

Name: Chandra Shekhar  
College: IIT Gandhinagar  
Subject: Chemistry  
Weightage: Regular  
Title: Halogen-Containing Organic Compound

## Halogen Containing Compounds

Compounds derived from hydrocarbons by replacing one or more hydrogen atoms with corresponding halogen atoms are termed halogen derivatives. They are broadly classified into three classes:

1. Halogen derivatives of saturated hydrocarbons (Alkanes) - Haloalkanes.
2. Halogen derivatives of unsaturated hydrocarbons (Alkenes and Alkynes) - Haloalkenes or Haloalkynes.
3. Halogen derivatives of aromatic hydrocarbons (Arenes) - Haloarenes.

### General Methods of Preparation of Alkyl Halides

#### 1. From Alkanes

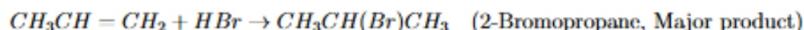
1. **By halogenation:** Reaction with halogens ( $Cl_2$ ) in the presence of UV light. This reaction proceeds via a free radical mechanism.



(Propane) (1-Chloropropane, 45%) (2-Chloropropane, 55%) Order of reactivity of  $X_2$  for a given alkane is:  $F_2 > Cl_2 > Br_2 > I_2$ . Order of reactivity of alkanes for a given halogen is: Tertiary > Secondary > Primary.

#### 2. From Alkenes

1. **By addition of HX:** Alkenes react with hydrogen halides (HCl, HBr, HI). This follows Markovnikov's rule.



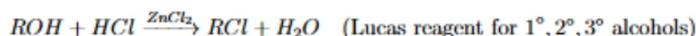
In the presence of peroxides, HBr adds anti-Markovnikov.

2. **By addition of Halogen:** Alkenes react with halogens ( $Br_2/CCl_4$ ) to form vicinal dihalides.



#### 3. From Alcohols

1. **By action of halogen acids:** Alcohols react with HCl, HBr, HI.



Order of reactivity of alcohols:  $3^\circ > 2^\circ > 1^\circ$ . Order of reactivity of halogen acids:  $HI > HBr > HCl$ .

2. **By action of phosphorus halides:**



3. **By action of thionyl chloride ( $SOCl_2$ ): Darzen's method.**



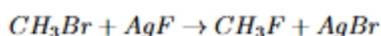
This is the best method as by-products are gases.

#### 4. Halogen Exchange Reactions

1. **Finkelstein Reaction:** For preparing alkyl iodides.



2. **Swarts Reaction:** For preparing alkyl fluorides.



Other reagents:  $Hg_2F_2, CoF_2, SbF_3$ .

## General Physical Properties of Alkyl Halides

1. **Boiling Points:** Increase with molecular mass. For same alkyl group,  $RI > RBr > RCl > RF$ . For isomeric alkyl halides, boiling point decreases with branching.
2. **Density:** Alkyl iodides, bromides, and polychloro derivatives are denser than water.
3. **Solubility:** Insoluble in water, soluble in organic solvents.

## General Chemical Properties of Alkyl Halides

### 1. Nucleophilic Substitution Reactions

Alkyl halides undergo nucleophilic substitution ( $S_N1$  and  $S_N2$ ).

- **$S_N1$  Reaction:** Unimolecular, two steps, carbocation intermediate. Order of reactivity:  $3^\circ > 2^\circ > 1^\circ$ . Favored by polar protic solvents.
- **$S_N2$  Reaction:** Bimolecular, one step, transition state. Order of reactivity:  $1^\circ > 2^\circ > 3^\circ$ . Favored by polar aprotic solvents.

$S_N1$ Reaction	$S_N2$ Reaction
Two steps	One step
Carbocation intermediate	Transition state
Racemization (partial)	Inversion of configuration
Order of reactivity: $3^\circ > 2^\circ > 1^\circ$	Order of reactivity: $1^\circ > 2^\circ > 3^\circ$
Favored by polar protic solvents	Favored by polar aprotic solvents
Rate depends only on substrate concentration	Rate depends on both substrate and nucleophile concentration

### 2. Elimination Reactions (Dehydrohalogenation)

Alkyl halides undergo elimination to form alkenes when heated with alcoholic KOH.



Follows Saytzeff's rule: more substituted alkene is the major product. Order of reactivity of alkyl halides:  $3^\circ > 2^\circ > 1^\circ$ . Order of reactivity of halogens:  $RI > RBr > RCl$ .

### 3. Reaction with Metals

1. **Wurtz Reaction:** Alkyl halides react with sodium in dry ether to form alkanes.



