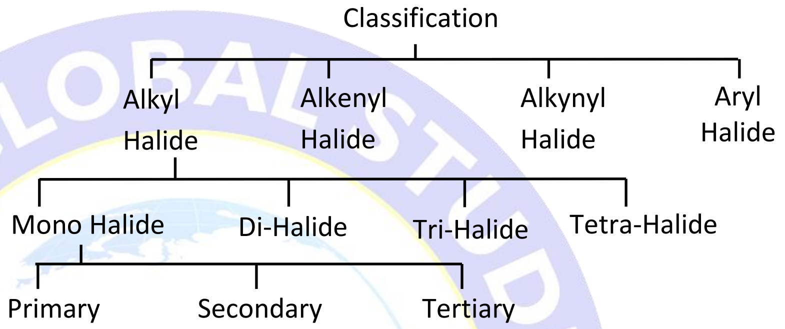
Chapter 01

Halogen Derivatives

CONTENT

INTRODUCTION

Halogen derivative from hydrocarbons by replacement of one or more H-atom by corresponding no. of halogen atom are known as Halogen derivative.



MONO HALIDES

General methods of preparation of monohalide (5 methods)

(1) From alcohol

(i) From ($SOCl_2$) in presence of pyridine

$$R-OH\xrightarrow[\Delta\text{pyridine}]{SOCl_2}R-Cl+SO_2+HCl$$

It is known as darzen's method

(ii) From PCl_5

$$R-OH+PCl_5\longrightarrow R-Cl+HCl+POCl_3$$

(iii) From PX_3

$$3R-OH+PX_3\xrightarrow{(X=Cl,Br,I)}3R-X+H_3PO_3$$

(iv) Lucas test

$R-OH+HX\xrightarrow{ZnCl_2}R-X+H_2O$ (anhydrous $ZnCl_2$ + conc.HCl is lucas reagents)

Rate of reaction tertiary alcohol > Secondary alcohol > Primary alcohol

(2) Halogenation of Alkane: –

Halogenation take place either at high temp. (573-773 K) or in presence of diffuse sun light or ultraviolet light Rate of reaction of alkane with halogen $F_2 > Cl_2 > Br_2 > I_2$

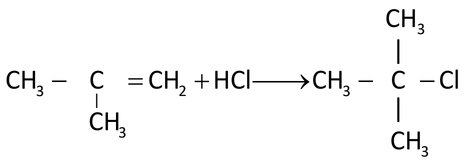
Eg. $CH_4+Cl_2\xrightarrow{Heat/light}CH_3Cl+HCl$

$R-H+Cl_2\xrightarrow{Heat/light}R-Cl+HCl$

(3) Addition of hydrogen halides: –

Hydrogen halide react with alkene to form alkyl halide. The order of reactivity of hydrogen halide is HI > HBr > HCl

$$CH_2=CH_2+HBr\longrightarrow CH_3-CH_2-Br$$



$$CH_3-\underset{\substack{|\\CH_3}}{C}=CH_2+HCl\longrightarrow CH_3-\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{C}}-Cl$$

(4) By halide exchange

(1) Finkelstein reaction

$R-Cl$ or $R-Br + KI \xrightarrow{\text{Acetone}} R-I + KCl$ or KBr

(2) Swartz reaction

$$2CH_3Cl + Hg_2F_2 \xrightarrow{\text{water}} 2CH_3-F + Hg_2Cl_2$$

SPOT LIGHT

- Finkelstein reaction can only be used to prepare $R-I$ and swart reaction can only be used to prepare $R-F$.
- Darzen method is best method to prepare pure halo alkane.
- $R-X$ gives Beliestein test except $R-F$.

(5) Borodine – Hunsdicker's reaction :

$$R-COOAg + X_2 \xrightarrow[\Delta]{CCl_4} R-X + CO_2 + AgX$$

Silver salt of fatty acid (Cl₂ or Br₂)

 # Physical Properties

(a) Lower member of alkyl Halides are gases at room temp

Eg. CH_3F, CH_3Cl, CH_3Br, C_2H_5Cl, C_2H_5F

(b) Boiling point is higher than parent alkane Decreasing order of Boiling point. is

$R-I > R-Br > R-Cl > R-F$

Among isomeric $R-X$, decreasing order of Boiling point. is primary > secondary > tertiary

(c) $R-F$ & $R-Cl \rightarrow$ lighter than water

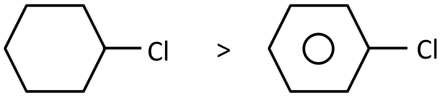
$R-Br$ & $R-I \rightarrow$ Heavier than water

Decreasing order of density is $R-I > R-Br > R-Cl > R-F$

(d) $R-X$ are polar co-valent compound but insoluble in water they dissolve in organic solvents

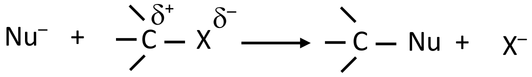
(e) Dipole moment order

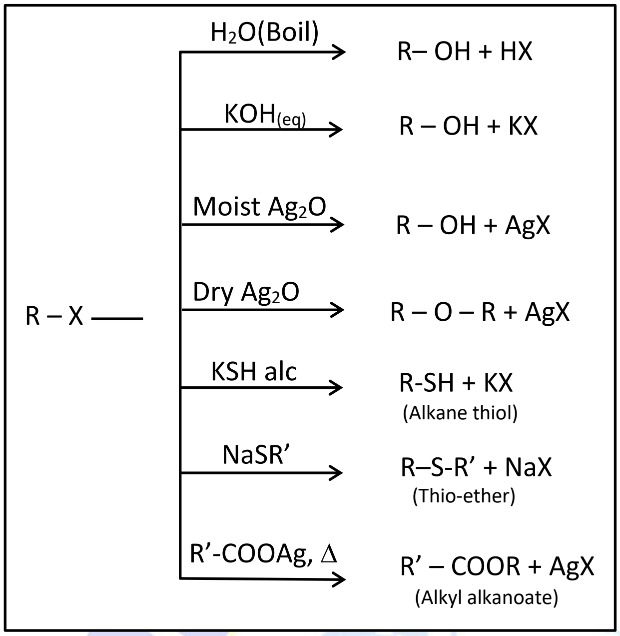
$CH_3Cl > CH_3F > CH_3Br > CH_3I$



- **Chemical Reactions**

(1) Nucleophilic substitution Reaction (S_N)





