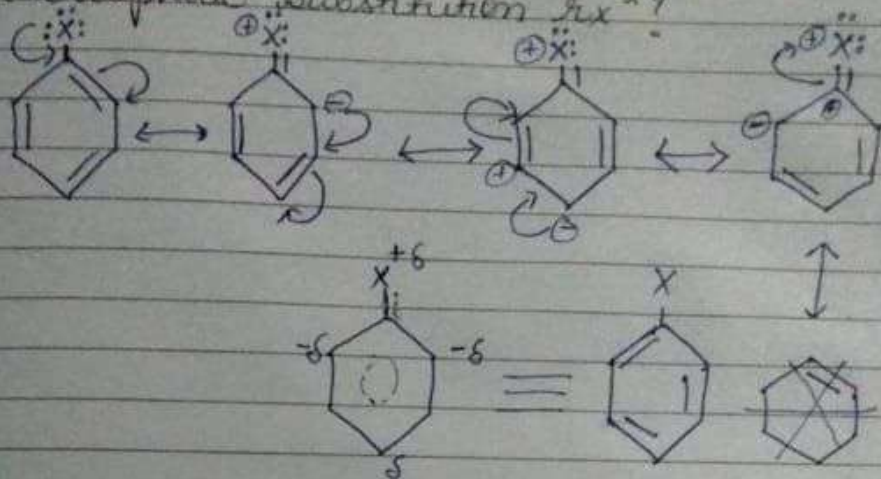


Ques- Why haloarenes are less reactive towards nucleophilic substitution  $S_N^2$ ?

Soln-



- i) Due to resonance the Carbon halogen bond of haloarene have partially double bond character that's why the cleavage of/breaking of C-X is difficult to break as compared to haloalkane.
- ii) In case of haloarene the carbon of C-X bond have  $sp^2$  hybridization due to which it has more electronegativity as compared to the carbon of haloalkane (having  $sp^3$  hybridization) hence, the e<sup>-</sup> pair of C-X bond is tightly held by  $sp^2$  hybridized carbon and bond length gets shorter therefore it is difficult to break the C-X bond in case of haloarene.
- iii) Instability of Phenyl Cation

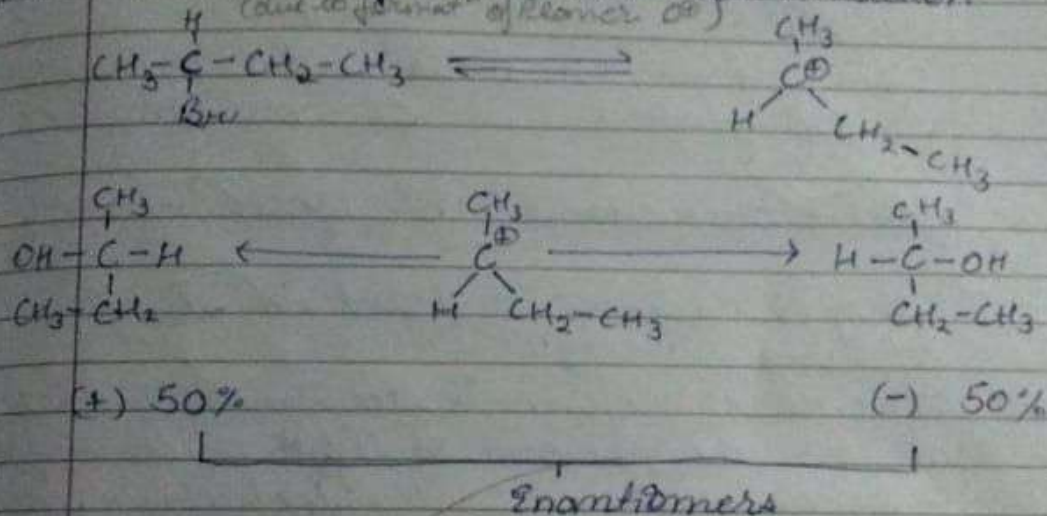
NOTE- Allylic & benzylic halide shows high reactivity towards  $S_N^1$   $S_N^2$  due to the resonance stabilized carbocation



**Racemic Mixture** - An equimolar mixture of enantiomers (dextro & laevo forms) is called racemic mixture.

Racemic mixture is optically inactive and it is represented as  $dl$  or  $\pm$

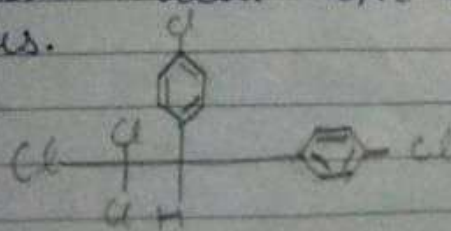
**NOTE** -  $SN^2$  rxn proceeds with racemisation (due to formation of Planar  $sp^2$ )



**NOTE 2** -  $SN^2$  rxn proceeds with inversion in configuration

\* **Polyhalogen Compounds** :-

- DDT - p,p-Dichloro-diphenyl-trichloro ethane  
**uses of DDT** :- DDT is a powerful insecticide and it is very effective against Anopheles mosquito causes malaria and lice which carry typhus.

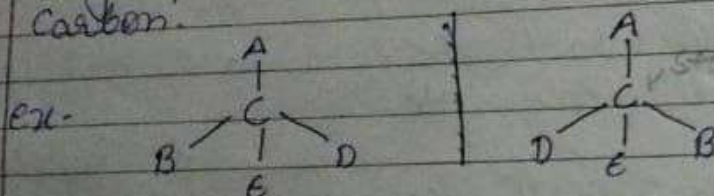




The D(+) and L(-) forms of a compound called optical isomers and this phenomenon is known as optical isomerism.

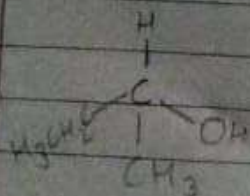
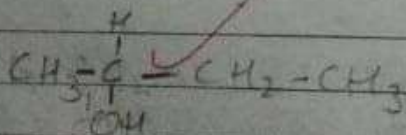
### \* Molecular Symmetry & Chirality :-

- Chiral or Asymmetric Carbon :- The carbon which is bonded to four different atoms or groups is called a chiral / Asymmetric Carbon.

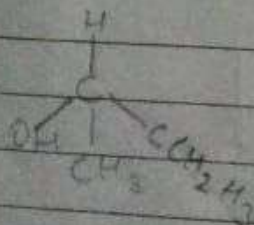


Enantiomers :- The optical isomers which are non superimposable mirror images of each other are called Enantiomers. & this phenomenon is known as Enantiomerism.

