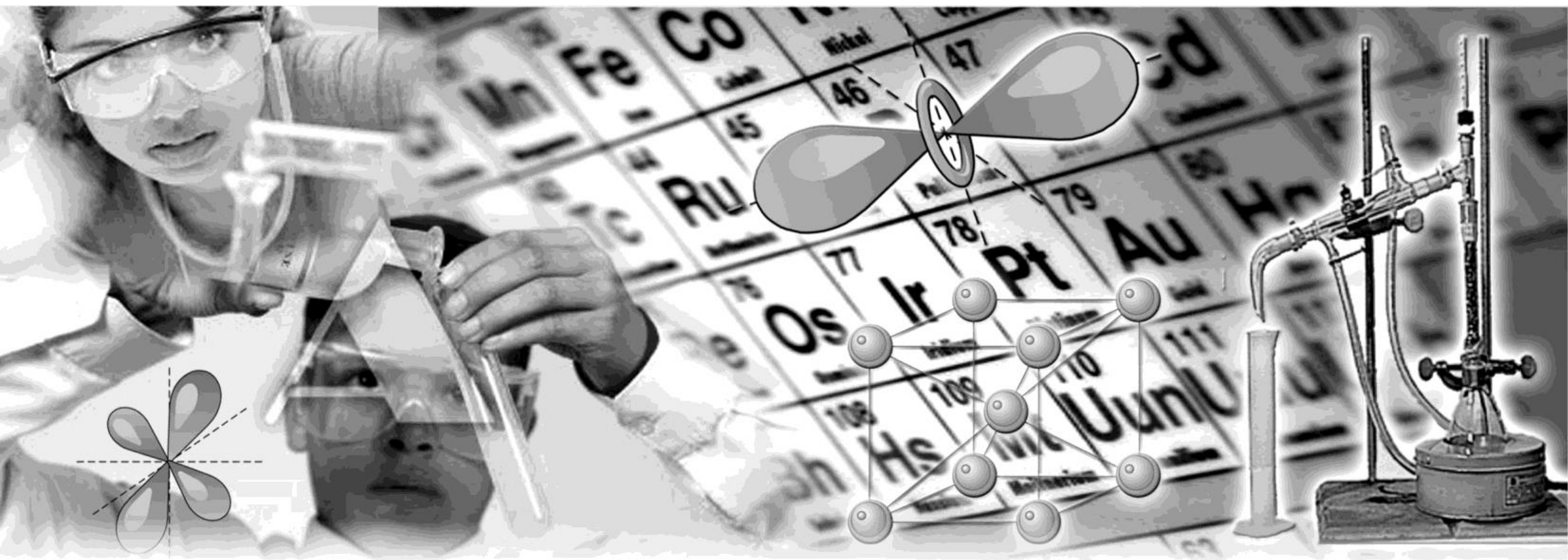


Chapter

25

Halogen Containing Compounds

Compounds derived from hydrocarbons by the replacement of one or more hydrogen atoms by the corresponding number of halogen atoms are termed as halogen derivatives. The halogen derivatives of the hydrocarbons are broadly classified into three classes:

Halogen derivatives of saturated hydrocarbons (Alkanes)- Halo-alkanes.

Halogen derivatives of unsaturated hydrocarbons (Alkenes and alkynes)-Halo-alkene or alkyne.

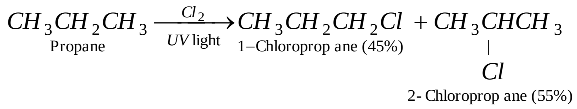
Halogen derivatives of aromatic hydrocarbons (Arenes)-Halo-arenes.

General methods of preparation of Alkyl Halides

(1) **From alkanes**

(i) ***By halogenation*** :

$$\underset{\text{Ethane}}{C_2H_6}\ \text{(Excess)} + Cl_2 \xrightarrow{hv} \underset{\text{Ethyl chloride (Major product)}}{C_2H_5Cl} + HCl$$



$$\underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow[UV\text{ light}]{Cl_2} \underset{\text{1–Chloropropane (45\%)}}{CH_3CH_2CH_2Cl} + \underset{\text{2- Chloropropane (55\%)}}{CH_3\underset{\substack{|\\ Cl}}{C}HCH_3}$$

This reaction proceed through free radical mechanism.

❐ Order of reactivity of X_2 for a given alkane is, $F_2 > Cl_2 > Br_2 > I_2$.

❐ The reactivity of the alkanes follows the order :

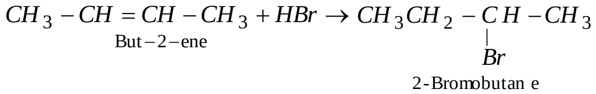
3°alkane > 2°alkane > 1°alkane.

(ii) ***With sulphuryl chloride*** :

$$R-H + SO_2Cl_2 \xrightarrow[\text{Organic peroxide}\,(R'CO_2)_2]{hv} R-Cl + SO_2 + HCl$$

❐ This reaction is a fast due to in presence of light and trace of an organic peroxide.

(2) **From alkenes** (Hydrohalogenation by Electrophillic addition)



$$\underset{\text{But}-2-\text{ene}}{CH_3-CH=CH-CH_3} + HBr \rightarrow \underset{\text{2-Bromobutane}}{CH_3CH_2-\underset{\substack{|\\ Br}}{C}H-CH_3}$$

❐ Addition of HBr to alkene in the presence of organic peroxide take place due to peroxide effect or Kharasch's effect.

❐ This addition take place by two mechanism, Peroxide initiates free radical mechanism.

Markownikoff's addition by electrophillic mechanism.

❐ The order of reactivity of halogen acids is, $HI > HBr > HCl$.

(3) **From alcohols**

(i) ***By the action of halogen acids***

Groove's process

$$\underset{\text{Alcohol}}{R-OH} + H-X \xrightarrow[300°C]{Anhy.\,ZnCl_2} \underset{\text{Haloalkane}}{RX} + H_2O$$

❐ The reactivity order of HX in the above reaction is : $HI > HBr > HCl > HF$.

❐ Reactivity order of alcohols $3° > 2° > 1° > MeOH$.

❐ 2° and 3° alcohols undergo S_{N^1} ; where as 1° and $MeOH$ undergo S_{N^2} mechanism.

❐ Concentrated HCl + *anhy*. $ZnCl_2$ is known as lucas reagent.

(ii) ***Using PCl_5 and PCl_3*** :

$$\underset{}{CH_3CH_2OH} + \underset{\text{Phosphorus pentachloride}}{PCl_5} \longrightarrow \underset{\text{Chloroethane}}{CH_3CH_2Cl} + \underset{\text{Phosphorus Oxychloride}}{POCl_3} + HCl$$

$$3CH_3CH_2OH + PCl_3 \longrightarrow \underset{\text{Chloroethane}}{3CH_3CH_2Cl} + \underset{\text{Phosphorus acid}}{H_3PO_3}$$

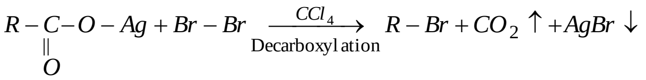
❐ Bromine and iodine derivatives cannot be obtain from the above reaction, because PBr_5 or PI_5 are unstable.

❐ This method gives good yield of primary alkyl halides but poor yields of secondary and tertiary alkyl halides.

(iii) ***By the action of thionyl chloride*** (Darzan's process) : Reaction takes place through SN^2 mechanism.

$$CH_3CH_2OH + SOCl_2 \xrightarrow{\text{Pyridine}} CH_3CH_2Cl + SO_2 + HCl$$

(4) **From silver salt of carboxylic acids** (Hunsdiecker reaction, Decarboxylation by Free radical mechanism)



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

❐ The reactivity of alkyl group is $1° > 2° > 3°$

❐ Only bromide are obtained in good yield.

❐ Not suitable for chlorination because yield is poor.

❐ In this reaction iodine forms ester instead of alkyl halide and the reaction is called Birnbourn-Simonini reaction,

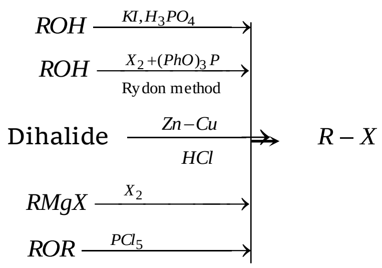
$$2R-COOAg + I_2 \longrightarrow RCOOR' + 2CO_2 + 2AgI\ .$$

(5) **By Finkelstein reaction** (Halide exchange method) **:** $R-X + NaI \xrightarrow[\text{Reflux}]{\text{Acetone}} R-I + NaX (X = Cl, Br)$

❐ Alkyl fluorides can not be prepared by this method. They can be obtained from corresponding chlorides by the action of Hg_2F_2 or antimony trifluoride. (swart reaction)

$$2CH_3Cl + Hg_2F_2 \rightarrow \underset{\text{Methyl fluoride}}{2CH_3F} + Hg_2Cl_2$$

(6) **Other method**



Properties of Alkyl Halides

(1) **Physical properties**

(i) CH_3F, CH_3Cl, CH_3Br and C_2H_5Cl are gases at room temperature. The alkyl halides upto C_{18} are colourless liquids while higher members are colourless solids.

(ii) Alkyl halides are insoluble in water but soluble in organic solvents.

(iii) They burn on copper wire with green edged flame (Beilstein test for halogens).

(iv) Alkyl bromides and iodides are heavier than water. Alkyl chlorides and fluorides are lighter than water.

(v) Alkyl iodides become violet or brown in colour on exposure as they decompose in light.

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

(vi) For a given alkyl group, the boiling points of alkyl halides are in the order $RI > RBr > RCl > RF$ and for a given halogen the boiling points of alkyl halides increase with the increase of the size of the alkyl group.

(vii) Alkyl halides are in general toxic compounds and bring unconsciousness when inhaled in large amounts.

(2) **Chemical properties :** The alkyl halides are highly reactive, the order of reactivity is,

Iodide > Bromide > Chloride (Nature of the halogen atom)

Tertiary > Secondary > Primary (Type of the halogen atom)

Amongst the primary alkyl halide, the order of reactivity is : $CH_3X > C_2H_5X > C_3H_7X$, etc.

The high reactivity of alkyl halides can be explained in terms of the nature of $C-X$ bond which is highly polarised covalent bond due to large difference in the electronegativities of carbon and halogen atoms. The halogen is far more electronegative than carbon and tends to pull the electrons away from carbon, *i.e.,* halogen acquires a small negative charge and carbon a small positive charge.

$$-\overset{\delta^+}{C}-\overset{\delta^-}{X}$$

This polarity is responsible for reactions,

(i) Nucleophilic substitution reactions (ii) Elimination reactions

(i) ***Nucleophilic substitution (S_N) reactions*** : The C^{δ^+} site is susceptible to attack by nucleophiles (An electron rich species).

$$Nu^- + R-X \longrightarrow Nu-R + X^-$$

$$R-X \xrightarrow[\text{Slow}]{-X^-} R^+ \xrightarrow[\text{Fast}]{Nu^-} R-Nu \quad (S_{N^1} \text{ reaction})$$

$$Nu^- + R-X \xrightarrow{\text{Slow}} \underset{\text{Transition state}}{Nu.....R.....X} \xrightarrow{\text{Fast}} Nu-R + X^-$$

(S_{N^2} reaction)

Examples of S_N reactions,

(a) *Hydrolysis* :

$$\underset{\text{Alkyl halide}}{RX} + AgOH \longrightarrow \underset{\text{Alcohol}}{ROH} + AgX$$

$$RX + KOH(aq) \longrightarrow ROH + KX$$

❒ With the help of this reaction an alkene can be converted into alcohol. Alkene is first reacted with *HBr* to form alkyl bromide and then hydrolysis is done.

$$\underset{\text{Ethylene}}{CH_2 = CH_2} \xrightarrow{HBr} \underset{\text{Ethyl bromide}}{CH_3CH_2Br} \xrightarrow{AgOH} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$

(b) *Reaction with alkoxides or dry silver oxide* :

$$RX + NaOR' \xrightarrow{Heat} \underset{\text{Unsym. ether}}{ROR'} + NaX$$

$$2RX + Ag_2O \longrightarrow \underset{\text{Sym. ether}}{R-O-R} + 2AgX$$

(c) *Reaction with sodium or potassium hydrogen sulphide* :

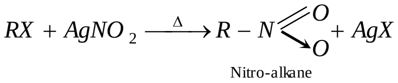
$$RX + \underset{\text{Sodium hydrogen sulphide}}{NaSH} \longrightarrow \underset{\substack{\text{Thioalcohol} \\ \text{or Alkanethiol} \\ \text{or Alkyl mercaptan}}}{RSH} + NaX$$

(d) *Reaction with alcoholic potassium cyanide and silver cyanide* :

$$RX + KCN \xrightarrow{Alcohol} \underset{\substack{\text{Alkyl cyanide or} \\ \text{Alkane nitrile}}}{RCN} + KX$$

(e) *Reaction with potassium nitrite or silver nitrite* :

$$RX + K-O-N=O \xrightarrow{\Delta} \underset{\text{Alkyl nitrite}}{R-O-N=O} + KX$$



$$RX + AgNO_2 \xrightarrow{\Delta} \underset{\text{Nitro-alkane}}{R-N\overset{\nearrow O}{\underset{\searrow O}{}}} + AgX$$

(f) *Reaction with ammonia* :

$$C_2H_5Br + H-NH_2 \longrightarrow \underset{\text{Ethylamine (p.)}}{C_2H_5NH_2} + HBr$$

$$C_2H_5NH_2 + BrC_2H_5 \longrightarrow \underset{\text{Diethylamine (sec.)}}{C_2H_5NHC_2H_5} + HBr$$

$$(C_2H_5)_2NH + BrC_2H_5 \longrightarrow \underset{\text{Triethylamine (tert.)}}{(C_2H_5)_3N} + HBr$$

$$(C_2H_5)_3N + BrC_2H_5 \longrightarrow \underset{\substack{\text{Tetraethylammonium} \\ \text{bromide (Quaternary)}}}{(C_2H_5)_4\overset{+}{N}\overset{-}{Br}}$$

(g) *Reaction with silver salts of fatty acids* :

$$R'COOAg + XR \longrightarrow \underset{\text{Ester}}{R'COOR} + AgX$$

(h) *Reaction with sodium acetylide* :

$$RX + \underset{\text{Sodium acetylide}}{NaC \equiv CH} \longrightarrow \underset{\text{Alkyne}}{R-C \equiv CH} + NaX$$

(i) *Reaction with sodium or potassium sulphide* :

$$2RX + Na_2S \longrightarrow \underset{\text{Thioether}}{R-S-R} + 2NaX$$

Thioethers can also be obtained by

$$RX - NaSR' \longrightarrow R-S-R' + NaX$$

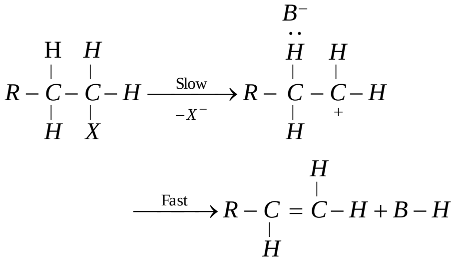
$$C_2H_5Br + NaSCH_3 \longrightarrow \underset{\text{Ethyl methyl thioether}}{C_2H_5-S-CH_3} + NaBr$$

(j) *Reaction with halides* :

$$\underset{\text{Alkyl chloride}}{RCl} + NaBr \longrightarrow \underset{\text{Alkyl bromide}}{RBr} \xrightarrow{NaI} \underset{\text{Alkyl iodide}}{RI}$$

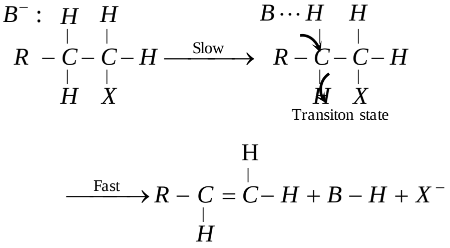
(ii) ***Elimination reactions*** : The positive charge on carbon is propagated to the neighbouring carbon atoms by inductive effect. When approached by a strongest base (*B*), it tends to lose a proton usually from the β-carbon atom. Such reactions are termed elimination reactions. They are also E_1 and E_2 reactions.

E_1 reaction :



$$R-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{X}{C}}-H \xrightarrow[-X^-]{\text{Slow}} R-\overset{H}{\underset{H}{C}}-\overset{\overset{B^-}{\ddot{H}}}{\underset{+}{C}}-H \xrightarrow{\text{Fast}} R-\underset{H}{C}=\overset{H}{C}-H + B-H$$

E_2 Reaction :



$$\overset{B^-:}{} R-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{X}{C}}-H \xrightarrow{\text{Slow}} \underset{\text{Transiton state}}{R-\overset{B\cdots H}{\underset{H}{C}}-\overset{H}{\underset{X}{C}}-H} \xrightarrow{\text{Fast}} R-\underset{H}{C}=\overset{H}{C}-H + B-H + X^-$$

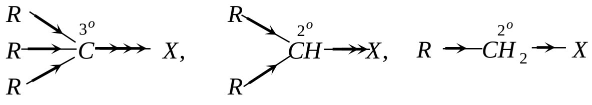
As the above reactions involve leaving of X^-, the reactivity of alkyl halides (Same alkyl group, different halogens) should be limited with $C-X$ bond strength.

Type of bond	$C-I$	$C-Br$	$C-Cl$
Bond strength (*kcal/mol*)	45.5	54	66.5

$$\xrightarrow[\text{increases}]{\text{Bond strength}}$$

The breaking of the bond becomes more and more difficult and thus, the reactivity decrease.

The order of reactivity (Tertiary > Secondary > Primary) is due to +*I* effect of the alkyl groups which increases the polarity of $C-X$ bond.



The primary alkyl halides undergo reactions either by S_{N^2} or E_2 mechanisms which involve the formation of transition state. The bulky groups cause steric hinderance in the formation of transition state. Therefore, higher homologues are less reactive than lower homologues. $CH_3X > C_2H_5X > C_3H_7X$, etc.

Example of elimination reaction

(a) *Dehydrohalogenation* :

$$C_nH_{2n+1}X + \underset{\text{(Alcoholic)}}{KOH} \longrightarrow \underset{\text{Alkene}}{C_nH_{2n}} + KX + H_2O$$

In this reactions, ether is a by-product as potassium ethoxide is always present in small quantity.

$$C_2H_5Br + KOC_2H_5 \longrightarrow C_2H_5 - O - C_2H_5 + KBr$$

(b) *Action of heat* :

$$RCH_2CH_2X \xrightarrow{300°C} \underset{\text{Alkene}}{RCH = CH_2} + HX$$

$$C_2H_5Br \xrightarrow{300°C} \underset{\text{Ethene}}{CH_2 = CH_2} + HBr$$

The decomposition follows the following order,

Iodide > Bromide > Chloride (When same alkyl group is present) and

Tertiary > Secondary > Primary (When same halogen is present).

(iii) ***Miscellaneous reactions***

(a) *Reduction* : Alkyl halides are reduced with nascent hydrogen obtained by Zn/HCl or sodium and alcohol or Zn/Cu couple or $LiAlH_4$.

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

Reaction is used for the preparation of pure alkanes

(b) *Wurtz reaction* : An ether solution of an alkyl halide (Preferably bromide or iodide) gives an alkane when heated with metallic sodium.

$$2RX + 2Na \longrightarrow R - R + 2NaX$$

(c) *Reaction with magnesium* : Alkyl halides form Grignard reagent when treated with dry magnesium powder in dry ether.

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

Grignard reagents are used for making a very large number of organic compounds.

(d) *Reaction with other metals* : Organometallic compounds are formed.

❑ When heated with zinc powder in ether, alkyl halides form dialkyl zinc compounds. These are called Frankland reagents.

$$2C_2H_5Br + 2Zn \xrightarrow[\text{Heat}]{\text{Ether}} (C_2H_5)_2Zn + ZnBr_2$$

❑ When heated with lead-sodium alloy, ethyl bromide gives tetra ethyl lead which is used an antiknock compound in petrol.

$$4C_2H_5Br + 4Pb(Na) \longrightarrow (C_2H_5)_4Pb + 4NaBr + 3Pb$$

❑ Reaction with lithium : Alkyl halides react with lithium in dry ether to form alkyl lithiums.

$$RX + 2Li \xrightarrow{\text{Ether}} R - Li + LiX \; ;$$

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + 2Li \longrightarrow C_2H_5 - Li + LiBr$$

Alkyl lithiums are similar in properties with Grignard reagents. These are reactive reagents also.

(e) *Friedel-Craft's reaction* :

$$\underset{\text{Benzene}}{C_6H_6} + RCl \xrightarrow{AlCl_3} \underset{\text{Alkylbenzene}}{C_6H_5R} + HCl$$

$$C_6H_6 + C_2H_5Br \xrightarrow{AlBr_3} C_6H_5C_2H_5 + HBr$$

(f) Substitution (Halogenation) : Alkyl halides undergo further halogenation in presence of sunlight, heat energy or peroxide.

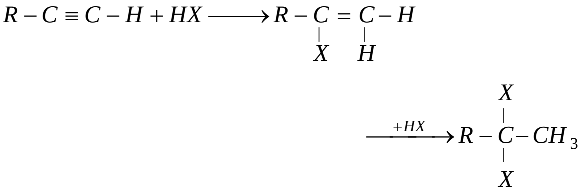
$$C_2H_5Br \xrightarrow[hv]{Br_2} C_2H_4Br_2 \xrightarrow[hv]{Br_2} C_2H_3Br_3 .....$$

Preparations and properties of Dihalides

(1) **Methods of preparation of dihalides**

(i) ***Methods of preparation of gemdihalide***

(a) *From alkyne (Hydrohalogenation)* :



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

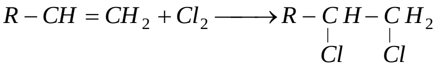
(b) *From carbonyl compound* :

$$RCHO + PCl_5 \longrightarrow \underset{\text{[Terminal dihalide]}}{RCHCl_2} + POCl_3$$

❒ If ketone is taken internal dihalide formed.

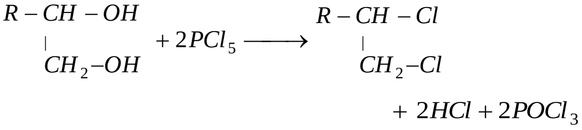
(ii) ***Methods of preparation of vicinal dihalide***

(a) From alkene [By halogenation] :



$$R - CH = CH_2 + Cl_2 \longrightarrow R - \underset{Cl}{\underset{|}{C}}H - \underset{Cl}{\underset{|}{C}}H_2$$

(b) From vicinal glycol :



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

(2) **Properties of dihalides**

(i) ***Physical properties***

(a) Dihalide are colourless with pleasant smell liquid. Insoluble in water, soluble in organic solvent.

(b) $M.P$ and $B.P \propto$ -molecular mass.

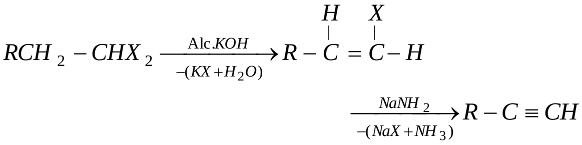
(c) Reactivity of vicinal dihalides > Gem dihalide.

(ii) ***Chemical properties of dihalide***

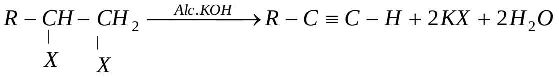
(a) *Reaction with aqueous KOH* :

$$RCHX_2 + 2KOH(aq.) \xrightarrow[-KX]{} RCH(OH)_2 \xrightarrow{-H_2O} RCHO$$

(b) *Reaction with alcoholic KOH* :



$$RCH_2 - CHX_2 \xrightarrow[-(KX + H_2O)]{\text{Alc.}KOH} R - \overset{H}{\overset{|}{C}} = \overset{X}{\overset{|}{C}} - H \xrightarrow[-(NaX + NH_3)]{NaNH_2} R - C \equiv CH$$



$$\underset{\substack{|\\X}}{R-CH}-\underset{\substack{|\\X}}{CH_2} \xrightarrow{Alc.KOH} R-C\equiv C-H+2KX+2H_2O$$

(c) *Reaction with Zn dust*

❑ Gem halide (*di*) form higer symmetrical alkene.

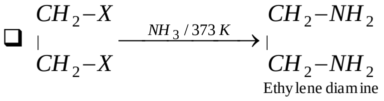
❑ Vicinal dihalide form respective alkene.

(d) *Reaction with KCN* :

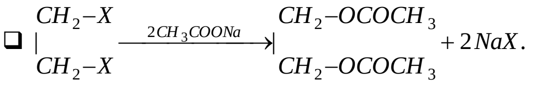
$$R-CHX_2+2KCN \xrightarrow[-2KX]{} RCH(CN)_2$$

$$\xrightarrow[\text{Hydrolysis}]{H_3O^{\oplus}} RCH(COOH)_2$$

(e) *Other substitution reaction*



❑ $$\begin{array}{l}CH_2-X\\ |\\ CH_2-X\end{array} \xrightarrow{NH_3/373\,K} \underset{\text{Ethylene diamine}}{\begin{array}{l}CH_2-NH_2\\ |\\ CH_2-NH_2\end{array}}$$



❑ $$\begin{array}{l}CH_2-X\\ |\\ CH_2-X\end{array} \xrightarrow{2CH_3COONa} \begin{array}{l}CH_2-OCOCH_3\\ |\\ CH_2-OCOCH_3\end{array} +2NaX.$$

Tri-halides (Chloroform and iodoform)

Chloroform or trichloromethane, $CHCl_3$

It is an important trihalogen derivative of methane. It was discovered by Liebig in 1831 and its name chloroform was proposed by Dumas as it gave formic acid on hydrolysis. In the past, it was extensively used as anaesthetic for surgery but now it is rarely used as it causes liver damage.

(1) **Preparation**

(i) Chloroform is prepared both in the laboratory and on large scale by distilling ethyl alcohol or acetone with bleaching powder and water. The yield is about 40%. The available chlorine of bleaching powder serves both as oxidising as well as chlorinating agent.

$$\underset{\text{Bleaching powder}}{CaOCl_2}+H_2O \longrightarrow Ca(OH)_2+Cl_2$$

(a) *From alcohol*

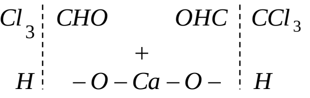
$$[Cl_2+H_2O \longrightarrow 2HCl+O]$$

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH}+O \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO}+H_2O$$

$$\underset{\text{Acetaldehyde}}{CH_3CHO}+3Cl_2 \longrightarrow \underset{\text{Chloral}}{CCl_3CHO}+3HCl$$

[So Cl_2 acts both as an oxidising and chlorinating agent]

Chloral, thus, formed, is hydrolysed by calcium hydroxide.

