UNIT - 1

ALIPHATIC HYDROCARBONS

CONTENTS

1.1 ALKANES

What are alkanes?

Alkanes are the simplest class of organic compounds. They are made of carbon and hydrogen atoms only. Alkanes form a homologous series with the general formula C_nH_{2n+2}, where n is the number of carbon atoms in the molecule. The first member of the family has the molecular formula CH_4(n=1) and is commonly known as methane and the second member with molecular formula C_2H_6(n=1) is called ethane. These compounds are also known as the **saturated hydrocarbons.**

GENERAL METHODS OF PREPARATION

The first five members of the alkane series can be obtained in the pure form by the fractional distillation of petroleum and natural gas. The alkanes can be prepared by the following general methods.

- **Hydrogenation of Alkenes and Alkynes**

Alkanes are formed by passing a mixture of an unsatured hydrocarbon and hydrogen over finely divided nickel at 200-300^{0}C (Sebatier and Senderens Reaction).

$$\underset{\text{Alkene}}{R\text{-}CH{=}CH_2} + H_2 \xrightarrow{Ni, 200-300^\circ C} \underset{\text{alkane}}{RCH_2CH_3}$$

$$CH_2{=}CH_2 \quad + H2 \xrightarrow{Ni, 200-300℃} CH_3CH_3$$

Ethene ethane

$$CH_3CH{=}CH_2 \quad + H_2 \xrightarrow{Ni, 200-300℃} CH_3CH_2CH_2$$

Propene propane

- **Decarboxylation of Carboxylic acids**

When the sodium salt of a carboxylic acid, RCOONa, is heated strongly with sodalime (NaOH + CaO), a molecule of carbon dioxide is split off as carbonate and an alkane is obtained.

$$RCOONa \quad + \quad NaOH \xrightarrow{\Delta} RH \quad + \quad Na_2CO_3$$

Sodium salt of a
arboxylic acid alkane

$$CH_3COONa \quad + \quad NaOH \xrightarrow{\Delta} CH_4 \quad + \quad Na_2CO_3$$

Sodium acetate methane

$$CH_3CH_2COONa + NaOH \xrightarrow{\Delta} CH_3CH_3 + Na_2CO_3$$

Sodium propionate ethane

- **Reduction of Alkyl halides**

When reduced with nascent hydrogen, alkyl halides are converted directly to the corresponding alkanes.

$$R{-}X \quad + 2[H] \longrightarrow R{-}H \quad + \quad HX$$

Alkyl halide alkane

$$CH_3I \quad + 2[H] \longrightarrow CH_4 \quad + \quad HI$$

Methyl iodide methane

The reaction occurs best with iodides and bromides.

- **Action of Sodium on alkyl halides (Wurtz Reaction)**

Higher alkanes are produced by heating an alkyl halide (RX) with sodium metal in dry ether solution.

$$R{-}X \; +2Na \; + \; XR \xrightarrow{\text{dry ether}} R{-}R \; + \; 2NaX$$

alkyl halide alkane

$$CH_3Br \; +2Na \; + \; BrCH_3 \xrightarrow{\text{dry ether}} CH_3{-}CH_3 \; +2NaBr$$

methyl bromide ethane

- **Hydrolysis of Grignard Reagent**

Alkylmagnesium halides on treatment with water, decompose to give alkanes containing the same number of carbon atoms as the original alkyl halide.

$$\text{R-X} + \text{Mg} \xrightarrow{\text{dry ether}} \text{R-Mg-X}$$

Alkyl halide   alkylmagnesium halide

$$\text{R-MgX} + \text{HO-H} \longrightarrow \text{R-H} + (\text{MgOH}^{+})\text{X}^{-}$$

water   alkane

$$CH_3CH_2Br + Mg \xrightarrow{\text{dry ether}} CH_3CH_2MgBr$$

ethyl bromide   ethylmagnesium halide

$$CH_3CH_2MgBr + H_2O \longrightarrow CH_3CH_3 + (MgOH^{+})X^{-}$$

ethane

PROPERTIES

Physical properties

(1) The first four alkanes(C_1 to C_4) i.e., four methane to butane are gases. The next thirteen members (C_5 to C_{17}) i.e., from pentane to heptadecane are liquids. The higher members (C_{18} onwards) are waxy solids.

(2) They are soluble in non polar solvents such as benzene and carbon tetrachloride.

(3) The boiling points of n-alkanes increase in a smooth manner with increasing molecular weight. The melting points do not increase in such a regular fashion.

(4) The branched chain isomer will have a lower boiling point than the corresponding n-isomer. Thus n-butane has a boiling point 0° while isobutene boils at -12°. Furthermore, more numerous the branches, the lower the boiling point. Thus isopentane with one branch chain boils at 28°, while neopentane with two branch chain boils at 9.5°,with branching the shape of the molecule tends to approach that of a sphere and thus the surface area decreses. As a result of the decrease of surface area, the intermolecular forces become weaker and can be overcome at a lower temperature.

(5) The density of alkanes also increases with the size of the molecule.

Chemical properties

Alkanes are relatively stable to most of the common reagents at room temperature.They do not react with acids,base,oxidizing agents,reducing agents and active metals.Alkanes undergo only two types of reactions.They are

a) Substitution reaction
b) Thermal and Catalytic reaction

(a) Substitution reaction

In this reaction, one or more of the H-atoms of alkane are substituted by either atoms like chlorine and bromine or by certain groups like nitro ($-NO_2$), Sulphonic ($-SO_3H$), etc.,

(1) Halogenation

It involves the substitution of H-atoms of alkanes by as many halogen atom i.e,by chlorine (chlorination) by bromine(bromination)

(a) Chlorination

The chlorination of alkanes can be brought about by the reaction of chlorine on them in the presence of diffused sunlight or ultraviolet light, or when heated to high temperature (300-400°C).

Methane react with chlorine in the presence of ultraviolet light, or at high temperature (300°) to yield methyl chloride or chloromethane and hydrogen chloride.

$$CH_4 \quad + \quad Cl_2 \xrightarrow{UV\ light\ or\ \Delta} CH_3Cl \qquad + \quad HCl$$

Methane methyl chloride

The reaction does not stop at this stage and the remaining three H-atoms of methyl chloride can be successively replaced by chlorine atoms.

$$CH_3\,Cl + Cl_2 \xrightarrow{UV\ light\ or\ \Delta} CH_2Cl_2 + HCl$$

methane methylene chloride

$$CH_2Cl_2 + C\,l_2 \longrightarrow CHCl_3 + HCl$$

trichloromethane

$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$

tetrachloromethane

In actual practice all the four (CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4) substitution products are obtained.The extent to which each product is formed depends on the initial chlorine to methane ratio.

Mechanism of chlorination

The chlorination of alkanes takes place through the formation of free radicals as intermediates.Thus, for the chlorination of methane the following steps have been proposed.

(1) $Cl \ :Cl \xrightarrow{h\gamma} Cl\cdot \ + Cl\cdot$ [Initiation step]

Free radicals

(2) $Cl\,. + H \ : CH_3 \longrightarrow HCl + \dot{C}H_3$ [Propagation step]

Methyl free radicals

(3) $Cl \ : Cl + \ .CH_3 \longrightarrow Cl\,. + CH_3Cl$

Methyl chloride

(4) $Cl^{\cdot} + Cl^{\cdot} \longrightarrow Cl\text{-}Cl$

(5) $Cl^{\cdot} + {}^{\cdot}CH_3 \longrightarrow CH_3\text{-}Cl$ } Termination step

(6) $CH_3^{\cdot} + {}^{\cdot}CH_3 \longrightarrow CH_3\text{-}CH_3$

The reaction is initiated in step 1 by the homolytic fission of the chlorine molecule due to the action of heat or light resulting in the production of chlorine free radicals.

In step (2), the chlorine free radicals attack a molecule of methane to form a stable molecule of HCl and methyl free radicals.

In step (3), the methyl free radicals react with chlorine molecule to yield methyl chloride and chlorine free radicals. The chlorine free radicals can again attack another molecule of methane as in step (2), The sequence of reaction in steps (2) and (3) is repeated over and over again ,and thus the chain reaction is propagated.A free radical mechanism,in general has three major steps namely initiation , propagation and termination.

(2) Nitration

When a mixture of an alkane and nitric acid vapours is heated at 400-500℃, one hydrogen atom on the alkane is substituted by a nitro group ($-NO_2$). The process is called **vapour phase nitration**, and yields a class of compounds called nitroalkanes.

$R\text{-}H \quad + \quad HO\text{-}NO_2 \quad \xrightarrow{400-500^\circ} \quad R\text{-}NO_2 + H_2O$
alkane nitric acid nitroalkane

$CH_3\text{-}H \quad + \quad HO\text{-}NO_2 \quad \xrightarrow{450^\circ} \quad CH_3\text{-}NO_2 + H_2O$
Methane nitromethane

(3) Sulphonation (substitution of $-SO_3H$ for H)

When alkanes are subjected to a prolonged reaction with fuming sulphuric acid,one hydrogen atom on the alkane is replaced by a sulphonic acid group($-SO_3H$).This process is called sulphonation and the products are alkylsulphonic acids.

$R\text{-}H \; + \; HOSO_3H \; \overset{\Delta}{\rightarrow} \; R\text{-}SO_3H + H_2O$
alkylsulphonic acid

Where,R is C_6H_{13}-or larger alkyl group

$C_6H_{13}\text{-}H \; + \; HOSO_3H \; \overset{\Delta}{\rightarrow} \; C_6H_{13}\text{-}SO_3H + H_2O$
n-hexane Hexylsulphonic acid

(4) **Chlorosulphonation** (Substitution of $-SO_2Cl$ for H)

When alkanes are treated with a mixture of sulphur dioxide and chlorine in the presence of ultraviolet light, a hydrogen atom of the alkane is replaced by a chlorosulphonyl group ($-SO_2Cl$)

(b) Thermal and Catalytic reaction

(5) Oxidation

When ignited in the presence of sufficient excess of oxygen, alkanes burn to form carbondioxide and water.

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3 + 25\ O_2 \longrightarrow 8CO_2 + 9H_2O$

(6) Pyrolysis (Cracking)

The decomposition of a compound by heat is called Pyrolysis.This process is known as cracking.When alkanes are heated to a high temperature in the absence of air, pyrolysis or a ‘thermal decomposition’ occurs.

Ethane when heated to 500° in the absence of air gives a mixture of methane, ethylene and hydrogen.

$$3CH_3CH_3 \xrightarrow{500^\circ} 2H_2C{=}CH_2 + H_2 + 2CH_4$$

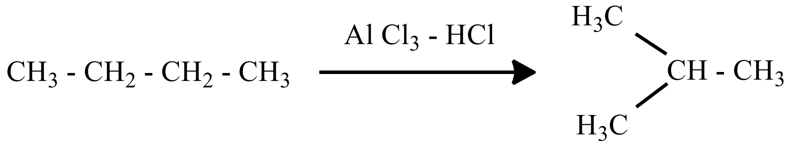
ethane ethylene methane

$$2CH_3CH_2CH_3 \xrightarrow{-600^\circ} CH_3\text{-}CH{=}CH_2 + H_2 + CH_2{=}CH_2 + CH_4$$

Propane propylene ethylene methane

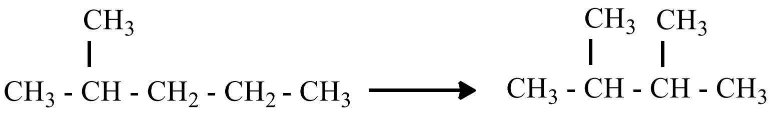
(7)Isomerisation

The molecular rearrangement of one isomer into one or more other isomers is called isomerisation. Normal alkanes are converted to their branched chain isomers in the presence of aluminium chloride and hydrogen chloride at 25°.



n-butane isobutane

Similary other less branched alkanes isomerise to the more branched ones. Thus

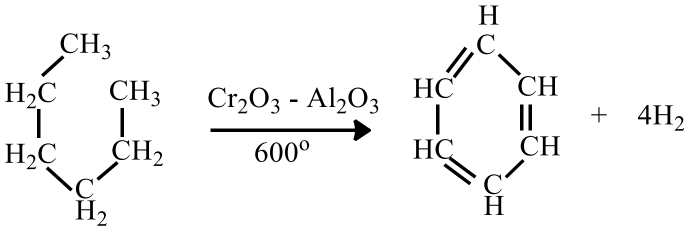


$$CH_3\text{-}\underset{}{\overset{CH_3}{\overset{|}{C}H}}\text{-}CH_2\text{-}CH_2\text{-}CH_3 \longrightarrow CH_3\text{-}\overset{CH_3}{\overset{|}{C}H}\text{-}\overset{CH_3}{\overset{|}{C}H}\text{-}CH_3$$

2-methylpentane 2,3-dimethylbutane

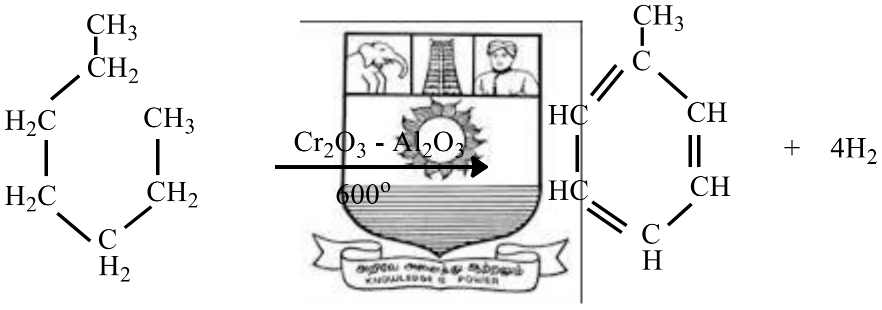
(8) Aromatisation

Alkanes containing six to ten carbon atoms are converted into benzene and its homologues at high temperature and in the presence of a catalyst.This process is called aromatisation.Thus when n-hexane is passed over Cr_2O_3 supported over alumina at 600°, benzene is produced.



n-hexane benzene

Under similar conditions, n-heptane yields toluene.



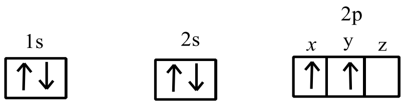
n-heptane Toluene

Hybridization

Structure of methane - Sp^3 Hybridization

If one **s** orbital and three **p**-orbitals take part hybridization then it is called **Sp^3 Hybridization.**

Let us consider the electronic configuration of carbon atom in the ground state;□



The electronic configuration of carbon atom in its excited state.

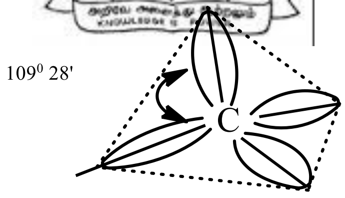
$$\overset{1s}{\boxed{\uparrow\downarrow}} \qquad \overset{2s}{\boxed{\uparrow}} \qquad \overset{x\quad y\quad z}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}$$

The electron configuration of carbon in methane molecule is

$$\boxed{\uparrow\downarrow} \qquad \underbrace{\boxed{\uparrow\downarrow} \qquad \boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}}_{\text{Sp}^3 \text{ hybridisation}}$$

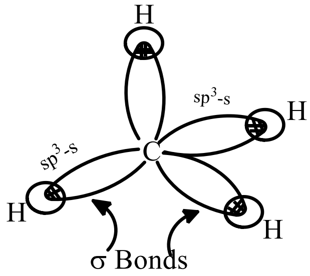
There are four unpaired electron in the valence shell of carbon in the excited state. Therefore four covalent bonds are formed .For this the carbon must contribute a set of four equivalent orbitals. The four equivalent orbitals are formed by the mixing of one 2s orbital and the three 2p orbitals in the excited state. These new orbitals are known as **Sp^3** hybridisation.

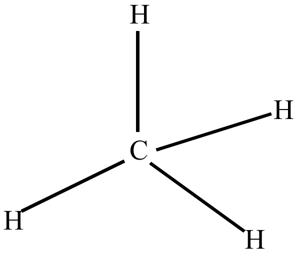
The four **Sp^3** hybridized orbitals obtained have same energy and shape. The four **Sp^3**hy orbitals arranged in such a way towards the corners of a regular tetrahedron with carbon at the center. The angle between the two obitals is 109° 28'.



Structure of methane (CH$_4$)

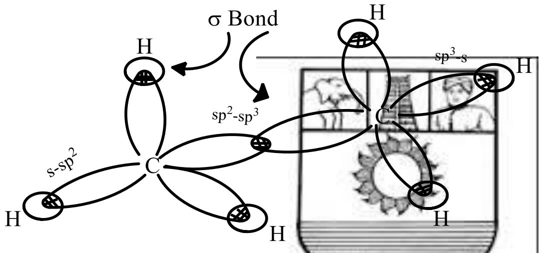
In methane the carbon atom is **Sp^3** hybridized.The carbon forms single covalent bonds with four hydrogen atom.Each C-H covalent bond is the result of the overlap of an **Sp^3** orbital form carbon and **1s** orbitals from hydrogen.The C-H bonds are directed to the corners of a tetrahedron with carbon at the centre.The bond angle between H-C-H bond is 109° 28'.

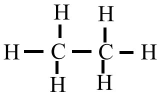




Structure of ethane (C_2H_6)

In ethane there are six C-H bonds and one C-C covalent bond. The C-H bond is the result of the overlap an Sp^3 hybrid orbitals from carbon and **1s** orbital from hydrogen. The C-C bond arises from the overlap Sp^3 orbitals, from each carbon atom.The C-C-H and H-C-H bond angle are 109° 28'.

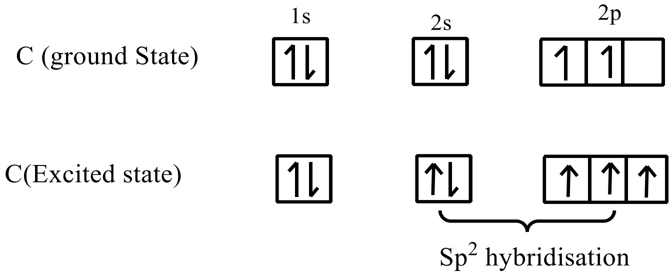




$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$$

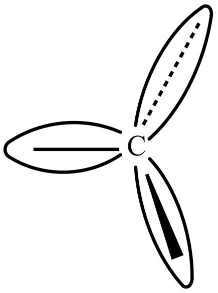
Sp^2- Hybridization

If one **s** orbital and two **p** orbital take part in hybridization then it is known as **Sp^2**hybridisation.Let us consider the electronic configuration of carbon in the ground state and excited state.



This process involves the mixing of one s orbital and two **p** orbitals.Hence three equivalent **Sp^2**hybridized orbitals are formed.Each **Sp^2** orbital contains an unpaired electron.The three **Sp^2**hybrid orbital lie in the same plane.The bond angle is 120° and the orientation

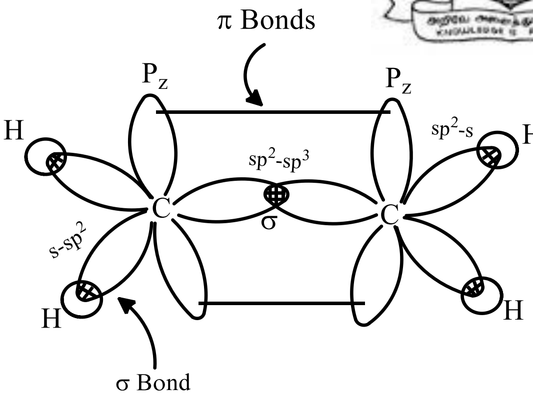
Sp^{2}hybridised orbitals is an equilateral triangle.The unhybridized **p$_z$** orbital lie perpendicular to the plane.

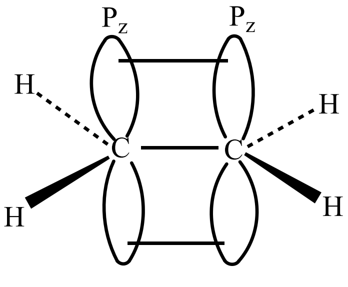


Structure of ethylene – (Sp^2 Hybridization)

In ethylene each carbon atom is attached to three other atoms.It uses **Sp^2**hybrid orbitals and an unhybridized **p** orbital to form its bonds.

There are four C-H single covalent bond are C-C double bond. Each C-H bonds is sigma bond.This is formed by the overlap of an **Sp^2** orbital from carbon and 1s orbital from hydrogen.One of the double bond is a π bond is which is formed by the overlap two unhybridized **p$_z$** orbitals.

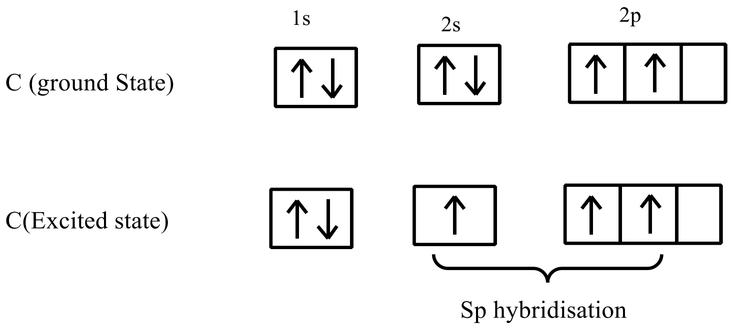




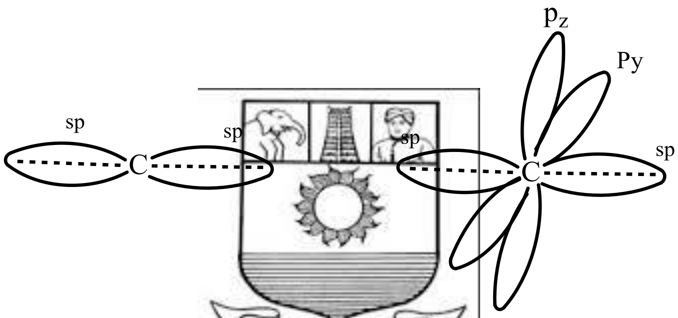
Sp - Hybridization

If one **'s'** orbital and one **'p'** orbitals part is hybridization then it is called **Sp** hybridization.

Let us consider the electronic configuration of carbon atom in the ground state and excited state.

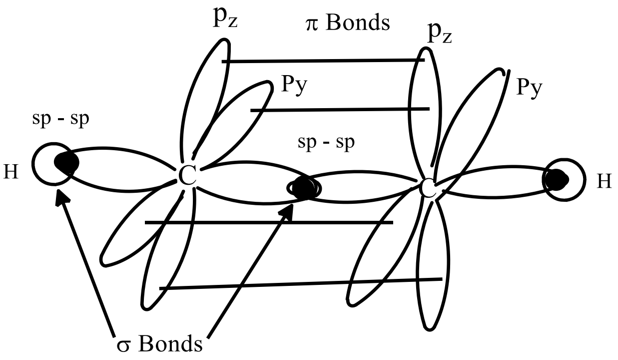


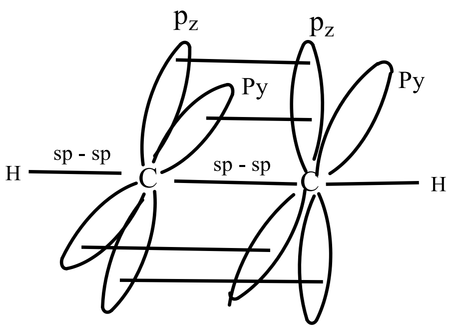
This process involves the mixing one **'s'** orbital and one **'p'** orbitals and the hybridization is **Sp** hybridization.Hence two equivalent Sp hybrid orbitals are formed. They lie is a straight line.The angle between the two Sp orbitals is 180°.The inhybridized Py and Pz orbitals lie at right angle to the **Sp** hybrid orbitals.



