

# E-CONTENT FOR COMPLETE COURSE

e-book:

## **PHARMACEUTICAL ORGANIC CHEMISTRY –I**

(BP202T)

(For B.Pharm 2<sup>nd</sup> Semester Student)

Editor: Dr.Alok Kumar Dash

Institute Of Pharmacy

V.B.S.P.University,Jaunpur,U.P.

Email:dr.alokdash@gmail.com

## COURSE CONTENT

General methods of preparation and reactions of compounds superscripted with asterisk (\*) to be explained To emphasize on definition, types, classification, principles mechanisms, applications, examples and differences

### UNIT-I

#### • Classification, nomenclature and isomerism

Classification of Organic Compounds

Common and IUPAC systems of nomenclature of organic compounds:

(up to 10 Carbons open chain and carbocyclic compounds)

Structural isomerisms in organic compounds

### UNIT-II

#### • Alkanes\*, Alkenes\* and Conjugated dienes\*

SP<sup>3</sup> hybridization in alkanes, Halogenation of alkanes, uses of paraffins:

Stabilities of alkenes, SP<sup>2</sup> hybridization in alkenes

E<sub>1</sub> and E<sub>2</sub> reactions – kinetics, order of reactivity of alkyl halides, rearrangement of carbocations, Saytzeff's orientation and evidences, E<sub>1</sub> versus E<sub>2</sub> reactions, Factors affecting E<sub>1</sub>

and E<sub>2</sub> reactions, Ozonolysis, electrophilic addition reactions of alkenes, Markownikoff's orientation, free radical addition reactions of alkenes, Anti Markownikoff's orientation,

Stability of conjugated dienes, Diels-Alder, electrophilic addition, free radical addition reactions of conjugated dienes, allylic rearrangement

### UNIT-III

#### • Alkyl halides\*

SN<sub>1</sub> and SN<sub>2</sub> reactions – kinetics, order of reactivity of alkyl halides, stereochemistry and rearrangement of carbocations

SN<sub>1</sub> versus SN<sub>2</sub> reactions, Factors affecting SN<sub>1</sub> and SN<sub>2</sub> reactions

Structure and uses of ethylchloride, Chloroform, trichloroethylene, tetrachloroethylene, dichloromethane, tetrachloromethane and iodoform.

• Alcohols\* - Qualitative tests, Structure and uses of Ethyl alcohol, Methyl alcohol, chlorobutanol, Cetosteryl alcohol, Benzyl alcohol, Glycerol, Propylene glycol

### UNIT-IV

#### • Carbonyl compounds\* (Aldehydes and ketones)

Nucleophilic addition, Electromeric effect, aldol condensation, Crossed Aldol condensation,

Cannizzaro reaction, Crossed Cannizzaro reaction, Benzoin condensation, Perkin

condensation, qualitative tests, Structure and uses of Formaldehyde, Paraldehyde, Acetone,

Chloral hydrate, Hexamine, Benzaldehyde, Vanillin, Cinnamaldehyde

### UNIT-V

#### • Carboxylic acids\*

Acidity of carboxylic acids, effect of substituents on acidity, inductive effect and qualitative tests for carboxylic acids, amide and ester

Structure and Uses of Acetic acid, Lactic acid, Tartaric acid, Citric acid, Succinic acid,

Oxalic

acid, Salicylic acid, Benzoic acid, Benzyl benzoate, Dimethyl phthalate, Methyl salicylate and

Acetyl salicylic acid

• Aliphatic amines\* - Basicity, effect of substituent on Basicity, Qualitative test, Structure and uses of Ethanolamine, Ethylenediamine, Amphetamine

## UNIT III

### Hydrocarbon:

Compounds containing only carbon and hydrogen as their constituent atoms are termed as hydrocarbons.

Depending upon their structures, it may be classified into two types:-

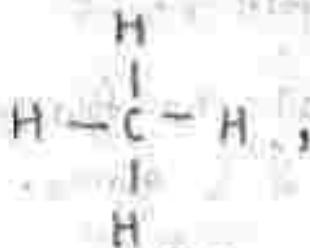
1- Aliphatic

2- Aromatic

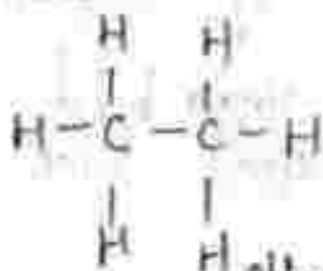
On the basis of no. of hydrogen atoms present in them or nature of bond present in them, aliphatic hydrocarbons may be classified into two types:-

i- Saturated hydrocarbons:- The hydrocarbons in which only single bonds are present, i.e., in which all the four valencies of carbon are satisfied with  $H_2$  or  $C$  atoms are called Saturated hydrocarbons.

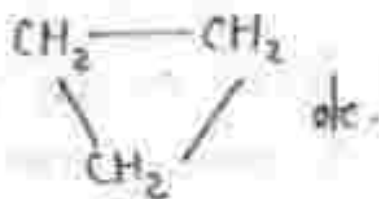
Ex:-



Methane



Ethane



Cyclopropane

It is classified into two types:-

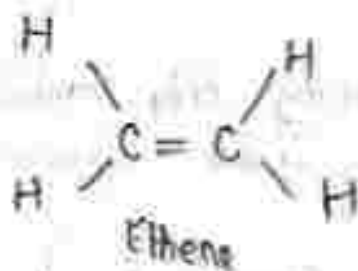
- 1- Alkanes, containing an open-chain structure.
- 2- Cycloalkanes, containing ring or cyclic structures.

ii- Unsaturated hydrocarbons:-

The compound in which

all the four valencies of carbon are not satisfied with H atom are called unsaturated hydrocarbon.

Ex:-



Ethyne

It is classified into two types:-

- 1- Alkenes, containing double bond.
- 2- Alkynes, containing triple bond.

## Alkanes

⇒ Due to chemical properties, it is also called as paraffin. It is derived from Latin word parum = little & affinis = affinity.

⇒ Alkanes are saturated compounds which constitute the simplest class of aliphatic hydrocarbons.

⇒ They contain only single bond i.e., all the four valencies of carbon are satisfied with H & C atoms.

Formula :-  $\boxed{\text{C}_n\text{H}_{2n+2}}$  or 2R or  $\text{C}_n\text{H}_{2n+1}\text{H}$

⇒ Alkanes are found naturally.

⇒ Main source of alkanes are petroleum and natural gas.

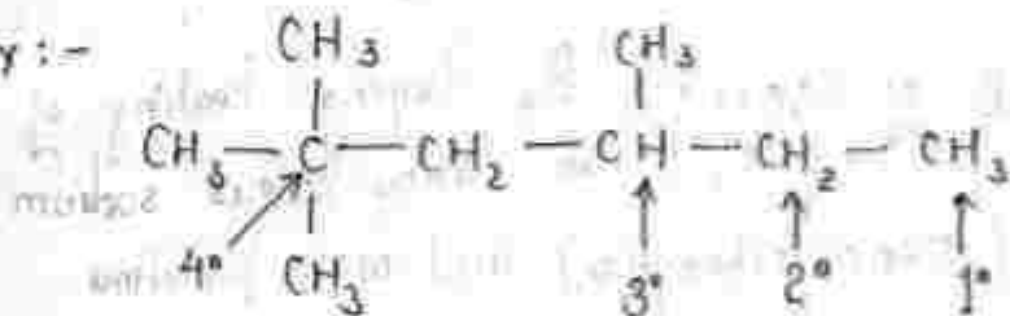
⇒ Methane is called "Marsh gas" which is produced by bacteria decomposition of organic material.



Classification :- According to degree, it is classified into four types :-

- i - Primary ( $1^\circ$ ) carbon atom, attached to only one carbon atom.
- ii - Secondary ( $2^\circ$ ) carbon atom, attached to two other carbon atoms.
- iii - Tertiary ( $3^\circ$ ) carbon atom, attached to three other carbon atoms.
- iv - Quaternary ( $4^\circ$ ) carbon atom, attached to four other carbon atoms.

Ex :-



=> Alkanes possess tetrahedral structure arising from  $\text{sp}^3$  hybridization.

=> The angle b/w each  $\text{H}-\text{C}-\text{H}$  is  $109^\circ.28'$

=> The distance b/w each  $\text{C}-\text{H}$  bond is  $1.09 \text{ \AA}$

=> The distance b/w  $\text{C}$  &  $\text{C}$  bond is  $1.54 \text{ \AA}$

Prep<sup>n</sup> of Alkane : ↓

1. B. Laboratory Method :-

Mix anhydrous sodium acetate with double of mixture is heated in gas is collected in the



Sodium  
acetate

methane

 $H_2O$ 

2- Decarboxylation of  $\text{COOH}$  :-

By drying heating of an anhydrous sodium

salt of a fatty (monocarboxylic) acid with sodalime.



Sol. salt of carboxylic acid

3. By Sabatier & Sanderons method:

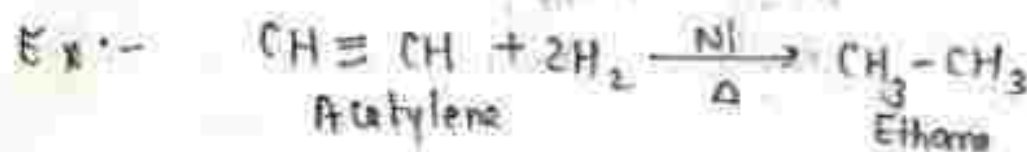
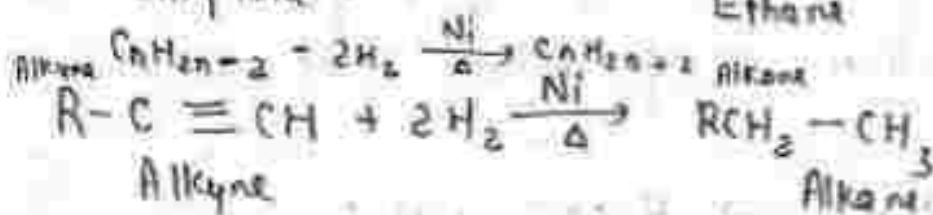
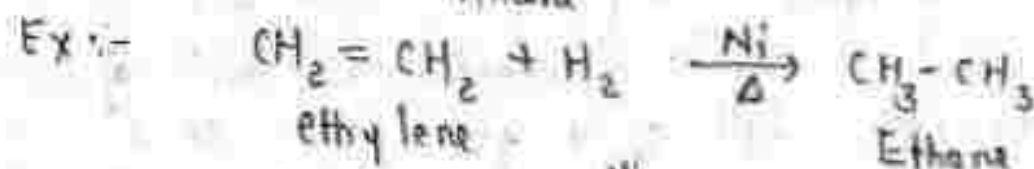
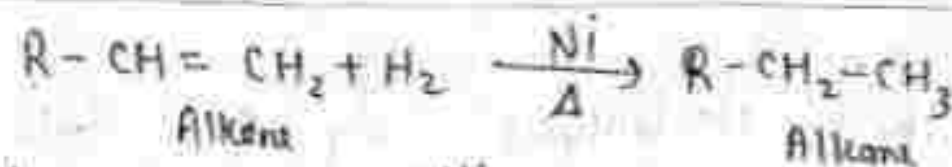
Unsaturated hydrocarbons are reacted with  $H_2$  in presence of metallic catalyst at  $200-300^\circ C$  to form

alkanes. Common catalysts used in this react<sup>n</sup> are finely divided Ni, Pt or Pd.

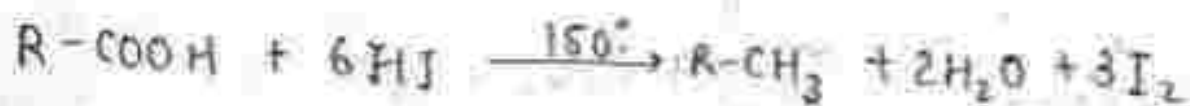


## Alkenes

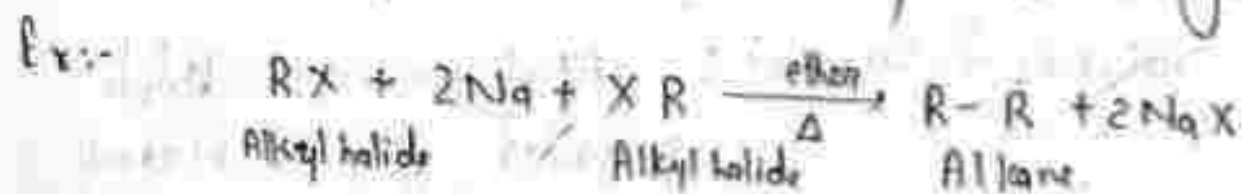
Alkanes



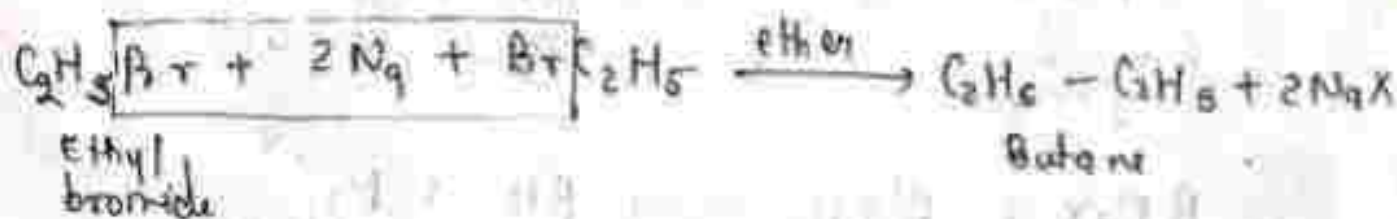
4- By the reduction of alcohol halides acid & aldehydes:-



5- Wurtz Method (1854):- Two molecules of alkyl halides are treated with two atoms of Na metal in dry ether to give alkane

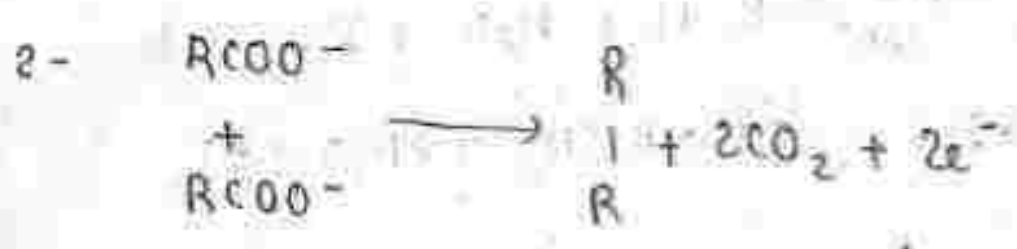
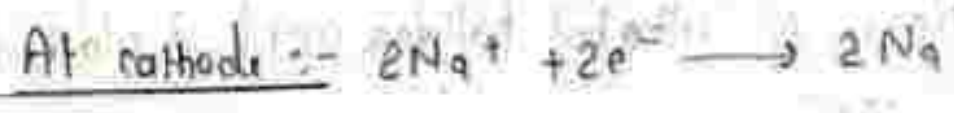
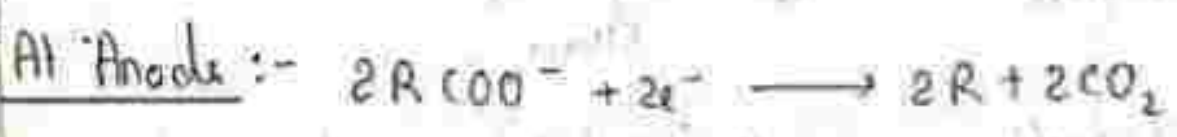
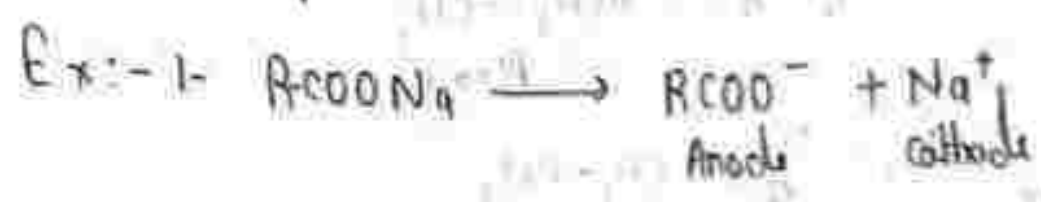


If two same alkyl halides are taken, the formed alkane has double no. of Carbon atoms as were present in the alkyl halides.





6- Kolbe's electrolysis:- By the electrolysis of a concentrated sol<sup>n</sup> of sodium or potassium salt of a fatty acid or a mixture of sodium or potassium salts of fatty acids.



At cathode hydrogen is evolved



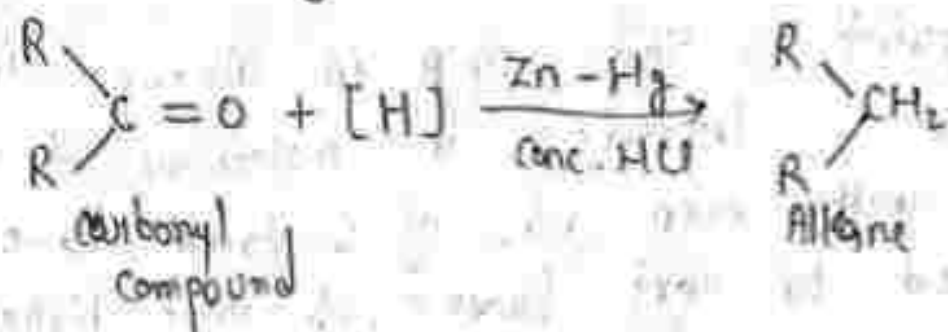
7- From Grignard reagent:- [Alkyl magnesium halide] is called grignard reagent.

Grignard reagent on react<sup>n</sup> with proton donors gives alkanes





8- By Clemmensen reduction: This method involves the reduction of carbonyl compounds with  $\text{Zn-Hg}$  & conc.  $\text{HCl}$ .



## Physical Properties:

1- Physical state: It is dependent upon wt. and composition etc of any compound. The first four members, i.e., from  $\text{C}_1$  to  $\text{C}_4$  are colourless & odourless gases, alkanes from  $\text{C}_5$  to  $\text{C}_{12}$  are colourless & odourless liquids while higher members are solids.

2- Solubility: Being weakly polar or non-polar in nature alkanes are insoluble in polar solvents like water & soluble in non-polar solvents like organic solvents as alcohol, ether, benzene etc.

3- Viscosity: Alkanes are less dense & float on water. Their viscosity increases with molecular wt.

4- Boiling point: Alkanes are non-polar molecules and weak van der Waals forces are present among the molecules.

B.P. increases with increase in the no. of carbon atoms. B.P. increases by  $20^\circ\text{C}$  to  $30^\circ\text{C}$  for each added C atom to the chain.

ie; for  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$ , the BP are  $-161.7^\circ$ ,  $-88.6^\circ$ ,  $-42.1^\circ$ ,  $-0.5^\circ$  respectively.

5- Melting point :- The m.p in alkanes increase with increase in molecular wt.

⇒ Alkanes with even no. of C atoms have higher M.p as compared to next lower & next higher alkanes with odd no. of carbon atoms.

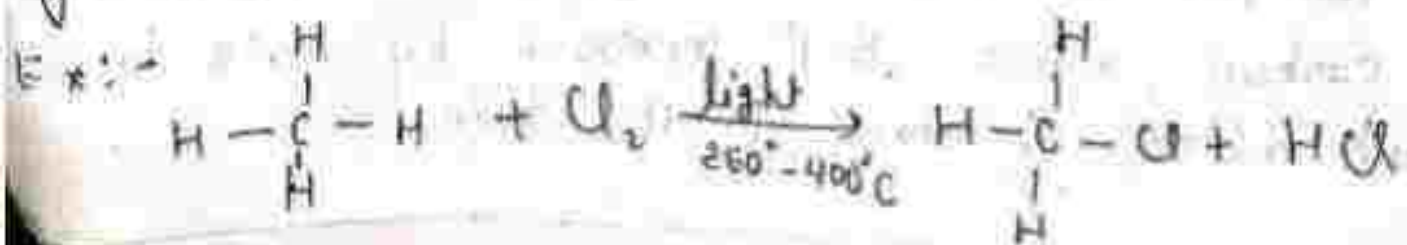
Ex- M.p of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$  are,  $(-182^\circ\text{C}) > \text{CH}_4 (-161.7^\circ\text{C}) > \text{C}_3\text{H}_8 (-190^\circ\text{C})$

Chemical properties :-

1- Substitution React<sup>n</sup> :- React<sup>n</sup> in which one or more H atoms of alkanes are substituted by any other group of atoms are called substitution react<sup>n</sup>. Generally, it is classified into three types :-

i- Halogenation :- Substitution of hydrogen atom of alkane by halogen is called halogenation. Halogenation of alkanes is carried out under controlled conditions.

A- Chlorination :- The addition of Cl in alkane is called chlorination. It is carried out by UV light at  $250^\circ - 400^\circ\text{C}$ . It depends upon the amount of a Cl used.





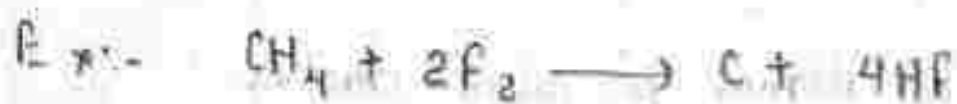
ii) Bromination :- It is similar to chlorination but occurs less vigorously than chlorination.

C-Iodination :- It is a reversible process.

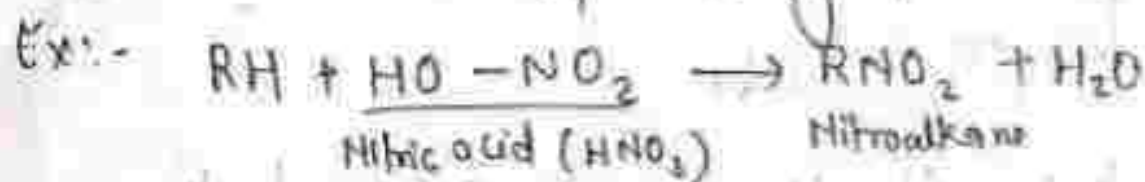


The reversibility of the react<sup>n</sup> is due to the reducing nature of HI formed in the react<sup>n</sup> which reduces iodoalkane back to alkane.

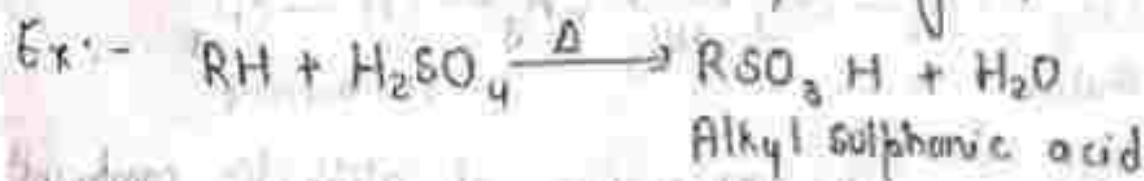
A-Fluorination :- It is an explosive process.



ii) Nitration :- The replacement of Hydrogen atom of alkane by nitro group is called nitration.



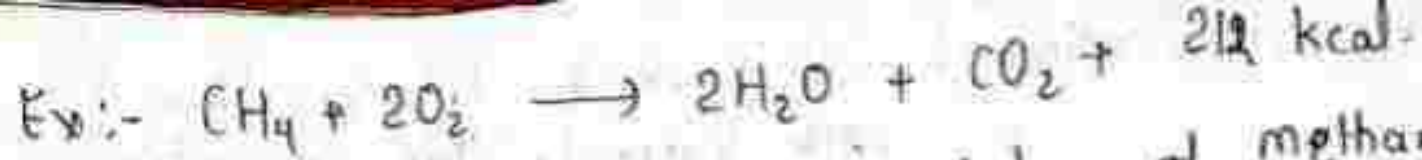
iii) Sulphonation :- The replacement of a 'H' atom of alkane by 'S' group is called sulphonation.



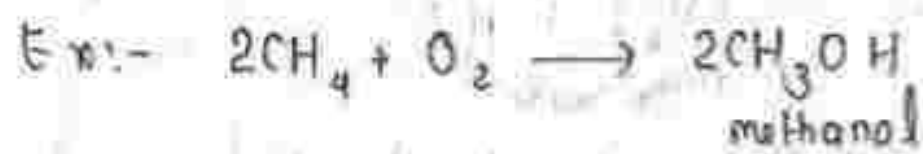
2 - Oxidation :-

a - Combustion :- In presence of excess  $\text{O}_2$ , alkanes are ignited to form  $\text{CO}_2$  &  $\text{H}_2\text{O}$ .



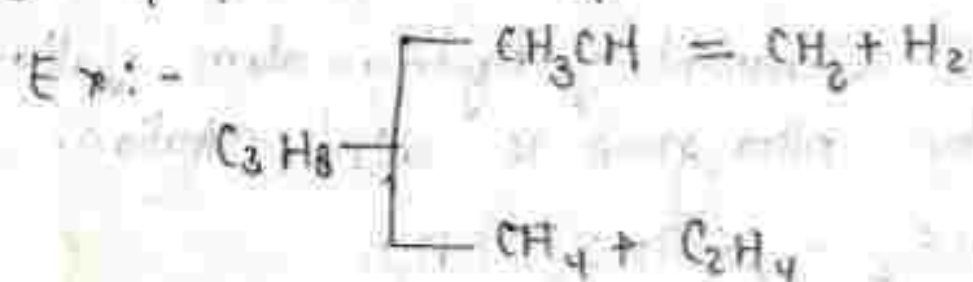


b- Catalytic oxidation:- when a mixture of methane and  $\text{O}_2(1:1)$  is compressed then alcohol evolved.

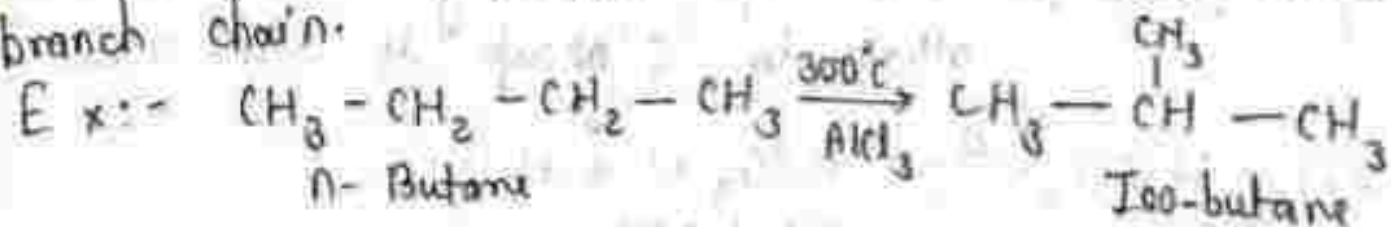


3- Cracking or pyrolysis:- Decomposition of a compound by the action of heat is called pyrolysis. This word has been taken from greek word - Pyro = 'fire' & lysis = 'loosening'.

⇒ Pyrolysis in case of alkanes is called cracking.

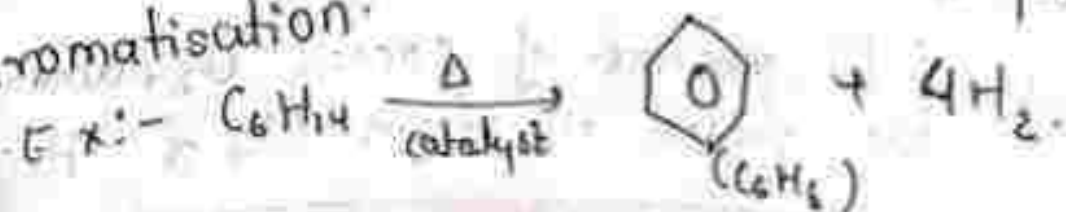


4- Isomerization:- Straight chain of RH on heating with  $\text{AlCl}_3$  at about  $300^\circ\text{C}$  is converted into branch chain.



5- Aromatisation:- The conversion of aliphatic compound into aromatic compound is called

aromatisation.

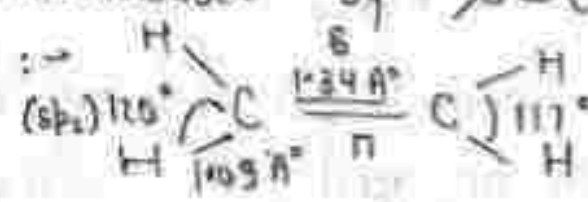


Use of Alkane :  $\rightarrow$  It is used :- in

- 1- It is used in explosives.
- 2- In rubber industry.
- 3- In the synthesis of a no. of organic compounds.
- 4- As solvents.

