# Chemistry Notes for class 12 Chapter 10 Haloalkanes and Haloarenes

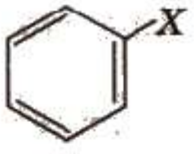
The replacement of hydrogen atom(s) in hydrocarbon, aliphatic or aromatic, by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene), respectively.

**Classification of Halogen Derivatives**

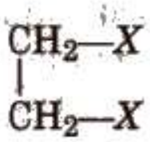
On the basis of number of halogen atoms present, halogen derivatives are classified as mono, di, tri, tetra, etc., halogen derivatives, e.g.,

$C_2H_5X$

monohaloalkane

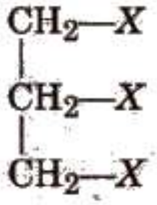


monohaloarene



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

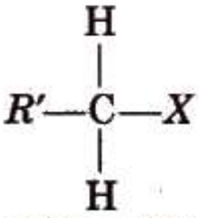
dihaloalkanes



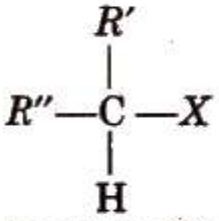
$$\begin{array}{l} CH_2-X \\ | \\ CH_2-X \\ | \\ CH_2-X \end{array}$$

trihaloalkane

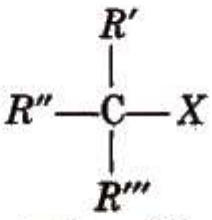
On the basis of the nature of the carbon to which halogen atom is attached, halogen derivatives are classified as 1°, 2°, 3°, allylic, benzylic, vinylic and aryl derivatives, e.g.,



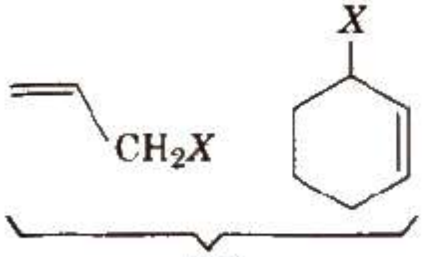
primary (1°)



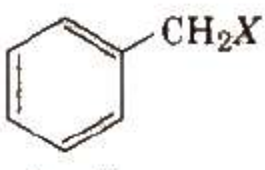
secondary (2°)



tertiary (3°)

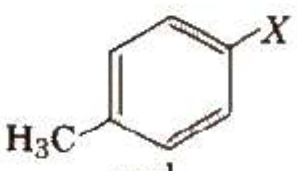


allylic



benzylic

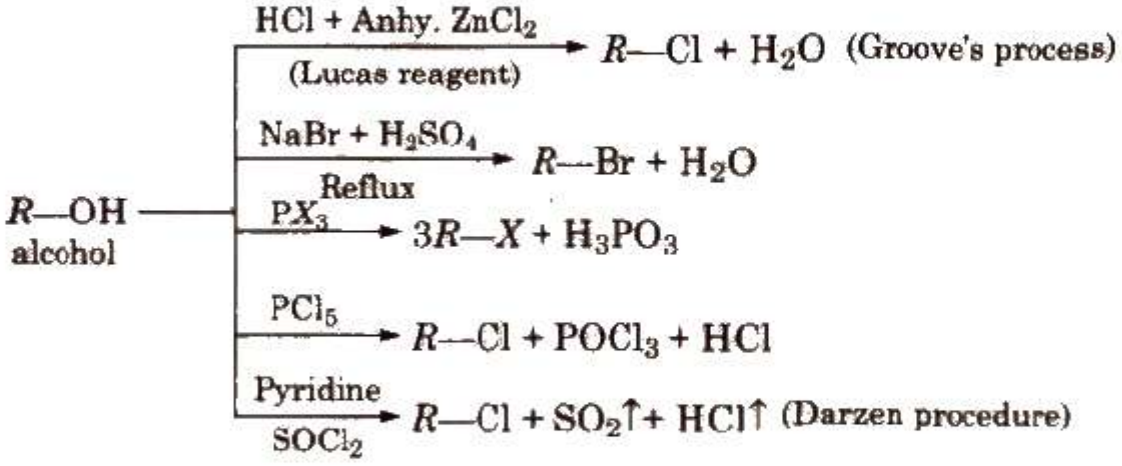
vinylic



aryl

## General Methods of Preparation of Haloalkanes

### 1. From Alcohols

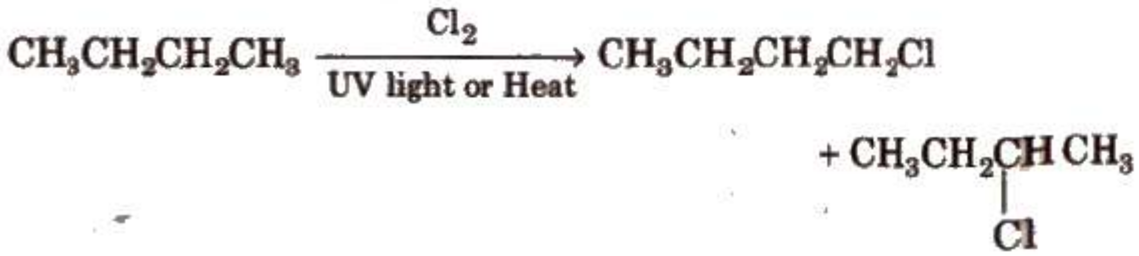


In Groove’s method, $ZnC1_2$ is used to weaken the C-OH bond. In case of 3° alcohols, $ZnC1_2$ is not required.

