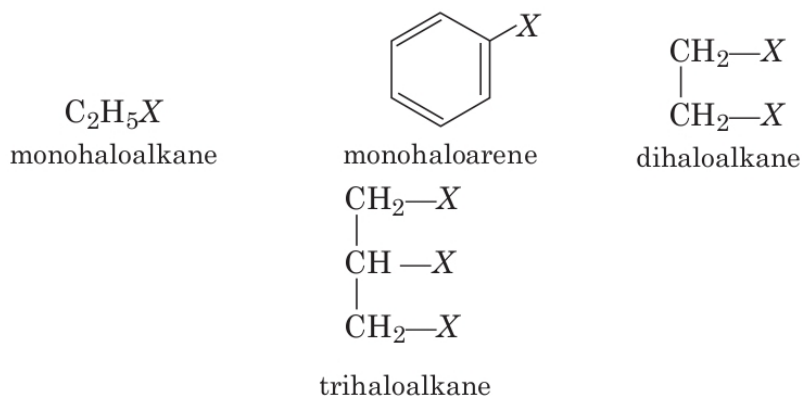


Haloalkanes and Haloarenes

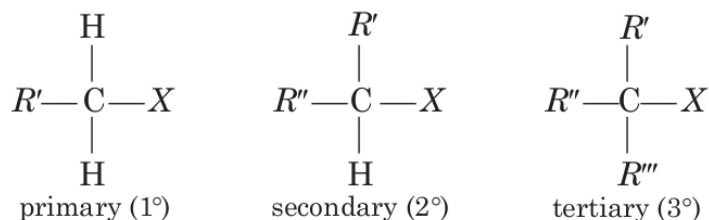
The replacement of hydrogen atom(s) in hydrocarbon, aliphatic or aromatic, by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene), respectively.

Classification of Halogen Derivatives

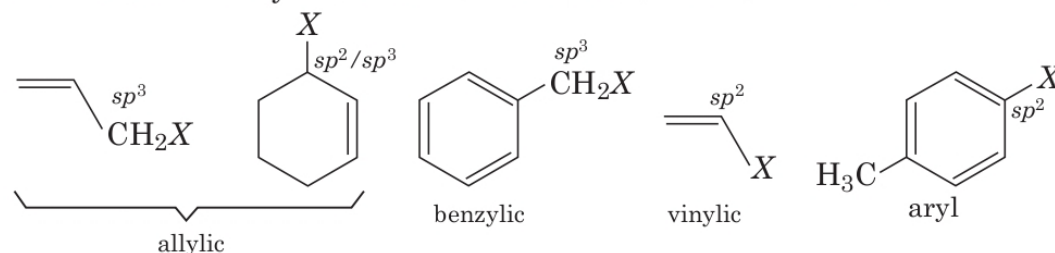
On the basis of number of halogen atoms present, halogen derivatives are classified as mono, di, tri, tetra, etc., halogen derivatives, e.g.



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.



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

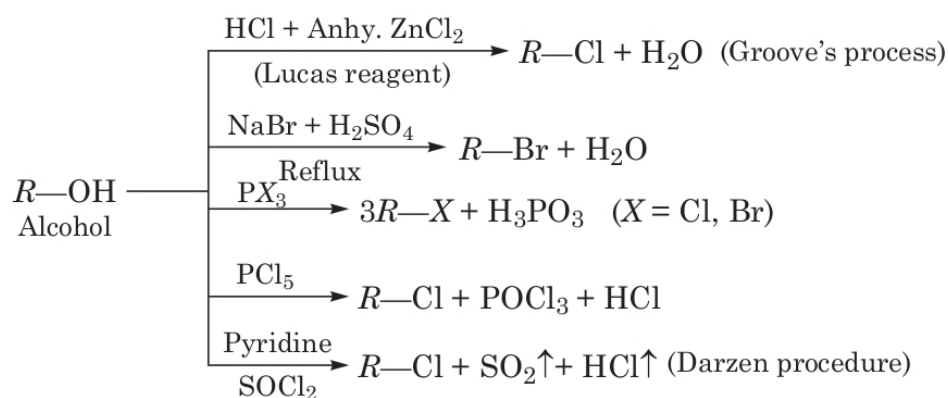


Nature of C—X Bond

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

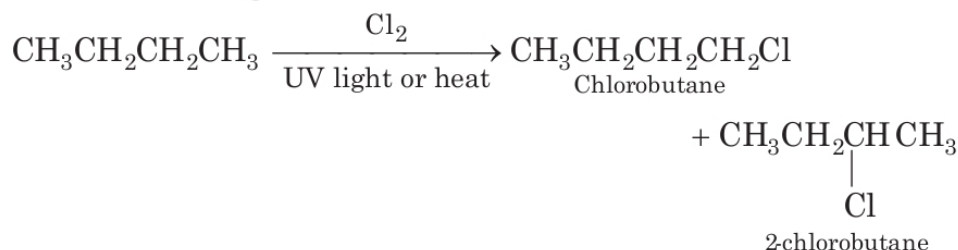


In Groove's method, ZnCl_2 is used to weaken the C—OH bond. In case of 3° alcohols, ZnCl_2 is not required.

