9

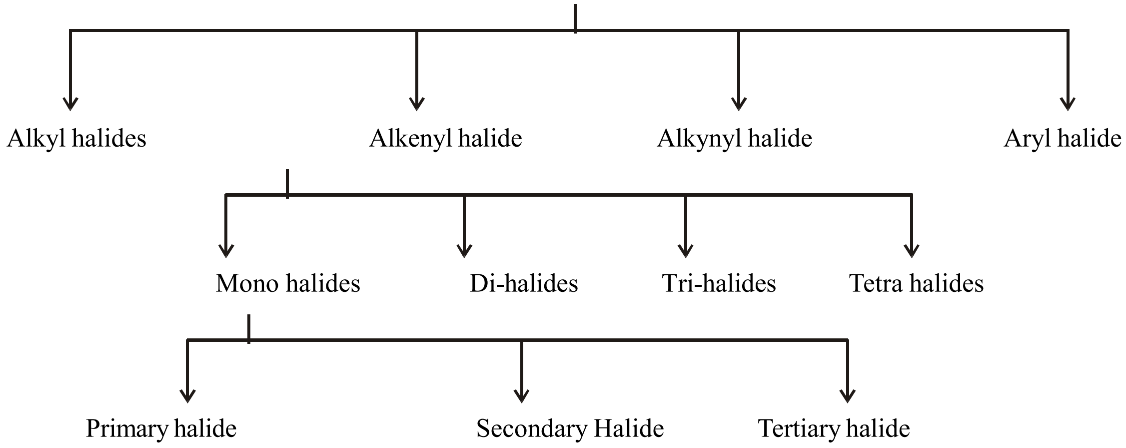
HALOALKANES AND HALOARENES

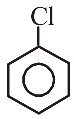
INTRODUCTION

The compounds formed by replacement of one or more Hydrogen atoms from hydrocarbon molecule by corresponding no. of halogen atoms called halogen derivative or halide.

$$\text{Hydrocarbon} \xrightarrow[\text{1 or more }(+)\text{X}]{\text{1 or more }(-)\text{H}} \text{Halogen Derivative}$$

Classification : On the basis of hydrocarbon part Halide classified as Halogen Derivatives



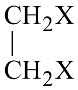
Halides	Example
(a) Alkyl halides (Halogen derivatives of alkanes)	CH_3CH_2Cl (Ethyl chloride)
(b) Alkenyl halide (Halogen derivative of alkenes)	$CH_2=CH-Cl$ (vinyl chloride) $CH_2=CH–CH_2–Cl$ (Allylchloride)
(c) Alkynyl halide (Halogen derivative of alkynes)	$CH\equiv C–CH_2-Cl$ (Propargyl chloride)
(d) Aryl halide (Halogen atom is directly attached with c-atom of aromatic nucleus)	 Chloro benzene

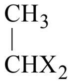
ALKYL HALIDE (HALOALKANE)

On the basis of No. of halogen atoms alkyl halides are -

(i) Mono halides : These involves replacement of one H-atom by halogen atom. Gen. formula $C_nH_{2n+1}X$
Type formula $R-X$
Ex. CH_3Cl methyl chloride (Chloro methane)
CH_3CH_2Br Ethyl bromide (Bromo ethane)

(ii) Dihalides : Replacement of two H-atom by halogen atoms.
Gen. formula $C_nH_{2n}X_2$
Type formula RX_2
Ex. CH_2X_2 Methylene Di halide


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


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

(iii) Trihalides : Replacement of three H-atoms by halogen atoms.
Gen. Formula – $C_2H_{2n-1}X_3$; Type formula – RX_3
Ex. CHX_3 Trihalo methane or haloform

(iv) Tetrahalides : Replacemnt of four H-atom by halogen atom. When all the H-atoms from an alkane are replaced by halogen atoms, then the compounds are called as perhalo compounds.
Gen. Formula – $C_nH_{2n-2}X_4$
Ex. CX_4 Perhalo methane
C_2X_6 (Perhalo ethane)

MONOHALIDES OR MONOHALOALKANE

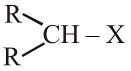
On the basis of position of Halogen atom monohalides classified into

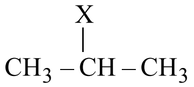
(a) Primary halide or 1° alkyl halide : Halogen atom attached with Primary c-atom. **Ex.** $R-CH_2-X$

CH_3X halomethane or methyl halide

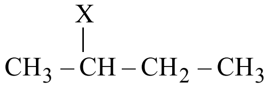
CH_3CH_2X haloethane or ethyl halide

(b) Secondary halide or 2° alkyl halide : Halogen atom attached with secondary c-atom. **Ex.**





$CH_3-\overset{\overset{X}{|}}{C}H-CH_3$ 2-halo propane or isopropyl halide

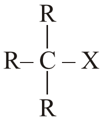


$CH_3-\overset{\overset{X}{|}}{C}H-CH_2-CH_3$

2-halobutane or secondary butyl halide

(c) Tertiary halide or 3° alkyl halide :
Halogen atom attached with t-c atom

Ex.



$R-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{C}}-X$ Tertiary alkyl halide

PREPARATION OF MONOHALIDES

(a) From alkane (Halogenation) :

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

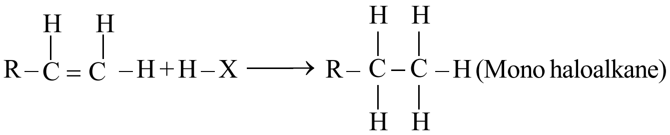
Alkane Monohaloalkane

The reactivity of the alkanes follows the following order :

Tertiary alkane > Secondary alkane > Primary alkane

(b) From alkene (Hydrohalogenation) :

According to markownikoff's rule



$$R-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-H+H-X\longrightarrow R-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H\ \text{(Mono haloalkane)}$$

- * The addition of halogen acid is electrophilic addition.
- * Addition of HBr to unsymmetrical alkene in the presence of organic peroxide violates Markownikov's rule. This is called Kharasch effect or peroxide effect.

$$\underset{\text{Propylene (Propene)}}{CH_3-CH=CH_2}+HBr\xrightarrow[(C_6H_5CO)_2O_2]{\text{Benzoyl peroxide}}\underset{\text{(1–Bromopropane)}}{CH_3CH_2CH_2Br}$$

- * Addition of HCl or HI does not show peroxide effect.
- * From alkyne we can obtain only di haloalkane.

(c) From alcohol :

(i) By action of dry H – X (Grove's Process) :

$$R–OH+H–X\xrightarrow[\Delta\ 300°]{\text{Anhydrous }ZnCl_2}R–X+H_2O$$

Alcohol

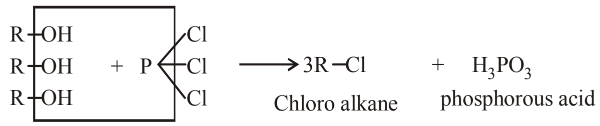
The reactivity order of HX in the above reaction is.

HI > HBr > HCl > HF

The reactivity order of alcohols in the above reaction is

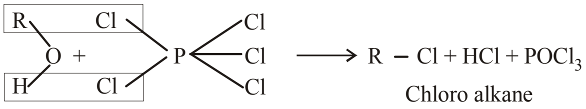
3° > 2° > 1° > MeOH

(ii) Action of PCl₃ :



Alcohol

(iii) Action of PCl₅ :

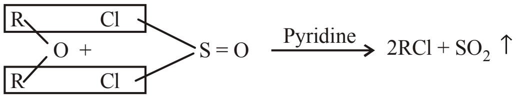


Alcohol

Bromine or Iodine derivatives can not be obtained from the above reaction because due to larger size of bromine or iodine, PBr_5 or PI_5 are unstable.

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

It is the best method for preparation of alkyl halide.



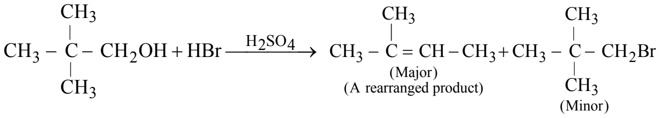
Ether Thionyl Chloride

(v) Alkyl bromides can be prepared by heating alcohol with potassium bromide or sodium bromide and concentrated sulphuric acid.

$$\underset{\substack{\text{Ethyl alcohol}\\\text{(Ethanol)}}}{C_2H_5OH}+KBr+H_2SO_4\rightarrow\underset{\substack{\text{Ethyl bromide}\\\text{(Bromoethane)}}}{C_2H_5Br}+KHSO_4+H_2O$$

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH}+HBr\xrightarrow{H_2SO_4}\underset{\text{Ethyl bromide}}{C_2H_5Br}+H_2O$$

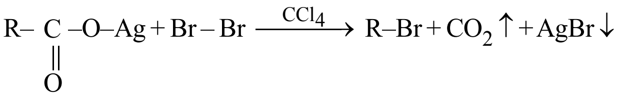
Note : Concentrated sulphuric acid should not be used in the preparation of alkyl bromides from 2°, 3° & neo alcohols as these undergo dehydration to form alkenes. For example,



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2OH+HBr\xrightarrow{H_2SO_4}\underset{\substack{\text{(Major)}\\\text{(A rearranged product)}}}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_3}+\underset{\text{(Minor)}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2Br}$$

(d) From silver salt of carboxylic acid ('Borodiene-Hunsdiecker') :

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



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

(ii) It is also an example of decarboxylation.

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

(e) From alkyl halide

(i) With NaI (Finkelstein Reaction') :

$$R–Cl+NaI\xrightarrow{\text{Acetone}}R-I\ \text{(Iodoalkane)}+NaCl$$

(ii) With AgF, (Swart Reaction) :

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

In these reaction only halogen exchange takes place.

(f) By reaction of alkane with sulphuryl chloride :

$$R{-}H + SO_2Cl_2 \xrightarrow[\text{organic peroxide}]{\text{light \&}} R{-}Cl + HCl + SO_2$$

PHYSICAL PROPERTIES

(i) Alkyl halides are colourless with sweet smell or pleasant oily liquid, where as CH_3F, CH_3Cl, CH_3-CH_2-F, CH_3-CH_2-Cl are gaseous in nature.

(ii) Alkyl halides having 18-carbon or more than it are solid in nature.

(iii) These are completely soluble in organic solvents but insoluble in H_2O

(iv) Reactivity order is $RI > RBr > RCl > RF$

(v) For same halide group reactivity order is
3° (halide) > 2° (halide) > 1° (halide)

(vi) Polarity order is $RF > RCl > RBr > RI$

(vii) M.P & B.P. $\propto$ molecular weight.
For same alkyl group the order of B.P. is : $RI > RBr > RCl > RF$
For isomeric alkyl halide order of boiling point
Primary > Secondary > Tertiary

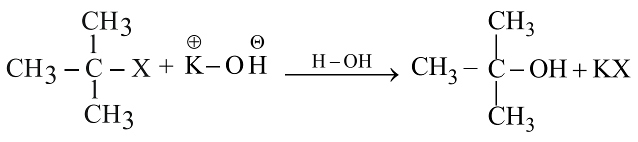
(viii) Fluorides and chlorides are lighter than water whereas bromides and iodides are heavier than H_2O due to more density of bromine than oxygen. CH_2I_2 is heavier liquid after Hg.

CHEMICAL PROPERTIES

Nucleophilic substitution reaction :

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

(1) S_N1 Reactions (Nucleophilic Unimolecular Substitution Reactions) : These reaction completes in two step. In first step a carbocation is formed from alkyl halide molecule. First step is slow step so it is also rate determining step. In second step an attacking nucleophile attacks on this carbocation and form a final product. In this reaction rate of reaction is dependent on the concentration of alkyl halide molecule only, not on the concentration of nucleophile. So the reaction is called as unimolecular substitution reaction. Molecularity of reaction is two but the order of reaction is one. All tertiary halides and sometimes secondary halides show this type of reaction. Polar medium is necessary for the reaction. **Example :**



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-X + \overset{\oplus}{K}-\overset{\ominus}{O}H \xrightarrow{H-OH} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH + KX$$

tertiary Butylhalide tertiary Butylalcohol

Rate of reaction $\propto [(CH_3)_3C-X]$

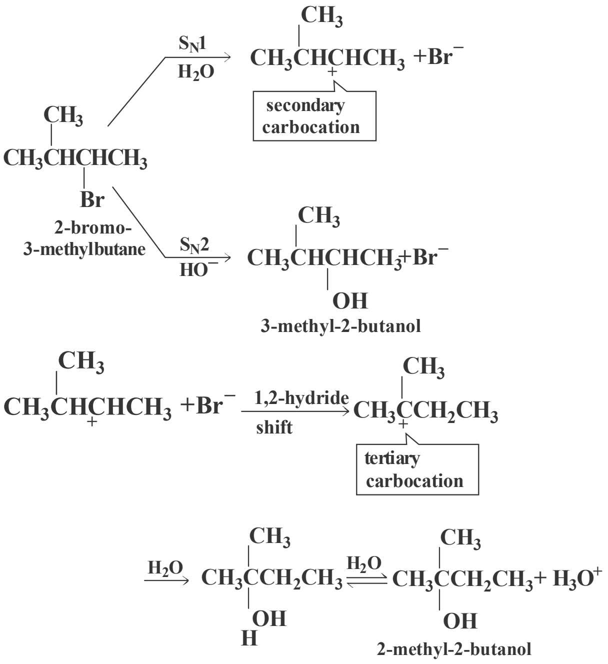
* **Relative reactivities of alkyl halides in an S_N1 reaction**
3° alkyl halide > 2° alkyl halide > 1° alkyl halide

* Relative reactivities of alkyl halides in an S_N1 reaction
$RI > RBr > RCl > RF$

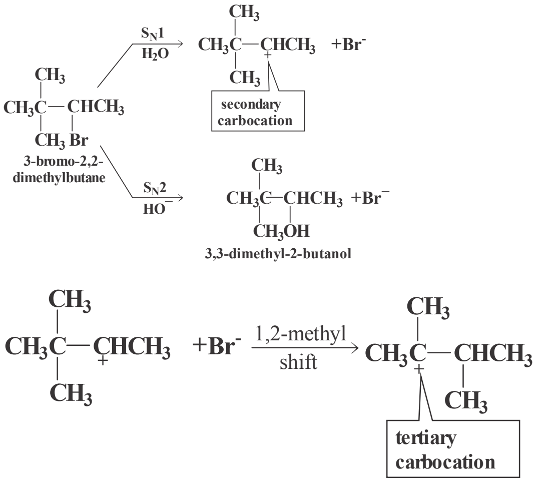
Carbocation rearrangements :

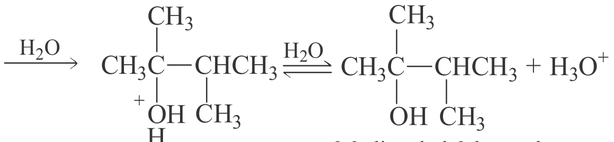
* A carbocation intermediate is formed in an S_N1 reaction.

* Carbocation will rearrange if it becomes more stable in the process. If the carbocation formed in an S_N1 reaction can rearrange, S_N1 and S_N2 reactions of the same alkyl halide can produce different constitutional isomers as products, since a carbocation is not formed in an S_N2 reaction and therefore the carbon skeleton cannot rearrange. For example, the product obtained when HO^- is substituted for Br^- in 2-bromo-3- methylbutane by an S_N1 reaction is different from the product obtained by an S_N2 reaction. When the reaction is carried out under conditions that favour an S_N1 reaction, the initially formed secondary carbocation undergoes a **1,2-hydride shift** to form a more stable tertiary carbocation.



* The product obtained from the reaction of 3-bromo-2,2-dimethylbutane with a nucleophile also depends on the conditions under which the reaction is carried out. The carbocation formed under conditions that favour an S_N1 reaction will undergo a **1,2-methyl shift**. Because a carbocation is not formed under conditions that favour an S_N2 reaction, the carbon skeleton does not rearrange.



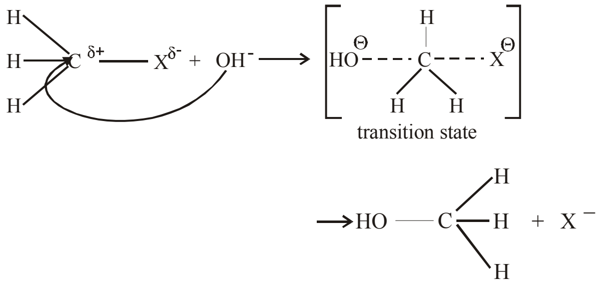


$$\xrightarrow{H_2O} CH_3\overset{CH_3}{\underset{\underset{H}{\overset{+}{O}H}}{C}}-\underset{CH_3}{CH}CH_3 \overset{H_2O}{\rightleftharpoons} CH_3\overset{CH_3}{\underset{OH}{C}}-\underset{CH_3}{CH}CH_3 + H_3O^+$$

2,3-dimethyl-2-butanol

(2) S_N2 Reactions (Nucleophilic Bimolecular Substitution Reactions) : These reaction completes in single step. In these reactions an attacking nucleophile attacks from back side of the central carbon atom of alkyl halide. This back side attack is called as 'Walden Inversion'. When nucleophile attacks on central atom then a transition state is formed in which attacking nucleophile and halogen atom both are linked with half bond with central atom. This stage is unstable stage, after sometime halogen atom attract bonded electrons towards itself and releases in the form of halide ion while attacking nucleophile forms complete bond with central carbon. In this reaction, bond breaking and bond forming process both can take place simultaneously and rate of reaction is dependent on the concentration of alkyl halide and concentration of attacking nucleophile both. So the reaction is called as biomolecular substitution reaction. Molecularity of reaction is two and the order of reaction is also two. In this reaction product is 100% opposite rotatory than reagent. Polar medium is not necessary for this type of reaction. All primary halides and sometimes 2° halide shows this type or reaction.

Example : $CH_3-X+K-OH \longrightarrow CH_3-OH+KX$



transition state

Rate of reaction ∝ $[CH_3X][OH^-]$

* **Relative reactivities of alkyl halides in an S_N2 reaction**

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

* **Relative reactivities of alkyl halides in an S_N2 reaction**

RI > RBr > RCl > RF

(A) Nucleophilic substitution reaction (SN^1) :

(i) Hydrolysis :

(a) With aqueous KOH : Alkyl halide are hydrolysed to corresponding alcohols by boiling with aqueous alkali solution. $R-X+K-OH \rightarrow R-OH$ (Alcohol) $+ K-X$

(b) Using moist Ag_2O :

$2R-X+Ag_2O+H_2O \rightarrow 2R-OH$ (Alcohol) $+ 2AgX$

(ii) Ether Synthesis :

(a) Reaction with NaOR :

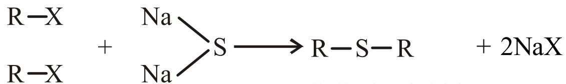
$R-X+NaOR \rightarrow R-O-R$ (Ether) $+ NaX$

Above reaction is called "Williamson's ether synthesis".

(b) Using dry Ag_2O : $2R-X+Ag_2O \rightarrow R-O-R+2AgX$

Ether

(iii) Reaction with Na_2S :



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

dialkyl sulphide

(iv) Reaction with KSH :

$R-X+K-SH \rightarrow R-SH + KX$

Alkane thiol

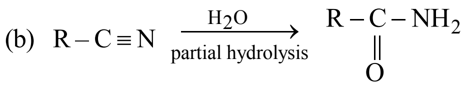
(v) Reaction with KCN : $R-X+KCN \rightarrow R-C\equiv N + KX$

Alkane nitrile

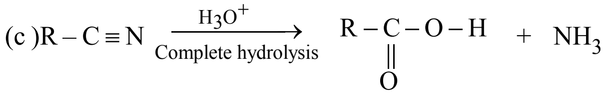
Alkane nitrile is an important compound which gives following products.

(a) $R-C\equiv N \xrightarrow{LiAlH_4/Reduction} R-CH_2-NH_2$

Alkane amine



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



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

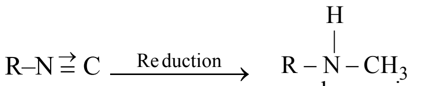
Carboxylic acid

(vi) Reaction with AgCN :

$R-X+AgCN \longrightarrow R-N\overset{\rightarrow}{=}C + AgX$

Alkane isocynide

$R-N\overset{\rightarrow}{=}C \xrightarrow{Hydrolysis} R-NH_2$ (Alkane amine) + HCOOH



$R-N\overset{\rightarrow}{=}C \xrightarrow{Reduction} R-\overset{\overset{H}{|}}{N}-CH_3$

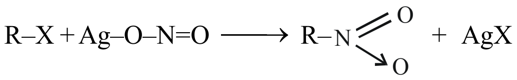
secondary amine

(vii) Reaction with KNO_2 :

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

alkyl nitrite

(viii) Reaction with $AgNO_2$:



$R-X+Ag-O-N=O \longrightarrow R-N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix} + AgX$

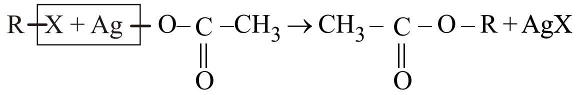
nitro alkane

(ix) Reaction with Na_2SO_3 :

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

alkyl sodium sulphonate

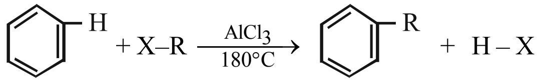
(x) Reaction with silver acetate (Esterification) :



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

silver acetate ester

(xi) Reaction with benzene 'Friedel-craft reaction' :



Alkyl benzene

Alkyl halide shows electrophilic substitution in the above reaction, which is exception in alkyl halide.

(B) Elimination Reaction :

(i) With alcoholic KOH : (Dehydrohalogenation) Alkyl halides undergo β-elimination on treatment with alcohol with KOH takes place and alkenes are formed.

$R-CH_2-CH_2-X + KOH\ (alc.) \rightarrow R-CH=CH_2$

(ii) Action of heat :

$$R—CH_2–CH_2–X \xrightarrow{300°C} \underset{\text{Alkene}}{R-CH=CH_2} + HX$$

The decomposition follows the following order :

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

and Tertiary > Secondary > Primary
(when same halogen is present)

(C) Reduction : Haloalkanes on reduction produces alkanes frequently. $R-X + 2H \rightarrow R-H\ (\text{Alkane}) + HX$

Reduction is done as follows.

(i) By nascent hydrogen liberated from Na/C_2H_5OH or Sn/HCl or Zn/HCl or Zn-Cu couple/C_2H_5OH etc.