Ex- Butane - 2-ol



(+)



(-)



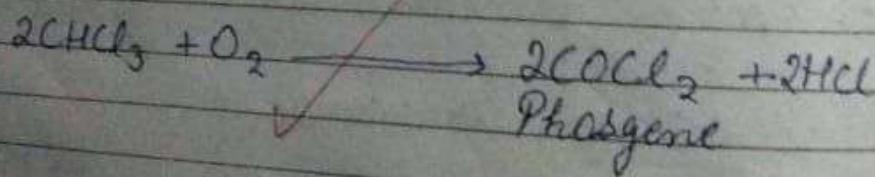
2. Freons: The chlorofluorocarbon compounds of methane and ethane are collectively known as Freons. Freon<sub>12</sub> ( $\text{CCl}_2\text{F}_2$ ) is one of the most common freons in industrial use. It can be prepared from tetrachloromethane ( $\text{CCl}_4$ ) by Swarts reaction.

Uses of Freons: It is used as refrigerant in refrigerators and air conditioners.

3. Trichloromethane (chloroform):  $[\text{CHCl}_3]$

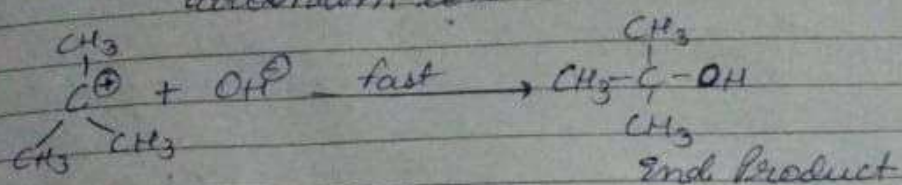
Why chloroform is stored in dark coloured bottles?

- ⇒ Because chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas, carbonyl chloride, also known as phosgene.





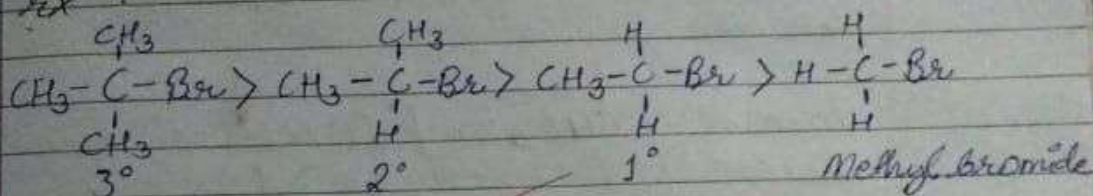
Step 2: It involves attack of nucleophile on carbocation ion.



$$\text{Rate} \propto [\text{C}(\text{CH}_3)_3 \text{Br}]$$

$$\text{Rate} = k [\text{C}(\text{CH}_3)_3 \text{Br}]$$

# Reactivity order of Alkyl halide towards  $\text{S}_\text{N}^1$  rx<sup>n</sup>:

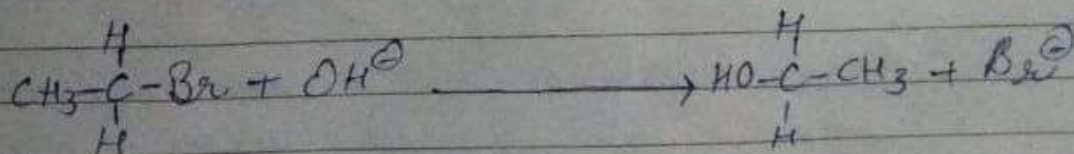


2-  $\text{S}_\text{N}^2$  rx<sup>n</sup> (Substituted bimolecular rx<sup>n</sup>):

In  $\text{S}_\text{N}^2$  rx<sup>n</sup> nucleophile approaches the substrate molecule from the back side to the leaving group.

In this mechanism old bond breaking and new bond formation takes place simultaneously. This rx<sup>n</sup> involves the formation of transition state.

Example: Rx<sup>n</sup> b/w ethyl bromide & hydroxide ion.





vibrates in only one plane.

\* Optical activity - The property of a substance by which it rotates the plane of polarised light is called optical activity.

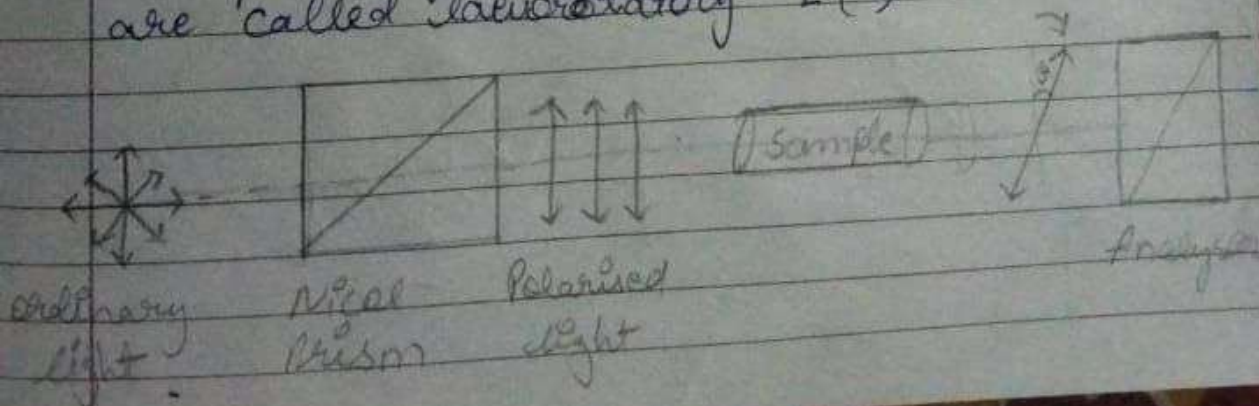
\* Optically Active compound:- These substances which rotate the plane of polarised light are called optically active compound.

Example:- Lactic Acid, tartaric Acid, glucose, fructose etc

\* Optically Inactive compound:- These substances which do not rotate the plane of polarised light are called optically inactive compound.

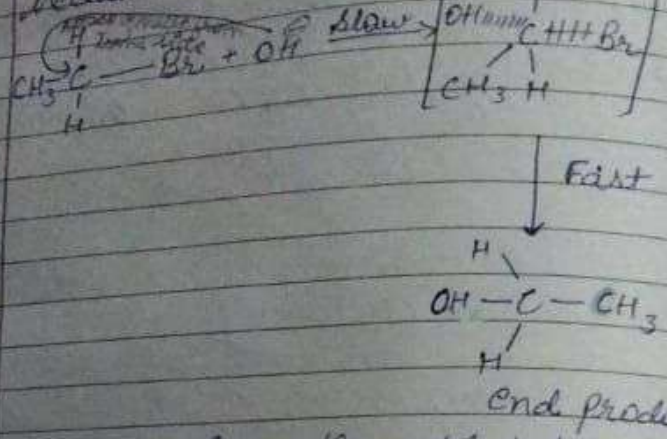
\* Dextrorotatory:- These substances which rotate the plane of polarised light clockwise are called dextrorotatory  $D(+)$ .

