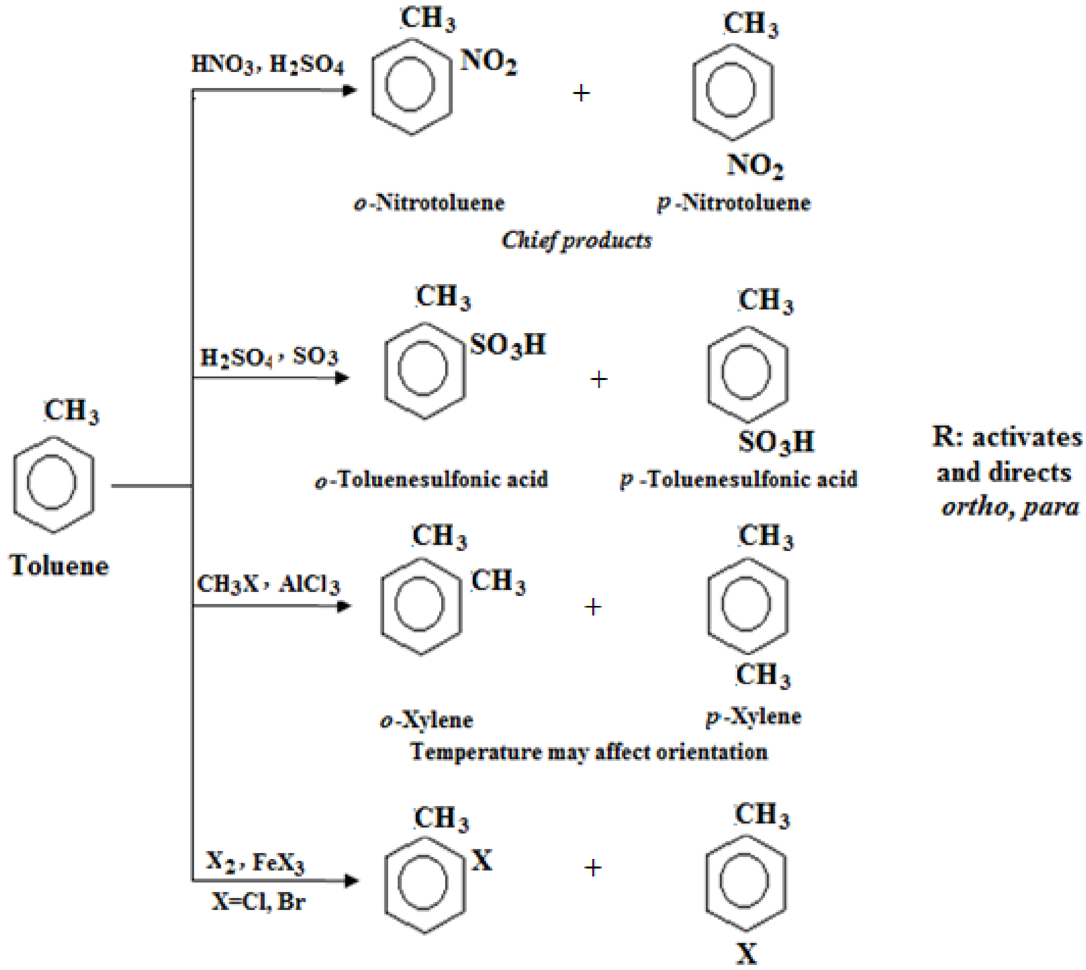


p-Xylene
b.p. 138 °C

Terephthalic acid
m.p. 300 °C

3- Substitution in the ring. Electrophilic aromatic substitution

Because of its electron-releasing effect, an alkyl group activates a benzene ring to which it is attached, and directs *ortho* and *para*.



4- Substitution in the side chain. Free-radical halogenation

Alkyl benzenes clearly offer two main areas to attack by halogens: the ring and the side chain. We can control the position of attack by choosing the proper reaction conditions.

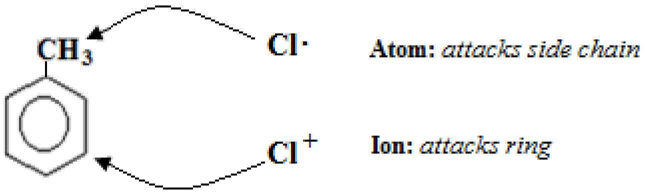
The side chain is alkane-like, and should undergo halogenation as alkanes do: via free-radical substitution. This reaction requires conditions under which halogen atoms are formed, that is, high temperatures or light.

