

# Haloalkanes and Haloarenes...

## Classification..

- Haloalkanes
  - monohalogen
  - dihalogen
  - trihalogen
  - tetrahalogen
- polyhalogen derivatives.

## # Vicinal dihalides..

- Halogen atoms are bonded to adjacent carbons IUPAC name: Alkylene halide.

example—  $\text{CH}_2-\text{CH}_2$   
 $\text{Cl} \quad \text{Cl}$  1,2-dichloroethane  
ethylene chloride

## # Gem dihalides..

- Halogen atoms bonded to same carbon.
- IUPAC name: Alkylidene halide.

example—  $\text{CH}_3-\text{CHCl}_2$

IUPAC name: 1,1-dichloroethane.

## \* Compounds containing $\text{sp}^3$ C-X bond. $\rightarrow$

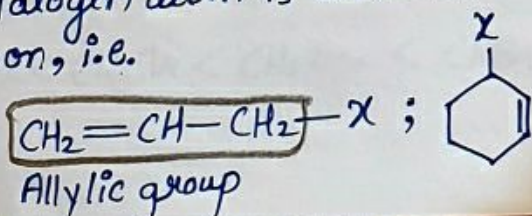
Classification based on type of group to which halogen atom is attached  $\rightarrow$

### (a) Alkyl halide.

- Halogen atom is attached to alkyl group i.e. R-X
- Halogen atom is attached to  $\text{sp}^3$  carbon.

### (b) Allylic halide.

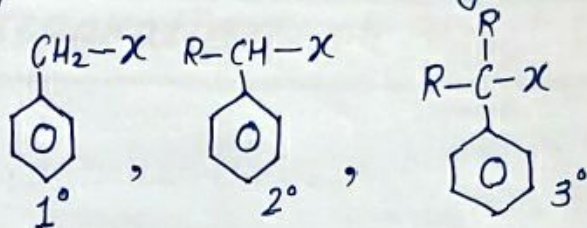
- Halogen atom is attached to allylic carbon, i.e.



- Halogen atom is attached to  $\text{sp}^3$  carbon.

### (c) Benzylic halide.

- Halogen atom is attached to carbon present on aromatic ring i.e.



- Halogen atom is attached to  $\text{sp}^3$  carbon.

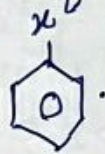
## \* Compounds containing $\text{sp}^2$ C-X bond :-

### (a) Vinyl Halide.

- Halogen atom is attached to vinyl group i.e.  $\text{CH}_2=\text{CH}-\text{X}$   
vinyl group
- Halogen atom is attached to  $\text{sp}^2$  carbon.

### (b) Aryl Halide.

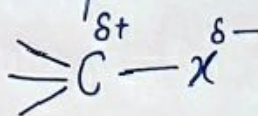
- Halogen atom is attached to carbon atom of aromatic ring i.e.



- Halogen atom is attached to  $\text{sp}^2$  carbon.

## Nature of C-X bond..

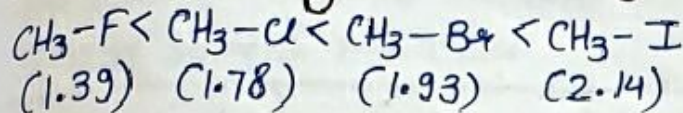
- Since, halogen atoms are more electronegative, carbon atom attains partial positive charge and halogen atom attains partial negative charge.



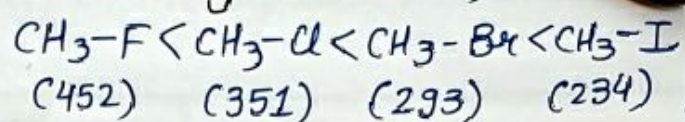


• As the size of halogen atom changes, following property changes →

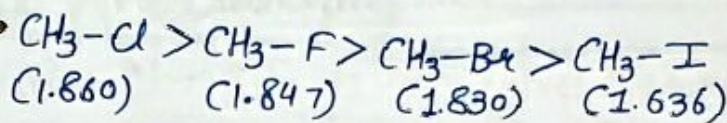
\* Carbon Halogen Bond length (Å)



