Chemistry Notes for class 12 Chapter 10 Haloalkanes and Haloarenes

The replacement of hydrogen atom(s) in hydrocarbon, aliphatic or aromatic, by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene), respectively.

Classification of Halogen Derivatives

On the basis of number of halogen atoms present, halogen derivatives are classified as mono, di, tri, tetra, etc., halogen derivatives, e.g.,



On the basis of the nature of the carbon to which halogen atom is attached, halogen derivatives are classified as 1° , 2° , 3° , allylic, benzylic, vinylic and aryl derivatives, e.g.,



U,

General Methods of Preparation of Haloalkanes

1. From Alcohols

$$R = OH$$
alcohol
$$R = OH$$

$$R$$

In Groove's method, $ZnC1_2$ is used to weaken the C-OH bond. In case of 3° alcohols, $ZnC1_2$ is not required.

The reactivity order of halogen acids is HI > HBr > HCl.

Darzen procedure is the best method for preparing alkyl halides from alcohols since both the by products (SO₂ and HCl) are gaseous and escape easily.

2. Free Radical Halogenation of Alkanes



Addition of Hydrogen Halides on Alkenes



1. Finkelstein Reaction

$$\begin{array}{c} R \xrightarrow{} X + \operatorname{NaI} \xrightarrow{\operatorname{Acetone}} R \xrightarrow{} I + \operatorname{NaX} \\ (X = \operatorname{Cl}, \operatorname{Br}) \end{array}$$

2. Swarts Reaction

 $H_3C - Br + AgF \rightarrow H_3C - F + AgBr$

 Hg_2F_2 , COF_2 and SbF_3 can also be used as a reagent for Swarts reaction.

3. Hunsdiecker Reaction

 $\mathrm{CH}_3\mathrm{COOAg} + \mathrm{Br}_2 \xrightarrow[]{\mathrm{CCl}_4} \mathrm{CH}_3\mathrm{Br} + \mathrm{AgBr} + \mathrm{CO}_2$

Physical Properties of Haloalkanes

1. Boiling point orders

- 1. R I > R Br > R CI > R F
- 2. $CH_3 (CH_2)_2 CH_2Br > (CH_3)_2 CHCH_2Br > (CH_3)_3CBr$
- 3. $CH_3CH_2CH_2 > CH_3CH_2X > CH_3X$

2. Bond strength of haloalkanes decreases as the size of the halogen atom increases. Thus, the order of bond strength is

 $CH_3F > CR_3Cl > CR_3Br > CH_3I$

3. Dipole moment decreases as the electronegativity of the halogen decreases.

4. Haloalkanes though polar but are insoluble in water as they do not form hydrogen bonding with water.

5. Density order is

RI > RBr > RCl > RF (For the same alkyl group)

 $CH_{3}I > C_{2}H_{5}I > C_{3}H_{7}I$

Chemical Reactions of Haloalkanes

1. Nucleophilic Substitution Reactions (S_N reactions)



kCN is predominantly ionic and provides cyanide ions in solution, which is ambident nucleophile and bind with carbon side to form as the major product, while AgCN is covalent and form isocyanide as the major product.

Like KCN, KNO₂ form R-ONO while AgNO₂ produces R-NO₂ as product. Vinyl chloride is less reactive towards nucleophilic substitution reactions due to resonance.

Nucleophilic substitution reactions are of two types

(a) S_N1 type (Unimolecular nucleophilic reactions proceed in two steps:



Rate, r = k [RX). It is a first order reaction.

Reactivity order of alkyl halide towards S_N1 mechanism

 $3^{\circ} > 2^{\circ} > 1^{\circ}$

Polar solvents, low concentration of nucleophiles and weak nucleophiles favour $S_N 1$ mechanism.

In S_N1 reactions, partial racemisation occurs due to the possibility of frontal as well as backside attack on planar carbocation.



(b) $S_N 2$ type (Bimolecular nucleophilic substitution) These reactions proceed in one step and is a second order reaction with r = k[RX] [Nu].

During $S_N 2$ reaction, inversion of configuration occurs (Walden inversion) i.e., starting with dextrorotatory halide a laevo product is obtained and vice-versa, e.g.,



Reactivity of halides towards S_N2 mechanism is

 $1^{\circ} > 2^{\circ} > 3^{\circ}$

Rate of reaction in $S_N 2$ mechanism depends on the strength of the attacking nucleophile. Strength of some common nucleophiles is

 $:CN^{-} > : I^{-} > : OR^{-} > : OH^{-} > CH^{3}COO : > H_{2}O > F^{-}$

Non-polar solvents, strong nucleophiles and high concentration of nucleophiles favour $S_N 2$ mechanism.

