Revision Notes on Organic Compounds Containing Halogens

Organic Compounds Containing Halogens can be devided into two groups:

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

$ROH + SOCl_2 \rightarrow HCl + ROSOCl$

$HCl + C_5H_5N \rightarrow C5H5NH^+ + Cl^-$

$ROSOCl + Cl^- \rightarrow RCl + SO_2 \quad (S_N2)$

- **Action of a phosphorus halide on the alcohol:** $ROH + PCl_5 \rightarrow RCl + HCl + POCl_3$.
- **By addition of Halogen to an alefins:** $R\text{-}CH{=}CH_2 + Br_2 + CCl_4 \rightarrow R\text{-}CH(Br)CH_2Br$
- **Photohalogenation:** $CH_4 + Cl_2 + hv \rightarrow CH_3Cl + HCl$
- **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=CH2 +HBr→RCH(Br)CH3
  - In presence of peroxide: $RCH{=}CH2 + HBr + Peroxide \rightarrow RCH_2CH_{2Br}$

Methods of Preparation of aryl halides

- **Halogenation:** Ar-H + X2 +Lewis Base → Ar-x + HX
- **From diazonium salts:**

- $C_6H_5N_2Cl + HBF_4 \rightarrow C_6H_5F$ (Schiemann Reaction)
- $C_6H_5N_2Cl + CuCl \rightarrow C_6H_5Cl$ (Sandmeyer Reaction)
- $C_6H_5N_2Cl + Cu$ powder $\rightarrow C_6H_5Cl$ (Gatterman Reaction)

S_N1 and S_N2 mechanism:

	S_N1	S_N2
Steps	Two : (1) $R:Xl \rightarrow R^+ + X^-$ (2) $R^+ + Nu^- l \rightarrow RNu$	One : $R:X + Nu^- l \rightarrow RNu + X^-$
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 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: :** $RX + OH^- \rightarrow ROH + X^-$
- **Williamson Synthasis:** $R\text{-}ONa + R'X \rightarrow R\text{-}R' + NaX$
- **Reaction with dry silver oxide:** $2R\text{-}X + Ag_2O \rightarrow R\text{-}O\text{-}R$
- **Reaction with sodio-Alkynides:** $R\text{-}C{\equiv}C\text{-}Na + X\text{-}R \rightarrow R\text{-}C{=}C\text{-}R + NaX$
- **Reaction with potassium-cyanide:** $KCN + X\text{-}R \rightarrow RCN + KX$
- **Reaction with silver-cyanide:** $AgCN + X\text{-}R \rightarrow RNC + AgX$
- **Reaction with silver-nitrite:** $AgNO_2 + X\text{-}R \rightarrow RNO_2 + AgX$
- **Reaction with potassium-nitrite:** $KNO_2 + X\text{-}R \rightarrow R\text{-}O\text{-}N{=}O + KX$

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

Substitution Versus Elimination:

CH_3X	RCH_2X	R_2CHX	R_3CX
Methyl	1°	2°	3°
Bimolecular reactions only			S_N1/E1 or E_2
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 gi S_N1/E1, and at lower temperatur $_N1$ is favoured. When a strong ba (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 a - 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:** $CHCl_3 + 1/2\ O_2 \rightarrow HCl + COCl_2$ (phosgene)
- **Hydrolysis:** $CHCl_3 + 4NaOH \rightarrow HCOONa + 3NaCl + 2H_2O$
- **Carbyl amine reactions:** $CHCl_3 + CH_3NH_2 + 3NaOH \rightarrow CH_3N{\equiv}C + 3NaCl + 3H_2O$