

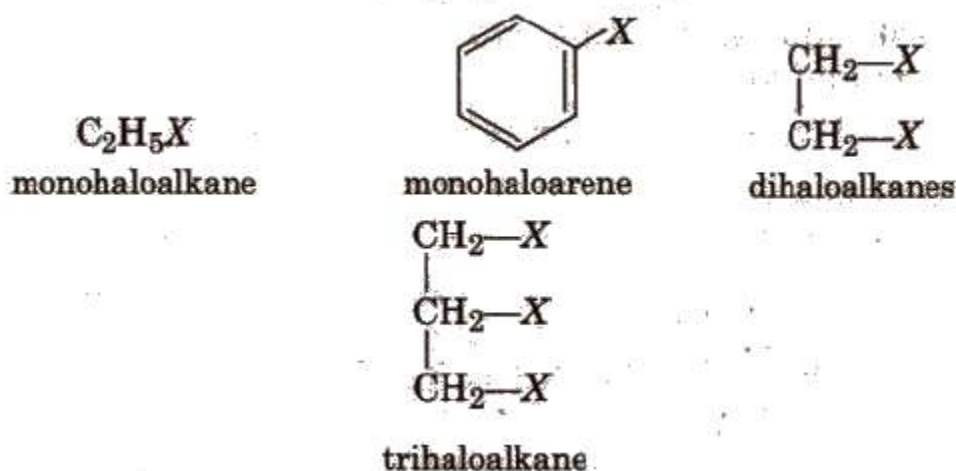
Chemistry Notes for class 12 Chapter 10

Haloalkanes and Haloarenes

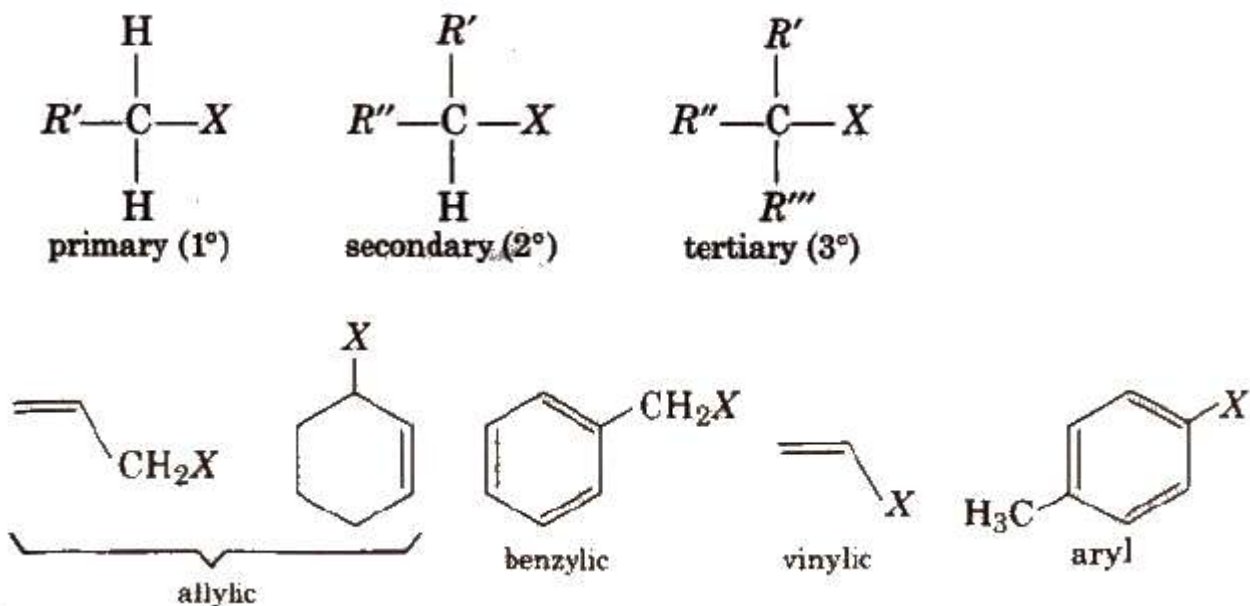
The replacement of hydrogen atom(s) in hydrocarbon, aliphatic or aromatic, by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene), respectively.

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.,

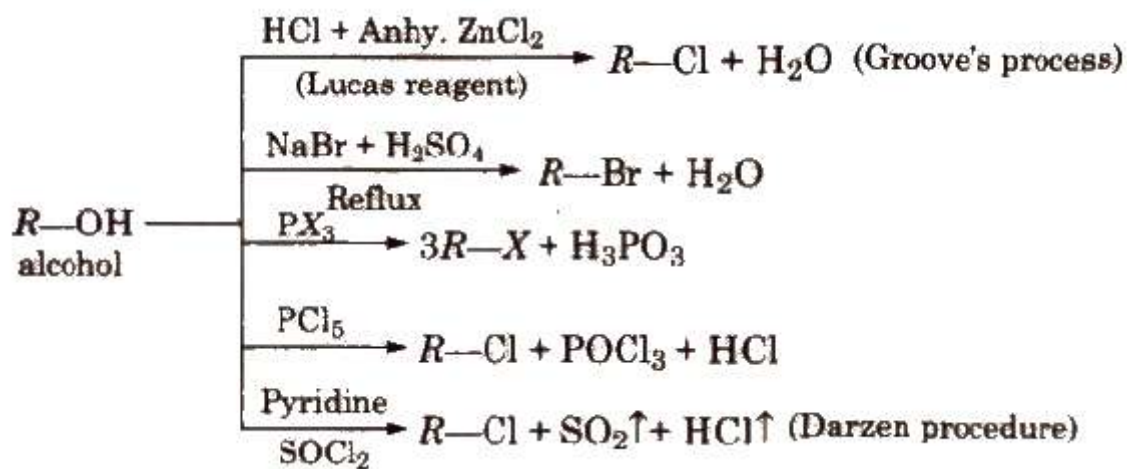


On the basis of the nature of the carbon to which halogen atom is attached, halogen derivatives are classified as 1° , 2° , 3° , allylic, benzylic, vinylic and aryl derivatives, e.g.,



General Methods of Preparation of Haloalkanes

1. From Alcohols

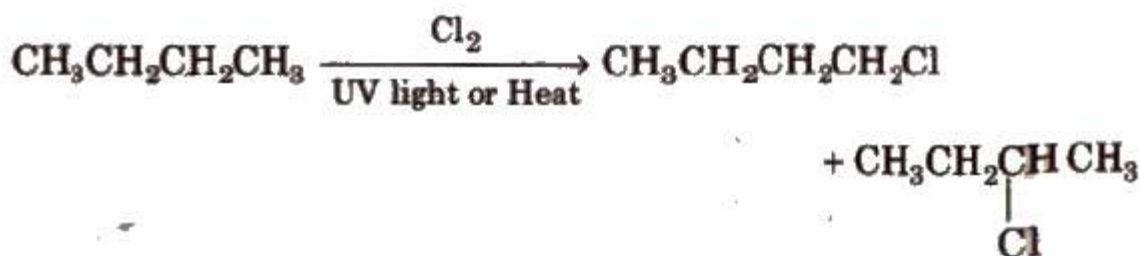


In Groove's method, $ZnCl_2$ is used to weaken the C-OH bond. In case of 3° alcohols, $ZnCl_2$ is not required.

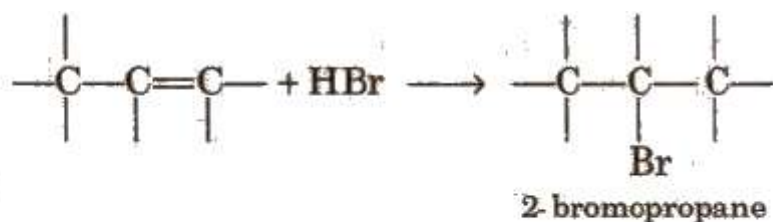
The reactivity order of halogen acids is $HI > HBr > HCl$.