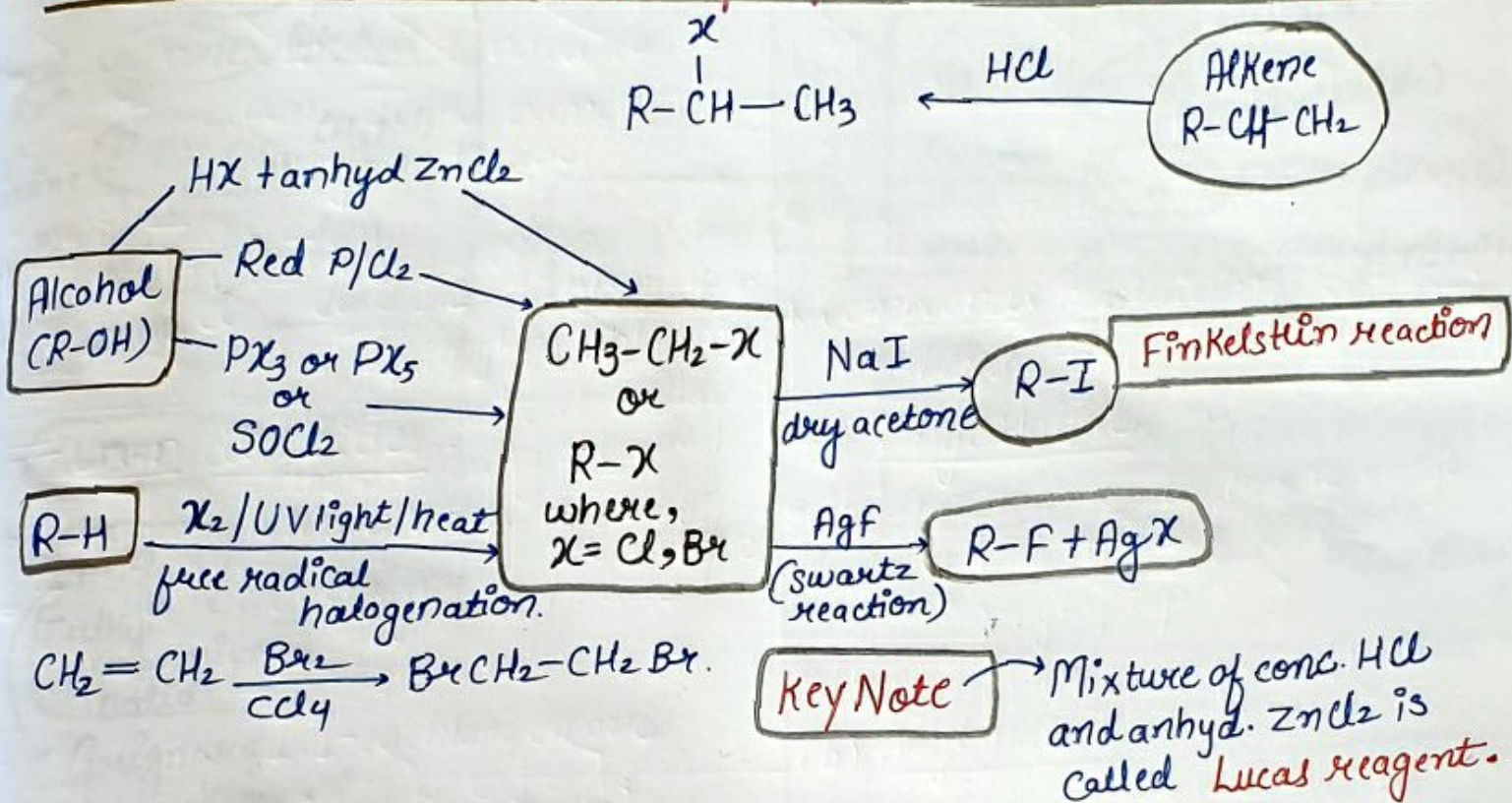
\* Bond length (KJmol<sup>-1</sup>)



\* Dipole Moment (Debye) →



## General Methods for preparation of Alkyl Halide

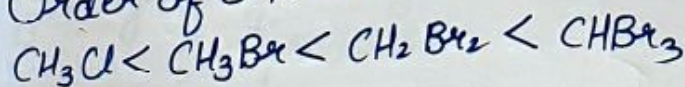


## Physical properties.

### # Boiling points.

- Alkyl halides are more polar and have high molecular masses when compared to parent hydrocarbons.
- So, in alkyl halides intermolecular forces are more. Hence, these have high M.P. and B.P.'s than hydrocarbons of comparable mass.