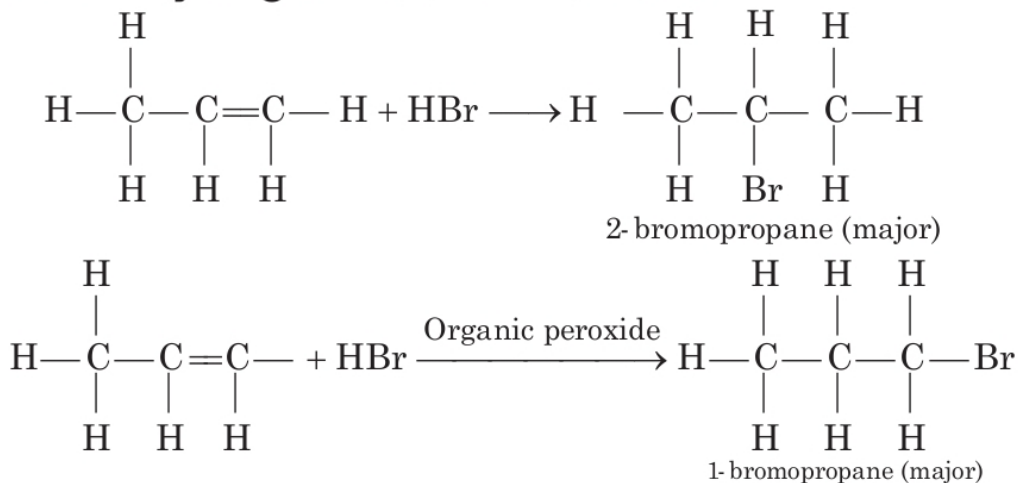
The reactivity order of halogen acids is $\text{HI} > \text{HBr} > \text{HCl}$.

┌ 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

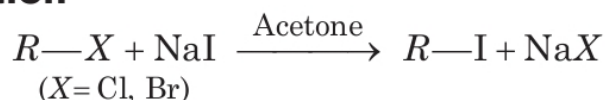


Addition of Hydrogen Halides on Alkenes



And from Alkynes

Finkelstein Reaction

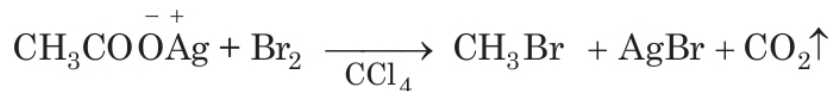


Swarts Reaction



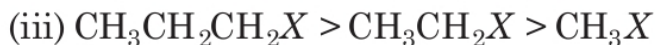
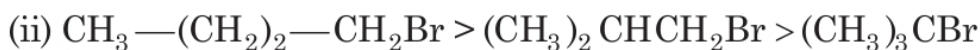
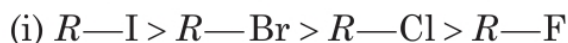
Hg_2F_2 , CoF_2 and SbF_3 can also be used as a reagent for Swarts reaction.

Hunsdiecker Reaction



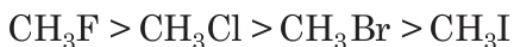
Physical Properties of Haloalkanes

1. Boiling point orders



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

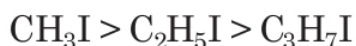
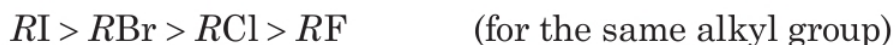
Thus, the order of bond strength is



3. Dipole moment decreases as the electronegativity of the halogen decreases.

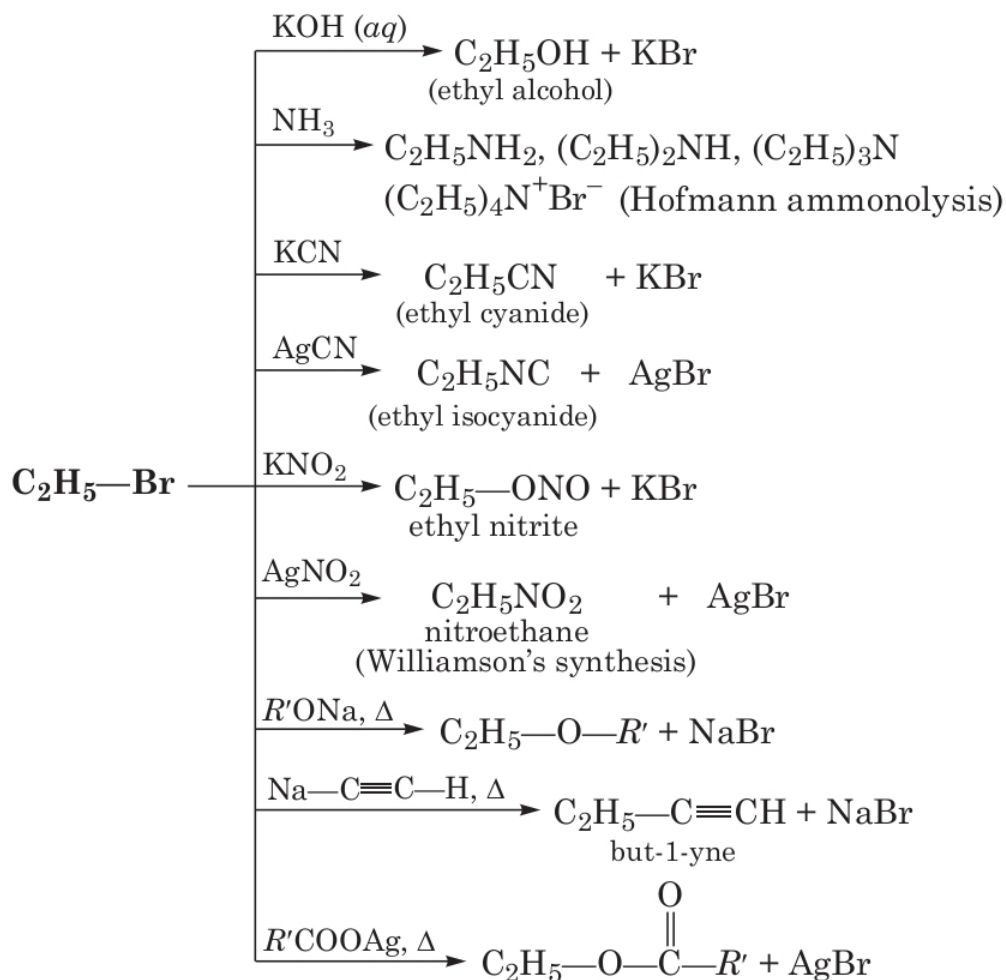
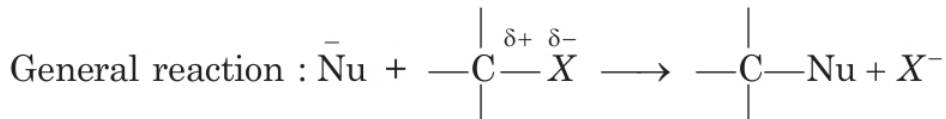
4. Haloalkanes though polar but are insoluble in water as they do not form hydrogen bonding with water.

