ORGANIC COMPOUNDS CONTAINING HALOGENS

METHODS OF PREPARATION OF ALKYL HALIDES

(I) From Alcohols

(a) By using hydrogen halide

$$R - OH \xrightarrow{HX} RX + H_2O$$

(b) By using phosphorous halides

$$ROH + PCl_5 \longrightarrow RCl + POCl_3 + HCl$$

$$3ROH + PCl_3 \longrightarrow 3RCl + H_3PO_3$$

$$3ROH + PBr_3 \longrightarrow 3RBr + H_3PO_3$$

$$3ROH + PI_3 \longrightarrow 3R - I + H_3PO_3$$

(c) By using $SOCl_2$ (thionyl chloride)

$$R - OH + SOCl_2 \xrightarrow{\text{Pyridine}} R - Cl + SO_2\uparrow + HCl\uparrow$$

(II) By Direct halogenation of hydrocarbons

$$R - H \xrightarrow[h\nu]{X_2} R - X + HX$$

Reactivity of hydrocarbon in the above reaction with respect to type of hydrogen to be replaced follows following order

Tertiary hydrogen > Secondary hydrogen > Primary hydrogen.

(III) By halide Exchange

$$R - Cl \xrightarrow[\text{Acetone}]{NaI} R - I + NaCl$$

$$R - Br \xrightarrow[\text{Acetone}]{NaI} R - I + NaBr$$

(IV) By addition of HX to alkenes

Alkyl chlorides, bromides and iodides can be prepared by treating an alkene with corresponding hydrogen halides (HCl, HBr and HI). The addition of these compounds to alkene takes place according to Markovnikov's rule.

(V) From silver salts of carboxylic Acid

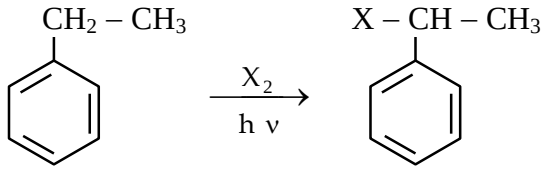
$$RCOOAg + X_2 \xrightarrow{CCl_4} RX + AgX + CO_2$$

($X_2 = Cl_2$ or Br_2)

This reaction is popularly known as *Hunsdieker reaction*.

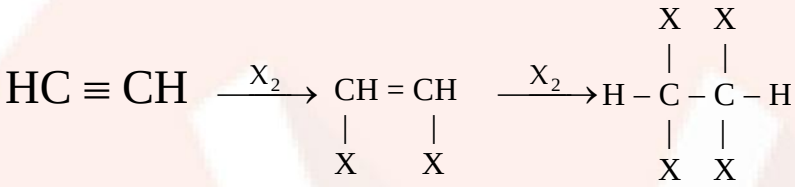
(VI) Preparation of allylic or benzylic halides

(i) Direct halogenation of any aromatic hydrocarbon preferably gives benzylic halide. This is because benzyl radical is resonance stabilized.

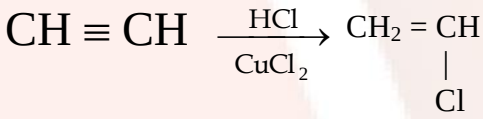


(VII) Preparation of Polyhalides

Addition of halogen (Cl_2 or Br_2) to alkynes produces tetrahaloderivatives.



(VIII) Preparation of Vinyl halides



PHYSICAL PROPERTIES

Because of small polarity in alkyl halides (carbon–halogen bond is polar due to difference in electronegativities of the two atoms) as well as greater molecular weights, alkyl halides have considerably higher boiling points than alkanes containing same number of carbon atoms.

CHEMICAL PROPERTIES

(I) Preparation of Organometallic compounds

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

(Grignard reagent)

$$R - X \xrightarrow[\text{ether}]{Li} R - Li + LiX$$

(Organo lithium compound)

(II) Reduction of alkyl halides

$$R - X \xrightarrow{\text{Reduction}} R - H$$

The reagents used for reduction of alkyl halide to alkane are Zn and CH_3COOH, Zn and HCl, Zn and NaOH, Zn – Cu couple and alcohol, aluminium amalgam and alcohol etc.

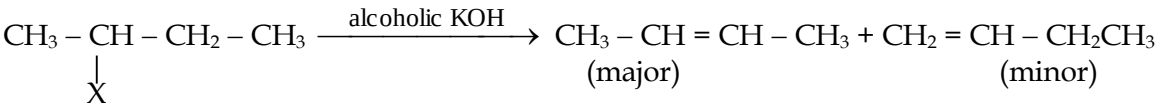
(III) Wurtz reaction

$$2R - X + 2Na \xrightarrow{\text{ether}} R - R + 2NaX$$

Details about this reaction had already been discussed during preparation of *alkanes*.

(IV) Dehydrohalogenation of alkyl halides

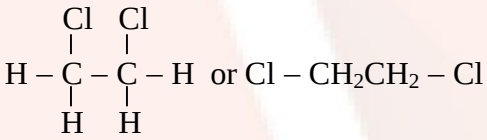
$$R - X \xrightarrow{\text{alcoholic KOH}} \text{Alkene}$$



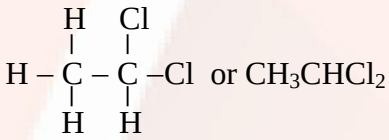
More substituted alkene is always obtained as a major product.

Dihalogen Derivatives

Two halogens may be linked to the same or different carbon atoms.



ethylene chloride
(1,2 or vic–dichloroethane)



ethylidene chloride
(1,1 or gem–dibromoethane)

Methods of Preparation

(i) By the action of phosphorus pentahalides on aldehydes or ketones

(ii) By the addition of halogen halides to alkynes

(iii) By the addition of halogens to alkenes

(iv) By the action of hydrogen halides or phosphorus halides on glycols.

Physical Properties

(i) They are sweet smelling colourless liquids, having comparatively high boiling point. Highest members are solids.

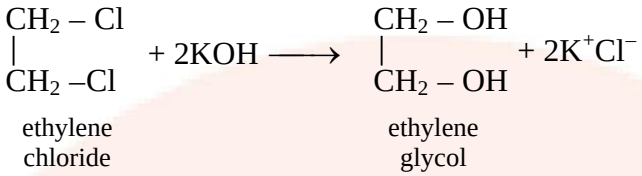
(ii) They are in general heavier than water. Methylene iodide is the densest organic liquid known, its density being 3.325.

(iii) They are insoluble in water and soluble in organic solvents.

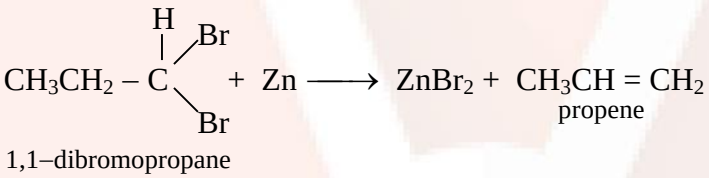
Chemical Properties

Chemically the dihalides are similar to monohalogen derivatives giving all the reactions of the halogen atom in duplicate. They however, differ from the latter in certain reactions in which both the halogens are involved together. Besides the usual reactions of alkyl halides, they give the following typical reactions.

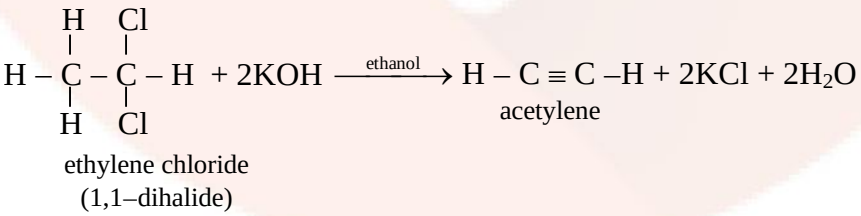
(i) Hydrolysis with aqueous alkalies: 1,2–dihalides upon heating with aqueous KOH give the respective glycols. Thus,



(ii) Dehalogenation with zinc dust and methanol: When treated with zinc dust and methanol, 1,1–dihalides eliminate a molecule of halogen, giving alkenes. Thus,



(iii) Dehydrohalogenation with ethanolic KOH: Both 1,1–dihalides and 1,2–dihalides when heated with ethanolic potassium hydroxide, give alkynes. Thus,



Trihalogen Derivatives

Chloroform, Trichloromethane, $CHCl_3$

The name chloroform was given to trichlormethane by Dumas who established that its molecule contained chlorine in union with 'formyl' an old name for CH ≡ group.

Preparation

(i) By heating ethanol or acetone with bleaching powder, Ca(ClO)Cl: The bleaching powder provides chlorine and the reaction takes place in three stages. Thus the formation of chloroform from ethanol occurs as follows.

(a) Oxidation of ethanol to acetaldehyde

$$CH_3 - CH_2OH + Cl_2 \longrightarrow CH_3 - CHO + 2HCl$$

ethanol acetaldehyde

(b) Chlorination of acetaldehyde to chloral

$$CH_3 - CHO + 3Cl_2 \longrightarrow CCl_3 - CHO + 3HCl$$

chloral

(c) Hydrolysis is of chloral by lime present in bleaching powder to form calcium formate and chloroform.

$$CCl_3 - CHO + HOH \longrightarrow CHCl_3 + HCOOH$$

chloroform formic acid

$$2HCOOH + Ca(OH)_2 \longrightarrow (HCOO^-)_2Ca^{2+} + 2H_2O$$

With acetone as the starting material, the conversion into chloroform takes place by similar steps.

$$CH_3 - CO - CH_3 + 3Cl_2 \longrightarrow CCl_3 - CO - CH_2 + 3HCl$$

acetone trichloroacetaone

$$CCl_3 - CO - CH_3 + HOH \longrightarrow CHCl_3 + CH_3COOH$$

acetic acid

Physical Properties

Chloroform is colourless liquid having a peculiar sickly smell and a sweetish burning taste, boiling point 61°C, sp gr 1.485. It is practically insoluble in water but soluble in most organic solvents. It acts as a solvent for many organic substances such as oils, fats and waxes. Chloroform vapour when inhalded causes temporary unconsciousness and hence its use as anaesthetic.

Chemical Properties

(i) Oxidation:

(a) In the presence of light, chloroform is oxidized slowly by the oxygen of air to form carbonyl chloride or phosgene.

(b) Fehling solution oxidizes chloroform when a red deposit of copper (I) oxide is produced.

(c) It is not inflammable but when a Bunsen burner is played on to the liquid chloroform it vaporizes and burns with a green–edged flame.

(ii) Reduction: Nascent hydrogen generated by the action of zinc on ethanolic hydrogen chloride, reduces chloroform to dichloromethane.

(iii) Hydrolysis with alkali: When treated with hot solution of NaOH (or KOH), chloroform is hydrolysed to form sodium chloride (or potassium chloride) and sodium formate or potassium formate.

(iv) Nitration: It reacts with concentrated nitric acid to form chloropicrin or mononition chloroform (boiling point = 120°C).

Chloropicrin is used as insecticide and also as a war gas.

(v) Carbylamine Reaction (Isocyanide Reaction): Chloroform when warmed with an ethanolic solution of potassium hydroxide, forms an isonitrile (carbylamine).

Isonitriles have characteristic powerful and unpleasant smell and their formation of sometimes used as a delicate test for primary amines.

(vi) Dehalogenation: When warmed with silver powder, chloroform gives acetylene.

(vii) Condensation with Acetone: Chloroform undergoes condensation with acetone in the presence of alkali to form chloretone which is used as hypnotic.

(viii)Action with Phenol and Sodium hydroxide (Reimer Tiemann Reaction): When heated with concentrated solution of KOH, chloroform gives salicylaldehyde.

Uses

(i)Chloroform can be used to some extent as an anesthetic, solvent and reagent.

(ii) Tricholromethane is used as solvent for iodine and fats.

(iii) Chloroform is used in the manufacture of freezing refrigerant.

Tetra-halogen Derivatives

Carbon Tetrachloride, Tetra-chloromethane, CCl_4

Preparation: It is prepared on industrial scale

(i)By chlorination of methane:

$$CH_4 + 4Cl_2 \longrightarrow CCl_4 + 4HCl$$

(ii) By the action of chlorine on carbon disulphide (CS_2) in the presence of aluminium chloride as a catalyst.

$$CS_2 + 3Cl_2 \xrightarrow{AlCl_3} CCl_4 + S_2Cl_2$$ sulphur monochloride

The products of this reaction, both liquids, are separated by fractional distillation.

Physical Properties

Carbon tetrachloride is a colourless liquid, boiling point 77°C. It is insoluble in water but soluble in all organic solvents. It is an excellent solvent for fatty substances.

Chemical Properties

Carbon tetrachloride is relatively inert substance. It gives following reactions.

(i) Action with Steam: Its vapours when mixed with steam react at high temperature to give phosgene gas.

(ii) Action with Alkalis: When boiled with ethanolic KOH soution, carbon tetrachloride is hydrolysed to form potassium carbonate.

(iii) Reduction: Carbon tetrachloride canbe reduced by moist iron fillings to chloroform. This is an industrial method for the preparation of chloroform.

(iv) Action with HF: When hydrogen fluoride is passed into carbon tetrachloride in presene of antimony pentachloride, the gas dichlorofluoromethane is obtained.

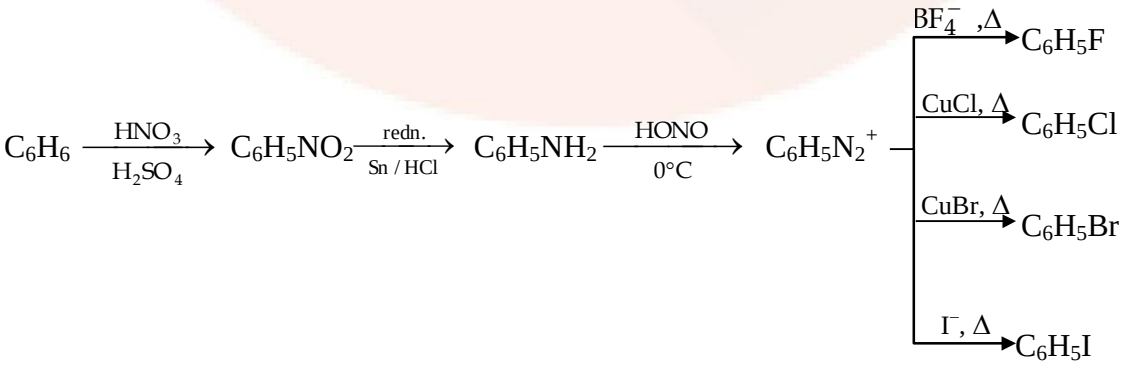
This gas (freon) is widely used as operating fluid for refrigerators and in air–conditioning equipment.

ARYL HALIDES

Aryl halides are halogen compounds directly linked to a fragrant ring. The general formula of aryl halides is *ArX,* where *Ar* is phenyl, substituted phenyl or aryl groups.

METHODS OF PREPARATION OF ARYL HALIDES

(I) From Diazonium Salts



(II) By Halogenation of Arenes or Substituted Arenes

$$ArH + X_2 \xrightarrow{\text{Lewis acid}} ArX + HX$$

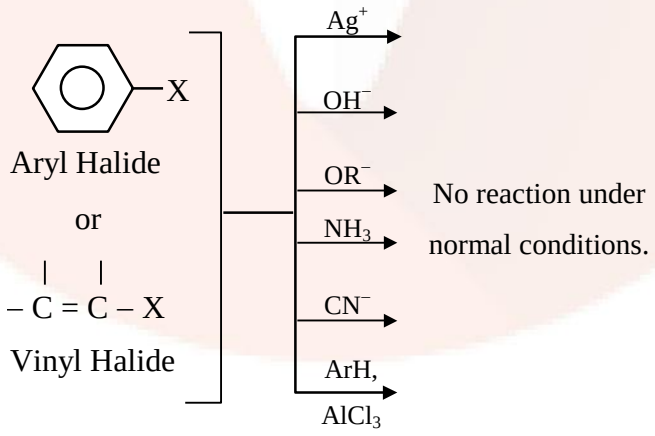
where $X_2 = Cl_2$ or Br_2

Lewis acid = $FeCl_3$, $AlCl_3$, $Tl(OAc)_3$ etc.

GENERAL CHEMICAL PROPERTIES OF THE ARYL HALIDES

Low reactivity of aryl and vinyl halides

An alkyl halide is conveniently detected by the precipitation of insoluble silver halides when it is warmed with alcoholic $AgNO_3$.



The typical reaction of alkyl halides, is nucleophilic substitution.

$R - X + :Z^- \longrightarrow R - Z + :X^-$

Where Z = OH^-, OR^-, NH_3, CN^-, NH_2^-, ROH, H_2O etc.

(I) Formation of Grignard Reagent

$ArBr + Mg \xrightarrow{\text{dry ether}} ArMgBr$

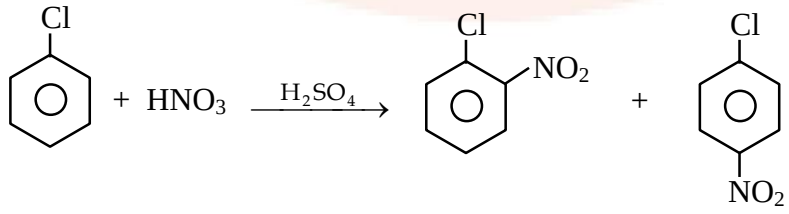
$ArCl + Mg \xrightarrow{\text{tetrahydrofuran}} ArMgCl$

(II) Electrophilic Aromatic Substitution

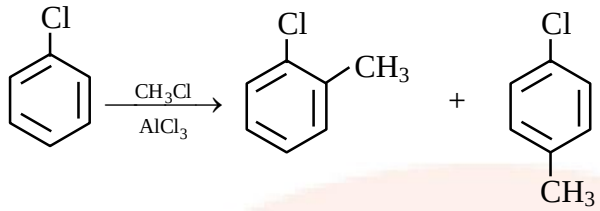
Although halogen is deactivating but still it directs the incoming electrophile to ortho and para position.

For example,

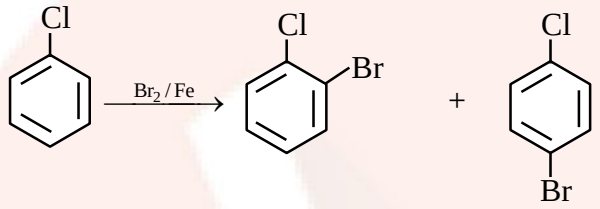
(i) Nitration



(ii) Friedal Craft's Alkylation

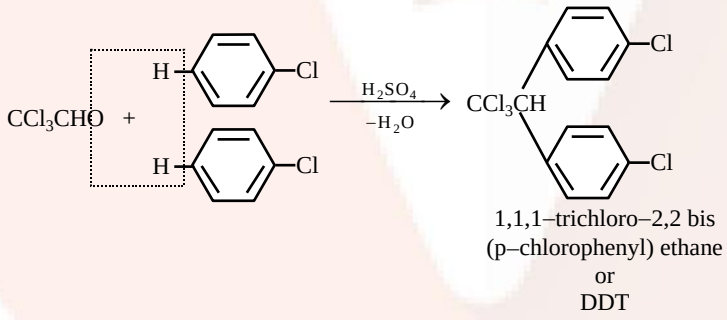


(iii) Bromination



Dichlorodiphenyl Trichloroethane (DDT)

DDT is prepared by heating chlorbenzene and chloral with concentrated sulphuric acid



1,1,1–trichloro–2,2 bis (p–chlorophenyl) ethane
or
DDT

DDT is a solid compound, melting point is 109–110°C.

Benzene Hexachloride (BHC)

1,2,3,4,5,6–hexachlorocyclohexane, can theoretically exist in nine stereoisomeric forms due to different arrangements of H and Cl on opposite sides of the plane of benzene ring