Order of B.P. →



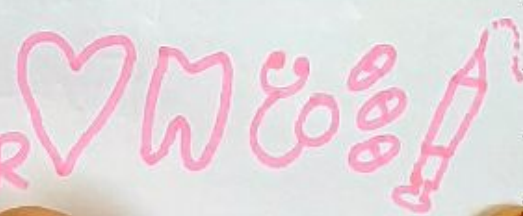
- In alkyl halides BP increase with increase of atomic weight of halogen.  
 $\text{R-F} < \text{R-Cl} < \text{R-Br} < \text{R-I}$ .

- Among isomeric alkyl halides BP. ~~increase~~ decrease with increase in branching.

### # Solubility.

- Solubility of haloalkanes in water is low.

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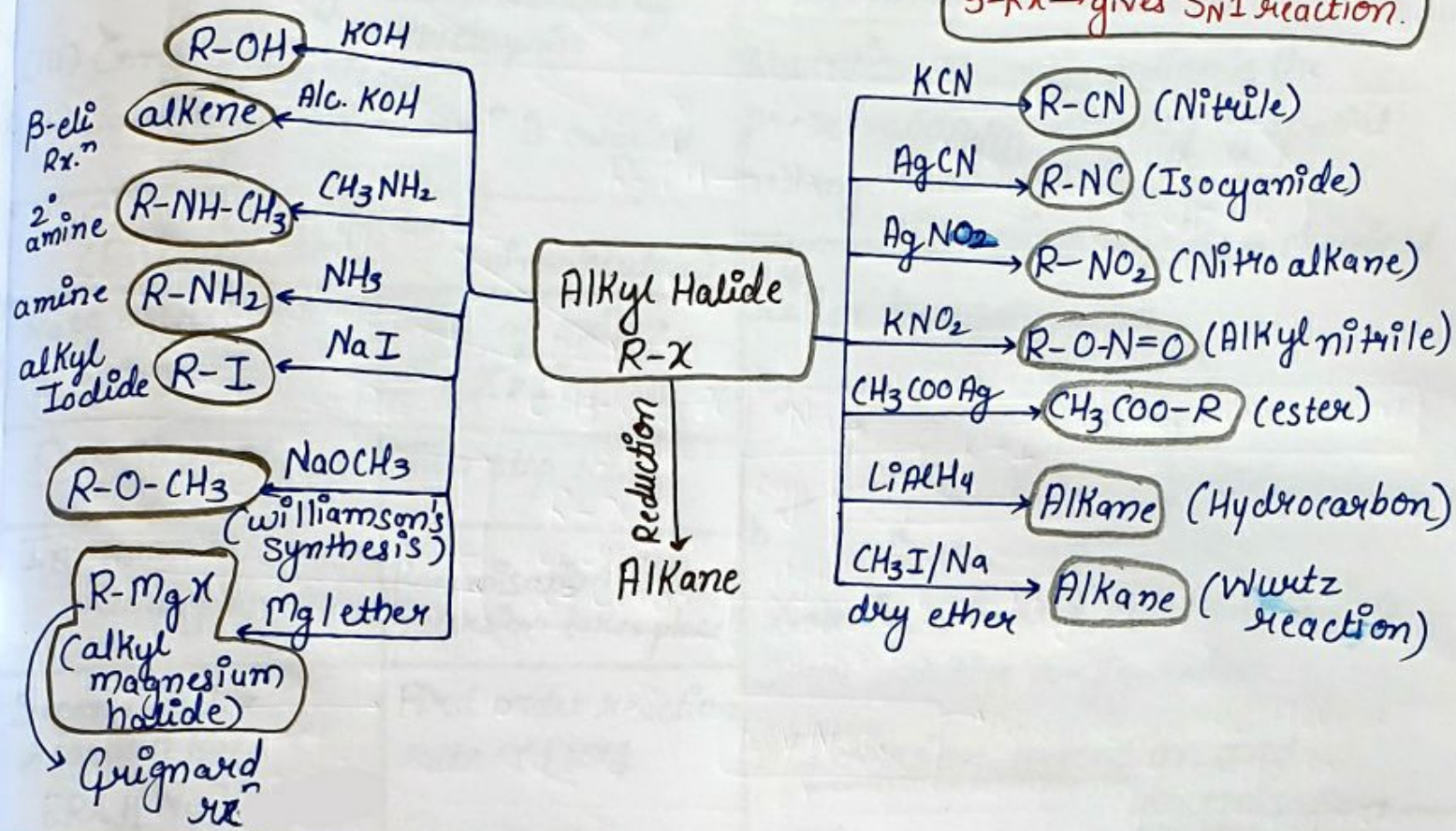