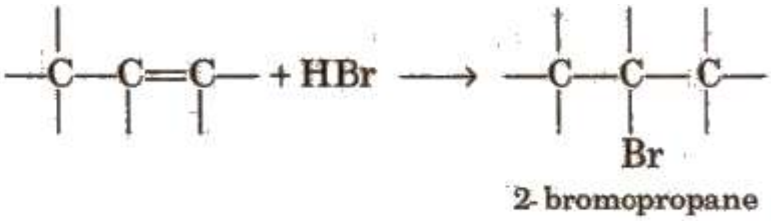
The reactivity order of halogen acids is HI > HBr > HCl.

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

### 2. Free Radical Halogenation of Alkanes



### Addition of Hydrogen Halides on Alkenes



### 1. Finkelstein Reaction

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

### 2. Swarts Reaction

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

$Hg_2F_2$, $COF_2$ and $SbF_3$ can also be used as a reagent for Swarts reaction.

### 3. Hunsdiecker Reaction

$$CH_3COOAg + Br_2 \xrightarrow[CCl_4]{} CH_3Br + AgBr + CO_2$$

## Physical Properties of Haloalkanes

### 1. Boiling point orders

1. $R - I > R - Br > R - Cl > R - F$
2. $CH_3 - (CH_2)_2 - CH_2Br > (CH_3)_2\,CHCH_2Br > (CH_3)_3CBr$
3. $CH_3CH_2CH_2 > CH_3CH_2X > CH_3X$

2. Bond strength of haloalkanes decreases as the size of the halogen atom increases. Thus, the order of bond strength is

$CH_3F > CR_3Cl > CR_3Br > CH_3I$

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.

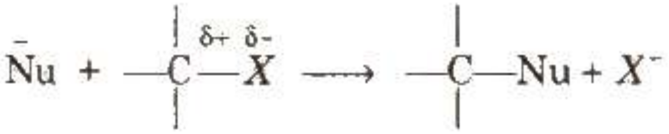
5. Density order is

$RI > RBr > RCl > RF$ (For the same alkyl group)

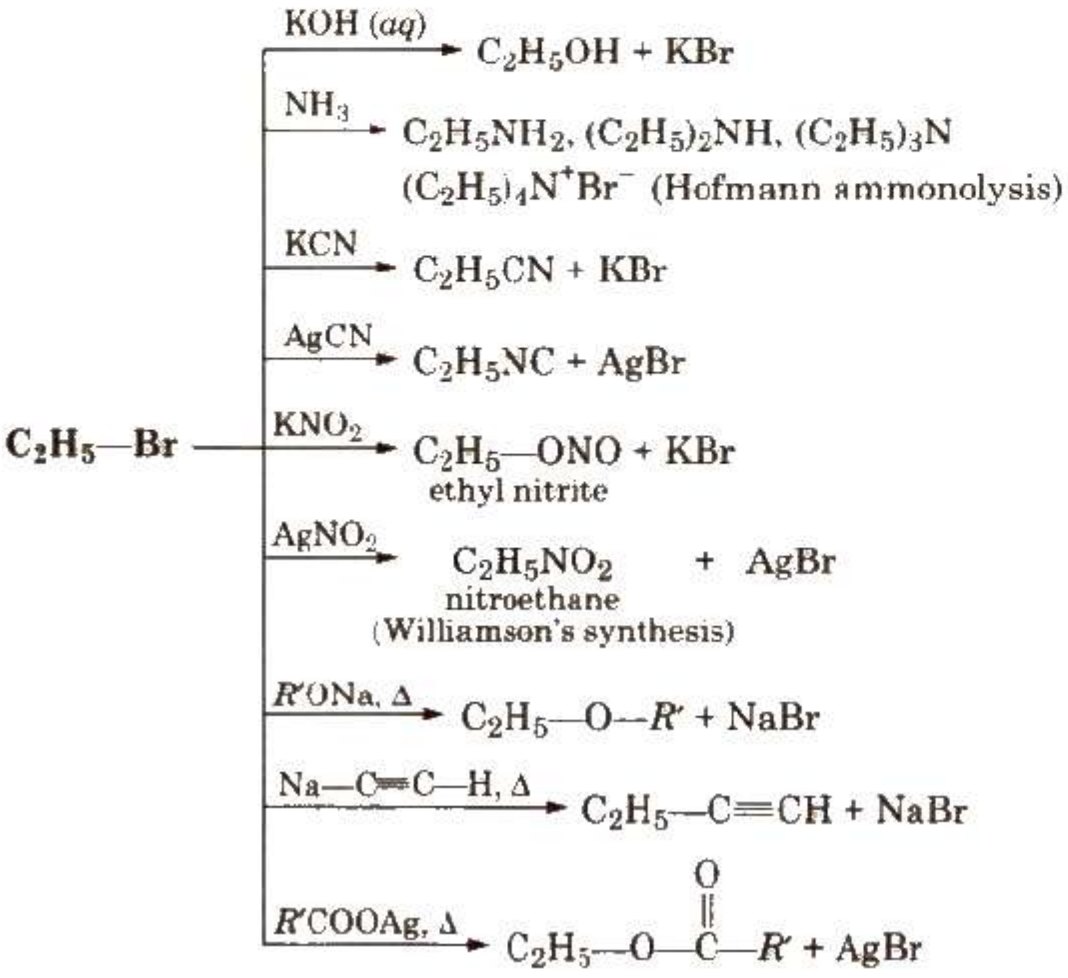
$CH_3I > C_2H_5I > C_3H_7I$

## Chemical Reactions of Haloalkanes

### 1. Nucleophilic Substitution Reactions ($S_N$ reactions)



$$\overset{-}{Nu} + -\overset{|}{\underset{|}{C}}\overset{\delta+\ \delta-}{-X} \longrightarrow -\overset{|}{\underset{|}{C}}-Nu + X^-$$

