10

Halogen Derivatives

Compounds which are obtained by the replacement of one or more hydrogen atoms of hydrocarbon by halogen atom are known as halogen derivatives.

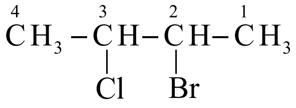
10.1 Haloalkane or Alkyl Halide

Compounds which are obtained by replacement of one or more hydrogen atoms of saturated hydrocarbons by halogen atom are known as alkyl halide. The general formula of alkyl halide is $C_nH_{2n+1}X$ or RX. Here X = Halogen atom (F, Cl, Br, I) and n = 1, 2, 3.....

10.1.1 Classification and Nomenclature –

Halogen derivatives are classified on different basis as given below. These are considered as halogen derivatives of corresponding alkane for nomenclature in IUPAC system. To show the position of halogen atom, numbering of carbon atoms is done. Minimum number is given to that carbon atom to which halogen atom is attached. During the writing of name, prefix is used for halogen atom. If there are two different halogen atoms in alkyl halide then priority is given to that halogen atom which comes first in english alphabetical order both in number and writting the name

Example - (2-bromo-3-chloro butane)



$$\overset{4}{C}H_3-\underset{\underset{Cl}{|}}{\overset{3}{C}H}-\underset{\underset{Br}{|}}{\overset{2}{C}H}-\overset{1}{C}H_3$$

(i) On the basis of number of halogen atoms in haloalkanes, these are classified as mono, di, tri, tetra, etc. For example-

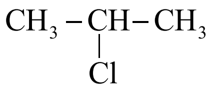
Formula	**CH_3–Cl**	**CH_2Cl_2**	**$CHCl_3$**	**CCl_4**
General Name	Methyl chloride	Methylene chloride	Chloroform	Carbon tetra-chloride
IUPAC Name	Chloro methane	dichloro methane	trichloro methane	tetrachloro methane
Category	Monohalo alkane	dihalo alkane	trihalo alkane	tetrahalo alkane

(ii) On the basis of carbon atom bonded to halogen atom in mono haloalkanes, these are classified into three categories-

Primary Alkyl Halides– Halogen atom is bonded with primary carbon atom. **Example**–

Formula	CH_3-Cl	CH_3-CH_2-Cl	CH_3-CH_2-CH_2-Cl
General name	Methyl chloride	ethyl chloride	propyl chloride
IUPAC name	chloro-methane	chloro ethane	1-chloro propane

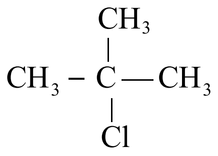
Secondary Alkyl Halides– Halogen atom is bonded with secondary carbon atom. Example -



$$CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3$$

Isopropyl chloride (2-chloropropane)

Tertiary Alkyl Halides– Halogen atom is bonded with tertiary carbon atom.



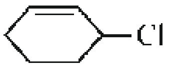
$$CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

Tertiary butyl chloride (2-chloro-2-methyl propane)

(iii) **Allylic Halides–** In these compounds, halogen atom is bonded to sp^3 hybridized carbon atom next to carbon-carbon double bond. This sp^3 hybridized carbon is known as allylic carbon

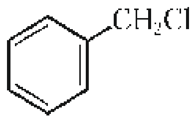
Example-

$$\underset{\text{allyl chloride}}{CH_2=CH-CH_2-Cl}$$



3-chloro cyclohexene

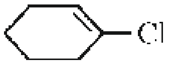
(iv) Benzylic Halides– In these compounds halogen atom is bonded to sp^3 hybridized carbon atom next to aromatic ring. This carbon is known as Benzylic carbon.



benzyl chloride

(v) Vinylic Halides– These are the compounds in which halogen atom is bonded to carbon atom of carbon-carbon double bond. Example -

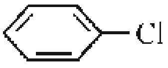
$CH_2=CH-Cl$ vinyl chloride



1-chlorocyclohexene

(vi) Aryl Halides or Haloarenes– Halogen atom is directly bonded to aromatic ring. These are shown as- Ar - X

Example –



chlorobenzene

10.1.2 Nature of C-X bond in haloalkanes–

In these compounds, C-X bond is formed by overlapping of sp^3 hybridized orbital of carbon atom and 3p (half filled) orbital of chlorine (sp^3-p). This overlapping can be shown as follows–

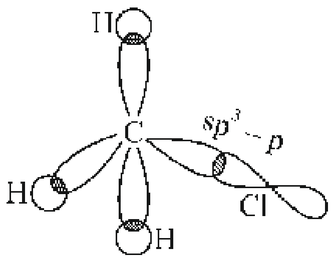
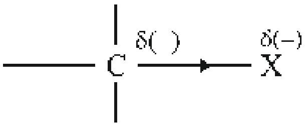


Fig. 10.1 : Molecular orbital diagram of CH_3Cl

Although C-X bond is a covalent bond but electronegativity of carbon atom (2.6) is less than halogen atom. Therefore due to the difference in electronegativities, C-X bond is polar in nature. By this way partial negative charge appears on halogen atom and partial positive charge on carbon atom.



Covalent but polar bond

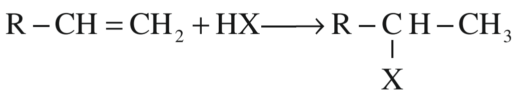
	CH_3-Cl	CH_3-Br	CH_3-I
μ =	1.86 D	1.79 D	1.62 D

10.1.3 Methods of Preparation of haloalkanes–

1. From alkanes– Methane reacts with chlorine in presence of sunlight to give CH_3Cl. But this method is not proper to get pure alkyl halide because by this way we get the mixture of mono, di, tri, tetra halogen derivatives. This method is more useful for industrial purpose where separation of alkyl halide mixture is not always necessary or separation is done by fractional distillation.

$$CH_4+Cl_2\xrightarrow{hv}CH_3-Cl+HCl$$

2. By addition of hydrogen halide on alkene– Alkyl halides are obtained by electrophilic addition reactions of alkenes with hydrogen halide according to Markownikoff's rule.



$$R-CH=CH_2+HX\longrightarrow R-\underset{\underset{X}{|}}{C}H-CH_3$$

R = alkyl group (–CH_3, –CH_2-CH_3 etc.)

X = Halogen atom (Cl, Br, I)

Order of reactivity HI > HBr > HCl

HBr reacts according to anti-Markownikoff's rule in the presence of peroxide. It is also known as peroxide effect.

$$R-CH=CH_2+HBr\xrightarrow[\text{R–O–O–R}]{\text{peroxide}}\underset{\text{1-bromopropane}}{R-CH_2-CH_2-Br}$$

3. From Alcohols –

(i) By the reaction of alcohol and halogen acids– Alcohol reacts with dry halogen acids to give alkyl halide. HCl reacts in the presence of anhydrous zinc chloride, while HBr or HI reacts in the presence of concentrated H_2SO_4, which absorbs water, formed during the reaction.

$$R-OH+HCl\xrightarrow[ZnCl_2]{\Delta}R-Cl+H_2O$$

Here, HBr or HI is prepared by the reaction of NaBr or NaI with concentrated H_2SO_4.

$$R-OH+HBr\xrightarrow[H_2SO_4]{\Delta}R-Br+H_2O$$

Order of reactivity of above reactions are as follows–

Halogen acids : HI > HBr > HCl

Alcohols : Tertiary > Secondary > Primary

(ii) By the reaction of thionyl chloride on alcohols– It is the best method for preparation of alkyl halide from alcohols because we get two gaseous by-products SO_2 and HCl along with alkyl halide. SO_2 gets evaporated and HCl is absorbed by pyridine (C_5H_5N). So alkyl halide is obtained in pure form. This reaction is known as **Darzen's reaction**

$$R-OH+\underset{\substack{\text{Thionyl}\\ \text{Chloride}}}{SOCl_2}\xrightarrow{C_5H_5N}R-Cl+SO_2+HCl$$

Alkyl bromides and alkyl iodide can not be prepared by this reaction because thionyl bromide is unstable and thionyl iodide is unknown.

(iii) By the reaction of alcohol with phosphorous halide– Phosphorous penta chloride (PCl_5) and phosphorous trichloride gives alkyl chloride as follows–

$$R-OH+PCl_5\xrightarrow{\Delta}R-Cl+POCl_3+HCl$$

$$3ROH+PCl_3\xrightarrow{\Delta}3R-Cl+H_3PO_3$$

PBr_3 or PI_3 are used to obtain alkyl bromide and alkyl iodide, which are prepared in reaction flask by the reaction of red phosphorous with Bromine and Iodine, respectively.

$$R-OH\xrightarrow[X_2=Br_2\text{ or }I_2]{\text{Red }P+X_2}R\text{ - }X+H_3PO_3$$

4. From Halogen Exchange–

In this reaction, alkyl halides are prepared from alkyl halides itself. Alkyl iodide is prepared by alkyl chloride or alkyl bromide. For this, solution of chloro or bromoderivatives reacts with sodium iodide in the presence of methanol or acetone to give alkyl iodide. This reaction is known as **Finkelstein Reaction.**

$$R-Cl+NaI\xrightarrow[\Delta]{\text{acetone}}R-I+NaCl$$

$$R-Br+NaI\xrightarrow[\Delta]{\text{acetone}}R-I+NaBr$$

NaCl or NaBr produced here are less soluble in methanol or acetone in comparison to NaI, therefore gets precipitated.

To obtain alkyl fluoride, alkyl iodide is reacted with AgF and this reaction is known as **Swart Reaction.**

$$RI+AgF\longrightarrow R-F+AgI$$

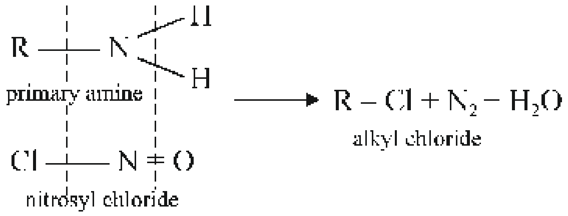
5. From Hunsdicker Reaction–

When silver salt of monocarboxylic acid reacts with Br_2 in presence of CCl_4 solution, decarboxylative bromination takes place and alkyl bromide is formed.

$$R-COOAg+Br_2\xrightarrow{CCl_4}R-Br+CO_2+AgBr$$

6. From Primary Amines–

When primary amines react with nitrosyl chloride (Tilden Reagent) alkyl chlorides are formed.



10.1.4 Physical Properties –

(i) All the alkyl halides are colourless in pure form but in presence of light alkyl bromide and iodide turn-yellowish.

(ii) Alkyl halides are insoluble in water but soluble in alcohol, ether and benzene.

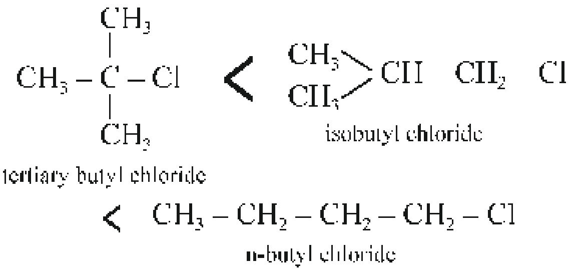
(iii) CH_3Cl, CH_3Br and C_2H_5Cl are in gaseous state where as CH_3I and other alkyl halides are in liquid or solid state.

(iv) Alkyl halides burn with a green colour flame.

(v) Alkyl halides are polar in nature hence their boiling points are more than corresponding hydrocarbons. Boiling point increases with increase in molecular mass. If alkyl group is same then order of boiling point is as follows :

$$CH_3F < CH_3Cl < CH_3Br < CH_3I$$

In isomeric alkyl halides boiling point of branched alkyl halide is less than unbranched alkyl halide.



(vi) Alkyl iodides are most reactive among alkyl halides and decompose in presence of sunlight into iodine and alkane.

$$2RI \xrightarrow{\text{sunlight}} \underset{\text{alkane}}{R-R} + \underset{\text{iodine}}{I_2}$$

10.1.5 Chemical Properties –

Alkyl halides show mainly four types of reactions.

(A) Nucleophilic Substitution Reactions

(B) Elimination Reactions

(C) Reactions with Metals

(D) Reduction Reactions

(A) Nucleophilic Substitution Reactions– The C–X bond in alkyl halides is polar in nature. Due to –I effect of X atom, a partial negative charge appears on halogen atom and partial positive charge on carbon atom. The strong nucleophile ($Nu^{\ominus}$) attacks on carbon atom and replaces halogen atom. Therefore these reactions are known as nucleophilic substitution (S_N) reactions.

$$\overset{\delta+}{R}-\overset{\delta-}{X}+\overset{\ominus}{Nu} \longrightarrow R-Nu+X^{\ominus}$$

Nucleophilic substitution reactions are classified in two categories–

1. Uni molecular Nucleophilic Substitution or S_N1

(i) These reactions are completed in two steps.

(ii) Carbocation (Carbonium ion $R^{\oplus}$) intermediate and halide ion ($X^{\ominus}$) are formed by the heterolysis of C–X bond in first step. The first step is slow and rate determining step.

$$\underset{\text{(rate determining step)}}{\text{First Step}} \quad R-X \xrightarrow[\text{I–step}]{\text{slow}} \underset{\substack{\text{carbocation}\\ \text{(Planar)}}}{R^{\oplus}} + \underset{\text{halide ion}}{X^{\ominus}}$$

(iii) Alkyl halide is used in first step of the reaction, therefore rate of reaction depends on concentration of alkyl halide

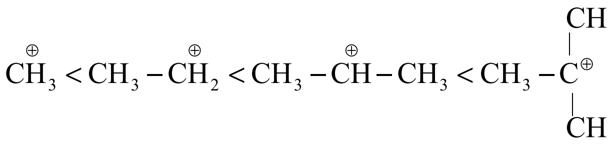
$$\text{Rate of reaction} \propto [R\text{–}X]$$

So this reaction is known as unimolecular nucleophilic substitution reaction (S_N1)

(iv) In II–step, attacking nucleophile reacts with carbocation and gives product. The rate of reaction in II–step is very fast in comparison to I–step.