## Alkenes

Formula :-  $C_nH_{2n}$

- ⇒ Alkenes are unsaturated hydrocarbons containing at least one double bond.
- ⇒ The open chain hydrocarbons which contain lesser no. of hydrogen atoms than the corresponding alkanes containing same no. of carbon atoms are called unsaturated hydrocarbons.
- ⇒ The members which contain two hydrogen atom less than the corresponding saturated hydrocarbons are known as 'olefins'.
- ⇒ The double bond is known as "olefinic bond" or "Ethylenic bond".
- ⇒ formula -  $C_nH_{2n}$
- ⇒ It is characterised by  $X=C'$
- ⇒ Structure :-  

- ⇒ The Alkenes are obtained during cracking of petroleum.
- ⇒ Ethylene ( $CH_2=CH_2$ ) is the first member of alkene series.

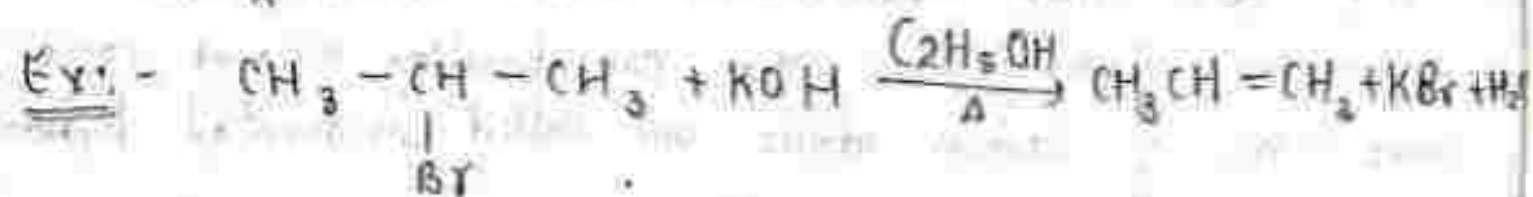


Classification:- It is classified into di, tri & tetra's term.

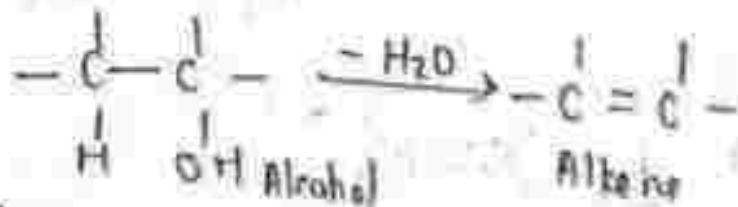
Method of prep<sup>n</sup>:-

1- By Dehydrohalogenation of Alkyl halides:-

Alkyl halides, when heated with a hot conc. alcoholic sol<sup>n</sup> of a strong base, as KOH, give alkenes, eliminating H<sub>2</sub> & halogen in the form of KBr & water, this method of prep<sup>n</sup> of alkenes is called dehydrohalogenation.



2- By dehydration of alcohols:- Alcohols can be converted into alkenes by the dehydration react<sup>n</sup> i.e., by elimination of water molecule from them.



Dehydration may be carried out by two methods:-

- 1- By heating alcohol with an acid, as H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub>.
- 2- By passing the alcohol vapours over a catalyst, as Al<sub>2</sub>O<sub>3</sub> at high temp.







## Physical properties :-

- 1- Physical state :- Alkenes containing 2-4 carbon atoms i.e., first four members of alkenes are gases, those containing 5-15 C atoms are liquids & higher members are solids.
- 2- Solubility :- They are insoluble in polar solvents like water but soluble in nonpolar solvents like organic solvents.
- 3- Boiling point :- B.P increases with mole. wt & each added C atoms adds 20-30°C to the B.P of the previous alkene.  
The B.P of straight chain alkenes are higher than those of branched alkenes.
- 4- Dipole moment :- Alkenes have greater dipole moment than for alkanes.
- 5- Isomerism :- Chemical properties :-

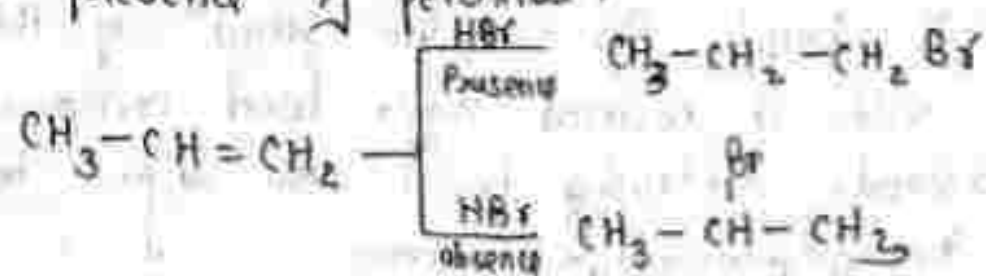
Alkenes are more reactive than alkanes due to the presence of double bond which contain one  $\pi$  bond and one  $\sigma$  bond.

Alkene behaves the following chemical property:-

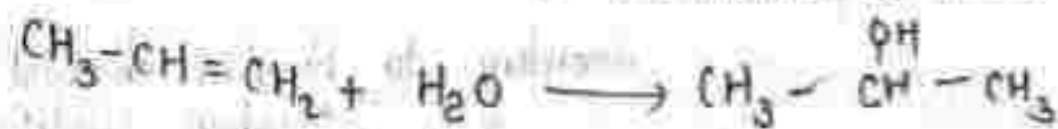




2. Addition of halogen acid: Alkene react with halogen acid to give alkyl halide, it gives both Markonikovs & Antimarkonikovs rule i.e; in the presence of & presence of peroxide.



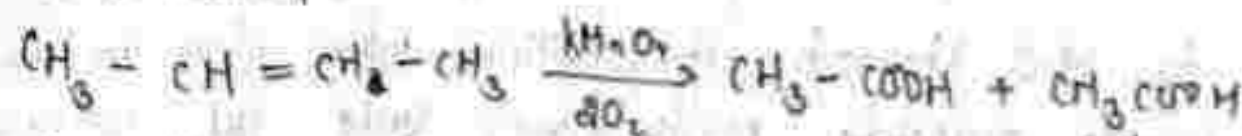
Addition of Water :- Addition of water takes place according to markonikovs rule.



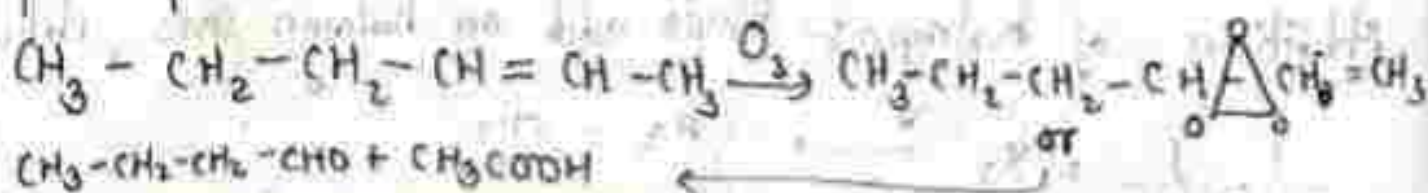
Hydroboration :- Alkene undergoes hydroboration with diboron to yield alkyl boron which on oxidation & treated with  $\text{H}_2\text{O}_2$  gives alcohol. it obey antimarkonikovs rule.



Oxidation with  $(\text{KMnO}_4)$  Mono substitute phylicarbon converted into  $-\text{COOH}$  group by  $\text{KMnO}_4$ .



Ozonolysis :- Addition of ozone to  $\text{C}=\text{C}$  followed by hydrolysis is called ozonolysis. On passing a strain of ozone through a sol<sup>n</sup> of an alkene in an organic solvent, ozonide obtained, then it is converted into two carbonyl compound.





# DIENE [C<sub>n</sub>H<sub>2n-2</sub>]

Compound containing two double bond are called dienes or alkydienes or diolefines.

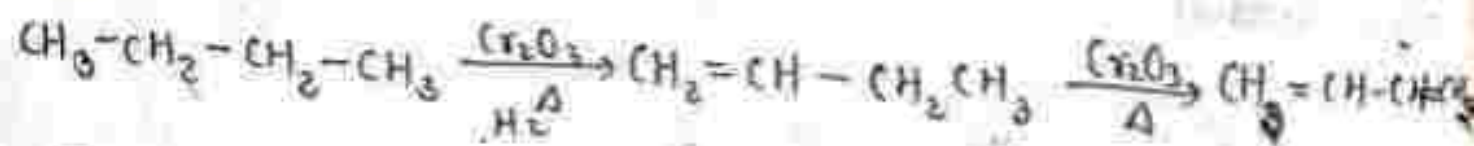
It is classified into three types:-

- i- Isolated dienes:- Here two double bonds are separated by two or more than two single bond.
- ii- Conjugated diene:- Two double bonds are separated by one single bond.
- iii- Cumulated diene:- Two double bonds are adjacent to each other.

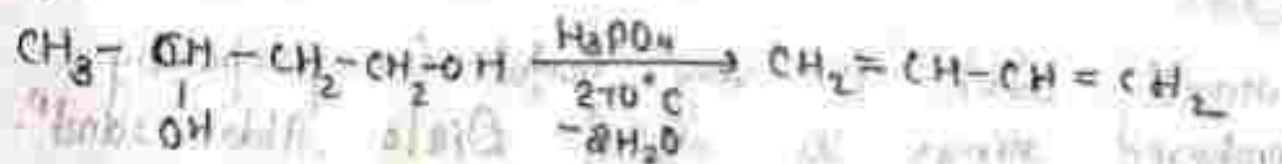
Order of Stability:- Conjugated diene > Isolated diene > cumulative diene.

## Preparation

1- Dehydrogenation:- When dehydrogenation of alkane occurs and it passes over a vapour over catalyst as chromium oxide at 530°-630°C, 1,3 butadiene is formed.

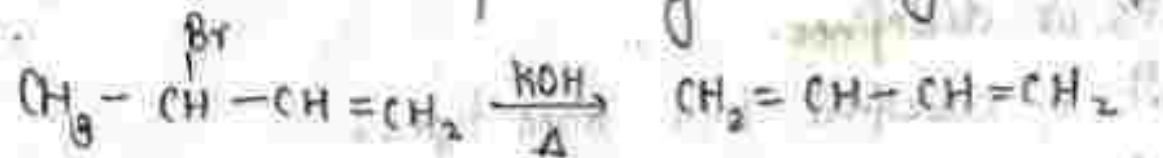


2- From Diols:- 1,3 or 1,4 butane diol on treatment with steam in presence of catalyst gives 1,3 butadiene.

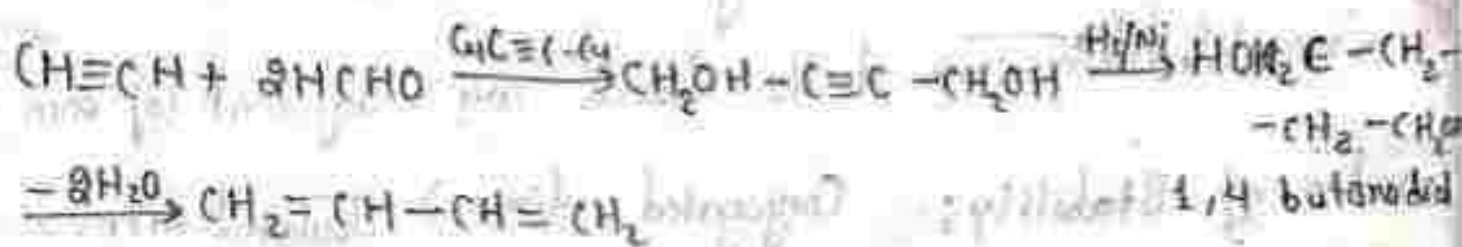




3- Dehydrohalogenation of 3-bromo-1-butene :  $\downarrow$  when 3-bromo-1-butene on dehydrohalogenation "gives conjugate diene"

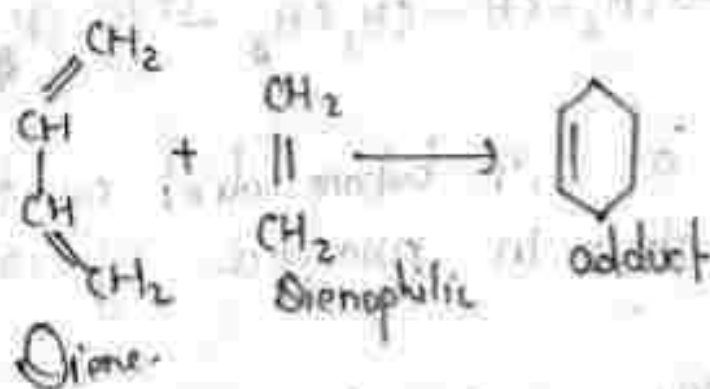


4- Acetylene :  $\downarrow$  A mixture of Acetylene and formalityde when pass over catalyst ~~and~~ as copper acetylide, it gives 1,3-butadiene.



## Chemical Property : $\downarrow$

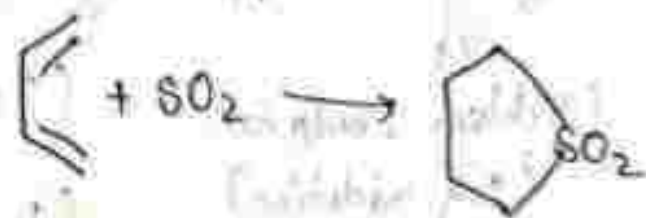
1- Diels - Alder react<sup>n</sup> : Conjugated dienes add to alkene by 1-4 addition to form cyclic compound. The alkene is called dienophilic and the product is adduct.



$\Rightarrow$  The react<sup>n</sup> which is very useful for preparing six membered rings is called Diels Alder react<sup>n</sup>.  
 $\Rightarrow$  This results in the formation of 2  $\sigma$  bond & one  $\pi$  bond at the expense of three original  $\pi$  bond.

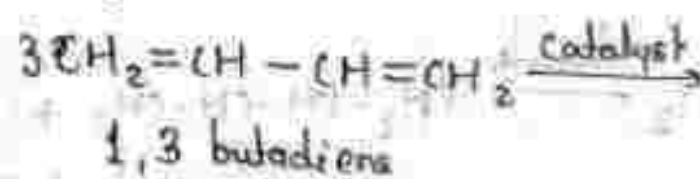
⇒ This react<sup>n</sup> is very useful for synthesis of complex system.

i- When it happen with  $\text{SO}_2$  then,

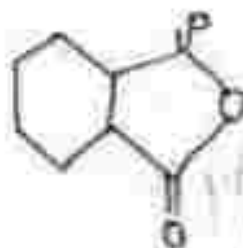
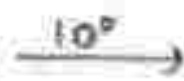
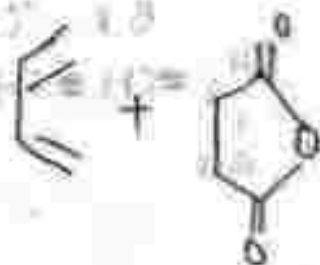


Sulpholene

ii- Polymerisation:- When 3 molecules of 1,3 butadiene combine with in the presence of catalyst to give cyclodecatriene.



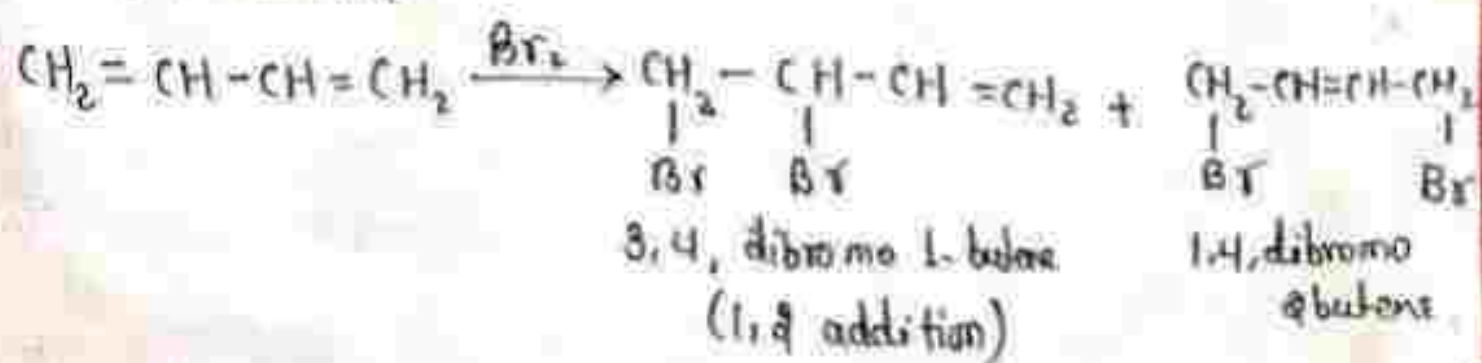
cyclodecatriene



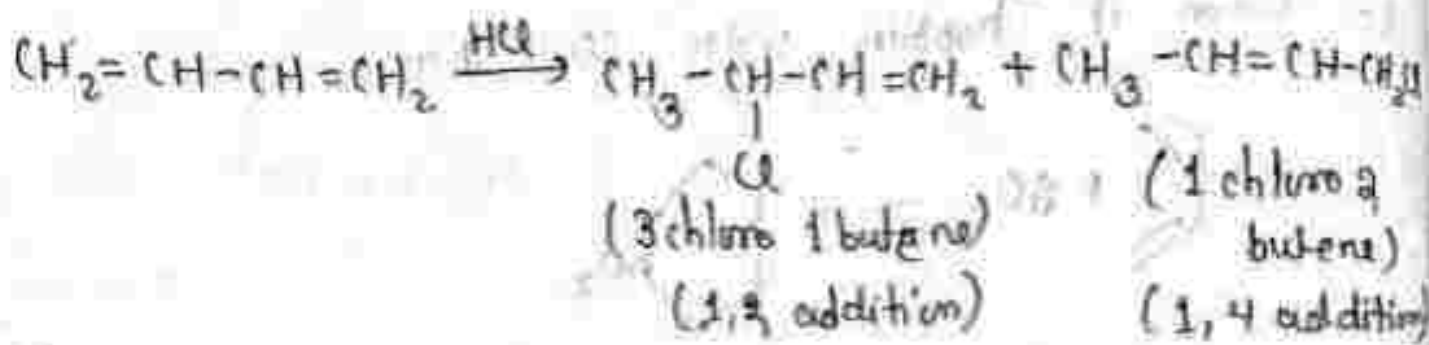
Adduct

2- Addition react<sup>n</sup>:-

1- Addition of halogen:- On addition of halogen, it gives two product i.e; 1,2 addition and 1,4 addition.

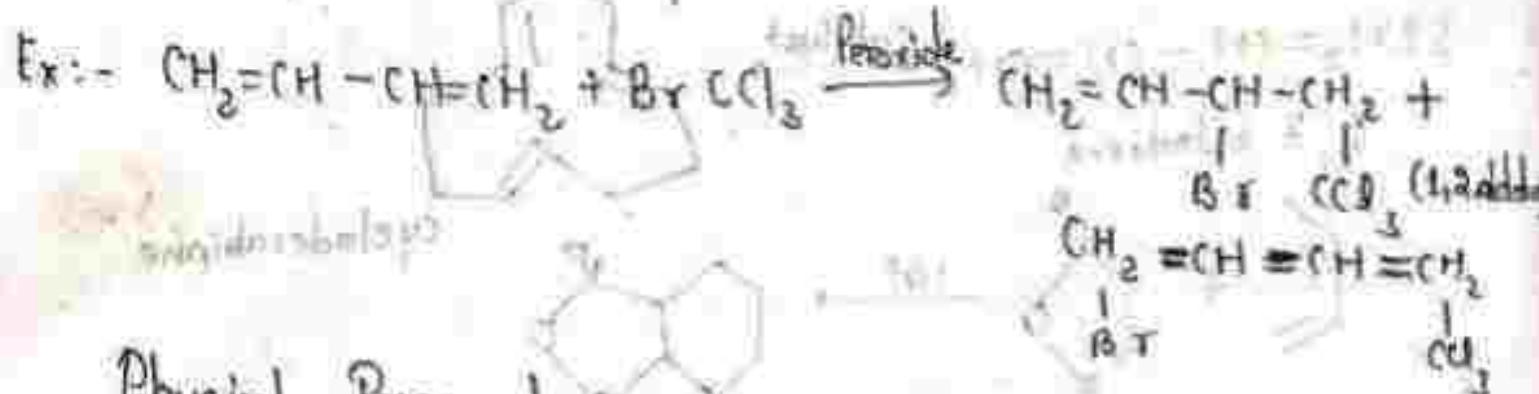


ii - Addition of halogen acid:- Similarly it happens in case of halogen acid.



3- Free radical addition:-

Conjugated dienes also undergoes free radical addition reaction and produces 1,2 & 1,4 addition product.



Physical Property:-

- 1) Butadiene is a colourless gas.
- 2) It is having the B.P.  $-1.4^\circ\text{C}$ , while isoprene is a liquid with B.P.  $35^\circ\text{C}$ .



# Alkynes

$$\text{Formula} = C_n H_{2n-2}$$

- ⇒ Alkyne constitute another class of unsaturated hydrocarbons. They are characterised by the presence of triple bond in them.
- ⇒ Acetylene is the first member of alkyne series.
- ⇒ In alkynes  $sp$  hybridization are found.
- ⇒ It is an explosive, present only in air.

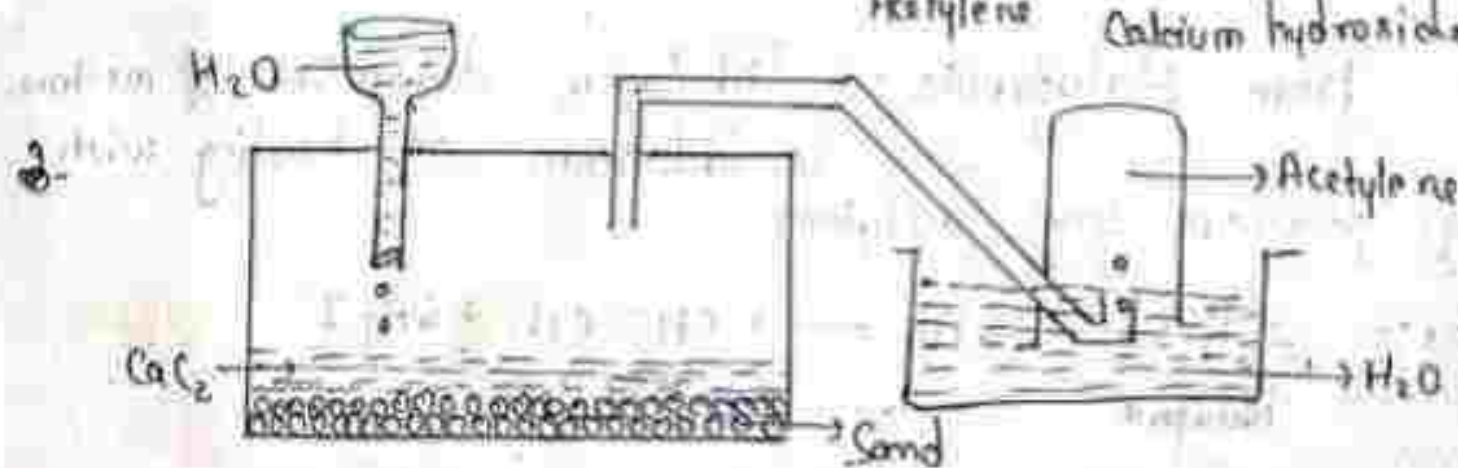
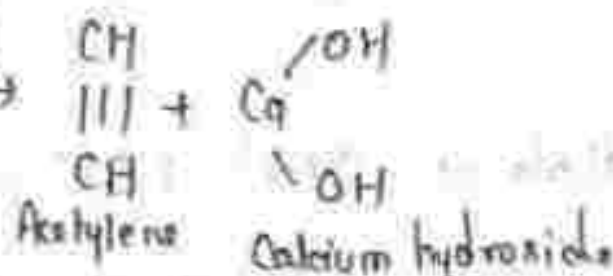
## Method of prep<sup>n</sup>:

### 1- Laboratory method from Calcium Carbide ( $CaC_2$ ):

When a molecule of  $CaC_2$  is treated with two molecules of  $H_2O$ , it gives acetylene.



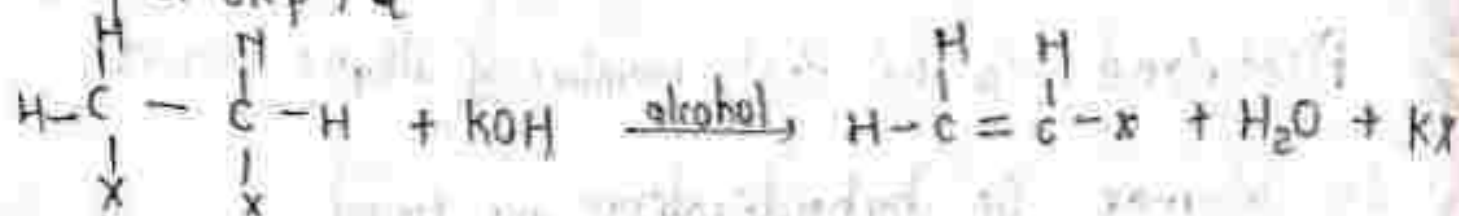
The react<sup>n</sup> occurs as follows:-



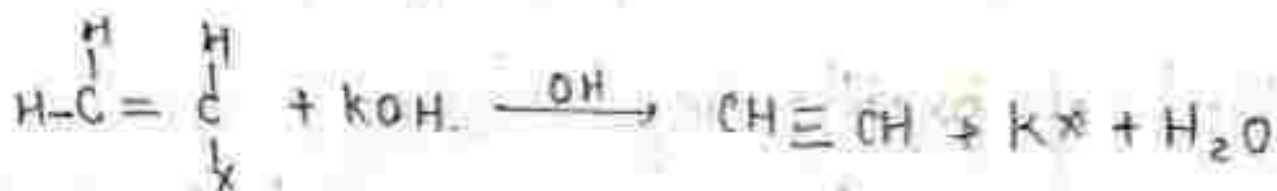
## 2. By Dehydrohalogenation of vicinal/gem dihalides:-

Dehydro halogenation of dihalides gives alkynes. The react<sup>n</sup> occurs in two steps:-

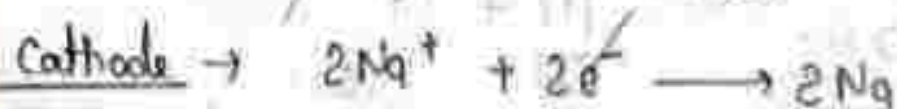
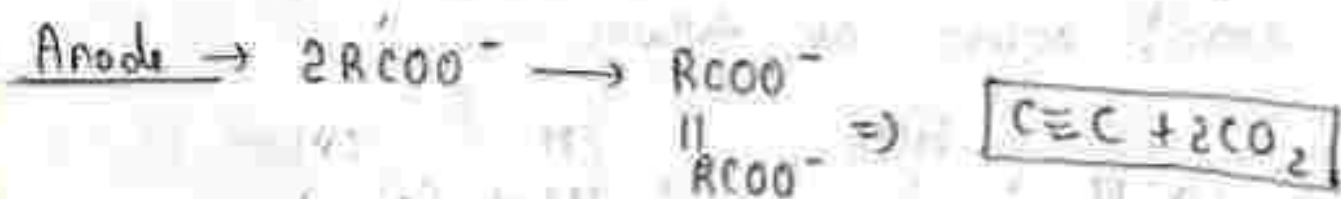
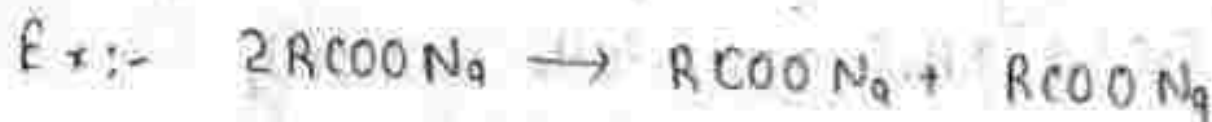
→ In first step, a



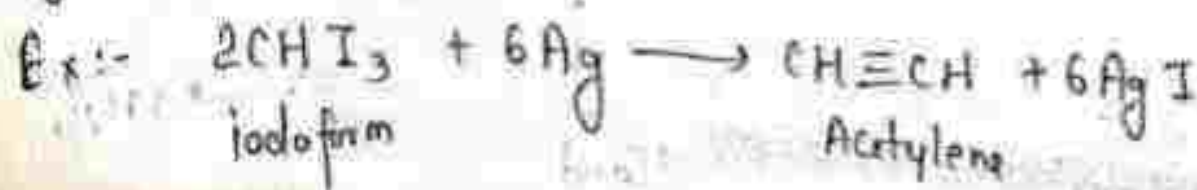
→ In second step,



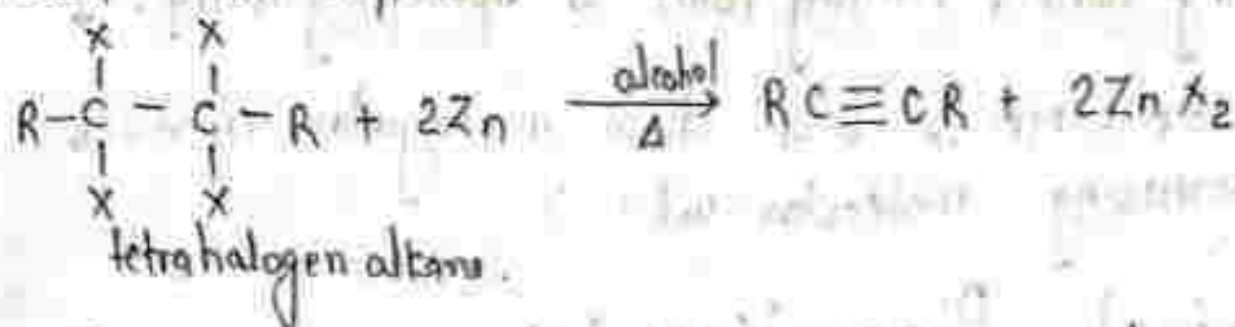
3. Kolbe's react<sup>n</sup>:- A conc. sol<sup>n</sup> of Na or K salt of an unsaturated acid is electrolysed so that alkyne is obtained at anode.



