Chapter

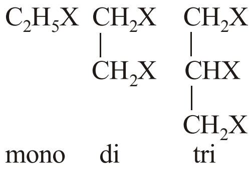
24 Haloalkanes and Haloarenes

The replacement of H-atom(s) in a hydrocarbon, aliphatic or aromatic, by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene).

CLASSIFICATION

On the Basis of No. of Halogen Atoms :

Mono, di, tri, tetra, etc. depending on whether they contain one, two, three, four halogen atoms in structures.



$$\begin{array}{ccc} C_2H_5X & \begin{array}{c} CH_2X \\ | \\ CH_2X \end{array} & \begin{array}{c} CH_2X \\ | \\ CHX \\ | \\ CH_2X \end{array} \\ \text{mono} & \text{di} & \text{tri} \end{array}$$

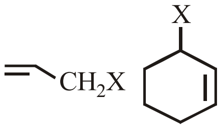
Classification Based on Nature of C – X Bond

(i) Compounds containing sp^3 hybridised C–X bond

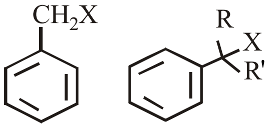
(a) **Alkyl halides or halo alkanes :**

$$\underset{1^\circ}{RCH_2X} \quad \underset{2^\circ}{R_2CH\,X} \quad \underset{3^\circ}{R_3CX}$$

(b) **Allylic halides :** In these compounds the halogen atom is linked to an sp^3 hybridised carbon atom which has a C = C bond attached to it.

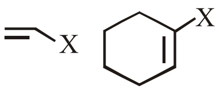


(c) **Benzylic halides :** The tetrahedral carbon involved in C – X bond is linked to an aromatic ring.

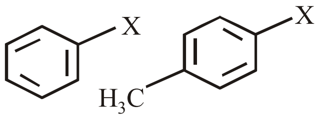


(ii) Compounds containing sp^2 hybridised C–X bond

(a) **Vinylic halides :** The halogen atom is attached to sp^2 hybridised carbon atom of C = C bond.



(b) **Aryl halides :** The halogen atom is attached directly to the carbon atom of the benzene ring.



Note :

(a) Down the group, size of X increases, ∴ C– X bond length increases down the group from F to I.

(b) Although F is more electronegative than Cl, yet dipole moment of CH_3Cl is more than CH_3F. This is because of small size of F due to which C-F bond distance (d) becomes small in comparison to C – Cl bond distance dipole moment is given as $\mu = q \times d$. Thus dipole moment of C – Cl bond is greater in comparison to dipole moment of C – F bond.

METHODS OF PREPARATION OF ALKYL HALIDES

(i) From Alcohols

$$R - OH + HX \longrightarrow RX + H_2O$$

$$3\,R - OH + PX_3 \longrightarrow 3R - X + H_3PO_3$$

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

$$R - OH + SOCl_2 \longrightarrow RCl + SO_2\uparrow + HCl\uparrow$$

Thionyl chloride method is preferred over hydrogen chloride or phosphorus pentachloride method for the preparation of chloroalkanes since both the by-products (SO_2 and HCl) in this reaction being gases escape out leaving behind the chloroalkanes in almost pure state.

Note :

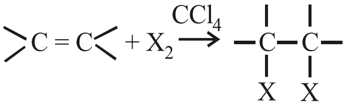
(a) Order of reactivity among HX : HI > HBr > HCl >> HF

(b) Order of reactivity among ROH : 3° > 2° > 1° > CH_3OH

(c) Mixture of conc. HCl and anhydrous $ZnCl_2$ is used for differentiating three types of alcohols (3° > 2° > 1°) under the name of ***Lucas reagent***.

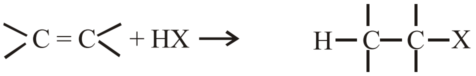
(d) $SOBr_2$ is less stable and SOI_2 does not exist, PBr_5 and PI_5 are highly unstable hence not used.

(ii) From Alkenes



A vic-dihalide
(X = Cl, Br)

When above reaction is carried out by using Br_2/CCl_4 the reddish brown colour of Br_2 is discharged. Therefore this reaction is used as a test for detection of unsaturation in organic molecules.



(with unsymmetrical alkenes,
Markovnikov's rule followed)

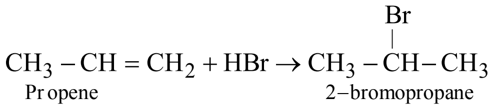
Alkenes react with halogen acids to form haloalkanes. The order of reactivity is

HI > HBr > HCl > HF

Markownikoff's rule :

When an unsymmetrical alkene or alkyne reacts with unsymmetrical reagent, then negative part of reagent attach with that carbon atom which contains lesser number of hydrogen atom during the addition.

For example:



$$\underset{\text{Propene}}{CH_3-CH=CH_2} + HBr \rightarrow \underset{\text{2-bromopropane}}{CH_3-\overset{\overset{Br}{|}}{C}H-CH_3}$$

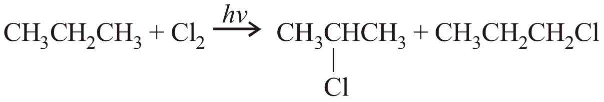
Anti-Markownikoff's rule :

Addition of HBr (not HCl, HI and HF) on alkenes in presence of peroxides takes place in ***anti-Markownikoff's way*** (***Peroxide effect***)**.** Here addition takes place via ***free-radical mechanism*****.**

$$CH_3CH=CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3CH_2CH_2Br$$

(iii) From Alkanes

By free radial halogenation



$$CH_3CH_2CH_3 + Cl_2 \xrightarrow{h\nu} \underset{\underset{Cl}{|}}{CH_3CHCH_3} + CH_3CH_2CH_2Cl$$

(a mixture of products
is obtained)

However, compounds containing only one type of hydrogen atom can be converted into monohalogenated products in good yield by taking excess of the concerned hydrocarbon; examples of such compounds are CH_4, CH_3CH_3, $(CH_3)_4C$, $C_6H_5CH_3$ etc. The reactivity of the alkanes follows the following order: Tertiary alkane > Secondary alkane > Primary alkane.

Note:

(a) Chlorination and bromination can be achieved by above method while iodination is done in presence of oxidising agent (i.e., HNO_3 or HIO_3). Direct flourination is highly exothermic. Thus it is done by heating alkyl chlorides with inorganic fluorides (Hg_2F_2, AgF, SbF_3 etc.).

(b) Benzylic hydrogens (hydrogen present on C attached directly to benzene) are more reactive, hence easily replaced than 1°, 2° or 3° hydrogens.

(iv) By Halogen Exchange

(a) Finkelstein reaction

$$R-X + NaI \xrightarrow[(X = Cl,\ Br)]{\text{acetone}} R-I + NaX$$

(b) Swarts reaction

Alkyl chlorides/ bromides is heated in presence of a metallic fluoride such as AgF, Hg_2F_2, CoF_2 or SbF_3 to form alkyl flourides.

$$R-X + AgF \xrightarrow{\Delta} R-F + AgX (X = Cl, Br)$$

PHYSICAL PROPERTIES OF ALKYL HALIDES

(i) Lower halides are gaseous in nature whereas higher halides are either liquid or solids (having 18 or more C–atoms)

(ii) Alkyl halides are colourless when pure. The bromides and iodides develop colour when exposed to light.

(iii) **Melting and Boiling points**

The m.pts and b.pts of chlorides, bromides and iodides are higher than those of analogous hydrocarbons due to presence of dipole-dipole interactions in them besides van der waal's forces.

The m.pts. and b.pt. follows the order: RI > RBr > RCl > RF. This is because with increase in size and mass of halogen, magnitude of van der Waal's forces also increases. The b.pts of isomeric haloalkanes decrease with increase in branching. For isomeric alkyl halides, order of boiling point is

Primary > Secondary > Tertiary

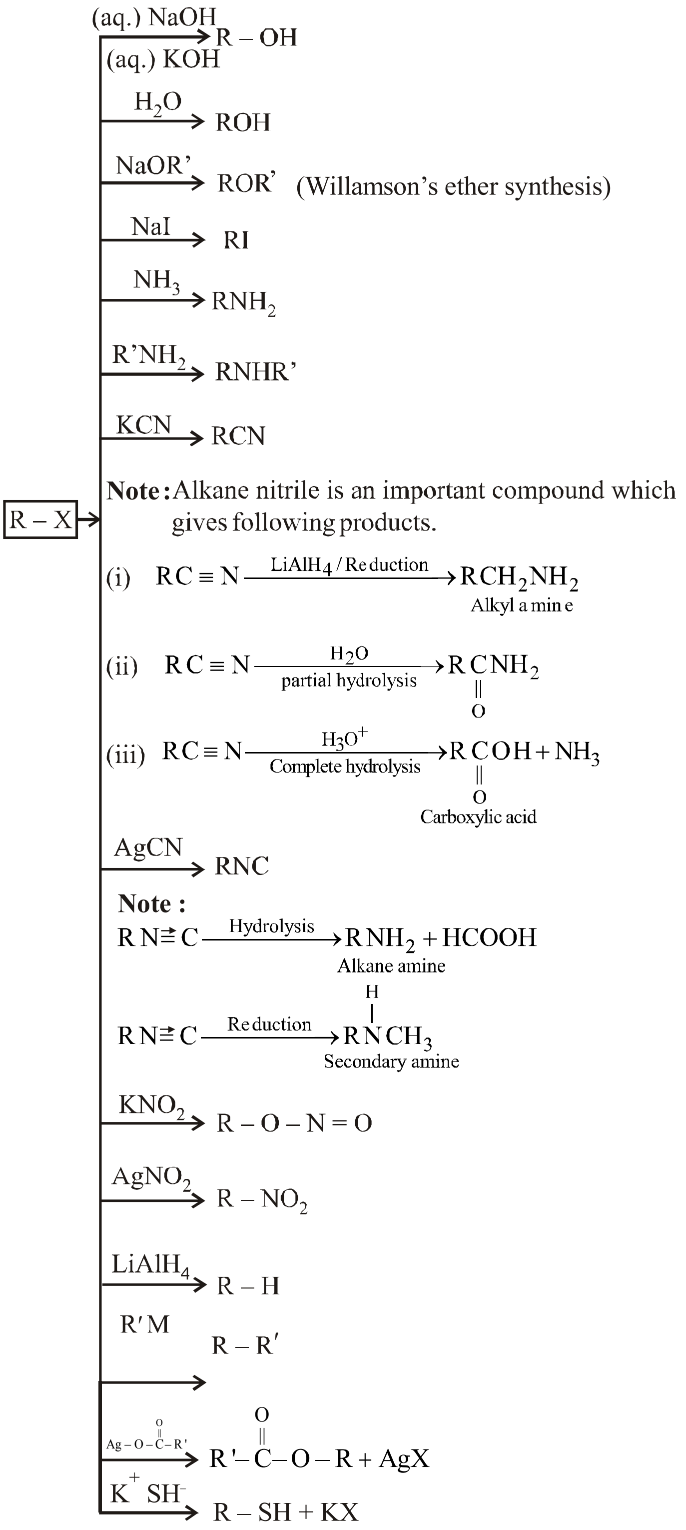
(iv) **Solubility**

The haloalkanes are only very slightly soluble in water. This is because less energy is released when new interactions are set up between haloalkane and water molecules and these are not as strong as original H-bonds in water. Haloalkanes are completely soluble in organic solvents.

CHEMICAL PROPERTIES OF ALKYL HALIDES

1. Nucleophilic Substitution Reactions

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



$\boxed{R-X} \rightarrow$

$\xrightarrow[\text{(aq.) KOH}]{\text{(aq.) NaOH}} R-OH$

$\xrightarrow{H_2O} ROH$

$\xrightarrow{NaOR'} ROR'$ (Willamson's ether synthesis)

$\xrightarrow{NaI} RI$

$\xrightarrow{NH_3} RNH_2$

$\xrightarrow{R'NH_2} RNHR'$

$\xrightarrow{KCN} RCN$

Note : Alkane nitrile is an important compound which gives following products.

(i) $RC\equiv N \xrightarrow{LiAlH_4/\text{Reduction}} \underset{\text{Alkyl amine}}{RCH_2NH_2}$

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

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

$\xrightarrow{AgCN} RNC$

Note :

$RN\rightleftarrows C \xrightarrow{\text{Hydrolysis}} \underset{\text{Alkane amine}}{RNH_2}+HCOOH$

$RN\rightleftarrows C \xrightarrow{\text{Reduction}} \underset{\text{Secondary amine}}{R\overset{\overset{H}{|}}{N}CH_3}$

$\xrightarrow{KNO_2} R-O-N=O$

$\xrightarrow{AgNO_2} R-NO_2$

$\xrightarrow{LiAlH_4} R-H$

$R'M \quad R-R'$

$\longrightarrow$

$\xrightarrow{Ag-O-\overset{\overset{O}{\|}}{C}-R'} R'-\overset{\overset{O}{\|}}{C}-O-R+AgX$

$\xrightarrow{K^+SH^-} R-SH+KX$

$Ar-H+AlCl_3 \rightarrow Ar-R$ (Friedel-craft reaction)

(ii) Elimination Reactions

Alkyl halide loses a molecule of hydrogen halide when heated with alc KOH and alkene is formed.

$$R-CH_2CH(Br)CH_3 \xrightarrow[\Delta]{\text{alc. KOH}}$$

$$\underset{\text{(major)}}{R-CH_2CH=CH_2}+\underset{\text{(minor)}}{R-CH=CH-CH_3}$$

This is also called β-elimination or Dehydrohalogenation reaction.

The product formed is determined by Saytzeff's rule i.e. the preferred alkene is that which has greater no. of alkyl groups attached to doubly bonded C-atoms. Ease of dehydrohalogenation among halides is : 3° > 2° > 1°

Note :

Elimination reactions dominate over substitution when strong base i.e., Bronsted base [*e.g.* NH_2^-, Me_3CO^-, $\overline{O}C_2H_5$ etc.) is used and alkyl halide is 3° or 2°.

(iii) Reaction with Metals

(a) Grignard reaction:

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

(b) Wurtz reaction:

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

(c) $4CH_3CH_2Cl+4\ Pb/Na \xrightarrow{\text{dry ether}}$

$$\underset{\text{TEL}}{(C_2H_5)_4Pb}+4NaCl+3Pb$$

(d) With Zn dust : (Frankland reaction)

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

(e) With Li :

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

Alkyl lithiums react with copper halides to form higher alkanes **(Corey-House synthesis)**

$$2RLi \xrightarrow[(-LiI)]{CuI} R_2CuLi \xrightarrow[(1^\circ\text{ halide})]{R'X} R-R'$$

(iv) Reduction

Haloalkanes on reduction produces alkanes frequently.

$$R-X+2H \longrightarrow \underset{\text{Alkane}}{R-H}+HX$$

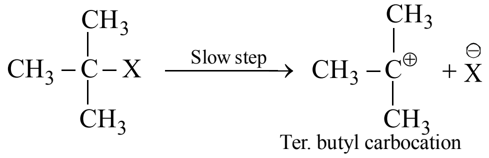
MECHANISM OF NUCLEOPHILIC SUBSTITUTION

Nucleophilic substitution rxns can proceed via two mechanism $S_N{}^1$ or $S_N{}^2$.

$S_N{}^1$ (Unimolecular Nucleophilic Substitution)

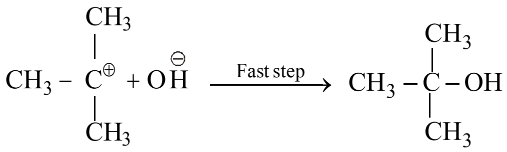
This reaction occurs in two steps. In first step, a carbocation is formed from alkyl halide molecule. First step is slow step so it is also rate determining step. In second step, an attacking nucleophile attacks on this carbocation and forms the final product.

