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Haloalkanes and Haloarenes

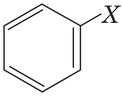
The replacement of hydrogen atom(s) in hydrocarbon, aliphatic or aromatic, by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene), respectively.

Classification of Halogen Derivatives

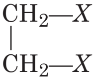
On the basis of number of halogen atoms present, halogen derivatives are classified as mono, di, tri, tetra, etc., halogen derivatives, e.g.

C_2H_5X

monohaloalkane

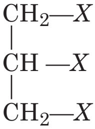


monohaloarene



$$\begin{array}{l} CH_2-X \\ | \\ CH_2-X \end{array}$$

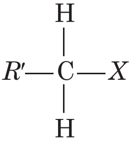
dihaloalkane



$$\begin{array}{l} CH_2-X \\ | \\ CH\ -X \\ | \\ CH_2-X \end{array}$$

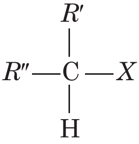
trihaloalkane

On the basis of the nature of the carbon to which halogen atom is attached, halogen derivatives are classified as 1°, 2°, 3°, allylic, benzylic, vinylic and aryl derivatives, e.g.



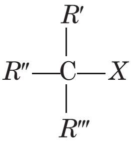
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ R' & - & C & - & X \\ & & | & & \\ & & H & & \end{array}$$

primary (1°)



$$\begin{array}{ccccc} & & R' & & \\ & & | & & \\ R'' & - & C & - & X \\ & & | & & \\ & & H & & \end{array}$$

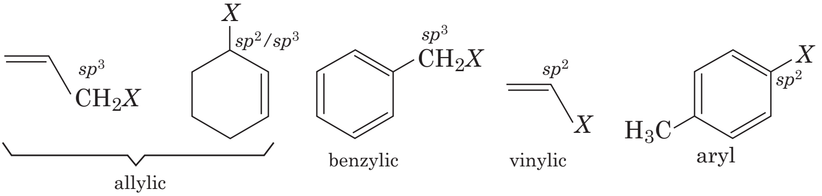
secondary (2°)



$$\begin{array}{ccccc} & & R' & & \\ & & | & & \\ R'' & - & C & - & X \\ & & | & & \\ & & R''' & & \end{array}$$

tertiary (3°)

On the basis of hybridisation of carbon atom of C—X bond

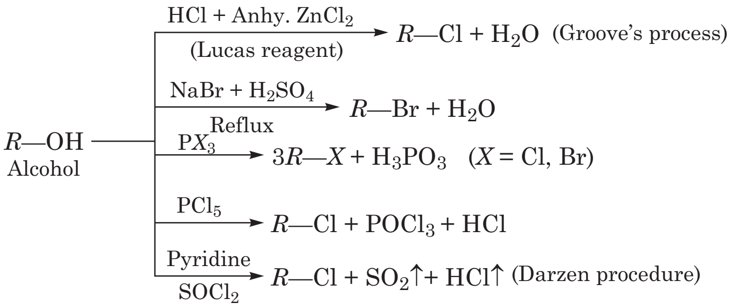


Nature of C—X Bond

Due to high electronegativity of halogen (X) atom, the C—X bond is polar. This bond of haloarene is less polar than that of haloalkanes.

General Methods of Preparation of Haloalkanes

From Alcohols



$$R\text{—OH} \xrightarrow[\text{(Lucas reagent)}]{\text{HCl + Anhy. ZnCl}_2} R\text{—Cl} + H_2O \quad \text{(Groove's process)}$$

$$R\text{—OH} \xrightarrow[\text{Reflux}]{\text{NaBr} + H_2SO_4} R\text{—Br} + H_2O$$

$$R\text{—OH} \xrightarrow{PX_3} 3R\text{—}X + H_3PO_3 \quad (X = \text{Cl, Br})$$

$$R\text{—OH} \xrightarrow{PCl_5} R\text{—Cl} + POCl_3 + HCl$$

$$R\text{—OH} \xrightarrow[SOCl_2]{\text{Pyridine}} R\text{—Cl} + SO_2\uparrow + HCl\uparrow \quad \text{(Darzen procedure)}$$

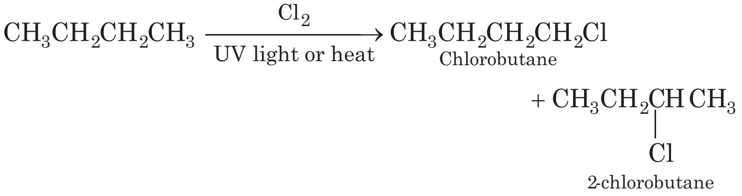
Alcohol

In Groove's method, $ZnCl_2$ is used to weaken the C—OH bond. In case of 3° alcohols, $ZnCl_2$ is not required.

