3

ORGANIC CHEMISTRY

HALOALKANES AND HALOARENES

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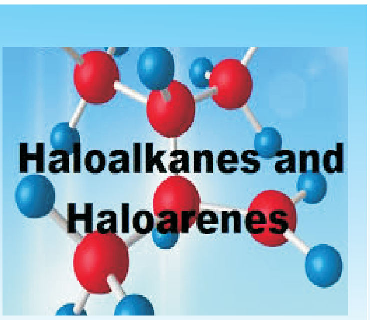


ALKYL HALIDES (HALOALKANES)

On the basis of no. of halogen atoms alkyl halides are classified as :

(i) Monohalides : They are formed by the replacement of one H-atom by halogen atom.

Gen. formula : $C_nH_{2n+1}X$ where $n = 1, 2, 3......$

Type formula : $R-X$

Ex. CH_3Cl, Methyl chloride (Chloromethane)

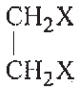
CH_3CH_2Br, Ethyl bromide (Bromoethane)

(ii) Dihalides : Obtained by replacement of two H-atoms by equal no. of halogen atoms.

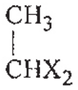
Gen. formula $C_nH_{2n}X_2$

Type formula RX_2

Ex. CH_2X_2 Methylene dihalide



$\begin{array}{c} CH_2X \\ | \\ CH_2X \end{array}$ Ethylene dihalide or Vicinal dihalide



$\begin{array}{c} CH_3 \\ | \\ CHX_2 \end{array}$ Ethylidene dihalide or geminal dihalide

(iii) Trihalides : Obtained by replacement of three H-atoms by equal no. of halogen atoms.

Gen. Formula : $C_2H_{2n-1}X_3$; Type formula : RX_3

Ex. CHX_3 Trihalomethane or haloform

(iv) Tetrahalides : Replacement of four H-atoms by equal no. of halogen atoms. When all the H-atoms from an alkane are replaced by halogen atoms, then the compounds are called perhalo compounds.

Gen. Formula – $C_nH_{2n-2}X_4$

MONOHALIDES OR MONOHALOALKANES

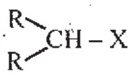
Depending on the attachment of the halogen atom to 1°, 2° or 3° carbon atom, monohalides are classified as :

(a) Primary or 1° alkyl halide : Where halogen atom is attached to primary C-atom

Ex. $R-CH_2-X$

(b) Secondary or 2° alkyl halide : Where halogen atom is attached to secondary C-atom

Ex.



R_2CH-X

(c) Tertiary halide or 3° alkyl halide :

Where halogen atom is attached to 3° C-atom

Preparation of Monohalides

(a) From alkanes (Halogenation) :

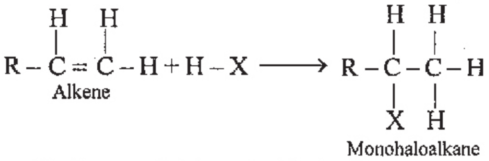
$$\underset{\text{Alkane}}{R-H} + X-X \xrightarrow{\text{Sunlight}} \underset{\text{Monohaloalkane}}{R-X} + H-X$$

The reactivity of the alkanes follows the following order :

Tertiary alkane > Secondary alkane > Primary alkane

(b) From alkenes (Hydrohalogenation) :

According to Markovnikoff's rule



$$\underset{\text{Alkene}}{R-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H} + H-X \longrightarrow \underset{\text{Monohaloalkane}}{R-\underset{X}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-H}$$

From alkynes we obtain only dihaloalkane.

(c) From alcohols :

(i) By action of dry H-X (Grove's process)

$$\underset{\text{Alcohol}}{R-OH} + H-X \xrightarrow[\Delta]{\text{Anhydrous } ZnCl_2} R-X + H_2O$$

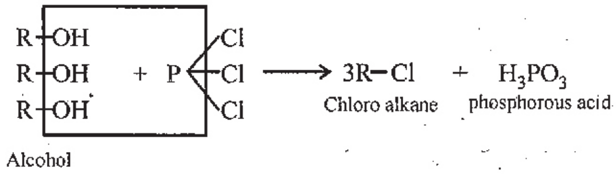
The reactivity order of HX in the above reaction is :

HI > HBr > HCl > HF

The reactivity order of alcohols in the above reaction is :

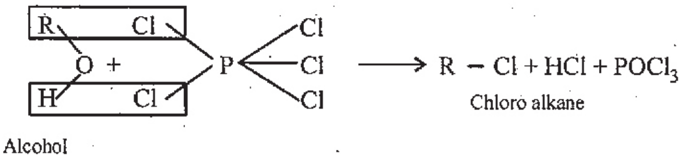
3° > 2° > 1° > MeOH

(ii) By action of PCl_3 :



$$3R-OH + PCl_3 \longrightarrow 3R-Cl + H_3PO_3$$

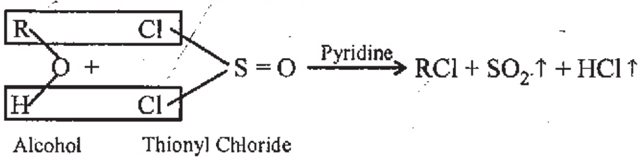
(iii) By action of PCl_5 :



$$R-OH + PCl_5 \longrightarrow R-Cl + HCl + POCl_3$$

(iv) Action of Thionyl chloride (Darzen's Process) :

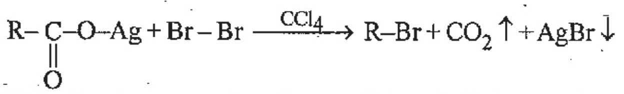
It is the best method for preparation of alkyl halide.



$$R-OH + SOCl_2 \xrightarrow{\text{Pyridine}} RCl + SO_2\uparrow + HCl\uparrow$$

(d) From silver salt of carboxylic acids :
(Borodine-Hunsdiecker reation) :

(i) A good method for obtaining alkyl halide, but from this reaction we obtain only bromo derivatives because reaction is based upon free radical mechanism.



$$R-\underset{O}{\underset{\|}{C}}-O-Ag + Br-Br \xrightarrow{CCl_4} R-Br + CO_2\uparrow + AgBr\downarrow$$

(ii) In the above reaction, the reactivity of alkyl group is 1° > 2° > 3°

(c) By halogen exchange

(i) With NaI (Finkelstein Reaction) :

$$R-Cl + NaI \xrightarrow{Acetone} \underset{\text{Iodoalkane}}{R-I} + NaCl$$

(ii) With AgF (Swarts Reaction) :

$$C_2H_5Cl + AgF \longrightarrow \underset{\text{Floroethane}}{C_2H_5F} + AgCl$$

In these reactions, only halogen exchange takes place.

(f) By reaction of alkene with sulphuryl chloride (Allylic chlorination) :

$$\underset{\text{Propene}}{CH_3-CH=CH_2} + SO_2Cl_2 \xrightarrow[\text{organic peroxide}]{\text{light \&}} \underset{\substack{\text{3-chloroprop-1-ene}\\ \text{(Allylchloride)}}}{Cl-CH_2-CH=CH_2} + HCl + SO_2$$

Physical Properties

(i) Polarity order is RF > RCl > RBr > RI

(ii) M.P & B.P. ∝ molecular weight.

For same alkyl group, the order of B.P. is

RI > RBr > RCl > RF

For isomeric alkyl halides, order of boiling point is

Primary > Secondary > Tertiary

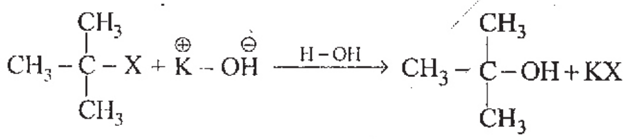
Chemical Properties

(A) Nucleophilic substitution reactions :

Main reaction of alkyl halides is nucleophilic substitution reaction. These are of two types–

(1) S_N1 Reaction (Substitution Nucleophilic Unimolecular)

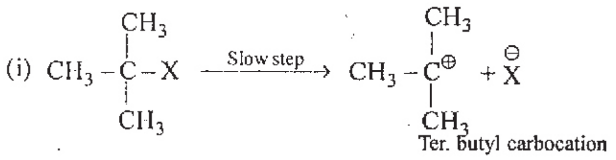
The reactivity of alkylhalides in S_N1 reaction is : 3° > 2° > 1°



$$\underset{\text{tertiary Butylhalide}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-X} + \overset{\oplus}{K}-\overset{\ominus}{OH} \xrightarrow{H-OH} \underset{\text{tertiary Butylalcohol}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH} + KX$$

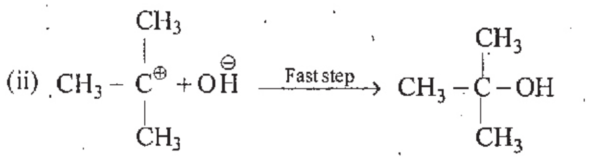
tertiary Butylhalide tertiary Butylalcohol

Mechanism L



$$\text{(i)}\ CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-X \xrightarrow{\text{Slow step}} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^{\oplus}}} + \overset{\ominus}{X}$$

Ter. butyl carbocation



$$\text{(ii)}\ CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^{\oplus}}} + \overset{\ominus}{OH} \xrightarrow{\text{Fast step}} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$$

Rate of reaction ∝ $[(CH_3)_3C-X]$

(2) S_N2 Reactions (Substitution Nucleophilic Bimolecular)

The reactivity of alkyl halides in S_N2 reactions is :

1° > 2° > 3°.

The order of reactivity among various 1° alkyl halides is

$$CH_3X > C_2H_5X > n-C_3H_7X, \text{etc.}$$

Bulkier the alkyl group, more is the steric hindrance in the formation of transition state and less is the reactivity of alkyl halide.

Remember that in case alkyl halide is optically active, $S_N{}^2$ **reactions lead to Walden inversion**

Thus in short, 3° alkyl halides react by $S_N{}^1$, 1° by $S_N{}^2$ and 2° by either or both of these mechanism depending upon the nature of the alkyl halide and the reagent.

For a given alkyl group, the order of reactivity is

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

Increasing bond energy ; Decreasing halogen reactivity.

The nucleophilic substitution reactions of alkyl halides are as follows :

(i) Hydrolysis :

(a) With aqueous KOH :

$$R-X + K-OH \longrightarrow \underset{\text{Alcohol}}{R-OH} + K-X$$

(b) Using moist Ag_2O :

$$2R-X + Ag_2O + H_2O \longrightarrow \underset{\text{Alcohol}}{2R-OH} + 2AgX$$

(a) Reaction with NaOR

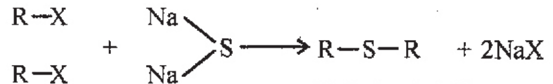
$$R-X + NaOR \longrightarrow \underset{\text{Ether}}{R-O-R} + NaX$$

The above reaction is called **"Williamson's ether synthesis"**.

(b) Using dry Ag_2O

$$2R-X + Ag_2O \longrightarrow \underset{\text{Ether}}{R-O-R} + 2AgX$$

(iii) Reaction with Na_2S



$$\begin{matrix} R-X \\ R-X \end{matrix} + \begin{matrix} Na \\ Na \end{matrix}\!\!>\!S \longrightarrow R-S-R + 2NaX$$

dialkyl sulphide

(iv) Reaction with KSH :

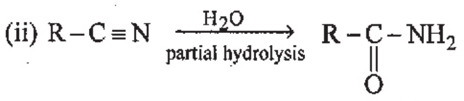
$$R-X + K-SH \longrightarrow \underset{\text{Alkane thiol}}{R-SH} + KX$$

(v) Reaction with KCN :

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

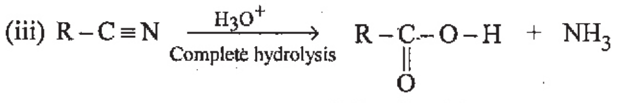
Alkane nitrile is an important compound which gives following products.

$$\text{(i)}\ R-C\equiv N \xrightarrow{LiAlH_4/\text{Reduction}} \underset{\text{Alkyl amine}}{R-CH_2-NH_2}$$



$$\text{(ii)}\ R-C\equiv N \xrightarrow[\text{partial hydrolysis}]{H_2O} R-\underset{\underset{O}{\|}}{C}-NH_2$$

Alkane amide



$$\text{(iii)}\ R-C\equiv N \xrightarrow[\text{Complete hydrolysis}]{H_3O^+} R-\underset{\underset{O}{\|}}{C}-O-H + NH_3$$

Carboxylic acid

(vi) Reaction with AgCN :

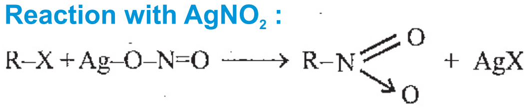
$$R-X + AgCN \longrightarrow \underset{\text{Alkane isocynide}}{R-N \overrightarrow{\equiv} C} + AgX$$

(vii) Reaction with KNO_2 :

$$R{-}X + \overset{+}{K}{-}\overset{-}{O}{-}N{=}O \longrightarrow R{-}O{-}N{=}O + KX$$

alkyl nitrite

(viii) Reaction with $AgNO_2$:



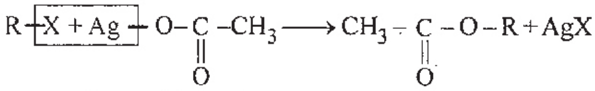
nitro alkane

(ix) Reaction with Na_2SO_3 :

$$R-X + Na_2SO_3 \longrightarrow RSO_3Na + NaX$$

alkyl sodium sulphonate

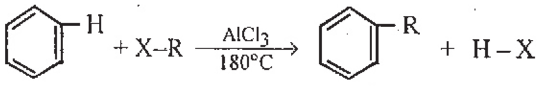
(x) Reaction with silver acetate (Esterification) :



$$R\boxed{-X + Ag-}O-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-O-R + AgX$$

silver acetate ester

(xi) Reaction with benzene (Friedel-Craft reaction) :



Alkyl benzene

(B) Elimination reactions

(i) With alcoholic KOH :

$$R-CH_2-CH_2-X + KOH\,(alc.) \longrightarrow R-CH=CH_2 + KX + H_2O$$

The elemination takes place in accordance with the **Saytzeff's rule.**

(ii) Action of heat :

$$R{-}CH_2{-}CH_2{-}X \xrightarrow{300°C} R-CH=CH_2 + HX$$

Alkene

The decomposition follows the following order :

Iodide > Bromide > chloride (when alkyl group is same)

and Tertiary > Secondary > Primary

(when same halogen is present)

(c) Reduction

Haloalkanes on reduction produces alkanes frequently.

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

Alkane

(D) Reaction with metals :

(i) With Na : (Wurtz reaction)

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

Alkane

(ii) With Mg : (Grignard reaction)

$$R-X + Mg \xrightarrow{\text{dry ether}} R-Mg-X$$

Grignard reagent

(iii) With Zn dust : (Frankland reaction)

$$R\boxed{-X + 2Zn + X-}R \longrightarrow R-R + ZnX_2$$

alkane

(iv) With Li :

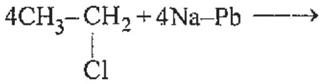
$$R-Cl + 2Li \xrightarrow{\text{dry ether}} RLi + LiCl$$

alkyl lithium

Note :

Isopropyl lithium is more reactive than Grignard reagent.

(v) With Na - lead alloy :



$$4CH_3-\underset{\underset{Cl}{|}}{CH_2} + 4Na{-}Pb \longrightarrow$$

$$(CH_3-CH_2)_4Pb + 4NaCl + 3Pb$$

TEL

(tetra ethyl lead)

Tetra ethyl lead is used as an antiknocking agent with gasoline.

Uses :

(a) As alkylation agent (Wurtz reaction)

(b) As synthetic reagent

(c) Lower members used as anaesthetic agent, refrigerant or solvent.

DIHALIDES OR DIHALOALKANES

Gen. formula $C_nH_{2n}X_2$

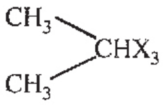
Two H-atoms of alkanes, replaced by two halogen atoms form dihalides.

Dihalides are classified as :

(a) Gem dihalides or Alkylidene halides

These are the halides in which two identical halogen atoms are attached to the same carbon atom.

Ex. CH_3CHX_2 Ethylidene dihalide (1, 1-dihaloethane)

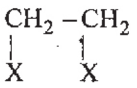


Isopropylidene dihalide (2, 2-dihalopropane)

(b) Vicinal dihalides or Alkylene halides

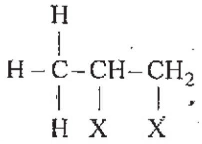
In these halides, two identical halogen atoms are attatched on adjacent carbon atoms.

Ex.



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

Ethylene dihalide

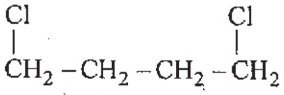


$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\underset{\underset{X}{|}}{CH}-\underset{\underset{X}{|}}{CH_2}$$

Propylene dihalide

(c) **α, ω dihalides :** Halogen atoms are attached with terminal C-atoms. They are separated by 3 or more C-atoms. They are also known as polymethylene halides.

Ex.



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

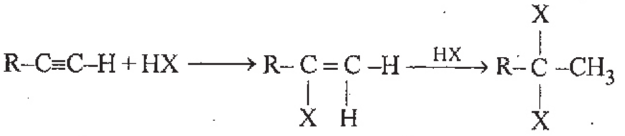
(1,4-Dichlorobutane)

Tetramethylene dichloride

Preparation of Dihalides

(a) Gem dihalides

(i) From alkynes (By hydrohalogenation) : Addition of halogen acid to alkynes. The addition follows **Markovnikov's rule.**



$$R{-}C{\equiv}C{-}H + HX \longrightarrow R-\underset{\underset{X}{|}}{C}=\underset{\underset{H}{|}}{C}-H \xrightarrow{HX} R-\overset{\overset{X}{|}}{\underset{\underset{X}{|}}{C}}-CH_3$$

Alkyne Alkylidine halide

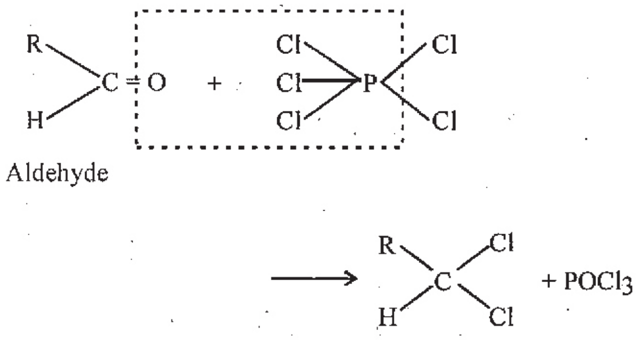
Ex.

$$CH{\equiv}CH + HBr \longrightarrow CH_2{=}CHBr \xrightarrow{HBr} CH_3CHBr_2$$

Vinyl bromide 1, 1-Dibromo ethane

(ii) From carbonyl compounds :

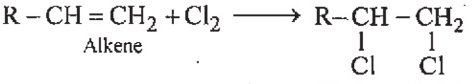
By action of phosphorous pentachloride on aldehydes and ketones.



(terminal gem dihalide)

(b) Vicinal dihalides

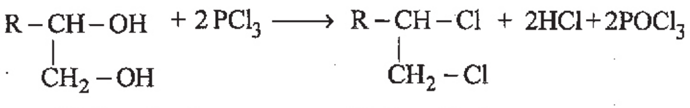
(i) From alkene (By halogenation) Addition of halogens to alkene.



$$\underset{\text{Alkene}}{R-CH=CH_2} + Cl_2 \longrightarrow R-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}$$

Alkylene chloride

(ii) From vicinal glycol : By the action of phosphorous pentahalide on glycol.



$$\underset{\text{Alkylene glycol}}{\begin{matrix}R-CH-OH\\ |\\ CH_2-OH\end{matrix}} + 2PCl_5 \longrightarrow \underset{\text{Alkylene chloride}}{\begin{matrix}R-CH-Cl\\ |\\ CH_2-Cl\end{matrix}} + 2HCl + 2POCl_3$$

(c) α-ω dihalides :

$$\underset{\text{Allyl bromide}}{CH_2=CH-CH_2Br} + HBr \longrightarrow \underset{\text{1,2-Dibromopropane}}{Br-CH_2-CH_2-CH_2Br}$$

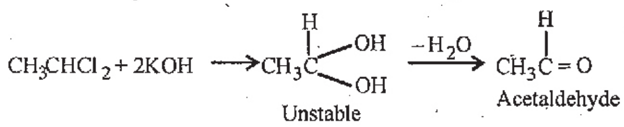
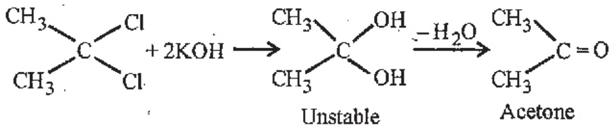
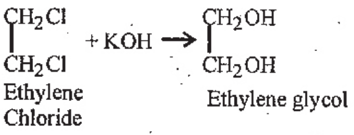
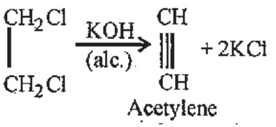
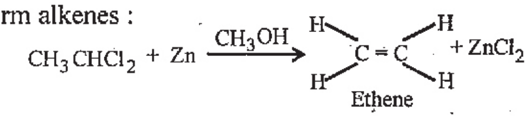
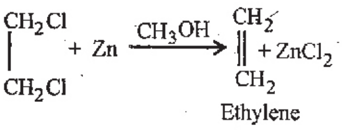
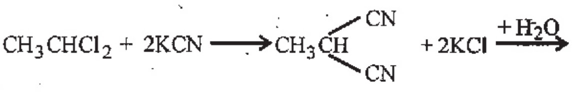
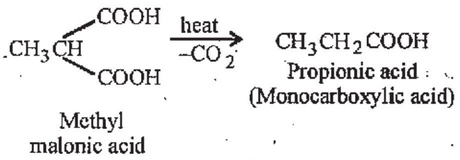
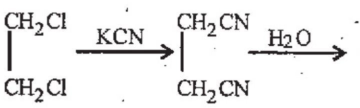
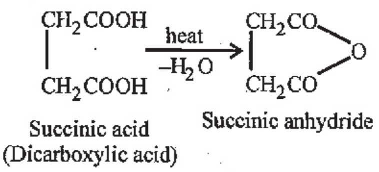
Physical Properties

(i) Dihalides of lower alkanes are colourless with sweet smelling liquids but higher homologues are solids.

(ii) Melting point and boiling points are directly proportional to molecular mass but boiling point of vicinal dihalides are more than gem dihalides. Also, reactivity of vicinal dihalides is more than gemdihalides, but they are less reactive than monohalides.

Chemical Properties

The important chemical properties of dihalides are given below in comparative form.

S.No.	Property	Alkylidene halides (Gem dihalide)	Alkylene halides (Vicinal dihalide)
1	**Hydrolysis** **(with aq. KOH)**	Form aldehydes or ketones :  $CH_3CHCl_2 + 2KOH \rightarrow CH_3CH(OH)_2 \xrightarrow{-H_2O} CH_3CH=O$ Unstable Acetaldehyde  $(CH_3)_2CCl_2 + 2KOH \rightarrow (CH_3)_2C(OH)_2 \xrightarrow{-H_2O} (CH_3)_2C=O$ Unstable Acetone	Form glycols :  $\underset{\text{Ethylene Chloride}}{\begin{matrix}CH_2Cl\\ \vert\\ CH_2Cl\end{matrix}} + KOH \rightarrow \underset{\text{Ethylene glycol}}{\begin{matrix}CH_2OH\\ \vert\\ CH_2OH\end{matrix}}$
2	**Reaction with alcoholic KOH (Dehydrohalogenation)**	Form alkynes : $CH_3CHCl_2 \xrightarrow[\text{(alc.)}]{KOH} \underset{\text{Acetylene}}{CH\equiv CH} + 2KCl$	Form alkynes :  $\begin{matrix}CH_2Cl\\ \vert\\ CH_2Cl\end{matrix} \xrightarrow[\text{(alc.)}]{KOH} \underset{\text{Acetylene}}{\begin{matrix}CH\\ \vert\vert\vert\\ CH\end{matrix}} + 2KCl$
3	**Reaction with Zn dust in methanol**	Form alkenes :  $CH_3CHCl_2 + Zn \xrightarrow{CH_3OH} H_2C=CH_2 + ZnCl_2$ Ethene	Form alkenes :  $\begin{matrix}CH_2Cl\\ \vert\\ CH_2Cl\end{matrix} + Zn \xrightarrow{CH_3OH} \underset{\text{Ethylene}}{\begin{matrix}CH_2\\ \vert\vert\\ CH_2\end{matrix}} + ZnCl_2$
4	**Reaction with alc. KCN followed by hydrolysis and heating the product**	 $CH_3CHCl_2 + 2KCN \rightarrow CH_3CH(CN)_2 + 2KCl \xrightarrow{+H_2O}$  $\underset{\text{Methyl malonic acid}}{CH_3CH(COOH)_2} \xrightarrow[-CO_2]{heat} CH_3CH_2COOH$ Propionic acid (Monocarboxylic acid)	 $\begin{matrix}CH_2Cl\\ \vert\\ CH_2Cl\end{matrix} \xrightarrow{KCN} \begin{matrix}CH_2CN\\ \vert\\ CH_2CN\end{matrix} \xrightarrow{H_2O}$  $\begin{matrix}CH_2COOH\\ \vert\\ CH_2COOH\end{matrix} \xrightarrow[-H_2O]{heat}$ Succinic acid (Dicarboxylic acid) Succinic anhydride

TRIHALIDES OR TRIHALOALKANES

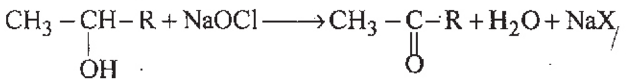
Gen formula $C_nH_{2n-1}X_3$

Three H-atoms of alkane replaced by three halogen atoms form trihalides. Trihalogen derivatives of methane are also known as haloforms.

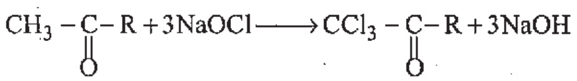
Preparation of $CHCl_3$

(i) Haloform reaction : In this reaction, when suitable aldehyde, ketone is treated with halogen, $X_2(Cl_2, Br_2$ or $I_2)$ and an alkali [NaOH, KOH, $Ca(OH)_2$ etc.], a halo form is produced.

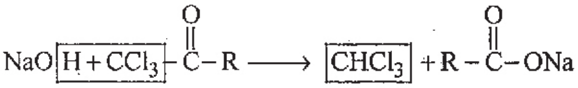
e.g. : $Cl_2 + 2NaOH \longrightarrow NaCl + NaOCl + H_2O$



$$CH_3-\underset{OH}{\underset{|}{CH}}-R + NaOCl \longrightarrow CH_3-\underset{O}{\underset{\|}{C}}-R + H_2O + NaX$$



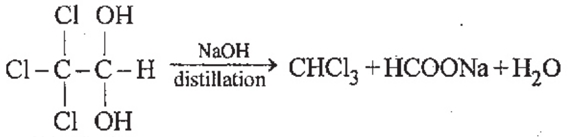
$$CH_3-\underset{O}{\underset{\|}{C}}-R + 3NaOCl \longrightarrow CCl_3-\underset{O}{\underset{\|}{C}}-R + 3NaOH$$



$$NaO\boxed{H + CCl_3}-\overset{O}{\overset{\|}{C}}-R \longrightarrow \boxed{CHCl_3} + R-\overset{O}{\overset{\|}{C}}-ONa$$

Chloroform

(ii) Preparation of pure chloroform : Alkaline solution of chloralhydrate on distillation gives pure chloroform as follows :



$$Cl-\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}-\underset{OH}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-H \xrightarrow[\text{distillation}]{NaOH} CHCl_3 + HCOONa + H_2O$$

Chloralhydrate

(iii) From carbon tetrachloride (Pyrene)

By reduction, i.e,

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

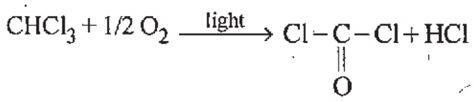
If reducing agent is $Fe + H_2O$, then complete reduction occurs and product becomes alkane.

(iv) From methane :

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl \xrightarrow[Cl_2]{h\nu} CH_2Cl_2 \xrightarrow[Cl_2]{h\nu} CHCl_3$$

Chemical Properties

(i) Oxidation : In the presence of light, $CHCl_3$ forms poisonous gas phosgene with atmospheric oxygen or with air.



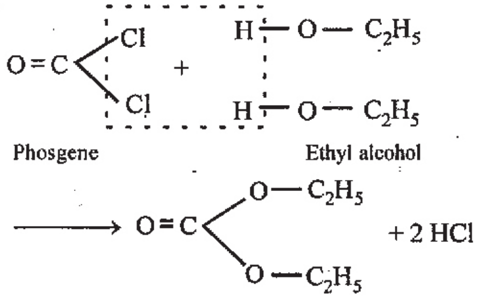
$$CHCl_3 + 1/2\ O_2 \xrightarrow{\text{light}} Cl-\underset{O}{\underset{\|}{C}}-Cl + HCl$$

Chloroform Phosgene

Precautions :

(i) It is stored in closed dark coloured bottles (to cutoff light) completely filled to the neck and well stoppered to exclude air.

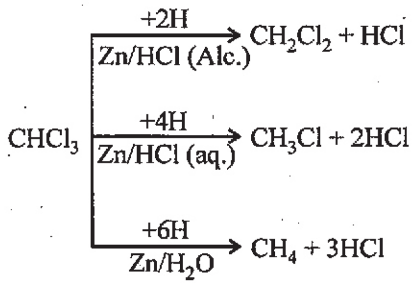
(ii) For removal of phosgene we can use 1% ethanol solution which converts poisonous phosgene into non–poisonous salt diethyl carbonate.



Phosgene Ethyl alcohol

Diethyl carbonate (Non–poisonous substance)

2. Reaction :

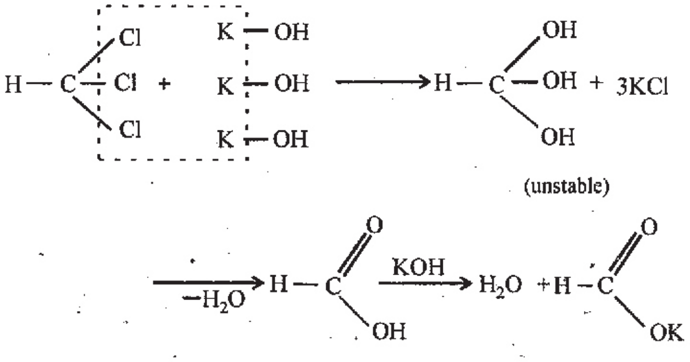


$$CHCl_3 \xrightarrow[Zn/HCl\ (Alc.)]{+2H} CH_2Cl_2 + HCl$$

$$CHCl_3 \xrightarrow[Zn/HCl\ (aq.)]{+4H} CH_3Cl + 2HCl$$

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

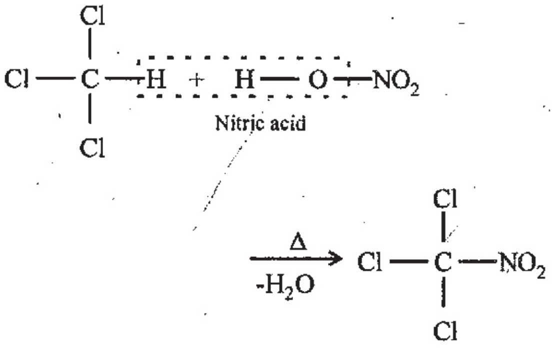
3. Reaction with Alcoholic KOH :



(unstable)

Formic acid Potassium formate

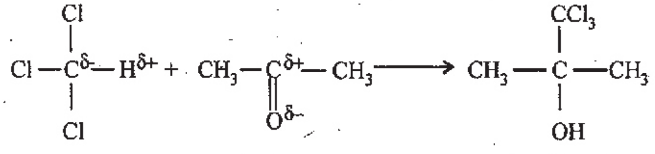
4. Reaction with Alcoholic KOH :



Nitric acid

Trichloronitromethane
(Chloropicrin) (Tear gas)

5. Reaction with Acetone :



Acetone Chloretone

Chloretone is used as a hypnotic agent

6. Reaction with silver powder (Dehalogenation) :

$$CHCl_3 + 6Ag + Cl_3CH \xrightarrow{\text{high temp.}} CH\equiv CH + 6AgCl$$

Acetylene

7. Reaction with Primary amine :

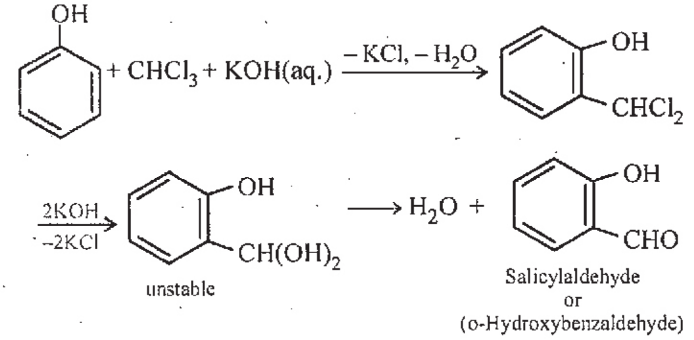
$$R\ddot{N}H_2 + CHCl_3 + KOH(alc.) \longrightarrow R-N \stackrel{\rightarrow}{=} C + KCl + H_2O$$

Alkane amine Alkyl isocyanide or carbylamine

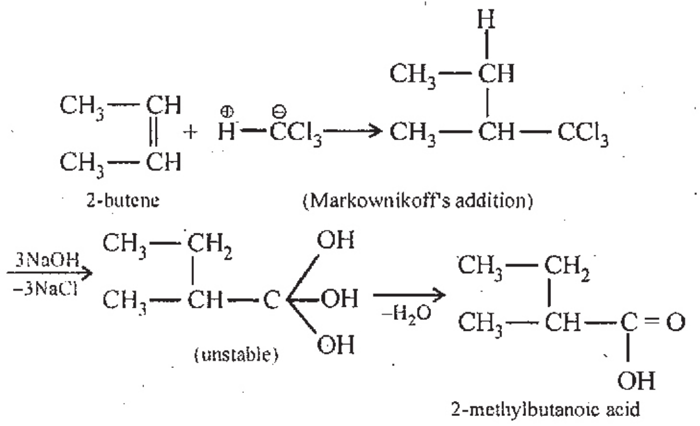
The reaction is called as “**carbylamine Reaction**’ or “**Isocyanide–test**’. It is not shown by 2° and 3° amines.

8. Reaction with Phenol :

The reaction is called as “**Reimer-Tiemann reaction**’.



9. Reaction with 2-Butene :



Uses

(a) As an anaesthetic agent. However, it has been replaced by less toxic and safer anaesthetic agents.

(b) $CHCl_3$ acts as a solvent for fat, waxes, rubber etc.

(c) In preparation of chloretone (drug, a hypnotic agent) and nitrochloroform (an insecticide, tear gas)

(d) $CHCl_3$ is used as a preservative for anatomical specimen.

(e) As lab. reagent to identity 1° amine and other analytical tests.

IODOFORM (TRIIODOMETYHANE) CHI_3

CHI_3 was earlier used as an antiseptic for dressing wounds. Its antiseptic properties are due to the liberation of iodine when iodoform comes in contact with skin but not due to iodoform itself.

TETRA HALIDES OR TETRAHALOALKANES

Gen formula → $C_nH_{2n-2}X_4$

Obtained by the replacement of 4-H atoms of an alkane by equal no. of halogen atoms.

Ex. CCl_4 [Carbon Tetrachloride (pyrene)]

Preparations

(i) From methane (CH_4) :

$$CH_4 + Cl_2 \longrightarrow CH_2Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$$

(ii) From carbon disulphide (CS_2) :

$$CS_2 + 3Cl-Cl \xrightarrow[\text{Fe dust, } I_2]{\Delta(500°C)} CCl_4 + S_2Cl_2$$

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

(iii) From $CHCl_3$ Chlorination of chloroform.

$$CHCl_3 + Cl-Cl \xrightarrow{\text{ultravioletlight}} CCl_4 + HCl$$

(iv) From propane :

$$C_3H_8 + 9Cl_2 \xrightarrow[\text{Pressure}]{400°C} CCl_4 + C_2Cl_6 + 8HCl$$

Propane Pyrene

PHYSICAL PROPERTIES

(i) It is colourless liquid with specific smell.

(ii) It is insoluble in water and soluble in organic solvent.

(iii) It is the only organic solvent which is non–combustible. So, it is used as fire-extinguisher called as ‘**Pyrene**’.

CHEMICAL PROPERTIES

(i) Oxidation :

$$CCl_4 + H_2O(g) \xrightarrow{\Delta} COCl_2 + 2HCl$$

Phosgene

(ii) Hydrolysis :

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

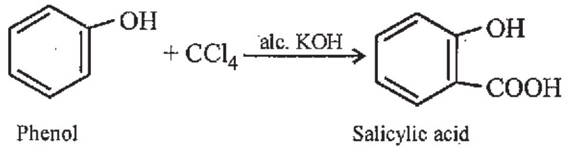
(unstable)

$$\xrightarrow{+2KOH} K_2CO_3 + H_2$$

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

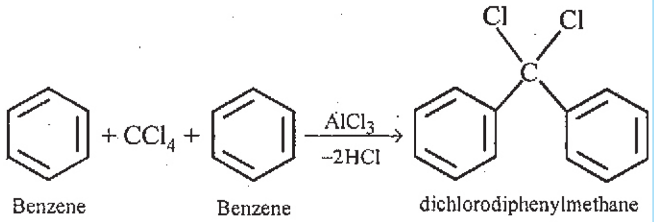
$$CCl_4 + 2H \xrightarrow{Fe/H_2O} CHCl_3 + HCl$$

(iv) It reacts with phenol and forms salicylic acid.



The reaction is called as “**Riemer-Tiemann Carboxylation**’.

(v) Reaction with benzene :



Uses :

(a) As a fire extinguisher (Pyrene)

(b) As a Lab reagent.

(c) As a solvent for fats, oils, resins. in dry cleaning

OTHER USEFUL HALOGEN DERIVATIVES

(A) Freons or CFC's (Chlorofluoro Carbons) :

(i) Preparation of freons :

The chlorofluoro derivatives of methane and ethane are called freons.

$$CCl_4 + HF \xrightarrow{SbCl_5} CCl_3F + HCl$$

Freon–11

$$CHCl_3 + HF \xrightarrow{SbCl_5} CHFCl_2 + HCl$$

Freon–21

$$C_2Cl_6 + 2HF \xrightarrow{SbCl_5} C_2F_2Cl_4 + 2HCl$$

Hexachloro ethane Freon–112

(ii) Properties

(i) Freons is a colourless, odourless, unreactive & non-corrossive and non-toxic gas.

(ii) It has low b.p., low specific heat and can be easily liquefied by applying pressure.

(iii) Uses of Freons : (i) They easily converted from gaseous state to liquid state, therefore they are used as a coolant in A.C. & refrigerators.

(ii) Used as a propellant in aerosols and foams.

(iv) Nomenclature of Freons : The common name of freons is Freon - cba or freon C - 1, H + 1, F

where c = no. of carbon atoms –1
b = no. of hydrogen atoms +1
a = total no. of atoms of fluorine

Example : $CFCl_3 : C-1=0, H+1=1, F=1$

$\therefore$ its name is : Freon – 11

Formula	C–1	H+1	F	Name
$CFCl_3$	1–1 = 0	0 + 1 = 1	1	Freon–11
CF_2Cl_2	1–1 = 0	0 + 1 = 1	2	Freon–12
$C_2F_2Cl_4$	2–1 = 1	0 + 1 = 1	2	Freon–112
$C_2F_3Cl_3$	2–1 = 1	0 + 1 = 1	3	Freon-113
$C_2F_4Cl_2$	2–1 = 1	0 + 1 = 1	4	Freon-114
C_2F_5Cl	2–1 = 1	0 + 1 = 1	5	Freon-115

(B) Teflon

(i) Preparation :

Produced by polymerisation of $CF_2=CF_2$ (Tetrafluoroethylene).

$$2CHCl_3 + SbF_3 \xrightarrow{-HF} 2CHF_2Cl \xrightarrow[-2HCl]{800°C} CF_2=CF_2$$

Polymerisation of $CF_2=CF_2$ gives Teflon.

$$n\,CF_2=CF_2 \xrightarrow{\text{Polymerisation}} (-CF_2-CF_2-)_n$$

Teflon

(ii) Properties :

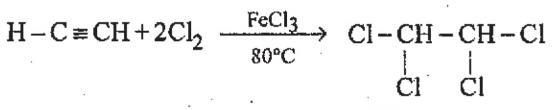
(i) It is chemically inert.
(ii) It is stable at high temp.
(iii) Unaffected by strong acids and by boiling aqua-regia.

(iii) Uses :

(i) Making acid containers.
(ii) For electrical insulation & lubricants.
(iii) Preparation of gasket materials.

(C) Westron (Acetylene Tetrachloride) : ($Cl_2CH\text{-}CHCl_2$)

(i) Preparation :

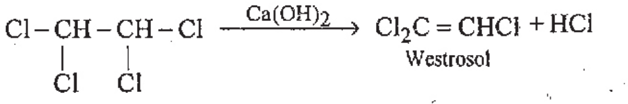


$$H-C\equiv CH + 2Cl_2 \xrightarrow[80°C]{FeCl_3} Cl-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH}}-Cl$$

Westron

(ii) Properties :

Heavy, nonflammable, highly toxic liquid, BP → 145°C, Chloroform like smell. When treated with lime water ($Ca(OH)_2$), it gives westrosol.



$$Cl-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH}}-Cl \xrightarrow{Ca(OH)_2} Cl_2C=CHCl + HCl$$

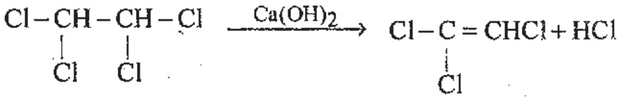
Westrosol

Uses :

(i) In the manufacture of westrosol.
(ii) As an insecticide.
(iii) As a solvent for oil, fats, paints etc.

(D) Westrosol : (Trichloro Ethylene)

(i) Preparation :



$$Cl-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH}}-Cl \xrightarrow{Ca(OH)_2} Cl-\underset{Cl}{\underset{|}{C}}=CHCl + HCl$$

(ii) Properties : It is less toxic than westron. B.P. 80°C

(iii) Uses :

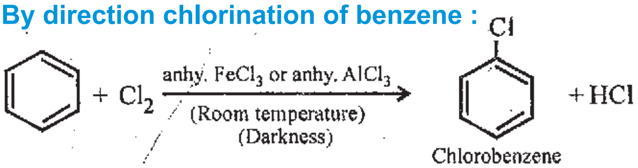
(i) As a refrigerants
(ii) As an aneasthetic
(iii) As a solvent for oil, fats etc.

HALOARENES (ARYL HALIDES)

They are obtained by replacement of one or more H–atoms of an aromatic hydrocarbon by an equal number of halogen atoms.

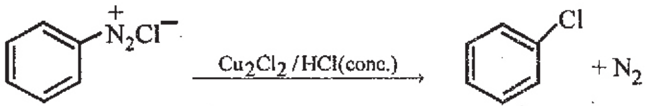
Preparation

(i) By direction chlorination of benzene :

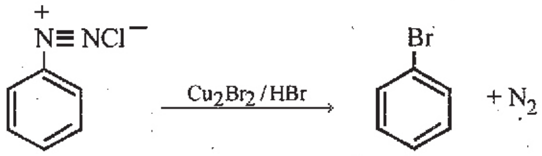


Chlorobenzene

(ii) By Sandmeyer's reaction :

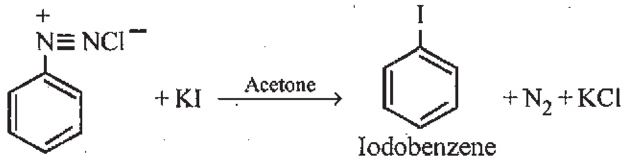


Benzene diazonium chloride Chlorobenzene

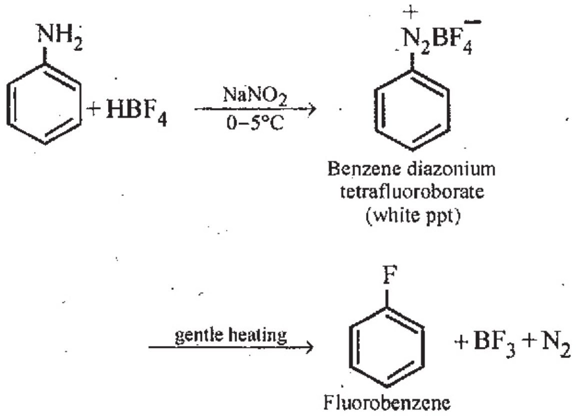


Bromobenzene

Iodobenzene can be prepared by reacting benzene diazonium chloride with KI solution.

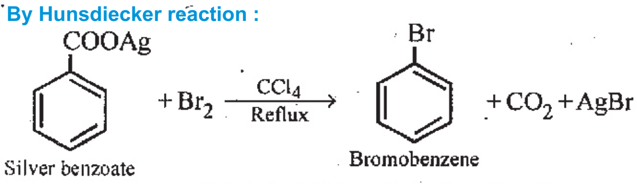


Fluorobenzene can be obtained from diazo salt as follows :

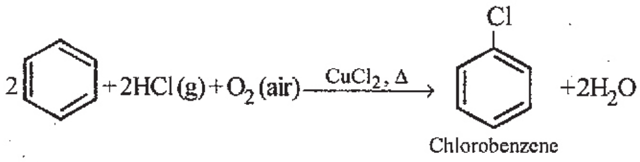


This reaction is called **Balz-Schiemann Reaction**

(iii) By Hunsdiecker reaction :



(iv) Rasching process : It is industrial method for chlorobenzene.

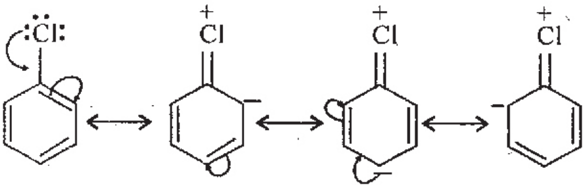


PHYSICAL PROPERTIES

Chlorobenzene is a colourless, pleasant smelling, heavy liquid. It is insoluble in water, but soluble in alcohol and ether.

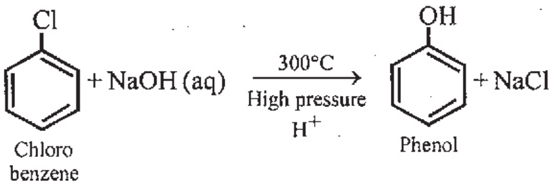
CHEMICAL PROPERTIES

1. **Nucleophilic substitution** The halogen atom is firmly attached with the benzene nucleus and acquires extra stability due to resonance (+M) effect. Hence, the halogen atom cannot be easily replaced by other atoms or group of atoms. So, aryl halides are less reactive the than alkyl halides.

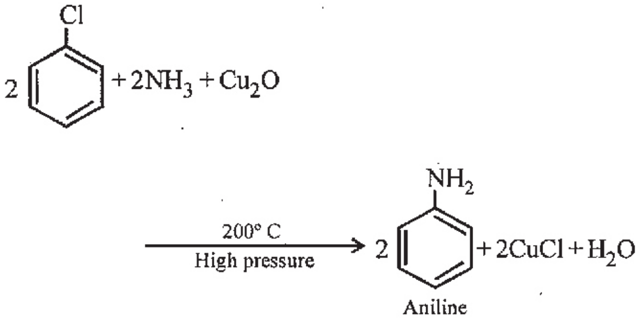


The halogen atom is replaced by other nucleophiles under drastic conditions.

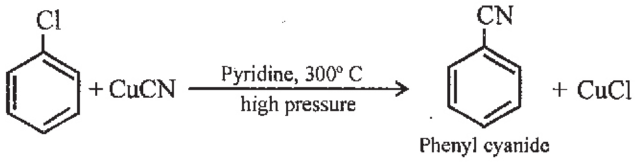
(i) Replacement by-OH group:



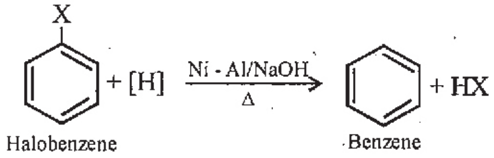
(ii) Replacement by-NH_2 group:

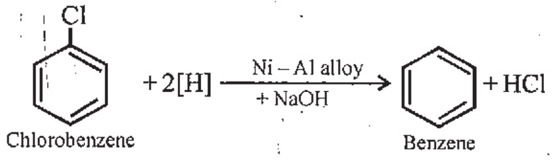


(iii) Replacement by-CN :

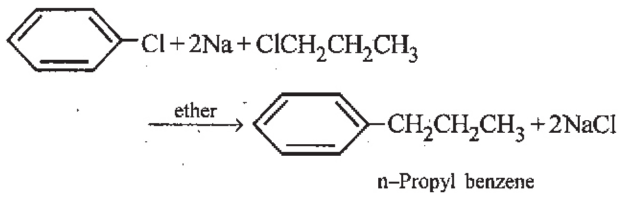


2. **Reduction :**

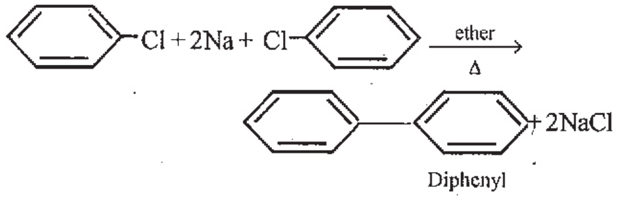




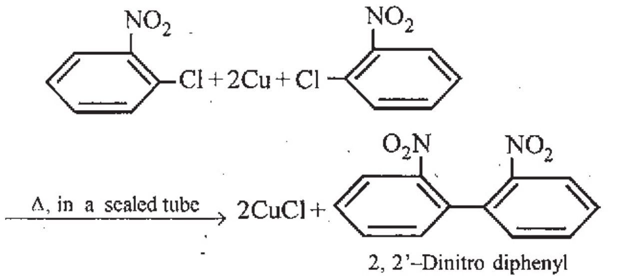
3. **Wurtz-Fittig reaction :** Aryl halide and alkyl halide when heated together in the presence of sodium and ether, yield homologues of benzene.

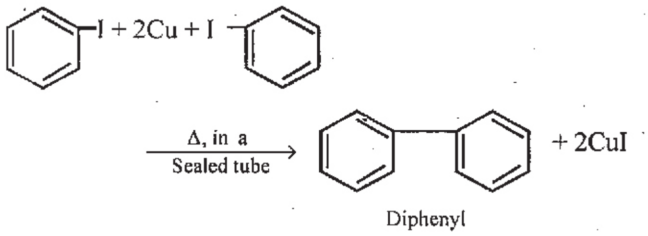


When only aryl halides are heated with metallic sodium, the reaction is known as Fittig reaction and the product is diaryl :

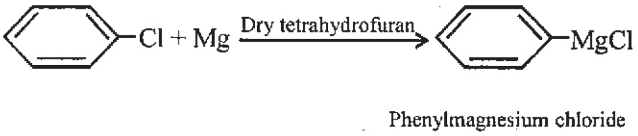


4. Ullmann Reaction : Chloro and bromo benzenes do not give this reaction. But when there is an electron withdrawing group at the ortho and/or para position of the halogen atom, Ullmann reaction is given by them :

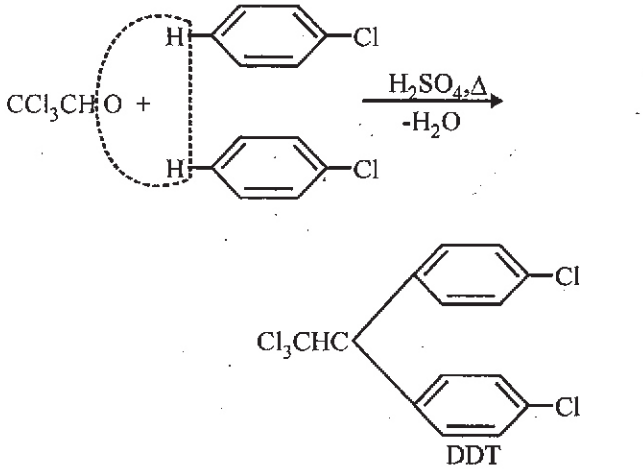




5. Formation of Grignard's reagents :

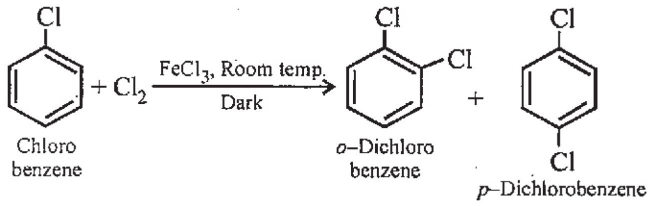


6. Reaction with chloral When chlorobenzene is heated with chloral in the presence of conc. H_2SO_4, a powerful insecticide, DDT is formed.

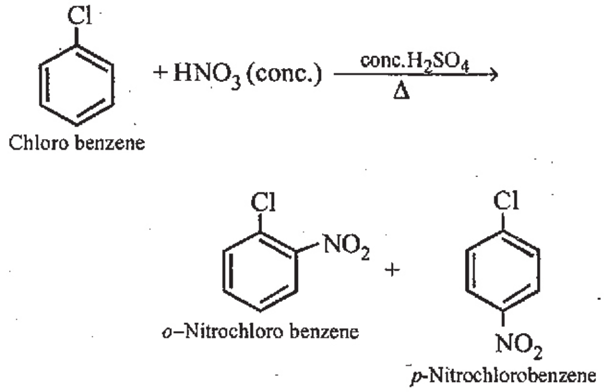


(p, p'-Dichlorodiphenyl trichloroethane)

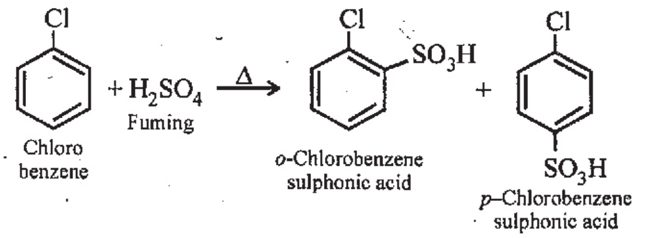
7. Reactions due to the benzene ring : The halogen atoms are *o*-, *p*-directing but deactivate the benzene ring towards electrophilic substitution reactions due to their strong –I effect.



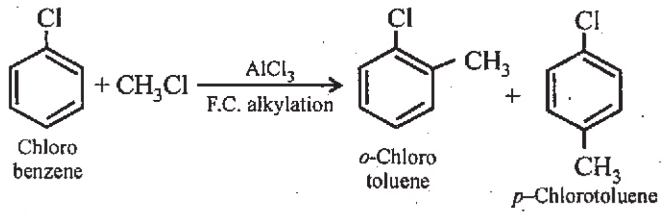
(b) Nitration :

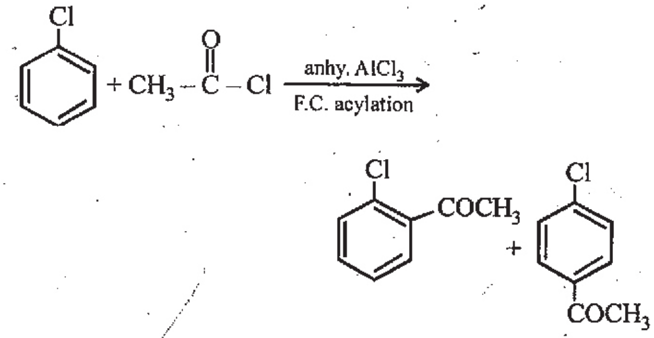


(c) Sulphonation :



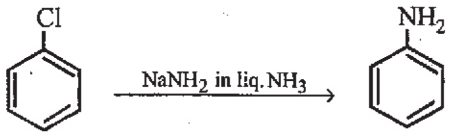
(d) Friedel -Crafts reaction :





8. Elimination addition reaction :

In absence of electron withdrawing substituents at *o*- and *p*-positions wrt the halogen, aryl halides can still be made to undergo nucleophillic substitution reactions but only in the presence of strong nucleophiles such as $NaNH_2$ in liq. NH_3.

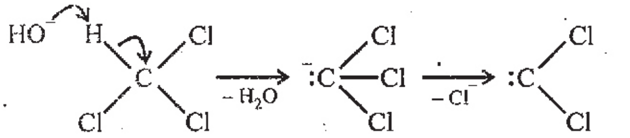


Chlorobenzene is used for preparation of aniline, phenol, picric acid, DDT, etc.

IMPORTANT POINTS

1. Elimination Reactions : They are classified into two categories : (a) α-Elimination reactions (b) β-Elimination reactions.

(a) α-Elimination reactions: are those in which the two groups are eliminated from the same carbon. For ex :



Chloroform Dichlorocarbene

(b) β-Elimination reactions: are those reactions in which the two groups are eliminated from the adjacent carbon atoms. H from β- and the X from the α-carbon. For ex :

$$\overset{\beta}{CH_3} - \overset{\alpha}{CH_2} - Br \xrightarrow{NaOC_2H_5} CH_2 = CH_2 + C_2H_5OH + NaBr$$

Depending upon the structure of the alkyl halide, strength of the base and polarity of the solvent, β-elimination reactions occur by the following three mechanisms :

(i) E_2 (Elimination, bimolecular)

(ii) E_1 (Elimination, unimolecular)

(iii) E_1CB (Elimination, unimolecular, conjugate base or carbanion mechanism)

2. Analysis of Alkyl and Ary Halides :

The presence of halogen in organic compounds is tested by the following two tests :

(i) Beilstein test : In this test, a copper strip is heated strongly in the Bunsen flame till it ceases to impart any greenish or bluish green flame. A pinch of the organic halide is then placed on this hot copper strip and then reintroduced into the flame.

If a green or bluish green flame reappears, it indicates the presence of halogen in the organic compound. [This test is very sensitive but does not indicate the nature of halogen (i.e., chlorine, bromine or iodine)].

(ii) Lassaigne's test : The test is carried out using Lassaigne's extract which is prepared by fusing the organic halide with sodium metal.

The extract is boiled with dil. HNO_3 to expel gases. The solution is then cooled and $AgNO_3$ solution added to it.

(a) A white ppt soluble in NH_4OH indicates the presence of chlorine.

(b) A pale yellow ppt partially soluble in NH_4OH indicates the presence of bromine.

(c) A bright yellow ppt insoluble in NH_4OH indicates the presence of iodine.

3. Organic halides contain three types of halogens.

(a) Ionic halogen as in benzene diazonium halides and quarternary ammonium halides, i.e.,

$C_6H_5N_2^+X^-$ and $R_4N^+X^-$ (where X = Cl, Br or I)

(b) Labile halogen as in alkyl, allyl or benzyl halides

i.e., $R-X$; $CH_2=CH-CH_2X$; $C_6H_5-CH_2X$

(c) Inert halogen as in aryl halides, i.e., chlorobenzene, bromobenzene, iodobenzene, etc. and vinyl halides i.e., vinyl chloride, vinyl bromide, etc.

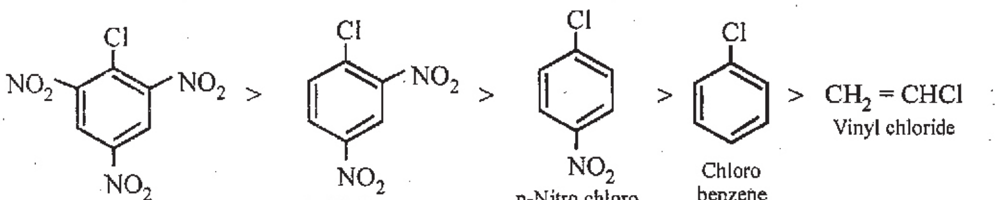
These halogens can be distinguished by **$AgNO_3$ test** :

(i) If a white or yellow ppt of AgX is formed with $AgNO_3$ solution in cold, it indicates ionic halogen.

(ii) If a white or yellow ppt of AgX is formed with $AgNO_3$ solution in the hot, labile halogen is indicated.

(iii) If both the above tests are negative, the presence of inert halogen is indicated.

The reactivity of halogen atom is increased by the presence of electron withdrawing group at ortho and or para positions wrt the halogen atom. Thus, the reactivity order of halogens is :



Picryl chloride 2, 4dinitro chlorobenzene p-Nitro chloro benzene Chloro benzene

MISCELLANEOUS SOLVED EXAMPLES

Example 1 : A dihalogen derivative 'X' of a hydrocarbon with three carbon atoms reacts with alcoholic KOH and produces another hydrocarbon which forms a red precipitate with ammoniacal Cu_2Cl_2. 'X' gives an aldehyde on reaction with aqueous KOH. The compound 'X' is

(a) 1, 3 – Dichloropropane (b) 1, 2 – Dichloropropane

(c) 2, 2 – Dichloropropane (d) 1, 1 – Dichloropropane

sol. **(d)** The reaction sequence is as follows

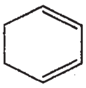
$$\underset{\text{aldehyde}}{CH_3CH_2CHO} \xleftarrow{\text{aq.KOH}} \underset{\text{1,1–dichloropropane}}{CH_3CH_2CHCl_2}$$

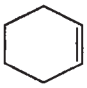
$$\xrightarrow{\text{alc.KOH}} \underset{\text{hydrocarbon}}{CH_3-C\equiv CH} + 2KCl + H_2O$$

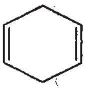
$$\Big\downarrow Cu_2Cl_2\,/\,NH_3$$

$$\text{Red ppt}$$

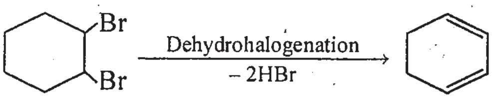
Example 2 : 1, 2-di-bromo cyclohexane on dehydrohalogenation gives

(a) 

(b) 

(c) 

(d) None of these

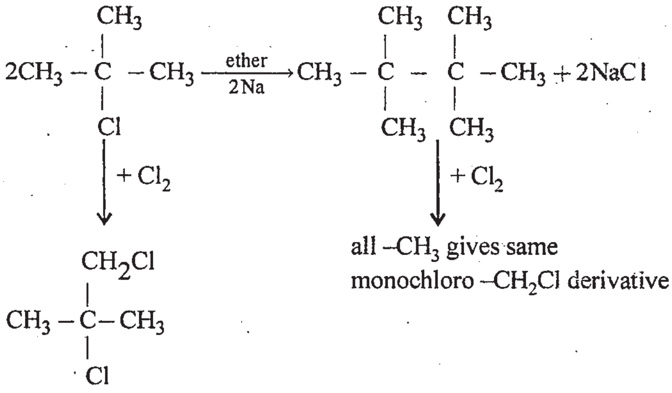
Sol. **(a)** 

Example 3 : An organic compound $A(C_4H_9Cl)$ on reaction with Na/diethyl ether gives a hydrocarbon, which on monochlorination gives only one chloro derivative. A is

(a) *t*-butyl chloride (b) *s*-butyl chloride

(c) Isobutyl chloride (d) *n*-butyl chloride

sol. **(a)**



all $-CH_3$ gives same monochloro $-CH_2Cl$ derivative

Example 4 : On heating diethyl ether with conc. HI, 2 moles of which of the following is formed

(a) Ethanol (b) Iodoform

(c) Ethyl iodide (d) Methyl iodide

sol. **(c)** $C_2H_5-O-C_2H_5 + \underset{\text{(conc.)}}{2HI} \rightarrow \underset{\text{Ethyl iodide}}{2C_2H_5I} + H_2O$

dpp

Daily **Practice** Problems

TARGET : IIT-JEE / NEET

1. When two halogen atoms are attached to same carbon atom then it is :
(a) *vic*-dihalide (b) *gem*-dihalide
(c) α, ω -halide (d) α, β -halide

2. Full name of DDT is
(a) 1, 1, 1-trichloro-2, 2-bis(*p*-chlorophenyl) ethane
(b) 1, 1-dichloro-2, 2-diphenyl trimethylethane
(c) 1, 1-dichloro-2, 2-diphenyl trichloroethane
(d) None of these

3. How many structural isomers are possible for a compound with molecular formula C_3H_7Cl
(a) 2 (b) 5
(c) 7 (d) 9

4. The compound which contains all the four 1°, 2°, 3° and 4° carbon atoms is
(a) 2, 3-dimethyl pentane
(b) 3-chloro-2, 3 dimethylpentane
(c) 2, 3, 4-trimethylpentane
(d) 3,3-dimethylpentane

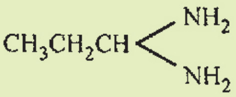
5. Gem-dibromide is
(a) $CH_3CH(Br)CH_2(Br)$ (b) $CH_3CBr_2CH_3$
(c) $CH_2(Br)CH_2CH_2$ (d) CH_2BrCH_2Br

6. When hydrochloric acid gas is treated with propene in presence of benzoyl peroxide, it gives
(a) 2-chloropropane (b) allyl chloride
(c) n-propyl chloride. (d) No reaction occurs

7. When chlorine is passed through propene at 400°C, which of the following is formed ?
(a) PVC (b) Allyl chloride
(c) Alkyl chloride (d) 1, 2-Dichloroethane

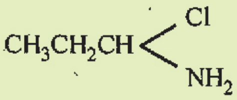
8. When $CH_3CH_2CHCl_2$ is treated with $NaNH_2$, the product formed is
(a) $CH_3-CH=CH_2$ (b) $CH_3-C\equiv CH$

(c)



$CH_3CH_2CH(NH_2)_2$

(d)



$CH_3CH_2CH(Cl)(NH_2)$

9. Elimination of bromine from 2-bromobutane results in the formation of –
(a) predominantly 2-butyne
(b) predominantly 1-butene
(c) predominantly 2-butene
(d) equimolar mixture of 1 and 2-butene

10. The reaction of tert-butyl bromide with sodium methoxide produces mainly –
(a) iso-butane (b) iso-butylene
(c) tert-butyl methyl ether (d) sodium tert butoxide

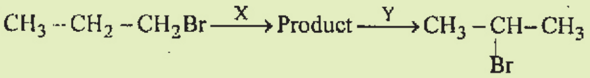
11. $CH_3-CH_2-CH_2-Cl \xrightarrow[KOH]{alc.} B \xrightarrow{HBr} C \xrightarrow[ether]{Na} D$
In the above sequence of reactions, the product D is –
(a) propane (b) 2, 3-dimethylbutane
(c) hexane (d) allyl bromide

12. Chlorobenzene gives aniline with :
(a) $NH_3 + Cu_2O$ (b) $NH_3 + H_2SO_4$
(c) $NaNH_2$ (d) None of these

13. In the following sequence of reactions
$C_2H_5Br \xrightarrow{AgCN} X \xrightarrow{Reduction} Y$; Y is
(a) *n*-propyl amine (b) isopropylamine
(c) ethylamine (d) ethylmethyl amine

14. 1-Chlorobutane on reaction with alcoholic potash gives
(a) 1-butene (b) 1-butanol
(c) 2-butene (d) 2-butanol

15. Identify the set of reagents 'X' and 'Y' in the following set of transformations



$CH_3-CH_2-CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y} CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$