2. **Grignard Reagents:** Alkyl halides react with magnesium in dry ether to form Grignard reagents ( $RMgX$ ).



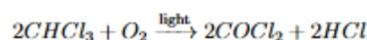
## Polyhalogen Compounds

### 1. Dichloromethane ( $CH_2Cl_2$ )

- **Uses:** Solvent, paint remover, propellant.

### 2. Chloroform ( $CHCl_3$ )

- **Preparation:** By chlorination of methane or by heating ethanol/acetone with bleaching powder.
- **Properties:** Oxidizes to phosgene ( $COCl_2$ ) in light/air. Stored in dark bottles.



- **Uses:** Solvent, anesthetic (now limited due to toxicity), in carbylamine reaction.

### 3. Iodoform ( $CHI_3$ )

- **Preparation:** By heating ethanol/acetone with iodine and NaOH.
- **Uses:** Antiseptic (due to liberated iodine).

### 4. Carbon Tetrachloride ( $CCl_4$ )

- **Uses:** Solvent, fire extinguisher (pyrene), refrigerant (Freon).

### 5. Freons (Chlorofluorocarbons, CFCs)

- **Uses:** Refrigerants, aerosols, propellants.
- **Environmental impact:** Deplete ozone layer.

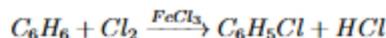
## 6. DDT (Dichlorodiphenyltrichloroethane)

- **Preparation:** From chloral and chlorobenzene.
- **Uses:** Insecticide (now banned in many countries due to environmental persistence).

## General Methods of Preparation of Haloarenes

### 1. By Electrophilic Substitution

Direct halogenation of benzene in the presence of a Lewis acid (e.g.,  $FeCl_3$ ).



### 2. From Diazonium Salts

#### 1. Sandmeyer Reaction:



#### 2. Gattermann Reaction:



## General Physical Properties of Haloarenes

- Colorless liquids or solids.
- Higher boiling points than corresponding alkanes.
- Insoluble in water, soluble in organic solvents.

## General Chemical Properties of Haloarenes

Haloarenes are less reactive towards nucleophilic substitution than alkyl halides due to resonance stabilization and  $sp^2$  hybridized carbon-halogen bond.

### 1. Nucleophilic Substitution Reactions

Require harsh conditions (high temperature, pressure).

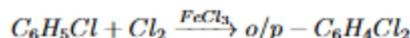


Electron-withdrawing groups (e.g.,  $-NO_2$ ) at ortho- and para-positions increase reactivity.

### 2. Electrophilic Substitution Reactions

Halogens are deactivating but ortho-para directing.

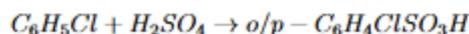
#### • Halogenation:



#### • Nitration:



#### • Sulphonation:

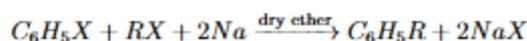


#### • Friedel-Crafts Reactions:

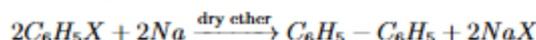


### 3. Reaction with Metals

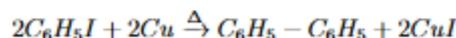
- **Wurtz-Fittig Reaction:** Alkyl halide and aryl halide react with sodium in dry ether to form alkylbenzene.



- **Fittig Reaction:** Two aryl halides react with sodium in dry ether to form biphenyl.



- **Ullmann Reaction:** Two aryl iodides react with copper powder to form biphenyl.



## Tips & Tricks

- $S_N1$  reactions often result in partial racemization with inverted product predominance.  $S_N2$  reactions form inverted products.
- Nucleophilicity order among halide ions:  $I^- > Br^- > Cl^- > F^-$ .
- In elimination reactions, the H atom is lost from the carbon with the minimum number of H atoms (Saytzeff's rule).
- Ethyl mercaptan ( $C_2H_5SH$ ) is added to LPG to detect leakage due to its typical smell.
- In Sandmeyer reaction, Cl of  $CuCl$  attaches to the benzene ring.
- Nuclear halogenation occurs via electrophilic substitution. Side chain halogenation occurs via free radical mechanism.
- Aryl halides and vinyl halides ( $CH_2 = CH - X$ ) are less reactive than alkyl halides and are not easily hydrolyzed.
- Pure chloroform (anaesthetic) does not give a precipitate with aqueous  $AgNO_3$ .
- Halothane ( $CF_3 - CHClBr$ ) is a general anaesthetic replacing diethyl ether.
- $CCL_4$  resists hydrolysis with boiling water due to non-availability of d-orbital in C.