$$R-X \xrightarrow{H_2O(Boil)} R-OH + HX$$

$$R-X \xrightarrow{KOH_{(eq)}} R-OH + KX$$

$$R-X \xrightarrow{Moist\ Ag_2O} R-OH + AgX$$

$$R-X \xrightarrow{Dry\ Ag_2O} R-O-R + AgX$$

$$R-X \xrightarrow{KSH\ alc} R\text{-}SH + KX$$

(Alkane thiol)

$$R-X \xrightarrow{NaSR'} R-S-R' + NaX$$

(Thio-ether)

$$R-X \xrightarrow{R'\text{-}COOAg,\ \Delta} R'-COOR + AgX$$

(Alkyl alkanoate)

Difference between S_N1 and S_N2 mechanism

S.NO.	**S_N1**	**S_N2**
(i)	First order reaction.	Second order reaction
(ii)	Rate = k [RX]	Rate = k[RX] [Nu]
(iii)	Racemic mixture	Inversion of configuration
(iv)	Two step reaction	One step reaction
(v)	Order: $CH_3X < 1° < 2° < 3°$	Order: $CH_3X > 1° > 2° > 3°$

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Important conversions

$R-X + KCN \rightarrow R-CN + KX$

$R-CN \xrightarrow{Na, C_2H_5OH \text{ or } LiAlH_4 \text{ or } Ni/H_2} R-CH_2NH_2 \xrightarrow{HONO} RCH_2OH$

$R-CN \xrightarrow{H_3O^+} R-COOH \xrightarrow{NH_3} R-CONH_2$

$R-COOH \xrightarrow{LiAlH_4} RCH_2OH$

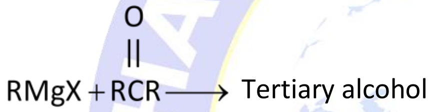
$R-COOH \xrightarrow{PCl_5 \text{ or } PCl_3 \text{ or } SOCl_2} R-COCl$

$R-X + Mg \xrightarrow{\text{Dry Ether}} RMgX$

$RMgX + CO_2 \longrightarrow RCOOH$

$RMgX + HCHO \longrightarrow$ Primary alcohol

$RMgX + RCHO \longrightarrow$ Secondary alcohol



$RMgX + R\overset{\overset{\displaystyle O}{\|}}{C}R \longrightarrow$ Tertiary alcohol

- **Reaction with KCN & AgCN**

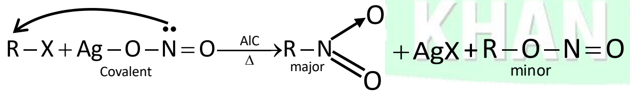
$\overset{\delta+}{R}-\overset{\delta-}{X} + \underset{\text{Ionic}}{\overset{+\ -}{KCN}} \xrightarrow[\Delta]{Alc} \underset{\text{major}}{R-CN} + \underset{\text{minor}}{R-NC} + KX$

$R-X + \underset{\text{Covalent}}{Ag\ddot{C}N} \rightarrow \underset{\text{major}}{R-\overset{+}{N}} \equiv \overset{-}{C} + \underset{\text{(minor)}}{R-CN} + AgX$

$R-X + \underset{\text{Covalent}}{Ag\ddot{C}N} \rightarrow \underset{\text{major}}{R-N\equiv C} + \underset{\text{(minor)}}{R-CN} + AgX$ ($:\overset{\ominus}{C}\equiv N:$ ion is an ambidentate nucleophile)

- **Reaction with KNO_2 & $AgNO_2$**

$R-X + \underset{\text{Ionic}}{\overset{+\ -}{KO}-NO} \xrightarrow[\Delta]{Alc} \underset{\text{major}}{R-O-N=O} + \underset{\text{minor}}{R-NO_2} + KX$

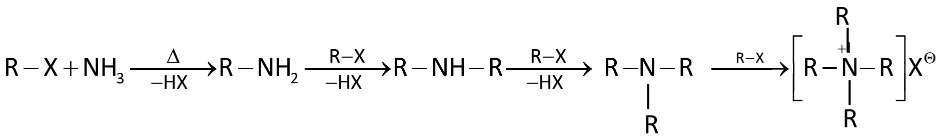


$R-X + \underset{\text{Covalent}}{Ag-O-\ddot{N}=O} \xrightarrow[\Delta]{Alc} \underset{\text{major}}{R-N(\rightarrow O)=O} + AgX + \underset{\text{minor}}{R-O-N=O}$

- **Reaction with sodium alkoxide (NaOR')**

$R-X + NaOR' \rightarrow \underset{\text{(williamson synthesis Reaction)}}{R-OR' + NaX}$

- **Reaction with NH_3**

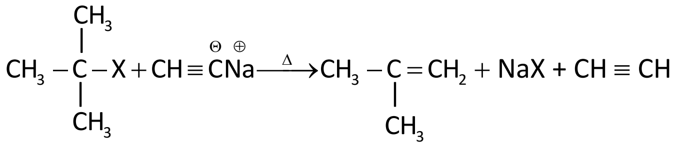


$R-X + NH_3 \xrightarrow[-HX]{\Delta} R-NH_2 \xrightarrow[-HX]{R-X} R-NH-R \xrightarrow[-HX]{R-X} R-\underset{\displaystyle R}{\underset{|}{N}}-R \xrightarrow{R-X} \left[R-\underset{\displaystyle R}{\underset{|}{\overset{\displaystyle R}{\overset{|}{\overset{+}{N}}}}}-R\right]X^{\ominus}$