$R-X + 2H \rightarrow R-H\ (\text{Alkane}) + HX$

(ii) By hydride ion $[H^{\ominus}]$ liberated from $LiAlH_4$ or $NaBH_4$. It is completed by nucleophilic substitution reaction.

$R-X + :H^{\ominus} \rightarrow R-H\ (\text{Alkane}) + :X^{\ominus}$

(iii) By catalytic hydrogenation of haloalkane.

$$R-X + H_2 \xrightarrow{\text{catalyst Pd}} R-H + HX$$

(iv) By reduction of RI with HI in presence of red P.

$$R-I + HI \xrightarrow{\text{red P}/150°C} R-H + I_2$$

(D) Reaction with metals : Organometallic compounds are formed.

(i) With Na : (Wurtz reaction)

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

(ii) With Mg : (Grignard reaction)

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

(iii) With Zn dust : (Frankland reaction)

$$R\boxed{-X + 2Zn + X-}R \rightarrow R–Zn–R\ (\text{dialkyl zinc}) + ZnX_2$$

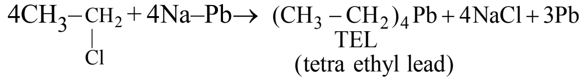
Dialkyl zinc is known as 'Frankland - Reagent'.

(iv) With Li : (Corey-House reaction)

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

Note: Isopropyl lithium is more reactive than grignard reagent.

(v) With Na-lead alloy :

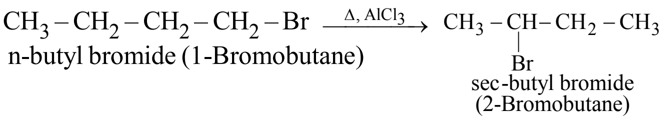


$$4CH_3-\underset{\underset{Cl}{|}}{CH_2} + 4Na–Pb \rightarrow \underset{\substack{\text{TEL} \\ \text{(tetra ethyl lead)}}}{(CH_3-CH_2)_4Pb} + 4NaCl + 3Pb$$

Tetra ethyl lead is used as antiknocking agent with gasoline.

(E) Rearrangement on heating (Isomerization)

When heated at 570 K in the presence of anhydrous aluminium chloride as a catalyst, alkyl halides undergo molecular rearrangement to form an isomeric haloalkanes.

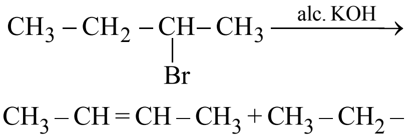


$$\underset{\text{n-butyl bromide (1-Bromobutane)}}{CH_3-CH_2-CH_2-CH_2-Br} \xrightarrow{\Delta,\ AlCl_3} \underset{\substack{\text{sec-butyl bromide} \\ \text{(2-Bromobutane)}}}{CH_3-\underset{\underset{Br}{|}}{CH}-CH_2-CH_3}$$

Note :

* The order of elimination reactions is 3° > 2° > 1°.

* During elimination reactions Saytzeff rule must be taken into consideration. e.g.,



$$CH_3-CH_2-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow{\text{alc. KOH}}$$

$$\underset{\text{2-butene (major)}}{CH_3-CH=CH-CH_3} + \underset{\text{But-1-ene (minor)}}{CH_3-CH_2-CH=CH_2}$$

It is explained on the basis of stability of alkene formed (Saytzeff's rule).

As per Saytzeff's rule, during elimination the most preferred alkene is that which is most alkylated.

$R_2C=CR_2 > R_2C=CHR > RCH=CHR$

or $R_2C=CH_2 > RCH=CH_2 > CH_2=CH_2$

Larger the number of alkyl groups attached to the doubly bonded carbon atoms more will be the stability and hence more will be the ease of its formation.

USES :

(a) As alkylation agent (Wurtz reaction)

(b) As synthetic reagent

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

DIHALIDES OR DIHALOALKANES

Gen. formula $C_nH_{2n}X_2$

Two H-atom of alkanes, replaced by two halogen atoms to form dihalides. Dihalides are classified as :

(a) Gem dihalide or Alkylidene halide :

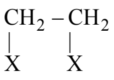
These are the halides in which two identical halogen atoms are attached on same carbon.

Ex. CH_3CHX_2 ethylidene dihalide (1, 1-dihalo ethane)

(b) Vicinal dihalide or Alkylene halides :

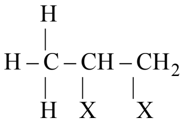
In these halides two identical halogen atoms are attatched on adjacent carbon atoms.

Ex.



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

Ethylene dihalide

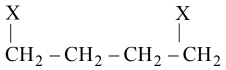


$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\underset{\underset{X}{|}}{CH}-\underset{\underset{X}{|}}{CH_2}$$

Propylene dihalide

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

Ex.



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

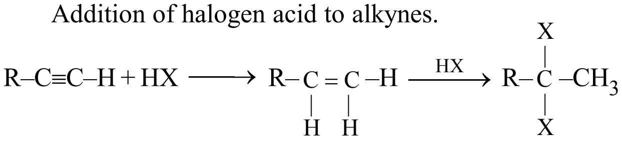
(1,4-dichlorobutane) Tetramethylene dichlorides

PREPARATION OF DIHALIDE

(a) Gem dihalides :

(i) From alkyne (By hydrohalogenation) :

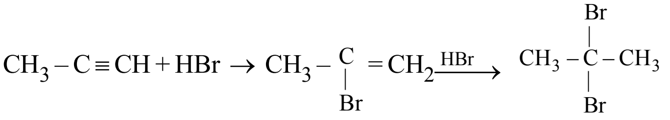
Addition of halogen acid to alkynes.



$$\underset{\text{Alkyne}}{R–C≡C–H} + HX \longrightarrow R–\underset{\underset{H}{|}}{C}=\underset{\underset{H}{|}}{C}–H \xrightarrow{HX} \underset{\text{Alkylidine halide}}{R–\overset{\overset{X}{|}}{\underset{\underset{X}{|}}{C}}–CH_3}$$

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

Vinyl bromide 1, 1-Dibromo ethane

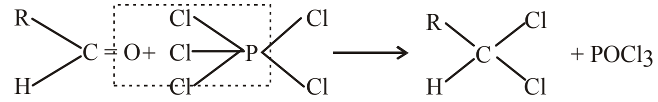


$$CH_3-C\equiv CH + HBr \rightarrow CH_3-\underset{Br}{C}=CH_2 \xrightarrow{HBr} CH_3-\underset{Br}{\overset{Br}{C}}-CH_3$$

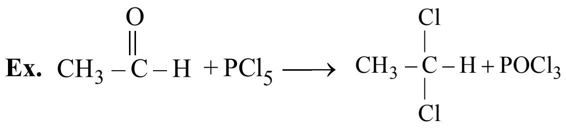
Propyne 2, 2-Dibromo propane

(ii) From carbonyl compounds :

By action of phosphorous pentachloride on aldehyde and ketones.



Aldehyde (terminal gem dihalide)

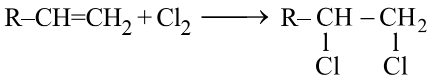


$$\textbf{Ex.}\ CH_3-\overset{O}{\overset{\|}{C}}-H + PCl_5 \longrightarrow CH_3-\underset{Cl}{\overset{Cl}{C}}-H + POCl_3$$

Acetaldehyde Ethylidene chloride

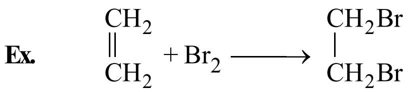
(b) Vicinal dihalides :

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



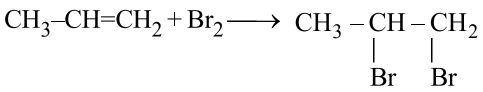
$$R{-}CH{=}CH_2 + Cl_2 \longrightarrow R-\underset{Cl}{CH}-\underset{Cl}{CH_2}$$

Alkene Alkylene chloride



$$\textbf{Ex.}\ \begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} + Br_2 \longrightarrow \begin{matrix}CH_2Br\\ |\\ CH_2Br\end{matrix}$$

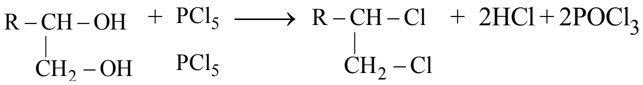
1, 2-dibromo ethane



$$CH_3{-}CH{=}CH_2 + Br_2 \longrightarrow CH_3-\underset{Br}{CH}-\underset{Br}{CH_2}$$

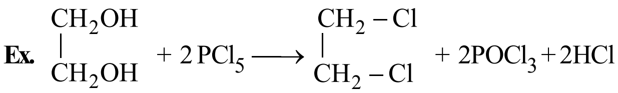
1, 2-dibromo propane

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



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

Alkylene glycol Alkylene chloride



$$\textbf{Ex.}\ \begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix} + 2\,PCl_5 \longrightarrow \begin{matrix}CH_2-Cl\\ |\\ CH_2-Cl\end{matrix} + 2POCl_3 + 2HCl$$

Ethylene glycol Ethylene chloride

(c) α-ω dihalides :

$CH_2=CH-CH_2Br + HBr \longrightarrow Br-CH_2-CH_2-CH_2Br$

1, 3-dibromo propane

PHYSICAL PROPERTIES

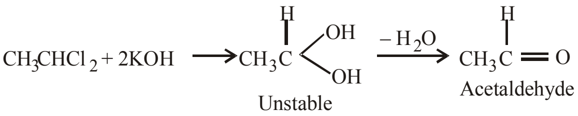
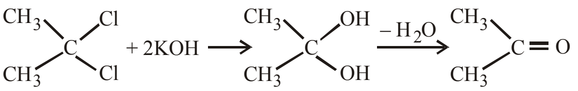
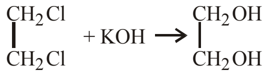
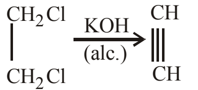
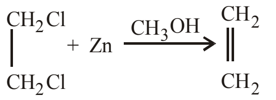
(i) Dihalides of lower alkane are colourless with sweet smelling liquids but higher homologues are solids

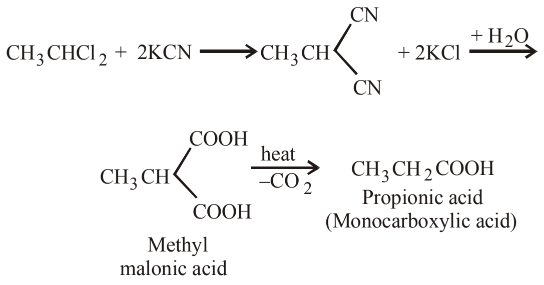
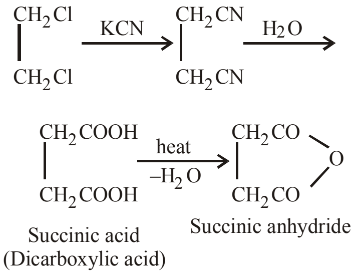
(ii) Insoluble in water but soluble in organic solvent.

(iii) Melting point and boiling points are directly proportional to molecular mass but boiling point of vicinal dihalides are more than gem dihalides. Also, reactivity of vicinal dihalide is more than gemdihalide, but these are less reactive than monohalide.

CHEMICAL PROPERTIES

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

	Property	**Alkylidene halides** (Gem dihalide)	**Alkylene halides** (Vicinal dihalide)
1	Hydrolysis (with aq. KOH)	Form aldehydes or ketones,  Unstable Acetaldehyde  Unstable Acetone	Form glycols,  $\begin{matrix}CH_2Cl\\ \mid\\ CH_2Cl\end{matrix} + KOH \rightarrow \begin{matrix}CH_2OH\\ \mid\\ CH_2OH\end{matrix}$ Ethylene Chloride Glycol
2	Reaction with alcoholic KOH (Dehydrohalogenation)	Form alkynes, $CH_3CHCl_2 \xrightarrow[(alc.)]{KOH} CH\equiv CH$ Acetylene	Form alkynes,  $\begin{matrix}CH_2Cl\\ \mid\\ CH_2Cl\end{matrix} \xrightarrow[(alc.)]{KOH} \begin{matrix}CH\\ \|\!\|\\ CH\end{matrix}$ Acetylene
3	Reaction with Zn dust in methanol	Form alkenes, $CH_3CHCl_2 + Zn \xrightarrow{CH_3OH} CH_3\,CH=CH\,CH_3$ 2-Butene	Form alkenes,  $\begin{matrix}CH_2Cl\\ \mid\\ CH_2Cl\end{matrix} + Zn \xrightarrow{CH_3OH} \begin{matrix}CH_2\\ \|\\ CH_2\end{matrix}$ Ethylene

4	Reaction with alc. KCN followed by hydrolysis and heating the product		

TRIHALIDES OR TRIHALOALKANES :

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

Three H-atom of alkane replaced by three halogen atoms.

Trihalogen of methane are also known as haloform

Chloroform,	bromoform,	Iodoform
$CHCl_3$	$CHBr_3$	CHI_3
Colourless liquid	Colourless	Yellow solid

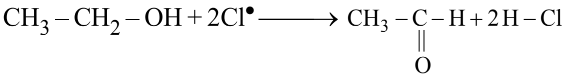
PREPARATIONS OF $CHCl_3$

(i) Haloform Reaction :

If any compound contains $CH_3-\underset{\underset{O}{\|}}{C}-H$ or $CH_3-\underset{\underset{O}{\|}}{C}-R$ group, (or may be oxidises in this group). When reacts with halogen and conc. alkali, trihalides are produced. Reaction is called as haloform reaction.

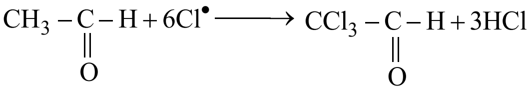
(a) $CaOCl_2+H_2O \longrightarrow Ca(OH)_2+2Cl^{\bullet}$

Bleaching Powder

(b) 

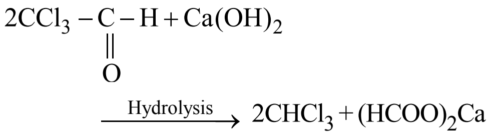
$$CH_3-CH_2-OH+2Cl^{\bullet} \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-H+2H-Cl$$

Ethyl alcohol　　Acetaldihyde

(c) 

$$CH_3-\underset{\underset{O}{\|}}{C}-H+6Cl^{\bullet} \longrightarrow CCl_3-\underset{\underset{O}{\|}}{C}-H+3HCl$$

chloral

(d) 

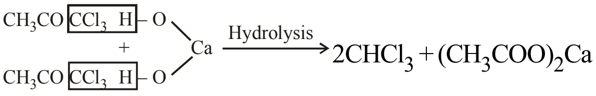
$$2CCl_3-\underset{\underset{O}{\|}}{C}-H+Ca(OH)_2 \xrightarrow{\text{Hydrolysis}} 2CHCl_3+(HCOO)_2Ca$$

Chloroform

From acetone :

(a) $CH_3COCH_3+6Cl^* \rightarrow CCl_3COCH_3+3HCl$

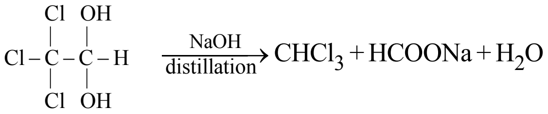
Acetone　　Trichloro acetone

(b) 

Chloroform

(ii) Preparation of pure Chloroform :

Alkaline solution of chlorohydrate is used in the formation of chloroform. Which on distillation gives pure chloroform:



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

chloral hydrate

(iii) From carbon tetra chloride (Pyrene) :

Reduction process

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

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

(iv) From Methane :

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

PHYSICAL PROPERTIES

(i) Chloroform is colourless with sweet smelling, liquid.

(ii) Inslouble in water and soluble in organic solvent.

(iii) Vapours of chloroform are poisonous in nature. It cause temporary unconsciousness, so used as an anasthetic agent.

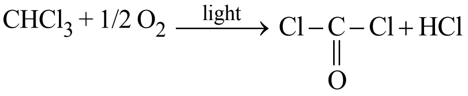
(iv) Boiling point of $CHCl_3$ is 61ºC.

(v) It is best solvent for fats, oil and wax.

(vi) Iodoform is yellow crystalline solid. It has melting point 119ºC.

CHEMICAL PROPERTIES

1. Oxidation : In presence of light it forms poisonous gas phosgene with atmospheric oxygen or with air.



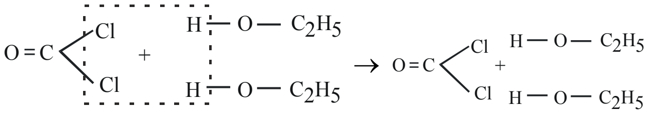
$$CHCl_3+1/2\,O_2 \xrightarrow{\text{light}} Cl-\underset{\underset{O}{\|}}{C}-Cl+HCl$$

Chloroform　　Phosgene

Precautions :

(i) It is kept into dark room in coloured bottle filling completely.

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



Phosgen　　Ethyl alcohol

diethyl carbonate (Non–poisonous substance)

Note : We use silver nitrate solution to check the impurity of phosgene in solution which will form white ppt. of AgCl with HCl.

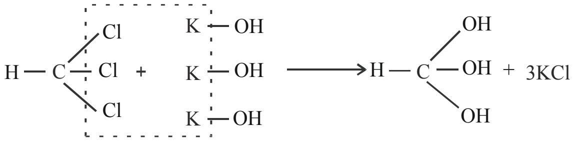
2. **Reduction :** $CHCl_3$

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

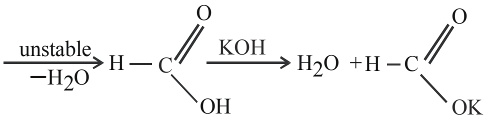
$$CHCl_3 \xrightarrow[Zn/HCl\ (aq.)]{+4H} CH_3Cl + 2HCl$$

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

3. **Reaction with Alcoholic KOH :**

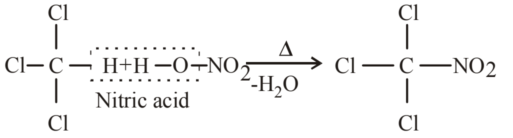


(unstable)



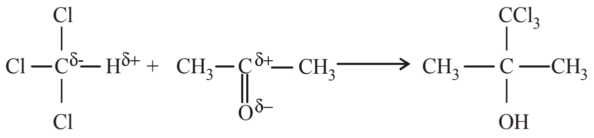
Formic acid Sodium formate

4. **Reaction with HNO_3 :**



Trichloro nitro methane
(chloropicrin) (Tear gas)

5. **Reaction with Acetone :**



Acetone Chloretone

Chloretone is used as a hypnotic agent

6. **Reaction with silver powder (Dehalogenation) :**

$$CHX_3 + 6Ag + X_3CH \xrightarrow{\text{high temp.}} CH \equiv CH + 6AgX$$

Acetylene

7. **Reaction with Primary amine :**

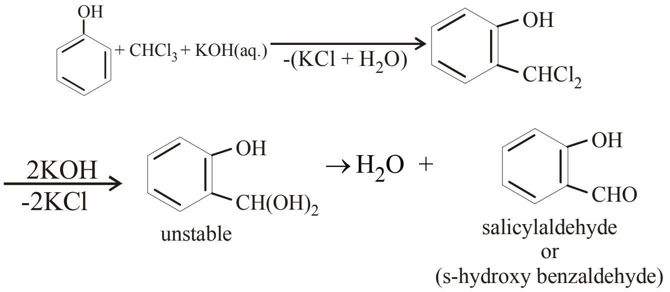
$$R\ddot{N}H_2 + CHCl_3 + KOH(alc.) \longrightarrow R\text{–}N \stackrel{\rightarrow}{=} C + KCl + H_2O$$

Alkane amine Alkane isocynide

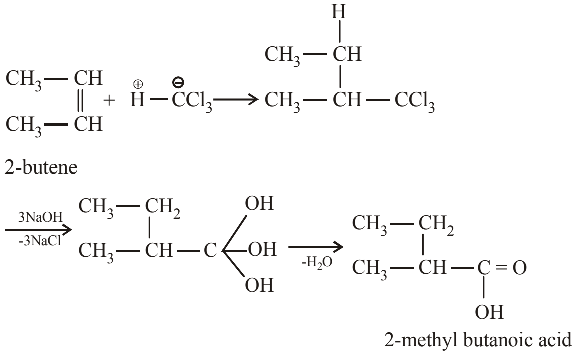
The reaction is called as "Hoffman–carbylamine Reaction' or "Isocyanide–test'. These isocyanides (product) has offensive smell. So, the reaction is used to test 1° amine. Reacting species of reaction is dichloro carbene.

8. **Reaction with Phenol :**

The reaction is called as "Reimer-tiemann Formylation'.



9. **Reaction with 2–Butene :**



USES

1. As an anaesthetic agent. ($CHCl_3$. Chloroform) and CHI_3 as antiseptic.
2. $CHCl_3$ as solvent for fat, waxes, rubber etc.
3. In preparation of chloroitone (drug, a hypnotic agent) and nitrochloroform (an insecticide, tear gas)
4. $CHCl_3$ as an preservative for antomical specimen.
5. As lab. reagent to identity pr. amine and other analytical test.

TETRA HALIDE OR TETRAHALOALKANE ($C_nH_{2n-2}X_4$)

Obtained by the replacement of 4-H atoms of an alkane by four C-atom. **Ex.** CCl_4 [Carbon Tetrachloride (pyrene)]

PREPARATIONS

(i) **From Methane (CH_4) :** Chlorination of methane with excess of chlorine at 400° C yields impure CCl_4.

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

(ii) **From carbon disulphide (CS_2) :**

This reaction used for industrial production of CCl_4.

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

sulphur monochloride

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

(iii) **From $CHCl_3$:** Chlorination of chloroform.

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

(iv) **From propane :**

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

Propane Pyrene

PHYSICAL PROPERTIES

(i) It is colourless liquid with specific smell.

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

(iii) It is the only organic solvent which is non–combustible. So used as fire-extinguisher called as 'Pyrene'.

CHEMICAL PROPERTIES

(i) **Oxidation :** It reacts with hot H_2O or with water vapour and forms poisonous gas 'Phosgene'.

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

(ii) **Hydrolysis :** It reacts with aqueous or alcoholic KOH and forms inorganic salt potassium carbonate.