Strucrure of Acetylene

In acetylene each carbon is attached to two other atoms. It uses Sp hybrid orbitals and two unhybridised ‘p’ orbitals. There are two C-H single bond and are C-C triple bond. Each C-H bond is a sigma bond. The two carbon-carbon-π bond is due to the sidewise overlap the inhybridised ‘p’ orbitals on each carbon atom.





1.2 ALKENES

Alkenes are hydrocarbons that contain a carbon –carbon double bond **(C=C)** in their molecules. They have the general formula **C_nH_{2n}** (n-number of C atoms). The first member of the series has the molecular formula **C_2H_4** and is commonly known as *ethylene.*

GENERAL METHOD OF PREPARATION

The general methods of preparation of alkenes are ;

1. By Dehydration of Alcohols

When an alcohol is heated in the presence of sulphuric acid, a molecule of water is eliminated and an alkene is formed.

$$R\text{-}CH_2\text{-}CH_2\text{-}OH \xrightarrow{H_2SO_4\,,\Delta} R\text{-}CH{=}CH_2 + H_2O$$

Alcohol alkene

$$HO\text{-}CH_2\text{-}CH_3 \xrightarrow{160-170°, Conc.H_2SO_4} CH_2{=}CH_2 + H_2O$$

Ethyl alohol ethylene

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}OH \xrightarrow{160-170°, Conc.H_2SO_4} CH_3\text{-}CH{=}CH_2 + H_2O$$

1° alcohol propene

n-propyl alcohol

2. By dehydrohalogenation of alkyl halides

When an alkyl halide is heated with an alcoholic solution of sodium or potassium hydroxide, a molecule of hydrogen halide is eliminated and an alkene is formed.

$$R\text{-}CH_2\text{-}CH_2\text{-}X + KOH \xrightarrow{Alcohol,\ \Delta} R\text{-}CH{=}CH_2 + KX + H_2O$$

Alkyl halide alkene

$$CH_3\text{-}CH_2\text{-}Br + NaOH \xrightarrow{Alcohol,\ \Delta} CH_2{=}CH_2 + NaBr + H_2O$$

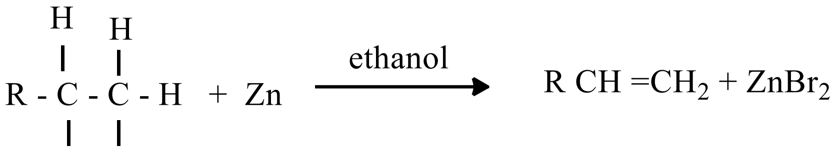
Ethyl bromide ethylene

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}Br + NaOH \xrightarrow{Alcohol,\ \Delta} CH_3\text{-}CH{=}CH_2 + NaBr + H_2O$$

1-bromopropane propene

3. By Dehalogenation of Vicinal dihalides

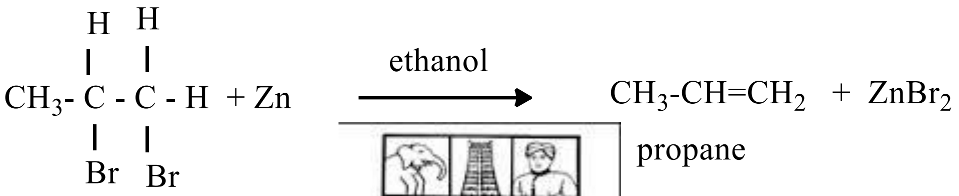
A compound having two halogen atoms on adjacent carbon atoms is called a vicinal dihalide (or vic-dihalide). The treatment of vic-dihalides with zinc dust using ethyl alcohol as solvent,results in dehalogenation and an alkene is formed



$$R-\overset{\displaystyle H}{\underset{\displaystyle Br}{C}}-\overset{\displaystyle H}{\underset{\displaystyle Br}{C}}-H + Zn \xrightarrow{\text{ethanol}} R\,CH=CH_2 + ZnBr_2$$

Alkene

vic-dihalide



$$CH_3-\overset{\displaystyle H}{\underset{\displaystyle Br}{C}}-\overset{\displaystyle H}{\underset{\displaystyle Br}{C}}-H + Zn \xrightarrow{\text{ethanol}} CH_3-CH=CH_2 + ZnBr_2$$

propane

1,2-dibromopropane

4. By Partial hydrogenation of Alkynes

Alkynes can be hydrogenated using *Raney nickel* or finely divided platinum or palladium to give alkene.

$R-C\equiv C-H \quad + \quad H_2 \quad \xrightarrow[Ni, 250-300°]{} \quad R-CH=CH_2$

alkyne alkene

$R-C\equiv C-H \quad +H_2 \quad \xrightarrow[\substack{Pd-CaCO_3,\\ Lead\ acetate}]{} \quad R-CH=CH_2$

alkyne alkene

$H-C\equiv C-H \quad + \quad H_2 \quad \xrightarrow[\substack{Pd-CaCO_3,\\ Lead\ acetate}]{} \quad CH_2=CH_2$

Acetylene ethylene

PHYSICAL PROPERTIES

(1). Unbranched alkenes containing 2 to 4 carbon atoms (ethylene, propylene, butenes) are gases at room temperature; those containing 5 to 18 carbon atoms are liquids; while those containing more than 18 carbons are solids.

(2). They are insoluble in water but are soluble in organic solvents such as ethers,alcohols, and carbon tetrachloride.

(3). They are lighter than water; the series has a limiting density of rather less than 0.8

(4). The melting points and boiling points rise with increasing molecular weight.Furthermore. branched chain alkenes have lower boiling points than straight-chain alkenes.

(5). In general , alkenes have higher melting points than the alkanes with the same carbon skeleton. This is attributed to the stronger attractive forces in alkenes than in alkanes. Due to the mobility of the electrons in the π bond, the double bond is more polarizable than single bond. This permits the ready formation of induced dipoles in alkenes molecules which are responsible for stronger intermolecular forces of attraction.

CHEMICAL PROPERTIES

General chemical properties of alkenes are as follows

1. Addition of hydrogen (Catalytic hydrogenation)

Alkenes add hydrogen in the presence of a metal catalyst forming the corresponding alkane.

$CH_2{=}CH_2 + H_2 \xrightarrow{Ni,\Delta} CH_3{-}CH_3$

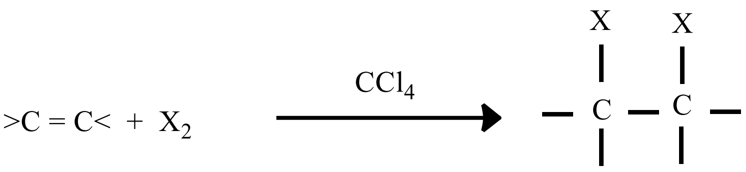
Ethane ethane

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

Propene propane

2. Addition of halogens(Halogenation)

When an alkene is treated with chlorine or bromine in carbon tetrachloride in dark, the halogen adds rapidly across the carbon-carbon double bond of the alkene to form 1,2-dihaloalkane or vicinal dihalide.



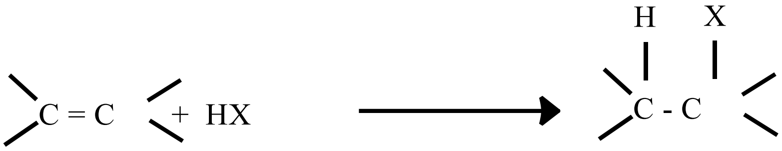
$$>C=C< + X_2 \xrightarrow{CCl_4} -\overset{X}{\underset{|}{C}}-\overset{X}{\underset{|}{C}}-$$

alkene

1, 2-dihaloalkane, or vic dihalide

3. Addition of hydrogen halide(Hydrohalogenation)

Alkenes react with hydrogen halides (HX) by addition across the carbon-carbon double bond to form alkyl halides.

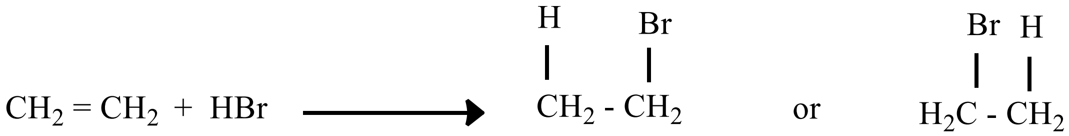


alkene

alkyl halide, or haloalkane

Addition to Symmetrical alkenes

The addition of a hydrogen halide to a symmetrical alkene gives only one product because it does not matter as to on which carbon of the double bond the halogen atom is placed.

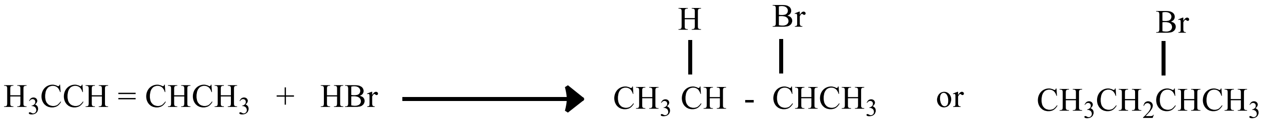


$$CH_2=CH_2 + HBr \longrightarrow \overset{H}{CH_2}-\overset{Br}{CH_2} \quad \text{or} \quad \overset{Br}{H_2C}-\overset{H}{CH_2}$$

ethylene

ethyl bromide

bromoethane



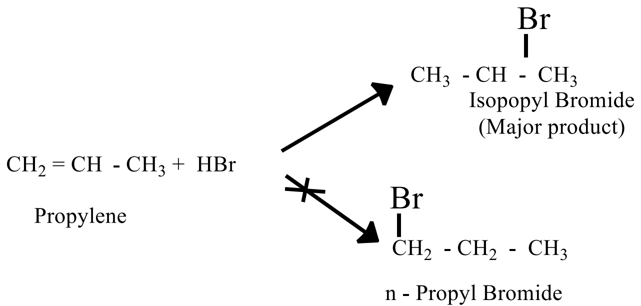
$$H_3CCH=CHCH_3 + HBr \longrightarrow CH_3\overset{H}{CH}-\overset{Br}{CH}CH_3 \quad \text{or} \quad CH_3CH_2\overset{Br}{CH}CH_3$$

2-butene

2- bromobutane

4. Markovnikov Rule (Addition to Unsymmetrical alkenes)

When a hydrogen halide reacts with an unsymmetrical alkene, there are two possible addition products according as the halogen atom is placed on one or the other carbon of the double bond. Thus propylene with HBr can form n-propyl bromide and isopropyl bromide .But it has been established experimentally that isopropyl bromide is obtained predominantly.



Markovnikov suggested a rule to predict the course of reaction for addition of hydrogen halides and other unsymmetrical reagents (HCl, HBr,HI, H_2SO_4, HOCl, etc) to unsymmetrical alkenes. The empirical rule named after him as **Markovnikov Rule** may be stated as below.

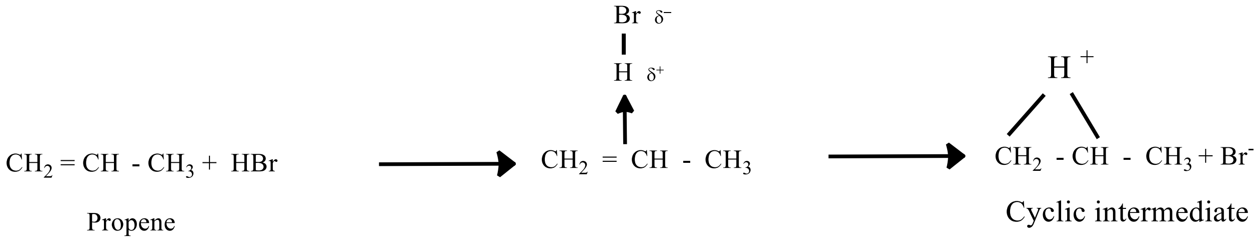
In the ionic addition of an unsymmetrical reagent(H-G), the hydrogen or positive end of the reagent becomes attached to the carbon atom of the double bond bearing the larger member of hydrogen atoms.

The addition reactions of an alkene which follow Markovinkov Rule are referred to as Markovnikov additions.

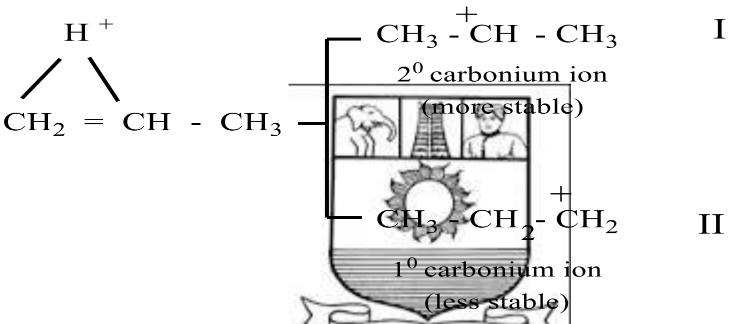
EXPLANATION;

The mechanism of addition of halogen halides to unsymmetrical alkenes involves the formation of carbonium ions as was described in the case of symmetrical alkenes(ethylene). It may be illustrated by taking example of addition of HBr to propylene. The various steps are;

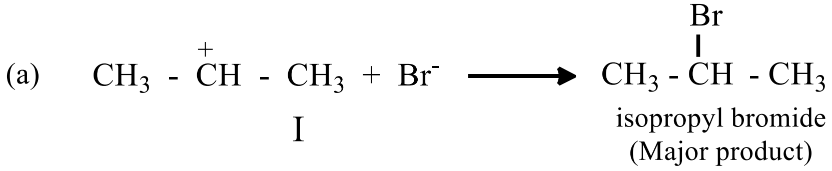
(i). Formation of π complex, giving a cyclic intermediate and Br^-



(ii) The cyclic intermediate is capable of forming two carbonium ions, one primary (1°) and one secondary (2°)



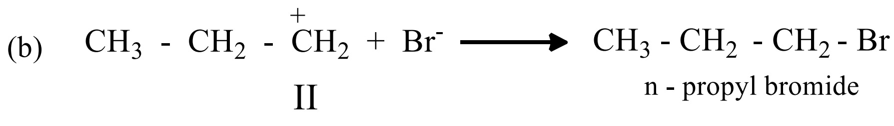
(iii) The carbonium ions I and II then react with the nucleophile Br^- Type equation here.from step (i) to give two possible alkyl bromides.



(a) $CH_3 - \overset{+}{C}H - CH_3 + Br^- \longrightarrow CH_3 - \overset{\overset{Br}{|}}{C}H - CH_3$

I

isopropyl bromide
(Major product)



(b) $CH_3 - CH_2 - \overset{+}{C}H_2 + Br^- \longrightarrow CH_3 - CH_2 - CH_2 - Br$

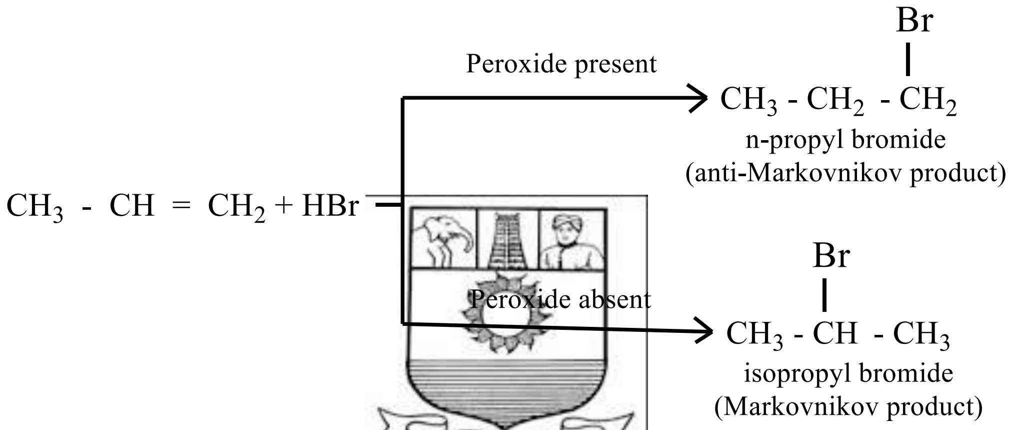
II

n - propyl bromide

We may recall that stabilities of carbonium ions are in the order3° >2° >1° . Thus the carbonium ion I dominates in step (ii) because it is more stable than II; and also because of its greater ease of formation compared to I. Then in step (iii), I reacts with Br$^-$ to form isopropyl bromide as the major product.

(5). Anti- Markovnikov addition; (Peroxide Effect)

The addition of HBr to unsymmetrical alkenes in the presence of organic peroxides (R-O-O-R) takes a course opposite to that predicted by Markovnikov Rule. This phenomenon of anti-Markovnikov addition caused by the presence of peroxide, is called Peroxide Effect. Thus when propylene reacts with hydrogen bromide in the presence of a peroxide, the product is mainly n-propyl bromide, where as in the absence of a peroxide, the main product is isopropyl bromide.

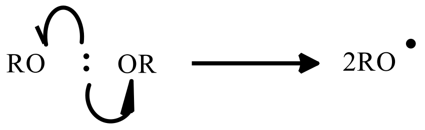


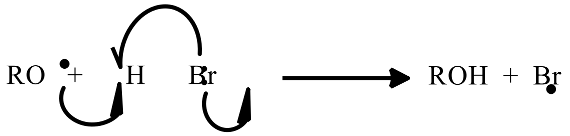
MECHANISM

Peroxides as well as ultraviolet light are able to initiate the chain reaction which results in the formation of anti-Markovnikov product. Thus propylene reacts with HBr to give n-propyl bromide by the following step.

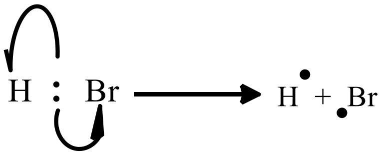
(i) Chain initiation step

(a) Peroxide dissociates to give two free alkoxy radicals which attack HBr to form bromine free radical(Br$^{\cdot}$)



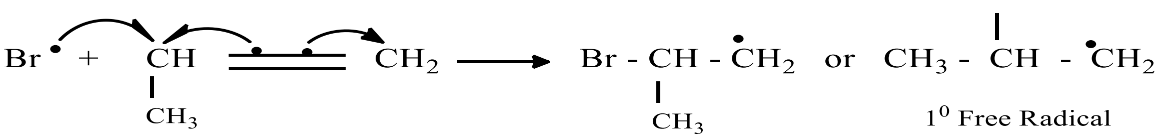


(b) HBr on photochemical dissociation (UV light) gives the free radicals H and Br



(ii) Bromine free radicals then attacks the alkene molecule giving two possible bromo-alkyl free radicals.

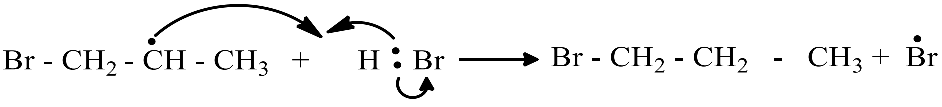
2⁰ Free Radical
(More stable)



1⁰ Free Radical
(Less stable)

The order of stability of free radicals is 3° >2° >1°. Therefore, 2° free radicals in this step is formed predominantly.

(iii) The more stable radical from step (ii) reacts with HBr forming anti-Markovnikov product , and another bromine free radical which propagates the chain reaction.

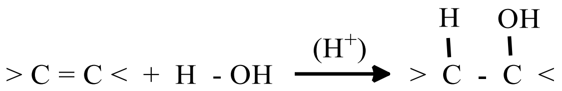


2⁰ Free Radical
(More stable)

n - Propyl Bromide
Anti - Markovnikov product

(6). Addition of water (Hydration)

Water adds to the more reactive alkenes in the presence of an acid catalyst (H_3PO_4/SiO_2) to form alcohols.



$$>C=C< + H-OH \xrightarrow{(H^+)} >\overset{H}{\overset{|}{C}}-\overset{OH}{\overset{|}{C}}<$$

Example

$$CH_2=CH_2 + H-OH \longrightarrow CH_3-CH_2-OH$$

ethene ethyl alcohol

$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + H-OH \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

isobutene,
2-methylpropylene

tert-butyl alcohol,
2-methyl-2-propanol

(7).Hydroboration

Boron hydrides add readily to alkenes across the double bond to form trialkylboranes. Diborane (B_2H_6) adds as borane (BH_3)

$$3R-CH=CH_2 + BH_3 \longrightarrow (R-CH_2-CH_2-)_3B$$

Alkene trialkylborane

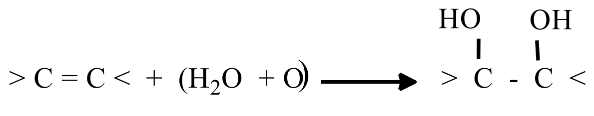
$$3CH_3-CH=CH_2 + BH_3 \longrightarrow (CH_3-CH_2-CH_2-)_3B$$

Propene tri-n-propyl borane

This reaction is called *hydroboration* of alkenes.

(8). Hydroxylation

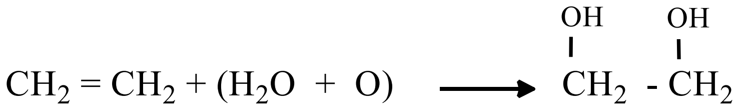
Alkenes on treatment with a cold aqueous solution of potassium permanganate add two hydroxyl groups across the double bond to form 1,2-hydroxy compounds known as glycols or 1,2-dihydroxyalkanes.



$$>C=C< + (H_2O + O) \longrightarrow >\overset{\overset{HO}{|}}{C} - \overset{\overset{OH}{|}}{C}<$$

glycol

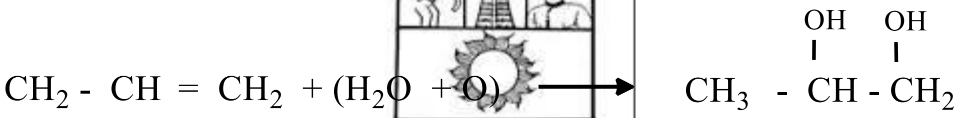
This reaction is known as hydroxylation of alkenes.



$$CH_2=CH_2 + (H_2O + O) \longrightarrow \overset{\overset{OH}{|}}{CH_2} - \overset{\overset{OH}{|}}{CH_2}$$

ethylene

ethylene glycol,
1, 2, -dihydroxyethane



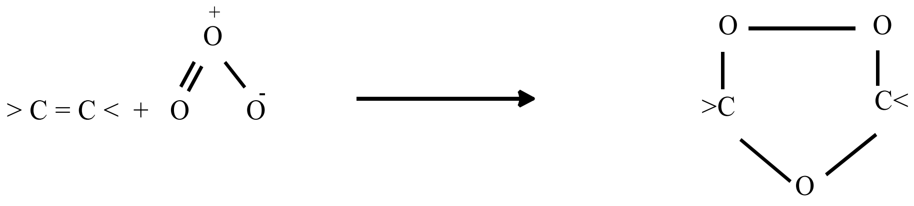
$$CH_2 - CH = CH_2 + (H_2O + O) \longrightarrow CH_3 - \overset{\overset{OH}{|}}{CH} - \overset{\overset{OH}{|}}{CH_2}$$

Propylene

propylene glycol,
1, 2, -dihydroxypropane

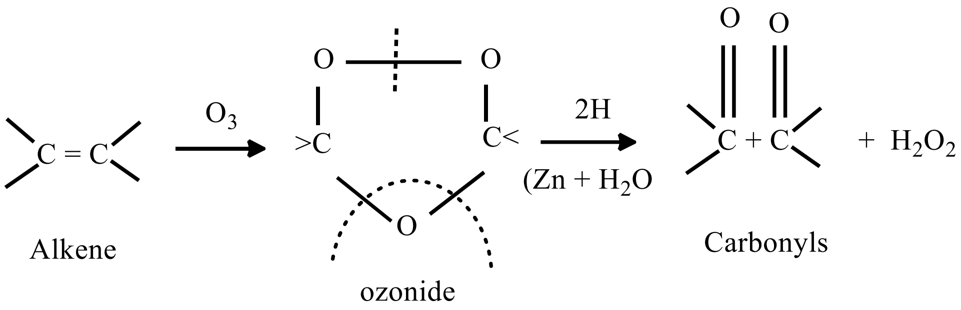
(9).Ozonolysis

When ozone is passed through a solution of an alkene in an inert solvent ($CHCl_3$ or CCl_4) at low temperature, it reacts by addition across the carbon-carbon double bond of the alkene, First an unstable intermediate, *molozonide is formed which spontaneously isomerizes to give the ozonide.*



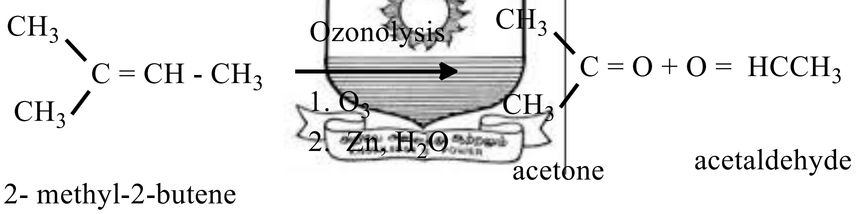
This reaction is known as Ozonization of alkenes.

