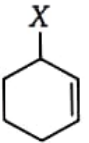
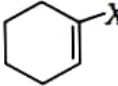
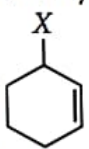
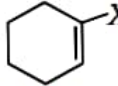
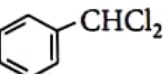
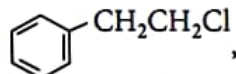


Previous Years' CBSE Board Questions

10.1 Classification

VSA (1 mark)

- Out of  and , which is an example of allylic halide? (AI 2017)
- Out of  and , which is an example of vinylic halide? (AI 2017)
- Out of  and , which is an example of a benzylic halide? (AI 2017)

10.2 Nomenclature

VSA (1 mark)

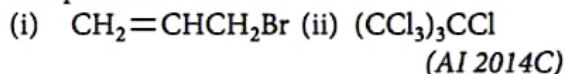
- Write the structure of 1-bromo-4-chlorobut-2-ene. (Delhi 2017)
- Write the structure of 3-bromo-2-methylprop-1-ene. (Delhi 2017)
- Draw the structure of 2-bromopentane. (Delhi 2014C)
- Write the IUPAC name of $\text{CH}_3-\underset{\text{Cl}}{\text{CH}}-\text{CH}_2-\text{CH}=\text{CH}_2$ (Delhi 2013)
- Write the IUPAC name of $\text{CH}_3\text{CH}=\underset{\text{Br}}{\overset{\text{CH}_3}{\text{C}}}-\text{CH}_3$ (Delhi 2013)
- Write the IUPAC name of $(\text{CH}_3)_2\text{CHCH}(\text{Cl})\text{CH}_3$. (Delhi 2013)
- Write the IUPAC name of the following compound:
 $\text{CH}_3-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-\underset{\text{Cl}}{\text{CH}}-\text{CH}_3$ (AI 2013)
- Write the IUPAC name of the following compound:
 $\text{CH}_3-\underset{\text{Br}}{\text{CH}}-\text{CH}_2-\underset{\text{Cl}}{\text{CH}}-\text{CH}_3$ (AI 2013)
- Write the IUPAC name of the following:
 $\text{CH}_3-\underset{\text{CH}_3}{\text{C}}=\underset{\text{Br}}{\text{C}}-\text{CH}_2\text{OH}$ (AI 2013C, 2012C, Foreign 2011)
- Give the IUPAC name of the following compound:
 $\text{CH}_2=\underset{\text{CH}_3}{\text{C}}-\text{CH}_2\text{Br}$ (Delhi 2012, AI 2011)
- Write the IUPAC name of the following compound:
 $(\text{CH}_3)_3\text{CCH}_2\text{Br}$ (Delhi 2011)
- Write the IUPAC name of the following compound:
 $\text{CH}_2=\text{CHCH}_2\text{Br}$ (AI 2011)
- Write the structure of the following compound:
 1, 4-dibromobut-2-ene (Delhi 2011C)
- Write the structure of the following compound:
 2-(2-Bromophenyl)butane (Delhi 2011C)
- Give IUPAC name of the following organic compound:
 $\text{CH}_3\text{CH}=\underset{\text{CH}_3}{\text{C}}-\underset{\text{Br}}{\text{CH}}-\text{CH}_3$ (Delhi 2011C)
- Write the structure of the following compound:
 2-(2-chlorophenyl)-1-iodooctane (AI 2011C)
- Write the structure of the following compound:
 1-bromo-4-sec-butyl-2-methylbenzene (AI 2011C)
- Write the structure of the compound:
 4-tert-butyl-3-iodoheptane (AI 2010C)
- Write the IUPAC name of the following compound:



23. Write the structure of the compound 1-chloro-4-ethylcyclohexane. (AI 2010C)

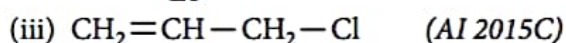
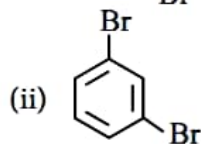
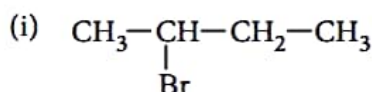
SA I (2 marks)

24. Write the IUPAC names of the following compounds:



SA II (3 marks)

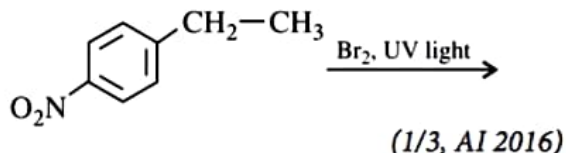
25. Give the IUPAC names of the following compounds:



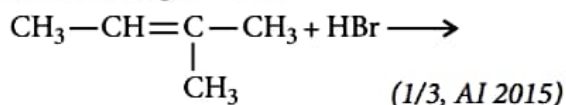
10.4 Methods of Preparation

VSA (1 mark)

26. How do you convert: Propene to 1-iodopropane? (1/3, AI 2016)
27. Write the major products in the following:

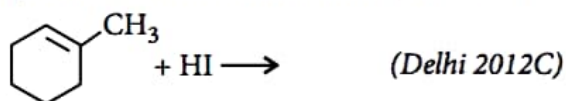


28. Write the structure of the major product in the following reaction:

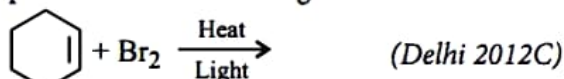


29. A hydrocarbon C_5H_{12} gives only one monochlorination product. Identify the hydrocarbon. (Delhi 2013C)

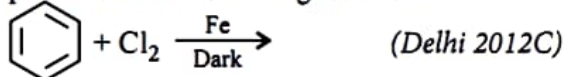
30. Draw the structure of major monohalogen product formed in the following reaction:



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



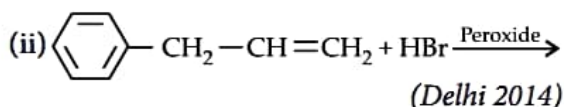
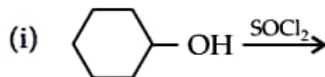
32. Draw the structure of major monohalogen product in the following reaction:



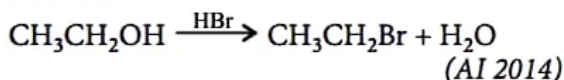
33. What happens when bromine attacks $\text{CH}_2=\text{CH}-\text{CH}_2-\text{C}\equiv\text{CH}$? (AI 2012)

SA I (2 marks)

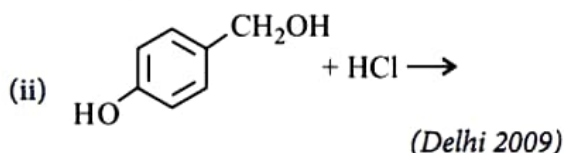
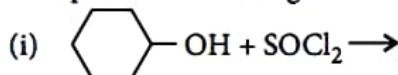
34. Draw the structure of major monohalogen product in each of the following reactions:



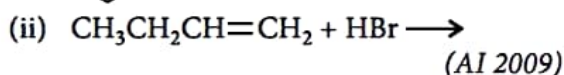
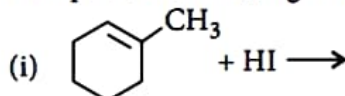
35. Write the mechanism of the following reaction:



36. Complete the following reaction equations:

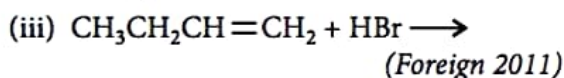
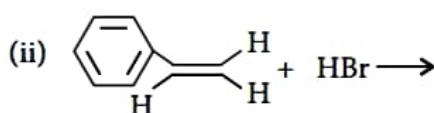
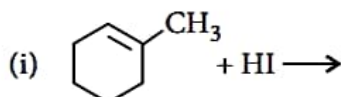


37. Complete the following reaction equations:

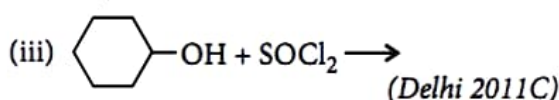
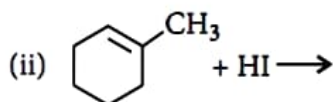
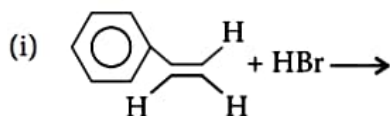


SA II (3 marks)

38. Complete the following reaction equations:



39. Complete the equations for the following reactions :



10.5 Physical Properties

VSA (1 mark)

40. Give reason :
n-Butyl bromide has higher boiling point than *t*-butyl bromide. (1/3, Delhi 2015)
41. Why are alkyl halides insoluble in water? (1/3, Foreign 2015)
42. Why does *p*-dichlorobenzene have a higher m.pt. than its *o*- and *m*-isomers? (1/2, Delhi 2013, 1/3, AI 2009C)
43. Explain the following :
 Alkyl halides, though polar, are immiscible with water. (1/3, Delhi 2013C, 1/3, AI 2010C)
44. Answer the following :
 Haloalkanes easily dissolve in organic solvents, why? (1/3, Delhi 2011)

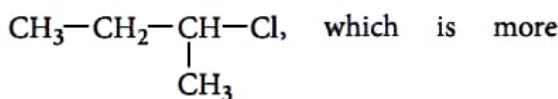
SA I (2 marks)

45. Explain why
 (i) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride? (1/3, Delhi 2016, 2013C, 2011 C, 1/2, Delhi 2010C, 1/3, AI 2010C)
 (ii) alkyl halides, though polar, are immiscible with water? (2/3, AI 2013C, 2012C)

10.6 Chemical Reactions

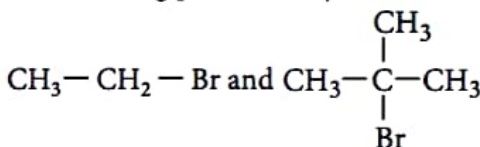
VSA (1 mark)

46. Out of chlorobenzene and benzyl chloride, which one gets easily hydrolysed by aqueous NaOH and why? (2018)
47. Out of $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{Cl}$ and



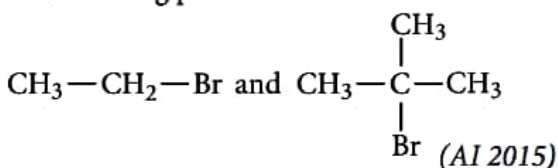
reactive towards S_N1 reaction and why? (Delhi 2016)

48. Write the structure of an isomer of compound C₄H₉Br which is most reactive towards S_N1 reaction. (AI 2016)
49. Which would undergo S_N2 reaction faster in the following pair and why?



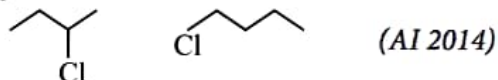
(Delhi 2015)

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



51. Which would undergo S_N2 reaction faster in the following pair and why?
 $\text{CH}_3-\text{CH}_2-\text{Br}$ and $\text{CH}_3-\text{CH}_2-\text{I}$ (Foreign 2015)

52. Identify the chiral molecule in the following pair:



53. Which halogen compound in each of the following pairs will react faster in S_N2 reaction:

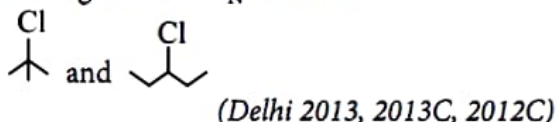
- (i) CH₃Br or CH₃I
 (ii) (CH₃)₃CCl or CH₃Cl (Delhi 2014C, AI 2014)

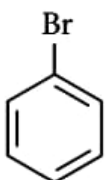
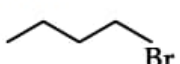
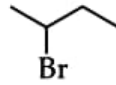
54. What happens when CH₃Br is treated with KCN? (Delhi 2013)

