Halogen Derivatives of Organic Compounds

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.

$$\begin{array}{ccc} \overrightarrow{ROH} + \overrightarrow{ZnCl_2} \longrightarrow & \overrightarrow{R} \xrightarrow{\frown} \overrightarrow{O} & \overrightarrow{ZnCl_2} \xrightarrow{S_N 1} & \overrightarrow{R} + [HO - \overrightarrow{ZnCl_2}] \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ \end{array}$$

The reaction follows $S_N 2$ mechanism when the concentration of zinc chloride is low.

Darzen Process: Reaction of thionyl chloride with straight-chain primary alcohols without presence or absence of pyridine.

In presence of pyridine:

 $\mathsf{ROH} + \mathsf{SOCI}_2 \rightarrow \mathsf{HCI} + \mathsf{ROSOCI}$

 $HCI+C_5H_5N \rightarrow C5H5NH^++CI^-$

 $ROSOCI + CI^{-} \rightarrow RCI + SO_2$ (S_N2)

- Action of a phosphorus halide on the alcohol: ROH + PCl₅ → RCl + HCl + POCl₃.
- By addition of Halogen to an alefins: $R-CH=CH_2+Br_2+CCI_4 \rightarrow R-CH(Br)CH_2Br$
- **Photohalogenation:** $CH_4 + Cl_2 + hv \rightarrow CH_3Cl + HCl$
- Displacement of one halogen atom by another:RCl + Nal →Rl + NaCl
- Bonodine Hünsdiecker Reaction: RCO₂Ag + Br₂→RBr + CO₂ + AgBr
- Hydrohalogenation of unsaturated hydrocarbons:
 - In absence of peroxide: $RCH=CH_2 + HBr \rightarrow RCH(Br)CH_3$
 - In presence of peroxide: RCH=CH₂ +HBr + Peroxide \rightarrow RCH₂CH_{2Br}

Methods of Preparation of aryl halides

- Halogenation: Ar-H + X_2 +Lewis Base \rightarrow Ar-x + HX
- From diazonium salts:
 - \circ C₆H₅N₂Cl + HBF₄ → C₆H₅F (Schiemann Reaction)
 - $\circ \quad C_6H_5N_2CI + CuCI \rightarrow C_6H_5CI \quad \text{(Sandmeyer Reaction)}$
 - $C_6H_5N_2CI + Cu \text{ powder } \rightarrow C_6H_5CI$ (Gatterman Reaction)
 - 0
- $S_{\rm N} 1$ and $S_{\rm N} 2$ mechanism:

	S _N 1	S _N 2	
Steps	Two : (1) R:XI \rightarrow R ⁺ + X ⁻ (2) R ⁺ + Nu ⁻ I \rightarrow RNu	One : R:X + Nu ⁻ I \rightarrow RNu + X ⁻	
Rate	=K [RX] (1st order)	=K[RX] [:Nu ⁻] (2nd order)	
TS of slow step	R CX ^{δ-} R	δ-NuX R	
Stereochemistry	Inversion and racemization	Inversion (backside attack)	
Molecularity	Unimolecular	Bimolecular	
Reactivity structure of R Determining Factor Nature of X Solvent effect on rate	3°> 2°> 1°> CH ₃ Stability of R ⁺ RI> RBr> RCI> RF Rate increases in polar solvent	CH ₃ > 1°> 2°> 3° Steric hindrance in R group RI> RBr> RCI> 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⁺, AlCl₃, ZnCl₂	None	
Competitive reaction	Elimination, rearrangement	Elimination	

Reactions of Alkyl Halides:

- **Hydrolysis:** : $RX + OH^- \rightarrow ROH + X^-$
- Williamson Synthasis: R-ONa +R'X \rightarrow R-R' + NaX
- Reaction with dry silver oxide: $2R-X + Ag_2O \rightarrow R-O-R$
- **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:** $AgNO_2+X-R \rightarrow RNO_2 + AgX$
- **Reaction with potassium-nitrite:** $KNO_2+X-R \rightarrow R-O-N=O+KX$
- Fridal Craft Reaction: $R-X + C_6H_6 + AlCl_3 \rightarrow C_6H_5-R$
- Malonic Ester Synthasis: $R-X + CH(CO_2C_2H_5)_2 \rightarrow R-CH(CO_2C_2H_5)_2 +HX$
- Acetoacetic Ester Synthasis: $R-X + CH(CO_2CH_3)_2 \rightarrow R-CH(CO_2CH_3)_2 + HX$
- **Reaction with Ammonia:** $R-X + NH_3 \rightarrow R-NH_2 + HX$
- Wurtz Reaction: $2R-I+ 2Na \rightarrow R-R + 2NaI$
- **Dehydrohalogenation:** $CH_3.CH_2.CH_2Br + alco.KOH \rightarrow CH_3-CH = CH_2 + KBr + H_2O$
- Reaction with alcoholic AgNO₃: R-X +AgNO₃ \rightarrow R⁺ + AgX \downarrow +HNO₃

Substitution Versus Elimination:

CH₃X	RCH₂X	R₂CHX	R₃CX
Methyl	1°	2°	3°
Bimolecular reactions only			$S_N1/E1$ 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 E2.	Gives mainly $S_N 2$ with weak bases (e.g., I ⁻ , CN^- , RCO_2^-) and mainly E2 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. E2 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 X₂and an alkali or Na₂CO₃.
- Laboratory Preparation of CHCl₃:

$$CH_{3}CH_{2}OH \xrightarrow{\text{oxidation by Cl}_{2}} CH_{3}CHO \xrightarrow{\text{chlorination}} CCl_{3}CHO \xrightarrow{\text{Ca(OH)}_{2}} CHCl_{3}$$