- Haloalkanes tend to dissolve in organic solvent becoz the new intermolecular attractions between haloalkanes and solvent molecules have much the same strength as the ones being broken in the separate haloalkane and solvent molecules.

## .. Chemical Reactions..

(A) Nucleophilic Substitution Reaction :-

$1^\circ\text{-RX} \rightarrow$  gives  $\text{S}_\text{N}2$  reaction.  
 $3^\circ\text{-RX} \rightarrow$  gives  $\text{S}_\text{N}1$  reaction.



### Key Note

$\text{KCN}$  is predominantly ionic, so both C and N atoms are free to donate electron pair.

As C-C bond is more stronger than C-N, attack occurs through carbon atom of cyanide to form alkyl cyanide as major product.

But  $\text{AgCN}$  is covalent so the electron pair on nitrogen is able to form bond with carbon atom giving alkyl isocyanide as major product.

Carbon compounds in which  $\text{sp}^3$  carbon is bonded to more electronegative atom/group undergo 2 types of rxn.

- $\rightarrow$  Substitution rxn
- $\rightarrow$  elimination rxn

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## # Substitution Reaction

- It's of 2 types  $\rightarrow$   $S_N1$  reaction  $\rightarrow$   $S_N2$  reaction.
- Nucleophilic substitution depends on  $\rightarrow$

- The structure of alkyl halide.
- The reactivity and structure of nucleophile.
- Conc. of nucleophile.
- Solvent in which, rxn. is carried out.

$S_N2$ (Bimolecular)	$S_N1$ (Unimolecular)
Rate of rxn. $\rightarrow$ $1^\circ > 2^\circ > 3^\circ$	Rate of rxn. $\rightarrow$ $3^\circ > 2^\circ > 1^\circ$
One step rxn.	Two step rxn.
Inversion of Configuration.	Racemisation and inversion takes place
Second order reaction Rate $\propto$ $[RX][Nu]$	First order reaction rate $\propto [RX]$
eg- $CH_3O^-$ , $CN^-$ , $OH^-$ ...	eg- $CH_3OH$ , $H_2O$

## # Stereo chemical aspects of Nucleophilic substitution reaction

- $S_N2$  reaction proceeds with complete stereochemical inversion, while  $S_N1$  reaction proceeds with racemisation.

## # Chiral center / Stereo Center

- Carbon which is tetrahedrally surrounded by four different groups.

## # Racemic mixture

Mixture of 50% d-form and 50% l-form.

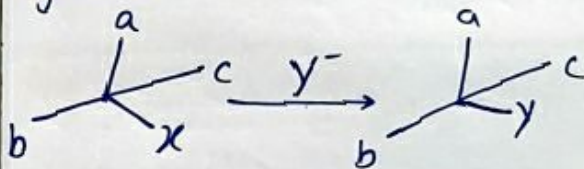
## # Enantiomers.

Two non superimposable mirror image compounds.

## # Retention.

Retention of configuration is the preservation of integrity of spatial arrangement of bonds to an asymmetric centre during a chemical rxn or transformation.

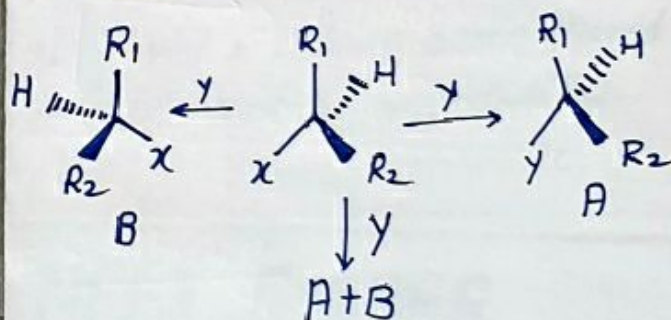
eg  $\rightarrow$



Xabc is converted into Yabc having same relative configuration.

## # Inversion, retention and racemisation

- There are three outcomes for a reaction at an asymmetric carbon atom. Consider the replacement of a group X by Y in the following reaction:



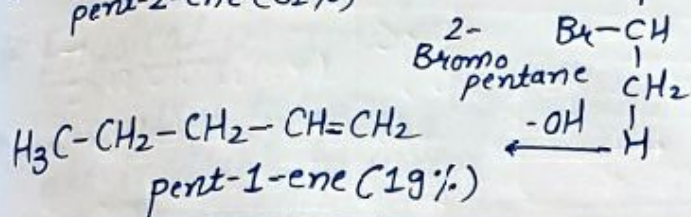
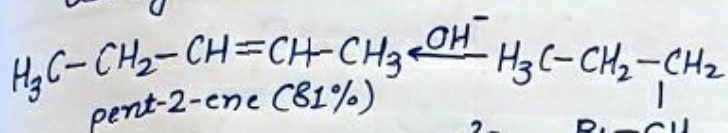
- If (A) is the only compound obtained, process is retention of configuration.
- If (B) is only compound obtained, process is called inversion of configuration.



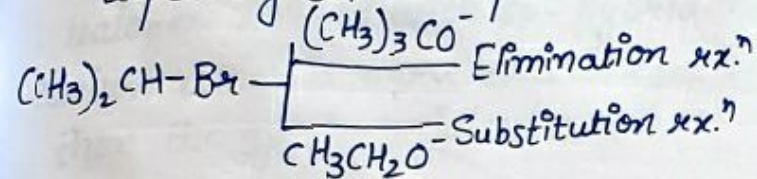
→ If a 50:50 mixture of the above two is obtained then the process is called **racemisation** and the product is optically inactive.

## (B) Elimination Reactions :-

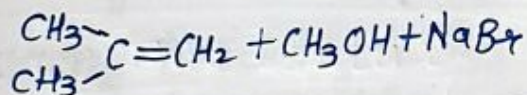
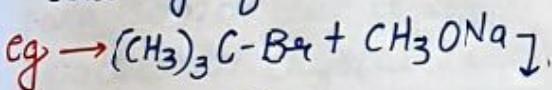
**Saytzeff rule** → In dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms.



**Key Note** → A secondary alkyl halide prefers for  $\text{S}_{\text{N}}1$  or elimination depending on nucleophile.

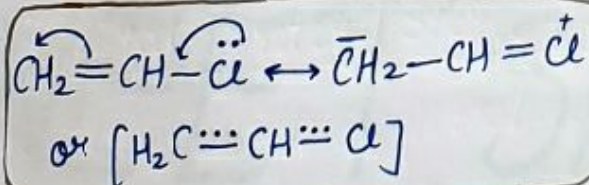


• A tertiary alkyl halide prefers  $\text{S}_{\text{N}}1$  or elimination depending on stability of carbocation or alkenes.



