

## Fundamental Principles of Organic Chemistry

### Old Concept about Organic Chemistry:

According to old concept "all those compounds which contain carbon atom (except  $\text{CO}_2$ ,  $\text{CO}$ , Carbonates, bicarbonates, cyanates, carbides etc.) are called as organic compounds and their study is known as organic chemistry.

The compounds like  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^{-}$  etc are considered as inorganic, by convention because of some basic reasons although these compounds contain carbon atom. One of the valid reasons, that why the compounds are not organic is that, "they do not undergo combustion".

### Modern Concept about Organic Chemistry:

According to modern concept, "All the hydrocarbons and their derivatives are called organic compounds and their study is known as organic chemistry".

### Vital Force Theory:

In 1807, Berzelius suggested that organic compounds always obtained from organisms (animals and plants) and therefore got the name "organic derived from ORGANISM". This concept appeared in the form of a theory which is known as Vital Force Theory and can be stated as, "Organic compounds are formed inside the body of organisms (animals & plants) and cannot be synthesized in laboratory".

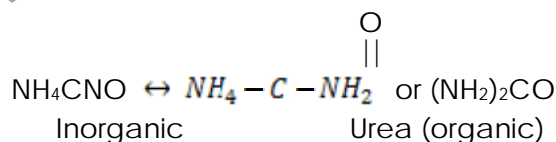
### Rejection of Vital Force Theory:

In 1828, a German chemist Friedrich Wholer synthesized urea (an organic compound) in laboratory and thus rejected Vital Force Theory.

Actually he was reacting Potassium Cyanate ( $\text{KOCN}$ ) with Ammonium Chloride ( $\text{NH}_4\text{Cl}$ ) (Both inorganic) to produce an inorganic compound, Ammonium Cyanate ( $\text{NH}_4\text{CNO}$ ). When he got  $\text{NH}_4\text{CNO}$ , he started heating it, to study its characteristics. But when he heated, Ammonium Cyanate, it converted into a new compound which was urea. Thus the concept of Vital Force Theory was rejected.



Then



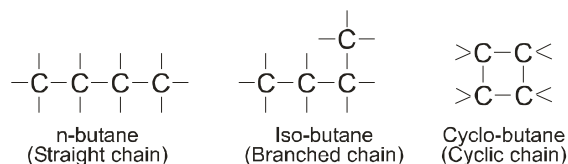
### Some Important Features of Organic Compounds:

Q: Why organic compounds are found in such a large number?

Ans: It is because of some qualities or characteristics of carbon. The most important ones are

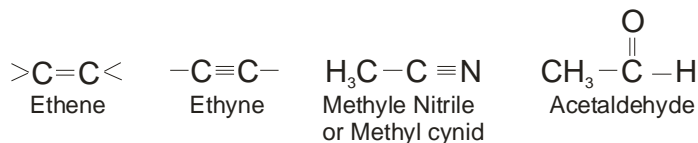
1) Catenation: The ability of carbon atom make bonds with other carbon atoms to form chains, which may be straight branched or cyclic, is known as catenation. This ability of carbon give rise to plenty of organic compounds.

e.g.



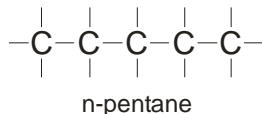
2) Multiple Bond Formation: Carbon has got the ability of multiple bond formation with other carbon atoms or even with other atoms like O, S, N etc. Due to this ability of carbon, so many organic compounds have been possible.

e.g



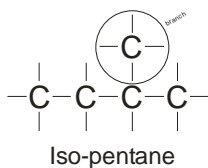
Q: What is normal, Iso and neo-hydrocarbon?

1) Normal Hydrocarbon: A hydrocarbon in which all carbon atoms are bonded in a straight chain, represented by "n". e.g



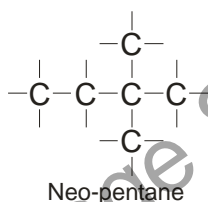
2) Iso – Hydrocarbon: A hydrocarbon in which there is a branch at the 2<sup>nd</sup> last carbon of the branch.

e.g



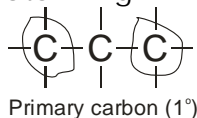
3) Neo-hydrocarbon: A hydrocarbon in which there are two branches attached to the 2<sup>nd</sup> last carbon of the chain.

e.g

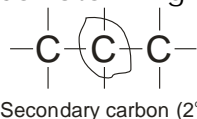


Q: Define primary, secondary and tertiary carbon atom?

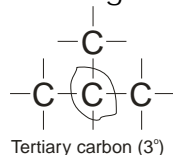
1) Primary Carbon (1°): That carbon of a hydrocarbon which is bonded with only one other carbon atom is known as primary carbon atom. E.g



2) Secondary Carbon Atom (2°): That carbon of a hydrocarbon which is bonded with two other carbon atoms is known as secondary carbon atom. E.g

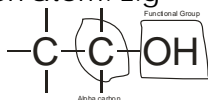


3) Tertiary Carbon Atom (3°): The carbon atom of a hydrocarbon which is bonded to three other carbon atoms is known as tertiary carbon atom. E.g

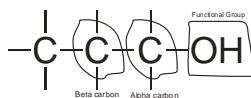


Q: What is alpha ( ), Beta ( ), Gamma ( ) and Sigma ( ) carbon atoms?

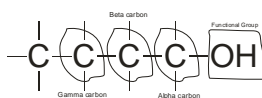
1) Alpha Carbon ( ): That carbon of an organic compound which is directly bonded with the functional group is known as alpha carbon atom. E.g



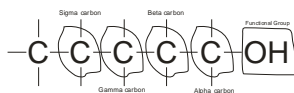
2) Beta Carbon ( ): That carbon atom of an organic compound which attached with an alpha carbon atom is known as Beta carbon. E.g



3) Gamma Carbon (  $\gamma$  ): That carbon atom of an organic compound which is bonded with a beta carbon. E.g



4) Sigma Carbon (  $\sigma$  ): That carbon atom of an organic compound which is bonded with a gamma carbon. E.g



### Natural Sources of Organic Compounds:

Petroleum, coal and natural gas are the fossil fuels and are formed over long period of time, from the decay of plants and animals. They are the natural reservoirs from which many organic compounds can be prepared.

These natural sources of organic compounds are discussed as;

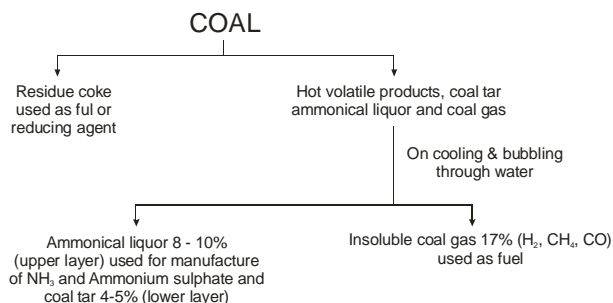
### COAL

Origin of Coal: Coal was formed from the remains of the trees, which were buried inside the earth crust some 500 years ago. Due to bacterial and chemical action on wood, it converts into "peat". Then due to high pressure and high temperature inside the earth crust "peat" converted into "coal". i.e



Destructive Distillation of Coal: During destructive distillation, coal is highly heated in the absence of air at about 500 – 1000 °C and it is converted into coke, coal and coal tar. Coal tar further contains, large number of organic compounds which are obtained by fractional distillation of coal tar.

The various components of coal, obtained by its fractional distillation are shown as;



### Uses:

About 80% of the coal is used for baking purposes of bricks in limekilns. Coal is also used for domestic purposes.

Coal contains more than 200 aromatic compounds. According to geological survey the total estimated coal resources of Pakistan are 184 billion tones.

### NATURAL GAS:

Natural gas is an important means of energy both for industrial as well as for domestic purposes.

Source: Natural gas is formed by the decomposition of organic matter. It is a mixture of low boiling hydrocarbons. Major portion (about 85%) of natural gas is methane ( $\text{CH}_4$ ).

Uses: Natural gas is used for power generation in various industries like cement & fertilizers industries as a fuel. It is also used as fuel for domestic purposes.

#### PETROLEUM

Sources: Refined form of mineral oil called petroleum. It is considered that petroleum is formed by slow chemical and biochemical decomposition of the remains of organic matter found between the earth crusts. When extracted from rocks, it appears like a liquid of blackish color known as "Crude Oil". Then it is refined to get different petroleum fractions.

So the process by which the various components of petroleum are separated from each other is known as "Refining of Petroleum". Currently four oil refineries are in operation in Pakistan. They are

- a. Attock Oil National Refinery
- b. Pak – Arab Refinery
- c. Pak Refinery
- d.

The various components of petroleum (crude oil) are separated from each other by means of fractional distillation which is explained as follows. This process is also known as Refining of Petroleum.

#### Fractional Distillation:

The process, by which the various liquid components of a mixture are separated on the basis of difference in their boiling points, is known as fractional distillation.

The various components of crude oil are separated by means of its fractional distillation, also called as refining of crude oil. A fractionating tower is used in this process. The tower has different temperature zones, where various components are obtained. The detailed data obtained by fractional distillation of petroleum, is shown in the table as follow.

Boiling Point Range	No. of Carbon Atoms in the Fraction	Name of the Fraction and Principle uses
Below $20^\circ\text{C}$	$\text{C}_1 - \text{C}_4$	Natural Gas: used as fuel, Raw material for other chemicals
$20 - 60^\circ\text{C}$	$\text{C}_5 - \text{C}_6$	Petroleum Ether: Used as a non-polar solvent & cleansing fluid
$60 - 100^\circ\text{C}$	$\text{C}_6 - \text{C}_7$	Ligroin or Light Naphtha: used as a non-polar solvent & cleansing fluid
$40 - 200^\circ\text{C}$	$\text{C}_5 - \text{C}_{10}$	Gasoline or Petrol: used as fuel for vehicles
$175 - 325^\circ\text{C}$	$\text{C}_{12} - \text{C}_{18}$	Kerosine: used for domestic purposes and jet fuel
$250 - 400^\circ\text{C}$	$\text{C}_{12}$ & higher	Gas Oil or Diesel: used as fuel for diesel engines
Residue	$\text{C}_{20}$ & Up $\text{C}_{30}$ & Up	Lubrication Oil: used for lubrication Asphalt: used for surface roads and roofs

OCTANE NUMBER:

"The percentage by volume of iso-octane and n-heptane which has the same knocking ability as the fuel under test is called Octane of fuel".

OR "As gasoline is usually a mixture of n-heptane and iso-octane molecules, thus the octane no. of fuel (gasoline or petrol) can also be defined as

"The number of iso-octane molecules, present in 100 molecules of gasoline, is known as octane number of the fuel or gasoline".

Greater is the octane number of fuel, greater will be its quality and vice versa. For example if we have a fuel (gasoline) such that it has 90% iso-octanes and 10% n-heptane. Then the octane number of this fuel is 90. With increase of octane number the engine is less likely to produce knocking. Straight chain hydro carbons have low octane number and are poor fuels.

Experiments have shown that iso-octane (or 2, 2, 4-trimethyl pentane) burns very smoothly in an engine and has been arbitrarily given an octane number of 100. For improving the octane number of a fuel (i-e converting n-heptane to iso-octane molecules) a process is used which is called as refining.

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#### KNOCKING:

Gasoline is a mixture of n-heptane and iso-octane. The straight chain hydrocarbons are easily ignited (ie, straight chain hydrocarbons undergo rapid combustion) as compared to branched chain hydrocarbon. Thus in low octane fuel (gasoline containing low octane number i.e, higher %age of n-heptane), pre-ignition of n-heptane molecule starts due to which a sharp metallic sound is produced in the internal combustion engine of vehicle and this sharp metallic sound produced in the internal combustion engine of vehicle due to low octane fuel is known as "Knocking".

To overcome the problem of knocking, two methods are applied:

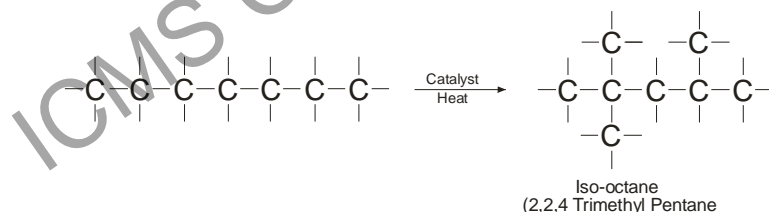
##### 1) Anti Knocking Agents:

The knocking in the combustion engine of vehicles can be reduced by using an anti-knocking material. An anti-knocking substance is a compound or element which slows down the combustion reaction of n-heptane of the low octane fuel. Thus pre-ignition of n-heptane molecules does not occur any more in the presence of an anti-knocking agent. Thus it is clear that an anti-knocking agent acts as a "negative catalyst", as it slows down the combustion reaction of n-heptane. The most common anti-knocking agent is tetraethyle lead  $((C_2H_5)_4Pb)$ . But use of tetra ethyle lead (TEL) as an anti knocking agent has a very major disadvantage. The combustion product of TEL i.e lead oxide is reduced to metallic lead (Pb) which is discharged into the air through exhaust pipe and causes air pollution. Therefore use of TEL as an anti-knocking is nowadays banned.

##### 2) Reforming of Petrol:

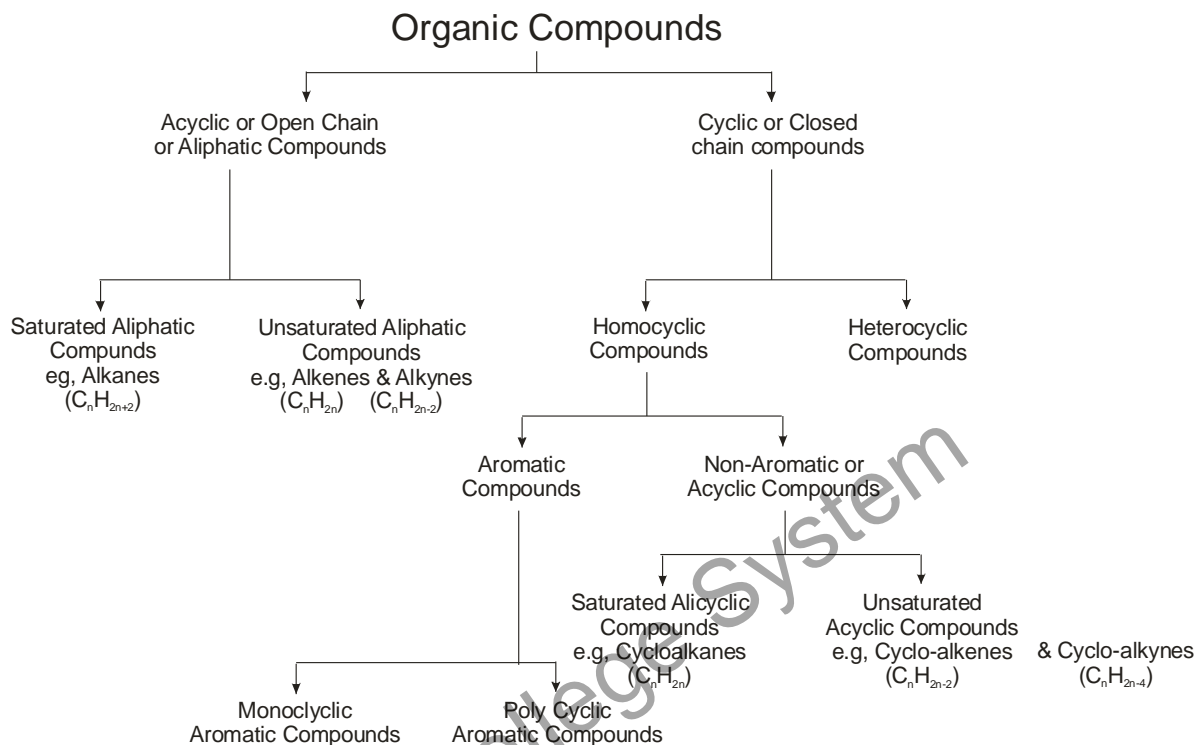
The conversion of straight chain hydrocarbon into branched chain hydrocarbons by heat in the absence of oxygen and in the presence of a catalyst is called as Refining.

The octane number of low octane petrol (Gasoline) is enhanced by the process known as Reforming of Petrol. In this process the n-heptane molecules are converted into iso-octane molecules by high heating in the presence of a catalyst and thus the octane number of gasoline is enhanced and knocking problem is reduced in minimum, i.e,



## CLASSIFICATION OF ORGANIC COMPOUNDS:

Organic compounds can be classified as follows:

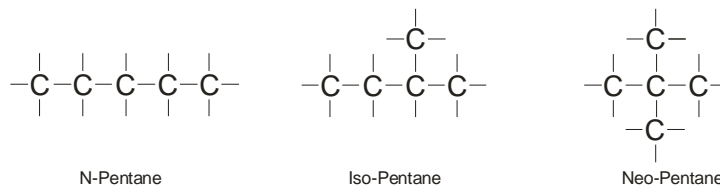


Now all these various types of organic compounds can be defined with examples as :

### 1) Open Chain or Acyclic or Aliphatic Organic Compounds:

Those organic compounds (hydrocarbons) in which carbon atoms are bonded in such a way that they form no cycle and the carbon chain is always an open chain, are called as open chain or aliphatic hydrocarbons.

e.g



Types:

Aliphatic hydrocarbons are of two types;

#### a) Aliphatic Saturated Hydrocarbons:

Those aliphatic compounds (organic compounds containing no cycle), in which the tetravalency of each carbon is fully satisfied i.e, each carbon has formed four single covalent bonds with other atoms, are known as aliphatic saturated hydrocarbons. The best example of aliphatic saturated hydrocarbons is "Alkanes". The general formula of alkanes is " $C_nH_{2n+2}$ ", where 'n' stands for the number of carbon atoms. On the basis of general formula, alkane series can be drawn as;

### Alkane Series:

General Formula,  $C_nH_{2n+2}$

$C_1H_{2 \times 1 + 2}$	=	$CH_4$	Methane
$C_2H_{2 \times 2 + 2}$	=	$C_2H_6$	Ethane
$C_3H_{2 \times 3 + 2}$	=	$C_3H_8$	Propane
$C_4H_{2 \times 4 + 2}$	=	$C_4H_{10}$	Butane
	=	$C_5H_{12}$	Pentane
	=	$C_6H_{14}$	Hexane
	=	$C_7H_{16}$	Heptane
	=	$C_8H_{18}$	Octane
	=	$C_9H_{20}$	Nonane
	=	$C_{10}H_{22}$	Decane
	=	$C_{11}H_{24}$	Undecane
	=	$C_{12}H_{26}$	Dodecane
	=	$C_{13}H_{28}$	Tridecane
	=	$C_{14}H_{30}$	Tetradecane
	=	$C_{15}H_{32}$	Pentadecane
	=	$C_{16}H_{34}$	Hexadecane
	=	$C_{17}H_{36}$	Heptadecane
	=	$C_{18}H_{38}$	Octadecane
	=	$C_{19}H_{40}$	Nonadecane
	=	$C_{20}H_{42}$	Eicosane
	=	$C_{21}H_{44}$	Heneicosane and so on.

### b) Aliphatic Unsaturated Hydrocarbons:

Those aliphatic hydrocarbons in which the tetravalency of each carbon is not fully satisfied i.e., there is at least one double or triple covalent bond between carbon atoms, are known as unsaturated hydrocarbons. The two well known examples of aliphatic unsaturated hydrocarbons are;

#### i) Alkenes:

Alkenes are those unsaturated hydrocarbons in which there is a double bond between carbon atoms. The general formula of alkenes is " $C_nH_{2n}$ " and their functional group is "double bond". The alkene series can be derived as:

Alkene Series:

$C_nH_{2n}$		
$C_1H_{2 \times 1}$	=	$CH_2$ Methylene gp = Not an alkene
$C_2H_{2 \times 2}$	=	$C_2H_4$ Ethene
$C_3H_{2 \times 3}$	=	$C_3H_6$ Propene
	=	$C_{10}H_{20}$ Decene

#### ii) Alkynes:

Those unsaturated aliphatic hydrocarbons in which there is a triple covalent bond between carbon atoms are known as alkynes. The functional group of alkynes is "triple bond". The general formula of alkynes is " $C_nH_{2n-2}$ ". Alkyne series can be derived as;

Alkyne Series:

$C_nH_{2n-2}$		
$C_1H_{2 \times 1 - 2}$	=	$CH_0$ Not possible
$C_2H_{2 \times 2 - 2}$	=	$C_2H_2$ Ethyne (Acetylene)
$C_3H_{2 \times 3 - 2}$	=	$C_3H_4$ Propyne
$C_{10}H_{2 \times 10 - 2}$	=	$C_{10}H_{18}$ Decyne

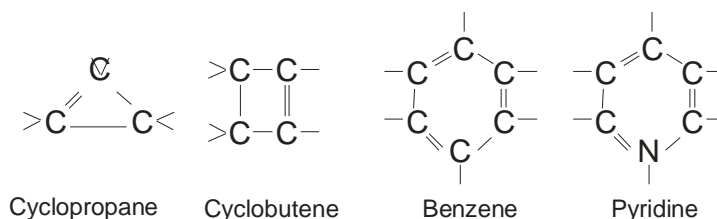


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## 2) Closed Chain or Cyclic Organic Compounds:

Those organic compounds in which there is a cycle or ring, which may be composed of only carbon atoms or may also have one or more atoms other than carbon, are known as chain or cyclic organic compounds.

e.g,



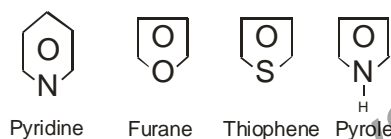
Types:

Close chain or cyclic organic compounds are of two types

### i) Heterocyclic Organic Compounds:

Those cyclic organic compounds in which the ring consists of at least one atom, other than carbon, are known as heterocyclic organic compounds.

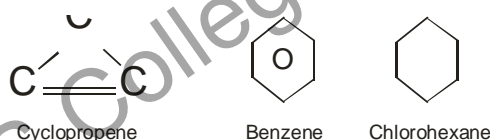
e.g,



### ii) Homocyclic Organic Compounds:

Those cyclic organic compounds in which the ring consists of carbon atoms only, are known as homocyclic organic compounds.

e.g,



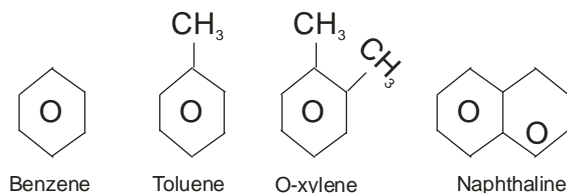
Types:

Homocyclic organic compounds are of two types.

### a) Aromatic Organic Compounds:

Those organic compounds which contain one or more aromatic or benzene rings are called as aromatic compounds. An aromatic or benzene ring is a ring containing six carbon atoms bonded together by means of alternate double and single bonds.

e.g,

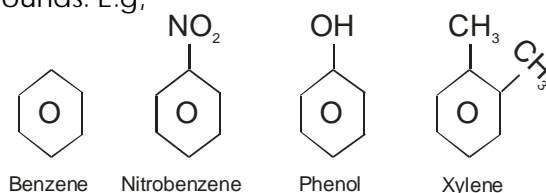


Types:

Aromatic compounds are of two types:

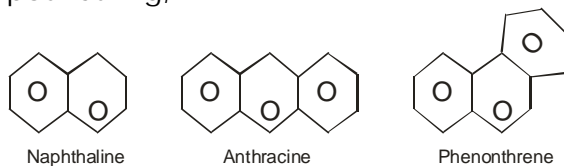
#### 1) Monocyclic Aromatic Compounds:

Those aromatic compounds which contain only one aromatic or benzene ring, are known as monocyclic aromatic compounds. E.g,



## II) Polycyclic Aromatic Compounds:

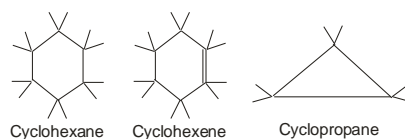
Those aromatic compounds which contain more than one aromatic or benzene rings, are known as polycyclic aromatic compounds. E.g,



## b) Non-Aromatic or Alicyclic Organic Compounds:

Those cyclic compounds which do not contain any aromatic ring, are known as non-aromatic or alicyclic compounds.

e.g,



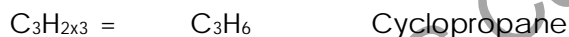
Types:

Alicyclic hydrocarbons are of two types;

### I) Alicyclic Saturated Organic Compounds:

Those cyclic compounds in which tetravalency of each carbon is fully satisfied, are known as alicyclic saturated organic compounds. The best examples of alicyclic saturated hydrocarbons is "Cycloalkanes". The general formula of cycloalkanes is " $C_nH_{2n}$ ". The cycloalkane series starts from three carbon atoms because the cycle needs a minimum of three carbon atoms. The cycloalkanes series can be drawn as;

Cycloalkane Series:



### II) Alicyclic Unsaturated Organic Compounds:

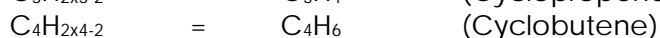
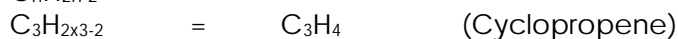
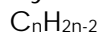
Those cyclic compounds in which the tetravalency of each carbon is not fully satisfied, i.e, there is one or more double or triple covalent bonds between carbon atoms, are known as alicyclic unsaturated organic compounds.

The best examples of unsaturated alicyclic organic compounds are;

#### a) Cycloalkenes:

Those alicyclic compounds in which there is a double covalent bond between any two carbon atoms. General formula of cycloalkenes is " $C_nH_{2n-2}$ ". The cyclo alkene series starts from three carbon atoms and can be derived as;

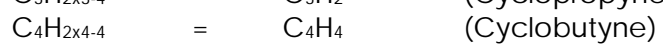
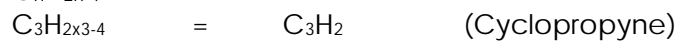
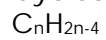
Cycloalkene Series:



#### b) Cycloalkynes:

Those alicyclic compounds in which there is a triple covalent bond between any two carbon atoms, are known as cycloalkynes. General formula of cycloalkynes is " $C_nH_{2n-4}$ ". The cycloalkynes series starts from three carbon atoms.

Cycloalkynes Series:



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## Functional Group:

An atom or group of atoms or a double or a triple bond which is responsible for the particular characteristics of an organic compound is known as Functional Group of that compound.

OR an atom or group of atoms or double or triple bond which serve distinguish compound from other compounds is known as Functional group of that compound.

The study of organic chemistry is organized around functional group. Each functional group defines an organic family. For example, millions of organic compounds have been derived into homologous series on the basis of functional group. Some important organic compound's families and their functional groups are shown in the table below;

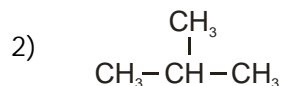
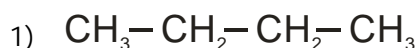
Functional Group		Class of Compounds	Examples
Formula	Name		
$\text{—C—C—}$	None	Alkanes	$\text{CH}_3 - \text{CH}_3$
$\text{>C=C<}$	Double Bond	Alkenes	$\text{H}_2\text{C} = \text{CH}_2$
$\text{—C}\equiv\text{C—}$	Triple Bond	Alkynes	$\text{HC}\equiv\text{CH}$
$\text{—X}$ (X = F, Cl, Br, I)	Halo gp.	Alkyl Halides	$\text{H}_3\text{C} - \text{CH}_2 - \text{I}$
$\text{—OH}$	Hydroxyl Group	Alcohols	$\text{H}_3\text{C} - \text{CH}_2 - \text{OH}$
$\text{—NH}_2$	Amino Group	Amines	$\text{H}_3\text{C} - \text{CH}_2 - \text{NH}_2$
$\text{R—O—R}$	Ether Linkage	Ethers	$\text{H}_3\text{C} - \text{O} - \text{CH}_3$
$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—H} \end{array} \text{ or } \text{—CHO}$	Formyl Group	Aldehydes	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C} - \text{C} - \text{H} \end{array}$
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R—C—R} \end{array}$	Carboxyl	Ketones	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C} - \text{C} - \text{CH}_3 \end{array}$
$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—OH} \end{array}$	Carboxylic Group	Carboxylic Acids	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C} - \text{C} - \text{OH} \end{array}$
$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—X} \end{array}$	Acid Halides	Acid Halides	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C} - \text{C} - \text{Cl} \end{array}$
$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—NH}_2 \end{array}$	Acidamide	Acidamides	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C} - \text{C} - \text{NH}_2 \end{array}$
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R—C—OR} \end{array}$	Carbalkoxy or Ester gp.	Esters	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C} - \text{C} - \text{O} - \text{CH}_3 \end{array}$
$\text{—C}\equiv\text{N}$	Cyano	Alkyl cyanides or Alkane nitrites	$\text{H}_3\text{C} - \text{C}\equiv\text{N}$
$\text{—N}_2\text{O}$	Nitro	Nitro Compounds	$\text{H}_5\text{C}_6\text{NO}_2$

## ISOMERISM

"ISO" means "same" & "mers" means "parts".

"Two or more than two compounds having same molecular formula but different arrangement of atoms, are known as isomerism".

For example, consider the following two molecules;



The molecular formula both the above mentioned molecules is " $\text{C}_4\text{H}_{10}$ ", so the above two molecules are isomers of each other, as they have same molecular formula but different arrangement of atoms.

Types of Isomerism:

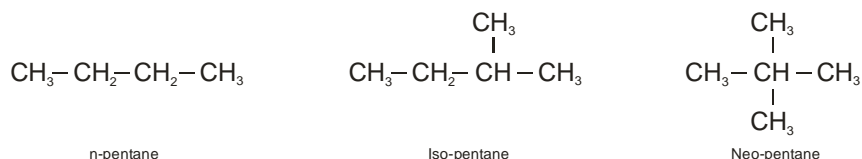
Isomerism has two major types;

- Structural Isomerism
- Geometric or Cis-trans Isomerism

### A) Structural Isomerism:

Two or more than two compounds having same molecular formula but different structural formula are known as structural isomers and the phenomenon is known as structural isomerism.

e.g, Consider the following three molecules;



All the above three molecules are structural isomers because they have same molecular formula but different structural formula.