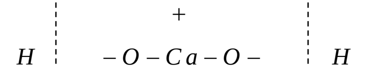


$$\begin{array}{ccccc} CCl_3 & \vdots\ CHO & & OHC\ \vdots & CCl_3\\ & & + & & \\ H & \vdots & -O-Ca-O- & \vdots & H\end{array}$$

$$\xrightarrow{\text{Hydrolysis}} \underset{\text{Chloroform}}{2CHCl_3}+\underset{\text{Calcium formate}}{(HCOO)_2Ca}$$

(b) *From acetone*

$$CH_3-CO-CH_3+3Cl_2 \longrightarrow \underset{\text{Trichloroacetone}}{CCl_3COCH_3}+3HCl$$



$$\begin{array}{ccccc} CCl_3 & \vdots\ COCH_3 & & H_3C.CO\ \vdots & CCl_3\\ & & + & & \\ H & \vdots & -O-Ca-O- & \vdots & H\end{array}$$

$$\xrightarrow{\text{Hydrolysis}} \underset{\text{Chloroform}}{2CHCl_3}+\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca}$$

(ii) ***From carbon tetrachloride*** : Now-a-days, chloroform is obtained on a large scale by the reduction of carbon tetrachloride with iron fillings and water.

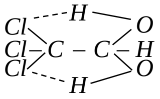
$$CCl_4+2H \xrightarrow{Fe/H_2O} CHCl_3+HCl$$

This chloroform is not pure and used mainly as a solvent.

(iii) Pure Chloroform is obtained by distilling chloral hydrate with concentrated sodium hydroxide solution.

$$\underset{\text{Chloral hydrate}}{CCl_3CH(OH)_2}+NaOH \longrightarrow CHCl_3+HCOONa+H_2O$$

❒ Chloral hydrate is a stable compound inspite of the fact that two $-OH$ groups are linked to the same carbon atom. This is due to the fact that intramolecular hydrogen bonding exists in the molecule between chlorine and hydrogen atom of $-OH$ group.



(2) **Physical properties**

(i) It is a sweet smelling colourless liquid.

(ii) It is heavy liquid. Its density is 1.485. It boils at 61°C.

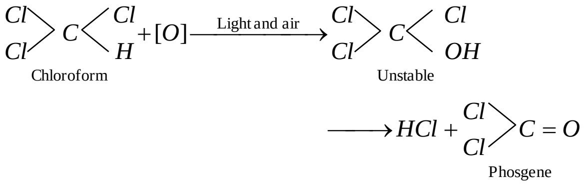
(iii) It is practically insoluble in water but dissolves in organic solvents such as alcohol, ether, etc.

(iv) It is non-inflammable but its vapours may burn with green flame.

(v) It brings temporary unconsciousness when vapours are inhaled for sufficient time.

(3) **Chemical properties**

(i) ***Oxidation*** :



Phosgene is extremely poisonous gas. To use chloroform as an anaesthetic agent, it is necessary to prevent the above reaction. The following two precautions are taken when chloroform is stored.

(a) It is stored in dark blue or brown coloured bottles, which are filled upto the brim.

(b) 1% ethyl alcohol is added. This retards the oxidation and converts the phosgene formed into harmless ethyl carbonate.

$$COCl_2+2C_2H_5OH \longrightarrow \underset{\text{Ethyl carbonate}}{(C_2H_5O)_2CO}+2HCl$$

(ii) ***Reduction*** :

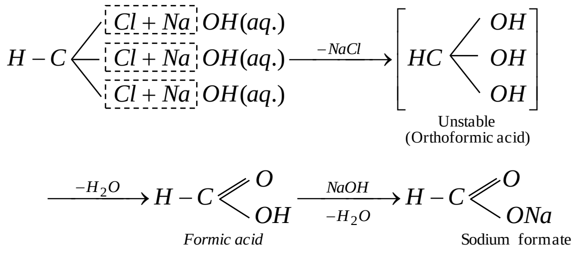
$$CHCl_3+2H \xrightarrow[\text{(alc.)}]{Zn/HCl} CH_2Cl_2+HCl$$

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

(iii) ***Chlorination*** :

$$CHCl_3 + Cl_2 \xrightarrow{\text{UV light}} \underset{\text{Carbon tetrachloride}}{CCl_4} + HCl$$

(iv) ***Hydrolysis*** :



$$H-C\begin{cases}\boxed{Cl+Na}OH(aq.)\\ \boxed{Cl+Na}OH(aq.)\\ \boxed{Cl+Na}OH(aq.)\end{cases}\xrightarrow{-NaCl}\underset{\substack{\text{Unstable}\\ \text{(Orthoformic acid)}}}{\left[HC\begin{matrix}OH\\OH\\OH\end{matrix}\right]}$$

$$\xrightarrow{-H_2O}\underset{\text{Formic acid}}{H-C\begin{matrix}\nearrow O\\ \searrow OH\end{matrix}}\xrightarrow[-H_2O]{NaOH}\underset{\text{Sodium formate}}{H-C\begin{matrix}\nearrow O\\ \searrow ONa\end{matrix}}$$

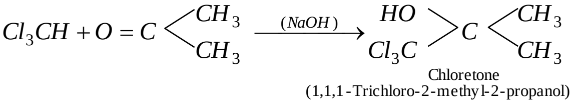
(v) ***Nitration*** : The hydrogen of the chloroform is replaced by nitro group when it is treated with concentrated nitric acid. The product formed is chloropicrin or trichloronitro methane or nitro chloroform. It is a liquid, poisonous and used as an insecticide and a war gas.

$$CHCl_3 + \underset{\text{Nitric acid}}{HONO_2} \longrightarrow \underset{\text{Chloropicrin (Tear gas)}}{CNO_2Cl_3} + H_2O$$

(vi) ***Heating with silver powder*** :

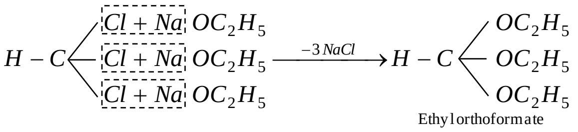
$$H-C-\boxed{Cl_3 + 6Ag + Cl_3 - C}-H \longrightarrow \underset{\text{Acetylene}}{CH \equiv CH} + 6AgCl$$

(vii) ***Condensation with acetone*** : Chloroform condenses with acetone on heating in presence of caustic alkalies. The product formed is a colourless crystalline solid called chloretone and is used as **hypnotic** in medicine.



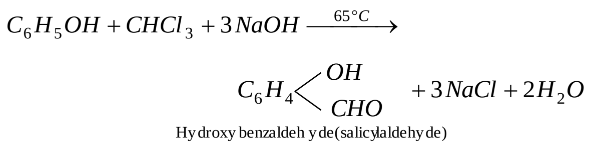
$$Cl_3CH + O = C\begin{matrix}CH_3\\CH_3\end{matrix}\xrightarrow{(NaOH)}\underset{\substack{\text{Chloretone}\\ \text{(1,1,1-Trichloro-2-methyl-2-propanol)}}}{\begin{matrix}HO\\Cl_3C\end{matrix}\!>\!C\begin{matrix}CH_3\\CH_3\end{matrix}}$$

(viii) ***Reaction with sodium ethoxide*** :



$$H-C\begin{cases}\boxed{Cl+Na}OC_2H_5\\ \boxed{Cl+Na}OC_2H_5\\ \boxed{Cl+Na}OC_2H_5\end{cases}\xrightarrow{-3NaCl}\underset{\text{Ethyl orthoformate}}{H-C\begin{matrix}OC_2H_5\\OC_2H_5\\OC_2H_5\end{matrix}}$$

(ix) ***Reimer-Tiemann reaction*** :



$$C_6H_5OH + CHCl_3 + 3NaOH \xrightarrow{65°C}$$

$$\underset{\text{Hydroxy benzaldehyde (salicylaldehyde)}}{C_6H_4\begin{matrix}OH\\CHO\end{matrix}} + 3NaCl + 2H_2O$$

(x) ***Carbylamine reaction*** (Isocyanide test) : This reaction is actually the test of primary amines. Chloroform, when heated with primary amine in presence of alcoholic potassium hydroxide forms a derivative called isocyanide which has a very offensive smell.

$$RNH_2 + CHCl_3 + 3KOH(alc.) \xrightarrow{\Delta} \underset{\substack{\text{Carbylaminoalkane}\\ \text{(Alkylisonitrile)}}}{RNC} + 3KCl + 3H_2O$$

This reaction is also used for the test of chloroform.

(4) **Uses**

(i) It is used as a solvent for fats, waxes, rubber, resins, iodine, etc.

(ii) It is used for the preparation of chloretone (a drug) and chloropicrin (Insecticide).

(iii) It is used in laboratory for the test of primary amines, iodides and bromides.

(iv) It can be used as **anaesthetic** but due to harmful effects it is not used these days for this purpose.

(v) It may be used to prevent putrefaction of organic materials, *i.e.,* in the preservation of anatomical species.

(5) **Tests of chloroform**

(i) It gives isocyanide test (Carbylamine test).

(ii) It forms silver mirror with Tollen's reagent.

(iii) Pure Chloroform does not give white precipitate with silver nitrate.

Iodoform or tri-iodomethane, CHI_3

Iodoform resembles chloroform in the methods of preparation and properties.

(1) **Preparation**

(i) ***Laboratory preparation*** :

From ethanol : $CH_3CH_2OH + I_2 \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + 2HI$

$$CH_3CHO + 3I_2 \longrightarrow \underset{Iodal}{CI_3CHO} + 3HI$$

$$\underset{Tri-iodoacetaldehyde}{CI_3CHO} + KOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Pot. formate}}{HCOOK}$$

From Acetone:

$$CH_3COCH_3 + 3I_2 \longrightarrow \underset{\text{Tri-iodoacetone}}{CI_3COCH_3} + 3HI$$

$$CI_3COCH_3 + KOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Pot. acetate}}{CH_3COOK}$$

Sodium carbonate can be used in place of KOH or $NaOH$. These reactions are called iodoform reactions.

(ii) ***Industrial preparation*** : Iodoform is prepared on large scale by electrolysis of a solution containing ethanol, sodium carbonate and potassium iodide. The iodine set free, combine with ethanol in presence of alkali to form iodoform. The electrolysis carried out in presence of CO_2 and the temperature is maintained at 60-70°C.

$$\begin{tikzcd} & KI \rightleftharpoons K^+ + I^- \arrow[dl, "\text{Cathod}"'] \arrow[dr, "\text{Anod}"] & \\ K^+ + e^- \to K & & 2I^- \to I_2 + 2e^- \end{tikzcd}$$

$$K + H_2O \longrightarrow KOH + \frac{1}{2}H_2$$

KOH is neutralised by CO_2 :

$$C_2H_5OH + 4I_2 + 3Na_2CO_3 \longrightarrow CHI_3 + HCOONa + 5NaI + 3CO_2 + 2H_2O$$

(2) **Physical properties**

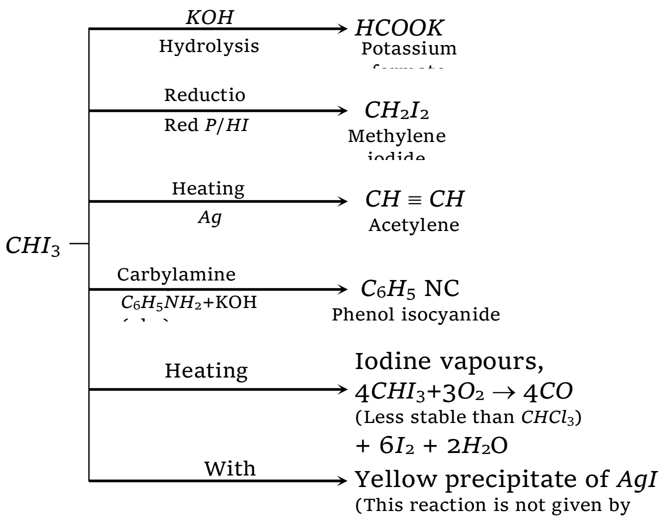
(i) It is a yellow crystalline solid.

(ii) It has a pungent characteristic odour.

(iii) It is insoluble in water but soluble in organic solvents such as alcohol, ether, etc.

(iv) It has melting point 119°C. It is steam volatile.

(3) **Chemical Reactions of iodoform**



(4) **Uses :** Iodoform is extensively used as an **antiseptic** for dressing of wounds; but the antiseptic action is due to the liberation of free iodine and not due to iodoform itself. When it comes in contact with organic matter, iodine is liberated which is responsible for antiseptic properties.

(5) **Tests of iodoform**

(i) ***With AgNO₃*** : CHI_3 gives a yellow precipitate of AgI .

(ii) ***Carbylamine reaction*** : CHI_3 on heating with primary amine and alcoholic KOH solution, gives an offensive smell of isocyanide (Carbylamine).

(iii) ***Iodoform reaction*** : With I_2 and $NaOH$ or I_2 and Na_2CO_3 , the iodoform test is mainly given by ethyl alcohol (CH_3CH_2OH), acetaldehyde $(CH_3-\overset{O}{\overset{||}{C}}-H)$, α-methyl ketone or 2-one $(-\overset{O}{\overset{||}{C}}-CH_3)$, secondary alcohols or 2-ol $(-CHOH \cdot CH_3)$ and secondary alkyl halide at $C_2(-CHClCH_3)$. Also lactic acid ($CH_3-CHOH-COOH$), Pyruvic acid $(CH_3-\overset{O}{\overset{||}{C}}-COOH)$ and methyl phenyl ketone $(C_6H_5-\overset{O}{\overset{||}{C}}-CH_3)$ give this test.

Tetra-halides (Carbon tetrachloride, CCl_4)

It is the most important tetrahalogen derivative of methane.

(1) **Manufacture**

(i) ***From methane*** :

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

(ii) ***From carbon disulphide*** :

$$CS_2 + 3Cl_2 \xrightarrow{Fe/I_2/AlCl_3} CCl_4 + \underset{\text{Sulphur monochloride}}{S_2Cl_2}$$

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

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

Carbon tetrachloride is separated out by fractional distillation. It is washed with sodium hydroxide and then distilled to get a pure sample.

(iii) ***From propane*** :

$$C_3H_8 + 9Cl_2 \xrightarrow[70\text{-}100]{400°C} \underset{\substack{\text{Carbon tetrachloride}\\ \text{(Liquid)}}}{CCl_4} + \underset{\substack{\text{Hexachloroethane}\\ \text{(Solid)}}}{C_2Cl_6} + 8HCl$$

(2) **Physical properties**

(i) It is a colourless liquid having characteristic smell.

(ii) It is non-inflammable and poisonous. It has boiling point 77°C.

(iii) It is insoluble in water but soluble in organic solvents.

(iv) It is an excellent solvent for oils, fats, waxes and greases.

(3) **Chemical properties :** Carbon tetrachloride is less reactive and inert to most organic reagents. However, the following reactions are observed.

(i) ***Reaction with steam*** (Oxidation**) :**

$$CCl_4 + H_2O \xrightarrow{500°C} \underset{\text{Phosgene (Carbonyl chloride)}}{COCl_2} + 2HCl$$

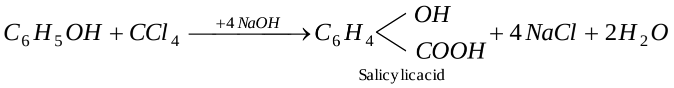
(ii) ***Reduction*** :

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

(iii) ***Hydrolysis*** :

$$CCl_4 + 4KOH \xrightarrow{-4KCl} \underset{\text{Unstable}}{[C(OH)_4]} \xrightarrow{-2H_2O} CO_2 \xrightarrow{2KOH} K_2CO_3 + H_2O$$

(iv) ***Reaction with phenol*** (Reimer-tiemann reaction) :



$$C_6H_5OH + CCl_4 \xrightarrow{+4\,NaOH} \underset{\text{Salicylic acid}}{C_6H_4\begin{cases}OH\\COOH\end{cases}} + 4NaCl + 2H_2O$$

(4) **Uses**

(i) It is used as a fire extinguisher under the name **pyrene**. The dense vapours form a protective layer on the burning objects and prevent the oxygen or air to come in contact with the burning objects.

(ii) It is used as a solvent for fats, oils, waxes and greases, resins, iodine etc.

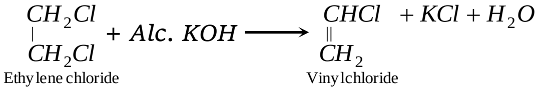
(iii) It finds use in medicine as **helmenthicide** for elimination of hook worms.

Unsaturated halides (Halo-alkene)

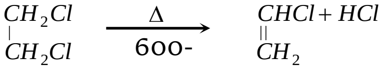
Vinyl chloride or chloroethene, $CH_2=CHCl$

(1) **Synthesis :** Vinyl chloride can be synthesised by a number of methods described below:

(i) ***From ethylene chloride*** :



$$\underset{\text{Ethylene chloride}}{\begin{matrix}CH_2Cl\\|\\CH_2Cl\end{matrix}} + \text{Alc. }KOH \longrightarrow \underset{\text{Vinyl chloride}}{\begin{matrix}CHCl\\\|\\CH_2\end{matrix}} + KCl + H_2O$$



$$\begin{matrix}CH_2Cl\\|\\CH_2Cl\end{matrix} \xrightarrow[600-]{\Delta} \begin{matrix}CHCl\\\|\\CH_2\end{matrix} + HCl$$

(ii) ***From ethylene*** :

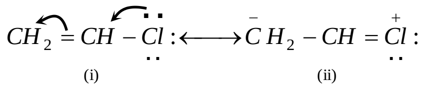
$$CH_2 = CH_2 + Cl_2 \xrightarrow{500°C} \underset{\text{Vinyl chloride}}{CH_2 = CHCl}$$

(iii) ***From acetylene*** :

$$CH \equiv CH + HCl \xrightarrow[70°C]{HgCl_2} \underset{\text{Vinyl chloride}}{CH_2 = CHCl}$$

(2) **Properties :** It is a colourless gas at room temperature. Its boiling point is –13°*C*. The halogen atom in vinyl chloride is not reactive as in other alkyl halides. However, $C=C$ bond of vinyl chloride gives the usual addition reactions.

The non-reactivity of chlorine atom is due to resonance stabilization. The lone pair on chlorine can participate in delocalization (Resonance) to give two canonical structures.



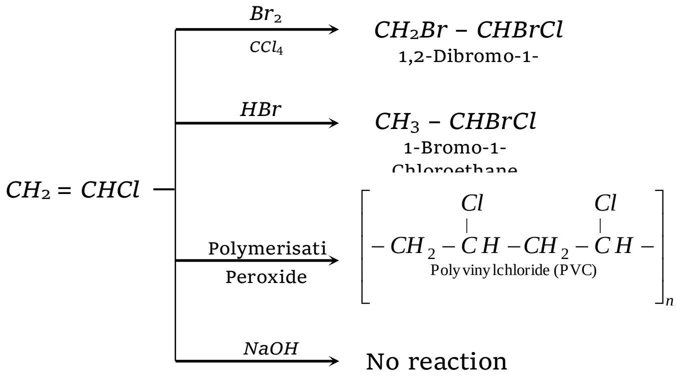
$$\underset{\text{(i)}}{CH_2 = CH - \ddot{\underset{\cdot\cdot}{Cl}}:} \longleftrightarrow \underset{\text{(ii)}}{\overset{-}{C}H_2 - CH = \overset{+}{\underset{\cdot\cdot}{Cl}}:}$$

The following two effects are observed due to resonance stabilization.

(i) Carbon-chlorine bond in vinyl chloride has some double bond character and is, therefore, stronger than a pure single bond.

(ii) Carbon atom is sp^2 hybridized and $C-Cl$ bond length is shorter (1.69$\mathring{A}$) and the bond is stronger than in alkyl halides (1.80$\mathring{A}$) due to sp^3 hybridization of the carbon atom.

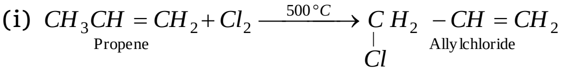
Addition reactions



(3) **Uses :** The main use of vinyl chloride is in the manufacture of polyvinyl chloride (PVC) plastic which is employed these days for making synthetic leather goods, rain coats, pipes, floor tiles, gramophone records, packaging materials, etc.

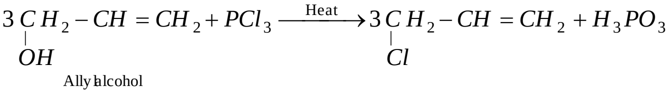
Allyl iodide or 3-iodopropene-1, $ICH_2CH = CH_2$

(1) **Synthesis :** It is obtained,

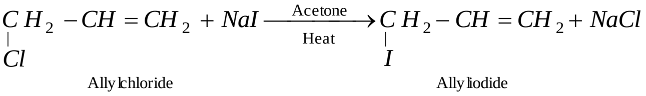


(i) $$\underset{\text{Propene}}{CH_3CH = CH_2} + Cl_2 \xrightarrow{500°C} \underset{\text{Allyl chloride}}{\underset{\underset{Cl}{|}}{CH_2} - CH = CH_2}$$

Or

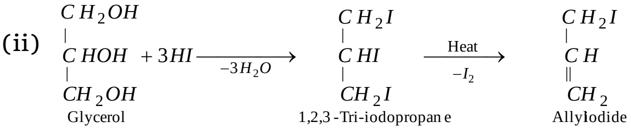


$$3\underset{\text{Allyl alcohol}}{\underset{\underset{OH}{|}}{CH_2} - CH = CH_2} + PCl_3 \xrightarrow{\text{Heat}} 3\underset{\underset{Cl}{|}}{CH_2} - CH = CH_2 + H_3PO_3$$



$$\underset{\text{Allyl chloride}}{\underset{\underset{Cl}{|}}{CH_2} - CH = CH_2} + NaI \xrightarrow[\text{Heat}]{\text{Acetone}} \underset{\text{Allyl iodide}}{\underset{\underset{I}{|}}{CH_2} - CH = CH_2} + NaCl$$

This is halogen- exchange reaction and is called ***Finkelstein reaction***.



(ii) $$\underset{\text{Glycerol}}{\begin{matrix}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{matrix}} + 3HI \xrightarrow[-3H_2O]{} \underset{\text{1,2,3-Tri-iodopropane}}{\begin{matrix}CH_2I\\|\\CHI\\|\\CH_2I\end{matrix}} \xrightarrow[-I_2]{\text{Heat}} \underset{\text{Allyl iodide}}{\begin{matrix}CH_2I\\|\\CH\\\|\\CH_2\end{matrix}}$$

(2) **Properties :** It is a colourless liquid. It boils at 103.1°*C*.The halogen atom in allyl iodide is quite reactive. The *p*-orbital of the halogen atom does not interact with π-molecular orbital of the double bond because these are separated by a saturated sp^3-hybridized carbon atom. Thus, the halogen atom in allyl halides can be easily replaced and the reactions of allyl halides are similar to the reaction of alkyl halides.

In terms of valence bond approach, the reactivity of halogen atom is due to ionisation to yield a carbonium ion which can stabilize by resonance as shown below,

$$CH_2 = CH - CH_2I \longrightarrow$$

$$[CH_2 = CH - \overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2 - CH = CH_2] + I^-$$

Substitution reactions : Nucleophilic substitution reactions occur,

$$CH_2 = CHCH_2I \xrightarrow{NaOH} \underset{\text{Allyl alcohol}}{CH_2 = CH - CH_2OH}$$

$$CH_2 = CHCH_2I \xrightarrow{KCN} \underset{\text{Allyl cyanide}}{CH_2 = CH - CH_2CN}$$

$$CH_2 = CHCH_2I \xrightarrow{NH_3} \underset{\text{Allyl amine}}{CH_2 = CH - CH_2NH_2}$$

$$CH_2 = CHCH_2I \xrightarrow{CH_3ONa} \underset{\text{Allyl methyl ether}}{CH_2 = CH - CH_2OCH_3}$$

$$CH_2 = CHCH_2I \xrightarrow{AgNO_2} \underset{\text{3-Nitropropene-1}}{CH_2 = CH - CH_2NO_2}$$

Addition reactions : Electrophilic addition reactions take place in accordance to Markownikoff's rule.

$$CH_2 = CH - CH_2I + Br_2 \longrightarrow \underset{\text{1,2-Dibromo-3-iodopropan e}}{CH_2Br \cdot CHBr \cdot CH_2I}$$

$$CH_2 = CH - CH_2I + HBr \longrightarrow \underset{\text{2-Bromo-1-iodopropan e}}{CH_3CHBrCH_2I}$$

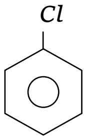
Allyl iodide is widely used in organic synthesis.

Halo-arenes

In these compounds the halogen is linked directly to the carbon of the benzene nucleus.

(1) **Nomenclature :** Common name is aryl halide *IUPAC* name is halo-arene.

Example :



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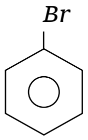
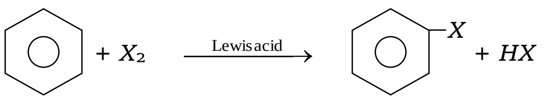


Benzylchloride
Chlorobenzen

Benzylbromide
Bromobenzene

(2) **Methods of preparation**

(i) ***By direct halogination of benzene ring***



Lewis acid $= FeX_3, AlX_3, Tl(OAC)_3$; $X_2 = Cl_2, Br_2$

(ii) ***From diazonium salts***

$$C_6H_5NH_2 \xrightarrow[5°C]{NaNO_2, HCl} C_6H_5N_2^{\oplus}\overset{\ominus}{Cl}$$

$$C_6H_5N_2^{\oplus}\overset{\ominus}{Cl} \xrightarrow{CuCl} C_6H_5Cl$$

$$C_6H_5N_2^{\oplus}\overset{\ominus}{Cl} \xrightarrow{CuBr} C_6H_5Br$$

$$C_6H_5N_2^{\oplus}\overset{\ominus}{Cl} \xrightarrow{KI} C_6H_5I$$

$$C_6H_5N_2^{\oplus}\overset{\ominus}{Cl} \xrightarrow{H^{\oplus}BF_4^-} C_6H_5F$$

(iii) ***Hunsdiecker reaction*** :

$$C_6H_5COO^-Ag^+ \xrightarrow{Br_2} C_6H_5Br + CO_2 + AgBr$$

(iv) ***From Aryl thalium compound*** :

$$ArH + Tl(OOCCF_3)_3 \xrightarrow[-CF_3CO_2H]{} \underset{\text{Aryl thallum trifluoroacetate}}{ArTl(OOCF_3)_2} \xrightarrow[\Delta]{KI} ArI$$

(3) **Physical properties**

(i) ***Physical state*** : Haloarenes are colourless liquid or crystalline solid.