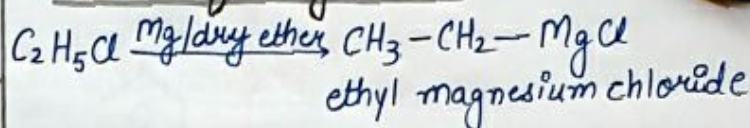
• Chlorine atom in vinyl chloride is non-reactive :-

**Reason** → The non-reactivity of chlorine atom in vinyl chloride is due to resonance stabilisation.

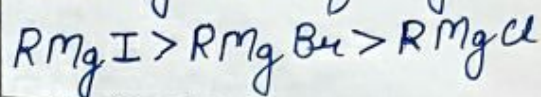


## (C) Reaction with metals :-

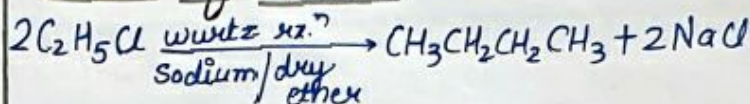
\* Action of Magnesium.



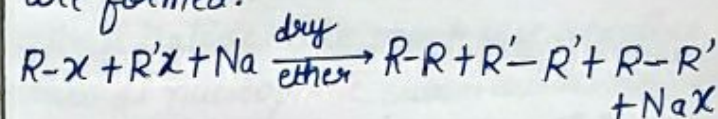
Reactivity order of Grignard reagent :-



\* Action of Sodium.



• When a mixture of 2 different alkyl halides is used 3 possible alkanes are formed.



**Note** :- Wurtz rxn. is not a suitable method for the preparation of alkane having odd number of carbon atoms.

## Haloarenes..

• Aryl halides are the compounds having halogen atom directly attached to the aromatic ring.

General formula →  $\text{Ar-X}$ .

\* Aryl Alkyl Halide

• All compounds containing aromatic ring and a halogen atom should not be considered as aryl halides.

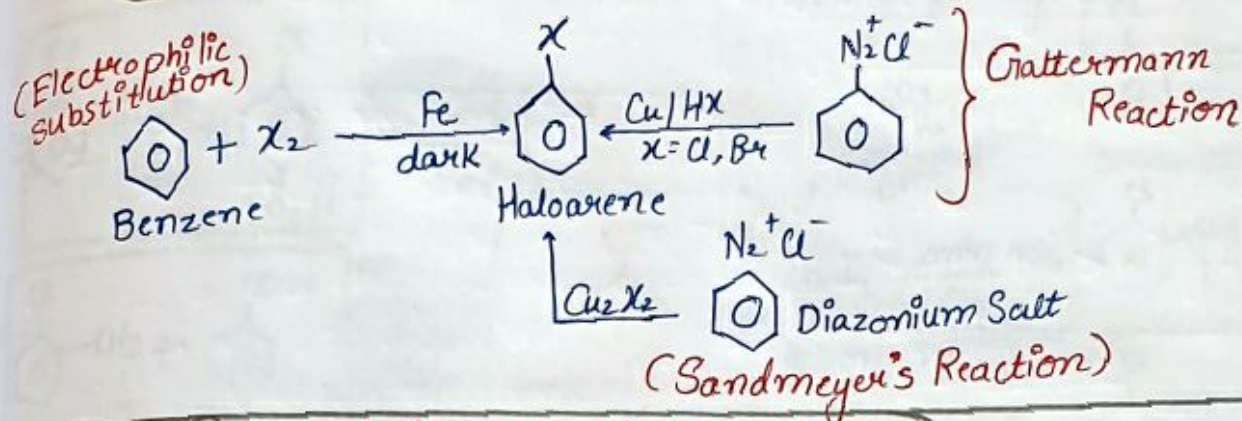
example — Benzyl chloride.

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# Preparation Of Haloarenes..



## Properties Of Haloarenes..

### # Physical properties :-

- Like alkyl halides, aryl halides are insoluble in water due to their incapability of forming H-bond.
- Aryl halides are less polar than alkyl halides as in aryl halides, halogen linked with  $sp^2$  hybridised carbon which is more electronegative than the  $sp^3$  hybridised carbon.
- p-isomer has higher melting point than the o and m-isomers. This is due to symmetrical structure of the para isomer due to which it is better packed in crystal lattice.
- Due to strong intercrystalline forces and higher melting point the para isomer is less soluble in a given solvent than the ortho isomer.