Types:

Structural isomerism is of four types;

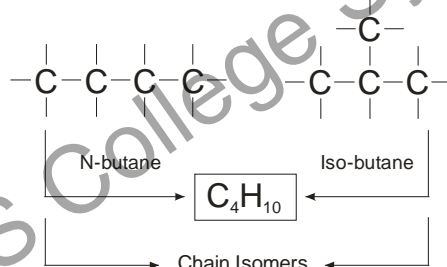
- 1) Chain Isomerism
- 2) Position Isomerism
- 3) Functional Group Isomerism
- 4) Meta merism

They can be explained as follows;

#### 1) Chain Isomerism:

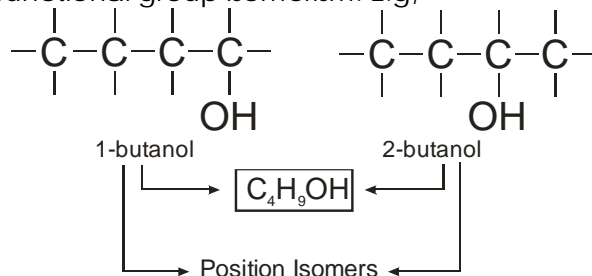
Two or more than two molecules having same molecular formula but have different carbon chain, are known as chain isomers and the phenomenon is known as chain isomerism.

e.g,



#### 2) Position Isomerism:

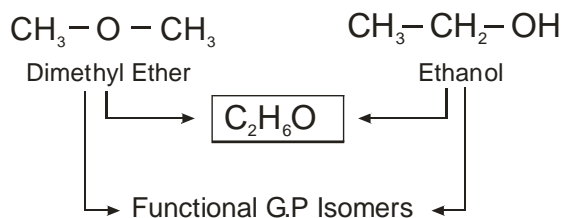
Two or more molecules having same molecular formula and have same functional group but have different positions of their functional group are known as position isomers and the phenomenon is known as functional group isomerism. E.g,



#### 3) Functional Group Isomerism:

Two or more molecules having same molecular formula but have different functional group, are known as functional group isomers and the phenomenon is known as functional group isomerism.

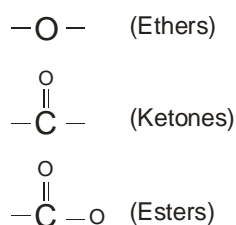
E.g,



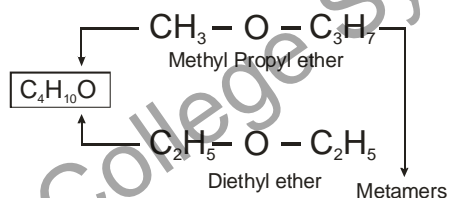
#### 4) Metamerism:

Two or more molecules having same molecular formula and same multivalent functional group but different number of carbon atoms attached to either side of the functional group, are known as metamers and the phenomenon is known as metamerism.

It is important to note that metamerism is shown only by those molecules (organic compounds) whose functional group is multivalent i.e, which can make more than one bonds. So either Ketones and esters can show the phenomenon of metamerism, because all of them have multivalent functional group, i.e



e.g,

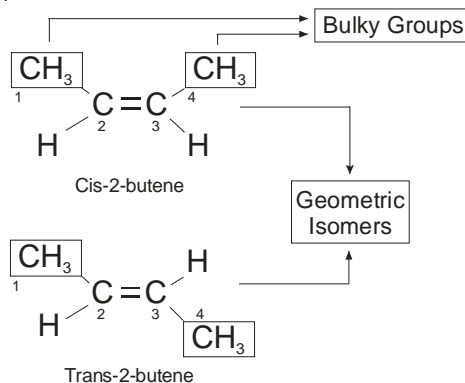


#### B) Geometric OR Cis-Trans Isomerism:

Two or more than two compounds having same molecular formula and same structural formula but different arrangement of its atoms or groups of atoms in space, are known as Geometric or Cis-Trans Isomers and the phenomenon is known as Geometric or Cis-Trans Isomerism. Such isomerism is mostly in alkenes in which both the double bonded carbon atoms having an alkyl group and a H attached with it. The alkyl group attached with the double bonded carbon atom of an alkene is known as "bulky group". That isomer in which the bulky groups (alkyl groups) attached with double bonded carbon atoms are at the same side i.e, either both are above or below, is known as Cis-Isomer or Cis-alkene.

On the other hand that isomer (alkene - ) in which the bulky groups lie at opposite sides i.e, one above and other below is known as "Trans alkene" or "Trans isomer".

For example consider the molecule butane ( $\text{C}_4\text{H}_8$ ). It has two geometric isomers i.e, one Cis-butene and other Trans-butene.



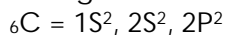
We cannot convert the trans-isomer into Cis-isomer by rotation because by doing so, the pi bond has to be broken.

ICMS College System



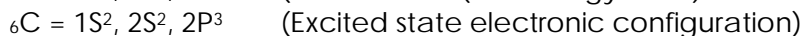
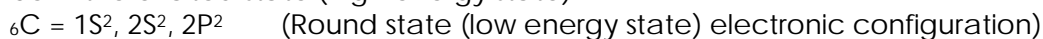
## HYBRIDIZATION:

The process in which atomic orbitals of different shape and energy mix and form an equivalent number of new atomic orbitals of same shape and energy is known as hybridization. These new orbitals are known as hybridization. The process of hybridization got its consideration when some problems were faced in case of bonding of some atoms. For example, the electronic configuration of carbon is;



$K = 2, L = 4$ , (2 paired and 2 unpaired)

As C has only 2 unpaired electrons in its valence shell, so it should always form only two bonds according to valence bond theory. But in all organic compounds, C has formed four covalent bonds. It is because of the transference of one of the 2S electron to the empty 2P. Thus due to greater number of unpaired electron (4 unpaired electrons) C gets more energetic and is said to be in the excited state (high energy state).



Now C can form 4 covalent bonds. But as in all the 4 bonds, one S orbital is involved whose shape is different from P orbitals and also its energy is lower (being closer to nucleus) than P orbitals, thus all 4 bonds C will not be same (same length and energy). Therefore, to avoid this problem and to form all bonds of same energy and length, carbon undergoes the process of hybridization after exciting and b/f bond formation.

The shape of a hybrid orbital is two lobed, one lobe is larger while the other one is smaller.

The energy of a hybrid orbital is less than the energy of P orbitals and larger than the energy of S orbitals, so we can say that the hybrid orbitals are closer to nucleus as compared to P orbitals, while away from the nucleus as compared to S orbitals.

### TYPES:

Although there are several types of hybridization, but the following three are the most simple and main types.

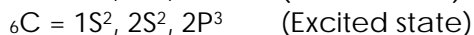
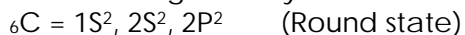
- 1)  $\text{SP}^3$  Hybridization
- 2)  $\text{SP}^2$  Hybridization
- 3)  $\text{SP}$  Hybridization

#### 1) $\text{SP}^3$ Hybridization:

The hybridization in which one S and three P orbitals intermix and form four hybrid orbitals of same shape and energy, is known as  $\text{SP}^3$  Hybridization and each hybrid orbital is known as an  $\text{SP}^3$  hybrid orbital. In each  $\text{SP}^3$  hybrid orbital, the S character is only 25% while P character is 75%, therefore, these 4  $\text{SP}^3$  hybrid orbitals will not be very much close to the nucleus as they will be near to P and away from S orbital.

These four  $\text{SP}^3$  hybrid orbitals arrange themselves in a tetrahedral geometry. The angle between any two  $\text{SP}^3$  hybrid orbitals is  $109.5^\circ$ .

Example: Methane ( $\text{CH}_4$ ) molecule, carbon undergoes  $\text{SP}^3$  hybridization, therefore,  $\text{CH}_4$  has a tetrahedral geometry with bond angle of  $109.5^\circ$ .



#### 2) $\text{SP}^2$ Hybridization:

The hybridization in which one S and two P orbitals of different shape and energy mix to form 3 hybrid orbitals, is known as  $\text{SP}^2$  Hybridization and each hybrid orbital is known as  $\text{SP}^2$  hybrid orbital.

In case of each  $\text{SP}^2$  hybrid orbital, S character is 33.33% while P character is 66.66%, therefore, each  $\text{SP}^2$  hybrid orbital will be a bit closer to the nucleus as compared to  $\text{SP}^3$  hybrid orbitals, due to increase of S character. Hence the sigma bond formed from  $\text{SP}^2$  hybrid orbital will be stronger than the sigma bond formed by  $\text{SP}^3$  hybrid orbitals and thus the  $\text{SP}^2$  hybridized carbon will more

electronegative than the  $sp^3$  hybridized carbon. The three  $sp^2$  hybrid orbitals arrange themselves in a "coplanar geometry". The angle between any two  $sp^2$  hybrid orbitals is  $120^\circ$ .

Example:

Ethylene or Ethene Molecule ( $C_2H_4$ ):

In ethene molecule, each carbon undergoes  $sp^2$  hybridization. Thus the geometry of ethene molecule is coplanar and the bond angle is  $120^\circ$ . Two of the 2P orbitals (i.e.,  $2p_x$  &  $2p_y$ ) undergo hybridization and their shape and energy changes. But the 3<sup>rd</sup> orbital i.e., ( $2p_z$ ) remains unhybrid, so its shape and energy remain unchanged and it lies perpendicular to the plane of hybrid orbitals with one lobe above and one lobe below the hybrid orbitals. Thus when the  $sp^2$  hybrid orbital of one C overlaps with the  $sp^2$  hybrid orbital of other carbon, a sigma bond is formed between the two carbon atoms, which brings them so closer to each other that the unhybrid  $2p_z$  orbital of both the carbon atoms undergo a sidewise overlap resulting in the formation of a bond.

### 3) SP Hybridization:

The hybridization in which one S and one P orbital of different shape and energy mix and form two SP hybrid orbitals of same shape and energy is known as SP Hybridization.

In each SP hybrid orbital, there is 50% S and 50% P character. Thus due to the increased S character in case of SP hybridization, each SP hybrid orbital is more closer to the nucleus of the hybridized atom as compared to  $sp^2$  &  $sp^3$  hybrid orbitals. The SP hybrid orbitals arrange themselves in a linear geometry and the angle between them is always  $180^\circ$ .

Example:

Acetylene or Ethyne ( $C_2H_2$ ):

In acetylene molecule, each carbon undergoes SP hybridization. Thus the geometry of acetylene is linear and its bond angle is  $180^\circ$ . As in SP hybridization, one S and only one P orbital get hybridized, thus the two P orbitals, i.e.,  $2p_y$  &  $2p_z$  orbitals of both the carbon atoms remain unhybrid and they are perpendicular to the plane of hybrid orbitals as well as mutually perpendicular.

The one SP hybrid orbital of one carbon atom overlap with the SP hybrid orbital of the other carbon atom forming a sigma covalent bond between them. Similarly the other SP hybrid orbital of each carbon overlap with the S orbital of hydrogen atoms producing two C - H sigma covalent bonds. Then due to the formation of sigma bond between carbon atoms, they come so close to each other that the  $2p_y$  of one carbon undergo a sidewise overlap with the  $2p_y$  of the other carbon and same case happens for  $2p_z$  orbital of both the carbon atoms thus producing two pi bonds between carbon atoms. Thus in acetylene molecule, there is a triple covalent bond between the carbon atoms. Out of these three bonds, one is sigma covalent bond while the remaining two are pi (  $\pi$  ) covalent bonds. As the sigma bond is formed due to linear overlap of the orbitals of carbon atoms, therefore, it is much more stronger. While the pi bonds are of equal strength and as they are formed by the sidewise overlap of the orbitals of carbon atoms therefore, they are much weaker than the sigma bond.

## CHEMISTRY OF ALIPHATIC HYDROCARBONS

### Contents:

- 8.1 Introduction to Hydrocarbons
- 8.2 Classification of Hydrocarbons
- 8.3 Introduction to Aliphatic Hydrocarbons
- 8.4 Chemistry of Alkanes  
(Introduction, Methods of Preparation, Physical & Chemical Properties and Uses)
- 8.5 Chemistry of Alkenes  
(Introduction, Methods of Preparation, Physical & Chemical Properties, Uses & Tests for Identification of Alkenes)
- 8.6 Chemistry of Alkynes  
(Introduction, Methods of Preparation, Physical & Chemical Properties, Uses & Tests for Identification of Terminal Alkynes)
- 8.7 Comparison of Reactivity of Alkanes, Alkenes & Alkynes

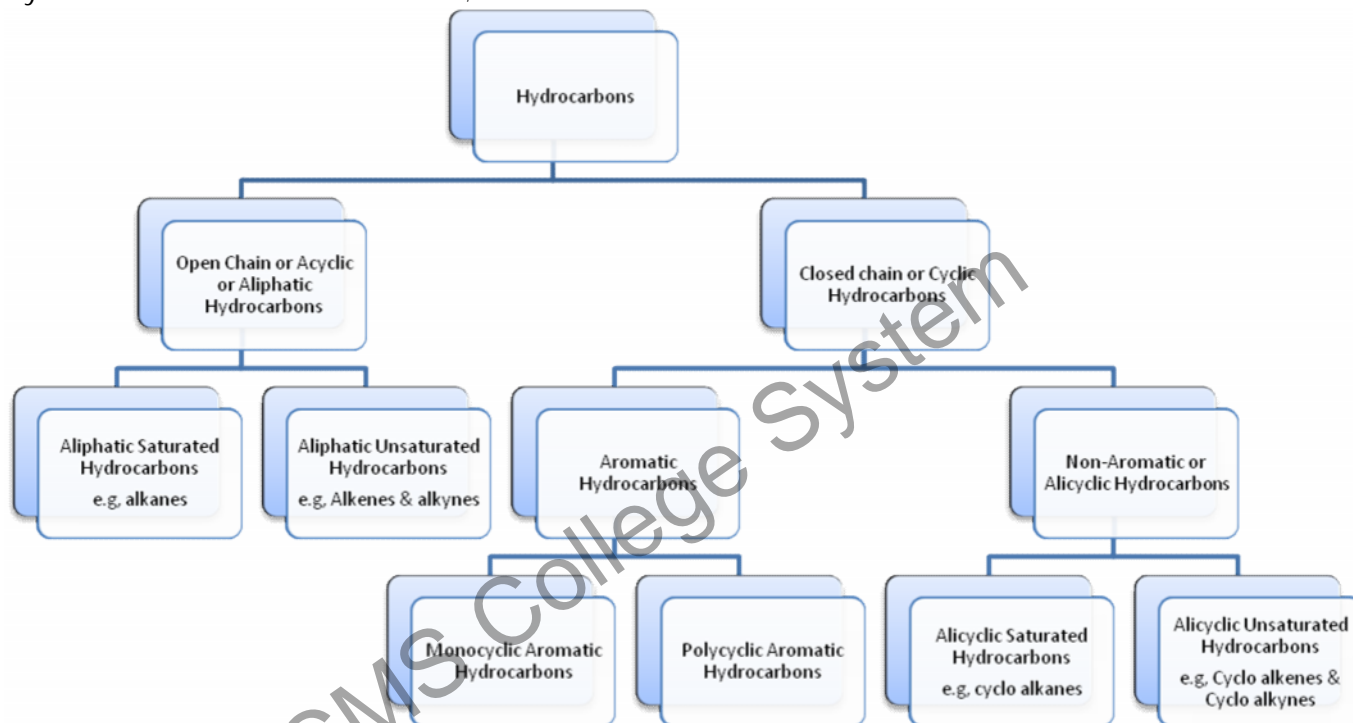
## 8.1 Introduction to Hydrocarbons:

Compounds containing only carbon and hydrogen elements are known as hydrocarbons. E.g, Methane ( $\text{CH}_4$ ), Ethane ( $\text{C}_2\text{H}_6$ ), Benzene ( $\text{C}_6\text{H}_6$ ) etc.

Hydrocarbons are the genuine organic compounds and all other organic compounds, which are not hydrocarbons are considered as the derivatives of hydrocarbons. So in short, the world of organic chemistry is made by hydrocarbons.

## 8.2 Classification of Hydrocarbons:

Hydrocarbons can be classified as;



### A) Open Chain Hydrocarbons OR Aliphatic Hydrocarbons:

The hydrocarbons in which the carbon atoms are bonded together in such a way that there is no ring or cycle, are known as Open chain hydrocarbons. Like Propane ( $\text{CH}_3 - \text{CH}_2 - \text{CH}_3$ ) is an open chain or aliphatic hydrocarbon.

Types:

Aliphatic hydrocarbons are of the following two types;

- i. Aliphatic Saturated Hydrocarbons
- ii. Aliphatic Unsaturated Hydrocarbons

#### i) Aliphatic Saturated Hydrocarbons:

The aliphatic hydrocarbons in which the tetravalency of each carbon is fully satisfied i.e., each carbon has formed four single covalent bonds with other carbon atoms or with hydrogen atoms, are known as saturated hydrocarbons.

The aliphatic saturated hydrocarbons are known as "alkanes". Thus alkanes are the aliphatic saturated hydrocarbons in which each carbon atom has formed four single covalent bonds or sigma covalent bonds.

Alkanes are also known as "paraffines" where "para" means "little" and "ffine" means "tendency". It means that alkanes show very little tendency towards reactivity i.e., reactivity of alkanes is very low. It is because of the fact that all bonds in alkanes are sigma covalent bonds which are very strong and thus acids, bases, oxidizing agents, reducing agents, in common

conditions cannot attack upon alkanes. The general formula of alkanes is  $C_nH_{2n+2}$ , where "n" is the number of carbon atoms. On the basis of general formula, alkanes series can be derived as;

General Formula,  $C_nH_{2n+2}$

$C_1H_{2 \times 1 + 2}$	=	$CH_4$	Methane
$C_2H_{2 \times 2 + 2}$	=	$C_2H_6$	Ethane
$C_3H_{2 \times 3 + 2}$	=	$C_3H_8$	Propane
$C_4H_{2 \times 4 + 2}$	=	$C_4H_{10}$	Butane
	=	$C_5H_{12}$	Pentane
	=	$C_6H_{14}$	Hexane
	=	$C_7H_{16}$	Heptane
	=	$C_8H_{18}$	Octane
	=	$C_9H_{20}$	Nonane
	=	$C_{10}H_{22}$	Decane

## ii) Aliphatic Unsaturated Hydrocarbons:

The aliphatic hydrocarbons in which the tetravalency of each carbon is not fully satisfied i.e, there is at least one double or triple covalent bond between any two carbon atoms, are known as aliphatic unsaturated hydrocarbons. Those unsaturated aliphatic hydrocarbons which contain a double covalent bond between carbon atoms, are known as "Alkenes". The general formula of alkenes is  $C_nH_{2n}$ , where "n" is the number of carbon atoms.

Those unsaturated hydrocarbons which contain a triple covalent bond between carbon atoms, are known as "alkynes". The general formula of alkynes is  $C_nH_{2n-2}$ , where "n" is the number of carbon atoms. The alkene and alkyne series are as follows;

Alkene Series:

$C_nH_{2n}$			
$C_1H_{2 \times 1}$	=	$CH_2$	Methylene gp = Not an alkene
$C_2H_{2 \times 2}$	=	$C_2H_4$	Ethene
$C_3H_{2 \times 3}$	=	$C_3H_6$	Propene
		$C_{10}H_{20}$	Decene

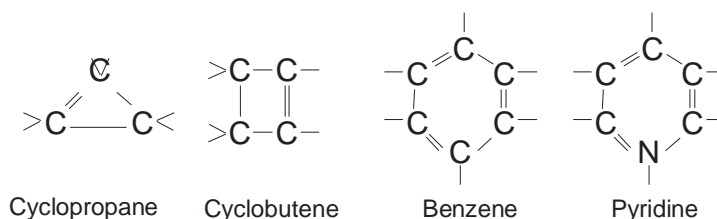
Alkyne Series:

$C_nH_{2n-2}$			
$C_1H_{2 \times 1 - 2}$	=	$CH_0$	Not possible
$C_2H_{2 \times 2 - 2}$	=	$C_2H_2$	Ethyne (Acetylene)
$C_3H_{2 \times 3 - 2}$	=	$C_3H_4$	Propyne
$C_{10}H_{2 \times 10 - 2}$	=	$C_{10}H_{18}$	Decyne

## B) Closed Chain OR Cyclic Hydrocarbons:

The hydrocarbons in which the carbon atoms are bonded together in such a ways that they form a ring or cycle, are known as closed chain or cyclic hydrocarbons.

e.g,



Types:

Cyclic hydrocarbons are of the following two types;

- a) Aromatic Hydrocarbons
- b) Non-Aromatic Cyclic OR Alicyclic Hydrocarbons

a) Aromatic Hydrocarbons:

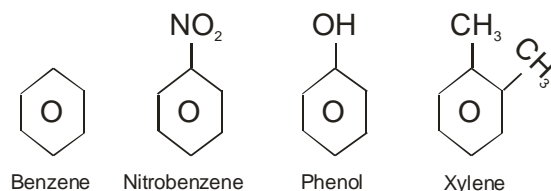
Those organic compounds (hydrocarbons) which contain one or more aromatic or benzene ring are known as aromatic hydrocarbons. Aromatic compounds are generally considered as derivatives of benzene.

**Aromatic or Benzene Ring:** The ring contains six carbon atoms bonded together by means of alternate double and single covalent bonds.

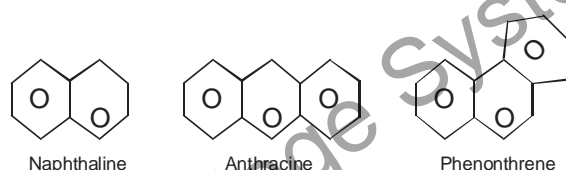
**Types of Aromatic Compounds:**

Aromatic compounds are of two types;

i) **Monocyclic Aromatic Compounds:** Those aromatic compounds which contain only one aromatic or benzene ring, are known as mono-cyclic aromatic compounds. E.g,



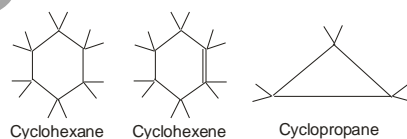
ii) **Polycyclic Aromatic Compounds:** Those aromatic compounds which contain more than one aromatic rings, are known as polycyclic aromatic compounds. E.g,



b) Non-Aromatic OR Alicyclic Hydrocarbons:

Those cyclic hydrocarbons, which do not have any aromatic or benzene ring are known as Alicyclic hydrocarbons.

e.g,



**Types:**

Alicyclic hydrocarbons are of two types;

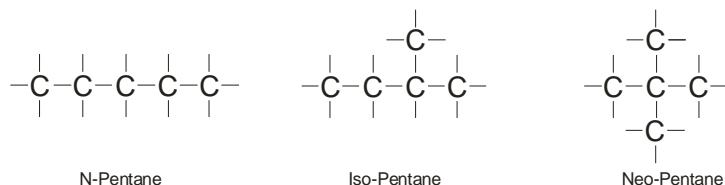
i) **Saturated Alicyclic Hydrocarbons:** Those alicyclic hydrocarbons in which the tetravalency of each carbon atom is fully satisfied i.e, each carbon has formed four single covalent bonds. The alicyclic saturated hydrocarbons are known as cycloalkanes. The general formula of cycloalkanes is  $\text{C}_n\text{H}_{2n}$ .

ii) **Alicyclic Unsaturated Hydrocarbons:** Those alicyclic hydrocarbons in which the tetravalency of each carbon is not fully satisfied i.e, there is at least one double or one triple covalent bond between any two carbon atoms are known as alicyclic unsaturated hydrocarbons. Those alicyclic unsaturated hydrocarbons which contain a double covalent bond between any two carbon atoms, are called "cycloalkenes". The general formula of cycloalkenes is  $\text{C}_n\text{H}_{2n-2}$ . Those alicyclic unsaturated hydrocarbons which contain a triple covalent bond between carbon atoms, are called as, "cycloalkynes". The general formula of cycloalkynes is  $\text{C}_n\text{H}_{2n-4}$ .

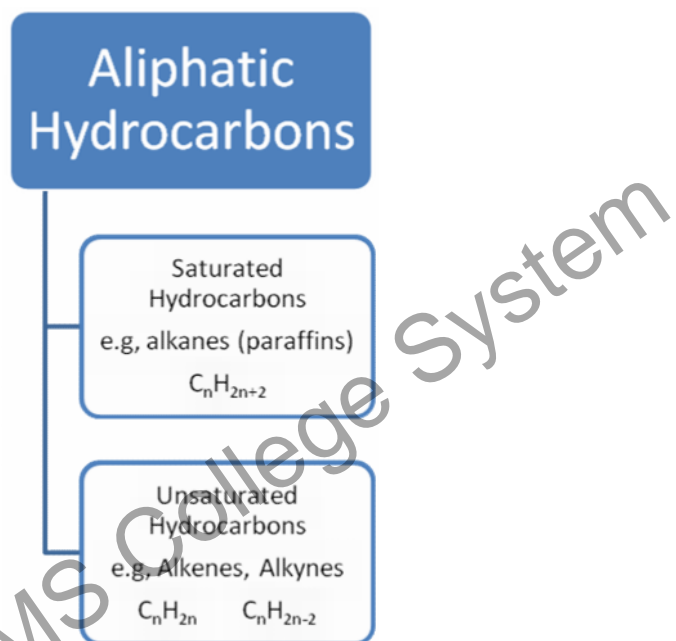
### 8.3 Introduction to Aliphatic Hydrocarbons:

Those hydrocarbons in which all the carbon atoms are bonded together in an open chain i.e, there is no ring or cycle, are known as aliphatic hydrocarbons.

e.g,



The classification of aliphatic hydrocarbons is as follows;



### 8.4 Chemistry of Alkanes:

Alkanes are the saturated aliphatic hydrocarbons in which the tetravalency of each carbon atom is fully satisfied i.e, each carbon atom has formed four single covalent bonds and there is no double or triple covalent bond between carbon atoms. The alkanes are also called as paraffin which means that alkanes show little tendency towards reactivity because of presence of all sigma covalent bonds which are very strong as compared to pi ( ) bonds. The general formula of alkanes is  $C_nH_{2n+2}$ , where "n" stands for the number of carbon atoms.

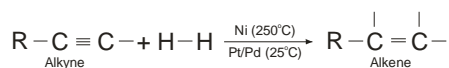
General Methods of Preparation of Alkanes:

Alkanes can be prepared by the following general methods;

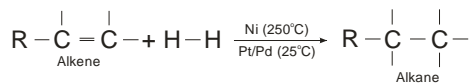
#### 1) By Hydrogenation of Unsaturated Hydrocarbons:

The addition of  $H_2$  gas into an alkyne or an alkene is known as hydrogenation of unsaturated hydrocarbons. When a mixture of an alkyne and  $H_2$  is passed over finely divided Ni catalyst (at 200 – 300°C) or Pt/Pd catalyst (at 25°C) first a hydrogen molecule adds into a double bond, thus producing an alkene. Then further  $H_2$  add into the double of alkene and produce an alkane as the final product. As alkanes have no pi ( ) bond, so further addition is not possible and the reaction stops at alkane.

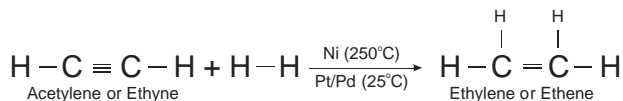
i.e,



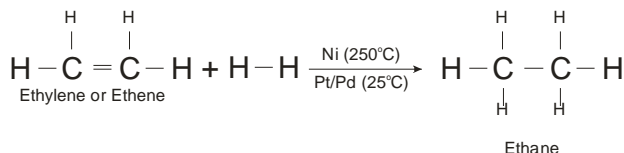
Then,



For example;



Then,



Note:

1) During Sabatier Senderens reaction Ni is mostly used as catalyst instead of Pt or Pd, although Ni needs heat. It is because of the fact that Ni is cheaper than Pt and Pd.

1) Methane cannot be prepared by Sabatier Senderens reaction because the alkyne or alkane series starts from C<sub>2</sub> not from C<sub>1</sub>.

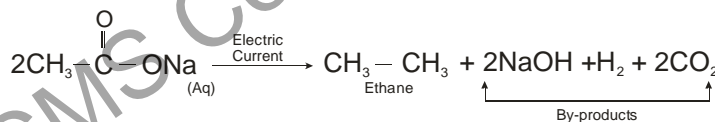
2) Electrolysis of Na/K Salt of a Monocarboxylic Acid:

Kolbe's Electrolytic Method:

When an electric current is passed through an aqueous solution of Na/K salt of a mono carboxylic acid, an alkane is produced, i.e.,



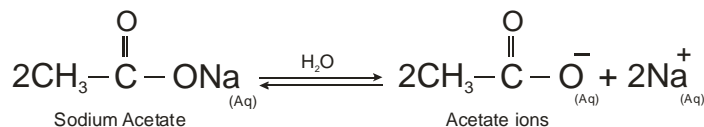
For example,



Mechanism:

The mechanism of the above reaction (Kolbe's Electrolytic Method) can be explained as;

Step 1: (Ionization): First of all the salt (CH<sub>3</sub>COONa) is dissolved to produce its aqueous solution, i.e.,

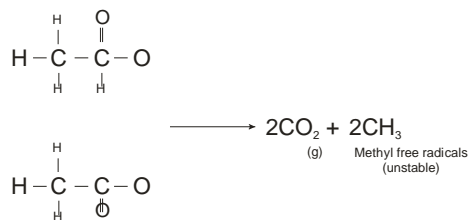


Step 2: (At anode (oxide half reaction): The acetate ions come to anode (positive electrode) where they lose their electron producing very unstable acetate free radicals, i.e.,

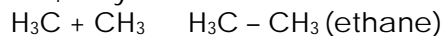


The acetate free radicals are very unstable, therefore they undergo the following change producing CO<sub>2</sub> molecules and methyl free radicals.

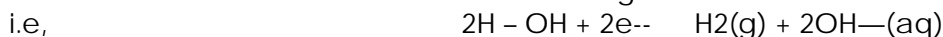




As methyl free radicals unstable thus, they combine and form ethane molecule.



Step 3: At cathode (reduction half reaction): As the reduction potential of  $\text{H}^+$  ions of  $\text{H}_2\text{O}$  is greater than  $\text{Na}^+$  ions, therefore,  $\text{H}^+$  ions of  $\text{H}_2\text{O}$  gain the electrons to form hydrogen atoms (H) which combine and form  $\text{H}_2$  molecules leaving  $\text{OH}^-$  ions free in solution.



Then finally the  $\text{Na}^+$  ions and  $\text{OH}^-$  ions combine and form  $\text{NaOH}$ .

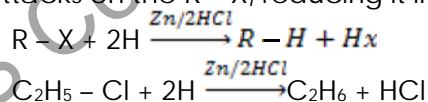


Note:

1. By Kolbe's Electrolytic methods we can prepare symmetrical alkanes only, symmetrically alkanes are those alkanes which contain even number of Carbon atoms. Thus alkanes containing odd number of carbon atoms cannot be prepared by Kolbe's electrolytic method. Thus alkanes like  $\text{CH}_4$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_5\text{H}_{12}$  etc cannot be prepared by this method.
2. The alkane produced by Kolbe's electrolytic method, contains double number of carbon atoms then the number of carbon atoms of the alkyl group (R) attached to the carboxyl ( $-\text{COOH}$ ) of the Na/K salt of the carboxylic acid.
3. Kolbe's electrolytic method has lost its attraction because of the production of large number of by-products.