Ozonides when treated with a reducing agent like zinc and water or hydrogen in the presence of palladium, are cleaved at the seat if the double bond to give two carbonylic fragments. The products are aldehydes, ketones or an aldehyde and a ketone (carbonyls),depending on the nature of the alkenes.



The two –step process of preparing the ozonide and then decomposing it to get the carbonyls compounds is called **Ozonolysis.**

For example,



(10). Polymerization of alkenes

Many simple alkenes give a peculiar reaction when two or more alkene molecules join together to form a new compound which is made up of several identical units. This reaction is called *Polymerrization.*

Example;

$$\text{n CH2=CH2} \xrightarrow[01\%O_2]{200°,high\ pressure} \text{-CH2-CH2-CH2-CH2-CH2-)-}$$

ethylene polyethylene(*n monomers*)

DIENES

These are open-chain alkenes which contain two double bond on the carbon chain and are, therefore, called **dienes.**

Dienes are of three types depending on the position of the two double bonds on the carbon chain.

(1). Conjugated dienes are those in which the double bonds are separated by one single bond.Since double and single bonds alternate on the carbon chain, they are also referred to as alternating dienes.

$-CH=CH-CH=CH-$ Conjugated dienes

For example

$CH_2=CH-CH=CH_2$ $CH_2=CH-CH=CH-CH_3$

1,3-butadiene 1,3-pentadiene

(2). Non-conjugated dienes or Isolated dienes are those in which the double bonds are separated by more than one single bond.

$CH_2=CH-CH_2-CH=CH_2$ $CH_2=CH-CH_2-CH_2-CH=CH_2$

1,4-pentadiene 1,5-hexadiene

(3). Cumulated dienes or allenes are those in which the bonds appear on successive carbon atoms, and one carbon is a part of the two double bonds.

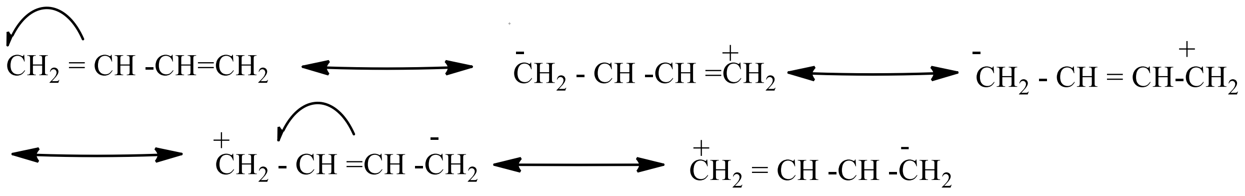
$-CH=C=CH-$ $CH_3CH_2CH=C=CH_2$

1,2-propadiene 1,2-pentadiene

Stability of conjugated dienes

Stability of conjugated dienes

In conjugated dienes the double and single bonds alternate along the chain . An example of conjugated diene is 1,3-butadiene.1,3-butadiene is regared as a resonance hybrid of several contributing structure as shown below.



$$CH_2 = CH - CH=CH_2 \longleftrightarrow \overset{-}{C}H_2 - CH - CH = \overset{+}{C}H_2 \longleftrightarrow \overset{-}{C}H_2 - CH = CH - \overset{+}{C}H_2$$

$$\longleftrightarrow \overset{+}{C}H_2 - CH = CH - \overset{-}{C}H_2 \longleftrightarrow \overset{+}{C}H_2 = CH - CH - \overset{-}{C}H_2$$

This shows grater stability of 1,3-butadiene (or) conjugated dienes.

The extra of conjugated dienes can be seen in analysis of heating of hydrogenation. The heat of hydrogenation as 1,3-butadiene is -239KJ. Where as the heat of hydrogenation of 2 molar equivalents of 1-butene is 2× -127 =254. The difference is 15 KJ. Thus the value is less than expected. Therefore conjugation imparts some extra stability to the conjugated system .

$2CH_2 = CH - CH_2 - CH_3 + 2H_2 \longrightarrow 2CH_3 - CH_2 - CH_2 - CH_3$ $\Delta H = 2 \times -127 = -254KJ$

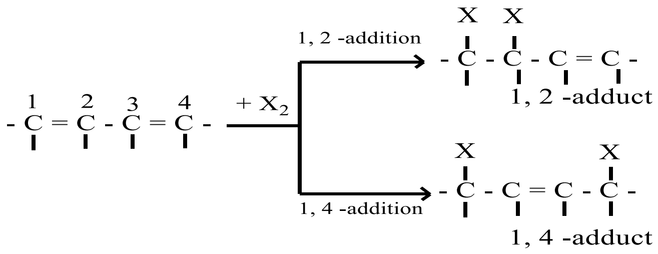
$CH_2 = CH - CH = CH_2 + 2H_2 \longrightarrow CH_3 - CH_2 - CH_2 - CH_3$ $\Delta H = -239$ difference

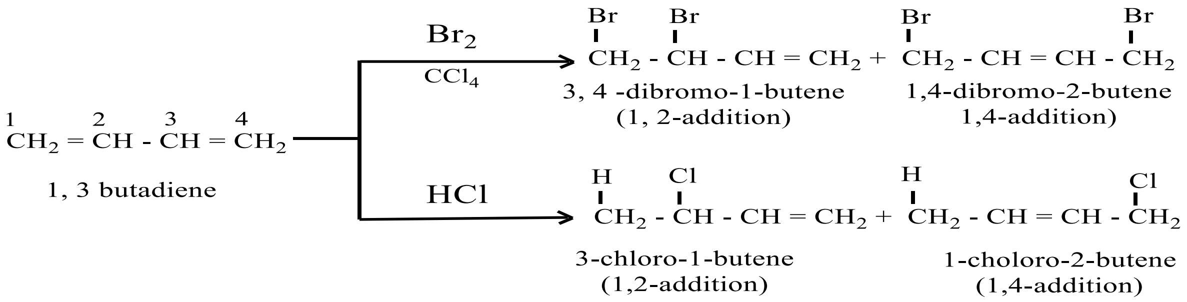
15 KJ mol^{-1}

Thus conjugated diene are more stable than isolated diene.

Mechanism of 1,2 and 1,4 –butadiene(Addition reaction)

1,3-Butadiene undergoes addition reactions with reagents such as halogens (Br_2, Cl_2), HBr and H_2. Although it contains two double bonds but only one molecule of the addendum is added either to 1,2-carbons (1,2-addition) or to 1,4-carbons (1,4-addition).





MECHANISM

Let us take the addition of HBr to 1,3-butadiene for illustrating the mechanism of the above reactions. This involves the formation of a carbonium ion stabilized by resonance.

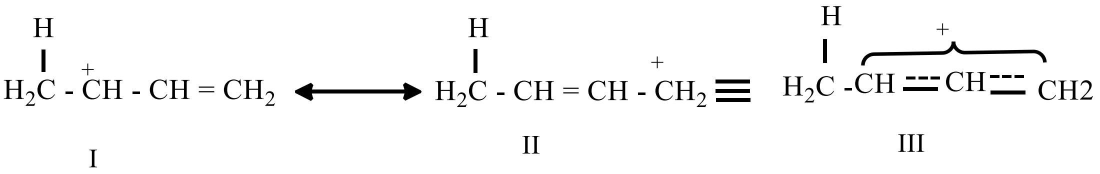
Formation of allylic carbonium ion.

$$H - Br \longrightarrow \overset{+}{H} + Br$$

$$CH_2 = CH - CH = CH_2 + \overset{+}{H} \longrightarrow \overset{H}{\underset{}{CH_2}} - \overset{+}{CH} - CH = CH_2$$

allylic carbonium ion

The allylic carbonium ion is a hybrid of two resonance structure (I and II) which are equivalent to structure III.

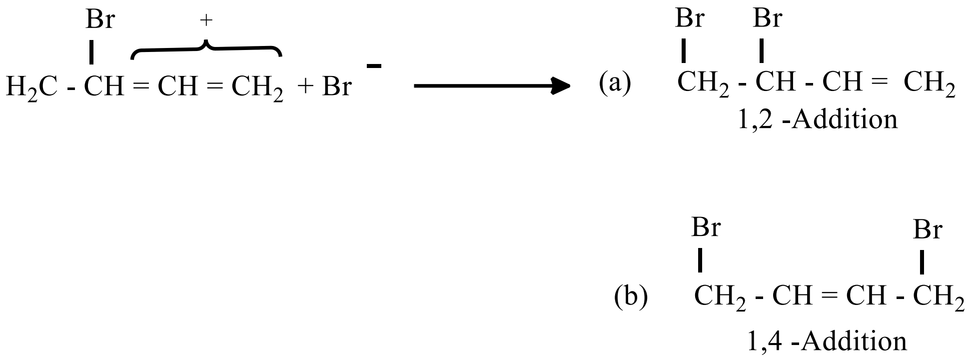


$$\overset{H}{H_2C} - \overset{+}{CH} - CH = CH_2 \longleftrightarrow \overset{H}{H_2C} - CH = CH - \overset{+}{CH_2} \equiv \overset{H}{H_2C} - \overbrace{CH \cdots CH \cdots CH2}^{+}$$

I II III

The allylic ion is thus said to be resonance stabilized.

(ii) Formation of 1,2- and 1,4-adducts, the nucleophilic Br^- adding either to C_2 or C_4 of the allylic carbonium ion.



$$\overset{Br}{\overset{|}{H_2C - CH}} - \overset{+}{\overbrace{CH = CH = CH_2}} + Br^- \longrightarrow \text{(a)}\ \overset{Br}{\overset{|}{CH_2}} - \overset{Br}{\overset{|}{CH}} - CH = CH_2$$

1,2 -Addition

$$\text{(b)}\ \overset{Br}{\overset{|}{CH_2}} - CH = CH - \overset{Br}{\overset{|}{CH_2}}$$

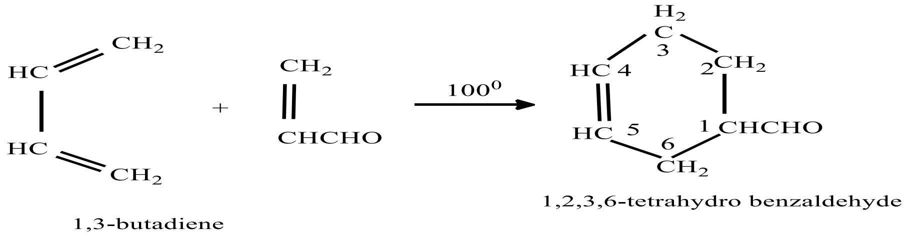
1,4 -Addition

The energy of activation of the carbonium ion IIIis higher for 1,4-addition than for 1,2-addition. Therefore 1,4-addition is favoured at high temperature and 1,2-addition at low temperature.

Diels-Alder Reaction

The Diels-Alder reaction consists in the 1,4-addition of the double bond of a suitable vinyl derivative(called the *dienophile)* to the two ends of a conjugated diene system. Thus

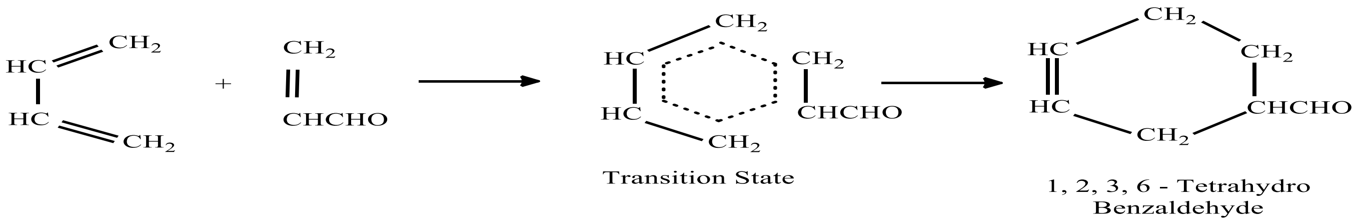
1,3-butadiene combines with acrolein at 100° to form tetrahydrobenzaldehyde.



This reaction is highly stereospecific and occurs exclusively in the *cis* fashion.

MECHANISM

The exact mechanism of Diels-Alder reaction is still uncertain. It has been suggested that a six-membered transition state compound is formed. That is,



1.3 ALKYNES

Alkynes are unsaturated hydrocarbons which contain a carbon-carbon triple bond (C≡C). The general formula of this class of compound is C_nH_{2n-2}

H-C ≡ C-H	R-C ≡ C-R
Acetylene	alkynes (acetylenes)

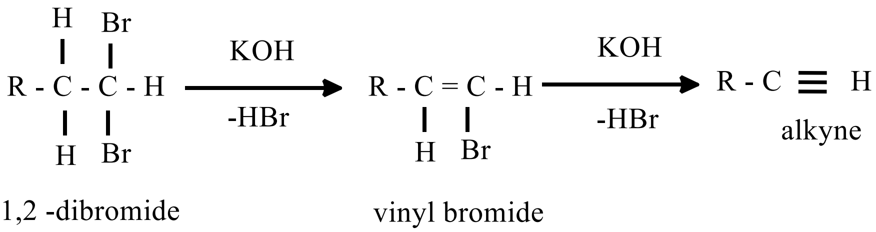
GENERAL METHODS OF PREPARATION

(1). Dehydrohalogenation of 1,2-dihalides

1,2-dihalides (vicinal dihalides) when treated with alcoholic KOH eliminate two molecules of hydrogen halide from adjacent carbons to yield an alkyne.

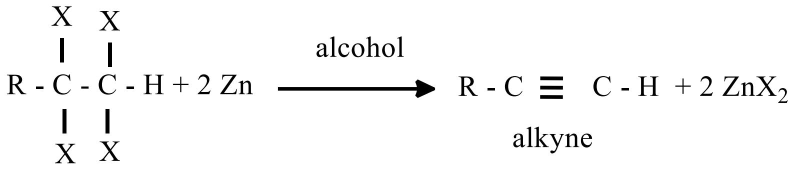
(2). Dehydrohalogenation of 1,1-dihalides

1,1-dihalides upon treatment with alcoholic KOH or with sodamide, bring about the double dehydrohalogenation yielding 1-alkynes.



(3).**Dehalogenation of tetrahalides**

Tetrahalides in which the halogen atoms are attached to adjacent carbon atoms (two on each carbon) when heated with zinc dust in alcohol yields alkynes.



$$R-\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}-H + 2\,Zn \xrightarrow{\text{alcohol}} \underset{\text{alkyne}}{R-C\equiv C-H} + 2\,ZnX_2$$

1,1,2,2-tetrahaloalkane

PROPERTIES

Physical properties

(1). The first three members ($C_1 \rightarrow C_3$) are gases, next eight ($C_4 \rightarrow C_{11}$) are liquids, and the higher alkynes (C_{12}) are solids.

(2). Alkynes are compounds of low polarity and hence they are slightly soluble in water.

(3). The boiling points, melting points, and specific gravities of alkynes are slightly higher than the corresponding alkanes and alkenes.

Chemical properties

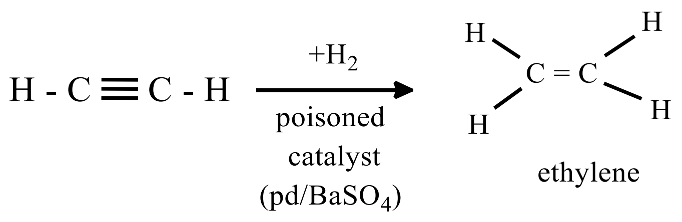
The different reaction of alkynes are described below under the following heads

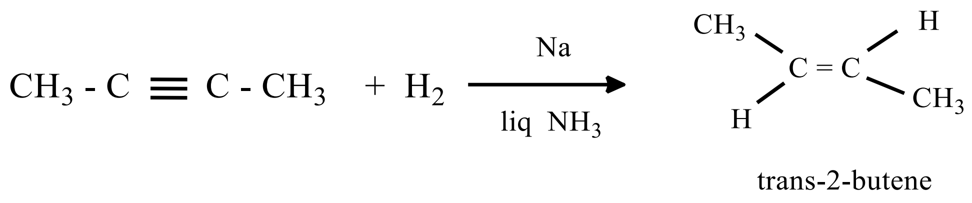
1. Addition reactions
2. Substitution Reaction
3. Oxidation Reaction
4. Polymerization
5. Isomerization

1. Addition reactions

a) Addition of Hydrogen (Catalytic Hydrogenation)

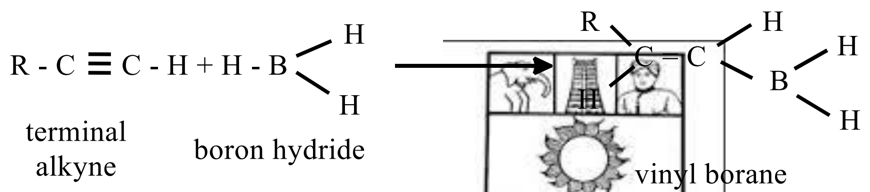
In the presence of catalysts like finely divided platinum, palladium or Raney nickel, alkynes add up two molecules of hydrogen first forming the corresponding alkenes and finally the alkanes.

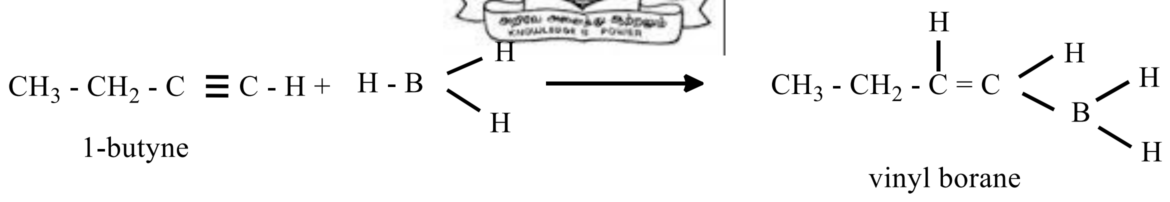


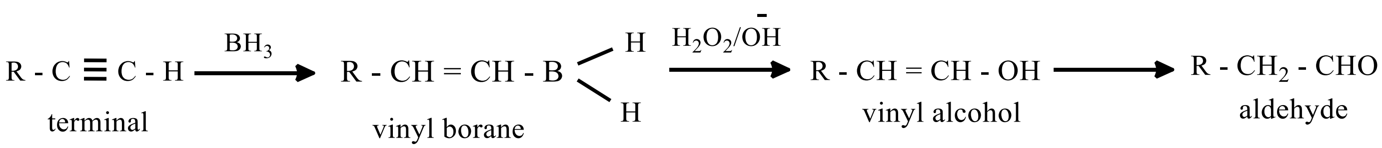


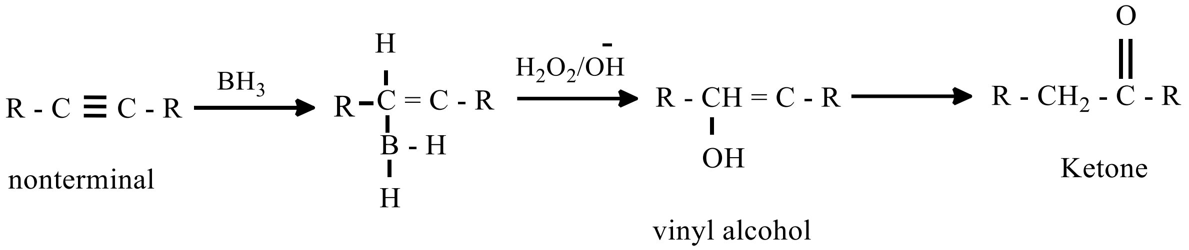
B) Addition of Boron hydride (Hydroboration)

Alkynes like alkenes add on boron hydride (BH_3), in a cis manner to form vinyl boranes.



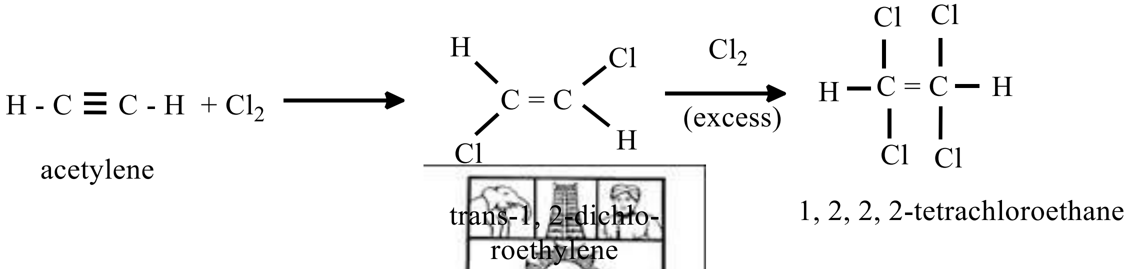


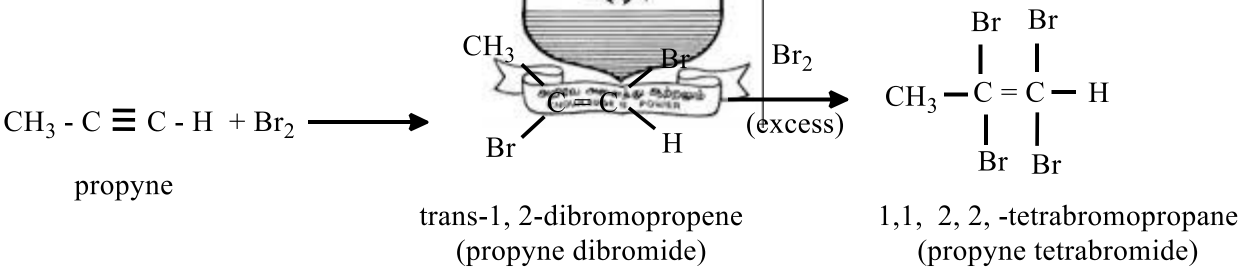




C) Addition of Halogens

Alkynes add on two molecules of halogens forming first a dihaloalkane and then a tetrahaloalkane.