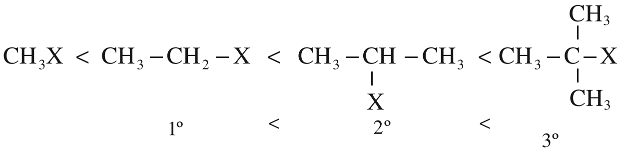
$$\underset{\substack{\text{carbocation}\\ \text{(intermediate)}}}{R^{\oplus}} + \underset{\substack{\text{attacking}\\ \text{nucleophile}}}{Nu^{\ominus}} \xrightarrow[\text{II–step}]{\text{fast}} \underset{\text{product}}{R-Nu}$$

(v) More the stability of carbocation formed during the first step of reaction, easier is the reaction. The order of stability of carbocations is as follows–



$$\overset{\oplus}{C}H_3 < CH_3-\overset{\oplus}{C}H_2 < CH_3-\overset{\oplus}{C}H-CH_3 < CH_3-\underset{\substack{|\\ CH_3}}{\overset{\substack{CH_3\\ |}}{C^{\oplus}}}$$

If halogen atom is same then the order of reactivity in S_N1 mechanism is as follows–



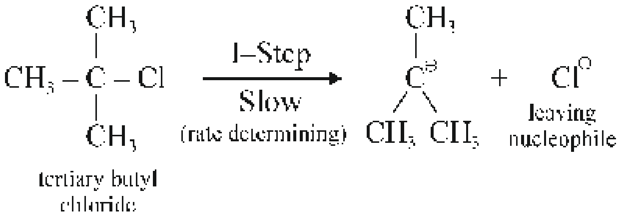
$$CH_3X < CH_3-CH_2-X < CH_3-\underset{X}{CH}-CH_3 < CH_3-\overset{CH_3}{\underset{CH_3}{C}}-X$$

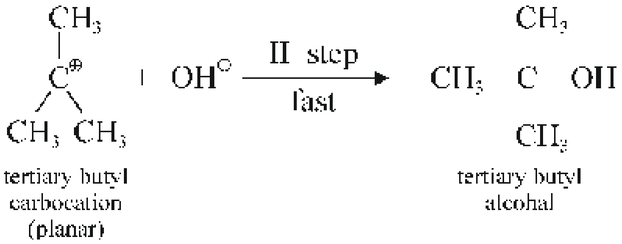
$$1^\circ < 2^\circ < 3^\circ$$

——————— Reactivity (S_N1) ———————→

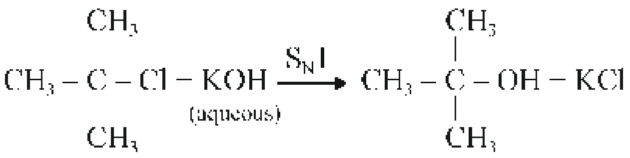
(vi) Geometry of carbocation formed during the reaction is planar, hence, attacking nucleophile ($Nu^{\ominus}$) can attack from both the sides of leaving nucleophile ($X^{\ominus}$) i.e. from same side or opposite side. Therefore if reactant is optically active then product formed will be a racemic mixture.

The S_N1 mechanism of the reaction in between tertiary butyl chloride and aqueous KOH is as follows–





The complete reaction is shown as follows–



2. Bimolecular Nucleophilic Substitution or S_N2

(i) These reactions are completed in one step (concerted).

(ii) In these reactions, only transition state is formed.

(iii) During the formation of transition state, attacking nucleophile ($Nu^{\ominus}$) attacks from opposite side of the leaving nucleophile ($X^{\ominus}$) making an angle of 180° with the C–X bond. It is known as back side attack or rear attack.

(iv) In transition state, attacking nucleophile ($Nu^{\ominus}$) and leaving nucleophile ($X^{\ominus}$) both are partially attached with central carbon atom.

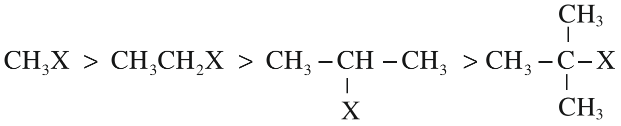
(v) Rate of reaction depends upon concentration of alkyl halide (RX) and concentration of attacking nucleophile ($Nu^{\ominus}$) both. Therefore this reaction is known as bimolecular nucleophilic substitution reaction (S_N2).

$$\text{Rate of reaction} \propto [R\text{-}X]\,[Nu^{\ominus}]$$

(vi) In these reactions, inversion in configuration takes place i.e. configuration of product is inverse of the configuration of reactant. It is known as **"Walden Inversion".**

(vii) In these reactions alkyl groups attached to carbon atom of C–X bond increase the steric hindrance for attacking nucleophile, hence, increase in number of alkyl groups attached with this carbon atom, decrease the rate of reaction. If halogen atom is same then order of reactivity of alkyl halides for S_N2 mechanism is as follows–

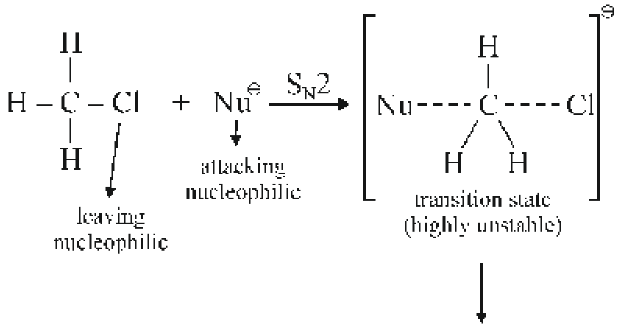
——————— Steric hindrance ———————→

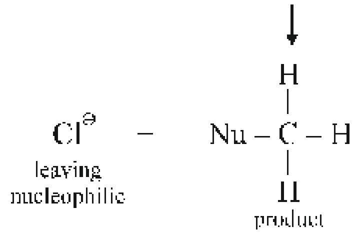


$$CH_3X > CH_3CH_2X > CH_3-\underset{X}{CH}-CH_3 > CH_3-\overset{CH_3}{\underset{CH_3}{C}}-X$$

←——————— Reactivity (S_N2) ———————

So, primary alkyl halide shows S_N2 mechanism and tertiary alkyl halide shows S_N1 mechanism. Which type of mechanism shown by secondary alkyl halide depends upon nucleophile and nature of solvent.





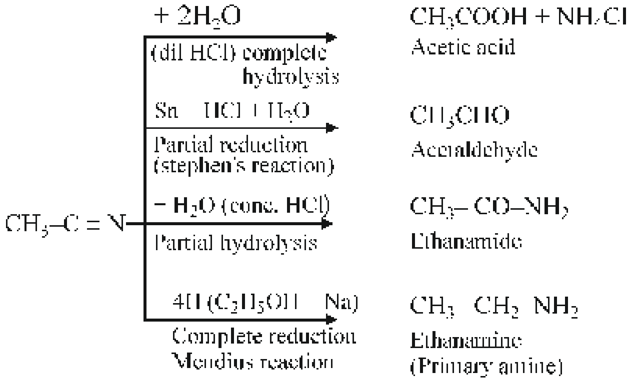
Some examples of nucleophilic substitution reactions are as follows–

(1) Synthesis of Alkyl Cyanide– When KCN reacts with alkyl halide it gives alkyl cyanide

$$R-X+KCN \longrightarrow \underset{\text{alkyl cyanide}}{R-C\equiv N}+KX$$

$$CH_3-Cl+KCN \longrightarrow CH_3-CN+KCl$$

Methyl cyanide so formed gives following important reactions–

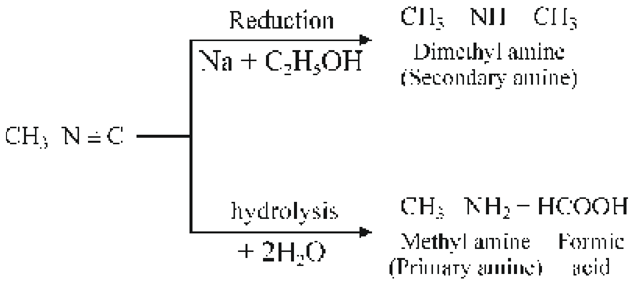


(2) Synthesis of alkyl isocyanide– When AgCN reacts with alkyl halide, it gives alkyl isocyanide.

$$R-X+AgCN \longrightarrow R-N\equiv C+AgX$$

$$CH_3-Cl+AgCN \longrightarrow CH_3-N\equiv C+AgCl$$

Alkyl isocyanide gives primary amine by hydrolysis and secondary amine by reduction process.



We can explain the formation of cyanide from KCN and isocyanide from AgCN as follows–

KCN is an ionic compound and by ionization process it liberates cyanide ions $(:\overset{\ominus}{C}\equiv N:)$ as an attacking nucleophile. In $:\overset{\ominus}{C}\equiv N:$ ion carbon atom is nucleophilic centre (point of attachment) hence gives alkyl cyanide. Ag – CN: is a polar covalent compound and nitrogen atom has a lone pair of electron, therefore nitrogen atom acts as a nucleophilic centre (point of attachment) and gives alkyl isocyanide $(R-N\equiv C)$.

(3) Synthesis of Alcohol– Alcohols are formed by the reaction of aqueous KOH, aqueous AgOH, aqueous Ag_2O, etc. with alkyl halides.

$$R-X+KOH\ (aq.) \longrightarrow R-OH+KX$$

$$CH_3-CH_2-Cl+KOH\ (aq.)$$
$$\downarrow$$
$$CH_3-\underset{\text{Ethanol}}{CH_2}-OH+KCl$$

Order of reactivity of alkyl halides–

3° alkyl halide > 2° alkyl halide > 1° alkyl halide

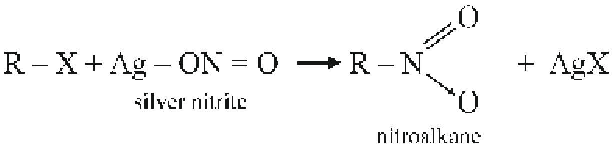
Tertiary alkyl halides are easily hydrolysed even by boiling with water and give alcohols, secondary alkyl halides are hydrolysed by weak bases like Na_2CO_3 or $CaCO_3$ and give alcohols.

(4) Synthesis of Alkyl Nitrite– When alkyl halides react with sodium or potassium nitrites gives alkyl nitrites.

$$RX+KNO_2 \longrightarrow \underset{\text{alkyl nitrite}}{R-O-N=O}+KX$$

$$CH_3Cl+KNO_2 \longrightarrow \underset{\text{methyl nitrite}}{CH_3-O-N=O}+KCl$$

(5) Synthesis of nitroalkane– Nitroalkanes are obtained by the reaction of silver nitrite with alkyl halides.



$$R-X+\underset{\text{silver nitrite}}{Ag-ON=O} \longrightarrow \underset{\text{nitroalkane}}{R-N\overset{O}{\underset{O}{\lessgtr}}} + AgX$$

$$CH_3-CH_2-Br+AgNO_2 \rightarrow \underset{\text{nitroethane}}{CH_3-CH_2-NO_2}-AgBr$$

(6) Synthesis of ether– When dry silver oxide reacts with alkyl halide, it gives ether.

$$2R-X+Ag_2O\longrightarrow R-O-R+2AgX$$

$$2CH_3-CH_2-Br+Ag_2O$$
$$\downarrow$$
$$\underset{\text{diethyl ether}}{CH_3-CH_2-O-CH_2-CH_3}+2AgBr$$

If Sodium alkoxide reacts with alkyl halide it gives ether and it is known as **williamson's ether Synthesis.**

$$C_2H_5Cl+\underset{\text{sodium ethoxide}}{NaOC_2H_5}$$
$$\downarrow$$
$$\underset{\text{diethyl ether}}{C_2H_5-O-C_2H_5}+NaCl$$

(7) Synthesis of thioether– Thioethers are formed by the reaction of sodium sulphide (Na_2S) or sodium mercaptide (NaSR) with alkyl halides.

$$2C_2H_5Cl+Na_2S\longrightarrow \underset{\text{diethyl thioether}}{C_2H_5-S-C_2H_5}+2NaCl$$

$$C_2H_5Cl+NaSC_2H_5\longrightarrow C_2H_5-S-C_2H_5+NaCl$$

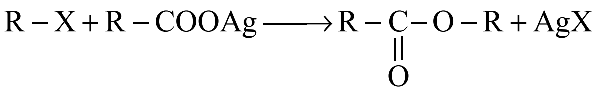
(8) Synthesis of alkane thiol– When sodium or potassium hydrogen sulphide reacts with alkyl halide, it gives alkane thiol.

$$R-X+NaSH\longrightarrow \underset{\text{alkane thiol}}{R-SH}+NaX$$

$$C_2H_5-Cl+NaSH\longrightarrow \underset{\text{ethane thiol}}{C_2H_5-SH}+NaCl$$

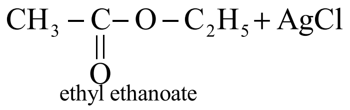
$$C_2H_5Cl+KSH\longrightarrow C_2H_5SH+KCl$$

(9) Synthesis of ester– By the reaction of silver salt of monocarboxylic acids with alkyl halides ester is obtained.



$$R-X+R-COOAg\longrightarrow R-\underset{\underset{O}{\|}}{C}-O-R+AgX$$

$$CH_3-CH_2-Cl+\underset{\text{silver acetate}}{CH_3-COOAg}\rightarrow$$



$$CH_3-\underset{\underset{O}{\|}}{C}-O-C_2H_5+AgCl$$

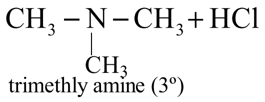
ethyl ethanoate

(10) Synthesis of amines– When alcoholic ammonia is heated with alkyl halide in sealed tube, alkylation of ammonia takes place and mixture of amines is formed. If alkyl halide is used in excess, then last product is a quaternary ammonium salt. For example, reaction of methyl chloride with ammonia is as follows–

$$CH_3-Cl+NH_3\longrightarrow \underset{\text{methyl amine (1°)}}{CH_3-NH_2}+HCl$$

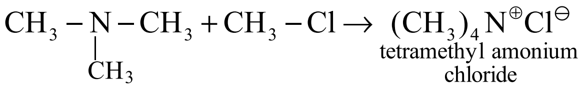
$$CH_3-NH_2+CH_3-Cl\longrightarrow \underset{\text{dimethyl amine (2°)}}{CH_3-NH-CH_3}+HCl$$

$$CH_3-NH-CH_3+CH_3-Cl$$
$$\downarrow$$



$$CH_3-\underset{\underset{CH_3}{|}}{N}-CH_3+HCl$$

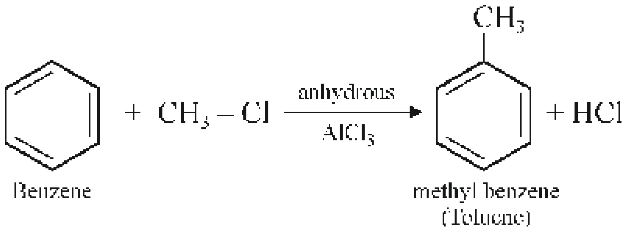
trimethly amine (3°)

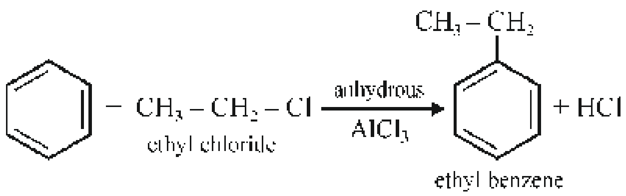


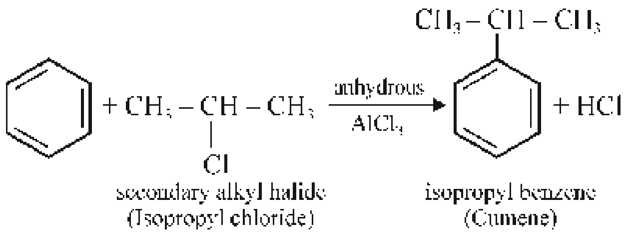
$$CH_3-\underset{\underset{CH_3}{|}}{N}-CH_3+CH_3-Cl\rightarrow (CH_3)_4N^{\oplus}Cl^{\ominus}$$

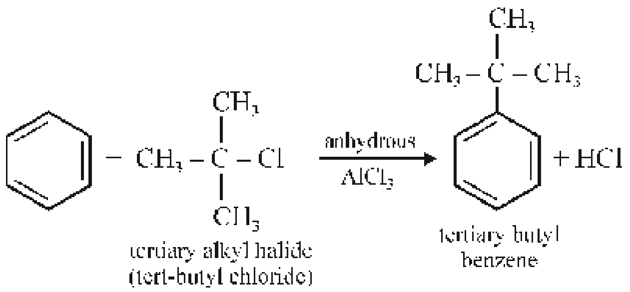
tetramethyl amonium chloride (quaternary salt)

(11) Friedel-Crafts Reaction– When alkyl halide reacts with benzene in presence of anhydrous $AlCl_3$, it gives alkyl benzene. In this reaction, alkylation of benzene takes place.