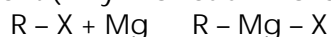
3) By Reduction of Alkyl Halides:

When an alkyl halide is reacted with Zn and HCl, the Zn and HCl react and produce nascent hydrogen (H) and  $\text{ZnCl}_2$ . The H, attacks on the  $\text{R}-\text{X}$ , reducing it into an alkane.



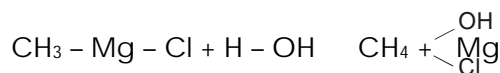
4) From Grignard Reagent:

In 1900, Victor Grignard synthesized a new organic compound by reacting an  $\text{R}-\text{X}$  with Mg, which is called as Grignard Reagent (Alkyl Magnesium halide).

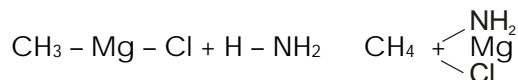


When a Grignard's reagent is reacted with some compound like  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  etc, an alkane is produced.

i) With  $\text{H}_2\text{O}$ :

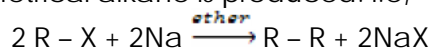


ii) With  $\text{NH}_3$ :

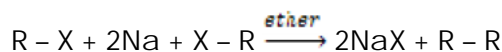


5) By Wurtz's Reaction:

When an alkyl halide ( $\text{R}-\text{X}$ ) is reacted with sodium metal (Na) in an ethereal solution i.e, in the presence of ether, a symmetrical alkane is produced. i.e,

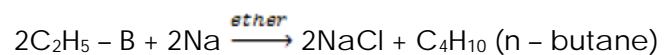


OR



A symmetrical alkane which is produced by joining of two similar alkyl groups.

For example:



This reaction was presented by Wurtz in 1885, therefore, it is known as Wurtz's Reaction.

Note:

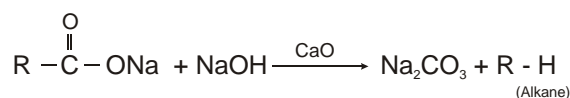
- 1) By Wurtz Reaction, a long chain alkane is produced from a small chain alkyl halide.
- 2) The alkane produced by Wurtz reaction, always contains an even number of carbon atoms.

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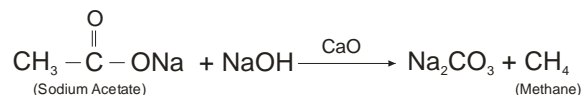
6) By Reaction of Na Salt of a Mono Carboxylic Acid With Soda Lime (NaOH + CaO):

When a sodium salt of a mono carboxylic acid is reacted with soda lime (NaOH + CaO), an alkane is produced.

i.e,



For Example:



Note:

The alkane produced by this method, contains the same number of carbon atoms as in the alkyl group bonded to the carboxylic group.

## GENERAL PROPERTIES OF ALKANES:

a) Physical Properties:

From Book

b) Chemical Properties:

As all the bonds present in alkanes are sigma covalent bonds (single covalent bonds), which are very strong, therefore, alkanes do not easily undergo reactions. That is why alkanes are also called "paraffines", where "para" means "little" and "ffine" means "tendency", i.e, alkanes show little tendency towards reactivity. However, in special conditions, alkanes undergo the following types of reactions:

I) Oxidation Reactions

II) Replacement or Substitution Reactions

III) Cracking or Pyrolysis Reactions

I) Oxidation Reaction:

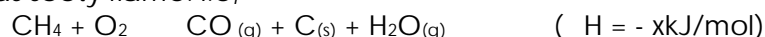
The reaction of alkanes with oxygen, are known as oxidation reactions of alkanes. Some important oxidation reactions of alkanes are;

a) Combustion: The process of burning of an alkane is known as combustion. When alkane burns in the presence of O<sub>2</sub>, it is converted into CO<sub>2</sub> or CO and H<sub>2</sub>O along with the production of heat. The combustion of an alkane may occur as;

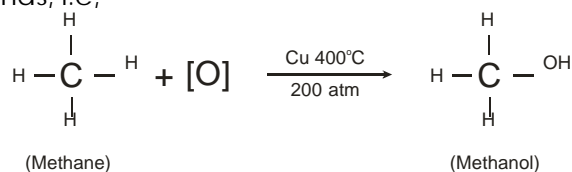
i) In excess of O<sub>2</sub>: When an alkane burns in excess of O<sub>2</sub>, complete oxidation of carbon takes place producing CO<sub>2</sub> & H<sub>2</sub>O and large amount of heat is produced. e.g,



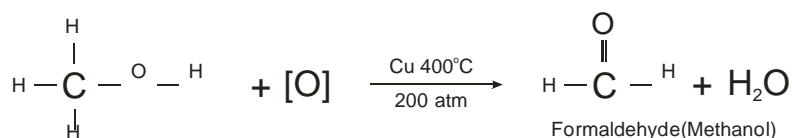
ii) In limited O<sub>2</sub>: When an alkane burns in limited supply of O<sub>2</sub>, then incomplete oxidation of carbon takes place producing CO and some carbon black (soot) and H<sub>2</sub>O. Here small amount of heat is produced. The carbon black causes smoke in such a flame and such a flame which contains smoke, is known as sooty flame. i.e,



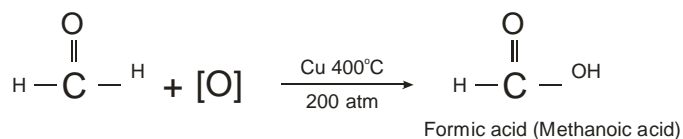
b) Catalytic Oxidation of Alkanes: When alkane (like CH<sub>4</sub>) is reacted with O<sub>2</sub> in the presence of Cu catalyst at 200 atmospheric pressure and 400°C, a chain reaction starts producing several important organic compounds, i.e,



Then,



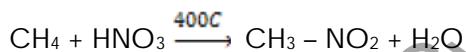
Then,



## II) Substitution OR Replacement Reaction:

The reaction of alkanes in which one or more of its H atoms are replaced by some other atom or group of atoms is called as replacement reactions of alkanes. Some important replacement reactions are as follows;

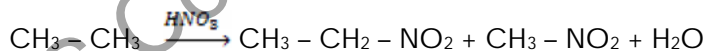
a) Nitration: The replacement of H of an alkane by a nitro group ( - NO<sub>2</sub>) is known as nitration of alkanes. When an alkane is mixed with excess of HNO<sub>3</sub> (Nitric Acid) in vapour phase and passed through narrow tubes at 400 – 450°C, a hydrogen of the alkane is replaced by the - NO<sub>2</sub> group of HNO<sub>3</sub> producing a nitro alkane. This process is also known as vapour phase nitration of alkanes.  
e.g,



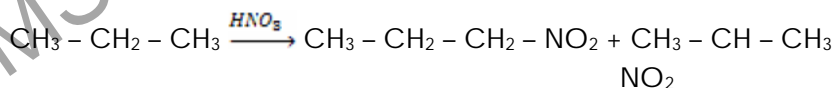
Note:

As nitration of alkanes occur at high temperature, therefore, sometimes (in case of higher alkanes), the C – C bond also breaks down and thus we get a mixture of different nitro alkanes. For example in case of ethane & propane, nitration occurs as;

i) Ethane:



ii) Propane:



Note:

During the nitration of CH<sub>4</sub>, only one H atom can be replaced by NO<sub>2</sub> group of HNO<sub>3</sub>.

b) Halogenation: The replacement of one or more H atoms of an alkane by halogens is known as halogenations of alkanes. For example Cl<sub>2</sub> reacts with CH<sub>4</sub> as follows;

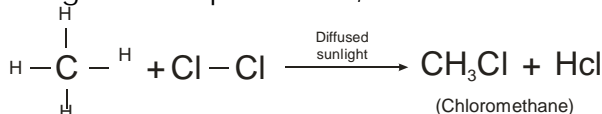
i) In dark: When CH<sub>4</sub> and Cl<sub>2</sub> are mixed together in diffused sunlight, no reaction takes place.

i.e,  $\text{CH}_4 + \text{Cl}_2 \xrightarrow{\text{dark}} \text{No products}$

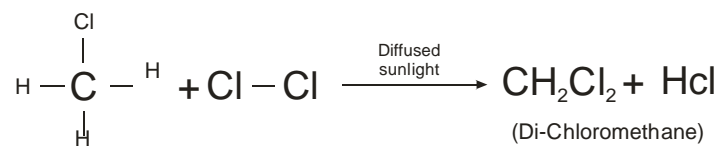
ii) In direct sunlight: When CH<sub>4</sub> and Cl<sub>2</sub> are reacted in direct sunlight, an explosive reaction takes place producing carbon black and HCl.

i.e,  $\text{CH}_4 + 2\text{Cl}_2 \xrightarrow{\text{direct sunlight}} \text{C}_{(\text{s})} + \text{HCl}$

iii) In diffused Sunlight: When CH<sub>4</sub> and Cl<sub>2</sub> are reacted in diffused sunlight, a chain reaction starts producing several important organic compounds. i.e,

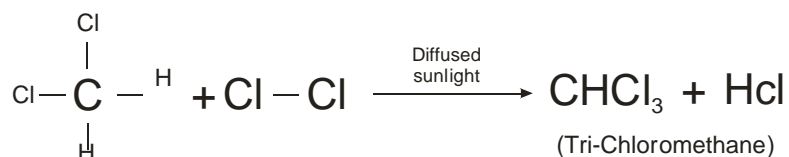


Then,

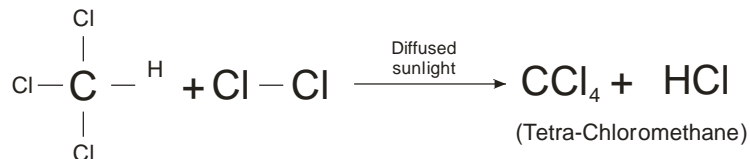


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Then,



Then,



Note:

Halogenation of alkanes follow a free radical mechanism which is explained as follows;

Free Radical Mechanism:

1) Initiation:

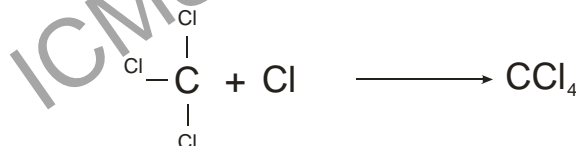


2) Propagation:



This step continues till all the H atoms are replaced by Cl atoms. The final step is

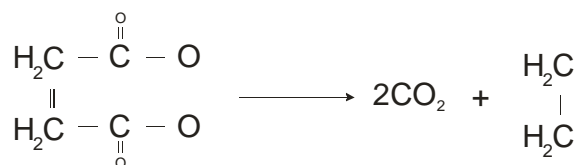
3) Termination:



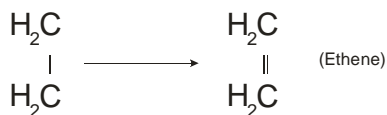
USES of ALKANES:

From book.





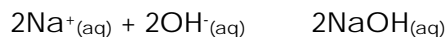
Then,



Step 3: At Cathode (RHR):

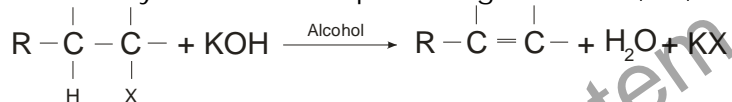


Then,

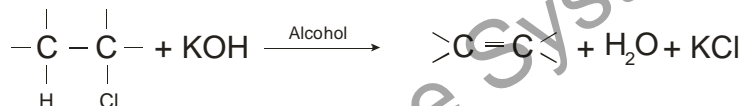


### 3) By Dehydro-halogenation of An Alkyl Halide:

The elimination of a X and H from the adjacent carbon atoms of an alkyl halide is known as dehydrohalogenation of that alkyl halide. When an alkyl halide is reacted with alcoholic KOH, dehydrohalogenation of the alkyl halide occurs producing an alkene, i.e.,

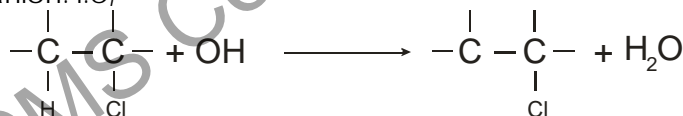


e.g.,

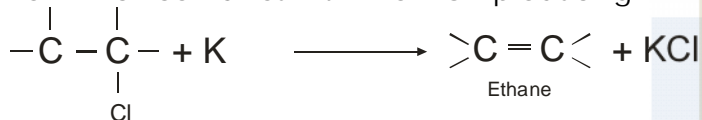


Mechanism:

Step 1: The OH<sup>-</sup> of KOH, attacks on a -H of the alkyl halide producing H<sub>2</sub>O and the alkyl halide is converted into a carbanion. i.e.,



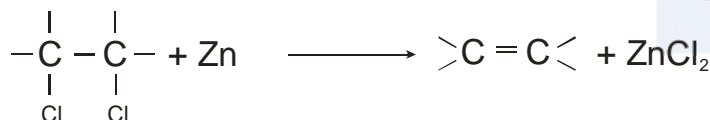
Step 2: The negatively charged C of the carbanion producing a double bond. As a result the carbon loses the Cl<sup>-</sup> ion which combines with K<sup>+</sup> of KOH producing KCl. i.e.,



### 4) Dehalogenation of Vicinal Dihalide:

When a vicinal dihalide is reacted with Zinc dust, the halogens are eliminated by Zn producing an alkane.

e.g.,



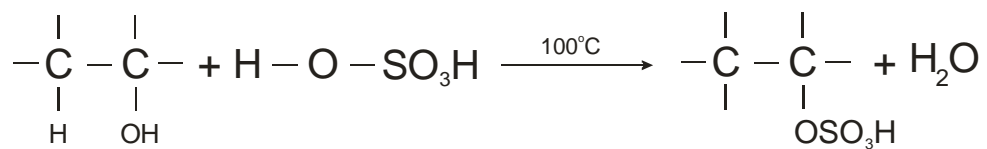
### 5) By Dehydration of Alcohols:

When alcohol is reacted with H<sub>2</sub>SO<sub>4</sub> (dehydrating agent), we get an alkyl hydrogen Sulphate e.g.,

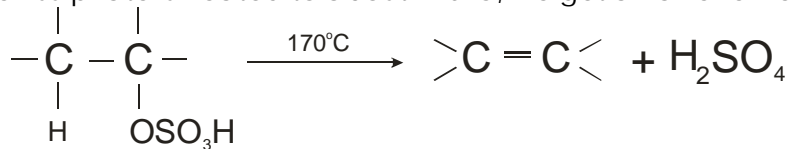
**Vicinal Dihalide:**  
The organic compounds containing two halogen atom bonded to two adjacent carbon atom, they are shortly called as Vicinal Dihalides.

**Gem dihalides:**  
The org. compounds containing two halogen atoms





When ethyl hydrogen sulphate is heated to about  $170^\circ\text{C}$ , we get an alkene. i.e.,



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## PROPERTIES OF ALKENES

### A) Physical Properties:

From book

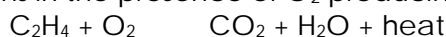
### B) Chemical Properties:

Due to the presence of pi ( ) bond, alkenes are the most reactive hydrocarbons. Alkenes undergo the following types of reactions;

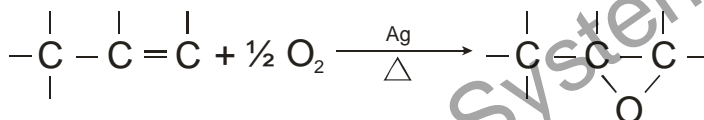
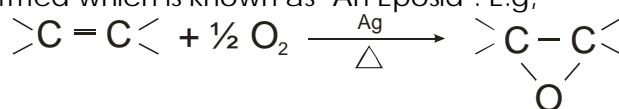
#### 1) Oxidation Reactions:

The reaction of alkene with oxygen are known as oxidation reactions of alkenes. The oxidation reactions of alkenes are;

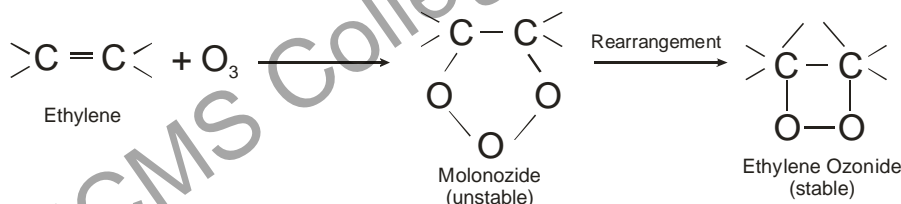
i) Combustion: Alkene burns in the presence of  $O_2$  producing  $CO_2$ ,  $H_2O$  and heat. i.e,



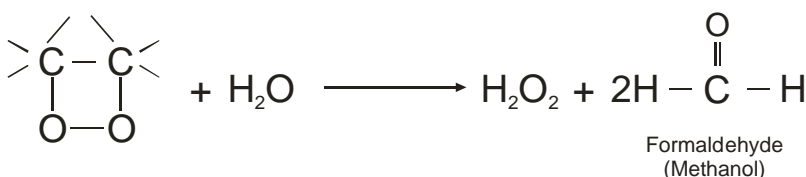
ii) Catalytic Oxidation: When an alkene is reacted with oxygen in the presence of Ag catalyst, a cyclic compound is formed which is known as 'An Eposid'. E.g,



iii) Ozonolysis: Reaction of an alkene with ozone ( $O_3$ ) is known as ozonolysis of alkenes. When an alkene is reacted with  $O_3$ , we get an unstable cyclic compound known as molonozide which rearranges and converts into a stable cyclic compound known as ozonide. E.g,



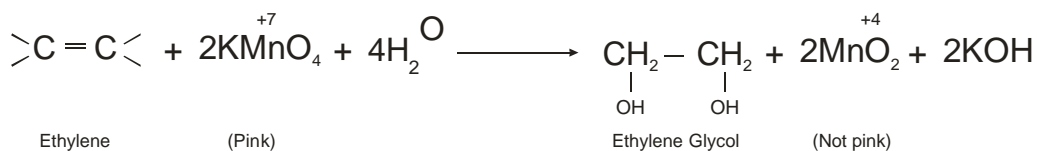
When ethylene ozonide is reacted with  $H_2O$  in the presence of Zn, we get carboxyl compound (aldehyde or ketones) and  $H_2O_2$ . Finally  $H_2O_2$  reacts with Zn producing ZnO. i.e,



Then,



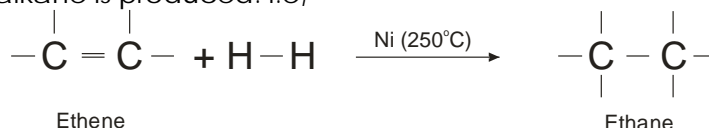
iv) Hydroxylation of Alkenes (Baeyer's Test): The addition of hydroxyl groups to the double bonded carbon atoms of an alkene is known as hydroxylation of alkene. During hydroxylation, two OH groups get attached with two adjacent C atoms producing a molecule which is generally called a 'Glycol'. When alkene is passed through a cold alkene solution of  $KMnO_4$ , hydroxylation of alkene takes place during which Mn is reduced from +7 to +4 oxidation state and thus the pink color of solution disappears. This proves the presence of alkene. This process is called as, Baeyer's Test for identification of alkenes. i.e,



## 2) Addition Reaction:

Due to the presence of a pi bond in alkenes, they are very reactive and always undergo addition reactions instead of substitution reactions. During addition reactions, two atoms or group of atoms, get attached to those two adjacent carbon atoms which carry double bond amongst them and thus the pi bond is broken down, as a result of which two new sigma bonds are formed. Some important addition reactions of alkenes are;

i) Hydrogenation: The addition of  $\text{H}_2$  into the double bond of an alkene is known as hydrogenation of alkene. For example when  $\text{H}_2$  is reacted with ethene in the presence of Ni catalyst at  $250^\circ\text{C}$ , an alkane is produced. i.e,



ii) Halogenation: The addition of a molecule of a halogen ( $\text{X}_2$ ) to the = bonded carbon atoms of an alkene is known as halogenations of alkenes. The addition of  $\text{Cl}_2$  (chlorination) and  $\text{Br}_2$  (bromination) is readily recommended.

Fluorination and iodination are not recommended for addition to an alkene.

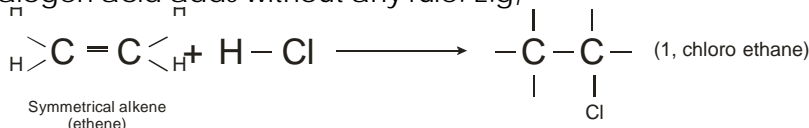
It is important to note that when a halogen adds into an alkene, a vicinal dihalide is formed, which is shortly called as vic-dihalide. (A vicinal dihalide is that in which two similar halogen atoms are attached to two adjacent carbon atoms). E.g,



iii) Addition of Halogen Acid: When a halogen acid adds to an alkene, an alkyl halide is produced. the order of addition of halogen acids to alkenes is as follows;



If the alkene, to which a halogen acid (a polar molecule) is added, is a symmetrical alkene (an alkane in which same number of hydrogen atoms is attached to the double bonded carbon atoms), then the halogen acid adds without any rule. E.g,



If the halogen acid is added to an unsymmetrical alkene (in which different number of carbon atoms is attached to the double bonded carbon atoms), then the addition occurs according to "Markonikov's Rule", which states that "when a polar molecule adds into an unsymmetrical alkene, then the negative part of the polar molecule will attach to that carbon atom which carries the least number of H - atoms".

e.g,

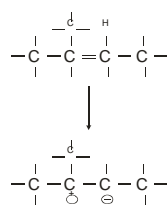


Note:

The reason for Markonikov's rule is based on the stability of carbonium ion, produced from alkane. The order of stability of carbonium ion is;

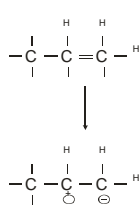
Tertiary Carbonium Ion > Secondary Carbonium Ion > Primary Carbonium Ion

e.g,



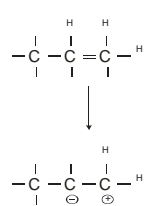
Tertiary Carbon-cation

(I)



Secondary Carbon-cation

(II)



Primary Carbon-cation

(III)

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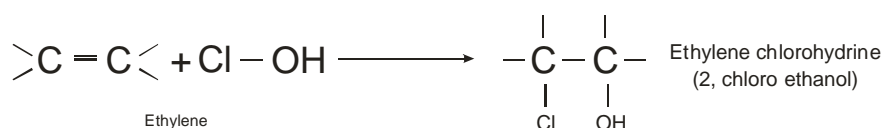
Now if tertiary, primary and secondary carbocations are available for the attack of a nucleophile (nucleus loving substance) i.e, negative part of polar compound, then this nucleophile will preferably attack on positive carbon of tertiary carbocation (because of its most stability) instead of positive C of secondary or primary carbocation. Similarly if only secondary and primary carbocation are available for the attack of a nucleophile, then it will attack on the positive carbon of secondary carbon cation instead of primary carbocation because of greater stability of secondary carbocation then primary carbocation.

Now as the positive carbon of tertiary carbocation carries number "H" that of secondary carbocation carries one "H" and that of primary carbocation carries two "H" atoms, therefore, Markonikov stated that the negative part (nucleophile) of a polar molecule will attack on that carbon of the double bond which carries smaller number of "H" atoms.

iv) Addition of Hypohalous Acids (X – OH): When a hypohalous acid is added into an alkene, a new organic compound is obtained, which is called as "Halohydrine".

(Halohydrine are those organic compounds which contain a halogen (X) and a hydroxyl group (OH) at their adjacent carbon atoms).

e.g,



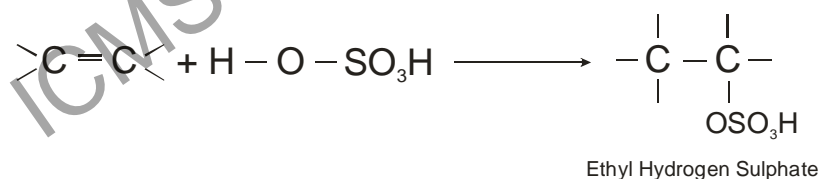
If a hypohalous acid is added to an unsymmetrical alkene, then the addition is according to Markonikov's rule.

e.g,

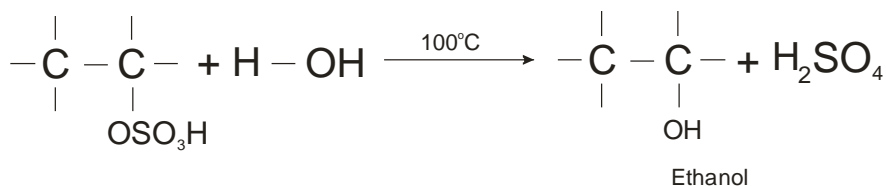


v) Addition of Sulphuric Acid: When an alkene is reacted with H<sub>2</sub>SO<sub>4</sub>, we get an organic compound known as alkyl hydrogen sulphate. When alkyl hydrogen sulphate is reacted with H<sub>2</sub>O at 100°C, we get an alcohol.

e.g,

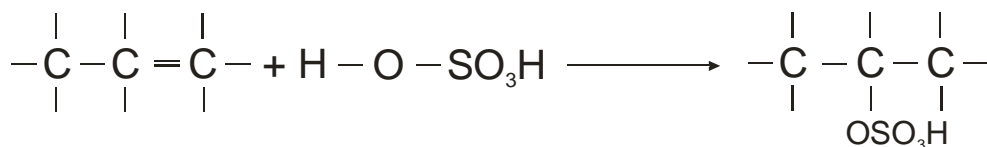


Then,



If a symmetrical alkene is present then addition of H<sub>2</sub>SO<sub>4</sub> take place according to Markonikov's Rule.

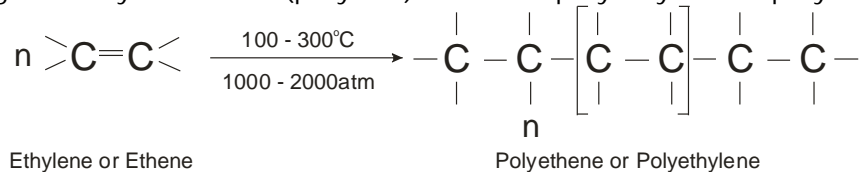
i.e,



### 3) Polymerization Reactions:

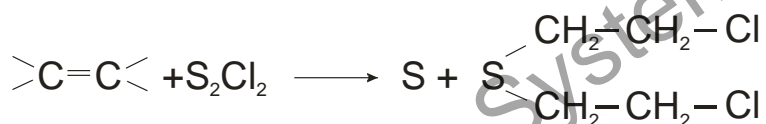
Due to the presence of pi bonds, alkene molecules combine together producing long chain hydrocarbons (polymers).

e.g, when n molecule of ethylene ( $\text{CH}_2 = \text{CH}_2$ ) are heated together at high temperature ( $100 - 300^\circ\text{C}$ ) and high pressure ( $1000 - 2000 \text{ atm}$ ) in the presence of catalyst, they combine together producing a long chain hydrocarbon (polymer) known as polyethylene or polyethene. i.e,



### USES OF ALKENES:

1) Mustard Gas Formation: When ethene is reacted with sulphurmonochloride ( $\text{S}_2\text{Cl}_2$ ) a poisonous gas known as mustard gas or , - dichloro ethyle sulphide is produced. Thus gas was used in World War I. i.e,



Note:

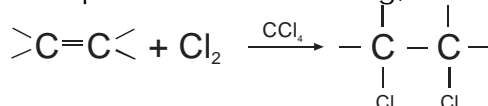
See other uses from book.

### TESTS FOR IDENTIFICATION OF ALKENES:

Following tests can be used for identification of alkenes.

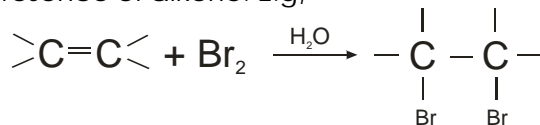
#### 1) Dutch Liquid Test:

When an alkene is passed through chlorinated  $\text{CCl}_4$ ,  $\text{Cl}_2$  adds into the alkene producing a vicinal dichloride which is oily and makes the surface of solution oily which looks like a dutch. The appearance of oily layer proves the presence of alkene. E.g,



#### 2) Bromine Water Test:

When  $\text{Br}_2$  gas is dissolved in water, the solution acquires a brown color due to the presence of  $\text{Br}_2$  gas. This is known as brown water test. When an alkene is passed through bromine water, all the  $\text{Br}_2$  adds into alkene and thus due the disappearance of  $\text{Br}_2$  from brown water, the brown color disappears. This proves the presence of alkene. E.g,



#### 3) Baeyer's Test:

Already discussed.

## CHEMISTRY OF ALKYNES

The unsaturated hydrocarbons which contain a triple covalent bond between carbon atoms are known as alkynes.

Alkynes are also called "Acetylene". It is because of the fact that the first member of alkyne series is acetylene ( $C_2H_2$ ) and all members of the series follow acetylene. The general formula of alkynes is " $C_nH_{2n-2}$ ". The unsaturated hydrocarbons which contain more than one triple bond are called "Diyne", "Triyne" and so on.

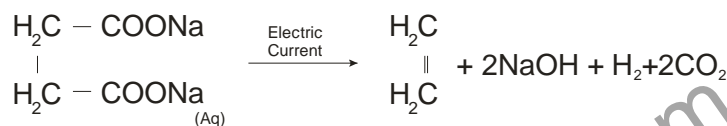
### Methods of Preparation

Some important methods of preparation of alkynes are as follows;

#### 1) Electrolysis of Na/K Salt of Unsaturated Dicarboxylic Acid (Kolbe's Electrolytic Method):

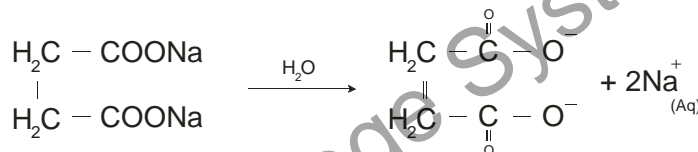
When an electric current is passed through an aqueous solution of Na/K salt of unsaturated dicarboxylic acid (like sodium Maleate), an alkyne is produced.

e.g,

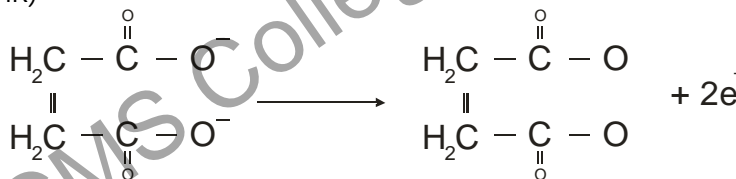


Mechanism:

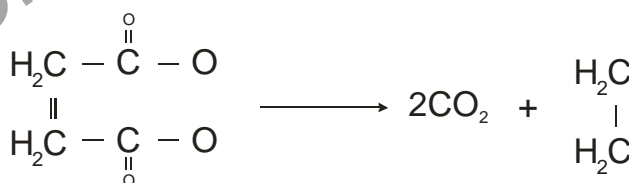
Step 1:



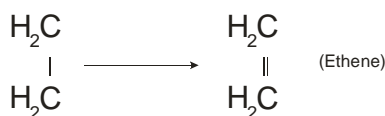
Step 2: At Anode (OHR)



Then,



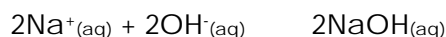
Then,



Step 3: At Cathode (RHR):

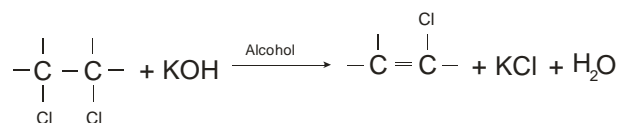


Then,

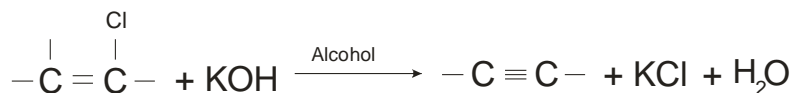


#### 2) By Dehydro-Halogenation of Vicinal Dihaloalkane:

When a vicinal dihalide is reacted with alcoholic KOH, an alkyne is obtained. Here elimination reaction takes place which completes in two steps. In each step a hydrogen and a halogen are eliminated from the adjacent carbon atoms. e.g,



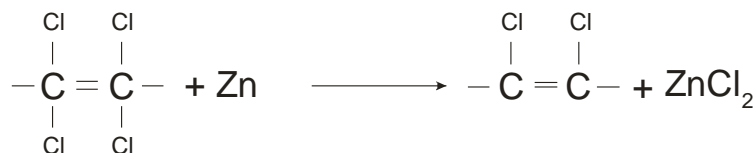
Then,



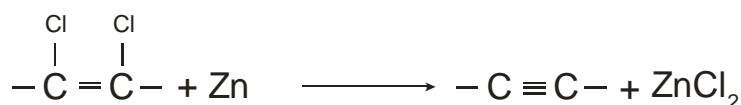
### 3) By Dehalogenation of Tetrahaloalkanes:

When a tetrahalo-alkane is reacted with Zn, an alkyne is produced. The reaction completes in two steps.

e.g,



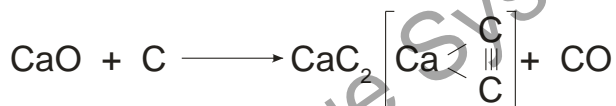
Then,



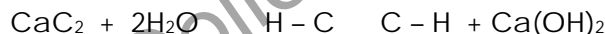
### 4) From Calcium Carbide ( $\text{CaC}_2$ ):

When lime ( $\text{CaO}$ ) is highly heated coke © in an electric furnace, calcium carbide is obtained.

i.e,



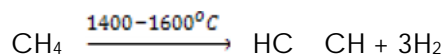
When this  $\text{CaC}_2$  is reacted with water, ethylene gas is obtained.



This method was introduced by an American scientist named, Wilson. In his method acetylene gas is produced from cheap materials therefore, this method is used as commercial method of preparation of acetylene.

### 5) From Methane:

Acetylene can be obtained commercially by heating natural gas ( $\text{CH}_4$ ) at high temperature. i.e,



## PROPERTIES OF ALKYNES:

### A) Physical Properties:

See from book

### B) Chemical Properties:

Alkynes undergo the following types of reactions.

- 1) Oxidation Reactions
- 2) Addition Reactions
- 3) Polymerization Reactions
- 4) Acidic Behaviour of Terminal Alkynes

#### 1) Oxidation Reactions:



Combustion: When alkynes burn in the presence of  $O_2$ , combustion occurs producing  $CO_2$  and  $H_2O$ .

e.g, when acetylene is reacted with  $O_2$  combustion takes place producing so much heat that the temperature reaches to about  $2800^\circ C$ . Therefore oxyacetylene flame is used for welding purposes.

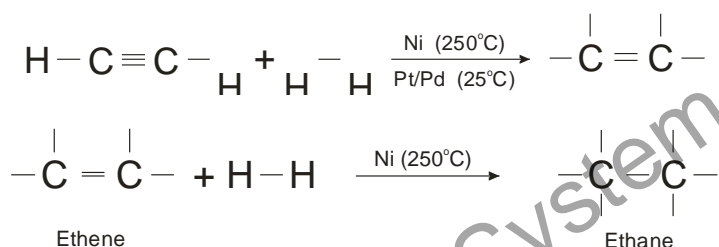
i.e,  $2H-C \equiv C-H + 5O_2 \rightarrow 4CO_2 + 2H_2O$   $\Delta H = -311 \text{ kcal/mol}$ .  
Combustion of acetylene produces high flame temperature than ethane ( $C_2H_6$ ) and ethene ( $C_2H_4$ ).

## 2) Addition Reactions:

Due to the presence of pi bonds, alkynes undergo addition reactions. Some important addition reactions of alkynes are;

### i) Hydrogenation (Sabatier – Sendren's Reaction):

When an alkyne is reacted with  $H_2$  in the presence of Ni catalyst (at  $250^\circ C$ ) or Pt/Pd catalyst ( $25^\circ C$ ), an alkene is produced which undergoes further hydrogenation and producing alkane as the final product. E.g,

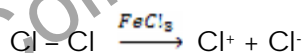


Then,

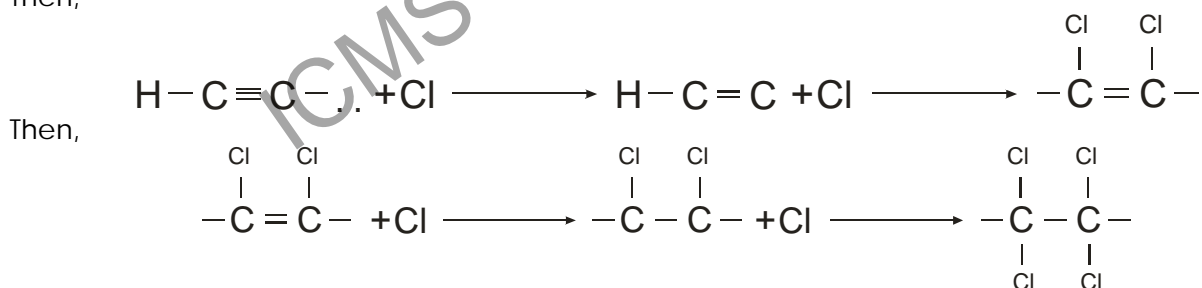
### ii) Halogenation:

When a halogen is reacted with an alkyne, a tetrahaloalkane is produced. This reaction completes in two steps. Here  $FeX_3$  is used as catalyst which turns the  $X_2$  polarized.

e.g,



Then,



Then,

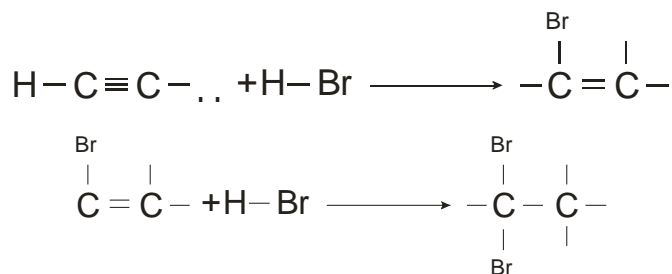
Note:

This reaction can be stopped at dihaloalkane stage by using proper conditions.

### iii) Addition of Hydrogen Halides:

When an alkyne is reacted with a halogen acid (HX), we get a Gem-dihalide. This reaction completes in two steps. The Gem-dihalide is formed according to Markovnikov's rule. Thus vicinal dihalide cannot be produced here.

e.g,

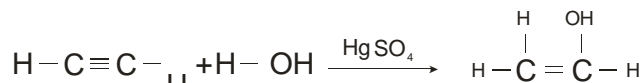


Then,

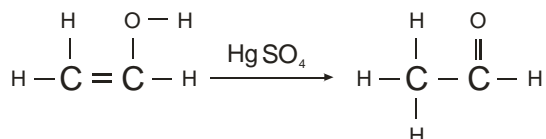
## iv) Addition of Water:

When an alkyne (like ethyne) is reacted with water in the presence of mercuric sulphate ( $\text{HgSO}_4$ ) and an unstable unsaturated alcohol is obtained which undergoes rearrangement producing a carboxyl compound.

e.g.,



Then,



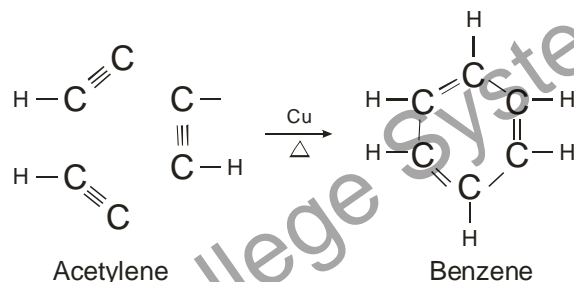
### 3) Polymerization Reactions:

Due to the presence of pi bonds, alkynes have got the ability of polymerization reactions. Alkynes undergo different polymerization reactions under different conditions producing different products. For example;

i) Formation of Benzene:

When acetylene molecules are passed through copper tube at high temperature, they undergo polymerization reaction producing benzene.

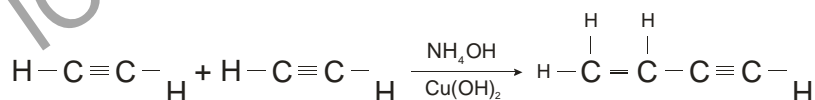
i.e.,



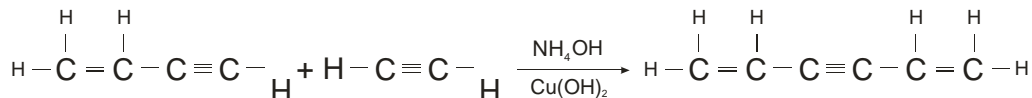
## ii) Formation of Divinyl Acetylene:

When acetylene molecules are reacted together in the presence of  $\text{NH}_4\text{OH}$  and  $\text{Cu}(\text{OH})_2$ , they undergo polymerization, producing vinyl acetylene which undergoes further polymerization producing divinyl acetylene as the final product.

i.e.,



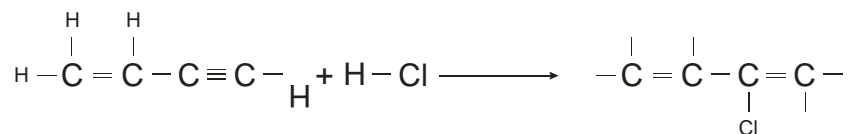
Then,



Note:

If we react vinylacetylene, we get a new organic compound known as Chloroprene.

i.e.,



When chloroprene undergoes polymerization, a polymer is obtained which is known as neoprene.

i.e.,

n Chloroprene (Monomer)

neoprene (polymer)

#### 4) Acidic Behaviour of Terminal Alkynes:

Those alkynes in which the triple bond is present at either end of the chain are known as terminal alkynes.

e.g.,  $\text{H}-\text{C}\equiv\text{C}-\text{H}$ ,  $-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H}$ , etc.

Those carbon atoms of an alkyne which have triple bond between them, undergo SP hybridization. In SP hybrid orbitals, the S character is maximum (i.e., 50%), therefore, the SP hybrid orbitals are very closer to nucleus of carbon atom and the thus SP hybridized carbon has got maximum ability to attract the shared pair of electrons in the SP hybrid orbitals i.e., SP hybrid orbitals have maximum electronegativity as compared to  $\text{SP}^2$  &  $\text{SP}^3$  hybridized carbon atoms. Now if the triple bond is terminal, then there will be a C – H bond. Due to high E.N of SP hybridized carbon, this C – H becomes polar i.e.,  $\text{C}^{\delta-}-\text{H}^{\delta+}$ . Due to this polarity, terminal alkynes have got the ability of producing hydrogen ion ( $\text{H}^+$ ) in aqueous solution and this is called as acidic behavior of terminal alkynes.

The acidic behavior of terminal alkynes can be used as a test for identification of terminal alkynes.

Test: When terminal alkyne (like acetylene) is passed through a solution containing metal ions, a metal acetylide is produced because the  $\text{H}^+$  ions of acetylene release into solution while metal ions ( $\text{M}^+$ ) get attached with "SP" hybridized carbon atoms of acetylene producing a metal acetylide. The metal acetylides are water insoluble and hence appear in the form of precipitate (ppt) of different colors depending upon the metal. The appearance of ppt proves the presence of terminal triple bond in an alkyne.

For example:

- 1) When acetylene is passed through an aqueous solution of  $\text{Cu}_2\text{Cl}_2$  and  $\text{NH}_4\text{OH}$ , a red ppt of copper acetylide ( $\text{Cu}-\text{C}\equiv\text{C}-\text{Cu}$ ) is produced.
- 2) When acetylene is passed through ammoniacal solution of silver nitrate ( $\text{AgNO}_3$ ), a white ppt of silver acetylide is produced.

Note:

Metal acetylides are explosive and are reconverted to a acetylene (or some other terminal alkynes) by reacting it with a strong acid like  $\text{H}_2\text{SO}_4$ .

The formation of ppt of metal acetylids is used as test for identification of terminal alkynes.

## USES OF ALKYNES:

See that from book.

## Comparison of Reactivity of Alkanes, Alkenes & Alkynes:

The general order of reactivity of alkanes, alkenes and alkynes is as follows;



The lowest reactivity of alkanes is because of the fact that all bonds in alkanes are sigma covalent bond and they have no pi bonds. As sigma bond is very strong, hence very stable, therefore, alkanes are less reactive as compared to alkenes and alkynes because both alkenes and alkynes contain pi bonds. Due to the presence of pi bonds alkenes and alkynes are very reactive hydrocarbons.

Alkenes contain one pi bond and alkynes contain two pi bonds but alkenes are more reactive than alkynes. It is because of the fact that the pi bond length of alkenes is greater than the pi bond length of alkynes. Bonds with smaller bond length are more stable and stronger than bonds with lower bond length. Bond order (number of covalent bonds between two bonded atoms) is one of the factors which controls the bond length and hence bond energy or stability. Greater the number of covalent bonds formed between two covalently bonded atoms, smaller will be the bond length and stronger and stable will be the bond.

As the bond order of alkenes is two and that of alkynes is three, therefore, the bond length of the triple covalent bond of alkynes is shorter than the bond length of the double covalent bond of

alkenes. That is why, we can say that pi bond of alkenes is weaker than the pi bond of alkynes and that is the reason that alkenes are more reactive than alkynes.

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## AROMATIC HYDROCARBONS

### Introduction:

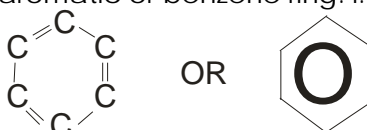
"Benzene and all those compounds which are structurally related to benzene, are known as aromatic hydrocarbons".

OR

"All those compounds which contain one or more than one aromatic ring, are known as aromatic compounds".

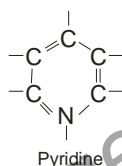
### Aromatic or Benzene Ring:

A ring which contains six carbon atoms bonded together by means of alternate double and single covalent bonds, is known as aromatic or benzene ring. i.e,



It is important to note that there are some aromatic rings which include one or more than one atom, other than carbon. Then such a ring may be called as Aromatic ring but not as benzene ring. However, such a molecule is an aromatic molecule but not an aromatic hydrocarbon.

e.g,



Broadly speaking, to decide whether a ring is an aromatic ring or not an aromatic ring, we use a rule which is called as "Huckle Rule". So to check the aromaticity of a ring we apply Huckle rule upon it and then decide whether the given ring is aromatic or not.

### Classification of Aromatic Hydrocarbons:

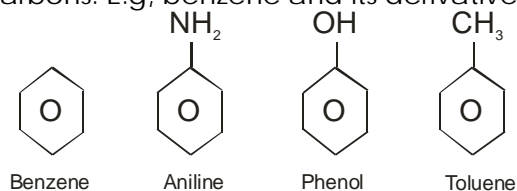
Based on the number of benzene rings, present in an aromatic hydrocarbon they are classified into two major groups.

- 1) Monocyclic Aromatic Hydrocarbons &
- 2) Polycyclic Aromatic Hydrocarbons

They are explained along with examples as follows:

#### 1) Monocyclic Aromatic Hydrocarbons:

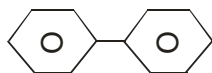
The aromatic hydrocarbons which contains only one benzene ring, per molecule, are known as Monocyclic Aromatic Hydrocarbons. E.g, benzene and its derivatives like;



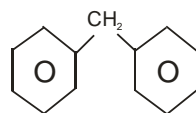
#### 2) Polycyclic Aromatic Hydrocarbons (Arenes):

Those aromatic hydrocarbons which contain more than one benzene ring, are known as Polycyclic Aromatic Hydrocarbons. They, further, are of two types. i.e, Those in which the benzene rings are not fused and are isolated,

e.g,

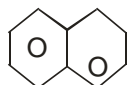


Biphenyl

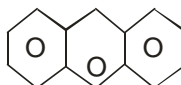


Biphenyl methane

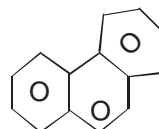
Those in which the benzene rings are fused together, e.g,



Naphthalene




Anthracene



Phenanthrene

## BENZENE

### Introduction:

Discovered By :	Michael Faraday
Isolated By:	Hoffmann
Molecular Formula:	C <sub>6</sub> H <sub>6</sub>
Structural Formula:	
Geometry:	Coplanar
Hybridization:	SP <sup>2</sup>
Bond Angle:	120°
Special Features:	i) Resonance      ii) Electrophilic Substitution Reaction

### Structure of Benzene:

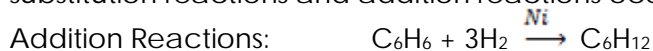
The empirical formula of benzene is determined as "CH". The molecular mass of benzene, determined by vapour density method is 78.108. Thus the molecular formula of benzene comes out to be "C<sub>6</sub>H<sub>6</sub>". Now it was a big problem to explain the structure of benzene. Different attempts have been made to explain the structure of benzene.

### Straight Chain Structure:

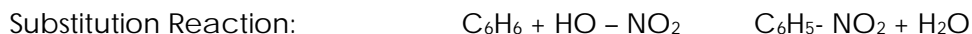
Two possible straight chain formulas were suggested for benzene which are;

- 1) HC = C - CH<sub>2</sub> - CH<sub>2</sub> - C = CH (1, 5 - Hexadiyne)
- 2) H<sub>2</sub>C = CH - C = C - CH = CH<sub>2</sub> (Hexa - 1, 5 - Diene - 3 - yne)

The above mentioned structures of benzene show that benzene should be highly unsaturated and must always undergo "addition reactions" like alkenes. And it should never undergo substitution or replacement reactions. But it was clearly seen that benzene mostly prefers electrophilic substitution reactions and addition reactions occur rarely in benzene, e.g,



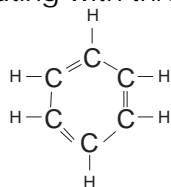
The above reaction (addition reaction) of benzene occurs much slower than that of an alkene.



Benzene shows greater affinity for substitution reactions rather than for addition reactions. But unsaturated hydrocarbons show greatest affinity for addition reactions and no affinity for substitution reactions. Therefore, it was concluded that the above mentioned structure of benzene are not possible.

### Kekule Structure:

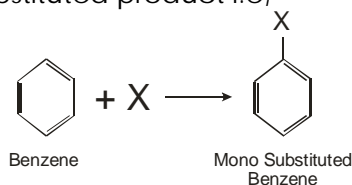
In 1865, a German Chemist, Kekule proposed a cyclic regular hexagonal structure for benzene, which contains three double bonds alternating with three single bonds. i.e,



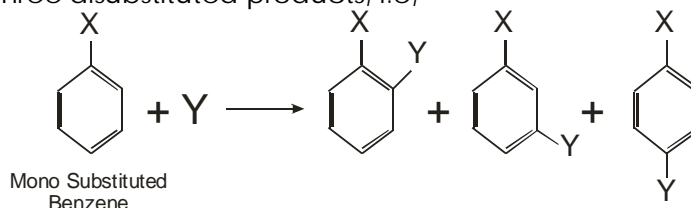
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Kekule supported his theory by the following arguments;

1) Benzene gives only one mono substituted product i.e.,

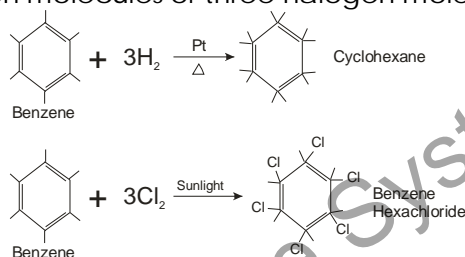


2) Benzene gives only three disubstituted products, i.e.,



The above two arguments confirm the regular hexagonal cyclic structure for benzene.

3) Benzene adds three hydrogen molecules or three halogen molecules. i.e.,



The above reactions confirm the presence of three double bonds in benzene.

X – Ray Studies of Structure of Benzene:

The x – rays studies of benzene have confirmed the hexagonal structure of benzene. These studies confirm that all carbon and hydrogen atoms of benzene are in same plane. All bond angles are of 120°. X – ray analysis of benzene has shown that all the C – C bonds have same length and same energy. The C – C bond length has been found out to 1.397°A and that of C – H bonds is 1.09°A.

Modern Concept about the Structure of Benzene by MOT:

According to Molecular Orbital Concept, in benzene, each carbon undergoes SP<sup>2</sup> hybridization, thus each carbon of benzene has three SP<sup>2</sup> hybrid orbitals with coplanar geometry and an angle of 120°. Similarly each carbon has one unhybrid half filled "P" orbital which lies perpendicular to the plane of hybrid orbitals. Benzene also contains six H – atoms such that each hydrogen atom has 1s half filled orbitals. Now each carbon gets, its one of the three SP<sup>2</sup> hybrid orbitals, overlapped with the 1s half filled orbital, benzene molecule has six C – H sigma bonds. On the other hand each C atoms overlaps the remaining two SP<sup>2</sup> hybrid orbital with the SP<sup>2</sup> hybrid orbital of the two neighbouring carbon atoms producing sigma bonds. Thus benzene molecule has 6 C – C sigma bonds. As the SP<sup>2</sup> hybrid orbital lie in same plane, therefore, benzene forms a cycle of C atoms attached with H atoms, all in same plane.

As each carbon has one half filled unhybrid "P" orbital which lies perpendicular to the plane of sigma bonds. These unhybrid "P" orbital undergo a sidewise overlap with each other to form three pi bonds. The six electrons of these three pi bonds form continuous circular sheath above and below the regular hexagonal planar ring of carbon atoms. Angle between any three adjacent carbon atoms is 120° (i.e., C – C – C = 120°). From x – rays analysis of benzene, it is confirmed that all C – C bond length of benzene are same. It is because of the resonance phenomenon which appears due to the process of delocalization of pi electrons upon benzene ring.

Stability of Benzene:



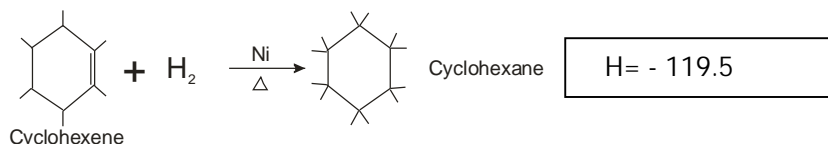
Although benzene has three pi bonds and thus should be highly unsaturated and hence highly reactive, but actually it has been come to know that benzene shows much more less reactivity than benzene and rarely undergoes addition reactions. This behavior of benzene is known as the stability of benzene. The stability of benzene shows that benzene is not a common unsaturated hydrocarbon like alkenes.

Actually the pi electrons of benzene are not fixed or localized between any two particular carbon atoms like that of alkenes, therefore, cannot be easily attacked by an electrophile. This phenomenon or process in which the pi electrons of a ring or open chain are not fixed between any two carbon atoms, is known as "Delocalization of pi electrons", which gives rise to various resonance structures of benzene thus making it stable (less reactive).

Stability of benzene can be shown by the following example.

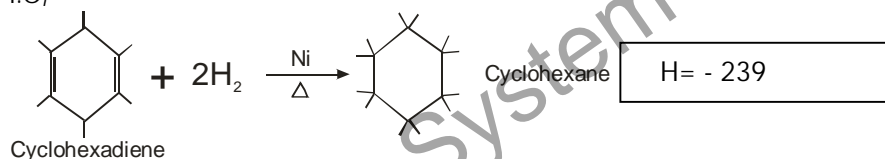
When we add one mole of  $H_2$  in one of cyclohexene, hydrogenation of cyclohexene occurs and 119.5 kJ/mole of heat is evolved because the reaction is exothermic.

i.e.,

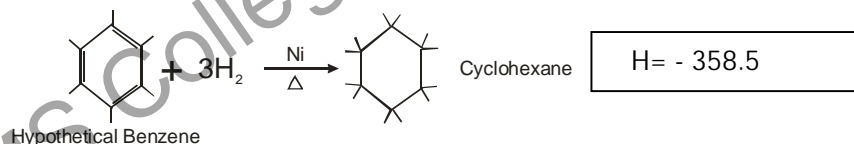


Similarly when we add two moles of  $H_2$  in one mole of cyclohexadiene then the amount of heat evolved is,

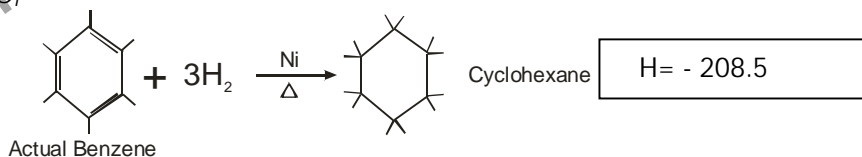
- 119.5 x 2 = - 239 kJ/mole. i.e.,



Now if we consider benzene as much reactive as alkene, then hypothetically benzene (hypothetical benzene) must release - 119.5 x 3 = - 358.5 kJ/mole of heat when it adds three moles of  $H_2$  in it. i.e.,



But whenever hydrogenation of benzene occurs, then the heat evolved is always 208.5 kJ/mole, rather than 358.5 kJ/mole. i.e.,



Thus it is proved that actual benzene is stable than hypothetical benzene (alkene) by an amount of energy which is

$$- 358.5 - (-208.5) = - 150 \text{ kJ/mole}$$

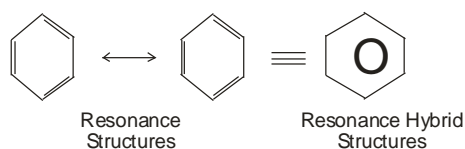
This energy by which benzene is stable (less reactive) than alkenes, is known as "stabilization energy" or "resonance energy". The stability of benzene is due to the phenomenon of resonance which appears as a result of delocalization of pi electrons upon benzene ring.

## RESONANCE:

The appearance of a compound in more than one possible structures, such that these structures differs only in the position of pi electrons is known as Resonance. All the possible structures of a molecule due to resonance phenomenon are known as resonance structures.

The resonance structures of a molecule do not have any change in any property except the position of pi electrons. The resonance structures of a molecule are separated by a double head arrow i.e., ( $\longleftrightarrow$ ). A molecule showing the phenomenon of resonance, is usually represented by a single structure known as resonance hybrid structure which has the characteristics of all the

resonance structures. For example benzene has two resonance structures as explained by Kekule too.



The phenomenon of resonance appears as a result of delocalization (the phenomenon in which the pi electrons are not fixed between any two particular atoms). Thus due to the delocalization and resonance phenomenon, the pi electrons of benzene cannot be easily attacked by a reagent thus making benzene stable (less reactive). Greater is the number of resonance structures of a molecule, greater will be its stability and vice versa.

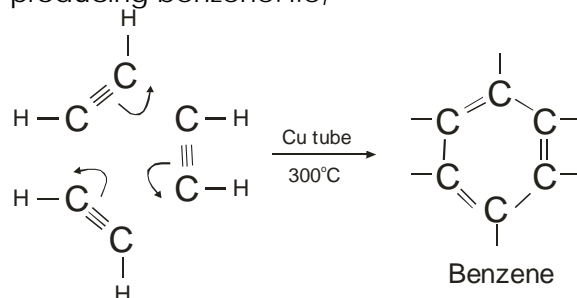
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## Methods of Preparation of Benzene:

Benzene can be prepared by several methods. Some important ones are;

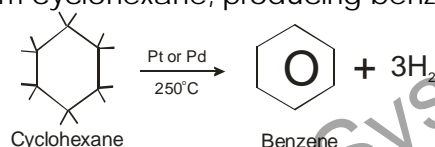
### 1) From Acetylene:

When acetylene is passed through Cu tube (acts as catalyst) at about 300°C and high pressure, acetylene gets polymerized producing benzene. i.e.,



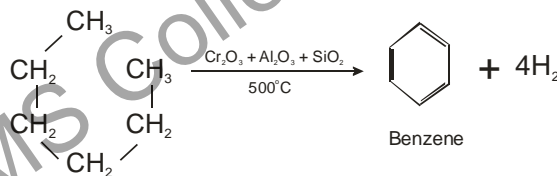
### 2) By Dehydrogenation of Cyclohexane:

When cyclohexane ( $C_6H_{12}$ ) is heated at 250°C in the presence of Pt or Pd catalyst, three moles of hydrogen gas are eliminated from cyclohexane, producing benzene. i.e.,



### 3) From Alkanes:

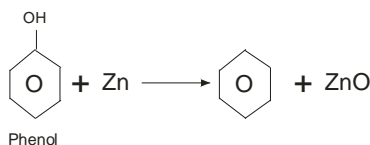
When n-hexane is heated at about 500°C in the presence of  $Cr_2O_3 + Al_2O_3 + SiO_2$ , benzene is produced. i.e.,



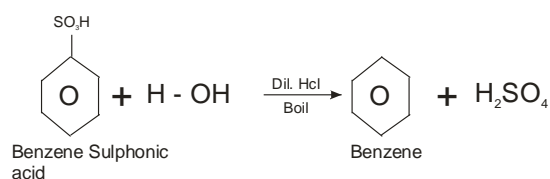
### 4) Laboratory Methods:

Along with the above mentioned commercial preparations of benzene, some laboratory preparations of benzene are explained as;

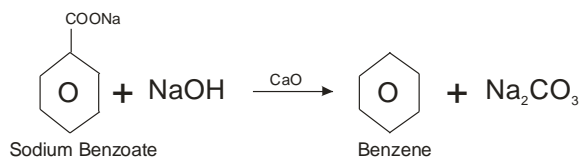
a) From Phenol: When vapors of phenol are passed over red hot zinc, phenol is reduced to benzene. i.e.,



b) From Benzene Sulphonic Acid: When benzene sulphonic acid is heated and reacted with boiling water or super heated steam in the presence of dil. HCl, we get benzene. i.e.,



c) From Sodium Benzoate: When sodium salt of benzoic acid (sodium benzoate) is reacted with soda lime ( $NaOH + CaO$ ), we get benzene. i.e.,



## Chemical Properties of Benzene:

Benzene shows the following types of chemical reactions.

- 1) Oxidation Reactions
- 2) Electrophilic Substitution Reactions
- 3) Addition Reactions

These reactions of benzene are discussed along with examples as follows;

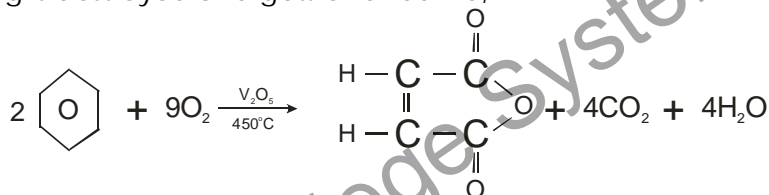
### 1) Oxidation Reactions:

Benzene shows the following oxidation reactions;

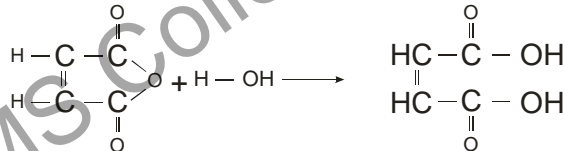
i) Combustion: When benzene is burnt in air, it produces  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and heat. i.e.,

$$\text{C}_6\text{H}_6 + 15/2 \text{O}_2 \rightarrow 6\text{CO}_2 + 3\text{H}_2\text{O}$$

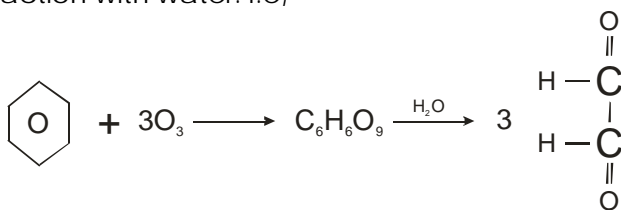
ii) Catalytic Oxidation: Benzene cannot be oxidized even by strong oxidizing agent like  $\text{KMnO}_4 + \text{H}_2\text{SO}_4$ , at room temperature. However, when benzene is strongly heated in air in the presence of  $\text{V}_2\text{O}_5$  catalyst, the ring is destroyed and gets oxidized. i.e.,



When maleic anhydride is reacted with  $\text{H}_2\text{O}$ , maleic acid is obtained. i.e.,



iii) Ozonolysis: When benzene is reacted with  $\text{O}_3$ , we get benzene triozone, which produces glyoxal upon reaction with water. i.e.,



### 2) Electrophilic Substitution Reactions of Benzene:

As benzene ring is rich in pi electrons, therefore, it is most suitable for electrophilic attack. But due to the resonance phenomenon, weak electrophiles cannot attack on benzene ring. Only strong electrophiles can attack upon benzene ring to break the continuous sheath of pi electron cloud in benzene.

The general pattern and mechanism of benzene can be shown as;

#### General Mechanism of Substitution in Benzene:

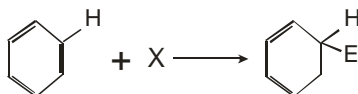
During electrophilic substitution reactions of benzene, following mechanism is followed;

Step1: In this step, an electrophile ( $\text{E}^+$ ) is produced. This is usually done with the help of a catalyst.

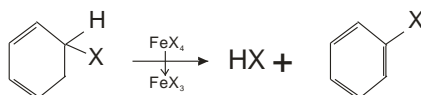
E.g.,



Step2: In this step, the electrophile attacks on the pi electrons of benzene ring to produce a carbocation. i.e,



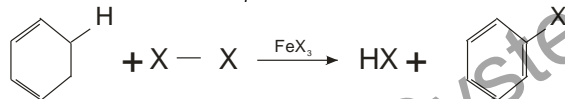
Step3: In this step, the benzene ring is regenerated and the H - atom is thus replaced by the electrophile. i.e,



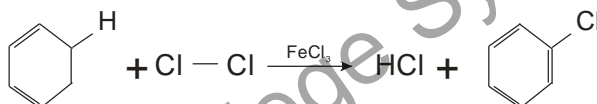
The most important electrophilic substitution reactions of benzene are discussed along with their suitable mechanisms as follows;

#### a) Halogenation of Benzene:

The replacement of a hydrogen of benzene by a halogen is known as halogenations of benzene. In case of halogenations of benzene where the halogen acts as an electrophile, the reaction is carried out in the presence of  $\text{FeX}_3$  catalyst. This such a halogenations of benzene may be called as catalytic halogenations. If catalyst is not available, then during halogenations of benzene, the halogen does not replace or substitute the H - atom of benzene, rather addition of halogen occurs in benzene and then the reaction will not be an electrophilic substitution reaction. When benzene is reacted with a halogen in the presence of  $\text{FeX}_3$  catalyst, a H of benzene is replaced by the halogen producing a halobenzene. i.e,



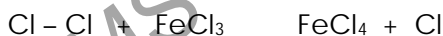
For example,



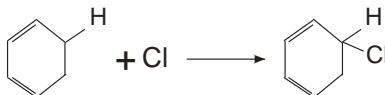
Note: Reaction of  $\text{F}_2$  is too violent and explosive while reaction of  $\text{I}_2$  is too slow to occur. That is why  $\text{Cl}_2$  and  $\text{Br}_2$  give the most suitable reactions with benzene.

Mechanism:

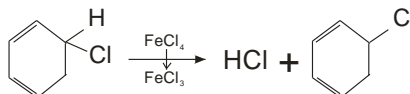
Step1:



Step2:



Step3:



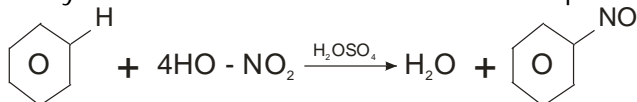
Note:

If an alkyl benzene is reacted with  $\text{Cl}_2$  or  $\text{Br}_2$  in the presence of sunlight, then the  $\text{X}_2$  substitutes with H - atoms of the alkyl group and does not replace the H - atom of benzene ring.

#### b) Nitration of Benzene:

When benzene is reacted with 1 : 1 ratio of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  (nitrating reagent), at  $50^\circ\text{C}$ , a H of benzene is replaced by the nitrogroup ( -  $\text{NO}_2$ ) of  $\text{HNO}_3$  producing a nitrobenzene. The reaction is called as nitration of benzene.

It is important to note that only one H - atom of benzene can be replaced by a nitrogroup. i.e,

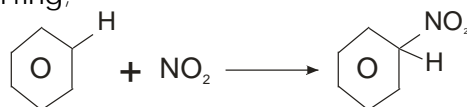


Mechanism:

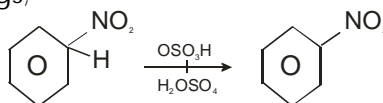
Step1:



Step2: Attack of electrophile on ring;



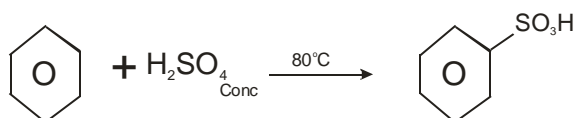
Step3: Reformation of benzene rings;



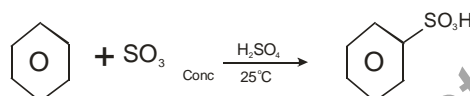
c) Sulphonation of Benzene:

When benzene is reacted with either concentrated  $\text{H}_2\text{SO}_4$  or with fuming  $\text{H}_2\text{SO}_4$  (it has free  $\text{SO}_3$  which is electron deficient and hence acts as an electrophile), at about  $80^\circ\text{C}$ , a H of benzene is replaced by a sulphonic group ( $-\text{SO}_3\text{H}$ ) producing benzene sulphonic acid and the reaction is called as sulphonation of benzene. i.e.,

When conc.  $\text{H}_2\text{SO}_4$  is used:



When fuming  $\text{H}_2\text{SO}_4$  is used:

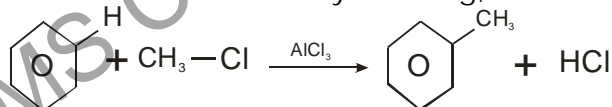


d) Friedel Craft's Reaction:

The reaction in which benzene is reacted with an alkyl halide ( $\text{R}-\text{X}$ ) or an acyl halide in the presence of a Lewis acid ( $\text{AlX}_3$ ), to produce an alkylated or acylated benzene, are known as Friedel Craft's Reactions. The F.C reactions are discussed as;

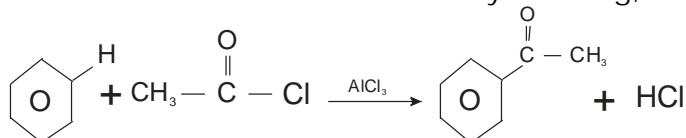
i) Friedel Craft Alkylation:

When benzene is reacted with an alkyl halide in the presence of  $\text{AlX}_3$  catalyst, an alkylated benzene is formed, this reaction is known as F.C alkylation. E.g.,



ii) Friedel Craft Acylation:

When benzene is reacted with an acid halide in the presence of  $\text{AlX}_3$  catalyst, we get an acylated benzene. This reaction is called as Friedel Craft Acylation. E.g.,

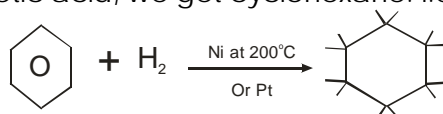


3) Addition Reactions of Benzene:

Due to the presence of pi bonds, benzene also shows addition reactions but not like alkenes. Addition reactions of benzene are much less suited than addition reactions of alkenes. Some important addition reactions of benzene are;

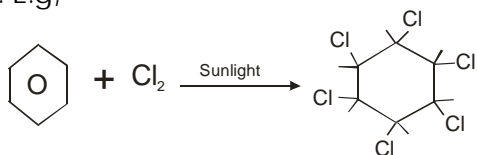
a) Hydrogenation (Reduction):

When  $\text{H}_2$  is heated with benzene in the presence of Ni catalyst at about  $200^\circ\text{C}$  or in the presence of Pt in an acidic solvent like acetic acid, we get cyclohexane. i.e.,



b) Halogenation:

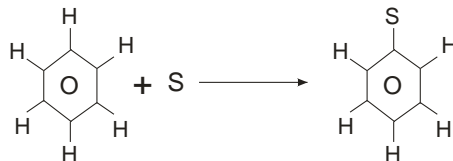
Benzene reacts with  $\text{Cl}_2$  or  $\text{Br}_2$  in the presence of sunlight to give an addition product.  $\text{F}_2$  is too vigorous while  $\text{I}_2$  is slow enough. E.g,



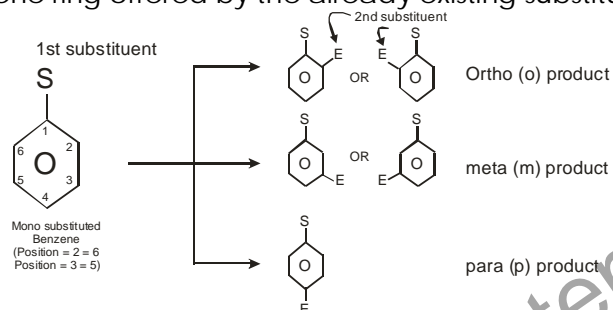
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### Effect of Substitutions on Further Substitution:

All six hydrogen atoms of benzene ring are equivalent. When an electrophile attacks on benzene ring, it can replace or substitute any of the six hydrogen atoms of benzene, thus, producing a mono-substituted benzene. E.g,



Once the 1<sup>st</sup> substituent comes on benzene ring, then the next incoming substituent is always directed by the already existing substituent to a particular position. The possible positions for the 2<sup>nd</sup> substituent upon benzene ring offered by the already existing substituent are:



A substituent already present on a mono-substituted benzene (1<sup>st</sup> substituent) has two effects on further substitution they are;

#### 1) Directive Effect:

The 1<sup>st</sup> substituent present on benzene ring i.e, substituent on a mono-substituted benzene, directs the next incoming substituent to either ortho or para or to meta positions. This effect of the 1<sup>st</sup> substituent is known as directive effect of that substituent. On the basis of directive effect of substituent (group) we have two types of substituent or groups.

##### a) Ortho-Para (O – P) Directing Groups:

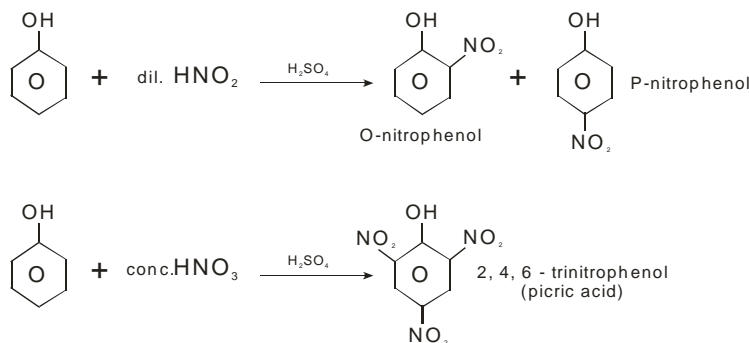
The groups or substituent, present on a mono-substituted benzene, which directs the next incoming groups or substituent to either ortho or para to both ortho and para positions and not to the meta position are called as ortho-para directing group. Ortho-para directing groups are electron rich and thus provide their lone pair of electrons to benzene ring through resonance and thus making ortho and para positions more stable for the attack of an electrophile (i.e, next incoming substituent). In an ortho-para directing group that atom which is directly attached to the benzene ring, always has at least one lone pair of electrons.

Note: A group or substituent, in which carbon atom of benzene ring, has greater electronegativity value than all other atoms of the group always acts as an ortho-para directing group. Some examples of ortho-para directing groups are; -OH, -NH<sub>2</sub>, -O – R, Cl, Br, F, I, -R etc.

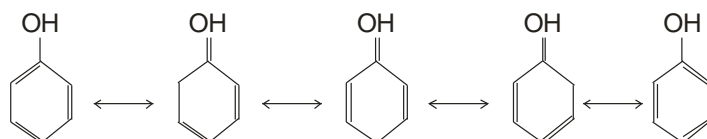
The alkyl group when attaches itself to benzene ring, it acts as an ortho-para directing groups. As mentioned earlier that the atom of the o – p directing which is bonded to benzene ring must have a lone pair of electrons, but the carbon atom of the alkyl group attached to benzene ring, has no lone pair of electrons to give it to benzene ring for resonance. But still the alkyl group acts as ortho-para directing group. The fact is that, that the alkyl group gets involved, one of its C – H sigma bond for resonance phenomenon to make ortho and para positions of the ring more suitable for the attack of next incoming groups (electrophile). This special types of resonance, where sigma bond is involved instead of lone pair of electrons, is known as "Hyperconjugation" or "No Bond Resonance".

Lets consider the concept of o – p directing group with an example. In phenol – OH group is an ortho-para directing group.





The fact that why, the ortho-para directing group makes ortho and para position suitable for the attack of next incoming electrophile, can be explained by resonance phenomenon as; Let's consider phenol where  $-\text{OH}$  is an o - p directing group, it makes the ortho and para positions more negative by providing a lone pair of electrons of oxygen to the ring to show resonance phenomenon.



It is clear that ortho and para positions are more negative more suitable for the attack of an electrophile, therefore,  $\text{OH}$  acts as o - p directing group. The o - p directing behavior of alkyl group (R) is due to hyper conjugation.

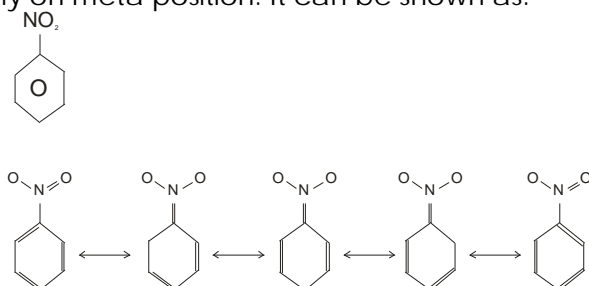
#### b) Meta Directing Group:

The group or substituent, present on a mono-substituted benzene, which directs the next incoming substituent to meta position only and not to ortho and para positions, is known as a meta directing group. The meta directing groups are usually electron deficient (i.e., electron withdrawing groups). These groups withdraw the pi electrons of benzene ring thus causing resonance in which the ortho and para positions of the ring become positively charged and are thus not suited for the attack of an electrophile. Therefore, the next incoming group can attack only on meta position.

Note: A group or substituent, in which that atom of benzene ring, has smaller electronegativity value than any other atom of the group, acts as a meta directing group. For example  $\text{NO}_2$  is a meta directing group because "N" of  $\text{NO}_2$  is attached with benzene ring and the other members of the  $\text{NO}_2$  group are oxygen atoms. As the electronegativity of oxygen is greater than that of "N", therefore we say  $-\text{NO}_2$  group is a meta directing group and it withdraws pi electrons from benzene ring. The best example of meta directing groups are;

$-\text{NO}_2$ ,  $-\text{COOH}$ ,  $-\text{CN}$ ,  $-\text{NH}_3$ ,  $-\text{CO}-$ ,  $-\text{CHO}$  etc.

Once a meta directing group attached with benzene ring, it withdraws the pi electron of the ring making ortho and para positions positive due to resonance and thus the next incoming electrophile can attack only on meta position. It can be shown as:



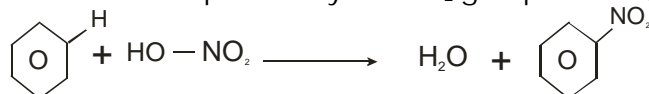
From the above resonance structures, it is clear that in the presence of a meta directing group ( $-\text{NO}_2$ ), the ortho and para positions on the ring are positive and not suited for the attack of an electrophile. Therefore, the electrophile can attack only on meta positions.

#### 2) Activity Effect:

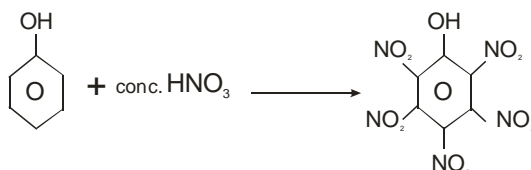
The substituent present on a mono substituted benzene also has a great effect on the reactivity of benzene ring. i.e., some substituents or groups when attach to benzene ring, make the ring more

reactive and such groups are called as "ring activators" while some substituents or groups when attach to benzene ring, make the ring less reactive i.e, decrease the reactivity of the ring. Such groups are known as "ring deactivators".

The ortho-para directing groups are ring activators. It means that when an ortho para directing group attaches to benzene ring, the reactivity of benzene ring is enhanced and then benzene ring can attach more groups with it. For example, when benzene is reacted with concentrated  $\text{HNO}_3$ , only one H of benzene can be replaced by a  $-\text{NO}_2$  group of  $\text{HNO}_3$  i.e,



But if an ortho-para directing group like  $-\text{OH}$  is attached to benzene ring then ring is more reactive and greater number of H - atoms of benzene can be replaced by other groups or atoms.



Halogens are exceptional. Although halogens ( $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ) are ortho-para directing group but they decrease the reactivity of benzene ring when attached to it. Thus halogens are ortho-para directing groups but they are "ring deactivators". This anomalous behavior of halogen is attributed to the fact that there are two opposing effects operating. (1) Halogen group is electron releasing by resonance but (2) it is electron withdrawing due to its high electronegativity i.e, Inductive Effect.

Here the inductive effect of shown by halogens dominates the resonance effect also shown by halogen, and as a result the ring becomes electron deficient and thus less liable to electrophilic attack. All meta directing groups being electron withdrawing groups, when attach to benzene ring, make the ring electron deficient and thus deactivate it. Thus all meta directing groups are ring deactivators.

#### Comparison of Reactivities of Alkanes, Alkenes and Benzene:

Alkanes are very much less reactive molecules because they have sigma bonds only, which are very stable. However alkanes show substitution reactions. Which involve a free radical. Alkanes never undergo addition reactions. Alkenes are very much reactive due to the presence of weak pi bond. They show addition reactions with great deal of reactivity but they never undergo substitution reactions. But benzene shows dual behavior in its reactivity i.e, it shows both addition as well as replacement or substitution reactions.

As benzene is highly unsaturated (has three pi bonds) but due to the phenomenon of delocalization of these pi electrons, it undergoes addition reactions much slower than those of alkenes. Thus benzene is more stable than alkenes. Similarly benzene also undergoes substitution reactions like alkanes. But substitution reactions of alkanes involve free radical while substitution reactions of benzene involve electrophiles and do not undergo free radical mechanism.

ENDED

## ALKYL HALIDES

### INTRODUCTION:

When one H – atom of an alkane is replaced by a halogen atom ( X = F, Cl, Br, I), a new organic compound is formed which is known as an “alkyl halide”. An alkyl halide is represented as “R – X” and its general formula is “C<sub>n</sub>H<sub>2n+1</sub>X”.

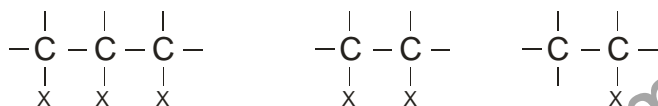
e.g,



### Halo Alkanes:

One or more hydrogen atoms of an alkane are replaced by halogen atoms, the resulting organic compounds are known as “Halo Alkanes”.

e.g,



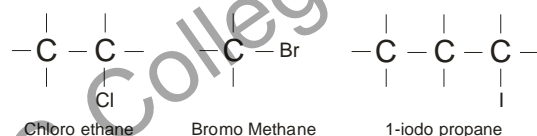
### Types:

On the basis of number of halogen atoms present in halo alkane, they are of three types,

#### 1) Mono Halo Alkanes (Alkyl Halides):

That halo alkanes which has only one atom attached to carbon atom, is known as a mono halo alkane. Mono halo alkane are also called alkyl halides.

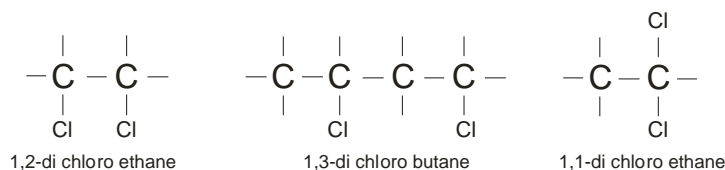
e.g,



#### 2) Di Halo Alkanes:

The halo alkane molecule in which two halogen atoms are present which are bonded either to same carbon atom (Gem di halide) or to two carbon atoms. (If to adjacent carbon atoms, then called as vicinal dihalides).

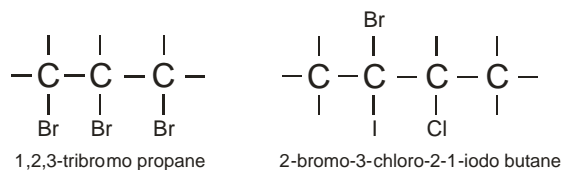
e.g,



#### 3) Poly Halo Alkanes:

The halo alkane molecule in which more than two halogen atoms are attached to carbon atoms, in known as poly halo alkane.

e.g,



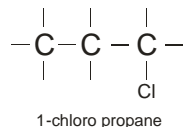
### Types of Alkyl Halides:

Alkyl halides are of three types.

#### 1) Primary Alkyl Halide:

An alkyl halide in which the halogen is attached to a primary carbon atom, is known as primary alkyl halide.

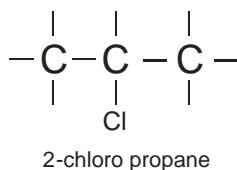
e.g,



#### 2) Secondary Alkyl Halide:

An alkyl halide in which the halogen atom is bonded to a secondary carbon atom, is known as a secondary alkyl halide.

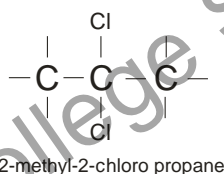
e.g,



#### 3) Tertiary Alkyl Halide:

An alkyl halide molecule in which the halogen atom is bonded to a tertiary carbon atom, is known as tertiary alkyl halide.

e.g,



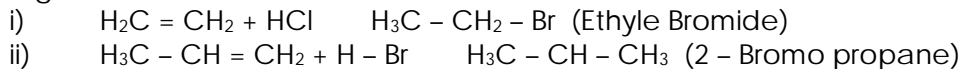
### General Methods of Preparation of Alkyl Halides:

The various methods of preparation of alkyl halides are discussed as follows;

#### 1) By Action of Halogen Acid on Alkenes:

When alkyl halide reacts with an alkene, we get an alkyl halide.

e.g,



Note: The order of reactivity of halogen acids with alkenes is  $\text{HI} > \text{HBr} > \text{HCl}$

#### 2) By Direct Hologenation of Alkanes:

When an alkane is reacted with  $\text{Cl}_2$  or  $\text{Br}_2$  in the presence of diffused sunlight, we get alkyl halides.

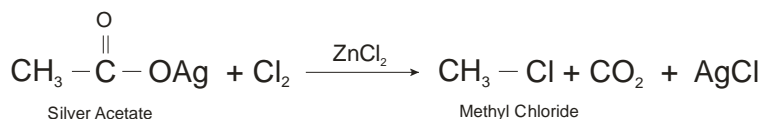
e.g,  $\text{H}_3\text{C} - \text{CH}_3 + \text{Cl}_2 \rightarrow \text{H}_3\text{C} - \text{CH}_2 - \text{Cl} + \text{HCl}$

By this method a pure alkyl halide cannot be obtained. Molecules containing two or more halogen atoms are also obtained or formed.

#### 3) By the Action of Halogens on Silver Salt of Carboxylic Acid:

When a halogen is reacted with silver salt of a carboxylic acid in the presence of  $\text{ZnX}_2$  catalyst, an alkyl halide is formed.

e.g,



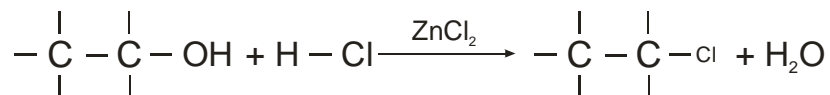
#### 4) From Alcohols:

From alcohols, alkyl halides can be formed by several methods.

##### a) Reaction of Alcohol with Halogen Acid:

When an alcohol is reacted with a halogen acid in the presence of  $ZnX_2$  as catalyst, an alkyl halide is formed.

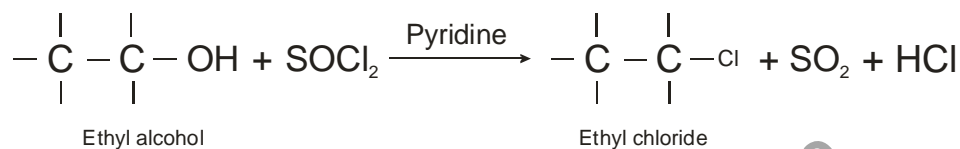
e.g,



##### b) Reaction of Alcohol with Thionyl Chloride:

When an alcohol is reacted with thionyl chloride ( $SOCl_2$ ) in pyridine which acts as solvent, an alkyl halide is formed.

e.g,



Note:

This method is more important one because the by-products formed (i.e.,  $SO_2$  &  $HCl$ ) are gases and thus escape leaving pure product (Alkyl Halide).

##### c) Reaction of an Alcohol with Phosphorous Trihalide & Pentahalide:

When an alcohol reacts with phosphorous trihalide ( $PX_3$ ) or phosphorous pentahalide ( $PX_5$ ), we get an alkyl halide in both cases.

e.g,



#### Reactivity of Alkyl Halides:

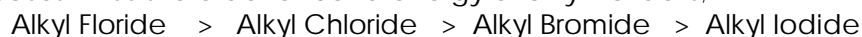
The reactivity of alkyl halides is controlled by the following two factors.

##### 1) Bond Polarity:

In an alkyl halide molecule the  $C - X$  bond is always polar because of electronegativity difference of  $C$  and  $X$  elements.  $X$  atom being more electronegative, attracts the shared pair of electrons a little more closer to its nucleus. As a result  $C$  atoms gains partial positive charge while  $X$  gets partial negative charge. Thus the  $X$  being negatively charged becomes a nucleophile and thus can be replaced or substituted by another strong nucleophile.

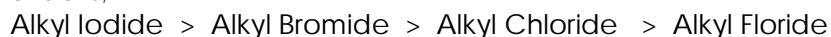
##### 2) Bond Energy:

As we go from  $R - F$  to  $R - I$ , the bond energy decreases. It is because of the fact that down the group (from  $F$  to  $I$ ) the electronegativity of  $X$  atoms decrease due to which the bond polarity of  $R - X$  decreases from  $R - F$  to  $R - I$ . Greater the bond polarity, stronger is the bond and hence bond energy also increases. Thus the order of bond energy of alkyl halide is;



Note:

It has been experimentally known that the bond energy is key factor which controls the reactivity of alkyl halides. The alkyl halide with least bond energy is the most reactive. Thus the order of reactivity of alkyl halide is;



## Reactions of Alkyl Halides:

Alkyl halides show two major types of reactions which are;

a) Nucleophilic Substitution (SN) Reactions and

b) Elimination (E) Reactions

Before discussing the above mentioned types of the alkyl halides, let's discuss some important terms related to these reactions.

### 1) Electrophile:

(Electro – electron, & Phile – loving)

Any positively charged species or a neutral species which is an electron pair deficient (Lewis Acid), is known as an electrophile. Examples:  $R^+$ ,  $AlCl_3$ ,  $BF_3$ ,  $H^+$

### 2) Nucleophile (Nu):

(Nucleo – Nucleus, Phile – loving)

Any negatively charged species or a neutral species with a lone pair of electrons available for bonding (Lewis Base), is known as Nucleophile. For example,  $OH^-$ ,  $C_2H_5O^-$ ,  $HS^-$ ,  $NH_2^-$ ,  $Cl^-$ ,  $Br^-$ ,  $NH_3$ ,  $H_2O$  etc.

### 3) Leaving Group:

When a strong nucleophile attacks on an alkyl halide molecule, it replaces the halogen group of the alkyl halide. The halogen group leaves the alkyl halide molecule and goes out as halide ion (i.e.,  $X^-$ ). This halogen group which leaves the alkyl halide molecule, as a result of nucleophile attack is known as leaving group.

The leaving group is also a nucleophile, so we can say that a nucleophile is a leaving group.

Note:

Strong nucleophiles are always poor leaving groups. For example,  $OH^-$ ,  $OR^-$ ,  $NH_2^-$ , etc are strong nucleophiles, hence poor leaving group. On the other hand a weak nucleophile is a good leaving group. For example,  $Cl^-$ ,  $Br^-$ ,  $HSO_4^-$ , etc. are weak nucleophiles hence good leaving group. Iodine is a good nucleophile as well as good leaving group.