- **Reaction with $CH\equiv CNa$**

$\overset{\delta+}{R}-\overset{\delta-}{X} + CH\equiv \overset{-\ +}{CNa} \xrightarrow{\Delta} R-C\equiv CH + NaX$

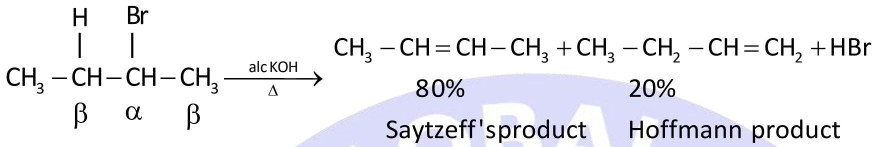
If 3° halide



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-X+CH\equiv\overset{\ominus}{C}\overset{\oplus}{Na}\xrightarrow{\Delta}CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2+NaX+CH\equiv CH$$

Dehydrohalogenation:- Alkyl halide undergo β elimination on treatment with alc KOH or $NaNH_2$

$$R-\overset{\beta}{CH_2}-\overset{\alpha}{CH_2}-X+KOH(alc)\xrightarrow{\Delta}R-CH=CH_2+KX+H_2O$$



$$CH_3-\underset{\beta}{\overset{H}{\overset{|}{C}H}}-\underset{\alpha}{\overset{Br}{\overset{|}{C}H}}-\underset{\beta}{CH_3}\xrightarrow[\Delta]{alc\,KOH}\underset{\underset{\text{Saytzeff'sproduct}}{80\%}}{CH_3-CH=CH-CH_3}+\underset{\underset{\text{Hoffmann product}}{20\%}}{CH_3-CH_2-CH=CH_2}+HBr$$

SPOT LIGHT

Substitution Vs Elimination reaction

Reaction	Solvent	Nucleophile/base	Leaving group	Substrate structure
S_N1	**Very strong effect :** Reaction favored by polar solvents.	**Weak effect:** Reaction favored by good nucleophile/weak base.	**Strong effect:** Reaction favored by good leaving group.	**Strong effect:** Reaction favored by 3°, allylic, and benzylic substrates.
S_N2	**Strong effect:** Reaction favored by polar aprotic solvents.	**Strong effect:** Reaction favored by good nucleophile/weak base.	**Strong effect:** Reaction favored by good leaving group.	**Strong effect:** Reaction favored by 1°, allylic, and benzylic substrates.
E_1	**Very strong effect:** Reaction favored by polar solvents.	**Weak effect:** Reaction favored by weak base.	**Strong effect:** Reaction favored by good leaving group.	**Strong effect:** Reaction favored by 3°, allylic, and benzylic substrates.
E_2	**Strong effect:** Reaction favored by polar aprotic solvents.	**Strong effect:** Reaction favored by poor nucleophile/strong base.	**Strong effect:** Reaction favored by good leaving group.	**Strong effect:** Reaction favored by 3° substrates.

Wurt'z Reaction :- $2RX+2Na\xrightarrow[\text{ether}]{\text{Dry}}R-R+2NaX$

when a mix of alkyl halides, (R_1-X) & (R_2-X) is used a mixture of alkane is formed

$R_1-X+2Na+X-R_2\xrightarrow[\Delta]{\text{Dry ether}}R_1-R_2+R_1-R_1+R_2-R_2$

- **Organometallic Compounds**

(1) Grignard reagent (RMgX)

$R-X+Mg\xrightarrow{\text{dry ether}}R-MgX$

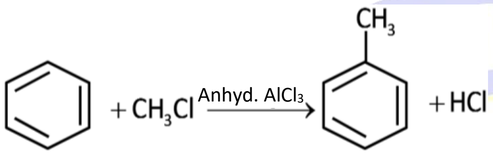
(2) Frankland reagent $(C_2H_5)_2Zn$

$2C_2H_5Br+2Zn\xrightarrow[\text{ether}]{\text{dry}}(C_2H_5)_2Zn+ZnBr_2$

(3) $4C_2H_5Cl + 4Na/Pb \rightarrow (C_2H_5)_4Pb + 4NaCl + 3Pb$

Tetra ethyl lead (used as antiknocking agent)

- **Friedel – craft reaction:**

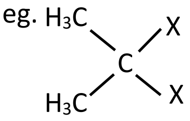
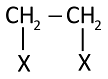
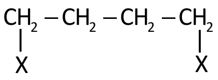


Toluene

DIHALIDES

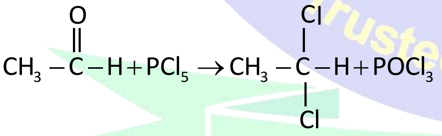
General formula $C_nH_{2n}X_2$. Two H-atom of alkanes, replaced by two halogen atom to form dihalides,

Classification

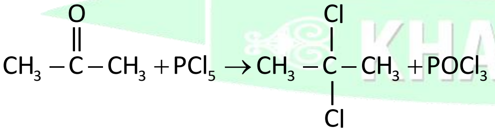
Gem dihalide	Vic dihalide	α, ω dihalide
Two similar halogen attached to same c – atom	Two halogen atoms are attached on adjacent carbon atom	Two halogen atoms separated by 3 or more C- atom. They are attached with terminal C-atom
eg. 	eg.  $\underset{X}{CH_2}-\underset{X}{CH_2}$	eg.  $\underset{X}{CH_2}-CH_2-CH_2-\underset{X}{CH_2}$