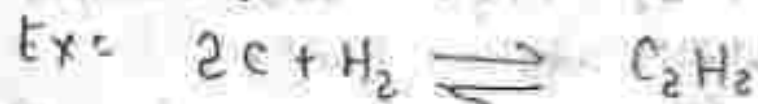
4. from Haloforms:- Trihalogen derivatives of methane as iodoform on heating with Ag powder give acetylene.



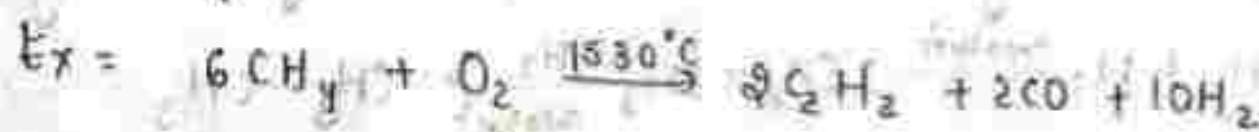
5 - By Dehalogenation of tetrahalide :- 1, 1, 2, 2-tetrahalides on heating with Zn dust in alcohol are dehalogenated to alkynes.



6 - Berthelot Synthesis :- Berthelot synthesised acetylene from its elements by striking an electric arc b/w two Carbon electrodes in an atmosphere of  $\text{H}_2$  gas.



7 - Industrial Method :- The prep<sup>n</sup> of acetylene by the hydrolysis of  $\text{CaC}_2$  is also used industrially as it is economic.



### Physical Properties :-

The physical property of alkynes resembles those of alkanes and alkenes.

1 - Physical state :- The first three members ( $\text{C}_2-\text{C}_4$ ) of alkynes are gases, next eight ( $\text{C}_5-\text{C}_{12}$ ) are liquids while higher (higher than  $\text{C}_{12}$ ) are solids. All of these are colourless & odourless. Acetylene has a garlic like odour due to presence of phosphine.



2- Solubility:- They are insoluble in polar solvent & soluble in non-polar solvent.

3- Boiling Point, Melting Point & Specific gravity:- ↓

Their BP, MP & S.G show a regular increase with increasing molecular wt.

Chemical Properties:- ↓

1- Combustion:- Combination of  $O_2$  in excess is called combustion.

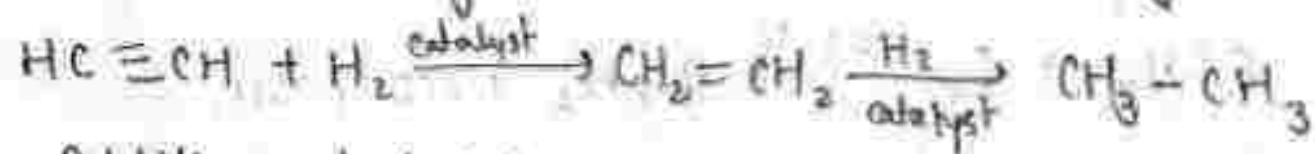
Ex:-  $2C_2H_2 + 5O_2 \longrightarrow 4CO_2 + 2H_2O + 309.5 \text{ kcal/mol}$

2- Addition react<sup>n</sup>:-

Electrophillic addition react<sup>n</sup>:- ↓

a- Addition of hydrogen:- Alkynes give the usual react<sup>n</sup> of unsaturated hydrocarbons.

i.e., addition react<sup>n</sup>. Alkyne adds on  $H_2$  in the presence of a catalyst, the react<sup>n</sup> proceeding in two stages:



b- Addition of haloform:- ↓

I step:-  $CH \equiv CH + Cl_2 \longrightarrow CHCl = CHCl$

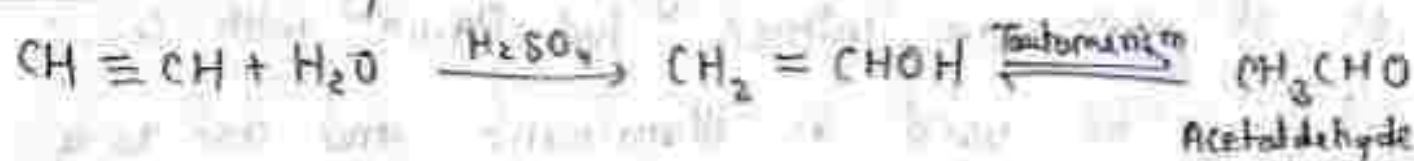
II step:-  $CHCl = CHCl \xrightarrow{Cl_2} \begin{array}{c} CHCl_2 \\ | \\ CHCl_2 \end{array}$

c- Addition of Halogen acid:- ↓

Halogen acids adds on alkynes to give alkylidene halides.

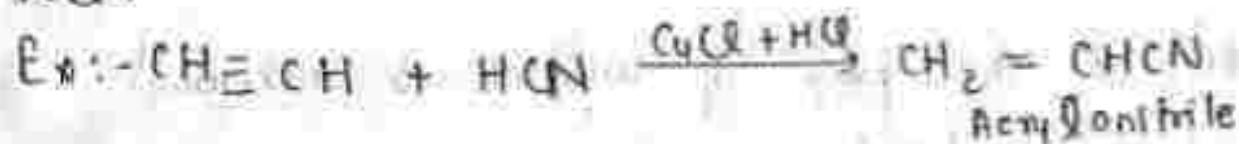


d- Addition of water:-

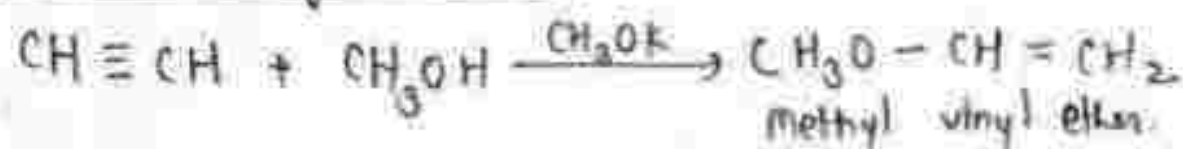


ii - Nucleophilic react<sup>n</sup>:-  $\rightarrow$  Nucleophilic addition on C-C multiple bond proceeds with difficulty due to the repulsion b/w  $e^-$  clouds of multiple bond & nucleophile.

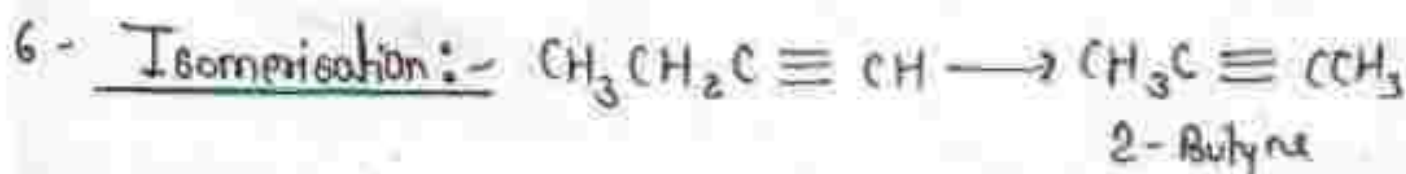
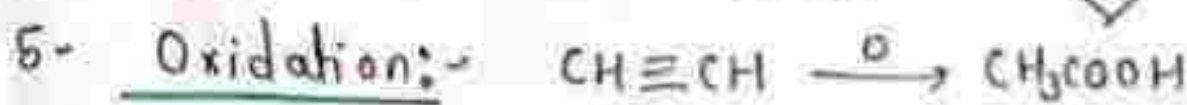
9- Addition of HCN:- HCN adds on alkynes in the presence of catalyst, as  $\text{CuCl}$  +  $\text{HCl}$ .



b- Addition of alcohol:-



3- Acid 3- Substitution react<sup>n</sup>:- Replacement of 'H' atom.



## Use of Alkyne:

1. It is used for cutting & welding of metals as it gives an intense hot flame with  $O_2$ .
2. It may be used as illuminant and act as a source of a no. of chemicals, as acrytic acid etc.
3. It is used in fruit industry.
4. HCN is used as a raw material for textile fibres.
5. It is used in the manufacture of plastics and synthetic rubber.
6. It is used in the prep<sup>n</sup> of oestron & oestrosol.
7. It is used as solvents.



# ALKYL HALIDES [RX]

⇒ Alkyl halides are compounds in which a halogen atom is attached to carbon.

OR

⇒ The halogen derivative of saturated hydrocarbon, is known as alkyl halide.

Formula: -  $C_nH_{2n+1}X$  or  $RX$

## Classification:

i- Based on the no. of halogen atoms present in molecule

a- Monohalogen derivatives containing only one halogen atom

Ex:-  $CH_3Cl$   
methyl chloride

b- Dihalogen derivative containing two halogen atoms:

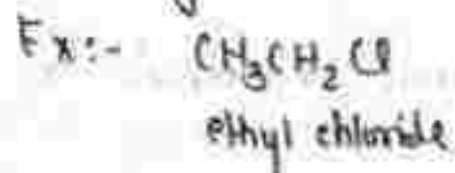
Ex:-  $CH_2Cl - CH_2Cl$   
1,2-dichloroethane

c- Trihalogen derivative containing three halogen atoms.

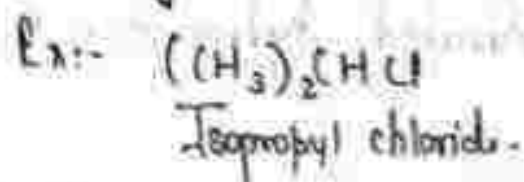
Ex:-  $CHCl_3$   
chloroform

ii- Based on the type of carbon atom bearing the halogen atom:-

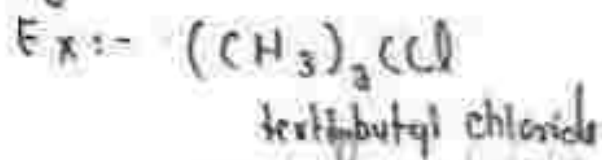
a. Primary alkyl halide represented as  $\text{RCH}_2\text{X}$ .



b. Secondary alkyl halide represented as  $\text{R}_2\text{CHX}$ .



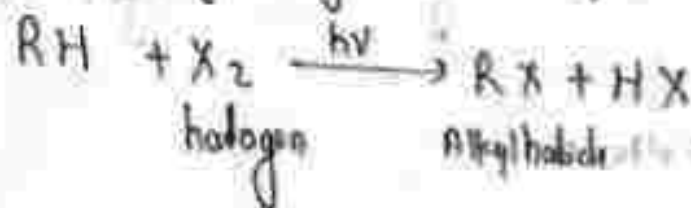
c. Tertiary alkyl halide represented as  $\text{R}_3\text{CX}$ .



### Preparation :-

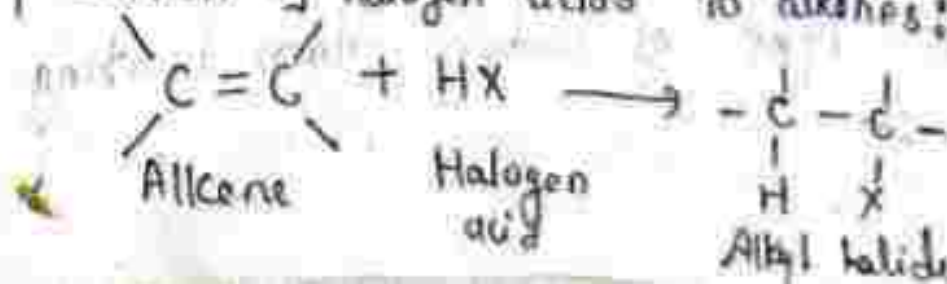
1. Dehydrogenation of alkane :- Alkanes can be halogenated to give alkyl halides in

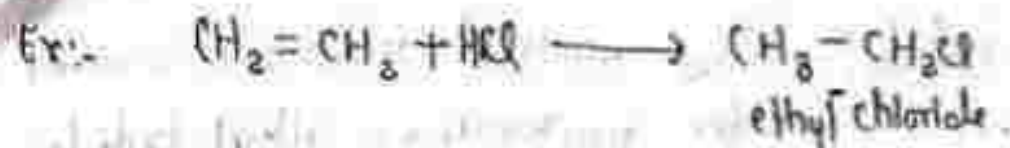
the presence of light or catalyst.



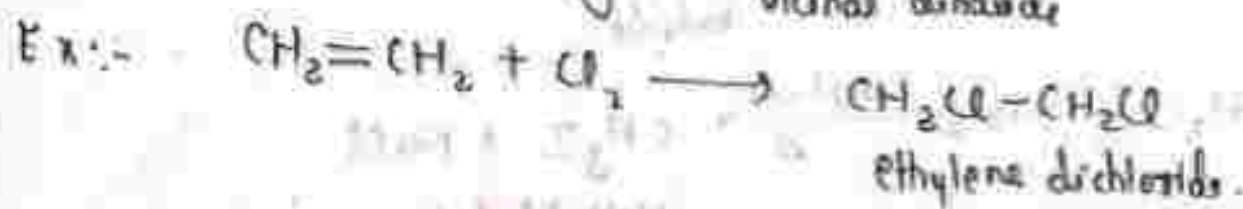
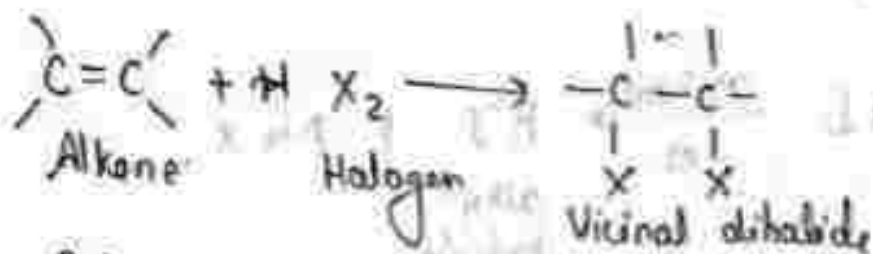
2. From alkenes :- Alkenes may be converted into alkyl halides by different methods.

i:- By addition of halogen acids to alkenes:-

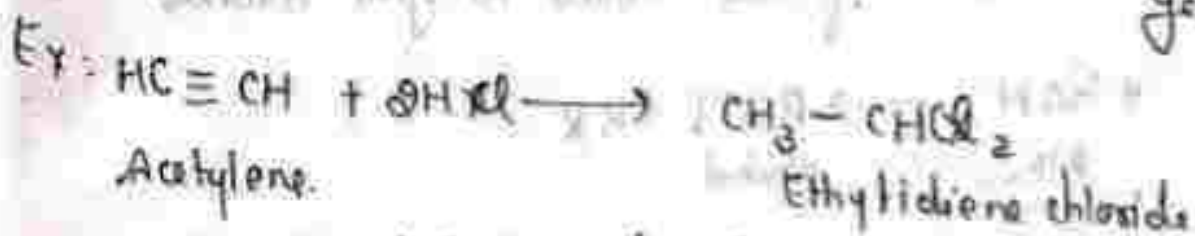
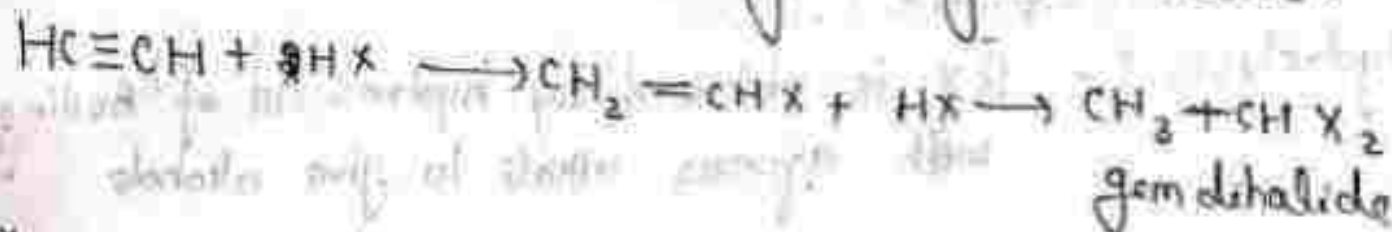




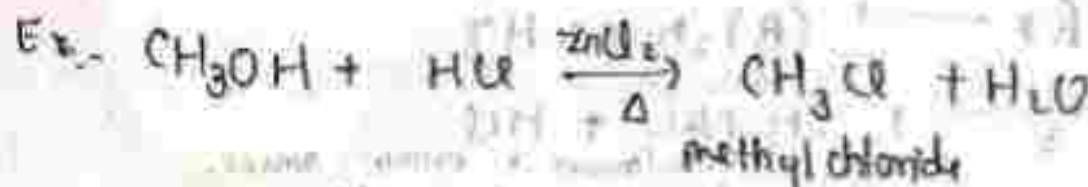
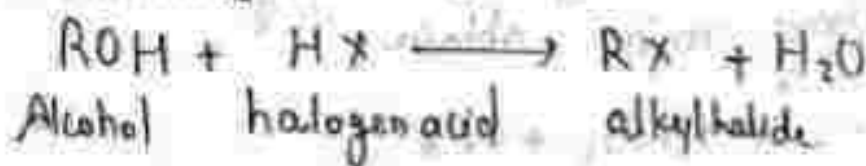
ii - By the addition of halogens to alkenes dihalogen derivatives of alkanes are obtained.



3- from alkyne :- when an alkyne reacts with halogen acids, it gives gem dihalides.



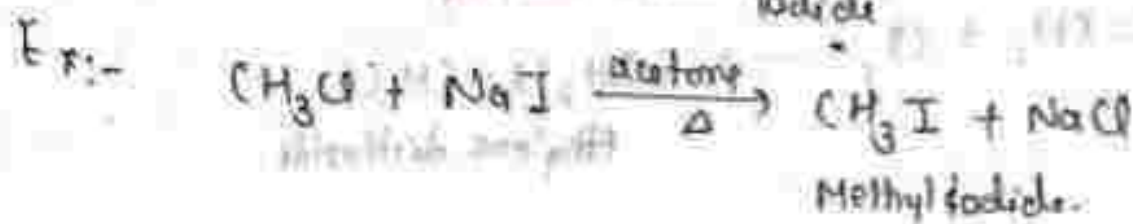
4- From alcohols :- Dehydrohalogenation of when alcohol reacts with halogen acid in the presence of  $\text{ZnCl}_2$  or  $\text{H}_2\text{SO}_4$ , it gives alkyl halide.





5. Exchange of halide:- This method is more suitable for preparing alkyl iodides.

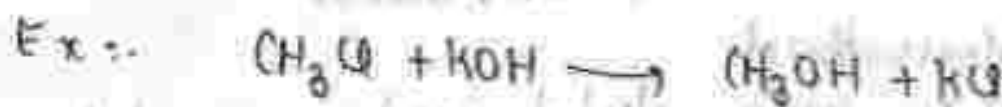
In this method, alkyl iodide is obtained by heating corresponding alkyl chloride or bromide with NaI in acetone.



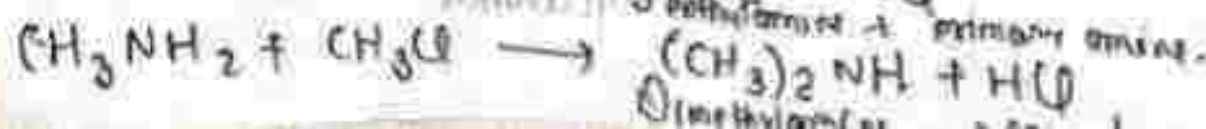
Chemical property:-

A. Nucleophilic Substitution:-

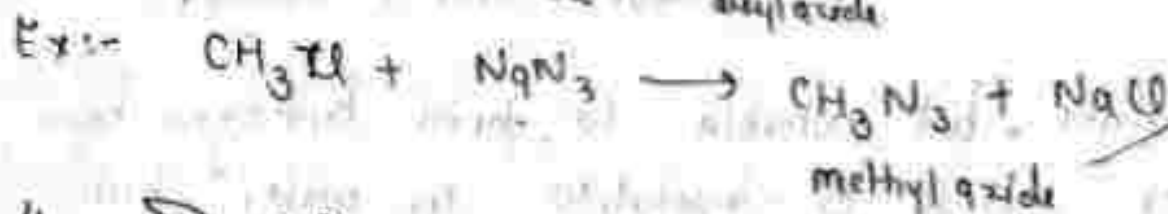
1. Hydrolysis:-  $RX$  is obtained by hydrolysis of Boiling with aqueous alkali to give alcohols.



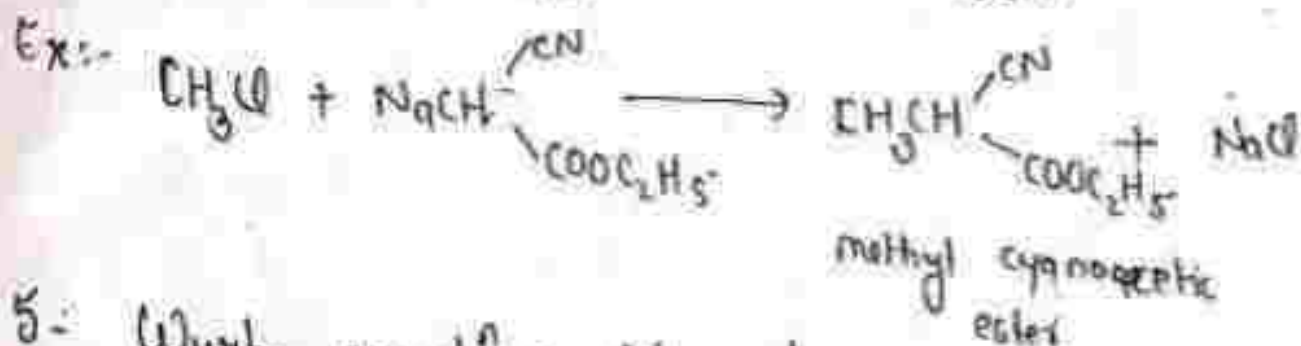
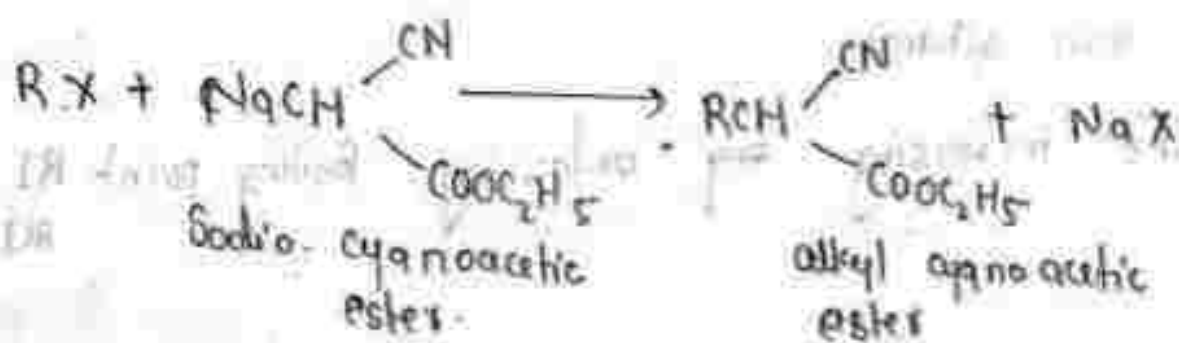
2. React with  $NH_3$ :- On heating alcoholic sol<sup>n</sup> of  $NH_3$  with alkyl halides  $\rightarrow$  Primary then secondary amine obtain.



3. React<sup>n</sup> with metal azide:- On treatment with metal azide alkyl halides give alkyl azides.



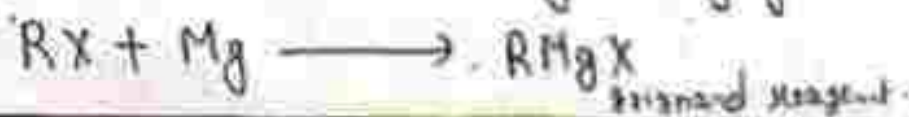
4. React<sup>n</sup> of Sodium cyanoacetic ester:- On treatment with sodium cyanoacetic ester, alkyl substituted cyanoacetic ester  $RX$  is obtained.



5. Wurtz react<sup>n</sup>:- When two molecule of alkyl halide react with two molecules of Na metal in presence of dry ether, it gives alkane.



6. React<sup>n</sup> with Mg:- Alkyl halide on react<sup>n</sup> with Mg gives Grignard reagent.

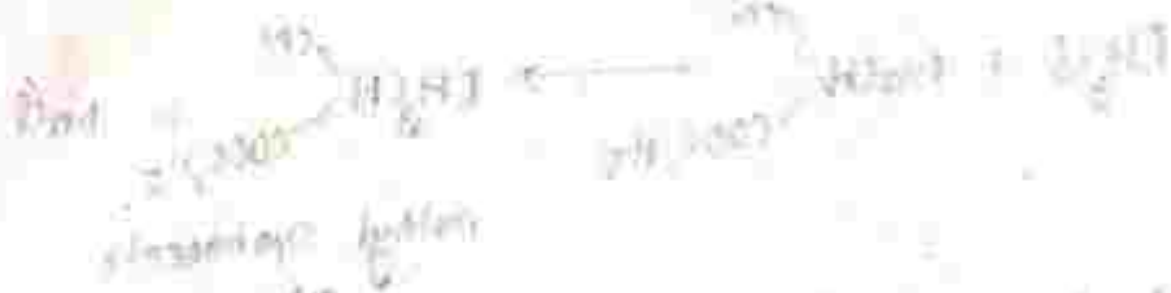


Physical Property : 1. Lower members upto  $C_2 \rightarrow$  gases  
 $\Rightarrow$  next members upto  $C_{18} \rightarrow$  liquids  
 $\Rightarrow$  and above are  $\rightarrow$  solids

2. Polar in nature, but unable to form hydrogen bond with water, so it is insoluble in water but soluble in organic compounds.

3. It has their B.P. increases and density increases with increase in molecular wt. They have higher B.P. than alkanes.

4.  $\Rightarrow$  The increasing order of Boiling point  $RI > RB_r > RC_l > RF$ .



Alkyl halides are colorless and volatile  $\rightarrow$  have strong dipole moment.

Alkyl halides are used in various industries.



Alkyl halides are used in various industries.



