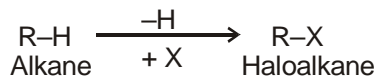


Halogen Derivatives of Alkanes

1. HALOGEN DERIVATIVES OF ALKANES

- Halogen derivatives of alkanes are formed by substitution of one or more hydrogen atoms of an alkane by halogen (F, Cl, Br or I).



(Halogen atom is normally represented by X)

- Halogen derivatives of Alkanes are divided into mono di, tri, etc. Substitution products according to the number of halogen atoms in the molecule.

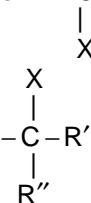
1.1 MONOHALO ALKANES

- (i) These are halogen derivatives of alkanes having general formula $C_nH_{2n+1}X$. where X = F, Cl, Br and I.
(ii) Monohalo alkanes are of three types :

(a) **Primary alkyl halides** in which halo group is present on primary carbon atom, i.e. $R-CH_2-X$

(b) **Secondary alkyl halides** in which halo group is present on secondary carbon atom, i.e. $R-CH(X)-R'$

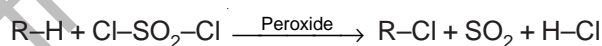
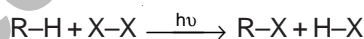
(c) **Tertiary alkyl halides** in which halo group is present on tertiary carbon atom, i.e. $R-C(X)(R')R''$



➤ Methods of Preparation of Alkyl Halide

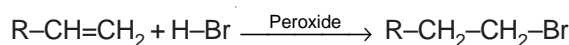
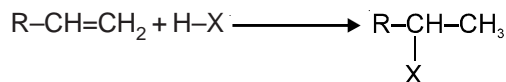
(a) By Halogenation of Alkanes

Halogenation of alkanes takes place by free radical mechanism.



(b) By Hydrohalogenation of Alkenes

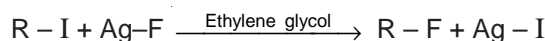
Alkyl halides are formed by addition of hydrogen halide on alkenes according to **Markownikoff's rule**.



(c) By halogen exchange in alkyl Halides :

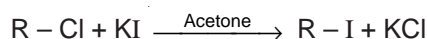
(i) By Silver Halide :

This reaction is called **Swart reaction**.



(ii) By Sodium or Potassium Halide :

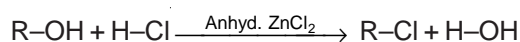
This reaction is called **Finkelstein reaction**.



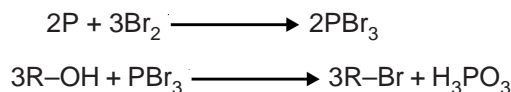
(d) **From Alkanols**

(i) **By Conc. HCl :**

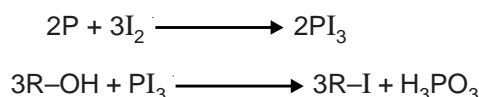
This is called **Grove's method**.



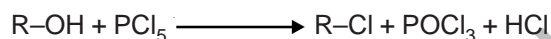
(ii) **By Red Phosphorus and Bromine :**



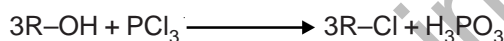
(iii) **By Red Phosphorus and Iodine :**



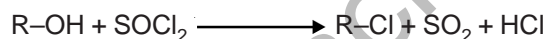
(iv) **By Phosphorus pentachloride :**



(v) **By Phosphorus trichloride :**



(vi) **By Thionyl chloride :**

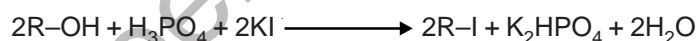


The above reaction is performed in the presence of pyridine. Called **Darzens reaction**.

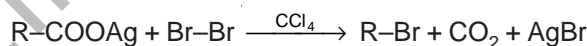
(vii) **From KBr and Conc. H₂SO₄ :**



(viii) **From KI and H₃PO₄ :**



(e) **From Alkanoic Acids :**



It is called **Hunsdiecker reaction**.

(f) **From Alkylamines :**

Alkyl chlorides are formed by the reaction of **Tilden's reagent** or **Nitrosyl chloride (NOCl)** on alkylamines.



➤ **Physical Properties**

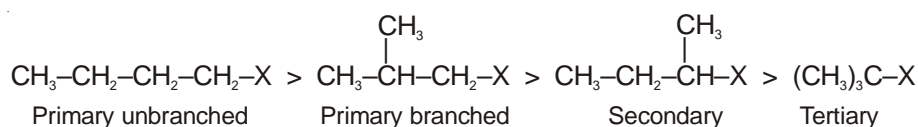
- (i) CH₃F, CH₃Cl, CH₃Br, C₂H₅F and C₂H₅Cl are found in gaseous state at room temperature.
- (ii) Alkyl halides are normally sweet-smelling gases and liquids, whereas odourless in solid state.
- (iii) All alkyl halides are insoluble in water.

(iv) Boiling points of alkyl halides change in the following order.