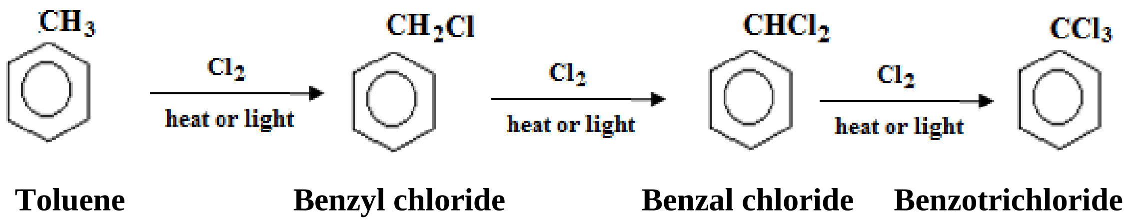
$$\mathbf{CH_4 + Cl_2 \xrightarrow{\text{heat or light}} CH_3Cl + HCl}$$

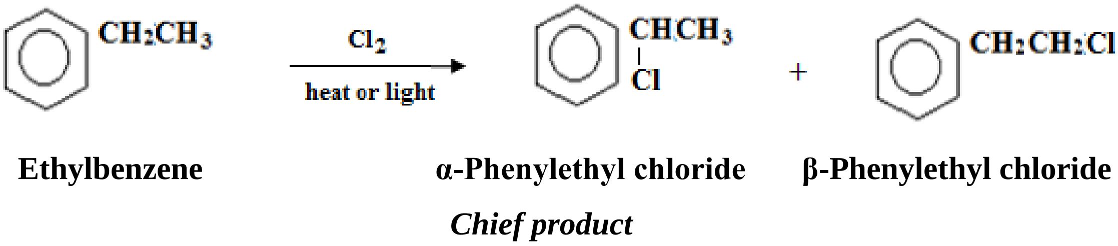
The ring should undergo substitution as benzene dose: via electrophlic substitution. This reaction involves transfer of positive halogen, which is promoted by acid catalysts like ferric chloride.

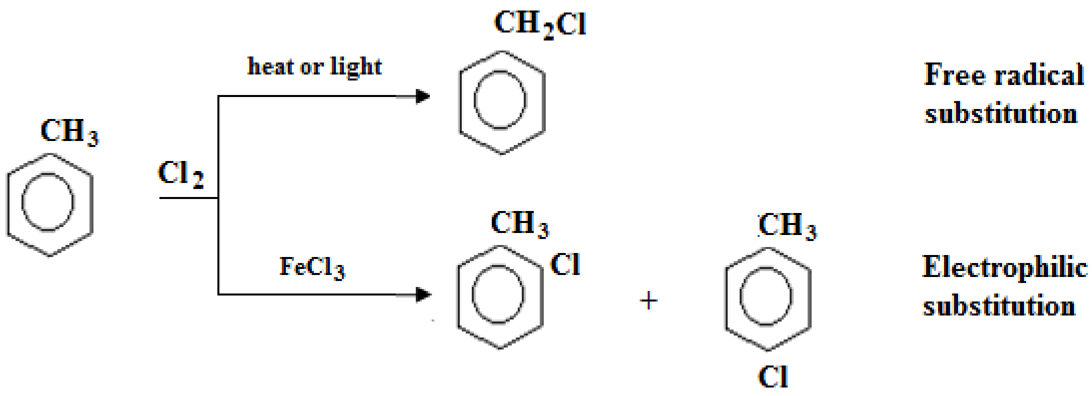
$$\mathbf{C_6H_6 + Cl_2 \xrightarrow{FeCl_3\text{, cold}} C_6H_5Cl + HCl}$$

We must expect, then, that the position of attack in, say, toluene would be governed by which attacking particles is involved, and therefore by the conditions employed. If chlorine is bubbled into boiling toluene that is exposed to U.V. light, substitution occurs in the side chain. In the absence of light and in the presence of ferric chloride, substitution occurs in the ring.




CH₃
Cl₂
heat or light
CH₂Cl
Cl₂
heat or light
CHCl₂
Cl₂
heat or light
CCl₃
Toluene
Benzyl chloride
Benzal chloride
Benzotrichloride


CH₂CH₃
Cl₂
heat or light
CHCH₃
Cl
+
CH₂CH₂Cl
Ethylbenzene
α-Phenylethyl chloride
Chief product
β-Phenylethyl chloride


CH₃
Cl₂
heat or light
CH₂Cl
Free radical substitution
FeCl₃
CH₃
Cl
+
CH₃
Cl
Electrophilic substitution