- **Preparation of gem-dihalides**

(i) By reaction of PCl_5 on carbonyl compound

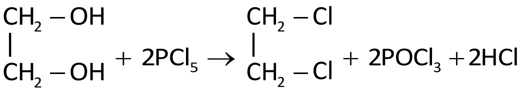


$CH_3-\overset{O}{\overset{\|}{C}}-H+PCl_5\rightarrow CH_3-\overset{Cl}{\underset{Cl}{C}}-H+POCl_3$



$CH_3-\overset{O}{\overset{\|}{C}}-CH_3+PCl_5\rightarrow CH_3-\overset{Cl}{\underset{Cl}{C}}-CH_3+POCl_3$

⇒ Preparation vic-halide

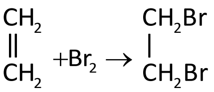


$\begin{matrix}CH_2-OH\\|\\CH_2-OH\end{matrix}+2PCl_5\rightarrow\begin{matrix}CH_2-Cl\\|\\CH_2-Cl\end{matrix}+2POCl_3+2HCl$

(ii) By addition of halogen acids on alkynes

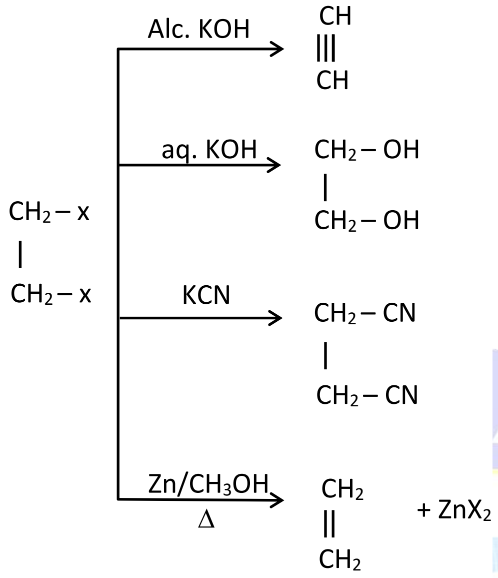
$CH\equiv CH+HBr\rightarrow \underset{\substack{\text{vinyl}\\\text{Bromiole}}}{CH_2=CHBr}\xrightarrow{HBr}CH_2BrCH_2Br$

(iii) By addition of halogen to alkenes.



$\begin{matrix}CH_2\\\|\\CH_2\end{matrix}+Br_2\rightarrow\begin{matrix}CH_2Br\\|\\CH_2Br\end{matrix}$

Chemical Reaction of dihalide



TRI-HALIDE (Halo form CHX_3)

- **Preparation**

(i) From CH_4: – $CH_4 + 3Cl_2 \xrightarrow{h\nu} CHCl_3 + 3HCl$

(ii) By halo form reaction

$$\left.\begin{array}{c} CH_3CH_2-OH \\ \text{or} \\ CH_3-CO-CH_3 \end{array}\right] \xrightarrow[{[CaOCl_2]H_2O/\Delta}]{\text{Bleaching powder}} CHCl_3 + (H_3COO)_2\,Ca \ \text{ or } \ (CH_3COO)_2\,Ca$$

Mechanism

$CaOCl_2 + H_2O \longrightarrow 2Cl + Ca(OH)_2$

$CH_3CH_2-OH + 2Cl \longrightarrow CH_3CHO + 2HCl(\text{oxidation})$

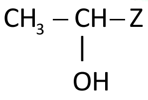
$CH_3CHO + 6Cl \longrightarrow CCl_3CHO + 3HCl(\text{Halogenation})$

$CH_3CHO + Ca(OH)_2 \longrightarrow CHCl_3 + (HCOO)_2Ca(\text{Hydrolysis})$

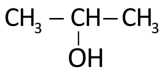
If CH_3COCH_3 is used then $CHCl_3$ is formed into 2 step (Chlorination & Hydrolysis)

Positive haloform reaction: – Reaction which give haloform with alkali & X_2 is called as (+ve) haloform reaction.

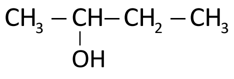
Eg. Alcohols: –



$CH_3-\underset{\underset{OH}{|}}{CH}-Z$



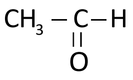
$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$



$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3$

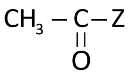
etc.

Aldehydes only acetaldehyde



$CH_3-\underset{\underset{O}{||}}{C}-H$

Ketone



$CH_3-\underset{\underset{O}{||}}{C}-Z$

($Z = CH_3, C_2H_5, COOH, CHO$)

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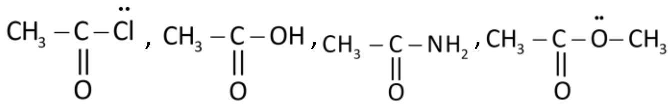
Negative haloform reaction:- Reaction in which haloform are not formed with X_2 & alkali.

Eg. 
$CH_3-\underset{\underset{O}{\|}}{C}-\ddot{Cl}$, $CH_3-\underset{\underset{O}{\|}}{C}-OH$, $CH_3-\underset{\underset{O}{\|}}{C}-NH_2$, $CH_3-\underset{\underset{O}{\|}}{C}-\ddot{O}-CH_3$

do not show haloform reaction

- **$CHCl_3$**

Preparation

$$\underset{\text{chloralhydrate}}{CCl_3.CHO.2H_2O} \xrightarrow[\Delta]{NaOH} \underset{\text{(pure chloroform)}}{CHCl_3} + HCOONa + 2H_2O$$

Industrial preparation

$$\begin{matrix}CH_3CH_2-OH\\ \text{or}\\ CH_3COCH_3\end{matrix} \xrightarrow[\text{electrolysis}]{\text{aq.NaCl}} CHCl_3 + \begin{matrix}HCOONa\\ \text{or}\\ CH_3COONa\end{matrix}$$

Physical properties

→ $CHCl_3$ is colourless
→ $CHCl_3$ sweet smelling liquid
→ Boiling point is 61°C
→ Insoluble in H_2O
→ Density more than H_2O
→ Used as Anaesthetic.