### # Chemical properties :-

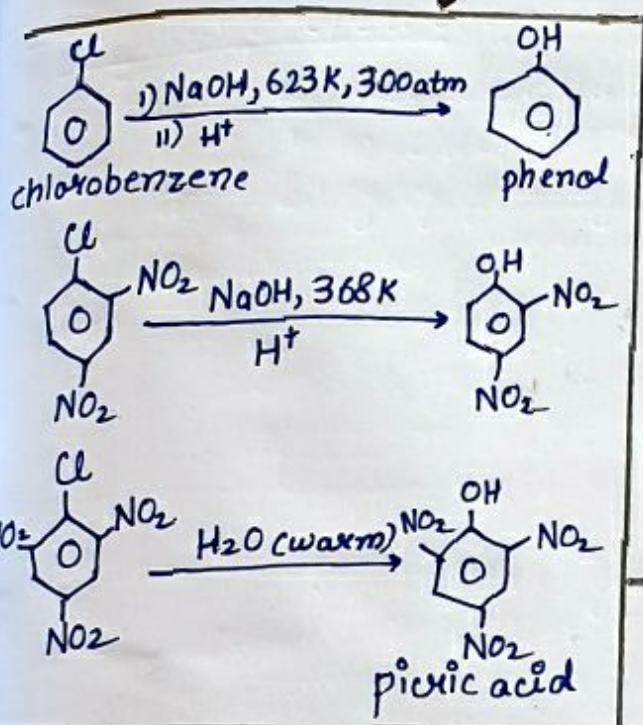
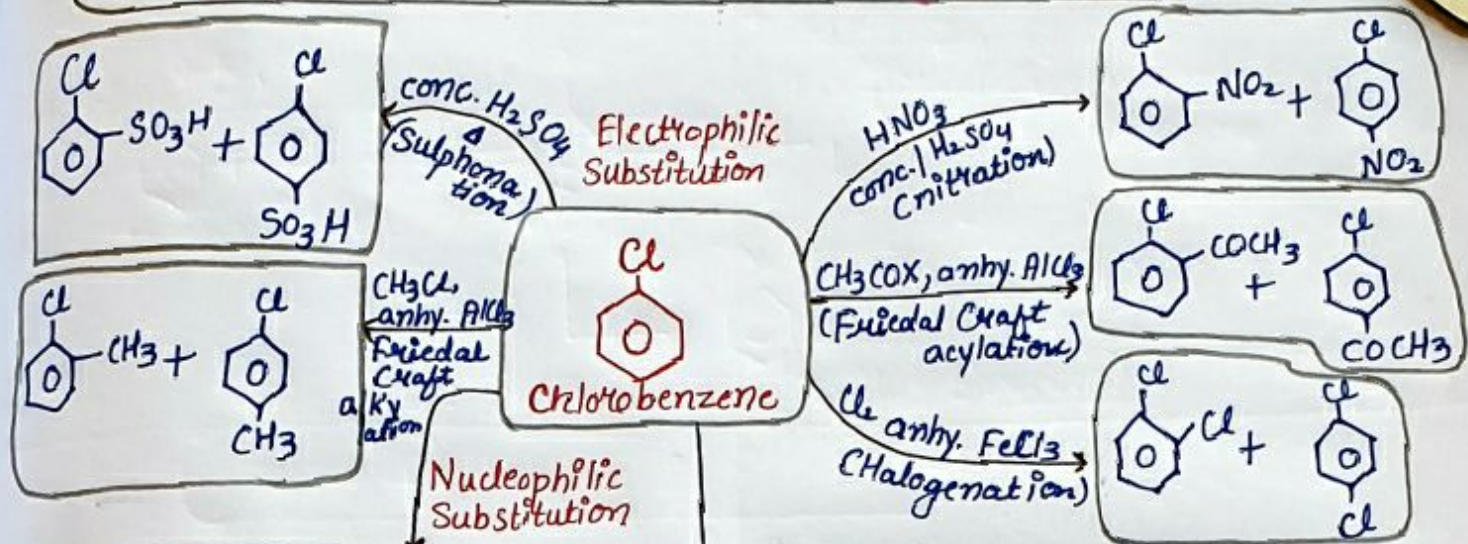
#### (1) Nature of C-X bond.