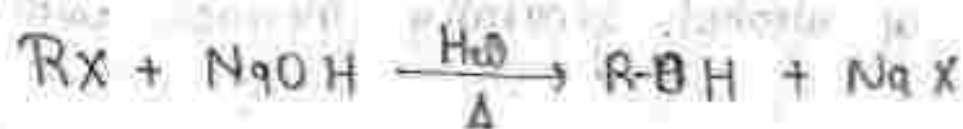


# ALCOHOL

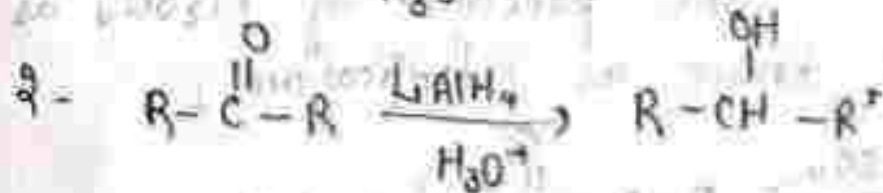
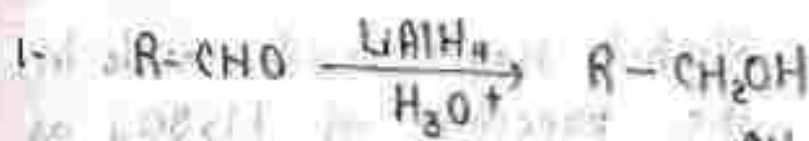
Alcohol are compound having general formula  $ROH$ , it is classified as monohydric, dihydric, trihydric & polyhydric alcohol. It is classified as primary, secondary and tertiary alcohol depending upon the no. of carbon atom attached to it.

## Prep<sup>n</sup> of alcohol:

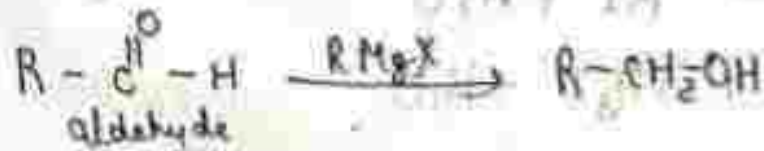
1- From alkyl halide:- Hydrolysis of alkyl halide with aqueous  $NaOH$  sol<sup>n</sup>, alcohol results.



2- Reduction with  $LiAlH_4$  and  $NaBH_4$ :- when we reduce aldehyde, ketones or acids in presence of  $LiAlH_4$ , we get alcohol.

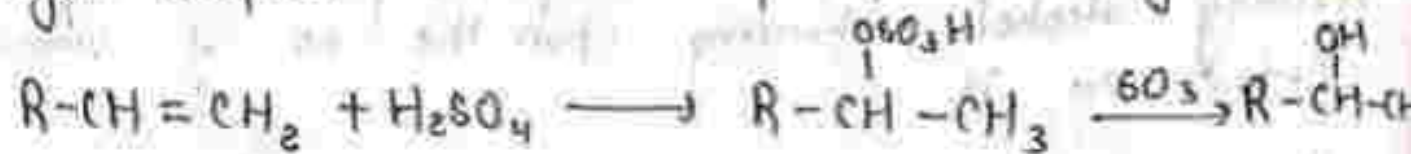


3- Grignard reagent:- when we react grignard reagent with aldehyde and ketone, we get alcohol.



#### 4. Addition of water to alkene: ↓

Most of the alkene are absorbed in conc.  $H_2SO_4$  to give alkyl hydrogen sulphate with on hydrolysis, we get alcohol.



#### Physical property of alcohol: ↓

##### 1. Melting point & Boiling point of alcohol: ↓

M.P. and B.P. of alcohol generally increase with increasing mol. wt.

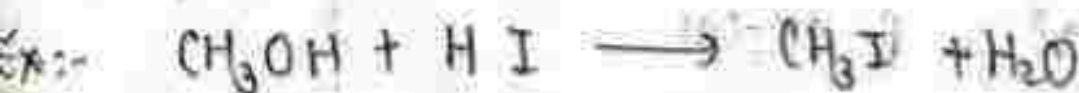
2. Lower mol. wt. of alcohol are water soluble and as mol. wt. increase, solubility decreases.

#### Chemical property: ↓

1. React<sup>n</sup> with  $COOH$ : Alcohol react with acids in the presence of  $H_2SO_4$  as catalyst, we get ester known as esterification.



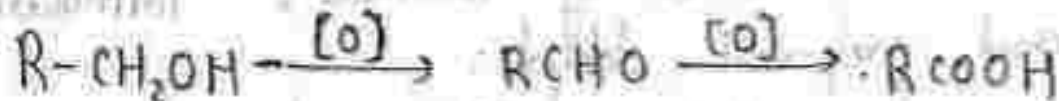
2. React<sup>n</sup> with alkyl halide: ↓ Alcohol react with  $HX$  to form corresponding alkyl halide.



3- React<sup>n</sup> with  $\text{SOCl}_2$  :- React<sup>n</sup> b/w alcohol & thionyl-chloride is treated and free of side react<sup>n</sup>.



4- Oxidation :- When we oxidise alcohol, we get aldehyde and on further oxidation, we get acids.



5- React<sup>n</sup> with acid chloride :-

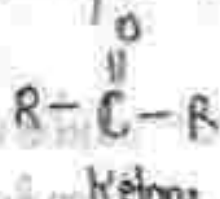
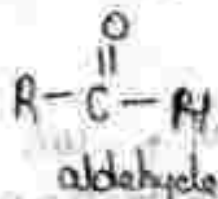
On react<sup>n</sup> with acid chloride, alcohol gives ether.





## UNIT V :- ALDEHYDE AND KETONE

Aldehyde and ketone are called carbonyl compound because both the compounds are attached with carbon and oxygen. The formula of aldehyde & ketone is :-



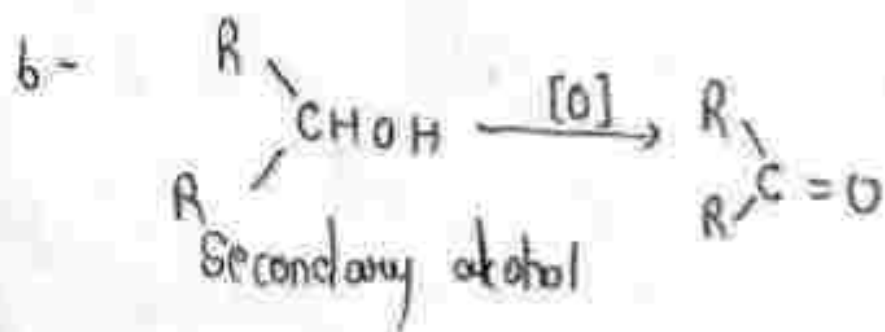
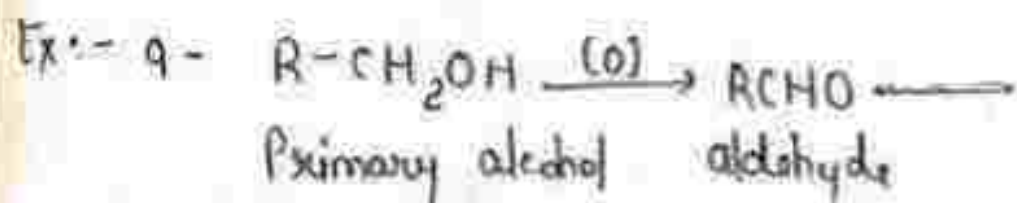
The members are in case of aldehyde :- formaldehyde, acetaldehyde and propanaldehyde.

In case of ketone :- The members are propanone, butanone and pentanone.

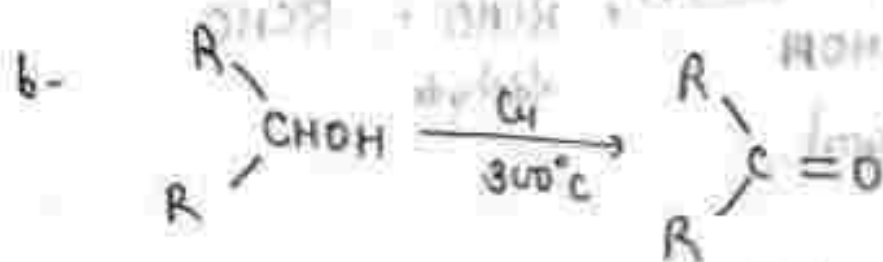
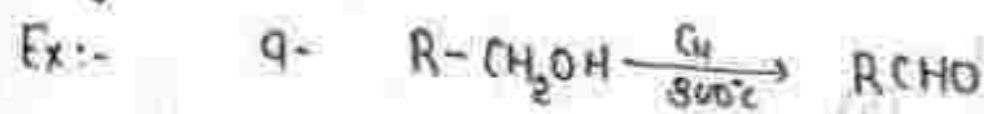
In case of aldehyde and ketone, there is  $sp^2$  hybridization occurs. The bond angle is  $120^\circ$ .

Brief of aldehyde, aliphatic and ketone :-

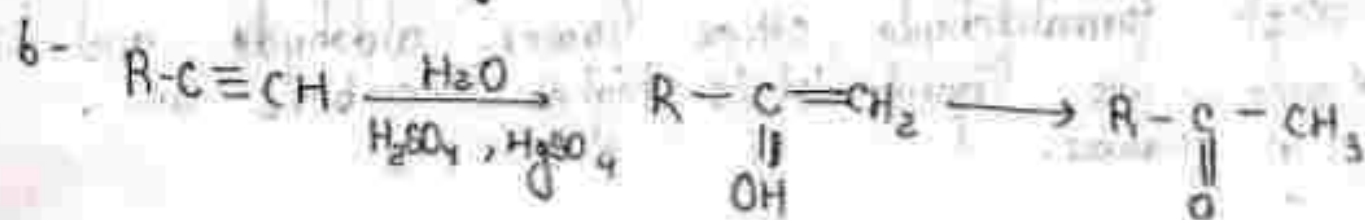
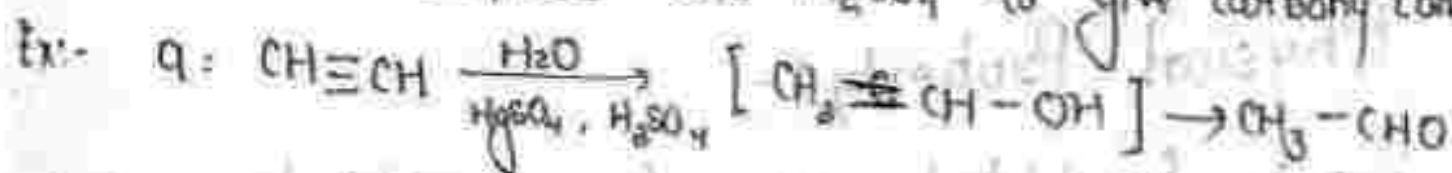
1- Oxidation of alcohol :- Primary alcohol gives aldehyde and secondary alcohol gives ketone on oxidation.



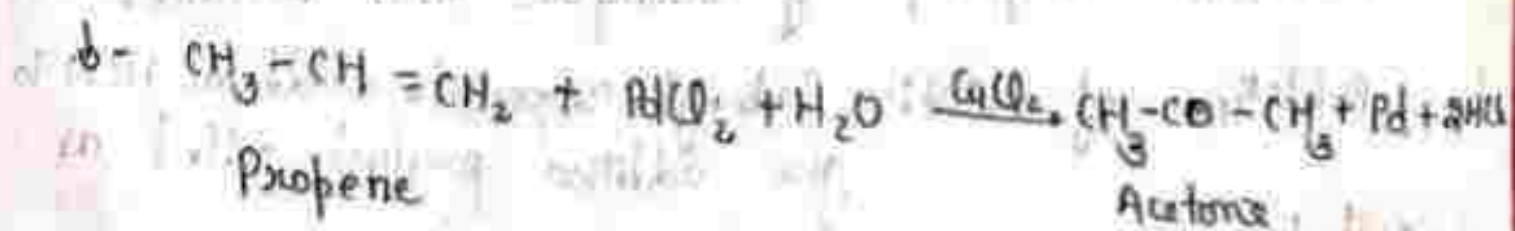
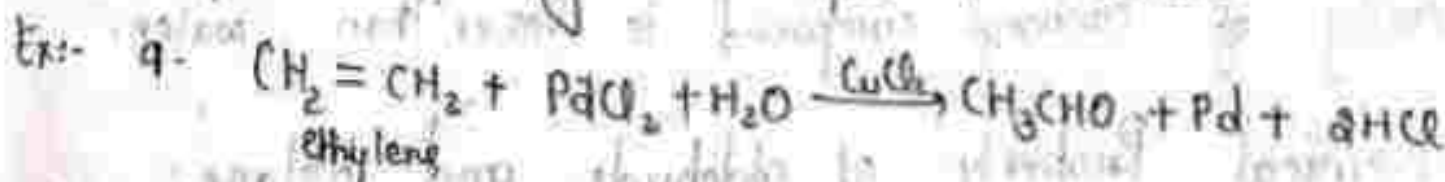
2- Catalytic hydrogenation of alcohol:- When vapours of alcohol are passed over heated copper at about  $300^{\circ}\text{C}$ , they are dehydrogenated to give their corresponding carbonyl compound.



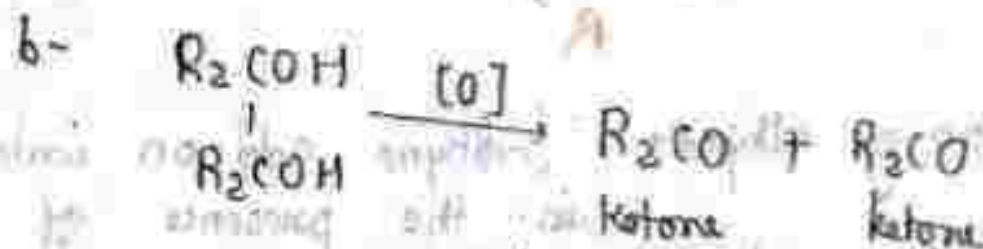
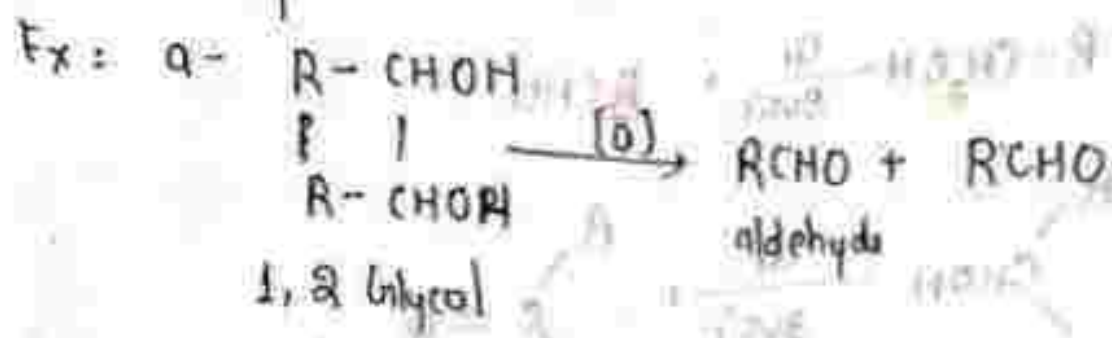
3- By hydration of alkyne:- Alkyne add on water in the presence of mercuric chloride sulphate and  $H_2SO_4$  to give carbonyl compound  
Ex:-  $C \equiv CH + H_2O \rightarrow CH_3COOH$



4- Wacker process :- Alkene on treatment with acidified aqueous sol<sup>n</sup> of palladium chloride and cupric chloride give aldehyde and ketone.



5 - By oxidation of 1,2 Glycol: Oxidation of 1,2 Glycol with lead tetracetate on periodic acid, we get aldehyde & ketone.



### Physical Property :-

1- Except formaldehyde, other lower aldehyde and ketones are liquid while higher members are Solid in nature.

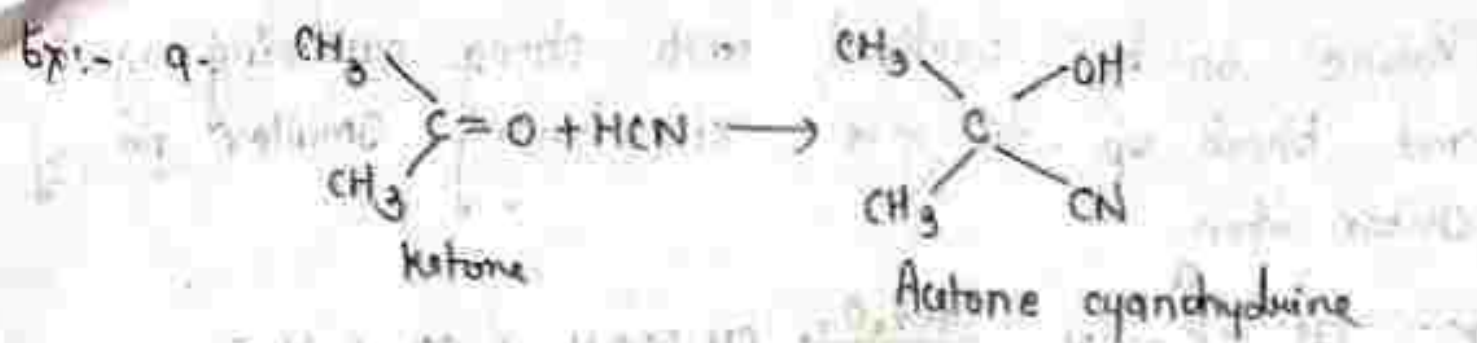
2- Lower aldehydes have an unpleasant odour, while higher have not.

3- Density of carbonyl compound is lesser than water.

### Chemical Property of aldehyde and ketone :-

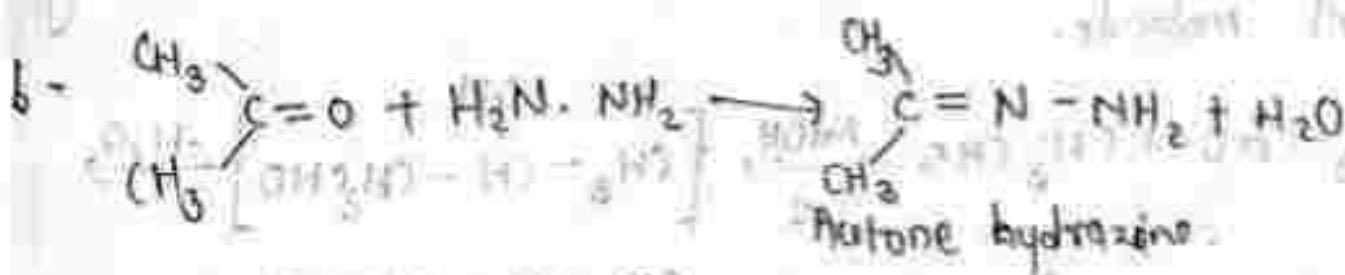
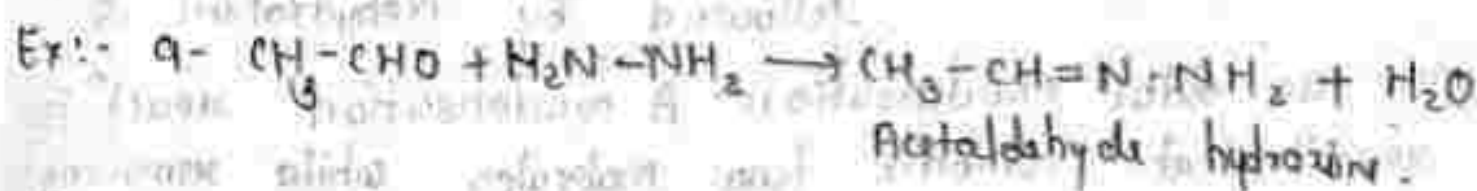
1- Addition of HCN: Carbonyl compounds add on HCN to give addition product called as cyanohydrines.



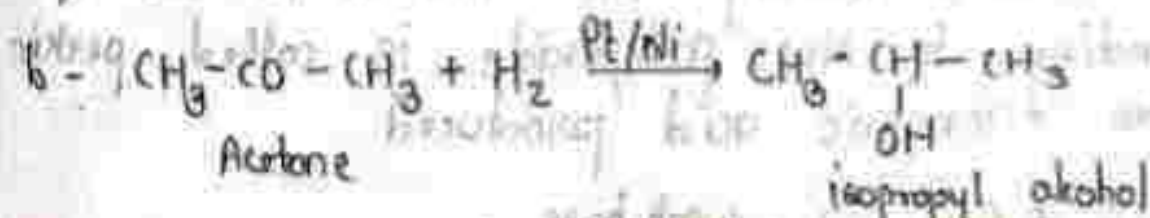
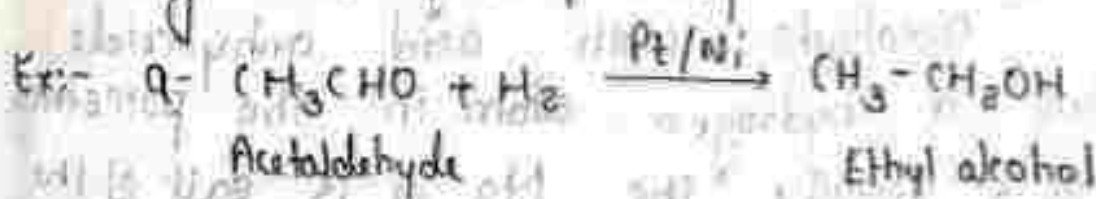


2- React<sup>n</sup> with hydrazine:-

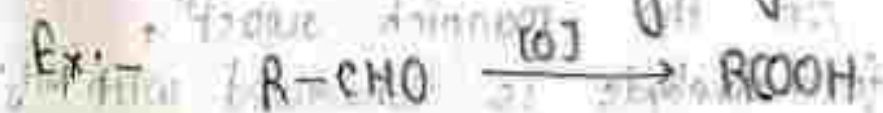
Hydrazone are obtained on react<sup>n</sup> of carbonyl compound with hydrazine.



3- Reduction:- Aldehyde and ketone reduced catalytically in the presence of Ni & Pt to give primary & secondary alcohol respectively.



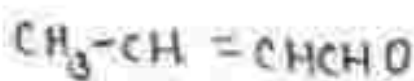
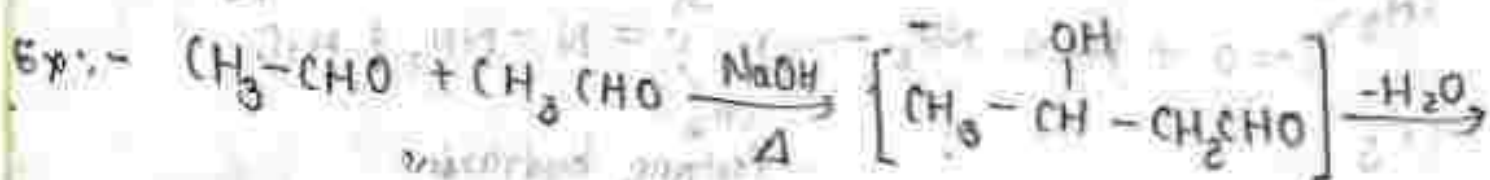
9- Oxidation:- Aldehyde can easily be oxidised with mild oxidising agent to give corresponding acid.



Ketone can be oxidised with strong oxidising agent and break up to give acid having smaller no. of carbon atom.

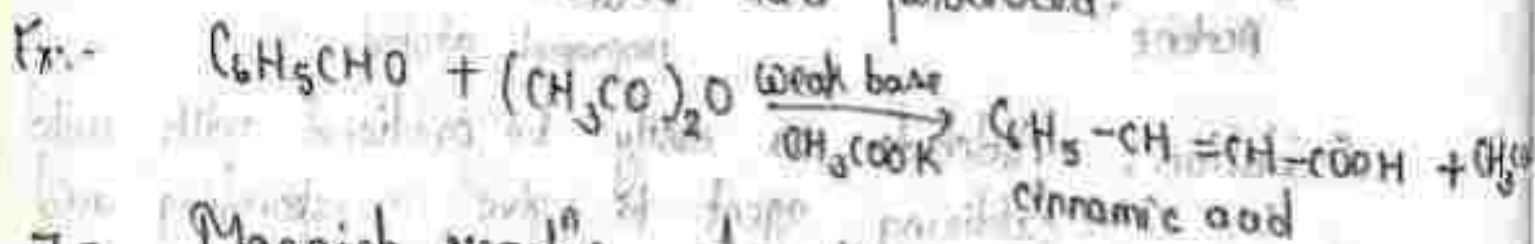


5 - Aldol condensation:- Aldol condensation addition followed by dehydration is known as aldol condensation. A condensation react<sup>n</sup> is a react<sup>n</sup> that combine two molecules while removing a small molecule.



$\alpha, \beta$ , Unsaturated aldehyde.

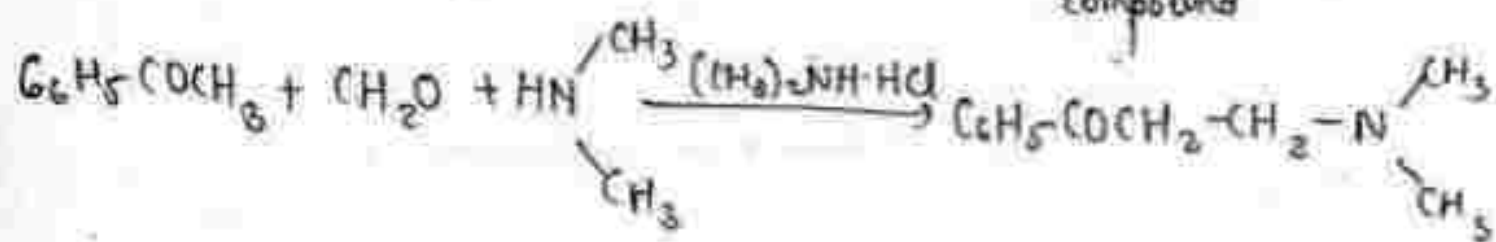
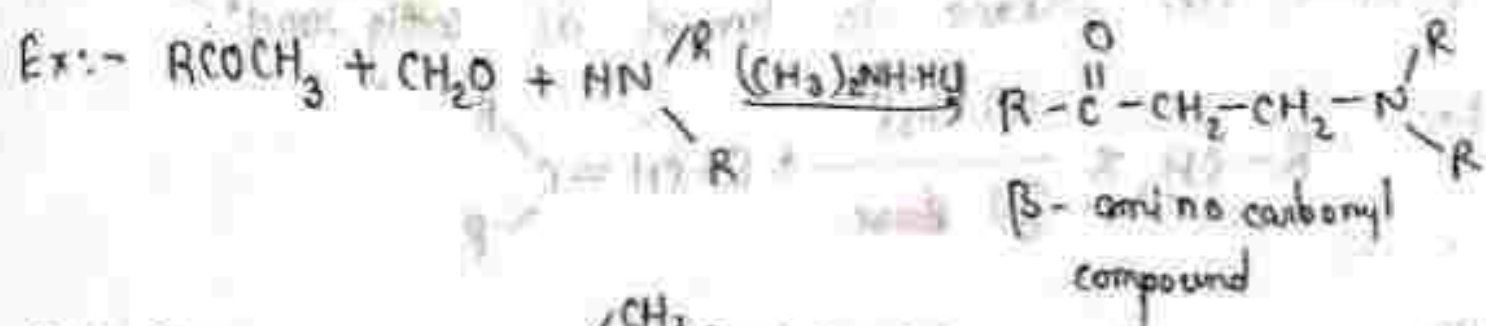
6 - Perkin react<sup>n</sup>:- The condensation of aromatic aldehyde with acid anhydride having atleast two  $\alpha$ -hydrogen atom in the presence of a weak base, usually the Na or K salt of the acid corresponding to the anhydride, is called perkin reaction. Here cinnamic acid produced.