(a) X = dilute aqueous NaOH, 20°C; Y = HBr/acetic acid, 20°C
(b) X = concentrated alcoholic NaOH, 80°C; Y = HBr/acetic acid, 20°C
(c) X = dilute aqueous NaOH, 20°C ; Y = $Br_2/CHCl_3$, 0°C
(d) X = concentrated alcoholic NaOH, 80°C; Y = $Br_2/CHCl_3$, 0°C

16. *n*-Propyl bromide on treatment with ethanolic potassium hydroxide produces
(a) propane (b) propene
(c) propyne (d) propanol

17. The number of structural and configurational isomers of a bromo compound, C_5H_9Br, formed by the addition of HBr to 2-pentyne respectively are
(a) 1 and 2 (b) 2 and 4
(c) 4 and 2 (d) 2 and 1

18. During debromination of *meso*-2,3-dibromobutane, the major compound formed is
(a) *n*-butane (b) 1-butene
(c) *cis*-2-butene (d) *trans*-2-butene

19. Benzene reacts with *n*-propyl chloride in the presence of anhydrous $AlCl_3$ to give
(a) 3 – Propyl – 1 – chlorobenzene
(b) *n*-Propylbenzene
(c) Isopropylbenzene.
(d) No reaction occurs

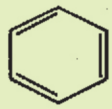
20. Phenyl magnesium bromide reacts with methanol to give
(a) a mixture of toluene and Mg(OH)Br
(b) a mixture of phenol and Mg(Me)Br
(c) a mixture of anisole and Mg(OH)Br
(d) a mixture of benzene and Mg(OMe)Br

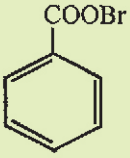
21. The reaction of $C_6H_5N_2^+Cl^-$ with CuCl gives
(a) C_6H_5Cl (b) C_6H_6
(c) $C_6H_5-C_6H_5$ (d) $C_6H_4Cl_2$

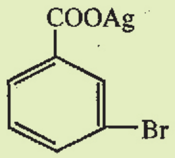
22. Bromination of toluene gives
(a) only *m*-substituted product
(b) only *p*-substituted product
(c) mixture of *o*-and *p*-substituted products
(d) mixture of *o*-and *m*-substituted products

23. On sulphonation of C_6H_5Cl
(a) *m*-chlorobenzenesulphonic acid is formed
(b) benzenesulphonic acid is formed
(c) *o*-chlorobenzenesulphonic acid is formed
(d) mixture of *o*- and *p*-Chlorobenzenesulphonic acid is formed

24. Silver benzoate reacts with bromine to form

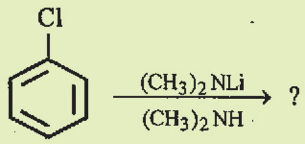
(a) 

(b) 

(c) 

(d) C_6H_5Br

25. What is the product of the following reaction ?

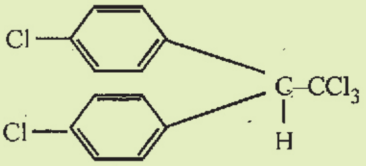


(a) N, N-dimethyl aniline
(b) phenyl lithium (C_6H_5Li)
(c) para chloro-N, N-dimethyl aniline
(d) meta chloro-N, N-dimethyl aniline

26. Chlorobenzene can be prepared by reacting aniline with :
(a) hydrochloric acid
(b) cuprous chloride
(c) chlorine in presence of anhydrous aluminium chloride
(d) nitrous acid followed by heating with cuprous chloride

27. When phenyl magnesium bromide reacts with *tert*–butanol, the product would be
(a) benzene (b) phenol
(c) *ter*–butylbenzene (d) *ter*–butyl phenyl ether

28. Chloropicrin is obtained by the reaction of
(a) steam on carbon tetrachloride
(b) nitric acid on chlorobenzene
(c) chlorine on picric acid
(d) nitric acid on chloroform

29. 

The above structural formula refers to
(a) BHC (b) DNA (c) DDT (d) RNA

30. If chloroform is left open in air in the presence of sunlight, it gives
(a) carbon tetrachloride (b) carbonyl chloride
(c) mustard gas (d) lewisite

31. On warming with silver powder, chloroform is converted into
(a) acetylene (b) hexachloroethane
(c) 1,1,2,2-tetrachloroethane (d) ethylene

32. Cl_2 reacts with CS_2 in presence of I_2 to form
(a) $CHCl_3$ (b) CCl_4
(c) C_2H_5Cl (d) Cl_3C-NO_2

33. Reaction of chloroform with KOH in presence of a primary aromatic amine is called :
(a) carbylamine reaction (b) reduction
(c) hydrolysis (d) Wurtz reaction

34. $AgNO_3$ does not give precipitate with chloroform because :
(a) $CHCl_3$ does not ionise in water
(b) $CHCl_3$ is insoluble in water
(c) $AgNO_3$ is insoluble in $CHCl_3$
(d) $CHCl_3$ is an organic compound

35. $CHCl_3$ and KOH on heating with a compound forms a bad smelling product (X), x is
(a) C_2H_5CN (b) C_2H_5NC (c) C_2H_5OH (d) $C_2H_5NH_2$

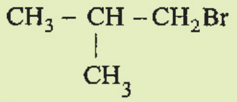
36. Ethyl alcohol is used as a preservative for chloroform because it :
(a) prevents aerial oxidation of chloroform
(b) prevents decomposition of chloroform
(c) decomposes phosgene to CO and Cl_2
(d) removes phosgene by converting it to ethyl carbonate

37. In a S_N2 substitution reaction of the type

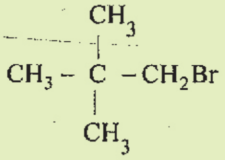
$$R-Br+Cl^- \xrightarrow{DMF} R-Cl+Br^-$$

which one of the following has the highest relative rate ?

(a) $CH_3-CH_2-CH_2Br$

(b) 

$CH_3-CH(CH_3)-CH_2Br$

(c) 

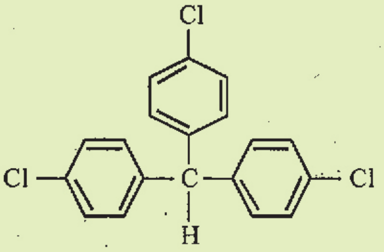
$CH_3-C(CH_3)_2-CH_2Br$

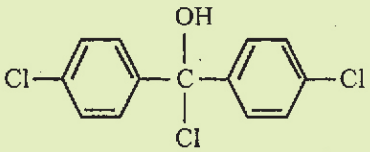
(d) CH_3CH_2Br

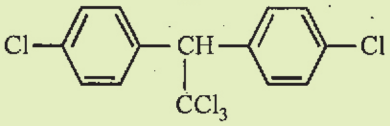
38. Which of the following reactions is an example of nucleophilic substitution reaction?
(a) $2\,RX+2\,Na \to R-R+2\,NaX$
(b) $RX+H_2 \to RH+HX$
(c) $RX+Mg \to RMgX$
(d) $RX+KOH \to ROH+KX$

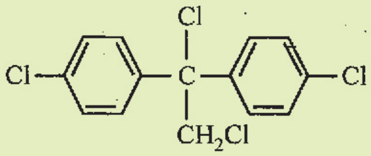
39. Benzene reacts with CH_3Cl in the presence of anhydrous $AlCl_3$ to form:
(a) chlorobenzene (b) benzylchloride
(c) xylene (d) toluene

40. Trichloroacetaldehyde, CCl_3CHO reacts with chlorobenzene in presence of sulphuric acid and produces :

(a) 

(b) 

(c) 

(d) 

41. The reaction of toluene with Cl_2 in presence of $FeCl_3$ gives 'X' and reaction in presence of light gives 'Y'. Thus, 'X' and 'Y' are :

(a) X = Benzal chloride, Y = o – Chlorotoluene
(b) X = m – Chlorotoluene, Y = p – Chlorotoluene
(c) X = o – and p – Chlorotoluene, Y = Trichloromethylbenzene
(d) X = Benzyl chloride, Y = m – Chlorotoluene

42. Which one is most reactive towards S_N1 reaction ?

(a) $C_6H_5CH(C_6H_5)Br$ (b) $C_6H_5CH(CH_3)Br$
(c) $C_6H_5C(CH_3)(C_6H_5)Br$ (d) $C_6H_5CH_2Br$

43. Consider the reactions :

(i) $(CH_3)_2CH-CH_2Br \xrightarrow{C_2H_5OH} (CH_3)_2CH-CH_2OC_2H_5 + HBr$

(ii) $(CH_3)_2CH-CH_2Br \xrightarrow{C_2H_5O^-} (CH_3)_2CH-CH_2OC_2H_5 + Br^-$

The mechanisms of reactions (i) and (ii) are respectively :

(a) S_N1 and S_N2 (b) S_N1 and S_N1
(c) S_N2 and S_N2 (d) S_N2 and S_N1

44. In the following sequence of reactions

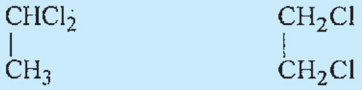
$CH_3-Br \xrightarrow{KCN} A \xrightarrow{H_3O^+}$

$B \xrightarrow[\text{ether}]{LiAlH_4} C$, the end product (C) is :

(a) acetone (b) methane
(c) acetaldehyde (d) ethyl alcohol

SOLUTION

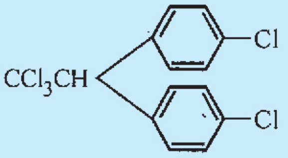
1. (b)



$$\underset{CH_3}{\overset{|}{CHCl_2}} \qquad \underset{CH_2Cl}{\overset{|}{CH_2Cl}}$$

(*gem*-dihalide) (*vic*-dihalide)

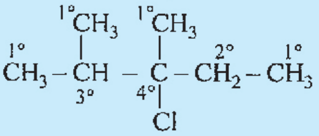
2. (a)



(DDT)

3. (a)

4. (b)



$$\overset{1°}{CH_3}-\underset{3°}{CH}(\overset{1°}{CH_3})-\underset{4°}{C}(\overset{1°}{CH_3})(Cl)-\overset{2°}{CH_2}-\overset{1°}{CH_3}$$

3-Chloro-2,3-dimethylpentane

5. (b) Gem-dihalides are those in which two halogen atoms are attached on the same carbon atom.

6. (a) Peroxide effect is observed only in case of HBr. Therefore, addition of HCl to propene even in the presence of benzoyl peroxide occurs according to Markonikov's rule :

$$CH_3-CH=CH_2 \xrightarrow[\text{Benzoyl peroxide}]{HCl} CH_3-CHCl-CH_3$$

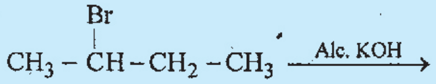
7. (b) At high temp. i.e., 400°C substitution occurs in preference to addition.

$$CH_3CH=CH_2 \xrightarrow[-HCl]{Cl_2,\,400°C} ClCH_2CH=CH_2$$

8. (b) $CH_3-CH_2-CHCl_2 \xrightarrow[\Delta]{NaNH_2}$

$$CH_3-CH=CHCl \xrightarrow[\Delta]{NaNH_2} \underset{\text{Final Product}}{CH_3-C\equiv CH}$$

9. (c)

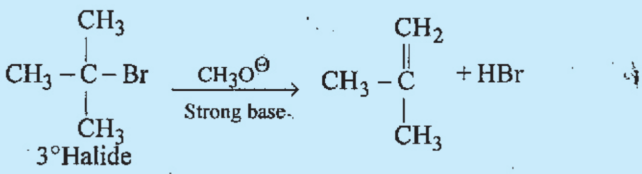


$$CH_3-\overset{\overset{Br}{|}}{CH}-CH_2-CH_3 \xrightarrow{\text{Alc. KOH}}$$

$$CH_3-CH=CH-CH_3 + HBr$$

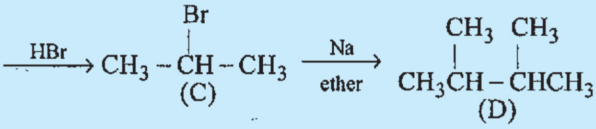
The formation of 2-butene is in accordance to **Saytzeff's rule**. The more substituted alkene is formed in major quantity.