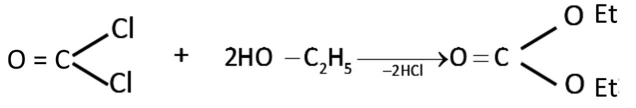
Chemical properties: –

(i) Oxidation: – $CHCl_3 + [O] \xrightarrow{\text{Air \& Light}} \underset{\text{Phosgene gas}}{COCl_2} + HCl$

Phosgene gas or carbonyl chloride (Poisonous gas)

Prevent oxidation

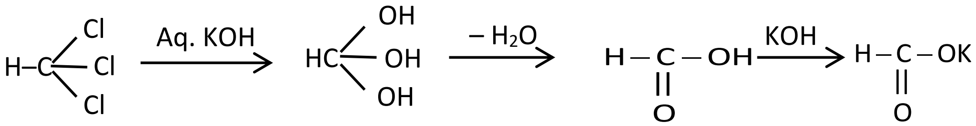
$CHCl_3$ is stored in dark colored bottle which are filled upto the brim to prevent oxidation of $CHCl_3$ into $COCl_2$ and 1 % ethanol is also added to chloroform.



Poisonous

Di-ethyl carbonate
[Non-Poisonous]

(ii) Hydrolysis



(iii) Carbyl amine reaction or isocyanide test:-

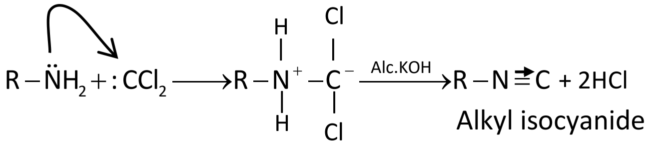
$$R-NH_2 \xrightarrow{CHCl_3+KOH} R-NC$$

Primary amines (Aliphatic or Aromatic) $\xrightarrow{CHCl_3+KOH}$ Isocyanides → (unpleasant or offensive smell)

Mechanism

$CHCl_3 \xrightarrow{KOH} :CCl_2$

(electrophile)



$$R-\ddot{N}H_2 + :CCl_2 \longrightarrow R-\overset{H}{\underset{H}{N^+}}-\overset{Cl}{\underset{Cl}{C^-}} \xrightarrow{Alc.KOH} R-N \overset{\rightarrow}{=} C + 2HCl$$

Alkyl isocyanide

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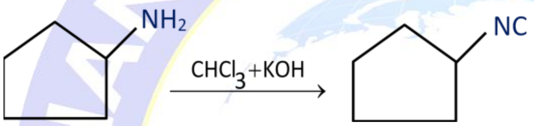
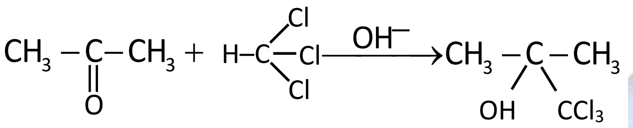
$CH_3CH_2-NH_2 \xrightarrow{CHCl_3+KOH} CH_3CH_2-NC$

$Ph-NH_2 \xrightarrow{CHCl_3+KOH} Ph-NC$



Reaction given by Only primary amine

(iv) Reaction with CH_3COCH_3



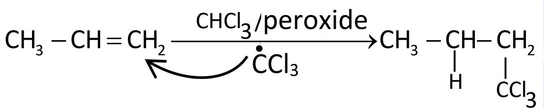
$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + H-C\begin{smallmatrix}Cl\\-Cl\\Cl\end{smallmatrix} \xrightarrow{OH^-} CH_3-\underset{OH\ \ CCl_3}{C}-CH_3$$

(v) Reaction with HNO_3

$CCl_3-\boxed{H+OH}-NO_2 \longrightarrow CCl_3-NO_2 + H_2O$

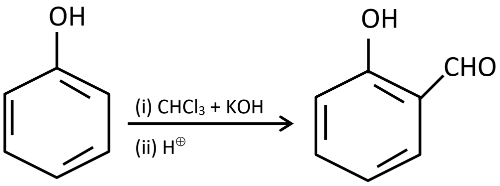
Chloropicrin

(vi) Reaction with $CH_3CH = CH_2$



$$CH_3-CH=CH_2 \xrightarrow[\dot{C}Cl_3]{CHCl_3/peroxide} CH_3-\underset{H}{CH}-\underset{CCl_3}{CH_2}$$

(vii) Reimer Tiemann's Reaction:-

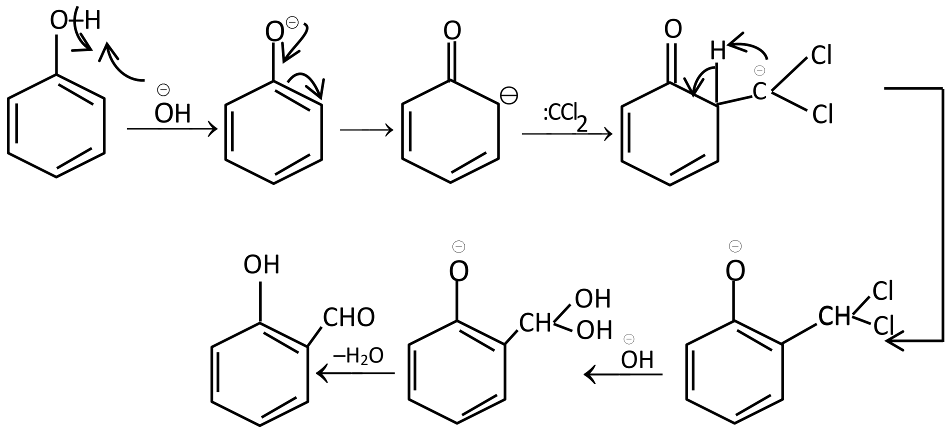


salicylaldehyde

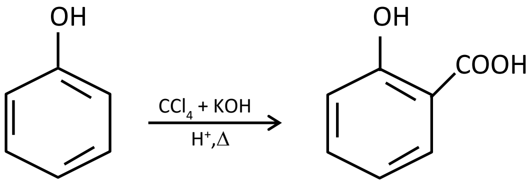
Mechanism

$CHCl_3 \xrightarrow{KOH} :CCl_2$

(dichlorocarbene)