(a) On having same alkyl group



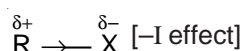
(b) On having same halogen atom



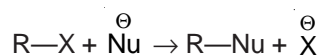
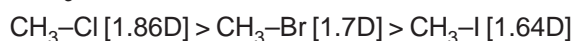
➤ REACTIONS

1. Nucleophilic substitution reaction [S_N] :

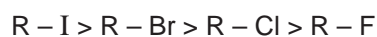
Bond polarity :



Order of dipole moment [CH₃X] :



In this reaction reactivity order is as follows :

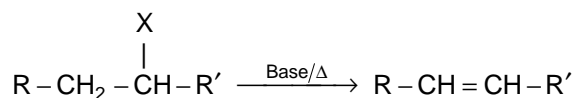


➤ R-X REACTION

Reagent	Product
Na/dry ether	R-R
KOH (aq.)	ROH
Ag ₂ O (moist)	ROH
NaI	RI
NaOR	ROR
R'COOAg	R'COOR
Ag ₂ O (dry)	ROR
KCN	RCN
AgCN	RN ≡ C
R'C ≡ CNa	R'C ≡ CR
KNO ₂	RONO
AgNO ₂	RNO ₂
Na ₂ SO ₃	RSO ₃ Na
NaSR'	RSR'
Na ₂ S	R ₂ S
KSH	RSH
NH ₃	RNH ₂
RNH ₂	R ₂ NH
R ₂ NH	R ₃ N
R ₃ N	R ₄ N ⁺ X ⁻

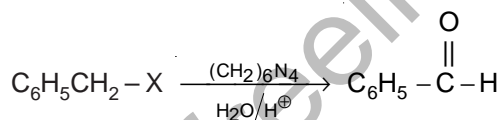
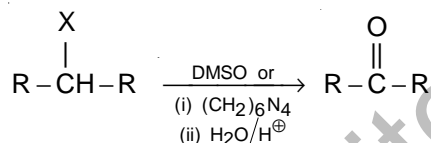
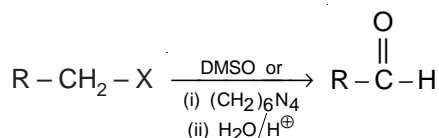
2. β -Elimination Reaction

Dehydrohalogenation : Alkyl halides give β -elimination reaction in the presence of strong base such as alc. KOH/ Δ , alc. NaOH/ Δ , $\text{RONa}^\ominus/\text{Ethanol}$, Δ , NaH/ Δ , NaNH_2/Δ



3. Oxidation reaction

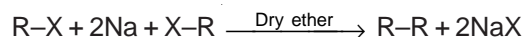
- (i) Only primary and secondary alkyl halides undergo oxidation. Tertiary alkyl halide does not undergo oxidation.
- (ii) Primary alkyl halides give aldehyde whereas secondary alkyl halides give ketone in this reaction.
- (iii) Oxidising agent is either :
 - (a) Dimethyl sulphoxide or
 - (b) Reaction with $(\text{CH}_2)_6\text{N}_4$ followed by hydrolysis.
- (iv) Reactivity \propto number of α -hydrogens.



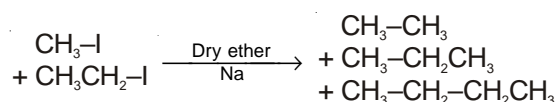
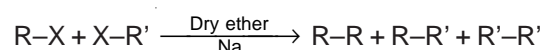
- Note :**
- (1) Oxidation of Benzyl halides by $(\text{CH}_2)_6\text{N}_4$ is known as **sommelet aldehyde synthesis**.
 - (2) Oxidation of alkyl halide with DMSO is known as **swern oxidation**.

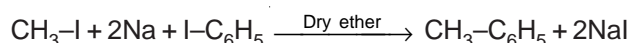
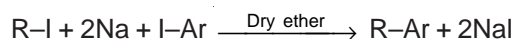
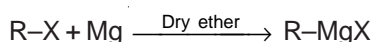
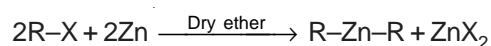
4. Coupling Reactions

- (A) **By Wurtz Reaction :** An alkane having even number of carbon atoms. This is called **Wurtz synthesis or Wurtz Reaction**.



Alkane having odd number of carbon atoms can be obtained by mixed **Wurtz synthesis**.



(B) By Wurtz-Fitting Reaction

5. Reaction with Metals
Synthesis of Grignard's Reagents

Synthesis of Frankland's Reagents

Synthesis of Tetraalkyllead

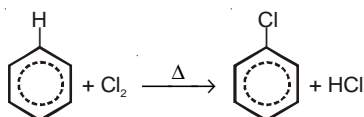

Tetraethyllead and tetramethyllead are high quality antiknock compounds.

➤ Uses of Alkyl Halides

- (i) Alkyl halides are used as **weak refrigerants**, but more suitable **freons** are now being used in place of alkyl halides.
- (ii) Synthesis of **detergents** is carried out from alkyl halides by Strecker's reaction.
- (iii) Synthesis of **antiknock compounds**.
- (iv) Alkyl halides, especially alkyl bromides and alkyl iodides are used for the synthesis of other organic compounds of almost all classes, in laboratory and in industry.
- (v) Alkyl halides are generally used as starting substances for the manufacture of **alcohols**, **ethers** and **esters**.
- (vii) Synthesis of important organometallic compounds, like Grignard's reagents, Frankland's reagents, etc., is carried out from alkyl halides.

1.2 HALOBENZENE
1. Chlorobenzene, C₆H₅Cl
1.1 Methods of Preparation :
[1] Chlorination of Benzene :

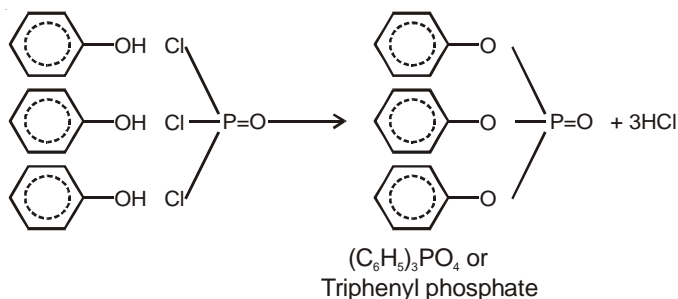
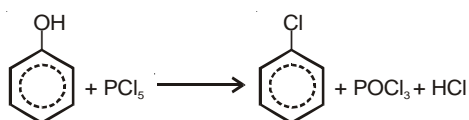
Chlorobenzene is obtained on reacting benzene with chlorine in the presence of a halogen carrier. Lewis acids (AlCl₃, FeBr₃, BF₃, etc) some elements (iron powder, iodine, etc.) or some tertiary amine bases (pyridine) can be used as halogen carriers.



Bromobenzene is obtained if bromine is used in place of chlorine in the above reaction.

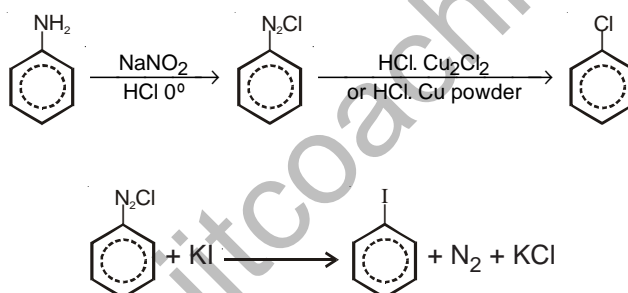
[2] Dehydroxylative Chlorination of Phenol :

Chlorobenzene is formed on reacting phenol with phosphorus pentachloride. Yields of chlorobenzene are low due to formation of triphenyl phosphate (C₆H₅)₃PO₄ as the major product.

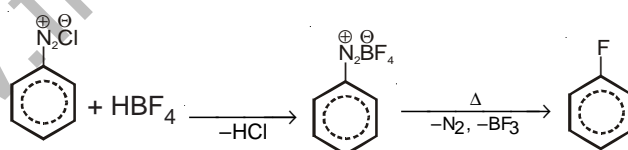


[3] Deaminative Chlorination of Aniline :

Chlorobenzene can be obtained by Sandmeyer's reaction (Cuprous chloride, in the presence of Cu₂Cl₂) or Gattermann reaction (in the presence of copper powder) of the benzenediazonium chloride salt obtained by diazotisation (reaction of aqueous NaNO₂ and aqueous HCl at 0° C) of aniline.

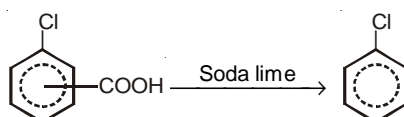


For the synthesis of fluorebenzene, benzenediazonium fluoroborate is heated. This is called Balz–Schiemann reaction.



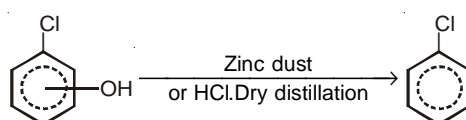
[4] Decarboxylation of Chlorobenzoic Acids :

Dry distillation of o-, m- or p-chlorobenzoic acid with soda lime gives chlorobenzene by **decarboxylation**.



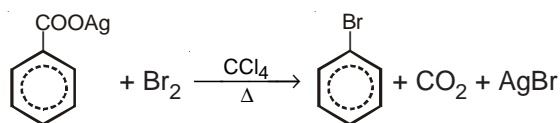
[5] Dehydroxylation of Chlorophenols :

On dry distillation of o-, m- or p-chlorophenol with zinc dust, chlorobenzene is obtained by **dehydroxylation**.



[6] Decarboxylative Bromination of Benzoic Acid :

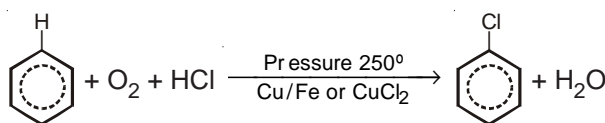
For the preparation of bromobenzene, silver salt of benzoic acid is heated with bromine in CCl_4 solution. This is called **Borodine–Hunsdiecker reaction**.



Flurobenzene, chlorobenzene and iodobenzene cannot be prepared by the above method.

[7] Raschig Process :

Manufacture of chlorobenzene on large scale is carried out by **Raschig process**. In this method, the mixture of benzene vapour, HCl gas and the oxygen (air) is passed over heated copper-iron catalyst or CuCl_2 catalyst with pressure at 250°C .


