

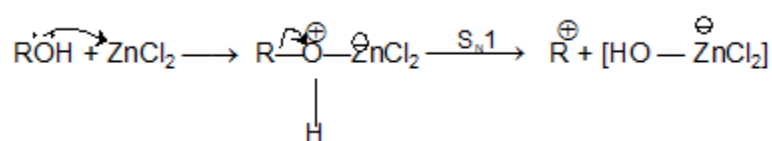
Organic Compounds Containing Halogens can be divided into two groups:

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:

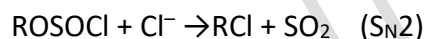
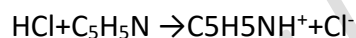
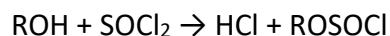
Grove's process: Replacement of "OH" group in primary and secondary alcohols with an "X" atom in presence of Zinc chloride.



The reaction follows 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: $\text{ROH} + \text{PCl}_5 \rightarrow \text{RCl} + \text{HCl} + \text{POCl}_3$.

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:

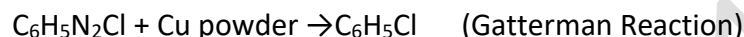
In absence of peroxide: $\text{RCH=CH}_2 + \text{HBr} \rightarrow \text{RCH(Br)CH}_3$

In presence of peroxide: $\text{RCH}=\text{CH}_2 + \text{HBr} + \text{Peroxide} \rightarrow \text{RCH}_2\text{CH}_2\text{Br}$

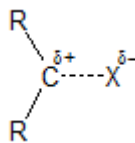
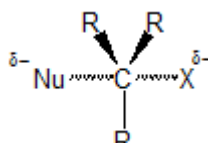
Methods of Preparation of aryl halides

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

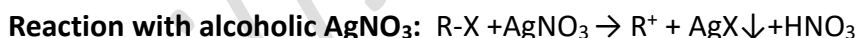
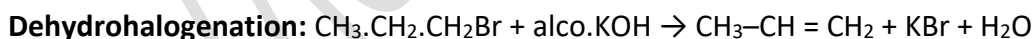
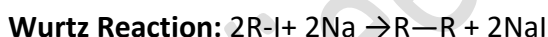
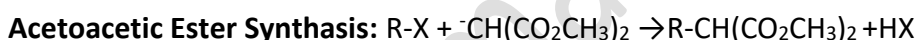
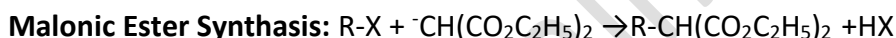
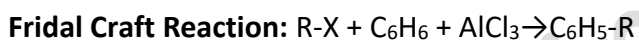
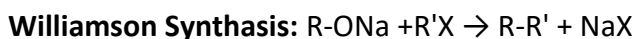
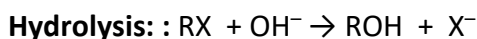
From diazonium salts:



$\text{S}_{\text{N}}1$ 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) $\text{R}^+ + \text{Nu}^- \text{I} \rightarrow \text{RNU}$	One : $\text{R:X} + \text{Nu}^- \text{I} \rightarrow \text{RNU} + \text{X}^-$
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	$3^\circ > 2^\circ > 1^\circ > \text{CH}_3$	$\text{CH}_3 > 1^\circ > 2^\circ > 3^\circ$
Determining Factor	Stability of R^+	Steric hindrance in R group
Nature of X	$\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$	$\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$
Solvent effect on rate	Rate increases in polar solvent	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 $\text{I}^- > \text{Br}^- > \text{Cl}^-$; $\text{RS}^- > \text{RO}^-$
Catalysis	Lewis acid, eg. Ag^+ , AlCl_3 , ZnCl_2	None
Competitive reaction	Elimination, rearrangement	Elimination

Reactions of Alkyl Halides:



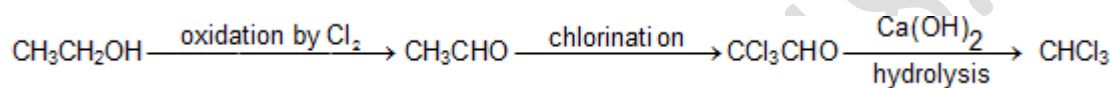
Substitution Versus Elimination:

CH_3X	RCH_2X	R_2CHX	R_3CX
Methyl	1°	2°	3°
Bimolecular reactions only			$\text{S}_\text{N}1/\text{E}1$ or 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 E_2 .	Gives mainly $\text{S}_\text{N}2$ with weak bases (e.g., I^- , CN^- , RCO_2^-) and mainly E_2 with strong bases (e.g., 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., RO^-) is used. 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 α - hydrogen atoms by the action of X_2 and an alkali or Na_2CO_3 .

Laboratory Preparation of CHCl_3 :



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

Hydrolysis: $\text{CHCl}_3 + 4\text{NaOH} \rightarrow \text{HCOONa} + 3\text{NaCl} + 2\text{H}_2\text{O}$

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