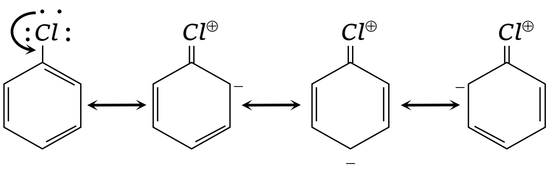
(ii) ***Solubility*** : They are insoluble in water, but dissolve readily in organic solvents. Insolubility is due to inability to form hydrogen bonding in water. Para isomer is less soluble than ortho isomer.

(iii) Halo-arenes are heavier than water.

(iv) B.P. of halo-arenes follow the trend. Iodo arene > Bromo arene > Chloro arene.

(4) **Chemical properties**

Inert nature of chlorobenzene **:** Aryl halides are unreactive as compared to alkyl halides as the halogen atom in these compounds is firmly attached and cannot be replaced by nucleophiles. Such as OH^-, NH_2^-, CN^- *etc.*

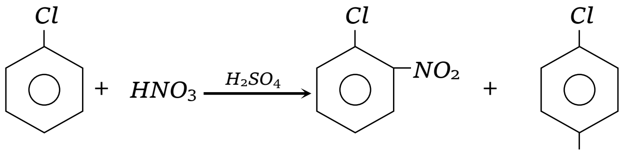


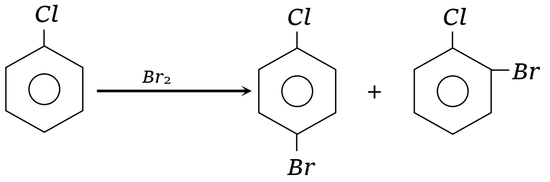
Thus delocalization of electrons by resonance in aryl halides, brings extra stability and double bond character between $C - X$ bond. This makes the bond stronger and shorter than pure single bond. However under vigorous conditions the following nucleophilic substitution reactions are observed,

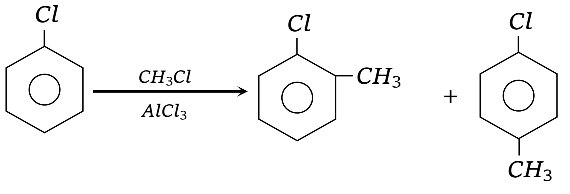
(i) ***Nucleophilic displacement*** :

$$C_6H_5Cl \xrightarrow[500\,atm.]{NaOH,\,350°C} C_6H_5OH + NaCl$$

(ii) ***Electrophilic aromatic substitution***







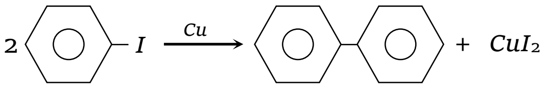
(iii) ***Wurtz – fittig reaction*** :

$$C_6H_5Br + CH_3Br \xrightarrow[\text{Ether}]{Na} C_6H_5CH_3 + 2NaBr$$

(iv) ***Formation of grignard reagent*** :

$$C_6H_5Br \xrightarrow[\text{Ether}]{Mg} C_6H_5MgBr$$

(v) ***Ullmann reaction***



Diphenyl

Some more important halogen derivatives

(1) **Freons :** The chloro fluoro derivatives of methane and ethane are called freons. Some of the derivatives are: CHF_2Cl (monochlorodifluoromethane), CF_2Cl_2 (dichlorodifluoro-methane), HCF_2CHCl_2 (1,1-dichloro-2,2-difluoroethane). These derivatives are non-inflammable, colourless, non-toxic, 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** and **freon-12**.

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

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

Or it can be obtained by reacting carbon tetrachloride with hydrofluoric acid in presence of antimony pentafluoride.

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

Under ordinary conditions freon is a gas. Its boiling point is –29.8°*C*. It can easily be liquified. It is chemically inert. It is used in air-conditioning and in domestic refrigerators for cooling purposes (As refrigerant). It causes depletion of ozone layer.

(2) **Teflon :** It is plastic like substance produced by the polymerisation of tetrafluoroethylene $(CF_2 = CF_2)$.

Tetrafluoroethylene is formed when chloroform is treated with antimony trifluoride and hydrofluoric acid.

$$CHCl_3 \xrightarrow[HF]{SbF_3} CHF_2Cl \xrightarrow[-HCl]{800°C} \underset{\text{(b.pt. -76°C)}}{CF_2 = CF_2}$$

On polymerisation tetrafluoroethylene forms a plastic-like material which is called **teflon**.

$$\underset{\text{Tetrafluoroethylene}}{nCF_2 = CF_2} \longrightarrow \underset{\text{Teflon}}{(-CF_2 - CF_2-)_n}$$

Teflon is chemically inert substance. It is not affected by strong acids and even by boiling aqua-regia. It is stable at high temperatures. It is, thus, used for electrical insulation, preparation of gasket materials and non-sticking frying pans.

(3) **Acetylene tetrachloride (Westron), *CHCl₂·CHCl₂* :** 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.

$$CH \equiv CH + 2Cl_2 \longrightarrow \underset{\text{(1,1,2,2 –Tetrachloroethane)}}{CHCl_2 \cdot CHCl_2}$$

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 a catalyst.

It is a heavy, non-inflammable liquid. It boils at 146°*C*. It is highly toxic in nature. Its smell is similar to chloroform. 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 useful product **westrosol** $(CCl_2 = CHCl)$.

$$\underset{\text{Westron}}{2CHCl_2 - CHCl_2} + Ca(OH)_2 \longrightarrow$$

$$\underset{\substack{\text{Westrosol}\\ \text{(Trichloroethene)}}}{2CHCl = CCl_2} + CaCl_2 + 2H_2O$$

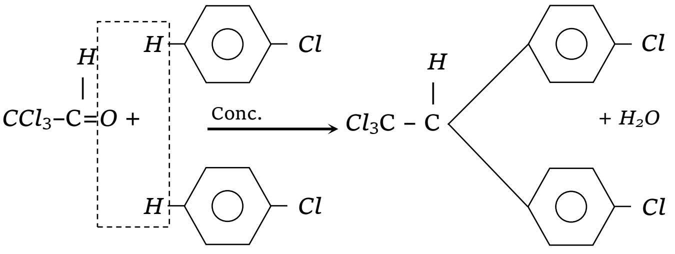
Both westron and westrosol are used as solvents for oils, fats, waxes, resins, varnishes and paints, etc.

(4) ***p*-Dichlorobenzene :** It is prepared by chlorination of benzene.

It is a white, volatile solid having melting point of 325 *K*, which readily sublimes. It resembles chlorobenzene in their properties.

It is used as general insecticides, germicide, soil fumigant deodorant. It is used as a larvicide for cloth moth and peach tee borer.

(5) **DDT; 2, 2-bis (*p*-Chlorophenyl) –1,1,1-trichloroethane :**



Chloral (1*mol*) Chlorobenzene (2*mol*) D.D.T.

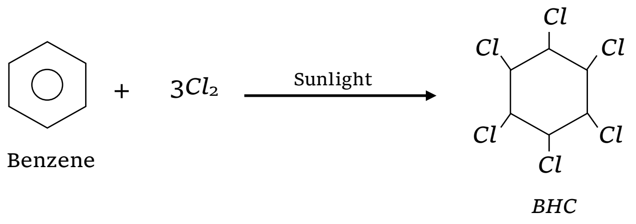
Properties and uses of D.D.T.

(i) D.D.T. is almost insoluble in water but it is moderately soluble in polar solvents.

(ii) D.D.T. is a powerful insecticide. It is widely used as an insecticide for killing mosquitoes and other insects.

Side Effects of D.D.T. : D.D.T. is not biodegradable. Its residues accumulate in environment and its long term effects could be highly dangerous. It has been proved to be toxic to living beings. Therefore, its use has been abandoned in many western countries. However, inspite of its dangerous side effects, D.D.T. is still being widely used in India due to non-availability of other cheaper insecticides.

(6) **BHC (Benzene hexachloride), $C_6H_6Cl_6$:**



Uses : It is an important agricultural pesticide mainly used for exterminating white ants, leaf hopper, termite, etc. It is also known by the common name **gammaxene or lindane or 666**.

❐ aaaeee conformation of $C_6H_6Cl_6$ is most powerful insecticide.

(7) **Perfluorocarbons (PFCs) :** Perfluorocarbons (C_nF_{2n+2}) are obtained by controlled fluorination of vapourized alkanes diluted with nitrogen gas in the presence of a catalyst.

$$\underset{}{C_7H_{16}} + 16F_2 \xrightarrow[CoF_2\text{(Catalyst)}]{\text{Vapour phase}, N_2, 573K} \underset{\text{Perfluoroheptane}}{C_7F_{16}} + 16HF$$

These are colourless, odourless, non-toxic, non-corrosive, non-flammable, non-polar, extremely stable and unreactive gases, liquids and solids. These are stable to ultraviolet radiations and other ionising radiations and therefore, they do not deplete the ozone layer like freons.

These are good electrical insulators. These have many important uses such as :

(i) These are used as lubricants, surface coatings and dielectrics.

(ii) These are used as heat transfer media in high voltage electrical equipment.

(iii) These are used for vapour phase soldering, gross leak detection of sealed microchips etc. in electronic industry.

(iv) These are also used in health care and medicine such as skin care cosmetics, wound healing, liquid ventilation, carbon monoxide poisoning and many medical diagnosis.

Organometallic compounds

Organic compounds in which a metal atom is directly linked to carbon or organic compounds which contain at least one carbon-metal bond are called organometallic compounds.

Example : Methyl lithium (CH_3Li), Dialkyl zinc (R_2Zn), Alkyl magnesium halide $(R-Mg-X)$

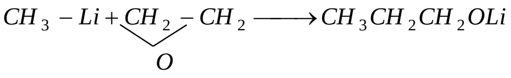
(1) **Methyl lithium :**

$$\underset{\text{Methyl iodide}}{CH_3I} + 2Li \xrightarrow[-10°C]{\text{Ether}} \underset{\text{Methyl lithium}}{CH_3Li} + LiI$$

❐ High reactivity of CH_3Li over grignard reagent is due to greater polar character of $C-Li$ bond in comparison to $C-Mg$ bond.

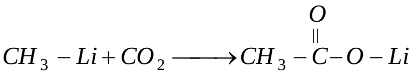
Chemical properties

(i) $CH_3-Li+H\cdot OH \longrightarrow CH_4+LiOH$

(ii)


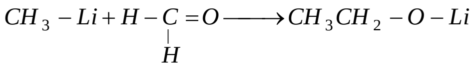
$CH_3-Li+CH_2-CH_2 \longrightarrow CH_3CH_2CH_2OLi$ (with O bridging the two CH_2)

$$\xrightarrow{H_2O} CH_3CH_2CH_2OH+LiOH$$

(iii)


$CH_3-Li+CO_2 \longrightarrow CH_3-\overset{\overset{O}{||}}{C}-O-Li$

$$\xrightarrow{H_2O} CH_3COOH+LiOH$$

(iv)


$CH_3-Li+H-\underset{\underset{H}{|}}{C}=O \longrightarrow CH_3CH_2-O-Li$

$$\xrightarrow{H_2O} CH_3CH_2OH+LiOH$$

❐ Unlike grignard reagents, alkyl lithium can add to an alkenic double bond.

❐ $R-Li+CH_2=CH_2 \longrightarrow R-CH_2-CH_2-Li$

(2) **Dialkyl zinc :** First organometallic compound discovered by Frankland in 1849.

$$2RI+2Zn \xrightarrow[CO_2]{Heat} 2R-Zn-I \xrightarrow[CO_2]{Heat} \underset{\text{Dialkyl zinc}}{R_2Zn} + ZnI_2$$

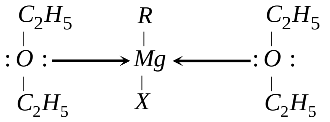
Chemical properties

Preparation of quaternary hydrocarbon :

$$(CH_3)_3CCl+(CH_3)_2Zn \longrightarrow \underset{\text{Neopentane}}{(CH_3)_4C} + CH_3ZnCl$$

(3) **Grignard reagent :** Grignard reagent are prepared by the action of alkyl halide on dry burn magnesium in presence of alcohol free dry ether.

Dry ether dissolves the grignard reagent through solvation.



$$\begin{array}{ccccc} C_2H_5 & & R & & C_2H_5\\ | & & | & & |\\ :O: & \longrightarrow & Mg & \longleftarrow & :O:\\ | & & | & & |\\ C_2H_5 & & X & & C_2H_5 \end{array}$$

Grignard reagents are never isolated in free sate on account of their explosive nature.

❒ For given alkyl radical the ease of formation of a grignard reagent is, Iodide > Bromide > Chloride

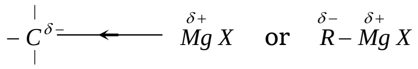
Usually alkyl bromides are used.

❒ For a given halogen, the ease of formation of grignard reagent is, $CH_3X > C_2H_5X > C_3H_7X$..........

❒ Since tertiary alkyl iodides eliminate HI to form an alkene, tertiary alkyl chlorides are used in place of tertiary alkyl iodides.

❒ Grignard reagent cannot be prepared from a compound which consists in addition to halogen, some reactive group such as $-OH$ because it will react rapidly with the grignard reagent.

The $C-Mg$ bond in grignard reagent is some what covalent but highly polar.



$$-\overset{|}{\underset{|}{C}}{}^{\delta-}\longleftarrow \overset{\delta+}{Mg}\,X \quad \text{or} \quad \overset{\delta-}{R}-\overset{\delta+}{Mg}\,X$$

The alkyl group acts as carbanion. The majority of reaction of grignard reagent fall into two groups:

(i) *Double decomposition with compound containing active hydrogen atom or reactive halogen atom*

$$RMgX + HOH \longrightarrow RH + Mg(OH)X$$

$$RMgX + D_2O \longrightarrow RD + Mg(OD)X$$

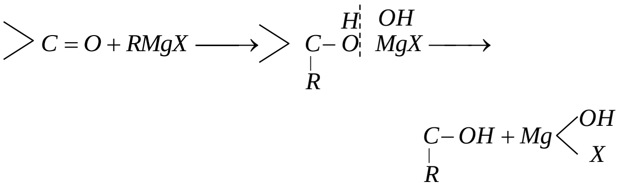
$$RMgX + R'OH \longrightarrow RH + Mg(OR')X$$

$$RMgX + R'NH_2 \longrightarrow RH + Mg(R'NH)X$$

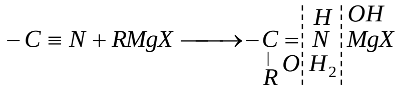
$$RMgX + R'I \longrightarrow R - R' + MgIX$$

$$RMgX + ClCH_2OR' \longrightarrow RCH_2OR' + MgClX$$

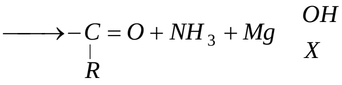
(ii) Addition reaction with compounds containing $>C=O$; $-C\equiv N$, $>C=S$ etc.



$$>C=O + RMgX \longrightarrow >\underset{R}{\underset{|}{C}}-\overset{H}{O}\ \overset{OH}{MgX} \longrightarrow \underset{R}{\underset{|}{C}}-OH + Mg\begin{smallmatrix}OH\\X\end{smallmatrix}$$



$$-C\equiv N + RMgX \longrightarrow -\underset{R}{\underset{|}{C}}=\overset{H}{N}\ \overset{OH}{MgX}\ \underset{O\ H_2}{}$$



$$\longrightarrow -\underset{R}{\underset{|}{C}}=O + NH_3 + Mg\begin{smallmatrix}OH\\X\end{smallmatrix}$$

Tips & Tricks

✍ Iodination of alkanes is a reversible process, therefore, formation of iodoalkanes is possible only in the presence of oxidising agents such as HIO_3.

✍ Iodination with methane does not take place at all.

✍ Fluorination of alkanes takes place with rupture of $C-C$ bonds in higher alkanes. Therefore alkyl fluorides are generally prepared by halide exchange reactions.

✍ Phosphorous halides are generally used to prepare lower alkyl bromides in the laboratory.

✍ $SOBr_2$ is less stable and SOI_2 does not exist. Thus, $R-Br$ and $R-I$ cannot be prepared by Darzan's method.

✍ Hunsdiecker reaction proceeds through free radical mechanism. It is used to reduce the length of carbon chain.

✍ Reactivity of halides towards $S_N{}^1$ mechanism is 3°>2°>1°.

✍ Reactivity of halides towards $S_N{}^2$ mechanism is 1°>2°>3°.

✍ Polar solvents favour $S_N{}^1$ mechanism.

✍ Non polar solvents favour $S_N{}^2$ mechanism.

✍ High concentration of nucleophile favour $S_N{}^2$ mechanism while low concentration of nucleophile favour $S_N{}^1$ mechanism.

✍ $S_N{}^1$ reactions partial racemisation occurs with inverted product predominant in yield whereas in $S_N{}^2$ reactions, inverted product is formed.

✍ Order of nucleophilicity among halide ions decreases in the order $I^- > Br^- > Cl^{-} > F^-$.

✍ During elimination reactions, the H atom is lost from the carbon atom carrying minimum number of H atom.

✍ C_2H_5SH (Ethyl mercaptan) is added to LPG (household cooking gas) to detect leakage. The compound has a typical smell.

✍ In Sandmeyer reaction, Cl of $CuCl$ is attached to benzene ring.

✍ Nuclear halogenation takes place by electrophilic substitution mechanism whereas side chain halogenation takes place by free radical mechanism.

✍ Aryl halides and vinyl halides ($CH_2 = CH - X$) are less reactive than alkyl halides and are not easily hydrolysed. Thus alkyl halides on reaction with $NaOH$ give coloured precipitate but aryl and vinyl halide does not.

✍ Before using the sample of chloroform as an anaesthetic it is tested by treating with aqueous solution of $AgNO_3$. A pure sample does not give ppt. with aq. $AgNO_3$.

✍ Halothane, $CF_3\text{-}CHClBr$, is a general anaesthetic which replace diethyl ether.

✍ CCl_4 resist hydrolysis with boiling water due to non availability of d-orbital in C.

✍ C_2Cl_6 is an solid and is known as atificial camphor.

✍ *Chlorobenzene commercially produced by Raschig process.*

Ordinary Thinking

Objective Questions

Introduction of Halogen containing compounds

1. How many structural isomers are possible for a compound with molecular formula C_3H_7Cl **[MH CET 2001]**

(a) 2 (b) 5

(c) 7 (d) 9

2. In CH_3CH_2Br, % of Br is **[DPMT 1996]**

(a) 80 (b) 75

(c) 70 (d) 7

3. Gem- dibromide is **[RPMT 2000]**

(a) $CH_3CH(Br)OH(Br)CH_3$ (b) $CH_3CBr_2CH_3$

(c) $CH_2(Br)CH_2CH_2$ (d) CH_2BrCH_2Br

4. Ethylidene dibromide is

(a) CH_3-CH_2-Br (b) $Br-CH_2-CH_2-Br$

(c) CH_3-CHBr_2 (d) $CH_2=CBr_2$

5. Benzylidene chloride is

(a) $C_6H_5CH_2Cl$ (b) $C_6H_5CHCl_2$

(c) $C_6H_4ClCH_2Cl$ (d) $C_6H_5CCl_3$

6. Which of the following halide is 2^o

(a) Isopropyl chloride (b) Isobutyl chloride

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

7. Haloforms are trihalogen derivatives of **[CPMT 1985]**

(a) Ethane (b) Methane

(c) Propane (d) Benzene

8. Benzene hexachloride is

(a) 1, 2, 3, 4, 5, 6-hexachlorocyclohexane

(b) 1, 1, 1, 6, 6, 6-hexachlorocyclohexane

(c) 1, 6-phenyl-1, 6-chlorohexane

(d) 1, 1-phenyl-6, 6-chlorohexane

9. Number of $\pi-$bonds present in *B.H.C.* (Benzene hexachloride) are **[RPMT 1999]**

(a) 6 (b) Zero

(c) 3 (d) 12

10. The general formula for alkyl halides is

(a) $C_nH_{2n+1}X$ (b) $C_nH_{2n+2}X$

(c) $C_nH_{n+1}X$ (d) $C_nH_{2n}X$

11. Which of the following is a primary halide **[DCE 2004]**

(a) Isopropyl iodide (b) Secondary butyl iodide

(c) Tertiary butyl bromide (d) Neo hexyl chloride

12. Full name of DDT is **[KCET 1993]**

(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

13. The compound which contains all the four $1^o, 2^o, 3^o$ and 4^o carbon atoms is **[J & K 2005]**

(a) 2, 3-dimethyl pentane

(b) 3-chloro-2, 3-dimethylpentane

(c) 2, 3, 4-trimethylpentane

(d) 3, 3-dimethylpentane

Preparation of Halogen containing compounds

1. The following reaction is known as

$$C_2H_5OH + SOCl_2 \xrightarrow{\text{Pyridine}} C_2H_5Cl + SO_2 + HCl$$

[AIIMS 2002]

(a) Kharasch effect

(b) Darzen's procedure

(c) Williamson's synthesis

(d) Hunsdiecker synthesis reaction

2. What is the main product of the reaction between 2-methyl propene with HBr **[RPMT 2002]**

(a) 1-bromo butane

(b) 1-bromo-2 methyl propane

(c) 2-bromo butane

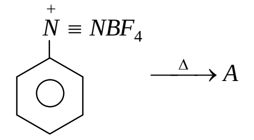
(d) 2-bromo-2 methyl propane

3. Halogenation of alkanes is **[KCET 2002]**

(a) A reductive process (b) An oxidative process

(c) An isothermal process (d) An indothermal process

4.



In the above process product A is **[Kerala (Engg.) 2002]**

(a) Fluorobenzene (b) Benzene

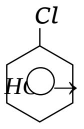
(c) 1, 4-difluorobenzene (d) 1, 3-difluorobenzene

5. Silver acetate $+ Br_2 \xrightarrow{CS_2}$. The main product of this reaction is **[Kurukshetra CET 2002]**

(a) CH_3-Br (b) CH_3COI

(c) CH_3COOH (d) None of these

6. Diazonium salts $+ Cu_2Cl_2 + HCl \rightarrow$



, the reaction is known as **[Kerala (Med.) 2002]**

(a) Chlorination (b) Sandmeyer's reaction

(c) Perkin reaction (d) Substitution reaction

7. When ethyl alcohol (C_2H_5OH) reacts with thionyl chloride, in the presence of pyridine, the product obtained is

[AIIMS; CBSE PMT 2001]

(a) $CH_3CH_2Cl + HCl$

(b) $C_2H_5Cl + HCl + SO_2$

(c) $CH_3CH_2Cl + H_2O + SO_2$

(d) $CH_3CH_2Cl + HCl + SO_2$

8. Preparation of alkyl halides in laboratory is least preferred by **[DPMT 2000]**

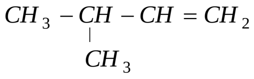
(a) Treatment of alcohols

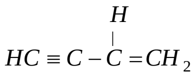
(b) Addition of hydrogen halides to alkenes

(c) Halide exchange

(d) Direct halogenation of alkanes

9. Which of the following organic compounds will give a mixture of 1-chlorobutane and 2-chlorobutane on chlorination **[CPMT 2001]**

(a) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2$

(b) 
$HC\equiv C-\overset{\overset{H}{|}}{C}=CH_2$

(c) $CH_2=CH-CH=CH_2$

(d) $CH_2=CH-CH_2-CH_3$

10. The chlorobenzene is generally obtained from a corresponding diazonium salt by reacting it with **[MP PMT 2000]**

(a) Cu_2Cl_2 (b) $CuSO_4$

(c) Cu (d) $Cu(NH_3)_4^{2+}$

11. Decreasing order of reactivity of HX in the reaction $ROH + HX \to RX + H_2O$

[RPET 2000; AIIMS 1983; MP PET 1996]

(a) $HI > HBr > HCl > HF$ (b) $HBr > HCl > HI > HF$

(c) $HCl > HBr > HI > HF$ (d) $HF > HBr > HCl > HI$

12. The product of the following reaction :

$CH_2=CH-CCl_3 + HBr$ **[RPET 2000]**

(a) $CH_3-CH(Br)-CCl_3$ (b) $CH_2(Br)-CH_2-CCl_3$

(c) $BrCH_2-CHCl-CHCl_2$ (d) $CH_3-CH_2-CCl_3$

13. Chlorobenzene is prepared commercially by

[JIPMER 2000; CPMT 1976; Pb. CET 2002]

(a) Raschig process (b) Wurtz Fitting reaction

(c) Friedel-Craft's reaction (d) Grignard reaction

14. In methyl alcohol solution, bromine reacts with ethylene to yield $BrCH_2CH_2OCH_3$ in addition to 1, 2-dibromoethane because **[Pb. PMT 1998]**

(a) The ion formed initially may react with Br^- or CH_3OH

(b) The methyl alcohol solvates the bromine

(c) The reaction follows Markownikoff's rule

(d) This is a free-radical mechanism

15. $C_3H_8 + Cl_2 \xrightarrow{\text{Light}} C_3H_7Cl + HCl$ is an example of which of the following types of reactions

[AFMC 1997; CPMT 1999]

(a) Substitution (b) Elimination

(c) Addition (d) Rearrangement

16. Which of the following would be produced when acetylene reacts with HCl **[MH CET 1999]**

(a) CH_3CH_2Cl (b) CH_3CHCl_2

(c) $CHCl=CHCl$ (d) $CH_2=CHCl$

17. $R-OH + HX \to R-X + H_2O$

In the above reaction, the reactivity of different alcohols is

[CPMT 1997]

(a) Tertiary > Secondary > Primary

(b) Tertiary < Secondary < Primary

(c) Tertiary < Secondary > Primary

(d) Secondary < Primary < Tertiary

18. $C_6H_6 + Cl_2 \xrightarrow{\text{UV Light}}$ Product. In above reaction product is **[CPMT 1997]**

(a) CCl_3CHO (b) $C_6H_6Cl_6$

(c) $C_6H_{12}Cl_6$ (d) $C_6H_9Cl_2$

19. Benzene reacts with chlorine to form benzene hexachloride in presence of **[MP PET 1999]**

(a) Nickel (b) $AlCl_3$

(c) Bright sunlight (d) Zinc

20. The final product obtained by distilling ethyl alcohol with the excess of chlorine and $Ca(OH)_2$ is**[MP PET**

(a) CH_3CHO (b) CCl_3CHO

(c) $CHCl_3$ (d) $(CH_3)_2O$

21. When ethyl alcohol and KI reacted in presence of Na_2CO_3, yellow crystals of...... are formed**[AFMC 1989]**

(a) CHI_3 (b) CH_3I

(c) CH_2I_2 (d) C_2H_5I

22. In preparation of $CHCl_3$ from ethanol and bleaching powder, the latter provides **[BHU 1986]**

(a) $Ca(OH)_2$ (b) Cl_2

(c) Both (a) and (b) (d) None of these

23. Which one of the following processes does not occur during formation of $CHCl_3$ from C_2H_5OH and bleaching powder

[DPMT 1984]