(2) Substitution Reaction

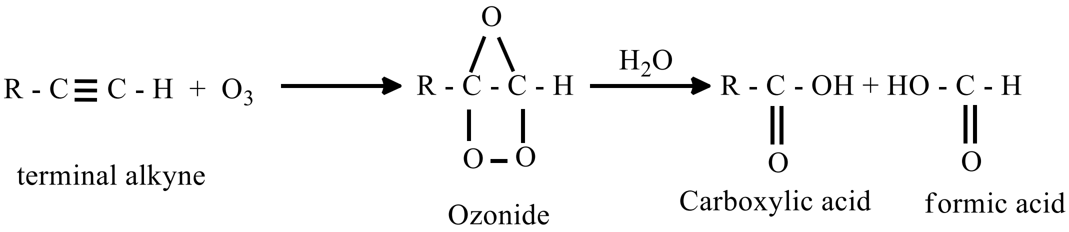
The acidic hydrogen of alkynes can be replaced by halogens under conditions which promote the formation of positive halogen. Thus, when acetylene is passed into ice-cold alkaline hypochlorite solution, dichloracetylene is produced.

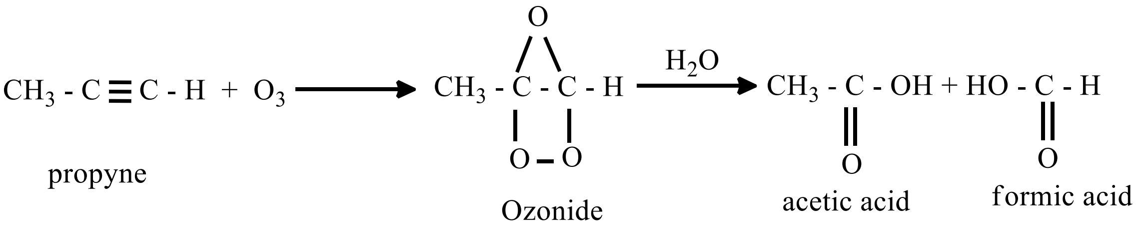
$$\text{H-C}\equiv\text{C-H} \quad + \quad 2\text{NaOCl} \longrightarrow \quad \text{Cl-C}\equiv\text{C-Cl} \quad + \quad 2\text{NaOH}$$

Dichloroacetylene

(3) Oxidation (Ozonolysis)

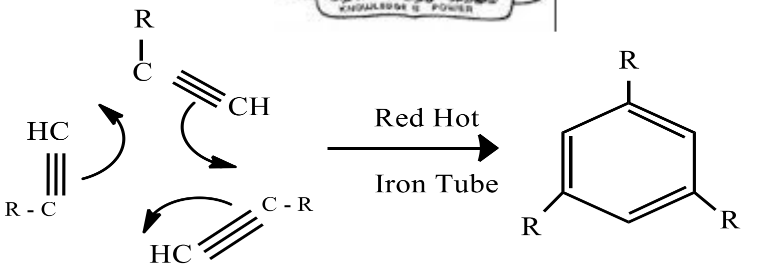
Alkynes react slowly with ozone to produce ozonides.These ozonides on decomposition with water yield carboxylic acids.





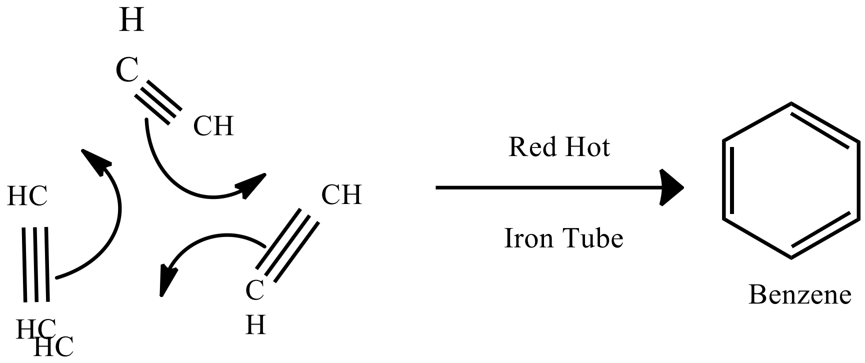
(3)Polymerization

Alkynes when passed through a red hot quartz or iron tube polymerize to yield benzene hydrocarbons.



Sym - TrialkylBenzene

Thus propyne gives mesitylene while acetylene furnishes benzene itself.



(6) Isomerization (Acetylene-Alkene Rearrangement)

1-Alkynes can be readily isomerized to the more stable 2-akynes on treatment with potassium hydroxide in enthanol.

$$R\text{-}CH_2\text{-}C\equiv C\text{-}H \xrightarrow{KOH,\text{enthanol.}} R\text{-}CH=C=CH_2 \longrightarrow R\text{-}C\equiv C\text{-}CH_3$$

1-alkyne alkene 2-alkyne

Acidity of Alkynes (Acetylene)

Alkynes having atleast on ≡ C-H bond show an acidic character .But disubstituted alkynes do not show acidic character.

We can explain the acidic character based on the hybridization stable of carbon atom in alkynes. The ≡ C-H bond in alkyne is Sp hybridized and have 50% S character. The Sp hybridized carbon would attract attack electron pair constituting the –C-H bond of alkyne more effectively. Thus the ≡ C-H bond is alkyne would be more ionic .Than in ethylene (Sp^2) and ethane(Sp^3).

1.4 Answer the Following Questions

PART-A

1. What are alkanes? Give two methods of preparation
2. Write a note an structure of methane
3. How will you prepare alkene from alcohol?
4. Write a note on Markovnikov rule with an example
5. Write the ozonide formation reaction
6. Write a short note on Diel’s Alder reaction
7. Explain the hydroboration reaction of alkynes?

PART-B

1. Explain the chemical properties of alkanes
2. Explain SP^3 and SP^2 hybridisation and structure of methane and ethylene
3. Write the mechanism of Anti-Markovnikov addition(or) peroxide effect

UNIT-II

HALOGEN DERIVATIVES

CONTENTS

2.1 Substitution reaction(SN)

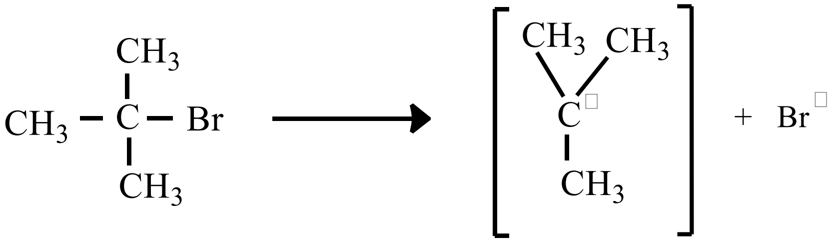
SN^1 Mechanism

SN^1 stands for unimolecular nucleophilic substitution. The rate of the reaction depends only on the concentration of the substrate. Hence the reaction is first order and is represented as SN^1.

Let us consider the hydrolysis of tertiary butyl bromide. This reaction consists of two steps.

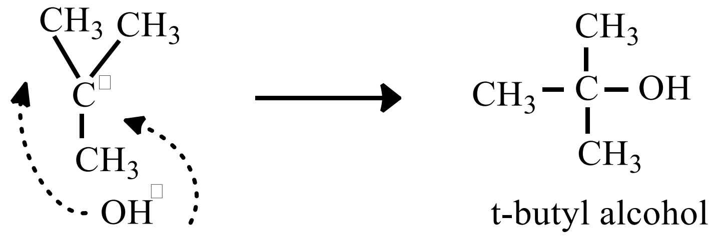
STEP I:

The alkyl halides ionizes slowly to produce the carbonium ion . The carbonium ion is planar. The carbonation in carbonium ion is Sp^2 hybridized.



STEP II:

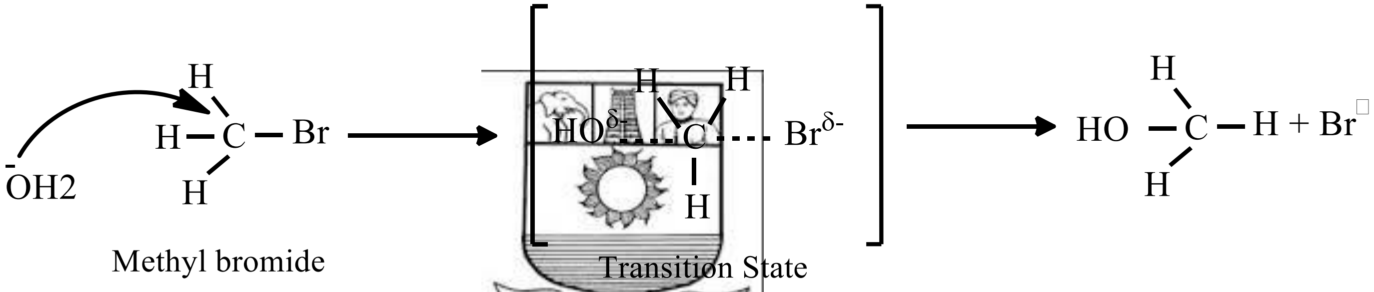
The second step involves the fast attack of the nucleophile to the carbonium ion.



SN^2 Mechanism

SN^2 stands for bimolecular nucleophilic substitution. The rate of the reaction depends on the concentration of both substrate and the nucleophile. Hence the reaction is of second order and is represented as **SN^2**

Consider the hydrolysis methyl bromide by aqueous NaOH. The reaction may be represented as follows.



The OH^- ion approaches the substrate carbon from the side opposite to the bromine atom. So a transition state is formed.In the transition state the three C-H bond lie in the same plane. The C-OH and C-Br bonds are perpendicular to the plane of the C-H bonds. The C-Br bond is not completely cleaved and C-OH bond is not completely formed. Hydroxide ion has a diminished negative charge because it has started to share its electrons with the substrate carbon. The bromine atom also carries a negative charge because it has started removing its shared pair of electrons from the carbon atom.

2.2 Elimination reactions

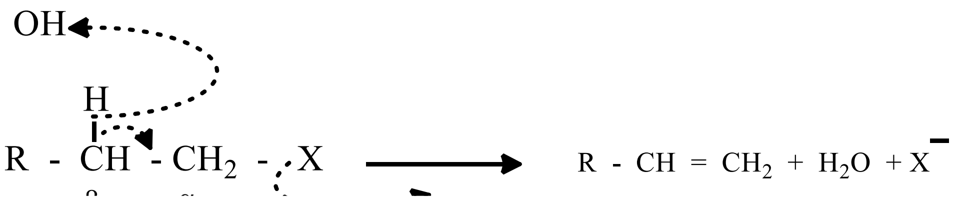
Elimination of reaction are reverse of addition reaction. Dehydrohalogenation of alkyl halides with alcoholic potash is an example.

$$R\text{-}CH2\text{-}CH2\text{-}X \xrightarrow{OH-,alcohol} R\text{-}CH{=}CH2{+}H2O{+}X^{-}$$

There are two types of elimination reactions.

1.E_2-Elimination

E_2 stands for bimolecular elimination. The rate of the reaction depends on the concentration substrate and nucleophile. Hence the reaction is second order and is represented as E2. E2 mechanism is a one step process in which the abstraction of proton from the β-carbon and expulsion of halide ion from the α-carbon occurs simultaneously. The mechanism is shown below.

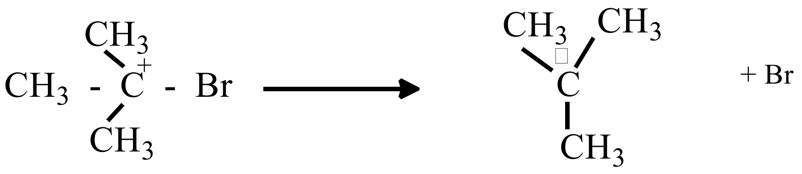


2. E_1-Elimination

E_1 stands for unimolecuolar elimination. The rate of the reaction depends only on the concentration of substrate. Hence the reaction is first order and is represented as E_1. E_1 reactions are two step process.

i. **STEP I**:

The alkyl halides ionizes to give the carbonium ion.

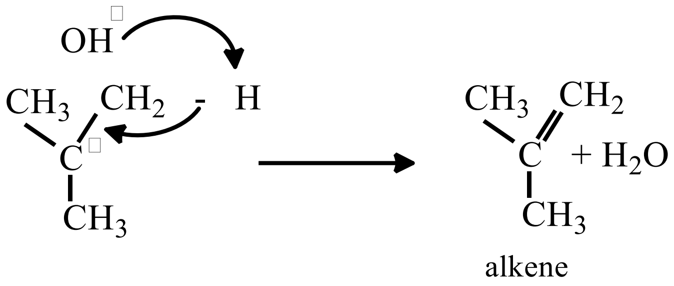


t-butyl bromide

carbonium ion

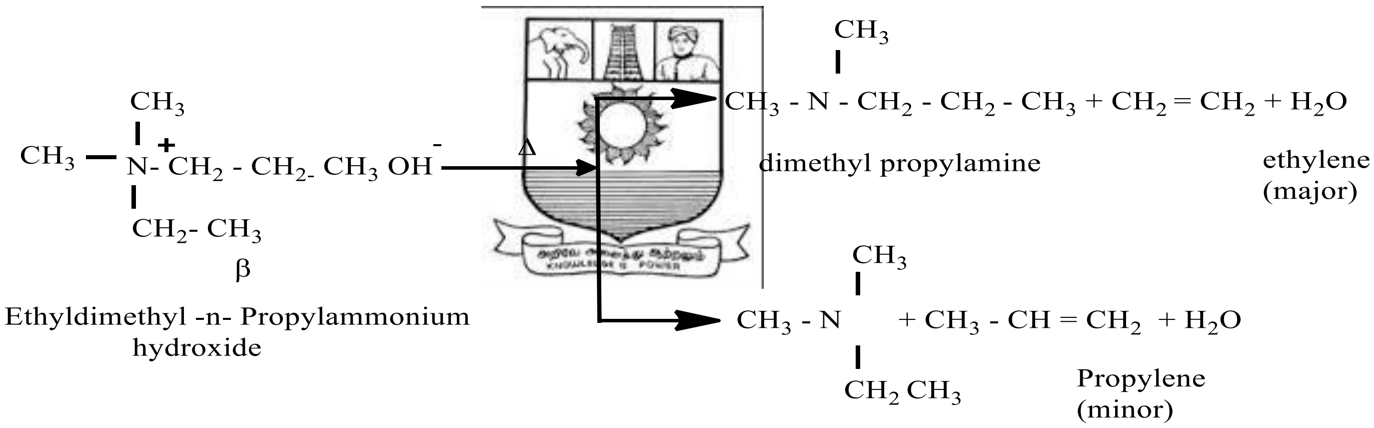
ii. **STEP II**:

The base(OH^-) abstract a proton and forms an alkene.



Hoffmann and Saytzeff Rule

When there are four different alkyl groups attached to the nitrogen atom of the ammonium ion, the pyrolysis of the tetraalkylammonium hydroxide may theoretically lead to the formation of more than one type of alkene. In such cases, the elimination takes place in a fashion that the major product is the alkene containing the least alkylated double bond i,e., the least substituted alkene(*Hoffmann Rue*). For example,



Unsymmetrical secondary(or tertiary) alcohols, elimination can proceed in two ways and a mixture of alkenes is obtained. Thus the dehydration of 2-butanol leads to the formation of 2-butene (major product) and 1-butene (minor product).

$CH_3\text{-}CH_2\text{-}CHOH\text{-}CH_3 \xrightarrow[\Delta]{H_2SO_4,} CH_3\text{-}CH{=}CH\text{-}CH_3$ (80%)

2-butanol 2-butene(major product)

$CH_3\text{-}CH_2\text{-}CHOH\text{-}CH_3 \xrightarrow[\Delta]{H_2SO_4,} CH_3\text{-}CH_2\text{-}CH{=}CH_2$ (20%)

2-butanol 1-butene(minor product)

When alternatives exist, hydrogen is preferentially eliminated from the carbon atom with fewer number of hydrogen atoms. Stated differently, the major product will be the alkene with larger number of alkyl groups attached to the double bond.

2.3 Preparation and properties of halogen derivatives

CHLOROFORM (*Trichloromethane,*$CHCl_3$)

Preparation

1. By heating enthanol or acetone with bleaching powder, Ca (ClO)Cl. The bleaching powder provides chlorine and the reaction takes place in three stages. Thus the formation of chloroform from ethanol occurs as follows.

(i). Oxidation of ethanol to acetaldehyde.

$$\underset{\text{Ethanol}}{CH_3\text{-}CH_2OH} + Cl_2 \longrightarrow \underset{\text{acetaldehyde}}{CH_3\text{-}CHO} + 2HCl$$

(ii) Chlorination of acetaldehyde to chloral

$$CH_3\text{-}CHO + 3Cl_2 \longrightarrow CCl_3\text{-}CHO + 3HCl$$

(iii) Hydrolsis is of chloral by lime present in bleaching powder to form calcium formate and chloroform

$$CCl_3\text{-}CHO + HOH \longrightarrow \underset{\text{chloroform}}{CHCl_3} + \underset{\text{formic acid}}{HCOOH}$$

$$2HCOOH + Ca(OH)_2 \longrightarrow (HCOO)^-{}_2Ca^{2+} + 2H_2O$$

2. Chloroform is also prepared on a large scale by the reduction of carbon tetrachloride with water and iron.

$$CCl_4 + H_2 \longrightarrow CHCl_3 + HCl$$

3. Pure Chloroform is obtained by treatment of chloral with aqueous alkali.

$CCl_3CHO + KOH \longrightarrow CHCl_3 + HCOOK$

Chloral

PROPERTIES

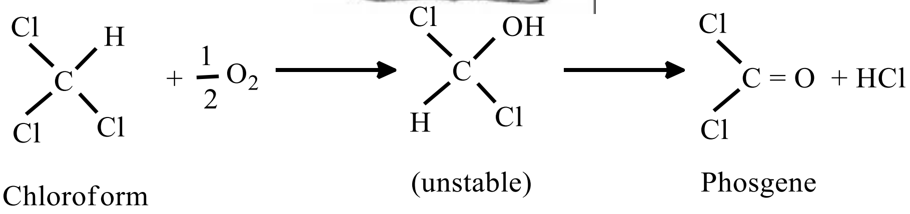
Physical properties

- Chloroform is colourless liquid having a peculiar sickly smell and a sweetish buring taste.
- It is practically insoluble in water but soluble in most organic solvents.
- It acts as a solvent for many organic substances such as oils,fats and waxes.
- Chloroform vapour when inhaled causes temporary unconsciousness and hence its use as anaesthetic.

Chemical properties

(1) Oxidation

In the presence of light, chloroform is oxidized slowly by the oxygen of air to form carbonyl chloride or phosgene.



Reduction

Nascent hydrogen generated by the action of zinc on ethanolic hydrogen chloride, reduces chloroform to dichloromethane.

$CHCl_3 + 2H \longrightarrow CH_2Cl_2 + HCl$

Dichloromethane

(2) Hydrolysis with alkali

When treated with hot solution of NaOH (or KOH), chloroform is hydrolysed to form sodium chloride (or potassium chloride) , and sodium formate or potassium formate.

$CHCl_3 + 4Na^+ OH^- \longrightarrow HCOO^- Na^+ + 3Na^+ Cl^- + 2H_2O$

Sodium formate

(3) Nitration

It reacts with concentrated nitric acid to form chloropicrin or mononitrochloroform (bp 120°).

$CCl_3CH + HONO_2 \longrightarrow CCl_3C\text{-}NO_2 + H_2O$

Chloropicrin

(4) Carbylamine Reaction (*Isocyanide Reaction*)

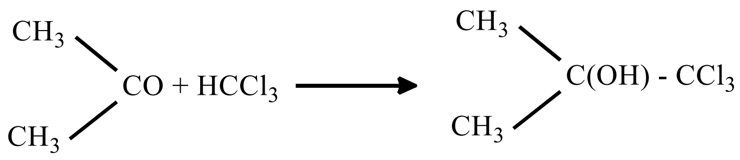
Chloroform when warmed with an ethanolic solution of potassium hydroxide, forms an isonitrile (*carbylamine*).

$CHCl_3 + 3KOH + R\text{-}NH_2 \longrightarrow R\text{-}N^+\equiv C^-: + 3H_2O + 3KCl$

Primary amine Isocyanide

(5) Condensation with Acetone

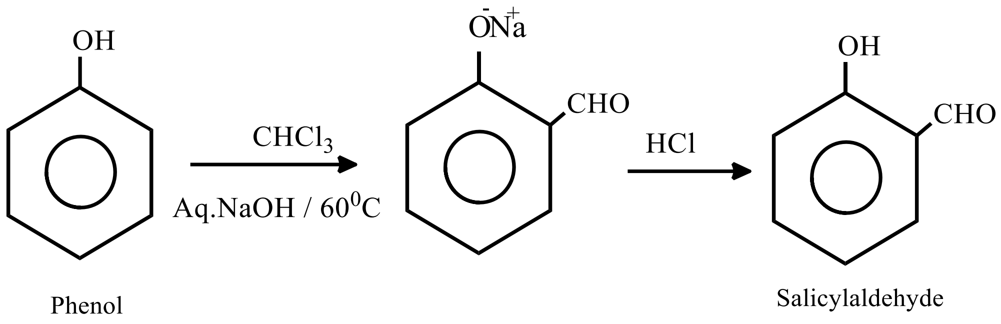
Chloroform undergoes condensation with acetone in the presence of alkali to form chloretone which is used as a hypnotic.



chloretone

(6) Action with Phenol and Sodium hydroxide (*Reimer Tiemann Reaction*)

When heated with concentrated solution of NaOH,chloroform gives salicylaldehyde.



USES

- Chloroform is to some extent used as anaesthetic, it has fallen into disrepute as slight overdoses are dangerously toxic.
- It is used as a solvent for fats and iodine.
- As a reagent for testing primary amines.
- It is added to decomposable organic materials to present putrefaction.

CARBON TETRACHLORIDE *(Tetrachloromethane,CCl_4)*

Preparation

It is prepared on industrial scale

(1) By chlorination of methane

$$CH_4 + 4Cl_2 \longrightarrow CCl_4 + 4HCl$$

(2) By the action of chlorine on carbon disulphide (CS_2) in the presence of aluminium chloride as a catalyst.

$$CS_2 + 3Cl \longrightarrow CCl_4 + S_2Cl_2$$

Suphurmonochloride

Properties

Physical Properties

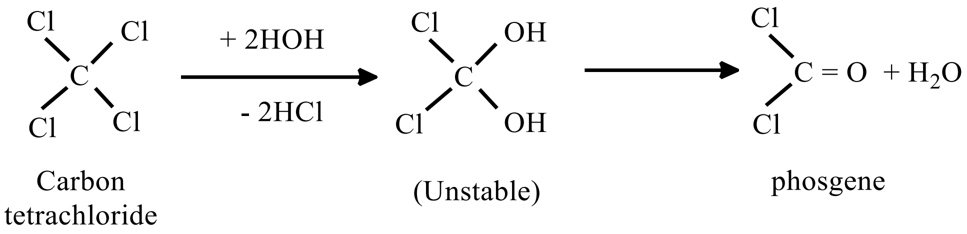
- Carbon tetrachloride is a colourless liquid.
- It is insoluble in water but soluble in all organic solvents.