### 4) Substrate:

The alkyl halide molecule which is being attacked by an attacking nucleophile is known as substrate.

All the above mentioned terms can be explained with the help of the following example.



Now let's discuss the chemical reactions of alkyl halides.

### a) Nucleophilic Substitution (SN) Reactions:

The reactions of an alkyl halide in which it is attacked by an attacking nucleophile to replace the halogen atom of the alkyl halide, are known as nucleophilic substitution reactions (SN reactions). These reactions are named as SN reactions because during reactions one nucleophile ( $X^-$ ) is replaced or substituted by other nucleophile (Nu). It must be kept in mind that during SN reactions, the attacking nucleophile must be stronger than the leaving nucleophile ( $X^-$ ). The overall SN reaction can be shown as;



The SN reactions are of two types i.e.,

#### 1) Bimolecular Nucleophilic Substitution Reactions (SN<sub>2</sub>)

A nucleophilic substitution reaction in which two molecules are involved in the rate determining step and which complete in single step is known as bimolecular nucleophilic substitution reactions (SN<sub>2</sub>). The rate of an SN<sub>2</sub> reaction depends upon the concentration of substrate as well as attacking nucleophile. Thus we say that the molecularity of SN<sub>2</sub> reactions is "2". i.e.,

$$\text{Rate} = K (\text{substate})^1 \times (\text{Nu})^1$$

$$\text{Molecularity} = 2$$

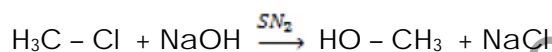
$$\text{Order} = 1 + 1 = 2$$

The  $\text{S}_\text{N}2$  reactions always occur in case of "primary alkyl halides".  $\text{S}_\text{N}2$  reactions never occur in "tertiary alkyl halides". In case of "secondary alkyl halides",  $\text{S}_\text{N}2$  reactions will occur only if the reaction is carried out in a non-polar medium. During  $\text{S}_\text{N}2$  reactions the attacking nucleophile always attacks on that site of the electrophilic carbon which is opposite to the halogen atom. During nucleophilic attack, Nu – C bond formation and the C – X bond breaking take place simultaneously. When the attacking nucleophile attacks on the electrophilic carbon (that carbon which is attached with halogen atom), a transition state or activated complex is formed, in which carbon changes its state of hybridization from  $\text{SP}^3$  (tetrahedral) to  $\text{SP}^2$  (co-planar).

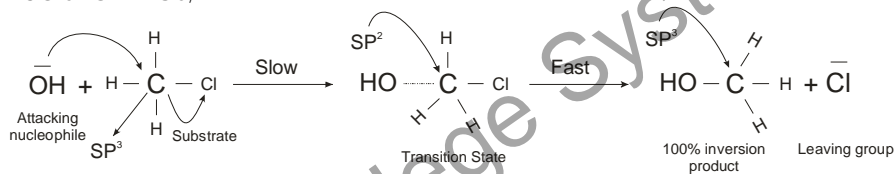
Finally the halogen atom (leaving group) detaches from carbon and goes out as halide ion ( $\text{X}^-$ ) which the attacking nucleophile makes a true covalent bond with the carbon. At this type carbon, once again changes from  $\text{SP}^2$  (co-planar) to  $\text{SP}^3$  (tetrahedral) hybridization. In the final product a complete inversion of the molecule takes place because the attacking nucleophile has attacked on that site of the electrophilic carbon which is opposite to the halogen atom. Thus during  $\text{S}_\text{N}2$  reaction, 100% inversion product is obtained. This whole process can be explained by the following example.

Consider the reaction of methyl alcohol (substrate) with aqueous NaOH or KOH (where OH is the attacking nucleophile) to form methyl alcohol.

i.e.,



The process can be shown as;



## 2) Unimolecular Nucleophilic Substitution Reactions ( $\text{S}_\text{N}1$ )

The  $\text{S}_\text{N}$  reactions in which only one molecule (substrate) is involved in the rate determining step and which complete in two steps are known as  $\text{S}_\text{N}1$  reactions.

In first step of the  $\text{S}_\text{N}1$  reaction the alkyl halide (substrate) molecule ionizes in an aqueous medium of acetone or alcohol to form a stable carbonium ion and halide ion ( $\text{X}^-$ ). Here the electrophilic carbon of the alkyl halide changes its state of  $\text{SP}^3$  (tetrahedral) hybridization to  $\text{SP}^2$  (planar) hybridization. This is slow step, hence called as rate determining step. During the second step, the attacking nucleophile attacks on the  $\text{SP}^2$  hybridized carbon of the carbocation, either from one side or from the other side producing 50% inversion products and 50% retention products. In the products, the carbon again acquires  $\text{SP}^3$  hybridization. The mixture of inversion products & retention products is known as "RACEMIC MIXTURE" and the process of formation of Racemic Mixture is called "RACEMIZATION". The rate equation for  $\text{S}_\text{N}1$  reactions is;

$$\text{Rate} = k [\text{substrate}]^1$$

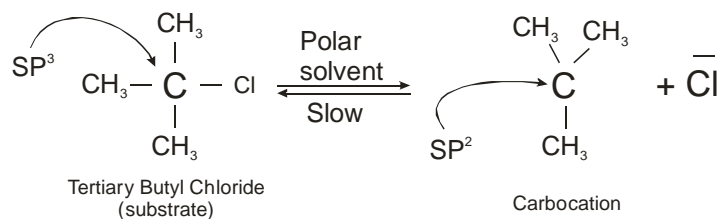
$$\text{Molecularity} = 1$$

$$\text{Order} = 1$$

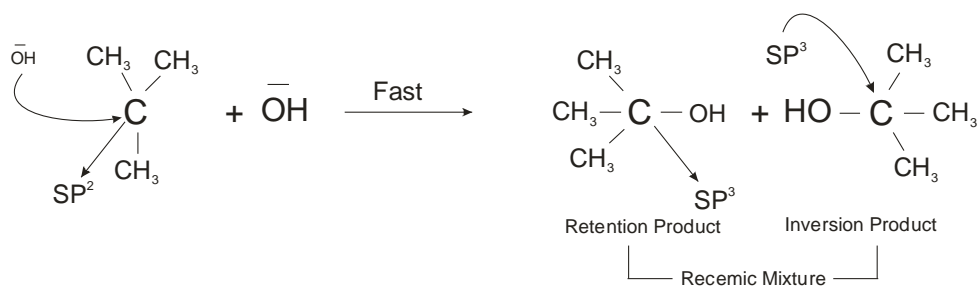
$\text{S}_\text{N}1$  reactions always occur in case of "tertiary alkyl halides". "Primary alkyl halides" never undergo  $\text{S}_\text{N}1$  reactions. Secondary alkyl halides undergo  $\text{S}_\text{N}1$  reaction, if the reaction is carried out in a polar medium. The whole process can be explained by the following example.

Consider a tertiary alkyl halide like tertiary butyl chloride, reacting with NaOH.

Step1:



Step2:



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## Differences between SN<sub>2</sub> and SN<sub>1</sub> Reactions:

The major differences between SN<sub>2</sub> and SN<sub>1</sub> reactions are shown as follow;

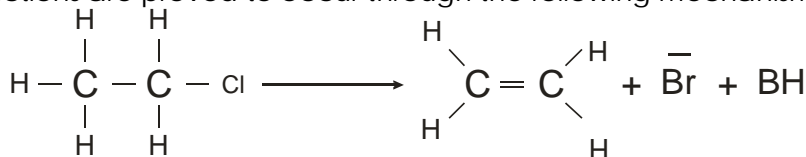
SN <sub>2</sub> Reactions	SN <sub>1</sub> Reactions
1) Always occur in Primary Alkyl Halides	1) Always occur in Secondary Alkyl Halides
2) They are called as Bimolecular nucleophilic substitution reactions.	2) They are called as unimolecular nucleophilic substitution reactions.
3) Two molecules are involved in the rate determining step.	3) One molecule is involved in the rate determining step.
4) Completes in single step.	4) Completes in two steps.
5) Rate depends upon the concentration of both the substrate as well as nucleophile, i.e, Rate [substrate] [Nu]	5) Rate depends upon the concentration of substrate only. i.e, Rate [substrate]
6) The overall order of the reaction is 2.	6) The overall order of the reaction is 1.
7) The attacking nucleophile, attack the carbon atom from the side which is opposite to leaving group.	7) The attacking nucleophile can attack on the carbon atom from any side.
8) Formation of new bond & breaking of old bond takes place simultaneously.	8) Old bond breaks down in 1 <sup>st</sup> step while new bond is formed in 2 <sup>nd</sup> step.
9) 100% inversion products is obtained.	9) Racemic Mixture (inversion + retention products) is obtained.

## b) - Elimination Reactions:

"The reactions of alkyl halides in which the removal of halogen and beta ( ) hydrogen (hydrogen bonded with beta carbon atom) takes place simultaneously, are called as - Elimination Reactions".

Sometimes when a stable carbonium ion and a strong base are available, then the attacking nucleophile attacks not upon the electrophilic carbon as in case of SN reactions, thus when the attacking nucleophile attacks on the - H atom, an elimination reaction occurs (instead of SN reaction) in which a H atom ( - H) and a halogen atom are removed from the adjacent carbon atoms of the R - X resulting in the formation of an alkene.

The elimination reactions are proved to occur through the following mechanism.



Elimination reactions follow two types of mechanisms.

### 1) Bimolecular Elimination Reactions (E<sub>2</sub> Mechanism):

The elimination reactions where the rate depends upon the concentration of two molecules and which completes in a single step, are said to follow E<sub>2</sub> Mechanism.

Here the attack of nucleophile upon - H of the alkyl halide molecule and the removal of the halogen atom (leaving group) take place simultaneously. Such reactions usually occur in case of primary alkyl halides.

The rate depends upon the concentration of both the substrate as well as attacking nucleophile,  
i.e,

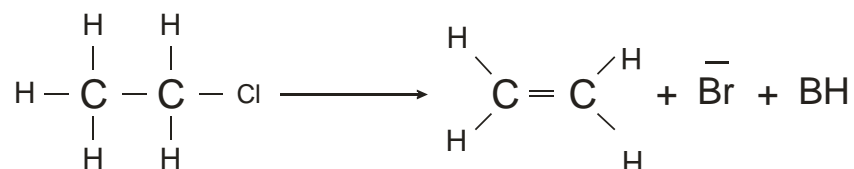
Rate =  $k$  [substrate] [Nu]

Molecularity = 2

Order = 2

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The whole process can be shown by the following example.



## 2) Unimolecular Elimination Reaction (E<sub>1</sub> Mechanism):

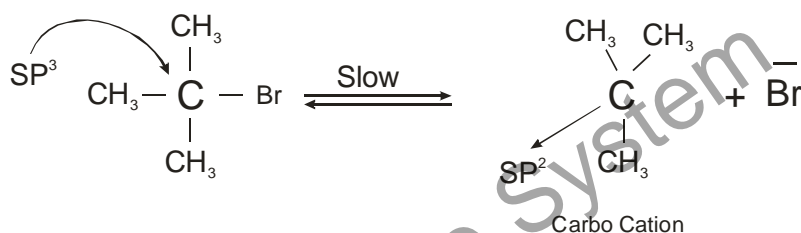
The elimination reactions in whose the rate depends upon the concentration of only one molecule i.e, substrate and complete in two steps, are known as E<sub>1</sub> reactions.

In step 1, the substrate (alkyl halide) loses the halogen atom forming a carbocation. The hybridization of the carbon atom, attached with halogen atom, changes from SP<sup>3</sup> to SP<sup>2</sup>. This is a slow step, hence rate determining step, i.e,

$$\text{Rate} \propto [\text{substrate}]$$

In step 2, the attacking nucleophile attacks on the  $\beta$ -H of the carbo cation forming an alkene. This is a fast step. E<sub>1</sub> reactions usually occur in tertiary alkyl halides. The whole process can be explained by the following example.

Step1:



Step2:



Differentiation Between Substitution & Elimination Reactions:

Substitution Reactions	Elimination Reactions
Substitution Reactions are favoured by	Elimination Reactions are favoured by
a) Weaker bases and	a) Strong bases and
b) Less stable carbonium ion.	b) Stable carbonium ion (carbo cation).

Note:

The order of stability of carbonium ions is

Tertiary Carbonium Ion > Secondary Carbonium Ion > Primary Carbonium Ion

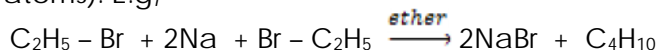
Thus we can say that elimination reactions occur most readily with tertiary carbonium ions.

## Some General Reactions of Alkyl Halides:

Some general reactions of alkyl halides are discussed as follows:

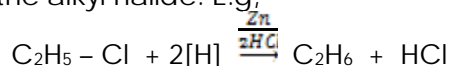
### 1) Wurtz Reaction or Synthesis:

When an alkyl halide reacts with sodium metal in ether used as solvent, the reaction is known as Wurtz Reaction. The reaction is very much useful in obtaining symmetrical alkanes (alkanes having even number of carbon atoms). E.g,



### 2) Reduction of Alkyl Halides:

The alkyl halides can be reduced to the corresponding alkane when reacted with (Zn + HCl). Zn and HCl react together producing ZnCl<sub>2</sub> and nascent hydrogen (H). This nascent hydrogen is responsible for the reduction of the alkyl halide. E.g,



### 3) Frankland's Reaction:

When an alkyl halide is reacted with Zn metal, we get a symmetrical alkane. E.g,



### 4) Reaction with Sodium Lead Alloy (Na<sub>4</sub>Pb):

When ethyl chloride or methyl chloride are reacted with Na<sub>4</sub>Pb, we get "tetra ethyl lead (TEL)" or "tetra methyl lead (TML)". TEL & TML are important anti-knock agents and were used as knock inhibitors in gasoline. i.e,



## GRIGNARD REAGENT (R - Mg - X):

In 1900, a chemist, Victor Grignard, synthesized a new organic compound, by reacting methyl iodide with magnesium metal. This new organometallic compound i.e, methyl magnesium iodide was named as Grignard Reagent.

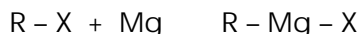
Later on it was confirmed that when even any alkyl group and any halogen get bonded to magnesium metal, we get an alkyl magnesium halide molecule. Now any alkyl magnesium halide (R - Mg - X) is known as Grignard Reagent and also called as "Organometallic Compounds". i.e, Grignard's Reagent be generally represented as;



Where 'R' is an alkyl group (- CH<sub>3</sub>, - C<sub>2</sub>H<sub>5</sub>, etc), 'X' is a halogen atom (F, Cl, Br, I).

### General Method of Preparation:

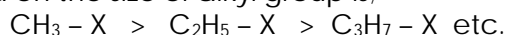
Grignard's reagent can be generally prepared by reacting an alkyl halide with magnesium metal. i.e,



The order of reactivity of alkyl halides with Mg is

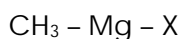


The reactivity of alkyl halides with Mg also depend upon the size of alkyl group. With the increase of the size of alkyl group, the reactivity of alkyl halide with Mg, decreases. Thus the order of reactivity of alkyl halide based on the size of alkyl group is;



### Structure & Reactivity of Grignard's Reagent:

The reactivity of Grignard reagent is due to the polar nature of C - Mg bond. The structure of a Grignard's reagent can be shown as;

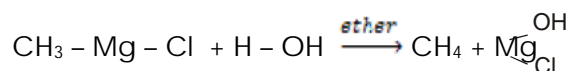


As magnesium metal is more electropositive than carbon hence the C – Mg bond become highly polar where the C atom gets partial negative and Mg gets partial positive charge. Due to the negative charge, the carbon atom of the alkyl group attached with Mg, the alkyl group is made highly reactive towards electrophilic center.

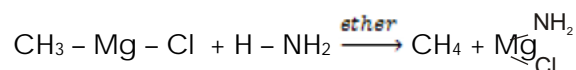
### Reactions (or Applications) of Grignard's Reagent:

Grignard's reagent reacts with so many compounds, producing other important compounds. For example:

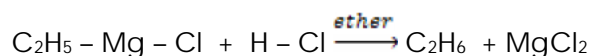
a) With Water: G.R. reacts with water in the presence of ether to form an alkane. E.g,



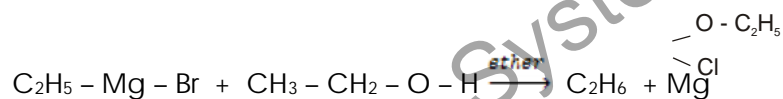
b) With Ammonia: G.R. when reacts with NH<sub>3</sub> in the presence of ether, we get an alkane. E.g,



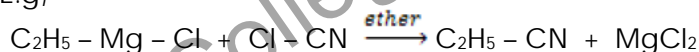
c) With Halogen Acid: When G.R. is reacted with a halogen acid, an alkane is obtained. E.g,



d) With an Alcohol: When G.R. reagent reacts with an alcohol in the presence of ether, we get an alkane. E.g,



e) With Cyanogen Chloride (Cl – CN): When G.R. reacts with cyanogen chloride, we get an alkyl cyanide or alkyl nitrile. E.g,

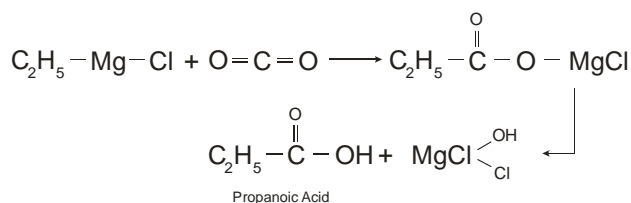


f) With Carbon Dioxide to a Carboxylic Acid: When a G.R is reacted with CO<sub>2</sub>, the G.R adds into the CO<sub>2</sub> molecule forming an addition product (adduct), which upon acid hydrolysis gives a carboxylic acid.

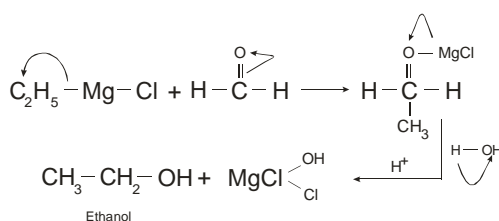
Note:

The carboxylic acid formed by this method is one carbon atom rich than the alkyl group attached with the Mg & G.R.

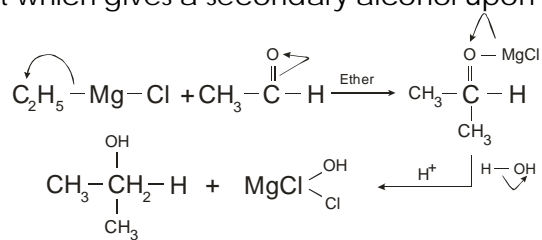
e.g,



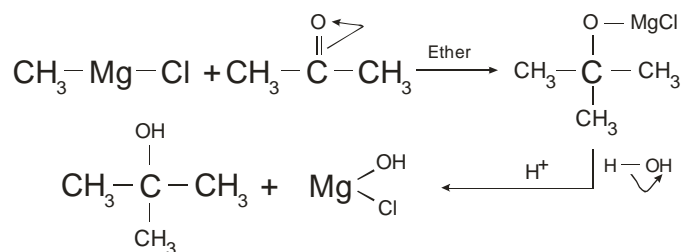
g) With Formaldehyde to form a Primary Alcohol: When G.R. is reacted with HCHO, the G.R adds into the carboxyl group of HCHO forming an adduct which upon acid hydrolysis gives a primary alcohol. E.g,



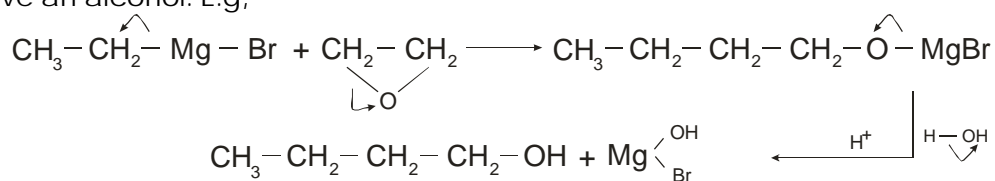
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i) With Acetone to form a Tertiary Alcohol: When a G.R reacts with acetone, we get an adduct, which upon acid hydrolysis gives a tertiary alcohol. E.g,



j) With an Epoxide: When a G.R reacts with an epoxide, we get an adduct, which upon acid hydrolysis give an alcohol. E.g,

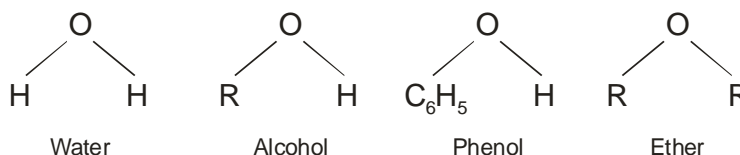


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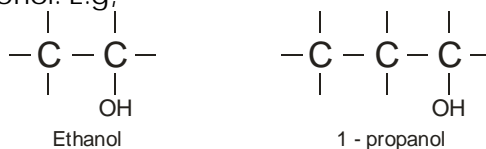
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## ALCOHOLS, PHENOLS &amp; ETHERS

Alcohols, phenols and ethers have much closer structures to water.

**Alcohols:**

When one or more H atoms of a hydrocarbon are replaced by hydroxyl groups, the resulting compound is known as an alcohol. E.g,

**Classification of Alcohols on the Basis of Number of – OH Groups:**

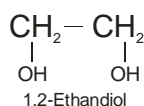
On the basis of number of – OH groups, alcohols are classified into the following three types;

**1) MONOHYDRIC ALCOHOLS:**

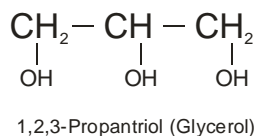
The alcohols containing only one – OH group bonded to carbon atom, are known as Monohydric alcohols. E.g,

**2) DIHYDRIC ALCOHOLS:**

The alcohols in which two – OH groups are bonded to one or two carbon atoms, are known as Dihydric alcohols. E.g,

**3) POLYHYDRIC ALCOHOLS:**

Alcohols containing more than two – OH groups bonded with carbon atoms of an alcohol, are known as Polyhydric alcohols. E.g,

**Classification of Monohydric Alcohols:**

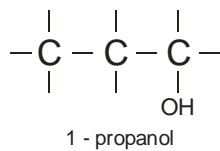
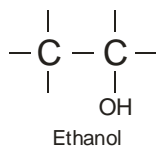
Monohydric alcohols are further classified as;

**a) Primary Alcohols:**

Monohydric alcohols in which the – OH group is bonded with a primary carbon, are known as Primary alcohols.

e.g,



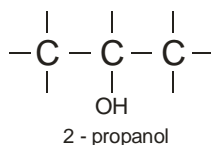


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### b) Secondary Alcohols:

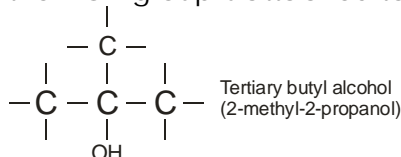
The monohydric alcohols, in which the – OH group is bonded to an secondary carbon atom is known as secondary alcohol.

e.g,



### c) Tertiary Alcohols:

The monohydric alcohols in which the – OH group is attached to a tertiary carbon atom. E.g,

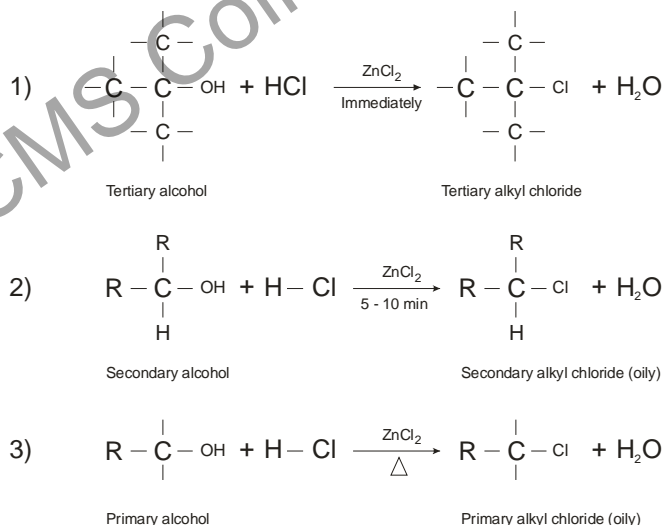


### LOCUS TEST (Distinction between Primary, Secondary & Tertiary Alcohols):

The primary, secondary and tertiary alcohols can be distinguished by means of Lucas test. In this test, we take primary, secondary and tertiary alcohols in three separate beakers and then add HCl and ZnCl<sub>2</sub> to all the three beakers at the same time. The alkyl group of alcohol combines with the Cl of HCl because the OH of the alcohol combines with H of HCl to form H<sub>2</sub>O. The alkyl halide formed is oily and thus makes the surface oily. The order of reactivity of alcohols with HCl to form the oily layer of alkyl chloride is;

Tertiary Alcohol > Secondary Alcohol > Primary Alcohol

The alcohol which forms oily layer with HCl & ZnCl<sub>2</sub> immediately, is tertiary alcohol. The alcohol which forms oily layer with HCl & ZnCl<sub>2</sub> after 5 – 10 minutes is secondary alcohol. The alcohol which forms oily layer with HCl and ZnCl<sub>2</sub> only after heating is primary alcohol. The reactions are shown as follows;



### Methods of Preparation of Alcohols:

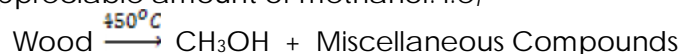
#### 1) Methanol:

Methanol can be prepared as;

##### a) From Wood:

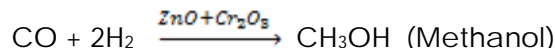
In 1661, Robert Boyle discovered methanol by the destructive distillation of wood. So formerly methanol was obtained by the destructive distillation of wood. Due to this fact methanol is commercially known as “wood spirit”. During this process wood is heated at 400°C in the absence of oxygen. Thus we get some gases and a liquid. The liquid produced here is a mixture of several

organic compounds. This liquid contains 5% methanol. Then we perform fractional distillation of the liquid and obtain appreciable amount of methanol. i.e,



b) From Water Gas (Catalytic Reduction of CO):

Now a days methanol is prepared by this method. In this method, water gas ( $\text{CO} + \text{H}_2$ ) is passed through  $\text{ZnO}$  and  $\text{Cr}_2\text{O}_3$  at about  $400 - 450^{\circ}\text{C}$  and at 200 atm pressure and methanol is produced. i.e,



c) From Natural Gas (Partial Oxidation of Natural Gas):

When a mixture of natural gas ( $\text{CH}_4$ ) and  $\text{O}_2$  is passed over copper catalyst at  $250^{\circ}\text{C}$  and 100 atm pressure, methanol is formed. i.e,



2) Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ):

Ethanol (grain spirit) is commercially prepared by a process known as fermentation.

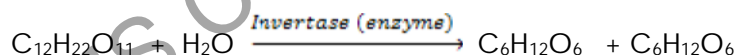
**Fermentation:** The process by which a carbohydrate (aqueous) is converted into alcohol with the evolution of  $\text{CO}_2$  by the action of enzymes (biological catalyst) secreted by a microorganism like yeast.

Optimum temperature for this process is  $25 - 30^{\circ}\text{C}$ . Proper aeration and absence of any preservative, are the essential conditions for fermentation.

Commercially, ethanol is synthesized by the fermentation of Molasses (the residue obtained after the crystallization of sugar from sugar cane juice) and starch. Fermentation of molasses and starch can be explained as;

i) From Molasses:

The process of fermentation of molasses to obtain ethanol is as follows;



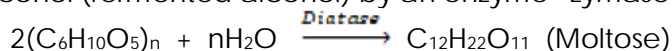
Then,



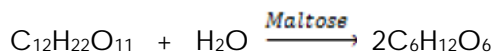
ii) From Starch:

The process of fermentation of starch to obtain alcohol (fermented alcohol) is as follow;

In this process the starch present in potatoes, barley etc is broken down by an enzyme "diastase", to maltose and then, maltose is broken down into glucose by an enzyme "maltase". The glucose is finally converted into alcohol (fermented alcohol) by an enzyme "zymase". i.e,



Then,



Then,



In Pakistan, alcohol is prepared from Molasses, starch grains or fruit juices. Due to the reason that ethanol is obtained from grains, it is also called as grain spirit.

**Note:**

By the process of fermentation we cannot obtain 100% pure alcohol. Fermented alcohol is 12 – 14% pure. It is because of the fact that after 14%, the enzymes become inactive and, therefore, we are not able to get any more alcohol. For purification purpose, the fermented alcohol is distilled again and again to obtain 95% alcohol. This 95% alcohol obtained by distillation of fermented alcohol, is known as "Rectified Spirit". When the rectified spirit is re-distilled in the

presence of CaO (which absorbs moisture) to get 100% alcohol, then such an alcohol is known as "Absolute Spirit".

### Denaturing of Alcohol:

The process of making alcohol unfit for human consumption (drinking purpose) by adding some poisonous substance to it, is known as denaturing of alcohol. Alcohol (ethanol) is denatured by adding 10% methanol (poisonous) into it. Such an alcohol which is being denatured by the addition of 10% methanol into it, is known as "Methylated Spirit". We can also add "Acetone" or "Pyridine" into alcohol for the denaturing purposes.

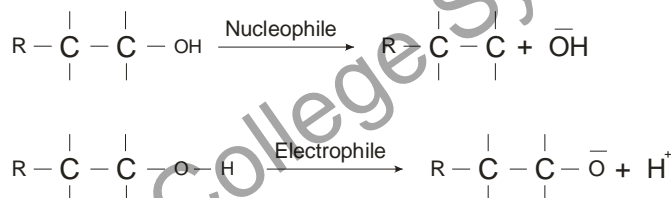
### Physical Properties:

From book.

