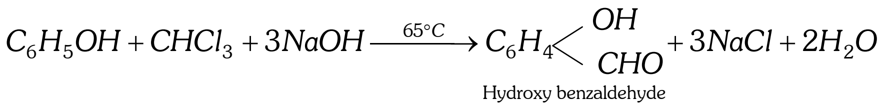
Halogen Derivatives Part 2

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



$$C_6H_5OH + CHCl_3 + 3NaOH \xrightarrow{65^\circ C} \underset{\text{Hydroxy benzaldehyde}}{C_6H_4\begin{matrix} OH \\ CHO \end{matrix}} + 3NaCl + 2H_2O$$

(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.

$$RNH_2 + CHCl_3 + 3KOH(alc.) \xrightarrow{\Delta} \underset{\substack{\text{Carbylaminoalkane} \\ \text{(Alkyl isonitrile)}}}{RNC} + 3KCl + 3H_2O$$

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*** : Iodoform is prepared in the laboratory by heating ethanol or acetone with iodine and alkali.

$$\text{Ethanol}: CH_3CH_2OH + I_2 \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + 2HI$$

$$CH_3CHO + 3I_2 \longrightarrow \underset{Iodal}{CI_3CHO} + 3HI$$

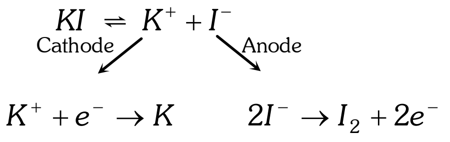
$$\underset{Tri-iodoacetaldehyde}{CI_3CHO} + KOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Pot. formate}}{HCOOK}$$

$$\text{Acetone}: CH_3COCH_3 + 3I_2 \longrightarrow \underset{\text{Tri-iodoacetone}}{CI_3COCH_3} + 3HI$$

$$CI_3COCH_3 + KOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Pot. acetate}}{CH_3COOK}$$

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 60-70°C.



$$KI \rightleftharpoons K^+ + I^-$$

$$K^+ + e^- \rightarrow K \qquad 2I^- \rightarrow I_2 + 2e^-$$

$$K + H_2O \longrightarrow KOH + \frac{1}{2}H_2$$

KOH is neutralised by CO_2: $C_2H_5OH + 4I_2 + 3Na_2CO_3 \longrightarrow CHI_3 + HCOONa + 5NaI + 3CO_2 + 2H_2O$

(2) Properties

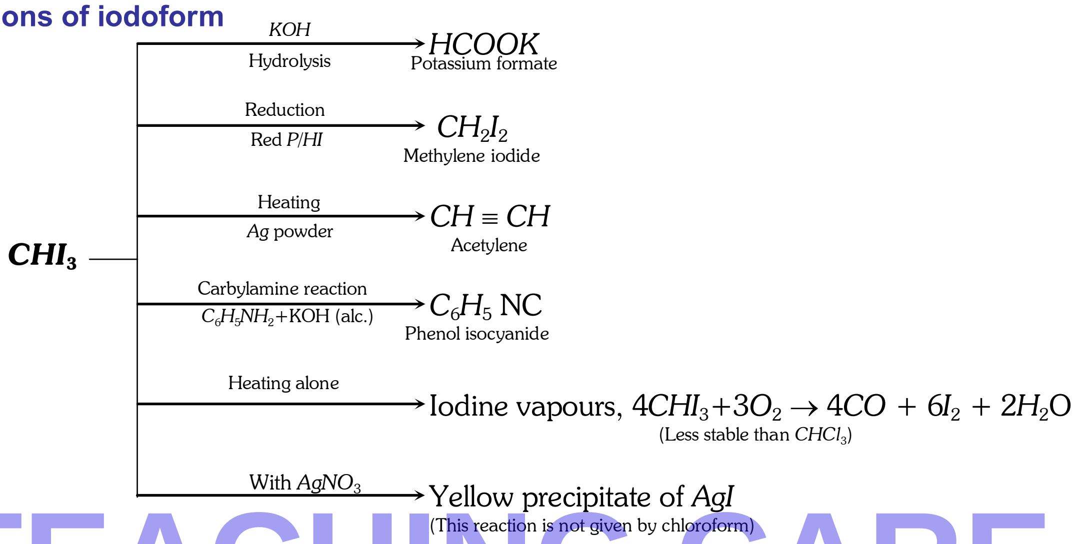
(i) It is a yellow crystalline solid.

(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) 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 (CH_3CH_2OH), acetaldehyde $(CH_3-\overset{O}{\overset{||}{C}}-H)$, α-methyl ketone or 2-one $(-\overset{O}{\overset{||}{C}}-CH_3)$, secondary alcohols or 2-ol $(-CHOH\cdot CH_3)$ and secondary alkyl halide at $C_2(-CHClCH_3)$. Also lactic acid $(CH_3-CHOH-COOH)$, Pyruvic acid $(CH_3-\overset{O}{\overset{||}{C}}-COOH)$ and methyl phenyl ketone $(C_6H_5-\overset{O}{\overset{||}{C}}-CH_3)$ give this test.

Tetra-halides (Carbon tetrachloride or tetrachloromethane, CCl_4).

It is the most important tetrahalogen derivative of methane.

(1) Manufacture

(i) ***From methane*** : Chlorination of methane with excess of chlorine at 400°C yields impure carbon tetrachloride.

$$CH_4 + 4Cl_2 \xrightarrow{400°C} CCl_4 + 4HCl$$

Methane used in this process is obtained from natural gas.

(ii) ***From carbon disulphide*** : Chlorine reacts with carbon disulphide in presence of catalysts like iron, iodine, aluminium chloride or antimony pentachloride.

$$CS_2 + 3Cl_2 \longrightarrow CCl_4 + \underset{\substack{\text{Sulphur}\\\text{monochloride}}}{S_2Cl_2}$$

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

$$CS_2 + 2S_2Cl_2 \longrightarrow CCl_4 + 6S$$

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

(iii) ***From propane*** : Propane is reacted with chlorine at about 400°*C* and at a pressure of 70-100 atmosphere.

$$C_3H_8 + 9Cl_2 \xrightarrow[\text{Pressure}]{\text{Heat}} \underset{\substack{\text{Carbon tetrachloride}\\\text{(Liquid)}}}{CCl_4} + \underset{\substack{\text{Hexachloroethane}\\\text{(Solid)}}}{C_2Cl_6} + 8HCl$$

(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) **:** Carbon tetrachloride vapours react with steam above 500°*C* to form phosgene, a poisonous gas.

$$CCl_4 + H_2O \xrightarrow{500^\circ C} \underset{\text{Phosgene (Carbonyl chloride)}}{COCl_2} + 2HCl$$

(ii) ***Reduction*** : It is reduced by moist iron filling into chloroform.

$$CCl_4 + 2H \xrightarrow{Fe/H_2O} CHCl_3 + HCl$$

(iii) ***Hydrolysis*** : On heating with aqueous potassium hydroxide it forms carbon dioxide which combines with potassium hydroxide to give *KCl* and potassium carbonate (Inorganic salts).

$$CCl_4 + 4KOH \xrightarrow{-4KCl} \underset{\text{Unstable}}{[C(OH)_4]} \xrightarrow{-2H_2O} CO_2 \xrightarrow{2KOH} K_2CO_3 + H_2O$$

(iv) ***Reaction with phenol*** (Reimer-tiemann reaction**)** : It combines with phenol in presence of sodium hydroxide to form salicylic acid.

$$C_6H_5OH + CCl_4 \xrightarrow{+4NaOH} \underset{\text{Salicylic acid}}{C_6H_4 \left\langle \begin{matrix} OH \\ COOH \end{matrix} \right.} + 4NaCl + 2H_2O$$

(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.

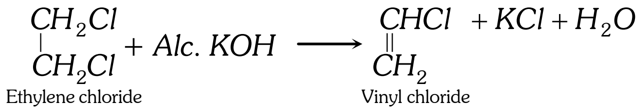
(iii) It finds use in medicine as **helmenthicide** for elimination of hook worms.

Unsaturated halides (Halo-alkene).

Vinyl chloride or chloroethene, $CH_2=CHCl$

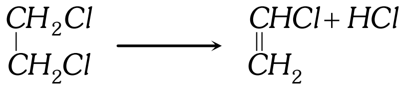
(1) **Synthesis :** Vinyl chloride can be synthesised by a number of methods described below:

(i) ***From ethylene chloride*** : It is easily prepared in the laboratory by the action of dilute alcoholic solution of potassium hydroxide on ethylene chloride.



$$\underset{\text{Ethylene chloride}}{\begin{matrix}CH_2Cl\\|\\CH_2Cl\end{matrix}} + Alc.\ KOH \longrightarrow \underset{\text{Vinyl chloride}}{\begin{matrix}CHCl\\||\\CH_2\end{matrix}} + KCl + H_2O$$

Vinyl chloride can also be obtained from ethylene chloride by thermal decomposition at 600-650°C.



$$\begin{matrix}CH_2Cl\\|\\CH_2Cl\end{matrix} \longrightarrow \begin{matrix}CHCl\\||\\CH_2\end{matrix} + HCl$$

(ii) ***From ethylene*** : Free radical chlorination of ethylene at 500°C yields vinyl chloride.

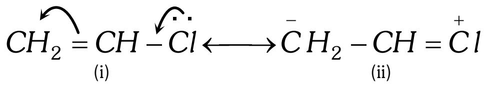
$$CH_2=CH_2+Cl_2 \xrightarrow{500°C} \underset{\text{Vinyl chloride}}{CH_2=CHCl}$$

(iii) ***From acetylene*** : Vinyl chloride is obtained by controlled addition of HCl on acetylene. Acetylene is passed through dilute hydrochloric acid at about 70°C in presence of $HgCl_2$ as a catalyst to form vinyl chloride. This method is also used for its manufacture.

$$CH\equiv CH+HCl \xrightarrow[70°C]{HgCl_2} \underset{\text{Vinyl chloride}}{CH_2=CHCl}$$

(2) **Properties :** It is a colourless gas at room temperature. Its boiling point is –13°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 structures.



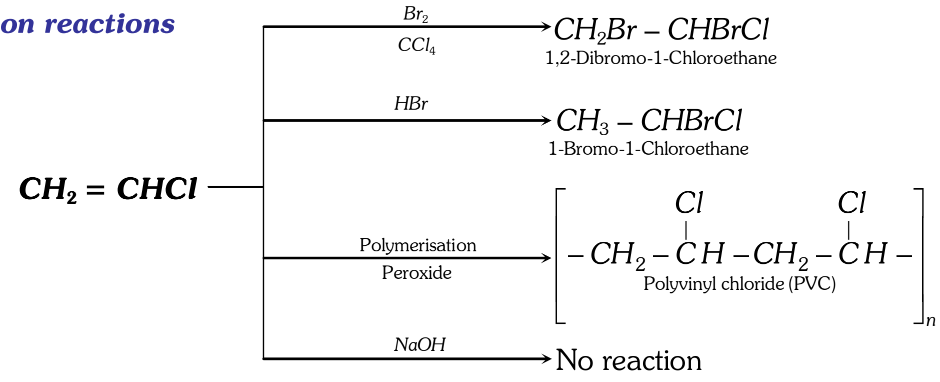
$$\underset{(i)}{CH_2=CH-\ddot{Cl}} \longleftrightarrow \underset{(ii)}{\overset{-}{C}H_2-CH=\overset{+}{Cl}}$$

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 (1.69Å) and stronger than in alkyl halides (1.80Å) due to sp^3 hybridization of the carbon atom.

Addition reactions

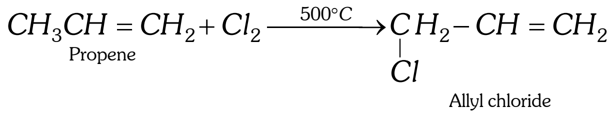


(3) Uses : The main use of vinyl chloride is in the manufacture of polyvinyl chloride **(PVC)** plastic which is employed these days for making synthetic leather goods, rain coats, pipes, floor tiles, gramophone records, packaging materials, etc.

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

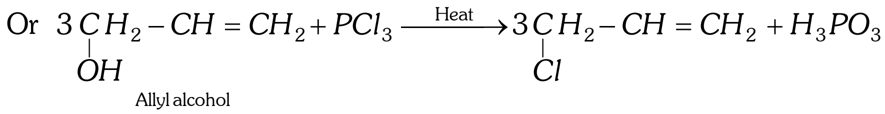
(1) Synthesis : It is obtained,

(i) By heating allyl chloride with sodium iodide in acetone. Allyl chloride required in the reactions is prepared either by chlorination of propene at 500°C or by action of PCl_3 on allyl alcohol.

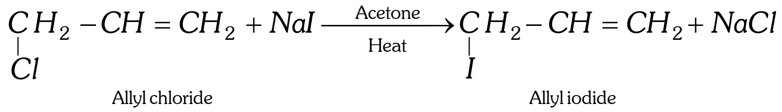


$$\underset{\text{Propene}}{CH_3CH=CH_2}+Cl_2\xrightarrow{500^\circ C}\underset{\text{Allyl chloride}}{\underset{\substack{|\\ Cl}}{CH_2}-CH=CH_2}$$

Or



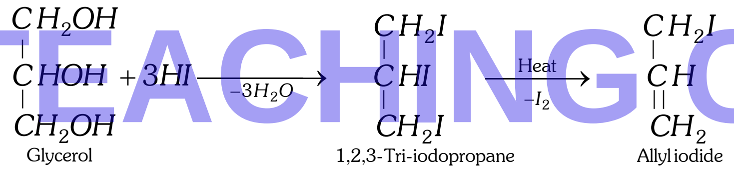
$$3\underset{\text{Allyl alcohol}}{\underset{\substack{|\\ OH}}{CH_2}-CH=CH_2}+PCl_3\xrightarrow{\text{Heat}}3\underset{\substack{|\\ Cl}}{CH_2}-CH=CH_2+H_3PO_3$$



$$\underset{\text{Allyl chloride}}{\underset{\substack{|\\ Cl}}{CH_2}-CH=CH_2}+NaI\xrightarrow[\text{Heat}]{\text{Acetone}}\underset{\text{Allyl iodide}}{\underset{\substack{|\\ I}}{CH_2}-CH=CH_2}+NaCl$$

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

(ii) By heating glycerol with HI.



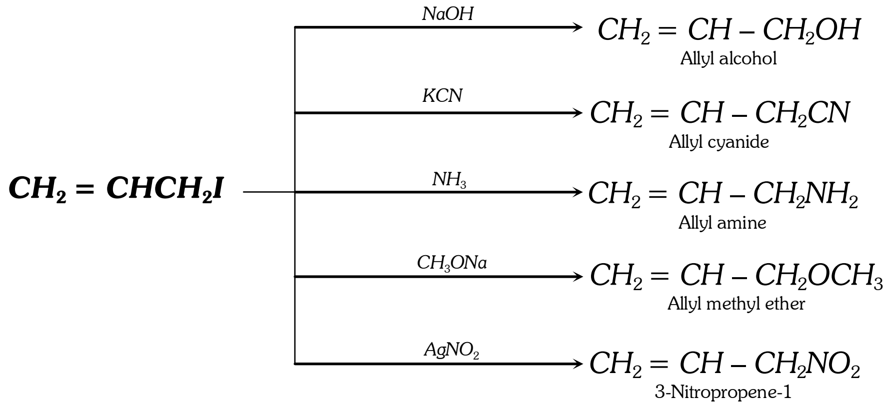
$$\underset{\text{Glycerol}}{\begin{array}{c}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array}}+3HI\xrightarrow{-3H_2O}\underset{\text{1,2,3-Tri-iodopropane}}{\begin{array}{c}CH_2I\\|\\CHI\\|\\CH_2I\end{array}}\xrightarrow[-I_2]{\text{Heat}}\underset{\text{Allyl iodide}}{\begin{array}{c}CH_2I\\|\\CH\\||\\CH_2\end{array}}$$

(2) Properties : It is a colourless liquid. It boils at 103.1°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,

$$CH_2=CH-CH_2I\longrightarrow[CH_2=CH-\overset{+}{C}H_2\longleftrightarrow\overset{+}{C}H_2-CH=CH_2]+I^-$$

Substitution reactions **:** Nucleophilic substitution reactions occur,



$CH_2=CHCH_2I\xrightarrow{NaOH}CH_2=CH-CH_2OH$ Allyl alcohol

$CH_2=CHCH_2I\xrightarrow{KCN}CH_2=CH-CH_2CN$ Allyl cyanide

$CH_2=CHCH_2I\xrightarrow{NH_3}CH_2=CH-CH_2NH_2$ Allyl amine

$CH_2=CHCH_2I\xrightarrow{CH_3ONa}CH_2=CH-CH_2OCH_3$ Allyl methyl ether

$CH_2=CHCH_2I\xrightarrow{AgNO_2}CH_2=CH-CH_2NO_2$ 3-Nitropropene-1

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

$$CH_2=CH-CH_2I+Br_2\longrightarrow \underset{\text{1,2-Dibromo-3-iodopropane}}{CH_2Br\cdot CHBr\cdot CH_2I}\ ;\ CH_2=CH-CH_2I+HBr\longrightarrow \underset{\text{2-Bromo-1-iodopropane}}{CH_3CHBrCH_2I}$$

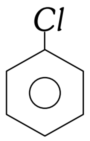
Allyl iodide is widely used in organic synthesis.

Halo-arenes.

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

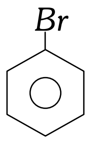
(1) **Nomenclature :** Common name is aryl halide *IUPAC* name is halo-arene.

Example :



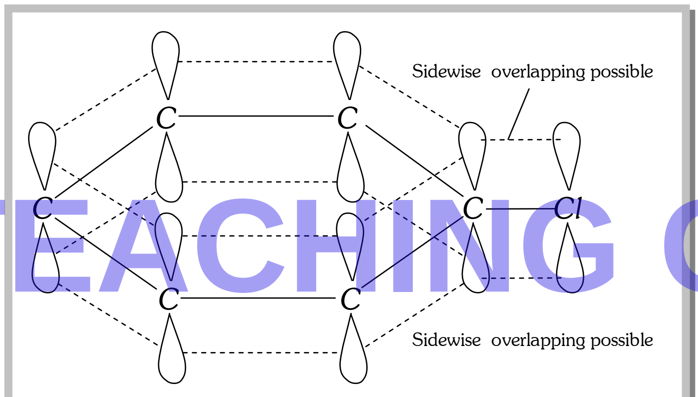
Benzylchloride
Chlorobenzene

;



Benzylbromide
Bromobenzene

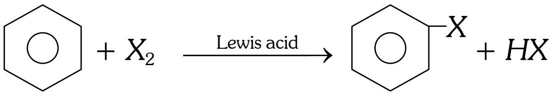
(2) **Structure**



Chlorobenzene

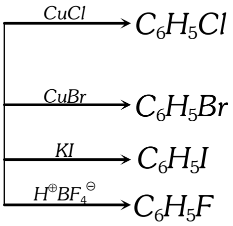
(3) **Methods of preparation**

(i) ***By direct halogination of benzene ring***



Lewis acid $=FeX_3, AlX_3, Tl(OAC)_3$; $X_2=Cl_2, Br_2$

(ii) ***From diazonium salts***



$$C_6H_5NH_2\xrightarrow[5°C]{NaNO_2,HCl}C_6H_5N_2^{\oplus}\overset{\ominus}{C}l-$$

(iii) ***Hunsdiecker reaction*** : $C_6H_5COO^-Ag^+ \xrightarrow{Br_2} C_6H_5Br + CO_2 + AgBr$

(iv) ***From Aryl thalium compound*** : $ArH + Tl(OOCCF_3)_3 \xrightarrow[-CF_3CO_2H]{} ArTl(OOCF_3)_2 \xrightarrow[\Delta]{KI} ArI$

Aryl thallium trifluoroacetate

(4) Physical properties

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

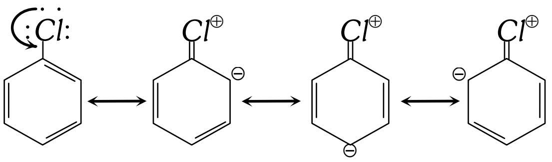
(ii) ***Solubility*** : They are insoluble in water, but dissolve readily in organic solvents. Insolubility is due to inability to break hydrogen bonding in water. Para isomer is less soluble than ortho isomer.

(iii) Halo-arenes are heavier than water.

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

(5) Chemical properties

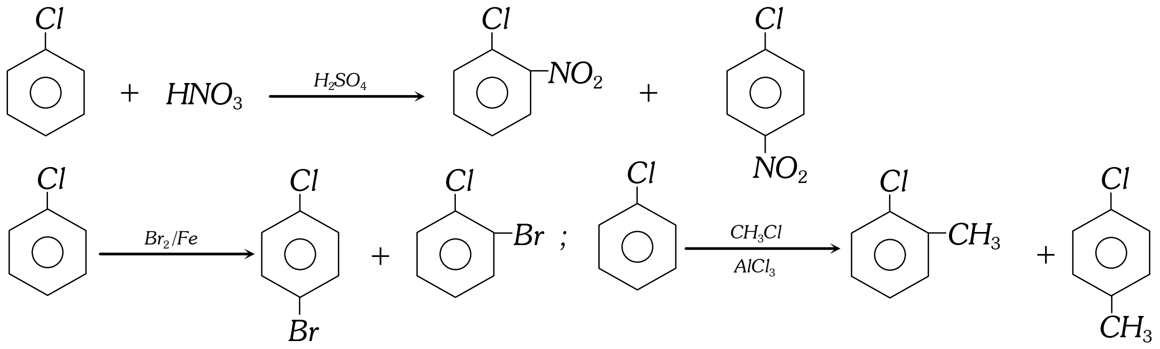
Inert nature of chlorobenzene : Aryl halides are unreactive as compared to alkyl halides as the halogen atom in these compounds is firmly attached and cannot be replaced by nucleophiles. Such as OH^-, NH_2^-, CN^- *etc.*



Thus delocalization of electrons by resonance in aryl halides, brings extra stability and double bond character between $C-X$ 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*** : $C_6H_5Cl \xrightarrow[500\,atm.]{NaOH,\,350°C} C_6H_5OH$

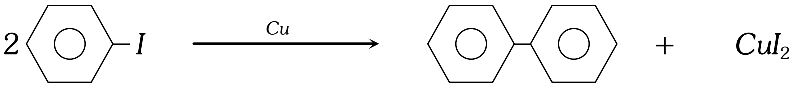
(ii) ***Electrophilic aromatic substitution***



(iii) ***Wurtz – fittig reaction*** : $C_6H_5Br + CH_3Br \xrightarrow[Ether]{Na} C_6H_5CH_3 + 2NaBr$

(iv) ***Formation of grignard reagent*** : $C_6H_5Br \xrightarrow[Ether]{Mg} C_6H_5MgBr$

(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 (dichlorodifluoromethane), HCF_2CHCl_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. $3CCl_4 + 2SbF_3 \xrightarrow[\text{Catalyst}]{SbCl_5} 3CCl_2F_2 + 2SbCl_3$

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

$$CCl_4 + 2HF \xrightarrow{SbF_5} CCl_2F_2 + 2HCl$$

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.

$$CHCl_3 \xrightarrow[HF]{SbF_3} CHF_2Cl \xrightarrow[-HCl]{800°C} \underset{\text{(b.pt.-76°C)}}{CF_2 = CF_2}$$

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

$$\underset{\text{Tetrafluoroethylene}}{nCF_2 = CF_2} \longrightarrow \underset{\text{Teflon}}{(-CF_2 - CF_2-)_n}$$

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.

$$CH \equiv CH + 2Cl_2 \longrightarrow \underset{\text{(1,1,2,2−Tetrachloroethane)}}{CHCl_2 \cdot CHCl_2}$$

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°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** $(CCl_2 = CHCl)$.

$$\underset{\text{Westron}}{2CHCl_2 - CHCl_2} + Ca(OH)_2 \longrightarrow \underset{\substack{\text{Westrosol} \\ \text{(Trichloroethene)}}}{2CHCl = CCl_2} + CaCl_2 + 2H_2O$$

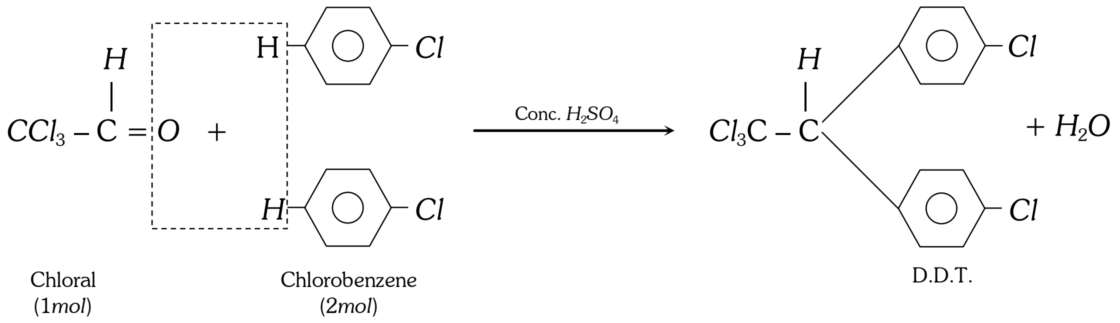
Both westron and westrosol are used as solvents for oils, fats, waxes, resins, varnishes and paints, etc.

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

It is a white, volatile solid having melting point of 325 K, which readily sublimes. 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 : It is synthesised by heating a mixture of chloral (1*mol*) with chlorobenzene (2*mol*) in the presence of concentrated H_2SO_4.



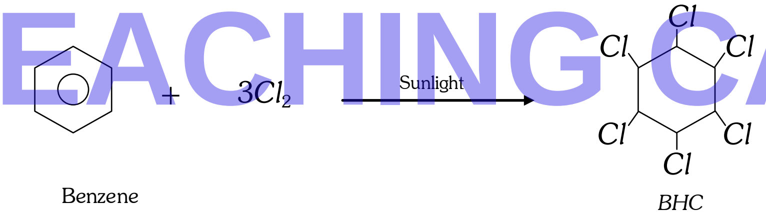
Properties and uses of D.D.T.

(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, inspite 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), $C_6H_6Cl_6$:** It is prepared by chlorination of benzene in the presence of sunlight.



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 gammaxene or lindane or 666.

Note : ✹ aaaeee 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.

$$C_7H_{16}+16F_2 \xrightarrow[CoF_2\text{ (Catalyst)}]{\text{Vapour phase, } N_2, 573K} \underset{\text{Perfluoroheptane}}{C_7F_{16}} + 16HF$$

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.

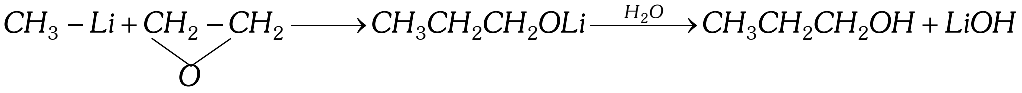
Example : Methyl lithium $\longrightarrow CH_3Li$; Dialkyl zinc $\longrightarrow R_2Zn$; Alkyl magnesium halide $\longrightarrow R-Mg-X$

(1) **Methyl lithium :** $\underset{\text{Methyl iodide}}{CH_3I} + 2Li \xrightarrow[-10^\circ C]{\text{Ether}} \underset{\text{Methyl lithium}}{CH_3Li} + LiI$

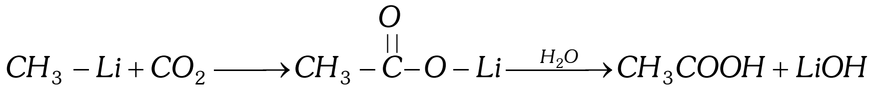
Note : ✸ High reactivity of CH_3Li over grignard reagent is due to greater polar character of $C-Li$ bond in comparison to $C-Mg$ bond.

Chemical properties

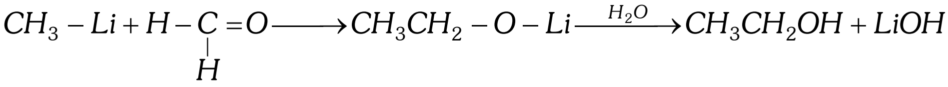
(i) $CH_3-Li+H\cdot OH \longrightarrow CH_4 + LiOH$

(ii) 

$CH_3-Li+\underset{\diagdown O \diagup}{CH_2-CH_2} \longrightarrow CH_3CH_2CH_2OLi \xrightarrow{H_2O} CH_3CH_2CH_2OH + LiOH$

(iii) 

$CH_3-Li+CO_2 \longrightarrow CH_3-\overset{\overset{\displaystyle O}{||}}{C}-O-Li \xrightarrow{H_2O} CH_3COOH + LiOH$

(iv) 

$CH_3-Li+H-\underset{\underset{\displaystyle H}{|}}{C}=O \longrightarrow CH_3CH_2-O-Li \xrightarrow{H_2O} CH_3CH_2OH + LiOH$

Note : ✸ Unlike grignard reagents, alkyl lithium can add to an alkenic double bond.

✸ $R-Li+CH_2=CH_2 \longrightarrow R-CH_2-CH_2-Li$

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

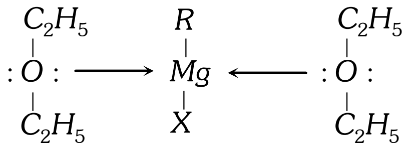
$2RI + 2Zn \xrightarrow[CO_2]{Heat} 2R-Zn-I \xrightarrow[CO_2]{Heat} \underset{\text{Dialkyl zinc}}{R_2Zn} + ZnI_2$

Chemical properties

Preparation of quaternary hydrocarbon : $(CH_3)_3CCl + (CH_3)_2Zn \longrightarrow \underset{\text{Neopentane}}{(CH_3)_4C} + CH_3ZnCl$

(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 solvolysis.



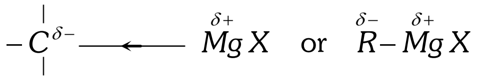
Grignard reagents are never isolated in free sate on account of their explosive nature.

Note : ✸ 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, $CH_3X > C_2H_5X > C_3H_7X$..........
- ✸ Since tertiary alkyl iodides eliminate HI to form an alkene, tertiary alkyl chlorides are used in their place.
- ✸ 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.



$$-\underset{|}{\overset{|}{C}}{}^{\delta-} \longleftarrow \overset{\delta+}{Mg}\,X \quad \text{or} \quad \overset{\delta-}{R}-\overset{\delta+}{Mg}\,X$$

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

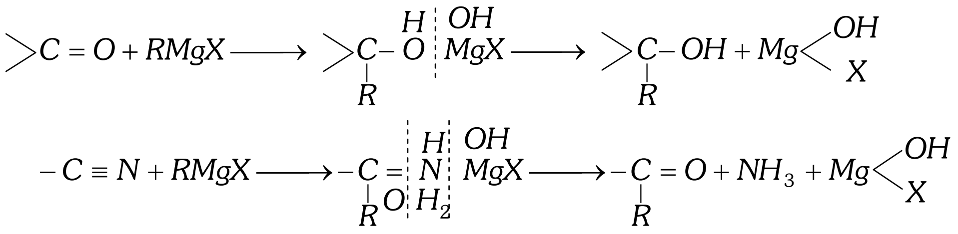
(i) *Double decomposition with compound containing active hydrogen atom or reactive halogen atom*

$$RMgX+HOH\longrightarrow RH+Mg(OH)X\ ;\ RMgX+D_2O\longrightarrow RD+Mg(OD)X$$

$$RMgX+R'OH\longrightarrow RH+Mg(OR')X\ ;\ RMgX+R'NH_2\longrightarrow RH+Mg(R'NH)X$$

$$RMgX+R'I\longrightarrow R-R'+MgIX\ ;\ RMgX+ClCH_2OR'\longrightarrow RCH_2OR'+MgClX$$

(ii) Addition reaction with compounds containing $>C=O$; $-C\equiv N, >C=S$ etc.



$$>C=O+RMgX\longrightarrow\ >\underset{R}{\underset{|}{C}}-\overset{H}{O}\,\vdots\,\overset{OH}{MgX}\longrightarrow\ >\underset{R}{\underset{|}{C}}-OH+Mg<^{OH}_{X}$$

$$-C\equiv N+RMgX\longrightarrow -\underset{R}{\underset{|}{C}}=\underset{O\,H_2}{\overset{H}{N}}\,\vdots\,\overset{OH}{MgX}\longrightarrow -\underset{R}{\underset{|}{C}}=O+NH_3+Mg<^{OH}_{X}$$