

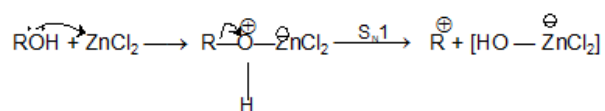
# Revision Notes on Organic Compounds Containing Halogens

Organic Compounds Containing Halogens can be divided into two groups:

- **Alkyl Halides:** Aliphatic carbon chain with halogen atom(s) as substitution. Example: Chlorobutane.
- **Aryl Halides:** Aromatic carbon ring with halogen atom(s) as substitution on ring. Example: Chlorobenzene.

## Methods of Preparation of Alkyl Halides:

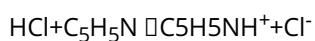
Grove's process: Replacement of "OH" group in primary and secondary alcohols with an "X" atom in presence of Zinc chloride.



The reaction follows  $\text{S}_{\text{N}}2$  mechanism when the concentration of zinc chloride is low.

**(b) Darzen Process:** Reaction of thionyl chloride with straight-chain primary alcohols without presence or absence of pyridine.

In presence of pyridine:



- **Action of a phosphorus halide on the alcohol:**  $\text{ROH} + \text{PCl}_5 \longrightarrow \text{RCl} + \text{HCl} + \text{POCl}_3$ .
- **By addition of Halogen to an alkenes:**  $\text{R-CH=CH}_2 + \text{Br}_2 + \text{CCl}_4 \longrightarrow \text{R-CH(Br)CH}_2\text{Br}$
- **Photohalogenation:**  $\text{CH}_4 + \text{Cl}_2 + h\nu \longrightarrow \text{CH}_3\text{Cl} + \text{HCl}$
- **Displacement of one halogen atom by another:**  $\text{RCl} + \text{NaI} \longrightarrow \text{RI} + \text{NaCl}$
- **Reimer-Tiemann Reaction:**  $\text{RCO}_2\text{Ag} + \text{Br}_2 \longrightarrow \text{RBr} + \text{CO}_2 + \text{AgBr}$
- **Hydrohalogenation of unsaturated hydrocarbons:**
  - In absence of peroxide:  $\text{RCH=CH}_2 + \text{HBr} \longrightarrow \text{RCH(Br)CH}_3$
  - In presence of peroxide:  $\text{RCH=CH}_2 + \text{HBr} + \text{Peroxide} \longrightarrow \text{RCH}_2\text{CH}_2\text{Br}$

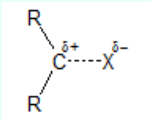
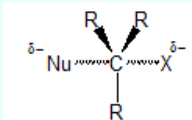
## Methods of Preparation of aryl halides

- **Halogenation:**  $\text{Ar-H} + \text{X}_2 + \text{Lewis Base} \rightarrow \text{Ar-X} + \text{HX}$

- **From diazonium salts:**

- $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{HBF}_4 \rightarrow \text{C}_6\text{H}_5\text{F}$  (Schiemann Reaction)
- $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{CuCl} \rightarrow \text{C}_6\text{H}_5\text{Cl}$  (Sandmeyer Reaction)
- $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{Cu powder} \rightarrow \text{C}_6\text{H}_5\text{Cl}$  (Gatterman Reaction)

## $\text{S}_\text{N}1$ and $\text{S}_\text{N}2$ mechanism:

	$\text{S}_\text{N}1$	$\text{S}_\text{N}2$
Steps	Two : (1) $\text{R-XI} \rightarrow \text{R}^+ + \text{X}^-$ (2) $\text{R}^+ + \text{Nu}^- \rightarrow \text{RNU}$	One : $\text{R-X} + \text{Nu}^- \rightarrow \text{RNU} + \text{X}^-$
Rate	$=k[\text{RX}]$ (1st order)	$=k[\text{RX}][\text{:Nu}^-]$ (2nd order)
TS of slow step		
Stereochemistry	Inversion and racemization	Inversion (backside attack)
Molecularity	Unimolecular	Bimolecular
Reactivity structure of R Determining Factor	$3^\circ > 2^\circ > 1^\circ > \text{CH}_3$	$\text{CH}_3 > 1^\circ > 2^\circ > 3^\circ$
Nature of X Solvent effect on rate	Stability of $\text{R}^+$ $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$ Rate increases in polar solvent	Steric hindrance in R group $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$ with $\text{Nu}^-$ there is a large rate increase in polar aprotic solvents.
Effect of nucleophile	No effect as it does not appear in the rate expression.	Rate depends on nucleophilicity $\text{I}^- > \text{Br}^- > \text{Cl}^-$ ; $\text{RS}^- > \text{RO}^-$
Catalysis	Lewis acid, eg. $\text{Ag}^+$ , $\text{AlCl}_3$ , $\text{ZnCl}_2$	None
Competitive reaction	Elimination, rearrangement	Elimination