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



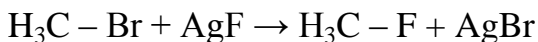
Addition of Hydrogen Halides on Alkenes



1. Finkelstein Reaction

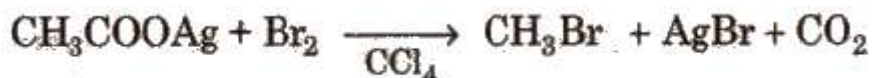


2. Swarts Reaction



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

3. Hunsdiecker Reaction

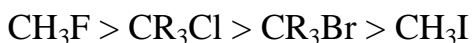


Physical Properties of Haloalkanes

1. Boiling point orders

1. $\text{R}-\text{I} > \text{R}-\text{Br} > \text{R}-\text{Cl} > \text{R}-\text{F}$
2. $\text{CH}_3-(\text{CH}_2)_2-\text{CH}_2\text{Br} > (\text{CH}_3)_2\text{CHCH}_2\text{Br} > (\text{CH}_3)_3\text{CBr}$
3. $\text{CH}_3\text{CH}_2\text{CH}_2 > \text{CH}_3\text{CH}_2\text{X} > \text{CH}_3\text{X}$

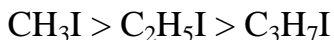
2. Bond strength of haloalkanes decreases as the size of the halogen atom increases. Thus, the order of bond strength is



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

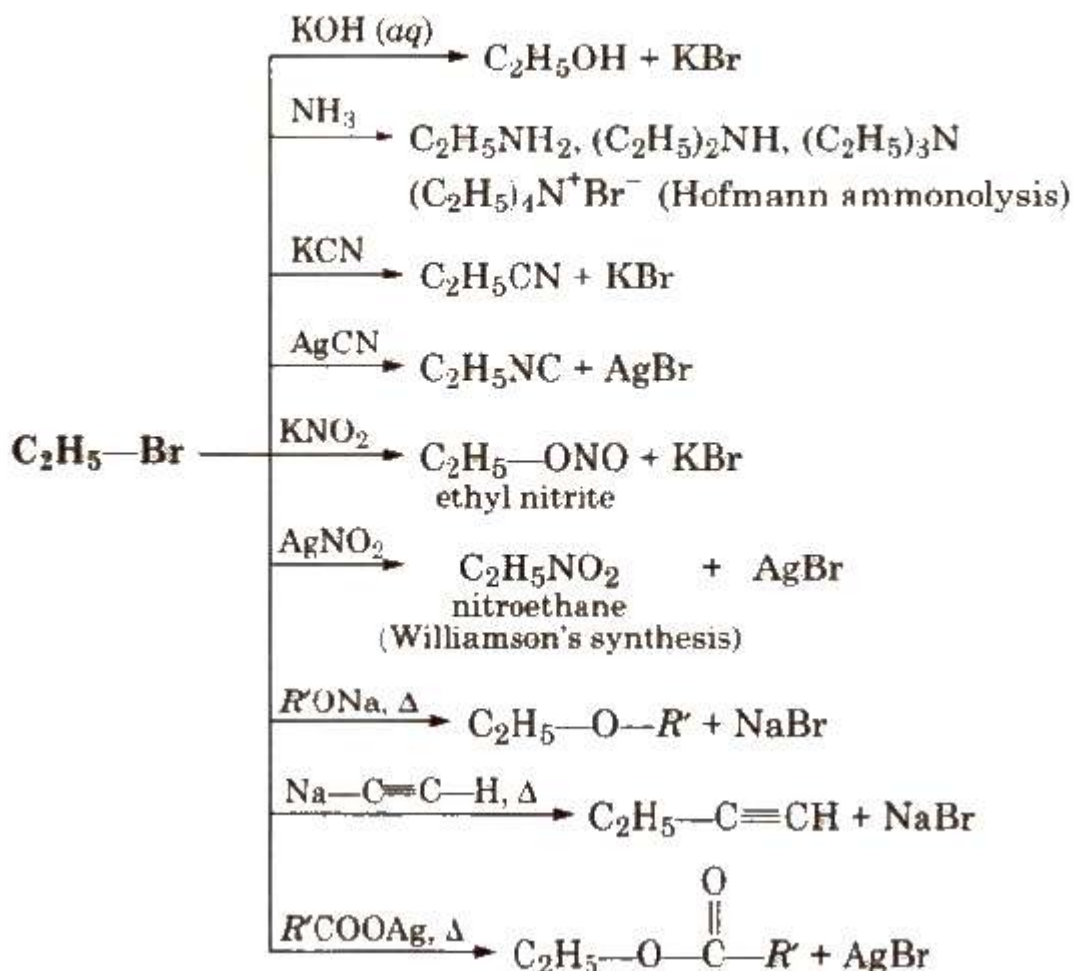
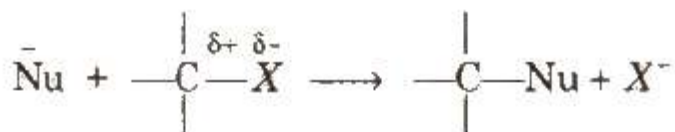
4. Haloalkanes though polar but are insoluble in water as they do not form hydrogen bonding with water.

5. Density order is



Chemical Reactions of Haloalkanes

1. Nucleophilic Substitution Reactions (S_N reactions)

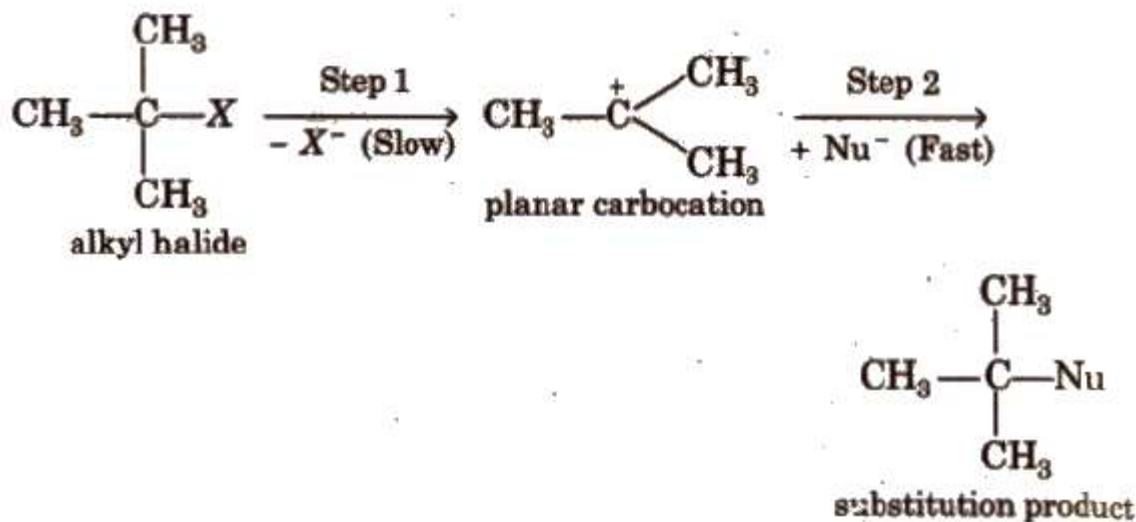


kCN is predominantly ionic and provides cyanide ions in solution, which is ambident nucleophile and bind with carbon side to form as the major product, while AgCN is covalent and form isocyanide as the major product.

Like KCN, KNO₂ form R-ONO while AgNO₂ produces R-NO₂ as product. Vinyl chloride is less reactive towards nucleophilic substitution reactions due to resonance.

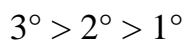
Nucleophilic substitution reactions are of two types

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



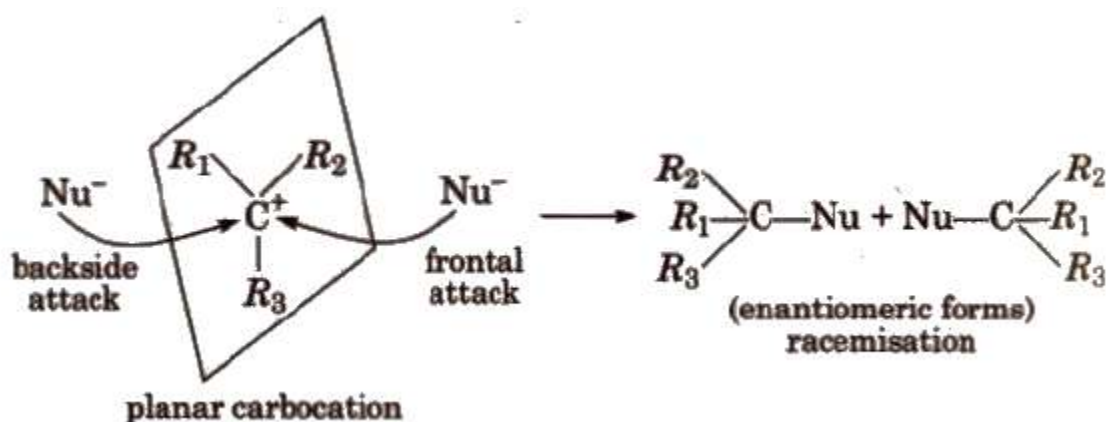
Rate, $r = k [RX]$. It is a first order reaction.

Reactivity order of alkyl halide towards S_N1 mechanism



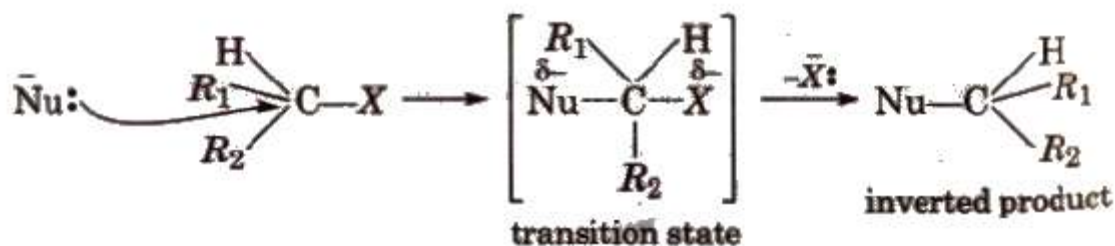
Polar solvents, low concentration of nucleophiles and weak nucleophiles favour S_N1 mechanism.

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

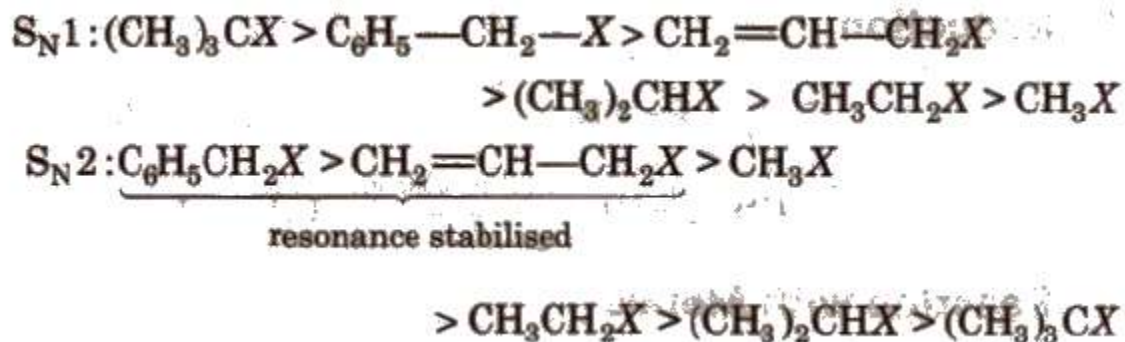


Rate of reaction in S_N2 mechanism depends on the strength of the attacking nucleophile. Strength of some common nucleophiles is

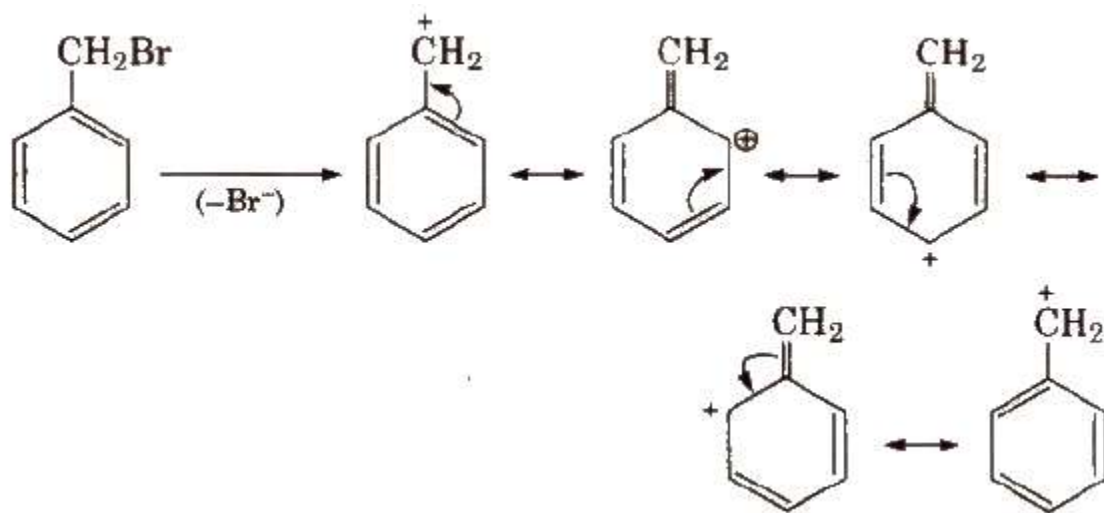


Non-polar solvents, strong nucleophiles and high concentration of nucleophiles favour S_N2 mechanism.

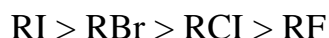
Relative rates of some alkyl halides in S_N1 and S_N2 reactions are in the order



Resonating structure of benzyl carbocations are

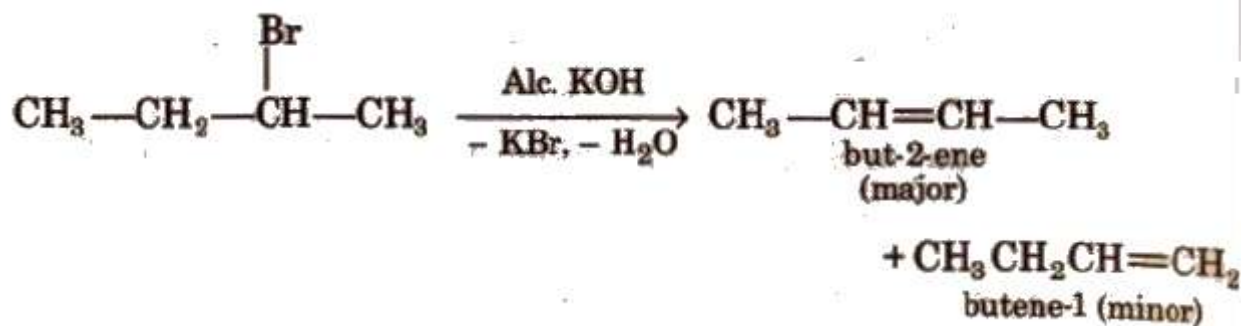


Relative reactivity of alkyl halides for same alkyl group is

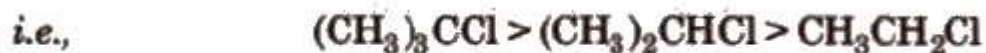
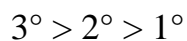