1.2 Physical Properties :

Chlorobenzene is a colourless, volatile, inflammable, liquid (boiling point = 132°) having faint smell resembling almonds. It is a little bit poisonous (less than benzene), insoluble in water and soluble in organic solvents.

1.3 Reactions :

[A] Reactions due to chlorine atom.

[B] Reactions due to Benzene ring.

1.3.1 Reactions Due to Chlorine Atom :

Reactivity of chlorobenzene towards nucleophilic substitution reactions is very less. This is mainly due to

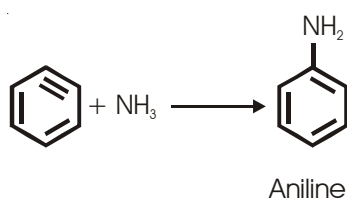
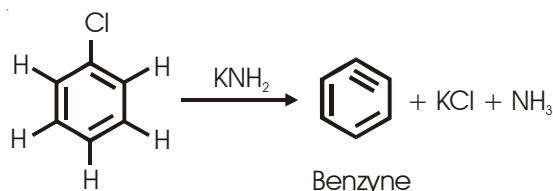
(i) Greater 'pi' electron density on ring carbons which repels the attacking nucleophile.

(ii) Chlorine bearing carbon of chlorobenzene is sp^2 hybridised and hence the polarity of $\text{C} - \text{Cl}$ bond in chlorobenzene is less than that of $\text{C} - \text{Cl}$ bond in ethyl chloride.

The reactivity of chlorobenzene increases when $-\text{M}$ or $-\text{I}$ effect causing groups are bonded at ortho or para positions of chlorobenzene. These groups decrease pi electron density on the ring and then nucleophile can attack easily on chloro benzene.

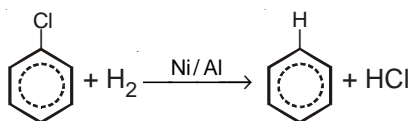
Thus is more reactive than towards nucleophilic substitution.

Nucleophilic substitution in chlorobenzene takes place by elimination-addition mechanism. In this reaction **Benzyne** is formed as an intermediate.



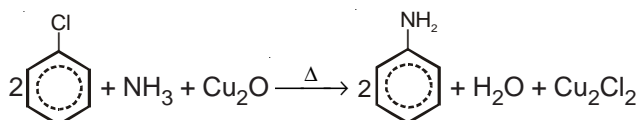
1. **Reduction or Dechlorination :**

Benzene is formed on reduction of chlorobenzene by nickel-aluminium alloy in the presence of small amounts of a base.



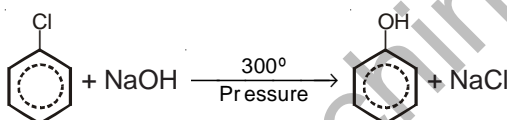
2. **Dechlorinative Amination :**

On heating with ammonia in the presence of cuprous oxide, aniline is formed.

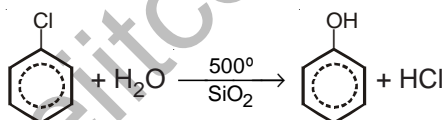


3. **Dechlorinative Hydroxylation :**

[a] By Dow process : Phenol is formed on heating chlorobenzene with caustic soda (NaOH) or washing soda (Na_2CO_3) solution at a high temperature (300°) under pressure in the presence of a copper salt. This method is used for the manufacture of phenol on large scale and is known as **Dow process**.

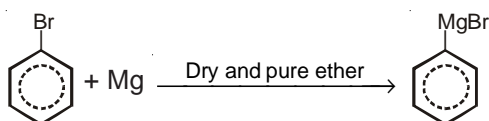


[b] By steam : On passing a mixture of chlorobenzene and steam through heated silica at 500° , phenol is formed.



4. **With Magnesium Metal :**

In order to obtain high yields of phenylmagnesium halide, iodobenzene (or bromobenzene) is reacted with magnesium in dry and pure ether. Fluorobenzene and chlorobenzene react very slowly. Therefore, they are practically not suitable for preparing a Grignard's reagent.

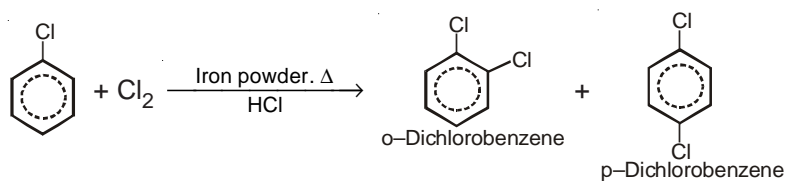


1.3.2 **Reactions Due to Benzene Ring :**

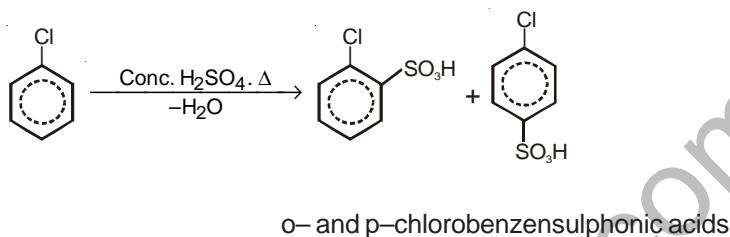
[i] Electrophilic Substitution or S_E Reactions :

Due to strong negative inductive effect ($-I$) of chloro substituent of chlorobenzene, it decreases electron density in benzene ring. As a result, the attacking electrophile is very weakly attracted by the benzene ring. Therefore, its electrophilic substitution occurs with slow rate as compared to unsubstituted benzene. Thus, chloro substituent deactivates the benzene ring. Due to the presence of nonbonded electron pair on chlorine. It is $o-$ and $p-$ directing by positive mesomeric ($+M$) effect. Thus chlorine atom directly bonded to benzene ring gives mainly $o-$ and $p-$ S_E products on electrophilic substitution.