- It is an excellent solvent for fatty substances.
- It is not flammable and hence was used as a fire extinguisher (Pyrene)

Chemical Properties

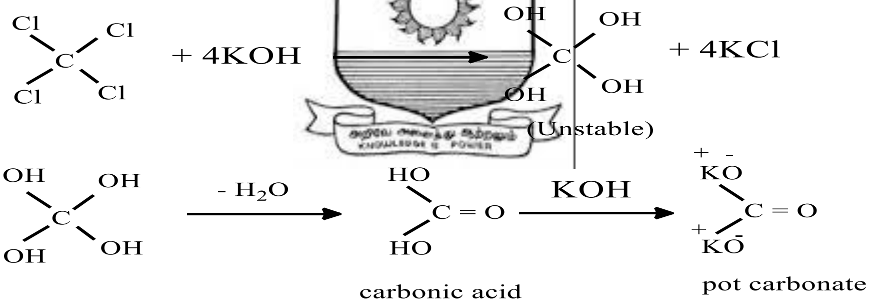
1) Action of steam

Its vapours when mixed with steam react at high temperature to give phosgene gas.



2) Action with alkali

When boiled with ethanolic KOH solution, carbon tetrachloride is hydrolysed to form potassium carbonate.



3) Reduction

Carbon tetrachloride can be reduced by moist iron filing to chloroform. This is an industrial method for the preparation of chloroform.

CCl_4 + H_2 ⟶ $CHCl_3$ + HCl

4) Action with HF

When hydrogen fluoride is passed into carbon tetrachloride in presence of antimony pentachloride, the gas dichlorodifluoromethane is obtained.

$CCl_4 + 2HF \xrightarrow{Sbcl_5} CCl_2F_2 + 2HCl$

Freon

USES

- It is used as a fire extinguisher
- It is also used for the preparation of Freon

VINYL CHLORIDE (*Chloroethene)*

Preparation

1) By the controlled addition of hydrogen chloride in the presence of mercury salts as catalyst.

$$CH\equiv CH \quad + \quad HCl \xrightarrow{Hg3+} CH_2=CH\text{-}Cl$$

Acetylene vinylchloride

2) By passing a mixture of ethylene, hydrogen chloride and oxygen at 250℃ over Copper (II) chloride.

$$CH_2=CH_2 \quad +HCl \quad + \frac{1}{2} O_2 \xrightarrow{\substack{CuCl_2 \\ 250℃}} CH_2=CH\text{-}Cl \quad + \quad H_2O$$

3) In the laboratory, vinyl chloride can conveniently be prepared by heating ethylene chloride with ethanolic KOH solution.

$$Cl\text{-}CH_2\text{-}CH_2\text{-}Cl \quad + \quad KOH \xrightarrow{ethanol} CH_2=CH\text{-}Cl \quad + \quad KCl \quad +H_2O$$

Ethylene chloride vinyl chloride

PROPERTIES

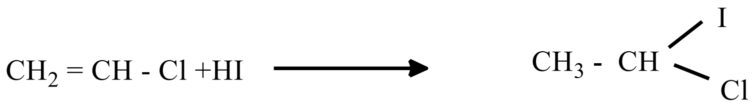
Vinyl chloride is a colouress gas under ordinary conditions.

1. Reaction of carbon-carbon double bond

Vinyl chloride gives the usual electrophilic reactions of alkenes.

$$CH_2 = CH - Cl + Cl_2 \longrightarrow CH_2Cl + CHCl_2$$

1, 1, 2 - trichlorethane



$$CH_2 = CH - Cl + HI \longrightarrow CH_3 - CH(I)(Cl)$$

1-chloro-1-iodoethane

2. Reactions of chlorine atom

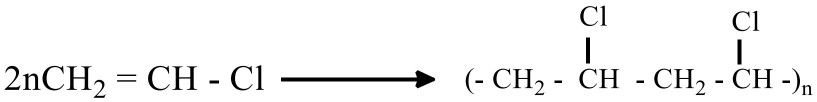
The reaction of vinyl chloride at the chlorine atom are strikingly different from those of alkyl chlorides. It does not react with nucleophilic reagents giving substitution products. For example, it is not hydrolysed by sodium hydroxide.

$$CH_2{=}CH{-}Cl \quad + NaOH \xrightarrow{\text{Water}} \text{No reaction}$$

$$(\text{Cf.}\, CH_3CH_2Cl + NaOH \xrightarrow{\text{Water}} CH_3CH_2OH + NaCl)$$

3. Polymerization to PVC

Vinyl chloride polymerizes when heated in an inert solvent in presence of dibenzoyl peroxide. The product is polyvinylchloride (PVC)



$$2nCH_2 = CH - Cl \longrightarrow (-CH_2 - \underset{}{\overset{Cl}{CH}} - CH_2 - \overset{Cl}{CH} -)_n$$

Allyl chloride

Preparation

Allyl chloride is prepared on a commercial scale by the action of chlorine on excess of propene at 500℃.

$$CH_3{-}CH{=}CH_2 \xrightarrow[500℃]{Cl_2} CH_2{=}CH{-}CH_2\,Cl$$

Properties

Allyl Chloride gives the reactions of both an alkene and an alkyl halide.

i). Reaction due to C=C bond:

Allyl chloride undergoes addition reaction with chlorine to form trichloropropane.

$$ClCH_2\text{-}CH{=}CH_2 + Cl_2 \longrightarrow ClCH_2\text{-}CHCl\text{-}CH_2Cl$$

ii). Reaction due to the chlorine atom:

The chlorine atom in allyl chloride is highly reactive. This is because of the stabilization of the allyl carbonium ion by resonance. This facilitates the removal of Cl atoms as Cl^- ion.

Thus, allyl chloride undergoes the usual substitution reactions of alkyl halides. For example, it is hydrolysed with dilute alkali forming allyl alcohol.

$$CH_2{=}CH\text{-}CH_2Cl \xrightarrow{KOH} CH_2{=}CH\text{-}CH_2OH + KCl$$

Uses:

1. Allyl chloride is an intermediate in the synthesis of glycerol from propene.
2. It is used to prepare allyl alcohol and epichlorohydrin.

WESTRON (1, 1, 2, 2-tetrachloroethane)

Preparation

Westron is prepared by the action of chlorine on acetylene in the presence of ferric chloride (catalyst) at 80℃.

$$CH{\equiv}CH \quad + \quad 2Cl_2 \xrightarrow[80℃]{FeCl_3} CHCl_2\text{-}CHCl_2$$

Acetylene Westron

Uses

1. It is used as a solvent for oils, fats, paints, varnishes and rubber.
2. It used to prepare *westrosol,* a non-toxic solvent widely used in dry cleaning.

Westrosol

Preparation

It is prepared by treating westron with lime.

$$\mathrm{CHCl_2\text{-}CHCl_2} \xrightarrow{Ca(OH)_2, -HCl} \mathrm{CHCl{=}CCl_2}$$

Uses

It is used as a non toxic solvent in dry cleaning.

Freon(Dichlorodifluroromethane)

Preparation

Freon is prepared by the action of anhydrous HF on CCl4 in the presence of antimony pentafluoride as catalyst.

$$\mathrm{CCl_4} + \mathrm{2HF} \xrightarrow{SbCl_5} \mathrm{CCl_2F_2} + \mathrm{2HCl}$$

Uses

1. It is used as a coolant in refrigerators and air-conditioners.
2. It is used as a propellant in aerosol sprays.
3. It is used to making foam plastics such as *thermocole.*

Chloroprene(2-chloro-1, 3-butadiene)

Preparation

When passed through an aqueous solution of ammonium chloride containing cuprous chloride, acetylene forms the dimer, vinyl acetylene.

$$\mathrm{2CH{\equiv}CH} \xrightarrow{Cu_2Cl_2, NH_4Cl} \mathrm{CH_2{=}CH\text{-}C{\equiv}CH}$$

Vinyl acetyene (gas) thus formed is then passed into dil.HCl when chloroprene is obtained.

$$\mathrm{CH_2{=}CH\text{-}C{\equiv}CH} + \mathrm{HCl} \longrightarrow \mathrm{CH_2{=}CH\text{-}CCl{=}CH_2}$$

Uses

Chloroprene is used as the strating materials for neoprene rubber.

2.4 Answer the Following Questions

PART-A

1. Discuss the mechanism of E_1 and E_2 elimination

2. Write a short note on Hoffmann and Stayzeff rule

3. Write the preparation of Carbon trtra chloride

4. How will you convert Westron into Westrosol

PART-B

1. Discuss SN_1 and SN_2 Mechanism

2. Explain the preparation , properties and uses of Chloroform

UNIT-III

ALICYCLIC COMPOUNDS

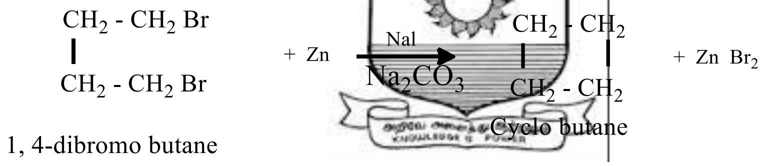
CONTENTS

3.1 Cyclo alkanes

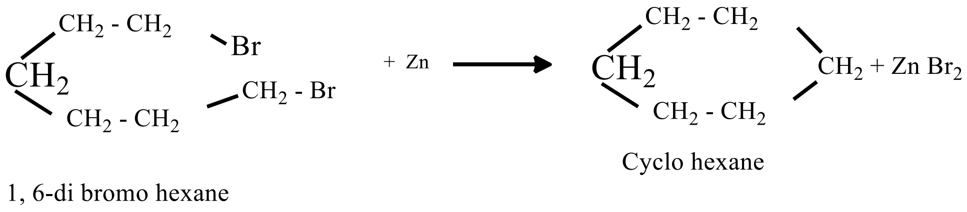
General methods of preparation

(1) **Freund's method**

This method involves the action of zinc on suitable dihalides.

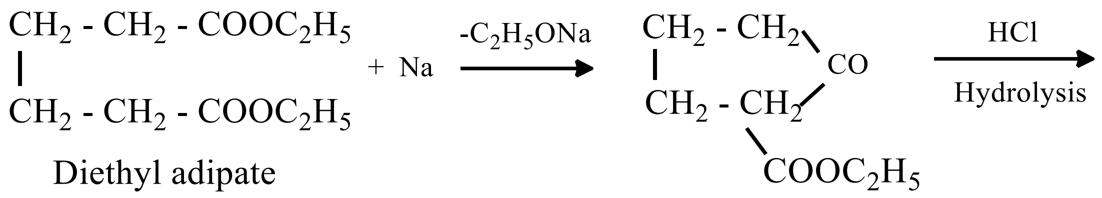


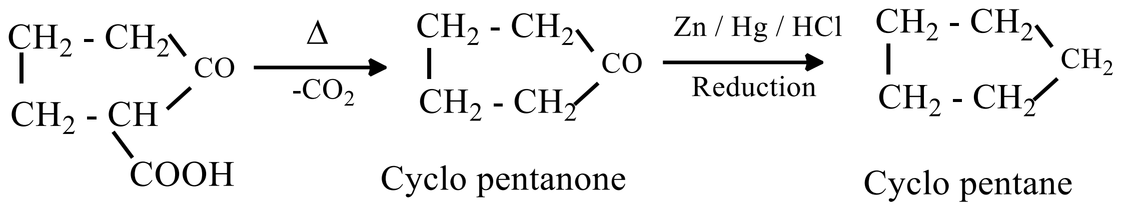
$$\begin{matrix} CH_2 - CH_2Br \\ | \\ CH_2 - CH_2Br \end{matrix} + Zn \xrightarrow[Na_2CO_3]{NaI} \begin{matrix} CH_2 - CH_2 \\ | \quad\quad | \\ CH_2 - CH_2 \end{matrix} + ZnBr_2$$



(2) **Dieckmann's meth**od

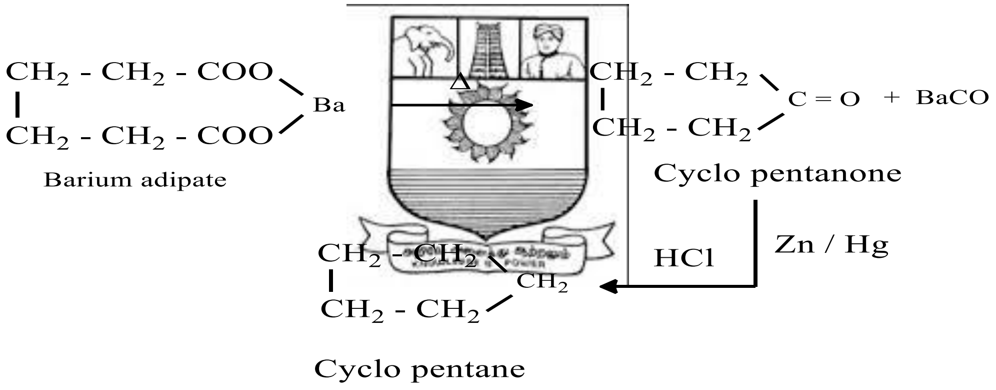
In this method esters of dicarboxylic acids when treated with sodium form cyclic ketones. Cyclic ketones on reduction give cyclo alkanes.





(3) **Wislienus method**

When calcium or barium salts of dicarboxylic acid is heated, a cyclic ketone is formed. The cyclic ketone on Clemensen’s reduction gives, cyclo akane is obtained.



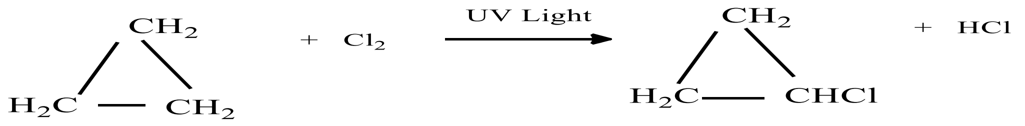
Properties

Physical Properties

- Cyclopropane and cyclobutane are gases at ordinary temperature, the remaining cycloalkanes are liquids.
- They are all lighter than water, the series has a limiting density of less than 0.9.
- They are insoluble in water but are soluble in organic solvents such as ethers and alcohols.

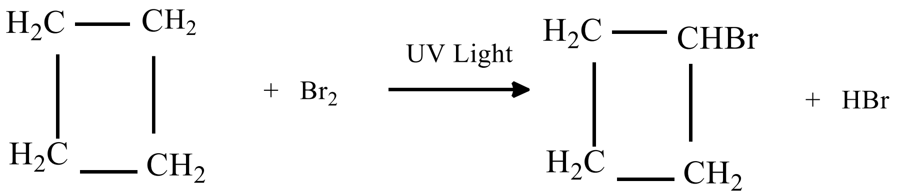
Chemical Properties

1. They undergo ring-opening and give addition product. The more important reactions of cycloakanes are given below.



Cyclopropane

Chlorocyclopropane

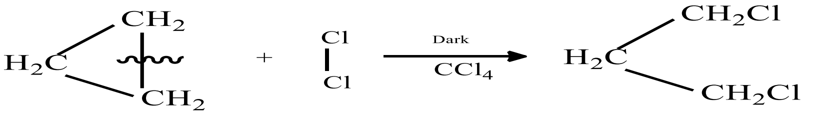


Cyclobutane

Bromocyclobutane

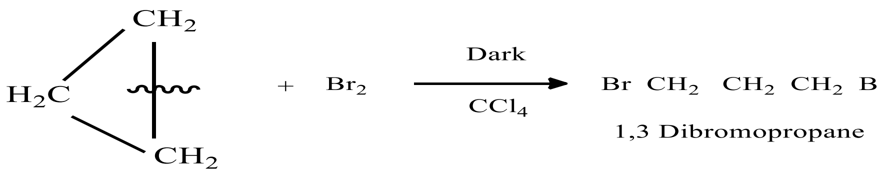
2. Addition of Cl_2 and Br_2

Cyclopropane reacts with Cl_2 and Br_2 at room temperature and in the absence of diffused sunlight to produce 1,3-dichlorocyclopropane and 1,3-dibromocyclopropane respectively.



Cyclopropane

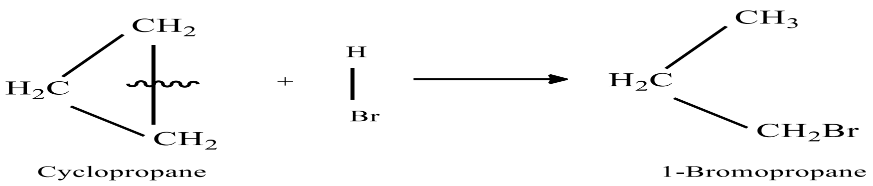
1,3 Dichloropropane

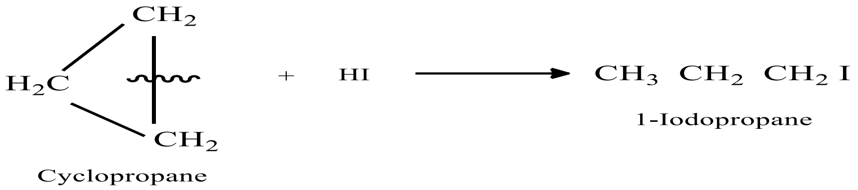


1,3 Dibromopropane

3. Addition of HBr and HI

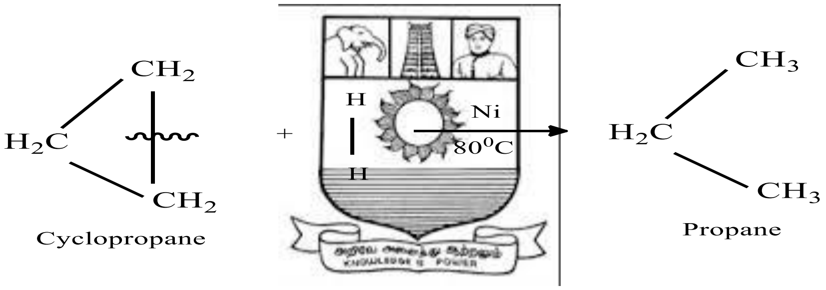
Cyclopropane reacts with conc.HBr and HI to give 1-bromopropane and 1-iodopropane respectively.

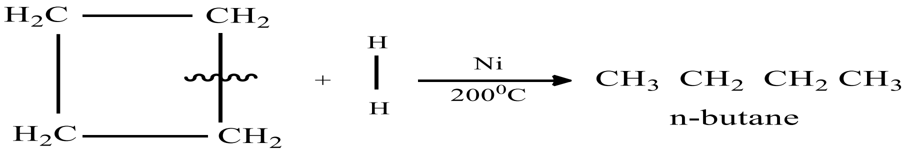




4.Addition of Hydrogen(*Catalytic Reduction*)

Cyclopropane and cyclobutane react with hydrogen in the presence of a nickel catalyst to produce propane and n-butane respectively.



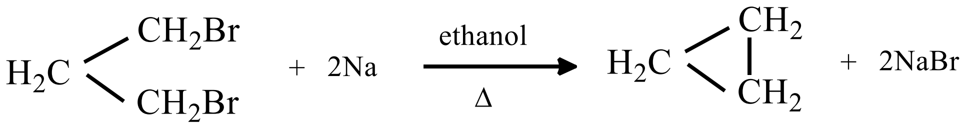


Cyclopropane

Preparation

1. From Dihalogen Compounds

Suitable dihalogen compounds on treatment with sodium or zinc corresponding cycloalkanes. For example,



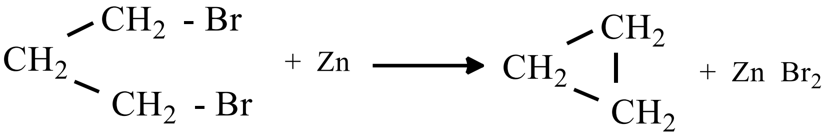
1, 3- dibromopropane

Cyclopropane

This reaction is an extension of *Wurtz Reaction* and may be regared as an **Internal Wurtz Reaction.**

2. Freund's method

In this method cycloalkane is prepared by the action of zinc on dihalides.



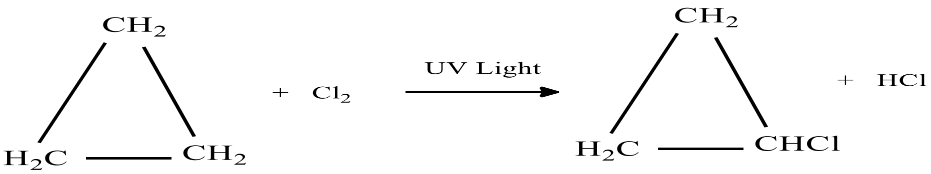
PROPERTIES

Physical properties

i. Cyclopropane is a gas at ordinary temperature.
ii. It is lighter than water.
iii. Soluble in organic solvents.

Chemical properties

1. They undergo ring-opening and give addition product. The more important reactions of cycloakanes are given below.



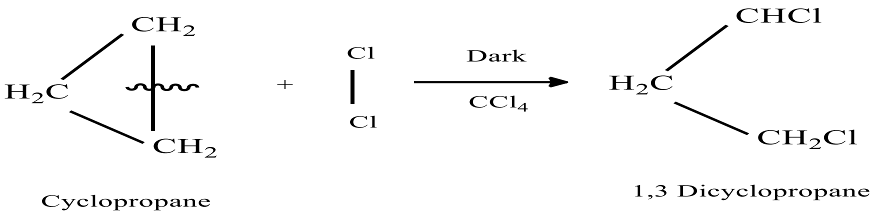
Cyclopropane

Chlorocyclopropane

2. Addition of Cl_2 and Br_2

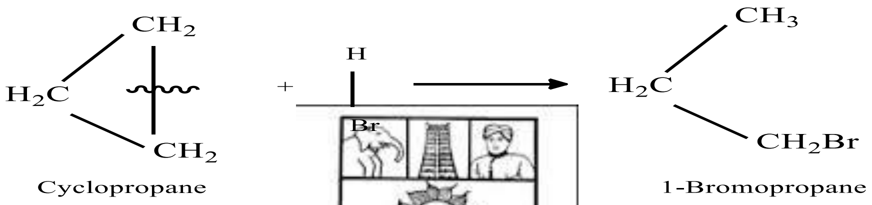
Cyclopropane reacts with Cl_2 and Br_2 at room temperature and in the absence of diffused sunlight to produce 1,3-dichlorocyclopropane and

1,3-dibromocyclopropane respectively.



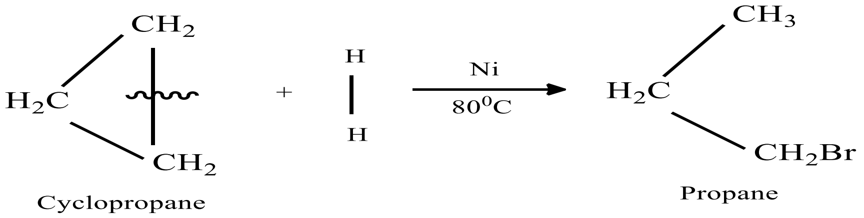
3. Addition of HBr and HI

Cyclopropane reacts with conc.HBr and HI to give 1-bromopropane and 1-iodopropane respectively.



4.Addition of Hydrogen(*Catalytic Reduction*)

Cyclopropane and cyclobutane react with hydrogen in the presence of a nickel catalyst to produce propane and n-butane respectively.