CCl_4 is used in place of $CHCl_3$



Salicylic acid

(viii) Reaction with Ag

$$2CHCl_3 + 6Ag \longrightarrow CH \equiv CH + 6AgCl$$

SPOT LIGHT

Iodoform Test

$$\left.\begin{matrix} CH_3CH_2OH \\ \text{or} \\ CH_3COCH_3 \end{matrix}\right\} \xrightarrow[\text{or } I_2 + Na_2CO_3 + H_2O]{I_2 + NaOH \text{ or } NaOI} \underset{\text{Yellow crystal of iodoform.}}{CHI_3}$$

- CHI_3 give yellow ppt of AgI with $AgNO_3$ but $CHCl_3$ does not give AgCl ppt because CHI_3 is thermally less stable than $CHCl_3$.

SPOT LIGHT

Iodoform test can be used to distinguish the following pairs of compound:-

(1) CH_3CH_2OH and CH_3OH

(2) CH_3CHO & CH_3CH_2CHO

(3) 2 Pentanol & Pentanol

(4) Acetophenone & Benzophenone

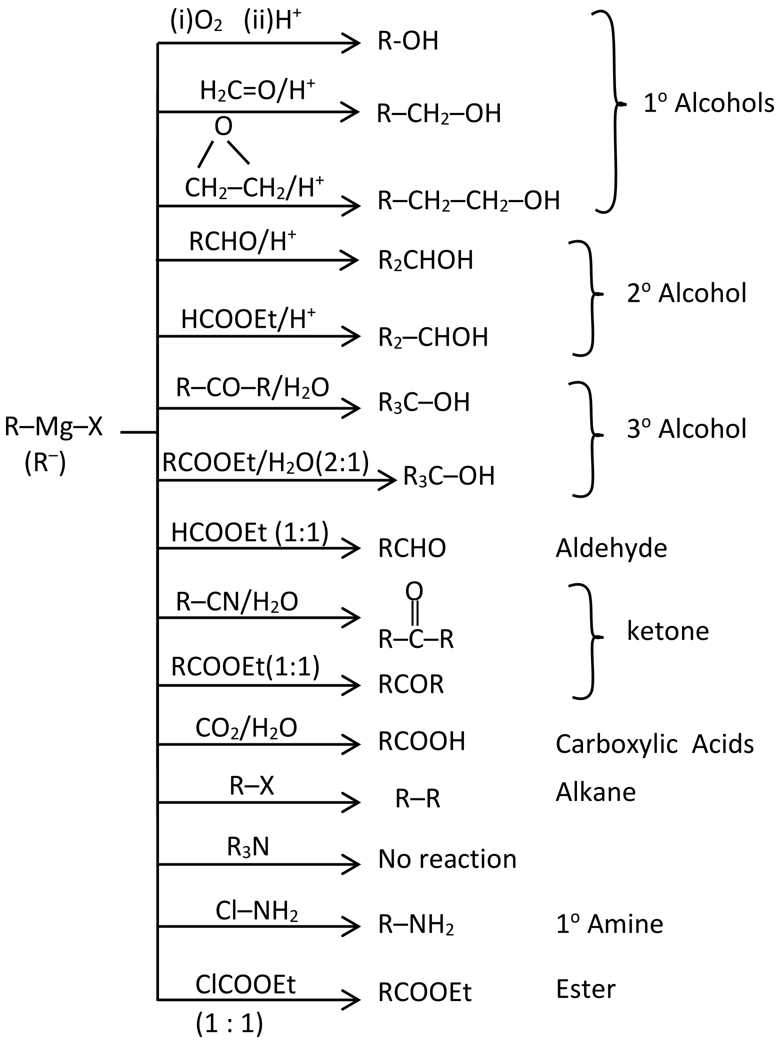
(5) 2 Propanol & 1 Propanol

- **Grignard Regent**

$$R-X+Mg\xrightarrow[\text{ether}]{\text{dry}}R-Mg-X$$

It is used to formation of many compound like 1°, 2°, 3° Alcohols, Aldehyde, Ketone, Acids, Alkane, Alkene etc.

Reaction



$R{-}Mg{-}X\ (R^-)$

$\xrightarrow{(i)O_2\ (ii)H^+}$ R-OH

$\xrightarrow{H_2C=O/H^+}$ $R{-}CH_2{-}OH$

$\xrightarrow{CH_2{-}CH_2\ (O)/H^+}$ $R{-}CH_2{-}CH_2{-}OH$

} 1° Alcohols

$\xrightarrow{RCHO/H^+}$ R_2CHOH

$\xrightarrow{HCOOEt/H^+}$ $R_2{-}CHOH$

} 2° Alcohol

$\xrightarrow{R{-}CO{-}R/H_2O}$ $R_3C{-}OH$

$\xrightarrow{RCOOEt/H_2O(2:1)}$ $R_3C{-}OH$

} 3° Alcohol

$\xrightarrow{HCOOEt\ (1:1)}$ RCHO Aldehyde

$\xrightarrow{R{-}CN/H_2O}$ $R{-}\overset{O}{\overset{\|}{C}}{-}R$

$\xrightarrow{RCOOEt(1:1)}$ RCOR

} ketone

$\xrightarrow{CO_2/H_2O}$ RCOOH Carboxylic Acids

$\xrightarrow{R{-}X}$ R–R Alkane

$\xrightarrow{R_3N}$ No reaction

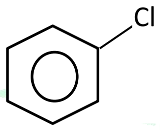
$\xrightarrow{Cl{-}NH_2}$ $R{-}NH_2$ 1° Amine