(i)



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-X \xrightarrow{\text{Slow step}} \underset{\text{Ter. butyl carbocation}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^\oplus}}}+\overset{\ominus}{X}$$

(ii)



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^{\oplus}}} + \overset{\ominus}{O}H \xrightarrow{\text{Fast step}} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$$

Rate of reaction $\propto$ $[(CH_3)_3C-X]$ It is a unimolecular substitution reaction.

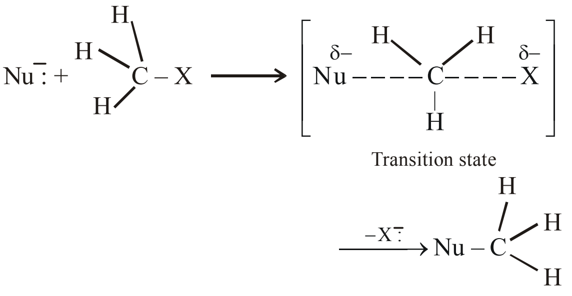
In S_N1 mechanism, carbocations are formed as intermediate, hence more the stability of the intermediate carbocation, greater are chances for their formation and hence more reactive will be the parent alkyl halide for S_N1 reaction. Hence the order of reactivity of alkyl halides toward S_N1 reaction follows the order : $3° > 2° > 1°$

When the intermediate carbocation is capable of undergoing rearrangement, lesser stable carbocation ($1° < 2° < 3°$) rearranges to the more stable carbocation and hence under such conditions unexpected product is formed.

Note: Allylic and benzylic halides show high reactivity towards the S_N1 reaction because carbocation formed gets stabilised via resonance.

S_N2 (Bimolecular Nucleophilic Substitution) :

The rate of S_N2 reactions depends on the concentration of alkyl halide as well as nucleophile, *i.e.* $r = k[RX][Nu]$. This implies that both the reactants are involved in the rate-determining step, i.e. the reaction occurs in one step only or it is a *concerted reaction.* Concerted reactions occur through a transition state (an imaginary state in which both the reactant molecules are partially linked to each other).



Inverted product

The nucleophile attacks from the back side of the halide ion, bulkier the alkyl group present on the carbon bearing halogen lesser will be its tendency to undergo S_N2 reaction. Thus the reactivity of alkyl halides towards S_N2 mechanism is

The reactivity of alkyl halides in S_N2 reactions is:

$$1° > 2° > 3°$$

The order of reactivity among various 1° alkyl halides is

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

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

Note :

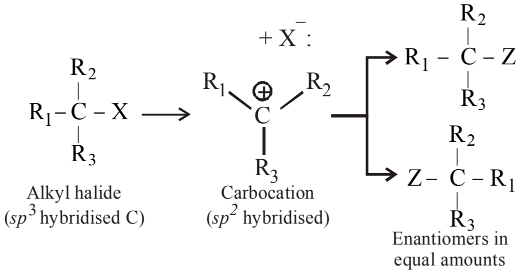
(a) 3° alkyl halides react by S_N1, 1° by S_N2 and 2° by either or both of these mechanism depending upon the nature of the alkyl halide and the reagent.

(b) For a given alkyl group, the reactivity of halide, $R-X$ follows the same order in both the mechanisms:
$R-I > R-Br > R-Cl > R-F$

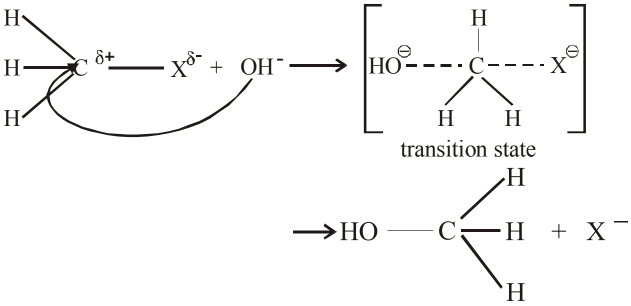
(c) Polar solvents favour S_N1 reactions while non-polar solvents favour S_N2 reactions.

Stereochemical aspects of nucleophilic substitution.

If the alkyl halide is optically active, the product formed in S_N1 reaction is always a racemic mixture. This is due to the formation of carbocations as intermediates which, being planar (sp^2 hybridised) can be equally attacked by the nucleophile on either side of the face forming two enantiomers.



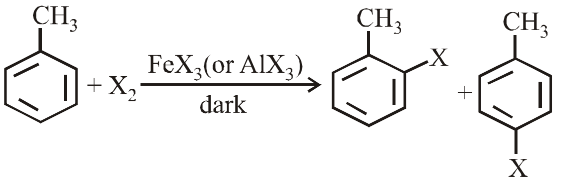
Since the nucleophile attacks from the back side and the halide ion leaves from the front side, the product obtained will have an ***inverted configuration [Walden inversion].*** This implies that if the alkyl halide is optically active, the product will also be optically active, although the sign of rotation may be same or different.



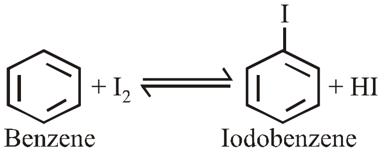
(Walden inversion)

METHODS OF PREPARATION OF ARYL AND ARALKYL HALIDES

(i) By Electrophilic Substitution



Chlorobenzene and bromobenzene can be prepared by above methods whereas iodobenzene cannot be done in the same way because HI formed in the reaction is a powerful reducing agent due to low bond dissociation enthalpy (299 kJ mol^{-1}). It will therefore, make the reaction reversible in nature.



On account of this, HI formed in the reaction is oxidised by carrying the reaction in the presence of iodic acid (HIO_3) or conc. HNO_3.

$$2HI + 2HNO_3 \xrightarrow{\text{heat}} 2NO_2 + 2H_2O + I_2$$

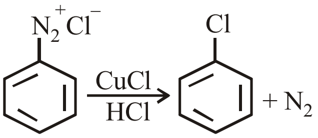
$$5HI + HIO_3 \xrightarrow{\text{heat}} 3H_2O + 3I_2$$

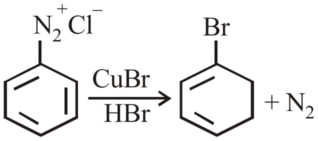
Fluorination being extremely violent is difficult to control.

Substitution in alkyl group

(ii) By the Decomposition of Diazonium Salts.

(a) Sandmeyer's reaction



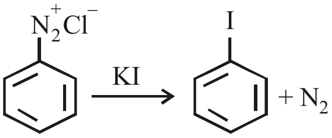


(b) Gattermann reaction:

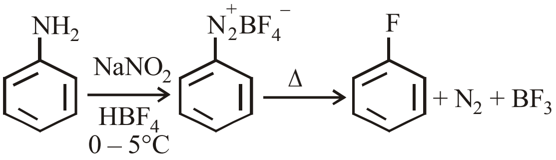
$$C_6H_5N_2^+Cl^- \xrightarrow{Cu/HCl} C_6H_5Cl$$

$$C_6H_5N_2^+Cl^- \xrightarrow{Cu/HBr} C_6H_5Br$$

(c)



(d)



Thermal decomposition of benzenediazonium tetrafluoroborate to give fluorobenzene is called *Balz-Schiemann reaction.*

(iii) Hunsdiecker Method :

$$C_6H_5COOAg + Cl_2 (\text{or } Br_2) \longrightarrow C_6H_5Cl + CO_2 + AgCl$$

PHYSICAL PROPERTIES OF ARYL AND ARALKYL HALIDES

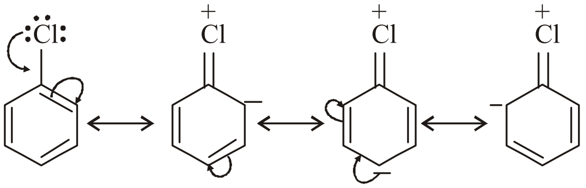
(i) Like alkyl halides, aryl halides are insoluble in water due to their incapability of forming H-bonds.

(ii) Aryl halides are less polar than alkyl halides because in aryl halides, halogen is present on *sp*^{2} hybridised carbon which is more electronegative than the *sp*^{3} hybridised carbon of alkyl halides.

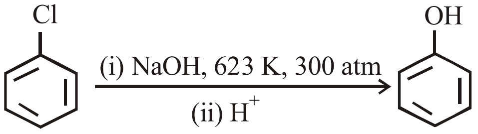
CHEMICAL PROPERTIES OF ARYL AND ARALKYL HALIDES

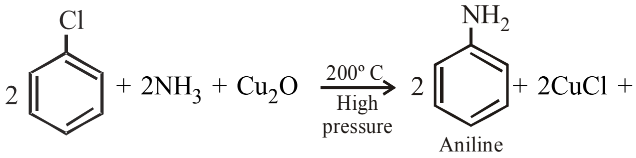
(i) Nucleophilic Substitution :

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

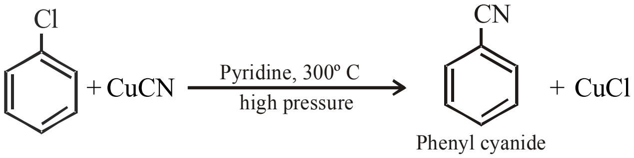


The halogen atom is replaced by other nucleophiles under drastic conditions.





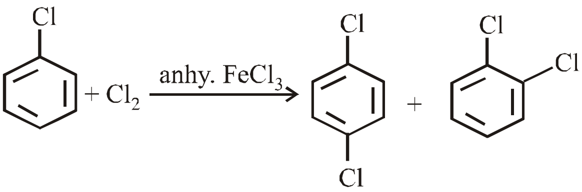
H_2O



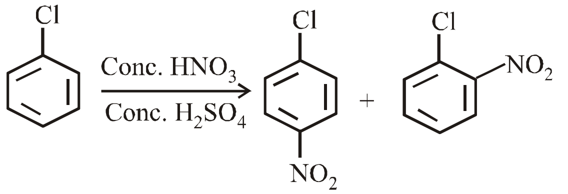
Note : Haloarenes does not undergo nucleophilic substitution as clevage of C – X bond is difficult. When electron withdrawing groups like –NO_2, – CN, – CHO, – COOH etc. are present at ortho or para positions the bond cleavage becomes easier.

(ii) Electrophilic Substitution Reactions

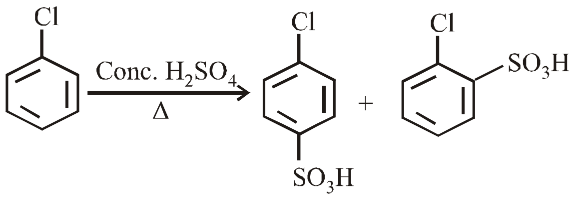
(a) Halogenation :



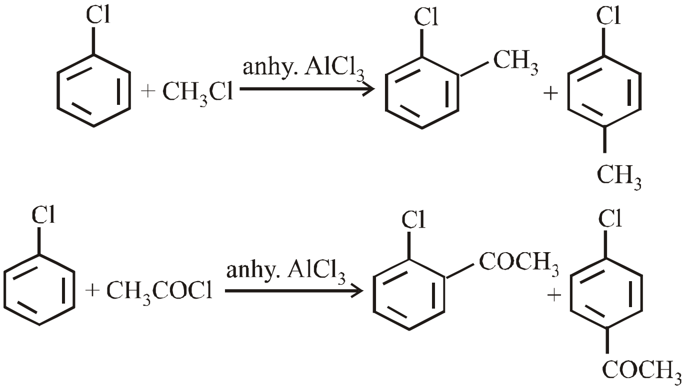
(b) Nitration :



(c) Sulfonation :

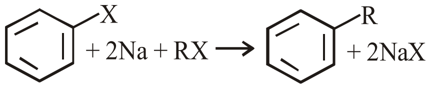


(d) Friedel-crafts reaction :

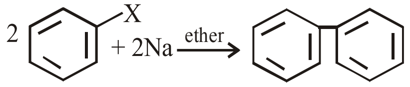


(iii) Reaction with Metals:

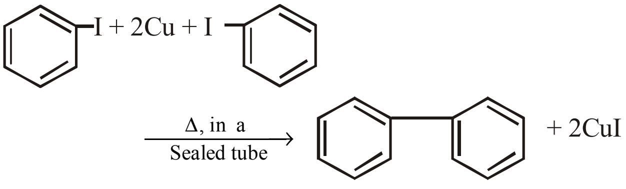
(a) **Wurtz-Fiting reaction**



(b) **Fittig reaction**



(iv) Ullmann Reaction:



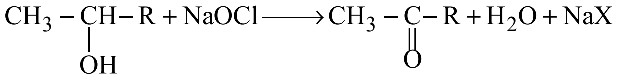
Diphenyl

POLYHALOGEN COMPOUNDS

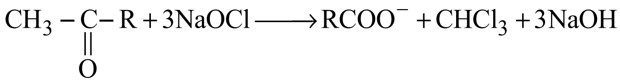
Chloroform

Preparation of $CHCl_3$

(i) **Haloform reaction :** Aldehydes and ketones with CH_3CO group, and alcohols with $CH_3CH(OH)$ group give this reaction.

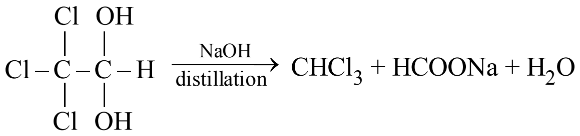


$$CH_3-\underset{\underset{OH}{|}}{C}H-R+NaOCl\longrightarrow CH_3-\underset{\underset{O}{||}}{C}-R+H_2O+NaX$$



$$CH_3-\underset{\underset{O}{||}}{C}-R+3NaOCl\longrightarrow RCOO^-+CHCl_3+3NaOH$$

(ii) **Preparation of pure chloroform :**



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

Chloralhydrate

(iii) **From carbon tetrachloride (Pyrene) :**

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

Properties

(i) Chloroform is colourless with sweet smelling, liquid.
(ii) Inslouble in water and soluble in organic solvent.
(iii) Boiling point of $CHCl_3$ is 61ºC.
(iv) It is best solvent for fats, oil and wax.
(v) On exposure to air and sunlight, chlorofrom, a colourless heavy liquid, oxidises to **carbonyl chloride (phosgene),** a highly poisonous gas used in warfare.

$$CHCl_3+\frac{1}{2}O_2\xrightarrow{\text{light}}\underset{\text{unstable}}{CCl_3(OH)}\longrightarrow COCl_2+HCl$$

To avoid this oxidation chlorofrom is always stored in dark coloured bottles filled to the brim to exclude any air. Further nearly 1% alcohol is also added to destroy traces of phosgene, if formed, to harmless diethyl carbonate.

$$2C_2H_5OH+Cl_2C=O\longrightarrow\underset{\text{Diethyl carbonate}}{(C_2H_5O)_2C=O}+2HCl$$

Uses :

(a) As an anaesthetic agent. However, it has been replaced by less toxic and safer anaesthetic agents.
(b) $CHCl_3$ acts as a solvent for fat, waxes, rubber etc.

Iodoform (Triiodomethane) CHI_3 :

CHI_3 was earlier used as an antiseptic for dressing wounds. Its antiseptic properties are due to the liberation of iodine when iodoform comes in contact with skin.

Any compound containing CH_3CO– or $CH_3CH(OH)$– group, when heated with iodine and aqueous NaOH or NaOI (sodium hypoiodite) gives yellow precipitate of iodoform, this reaction is called **iodoform reaction.**

$$CH_3.CH(OH).R\xrightarrow{I_2/NaOH}CH_3.CO.R$$

$$\xrightarrow{I_2/NaOH}I_3C.CO.R\xrightarrow{I_2/NaOH}\underset{\text{Iodoform}}{CHI_3}+RCOONa$$

Carbon Tetrachloride (Tetrachloro Methane or Perchloromethane) :

Preparation :

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

Properties :

(i) It is a colourless, non-inflammable, poisonous liquid, soluble in alcohol and ether.
(ii) On heating with steam at about 773K, it undergoes ***oxidation*** forming carbonyl chloride.