\* Laevorotatory:- The compounds which rotate the plane of polarised light anti clockwise are called laevorotatory  $L(-)$ .





Mechanism:-



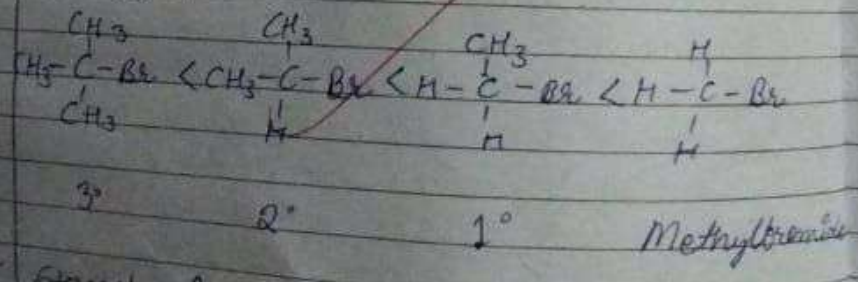
Inversion in configuration takes place called Walden inversion.

$$\text{Rate} \propto [\text{CH}_3\text{CH}_2\text{Br}] [\text{OH}^-]$$

$$\text{Rate} = k [\text{CH}_3\text{CH}_2\text{Br}] [\text{OH}^-]$$

$$\text{order of } k_x = 2$$

\* Reactivity order of Alkyl halide towards  $\text{SN}^2$  rxn:-



# Stereochemical aspects of nucleophilic substitution reactions:-

\* Plane Polarised Light:- when a beam of ordinary light passed through a nicol prism it becomes plane polarised which

vibrates

\* Optical which is called

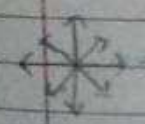
\* Optical which light

Example

\* Optical which light

\* Deuterium isotopes are

\* Laves the are

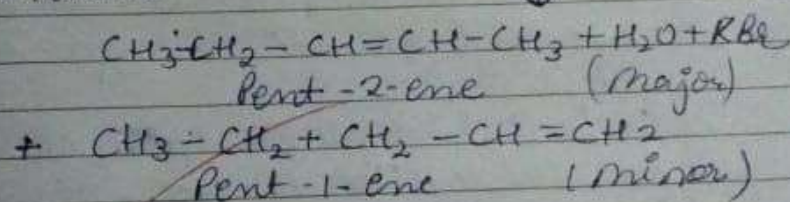
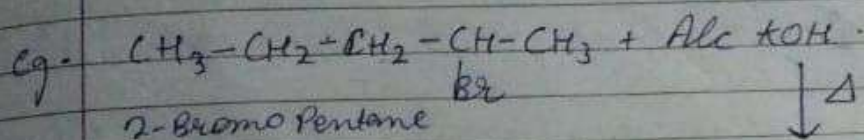
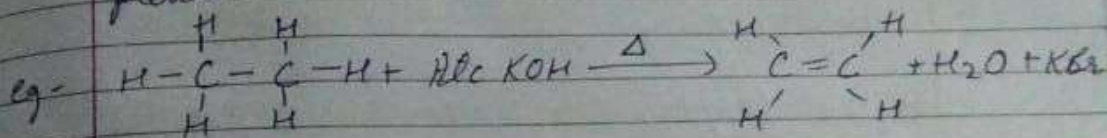


Ordinary light



### (iii) Elimination Rx<sup>n</sup>:-

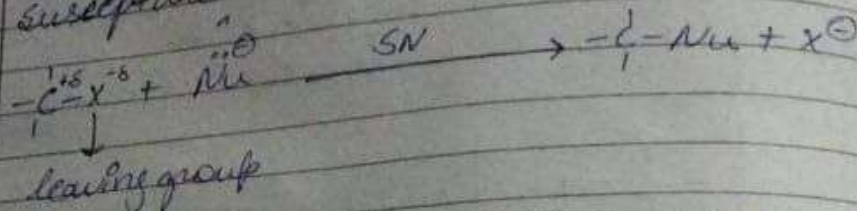
Dehydrohalogenation react<sup>n</sup>:- In this rx<sup>n</sup> halogenoalkane containing Beta ( $\beta$ ) hydrogen is treated with alc KOH. Removal of  $\beta$  hydrogen & formation of alkene take place.





## # Nucleophilic Substitution $S_N$ :-

In alkyl halides the carbon of C-X bond remains electropositive & thus becomes susceptible for nucleophilic attack.



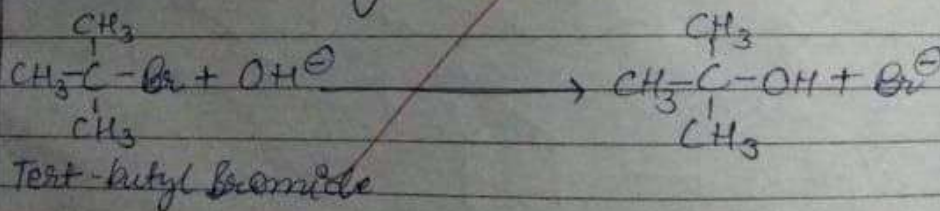
Depending upon the mechanism of the  $S_N$  nucleophilic substitution  $S_N$  are of two types

1.  $S_N^1$   $S_N$  (Nucleophilic Substitution unimolecular  $S_N$ )

In  $S_N^1$  mechanism old bond breaking and new bond formation takes place in two steps.

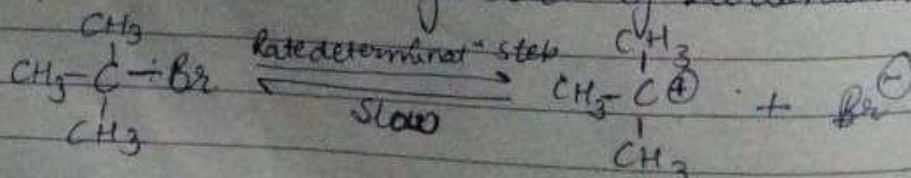
$S_N^1$   $S_N$  is carried out in polar protic solvents (can donate  $H^+$  ion - water, alcohols, amines)

Example - The  $S_N$  b/w tertiary butyl bromide & hydroxide ion.



Mechanism:-

Step I - It involves generation of Carbonium ion.



$3^\circ$  Carbonium ion

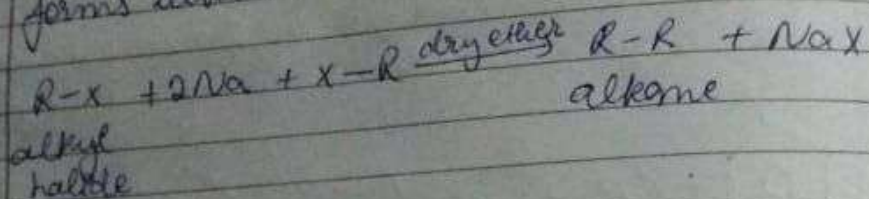


i)  $Rx^n$  with Sodium (Wurtz  $2x^n$ )

$Rx^+$  with sodium

In this  $Rx^+$  alkyl halide is treated with sodium in the presence of dry ether and forms alkane.

Another  $R-R + NaX$

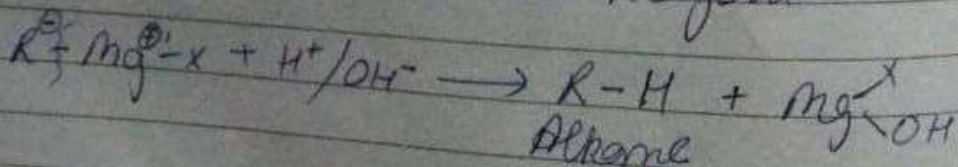
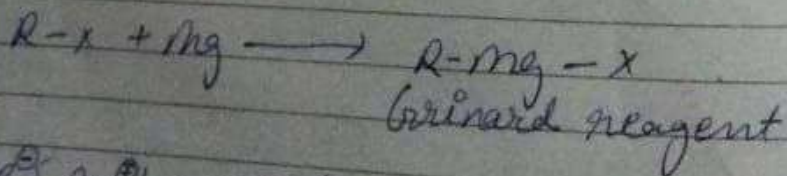


→ This rx<sup>n</sup> is useful for the preparat<sup>n</sup> of symmetrical alkane.

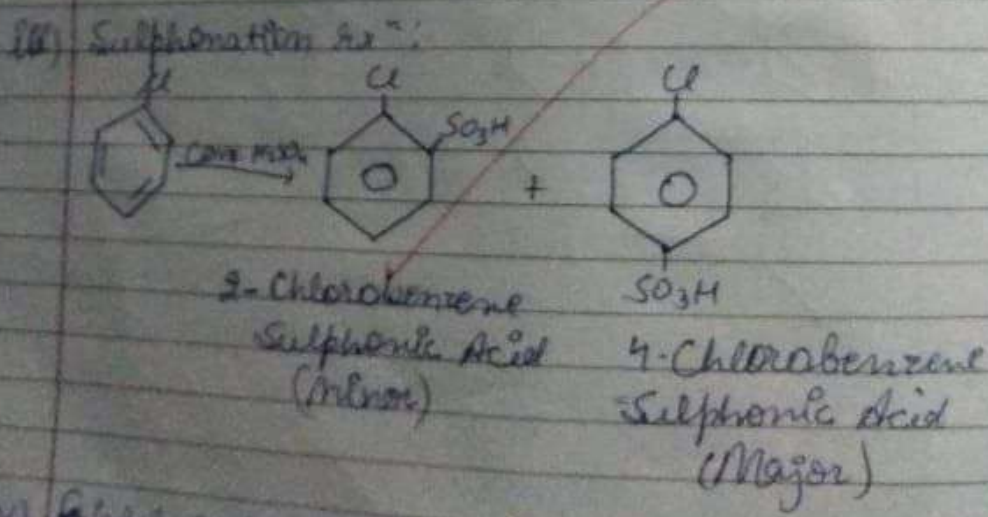
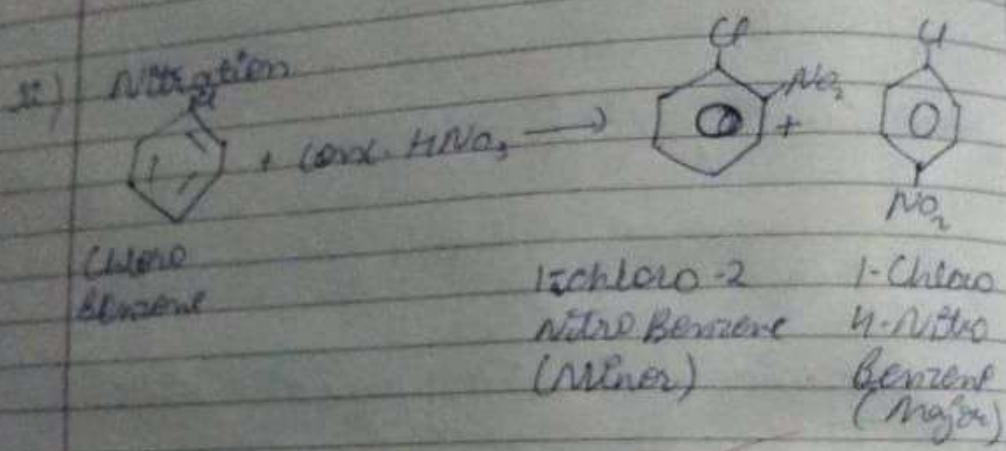
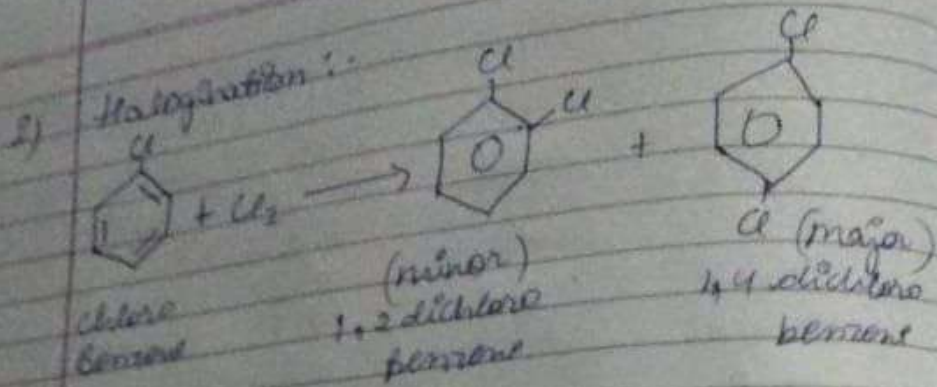
- Tertiary halide does not give this rxn.

ii)  $Rx^u$  with Magnesium

Alkyl halide on treating with magnesium forms Grignard reagent i.e. alkyl magnesium halide. This is highly reactive substance and reacts with any source of proton to give alkane.



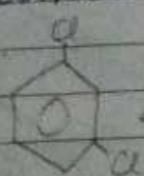




iv) Friedel Craft Alkylation :-



lactic battle is compared to ortho and meta isomer.



249 K

meta-di  
chloro  
benzene



256 K

ortho-di  
chloro  
benzene



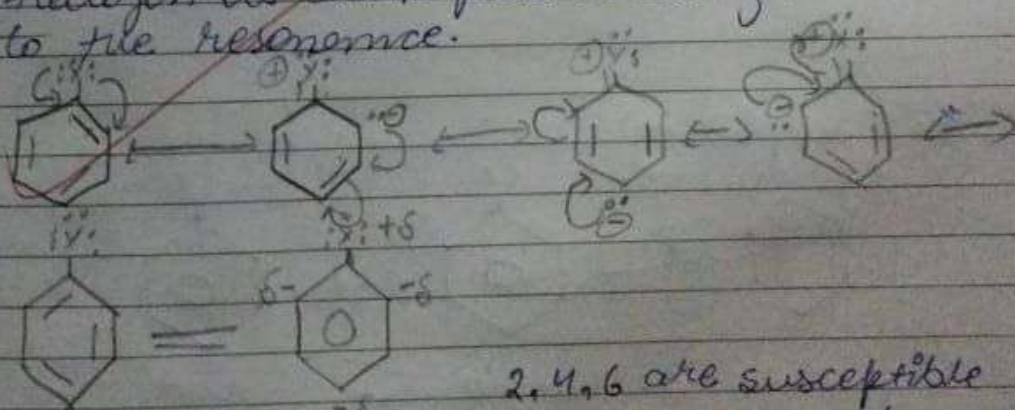
323 K

Para dichloro benzene

## # Electrophilic Substitution reaction of Halobenzenes

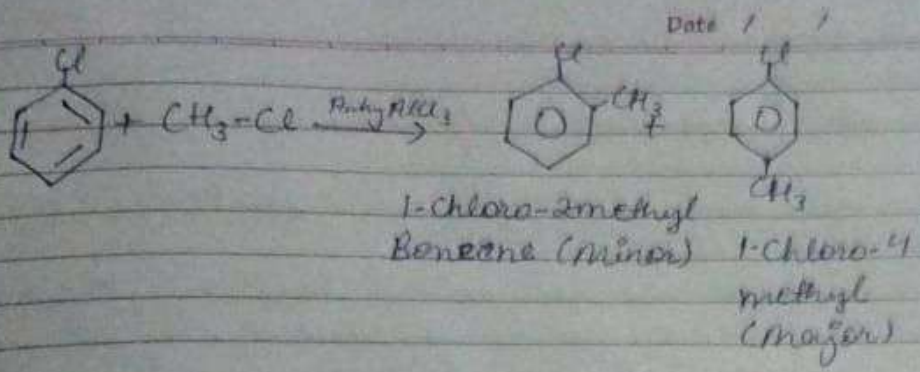
Halobenzenes undergoes the usual electrophilic substitution rx<sup>n</sup> of the benzene and ~~finds a graft rx<sup>n</sup>~~.

Halogen is ortho para directing in rx<sup>n</sup> due to the resonance.

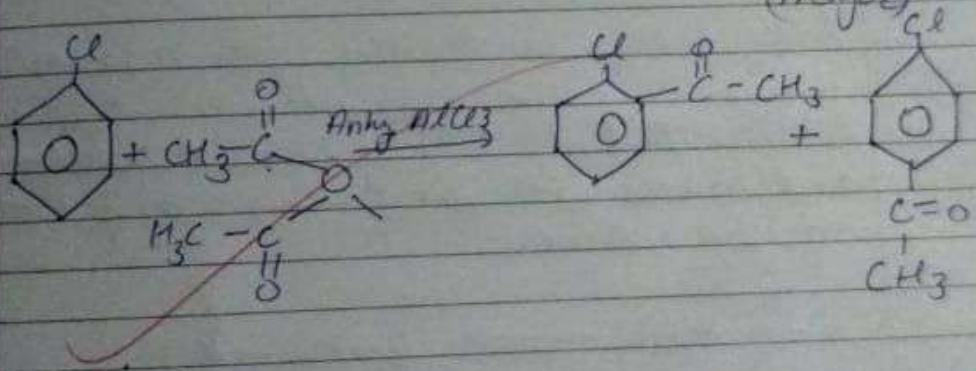
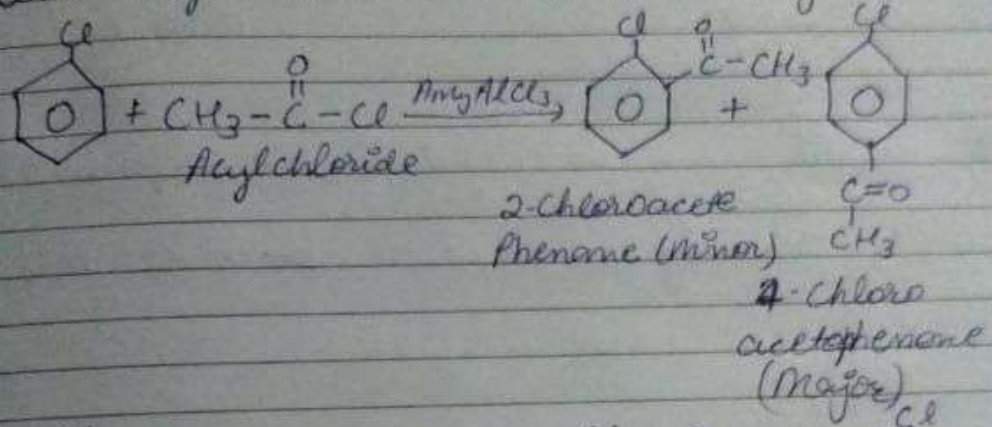


2, 4, 6 are susceptible site for the attack of electrophile.





It can be carried out by treating halobenzenes with acyl chloride or acetic anhydride

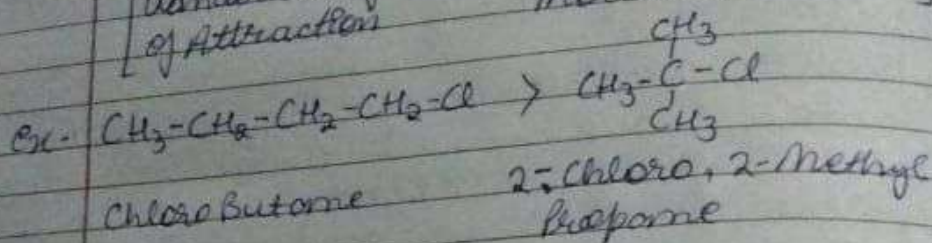




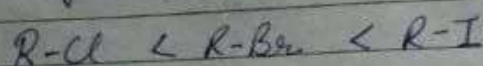
→ For isomeric alkyl. halides the boiling point is decrease with increase in branch.

Boiling point  $\propto$  van der Waals force of attraction

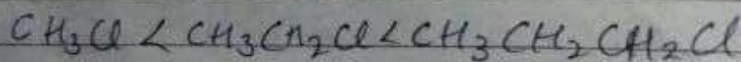
Intermolecular force  $\propto$  molecular size or molecular mass



For the same alkyl group the order of B.P. is followed as:-



→ For the same halogen the B.P is decreased with decrease in the size of alkyl group.

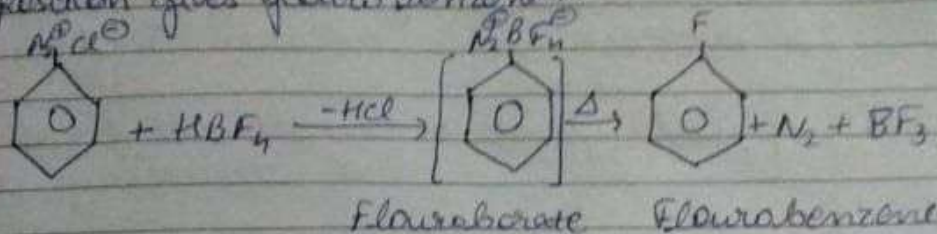


Ques. Why the Para isomer of dihalo-alkane have high melting point as compare to ortho and meta isomer.

Ans. - This is because the symmetry of para-isomers molecule that fits in the crystal.



acid and form fluoborate which on decomposition gives fluorobenzene:-



## # Physical properties of haloalkane & haloarenes:-

1. Solubility - Haloalkanes are very less soluble in water, because energy is required to overcome the interaction b/w haloalkane molecule & break the hydrogen bond b/w water molecule. As less energy is released when new interaction set up b/w the haloalkane and water molecule as these are not strong as the hydrogen bond.

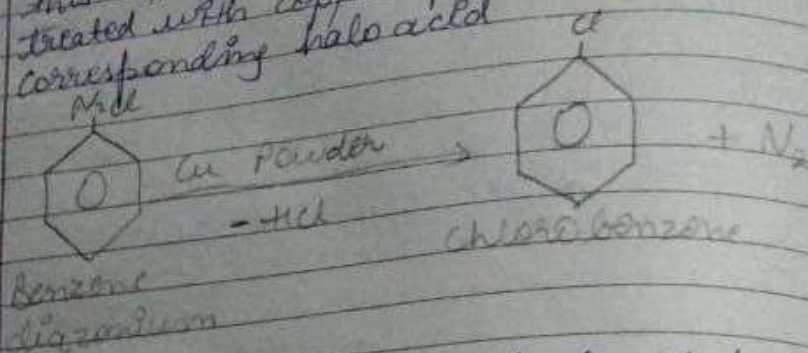
However haloalkanes can be dissolved in organic solvents.

Haloarenes - Haloarenes are also less soluble in water due to the presence of water repellent Benzene ring.

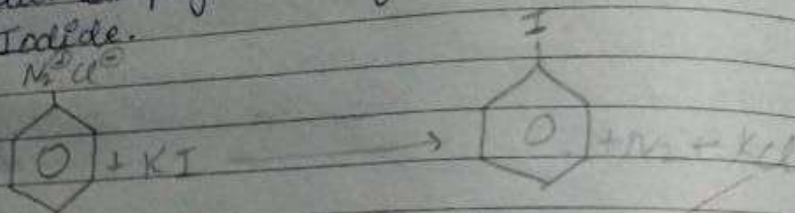
2. Melting and Boiling Point :- M.P & B.P of Haloalkanes are greater than those Hydrocarbons due to the presence of dipole-dipole interaction and vander waal's force of attraction.



c) Crattermann React<sup>n</sup>  
 This is the modified form of Rea<sup>n</sup> -  
 this is benzene diazonium salt  
 treated with copper powder and forms  
 corresponding halo acid

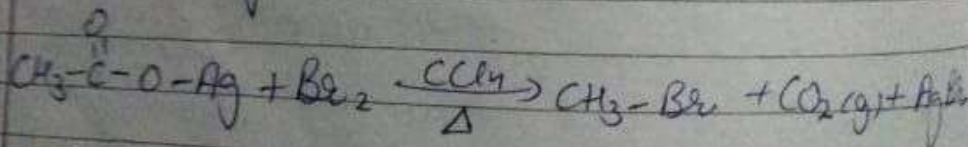


→ Iodo Benzene can be prepared by diazonium salt simply, shaking it with potassium Iodide.



### \* Preparation of Haloalkane :-

Siodine Hund's diecker reaction :- when silver salt of Carboxylic acid is treated with bromine in presence of CCl<sub>4</sub> then Bromo alkane is form.



→ Bolz Schiemann Reaction :- In this is benzene diazonium salt is treated with Fluoro - Boric



2. On the basis of Nature of Carbon in C-X bond i.e. according to the hybridisation of C atom to which halogen is bonded

a) Compound containing  $sp^3$  C-X bond

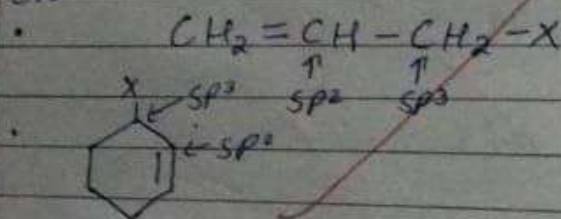
ex.  $\begin{array}{c} H \\ | \\ R-C-X \\ | \\ H \end{array}$   $1^\circ$  haloalkane or  $1^\circ$  alkyl halide

$\begin{array}{c} R \\ | \\ R-C-X \\ | \\ H \end{array}$   $2^\circ$  haloalkane

$\begin{array}{c} R \\ | \\ R-C-X \\ | \\ R \end{array}$   $3^\circ$  haloalkane

- b) Allylic Halide - In these halides the halogen atom is attached to  $sp^3$  C-atom which is also attached to  $sp^2$  C-atom.

Ex-



- (iii) Benzylic Halide - In these halides the halogen atom is attached to  $sp^3$  hybridised C-atom next to aromatic ring (Benzene ring).

Ex-  $H-C-X$

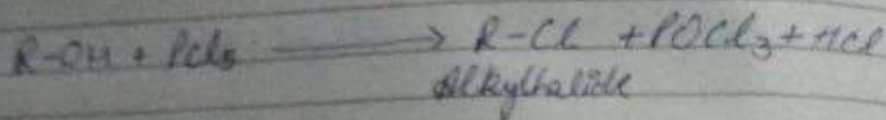
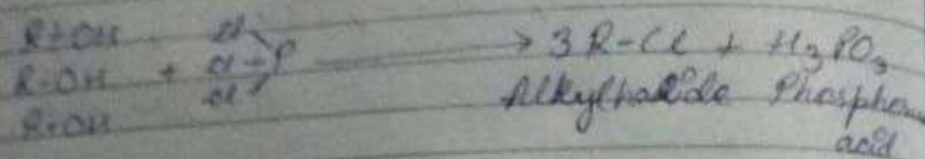


$1^\circ$  Benzylic halide

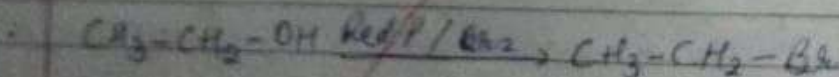


Here, Anhydrous  $ZnCl_2$  helps to break C-O bond because Anhydrous  $ZnCl_2$  is a Lewis acid & it forms coordinate bond with Oxygen.