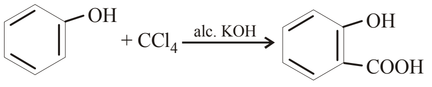
$$CCl_4 + 4KOH\,(aq.) \xrightarrow[-4KCl]{} \underset{\text{(unstable)}}{C(OH)_4} \xrightarrow[-2H_2O]{} CO_2$$

$$\xrightarrow{+2KOH} K_2CO_3 + H_2O$$

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

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

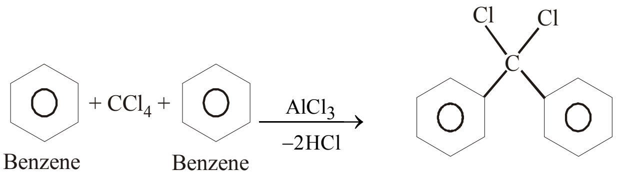
(iv) It reacts with phenol and forms salicylic acid.



Phenol Salicylic acid

The reaction is called as **"Riemer-Tieman Carboxylation'.**

(v) **Reaction with benzene :**



Benzene Benzene dichloro diphenyl methane

USES : (a) As a fire extinguisher (Pyrene)

(b) As a Lab reagent.

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

(d) In medicine a helminthicide. (e) As a tumigant.

OTHER USEFUL HALOGEN DERIVATIVES

(a) **Freons or cfc [Chlorofloro carbon] :** The chloro fluoro derivatives of methane and ethane are called freons.

Preparation of freons :

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

$$CHCl_3 + HF \xrightarrow{SbCl_5} \underset{\text{freon–21}}{CHFCl_2} + HCl$$

$$\underset{\text{hexachloro ethane}}{C_2Cl_6} + 2HF \xrightarrow{SbCl_5} \underset{\text{freon–112}}{C_2F_2Cl_4} + 2HCl$$

Properties

(i) Freons are colourless, odourless, unreactive & non-combustible liquids.

(ii) Also used as a solvent.

Uses of freons : (1) Having very low boiling points. They easily converted from gaseous state to liquid state, therefore they used as a coolant in A.C. & Refrigerator.

(2) Used as a aerosole propellant in aeroplane & rockets.

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

where c = no. of carbon atom –1, b = no. hydrogen atom +1

a = total no. of atoms of fluorine

Example : $CFCl_3$

C – 1 = 0, H + 1 = 1, F = 1 Freon – 11

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

(b) **Teflon :** Produced by polymerisation of $CF_2 = CF_2$ (tetrafluoro ethylene).

$CF_2 = CF_2$ obtained by following reaction -

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

Polymerisation of $CF_2 = CF_2$ –

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

Properties :

(i) It is chemically inert. (ii) It is stable at high temp.

(iii) Unaffected by strong acids and by boiling aqua-regia.

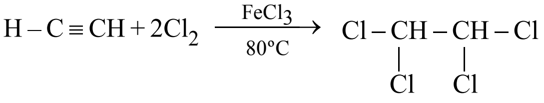
Uses : (i) Making acid containers.

(ii) For electrical insulation & lubricants.

(iii) Preparation of gasket materials.

(c) **Westron (Acetylene tetra chloride) :** $(Cl_2CH - CHCl_2)$

Preparation :

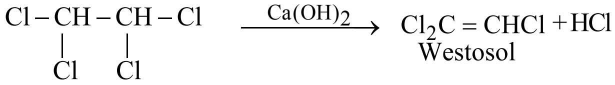


$$H - C \equiv CH + 2Cl_2 \xrightarrow[80°C]{FeCl_3} \underset{\text{Cl}}{\underset{|}{Cl - CH}} - \underset{\text{Cl}}{\underset{|}{CH - Cl}}$$

Westron

Properties :

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



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

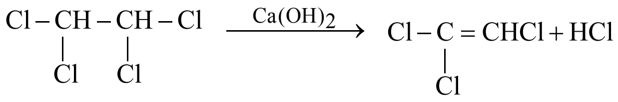
Uses : (i) In the manufacture of westrosol.

(ii) As an insecticide.

(iii) As a solvent for oil, fats, paints etc.

(d) **Westrosol :** (Trichloro ethylene)

Preparation :



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

Properties : It is less toxic than westron. B.P. 80ºC

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

(e) **BHC :** $C_6H_6 + 3Cl_2 \xrightarrow{Light} C_6H_6Cl_6$ (BHC)

It is also called Gammexene or Lindane or 666 and is used as pesticide.

ARYL HALIDES

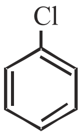
* Those compounds in which halogen in directly attached to benzene nucleus are called aryl halides.

* **Physical properties :** They are generally colourless liquids or solids at room temperature. Boiling and melting points are in the order ArI > ArBr > ArCl.

In case of aromatic dihalides p-isomer has much higher melting point due to symmetrical structure which leads to the stronger interparticle forces in the lattice.

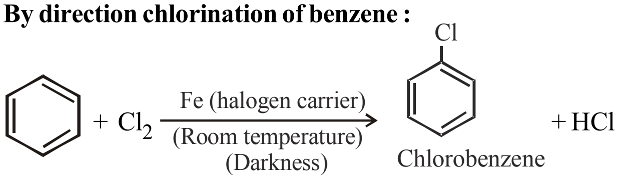
Aromatic halides are insoluble in water.

CHLOROBENZENE, PHENYL CHLORIDE



Preparation :

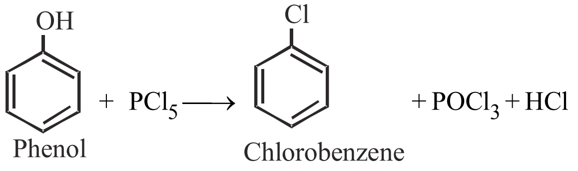
(i) **By direction chlorination of benzene :**



Low temperature and presence of halogen carrier favour nuclear substitution.

(ii) **From phenol :**

$C_6H_5OH \xrightarrow[SOCl_2]{HX,PX_3} X$ (No reaction)

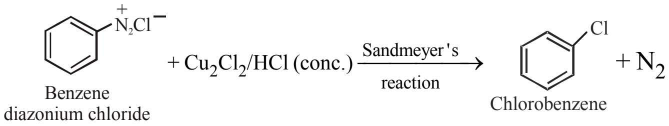


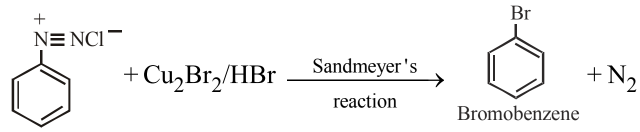
Yield of chlorobenzene in this reaction is poor because $POCl_3$ reacts with phenol giving triphenyl phosphate.

$$3C_6H_5OH + POCl_3 \longrightarrow \underset{\text{Triphenyl phosphate}}{(C_6H_5)_3PO_4} + 3HCl$$

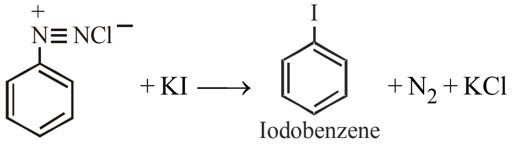
(iii) **By Sandmeyer's reaction :**

When benzene diazonium chloride is treated with Cu_2Cl_2 in conc. HCl, the N_2Cl group is replaced by chlorine atom. This reaction is called Sandmeyer's reaction.

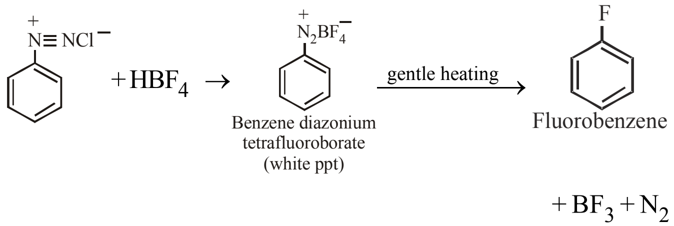




Iodobenzene can be prepared by reacting benzene diazonium chloride with KI solution.

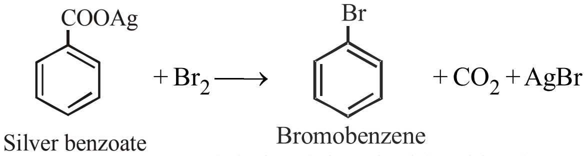


Fluorobenzene can be obtained from diazo salt as follows :

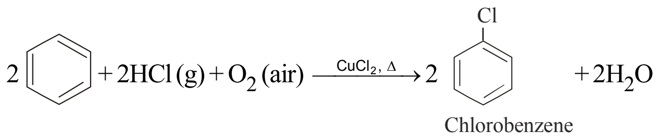


This reaction is called Schiemann Reaction

(iv) **By Hunsdiecker reaction :**



(v) **Raschig process :** It is industrial method for chlorobenzene.

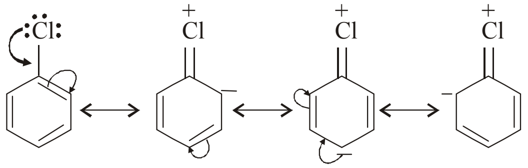


PHYSICAL PROPERTIES

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

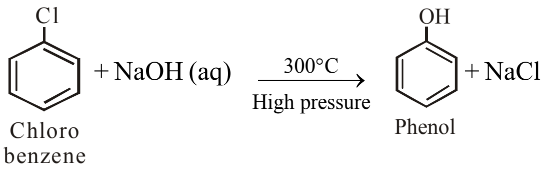
CHEMICAL PROPERTIES

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

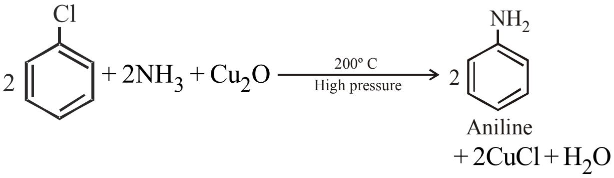


The halogen atom is replaced by other nucleophiles under forcing conditions.

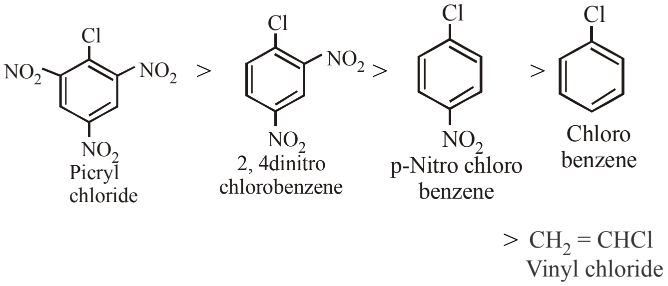
(i) Replacement by –OH group :



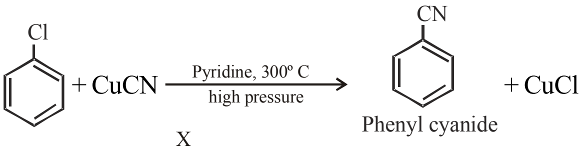
(ii) Replacement by –NH_2 group :



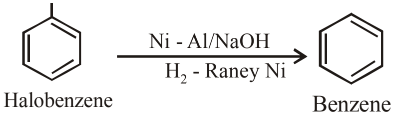
The reactivity of halogen atom is increased by the presence of electron attracting atom or group of atoms at ortho and or para position of the halogen atom. Thus, the reactivity order of halogens is :

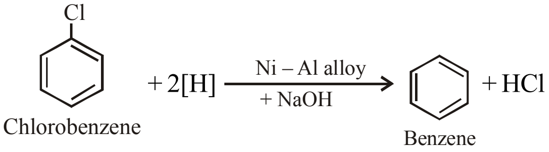


(iii) Replacement by –CN :

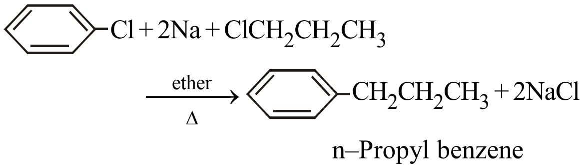


2. Reduction :

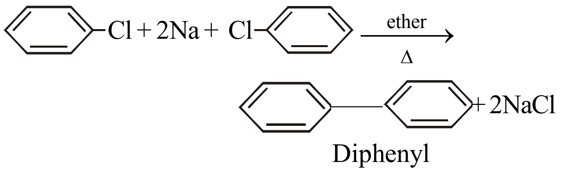




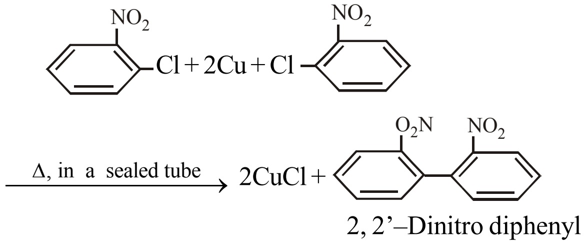
3. Wurtz–Fittig reaction : Aryl halide and alkyl halide when heated together in the presence of sodium and ether, yield homologues of benzene.



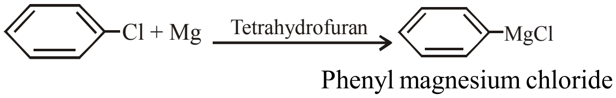
When only aryl halides are heated with metallic sodium, the reaction is known as Fittig reaction and the product is diaryl,



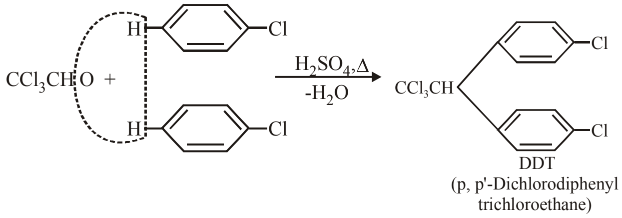
4. Ullmann Reaction : Chloro and bromo benzenes do not give this reaction. But when there is an electron attracting group at the ortho and/or para position of the halogen atom, Ullmann reaction is responded to by them.



5. Formation of Grignard's reagents :

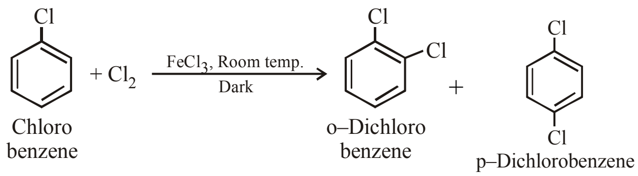


6. Reaction with chloral : When chlorobenzene is heated with chloral in the presence of conc. H_2SO_4, a powerful insecticide, DDT is formed.

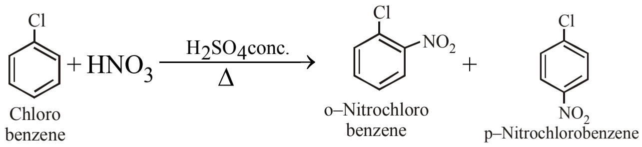


7. Reactions due to the benzene ring : The halogen atoms are ortho–para directing but deactivate the benzene ring towards electrophilic substitution reactions. It is due to their strong –I effect ; o–, p–direction is due to +E and +M effects.

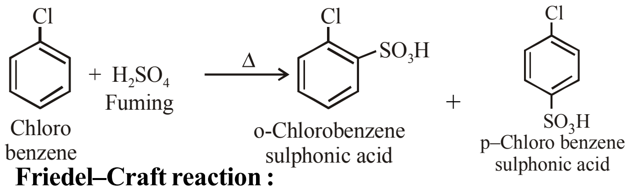
(a) Halogenation :



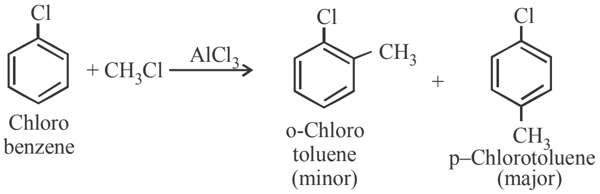
(b) Nitration :



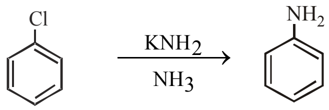
(c) Sulphonation :

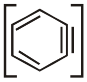


(d) Friedel–Craft reaction :



(e) Elimination addition Reaction :



This reaction known as ceny substitution and complete through benzyne inter mediate 

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

TRY IT YOURSELF

Q.1 Identify B, $CH_3-CH_2-Cl \xrightarrow[C_2H_5OH]{KF} B$

Q.2 Hunsdiecker reaction is used to prepare alkyl chloride and alkyl bromide starting from –
(A) Diazonium salt
(B) Silver salt of carboxylic acid
(C) Sodium salt of carboxylic acids
(D) Alcohols

Q.3 The best reagent for converting an alcohol into the corresponding chloride is –
(A) PCl_5 (B) PCl_3
(C) $HCl/ZnCl_2$ (D) $SOCl_2$

Q.4 What is the decreasing order of reactivity of following compounds through S_N2 mechanism?
CH_3I, CH_3Br, CH_3Cl, CH_3CH_2Cl
(I) (II) (III) (IV)

Q.5 Most reactive halide towards S_N1 reaction is
(A) n-butyl chloride (B) sec-butyl chloride
(C) tert-butyl chloride (D) Allyl chloride

Q.6 Which of the following is most reactive towards nucleophilic substitution reaction?
(A) $CH_2=CH-Cl$ (B) C_6H_5Cl
(C) $CH_3-CH=CH-Cl$ (D) $Cl-CH_2-CH=CH_2$

Q.7 Which of the following does not form Grignard reagent on reaction with Mg in the presence of ether?
(A) Chloroethane (B) 1-chloropropane
(C) Bromobenzene (D) Vinyl chloride

Q.8 In chlorination of benzene to form chlorobenzene, the attacking species is –
(A) Cl_2 (B) $Cl^{\bullet}$
(C) Cl^- (D) Cl^+

Q.9 IUPAC name of gammexene is –
(A) Hexachlorobenzene
(B) Benzene hexachloride
(C) 1, 2, 3, 4, 5, 6-hexachlorocyclohexane
(D) All of these

Q.10 'Pyrene' is the trade name of __ when used as fire extinuisher –
(A) CO_2 (B) $CHCl_3$
(C) CCl_4 (D) CH_2Cl_2

ANSWERS

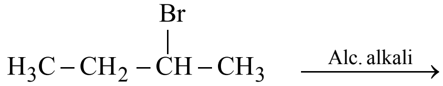
(1) No product **(2)** (B) **(3)** (D)
(4) I > II > III > IV **(5)** (D) **(6)** (D)
(7) (D) **(8)** (D) **(9)** (C) **(10)** (C)

ADDITIONAL EXAMPLES

Example 1 :

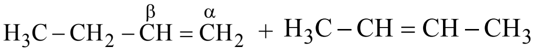
2-Bromobutane on heating with alcoholic alkali forms –
(A) α-Butylene only
(B) β-Butylene only
(C) 20% of β-Butylene + 80% of α-Butylene
(D) 80% of β-Butylene + 20% of α-Butylene

Sol. **(D).**



$H_3C-CH_2-\overset{Br}{\overset{|}{C}H}-CH_3 \xrightarrow{\text{Alc. alkali}}$

(Reaction occur by Saytzeff's rule)

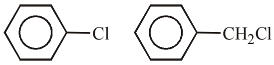


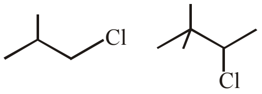
$H_3C-CH_2-\overset{\beta}{C}H=\overset{\alpha}{C}H_2 + H_3C-CH=CH-CH_3$

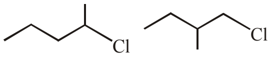
α-Butylene (20%) β-Butylene (80%)

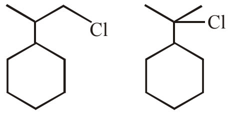
Example 2 :

In the given pair in which pair the first compound is more reactive than second for S_N1 reaction.

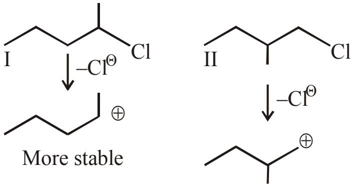
(A) 

(B) 

(C) 

(D) 

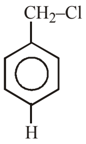
Sol. **(C).** Reactivity of alkyl halide increases with increase of stability of intermediate carbocation. Stability of carbocation of I is more than II only in (C) option due to more hyperconjugation.

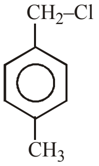


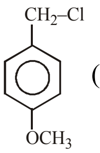
More stable Less stable

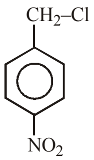
Example 3 :

Which of the following is most reactive toward S_N2.

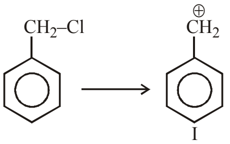
(A) 

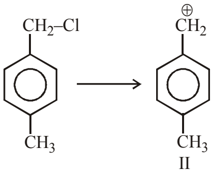
(B) 

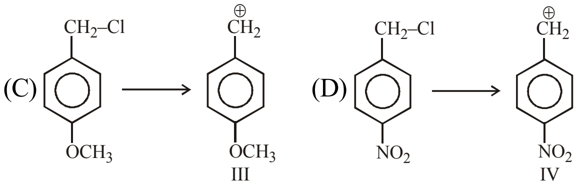
(C) 

(D) 

Sol. **(D).** Alkyl halide which produces less stable carbocation are less reactive towards S_N1 – Reaction but more reactive towards S_N2 reaction.

(A) 

(B) 



Stability order of carbocation = III > II > I > IV

Example 4 :

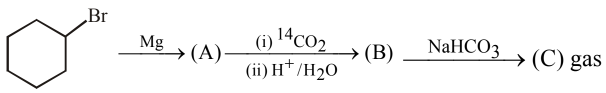
The order of reactivity of alkyl halide in the reaction : $R - X + Mg \rightarrow RMgX$ is –

(A) $RI > RBr > RCl$ (B) $RCl > RBr > RI$

(C) $RBr > RCl > RI$ (D) $RBr > RI > RCl$

Sol. **(A).** Smaller the bond dissociation energy of R – X bond greater will reactivity of R – X towards Mg.

Example 5:

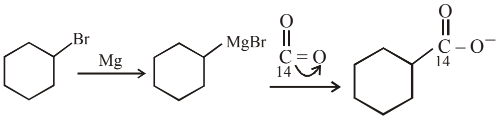


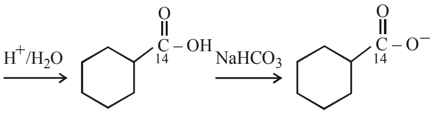
Product C is –

(A) CO (B) $^{14}CO_2$

(C) CO_2 (D) A mixture of $^{14}CO_2$ & CO_2

Sol. **(C).**





$+ H_2CO_3 \rightarrow H_2O + CO_2$

QUESTION BANK

CHAPTER 9 : HALOALKANES AND HALOARENES

EXERCISE - 1 [LEVEL-1]

Choose one correct response for each question.

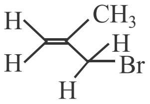
PART - 1 : CLASSIFICATION AND NOMENCLATURE

Q.1 Which of the following halide is 2°
(A) Isopropyl chloride (B) Isobutyl chloride
(C) n-propyl chloride (D) n-butyl chloride

Q.2 Which of the following is not an allylic halide?
(A) 4-Bromopent-2-ene
(B) 3-Bromo-2-methylbut-1-ene
(C) 1-Bromobut-2-ene
(D) 4- Bromobut -1-ene

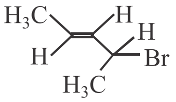
Q.3 The IUPAC name of
$(CH_3)_2CH-CH_2-CH_2Br$ is –
(A) 1-bromopentane
(B) 1-bromo-3-methylbutane
(C) 2-methyl-4-bromobutane
(D) 2-methyl-3-bromopropane.

Q.4 Which of the following is a primary halide
(A) Isopropyl iodide
(B) Secondary butyl iodide
(C) Tertiary butyl bromide
(D) Neo hexyl chloride

Q.5 The IUPAC name of  is –

(A) 3-bromo-2-methylpropene
(B) 1-bromo-2-methylbut-2-ene
(C) 4-bromopent-2-ene
(D) 4-bromopent-1-ene

Q.6 IUPAC name of m-Dibromobenzene is –
(A) 1,3-Dibromobenzene (B) 1,2-Dibromobenzene
(C) 1,4-Dibromobenzene (D) 1,3,5-Dibromobenzene

Q.7 The IUPAC name of  is –

(A) 2-bromopent-4-ene (B) 2-bromopent-3-ene
(C) 4-bromopent-2-ene (D) 4-bromopent-1-ene

Q.8 Common name given to 2-chloropropane
(A) n-propyl chloride (B) isopropyl chloride
(C) isobutyl chloride (D) None of these

Q.9 Which of the following is an example of vic-dihalide?
(A) Dichloromethane (B) 1,2-dichloroethane
(C) Ethylidene chloride (D) Allyl chloride

Q.10 Choose the correct statement –
(A) o-Br-$C_6H_4CH(CH_3)CH_2CH_3$ is a aryl halide.
(B) m-$ClCH_2C_6H_4CH_2C(CH_3)_3$ is a benzylic, primary halide.
(C) $CH_3CH=CHC(Br)(CH_3)_2$ is a allylic, tertiary halide.
(D) All of these

Q.11 The position of – Br in the compound in
$CH_3CH=CHC(Br)(CH_3)_2$ can be classified as –
(A) allyl (B) aryl
(C) vinyl (D) secondary

Q.12 Which of the following statement{s} is/are true for geminal halide?
(A) Alkylene dihalide
(B) Halogen present on adjacent carbon atom
(C) Alkylidene dihalide
(D) Both (B) and (C)

Q.13 The IUPAC name of tertiary butyl chloride is
(A) 2-chloro-2-methylpropane
(B) 3-chlorobutane
(C) 4-chlorobutane
(D) 1,2-chloro-3-methylpropane

PART - 2 : METHODS OF PREPARATION

Q.14 Silver acetate + $Br_2 \xrightarrow{CS_2}$. The main product of this reaction is
(A) CH_3-Br (B) CH_3COI
(C) CH_3COOH (D) None of these

Q.15 The reaction of alkyl chlorides/bromides with NaI in dry acetone produces –
(A) Alkyl iodides (B) Alkyl fluorides
(C) Alkyl bromides (D) None of these

Q.16 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.

Q.17 When ethyl alcohol and KI reacted in presence of Na_2CO_3, yellow crystals of...... are formed
(A) CHI_3 (B) CH_3I
(C) CH_2I_2 (D) C_2H_5I

Q.18 On heating diethyl ether with conc. HI, 2 moles of which of the following is formed
(A) Ethanol (B) Iodoform
(C) Ethyl iodide (D) Methyl iodide

Q.19 Acetone reacts with I_2 in presence of NaOH to form
(A) C_2H_5I (B) $C_2H_4I_2$
(C) CHI_3 (D) CH_3I

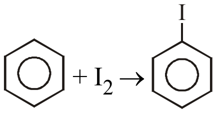
Q.20 Ethanol is converted into ethyl chloride by reacting with
(A) Cl_2 (B) $SOCl_2$
(C) HCl (D) NaCl

Q.21 Propene on treatment with HBr gives
(A) Isopropyl bromide (B) Propyl bromide
(C) 1, 2-dibromoethane (D) None of the above

Q.22 Benzene reacts with chlorine to form benzene hexachloride in presence of –
(A) Nickel (B) $AlCl_3$
(C) Bright sunlight (D) Zinc

Q.23 In the reaction, $CH_3CH = CH_2 + HI$, major product is –
(A) CH_3CHICH_3
(B) $CH_3CH_2CH_2I$
(C) Both (A) and (B) are formed in equal proportion..
(D) None of these

Q.24 Name the reagent used in this reaction.



(A) HNO_3 (B) HF
(C) H_2O (D) SO_2

Q.25 Which of the following compounds can yield only one monochlorinated product upon free radical chlorination?
(A) 2,2-Dimethylpropane (B) 2-Methylpropane
(C) 2-Methylbutane (D) n-Butane

Q.26 Alkyl chloride is prepared by passing the ____ gas through solution of alcohol.
(A) H_2SO_4 (B) HCl
(C) dry HCl (D) None of these

PART - 3 : PHYSICAL PROPERTIES

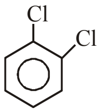
Q.27 Which of the following compounds will have highest melting point?
(A) Chlorobenzene (B)o-Dichlorobenzene
(C) m-Dichlorobenzene (D) p-Dichorobenzene

Q.28 Arrange the following compounds in increasing order of their density.
(i) CH_2Cl_2 (ii) $CHCl_3$ (iii) CCl_4
(A) (iii) < (ii) < (i) (B) (iii) < (i) < (ii)
(C) (iii) < (i) = (ii) (D) (i) < (ii) < (iii)

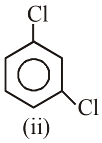
Q.29 Which of the following compounds has the highest boiling point?
(A) $CH_3CH_2CH_2Cl$ (B) $CH_3CH_2CH_2CH_2Cl$
(C) $CH_3CH(CH_3)CH_2Cl$ (D) $(CH_3)_3CCl$

Q.30 Which is the correct increasing order of boiling points of the following compounds?
1-Iodobutane, 1-Brornobutane, 1-Chlorobutane, Butane
(A) Butane < 1-Chlorobutane < 1-Bromobutane < 1-Iodobutane
(B) 1-Iodobutane < 1-Bromobutane < 1-Chlorobutane < Butane
(C) Butane < 1-Iodobutane < 1-Bromobutane < 1-Chlorobutane
(D) Butane < 1-Chlorobutane < 1-Iodobutane < 1-Bromobutane

Q.31 Arrange the following compounds in the increasing order of their melting point.



(i)



(ii)

(iii)

(A) (i) > (ii) > (iii) (B) (iii) > (i) = (ii)
(C) (iii) > (i) ≥ (ii) (D) (iii) > (i) > (ii)

Q.32 Alkyl halides are immiscible in water though they are polar because
(A) they react with water to give alcohols.
(B) they cannot form hydrogen bonds with water.
(C) C – X bond cannot be broken easily.
(D) they are stable compounds and are not reactive.

PART - 4 : CHEMICAL PROPERTIES

Q.33 A Grignard's reagent may be made by reacting magnesium with
(A) Methyl amine (B) Diethyl ether
(C) Ethyl iodide (D) Ethyl alcohol

Q.34 Ethyl bromide can be converted into ethyl alcohol by
(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

Q.35 Reaction of ethyl chloride with sodium leads to
(A) Ethane (B) Propane
(C) n-butane (D) n-pentane

Q.36 $2CHCl_3 + O_2 \xrightarrow{X} 2COCl_2 + 2HCl$
In the above reaction, X stands for
(A) An oxidant (B) A reductant
(C) Light and air (D) None of these

Q.37 The reactivity of ethyl chloride is
(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

Q.38 The reactivities of methyl chloride, propyl chloride and chlorobenzene are in the order
(A) Methyl chloride > propyl chloride > chlorobenzene
(B) Propyl chloride > methyl chloride > chlorobenzene
(C) Methyl chloride > chlorobenzene > propyl chloride
(D) Chlorobenzene > propyl chloride > methyl chloride

Q.39 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

Q.40 Ethyl bromide reacts with lead-sodium alloy to form
(A) Tetraethyl lead (B) Tetraethyl bromide
(C) Both (A) and (B) (D) None of the above

Q.41 1-chlorobutane reacts with alcoholic KOH to form
(A) 1-butene (B) 2-butane
(C) 1-butanol (D) 2-butanol

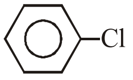
Q.42 Which metal is used in Wurtz synthesis
(A) Ba (B) Al
(C) Na (D) Fe

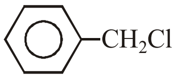
Q.43 The reaction of an aromatic halogen compound with an alkyl halides in presence of sodium and ether is called
(A) Wurtz reaction (B) Sandmeyer's reaction
(C) Wurtz-fittig reaction (D) Kolbe reaction

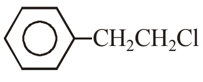
Q.44 The reaction, $CH_3Br + Na \rightarrow$ Product is called
(A) Perkin reaction (B) Levit reaction
(C) Wurtz reaction (D) Aldol condensation

Q.45 Which one of the following chlorohydrocarbons readily undergoes solvolysis?

(A) $CH_2=CHCl$

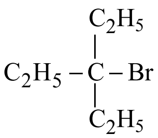
(B) 

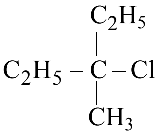
(C) 

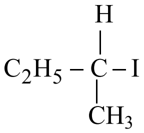
(D) 

Q.46 An alkyl halide, RX reacts with KCN to give propane nitrile. RX is –
(A) C_3H_7Br (B) C_4H_9Br
(C) C_2H_5Br (D) $C_5H_{11}Br$

Q.47 Which of the following will give enantiomeric pair on reaction with water due to presence of asymmetric carbon atom?

(A) 
$C_2H_5-\overset{C_2H_5}{\underset{C_2H_5}{C}}-Br$

(B) 
$C_2H_5-\overset{C_2H_5}{\underset{CH_3}{C}}-Cl$

(C) 
$C_2H_5-\overset{H}{\underset{CH_3}{C}}-I$

(D) None of these

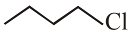
Q.48 The allylic and benzylic halides undergoe
(A) S_N1 mechanism
(B) S_N2 mechanism
(C) Both S_N1 and S_N2 mechanism
(D) None of the above

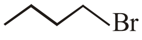
Q.49 Which of the following haloalkanes is most reactive?
(A) 1-Chloropropane (B) 1-Bromopropane
(C) 2-Chloropropane (D) 2-Bromopropane

Q.50 Which of the following molecule is chiral?
(A) Butan-1-ol (B) Butan-2-ol
(C) Butan-4-ol (D) All of these

Q.51 Which would undergo S_N2 reaction faster ?

(A) 

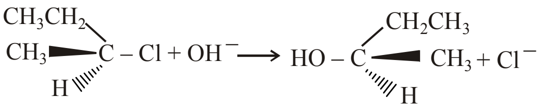
(B) 

(C) 

(D) 

Q.52 Which of the following is most reactive towards aqueous NaOH?
(A) C_6H_5Cl (B) $C_6H_5CH_2Cl$
(C) C_6H_5Br (D) C_6H_4Br

Q.53 In the reaction given below:



Which of the following statements is correct?
(A) The reaction proceeds via S_N2 mechanism hence inversion of configuration takes place.
(B) The reaction proceeds via S_N1 mechanism hence inversion of configuration takes place.
(C) The reaction proceeds via S_N2 mechanism hence their is no change in the configuration.
(D) The reaction proceeds via S_N1 mechanism hence there is no change in the configuration.

Q.54 Ethyl alcohol is obtained when ethyl chloride is boiled with –
(A) alcoholic KOH (B) aqueous KOH
(C) water (D) aqueous $KMnO_4$

Q.55 $C_3H_8 + Cl_2 \xrightarrow{Light} C_3H_7Cl + HCl$ is an example of which of the following types of reactions
(A) Substitution (B) Elimination
(C) Addition (D) Rearrangement

Q.56 Which of the following is the most reactive towards nucleophilic substitution reaction?
(A) $ClCH_2-CH=CH_2$ (B) $CH_2=CH-Cl$
(C) $CH_3CH=CH-Cl$ (D) C_6H_5Cl

Q.57 2-Chloro-2-methylpropane on reaction with alc. KOH gives X as the product. X is –
(A) but-2-ene (B) 2-methylbut-l-ene
(C) 2-methylprop-1-ene (D) 2-methylbutan-2-ol

Q.58 Ethyl iodide on reduction with Zn-Cu couple and alchol produces –
(A) ethane (B) methane
(C) butane (D) propane

PART - 5 : POLYHALOGEN COMPOUNDS

Q.59 Haloforms are trihalogen derivatives of
(A) Ethane (B) Methane
(C) Propane (D) Benzene

Q.60 Which compound needs chloral in its synthesis
(A) D. D. T. (B) Gammexane
(C) Chloroform (D) Michler's Ketone

Q.61 It exposure in air causes impaired hearing and vision. Higher level exposure causes nausea and numbness in finger and trees. Direct skin contact causes intense burning and mild redness of skin, and even burn cornea. Which of the following solvent is responsible for it?
(A) Methylene chloride (B) Chloroform
(C) Iodoform (D) Carbon tetrachloride

Q.62 Chloroform for anesthetic purposes is tested for its purity with the reagent
(A) Silver nitrate (B) Lead nitrate
(C) Ammoniacal Cu_2Cl_2 (D) Lead nitrate

Q.63 Chloroform, when kept open, is oxidised to
(A) CO_2 (B) $COCl_2$
(C) CO_2, Cl_2 (D) None of these

Q.64 Freon (dichlorodifluoro methane) is used
(A) As local anaesthetic
(B) For dissolving impurities in metallurgical process
(C) In refrigerator
(D) In printing industry

Q.65 In fire extinguisher, pyrene is
(A) CO_2 (B) CCl_4
(C) CS_2 (D) $CHCl_3$

Q.66 At normal temperature iodoform is
(A) Thick viscous liquid (B) Gas
(C) Volatile liquid (D) Solid

Q.67 The molecular formula of DDT has
(A) 5 chlorine atoms (B) 4 chlorine atoms
(C) 3 chlorine atoms (D) 2 chlorine atoms

Q.68 Iodoform can be used as
(A) Anaesthetic (B) Antiseptic
(C) Analgesic (D) Antifebrin

Q.69 Which of the following is an anaesthetic
(A) C_2H_4 (B) $CHCl_3$
(C) CH_3Cl (D) C_2H_5OH

Q.70 Use of chlorofluoro carbons is not encouraged because
(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.

Q.71 An organic halogen compound which is used as refrigerant in refrigerators and air conditioners is
(A) BHC (B) CCl_4
(C) freon (D) $CHCl_3$

Q.72 Which one is correct?
(A) Freon-14 is CF_4, Freon-13 is CF_3Cl, Freon-12 is CF_2Cl_2 & Freon-11 is $CFCl_3$.
(B) Freons are chlorofluorocarbons.
(C) Freons are used as refrigerants.
(D) All the above.

EXERCISE - 2 [LEVEL-2]

Choose one correct response for each question.

Q.1 What is the main product of the reaction between 2-methyl propene with HBr
(A) 1-bromo butane
(B) 1-bromo-2 methyl propane
(C) 2-bromo butane
(D) 2-bromo-2 methyl propane

Q.2 In methyl alcohol solution, bromine reacts with ethylene to yield $BrCH_2CH_2OCH_3$ in addition to 1, 2 dibromo-ethane because
(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.

Q.3 The product formed on reaction of ethyl alcohol with bleaching powder is
(A) $CHCl_3$ (B) CCl_3CHO
(C) CH_3COCH_3 (D) CH_3CHO

Q.4 Which of the following compound will make precipitate most readily with $AgNO_3$
(A) CCl_3CHO (B) $CHCl_3$
(C) $C_6H_5CH_2Cl$ (D) CHI_3

Q.5 $C_6H_5CH_2Cl + KCN(aq.) \rightarrow X + Y$
Compounds X and Y are
(A) $C_6H_6 + KCl$ (B) $C_6H_5CH_2CN + KCl$
(C) $C_6H_5CH_3 + KCl$ (D) None of these

Q.6 Iodoform heated with Ag powder to form
(A) Acetylene (B) Ethylene
(C) Methane (D) Ethane

Q.7 Which of the following reactions gives $H_2C=C=C=CH_2$
(A) $CH_2Br-CBr=CH_2 \xrightarrow{Zn/CH_3OH}$
(B) $HC\equiv C-CH_2-COOH \xrightarrow[40^oC]{Aq.K_2CO_3}$
(C) $CH_2Br-C\equiv C-CH_2Br \xrightarrow[Heat]{Zn}$
(D) $2CH_2=CH-CH_2I \longrightarrow$

Q.8 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
(A) $C_6H_4(CH_3)Br$ (B) $C_6H_5CH_2Cl$
(C) C_6H_5Cl (D) None of these

Q.9 When chloroform is treated with conc. HNO_3 it gives –
(A) $CHCl_2NO_2$ (B) CCl_3NO_2
(C) $CHCl_2HNO_3$ (D) None of these

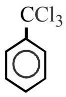
Q.10 2, 6 - Dimethylheptane on monochlorination produces ____ derivatives
(A) 5 (B) 6
(C) 3 (D) 4

Q.11 Vinyl chloride reacts with HCl to form
(A) 1, 1- dichloro ethane
(B) 1, 2- dichloro ethane
(C) Tetrachloro ethylene
(D) Mixture of 1, 2 and 1, 1-dichloro ethane

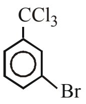
Q.12 Elimination of hydrogen bromide from 2-bromobutane results in the formation of –
(A) equimolar mixture of 1 and 2-butene
(B) predominantly 2-butene
(C) predominantly 1-butene
(D) predominantly 2-butyne

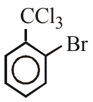
Q.13 Which of the following is obtained when chloral is boiled with NaOH –
(A) CH_3Cl (B) $CHCl_3$
(C) CCl_4 (D) None of these

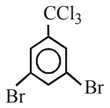
Q.14 Acetone is mixed with bleaching powder to give
(A) Chloroform (B) Acetaldehyde
(C) Ethanol (D) Phosgene

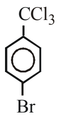
Q.15 

$\xrightarrow{\text{1 eqv. of } Br_2/Fe}$ A. Compounds A is

(A) 

(B) 

(C) 

(D) 

Q.16 Reaction of t-butyl bromide with sodium methoxide produces
(A) Isobutane (B) Isobutylene
(C) Sodium t-butoxide (D) t-butyl methyl ether

Q.17 Alcoholic caustic potash on chloroform and aniline gives
(A) Phenyl isocyanide (B) Nitrobenzene
(C) Phenyl cyanide (D) Phenyl isocyanate

Q.18 Chlorine reacts with ethanol to give –
(A) Ethyl chloride (B) Chloroform
(C) Acetaldehyde (D) Chloral

Q.19 $C_6H_6Cl_6$ on treatment with alcoholic KOH, yields –
(A) C_6H_6 (B) $C_6H_3Cl_3$
(C) $(C_6H_6)OH$ (D) $C_6H_6Cl_4$

Q.20 For a given alkyl group the densities of the halides follow the order
(A) $RI < RBr < RCl$ (B) $RI < RCl < RBr$
(C) $RBr < RI < RCl$ (D) $RCl < RBr < RI$

Q.21 Two percent of ethanol is added during the oxidation of chloroform to stop the formation of carbonyl chloride. In this reaction ethanol acts as
(A) Auto catalyst (B) Negative catalyst
(C) Positive catalyst (D) None of these

Q.22 Among the following, the molecule with the highest dipole moment is
(A) CH_3Cl (B) CH_2Cl_2
(C) $CHCl_3$ (D) CCl_4

Q.23 Among the following one with the highest percentage of chlorine is
(A) Chloral (B) Pyrene
(C) PVC (D) Gammexene

Q.24 Reduction of acetyl chloride with H_2 in presence of Pd gives
(A) CH_3COCH_3 (B) C_2H_5OH
(C) CH_3COOH (D) CH_3CHO

Q.25 The compound added to prevent chloroform to form phosgene gas is
(A) C_2H_5OH (B) CH_3COOH
(C) CH_3COCH_3 (D) CH_3OH

Q.26 Chloroform, on warming with Ag powder, gives
(A) C_2H_6 (B) C_4H_8
(C) C_2H_4 (D) C_2H_2

Q.27 When alkyl halide is heated with dry Ag_2O, it produces
(A) Ester (B) Ether
(C) Ketone (D) Alcohol

Q.28 In the following reaction X is

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

(A) CH_2Cl_2 (B) $CHCl_3$
(C) CH_3Cl (D) CCl_4

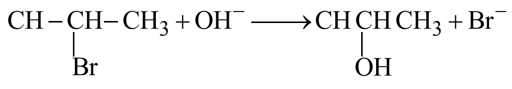
Q.29 Which of the following is liquid at room temperature
(A) CH_3I (B) CH_3Br
(C) C_2H_5Cl (D) CH_3F

Q.30 The hybridization state of carbon atoms in the product formed by the reaction of ethyl chloride with aqueous potassium hydroxide is
(A) sp (B) sp^2
(C) sp^3 (D) sp^3d

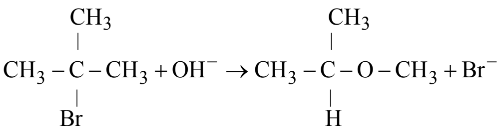
Q.31 Which of the following compounds does not undergo nucleophilic substitution reactions
(A) Vinyl chloride (B) Ethyl bromide
(C) Benzyl chloride (D) Isopropyl chloride

Q.32 Which of the following is the example of S_N2 reaction

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

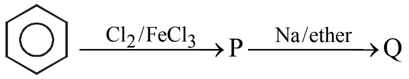
(B)

$CH-\underset{\substack{|\\Br}}{CH}-CH_3+OH^-\longrightarrow CH\underset{\substack{|\\OH}}{CH}CH_3+Br^-$

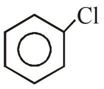
(C) $CH_3CH_2OH \xrightarrow{-H_2O} CH_2 = CH_2$

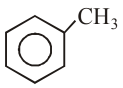
(D)

$CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\Br}}{C}}-CH_3+OH^-\to CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\H}}{C}}-O-CH_3+Br^-$

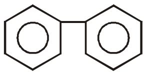
Q.33 Which of these do not form Grignard reagent
(A) CH_3F (B) CH_3Cl
(C) CH_3Br (D) CH_3I

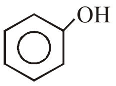
Q.34 The end product (Q) in the following sequence of reactions is


$\xrightarrow{Cl_2/FeCl_3} P \xrightarrow{Na/ether} Q$

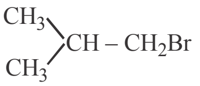
(A)


(B)


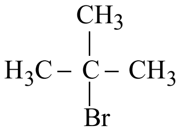
(C)


(D)


Q.35 Arrange the following compounds in increasing order of their boiling points.