10. (b) 3° halide on reaction with strong base ($CH_3O^{\ominus}$) undergo elimination reaction and forms alkene as major product.



$$\underset{3°\text{Halide}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br} \xrightarrow[\text{Strong base}]{CH_3O^{\ominus}} CH_3-\overset{\overset{CH_2}{\|}}{\underset{\underset{CH_3}{|}}{C}} + HBr$$

11. (b) $CH_3-CH_2-CH_2-Cl \xrightarrow[KOH]{alc.} \underset{(B)}{CH_3CH=CH_2}$



$$\xrightarrow{HBr} \underset{(C)}{CH_3-\overset{\overset{Br}{|}}{CH}-CH_3} \xrightarrow[ether]{Na} \underset{(D)}{CH_3\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}CH_3}$$

12. (a) $C_6H_5Cl+NH_3+Cu_2O \xrightarrow[pressure]{200°C}$

$$C_6H_5NH_2+2CuCl+H_2O$$

13. (d) $\underset{\text{Ethyl bromide}}{C_2H_5Br} \xrightarrow{AgCN} \underset{\text{Ethyl isocyanide}}{C_2H_5NC} \xrightarrow{\text{Reduction}}$

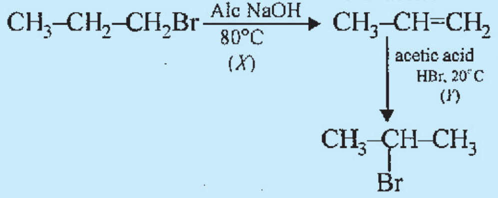
$$\underset{\text{Ethyl methyl amine}}{C_2H_5NHCH_3}$$

14. (a) $\underset{\text{1-Chlorobutane}}{CH_3—CH_2—CH_2—CH_2—Cl}+KOH\ (Alc) \longrightarrow$

$$\downarrow$$

$$\underset{\text{1-Butene}}{CH_3—CH_2—CH=CH_2}+KCl+H_2O$$

15. (b)



$$CH_3—CH_2—CH_2Br \xrightarrow[\substack{80°C\\(X)}]{\text{Alc NaOH}} CH_3—CH=CH_2 \xrightarrow[\substack{HBr,\ 20°C\\(Y)}]{\text{acetic acid}} CH_3—\underset{\underset{Br}{|}}{CH}—CH_3$$

16. (b) $\underset{n-\text{Propyl bromide}}{CH_3-CH_2-CH_2Br} \xrightarrow[-HBr]{\text{ethanolic KOH}} \underset{\text{Propene}}{CH_3-CH=CH_2}$

17. (b) Addition of HBr to 2-pentyne gives two structural isomers (I) and (II)

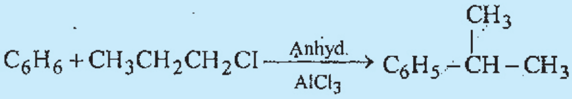
$$CH_3-C\equiv C-CH_2CH_3 \xrightarrow{HBr}$$

$$\underset{(I)}{CH_3C(Br)=CHCH_2CH_3}+\underset{(II)}{CH_3CH=C(Br)CH_2CH_3}$$

Each one of these will exist as a pair of geometrical isomers. Thus, there are two structural and four configurational isomers.

18. (d) Debromination is a *trans*-elimination reaction. *meso*- 2, 3-Dibromobutane on debromination gives *trans*-2-butene.

19. (c)



$$C_6H_6+CH_3CH_2CH_2Cl \xrightarrow[AlCl_3]{Anhyd.} C_6H_5-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

Isopropyl benzene

20. (d) $CH_3OH+C_6H_5MgBr \longrightarrow CH_3O.MgBr+C_6H_6$

21. (a) $C_6H_5N_2^+Cl^- \xrightarrow{CuCl} C_6H_5Cl$ (Sandmeyer reaction)

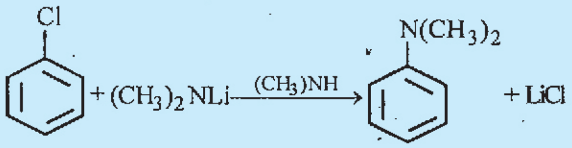
22. (c) $-CH_3$ group is *o*, *p*–directing.

23. (d) –Cl is *o*, *p*–directing.

24. (d) $C_6H_5COOAg+Br_2 \xrightarrow{\text{Hunsdiecker reaction}}$

$$C_6H_5Br+CO_2+AgBr$$

25. (a)



26. (d) $C_6H_5NH_2 \xrightarrow[HCl]{HONO} C_6H_5N_2Cl \xrightarrow{CuCl} C_6H_5Cl$

27. (a) Grignard reagents react with compounds containing active hydrogen to form hydrocarbons corresponding to alkyl (or aryl) part of the Grignard reagent.

$$C_6H_5MgBr + Me_3COH \longrightarrow C_6H_6 + Me_3COMgBr$$

28. (d) Chloropicrin is nitrochloroform. It is obtained by the nitration of chloroform with HNO_3.

$$\underset{\text{Chloroform}}{HCCl_3} \xrightarrow{\text{(conc.) } HNO_3} \underset{\text{Chloropicrin}}{O_2NCCl_3}$$

29. (c)

30. (b) $CHCl_3 + \frac{1}{2}O_2 \xrightarrow{\text{Light}} \underset{\text{unstable}}{CCl(OH)_3} \rightarrow COCl_2 + HCl$

31. (a) $HCCl_3 + 6Ag + HCCl_3 \xrightarrow{\Delta} HC \equiv CH + 6AgCl$

32. (b) $CS_2 + 3Cl_2 \xrightarrow[\text{or } SbCl_5]{\text{anhy. } AlCl_3} CCl_4 + S_2Cl_2$

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

33. (a) This is carbylamine reaction

$$\underset{1^\circ \text{ aromatic amine}}{ArNH_2} + CHCl_3 + 3KOH$$

$$HCOOK \xleftarrow{KOH} \longrightarrow \underset{\text{isocyanide}}{Ar-N\equiv C} + 3KCl + 3H_2O$$

34. (a) Since $CHCl_3$ is covalent compound it does not produce Cl^- ion in H_2O, hence no white ppt is formed during reaction with $AgNO_3$.

35. (b) This is carbylamine reation which is used to detect presence of 1° amine in organic compounds. The bad smelling compound is isocyanide.

$$\underset{\text{Chloroform}}{CHCl_3} + 3KOH + \underset{\text{Ethyl amine}}{C_2H_5NH_2} \longrightarrow$$

$$\underset{\text{Ethylisocyanide}}{C_2H_5N \equiv C} + 3KCl + 3H_2O$$

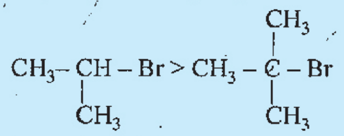
36. (d) $CHCl_3$ on exposure to air forms phosgene which is poisonous gas and removed by converting it into diethyl carbonate (which is non-poisonous substance).

$$CHCl_3 \xrightarrow{O_2/\text{light}} \underset{\text{Phosgene (Poisonous)}}{COCl_2} + HCl$$

$$COCl_2 + 2C_2H_5OH \longrightarrow \underset{\text{Diethyl carbonate (non-poisonous)}}{(C_2H_5)_2CO_3} + 2HCl$$

37. (d) For such a reaction the rate of S_N2 substitution reaction is maximum in case of CH_3CH_2Br because S_N2 mechanism is followed in case of primary and secondary halides i.e., S_N2 reaction is favoured by small groups on the carbon atom attached to halogens so order of S_N2 substitution reaction will be

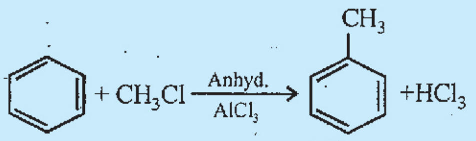
$$CH_3CH_2Br > CH_3CH_2CH_2Br >$$



$$CH_3-\underset{\underset{CH_3}{|}}{CH}-Br > CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br$$

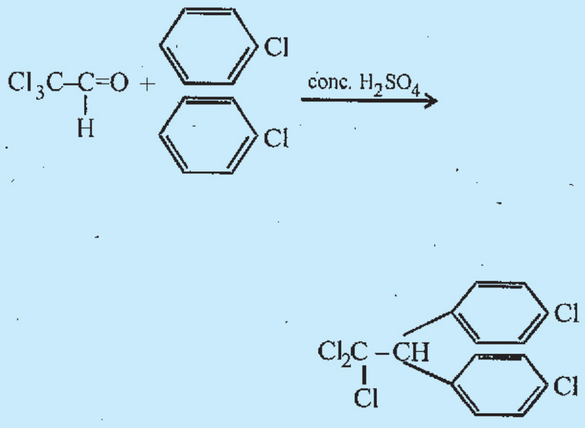
i.e. option (d) is correct.

38. (d) It is a nucleophilic substitution reaction as here stronger nucleophile OH^- is replacing weaker nucleophile X^-

39. (d) 

Toluene

Friedel Craft's reaction.

40. (c) 

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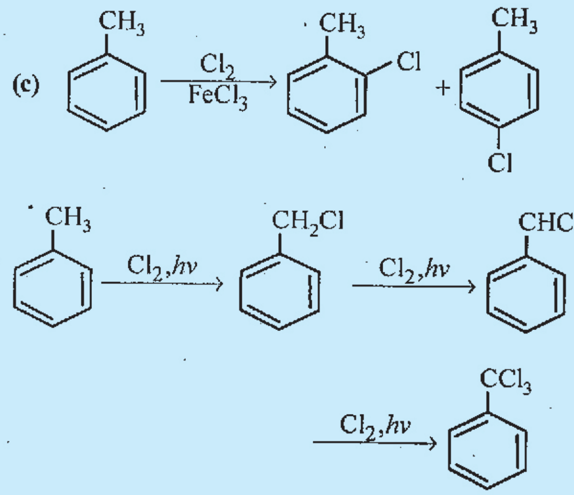
41. (c) 

42. (c) S_N1 reactions involve the formation of carbocations, order of stability of carbocation is 3° > 2° > 1° hence higher the stability of carbocation, more will be the reactivity of the parent alkyl halide. Moreover the tertiary carbocation formed from (c) is stabilized by two phenyl groups.

43. (a) A strong nucleophile favours the S_N2 reaction and a weak nucleophile favours the S_N1 reaction.
First reaction is S_N1 reaction because C_2H_5OH is used as solvent which is a weak nucleophile.
Second reaction is S_N2 reaction because $C_2H_5O^-$ is strong nucleophile.

44. (d) $CH_3-Br \xrightarrow{KCN} \underset{(A)}{CH_3-CN} \xrightarrow{H_3O^+}$

$$\underset{(B)}{CH_3-COOH} \xrightarrow{LiAlH_4} \underset{\substack{(C)\\ \text{Ethyl alcohol}}}{CH_3-CH_2-OH}$$