The reactivity order of halogen acids is HI > HBr > HCl.

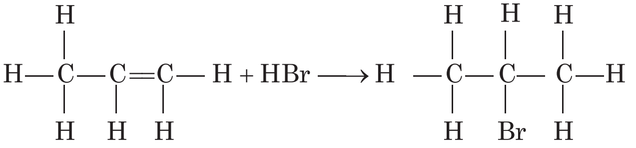
> Darzen procedure is the best method for preparing alkyl halides from alcohols since both the byproducts (SO_2 and HCl) are gaseous and escape easily.

Free Radical Halogenation of Alkanes



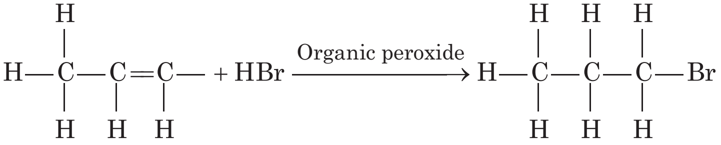
$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{UV light or heat}]{Cl_2} \underset{\text{Chlorobutane}}{CH_3CH_2CH_2CH_2Cl} + \underset{\text{2-chlorobutane}}{CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}H\,CH_3}$$

Addition of Hydrogen Halides on Alkenes



$$\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\underset{\text{H}}{\text{C}}=\underset{\text{H}}{\text{C}}-\text{H}+\text{HBr}\longrightarrow \text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{Br}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{H}$$

2- bromopropane (major)



$$\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\underset{\text{H}}{\text{C}}=\underset{\text{H}}{\text{C}}-+\text{HBr}\xrightarrow{\text{Organic peroxide}}\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{Br}$$

1- bromopropane (major)

And from Alkynes

Finkelstein Reaction

$$\underset{(X=\text{Cl, Br})}{R-X+\text{NaI}}\xrightarrow{\text{Acetone}}R-\text{I}+\text{Na}X$$

Swarts Reaction

$$H_3C-Br+AgF\longrightarrow H_3C-F+AgBr$$

Hg_2F_2, CoF_2 and SbF_3 can also be used as a reagent for Swarts reaction.

Hunsdiecker Reaction

$$CH_3CO\overset{-}{O}\overset{+}{Ag}+Br_2\xrightarrow[CCl_4]{}CH_3Br+AgBr+CO_2\uparrow$$

Physical Properties of Haloalkanes

1. Boiling point orders

   (i) $R-I > R-Br > R-Cl > R-F$

   (ii) $CH_3-(CH_2)_2-CH_2Br > (CH_3)_2CHCH_2Br > (CH_3)_3CBr$

   (iii) $CH_3CH_2CH_2X > CH_3CH_2X > CH_3X$

2. Bond strength of haloalkanes decreases as the size of the halogen atom increases.

   Thus, the order of bond strength is

   $$CH_3F > CH_3Cl > CH_3Br > CH_3I$$

3. Dipole moment decreases as the electronegativity of the halogen decreases.
4. Haloalkanes though polar but are insoluble in water as they do not form hydrogen bonding with water.