5. Density order is



Chemical Reactions of Haloalkanes

Nucleophilic Substitution Reactions (S_N reactions)



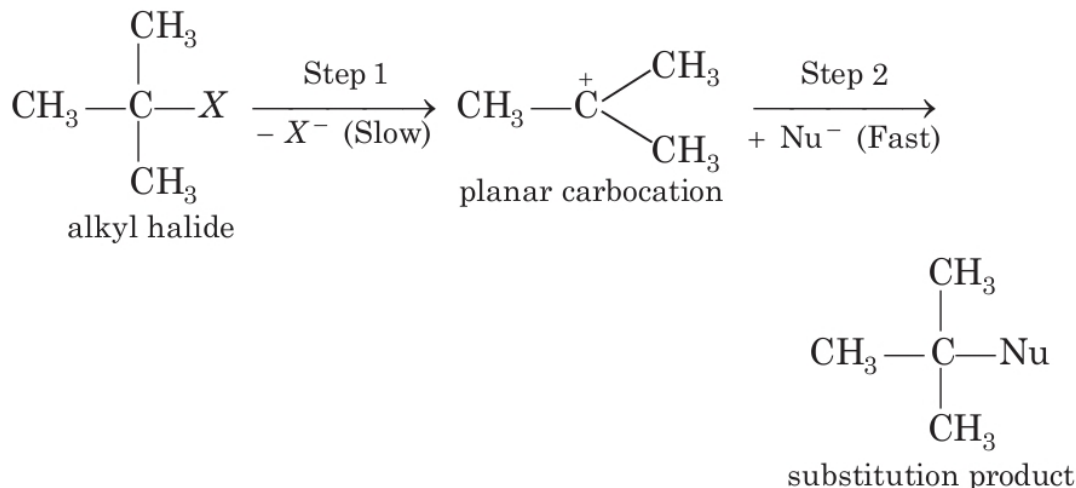
KCN is predominantly ionic and provides cyanide ions in solution, which is ambident nucleophile and bind with carbon side to form cyanide as the major product, while AgCN is covalent and form isocyanide as the major product.

Like KCN, KNO_2 form $R\text{---ONO}$ as K---O bond is ionic while AgNO_2 produces $R\text{---NO}_2$ 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_N1 **type** (Unimolecular nucleophilic substitution)

These reactions proceed in two steps:



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

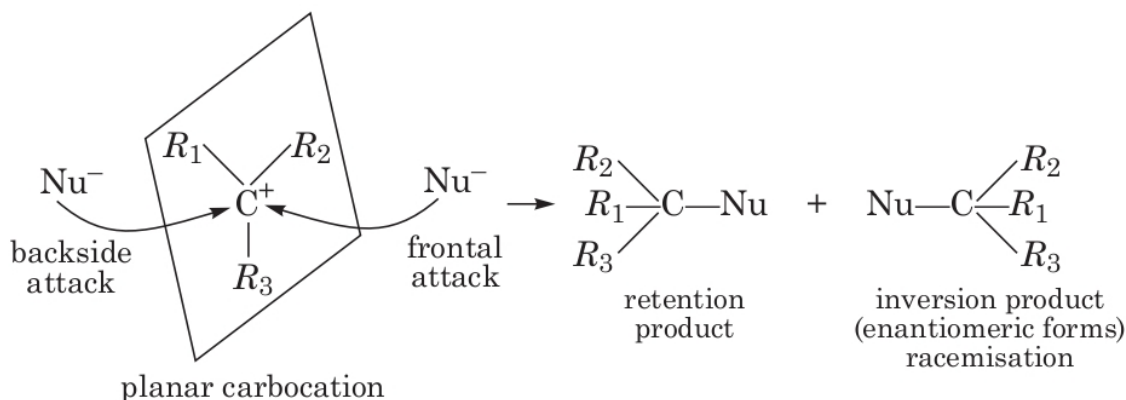
Rate of S_N1 reaction depends upon the stability of carbocation formed.

Reactivity order of alkyl halide towards S_N1 mechanism



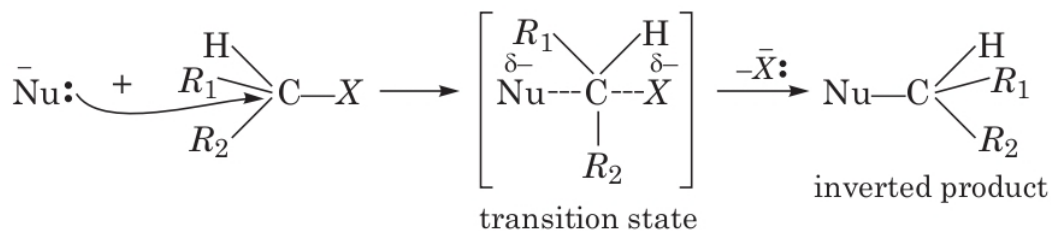
Polar solvents, low concentration of nucleophiles and weak nucleophiles favours S_N1 mechanism.

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



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

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.,



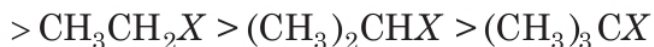
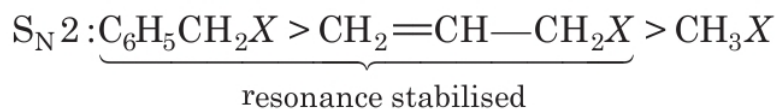
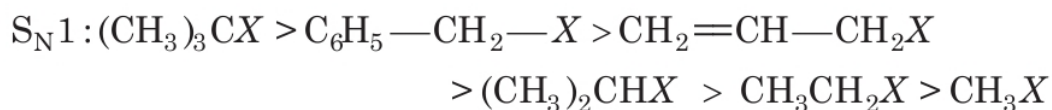
Reactivity of alkyl halides toward $\text{S}_{\text{N}}2$ mechanism is $1^\circ > 2^\circ > 3^\circ$

Rate of reaction in $\text{S}_{\text{N}}2$ mechanism depends on the strength of the attacking nucleophile. Strength of some common nucleophiles is

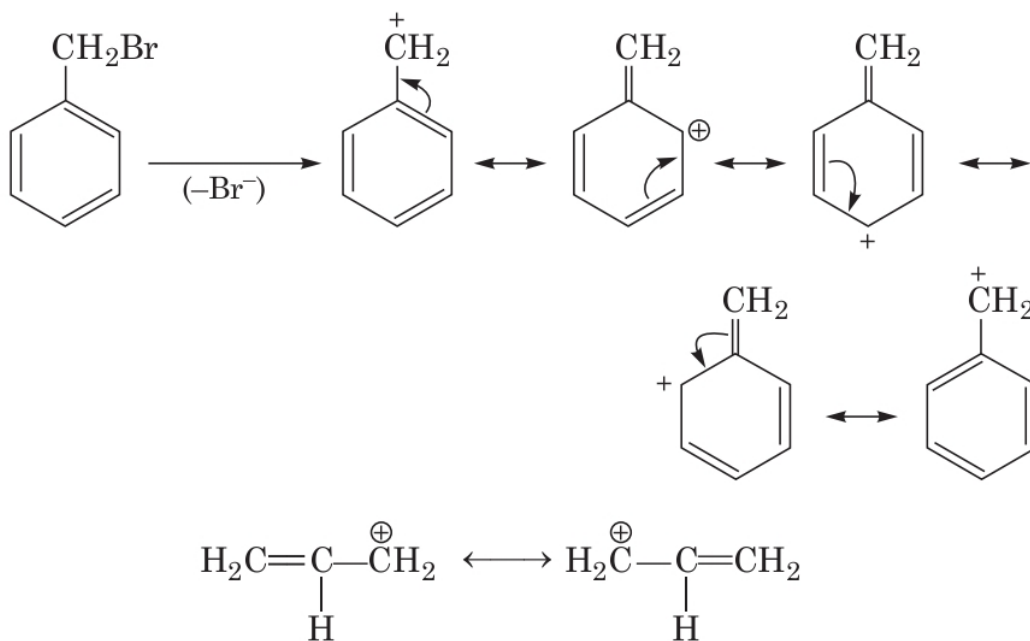


Non-polar solvents, strong nucleophiles and high concentration of nucleophiles favour $\text{S}_{\text{N}}2$ mechanism.

Relative rates of some alkyl halides in $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ reactions are in the order



Resonating structures of benzyl carbocations and allylic carbocation are

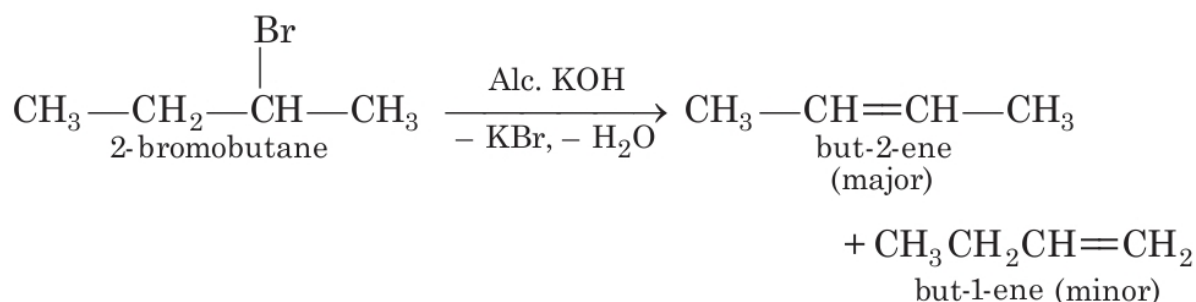


Relative reactivity of alkyl halides having same alkyl group is



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.

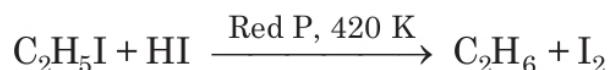
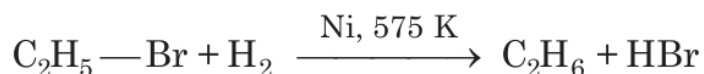


Ease of dehydrohalogenation among alkyl halides



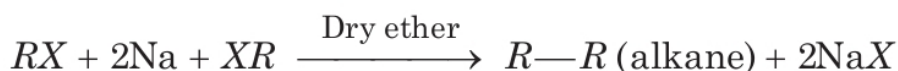
i.e. $(\text{CH}_3)_3\text{CCl} > (\text{CH}_3)_2\text{CHCl} > \text{CH}_3\text{CH}_2\text{Cl}$

Reduction

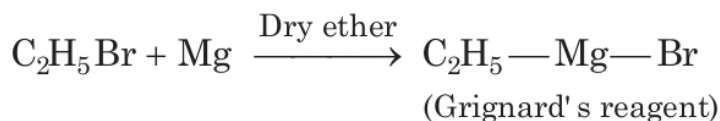


Reaction with Metals

(i) **Wurtz reaction**

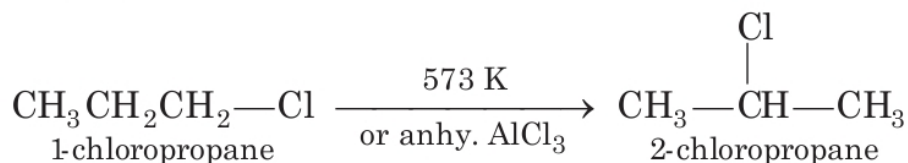


(ii) **Reaction with Mg**



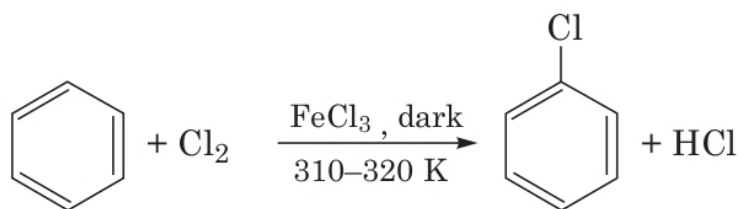
Grignard reagent is never isolated in the solid state as it explodes in dry state. So it is used in ethereal solution.

Isomerisation



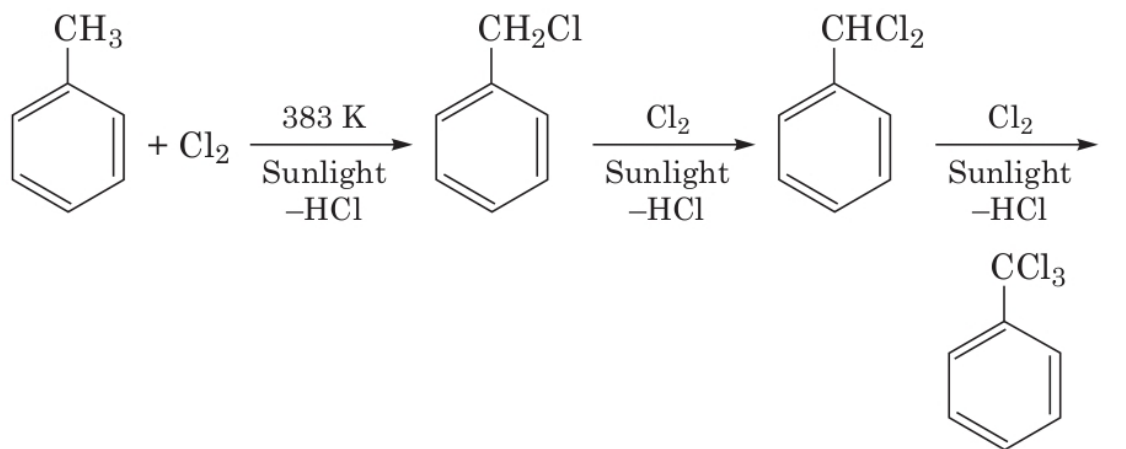
General Methods of Preparation of Aryl Halides (Haloarenes)

By Halogenation of Aromatic Hydrocarbons



It is an electrophilic substitution reaction.

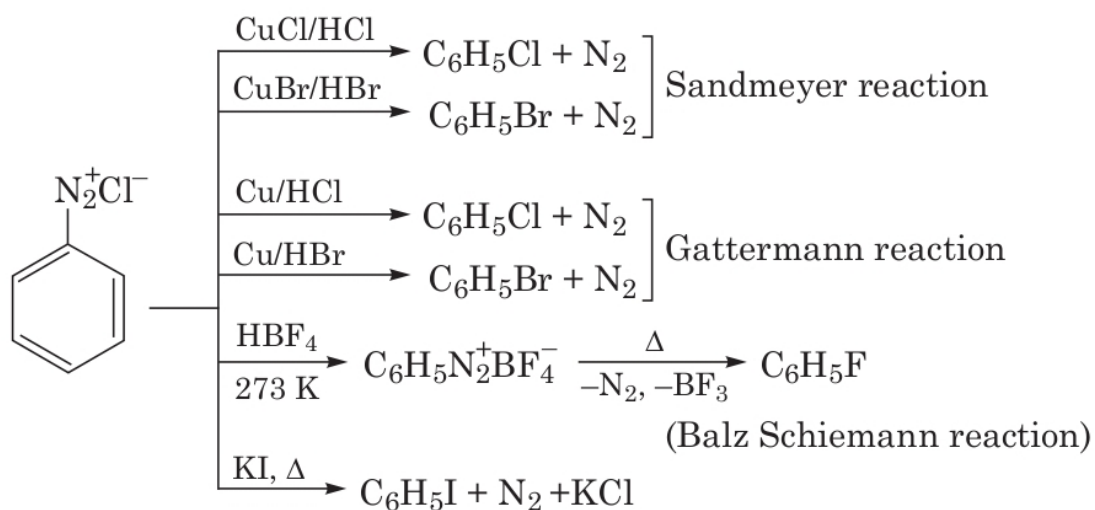
By Side Chain Halogenation



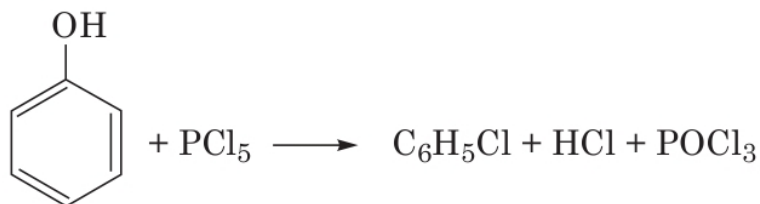
Benzotrichloride

(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
$$\text{Ar—I} > \text{Ar—Br} > \text{Ar—Cl} > \text{Ar—F}$$
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.

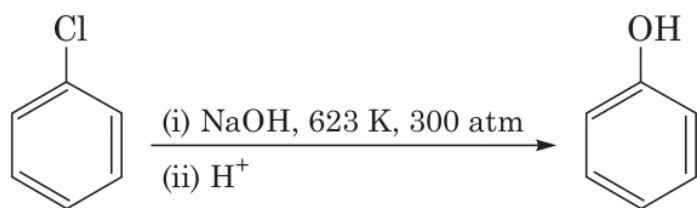
Chemical Properties of Aryl Halides

1. Nucleophilic Substitution Reactions

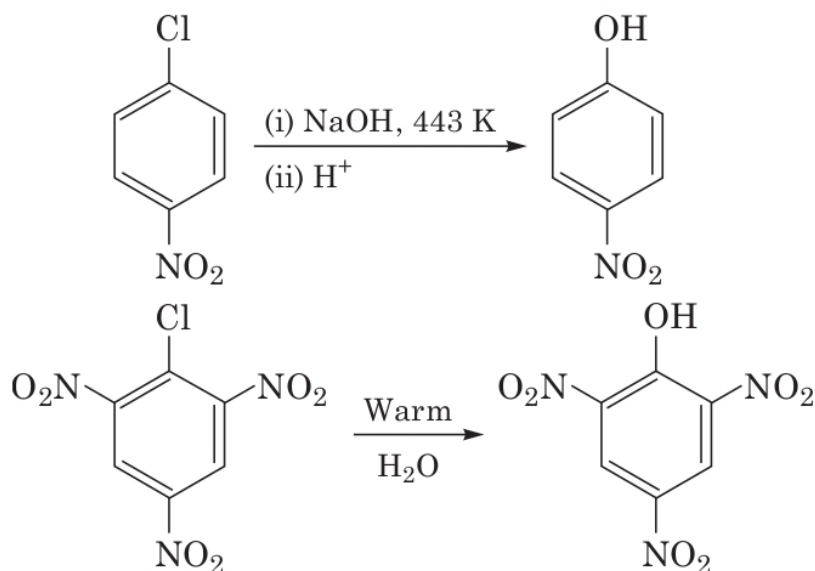
Aryl halides are less reactive towards nucleophilic substitution reaction. Their low reactivity is attributed due to the following reasons:

- (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 , $\text{—SO}_3\text{H}$, etc.) at *ortho* and *para* positions undergo nucleophilic substitution reaction easily.



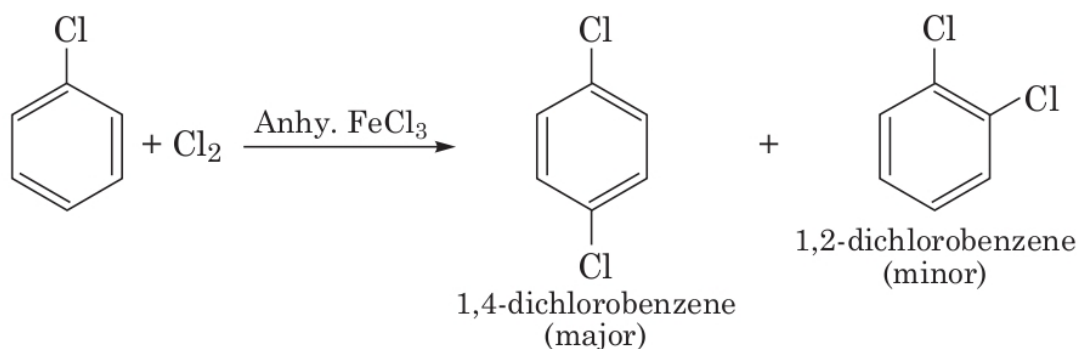
Presence of electron withdrawing group (—NO_2) increases the reactivity.



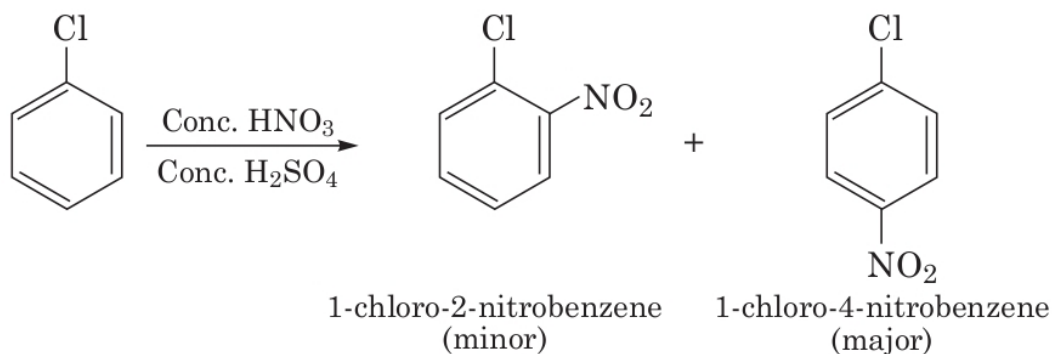
2. Electrophilic Substitution Reactions

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.

