

Organic Compounds Containing Halogens

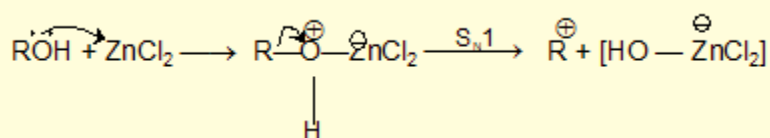
Organic Compounds Containing Halogens can be divided into two groups:

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:

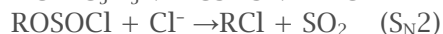
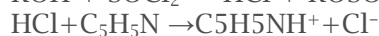
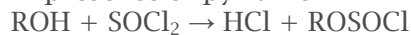
Grove's process: Replacement of "OH" group in primary and secondary alcohols with an "X" atom in presence of Zinc chloride.



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:

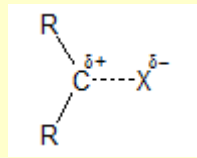
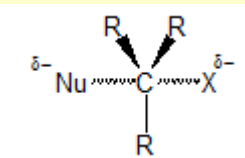


- **Action of a phosphorus halide on the alcohol:** $\text{ROH} + \text{PCl}_5 \rightarrow \text{RCl} + \text{HCl} + \text{POCl}_3$.
- **By addition of Halogen to an alkenes:** $\text{R}-\text{CH}=\text{CH}_2 + \text{Br}_2 + \text{CCl}_4 \rightarrow \text{R}-\text{CH}(\text{Br})\text{CH}_2\text{Br}$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

Methods of Preparation of aryl halides

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

S_N1 and S_N2 mechanism:

	S_N1	S_N2
Steps	Two : (1) R:Xl → R ⁺ + X ⁻ (2) R ⁺ + Nu ⁻ l → RNu	One : R:X + Nu ⁻ l → 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 Nature of X Solvent effect on rate	3 ^o > 2 ^o > 1 ^o > CH ₃ Stability of R ⁺ RI > RBr > RCl > RF Rate increases in polar solvent	CH ₃ > 1 ^o > 2 ^o > 3 ^o 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⁻ → ROH + X⁻
- **Williamson Synthesis:** R-ONa + R'X → R-R' + NaX
- **Reaction with dry silver oxide:** 2R-X + Ag₂O → R-O-R
- **Reaction with sodio-Alkynides:** R-C≡C-Na + X-R → R-C=C-R + NaX
- **Reaction with potassium-cyanide:** KCN + X-R → RCN + KX
- **Reaction with silver-cyanide:** AgCN + X-R → RNC + AgX
- **Reaction with silver-nitrite:** AgNO₂ + X-R → RNO₂ + AgX
- **Reaction with potassium-nitrite:** KNO₂ + X-R → R-O-N=O + KX
- **Fridal Craft Reaction:** R-X + C₆H₆ + AlCl₃ → C₆H₅-R
- **Malonic Ester Synthesis:** R-X + ⁻CH(CO₂C₂H₅)₂ → R-CH(CO₂C₂H₅)₂ + HX
- **Acetoacetic Ester Synthesis:** R-X + ⁻CH(CO₂CH₃)₂ → R-CH(CO₂CH₃)₂ + HX
- **Reaction with Ammonia:** R-X + NH₃ → R-NH₂ + HX
- **Wurtz Reaction:** 2R-I + 2Na → R-R + 2NaI
- **Dehydrohalogenation:** CH₃.CH₂.CH₂Br + alco.KOH → CH₃-CH = CH₂ + KBr + H₂O

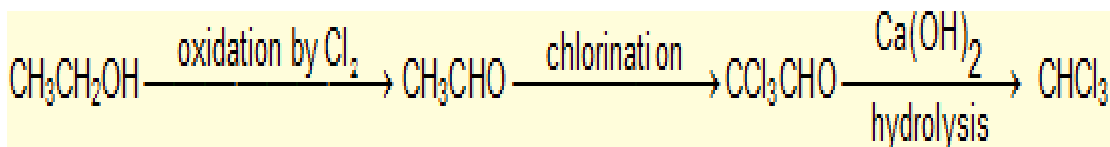
- **Reaction with alcoholic AgNO₃:** $R-X + AgNO_3 \rightarrow R^+ + AgX\downarrow + HNO_3$

Substitution Versus Elimination:

CH ₃ X	RCH ₂ X	R ₂ CHX	R ₃ CX
Methyl	1°	2°	3°
Bimolecular reactions only			S _N 1/E1 or E ₂
Gives S _N 2 reactions	Gives mainly S _N 2 except with a hindered strong base [e.g., (CH ₃) ₃ CO ⁻] and then gives mainly E ₂ .	Gives mainly S _N 2 with weak bases (e.g., I ⁻ , CN ⁻ , RCO ₂ ⁻) and mainly E ₂ with strong bases (e.g., RO ⁻)	No S _N 2 reaction. In solvolysis gives S _N 1/E1, and at lower temperature S _N 1 is favoured. When a strong base (e.g., RO ⁻) is used. E ₂ predominates.

Haloform(Tri halide):

- **Preparation:** It can be prepared from any alcohol having -CH(OH)CH₃ group or from the aldehydes and ketones formed from above type of alcohols i.e, from a carbonyl compound having three a - hydrogen atoms by the action of X₂ and an alkali or Na₂CO₃.
- **Laboratory Preparation of CHCl₃:**



- **Physical properties of CHCl₃:** 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 CHCl₃:

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