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Educational Services Private Limited
NEET, JEE(Mains/Advanced)
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Haloalkanes and Haloarenes

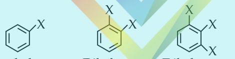
Racemisation S_n1
- Chiral : Objects which are non-superimposable
- Achiral : objects which are superimposable

Classification

- No. of halogen atoms

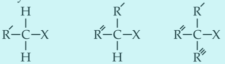
C_2H_5X — Monohaloalkane

CH_2X-CH_2X — Dihaloalkane

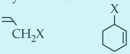


Monohaloarene   Dihaloarene   Trihaloarene

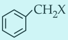
- Compounds containing sp^3 C–X bond
  - (a) Alkyl halides



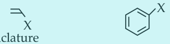
  - (b) Allylic halides



  - (c) Benzylic halides



- Compounds containing sp^2 C–X bond
  - (a) Vinylic halides   (b) Aryl halides



- Nomenclature

  Common name : alkyl group followed by halides. Dihalogen derivatives, prefixes o–, m–, p– are used.

  IUPAC name : numerals are used
- Nature of C –X bond

  : Carbon –halogen bond is polarized

$$\overset{\delta+}{C}-\overset{\delta-}{X}$$

Haloalkanes

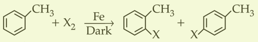
- Preparation
  - From alcohol :

$$R-OH + HCl \xrightarrow{ZnCl_2} R-Cl + H_2O$$
$$3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3$$
$$ROH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCl$$

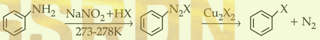
  - From hydrocarbons :
    - (a) By free radical halogenations

$$CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2/UV} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

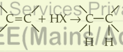
    - (b) By electrophilic substitution



    - (c) Sand meyer's reaction



    - (d) From alkenes



$$H_2C=CH_2 + Br_2 \xrightarrow{CCl_4} BrCH_2-CH_2Br$$

  - Halogen exchange :

$$R-X + NaI \rightarrow R-I + NaX$$

- Properties
  - Physical : Colourless, volatile, sweet smell.

    Lower members are gases at room temperature while higher are solids.

    B.P : RI > R Br > RCl > RF.

    M.P : Para isomers have high m.p. than ortho and meta – isomers.

    Density : Increases with increase in number of C/X atoms and atomic masses of the X atoms.

    Solubility : Very slightly soluble in water.
  - Chemical :
    - (a) Nucleophilic substitution

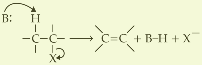
$$Nu^- + \overset{\delta+}{C}-\overset{\delta-}{X} \longrightarrow C-Nu + X^-$$

For S_N2 reaction →

Tertiary, Secondary, Primary

← For S_N1 reaction

    - (b) Elimination reaction



B = Base; X = Leaving group

    - (c) Reaction with metals

$$CH_3CH_2Br + M \longrightarrow CH_3CH_2MgBr$$

Wurtz reaction :

$$2RX + 2Na \xrightarrow{\text{Dry ether}} RR + 2NaX$$

Carbon tetrachloride
- Manufacture of refrigerants and propellants.
- Cleaning fluid

Chloroform
- Solvent for fats, alkaloids, I etc.
- Production of Freon

Dichloromethane
- Paint remover
- Propellant in aerosols
- Metal cleaning and finishing solvent.

Freon's
For aerosol propellants, refrigeration and air conditioning purposes

D. DT.
As insecticide

Iodoform
Antiseptic

Polyhalogen compounds

Haloalkanes and Haloarenes

$S_{n}2$ Stereochemical inversion
(a) Dextro (+/d)
(b) laevo (–/l)

Haloarenes

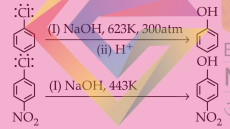
Reactions :

• (a) Nucleophilic substitution

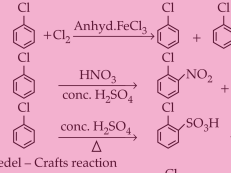
(i) Resonance effect

(ii) Hybridization of C – X bond in :
Haloalkane –sp^3; Haloarence –sp^2

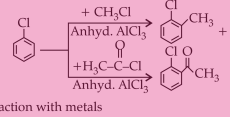
(iii) Phenyl cation unstabilised by resonance



(b) Electrophilic substitution

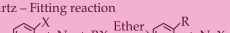


Friedel – Crafts reaction

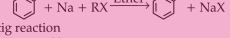


• (c) Reaction with metals

Wurtz – Fitting reaction



Fittig reaction



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