Haloalkanes and Haloarenes

Haloalkanes :- Methods of Preparation

. From alcohols: $R\text{-}OH + HX \rightarrow R\text{-}X + H_2O$

(in presence of anhydrous $ZnCl_2$ catalyst for conc. HCl)

From alkanes (halogenation):

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ (in presence of sunlight)

3. Finkelstein reaction: $R\text{-}Cl + NaI$ (acetone) $\rightarrow R\text{-}I + NaCl$ (ppt)

4.From alkenes (addition reaction):

$CH_2{=}CH_2 + HCl \rightarrow CH_3\text{-}CH_2Cl$

(Markovnikov's Rule)

Unsymmetrical alkene + HX → H goes to C with more H, X goes to C with less H.

(Rich get richer rule)Example:

$CH_2{=}CH\text{-}CH_3 + HBr \rightarrow CH_3\text{-}CHBr\text{-}CH_3$ (2-Bromopropane)

(B) Chemical Properties

1. Reaction with aqueous KOH (Nucleophilic substitution):

R-X + KOH (aq) → R-OH + KX

SN1 mechanism (tertiary halides, carbocation formation).

SN2 mechanism (primary halides, backside attack).

2. Reaction with alcoholic KOH (Elimination):

$R\text{-}CH_2\text{-}CH_2\text{-}X$ + alc. KOH → $R\text{-}CH{=}CH_2$ + HX

Follows Saytzeff's rule: Major product is more substituted alkene.

1.Reaction with metals (Wurtz reaction):

2R-X + 2Na → R-R + 2NaX

2. Reaction with NaOR (Williamson synthesis):

R-X + NaOR' → R-OR' + NaX

Reaction with Ag powder:

2R-X + 2Ag → R-R + 2AgX

© Physical Properties

Haloalkanes are colorless liquids or solids.

Boiling point increases with molecular mass and decreases with branching.

They are heavier than water (except chloromethane, which is lighter).

They are insoluble in water but soluble in organic solvents.

Haloarenes

Methods of Preparation

From benzene:

$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$ (in presence of $FeCl_3$)

From diazonium salts (Sandmeyer reaction):

$C_6H_5\text{-}N_2^+Cl^- + CuCl \rightarrow C_6H_5Cl + N_2$

Chemical Properties

Electrophilic substitution reactions:

Nitration: $C_6H_5Cl + HNO_3 \rightarrow$ o- & p-nitrochlorobenzene

Sulphonation: $C_6H_5Cl + H_2SO_4 \rightarrow$ o- & p-chlorobenzenesulphonic acid

Nucleophilic substitution (very difficult due to resonance and partial double bond character of C-Cl bond).

© Physical Properties

Haloarenes are colorless liquids or crystalline solids.

Insoluble in water but soluble in organic solvents.

Boiling point increases with increase in halogen atomic mass.

Chloroform ($CHCl_3$)

Preparation

From ethanol/acetone by chlorination:

$CH_3CH_2OH + 4Cl_2 \rightarrow CHCl_3 +$ other products

Chemical Properties

Oxidation:

$2CHCl_3 + O_2 \rightarrow 2COCl_2 + 2HCl$ (phosgene gas)

With Ag powder:

$CHCl_3 + 6Ag \rightarrow C + 6AgCl$

With Acetone (haloform reaction):

$CHCl_3 + CH_3COCH_3 + 3NaOH \rightarrow CH_2=C(OH)-CCl_3 + 3NaCl + 3H_2O$

With Cl_2 (sunlight):

$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$

Physical Properties Sweet smelling liquid.Non-flammable.Heavier than water.Volatile, used as solvent.

Iodoform (CHI_3)

Preparation From ethanol or acetone with iodine and alkali:

$CH_3CH_2OH + I_2 + NaOH \rightarrow CHI_3 +$ other products

Chemical Properties

.1 Iodoform test:

$R\text{-}CO\text{-}CH_3 + 3I_2 + 4NaOH \rightarrow R\text{-}COONa + CHI_3$ (yellow ppt) $+ 3NaI + 3H_2O$

2. Oxidation:

$CHI_3 + 3Cl_2 \rightarrow CCl_4 + 3ICl$

Physical Properties :- Yellow crystalline solid.Characteristic antiseptic smell.Insoluble in water but soluble in organic solvents.

Carbon Tetrachloride (CCl_4)

Preparation :- $CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$ (in presence of sunlight)

Chemical Properties Very stable, non-flammable.

Hydrolysed by sunlight into phosgene gas:

$CCl_4 + O_2$ (UV light) $\rightarrow COCl_2 + Cl_2$

© Physical Properties Colorless liquid.nNon-inflammable. Good solvent for fats, oils, and wax.

DDT (p,p'-dichloro diphenyl trichloroethane)

Preparation :- $C_6H_5Cl + CCl_3CHO \rightarrow$ DDT

Properties :-;White solid, insoluble in water. Highly stable and non-biodegradable. Used as insecticide.

BHC (Benzene hexachloride, $C_6H_6Cl_6$)

Preparation :- $C_6H_6 + 3Cl_2 \rightarrow C_6H_6Cl_6$ (in presence of UV light)

Properties :- White crystalline solid. Used as insecticide (commonly called gammexane).

Nature of C-X Bond

C-X bond in haloalkanes is polar due to electronegativity difference. In haloarenes, C-Cl bond acquires partial double bond character due to resonance.Hence, haloalkanes are more reactive than haloarenes in nucleophilic substitution.

Important Rules :- Saytzeff's Rule (Elimination): Major product is more substituted alkene

. SN1 Mechanism: Carbocation intermediate, rate depends on substrate.

SN2 Mechanism: Backside attack, inversion of configuration, rate depends on both substrate and nucleophile.

Extra - What Happens When

CH_3CH_2Cl is treated with aqueous KOH $\rightarrow CH_3CH_2OH$ forms.

CH_3CH_2Cl is treated with alcoholic KOH → $CH_2=CH_2$ forms.

CH_3Cl + NaI (acetone) → CH_3I + NaCl ppt.

$CHCl_3$ exposed to air → forms phosgene gas.

$CHCl_3$ + Ag powder → C + AgCl.

$CHCl_3$ + Cl_2 (sunlight) → CCl_4 + HCl.

Acetone + I_2 + NaOH → yellow ppt of iodoform.

Ethanol + I_2 + NaOH → yellow ppt of iodoform.

Benzene + Cl_2 + $FeCl_3$ → chlorobenzene.

Chlorobenzene + conc. HNO_3 + H_2SO_4 → nitrochlorobenzene.

Chlorobenzene + conc. H_2SO_4 → chlorobenzenesulphonic acid.

C_2H_5Br + NaOEt → $C_2H_5OC_2H_5$.

$2CH_3Cl$ + 2Na → C_2H_6 + 2NaCl.

Chlorobenzene + CuCN → benzonitrile.

Chlorobenzene + NaOH (at 623K, 300 atm) → phenol.

CCl_4 + O_2 (UV) → $COCl_2$ + Cl_2.

BHC exposed to air → slowly decomposes.

DDT sprayed in fields → accumulates in food chain.

CH_3CH_2Br + Mg (ether) → C_2H_5MgBr.

C_2H_5Cl + NH_3 → $C_2H_5NH_2$ + HCl.

C_2H_5Cl + KCN → C_2H_5CN + KCl.

C_2H_5Cl + AgCN → C_2H_5NC + AgCl.

$CH_3Cl + 2Cl_2$ (sunlight) $\rightarrow CCl_4 + 3HCl$.

Chlorobenzene + Cl_2 ($FeCl_3$) $\rightarrow$ p-dichlorobenzene.