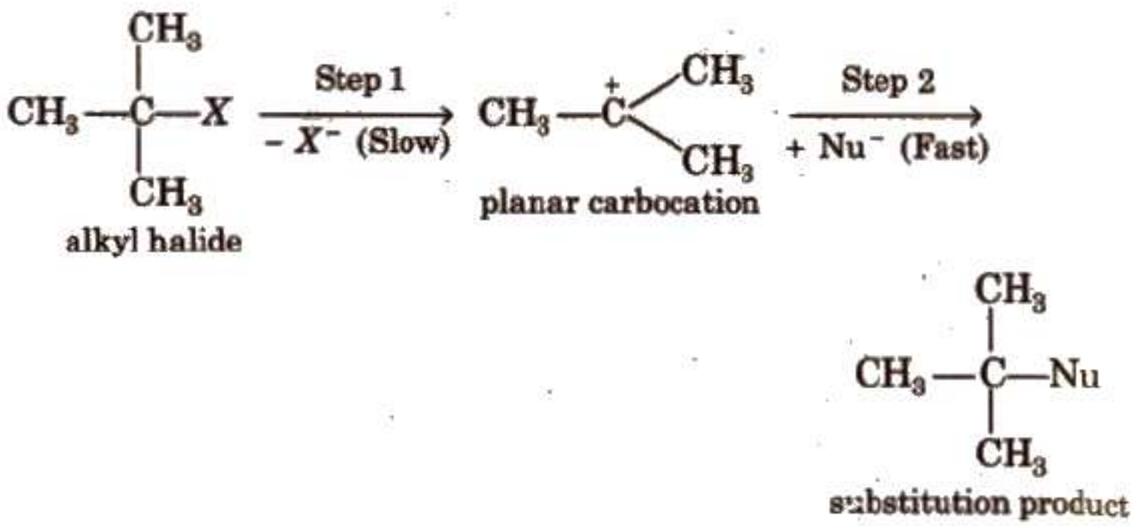


kCN is predominantly ionic and provides cyanide ions in solution, which is ambident nucleophile and bind with carbon side to form as the major product, while AgCN is covalent and form isocyanide as the major product.

Like KCN, $KNO_2$ form R-ONO while $AgNO_2$ produces $R\text{-}NO_2$ as product. Vinyl chloride is less reactive towards nucleophilic substitution reactions due to resonance.

Nucleophilic substitution reactions are of two types

**(a) $S_N1$ type** (Unimolecular nucleophilic reactions proceed in two steps:



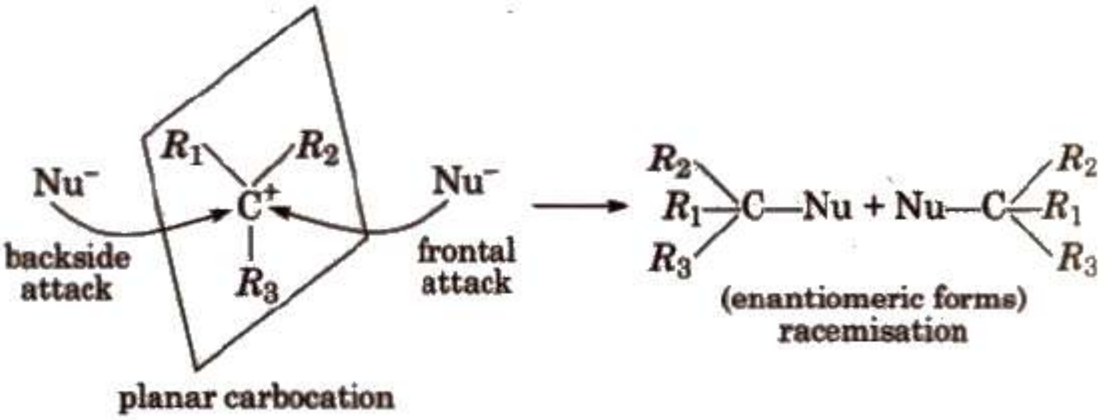
Rate, r = k [RX). It is a first order reaction.

Reactivity order of alkyl halide towards $S_N1$ mechanism

3° > 2° > 1°

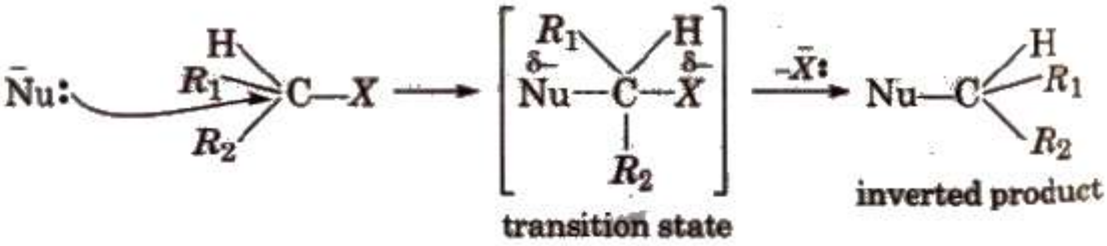
Polar solvents, low concentration of nucleophiles and weak nucleophiles favour $S_N1$ mechanism.

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



(b) $S_N2$ type (Bimolecular nucleophilic substitution) These reactions proceed in one step and is a second order reaction with r = k[RX] [Nu].

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



Reactivity of halides towards $S_N2$ 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

$:CN^- > :I^- > :OR^- > :OH^- > CH^3COO: > H_2O > F^-$

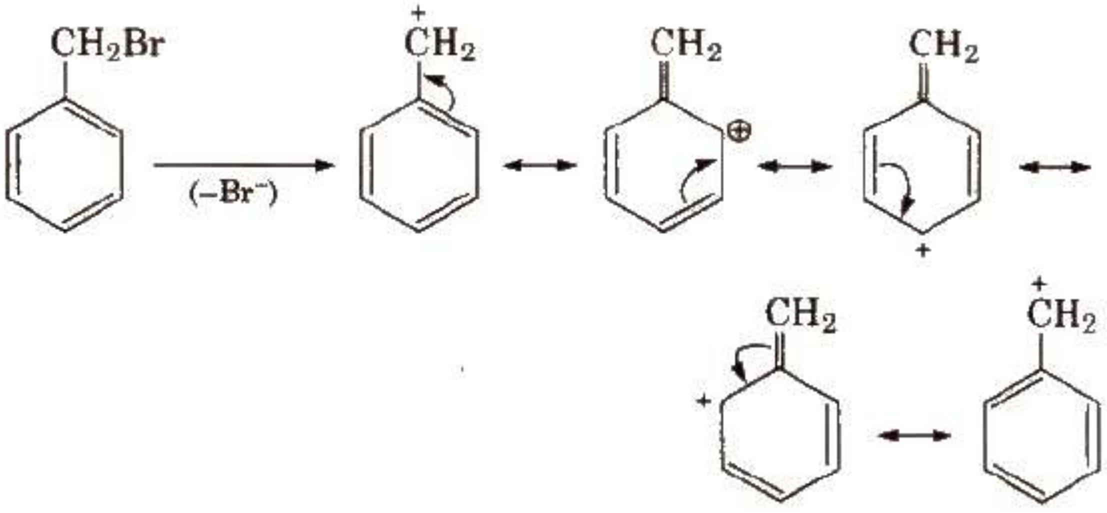
Non-polar solvents, strong nucleophiles and high concentration of nucleophiles favour $S_N2$ mechanism.

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 structure of benzyl carbocations are

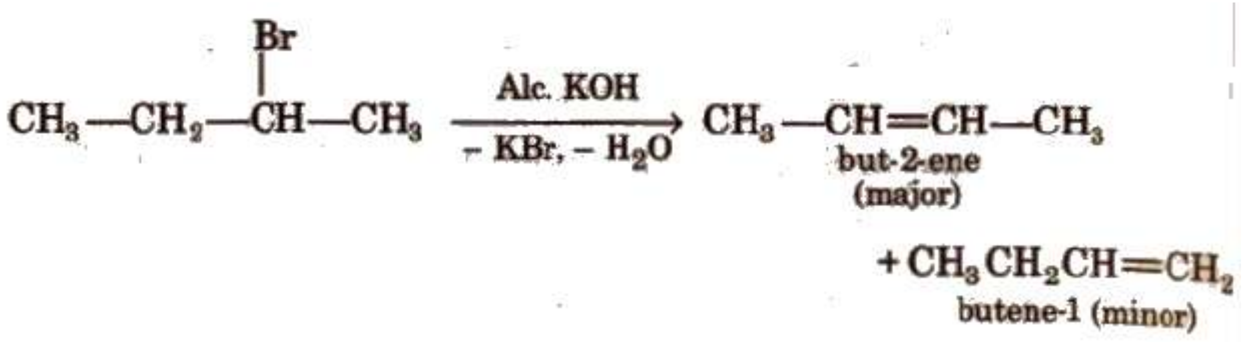


Relative reactivity of alkyl halides for same alkyl group is

RI > RBr > RCI > RF

## 2. Elimination Reactions

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



$$CH_3-CH_2-\overset{\overset{Br}{|}}{CH}-CH_3 \xrightarrow[-KBr,\ -H_2O]{Alc.\ KOH} \underset{\substack{\text{but-2-ene}\\ \text{(major)}}}{CH_3-CH=CH-CH_3} + \underset{\text{butene-1 (minor)}}{CH_3CH_2CH=CH_2}$$

Ease of dehydrohalogenation among halides

3° > 2° > 1°

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

## 3. Reduction

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

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

## 4. Reaction with Metals

**(i) Wurtz reaction**

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

**(ii) Wurtz-Fittig reaction**

$$C_6H_5 \boxed{—Cl + 2Na + Cl} CH_3 \xrightarrow{\text{Dry ether}} C_6H_5\text{—}CH_3 + 2NaCl$$

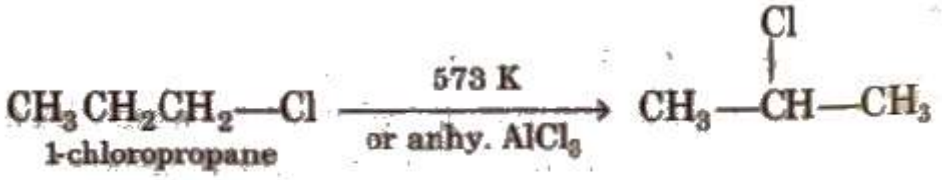
**(iii) Reaction with Mg**

$$C_2H_5Br + Mg \xrightarrow{\text{Dry ether}} C_2H_5\text{—}Mg\text{—}Br$$

(Grignard' s reagent)

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

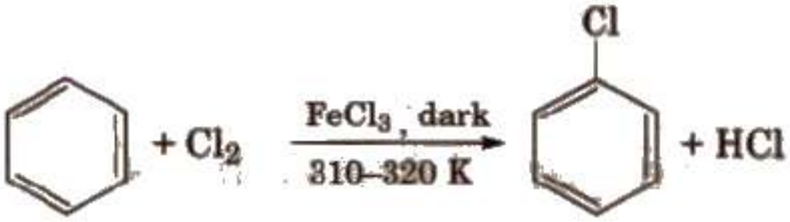
### 5. lsomerisation



$$\underset{\text{1-chloropropane}}{CH_3CH_2CH_2\text{—}Cl} \xrightarrow[\text{or anhy. }AlCl_3]{573\text{ K}} CH_3\text{—}\overset{\overset{\large Cl}{|}}{CH}\text{—}CH_3$$

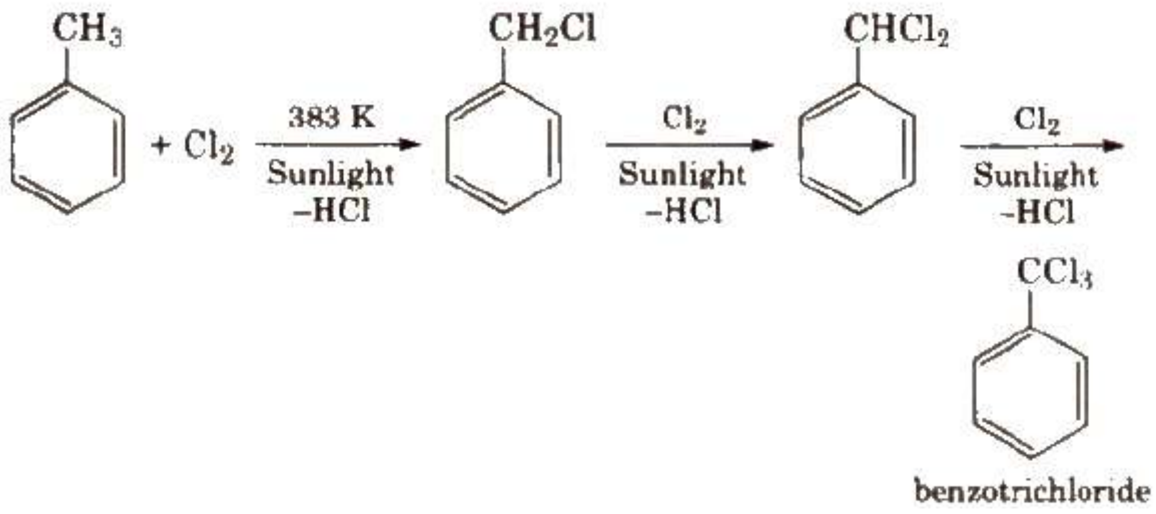
## General Methods of Preparation of Aryl Halides

### 1. By Halogenation of Aromatic Hydrocarbons



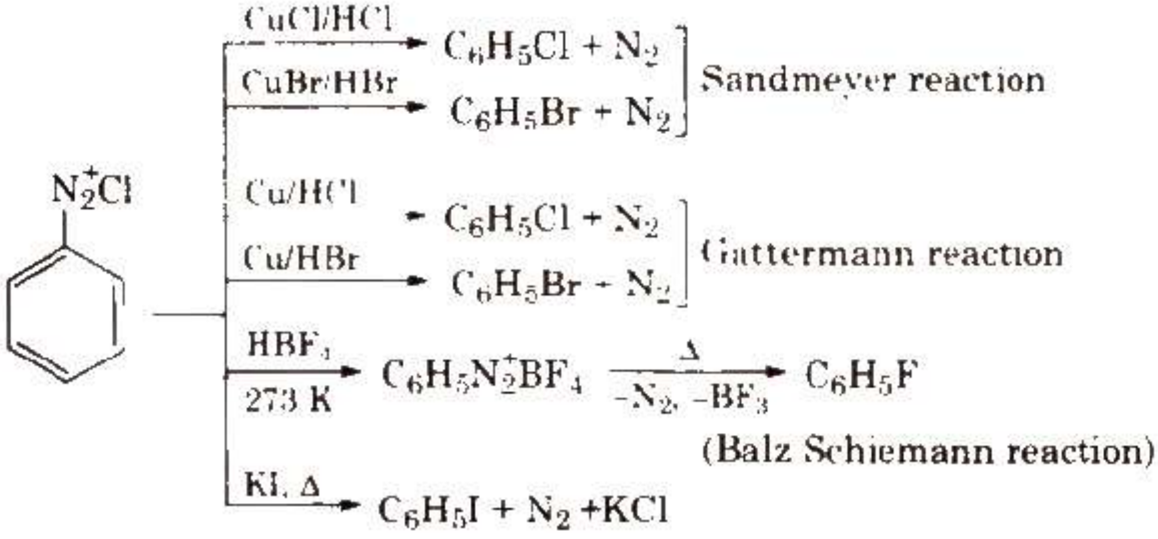
It is an electrophilic substitution reaction.