(a) Hydrolysis (b) Oxidation

(c) Reduction (d) Chlorination

24. Which of the following is obtained when chloral is boiled with $NaOH$ **[CBSE PMT 1991; RPMT 1999]**

(a) CH_3Cl (b) $CHCl_3$

(c) CCl_4 (d) None of these

25. Chloroform can be obtained from **[MNR 1986]**

(a) Methanol (b) Methanal

(c) Propanol-1 (d) Propanol-2

26. Chlorine reacts with ethanol to give

[MP PMT 1989; CPMT 1997; KCET 1998; JIPMER 1999]

(a) Ethyl chloride (b) Chloroform

(c) Acetaldehyde (d) Chloral

27. On heating diethyl ether with conc. HI, 2 moles of which of the following is formed
[IIT-JEE 1983; MP PET 1990; EAMCET 1990; AFMC 1993; JIPMER 2001]
(a) Ethanol (b) Iodoform
(c) Ethyl iodide (d) Methyl iodide

28. Lucas reagent is **[MP PMT 1996; MP PET 1992, 95; CPMT 1986, 89; AIIMS 1980; Kurukshetra CEE 2002]**
(a) Concentrated $HCl + \text{anhydrous } ZnCl_2$
(b) Dilute $HCl + \text{hydrated } ZnCl_2$
(c) Concentrated $HNO_3 + \text{anhydrous } ZnCl_2$
(d) Concentrated $HCl + \text{anhydrous } MgCl_2$

29. Which compound does not form iodoform with alkali and iodine **[IIT-JEE 1985]**
(a) Acetone (b) Ethanol
(c) Diethyl ketone (d) Isopropyl alcohol

30. Which compound gives yellow ppt. with iodine and alkali
[IIT-JEE 1984]
(a) 2-hydroxy propane (b) Acetophenone
(c) Methyl acetone (d) Acetamide

31. Acetone reacts with I_2 in presence of $NaOH$ to form
[MP PMT 1992]
(a) C_2H_5I (b) $C_2H_4I_2$
(c) CHI_3 (d) CH_3I

32. Ethanol is converted into ethyl chloride by reacting with
[MP PET 1991; MP PMT 1990; BHU 1997]
(a) Cl_2 (b) $SOCl_2$
(c) HCl (d) $NaCl$

33. C_6H_5Cl prepared by aniline with **[IIT-JEE 1984]**
(a) HCl
(b) Cu_2Cl_2
(c) Cl_2 in presence of anhydrous $AlCl_3$
(d) HNO_2 and then heated with Cu_2Cl_2

34. The starting substance for the preparation of CH_3I is
[CPMT 1975]
(a) CH_3OH (b) C_2H_5OH
(c) CH_3CHO (d) $(CH_3)_2CO$

35. A Grignard's reagent may be made by reacting magnesium with **[CPMT 1973, 83, 84]**
(a) Methyl amine (b) Diethyl ether
(c) Ethyl iodide (d) Ethyl alcohol

36. Which of the following is responsible for iodoform reaction
[CPMT 1980; RPMT 1997]
(a) Formalin (b) Methanol
(c) Acetic acid (d) Ethanol

37. When a solution of sodium chloride containing ethyl alcohol is electrolysed, it forms
(a) Ethyl alcohol (b) Chloral
(c) Chloroform (d) Acetaldehyde

38. Which reagent cannot be used to prepare an alkyl halide from an alcohol **[CPMT 1989, 94]**
(a) $HCl + ZnCl_2$ (b) $NaCl$
(c) PCl_5 (d) $SOCl_3$

39. Ethyl benzoate reacts with PCl_5 to give**[KCET 2003]**
(a) $C_2H_5Cl + C_6H_5COCl + POCl_3 + HCl$
(b) $C_2H_5Cl + C_6H_5COCl + POCl_3$
(c) $CH_3COCl + C_6H_5COCl + POCl_3$
(d) $C_2H_5Cl + C_6H_5COOH + POCl_3$

40. On treatment with chlorine in presence of sunlight, toluene giv.es the product
[Orissa JEE 2003; MH CET 1999, 2002]
(a) *o*-chloro toluene (b) 2, 5-dichloro toluene
(c) *p*-chloro toluene (d) Benzyl chloride

41. When chlorine is passed through warm benzene in presence of the sunlight, the product obtained is**[KCET 20**
(a) Benzotrichloride (b) Chlorobenzene
(c) Gammexane (d) DDT

42. Which of the following acids adds to propene in the presence of peroxide to give anti-Markownikoff's product
[MP PET 2003]
(a) HF (b) HCl
(c) HBr (d) HI

43. Propene on treatment with HBr gives **[CPMT 1986]**
(a) Isopropyl bromide (b) Propyl bromide
(c) 1, 2-dibromoethane (d) None of the above

44. The catalyst used in Raschig's process is
(a) $LiAlH_4$ (b) Copper chloride
(c) Sunlight (d) $\text{Ethanol}/Na$

45. The compound formed on heating chlorobenzene with chloral in the presence of concentrated sulphuric acid, is
[AIEEE 2004]
(a) Freon (b) DDT
(c) Gammexene (d) Hexachloroethane

46. Acetone is mixed with bleaching powder to give
[AFMC 2004]
(a) Chloroform (b) Acetaldehyde
(c) Ethanol (d) Phosgene

47. Which of the following compounds gives trichloromethane on distilling with bleaching powder
[KCET 2004; EAMCET 1986]
(a) Methanal (b) Phenol
(c) Ethanol (d) Methanol

48. The product formed on reaction of ethyl alcohol with bleaching powder is**[Orissa JEE 2004; DPMT 1978; AIIM**
(a) $CHCl_3$ (b) CCl_3CHO
(c) CH_3COCH_3 (d) CH_3CHO

49. Ethylene reacts with bromine to form **[Pb. CET 2000]**

(a) Chloroethane (b) Ethylene dibromide

(c) Cyclohexane (d) 1-bromo propane

50. Best method of preparing alkyl chloride is **[MH CET 2004]**

(a) $ROH + SOCl_2 \longrightarrow$

(b) $ROH + PCl_5 \longrightarrow$

(c) $ROH + PCl_3 \longrightarrow$

(d) $ROH + HCl \xrightarrow{\text{anhy. } ZnCl_2}$

51. *DDT* is prepared by reacting chlorobenzene with **[BHU 1998, 2005]**

(a) CCl_4 (b) $CCl_3 - CHO$

(c) $CHCl_3$ (d) Ethane

52. Which compound needs chloral in its synthesis **[Pb. PET 2003]**

(a) *D. D. T.* (b) Gammexane

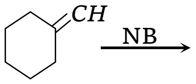
(c) Chloroform (d) Michler's Ketone

53. To get *DDT*, chlorobenzene has to react with which of the following compounds in the presence of concentrated sulphuric acid **[KCET (Engg/Med.) 2001]**

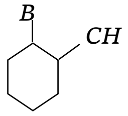
(a) Trichloroethane (b) Dichloroacetone

(c) Dichloroacetaldehyde (d)Trichloroacetaldehyde

54. What will be the product in the following reaction



[BHU 2005]

(a)


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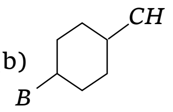

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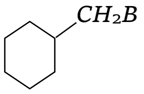

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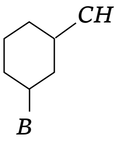

Properties of Halogen containing compounds

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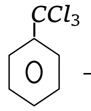
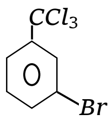


$\xrightarrow{1 \text{ eqv. of } Br_2 / Fe} A$. Compounds *A* is **[Orissa JEE 2005]**

(a)


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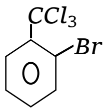

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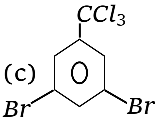

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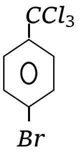


2. Ethyl bromide can be converted into ethyl alcohol by **[KCET 1989]**

(a) Heating with dilute hydrochloric acid and zinc

(b) Boiling with an alcoholic solution of *KOH*

(c) The action of moist silver oxide

(d) Refluxing methanol

3. Reaction of ethyl chloride with sodium leads to **[NCERT 1984]**

(a) Ethane (b) Propane

(c) *n*-butane (d) *n*-pentane

4. Treatment of ammonia with excess of ethyl chloride will yield **[AIIMS 1992]**

(a) Diethyl amine

(b) Ethane

(c) Tetraethyl ammonium chloride

(d) Methyl amine

5. $2CHCl_3 + O_2 \xrightarrow{X} 2COCl_2 + 2HCl$

In the above reaction, *X* stands for

(a) An oxidant (b) A reductant

(c) Light and air (d) None of these

6. Phosgene is the common name for **[DPMT 1983; CPMT 1993; MP PMT 1994; Kurukshetra CEE 1998; RPMT 2000, 02]**

(a) CO_2 and PH_3 (b) Phosphoryl chloride

(c) Carbonyl chloride (d) Carbon tetrachloride

7. When chloroform is treated with amine and *KOH*, we get **[CPMT 1979]**

(a) Rose odour smell

(b) Sour almond like smell

(c) Offensive odour

(d) Sour oil of winter green like smell

8. A mixture of two organic chlorine compounds was treated with sodium metal in ether solution. Isobutane was obtained as a product. The two chlorine compounds are **[KCET 1988]**

(a) Methyl chloride and propyl chloride

(b) Methyl chloride and ethyl chloride

(c) Isopropyl chloride and methyl chloride

(d) Isopropyl chloride and ethyl chloride

9. Alkyl halides can be converted into Grignard reagents by **[KCET 1989]**

(a) Boiling them with *Mg* ribbon in alcoholic solution

(b) Warming them with magnesium powder in dry ether

(c) Refluxing them with $MgCl_2$ solution

(d) Warming them with $MgCl_2$

10. Which is not present in Grignard reagent **[CBSE PMT 1991]**

(a) Methyl group (b) Magnesium

(c) Halogen (d) $-COOH$ group

11. The reactivity of ethyl chloride is **[KCET 1986]**

(a) More or less equal to that of benzyl chloride

(b) More than that of benzyl chloride

(c) More or less equal to that of chlorobenzene

(d) Less than that of chlorobenzene

12. The reactivity of halogen atom is minimum in **[KCET 1985]**

(a) Propyl chloride (b) Propyl iodide

(c) Isopropyl chloride (d) Isopropyl bromide

13. Chlorobenzene is

(a) Less reactive than benzyl chloride

(b) More reactive than ethyl bromide

(c) Nearly as reactive as methyl chloride

(d) More reactive than isopropyl chloride

14. The reactivities of methyl chloride, propyl chloride and chlorobenzene are in the order **[KCET 1988]**

(a) Methyl chloride > propyl chloride > chlorobenzene

(b) Propyl chloride > methyl chloride > chlorobenzene

(c) Methyl chloride > chlorobenzene > propyl chloride

(d) Chlorobenzene > propyl chloride > methyl chloride

15. Which of the following compound will make precipitate most readily with $AgNO_3$ **[CPMT 1992]**

(a) CCl_3CHO (b) $CHCl_3$

(c) $C_6H_5CH_2Cl$ (d) CHI_3

16. Carbylamine is liberated when..... is heated with chloroform and alcoholic potash **[KCET 1992]**

(a) An aldehyde (b) A primary amine

(c) A secondary amine (d) A phenol

17. Salicylic acid can be prepared using Reimer-Tiemann's reaction by treating phenol with **[KCET 1989]**

(a) Methyl chloride in the presence of anhydrous aluminium chloride

(b) Carbon dioxide under pressure in sodium hydroxide solution

(c) Carbon tetrachloride and concentrated sodium hydroxide

(d) Sodium nitrite and a few drops of concentrated sulphuric acid

18. Grignard reagent is prepared by the reaction between

[CBSE PMT 1994; DPMT 1996; Pb. PMT 1999; MH CET 1999]

(a) Zinc and alkyl halide

(b) Magnesium and alkyl halide

(c) Magnesium and alkane

(d) Magnesium and aromatic hydrocarbon

19. Reaction of *t*-butyl bromide with sodium methoxide produces **[CBSE PMT 1994]**

(a) Isobutane (b) Isobutylene

(c) Sodium *t*-butoxide (d) *t*-butyl methyl ether

20. War gas is formed from **[BHU 1995]**

(a) PH_3 (b) C_2H_2

(c) Zinc phosphate (d) Chloropicrin

21. What happens when CCl_4 is treated with $AgNO_3$

[EAMCET 1987; CBSE PMT 1988; MP PET 2000]

(a) NO_2 will be evolved

(b) A white ppt. of $AgCl$ will be formed

(c) CCl_4 will dissolve in $AgNO_3$

(d) Nothing will happen

22. If we use pyrene (CCl_4) in the Riemer-Tiemann reaction in place of chloroform, the product formed is

[CBSE PMT 1989; MP PMT 1990; MH CET 1999]

(a) Salicylaldehyde (b) Phenolphthalein

(c) Salicylic acid (d) Cyclohexanol

23. $C_6H_5CH_2Cl + KCN(aq.) \rightarrow X + Y$

Compounds *X* and *Y* are **[BHU 1979]**

(a) $C_6H_6 + KCl$ (b) $C_6H_5CH_2CN + KCl$

(c) $C_6H_5CH_3 + KCl$ (d) None of these

24. The bad smelling substance formed by the action of alcoholic caustic potash on chloroform and aniline is

[MP PMT 1971, 92, 2001; CPMT 1971, 86; AFMC 2002; RPMT 1999]

(a) Phenyl isocyanide (b) Nitrobenzene

(c) Phenyl cyanide (d) Phenyl isocyanate

25. Ethylidene chloride on treatment with aqueous *KOH* gives

[MP PMT 1986]

(a) Ethylene glycol (b) Acetaldehyde

(c) Formaldehyde (d) None

26. Reaction

$C_2H_5I + C_5H_{11}I + 2Na \rightarrow C_2H_5 - C_5H_{11} + 2NaI$ is called

[MP PMT 1992]

(a) Hoffmann's reaction

(b) Dow's reaction

(c) Wurtz's reaction

(d) Riemer-Tiemann's reaction

27. In presence of $AlCl_3$, benzene and *n*-propyl bromide react in Friedal-Craft's reaction to form **[MP PMT**

(a) *n*-propyl benzene

(b) 1, 2-dinormal propyl benzene

(c) 1, 4-dinormal propyl benzene

(d) Isopropyl benzene

28. The dehydrobromination of 2-bromobutane gives $CH_3CH = CHCH_3$. The product is

(a) Hofmann product

(b) Saytzeff product

(c) Hoffmann-Saytzeff product

(d) Markownikoff product

29. Ethylene difluoride on hydrolysis gives

(a) Glycol (b) Fluoroethanol

(c) Difluoroethanol (d) Freon

30. Benzyl chloride when oxidised by $pb(NO_3)_2$ gives **[MP PMT 1989]**

(a) Benzoic acid (b) Benzaldehyde

(c) Benzene (d) None

31. Which of the following statements about chloroform is false **[Manipal MEE 1995]**

(a) It is a colourless, sweet-smelling liquid

(b) It is almost insoluble in water

(c) It is highly inflammable

(d) It can be used as an inhalational anaesthetic agent

32. CCl_4 cannot give precipitate with $AgNO_3$ due to **[CPMT 1979]**

(a) Formation of complex with $AgNO_3$

(b) Evolution of Cl_2 gas

(c) Chloride ion is not formed

(d) $AgNO_3$ does not give silver ion

33. On heating $CHCl_3$ with aq. $NaOH$, the product is **[CPMT 1971, 78; BHU 1997; EAMCET 1998; JIPMER (Med.) 2002]**

(a) CH_3COONa (b) $HCOONa$

(c) Sodium oxalate (d) CH_3OH

34. Ethyl bromide reacts with lead-sodium alloy to form **[MP PMT/PET 1988; MP PET 1997]**

(a) Tetraethyl lead (b) Tetraethyl bromide

(c) Both (a) and (b) (d) None of the above

35. Iodoform heated with Ag powder to form **[DPMT 1985]**

(a) Acetylene (b) Ethylene

(c) Methane (d) Ethane

36. Ethyl bromide reacts with silver nitrite to form **[DPMT 1985; IIT-JEE 1991]**

(a) Nitroethane

(b) Nitroethane and ethyl nitrite

(c) Ethyl nitrite

(d) Ethane

37. Which of the following reactions leads to the formation of chloritone **[RPMT 2003]**

(a) $CHCl_3 + CH_3COCH_3$ (b) CCl_4 + Acetone

(c) $CHCl_3 + KOH$ (d) $CHCl_3 + HNO_3$

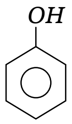
38. $CH_3 - CH_2 - CH_2Br + KOH\,(\text{alc.}) \rightarrow \text{Product}$ Product in above reaction is **[RPMT 2003]**

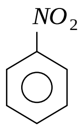
(a) $CH_3 - CH = CH_2$ (b) $CH_3 - CH_2 - CH_3$

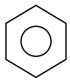
(c) (*a*) and (*b*) both (d) None of these

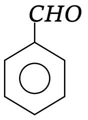
39. $A + CCl_4 + KOH \rightarrow$ Salicylic acid

'*A*' in above reaction is **[RPMT 2003]**

(a) 

(b) 

(c) 

(d) 

40. Identify X and Y in the following sequence

$C_2H_5Br \xrightarrow{X} \text{product} \xrightarrow{Y} C_3H_7NH_2$ **[Orissa JEE 2005]**

(a) $X = KCN, Y = LiAlH_4$

(b) $X = KCN, Y = H_3O^+$

(c) $X = CH_3Cl, Y = AlCl_3 / HCl$

(d) $X = CH_3NH_2, Y = HNO_2$

41. 1-chlorobutane reacts with alcoholic KOH to form **[IIT-JEE 1991; AFMC 1998]**

(a) 1-butene (b) 2-butane

(c) 1-butanol (d) 2-butanol

42. Which of the following reactions gives $H_2C = C = C = CH_2$ **[Roorkee Qualifying 1998]**

(a) $CH_2Br - CBr = CH_2 \xrightarrow{Zn / Ch_3OH}$

(b) $HC \equiv C - CH_2 - COOH \xrightarrow[40^o C]{Aq.K_2CO_3}$

(c) $CH_2Br - C \equiv C - CH_2Br \xrightarrow[\text{Heat}]{Zn}$

(d) $2CH_2 = CH - CH_2I \longrightarrow$

43. When ethyl amine is heated with chloroform and alcoholic KOH, a compound with offensive smell is obtained. This compound is **[CPMT 1983, 84; RPMT 2002]**

(a) A secondary amine (b) An isocyanide

(c) A cyanide (d) An acid

44. Chlorobenzene on fusing with solid $NaOH$ gives **[DPMT 1981; CPMT 1990]**

(a) Benzene (b) Benzoic acid

(c) Phenol (d) Benzene chloride

45. DDT can be prepared by reacting chlorobenzene (in the presence of conc. H_2SO_4) with

(a) Cl_2 in ultraviolet light (b) Chloroform

(c) Trichloroacetone (d) Chloral hydrate

46. When phenol reacts with $CHCl_3$ and KOH, the product obtained would be **[RPMT 1997]**

(a) Salicylaldehyde (b) *p*-hydroxy benzaldehyde

(c) Both (a) and (b) (d) Chloretone

47. Ethyl chloride on heating with silver cyanide forms a compound *X*. The functional isomer of *X* is **[EAMCET 1997; KCET 2005]**

(a) C_2H_5NC (b) C_2H_5CN

(c) $H_3C - NH - CH_3$ (d) $C_2H_5NH_2$

48. Which of the following statements is incorrect **[CPMT 1977**

(a) C_2H_5Br reacts with alco. KOH to form C_2H_5OH

(b) C_2H_5Br when treated with metallic sodium gives ethane

(c) C_2H_5Br when treated with sodium ethoxide forms diethyl ether

(d) C_2H_5Br with $AgCN$ forms ethyl isocyanide

49. When chloroform is exposed to air and sunlight, it gives

[NCERT 1984; CPMT 1978, 87; CBSE PMT 1990; EAMCET 1993; MNR 1994; MP PET 1997, 2000; BHU 2001; AFMC 2002]

(a) Carbon tetrachloride (b) Carbonyl chloride

(c) Mustard gas (d) Lewsite

50. An organic halide is shaken with aqueous $NaOH$ followed by the addition of dil. HNO_3 and silver nitrate solution gave white ppt. The substance can be **[JIPMER 1997]**

(a) $C_6H_4(CH_3)Br$ (b) $C_6H_5CH_2Cl$

(c) C_6H_5Cl (d) None of these

51. A compound A has a molecular formula C_2Cl_3OH. It reduces Fehling solution and on oxidation gives a monocarboxylic acid (B). A is obtained by action of chlorine on ethyl alcohol. A is

[CBSE PMT 1994; MP PET 1997; KCET 2005]

(a) Chloral (b) $CHCl_3$

(c) CH_3Cl (d) Chloroacetic acid

52. Following equation illustrates

$$C_6H_5Cl + 2NaOH \xrightarrow[200\ atm]{200-250^oC} C_6H_5ONa + NaCl + H_2O$$

[Bihar CEE 1995]

(a) Dow's process (b) Kolbe's process

(c) Carbylamine test (d) Haloform reaction

53. One of the following that cannot undergo dehydro-halogenation is **[J & K 2005]**

(a) Iso-propyl bromide (b) Ethanol

(c) Ethyl bromide (d) None of these

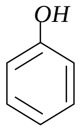
54. A compound X on reaction with chloroform and $NaOH$ gives a compound with a very unpleasant odour. X is

[MP PMT 1999]

(a) $C_6H_5CONH_2$ (b) $C_6H_5NH_2$

(c) $C_6H_5CH_2NHCH_3$ (d) $C_6H_5NHCH_3$

55.



$$+ C_2H_5I \xrightarrow[\text{Anhydrous}(C_2H_5OH)]{O^-C_2H_5} \text{Product}$$

In the above reaction product is

(a) $C_6H_5OC_2H_5$ (b) $C_2H_5OC_2H_5$

(c) $C_6H_5OC_6H_5$ (d) C_6H_5I

56. $C_2H_5Cl + KCN \longrightarrow X \xrightarrow{\text{Hydrolysis}} Y$. '$X$' and '$Y$' are

[MP PET 1995]

(a) C_2H_6 and C_2H_5CN

(b) C_2H_5CN and C_2H_6

(c) C_2H_5CN and $C_2H_5CH_2NH_2$

(d) C_2H_5CN and C_2H_5COOH

57. Iodoform is formed on warming I_2 and $NaOH$ with

[MP PET 1995; DCE 1999; RPET 1999; RPMT 2002]

(a) C_2H_5OH (b) CH_3OH

(c) $HCOOH$ (d) C_6H_6

58. Which of the following reacts with phenol to give salicylaldehyde after hydrolysis **[MP PMT 1995]**

(a) Dichloromethane (b) Trichloromethane

(c) Methyl chloride (d) None of these

59. Dehydrohalogenation in monohaloalkanes produces

(a) A single bond (b) A double bond

(c) A triple bond (d) Fragmentation

60. When chloroform is treated with conc. HNO_3 it gives

[CPMT 1986; MP PMT 1989; AFMC 1998, 99; EAMCET 1991; BHU 1999]

(a) $CHCl_2NO_2$ (b) CCl_3NO_2

(c) $CHCl_2HNO_3$ (d) None of these

61. A sample of chloroform being used as anaesthetic is tested by **[AIIMS 1980; CPMT 1983]**

(a) Fehling solution

(b) Ammoniacal Cu_2Cl_2

(c) $AgNO_3$ solution

(d) $AgNO_3$ solution after boiling with alcoholic KOH solution

62. Dehydrohalogenation of an alkyl halide is **[MP PMT 1996]**

(a) An addition reaction (b) A substitution reaction

(c) An elimination reaction (d)An oxidation reaction

63. Reaction of aqueous sodium hydroxide on (i) ethyl bromide and (ii) chlorobenzene gives

(a) (i) Ethene and (ii) *o*-chlorophenol

(b) (i) Ethyl alcohol and (ii) *o*-chlorophenol

(c) (i) Ethyl alcohol and (ii) phenol

(d) (i) Ethyl alcohol and (ii) no reaction

64. 2-bromopentane is heated with potassium ethoxide in ethanol. The major product obtained is **[CBSE PMT 1998]**

(a) Pentene-1 (b) *cis* pentene-2

(c) *trans* pentene-2 (d) 2-ethoxypentane

65. What is the product formed in the following reaction $C_6H_5OH + CCl_4 \xrightarrow[(2)\ H^+]{(1)\ NaOH}$ **[KCET 1998]**

(a) *p*-hydroxybenzoic acid (b)*o*-hydroxybenzoic acid

(c) Benzaldehyde (d) Salicylaldehyde

66. When chloroform is treated with excess oxygen it forms **[MH CET 1999]**

(a) $COCl_2 + HCl$

(b) $COCl_2 + Cl_2 + H_2$

(c) $COCl_2 + Cl_2 + H_2O$

(d) No product will be formed

67. Which isomer of cyclohexane hexachloride is a very strong insecticide **[MP PET 2003]**

(a) α (b) β

(c) γ (d) δ

68. Haloalkane in the presence of alcoholic KOH undergoes **[KCET (Engg/Med.) 2002]**

(a) Elimination (b) Polymerisation

(c) Dimerisation (d) Substitution

69. The set of compounds in which the reactivity of halogen atom in the ascending order is **[KCET (Engg.) 2002]**

(a) Vinyl chloride, chlorethane, chlorobenzene

(b) Vinyl chloride, chlorobenzene, chloroethane

(c) Chloroethane, chlorobenzene, vinyl chloride

(d) Chlorobenzene, vinyl chloride chloroethane

70. Alkyl halides react with *Mg* in dry ether to form **[DPMT 2000; MP PET 2001]**

(a) Magnesium halide (b) Grignard's reagent

(c) Alkene (d) Alkyne

71. In the following sequence of reactions

$CH_3CH_2CH_2Br \xrightarrow{KOH(alc)} (A) \xrightarrow{HBr} (B) \xrightarrow{KOH\ (aq.)} (C)$,

The product (*C*) is **[JIPMER 2001]**

(a) Propan – 2 - *ol* (b) Propan – 1 – *ol*

(c) Propyne (d) Propene

72. Alkyl halide on heating with alc. NH_3 in a sealed tube results... **[Orissa JEE 2002]**

(a) 1° amine (b) 2° amine

(c) 3° amine (d) All of these

73. When $CH_3CH_2CHCl_2$ is treated with $NaNH_2$, the product formed is **[CBSE PMT 2002]**

(a) $CH_3 - CH = CH_2$ (b) $CH_3 - C \equiv CH$

(c) $CH_3CH_2CH(NH_2)(Cl)$ (d) $CH_3CH_2C(NH_2)_2$

74. By heating a mixture of $CHCl_3$ with silver powder, the compound formed is **[Kurukshetra CET 2002]**

(a) Acetylene (b) Silver acetate

(c) Methanol (d) None of these

75. Chloropicrin is **[Kurukshetra CET 2002]**

(a) Trichloro acetaldehyde (b) Nitrochloroform

(c) 2,4,6-trinitro phenol (d) None of these

76. Which of the following are correct statements about C_2H_5Br **[Roorkee 1999]**

(a) It reacts with metallic *Na* to give ethane

(b) It gives nitroethane on heating with aqueous ethanolic solution of $AgNO_2$

(c) It gives C_2H_5OH on boiling with alcoholic potash

(d) It forms ethylacetate on heating with silver acetate

77. Aryl halide is less reactive than alkyl halide towards nucleophilic substitution because **[RPMT 2002]**

(a) Less stable carbonium ion

(b) Due to large $C - Cl$ bond energy

(c) Inductive effect

(d) Resonance stabilization and sp^2 - hybridisation of *C* attached to halide

78. Methyl chloride reacts with silver acetate to yield **[BVP 2003]**

(a) Acetaldehyde (b) Acetyl chloride

(c) Methyl acetate (d) Acetic acid

79. Chloroform for anesthetic purposes is tested for its purity with the reagent **[DPMT 2001]**

(a) Silver nitrate (b) Lead nitrate

(c) Ammoniacal Cu_2Cl_2 (d) Lead nitrate

80. 2, 6 - Dimethylheptane on monochlorination produces....... derivatives **[DPMT 2001]**

(a) 5 (b) 6

(c) 3 (d) 4

81. The less reactivity of chlorine atom in $CH_2 = CH - Cl$ is due to **[DCE 2001]**

(a) Inductive effect (b) Resonance stabilization

(c) Electromeric effect (d) Electronegativity

82. $CH_3 - CH_2 - Br \xrightarrow{\text{alc.KCN}} CH_3CH_2CN \xrightarrow{\text{HOH}} X$

In this reaction, product *X* is

(a) Acetic acid (b) Propionic acid

(c) Butyric acid (d) Formic acid

83. In alkaline hydrolysis of a tertiary alkyl halide by aqueous alkali if concentration of alkali is doubled, then the reaction **[MH CET 2002]**

(a) Will be doubled (b) Will be halved

(c) Will remain constant (d) Can't say

84. $AgNO_3$ does not give precipitate with $CHCl_3$ because **[MP PET 1999; CPMT 2002]**

(a) $CHCl_3$ does not ionise in water

(b) $AgNO_3$ does not reacts with $CHCl_3$

(c) $CHCl_3$ is chemically inert

(d) None of these

85. The reaction between chlorobenzene and chloral in the presence of concentrated sulphuric acid produces **[Pb. PMT 2001]**

(a) Gammexane

(b) *p,p*-dichloro diphenyl trichloro ethane

(c) Chloropicrin

(d) Benzene hexachloride

86. False statement is **[RPET 1999]**

(a) Chloroform is heavier than water

(b) CCl_4 is non-inflammable

(c) Vinyl chloride is more reactive than allyl chloride

(d) Br^- is a good nucleophile as compared to I^-

87. Chloroform is slowly oxidise by air in presence of light to form **[MH CET 1999; UPSEAT 2001, 02; RPMT 2003]**

(a) Formyl chloride (b) Phosgene

(c) Trichloroacetic acid (d) Formic acid

88. Alcoholic potash is used to bring about **[KCET (Engg.) 2001]**

(a) Dehydrogenation (b) Dehydration

(c) Dehydrohalogenation (d) Dehalogenation

89. Vinyl chloride reacts with HCl to form **[JIPMER 2000]**

(a) 1, 1- dichloro ethane

(b) 1, 2- dichloro ethane

(c) Tetrachloro ethylene

(d) Mixture of 1, 2 and 1, 1 – dichloro ethane

90. $R-X+NaOH \longrightarrow ROH+NaX$

The above reaction is classified as **[BHU 1982; CBSE PMT 1991; RPET 2000]**

(a) Nucleophilic substitution

(b) Electrophilic substitution

(c) Reduction

(d) Oxidation

91. Reduction of acetyl chloride with H_2 in presence of Pd gives **[MP PMT 2001]**

(a) CH_3COCH_3 (b) C_2H_5OH

(c) CH_3COOH (d) CH_3CHO

92. When methyl bromide is heated with Zn it gives **[MP PMT 2001]**

(a) CH_4 (b) C_2H_6

(c) C_2H_4 (d) CH_3OH

93. Phenol reacts with $CHCl_3$ and $NaOH$ (at $340\,K$) to give **[MP PMT 1997; CBSE PMT 2002]**

(a) *o*-chlorophenol (b) Salicylaldehyde

(c) Benzaldehyde (d) Chlorobenzene

94. Iodoform on heating with KOH gives **[MP PMT 2000]**

(a) CH_3CHO (b) CH_3COOK

(c) $HCOOK$ (d) $HCHO$

95. Which reaction is correct in the conversion of chloroform to acetylene **[Pb. PMT 2000]**

(a) $CHCl_3+AgNO_3$ (b) $CHCl_3+O_2$

(c) $CHCl_3+HNO_3$ (d) $CHCl_3+Ag$

96. Which of the following gases are poisonous **[Pb. PMT 2000]**

(a) $CHCl_3$ (b) CO_2

(c) None of these (d) CO

97. Which of the following alkyl halide is used as a methylating agent **[KCET (Med.) 2000; MP PET 1999]**

(a) CH_3I (b) C_2H_5Br

(c) C_2H_5Cl (d) C_6H_5Cl

98. $C_6H_6Cl_6$, on treatment with alcoholic KOH, yields **[AFMC 2000]**

(a) C_6H_6 (b) $C_6H_3Cl_3$

(c) $(C_6H_6)OH$ (d) $C_6H_6Cl_4$

99. When ethyl iodide is heated with silver nitrate, the product obtained is **[CPMT 2000]**

(a) C_2H_5Ag (b) $Ag-O-NO_2$

(c) $C_2H_5O-NO_2$ (d) $C_2H_5I-NO_2$

100. $CHCl_3$ and HF lead to the formation of a compound of fluorine of molecular weight 70. The compound is **[RPET 2000]**

(a) Fluoroform (b) Fluorine monoxide

(c) Fluorine dioxide (d) FlurometHanol

101. Chloroform with zinc dust in water gives **[UPSEAT 2000]**

(a) CH_4 (b) Chloropicrin

(c) CCl_4 (d) CH_2Cl_2

102. Which of the following is used as a catalyst for preparing Grignard reagent **[KCET 1998]**

(a) Iron powder (b) Iodine powder

(c) Activated charcoal (d) Manganese dioxide

103. For a given alkyl group the densities of the halides follow the order **[MP PMT 1997]**

(a) $RI<RBr<RCl$ (b) $RI<RCl<RBr$

(c) $RBr<RI<RCl$ (d) $RCl<RBr<RI$

104. Which halide will be least reactive in respect to hydrolysis **[MP PET 2003]**

(a) Vinyl chloride (b) Allyl chloride

(c) Ethyl chloride (d) *t*-Butyl chloride

105. In nucleophilic aliphatic substitution, the nucleophiles are generally

(a) Acids (b) Bases

(c) Salts (d) Neutral molecules

106. Which one of the following compounds does not react with bromine **[DPMT 1983]**

(a) Ethylamine (b) Propene

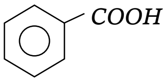
(c) Phenol (d) Chloroform

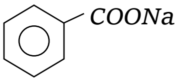
107. Allyl chloride on dehydro chlorination gives **[Kerala (Med.) 2003]**

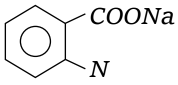
(a) Propadiene (b) Propylene

(c) Acetylchloride (d) Acetone

108. Toluene reacts with excess of Cl_2 in presence of sunlight to give a product which on hydrolysis followed by reaction with $NaOH$ gives **[Orissa JEE 2004]**

(a) 

(b) 

(c) 

(d) None of these

109. An alkyl bromide produces a single alkene when it reacts with sodium ethoxide and ethanol. This alkene undergoes hydrogenation and produces 2-methyl butane. What is the identity of the alkyl bromide **[Kerala PMT 2004]**

(a) 1-bromo-2, 2-dimethylpropane

(b) 1-bromobutane

(c) 1-bromo-2-methylbutane

(d) 2-bromo-2-methylbutane

(e) 2-bromopentane

110. On treating a mixture of two alkyl halides with sodium metal in dry ether, 2-methyl propane was obtained. The alkyl halides are **[KCET 2004]**

(a) 2-chloropropane and chloromethane

(b) 2-chloropropane and chloroethane

(c) Chloromethane and chloroethane

(d) Chloromethane and 1-chloropropane

111. In which case formation of butane nitrile is possible

[Orissa JEE 2004]

(a) $C_3H_7Br + KCN$ (b) $C_4H_9Br + KCN$

(c) $C_3H_7OH + KCN$ (d) $C_4H_9OH + KCN$

112. The reaction of an aeromatic halogen compound with an alkyl halides in presence of sodium and ether is called

[MP PMT 2004]

(a) Wurtz reaction

(b) Sandmeyer's reaction

(c) Wurtz-fittig reaction

(d) Kolbe reaction

113. The compound added to prevent chloroform to form phosgene gas is **[MP PET 2004]**

(a) C_2H_5OH (b) CH_3COOH

(c) CH_3COCH_3 (d) CH_3OH

114. Among the following, the one which reacts most readily with ethanol is **[AIIMS 2004]**

(a) *p*-nitrobenzyl bromide

(b) *p*-chlorobenzyl bromide

(c) *p*-methoxybenzyl bromide

(d) *p*-methylbenzyl bromide

115. Chloropicrin is obtained by the reaction of

[CBSE PMT 2004]

(a) Chlorine on picric acid

(b) Nitric acid on chloroform

(c) Steam on carbon tetrachloride

(d) Nitric acid on chlorobenzene

116. In Wurtz reaction alkyl halide react with**[MH CET 2004]**

(a) Sodium in ether (b) Sodium in dry ether

(c) Sodium only (d) Alkyl halide in ether

117. Chloroform, when kept open, is oxidised to **[CPMT 2004]**

(a) CO_2 (b) $COCl_2$

(c) CO_2, Cl_2 (d) None of these

118. Chloroform reacts with concentrated HNO_3 to give

[Pb. CET 2000]

(a) Water gas (b) Tear gas

(c) Laughing gas (d) Producer gas

119. When ethyl chloride and alcoholic KOH are heated, the compound obtained is **[MH CET 2003]**

(a) C_2H_4 (b) C_2H_2

(c) C_6H_6 (d) C_2H_6

120. Chloroform, on warming with *Ag* powder, gives

[MH CET 2003]

(a) C_2H_6 (b) C_3H_8

(c) C_2H_4 (d) C_2H_2

121. When alkyl halide is heated with dry Ag_2O, it produces

[CPMT 1997; BHU 2004]

(a) Ester (b) Ether

(c) Ketone (d) Alcohol

122. Reaction of alkyl halides with aromatic compounds in presence of anhydrous $AlCl_3$ is known as **[UPSEAT 2004]**

(a) Friedal-Craft reaction

(b) Hofmann degradation

(c) Kolbe's synthesis

(d) Beckmann rearrangement

123. Two percent of ethanol is added during the oxidation of chloroform to stop the formation of carbonyl chloride. In this reaction ethanol acts as**[Pb. CET**

(a) Auto catalyst (b) Negative catalyst

(c) Positive catalyst (d) None of these

124. When benzene is heated with chlorine in the presence of sunlight, it forms **[Pb. CET 2000]**

(a) B.H.C. (b) Cyclopropane

(c) *p*-dichlorobenzene (d) None of these

125. Ethylene di bromide on heating with metallic sodium in ether solution yields **[Pb. CET 2004]**

(a) Ethene (b) Ethyne

(c) 2-butene (d) 1-butene

126. The reaction, $CH_3Br + Na \rightarrow \text{Product}$, is called

[Pb. CET 2003]

(a) Perkin reaction (b) Levit reaction

(c) Wurtz reaction (d) Aldol condensation

127. At normal temperature iodoform is **[MP PET 2004]**

(a) Thick viscous liquid (b) Gas

(c) Volatile liquid (d) Solid

128. Which of the following statements about benzyl chloride is incorrect **[KCET 2004]**

(a) It is less reactive than alkyl halides

(b) It can be oxidised to benzaldehyde by boiling with copper nitrate solution

(c) It is a lachrymatory liquid and answers Beilstein's test

(d) It gives a white precipitate with alcoholic silver nitrate

129. Ethylene dichloride and ethylidine chloride are isomeric compounds. The false statement about these isomers is that they **[DCE 2003]**

(a) React with alcoholic potash and give the same product

(b) Are position isomers

(c) Contain the same percentage of chlorine

(d) Are both hydrolysed to the same product

130. An alkyl bromide (X) reacts with Na to form 4, 5-diethyloctane. Compound X is **[Roorkee 1999]**

(a) $CH_3(CH_2)_3Br$

(b) $CH_3(CH_2)_5Br$

(c) $CH_3(CH_2)_3CH.Br.CH_3$

(d) $CH_3(CH_2)_2CH.Br.CH_2CH_3$

131. In the following reaction X is

$CH_3NH_2 + X + KOH \rightarrow CH_3NC$ (highly offensive odour)

[MP PET 1994]

(a) CH_2Cl_2 (b) $CHCl_3$

(c) CH_3Cl (d) CCl_4

132. Which metal is used in Wurtz synthesis

[CPMT 1986; DPMT 1979; MP PET 2002]

(a) Ba (b) Al

(c) Na (d) Fe

133. Which of the following is boiled with ethyl chloride to form ethyl alcohol **[MNR 1982]**

(a) Alcoholic KOH (b) Aqueous KOH

(c) H_2O (d) H_2O_2

134. Why is chloroform put into dark coloured bottles

[MP PET 2002]

(a) To prevent evaporation

(b) To prevent from moisture

(c) To prevent it from oxidation to form phosgene

(d) To prevent its reaction with glass

135. DDT is

(a) A solid (b) A liquid

(c) A gas (d) A solution

136. Bottles containing C_6H_5I and $C_6H_5CH_2I$ lost their original labels. They were labelled A and B for testing. A and B were separately taken in test tubes and boiled with $NaOH$ solution. The end solution in each tube was made acidic with dilute HNO_3 and then some $AgNO_3$ solution was added. Substance B give a yellow precipitate. Which one of the following statements is true for this experiment

[AIEEE 2003]

(a) A was C_6H_5I

(b) A was $C_6H_5CH_2I$

(c) B was C_6H_5I

(d) Addition of HNO_3 was unnecessary

137. Which of the following statements is incorrect regarding benzyl chloride **[KCET 2003]**

(a) It gives white precipitate with alcoholic $AgNO_3$

(b) It is an aromatic compound with substitution in the side chain

(c) It undergoes nucleophilic substitution reaction

(d) It is less reactive than vinyl chloride

138. Alkyl halide can be converted into alkene by

[BCECE 2005]

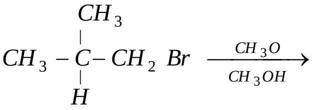
(a) Nucleophilic substitution reaction

(b) Elimination reaction

(c) Both nucleophilic substitution and elimination reaction

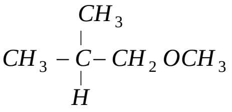
(d) Rearrangement

139. The major product formed in the following reaction is



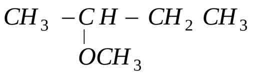
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-CH_2Br \xrightarrow[CH_3OH]{CH_3O} $ **[AIIMS 2005]**

(a)



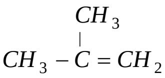
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-CH_2OCH_3$

(b)



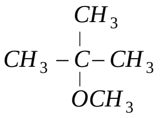
$CH_3-\underset{\underset{OCH_3}{|}}{CH}-CH_2CH_3$

(c)



$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2$

(d)



$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OCH_3}{|}}{C}}-CH_3$

140. The major product obtained on treatment of $CH_3CH_2CH(F)CH_3$ with CH_3O^-/CH_3OH is

[AIIMS 2005]

(a) $CH_3CH_2CH(OCH_3)CH_3$

(b) $CH_3CH=CHCH_3$

(c) $CH_3CH_2CH=CH_2$

(d) $CH_3CH_2CH_2CH_2OCH_3$

141. When phenyl magnesium bromide reacts with *t*–butanol, the product would be **[IIT 2005]**

(a) Benzene (b) Phenol

(c) *t*–butyl benzene (d) *t*–butyl phenyl ether

142. Alkyl halides react with dialkyl copper reagents to give

[AIEEE 2005]

(a) Alkenes (b) Alkyl copper halides

(c) Alkanes (d) Alkenyl halides

143. Which of the following is liquid at room temperature

[AFMC 2005]

(a) CH_3I (b) CH_3Br

(c) C_2H_5Cl (d) CH_3F

144. Which of the following haloalkanes is most reactive

[KCET 2005]

(a) 1-chloropropane (b) 1-bromopropane

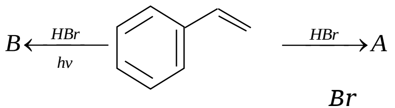
(c) 2-chloropropane (d) 2-bromopropane

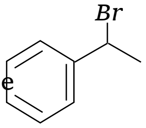
145. Grignard reagent adds to **[KCET 2005]**

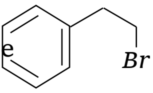
(a) $> C=O$ (b) $-C\equiv N$

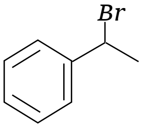
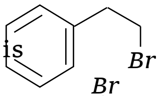
(c) $> C=S$ (d) All of the above

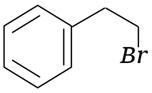
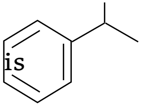
146. Analyse the following reaction and identify the nature of A and B **[Kerala CET 2005]**

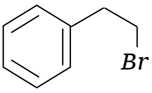
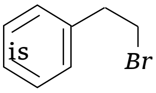


(a) Both A and B are 

(b) Both A and B are 

(c) A is  & B is 

(d) A is  & B is 

(e) A is  & B is 

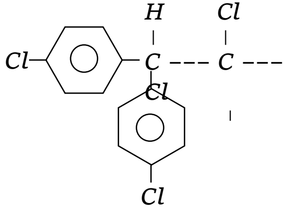
Uses of Halogen Containing Compounds

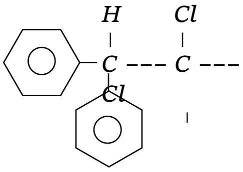
1. Which of these can be used as moth repellant **[CPMT 1987]**

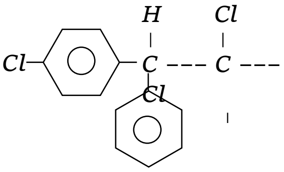
(a) Benzene hexachloride (b) Benzal chloride

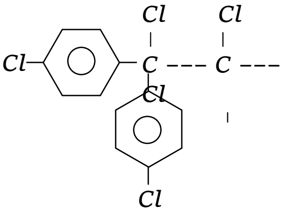
(c) Hexachloroethane (d) Tetrachloroethane

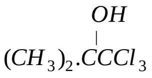
2. Which one of the following is the correct formula of dichlorodiphenyl trichloroethane **[AIIMS 1982]**

(a) 

(b) 

(c) 

(d) 

3. The compound  $(CH_3)_2.\overset{OH}{\overset{|}{C}}CCl_3$ is

(a) Chloretone (b) Chloroquin

(c) Chloropicrin (d) Chloropropyl chloride

4. Depletion of ozone layer is caused by **[RPMT 2002]**

(a) Freon (b) Alkane

(c) Gringard reagent (d) All of these

5. Which of the following is Teflon **[RPMT 2002]**

(a) $[-CF_2-CF_2-]_n$ (b) $CF_2=CF_2$

(c) $CF\equiv CF$ (d) None of these

6. Statement "Ozone in atmosphere is decreased by chloro-fluoro-carbon (Cl_2F_2C)" **[RPET 1999]**

(a) Is true

(b) Is false

(c) Only in presence of CO_2

(d) Only in absence of CO_2

7. CF_xCl_y [where x + y = 4]. These compounds are not used because **[RPET 2000]**

(a) These are fluoro carbons

(b) These are difficult to synthesise

(c) They deplete ozone layer

(d) None of the these

8. The molecular formula of DDT has **[MP PMT 1997]**

(a) 5 chlorine atoms (b) 4 chlorine atoms

(c) 3 chlorine atoms (d) 2 chlorine atoms

9. What is the reagent used for testing fluoride ion in water **[EAMCET 2003]**

(a) Alizarin - S (b) Quinalizarin

(c) Phenolphthalein (d) Benzene

10. Chloropicrin is used as **[UPSEAT 2000]**

(a) Solvent (b) Anaesthetic

(c) Perfume (d) Tear gas

11. Which is used in the manufacture of plastic

(a) $CH_2=CHCl$ (b) $CH\equiv CH$

(c) $CH_2=CH-CH_2I$ (d) CCl_4

12. Freon (dichlorodifluoro methane) is used **[CPMT 1986; DPMT 1983; CBSE PMT 2001]**

(a) As local anaesthetic

(b) For dissolving impurities in metallurgical process

(c) In refrigerator

(d) In printing industry

13. Which of the following is known as freon which is used as a refrigerant**[DPMT 1982; CPMT 1979, 81, 89; AFMC Manipal MEE 1995; MP PET 1995, 2004]**

(a) CCl_2F_2 (b) $CHCl_3$

(c) CH_2F_2 (d) CF_4

14. Benzene hexachloride (BHC) is used as **[MP PMT 1994; KCET 1999]**

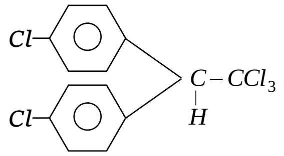
(a) Dye (b) Antimalerial drug

(c) Antibiotic (d) Insecticide

15. Which plastic is obtained from $CHCl_3$ as follows

$$CHCl_3 \xrightarrow[SbF_3]{HF} X \xrightarrow{800^o C} Y \xrightarrow{Polymerisation} \text{Plastic}$$

(a) Bakelite (b) Teflon
(c) Polythene (d) Perspex

16.  . The above structural formula refers to **[MP PET 1997]**

(a) BHC (b) DNA
(c) DDT (d) RNA

17. The commercial uses of DDT and benzene hexachloride are

(a) DDT is a herbicide, benzene hexachloride is a fungicide
(b) Both are insecticides
(c) Both are herbicides
(d) DDT is a fungicide and benzene hexachloride is a herbicide

18. Which of the following is used in fire extinguishers **[AFMC 1993]**

(a) CH_4 (b) $CHCl_3$
(c) CH_2Cl_2 (d) CCl_4

19. Iodoform can be used as **[NCERT 1981]**

(a) Anaesthetic (b) Antiseptic
(c) Analgesic (d) Antifebrin

20. Which of the following is an anaesthetic **[AFMC 1989]**

(a) C_2H_4 (b) $CHCl_3$
(c) CH_3Cl (d) C_2H_5OH

21. An important insecticide is obtained by the action of chloral on chlorobenzene. It is **[KCET 1989]**

(a) BHC (b) Gammexene
(c) DDT (d) Lindane

22. In fire extinguisher, pyrene is **[DPMT 1985]**

(a) CO_2 (b) CCl_4
(c) CS_2 (d) $CHCl_3$

23. B.H.C. is used as **[Pb. CET 2002]**

(a) Insecticide (b) Pesticide
(c) Herbicide (d) Weedicide

24. The use of the product obtained as a result of reaction between acetone and chloroform is **[RPMT 1999]**

(a) Hypnotic (b) Antiseptic
(c) Germicidal (d) Anaesthetic

25. Use of chlorofluoro carbons is not encouraged because **[KCET 2005]**

(a) They are harmful to the eyes of people that use it
(b) They damage the refrigerators and air conditioners
(c) They eat away the ozone in the atmosphere
(d) They destroy the oxygen layer

Critical Thinking

Objective Questions

1. Among the following, the molecule with the highest dipole moment is **[IIT-JEE (Screening) 2003]**

(a) CH_3Cl (b) CH_2Cl_2
(c) $CHCl_3$ (d) CCl_4

2. When $CHCl_3$ is boiled with $NaOH$, It gives **[Orissa JEE 2003]**

(a) Formic acid (b) Trihydroxy methane
(c) Acetylene (d) Sodium formate

3. The hybridization state of carbon atoms in the product formed by the reaction of ethyl chloride with aqueous potassium hydroxide is **[EAMCET 1997]**

(a) sp (b) sp^2
(c) sp^3 (d) sp^3d

4. Which of the following compounds does not undergo nucleophilic substitution reactions **[KCET 1998]**

(a) Vinyl chloride (b) Ethyl bromide
(c) Benzyl chloride (d) Isopropyl chloride

5. Replacement of Cl of chlorobenzene to give phenol requires drastic conditions but chlorine of 2, 4-dinitrochlorobenzene is readily replaced because **[CBSE PM**

(a) NO_2 make ring electron rich at ortho and para
(b) NO_2 withdraws e^- from meta position
(c) denotes e^- at meta position
(d) NO_2 withdraws e^- from ortho/para positions

6. Among the following one with the highest percentage of chlorine is **[MNR 1989; BHU 1998; MH CET 199**

(a) Chloral (b) Pyrene
(c) PVC (d) Gammexene

7. In which alkyl halide, SN^2 mechanism is favoured maximum **[RPMT 1997]**

(a) CH_3Cl (b) CH_3CH_2Cl
(c) $(CH_3)_2CHCl$ (d) $(CH_3)_3C-Cl$

8. Which conformation of $C_6H_6Cl_6$ is most powerful insecticide

(a) $aaeeee$ (b) $aaaeee$
(c) $aaaaee$ (d) $aaaaaa$

9. The odd decomposition of carbon chlorine bond form **[UPSEAT 1999]**

(a) Two free ions (b) Two-carbanium ion
(c) Two carbanion (d) A cation and an anion

10. A new carbon-carbon bond formation is possible in

[IIT-JEE 1998]

(a) Cannizzaro reaction (b) Friedel-Craft's alkylation

(c) Clemmensen reduction (d)Reimer-Tiemann reaction

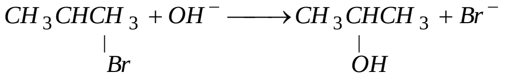
11. An isomer of $C_3H_6Cl_2$ on boiling with aqueous KOH gives acetone. Hence, the isomer is **[UPSEAT 2000]**

(a) 2, 2-dichloropropane (b) 1, 2-dichloropropane

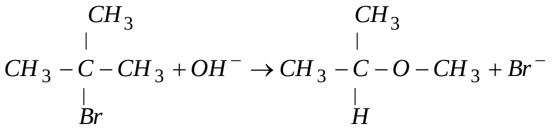
(c) 1, 1-dichloropropane (d) 1, 3-dichloropropane

12. Which of the following is the example of SN^2 reaction **[CPMT 1999]**

(a) $CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$

(b) 
$CH_3\underset{\underset{Br}{|}}{C}HCH_3 + OH^- \longrightarrow CH_3\underset{\underset{OH}{|}}{C}HCH_3 + Br^-$

(c) $CH_3CH_2OH \xrightarrow{-H_2O} CH_2 = CH_2$

(d) 
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-CH_3 + OH^- \rightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-O-CH_3 + Br^-$

13. Wurtz reaction of methyl iodide yields an organic compound X. Which one of the following reactions also yields X **[EAMCET 2003]**

(a) $C_2H_5Cl + Mg \xrightarrow{\text{dry ether}}$

(b) $C_2H_5Cl + LiAlH_4 \longrightarrow$

(c) $C_2H_5Cl + C_2H_5ONa \longrightarrow$

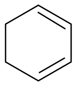
(d) $CHCl_3 \xrightarrow[\Delta]{Ag\text{ powder}}$

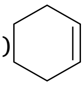
14. Ethyl orthoformate is formed by heating with sodium ethoxide **[EAMCET 2003]**

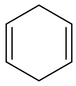
(a) $CHCl_3$ (b) C_2H_5OH

(c) $HCOOH$ (d) CH_3CHO

15. 1 , 2 di-bromo cyclohexane on dehydro halogenation gives **[UPSEAT 2003]**

(a) 

(b) 

(c) 

(d) None of these

16. In which one of the following conversions phosphorus pentachloride is used as a reagent **[EAMCET 1997]**

(a) $H_2C = CH_2 \rightarrow CH_3CH_2Cl$

(b) $H_3C-O-CH_3 \rightarrow CH_3Cl$

(c) $CH_3CH_2OH \rightarrow CH_3CH_2Cl$

(d) $HC \equiv CH \rightarrow CH_2 = CHCl$

17. When but –3-*en* -2- *ol* reacts with *aq*. HBr, the product formed is **[DCE 2001]**

(a) 3 - bromobut - 1- ene

(b) 1 - bromobut - 2- ene

(c) *A* mixture of both *a* and *b*

(d) 2 - bromobut - 2 - ene

18. Which of these do not form Grignard reagent

(a) CH_3F (b) CH_3Cl

(c) CH_3Br (d) CH_3I

19. An organic compound $A(C_4H_6Cl)$ on reaction with Na/diethyl ether gives a hydrocarbon, which on monochlorination gives only one chloro derivative. *A* is **[Kerala PMT 2004]**

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

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

(e) None of these

20. Among the following the most reactive towards alcoholic KOH is **[AIIMS 2004]**

(a) $CH_2 = CHBr$ (b) $CH_3COCH_2CH_2Br$

(c) CH_3CH_2Br (d) $CH_3CH_2CH_2Br$

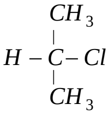
21. Which one of the following possess highest m.pt. **[Pb. CET 2004]**

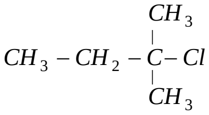
(a) Chlorobenzene (b) *o*-dichlorobenzene

(c) *m*-dichlorobenzene (d) *p*-dichlorobenzene

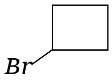
22. Which chlorine atom is more electronegative in the following **[UPSEAT 2004]**

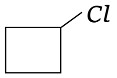
(a) CH_3-Cl (b) CH_3-CH_2-Cl

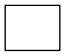
(c) 
$H-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Cl$

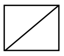
(d) 
$CH_3-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Cl$

23. What would be the product formed when 1-Bromo-3-chloro cyclobutane reacts with two equivalents of metallic sodium in ether **[IIT-JEE (Screening]**

(a) 

(b) 

(c) 

(d) 

AR Assertion & Reason

For AIIMS Aspirants

Read the assertion and reason carefully to mark the correct option out of the options given below:

(a) If both assertion and reason are true and the reason is the correct explanation of the assertion.

(b) If both assertion and reason are true but reason is not the correct explanation of the assertion.

(c) If assertion is true but reason is false.

(d) If the assertion and reason both are false.

(e) If assertion is false but reason is true.

1. Assertion : $CHCl_3$ is stored in transparent bottles.

Reason : $CHCl_3$ is oxidised in dark. **[AIIMS 1996]**

2. Assertion : Addition of bromine to trans-2-butene yields meso-2, 3-dibromobutane

Reason : Bromine addition to an alkene is an electrophilic addition.

[IIT-JEE (Screening) 2001]

3. Assertion : Alkyl halides are soluble in organic solvents.

Reason : *p*-dichlorobenzene possesses low melting point.

4. Assertion : CCl_4 is not a fire extinguisher.

Reason : CCl_4 is insoluble in water.

5. Assertion : Aqueous hydrohalogen acids are used to prepare alkyl halides from alkenes.

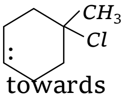
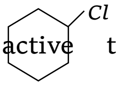
Reason : Hydrogen iodide readily reacts with alkenes to form alkyl halides.

6. Assertion : Alkyl halides form alkenes when heated above 300°*C*.

Reason : CH_3CH_2I react slowly with strong base when compared to CD_3CH_2I.

7. Assertion : Halogen acids react with alcohols to form haloalkanes.

Reason : Order of reactivity of halogen acids $HCl > HBr > HI$

8. Assertion :  is less reactive than  towards reactions.

Reason : Tertiary alkyl halides react predominantly by S_N1 mechanism.

9. Assertion : Electron withdrawing groups in aryl halides decrease the reactivity towards nucleophilic substitution.

Reason : 2, 4-Dinitrochlorobenzene is less reactive than chlorobenzene.

10. Assertion : Aryl halides undergo electrophilic substitutions more readily than benzene.

Reason : Aryl halide gives a mixture of *o*- and *p*- products.

11. Assertion : Addition of Br_2 to cis-but-2-ene is stereoselective.

Reason : SN^2 reactions are stereospecific as well as stereoselective.

12. Assertion : Optically active 2-iodobutane on treatment with *NaI* in acetone undergoes recemization.

Reason : Repeated Walden inversions on the reactant and its product eventually gives a racemic mixture.

13. Assertion : Nucleophilic substitution reaction on an optically active alkyl halide gives a mixture of enantiomers.

Reason : The reaction occurs by SN^1 mechanism.

Answers

Introduction of Halogen containing compounds

1	a	2	b	3	b	4	c	5	b
6	a	7	b	8	a	9	b	10	a
11	d	12	a	13	b				

Preparation of Halogen containing compounds

1	b	2	d	3	b	4	a	5	a
6	b	7	d	8	d	9	b	10	a
11	a	12	b	13	a	14	a	15	a
16	b	17	a	18	b	19	c	20	c
21	a	22	c	23	c	24	b	25	d
26	d	27	c	28	a	29	c	30	b
31	c	32	b	33	d	34	a	35	c
36	d	37	c	38	b	39	b	40	d
41	c	42	c	43	a	44	b	45	b
46	a	47	c	48	a	49	b	50	a
51	b	52	a	53	d	54	a		

Properties of Halogen containing compounds

1	a	2	c	3	c	4	c	5	c
6	c	7	c	8	c	9	b	10	d
11	b	12	c	13	a	14	a	15	d
16	b	17	c	18	b	19	b	20	d
21	d	22	c	23	b	24	a	25	b
26	c	27	d	28	b	29	a	30	b
31	c	32	c	33	b	34	a	35	a
36	a	37	a	38	a	39	a	40	a
41	a	42	c	43	b	44	c	45	d
46	c	47	b	48	ab	49	b	50	b
51	a	52	a	53	b	54	b	55	a
56	d	57	a	58	b	59	b	60	b
61	c,d	62	c	63	c	64	c	65	b
66	c	67	c	68	a	69	d	70	b
71	a	72	d	73	d	74	a	75	b
76	b,d	77	d	78	c	79	a	80	d

81	b	82	b	83	c	84	a	85	b
86	cd	87	b	88	c	89	a	90	a
91	d	92	b	93	b	94	c	95	d
96	d	97	a	98	b	99	c	100	a
101	a	102	b	103	d	104	a	105	b
106	d	107	a	108	b	109	c	110	a
111	a	112	c	113	a	114	c	115	b
116	a	117	b	118	b	119	a	120	d
121	b	122	a	123	b	124	a	125	c
126	c	127	d	128	a	129	d	130	d
131	b	132	c	133	b	134	c	135	a
136	a	137	d	138	b	139	d	140	b
141	a	142	c	143	a	144	d	145	d
146	c								

Uses of Halogen containing compounds

1	c	2	a	3	a	4	a	5	a
6	a	7	c	8	a	9	a	10	d
11	a	12	c	13	a	14	d	15	b
16	c	17	b	18	d	19	b	20	b
21	c	22	b	23	a	24	a	25	c

Critical Thinking Questions

1	a	2	b	3	c	4	a	5	d
6	b	7	a	8	b	9	d	10	bd
11	a	12	a	13	b	14	a	15	d
16	bc	17	c	18	a	19	a	20	d
21	d	22	d	23	d				

Assertion and Reason

1	d	2	b	3	c	4	e	5	e
6	c	7	c	8	e	9	d	10	e
11	b	12	a	13	a				

Answers and Solutions

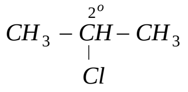
Introduction of Halogen containing compounds

2. (b) $$\% \text{ of } Br = \frac{\text{Mass of } Br}{\text{Mass of organic compound}} \times 100$$

$$= \frac{80}{109} \times 100 = 73.39\,\%$$ or approx. 75%

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

6. (a) Isopropyl chloride

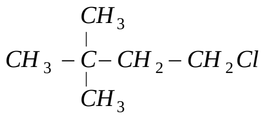


$$CH_3 - \underset{Cl}{\underset{|}{\overset{2^o}{CH}}} - CH_3$$

chlorine atom is attached to 2^o carbon atom.

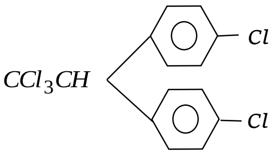
7. (b) $CH_4 \xrightarrow[+3X]{-3H} CHX_3$ $(X = Cl, Br, I)$

11. (d) Neohexyl chloride is a primary halide as in it Cl-atom is attached to a primary carbon.



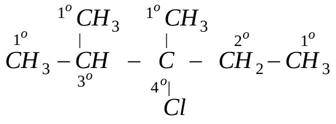
$$CH_3 - \underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}} - CH_2 - CH_2Cl$$

12. (a)



(DDT)

13. (b)

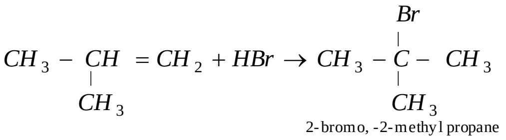


$$\overset{1^o}{CH_3} - \underset{3^o}{\overset{1^o CH_3}{\overset{|}{CH}}} - \underset{Cl}{\underset{4^o|}{\overset{1^o CH_3}{\overset{|}{C}}}} - \overset{2^o}{CH_2} - \overset{1^o}{CH_3}$$

3-chloro-2,3-dimethylpentane

Preparation of Halogen containing compounds

2. (d)

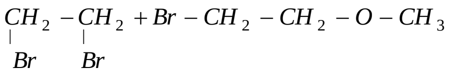


$$CH_3 - \underset{CH_3}{\underset{|}{CH}} = CH_2 + HBr \rightarrow \underset{\text{2-bromo, -2-methyl propane}}{CH_3 - \underset{CH_3}{\underset{|}{\overset{Br}{\overset{|}{C}}}} - CH_3}$$

5. (a) $CH_3COOAg + Br_2 \xrightarrow{CS_2} CH_3Br + AgBr + CO_2$

7. (d) $C_2H_5OH + SOCl_2 \xrightarrow{\text{Pyridine}} C_2H_5Cl + SO_2 + HCl$

14. (a) $CH_2 = CH_2 + Br_2 \xrightarrow{CH_3OH}$



$$\underset{Br}{\underset{|}{CH_2}} - \underset{Br}{\underset{|}{CH_2}} + Br - CH_2 - CH_2 - O - CH_3$$

15. (a) $C_3H_8 + Cl_2 \xrightarrow{\text{Light}} C_3H_7Cl + HCl$

This is an example of substitution reaction. Hydrogen atom of alkane is replaced by halogen atom.

16. (b) $CH \equiv CH + HCl \rightarrow CH_2 = CHCl \xrightarrow{+HCl} CH_3CHCl_2$

17. (a) $R - OX + HX \rightarrow R - X + H_2O$

Reactivity order of alcohols for this reaction

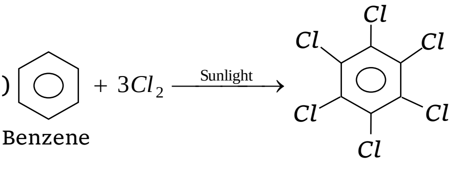
$3^o > 2^o > 1^o$

Reactivity order of halogen acids

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

18. (b) $\underset{\text{Benzene}}{C_6H_6} + 3Cl_2 \xrightarrow{\text{U.V light}} \underset{\text{BHC}}{C_6H_6Cl_6}$

19. (c)



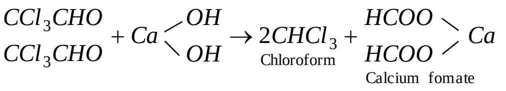
21. (a) $C_2H_5OH \xrightarrow[Na_2CO_3]{KI} CHI_3$

22. (c) $\underset{\text{Bleaching powder}}{CaOCl_2} + H_2O \rightarrow Ca(OH)_2 + Cl_2$

23. (c) $CaOCl_2 + H_2O \xrightarrow{\text{Hydrolysis}} Ca(OH)_2 + Cl_2$

$CH_3CH_2OH + Cl_2 \xrightarrow{\text{Oxidation}} CH_3CHO + 2HCl$

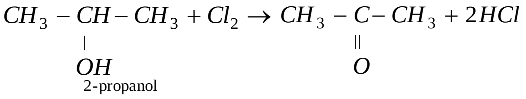
$CH_3CHO + 3Cl_2 \xrightarrow{\text{Chlorination}} CCl_3CHO + 3HCl$



$$\begin{array}{l} CCl_3CHO \\ CCl_3CHO \end{array} + Ca \begin{array}{l} \diagup OH \\ \diagdown OH \end{array} \rightarrow \underset{\text{Chloroform}}{2CHCl_3} + \underset{\text{Calcium fomate}}{\begin{array}{l} HCOO \diagdown \\ HCOO \diagup \end{array} Ca}$$

24. (b) $\underset{\text{Chlorol}}{CCl_3CHO} + NaOH \xrightarrow{\text{Boil}} \underset{\text{Chloroform}}{CHCl_3} + HCOONa$

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



$$\underset{\text{2-propanol}}{CH_3 - \underset{OH}{\underset{|}{CH}} - CH_3} + Cl_2 \rightarrow CH_3 - \underset{O}{\underset{||}{C}} - CH_3 + 2HCl$$

$$CH_3 - \underset{\underset{O}{||}}{C} - CH_3 + 3Cl_2 \rightarrow CCl_3 - CO - CH_3 + 3HCl$$

$$\begin{matrix} CCl_3COCH_3 \\ CCl_3COCH_3 \end{matrix} + Ca\begin{matrix} \diagup OH \\ \diagdown OH \end{matrix} \rightarrow 2CHCl_3 + \begin{matrix} CH_3COO \diagdown \\ CH_3COO \diagup \end{matrix} Ca$$

26. (d) $CH_3CH_2OH + Cl_2 \rightarrow CH_3CHO + 2HCl$

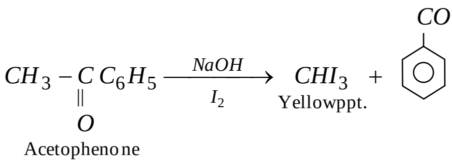
$CH_3CHO + 3Cl_2 \rightarrow \underset{\text{Chloral}}{CCl_3\,CHO} + 3HCl$

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

29. (c) $CH_3CH_2 - CO - CH_2 - CH_3 \xrightarrow{NaOH / I_2}$ No yellow ppt

$$\left.\begin{array}{l} CH_3COCH_3 \xrightarrow{NaOH / I_2} CHI_3 \\ C_2H_5OH \xrightarrow{NaOH / I_2} CHI_3 \\ CH_3 - \underset{\underset{OH}{|}}{CH} - CH_3 \xrightarrow{NaOH / I_2} CHI_3 \end{array}\right\} \text{yellow ppt.}$$

30. (b)

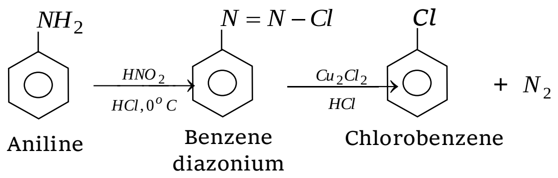


31. (c) $CH_3COCH_3 + 3I_2 + 4NaOH \rightarrow$

$CHI_3 + 3Na + CH_3COONa + 3H_2O$

32. (b) $C_2H_5OH + SOCl_2 \xrightarrow{\text{Pyridine}} C_2H_5Cl + SO_2 + HCl$

33. (d)

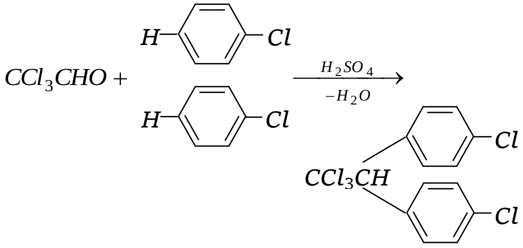


34. (a) $CH_3OH + HI \xrightarrow{ZnCl_2} CH_3I + H_2O$

35. (c) $\underset{\text{Ethyl iodide}}{C_2H_5I + Mg} \xrightarrow{\text{Dry ether}} \underset{\text{Ethyl magnesium iodide}}{C_2H_5 - Mg - I}$

43. (a) $CH_3 - CH = CH_2 + HBr \xrightarrow[\text{Markownikoff's rule}]{} CH_3 - \underset{\underset{Br}{|}}{CH} - CH_3$

45. (b) DDT is prepared by heating chlorobenzene and chloral with concentrated sulphuric acid



1, 1, 1-trichloro-2, 2 bis (*P*-chlorophenyl) ethane or

46. (a) Acetone forms chloroform when heated with bleaching powder.

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

$CH_3COCH_3 + 3Cl_2 \rightarrow CCl_3COCH_3 + 3HCl$

$2CCl_3COCH_3 + Ca(OH)_2 \rightarrow \underset{\text{chloroform}}{2CHCl_3} + (CH_3COO)_2Ca$

47. (c) $\underset{\text{Bleaching powder}}{CaOCl_2} + H_2O \rightarrow Ca(OH)_2 + Cl_2$

$Cl_2 + H_2O \rightarrow 2HCl + O$

$\underset{\text{ethanol}}{C_2H_5OH} + O \rightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2O$

$CH_3CHO + 3Cl_2 \rightarrow \underset{\text{chloral}}{CCl_3CHO} + 3HCl$

$2CCl_3CHO + Ca(OH)_2 \rightarrow \underset{\substack{\text{chloroform or} \\ \text{trichloromethane}}}{2CHCl_3} + (HCOO)_2Ca$

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

$CH_3CH_2OH + Cl_2 \rightarrow CH_3CHO + HCl$

$CH_3CHO + Cl_2 \xrightarrow{Ca(OH)_2} CHCl_3 + (CH_3COO)_2Ca$

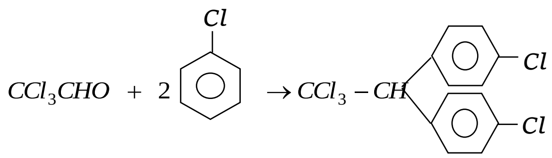
49. (b) When ethylene reacts with bromine, it forms ethylene dibromide.

$$\underset{\text{Ethylene}}{H_2C = CH_2} + \underset{\text{Bromine}}{Br_2} \rightarrow \underset{\text{Ethylene dibromide}}{H_2\underset{\underset{Br}{|}}{C} - \underset{\underset{Br}{|}}{CH_2}}$$

50. (a) The chlorination of alcohol by $SOCl_2$ (thionyl chloride) is the best method for the preparation of alkyl halides as in this method all the other product are gaseous and thus halides are obtained on quite pure state

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

51. (b)

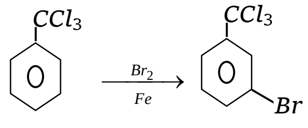


52. (a) DDT is formed by reaction of chloral with chloro benzene.

54. (a) *NBS* is a selective brominating reagent since it normally brominates the ethylenic compounds in the allylic position.

Properties of Halogen containing compounds

1. (a)



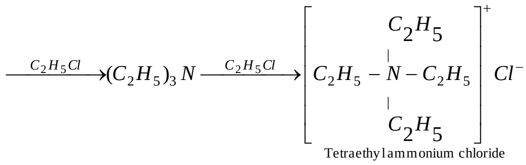
As $–CCl_3$ is a *m*-directing group.

2. (c) $Ag_2O + H_2O \rightarrow 2AgOH$

$C_2H_5Br + AgOH \rightarrow C_2H_5OH + AgBr$

3. (c) $C_2H_5Cl + 2Na + ClC_2H_5 \xrightarrow[\text{Ether}]{\text{Dry}} C_2H_5 - C_2H_5 + 2NaCl$

4. (c) $C_2H_5Cl \xrightarrow{NH_3} C_2H_5 - NH_2 \xrightarrow{C_2H_5Cl} (C_2H_5)_2 - NH$



$\xrightarrow{C_2H_5Cl} (C_2H_5)_3N \xrightarrow{C_2H_5Cl} \underset{\text{Tetraethylammonium chloride}}{\left[C_2H_5 - \overset{C_2H_5}{\underset{C_2H_5}{N}} - C_2H_5 \right]^+ Cl^-}$

If NH_3 is in excess, then 1^o amine will be the main product, if C_2H_5Cl is in excess then mixture of $1^o, 2^o, 3^o$ and quaternary amine is obtained.

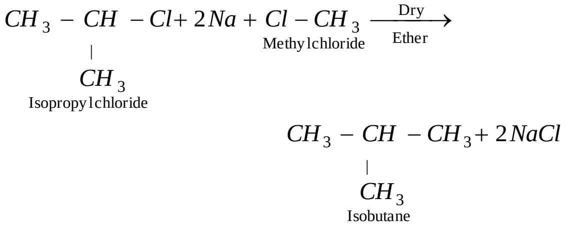
5. (c) $2CHCl_3 + O_2 \xrightarrow[\text{air}]{\text{Light}} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$

6. (c) $COCl_2$ carbonyl chloride is commonly called as phosgene.

7. (c) $C_2H_5NH_2 + CHCl_3 + 3KOH \rightarrow$

$\underset{\text{Ethylisocyanide(offensive odour)}}{C_2H_5 - N \equiv C} + 3KCl + 3H_2O$

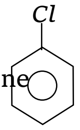
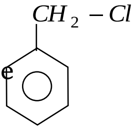
8. (c)



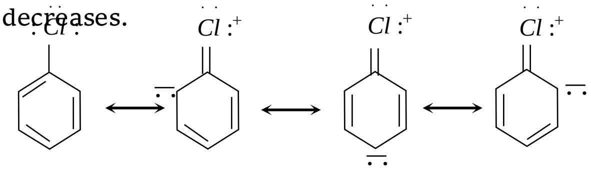
$\underset{\text{Isopropylchloride}}{CH_3 - \underset{CH_3}{CH} - Cl} + 2Na + \underset{\text{Methylchloride}}{Cl - CH_3} \xrightarrow[\text{Ether}]{\text{Dry}} \underset{\text{Isobutane}}{CH_3 - \underset{CH_3}{CH} - CH_3} + 2NaCl$

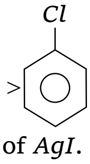
9. (b) $RX + Mg \xrightarrow{\text{Dry ether}} R - Mg - X$

11. (b) $\underset{\text{more reactive}}{C_2H_5 - Cl} > \underset{\text{less reactive}}{C_6H_5 - CH_2 - Cl}$

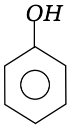
13. (a) Chlorobenzene  is less reactive than benzyl chloride 

In chlorobenzene the lone pairs present on Cl atom get involved in resonance with π electrons of benzene due to which $C-Cl$ bond acquires double bond character Hence, reactivity decreases.

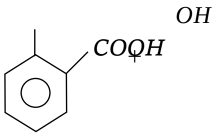


14. (a) $CH_3 - Cl > CH_3 - CH_2 - Cl >$ 

15. (d) CHI_3 gives a yellow ppt. of AgI.



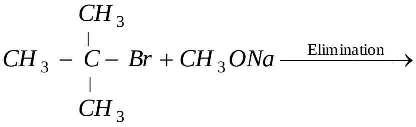
17. (c) $+ CCl_4 + 4NaOH \rightarrow 4NaCl + 2H_2O$



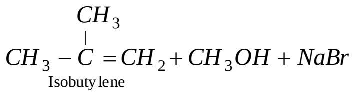
salicylicacid

18. (b) $RX + Mg \xrightarrow[\text{ether}]{\text{Dry}} \underset{\text{Grignard's reagent}}{R - Mg - X} \quad (X = Cl, Br, I)$

19. (b)



$CH_3 - \overset{CH_3}{\underset{CH_3}{C}} - Br + CH_3ONa \xrightarrow{\text{Elimination}}$



$\underset{\text{Isobutylene}}{CH_3 - \overset{CH_3}{C} = CH_2} + CH_3OH + NaBr$

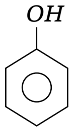
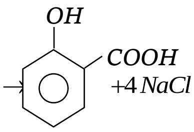
$CH_3ONa \rightarrow CH_3O^- + Na^+$

methoxide ion (CH_3O^-) is a strong base, therefore it abstract proton from 3^o alkyl halide and favours elimination reaction.