$\xrightarrow[(1:1)]{ClCOOEt}$ RCOOEt Ester

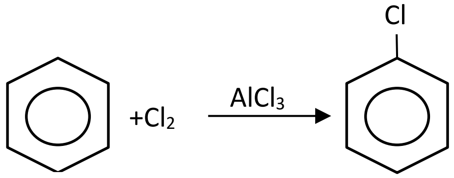
HALOARENE

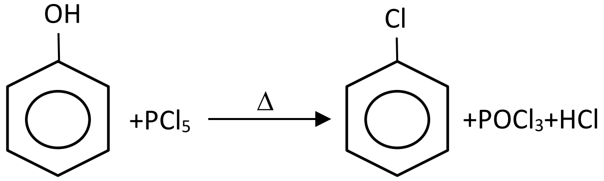
If halogen is directly attached to the benzene ring, compound is called as Haloarene

Ex.



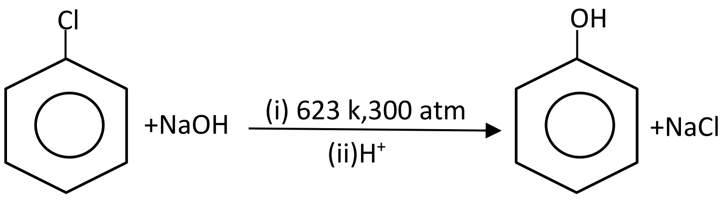
Preparation





Chemical properties

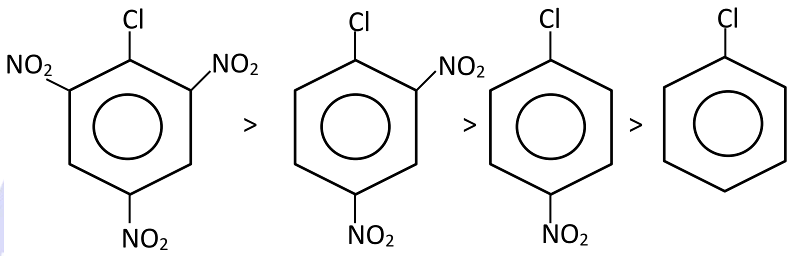
(1)



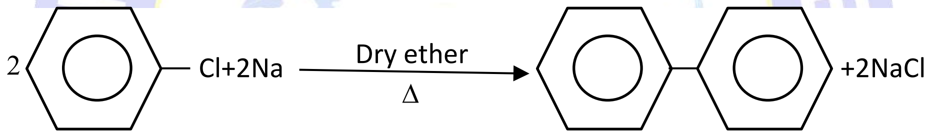
Presence of electron withdrawing group on ring makes the nucleophilic substitution easier.

- **Reactivity order :-**

  Towards nucleophilic substitution

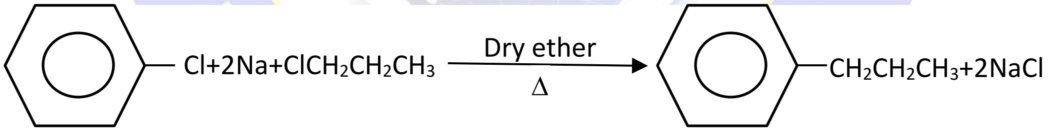


Fittig Reaction



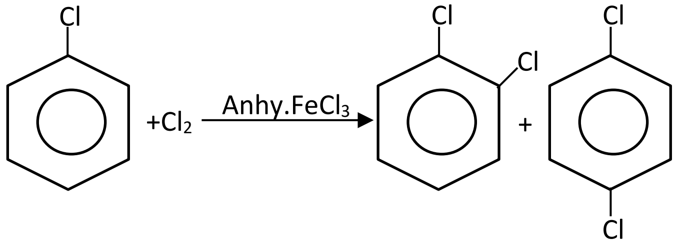
Diphenyl

Wurtz fittig Reaction



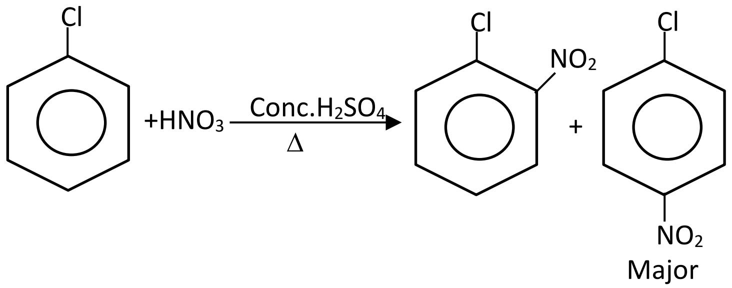
Electrophilic substitution reaction

(i)

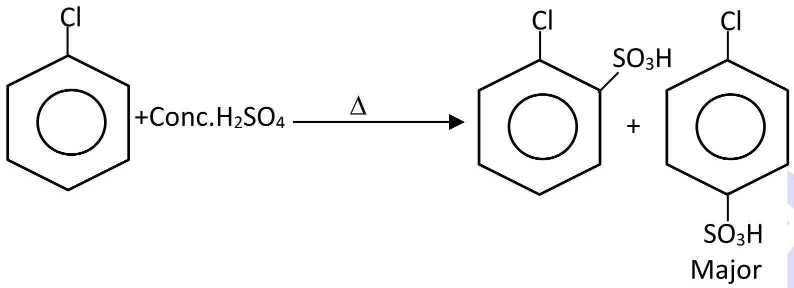


Major

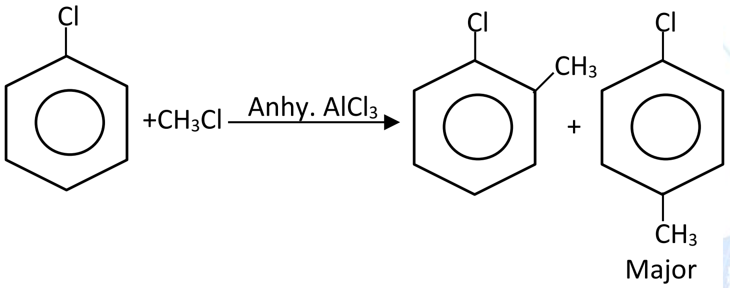
(ii)