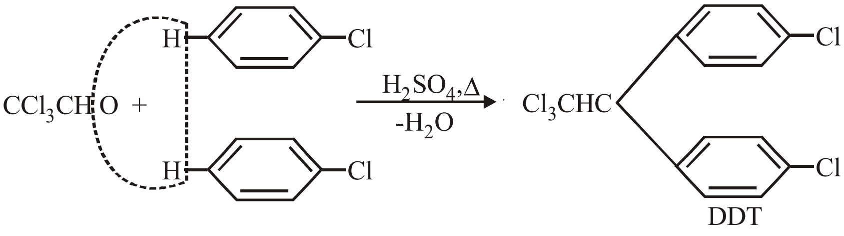
$$CCl_4+H_2O\ (\text{steam})\xrightarrow{773K}COCl_2+2HCl$$

Uses :

Carbon tetrachloride is used
(i) as a solvent for oils, fats, resins
(ii) in dry cleaning
(iii) as a laboratory reagent
(iv) as anthelmentic (removal of worms) for hook worms and
(v) as a fire extinguisher under the name of **pyrene**.

DDT

Preparation:



(p, p'-Dichlorodiphenyl trichloroethane)

Uses

It is priorly widely used as a insecticide but later researches have shown that DDT is very harmful for aquatic life as it is non-biodegradeble.

CONCEPT MAP

HALOALKANES AND HALOARENES

Haloalkanes

Preparation

From alcohols:

- $ROH + HX \longrightarrow RX + H_2O$
- $ROH + PCl_5 \longrightarrow PCl + POCl + HCl$
- $ROH + SOCl_2 \longrightarrow RCl + SO_2 + HCl$

From hydrocarbons:

- $CH_2 = CH_2 + HX \longrightarrow CH_3CH_2X$
- Order of reactivity HI > HBr > HCl > HF
  In case of unsymmetrical alkenes addition occurs according to Markownikoff's rule only in case of HBr in presence of peroxides addition occurs according to anti Markownikoff's rule
- $CH_2 = CH_2 + Br_2 \xrightarrow{CCl_4} BrCH_2CH_2Br$
- $CH_4 \xrightarrow[hv]{Cl_2} CH_3Cl + CH_2Cl + CHCl_3 + CCl_4$

From Halogen Exchange

With NaI (Finkelstein reaction):

$$\underset{(X=Cl,\,Br)}{R-X} + NaI \xrightarrow{Acetone} \underset{Iodoalkane}{R-I} + NaX$$

With AgF (Swarts reaction):

$$C_2H_5Cl + AgF \longrightarrow \underset{Flouroetane}{C_2H_5F} + AgCl$$

Properties

- **Nucleophilic substitution**
  $RX + KOH \longrightarrow ROH + KX$
  $RX + H_2O \longrightarrow ROH + HX$
  $RX + NaOR' \longrightarrow ROR' + NaX$
  $RCl + NaI \xrightarrow{Acetope} RI + NaCl$
  $RX + Li\,AlH_4 \longrightarrow RH + LiX + AlX_3$
- **Elimination reaction**
  $CH_2CH_2Br \xrightarrow{OH^-} CH_2CH_2 + H_2O + Br^-$
- **Reaction with metal**
  $CH_3CH_2Br + Mg \xrightarrow{Dry\ Ether} CH_2CH_2MgBr$
- **Wurtz reaction :**
  $2RX + 2Na \longrightarrow RR + 2NaX$

Haloarenes

Preparation

- **From arenes**
  $C_6H_6 + Cl_2 \xrightarrow[dark]{Fe} C_6H_5Cl$
- **Sandmeyer's reaction**
  $C_6H_5\overset{+}{N}_2Cl^- \xrightarrow{Cu_2Cl_2/HCl} C_6H_5Cl + N_2$
- **By Gattermann reaction**
  $C_6H_5\overset{+}{N}_2Cl^- \xrightarrow{Cu/HCl} C_6H_5Cl + N_2$
- **Hunsdiecker reaction**
  $C_6H_5COOAg + Br_2 \xrightarrow[Reflux]{CCl_4}$
  $C_6H_5Br + CO_2 + AgBr$

Properties

Nucleophilic substitution reactions

Electron withdrawing group present at o- and p-position increases the reactivity towards nucleophlic substitution.

Nucleophilic substitution involves replacement of –X group with –OH, $-NH_2$ and –CN groups.

Electrophilic substitution

Haloarenes are o, p-directing, due to + I effect of halogen group electrondensity increases at ortho and para positions.

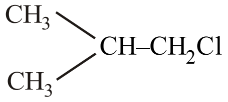
(a) Halogenation
(b) Nitration
(c) Sulphonation
(d) Friedel-crafts reaction

EXERCISE - 1

Conceptual Questions

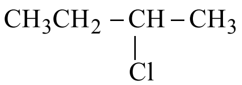
1. Under basic conditions which one suffers elimination the most

(a) $(CH_3)_3\,CCl$ (b)



$(CH_3)_2CH-CH_2Cl$

(c)



$CH_3CH_2-CH(Cl)-CH_3$

(d) $CH_3CH_2CH_2-CH_2-Cl$

2. The total number of acyclic isomers including the stereoisomers with the molecular formula C_4H_7Cl

(a) 11 (b) 12
(c) 9 (d) 10

3. Gem dihalides on treatment with alcoholic KOH give :

(a) alkyne (b) alkene
(c) alkane (d) all of these

4. When two halogen atoms are attached to same carbon atom then it is :

(a) *vic*-dihalide (b) *gem*-dihalide
(c) α, ω -halide (d) α, β -halide

5. Full name of DDT is

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

6. How many structural isomers are possible for a compound with molecular formula C_3H_7Cl

(a) 2 (b) 5
(c) 7 (d) 9

7. Which one of the following is least reactive in a nucleophilic substitution reaction?

(a) CH_3CH_2Cl (b) $CH_2 = CHCH_2Cl$
(c) $(CH_3)_3\,C-Cl$ (d) $CH_2 = CHCl$

8. The compound which contains all the four 1°, 2°, 3° and 4° carbon atoms is

(a) 2, 3-dimethyl pentane
(b) 3-chloro-2, 3 dimethylpentane
(c) 2, 3, 4-trimethylpentane
(d) 3,3-dimethylpentane

9. Benzene hexachloride is

(a) 1, 2, 3, 4, 5, 6-hexachlorocyclohexane
(b) 1, 1, 1, 6, 6, 6-hexachlorocyclohexane
(c) 1, 6-phenyl-1, 6-chlorohexane
(d) 1, 1-phenyl-6, 6-chlorohexane

10. A compound on treatment with NaOH followed by addition of $AgNO_3$ produces white precipitate at room temperature. The precipitate is soluble in NH_4OH . The compound is identified as

(a) vinyl chloride (b) benzyl chloride
(c) chlorobenzene (d) ethyl bromide

11. When hydrochloric acid gas is treated with propene in presence of benzoyl peroxide, it gives

(a) 2-chloropropane (b) allyl chloride
(c) n-propyl chloride (d) No reaction occurs

12. $C_6H_6Cl_6$ on treatment with KOH produces

(a) C_6H_6 (b) $C_6H_6Cl_4$
(c) $C_6H_3Cl_3$ (d) C_6H_6OH

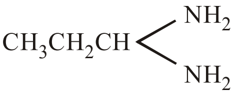
13. 2-Bromopentane is heated with potassium ethoxide in ethanol. The major product obtained is

(a) 2-ethoxypentane (b) pentene-1
(c) trans-2-pentene (d) cis-pentene-2

14. When $CH_3CH_2CHCl_2$ is treated with $NaNH_2$, the product formed is

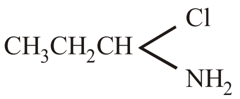
(a) $CH_3 - CH = CH_2$ (b) $CH_3 - C \equiv CH$

(c)



$CH_3CH_2CH(NH_2)_2$

(d)



$CH_3CH_2CH(Cl)(NH_2)$

15. When 2-bromobutane reacts with alcoholic KOH, the reaction is called

(a) halogenation (b) chlorination
(c) hydrogenation (d) dehydro-halogenation

16. Elimination of bromine from 2-bromobutane results in the formation of –

(a) predominantly 2-butyne
(b) predominantly 1-butene
(c) predominantly 2-butene
(d) equimolar mixture of 1 and 2-butene

17. $C_3H_8 + Cl_2 \xrightarrow{\text{Light}} C_3H_7Cl + HCl$ is an example of

(a) substitution (b) elimination
(c) addition (d) rearrangement reaction

18. The reaction of tert-butyl bromide with sodium methoxide produces mainly –

(a) iso-butane (b) iso-butylene
(c) tert-butyl methyl ether (d) sodium tert butoxide

19. $CH_3 - CH_2 - CH_2 - Cl \xrightarrow[\text{KOH}]{\text{alc.}} B \xrightarrow{\text{HBr}} C \xrightarrow[\text{ether}]{\text{Na}} D$

In the above sequence of reactions, the product D is –

(a) propane (b) 2, 3-dimethylbutane
(c) hexane (d) allyl bromide

20. The compounds $CHCl_3$ and HF lead to the formation of a compound of fluorine of molecular weight 70. The compound is

(a) fluoroform (b) fluoric monoxide
(c) fluoride dioxide (d) fluoro methanol

21. When two halogens are attached to same carbon atom, it is known as :
(a) *vic*-dihalide (b) *gem*-dihalide
(c) α, ω-dihalide (d) α, β-dihalide

22. Reaction of alkyl halides with aromatic compounds in presence of anhydrous $AlCl_3$ is known as :
(a) Friedel Craft reaction (b) Corey house synthesis
(c) Kolbe's synthesis (d) Beckmann rearrangement

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

24. In the following sequence of reactions

$$C_2H_5Br \xrightarrow{AgCN} X \xrightarrow{Reduction} Y \text{ ; Y is}$$

(a) *n*-propyl amine (b) isopropylamine
(c) ethylamine (d) ethylmethyl amine

25. Ethanol can be prepared more easily by which reaction ?

(i) $CH_3CH_2Br + H_2O \longrightarrow CH_3CH_2OH$

(ii) $CH_3CH_2Br + Ag_2O$ (in boiling water) $\longrightarrow CH_3CH_2OH$

(a) by (i) reaction
(b) by (ii) reaction
(c) Both reactions proceed at same rate
(d) by none

26. The reaction conditions leading to the best yields of C_2H_5Cl are :

(a) C_2H_6 (excess) + $Cl_2 \xrightarrow{\text{UV } light}$

(b) $C_2H_6 + Cl_2 \xrightarrow[\text{room temperature}]{\text{dark}}$

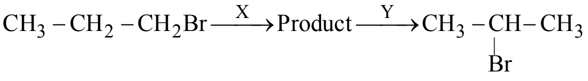
(c) $C_2H_6 + Cl_2$ (excess) $\xrightarrow{\text{UV } light}$

(d) $C_2H_6 + Cl_2 \xrightarrow{\text{UV } light}$

27. The best method for the conversion of an alcohol into an alkyl chloride is by treating the alcohol with
(a) PCl_5
(b) dry HCl in the presence of anhydrous $ZnCl_2$
(c) $SOCl_2$ in presence of pyridine
(d) None of these

28. $(CH_3)_3CMgCl$ on reaction with D_2O produces :
(a) $(CH_3)_3\,CD$ (b) $(CH_3)_3OD$
(c) $(CD_3)_3CD$ (d) $(CD_3)_3OD$.

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



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

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

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

31. The compound which forms acetaldehyde when heated with dilute NaOH, is
(a) 1, 1-dichloroethane (b) 1, 1, 1-trichloroethane
(c) 1-chloroethane (d) 1, 2-dichloroethane

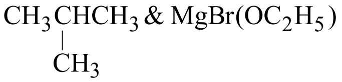
32. The number of structural and configurational isomers of a bromo compound, C_5H_9Br, formed by the addition of HBr to 2-pentyne respectively are
(a) 1 and 2 (b) 2 and 4
(c) 4 and 2 (d) 2 and 1

33. Chlorination of toluene in the presence of light and heat followed by treatment with aqueous KOH gives
(a) *o*-cresol (b) *m*-cresol
(c) *p*-cresol (d) benzyl alcohol

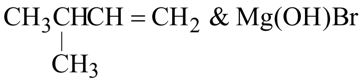
34. Isobutyl magnesium bromide with dry ether and ethyl alcohol gives :

(a)

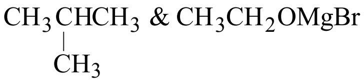

$$CH_3\underset{\substack{|\\CH_3}}{CH}CH_2OH \ \& \ CH_3CH_2MgBr$$

(b)


$$CH_3\underset{\substack{|\\CH_3}}{CH}CH_3 \ \& \ MgBr(OC_2H_5)$$

(c)


$$CH_3\underset{\substack{|\\CH_3}}{CH}CH=CH_2 \ \& \ Mg(OH)Br$$

(d)


$$CH_3\underset{\substack{|\\CH_3}}{CH}CH_3 \ \& \ CH_3CH_2OMgBr$$

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

36. Which of the following isomeric heptanes can yield seven different monochlorinated products upon free radical chlorination?
(a) 3-methylhexane (b) 2,2-dimethylpentane
(c) 2-methylhexane (d) 2,3-dimethylpentane

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

38. Methyl bromide reacts with AgF to give methyl fluoride and AgBr. This reaction is called
(a) Finkelstein reaction (b) Swarts reaction
(c) Fittig reaction (d) Wurtz reaction

39. Bromobenzene reacts with Mg in dry ether to give a compound (A) which further reacts with ethanol to yield
(a) phenol (b) benzene
(c) ethylbenzene (d) phenyl ether.

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

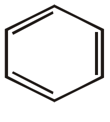
41. In alkaline hydrolysis of a tertiary alkyl halide by aqueous alkali, if concentration of alkali is doubled, then the reaction rate of constant temperature
(a) will be doubled
(b) will be halved
(c) will become four times greater
(d) will remain constant

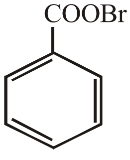
42. Bromination of toluene gives
(a) only *m*-substituted product
(b) only *p*-substituted product
(c) mixture of *o*-and *p*-substituted products
(d) mixture of *o*-and *m*-substituted products

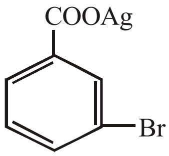
43. On sulphonation of C_6H_5Cl
(a) *m*-chlorobenzenesulphonic acid is formed
(b) benzenesulphonic acid is formed
(c) *o*-chlorobenzenesulphonic acid is formed
(d) mixture of *o*- and *p*-Chlorobenzenesulphonic acid is formed

44. An alkyl halide with molecular formula $C_6H_{13}Br$ on dehydrohalogenation gave two isomeric alkenes X and Y with molecular formula C_6H_{12}. On reductive ozonolysis, X and Y gave four compounds CH_3COCH_3, CH_3CHO, CH_3CH_2CHO and $(CH_3)_2CHCHO$. The alkyl halide is
(a) 2-bromohexane
(b) 2, 2-dimethyl-1-bromobutane
(c) 4-bromo-2-methylpentane
(d) 3-bromo-2-methylpentane

45. Silver benzoate reacts with bromine to form

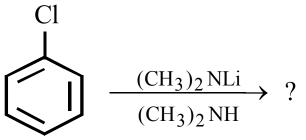
(a) 

(b) 

(c) 

(d) C_6H_5Br

46. What is the product of the following reaction ?



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

47. To prepare 3-ethylpentan-3-ol the reagents needed are –
(a) $CH_3CH_2MgBr + CH_3COCH_2CH_3$
(b) $CH_3MgBr + CH_3CH_2CH_2COCH_2CH_3$
(c) $CH_3CH_2MgBr + CH_3CH_2COCH_2CH_3$
(d) $CH_3CH_2CH_2MgBr + CH_3COCH_2CH_3$

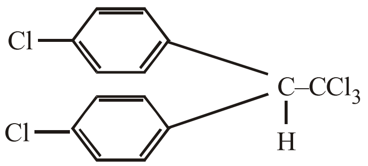
48. Which one of the following alkyl halides has the lowest boiling point?
(a) *n*-Butyl chloride (b) *iso*-Butyl chloride
(c) *sec*-Butyl chloride (d) *tert*-Butyl chloride

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

50. Which Chloride is least reactive with the hydrolysis point of view
(a) CH_3Cl (b) CH_3CH_2Cl
(c) $(CH_3)_3CCl$ (d) $CH_2 = CH - Cl$

51. 2-Bromopentane is treated with alcoholic KOH solution. The major product formed in this reaction and the type of reaction respectively are
(a) pent-2-ene, β-elimination
(b) pent-1-ene, β-elimination
(c) 2-pentanol, nucleophilic substitution
(d) pent-1-ene, nucleophilic substitution

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

53. 

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

54. The pesticide DDT slowly changes to
(a) CCl_3-CHO and chlorobenzene
(b) *p, p*′-Dichlorodiphenylethene
(c) *p, p*′-Dichlorodiphenyldichloroethane
(d) *p, p*′-Dichlorodiphenyldichloroethene

55. Which one of the following on hydrolysis produces a ketone?
(a) Isobutylidene chloride
(b) Secondarybutylidene chloride
(c) Benzylidene chloride
(d) Ethylidene chloride

56. Pure chloroform is prepared by

(a) distilling chloral hydrate with aqueous sodium hydroxide
(b) heating ethanol with bleaching powder
(c) heating acetone with bleaching powder
(d) reducing carbon tetrachloride

57. The organic compound used as feedstock in the synthesis of chlorofluorocarbons is

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

58. If chloroform is left open in air in the presence of sunlight, it gives

(a) carbon tetrachloride (b) carbonyl chloride
(c) mustard gas (d) lewisite

59. On warming with silver powder, chloroform is converted into

(a) acetylene
(b) hexachloroethane
(c) 1,1,2,2-tetrachloroethane
(d) ethylene

60. Cl_2 reacts with CS_2 in presence of I_2 to form

(a) $CHCl_3$ (b) CCl_4
(c) C_2H_5Cl (d) Cl_3C-NO_2

61. Reaction of chloroform with KOH in presence of a primary aromatic amine is called :

(a) carbylamine reaction (b) reduction
(c) hydrolysis (d) Wurtz reaction

62. The product formed by heating iodoform with KOH is :

(a) HCHO (d) HCOOK
(c) CH_3COOK (d) CH_3CHO

63. Ethyl alcohol is used as a preservative for chloroform because it :

(a) prevents aerial oxidation of chloroform
(b) prevents decomposition of chloroform
(c) decomposes phosgene to CO and Cl_2
(d) removes phosgene by converting it to ethyl carbonate

64. When chlorobenzene is reacted with acetyl chloride in the presence of anhydrous $AlCl_3$, the major product formed is

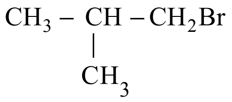
(a) 2-chloroacetophenone
(b) 3-chloroacetophenone
(c) 4-chloroacetophenone
(d) 1, 4-dichlorobenzene

65. In a S_N2 substitution reaction of the type

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

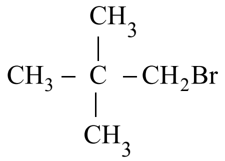
which one of the following has the highest relative rate ?

(a) $CH_3-CH_2-CH_2Br$ (b)



$CH_3-CH(CH_3)-CH_2Br$

(c)



$CH_3-C(CH_3)_2-CH_2Br$

(d) CH_3CH_2Br

66. Which of the following reactions is an example of nucleophilic substitution reaction?

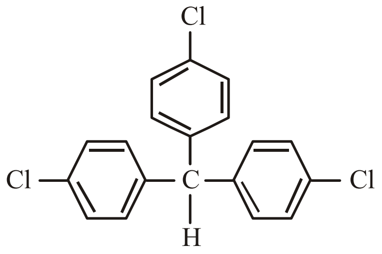
(a) $2RX+2Na \rightarrow R-R+2NaX$
(b) $RX+H_2 \rightarrow RH+HX$
(c) $RX+Mg \rightarrow RMgX$
(d) $RX+KOH \rightarrow ROH+KX$

67. Benzene reacts with CH_3Cl in the presence of anhydrous $AlCl_3$ to form:

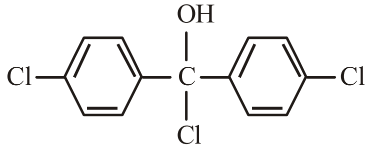
(a) chlorobenzene (b) benzylchloride
(c) xylene (d) toluene

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

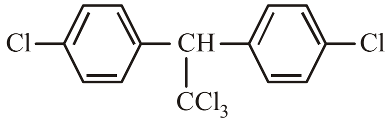
(a)



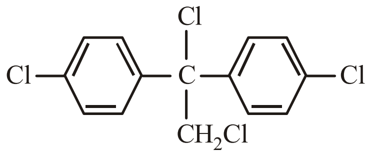
(b)



(c)



(d)



69. Which one is most reactive towards S_N1 reaction ?

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

70. In the following sequence of reactions

$$CH_3-Br \xrightarrow{KCN} A \xrightarrow{H_3O^+} B \xrightarrow[\text{ether}]{LiAlH_4} C,$$ the end product (C) is :

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

71. Which of the following is the correct order of decreasing S_N2 reactivity?

(a) $R_2CHX > R_3CX > RCH_2X$
(b) $RCHX > R_3CX > R_2CHX$
(c) $RCH_2X > R_2CHX > R_3CX$
(d) $R_3CX > R_2CHX > RCH_2X$.
(X is a halogen)

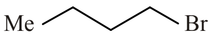
72. Iodoform can be prepared from all except :

(a) Ethyl methyl ketone
(b) Isopropyl alcohol
(c) 3-Methyl 2-butanone
(d) Isobutyl alcohol

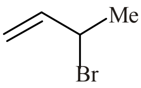
73. Which one of the following is not an allylic halide?
(a) 4-Bromopent-2-ene
(b) 3-Bromo-2-methylbut-1-ene
(c) 1-Bromobut-2-ene
(d) 4-Bromobut-1-ene

74. The organic chloro compound, which shows complete stereochemical inversion during a S_N2 reaction, is
(a) $(C_2H_5)_2CHCl$ (b) $(CH_3)_3CCl$
(c) $(CH_3)_2CHCl$ (d) CH_3Cl

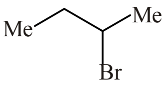
75. Consider the following bromides :



(A)



(B)

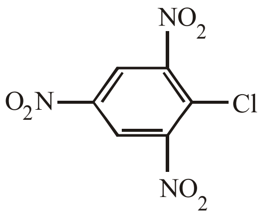


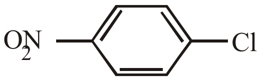
(C)

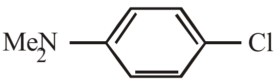
The correct order of S_N1 reactivity is
(a) $B > C > A$ (b) $B > A > C$
(c) $C > B > A$ (d) $A > B > C$

EXERCISE - 2
Applied Questions

1. Which chloro derivative of benzene among the following would undergo hydrolysis most readily with aqueous sodium hydroxide to furnish the corresponding hydroxy derivative?

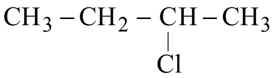
(a)


(b)


(c)


(d) C_6H_5Cl.

2. The alkyl halide that undergoes S_N1 reaction more readily is
(a) ethyl bromide (b) isopropyl bromide
(c) vinyl bromide (d) n=propyl bromide

3.

$CH_3-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$
obtained by chlorination of n-butane, will be
(a) *l*-form (b) d-form
(c) meso form (d) racemic mixture

4. Aryl halides do not undergo nucleophilic substitution reactions under ordinary conditions because
1. approach of nucleophile is retarded
2. carbon carrying halogen atom is sp^3 hybridised
3. the substrate molecule is destabilised due to resonance
4. partial double bond character between carbon and halogen

(a) 2 and 4 only (b) 1 and 4 only
(c) 2 and 3 only (d) 2, 3 and 4 only

5. $CH_3CH_2Cl \xrightarrow{NaCN} X \xrightarrow{Ni/H_2} Y$

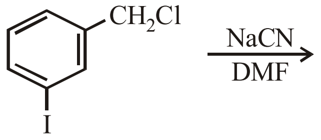
$Y \xrightarrow[\text{anhydride}]{\text{Acetic}} Z$

Z in the above reaction sequence is
(a) $CH_3CH_2CH_2NHCOCH_3$
(b) $CH_3CH_2CH_2NH_2$
(c) $CH_3CH_2CH_2CONHCH_3$
(d) $CH_3CH_2CH_2CONHCOCH_3$

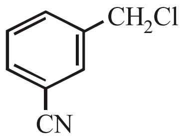
6. Bottles containing C_6H_5I and $C_6H_5CH_2I$ lost their original labels. They were labelled A and B for testing. A and B were separately taken in test tubes and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and then some $AgNO_3$ solution was added. Substance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

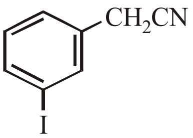
7. Which of the following is the correct method of preparation of methyl fluoride?
(a) $CH_4 + HF \rightarrow$ (b) $CH_3OH + HF \rightarrow$
(c) $CH_4 + F_2 \rightarrow$ (d) $CH_3Br + AgF \rightarrow$

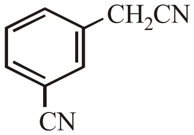
8. The structure of the major product formed in the following reaction

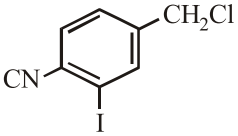


is

(a)


(b)


(c)


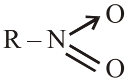
(d)


9. Identify Z in the following series

$$C_2H_5I \xrightarrow{\text{Alc. KOH}} X \xrightarrow{Br_2} Y \xrightarrow{KCN} Z$$

(a) CH_3CH_2CN (b) $NCCH_2–CH_2CN$
(c) $BrCH_2–CH_2CN$ (d) $BrCH=CHCN$

10. Which of the following pairs is/are correctly matched?

	Reaction	**Product**
I.	$RX + AgCN$	RNC
II.	$RX + KCN$	RCN
III.	$RX + KNO_2$	
IV.	$RX + AgNO_2$	R–O–N = O

(a) Only I (b) I and II
(c) III and IV (d) I, II, III and IV

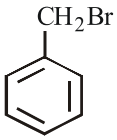
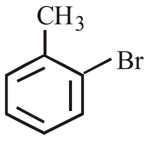
11. Identify Z in

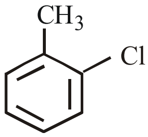
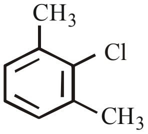
$$CH_3CH_2CH_2Br \xrightarrow{\text{aq. NaOH}} X$$

$$\xrightarrow{Al_2O_3} Y \xrightarrow{Cl_2/H_2O} Z$$

(a) Mixture of $CH_3CHClCH_2Cl$ and $CH_3CHOHCH_2Cl$
(b) $CH_3CHOHCH_2Cl$
(c) $CH_3CHClCH_2OH$
(d) $CH_3CHClCH_2Cl$

12. Which compound in each of the following pairs is most reactive to the conditions indicated ?

(A)

and (B)

(KOH in CH_3OH)

(C)

and (D)

($NaNH_2$ in NH_3)

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

13. The correct kinetic rate equation for the addition-elimination mechanism of nucleophilic aromatic substitution

(a) rate = K [aryl halide] [nucleophile]
(b) rate = K [aryl halide]
(c) rate = K [aryl halide] $[\text{nucleophile}]^2$
(d) rate = K [nucleophile]

14. Which of the following reagents react readily with bromobenzene ?

(a) $NaNH_2 / NH_3$ at $-33°C$
(b) $(CH_3)_2NH$ at. 25°C
(c) CH_3CH_2ONa at. 25°C
(d) NaCN / DMSO at. 25°C

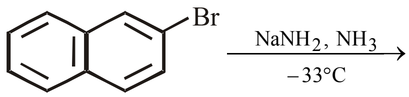
15. Isobutene $\xrightarrow[\text{peroxide}]{HBr}$ A $\xrightarrow{KCN}$

B $\xrightarrow{\text{dil. } H_2SO_4}$ C + inorganic salt D

C and D are

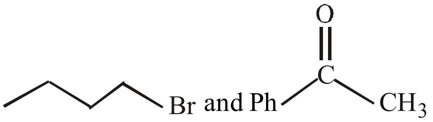
(a) $Me_2CH.CH_2COOH, (NH_4)_2SO_4$
(b) $Me_2CH.COOH, (NH_4)_2SO_4$
(c) $Me_2CH.CH_2COOK, NH_4OH$
(d) $Me_2CH.CH_2COOK, K_2SO_4$

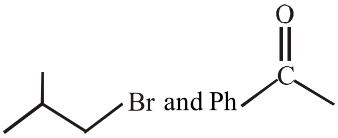
16. How many isomeric naphthylamines are expected in the following reaction ?

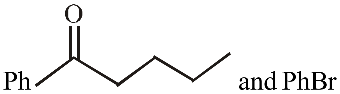


(a) two (b) only single product
(c) four (d) three

17. 2-phenyl-2-hexanol can be prepared by Grignard synthesis. The pair of compounds giving the desired product is

(a)


(b)


(c)


(d) None of these

18. Which will undergo S_N2 reaction fastest among the following halogen compounds?

(a) CH_3CH_2F (b) CH_3CH_2Cl
(c) CH_3CH_2Br (d) CH_3CH_2I

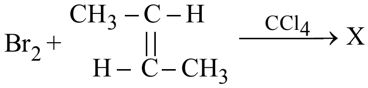
19. In the following sequence of reactions

$$CH_3CH_2OH \xrightarrow{P+I_2} A \xrightarrow[\text{ether}]{Mg} B \xrightarrow{HCHO} C \xrightarrow{H_2O} D$$

the compound D is

(a) propanal (b) butanal
(c) *n*-butyl alcohol (d) *n*-propyl alcohol.

20. X in the following reaction is –



$$Br_2 + \begin{matrix} CH_3-C-H \\ \| \\ H-C-CH_3 \end{matrix} \xrightarrow{CCl_4} X$$

(a) (+) 2, 3-Dibromobutane
(b) (–) 2, 3-Dibromobutane
(c) Rac. 2, 3-Dibromobutane
(d) Meso-2, 3-Dibromobutane

21. Consider the reactions :

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

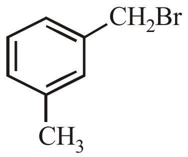
(ii) $(CH_3)_2CH-CH_2Br \xrightarrow{C_2H_5O^-} (CH_3)_2CH-CH_2OC_2H_5 + Br^-$

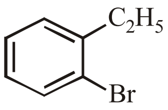
The mechanisms of reactions (i) and (ii) are respectively :

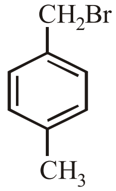
(a) S_N1 and S_N2 (b) S_N1 and S_N1

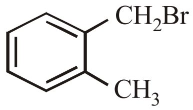
(c) S_N2 and S_N2 (d) S_N2 and S_N1

22. 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).

(a) 

(b) 

(c) 

(d) 

DIRECTIONS for Qs. 23 to 25 : These are Assertion-Reason type questions. Each of these question contains two statements : Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

(a) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement-1

(b) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1

(c) Statement-1 is True, Statement-2 is False

(d) Statement-1 is False, Statement-2 is True

23. **Statement-1 :** $CHCl_3$ is stored in dark bottles.
Statement-2 : $CHCl_3$ is oxidised in dark.

24. **Statement-1 :** Addition of bromine to trans-2-butene yields meso-2, 3-dibromobutane
Statement-2 : Bromine addition to an alkene is an electrophilic addition.

25. **Statement-1 :** CCl_4 is not a fire extinguisher.
Statement-2 : CCl_4 is insoluble in water.