- Aryl halides are much less reactive towards nucleophilic substitution rxn than alkyl halides. The less reactivity of aryl halides is due to following reasons. In haloarenes, halogen atom is attached to  $sp^2$  hybridized carbon of arene but in haloalkanes, halogen is attached to  $sp^3$  carbon.  $sp^2$  orbital has more 's' character than  $sp^3$  orbital.
- Hence, C-X bond in haloarenes has shorter distance (169pm) than in haloalkanes (177pm). So in haloarenes C-X is stronger bond. Thus, it is less reactive towards nucleophilic substitution reactions.
- Due to resonance effect, C-X bond in haloarenes acquires a partial double bond character and the cleavage of C-X bond becomes more difficult than in haloalkanes.

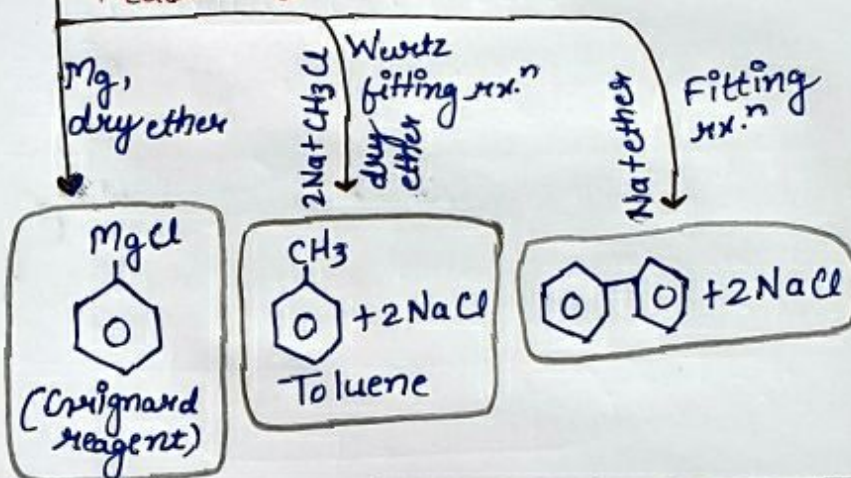
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# ..... Chemical Reactions Of Aryl Halides .....



## Reaction with metals

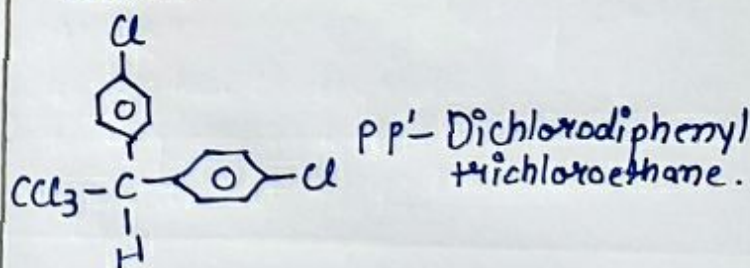


## Poly halogen Atoms..

Chloroform is used in production of Freon refrigerant R-22.  $[\text{CHClF}_2]$ .

### # DDT.

1 molecule of DDT has 5 chlorine atoms.

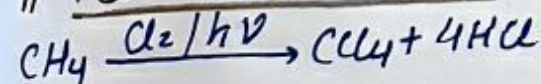


IUPAC Name — 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane

### # Iodoform ( $\text{CHI}_3$ )

Use  $\rightarrow$  Antiseptic. Antiseptic properties are due to liberated iodine but not due to iodo form. Its dirty odour made it replaced by other formulation.

### # Tetrachloromethane ( $\text{CCl}_4$ )



Uses  $\rightarrow$  production of refrigerants, propellants for aerosol cans.

### # Freons.

Freon 12 ( $\text{CCl}_2\text{F}_2$ ) is prepared from  $\text{CCl}_4$ . It is used as aerosol propellant, refrigerant in air.C.