• **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 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: CHCl₃ + CH₃NH₂ + 3NaOH →CH₃N≡C +3NaCl +3H
- 5. Hydroboration-Oxidation:



Examples:



6. Halogen Addition in Non-polar Solvent:



7. Halogen Addition in Aqueous Medium:





9. Ozonolysis of Alkenes:



Alkyne

- Saturated open chain hydrocarbon with general formula (C_nH_{2n-2}).
- At least one -c=c- (triple bond) group i.e. sp hybridisation, is present throughout the chain.
- Physical properties of alkynes are similar to those of the corresponding alkenes

Preparation

1. Dehydrohalogenation of vic-Dihalides or gem-Dihalides



2. Dehalogenation of vic-Tetrahalogen Compounds

$$\begin{array}{c} CH_{3} \longrightarrow CBr_{2} \longrightarrow CBr_{2} \longrightarrow CH_{3} + 2Zn \xrightarrow{EtOH} cH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3} + 2ZnBr_{2} \\ 2,2,3,3 \xrightarrow{Tetrabromobutane} & cH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3} + 2ZnBr_{2} \\ 2-butyne \end{array}$$

3. Alkyl Substitution in Acetylene; Acidity of ^o C-H

$$HC = CH + NaNH_2 \xrightarrow{Iiq. NH_3} HC = CNa^{+} \xrightarrow{n-C_4H_9Br} CH_3(CH_2)_3C = CH_$$

4. From Calcium Carbide:

 $CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$

5. Kolbe's Electrolysis:

$$\begin{array}{c} \mathsf{CHCO}_2\mathsf{Na} \\ || \\ \mathsf{CHCO}_2\mathsf{Na} \end{array} \xrightarrow{+2\mathsf{H}_2\mathsf{O}, \texttt{ourrent}} & \mathsf{CH} \\ \mathsf{CHCO}_2\mathsf{Na} \end{array} \xrightarrow{+2\mathsf{H}_2\mathsf{O}, \texttt{ourrent}} & \mathsf{CH} \\ \mathsf{CH} \\ \mathsf{CH} \end{array} + 2\mathsf{CO}_2 + 2\mathsf{Na}\mathsf{OH} + \mathsf{H}_2 \\ \mathsf{CH} \end{array}$$

Chemical Properties

- 1. Hydrogenation: RC = CCH₂CH₃ + 2H₂ \rightarrow CH₃CH₂CH₂CH₂CH₃
- 2. Hydro-halogenation:

 $\textbf{Markovnikov addition: } RC{=}CH + HBr \rightarrow RCBr{=}CH_2 + HBr \rightarrow RCBr_2 - CH_3$

Anti-markovnikov addition: RC=CH +HBr +peroxide \rightarrow RCH=CHBr

3. Hydration:

$$CH = CH + H_2O \xrightarrow{H_2SO_4} [CH_2 = CHOH] \longrightarrow CH_3CHO$$

4. Addition of boron hydride:

$$R'-C = C - H + R_2BH \xrightarrow{R'} C = C + H \xrightarrow{H_2O_2, NaOH} R'CH_2CHO$$

$$H = BR_2 \xrightarrow{CH_3COOH} R'CH= CH_2$$

5. Dimerization:

$$2 \text{ H} - \text{C} = \text{C} - \text{H} \xrightarrow{\text{Cu(NH_3)_2}^+\text{Cl}^-}_{\text{H_2O}} \text{H_2C} = \text{CH} - \text{C} = \text{CH}$$

Vinylacetylene

6. Oxidation:

 $\begin{array}{c} CH_{3}CH_{2}C \equiv C-CH_{3} + 2KMnO_{4} \rightarrow CH_{3}CH_{2}COOK + CH_{3}COOK + 2MnO_{2} + 2H_{2}O \\ CH_{3} \\ \vdots \\ CH_{3}-CH-C \equiv C CH_{2} CH_{2}CH_{3} \xrightarrow{\text{ox dn.}} CH_{3}CH_{2}CH_{2}CO_{2}H + CH_{3}CH_{2}CH_{2}CO_{2}H \\ (Two isomeric acids each having M.F. C_{4}H_{8}O_{2}) \end{array}$

7. Ozonolysis Hydrolysis:

$$\begin{array}{c} CH_{3}C \equiv CCH_{2}CH_{3} & \xrightarrow{1. O_{3}} \\ 2\text{-Pentyne} & 2\text{-hydrolysis} \end{array} \xrightarrow{CH_{3}COOH + HOOCCH_{2}CH_{3}} \\ Acetic acid & Propanoic acid \end{array}$$

8. Cyclic polymerization:



Aromatic Hydrocarbons:

For being aromatic a hydrocarbon should

- be a cyclic compounds.
- have planarity in geometry.
- have complete delocalization of electrons over ring.
- follow Huckel Rule i.e. number of ?? electrons in ring = (4n+2).









:

Benzene

Toluene

(Cumene)

Isopropyl benzene

Benzene (C₆H₆)

1. Structure:



2. Chemical Reactions of Benzene:



Benzene hexachloride

Anti-aromatic Hydrocarbons:

Highly unstable compounds.

Number of π electrons in ring = 4n.

Example: