



Haloalkanes and Haloarenes

Haloalkanes :- Methods of Preparation

. From alcohols: $\text{R-OH} + \text{HX} \rightarrow \text{R-X} + \text{H}_2\text{O}$

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

From alkanes (halogenation):

$\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$ (in presence of sunlight)

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

4. From alkenes (addition reaction):

$\text{CH}_2=\text{CH}_2 + \text{HCl} \rightarrow \text{CH}_3-\text{CH}_2\text{Cl}$

(Markovnikov's Rule)

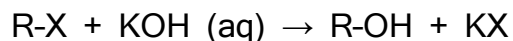
Unsymmetrical alkene + $\text{HX} \rightarrow$ H goes to C with more H, X goes to C with less H.

(Rich get richer rule) Example:

$\text{CH}_2=\text{CH-CH}_3 + \text{HBr} \rightarrow \text{CH}_3-\text{CHBr-CH}_3$ (2-Bromopropane)

(B) Chemical Properties

1. Reaction with aqueous KOH (Nucleophilic substitution):



SN1 mechanism (tertiary halides, carbocation formation).

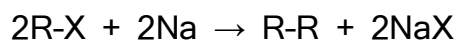
SN2 mechanism (primary halides, backside attack).

2. Reaction with alcoholic KOH (Elimination):

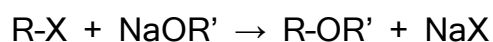


Follows Saytzeff's rule: Major product is more substituted alkene.

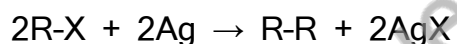
1. Reaction with metals (Wurtz reaction):



2. Reaction with NaOR (Williamson synthesis):



Reaction with Ag powder:



© Physical Properties

Haloalkanes are colorless liquids or solids.

Boiling point increases with molecular mass and decreases with branching.

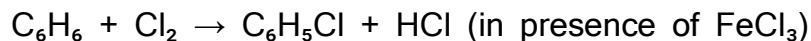
They are heavier than water (except chloromethane, which is lighter).

They are insoluble in water but soluble in organic solvents.

Haloarenes

Methods of Preparation

From benzene:

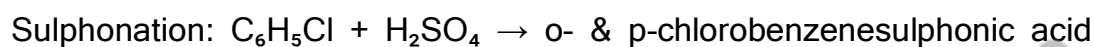
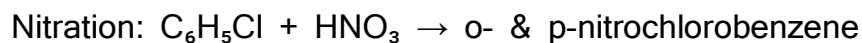


From diazonium salts (Sandmeyer reaction):



Chemical Properties

Electrophilic substitution reactions:



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 (CHCl₃)

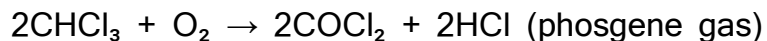
Preparation

From ethanol/acetone by chlorination:

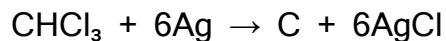


Chemical Properties

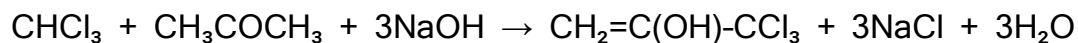
Oxidation:



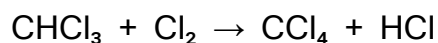
With Ag powder:



With Acetone (haloform reaction):



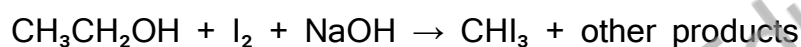
With Cl_2 (sunlight):



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:

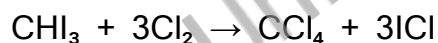


Chemical Properties

.1 Iodoform test:



2. Oxidation:



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

Carbon Tetrachloride (CCl_4)

Preparation :- $\text{CHCl}_3 + \text{Cl}_2 \rightarrow \text{CCl}_4 + \text{HCl}$ (in presence of sunlight)

Chemical Properties Very stable, non-flammable.

Hydrolysed by sunlight into phosgene gas:



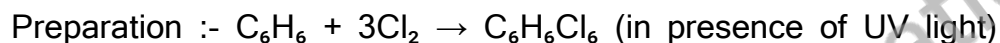
© Physical Properties Colorless liquid. Non-inflammable. Good solvent for fats, oils, and wax.

DDT (p,p'-dichloro diphenyl trichloroethane)



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

BHC (Benzene hexachloride, $\text{C}_6\text{H}_6\text{Cl}_6$)



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



$\text{CH}_3\text{CH}_2\text{Cl}$ is treated with alcoholic $\text{KOH} \rightarrow \text{CH}_2=\text{CH}_2$ forms.

$\text{CH}_3\text{Cl} + \text{NaI}$ (acetone) $\rightarrow \text{CH}_3\text{I} + \text{NaCl}$ ppt.

CHCl_3 exposed to air \rightarrow forms phosgene gas.

$\text{CHCl}_3 + \text{Ag}$ powder $\rightarrow \text{C} + \text{AgCl}$.

$\text{CHCl}_3 + \text{Cl}_2$ (sunlight) $\rightarrow \text{CCl}_4 + \text{HCl}$.

Acetone + $\text{I}_2 + \text{NaOH} \rightarrow$ yellow ppt of iodoform.

Ethanol + $\text{I}_2 + \text{NaOH} \rightarrow$ yellow ppt of iodoform.

Benzene + $\text{Cl}_2 + \text{FeCl}_3 \rightarrow$ chlorobenzene.

Chlorobenzene + conc. $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow$ nitrochlorobenzene.

Chlorobenzene + conc. $\text{H}_2\text{SO}_4 \rightarrow$ chlorobenzenesulphonic acid.

$\text{C}_2\text{H}_5\text{Br} + \text{NaOEt} \rightarrow \text{C}_2\text{H}_5\text{OC}_2\text{H}_5$.

$2\text{CH}_3\text{Cl} + 2\text{Na} \rightarrow \text{C}_2\text{H}_6 + 2\text{NaCl}$.

Chlorobenzene + $\text{CuCN} \rightarrow$ benzonitrile.

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

$\text{CCl}_4 + \text{O}_2$ (UV) $\rightarrow \text{COCl}_2 + \text{Cl}_2$.

BHC exposed to air \rightarrow slowly decomposes.

DDT sprayed in fields \rightarrow accumulates in food chain.

$\text{CH}_3\text{CH}_2\text{Br} + \text{Mg}$ (ether) $\rightarrow \text{C}_2\text{H}_5\text{MgBr}$.

$\text{C}_2\text{H}_5\text{Cl} + \text{NH}_3 \rightarrow \text{C}_2\text{H}_5\text{NH}_2 + \text{HCl}$.

$\text{C}_2\text{H}_5\text{Cl} + \text{KCN} \rightarrow \text{C}_2\text{H}_5\text{CN} + \text{KCl}$.

$\text{C}_2\text{H}_5\text{Cl} + \text{AgCN} \rightarrow \text{C}_2\text{H}_5\text{NC} + \text{AgCl}$.

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