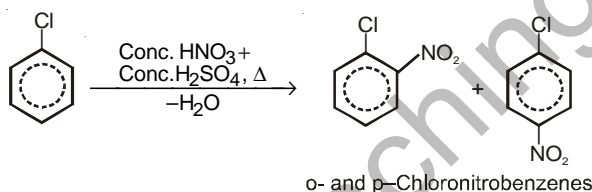
5. Halogenation :



6. Sulphonation :



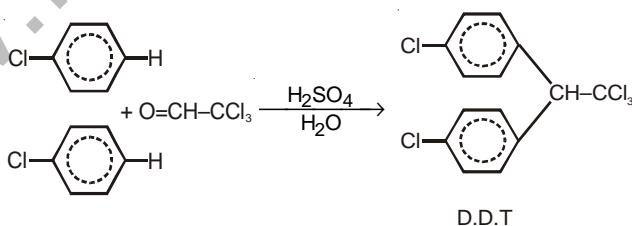
7. Nitration :



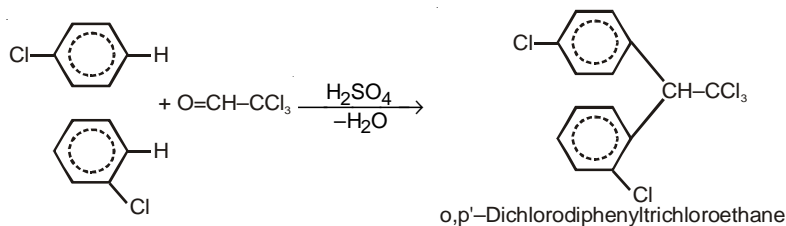
[ii] Condensation Reaction :

8. Bimolecular Condensation with Chloral :

On heating mixture of chlorobenzene and chloral hydrate in the presence of small amount of concentrated sulphuric acid, p, p'-dichlorodiphenyltrichloroethane, whose abbreviated name is **D.D.T**. It is a strong germicide and its IUPAC name is 1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane.



In the above reaction o, p'-dichloro isomer is also formed in minor amount (about 25%) as a by-product.

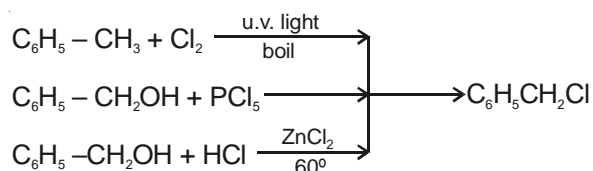


1.4 Uses :

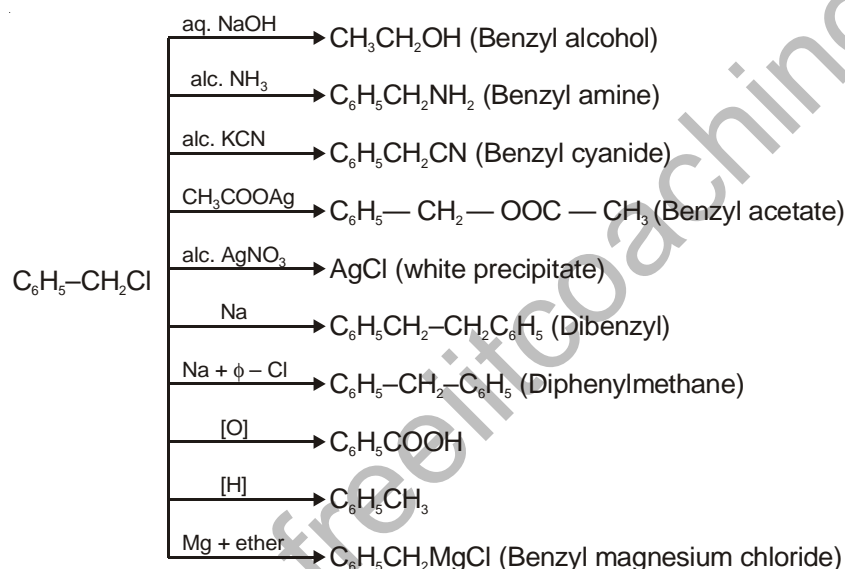
- [1] In the manufacture of strong germicide, D.D.T.
- [2] In the manufacture of many medicines and compounds (phenol, aniline, alkylbenzenes, dichlorobenzenes, phenylmagnesium halides, etc.) and as intermediate in several reactions.
- [3] As a solvent.