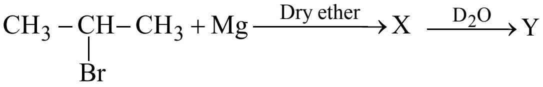
(I)

$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH-CH_2Br$

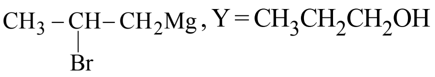
(II) $CH_3CH_2CH_2CH_2Br$

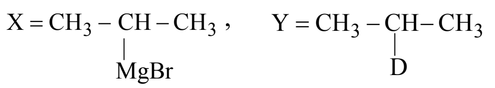
(III)

$H_3C-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\Br}}{C}}-CH_3$

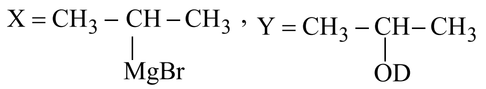
(A) (II) < (I) < (III) (B) (I) < (II) < (III)
(C) (III) < (I) < (II) (D) (III) < (II) < (I)

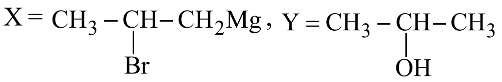
Q.36 Identify the products X & Y in the given reaction,


$CH_3-\underset{\substack{|\\Br}}{CH}-CH_3+Mg\xrightarrow{\text{Dry ether}}X\xrightarrow{D_2O}Y$

(A)

$X = CH_3-\underset{\substack{|\\Br}}{CH}-CH_2Mg,\ Y=CH_3CH_2CH_2OH$

(B) 
$X = CH_3-CH(MgBr)-CH_3$, $Y = CH_3-CH(D)-CH_3$

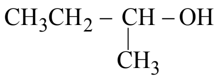
(C) 
$X = CH_3-CH(MgBr)-CH_3$, $Y = CH_3-CH(OD)-CH_3$

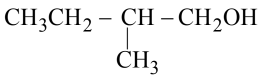
(D) 
$X = CH_3-CH(Br)-CH_2Mg$, $Y = CH_3-CH(OH)-CH_3$

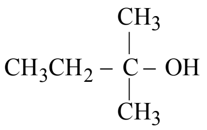
Q.37 The reaction of toluene with chlorine in presence of $FeCl_3$ gives predominantly –
(A) a mixture of o-and p-chlorotoluene.
(B) benzyl chloride
(C) m-Chlorotoluene
(D) benzoyl chloride.

Q.38 Ethylene dichloride and ethylidene chloride are isomeric compounds. The false statement about these isomers is that they
(A) are both hydrolysed to the same product.
(B) contain the same percentage of chlorine.
(C) are position isomers.
(D) react with alcoholic potash and give the same product.

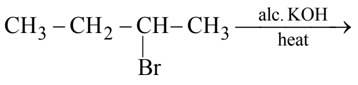
Q.39 Which of the following alcohols will yield the corresponding alkyl chloride on reaction with concentrated HCl at room temperature?
(A) $CH_3CH_2-CH_2-OH$

(B) 
$CH_3CH_2-CH(CH_3)-OH$

(C) 
$CH_3CH_2-CH(CH_3)-CH_2OH$

(D) 
$CH_3CH_2-C(CH_3)_2-OH$

Q.40 Which of the following reactions will give the major and minor products?

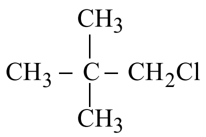

$CH_3-CH_2-CH(Br)-CH_3 \xrightarrow[\text{heat}]{\text{alc. KOH}}$

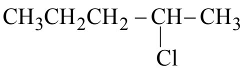
$CH_3-CH=CH-CH_3$ (a)
$+ CH_3-CH_2-CH=CH_2$ (b)

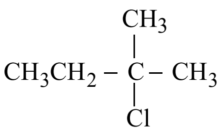
(A) (a) is major product & (b) is minor product.
(B) (a) is minor product & (b) is major product.
(C) Both (a) and (b) are major products.
(D) Only (b) is formed and (a) is not formed.

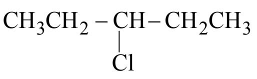
Q.41 Classify the following compounds as primary, secondary and tertiary halides.
(i) 1-Bromobut-2-ene
(ii) 4-Bromopent-2-ene
(iii) 2-Bromo-2-methylpropane
(A) (i) secondary, (ii) tertiary, (iii) primary
(B) (i) secondary, (ii) primary, (iii) tertiary
(C) (i) primary, (ii) tertiary, (iii) secondary
(D) (i) primary, (ii) secondary, (iii) tertiary

Q.42 Among the isomers of $C_5H_{11}Cl$, the one which is chiral is –

(i) 
$CH_3-C(CH_3)_2-CH_2Cl$
2,2-Dimethyl-1-chloropropane

(ii) 
$CH_3CH_2CH_2-CH(Cl)-CH_3$
2-Chloropentane

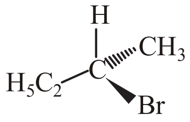
(iii) 
$CH_3CH_2-C(CH_3)(Cl)-CH_3$
2-Methyl-2-chlorobutane

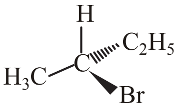
(iv) 
$CH_3CH_2-CH(Cl)-CH_2CH_3$
3-Chloropentane

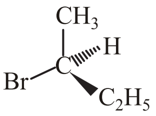
(A) (i) and (ii) (B) (i), (ii) and (iii)
(C) (i) and (iii) (D) only (ii)

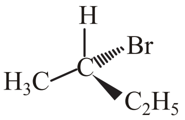
Q.43 Compound X reacts with alcoholic KOH to yield compound Y which on ozonlysis followed by reaction with Zn/H_2O gives methanal and propanal. Compound X is –
(A) 1-propanol (B) 1-butanol
(C) 1-chlorobutane (D) 1-chloropentane

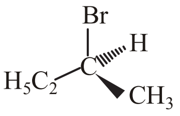
Q.44 Which of the following structures is enantiomeric with the molecule (I) given below:

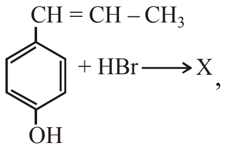

(I)

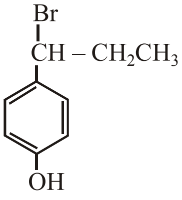
(A) 

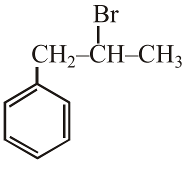
(B) 

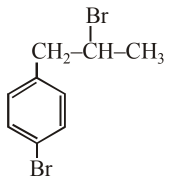
(C) 

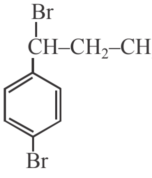
(D) 

Q.45  X in the reaction is

(A) 

(B) 

(C) 

(D) 

Q.46 The main difference in C – X bond of a haloalkane and a haloarene is –

(A) C– X bond in haloalkanes is shorter than haloarenes.

(B) In haloalkanes the C attached to halogen in C – X bond is sp^3 hybridised while in haloarenes it is sp^2 hybridised.

(C) C–X bond in haloarenes acquires a double bond character due to higher electronegativity of X than haloalkanes.

(D) haloalkanes are less reactive than haloarenes due to difficulty in C–X cleavage in haloalkanes.

Q.47 A mixture of 1-chloropropane and 2-chloropropane when treated with alcoholic KOH gives –

(A) prop-1-ene (B) prop-2-ene

(C) propanol. (D) None of these

Q.48 Which alkyl halide is preferentially hydrolysed by S_N1 mechanism?

(A) $(CH_3)_3CCl$ (B) $CH_3CH_2CH_2Cl$

(C) CH_3CH_2Cl (D) CH_3Cl

Q.49 Which one of the following is not correct order of boiling points of the alkyl/aryl halides?

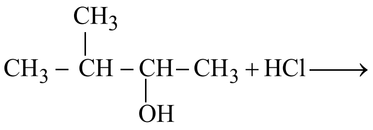
(A) $CHCl_3 > CH_2Cl_2$

(B) $CH_3(CH_2)_3Cl > CH_3(CH_2)_2Cl$

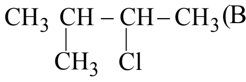
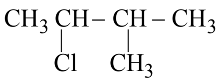
(C) $(CH_3)_3CCl > (CH_3)_2CHCH_2Cl$

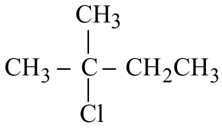
(D) $CH_3(CH_2)_3Cl > CH_3CH_2CHClCH_3$

Q.50 Halogen acids react with alcohols to form alkyl halides. The reaction follows a nucleophilic substitution mechanism. What will be the major product of the following reaction?



$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{CH}}}-\underset{\underset{OH}{|}}{CH}-CH_3 + HCl \longrightarrow$$

(A)  $CH_3\ \underset{\underset{CH_3}{|}}{CH}-\underset{\underset{Cl}{|}}{CH}-CH_3$ (B)  $CH_3\ \underset{\underset{Cl}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

(C)  $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_2CH_3$ (D) $CH_3CH_2CH_2CH_2CH_2Cl$

Q.51 Arrange the following alkyl halides in order of dehydrohalogenation; C_2H_5I, C_2H_5Cl, C_2H_5Br, C_2H_5F

(A) $C_2H_5F > C_2H_5Cl > C_2H_5Br > C_2H_5I$

(B) $C_2H_5I > C_2H_5Br > C_2H_5Cl > C_2H_5F$

(C) $C_2H_5I > C_2H_5Cl > C_2H_5Br > C_2H_5F$

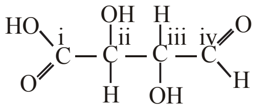
(D) $C_2H_5F > C_2H_5I > C_2H_5Br > C_2H_5Cl$

Q.52 An alkyl chloride produces a single alkene on reaction with sodium ethoxide and ethanol. The alkene further undergoes hydrogenation to yield 2-methylbutane. Identify the alkyl chloride from amongst the following

(A) $ClCH_2CH(CH_3)CH_2CH_3$ (B) $ClCH_2CH_2CH_2CH_3$

(C) $ClCH_2CH(CH_3)CH_2CH_3$ (D) $CH_3C(Cl)(CH_3)CH_2CH_3$

Q.53 Which of the carbon atoms present in the molecule given below are asymmetric?



(A) (i), (ii), (iii), (iv) (B) (ii), (iii)

(C) (i), (iv) (D) (i), (ii), (iii)

Q.54 A mixture of two haloalkanes was treated with sodium metal in ether solution. After the reaction, the product formed was 2-methylpropane. The two haloalkanes present in the mixture were

(A) 2-chloropropane and chloromethane

(B) chloropropane and chloroethane

(C) 2-chloropropane and chloroethane

(D) chloroethane and chloromethane.

Q.55 Which of the following alkyl halides will undergo S_N1 reaction most readily?

(A) $(CH_3)_3C–F$ (B) $(CH_3)_3C–Cl$

(C) $(CH_3)_3C–Br$ (D) $(CH_3)_3C–I$

Q.56 Identify the products in the reactions.

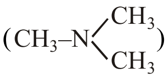
$RX + AgCN \rightarrow \_\_\_\_ + AgX;$

$RX + KCN \rightarrow \_\_\_\_ + KX$

(A) RCN, RCN (B) RCN, RNC

(C) RNC, RCN (D) RNC, RNC

Q.57 Chloromethane on treatment with excess of ammonia yields mainly

(A) N, N-dimethylmethanamine  $(CH_3–N\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix})$

(B) N-methylmethanamine ($CH_3–NH–CH_3$)

(C) methanamine (CH_3NH_2)

(D) mixture containing all these in equal proportion.

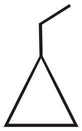
Q.58 Which of the following alkyl halides undergoes hydrolysis with aqueous KOH at the fastest rate?

(A) $CH_3CH_2CH_2Cl$ (B) CH_3CH_2Cl

(C) $CH_3CH_2CH_2CH_2Cl$ (D) $CH_3CH_2CH(Br)CH_3$

EXERCISE - 3 (NUMERICAL VALUE BASED QUESTIONS)

NOTE : The answer to each question is a NUMERICAL VALUE.

Q.1  $\xrightarrow[h\nu\text{ (monochlorination)}]{Cl_2}$ Products

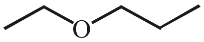
Total number of theoratically products (including stereo) are :

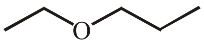
Q.2 In above question how many products are resolvable.

Q.3 In Q.1, how many fractions are present on fractional distillation.

Q.4 How many isomeric bromides having molecular formula $C_6H_{13}Br$ on conversion into Grignard reagent followed by treatment with water would yield 2,3-dimethylbutane?

Q.5 Sum of molecular mass of iodides produced in following reaction is

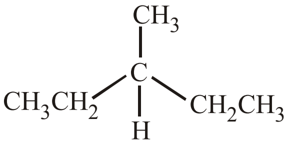
(a)  $\xrightarrow{\text{Conc. HI}}$

(b)  $\xrightarrow[\text{HI}]{\text{anhydrous}}$

(c) Ph – O – Me $\xrightarrow[\text{excess}]{\text{HI}}$

Q.6 The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is

Q.7 The maximum number of isomers (including stereoisomers) that are possible on monochlorination of the fol-



$CH_3CH_2-\overset{CH_3}{\underset{H}{C}}-CH_2CH_3$

EXERCISE - 4 [PREVIOUS YEARS JEE MAIN QUESTIONS]

Q.1 The reaction $(CH_3)_3\,CBr + H_2O \rightarrow (CH_3)_3\,COH + HBr$ is a **[AIEEE-2002]**

(A) Substitution reaction (B) Debromination reaction
(C) Rearrangement reaction (D) Elimination reaction

Q.2 The compound formed on heating chlorobenzene with chloral in the presence of concentrated sulphuric acid is

(A) gammexane (B) DDT **[AIEEE-2004]**
(C) freon (D) hexachloroethane

Q.3 Acetyl bromide reacts with excess of CH_3MgI followed by treatment with a saturated solution of NH_4Cl gives – **[AIEEE-2004]**

(A) acetone (B) acetamide
(C) 2-methyl-2-propanol (D) acetyl iodide

Q.4 The correct order of the thermal stability of hydrogen halides (H – X) is – **[AIEEE-2005]**

(A) $HF > HCl > HBr > HI$ (B) $HI > HBr > HCl > HF$
(C) $HI > HCl < HF > HBr$ (D) $HCl < HBr > HBr < HI$

Q.5 Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of – **[AIEEE-2005]**

(A) instability (B) insolubility
(C) steric hindrance (D) inductive effect

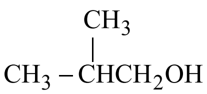
Q.6 Alkyl halides react with dialkyl copper reagents to give

(A) alkyl copper halides (B) alkenes **[AIEEE-2005]**
(C) alkenyl halides (D) alkanes

Q.7 Elimination of bromine from 2–bromobutane results in the formation of – **[AIEEE-2005]**

(A) predominantly 2–butene
(B) equimolar mixture of 1 and 2–butene
(C) predominantly 2–butyne
(D) predominantly 1–butene

Q.8 Among the following the one that gives positive iodoform upon reaction with I_2 and NaOH is – **[AIEEE 2006]**

(A) $C_6H_5CH_2CH_2OH$ (B) 

$CH_3-\overset{CH_3}{\overset{|}{C}}HCH_2OH$

(C) $PhCHOHCH_3$ (D) $CH_3CH_2CH(OH)CH_2CH_3$

Q.8 Which of the following is the correct order of decreasing S_N2 reactivity ? **[AIEEE 2007]**

(A) $RCH_2X > R_3CX > R_2CHX$
(B) $RCH_2X > R_2CHX > R_3CX$
(C) $R_3CX > R_2CHX > RCH_2X$
(D) $R_2CHX > R_3CX > RCH_2X$
(X = a halogen)

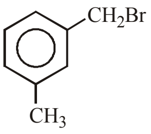
Q.10 The organic chloro compound, which shows complete stereochemical inversion during a S_N2 reaction , is **[AIEEE 2008]**

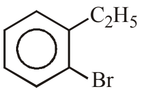
(A) $(CH_3)_3CCl$ (B) $(CH_3)_2CHCl$
(C) CH_3Cl (D) $(C_2H_5)_2CHCl$

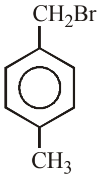
Q.11 A solution of (–) – 1-chloro-1–phenylethane in toluene racemises slowly in the presence of a small amount of $SbCl_5$, due to the formation of – **[JEE MAIN 2013]**

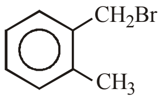
(A) carbanion (B) carbene
(C) carbocation (D) free radical

Q.12 Compound (A), C_8H_9Br, gives a white precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A). **[JEE MAIN 2013]**

(A) 

(B) 

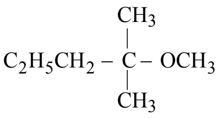
(C) 

(D) 

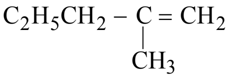
Q.13 The synthesis of alkyl fluorides is best accomplished by **[JEE MAIN 2015]**

(A) Sandmeyer's reaction (B) Finkelstein reaction
(C) Swarts reaction (D) Free radical fluorination

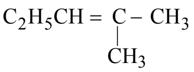
Q.14 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields : **[JEE MAIN 2016]**

(a) 

$C_2H_5CH_2-\overset{CH_3}{\underset{CH_3}{C}}-OCH_3$

(b) 

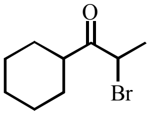
$C_2H_5CH_2-\underset{CH_3}{C}=CH_2$

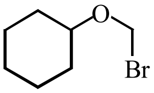
(c) 

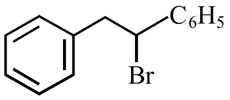
$C_2H_5CH=\underset{CH_3}{C}-CH_3$

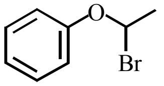
(A) (a) and (c) (B) (c) only
(C) (a) and (b) (D) All of these

Q.15 Which of the following, upon treatment with tert-BuONa followed by addition of bromine water, fails to decolourize the colour of bromine? **[JEE MAIN 2017]**

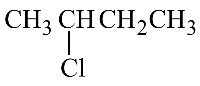
(A) 

(B) 

(C) 

(D) 

Q.16 The increasing order of the reactivity of the following halides for the S_N1 reaction is: **[JEE MAIN 2017]**

I. 

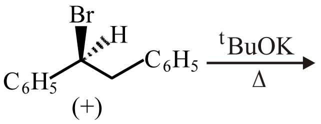
$CH_3\underset{Cl}{C}HCH_2CH_3$

II. $CH_3CH_2CH_2Cl$

III. $p-H_3CO-C_6H_4-CH_2Cl$

(A) (II) < (III) < (I) (B) (III) < (II) < (I)
(C) (II) < (I) < (III) (D) (I) < (III) < (II)

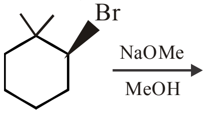
Q.17 The major product obtained in the following reaction is



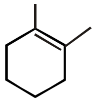
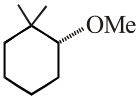
[JEE MAIN 2017]

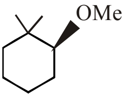
(A) (–) $C_6H_5CH(O^tBu)CH_2C_6H_5$
(B) (±) $C_6H_5CH(O^tBu)CH_2C_6H_5$
(C) $C_6H_5CH=CHC_6H_5$
(D) (+) $C_6H_5CH(O^tBu)CH_2C_6H_5$

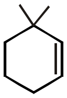
Q.18 The major product of the following reaction is



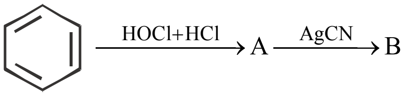
[JEE MAIN 2018]

(A) 
(B) 

(C) 

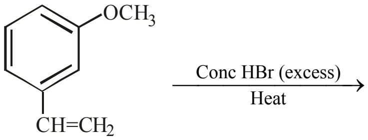
(D) 

Q.19 The compounds A and B in the following reaction are, respectively: **[JEE MAIN 2019 (Jan)]**

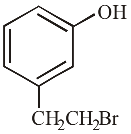


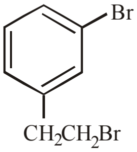
(A) A = Benzyl alcohol, B = Benzyl isocyanide
(B) A = Benzyl alcohol, B = Benzyl cyanide
(C) A = Benzyl chloride, B = Benzyl cyanide
(D) A = Benzyl chloride, B = Benzyl isocyanide

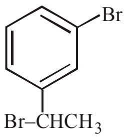
Q.20 The major product of the following reactions:

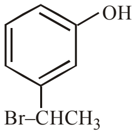


[JEE MAIN 2019 (April)]

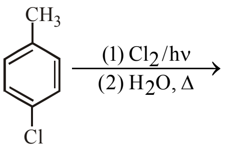
(A) 

(B) 

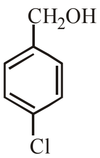
(C) 

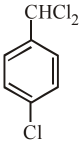
(D) 

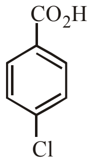
Q.21 The major product of the following reaction is:

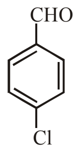


[JEE MAIN 2019 (APRIL)]

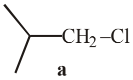
(A) 

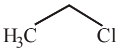
(B) 

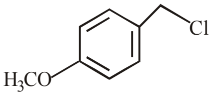
(C) 

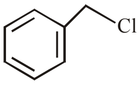
(D) 

Q.22 Increasing order of reactivity of the following compounds for S_N1 substitution is: **[JEE MAIN 2019 (APRIL)]**



a


b


c


d

(A) b < c < d < a (B) a < b < d < c
(C) b < a < d < c (D) b < c < a < d

Q.23 An ' Assertion' and a 'Reason' are given below. Choose the correct answer from the following options. **[JEE MAIN 2019 (APRIL)]**

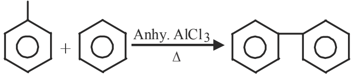
Assertion (A) : Vinyl halides do not undergo nucleophilic substitution easily.