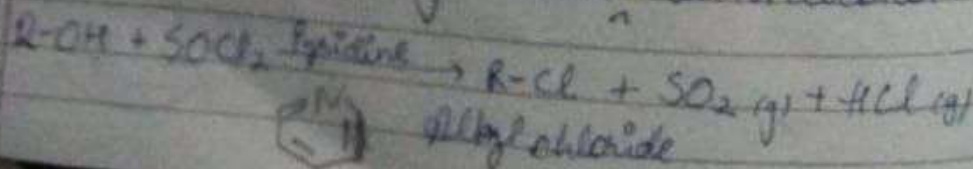
b) By the react<sup>n</sup> with Phosphorus halide :-



Bromalkanes & Iodoalkanes are prepared by react<sup>n</sup> of alcohols with red  $PBr_3$  &  $PI_3$  which are produced by the react<sup>n</sup> of  $Br_2$  or  $I_2$  with red Phosphorus during the react<sup>n</sup>.



c) By the react<sup>n</sup> of thionyl <sup>chloride</sup> with alcohol :-



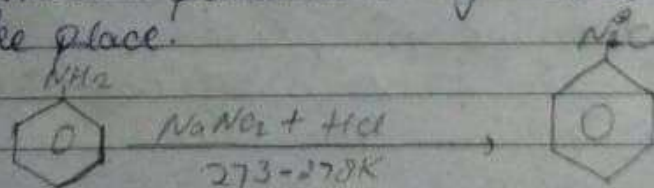


NOTE- Fluoro Benzene cannot directly prepared by this method due to high reactivity of Fluorine.

- React<sup>n</sup> with Iodine is reversible in nature and require the presence of agent  $\text{HNO}_3$ ,  $\text{HIO}$  to oxidised the  $\text{HI}$  to  $\text{I}_2$  during Iodinat<sup>n</sup>.

b) Sandmeyer's Rxn :-

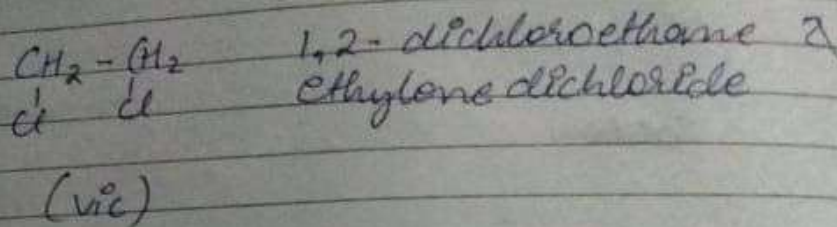
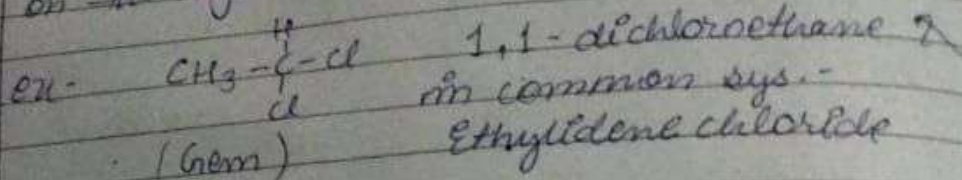
when a freshly prepared diazonium salt is treated with cuprous chloride or cuprous bromide replacement of diazonium group take place.



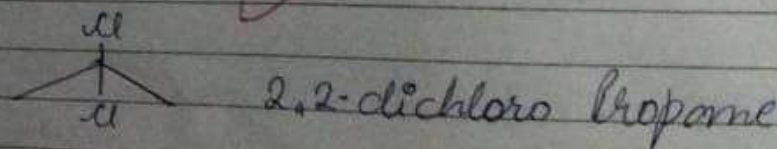
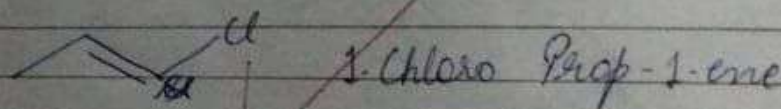
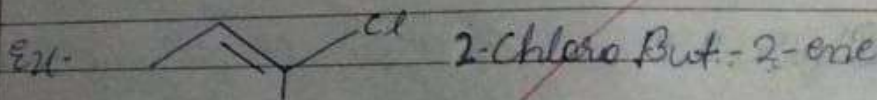


both the halogen atoms present on the same C-atom. (These are also called alkylidene)

- (ii) Vicinal or *vic* dihalides (Alkylene):- In these halides both the halogen atoms are present on the adjacent C-atoms.



### # Nomenclature



# Nature of C-x Bond :- Due to the higher electronegativity of halogen atom C-x bond is polar in nature

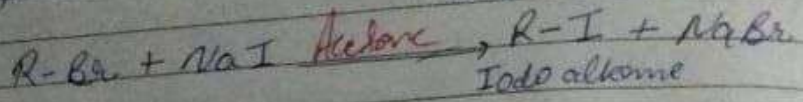
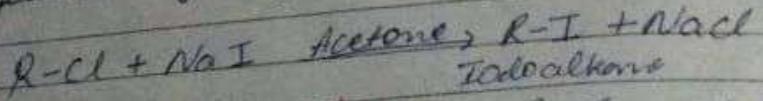


In the molecule.

c) Preparation by halogen exchange :-

i) Finkelstein Rxn :-

In this rxn alkylhalides (chlorides or bromides) on heating with sodium Iodide [NaI] in the presence of dry acetone gives Iodo alkane



NOTE-

ii) Swarts Rxn :-

In this rxn alkylhalide (chloride or bromide) are treated with metallic fluoride like  $HgF$ ,  $Hg_2F_2$ ,  $COF_2$  or  $SbF_3$  & forms fluoro alkane.



b)

(Halobenzenes)

a) from hydrocarbon by electrophilic substitution rxn :-

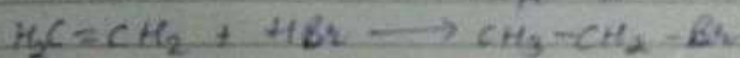
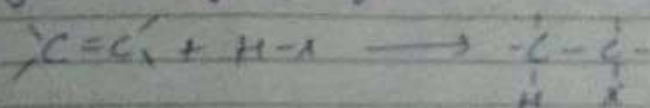
Chloride and Bromide can easily prepared by an electrophilic substitution of arenes in the presence of Lewis Acid such as anhydrous  $AlCl_3$ ,  $ZnCl_2$ ,  $FeCl_3$



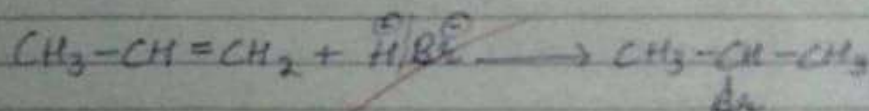
This method is the best method for the preparation of alkyl chloride / alkyl halide because all the other products are formed in the gaseous state.

a) from alkenes:-

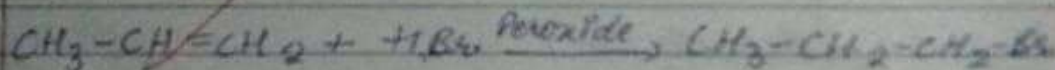
i) by addition of hydrogen halide:-



In case of unsymmetrical alkene addition of hydrogen halide over alkene takes place acc. to Markovnikov's rule

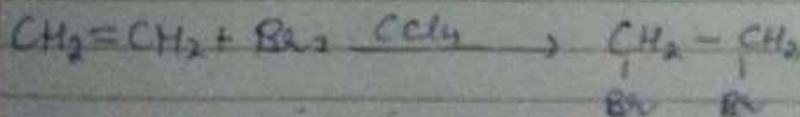


In case of peroxide addition of HBr over unsymmetrical alkene takes place acc. to anti Markovnikov's rule



ii) Addition of halogen to alkene:-

On adding  $\text{Br}_2$  /  $\text{Cl}_2$  to alkene, the addition occurs at the double bond forming vic dihalide



This rxn is used for the detection of double bond



## Chapter-

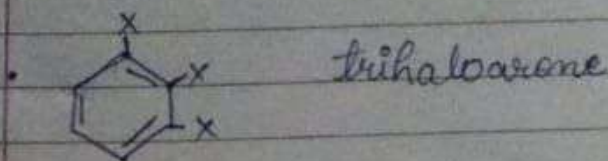
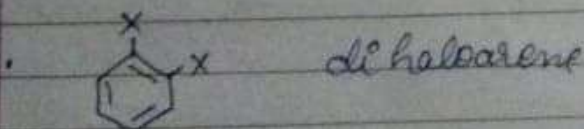
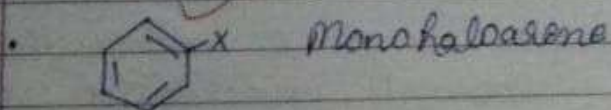
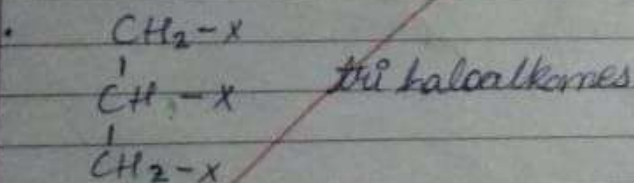
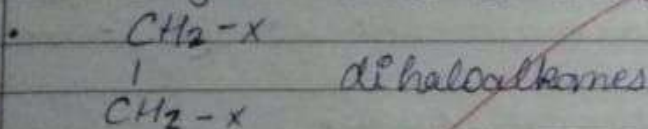
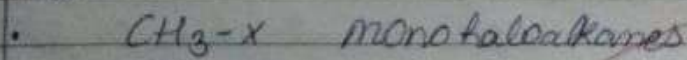
## Haloalkanes &amp; Haloarenes

# Halogen derivatives of Alkanes are known as Haloalkanes while halogen derivative of arenes are known as Haloarenes.

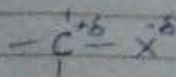
# Classification of Haloalkanes & Haloarenes:-

1. On the basis of no. of halogen atoms - depending on the no. of halogen atoms in the str., haloalkanes & haloarenes may be mono, di, tri, or polyhalogen (tetra, penta etc) polyhalogen compounds.

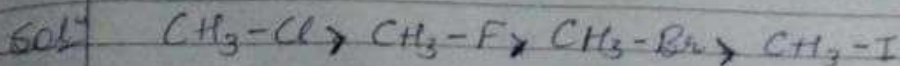
Ex:-







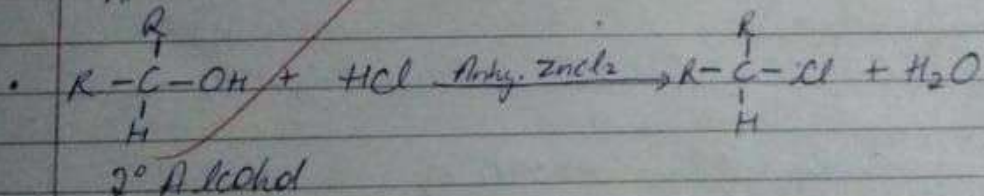
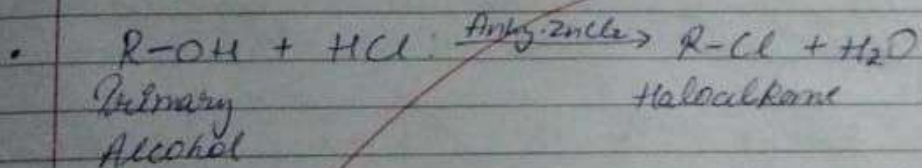
Q- Arrange the following in increasing order of dipole moment :-



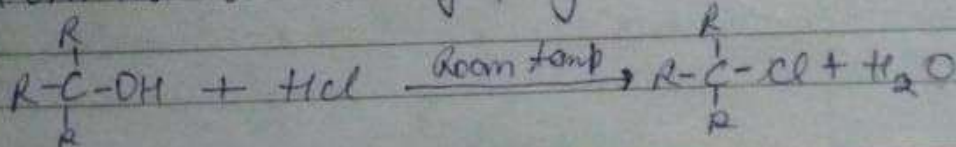
# Method of preparat<sup>n</sup> of Haloalkanes & Haloarenes :-  
(Haloalkanes)

a) Preparat<sup>n</sup> from Alcohols :-

b) by the action of halogen acid / Haloacid :-  
Primary and Secondary alcohol on treating with halogen acid in the presence of anhydrous  $\text{ZnCl}_2$  forms haloalkane.



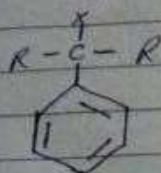
• 3° Alcohol are very reactive, therefore there rx<sup>n</sup> can be conducted by simply shaking with HCl even in the absence of Anhy.  $\text{ZnCl}_2$ .







2° Benzylic halide



3° Benzylic halide

- b) Compound containing  $\text{sp}^2$  C-X Bond  
In these compounds halogen atom is directly attached to double bonded C-atom.

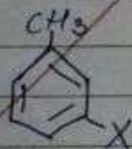
- (i) Vinylic Halide - In these halides halogen atom is directly attached to  $\text{sp}^2$  hybrid double bonded C-atom.

EX -



- (ii) Aryl halide - In these halide the halogen atom is directly attached to benzene ring.

EX -



### # Disubstituted Haloalkanes:-

The dihaloalkanes having the same types of halogen atoms are named as alkylidene or alkylene dihalides.

- i) Geminal or Gem dihalides:- In the halides