## Reactions of Alkyl Halides:

- **Hydrolysis:**  $\text{RX} + \text{OH}^- \rightarrow \text{ROH} + \text{X}^-$
- **Williamson Synthesis:**  $\text{R-ONa} + \text{R}'\text{X} \rightarrow \text{R-R}' + \text{NaX}$
- **Reaction with dry silver oxide:**  $2\text{R-X} + \text{Ag}_2\text{O} \rightarrow \text{R-O-R}$
- **Reaction with sodio-Alkynides:**  $\text{R-C}\equiv\text{C-Na} + \text{X-R} \rightarrow \text{R-C}\equiv\text{C-R} + \text{NaX}$

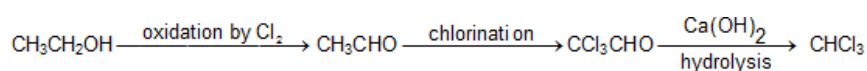
- **Reaction with potassium-cyanide:**  $\text{KCN} + \text{X-R} \rightarrow \text{RCN} + \text{KX}$
- **Reaction with silver-cyanide:**  $\text{AgCN} + \text{X-R} \rightarrow \text{RNC} + \text{AgX}$
- **Reaction with silver-nitrite:**  $\text{AgNO}_2 + \text{X-R} \rightarrow \text{RNO}_2 + \text{AgX}$
- **Reaction with potassium-nitrite:**  $\text{KNO}_2 + \text{X-R} \rightarrow \text{R-O-N=O} + \text{KX}$
- **Fridal Craft Reaction:**  $\text{R-X} + \text{C}_6\text{H}_6 + \text{AlCl}_3 \rightarrow \text{C}_6\text{H}_5\text{-R}$
- **Malonic Ester Synthesis:**  $\text{R-X} + ^-\text{CH}(\text{CO}_2\text{C}_2\text{H}_5)_2 \rightarrow \text{R-CH}(\text{CO}_2\text{C}_2\text{H}_5)_2 + \text{HX}$
- **Acetoacetic Ester Synthesis:**  $\text{R-X} + ^-\text{CH}(\text{CO}_2\text{CH}_3)_2 \rightarrow \text{R-CH}(\text{CO}_2\text{CH}_3)_2 + \text{HX}$
- **Reaction with Ammonia:**  $\text{R-X} + \text{NH}_3 \rightarrow \text{R-NH}_2 + \text{HX}$
- **Wurtz Reaction:**  $2\text{R-I} + 2\text{Na} \rightarrow \text{R-R} + 2\text{NaI}$
- **Dehydrohalogenation:**  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{Br} + \text{alco.KOH} \rightarrow \text{CH}_3\text{-CH=CH}_2 + \text{KBr} + \text{H}_2\text{O}$
- **Reaction with alcoholic  $\text{AgNO}_3$ :**  $\text{R-X} + \text{AgNO}_3 \rightarrow \text{R}^+ + \text{AgX} + \text{HNO}_3$

## Substitution Versus Elimination:

$\text{CH}_3\text{X}$	$\text{RCH}_2\text{X}$	$\text{R}_2\text{CHX}$	$\text{R}_3\text{CX}$
Methyl	1°	2°	3°
Bimolecular reactions only			$\text{S}_{\text{N}}1/\text{E}1$ or $\text{E}_2$
Gives $\text{S}_{\text{N}}2$ reactions	Gives mainly $\text{S}_{\text{N}}2$ except with a hindered strong base [e.g., $(\text{CH}_3)_3\text{CO}^-$ ] and then gives mainly $\text{E}_2$ .	Gives mainly $\text{S}_{\text{N}}2$ with weak bases (e.g., $\text{I}^-$ , $\text{CN}^-$ , $\text{RCO}_2^-$ ) and mainly $\text{E}_2$ with strong bases (e.g., $\text{RO}^-$ )	No $\text{S}_{\text{N}}2$ reaction. In solvolysis gives $\text{S}_{\text{N}}1/\text{E}1$ , and at lower temperature $\text{S}_{\text{N}}1$ is favoured. When a strong base (e.g., $\text{RCO}_2^-$ ) is used, $\text{E}_2$ predominates.

## Haloform(Tri halide):

- **Preparation:** It can be prepared from any alcohol having  $-\text{CH}(\text{OH})\text{CH}_3$  group or from the aldehydes and ketones formed from above type of alcohols i.e, from a carbonyl compound having three  $\alpha$ -hydrogen atoms by the action of  $\text{X}_2$  and an alkali or  $\text{Na}_2\text{CO}_3$ .
- **Laboratory Preparation of  $\text{CHCl}_3$ :**



- **Physical properties of  $\text{CHCl}_3$ :** colourless liquid with sweet smell and test. It is heavier than water and insoluble in it but soluble in alcohol and ether.

## Chemical Reactions of $\text{CHCl}_3$ :

- **Oxidation:**  $\text{CHCl}_3 + 1/2 \text{O}_2 \rightarrow \text{HCl} + \text{COCl}_2$  (phosgene)

- **Hydrolysis:**  $\text{CHCl}_3 + 4\text{NaOH} \rightarrow \text{HCOONa} + 3\text{NaCl} + 2\text{H}_2\text{O}$
- **Carbyl amine reactions:**  $\text{CHCl}_3 + \text{CH}_3\text{NH}_2 + 3\text{NaOH} \rightarrow \text{CH}_3\text{N}\equiv\text{C} + 3\text{NaCl} + 3\text{H}_2\text{O}$