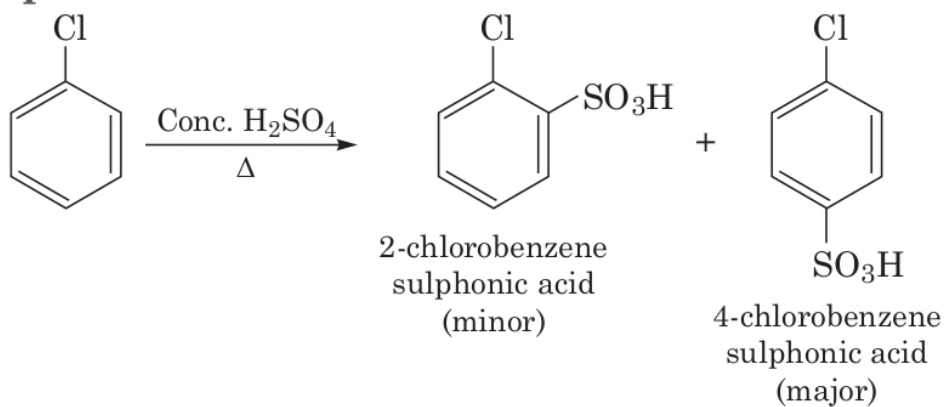
(i) Halogenation



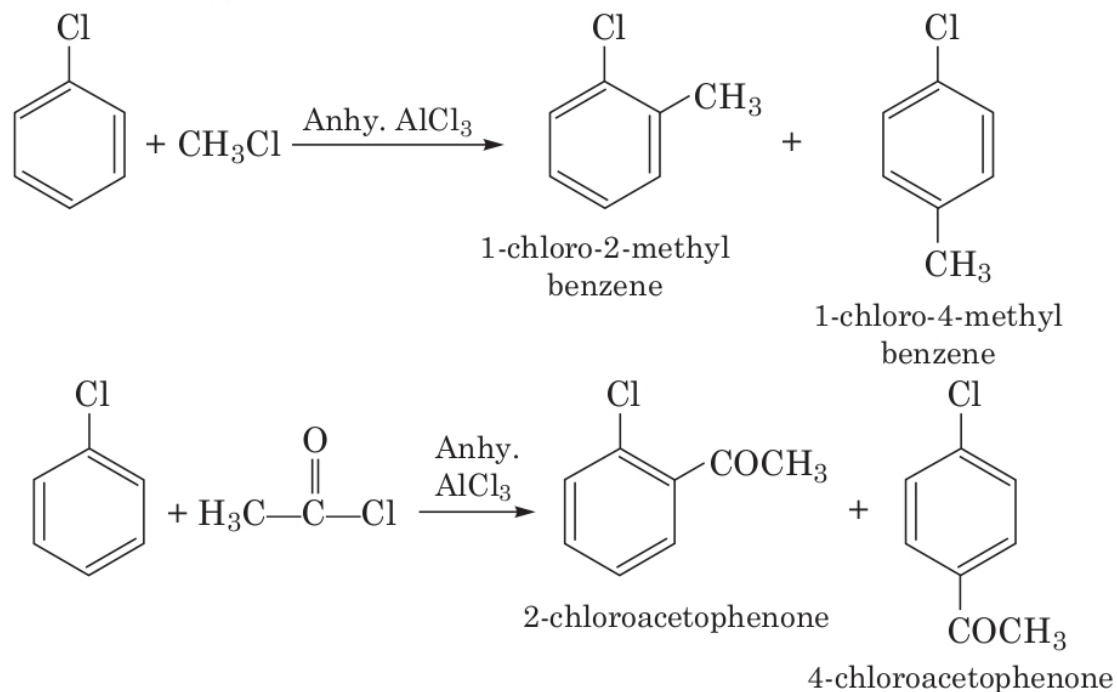
(ii) Nitration



(iii) Sulphonation

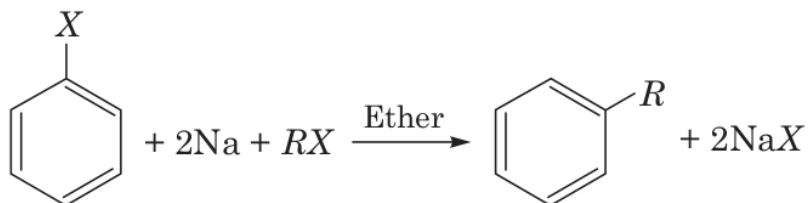


(iv) Friedel-Crafts reaction

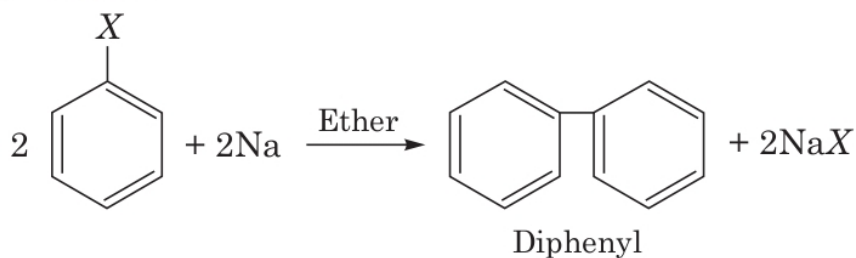


3. Reaction with Metals

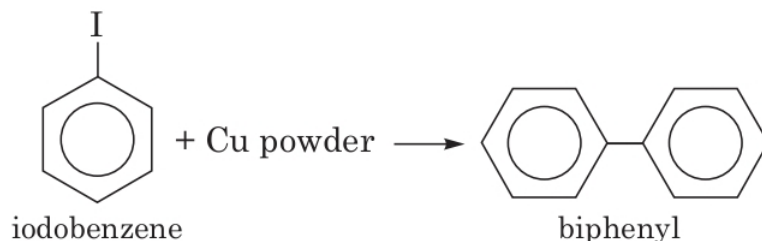
(i) Wurtz Fittig reaction



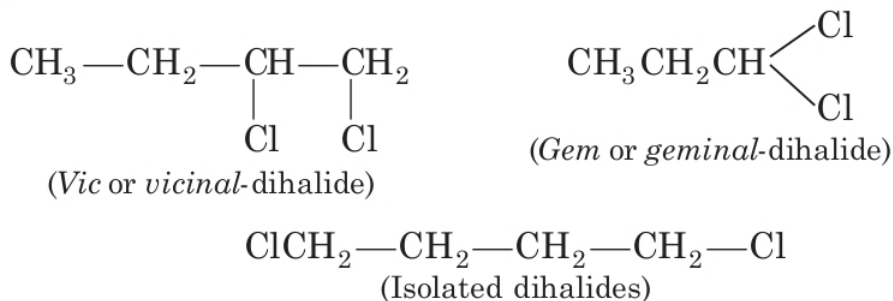
(ii) Fittig reaction



(iii) Ullmann reaction



Dihalogen Derivatives

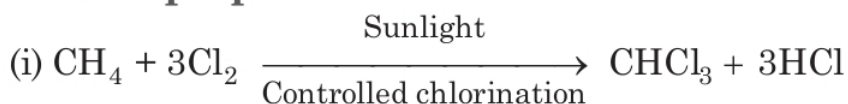


Dichloromethane (CH_2Cl_2) is widely used as a solvent, as a propellant in aerosols. Direct contact of dichloromethane in humans causes intense burning and mild redness of the skin.

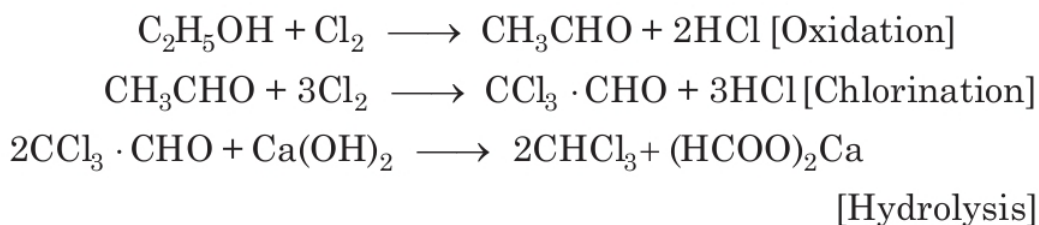
Trihalogen Derivatives

1. Chloroform [Trichloromethane, CHCl_3]

Methods of preparation

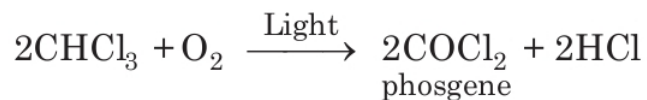


(ii) Haloform reaction



Properties

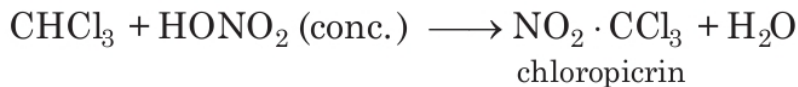
- (i) Oxidation of CHCl_3 gives poisonous gas phosgene (carbonyl chloride).



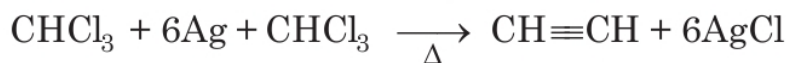