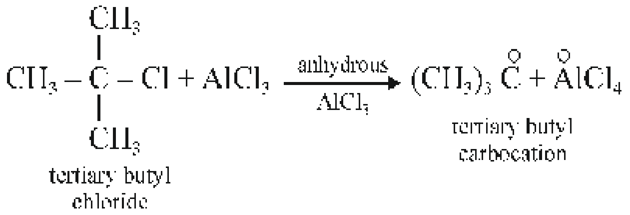




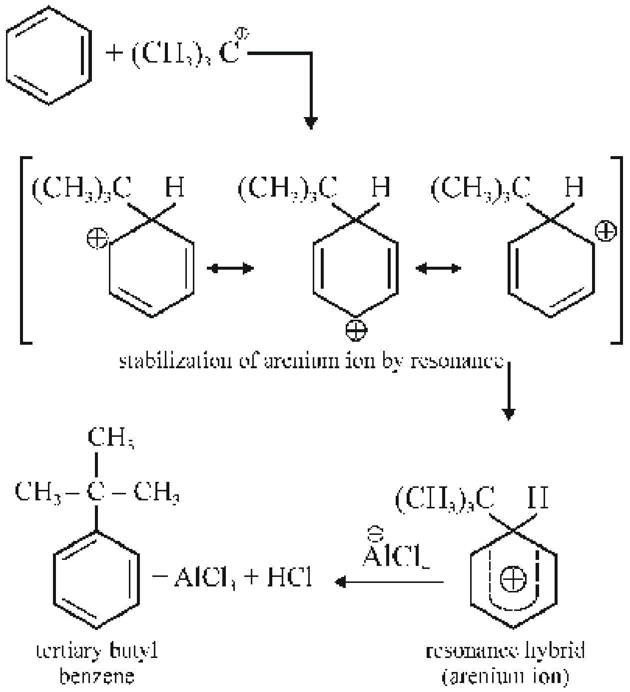




Mechanism– Friedel-Crafts reaction is an example of electrophilic substitution reaction of benzene. In this reaction, secondary and tertiary alkyl halide gives carbocation as an intermediate in the presence of anhydrous $AlCl_3$, which acts as an electrophile (lewis acid). While primary alkyl halide gives $R-\overset{\oplus}{\ddot{X}}-\overset{\ominus}{AlCl_3}$ complex (alkyl halide aluminium chloride complex) in the presence of $AlCl_3$, which acts as an electrophile.

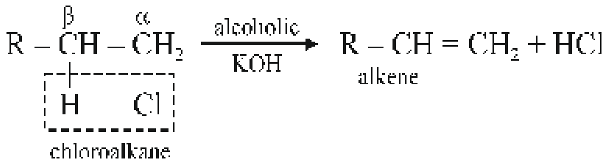


$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl+AlCl_3\xrightarrow[AlCl_3]{\text{anhydrous}}(CH_3)_3\overset{\oplus}{C}+\overset{\ominus}{AlCl_4}$$

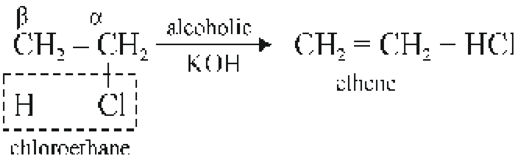


If positive charge appears on carbon atom in aromatic system, it is known as arenium ion (cyclohexa dienyl cation)

(B) Elimination Reactions– "In an elimination reaction two substituents are removed from a molecule with the formation of a multiple bond (a double or triple bond)". When alcoholic KOH reacts with alkyl halide, HX molecule is removed by β-elimination and alkene is formed. In this reaction hydrogen atom is removed from adjacent carbon atom (β-carbon) with respect to carbon atom bonded to halogen atom (α-carbon). Therefore it is known as β–elimination and HX is removed from alkyl halide, so process is known as "dehydrohalogenation".



$$R-\overset{\beta}{C}H-\overset{\alpha}{C}H_2\xrightarrow[KOH]{\text{alcoholic}}R-CH=CH_2+HCl$$



$$\overset{\beta}{C}H_2-\overset{\alpha}{C}H_2\xrightarrow[KOH]{\text{alcoholic}}CH_2=CH_2-HCl$$

Order of reactivity in elimination reaction–

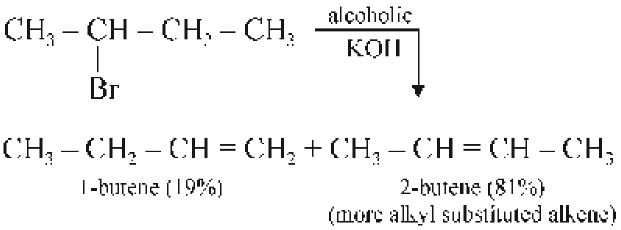
If halogen atom (X) is same then–

$$\underset{(1°)}{R-CH_2X}<\underset{(2°)}{R_2CHX}<\underset{(3°)}{R_3CX}$$

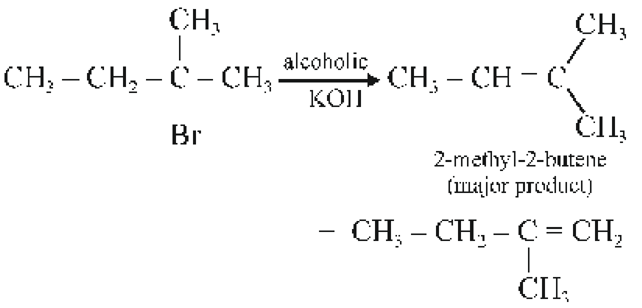
If alkyl group (R) is same, then–

$$RF<RCl<RBr<RI$$

If two isomeric alkenes are formed during the elemination reaction, then more alkyl substituted alkene is formed as a major product. It is known as **"Saytzeff's Rule".**



$$CH_3-\underset{Br}{CH}-CH_2-CH_3\xrightarrow[KOH]{\text{alcoholic}}CH_3-CH_2-CH=CH_2+CH_3-CH=CH-CH_3$$



2-methyl-2-butene (major product)

2-methyl-1-butene (minor product)

(C) Reactions with Metals

1. **Wurtz Reaction–** When two molecules of alkyl halide react with sodium metal in presence of dry ether; alkane is formed. Number of carbon atoms in alkane are double of number of carbon atoms present in alkyl halide.

$$R-X-2Na+X-R \xrightarrow{\text{dry ether}} R-R+2NaX$$

$$\underset{(1C)}{CH_3}-I+2Na+I-CH_3 \xrightarrow[\text{ether}]{\text{dry}} \underset{(2C)}{CH_3-CH_3}+2NaI$$

A mixture of three probable alkanes is obtained if two different alkyl halides are used in the reaction.

$$R-X+R^1X \xrightarrow[\text{dry ether}]{Na} R-R+R-R^1+R^1-R^1$$

2. **Reaction with Lithium–** Alkyl lithium is formed when lithium reacts with alkyl halide in presence of ether.

$$CH_3-CH_2Br+2Li \xrightarrow{\text{ether}} \underset{\substack{\text{ethyl lithium} \\ \text{(organometallic compound)}}}{CH_3-CH_2Li}+LiBr$$

3. **Reaction with zinc–** Dialkyl zinc **(Frankland-reagent)** is formed when haloalkanes react with zinc metal.

$$2CH_3-CH_2-Br+2Zn$$
$$\downarrow$$
$$\underset{\text{diethyl zinc (frankland reagent)}}{CH_3-CH_2-Zn-CH_2-CH_3}+ZnBr_2$$

4. **Synthesis of Grignard Reagent–** When alkyl halide reacts with Mg-metal in presence of dry ether it gives Grignard Reagent.

$$RX+Mg \xrightarrow{\text{dry ether}} \underset{\text{(Grignard reagent)}}{R-Mg-X}$$

$$CH_3I+Mg \xrightarrow{\text{dry ether}} CH_3-Mg-I$$

$$CH_3-CH_2-Br+Mg \xrightarrow{\text{dry ether}} \underset{\substack{\text{ethyl magnesium bromide} \\ \text{(Grignard reagent)}}}{CH_3-CH_2-Mg-Br}$$

5. **Reaction with Lead-Sodium alloy–** When ethyl bromide reacts with lead sodium alloy, it gives "Tetraethyl lead" (TEL).

$$4C_2H_5Br+4Pb.Na \xrightarrow{\text{ether}} \underset{\text{tetra ethyl lead (TEL)}}{(C_2H_5)_4Pb}+3Pb+4NaBr$$

(D) Reduction– Alkanes are formed by reduction of alkyl halides.

$$R-X+2H \longrightarrow R-H+HX$$

$$C_2H_5Cl+2H \longrightarrow C_2H_6+HCl$$

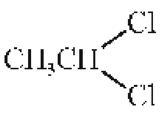
Following reagents are used for reduction–

Zn/HCl, Na/C_2H_5OH, $LiAlH_4$, Red P/HI, etc.

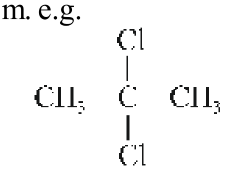
10.2 Dihalogen derivatives–

When two hydrogen atoms of an alkane are substituted by two halogen atoms, compound so formed is known as dihalogen derivatives. These are classified in three categories on the basis of relative position of two halogen atoms in dihaloalkane.

(i) Gem-dihalides– (gemini-twins)– In these dihalides, both the halogen atoms are attached to the same carbon atom. e.g.



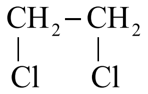
ethylidene chloride



$$CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_3$$

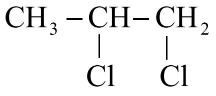
isopropylidene chloride

(ii) Vic dihalides– (vicinal-adjacent)– In these dihalides, both the halogen atoms are attached to adjacent carbon atoms. e.g.



$$\underset{\underset{Cl}{|}}{CH_2}-\underset{\underset{Cl}{|}}{CH_2}$$

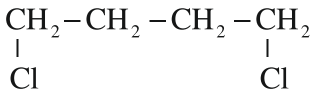
Ethylene chloride (1, 2-dichloro ethane)



$$CH_3-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{Cl}{|}}{CH_2}$$

Propylene chloride. (1,2-dichloro propane)

(iii) α, ω-dihalide– In these dihalides, both the halogen atoms are attached to first and last carbon atom of the carbon chain. e.g.



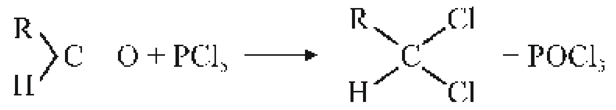
$$\underset{\displaystyle Cl}{CH_2} - CH_2 - CH_2 - \underset{\displaystyle Cl}{CH_2}$$

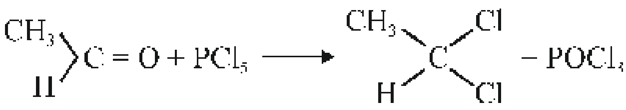
α, ω-dichloro butane (1,4-dichloro butane)

10.2.1 Methods of preparation–

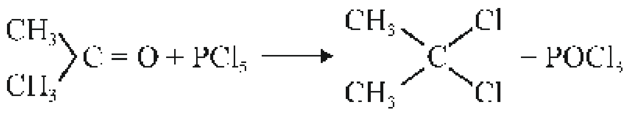
(A) Gem-dihalides–

(i) From carbonyl compounds– By the reaction of PCl_5–





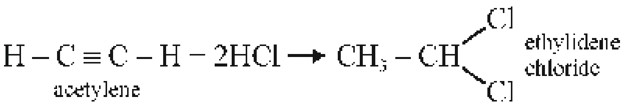
ethylidene chloride



acetone

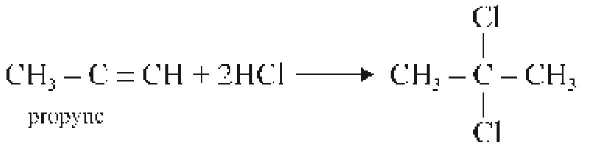
Iso propylidene chloride

(ii) From alkynes– By the reaction of halogen acids.



acetylene

ethylidene chloride



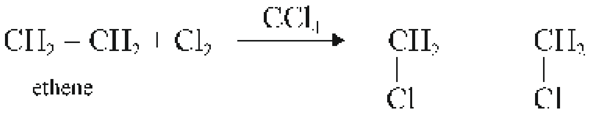
$$CH_3 - C = CH + 2HCl \longrightarrow CH_3 - \overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}} - CH_3$$

propyne

Iso propylidene chloride

(B) Vic-dihalides–

(i) From alkenes– When alkenes react with halogens in presence of CCl_4 it gives vic-dihalides.

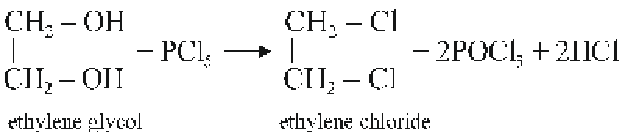


$$CH_2 - CH_2 + Cl_2 \xrightarrow{CCl_4} \underset{\displaystyle Cl}{CH_2} \quad \underset{\displaystyle Cl}{CH_2}$$

ethene

1,2-dichloroethane

(ii) From glycol– Vic-dihalides are obtained by the reaction of glycol with PCl_5.

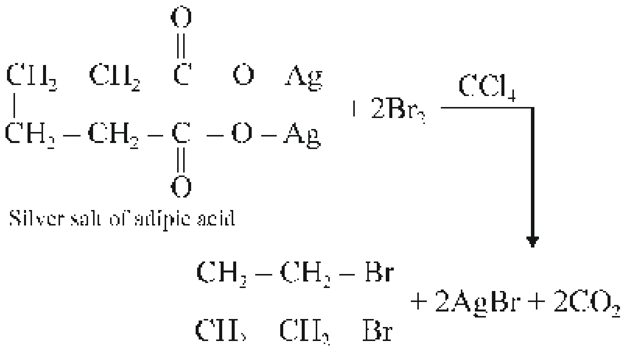


$$\begin{matrix} CH_2 - OH \\ | \\ CH_2 - OH \end{matrix} - PCl_5 \longrightarrow \begin{matrix} CH_2 - Cl \\ | \\ CH_2 - Cl \end{matrix} - 2POCl_3 + 2HCl$$

ethylene glycol

ethylene chloride

(C) α, ω-dihalide– When silver salt of dicarboxylic acids react with bromine in presence of CCl_4 it gives α,ω–dihalides. It is known as **Hunsdiecker reaction.**



$$\begin{matrix} CH_2 & CH_2 & \overset{\displaystyle O}{\overset{\|}{C}} & O & Ag \\ | & & & & \\ CH_2 - & CH_2 - & \underset{\displaystyle O}{\underset{\|}{C}} & - O - & Ag \end{matrix} + 2Br_2 \xrightarrow{CCl_4} \begin{matrix} CH_2 - CH_2 - Br \\ CH_2 \quad CH_2 \quad Br \end{matrix} + 2AgBr + 2CO_2$$

Silver salt of adipic acid

1, 4- dibromobutane (α, ω - dihalide)

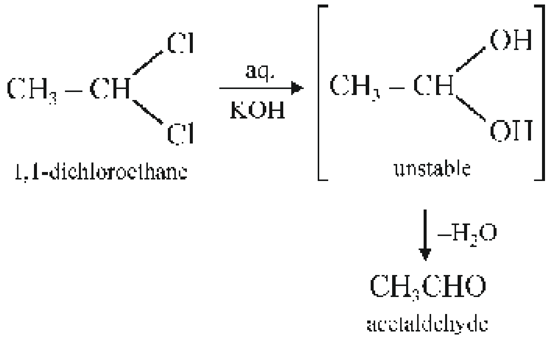
10.2.2 Physical Properties–

Dihaloderivatives are generally colourless liquids with sweet smell. These are insoluble in water but soluble in organic solvents. Dihalides are heavier than water.

