CHAPTER

10

Haloalkanes and Haloarenes

10.1 Classification

10.2 Nomenclature

10.3 Nature of C—*X* Bond

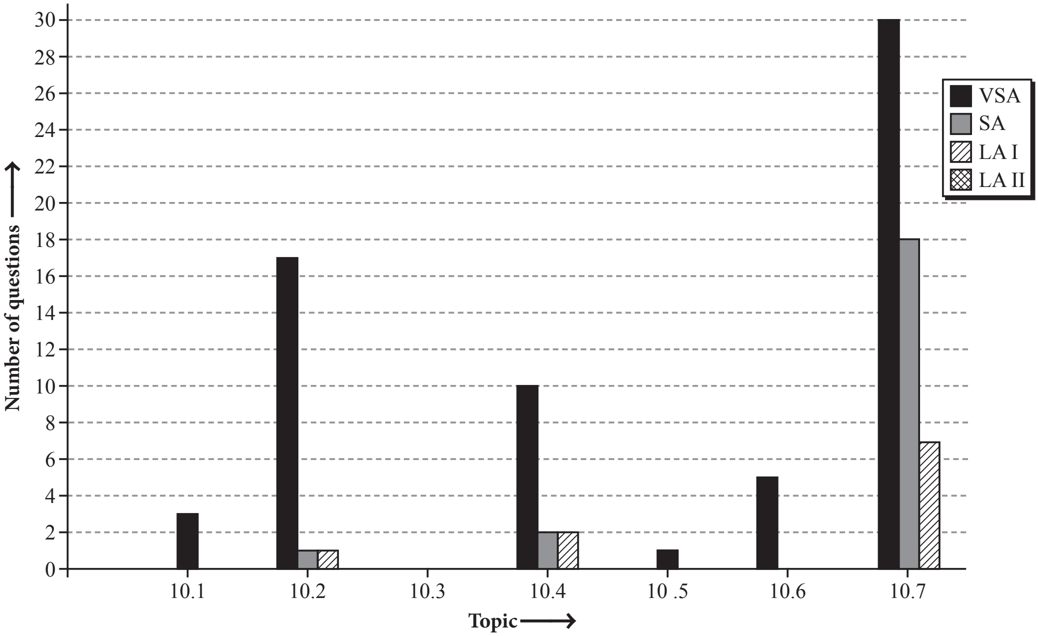
10.4 Methods of Preparation of Haloalkones

10.5 Methods of Preparation of Haloarenes

10.6 Physical Properties

10.7 Chemical Reactions

Topicwise Analysis of Last 10 Years' CBSE Board Questions (2020-2011)

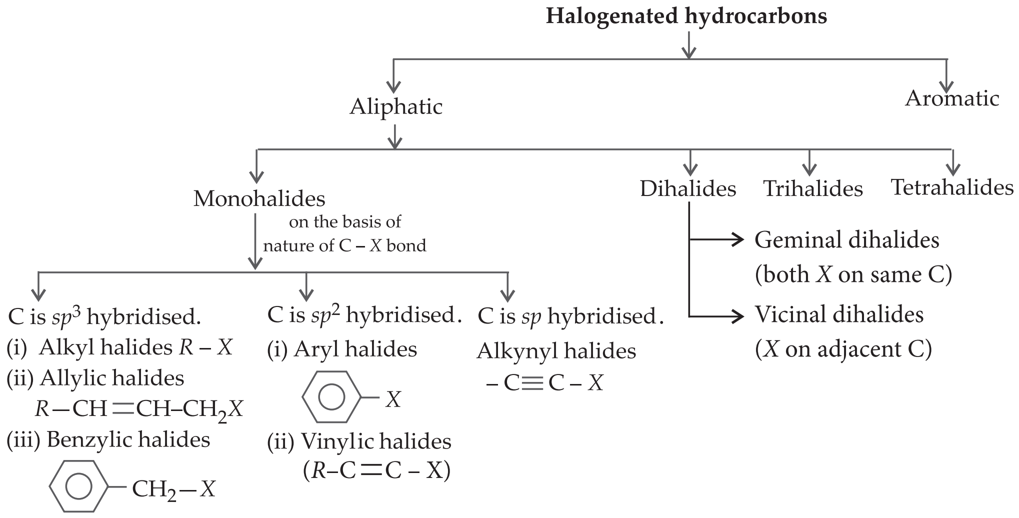


- Maximum total weightage is of *Chemical Reactions.*
- Maximum VSA type questions were asked from *Chemical Reactions.*
- Maximum SA and LA I type questions were asked from *Chemical Reactions.*

QUICK RECAP

- **Haloalkanes and haloarenes :** The replacement at hydrogen atom(s) in a hydrocarbon, aliphatic or aromatic, by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene) respectively.

Classification :



HALOALKANES

Alkyl halides : General formula is RX, where R = alkyl group.

General methods of preparation :

▶ **From alcohols :** Alkyl halides can be prepared from alcohols in a number of ways :

– **Action of hydrogen halides :**

$$R\text{–}OH \begin{cases} \xrightarrow{\text{HCl/anhyd. ZnCl}_2} RCl + H_2O \\ \xrightarrow[\text{or KBr + conc. H}_2\text{SO}_4\text{ reflux}]{\text{HBr/H}_2\text{SO}_4\text{ reflux}} R\text{–}Br + H_2O \\ \xrightarrow[\text{or KI + H}_3\text{PO}_4\text{ reflux}]{\text{HI reflux}} R\text{–}I + H_2O \end{cases}$$

- Order of reactivity of halogen acids towards the above reaction is :

  HI > HBr > HCl

- Order of reactivity of different alcohols towards the above reaction is :

  tertiary > secondary > primary

– **Action of phosphorus halides :**

$$R\text{–}OH \begin{cases} \xrightarrow{PCl_5} R\text{–}Cl + POCl_3 + HCl \\ \xrightarrow{PCl_3} R\text{–}Cl + H_3PO_3 \\ \xrightarrow[(P + Br_2)]{PBr_3} R\text{–}Br + H_3PO_3 \\ \xrightarrow[(P + I_2)]{PI_3} R\text{–}I + H_3PO_3 \end{cases}$$

– **Action of thionyl chloride (Darzen's process) :**

$$R\text{—}OH + SOCl_2 \xrightarrow{\text{Pyridine}} R\text{—}Cl + SO_2\uparrow + HCl\uparrow$$

▶ **Halogenation of alkanes :**

$$R\text{—}H + X_2 \xrightarrow[\text{or } 250 - 400\ ^\circ\text{C}]{h\upsilon} RX + HX$$

– Abstraction of hydrogen for a particular halogen follows the order

allylic > 3° > 2° > 1° > CH_4

– Reactivity of halogens for the above reaction follows the order :

$F_2 > Cl_2 > Br_2 > I_2$

▶ **Halide exchange method :**

$$R\text{—}Cl + NaI \xrightarrow{\text{dry acetone}} R\text{—}I + NaCl$$

This is known as *Finkelstein reaction.*

– Fluoroalkanes can also be prepared by halide exchange method by reacting alkyl chloride with inorganic fluorides. This is known as *Swart's reaction.*

$$2CH_3CH_2Cl + \underset{\text{Mercurous fluoride}}{Hg_2F_2} \longrightarrow 2CH_3CH_2F + \underset{\text{Mercurous chloride}}{Hg_2Cl_2}$$

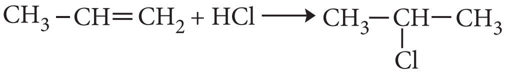
▶ **Action of hydrogen halides on ethers :**

$$R\text{—}O\text{—}R + 2HX \longrightarrow 2R - X + H_2O$$

▶ **Addition of hydrogen halides to alkene :**

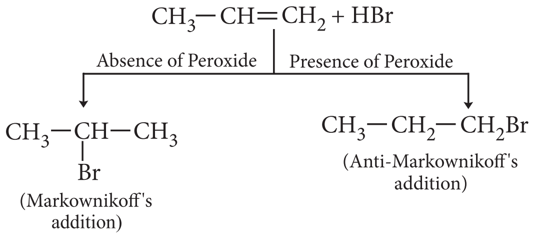
Alkenes add on a molecule of hydrogen halide to form alkyl halide.

$$>C=C< + HX \longrightarrow -\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{X}{\overset{|}{\underset{|}{C}}}-$$



$$CH_3-CH{=}CH_2 + HCl \longrightarrow CH_3-\underset{\displaystyle Cl}{\underset{|}{C}}H-CH_3$$

- Reaction follows electrophilic addition mechanism and takes place as per Markownikoff's rule. However, in presence of peroxide, addition of HBr takes place as per anti-Markownikoff's rule.



Anti-Markownikoff's rule is also known as *Peroxide effect* or *Kharasch effect*. HCl and HI do not show peroxide effect.

Physical properties :

- Alkyl halides being polar in nature are insoluble in water as they cannot break H-bonding already existing in water.
- They have higher melting and boiling points, than those of the hydrocarbons of comparable molecular mass. For the same alkyl group boiling point follows the order as :

  $R—I > R—Br > R—Cl > R—F$
- Decreasing order of boiling points among the isomeric alkyl halides follows the order : 1° > 2° > 3° alkyl halides
- Decreasing order of density among the alkyl halides is $RI > RBr > RCl > RF$.

  For alkyl iodide decreasing order of density is as follows :

  $CH_3I > CH_3CH_2I > CH_3CH_2CH_2I$.
- Bond strength of C—X bond follows the order

  $CH_3—F > CH_3—Cl > CH_3—Br > CH_3—I$

  i.e., bond strength of C—X bond decreases as the size of halogen atoms increases.
- Correct stability order of RX is as follows :

  $R—F > R—Cl > R—Br > R—I$

Chemical properties :

- **Nucleophilic substitution reactions :** The reactions in which a stronger nucleophile displaces a weaker nucleophile are called nucleophilic substitution reactions. Better the leaving group, more facile is the nucleophilic substitution reaction.
- **S_N1 and S_N2 mechanisms :** The nucleophilic substitution can proceed via S_N1 mechanism or S_N2 mechanism.

Unimolecular (S_N1)	Bimolecular (S_N2)
It is first order reaction.	It is second order reaction.
Generally carried out in polar protic solvents like water, alcohol and acetic acid.	Carried out in polar aprotic solvents like acetone, DMSO, acetonitrile or DMF.
Takes place in two steps through carbocation as the intermediate.	Takes place in one step through transition state.
Rate of reaction : 3° > 2° > 1° > CH_3 halides (fastest) (slowest) Greater the stability of carbocation, faster will be the reaction.	Rate of reaction : CH_3 > 1° > 2° > 3° halides (fastest) (slowest) Less the steric hindrance in transition state, faster will be the reaction.
Tends to proceed with weak nucleophiles, *e.g.*, CH_3OH, H_2O, CH_3CH_2OH, etc.	Tends to proceed with strong nucleophiles, *e.g.*, CH_3O^-, CN^-, OH^-, etc.
Both retention and inversion of configuration takes place.	Inversion of configuration takes place (Walden inversion).

- Primary allylic and primary benzylic halides show higher reactivity in S_N1 reactions than other primary alkyl halides due to the greater stabilisation of allylic and benzylic carbocation intermediates by resonance.
- Vinylic and aryl halides are unreactive in nucleophilic substitution reactions. This is because of double bond character of C — X bond due to resonance.

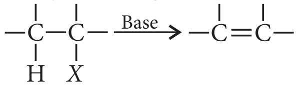
Optical isomerism/Enantiomerism :

- Optical isomer is known as *dextrorotatory isomer* (latin : *dexter* means right) (*d*-form or +ve) if it rotates the plane polarised light to the right (clockwise) and *laevorotatory* *isomer* (latin : *laevo* means left) (*l*-form or –ve) if it rotates the plane polarised light to the left (anticlockwise).

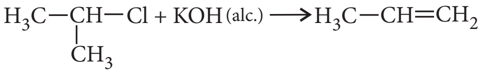
- An equimolar mixture of the *d*-form and *l*-form will be optically inactive and is called *racemic mixture* (or *dl- form or* (±)*-mixture*).
- The process of conversion of an enantiomer into racemic mixture is known as *racemisation.*
- **Chirality :** The compound is said to have chirality if the central carbon atom is attached to four different groups and this centre is called *chiral* (*asymmetric*) *centre* or *stereogenic centre* or *stereocentre*.
- **Achirality :** The compound is said to have achirality if the central carbon atom have atleast two identical groups and this centre is called *achiral* (*symmetric*).
- If molecule has a plane of symmetry it is *achiral* (*not chiral*) and if molecule has no plane of symmetry it is *chiral.*
- **Enantiomers/*d*- and *l*-isomers :** They are the optical isomers which are non-superimposable mirror images (or dissymmetric).
- **Diastereomers :** They are the optical isomers which are not mirror images of each other. They have different physical properties and magnitude of specific rotation.
- **Meso compounds :** These compounds have two or more even number of chiral carbon atoms and have an internal plane of symmetry. They are optically inactive due to internal compensation.

Elimination reactions:

- **Dehydrohalogenation :**



$$-\underset{H}{\overset{|}{C}}-\underset{X}{\overset{|}{C}}- \xrightarrow{Base} -\overset{|}{C}=\overset{|}{C}-$$

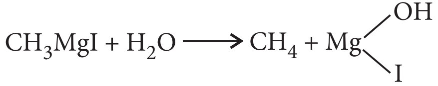


$$H_3C-\underset{CH_3}{CH}-Cl + KOH\,(alc.) \longrightarrow H_3C-CH=CH_2$$

Reaction with metals:

- **Reaction with Mg metal :**

$$CH_3I + Mg \xrightarrow{Ether} CH_3MgI$$



$$CH_3MgI + H_2O \longrightarrow CH_4 + Mg\begin{matrix} OH \\ I \end{matrix}$$

- **Wurtz reaction :**

$$R\boxed{-X + 2Na + X-}R \xrightarrow{Ether} R-R + 2NaX$$

Reduction of alkyl halides :

$$2R-X + 2[H] \xrightarrow{Zn/HCl} 2R-H + ZnX_2$$

HALOARENES

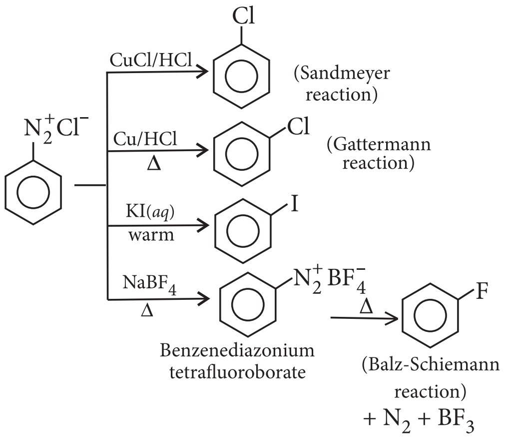
Aryl halides : General formula is Ar*X*, where Ar = aryl group.

General methods of preparation :

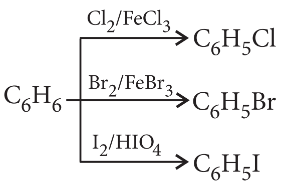
- **By Raschig process :**

$$2C_6H_6 + 2HCl + O_2 \xrightarrow[500\ K]{CuCl_2} 2C_6H_5Cl + 2H_2O$$

- **From benzenediazonium salt :**



- **By direct halogenation of benzene :**



$$C_6H_6 \xrightarrow{Cl_2/FeCl_3} C_6H_5Cl$$

$$C_6H_6 \xrightarrow{Br_2/FeBr_3} C_6H_5Br$$

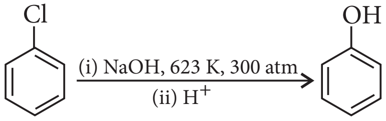
$$C_6H_6 \xrightarrow{I_2/HIO_4} C_6H_5I$$

Physical properties :

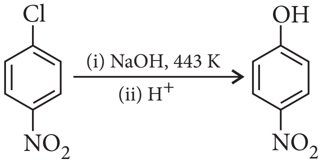
- Aryl halides are colourless stable liquids with pleasant odour.
- These are insoluble in water but readily miscible with organic solvents.
- Most of them are steam volatile, heavier than water.
- Their boiling points are higher than corresponding alkyl halides. The boiling points rise gradually from fluoro to iodo compounds.

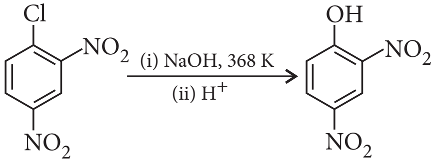
Chemical properties :

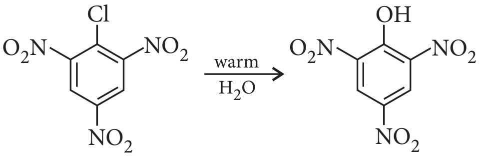
Nucleophilic substitution reactions :



The presence of an electron withdrawing group (—NO_2) at *ortho*- and *para*-positions increases the reactivity of haloarenes.

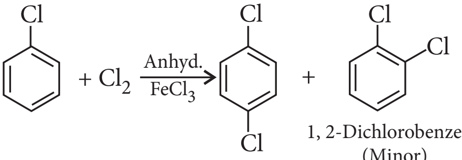






Electrophilic substitution reactions :

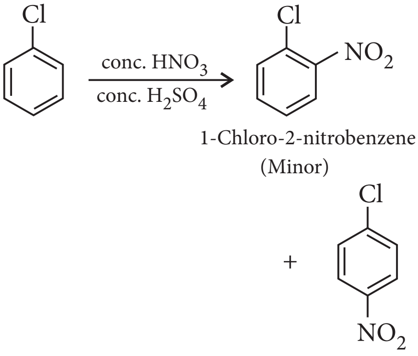
– Halogenation :



1, 4-Dichlorobenzene (Major)

1, 2-Dichlorobenzene (Minor)

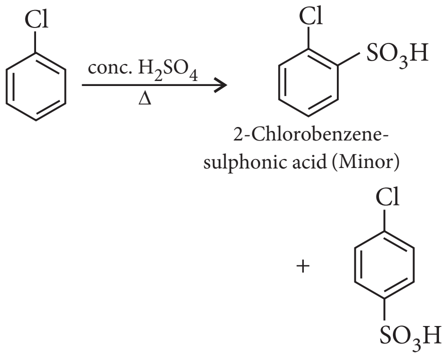
– Nitration :



1-Chloro-2-nitrobenzene (Minor)

1-Chloro-4-nitrobenzene (Major)

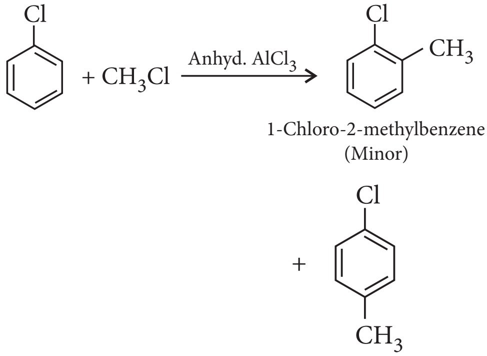
– Sulphonation :



2-Chlorobenzene-sulphonic acid (Minor)

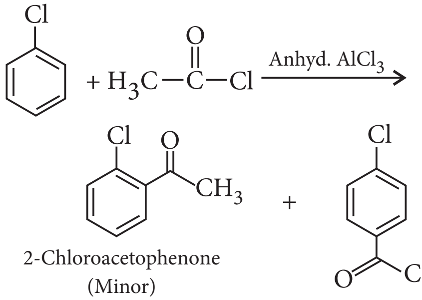
4-Chlorobenzene-sulphonic acid (Major)

– Friedal–Crafts reaction :



1-Chloro-2-methylbenzene (Minor)

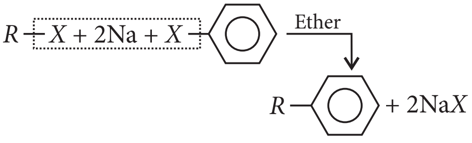
1-Chloro-4-methylbenzene (Major)



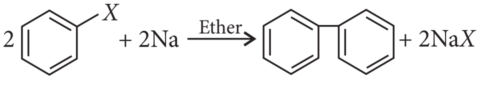
2-Chloroacetophenone (Minor)

4-Chloroacetophenone (Major)

Wurtz Fittig reaction :



Fittig reaction :



Diphenyl

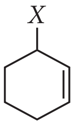
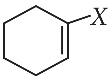
Uses and environmental effects of some important compounds :

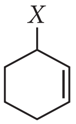
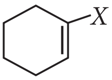
Compounds	Uses	Effects
Chloroform ($CHCl_3$)	– Its major use is in the production of Freon refrigerant, R-22. – It is used as a solvent for resins, rubbers, oils and fats, alkaloids, iodine and many other substances. – In the past, it was extensively used as anaesthetic for surgery but now it is rarely used as it causes liver damage. – It is used in preparation of chloretone (drug) and chloropicrin (insecticide). – It is used to preserve anatomical species.	– It is oxidised to poisonous gas, carbonyl chloride, known as *phosgene*. $2CHCl_3 + O_2 \xrightarrow{\text{Light}} 2COCl_2 + 2HCl$ Phosgene gas causes liver and kidney damage. – Inhaling chloroform vapours depresses the central nervous system, causes dizziness, fatigue and headache.
Iodoform (CHI_3)	– It was earlier used as an antiseptic in dressing of wounds due to liberation of iodine. Due to its objectionable smell, it has been replaced by other formulations containing iodine. – It is used as methylating agent in organic synthesis.	– It has strong smell.
Carbon tetrachloride (CCl_4)	– It is used in the manufacture of refrigerants and propellants for aerosol cans. – It is used as feed stock in the synthesis of CFC's and other chemicals.	– Exposure CCl_4 causes liver cancer. – It causes Diziness, light headness, nausea and vomiting, which can cause permanent damage to nerve cells. – It depletes the ozone layer.
Freons	– They are used as refrigerants, blowing agents, propellants in medical applications and degreasing solvent.	– Freons cause disruption of ozone layer by initiating radical chain reactions in stratosphere. – This anthropogenic compound is a green-house gas and its effect is more than CO_2.
DDT	– In 1940, it was used as a pesticide.	– It is a persistent organic pollutant, strongly absorbed by soil. – It is lipophilic so has a high potential to bioaccumulate. – It may be directly genotoxic but may also induce enzymes to produce other genotoxic intermediates and DNA adducts.

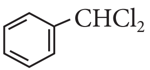
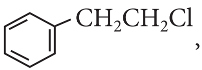
Previous Years' CBSE Board Questions

10.1 Classification

VSA (1 mark)

1. Out of  and , which is an example of allylic halide? *(AI 2017)*

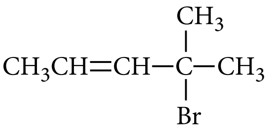
2. Out of  and , which is an example of vinylic halide? *(AI 2017)*

3. Out of  and , which is an example of a benzylic halide? *(AI 2017)*

10.2 Nomenclature

VSA (1 mark)

4. Write the IUPAC name of



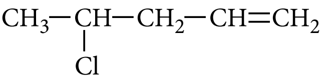
$$CH_3CH{=}CH{-}\underset{Br}{\overset{CH_3}{C}}{-}CH_3$$ *(AI 2019, Delhi 2013)*

5. Write the structure of 1-bromo-4-chlorobut-2-ene. *(Delhi 2017)*

6. Write the structure of 3-bromo-2-methylprop-1-ene. *(Delhi 2017)*

7. Draw the structure of 2-bromopentane. *(Delhi 2014C)*

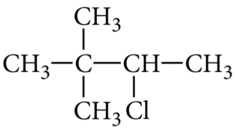
8. Write the IUPAC name of



$$CH_3{-}\underset{Cl}{CH}{-}CH_2{-}CH{=}CH_2$$ *(Delhi 2013)*

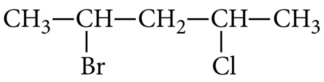
9. Write the IUPAC name of $(CH_3)_2CHCH(Cl)CH_3$. *(Delhi 2013)*

10. Write the IUPAC name of the following compound:



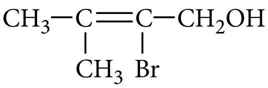
$$CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\underset{Cl}{CH}{-}CH_3$$ *(AI 2013)*

11. Write the IUPAC name of the following compound:



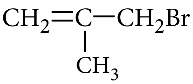
$$CH_3{-}\underset{Br}{CH}{-}CH_2{-}\underset{Cl}{CH}{-}CH_3$$ *(AI 2013)*

12. Write the IUPAC name of the following:



$$CH_3{-}\underset{CH_3}{C}{=}\underset{Br}{C}{-}CH_2OH$$ *(AI 2013C, 2012C, Foreign 2011)*

13. Give the IUPAC name of the following compound:



$$CH_2{=}\underset{CH_3}{C}{-}CH_2Br$$ *(Delhi 2012, AI 2011)*

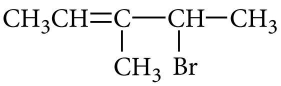
14. Write the IUPAC name of the following compound:
$(CH_3)_3CCH_2Br$ *(Delhi 2011)*

15. Write the IUPAC name of the following compound:
$CH_2{=}CHCH_2Br$ *(AI 2011)*

16. Write the structure of the following compound:
1, 4-dibromobut-2-ene *(Delhi 2011C)*

17. Write the structure of the following compound:
2-(2-Bromophenyl)butane *(Delhi 2011C)*

18. Give IUPAC name of the following organic compound:



$$CH_3CH{=}\underset{CH_3}{C}{-}\underset{Br}{CH}{-}CH_3$$ *(Delhi 2011C)*

19. Write the structure of the following compound:
2-(2-chlorophenyl)-1-iodooctane *(AI 2011C)*

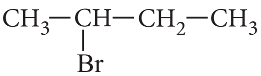
20. Write the structure of the following compound:
1-bromo-4-*sec*-butyl-2-methylbenzene *(AI 2011C)*

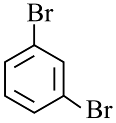
SA (2 marks)

21. Write the IUPAC names of the following compounds :
(i) $CH_2{=}CHCH_2Br$ (ii) $(CCl_3)_3CCl$
(AI 2014C)

LA I (3 marks)

22. Give the IUPAC names of the following compounds :

(i)

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

(ii)


(iii) $CH_2{=}CH-CH_2-Cl$ *(AI 2015C)*

10.4 Methods of Preparation of Haloalkanes

VSA (1 mark)

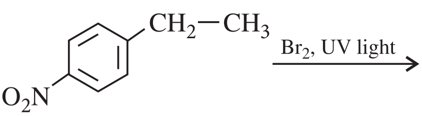
23. How can you convert the following?
But-1-ene to 1-iodobutane *(1/3, 2020)*

24. Give reason for the following:
Thionyl chloride method is preferred for preparing alkyl chloride from alcohols.
(1/3, AI 2019)

25. Write equation for preparation of 1-iodobutane from 1-chlorobutane. *(1/3, AI 2019)*

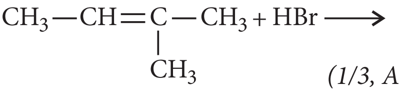
26. How do you convert:
Propene to 1-iodopropane? *(1/3, AI 2016)*

27. Write the major product in the following :



(1/3, AI 2016)

28. Write the structure of the major product in the following reaction :

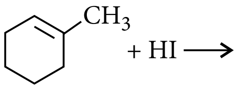

$CH_3-CH=\underset{\underset{CH_3}{|}}{C}-CH_3+HBr\longrightarrow$

(1/3, AI 2015)

29. A hydrocarbon C_5H_{12} gives only one monochlorination product. Identify the hydrocarbon. *(Delhi 2013C)*

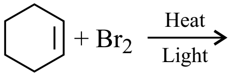
30. What happens when bromine attacks $CH_2{=}CH-CH_2-C{\equiv}CH$? *(AI 2012)*

31. Draw the structure of major monohalogen product formed in the following reaction :



(Delhi 2012C)

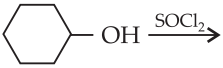
32. Draw the structure of major monohalogen product in the following reaction :

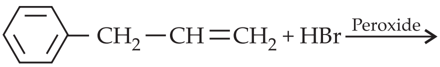


(Delhi 2012C)

SA (2 marks)

33. Draw the structure of major monohalo product in each of the following reactions :

(i)


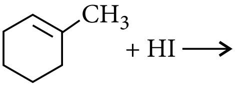
(ii)


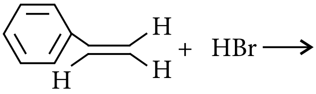
(Delhi 2014)

34. Write the mechanism of the following reaction:
$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$
(AI 2014)

LA I (3 marks)

35. Complete the following reaction equations :

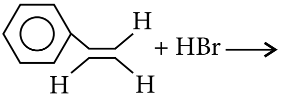
(i)


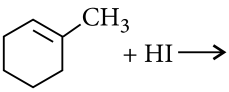
(ii)


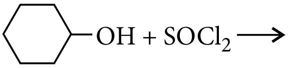
(iii) $CH_3CH_2CH{=}CH_2 + HBr \longrightarrow$

(Foreign 2011)

36. Complete the equations for the following reactions :

(i)


(ii)


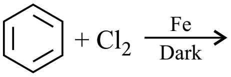
(iii)


(Delhi 2011C)

10.5 Methods of Preparation of Haloarenes

VSA **(1 mark)**

37. Draw the structure of major monohalo product in the following reaction :



(Delhi 2012C)

10.6 Physical Properties

VSA **(1 mark)**

38. Give reason for the following :
p-dichlorobenzene has higher melting point than that of *ortho* or *meta* isomer.
(1/3, AI 2019, 1/2, Delhi 2013)

39. Explain the following :
Alkyl halides, though polar, are immiscible with water.
(1/2, AI 2017C, 1/3, Foreign 2015, Delhi 2013C, AI 2013C, 2012C)

40. Explain why the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.
(1/3, Delhi 2016, 2013C, 2011C)

41. Give reason :
n-Butyl bromide has higher boiling point than *t*-butyl bromide. *(1/3, Delhi 2015)*

42. Answer the following :
Haloalkanes easily dissolve in organic solvents, why? *(1/3, Delhi 2011)*

10.7 Chemical Reactions

VSA **(1 mark)**

Read the given passage and answer the questions number (43 - 47) that follow.

The substitution reaction of alkyl halide mainly occurs by S_N1 or S_N2 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 S_N1 reactions are governed by the stability of carbocation whereas for S_N2 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. *(2020)*

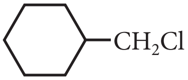
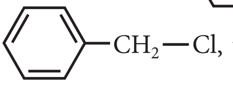
43. Predict the stereochemistry of the product formed if an optically active alkyl halide undergoes substitution reaction by S_N1 mechanism.

44. Name the instrument used for measuring the angle by which the plane polarised light is rotated.

45. Predict the major product formed when 2-bromopentane reacts with alcoholic KOH.

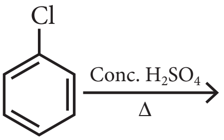
46. Give one use of CHI_3.

47. Write the structures of the products formed when anisole is treated with HI.

48. Out of  and , which will react faster in S_N1 reaction with OH^-? *(One word, 2020)*

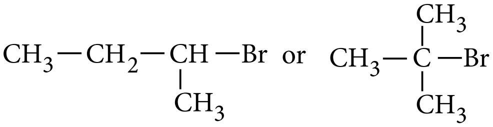
49. Racemisation occurs in
(a) S_N2 reaction
(b) S_N1 reaction
(c) Neither S_N2 nor S_N1 reactions
(d) S_N2 reaction as well as S_N1 reaction.
(2020)

50. Write the major product(s) of the following reaction :



(1/3, 2020)

51. Which alkyl halide from the following pair would you expect to react more rapidly by an S_N2 mechanism?



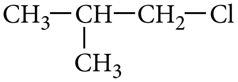
$$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-Br \quad \text{or} \quad CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-Br$$

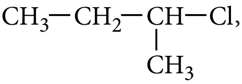
(AI 2019)

52. Give reason for the following:
The presence of $-NO_2$ group at *ortho* and *para* position increases the reactivity of haloarenes towards nucleophilic substitution reactions. *(1/3, AI 2019)*

53. Out of 2-bromopentane, 2-bromo-2-methyl butane, and 1-bromopentane, which compound is most reactive towards elimination reaction and why? *(1/3, AI 2019)*

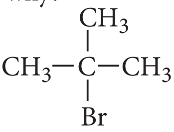
54. Out of chlorobenzene and benzyl chloride, which one gets easily hydrolysed by aqueous NaOH and why? *(2018)*

55. Out of 
$CH_3-CH(CH_3)-CH_2-Cl$ and


$CH_3-CH_2-CH(CH_3)-Cl$, which is more reactive towards S_N1 reaction and why? *(Delhi 2016)*

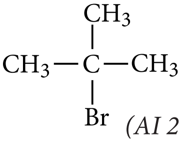
56. Write the structure of an isomer of compound C_4H_9Br which is most reactive towards S_N1 reaction. *(AI 2016)*

57. Which would undergo S_N2 reaction faster in the following pair and why?

CH_3-CH_2-Br and 
$CH_3-C(CH_3)(Br)-CH_3$

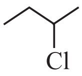
(Delhi 2015)

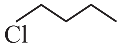
58. Which would undergo S_N1 reaction faster in the following pair :

CH_3-CH_2-Br and 
$CH_3-C(CH_3)(Br)-CH_3$ *(AI 2015)*

59. Which would undergo S_N2 reaction faster in the following pair and why?
CH_3-CH_2-Br and CH_3-CH_2-I *(Foreign 2015)*

60. Identify the chiral molecule in the following pair:





(AI 2014)

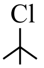
61. Which halogen compound in each of the following pairs will react faster in S_N2 reaction:
(i) CH_3Br or CH_3I
(ii) $(CH_3)_3CCl$ or CH_3Cl
(AI 2014, Delhi 2014C)

62. What happens when CH_3-Br is treated with KCN? *(Delhi 2013)*

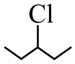
63. What happens when ethyl chloride is treated with aqueous KOH? *(Delhi 2013)*

64. Why is (±)-butan-2-ol is optically inactive? *(1/2, Delhi 2013)*

65. Which compound in the following pair undergoes faster S_N1 reaction?



and



(Delhi 2013, 2013C, 2012C)

66. How may methyl bromide be preferentially converted to methyl isocyanide? *(Delhi 2013C)*

67. Account for the following :
Grignard's reagents should be prepared under anhydrous conditions. *(1/3, Delhi 2013C, 1/3, AI 2012C)*

68. Predict the order of reactivity of four isomeric bromobutanes in S_N1 reaction. *(Delhi 2012C)*

69. Predict the order of reactivity of the following compounds in S_N1 reaction.
$C_6H_5CH_2Br$, $C_6H_5C(CH_3)(C_6H_5)Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$ *(Delhi 2012C)*

70. Give a chemical test to distinguish between C_2H_5Br and C_6H_5Br. *(AI 2012C)*

71. Which will react faster in S_N2 displacement, 1-bromopentane or 2-bromopentane and why? *(Foreign 2011)*

72. Which will react faster in S_N1 displacement reaction :
1-Bromobutane or 2-bromobutane and why? *(Foreign 2011)*

SA (2 marks)

73. Write the mechanism of the following S_N1 reaction

$$(CH_3)_3\,C-Br \xrightarrow{\text{Aq. NaOH}} (CH_3)_3\,C-OH + NaBr$$

(2/3, 2020)

74. Give reasons :

(i) C—Cl bond length in chlorobenzene is shorter than C—Cl bond length in CH_3—Cl.

(ii) S_N1 reactions are accompanied by racemization in optically active alkyl halides. *(2/3, Delhi 2016)*

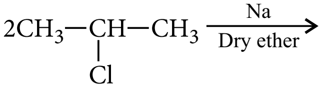
75. How do you convert?

(i) Chlorobenzene to biphenyl

(ii) 2-Bromobutane to but-2-ene

(2/3, AI 2016)

76. Write the major product(s) in the following :

(i) 

$2CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3 \xrightarrow[\text{Dry ether}]{Na}$

(ii) $CH_3-CH_2-Br \xrightarrow{AgCN}$ *(2/3, AI 2016)*

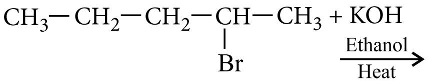
77. Give reasons:

(i) Racemic mixture is optically inactive.

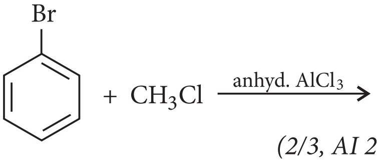
(ii) The presence of nitro group (—NO_2) at *o*/*p* positions increases the reactivity of haloarenes towards nucleophilic substitution reactions.

(2/3, Delhi 2015)

78. Write the structure of the major product in each of the following reactions :

(i) 

$CH_3-CH_2-CH_2-\underset{\underset{Br}{|}}{CH}-CH_3 + KOH \xrightarrow[\text{Heat}]{\text{Ethanol}}$

(ii) 

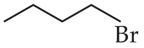
(2/3, AI 2015)

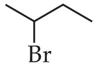
79. (i) Why is butan-1-ol optically inactive but butan-2-ol is optically active?

(ii) Although chlorine is an electron withdrawing group, yet it is *ortho*-, *para*-directing in electrophilic aromatic substitution reactions. Why?

(2/3, Foreign 2015, Delhi 2012)

80. (i) Which alkyl halide from the following pair is chiral and undergoes faster S_N2 reaction?

(a) 

(b) 

(ii) Out of S_N1 and S_N2, which reaction occurs with

(a) inversion of configuration

(b) racemisation? *(2/3, Delhi 2014)*

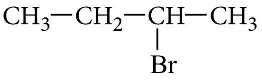
81. Write chemical equations when

(i) ethyl chloride is treated with aqueous KOH.

(ii) chlorobenzene is treated with CH_3COCl in presence of anhydrous $AlCl_3$.

(Foreign 2014)

82. (i) Which alkyl halide from the following pairs would you expect to react more rapidly by an S_N2 mechanism and why?



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

$CH_3-CH_2-CH_2-CH_2-Br$

(ii) Racemisation occurs in S_N1 reactions. Why? *(Foreign 2014)*

83. Write chemical equations when

(i) methyl chloride is treated with $AgNO_2$.

(ii) bromobenzene is treated with CH_3Cl in the presence of anhydrous $AlCl_3$.

(Foreign 2014)

84. What are ambident nucleophiles? Explain with an example. *(2/3, AI 2014C)*

85. Chlorobenzene is extremely less reactive towards a nucleophilic substitution reaction. Give two reasons for the same. *(Delhi 2013)*

86. Account for the following:

(i) The C—Cl bond length in chlorobenzene is shorter than that in CH_3—Cl.

(ii) Chloroform is stored in closed dark brown bottles. *(Delhi 2013)*

87. Give reasons for the following :

(i) Ethyl iodide undergoes S_N2 reaction faster than ethyl bromide.

(ii) C—X bond length in halobenzene is smaller than C—X bond length in CH_3—X. *(2/3, AI 2013)*

88. Haloalkanes undergo nucleophilic substitution whereas haloarenes undergo electrophilic substitution. Explain. *(2/3, Delhi 2012C)*

89. Answer the following :

(i) What is known as a racemic mixture? Give an example.

(ii) Of the two bromo derivatives, $C_6H_5CH(CH_3)Br$ and $C_6H_5CH(C_6H_5)Br$, which one is more reactive in S_N1 substitution reaction and why?

(2/3, Delhi 2011)

90. Write the mechanism of the following reaction :

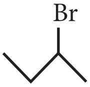
$$n\text{-BuBr} + \text{KCN} \xrightarrow{\text{EtOH, } H_2O} n\text{-BuCN}$$

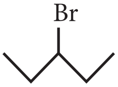
(1/3, Delhi 2011C)

LA I (3 marks)

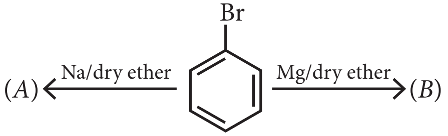
91. (i) Write the structure of major alkene formed by β-elimination of 2, 2, 3-trimethyl-3-bromopentane with sodium ethoxide in ethanol.

(ii) Which one of the compounds in the following pairs is chiral?





(iii) Identify (*A*) and (*B*) in the following :



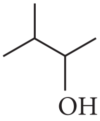
(2020)

92. (i) Out of $(CH_3)_3C-Br$ and $(CH_3)_3C-I$, which one is more reactive towards S_N1 and why?

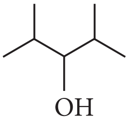
(ii) Write the product formed when *p*-nitrochlorobenzene is heated with aqueous NaOH at 443 K followed by acidification.

(iii) Why *dextro* and *laevo*-rotatory isomers of Butan-2-ol are difficult to separate by fractional distillation? *(Delhi 2019)*

93. (a) Identify the chiral molecule in the following pair :



and



(i) (ii)

(b) Write the structure of the product when chlorobenzene is treated with methyl chloride in the presence of sodium metal and dry ether.

(c) Write the structure of the alkene formed by dehydrohalogenation of 1-bromo-1-methylcyclohexane with alcoholic KOH. *(2018)*

94. Following compounds are given to you:
2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane

(i) Write the compound which is most reactive towards S_N2 reaction.

(ii) Write the compound which is optically active.

(iii) Write the compound which is most reactive towards β-elimination reaction.

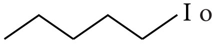
(Delhi 2017)

95. Answer the following questions:

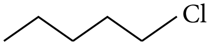
(i) What is meant by chirality of a compound? Give an example.

(ii) Which one of the following compounds is more easily hydrolysed by KOH and why?
$CH_3CHClCH_2CH_3$ or $CH_3CH_2CH_2Cl$

(iii) Which one undergoes S_N2 substitution reaction faster and why?



or



(AI 2012)

96. Rearrange the compounds of each of the following sets in order of reactivity towards S_N2 displacement:

(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane,3-bromo-2-methylbutane

(iii) 1-Bromobutane, 1-Bromo-2, 2-dimethyl propane, 1-Bromo-2-methylbutane

(AI 2011)

97. (a) Write a chemical test to distinguish between:

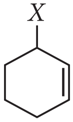
(i) Chlorobenzene and benzyl chloride

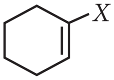
(ii) Chloroform and carbon tetrachloride

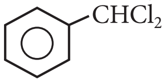
(b) Why is methyl chloride hydrolysed more easily than chlorobenzene?

(Delhi 2011C)

Detailed Solutions

1.  is an allylic halide as the halogen is attached to sp^3-hybridised carbon atom which is next to carbon-carbon double bond.

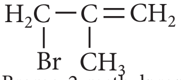
2.  is a vinylic halide as the halogen is attached to sp^2-hybridised carbon.

3.  is a benzylic halide as the halide group is attached to sp^3-hybridised carbon atom next to aromatic ring.

4. 4-Bromo-4-methylpent-2-ene

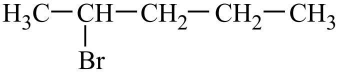
5. $Cl-\overset{4}{CH_2}-\overset{3}{CH}=\overset{2}{CH}-\overset{1}{CH_2}-Br$

1-Bromo-4-chlorobut-2-ene

6. 

$$\underset{\overset{|}{Br}}{H_2C}-\underset{\overset{|}{CH_3}}{C}=CH_2$$

3-Bromo-2-methylprop-1-ene

7. 

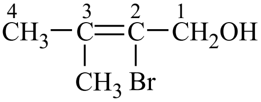
$$H_3C-\underset{\overset{|}{Br}}{CH}-CH_2-CH_2-CH_3$$

8. 4-Chloropent-1-ene

9. 2-Chloro-3-methylbutane

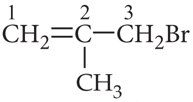
10. 3-Chloro-2,2-dimethylbutane

11. 2-Bromo-4-chloropentane

12. 

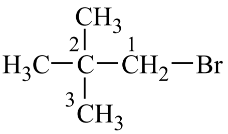
$$\overset{4}{CH_3}-\underset{\overset{|}{CH_3}}{\overset{3}{C}}=\underset{\overset{|}{Br}}{\overset{2}{C}}-\overset{1}{CH_2OH}$$

2-Bromo-3-methylbut-2-en-1-ol

13. 

$$\overset{1}{CH_2}=\underset{\overset{|}{CH_3}}{\overset{2}{C}}-\overset{3}{CH_2Br}$$

3-Bromo-2-methylpropene

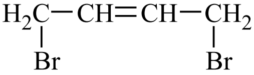
14. 

$$H_3C-\underset{\overset{|}{{}^{3}CH_3}}{\overset{\overset{CH_3}{2|}}{C}}-\overset{1}{CH_2}-Br$$

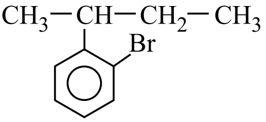
1-Bromo-2,2-dimethylpropane

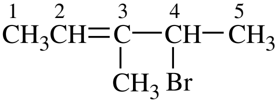
15. $\overset{1}{CH_2}=\overset{2}{CH}\overset{3}{CH_2}Br$

3-Bromoprop-1-ene

16. 

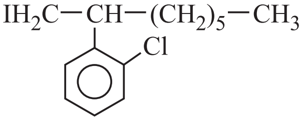
$$\underset{\overset{|}{Br}}{H_2C}-CH=CH-\underset{\overset{|}{Br}}{CH_2}$$

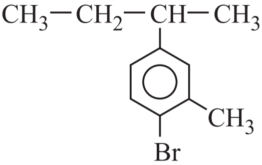
17. 

18. 

$$\overset{1}{CH_3}\overset{2}{CH}=\underset{\overset{|}{CH_3}}{\overset{3}{C}}-\underset{\overset{|}{Br}}{\overset{4}{CH}}-\overset{5}{CH_3}$$

4-Bromo-3-methylpent-2-ene

19. 

20. 

21. (i) *Refer to answer 15.*

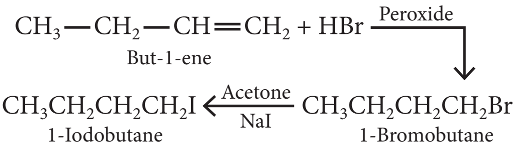
(ii) 2-(Trichloromethyl)-1,1,1,2,3,3,3-heptachloropropane

22. (i) 2-Bromobutane

(ii) 1,3-Dibromobenzene

(iii) 3-Chloropropene

23.



$$\underset{\text{But-1-ene}}{CH_3-CH_2-CH=CH_2} + HBr \xrightarrow{\text{Peroxide}}$$

$$\underset{\text{1-Iodobutane}}{CH_3CH_2CH_2CH_2I} \xleftarrow[\text{NaI}]{\text{Acetone}} \underset{\text{1-Bromobutane}}{CH_3CH_2CH_2CH_2Br}$$

24. Thionyl chloride is preferred because in this reaction alkyl halide is formed along with gases SO_2 and HCl. These two gaseous products are escapable, hence the reaction gives pure alkyl halides.

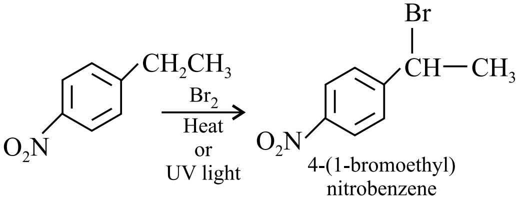
25. Alkyl iodides are often prepared by the reaction of alkyl chlorides/bromides with NaI in dry acetone. This is known as Finkelstein reaction.

$$CH_3CH_2CH_2CH_2Cl \xrightarrow[\text{Acetone}]{\text{NaI}} CH_3CH_2CH_2CH_2I$$

26. $\underset{\text{Propene}}{CH_3CH=CH_2} + HBr \xrightarrow{\text{Peroxide}} CH_3CH_2CH_2Br$

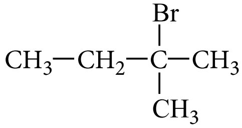
$$\xrightarrow[\text{Acetone}]{\text{NaI}} \underset{\text{1-Iodopropane}}{CH_3-CH_2-CH_2I}$$

27.



4-(1-bromoethyl) nitrobenzene

28.

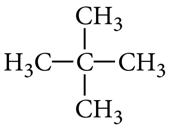


$$CH_3-CH_2-\overset{\overset{\large Br}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-CH_3$$

2-Bromo-2-methylbutane

(Markovnikov's addition)

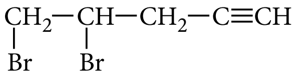
29.



$$H_3C-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-CH_3$$

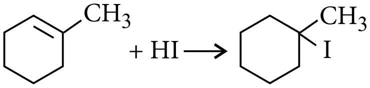
2,2-Dimethylpropane

30.

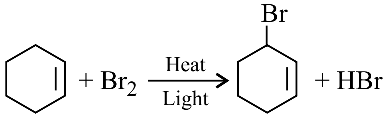


$$\underset{\underset{\large Br}{|}}{CH_2}-\underset{\underset{\large Br}{|}}{CH}-CH_2-C\equiv CH$$

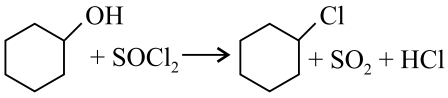
31.



32.

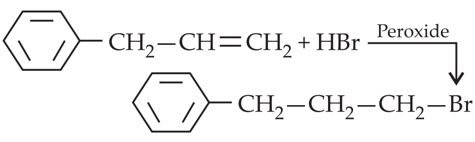


33. (i)

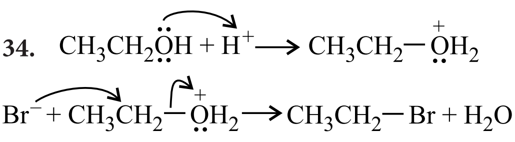


Chlorocyclohexane

(ii)



34.

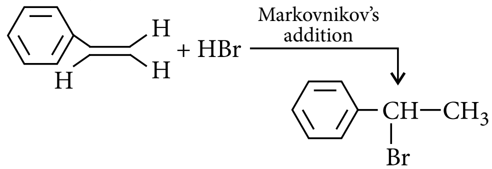


$$CH_3CH_2\ddot{O}H + H^+ \longrightarrow CH_3CH_2-\overset{+}{\ddot{O}}H_2$$

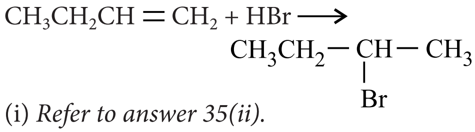
$$Br^- + CH_3CH_2-\overset{+}{\ddot{O}}H_2 \longrightarrow CH_3CH_2-Br + H_2O$$

35. (i) *Refer to answer 31.*

(ii)



(iii)



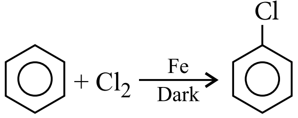
$$CH_3CH_2CH=CH_2 + HBr \longrightarrow CH_3CH_2-\underset{\underset{\large Br}{|}}{CH}-CH_3$$

36. (i) *Refer to answer 35(ii).*

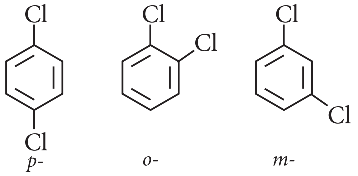
(ii) *Refer to answer 31.*

(iii) *Refer to answer 33(i).*

37.



38. *p*-Dichlorobenzene has higher melting point than those of *o*-and *m*-isomers because it is more symmetrical and packing is better in solid form. Hence, it has stronger intermolecular forces of attraction than *o*-and *m*-isomers.



p- *o*- *m*-

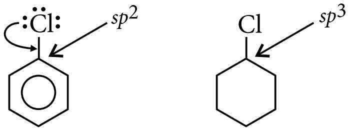
39. Alkyl halides are polar but are insoluble in water because energy required to break the intermolecular H – bond among water molecules is much higher than energy released by water halide interaction.

40. There are two reasons :

(i) In case of chlorobenzene, carbon to which chlorine is attached is sp^2-hybridised and is more electronegative than the corresponding carbon in cyclohexyl chloride which is sp^3-hybridised. So the net dipole moment is lower in chlorobenzene.

(ii) In chlorobenzene C—Cl bond has some double bond character so its bond length is smaller.

Hence dipole moment is smaller than cyclohexyl chloride which has a longer C—Cl single bond.



Chlorobenzene Cyclohexyl chloride

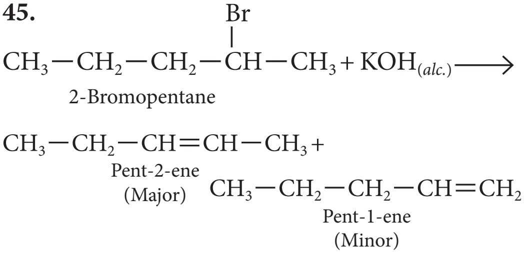
41. *n*-Butyl bromide, being a straight chain molecule have strong intermolecular forces whereas *t*-butyl bromide being a branched chain molecule have weaker intermolecular forces due to smaller surface area.
Hence, boiling point of *n*-butyl bromide is higher than that of *t*-butyl bromide.

42. Haloalkanes dissolve in organic solvents because the intermolecular attractions between haloalkanes and organic solvent molecules have the same strength as in the separate haloalkanes and solvent molecules.

43. Stereochemical aspects of nucleophilic substitution reaction in S_N1 proceeds with racemisation.

44. Polarimeter is used for measuring the angle by which the plane polarised light is rotated.

45.

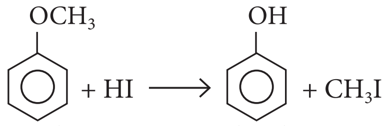


$$\underset{\text{2-Bromopentane}}{CH_3-CH_2-CH_2-\overset{\overset{\displaystyle Br}{|}}{C}H-CH_3} + KOH_{(alc.)} \longrightarrow$$

$$\underset{\substack{\text{Pent-2-ene}\\\text{(Major)}}}{CH_3-CH_2-CH{=}CH-CH_3} + \underset{\substack{\text{Pent-1-ene}\\\text{(Minor)}}}{CH_3-CH_2-CH_2-CH{=}CH_2}$$

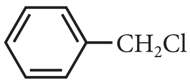
46. Iodoform (CHI_3) is used as a mild antiseptic.

47.



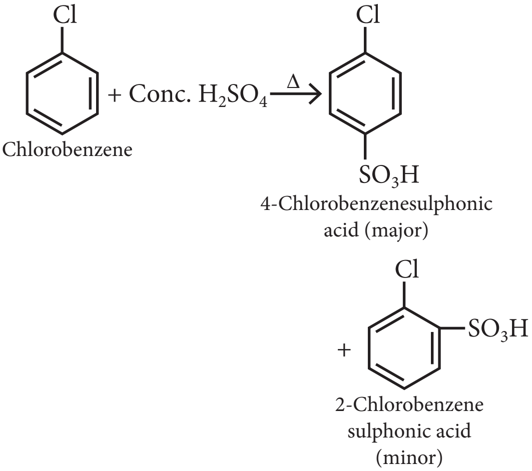
Anisole Phenol

48.



49. **(b)** : S_N1 reactions are accompanied by racemisation.

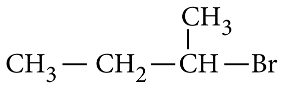
50.



Chlorobenzene

4-Chlorobenzenesulphonic acid (major)

2-Chlorobenzene sulphonic acid (minor)



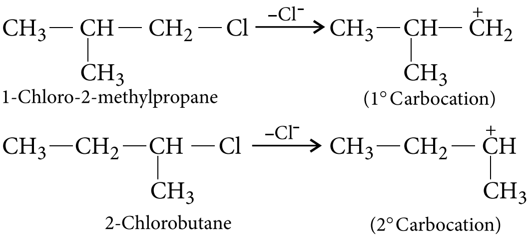
51. 2° alkyl halide *i.e.*, $CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}H-Br$ would undergo S_N2 reaction faster than compared to 3° alkyl halide *i.e.*, $(CH_3)_3CBr$ due to formation of less sterically hindered transition state.

52. The presence of nitro group at *o*-and *p*-positions withdraws electrons from the benzene ring and thus, facilitates the attack of the nucleophile on haloarenes. The carbanion thus formed is further stabilised by resonance.

53. 2-Bromo-2-methylbutane will give fastest elimination reaction because it is a *tert*-halide and *tert*-halides prefer elimination reaction.

54. Benzyl chloride gets easily hydrolysed by aq. NaOH due to formation of stable benzyl carbocation. But due to partial double bond character of C—Cl bond in chlorobenzene, it does not hydrolyse.

55. The S_N1 reaction proceeds through carbocation formation thus, the compound which forms more stable carbocation will be more reactive.

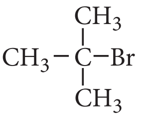


$$\underset{\text{1-Chloro-2-methylpropane}}{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}H-CH_2-Cl} \xrightarrow{-Cl^-} \underset{\text{(1° Carbocation)}}{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}H-\overset{+}{C}H_2}$$

$$\underset{\text{2-Chlorobutane}}{CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{C}H-Cl} \xrightarrow{-Cl^-} \underset{\text{(2° Carbocation)}}{CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{\overset{+}{C}}H}$$

As, 2° carbocation is more stable than 1° carbocation thus, 2-chlorobutane is more reactive towards S_N1 reaction.

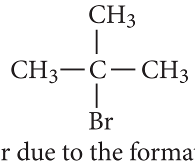
56.



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

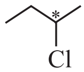
tert-butyl bromide

57. CH_3-CH_2-Br would undergo S_N2 reaction faster due to formation of less sterically hindered transition state.



58. $CH_3-\underset{\underset{\displaystyle Br}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$ will undergo S_N1 reaction faster due to the formation of stable carbocation.

59. Since I^- is a better leaving group than Br^-, thus, CH_3CH_2I undergoes S_N2 reaction faster than CH_3CH_2Br.

60.  is a chiral molecule.

61. (i) CH_3I will give faster S_N2 reaction.
(ii) CH_3Cl will give faster S_N2 reaction.

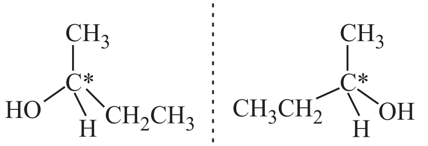
62. CH_3CN is formed by nucleophilic substitution reaction.

$$CH_3Br + KCN \rightarrow CH_3CN + KBr$$

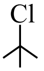
63. When ethyl chloride is treated with aqueous KOH, ethanol is formed,

$$CH_3CH_2Cl + KOH_{(aq)} \longrightarrow CH_3CH_2OH + KCl$$

64. (±)-Butan-2-ol is optically inactive because the two enantiomeric forms are present in equal amounts therefore, it does not rotate the plane of polarized light and is optically inactive.



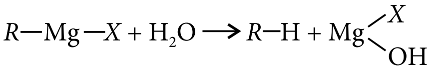
50% – (+) Butan-2-ol 50% – (–) Butan-2-ol

65. Tertiary halide  reacts faster than the secondary halide because of the greater stability of *tert*-carbocation.

66. AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as main product.

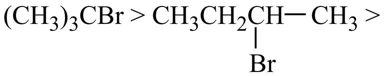
$$\underset{\text{Methyl bromide}}{CH_3Br} + AgCN \longrightarrow \underset{\text{Methyl isocyanide}}{CH_3N \equiv C} + AgBr$$

67. Grignard reagents react with water to form alkanes.



$$R{-}Mg{-}X + H_2O \longrightarrow R{-}H + Mg\begin{matrix}X\\OH\end{matrix}$$

So, they must be prepared under anhydrous conditions.

68. 

$$(CH_3)_3CBr > CH_3CH_2\underset{\substack{|\\Br}}{CH}{-}CH_3 >$$

$$(CH_3)_2CHCH_2Br > CH_3CH_2CH_2CH_2Br$$

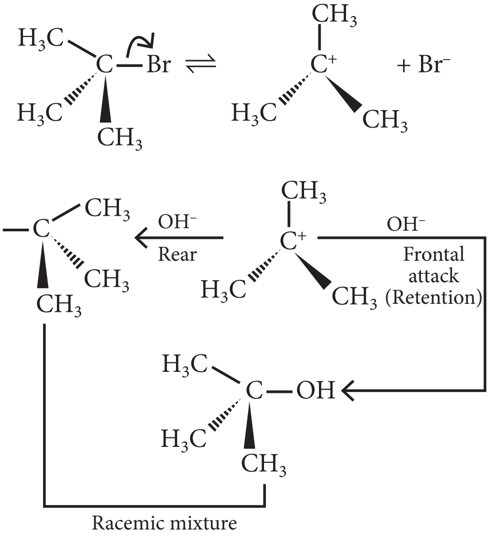
69. $C_6H_5C(CH_3)(C_6H_5)Br > C_6H_5CH(C_6H_5)Br > C_6H_5CH(CH_3)Br > C_6H_5CH_2Br$

70. C_2H_5Br reacts with $AgNO_3$ to give yellow precipitate of AgBr while C_6H_5Br will not.

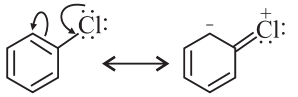
71. 1-Bromopentane is a primary alkyl halide, hence reacts faster in S_N2 displacement than secondary halide 2-bromopentane due to less steric hindrance in 1° alkyl halide than 2° alkyl halide.

72. 2-Bromobutane will react faster in S_N1 displacement reaction because it will form more stable secondary carbocation intermediate.

73. **(a)**

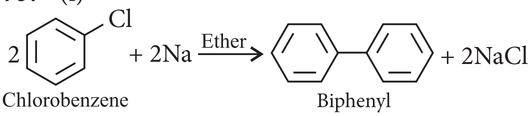


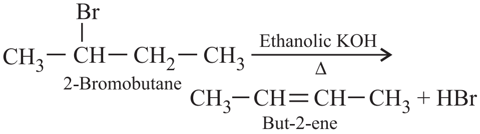
74. (i) In halobenzene C—X bond has partial double bond character due to resonance while $CH_3{-}X$ bond is single bond.
Thus, bond length of C—X bond in halobenzene is smaller than that in $CH_3{-}X$.



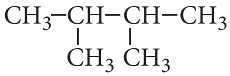
(ii) In S_N1 reaction carbocation intermediate is formed which is a planar molecule so, an incoming nucleophile can attack from either side and a equimolar mixture of two components are formed and resulting mixture is optically inactive.

75. (i)



(ii) 

$$CH_3-\underset{\text{2-Bromobutane}}{\overset{Br}{\overset{|}{C}H}}-CH_2-CH_3 \xrightarrow[\Delta]{\text{Ethanolic KOH}} \underset{\text{But-2-ene}}{CH_3-CH=CH-CH_3} + HBr$$

76. (i) 

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

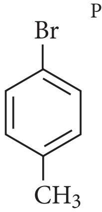
(ii) CH_3CH_2NC

77. (i) Racemic mixture contains equal amount of *d*- and *l*-forms, hence rotation due to one enantiomer is cancelled by another.

(ii) *Refer to answer 52.*

78. (i) $CH_3-CH_2-CH=CH-CH_3$

Pent-2-ene (Saytzeff rule)

(ii) 

4-Bromotoluene

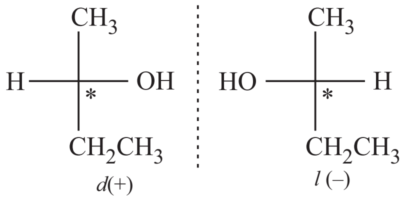
(Friedel—Crafts alkylation)

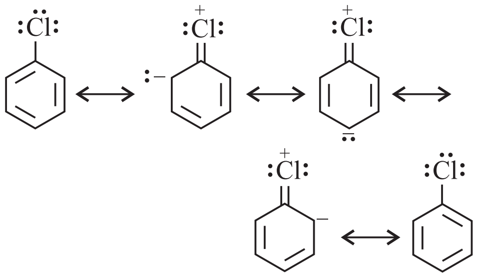
79. (i) Butan-1-ol is achrial, *i.e.*, does not have chiral 'C' atom which is attached to four different groups, therefore, it is optically inactive.

$$CH_3-CH_2-CH_2-CH_2OH$$

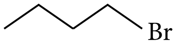
Butan-1-ol
(Optically inactive)
(No chiral carbon)

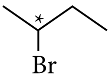
Butan-2-ol is chiral, *i.e.*, has chiral 'C' atom, attached to four different groups.



(ii) 

Although Cl is electron withdrawing (-*I* effect) but still *o*- and *p*-directing as due to +*R* effect, electron density is maximum at *o*- and *p*-positions.

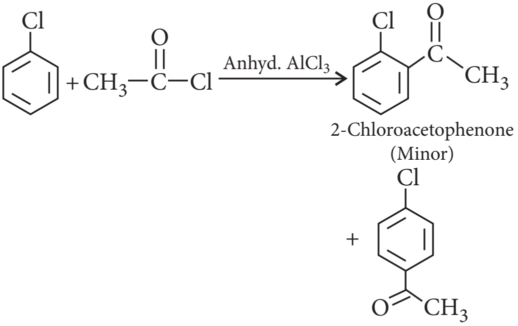
80. (i) (a)  undergoes faster S_N2 reaction.

(b)  is chiral.

(ii) (a) S_N2 reaction occurs with inversion of configuration.

(b) S_N1 reaction occurs with racemisation.

81. (i) *Refer to answer 63.*

(ii) 

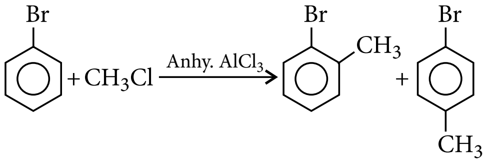
2-Chloroacetophenone
(Minor)

4-Chloroacetophenone
(Major)

82. (i) 1-Bromobutane is 1° alkyl halide while 2-bromobutane is 2° alkyl halide. Due to steric hindrance in 2° alkyl halides, 1° alkyl halide will react faster than 2° alkyl halide in S_N2 reaction.

(ii) *Refer to answer 74(ii).*

83. (i) $CH_3Cl + AgNO_2 \longrightarrow CH_3NO_2 + AgCl$

(ii) 

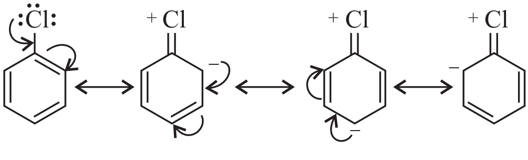
84. A nucleophile which can attack from more than one centres, is known as ambident nucleophile, *e.g.*, $^{-}\ddot{C}\equiv N\text{:}$ cyanide ion

$R-X + AgCN \longrightarrow R-NC + AgX$

$R-X + KCN \longrightarrow R-CN + KX$

85. Haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions due to the following reasons.

(i) Resonance effect : In haloarenes the electron pairs on halogen atom are in conjugation with π-electrons of the ring and the following resonating structures are possible.



C—Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, are less reactive towards nucleophilic substitution reaction.

(ii) In halorenes, halogen is attached to sp^2-hybridised carbon while in haloalkanes, halogen is attached to sp^3-hybridised carbon.

86. (i) *Refer to answer 74(i).*

(ii) Chloroform when exposed to air and sunlight changes to phosgene which is a poisonous gas.

$$CHCl_3 + \frac{1}{2}O_2 \rightarrow \underset{\text{Phosgene}}{COCl_2} + HCl$$

Thus, it is kept in dark coloured bottles to prevent the oxidation.

87. (i) *Refer to answer 59.*

(ii) *Refer to answer 74(i).*

88. In haloarenes –ve charge gets localised on arenes using resonance, therefore they undergo electrophilic substitution.

Haloalkanes have electrophilic carbon centre due to polarity of $C \rightarrow X$ bond.

89. (i) An equimolar mixture of a pair of enantiomers is called racemic mixture. A racemic mixture is optically inactive due to external compensation.

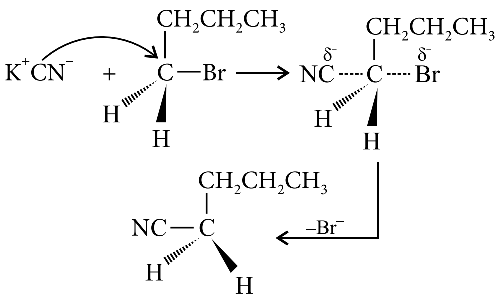
Example :

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

Butan-2-ol (50% mixture of *d*- and *l*-form)

(ii) Of the two bromo derivatives, $C_6H_5CH(C_6H_5)Br$ is more reactive than $C_6H_5CH(CH_3)Br$ for S_N1 reaction because its carbocation is resonance stabilised by two phenyl groups.

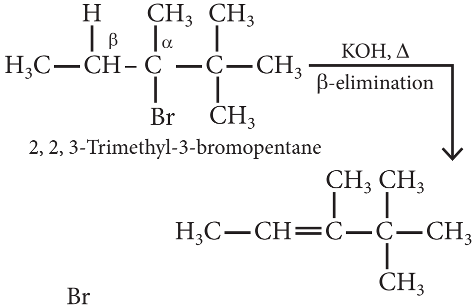
90. Normal butyl bromide will give S_N2 reaction :



n-Butyl cyanide

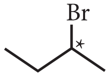
91.

(i)

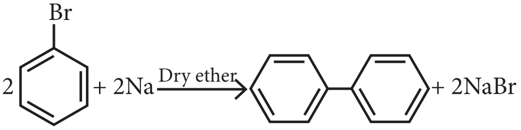


2, 2, 3-Trimethyl-3-bromopentane

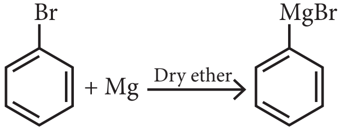
(ii)



(iii)



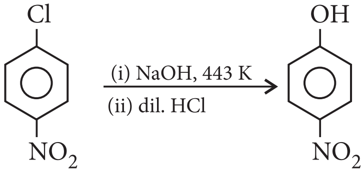
Biphenyl
(*A*)



Phenylmagnesium bromide
(*B*)

92. (i) $(CH_3)_3C—I$ is more reactive because C—I bond has the minimum bond dissociation enthalpy.

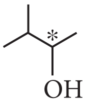
(ii)



4-Nitrophenol

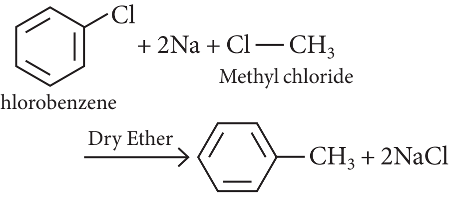
(iii) *Dextro* and *laevo*-rotatory isomers of butan-2-ol are difficult to separate by fractional distillation because they have almost same boiling point.

93. (a)



(i)

(b)

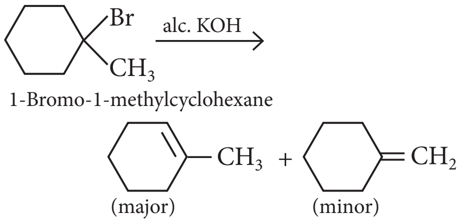


Chlorobenzene

Methyl chloride

Toluene

(c)

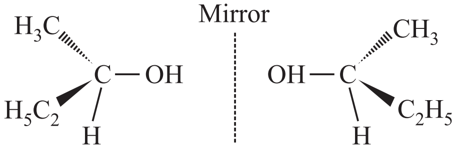


94. (i)1-Bromopentane

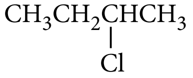
(ii) 2-Bromopentane

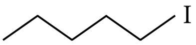
(iii) 2-Bromo-2-methylbutane

95. (i) The molecules which are not superimposable on their mirror images are called chiral molecules. The property of non-superimposability of a structure on its mirror image is called chirality.

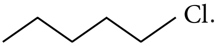


Non superimposable mirror image of 2-butanol

(ii) 
$\underset{\textstyle Cl}{CH_3CH_2CHCH_3}$ hydrolyses easily with KOH because it is secondary halide.

(iii) As iodide is a better leaving group because of its large size, therefore, 

undergoes S_N2 reaction faster than



96. (i) 1-Bromopentane > 2-Bromopentane > 2-Bromo-2-methylbutane.

(ii) 1-Bromo-3-methylbutane > 3-Bromo-2-methylbutane > 2-Bromo-2-methylbutane

(iii) 1-Bromobutane > 1-Bromo-2-methylbutane > 1-Bromo-2,2-dimethylpropane

97. (a) (i) Benzyl chloride gives white precipiate with $AgNO_3$ solution while chlorobenzene does not.

(ii) $CHCl_3$ with aniline in presence of alc. KOH gives foul smelling isocyanides whereas CCl_4 does not.

(b) CH_3Cl is hydrolysed easily than C_6H_5Cl as chlorobenzene has partial double bond character between C—Cl bond which is difficult to break.