20. (d) $CHCl_3 + HO - NO_2 \rightarrow \underset{\text{Chloropicrin (war gas)}}{CCl_3NO_2} + H_2O$

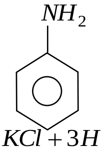
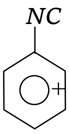
21. (d) $CCl_4 + AgNO_3 \rightarrow$ No reaction

CCl_4 is a covalent compound. Therefore does not provide Cl^- ions.

22. (c)  $+ CCl_4 + 4NaOH \rightarrow$  $+4NaCl + 2H_2O$

Salicylic acid

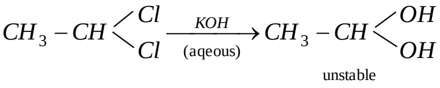
23. (b) $C_6H_5 - CH_2 - Cl + KCN\,(aq) \rightarrow C_6H_5 - CH_2 - C \equiv N + KCl$

24. (a)   $+ CHCl_3 + 3KOH \underset{\text{alcoholic}}{\rightarrow}$

$+ 3KCl + 3H_2O$

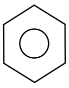
Phenyl isocyanide

25. (b)

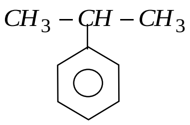


$CH_3 - CH \genfrac{}{}{0pt}{}{Cl}{Cl} \xrightarrow[\text{(aqeous)}]{KOH} \underset{\text{unstable}}{CH_3 - CH \genfrac{}{}{0pt}{}{OH}{OH}}$

$\xrightarrow[-H_2O]{} CH_3 - CHO + H_2O$

27. (d)  $+ \underset{n\text{-propyl bromide}}{CH_3 - CH_2 - CH_2 - Br} \xrightarrow{AlCl_3}$

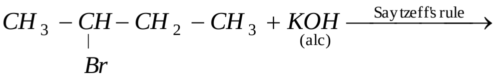
Benzene



+ HBr

Isopropyl

28. (b)

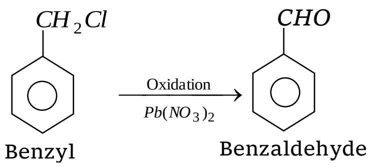


$CH_3 - \underset{Br}{CH} - CH_2 - CH_3 + KOH \xrightarrow[\text{(alc)}]{\text{Saytzeff's rule}}$

$CH_3 - CH = CH - CH_3 + KBr + H_2O$

29. (a) $\begin{array}{l}CH_2-F\\ |\\ CH_2-F\end{array} \xrightarrow{\text{Hydrolysis}} \begin{array}{l}CH_2-OH\\ |\\ CH_2-OH\end{array}$

30. (b)



32. (c) CCl_4 is a covalent compound, Hence it does not give Cl^- ion in solution.

$CCl_4 + AgNO_3 \rightarrow$ No reaction

33. (b) $CHCl_3 + 3NaOH \xrightarrow[-3HCl]{} CH\begin{matrix}OH\\OH\\OH\end{matrix} \xrightarrow[-H_2O]{}$

$$HCOOH \xrightarrow[-H_2O]{NaOH} HCOONa$$

34. (a) $4C_2H_5Br + 4Pb/Na \rightarrow \underset{\substack{\text{Tetra Ethyl lead}\\ \text{(TEL)}}}{(C_2H_5)_4Pb} + 4NaBr$

35. (a) $CHI_3 + 6Ag + I_3CH \rightarrow \underset{\text{Acetylene}}{CH \equiv CH} + 6AgI$

36. (a) $C_2H_5Br + Ag-O-N=O \rightarrow \underset{\text{Nitro ethane}}{C_2H_5-N\begin{matrix}\nearrow O\\ \searrow O\end{matrix}} + AgBr$

$Ag-O-N=O$ is a covalent compound. Therefore, attack of nucleophile occurs through Nitrogen atom. Hence, nitroethane is formed.

40. (a) $C_2H_5Br \xrightarrow{KCN(X)} C_2H_5CN \xrightarrow{LiAlH_4(Y)}$

$$C_2H_5CH_2NH_2(C_3H_7NH_2)$$

$X = KCN, Y = LiAlH_4$

41. (a) $CH_3CH_2CH_2CH_2-Cl + KOH(\text{alc.}) \rightarrow$

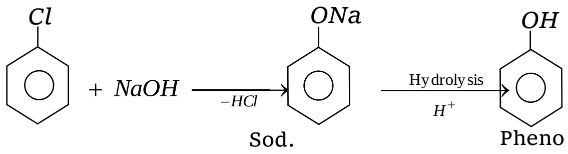
$$\underset{\text{1-butene}}{CH_3CH_2-CH=CH_2} + KCl + H_2O$$

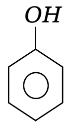
42. (c) $CH_2Br-C\equiv C-CH_2Br \xrightarrow[\Delta]{Zn} CH_2=C=C=CH_2$

43. (b) $\underset{\text{ethylamine}}{C_2H_5NH_2} + \underset{\text{Reaction}}{CHCl_3} + 3KOH \rightarrow \underset{\substack{\text{Ethylisocyanide}\\ \text{(Unpleasant smell)}}}{C_2H_5N \equiv C}$

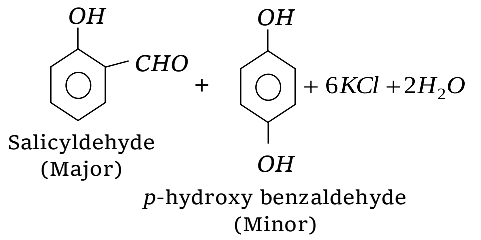
$$+3KCl + 3H_2O$$

44. (c)





46. (c) $+ 2CHCl_3 + 6KOH \rightarrow$



47. (b) $C_2H_5Cl + AgCN \rightarrow \underset{\substack{\text{Ethyl isocyanide}\\ (X)}}{C_2H_5-N \equiv C} + AgCl$

The functional isomer of ethyl isocyanide is ethyl cyanide $C_2H_5-C\equiv N$.

48. (a,b) $C_2H_5Br + alc.KOH \rightarrow C_2H_4 + H_2O + KBr$

$C_2H_5\boxed{Br + 2Na + Br}-C_2H_5 \rightarrow \underset{\text{Butane}}{C_2H_5-C_2H_5} + 2NaBr$

49. (b) $CHCl_3 + \frac{1}{2}O_2 \xrightarrow{\text{Sunlight}} \underset{\text{Phosgene or carbonylchloride}}{COCl_2} + HCl$

50. (b) $C_6H_5-CH_2-Cl \xrightarrow[\text{(aq)}]{NaOH} C_6H_5-CH_2-OH$

$$\xrightarrow{\text{dil } HNO_3} C_6H_5-CHO$$

White *ppt* of *AgCl* are obtained.

51. (a) $\underset{A}{C_2Cl_3OH} + \text{Fehling sol.} \rightarrow \underset{\text{Red ppt}}{Cu_2O}$

It means –*CHO* group is present.

$\underset{A}{C_2Cl_3OH} \xrightarrow{\text{Oxidation}} \underset{\text{Monocarboxylic acid}}{CCl_3-COOH}$

It means only one –*CHO* group is present.

$C_2H_5OH + Cl_2 \rightarrow CH_3CHO + 2HCl$

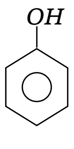
$CH_3CHO + 3Cl_2 \rightarrow \underset{\text{Chloral}}{CCl_3CHO} + 3HCl$

53. (b) Ethanol cannot undergo dehydrohalogenation.

54. (b) $\underset{\substack{\text{(Aniline)}\\ X}}{C_6H_5NH_2} + CHCl_3 + 3NaOH \rightarrow$

$$3NaCl + 3H_2O + \underset{\text{Phenyl isocyanide}}{C_6H_5-N\equiv C}$$

55. (a)



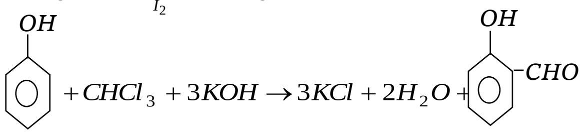
$+ C_2H_5I \xrightarrow[C_2H_5OH]{\text{Anhy.}} C_6H_5OC_2H_5$

56. (d)

$C_2H_5Cl + KCN \rightarrow \underset{\substack{\text{Ethyl cyanide}\\ (X)}}{C_2H_5CN} \xrightarrow{\text{Hydrolysis}} \underset{\substack{\text{Propanoic acid}\\ (Y)}}{C_2H_5COOH}$

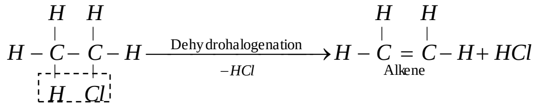
57. (a) $C_2H_5OH \xrightarrow[I_2]{NaOH} CHI_3$

58. (b)



Salicyaldehyde

59. (b)



$$H-\underset{H}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-H \xrightarrow[-HCl]{\text{Dehydrohalogenation}} \underset{\text{Alkene}}{H-\overset{H}{C}=\overset{H}{C}-H} + HCl$$

60. (b) $\underset{\text{Chloroform}}{CHCl_3} + \text{conc. } HNO_3 \rightarrow \underset{\text{Chloropicrin}}{CCl_3-NO_2} + H_2O$

61. (c,d) Before using the sample of chloroform as an anaesthetic, it is tested by treating with *aq*. solution of $AgNO_3$. A pure sample does not give *ppt* with *aq*. $AgNO_3$.

62. (c) Alkyl halide gives alkene on elimination, reaction takes place in presence of alc. *KOH*.

$CH_3CH_2Br + Alc.KOH \rightarrow CH_2 = CH_2 + KBr + H_2O$

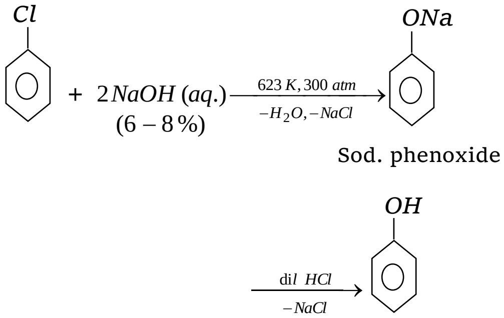
There are two types of elimination reactions.

(a) E_1 → Unimolecular elimination

(b) E_2 → Bimolecular elimination

63. (c) (i) Ethyl alcohol (ii) Phenol

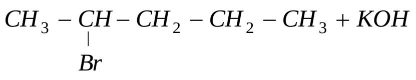
$C_2H_5Br + \underset{\text{(aq)}}{NaOH} \rightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + NaBr$



Sod. phenoxide

Phenol

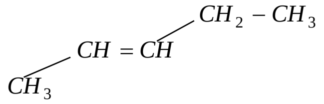
64. (c)



$$CH_3-\underset{Br}{CH}-CH_2-CH_2-CH_3+KOH$$

$$\xrightarrow[\text{Elimination reaction}]{C_2H_5OH} \underset{\text{2-Pentene}}{CH_3-CH=CH-CH_2-CH_3}$$

When alkyl halide reacts with alc. *KOH* then it favours elimination reaction (Dehydrohalogenation). Since, *trans* pentene-2 is more symmetrical than *cis* isomers. Hence, it is main product.



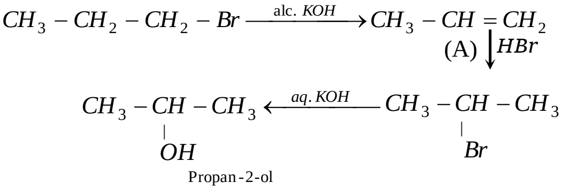
Trans-pentene -2
(Main product)

66. (c) $CHCl_3 + O_2 \xrightarrow{hv} COCl_2 + Cl_2 + H_2O$

70. (b) Alkyl halide reacts with *Mg* in presence of dry ether to give alkyl magnesium halide which is also called as Grignard reagent. This reaction is also called as Grignard's reaction.

$R-X+Mg \xrightarrow[\text{ether}]{\text{dry}} \underset{\text{Grignard's reagent}}{R-Mg-X}$

71. (a)



$$CH_3-CH_2-CH_2-Br \xrightarrow{\text{alc. } KOH} \underset{(A)}{CH_3-CH=CH_2} \;\downarrow HBr$$

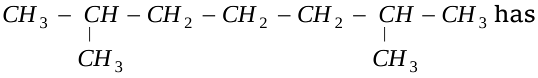
$$\underset{\text{Propan-2-ol}}{CH_3-\underset{OH}{CH}-CH_3} \xleftarrow{aq.KOH} CH_3-\underset{Br}{CH}-CH_3$$

76. (b,d) $C_2H_5Br + \text{alc. } AgNO_2 \rightarrow \underset{\text{nitro ethane}}{C_2H_5-NO_2} + AgBr$

$C_2H_5Br + CH_3COOAg \rightarrow \underset{\text{Ester}}{CH_3-COO-C_2H_5} + AgBr$

79. (a) If $CHCl_3$ sample contains phosgene $(COCl_2)$ then it will give a white *ppt*. When treated with cold $AgNO_3$.

80. (d) Because



$CH_3-\underset{CH_3}{CH}-CH_2-CH_2-CH_2-\underset{CH_3}{CH}-CH_3$ has four methyl groups on the corner so it can produce for derivatives.

84. (a) $CHCl_3 + AgNO_3 \rightarrow$ No react

$CHCl_3$ is a covalent compound. It does not ionize in water.

86. (c,d) Vinyl chloride is less reactive than allyl chloride due to resonance effect.

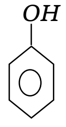
Order of nucleophilicity amongst the halide ion are as $I^- > Br^- > Cl^-$.

87. (b) $CHCl_3 + O_2 \rightarrow \underset{\text{Phosgene}}{COCl_2} + HCl$

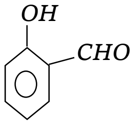
89. (a) $CH_2 = CH-Cl + HCl \rightarrow \underset{\text{1,1-dichloro ethane}}{CH_3-CHCl_2}$

91. (d) $CH_3COCl + H_2 \xrightarrow[\text{Reduction}]{Pd} CH_3CHO + HCl$

92. (b) $CH_3Br + Zn + BrCH_3 \xrightarrow{\Delta} C_2H_6 + ZnBr_2$



Phenol



Salicyldehyde

93. (b) $+ CHCl_3 + 3NaOH \rightarrow$
$+ 3NaCl + 2H_2O$

94. (c) $CHI_3 + 4KOH(\text{aq.}) \rightarrow \underset{\text{Potassium formate}}{HCOOK} + 3KCl + 2H_2O$

95. (d) $CHCl_3 + 6Ag + Cl_3CH \rightarrow CH \equiv CH + 6AgCl$

96. (d) CO is poisonous gas.

98. (b) $C_6H_6Cl_6 + 3KOH \rightarrow C_6H_3Cl_3 + 3KCl + 3H_2O$

Thus Benzene hexahalides decomposes when heated with alc. KOH and yield trichloro benzene.

99. (c) $C_2H_5 - I + AgNO_3 \rightarrow C_2H_5ONO_2 + AgI$

100. (a) We know that $CHCl_3 + HF \rightarrow CHF_3 + 3HCl$. Thus in this reaction the compound obtained in fluoroform (CHF_3). As we know molecular weight of $CHF_3 = 70$.

102. (b) $RX + Mg \xrightarrow[I_2 \text{ powder}]{\text{Dry ether}} R - Mg - X$

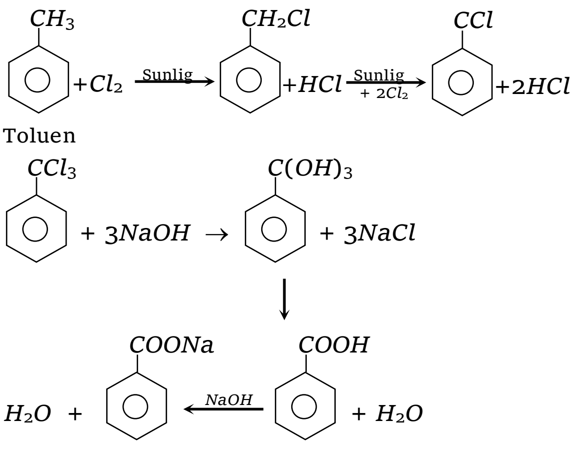
103. (d) Density of alkyl halide increases as the size of halogen atom increases.

$RF < RCl < RBr < RI$

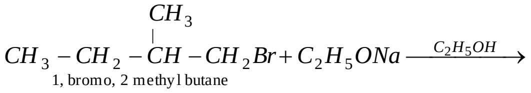
104. (a) Due to resonance partial double bond character is created on vinyl chloride. So, chlorine atom is not replaced easily.

105. (b) $R - X + \underset{\substack{\text{Nucleophile} \\ \text{or base}}}{OH^-} \rightarrow R - OH + X^-$

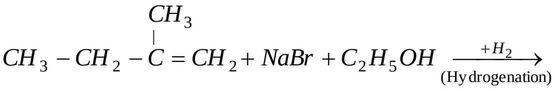
108. (b)



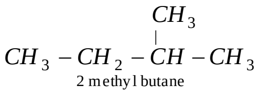
109. (c)



$\underset{\text{1, bromo, 2 methyl butane}}{CH_3 - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{C}H - CH_2Br} + C_2H_5ONa \xrightarrow{C_2H_5OH}$

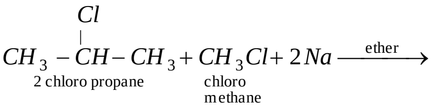


$CH_3 - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2 + NaBr + C_2H_5OH \xrightarrow[\text{(Hydrogenation)}]{+H_2}$

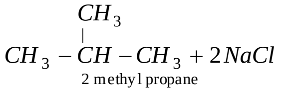


$\underset{\text{2 methyl butane}}{CH_3 - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{C}H - CH_3}$

110. (a) It is Wurtz reaction in which hydrocarbon formed when alkyl halide react with Na metal in dry ether.



$\underset{\text{2 chloro propane}}{CH_3 - \overset{\overset{\displaystyle Cl}{|}}{C}H - CH_3} + \underset{\substack{\text{chloro} \\ \text{methane}}}{CH_3Cl} + 2Na \xrightarrow{\text{ether}}$



$\underset{\text{2 methyl propane}}{CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C}H - CH_3} + 2NaCl$

111. (a) $C_3H_7Br + KCN \rightarrow C_3H_7CN + KBr$

In IUPAC system the carbon of functional group also take in numbering. So C_3H_7CN is butane nitrile.

112. (c) It is Wurtz fittig reaction

$C_6H_5Br + CH_3Br \xrightarrow[\text{Ether}]{Na} C_6H_5CH_3 + 2NaBr$

113. (a) Because it float over chloroform and prevent its oxidation.

114. (c) Due to the presence of electron rich methoxy group $(+I)$ at *p*-position the polarity increase on *C-X* bond by which it becomes more reactive towards nucleophillic attack of ethanol, *p*-nitro and chloro are electron deficient group decrease the polarity of *C-X* bond. Hence by them it become difficult to react with ethanol due to less polarity. Methyl group is less electron rich than methoxy group.

115. (b) When chloroform is treated with concentrated nitric acid, its hydrogen is replaced by nitro group.

$CHCl_3 + HONO_2 \rightarrow \underset{\text{chloropicrin}}{CNO_2Cl_3} + H_2O$

116. (a) Alkyl halides give alkane when react with sodium in ether. This is called Wurtz reaction.

$R - Cl + 2Na + R - Cl \xrightarrow{\text{ether}} \underset{\text{alkane}}{R - R} + 2NaCl$

117. (b) Chloroform is oxidised to a poisonous gas, phosgene $(COCl_2)$ by atmospheric gas.

$CHCl_3 + O \rightarrow COCl_2 + HCl$

118. (b) When chloroform reacts with HNO_3 product formed are chloropicrin or tear gas and water.

$$\underset{\text{chloroform}}{CHCl_3} + \underset{\text{conc.}}{HNO_3} \rightarrow \underset{\text{chloropicrin}}{CCl_3NO_2} + \underset{\text{water}}{H_2O}$$

119. (a) We know that

$$CH_3CH_2Cl + KOH \rightarrow CH_2 = CH_2 + KCl + H_2O$$

Thus in this reaction ethene (C_2H_4) is produced.

120. (d) We know that

$$\underset{\text{chloroform}}{HCCl_3} + 6Ag + \underset{\text{chloroform}}{Cl_3CH} \xrightarrow{\text{heat}} \underset{\text{Acetylene}}{HC \equiv CH} + 6AgCl$$

Thus in this reaction acetylene $(HC \equiv CH)$ is produced.

121. (b) Alkyl halide on reaction with dry silver oxide furnish ether.

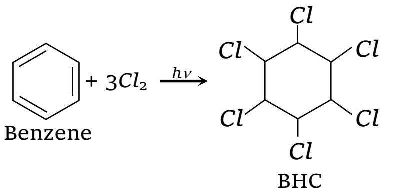
$$2CH_3Cl + Ag_2O \xrightarrow{\Delta} \underset{\text{(methoxy methane)}}{CH_3OCH_3} + 2AgCl$$

122. (a) Acylation or alkylation of aromatic compound in presence of $AlCl_3$ is known as Friedal-craft reaction.

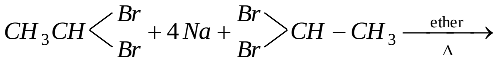
$$\underset{\text{Benzene}}{C_6H_6} + \underset{\substack{\text{chloro}\\\text{methane}}}{CH_3Cl} \xrightarrow[AlCl_3]{\text{dry}} \underset{\text{Toluene}}{C_6H_5CH_3} + HCl$$

123. (b) Any substance which when added to a chemical reaction inhibit or decrease the rate of reaction is called negative catalyst. In $CHCl_3$ when two percent ethanol is added, it stops the formation of carbonyl chloride. So ethanol acts as negative catalyst.

124. (a) When benzene is heated with chlorine in the presence of sunlight, it form benzene hexachloride.



125. (c)



$$CH_3CH\left\langle\begin{matrix}Br\\Br\end{matrix}\right. + 4Na + \left.\begin{matrix}Br\\Br\end{matrix}\right\rangle CH - CH_3 \xrightarrow[\Delta]{\text{ether}}$$

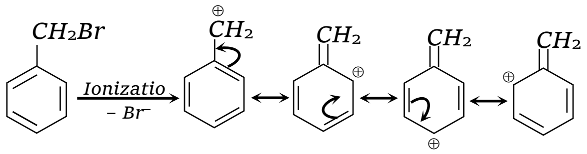
$$\underset{\text{2-butene}}{CH_3 - CH = CH - CH_3} + 4NaBr$$

126. (c) It is a common method to prepare alkanes. Methane cannot be prepared by Wurtz reaction.

$$CH_3Br + 2Na + BrCH_3 \rightarrow \underset{\text{ethane}}{C_2H_6} + 2NaBr$$

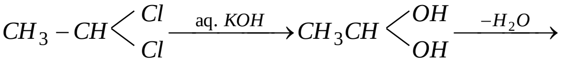
127. (d) At room temperature iodoform is the yellow solid.

128. (a) Benzyl chloride are far more reactive than alkyl halide towards nucleophilic substitution reaction due to the reason that the carbocation formed after the removal of halide ion is stabilized by resonance.



129. (d) On hydrolysis, ethylene dichloride gives ethylene glycol. While ethylidine chloride give acetaldehyde.

$$\underset{\text{ethylene dichloride}}{CH_2Cl.CH_2Cl} \xrightarrow{\text{aq. } KOH} \underset{\text{glycol}}{CH_2OH - CH_2OH}$$



$$\underset{\text{ethylidinechloride}}{CH_3 - CH\left\langle\begin{matrix}Cl\\Cl\end{matrix}\right.} \xrightarrow{\text{aq. } KOH} CH_3CH\left\langle\begin{matrix}OH\\OH\end{matrix}\right. \xrightarrow{-H_2O}$$

$$\underset{\text{acetaldehyde}}{CH_3CHO}$$

131. (b) $\underset{(X)}{CH_3NH_2} + CHCl_3 + 3KOH \rightarrow 3KCl + CH_3NC + 3H_2O$

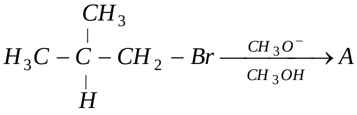
132. (c) $CH_3Br + 2Na + Br - CH_3 \xrightarrow[\text{Ether}]{\text{Dry}} CH_3CH_3 + 2NaBr$

133. (b) $C_2H_5Cl + \underset{(aq)}{KOH} \rightarrow C_2H_5OH + KCl$

138. (b) Alkyl halide is best converted to alkene by mean of elimination reaction in form of dehydrohalogenation.

$$R - CH_2 - CH_2 - X \xrightarrow{\text{dehydrohalogenation}} R - CH = CH_2$$

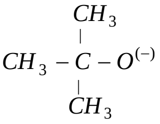
139. (d)



$$H_3C - \underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2 - Br \xrightarrow[CH_3OH]{CH_3O^-} A\ ?$$

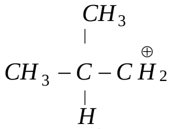
Alkyl halide is 1°.

Keep in mind 1° halide give product by S_N2 / $E-2$ mechanism and 1° halide always gives substitution reaction except when strongly hindered base is used.



ex.: With $CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - O^{(-)}$ it gives mainly elimination.

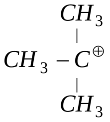
The reaction involves carbocation intermediate.

i.e. 

$$CH_3-\underset{H}{\overset{CH_3}{C}}-\overset{\oplus}{C}H_2$$

(primary carbocation)

but as it is a primary carbocation it will rearrange to give a tertiary carbocation, which completes the reaction



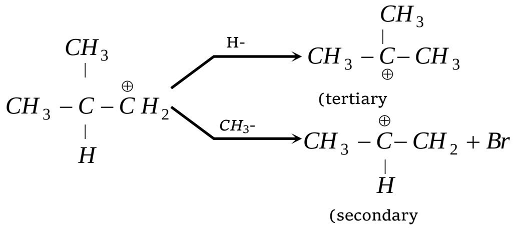
$$CH_3-\underset{CH_3}{\overset{CH_3}{C^{\oplus}}}$$

teritiary carbocation

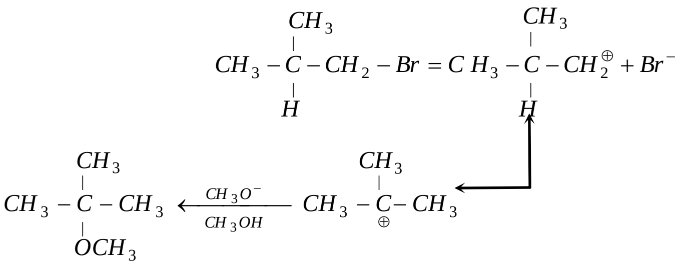
Stability of carbocation : 3° > 2° > 1° > $\overset{\oplus}{C}H_3$

It is because the stability of a charged system is increased by dispersal of the charge. The more stable the carbocation, the faster it is formed.