2. Elimination Reactions

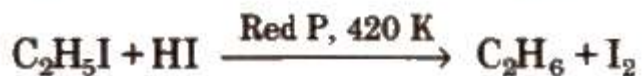
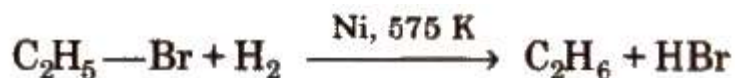
Dehydrohalogenation is a β – elimination reaction in which halogen is from α -carbon atom and the hydrogen from the α -carbon according to Saytzeff rule, e.g.,



Ease of dehydrohalogenation among halides

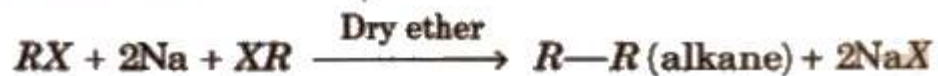


3. Reduction



4. Reaction with Metals

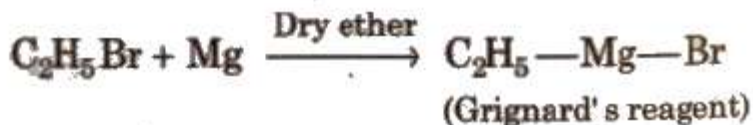
(i) Wurtz reaction



(ii) Wurtz-Fittig reaction

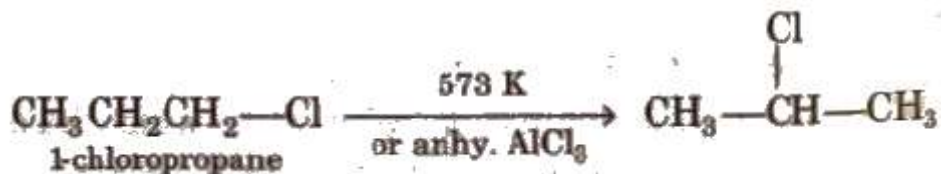


(iii) Reaction with Mg



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

5. Isomerisation



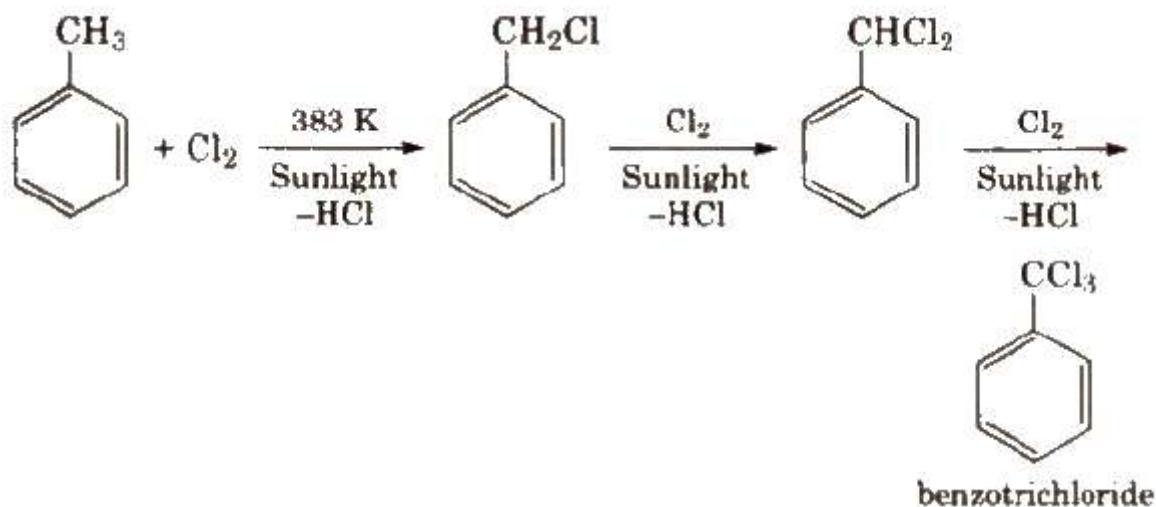
General Methods of Preparation of Aryl Halides

1. By Halogenation of Aromatic Hydrocarbons



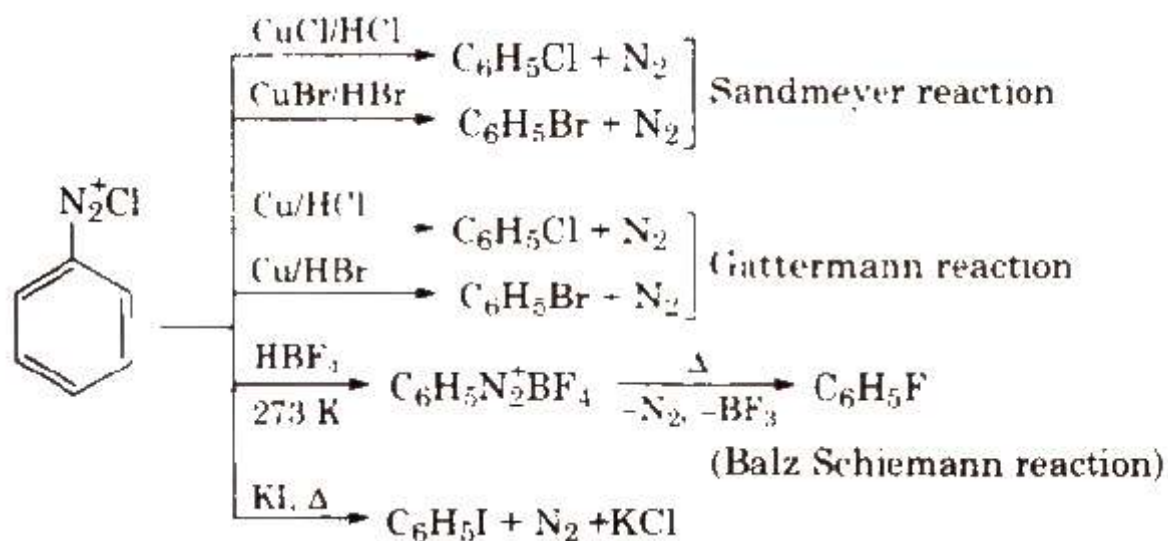
It is an electrophilic substitution reaction.

2. By Side Chain Halogenation

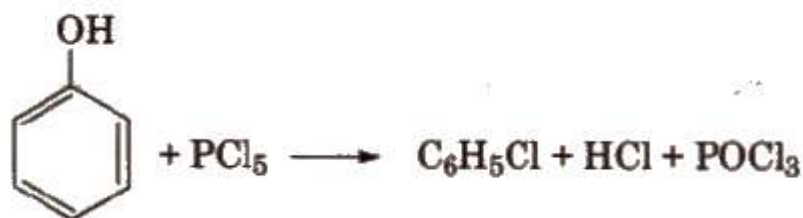


(It involves free radical mechanism.)

3. From Benzene Diazonium Salt



4. From Phenol

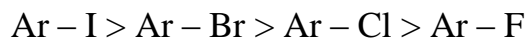


Physical Properties of Aryl Halides

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



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 cyclohexyl chloride.