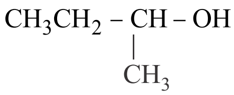
EXERCISE - 3

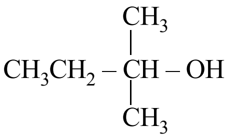
Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

1. The order of reactivity of following alcohols with halogen acids is ....

(A) $CH_3CH_2-CH_2-OH$

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

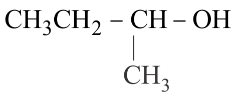
(C) 
$CH_3CH_2-C(CH_3)_2-OH$

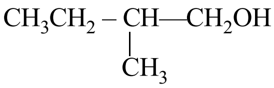
(a) (A) > (B) > (C) (b) (C) > (B) > (A)

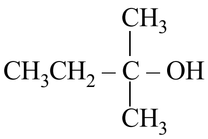
(c) (B) > (A) > (C) (d) (A) > (C) > (B)

2. Which of the following alcohols will yield the corresponding alkyl chloride on reaction with concentrated HCl at room temperature?

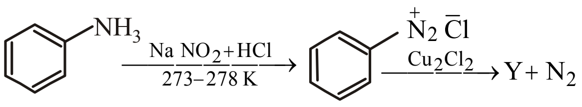
(a) $CH_3CH_2-CH_2-OH$

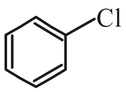
(b) 
$CH_3CH_2-CH(CH_3)-OH$

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

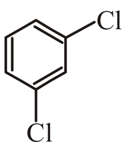
(d) 
$CH_3CH_2-C(CH_3)_2-OH$

3. Identify the compound Y in the following reaction.



(a) 

(b) 

(c) 

(d) 

4. Toluene reacts with a halogen in the presence of iron (III) chloride giving ortho and para halo compounds. The reaction is

(a) electrophilic elimination reaction

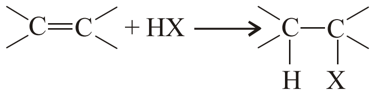
(b) electrophilic substitution reaction

(c) free radical addition reaction

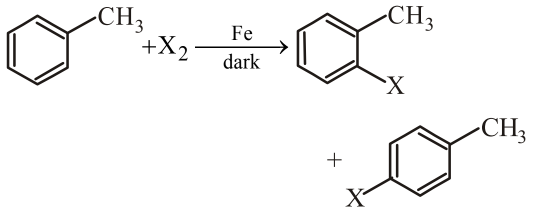
(d) nucleophilic substitution reaction

5. Which of the following is halogen exchange reactions?

(a) $RX + NaI \rightarrow RI + NaX$

(b) 

(c) $R-OH + HX \xrightarrow{ZnCl_2} R-X + H_2O$

(d) 

6. Which reagent will you use for the following reaction?

$CH_3CH_2CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$

(a) Cl_2/UV light

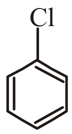
(b) $NaCl + H_2SO_4$

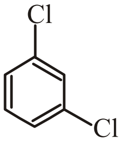
(c) Cl_2 gas in dark

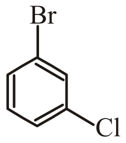
(d) Cl_2 gas in the presence of iron in dark

7. Arrange the following compounds in the increasing order of their densities.

(i) 

(ii) 

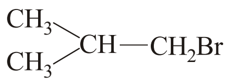
(iii) 

(iv) 

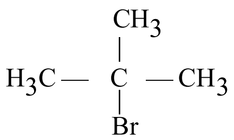
(a) (i) < (ii) < (iii) < (iv) (b) (i) < (iii) < (iv) < (ii)

(c) (iv) < (iii) < (ii) < (i) (d) (ii) < (iv) < (iii) < (i)

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

(i) 

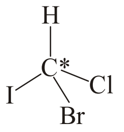
(ii) $CH_3CH_2CH_2CH_2Br$

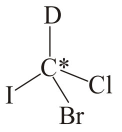
(iii) 

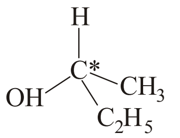
(a) (ii) < (i) < (iii) (b) (i) < (ii) < (iii)

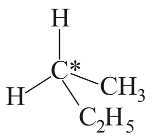
(c) (iii) < (i) < (ii) (d) (iii) < (ii) < (i)

9. In which of the following molecules carbon atom marked with asterisk (*) is asymmetric?

(i) 

(ii) 

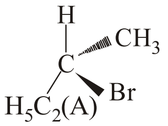
(iii) 

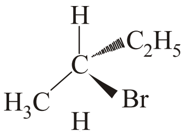
(iv) 

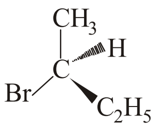
(a) (i), (ii), (iii) and (iv) (b) (i), (ii) and (iii)

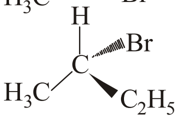
(c) (ii), (iii) and (iv) (d) (i), (iii) and (iv)

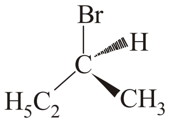
10. Which of the following structures is enantiomeric with the molecule (A) given below?



(a) 

(b) 

(c) 

(d) 

11. Which of the following is an example of *vic*-dihalide?

(a) Dichloromethane (b) 1, 2-dichloroethane

(c) Ethylidene chloride (d) Allyl chloride

12. The position of Br in the compound $CH_3CH = CHC(Br)(CH_3)_2$ can be classified as ....

(a) allyl (b) aryl

(c) vinyl (d) secondary

13. Chlorobenzene is formed by reaction of chlorine with benzene in the presence of $AlCl_3$. Which of the following species attacks the benzene ring in this reaction?

(a) Cl^- (b) Cl^+

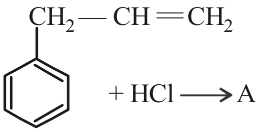
(c) $AlCl_3$ (d) $[AlCl_4]^-$

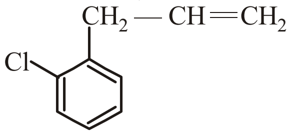
14. Ethylidene chloride is a/an ....

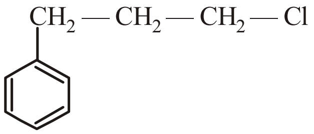
(a) *vic*-dihalide (b) *gem*-dihalide

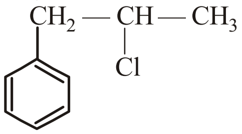
(c) allylic halide (d) vinylic halide

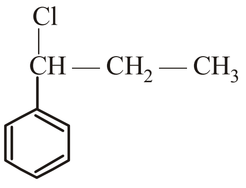
15. What is 'A' in the following reaction?



(a) 

(b) 

(c) 

(d) 

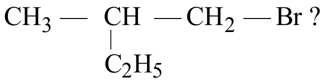
16. A primary alkyl halide would prefer to undergo ....

(a) S_N1 reaction (b) S_N2 reaction

(c) α-elimination (d) racemisation

17. 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) $(CH_3)_3C—I$

18. Which is the correct IUPAC name for

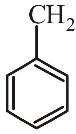
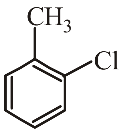
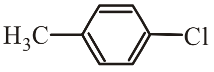


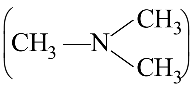
$$CH_3—\underset{\substack{|\\C_2H_5}}{CH}—CH_2—Br\ ?$$

(a) 1-bromo-2-ethylpropane
(b) 1-bromo-2-ethyl-2-mehylethane
(c) 1-bromo-2-methylbutane
(d) 2-methyl-1-bromobutane

19. What should be the correct IUPAC name for diethylbromomethane?
(a) 1-bromo-1, 1-diethylmethane
(b) 3-bromopentane
(c) 1-bromo-1-ethylpropane
(d) 1-bromopentane

20. The reaction of toluene with chlorine in the presence of iron and in the absence of light yields ....

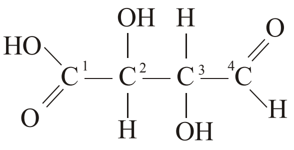
(a) 
(b) 
(c) 
(d) Mixture of (b) and (c)

21. Chloromethane on treatment with excess of ammonia yields mainly
(a) N, N-dimethylmethanamine 
(b) N - methylmethanamine $(CH_3—NH—CH_3)$
(c) methanamine (CH_3NH_2)
(d) mixture containing all these in equal proportion

22. Molecules whose mirror image is non – superimposable over them are known as chiral. Which of the following molecules is chiral in nature?
(a) 2 - bromobutane (b) 1 - bromobutane
(c) 2 - bromopropane (d) 2 -bromopropan - 2 - ol

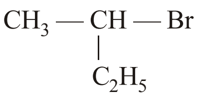
23. Reaction of $C_6H_5CH_2Br$ with aqueous sodium hydroxide follows ....
(a) S_N1 mechanism
(b) S_N2 mechanism
(c) Any of the above two depending upon the temperature of reaction
(d) Saytzeff rule

24. Which of the carbon atoms presents in the molecule given below are asymmetric?

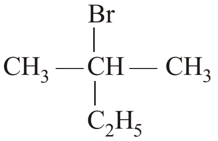


(a) 1, 2, 3, 4 (b) 2, 3
(c) 1, 4 (d) 1, 2, 3

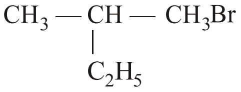
25. Which of the following compounds will give racemic mixture on nucleophilic substitution by OH^- ion?

(i) 

$$CH_3—\underset{\substack{|\\C_2H_5}}{CH}—Br$$

(ii) 

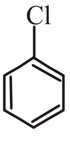
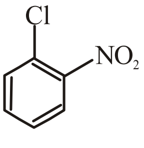
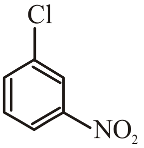
$$CH_3—\overset{\substack{Br\\|}}{\underset{\substack{|\\C_2H_5}}{CH}}—CH_3$$

(iii) 

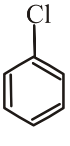
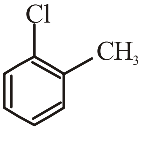
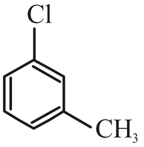
$$CH_3—\underset{\substack{|\\C_2H_5}}{CH}—CH_2Br$$

(a) (i) (b) (i), (ii) and (iii)
(c) (ii) and (iii) (d) (i) and (iii)

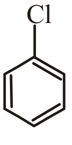
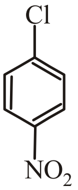
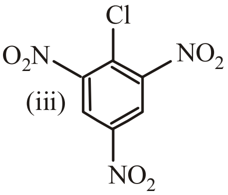
Direction (Q. No. 26 to 29) : In the questions 26 to 29 arrange the compounds in increasing order of rate of reaction towards nucleophilic substitution.

26. (i)  (ii)  (iii) 

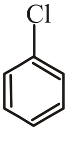
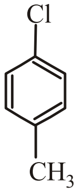
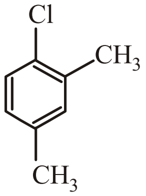
(a) (i) < (ii) < (iii) (b) (iii) < (ii) < (i)
(c) (i) < (iii) < (ii) (d) (iii) < (i) < (ii)

27. (i)  (ii)  (iii) 

(a) (i) < (ii) < (iii) (b) (i) < (iii) < (ii)
(c) (iii) < (ii) < (i) (d) (ii) < (iii) < (i)

28. (i)  (ii)  (iii) 

(a) (iii) < (ii) < (i) (b) (ii) < (iii) < (i)
(c) (i) < (iii) < (ii) (d) (i) < (ii) < (iii)

29. (i)  (ii)  (iii) 

(a) (iii)<(ii)<(i) (b) (ii)<(i)<(iii)
(c) (iii)<(ii)<(i) (d) (i)<(iii)<(ii)

30. Which is the correct increasing order of boiling points of the following compounds?
1 - iodobutane, 1 - bromobutane, 1 - chlorobutane, Butane
(a) Butane < 1-chlorobutane < 1- bromobutane < 1 - iodobutabe
(b) 1 - iodobutane < 1 - bromobutane < 1 - chloroubutane < Butane

(c) Butane < 1 - iodobutane < 1 - bromobutane < 1 - chlorobutane

(d) Butane < 1 - chlorobutane < 1 - iodobutane < 1 - bromobutane

31. Which is the correct increasing order of boiling points of the following compounds?

1 - bromoethane, 1 - bromopropane, 1 - bromobutane, Bromobenzene

(a) Bromobenzene < 1 - bromobutane < 1 - bromopropane < 1- bromoethane

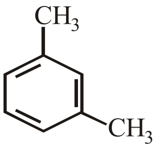
(b) Bromobenzene < 1 - bromobutane < 1 - bromopropane < 1- bromobutane

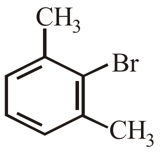
(c) 1 - bromopropane < 1 - bromorpropane < 1 - bromoethane < Bromobenzene

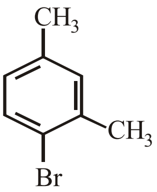
(d) 1 - bromoethane < 1 - bromopropane < 1 - bromobutane < Bromobenzene

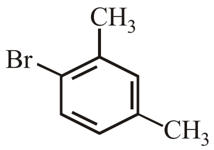
NEET/AIPMT (2013-2017) Questions

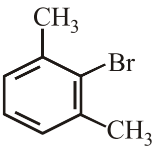
32. What products are formed when the following compounds is treated with Br_2 in the presence of $FeBr_3$? *[2014]*

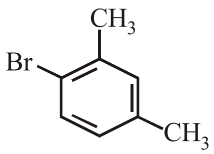


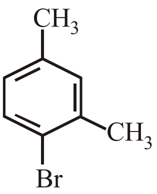
(a) 

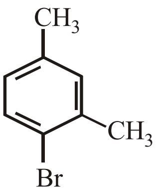
and 

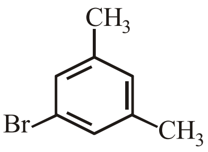
(b) 

and 

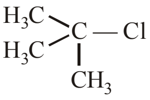
(c) 

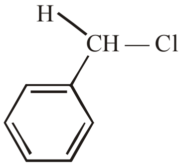
and 

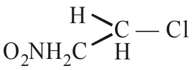
(d) 

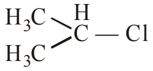
and 

33. In which of the following compounds, the C - Cl bond ionisation shall give most stable carbonium ion? *[2015]*

(a) 

(b) 

(c) 

(d) 

34. In an S_N1 reaction on chiral centres there is : *[2015 RS]*

(a) 100 % racemization

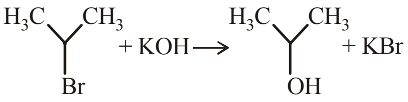
(b) inversion more than retention leading to partial racemization

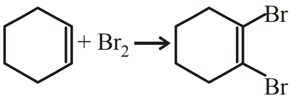
(c) 100 % retention

(d) 100 % inversion

35. For the following reactions : *[2016]*

(1) $CH_3CH_2CH_2Br + KOH \rightarrow CH_3CH{=}CH_2 + KBr + H_2O$

(2) 

(3) 

Which of the following statements is correct ?

(a) (1) and (2) are elimination reaction and (3) is addition reaction

(b) (1) is elimination, (2) is substitution and (3) is addition reaction

(c) (1) is elimination, (2) and (3) are substitution reactions

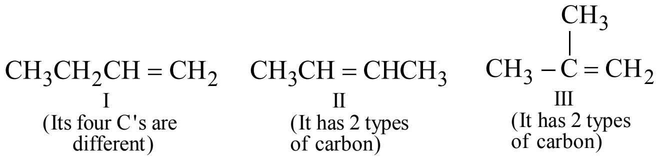
(d) (1) is substitution, (2) and (3) are addition reaction

Hints & Solutions

EXERCISE - 1

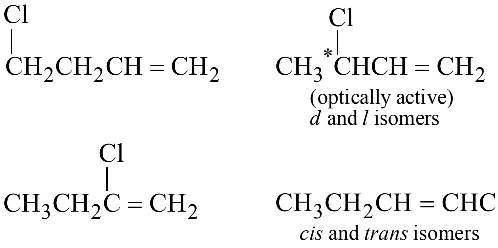
1. **(b)** In basic conditions, the reactivity by elimination increases from 1° carbocation to 3° carbocation. So, $(CH_3)_3CCl$ suffers elimination the most among the given choices.
Note: Elimination reactions are of two types E_1 and E_2. Reactivity by E_1 and E_2 mechanism increases in the same order but due to different reasons. The rate of E_2 depends upon the concentration of base and rate of E_1 depends upon the nature of base.
Here we can not decide whether the reaction is proceed via E_1 mechanism or E_2 mechanism because nothing is given about the basic conditions.

2. **(b)** C_4H_7Cl is a monochloro derivative of C_4H_8 which itself exists in three acyclic isomeric forms.



$CH_3CH_2CH=CH_2$ I (Its four C's are different) $CH_3CH=CHCH_3$ II (It has 2 types of carbon) $CH_3-C(CH_3)=CH_2$ III (It has 2 types of carbon)

Four monochloro derivatives of I

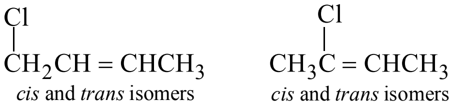


$ClCH_2CH_2CH=CH_2$ $CH_3\overset{*}{C}H(Cl)CH=CH_2$ (optically active) *d* and *l* isomers

$CH_3CH_2C(Cl)=CH_2$ $CH_3CH_2CH=CHCl$ *cis* and *trans* isomers

Hence total isomers from I = 6

Two monochloro derivatives of II



$ClCH_2CH=CHCH_3$ *cis* and *trans* isomers $CH_3C(Cl)=CHCH_3$ *cis* and *trans* isomers

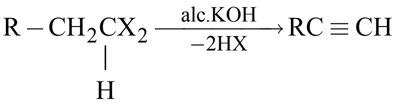
Hence total isomers from II = 4

Two monochloro derivatives from III

$CH_3-C(CH_2Cl)=CH_2$ $CH_3-C(CH_3)=CHCl$

Grand total of acyclic isomers = 6 + 4 + 2 = 12

3. **(a)** Gem dihalides on treatment with alcoholic KOH gives alkyne as follows :

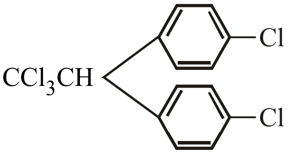


$$R-\underset{\displaystyle H}{\underset{|}{C}}H_2CX_2 \xrightarrow[-2HX]{alc.KOH} RC\equiv CH$$

4. **(b)**

$CHCl_2-CH_3$ (*gem*-dihalide) CH_2Cl-CH_2Cl (*vic*-dihalide)

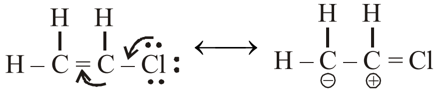
5. **(a)**



(DDT)

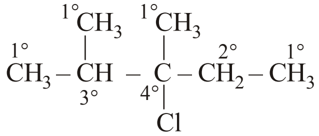
6. **(a)**

7. **(d)** Among the given structures, $CH_2=CHCl$ is least reactive.
As reaction of substitution involves breakage of carbon-halogen bond. Here the carbon is vinylic carbon hence is sp^2 hybridised. The bond length is shorter than single bond and has a very high bond energy. This is because of resonance:



Also vinylic carbocation is very less stable.
Thus option (d) is correct choice.
In structure $CH_2=CHCH_2Cl$, allylic carbon is present.
Allylic carbocation is infact stabilized by resonance.

8. **(b)**



3-Chloro-2,3-dimethylpentane

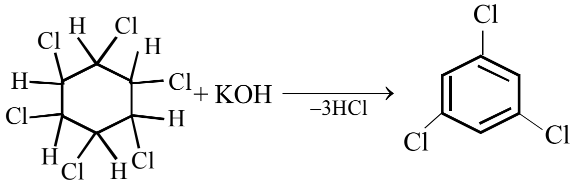
9. **(a)**

10. **(b)** Halides Cl^-, Br^-, I^- React with $AgNO_3$ to give
$AgCl \longrightarrow$ soluble in NH_4OH
$AgBr \longrightarrow$ spraringly soluble in NH_4OH
$AgI \longrightarrow$ Insoluble
and the C – Cl bond is weakest in benzyl chloride [(sp^3) hybridised carbon is attached to Cl]

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

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

12. **(c)**



13. **(c)** Potassium ethoxide is a strong base, and 2-bromopentane is a 2º bromide, so elimination reaction predominates

$$CH_3CH(Br)CH_2CH_2CH_3 \xrightarrow{OC_2H_5^-}$$

$$\underset{\text{Pentene - 2(major) } trans}{CH_3CH=CHCH_2CH_3} + \underset{\text{Pentene–1(min or) } cis}{CH_2=CHCH_2CH_2CH_3}$$

Since *trans*- alkene is more stable than *cis.thus* *trans*-pentene -2 is the main product.

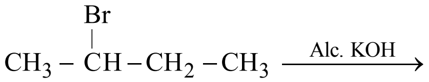
14. **(b)** $CH_3-CH_2-CHCl_2 \xrightarrow[\Delta]{NaNH_2}$

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

15. (d) Alcoholic KOH, reduces haloalkane into alkene by the process dehydrohalogenation

$$CH_3-CHBr-CH_2-CH_3+KOH\ (Alc)$$

$$\xrightarrow[-HBr]{} CH_3-CH=CH-CH_3$$

16. **(c)** 

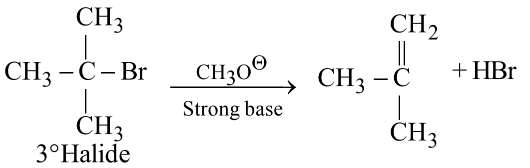
$$CH_3-\overset{Br}{\overset{|}{C}}H-CH_2-CH_3 \xrightarrow{\text{Alc. KOH}}$$

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

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

17. **(a)**

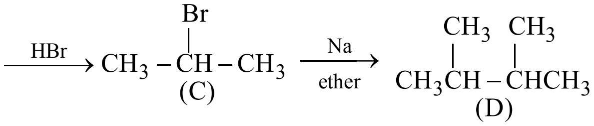
18. **(b)** 3° halide on reaction with strong base $(CH_3O^{\ominus})$ undergo elimination reaction and forms alkene as major product.



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

3°Halide

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



$$\xrightarrow{HBr} \underset{(C)}{CH_3-\overset{Br}{\overset{|}{C}}H-CH_3} \xrightarrow[ether]{Na} \underset{(D)}{CH_3\overset{CH_3}{\overset{|}{C}}H-\overset{CH_3}{\overset{|}{C}}HCH_3}$$

20. **(a)** $CHCl_3+3HF \longrightarrow CHF_3+3HCl$

wt. of $CHF_3 = (12 + 1 + 19 \times 3) = 70$

21. **(b)** 

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

gem-dihalide *vic*–dihalide

22. **(a)** Friedel Craft reactions are examples of aromatic electrophilic substitution. In this, a Lewis acid (like $AlCl_3, FeBr_3$ etc.) is used as catalyst.

$$C_6H_6+CH_3Cl \xrightarrow{AlCl_3} C_6H_5CH_3+HCl$$

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

$$C_6H_5NH_2+2CuCl+H_2O$$

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

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

25. **(b)** Heavy metal ions, particularly Ag^+, catalyse S_N1 reaction because of presence of empty orbital.

$$CH_3CH_2Br+Ag^+ \rightleftharpoons$$

$$[CH_3CH_2 .... Br .... Ag]^+$$

$$\xrightarrow[(-AgBr)]{slow} CH_3CH_2^+ \xrightarrow[\text{from } H_2O]{OH^-} CH_3CH_2OH$$

26. **(a)** $C_2H_6+Cl_2 \xrightarrow{\text{UV light}} C_2H_5Cl+HCl$

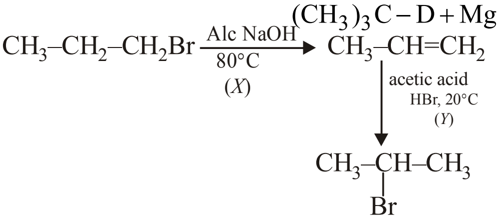
27. **(c)** The best method for the conversion of an alcohol into an alkyl chloride is reaction of the alcohol with thionyl chloride ($SOCl_2$) in the presence of pyridine.

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

SO_2 and HCl being gases escape leaving behind pure alkyl halide.

28. **(a)** $(CH_3)_3C-MgCl+D_2O \longrightarrow$

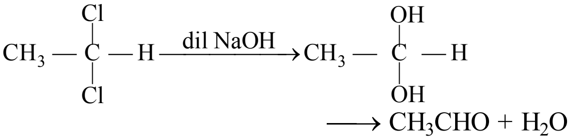
$$(CH_3)_3C-D+Mg(OD)Cl$$

29. **(b)** 

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

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

31. **(a)** 1, 1-dichloroethane on heating with dil. NaOH gives acetaldehyde.



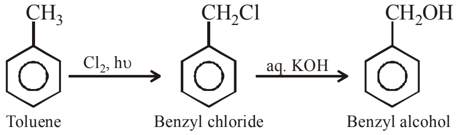
$$CH_3-\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}-H \xrightarrow{\text{dil NaOH}} CH_3-\underset{OH}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-H \longrightarrow CH_3CHO+H_2O$$

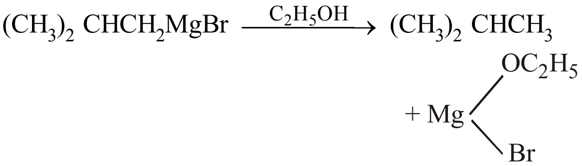
32. **(b)** Addition of HBr to 2-pentyne gives two structural isomers (I) and (II)

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

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

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

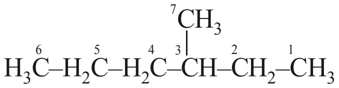
33. **(d)** 

34. **(b)** 

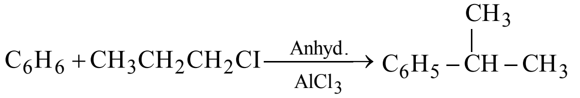
$$(CH_3)_2\ CHCH_2MgBr \xrightarrow{C_2H_5OH} (CH_3)_2\ CHCH_3 + Mg\begin{matrix} OC_2H_5 \\ Br \end{matrix}$$

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

36. **(a)** 3-methlhexane can yield seven different monochlorinated products upon free radical chlorination.



$$H_3\overset{6}{C}-H_2\overset{5}{C}-H_2\overset{4}{C}-\overset{^7CH_3}{\overset{3\,|}{C}}H-\overset{2}{C}H_2-\overset{1}{C}H_3$$

37. **(c)** 

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

Isopropyl benzene

38. **(b)** $CH_3Br+AgF \longrightarrow CH_3F+AgBr$

39. **(b)** $C_6H_5Br \xrightarrow{Mg} C_6H_5MgBr$

$\xrightarrow{CH_3CH_2OH} C_6H_6 + CH_3CH_2OMgBr$

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

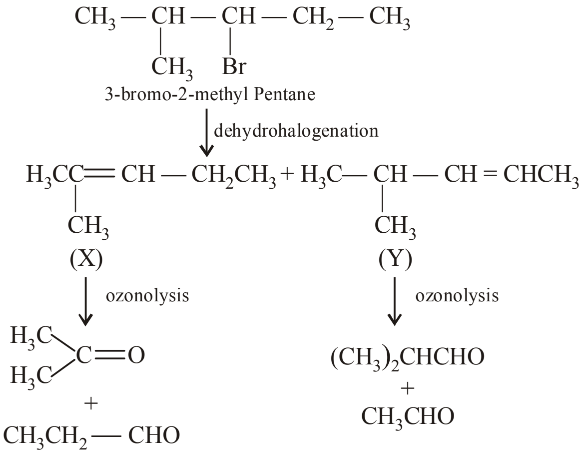
41. **(d)** **S_N1 (Unimolecular nucleophilic substitution)** : Although it is a two step process, the rate of reaction depends only upon the **first (slow)** step which involves ionization of the alkyl halide to form carbocation. Hence rate of reaction depends only upon the concentration of the alkyl halides, $r = k[RX]$ and is independent of the concentration of the nucleophile which adds on the carbocation in the ***second (fast)*** step.

$$R-X \xrightarrow[\text{(slow)}]{-X^-} R^+ \xrightarrow[\text{(fast)}]{:Z} R-Z$$

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

43. **(d)** $-Cl$ is *o, p*–directing.

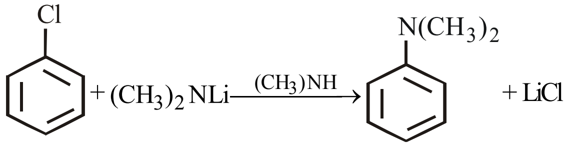
44. **(d)**



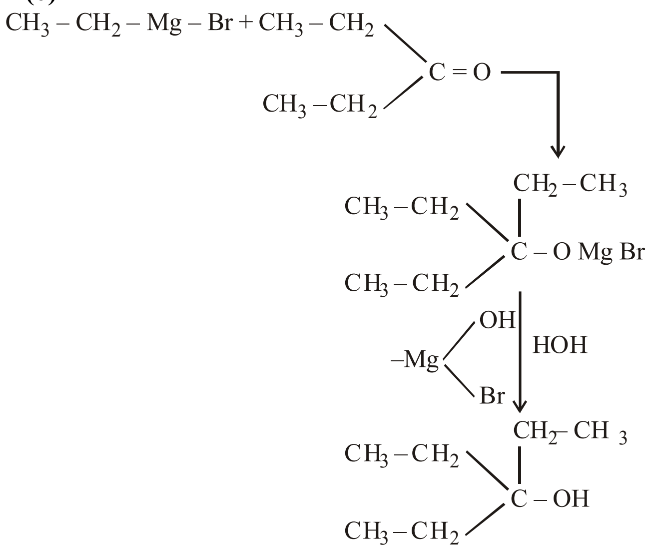
45. **(d)** $C_6H_5COOAg + Br_2 \xrightarrow{\text{Hunsdiecker reaction}}$

$C_6H_5Br + CO_2 + AgBr$

46. **(a)**



47. **(c)**



3-ethylpentan-3-ol

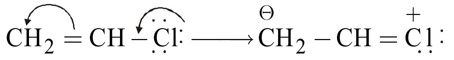
48. **(d)** The boiling points of alkyl chlorides increases with increase in molecular weight. In case of isomeric alkyl chloride, the order of boiling point is
primary > secondary > tertiary

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

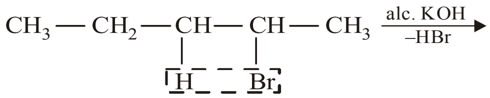
$C_6H_5MgBr + Me_3COH \longrightarrow C_6H_6 + Me_3COMgBr$

50. **(d)** $CH_2 = CH-Cl$
(Vinyl Chloride)

The halogen atom in vinyl chloride is not reactive as in other alkyl halides. The non-reactivity of chlorine atom is due to resonance stabilisation. The *ℓ.P.* on Cl-atom can participate in delocalisation (Resonance) to give two canonical structure.



51. **(a)**



2-bromopentane

$CH_3-CH_2-CH=CH-CH_3$
2-pentene

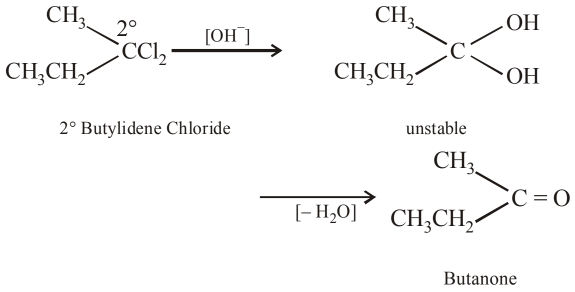
These reactions are known as β-elimination.

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

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

53. **(c)** **54.** (d)

55. **(b)**



56. **(a)** $CCl_3{\cdot}CH(OH)_2 + NaOH \xrightarrow{\text{distil}} CHCl_3 + HCOONa + H_2O$

57. **(d)** $3CCl_4 + 2\,SbF_5 \xrightarrow{SbCl_5} 2SbCl_3 + 3CCl_2F_2$
freon–12

$CCl_4 + 2H \xrightarrow{C,FeCl_3} 2HCl + CCl_2F_2$

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

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

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

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

61. **(a)** This is carbylamine reaction

$ArNH_2 + CHCl_3 + 3KOH$
1° aromatic amine

$\longrightarrow Ar-N\overset{\rightarrow}{\equiv}C + 3KCl + 3H_2O$
isocyanide

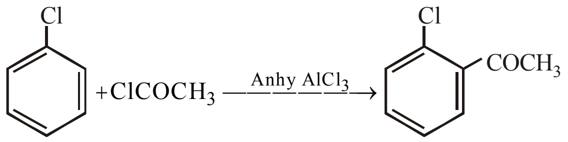
62. **(b)**
$$\begin{tikzcd} \underset{\text{iodoform}}{CHI_3} + 3KOH \arrow[r] & CH(OH)_3 + 3KI \arrow[d] \\ HCOOK & HCOOH + H_2O \arrow[l, "KOH"'] \end{tikzcd}$$

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

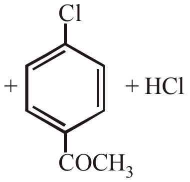
$$CHCl_3 \xrightarrow{O_2/\text{light}} \underset{\text{Phosgene (Poisonous)}}{COCl_2} + HCl$$

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

64. **(c)**



2-Chloro acetophenone (minor)

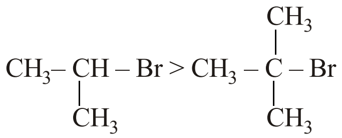


4-Chloro acetophenone (major)

[**Note :** Para product predominates over the ortho product]

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

$CH_3\,CH_2\,Br > CH_3\,CH_2\,CH_2\,Br >$

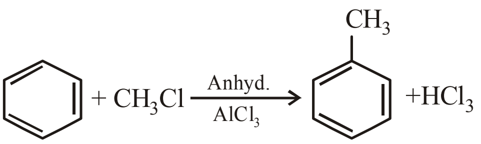


$$\underset{\displaystyle CH_3}{CH_3-\underset{|}{CH}-Br} > CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Br$$

i.e. option (d) is correct.

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

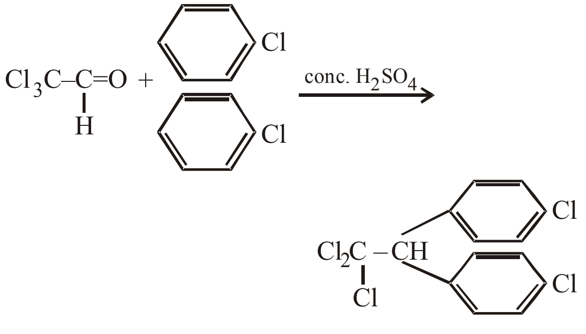
67. **(d)**



Toluene

Friedel Craft's reaction.

68. **(c)**



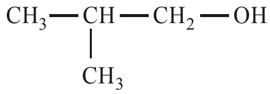
DDT

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

70. **(d)** $$CH_3-Br \xrightarrow{KCN} \underset{(A)}{CH_3-CN} \xrightarrow{H_3O^+}$$
$$\underset{(B)}{CH_3-COOH} \xrightarrow{LiAlH_4} \underset{\substack{(C)\\ \text{Ethyl alcohol}}}{CH_3-CH_2-OH}$$

71. **(c)** In S_N2 mechanism transition state is pentavalent. Thus bulky alkyl group will be sterically hindered and smaller alkyl group will favour the S_N2 mechanism. So the decreasing order of reactivity of alkyl halides is $RCH_2X > R_2CHX > R_3CX$

72. **(d)** Iodoform test is given by methyl ketones, acetaldehyde and methyl secondary alcohols.



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-OH$$

Isobutyl alcohol is a primary alcohol hence does'nt give positive iodoform test.

73. **(d)** 4-Bromobut-l-ene is not an allylic halide

$$\underset{\text{4–Bromobut–1–ene}}{BrH_2C-CH_2-CH=CH_2}$$

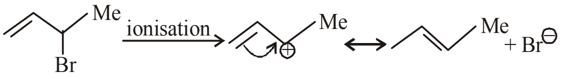
74. **(d)** S_N2 reaction is favoured by small groups on the carbon atom attached to halogen.
So, the order of reactivity is

$$CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl > (C_2H_5)_2CHCl$$

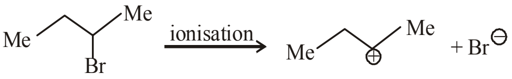
S_N2 reaction is shown to maximum extent by primary halides. The only primary halides given is CH_3Cl so the correct answer is (d).

75. **(a)**

(A)



(B)



(C)

Since S_N1 reactions involve the formation of carbocation as intermediate in the rate determining step, more is the stability of carbocation higher will be the reactivity of alkyl halides towards S_N1 route. Now we know that stability of carbocations follows the order : 3° > 2° > 1°, so S_N1 reactivity should also follow the same order.

3° > 2° > 1° > Methyl **(S_N1 reactivity)**

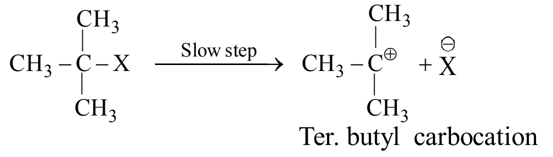
EXERCISE - 2

1. **(a)** Cl in 2, 4, 6-trinitrochlorobenzene is activated by three NO_2 groups at *o*, and *p*-positions and hence undergoes hydrolysis most readily.

2. **(d)** This reaction occurs in two steps. 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 forms the final product.

Thus the stability of the carbocation influences the rate of reaction. More stable the carbocation, higher is its rate of formation. Thus those alkyl halides which form stable, 3° carbocations undergo S_N1 reaction readily. Thus, t-butyl bromide is the favourable substrate.

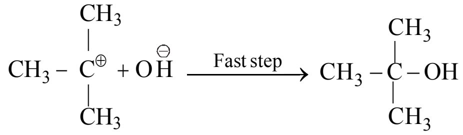
(i)



$$CH_3-C(CH_3)_2-X \xrightarrow{\text{Slow step}} CH_3-\overset{\oplus}{C}(CH_3)_2 + \overset{\ominus}{X}$$

Ter. butyl carbocation

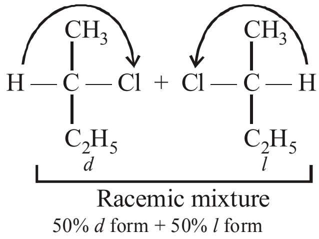
(ii)



$$CH_3-\overset{\oplus}{C}(CH_3)_2 + \overset{\ominus}{OH} \xrightarrow{\text{Fast step}} CH_3-C(CH_3)_2-OH$$

Rate of reaction ∝ $[(CH_3)_3C-X]$

3. **(d)** $CH_3-CH_2-CH_2-CH_3 \xrightarrow{Cl_2/hv}$



$Cl^{\bullet}$ may attack on either side and give a racemic mixture of 2-chloro butane which contain 50% *d* form and 50% *l*-form.

4. **(b)** Aryl halides are less reactive towards nucleophilic substitution because of the partial double bond character of carbon-halogen bonds. It is also partly due to repulsion between the electron cloud of the benzene ring and the nucleophile.

5. **(a)** $CH_3CH_2Cl \xrightarrow{NaCN}$

$$\underset{(X)}{CH_3CH_2CN} + NaCl \xrightarrow{Ni/H_2}$$

$$\underset{(Y)}{CH_3CH_2CH_2NH_2} \xrightarrow[(CH_3CO)_2O]{}$$

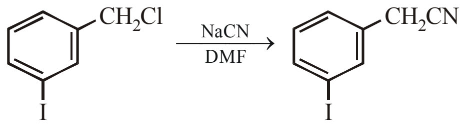
$$\underset{(Z)}{CH_3CH_2CH_2NHCOCH_3} + CH_3COOH$$

6. **(d)**

7. **(d)** Fluoroalkanes are difficult to prepare directly because flourination of hydrocarbons with pure F_2 gas occurs explosively. Therefore these are prepared by treating alkyl chloride or bromide with salts such as Hg_2F_2, AgF. The reaction is called swarts reaction.

$$CH_3Br + AgF \rightarrow CH_3F + AgBr$$

8. **(b)**



Nuclear substitution will not take place.

9. **(b)** $C_2H_5I \xrightarrow{\text{alc. KOH}} CH_2=CH_2 \xrightarrow{Br_2}$

$$BrCH_2-CH_2Br \xrightarrow{KCN} CNCH_2.CH_2CN$$

10. **(b)**

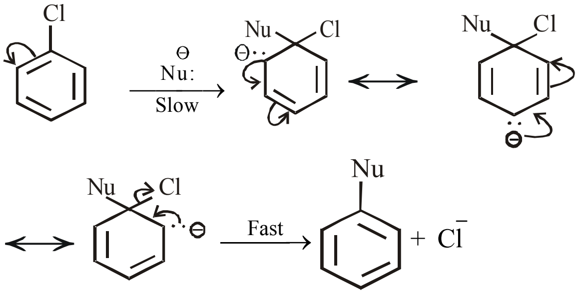
11. **(b)**

$$CH_3CH_2CH_2Br \xrightarrow{\text{aq. KOH}} CH_3CH_2CH_2OH \xrightarrow[\text{heat}]{Al_2O_3}$$

$$CH_3CH=CH_2 \xrightarrow{Cl_2/H_2O} CH_3.CHOH.CH_2Cl$$

12. **(a)** In the first case the reaction gives side chain substitution product which is easier in A. In the second case the reaction will proceed by benzyne mechanism for which ortho position w. r. to Cl must have H-atoms.

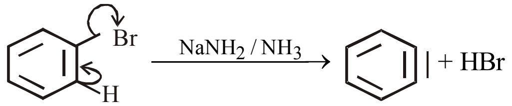
13. **(a)**



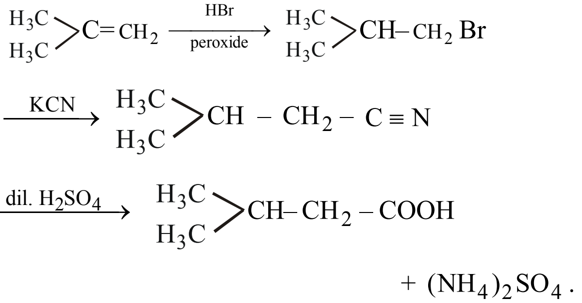
Rate ∝ $[C_6H_5Cl][\bar{Nu}:] =$

K [Aryl halide] [nucleophile]

14. **(a)**



15. **(a)**

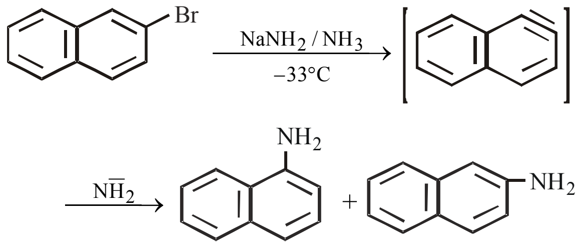


$$(H_3C)_2C=CH_2 \xrightarrow[\text{peroxide}]{HBr} (H_3C)_2CH-CH_2Br$$

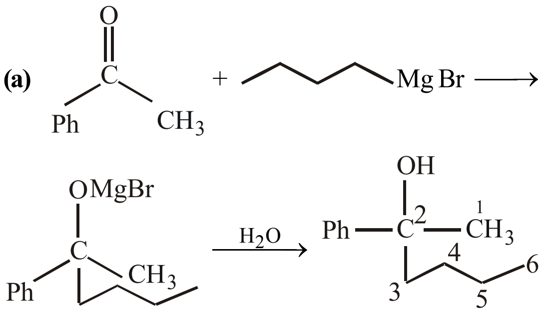
$$\xrightarrow{KCN} (H_3C)_2CH-CH_2-C\equiv N$$

$$\xrightarrow{\text{dil. } H_2SO_4} (H_3C)_2CH-CH_2-COOH + (NH_4)_2SO_4.$$

16. **(a)**



17. (a)



2 – phenyl -2-hexanol

18. (d) Smaller the R group reactivity will be higher towards S_N2 reaction. For alkyl halides containing similar alkyl group better will be the leaving group, more facile is the nucleophilic substitution reaction.

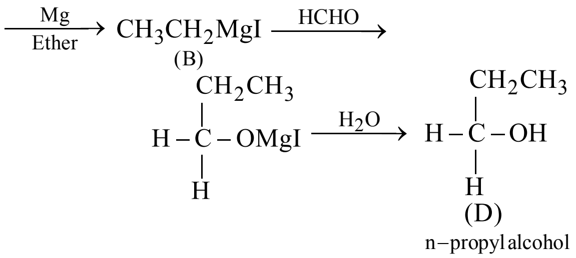
Amongst the halide ions, the order in which the leaving groups depart follows the sequence :

$$I^- > Br^- > Cl^- > F^-$$

It is because of this reason that the order of reactivity of haloalkanes follows the sequence :

iodoalkanes > bromoalkanes > chloroalkanes > fluoroalkanes

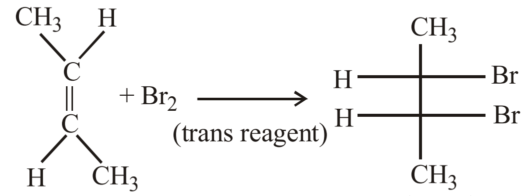
19. (d) $\underset{A}{CH_3CH_2OH \xrightarrow{P+I_2} CH_3CH_2I}$



$$\xrightarrow[\text{Ether}]{Mg} \underset{(B)}{CH_3CH_2MgI} \xrightarrow{HCHO} H-\underset{H}{\overset{CH_2CH_3}{C}}-OMgI \xrightarrow{H_2O} \underset{(D)}{H-\underset{H}{\overset{CH_2CH_3}{C}}-OH}$$

n–propyl alcohol

20. (d)



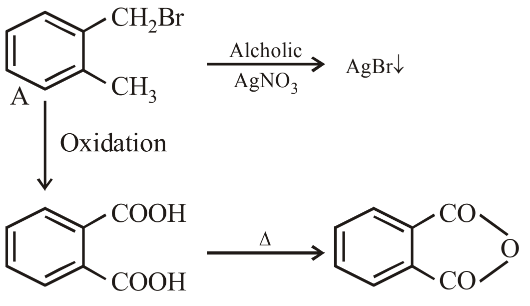
(trans-2-butene) (Meso)

21. (a) A strong nucleophile favours the S_N2 reaction and a weak nucleophile favours the S_N1 reaction.

First reaction is S_N1 reaction because C_2H_5OH is used as solvent which is a weak nucleophile.

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

22. (d)



Acid (B) Phthalic Anhydride

23. (c) $CHCl_3$ is stored in dark bottles to prevent oxidation of $CHCl_3$ in presence of sunlight.

24. (b)

25. (d) CCl_4 is used as a fire extinguisher. The dense, non combustible vapours cover the burning substance and prevents the availability of oxygen around burning material.

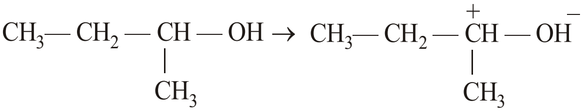
EXERCISE - 3

Exemplar Questions

1. (b) Alchols and halogen acid react through S_N1 mechanism.

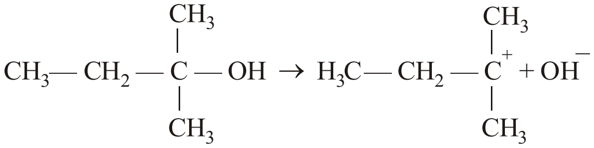
$$CH_3—CH_2—CH_2—OH \rightarrow CH_3—CH_2—\overset{+}{C}H + OH^-$$

In this case, 1° carbocation is formed. It is least stable. So, here S_N2 mechanism is followed. In this S_N2 mechanism a transition state is observed in which α - carbon is linked with two nucleophilies.



$$CH_3—CH_2—\underset{CH_3}{CH}—OH \rightarrow CH_3—CH_2—\underset{CH_3}{\overset{+}{C}H}—\overset{-}{OH}$$

2° Carbocation (more stable than 1° carbocation)



$$CH_3—CH_2—\underset{CH_3}{\overset{CH_3}{C}}—OH \rightarrow H_3C—CH_2—\underset{CH_3}{\overset{CH_3}{C^+}} + \overset{-}{OH}$$

3° carbocation (most stable)

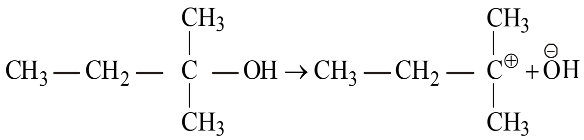
Greater the stability of carbocation, greater will be the possibilities of attack of X⁻ ion on the carbocation. Order of stability of carbocation is : 3° > 2° > 1.

So order of reactivity will be C > B > A.

2. (d) Reaction of alcohols with conc. HCl at room temperature follows S_N1 mechanism.

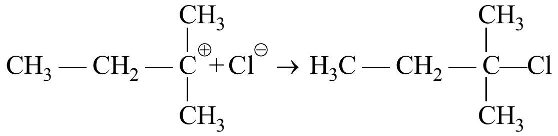
The attack of nucleophile to the carbocation is possible only on stable carbocation as at room temperature only 3° carbocation is stable.

Step I



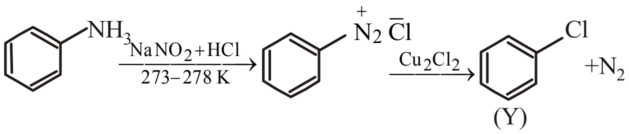
$$CH_3—CH_2—\underset{CH_3}{\overset{CH_3}{C}}—OH \rightarrow CH_3—CH_2—\underset{CH_3}{\overset{CH_3}{C^{\oplus}}} + \overset{\ominus}{O}H$$

Step II



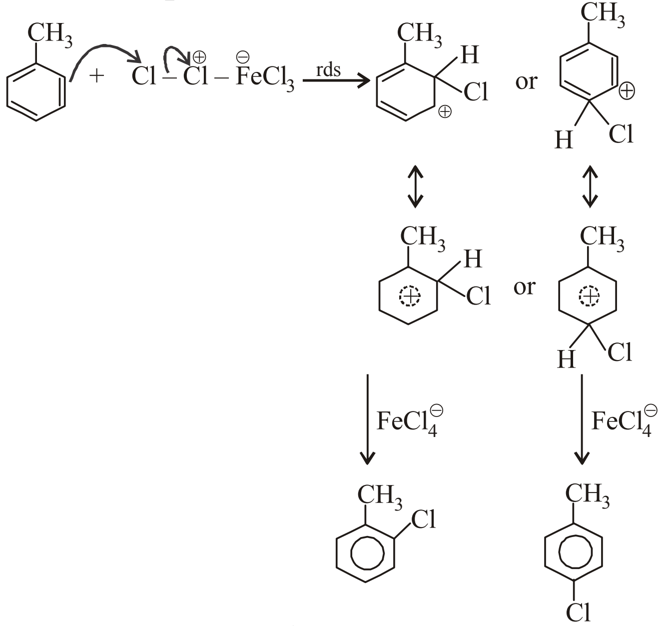
$$CH_3—CH_2—\underset{CH_3}{\overset{CH_3}{C^{\oplus}}} + Cl^{\ominus} \rightarrow H_3C—CH_2—\underset{CH_3}{\overset{CH_3}{C}}—Cl$$

3. (a) Sand meyer's Reaction



4. (b)

$$Cl-Cl \xrightleftharpoons{FeCl_3} \left[Cl-\overset{\oplus}{Cl}-\overset{\ominus}{Fe}Cl_3 \longleftrightarrow \overset{\oplus}{Cl}+\overset{\ominus}{Fe}Cl_4\right]$$



As electrophile Cl^+ attacks on electron rich benzene ring and substitutes hydrogen. So, the reaction is electrophilic substitution reaction.

5. (a) Halogen exchange reactions are those reactions in which one hailde replaces another (Finkelstein reaction).

6. (a) It is a substitution reaction which involves the replacement of 1° and 2° hydrogen of alkanes by chlorine. It occurs in presence of ultraviolet light.

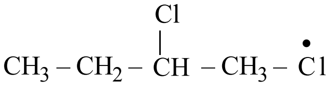
Step 1 : $Cl-Cl \xrightarrow[\text{light}]{\text{UV}} 2\dot{C}l$

$\dot{C}l + CH_3-CH_2-CH_2-CH_3 \rightarrow CH_3CH_2CH_2-\dot{C}H_2 + HCl$

Step 2 :

$CH_3-CH_2-CH_2-\dot{C}H_2 + Cl_2 \rightarrow CH_3-CH_2-CH_2-CH_2Cl + \dot{C}l$

$CH_3-CH_2-\dot{C}H-CH_3 + Cl_2 \rightarrow$

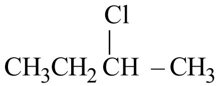


$CH_3-CH_2-\underset{}{\overset{Cl}{\overset{|}{C}H}}-CH_3-\dot{C}l$

Step 3 :

$CH_3-CH_2-CH_2-\dot{C}H_2 + \dot{C}l \rightarrow CH_3CH_2CH_2CH_2Cl$

$CH_3-CH_2-\dot{C}H-CH_3 + \dot{C}l \rightarrow$

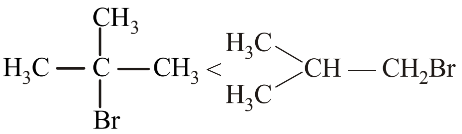


$CH_3CH_2\overset{Cl}{\overset{|}{C}H}-CH_3$

7. (a) Density is directly related to molecular mass. More the molecular mass, more will be the density of the compound. The order of molecular mass is benzene < chlorobenzene < dichlorobenzene < bromochlorbenzene

8. (c) Greater the surface area, greater will be the boiling point of a compound. Surface area decreases with increases in branching.

Increasing order of boiling point



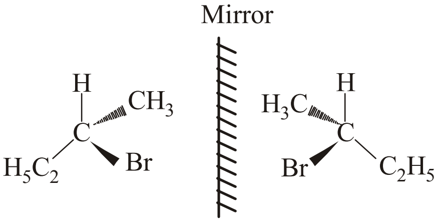
$H_3C-\underset{Br}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3 < (H_3C)_2CH-CH_2Br$

$< CH_3CH_2CH_2CH_2Br$

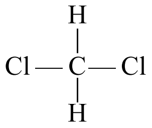
9. (b) Carbon atom in which all four valencies are different is known as Asymmetrical/chiral.

10. (a) Enantiomers are the steroismers which are related to each other as non – superimposable mirror images.

The enantiomer of molecule (A) is

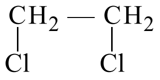


11. (b) Halides in which two halogen atoms are present on the two adjacent carbon atoms are known as *vic* - dihalides.



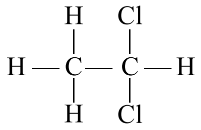
$Cl-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-Cl$

Dichloromethane



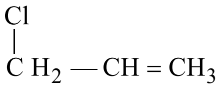
$\underset{Cl}{\underset{|}{CH_2}}-\underset{Cl}{\underset{|}{CH_2}}$

1, 2 – dichloroethane



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

Ethylidene chloride



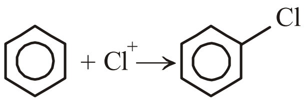
$\overset{Cl}{\overset{|}{C}H_2}-CH=CH_3$

Allyl chloride

12. (a) Compounds in which the halogen atom is bonded to sp^3 hybridised carbon atom next to carbon carbon-double bond are known as allyl halides.

$CH_3CH=CHC(Br)(CH_3)_2$

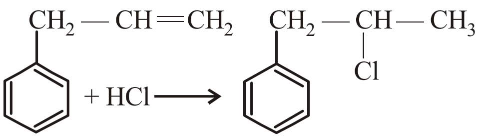
13. (b) $AlCl_3 + Cl_2 \longrightarrow [AlCl_4]^- + Cl^+$



Chlorobenzene

14. (b) If halogen atoms present on the same carbon atom then they are known as gem – dihalides or alkylidene halides.

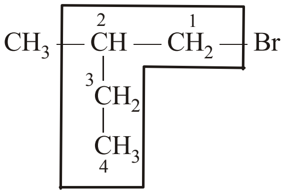
15. (c) Addition of HCl takes place in accordance with Markownikoff's rule.



16. (b) It would prefer to undergo S_N2 reaction.
S_N2 reactions occur if there is less steric crowding on α - carbon of alkyl halide. In case of primary aklyl halides, steric crowding is very less. So, it would prefer to undergo S_N2 reaction.

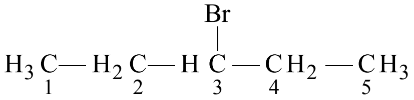
17. (d) All compounds are tertiary alkyl but bond formed between carbon and iodine (C — I) is weakest bond due to higher difference in size of carbon and iodine.

18. (c) IUPAC name



1-bromo-2 methylbutane

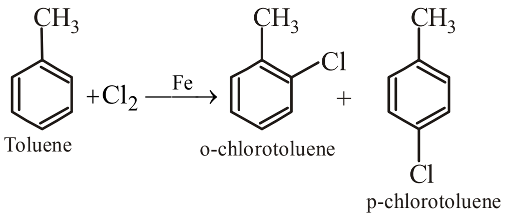
19. (b)



$$\underset{1}{H_3C}—\underset{2}{H_2C}—H\underset{3}{\overset{Br}{C}}—\underset{4}{CH_2}—\underset{5}{CH_3}$$

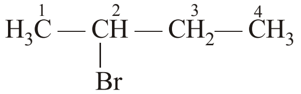
IUPAC name is 3-bromopentane.

20. (d) Toluene react with chlorine in presence of iron and in absence of light, by substitution on benzene ring.



21. (c) $CH_3Cl + \underset{\text{Excess}}{NH_3} \rightarrow \underset{\text{Methanamine}}{CH_3NH_2} + HCl$

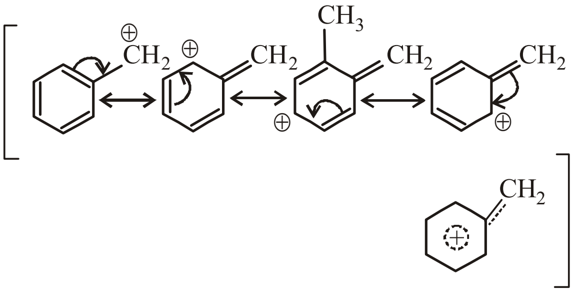
22. (a) Carbon in which four bonds are different is known as Chiral carbon.



$$\overset{1}{H_3C}—\underset{Br}{\overset{2}{CH}}—\overset{3}{CH_2}—\overset{4}{CH_3}$$

(2- bromobutane)

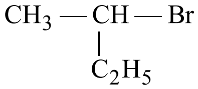
23. (a) In $C_6H_5CH_2Br$ carbocation is $C_6H_5\overset{\oplus}{C}H_2$ which is stable due to resonance.



24. (b) If carbon atom has all four valencies with four different groups then it is called as asymmetric/chiral carbon.

25. (a) All those compounds which follow S_N1 mechanism during nucleophilic subsitution reaction will give racemic mixture.
Order of reactivity of alkyl halides for S_N1.

$$3° > 2° > 1°\ CH_3\ X$$

Thus,  $CH_3—\underset{C_2H_5}{CH}—Br$ contains a 2° carbon so gives a racemic product.

26. (c) The substitution is faster if the electron withdrawing group is at ortho and para position because electron density is high at these positions as chlorine is electron donating group which increase electron density at ortho and para position. Therefore, it has partial double bond character, and is not easy to break. In compound (ii) and (iii) both has one electron withdrawing group but in compound (ii) electron withdrawing (— NO_2) group is present at ortho position, so rate of reaction in compound (ii) is more than that of (iii) while (i) has no electron withdrawing group.

27. (d) If electron releasing group is present at ortho or para position it decreases the rate of nucleophilic substitution reaction. In compound (iii) electron releasing group is present at meta position w.r.t. chlorine, so the impact is nothing but in compound (ii) it is present at ortho position.

28. (d) If electron withdrawing group is present at ortho and para position then the nucleophilic substitution reaction rate increases.

29. (c) If electron releasing group is present at ortho and para position w.r.t. to chlorine it decreases the rate of nucleophilic substitution reaction.

30. (a) Greater the surface area, greater will be the intermolecular forces of attraction and intermolecular forces of attraction is directly proportional to boiling point. Surface area is larger for larger size of halogen.

31. (d) Boiling point is directly proportional to size of the molecule. All contains same halogen atom but different hydrocarbon part. Larger the different hydrocarbon part larger the boiling point.

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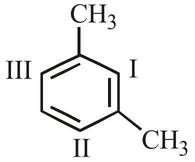
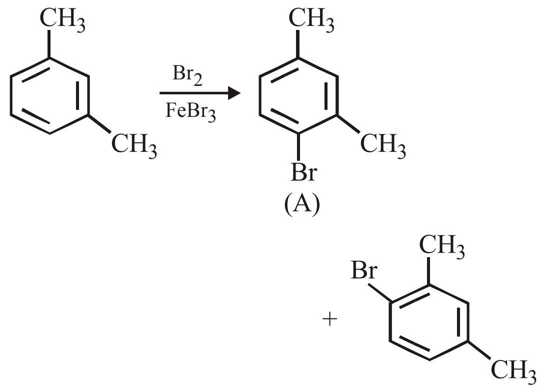
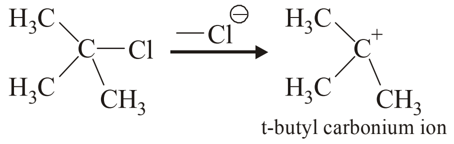
32. **(c)** Methyl group is ortho para directing but due to steric hind rance effect, generated by two CH_3 groups substitution will not take place on position (I). Hence only two products are possible.



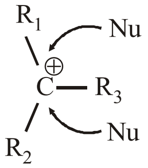
i.e.



33. **(a)** Tertiary butyl chloride will give the most stable tertiary carbonium ion among the other given compounds



34. **(b)** In S_N1 reaction, carbocation a planar species as intermediate is formed.



So attack from below or above the plane can take place.

If 50% attack below and above the plane of carbocation take place than 100% racemization occurs but it may not be highly probable.

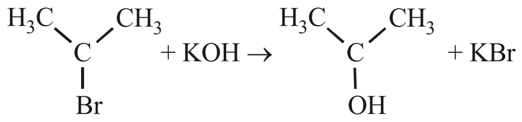
i.e. if inversion occurs more than retention leading to partial racemization.

35. **(b)** (1) $CH_3CH_2CH_2{-}Br + KOH$

$$\rightarrow CH_3CH{=}CH_2 + KBr + H_2O$$

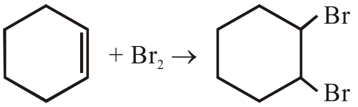
This is dehydrohalogenation reaction which is an example of elimination reaction.

(2)



Replacement of Br^- by OH^- is substitution reaction thus it is a nucleophilic substitution reaction.

(3)



Above reaction involves addition of Br_2 across double bond. Thus it is called addition reaction.