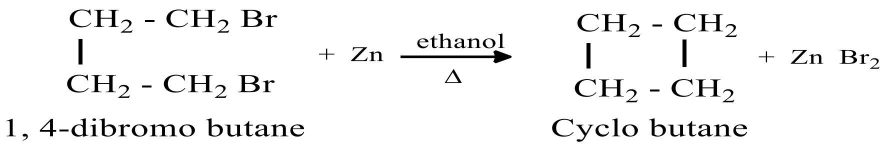


Uses of cyclopropane

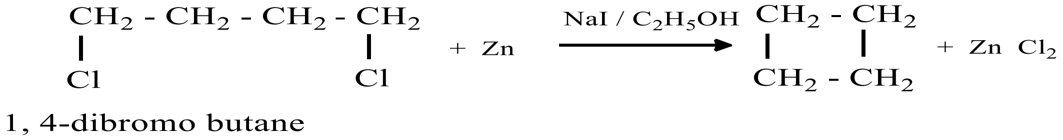
Cyclobutane

Preparation

1. From Dihalogen compounds : Suitable dihalogen compounds on treatment with sodium or zinc corresponding cycloalkanes. For example.



2. Cyclobutane is obtained by refluxing a mixture of 1,4-dichlorobutane, zinc dust, sodium iodide and alcohol. Cyclobutane is a colourless gas (bp12.5℃). It reacts with Cl2 and Br2 in the presence of diffused sunlight to give chlorocyclobutane and bromocyclobutane respectively. It reacts with H2 in the presence of a nickel catalyst at 200℃ to give n-butane.



PROPERTIES

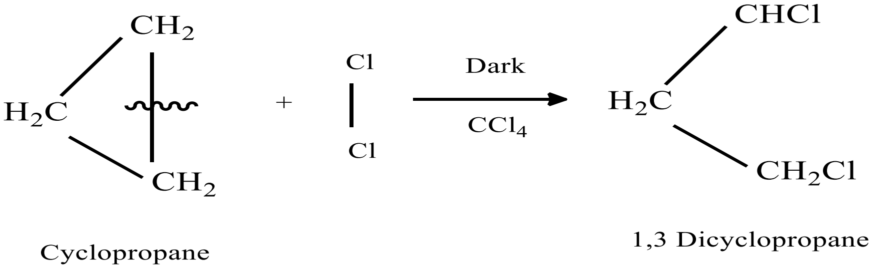
Physical properties

i. Cyclobutane is a gas at ordinary temperature.
ii. It is lighter than water.
iii. Soluble in organic solvents.

Chemical properties

1. Addition of Cl_2 and Br_2

Cyclopropane reacts with Cl_2 and Br_2 at room temperature and in the absence of diffused sunlight to produce 1,3-dichlorocyclopropane and
1,3-dibromocyclopropane respectively.



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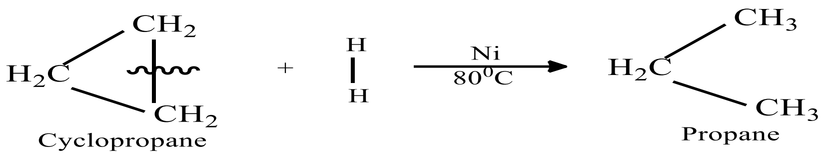


Relative stability of cycloalkanes (*Baeyer’s strain Theory*)

To explain the relative stabilities of cycloalkanes. Adolf Von Baeyer’s proposed a theory in 1885 known as Baeyer’s Strain theory. The important postulates of Baeyer’s Strain theory are;

(i) The carbon atoms of cycloalkanes(ring) lie in the same plane.

(ii) The bond angles between two adjacent carbon atoms in a ring are no longer equal to the tetrahedral bond angle 109° 28’.

(iii) The deviation (or) distortion from the normal bond angle (109° 28’) causes a strain in the molecule. This strain is known as angle strain.

(iv) Greater the angle strain, greater is the instability of the ring.

(v) More stable is the ring system, more easily it is formed.

Sachse-Mohr theory of Strainless Rings

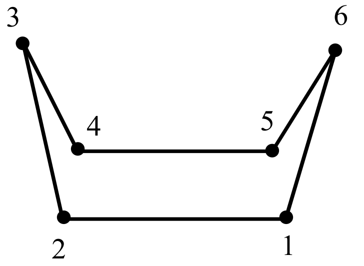
The stability of cycloalkanes larger than cyclopentane can be explained by Sachse and Mohr theory (1918). According to this

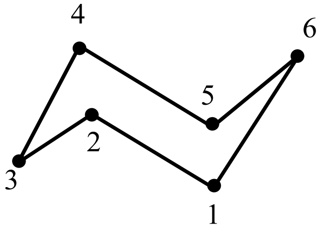
(i) The rings with six or more carbon atoms are not planar but they are puckered.

(ii) In puckered from the ring carbon lie in different planes.

(iii) The normal tetrahedral angle 109°28’ is retained in puckered form and the rings are known as strainless rings.

Thus cyclo alkane exist in two non-planar strainless forms. They are boat form and the chair form.

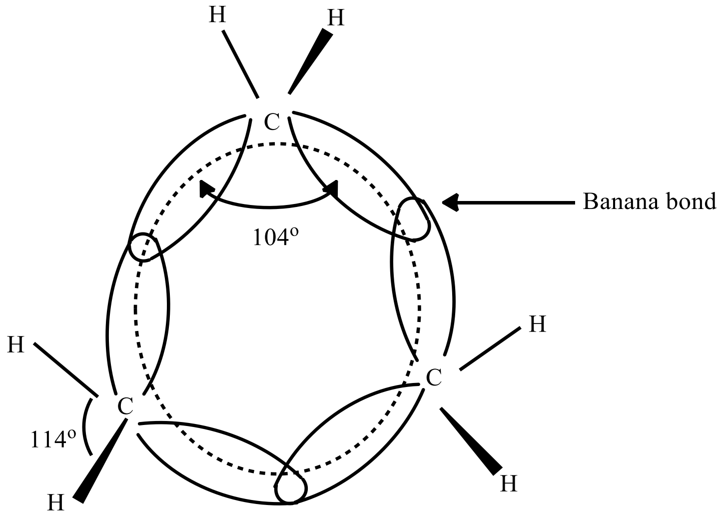




In boat form carbons 1, 2, 4 and 5 lie in the sample plane and in the same plane and carbons 3 and 6 above the plane. In the chair form, carbons 1, 2, 4 and 5 lie in the sample plane, but carbon 6 is above the plane and carbon 3 is below the plane. It is not possible to isolate these forms. Because they are readily inter convertible. Thus larger ring compounds are stable with non-planar strainless rings with normal tetrahedral angle.

Coulson and Moffit concept (Banana bond)

This concept explains the decrease in stability of a ring compounds.The decrease in stability of ring compounds is due to poor overlapping of atomic orbitals in the formation of C-C bonds and hence weakers such bonds to behave as π-bonds in cycloalkanes. These concept supports the following orbital picture for cyclo propane. This can be explained as follows.



In cyclo propane the carbon atoms are in Sp^3 hybridized state. The bond angles between C-C-C is expected to be 109°5'.The critically in such ring system the tetrahedral angle (109°5') is not possible and it should be 60°. So that the carbon atoms is cyclo propane can not be assigned structure similar to open chain C-C bond. However these can be placed in such a manner that only a partial overlap of SP^3 hybrid orbital occurs to relieve the strain by decreases the deviation from tetrahedral angle (109°5') and H-C-H angle is increased from 109°5' to 114°.Such SP^3 hybrid orbitals with best bond causes poor overlapping of orbitals to relieve angle strain are called banana bonds. So bonds increases the internal bond angle from 60° to 104°to release strain but such orbitals have less diffical overlapping.

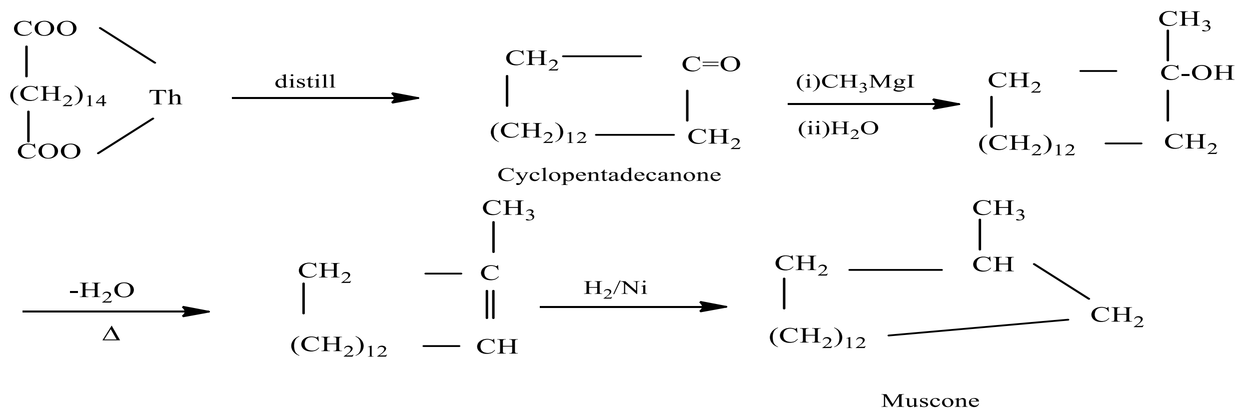
Conformations of cyclo butanes

The carbon atoms of cyclo alkanes are Sp^3 hybridized. The normal tetrahedral bond angle of an Sp^3 hybridized atom is 109°5'. But cyclobutane has considerable angle strain because the interal bond angle are 88°and decrease more than 21° from the normal tetrahedral bond angle. Hence the cyclobutane ring is not planar but slightly folded. In the cyclobutane ring were planar, the angle strain would be less, but torsional strain would be considerables larger because as all eight C-H bonds would be eclipsed. So cyclobutane ring slightly folded to relieve from its angle strain and torsional strain.

3.2 Large ring compounds

Synthesis and structure of Muscone ($C_{16}H_{30}O$)

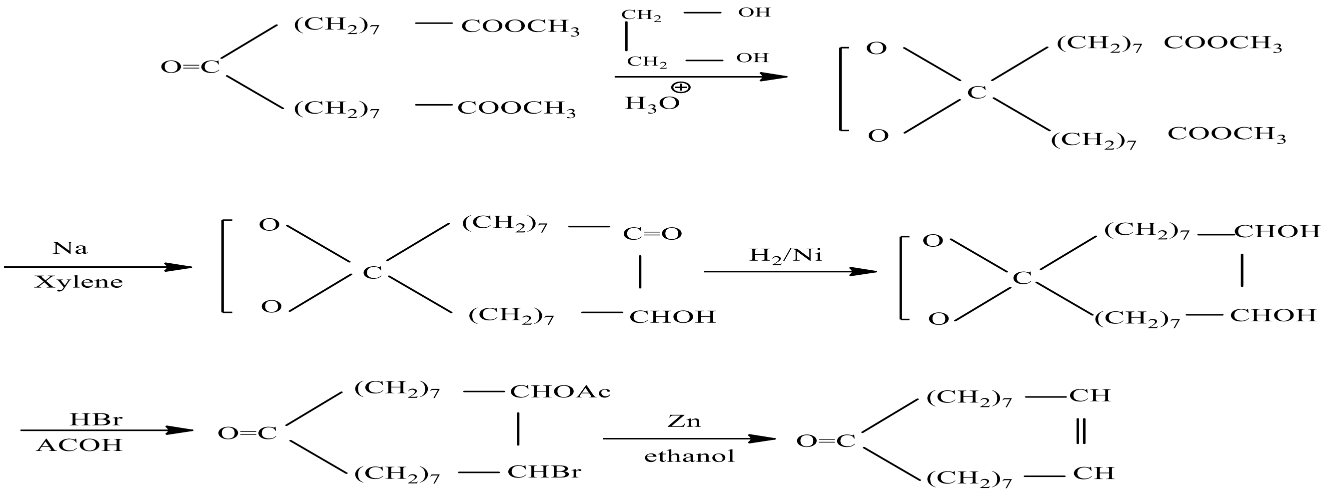
It is found in natural musck. It is a colourless oil and is optically active. It was prepared from cyclopentadecanone. Cyclopentadecanone was prepared by the distillation of thorium salt of tetradecane -1,14-dicarboxylic acid.



Civatone ($C_{17}H_{30}O$)

Synthesis

Stoll synthesized civatone by following sequence of reaction



Cis and trans civatone

3.3 Answer the Following Questions

PART-A

1. Give any two methods pf preparation of cyclo alkanes
2. Discuss the stability of cycloalkanes
3. Write the properties of cyclo propane

PART-B

1. Write a note on Bayer's Strain Theory
2. Give the stability and general methods of preparation of cyclo alkanes
3. Write a note on Sache-Mohr strainless rings
4. Explain the coulson and Moffit's concept
5. Discuss the synthesis of muscone and civatone

UNIT-IV

AROMATIC COMPOUNDS

4.1 AROMATICITY

The term ‘ aromatic character’ or Aromaticity was adopted to signify the characteristic physical and chemical behaviour of benzene and the related compounds undergo substitution reactions.

Originally the aromatic character was attributed to the presence of a planar, cyclic conjugated π bond system as in benzene. Thus cyclic polyenes possessing alternate double and single bonds, with a planar carbon skeleton were shown to have aromatic character.

It was Robinson who first pointed out that the presence of alternate double and single bonds conferred aromaticity on the benzene ring owing to delocalization of the six π electrons over the carbon-sextet. Thus the aromaticity of benzene was attributed to the six carbon planar hexagon having a sextet of π electrons in a continuous cloud above and below it.

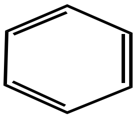
Characteristics of aromatic compounds

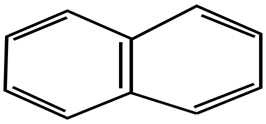
The π electrons are now said to be completely delocalized and can freely move about the six positive carbon nuclei instead of any two as in Kekule structure. The aromatic hydrocarbons resist addition and oxidation reactions since these destroy the extensive overlap and the stability of the system.

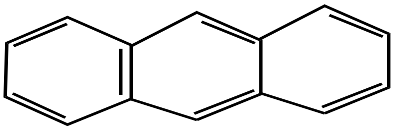
HUCKEL’S RULE

According to this rule, in a cyclic system of overlapping p orbitals if the number of π electrons is 4n+2, the system will have aromatic character, otherwise not. Here n=0, 1, 2, 3 etc. Thus

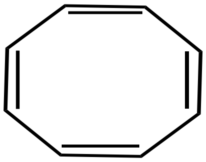
(a) Benzene, naphthalene and anthracene containing 6, 10 and 14 π electrons respectively satisfy Huckel Rule and are aromatic.

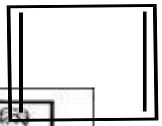

benzene
6π electrons
($n = 1; 4 \times 1 + 2 = 6$)
$4n + 2$ rule satisfied
AROMATIC


Naphthalene
10π electrons
($n = 2; 4 \times 2 + 2 = 10$)
$4n + 2$ rule satisfied
AROMATIC


Anthracene
14π electrons
($n = 3; 4 \times 3 + 2 = 14$)
$4n + 2$ rule satisfied
AROMATIC

(b) 1, 3-cyclobutadiene and 1, 3, 5, 7-cyclooctatetrene containing 4π electrons and 8π electrons respectively do not satisfy Huckel Rule and are nonaromatic.

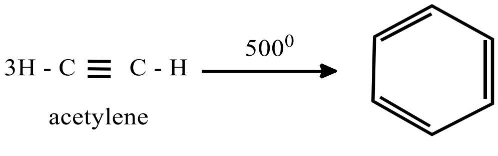

1, 3, 5, 7 - cyclooctatetrene
8π electrons
$4n + 2$ rule not satisfied
NON AROMATIC

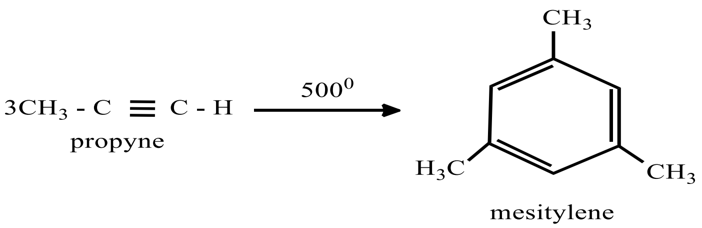

1, 3 - cyclobutadiene
4π electrons
$4n + 2$ rule not satisfied
NON AROMATIC

General methods of preparation of benzene and its homologues

1. From Alkynes

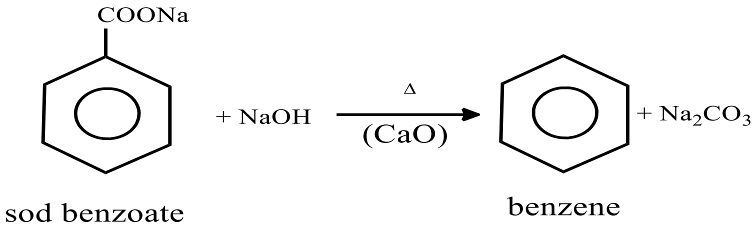
Benzene and many of its homologues cab be prepared by polymerization of appropriate alkynes. Acetylenes will polymerise at high temperature to yield arenes. Thus,

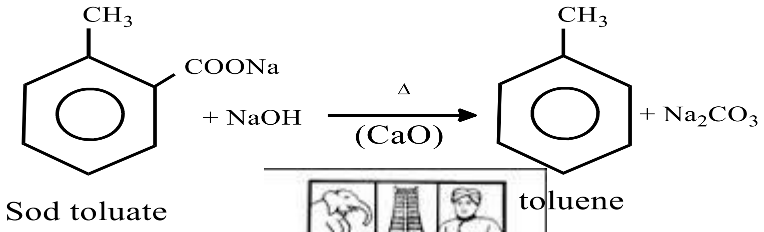




2. Decarboxylation of Aromatic acids

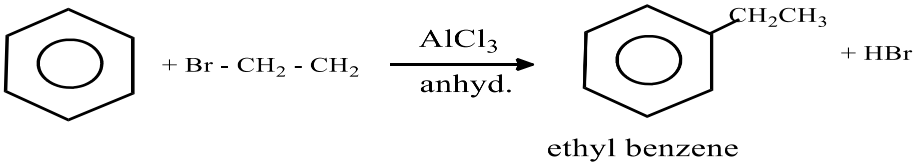
Arenes can be prepared by heating aromatic acids or their sodium salts with sodalime.





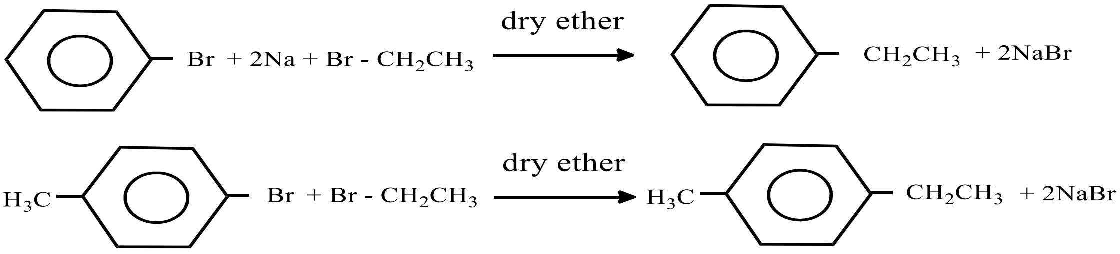
3. By Friedel-Crafts Reaction

Alkylbenzenes can be best prepared by the action of alkyl halides on benzene and its homologues in the presence of anhydrous aluminium chloride as catalyst. For example,



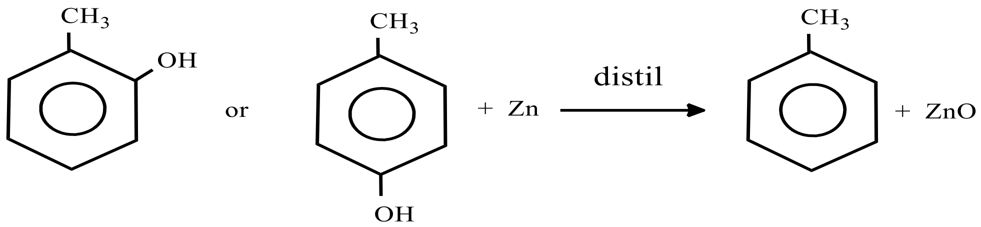
(4) By Wurtz-Fitting Reaction

Arenes can be obtained by the action of sodium metal on a mixture of alkyl halide and aryl halide in ether solution.



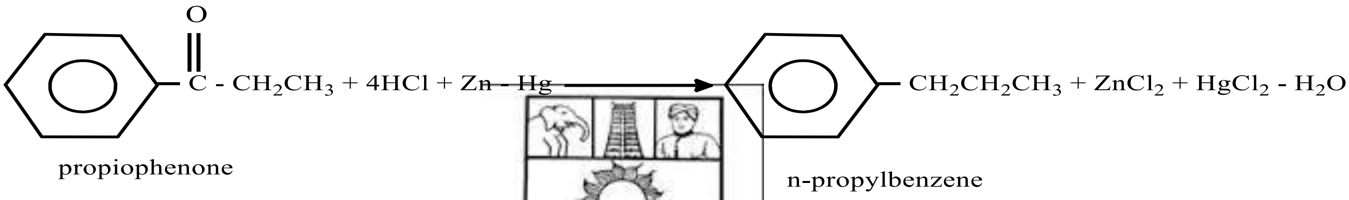
(5) **By Deoxygenation of phenols**

When distilled with zinc dust, phenols are deoxygenated to yield the respective parent arene.



(6) **By Clemmensen Reduction of ketones**

Higher homologues of benzene can be prepared easily by reduction of appropriate aromatic-aliphatic ketones with zinc amalgam and conc. Hydrochloric acid.



PROPERTIES

Physical properties

1. Monocyclic arenes are colourless mobile liquids which have pleasant odours. The higher homologues are crystalline solids.
2. They are lighter than and insoluble in water but are miscible in all proportions with organic solvents such as ethanol, ether, petrol etc.
3. They dissolve fats and many other organic substances which are insoluble in water.
4. The lower members are quite toxic, and prolonged inhalation of their vapours should be avoided.
5. Their boiling points increase fairly regularly with the rise of molecular weight.

4.3 Electrophilic Aromatic Substitution:

It means replacement of an atom generally hydrogen or a group attached to the carbon of a benzene ring by another group .Substitution reaction of aromatic compounds are mainly classified as

i)Electrophilic Substitution(SE)

ii)Necleophilic Substitution(SN) and

iii)Free radical Substitution(SF)

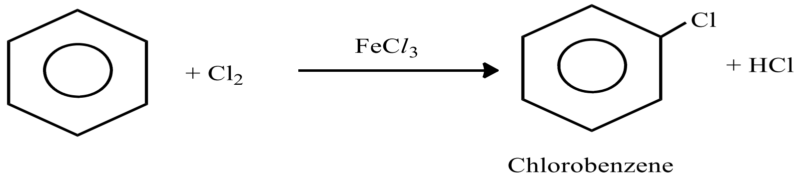
Electrophilic Substitution (SE) Reactions

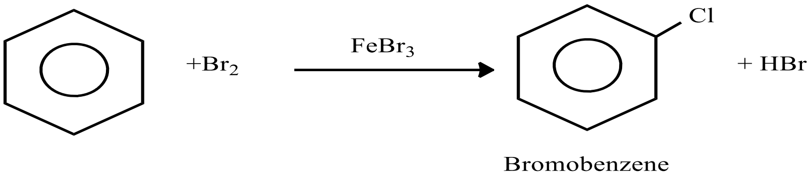
The benzene ring with its six π electrons in a delocalized state acts as a source of electrons .The electrons on the π clouds are readily available to form new bonds with electrons deficient substituents – called electrophiles (E^+)

Mechanism of electrophilic substitution reactions of benzene

1)Halogenation:

The halogenations of benzene is carried out with halogens in the presence of a Lewis acid catalyst such as $AlCl_3$,$FeCl_3$, *or* $FeBr_3$ by the elimination of a protons as HCl or HBr.