### Chemical Properties:

Most of the reactions of alcohol are due to either C – O bond or due to O – H bond of an alcohol depends upon the nature of the attacking reagent. If the attacking reagent is a nucleophile, then the C – O bond breaks down because the attacking nucleophile will attack on the partial positive carbon of the C – O bond. On the other hand, if the attacking reagent is an electrophile, then the O – H bond breaks down because the attacking electrophile will attack on the partial negative oxygen of the O – H bond.

i.e,



In case of reactions of alcohols, where the C – O bond is involved, their order of reactivity is;

Tertiary Alcohol > Secondary Alcohol > Primary Alcohol

In case of reactions of alcohols, where the O – H bond is involved, their order of reactivity is;

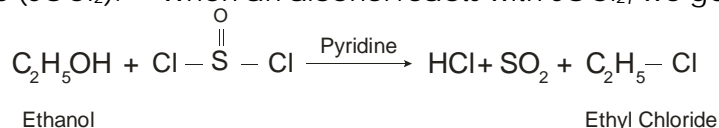
CH<sub>3</sub>OH > Primary Alcohol > Secondary Alcohol > Tertiary Alcohol

The various types of reactions of alcohols are discussed as follows;

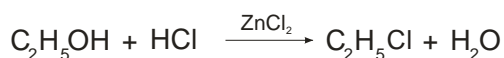
#### a) Reactions Involving Cleavage of C – O Bond:

some important reactions of alcohols in which the C – O bond breaks i.e, when an alcohol is attacked by a nucleophile, are as follows;

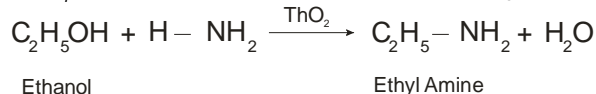
i) With Thionyl Chloride (SOCl<sub>2</sub>): When an alcohol reacts with SOCl<sub>2</sub>, we get an alkyl halide. E.g,



ii) With an Acid Halide (HX): We get an alkyl halide when an alcohol reacts with HX in the presence of ZnCl<sub>2</sub>. E.g,



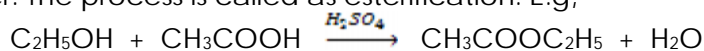
iii) With NH<sub>3</sub>: We get an amide, when an alcohol reacts with NH<sub>3</sub> in the presence of ThO<sub>2</sub>. E.g,



#### b) Reactions Involving the Cleavage of O – H bonds:

Some important reactions of alcohol in which the O – H bond breaks i.e, alcohol is attacked by an electrophile, are as follows;

i) With Carboxylic Acid: When an alcohol reacts with a carboxylic acid in the presence of H<sub>2</sub>SO<sub>4</sub>, we get an ester. The process is called as esterification. E.g,

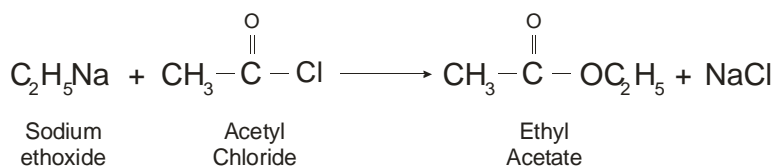


ii) With Metal: When an alcohol reacts with a reactive metal like Na, we get metal alkoxide with the evolution of H<sub>2</sub> gas. E.g,



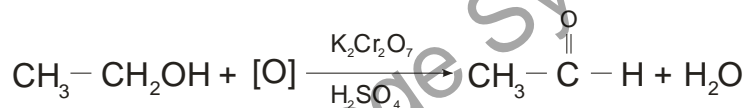
When sodium ethoxide is reacted with an acid halide, we get an ester which is an important commercial compound.

e.g,

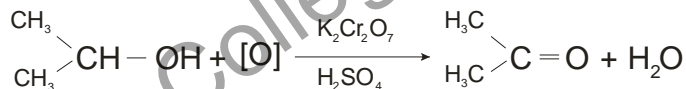


c) Some Other Reactions of Alcohols:

i) Oxidation: Primary and secondary alcohols are easily oxidized to carbonyl compound (aldehydes & Ketones) by strong oxidizing agents like K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + H<sub>2</sub>SO<sub>4</sub> or KMnO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub>, e.g,



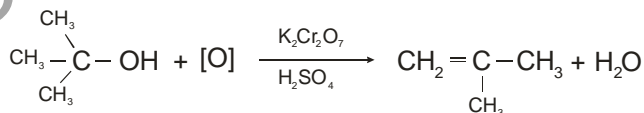
Similarly,



Note:

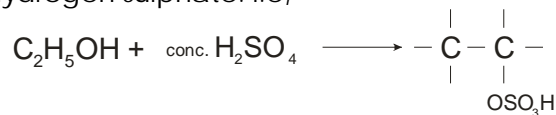
Tertiary alcohols are not oxidized easily. When they are treated with strong oxidizing agents, we get an alkene instead of a carboxyl compound.

e.g,



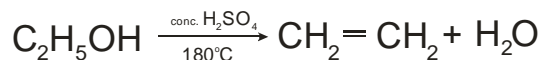
ii) With Sulphuric Acid (Dehydration): Alcohols react with conc. H<sub>2</sub>SO<sub>4</sub> (dehydrating agent) and give different products at different conditions of temperatures.

a) At Ordinary Temperature: When an alcohol reacts with Conc. H<sub>2</sub>SO<sub>4</sub> at ordinary temperature, we get ethyl hydrogen sulphate. i.e,

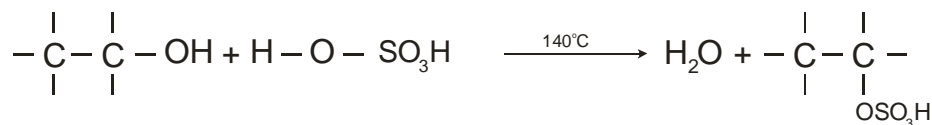


b) At Higher Temperature: When an alcohol is reacted with conc. H<sub>2</sub>SO<sub>4</sub> at about 180°C, we get an alkane.

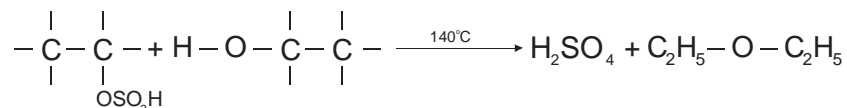
e.g,



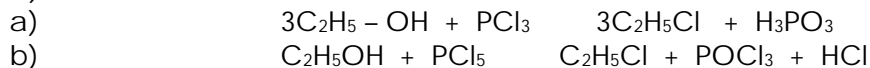
c) At a Little Lower Temperature with Excess Alcohol: When an excess of alcohol is reacted with conc. H<sub>2</sub>SO<sub>4</sub> at about 140°C, we get an ether. The process completes in two steps. i.e,



Then,



iii) With  $PX_3$  &  $PX_5$ :

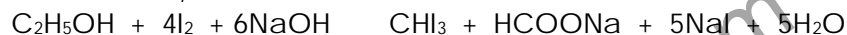


USES of ALCOHOLS:

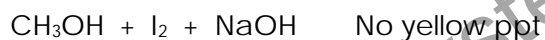
From book

Distinction between Ethanol & Methanol:

Ethanol and methanol can be distinguished by iodoform test. During this test, we take ethanol & methanol in two beakers and crystals of iodine along with NaOH in both the beakers. Ethanol reacts with  $I_2$  and NaOH forming a yellow ppt of iodoform ( $CHI_3$ ) while methanol does not form any yellow ppt of iodoform. i.e.,



And

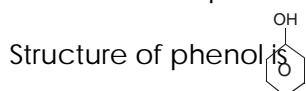


PHENOLS:

The aromatic compounds in which one or more -OH groups are directly bonded with the carbon atoms of an aromatic ring are known as Phenols.

Phenol (or carbolic acid) is the simplest member of phenols. Phenol was first obtained by Runge in 1834, from coaltar.

The formula of phenol is  $C_6H_5OH$

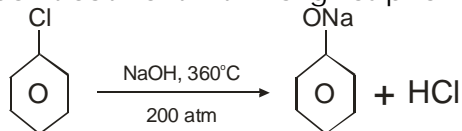


Methods of Preparation:

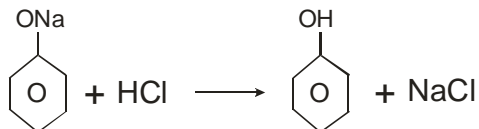
Some important methods of preparation of phenol are:

1) Dow's Method:

In this method, chlorobenzene is reacted with 10% NaOH at  $360^\circ C$  and 200 atm pressure. First we get sodium phenoxide which upon treatment with HCl gives phenol. i.e.,

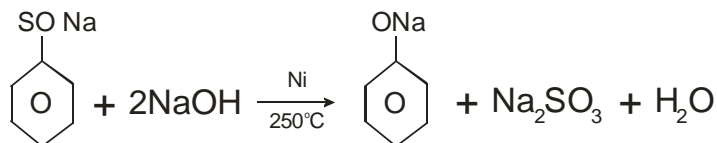


Then,

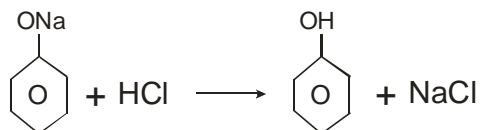


2) From Sodium Salt of Benzene Sulphonic Acid:

When sodium salt of benzene sulphonic acid is reacted with NaOH at about  $250^\circ C$  in the presence of Ni catalyst, we get sodium phenoxide, which upon treatment with HCl gives phenol. i.e.,

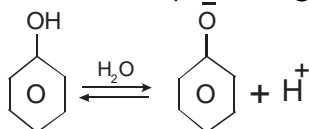


Then,

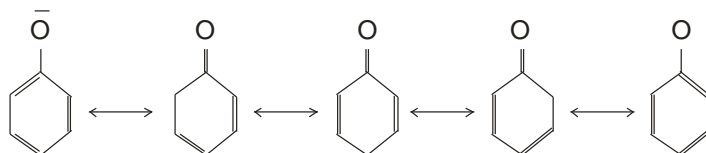


#### Acidic Behaviour of Phenol:

Phenol acts as an acid because it ionizes in water producing  $\text{H}^+$  and a phenoxide ion, i.e.,



The acidic behavior of phenol is due to the stability of phenoxide ion. The negative charge of oxygen of phenoxide ion involves with the pi electrons of benzene ring and thus this negative charge is delocalized on the ring causing resonance phenomenon that makes the phenoxide ion relatively stable. i.e.,



However phenol is so weak acid that it cannot affect the litmus paper and is also unable to evolve  $\text{CO}_2$  from metal carbonates. The ionization constant ( $K_a$ ) for phenol is very small i.e.,  $1.3 \times 10^{-10}$ . The order of acidic strength of phenol alcohol a carboxylic acids and water is;



#### Properties of Phenol:

##### 1) Physical Properties:

From book

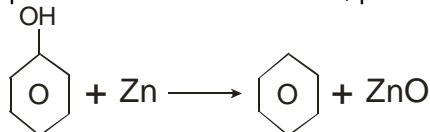
##### 2) Chemical Properties:

Phenol shows two types of chemical reactions.

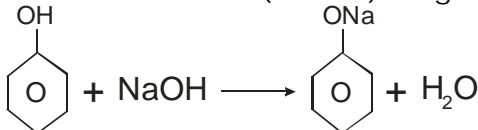
##### a) Reactions due to -OH Group:

Some important reactions of phenol which are due to -OH group, are

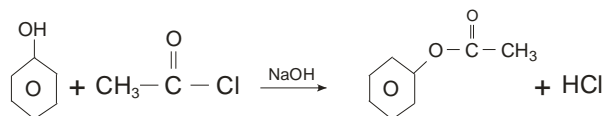
i) Reduction with Zinc: When phenol is reacted with Zn, phenol is reduced to benzene i.e.,



ii) Salt Formation: When phenol reacts with bases (alkalies) we get its salts. E.g,



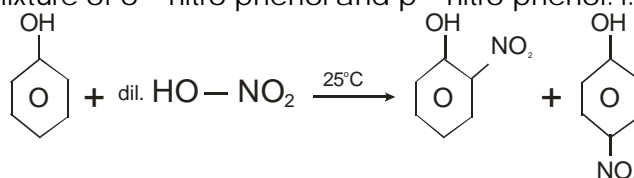
iii) Ester Formation: When phenol reacts with an acid halide in the presence of a base, we get an aromatic ester. E.g,



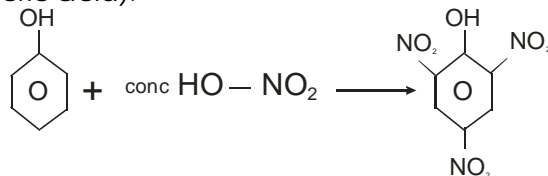
##### b) Reactions Due to Benzene Ring:

The reactions of phenol in which the benzene ring is involved are "Electrophilic Substitution Reactions". Some important electrophilic substitution reactions of phenol are;

i) Nitration: The replacement of one or more H – atoms of phenol by nitro groups ( - NO<sub>2</sub>) when reacted with HNO<sub>3</sub> is known as nitration of phenol. Phenol when reacted with HNO<sub>3</sub> of different concentrations, gives different products. When phenol is reacted with diluted HNO<sub>3</sub> at room temperature, we get a mixture of o – nitro phenol and p – nitro phenol. i.e,

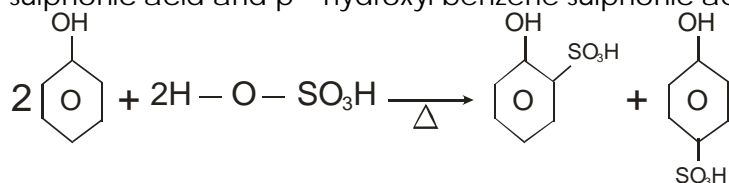


When phenol is reacted with concentrated HNO<sub>3</sub> at high temperature, we get a single product, i.e, 2, 4, 6 – trinitro phenol (picric acid).

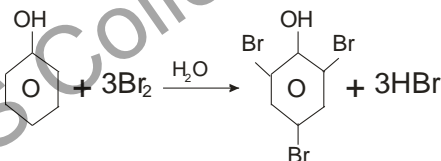


ii) Sulphonation: The replacement of a H of phenol by a sulphonic group ( - SO<sub>3</sub>H) when reacted with concentrated H<sub>2</sub>SO<sub>4</sub> is known as sulphonation of phenol.

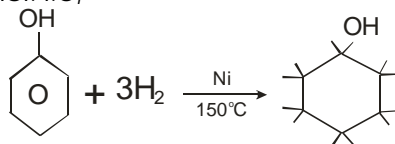
When phenol is reacted with concentrated H<sub>2</sub>SO<sub>4</sub>, we get a mixture of o – hydroxyl benzene sulphonic acid and p – hydroxyl benzene sulphonic acid. i.e,



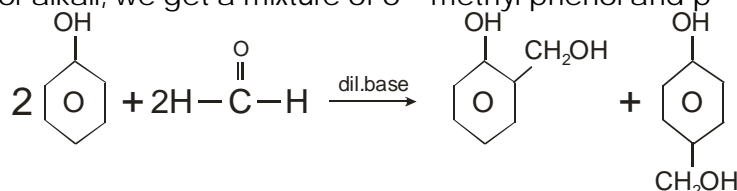
iii) Halogenation: When phenol is reacted with bromine water, a white ppt of 2, 4, 6 – tribromo phenol is obtained. i.e,



iv) Hydrogenation: When hydrogen gas is passed through phenol at about 150°C in the presence of Ni catalyst, we get cyclo-hexanol. i.e,

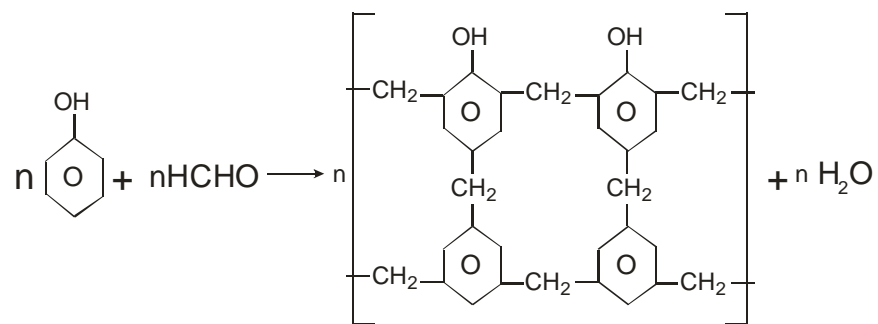


v) With Formaldehyde (HCHO): When phenol reacts with formaldehyde (methanol) in the presence of an acid or alkali, we get a mixture of o – methyl phenol and p – methyl phenol. i.e,



When 'n' molecules of phenol are reacted with 'n' molecules of methanol at high temperature, we get a polymer known as Bakelite. i.e,





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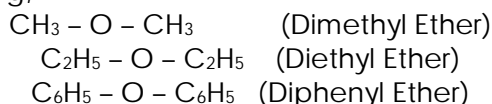
## ETHERS

The organic compounds in which alkyl or aryl groups are attached to both sides of oxygen, are known as ethers.

Types:

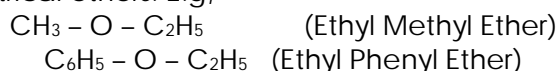
### 1) Simple or Symmetrical Ethers:

The ether in which same alkyl groups are attached to both sides of the oxygen atom are called simple or symmetrical ethers. E.g,



### 2) Mixed or Asymmetrical Ethers:

Those ether molecules in which different alkyl groups are bonded to both sides of "O" atom, are known as mixed or asymmetrical ethers. E.g,



## Methods of Preparation:

Various methods of preparation of ethers are:

### 1) Williamsons Synthesis:

This process completes in two steps. In first step, an alcohol is reacted with sodium metal (Na) to get sodium alkoxide. i.e,

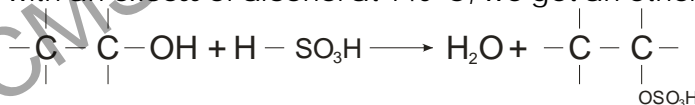


The sodium alkoxide is then reacted with an alkyl halide to get the ether. i.e,

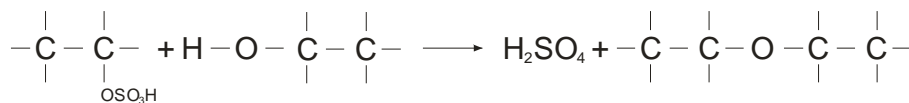


### 2) From Alcohols:

When  $\text{H}_2\text{SO}_4$  is reacted with an excess of alcohol at  $140^\circ\text{C}$ , we get an ether. E.g,

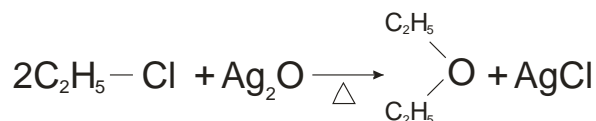


Then,



### 3) Reaction of Alkyl Halide with Silver Oxide:

When silver oxide ( $\text{Ag}_2\text{O}$ ) is reacted with an alkyl halide, in the absence of moisture, we get an ether. E.g,



## Physical Properties:

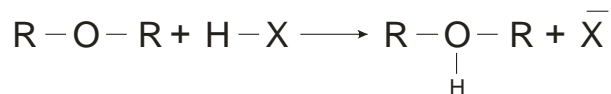
From book.

## Chemical Properties:

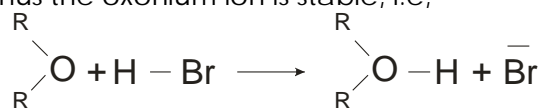
Ethers are usually less reactive.

### Reaction with $\text{H} - \text{X}$ :

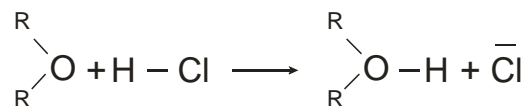
When an ether reacts with a halogen acid ( $\text{H} - \text{X}$ ), the  $\text{H}^+$  of  $\text{H} - \text{X}$  attaches with the "O" of ether by means of a coordinate covalent bond thus producing an oxonium ion and a halide ion. i.e,



The stability of oxonium ion depends upon the nature of  $\text{X}^-$ . If the  $\text{X}^-$  is  $\text{Cl}^-$ , or  $\text{Br}^-$ , then they do not attack on oxonium ion and thus the oxonium ion is stable, i.e.,



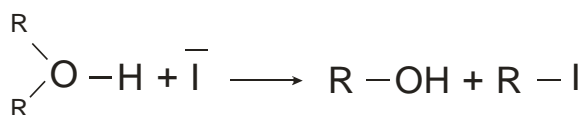
Similarly,



But if the  $\text{X}^-$  is  $\text{I}^-$ , then  $\text{I}^-$  makes the oxonium ion unstable as the  $\text{I}^-$  attacks on the oxonium ion converting it into an alcohol and an alkyl iodide. i.e.,



Then,



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## CARBONYL COMPOUNDS (ALDEHYDES & KETONES)

### Contents:

1. Introduction to Carbonyl Compounds
2. Introduction of Aldehydes & Ketones
3. Various Methods of Preparation of Aldehydes & Ketones
4. A Note of the Reactivity of Carbonyl Compounds
5. Various Chemical Reactions of Carbonyl Compounds including various test for identification of Aldehydes and Iodoform test.

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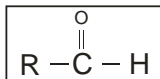
## ALDEHYDES & KETONES

### Carbonyl Compounds:

The organic compounds containing carbonyl group as their functional group or a main part of their functional group are known as carbonyl compounds. Aldehydes and Ketones are carbonyl compounds. A brief introduction of aldehydes and ketones is as follows;

### Aldehydes:

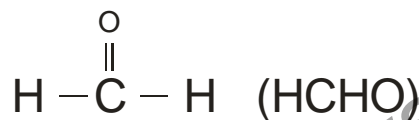
The carbonyl compounds in which the carbon of the carbonyl group is directly bonded to at least one H – atom, are known as aldehydes. The functional group of aldehydes is “Formyl group” (-CHO). The general formula of aldehydes is “ $C_nH_{2n}O$ ”. The general structure of an aldehyde is



Where R = H or an alkyl groups.

Aldehyde groups are present in most sugars. The aldehyde groups are also the main constituents of many essential oils used as fragrances and flavors.

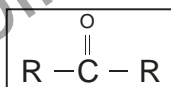
Examples:



### Ketones:

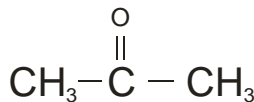
The carbonyl compounds in which the carbon atom of carbonyl group is bonded to two alkyl groups, are known as ketones.

Thus  $-\overset{\text{O}}{\parallel}{\text{C}}-$  is the functional group of ketones. General formula of ketones is “ $C_nH_{2n}O$ ”. The general formula structure of ketones is



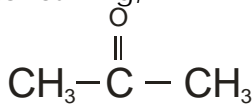
The ketonic group is present in fructose and camphor.

Examples:

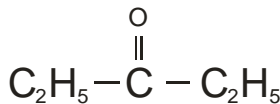


Propanone or Dimethyl Ketone or

Ketones in which two similar alkyl groups (R) are bonded to the carbonyl carbon, are known as “simple or symmetrical ketones”. E.g,

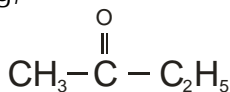


Dimethyl Ketone

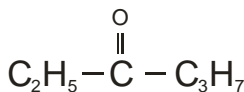


Diethyl Ketone

Ketones in which two different alkyl groups are bonded to carbonyl carbon, are known as “Mixed or Asymmetrical Ketones”. E.g,



Ethyl Methyl Ketone



Ethyl-n-propyl Ketone

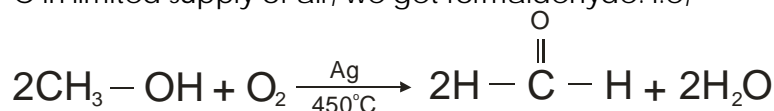
## Methods of Preparation of Aldehydes

### 1) Formaldehyde (HCHO):

Formaldehyde can be prepared by various industrial and laboratory methods. Some important ones are;

#### a) Industrial Methods:

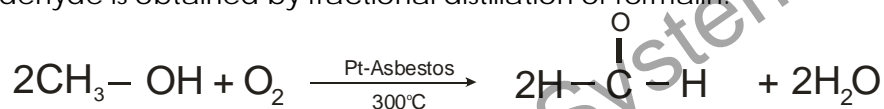
i) By Oxidation of Methanol with Air: When vapours of methanol (CH<sub>3</sub>OH) are passed over silver catalyst at 450°C in limited supply of air, we get formaldehyde. i.e.,



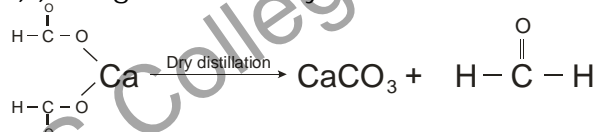
#### b) Laboratory Methods:

i) When a mixture of methanol and air is passed through platinized asbestos catalyst at about 300°C, we get "formalin". Formalin is mixture of 40% formaldehyde (HCHO), 8% methanol (CH<sub>3</sub>OH) and 52% water.

The pure formaldehyde is obtained by fractional distillation of formalin.



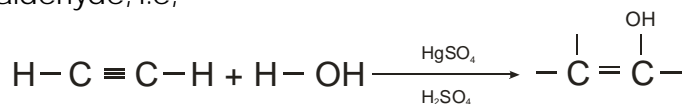
ii) By dry distillation of Calcium Formate: When we perform the process of dry distillation of Calcium Formate (Ca(HCOO)<sub>2</sub>), we get formaldehyde. i.e.,



### 2) Acetaldehyde:

#### a) Industrial Methods:

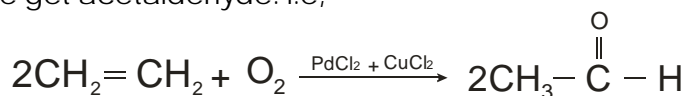
i) From Acetylene (C<sub>2</sub>H<sub>2</sub>): When acetylene reacts with H<sub>2</sub>O in the presence of HgSO<sub>4</sub> & H<sub>2</sub>SO<sub>4</sub> (10%) catalyst, we get an unstable compound, vinyl alcohol, which undergoes rearrangement and converts into acetaldehyde, i.e.,



Then,

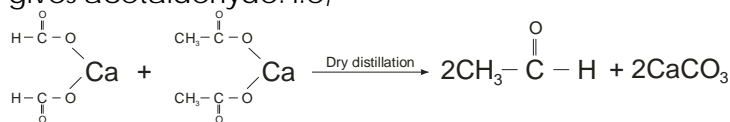


ii) From Ethylene (C<sub>2</sub>H<sub>4</sub>): When ethylene is reacted with air (O<sub>2</sub>) in the presence of PdCl<sub>2</sub> catalyst and CuCl<sub>2</sub> promoter, we get acetaldehyde. i.e.,

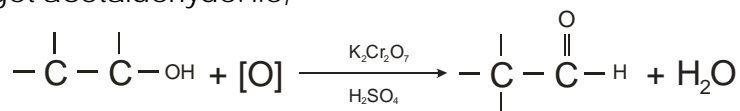


#### b) Laboratory Methods:

i) By dry distillation of Ca – format & acetate: The dry distillation of a mixture of calcium format and calcium acetate gives acetaldehyde. i.e,



ii) By oxidation of ethanol (C<sub>2</sub>H<sub>5</sub>OH): When ethanol is reacted with a strong oxidizing agent like K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + H<sub>2</sub>SO<sub>4</sub>, we get acetaldehyde. i.e,



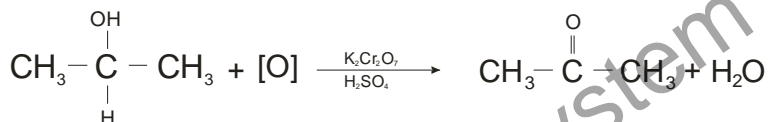
## Methods of Preparation of Ketones:

Acetone (CH<sub>3</sub>)<sub>2</sub>CO:

Various methods for the preparation of acetone are as follows;

1) By Oxidation of Secondary Alcohol (Isopropyl alcohol):

When isopropyl alcohol (2 – propanol) is reacted with a strong oxidizing agent like K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + H<sub>2</sub>SO<sub>4</sub>, we get actone. i.e,



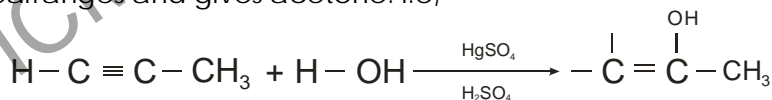
2) By Dry Distillation of Calcium Acetate:

Dry distillation of calcium acetate give acetone. i.e,

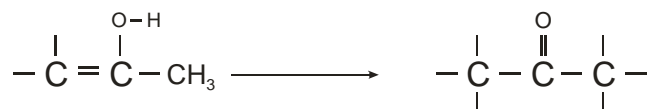


3) By Hydration of Propyne:

When propyne is reacted with H<sub>2</sub>O in the presence of HgSO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>, we get an unstable compound which rearranges and gives acetone. i.e,



Then,



Note:

Study Physical properties & uses of Aldehydes and Ketones from book.

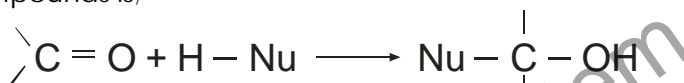
### Reactivity of Carbonyl Group:

A carbonyl group has a double covalent bond between C & oxygen atoms, in which one is sigma bond and the other is pi bond. As O is more electronegative than C, therefore, O pulls the pi electron density, more towards itself as compared to carbon atom. Thus oxygen gets a partial negative charge and carbon gets a partial positive charge. Thus we can say that oxygen gets nucleophilic character while carbon gets electrophilic character.

Due to the presence of polar bond in carbonyl group, a nucleophile can attack on its carbon and an electrophile can attack on its oxygen atom. Thus we say that, "Nucleophilic addition reactions" can easily occur in carbonyl compounds. The nucleophilic addition reactions of carbonyl compounds are usually catalysed by an acid or base.

The acid catalyst promotes the nucleophilic attack on carbonyl group because it (acid) provides  $H^+$  which combines with oxygen of carbonyl group, the increasing the electrophilic character of the carbonyl carbon and thus carbon can now easily be attacked by the attacking nucleophile.

A base catalyst increases the nucleophilic character of the reagent (compound which reacts with carbonyl compound). The base reacts with reagent taking out the positive portion of the reagent thus making the nucleophilic portion ( - ve part) of the reagent free which immediately attacks on the carbon of the carbonyl group. The general representation of nucleophilic addition reaction of carbonyl compounds is;



The carbonyl carbon has got  $sp^2$  hybridization. Thus the carbonyl group has a planar geometry with each bond angle of  $120^\circ$ .

### Reactions of Carbonyl Compounds:

The major reactions of carbonyl compounds are nucleophilic addition reactions. Other important reactions of carbonyl compounds are oxidation reactions and reduction reactions. These reactions of carbonyl compounds are discussed as;

#### 1) Nucleophilic Addition Reactions:

On the basis of nature of catalyst used, there are two types of nucleophilic addition reactions of carbonyl compounds;

##### a) Base Catalysed Nucleophilic Addition Reactions:

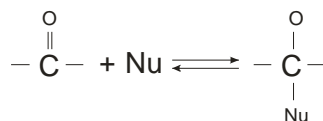
The base catalysed addition reactions of carbonyl compounds occur with a strong nucleophilic reagent (compound containing a strong nucleophile). Here the base reacts with the reagent takes away its positive portion and thus a strong nucleophile is generated. The nucleophile is actually the negative part of the reagent. Then this strong nucleophile attacks on the carbonyl carbon thus making the addition reaction possible.

