

ORGANIC CHEMISTRY

BASED ON FUNCTIONAL GROUP –I

HALO ALKANES AND HALOARENES

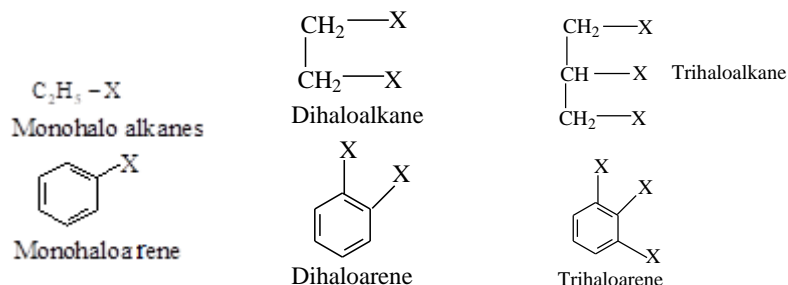
Haloalkanes have the general formula $R-X$, where 'X' is a halogen atom and 'R' is an alkyl group. They are also known as alkyl halides (Eg : CH_3-Cl).

Haloarenes are aromatic compounds in which the halogen is directly attached to an aromatic ring (eg: C_6H_5-Cl). They are also known as arylhalides.

Classification

1. On the basis of number of halogen atoms.

On the basis of number of halogen atoms haloalkanes and haloarenes are classified into mono, di and poly halogen compounds depending on whether they contain one, two or more halogen atoms .



2. On the basis of hybridization of carbon attached to halogen

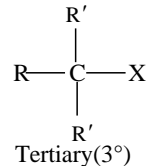
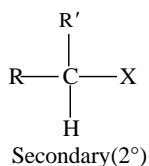
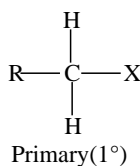
Mono halo compounds are further classified on the basis of hybridization

(1) Compounds containing sp^3 C-X bond

This includes

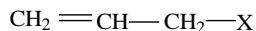
(a) Alkyl halides or haloalkanes ($R-X$)

Here halogen is attached to an alkyl group. They are represented by the general formula $C_nH_{2n+1}X$. These are further classified as **primary**, **secondary** or **tertiary** depending on the nature of the carbon to which halogen is attached.



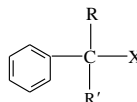
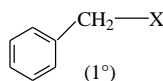
(b) Allylic halides

Here halogen is attached to a sp^3 - hybridized carbon next to carbon-carbon double bond.



(c) Benzylic halides

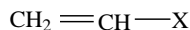
Here halogen is attached to a sp^3 - hybridized carbon next to an aromatic ring.



(2) Compounds containing sp^2 C-X bond

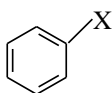
(a) Vinylic halides

Here halogen is attached to a sp^2 hybridised carbon atom of a carbon-carbon double bond.



(b) Aryl halides

Here halogen is attached to a sp^2 - hybridized carbon atom of a benzene ring.



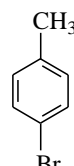
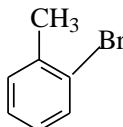
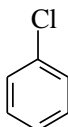
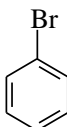
Nomenclature

In common or trivial system, monohalogen derivatives of alkanes are named as alkyl halides.

In IUPAC system, the monohalogen derivatives are named as haloalkanes. The prefixed fluoro, chloro, bromo and iodo are attached to the name of the longest carbon chain.

Compounds	Common Name	IUPAC Name
$\text{CH}_3 - \text{Cl}$	Methyl chloride	Chloromethane
$\text{CH}_3 - \text{CH}_2 - \text{Cl}$	Ethyl chloride	Chloro ethane
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{Cl}$	n-propyl chloride	1-chloropropane
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \\ \text{Cl} \end{array}$	Iso-propylchloride	2-chloropropane
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{Cl}$	n-butyl chloride	1-chlorobutane
$\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{CH}_3 \\ \\ \text{Cl} \end{array}$	sec - butylchloride	2-chlorobutane
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{Cl} \\ \\ \text{CH}_3 \end{array}$	Iso-butyl chloride	1-chloro-2-methyl propane
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{Cl} \\ \\ \text{CH}_3 \end{array}$	Tert-butyl chloride	2- chloro-2-methyl propane
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{Cl} \\ \\ \text{CH}_3 \end{array}$	Neo-Pentyl bromide	1-Bromo -2,2-dimethyl propane
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{Br} \\ \\ \text{CH}_3 \end{array}$	Vinyl chloride	Chloro ethene
$\text{CH}_2 = \text{CH} - \text{Cl}$	Allyl bromide	3-Bromo propene
$\text{CH}_2 = \text{CH} - \text{CH}_2 \text{ Br}$		

Haloarenes are named by adding the prefix halo (fluoro, chloro, bromo, iodo) before the name of the aromatic hydrocarbon. The relative positions of the substituents 1,2 ; 1,3 and 1,4 are indicated by the prefixes ortho (-o), meta (m-) and para (p-) respectively.

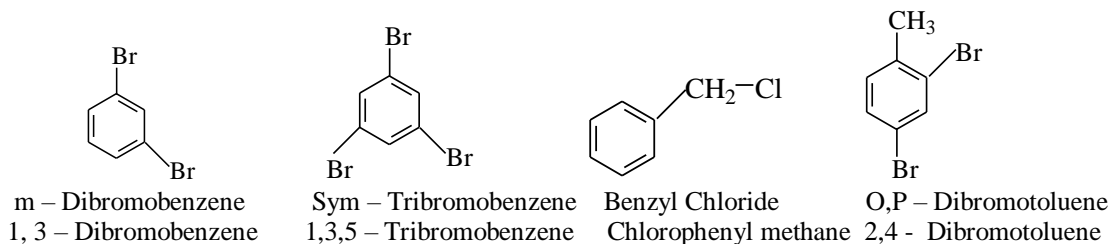


Common Name: Bromo benzene
IUPAC : Bromo Benzene

Chlorobenzene
Chlorobenzene

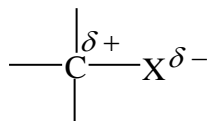
O - bromptoluene
2 - bromotoluene

P - bromotoluene
4 - bromotoluene



Nature of carbon-halogen bond

Halogen atoms are more electronegative than carbon. Therefore C—X bond is polar in nature. Carbon has a partial positive charge and halogen has a partial negative charge.



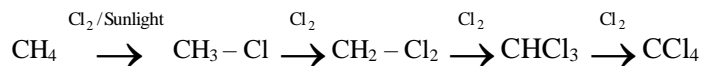
The bond strength decreases in the order
C—F > C—Cl > C—Br > C—I

Methods of preparation of Haloalkanes

Haloalkanes are generally prepared either from hydrocarbons or alcohols.