To avoid this oxidation, CHCl_3 is stored in dark brown bottles and filled to the brim. 1% ethanol is added to chloroform which converts harmful phosgene gas into diethyl carbonate.

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

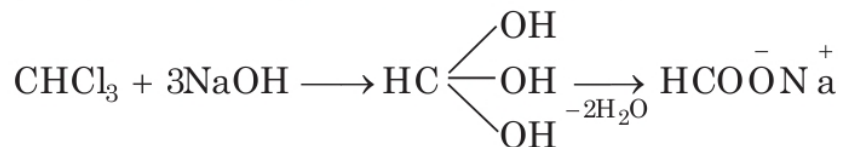
(iii) On nitration, it gives tear producing insecticide substance chloropicrin.



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

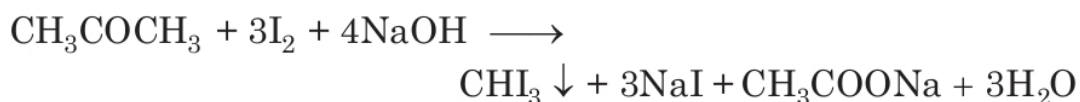


(v) When subjected to hydrolysis, it gives formate.



2. Iodoform (tri-iodomethane, CHI_3)

Iodoform is prepared by iodoform reaction.



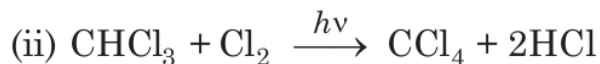
Compounds containing either CH_3CO — or $\text{CH}_3\text{CH}(\text{OH})$ group form yellow coloured iodoform with I_2 and NaOH .

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



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

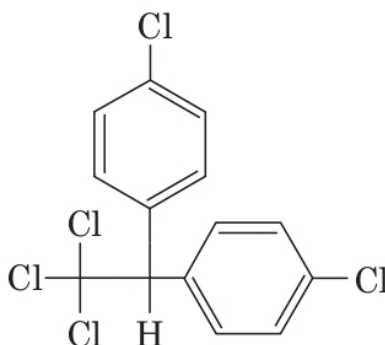
(ii) in dry cleaning

(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, dichlorofluoromethane (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 repellent and is also known as artificial camphor.