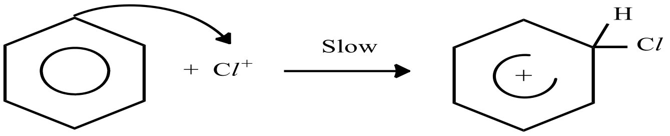
Mechanism:

i)Generation of the electrophile

$$FeCl_3 + Cl_2 \rightleftharpoons Cl - Cl \cdots FeCl_3 \longrightarrow Cl^+ + FeCl^{4-}$$

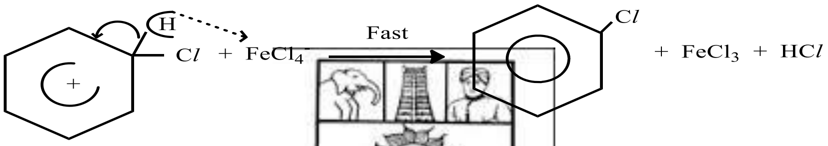
(Chloronium ion electrophile)

ii)Formation of a σ – Complex



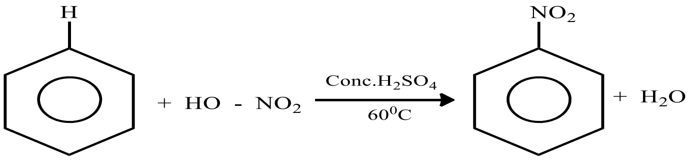
σ- Complex (Carbocation)

iii) Elimination of a proton



2)Nitration:

Benzene reacts with nitric acid in the presence of sulpuric acid 60° C to form nitrobenzene.



Mechanism

i)Generation of electrophilic nitronium ion(NO_2^+)

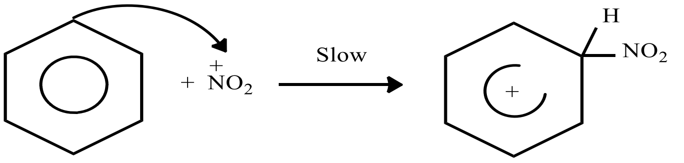
$$H_2SO_4 + HNO_3 \rightleftharpoons HSO_4^- + H_2O^+NO_2$$

$$H_2O^+NO_2 \rightleftharpoons H_2O + NO_2^+ \text{ (Nitronium ion)}$$

The overall reaction is

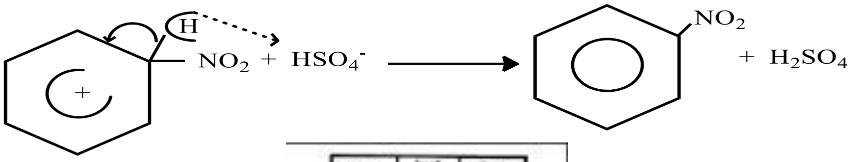
$$HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H2O$$

ii)Formation of σ – Complex



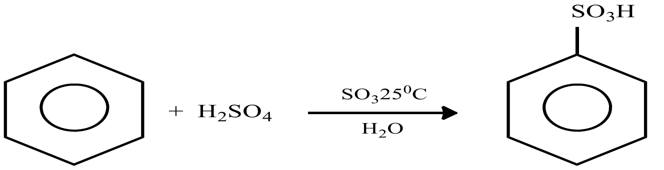
stable resonance hybrid (σ - complex)

ii)Eliminatiom of proton



3)Sulphonation:

Benzene reacts with concentrated or fuming sulpuric acid to form benzene sulphonic acid.



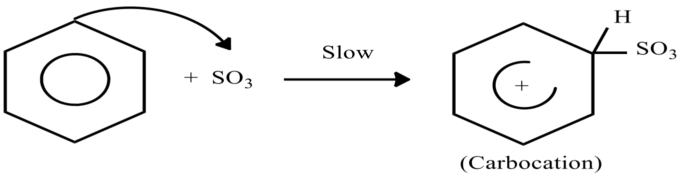
Benzene sulphonic acid

Mechanism:

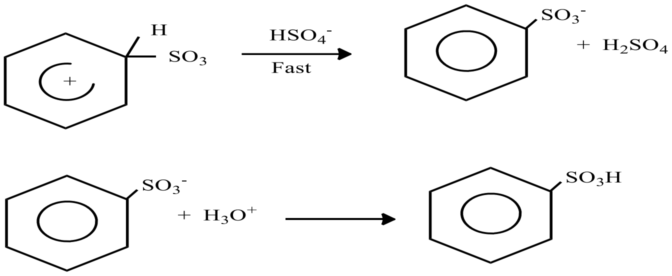
i)Generation of the electrophile

$$2H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- + \underset{\text{electrophile}}{SO_3}$$

ii) Formation of σ –Complex



iii) Elimination of proton

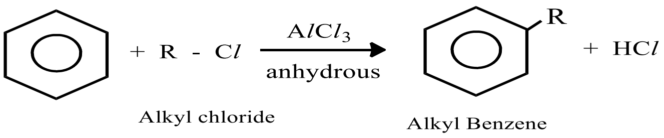


4. Friedel Craft's reaction:

Benzene reacts with alkyl halide(Friedel Craft's alkylation) or acyl halide (FriedelCraft's acylation)in the presence of Lewis acid like $AlCl_3$,BF_3,$AlBr_3$ etc.

Friedel crafts alkylation :

Benzene reacts with an alkyl halide R-C*l* or R-Br in the presence of anhydrous $AlCl_3$ as catalyst,one of the hydrogen atoms of the ring is substituted by the alkyl group(R).

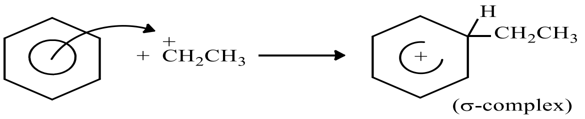


Mechanism:

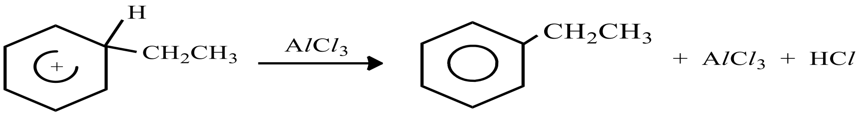
1.Generation of elctrophile:

$$CH_3CH_2 \vdots Cl + AlCl_3 \rightarrow \underset{\text{Carbonium ion}}{CH_3CH_2^+ \cdots [AlCl_4]^-} \rightarrow CH3 - CH2^+ + AlCl^-_4$$

2.Formation of the complex:

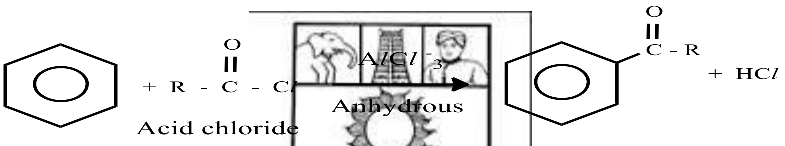


3.Elimination of proton



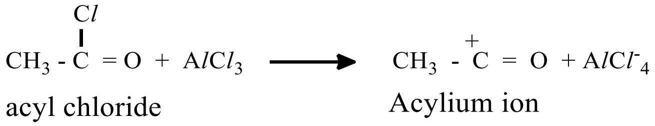
Friedel crafts acylation

Benzene reacts with acid chloride,the acyl group(RCO)is introduced in the aromatic ring in the presence of anhydrous $AlCl_3$, BF_3, $FeCl_3$, $ZnCl_2$ etc(Lewis acid catalysts)



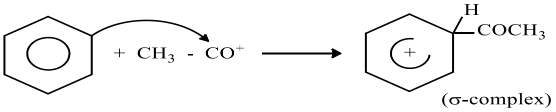
Mechanism

1.Generation of electrophile (acylium ion)

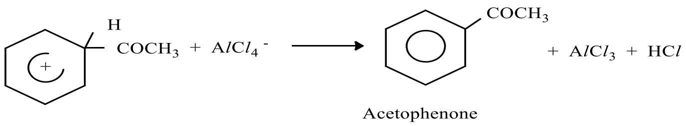


$$\underset{\text{acyl chloride}}{CH_3-\overset{Cl}{\overset{|}{C}}=O} + AlCl_3 \longrightarrow \underset{\text{Acylium ion}}{CH_3-\overset{+}{C}=O} + AlCl_4^-$$

2.Formation of σ –Complex



3.Elimination of proton(H⁺)



4.4 Directing effect of groups

When substituted benzenes undergo electrophilic attack , the substitution influence the orientation of attack by the incoming electrophile. It the substitution tend to direct the incoming group into the ortho and para positions they are known as ortho para directors. If the substitution tend to direct the incoming group in meta position , they are known as meta direction. The groups such as $–NH_2$, -OH, $-CH_3$, -F, $-C_2H_5$ are some examples of ortho para directing groups .Where as the groups such as –COOH, -CHO, -COR, -CN,$-NO_2$ are the some examples of meta directing groups.Inductive effect and resonance effects are the two factors determine the orientation of aromatic substitution reactions.

Answer the Following Questions

PART_A

1. State and explain Huckel rule with examples
2. Write a characteristic of aromatic compound
3. What is Clemmensen reduction with example
4. How will you prepare mesitylene from alkynes

PART-B

1. Give any three methods of preparation of benzene and its homologus
2. Write a short notes on directing effects of groups
3. Explain the mechanism of electrophilic substitution reaction of benzene

UNIT-V

ORGANO METALLIC COMPOUNDS AND SULPHUR COMPOUNDS

5.1 Preparation of Organo metallic compounds

GRIGNARD REAGENTS

Preparation

Grignard reagents are prepared in the laboratory by the action of alkyl halides on magnesium metal in the presence of dry ether.

$$\underset{\text{Alkyl halide}}{R\text{-}X + Mg} \xrightarrow{dry\ ether} \underset{\text{Grignard reagent}}{R\text{-}Mg\text{-}X}$$

Example

$$\underset{\text{Methyl iodide}}{CH_3\text{-}I + Mg} \xrightarrow{dry\ ether} \underset{\text{Methyl magnesium iodide}}{CH_3\text{-}Mg\text{-}I}$$

In actual practice a Grignard reagent is produced by dropping a solution of the alkyl halide in dry ether into the reaction flask containing magnesium ribbon suspended in dry ether. The ether solution of the Grignard reagent thus obtained is used immediately in the flask in which it is prepared.

MECHANISM OF FORMATION

The formation of Grignard reagents by the above procedure probably occurs via free radical mechanism as given below.

$$2R - X + Mg \longrightarrow R - R + Mg\,X_2$$

$$Mg + MgX_2 \rightleftharpoons 2Mg - X$$

$$R - X + Mg\,X \longrightarrow R + Mg\,X_2$$

$$R + Mg\,X \longrightarrow R - Mg - X$$

Structure

The role of ether here is not only to provide a medium for the function of GrignarD reagent but it also makes them dissolve (in ether) through solvolysis.

If the function of ether is to dissolve the Grignard reagent by coordination of the type shown above, then it should be possible to prepare a Grignard reagent even in benzene in presence of a base like triethylamine. It has actually been found to be so. Only one mole of the base per mole of the alkyl halide is required.

Grignard reagent in ether can exist EITHER in structure I or II. It has been pointed out recently that there is established an equilibrium between alkylmagnesium halide(Grignard reagent) and the corresponding dialkyl magnesium in ether solution as

$$2R\,Mg - X \rightleftharpoons R_2 - Mg + Mg\,X_2$$

In right of the above fact, structure II seems to be more probable. Further, since the reaction of R_2Mg in presence of MgX_2 are the same as those of RMgX, it seems reasonable to represent Grignard reagent solvated in ether by the formulation I.

SYNTHETIC USES

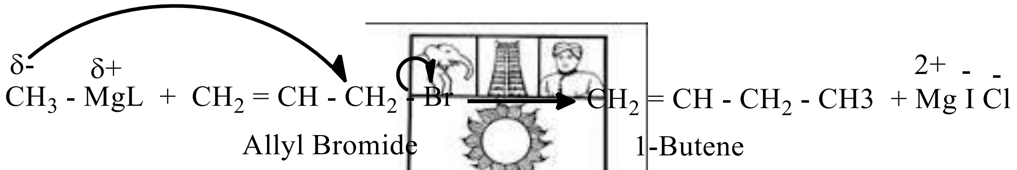
1. Preparation of hydrocarbon

Compounds like water, alcohols, carboxylic acids and amines which contain active hydrogens react with Grignard reagents to produce *hydrocarbons.*

$$\overset{\delta-}{R} - \overset{\delta+}{MgX} + \underset{\substack{\text{a compound having}\\ \text{acidic hydrogen}}}{H - A} \longrightarrow \underset{\text{alkane}}{R - H} + \overset{2+}{Mg}\overset{-}{O}H\overset{-}{X}$$

2. Preparation of alkene

Grignard reagents react with reactive halides like benzyl chloride and allyl bromide to form alkanes and alkene respectively.



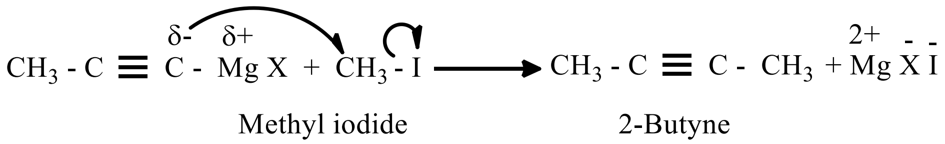
$$\overset{\delta-}{CH_3} - \overset{\delta+}{MgL} + \underset{\text{Allyl Bromide}}{CH_2 = CH - CH_2 - Br} \longrightarrow \underset{\text{1-Butene}}{CH_2 = CH - CH_2 - CH3} + \overset{2+}{Mg}\ \overset{-}{I}\ \overset{-}{Cl}$$

These reaction probably proceed by SN^2 mechanism.

3. Preparation of alkynes

The terminal alkynes react with Grignard reagents to produce alkylmagnesium halide which on subsequent treatment with alkyl halides undergo SN^2 displacements to form higher *alkynes*.

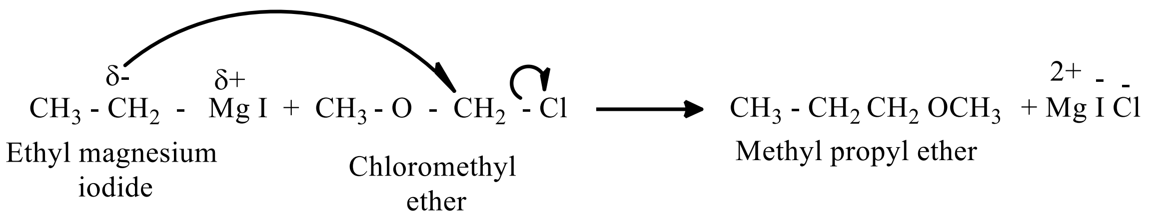
$$\underset{\text{propyne}}{CH_3 - C \equiv C - H} + R - MgX \longrightarrow \underset{\text{propynylmagnesium halide}}{CH_3 - C \equiv C - MgX} + RH$$



$$CH_3 - C \equiv \overset{\delta-}{C} - \overset{\delta+}{Mg\,X} + \underset{\text{Methyl iodide}}{CH_3 - I} \longrightarrow \underset{\text{2-Butyne}}{CH_3 - C \equiv C - CH_3} + \overset{2+}{Mg}\ \overset{-}{X}\ \overset{-}{I}$$

4. Preparation of ethers

Grignard reagents react with lower halogenated ethers to produce higher ethers.



$$\overset{\delta-}{CH_3-CH_2}-\overset{\delta+}{Mg\,I} + CH_3-O-CH_2-Cl \longrightarrow CH_3-CH_2CH_2OCH_3 + \overset{2+}{Mg}\,\overset{-}{I}\,\overset{-}{Cl}$$

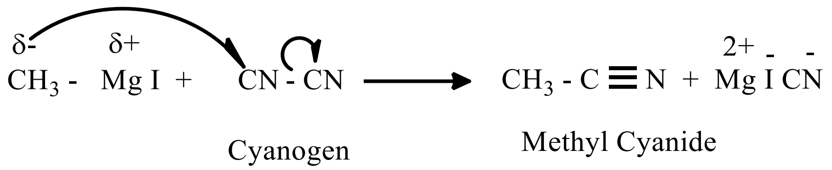
Ethyl magnesium iodide

Chloromethyl ether

Methyl propyl ether

5. Preparation of alkyl cyanides

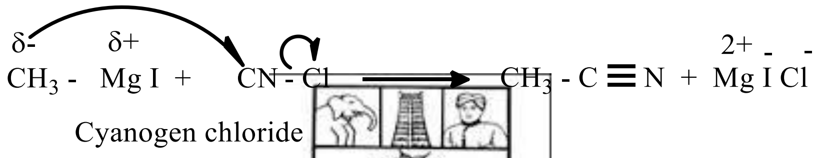
Alkyl cyanides are produced when Grignard reagents react with cyanogens and cyanogens chlorides.



$$\overset{\delta-}{CH_3}-\overset{\delta+}{Mg\,I} + CN-CN \longrightarrow CH_3-C\equiv N + \overset{2+}{Mg}\,\overset{-}{I}\,\overset{-}{CN}$$

Cyanogen

Methyl Cyanide



$$\overset{\delta-}{CH_3}-\overset{\delta+}{Mg\,I} + CN-Cl \longrightarrow CH_3-C\equiv N + \overset{2+}{Mg}\,\overset{-}{I}\,\overset{-}{Cl}$$

Cyanogen chloride

6. Preparation of primary amine

Grignard reagents react with chloroamines to give *primary amines.*

$$CH_3-Mg\,I + NH_2-Cl \longrightarrow CH_3NH_2 + \overset{2+}{Mg}\,\overset{-}{I}\,\overset{-}{Cl}$$

Methyl magnesium iodide

chloroamine

Methylamine

7. Preparation of alkyl iodide

When an alkyl magnesium chloride or bromide is treated with iodine, *alkyl iodides* are formed.

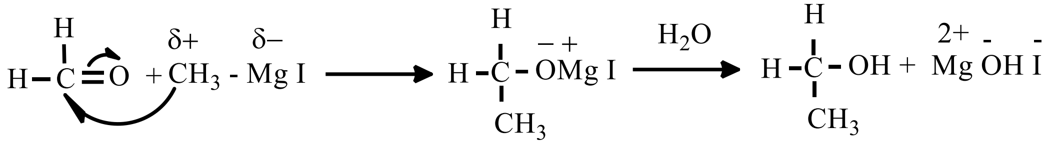
$$CH_3-Mg\,CI + I_2 \longrightarrow CH_3-I + \overset{2+}{Mg}\,\overset{-}{I}\,\overset{-}{Cl}$$

Methyl magnesium chloride

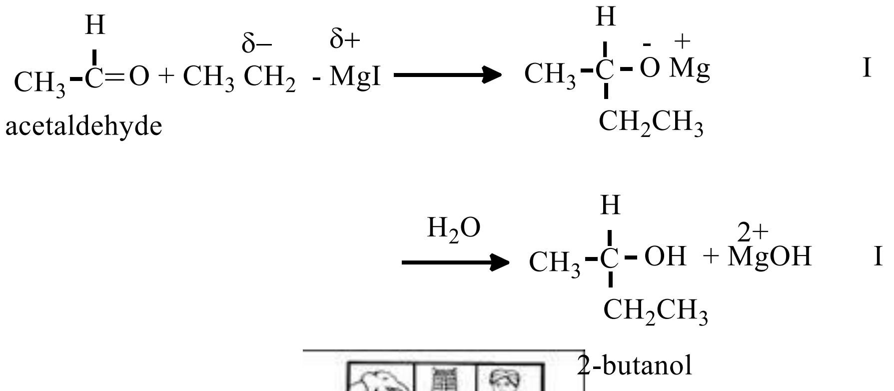
Methyl iodide

8. Preparation of 1°, 2°, 3° alcohols

Grignard reagents react with aldehydes to produces alcohols. The reaction with formaldehydes gives *primary alcohols*, while with other aldehydes *secondary alcohols* are produced.



$$H-\overset{H}{C}=O + \overset{\delta+}{C}H_3-\overset{\delta-}{Mg}I \longrightarrow H-\underset{CH_3}{\overset{H}{C}}-\overset{-}{O}\overset{+}{Mg}I \xrightarrow{H_2O} H-\underset{CH_3}{\overset{H}{C}}-OH + \overset{2+}{Mg}\overset{-}{OH}\overset{-}{I}$$

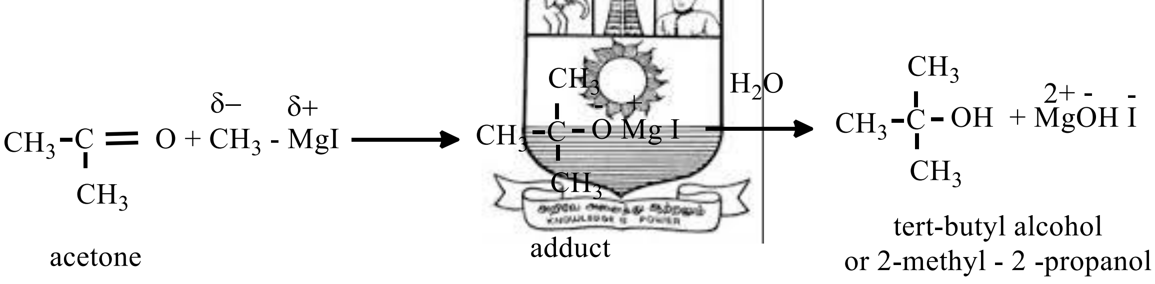


$$CH_3-\overset{H}{C}=O + CH_3\overset{\delta-}{C}H_2-\overset{\delta+}{Mg}I \longrightarrow CH_3-\underset{CH_2CH_3}{\overset{H}{C}}-\overset{-}{O}\overset{+}{Mg}\quad I$$

$$\xrightarrow{H_2O} CH_3-\underset{CH_2CH_3}{\overset{H}{C}}-OH + \overset{2+}{Mg}OH \quad I$$

acetaldehyde

2-butanol



$$CH_3-\underset{CH_3}{C}=O + \overset{\delta-}{C}H_3-\overset{\delta+}{Mg}I \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{-}{O}\overset{+}{Mg}I \xrightarrow{H_2O} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH + \overset{2+}{Mg}\overset{-}{OH}\overset{-}{I}$$

acetone

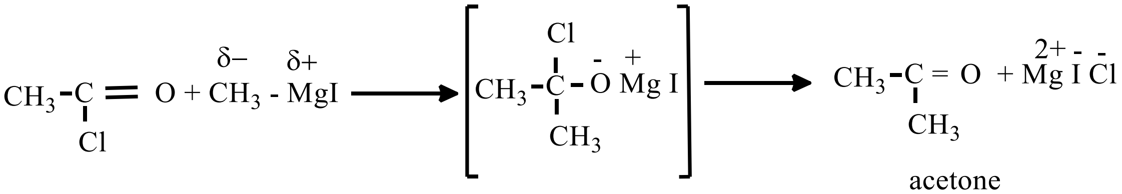
adduct

tert-butyl alcohol
or 2-methyl - 2 -propanol

9. Preparation of ketone

Ketones react with Grignard reagents to form *tertiary alcohols.*

Grignard reagents(1 mole) and an acid chloride (1 mole) react readily to form ketones.