The general mechanism of the base catalysed addition reactions of carbonyl compounds is;

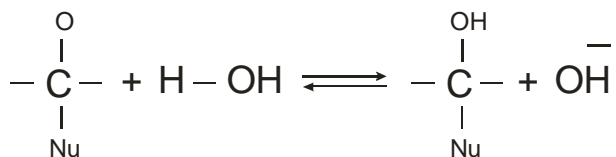
Step 1



Step 2



Step 3

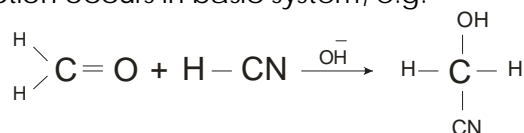


Some important base catalysed addition reactions of carbonyl compounds are;

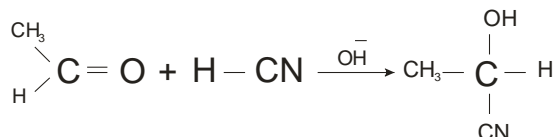


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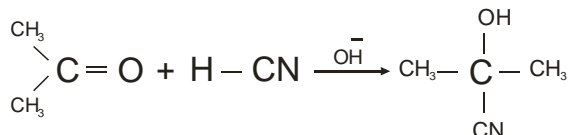
i) Addition of Hydrogen Cyanide: Hydrogen cyanide (HCN) adds into aldehydes and ketones to form cyanohydrins. The reaction occurs in basic system, e.g.



Similarly,



Similarly,



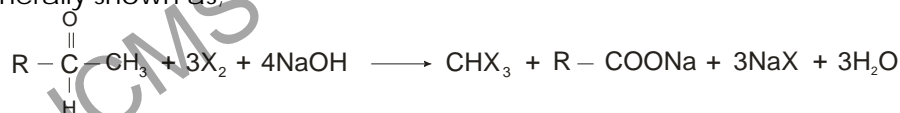
ii) Addition of Grignard's Reagent: When G.R. reacts with an aldehyde or ketone, the Grignard reagent adds into the carbonyl group forming an addition product (adduct). The addition product, gives an alcohol upon acid hydrolysis.

Note: Reactions are already discussed in [Chapter 10](#), see there.

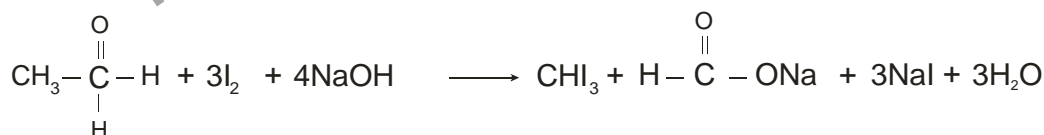
iii) Haloform Reaction: In case of aldehydes only acetaldehyde ( $\text{CH}_3\text{CHO}$ ) and in case of Ketones, all methyl ketones react with halogens ( $\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ) in the presence of  $\text{NaOH}$  and form a compound known as "Haloform ( $\text{CHX}_3$ )". The haloform may be chloroform ( $\text{CHCl}_3$ ), bromoform ( $\text{CHBr}_3$ ) or iodoform ( $\text{CHI}_3$ ). Such reactions of carbonyl compounds is known as haloform reactions.

Note:

Iodoform is yellow colored solid compound which is water insoluble. Therefore the iodoform reaction can be used as test for identification of acetaldehyde and methyl ketones. The haloform reaction be generally shown as:



Example,

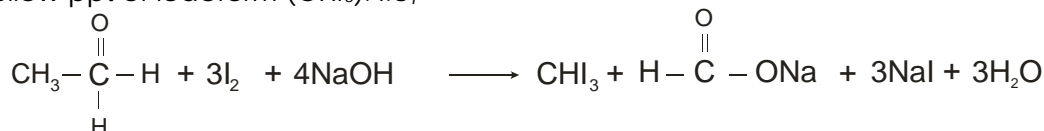


#### ODOFORM TEST:

The reaction of iodine crystals ( $\text{I}_2$ ) with a compound in the presence of  $\text{NaOH}$  to form a yellow ppt (precipitate) of iodoform ( $\text{CHI}_3$ ) is known as iodoform test. Iodoform test can be used for the identification of the following compounds;

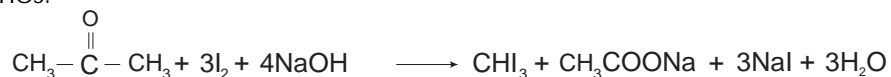
##### 1) Acetaldehyde ( $\text{CH}_3\text{CHO}$ ):

Acetaldehyde is the only aldehyde molecule, which reacts with  $\text{I}_2$  in the presence of  $\text{NaOH}$  and forms a yellow ppt of iodoform ( $\text{CHI}_3$ ). i.e.,



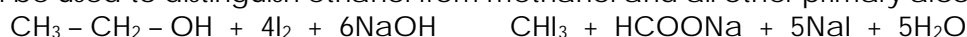
##### 2) Methyl Ketones:

Only methyl ketones (ketones containing methyl group) react with  $I_2$  in the presence of NaOH to form a yellow ppt of iodoform. Thus the reaction can be used for distinguishing a methyl ketone from other ketones.



### 3) Ethanol ( $C_2H_5OH$ ):

Ethanol is the only primary alcohol which reacts with  $I_2$  in the presence of NaOH to form a yellow ppt of iodoform. All other primary alcohols and methanol do not undergo this reaction. Thus this reaction can be used to distinguish ethanol from methanol and all other primary alcohols. i.e.

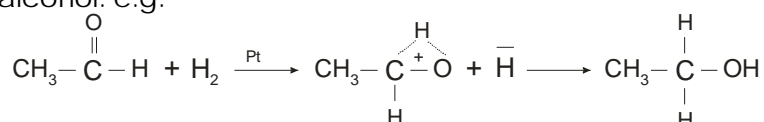


Note:

Secondary alcohols containing methyl group also undergo this reaction.

### 4) Addition of Hydrogen:

$H_2$  is added in the carbonyl group of a carbonyl compound in the presence of Pt or Ni catalyst and thus we get an alcohol. e.g.



### 5) Aldol Condensation:

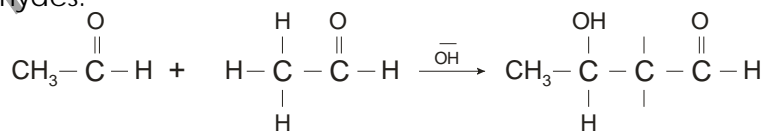
**Condensation Reaction:** A reaction in which two similar or different molecules combine producing a new compound with or without the formation of a small molecule like  $H_2O$ ,  $NH_3$  etc. is known as condensation reaction.

A reaction in which two similar or different carbonyl compounds containing  $\alpha$ -hydrogen, combine to form an "aldol" (a molecule containing aldehydic group and alcoholic group) or "Ketol" (a molecule containing a ketonic group and alcoholic group), with the elimination of  $H_2O$ , is known as "Aldol Condensation".

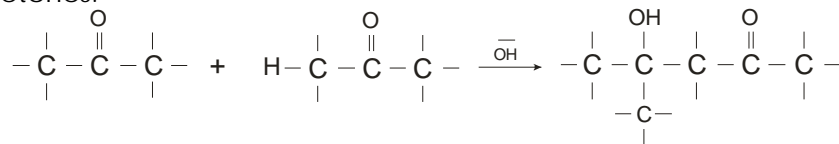
Aldol condensation takes place only when two carbonyl compounds, containing  $\alpha$  hydrogen atom, combine in mild alkaline conditions. Aldol condensation can occur

- Between two aldehydes (similar or different)
- Between an aldehyde and a ketone
- Between two ketones (similar or different)

#### i) Between two Aldehydes:



#### ii) Between two Ketones:



Note:

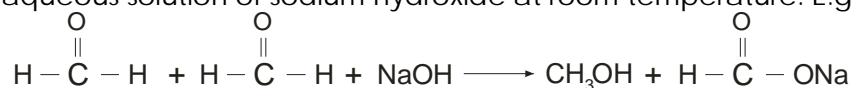
Upon heating an aldol, loses a molecule of  $H_2O$  to form an unsaturated aldehyde.

Carbonyl compounds having no  $\alpha$  hydrogen atom do not form an aldol, when they combine, and thus do not undergo Aldol Condensation.

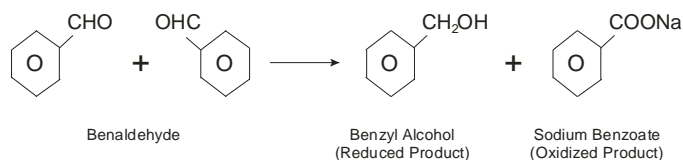
Formaldehyde ( $HCHO$ ) and Benzaldehyde ( $C_6H_5CHO$ ) are the carbonyl compounds which do not have  $\alpha$  hydrogen. When the carbonyl compounds containing no  $\alpha$  hydrogen, combine, they undergo "Cannizzaro's Reaction" instead of "Aldol Condensation". Cannizzaro's reaction can be explained as,

**Cannizzaro's Reaction:** Aldehydes having no  $\alpha$  hydrogen atom when combine, they undergo Cannizzaro's reaction. It is a disproportionate (self oxidation – reduction) product and the

other is oxidized product. The reduced product is a carboxylic acid. This reaction occurs in the presence of 50% aqueous solution of sodium hydroxide at room temperature. E.g.



Similarly,



#### b) Acid Catalysed Nucleophilic Addition Reaction:

In these reactions, the acid (catalyst) increases the electrophilic character of the carbonyl carbon and thus the attack of the weaker nucleophilic carbon of carbonyl carbon becomes easier.

Here the  $\text{H}^+$  of the acid attacks on the oxygen of carbonyl group and thus makes the carbonyl carbon positive and we say that the electrophilic character of the carbonyl carbon is increased. The general mechanism of such reactions is ;



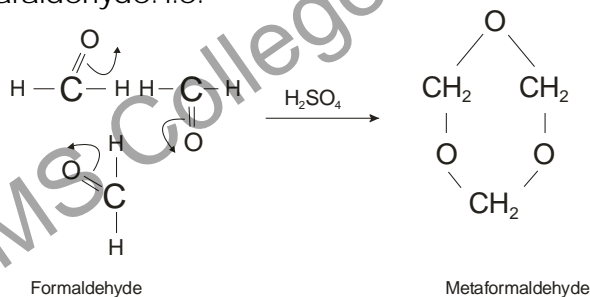
Then,



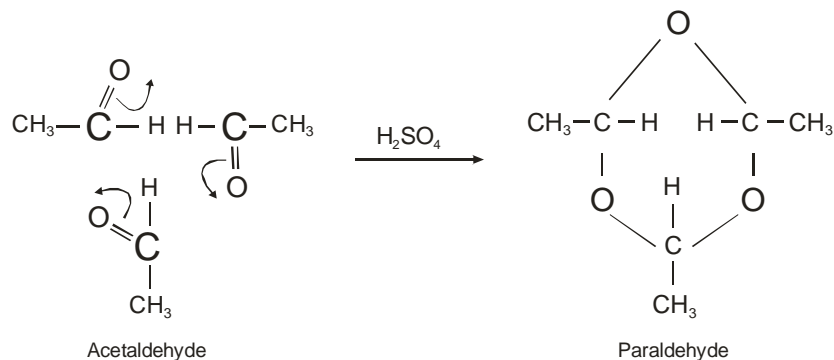
Some important acid catalysed nucleophilic addition reactions of carbonyl compounds are:

#### 1) Polymerization:

Formaldehyde and acetaldehyde undergo polymerization in the presence of  $\text{dil. H}_2\text{SO}_4$  to form metaformaldehyde and paraldehyde. i.e.

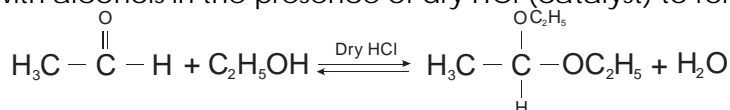


And,



#### 2) Addition of Alcohols:

Aldehydes combine with alcohols in the presence of dry  $\text{HCl}$  (catalyst) to form an acetal. E.g.



Ketones do not give this reaction under these conditions.

## OXIDATION REACTIONS:

Due to the presence of C – H bond (i.e. carbon is carbonyl carbon), the aldehydes can easily be oxidized both by strong as well as mild oxidizing reagents. On the other hand due to the C – C bond, ketones are not easily oxidized. Ketones are only oxidized by strong oxidizing agents and cannot be oxidized by mild oxidizing agents. The oxidizing reactions of aldehydes and ketones are explained as;

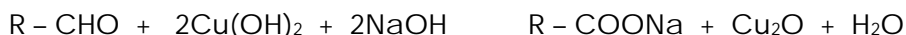
### Oxidation of Aldehydes:

Due to the presence of C – H bond, aldehydes can easily be oxidized by mild oxidizing agents like Fehling Solution, Tollen's reagent etc.

#### 1) With Fehling's Solution:

(Test for identification of aldehydes)

Aqueous solution of cuprihydroxide ( $\text{Cu}(\text{OH})_2$ ) and NaOH is known as Fehling's Solution. When an aliphatic aldehyde, reacts with Fehling's solution, the aldehyde gets oxidized to the Na salt of the corresponding acid (carboxylic acid) and ( $\text{Cu}_2\text{O}$ ) is formed which proves the presence of aldehyde. i.e.



- Ketones do not give this reaction.

#### 2) With Tollen's Reagent:

(Silver mirror test for identification of aldehydes)

Aqueous ammoniacal solution of silver nitrate ( $\text{AgNO}_3 + \text{NH}_4\text{OH}$ ) is known as Tollen's reagent. When an aldehyde is reacted with Tollen's reagent in a test tube, the aldehyde is oxidized to ammonium salt of the corresponding carboxylic acid and silver gets reduced from +1 to 0 oxidation state. The silver metal (Ag) formed, accumulates on the walls of the test tube and looks like mirror, which proves the presence of aldehyde. This test is called as Silver mirror test for aldehydes.



- \* Ketones do not give this reaction because ketones can be oxidized by Tollen's reagent.

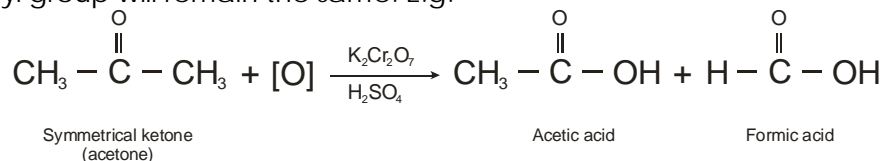
Aldehydes can also be oxidized by strong oxidizing agents like  $\text{KMnO}_4 + \text{H}_2\text{SO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$  or dil.  $\text{HNO}_3$ , to the corresponding carboxylic acid.

### Oxidation of Ketones:

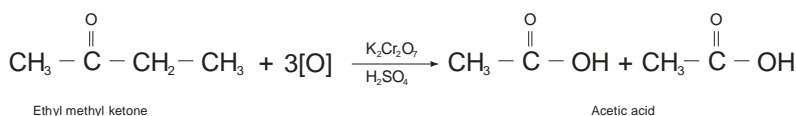
Ketones cannot be oxidized by mild oxidizing agents like Tollen's reagent or Fehling's solution, because the C – C bond is not easy to be oxidized.

Ketones are oxidized only by strong oxidizing agents like  $\text{KMnO}_4 + \text{H}_2\text{SO}_4$ , dil.  $\text{HNO}_3$ ,  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ . The ketones are oxidized by strong oxidizing agents to carboxylic acids.

If there is a symmetrical ketone (both alkyl groups bonded to carbonyl groups are same), then only one of the two carbon atoms bonded to carbonyl carbon will be oxidized to carboxylic acid and the carbonyl group will remain the same. E.g.



If there is an unsymmetrical ketone, where the two carbon atoms bonded to carbonyl carbon, do not have same number of hydrogen atoms, then that carbon atom (of the two bonded with carbonyl carbon) will be oxidized to a carboxylic acid, which has smaller number of hydrogen atoms. E.g.



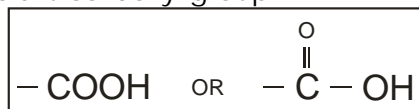
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## CARBOXYLIC ACIDS

### INTRODUCTION TO CARBOXYLIC ACIDS:

The organic compounds containing carboxylic group (-COOH) are known as carboxylic acids. Functional group of carboxylic acid is carboxyl group.

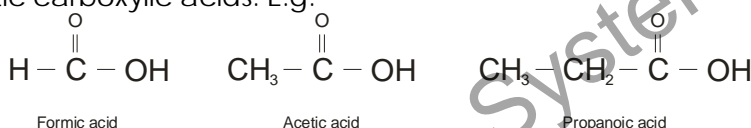


The carboxyl group is a combination of two group, i.e. carbonyl group and hydroxyl groups (-OH). Therefore, the carbonyl group has got its name, "Carboxyl Group", where "carbo" is for "carbonyl" and "xyl" is for "hydroxyl".

Based on the nature of atom of group of atoms bonded with the carbon atom of the carboxyl group we have two types of carboxylic acids.

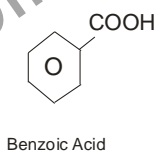
#### 1) Aliphatic Carboxylic Acids:

Those carboxylic acids in which a "H" or an "alkyl group (R)" is bonded with the carboxyl group are known as aliphatic carboxylic acids. E.g.



#### 2) Aromatic Carboxylic Acids:

Those carboxylic acids in which an aryl group is bonded with the carboxyl group are known as aromatic carboxylic acids. E.g.

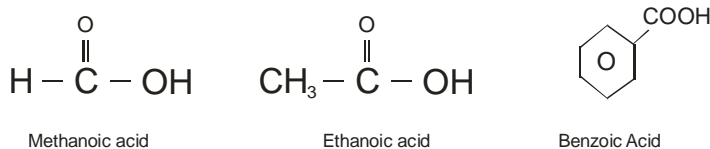


### CLASSIFICATION OF CARBOXYLIC ACIDS:

Based on the number of carboxyl groups, carboxylic acids are classified into the following types;

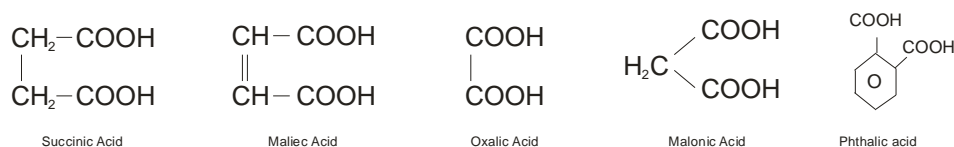
#### 1) Mono - Carboxylic Acids:

The carboxylic acids containing one carboxylic group (-COOH) are known as mono-carboxylic acids. E.g.



#### 2) Di - Carboxylic Acids:

The carboxylic acids containing two carboxyl groups are known as di - carboxylic acids. E.g.



## GENERAL METHODS OF PREPARATION:

Carboxylic acids can be prepared by the following general methods.

### A) Laboratory Methods:

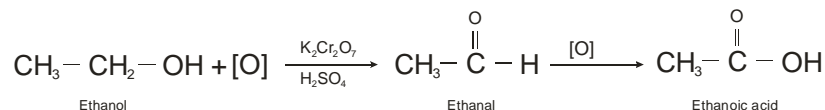
Some important laboratory methods for the preparation of carboxylic acids are;

#### 1) By Oxidation of Primary Alcohols & Aldehydes:

The alcohols and aldehydes can easily be oxidized to carboxylic acids by strong oxidizing agents like  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ ,  $\text{KMnO}_4 + \text{H}_2\text{SO}_4$  etc.

The aldehydes being more reactive, can also be oxidized to carboxylic acids by mild oxidizing agents like Tollen's reagent, Fehling Solution etc.

e.g.

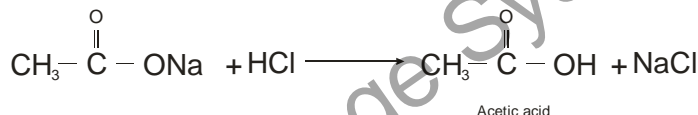


#### 2) By Hydrolysis of Esters:

When an ester is boiled with concentrated sodium hydroxide, we get sodium salt of a carboxylic acid. This sodium salt of the carboxylic acid upon treatment with dil. HCl gives a carboxylic acid.



Then,



#### 3) From Alkyl Nitriles:

When an alkyl nitrile ( $\text{R} - \text{CN}$ ) is boiled with an acid ( $\text{H}^+$ ) or alkali ( $\text{OH}^-$ ), a carboxylic acid is produced.

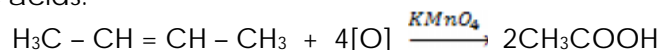


#### 4) From Girgnard's Reagent:

Already discussed in Chapter No. 10, plz see from there.

#### 5) By Oxidative Cleavage of Alkenes:

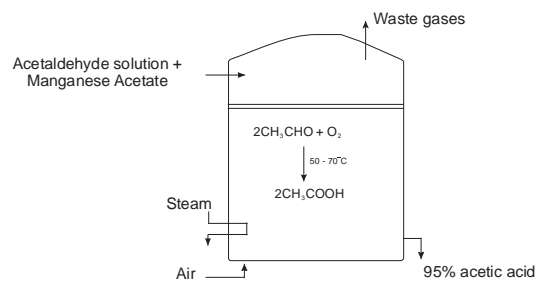
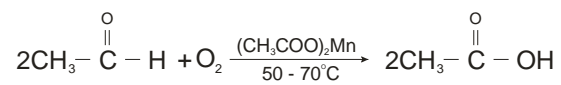
When alkenes are heated with alkaline  $\text{KMnO}_4$  solution, the alkenes are cleaved at the double bond to form carboxylic acids.



### B) Industrial Preparation:

Industrially or commercially, acetic acid is prepared by the oxidation of acetaldehyde ( $\text{CH}_3\text{CHO}$ ) with air ( $\text{O}_2$ ). In this method, a high pressurized air is passed through a concentrated solution of acetaldehyde in a stainless steel vessel. A small amount of manganese acetate ( $(\text{CH}_3\text{COO})_2\text{Mn}$ ) is added to prevent the formation of paracetic acid. The process is carried out at  $50 - 70^\circ\text{C}$ . The crude acetic acid obtained is purified by the process of distillation. The chemical reaction occurring during the process is;





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## PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS:

- First three members are colorless liquids having a pungent smell. Next three members have unpleasant smell.
- Due to hydrogen bonding, first four carboxylic acids are water soluble.
- Melting points are irregular but boiling points increase with increasing molecular mass of aliphatic carboxylic acids.
- Due to the hydrogen bonding, carboxylic acids exist as cyclic dimers i.e. each cycle has two molecules of a carboxylic acid.

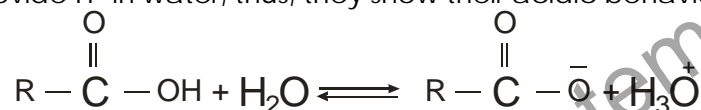
## CHEMICAL PROPERTIES OF CARBOXYLIC ACIDS:

As the functional group of carboxylic acids (-COOH) contains both a carbonyl group and a hydroxyl group, therefore, carboxylic acids show the chemistry of both the carbonyl and the hydroxyl groups. However, in most of the reactions of carboxylic acids, the carboxyl group, as a whole, is rarely involved.

Carboxylic acids show following types of chemical reactions:

A) As an acid (Reactions in which "H" of Carboxyl group is involved):

As carboxylic acids provide  $H^+$  in water, thus, they show their acidic behavior. i.e.



Some examples are as follow;

i) Reaction with Base: Carboxylic acids react with bases to form salt and water.  
e.g.



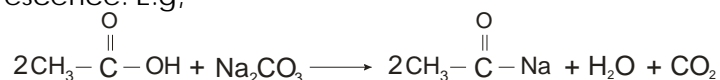
ii) Reaction with Metals: Carboxylic acids react with active metals like Na, K, Mg etc. to form their salts with the evolution of  $H_2$  gas. E.g.



Similarly,



iii) Reaction with Carbonates & Bicarbonates: When carboxylic acids react with metal carbonates and bicarbonates salts of the corresponding metals are produced and  $CO_2$  gas is liberated with effervescence. E.g,

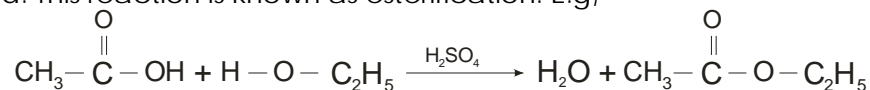


## B) Reactions Involving "-OH" Group of Carboxyl Group:

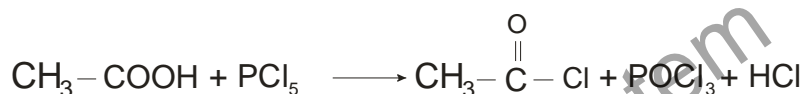
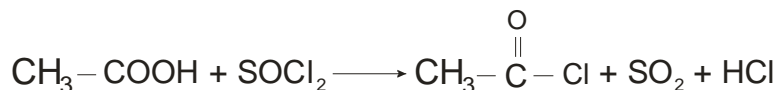
As carboxylic group (-COOH) of carboxylic acids contain carboxylic group which can easily be attacked by a nucleophile due to positive charge on carbon. So when a nucleophile attacks on the carbonyl carbon of the carboxyl group, the elimination of -OH group takes place, and thus a derivative of the carboxylic acid is produced.

Some examples of such reactions are;

i) Esterification: When a carboxylic acid reacts with an alcohol in the presence of an acid, an ester is formed. This reaction is known as esterification. E.g,



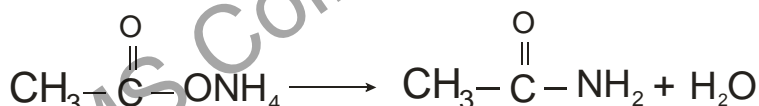
ii) With PCl<sub>5</sub> & SOCl<sub>2</sub>: When a carboxylic acid reacts with PCl<sub>5</sub> or SOCl<sub>2</sub>, an acid halide is formed. i.e,



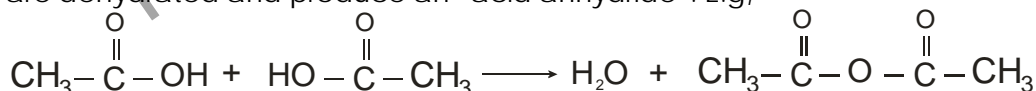
iii) Formation of Amide (Reaction with NH<sub>3</sub>): When a carboxylic acid reacts with NH<sub>3</sub>, an ammonium salt is formed which on heating produce an acid amide. E.g,



Then,



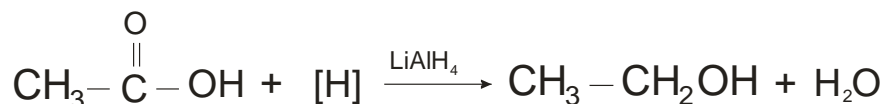
iv) Formation of Acid Anhydride: When carboxylic acids are strongly heated in the presence of P<sub>2</sub>O<sub>5</sub>, they are dehydrated and produce an "acid anhydride". E.g,



## C) Reactions Involving Carboxyl Group:

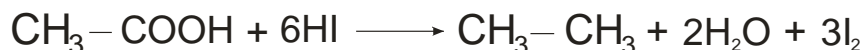
i) Partial Reduction of Alcohols: Carboxylic acids on reaction with lithium aluminium hydride (LiAlH<sub>4</sub>) are reduced to alcohols.

e.g,



ii) Complete Reduction to Alkanes: Carboxylic acids on reduction with HI and red phosphorous give alkanes.

e.g,



## AMINO ACIDS:

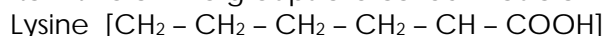
When  $\alpha$ ,  $\beta$  or  $\gamma$  - H of a carboxylic acid is replaced by an amino group ( $-\text{NH}_2$ ) we get a new organic compound which is known as "Amino acid". The amino acids are actually the substitute product of carboxylic acids depending upon the nature of carbon atom, to which amino group is bonded the amino acids may be "alpha amino acids", "beta amino acids" or "gamma amino acids".

Almost all the naturally occurring amino acids are  $\alpha$  - amino acids. These amino acids are very important because they are the building blocks of proteins.

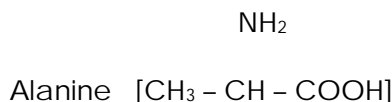
The amino acids which contain two carboxyl groups are called "acidic amino acids". E.g,



The amino acids which contain two amino groups are called "Basic amino acids". E.g,



The amino acids which contain one amino group and one carboxyl group are called "neutral amino acids". E.g,



Note:

About 20 of the amino acids have been identified as the constituents of most of the animal and plants proteins.

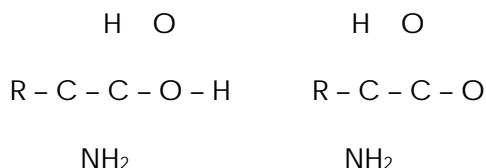
## Essential and Non-essential Amino Acids:

Out of the 20 amino acids, which are required for protein synthesis, the human body can synthesis 10. These 10 amino acids are called as "essential amino acids".

The remaining 10 amino acids, which the human body is not able to synthesis, and are got by the human body through diet, are called "non-essential amino acids".

## Structure of Amino Acids:

The amino acids usually exist as dipolar ion which is called as "ZWITTER ION". The zwitter ion has positive and negative ends within the same molecule. A zwitter ion is formed because of the transformation of the proton ( $\text{H}^+$ ) of the carboxy group ( $-\text{COOH}$ ) to the amino group ( $-\text{NH}_2$ ) due to the lone pair of "N". i.e,

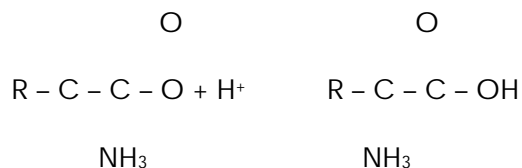


The dipolar structure is also called as "internal salt". All  $\alpha$  - amino acids exist largely in dipolar ionic form (zwitter ion).

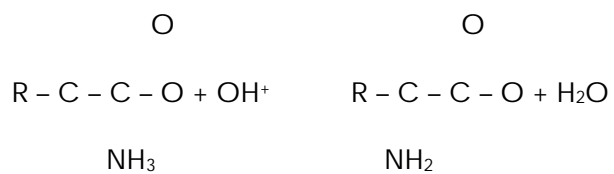
## Acidic and Basic Character of Amino Acids:

Due to dipar ionic structure, the amino acids can possess both acidic and basic character, like

a) when an acid is added to an amino acid, the carboxyl group accept the  $\text{H}^+$  of acid and thus acts as a base, i.e,



b) When a base is added to an amino acid, the  $\text{NH}_3$  group of the amino acid gives a proton to the OH of base. i.e,



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