2. Benzyl chloride [C₆H₅CH₂Cl]

2.1 Preparation :



2.2 Chemical Properties :



2.3 Uses :

- Chlorobenzene is used in the manufacture of phenols, aniline.
- Chlorobenzene is used as a solvent.
- In the manufacture of DDT, used as an insecticide.
- Benzyl chloride is used for the introduction of benzyl group in organic compounds.
- As a starting material in the manufacture of benzyl alcohol, benzylamine and benzaldehyde.

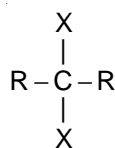
1.3 DIHALOALKANES

Dihalides are classified as :

- (a) Gem dihalides (b) Vicinal dihalides (c) α, ω-dihalides

(a) **Gem dihalides** : Dihalides having two halo groups on same carbon atom is known as gem dihalide

eg. $R-CH_2-CHX_2$ Terminal gem dihalide



Non-terminal gem dihalide

(b) **Vicinal dihalides** : Vicinal dihalides contains two halogen atoms on adjacent carbon atom. i.e vicinal position.

eg. $R-\overset{\overset{X}{|}}{CH}-\overset{\overset{X}{|}}{CH}-R$ vicinal positions

(c) **α, ω -dihalides** : They have two halogens on first and last carbon atoms.

eg. $(CH_2)_n$ $\begin{array}{l} \text{CH}_2 - Br \\ \text{CH}_2 - Br \end{array}$

➤ **General Methods of Preparation :**

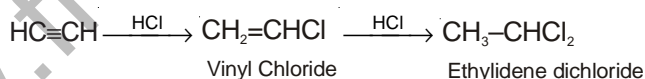
1. By halogenation of Alkenes :

vic-Dihalides are formed by electrophilic addition of halogens on alkenes.

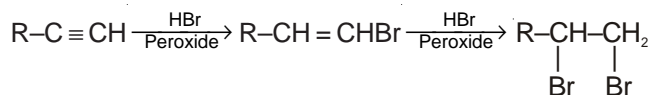


2. By Hydrohalogenation of Alkynes :

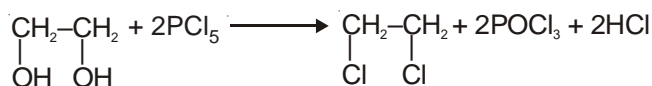
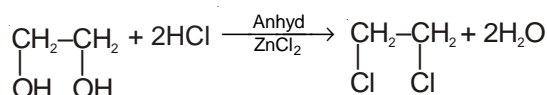
gem-Dihalides are formed by electrophilic addition of halogen acids on alkynes.



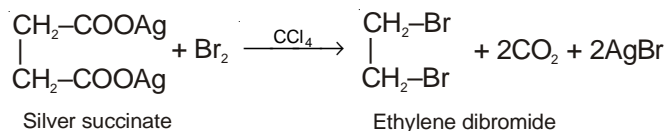
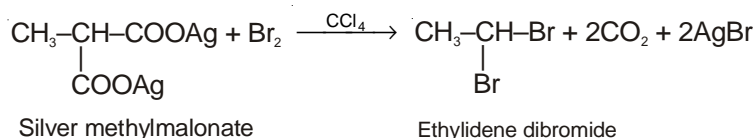
vic-Dibromide is formed by addition of HBr in the presence of a peroxide.



3. By the Action of Halogen Acids on Glycols :



4. By Hunsdiecker Reaction of Dicarboxylic acids :

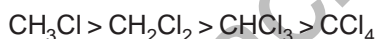


5. By Reaction of PCl_5 on Carbonyl Compounds : Gem dichlorides are obtained.



➤ **Physical Properties of Dihaloalkanes**

- (i) They all are colourless
- (ii) CH_2F_2 is a gas at room temperature.
- (iii) They are heavier than water, insoluble in water and soluble in nonpolar solvents.
- (iv) Reactivity of alkyl halide

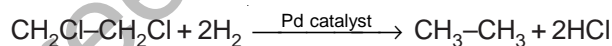


- (v) Reactivity of *vic*-dihaloalkanes is more than that of *gem*-dihaloalkanes.

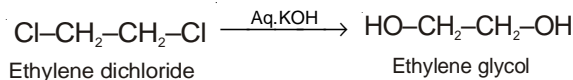
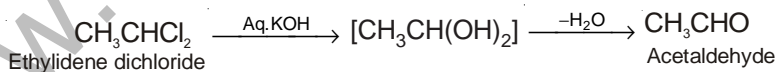


➤ **Reactions**

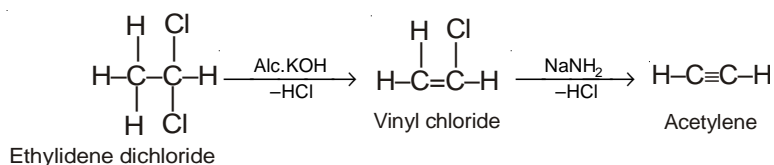
1. Reduction : Both on reduction form alkanes.



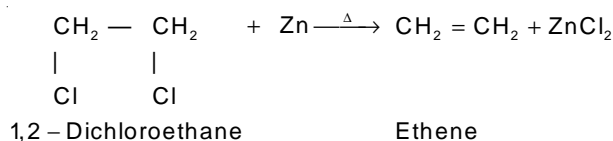
2. Hydrolysis



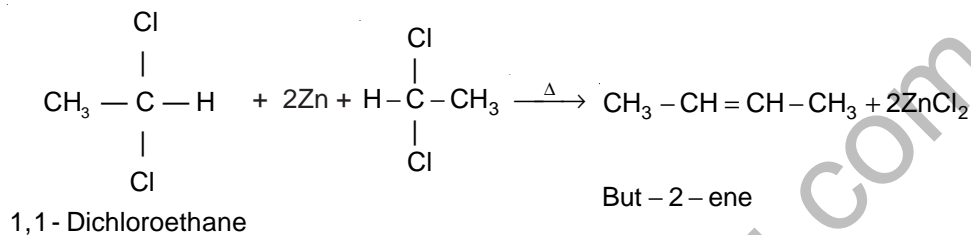
3. Dehydrohalogenation : Both on dehydrohalogenation form alkynes containing same number of carbon.



4. Reaction with Zn : Vicinal dihalides on reaction with zinc metal form alkenes containing same number of carbons.



Geminal dihalides on reaction with zinc metal form alkene containing double the number of carbon atoms.

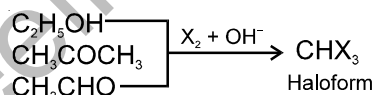


➤ **Uses of Dihaloalkanes**

1. As **solvents** for non-polar compounds.
2. As **fumigants** for grains and fruits.
3. Ethylene dibromide is used to remove lead from gasoline containing tetraethyllead.

1.4 TRIHALOALKANES : HALOFORM : CHX₃

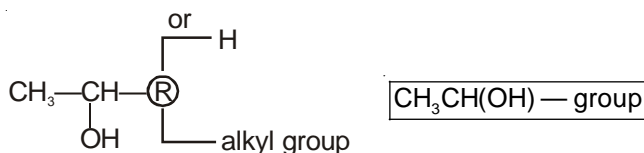
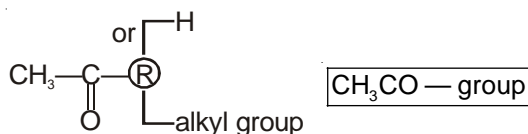
➤ **Preparation of Haloform**



* The following compound give haloform reaction.

* Acetaldehyde, all methyl ketones, acetone, ethylalcohol, all 2-alkanols etc.

When the following compounds are heated with alkali and halogen haloform is obtained.



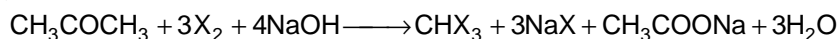
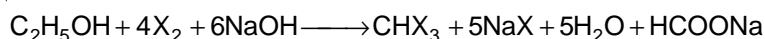
Acetone (CH₃-CO-CH₃)

Butanone (CH₃-CO-CH₂-CH₃)

2-Pentanone (CH₃-CO-CH₂-CH₂-CH₃)

3-Methylbutanone {CH₃-CO-CH(CH₃)₂}

➤ **Haloform Reaction**



(I) Chloroform : CHCl₃

➤ **Preparation of Chloroform**

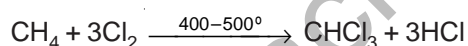
1. Laboratory Methods – Chloroform Reaction

On heating ethyl alcohol with bleaching powder, the reaction occurs in the followings steps :

- (i) $CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + 2Cl$
- (ii) $CH_3CH_2OH + 2Cl \rightarrow CH_3CHO + 2HCl$
- (iii) $CH_3CHO + 6Cl \rightarrow \underset{\text{Chloral}}{CCl_3CHO} + 3HCl$
- (iv) $2CCl_3CHO + Ca(OH)_2 \rightarrow 2CHCl_3 + (HCOO)_2Ca$

2. Industrial Methods :

(i) By Chlorination of Methane :



(ii) By Reduction of Carbon tetrachloride :



3. Methods of Preparation of Pure Chloroform :



➤ **Physical Properties**

Chloroform is a colourless sweet-smelling volatile and nonflammable liquid, which is immiscible with water and heavier than water. It is miscible with organic liquids, like alcohol, ether, etc., and is a very good solvent for non-polar compounds. Its boiling point is 61°.

➤ **Reaction**

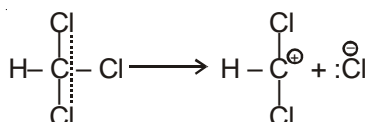
A. Due to Breaking of Carbon-Hydrogen Bond.

(i) By Heterolysis (In the presence of caustic alkali)

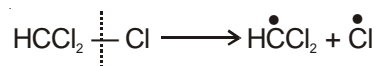
(ii) By Homolysis (At high temperature)

B. Due to Breaking of Carbon-Chlorine Bond

(i) In the presence of a Lewis acid (Heterolysis)

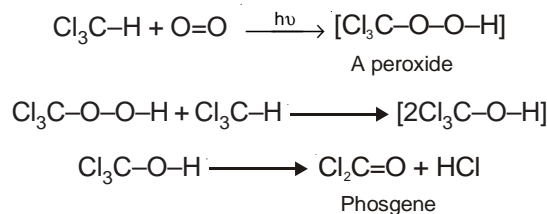


(ii) At high temperature (Homolysis)



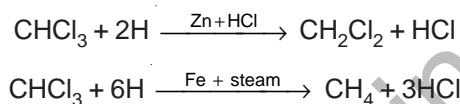
1. Oxidation :

Chloroform undergoes oxidation to form carbonyl chloride (phosgene) by oxygen on keeping it in contact with air in the presence of light

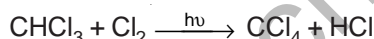


Phosgene (COCl_2) is a highly poisonous compound. This is the reason why the sample of chloroform exposed to air and light is not used as an anaesthetic.