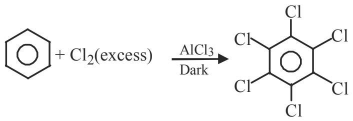
Reason (R) : Even though the intermediate carbocation is stabilized by loosely held π-electrons, the cleavage is difficult becuase of strong bonding.

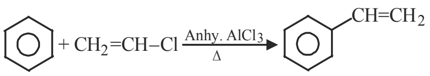
(A) Both A and R are wrong statements.
(B) Both A and R are correct statements and R is the correct explanation of A.
(C) Both A and R are correct statements but R is not the correct explanation of A.
(D) A is a correct statement but R is a wrong statement.

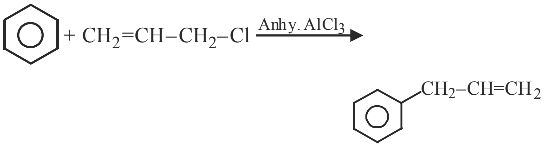
Q.24 The number of chiral carbons in chloramphenicol is ________ . **[JEE MAIN 2020 (JAN)]**

Q.25 Which of the following reactions are possible ? **[JEE MAIN 2020 (JAN)]**

(a) 

(b) 

(c) 

(d) 

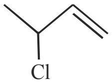
(A) a, b, c (B) b, d
(C) a, c, d (D) a, c

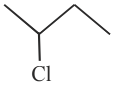
Q.26 Arrange the following compounds in order of dehydrohalogenation (E1) reaction.

[JEE MAIN 2020 (JAN)]

(a) 

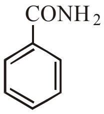
(b) 

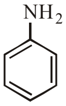
(c) 

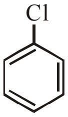
(d) 

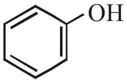
(A) c > b > d > a
(B) d > b > c > a
(C) b > c > d > a
(D) a > b > c > d

Q.27 Which of these will produce the highest yield in Friedel Crafts reaction? **[JEE MAIN 2020 (JAN)]**

(A) 

(B) 

(C) 

(D) 

EXERCISE - 5 [PREVIOUS YEARS AIPMT / NEET QUESTIONS]

Q.1 Which of the following undergoes nucleophilic substitution exclusively by S_N1 mechanism – **[AIPMT 2005]**

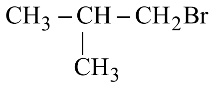
(A) Ethyl chloride (B) Isopropyl chloride
(C) Chlorobenzene (D) Benzyl chloride

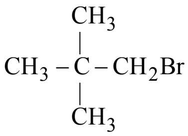
Q.2 In a S_N2 substitution reaction of the type

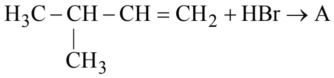
$R-Br+Cl^- \xrightarrow{DMF} R-Cl+Br^-$,

which one of the following has the highest relative rate? **[AIPMT 2008]**

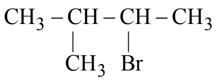
(A) CH_3CH_2Br (B) $CH_3-CH_2-CH_2Br$

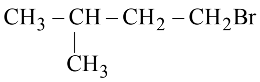
(C) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2Br$

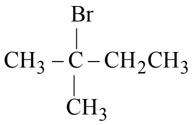
(D) 
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2Br$

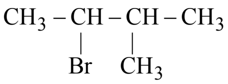
Q.3 
$H_3C-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2+HBr\rightarrow A$

A (Predominantly) is: **[AIPMT 2008]**

(A) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{Br}{|}}{CH}-CH_3$

(B) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2Br$

(C) 
$CH_3-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2CH_3$

(D) 
$CH_3-\underset{\underset{Br}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

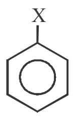
Q.4 Which of the following reactions is an example of nucleophilic susbtitution reaction? **[AIPMT 2009]**

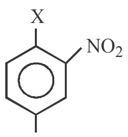
(A) $2\,RX+2\,Na \longrightarrow R-R+2\,NaX$
(B) $RX+H_2 \longrightarrow RH+HX$
(C) $RX+Mg \longrightarrow RMgX$
(D) $RX+KOH \longrightarrow ROH+KX$

Q.5 Which one is most reactive towards S_N1 reaction? **[AIPMT 2009]**

(A) $C_6H_5CH(C_6H_5)Br$ (B) $C_6H_5CH(CH_3)Br$
(C) $C_6H_5C(CH_3)(C_6H_5)Br$ (D) $C_6H_5CH_2Br$

Q.6 The correct order of increasing reactivity of C – X bond towards nucleophile in the following compounds is: **[AIPMT (PRE) 2010]**


I


II

$(CH_3)_3C-X$
III

$(CH_3)_2CH-X$
IV

(A) I < II < IV < III (B) II < III < I < IV
(C) IV < III < I < II (D) III < II < I < IV

Q.7 In the following reaction,

$C_6H_5CH_2Br \xrightarrow[2.\ H_3O^+]{1.\ Mg\ Ether} X$, the product 'X' is

[AIPMT (MAINS) 2010]

(A) $C_6H_5CH_2OCH_2C_6H_5$ (B) $C_6H_5CH_2OH$
(C) $C_6H_5CH_3$ (D) $C_6H_5CH_2CH_2C_6H_5$

Q.8 Consider the reactions :

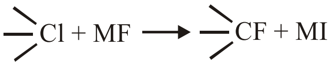
(i) $(CH_3)_2CH-CH_2Br \xrightarrow{C_2H_5OH} (CH_3)_2CH-CH_2OC_2H_5+HBr$

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

The mechanisms of reactions (i) and (ii) are respectively **[AIPMT (MAINS) 2011]**

(A) S_N1 and S_N2 (B) S_N1 and S_N1
(C) S_N2 and S_N2 (D) S_N2 and S_N1

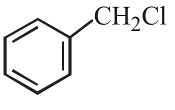
Q.9 In the replacement reaction



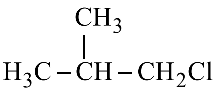
The reaction will be most favourable if M happens to be: **[AIPMT (MAINS) 2012]**

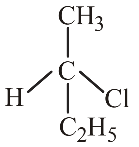
(A) Na (B) K
(C) Rb (D) Li

Q.10 Which of the following compounds will undergoes racemisation when solution of KOH hydrolyses? **[AIPMT 2014]**

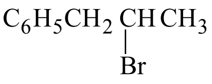
(A) 

(B) $CH_3CH_2CH_2Cl$

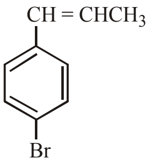
(C) 
$H_3C-\overset{\overset{CH_3}{|}}{CH}-CH_2Cl$

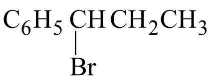
(D) 

Q.11 The reaction of $C_6H_5CH=CHCH_3$ with HBr produces **[AIPMT 2015]**

(A) 
$C_6H_5CH_2\underset{\underset{Br}{|}}{CH}CH_3$

(B) $C_6H_5CH_2CH_2CH_2Br$

(C) 

(D) 
$C_6H_5\underset{\underset{Br}{|}}{CH}CH_2CH_3$

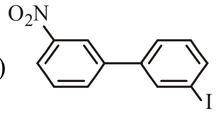
Q.12 Two possible stereo-structures of $CH_3CHOH.COOH$, which are optically active, are called **[RE-AIPMT 2015]**

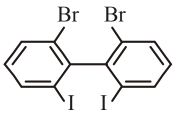
(A) Enantiomers (B) Mesomers
(C) Diastereomers (D) Atropisomers

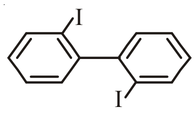
Q.13 In an S_N1 reaction on chiral centres, there is : **[RE-AIPMT 2015]**

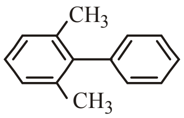
(A) 100% retention
(B) 100% inversion
(C) 100% racemization
(D) inversion more than retention leading to partial recemization.

Q.14 Which of the following biphenyl is optically active? **[NEET 2016 PHASE 1]**

(A)


(B)


(C)


(D)


Q.15 Which of the following can be used as the halide component for Friedel Crafts reaction? **[NEET 2016 PHASE 2]**

(A) Chlorobenzene (B) Bromobenzene
(C) Chloroethene (D) Isopropyl chloride

Q.16 Consider the reaction

$CH_3CH_2CH_2Br + NaCN \rightarrow CH_3CH_2CH_2CN + NaBr$

This reaction will be the fastest in **[NEET 2016 PHASE 2]**

(A) Ethanol (B) Methanol
(C) N, N'-dimethylformamide (DMF) (D) Water

Q.17 An example of a sigma bonded organometallic compound is : **[NEET 2017]**

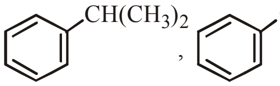
(A) Grignard's reagent (B) Ferrocene
(C) Cobaltocene (D) Ruthenocene

Q.18 Identify the major products P, Q and R in the following sequence of reactions: **[NEET 2018]**

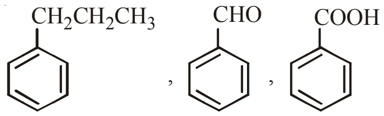

$+ CH_3CH_2CH_2Cl \xrightarrow{\text{Anhydrous AlCl}_3}$

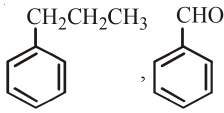
$P \xrightarrow[\text{(ii) } H_3O^+/\Delta]{\text{(i) } O_2} Q + R$

P Q R

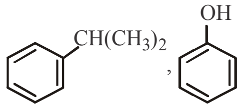
(A)


, $CH_3CH(OH)CH_3$

(B)


(C)


, $CH_3CH_2–OH$

(D)


, $CH_3 – CO – CH_3$

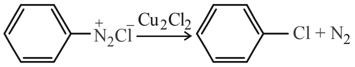
Q.19 The compound C_7H_8 undergoes the following reactions:

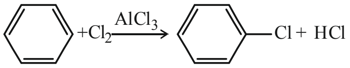
$$C_7H_8 \xrightarrow{3Cl_2/\Delta} A \xrightarrow{Br_2/Fe} B \xrightarrow{Zn/HCl} C$$

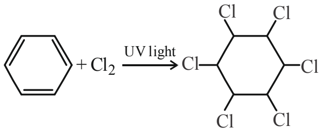
The product 'C' is **[NEET 2018]**

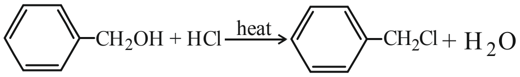
(A) 3-bromo-2,4,6-trichlorotoluene
(B) o-bromotoluene
(C) m-bromotoluene
(D) p-bromotoluene

Q.20 Among the following, the reaction that proceeds through an electrophilic substitution, is: **[NEET 2019]**

(A)


(B)


(C)


(D)


ANSWER KEY

EXERCISE - 1

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	A	D	B	D	A	A	C	B	B	D	A	C	A	A	A	B	A	C	C	B	A	C	A	A	A
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
A	C	D	D	B	A	C	B	C	C	C	C	B	A	B	A	A	C	C	C	C	C	C	A	D	B
Q	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72			
A	D	B	A	B	A	A	C	A	B	A	A	A	B	C	B	D	A	B	B	C	C	D			

EXERCISE - 2

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	D	A	A	D	B	A	C	B	B	D	A	B	B	A	A	B	A	D	B	D	B	A	B	D	A
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
A	D	B	B	A	C	A	A	A	C	C	C	A	A	D	A	D	D	C	A	A	B	A	A	C	C
Q	51	52	53	54	55	56	57	58																	
A	B	C	B	A	D	C	C	D																	

EXERCISE - 3

Q	1	2	3	4	5	6	7
A	8	6	5	2	454	5	8

EXERCISE - 4

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
A	A	B	C	A	C	D	A	C	B	C	C	D	C	D	B	C	C	D	D	D	D	C	D	2	B	B	C

EXERCISE - 5

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
A	D	A	C	D	C	A	C	A	C	D	D	A	D	B	D	C	A	D	C	B

HALOALKANES AND HALOARENES

TRY IT YOURSELF

(1) No product because KF in C_2H_5OH cannot replace – Cl.

(2) (B)

(3) (D)

(4) I > II > III > IV

From I to III C – X bond energy increases hence S_N2 reactivity decreases. In IV compound alkyl group is large.

(5) (D)

(6) (D)

(7) (D)

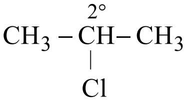
(8) **(D).** Electrophillic attack of Cl^+

(9) (C)

(10) (C)

CHAPTER-9 :
HALOALKANES AND HALOARENES
EXERCISE-1

(1) **(A)**. Isopropyl chloride



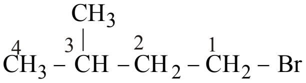
$CH_3-\underset{\underset{Cl}{|}}{\overset{2^\circ}{CH}}-CH_3$

chlorine atom is attached to 2°carbon atom.

(2) **(D).** An allylic halide is an alkyl halide in which there are one or more halogen atoms on allylic carbons. Except 4- Bromobut -1-ene, all are allylic halides.

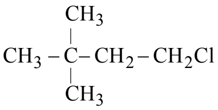
$Br-CH_2-CH_2-CH=CH_2$

(3) **(B).**



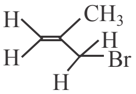
$\overset{4}{C}H_3-\overset{\overset{CH_3}{|}}{\overset{3}{C}H}-\overset{2}{C}H_2-\overset{1}{C}H_2-Br$

(4) **(D).** Neohexyl chloride is a primary halide as in it Cl-atom is attached to a primary carbon.



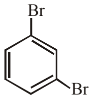
$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_2Cl$

(5) **(A).** The IUPAC name of

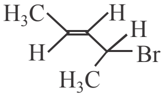


is 3-bromo-2-methylpropene

(6) **(A).** IUPAC name of m-Dibromobenzene is 1,3-Dibromobenzene



(7) **(C).** The IUPAC name of



is 4-bromopent-2-ene.

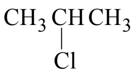
(8) **(B).**

(i) $CH_3CH_2CH_2Cl$

Common name : n-propyl chloride

IUPAC name : 1-chloro propane

(ii)

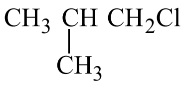


$CH_3\underset{\underset{Cl}{|}}{CH}CH_3$

Common name : Isopropyl chloride

IUPAC name : 2-chloro propane

(iii)

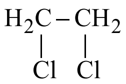


$CH_3\underset{\underset{CH_3}{|}}{CH}CH_2Cl$ Common name : Isobutylchloride

IUPAC name : 1-chloro-2-methylpropane

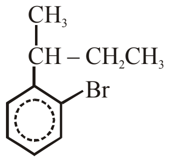
(9) **(B).** Vicinal dihalides (halogen atoms are present on the adjacent carbon atoms).

It is also known as alkylene dihalide.



$\underset{\underset{Cl}{|}}{H_2C}-\underset{\underset{Cl}{|}}{CH_2}$

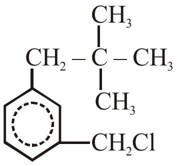
(10) **(D).** (i)



1-bromo-2-(1-methylpropyl) benzene

(Aryl halide)

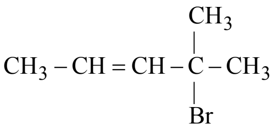
(ii)



3-(2, 2-dimethyylpropyl) benzylchloride

(Benzylic, Primary)

(iii)



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

4-bromo-4-methylpent-2-ene

(Allylic, Tertiary)

(11) **(A).** Allylic halides are the compounds in which the halogen atom is bonded to an sp^3-hybridised carbon atom next to carbon-carbon double bond (C = C) i.e. to an allylic carbon.

(12) **(C).** The dihalo-compounds having same type of halogen atoms on same carbon atom are known as geminal halides (halogen atoms are present on the same carbon atom). These are also called alkylidene dihalides.

(13) **(A).** The IUPAC name of tertiary butyl chloride is 2-chloro-2-methypropane $(CH_3)_3CCl$

(14) **(A).** $CH_3COOAg+Br_2\xrightarrow{CS_2}CH_3Br+AgBr+CO_2$

(15) **(A).** Alkyl iodides are often prepared by the reaction of alkyl chlorides/bromides with NaI in dry acetone.

$R-X+NaI\rightarrow R-I+NaX$

$X=Cl, Br$

(16) **(B).** Direct halogenation of alkanes give mixture of alkyl halides. For example,

$$CH_4+Cl_2\xrightarrow{h\nu}CH_3Cl+CH_2Cl_2+CHCl_3+CCl_4$$

(17) **(A).** $C_2H_5OH\xrightarrow[Na_2CO_3]{KI}CHI_3$

(18) **(C).** $C_2H_5-O-C_2H_5+2HI\rightarrow\underset{\text{Ethyliodide}}{2C_2H_5I}+H_2O$

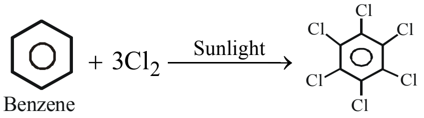
(19) **(C).** $CH_3COCH_3+3I_2+4NaOH\rightarrow$

$CHI_3+3Na+CH_3COONa+3H_2O$

(20) **(B).** $C_2H_5OH+SOCl_2\xrightarrow{\text{Pyridine}}C_2H_5Cl+SO_2+HCl$

(21) **(A).**

$CH_3-CH=CH_2+HBr\xrightarrow[\text{rule}]{\text{Markovnikov's}}CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$

(22) **(C).** 
Benzene BHC

(23) **(A).** $CH_3CH{=}CH_2 + H{-}I \rightarrow \underset{\text{(Minor)}}{CH_3CH_2CH_2I} + \underset{\text{(Major)}}{CH_3CHICH_3}$

(24) **(A).** Iodination of benzene occur in the presence of oxidising agent i.e., HNO_3.

(25) **(A).** All the hydrogen atoms in 2, 2-dimethylpropane are equivalent, hence it can form only one monochlorinated product.

(26) **(C).** The preparation of alkyl chloride is carried out either by passing dry hydrogen chloride gas through a solution of alcohol or by heating a solution of alcohol in concentrated aqueous acid.

(27) **(D).** p- isomer is symmetrical hence closely packed due to which it shows higher boiling point than o- and m-isomers.

(28) **(D).** The density increases with increase in number of carbon atoms, halogen atoms and atomic mass of halogen atoms.
(i) < (ii) < (iii)

(29) **(B).** For the same halogen, boiling point of alkyl halide decreases as the size of the alkyl group decreases. For isomeric alkyl halides, boiling point decreases as branching increases. So the decreasing order of boiling point is
$CH_3CH_2CH_2CH_2Cl > CH_3CH_2CH_2Cl$
$> CH_3CH(CH_3)CH_2Cl > (CH_3)_3CCl$

(30) **(A).** For the same alkyl halide, boiling point increases as the mass of halogen increases.

(31) **(C).** Boiling point of isomeric dihalobenzenes are very nearly the same. However, the para-isomers are high melting as compared to their ortho and meta-isomer. It is due to symmetry of para-isomer that fits in crystal lattice better as compared to ortho and meta-isomers.
(iii) > (i) ≥ (ii)

(32) **(B).** Though polar, alkyl halides cannot form hydrogen bonds with water hence they are insoluble in water.

(33) **(C).** $\underset{\text{Ethyl iodide}}{C_2H_5I} + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Ethyl magnesium iodide}}{C_2H_5-Mg-I}$

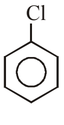
(34) **(C).** $Ag_2O + H_2O \rightarrow 2AgOH$

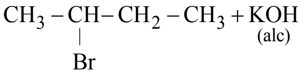
$C_2H_5Br + AgOH \rightarrow C_2H_5OH + AgBr$

(35) **(C).** $C_2H_5Cl + 2Na + ClC_2H_5 \xrightarrow[\text{Ether}]{\text{Dry}} C_2H_5-C_2H_5 + 2NaCl$

(36) **(C).** $2CHCl_3 + O_2 \xrightarrow[\text{air}]{\text{Light}} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$

(37) **(B).** $\underset{\text{more reactive}}{C_2H_5-Cl} > \underset{\text{less reactive}}{C_6H_5-CH_2-Cl}$

(38) **(A).** $CH_3-Cl > CH_3-CH_2-Cl >$ 

(39) **(B).** 
$\underset{\displaystyle Br}{CH_3-\underset{|}{CH}}-CH_2-CH_3 + \underset{\text{(alc)}}{KOH}$

$\xrightarrow{\text{Saytzeff's rule}} CH_3-CH=CH-CH_3 + KBr + H_2O$

(40) **(A).** $4C_2H_5Br + 4Pb/Na \rightarrow \underset{\substack{\text{Tetra Ethyl lead}\\\text{(TEL)}}}{(C_2H_5)_4Pb} + 4NaBr$

(41) **(A).** $CH_3CH_2CH_2CH_2-Cl + KOH(alc.)$

$\rightarrow \underset{\text{1-butene}}{CH_3CH_2-CH=CH_2} + KCl + H_2O$

(42) **(C).** $CH_3Br + 2Na + Br-CH_3 \xrightarrow[\text{Ether}]{\text{Dry}} CH_3CH_3 + 2NaBr$

(43) **(C).** It is Wurtz fittig reaction

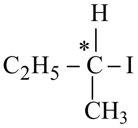
$C_6H_5Br + CH_3Br \xrightarrow[\text{Ether}]{\text{Na}} C_6H_5CH_3 + 2NaBr$

(44) **(C).** It is a common method to prepare alkanes. Methane cannot be prepared by Wurtz reaction.

$CH_3Br + 2Na + BrCH_3 \rightarrow \underset{\text{ethane}}{C_2H_6} + 2NaBr$

(45) **(C).** Solvolysis is related to stability of carbocation formed and among these benzyl carbocation is most stable. So, it will undergo solvolysis readily.