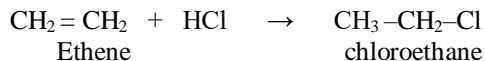
(i) From alkanes:

Halogens react with alkanes in the presence of UV-light to form haloalkanes. In this method generally polysubstituted halides are obtained, which is difficult to be separated. They can be separated by fractional distillation.

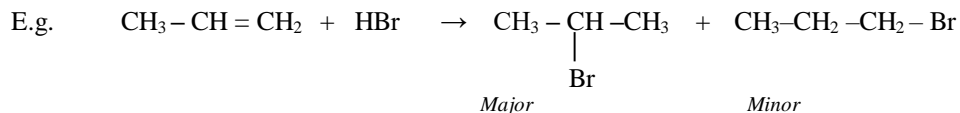


(ii) From alkenes

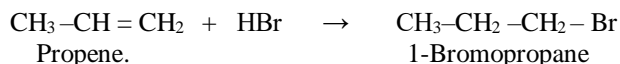
Alkyl halides can be prepared by the addition of hydrogen halides on alkenes.



But in the case of unsymmetrical alkenes addition take place according to **Markownikoff's rule**. This rule states that during the addition across unsymmetrical double bond, the negative part of the attacking reagent attaches itself to the carbon carrying lesser number of hydrogen atoms.



But when HBr is added to an unsymmetrical alkene, in the presence of organic peroxides such as benzoyl-peroxide (C₆H₅—CO—O—O—COC₆H₅), the reaction takes place against the markownikoff's rule. This is known as **Peroxide effect** or **Kharasch effect**

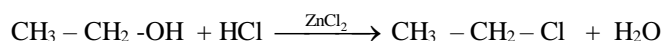


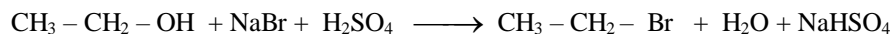
3) From Alcohols

This is the most widely used method for the preparation of alkyl halides. It can be done by the following methods.

(i) Reaction with hydrogen halides:

Alcohols can be converted into alkyl halides by treatment with halogen acids in the presence of dehydrating agents like anhydrous ZnCl₂ and H₂SO₄.





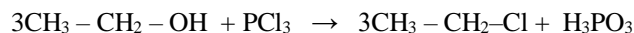
Alkyl iodides are obtained by heating alcohols with NaI or KI in 95% phosphoric acid.

The reactivity of alcohols is in the order

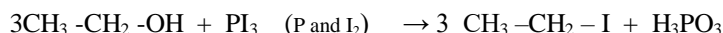
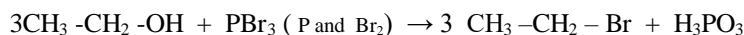
Tertiary > Secondary > Primary

(2) Reaction with phosphorus halides

Chloroalkanes can be prepared by the action of PCl_5 or PCl_3 on alcohols.

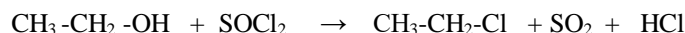


Bromoalkanes and iodoalkanes can be prepared by the action of PBr_3 and PI_3 respectively on alcohols. Since PBr_3 and PI_3 are unstable compounds, they are produced in situ by the action of red phosphorus on Br_2 or I_2



(3) By the action of thionyl chloride (SOCl_2)

Chloroalkanes can be prepared from alcohols by refluxing it with thionyl chloride in the presence of pyridine.

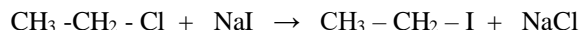


This method is preferred in the preparation of chloro alkanes since both the by-products (SO_2 and HCl) are gases and makes the purification of final products easy.

This method is called **Darzen's method**

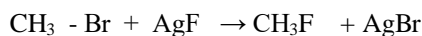
(4) By halide exchange reaction [Finkelstein Reaction]

This method is used for the preparation of iodo alkanes. Here chloro or bromo alkanes is heated with sodium iodide solution in acetone.



(5) Preparation of Alkyl fluorides [Swarts Reaction]

Fluoro alkanes are prepared by treating alkyl chloride with metallic fluorides such as Hg_2F_2 , AgF , SbF_3 etc.



(6) From silver salts of carboxylic acids

A solution of silver salt of an organic acid in CCl_4 on reaction with bromine produces bromoalkane. This reaction is called **Borodine Hunsdiecker reaction**

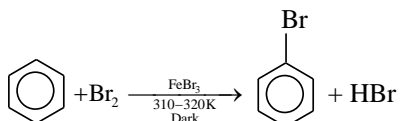
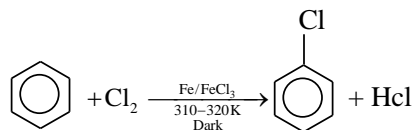


PREPARATION OF HALOARENES:

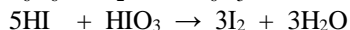
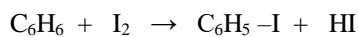
Haloarenes are usually prepared by the following methods.

(i) By direct halogenation

Chloroarenes and bromoarenes are prepared by direct chlorination or bromination of aromatic hydrocarbons in the presence of iron or iron halides as catalyst. These reactions are carried out in dark at ordinary temp:

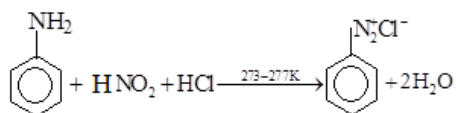
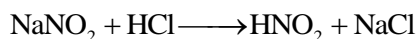


Fluoro-and iodo-compounds cannot be prepared by this method. With iodine this reaction is reversible. Since HI is a good reducing agent. So iodination is carried out in the presence of an oxidizing agent like HIO_3 or HNO_3 . This will oxidize the HF produced.



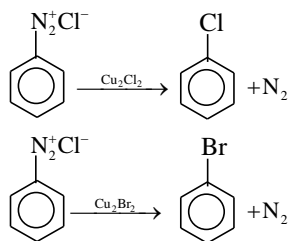
(ii) From Diazonium salts

When aromatic primary amines are heated with nitrous acid ($\text{NaNO}_2 + \text{HCl}$) at low temperature ($0^\circ - 4^\circ\text{C}$), diazonium salts are obtained.



This reaction is known as a diazotisation. The diazonium salts are unstable compounds.

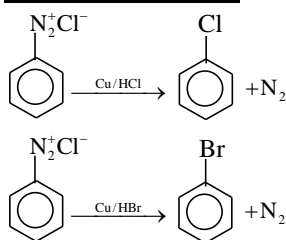
When this diazonium compound is treated with Cu_2Cl_2 or Cu_2Br_2 they are converted into the corresponding halide.



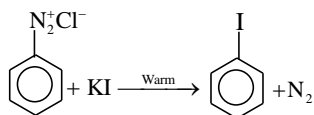
This reaction is known as Sandmeyer reaction

If instead of Cu_2Cl_2 and Cu_2Br_2 , *copper powder and HCl or HBr* is used, the reaction is called

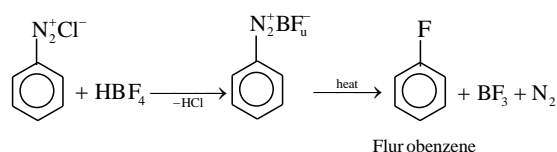
Gatterman's reaction



Iodoarenes are obtained by warming benzene diazonium salts with KI.



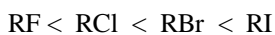
Fluoroarenes are obtained by the reaction of diazonium salt with fluoboric acid to produce diazonium tetra fluoroborate which on heating produces fluorobenzene.



This reaction is called Balz-Schiemann reaction.

Physical Properties:

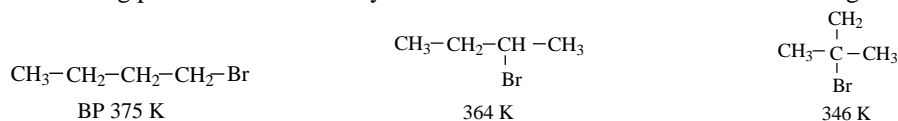
The melting points and boiling points of alkyl halides are several degrees higher than the parent alkanes. This is because the molecular masses of alkyl halides are higher than that of the corresponding alkanes. The boiling points of alkyl halides increase in the order.



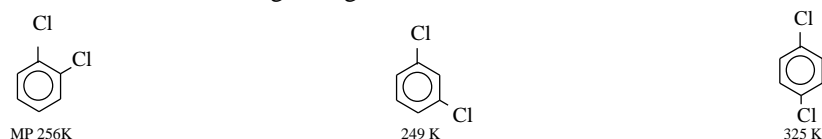
For same halogen, the B.P increases with increase in molecular mass.

Haloalkanes are polar molecules and strong dipole-dipole attractive interactions between the molecules also increase the boiling point.

The boiling points of isomeric alkyl halides decrease with increase in branching.



The boiling points of dihalobenzenes are nearly the same. But among haloarenes, the para isomer melts at about 70-100 degree higher than the ortho and meta isomer.



This is because the para isomer is more symmetrical and, therefore, can fit better in the crystal lattice of the solid.

Solubility:

Although polar in nature, alkyl halides and aryl halides are insoluble in water. This is because they are not able to form hydrogen bonds with water molecular or to break the hydrogen bonds already existing in water.

But they are soluble in organic solvents.

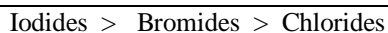
Density:

Alkyl chlorides are generally lighter than water whereas bromides and iodides are heavier. Their densities are in the order. Density increases with increase in carbon number.



Chemical Properties

Alkyl halides are highly reactive compounds. The reactivity is due to the presence of polar carbon-halogen bond in these molecules. The order of reactivity decreases as



This is because, most of the reactions of alkyl halides involve the cleavage of C-X bond. Now larger the bond dissociation energy of C-X bond, smaller is the reactivity. The bond dissociation energy decreases in the order $\text{C-Cl} > \text{C-Br} > \text{C-I}$

Hence the reactivity increases from chlorides to iodides.

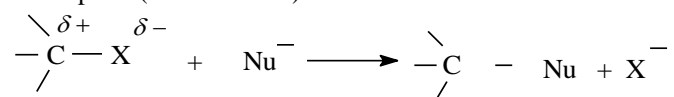
The chemical reactions of alkyl halides are:

- (i) Nucleophilic substitution reactions.
- (ii) Dehydrohalogenation
- (iii) Reaction with metals.
- (iv) Reduction.

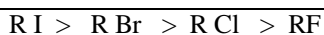
(i) Nucleophilic substitution reactions

In alkyl halides, the halogen is attached to the carbon atom. Since halogen is more electro negative than carbon, the carbon-halogen bond is polar in character (Dipole moment 2-2.2D)

Therefore the nucleophiles can attack on electron deficient carbon resulting in the displacement of weaker nucleophile (the halide ion)



The order of reactivity of alkyl halides is



Such reactions in which a strong nucleophile displaces a weaker nucleophile from the substrate are called nucleophilic substitution reactions (S_N reactions)

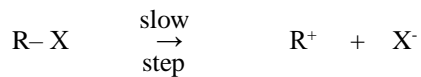
Mechanism of Nucleophilic substitution

The nucleophilic substitution can occur by two mechanisms – S_N 1 and S_N 2 mechanisms.

(i) S_N 1 Mechanism.

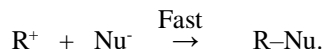
It occurs in two steps.

Step-1 : In the first step the alkyl halide undergoes heterolytic fission to produce a carbocation.



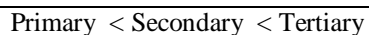
A carbocation is highly reactive species

Step II : The carbocation readily combines with the nucleophile to give the substituted product.



Step I being the slow step it is the rate determining step. Since only one reactant is present at this stage, the reaction is a first order reaction.

The order of reactivity of alkyl halide by S_N1 mechanism is

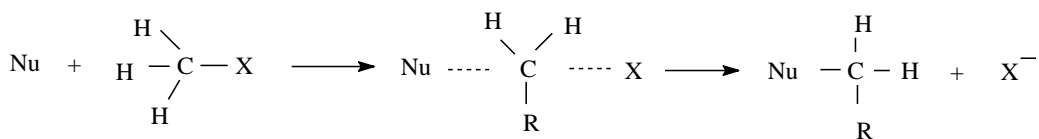


This is because the most stable carbocation is tertiary carbocation.

S_N1 mechanism is facilitated by Polar solvents such as water, alcohol etc. Such solvents promote the ionization step by stabilizing the ions by solvation.

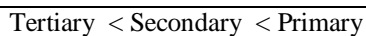
(II) S_N 2 mechanism

It occurs in one step. In this mechanism, the nucleophile, Nu⁻, attacks the partially positive carbon of the C-X bond from the backside of the C-X bond. The X⁻ departs simultaneously.



Here the reaction is of second order.

The order of reactivity of alkyl halide by S_N 2 mechanism is



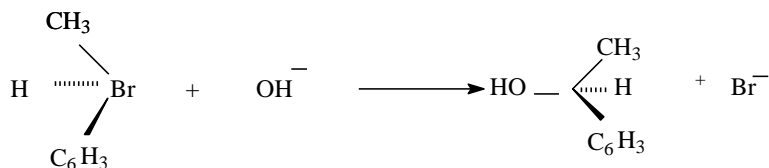
This is because in tertiary alkyl halide, the bulky alkyl groups in the transition state makes it unstable due to steric hindrance.

In S_N 2 mechanism, there is inversion in configuration as the attacking group approaches the molecule from the opposite side of the leaving group.

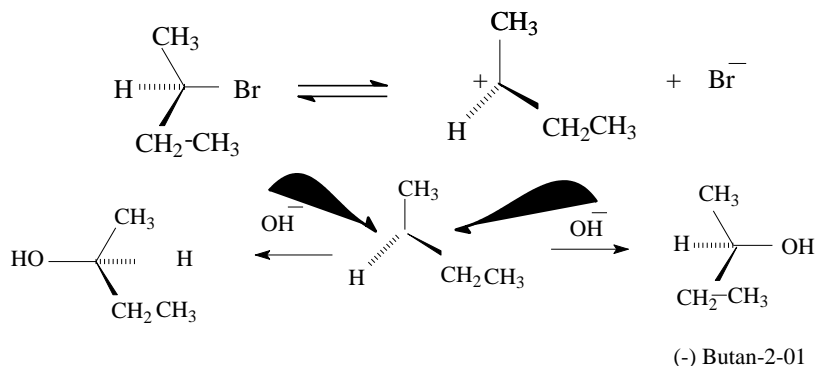
Thus primary alkyl halides react mainly by S_N 2 mechanism whereas tertiary alkyl halides react mainly by S_N 1 mechanism.

Stereochemistry of S_N1 and S_N2 mechanism

S_N2 reactions of optically active halides are accompanied by *inversion of configuration*. This is because the nucleophile is attached to the opposite side of the halogen which is removed. For example when (–) -2-bromooctane is allowed to react with NaOH, (+)-octane-2-ol is formed



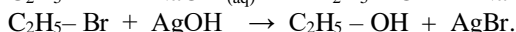
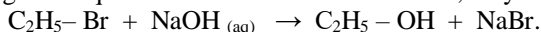
But $\text{S}_\text{N}1$ mechanism is accompanied by **racemisation**. Here the carbocation formed as intermediate being sp^2 hybridised is planar and achiral. The nucleophile may attack from either side resulting in a mixture of products- one having the same configuration and the other having opposite configuration. For example hydrolysis of optically active 2-bromobutane results in the formation of (\pm) -butan-2-ol.



Important nucleophilic substitution reactions are

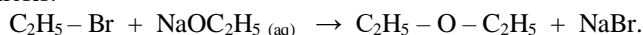
(a) Reaction with aqueous alkali or moist silver oxide [Formation of alcohols]

On boiling with aqueous alkali or moist silver oxide, alkyl halides give alcohols.



(b) Replacement by Alkoxy group: [formation of ethers] - Williamson's synthesis

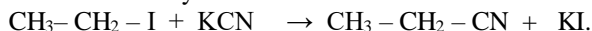
Alkyl halides on treatment with alcoholic sodium alkoxide form ethers. This reaction is known as Williamson's synthesis.



Ethers can also be prepared by heating alkyl halides with dry silver oxide. Ag_2O

(c) Replacement by cyanogroup [Formation of cyanides or nitriles]

Alkyl halides on treatment with alcoholic KCN solution, alkyl cyanides are formed as major product. A small amount of isocyanide is also formed.

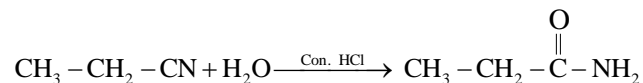


Alkyl cyanides can be converted into a number of compounds.

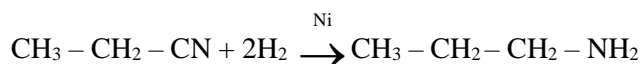
- (1) On complete hydrolysis with dil. HCl , acids are formed.



- (2) On partial hydrolysis with con. HCl or alkaline solution of H_2O_2 , amides are formed.



- (3) On catalytic reduction with H_2/Ni or Na/ethyl alcohol (Mendius reaction) give primary amines.



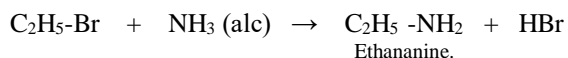
(d) Replacement with isocyanide group

Alkyl halides on treatment with alcoholic silver cyanide solution, alkyl isocyanides (carbylamine) are formed as major product. A small amount of alkyl cyanides is also formed.

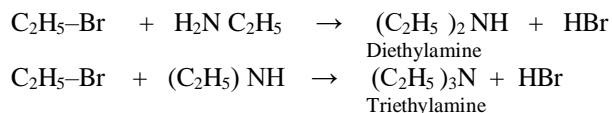


(e) **Replacement by Amino group [Formation of amines]**

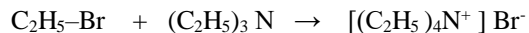
Alkyl halides when treated with alcoholic solution of ammonia under pressure, amines are formed.



If alkyl halides are in excess the hydrogen atoms of amino group are replaced by alkyl group to form secondary and tertiary amines.



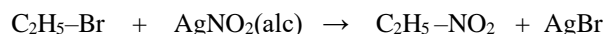
Tertiary amine further combine with another alkyl halide molecule to form quaternary ammonium salt.



This reaction is called **Hoffmann ammonolysis** of alkyl halides

(f) **Formation of Nitroalkane**

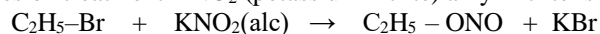
Alkyl halides on treatment with alcoholic silver nitrite (Ag-O-N=O), nitroalkane is formed.



This is because, the bond between Ag-O is covalent and the lone pair on nitrogen acts as attacking site for nucleophilic substitution.

(g) **Formation of Alkyl nitrites**

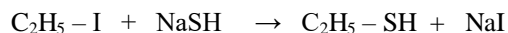
Alkyl halides on treatment KNO_2 (potassium nitrite) alkyl nitrite is formed.



This is because the bond between K-O is ionic in nature. Therefore the negative charge on oxygen serves as attacking site.

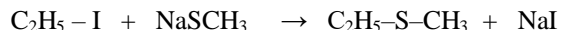
(h) **Replacement by-SH group [Formation of thiols or mercaptans]**

Alkyl halides on treatment with sodium hydrogen sulphide, mercaptans or thioalcohols are formed.



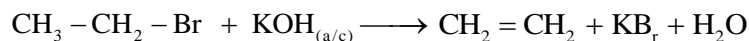
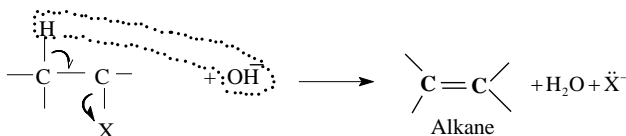
(i) **Formation of thioether**

Alkyl halides on treatment with sodium mercaptide, thioethers are formed.

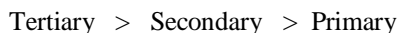


II Elimination reactions [Dehydrohalogenation]

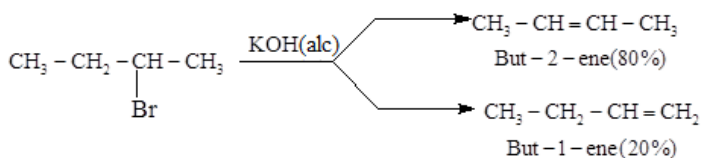
Alkyl halides on treatment with alcoholic solution of KOH undergo elimination reaction to form alkenes. These reactions are called β -elimination reactions, because the H atom present at β -position of the alkyl halide is removed.



The reactivity of alkyl halides towards elimination reaction is

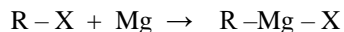


In the case of alkyl halides, which can eliminate hydrogen in more than one ways, the preferred alkenes is one which carries more number of alkyl groups attached to the doubly bounded carbon atoms. This rule is called **saytzeff's Rule**

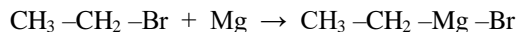


Reaction with magnesium

Alkyl halides form alkyl magnesium halides (***Grignard reagents***) when treated with magnesium in dry ether as solvent.



Grignard reagents are highly reactive compounds. They are used in the preparation of a large number of organic compounds.



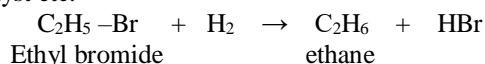
Reaction with sodium – Wurtz reaction

Alkyl halides react with metallic sodium in dry ether to form alkanes. This reaction is known as Wurtz reaction



Reduction

Alkyl halides can be reduced to alkanes by using suitable reducing agents like red P+HI, Zn+HCl, H₂ + catalyst etc.



Chemical Properties of Arylhalides

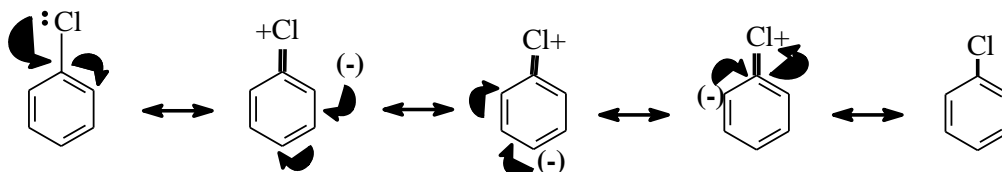
Haloarenes are less reactive than haloalkanes. This is due to the following reasons

(1) Hybridisation:

In haloalkanes, the carbon atom of C–X bond is sp³ hybridized. But in haloarenes the carbon atom is sp² hybridised. The sp² hybridized carbon has more S-character and can hold the electron pair of the bond more firmly than sp³ hybridised C-atom. So the bond cleavage in haloarene is more difficult and it is less reactive.

(2) Resonance effect:

In haloarenes, the electron pair of halogen atom is in conjugation with pi electrons of benzene ring. Thus haloarene is a resonance hybrid of the following structures.



In these resonance structures the C - X bond has partial double bond character so the cleavage of bond is more difficult and haloarenes are less reactive.

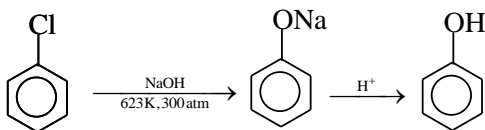
(3) Instability of phenyl cation

The phenyl cation formed as a result of self ionization will not be stabilized by resonance. Therefore S_N-1 mechanism is not possible.

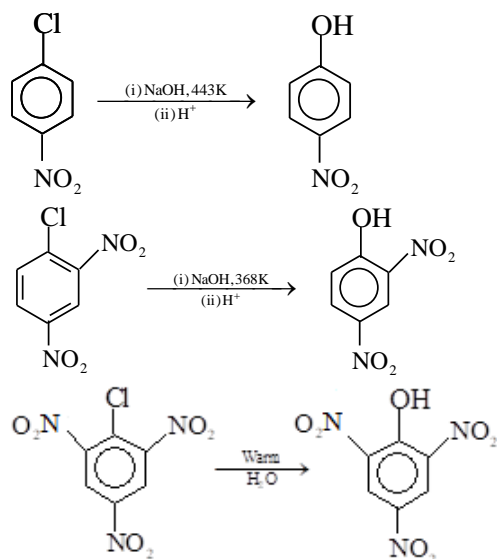
(4) Due to repulsion between electron rich nucleophile and electron rich benzene ring.

However under drastic conditions haloarenes undergo nucleophilic substitution reactions.

(i) On heating with aq. NaOH under pressure followed by acidification, phenol is formed.

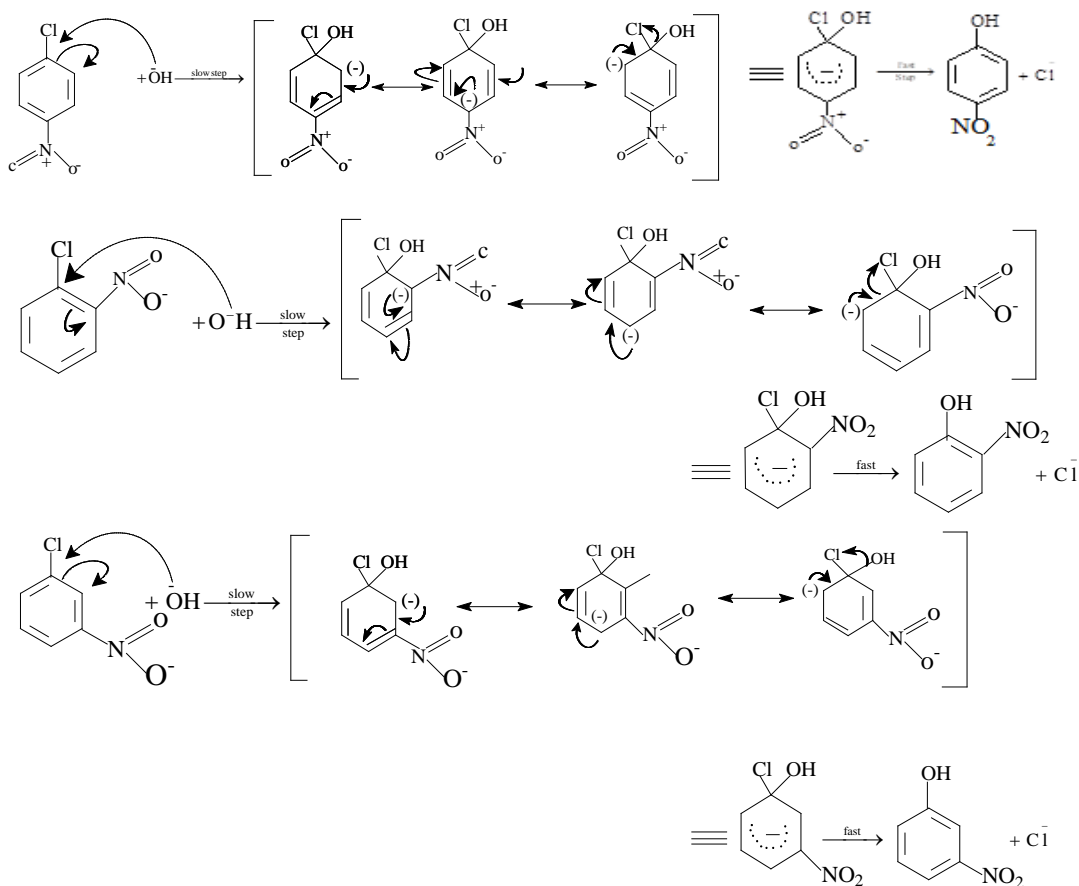


Presence of electron withdrawing group like nitro group, increases the reactivity towards nucleophilic substitution.



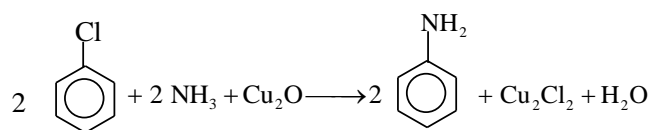
The effect is pronounced when $-NO_2$ group is introduced at ortho and para positions. No reactivity is observed when $-NO_2$ group is present at meta position.

The mechanism is



In the resonance structures the negative charge is present at ortho and para positions. The presence of $-NO_2$ group at ortho and para positions withdraws the electron density and facilitates the attack of the nucleophile. But in m-nitrobenzene, none of the resonating structures bear negative charge on carbon atom bearing the $-NO_2$ group. Therefore the $-NO_2$ group at meta position does not stabilize the negative charge and has no effect on reactivity.

(ii) On boiling with aq. ammonia in presence of Cu_2O and water pressure, aniline is formed.

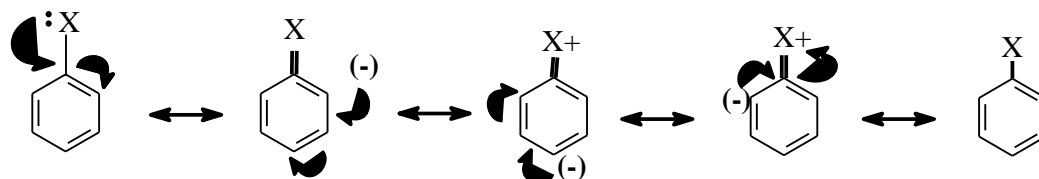


Electrophilic substitution Reactions

Haloarenes contain an electron rich benzene ring. Therefore haloarenes undergo electrophilic substitution reactions. **The substitution takes place at ortho and para with respect to the halogen atom.**

Halogen atom attached to benzene ring is slightly **deactivating** due to its $-\text{I}$ effect. Due to its $-\text{I}$ effect, halogen atom has some tendency to withdraw electron from benzene ring. Hence electrophilic substitution in haloarene occurs *slowly than those in benzene*.

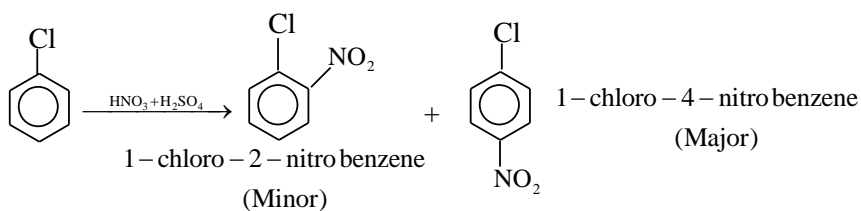
But the halogen atom present in benzene ring is ortho/para -directing. This is due to the existence of the following resonance structures.



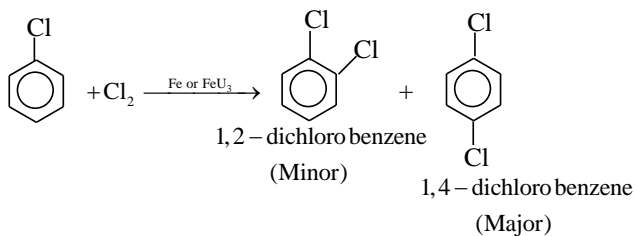
In these resonance structures electron density is more at ortho and para positions than meta position. Therefore the electrophile will attack only at o/p positions.

The inductive effect is stronger than resonance and causes net deactivation. Thus reactivity is controlled by stronger inductive effect and orientation is controlled by resonance

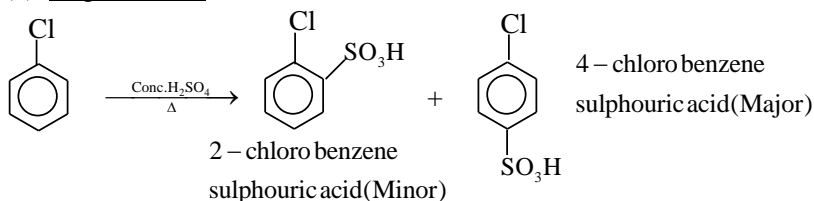
(1) Nitration : On nitration, chlorobenzene forms a mixture of 2-nitro chlorobenzene and 4-nitro chlorobenzene



(2) Halogenation : Halogenation takes place in the presence of iron or FeCl_3 or anhydrous AlCl_3 as a catalyst.

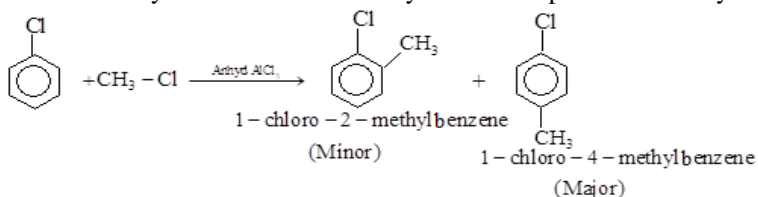


(3) Sulphonation :



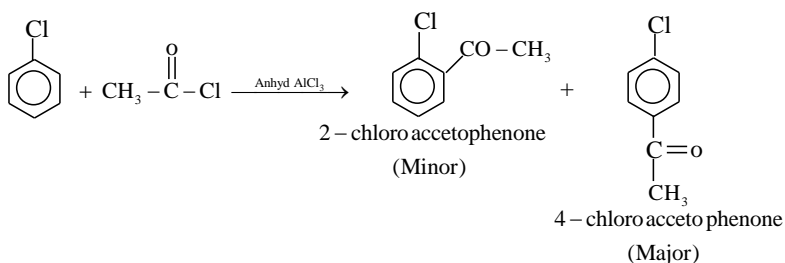
(4) Friedel Craft's Alkylation

When Aryl halides react with alkyl halides in presence of anhydrous AlCl_3 alkylation takes place.



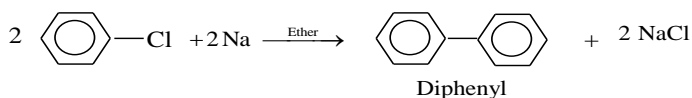
(5) Friedel Craft's Acylation

Acylation of haloarenes can be carried out with the reaction of acylchlorides in the presence of anhydrous AlCl_3

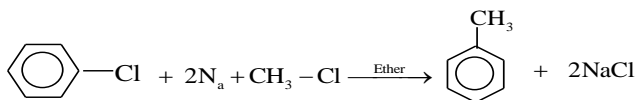


Reaction with sodium [Fittig reaction]

Haloarenes react with sodium in the presence of ether. During this reaction two phenyl rings unite. This reaction is called Fittig reaction.

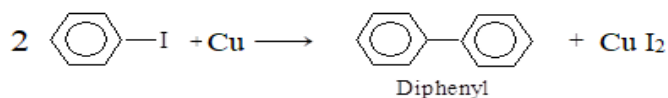


However, aryl halides when treated with haloalkane and sodium in dry ether undergo Wurtz Fittig reaction



Reaction with copper powder [Ulmann reaction]

Iodobenzene when heated with copper powder in a sealed tube gives diphenyl



This reaction is called Ulmann reaction

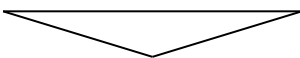
Distinction between alkyl and aryl halides

Halogen attached to saturated (sp^3 hybridized) carbon atom gives a precipitate of silver halides with alcoholic silver nitrate.

Eg: $\text{CH}_3-\text{CH}_2-\text{Cl}$, $\text{C}_6\text{H}_5-\text{CH}_2-\text{Cl}$, etc give precipitate of AgCl on treatment with AgNO_3 .

Halogen attached to unsaturated carbon atom (sp^2 or sp hybridised) does not give a precipitate with alcoholic AgNO_3 .

Eg: $\text{C}_6\text{H}_5-\text{Cl}$, $\text{CH}_2=\text{CH}-\text{Cl}$ etc will not give precipitate with AgNO_3 .



POLYHALOGEN COMPOUNDS

Organic compounds containing more than one halogen atom are called poly halogen compounds.

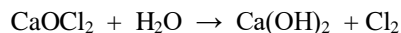
(1) Chloroform [Trichloro methane] CHCl₃

Chloroform is a sweet-smelling colourless liquid. (B.P. 334K). It is manufactured by chlorination of methane. The mixture so obtained is separated by fractional distillation.

Laboratory method of preparation

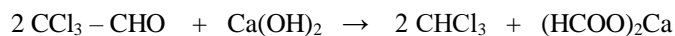
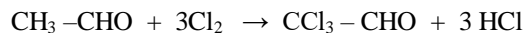
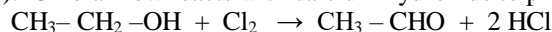
Chloroform can be prepared by the action of a paste of bleaching powder in water on ethyl alcohol or acetone.

Bleaching powder liberates Cl₂ and calcium hydroxide.



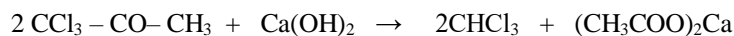
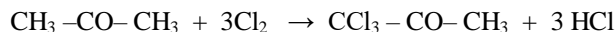
(i) From ethanol

Cl₂ oxidises ethyl alcohol to acetaldehyde. It is then chlorinated to trichloro acetaldehyde (*chloal*). Chloal now reacts with calcium hydroxide to produce chloroform and calcium formate



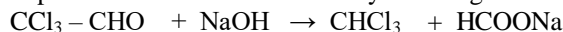
(ii) From Acetone

Acetone is chlorinated to trichloro acetone. It is then hydrolysed by calcium hydroxide to produce chloroform and calcium formate.



Preparation of pure chloroform

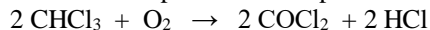
A pure sample of chloroform is obtained by distilling chloal with sodium hydroxide.



Chemical Properties.

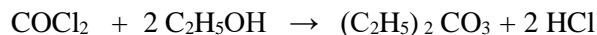
(i) Oxidation

When chloroform is exposed to air in presence of sunlight it is oxidized to poisonous phosgene.



In order to prevent this oxidation chloroform is stored in amber coloured bottles (to protect from light) and filled up to the neck.

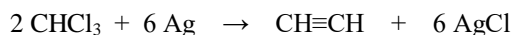
A little ethyl alcohol is also added into it in order to convert phosgene to non-poisonous ethyl carbonate



The formation of phosgene in a sample of chloroform can be tested by adding a small quantity of silver nitrate solution. A sample which contains phosgene will give a white precipitate (Due to the presence of HCl)

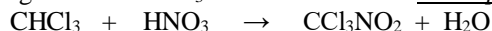
(ii) Reaction with silver

On warming with silver powder, chloroform is converted into ethyne. (acetylene)



(iii) Nitration

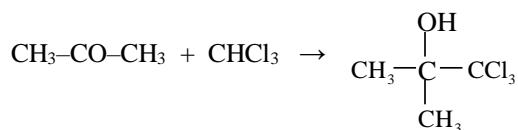
On heating with con.HNO₃ nitrochloroform or *chloropicrin* is formed.



Chloropicrin is used as an ***insecticide*** and a ***war gas***

(iv) Condensation with acetone

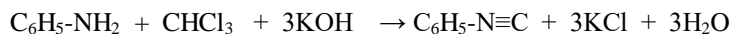
Chloroform condense with acetone to form *chloretone*



It is a colourless solid and is used as a hypnotic.

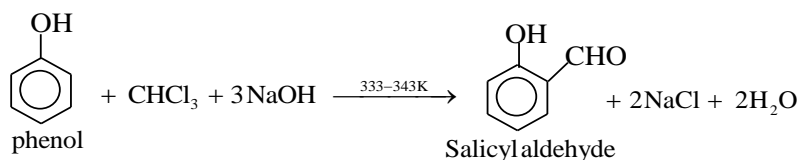
(v) Test for Chloroform [Isocyanide test] [Hofmann's carbyl amine reaction]

When chloroform is heated with ethanolic KOH and a primary amine (eg: ethylamine or aniline) an isocyanide is formed. It is readily detected by its disagreeing smell.



(vi) Reimer-Teimann reaction

Chloroform reacts with phenol and alc.KOH to form salicylaldehyde.



Uses of chloroform.

1. Chloroform is used as an anaesthetic.
2. It is used as a solvent for fats, alkaloids, iodine and varnishes.
3. It is widely used in the production of the Freon refrigerant R-22.
4. It is also used as a preservative for biological specimens.

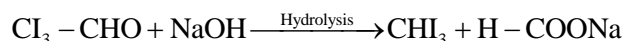
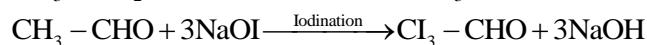
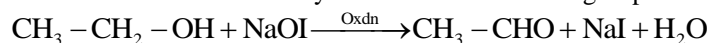
[Now **chloroform** is replaced by safer anaesthetic such as **ether**. Inhaling chloroform vapours depresses the central nervous system. Inhaling chloroform for short time can cause dizziness, fatigue and headache. Chronic chloroform exposure may cause damage to the liver and kidneys. In liver chloroform is metabolized to phosgene.]

II. Iodoform [Triiodomethane] CHI₃

Iodoform is prepared by treating ethanol or acetone with sodium hydroxide and iodine (or sodium carbonate and iodine). Sodium hypoiodite is formed during the reaction.



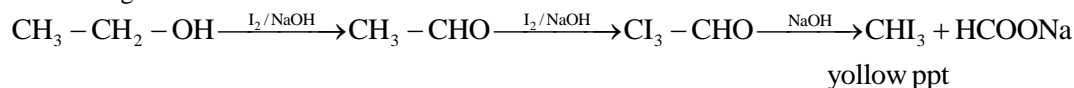
Iodoform is formed from ethyl alcohol in the following steps.



Iodoform

Iodoform test

It is a test to identify the presence of CH₃-CO- and CH₃-CH- groups in organic compounds. This test is performed by heating the substance with aqueous alkali and iodine solution. On warming the reaction mixture, a yellow precipitate of iodoform is formed. The reaction involves oxidation, halogenation and cleavage.

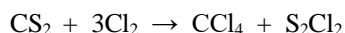


Uses of iodoform

Iodoform is used as an antiseptic. Antiseptic property of iodoform is due to the liberation of free iodine.

III. Carbon tetra chloride (CCl₄)

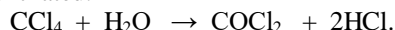
It is prepared by passing chlorine through carbon disulphide (CS₂) in presence of AlCl₃



It is also obtained by chlorination of methane in diffused sunlight.

Carbon tetrachloride is a colourless non-inflammable liquid. It is used as a fire extinguisher under the name pyrene.

CCl_4 react with steam to produce phosgene. So after extinguishing fire with pyrene, the room should be well ventilated.



Uses:

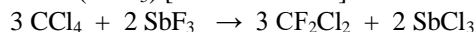
1. CCl_4 is used as an industrial solvent for oils, fats, resins, lacquers etc.
2. It is also used as a cleaning fluid in industry and home.
3. It is used as a fire extinguisher under the name pyrene
4. It is used in the manufacture refrigerants and propellants for aerosol cans.

[Exposure to CCl_4 causes liver cancer in humans. The common effects are dizziness, headache, nausea and vomiting. It causes permanent damage to nerve cells. Severe exposure of CCl_4 can lead to coma, unconsciousness or death. Exposure to CCl_4 can make heart beat irregular and may irritate the eyes on contact. When released in to the air, it depletes the ozone layer.]

IV. Freon [Dichlorodifluoro methane] [CF_2Cl_2]

Chlorofluorocarbon compounds of methane and ethane are collectively known as *freons*. They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases. Freon 12 [CF_2Cl_2] is the most common freon in industrial use.

Freon is prepared by the reaction of antimony trifluoride on carbon tetrachloride in presence of antimony pentachloride (SbCl_5) [Swarts reaction]



It is used as a refrigerant. Freon released into the atmosphere diffuses into the stratosphere and initiate radical chain reaction that can upset the natural ozone balance.

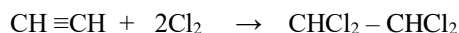
Dichloromethane (Methylene chloride) [CH_2Cl_2]

It is widely used as a solvent, as a paint remover, as a propellant in aerosols. It is also used as a metal cleaning and finishing solvent.

Methylene chloride is harmful to central nervous system. It causes intense burning and mild redness of the skin. Direct contact with eyes can burn the cornea.

V. Westron [Acetylene tetrachloride] [$\text{CHCl}_2 - \text{CHCl}_2$]

Westron is prepared by the action of chlorine on acetylene.



It is used as solvent for oils, paints, varnishes, rubber etc. It is highly toxic.

VI. Westrosol [trichloroethylene] [$\text{CHCl} = \text{CCl}_2$]

It is prepared by passing westron over heated BaCl_2 or $\text{Ba}(\text{OH})_2$

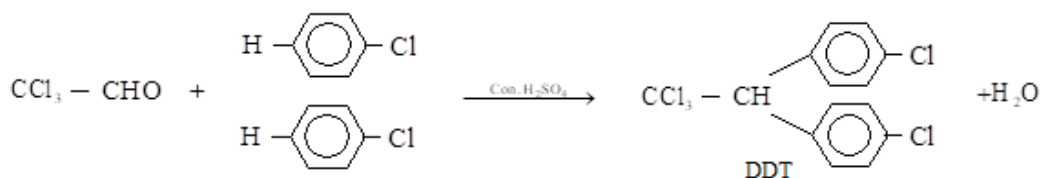


It is also used as solvent for oils, paints, varnishes, rubber etc. It is less toxic compared to westron.

VII. DDT [Dichloro diphenyl trichloro ethane]

1,1,1 – Trichloro-2,2-bis (4- chloro phenyl)ethane

DDT is prepared by heating chloral with chlorobenzene in presence of conc. H_2SO_4

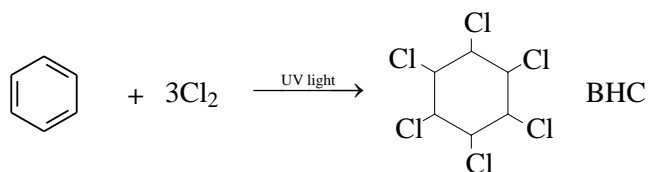


DDT is used as an *insecticide*.

But many species of insects develop resistance to DDT. It has high toxicity towards fish. It is not bio-gradable. DDT is not metabolized rapidly by animals and it is stored in the fatty tissues because it is fat soluble.

VIII. B.H.C [Benzene hexachloride]

BHC is prepared by passing chlorine through benzene in presence of UV light.



It is used as a powerful pesticide in agriculture. It is known by the trade name Gammexane. It is also known as 666 or Lindane