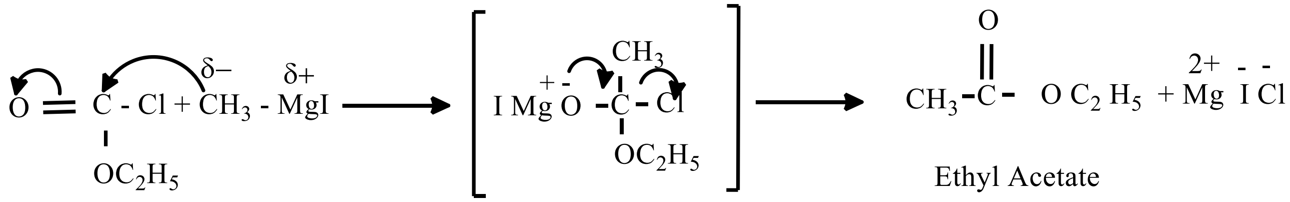


$$CH_3-\underset{Cl}{C}=O + \overset{\delta-}{C}H_3-\overset{\delta+}{Mg}I \longrightarrow \left[CH_3-\underset{CH_3}{\overset{Cl}{C}}-\overset{-}{O}\overset{+}{Mg}I\right] \longrightarrow CH_3-\underset{CH_3}{C}=O + \overset{2+}{Mg}\overset{-}{I}\overset{-}{Cl}$$

acetone

10. Preparation of esters

Higher esters are obtained by the action of Grignard reagent (1 mole) and ethyl chloroformate(1 mole).



Ethylchloroformate

Ethyl Acetate

METHYL LITHIUM (CH_3Li)

Preparation

Organolithium compounds are obtained by the reaction of alkyl halides with metallic lithium in ether in an inert atmosphere of nitrogen or helium.

$$CH_3\text{-}Br \quad + 2Li \xrightarrow{dry\ ether, -10°, N_2} CH_3\text{-}Li \quad + \ LiBr$$

n-methyl bromide methyl lithium

PROPERTIES

Physical properties

Organolithium compounds are particularly sensitive towards air and moisture. These react with cyclic ethers, alkyl halides, active halogen compounds and carbonyl compounds much in the same fashion as do Grignard reagents.

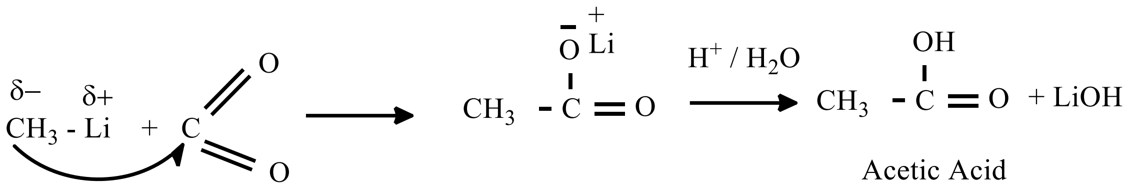
Chemical properties

(a). With water they give alkanes

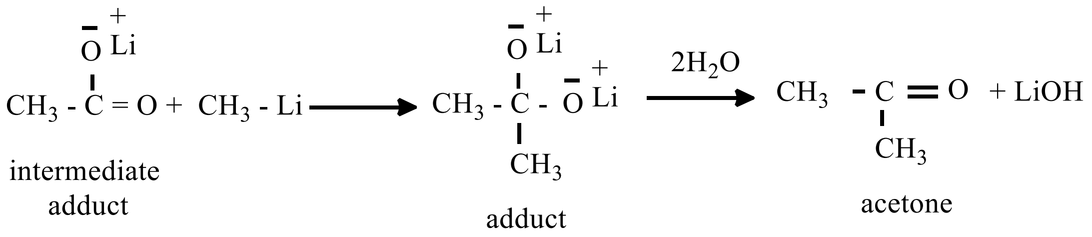
$$CH_3\text{-}Li \quad + \quad H\text{-}OH \longrightarrow CH_4 \ + LiOH$$

Methyllithium methane

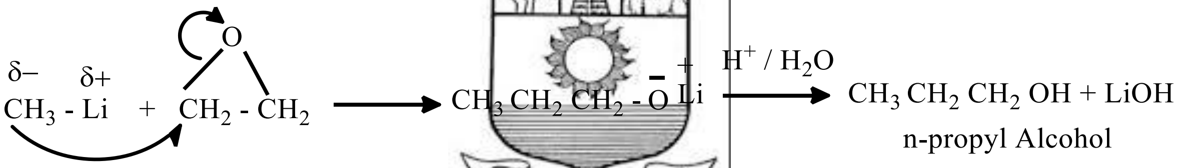
(b). With carbon dioxide they produce carboxylic acids.



However, if excess of CH_3Li is present, the acid obtained is contaminated with ketone.



(c). With epoxyethane (ethylene oxide) they produce primary alcohols.



5.3 DIETHYL ZINC $(C_2H_5)_2$ Zn

Preparation

Dialkylzincs are prepared by heating alkyl iodides with zinc in an atmosphere of CO_2, and then distilling the product (alkylzinc iodide) in an inert atmosphere of CO_2.

$C_2H_5\text{-}I \quad + \quad Zn \xrightarrow{CO_2} C_2H_5\text{-}ZnI$

Ethyl iodide ethyl zinc iodide

$2C_2H_5\text{-}ZnI \xrightarrow{CO^2,distill} C_2H_5\text{-}Zn\text{-}C_2H_5 \quad + ZnI_2$

Properties

Dialkylzincs are colourless, unpleasant smelling liquids which have comparatively low boiling points.

They are spontaneously inflammable in air and produce painful burns when brought into contact with skin.

They give reaction similar to those of Grignard reagents but being difficult to handle are sparingly used in organic synthesis.

Chemical properties of diethyl Zinc [$(C_2H_5)_2Zn$]

1. **With water and alcohol**

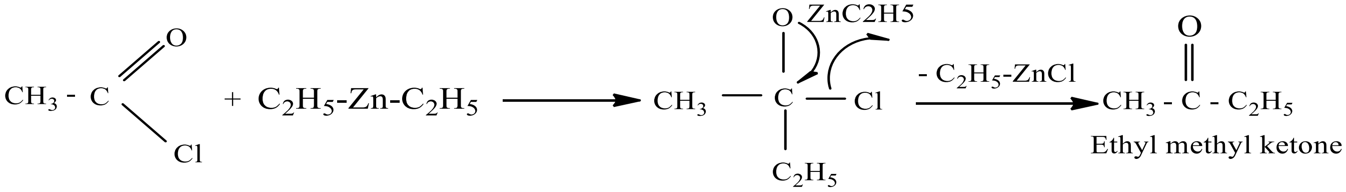
   Diethyl Zinc readily decomposed by water and alcohol gives ethane.

$$(C_2H_5)Zn + 2H_2O \longrightarrow 2C_2H_6 + Zn(OH)_2$$

$$(C_2H_5)Zn + 2C_2H_5OH \longrightarrow 2C_2H_6 + \underset{\text{Zinc ethylate}}{(C_2H_50)_2Zn}$$

2. **With acetyl chloride**

   With acetyl chloride it gives ethyl methyl ketone.



3. **Reaction with HgCl₂**

It gives diethyl mercury with $HgCl_2$

$$Zn(C_2H_5)_2 + HgCl_2 \longrightarrow (C_2H_5)_2Hg + ZnCl_2$$

3. **With SiCl₄**

   It gives tetraalkyl silane with $SiCl_4$

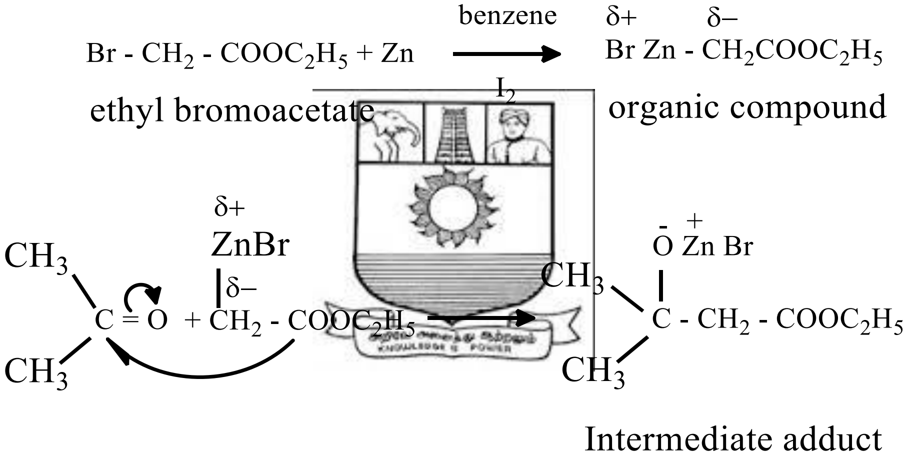
$$(C_2H_5)_2\,Zn + Si\,Cl_4 + (C_2H_5)_2\,Zn \longrightarrow (C_2H_5)_4Si + 2ZnCl2$$

Tetraethyl silane

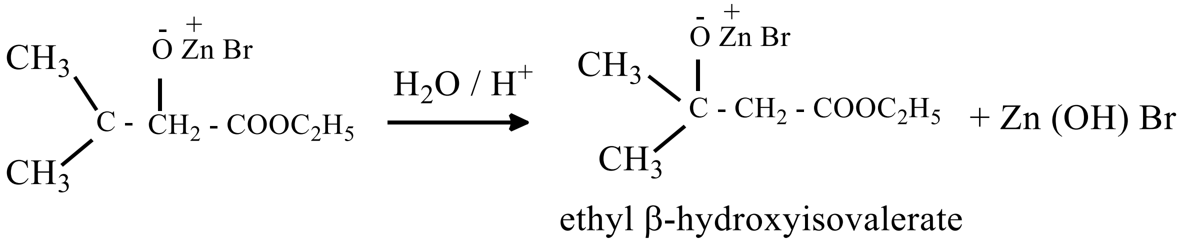
5.4 Reformatsky Reaction

This reaction involves the interaction of an α-bromoester with carbonyl compound (aldehyde and ketone) I presence of metallic zinc. An intermediate organo-zinc compound is first formed. This then adds on to the carbonyls group of aldehyde or ketone producing β-hydroxyester. These can be readily dehydrated to α,β-unsaturated acids by heating with concentrated sulphuric acids.

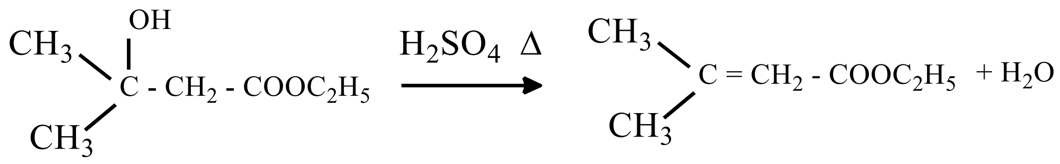
(i). Formation of organozinc compound



Acid hydrolysis of the adduct



Dehydration to form α, β – unsaturated ester



Tetra ethytl Lead (TEL)

Tetramethyl Tin

Preparation :

It is prepared by the reaction between methyl chloride and a tin – sodium alloy.

$$4CH_3\,Cl + 4\ Na / Sn \rightarrow (CH_3)_4\,Sn + 3\,Sn + 4\,NaCl$$

It may also be prepared by the interaction of methyl magnesium bromide (Grignard reagent) and $SnCl_4$.

$$SnCl_4 + 4\,CH_3MgCl \rightarrow (CH_3)_4\,Sn + 4MgClBr$$

Properties

1. Tetramethyl tin reacts with halogens to form organo tin halides

$$(CH_3)_4\,Sn + X_2 \rightarrow (CH_3)_3\,SnX + CH_3X$$

2. It reacts slowly with hydrogen halides to form organo tin halides

$$(CH_3)_4\,Sn + HX \rightarrow (CH_3)_3\,SnX + CH_4$$

3. It reacts with stannic chloride to give a variety of organotin halides.

$$(CH_3)_4\,Sn + SnCl_4 \xrightarrow{20^0C} (CH_3)_3\,SnCl + CH_3SnCl_3$$

$$(CH_3)_4\,Sn + SnCl_4 \xrightarrow{180^0C} 2\,(CH_3)_2\,SnCl_2$$

Uses

It is used as a catalyst in polymerization reactions.

5.5 Preparation of Organo sulphur compounds

THIOALCOHOLS

The sulphur analogues of alcohols are called *thioalcohols or thiols (thio*=sulphur). They have the functional group –SH. Since thiols react with mercury oxide forming insoluble salts, they are commonly known as *mercaptans (mercurius*=mercury; *captans*=catching). Examples

CH_3SH	Methyl mercaptan(methanethiol)
CH_3CH_2SH	Ethyl mercaptan (ethanethiol)

General methods of preparation

1. From alkyl halides

Thiols may be prepared by heating an alkyl halide with an alcoholic solution of sodium or potassium hydrogen sulphide.

$$C_2H_5Cl + KSH \longrightarrow C_2H_5SH + KCl$$

Ethyl mercaptan

2. From alcohols

Alcohols when heated with phosphorus pentasulphide from thioalcohols.

$$5C_2H_5OH + P_2S_5 \longrightarrow 5C_2H_5SH + P_2O_5$$

Ethanol Ethanethiol

A more satisfactory method is to pass a mixture of alcohol vapour and hydrogen sulphide over heated thioria (catalyst).

$$C_2H_5OH \quad + \quad H_2S \xrightarrow{ThO_2, 400℃} \quad C_2H_5SH \quad + \quad H_2O$$

3. From alkyl *iso-thiouronium* salts

The best method for preparing thiols is to decompose s-alkyl iso-thiouronium salts with alkali. These salts may be obtained by the interaction of an alkyl halide and thiourea.

$$C_2H_5Br + SC(NH_2)_2 \longrightarrow [C_2H_5SC(NH_2)_2]^+Br^- \longrightarrow C_2H_5SH + NH_2CN + NaBr + H_2O$$

Ethyl bromide s-ethyl iso-thiouronium bromide Ethanethiol

General properties

1. Reaction with metals

Thiols react with alkali metals like sodium, potassium etc to form mercaptides with the evolution of hydrogen.

$$2C_2H_5SH \quad + 2Na \longrightarrow \quad 2C_2H_5SNa \quad + \quad H_2$$

Sodium ethyl mercaptide

2. Reaction with acids

Thiols react with acids and acid chlorides to form thioesters

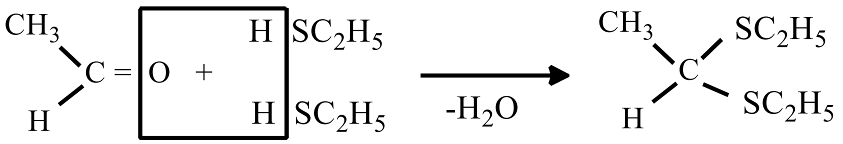
$$CH_3COOH \quad + HSC_2H_5 \longrightarrow \quad CH_3COSC_2H_5 + H_2O$$

$$CH_3COCl \quad + HSC_2H_5 \longrightarrow \quad CH_3COSC_2H_5 + HCl$$

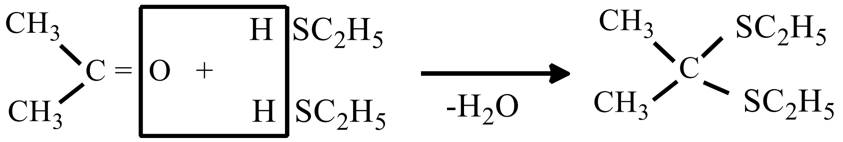
Ethyl thioacetate

3. Reaction with aldehydes and ketones

Thiols react with aldehydes and ketones in the presence of HCl to form mercaptals and mercaptols respectively.



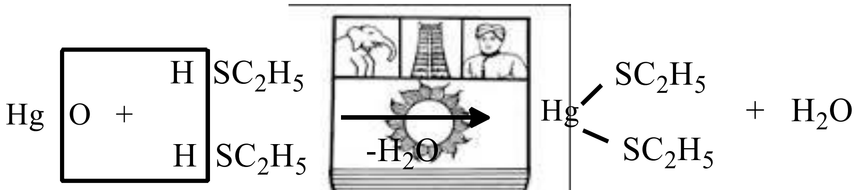
Diethyl methyl mercaptal



Diethyl dimethyl mercaptal

4. Reaction with mercuric oxide

Thiols precipitate mercury mercaptides on treatment with mercuric oxide in aqueous solution



5. Oxidation

i). With mild oxidizing agents like H_2O_2, thiols are oxidized to disulphides.

$2C_2H_5SH + H_2O_2 \longrightarrow C_2H_5\text{-}S\text{-}S\text{-}C_2H_5 + 2H_2O$

ii). Strong oxidizing agents like HNO_3 oxidise thiols to sulphonic acids.

$C_2H_5SH + 3(O) \longrightarrow C_2H_5SO_3H$

THIOETHERS

These are the sulphur analogues of ethers. They may be considered as the dialkyl derivatives of hydrogen sulphide.

General methods of preparation

1. From alkyl halides

Thioethers may be prepared by heating alkyl halide with potassium sulphide.

$$2C_2H_5I + K_2S \longrightarrow \underset{\text{Diethyl thioether}}{C_2H_5SC_2H_5} + 2KI$$

2. From ethers

Ethers when heated with phosphorus pentasulphide form thioethers.

$$5C_2H_5OC_2H_5 + P_2S_5 \longrightarrow 5C_2H_5SC_2H_5 + P_2O_5$$

3. From thioalcohols

Thioethers are obtained when thioalcohol vapour is passed over alumina-zinc sulphide catalyst at 300℃(cf.formation of ethers).

$$2C_2H_2SH \xrightarrow{Al_2O_3/ZnS,300℃} 5C_2H_5SC_2H_5 + H_2S$$

4. From mercaptides

Sodium mercaptide when heated with an alkyl halide also forms thioether (cf.Williamson's synthesis). This is the best method of preparation of thioethers.

$$CH_3I + NaSC_2H_5 \longrightarrow CH_3SC_2H_5 + NaI$$

General properties

1. Reaction with Br_2

Thioethers form addition compound with bromine.

$$\underset{\text{Diethyl sulphide}}{(C_2H_5)_2S} + Br_2 \longrightarrow \underset{\text{Diethyl sulphide dibromide}}{(C_2H_5)_2SBr_2}$$

2. **Reaction with alkyl halide**

Thioethers combine with alkyl halides forming sulphonium salts.

$$(C_2H_5)_2S + C_2H_5I \longrightarrow (C_2H_5)_3S^+I^-$$

Diethyl sulphide Triethyl sulphonium iodide

3. **Oxidation**

i). With mild oxidizing agents like H_2O_2, thioethers are oxidized to *sulphoxides* which on further oxidation yield *sulphone* at about 100℃.

$$(C_2H_5)_2S \xrightarrow{(O)H_2O_2} (C_2H_5)_2SO \xrightarrow{(O)} (C_2H_5)_2SO_2$$

Diethyl sulphide Diethyl sulphoxide Diethyl sulphone

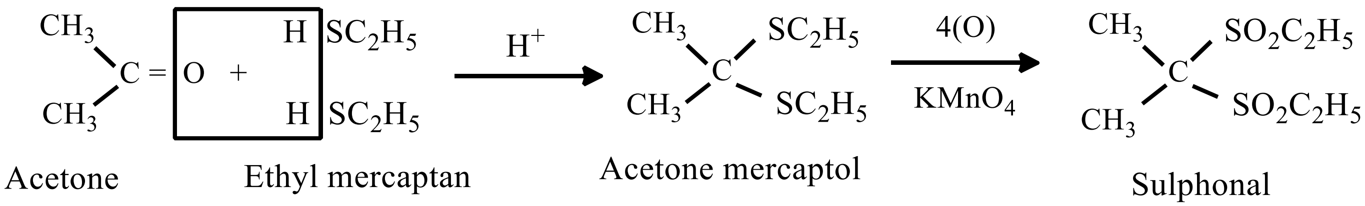
ii) . With strong oxidizing agents like conc.HNO_3, they are directly oxidized to sulphones.

$$(C_2H_5)_2S \xrightarrow{(O)HNO_3} (C_2H_5)_2SO_2$$

SULPHONAL

Preparation

Acetone diethylsulphone (or diethyl dimethylsulphone) is called sulphonal. It is prepared by the oxidation of acetone mercaptol (diethyl dimethylmercaptol) with potassium permanganate. Acetone mercaptol required for the reaction is obtained by the condensation of acetone with ethyl mercaptan in presence of HCl.



Use

Sulphonal is used as a hypnotic (sleep inducing drug).

SULPHONES

Preparation

Sulphones are the oxidation products of sulphoxides obtained from thioethers. Alkyl sulphones may be prepared by oxidizing alkyl sulphides (thioethers) with hydrogen peroxide in excess at 100℃ or with conc.HNO_3

$$R_2S + 2H_2O_2 \xrightarrow{100℃, HAC} R_2SO_2 + 2H_2O$$

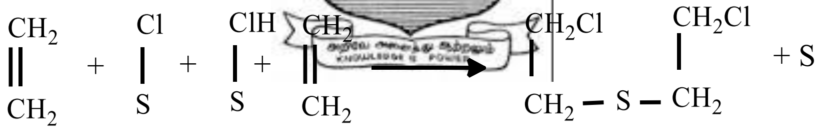
Use

Sulphones are crystalline solids used to characterise thioethers.

MUSTARD GAS

Preparation

2, 2’-dichlorodiethylsulphide is known as *mustard gas*. It may be prepared by the action of sulphur monochloride on ethylene.



$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + \begin{matrix} Cl \\ | \\ S \end{matrix} + \begin{matrix} ClH \\ | \\ S \end{matrix} + \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} \longrightarrow \begin{matrix} CH_2Cl & & CH_2Cl \\ | & & | \\ CH_2 & - S - & CH_2 \end{matrix} + S$$

$$\text{(or) } 2CH_2 = CH_2 + S_2Cl_2 \longrightarrow ClCH_2CH_2SCH_2CH_2Cl + S$$

Uses

Mustard gas is not a gas but an oily liquid with the smell of crushed mustard seed. It is different from *mustard oils* which are *alkyl isothiocyanates*, R-N=C=S. The vapours of mustard gas are extremely poisonous and produce blisters on skin and irritation in eyes. It was used as a chemical weapon (poisonous gas) in the first World War (1914-1918) by Germany.

5.6 Answer the Following Questions

PART-A

1. Discuss the preparation and properties of diethyl zinc
2. Describe Reformatsky reaction
3. How will you prepare Sulphonal and their uses

PART-B

1. What are Grignard reagents ? How are they prepared ? Discuss any four of its synthetic applications
2. What are thioalcohols and thioethers ? Explain their methods of preparation and their uses.