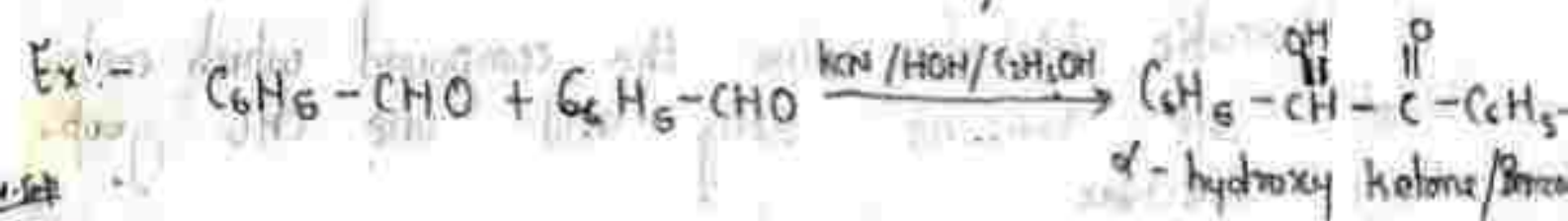
7 - Mannich react<sup>n</sup>:- In the mannich react<sup>n</sup>, formaldehyde is condensed with  $\text{NH}_3$



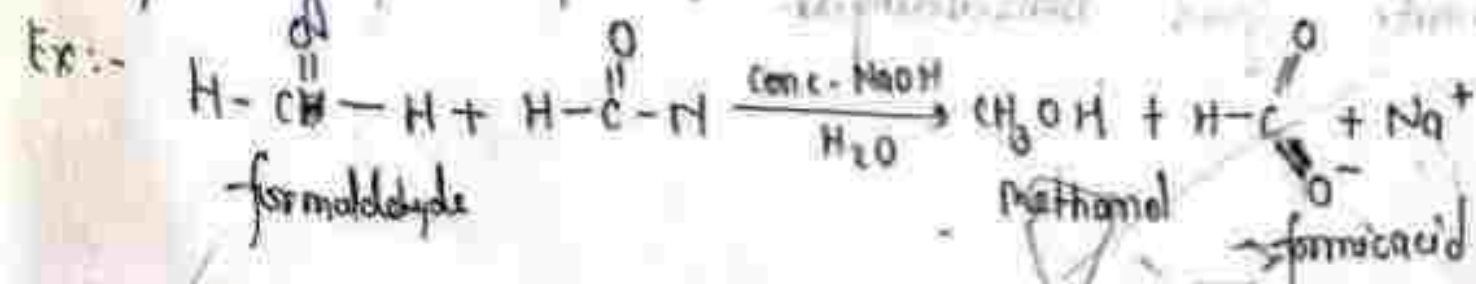
A primary or secondary amine and a compound containing at least one active hydrogen atom, the react<sup>n</sup> is and as well as having base catalyst.



8- Benzoin condensation:- Aromatic aldehyde when refluxed with alcoholic sol<sup>n</sup> of KCN undergoes self condensation to form an  $\alpha$ -hydroxy ketone.

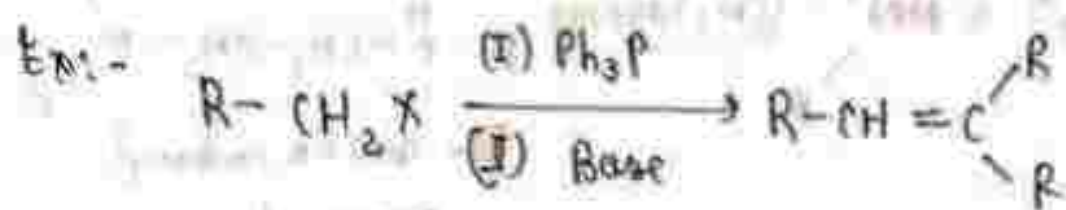


9- Cannizzaro react<sup>n</sup>:- When an aldehyde that has no hydrogen,  $\alpha$  to the carbonyl group is treated with conc. aqueous base, a disproportionation react<sup>n</sup> occurs, then one of the aldehyde is reduced to primary alcohol and the other is oxidised to the corresponding carboxylic acid.





10 - Wittig react<sup>n</sup> :- The react<sup>n</sup> of carbonyl compound with phosphorus ylide ( $\text{Ph}_3\text{P}$ ) to produce an alkene is known as Wittig react<sup>n</sup>.



## Aromatic Aldehyde

Ex:- Benzaldehyde

Structure:-



Def: Aromatic aldehydes are the compound which contain at least one benzene ring and one CHO group in their structure.

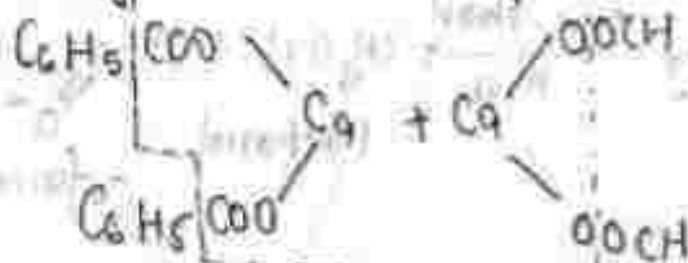
Ex:- Benzaldehyde

### Methods of Prep<sup>n</sup> of Benzaldehyde:-

1. From Calcium benzoate:-

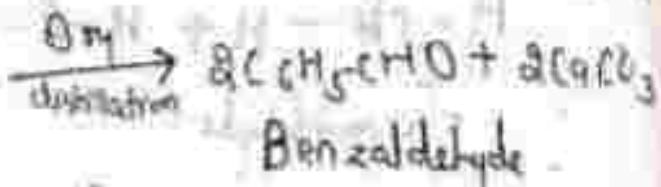
Calcium benzoate on dry distillation with calcium

formate gives benzaldehyde.

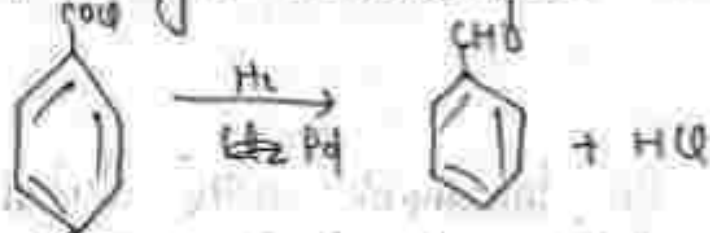


Calcium benzoate

Calcium formate

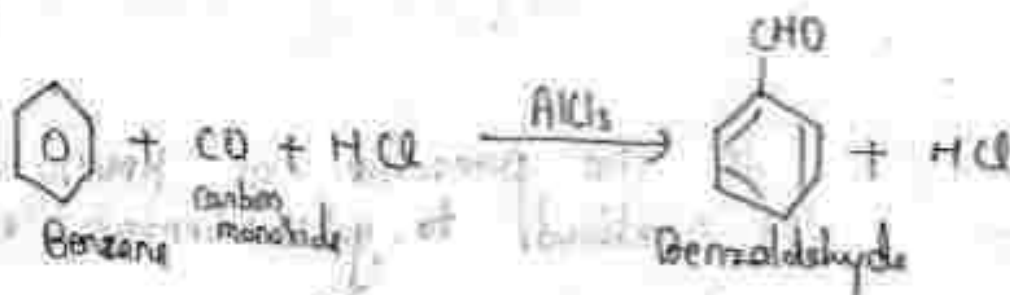


2- Rosenmund React<sup>n</sup> & Reduction: - Benzyl chloride in xylene sol<sup>n</sup> on reduction with hydrogen in the presence of catalyst, we get benzaldehyde.

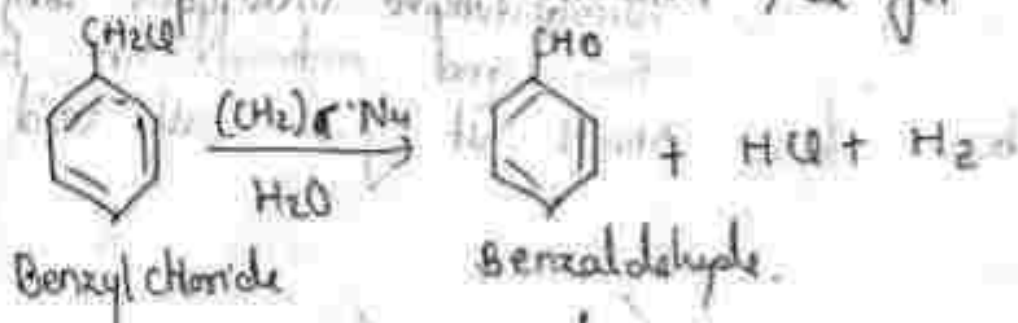


Xylene benzyl chloride      Benzaldehyde

3- Gatterman Koch Reduction: - when benzene treated with CO and HCl under high pressure in the presence of  $\text{AlCl}_3$ , the benzaldehyde obtained.



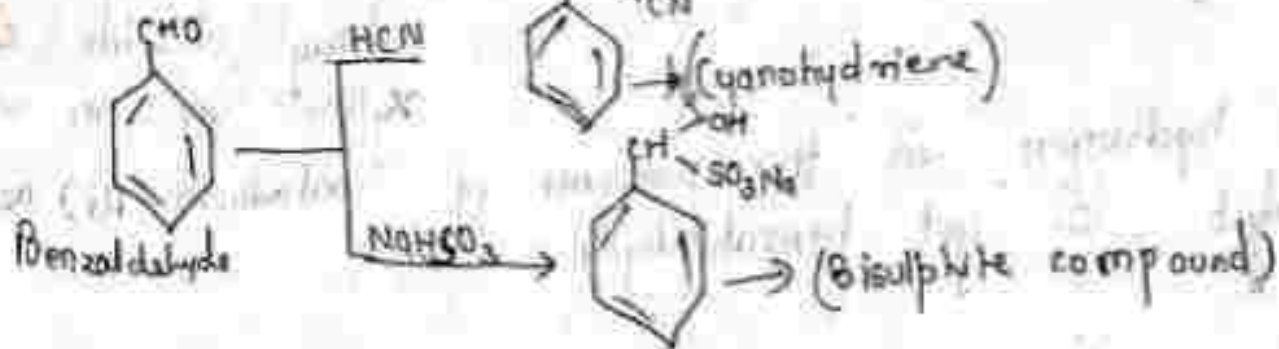
4- Somlet react<sup>n</sup>: - Benzyl chloride on refluxing with hexamethylene tetraamine in alcohol sol<sup>n</sup> and by stream distillation, we get benzaldehyde.



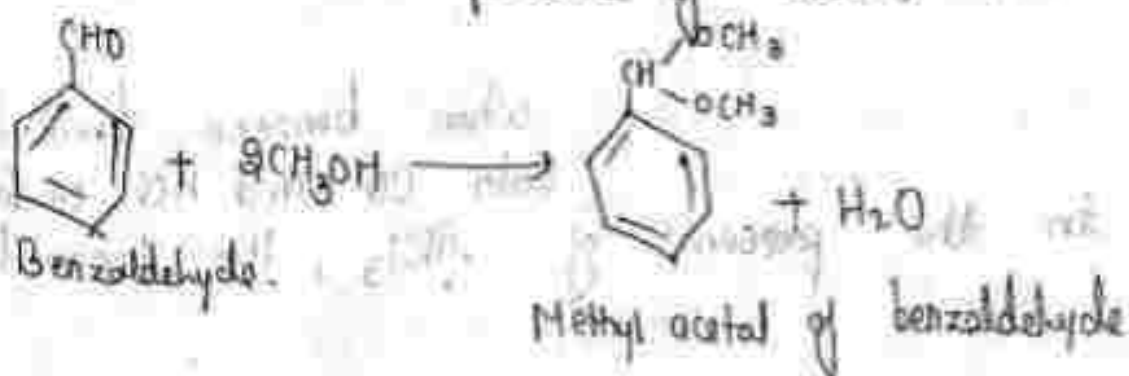
## Chemical Property

1- Addition react<sup>n</sup>: - Due to the presence of carbonyl group benzaldehyde also gives nucleophilic addition react<sup>n</sup>.

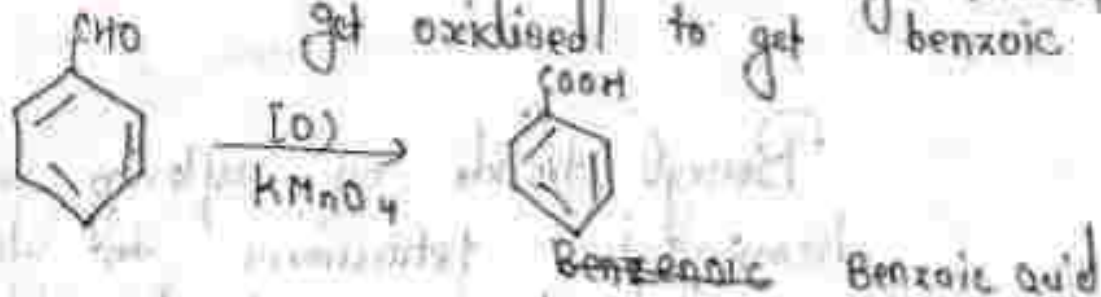




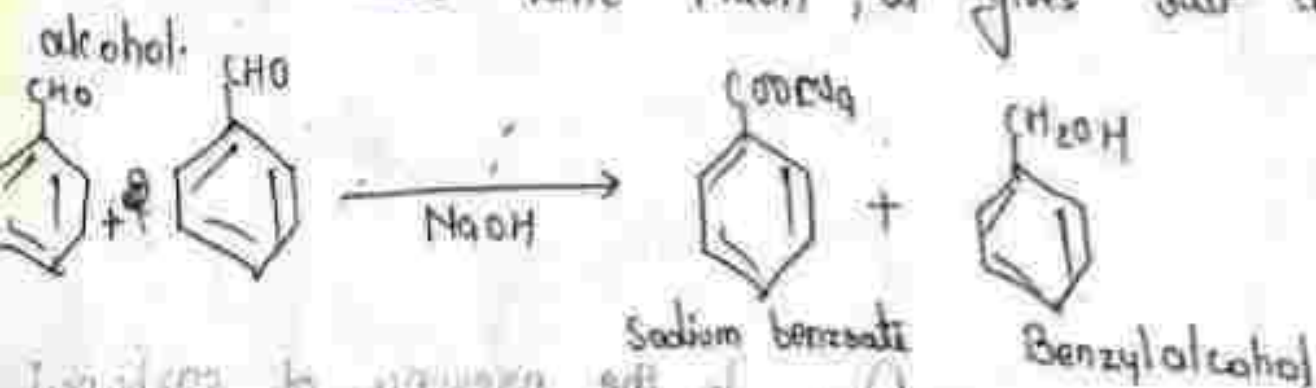
2. Acetal formation:- On treatment with alcohol in the presence of acid, acetal obtained.



3. Oxidation:- In the presence of  $\text{KMnO}_4$ , benzaldehyde get oxidised to get benzoic acid.



4. Cannizzaro reaction:- Benzaldehyde undergoes self oxidation and reduction on heating with conc. base like  $\text{NaOH}$ , it gives salt acid and

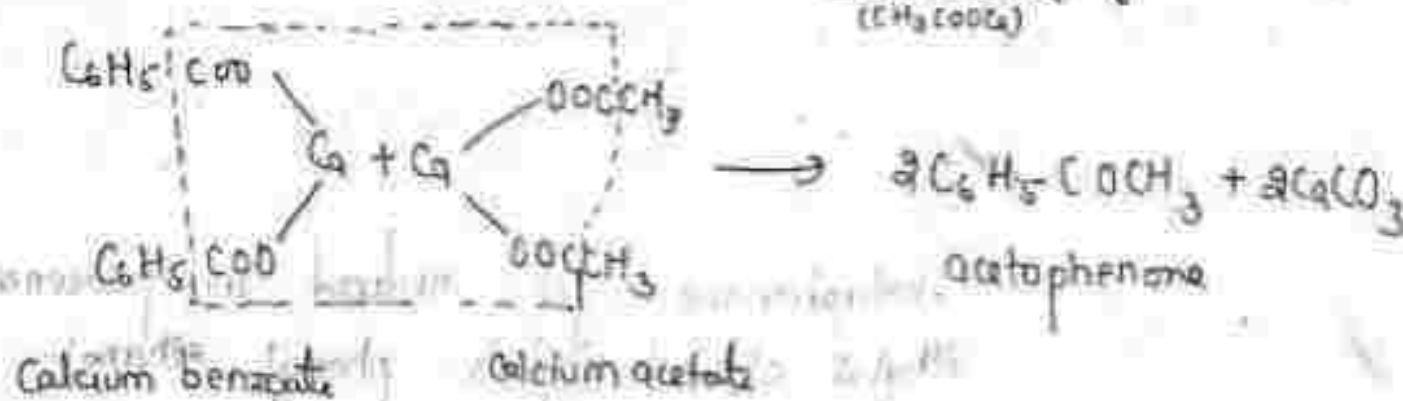


- Uses :- 1- It is used in the manufacturing of dyes & prep<sup>n</sup> of cinnamic acid.  
 2- It is used as a flavouring agent.

## Aromatic ketone

Prep<sup>n</sup> :-

- 1- From calcium benzoate :- Calcium benzoate on dry distillation with  $\text{CaCO}_3$  gives acetophenone.

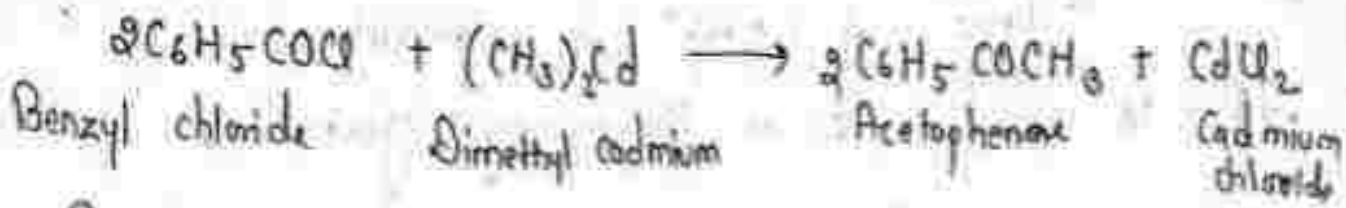


- 2- Friedel Craft react<sup>n</sup> :- Benzene on treated with acetyl chloride in presence of  $\text{AlCl}_3$  gives acetophenone.



when we add  $\text{AlCl}_3$  as a catalyst, there is added one to a free radical react<sup>n</sup> i.e., one hydrogen atom is added.

- 3- From Dimethyl cadmium :- Dimethyl cadmium on treated with benzyl chloride gives acetophenone.

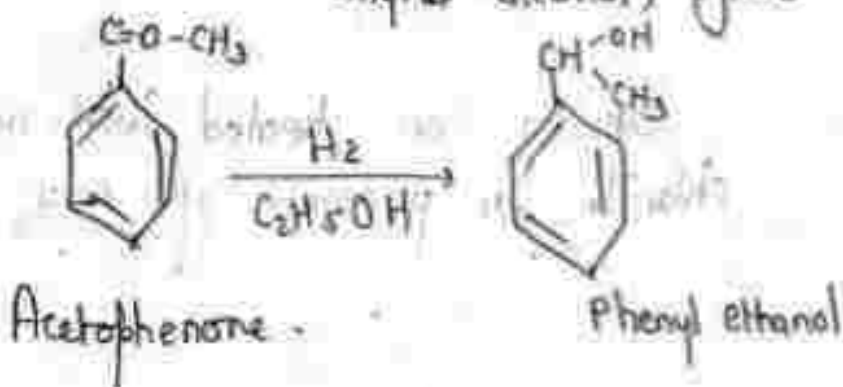


4- Brom Ethyl benzene:- Ethyl benzene get oxidised at  $186^{\circ}\text{C}$  in presence of magnesium acetate gives acetophenone.

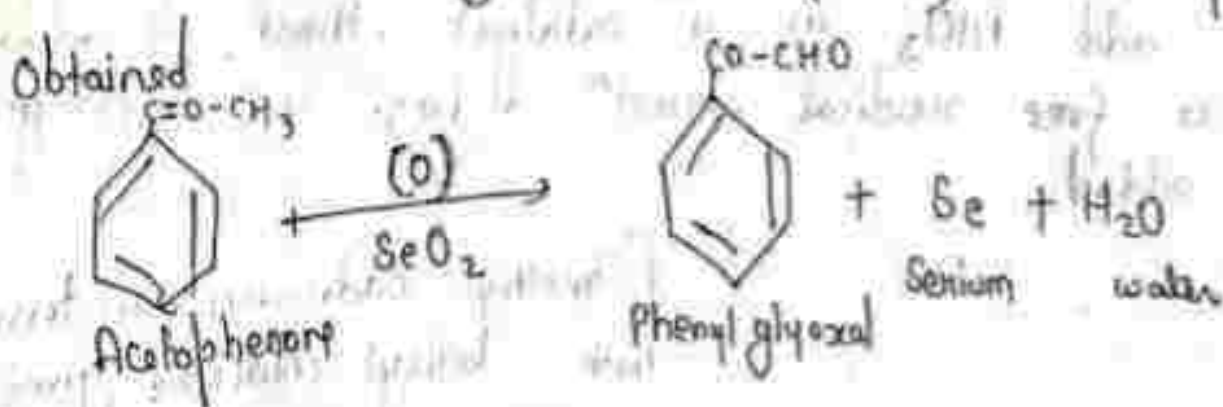


### ✓ Chemical Property

✓ Reduction :- Acetophenone get reduced in presence of ethyl alcohol, gives phenyl ethanol.

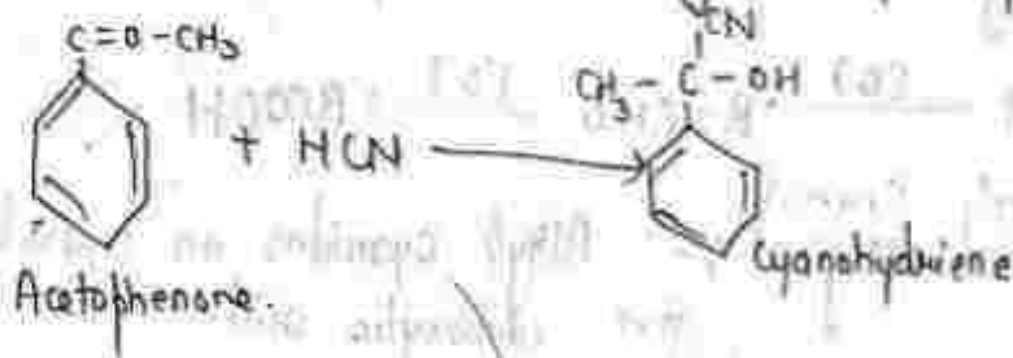


Q- Oxidation :- When acetophenone get oxidised with cerium oxide ( $\text{CeO}_2$ ), then phenyl glyoxal

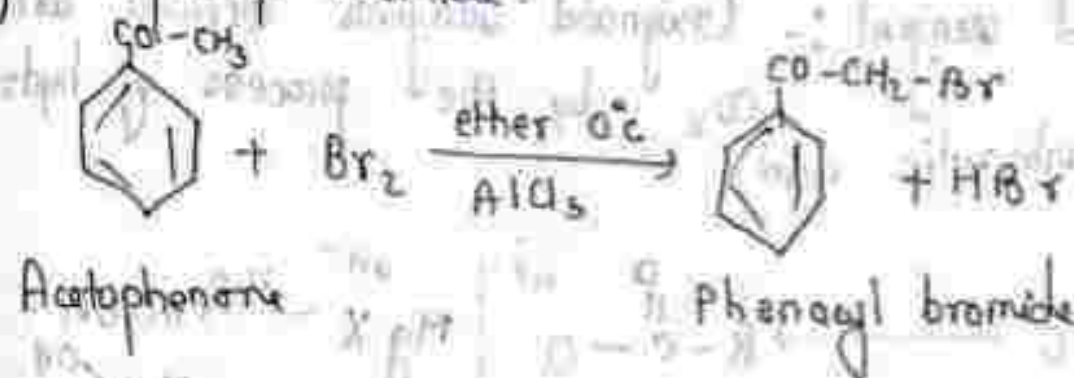




3- Addition react<sup>n</sup>:- Acetophenone under goes addition with HCN gives cyanohydrine



4- Halogenation:- Acetophenone on treatment with Bromine in ether at 0°C in presence of AlCl<sub>3</sub> gives phenyl bromide.



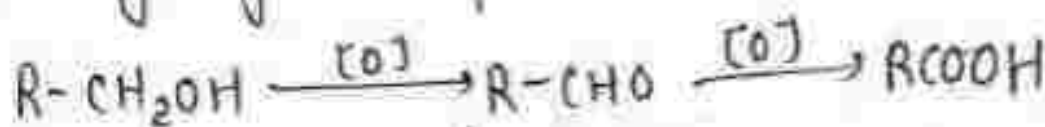
## Carboxylic Acid [C<sub>n</sub>H<sub>2n+1</sub>COOH]

Carbonyl + hydroxy = carboxy

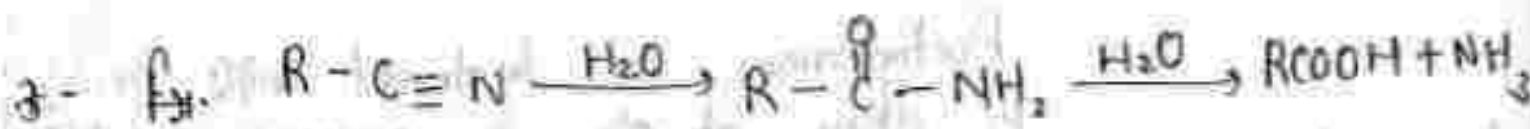
- Organic compounds containing COOH group are called carboxylic acid. Having general formula C<sub>n</sub>H<sub>2n+1</sub>COOH.
- Mono carboxylic acid are also called fatty acid because some the higher member of carboxylic acid like palmitic acid (C<sub>15</sub>H<sub>31</sub>COOH) & stearic acid (C<sub>17</sub>H<sub>35</sub>COOH) etc. They were first obtained from fats.

## Method of Prep<sup>n</sup>

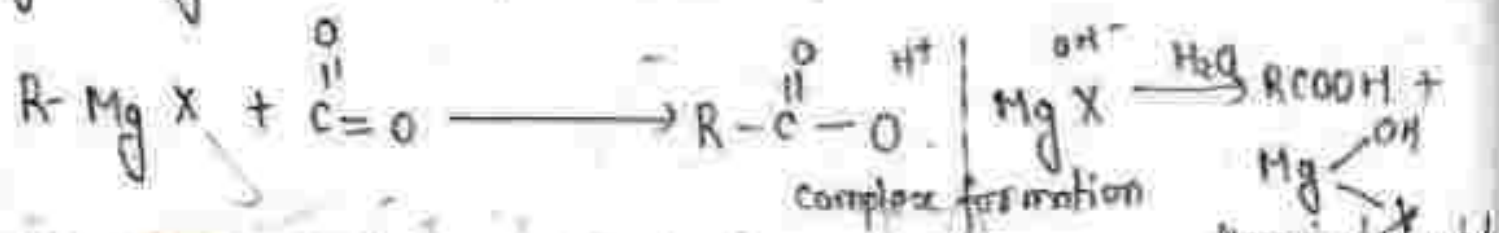
1- From alcohol and aldehyde :- Primary alcohol and aldehyde undergoes oxidation with oxidising agent to form carboxylic acid.



2- From alkyl cyanide :- Alkyl cyanides on hydrolysis give carboxylic acid.



3- From Grignard reagent :- Grignard reagents treated with  $CO_2$  by the process of hydrolysis gives carboxylic acid.



4- From ester :- On boiling an ester with conc. aqueous sodium hydroxide treated with HCl.

HCl gives carboxylic acid.



Physical property of mono carboxylic acid :-

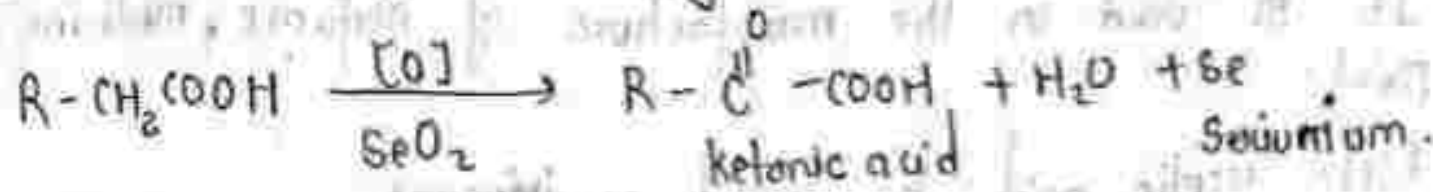
1)  $C_1$  to  $C_{10}$  are liquid in nature & higher members are solid in nature.

2) As it is polar in nature, it dissolve in water but the solubility decreases with increase in molecular wt.