(46) **(C).** $C_2H_5Br + KCN \rightarrow \underset{\text{Propane nitrile}}{C_2H_5CN} + KBr$

(47) **(C).** It has asymmetric carbon atom which is joined to four different groups hence it will give optically active products or a pair of enantiomers. 
$C_2H_5-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{\overset{*}{C}}}-I$

(48) **(A).** Allylic and benzylic halides show high reactivity towards the S_N1 reaction. The carbocation thus formed gets stabilised through resonance.

(49) **(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 most reactive.

(50) **(B).** Butan-2-ol has four different groups attached to the tetrahedral carbon and as expected is chiral.

(51) **(D).** I is good leaving group so S_N2 reaction occur faster.

(52) **(B).** Aromatic halides are less reactive than alkyl or aralkyl halides.

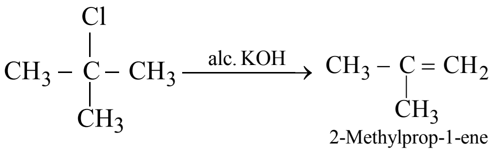
(53) **(A).** Inversion of configuration takes place in S_N2 mechanism.

(54) **(B).** $C_2H_5Cl + KOH\,(aq) \rightarrow C_2H_5OH + KCl$

(55) **(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.

(56) **(A).** Order of reactivity of different halo compounds towards nucleophilic substitution reactions are:
Allyl chloride > Vinyl chloride > Chlorobenzene

(57) **(C).** 

$$CH_3-\underset{CH_3}{\overset{Cl}{C}}-CH_3 \xrightarrow{\text{alc. KOH}} CH_3-\underset{CH_3}{C}=CH_2$$

2-Methylprop-1-ene

(58) **(A).** $C_2H_5I \xrightarrow[\text{alcohol}]{Zn-Cu} C_2H_6 + HI$

(59) **(B).** $CH_4 \xrightarrow[+3X]{-3H} CHX_3 \ (X = Cl, Br, I)$

(60) **(A).** DDT is formed by reaction of chloral with chloro benzene.

(61) **(A).** Methylene chloride harms the human central nervous system.

(62) **(A).** If $CHCl_3$ sample contains phosgene $(COCl_2)$ then it will give a white ppt. When treated with cold $AgNO_3$.

(63) **(B).** Chloroform is oxidised to a poisonous gas, phosgene $(COCl_2)$ by atmospheric gas.

$$CHCl_3 + O \rightarrow COCl_2 + HCl$$

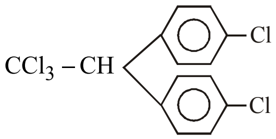
(64) **(C).** Freon (CCl_2F_2) is an odourless, non-corrosive, non toxic gas which is stable even at high temperatures and pressures. It has low boiling point, low specific heat and can be easily liquified by applying pressure at room temperature. It is therefore, widely used in refrigerant (cooling agent) in refrigerators and air conditioners.

(65) **(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 vapours. It forms highly poisonous phosgene gas

$$CCl_4 + H_2O \rightarrow \underset{\text{Phosgene}}{COCl_2} + 2HCl$$

(66) **(D).** At room temperature iodoform is the yellow solid.

(67) **(A).** DDT



5 chlorine atoms.

(68) **(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.

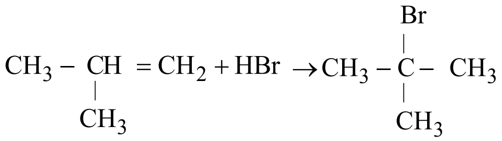
(69) **(B).** Inhalation of $CHCl_3$ vapours produces loss of consciousness and is therefore, used as a general anaesthetic agent in surgery.

(70) **(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.

(71) **(C).** Chlorofluorocarbons (CFC's) or freons are used as refrigerant in refrigerators and air conditioners.

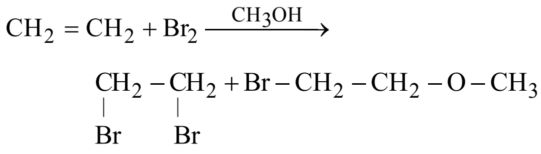
(72) **(D).** All the given points about freons are correct.

EXERCISE-2

(1) **(D).** 

$$CH_3-\underset{CH_3}{CH}=CH_2 + HBr \rightarrow CH_3-\underset{CH_3}{\overset{Br}{C}}-CH_3$$

2-bromo-2-methyl propane

(2) **(A).** 

$$CH_2=CH_2 + Br_2 \xrightarrow{CH_3OH} \underset{Br}{CH_2}-\underset{Br}{CH_2} + Br-CH_2-CH_2-O-CH_3$$

(3) **(A).** $CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2$

$$CH_3CH_2OH + Cl_2 \rightarrow CH_3CHO + HCl$$

$$CH_3CHO + Cl_2 \xrightarrow{Ca(OH)_2} CHCl_3 + (CH_3COO)_2Ca$$

(4) **(D).** CHI_3 gives a yellow ppt. of AgI.

(5) **(B).** $C_6H_5-CH_2-Cl + KCN(aq) \rightarrow C_6H_5-CH_2-C\equiv N + KCl$

(6) **(A).** $CHI_3 + 6Ag + I_3CH \rightarrow \underset{\text{Acetylene}}{CH\equiv CH} + 6AgI$

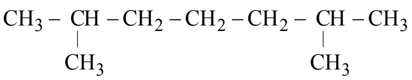
(7) **(C).** $CH_2Br-C\equiv C-CH_2Br \xrightarrow[\Delta]{Zn} CH_2=C=C=CH_2$

(8) **(B).** $C_6H_5-CH_2-Cl \xrightarrow[(aq)]{NaOH}$

$$C_6H_5-CH_2-OH \xrightarrow{\text{dil } HNO_3} C_6H_5-CHO$$

White ppt of AgCl are obtained.

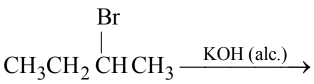
(9) **(B).** $\underset{\text{Chloroform}}{CHCl_3} + \underset{\text{Conc.}}{HNO_3} \rightarrow \underset{\text{Chloropicrin}}{CCl_3-NO_2} + H_2O$

(10) **(D).** 

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

has four methyl groups on the corner so it can produce four derivatives.

(11) **(A).** $CH_2=CH-Cl + HCl \rightarrow \underset{\text{1,1-dichloro ethane}}{CH_3-CHCl_2}$

(12) **(B).** 

$$\underset{\text{2-Bromobutane}}{CH_3CH_2\overset{Br}{CH}CH_3} \xrightarrow{\text{KOH (alc.)}}$$

$$\underset{\text{2-Butene (80\%)}}{CH_3CH=CHCH_3} + \underset{\text{1-Butene (20\%)}}{CH_3CH_2CH=CH_2}$$

In elimination reaction of alkyl halide major product is obtained according to Saytzeff's rule, which states that when two alkenes may be formed, the alkene which is most substituted one predominates.

(13) **(B).** $\underset{\text{Chlorol}}{CCl_3CHO} + NaOH \xrightarrow{\text{Boil}} \underset{\text{Chloroform}}{CHCl_3} + HCOONa$

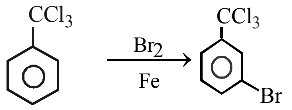
(14) **(A).** Acetone forms chloroform when heated with bleaching powder.

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

$$CH_3COCH_3 + 3Cl_2 \rightarrow CCl_3COCH_3 + 3HCl$$

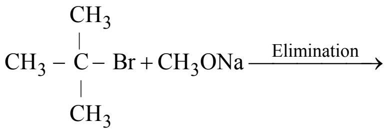
$$2CCl_3COCH_3 + Ca(OH)_2 \rightarrow \underset{\text{Chloroform}}{2CHCl_3} + (CH_3COO)_2Ca$$

(15) **(A).**

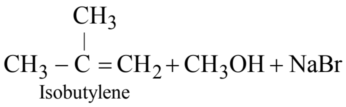


As –CCl_3 is a m-directing group.

(16) **(B).**



$$CH_3 - \overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}} - Br + CH_3ONa \xrightarrow{\text{Elimination}}$$

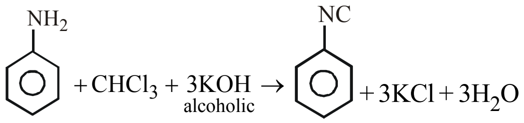


$$\underset{\text{Isobutylene}}{CH_3 - \overset{\overset{\large CH_3}{|}}{C} = CH_2} + CH_3OH + NaBr$$

$$CH_3ONa \rightarrow CH_3O^- + Na^+$$

Methoxide ion (CH_3O^-) is a strong base, therefore it abstract proton from 3° alkyl halide and favours elimination reaction.

(17) **(A).**



(18) **(D).** $CH_3CH_2OH + Cl_2 \rightarrow CH_3CHO + 2HCl$

$$CH_3CHO + 3Cl_2 \rightarrow \underset{\text{Chloral}}{CCl_3\,CHO} + 3HCl$$

(19) **(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.

(20) **(D).** Density of alkyl halide increases as the size of halogen atom increases. $RF < RCl < RBr < RI$

(21) **(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.

(22) **(A).** CH_3Cl have one Cl atom which is more electronegative so it will have highest dipole moment.

(23) **(B).** $\%\text{ of chlorine} = \dfrac{\text{Mass of chlorine}}{\text{Mass of organic compound}} \times 100$

$$\text{Chloral } (CCl_3CHO) = \frac{106.5}{147.5} \times 100 = 72.20$$

$$\text{Pyrene } (CCl_4) = \frac{142}{154} \times 100 = 92.20$$

$$\text{Gammexene } (C_6H_6Cl_6) = \frac{213}{291} \times 100 = 73.19$$

(24) **(D).** $CH_3COCl + H_2 \xrightarrow[\text{Reduction}]{\text{Pd}} CH_3CHO + HCl$

(25) **(A).** Because it float over chloroform and prevent its oxidation.

(26) **(D).** $\underset{\text{chloroform}}{HCCl_3} + 6Ag + \underset{\text{chloroform}}{Cl_3CH} \xrightarrow{\text{heat}} HC \equiv \underset{\text{Acetylene}}{CH} + 6AgCl$

Thus in this reaction acetylene (HC≡CH) is produced.

(27) **(B).** Alkyl halide on reaction with dry silver oxide furnish ether. $2CH_3Cl + Ag_2O \xrightarrow{\Delta} \underset{\text{(methoxy methane)}}{CH_3OCH_3} + 2AgCl$

(28) **(B).**

$$\underset{\text{(X)}}{CH_3NH_2} + CHCl_3 + 3KOH \rightarrow 3KCl + CH_3NC + 3H_2O$$

(29) **(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.

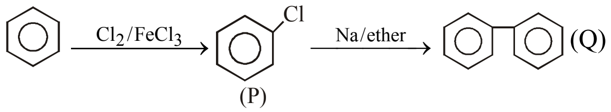
(30) **(C).** $CH_3 - CH_2 - Cl + \text{aq. KOH} \rightarrow \underset{\text{Ethyl alcohol}}{\overset{sp^3}{CH_3} - \overset{sp^3}{CH_2} - OH} + KCl$

(31) **(A).** As a result of resonance, the carbon-chloride bond acquires some double bond character. Hence, vinyl chloride does not undergo nucleophillic substitution reactions.

(32) **(A).** Only 1° alkyl halides, i.e. CH_3Br undergoes S_N2 reaction.

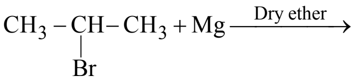
(33) **(A).** The C–F bond energy is maximum in CH_3F. Thus fluoride is the less reactive to form the grignard reagent with Mg.

(34) **(C).**

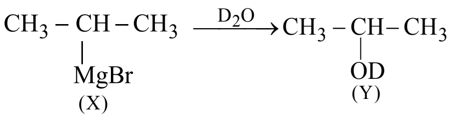


(35) **(C).** Boiling point increases as the branching decreases.

(36) **(C).**

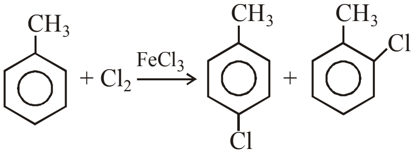


$$CH_3 - \underset{\underset{\large Br}{|}}{CH} - CH_3 + Mg \xrightarrow{\text{Dry ether}}$$



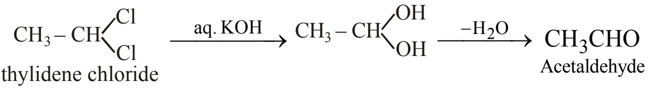
$$\underset{\text{(X)}}{CH_3 - \underset{\underset{\large MgBr}{|}}{CH} - CH_3} \xrightarrow{D_2O} \underset{\text{(Y)}}{CH_3 - \underset{\underset{\large OD}{|}}{CH} - CH_3}$$

(37) **(A).**



(38) **(A).** On hydrolysis both gives different compounds.

$$\underset{\text{(Ethylene dichloride)}}{CH_2Cl - CH_2Cl} \xrightarrow{\text{aq. KOH}} \underset{\text{(Glycol)}}{CH_2OH - CH_2OH}$$



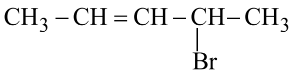
$$CH_3-CH\begin{matrix}Cl\\Cl\end{matrix}\xrightarrow{\text{aq. KOH}}CH_3-CH\begin{matrix}OH\\OH\end{matrix}\xrightarrow{-H_2O}CH_3CHO$$

Ethylidene chloride   Acetaldehyde

(39) **(D).** 3° alcohols being most reactive, react with conc. HCl at room temperature.

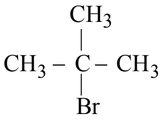
(40) **(A).** According to Saytzeff's rule, the more substituted product is more stable and is formed as major product. Hence (a) is the major product (80%) while (b) is the minor (20%) and less stable product.

(41) **(D).** $CH_3CH=CH-CH_2Br$,
1-Bromobut-2-ene (primary)



$$CH_3-CH=CH-\underset{\substack{|\\Br}}{CH}-CH_3$$

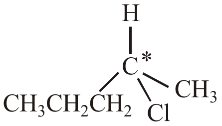
4-Bromopent-2-ene (secondary)



$$CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\Br}}{C}}-CH_3$$

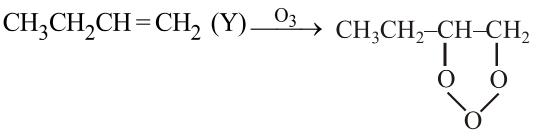
2-Bromo-2-methylpropane (tertiary)

(42) **(D).**



2-Chloropentane has a chiral carbon atom.

(43) **(C).** $CH_3CH_2CH_2CH_2Cl\ (X)\xrightarrow[\Delta]{\text{alc. KOH}}$

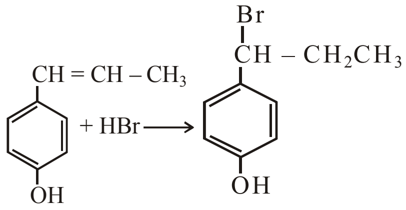


$$CH_3CH_2CH=CH_2\ (Y)\xrightarrow{O_3}CH_3CH_2-CH-CH_2 \text{ (ozonide: O–O–O bridge)}$$

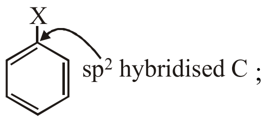
$$\xrightarrow{Zn/H_2O}CH_3CH_2CHO+HCHO$$

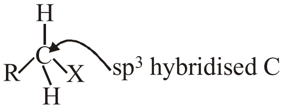
(44) **(A).** Compound (A) is enantiomer of compound (I) because the configuration of two groups, i.e., CH_3 and C_2H_5 in them is reversed at the chiral carbon.

(45) **(A).**

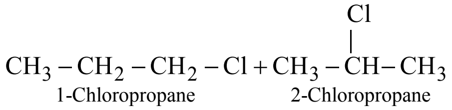


(46) **(B).** In haloarenes, carbon of C – X is sp^2 hybridised while in haloalkanes it is sp^3 hybridised,





(47) **(A).**



$$CH_3-CH_2-CH_2-Cl+CH_3-\overset{\substack{Cl\\|}}{CH}-CH_3$$

1-Chloropropane   2-Chloropropane

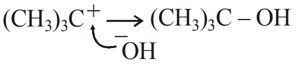
$$\xrightarrow{\text{alc. KOH}}CH_3-CH=CH_2$$

Prop-1-ene

(48) **(A).** S_N1 mechanism

(i) $(CH_3)_3CCl\rightarrow(CH_3)_3C^++Cl^-$
3° carbocation

(ii)

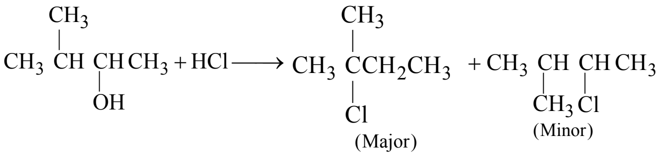


$$(CH_3)_3C^+\xrightarrow{\ \ }(CH_3)_3C-OH \quad (\overset{-}{O}H)$$

For S_N1 mechanism the reactivity of carbocation are 3° > 2° > 1°.

(49) **(C).** $(CH_3)_3CCl > (CH_3)_2CHCH_2Cl$ is not correct as boiling point of $(CH_3)_3CCl$ is smaller than $(CH_3)_2CHCH_2Cl$. It is due to large surface area and shorter alkyl chain.

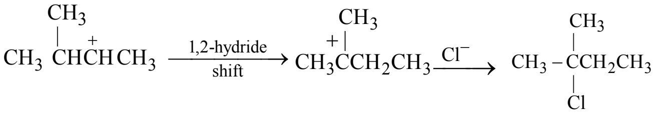
(50) **(C).**



$$CH_3\overset{\substack{CH_3\\|}}{CH}\underset{\substack{|\\OH}}{CH}CH_3+HCl\longrightarrow CH_3\overset{\substack{CH_3\\|}}{\underset{\substack{|\\Cl}}{C}}CH_2CH_3+CH_3\underset{\substack{|\\CH_3}}{CH}\underset{\substack{|\\Cl}}{CH}CH_3$$

(Major)   (Minor)

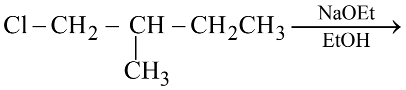
The intermediate in the reaction is secondary carbocation that can change to more stable tertiary carbocation by 1, 2-hydride shift.



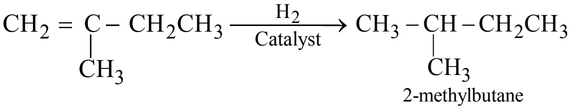
$$CH_3\overset{\substack{CH_3\\|}}{CH}\overset{+}{C}HCH_3\xrightarrow[\text{shift}]{\text{1,2-hydride}}CH_3\overset{\substack{CH_3\\+|}}{C}CH_2CH_3\xrightarrow{Cl^-}CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\Cl}}{C}}CH_2CH_3$$

(51) **(B).** The reactivity order can be explained on the basis of C – X bond strength. Lower the bond strength, higher is the reactivity.

(52) **(C).**



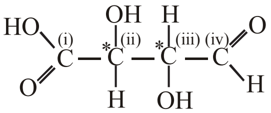
$$Cl-CH_2-\underset{\substack{|\\CH_3}}{CH}-CH_2CH_3\xrightarrow[\text{EtOH}]{\text{NaOEt}}$$



$$CH_2=\underset{\substack{|\\CH_3}}{C}-CH_2CH_3\xrightarrow[\text{Catalyst}]{H_2}CH_3-\underset{\substack{|\\CH_3}}{CH}-CH_2CH_3$$

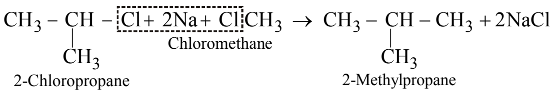
2-methylbutane

(53) **(B).**



(ii) and (iii) carbon atoms are asymmetric.

(54) **(A).**



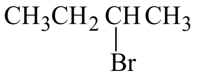
$$CH_3-\underset{\substack{|\\CH_3}}{CH}-\boxed{Cl+2Na+Cl}CH_3\rightarrow CH_3-\underset{\substack{|\\CH_3}}{CH}-CH_3+2NaCl$$

2-Chloropropane   Chloromethane   2-Methylpropane

(55) **(D).** As C – I bond is weakest, $(CH_3)_3C–I$ will undergo S_N1 reaction most readily.

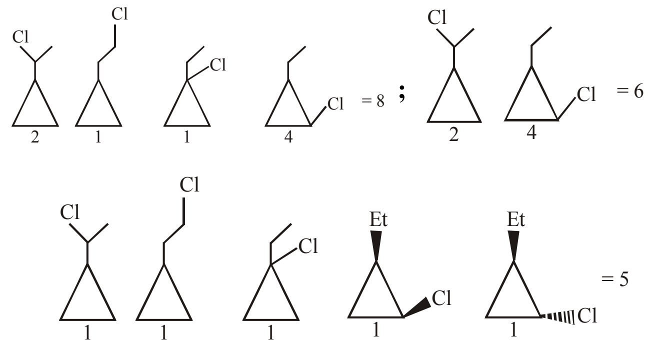
(56) **(C).** $RX + AgCN \rightarrow RNC + AgX; RX + KCN \rightarrow RCN + KX$
Both C and N can donate electron pairs. Since KCN is predominantly ionic and C – C bond is more stable than C – N bond in case of KCN, attack takes place through carbon atom.
AgCN is predominantly covalent hence only nitrogen pair is available for bonding resulting in formation of isocyanide.

(57) **(C).** $$\underset{\text{Chloromethane}}{CH_3Cl} + \underset{\text{(excess)}}{NH_3} \rightarrow \underset{\text{Methanamine}}{CH_3NH_2} + HCl$$
Primary amine is obtained as a major product by taking large excess of ammonia.

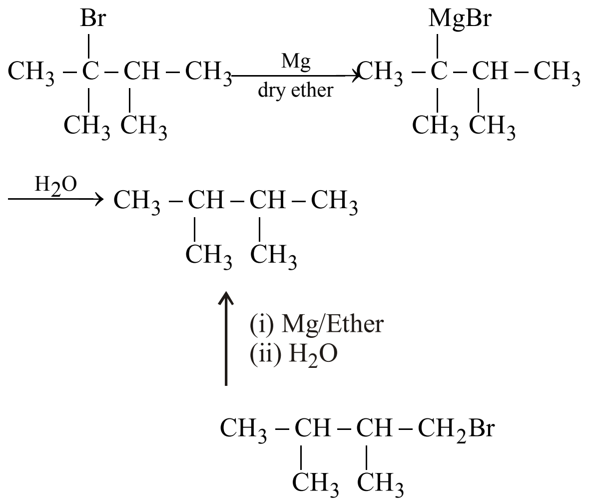
(58) **(D).** 
$\underset{\underset{Br}{|}}{CH_3CH_2CHCH_3}$ will undergo hydrolysis at the fastest rate because rate of reaction for hydrolysis of alkyl halides is in the order 3° > 2° > 1°.