10.2.3 Chemical Properties–

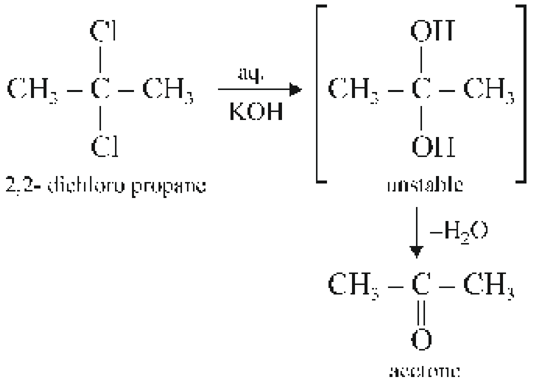
The chemical reactions of dihaloalkanes are similar to monohaloalkanes. Some reactions are as follows–

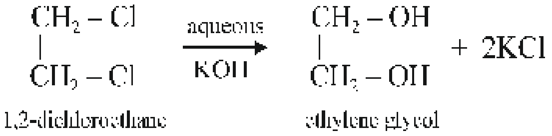
1. **Hydrolysis–** Aldehydes or ketones are formed by reaction of gem-dihalides with aqueous KOH or AgOH while reaction with vic-dihalides gives glycol.



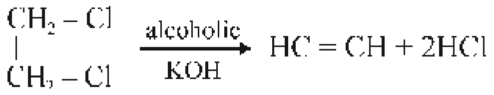
1,1-dichloroethane

acetaldehyde

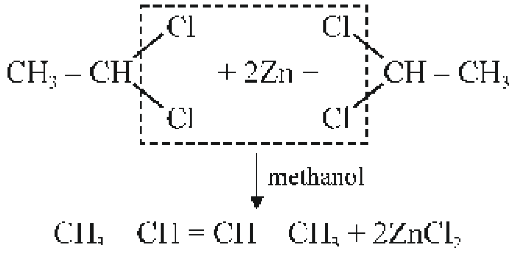


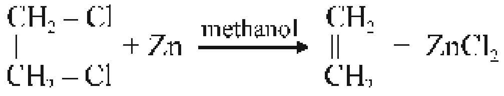


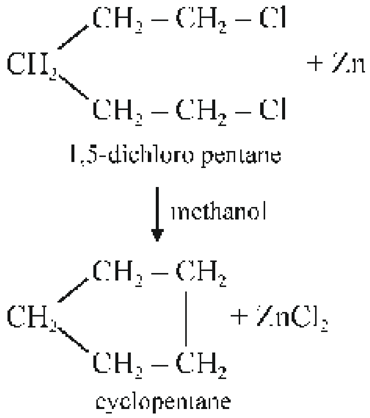
2. **Dehydrohalogenation–** Corresponding alkynes are formed by reaction of vic- or gem-dihalides with alcoholic KOH.



3. **Dehalogenation–** By reaction with Zn, gem–dihalide gives alkenes having double number of carbon atoms, vic–dihalide gives alkene having same number of carbon atoms and α, ω-dihalide gives cycloalkane of same number of carbon atoms as present in dihalides.







10.2.4 Uses-

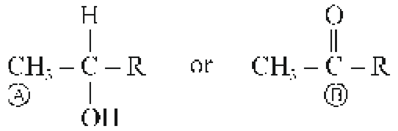
Mono and di-halo derivatives are generally used as follows–

1. Methyl chloride and ethyl chloride are used to prepare methyl cellulose and ethyl cellulose.
2. Ethyl chloride is used to synthesize tetra ethyl lead (TEL).
3. Methyl and ethyl chlorides are used as refrigerants and anaesthetics.
4. Mono halogen derivatives are used to synthesize many important organic compounds.
5. Dihalogen derivatives are used as a solvent for rubber.
6. Methylene chloride is used as extraction solvent in drug and food industries.

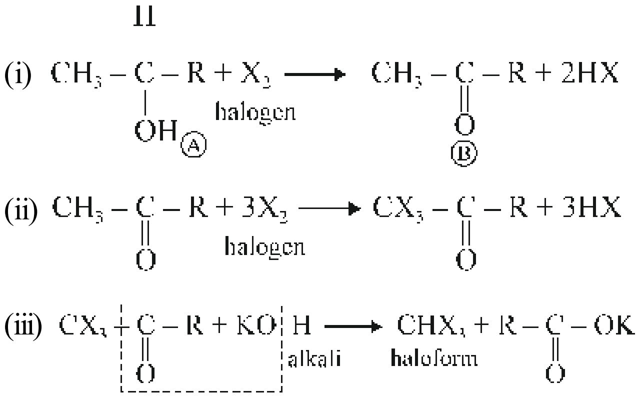
10.3 Tri Halogen Derivatives

Chloroform ($CHCl_3$) and Iodoform (CHI_3) are two important trihalogen derivatives which are also called Haloforms. These are synthesized by haloform reaction.

Haloform Reaction– The compounds having



Structure, show haloform reaction. Where R– is an alkyl group or hydrogen atom (H). Compounds having structure (A) are converted into (B) by oxidation. When compounds having structure (A) or (B) are heated with halogen and alkali, gives haloform by haloform reaction. This reaction is completed in following steps –

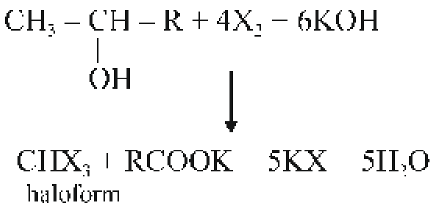


$$\text{(i)}\ CH_3-\underset{\underset{OH}{|}}{\overset{H}{C}}-R+\underset{\text{halogen}}{X_2}\longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-R+2HX$$

$$\text{(ii)}\ CH_3-\underset{\underset{O}{\|}}{C}-R+\underset{\text{halogen}}{3X_2}\longrightarrow CX_3-\underset{\underset{O}{\|}}{C}-R+3HX$$

$$\text{(iii)}\ CX_3-\underset{\underset{O}{\|}}{C}-R+\underset{\text{alkali}}{KOH}\longrightarrow \underset{\text{haloform}}{CHX_3}+R-\underset{\underset{O}{\|}}{C}-OK$$

Overall reaction is–



$$CH_3-\underset{\underset{OH}{|}}{CH}-R+4X_2+6KOH\longrightarrow \underset{\text{haloform}}{CHX_3}+RCOOK+5KX+5H_2O$$

10.3.1 Trichloromethane (Chloroform) $CHCl_3$–

Methods of preparation–

1. **Laboratory method–** Chloroform is obtained by heating ethyl alcohol or acetone with bleaching powder and water. This reaction is called "Haloform Reaction" and completed in following steps–

(i) Bleaching powder ($CaOCl_2$) reacts with water to produce nascent chlorine and calcium hydroxide

$$CaOCl_2+H_2O\rightarrow Ca(OH)_2+\underset{\substack{\text{nascent}\\\text{chlorine}}}{2Cl}$$

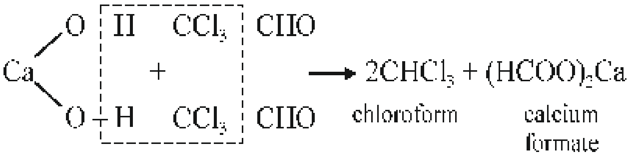
(ii) Nascent chlorine oxidizes ethyl alcohol into acetaldehyde

$$CH_3-CH_2-OH_2+2Cl\longrightarrow CH_3CHO+2HCl$$

(iii) Acetaldehyde is chlorinated by nascent chlorine and trichloroacetalehyde (chloral) is obtained.

$$CHCHO+6Cl\longrightarrow \underset{\text{chloral}}{CCl_3-CHO}+3HCl$$

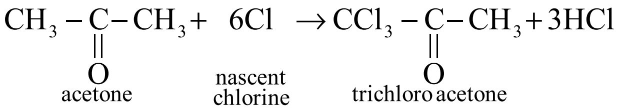
(iv) Chloral forms chloroform on hydrolysis by calcium hydroxide.



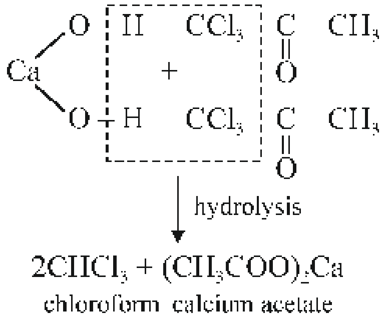
$$Ca\begin{matrix}O\,H & CCl_3\,CHO\\ + & \\ O\,H & CCl_3\,CHO\end{matrix}\longrightarrow \underset{\text{chloroform}}{2CHCl_3}+\underset{\substack{\text{calcium}\\\text{formate}}}{(HCOO)_2Ca}$$

If acetone is used as starting material instead of ethyl alcohol, reaction will proceed as follow–

$$CaOCl_2+H_2O\longrightarrow Ca(OH)_2+2Cl$$



$$\underset{\text{acetone}}{CH_3-\underset{\underset{O}{\|}}{C}-CH_3}+\underset{\substack{\text{nascent}\\\text{chlorine}}}{6Cl}\rightarrow \underset{\text{trichloro acetone}}{CCl_3-\underset{\underset{O}{\|}}{C}-CH_3}+3HCl$$



$$Ca\begin{matrix}O\,H & CCl_3\,\underset{\underset{O}{\|}}{C}\,CH_3\\ + & \\ O\,H & CCl_3\,\underset{\underset{O}{\|}}{C}\,CH_3\end{matrix}\xrightarrow{\text{hydrolysis}}\underset{\text{chloroform}}{2CHCl_3}+\underset{\text{calcium acetate}}{(CH_3COO)_2Ca}$$

Laboratory Method– 100 g bleaching powder, 200mL water and 25 mL ethyl alcohol or acetone is heated on sand bath in a 500mL round bottom flask as shown in figure below. Chloroform is collected in a water-containing receiver after passing through condenser. It is separated from water by separating funnel. Chloroform so obtained is washed with dil./ NaOH; dried with anhydrous $CaCl_2$ and redistilled to obtain pure chloroform.

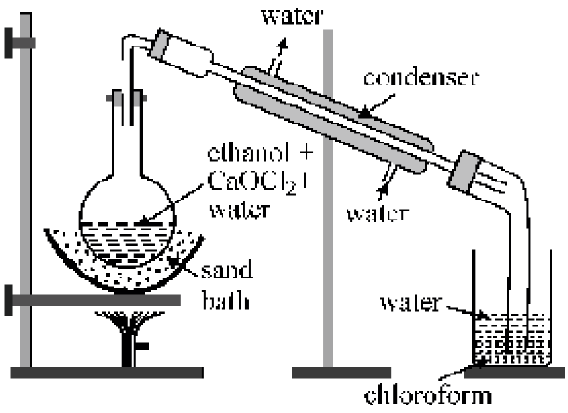
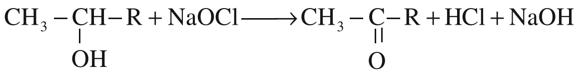


Fig. 10.2 : Preparation of chloroform in Laboratory

2. **From Sodium Hypochlorite (NaOCl)–** By haloform reaction, sodium hypochorite solution forms chloroform as follows

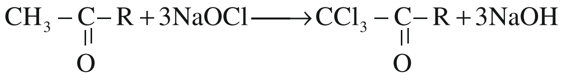
(i) $$2NaOH + Cl_2 \rightleftharpoons \underset{\text{sodium hypochlorite}}{NaOCl} + NaCl + H_2O$$

(ii)



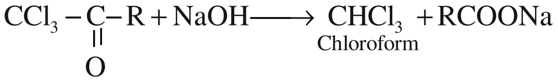
$$CH_3-\underset{\underset{OH}{|}}{CH}-R + NaOCl \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-R + HCl + NaOH$$

(iii)



$$CH_3-\underset{\underset{O}{\|}}{C}-R + 3NaOCl \longrightarrow CCl_3-\underset{\underset{O}{\|}}{C}-R + 3NaOH$$

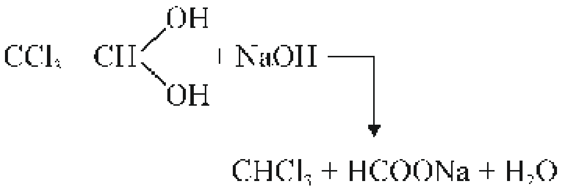
(iv)



$$CCl_3-\underset{\underset{O}{\|}}{C}-R + NaOH \longrightarrow \underset{\text{Chloroform}}{CHCl_3} + RCOONa$$

Here, R= alkyl group or H- atom.

3. **From chloral hydrate–** Chloral hydrate is hydrolysed with aqueous NaOH to give pure chloroform.



4. **From carbon tetra chloride–** Carbon tetrachoride is partially reduced into chloroform by Fe + H_2O.

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

5. **By Chlorination of Methane–** This method is used for industrial production of chloroform.

$$CH_4 + Cl_2 \xrightarrow{hv} CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 \xrightarrow{hv} CH_2Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{hv} \underset{\text{chloroform}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow{hv} CCl_4 + HCl$$

Chloroform is obtained by the partial distillation of this mixture ($CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$).

10.3.2 Physical Properties–

Chloroform is a colourless sweet smelling liquid. It is partially soluble in water and heavier than water. It is soluble in ether and alcohol. Chloroform causes unconsciousness on excess inhalation.

Purity Test of Chloroform : Pure chloroform do not gives white precipitate with $AgNO_3$ solution. While impure chloroform gives white precipitate of AgCl with $AgNO_3$ due to the presence of HCl gas. Chloroform gives HCl gas on oxidation in presence of air and light.

$$AgNO_3 + HCl \longrightarrow \underset{\text{(white precipitate)}}{AgCl\downarrow} + HNO_3$$

10.3.3 Chemical Properties –

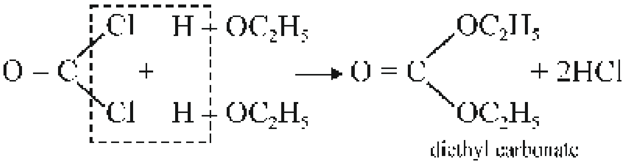
1. **Oxidation–** In presence of light and atomospheric oxygen, chloroform is oxidized into a poisnous gas carbonyl chloride (Phosgene)

$$2CHCl_3 + O_2 \xrightarrow{\text{Light}} \underset{\text{phosgene}}{2COCl_2} + 2HCl$$

Therefore, impure chloroform can not be used for anaesthetic purposes. To prevent oxidation of chloroform following precautions are taken into account–

(i) Chloroform is stored in dark brown (coloured) bottles filled upto the brim to prevent the contact of air and light.

(ii) 1% ethyl alcohol (small amount) is added with chloroform. If small amount of phosgene is formed then it is converted into non-poisnous diethyl carbonate by ethyl alcohol.

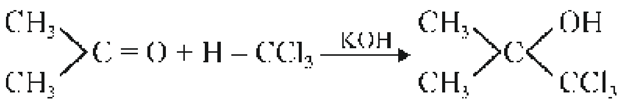


2. **Reduction–** Chloroform gives different products on reduction with various reducing agents. Dichloromethane is obtained with Zn + HCl and methane is obtained with Zn and water vapour.

$$CHCl_3 + 2H \xrightarrow[\text{reduction}]{Zn+HCl} CH_2Cl_2 + HCl$$

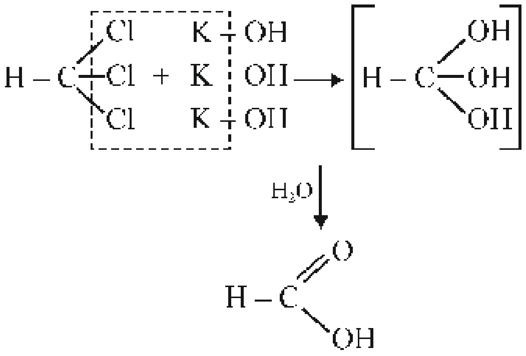
$$CHCl_3 + 6H \xrightarrow[\text{reduction}]{Zn+H_2O} CH_4 + 3HCl$$

3. **Reaction with Acetone–** Chloretone is obtained by the addition reaction of acetone and chlororform in presence of KOH. Chloretone is a hypnotic drug.



chloretone

4. **Hydrolysis–** Chloroform reacts with aqueous KOH to give formic acid.



formic acid

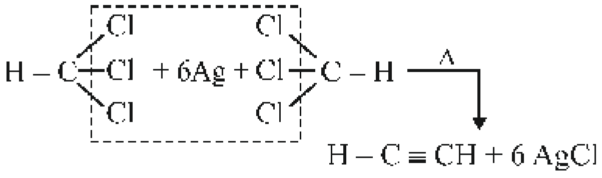
5. **Nitration–** By the reaction of concentrated HNO_3 with chloroform, chloropicrin or nitrochloroform is formed. It has been used as war gas.

$$CHCl_3 + HO-NO_2 \longrightarrow \underset{\text{Chloropicrin}}{Cl_3CNO_2} + H_2O$$

6. **Chlorination–** In presence of sun-light chloroform reacts with chlorine and gives carbon tetra chloride.

$$CHCl_3 + Cl_2 \xrightarrow{hv} CCl_4 + HCl$$

7. **Reaction with silver powder–** It gives acetylene



acetylene

8. **Hofmann's Carbyl amine Reaction or Isocyanide Test–**

When chloroform is heated with primary amine and alcoholic KOH. It gives isocyanide having an offensive smell. It is also called carbylamine.

$$CHCl_3 + \underset{\text{methyl amine}}{CH_3-NH_2} + 3KOH$$

$$\downarrow$$

$$\underset{\text{methyl isocyanide}}{CH_3-N \equiv C} + 3KCl + 3H_2O$$

$$CHCl_3 + \underset{\text{aniline}}{C_6H_5NH_2} + 3KOH$$

$$\downarrow$$

$$\underset{\text{phenyl isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$$

This reaction is used to test primary amine and chloroform. So this is also called isocyanide test.

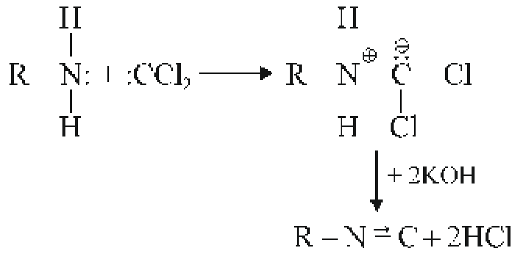
Mechanism of reaction–

(i) $KOH \rightleftharpoons \overset{\oplus}{K} + \overset{\ominus}{OH}$

(ii) $CHCl_3 + \overset{\ominus}{OH} \longrightarrow \underset{\text{trichloro carbanion}}{:\overset{\ominus}{C}Cl_3} + H_2O$

(iii) $:\overset{\ominus}{C}Cl_3 \xrightarrow{\overset{\ominus}{Cl}} :CCl_2$

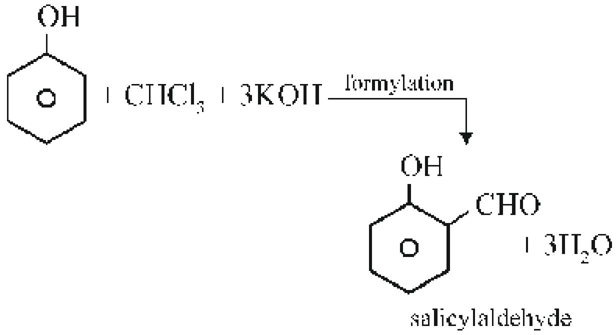
dichlorocarbene free radical

(iv) 

alkyl isocyanide

9. **Reimer-Tiemann Reaction–**

Salicylaldehyde is formed by heating chloroform and phenol with alcoholic KOH.



This is an electrophilic substitution reaction of phenol, here, dichlorocarbene free radical (:CCl_2) acts as an electrophile in this reaction.

10. **Addition with alkenes–** Addition reactions of alkenes with chloroform are according to anti Markownikoff's rule in presence of peroxide.

$$CH_3-CH_2-CH=CH_2+HCCl_3 \xrightarrow{\text{peroxide}} \underset{\text{1,1,1–trichloropentane}}{CH_3-CH_2-CH_2-CH_2-CCl_3}$$

10.3.3 Uses of chloroform– Chloroform is used

1. as an anaesthetic
2. as a solvent
3. as a laboratory reagent
4. as a germicide
5. in manufacturing of chloropicrin, chloretone etc.

10.4 Iodoform (CHI_3) or Tri-iodomethane : Method of Preparation–

1. Laboratory method–

By haloform reaction– When acetone or ehtyl alcohol is heated with iodine and aqueous solution of NaOH, yellow precipitate of iodoform is obtained. This reaction is also known as iodoform reaction and completed as follows–

$$2NaOH+I_2 \longrightarrow \underset{\substack{\text{sodium}\\\text{hypoiodite}}}{NaOI}+NaI+H_2O$$

$$CH_3-CH_2-OH+NaOI \longrightarrow CH_3CHO+NaI+H_2O$$

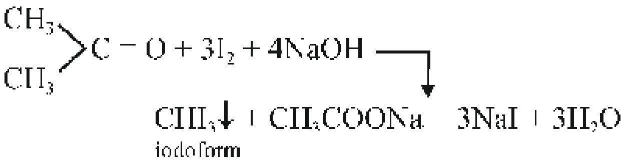
$$CH_3CHO+3NaOI \longrightarrow \underset{\substack{\text{Iodal}\\\text{(triiodoacetaldehyde)}}}{CI_3CHO}+3NaOH$$

$$CI_3CHO+NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3}+HCOONa$$

Overall reaction is written as–

$$CH_3-CH_2-OH+4I_2+6NaOH$$
$$\downarrow$$
$$CHI_3+5NaI+HCOONa+5H_2O$$

If acetone is used then overall reaction is as follows–



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C-O+3I_2+4NaOH \longrightarrow \underset{\text{iodoform}}{CHI_3\downarrow}+CH_3COONa+3NaI+3H_2O$$

10.4.1 Physical properties–

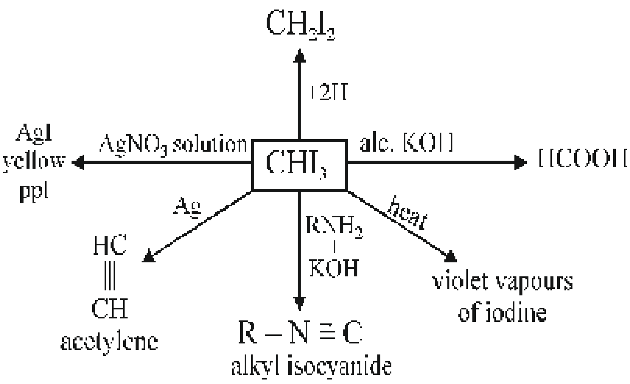
Iodoform is yellow coloured solid. It is insoluble in water but soluble in alcohol, ether, $CHCl_3$, etc. It is more reactive than chloroform and dissociates into iodine even at normal temperature. Melting point of iodoform is 392K.

10.4.2 Chemical properties–

Maximum reactions of iodoform are similar to chloroform.

Pure chloroform do not give white precipitate with $AgNO_3$ solution while iodoform gives yellow precipitate of AgI with $AgNO_3$ solution because iodoform dissociates into I_2 easily.

Some reactions of Iodoform are as follows–



10.4.3 Uses–

Iodoform is used as Antiseptic and Disinfectant.

10.5 Carbon tetra chloride (CCl_4) or Tetrachloromethane : Method of preparation–

1. By chlorination of chloroform

$$CHCl_3 + Cl_2 \xrightarrow[\text{Sunlight}]{hv} CCl_4 + HCl$$

2. By chlorination of carbon di sulphide (CS_2)

$$CS_2 + 3Cl_2 \xrightarrow{AlCl_3} CCl_4 + S_2Cl_2$$

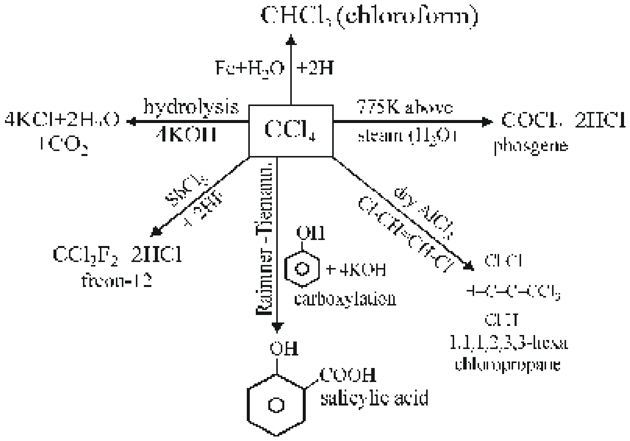
$$CS_2 + 2S_2Cl_2 \xrightarrow{AlCl_3} CCl_4 + 6S$$

10.5.1 Physical properties–

Carbon tetra chloride is a colourless, pleasant smelling volatile liquid. It is insoluble in water but soluble in alcohol and ether. It is non-inflammable and non-explosive. The trade name of carbon tetra chloride is "Pyrene".

10.5.2 Chemical properties–

Main chemical reactions of carbon tetrachloride are as follows–

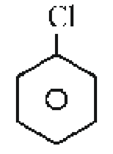


10.5.3 Uses– It is used

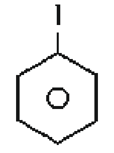
1. as a fire extinguisher under the trade name "Pyrene"
2. in dry cleaning and de-greasing agent.
3. in manufacturing of salicylic acid and freons.
4. as a solvent for fats, oils, etc.
5. in the treatment of tapeworm and hookworm.
6. as an insecticides and fumigant.
7. as a laboratory reagent.

10.6 Haloarenes

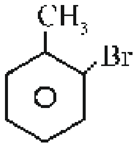
In these compounds halogen atom is directly attached with carbon atom of aromatic ring. These are shown as Ar-X.



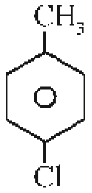
chlorobenzene



iodobenzene

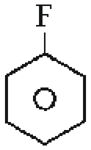


2-bromo toluene

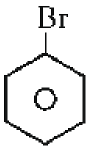


p-chlorotoluene

These compounds are treated as derivatives of benzene for IUPAC nomenlature and prefix of halogen atom is used e.g.



fluorobenzene

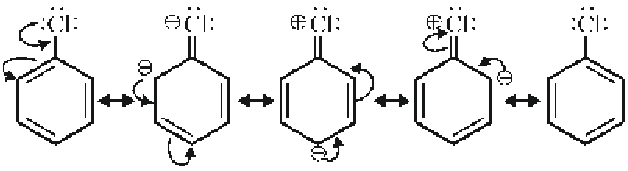


bromobenzene

10.6.1 Nature of C-X bond in haloarenes or arylhalides–

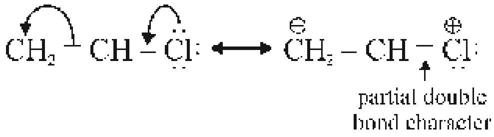
In aryl halides, halogen atom is attached with sp^2 hybrid carbon atom of benzene ring e.g. C_6H_5Cl. Due to +R effect of halogen atom, carbon halogen bond gets partial double bond character. Therefore, it is not broken easily. C-Cl bond length in chlorobenzene is 1.60 Å while bond length of C-Cl single bond is 1.77Å.

Decrease in value of bond length proves the presence of partial double bond character in C-Cl bond. The canonical forms of chlorobenzene can be shown as follows–



Canonical forms of Chlorobenzene (resonating structures)

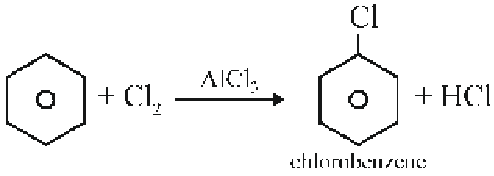
Similarly, vinyl chloride gets, partial double bond character in C-Cl bond. The C-Cl bond length in vinyl chloride is 1.69 Å whereas bond length of C-Cl single bond is 1.77Å. In vinyl chloride, halogen atom is attached to sp^2 hybrid carbon atom, therefore partial double bond character appears due to resonance.

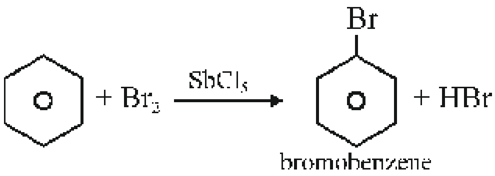


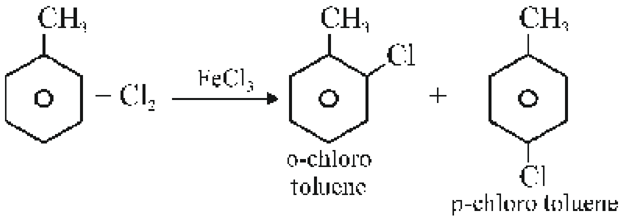
10.6.2 Methods of preparation of haloarenes

1. By halogenation–

(A) Halogenation in benzene ring– Chlorobenzene or bromobenzene is obtained by the chlorination and bormination of benzene. When bromine or chlorine reacts with benzene in presence of anhydrous lewis acids or halogen carrier like $AlCl_3$, $SbCl_5$, $FeCl_3$, etc. gives bromobenzene or chlorobenzene through electrophilic substituion reactions.







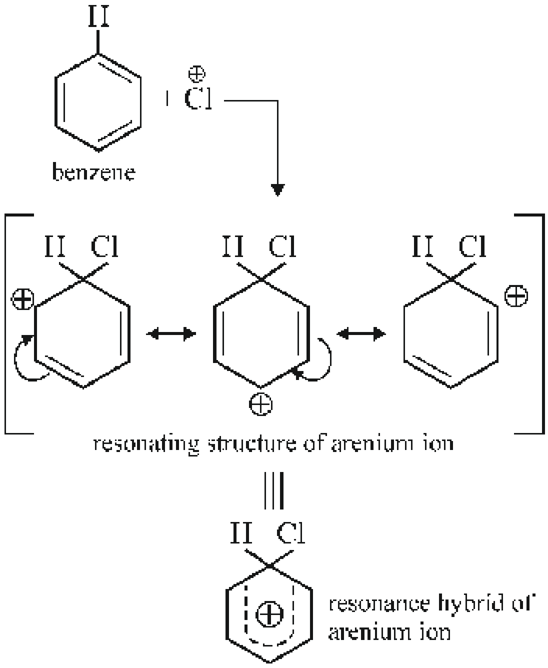
Reaction of iodine with benzene is reversible, hence, oxidising agents (HNO_3, HIO_3) are used to oxidise HI, formed in this reaction.

Mechanism– The mechanism of electrophilic substitution reaction of benzene with chlorine can be explained as follows–

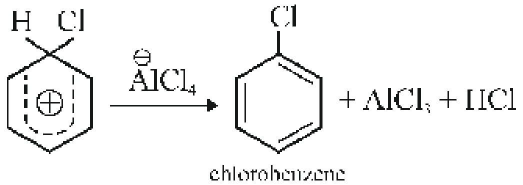
(i) $AlCl_3 + Cl_2 \longrightarrow \overset{\ominus}{AlCl_4} + \overset{\oplus}{Cl}$

chloronium ion (electrophile)

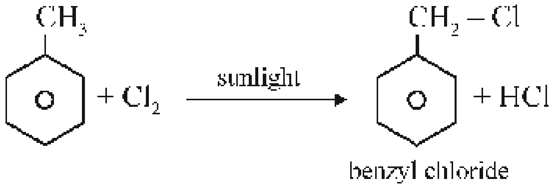
(ii)



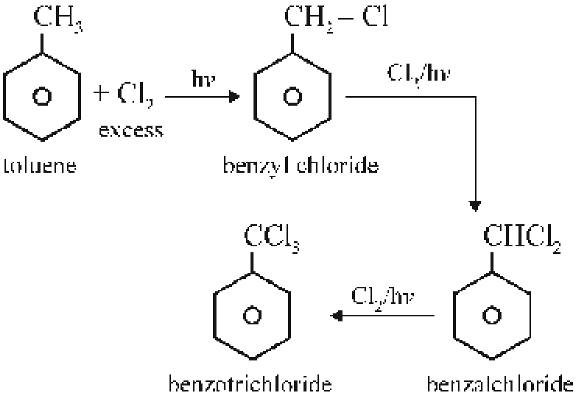
(iii)



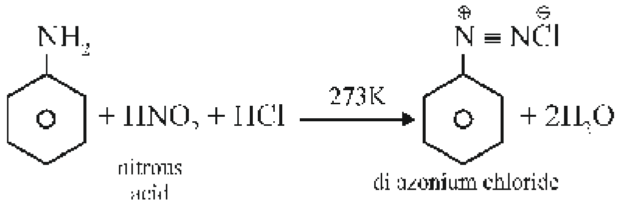
(B) Side chain halogenation– If alkyl benzene reacts with chlorine in absence of halogen carrier and in presence of sun-light, it gives benzly chloride.



If chlorine is used in excess, the benzotrichloride is formed.



2. **From aniline–** In this reaction aniline is intially converted into diazonium salt and it is known as "Diazotization".

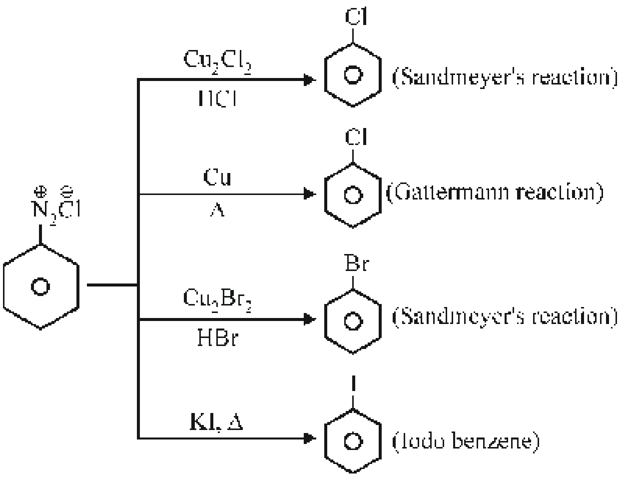


The HNO_2 used here is prepared within the reaction, by the reaction of $NaNO_2 + HCl$.

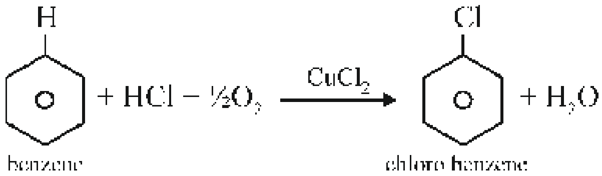
$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$

When benzene diazonium chloride reacts with Cu_2Cl_2 + HCl or Cu_2Br_2 + HBr, it gives chlorobenzene and bromobenzene respectively. It is called **Sandmeyer's Reaction.**

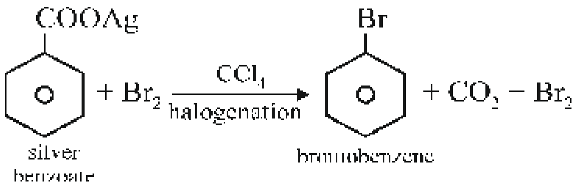
If benzene diazonium chloride is heated with copper powder also gives chlorobenzene and this reaction is called Gattermann Reaction. Iodobenzene is obtained by the reaction of benzene diazonium chloride with KI.



3. **Rasching Process–** It is the industrial method for preparation of chlorobenzene. When a mixture of benzene vapours, air and hydrogen chloride vapours is passed through copper chloride catalyst, it gives chlorobenzene.



4. **By Hunsdiecker Reaction–** When silver salt of monocarboxylic aromatic acids reacts with bromine in presence of CCl_4, it gives bromobenzene by decarboxylative bromination.



10.6.3 Physical properties–

Aryl halides are generally colourless, oily liquid or solid substances. These are insoluble in water but soluble in organic solvents. Density of these compounds is higher than water and possess a characteristic smell. Decreasing order of melting and boiling points of these compounds is as follows–

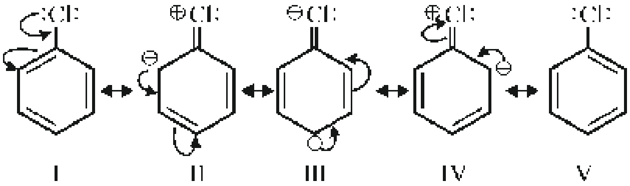
aryl iodide > aryl bromide > aryl chloride > aryl fluoride

10.6.4 Chemical properties–

Haloarenes show four types of reactions–

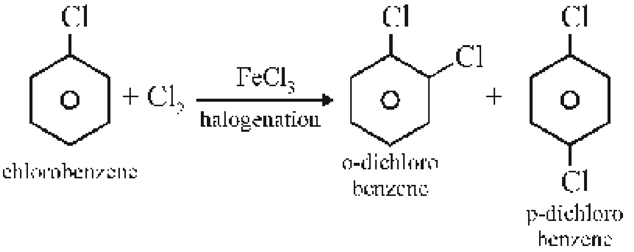
1. Electrophilic substitution reactions on benzene ring.
2. Reactions with metals.
3. Reduction
4. Nucleophilic substitution

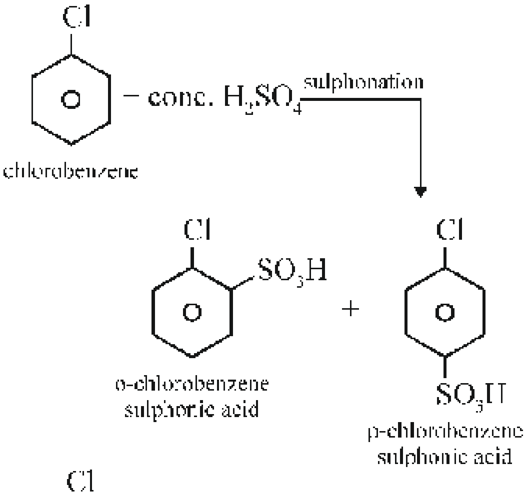
1. **Electrophilic substitution reaction on benzene ring–** The chlorine atom in chlorobenzene shown +R effect. It is ortho and para directing in nature. It directs attacking electrophile at ortho and para-positions. It can be explained by resonance, as follows–

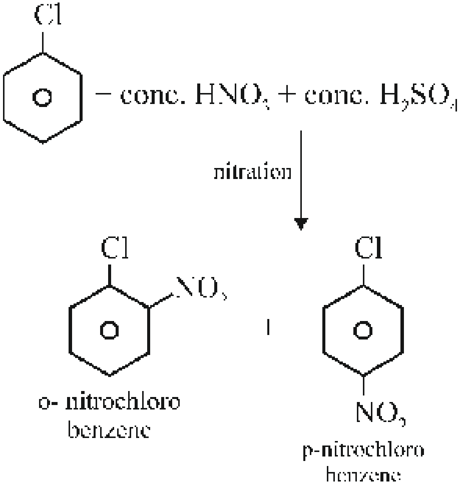


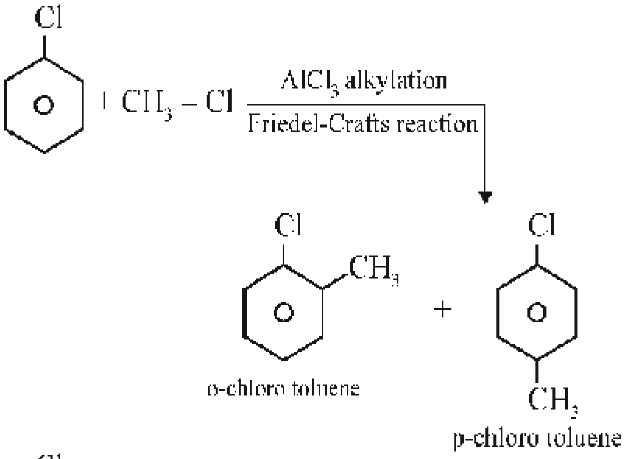
In above II, III and IV structures, negative charge appears at ortho and para positions of chlorine atom, hence, these positions have more electron density in comparison to other positions. This is the cause that attacking electrophile attacks at ortho and para positions. Therefore, o- and p- products are formed.

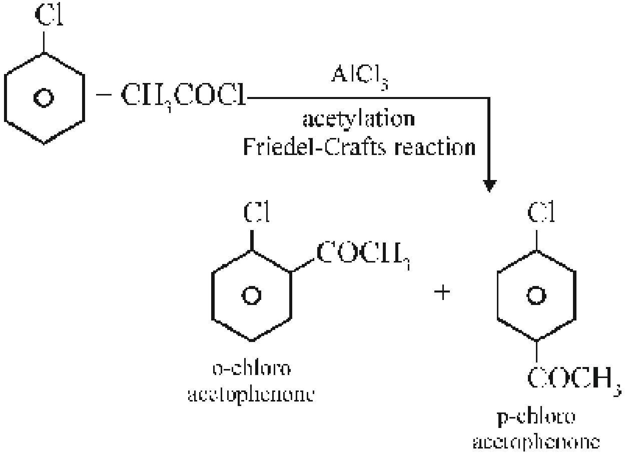
Halobenzene is less reactive than benzene towards electrophilic substitution reactions because -I effect of halo atom decreases electron density on the benzene ring and attack of electrophile becomes difficult. Some electrophilic substitution reactions are given below–

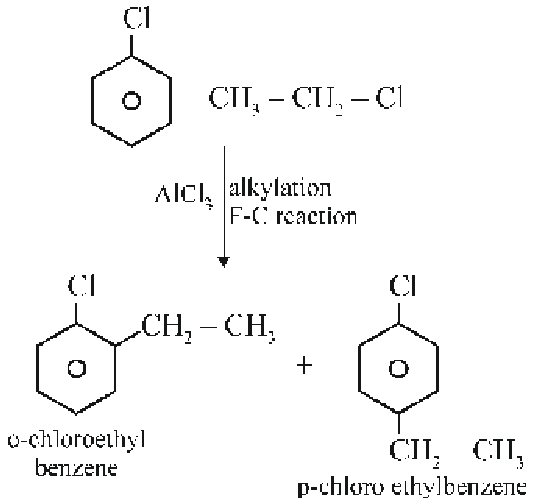






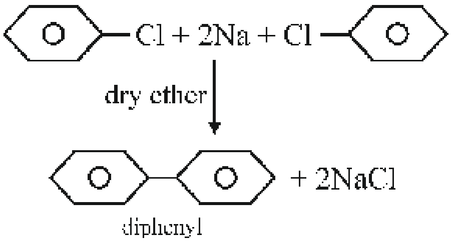




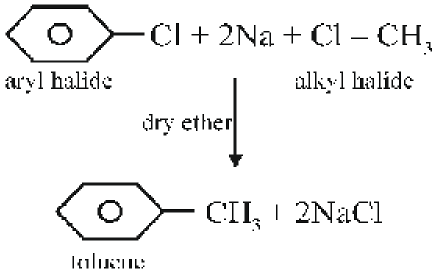


2. Reaction with Metals–

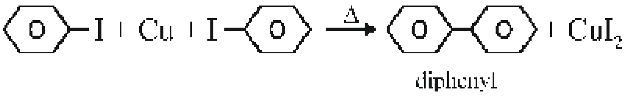
(i) **Reaction with Sodium–** Aryl halides react with sodium, similar to alkyl halide in Wurtz reaction. In this reaction two benzene rings connect to each other by one σ (sigma) bond and diphenyl is formed. It is known as **Fittig Reaction.**



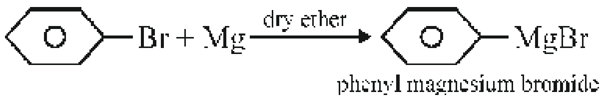
If a mixture of alkyl halide and aryl halide is used here then alkyl benzene is formed. This reaction is known as **Wurtz Fittig Reaction.**



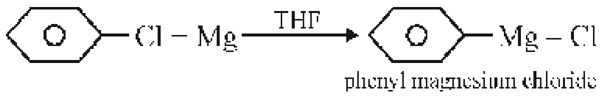
(ii) Reaction with copper metal– Diphenyl is formed if iodobenzene reacts with copper power and reaction is known as **"Ullmann reaction".**



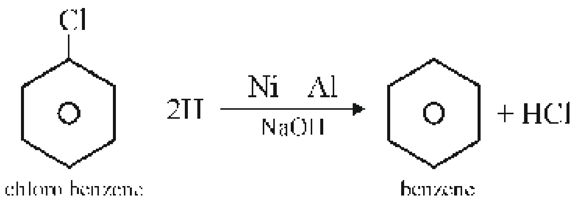
(iii) Reaction with magnesium– Grignard reagent is formed.



Tetrahydrofuran (THF) is used in place of dry ether to form Girgnard reagent from chlorobenzene.



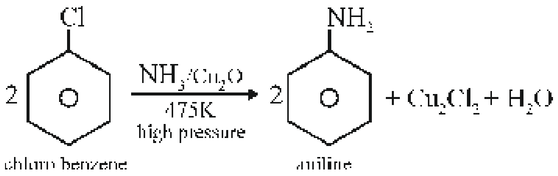
3. Reduction– Chlorobenzene is reduced to benzene by Ni-Al alloy in presence of a base.



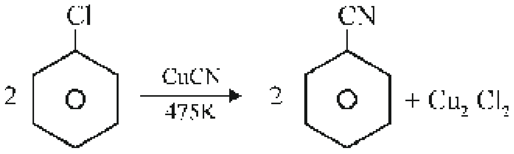
4. Nucleophilic Substitution Reaction– Aryl halides are less reactive than alkyl halides towards nucleophilic substitution reactions because due to resonance there is a partial double bond character in C-X bond and it is not easily broken. Nucleophilic substitution in aryl halide occurs in special condition such as at high temperature.

Some reactions are as follows–

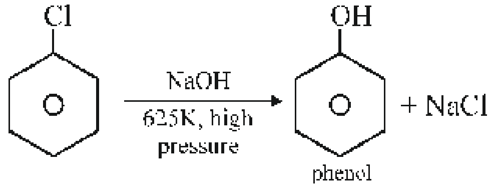
(i)



(ii)



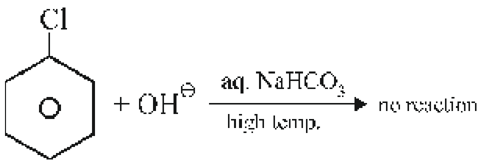
(iii)



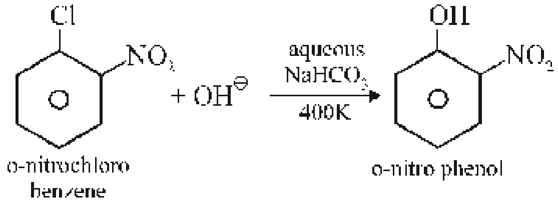
If electron attracting groups such as $-NO_2$, $-SO_3H$, -CN, -COOH, etc. are present at the ortho or para positions or both positions (ortho and para) in chloro-benzene then these groups attract the electron density from benzene ring.

Now benzene ring becomes more reactive towards nucleophilic substitution reactions and these reactions take place even in mild conditions. For example effect of $-NO_2$ group is shown below-

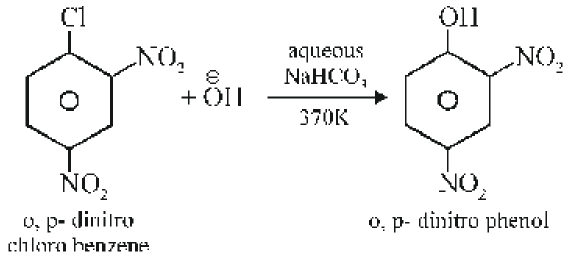
(i)



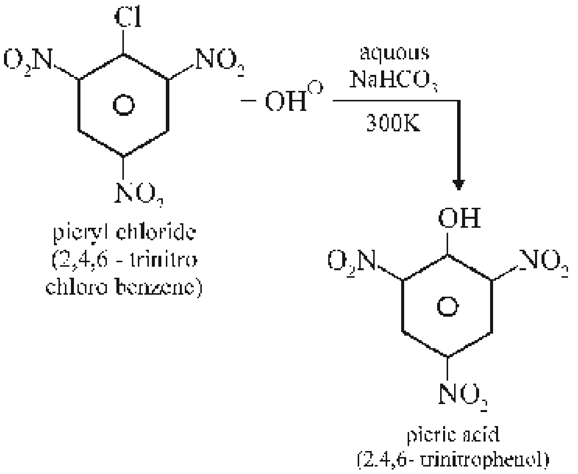
(ii)



(iii)

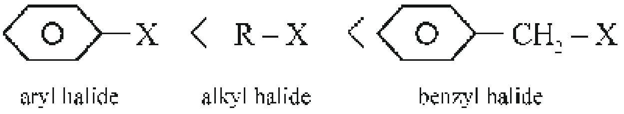


(iv)

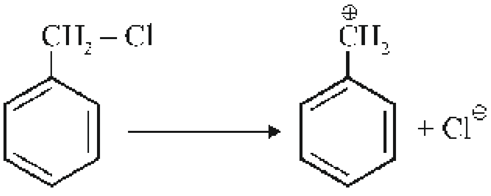


Order of reactivity among halogen derivatives–

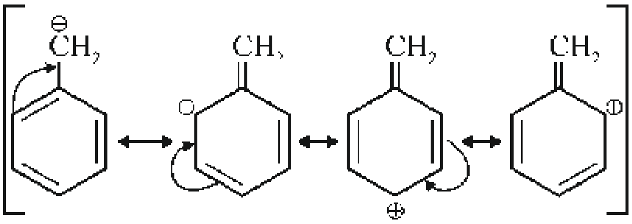
Order of reactivity of monohalogen derivatives towards nucleophilic substitution reactions is as follows–



Benzyl halide give S_N1 type nucleophilic substitution reactions because benzyl carbocation formed during the reaction is stabilised by resonance.



benzyl carbocation



stabilization of benzyl carbocation by resonance

Hence benzyl halides are very much reactive towards nucleophilic substitution reactions.

10.7 Freons

"Freons are poly chlorofluoroalkanes." Compounds in which carbon atom is linked with chlorine and fluorine are known as chlorofluoro carbon (CFC) or freons.

Synthesis of Freons–

Chlorofluoro derivatives of methane and ethane are prepared by the reaction of carbon tetra chloride (CCl_4) and hexachloroethane, respectively with HF in presence of $SbCl_5$.

$$CCl_4 + HF \xrightarrow{SbCl_5} \underset{\text{Freon–11}}{CCl_3F} + HCl$$

$$CCl_3F + HF \xrightarrow{SbCl_5} \underset{\text{Freon–12}}{CCl_2F_2} + HCl$$

$$\underset{\substack{\text{hexachloro}\\\text{ethane}}}{C_2Cl_6} + 2HF \xrightarrow{SbCl_5} \underset{\substack{\text{Freon–112}\\\text{(tetrachloro}\\\text{difluoroethane)}}}{C_2Cl_4F_2} + 2HCl$$

Nomenclature of Freons–

The number of carbon, hydrogen and fluorine atoms present in the molecular formula of freons are used for nomenclature of freons as follows–

Freon - XYZ

Table 10.1 : Nomenclature of some important Freons

Molecular Formula	X	Y	Z	Nomenclature of Freon
$CFCl_3$	0	1	1	Freon–11
CF_2Cl_2	0	1	2	Freon–12
C_2FCl_5	1	1	1	Freon–111
$C_2F_2Cl_4$	1	1	2	Freon–112
$C_2F_3Cl_3$	1	1	3	Freon–113
$C_2F_4Cl_2$	1	1	4	Freon–114

Here, X = One less than the number of carbon atoms in Freon molecule (C-1)

Y = One more than the number of hydrogen atoms in Freon molecule (H+1)

Z = Number of fluorine atoms in Freon molecule.

Properties of Freons– Freons are colourless, odourless, volatile liquids. These ae highly inert and stable even at high temperature and high pressure.

10.7.1 Uses of Freons–

1. Freons are used as inert solvents.
2. Freons are used as refrigerants in refrigerator, airconditioner and cold storages.
3. Freons are used as Aerosol Propellent.

10.7.2 Environmental Impact of Freons–

Depletion of ozone layer is mainly due to Freons. Although ozone gas is toxic but 90% part of ozone layer is in the stratosphere where it acts as life saving gas for us. 95% of harmful ultraviolet rays coming from the sunlight is absorbed by the ozone layer and it protects the earth's atmosphere. Due to excess of UV rays on the earth, following harmful effects are there,

1. Skin cancer increases.
2. Plants are damaged.
3. Population of plankten decreases in photic zone of ocean.
4. Possibility of eye disease called catract increases.
5. Reduces human immunity.

Freons (chlorofluorocarbons) due to their less reactivity reaches in stratosphere, without getting destroyed in troposphere. By reaction with increased ultraviolet rays due to ozone depletion, the atom of chlorine (free radical) becomes free from parent compound.

$$CFCl_3 \xrightarrow{UV} \dot{C}FCl_2 + \dot{C}l \quad \text{Chlorine free radical}$$

Now the atoms of chlorine destroy the ozone molecules by several destruction cycles. In the simplest example of such a cycle, a chlorine atom reacts with an ozone molecule and makes ClO (Chlorine monoxide) by taking its one oxygen atom. chlorine monoxide reacts with another molecule of ozone to give another chlorine atom (free radical) and two oxygen molecule.

$$\dot{C}l + \underset{\text{(ozone)}}{O_3} \longrightarrow \underset{\substack{\text{Chlorine monoxide}\\ \text{(free radical)}}}{\dot{C}lO + O_2}$$

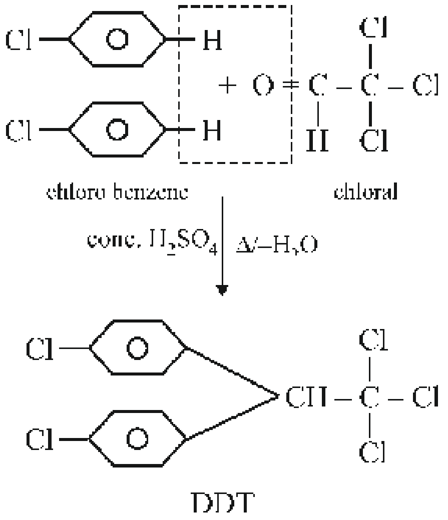
$$Cl\dot{O} + O_3 \longrightarrow \underset{\substack{\text{Chlorine}\\ \text{free radical}}}{\dot{C}l} + 2O_2$$

This chain reaction is a continuous process and only one chlorine atom reacts with one lakh (100000) ozone molecules and destroys them. Thus by decrease in quantity of ozone due to Freon, ozone layer is being depleted and it has been adversely affecting Earth's atmosphere.

To prevent the depletion of ozone layer, the production of gases that damage the ozone layer should be stopped or minimized gradually. Production and use of CFC is decreasing in the whole world. Ozone conservation day is celebrate on 16th september every year to generate awareness about ozone conservation in the public.

10.8 D.D.T. (p, p^1–Dichloro Diphenyl Trichloro Ethane)–

It is prepared by heating the mixture of chlorobenzene and chloral in the presence of sulphuric acid.

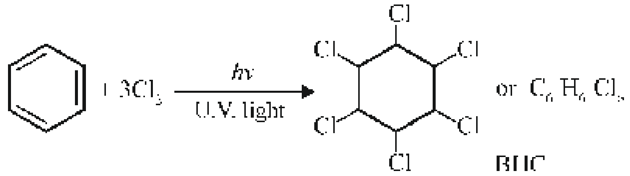


DDT is a white solid compound. It is used as insecticide for controlling mosquitoes, bedbugs, etc.

10.9 B.H.C. (Benzene Hexa Chloride)–

It has many commercial names such as gammaxane, Lindane, 666, etc. Its IUPAC name is 1,2,3,4,5,6-hexachloro-cyclohexane.

It is prepared by reaction of benzene with chlorine in the presence of ultraviolet rays.



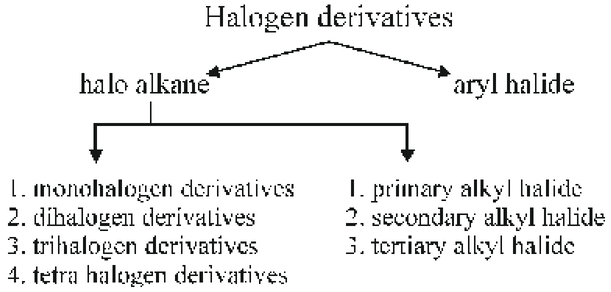
It is a mixture of many isomers (α, β, γ, δ, ε, η and θ) B.H.C. is used as insecticide in agriculture sector. γ-isomer is most reactive as insecticide. Penetrating power of γ-isomer is more in comparison to other isomers due to its relative small size.

10.9.1 Environmental Impact of DDT & BHC–

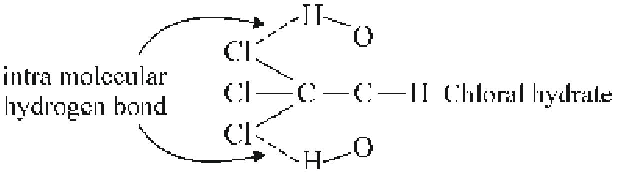
1. DDT and BHC are harmful and toxic substances and do not decompose easily. When these are used in agricultural field as insecticide for crops then these chemicals accumulate gradually in soil and water. These chemicals enter in the human food chain by the means of crops, vegetables, eggs, milk, etc and cause many diseases.
2. **Soil Pullution–** Excess usage of chlorine containing hydrocarbons like DDT and BHC leads to the high accumulation of chemicals in the soil itself and leads to land pollution. Soil pollution decreases the fertility of soil.
3. Some part of the BHC usage enters directly in the soil, 12-30 percent part evaporates and spreads in the environment which returns to earth's surface and depth alongwith water through rains. From here it accumulates in the food chain which is known as bioaccumulation. This is how it harms the living organisms.
4. Nervous system of living organisms is likely to be affected by excess B.H.C.

Important Points

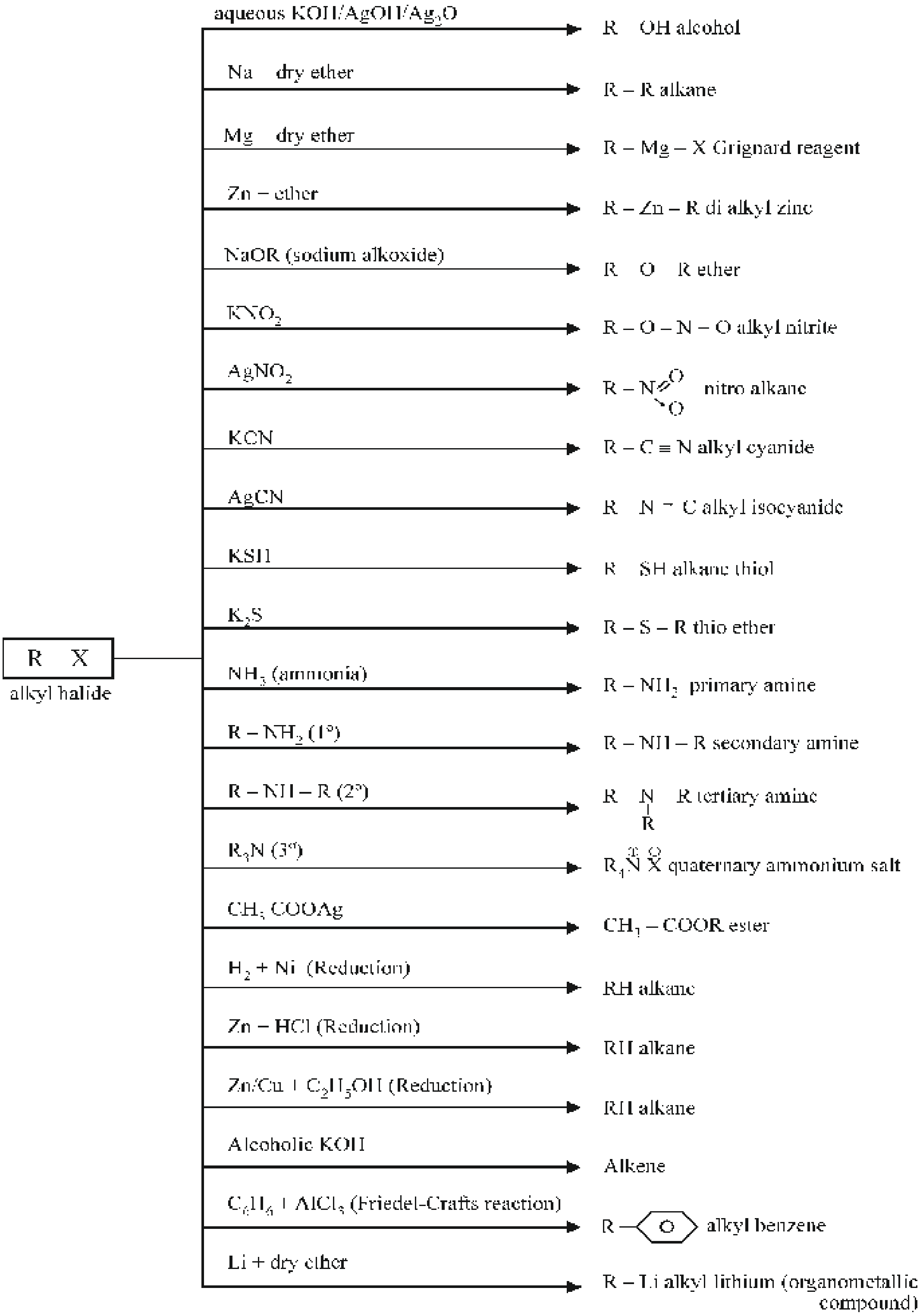
1. Classification–



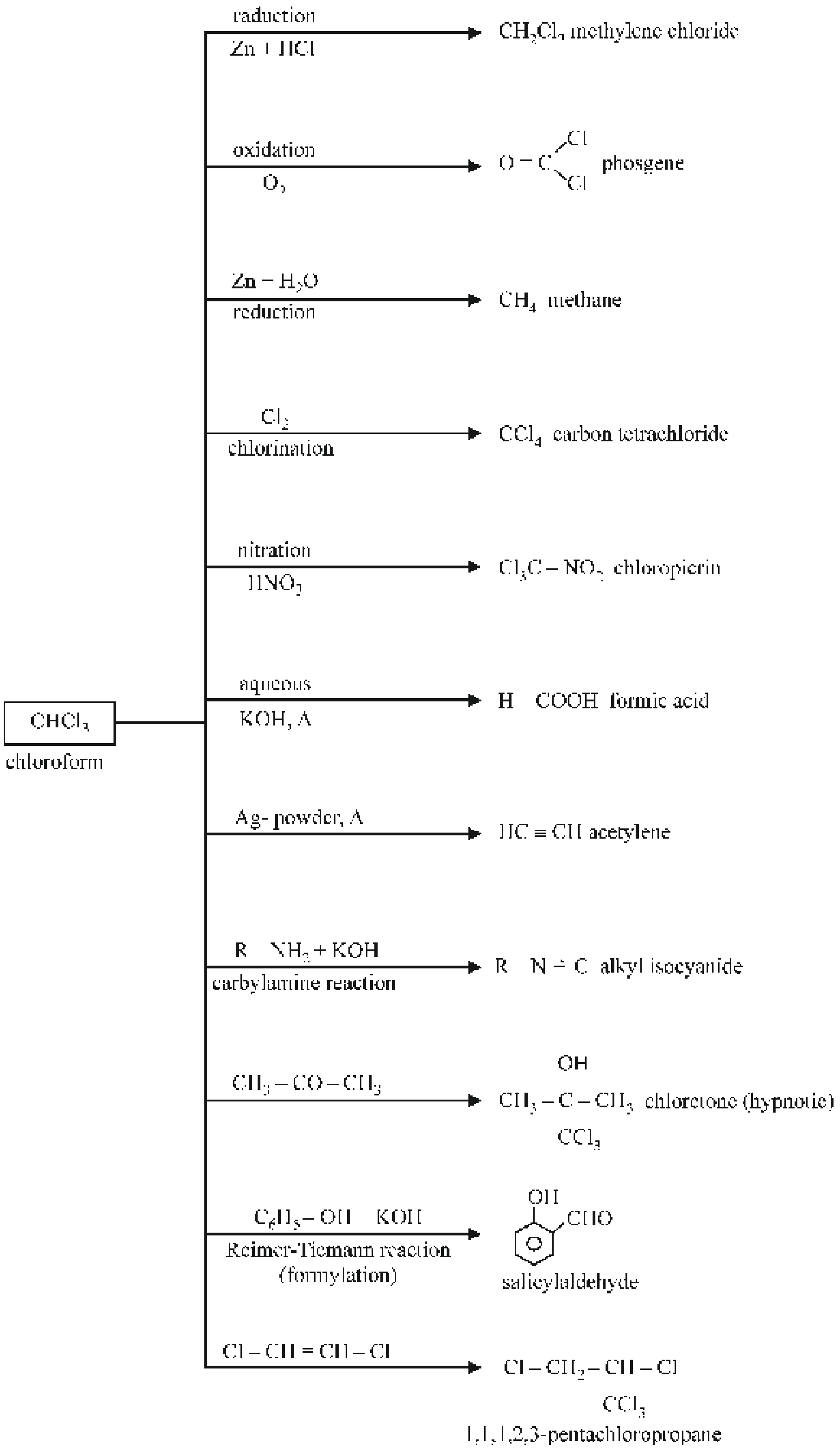
2. C–X bond is polar $(\overset{\delta\oplus}{C}-\overset{\delta\ominus}{X})$ in nature due to large difference in electronegativity of carbon and halogen.
3. The main reactions of alkyl halides are nucleophilic substitution reactions which are classified as S_N1 and S_N2.
4. Aryl halides mainly show electrophilic and nucleophilic substitution reactions.
5. Partial double bond characer is developed in C–X bond due to resonance. So nucleophilic substituion is not easy in aryl halides.
6. Halogen atom is ortho- and para- directing in electrophilic substitution reactions of aryl halides.
7. There are many industrial uses of polyhalogen compounds like Freons, DDT, BHC, but these are harmful to the environment because they do not decompose easily.
8. Although two -OH groups are attached to the same carbon atom in chloral hydrate but it is stable due to intramolecular hydrgoen bonding.



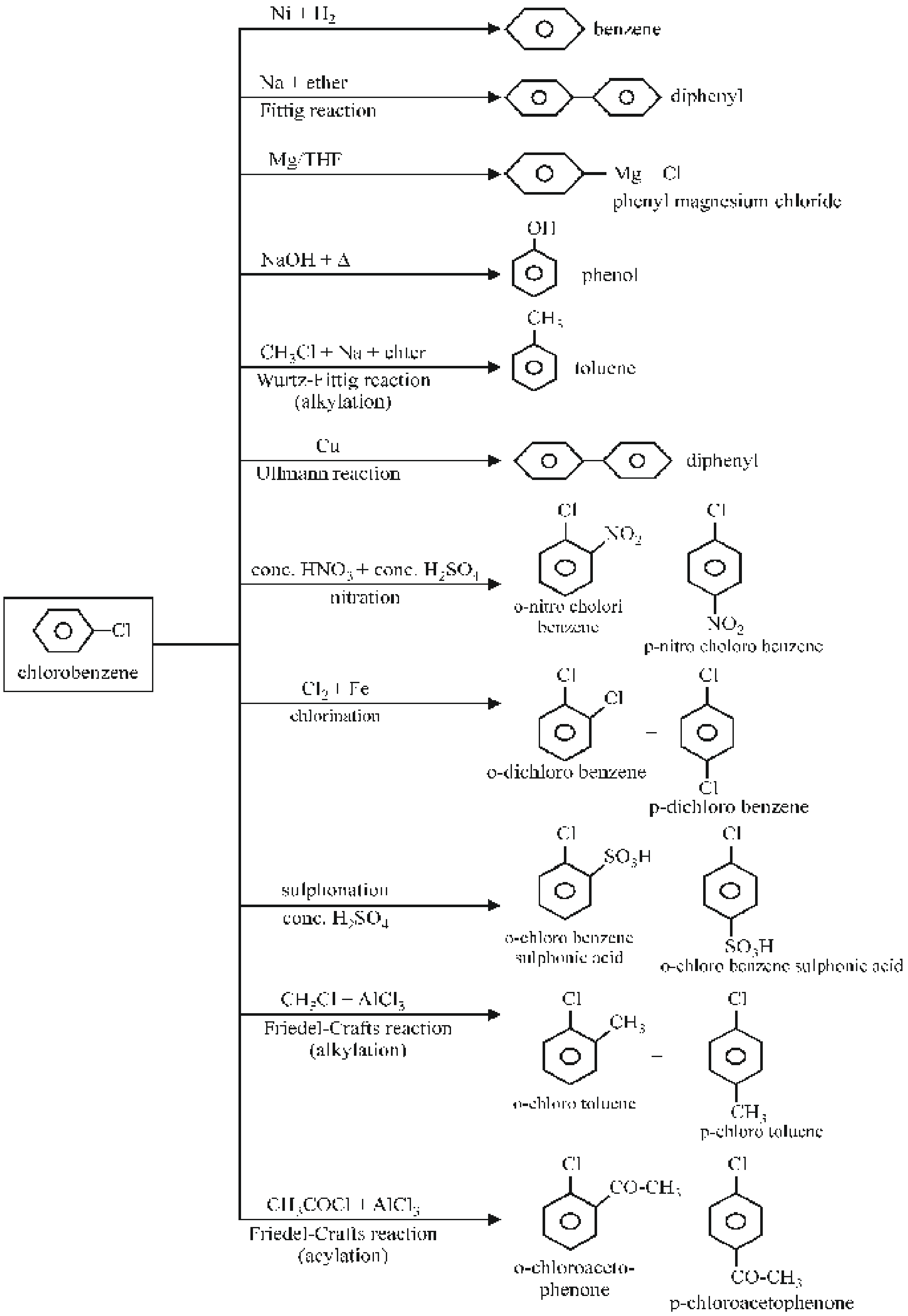
9. Main chemical properties of alkyl halides are as follows–



10. Main chemical properties of chloroform–



11. Taking chlorobenzene as an example we can expalin main properties of halobenzene as follows–



EXERCISE QUESTIONS

Multiple Choice Questions

1. Which of the following compounds show haloform reaction–

(A) Methanol (B) Ethanol

(C) 1–Propanol (D) 1–Butanol

2. What happens in Finkelstein Reaction–

(A) Dehydrohalogenation

(B) Hydrogenation

(C) Halogen Exchange

(D) Oxidation

3. Which is the example of haloarene–

(A) CH_3Cl (B) $C_6H_5CH_2Cl$

(C) $C_6H_6Cl_6$ (D) C_6H_5Cl

4. Which compound gives yellow precipitate with $AgNO_3$–

(A) CHI_3 (B) CH_3I

(C) $CHCl_3$ (D) $CH_3–CH_2I$

5. Which intermediate is formed in carbylamine reaction–

(A) $CN^{(-)}$ (B) $N \equiv C^{(-)}$

(C) $:CCl_2$ (D) $Cl^{(-)}$

6. What is formed in S_N2 reaction–

(A) Transition state (B) Carbonium ion

(C) Carbanion (D) Free radical

7. Which of the following compound has zero dipole moment–

(A) CH_3Cl (B) $CHCl_3$

(C) CCl_4 (D) CHI_3

Very Short Answer Questions

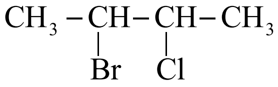
8. Write full name for DDT and BHC.

9. Write name and formula of any one tertiary alkyl halide.

10. Write name and formula of one alcohol and one ketone which gives haloform reaction.

11. Which reagent is used to prepare methanol from methyl chloride.

12. Write IUPAC name of



$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$

13. Give example of any three nucleophiles and one electrophile.

14. which compound is used as fire extinguisher.

15. Write the formula of DDT and BHC.

16. Write down the probable dichloro derivatives of propane.

17. Write Hunsdiecker reaction.

18. Write formula and uses of chloropicrin and chloretone.

19. Which is the best reagent to obtain pure chloroform.

20. Which gas is formed when chloroform is left open in the air.

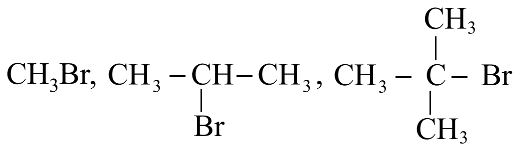
21. Out of methyl chloride and methyl iodide, which is more reactive.

22. Write the stucture of C_5H_{12} which gives only one monochloro derivatie.

23. What is the use of DDT.

24. Write two examples of secondary alkyl halide.

25. Arrange the following in the orer of increasing reactivity towards S_N1 reaction–



$CH_3Br,\ CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3,\ CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-Br$

Short Answer Type Questions

26. C_6H_5Cl is less reactive than C_2H_5Cl towards nucleophilic substitution reactions. Explain.

27. How Grignard reagent is prepared by ethyl bromide.

28. Write down the chemical equation for preparation of BHC.

29. How are following obtained from chlorobenzene.

(a) Phenol (b) Diphenyl

(c) Toluene

30. Explain β- elimination.

31. Write down mechanism of Hoffmann carbyl amine reaction.

32. How are following obtained from chloroform–
    (A) Acetylene
    (B) CCl_4
    (C) Salicylaldehyde

33. Write down four uses of carbon tetra chloride.

34. How are the followings obtained from aniline
    (a) Chlorobenzene
    (b) Bromobenzene
    (c) Iodobenzene

35. Write the chemical formula of followings–
    (a) Freon–11
    (b) Freon–12
    (c) Freon–111

36. What happens when–
    (a) Ethyl bromide reacts with silver cyanide
    (b) Iodoform is heated with silver powder

37. Why benzyl chloride is more reactive than chlorobenzene.

Long Answer Questions

38. Explain following–
    (A) Classification of halogen derivatives
    (B) Nature of C–X bond in halogen derivatives.
    (C) Directional nature of halogen atom in haloarenes.

39. How will you obtain from the following–
    (A) Alkyl halide from alcohol.
    (B) Alkyl halide from halogen exchange
    (C) Chloroform from acetone
    (D) Salicylic acid from CCl_4.

40. Write a note on following–
    (A) Haloform Reaction
    (B) Carbylamine Reaction
    (C) Darzen's Reaction
    (D) Sandmeyer's Reaction

41. Explain the Mechanism of S_N1 and S_N2.

42. Write short notes on following–
    (i) Freon
    (ii) D.D.T.
    (iii) B.H.C.

43. Explain the electrophilic and nucleophilic substitution reactions of chlorobenzene.

44. How will you obtain following from alkyl halide.
    (i) Alkyl isocyanide
    (ii) Alkyl cyanide
    (iii) Nitroalkane
    (iv) Alkyl nitrite
    (v) Isopropyl benzene
    (vi) Tetramethyl ammonium chloride

Answers (Multiple Choice Questions)

1.	(B)	2.	(C)	3.	(D)
4.	(A)	5.	(C)	6.	(A)
7.	(C)				

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