### 2. By Side Chain Halogenation

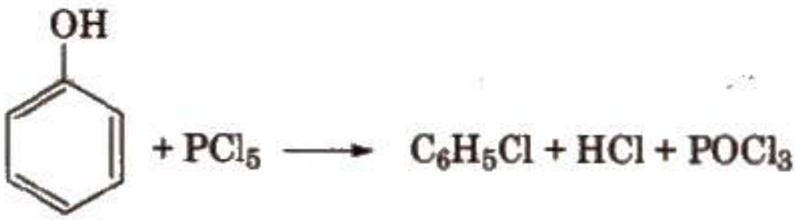


(It involves free radical mechanism.)

**3. From Benzene Diazonium Salt**



4. 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 0- and m-isomer.

This is because of more symmetrical nature of p-isomer.

4. Due to resonance in chlorobenzene, C-CI bond is shorter and hence, its dipole moment is less than that ofcyclohexylchloride.

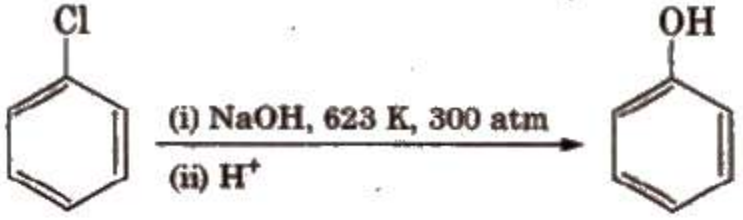
**Chemical Properties of Aryl Halides**

**1. Nucleophilic Substitution Reaction**

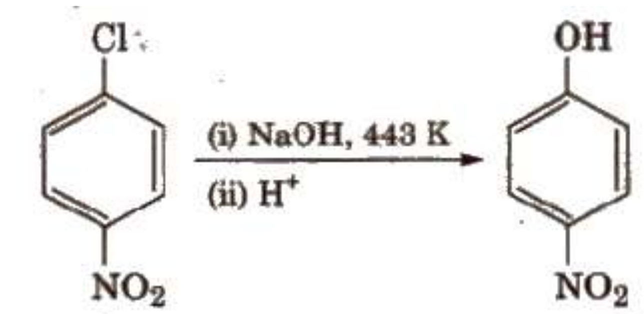
Aryl halides are less reactive towards nucleophilic substitution reaction. Their low reactivity is attributed due to the following reasons:

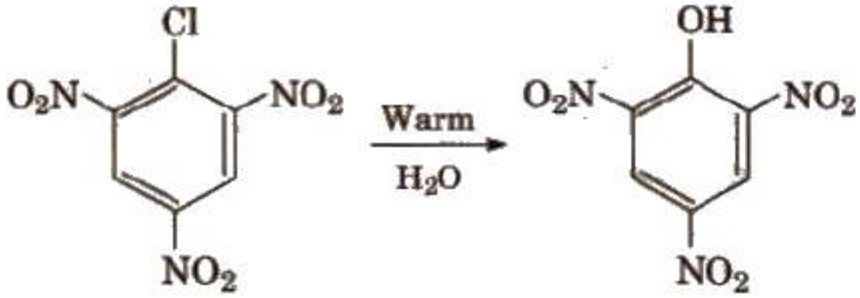
1. Due to resonance, C-X bond has partial double bond character.
2. Stabilisation of the molecule by delocalisation of electrons.
3. (Instability of phenyl carbocation.

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.