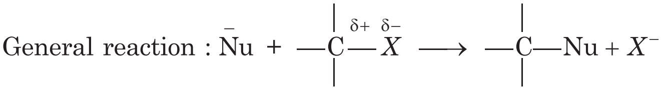
5. Density order is

$$RI > RBr > RCl > RF \qquad \text{(for the same alkyl group)}$$

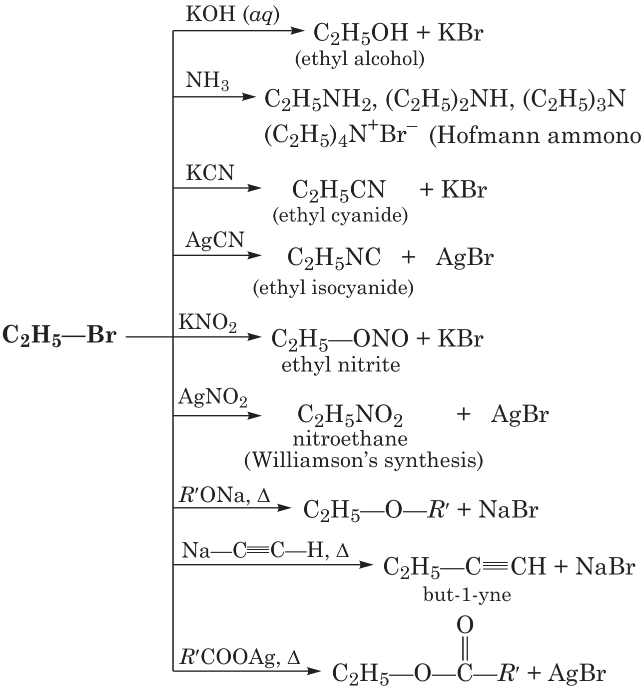
$$CH_3I > C_2H_5I > C_3H_7I$$

Chemical Reactions of Haloalkanes

Nucleophilic Substitution Reactions (S_N reactions)



$$\text{General reaction : } \overset{-}{Nu} + -\overset{|}{\underset{|}{C}}-\overset{\delta+\ \delta-}{X} \longrightarrow -\overset{|}{\underset{|}{C}}-Nu + X^-$$



$$C_2H_5-Br \xrightarrow{KOH\,(aq)} \underset{\text{(ethyl alcohol)}}{C_2H_5OH} + KBr$$

$$C_2H_5-Br \xrightarrow{NH_3} C_2H_5NH_2,\ (C_2H_5)_2NH,\ (C_2H_5)_3N,\ (C_2H_5)_4N^+Br^- \text{ (Hofmann ammonolysis)}$$

$$C_2H_5-Br \xrightarrow{KCN} \underset{\text{(ethyl cyanide)}}{C_2H_5CN} + KBr$$

$$C_2H_5-Br \xrightarrow{AgCN} \underset{\text{(ethyl isocyanide)}}{C_2H_5NC} + AgBr$$

$$C_2H_5-Br \xrightarrow{KNO_2} \underset{\text{ethyl nitrite}}{C_2H_5-ONO} + KBr$$

$$C_2H_5-Br \xrightarrow{AgNO_2} \underset{\text{nitroethane}}{C_2H_5NO_2} + AgBr$$

(Williamson's synthesis)

$$C_2H_5-Br \xrightarrow{R'ONa,\ \Delta} C_2H_5-O-R' + NaBr$$

$$C_2H_5-Br \xrightarrow{Na-C\equiv C-H,\ \Delta} \underset{\text{but-1-yne}}{C_2H_5-C\equiv CH} + NaBr$$

$$C_2H_5-Br \xrightarrow{R'COOAg,\ \Delta} C_2H_5-O-\overset{\overset{O}{\|}}{C}-R' + AgBr$$

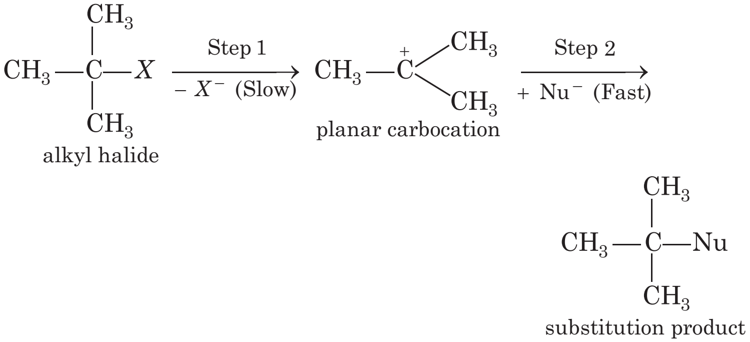
KCN is predominantly ionic and provides cyanide ions in solution, which is ambident nucleophile and bind with carbon side to form cyanide as the major product, while AgCN is covalent and form isocyanide as the major product.

Like KCN, KNO_2 form R—ONO as K—O bond is ionic while $AgNO_2$ produces $R—NO_2$ as product because Ag—O bond is covalent in nature. Vinyl chloride is less reactive towards nucleophilic substitution reactions due to resonance.

Nucleophilic substitution reactions are of two types :

(a) ***$S_N 1$* type** (Unimolecular nucleophilic substitution)

These reactions proceed in two steps:



Rate, $r = k\,[RX]$. It is a first order reaction.

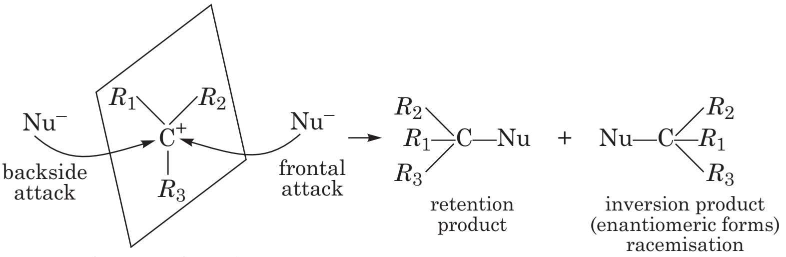
Rate of S_N1 reaction depends upon the stability of carbocation formed.

Reactivity order of alkyl halide towards S_N1 mechanism

$$3° > 2° > 1°$$

Polar solvents, low concentration of nucleophiles and weak nucleophiles favours S_N1 mechanism.

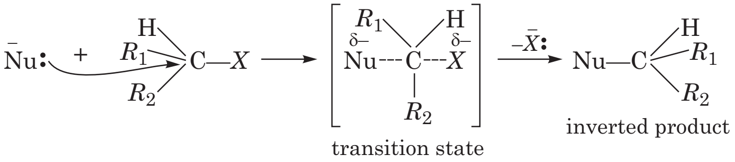
In S_N1 reactions, partial racemisation occurs due to the possibility of frontal as well as backside attack on planar carbocation.



planar carbocation

(b) ***$S_N 2$* type** (Bimolecular nucleophilic substitution) These reactions proceed in one step and is a second order reaction with $r = k[RX]\,[\overset{-}{\text{Nu}}]$.

During S_N2 reaction, inversion of configuration occurs **(Walden inversion)** i.e. starting with *dextro*rotatory halide a *laevo* product is obtained and *vice-versa, e.g.*,



Reactivity of alkyl halides toward S_N2 mechanism is $1° > 2° > 3°$

Rate of reaction in S_N2 mechanism depends on the strength of the attacking nucleophile. Strength of some common nucleophiles is

$$:CN^- > :I^- > :OR^- > :OH^- > CH_3CO\bar{O}: > H_2O > F^-$$

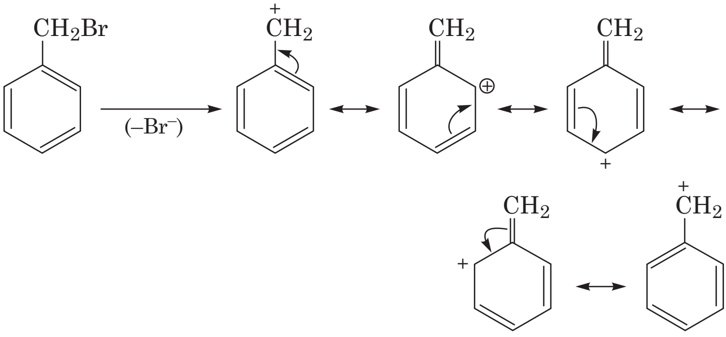
Non-polar solvents, strong nucleophiles and high concentration of nucleophiles favour S_N2 mechanism.

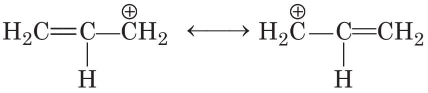
Relative rates of some alkyl halides in S_N1 and S_N2 reactions are in the order

$$S_N1 : (CH_3)_3CX > C_6H_5—CH_2—X > CH_2{=}CH—CH_2X$$
$$> (CH_3)_2CHX > CH_3CH_2X > CH_3X$$

$$S_N2 : \underbrace{C_6H_5CH_2X > CH_2{=}CH—CH_2X}_{\text{resonance stabilised}} > CH_3X$$
$$> CH_3CH_2X > (CH_3)_2CHX > (CH_3)_3CX$$

Resonating structures of benzyl carbocations and allylic carbocation are





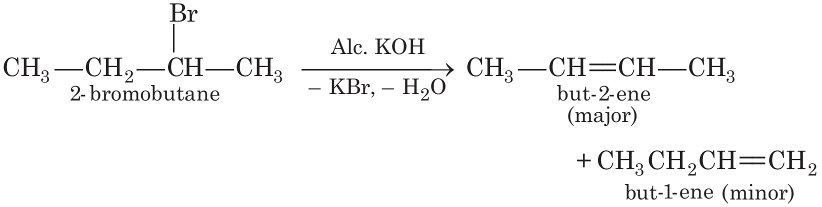
$$H_2C{=}\underset{\substack{|\\H}}{C}—\overset{\oplus}{C}H_2 \longleftrightarrow H_2\overset{\oplus}{C}—\underset{\substack{|\\H}}{C}{=}CH_2$$

Relative reactivity of alkyl halides having same alkyl group is

$$RI > RBr > RCl > RF$$

Elimination Reactions

Dehydrohalogenation is a β-elimination reaction in which halogen is lost from α-carbon atom and the hydrogen from the β-carbon according to Saytzeff rule, e.g.



$$\underset{\text{2-bromobutane}}{CH_3—CH_2—\overset{\overset{\displaystyle Br}{|}}{C}H—CH_3} \xrightarrow[-\text{ KBr, }-\text{ H}_2\text{O}]{\text{Alc. KOH}} \underset{\substack{\text{but-2-ene}\\ \text{(major)}}}{CH_3—CH{=}CH—CH_3}$$

$$+ \underset{\text{but-1-ene (minor)}}{CH_3CH_2CH{=}CH_2}$$

Ease of dehydrohalogenation among alkyl halides

$$3° > 2° > 1°$$

i.e. $$(CH_3)_3CCl > (CH_3)_2CHCl > CH_3CH_2Cl$$

Reduction

$$C_2H_5—Br + H_2 \xrightarrow{\text{Ni, 575 K}} C_2H_6 + HBr$$

$$C_2H_5I + HI \xrightarrow{\text{Red P, 420 K}} C_2H_6 + I_2$$

Reaction with Metals

(i) **Wurtz reaction**

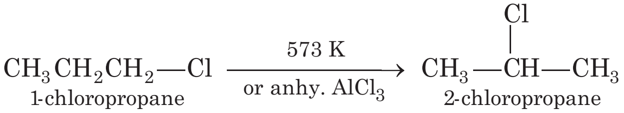
$$RX + 2Na + XR \xrightarrow{\text{Dry ether}} R—R\,(\text{alkane}) + 2NaX$$

(ii) **Reaction with Mg**

$$C_2H_5Br + Mg \xrightarrow{\text{Dry ether}} \underset{\text{(Grignard's reagent)}}{C_2H_5—Mg—Br}$$

Grignard reagent is never isolated in the solid state as it explodes in dry state. So it is used in ethereal solution.

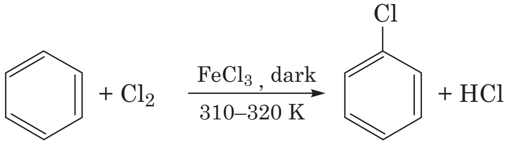
Isomerisation



$$\underset{\text{1-chloropropane}}{CH_3CH_2CH_2—Cl} \xrightarrow[\text{or anhy. AlCl}_3]{\text{573 K}} \underset{\text{2-chloropropane}}{CH_3—\overset{\overset{\displaystyle Cl}{|}}{C}H—CH_3}$$

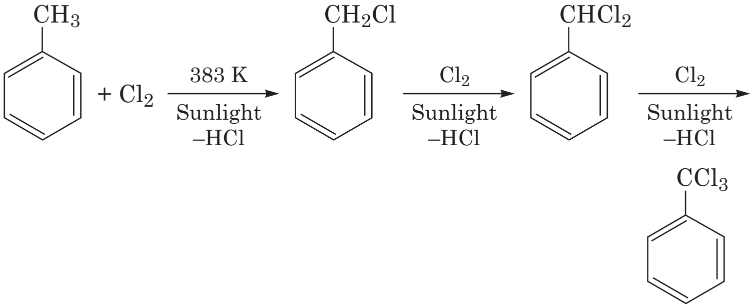
General Methods of Preparation of Aryl Halides (Haloarenes)

By Halogenation of Aromatic Hydrocarbons



It is an electrophilic substitution reaction.

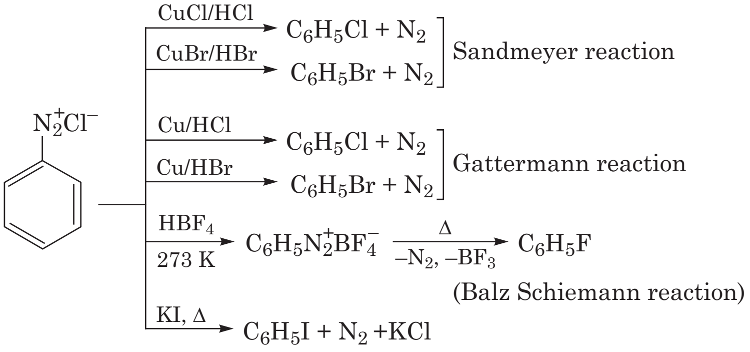
By Side Chain Halogenation



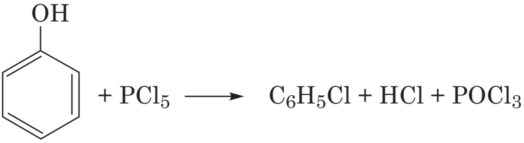
Benzotrichloride

(It involves free radical mechanism.)

From Benzene Diazonium Salt



From Phenol



Physical Properties of Aryl Halides

1. Aryl halides are colourless liquids or colourless solids with characteristic odour.
2. Boiling point generally increases with increase in the size of aryl group or halogen atom. Boiling point order

   Ar—I > Ar—Br > Ar—Cl > Ar—F
3. The melting point of *p* -isomer is more than *o*- and *m*-isomer. This is because of more symmetrical nature of *p*-isomer.
4. Due to resonance in chlorobenzene, C—Cl bond is shorter and hence, its dipole moment is less than that of cyclohexylchloride.

Chemical Properties of Aryl Halides

1. Nucleophilic Substitution Reactions

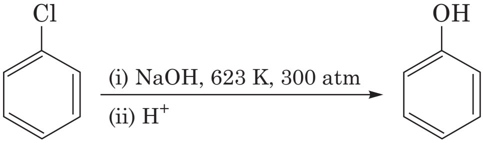
Aryl halides are less reactive towards nucleophilic substitution reaction. Their low reactivity is attributed due to the following reasons:

(i) Due to resonance, C—*X* bond has partial double bond character.

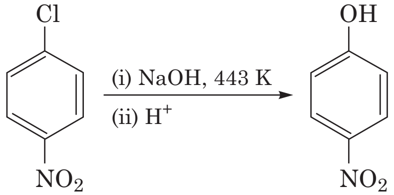
(ii) Stabilisation of the molecule by delocalisation of electrons.

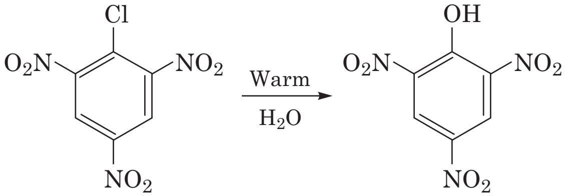
(iii) Instability of phenyl carbocation.

However, aryl halides having electron withdrawing groups (like $—NO_2$, $—SO_3H$, etc.) at *ortho* and *para* positions undergo nucleophilic substitution reaction easily.



Presence of electron withdrawing group ($—NO_2$) increases the reactivity.

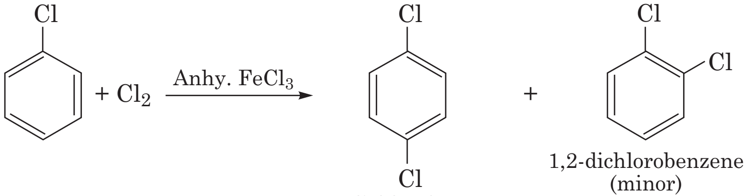




2. **Electrophilic Substitution Reactions**

Halogens are deactivating but *o, p*-directing. Thus, chlorination, nitration, sulphonation and Friedel Craft's reaction give a mixture of *o*- and *p*- chloro substituted derivatives.

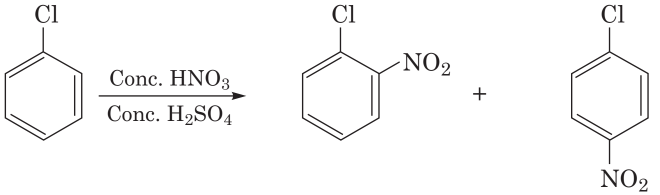
(i) **Halogenation**



1,2-dichlorobenzene (minor)

1,4-dichlorobenzene (major)

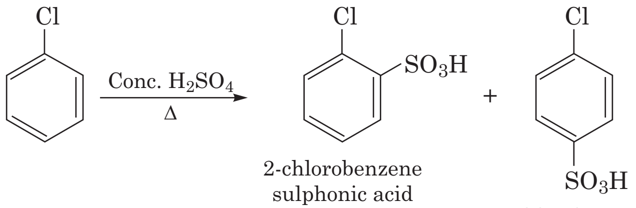
(ii) **Nitration**



1-chloro-2-nitrobenzene (minor)

1-chloro-4-nitrobenzene (major)

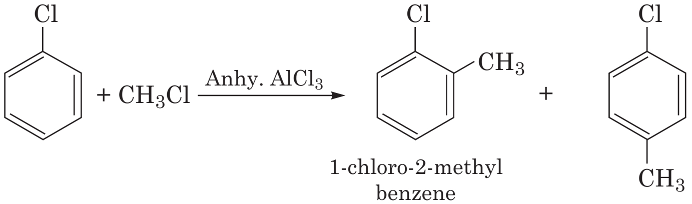
(iii) **Sulphonation**



2-chlorobenzene sulphonic acid (minor)

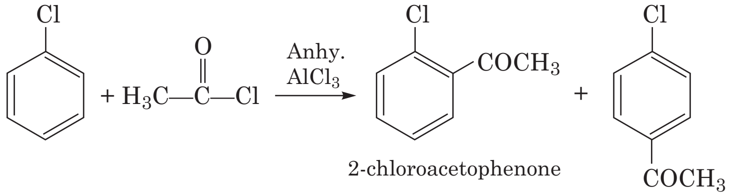
4-chlorobenzene sulphonic acid (major)

(iv) **Friedel-Crafts reaction**



1-chloro-2-methyl benzene

1-chloro-4-methyl benzene

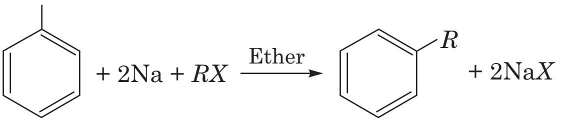


2-chloroacetophenone

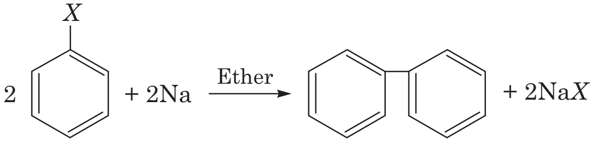
4-chloroacetophenone

3. **Reaction with Metals**

(i) **Wurtz Fittig reaction**

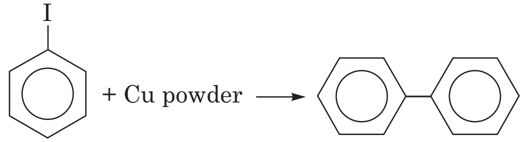


(ii) **Fittig reaction**



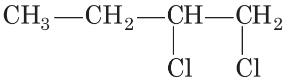
Diphenyl

(iii) **Ullmann reaction**



iodobenzene biphenyl

Dihalogen Derivatives



$$CH_3—CH_2—\underset{Cl}{CH}—\underset{Cl}{CH_2}$$

(*Vic* or *vicinal*-dihalide)

$$CH_3CH_2CH\begin{matrix}Cl\\Cl\end{matrix}$$

(*Gem* or *geminal*-dihalide)

$ClCH_2—CH_2—CH_2—CH_2—Cl$

(Isolated dihalides)

Dichloromethane (CH_2Cl_2) is widely used as a solvent, as a propellant in aerosols. Direct contact of dichloromethane in humans causes intense burning and mild redness of the skin.

Trihalogen Derivatives

1. **Chloroform** [Trichloromethane, $CHCl_3$]

Methods of preparation

(i) $$CH_4 + 3Cl_2 \xrightarrow[\text{Controlled chlorination}]{\text{Sunlight}} CHCl_3 + 3HCl$$

(ii) Haloform reaction

$$C_2H_5OH + Cl_2 \longrightarrow CH_3CHO + 2HCl \text{ [Oxidation]}$$

$$CH_3CHO + 3Cl_2 \longrightarrow CCl_3 \cdot CHO + 3HCl \text{ [Chlorination]}$$

$$2CCl_3 \cdot CHO + Ca(OH)_2 \longrightarrow 2CHCl_3 + (HCOO)_2Ca$$

[Hydrolysis]

Properties

(i) Oxidation of $CHCl_3$ gives poisonous gas phosgene (carbonyl chloride).

$$2CHCl_3 + O_2 \xrightarrow{\text{Light}} \underset{\text{phosgene}}{2COCl_2} + 2HCl$$

To avoid this oxidation, $CHCl_3$ is stored in dark brown bottles and filled to the brim. 1% ethanol is added to chloroform which converts harmful phosgene gas into diethyl carbonate.

(ii) $CHCl_3$ is widely used in the production of freon refrigerant R—22.

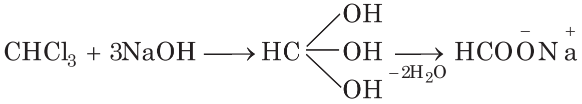
(iii) On nitration, it gives tear producing insecticide substance chloropicrin.

$$CHCl_3 + HONO_2\,(\text{conc.}) \longrightarrow \underset{\text{chloropicrin}}{NO_2 \cdot CCl_3} + H_2O$$

(iv) On dehalogenation, it gives C_2H_2 (acetylene).

$$CHCl_3 + 6Ag + CHCl_3 \xrightarrow[\Delta]{} CH{\equiv}CH + 6AgCl$$

(v) When subjected to hydrolysis, it gives formate.



$$CHCl_3 + 3NaOH \longrightarrow HC\begin{cases} OH \\ OH \\ OH \end{cases} \xrightarrow[-2H_2O]{} HCO\overset{-}{O}N\overset{+}{a}$$

2. **Iodoform** (tri-iodomethane, CHI_3)

Iodoform is prepared by iodoform reaction.

$$CH_3COCH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3\downarrow + 3NaI + CH_3COONa + 3H_2O$$

Compounds containing either CH_3CO— or $CH_3CH(OH)$ group form yellow coloured iodoform with I_2 and NaOH.

Iodoform when comes in contact with organic matter, decomposes easily to free iodine, an antiseptic. Due to its objectionable smell, it has been replaced by other formulations containing iodine.

Polyhalogen Derivatives

1. **Tetrachloromethane** (Carbon Tetrachloride, CCl_4)

Preparation

(i) $CH_4 + 4Cl_2 \xrightarrow{\text{Sunlight}} CCl_4 + 4HCl$

(ii) $CHCl_3 + Cl_2 \xrightarrow{h\nu} CCl_4 + 2HCl$

CCl_4 is a colourless, non-inflammable, poisonous liquid, soluble in alcohol and ether.

Uses

Carbon tetrachloride is used

(i) as a solvent for oils, fats, resins

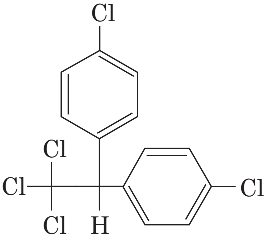
(ii) in dry cleaning

(iii) as fire extinguisher under the name **'pyrene'**.

2. **Freons**

The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. These are usually produced for aerosol propellants, refrigeration and air conditioning purposes. Carbon tetra chloride when reacts with antimony trifluoride in the presence of $SbCl_5$ as catalyst, dichlorofluromethane (freon) is obtained.

3. **DDT** (p, p′-Dichlorodiphenyltrichloroethane)



2,2- bis (4-chlorophenyl) -1,1,1- trichloroethane

DDT is the first chlorinated organic insecticide. Its stability and fat solubility is a great problem.

It is prepared from chloral and chlorobenzene in the presence of conc. H_2SO_4.

4. **Perchloroethane** (C_2Cl_6)

It is used as moth repellant and is also known as artificial camphor.