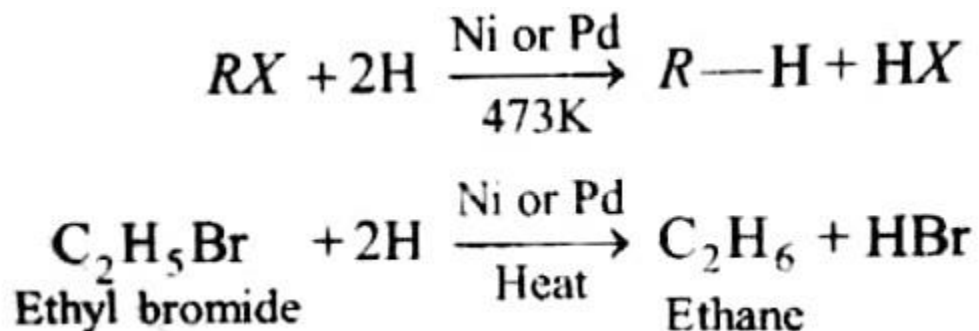


3. Miscellaneous Reactions

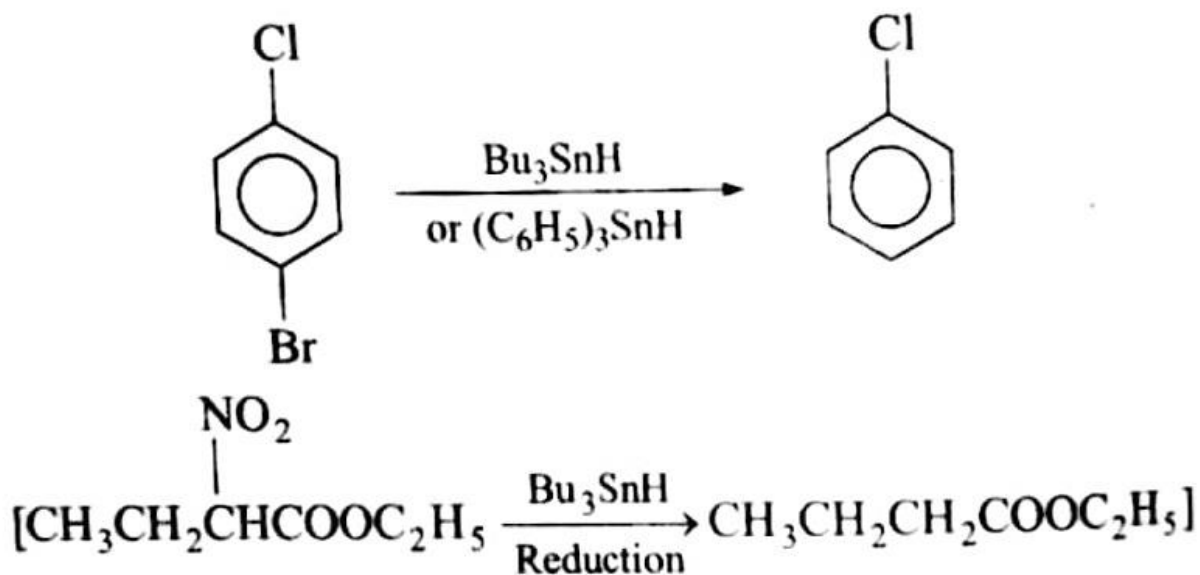
(xiii) Reduction (Formation of alkanes): Alkanes are formed when alkyl halides are reduced with nascent hydrogen obtained by Zn/HCl or sodium and alcohol or Zn/Cu couple on alcohol or Laugher or palladium carbon or Mg-Hg/water or tributyl tin hydride (Bu_3SnH) etc.



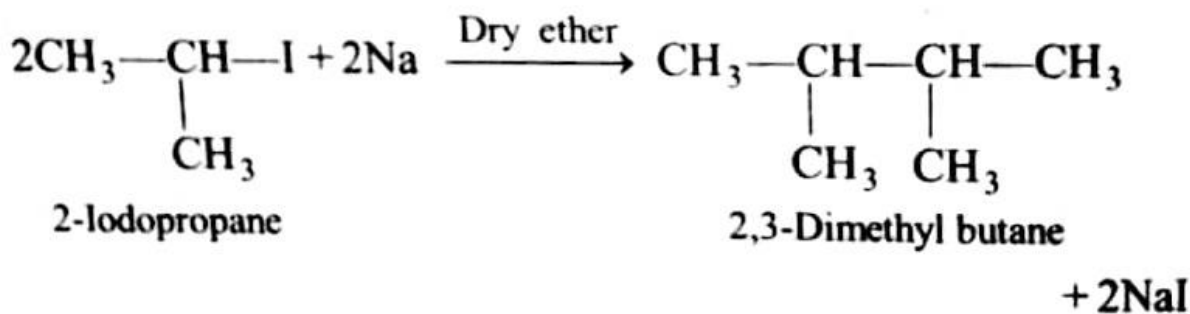
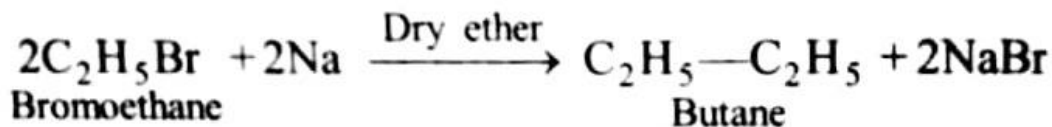
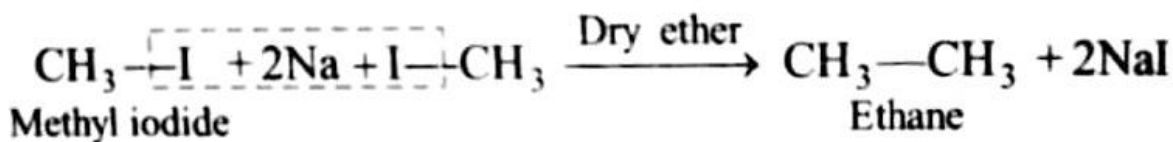
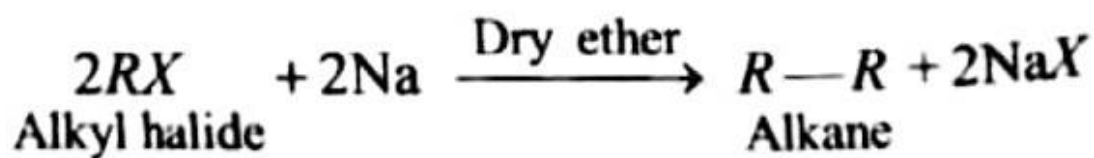
The reaction is used for the preparation of pure alkanes. Metal catalyst such as Ni, Pd or Pt at 473-523K, or HI in presence of red phosphorus at 423K can also be used for the reduction of alkyl halides into corresponding alkanes.

Bu_3SnH is a selective reducing agent because it reduces only halides (and nitroalkanes) and has no effect on any other functional groups.

Among halides, $\text{RI} > \text{RBr} > \text{RCl}$. Due to this reason, the reagent tributyl tin hydride (Bu_3SnH) shows substantial selectivity towards polyhalogenated compounds.



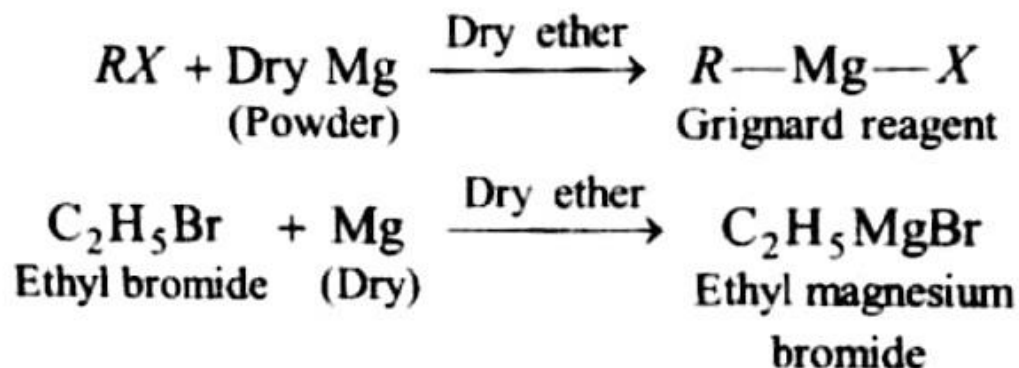
(xiv) Wurtz reaction : An ether solution of an alkyl halide (preferably bromide or iodide) forms symmetrical alkanes when heated with metallic sodium.



Tertiary halides do not undergo this reaction. Unsymmetrical alkanes can be conveniently prepared by

Corey-House reaction.

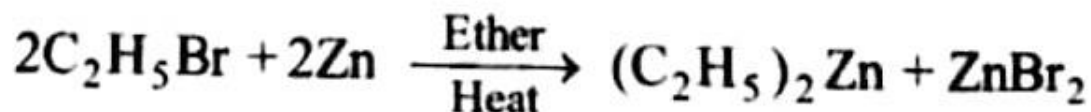
(xv) Reaction with magnesium : Alkyl halides form **Grignard reagents** when treated with dry magnesium powder in dry ether.



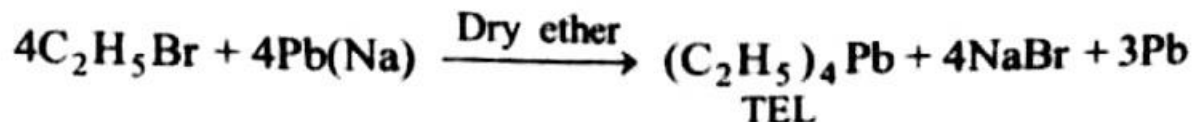
Grignard reagents are used for making a very large number of organic compounds. Reactivity order is $RI > RBr > RCl$.

(xvi) Reaction with other metals : Organometallic compounds are formed.

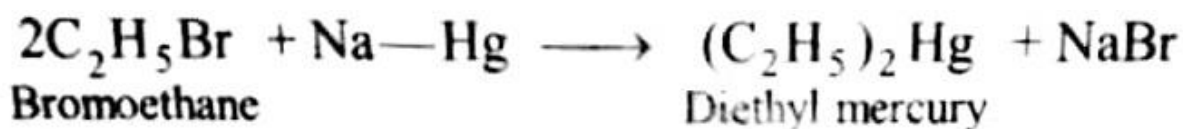
(a) When heated with zinc powder in ether, alkyl halides form dialkyl zinc compounds. These are called **Frankland reagents**.



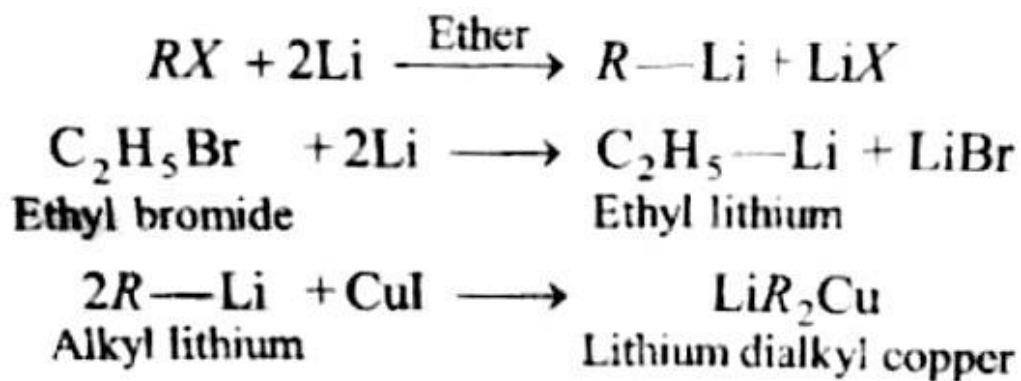
(b) When heated with lead-sodium alloy, ethyl bromide gives tetra ethyl lead (TEL) which is used as antiknock compound in petrol.



(c) Alkyl halides form dialkyl mercury compounds when treated with sodium amalgam.

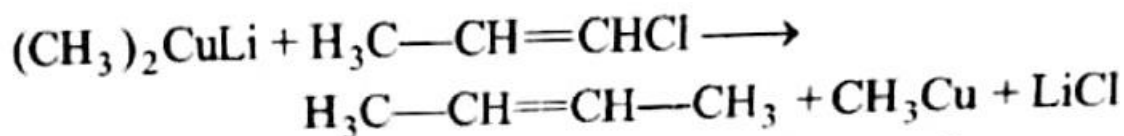
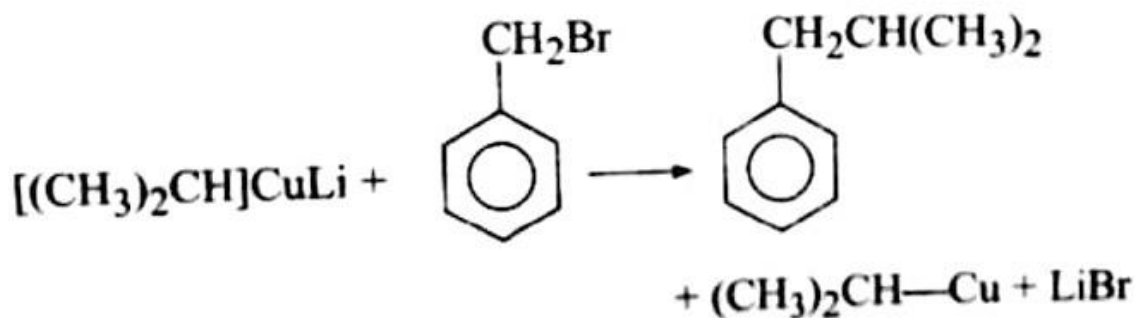
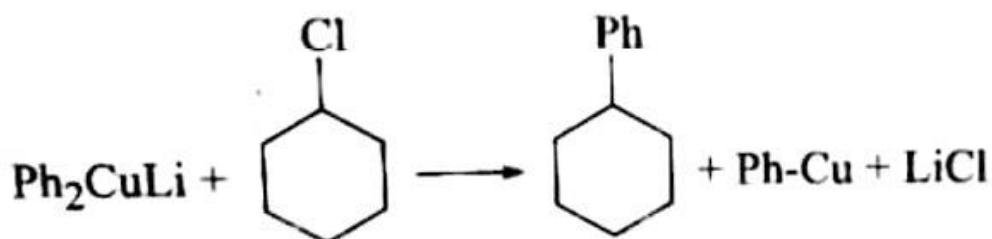
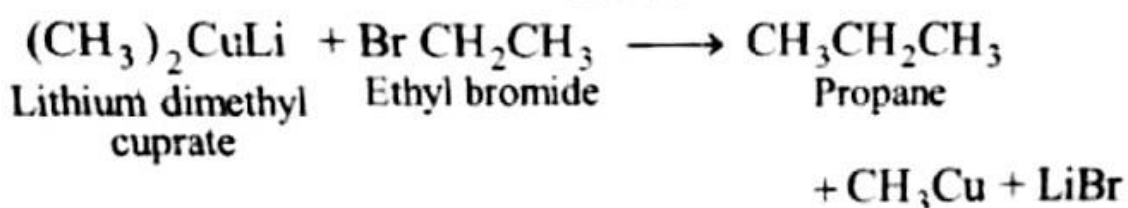
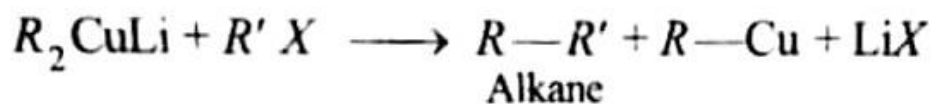


(d) Reaction with Lithium: Alkyl halides react with lithium in dry ether to form alkyl lithiums.

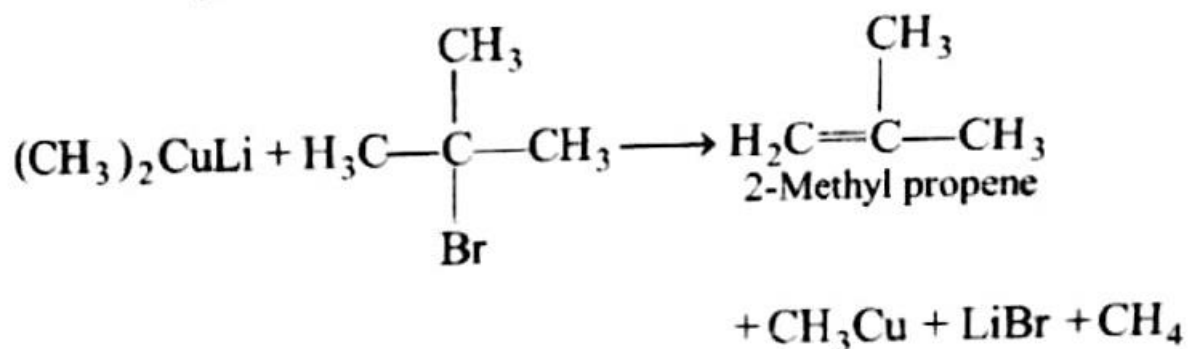


Alkyl lithiums are similar in properties with Grignard reagents. These are reactive reagents also and serve as strong bases.

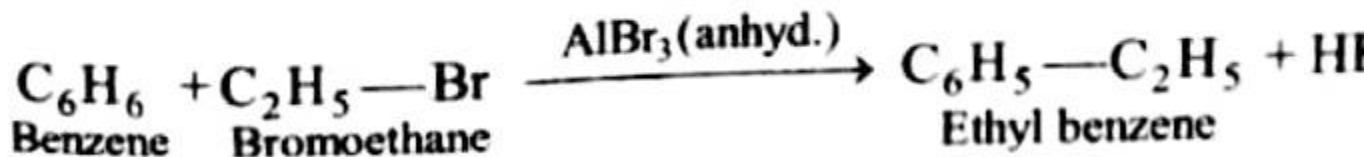
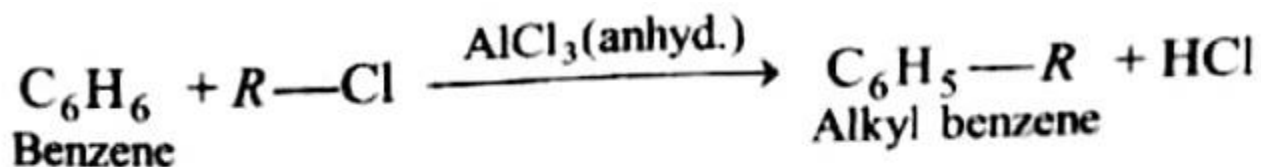
(e) Corey-House reaction : Alkyl halide reacts with lithium dialkyl cuprate (R_2CuLi) to form unsymmetrical alkanes.



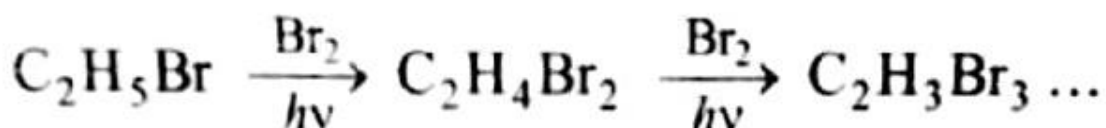
3° alkyl halide on reaction with R_2CuLi give alkenes.



(xvii) Friedel-Crafts reaction : Alkyl halides react with benzene in presence of anhydrous aluminium halides to form a homologue of benzene.

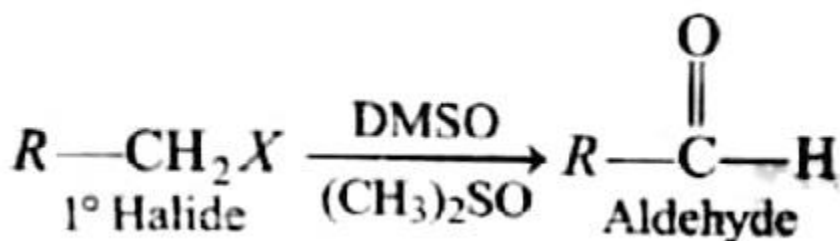


(xviii) Substitution (Halogenation) : Alkyl halides undergo further halogenation in presence of sunlight, heat energy or peroxide.

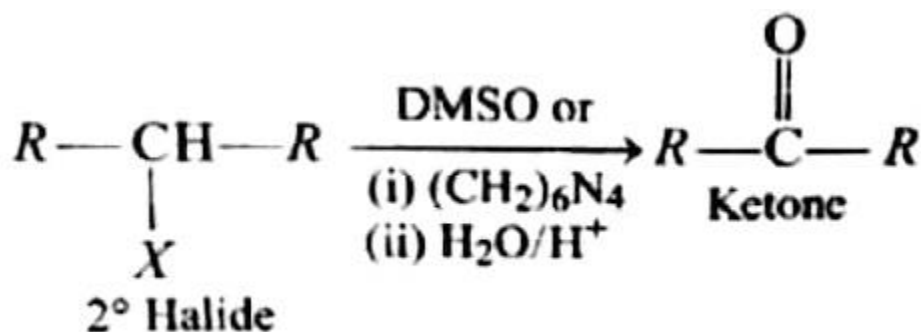


(xix) Oxidation reaction : Only primary and secondary alkyl halides undergo oxidation while tertiary alkyl halide does not.

Primary (1°) alkyl halides on oxidation with dimethyl sulphoxide, (CH₃)₂SO (DMSO) give aldehydes (**Swern oxidation**).



Oxidation can also be done with hexamethylene tetramine, (CH₂)₆N followed by hydrolysis. Secondary (2°) alkyl halides give ketone in this reaction.



Oxidation of benzyl halides with $(\text{CH}_2)_6\text{N}_4$, N is known as **Sommelet aldehyde synthesis**.

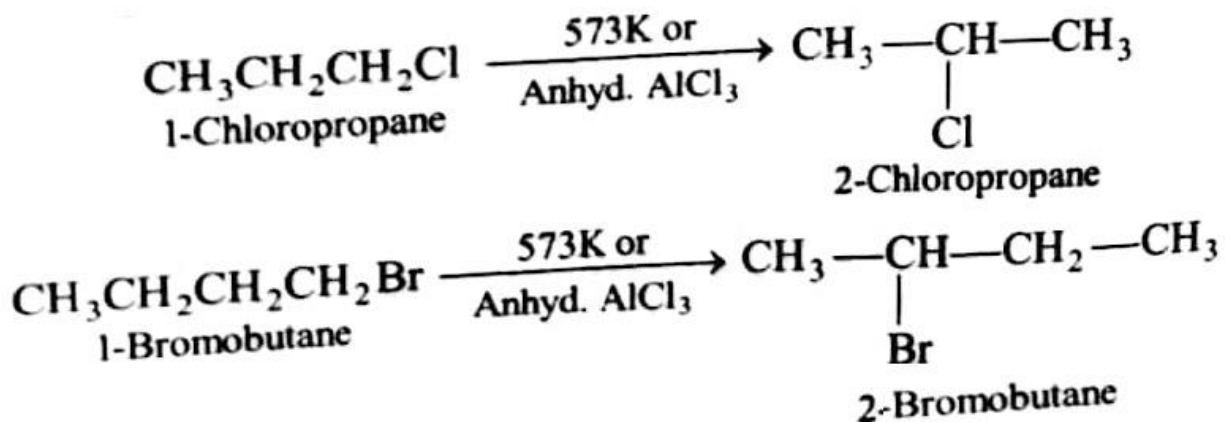
(a) Reactivity for oxidation reaction depends on the number of hydrogen atoms on alpha (α-) carbon of alkyl halides:

Reactivity ∝ number of α-hydrogen

(b) Reactivity of different halides in decreasing order is as follows:

Benzyl halides > Alkyl halides > Alkyl halides

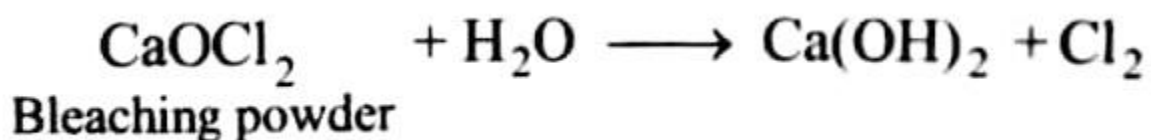
(xx) Isomerisation: Haloalkanes on heating at 573K or in presence of anhydrous AlCl_3 at low temperature undergo molecular rearrangement to form an isomeric haloalkane. For example,



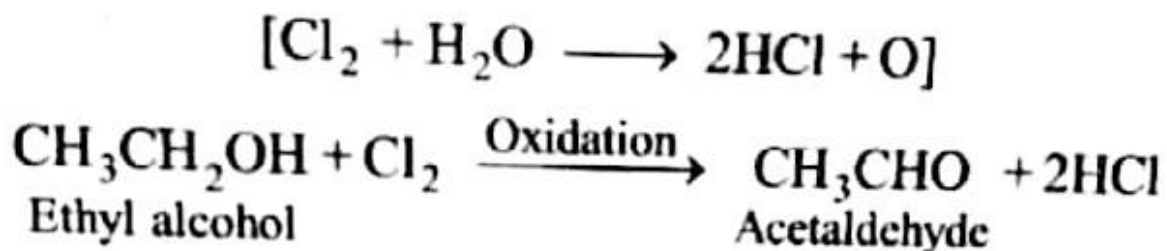
Chloroform or Trichloromethane (CHCl₃)

It is an important trihalogen derivative of methane. It was discovered by Liebig in 1831 and its name chloroform was proposed by Dumas as it gave formic acid on hydrolysis. In the past, it was extensively used as anaesthetic for surgery but now it is rarely used as it causes liver damage.

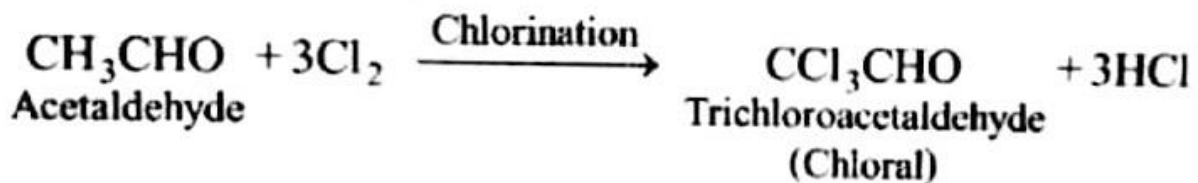
Preparation : 1. Chloroform is prepared both in the laboratory and on large scale by distilling ethyl alcohol or acetone with bleaching powder and water. The yield is about 40%. The available chlorine of bleaching powder serves as oxidising as well as chlorinating agent.



From alcohol : (i) Alcohol is first oxidised to acetaldehyde by chlorine.



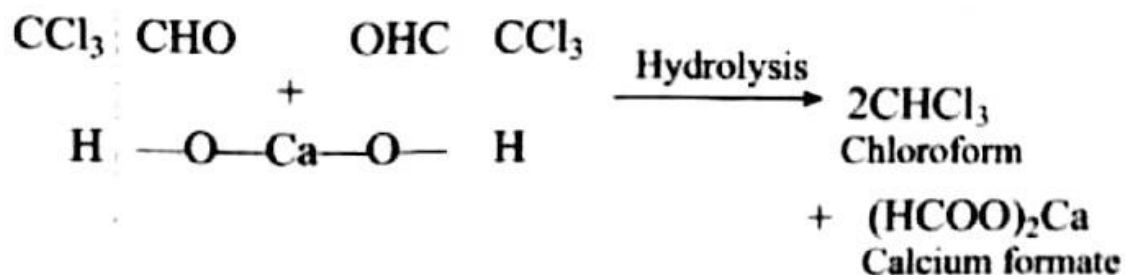
(ii) Acetaldehyde then reacts with chlorine to form chloral (trichloro acetaldehyde).



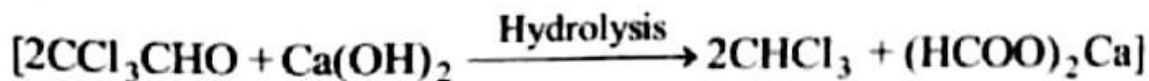
[So, Cl₂ acts both as an oxidising (i) and chlorinating agent

(ii)]

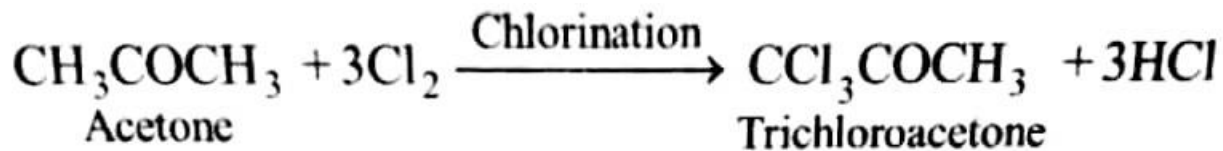
(iii) Chloral thus formed, is hydrolysed by calcium hydroxide.



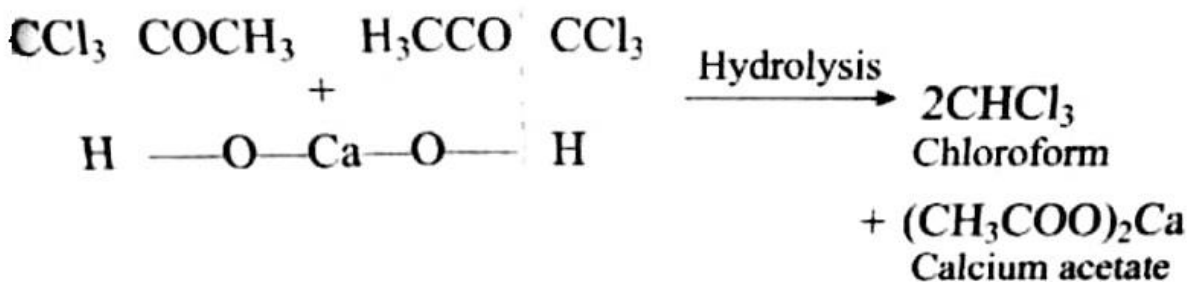
or



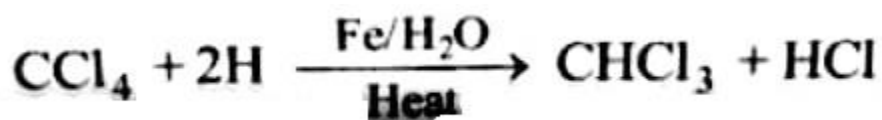
From acetone : (i) Acetone first reacts with chlorine to form trichloroacetone.



(ii) Trichloroacetone is then hydrolysed by calcium hydroxide.

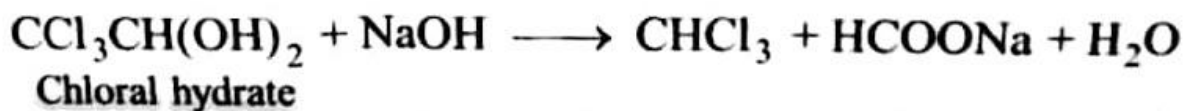


2. From carbon tetrachloride : Now-a-days, chloro- form is obtained on a large scale by the reduction of carbon tetrachloride with iron fillings and water. This method is used in countries like USA.



This chloroform is not pure and used mainly as a solvent.

3. Pure chloroform : It is obtained by distilling chloral hydrate with concentrated sodium hydroxide Solution.



Physical properties:

(i) It is a sweet smelling colourless liquid.

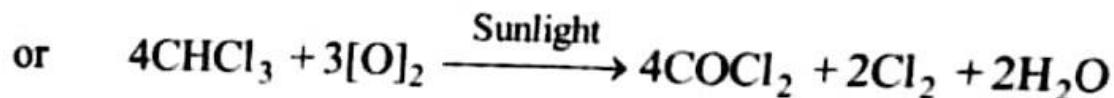
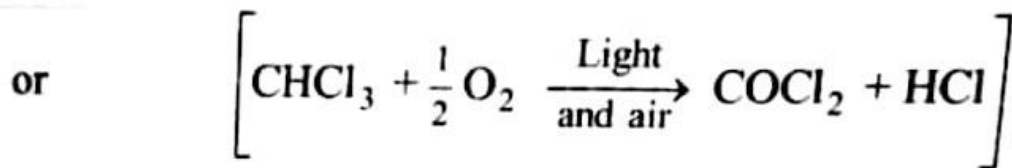
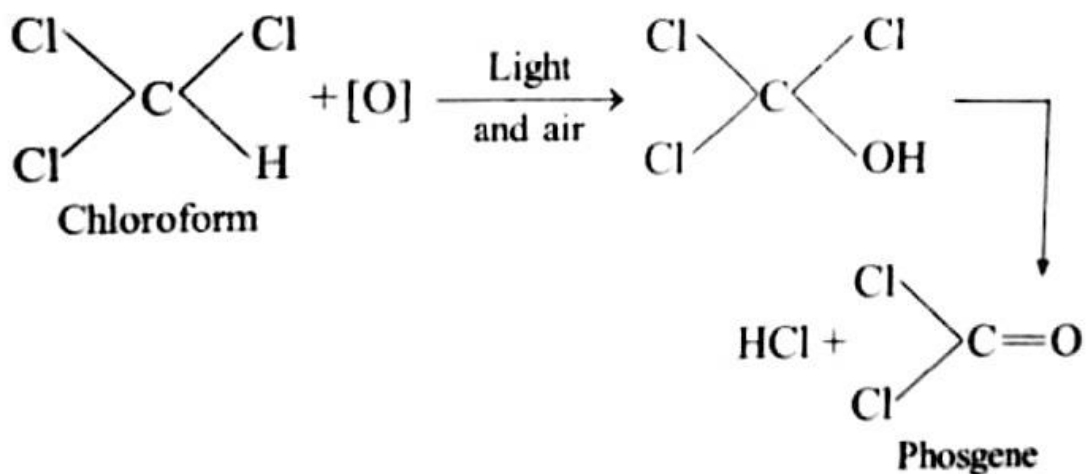
(ii) It is heavy liquid. Its density is 1.485. It boils at 334K.

(iii) It is practically insoluble in water but dissolves in organic solvents such as alcohol, ether, etc.

(iv) It is non-inflammable but its vapours may burn with green flame.

(v) It brings temporary unconsciousness when vapours are inhaled for sufficient time.

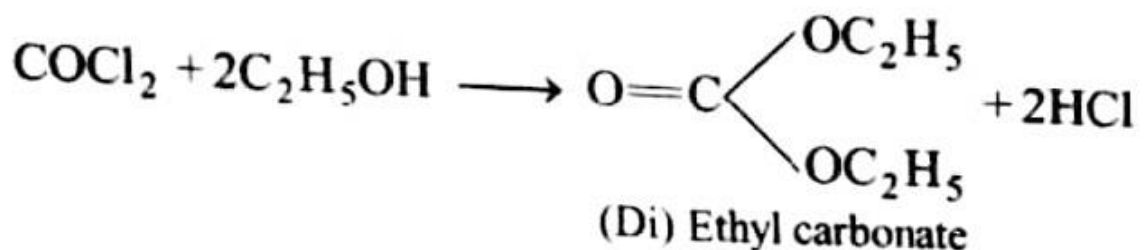
Chemical properties : (i) Oxidation : When exposed to sunlight and air, it slowly decomposes into phosgene (carbonyl chloride) and hydrogen chloride.



Phosgene is extremely poisonous gas. To use chloroform as an anaesthetic agent, it is necessary to prevent the above reaction. The following two precautions are taken when chloroform is stored.

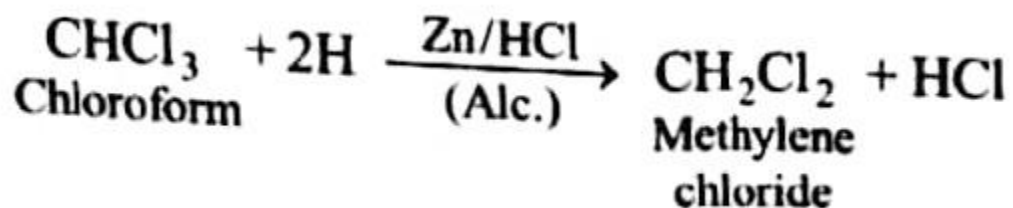
(a) It is stored in dark blue or brown coloured bottles which are filled upto the brim.

(b) 1% ethyl alcohol is added. This retards the oxidation and converts the phosgene formed into harmless ethyl carbonate.

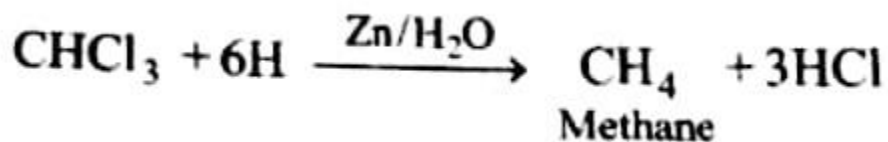


(ii) Reduction : When reduced with zinc and hydrochloric acid in presence of ethyl alcohol, it forms

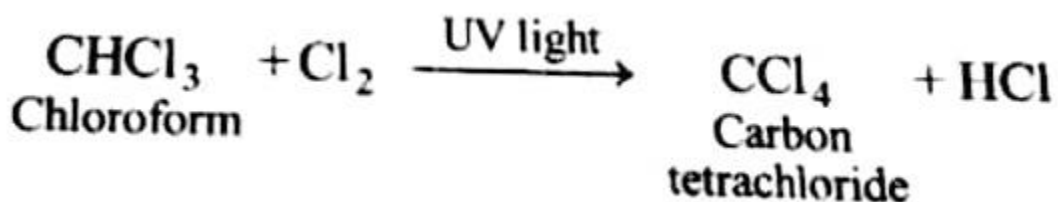
methylene chloride.



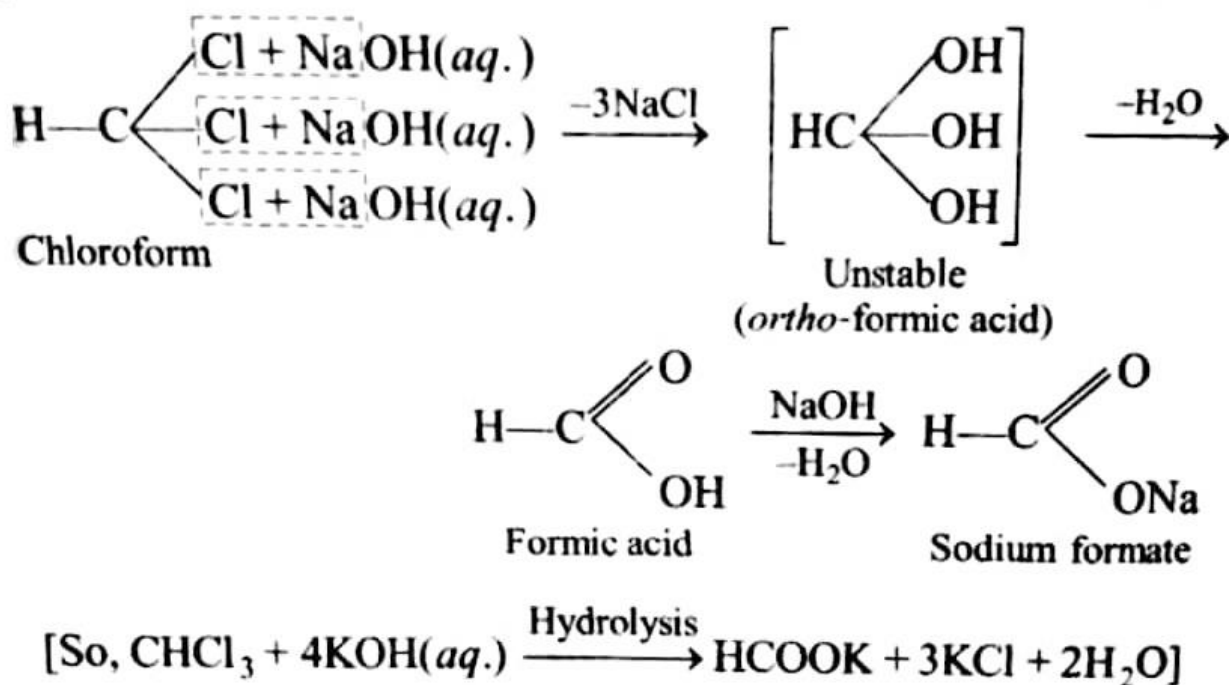
When reduced with zinc dust and water, methane is the



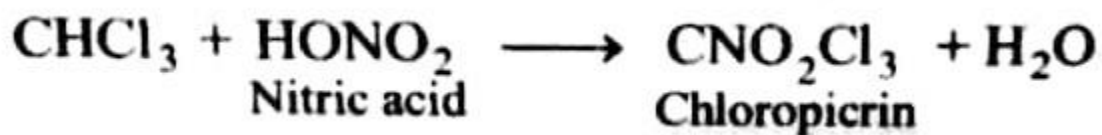
(iii) Chlorination : Chloroform reacts with chlorine in presence of diffused sunlight or UV light to form carbon tetrachloride.



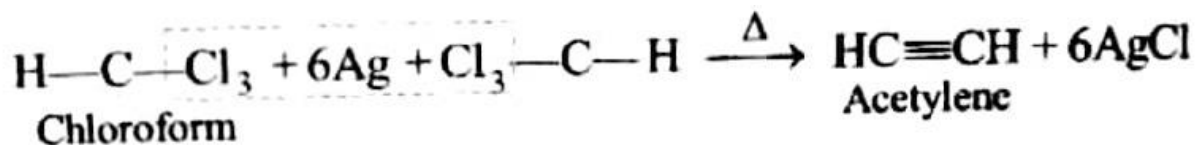
(iv) Hydrolysis : Chloroform is hydrolysed when treated with hot aqueous solution of sodium hydroxide or potassium hydroxide. The final product is sodium or potassium salt of formic acid.



(v) Nitration : The hydrogen of the chloroform is replaced by nitro group when it is treated with concentrated nitric acid. The product formed is chloropicrin or trichloro nitro methane or nitro chloroform. It is a liquid, poisonous and used as an insecticide and a war gas (tear gas).

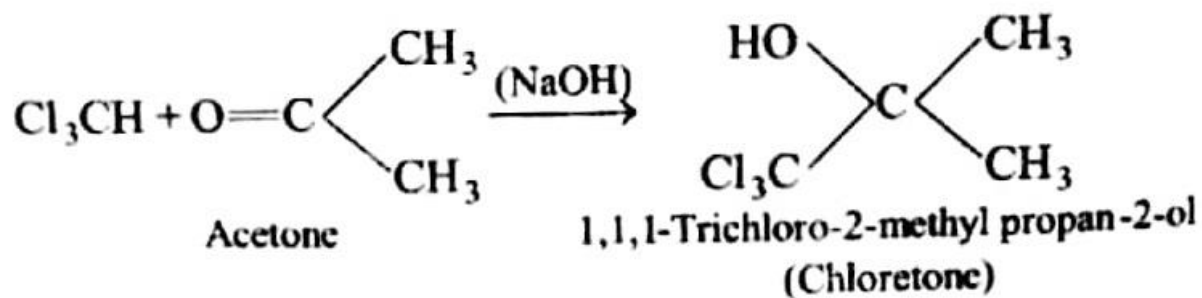


(vi) Heating with silver powder : Acetylene is formed when chloroform is heated at high temperature with silver powder.

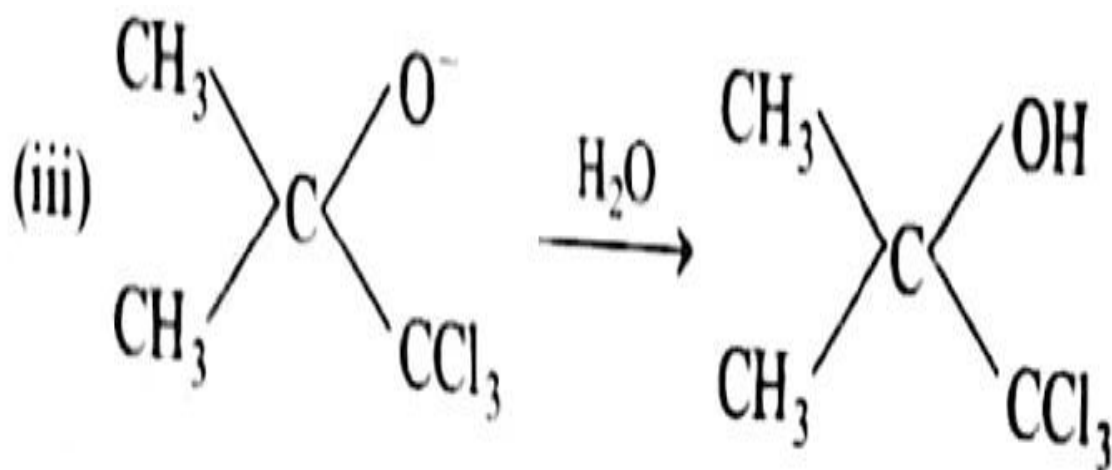
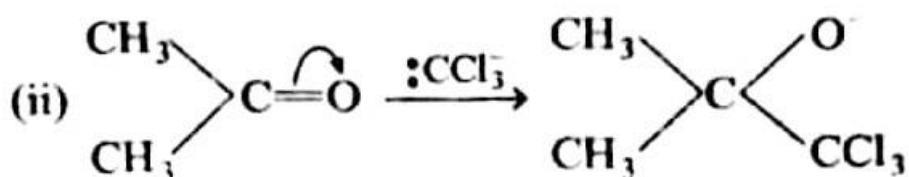
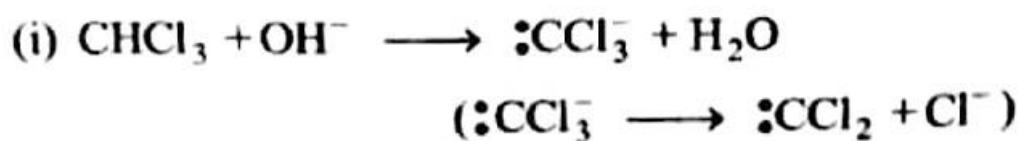


(vii) Condensation with acetone : Chloroform condenses with acetone on heating in presence of caustic

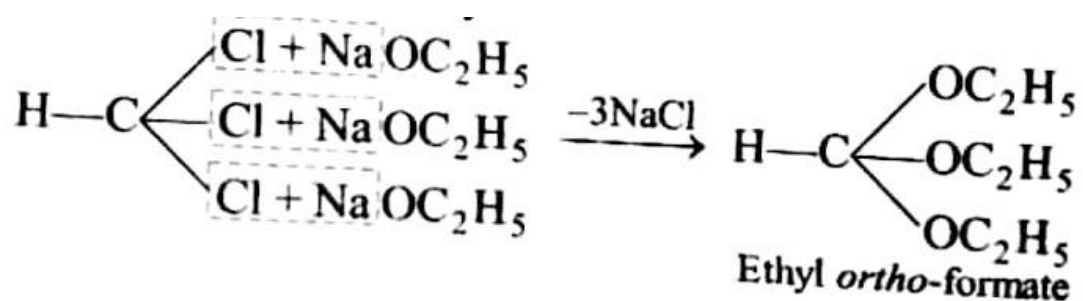
alkalies. The product formed is a colourless crystalline solid called chloretone and is used as a hypnotic (drug) in medicine.



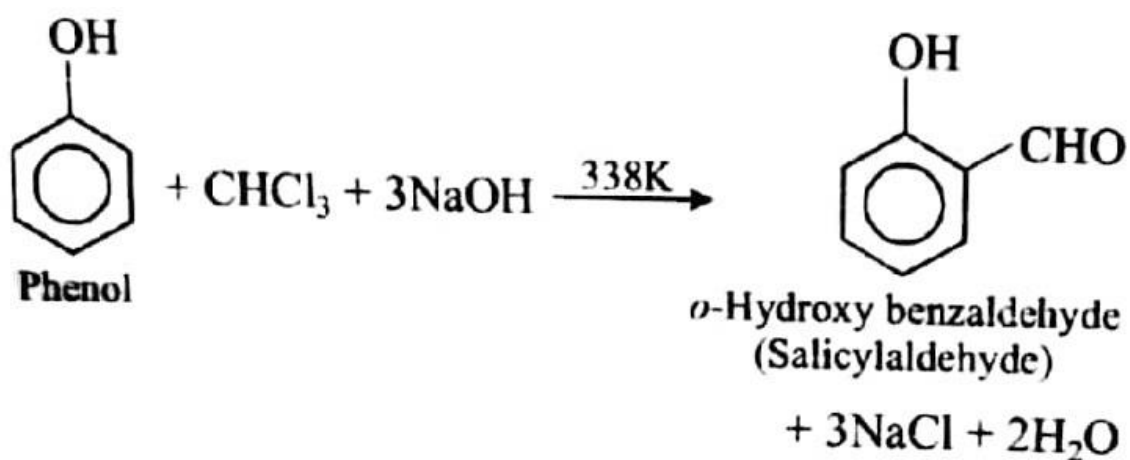
Mechanism :



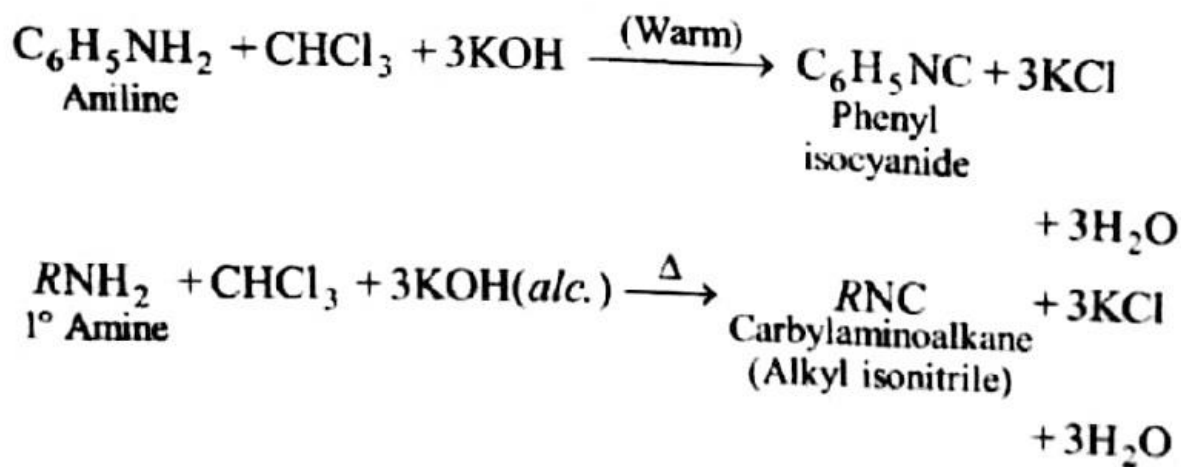
(viii) Reaction with sodium ethoxide : When heated with sodium ethoxide, ethyl ortho-formate is formed



(ix) Reimer-Tiemann reaction : Chloroform reacts with phenol when heated in presence of sodium hydroxide or potassium hydroxide. The product formed is salicylaldehyde.



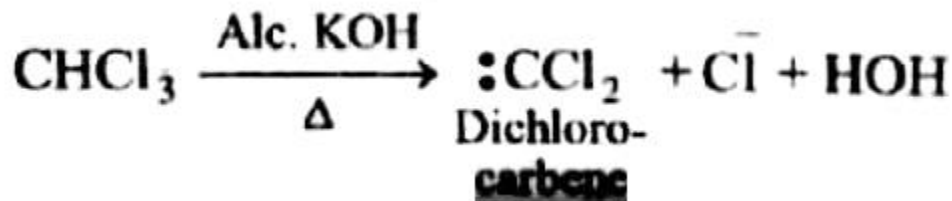
(x) Carbylamine reaction (isocyanide test) : This reaction is actually a test of primary amines. Chloroform, when heated with primary amine in presence of alcoholic potassium hydroxide forms a derivative called isocyanide (carbylamine) which has a very offensive smell.



This reaction is also used for the test of chloroform.

(xi) a-Elimination reaction: Chloroform undergoes α -elimination reaction to give dichlorocarbene (sing

let) which is a reaction intermediate.



Uses : (i) It is used as a solvent for fats, waxes, rubber, resins, iodine, etc.

(ii) It is used for the preparation of chloretone (a drug) and chloropicrin (insecticide).

(iii) It is used in laboratory for the test of primary amines iodides and bromides.

(iv) It can be used as anaesthetic but due harmful effects it is not used these days for this purpose. It causes lives damage when inhaled in excess (SO is CCl

Halothane (CF, CHClBr) is less toxic than CHCl, and hence is widely used these days.

(v) It may be used to prevent putrefaction of organic materials, i. e., in the preservation of anatomical species.

Tests of chloroform : (i) It gives isocyanide test (carbylamine test).

(ii) It forms silver mirror with Tollens' reagent.

(iii) Pure chloroform does not give white precipitate with silver nitrate.