

# 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:

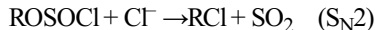
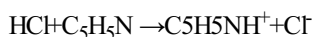
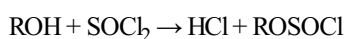
Grove's process: Replacement of "OH" group in primary and secondary alcohols with an "X" atom in presence of Zinc chloride.

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The reaction follows  $S_N2$  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:**  $ROH + PCl_5 \rightarrow RCl + HCl + POCl_3$ .
- **By addition of Halogen to an alkenes:**  $R-CH=CH_2 + Br_2 + CCl_4 \rightarrow R-CH(Br)CH_2Br$
- **Photohalogenation:**  $CH_4 + Cl_2 + h\nu \rightarrow CH_3Cl + HCl$
- **Displacement of one halogen atom by another:**  $RCl + NaI \rightarrow RI + NaCl$
- **Bonodine – Hünsdiecker Reaction:**  $RCO_2Ag + Br_2 \rightarrow RBr + CO_2 + AgBr$
- **Hydrohalogenation of unsaturated hydrocarbons:**
  - In absence of peroxide:  $RCH=CH_2 + HBr \rightarrow RCH(Br)CH_3$
  - In presence of peroxide:  $RCH=CH_2 + HBr + Peroxide \rightarrow RCH_2CH_2Br$

## Methods of Preparation of aryl halides

- **Halogenation:**  $Ar-H + X_2 + \text{Lewis Base} \rightarrow Ar-X + HX$
- **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)

## **S<sub>N</sub>1 and S<sub>N</sub>2 mechanism:**

	<b>S<sub>N</sub>1</b>	<b>S<sub>N</sub>2</b>
Steps	Two : (1) $\text{R:Xl} \rightarrow \text{R}^+ + \text{X}^-$ (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 Nature of X Solvent effect on rate	$3^\circ > 2^\circ > 1^\circ > \text{CH}_3$ Stability of $\text{R}^+$ $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$ Rate increases in polar solvent	$\text{CH}_3 > 1^\circ > 2^\circ > 3^\circ$ 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:**  $\text{KNO}_2 + \text{X-R} \rightarrow \text{R-O-N=O} + \text{KX}$

- **Friedel Craft Reaction:**  $R-X + C_6H_6 + AlCl_3 \rightarrow C_6H_5-R$
- **Malonic Ester Synthesis:**  $R-X + ^-CH(CO_2C_2H_5)_2 \rightarrow R-CH(CO_2C_2H_5)_2 + HX$
- **Acetoacetic Ester Synthesis:**  $R-X + ^-CH(CO_2CH_3)_2 \rightarrow R-CH(CO_2CH_3)_2 + HX$
- **Reaction with Ammonia:**  $R-X + NH_3 \rightarrow R-NH_2 + HX$
- **Wurtz Reaction:**  $2R-I + 2Na \rightarrow R-R + 2NaI$
- **Dehydrohalogenation:**  $CH_3-CH_2-CH_2Br + \text{alko.KOH} \rightarrow CH_3-CH=CH_2 + KBr + H_2O$
- **Reaction with alcoholic  $AgNO_3$ :**  $R-X + AgNO_3 \rightarrow R^+ + AgX \downarrow + HNO_3$

## Substitution Versus Elimination:

$CH_3X$	$RCH_2X$	$R_2CHX$	$R_3CX$
Methyl	1°	2°	3°
Bimolecular reactions only			$S_N1/E1$ or $E2$
Gives $S_N2$ reactions	Gives mainly $S_N2$ except with a hindered strong base [e.g., $(CH_3)_3CO^-$ ] and then gives mainly $E2$ .	Gives mainly $S_N2$ with weak bases (e.g., $I^-$ , $CN^-$ , $RCO_2^-$ ) and mainly $E2$ with strong bases (e.g., $RO^-$ )	No $S_N2$ reaction. In solvolysis gives $S_N1/E1$ , and at lower temperature $S_N1$ is favoured. When a strong base (e.g., $RO^-$ ) is used, $E2$ predominates.

## Haloform(Tri halide):

- **Preparation:** It can be prepared from any alcohol having  $-CH(OH)CH_3$  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  $X_2$  and an alkali or  $Na_2CO_3$ .
- **Laboratory Preparation of  $CHCl_3$ :**

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- **Physical properties of  $CHCl_3$ :** 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 $CHCl_3$ :

- **Oxidation:**  $CHCl_3 + 1/2 O_2 \rightarrow HCl + COCl_2$  (phosgene)
- **Hydrolysis:**  $CHCl_3 + 4NaOH \rightarrow HCOONa + 3NaCl + 2H_2O$
- **Carbyl amine reactions:**  $CHCl_3 + CH_3NH_2 + 3NaOH \rightarrow CH_3N \equiv C + 3NaCl + 3H_2O$