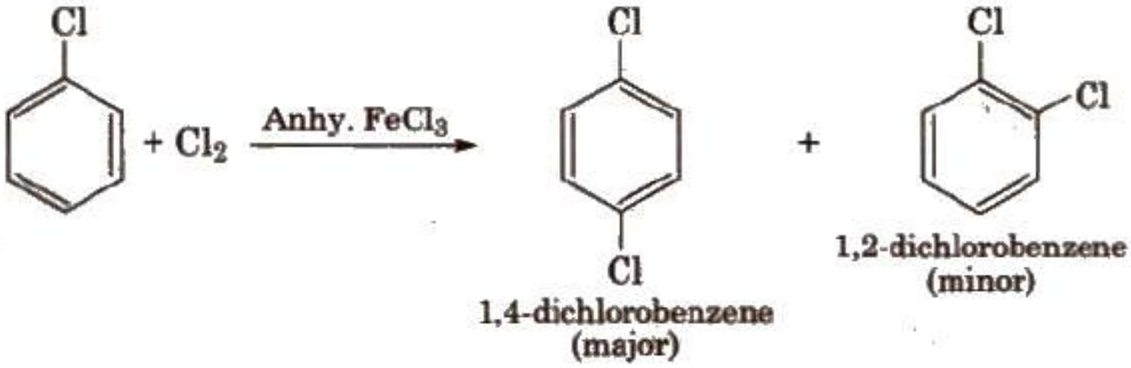




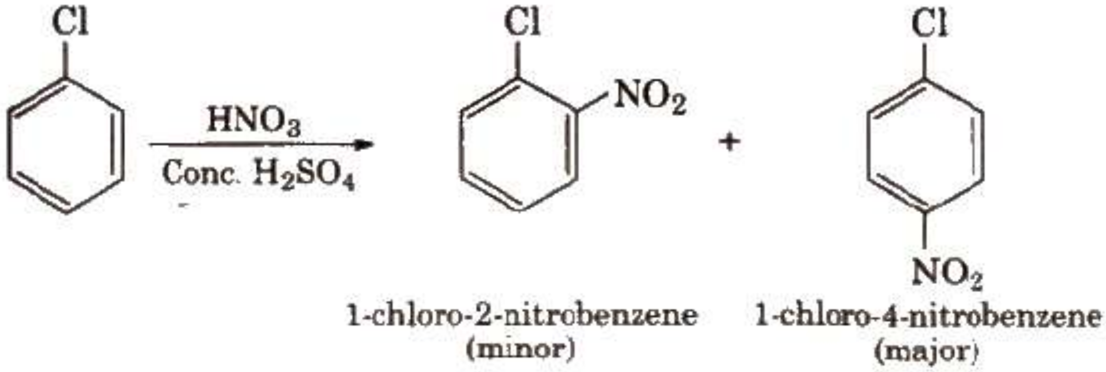
## 2. Electrophilic Substitution Reactions

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.

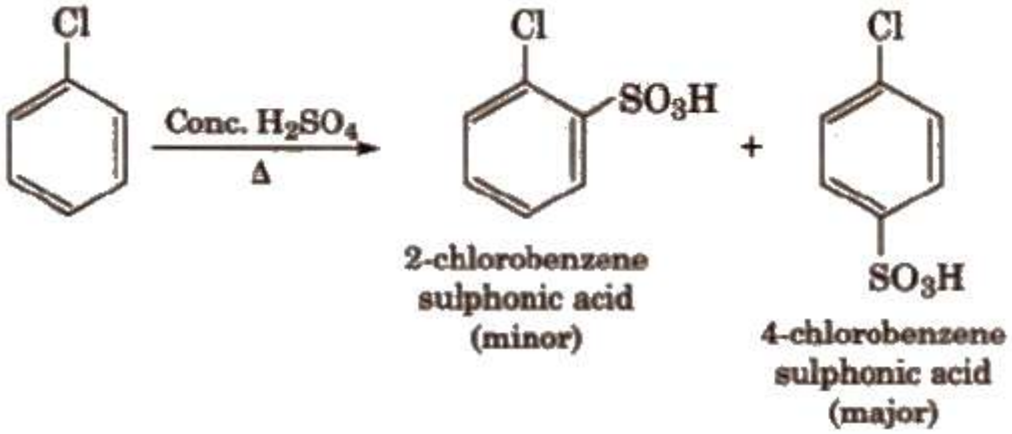
### (i) Halogenation



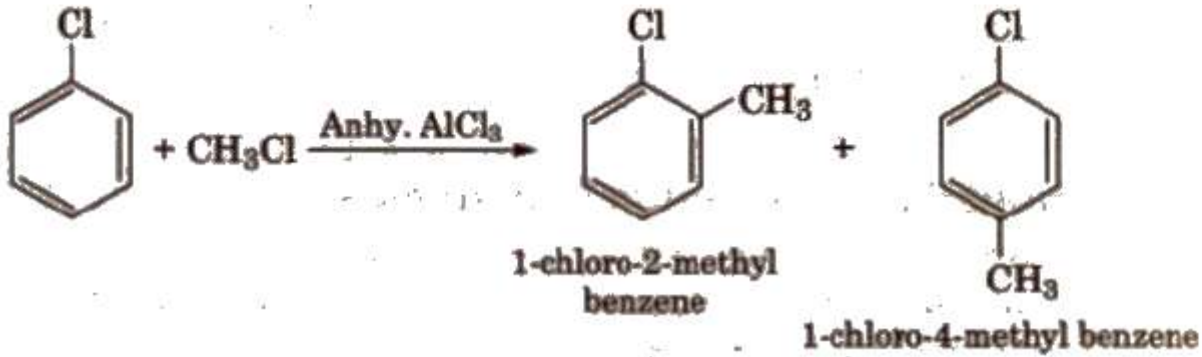
### (ii) Nitration

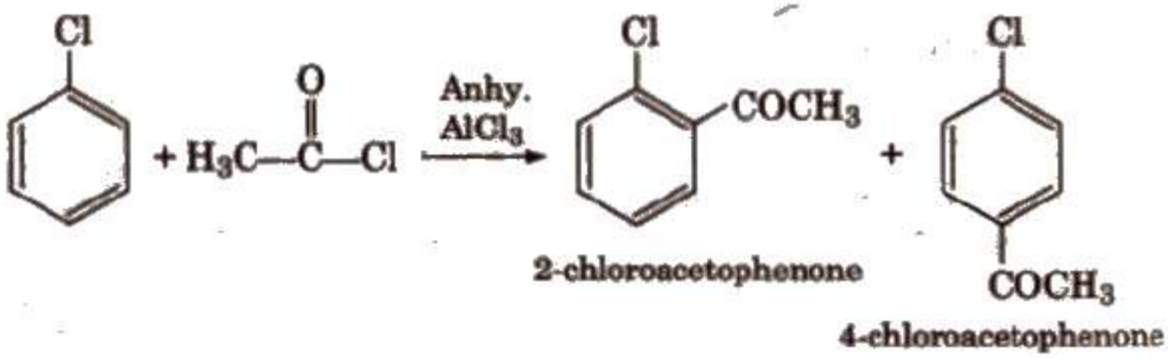


### (iii) Sulphonation



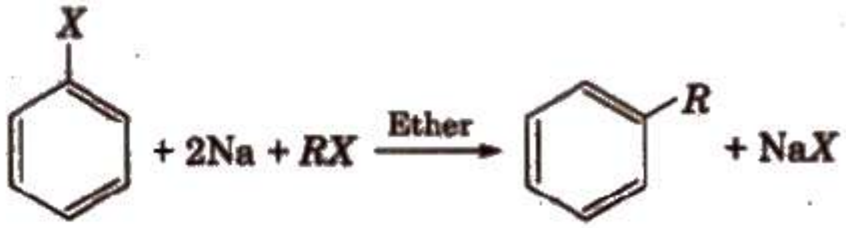
### (iv) Friedel-Crafts reaction



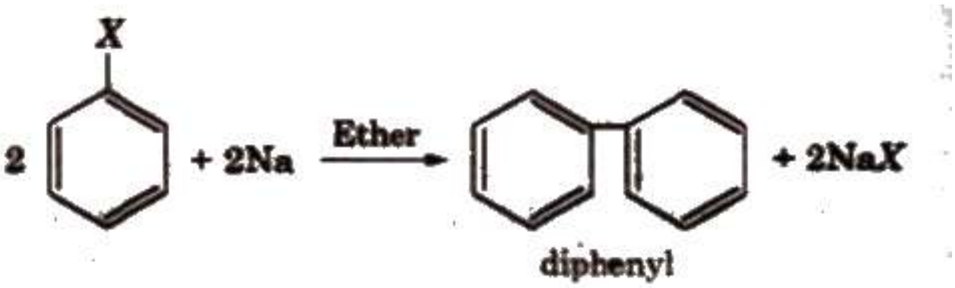


### 3. Reaction with Metals

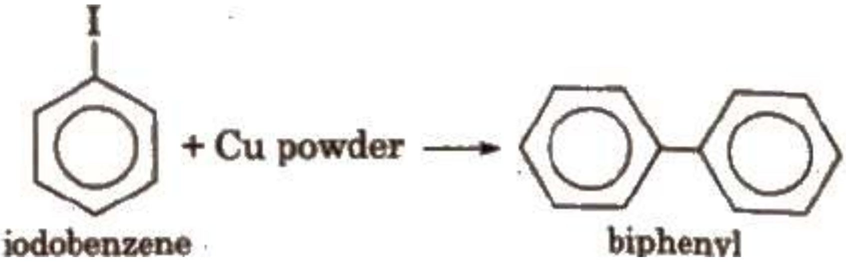
(i) Wurtz Fittig reaction



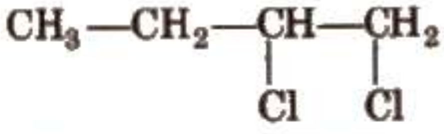
**(ii) Fitting reaction**



(iii) Ullmann reaction

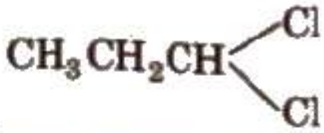


**Dlhalogen Derivatives**



$CH_3-CH_2-CH(Cl)-CH_2(Cl)$

(*Vic* or *vicinal*-dihalide)



(*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 milk redness of the skin.

**Trihalogen Derivatives**

1. Chloroform [Trichloromethane, $CHCl_3$]

**Methods of preparation**

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

(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**

1. 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 $CHCl_3$ iI .toreci in dark brown bottles and filled to the brim. 1% ethanol is added to chloroform which converts harmful phosgene gas into diethyl carbonate.

2. $CHCl_3$ is widely used in the production of freon refrigerant R-22.

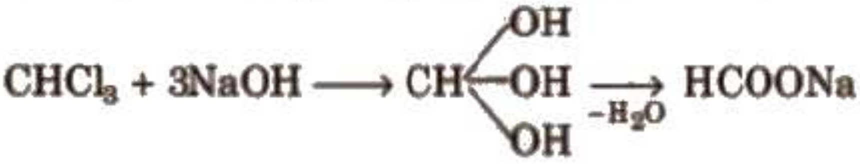
3. On nitration, it gives tear producing insecticide substance chloropicrin.

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

4. On dehalogenation, it gives $C_2H_2$ (acetylene).

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

5. When subjected to hydrolysis, it gives formate.



$$CHCl_3 + 3NaOH \longrightarrow CH(OH)_3 \xrightarrow[-H_2O]{} HCOONa$$

**2. Iodoform (tri-iodornethane, $CHI_3$)**

Iodoform is prepared by iodoform reaction.

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

Compounds containing either $CH_3CO$- or $CH_3CH(OH)$ group form yellow colour 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

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

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

$CCI_4$ is a colourless, non-inflammable, poisonous liquid, soluble in alcohol and ether.

### Uses

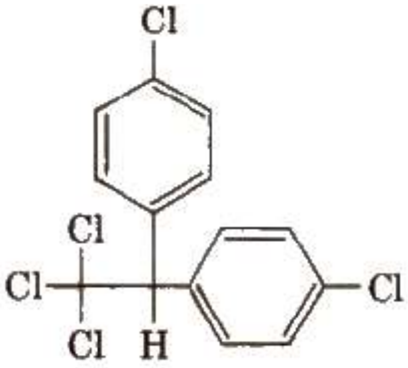
Carbon tetrachloride is used

1. as a solvent for oils, fats, resins
2. in dry cleaning
3. 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.