EXERCISE-3

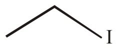
(1) (8), (2) (6), (3) (5).

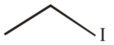


(4) **2.**


$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}-\underset{\underset{CH_3}{|}}{CH}-CH_3 \xrightarrow[\text{dry ether}]{Mg} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{MgBr}{|}}{C}}-\underset{\underset{CH_3}{|}}{CH}-CH_3$$
$$\xrightarrow{H_2O} CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$$
$$\uparrow \text{(i) Mg/Ether} \quad \text{(ii) } H_2O$$
$$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_2Br$$

(5) **454.**

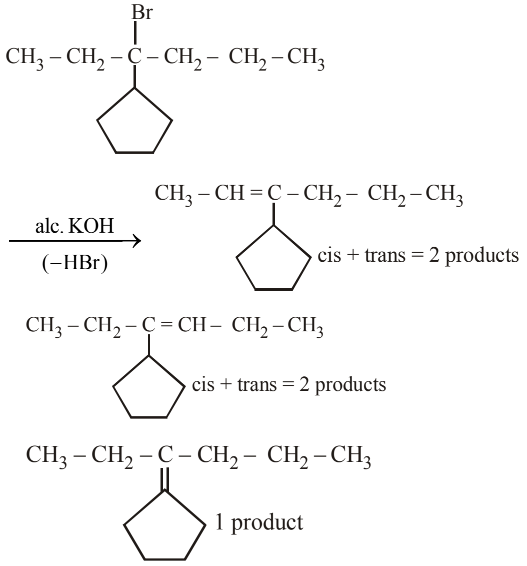
(a)  156 $I = 127$ $C_2H_5 = 29$

(b)  156 $I = 127$ $Me = 15$

(c) Me-I 142

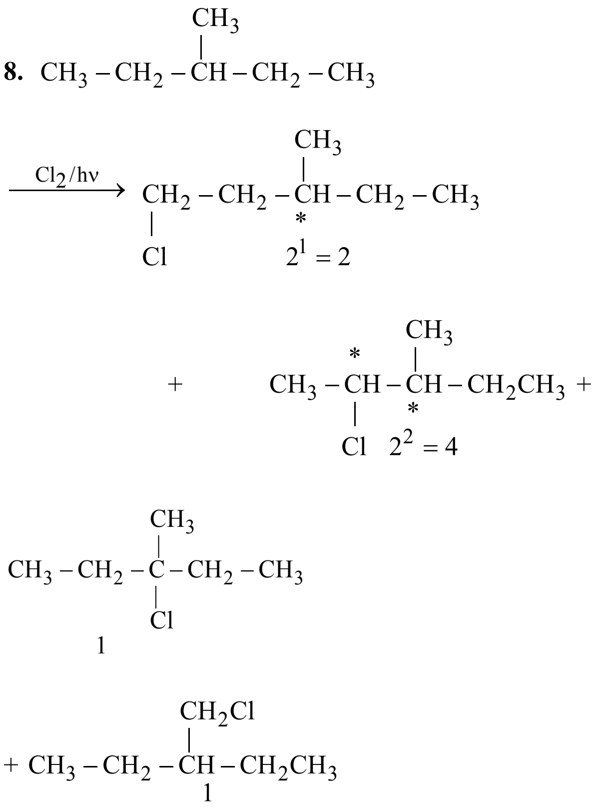
$156 + 156 + 142 = 454$

(6) **5.**



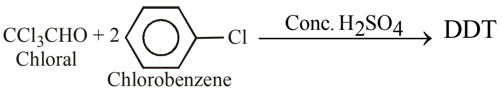
Total 5 products.

(7) **8.**

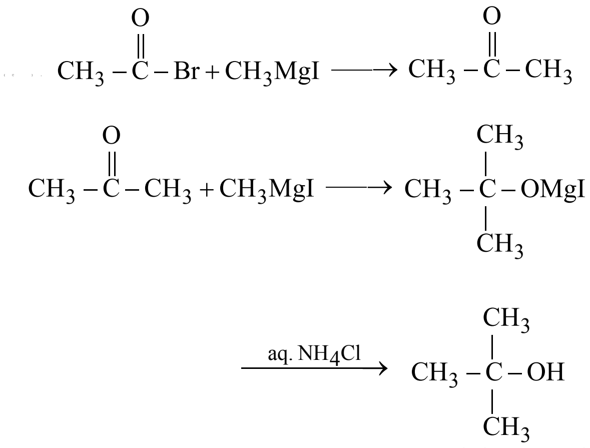

$$CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_3$$
$$\xrightarrow{Cl_2/h\nu} \underset{\underset{Cl}{|}}{CH_2}-CH_2-\underset{*}{\overset{\overset{CH_3}{|}}{CH}}-CH_2-CH_3 \quad 2^1 = 2$$
$$+ \quad CH_3-\underset{\underset{Cl}{|}}{\overset{*}{CH}}-\underset{*}{\overset{\overset{CH_3}{|}}{CH}}-CH_2CH_3 + \quad 2^2 = 4$$
$$CH_3-CH_2-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_3 \quad 1$$
$$+ CH_3-CH_2-\overset{\overset{CH_2Cl}{|}}{CH}-CH_2CH_3 \quad 1$$

EXERCISE-4

(1) **(A).**

(2) **(B).** 

(3)



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Br+CH_3MgI\longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3+CH_3MgI\longrightarrow CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-OMgI$$

$$\xrightarrow{\text{aq. }NH_4Cl} CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-OH$$

2-methyl-2-propanol

(4) **(A).** HF > HCl > HBr > HI

(5) **(C).**

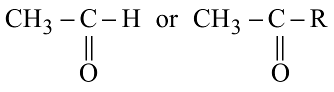
(6) **(D).** Corey-House synthesis

$$\underset{\text{(Alkyl halide)}}{R-X}\xrightarrow[Et_2O]{Li}R-Li\xrightarrow{CuI}\underset{\text{(Gilman reagent)}}{R_2CuLi}$$

$$\xrightarrow[R'X]{\text{Methyl,1°alkyl, 2°cycloalkyl}}\underset{\text{(Alkane)}}{R-R'}+R-Cu+LiX$$

(7) **(A).**

(8) **(C).** If any compound contains

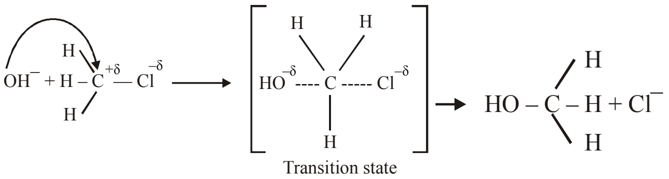


$$CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-H\ \text{ or }\ CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-R$$

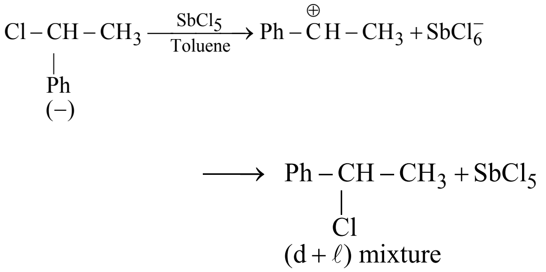
group or may be oxidized in this group gives the positive iodoform test.

(9) **(B).** 1° > 2° > 3° activity of alkyl halide

(10) **(C).** S_N2 **mechanism**



(11) **(C).**



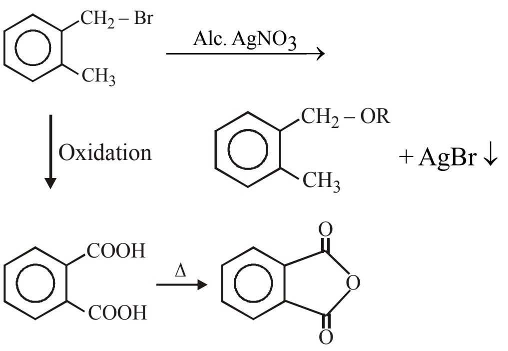
$$\underset{\underset{\displaystyle Ph}{|}}{Cl-CH}-CH_3\xrightarrow[\text{Toluene}]{SbCl_5}Ph-\overset{\oplus}{C}H-CH_3+SbCl_6^-$$

(−)

$$\longrightarrow Ph-\underset{\underset{\displaystyle Cl}{|}}{CH}-CH_3+SbCl_5$$

(d + ℓ) mixture

(12) **(D).**

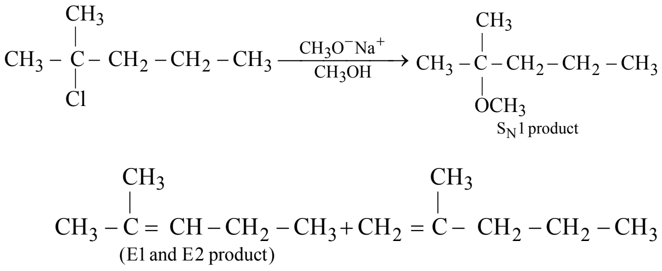


(Phthalic anhydride)

(13) **(C).** Swart's reaction

$$CH_3-Cl+AgF\xrightarrow{\Delta}CH_3F+AgCl$$

(14) **(D).**

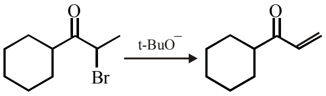


$$CH_3-\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-CH_2-CH_3\xrightarrow[CH_3OH]{CH_3O^-Na^+}\underset{S_N1\text{ product}}{CH_3-\underset{\underset{\displaystyle OCH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-CH_2-CH_3}$$

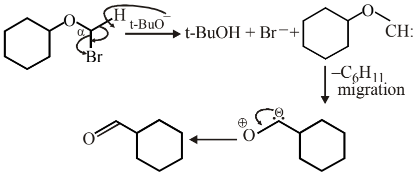
$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2-CH_3+CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_2-CH_2-CH_3$$

(E1 and E2 product)

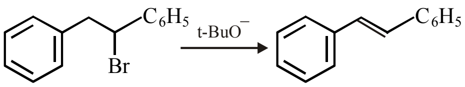
(15) **(B).**



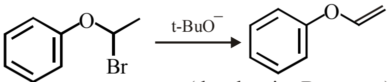
(decolourizes Br_2 water)



(cannot be decolorize Br_2 water)

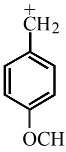


(decolourise Br_2 water)



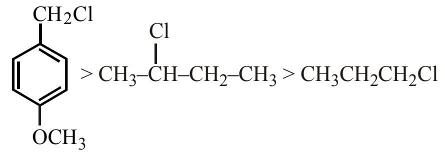
(decolourise Br_2 water)

(16) **(C).** Order of reactivity for S_N1 mechanism is in accordance with order of stability of carbocation involved :

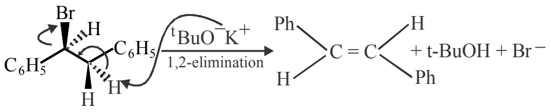


$$>CH_3-\overset{+}{C}H-CH_2-CH_3>CH_3CH_2\overset{+}{C}H_2$$

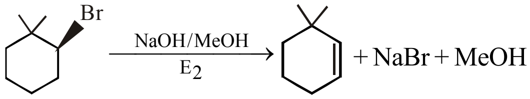
So, order of reactivity



(17) **(C).** Elimination reaction is highly favoured if
(a) Bulkier base is used
(b) Higher temperature is used
Hence in given reaction biomolecular ellimination reaction provides major product.

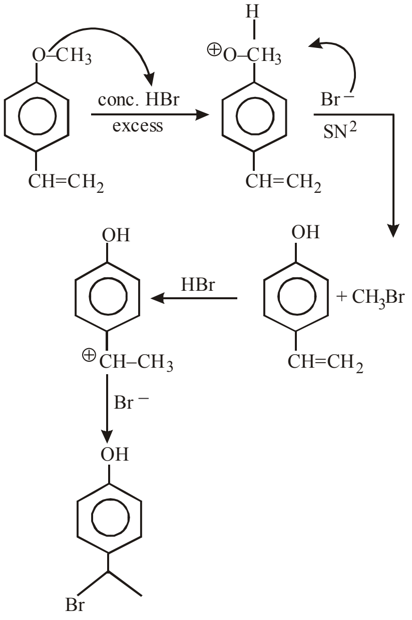


(18) **(D).**

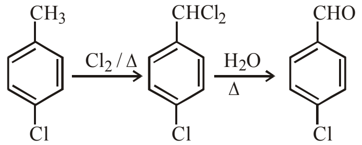


(19) **(D).**

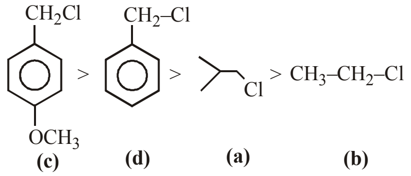
(20) **(D).**



(21) **(D).**



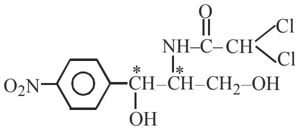
(22) **(C).** S_N1 Reactivity order



Order : c > d > a > b

(23) **(D).** Vinyl halide $CH_2 = CH - Cl$ do not undergo SN reaction. This is due to formation of highly unstable carbocation ($CH_2 = C^{\oplus}H$) ; which cannot be delocalised by the π-electron, also C–Cl has double bond character because of resonance. Hence statement (B) is wrong.

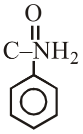
(24) **02.00**



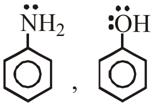
(25) **(B).** Vinyl halides and aryl halides do not give Friedel craft's reaction.

(26) **(B).** Carbocation formed from d is most stable Carbocation formed from a is least stable.

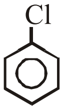
(27) **(C).**



(Deactivated ring due to –R effect of amide)



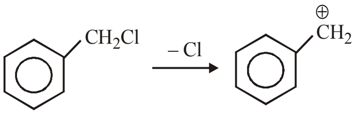
(l.p.e. of $-NH_2$ and –OH group do acid-base reaction with lewis acid $AlCl_3$, so ring is deactivated)



(Highest yield produced)

EXERCISE-5

(1) **(D).** S_N1 reaction is favoured by heavy groups on the carbon atom attached to halogen i.e.
Benzyl > allyl > tertiary > primary > secondary > primary > alkyl halides

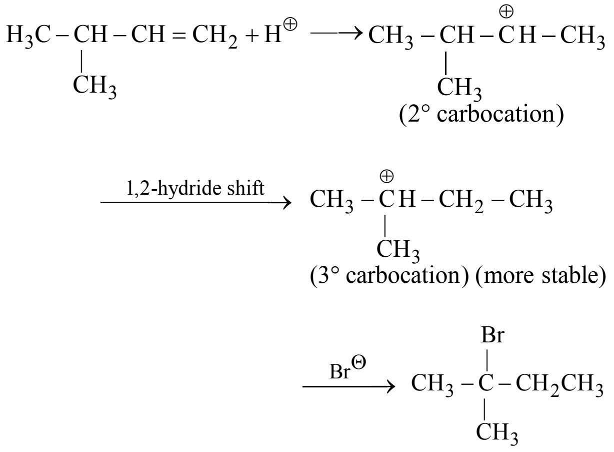


(Benzyl cation)

Obtained from S_N1 path.
This molecule is resonance stabilised.

(2) **(A).** S_N2 mechanism is followed in case of primary and secondary alkyl halides i.e., S_N2 reaction is favoured by small groups on the carbon atoms attached to halogen so,
$CH_3-X > R-CH_2-X > R_2CH-X > R_3C-X$
Primary is more reactive than secondary and tertiary alkyl halides.
S_N2 order : Methyl > Ethyl > Isopropyl > Tertiary butyl > Allyl > Benzyl

(3) **(C).**



$$H_3C-\underset{CH_3}{CH}-CH=CH_2+H^{\oplus}\longrightarrow CH_3-\underset{CH_3}{CH}-\overset{\oplus}{C}H-CH_3$$

(2° carbocation)

$$\xrightarrow{\text{1,2-hydride shift}} CH_3-\underset{CH_3}{\overset{\oplus}{C}}H-CH_2-CH_3$$

(3° carbocation) (more stable)

$$\xrightarrow{Br^{\ominus}} CH_3-\overset{Br}{\underset{CH_3}{C}}-CH_2CH_3$$

(4) **(D).** Nucleophiles are either negative charge or lone pair of electrons bearing species, X^- is replaced by OH^-

(5) **(C).** S_N1 reaction involves the formation of carbocation intermediate. More the stability of carbocation, more is the reactivity of alkyl/aryl haldies towards S_N1 reaction. The intermediate carbocations formed by given halides are as

(1) $C_6H_5CH(C_6H_5)Br \rightarrow (C_6H_5)_2\overset{+}{C}H+Br^-$

(2) ${}_6H_5CH(CH_3)Br \rightarrow C_6H_5\overset{+}{C}H(CH_3)+Br^-$

(3) $C_6H_5C(CH_3)(C_6H_5)Br \rightarrow (C_6H_5)_2\overset{+}{C}(CH_3)+Br^-$

(4) $C_6H_5CH_2Br \rightarrow C_6H_5\overset{+}{C}H_2+Br^-$

The order of stability of these carbocations is as

$$(C_6H_5)_2\overset{+}{C}(CH_3) > (C_6H_5)_2\overset{+}{C}H >$$

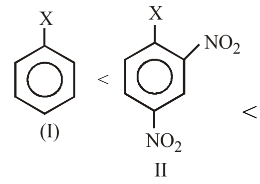
$$(C_6H_5)_2\overset{+}{C}H(CH_3) > \overset{+}{C}H_2$$

Thus, $C_6H_5C(CH_3)(CH_3)(C_6H_5)Br$

Br is most reactive towards S_N1 reaction.

(6) **(A).** Alkyl halides are more reactive toward nucleophilic substitution. Reactivity depends upon the stability of carbocation intermediate formed.

Among the given halides, aryl halide (C_6H_5X) is least reactive towards nucleophile as in it the C – X bond acquire some double bond character due to resonance. Presence of electron withdrawing groups like – NO_2 at ortho and para positions facilitate the nucleophilic displacement of –X of aryl halide. Among alkyl halides, 3° halides are more reactive as compared to 2° halides due to the formation of more stable carbocation. Hence, the order of reactivity of C – X bond towards nucleophile is as



$$< \underset{IV}{(CH_3)_2CH-X} < \underset{III}{(CH_3)_3C-X}$$

(7) **(C).** $C_6H_5CH_2Br \xrightarrow{Mg,\ Ether} \underset{\text{Grignard reagent}}{C_6H_5CH_2MgBr}$

$$\xrightarrow{H_3O^+} \underset{\text{Toluene}}{C_6H_5CH_3} + Mg\begin{smallmatrix}Br\\OH\end{smallmatrix}$$

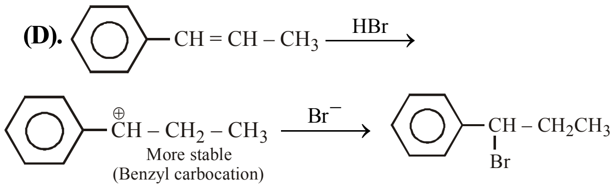
(8) **(A).** First reaction is S_N1 reaction because C_2H_5OH used as solvent which is a weak nucleophile.

Second reaction is S_N2 reaction because $C_2H_5O^-$ is strong nucleophile.

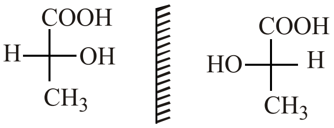
(9) **(C).** Tertiary halide can show ionic reaction with MF so, MF should be most ionic for reaction to proceed forward. Hence 'M' should be 'Rb'. Lattice energy of RbF less than LiF, NaF, KF.

(10) **(D).** Out of the compound (C) or (D), the (D) results in formation of racemic product due to chirality.

(11) **(D).**



(12) **(A).**

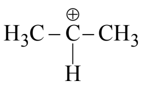


Both are enantiomers.

(13) **(D).** S_N1 reaction gives racemic mixture with slight predominance of that isomer which corresponds to inversion because S_N1 also depends upon the degree of 'shielding' of the front side of the reacting carbon..

(14) **(B).** Due to steric hindrance, arising due to presence of bulkier groups at ortho-positions of benzene rings, the biphenyl system becomes non-planar i.e., optically active.

(15) **(D).** Isopropyl chloride would form stable carbocation.

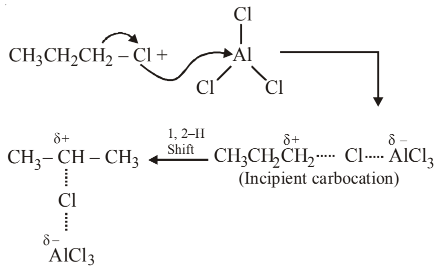


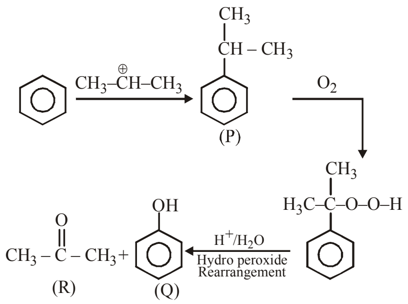
$$H_3C-\underset{H}{\overset{\oplus}{C}}-CH_3$$

(16) **(C).** The reaction is S_N2, most suitable solvent should be polar aprotic i.e., DMF.

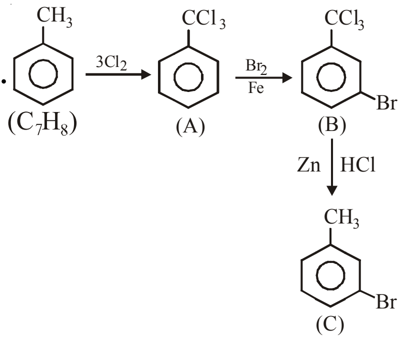
(17) **(A).** $RMgX_2$ is a organometallic compound and it has only sigma bonds.

(18) **(D).**

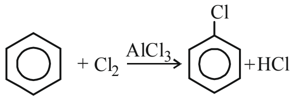




(19) **(C).**



(20) **(B).**



Generation of electrophile: