

Chapter 25

Halogen Containing Compounds

Compounds derived from hydrocarbons by the replacement of one or more hydrogen atoms by the corresponding number of halogen atoms are termed as halogen derivatives. The halogen derivatives of the hydrocarbons are broadly classified into three classes:

Halogen derivatives of saturated hydrocarbons (Alkanes)-Halo-alkanes.

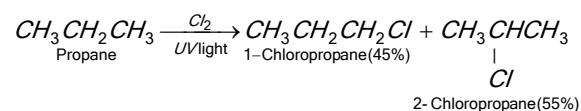
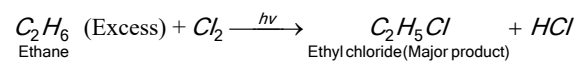
Halogen derivatives of unsaturated hydrocarbons (Alkenes and alkynes)-Halo-alkene or alkyne.

Halogen derivatives of aromatic hydrocarbons (Arenes)-Halo-arenes.

General methods of preparation of Alkyl Halides

(1) From alkanes

(i) By halogenation :

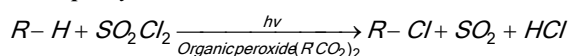


This reaction proceed through free radical mechanism.

□ Order of reactivity of X_2 for a given alkane is,
 $F_2 > Cl_2 > Br_2 > I_2$.

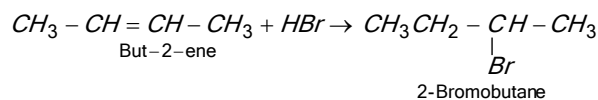
□ The reactivity of the alkanes follows the order :
 $3^\circ\text{alkane} > 2^\circ\text{alkane} > 1^\circ\text{alkane}$.

(ii) With sulphuryl chloride :



□ This reaction is a fast due to in presence of light and trace of an organic peroxide.

(2) From alkenes (Hydrohalogenation by Electrophillic addition)



□ Addition of HBr to alkene in the presence of organic peroxide take place due to peroxide effect or Kharasch's effect.

□ This addition take place by two mechanism, Peroxide initiates free radical mechanism.

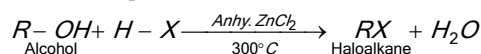
Markownikoff's addition by electrophillic mechanism.

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

(3) From alcohols

(i) By the action of halogen acids

Groove's process



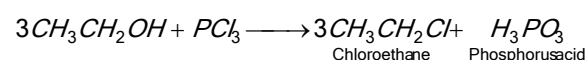
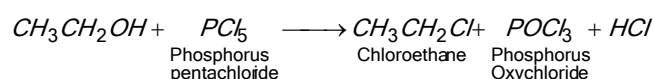
□ The reactivity order of HX in the above reaction is :
 $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$.

□ Reactivity order of alcohols $3^\circ > 2^\circ > 1^\circ > \text{MeOH}$.

□ 2° and 3° alcohols undergo S_N1 ; where as 1° and MeOH undergo S_N2 mechanism.

□ Concentrated $\text{HCl} + \text{anhy. ZnCl}_2$ is known as lucas reagent.

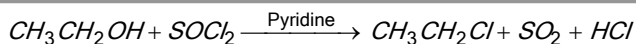
(ii) Using PCl_5 and PCl_3 :



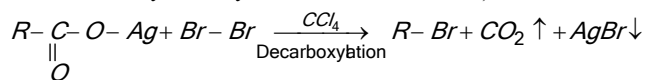
□ Bromine and iodine derivatives cannot be obtain from the above reaction, because PBr_5 or PI_5 are unstable.

□ This method gives good yield of primary alkyl halides but poor yields of secondary and tertiary alkyl halides.

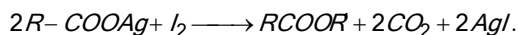
(iii) By the action of thionyl chloride (Darzan's process) :
Reaction takes place through S_N2 mechanism.



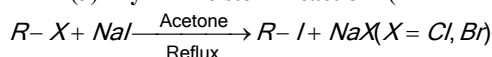
(4) From silver salt of carboxylic acids (Hunsdiecker reaction, Decarboxylation by Free radical mechanism)



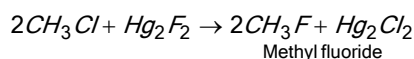
- The reactivity of alkyl group is $1^\circ > 2^\circ > 3^\circ$
- Only bromide are obtained in good yield.
- Not suitable for chlorination because yield is poor.
- In this reaction iodine forms ester instead of alkyl halide and the reaction is called Birnboorn-Simonini reaction,



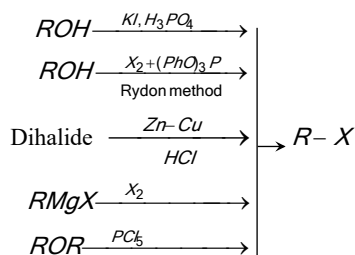
(5) By Finkelstein reaction (Halide exchange method) :



- Alkyl fluorides can not be prepared by this method. They can be obtained from corresponding chlorides by the action of Hg_2F_2 or antimony trifluoride. (swart reaction)



(6) Other method



Properties of Alkyl Halides

(1) Physical properties

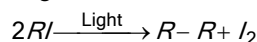
(i) CH_3F , CH_3Cl , CH_3Br and C_2H_5Cl are gases at room temperature. The alkyl halides upto C_{18} are colourless liquids while higher members are colourless solids.

(ii) Alkyl halides are insoluble in water but soluble in organic solvents.

(iii) They burn on copper wire with green edged flame (Beilstein test for halogens).

(iv) Alkyl bromides and iodides are heavier than water. Alkyl chlorides and fluorides are lighter than water.

(v) Alkyl iodides become violet or brown in colour on exposure as they decompose in light.



(vi) For a given alkyl group, the boiling points of alkyl halides are in the order $RI > RBr > RCl > RF$ and for a given halogen the boiling points of alkyl halides increase with the increase of the size of the alkyl group.

(vii) Alkyl halides are in general toxic compounds and bring unconsciousness when inhaled in large amounts.

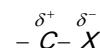
(2) Chemical properties : The alkyl halides are highly reactive, the order of reactivity is,

Iodide > Bromide > Chloride (Nature of the halogen atom)

Tertiary > Secondary > Primary (Type of the halogen atom)

Amongst the primary alkyl halide, the order of reactivity is : $CH_3X > C_2H_5X > C_3H_7X$, etc.

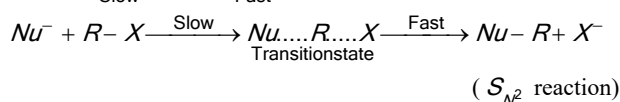
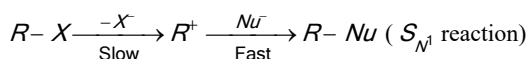
The high reactivity of alkyl halides can be explained in terms of the nature of $C-X$ bond which is highly polarised covalent bond due to large difference in the electronegativities of carbon and halogen atoms. The halogen is far more electronegative than carbon and tends to pull the electrons away from carbon, i.e., halogen acquires a small negative charge and carbon a small positive charge.



This polarity is responsible for reactions,

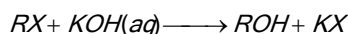
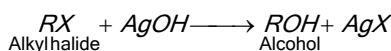
(i) Nucleophilic substitution reactions (ii) Elimination reactions

(i) **Nucleophilic substitution (S_N) reactions** : The $C^{\delta+}$ site is susceptible to attack by nucleophiles (An electron rich species).

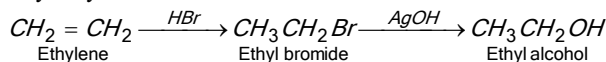


Examples of S_N reactions,

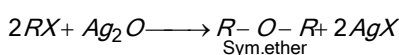
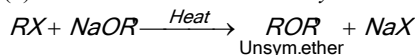
(a) Hydrolysis :



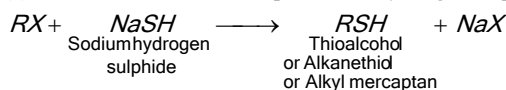
□ With the help of this reaction an alkene can be converted into alcohol. Alkene is first reacted with HBr to form alkyl bromide and then hydrolysis is done.



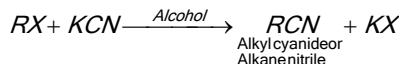
(b) Reaction with alkoxides or dry silver oxide :



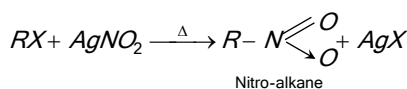
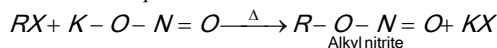
(c) Reaction with sodium or potassium hydrogen sulphide :



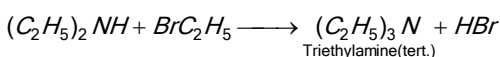
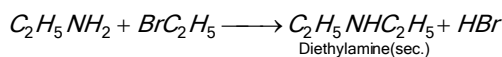
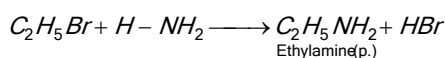
(d) Reaction with alcoholic potassium cyanide and silver cyanide :

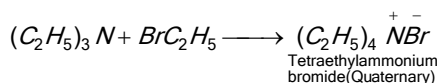


(e) Reaction with potassium nitrite or silver nitrite :

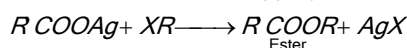


(f) Reaction with ammonia :

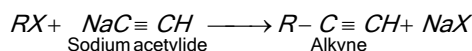




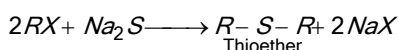
(g) Reaction with silver salts of fatty acids :



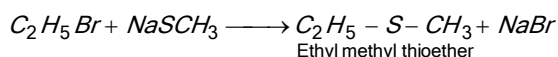
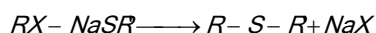
(h) Reaction with sodium acetylide :



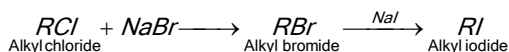
(i) Reaction with sodium or potassium sulphide :



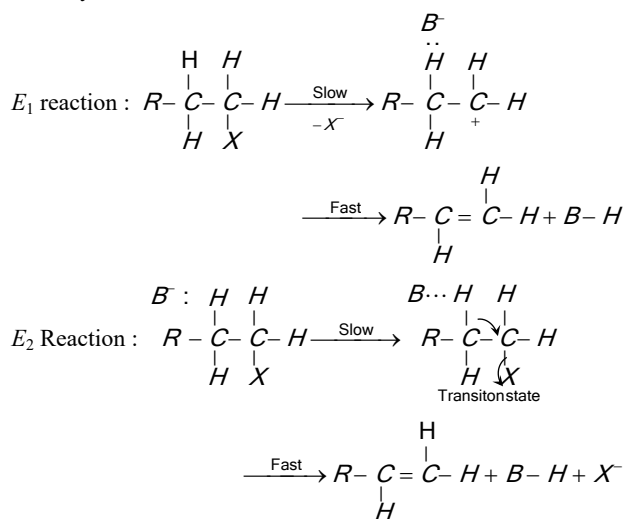
Thioethers can also be obtained by



(j) Reaction with halides :



(ii) **Elimination reactions** : The positive charge on carbon is propagated to the neighbouring carbon atoms by inductive effect. When approached by a strongest base (*B*), it tends to lose a proton usually from the β -carbon atom. Such reactions are termed elimination reactions. They are also E_1 and E_2 reactions.

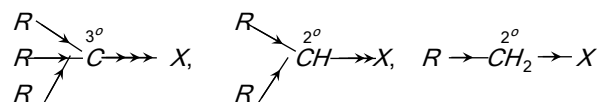


As the above reactions involve leaving of X^- , the reactivity of alkyl halides (Same alkyl group, different halogens) should be limited with $C-X$ bond strength.

Type of bond	$C-I$	$C-Br$	$C-Cl$
Bond strength (kcal/mol)	45.5	54	66.5
	Bond strength increases \longrightarrow		

The breaking of the bond becomes more and more difficult and thus, the reactivity decrease.

The order of reactivity (Tertiary > Secondary > Primary) is due to +I effect of the alkyl groups which increases the polarity of $C-X$ bond.



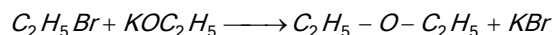
The primary alkyl halides undergo reactions either by S_N2 or E_2 mechanisms which involve the formation of transition state. The bulky groups cause steric hindrance in the formation of transition state. Therefore, higher homologues are less reactive than lower homologues. $CH_3X > C_2H_5X > C_3H_7X$, etc.

Example of elimination reaction

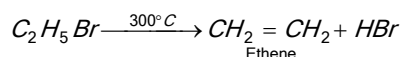
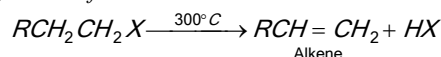
(a) Dehydrohalogenation :



In this reactions, ether is a by-product as potassium ethoxide is always present in small quantity.



(b) Action of heat :

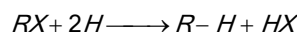


The decomposition follows the following order, Iodide > Bromide > Chloride (When same alkyl group is present) and

Tertiary > Secondary > Primary (When same halogen is present).

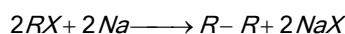
(iii) **Miscellaneous reactions**

(a) **Reduction** : Alkyl halides are reduced with nascent hydrogen obtained by Zn/HCl or sodium and alcohol or Zn/Cu couple or $LiAlH_4$.

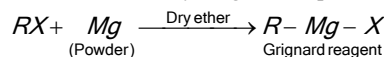


Reaction is used for the preparation of pure alkanes

(b) **Wurtz reaction** : An ether solution of an alkyl halide (Preferably bromide or iodide) gives an alkane when heated with metallic sodium.



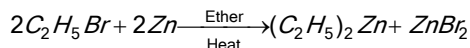
(c) **Reaction with magnesium** : Alkyl halides form Grignard reagent when treated with dry magnesium powder in dry ether.



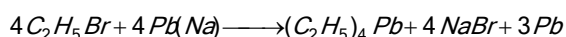
Grignard reagents are used for making a very large number of organic compounds.

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

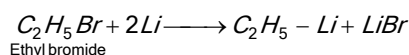
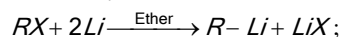
□ When heated with zinc powder in ether, alkyl halides form dialkyl zinc compounds. These are called Frankland reagents.



□ When heated with lead-sodium alloy, ethyl bromide gives tetra ethyl lead which is used as an antiknock compound in petrol.

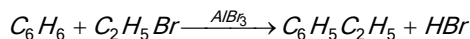
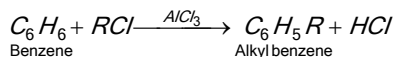


□ Reaction with lithium : Alkyl halides react with lithium in dry ether to form alkyl lithiums.

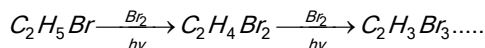


Alkyl lithiums are similar in properties with Grignard reagents. These are reactive reagents also.

(e) *Friedel-Craft's reaction* :



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

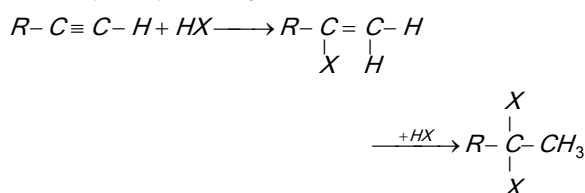


Preparations and properties of Dihalides

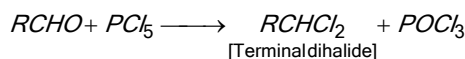
(1) **Methods of preparation of dihalides**

(i) **Methods of preparation of gemdihalide**

(a) *From alkyne (Hydrohalogenation)* :



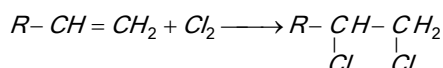
(b) *From carbonyl compound* :



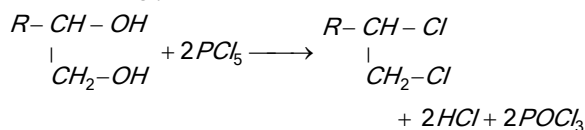
□ If ketone is taken internal dihalide formed.

(ii) **Methods of preparation of vicinal dihalide**

(a) *From alkene [By halogenation]* :



(b) *From vicinal glycol* :



(2) **Properties of dihalides**

(i) **Physical properties**

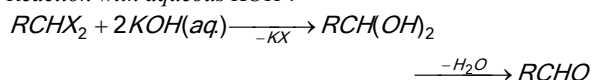
(a) Dihalide are colourless with pleasant smell liquid. Insoluble in water, soluble in organic solvent.

(b) *M.P* and *B.P* \propto -molecular mass.

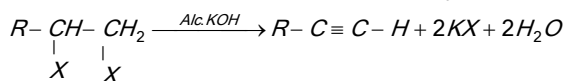
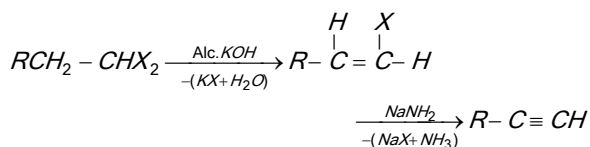
(c) Reactivity of vicinal dihalides > Gem dihalide.

(ii) **Chemical properties of dihalide**

(a) *Reaction with aqueous KOH* :



(b) *Reaction with alcoholic KOH* :

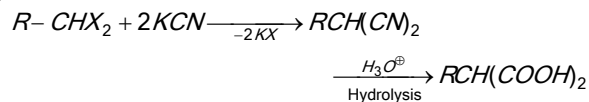


(c) *Reaction with Zn dust*

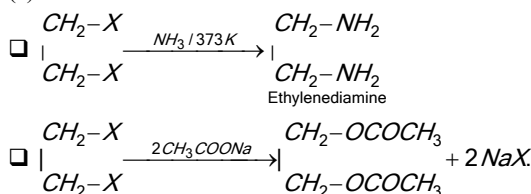
□ Gem halide (*di*) form higher symmetrical alkene.

□ Vicinal dihalide form respective alkene.

(d) *Reaction with KCN* :



(e) *Other substitution reaction*



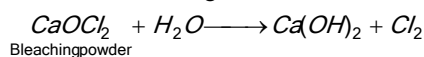
Tri-halides (Chloroform and iodoform)

Chloroform or trichloromethane, $CHCl_3$

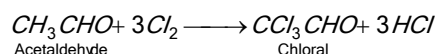
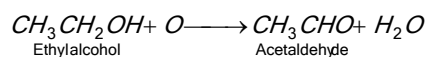
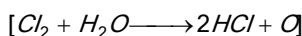
It is an important trihalogen derivative of methane. It was discovered by Liebig in 1831 and its name chloroform was proposed by Dumas as it gave formic acid on hydrolysis. In the past, it was extensively used as anaesthetic for surgery but now it is rarely used as it causes liver damage.

(1) **Preparation**

(i) 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 both as oxidising as well as chlorinating agent.

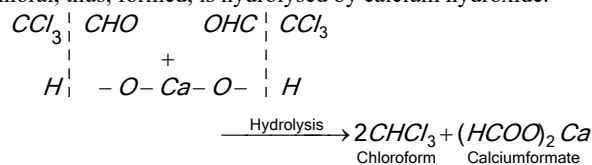


(a) *From alcohol*

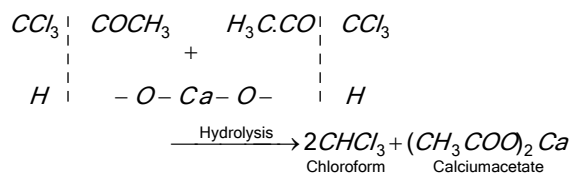
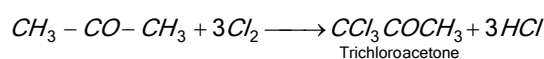


[So Cl_2 acts both as an oxidising and chlorinating agent]

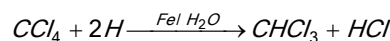
Chloral, thus, formed, is hydrolysed by calcium hydroxide.



(b) *From acetone*

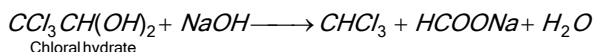


(ii) *From carbon tetrachloride* : Now-a-days, chloroform is obtained on a large scale by the reduction of carbon tetrachloride with iron filings and water.

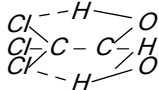


This chloroform is not pure and used mainly as a solvent.

(iii) Pure Chloroform is obtained by distilling chloral hydrate with concentrated sodium hydroxide solution.



Chloral hydrate is a stable compound inspite of the fact that two $-\text{OH}$ groups are linked to the same carbon atom. This is due to the fact that intramolecular hydrogen bonding exists in the molecule between chlorine and hydrogen atom of $-\text{OH}$ group.

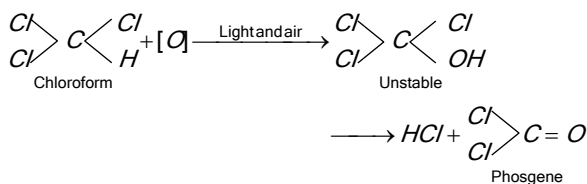


(2) Physical properties

- (i) It is a sweet smelling colourless liquid.
- (ii) It is heavy liquid. Its density is 1.485. It boils at 61°C .
- (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.

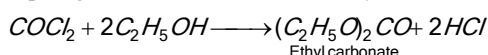
(3) Chemical properties

(i) Oxidation :

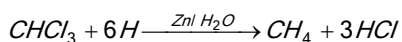
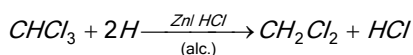


Phosgene is extremely poisonous gas. To use chloroform as an anaesthetic agent, it is necessary to prevent the above reaction. The following two precautions are taken when chloroform is stored.

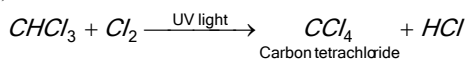
- (a) It is stored in dark blue or brown coloured bottles, which are filled upto the brim.
- (b) 1% ethyl alcohol is added. This retards the oxidation and converts the phosgene formed into harmless ethyl carbonate.



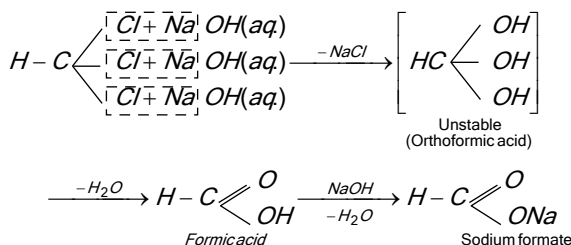
(ii) Reduction :



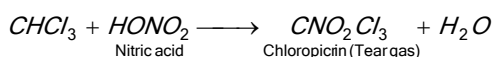
(iii) Chlorination :



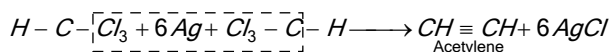
(iv) Hydrolysis :



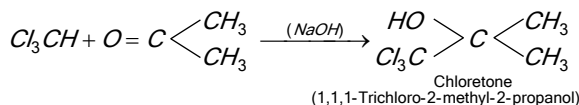
(v) **Nitration** : The hydrogen of the chloroform is replaced by nitro group when it is treated with concentrated nitric acid. The product formed is chloropicrin or trichloronitro methane or nitro chloroform. It is a liquid, poisonous and used as an insecticide and a war gas.



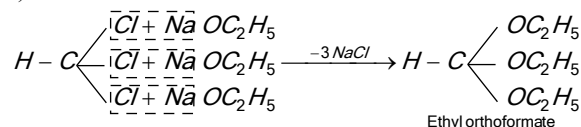
(vi) Heating with silver powder :



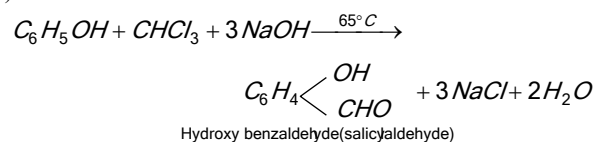
(vii) **Condensation with acetone** : Chloroform condenses with acetone on heating in presence of caustic alkalis. The product formed is a colourless crystalline solid called chloretone and is used as **hypnotic** in medicine.



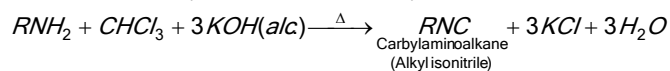
(viii) Reaction with sodium ethoxide :



(ix) Reimer-Tiemann reaction :



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



This reaction is also used for the test of chloroform.

(4) 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 to harmful effects it is not used these days for this purpose.
- (v) It may be used to prevent putrefaction of organic materials, *i.e.*, in the preservation of anatomical species.

(5) Tests of chloroform

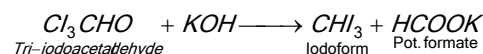
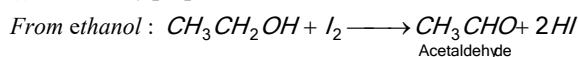
- (i) It gives isocyanide test (Carbylamine test).
- (ii) It forms silver mirror with Tollen's reagent.
- (iii) Pure Chloroform does not give white precipitate with silver nitrate.

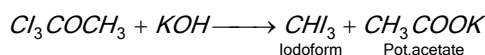
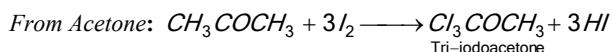
Iodoform or tri-iodomethane, CHI_3

Iodoform resembles chloroform in the methods of preparation and properties.

(1) Preparation

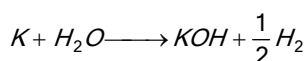
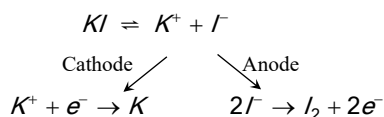
(i) Laboratory preparation :



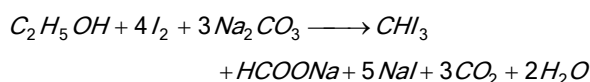


Sodium carbonate can be used in place of KOH or NaOH . These reactions are called iodoform reactions.

(ii) **Industrial preparation** : Iodoform is prepared on large scale by electrolysis of a solution containing ethanol, sodium carbonate and potassium iodide. The iodine set free, combine with ethanol in presence of alkali to form iodoform. The electrolysis carried out in presence of CO_2 and the temperature is maintained at $60\text{-}70^\circ\text{C}$.



KOH is neutralised by CO_2 :

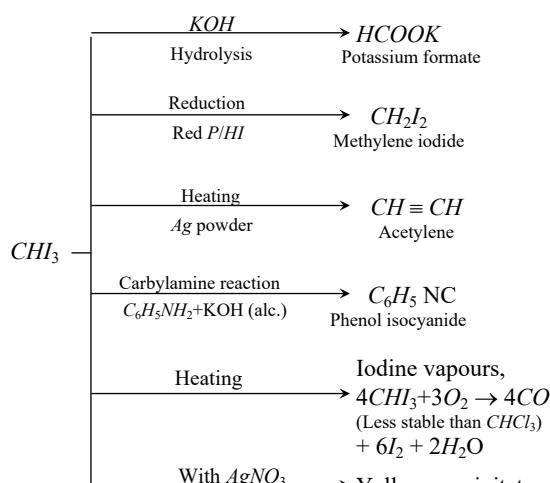


(2) Physical properties

- (i) It is a yellow crystalline solid.
- (ii) It has a pungent characteristic odour.
- (iii) It is insoluble in water but soluble in organic solvents such as alcohol, ether, etc.

(iv) It has melting point 119°C . It is steam volatile.

(3) Chemical Reactions of iodoform



(4) **Uses** : Iodoform is extensively used as an antiseptic for dressing of wounds; but the antiseptic action is due to the liberation of free iodine and not due to iodoform itself. When it comes in contact with organic matter, iodine is liberated which is responsible for antiseptic properties.

(5) Tests of iodoform

(i) **With AgNO_3** : CHI_3 gives a yellow precipitate of AgI .

(ii) **Carbylamine reaction** : CHI_3 on heating with primary amine and alcoholic KOH solution, gives an offensive smell of isocyanide (Carbylamine).

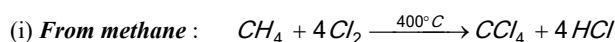
(iii) **Iodoform reaction** : With I_2 and NaOH or I_2 and Na_2CO_3 , the iodoform test is mainly given by ethyl alcohol

$(\text{CH}_3\text{CH}_2\text{OH})$, acetaldehyde ($\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$), α -methyl ketone or 2-one ($-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$), secondary alcohols or 2-ol ($-\text{CHOH}\cdot\text{CH}_3$) and secondary alkyl halide at $\text{C}_2(-\text{CHClCH}_3)$. Also lactic acid ($\text{CH}_3-\text{CHOH}-\text{COOH}$), Pyruvic acid ($\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{COOH}$) and methyl phenyl ketone ($\text{C}_6\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$) give this test.

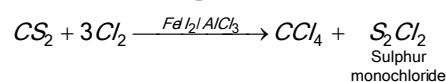
Tetra-halides (Carbon tetrachloride, CCl_4)

It is the most important tetrahalogen derivative of methane.

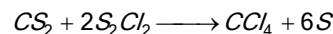
(1) Manufacture



(ii) **From carbon disulphide** :



S_2Cl_2 further reacts with CS_2 to form more of carbon tetrachloride.



Carbon tetrachloride is separated out by fractional distillation. It is washed with sodium hydroxide and then distilled to get a pure sample.

(iii) **From propane** :



(2) Physical properties

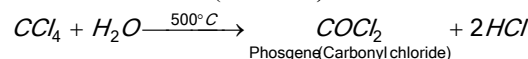
- (i) It is a colourless liquid having characteristic smell.
- (ii) It is non-inflammable and poisonous. It has boiling point 77°C .

(iii) It is insoluble in water but soluble in organic solvents.

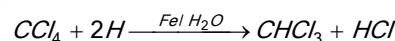
(iv) It is an excellent solvent for oils, fats, waxes and greases.

(3) **Chemical properties** : Carbon tetrachloride is less reactive and inert to most organic reagents. However, the following reactions are observed.

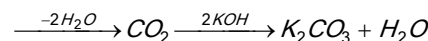
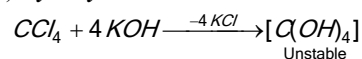
(i) **Reaction with steam** (Oxidation) :



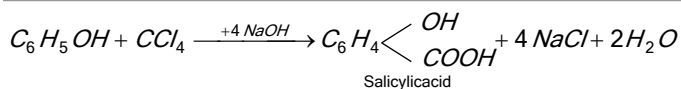
(ii) **Reduction** :



(iii) **Hydrolysis** :



(iv) **Reaction with phenol** (Reimer-tiemann reaction) :

**(4) Uses**

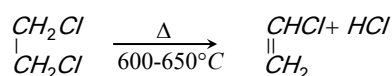
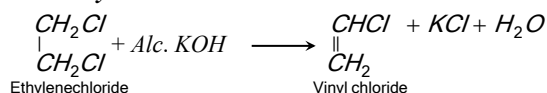
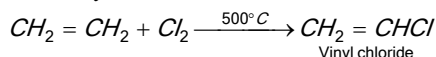
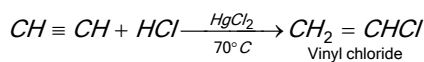
(i) It is used as a fire extinguisher under the name **pyrene**. The dense vapours form a protective layer on the burning objects and prevent the oxygen or air to come in contact with the burning objects.

(ii) It is used as a solvent for fats, oils, waxes and greases, resins, iodine etc.

(iii) It finds use in medicine as **helmenthicide** for elimination of hook worms.

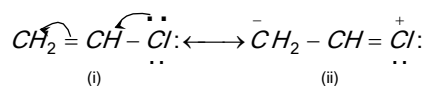
Unsaturated halides (Halo-alkene)**Vinyl chloride or chloroethene, $CH_2=CHCl$**

(1) **Synthesis** : Vinyl chloride can be synthesised by a number of methods described below:

(i) From ethylene chloride :**(ii) From ethylene :****(iii) From acetylene :**

(2) **Properties** : It is a colourless gas at room temperature. Its boiling point is $-13^\circ C$. The halogen atom in vinyl chloride is not reactive as in other alkyl halides. However, $C=C$ bond of vinyl chloride gives the usual addition reactions.

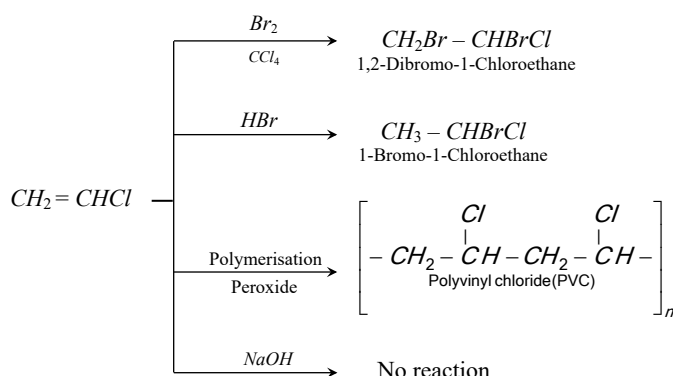
The non-reactivity of chlorine atom is due to resonance stabilization. The lone pair on chlorine can participate in delocalization (Resonance) to give two canonical structures.



The following two effects are observed due to resonance stabilization.

(i) Carbon-chlorine bond in vinyl chloride has some double bond character and is, therefore, stronger than a pure single bond.

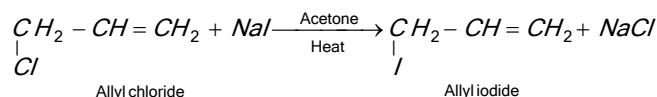
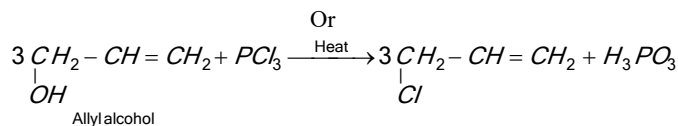
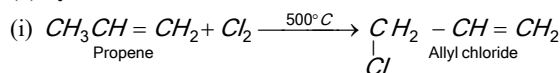
(ii) Carbon atom is sp^2 hybridized and $C-Cl$ bond length is shorter (1.69\AA) and the bond is stronger than in alkyl halides (1.80\AA) due to sp^3 hybridization of the carbon atom.

Addition reactions

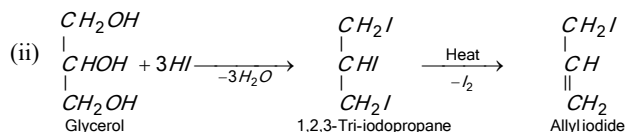
(3) **Uses** : The main use of vinyl chloride is in the manufacture of polyvinyl chloride (PVC) plastic which is employed these days for making synthetic leather goods, rain coats, pipes, floor tiles, gramophone records, packaging materials, etc.

Allyl iodide or 3-iodopropene-1, $ICH_2CH=CH_2$

(1) **Synthesis** : It is obtained,

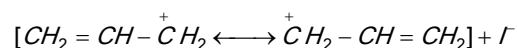
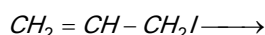


This is halogen-exchange reaction and is called **Finkelstein reaction**.

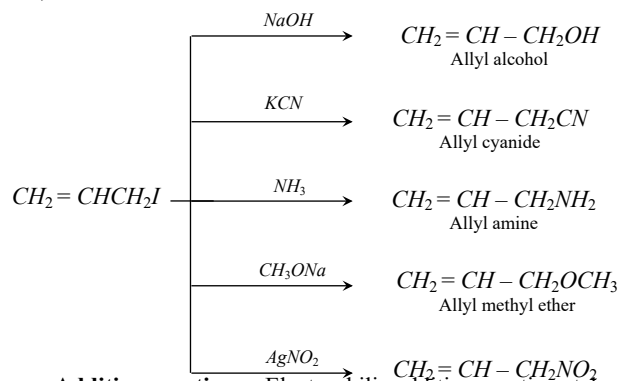


(2) **Properties** : It is a colourless liquid. It boils at $103.1^\circ C$. The halogen atom in allyl iodide is quite reactive. The p -orbital of the halogen atom does not interact with π -molecular orbital of the double bond because these are separated by a saturated sp^3 -hybridized carbon atom. Thus, the halogen atom in allyl halides can be easily replaced and the reactions of allyl halides are similar to the reaction of alkyl halides.

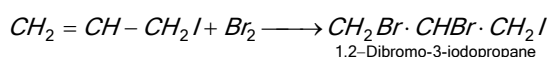
In terms of valence bond approach, the reactivity of halogen atom is due to ionisation to yield a carbonium ion which can stabilize by resonance as shown below,

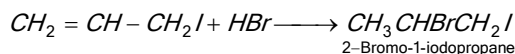


Substitution reactions : Nucleophilic substitution reactions occur,



Addition reactions : Electrophilic addition reactions take place in accordance to Markownikoff's rule.





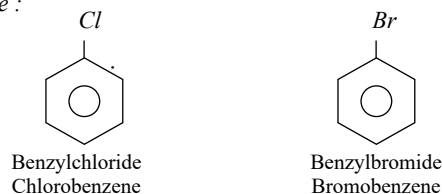
Allyl iodide is widely used in organic synthesis.

Halo-arenes

In these compounds the halogen is linked directly to the carbon of the benzene nucleus.

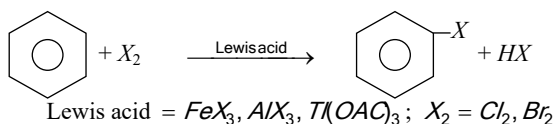
(1) **Nomenclature** : Common name is aryl halide *IUPAC* name is halo-arene.

Example :

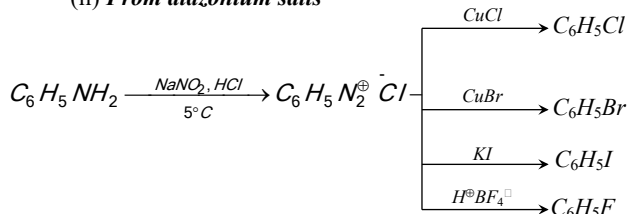


(2) Methods of preparation

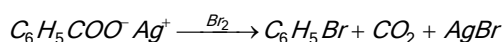
(i) By direct halogenation of benzene ring



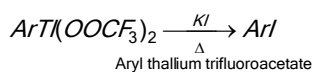
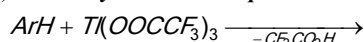
(ii) From diazonium salts



(iii) Hunsdiecker reaction :



(iv) From Aryl thallium compound :



(3) Physical properties

(i) **Physical state** : Haloarenes are colourless liquid or crystalline solid.

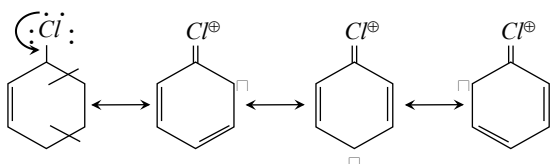
(ii) **Solubility** : They are insoluble in water, but dissolve readily in organic solvents. Insolubility is due to inability to form hydrogen bonding in water. Para isomer is less soluble than ortho isomer.

(iii) Halo-arenes are heavier than water.

(iv) B.P. of halo-arenes follow the trend. Iodo arene > Bromo arene > Chloro arene.

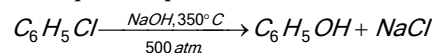
(4) Chemical properties

Inert nature of chlorobenzene : Aryl halides are unreactive as compared to alkyl halides as the halogen atom in these compounds is firmly attached and cannot be replaced by nucleophiles. Such as OH^- , NH_2^- , CN^- etc.

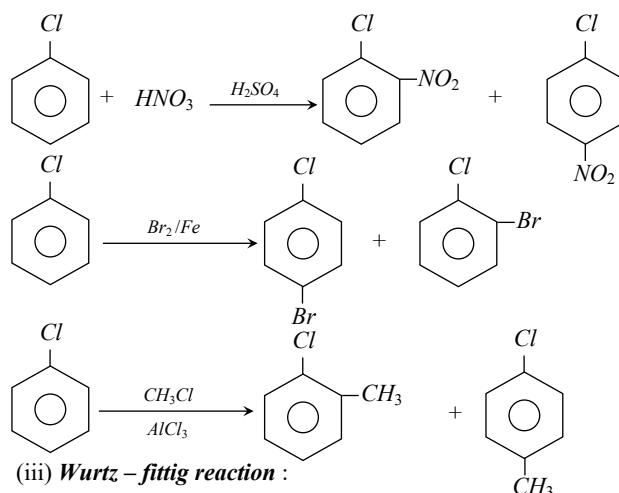


Thus delocalization of electrons by resonance in aryl halides, brings extra stability and double bond character between $\text{C}-\text{X}$ bond. This makes the bond stronger and shorter than pure single bond. However under vigorous conditions the following nucleophilic substitution reactions are observed,

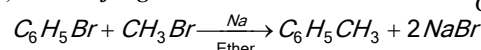
(i) Nucleophilic displacement :



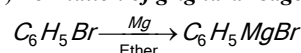
(ii) Electrophilic aromatic substitution



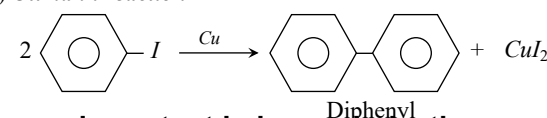
(iii) Wurtz - fittig reaction :



(iv) Formation of grignard reagent :



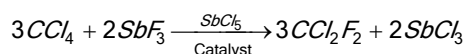
(v) Ullmann reaction



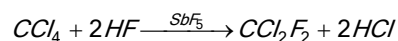
Some more important halogen derivatives

(1) **Freons** : The chloro fluoro derivatives of methane and ethane are called freons. Some of the derivatives are: CHF_2Cl (monochlorodifluoromethane), CF_2Cl_2 (dichlorodifluoro-methane), $\text{HCF}_2\text{CHCl}_2$ (1,1-dichloro-2,2-difluoroethane). These derivatives are non-inflammable, colourless, non-toxic, low boiling liquids. These are stable upto 550°C . The most important and useful derivative is CF_2Cl_2 which is commonly known as **freon** and **freon-12**.

Freon or freon-12 (CF_2Cl_2) is prepared by treating carbon tetrachloride with antimony trifluoride in the presence of antimony pentachloride as a catalyst.



Or it can be obtained by reacting carbon tetrachloride with hydrofluoric acid in presence of antimony pentafluoride.

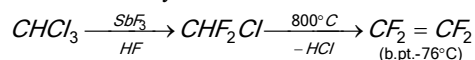


Under ordinary conditions freon is a gas. Its boiling point is -29.8°C . It can easily be liquified. It is chemically inert. It is used in

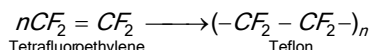
air-conditioning and in domestic refrigerators for cooling purposes (As refrigerant). It causes depletion of ozone layer.

(2) **Teflon** : It is plastic like substance produced by the polymerisation of tetrafluoroethylene ($CF_2 = CF_2$).

Tetrafluoroethylene is formed when chloroform is treated with antimony trifluoride and hydrofluoric acid.

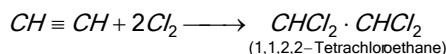


On polymerisation tetrafluoroethylene forms a plastic-like material which is called **teflon**.



Teflon is chemically inert substance. It is not affected by strong acids and even by boiling aqua-regia. It is stable at high temperatures. It is, thus, used for electrical insulation, preparation of gasket materials and non-sticking frying pans.

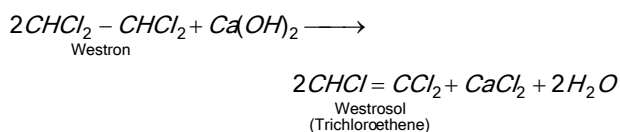
(3) **Acetylene tetrachloride (Westron), $CHCl_2 \cdot CHCl_2$** : Acetylene tetrachloride is also known as sym. tetrachloroethane. It is prepared by the action of chlorine on acetylene in presence of a catalyst such as ferric chloride, aluminium chloride, iron, quartz or kieselguhr.



In absence of catalyst, the reaction between chlorine and acetylene is highly explosive producing carbon and HCl . The reaction is less violent in presence of a catalyst.

It is a heavy, non-inflammable liquid. It boils at $146^\circ C$. It is highly toxic in nature. Its smell is similar to chloroform. It is insoluble in water but soluble in organic solvents.

On further chlorination, it forms penta and hexachloroethane. On heating with lime (Calcium hydroxide), it is converted to useful product **westrosol** ($CCl_2 = CHCl$).



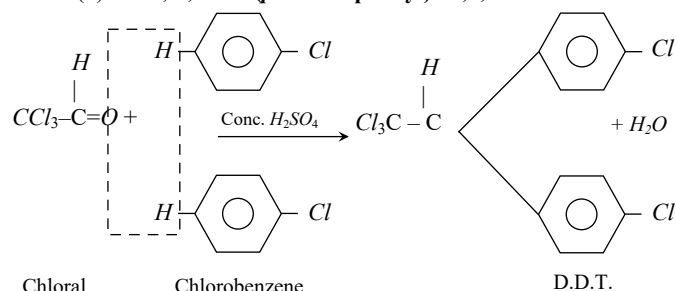
Both westron and westrosol are used as solvents for oils, fats, waxes, resins, varnishes and paints, etc.

(4) **p-Dichlorobenzene** : It is prepared by chlorination of benzene.

It is a white, volatile solid having melting point of $325 K$, which readily sublimates. It resembles chlorobenzene in their properties.

It is used as general insecticides, germicide, soil fumigant deodorant. It is used as a larvicide for cloth moth and peach tee borer.

(5) **DDT; 2, 2-bis (p-Chlorophenyl) -1,1,1-trichloroethane** :



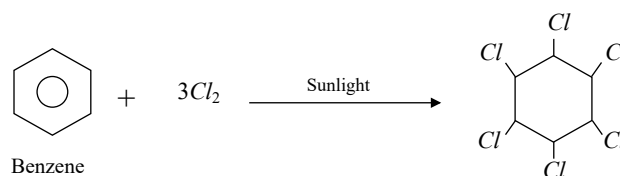
Properties and uses of D.D.T.

(i) D.D.T. is almost insoluble in water but it is moderately soluble in polar solvents.

(ii) D.D.T. is a powerful insecticide. It is widely used as an insecticide for killing mosquitoes and other insects.

Side Effects of D.D.T. : D.D.T. is not biodegradable. Its residues accumulate in environment and its long term effects could be highly dangerous. It has been proved to be toxic to living beings. Therefore, its use has been abandoned in many western countries. However, in spite of its dangerous side effects, D.D.T. is still being widely used in India due to non-availability of other cheaper insecticides.

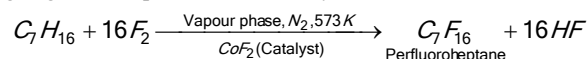
(6) **BHC (Benzene hexachloride), $C_6H_6Cl_6$** :



Uses : It is an important agricultural pesticide mainly used for exterminating white ants, leaf hopper, termite, etc. It is also known by the common name **gammexene or lindane or 666**.

□ aaccc conformation of $C_6H_6Cl_6$ is most powerful insecticide.

(7) **Perfluorocarbons (PFCs)** : Perfluorocarbons (C_nF_{2n+2}) are obtained by controlled fluorination of vapourized alkanes diluted with nitrogen gas in the presence of a catalyst.



These are colourless, odourless, non-toxic, non-corrosive, non-flammable, non-polar, extremely stable and unreactive gases, liquids and solids. These are stable to ultraviolet radiations and other ionising radiations and therefore, they do not deplete the ozone layer like freons.

These are good electrical insulators. These have many important uses such as :

(i) These are used as lubricants, surface coatings and dielectrics.

(ii) These are used as heat transfer media in high voltage electrical equipment.

(iii) These are used for vapour phase soldering, gross leak detection of sealed microchips etc. in electronic industry.

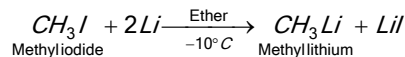
(iv) These are also used in health care and medicine such as skin care cosmetics, wound healing, liquid ventilation, carbon monoxide poisoning and many medical diagnosis.

Organometallic compounds

Organic compounds in which a metal atom is directly linked to carbon or organic compounds which contain at least one carbon-metal bond are called organometallic compounds.

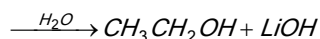
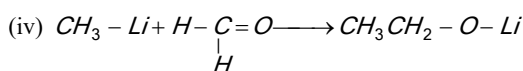
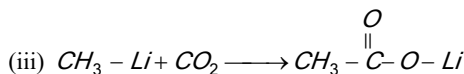
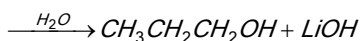
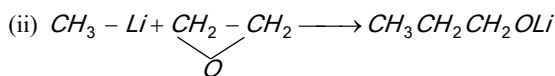
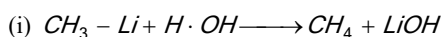
Example : Methyl lithium (CH_3Li), Dialkyl zinc (R_2Zn), Alkyl magnesium halide ($R-Mg-X$)

(1) **Methyl lithium** :

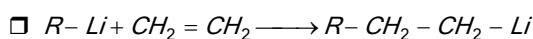


□ High reactivity of CH_3Li over grignard reagent is due to greater polar character of $C-Li$ bond in comparison to $C-Mg$ bond.

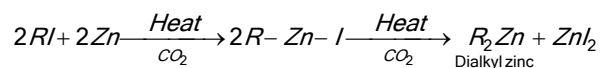
Chemical properties



□ Unlike grignard reagents, alkyl lithium can add to an alkenic double bond.

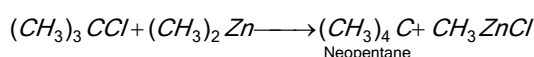


(2) **Dialkyl zinc** : First organometallic compound discovered by Frankland in 1849.



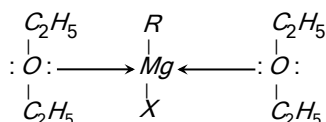
Chemical properties

Preparation of quaternary hydrocarbon :



(3) **Grignard reagent** : Grignard reagent are prepared by the action of alkyl halide on dry burn magnesium in presence of alcohol free dry ether.

Dry ether dissolves the grignard reagent through solvation.



Grignard reagents are never isolated in free state on account of their explosive nature.

□ For given alkyl radical the ease of formation of a grignard reagent is, Iodide > Bromide > Chloride

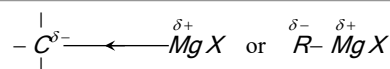
Usually alkyl bromides are used.

□ For a given halogen, the ease of formation of grignard reagent is, $CH_3X > C_2H_5X > C_3H_7X \dots\dots\dots$

□ Since tertiary alkyl iodides eliminate HI to form an alkene, tertiary alkyl chlorides are used in place of tertiary alkyl iodides.

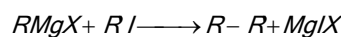
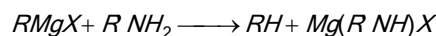
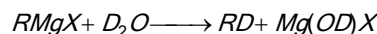
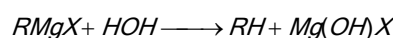
□ Grignard reagent cannot be prepared from a compound which consists in addition to halogen, some reactive group such as $-OH$ because it will react rapidly with the grignard reagent.

The $C-Mg$ bond in grignard reagent is some what covalent but highly polar.

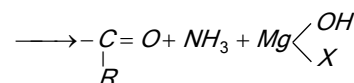
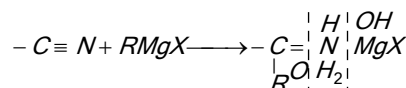
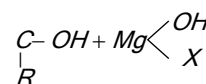
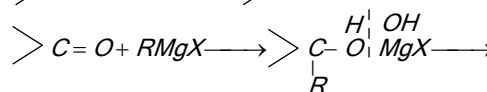
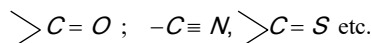


The alkyl group acts as carbanion. The majority of reaction of grignard reagent fall into two groups:

(i) *Double decomposition with compound containing active hydrogen atom or reactive halogen atom*



(ii) *Addition reaction with compounds containing*



Tips & Tricks

✍ Iodination of alkanes is a reversible process, therefore, formation of iodoalkanes is possible only in the presence of oxidising agents such as HIO_3 .

✍ Iodination with methane does not take place at all.

✍ Fluorination of alkanes takes place with rupture of $C-C$ bonds in higher alkanes. Therefore alkyl fluorides are generally prepared by halide exchange reactions.

✍ Phosphorous halides are generally used to prepare lower alkyl bromides in the laboratory.

✍ $SOBr_2$ is less stable and SOI_2 does not exist. Thus, $R-Br$ and $R-I$ cannot be prepared by Darzan's method.

✍ Hunsdiecker reaction proceeds through free radical mechanism. It is used to reduce the length of carbon chain.

✍ Reactivity of halides towards S_N^1 mechanism is $3^\circ > 2^\circ > 1^\circ$.

✍ Reactivity of halides towards S_N^2 mechanism is $1^\circ > 2^\circ > 3^\circ$.

- ✍ Polar solvents favour S_N^1 mechanism.
- ✍ Non polar solvents favour S_N^2 mechanism.
- ✍ High concentration of nucleophile favour S_N^2 mechanism while low concentration of nucleophile favour S_N^1 mechanism.
- ✍ S_N^1 reactions partial racemisation occurs with inverted product predominant in yield whereas in S_N^2 reactions, inverted product is formed.
- ✍ Order of nucleophilicity among halide ions decreases in the order $I^- > Br^- > Cl^- > F^-$.
- ✍ During elimination reactions, the H atom is lost from the carbon atom carrying minimum number of H atom.
- ✍ C_2H_5SH (Ethyl mercaptan) is added to LPG (household cooking gas) to detect leakage. The compound has a typical smell.
- ✍ In Sandmeyer reaction, Cl of $CuCl$ is attached to benzene ring.
- ✍ Nuclear halogenation takes place by electrophilic substitution mechanism whereas side chain halogenation takes place by free radical mechanism.
- ✍ Aryl halides and vinyl halides ($CH_2 = CH - X$) are less reactive than alkyl halides and are not easily hydrolysed. Thus alkyl halides on reaction with $NaOH$ give coloured precipitate but aryl and vinyl halide does not.
- ✍ Before using the sample of chloroform as an anaesthetic it is tested by treating with aqueous solution of $AgNO_3$. A pure sample does not give ppt. with aq. $AgNO_3$.
- ✍ Halothane, $CF_3-CHClBr$, is a general anaesthetic which replace diethyl ether.
- ✍ CCl_4 resist hydrolysis with boiling water due to non availability of d -orbital in C .
- ✍ C_2Cl_6 is a solid and is known as artificial camphor.
- ✍ Chlorobenzene commercially produced by Raschig process.