

# 6

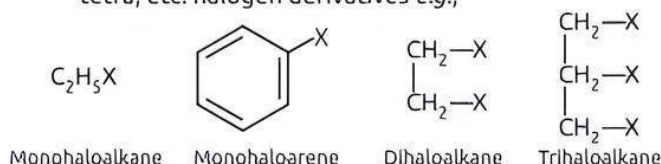
## Haloalkanes and Haloarenes

### Fastrack® Revision

- When a hydrogen attached to a carbon atom in the aliphatic hydrocarbons is replaced by a halogen atom (i.e. F, Cl, Br, I), then the compounds formed are called haloalkanes while in benzene ring, they are called haloarenes.

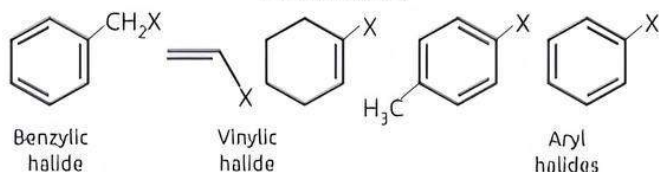
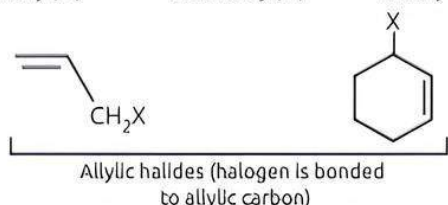
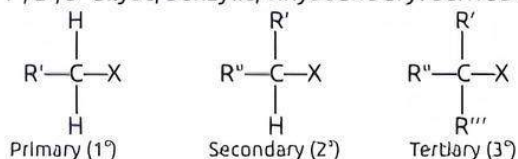
#### Classification of Haloalkanes and Haloarenes

- On the basis of number of halogen atoms present, halogen derivatives are classified as mono, di, tri, tetra, etc. halogen derivatives e.g.,



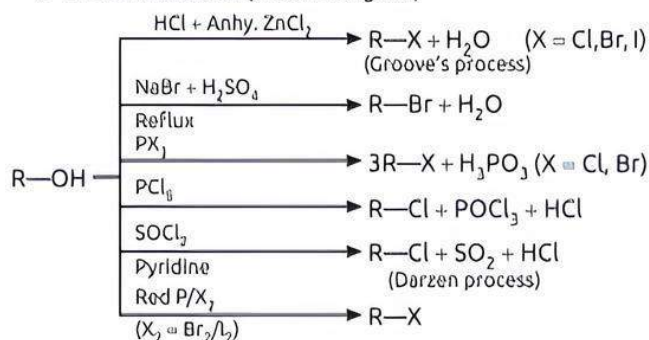
(where, X = halogen atom)

- On the basis of the nature of carbon to which halogen atom is attached, halogen derivatives are classified as 1°, 2°, 3° allylic, benzylic, vinylic and aryl derivatives, e.g.



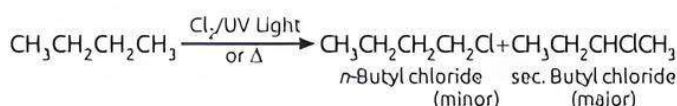
#### General Methods of Preparation of Haloalkanes and Haloarenes

##### From Alcohols: (Lucas Reagent)

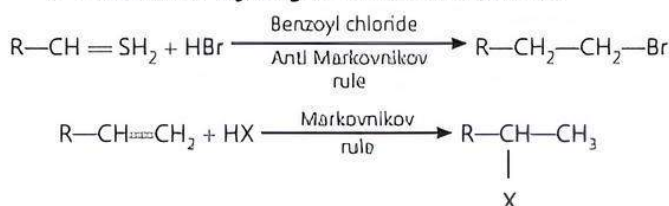


The reactivity order of halogen acids is  $HI > HBr > HCl$ .

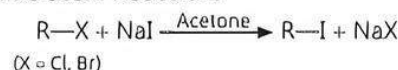
##### From Alkanes:



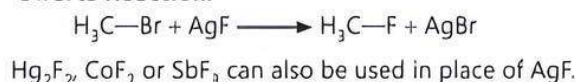
##### Addition of Hydrogen Halides on Alkenes:



##### Finkelstein Reaction:



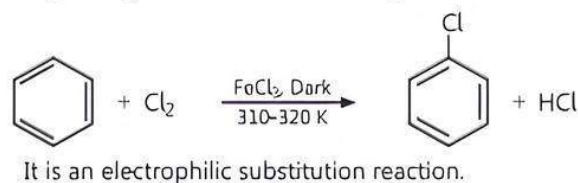
##### Swarts Reaction:



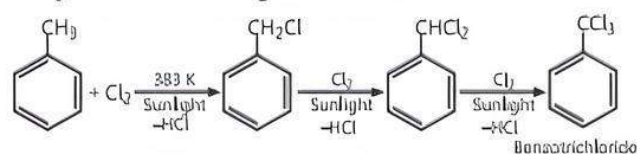
##### Hunsdiecker Reaction:



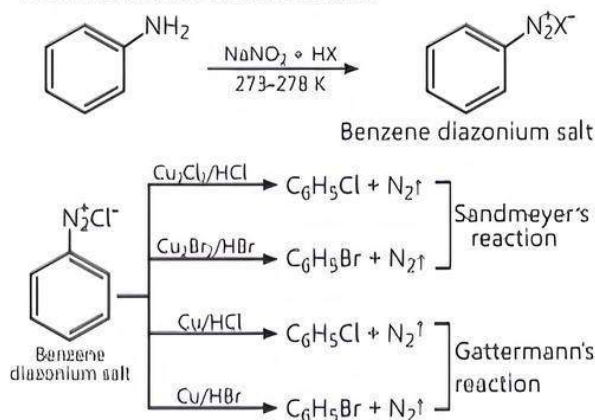
##### By Halogenation of Aromatic Hydrocarbon:



##### By Side Chain Halogenation:



##### From Benzene Diazonium Salt:



## ► Properties of Haloalkanes and Haloarenes

### Physical Properties:

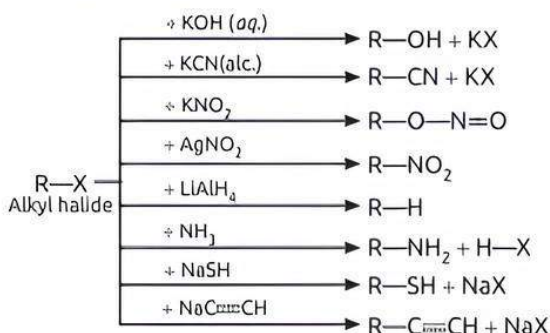
- Haloalkanes are colourless when pure but compounds of bromine are coloured.
- Haloalkanes have higher B.P. and M.P.
- The density of haloalkanes increases with increase in carbon atoms and halogen atoms.
- Isomeric haloarenes have similar boiling points but para isomer have higher melting point than other two.

### Chemical Properties:

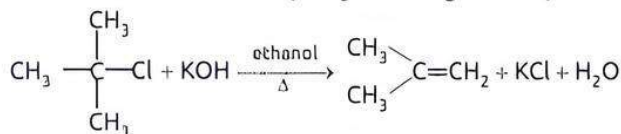
#### 1. Haloalkanes: Reactivity order of haloalkanes is:

Chlorides < Bromides < Iodides

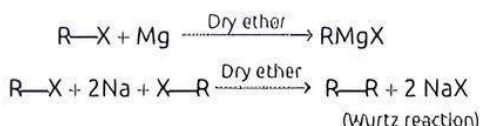
#### ► Nucleophilic Substitution Reaction:



#### ► Elimination Reaction (Dehydrohalogenation):



#### ► Reaction with Metals:

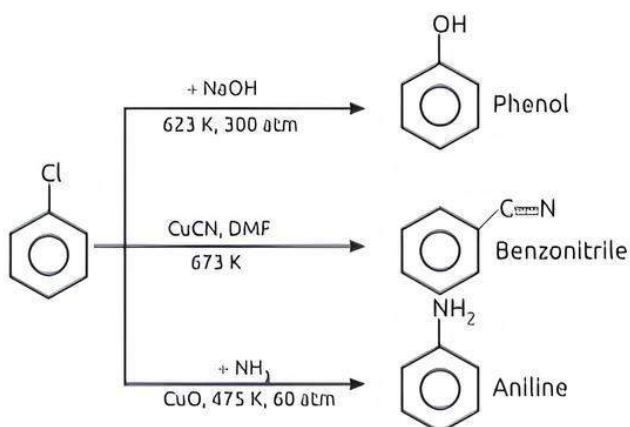


#### ► Reduction:

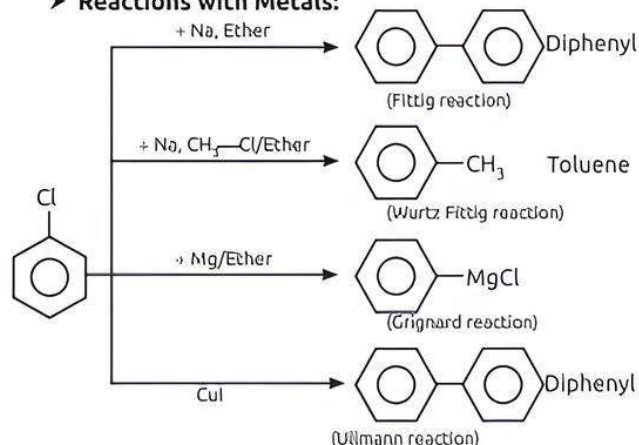


2. **Haloarenes:** Nucleophilic substitution reactions are very less possible with haloarenes as C-X bond attains partial double bond character because of resonance effect, difference in hybridisation, etc.

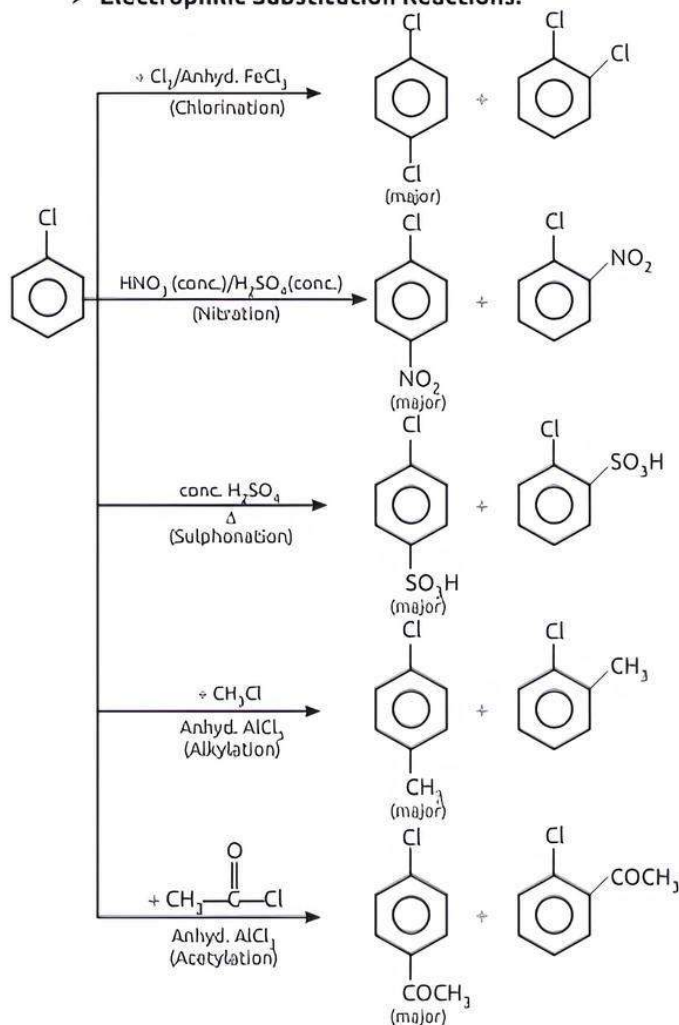
#### ► Substitution Reactions:



#### ► Reactions with Metals:



#### ► Electrophilic Substitution Reactions:



#### ► Polyhalogen Compounds:

- Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) is used as propellant in aerosols, as paint remover. Exposure to higher levels causes nausea, dizziness.
- The trihalogen derivatives of methane are called haloforms, e.g. CHCl<sub>3</sub> (chloroform), CHI<sub>3</sub> (iodoform), etc.
- Chloroform is stored in dark coloured bottles as in presence of light, it gets converted into highly poisonous substance, phosgene (COCl<sub>2</sub>).
- DDT is 1, 1, 1-trichloro-2, 2-bis (4-chlorophenyl) ethane and is used as a powerful insecticide.
- CCl<sub>4</sub> is used as a fire extinguisher under the name pyrene.
- Freon-12 (CF<sub>2</sub>Cl<sub>2</sub>) is used as a refrigerant and for air conditioning purposes.





## Practice Exercise



### Multiple Choice Questions

Q 1. The number of possible isomers of compound  $C_3H_6Cl_2$  is:

- a. 2                                      b. 4  
c. 6                                      d. 8

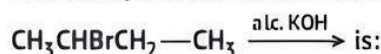
Q 2. What should be the correct IUPAC name for diethylbromomethane? (NCERT EXEMPLAR)

- a. 1-bromo-1, 1-diethylmethane  
b. 3-bromopentane  
c. 1-bromo-1-ethylpropane  
d. 1-bromopentane

Q 3. A primary alkyl halide would prefer to undergo: (NCERT EXEMPLAR)

- a.  $S_N1$  reaction                      b.  $S_N2$  reaction  
c.  $\alpha$ -elimination                    d. racemisation

Q 4. The main product of the reaction



- a. propene-1                          b. butene-2  
c. butane                              d. butyne-1

Q 5. Which one of the following halides contains  $C_{sp^2}-X$  bond? (CBSE 2021 Term-1)

- a. Allyl halide                        b. Alkyl halide  
c. Benzyl halide                    d. Vinyl halide

Q 6. Which of the following isomer has the highest melting point? (CBSE SQP 2021 Term-1)

- a. 1,2-dichlorobenzene  
b. 1,3-dichlorobenzene  
c. 1,4-dichlorobenzene  
d. All isomers have same melting points

Q 7. Which of the following has highest boiling point? (CBSE 2021 Term-1)

- a.  $C_2H_5-F$                               b.  $C_2H_5-Cl$   
c.  $C_2H_5-Br$                             d.  $C_2H_5-I$

Q 8. Which of the following is not correct?

(CBSE SQP 2023-24)

- a. In haloarenes, the electron pairs on halogen atom are in conjugation with  $\pi$ -electrons of the ring.  
b. The carbon-magnesium bond is covalent and non-polar in nature.  
c. During  $S_N1$  reaction, the carbocation formed in the slow step being  $sp^2$  hybridised is planar.  
d. Out of  $CH_2=CH-Cl$  and  $C_6H_5CH_2Cl$ ,  $C_6H_5CH_2Cl$  is more reactive towards  $S_N1$  reaction.

Q 9. Reaction of 1-phenyl-2-chloropropane with alcoholic KOH gives mainly: (CBSE 2023)

- a. 1-phenylpropene                  b. 3-phenylpropene  
c. 1-phenylpropan-3-ol              d. 1-phenylpropan-2-ol

Q 10. Which of the following belongs to the class of alkyl halides? (CBSE 2023)

- a.  $CH_2=CH-Cl$   
b.  $CH_2=CH-CH_2-CH_2-Cl$   
c.  $CH_2=CH-\underset{\substack{| \\ Cl}}{CH}-CH_3$   
d.  $CH\equiv C-CH_2-Cl$

Q 11. The synthesis of alkyl fluoride is best obtained from: (CBSE 2023)

- a. free radicals  
b. Swartz reaction  
c. Sandmeyer reaction  
d. Finkelstein reaction

Q 12. Which of the following is a correct statement for  $C_2H_5Br$ ? (CBSE SQP 2021 Term-1)

- a. It reacts with metallic Na to give ethane  
b. It gives nitroethane on heating with aqueous solution of  $AgNO_3$   
c. It gives  $C_2H_5OH$  on boiling with alcoholic potash  
d. It forms diethylthioether on heating with alcoholic KSH

Q 13. Which reagents are required for one step conversion of chlorobenzene to toluene? (CBSE SQP 2021 Term-1)

- a.  $CH_3Cl / AlCl_3$                       b.  $CH_3Cl, Na, \text{Dry ether}$   
c.  $CH_3Cl / Fe, \text{dark}$                   d.  $NaNO_2 / HCl / 0-5^\circ C$

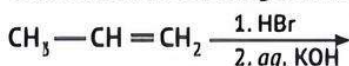
Q 14. Which of the following belongs to the class of vinyl halides? (CBSE 2023)

- a.  $CH_2=CHCH_2CH_2Cl$   
b.  $CH_2=\underset{\substack{| \\ Br}}{C}-CH_3$   
c.  $CH_2=CH-CH_2-Br$   
d.  $CH\equiv C-Br$

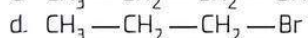
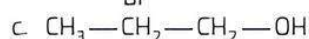
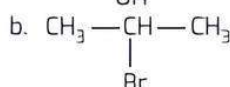
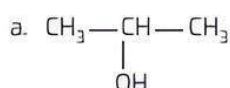
Q 15. Which of the following reactions are feasible? (CBSE 2023)

- a.  $CH_3CH_2Br + Na^+ O-C(CH_3)_3 \longrightarrow CH_3CH_2-O-C(CH_3)_3$   
b.  $(CH_3)_3C-Cl + Na^+ O-CH_2CH_3 \longrightarrow CH_3CH_2-O-C(CH_3)_3$   
c. Both a. and b.  
d. Neither a. nor b.

Q 16. Consider the following reaction:



The major end product is: (CBSE 2021 Term-1)



- Q 17. The reaction of toluene with  $\text{Cl}_2$  in presence of  $\text{FeCl}_3$  gives 'X' while the toluene with  $\text{Cl}_2$  in presence of light gives 'Y'. Thus 'X' and 'Y' are:

(CBSE SQP 2021 Term-1)

- a. X = benzyl chloride Y = o and p-chlorotoluene  
 b. X = m-chlorotoluene Y = p-chlorotoluene  
 c. X = o and p-chlorotoluene Y = trichloromethylbenzene  
 d. X = benzyl chloride, Y = m-chlorotoluene

- Q 18. Chlorobenzene is formed by reaction of chlorine with benzene in the presence of  $\text{AlCl}_3$ . Which of the following species attacks the benzene ring in this reaction?

(NCERT EXEMPLAR)

- a.  $\text{Cl}^-$       b.  $\text{Cl}^\cdot$       c.  $\text{AlCl}_3$       d.  $[\text{AlCl}_4]^-$

- Q 19. Reaction of chlorobenzene with  $\text{NH}_3$  in the presence of cuprous oxide, gives:

- a. phenol      b. aniline  
 c. benzene      d. benzoic acid

- Q 20. The conversion of an alkyl halide into an alkene by alcoholic KOH is classified as:

(CBSE 2023)

- a. a substitution reaction  
 b. an addition reaction  
 c. a dehydrohalogenation reaction  
 d. a dehydration reaction.

- Q 21. Which one of the following compounds is more reactive towards  $\text{S}_\text{N}1$  reaction?

(CBSE SQP 2022-23)

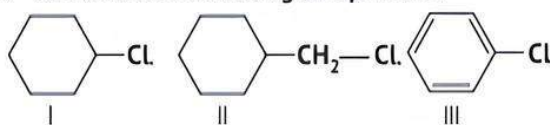
- a.  $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{Br}$       b.  $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$   
 c.  $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$       d.  $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$

- Q 22. Inversion of configuration occurs in:

(CBSE 2023)

- a.  $\text{S}_\text{N}2$  reaction  
 b.  $\text{S}_\text{N}1$  reaction  
 c. Neither  $\text{S}_\text{N}2$  nor  $\text{S}_\text{N}1$  reaction  
 d.  $\text{S}_\text{N}1$  as well as  $\text{S}_\text{N}2$  reaction.

- Q 23. Consider the following compounds:



The correct order of reactivity towards  $\text{S}_\text{N}2$  reaction.

(CBSE 2021 Term-1)

- a. I > III > II      b. II > III > I  
 c. II > I > III      d. III > I > II

- Q 24. Major product obtained on reaction of 3-phenyl propene with HBr in presence of organic peroxide is:

(CBSE SQP 2021 Term-1)

- a. 3-phenyl-1-bromopropane  
 b. 1-phenyl-3-bromopropane  
 c. 1-phenyl-2-bromopropane  
 d. 3-phenyl-2-bromopropane

- Q 25. Molecules whose mirror image is non-superimposable over them are known as chiral. Which of the following molecules is chiral in nature?

(NCERT EXEMPLAR)

- a. 2-bromobutane      b. 1-bromobutane  
 c. 2-bromopropane      d. 2-bromopropan-2-ol

- Q 26. Complete the following analogy:

Same molecular formula but different structures:

A :: Non-superimposable mirror images: B

(CBSE SQP 2021 Term-1)

- a. A : Isomers, B: Enantiomer  
 b. A : Enantiomers, B: Racemic mixture  
 c. A : Stereoisomers, B: Retention  
 d. A : Isomers, B: Stereoisomers

- Q 27. Enantiomers differ only in:

(CBSE 2021 Term-1)

- a. boiling point  
 b. rotation of polarised light  
 c. melting point  
 d. solubility

- Q 28. On oxidation chloroform gives or chloroform gets slowly oxidized by air in the presence of sunlight to give:

- a. phosgene  
 b. formic acid  
 c. carbon tetrachloride  
 d. chloropicrin

- Q 29. Auto oxidation of chloroform in air and sunlight produces a poisonous gas known as:

(CBSE 2023)

- a. tear gas      b. mustard gas  
 c. phosgene gas      d. chlorine gas

- Q 30. Iodoform test is not given by:

- a. ethanol      b. benzophenone  
 c. ethanal      d. acetophenone



## Assertion & Reason Type Questions

Directions (Q. Nos. 31-41): Each of the following questions consists of two statements, one is Assertion (A) and the other is Reason (R). Give answer:

- a. Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).  
 b. Both Assertion (A) and Reason (R) are true but Reason (R) is not a correct explanation of Assertion (A).  
 c. Assertion (A) is true but Reason (R) is false.  
 d. Assertion (A) is false but Reason (R) is true.

- Q 31. Assertion (A): Chlorobenzene is less reactive towards nucleophilic substitution reaction.

Reason (R): Nitro group in chlorobenzene increases its reactivity towards nucleophilic substitution reaction.

(CBSE 2021 Term-1)

- Q 32. Assertion (A): Chlorobenzene is resistant to nucleophilic substitution reaction at room temperature.

Reason (R): C—Cl bond gets weaker due to resonance.

(CBSE 2023)

- Q 33. Assertion (A): Alkyl halides are insoluble in water.

Reason (R): Alkyl halides have halogen attached to  $\text{sp}^3$  hybrid carbon.

(CBSE SQP 2021 Term-1)



**Q 34. Assertion (A):** It is difficult to replace chlorine by —OH in chlorobenzene in comparison to that in chloroethane.

**Reason (R):** Chlorine-carbon (C—Cl) bond in chlorobenzene has a partial double bond character due to resonance. (NCERT EXEMPLAR)

**Q 35. Assertion (A):** The boiling points of alkyl halides decrease in the order: RI > RBr > RCl > RF.

**Reason (R):** The boiling points of alkyl chlorides, bromides and iodides are considerably higher than that of the hydrocarbon of comparable molecular mass. (NCERT EXEMPLAR)

**Q 36. Assertion (A):** KCN reacts with methyl chloride to give methyl isocyanide.

**Reason (R):** CN<sup>-</sup> is an ambident nucleophile. (NCERT EXEMPLAR)

**Q 37. Assertion (A):** Nucleophilic substitution of iodoethane is easier than chloroethane.

**Reason (R):** Bond enthalpy of C—I bond is less than that of C—Cl bond. (CBSE 2023)

**Q 38. Assertion (A):** *tert*-Butyl bromide undergoes Wurtz reaction to give 2, 2, 3, 3-tetramethylbutane.

**Reason (R):** In Wurtz reaction, alkyl halides react with sodium in dry ether to give hydrocarbon containing double the number of carbon atoms present in the halide. (NCERT EXEMPLAR)

**Q 39. Assertion (A):** Presence of a nitro group at *ortho* or *para* position increases the reactivity of haloarenes towards nucleophilic substitution.

**Reason (R):** Nitro group, being an electron withdrawing group decreases the electron density over the benzene ring. (NCERT EXEMPLAR)

**Q 40. Assertion (A):** In monohaloarenes, further electrophilic substitution occurs at *ortho* and *para* positions.

**Reason (R):** Halogen atom is a ring deactivator. (NCERT EXEMPLAR)

**Q 41. Assertion (A):** Aryl iodides can be prepared by reaction of arenes with iodine in the presence of an oxidising agent.

**Reason (R):** Oxidising agent oxidises I<sub>2</sub> into HI. (NCERT EXEMPLAR)

## Answers

1. (b) 4

Possible isomers are:

CH<sub>3</sub>—CH<sub>2</sub>—CHCl<sub>2</sub>    1, 1-dichloropropane

CH<sub>3</sub>—CCl<sub>2</sub>—CH<sub>3</sub>    2, 2-dichloropropane

CH<sub>3</sub>—CHCl—CH<sub>2</sub>Cl    1, 2-dichloropropane

ClCH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>Cl    1, 3-dichloropropane

2. (b) 3-bromopentane

3. (b) S<sub>N</sub>2 reaction

9. (a) 1-phenylpropene

10. (d) The compounds that contain a halogen atom bonded to a sp<sup>3</sup>-hybridised carbon atom of an alkyl group are alkyl halides. In CH<sub>3</sub>—C—CH<sub>2</sub>—Cl, the halogen atom (Cl) is attached to a sp<sup>3</sup>-hybridised carbon atom of an alkyl group making it an alkyl halide.

11. (b) Swartz reaction is the best way to prepare alkyl fluoride in which inorganic fluorides like silver fluoride or antimony trifluorides are used with a corresponding alkyl halide.

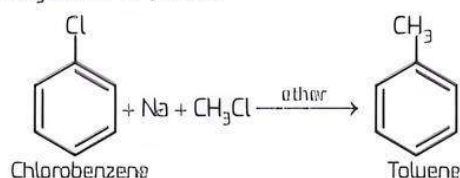
12. (b) It gives nitroethane on heating with aqueous solution of AgNO<sub>2</sub>.

C<sub>2</sub>H<sub>5</sub>Br reacts with metallic Na to give butane.

C<sub>2</sub>H<sub>5</sub>Br gives ethane on boiling with alcoholic potash.

C<sub>2</sub>H<sub>5</sub>Br forms C<sub>2</sub>H<sub>5</sub>SH (thiol) on heating with alcoholic KSH.

13. (b) CH<sub>3</sub>Cl, Na, Dry ether



14. (b)  $\text{CH}_2=\text{C}(\text{Br})-\text{CH}_3$

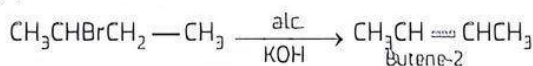
15. (a) The reactivity of primary halides is in the order, —CH<sub>3</sub> > CH<sub>3</sub>CH<sub>2</sub>— > CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>— and the tendency of alkyl halides to undergo elimination is 3° > 2° > 1°. Hence, for better yield, the alkyl halide should be primary and alkoxide should be secondary or tertiary.



## TiP

Higher the number of alkyl groups attached to carbon atom of the C—X bond, more is the steric hindrance and consequently lesser is the reactivity of the alkyl halide towards S<sub>N</sub>2 reactions.

4. (b) Butene-2



It is an example of elimination reaction.

5. (d) Vinyl halide

Vinyl halide and aryl halide contains C<sub>sp</sub><sup>2</sup>—X bond.

6. (c) 1, 4-dichlorobenzene.

1,4-dichlorobenzene is a *para* isomer and *para* isomers are more symmetric than *ortho* and *meta* isomers. Hence, it has highest melting point.

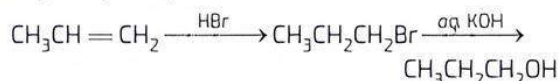
7. (d) C<sub>2</sub>H<sub>5</sub>—I

For the same alkyl group, the boiling points of alkyl halides decrease in the order RI > RBr > RCl > RF. Thus, C<sub>2</sub>H<sub>5</sub>—I has the highest boiling point.

8. (b) The carbon-magnesium bond is covalent and non-polar in nature.



16. (c)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

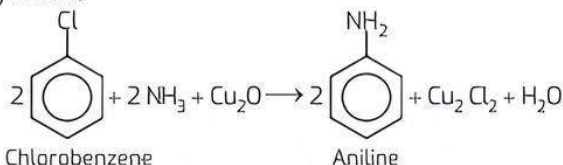


17. (c) X = *o*- and *p*-chlorotoluene.  
Y = trichloromethylbenzene

The reaction of toluene with  $\text{Cl}_2$  in presence of  $\text{FeCl}_3$  gives 'X' due to electrophilic substitution reaction taking place at ortho and para positions and reaction in the presence of light gives 'Y', due to substitution reaction occurring via free radical mechanism. Thus, 'X' and 'Y' are *o*- and *p*-chlorotoluene and trichloromethyl benzene respectively.

18. (b)  $\text{Cl}^+$

19. (b) aniline



20. (c) Alkyl halides ( $\text{R}-\text{X}$ ) on heating with alcoholic potash ( $\text{KOH}$ ) dissolved in alcohol eliminate one molecule of halogen acid to form alkenes. This reaction is known as dehydrohalogenation reaction.

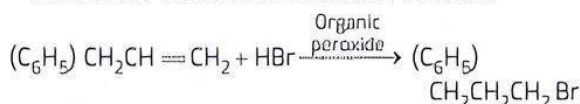
21. (c)  $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$   
 $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)^+$  carbocation formed in this compound is more stable as compared to other compounds so, it is more reactive towards  $\text{S}_{\text{N}}1$  reaction.

22. (a)  $\text{S}_{\text{N}}2$  reaction

23. (b)  $\text{II} > \text{III} > \text{I}$

24. (b) 1-phenyl-3-bromopropane.

It is an anti-Markovnikov addition reaction.



25. (a) 2-bromobutane

26. (a) A: Isomers B: Enantiomer

27. (b) Rotation of polarised light

28. (a) Phosgene

29. (c) When chloroform reacts with air and sunlight, it produces a toxic gas known as phosgene gas along with hydrochloric acid.

30. (b) benzophenone

31. (b) Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).

32. (b) The electron pair on chlorine atom is in conjugation with the electrons of the benzene ring. This results in delocalisation of the electrons of  $\text{C}-\text{Cl}$  bond and a partial double bond character develop in the bond which makes it difficult for the nucleophile to cleave the  $\text{C}-\text{Cl}$  bond. Hence, assertion is true but reason is false.

33. (b) Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).

34. (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

35. (b) Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).

36. (d) Assertion (A) is false because  $\text{KCN}$  reacts with methyl chloride to give methyl cyanide as the main product along with a small amount of methyl isocyanide.

37. (a) In iodoethane, there is bonding between the *s* orbital and  $3p$  orbitals whereas in chloroethane, the bonding is in between  $2p$  and  $3p$  orbital. The bonding between  $2p$  and  $3p$  orbital is more effective than *s* and  $3p$  orbital. Since, there is less bond energy in the  $\text{C}-\text{I}$  bond than in the  $\text{C}-\text{Cl}$  bond, therefore it is easier to break the  $\text{C}-\text{I}$  bond in iodoethane and hence easier is the nucleophilic substitution.

So, both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).

38. (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

39. (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

40. (b) Halogen being more electronegative acts as ring deactivator as it dominates -I effect over +*m*. However, lone pairs on halogen delocalises in the ring which enable further electrophilic substitution at *ortho* and *para* positions. Thus, assertion and reason both are true and reason is the correct explanation of assertion.

41. (c) Aryl iodide can be prepared by the reaction of arenes with iodine in the presence of an oxidising agent. So, assertion is true.  
Also,  $\text{HI}$  convert into  $\text{I}_2$  by the oxidising agent such as  $\text{HIO}_3$  although  $\text{HI}$  can convert aryl halides into arenes.



## Case Study Based Questions

### Case Study 1

Substitution reactions involve the replacement of one atom or group (*X*) by another (*Y*):



The halogenation of alkanes is a substitution reaction, in which a hydrogen atom is replaced by a halogen atom ( $\text{X} = \text{H}$ ,  $\text{Y} = \text{halogen}$ ).

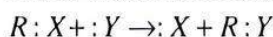
Reactions of this type proceed by radical-chain mechanisms in which the bonds are broken and formed by atoms or radicals as reactive intermediates. This mode of bond-breaking, in which one electron goes with *R* and the other with *X*, is called homolytic bond cleavage:





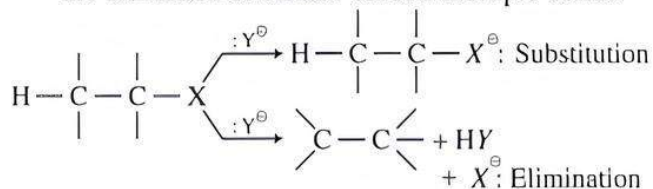
(a homolytic substitution reaction)

There are a large number of reactions, usually occurring in solution, that do not involve atoms or radicals but rather involve ions. They occur by heterolytic cleavage as opposed to homolytic cleavage of electron-pair bonds. In heterolytic bond cleavage, the electron pair can be considered to go with one or the other of the group  $R$  and  $X$  when the bond is broken. As one example,  $Y$  is a group such that it has an unshared electron pair and also is a negative ion. A heterolytic substitution reaction in which the  $R: X$  bonding pair goes with  $X$  would lead to  $RY$  and  $X^\ominus$ .



(a heterolytic substitution reaction.)

Substitution reactions can proceed by ionic or polar mechanism in which the bonds cleave heterolytically elimination reactions that result in the formation of carbon-carbon multiple bonds:

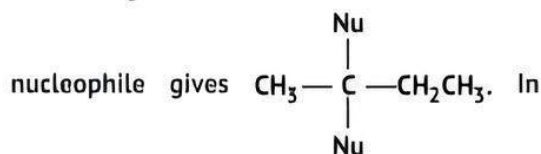
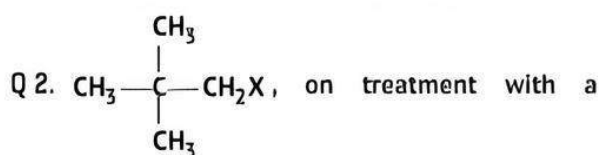


These reactions often are influenced profoundly by seemingly minor variations in the structure of the reactants, in the solvent, or in the temperature.

**Read the given passage carefully and give the answer of the following questions.**

**Q 1. In a nucleophilic substitution reaction, the least reactive compound is:**

- a.  $\text{CH}_3\text{CH}_2\text{Cl}$                       b.  $(\text{CH}_3)_3\text{CCl}$   
c.  $\text{CH}_2=\text{CHCl}$                       d.  $\text{CH}_2=\text{CHCH}_2\text{Cl}$



which condition, the product yield will be maximum?

- a.  $\text{CCl}_4$  as a solvent.  $\text{X} = \text{Cl}$   
b.  $\text{H}_2\text{O}$  as a solvent.  $\text{X} = \text{Cl}$   
c.  $\text{CCl}_4$  as a solvent.  $\text{X} = \text{I}$   
d.  $\text{H}_2\text{O}$  as a solvent.  $\text{X} = \text{I}$

**Q 3.  $n$ -butane on monobromination gives three isomers. The product obtained when the major monobromo product is heated with alc. KOH will be:**

- a. but-1-ene                      b. but-2-ene  
c. 2-ethoxybutane              d. butan-2-ol

**Q 4. Reaction of tert-butyl bromide with aqueous sodium hydroxide follows:**

- a.  $\text{S}_{\text{N}}1$  mechanism  
b.  $\text{S}_{\text{N}}2$  mechanism  
c. Any of the above two depending upon temperature of reaction  
d.  $\text{E}_1$  mechanism

## Answers

1. (c)  $\text{CH}_2=\text{CHCl}$   
2. (d)  $\text{H}_2\text{O}$  as a solvent,  $\text{X} = \text{I}$   
3. (b) but-2-ene  
4. (a)  $\text{S}_{\text{N}}1$  mechanism

## Case Study 2

The substitution reaction of alkyl halide mainly occurs by  $\text{S}_{\text{N}}1$  or  $\text{S}_{\text{N}}2$  mechanism. Whatever mechanism alkyl halides follow for the substitution reaction to occur, the polarity of the carbon halogen bond is responsible for these substitution reactions. The rate of  $\text{S}_{\text{N}}1$  reactions are governed by the stability of carbocation whereas for  $\text{S}_{\text{N}}2$  reactions steric factor is the deciding factor. If the starting material is a chiral compound, we may end up with an inverted product or racemic mixture depending upon the type of mechanism followed by alkyl halide. Cleavage of ethers with HI is also governed by steric factor and stability of carbocation, which indicates that in organic chemistry, these two major factors help us in deciding the kind of product formed.

**Read the given passage carefully and give the answer of the following questions:** (CBSE 2020)

- Q 1.** Predict the stereochemistry of the product formed if an optically active alkyl halide undergoes substitution reaction by  $\text{S}_{\text{N}}1$  mechanism.  
**Q 2.** Name the instrument used for measuring the angle by which the plane polarised light is rotated.  
**Q 3.** Predict the major product formed when 2-bromopentane reacts with alcoholic KOH.  
**Q 4.** Write the structures of the products formed when anisole is treated with HI.

## Answers

1. During  $\text{S}_{\text{N}}1$  reactions, optically active alkyl halides give racemic products.

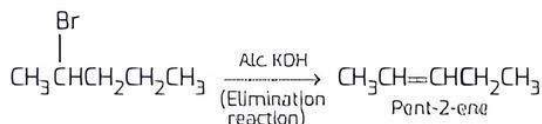


## TIP

$\text{S}_{\text{N}}1$  is shown by  $3^\circ$  alkyl halides.  $\text{S}_{\text{N}}2$  is shown by  $1^\circ$  alkyl halides.

2. A polarimeter is used for measuring the angle by which the plane polarised light is rotated.

3. Pent-2-ene.



4.  $\text{CH}_3\text{I}$  and  $\text{C}_6\text{H}_5\text{OH}$  are the products formed.

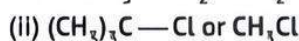
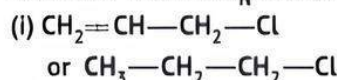
### Case Study 3

The polarity of  $\text{C}-\text{X}$  bond of alkyl halides is responsible for their nucleophilic substitution, elimination and their reaction with metal atoms to form organometallic compounds. Alkyl halides are prepared by the free radical halogenation of alkanes, addition of halogen acids to alkenes, replacement of  $-\text{OH}$  group of alcohols with halogens using phosphorus halides, thionyl chloride or halogen acids. Aryl halides are prepared by electrophilic substitution of arenes. Nucleophilic substitution reactions are categorised into  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$  on the basis of their kinetic properties. Chirality has a profound role in understanding the  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$  mechanism.

**Read the given passage carefully and give the answer of the following questions:** (CBSE 2023)

Q 1. What happens when bromobenzene is treated with Mg in the presence of dry ether?

Q 2. Which compound in each of the following pairs will react faster in  $\text{S}_{\text{N}}1$  reaction with  $\text{OH}^-$ ?

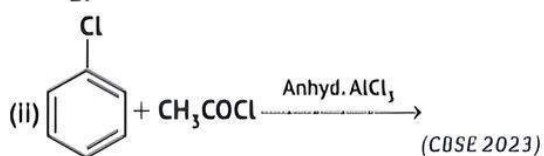
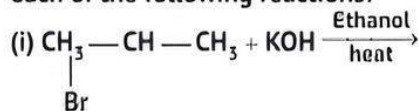


Q 3. Write the equations for the preparation of 1-iodobutane from:

(i) 1-chlorobutane and (ii) but-1-ene.

OR

Write the structure of the major products in each of the following reactions:

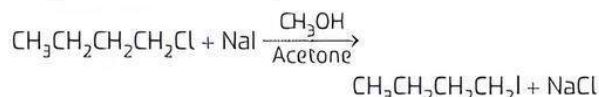


### Answers

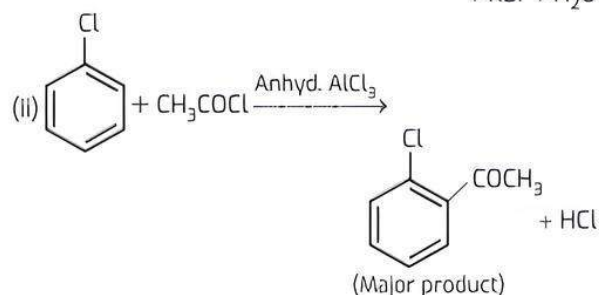
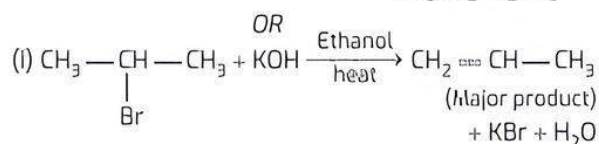
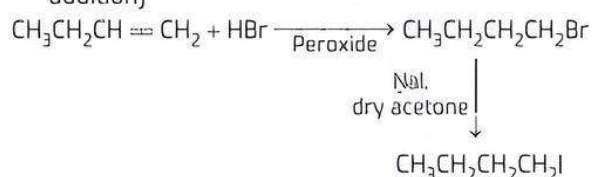
- When bromobenzene is treated with Mg in the presence of dry ether, phenylmagnesium bromide is formed.
- (i)  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Cl}$  will react faster because allylic halides show high reactivity towards the  $\text{S}_{\text{N}}1$  reaction

(ii)  $(\text{CH}_3)_3\text{C}-\text{Cl}$  will react faster because the rate of reaction depends only on the concentration of alkyl halide and not on the concentration of hydroxide ion. Greater the stability of carbocation, greater will be its ease of formation from alkyl halide and faster will be the rate of reaction.

3. (i) **Preparation of 1-iodobutane from 1-chlorobutane:**  
It occurs in the presence of dry acetone [Finkelstein reaction].



(ii) **Preparation of 1-iodobutane from but-1-ene:**  
It occurs by using peroxide [Anti-Markovnikov's addition]



### Very Short Answer Type Questions

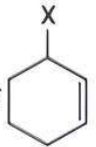
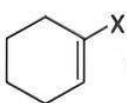
Q 1. Write IUPAC name of:  $\text{CH}_3-\text{CH}=\text{C}(\text{CH}_3)-\text{CH}(\text{Br})-\text{CH}_3$

Ans.  $\begin{array}{cccccc} 1 & 2 & 3 & 4 & 5 \\ \text{CH}_3 & -\text{CH} & =\text{C} & -\text{CH} & -\text{CH}_3 \\ & & | & | & \\ & & \text{CH}_3 & \text{Br} & \end{array}$  : 4-Bromo-3-methylpent-2-ene

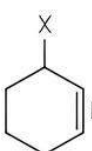
Q 2. Write the IUPAC name of the compound:

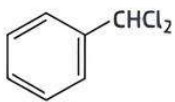
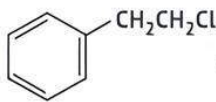


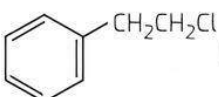
Ans.  $\begin{array}{cccccc} 1 & 2 & 3 & 4 & 5 \\ \text{CH}_3 & -\text{C} & =\text{C} & -\text{CH} & -\text{CH}_3 \\ & & & | & \\ & & & \text{Cl} & \end{array}$   
4-Chloropent-2-yne

Q 3. Out of  and , which is an example of allylic halide? (CBSE 2017)

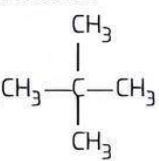


Ans.  is an example of allylic halide.

Q 4. Out of  and , which is an example of a benzylic halide? (CBSE 2017)

Ans.  is an example of a benzylic halide.

Q 5. Among the isomers of pentane ( $C_5H_{12}$ ), write the one which on photochemical chlorination yields a single monochloride. (CBSE 2017)

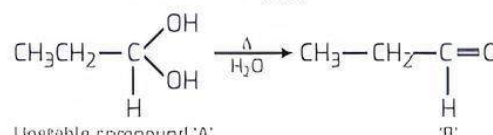
Ans. Neopentane.  as all the hydrogen atoms are equivalent and replacement of any hydrogen atom will give the same product.

**TiP**  
When alkyl groups are attached to a carbon atom at its centre, its name includes 'Neo'.

Q 6. Complete the following reaction sequence:

Ans.  $RX \xrightarrow{KCN} RCN \xrightarrow{H} RCH_2NH_2$   
alkyl cyanide 'A' alkylamine 'B'

Q 7. Complete the following chemical reaction:

Ans.  $CH_3CH_2CHBr_2 \xrightarrow{KOH(aq)} A \xrightarrow{\Delta} B$   
  
Unstable compound 'A'

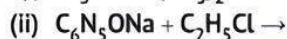
Q 8. Complete the following equations:

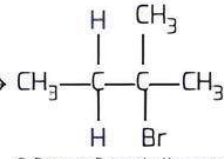
(i)  $C_6H_5N_2Cl + KI \rightarrow \dots$   
Benzene diazonium chloride iodobenzene  
(ii)  $H_2C=CH_2 + Br_2 \xrightarrow{CCl_4} \dots$   
Ethene 1,2-Dibromoethane

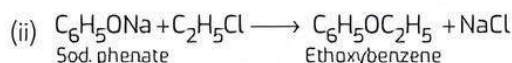
Q 9. Complete the following reaction:

Ans.  $CH_3-CH=CH_2 \xrightarrow{HBr, Peroxide} CH_3-CH_2-CH_2-Br \xrightarrow{NaI, Acetone} CH_3-CH_2-CH_2-I$   
Propene 1-Bromopropane (X) 1-Iodopropane (Y)

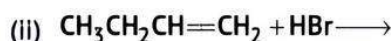
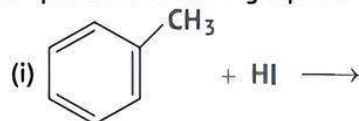
Q 10. Write the structures of the products of the following reactions:



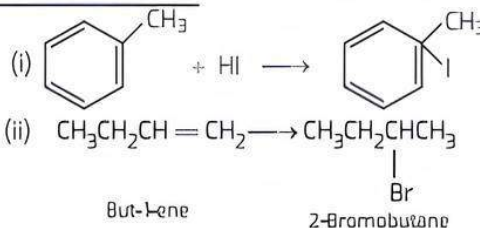
Ans. (i)  $CH_3CH=C(CH_3)_2 + HBr \rightarrow$    
2-Methylbut-2-ene 2-Bromo-2-methylbutane



Q 11. Complete the following equations:



Ans. Both additions to unsymmetrical carbon are guided by Markovnikov's rule.

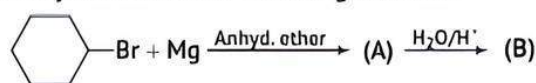


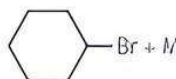
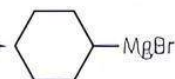

Q 12. Complete the following:



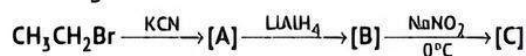
Ans. (i)  $C_6H_5N \rightleftharpoons C + AgCl$   
(ii) A mixture of o-chloronitrobenzene and p-chloronitrobenzene is formed.

Q 13. Identify A and B in the following reaction:



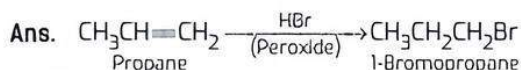
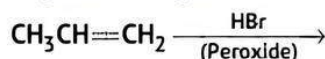
Ans.  + Mg  $\xrightarrow{\text{Anhyd. ether}}$    $\xrightarrow{H_2O/H^+}$    
Bromocyclohexane Cyclohexylmagnesium bromide (A) Cyclohexanol (B)

Q 14. Give the structures of the products A, B and C in the following reaction:

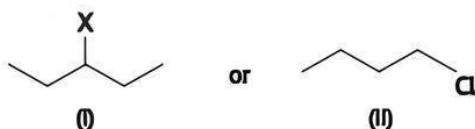


Ans.  $CH_3CH_2Br \xrightarrow{KCN} CH_3CH_2C \equiv N [A] \xrightarrow{LiAlH_4} CH_3CH_2CH_2NH_2 [B] \xrightarrow[0^\circ C]{NaNO_2} CH_3CH_2CH_2OH [C]$

Q 15. Complete the equation:

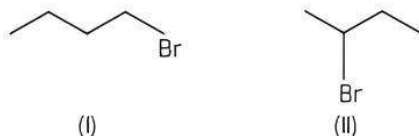


Q 16. Which of the following compounds will react faster in the  $\text{S}_\text{N}1$  reaction and why?



Ans. The compound (I) being a secondary alkyl halide will react faster than the compound (II) which is a primary alkyl halide in nature.

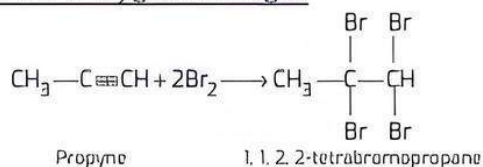
Q 17. Which alkyl halide from the following pair is chiral and undergoes  $\text{S}_\text{N}2$  reaction faster?



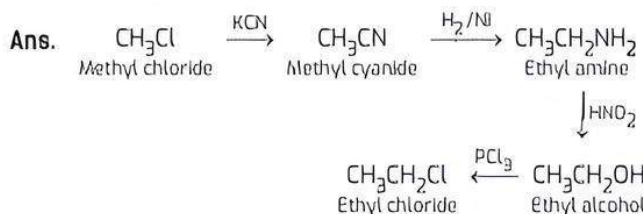
Ans. The isomer (II) has a chiral carbon while isomer (I) with less steric hindrance undergoes  $\text{S}_\text{N}2$  reaction faster.

Q 18. What happens when bromine reacts with  $\text{CH}_3\text{C}\equiv\text{CH}$ ?

Ans. Two moles of bromine participate in the reaction. The yellow colour of  $\text{Br}_2$  gets discharged.



Q 19. How will you convert methyl chloride into ethyl chloride?

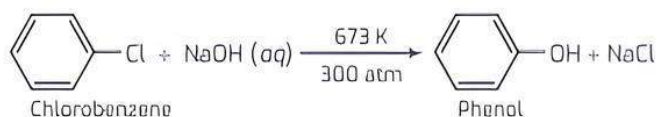


Q 20. What happens when  $\text{CH}_3\text{Br}$  is treated with KCN?

Ans. Methyl cyanide is formed  
 $\text{CH}_3\text{Br} + \text{KCN} \longrightarrow \text{CH}_3\text{C}\equiv\text{N} + \text{KBr}$

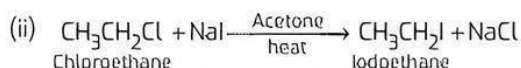
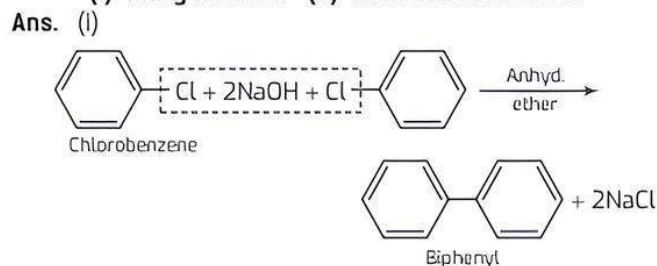
Q 21. What happens when chlorobenzene is subjected to hydrolysis?

Ans. Phenol is formed.



Q 22. Write chemical equations to illustrate the following reactions:

(i) Fittig reaction (ii) Finkelstein reaction.

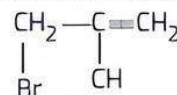


Q 23. How will you convert methyl chloride to ethyl amine?

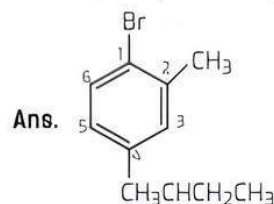


Q 24. Write the structure of 3-bromo-2-methylprop-1-ene. (CBSE 2017)

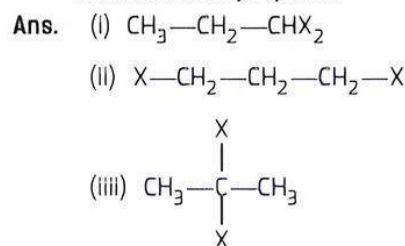
Ans. Structure of 3-bromo-2-methylprop-1-ene



Q 25. Write the structure of the compound 1-bromo-4-sec-butyl-2-methylbenzene.

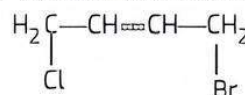


Q 26. Write the structures of different dihalogen derivatives of propane.



Q 27. Write the structures of 1-bromo-4-chlorobut-2-ene. (CBSE 2017)

Ans. Structure of 1-bromo-4-chlorobut-2-ene



Q 28. Out of chlorobenzene and benzyl chloride, which one gets easily hydrolysed by aqueous NaOH and why? (CBSE 2018)

Ans. C—Cl bond in chlorobenzene is stronger than C—Cl bond in benzyl chloride. Therefore, hydrolysis of benzyl chloride is easy. It is due to the fact that in



chlorobenzene, the lone pair of electrons on halogen atom are delocalised. Consequently, C—Cl bond have some double bond character. Whereas in benzyl chloride, C—Cl bond is weak. On cleavage it forms benzyl cation which is stable due to resonance.

**Q 29.** Which compound in the following couples will react faster in  $S_N2$  displacement and why?

- (i) 1-bromopentane or 2-Bromopentane  
(ii) 1-bromo-2-methylbutane or 2-bromo-2-methylbutane?

**Ans.** (i) 1-bromopentane since it is a primary alkyl halide and not 2-bromopentane it is a secondary alkyl halide.

(ii) 1-bromo-2-methylbutane since it is a primary alkyl halide and not 2-bromo-2-methyl butane since it is a tertiary alkyl halide.

**Q 30. Which will react faster in  $S_N2$  displacement reaction; 1-bromopentane or 2-bromopentane and why?**

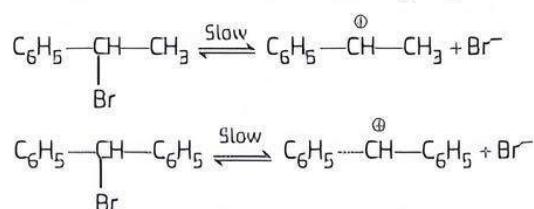
**Ans.** The order of reactivity of alkyl halides towards  $S_N2$  displacement reaction is:

Primary > secondary > tertiary.

Therefore 1-bromopentane will react faster.

Q 31. Out of the two bromoderivatives,  $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$ , and  $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$ , which one is more reactive in  $\text{S}_{\text{N}}1$  reaction and why?

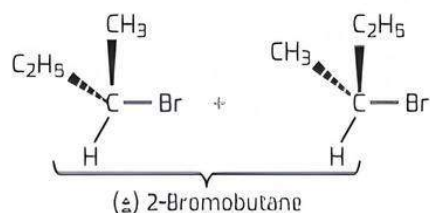
**Ans.** In the  $S_N1$  reaction, the reactivity of an alkyl halide depends upon the stability of the carbocation which is formed in the slow or rate determining step.



Although both the carbocations are secondary in nature, the carbocation formed in the second reaction is more resonance stabilised due to the presence of two phenyl groups that are involved in conjugation. Therefore, the corresponding halogen derivative is more reactive.

**Q 32. What is a racemic mixture? Give an example.**

**Ans.** An equimolar mixture of two enantiomers of an optically active compound is known as a racemic mixture.



Q 33. Chlorobenzene is extremely less reactive towards nucleophilic substitution reactions. Give two reasons for the same.

**Ans.** (i) The C—Cl bond has partial double bond character on account of conjugation.

(ii) The carbon atom in C—Cl bond is  $sp^2$  hybridised and is sufficiently electronegative in nature.

Therefore, the bond cleavage is quite difficult.

Q 34. Which one of the following compounds is more easily hydrolysed by aqueous KOH and why?  
 $\text{CH}_3\text{CH}_2\text{Cl}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$  or  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$

**Ans.**  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$  is hydrolysed more easily since it is a primary alkyl halide while the other alkyl halide is of secondary nature. The hydrolysis proceeds by  $\text{S}_{\text{N}}2$  mechanism.

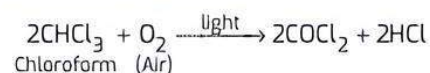
Q 35. Out of  $S_N1$  and  $S_N2$  which reaction occurs with (i) Inversion of configuration (ii) racemisation.

**Ans.** (i)  $S_N2$  reaction occurs with inversion of configuration.

(ii)  $S_N1$  reaction occurs with racemisation.

**Q 36. Why is chloroform kept in coloured bottles?**

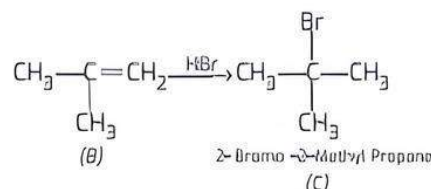
**Ans.** In the presence of light, chloroform is oxidised to a highly poisonous gas, phosgene.



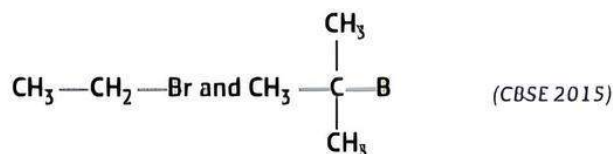
In order to check this, chloroform must be kept in dark brown coloured bottles. Moreover, the bottles must be completely filled and well stoppered to check the entry of air.

Q 37. Primary alkyl halide  $C_4H_9Br$  (A) is reacted with alcoholic KOH to give compound (B). The compound (B) is reacted with HBr to give (C) which is an isomer of compound (A). Write the structures of the compounds (A), (B) and (C).

Ans.  $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2 - \text{Br} \xrightarrow[\Delta]{\text{alc. KOH}} \text{CH}_3 - \underset{\text{CH}_3}{\text{C}} = \text{CH}_2$   
 (A) 2-methyl propene (B)



Q 38. Which would undergo  $S_N2$  reaction faster in the following pair and why?



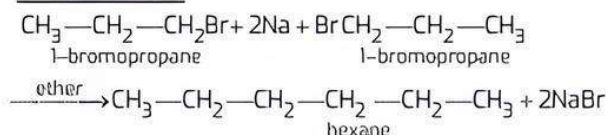
**Ans.**  $\text{CH}_3\text{—CH}_2\text{—Br}$  because It is a primary alkyl halide and offers less steric hindrance to the attacking nucleophile as compared to the other alkyl halide which is of tertiary nature.



### Short Answer Type-I Questions

**Q 1.** Write the structural formula and IUPAC name of the alkane obtained by the reaction of 1-bromopropane with sodium in the presence of ether. What is the name of the reaction?

**Ans.** 1-bromopropane in the presence of dry ether, reacts with sodium to give hexane. This reaction is called Wurtz reaction.



Q 2. Which compound in each of the following pairs will react faster in  $S_N2$  reaction with  $\text{OH}^-$ ?

(NCERT EXERCISE)

- (i)  $\text{CH}_3\text{Br}$  or  $\text{CH}_3\text{I}$   
(ii)  $(\text{CH}_3)_3\text{CCl}$  or  $\text{CH}_3\text{Cl}$

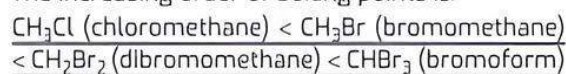
Ans. (i) Since  $I^-$  is a better leaving group as compared to  $Br^-$ . So,  $CH_3I$  reacts faster in  $S_N2$  reaction with  $OH^-$  as compared to  $CH_3Br$ .

(ii) On the basis of steric effect, in  $S_N2$  reactions  $1^\circ$  alkyl halides are much more reactive as compared to tertiary ( $3^\circ$ ) alkyl halides. So,  $\text{CH}_3\text{Cl}$  reacts faster with  $\text{OH}^-$  in  $S_N2$  reaction as compared to  $(\text{CH}_3)_3\text{CCl}$  ( $3^\circ$  alkyl halide).

Q 3. Arrange each set of compounds in order of increasing boiling points:

- (i) Bromomethane, bromoform, chloromethane, dibromomethane  
(ii) 1-chloropropane, isopropylchloride, 1-chlorobutane. (NCERT TEXT)

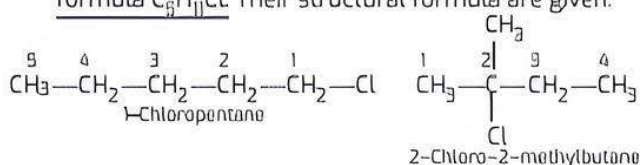
**Ans. (i)** The boiling points of organic compounds are linked with the van der Waals' forces of attraction which depend upon the molecular size. In the present case, all the compounds contain only one carbon atom. The molecular size depends upon size of the halogen atom and also upon the number of halogen atoms present in different molecules. The increasing order of boiling points is:



(ii) The same criteria is followed in this case. We all know that the branching of the carbon atom chain decreases the size of the isomer and this decreases its boiling point as compared to straight chain isomer. The increasing order of boiling point is:  
 $(\text{CH}_3)_2\text{CHCl}$  (isopropyl chloride or 2-chloropropane)  $< \text{ClCH}_2\text{CH}_2\text{CH}_3$  (1-chloropropane)  $< \text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  (1-chlorobutane)

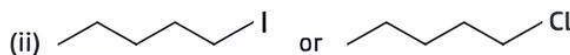
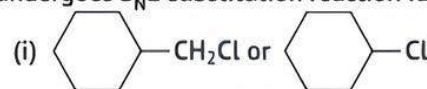
Q 4. Which will have a higher boiling point: 1-chloropentane or 2-chloro-2-methylbutane?

**Ans.** Both the isomeric haloalkanes have the molecular formula  $C_6H_{11}Cl$ . Their structural formula are given:




We know that the branching of the carbon atom chain tends to decrease the molecular size and van der Waals' forces of attraction leading to decrease in boiling point. This means that straight chain isomer has higher boiling point than the branched chain isomer.

Q 5. Which one of the following pairs of substances undergoes  $S_N2$  substitution reaction faster and why?

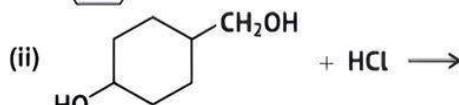
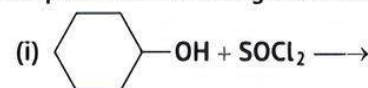


**Ans.** (i)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$  being a primary alkyl halide

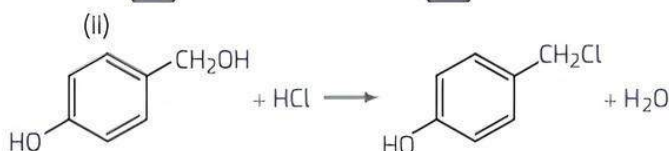
will react faster as compared to the other substance which is a tertiary alkyl halide. This is on account of lesser steric hindrance involved in the first substance when nucleophile attacks.

(ii)  will react faster as compared to the other substance since the cleavage of C—I bond is easier as compared to that of C—I bond due to less bond dissociation enthalpy.

**Q 6. Complete the following reaction equations:**



**Ans.** (i)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{SOCl}_2 \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{SO}_2 + \text{HCl}$

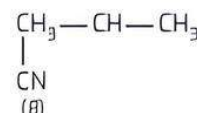


Q 7. (i)  $\text{CH}_3\text{CH}=\text{CH}_2 \xrightarrow{\text{PCl}_5} \text{'A'} \xrightarrow{\text{AgCN}} \text{'B'}$

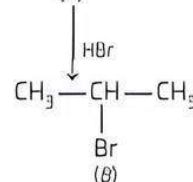


Identify 'A' and 'B' in the above reactions.

Ans. (i)  $\text{CH}_3\underset{\text{OH}}{\text{CH}}-\text{CH}_3 \xrightarrow{\text{PCl}_5} \text{CH}_3-\underset{\text{Cl (A)}}{\text{CH}}-\text{CH}_3 \xrightarrow{\text{AgCN}}$


$$(ii) \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{KOH} \xrightarrow{\text{ethanol}} \text{CH}_3\text{CH}=\text{CH}_2$$

(A)





Q 8. Give reason for the following:

(i) During the electrophilic substitution reaction of haloarenes, para substituted derivative is the major product.

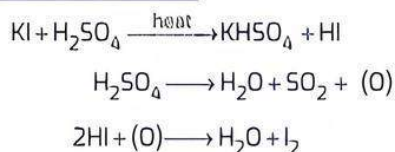
(ii) The product formed during  $S_N1$  reaction is a racemic mixture. (CBSE SQP 2022-23)

Ans. (i) During the electrophilic substitution of haloarenes, higher steric hindrance is there at the *ortho* position, hence *para* isomer is usually predominated and is obtained in the major amount. So we can say that *para* substituted derivative is the major product in this reaction.

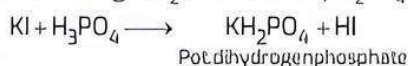
(ii) During the  $S_N1$  mechanism intermediate carbocation i.e., the product formed is  $sp^2$  hybridised and planar in nature. This allows the attack of nucleophile from either side of the plane resulting in a racemic mixture.

Q 9. Why is sulphuric acid not used during the reaction of alcohols with KI? (NCERT INTEXT)

Ans. KI is expected to give HI on reacting with  $H_2SO_4$  which will convert alcohols  $R-OH$  to alkyl iodides  $R-I$ . However,  $H_2SO_4$  is a strong oxidising agent and it oxidises HI formed during the reaction to  $I_2$  which does not react with alcohol.

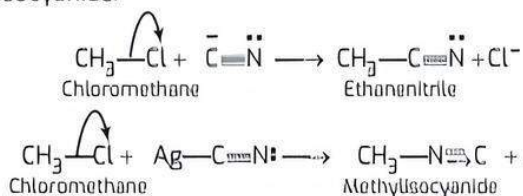


To solve the problem,  $H_2SO_4$  is replaced by phosphoric acid ( $H_3PO_4$ ) which provides HI for the reaction and does not give  $I_2$  as is done by  $H_2SO_4$ .



Q 10. Account for the following: Chloromethane reacts with KCN to form ethanenitrile as the main product and with AgCN to form methyl isocyanide as the chief product.

Ans. KCN ( $\overset{+}{K} \overset{-}{C} \equiv \overset{..}{N}$ ) is mainly an ionic compound and provides cyanide ion ( $\overset{-}{C} \equiv \overset{..}{N}$ ) for the nucleophile attack. On the other hand, silver cyanide ( $Ag-C \equiv N:$ ) is mainly covalent in nature and only nitrogen atom is free to donate the electron pair for the nucleophile attack. This results in the formation of methyl isocyanide.

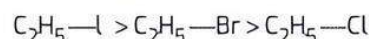


Q 11. Arrange the following compounds in decreasing order of reactivity towards  $S_N2$  displacement reaction and give reasons in support of your answer.

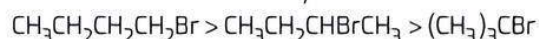
(i)  $C_2H_5Br$ ,  $C_2H_5I$ ,  $C_2H_5Cl$

(ii)  $(CH_3)_3CBr$ ,  $CH_3CH_2CHBrCH_3$ ,  $CH_3CH_2CH_2CH_2Br$ .

Ans. (i) The cleavage of  $C-X$  bond is linked with bond dissociation enthalpy. It is the order:  
 $C-Cl > C-Br > C-I$



(ii) The cleavage of  $C-Br$  bond is related to steric hindrance by alkyl group. Lesser the steric hindrance, more is the reactivity. In the light of this, the order of reactivity is:



Q 12. (i) Arrange the isomeric dichlorobenzene in the increasing order of their boiling point and melting points.

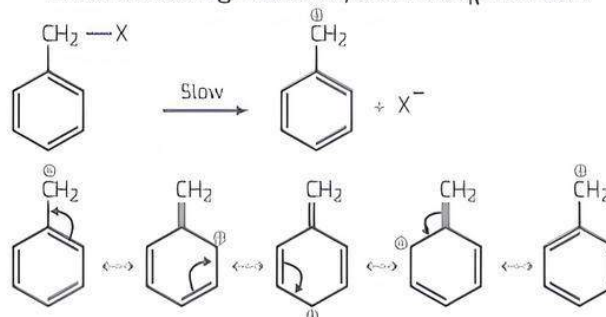
(ii) Explain why the electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene. (CBSE SQP 2023-24)

Ans. (i) *m*-dichlorobenzene < *o*-dichlorobenzene < *p*-dichlorobenzene. Symmetrical structure and close packing is seen in *para* isomer while *ortho* has a stronger dipole-dipole interaction as compared to *meta*.

(ii) The halogen atom because of its  $I$  effect, has some tendency to withdraw electrons from the benzene ring. As a result, the ring gets somewhat deactivated as compared to benzene and hence the electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene.

Q 13. Benzylic halides show high reactivity towards  $S_N1$  reactions. Why?

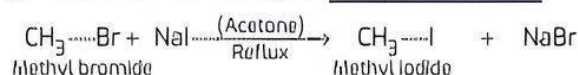
Ans.  $S_N1$  reactions, as we all know, proceed in two steps. In the slow step (rate determining step), a carbocation intermediate is formed. In benzylic halides, the benzylic carbocation is resonance stabilised. Therefore, benzylic halides show high reactivity towards  $S_N1$  reaction.



Q 14. (i) How will you convert methyl bromide into methyl iodide?

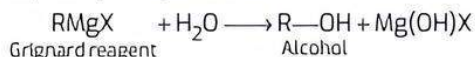
(ii) Grignard reagents should be prepared under anhydrous conditions. Explain.

Ans. (i) It is done with the help of Finkelstein reaction





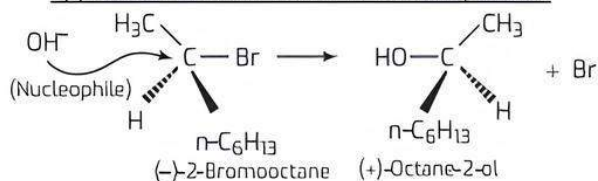
- (ii) In the presence of moisture, Grignard reagent formed gets hydrolysed to form alkane. Therefore, it should be prepared under completely anhydrous conditions.



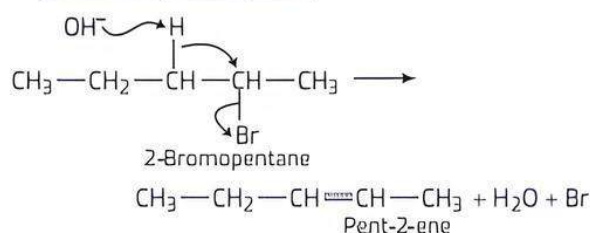
**Q 15. Propose the mechanism of the reaction taking place when:**

- (i) (-)-2-Bromooctane reacts with sodium hydroxide to form (+)-Octane-2-ol.  
 (ii) 2-Bromopentane is heated with KOH(alc.) to form alkene.

**Ans.** (i) In this reaction, there is an inversion of configuration since OH<sup>-</sup> ion (nucleophile) attacks from a side opposite to the side where Br atom is present.



- (ii) In this reaction, bimolecular elimination (E<sub>2</sub>-elimination) takes place.



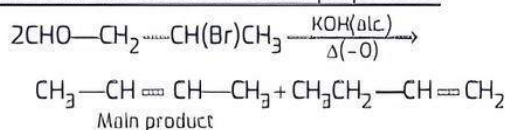
- Q 16. (i) Name the suitable alcohol and reagent, from which 2-chloro-2-methyl propane can be prepared.**  
 (ii) Out of the chloromethane and fluoromethane, which one has higher dipole moment and why?

**Ans.** (i) The alcohol and reagent used to prepare 2-chloro-2-methyl propane are tert butyl alcohol or 2-methyl propan-2-ol and Lucas reagent i.e. a mixture of conc. HCl and ZnCl<sub>2</sub>. The reaction will follow the S<sub>N</sub>1 pathway.

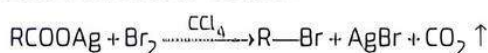
- (ii) Chloromethane has the higher dipole moment. Due to smaller size of fluorine, the dipole moment of fluoromethane is comparatively lesser.

**Q 17. Explain Saytzeff's law and Hunsdiecker reaction with chemical equations.**

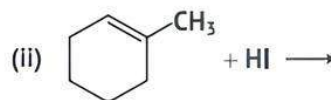
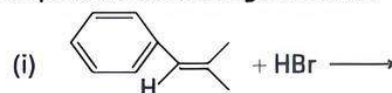
**Ans. Saytzeff's law:** This law states that in elimination reactions of organic compounds, among the various alkenes obtained by the effect of eliminating reagent, most substituted alkene is the major product.



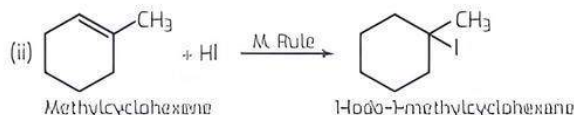
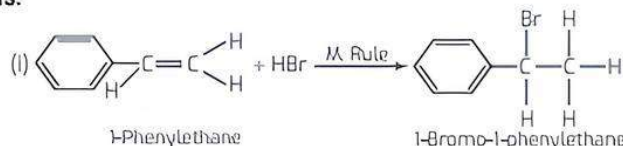
**Hunsdiecker reaction:** In the solution of silver salt of monocarboxylic acid, prepared in CCl<sub>4</sub>, when bromine is passed, bromoalkane is obtained. This reaction is called Hunsdiecker reaction.



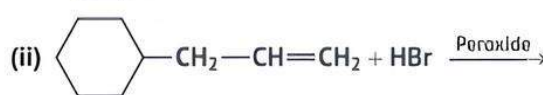
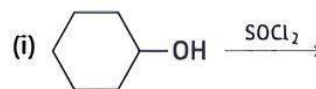
**Q 18. Complete the following reactions:**



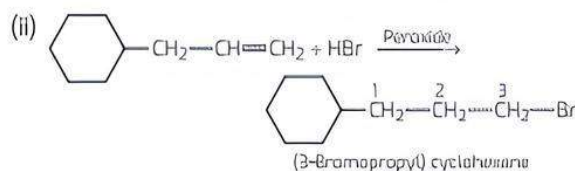
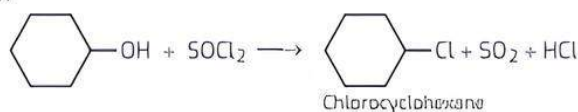
**Ans.**



**Q 19. Draw the structures of the major nucleophilic products in each of the following:**



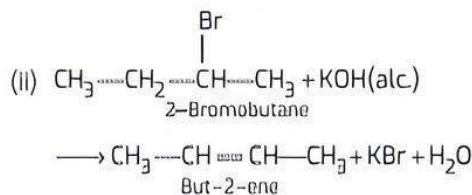
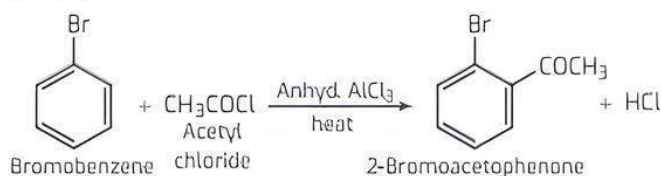
**Ans.** (i)



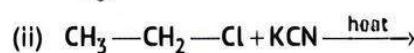
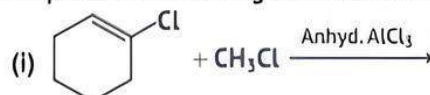
**Q 20. How will you convert:**

- (i) Bromobenzene to 2-bromoacetophenone?  
 (ii) 2-Bromobutane to But-2-ene?

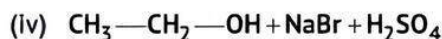
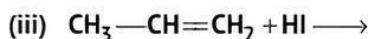
**Ans.** (i)



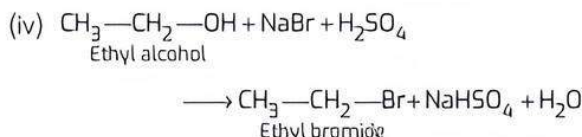
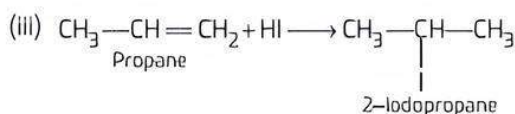
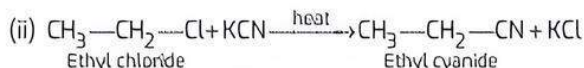
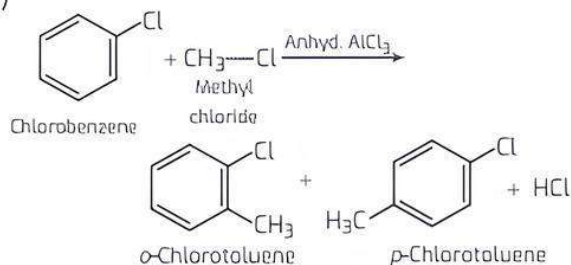
**Q 21. Complete the following chemical reactions:**







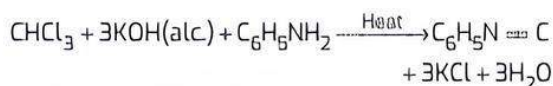
Ans. (i)



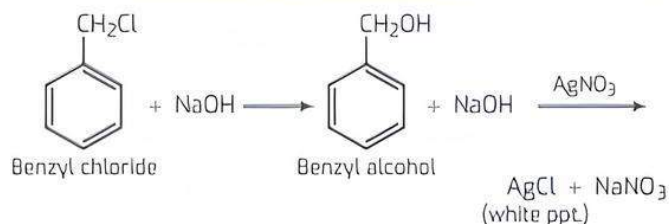
Q 22. How will you distinguish between the following pairs of compounds?

- (i) Chloroform and carbon tetrachloride  
 (ii) Benzyl chloride and chlorobenzene.

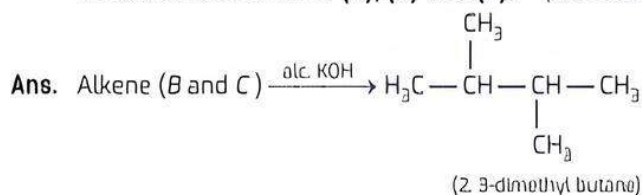
Ans. (i) Heat the two compounds separately with aniline and alcohol KOH. Chloroform gives pungent and irritating smell of an isocyanide while carbon tetrachloride does not.



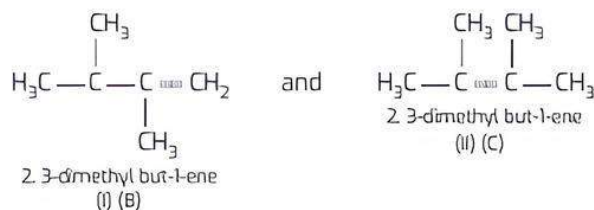
(ii) Add a few drops of NaOH and  $\text{AgNO}_3$  separately to both the compounds. Benzyl chloride gives a white precipitate while chlorobenzene does not.



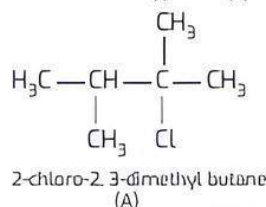
Q 23. An alkyl halide (A) of molecular formula  $\text{C}_6\text{H}_{13}\text{Cl}$  on treatment with alcoholic KOH gives two isomeric alkenes (B) and (C) of molecular formula  $\text{C}_6\text{H}_{12}$ . Both alkenes on hydrogenation give 2, 3-dimethylbutane. Write the structures of (A), (B) and (C). (CBSE 2023)



Only two alkenes are possible.



Only one alkyl halide is possible which gives the above two alkenes (I) and (II) and that is:

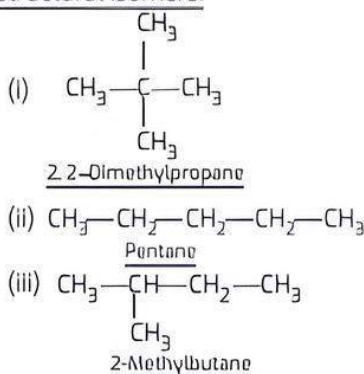


## Short Answer Type-II Questions

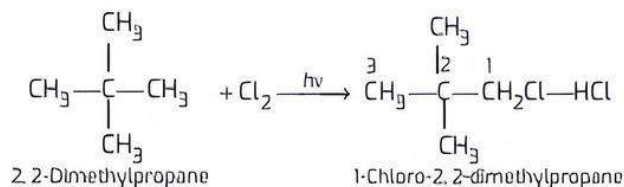
Q 1. Among the isomeric alkanes of molecular formula  $\text{C}_5\text{H}_{12}$ , identify the one which on photochemical chlorination yields:

- (i) A single monochloride  
 (ii) Three isomeric monochlorides  
 (iii) Four isomeric monochlorides. (NCERT INTEXT)

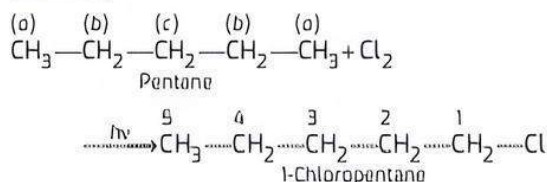
Ans. The molecular formula  $\text{C}_5\text{H}_{12}$  represents three structural isomers.

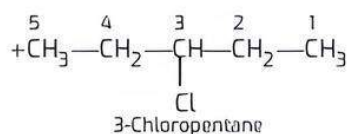
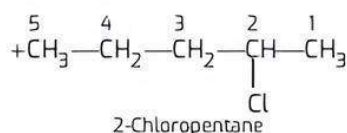


(i) The isomer is symmetrical with four primary ( $1^\circ$ ) carbon atoms and one quaternary ( $4^\circ$ ) carbon atom. Since all the hydrogen atoms are equivalent, it will yield only one monochloride upon photochlorination i.e., chlorination carried in the presence of ultra-violet light.

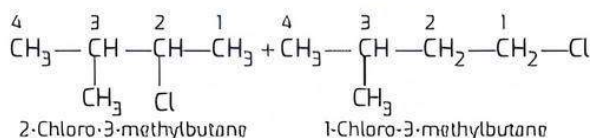
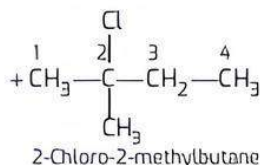
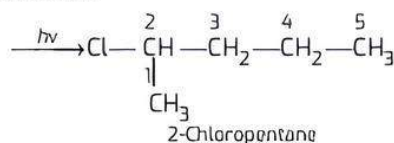
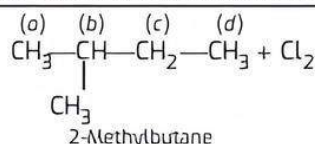


(ii) In the straight chain isomer pentane, there are three groups of equivalent hydrogen atoms. As a result, three isomeric monochlorides are possible.





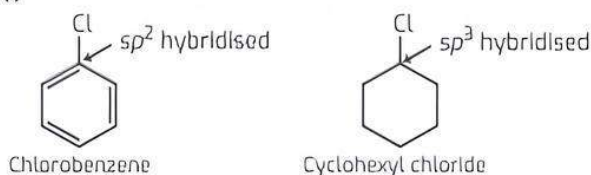
- (iii) The branched chain isomer has four types of equivalent hydrogen atoms present. It will give four isomeric monochlorides upon chlorination.



## Q 2. Explain why:

- Dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.
- Alkyl halides though polar are immiscible with water.
- Grignard reagents should be prepared under anhydrous conditions. (NCERT EXERCISE)

Ans. (i)

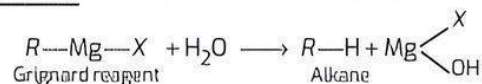


The polarity of C—Cl bond in chlorobenzene is less than that of same bond in cyclohexyl chloride because of carbon atom involved in chlorobenzene which is more electronegative (greater s-character) as compared to the carbon atom in case of cyclohexyl chloride (lesser s-character). Therefore, the dipole moment of chlorobenzene is less with respect to cyclohexyl chloride.

- (ii) In water,  $\text{H}_2\text{O}$  molecules are linked to each other by intermolecular hydrogen bonding. Although alkyl halides also contain polar C—X bonds, they cannot break the hydrogen bonding in  $\text{H}_2\text{O}$  molecules. This means that there is hardly any scope for association between molecules of

alkyl halides and water. They therefore, exist as separate layers and are immiscible with each other.

- (iii) Grignard reagents ( $\text{R—Mg—X}$ ) should be prepared under anhydrous conditions because these are readily decomposed by water to form alkanes.



That is why ether used as solvent in the preparation of Grignard reagent is completely anhydrous in nature.

## Q 3. (i) Define the following terms:

- (a) Enantiomers                      (b) Racemic mixture

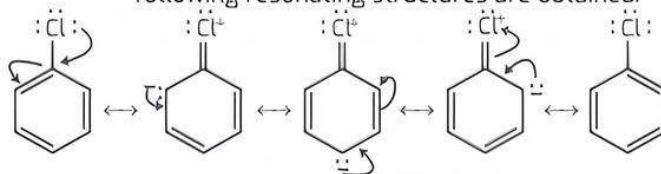
- (ii) Why is chlorobenzene resistant to nucleophilic substitution reaction? (CBSE 2019)

Ans. (i) (a) **Enantiomers:** The stereoisomers related to each other as non-superimposable mirror images are called enantiomers.

- (b) **Racemic Mixture:** Equimolar mixture of *d* and *l* form is known as racemic mixture.

- (ii) Two reasons for the resistivity or less reactivity of chlorobenzene towards a nucleophilic substitution reaction are as follows:

- (a) **Resonance Effect:** The electron pair of chlorine atom is involved in conjugation with the  $\pi$ -electrons of the benzene ring and the following resonating structures are obtained.



As a result, electrons of C—Cl bond get delocalised and a partial double bond character develops in the bond and hence, it becomes difficult for the nucleophile to cleave the C—Cl bond.

- (b) **Increased Electron Density:** A repulsion is suffered by the nucleophile due to increased electron density on the benzene ring which prohibits the nucleophile to make a close access for the attack on the molecule.

## Q 4. Arrange the compounds of each set in order of decreasing reactivity towards ( $\text{S}_{\text{N}}2$ ) displacement:

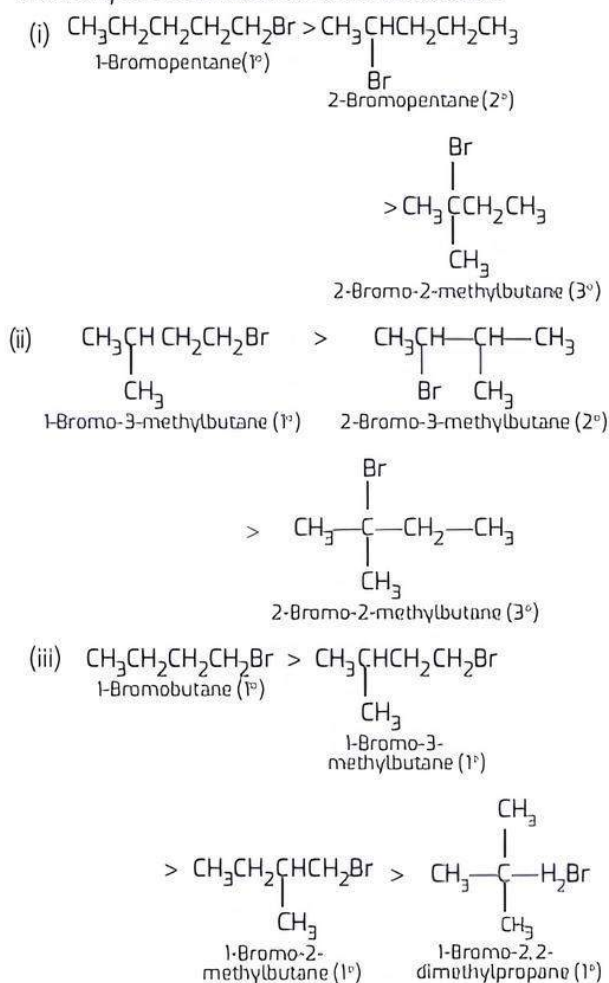
- 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane
- 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3-methylbutane
- 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane.

(NCERT EXERCISE)

Ans. The reactivity of a particular haloalkane towards  $\text{S}_{\text{N}}2$  reaction is inversely proportional to the steric hindrance around the carbon atom involved in C—X



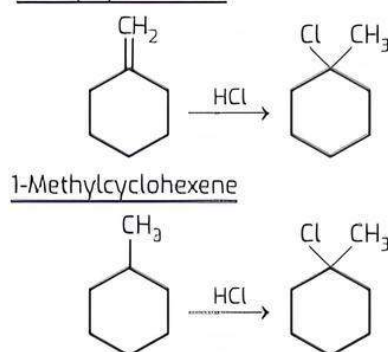
bond. More the steric hindrance, lesser will be the reactivity. In the light of this, the decreasing order of reactivity in all the three cases is as follows:



Q 5. (i) Name the possible alkenes which will yield 1-chloro-1-methylcyclohexane on their reaction with HCl. Write the reactions involved.

(ii) Allyl chloride is hydrolysed more readily than *n*-propyl chloride. Why? (CBSE SQP 2022-23)

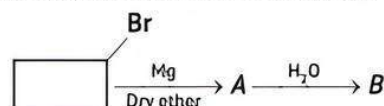
Ans. (i) The possible alkenes which will yield 1-chloro-1-methylcyclohexane on their reaction with HCl are Methylcyclohexene



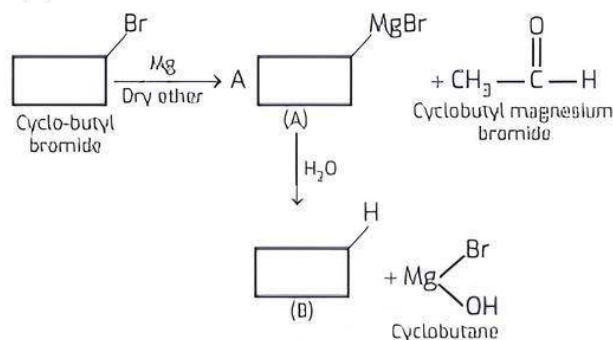
(ii) Allyl chloride shows high reactivity as the carbocation formed in the first step is stabilised by resonance while no such stabilisation of carbocation exists in the case of *n*-propyl chloride. So, allyl chloride is hydrolysed more readily than *n*-propyl chloride.

Q 6. Answer any three of the following:

- Which isomer of  $\text{C}_5\text{H}_{10}$  gives a single monochloro compound  $\text{C}_5\text{H}_9\text{Cl}$  in bright sunlight?
- Arrange the following compounds in increasing order of reactivity towards  $\text{S}_\text{N}2$  reaction: 2-Bromopentane, 1-Bromopentane, 2-Bromo-2-methylbutane
- Why *p*-dichlorobenzene has higher melting point than those of *ortho* and *meta*-isomers? (CBSE 2023)
- Identify A and B in the following:



- Ans. (i) Cyclopentane isomer of  $\text{C}_5\text{H}_{10}$  gives a single monochloro compound  $\text{C}_5\text{H}_9\text{Cl}$  in bright sunlight.
- (ii) The increasing order of reactivity is 2-Bromo-2-methylbutane < 2-Bromopentane < 1-Bromopentane
- (iii) This is due to the greater symmetry of *para*-isomer that fits in the crystal better as compared to *ortho* and *meta*-isomers.
- (iv)

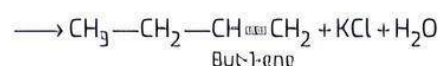
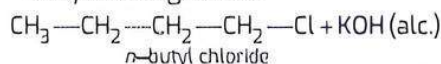


Q 7. What happens when:

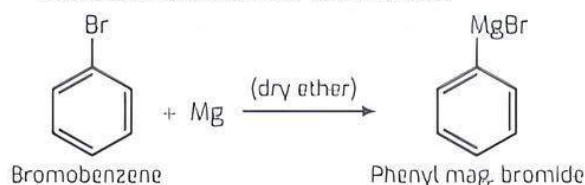
- n*-butyl chloride is treated with alcoholic KOH,
- bromobenzene is treated with Mg in the presence of dry ether,
- chlorobenzene is subjected to hydrolysis,
- ethyl chloride is treated with (aq.) KOH,
- methyl bromide is treated with sodium in the presence of dry ether,
- methyl chloride is treated with KCN?

(NCERT EXERCISE)

Ans. (i) But-1-ene is formed as the product as a result of dehydrohalogenation.



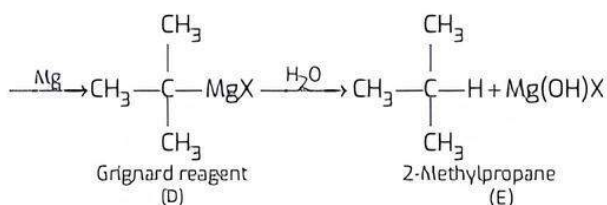
(ii) Phenyl magnesium bromide (Grignard reagent) is formed as a result of the reaction.



- $$\begin{array}{ccc} \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \\ \text{CH}_3 - \text{C} - \text{C} - \text{CH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array} & \begin{array}{c} \text{Na/ether} \\ \text{Wurtz reaction} \end{array} & \begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} - \text{X} \\ | \\ \text{CH}_3 \end{array} \end{array}$$

2,2,3,3-tetramethylbutane





Q 11. Write main product formed when:

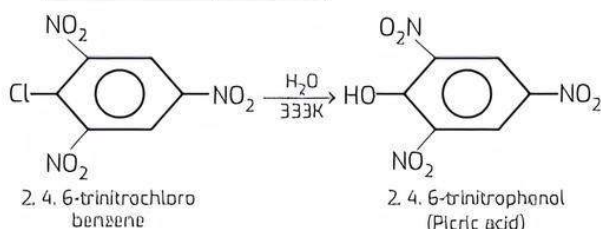
- (i) Methyl chloride is treated with NaI/Acetone.
- (ii) 2,4,6-trinitrochlorobenzene is subjected to hydrolysis.
- (iii) *n*-butyl chloride is treated with alcoholic KOH.

(CBSE 2023)

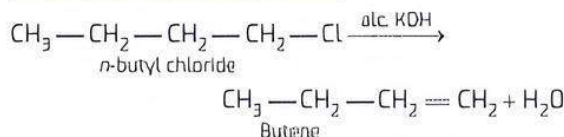
Ans. (i) Methyl iodide is formed when methyl chloride is treated with NaI/Acetone.



- (ii) The 'Cl' group leaves and is replaced by 'OH' group thereby forming 2, 4, 6 -trinitrophenol which is also known as picric acid.



- (iii) The product formed is butene and the reaction is known as hydrohalogenation:

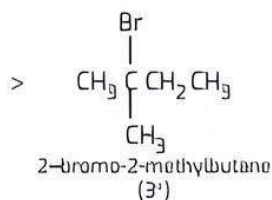
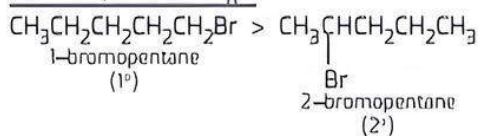


Q 12. The following compounds are given to you:

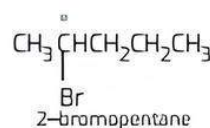
2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane

- (i) Write the compound which is most reactive towards  $\text{S}_{\text{N}}2$  reaction.
- (ii) Write the compound which is optically active.
- (iii) Write the compound which is most reactive towards  $\beta$  elimination reaction. (CBSE 2017)

Ans. (i)  $\text{S}_{\text{N}}2$  reaction involve the formation of transition state. Higher the steric hindrance, lesser the stability of transition state and lower is their reactivity towards  $\text{S}_{\text{N}}2$



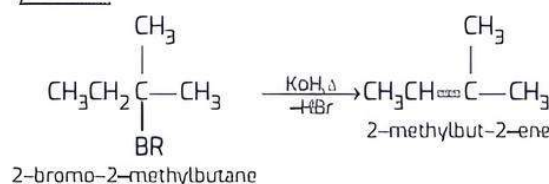
- (ii) Among the given compounds, 2-bromopentane is optically active due to the presence of chiral carbon (\*)



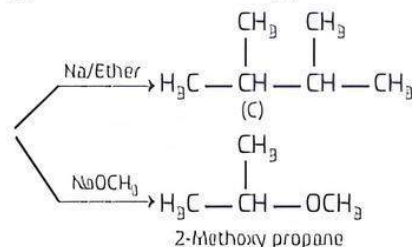
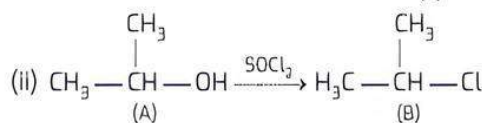
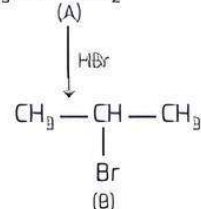
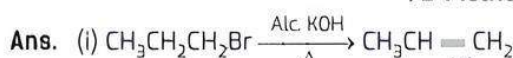
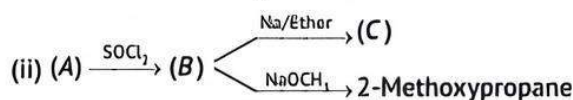
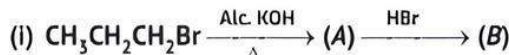
**TiP**

Achiral or asymmetric carbon is a carbon atom that is attached to four different types of atoms or group of atoms.

- (iii) 2-bromo-2-methylbutane is most reactive towards  $\beta$ -elimination reaction because in this case more substituted alkene is the major product.



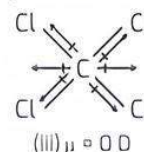
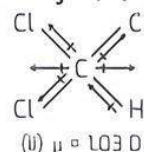
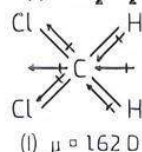
Q 13. Complete the following reactions:



Q 14. Which one of the following has highest dipole moment?

- (i)  $\text{CH}_2\text{Cl}_2$  (ii)  $\text{CHCl}_3$  (iii)  $\text{CCl}_4$  (NCERT EXERCISE)

Ans.



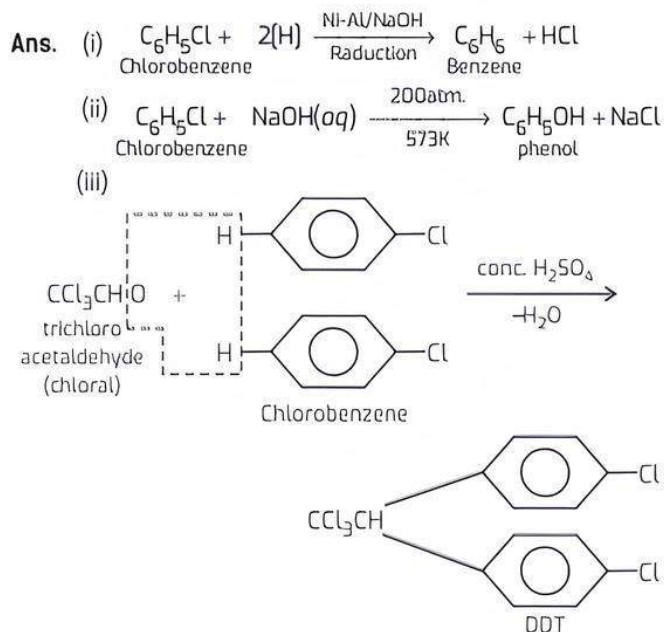
- (i) Tetrachloromethane ( $\text{CCl}_4$ ) is a symmetrical molecule and has zero dipole moment.

(ii) In chloroform ( $\text{CHCl}_3$ ), the resultant dipole moment of two  $\text{C—Cl}$  bonds is opposed by resultant dipole moment of  $\text{C—Cl}$  and  $\text{C—H}$  bonds. Since the latter resultant dipole moment is smaller, the molecule as a whole has dipole moment ( $\mu$ ) = 1.03D.

(iii) In dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), the resultant dipole moments of two  $\text{C—Cl}$  and two  $\text{C—H}$  bonds reinforce one another. The molecule has maximum dipole moment ( $\mu$ ) = 1.62 D.  $\text{CH}_2\text{Cl}_2$  has the maximum dipole moment value.

**Q 15. Clarify how will you prepare the following, starting from chlorobenzene by giving chemical equation:**

(i) Benzene (ii) Phenol (iii) DDT



**Q 16. What is chlorofluorocarbon? What is its effect on the environment?**

Ans. Chlorofluorocarbon or polychlorofluoro derivatives of alkane are called freon. Polychlorofluoro methane and polychlorofluoro ethane are important freons, e.g.,

- (i)  $\text{CFCl}_3$  (trichlorofluoromethane (Freon-11))
- (ii)  $\text{CF}_2\text{Cl}_2$  (dichlorodifluoromethane (Freon-12))
- (iii)  $\text{C}_2\text{F}_2\text{Cl}_4$  (tetrachlorodifluoroethane (Freon-112))

**Uses and effect in the environment:** Freons are colourless, odourless, non-poisonous, very less reactive and low boiling (at  $30^\circ\text{C}$ ) liquids. These get converted into gaseous state at very low pressure. That's why these are used as coolant in refrigerators and air conditioners. These are also used as aerosol propellant in aeroplanes. These also acts as solvent. In short form, these are called chlorofluorocarbon (CFC). These have harmful effect on the environment. These are assumed to be responsible for destroying ozone layer. These get diffused as pollutant and reached at the stratosphere, where it initiates free radical reaction. Consequently, these react with ozone and destroy it.

**Q 17. Write short note on the following:**

(i) Carbon tetrachloride and its uses

(ii) Iodoform and its uses

Ans. (i) **Carbon tetrachloride:** It is obtained by replacing all the four hydrogen atoms of methane by four chlorine atoms. Since it extinguishes fire, so it is also known by the name **pyrene**. It is used as a solvent in dry cleaning. It also gives Freon-12. It is used as a cleaning agent for removing stains from the clothes.

(ii) **Iodoform:** It is obtained by displacing three hydrogen atoms of methane by three iodine atoms. Thus, it is used in the test of primary amines and in the formation of acetylene.

**Q 18. Account for the following:**

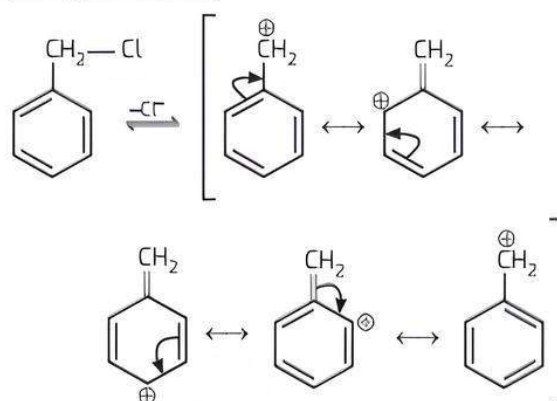
(i) Benzyl chloride is highly reactive towards  $\text{S}_{\text{N}}1$  reaction.

(ii) ( $\pm$ )-Butan-2-ol is optically inactive, though it contains a chiral carbon atom.

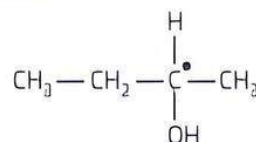
(iii) Chloroform is stored in closed dark coloured bottles.

(CBSE 2023)

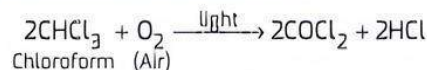
Ans. (i) Benzyl chloride is highly reactive towards  $\text{S}_{\text{N}}1$  reaction because the intermediate benzylic carbocation formed in the slowest step is stabilised through resonance



(ii) Butan-2-ol has a chiral centre that is butan-2-ol has a carbon atom bonded to four different substituents. So, it is optically active.



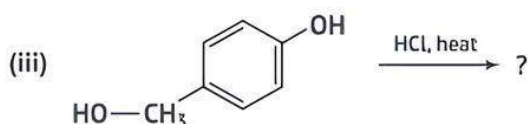
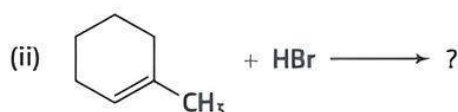
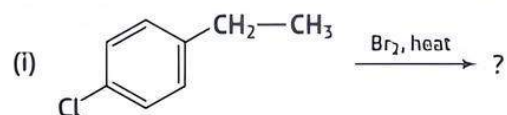
(iii) In the presence of light, chloroform is oxidised to a highly poisonous gas, phosgene.



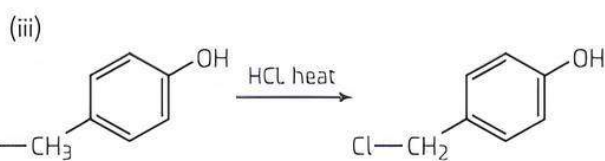
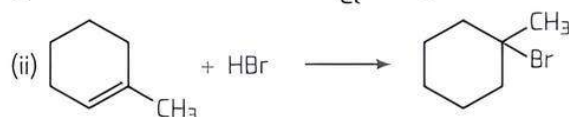
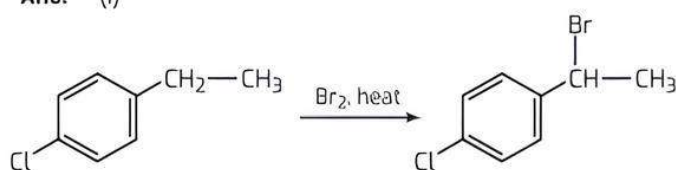
In order to check this, chloroform must be kept in dark brown coloured bottles. Moreover, the bottles must be completely filled and well stoppered to check the entry of air.



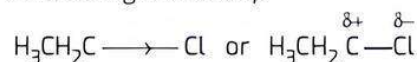
**Q 19. Draw the structures of the major monohalo product for each of the following reactions:** (CBSE 2017)



**Ans.** (i)



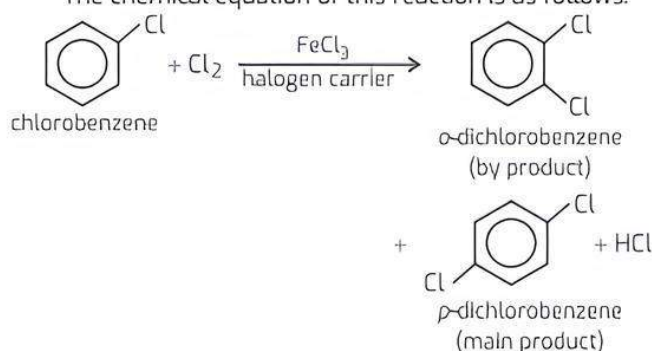
On the other hand, in  $\text{CH}_3\text{CH}_2\text{Cl}$ , carbon of  $\text{C}-\text{Cl}$  bond is  $\text{sp}^2$ -hybridised due to which it does not exhibit resonance. Although, here Cl carries partial negative charge ( $\delta^-$ ) and C carries partial positive charge ( $\delta^+$ ) due to  $-I$  effect of Cl hence Cl gets easily substituted by nucleophilic reagents. Thus, it shows high reactivity.



(ii) **Electrophilic substitution reactions:** The reactions in which an electrophilic reagent displaces another electrophile from its place are called electrophilic substitution reactions. These reactions are very common in the benzene ring in haloarenes. This is because benzene nucleus of haloarenes being electron rich acts as a source of electrons and invites the electrophile to attack on it.

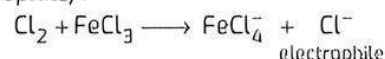
**Electrophilic substitution in aryl halides or haloarenes:** By the reaction of aryl halide (like chlorobenzene), with chlorine in the presence of halogen carrier (e.g. Fe or  $\text{FeCl}_3$ ), a mixture of *p*-dichlorobenzene (main product) and *o*-dichlorobenzene is obtained. This reaction is an example of electrophilic substitution reaction.

The chemical equation of this reaction is as follows:

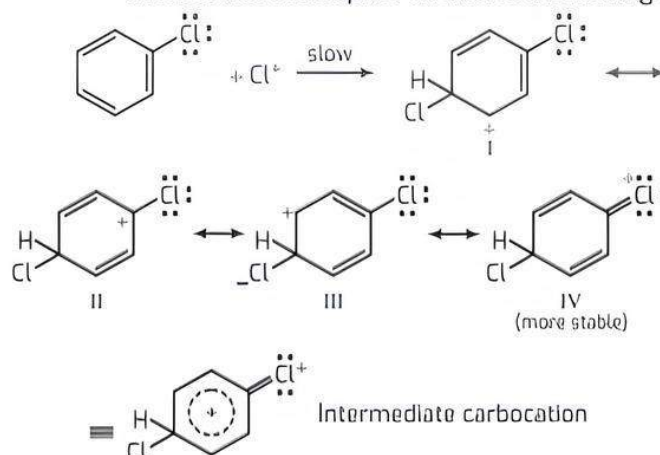


**Mechanism:** The mechanism of the above reaction can be explained by following steps:

**Step 1.** Formation of activated species *i.e.*, chloronium ion of the reaction (which acts as electrophile):



**Step 2.** Formation of intermediate carbocation by the attack of electrophile on chlorobenzene ring:

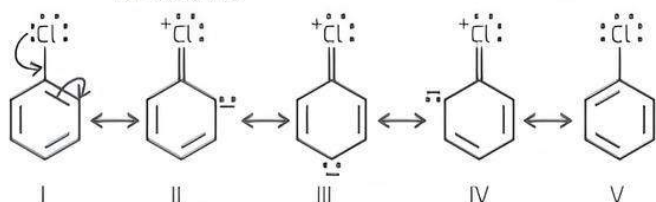


## Long Answer Type Questions

**Q 1. (i) Chlorine atom of chlorobenzene is much less reactive as compared to chlorine atom of ethyl chloride. Why?**

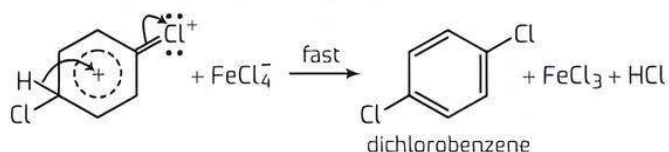
**(ii) What are electrophilic substitution reactions? Explain its mechanism with an example of aryl halide.**

**Ans.** (i) In chlorobenzene, chlorine atom is directly attached with carbon ( $\text{sp}^2$ -hybridised) of benzene nucleus and hence, chlorobenzene exhibits following resonating structures due to  $+M$  effect of chlorine.



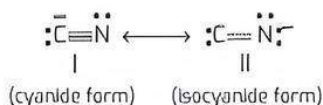
In the above resonating structures II, III and IV, Cl carries positive charge and partial double bond character is generated in carbon-chlorine bond (due to which bond distance decreases). Thus, chlorine is bound with carbon of benzene nucleus by strong attractive forces and hence, can not be substituted by nucleophile under normal conditions. Thus, it is very less reactive.

**Step 3.** Formation of product by the loss of proton from intermediate carbocation under the influence of  $\text{FeCl}_4^-$ .



- Q 2. (i) What are ambident nucleophiles? Explain with an example.
- (ii) Primary alkyl halide  $\text{C}_4\text{H}_9\text{Br}$  (a) reacted with alcoholic KOH to give compound (b). Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal, it gives compound (d),  $\text{C}_8\text{H}_{18}$  which is different from the compound formed when *n*-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions. (NCERT EXERCISE)

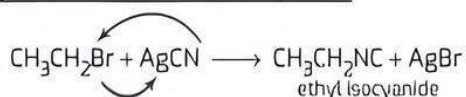
Ans. (i) **Ambidentate Nucleophiles:** The molecules/ions having two nucleophilic sites are called ambidentate nucleophiles. e.g., cyanide ion ( $\text{CN}^-$ ). It can attack either through carbon to form alkyl cyanide or through nitrogen to form alkyl isocyanide.



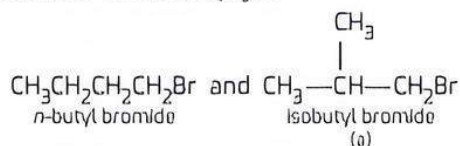
The carbon of  $\text{CN}^-$  ion attacks at the electron deficient site to form alkyl cyanide.



On the other hand,  $\text{AgCN}$  is a covalent compound so it does not ionise. Hence, its carbon is not free to attack. Thus, in this situation attack takes place by N resulting in the formation of isocyanide.

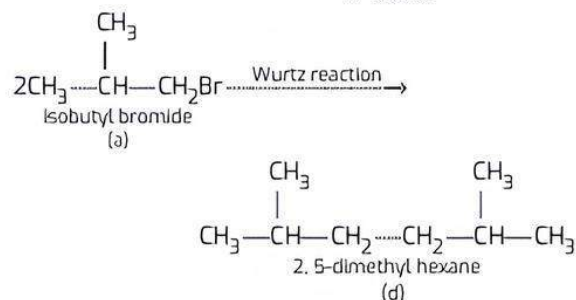
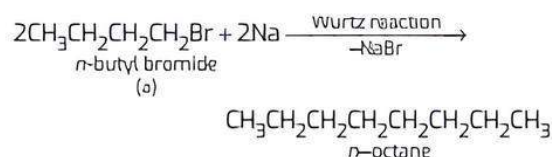


- (ii) Following two primary halides are possible for the molecular formula  $\text{C}_4\text{H}_9\text{Br}$ :

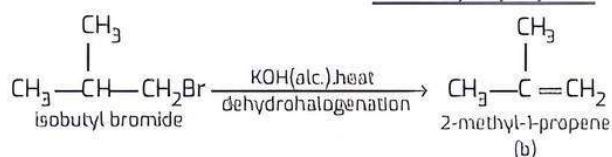


Thus, the compound 'a' is either *n*-butyl bromide or isobutyl bromide.

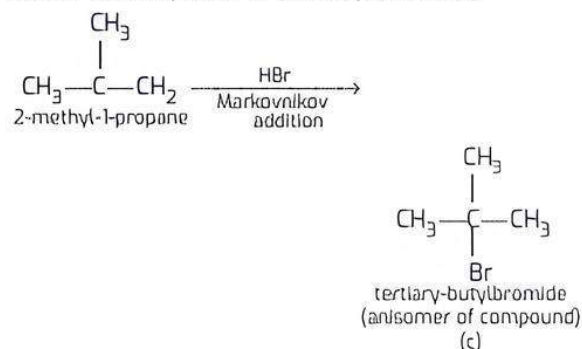
Since compound 'd' reacts with sodium metal to give compound 'd' (molecular formula  $\text{C}_8\text{H}_{18}$ ), which is different from the compound that is formed by the reaction of *n*-butyl bromide with sodium. Thus, compound 'a' must be isobutyl bromide and compound 'd' be 2, 5-dimethylhexane.



If compound 'a' is isobutyl chloride, the compound 'b' which is obtained by the reaction of compound 'a' with alcoholic KOH, should be 2-methyl-1-propene.

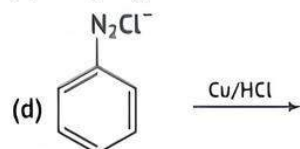
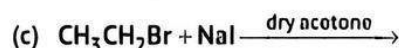
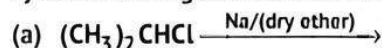


Compound 'b' reacts with HBr according to Markovnikov's rule to give compound 'c'. So compound 'c' is tertiary-butyl bromide which is an isomer of compound 'a' (isobutyl bromide).



Thus, compound 'a' is isobutyl bromide, 'b' is 2-methyl-1-propene, 'c' is tertiary-butyl bromide (isomer of 'a') and 'd' is 2, 5-dimethylhexane.

- Q 3. (i) Write the formula of the main products formed by the following chemical reactions:



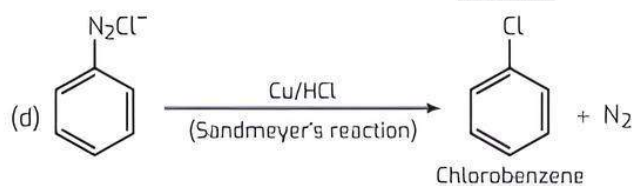
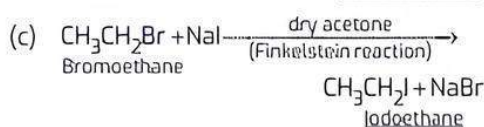
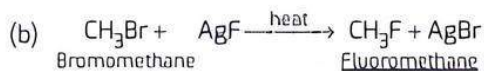
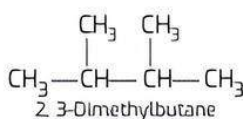
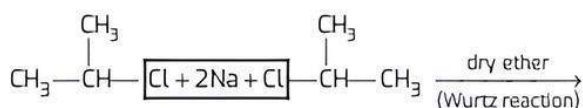
- (ii) What happens when:

- ethyl chloride is treated with NaI in the presence of acetone
- chlorobenzene is treated with Na metal in the presence of dry ether
- methyl chloride is treated with  $\text{KNO}_2$ .

Write chemical equations in support of your answer.



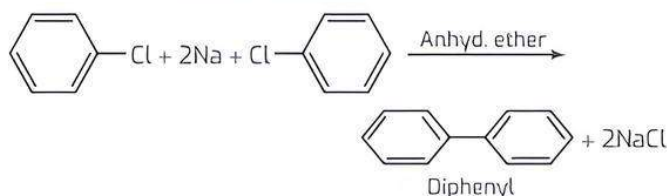
Ans. (i) (a)



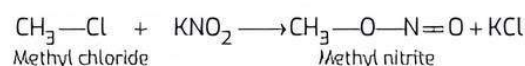
(ii) (a) Ethyl iodide is formed as a result of halogen exchange and the reaction is known as Finkelstein reaction.



(b) Diphenyl is formed and the reaction is known as Fittig reaction.



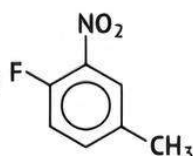
(c) Methyl nitrite is formed as a result of nucleophilic substitution.



## Chapter Test

### Multiple Choice Questions

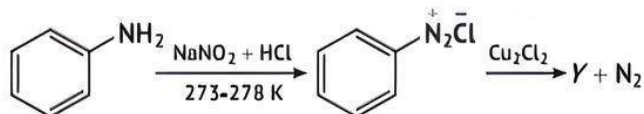
Q 1. The IUPAC name of the compound is:

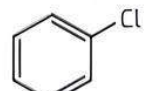
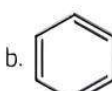
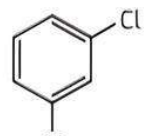
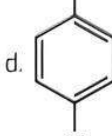


- 1-fluoro-4-methyl-2-nitrobenzene
- 4-fluoro-1-methyl-3-nitrobenzene
- 4-methyl-1-fluoro-2-nitrobenzene
- 2-fluoro-5-methyl-1-nitrobenzene

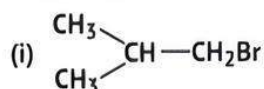
Q 2. Identify the compound 'Y' in the following reaction.

(NCERT EXEMPLAR)

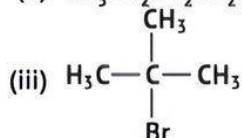


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Q 3. Arrange the following compounds in increasing order of their boiling points.

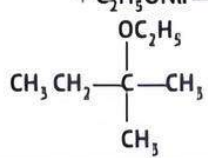


(ii)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$



- (ii) < (i) < (iii)
- (i) < (ii) < (iii)
- (iii) < (i) < (ii)
- (iii) < (ii) < (i)

Q 4. Match the column I with column II and mark the appropriate choice.

Column I	Column II
(A) $\text{CH}_3-\text{CH}(\text{Br})-\text{CH}(\text{CH}_3)-\text{CH}_3 \xrightarrow{+\text{C}_2\text{H}_5\text{ONa}}$ 	(i) $\beta$ -elimination
(B) $\text{CH}_3\text{CH}_2\text{Br} \xrightarrow{\text{AgOH}} \text{CH}_3\text{CH}_2\text{OH}$	(ii) $\text{S}_\text{N}1$ nucleophilic substitution
(C) $\text{CH}_3\text{CH}=\text{CH}_2 + \text{HBr} \xrightarrow{\text{Peroxide}}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$	(iii) $\text{S}_\text{N}2$ nucleophilic substitution
(D) $\text{CH}_3-\text{CH}_2\text{Br} + \text{alc. KOH} \rightarrow \text{CH}_2=\text{CH}_2$	(iv) Kharasch effect

- (A)→(iv), (B)→(i), (C)→(ii), (D)→(iii)
- (A)→(ii), (B)→(iii), (C)→(iv), (D)→(i)
- (A)→(i), (B)→(ii), (C)→(iv), (D)→(iii)
- (A)→(iii), (B)→(i), (C)→(ii), (D)→(iv)

### Assertion and Reason Type Questions

**Directions (Q. Nos. 5-6):** Each of the following questions consists of two statements, one is Assertion (A) and the other is Reason (R). Give answer:

- Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).
  - Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).
  - Assertion (A) is true but Reason (R) is false.
  - Assertion (A) is false but Reason (R) is true.
- Q 5. Assertion (A):** Hydrolysis of (–)-2-bromo octane proceeds with inversion of configuration.  
**Reason (R):** This reaction proceeds through the formation of a carbocation.
- Q 6. Assertion (A):** Nitration of chlorobenzene leads to the formation of *m*-nitrochlorobenzene.  
**Reason (R):**  $-\text{NO}_2$  group is a *m*-directing group.

### Case Study Based Question

- Q 7.** Nucleophilic substitution reaction of haloalkane can be conducted according to both  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$  mechanisms. However, which mechanism it is based on is related to such factors as the structure of haloalkane, and properties of leaving group, nucleophilic reagent and solvent.

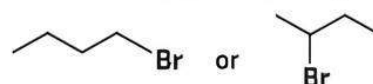
**Influences of halogen:** No matter which mechanism the nucleophilic substitution reaction is based on, the leaving group always leave the central carbon atom with electron pair. This is just the opposite of the situation that nucleophilic reagent attacks the central carbon atom with electron pair. Therefore, the weaker the alkalinity of leaving group is, the more stable the anion formed is and it will be more easier to be substituted. The alkalinity order of halogen ion is  $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^-$  and the order of their leaving tendency should be  $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$ . Therefore, in four halides with the same alkyl and different halogens, the order of substitution reaction rate is  $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$ . In addition, if the leaving group is very easy to leave, many carbocation intermediates are generated in the reaction and the reaction is based on  $\text{S}_{\text{N}}1$  mechanism. If the leaving group is not easy to leave, the reaction is based on  $\text{S}_{\text{N}}2$  mechanism.

**Influences of solvent polarity:** In  $\text{S}_{\text{N}}1$  reaction, the polarity of the system increases from the reactant to the transition state, because polar solvent has a greater stabilizing effect on the

transition state than the reactant, thereby reduce activation energy and accelerate the reaction. In  $\text{S}_{\text{N}}2$  reaction, the polarity of the system generally does not change from the reactant to the transition state and only charge dispersion occurs. At this time, polar solvent has a great stabilising effect on Nu than the transition state, thereby increasing activation energy and slow down the reaction rate. For example, the decomposition rate ( $\text{S}_{\text{N}}1$ ) of tertiary chlorobutane in  $25^\circ\text{C}$  water (dielectric constant 79) is 300000 times faster than in ethanol (dielectric constant 24). The reaction rate ( $\text{S}_{\text{N}}2$ ) of 2-bromopropane and NaOH in ethanol containing 40% water is twice slower than in absolute ethanol. In a word, the level of solvent polarity has influence on both  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$  reactions, but with different results. Generally speaking, weak polar solvent is favourable for  $\text{S}_{\text{N}}2$  reaction, while strong polar solvent is favourable for  $\text{S}_{\text{N}}1$  reaction, because only under the action of polar solvent can halogenated hydrocarbon dissociate into carbocation, and halogen ion and solvents with a strong polarity is favourable for solvation of carbocation increasing its stability. Generally speaking, the substitution reaction of tertiary haloalkane is based on  $\text{S}_{\text{N}}1$  mechanism in solvents with a strong polarity (for example, ethanol containing water).

**Read the given passage carefully and give the answer of the following questions:**

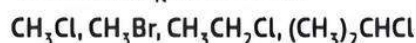
- (i) Which alkyl halide from the following pair is chiral and undergoes faster  $\text{S}_{\text{N}}2$  reaction?



- (ii) Give reason why ethyl iodide undergoes  $\text{S}_{\text{N}}2$  reaction.
- (iii) Why are  $\text{S}_{\text{N}}1$  reactions accompanied by racemisation in optically active alkyl halides?

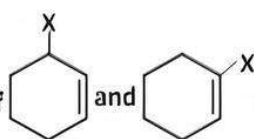
OR

Why do the  $\text{C}-\text{Cl}$  bond length in chlorobenzene is shorter than in  $\text{CH}_3\text{Cl}$ ? Also, arrange the following halides in the order of increasing  $\text{S}_{\text{N}}2$  reactivity:



### Very Short Answer Type Questions

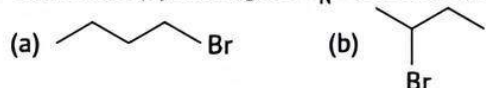
- Q 8.** Write the structure of an isomer of compound  $\text{C}_4\text{H}_9\text{Br}$  which is most reactive towards  $\text{S}_{\text{N}}1$  reaction.

- Q 9.** Out of , which is an example of allylic halide?

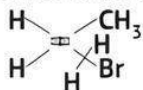


### Short Answer Type-I Questions

- Q 10. Which alkyl halide from the following pair is  
(i) chiral and (ii) undergoes  $S_N2$  reaction faster?



- Q 11. (i) Write the IUPAC name of the following:



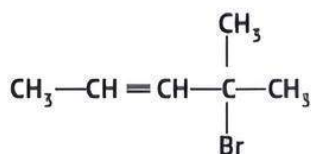
- (ii) Among the isomers of pentane ( $C_5H_{12}$ ), write the one which on photochemical chlorination yields a single monochloride.

- Q 12. Draw the structures of the following organic halogen compounds:

- (i) 4-tert-butyl-3-iodoheptane  
(ii) 4-bromo-3-methylpent-2-ene

### Short Answer Type-II Questions

- Q 13. (i) Write equation for preparation of 1-iodobutane from 1-chlorobutane.  
(ii) Out of 2-bromopentane, 2-bromo-2-methylbutane and 1-bromopentane, which compound is most reactive towards elimination reaction and why?  
(iii) Give IUPAC name of



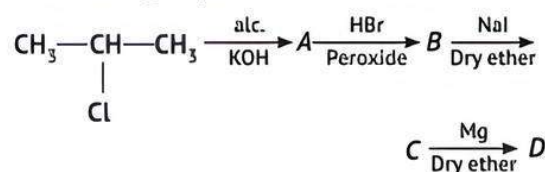
- Q 14. Give reasons for the following:

- (i) The presence of  $-\text{NO}_2$  group at *ortho* or *para* position increases the reactivity of haloarenes towards nucleophilic substitution reactions.  
(ii) *p*-dichlorobenzene has higher melting point than that of *ortho* or *meta* isomer.  
(iii) Thionyl chloride method is preferred for preparing alkyl chloride from alcohols.

- Q 15. (i) Out of  $(\text{CH}_3)_3\text{C}-\text{Br}$  and  $(\text{CH}_3)_3\text{C}-\text{I}$ , which one is more reactive towards  $S_N1$  and why?  
(ii) Write the product formed when *p*-nitrochlorobenzene is heated with aqueous  $\text{NaOH}$  at 443 K followed by acidification.  
(iii) Why *dextro* and *laevo*-rotatory isomers of butan-2-ol are difficult to separate by fractional distillation?

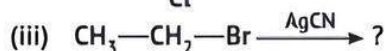
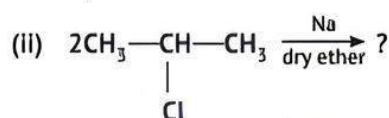
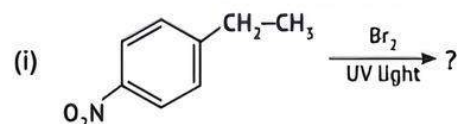
### Long Answer Type Questions

- Q 16. (i) Write the structural formula of A, B, C and D in the following sequence of reaction.



- (ii) Illustrate Sandmeyer's reaction with the help of a suitable example.  
(iii) A compound is formed by the substitution of two chlorine atoms for two hydrogen atoms in propane. Write the structures of the possible isomers. Give the IUPAC name of the isomer which can exhibit enantiomerism.

- Q 17. (a) Write the major product (s) in the following:



- (b) Account for the following:

- (i) The  $\text{C}-\text{Cl}$  bond length in chlorobenzene is shorter than that in  $\text{CH}_3-\text{Cl}$ .  
(ii) Chloroform is stored in closed dark brown bottles.