2. Reduction :



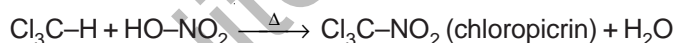
3. Chlorination :



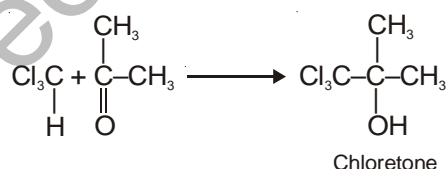
4. Dechlorination :



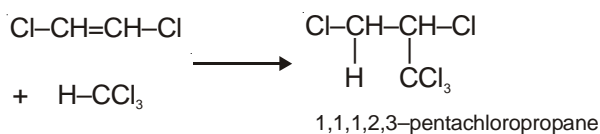
5. Nitration :



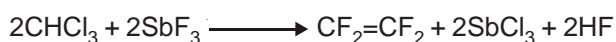
6. Addition on Acetone :



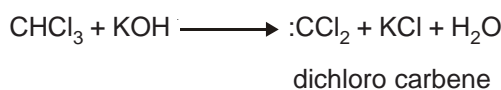
7. Addition on Acetylene dichloride :



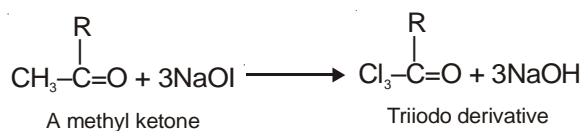
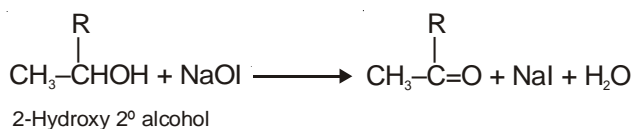
8. With Antimony trifluoride :



9. Hofmann Carbylamine Reaction :



It is called **isocyanide test**.

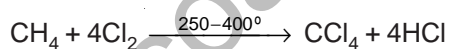


1.5 Tetrahaloalkane

Carbontetrachloride, Tetrachloromethane, CCl_4

➤ PREPARATION :

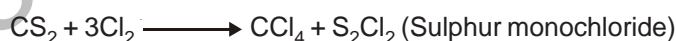
1. By Chlorination of Methane :



2. By Chlorination of Chloroform :

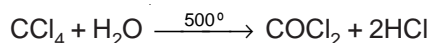


3. By Chlorination of Carbon disulphide :

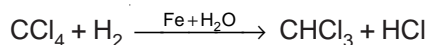


➤ Reactions

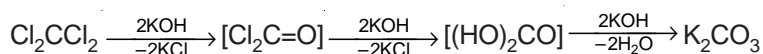
1. Oxidation :



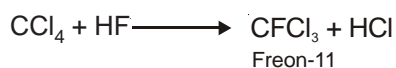
2. Reduction :



3. Alkaline Hydrolysis :

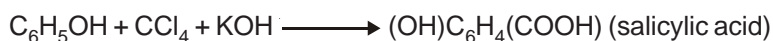


4. Dechlorinative Fluorination :

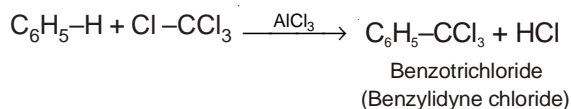


5. Reimer-Tiemann Carboxylation :

When phenol is heated with carbon tetrachloride and KOH, then salicylic acid (o-hydroxybenzoic acid) is obtained.



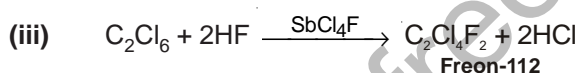
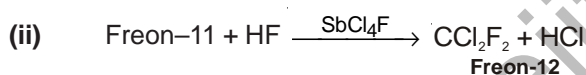
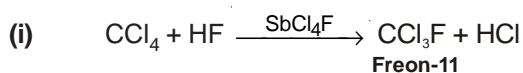
6. Friedel-Crafts Reaction :



➤ **Uses**

1. As an industrial solvent for fats, oils, waxes, gums, resins, rubbers, etc.
2. As a laboratory solvent and reagent
3. In dry cleaning
4. As fire extinguisher under the commercial name, 'Pyrene'.
5. In the manufacture of refrigerants, like Freon-11 and Freon-12
6. As a fumigant, anthelmintic and insecticide.

1.6 Freons (Polychlorofluoro Alkane)



Bromine-containing compounds are popularly used to extinguish fires and are called **Halons**

e.g.

CBrClF_2	Bromochloro difluoromethane	Halon – 1211
CBrF_3	Bromotrifluoro Methane	Halon – 1301

➤ **Uses**

1. As refrigerants in refrigerators, air conditioners, cold storages, etc.
2. As inert solvents.
3. As aerosol propellants