CONCEPT MAP

HALOALKANES AND HALOARENES

1 Classification

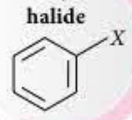
On the basis of number halgoen atoms

- **Monohalogen** *e.g.*, RCH_2X
- **Dihalogen** *e.g.*, $X—CH_2CH_2—X$
- **Trihalogen** *e.g.*, CHX_3

Compounds containing sp^2 C—X bond

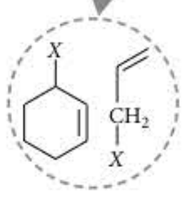
- **Vinylic halide**

- **Aryl halide**

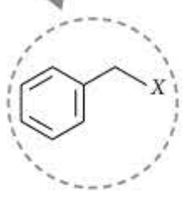


Compounds containing sp^3 C—X bond

- **Haloalkanes** $R—X$
- **Allylic halide**



- **Benzylic halide**



2 Nature of C—X Bond

C—F, C—Cl, C—Br, C—I ⟶

Size of halogen atoms increases

C—X bond length increases

Bond enthalpy decreases

3 Methods of Preparation

Alkyl halide

- **From Alkanes :**

$RH \xrightarrow{\text{By halogenation}}$ $\xrightarrow{Br_2, AlBr_3} R—Br + HBr$; $\xrightarrow{Cl_2, \text{Sunlight}} R—Cl + HCl$

- **From Alcohols :**

$R—OH \xrightarrow{PCl_5} R—Cl + POCl_3 + HCl$

$R—OH \xrightarrow{\text{Red } P/Br_2} R—Br + H_3PO_3$

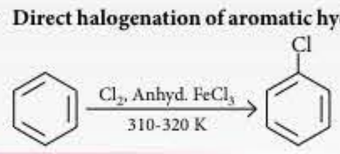
$R—OH \xrightarrow[\text{Pyridine}]{SOCl_2} R—Cl + SO_2\uparrow + HCl\uparrow$

- **Finkelstein Reaction :** $R—X + NaI \xrightarrow{\text{Dry acetone}} R—I + NaX$
- **Swarts Reaction :** $RBr + AgF \longrightarrow R—F + AgBr$
- **Hunsdiecker Reaction :**

$RCOOAg + Br_2 \xrightarrow{CCl_4/\text{Reflux}} R—Br + CO_2 + AgBr$

Aryl halide

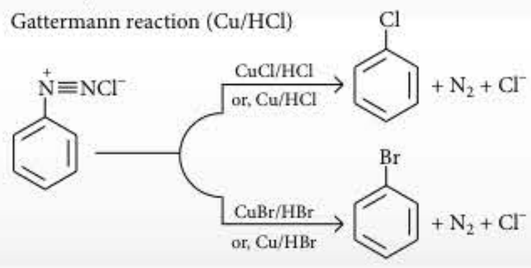
- **Direct halogenation of aromatic hydrocarbons :**



- **From diazonium salts :**

Sandmeyer's reaction (CuCl/HCl) and

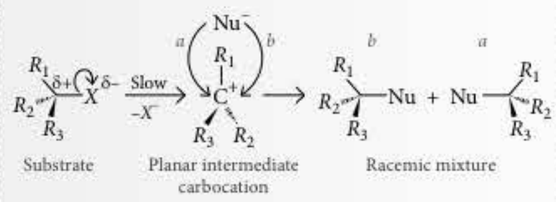
Gattermann reaction (Cu/HCl)



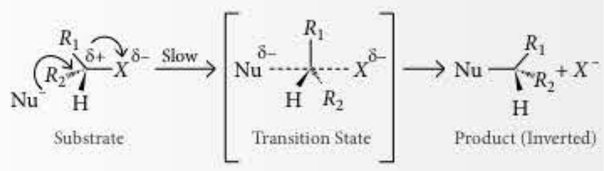
4 Chemical Properties

Nucleophilic Substitution Reactions

S_N1 (Racemisation)



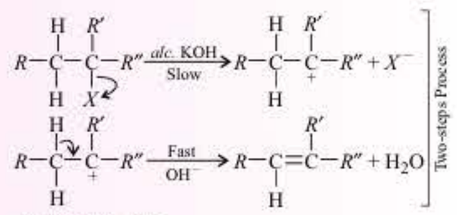
S_N2 (Inversion of Configuration)



Elimination Reactions

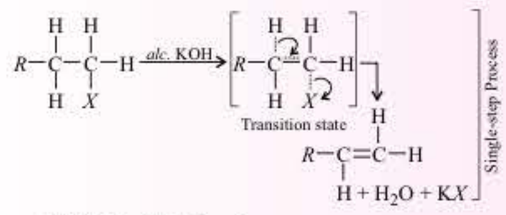
Alkyl halides undergo β-elimination reaction in the presence of potassium hydroxide in ethanol (high temperature) to yield alkenes.

E1 mechanism



Rate = k [Alkyl halide]

E2 mechanism



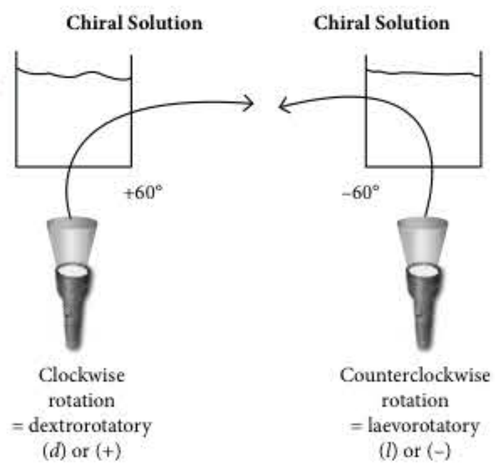
Rate = k [Alkyl halide] [base]

5 Stereochemistry

Optical Activity

Plane polarised light produced by passing ordinary light through nicol prism is rotated when it is passed through the solutions of certain compounds. Such compounds are called optically active compounds.

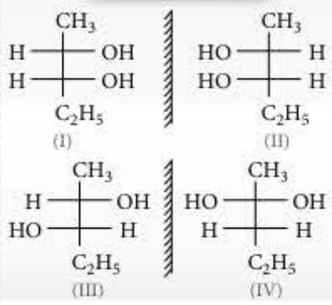
Chirality : The objects which are non-superimposable on their mirror images are said to be chiral.



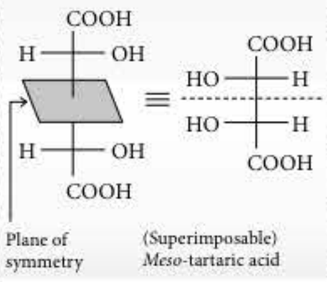
The direction and magnitude of rotation must be determined experimentally. There is no correlation between (*R*) and (*S*) configuration and the direction of rotation.

Enantiomers : Compounds having non-superimposable mirror images with same physical and chemical properties.

Diastereomers : Compounds which are not mirror images (I and III, II and IV) of each other with different physical properties but same chemical properties.



Meso compounds : These are optically inactive compounds as there exists a plane of symmetry which divides the molecule into two identical halves.



Racemic mixture : A mixture of equal amounts of two enantiomers is called *racemic mixture* or *racemic modification*.

A racemic mixture is always optically inactive because the rotation caused by the molecules of one enantiomer is exactly cancelled by equal and opposite rotation caused by the same number of molecules of the other enantiomer. It is represented by prefixing *dl* or (±) before the name. For example, (±) butan-2-ol.