

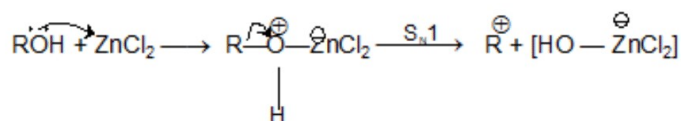
## Organic Compounds Containing Halogens:

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:

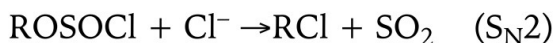
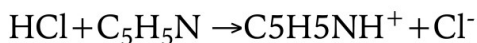
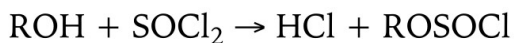
Grove's process: Replacement of "OH" group in primary and secondary alcohols with an "X" atom in presence of Zinc chloride.



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:



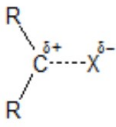
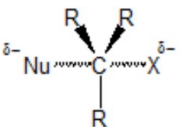
- **Action of a phosphorus halide on the alcohol:**  $\text{ROH} + \text{PCl}_5 \rightarrow \text{RCl} + \text{HCl} + \text{POCl}_3$ .
- **By addition of Halogen to an alkenes:**  $\text{R-CH=CH}_2 + \text{Br}_2 + \text{CCl}_4 \rightarrow \text{R-CH(Br)CH}_2\text{Br}$
- **Photohalogenation:**  $\text{CH}_4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

### 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 :	One :

	(1) $R:Xl \rightarrow R^+ + X^-$ (2) $R^+ + Nu^- l \rightarrow RNu$	$R:X + Nu^- l \rightarrow RNu + X^-$
Rate	$=K [RX]$ (1st order)	$=K[RX] [:Nu^-]$ (2nd order)
TS of slow step		
Stereochemistry	Inversion and racemization	Inversion (backside attack)
Molecularity	Unimolecular	Bimolecular
Reactivity structure of R Determining Factor	$3^\circ > 2^\circ > 1^\circ > CH_3$	$CH_3 > 1^\circ > 2^\circ > 3^\circ$
Nature of X Solvent effect on rate	Stability of $R^+$ $RI > RBr > RCl > RF$ Rate increases in polar solvent	Steric hindrance in R group $RI > RBr > RCl > RF$ with $Nu^-$ 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 $I^- > Br^- > Cl^-$ ; $RS^- > RO^-$
Catalysis	Lewis acid, eg. $Ag^+$ , $AlCl_3$ , $ZnCl_2$	None
Competitive reaction	Elimination, rearrangement	Elimination

## Reactions of Alkyl Halides:

- **Hydrolysis:**  $RX + OH^- \rightarrow ROH + X^-$

- **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:**  $\text{R-C}\equiv\text{C-Na} + \text{X-R} \rightarrow \text{R-C}=\text{C-R} + \text{NaX}$
- **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  $\text{AgNO}_3$ :**  $\text{R-X} + \text{AgNO}_3 \rightarrow \text{R}^+ + \text{AgX}\downarrow + \text{HNO}_3$

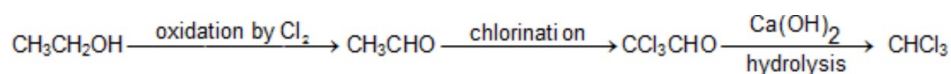
### Substitution Versus Elimination:

$\text{CH}_3\text{X}$	$\text{RCH}_2\text{X}$	$\text{R}_2\text{CHX}$	$\text{R}_3\text{CX}$
Methyl	1°	2°	3°

Bimolecular reactions only			S <sub>N</sub> 1/E1 or E <sub>2</sub>
Gives S <sub>N</sub> 2 reactions	Gives mainly S <sub>N</sub> 2 except with a hindered strong base [e.g., (CH <sub>3</sub> ) <sub>3</sub> CO <sup>-</sup> ] and then gives mainly E2.	Gives mainly S <sub>N</sub> 2 with weak bases (e.g., I <sup>-</sup> , CN <sup>-</sup> , RCO <sub>2</sub> <sup>-</sup> ) and mainly E2 with strong bases (e.g., RO <sup>-</sup> )	No S <sub>N</sub> 2 reaction. In solvolysis gives S <sub>N</sub> 1/E1, and at lower temperature S <sub>N</sub> 1 is favoured. When a strong base (e.g., RO <sup>-</sup> ) is used. E2 predominates.

### Haloform(Tri halide):

- **Preparation:** It can be prepared from any alcohol having – CH(OH)CH<sub>3</sub> group or from the aldehydes and ketones formed from above type of alcohols i.e, from a carbonyl compound having three α - hydrogen atoms by the action of X<sub>2</sub> and an alkali or Na<sub>2</sub>CO<sub>3</sub>.
- **Laboratory Preparation of CHCl<sub>3</sub>:**



- **Physical properties of CHCl<sub>3</sub>:** 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<sub>3</sub>:

- **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:**  $\text{CHCl}_3 + \text{CH}_3\text{NH}_2 + 3\text{NaOH} \rightarrow \text{CH}_3\text{N}\equiv\text{C} + 3\text{NaCl} + 3\text{H}_2\text{O}$