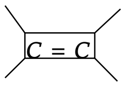
N.B. – Rearrangement can be done in two ways.

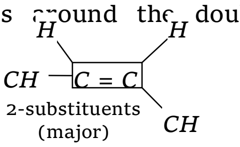


Therefore,

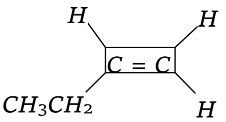


140. (b) According to Saytzeff's rule, the major product will be that one which contains more number of substituents around the double bond.





2-substituents (major)



One substituent

141. **(a)** $(CH_3)_3COH + PhMgBr \longrightarrow PhH + (CH_3)_3COMgBr$

142. (c) $R_2CuLi + R'X \longrightarrow R-R' + R-Cu + LiX$

143. (a) CH_3F, CH_3Cl, CH_3Br and C_2H_5Cl are gases at room temperature. CH_3I is a liquid at room temperature and solidifies at –66.5°C.

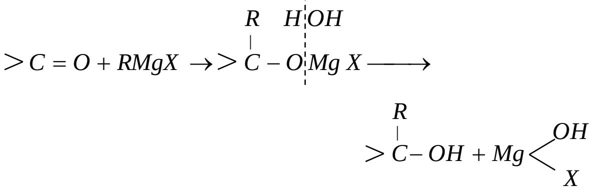
144. (d) The alkyl halides are highly reactive, the order of reactivity is

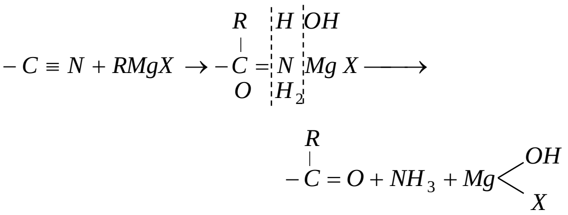
Iodide > bromide > chloride > (nature of the halogen atom).

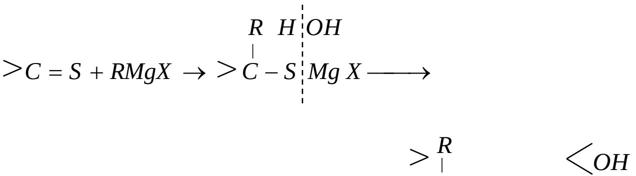
Tertiary > secondary > primary.

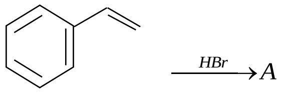
Thus 2-bromopropane is the given option.

145. (d) Grignard reagent gives addition reactions with compounds containing $C=O, >C\equiv N$ and $C=S$ groups.



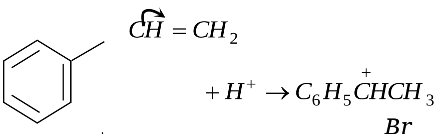


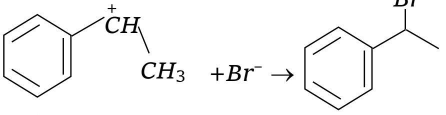


146. (c) 

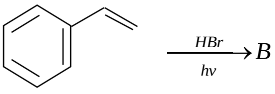
Formation of A is a electrophilic addition reaction

(i) $HBr \rightarrow H^+ + Br^-$

(ii) 

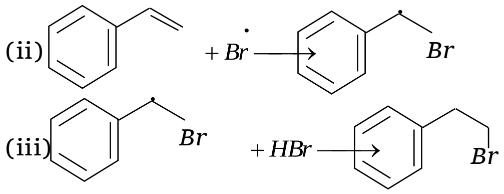


(A)



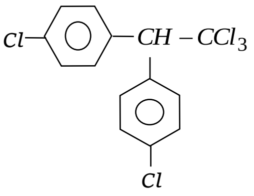
Formation of B is a free radical addition reaction

(i) $HBr \xrightarrow{h\nu} \dot{H} + \dot{Br}$



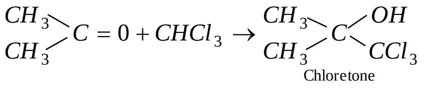
Uses of Halogen Containing Compounds

2. (a)



DDT

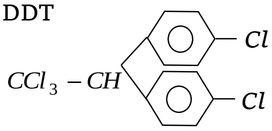
3. (a)



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=0+CHCl_3 \rightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C<\!\!\begin{matrix}OH\\CCl_3\end{matrix}$$

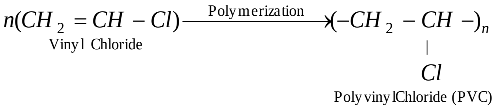
Chloretone

8. (a) DDT



5 chlorine atoms.

11. (a)



$$\underset{\text{Vinyl Chloride}}{n(CH_2=CH-Cl)} \xrightarrow{\text{Polymerization}} \underset{\text{Polyvinyl Chloride (PVC)}}{(-CH_2-\underset{|}{\underset{Cl}{CH}}-)_n}$$

12. (c) Freon (CCl_2F_2) is an odourless, non-corrosive, non toxic gas which is stable even at high temperatures and pressures. It has low b.Pt, low specific heat and can be easily liquified by applying pressure at room temperature. It is therefore, widely used in refrigerant (cooling agent) in refrigerators and air conditioners.

15. (b) $2CHCl_3 \xrightarrow[SbF_3]{HF} 2CHF_2Cl \xrightarrow[-2HCl]{800^0C}$

$$CF_2=CF_2 \xrightarrow{\text{Polymari}} (-CF_2-CF_2-)_r$$

18. (d) Its vapours are non inflammable (*i.e.* do not catch fire). Hence used as fire extinguishers under the name pyren.

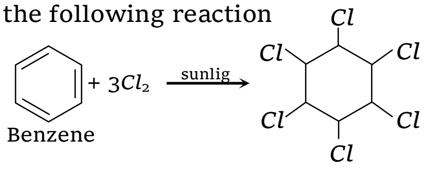
19. (b) Iodoform is used as an antiseptic for dressing wounds. When it comes in contact with skin (organic matter), Iodine is set free which responsible for antiseptic action.

20. (b) Inhalation of $CHCl_3$ vapours produces loss of consciousness and is therefore, used as a general anaesthetic agent in surgery.

22. (b) CCl_4 is stable to red heat. Its vapours are highly non-inflammable *i.e.* do not catch fire. It is because of this property CCl_4 is used as a fire extinguisher. But now a days its use as a fire extinguisher is restricted because with water vaporous. It forms highly poisonous phosgene gas

$$CCl_4 + H_2O \rightarrow \underset{\text{Phosgene}}{COCl_2} + 2HCl$$

23. (a) Benzene hexachloride is an insecticide generally known as gammexane. It is obtained by the following reaction



Benzene

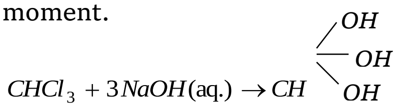
BHC

25. (c) Chlorofluorocarbon is used in air-conditioning and in domestic refrigerators for cooling purposes. Its main drawback is this, it is responsible for ozone depletion.

Critical Thinking Questions

1. (a) CH_3Cl have one Cl atom which is more electronegative so it will have highest dipole moment.

2. (b)



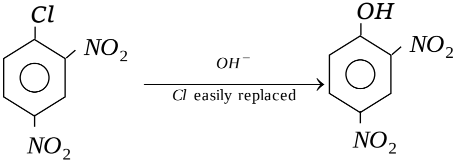
$$CHCl_3 + 3NaOH(\text{aq.}) \rightarrow CH(OH)_3$$

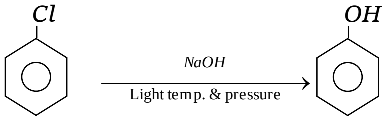
Unstable

3. (c) $CH_3-CH_2-Cl+\underset{(aq)}{KOH} \rightarrow \underset{\text{Ethyl alcohol}}{\overset{sp^3}{CH_3}-\overset{sp^3}{CH_2}-OH}+KCl$

4. (a) As a result of resonance, the carbon-chloride bond acquires some double bond character. Hence, vinyl chloride does not undergo nucleophillic substitution reactions.

5. (d)





6. (b) % of chlorine $= \dfrac{\text{Mass of chlorine}}{\text{Mass of organic compound}} \times 100$

Chloral $(CCl_3CHO) = \dfrac{106.5}{147.5} \times 100 = 72.20$

Pyrene $(CCl_4) = \dfrac{142}{154} \times 100 = 92.20$ Highest

Gammexene $(C_6H_6Cl_6) = \frac{213}{291} \times 100 = 73.19$

7. (a) SN^2 Substitution nucleophilic bimolecular order of different alkyl halides. $1^o > 2^o > 3^o$

SN^1 Substitution nucleophilic unimolecular order of different alkyl halides , $3^o > 2^o > 1^o$.

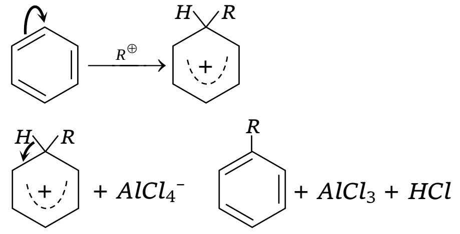
8. (b) aaaeee form is the most powerful insecticide form of $C_6H_6Cl_6$.

9. (d) $R - CH_2 - Cl \xrightarrow{\text{Heterolytic bond fission}} \underset{\text{cation}}{RCH_2^{\oplus}} + \underset{\text{anion}}{Cl^{-}}$

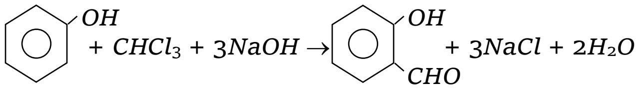
Cl is more electronegative than *C* by which it form anion and hydrocarbon form cation.

10. (b,d) New carbon-carbon bond formation take place in Friedel Craft's alkylation and Reimer-Tiemann reaction. In Friedel Craft's alkylation following mechanism involve

$$R - Cl + AlCl_3 \rightleftharpoons \underset{\text{Alkylcarbonium ion}}{R^{\oplus}} + AlCl_4^{-} + HCl$$



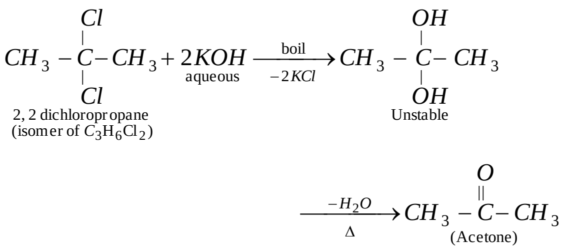
Here new *C–C* bond formed between carbon of benzene ring and alkyl group.
Similarly in Reimer-Tiemann reaction.



Salicylaldehy

Here new *C–C* bond formed between carbon of benzene ring and *–CHO* group.

11. (a)



$$\underset{\substack{\text{2, 2 dichloropropane}\\ \text{(isomer of } C_3H_6Cl_2)}}{CH_3 - \underset{Cl}{\overset{Cl}{C}} - CH_3} + \underset{\text{aqueous}}{2KOH} \xrightarrow[-2KCl]{\text{boil}} \underset{\text{Unstable}}{CH_3 - \underset{OH}{\overset{OH}{C}} - CH_3}$$

$$\xrightarrow[\Delta]{-H_2O} \underset{\text{(Acetone)}}{CH_3 - \overset{\overset{O}{\|}}{C} - CH_3}$$

12. (a) Only 1° alkyl halides, *i.e.* CH_3Br undergoes S_N2 reaction.

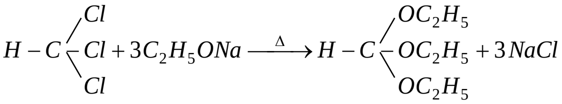
13. (b) Wurtz reaction gives ethane

$$2CH_3I + 2Na \xrightarrow[\text{ether}]{\text{dry}} C_2H_6 + 2NaI$$

Similarly C_2H_5Cl reduced by $LiAlH_4$ to give ethane

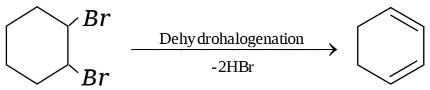
$$C_2H_5Cl + 2H \xrightarrow{LiAlH_4} C_2H_6 + HCl$$

14. (a)



Ethyl orthoformate

15. (d)



1, 2 dibromo

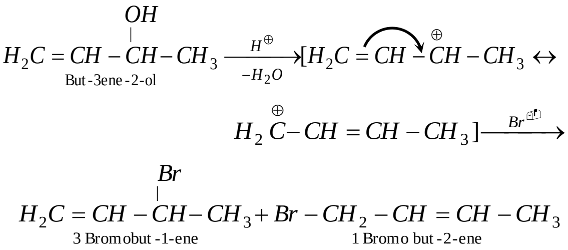
Cyclohex-

16. (b, c) $CH_3 - O - CH_3 + PCl_5 \rightarrow 2CH_3Cl + POCl_3$

$CH_3CH_2OH + PCl_5 \rightarrow CH_3CH_2Cl + HCl + POCl_3$

So, both reaction carried out by PCl_5

17. (c)



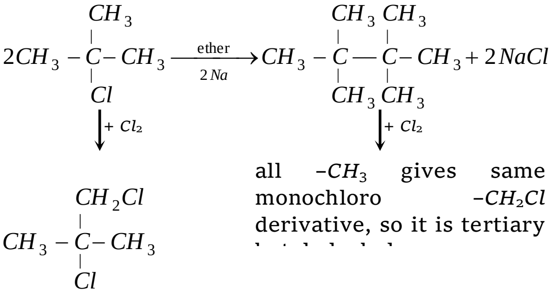
$$\underset{\text{But-3ene-2-ol}}{H_2C = CH - \overset{\overset{OH}{|}}{C}H - CH_3} \xrightarrow[-H_2O]{H^{\oplus}} [H_2C = CH - \overset{\oplus}{C}H - CH_3 \leftrightarrow$$

$$H_2\overset{\oplus}{C} - CH = CH - CH_3] \xrightarrow{Br^{-}}$$

$$\underset{\text{3 Bromobut-1-ene}}{H_2C = CH - \overset{\overset{Br}{|}}{C}H - CH_3} + \underset{\text{1 Bromo but-2-ene}}{Br - CH_2 - CH = CH - CH_3}$$

18. (a) The *C–F* bond energy is maximum in CH_3F . Thus fluoride is the less reactive to form the grignard reagent with *Mg*.

19. (a)



$$2CH_3 - \underset{Cl}{\overset{CH_3}{C}} - CH_3 \xrightarrow[2Na]{\text{ether}} CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - \underset{CH_3}{\overset{CH_3}{C}} - CH_3 + 2NaCl$$

$$\downarrow + Cl_2 \qquad\qquad \downarrow + Cl_2$$

$$CH_3 - \underset{Cl}{\overset{CH_2Cl}{C}} - CH_3$$

all $-CH_3$ gives same monochloro $-CH_2Cl$ derivative, so it is tertiary

20. (d) The polarity between *C-X* bond increase by increasing the *+I* effect which increase by increasing the alkyl group by which *X* of *C-X* easily eliminate. In $CH_3CH_2CH_2Br$ the polarity is maximum due to 3 alkyl group while in rest polarity decrease due to the presence of double bond, presence of *–CO* group (*–I*) and less no. of alkyl group.

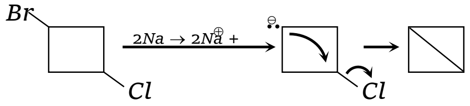
$$CH_3CH_2CH_2Br + KOH \xrightarrow{\text{alc.}}$$

$$CH_3CH = CH_2 + KBr + H_2O$$

21. (d) *p*-dichlorobenzene molecule has symmetrical structure. It can fit well in its crystal lattice. The intermolecular forces of attraction are strong. Hence, it possesses highest melting point.

22. (d) Due to +*I* effect of 3 alkyl group in option (d), the chlorine atom occupy the maximum charge in it so it is more electronegative.

23. (d) It is the example of Wurtz reaction.



Assertion and Reason

1. (d) $CHCl_3$ is stored in dark bottles of prevent oxidation of $CHCl_3$ in presence of sunlight.

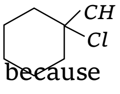
3. (c) Due to symmetrical nature and more closer packing *p*-dichlorobenzene has highest melting point.

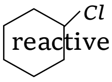
4. (e) CCl_4 is used as a fire extinguisher. The dense, non combustible vapours cover the burning substance and prevents the availability of oxygen round burning material.

5. (e) Dry gaseous hydrohalogen acids are better electrophile. Also in aqueous solution, H_2O, acting as nucleophile may produce alcohol.

6. (c) CH_3CH_2I reacts more rapidly with strong base in comparison to CD_3CH_2I. The elimination of *HI* (or *DI*) in presence of strong base shows E_2 elimination. The rate determining step involves the breaking up of *C-H* (or *C-D*) bond. The *C-D* bond being stronger than *C-H* and thus elimination is faster in case of CH_3CH_2I.

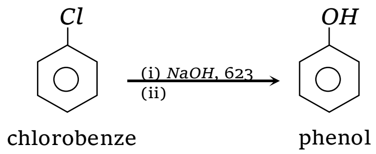
7. (c) For a given alcohol the order of reactivity of halogen acids follows the sequence *HI* > *HBr* > *HCl*. It is because of the fact that I^- is a stronger nucleophile than Br^- which in turn is a stronger nucleophile than Cl^-.

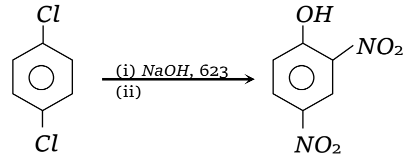
8. (e) 

is more reactive than 

because the former is a tertiary alkyl halide and the latter is a secondary alkyl halide. Tertiary alkyl halides react predominantly by S_N1 mechanism.

9. (d) Halobenzenes become reactive to nucleophilic substitution reactions when electron withdrawing groups (nitro, cyano) are present at ortho/para position. This is evident from the milder conditions required for hydrolysis in 2, 4-dinitrochlorobenzene than chlorobenzene.





2, 4-   2, 4-

10. (e) Halogens are somewhat deactivating but *o*, *p*-directing. As a result, aryl halides undergo the usual electrophilic substitution reactions less readily than benzene.

11. (b) A reaction is said to be stereo selective if a particular stereoisomer can give two or more stereoisomeric products but gives one of them in greater amount than the other or even to the exclusion of the other. So, addition of Br_2 to cis-but-2-ene is stereoselective since it gives only (±) 2, 3-dibromobutane.

13. (a) In SN^1 mechanism, recemization takes place, which is due to inverting nucleophilic displacement of halogen atom from the alkyl halide by the halide in solution.

Halogen Containing compounds

SET Self Evaluation Test -25

1. Preparation of alkyl halides in laboratory is least preferred by

(a) Halide exchange

(b) Direct halogenation of alkanes

(c) Treatment of alcohols

(d) Addition of hydrogen halides to alkenes

2. An alkyl halide may be converted into an alcohol by

[EAMCET 1980; CBSE PMT 1997; BHU 1999; AIIMS 2001]

(a) Addition (b) Substitution

(c) Dehydrohalogenation (d) Elimination

3. The $C-Cl$ bond in chlorobenzene as compared with $C-Cl$ bond in methyl chloride is **[MP PMT 1995]**

(a) Longer and weaker

(b) Shorter and weaker

(c) Shorter and stronger

(d) Longer and stronger

4. A salt solution is treated with chloroform drops. Then it is shaked with chlorine water. Chloroform layer becomes violet. Solution contains **[CPMT 1982]**

(a) NO_2^- ion (b) NO_3^- ion

(c) Br^- ion (d) I^- ion

5. The following reaction belongs to

$(CH_3)_3C-Br \xrightarrow{H_2O} (CH_3)_3-C-OH$ **[AIEEE 2002]**

(a) Elimination reaction (b) Substitution reaction

(c) Free radical reaction (d) Displacement reaction

6. The order of reactivities of methyl halides in the formation of Grignard reagent is **[KCET 2003]**

(a) $CH_3I > CH_3Br > CH_3Cl$

(b) $CH_3Cl > CH_3Br > CH_3I$

(c) $CH_3Br > CH_3Cl > CH_3I$

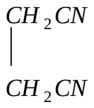
(d) $CH_3Br > CH_3I > CH_3Cl$

7. Identify Z in the following series

$C_2H_5I \xrightarrow{Alco.\ KOH} X \xrightarrow{Br_2} Y \xrightarrow{KCN} Z$

[AIIMS 1983; AFMC 1998; MP PET 1997]

(a) CH_3CH_2CN (b)



$\begin{matrix} CH_2CN \\ | \\ CH_2CN \end{matrix}$

(c) $BrCH_2-CH_2CN$ (d) $BrCH=CHCN$

8. The total number of stereoisomeric forms of $C_6H_6Cl_6$ known is

(a) 6 (b) 7

(c) 8 (d) None of these

9. The correct order of $C-X$ bond polarity is **[RPMT 2000]**

(a) $CH_3Br > CH_3Cl > CH_3I$

(b) $CH_3I > CH_3Br > CH_3Cl$

(c) $CH_3Cl > CH_3Br > CH_3I$

(d) $CH_3Cl > CH_3I > CH_3Br$

10. The order of reactivities of the following alkyl halides for a SN^2 reaction is **[IIT-JEE (Screening) 2000]**

(a) $RF > RCl > RBr > RI$

(b) $RF > RBr > RCl > RI$

(c) $RCl > RBr > RF > RI$

(d) $RI > RBr > RCl > RF$

11. Which of the following reactions doesn't give benzene

[RPMT 2003]

(a) $C_6H_5N_2Cl \xrightarrow[H_2O]{\text{boiling}}$

(b) $C_6H_5N_2Cl \xrightarrow[\Delta]{C_2H_5OH}$

(c) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$

(d) All of these

12. Benzene hexachloride is prepared from benzene and chlorine in sunlight by

(a) Substitution reaction (b) Elimination reaction

(c) Addition reaction (d) Rearrangement

13. Carbon-halogen bond is strongest among the following

[MP PMT 1995]

(a) CH_3Cl (b) CH_3Br

(c) CH_3F (d) CH_3I

14. Which of these do not undergo Wurtz reaction

(a) C_2H_5F (b) C_2H_5Br

(c) C_2H_5Cl (d) C_2H_5I

15. When ethyl bromide reacts with sodium acetylide the main product is **[Pb. CET 2002]**

(a) 1-butane (b) 1-butene

(c) 1-butyne (d) 2-butene

16. C_2H_5I and Ag_2O reacts to produce **[Pb. PMT 2004]**

(a) C_2H_6 (b) $C_2H_5-C_2H_5$ (c) $C_2H_5-O-C_2H_5$ (d) $C_2H_5-CH_3$

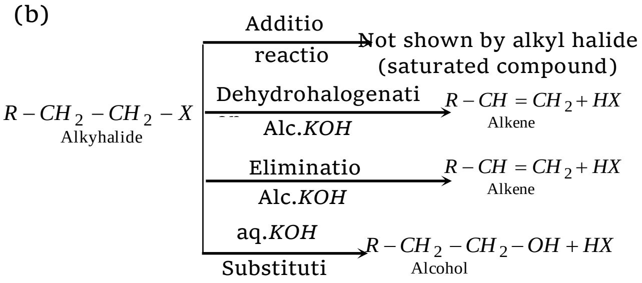
Answers and Solutions

(SET -25)

1. (b) Direct halogenation of alkenes is not preferred because in it a mixture of monohalogen, dihalogen, trihalogen and tetrahalogen substituted product is obtained which is difficult to separate.

e.g. $CH_4 \xrightarrow{Cl_2} CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$

2. (b)



3. (c) In chlorobenzene C – Cl bond acquires partial double bond character because of resonance.

4. (d) $2NaI + Cl_2 \rightarrow 2NaCl + I_2$ (Dissolves in $CHCl_3$ to give violet colour)

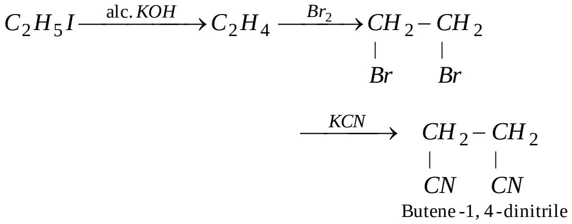
Chlorine displaces iodine from salt. The iodine get dissolve in $CHCl_3$ or CCl_4 to produce violet colour.

5. (b) $(CH_3)_3C-Br \xrightarrow{H_2O} (CH_3)_3-C-OH$

Here Br substitute by $-OH$ group.

6. (a) Reactivity towards grignard reagent are as under $CH_3I > CH_3Br > CH_3Cl$

7. (b)



$$C_2H_5I \xrightarrow{\text{alc.}KOH} C_2H_4 \xrightarrow{Br_2} \underset{Br}{\underset{|}{CH_2}}-\underset{Br}{\underset{|}{CH_2}} \xrightarrow{KCN} \underset{CN}{\underset{|}{CH_2}}-\underset{CN}{\underset{|}{CH_2}}$$

Butene-1, 4-dinitrile

8. (c) $C_6H_6Cl_6$ has 8 stereoisomer.

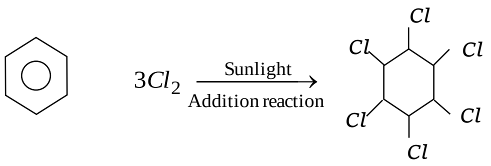
9. (c) The $C-X$ bond polarity order are as under $CH_3Cl > CH_3Br > CH_3I$

10. (d) The order of reactivity of alkyl holides for SN^2 reaction is

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

11. (a) $C_6H_5N_2Cl \xrightarrow[H_2O]{\text{Boiling}} C_6H_5OH + N_2 + HCl$

12. (c)



BHC

13. (c) $CH_3F > CH_3Cl > CH_3Br > CH_3I$

14. (a) $C_2H_5F + 2Na + FC_2H_5 \xrightarrow[\text{ether}]{\text{Dry}}$ No reaction

15. (c) $\underset{\text{Ethyl bromide}}{C_2H_5Br} + \underset{\text{sodium acetylide}}{NaC \equiv CH} \rightarrow \underset{\text{1-butyne}}{C_2H_5C \equiv CH} + \underset{\text{sodium bromide}}{NaBr}$

Thus in this reaction 1-butyne is main product.

16. (c) C_2H_5I and Ag_2O reacts as below

$2C_2H_5I + Ag_2O \rightarrow \underset{\text{ether}}{C_2H_5OC_2H_5} + I_2$

Thus, $C_2H_5-O-C_2H_5$ is produced.

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