## Chemical Property:

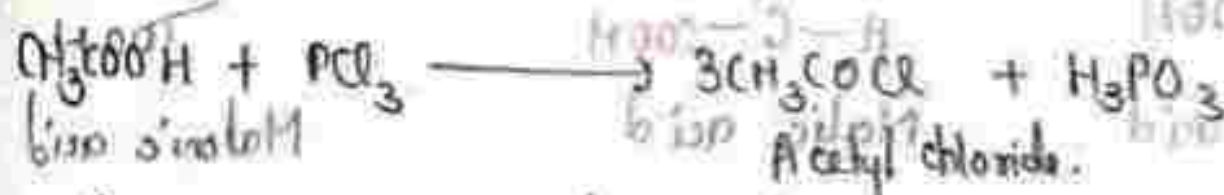
- 1- Oxidation: - When carboxylic acid get oxidised in presence of  $\text{SeO}_2$  it gives keto acid.



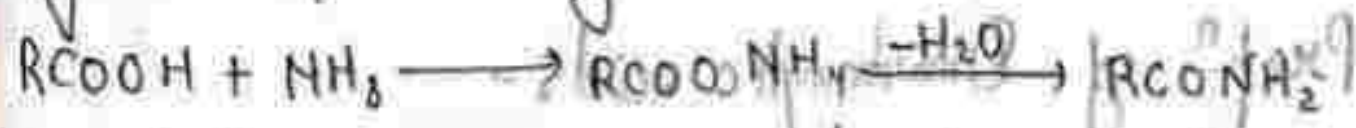
- 2- Esterification: → Acid on refluxing with alcohol in the presence of  $\text{H}_2\text{SO}_4$  as catalyst give ester, this is called fisher esterification. This reaction is reversible.



- 3- Formation of alkyl halide: - Acid on treatment with  $\text{PCl}_3$  gives alkyl halides by the replacement of OH group.

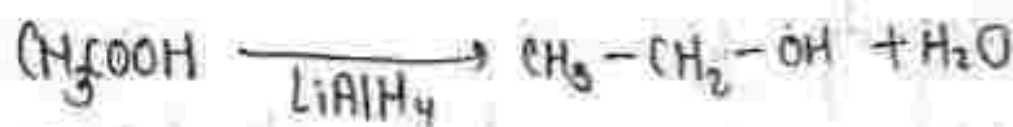


- 4- Formation of acid amide: - Acid on treatment with ammonia form ammonium salts which on heating strongly undergoes dehydration give acid amide.



- 5- Reduction: - Carboxylic acid can be reduced in presence of  $\text{LiAlH}_4$  (Lithium aluminium hydride) gives primary alcohol.





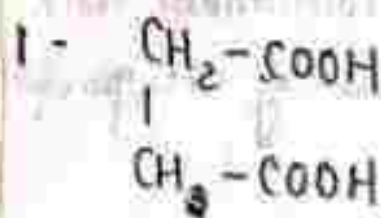
Uses: ↓

- ⇒ It is used in the manufacture of perfume, medicine, & paint.
- ⇒ Dil. acetic acid is used as vinegar.

## Dicarboxylic Acid

It contains two molecules of carboxylic acid called dicarboxylic acid.

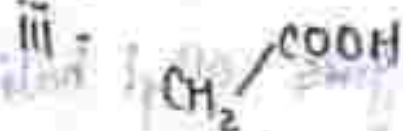
General formula:  $\text{C}_n\text{H}_{2n}(\text{COOH})_2$



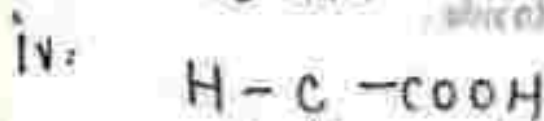
Succinic acid



Malic acid



Malonic acid



fumaric acid

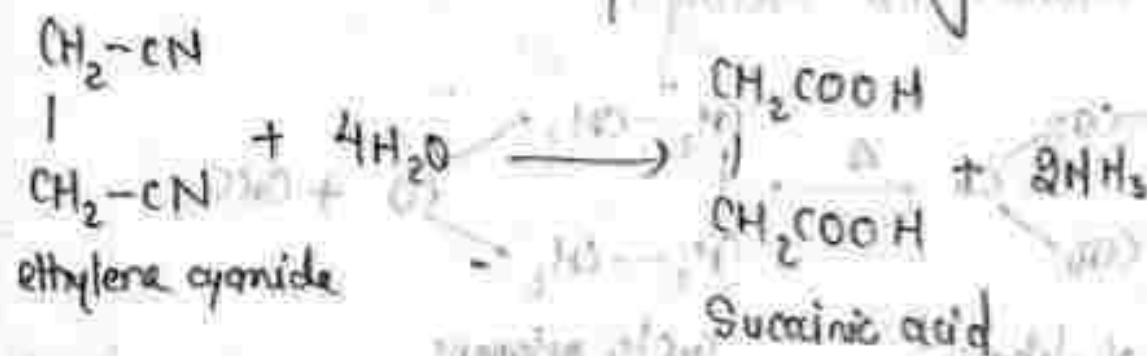
## Prep<sup>n</sup> of Dicarboxylic acid:-

1- Oxidation of diol:-

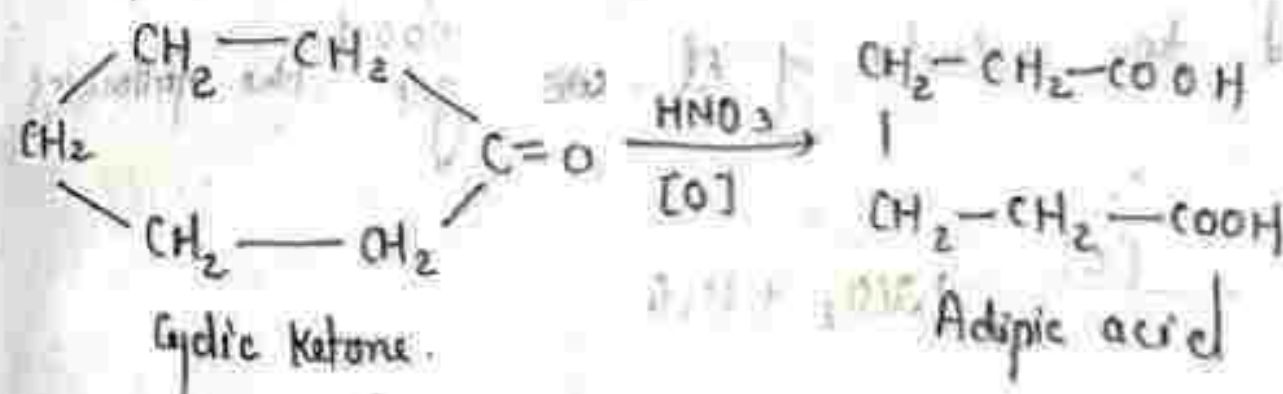
Primary Diol on oxidation gives dicarboxylic acid.



2. Cyanide synthesis:- In this method, ethylene cyanide get hydrolysed to give dicarboxylic acid.

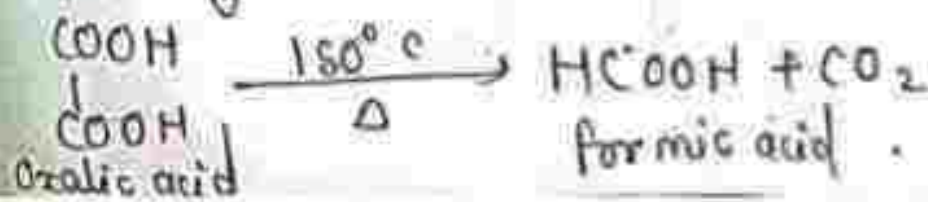


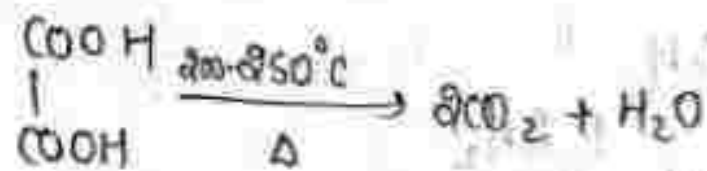
3. From cyclic ketone:- Oxidation of cyclic ketone in the presence of nitric acid produce carboxylic acid.



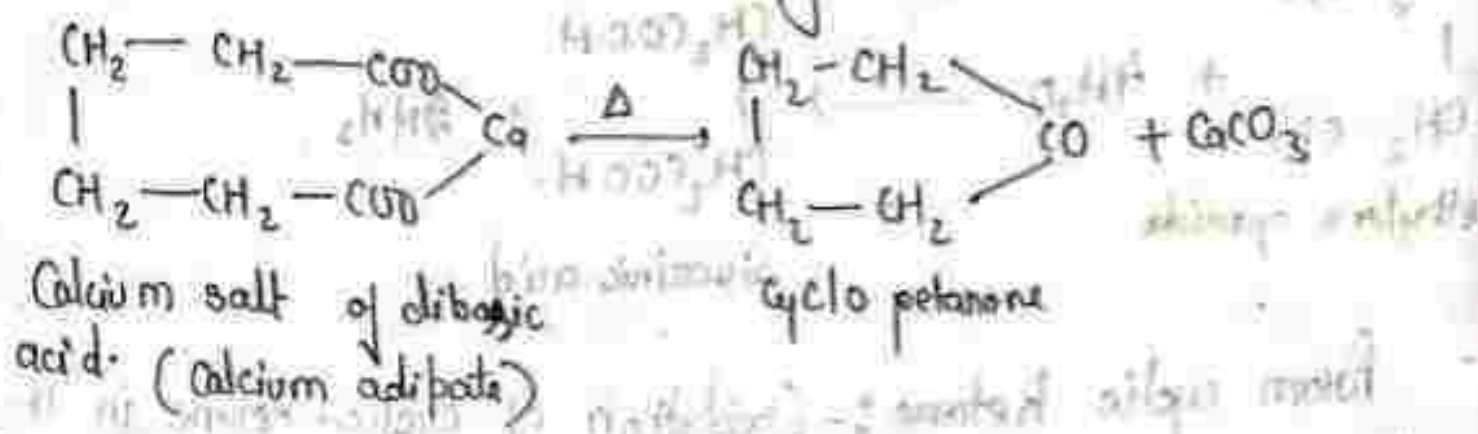
### Chemical Property:-

1. Action of heat:- Acid which contain two carboxylic group, on heating undergoes decarboxylation gives mono carboxylic acid and by increasing the temp<sup>r</sup>. it gives  $\text{CO}_2$  &  $\text{H}_2\text{O}$ .

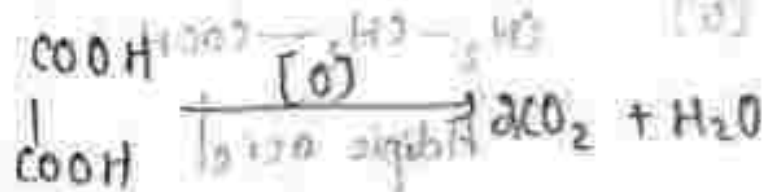




2. Action of heat on calcium salt:- Calcium salt of higher dibasic acid gives cyclic ketones on heating.



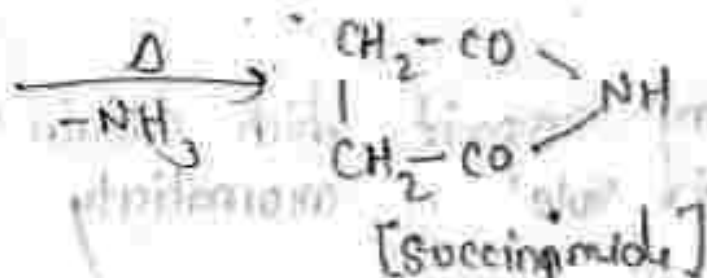
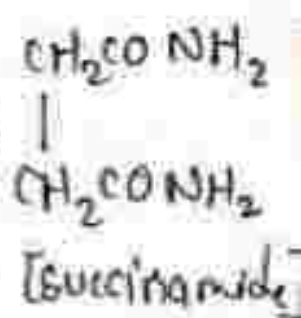
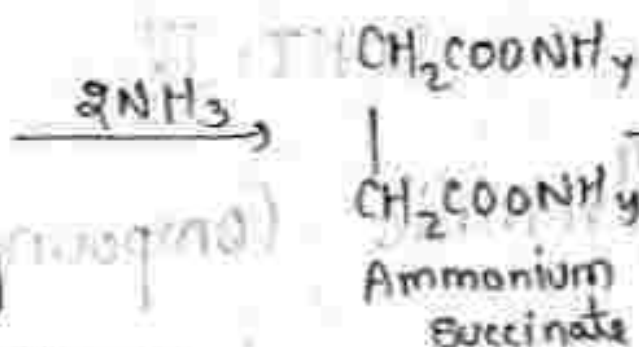
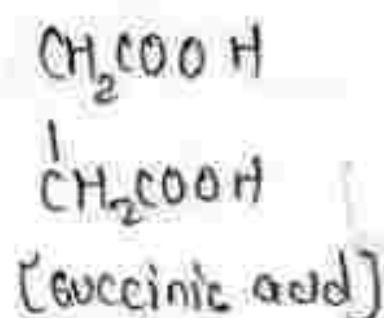
3. Addition of Oxygen and chlorine:- When we treat acid with oxygen and two molecule of Cl we get the following product.



oxalic acid

4. Treatment with  $\text{NH}_3$ :- On treatment with ammonia it gives ammonium succinate which undergoes dehydration give succinamide.





Benzene



Naphthalene

## ORGANOLITHIUM COMPOUNDS

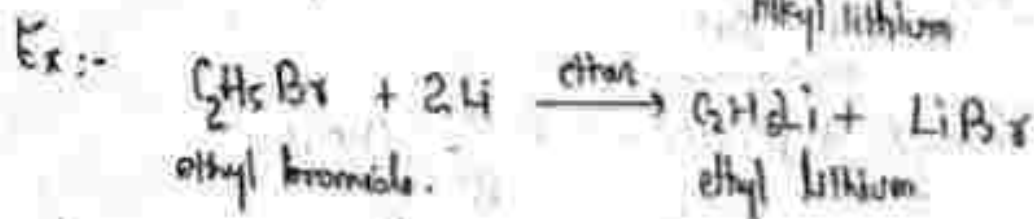
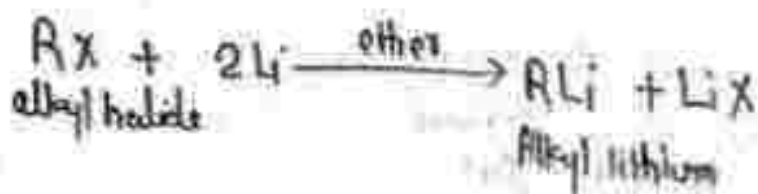
Organometallic compounds in which carbon atom is directly linked to lithium, an alkali metal, are called organolithium compounds.

Formula:-  $R-Li$

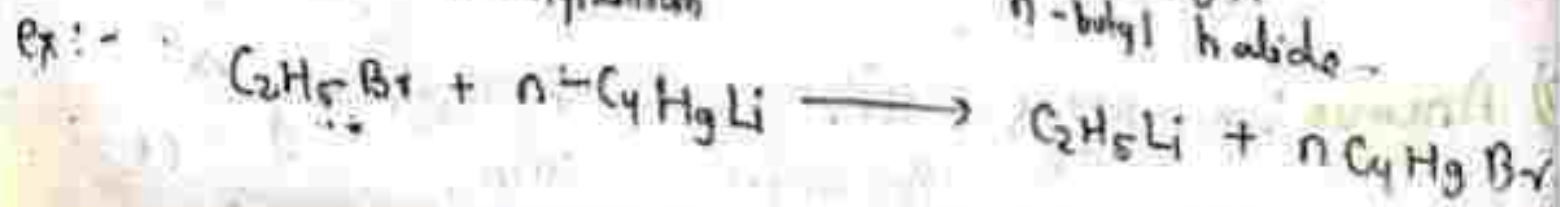
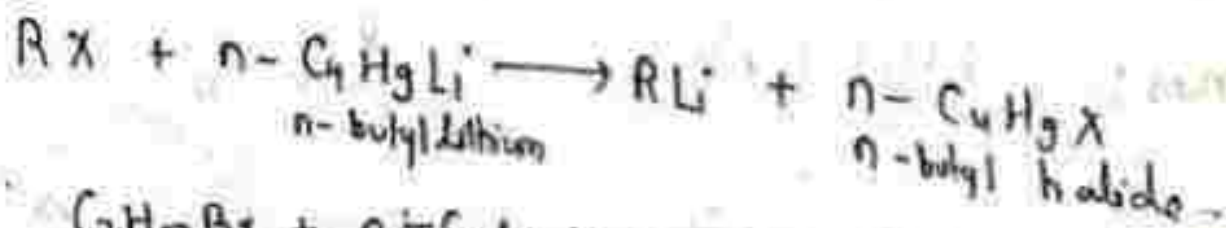
- ⇒ Organolithium compounds are more ionic & highly reactive as compared to Grignard reagents. This is due to the smaller size and greater polarising power of lithium.
- ⇒ They are very useful synthetic reagents.

### Prep<sup>n</sup> of Organolithium compounds:-

1. Organolithium compounds may be prepared by heating an alkyl or aryl halide with metallic lithium in ether or benzene.



2. Organolithium compounds may also be prepared by heating alkyl halide with a suitable alkyl lithium, usually n-butyl lithium.



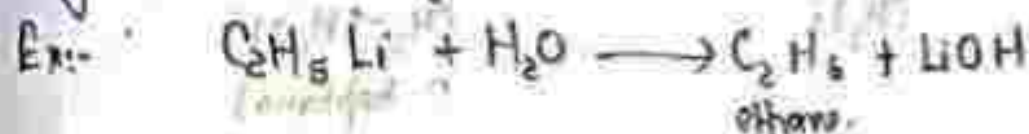
Physical property :-

- 1- Alkyl lithiums are colourless liquids or solids.
- 2- They have low M.P.
- 3- They are insoluble covalent compounds, with partial ionic character.

Chemical properties & Synthetic uses:-

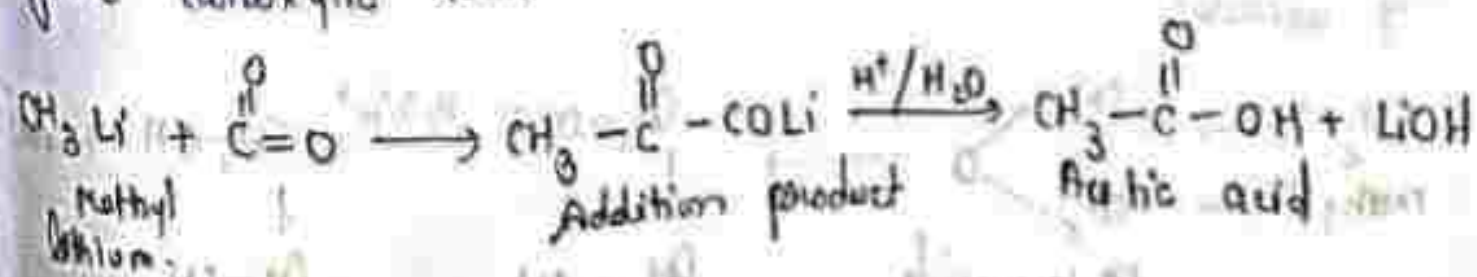
1. Organolithium compounds are more selective than Grignard reagents which is due to the greater polarity of  $C-Li$  bond than  $C-Mg$  bond.
2. They are highly sensitive towards air & moisture.

1. React<sup>n</sup> with compounds containing active hydrogen atoms (formation of hydrocarbons):  
Organolithium compounds react with water, to give corresponding hydrocarbons.



2. React<sup>n</sup> with  $O_2$  (formation of ~~carb~~ carboxylic acid & ketone):

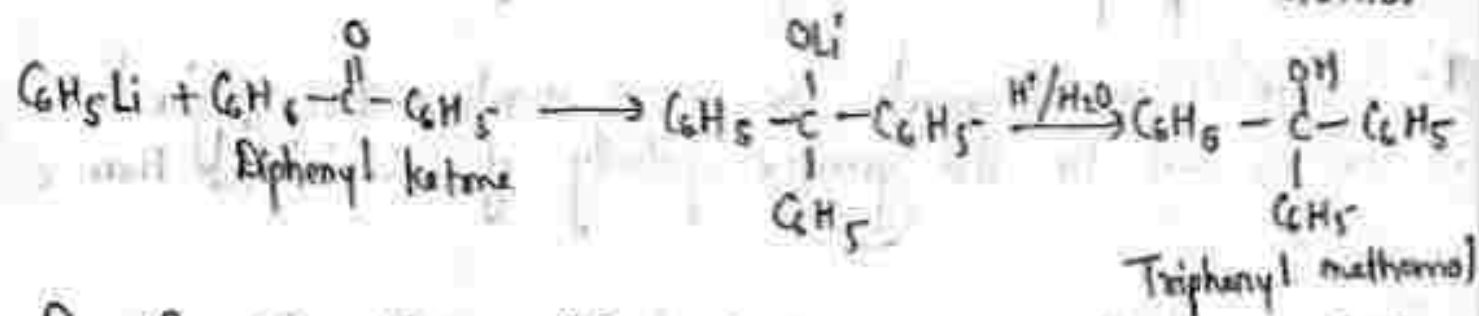
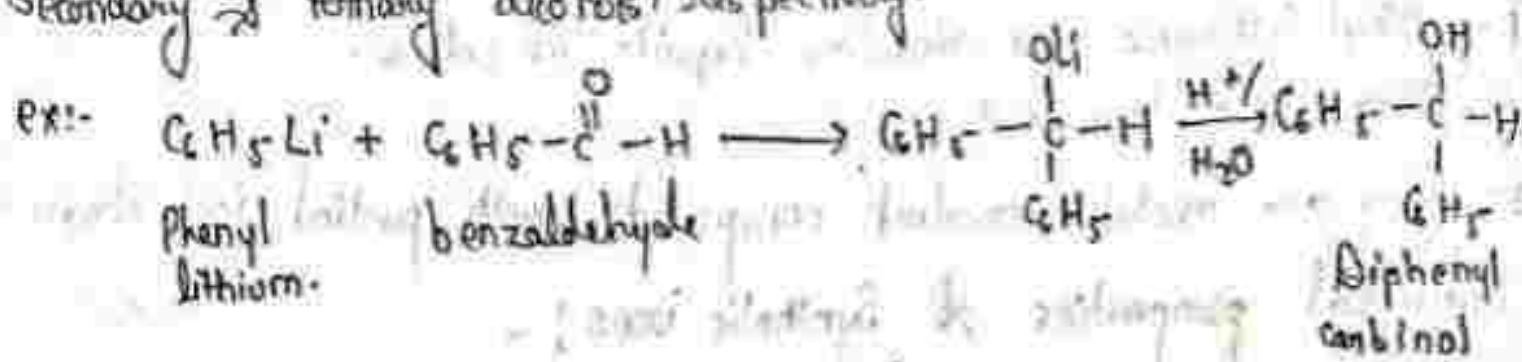
Alkyl lithiums react with  $\text{CO}_2$  under the process called carbo-  
nation to give  $\text{Li}$  salts of carboxylic acids which on hydrolysis  
give carboxylic acids.



3. React<sup>n</sup> with carbonyl compounds (formation of secondary & tertiary alcohols): ↓

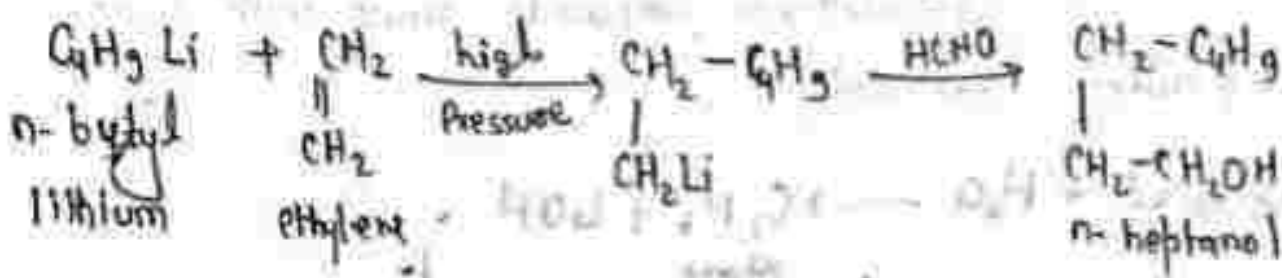


Organolithium compounds react with aldehydes & ketones to give secondary & tertiary alcohols, respectively.



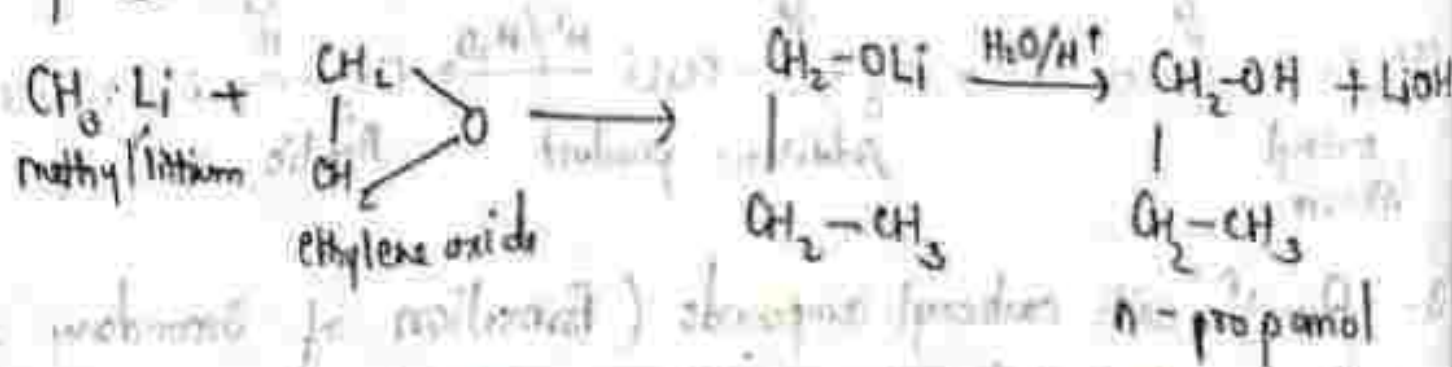
#### 4- React<sup>n</sup> with alkenes (formation of primary alcohols):

Organolithium compounds react with Alkenes to give addition product which reacts with formaldehyde to give primary alcohols.



#### 5- React<sup>n</sup> with ethylene oxide (formation of primary alcohols):

An addition product is obtained by the react<sup>n</sup> of organolithium compounds & ethylene oxide which on hydrolysis gives primary alcohols.



## UNIT = IV

### Aromatic Compound



According to Huckel any compound which contain  $4n+2$   $\pi$  rule is called Huckel rule of aromaticity.

Huckel's Rule:- According to Huckel, "A compound will be aromatic, if it has a cyclic  $\pi$   $e^-$  on the plane in the ring & it obey  $(4n+2)\pi$   $e^-$  rule, where  $n=0, 1, 2, 3$ ."

### Classification of Aromatic compound:-

Aromatic compound is classified into two types:-

1. Benzenoid compounds:- The compounds which are aromatic in nature & contain atleast one benzene ring are called Benzenoid compounds.

Ex:- Naphthalene :-  & Benzene - 

2. Non Benzenoid compounds:- Compounds which are aromatic in nature but do not contain any benzene ring in them is called non-benzenoid compounds.

Ex:-  Pyrrole  Furan  Thiophene



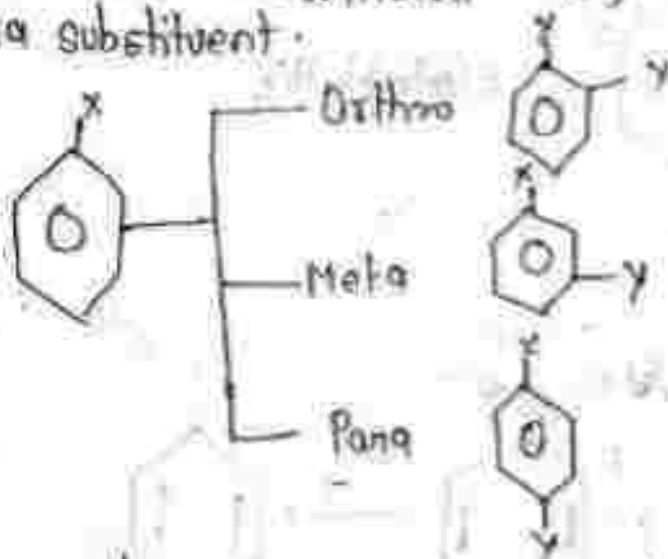
Although furone & thiophene contain  $8 \pi e^-$  & two  $\pi e^-$  are away from the plane so it obey Huckel rule, i.e.,  $(4n+2)\pi$ .

## Oriention in aromatic electrophillic substitution

As treated in the structure of benzene, all the position in the benzene ring are equivalent, so if we add a monosubstituent then the structure is :-



If we add polysubstituent, then there is three options to add another substituent i.e., Ortho substituent, Meta- & para substituent.



Depending upon the position to which new incoming group is directed groups may be classified into two types.

- 1- O, P directing group
- 2- M directing group

1- O, P directing groups: The groups which direct the new incoming groups to occupy O & P position in the benzene ring are called O, P directing group.

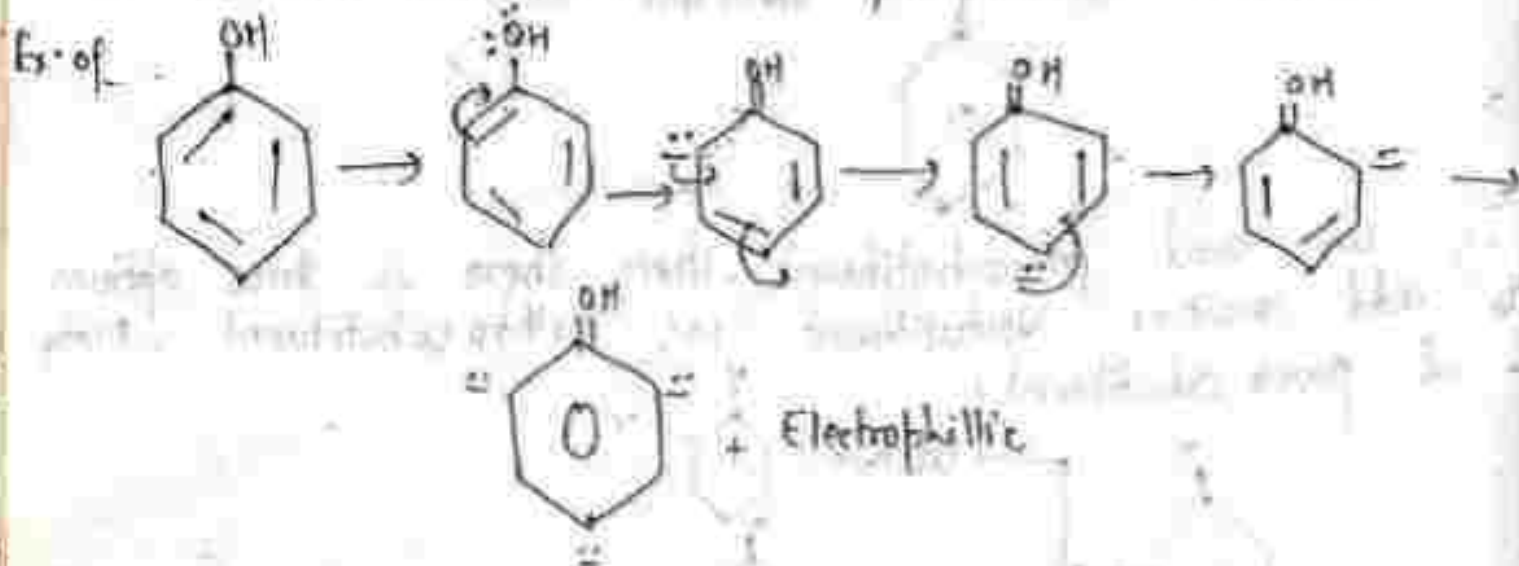
Important O, P directing groups are  $-NH_2$ ,  $-OH$ ,  $-OR$ ,  $-SH$ ,



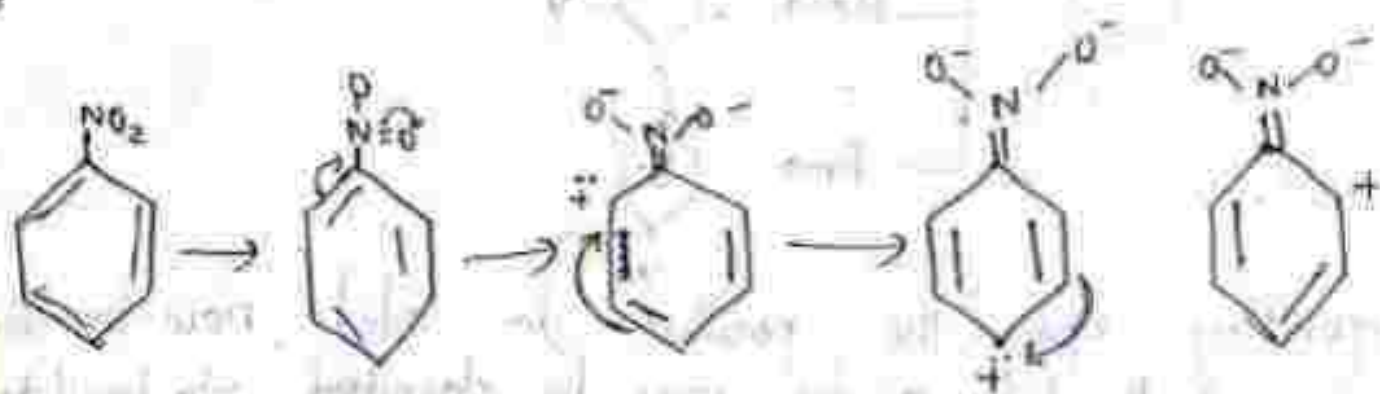
$-SR$ ,  $-COO^-$  etc.

Q. M-directing groups - The groups which direct the new incoming groups to occupy 'M-' position in the benzene ring are called M-directing groups.

Some important M directing groups are  $-NO_2$ ,  $-CN$ ,  $-NC$ ,  $-CHO$ ,  $-COOH$ ,  $-COCl$ ,  $COOR$  etc.



Q.



## Theory of Orientation:

Theory of orientation based on three principles:

1. Inductive effect:- In a covalent bond, the share pair of electrons is slightly shifted towards the more

electronegativity atom. It is classified into 2 types.  
1-  $\Delta$  +ve I effect      2- -ve I effect.

2. Electromeric effect :- [E-effect] :- The groups which have a tendency to donate or accept the lone pair of  $\pi$   $e^-$  from the ring, is called electromeric effect. It is classified as:-

i- +ve E      -ve E

3. Mesomeric effect :- The involvement of delocalization of  $e^-$  through resonance in a  $\pi$  system is called as mesomeric effect or resonance effect. It is classified as.

+ve M effect      -ve M effect.

⇒ Electromeric & Mesomeric effect are collectively called as Tautomeric effect, [T-effect].

## Aromatic Hydrocarbons

The word aromatic hydrocarbon means, "a benzene ring containing hydrocarbon i.e., addition of Hydrogen & Carbon atom."

Formula :-  $C_nH_{2n-6}$

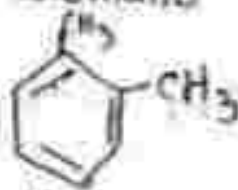
Ex:- Some example of aromatic hydrocarbon are:-



Benzene



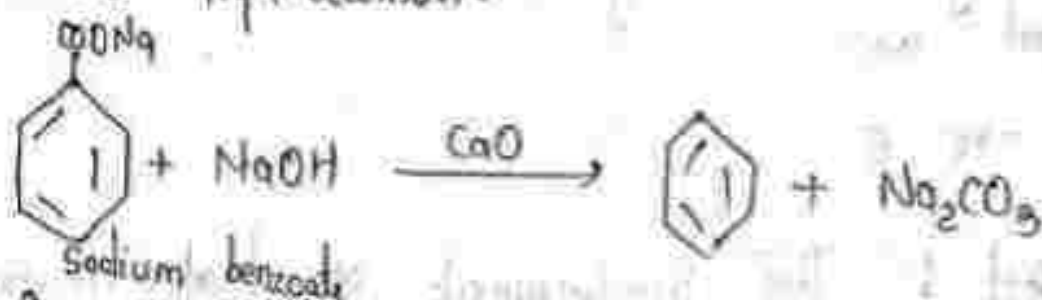
Toluene



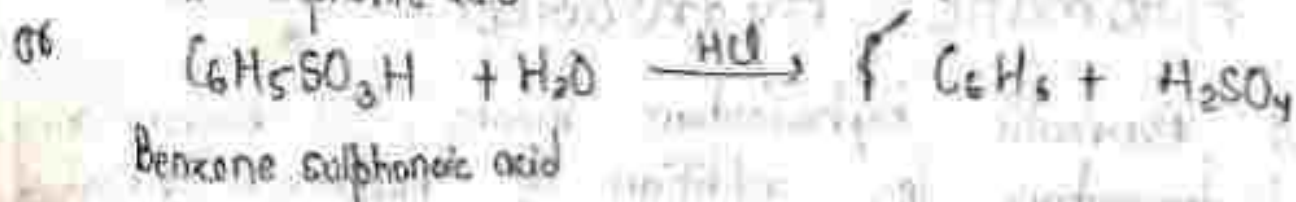
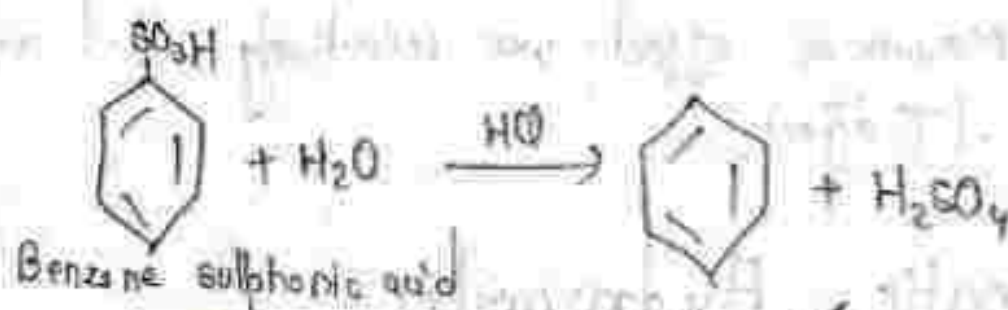
Xylene

## Method of Prep<sup>n</sup> of Aromatic hydrocarbon:-

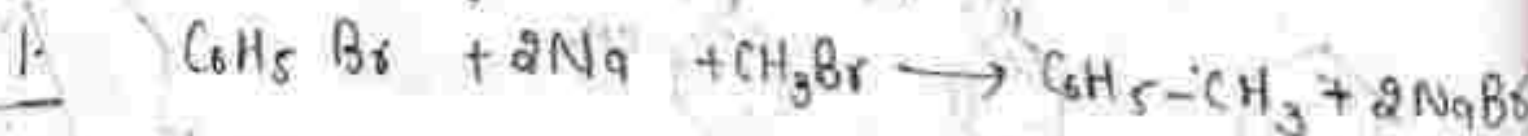
1. From Aromatic acid:- Aromatic acid undergoes heating with soda lime gives corresponding aromatic hydrocarbon.



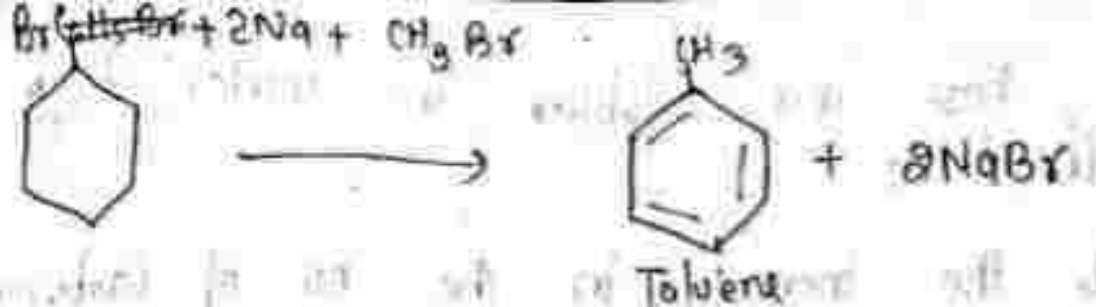
2. From Aromatic Sulphonic acid:- Aromatic sulphonic acid undergoes hydrolysis in presence of  $\text{HCl}$ , gives aromatic hydrocarbon.



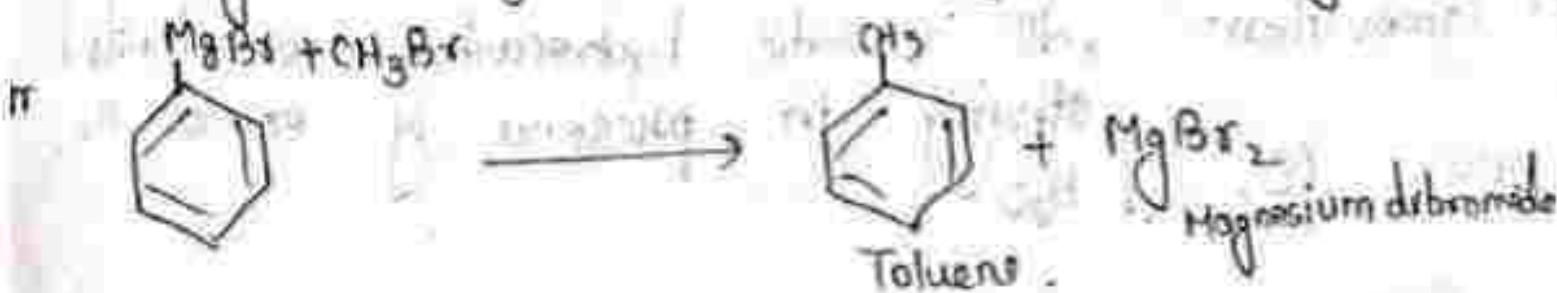
3. Wurtz fitting react<sup>n</sup>:- Aryl halides treated with alkyl halides in presence of sodium gives corresponding aromatic hydrocarbon.



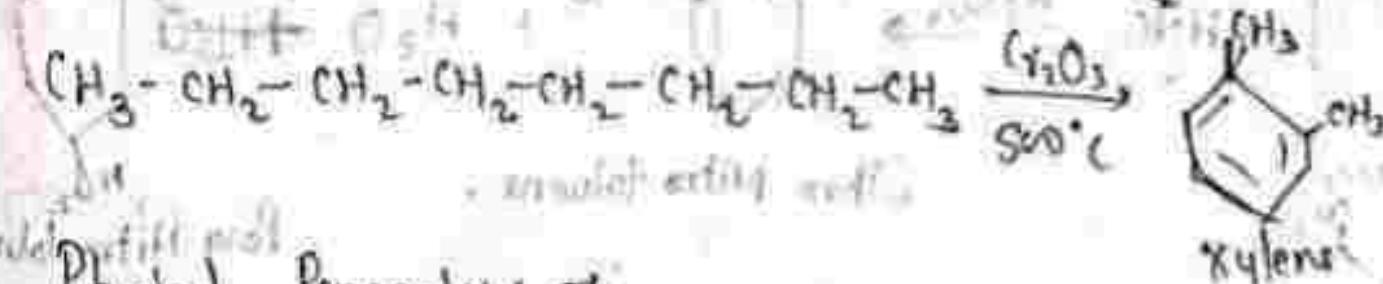
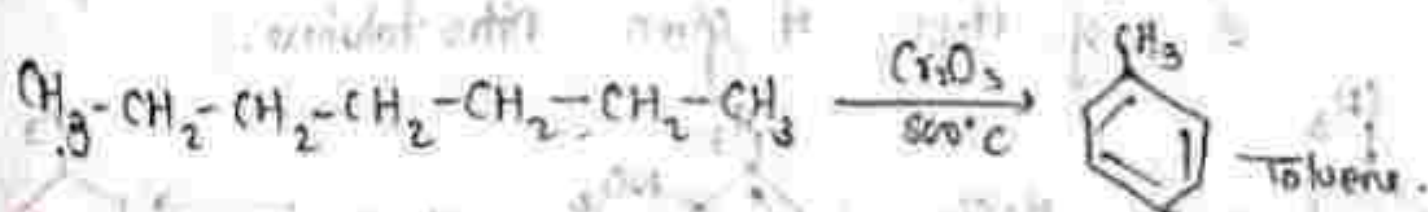
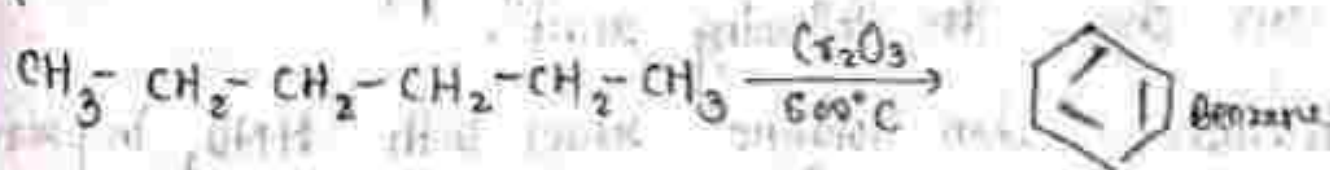




4. From Grignard reagent:- Aromatic grignard reagent treated with alkyl halide gives aromatic hydrocarbon.



5. Aromatisation:- When vapours of long chain of alkane are passed over chromic oxide as a catalyst and at  $500^\circ\text{C}$  then we get corresponding aromatic hydrocarbon.



Physical Property:-

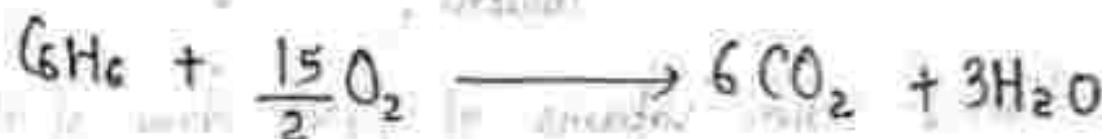
1- Lower members of this series are colourless & pleasant liquid but higher members are solid in nature.

2. Solubility:- These are soluble in water & b. insoluble

3. BP & M.P.:- As the increase in the no. of carbon atoms, the boiling & melting point are gradually increased.

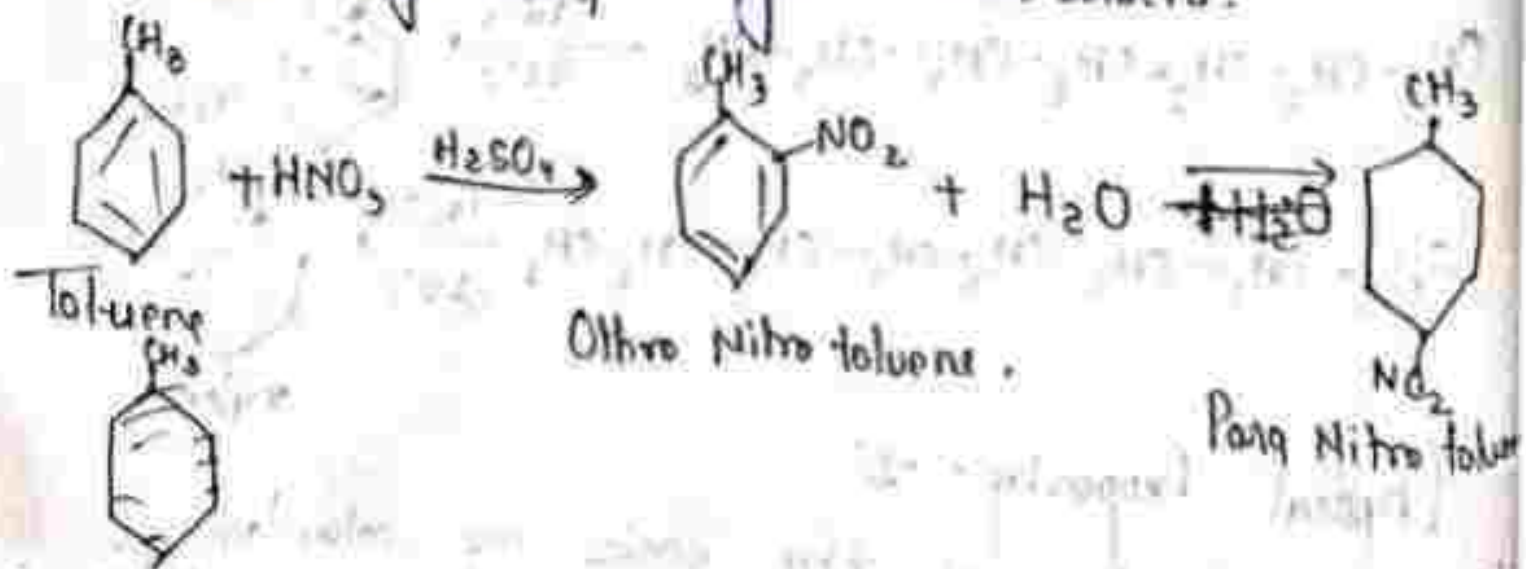
Chemical property:-

1. Combustion:- All aromatic hydrocarbon are heated strongly in presence of excess  $O_2$ , gives  $CO_2$  &  $H_2O$ .



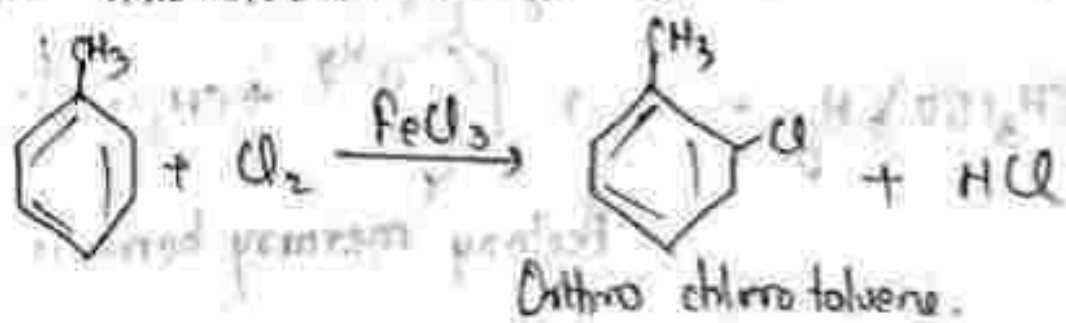
2. Electrophillic Substitution react<sup>n</sup>:- Aries undergoes electrophillic substitution react<sup>n</sup> can show the following react<sup>n</sup>.

A. Nitration:- When toluene react with  $HNO_3$  in presence of  $H_2SO_4$ , it gives Nitro toluene.

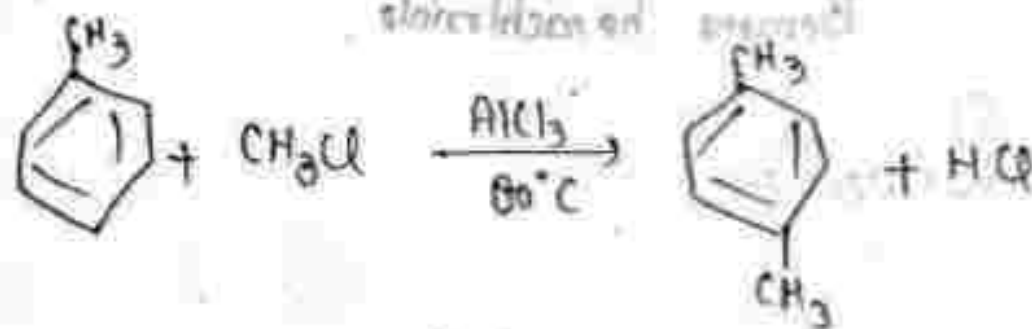
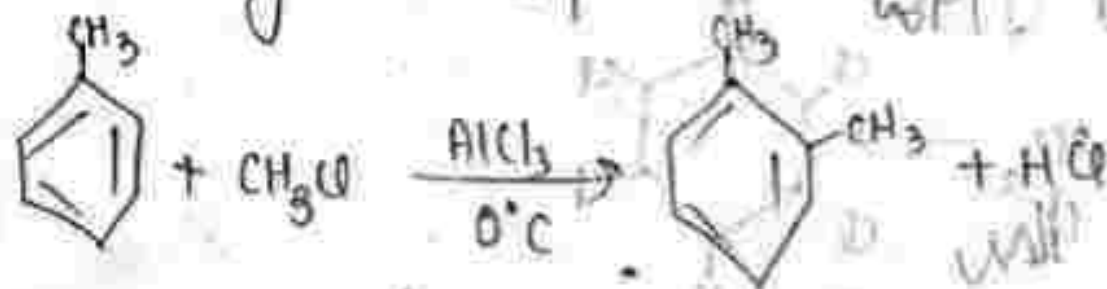




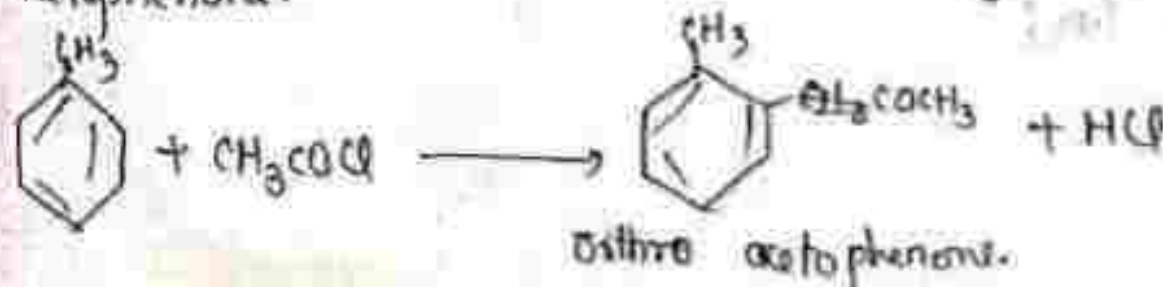
B- Halogenation:- Toluene react with two molecule of halogen group in presence of  $FeCl_3$  give halo toluene.



C- Friedel craft Alkylation:- when toluene treated with alkyl halide in presence of  $AlCl_3$  at  $0^\circ\text{C}$ , it gives ortho xylene & para xylene & at  $80^\circ\text{C}$  gives meta xylene.

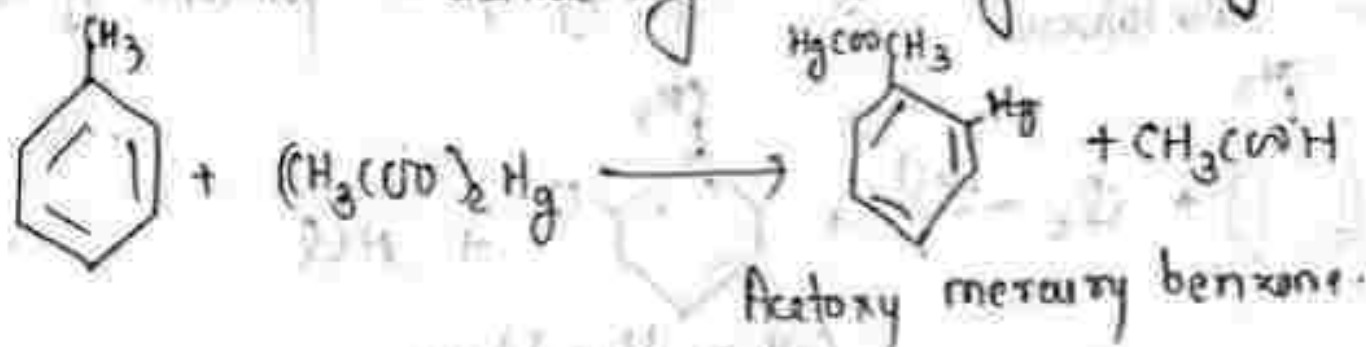


D- Friedel Craft Acylation:- Toluene react with acetyl chloride gives ortho & para -acetophenone.



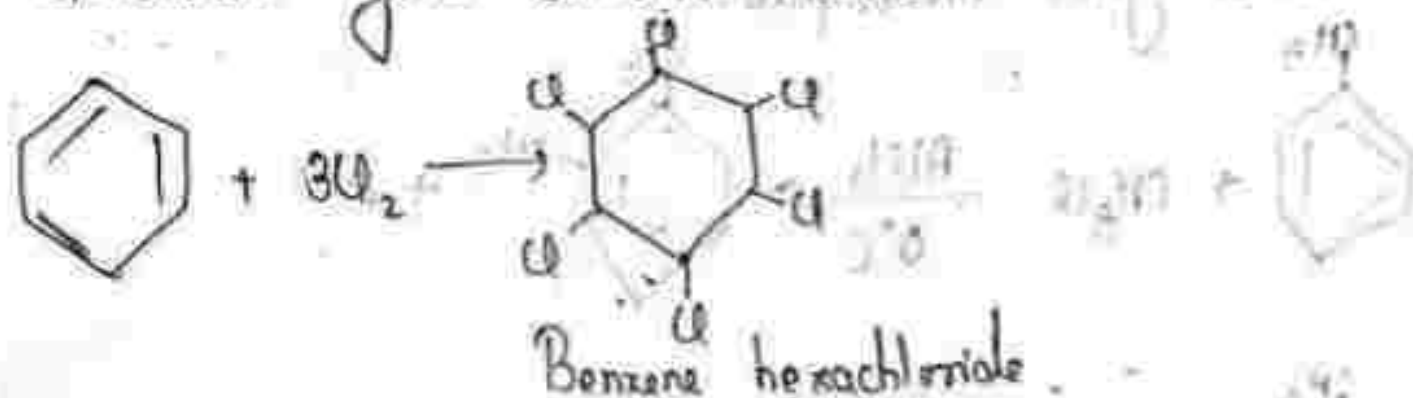


3- Mercuriation:- Benzene react with mercuric acetate, gives acetoxy mercury benzene.



4- Addition reaction:- 1- Addition of halogen:-

Benzene in presence of UV light adds on 3 molecules of chlorine gives benzene hexachloride.



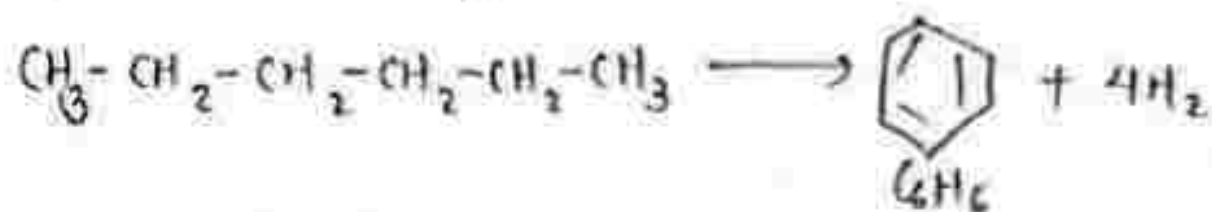
## Benzene

Benzene is the first and most important aromatic compound, it was discovered by Faraday in 1825.

Prep:-

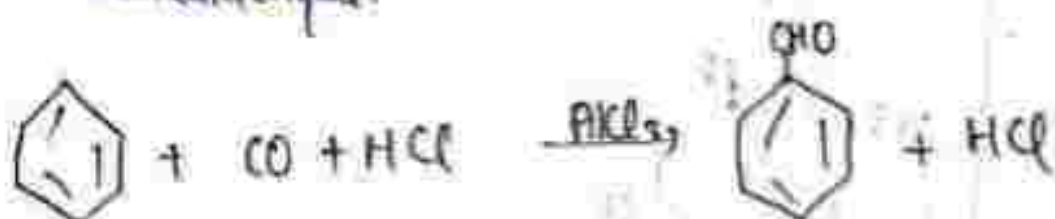
1. from coal Tar:- Coal tar is the main source of benzene. We can prepare benzene by boiling the coal tar, then by fractional distillation in presence of  $H_2SO_4$ .

2. From petroleum :- Different hydrocarbons present in petroleum on aromatization in presence of  $\text{Cr}_2\text{O}_3$  gives benzene.

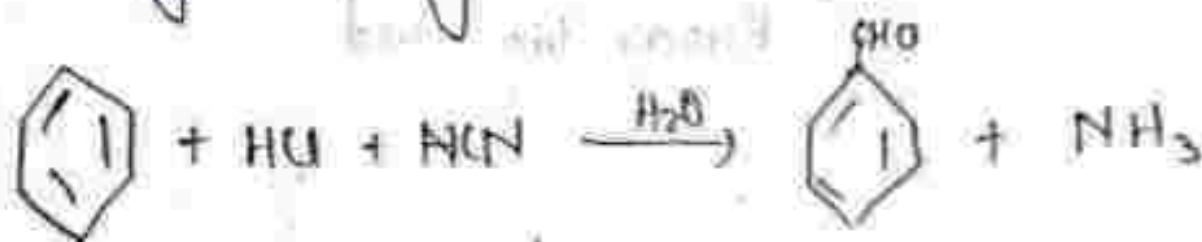


### Chemical Property:-

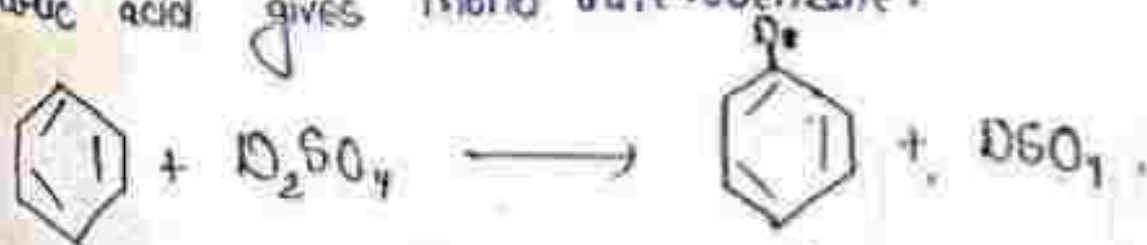
1- Gatterman coash react<sup>n</sup> :- Benzene on treatment with CO and HCl in presence of  $\text{AlCl}_3$  gives benzaldehyde.



2- Gatterman Aldehyde synthesis :- Benzene react with HCl & HCN in presence of water gives benzaldehyde.



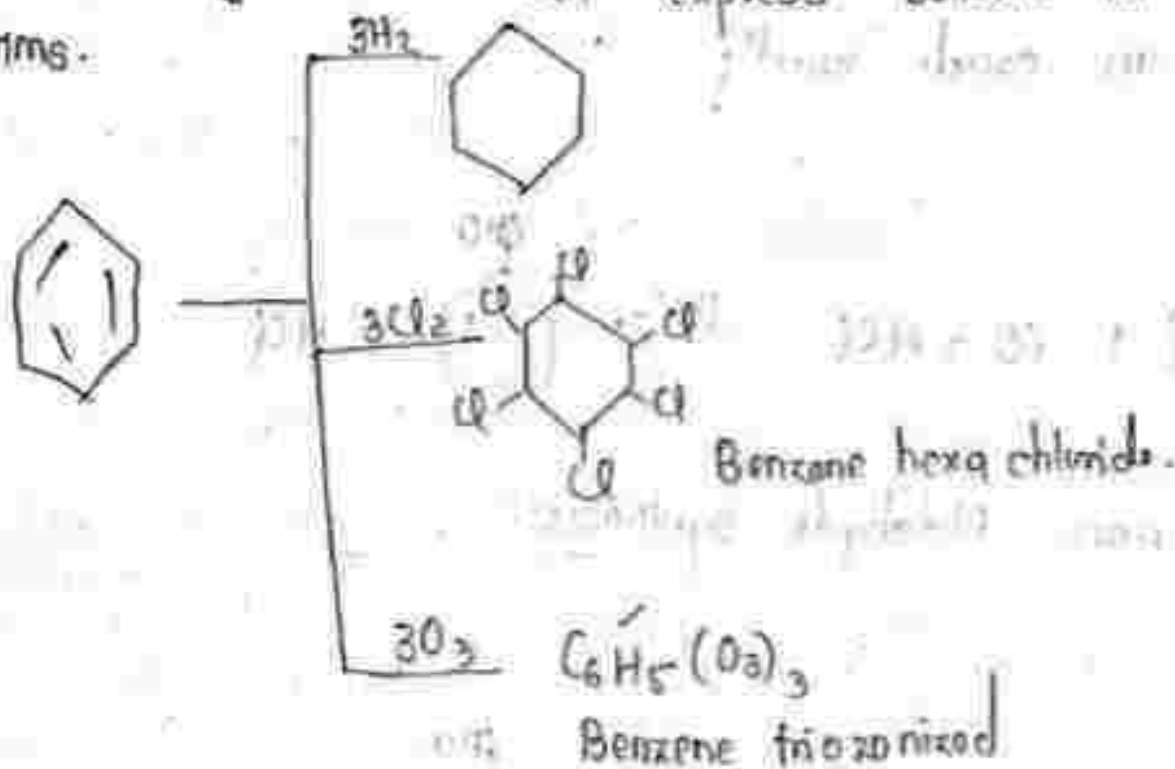
3- React<sup>n</sup> with deuterio Sulphuric acid :- Benzene treated with deuterio sulphuric acid gives mono deuterobenzene.



Use of benzene - Benzene is used as a solvent for threads, fats & resin.

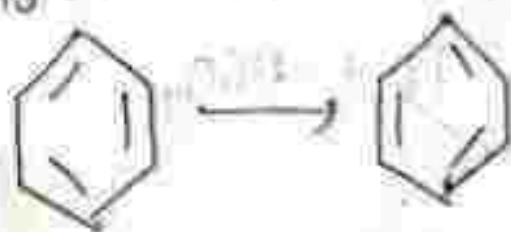
2. In prep<sup>n</sup> of inter insecticide as BHC.
3. Used in prep<sup>n</sup> of drycleaning.
4. It is used as a water motor fuel.

Structure of Benzene: The mol. formula is  $C_6H_6$ . We can express benzene in following forms.



We can express benzene in the form of Kekule structure & Dewar structure.

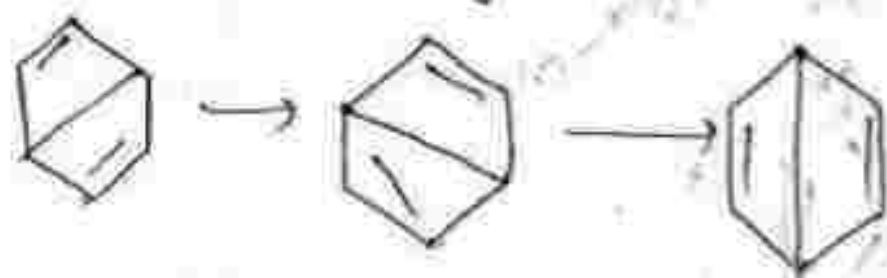
Kekule Structure: According to Kekule, In benzene there is simple single rotation of  $\pi e^-$  occur, so the structure is :-





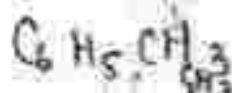
## Dewar structure:-

Dewar structure is the structure of benzene into two equal halves. <sup>Partition</sup>



## Toluene

Formula:-



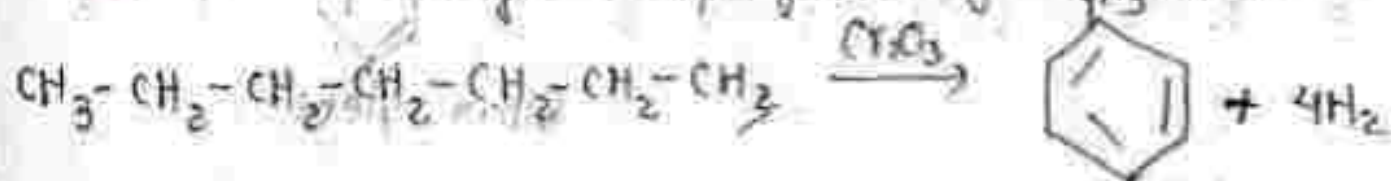
Structure:-



## Methods of prep<sup>n</sup>:-

1- From coal Tar:- We can prepare toluene by the distillation of coal tar at  $108-110^\circ C$ .

2- From petroleum:- n-heptane is obtained from petroleum or catalytic dehydrogenation gives toluene.

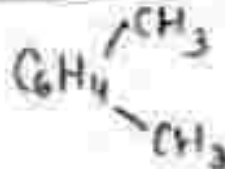
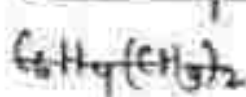


## Physical property:-

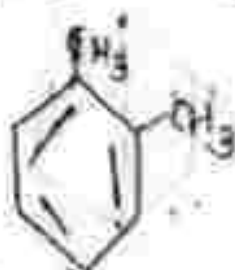
1. Toluene is a colourless liquid having B.P  $110^\circ C$ .
2. It is insoluble in water but soluble in organic solvent.
3. It has an odour resembling to benzene.

# Xylene

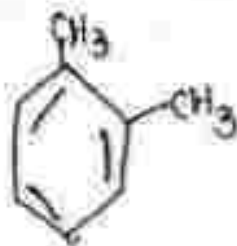
Formula:-



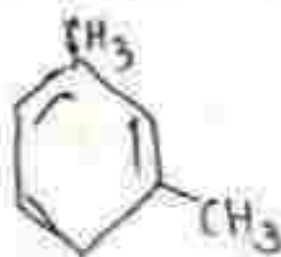
Structure:-



Xylene is classified into three types:-



Ortho Xylene



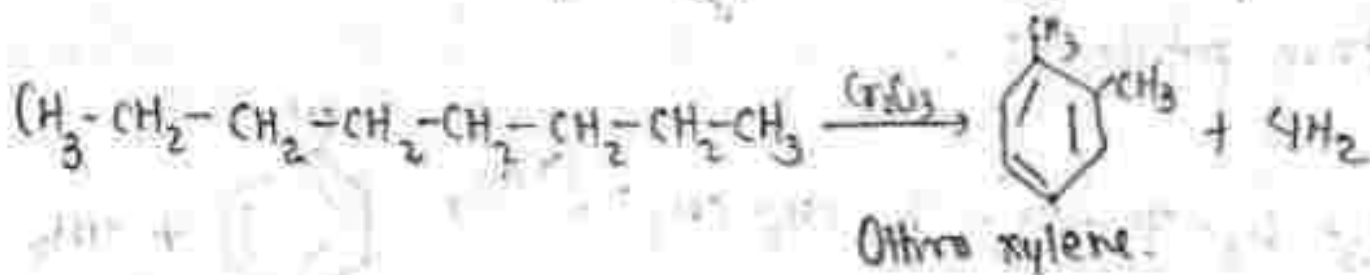
Meta Xylene



Para Xylene

Prep<sup>n</sup> of Xylene:-

1- n-octane obtained from petroleum, give Xylene.



Uses :- 1) Their amino derivatives are used in the prep<sup>n</sup> of dyes.

2) Xylene is used in the prep<sup>n</sup> of phthalic anhydride.

3) Xylene is also used in the medical to dressing the wound.

Physical properties:- 1- Xylenes are colourless liquids.

2- They are immiscible with water & miscible with organic solvents.

3- The B.P of o, m & p xylene are  $144^\circ C$ ,  $139^\circ C$  &  $138^\circ C$  respectively.

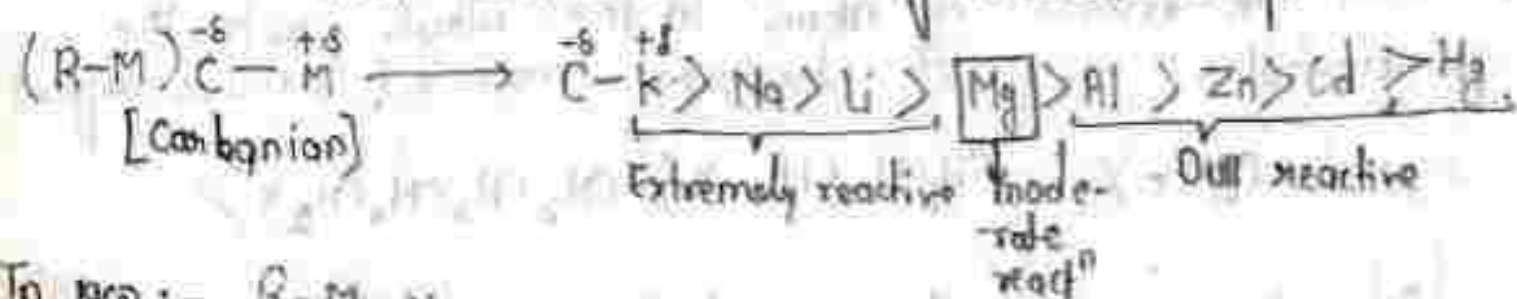
ORGANOMETALLIC COMPOUNDS

Carbon + Metal  $\longrightarrow$  Organometallic compound.

Organic compound in which a metal is bonded with carbon is called organometallics or organometallic compounds.

or

Compound generated through the establishment of bond b/w a metal and carbon atom is known as organometallic compound.



In AOC :-  $R-Mg-X$

Ex:- i-  $CH_3-Li \longrightarrow$  Methyl lithium

ii-  $(CH_3CH_2)_2Mg \longrightarrow$  Diethyl magnesium

iii-  $CH_3-CH_2-Li \longrightarrow$  (Ethyl lithium)

A series of compound in which Mg was linked with carbon of alkyl group & any halogen (Cl, Br, I not F) on another side were prepared by Gignard in yr 1900. The synthetic applications of Gignard reagent awarded him the prestigious Nobel prize in 1912.

### Important points about Organometallics:-

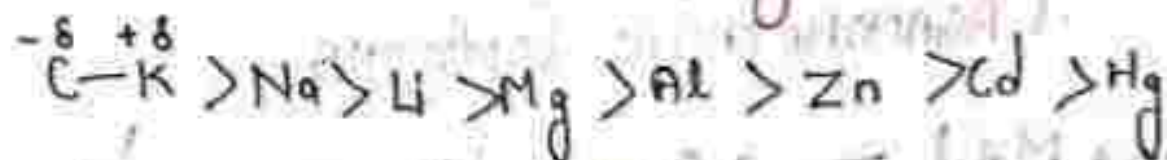
In organometallic, carbon behaves as more electronegative than H & metal. Such compounds formed may be fully or partially ionic or they may be covalent in nature.

The ionic character of metal in organometallic has the following



order:-

Rag 12345

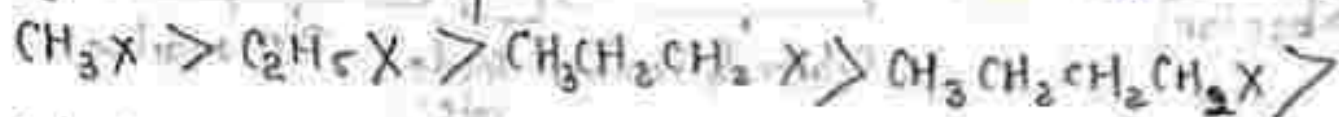


3- Ease of formation of organometallic has the following order:-

Iodide > Bromide > Chloride not with fluoride.

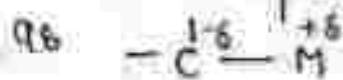
No organometallic involving fluoride.

4- With the increase of atoms in the alkyl group, the organometallic compound becomes more & more difficult.



Mechanism of action of organometallics:-

⇒ The development of charge on organometallics take place as



⇒ If the compound is fully ionic, it will dissociate into the +ve metal ion & -vely charged alkyl group.

⇒ The react<sup>n</sup> will be very fast in which two constituent group will take part separately.

⇒ If the compound is partially ionic, carbon of alkyl group becoming -ve will behave like a carbanion.

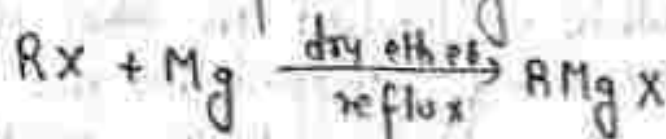
⇒ There will be nucleophilic substitution & nucleophilic addition react<sup>n</sup> at this carbon.

Prop<sup>n</sup> of Grignard Reagent:-

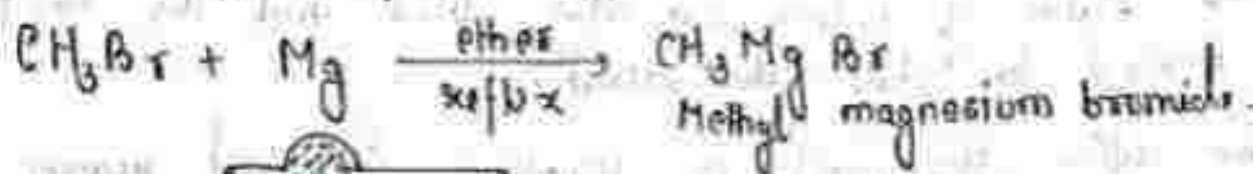
Alkyl magnesium halides,  $R-Mg-X$  are the most important organometallic compounds and in general are known as Grignard reagents as they were discovered by a French chemist, Victor Grignard. They are highly reactive organometallic compounds & are of great synthetic value.

### Prep<sup>n</sup> of Grignard Reagent:

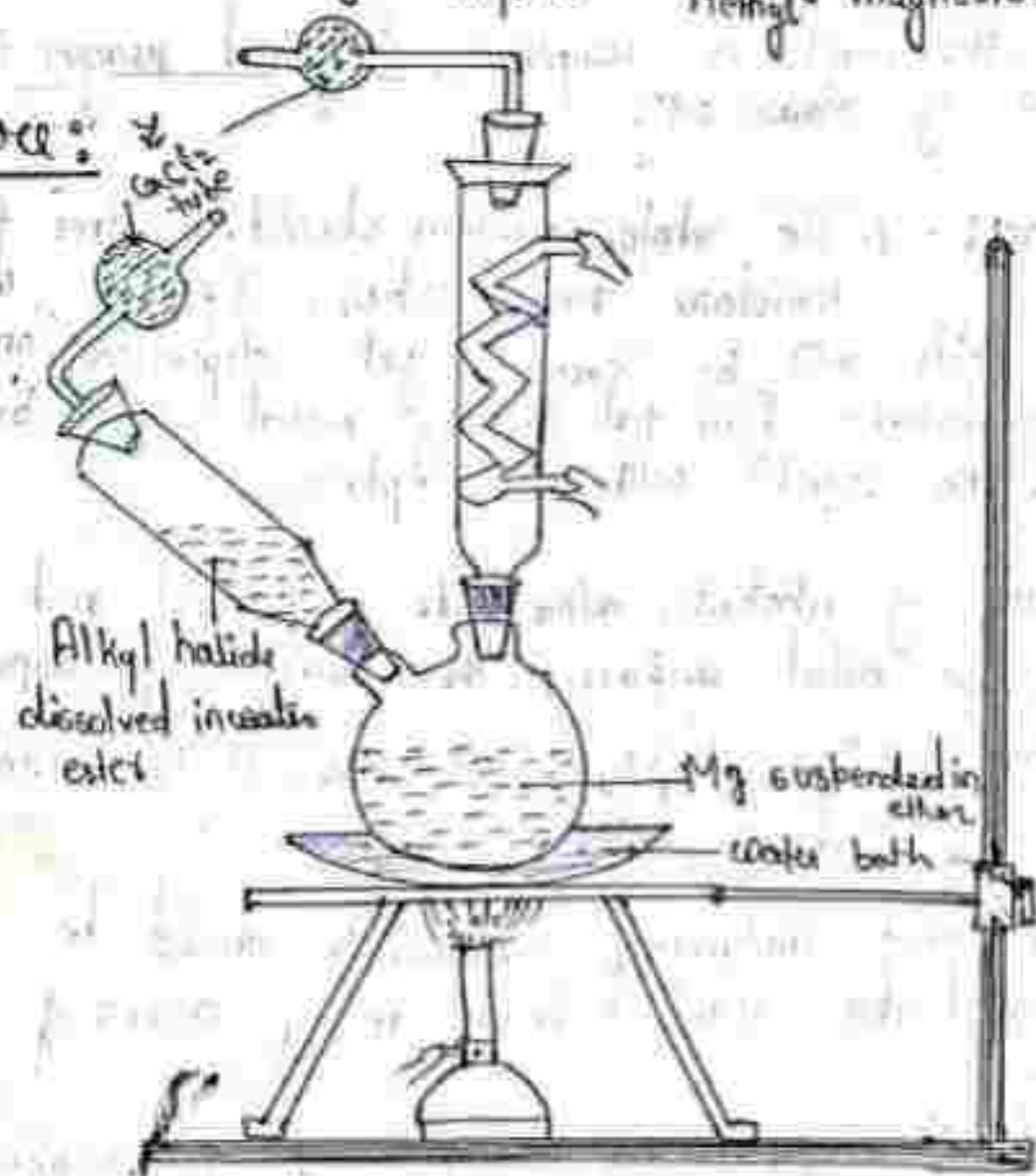
Grignard reagent is prepared in the laboratory by refluxing dry  $Mg$  turning with an alkyl or aryl halide in presence of a solvent such as dry ether.



ex:-



### Procedure:





- ⇒ The apparatus consist of a round bottom flask, fitted with a reflux condenser and a dropping funnel.
- ⇒ Clean <sup>clean</sup> magnesium turnings and dry ether are taken in 1:5 to 1:10 ratio by wt in a two necked round bottom flask.
- ⇒ The flask is fitted with a reflux condenser containing  $\text{CaH}_2$  tube at its upper end in one neck and a dropping funnel containing  $\text{CaH}_2$  tube at its upper end in the other neck.
- ⇒ Now, one mole of alkyl halide, dissolved in ether is taken in the dropping funnel and its slowly dropped into the flask.
- ⇒ Some flakes of iodine are also added and the react<sup>n</sup> mixture is heated to start the react<sup>n</sup>.
- ⇒ ~~The~~ When the react<sup>n</sup> is complete, Grignard reagent is obtained in the form of clear sol<sup>n</sup>.

Precautions: - 1- The whole system should be free from moisture and alcohol. If not, with moisture metal oxide will be formed, get deposited on the surface of the metal. Due to coating metal will become inactive & no react<sup>n</sup> will take place.

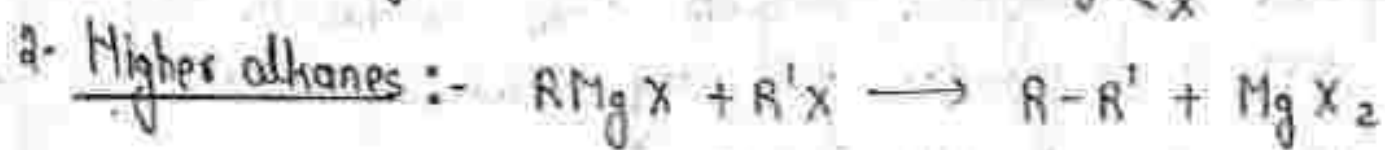
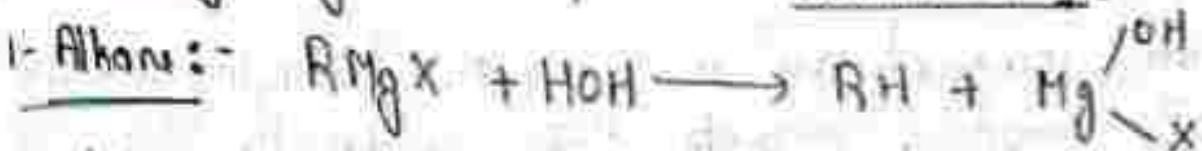
- \* In presence of alcohol, alkoxide is formed and due to its coating on metal surface, the react<sup>n</sup> again stops.
- 2- Since the react<sup>n</sup> is highly exothermic, it is cooled dipping into dry ice (solid  $\text{CO}_2$ ).
- 3- The nitro group containing compounds should be totally prohibited as the react<sup>n</sup> leads to a series of compounds formation.
- 4- The organometallics are highly reactive compounds, therefore their prep<sup>n</sup> is advised.



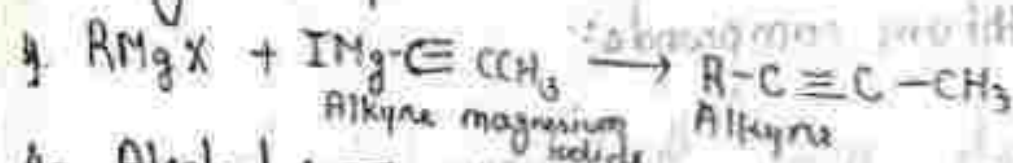
## Synthetic application of Grignard's reagents:-

From Grignard reagent, alkanes, alkenes, alkynes, alcohol, amines, aldehydes, ketones, carboxylic acid, nitriles, cyanides, thioalcohols, esters, other organometallic etc can be synthesised.

### Class of Organic compounds:- formation of:-



### 3- Higher alkynes:-



### 4- Alcohol:-

i- Primary:- By these method,  $CH_3OH$  is not possible