Relative rates of some alkyl halides in S_N1 and S_N2 reactions are in the order



 $> CH_3CH_2X > (CH_3)_2CHX > (CH_3)_3CX$

Resonating structure of benzyl carbocations are



Relative reactivity of alkyl halides for same alkyl group is

RI > RBr > RCI > RF

2. Elimination Reactions

Dehydrohalogenation is a β – elimination reaction in which halogen is from α -carbon atom and the hydrogen from the α -carbon according to Saytzeff rule, e.g.,

$$\begin{array}{c} & \operatorname{Br} & & \operatorname{Alc. \ KOH} \\ \operatorname{CH}_{3} - \operatorname{CH}_{2} - \operatorname{CH} - \operatorname{CH}_{3} & \xrightarrow{\operatorname{Alc. \ KOH}} & \operatorname{CH}_{3} - \operatorname{CH} = \operatorname{CH}_{-\operatorname{CH}_{3}} \\ & \xrightarrow{\operatorname{but-2-ene}} \\ & & \operatorname{but-2-ene} \\ & & \operatorname{(major)} \\ & + \operatorname{CH}_{3} \operatorname{CH}_{2} \operatorname{CH} = \operatorname{CH}_{2} \\ & & \operatorname{butene-1} (\operatorname{minor}) \end{array}$$

Ease of dehydrohalogenation among halides

$$3^{\circ} > 2^{\circ} > 1^{\circ}$$

i.e.,
$$(CH_3)_3 CCl > (CH_3)_2 CHCl > CH_3 CH_2 Cl$$

3. Reduction

1

$$C_{2}H_{5} \longrightarrow Br + H_{2} \xrightarrow{Ni, 575 \text{ K}} C_{2}H_{6} + HBr$$

$$C_{2}H_{5}I + HI \xrightarrow{\text{Red P, 420 K}} C_{2}H_{6} + I_{2}$$

4. Reaction with Metals



Grignard reagent is never isolated in the solid state as it explodes in dry state. So it is used as ethereal solution.

5. Isomerisation



General Methods of Preparation of Aryl Halides

1. By Halogenation of Aromatic Hydrocarbons



It is an electrophilic substitution reaction.

2. By Side Chain Halogenation



(It involves free radical mechanism.)

3. From Benzene Diazonium Salt

$$\frac{CuCl/HCl}{CuBr/HBr} = \frac{C_{6}H_{5}Cl + N_{2}}{C_{6}H_{5}Br + N_{2}}$$
Sandmeyer reaction

$$\frac{N_{2}^{+}Cl}{Cu/HCl} = \frac{C_{6}H_{5}Br + N_{2}}{C_{6}H_{5}Br + N_{2}}$$
Gattermann reaction

$$\frac{HBF_{4}}{C_{73}K} = \frac{C_{6}H_{5}N_{2}^{+}BF_{4}}{C_{6}H_{5}N_{2}^{+}BF_{4}} = \frac{\Delta}{-N_{2}, -BF_{3}} = C_{6}H_{5}F$$
(Balz Schiemann reaction)

$$\frac{KI, \Delta}{C_{6}H_{5}I + N_{2} + KCI}$$

4. From Phenol



Physical Properties of Aryl Halides

1. Aryl halides are colourless liquids or colourless solids with characteristic odour.

2. Boiling point generally increases with increase in the size of aryl group or halogen atom. Boiling point order

Ar-I>Ar-Br>Ar-Cl>Ar-F

3. The melting point of p -isomer is more than 0- and m-isomer.

This is because of more symmetrical nature of p-isomer.

4. Due to resonance in chlorobenzene, C-CI bond is shorter and hence, its dipole moment is less than that of cyclohexylchloride.

Chemical Properties of Aryl Halides

1. Nucleophilic Substitution Reaction

Aryl halides are less reactive towards nucleophilic substitution reaction. Their low reactivity is attributed due to the following reasons:

- 1. Due to resonance, C-X bond has partial double bond character.
- 2. Stabilisation of the molecule by delocalisation of electrons.
- 3. (Instability of phenyl carbocation.

However, aryl halides having electron withdrawing groups (like $-NO_2$, $-SO_3H$, etc.) at ortho and para positions undergo nucleophilic substitution reaction easily.



Presence of electron withdrawing group (-NO₂) increases the reactivity.



2. Electrophilic Substitution Reactions

Halogens are deactivating but O, p-directing. Thus, chlorination, nitration, sulphonation and Friedel Craft's reaction give a mixture of o- and P- chloro substituted derivatives.

(i) Halogenation



(iii) Sulphonation



3. Reaction with Metals

(i) Wurtz Fittig reaction



(ii) Fitting reaction



(iii) Ullmann reaction





Dichloromethane (CH_2Cl_2) is widely used as a solvent, as a propellant in aerosols. Direct contact of dichloromethane in humans causes intense burning and milk redness of the skin.

Trihalogen Derivatives

1. Chloroform [Trichloromethane, CHCl₃]

Methods of preparation



Properties

1. Oxidation of CHCl₃ gives poisonous gas phosgene (carbonyl chloride).



To avoid this oxidation $CHCl_3$ iI .toreci in dark brown bottles and filled to the brim. 1% ethanol is added to chloroform which converts harmful phosgene gas into diethyl carbonate.

2. CHCl₃ is widely used in the production of freon refrigerant R-22.

3. On nitration, it gives tear producing insecticide substance chloropicrin.

 $\begin{array}{c} \mathrm{CHCl}_8 + \mathrm{HONO}_2 \ (\mathrm{conc.}) &\longrightarrow \mathrm{NO}_2 \cdot \mathrm{CCl}_8 + \mathrm{H}_2\mathrm{O} \\ & \mathrm{chloropicrin} \end{array}$ 4. On dehalogenation, it gives $\mathrm{C}_2\mathrm{H}_2 \ (\mathrm{acetylene}).$ $\begin{array}{c} \mathrm{CHCl}_8 + 6\mathrm{Ag} + \mathrm{CHCl}_8 & \longrightarrow & \mathrm{CH} \Longrightarrow \mathrm{CH} + 6\mathrm{Ag}\mathrm{Cl} \end{array}$ 5. When subjected to hydrolysis, it gives formate. $\begin{array}{c} \mathrm{OH} \end{array}$

$$CHCl_3 + 3NaOH \longrightarrow CH \xrightarrow{OH} OH \xrightarrow{-H_2O} HCOONa$$

2. Iodoform (tri-iodornethane, CHl₃)

Iodoform is prepared by iodoform reaction.

$$\begin{array}{rl} \mathrm{CH}_{3}\mathrm{COCH}_{3}+3\mathrm{I}_{2}+4\mathrm{NaOH} & \longrightarrow \\ & & \mathrm{CHI}_{3}+3\mathrm{NaI}+\mathrm{CH}_{3}\mathrm{COONa}+3\mathrm{H}_{2}\mathrm{O} \end{array}$$

Compounds containing either CH_3CO - or $CH_3CH(OH)$ group form yellow colour iodoform with I_2 and NaOH.

Iodoform when comes in contact with organic matter, decomposes easily to free iodine, an antiseptic. Due to its objectionable smell, it has been replaced by other formulations containing iodine.

Polyhalogen Derivatives

1. Tetrachloromethane (Carbon Tetrachloride, CCl₄)

Preparation



CCI₄ is a colourless, non-inflammable, poisonous liquid, soluble in alcohol and ether.

Uses

Carbon tetrachloride is used

- 1. as a solvent for oils, fats, resins
- 2. in dry cleaning
- 3. as fire extinguisher under the name 'pyrene'.

2. Freons

The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. These are usually produced for aerosol propellants, refrigeration and air conditioning purposes. Carbon tetra chloride when reacts with antimony trifluoride in the presence of SbCl₅ as catalyst, dichlorofluromethane (freon) is obtained.

3. DDT (p, p'-Dichlorodiphenyltrichloroethane)



2,2- bis (4-chlorophenyl) -1,1,1- trichloroethane

DDT is the first chlorinated organic insecticide. Its stability and fat solubility'is a great problem.

It is prepared from chloral and chlorobenzene in the presence of conc. H_2SO_4 .

4. Perchloroethane (C₂Cl₆)

It is used as moth repellant and is also known as artificial camphor.