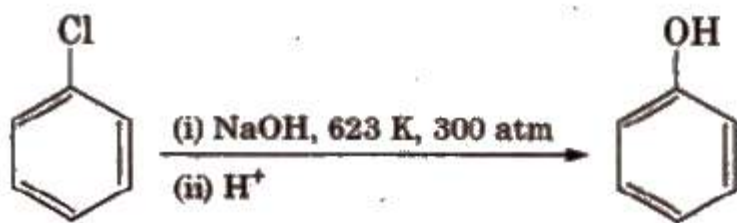
Chemical Properties of Aryl Halides

1. Nucleophilic Substitution Reaction

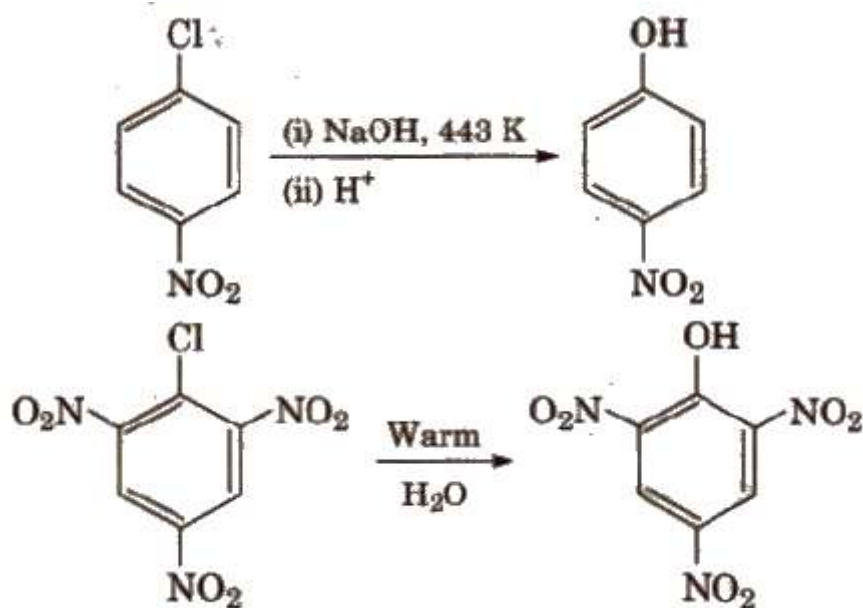
Aryl halides are less reactive towards nucleophilic substitution reaction. Their low reactivity is attributed due to the following reasons:

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 $-\text{NO}_2$, $-\text{SO}_3\text{H}$, etc.) at ortho and para positions undergo nucleophilic substitution reaction easily.



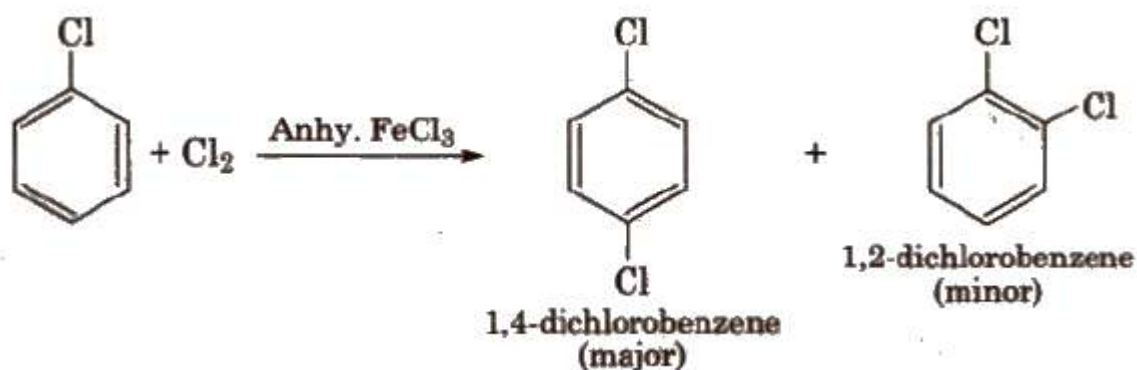
Presence of electron withdrawing group ($-\text{NO}_2$) increases the reactivity.



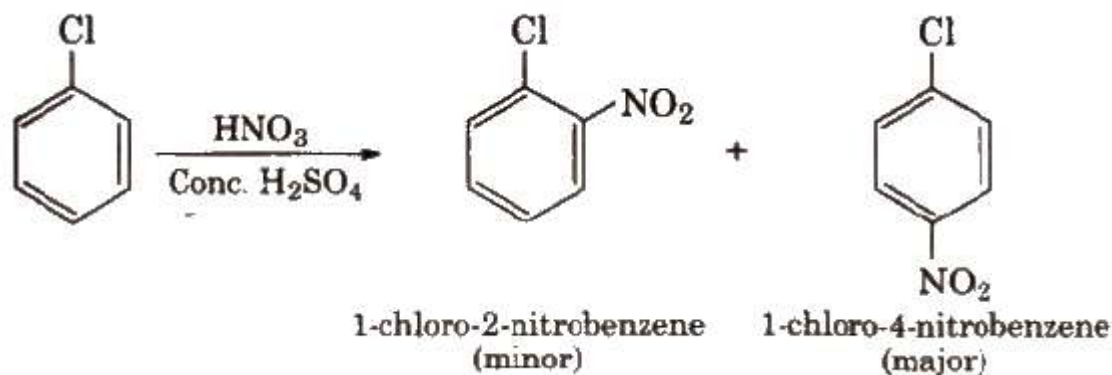
2. Electrophilic Substitution Reactions

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.

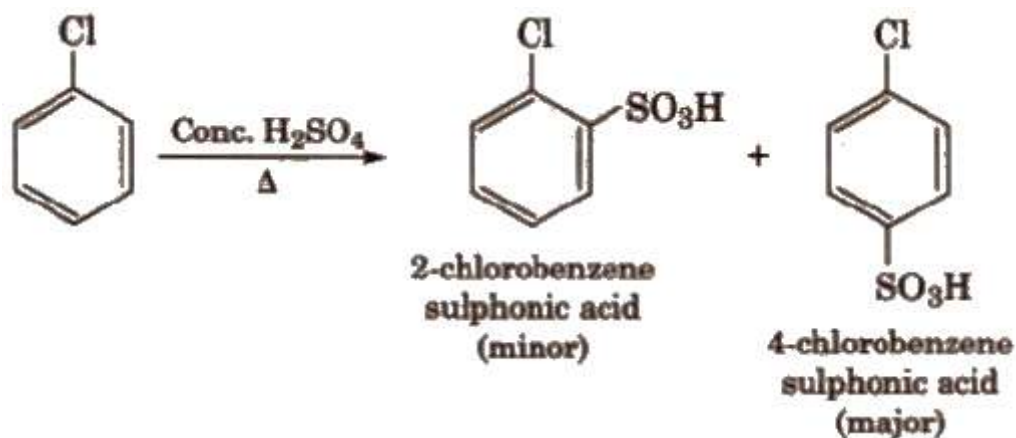
(i) Halogenation



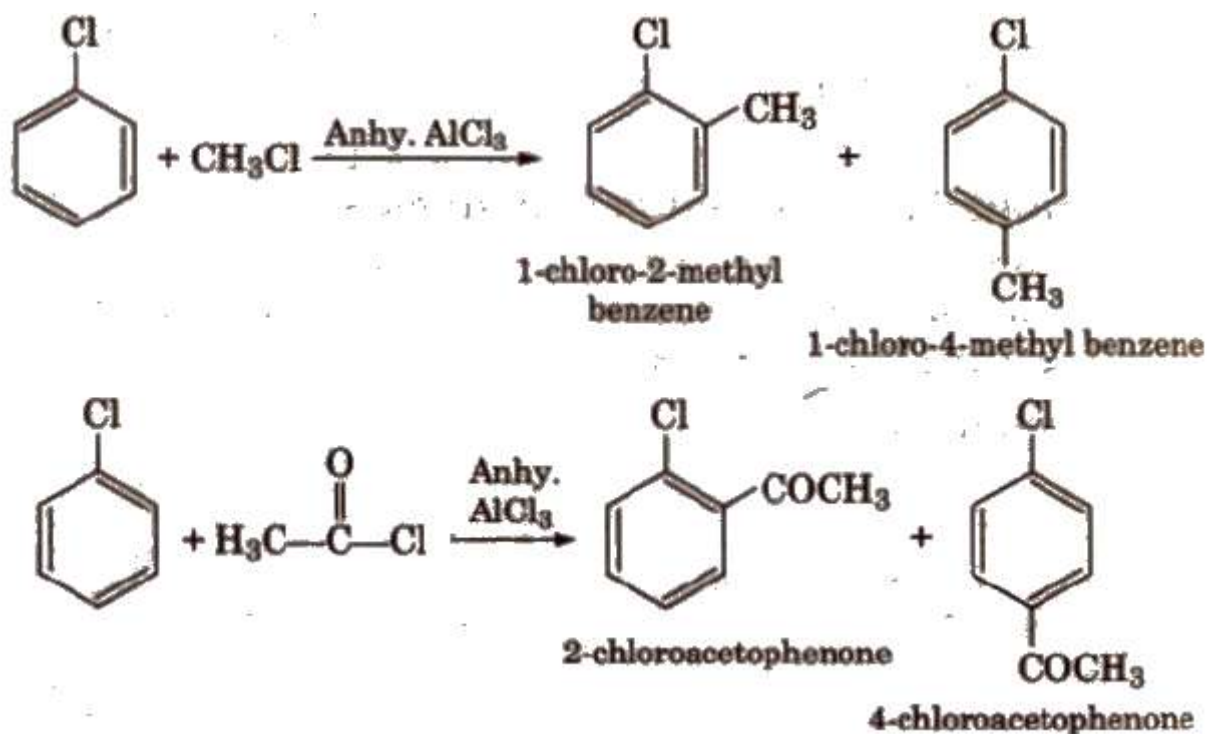
(ii) Nitration



(iii) Sulphonation

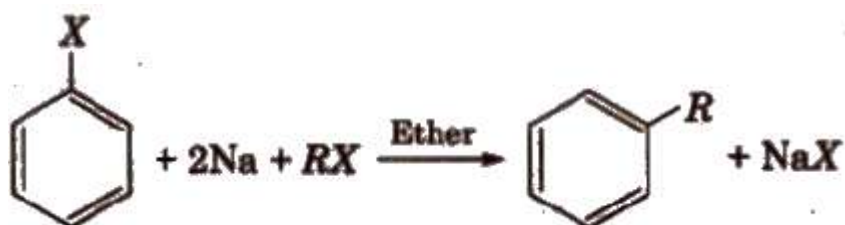


(iv) Friedel-Crafts reaction

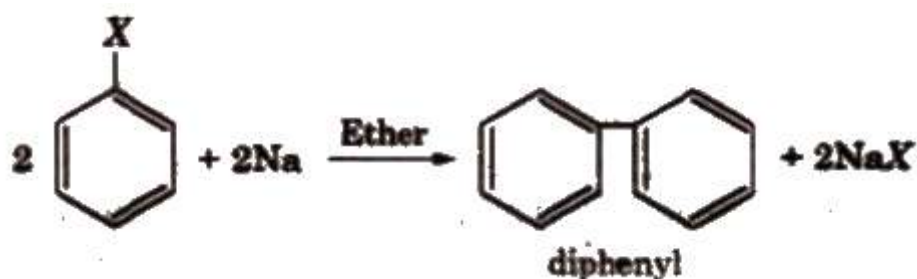


3. Reaction with Metals

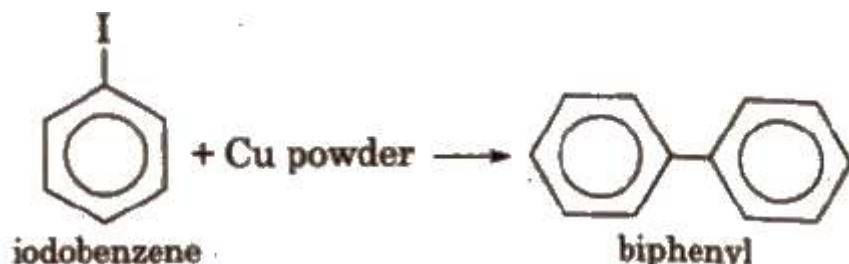
(i) Wurtz Fittig reaction



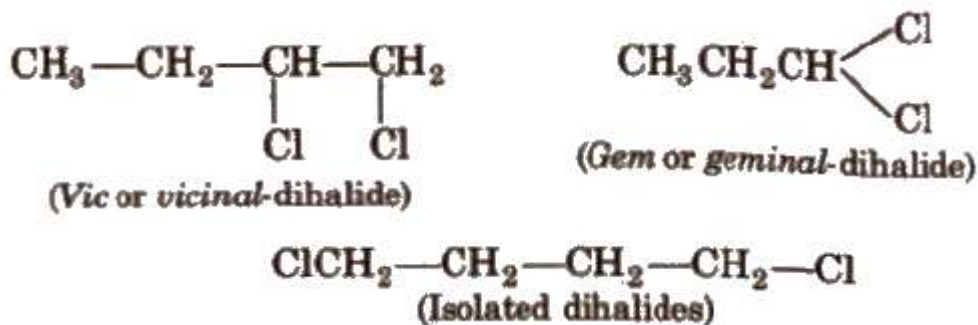
(ii) Fitting reaction



(iii) Ullmann reaction



Dihalogen Derivatives

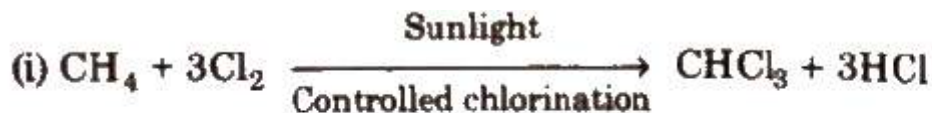


Dichloromethane (CH_2Cl_2) is widely used as a solvent, as a propellant in aerosols. Direct contact of dichloromethane in humans causes intense burning and milk redness of the skin.

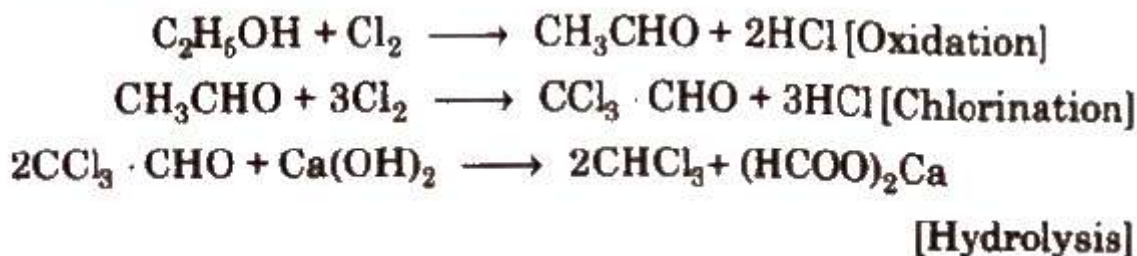
Trihalogen Derivatives

1. Chloroform [Trichloromethane, CHCl_3]

Methods of preparation

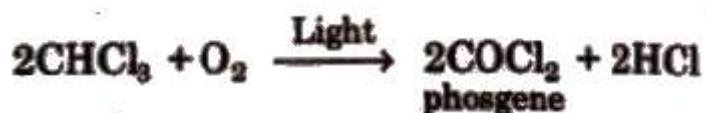


(ii) Haloform reaction



Properties

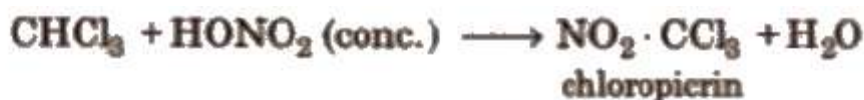
1. Oxidation of CHCl_3 gives poisonous gas phosgene (carbonyl chloride).



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.

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

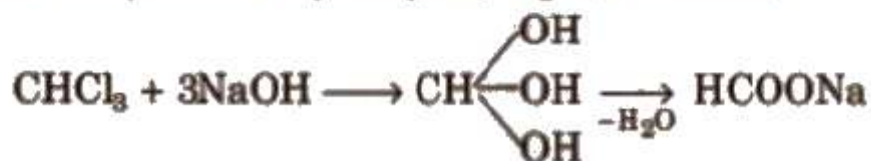
3. On nitration, it gives tear producing insecticide substance chloropicrin.



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



5. When subjected to hydrolysis, it gives formate.



2. Iodoform (tri-iodomethane, CHI_3)

Iodoform is prepared by iodoform reaction.



Compounds containing either $\text{CH}_3\text{CO}-$ or $\text{CH}_3\text{CH}(\text{OH})$ 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



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

Uses

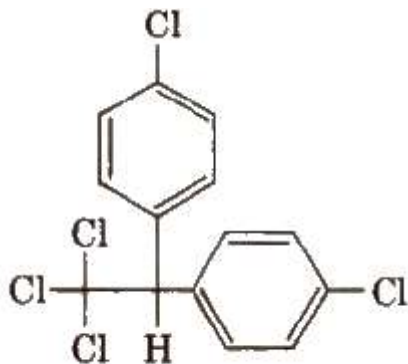
Carbon tetrachloride is used

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, 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.

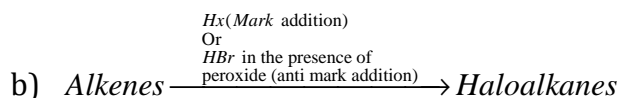
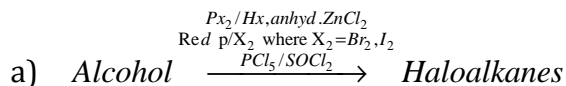
SUMMARY

CBSE Class-12 Chemistry Quick Revision Notes
Chapter-10: Haloalkanes and Haloarenes

- **Nature of C-X bond in alkyl halides:**

X is more electronegative than carbon. So, the C-X bond is polarized with C having a partial positive charge and X having a partial negative charge.

- **Preparation of haloalkanes:**

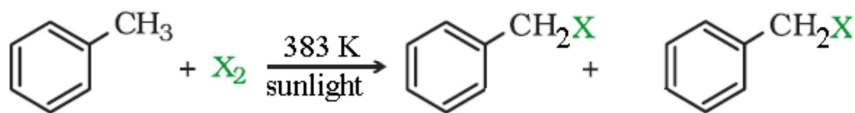
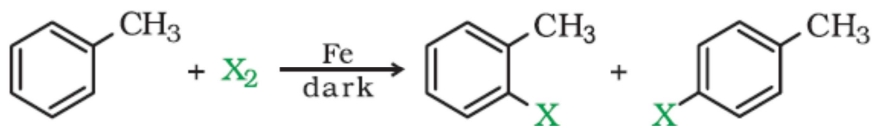


d) **Halogen Exchange Method:**

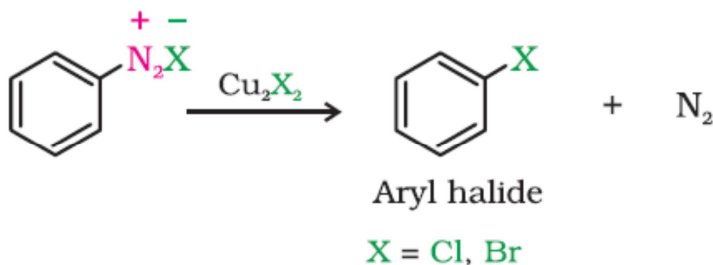
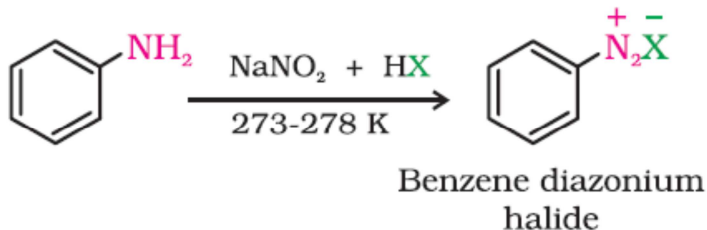


- **Preparation of haloarenes:**

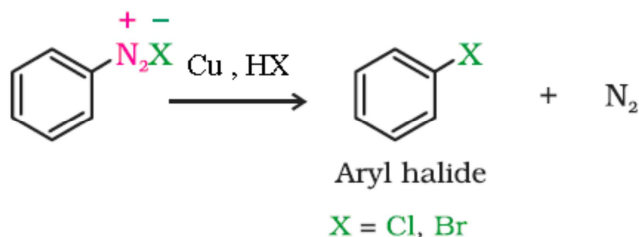
a) By electrophilic substitution reaction:



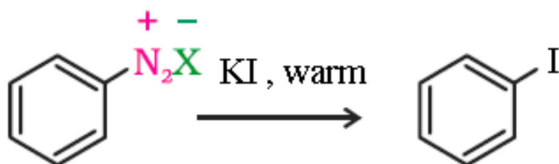
b) Sandmeyer's reaction:



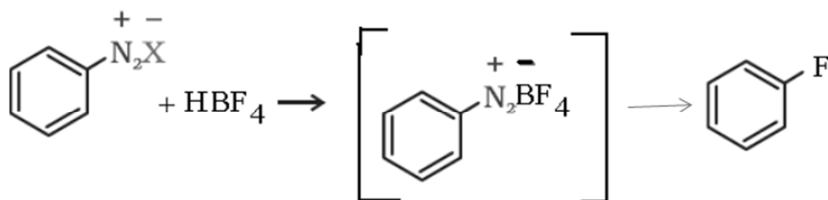
c) Gattermann reaction:



d) From Diazonium Chloride:



e) Balz – Schiemann reaction:



- **Physical properties of haloalkanes:**

a) Solubility

- i. Although haloalkanes are polar in nature, yet they are practically very slightly soluble in water.
- ii. In order for a haloalkane to dissolve in water, energy is required to overcome the attractions between the haloalkane molecules and break the hydrogen bonds between water molecules.
- iii. However Haloalkanes are not able to form hydrogen bonds with water and therefore, less energy is released when new attractions are set up between the haloalkane and the water molecules because these are not as strong as the original hydrogen bonds in water molecules.
- iv. As a result, solubility of haloalkanes in water is low.

b) Density

- i. Simple fluoro and chloroalkanes are lighter than water while bromides and polychloro derivatives are heavier than water.
- ii. With the increase in number of carbon atoms, the densities go on increasing. With the increase in number of halogen atoms, the densities go on increasing. The densities increase in the order: Fluoride < chloride < bromide < iodide
- iii. The density also increases with increasing number and atomic mass of the halogen.

c) Boiling Points

- i. Molecules of organic halogen compounds are generally polar.

- ii. Due to the polarity as well as higher molecular mass as compared to the parent hydrocarbon, the intermolecular forces of attraction (dipole – dipole and van der Waals) between the molecules are stronger in halogen derivatives of alkanes.
- iii. As a result melting and boiling points of chlorides, bromides and iodides are considerably higher than those of the parent hydrocarbon of comparable molecular mass.
- iv. For the same alkyl group the boiling points of alkyl chlorides, bromides and iodides follow the order $RI > RBr > RCl > RF$ where R is an alkyl group. This is because with the increase in the size of the halogen, the magnitude of van der Waals force increase.
- v. In general, the boiling points of chloro, bromo and iodo compounds increase with increase in the number of halogen atoms.
- vi. For the same halogen atom, the boiling points of haloalkanes increase with increase in the size of alkyl groups.
- vii. For isomeric alkyl halides, the boiling points decrease with branching. This is because branching of the chain makes the molecule more compact and, therefore, decrease the surface area. Due to decrease in surface area, the magnitude of van der Waals forces of attraction decreases and consequently, the boiling points of the branched chain compound is less than those of the straight chain compounds.

- **Physical Properties of Haloarenes:**

- a. These are generally colourless liquids or crystalline solids.
- b. These are heavier than water.
- c. Melting and boiling points of haloarenes
 - i. Melting and boiling points of haloarenes are nearly the same as those of alkyl halides containing the same number of carbon atoms.
 - ii. The boiling points of monohalogen derivatives of benzene are in the order: iodo > bromo > chloro > fluoro
 - iii. For the same halogen atom, the melting and boiling points increase as the size of the aryl group increases.
 - iv. The melting point of para isomer is quite higher than that of ortho or meta isomers. This is due to the fact that it has symmetrical structure and therefore, its molecules can easily pack loosely in the crystal lattice. As a result intermolecular forces of attraction are stronger and therefore, greater energy is required to break its lattice and it melts at higher temperature.

- **Chemical properties of haloalkanes:**

Nucleophilic substitution reaction:



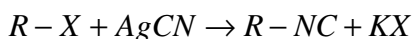
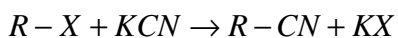
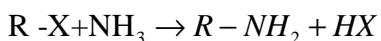
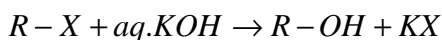
Mechanism of Nucleophilic Substitution Reaction:

S_N1 Mechanism

- a) First order reaction.
- b) Rate = $k [RX] [Nu]$
- c) Racemic mixture
- d) One step reaction
- e) Order: $CH_3X < 1^\circ < 2^\circ < 3^\circ$

S_N2 Mechanism

- a) Second order reaction
- b) Rate = $k [RX]$
- c) Inversion of configuration
- d) Two step reaction
- e) Order: $CH_3X > 1^\circ > 2^\circ > 3^\circ$

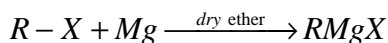


- Elimination reaction: Dehydrohalogenation (β - elimination):

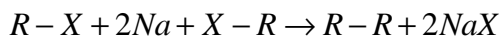
When a haloalkane with β-hydrogen atom is heated with alcoholic solution of potassium hydroxide, there is elimination of hydrogen atom from β-carbon and a halogen atom from the α-carbon atom. As a result, an alkene is formed as a product. Zaitsev rule (also pronounced as Saytzeff) is followed. It states that "In dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms."

- Reaction with metals:

- a) Reaction with Magnesium

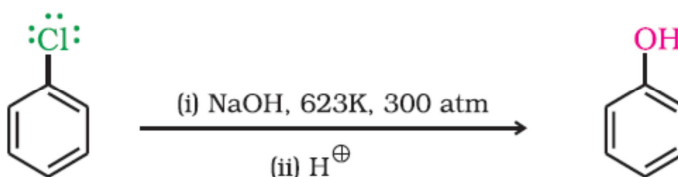


- b) Wurtz reaction

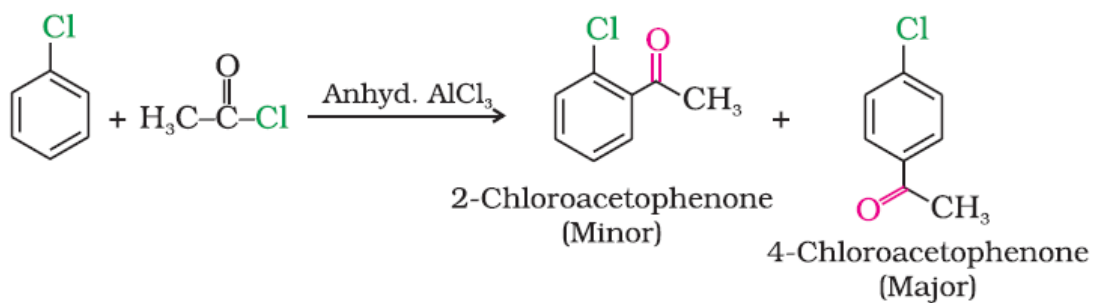
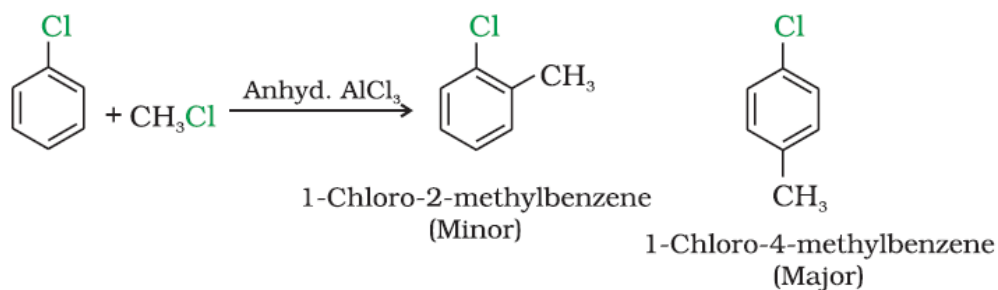
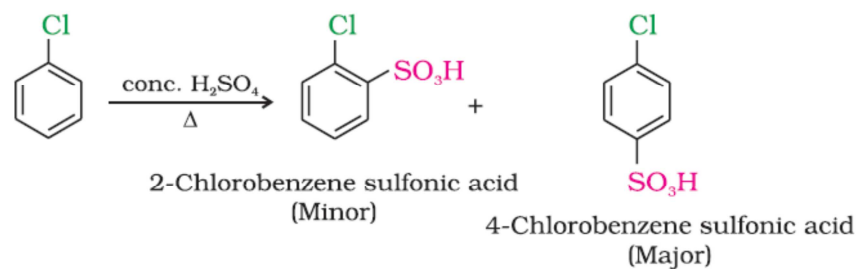
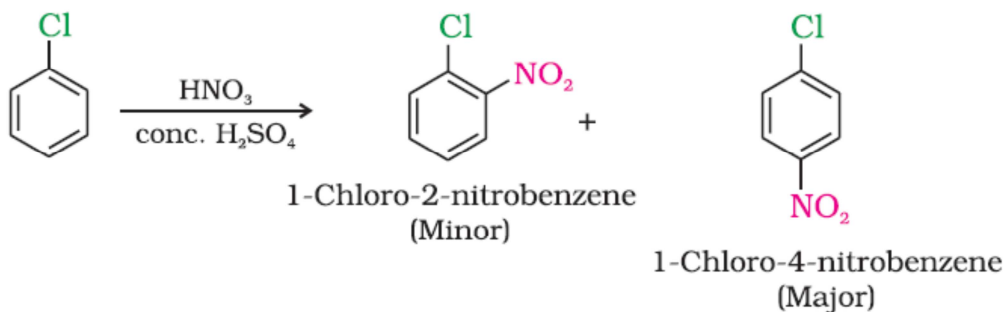
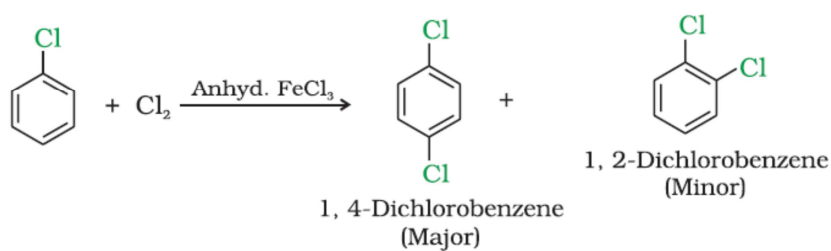


- **Chemical properties of haloarenes:**

- a) Dow's Process



- b) With halogens



g) Fittig reaction:



h) Wurtz – fittig reaction:



i) Other conversions:

