HALOALKANES AND HALOARENES

1. NOMENCLATURE

Compounds derived from hydrocarbons by the replacement of one or more hydrogen atom(s) by the corresponding number of halogen atom(s) are known as halogen derivatives. The halogen derivatives are classified on the basis of nature of hydrocarbon from which they are obtained as

(i) Alkyl halides(Haloalkanes) : Halogen derivative of alkanes.

(ii) Alkenyl halides : Halogen derivative of alkenes.

(iii) Alkynyl halides : Halogen derivative of alkynes.

(iv) Aryl halides : Halogen derivative of arenes.

In Alkyl halides, the halogen atom(s) is(are) attached to the sp^{3-} hybridized carbon atom(s) of an alkyl group whereas in Aryl halides, the halogen atom(s) is(are) attached to sp^{2-} hybridized carbon atom(s) of an aryl group.

Alkyl halides are further classified as

(i) **Mono halides :** These involve replacement of one H atom by halogen atoms i.e., $C_9H_{2n+1}X$.

CH_3Cl : methyl chloride or chloromethane

C_2H_5Cl : ethyl chloride or chloroethane

(ii) **Di halides :** These involve replacement of two H atoms by halogen atoms i.e., $C_8H_{2n}X_2$

CH_2X_2: methylene halide

CH_2X
|
CH_2X: ethylene dihalide or vicinal dihalides

CH_3
|
CHX_2 : ethylidene dihalide or geminal dihalides

(iii) **Tri halides :** These involve replacement of three H atoms by halogen atoms i.e. $C_nH_{2n-1}X_3$ e.g.,

CHX_3 : trihalo methane or haloform

(iv) **Tetra halide :** These involve replacement of four H atoms by halogen atoms i.e. $C_nH_{2n-2}X_4$ e.g., CCl_4.

Monohalides or Alkyl halides

(1) General formula $C_nH_{2n+1}X$ e.g., CH_3X, C_2H_5X, ...

(2) Mono halides are further classified as

(A) Primary halides : Halogen atom attached on 1° carbon or methyl carbon

e.g. CH_3X : halomethane or methyl halide

CH_3CH_2X : haloethane or ethyl halide

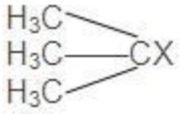
$CH_3CH_2CH_2X$: 1-halopropane or n-propyl halide

(B) Secondary halides : Halogen atoms are attached on 2° carbon atom

CH_3CHXCH_3 : 2-halopropane or sec. propyl halide or isopropyl halide

$CH_3CHXCH_2CH_3$: 2-halobutane or sec. butyl halide

(C) Tertiary halides : Halogen atoms are attached on 3° carbon atom



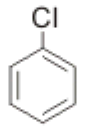
: 2-methyl, 2-halopropane or t.butyl halide

(d) Aromatic halogen compounds:

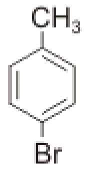
These are obtained by replacement of one or more hydrogen atoms of an aromatic hydrocarbon by an equal number of halogen atoms. These have been further classified into the following two major categories:

(**1) Nuclear halogen derivatives:**

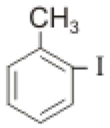
Halogen derivatives of aromatic hydrocarbons in which the halogen atom(F, Cl, Br or I) is directly attached to an aromatic ring are called aryl halides. Their general formula is $Ar - X$. Some examples of ary halides are:



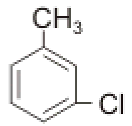
Chlorobenzene



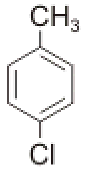
1 – Bromo–
4 – methylbenzene
or 4 – Bromotoluene
(p–Bromotoluene)



2 – Iodo – 1 – methylbenzene
or 2 – Iodotoluene
(o–Iodotoluene)



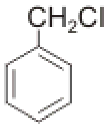
1– Chloro – 3 – methylbenzene
or 3–Chlorotoluene
(m–Chlorotoluene)



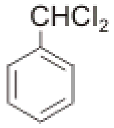
1 – Chloro –
4 – methylbenzene
or 4–Chlorotoluene
(p–Chlorotoluene)

(2) Side chain halogen derivatives:

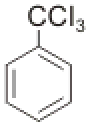
Aromatic hydrocarbons in which the halogen atom is linked to one of the carbon atoms of the side chain carrying the aryl group are called aralkyl halides. For example,



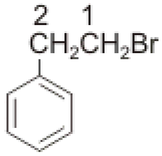
1 – Chloro–1–
phenylmethane
(Benzyl chloride)



1, 1 – Dichloro–
1 – phenylmethane
(Benzal dichloride)



1, 1, 1–Trichloro–1–
phenylmethane
(Benzotrichloride)



1–Bromo–2–phenylethane
(β–Phenylethyl bromide)

Like alkyl halides, aralkyl halides are very reactive and thus undergo a number of substitution reactions. On the other hand, aryl halides are far less reactive and thus undergo only a few substitution reactions and that too under drastic conditions.

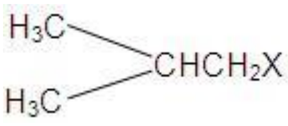
2. ISOMERISM :

Alkyl halides show chain and position isomerism e.g.

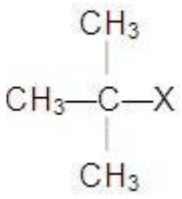
C_3H_7Cl : $CH_3CH_2CH_2X$ and CH_3CHXCH_3 are position isomers.

1-halopropane 2-halopropane

C_4H_9Cl : (a) $CH_3CH_2CH_2CH_2X$: n-butyl halide or 1-halobutane

(b)  iso-butyl halide or 1-halo, 2-methylpropane

(c) $CH_3CH_2CHXCH_3$: sec. butyl halide or 2-halobutane

(d) 

$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-X$$

tert-butyl halide or 2-halo, 2-methylpropane

a & b are chain isomers.

a & c are position isomers.

a & d are chain as well as position isomers.

b & c are chain isomers as well as position isomers.

b & d are position isomers.

c & d are chain isomers.

Note :

(i) n-propyl halide and isopropyl halide are position isomers where n-butyl halide and isobutyl halide are chain isomers.

(ii) Isopropyl halide is 2° halide whereas isobutyl halide is 1° halide

(iii) Secondary butyl halide possesses asymmetric carbon atom and thus shows optical isomerism.

$CH_3CH_2{}^{*}CHXCH_3$ $^{*}C$=Asymmetric carbon atom

3. NATURE OF THE C – X BOND:

Due to electronegativity difference between the carbon and the halogen, the shared pair of electron lies closer to the halogen atom.

As a result, the halogen carries a small negative charge, i.e. $\delta -$ while the carbon carries a small positive charge, i.e. $\delta +$. Consequently C – X bond is a polar covalent bond.

Since the size of halogen atom increases as we move down the group in the periodic table, fluorine atom is the smallest and iodine the largest. Consequently, the carbon-halogen bond length increases and bond enthalpy decreases from C – F to C – I.

Further, as we move from F to I, the electronegativity of the halogen decreases, therefore, the polarity of the C – X bond and hence the dipole moment of the haloalkane should also decrease accordingly. But the dipole moment of CH_3F is slightly lower than that of CH_3Cl. The reason being that although the magnitude of –ve charge on the F atom is much higher than that on the Cl atom but due to small size of F as compared to Cl the C – F bond distance is so small that the product of charge and distance, i.e., dipole moment of CH_3F turns out to be slightly lower than that of CH_3Cl.

3.1 Dipole moments:

Haloalkanes: Hence, the actual order of dipole moment of haloalkanes is CH_3Cl(1.860 D) > CH_3F (1.847 D) > CH_3Br(1830 D) > CH_3I(1.636D).

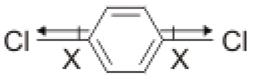
Haloarenes: Fluorobenzne (1.60 D), chlorobenzene (1.69 D) and bromobenzene (1.70 D) have lower dipole moments than the corresponding methyl halides. Iodobenzene, however, has higher dipole moment (1.70 D) than CH_3I (1.636 D). The lowest dipole moment of fluorobenzene is probably due to its small size.

Amongst isomeric dichlorobenzenes, the p-isomer being symmetrical has zero dipole cancel each other. The dipole moments of the o- and m-isomer decreases as the angle between the two halogen atoms increases in accordance with parallelogram law of forces, i.e.,

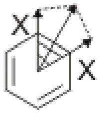
$$\mu = \sqrt{X^2 + X^2 + 2X^2 cos\theta}$$

Where X is the dipole moment of a C – Cl bond.

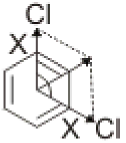
Thus, o-isomer with a bond angle of 60° between the two chlorine atoms has the highest dipole moment (2.54 D) while the m-isomer with a bond angle of 120° between the two chlorine atoms has a dipole moment of 1.72 D which is approximately equal to that of the chlorobenzene (1.69D).



p-Dichlorobenzene
(μ = 0 D)



o-Dichlorobenzene
(μ = 2·54 D)



m-Dichlorobenzene
(μ = 1·72 D)

4. MONOHALIDES

4.1 Preparation of Monohalides:

(1) By direct halogenations of alkanes :

$$R - H + X_2 \xrightarrow[\text{or heat}]{\text{U.V.light}} R\text{-}X + HX$$

(2) By the addition of HX on alkenes :

$RCH{=}CHR + HX \rightarrow RCH_2\text{-}CHXR$

$CH_2{=}CH_2 + HX \rightarrow CH_3\text{-}CH_2X$

$CH_3CH{=}CH_2 + HX \rightarrow CH_3CHXCH_3$ (Acc. to Markownikoff rule).

(3) By alcohols :

(a) Action of halogen acids :

$$R\text{—}OH + HCl_g \text{ or } HCl_{conc} \xrightarrow[\text{primary and secondary alcohols}]{} \underset{\text{ZnCl}_2 \text{ is needed for}}{} RCl + H_2O$$

$$R\text{—}OH + \underset{48\%}{HBr} \xrightarrow[\text{needed for primary alcohols}]{ZnCl_2 \text{ or } H_2SO_4 \text{ is}} RBr$$

$$R\text{—}OH + \underset{57\%}{HI} \rightarrow RI$$

The reactivity order for alcohols is: tertiary > secondary > primary alcohol

The reactivity order for halogen acid is: HI > HBr > HCl

Note : Bromides and iodides are also obtained as :

$$ROH + KBr + H_2SO_4 \xrightarrow{\Delta} RBr + KHSO_4 + H_2O$$

$$ROH + KI + H_2SO_4 \xrightarrow{\Delta} RI + KHSO_4 + H_2O$$

(b) Action of phosphorus halides :

$3ROH + PCl_3 \rightarrow 3RCl + H_3PO_3$

$ROH + PCl_5 \rightarrow RCl + POCl_3 + HCl$

Note : PBr_3 & PI_3 being less stable & thus for bromides & iodines, $P + Br_2$ or $P + I_2$ mixture is used.

(c) Action of thionyl chloride : or Darzen's method

$$R{-}OH + SOCl_2 \xrightarrow{pyridine} R{-}Cl + SO_2\uparrow + HCl\uparrow$$

Note : $SOBr_2$ is less stable & SOI_2 does not exist and thus bromides & iodides are prepared by this method.

4. Borodine-Hunsdicker reaction: Alkyl chlorides and alkyl bromides are obtained by the action of Cl_2 or Br_2 in CCl_4 on silver salt of the fatty acids. The reaction proceeds through free radical mechanism.

$$\underset{\text{(in xylene)}}{RCOOAg} + \underset{(Cl_2 \text{ or } Br_2)}{X_2} \rightarrow R{-}X + CO_2 + AgX$$

Note :

1. The yield of alkyl halide is primary > secondary > tertiary.
2. Hunsdiecker reaction is used to reduce the length of carbon chain (descent of series).

3. Only bromides are obtained in good yield in this reaction. The chlorides can also be obtained by this reaction but the yield is poor. Iodides however cannot be obtained because these form esters with silver salts.

$$2RCO_2Ag + I_2 \rightarrow RCO_2R + CO_2 + 2AgI$$

This reaction is called Birnbaum-Simonini reaction.

5. By halide exchange : Iodides are usually prepared by this method. The halogen exchange reaction is called Finkelstein reaction.

$$R{-}Cl \text{ or } RBr \xrightarrow[\text{Acetone}]{NaI} R{-}I$$

6.Flourination of organic halides: This method is used to prepare fluorides.

$$2CH_3Cl + Hg_2F_2 \rightarrow 2CH_3F + Hg_2Cl_2$$

The reaction is known as Swart reaction.

4.2 Physical Properties of Monohalides:

1. Physical state :

(a) CH_3Cl, C_2H_5Cl, CH_3Br only are gases at room temperature. The alkyl halides up to C_{18} are colourless liquids, while higher are colourless solids.

(b) The b.pt of halides shows following order :

alkyl iodide > alkyl bromide > alkyl chloride (for a given alkyl gp.)

methyl halide < ethyl halide < propyl halide (for a given halide)

1^o halide > 2^o halide > 3^o halide (for a given halide and alkyl gp)

2. Alkyl fluorides & alkyl chlorides are lighter than water, alkyl bromides and alkyl iodides are heavier than water. The density of halides thus follow the order : iodide > bromide > chloride > fluoride.

3. Alkyl halides are soluble in organic solvents but insoluble in water.

4. Alkyl halides burn on Cu wire with green edge flame. This is Beilstein test for halogens. The green or blue colour to flame is due to interaction of halogens with Cu wire.

It is often possible to distinguish between chlorine, bromine and iodine. Chlorine gives a green color to the flame. The color from a bromine compound is usually more blue than that from chlorine. Iodine compounds usually give an unmistakable blue flame.

5. Alkyl iodides are less stable and darken their colour on exposure to light on standing due to adsorption of liberated iodine.

$$2RI \xrightarrow{hv} R\text{-}R + I_2$$

4.3 Chemical properties of monohalides:

The reactions of haloalkanes may be divided into the following three categories:

1.Nucleophilic substitution reactions

2.Elimination reactions

3.Reactions with metals

(1).Nucleophilic substitution reactions:

(a) The alkyl halides are highly reactive due to the high electronegativity difference between carbon & halogen atom which provides polarity in $C^{+\delta}$ - $X^{-\delta}$ bond & thus carbon atom of C-X bond is easily attacked by a nucleophile to show nucleophilic substitution.
$R\text{-}X + :Nu \rightarrow R\text{-}Nu + X:$
The nucleophilic substitution may follow S_N1 or S_N2 mechanism.

(b) Furthermore the reactivity order of alkyl halide is :

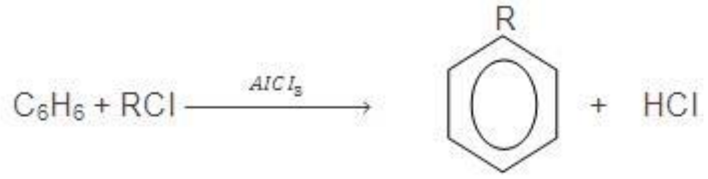
R-I > R-Br > R-Cl > R-F

The reactivity does not follow the polarity order of bond. On the contrary it has been explained in terms of increasing bond length of C-X bond (maximum in C-I) which gives rise to lower bond energy and thus less stability to C-C bond.

(c) The reactivity order for given alkyl halide also shows the order :
3^o halide > 2^o halide > 1^o halide
This has been explained in terms of +ve inductive effect of alkyl groups which increases the polarity of C-X bond & thereby making it more reactive.

(d) Primary alkyl halides undergo reactions by S_N2 mechanism. The presence of bulky groups in primary halides (inspite of more +ve I.E.) cause steric hindrance & bring them less reactive towards.
S_N2 mechanism : $CH_3X > C_2H_5X > C_3H_7X$

(i) Friedel-Crafts reaction : Alkyl halides react with benzene in presence of anhydrous $AlCl_3$ to form homologues of C_6H_6.



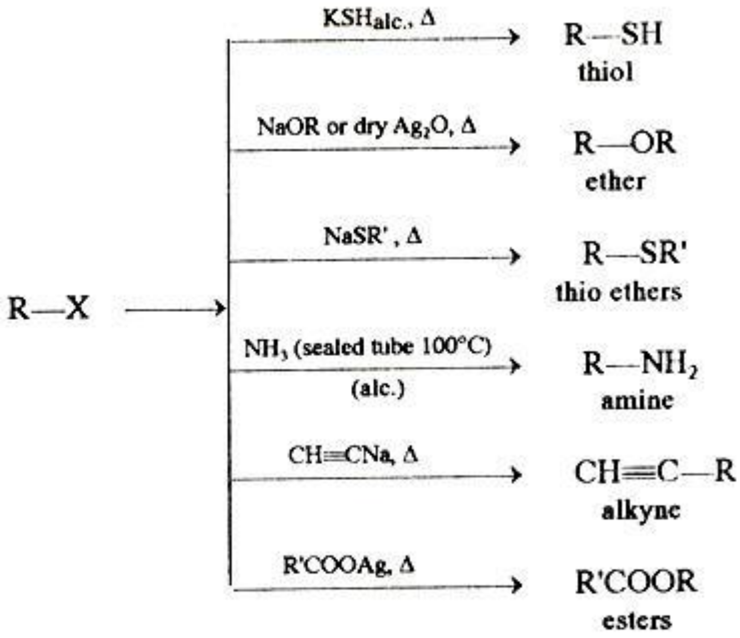
(ii) Action of halogen :

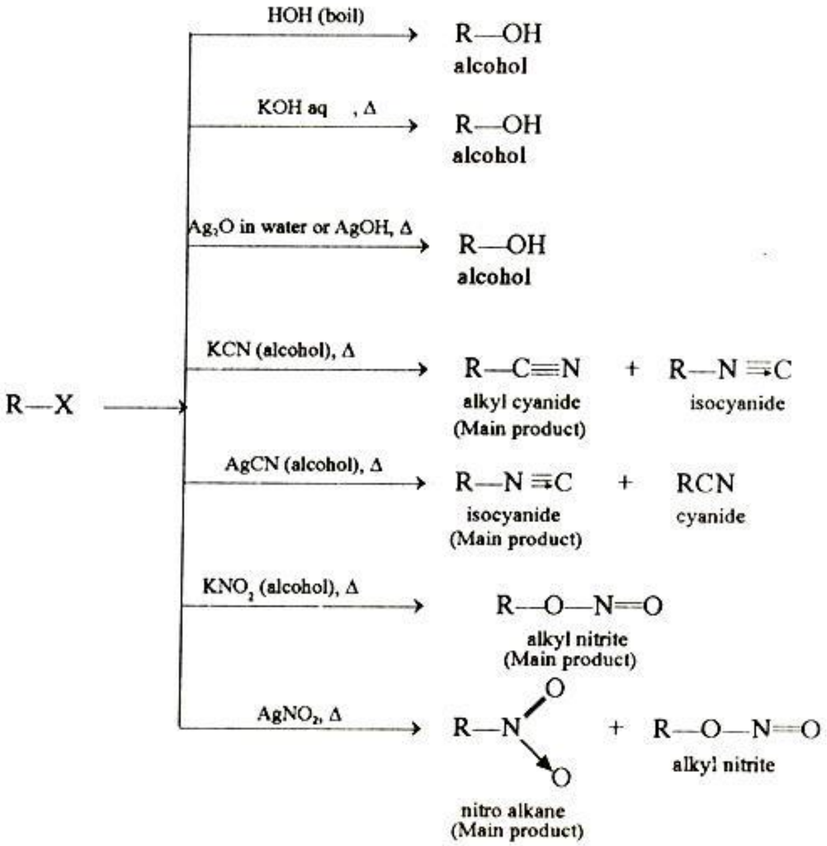
$$CH_3X + X_2 \xrightarrow[\text{u.v. light}]{hv.} CH_2X_2 \xrightarrow{X_2} CHX_3 \xrightarrow{X_2} CX_4$$

Note : C_2Cl_6 (hexachloroethane) is a solid and is known as artificial camphor.

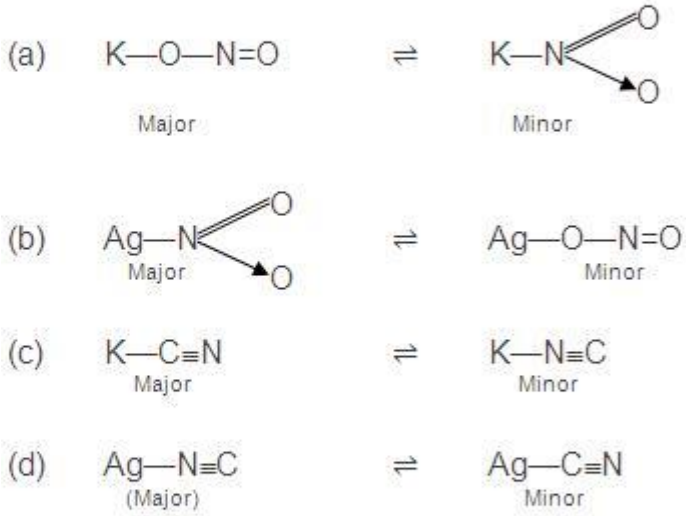
(iii) Reduction : $R\text{-}X + 2H \xrightarrow{\text{Reducing agent}} R\text{-}H + HX$

(iv) Other nucleophilic substitution on alkyl halides : Halogen atom of alkyl halides is easily replaced by other nucleophiles to give a large variety of S_N reactions.


R—X
KSHalc., Δ
R—SH
thiol
NaOR or dry Ag₂O, Δ
R—OR
ether
NaSR', Δ
R—SR'
thio ethers
NH₃ (sealed tube 100°C)
(alc.)
R—NH₂
amine
CH≡CNa, Δ
CH≡C—R
alkyne
R'COOAg, Δ
R'COOR
esters


R—X
HOH (boil)
R—OH
alcohol
KOH aq , Δ
R—OH
alcohol
Ag₂O in water or AgOH, Δ
R—OH
alcohol
KCN (alcohol), Δ
R—C≡N + R—N⇄C
alkyl cyanide
(Main product)
isocyanide
AgCN (alcohol), Δ
R—N⇄C + RCN
isocyanide
(Main product)
cyanide
KNO₂ (alcohol), Δ
R—O—N=O
alkyl nitrite
(Main product)
AgNO₂, Δ
R—N(O)→O + R—O—N=O
nitro alkane
(Main product)
alkyl nitrite

Note : The two products formed on reaction of R-X with KNO_2 and $AgNO_2$ as well as with KCN and AgCN are due to tautomerism in these molecules.



2.Elimination reactions:

(i) Dehydrogalogenation : An α, β-elimination of HX by KOH alc.

$$CH_3CH_2X \xrightarrow[-HX,\ \Delta]{KOH_{alc},\ or\ NaNH_2} CH_2{=}CH_2$$

$$CH_3CHXCHCH_3 \xrightarrow[-HX]{KOH_{alc},} \underset{\text{Minor}}{CH_2{=}CHCH_2CH_3} + \underset{\text{Major}}{CH_3{-}CH{=}CHCH_3}$$

(Acc. to Saytzeff rule)

(ii) Action of heat : $RCH_2CH_2X \xrightarrow[300^oC]{} RCH{=}CH_2 + HX$

3.Reactions with metals :

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

(b) $$2C_2H_5Br + \underset{\text{(powder)}}{2Zn} \xrightarrow[\Delta]{\text{ether}} \underset{\text{diethyl zinc}}{(C_2H_5)2Zn} + ZnBr_2$$

(c) $$4C_2H_5Br + \underset{\text{sodium-lead alloy}}{4Pb(Na)} \rightarrow \underset{\substack{\text{tetra ethyl lead} \\ \text{(an antiknock compounds)}}}{(C_2H_5)_4Pb} + 4NaBr + 3Pb$$

(d) $$2C_2H_5Br + \underset{\text{sodium amalgam}}{Hg(Na)} \rightarrow (C_2H_5)_2Hg + NaBr$$

(e) Wurtz reaction :

$$2RX \xrightarrow[\text{dry ether}]{2Na} R{-}R + 2NaX$$

$$2RX \xrightarrow[\text{Frankland reaction}]{Zn} R{-}R + ZnX_2$$

4.4 Uses of monohalides:

(i) As alkylating agent i.e. to introduce alkyl gp in a molecule.

(ii) Lower members are used as unaesthetic agent, refrigerant and solvents.

(iii) As synthetic reagent.

5. DIHALIDES:

(i) Two H atoms of alkanes are replaced by two halogen atoms to form dihalides.

(ii) General formula $C_nH_{2n}X_2$.

(iii) Dihalides are classified as :

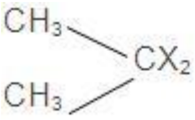
(a) Gem dihalides :

(i) The term gem has derived from geminal meaning for same position.

(ii) The two similar halogen atoms are attached to same carbon atom e.g.

CH_3CHX_2 ethylidene dihalide or 1, 1-dihaloehtane

$CH_3CH_2CHX_2$ propylidene dihalide or 1, 1-dihalopropane



isopropylidene dihalide or 2, 2-dihalopropane

(b) vic dihalides :

(i) The term vic has been derived from vicinal meaning for adjacent carbon atoms.

(ii) The two halogens are attached one each on adjacent carbon atoms e.g.

CH_2XCH_2X ethylene dihalide or 1, 2-dihaloethane

CH_3CHXCH_2X propylene dihalide or 1, 2-diahlopropane

(c) α-ω diahlides :

In these compounds halogen atoms are attached to terminal carbon atoms and are separated by three or more carbon atoms. They are also known as polymethylene halides e.g.

$CH_2X\text{-}CH_2\text{-}CH_2\text{-}CH_2X$ tetra methylene dichloride or 1, 4-dihalobutane

(iv) Vic and gem diahalides are position isomers to each other.

5.1 Preparation of dihalides:

(i) By alkenes and alkynes :

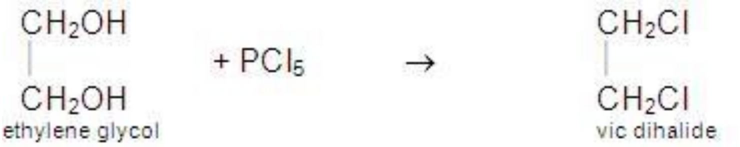
$CH_2{=}CH_2 + X_2 \rightarrow XCH_2\text{-}CH_2X$

vicinal dihalide

$CH \equiv CH + 2HX \rightarrow CH_3\text{-}CHX_2$

geminal dihalide

(ii) By the action of PCl_5 :



$$\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} + PCl_5 \rightarrow \begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix}$$

ethylene glycol vic dihalide

$$\begin{matrix} CH_3 \\ | \\ CHO \end{matrix} + PCl_5 \rightarrow \begin{matrix} CH_3 \\ | \\ CHCl_2 \end{matrix}$$

ethanol gem dihalide

5.2 Physical Properties of Dihalides:

(i) Dihalide are colourless with pleasant smell liquid. These are insoluble in water, soluble in organic solvent.

(i) Lower members are colourless, oily liquids with sweat smell. Higher members are solid.

(iii) These are heavier than water. The relative density of CH_2I_2 is 3.325 g/ml which is the 2nd heaviest liquid known after Hg.

(iv) $\text{m.p. and b.p. } \alpha \ \dfrac{1}{\text{molecular mass}}$.

5.3 Chemical Properties of Dihalides:

(ii) The reactivity of gem dihalides is lesser than alkyl halides, which might be due to the fact that in presence of one halogen atom (with a strong attracting effect i.e. -I effect), the other cannot be so easily replaced. However vic dihalides have same order of reactivity as alkyl halides.

Thus reactivity order : vic dihalides > gem dihalides

(iv) Some of the important reactions of dihalides are given below.

(a) Action of KOH_{alc} : Both vic and gem dihalides give same products.

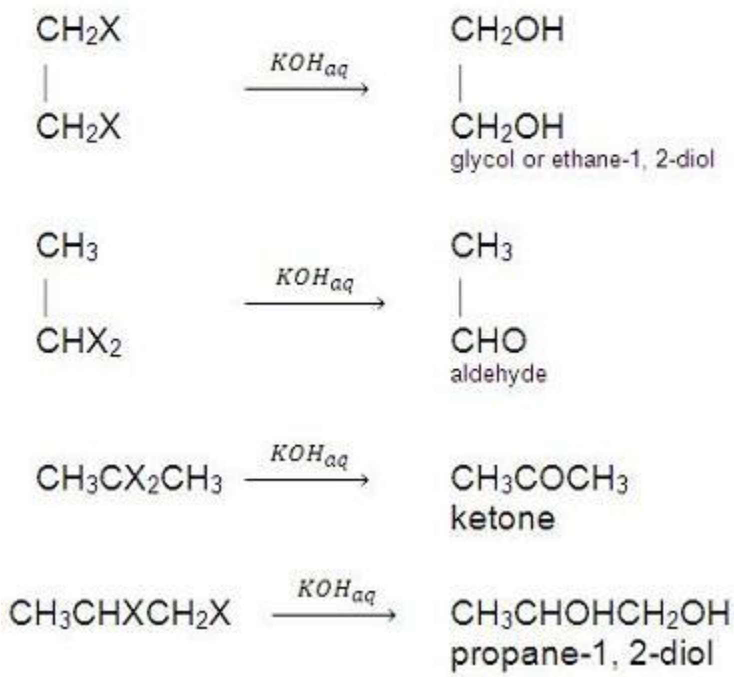
$$CH_2X - CH_2X \text{ or } CH_3\text{-}CHX_2 \xrightarrow[-2HX]{KOH_{alc}} CH \equiv CH$$

(b) Action of Zn dust : Both vic and gem dihalides give same products.

$$CH_2CHX_2 \text{ or } XH_2C\text{-}CH_2X \xrightarrow[\text{alcohol}]{\text{Zn dust}} CH_2{=}CH_2$$

(c) Action of KOH_{aq}

(i) It is a distinction test for gem & vic dihalides.



$$\begin{matrix} CH_2X \\ | \\ CH_2X \end{matrix} \xrightarrow{KOH_{aq}} \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$$

glycol or ethane-1, 2-diol

$$\begin{matrix} CH_3 \\ | \\ CHX_2 \end{matrix} \xrightarrow{KOH_{aq}} \begin{matrix} CH_3 \\ | \\ CHO \end{matrix}$$

aldehyde

$$CH_3CX_2CH_3 \xrightarrow{KOH_{aq}} CH_3COCH_3$$

ketone

$$CH_3CHXCH_2X \xrightarrow{KOH_{aq}} CH_3CHOHCH_2OH$$

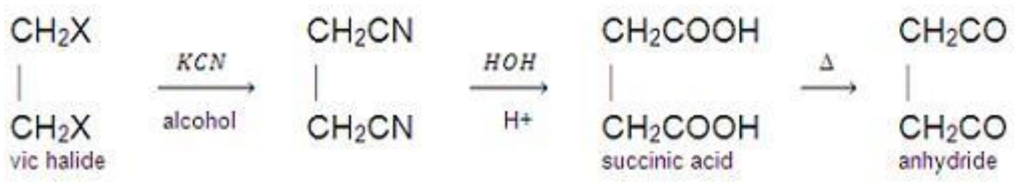
propane-1, 2-diol

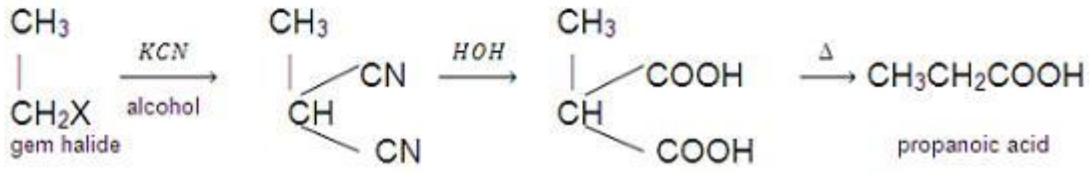
(ii) A gem dihalide gives either aldeyde or ketone on hydrolysis by KOH_{aq} ; A vicinal dihalide gives 1, 2-diol.

(d) Action of KCN followed with hydrolysis and heating the product formed.

(i) A distinction test for geminal and vicinal dihalides.

(ii) A geminal dihalide gives acid whereas vicinal dihalide gives anhydride if subjected to action of KCN followed with hydrolysis & heating the product formed.





Note :

(i) -CN gp on acid hydrolysis always converts to -COOH.

(ii) Two -COOH gp on one carbon atom on heating always lose CO_2 to form mono carboxylic acid.

(iii) Two -COOH gp on vicinal carbon atom, on heating always lose H_2O to form anhydride of acid.

5.4 Uses of Dihalides:

(1) 1,2-dichloroethane is used as a good apolar aprotic solventfor chemical reactions.

(2) It is also used as degreaser and paint remover.

(3) In the laboratory it is occasionally used as a source of chlorine, with elimination of ethene and chloride.

(4) The greatest use of 1,2-dichloroethane is in making chemicals involved in plastics, rubber and synthetic textile fibers. Other uses include: as a solvent for resins and fats, photography, photocopying, cosmetics, drugs; and as a fumigant for grains and orchards.

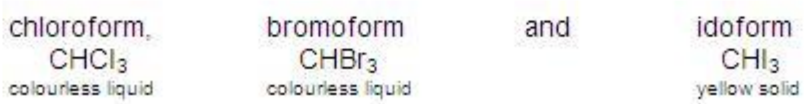
6. TIRHALIDES

6.1 Preparation of Trihalides:

(i) The trihalogen derivative of alkanes are prepared by replacement of three hydrogen atoms by three halogen atoms.

(ii) Their general formula is $C_nH_{2n-1}X_3$:

(iii) The trihalogen derivative of methane are also known as haloform



chloroform, $CHCl_3$ colourless liquid   bromoform $CHBr_3$ colourless liquid   and   idoform CHI_3 yellow solid

Haloform or trihalo methane CHX_3 vis a vis chloroform ($CHCl_3$)

Preparation :

(i) Lab method and Industrial method: By the distillation of ethyl alcohol or acetone with bleaching Powder:

(a) Bleaching powder on hydrolysis gives slaked lime and Cl_2 which acts as oxidizing agent as well as chlorinating agent.

$$CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2$$

By ethanol :

$Cl_2 + CH_3CH_2OH \rightarrow CH_3CHO + 2HCl$ (Cl_2 acts as oxidant)

$CH_3CHO + 3Cl_2 \rightarrow CCl_3CHO + 3HCl$ (Cl_2 acts as substituent)

$2CCl_3CHO + Ca(OH)_2 \rightarrow 2CHCl_3 + (HCOO)_2Ca$ (hydrolysis)

chloroform   Calcium formate

By acetone :

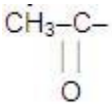
$CH_3COCH_3 + 3Cl_2 \rightarrow CCl_3COCH_3 + 3HCl$ (Cl_2 acts as substituent)

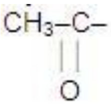
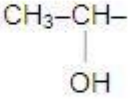
$2\ CCl_3COCH_3 + Ca(OH)_2 \rightarrow 2\ CHCl_3 + (CH_3COO)_2Ca$ (hydrolysis)

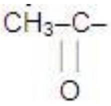
(b) Chloroform is collected with water in lower layer. It is washed with dilute alkali and dried over $CaCI_2$ and then redistilled at 60-65°C.

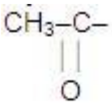
(c) The yield is better if acetone is used.

(ii) By haloform reaction :

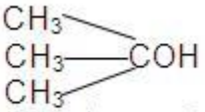
(a) Acetaldehyde and all methyl ketones (2-ones) or carbonyl compounds having  $CH_3-\underset{\underset{O}{||}}{C}-$ units as well as alcohols [primary (only ethanol) and secondary (only 2-ol) which produce this unit on oxidation by halogen undergo haloform reaction on heating with halogen and NaOH to give haloform.

(b) If I_2 + NaOH is used, the haloform reaction yields yellow solid as precipitate confirming the presence of  $CH_3-\underset{\underset{O}{||}}{C}-$ unit or  $CH_3-\underset{\underset{OH}{|}}{CH}-$ in the molecule attached to C or H.

This is known as iodoform test for confirming the presence of acetaldehyde, methyl ketones and alcohols (which produce  $CH_3-\underset{\underset{O}{||}}{C}-$ unit on oxidation) e.g.

Reactants which give iodoform test because of  $CH_3-\underset{\underset{O}{||}}{C}-$ unit or producing this unit during oxidation :

HCHO, methanal	CH_3CH_2CHO propanal	$CH_3CH_2COCH_2CH_3$ pentan-3-one
CH_3OH, methanol	$CH_3CH_2CH_2OH$ propanol	$CHCH_2OH$ 2-methylpropanol-1


2-methyl propan-2-ol

(Since it is not oxidised by I_2)

(c) In general, acetaldehyde,ket-2-one, ethanol & sec alcohols (2-ol) give the idoform test. Also pyruvic acid ($CH_3COCOOH$), lactic acid ($CH_3CHOHCOOH$) and acetophenone ($C_6H_5COCH_3$)give this test.

(d) The reactions are :

By ethanol

$$CH_3CH_2OH + X_2 \rightarrow CH_3CHO + 2HX$$

$$CH_3CHO + 3X_2 \rightarrow CX_3CHO + 3HX$$

$$CX_3CHO + NaOH \rightarrow CHX_3 + HCOONa$$

$$5HX + 5NaOH \rightarrow 5NaX + H_2O$$

$$CH_3CH_2OH + 4X_2 + 6 \rightarrow CHX_3 + HCOONa + 5NaX + 5H_2O$$

By ethanal :

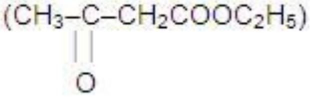
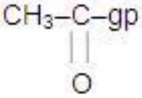
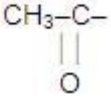
$$CH_3CHO + 3X_2 \rightarrow CX_3CHO + 3HX$$

$$CX_3CHO + NaOH \rightarrow CHX_3 + HCOONa$$

$$3HX + 3NaOH \rightarrow 3NaX + 3H_2O$$

$$CH_3CHO + 3X_2 + 4NaOH \rightarrow CHX_3 + HCOONa + 3NaX + 3H_2O$$

Note :

(a) Ethyl acetoacetate  $(CH_3-\underset{\underset{O}{||}}{C}-CH_2COOC_2H_5)$ does not give iodoform test, although it contains  $CH_3-\underset{\underset{O}{||}}{C}-gp$ attached to carbon (methylene gp). This is due to active nature of methylene group at which iodination occurs and not on the methyl group of  $CH_3-\underset{\underset{O}{||}}{C}-$ unit.

(b) Certain quinines, quinols and m-dihydric phenols also give positive iodoform test.

(iii) Pure chloroform is obtained by heating chloral hydrate with concentrate sodium hydroxide solution.

$$CCl_3CH(OH)_2 + NaOH \xrightarrow{\Delta} CHCl_3 + HCOONa + H_2O$$

(iv) By chlorination of methane :

$$CH_4 + Cl_2 \xrightarrow{U.V.light} CHCl_3 + 3HCl$$

(v) By CCl_4 (a commercial method) : Commerically it is obtained by the partial reduction of CCl_4 with iron fillings and water (steam). This chloroform is not pure and is used only as solvent.

$$CCl_4 + 2H \xrightarrow{Fe/H_2O_{(v)}} CHCl_3 + HCl$$

Note : Iodoform is commercially obtained by electrolysis of a solution containing ethanol, Na_2CO_3 and KI. The liberated I_2 during electrolysis brings in iodoform reaction with C_2H_5OH in presence of Na_2CO_3.

6.2 Physical Properties of Trihalides:

(i) Pure chloroform and bromoform are colourless liquids, and iodoform is yellow solids.

(ii) All are heavier than water and soluble in organic solvents, but insoluble in water.

(iii) $CHCl_3$ brings temporary unconsciousness when vapours are inhaled for sufficient time and thus used as an aesthetic agent.

(iv) $CHCl_3$ is non inflammable but like other halides its vapours when ignited on Cu wire burn with green edge flame. (Beilstein test).

6.3 Chemical Properties of Trihalides:

1. Oxidation :

(a) On exposure to air and sunlight, chloroform is slowly oxidized to a poisonous gas carbonyl chloride i.e. phoszene

$$2CHCl_3 + O_2 \xrightarrow{air+hv} 2COCl_2 + 2HCl$$

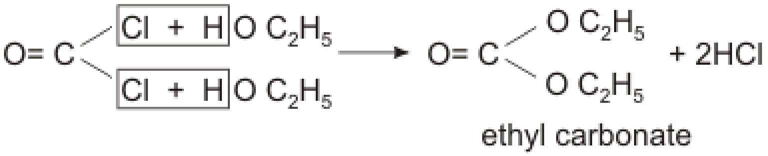
$$\text{or} \quad 4CHCl_3 + 3O_2 \xrightarrow[\text{light}]{excess\ of\ air} \underset{\text{phoszene}}{4COCl_2} + 2Cl_2 + 2H_2O$$

(b) Therefore purity of chloroform should be checked before its use as an aesthetic agent. Pure $CHCl_3$ does not give white ppt. of AgCl with $AgNO_3$. Also pure chloroform neither turns blue litmus to red nor give black colour on shaking with H_2SO_4 conc.

(c) Also following precautions are necessary to store $CHCl_3$ to be used as an aesthetic agent -

(i) It is kept in brown or blue coloured bottles which are filled upto the brim in order to protect the action of light & air.

(ii) 1% ethanol is also added which acts as negative catalyst for oxidation of $CHCl_3$ as well as converts carbonyl chloride into harmless ethyl carbonate.



2. Reduction :

$$CHCl_3 + 2H \xrightarrow{Zn/HCl\ (alc)} CH_2Cl_2 + HCl$$

$$CHCl_3 + 4H \xrightarrow{Zn/HCl\ (alc)} CH_2Cl_2 + 2HCl$$

$$CHCl_3 + 6H \xrightarrow{Zn/HCl\ (alc)} CH_4 + 3HCl$$

3. **Hydrolysis or action of KOH_{aq} :**

$$CHCl_3 + 3KOH_{aq} \xrightarrow[-3KCl]{} CH(OH)_3 \xrightarrow{-H_2O} HCOOH \xrightarrow{KOH_{aq}} HCOOK + H_2O$$

or $CHCl_3 + 4KOH \rightarrow HCOOK + 3KCl + 2H_2O$

4. **Chlorination :**

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

5. **Action of Ag powder :**

$$CHX_3 + \underset{\text{powder}}{6Ag} + X_3HC \xrightarrow[\text{high T}]{\Delta} CH{\equiv}CH + 6AgX$$

6. **Action of HNO_3 :** The H atom of $CHCl_3$ is replaced by $-NO_2$ gp if heated with conc. HNO_3.

$$CHCl_3 + HNO_3 \rightarrow CCl_3NO_2 + H_2O$$

(Chloropicrin or nitrochloroform, liquid, poisonous and used as insecticide & war gas)

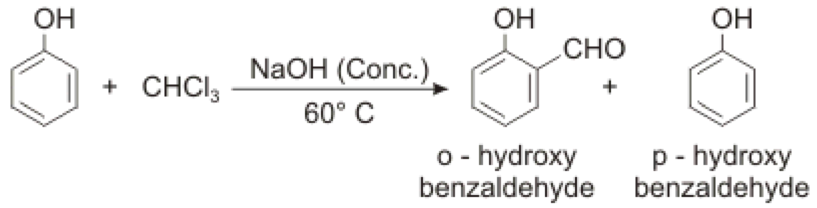
7. **Condensation with acetone :**

(chlorotone, solid, a hypnotic agent)

8. **Reaction with sodium ethoxide :**

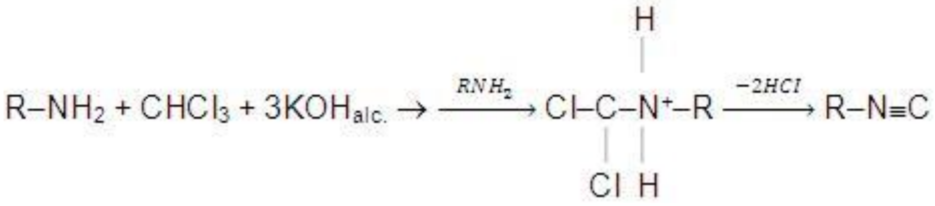
ethyl ortho formate

9. Riemer - Tiemann reacton :



10. Carbylamine reaction :

(i) All primary amines (may be aliphatic R-NH_2 or aromatic Ar-NH_2) on warming with $CHCl_3$ and $KOH_{alc.}$ undergo carbylamne reaction to give an offensive or unpleasant odour of isonitrile or carbylamines.



$$R{-}NH_2 + CHCl_3 + 3KOH_{alc.} \rightarrow \xrightarrow{RNH_2} Cl{-}\underset{Cl}{C}{-}\overset{H}{\underset{H}{N^{+}}}{-}R \xrightarrow{-2HCl} R{-}N{\equiv}C$$

6.4 Uses of Trihalides:

(i) $CHCl_3$, an an aesthetic agent; CHI_3 as antiseptic due to liberation of I_2.

(ii) $CHCl_3$ as solvent for fat, waxes rubbers, resins etc.

(iii) In preparation of chlorotone (drug, a hypnotic agent) and nitrochloroform (an insecticide).

(iv) $CHCl_3$ as preservative for anatomical specimens

(v) As laboratory reagent to identify primary amines & other analytical tests.

Note :

1. Iodoform on heating with $AgNO_3$ gives yellow ppt. of AgI whereas chloroform does not give this test because of stable nature.

2. Iodoform has antiseptic properties because on coming in contact with organic matter of skin it decomposes to give free iodine which acts as an antiseptic.

3. Halothane, CF_3-CHClBr, is used as a general anaesthetic which has replaced diethyl ether.

7. TETRAHALIDES

Tetrachloromethane (CCl_4)

7.1 Preparation of Tetrahalides (Tetrachloromethane):

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

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

Methane used in this process is obtained from natural gas.

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

$$CS_2 + 3Cl_2 \rightarrow CCl_4 + \underset{\text{sulphur dichloride}}{S_2Cl_2}$$

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

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

CCl_4 is washed with NaOH solution and then distilled to get pure sample.

(iii) By the action of chlorine on chloroform.

$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$$

(iv) From propane : Propane is allowed to react with Cl_2 at about 400°C and at a pressure of 70-100 atmosphere.

$$C_3H_8 + 9Cl_2 \xrightarrow[\text{pressure}]{heat} \underset{\substack{\text{carbon}\\\text{tetra}\\\text{chloride}}}{CCl_4} + \underset{\substack{\text{hexa chloro}\\\text{ethane}}}{C_2Cl_6} + 8HCl$$

7.2 Physical properties of Tetrahalides (Tetrachloromethane):

(i) It is colourless, non-inflammable, poisonous liquid with characteristic smell.

(ii) Insoluble in water but soluble in ethanol and ether.

(iii) It is a good solvent for oils, fats and greases.

7.3 Chemical properties of Tetrahalides (Tetrachloromethane):

Less reactive than other halogen derivatives.

1. **Oxidation or reaction with steam :**

$$CCl_4 + \underset{\text{(stream)}}{H_2O} \xrightarrow{500^oC} \underset{\text{phoszene}}{COCl_2} + 2HCl$$

2. **Reduction :** mostly iron fillings reduce CCI_4 to $CHCl_3$

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

3. **Hydrolysis (action of aqueous KOH) :**

$$CCl_4 + 4\,KOH \xrightarrow{-4\,KCl} C\,(OH)_4 \xrightarrow{-2H_2O} CO_2 \xrightarrow{2\,KOH} K_2CO_3 + H_2O$$

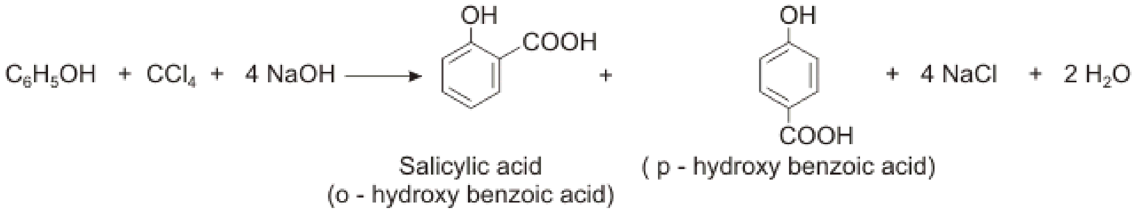
or $CCl_4 + 6KOH_{(aq.)} \rightarrow 4KCl + K_2CO_3 + 3H_2O$

Freon-12 (dichlorodifluoromethane) is widely used as a refrigerant and propellant in aerosol sprays of all kinds.

4. **Action of hydrogen fluoride in the presence of SbF_5.**

$$CCl_4 + 2HF \xrightarrow{SbF_5} CCl_3F_2 + 2HCl$$

5. **Reaction with phenol and alkali** (Reimer-Tiemann reaction).



7.4 Uses of Tetrahalides (Tetrachloromethane)::

Carbon tetrachloride is used:

(i) As fire extinguisher under the name pyrene. Then dense, non combustile vapours over the burning substances and prevents oxygen from reaching them. However, since CCI_4 forms phosgene, after the use of pyrene to extinguisher a fire the room should be well ventilated.

(ii) As a laboratory reagent.

(iii) As a solvent for oils, fats, resins iodine and in dry-cleaning.

(iv) As a fumigant.

(v) In medicine for the elimination of hookworms as helmenthicide due to antihelminthic nature.

8. SOME USEFUL HALOGEN DERIVATIVES

8.1 Freons : The chloro fluoro derivatives of methane and ethane are called freons. Some of the derivatives are : CHF_2Cl (monochlorodifluoromethane), CF_2Cl_2 (dichloro difluro methane), HCF_2CHCl_2 (1, 1-dichloro 2, 2-difluoroethane). These are non-inflammable, colourless, non-toxic and low boiling liquids. These are stable upto 550°C. The most important and useful derivative is CF_2Cl_2 which is commonly known as **Freon** on **Freon-12**.

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

$$3CCl_4 + 2SbF_3 \xrightarrow[\text{catalyst}]{SbCl_5} 3CCl_2F_2 + 2SbCl_3$$

or by reacting carbon tetrachloride with hydrofluoric acid in presence of antimony penta fluoride.

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

Under normal conditions Freon is a gas. (b.pt. - 29.8°C). It can easily be liquefied. It is chemically inert and is used in air-conditioning and in domestic refrigerators.

Note : Freon-14 is CF_4, Freon-13 is CF_3Cl, Freon-11 is $CFCl_3$. All these are used as refrigerant.

8.2 Teflon : A plastic like substance produced by the polymerization of tetrafluoroethylene ($CF_2=CF_2$). Tetrafluoroethylene is formed when chloroform is treated with antimony trifluoride and hydrofluoric acid.

$$2\ CHCl_3 \xrightarrow[HF]{SbF_5} 2\ CHF_2Cl \xrightarrow[-2\ HCl]{800°C} CF_2 = CF_2\ (\text{gas, b.pt.} = -76°C)$$

On polymerization, tetrafluoro ethylene forms a plastic-like material which is called teflon.

$$\underset{\text{tetrafluoro ethylene}}{nCF_2=CF_2} \rightarrow \underset{\text{Teflon}}{(CF_2\text{-}CF_2)_n}$$

Teflon is chemically inert substances. It is not affected by strong acids and even by boiling aqua-regia. It is stable at high temperature and thus, used for electrical insulation and preparation of gasket materials.

8.3 Acetylene tetrachloride (Westron), $CHCl_2CHCl_2$:

Acetylene tetrachloride is also known as sym. tetrachloroethane. It is prepared by the action of chlorine on acetylene in presence of a catalyst such as ferric chloride, aluminium chloride, iron, quartz or kieselguhr.

$$CH{\equiv}CH + 2Cl_2 \rightarrow CHCl_2CHCl_2$$

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

It is a heavy, non-inflammable toxic liquid with smell like $CHCl_3$. It is insoluble in water but soluble in organic solvents.

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

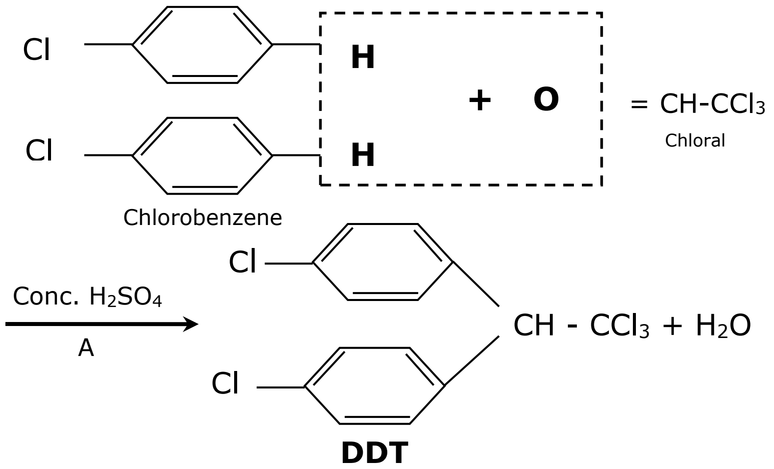
$$2C_2H_2Cl_4 + Ca(OH)_2 \rightarrow 2CHCl_2{=}CCl_2 + CaCl_2 + 2H_2O$$

Both westron and westrosol are used as solvent for oils, fats and varnishes.

8.4 P,p'-Dichlorodiphenyltrichloroethane (DDT):

The name *p,p'* -dichlorodiphenyltrichloroethane is a misnomer. Its actual name is 2, 2.-bis(4-chloropheny)-1, 1, 1- trichloroethane.

DDT was first prepared in 1873 but it was not until 1939 that Paul Muller, at Geigy pharmaceutical in Switzerland, discovered the effectiveness of DDT as an insecticide. Paul Muller was awarded the Nobel Prize in medicine and physiology in 1948 for this discovery.
Preparation: It is prepared by heating chlorobenzene with chloral (trichloroacetaldehyde) in presence of conc. H_2SO_4.



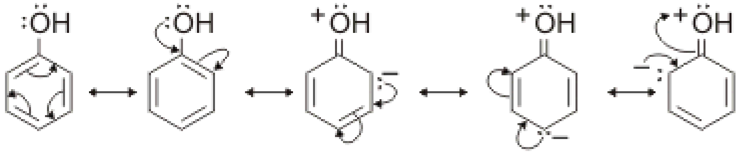
Uses: DDT is a cheap but powerful insecticide. It is widely used for sugarcane and fodder crops and to kill mosquitoes and other insects. It is particularly very effective against *Anopheles mosquitoes* which spread malaria and lice that carry typhus. Through its use, malaria has virtually been eliminated from India and large part of the world.

Tragic side effects: The use of DDT increased enormously on a worldwide basis after World War II. However, problems related to extensive use of DDT began to appear in the late 1940s. Many species of insects developed resistance to DDT and DDT was also discovered to have a high toxicity towards fish. The chemical stability of DDT and its fat solubility further increased the problems. DDT is not completely *biodegradable*, *i.e.*, it is not very rapidly metabolized by animals. Instead, it gets deposited and stored in fatty tissue. If this ingestion continues at a steady rate, DDT builds up within the animal over time. This affects the reproductive system of animals. Because of these tragic side effects, the use of DDT was banned in USA in 1973. However, in India and in many other Asian countries, DDT is still being widely used due to the non-availability of any other cheaper insecticide.

9. HALOARENES

9.1 Preparation of Haloarenes:

Haloarenes or aryl halides cannot be prepared from phenols because it is difficult to replace the hydroxyl group of phenols by a halogen atom. This is due to the reason that because of resonance.



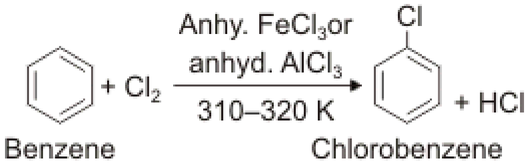
Therefore, these are usually prepared by the following methods:

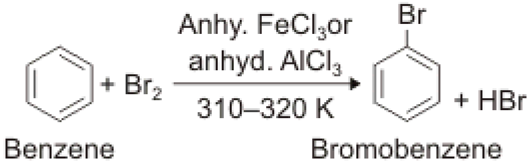
<u>(1) From aromatic hydrocarbons – by direct halogenations</u>:

(A) Nuclear halogenations:

The direct chlorination or bromination of aromatic hydrocarbons is usually carried out at a low temperature (310-320 K), in the absence of sunlight and in the presence of a Lewis acid such as anhydrous ferric or aluminium halide as catalyst.

$$2Fe + 3Cl_2 \longrightarrow 2FeCl_3$$





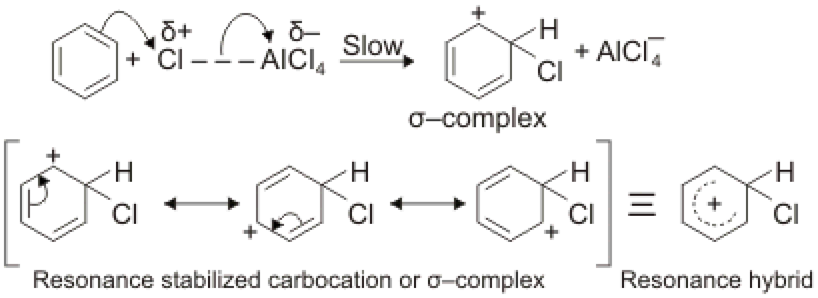
Mechanism:
Halogenation of benzene and other arenes occurs by the following mechanism:

Step I. Generation of electrophile

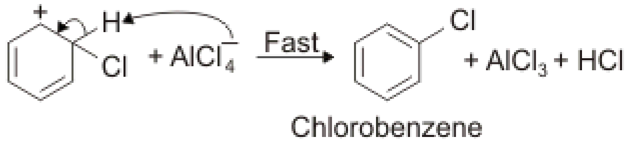
$$\mathrm{Cl{-}Cl + AlCl_3 \longrightarrow \underset{\text{Electrophile}}{\overset{\delta+}{Cl} \ldots\ldots \overset{\delta-}{AlCl_4}}}$$

Step II. Formation of σ-complex or carbocation intermediate.

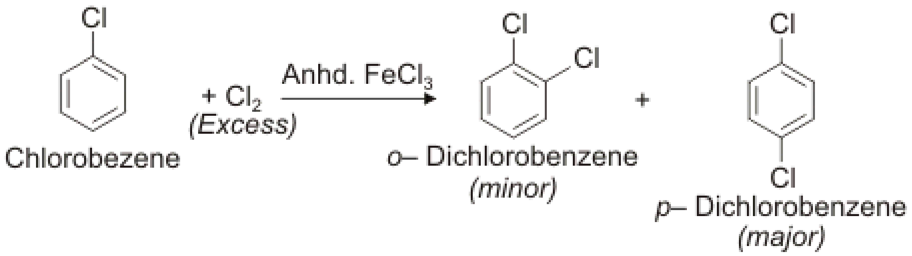
This step is slow and hence is the rate-determining step of the reaction.



Step III. Loss of a proton from the carbocation intermediate.
This step is fast and hence does not affect the rate of reaction.

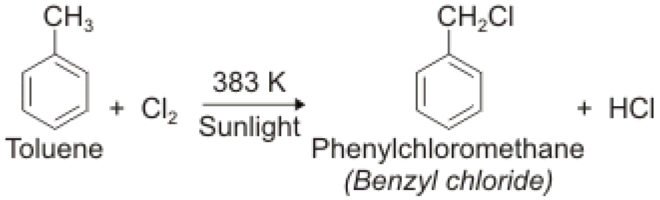


If excess of halogen is used – a second halogen is introduced in the ring mainly at o- and p-positions w.r.t. to the first since halogens are o, p- directing.

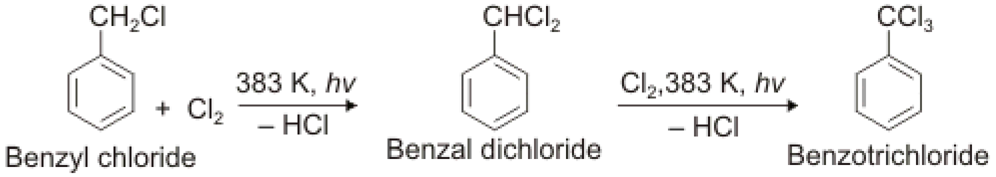


(B) Side chain halogenation:

When Cl_2 is passed through boiling toluene in the presence of sunlight and absence of halogen carrier, phenylchloromethane (benzyl chloride) is formed.



If Cl_2 is passed for a longer time, the initially formed benzyl chloride reacts further to form first benzal dichloride and then benzotrichloride.



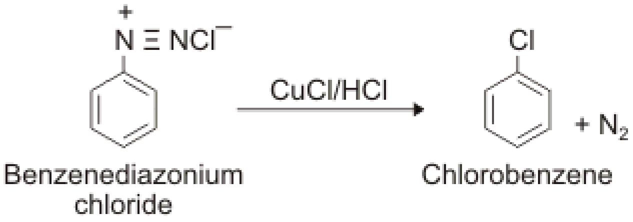
Instead of Cl_2, sulphuryl chloride (SO_2Cl_2) at 475 K in presence of light and traces of peroxide can also be used for benzylic halogenations of arenes. For example,

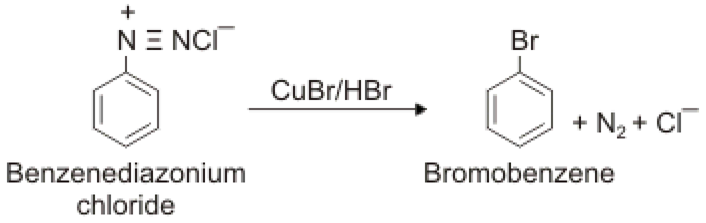
$$\underset{\text{Toluene}}{C_6H_5CH_3} + SO_2Cl_2 \xrightarrow[\text{traces of peroxide}]{475\text{ K}, h\nu} \underset{\text{Benzyl chloride}}{C_6H_5-CH_2Cl} + SO_2\uparrow + HCl\uparrow$$

(2) From diazonium salts :

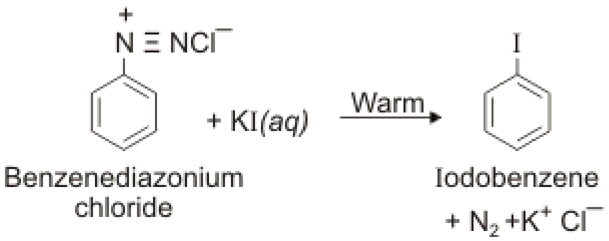
(A) By Sandmeyer reaction:

When the diazonium salts are treated with CuCl dissolved in HCl or CuBr dissolved in HBr, chloroarenesand bromoarenes are prepared.

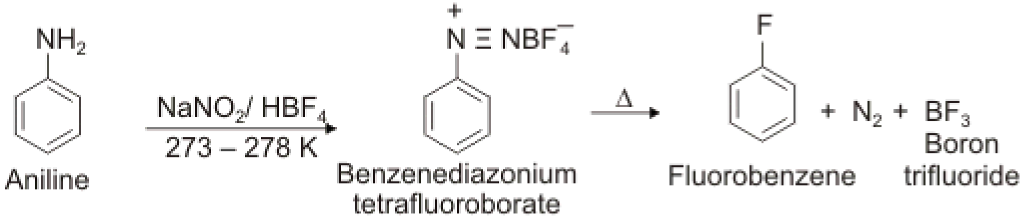




Iodoarenes are prepared by warming the diazonium salt with aqueous KI solution.

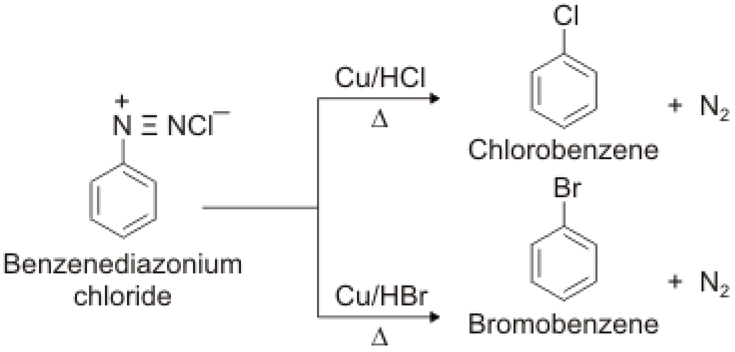


Fluoroarenes are prepared by heating the corresponding diazonium tetrafluoroborates.



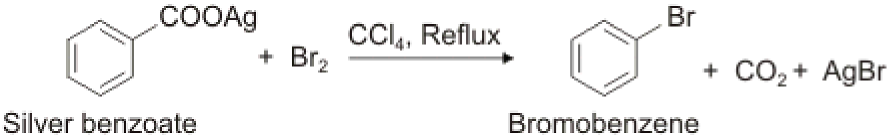
(B) By Gattermann reaction:

In this reaction, a mixture of freshly prepared copper powder in the presence of corresponding halogen acid (HCl or HBr) is used. The yields are often around 40%. Thus,



(C) From silver salt of aromatic acids(Hunsdiecker reaction):

Aryl bromides can be prepared by refluxing the silver salt of aromatic acids with bromine in carbon tetrachloride.



(D) Commercial preparation of chlorobenzene (Raschig process):

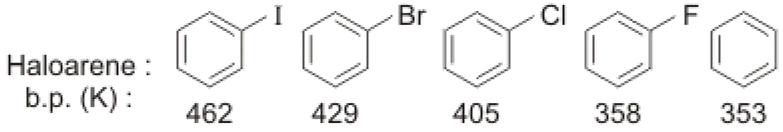
In this process, a mixture of benzene vapours, air and hydrogen chloride is passed over heated cupric chloride.

$$2\ C_6H_6 + 2HCl + O_2 \xrightarrow{CuCl_2,\ \Delta} 2\ C_6H_5Cl + 2H_2O$$

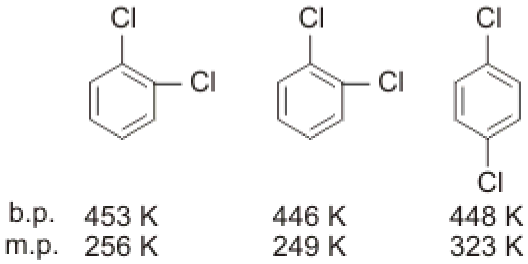
9.2 Physical Properties of Haloarenes:

(1) Melting points and boiling points:

For the same aryl group, the melting and boiling points increases as the size of the halogen atom increases,i.e.,iodoarenes > bromoarenes > chloroarenes > fluoroarenes > arenas.Thus,



The boiling points of isomeric dihalobenzenes are nearly the same but their melting points are quite different.



Intermolecular attraction is stronger in p-isomer, hence it melts at a higher temperature.

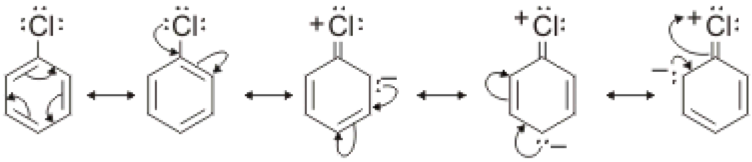
(2) Solubility:

Aryl halides are insoluble in water, because less energy is realesed when new attractions are set up between the haloarenes and water molecules.However,they are quite soluble in organic solvents.

9.3 Chemical Properties of Haloarenes:

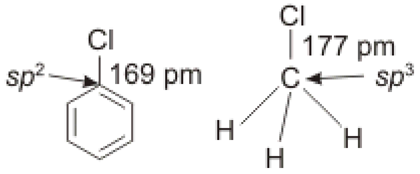
Haloarenes are extremely less reactive than haloalkanes towards nucleophilic substitution reactions. The following reasons can be given to account for the low reactivity of aryl and vinyl halides.

(1) Resonance effect: In haloarenes (e.g., chlorobenzene), the lone pairs of electrons on the halogen atom are delocalized on the benzene ring as shown below:

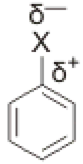


As a result, C Cl bond acquires some double bond character, i.e., Cl is attached to C by little more than a single pair of electrons.

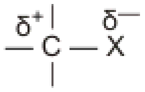
(2) Difference in hybridization of carbon atom in C -X bond: In haloalkanes the halogen is attached to sp^{3-} hybridized carbon while in haloarenes the halogen is attached to sp^{2-} hybridized carbon. therefore, the C - Cl bond in chlorobenzene should be shorter and hence stronger than in methyl chloride.



(3) Polarity (or Nature) of the carbon-halogen bond: Another reason for the low reactivity of aryl halides over alkyl halides is their lesser polar character. The sp^{2-} hybrid carbon of C - X bond in an aryl halides due to greater s- character is more electronegative and has less tendency to release electrons than a sp^{3-} hybrid carbon in alkyl halides.

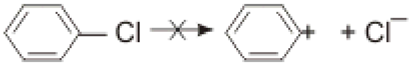


Haloarene or aryl halide
(C—X bond is less polor and hence X cannot be displaced casily by nucleophiles.)



Haloalkane or alkyl halide
(C—X bond is more polar than in aryl halides and hence X can be easily displaced by nucleophiles.)

(4) Instability of phenylcation: In haloarenes, the phenyl cation formed as a result of self-ionization is not stabilized by resonance because the sp^{2-} hybridized orbital of carbon having the +ve charge is perpendicular to the p-orbitals of the phenyl ring .

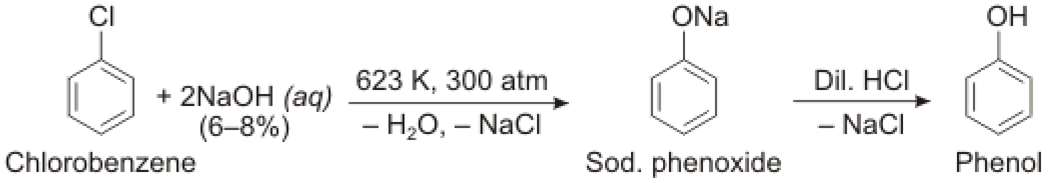


(5) Electronic repulsions: Since arenes are electron rich molecules due to the presence of π - bond, they repel the electron rich nucleophiles from attacking them.

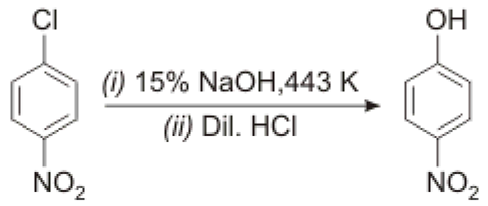
Some important reactions of haloarenes are discussed below:

(i) Replacement by hydroxyl group:

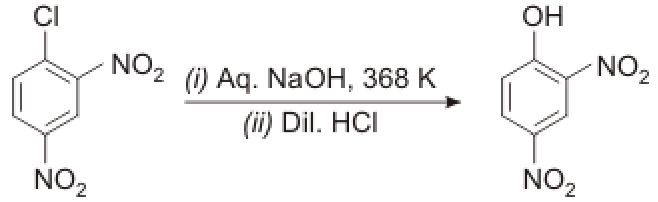
Chlorobenzene when heated with an aqueous solution of NaOH at 623 K and under a pressure of 300 atmospheres, gives sodium phenoxide which upon acidification gives phenol.(Dow process)



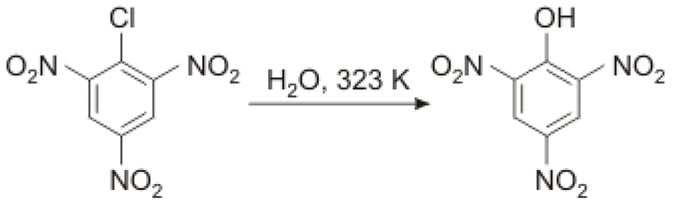
However, it has been observed that the presence of electron with drawing groups such as -NO_2, -CN, etc. at o- and p-position w.r.t. the halogen greatly activates it towards nucleophilic displacement.



Chloro– 4 –nitrobenzene 4–Nitrophenol



2, 4–Dinitro–chlorobenzene 2, 4–Dinitrophenol

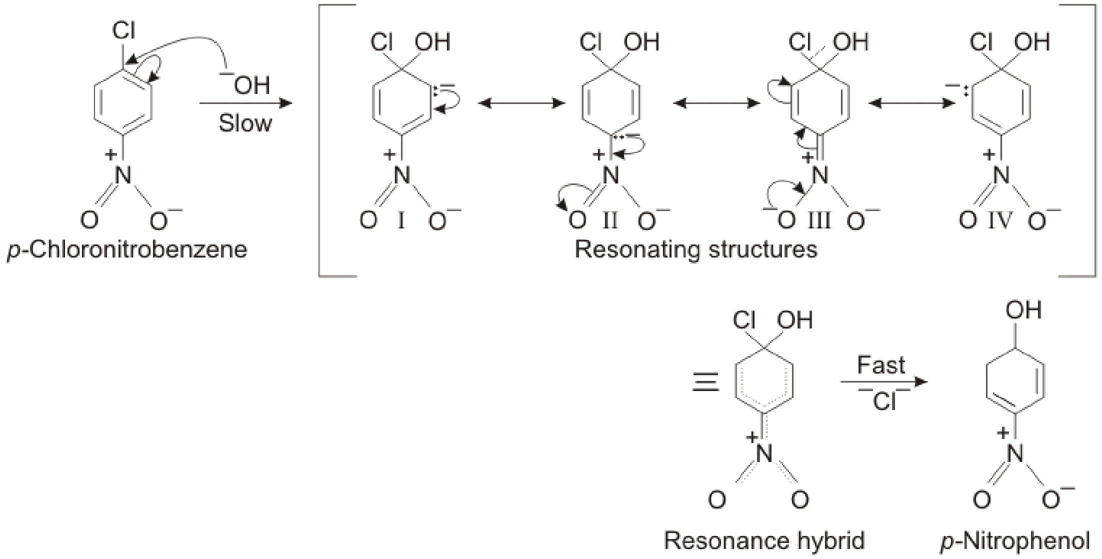


2, 4, 6–Trinitrochlorobenzene *(Picryl chloride)* 2, 4, 6–Trinitrophenol *(Picric acid)*

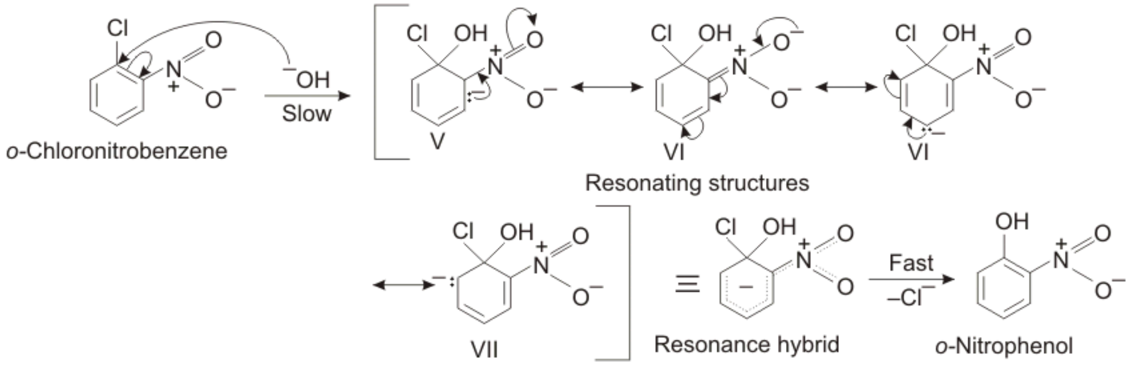
Mechanism and explanation:

The presence of NO_2 groups at o- and p- position withdraws electrons from the benzene ring and thus facilitates the attack of the nucleophile on haloarenes. The carbanion thus formed is stabilized by resoance as shown below: Therefore, in case of m-chloronitrobenzene, carbanion is not stabilized by the π electrons of the benzene ring.