Cl
+HNO3
Conc.H2SO4
Δ
Cl
NO2
+
Cl
NO2
Major

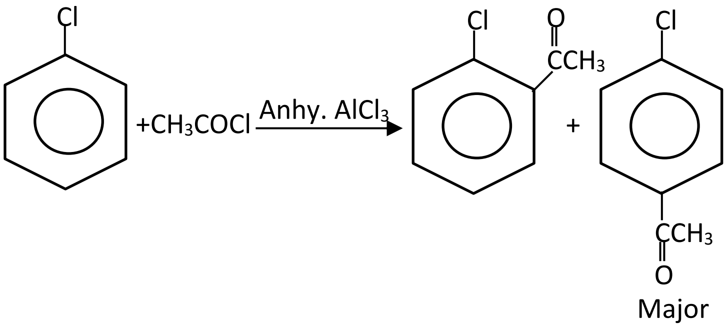
(iii)


Cl
+Conc.H2SO4
Δ
Cl
SO3H
+
Cl
SO3H
Major

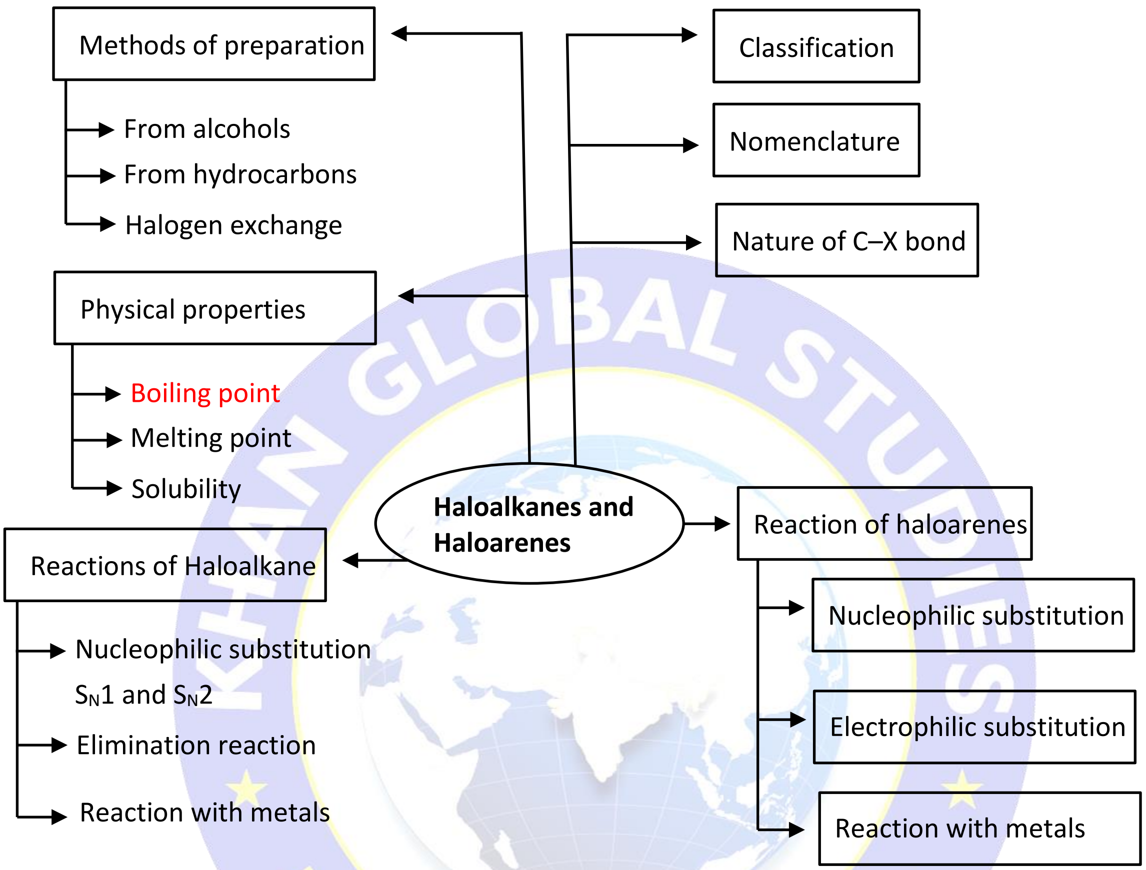
(iv)


Cl
+CH3Cl
Anhy. AlCl3
Cl
CH3
+
Cl
CH3
Major

(v)


Cl
+CH3COCl
Anhy. AlCl3
Cl
O
CCH3
+
Cl
CCH3
O
Major

QUICK FOLLOW UP



Haloalkanes and Haloarenes

- Methods of preparation
  - From alcohols
  - From hydrocarbons
  - Halogen exchange
- Physical properties
  - Boiling point
  - Melting point
  - Solubility
- Reactions of Haloalkane
  - Nucleophilic substitution S_N1 and S_N2
  - Elimination reaction
  - Reaction with metals
- Classification
- Nomenclature
- Nature of C–X bond
- Reaction of haloarenes
  - Nucleophilic substitution
  - Electrophilic substitution
  - Reaction with metals