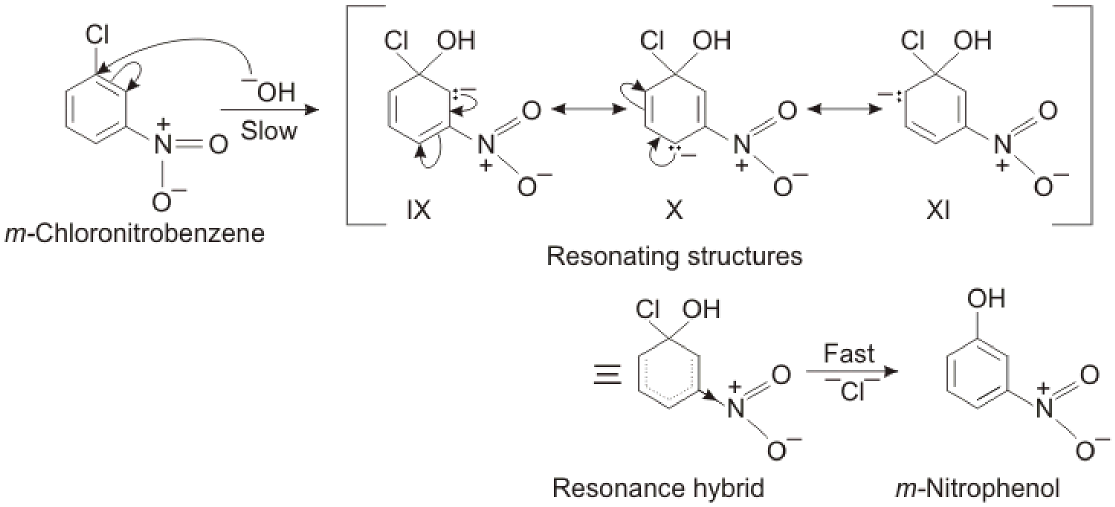
Attack at *p*-position



Attack at *o*-position



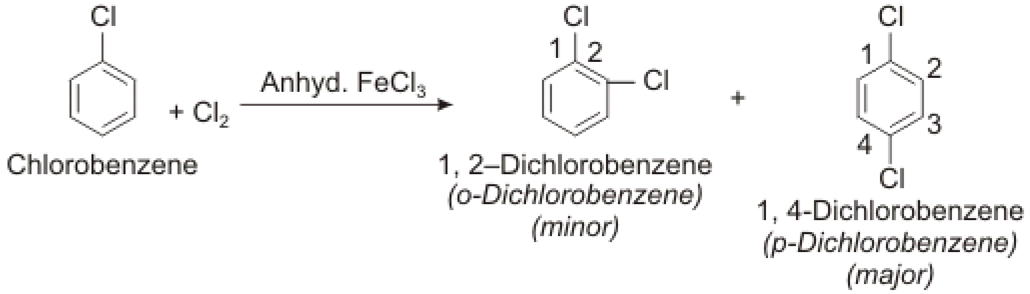
Attack at *m*-position



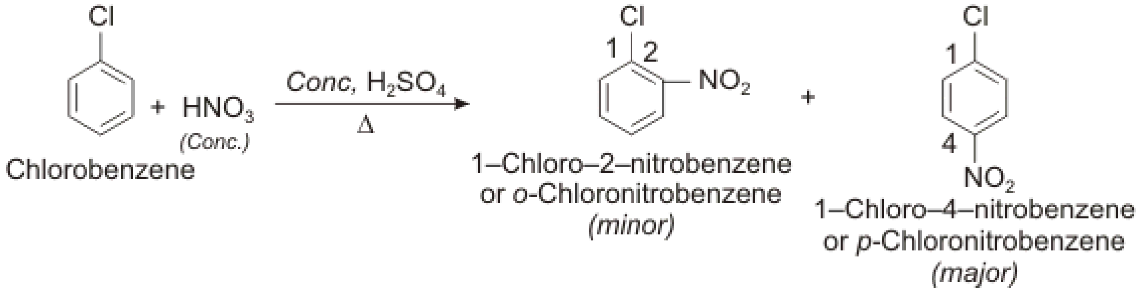
(ii) Electrophilic substitution reactions:

Haloarenes undergo the usual electrophilic substitution reactions of the benzene ring such as halogenation, nitration, sulphonation and Friedel-Crafts reactions.

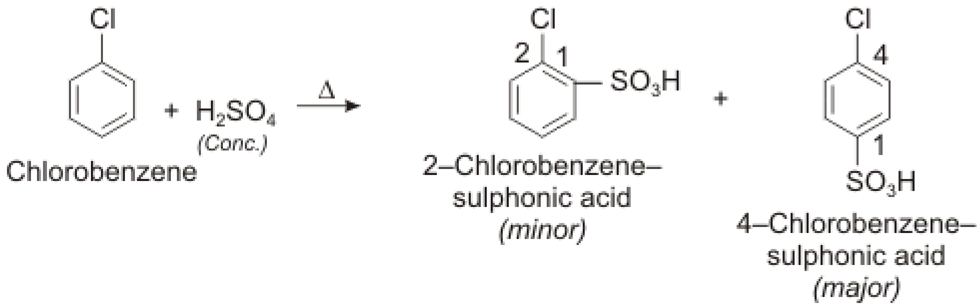
(a) Halogenation:



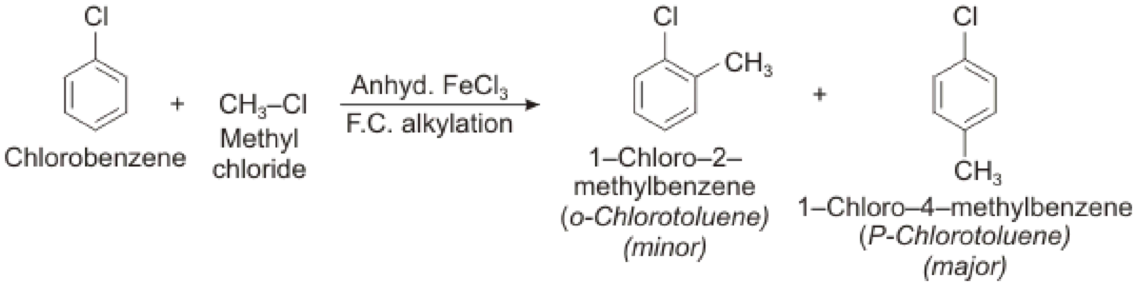
(b) Nitration:

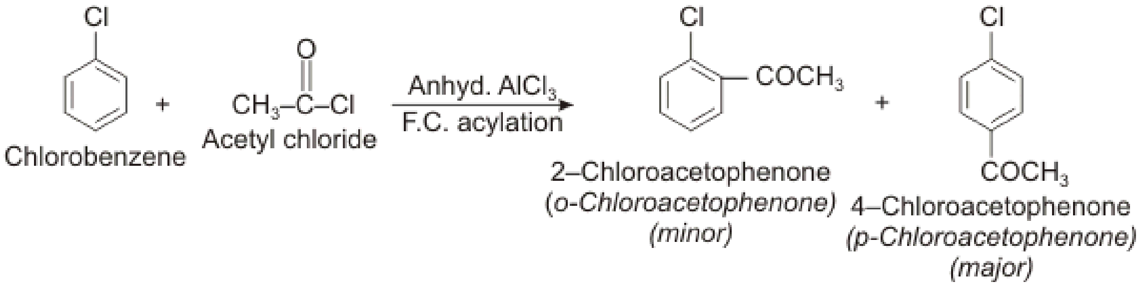


(b) Sulphonation:



(c) Friedel-Crafts reactions:



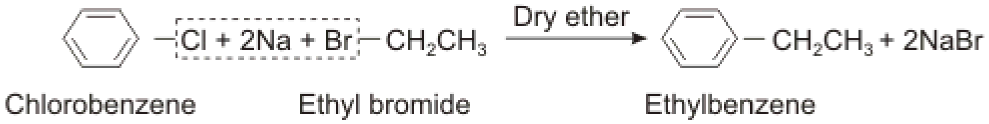


(2) Miscellaneous reactions:

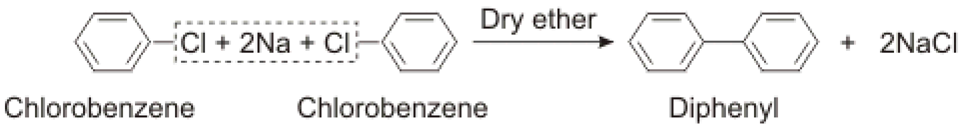
Besides these nucleophilic and electrophilic substitution reactions, haloarenes undergo a number of other reactions
as described below:

(i)Reaction with sodium:

(a) Wurtz-Fittig reaction: Haloarenes when treated with an ethereal solution of an alkyl halide in presence of sodium, form alkyl derivatives of benzene. This reaction is called Wurtz-Fittig reaction.

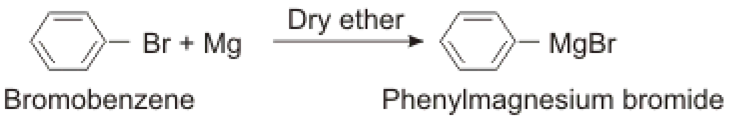


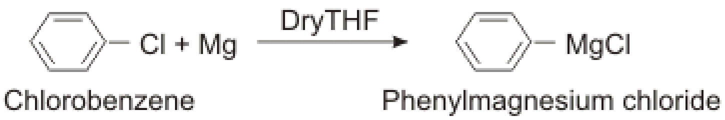
(b) Fittig reaction: When only haloarenes are treated with sodium, diaryls are produced. This reaction is called Fittig reaction.



(ii)Reactions with copper powder – Ullmann biaryl synthesis: When an iodoarene is heated with copper powder in a sealed tube, diaryl is formed.This is called Ullmann biaryl synthesis.

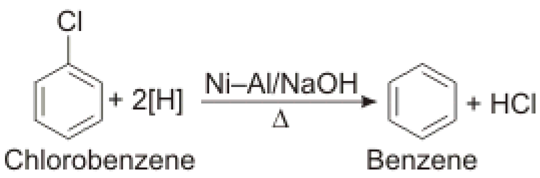
(iii)Reaction with magnesisum: Bromo-and iodoarenes form Grignard reagents when their ethereal solution is treated with magnesium turnings Chloroarenes form Grignard reagents only if the reaction is carried out in dry tetrahydrofuran (THF) as solvent.





(iv) Reaction with Lithium: Bromo- and iodoarenes also react with lithium,metal in presence of dry ether to form the corresponding organometallic compounds. For examples,

(v) Reduction: Haloarenes can be converted into the corresponding arenas by reduction with nickel-aluminium alloy in presence of alkali.



9.3 Uses of Haloarenes:

(i) Chlorobenzene once was used in the manufacture of certain pesticides, most notably DDT by reaction with chloral (trichloroacetaldehyde), but this application has declined with the diminished use of DDT.

(ii) The major use of chlorobenzene is as an intermediate in the production of commodities such as herbicides, dyestuffs, and rubber.

(iii) Chlorobenzene is also used as a high-boiling solvent in many industrial applications as well as in the laboratory.

(iv)Benzyl chloride is used as a chemical intermediate in the manufacture of certain dyes and pharmaceutical, perfume and flavor products. It is also used as a photographic developer.

(v) Benzyl chloride can be used in the manufacture of synthetic tannins and as a gum inhibitor in petrol.

(vi) Benzyl chloride has been used as an irritant gas in chemical warfare.