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

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

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



58. How may methyl bromide be preferentially converted to methyl isocyanide?
(Delhi 2013C)
59. Account for the following :
Grignard's reagents should be prepared under anhydrous conditions.
(1/3, Delhi 2013C, 1/3, AI 2012C)
60. Predict the order of reactivity of four isomeric bromobutanes in S_N1 reaction.
(Delhi 2012C)
61. Predict the order of reactivity of the following compounds in S_N1 reaction.
 $C_6H_5CH_2Br$, $C_6H_5C(CH_3)(C_6H_5)Br$,
 $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH_2CH_2Br$
(Delhi 2012C)
62. Give a chemical test to distinguish between C_2H_5Br and C_6H_5Br .
(AI 2012C)
63. Which will react faster in S_N2 displacement, 1-bromopentane or 2-bromopentane and why?
(Foreign 2011)
64. Which will react faster in S_N1 displacement reaction :
1-Bromobutane or 2-bromobutane and why?
(Foreign 2011)
65. A solution of KOH hydrolyses $CH_3CHClCH_2CH_3$ and $CH_3CH_2CH_2CH_2Cl$. Which one of these is more easily hydrolysed?
(Delhi 2010)
66. Explain the following reaction with an example:
Friedel-Crafts reaction. (1/2, Delhi 2010)
67. Why is the following occur :
Chloroform is stored in closed dark coloured bottles completely filled so that air is kept out.
(1/2, Delhi 2010C)
68. Explain why in the pair, $(CH_3)_3CCl$ and CH_3Cl , CH_3Cl will react faster in S_N2 reaction with OH^- ?
(1/3, AI 2010C)
- (ii) S_N1 reactions are accompanied by racemization in optically active alkyl halides. (2/3, Delhi 2016)
70. How do you convert?
(i) Chlorobenzene to biphenyl
(ii) 2-Bromobutane to but-2-ene
(2/3, AI 2016)
71. Write the major product(s) in the following :
(i) $2CH_3-\underset{\text{Cl}}{\underset{|}{CH}}-CH_3 \xrightarrow[\text{Dry ether}]{Na}$
(ii) $CH_3-CH_2-Br \xrightarrow{AgCN}$ (2/3, AI 2016)
72. 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)
73. Write the structure of the major product in each of the following reactions :
(i) $CH_3-CH_2-CH_2-\underset{\text{Br}}{\underset{|}{CH}}-CH_3 + KOH \xrightarrow[\text{Heat}]{\text{Ethanol}}$
(ii)  + $CH_3Cl \xrightarrow{\text{anhyd. AlCl}_3}$
(2/3, AI 2015)
74. (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)
75. (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

SA I (2 marks)

69. Give reasons :
(i) C—Cl bond length in chlorobenzene is shorter than C—Cl bond length in CH_3-Cl .

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

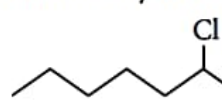
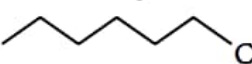
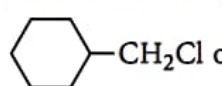
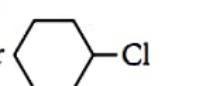
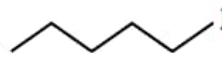
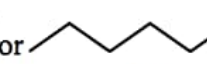
- (a) inversion of configuration
(b) racemisation? (2/3, Delhi 2014)
76. Write chemical equations when
(i) ethyl chloride is treated with aqueous KOH.
(ii) chlorobenzene is treated with CH_3COCl in presence of anhydrous AlCl_3 .
(Foreign 2014)
77. (i) Which alkyl halide from the following pairs would you expect to react more rapidly by an $\text{S}_{\text{N}}2$ mechanism and why?

$$\begin{array}{c} \text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}_3 \\ | \\ \text{Br} \end{array}$$

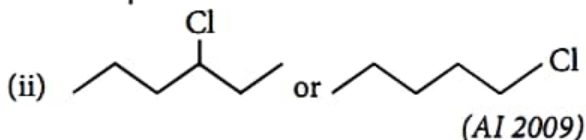
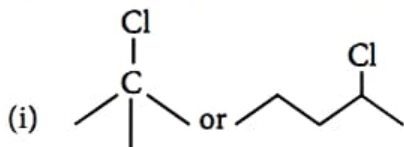
$$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Br}$$

 (ii) Racemisation occurs in $\text{S}_{\text{N}}1$ reactions. Why?
(Foreign 2014)
78. 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)
79. What are ambident nucleophiles? Explain with an example. (2/3, AI 2014C)
80. Chlorobenzene is extremely less reactive towards a nucleophilic substitution reaction. Give two reasons for the same. (Delhi 2013)
81. Account for the following:
(i) The $\text{C}-\text{Cl}$ bond length in chlorobenzene is shorter than that in CH_3-Cl .
(ii) Chloroform is stored in closed dark brown bottles. (Delhi 2013)
82. Give reasons for the following :
(i) Ethyl iodide undergoes $\text{S}_{\text{N}}2$ reaction faster than ethyl bromide.
(ii) $\text{C}-\text{X}$ bond length in halobenzene is smaller than $\text{C}-\text{X}$ bond length in CH_3-X . (2/3, AI 2013)
83. Haloalkanes undergo nucleophilic substitution whereas haloarenes undergo electrophilic substitution. Explain.
(2/3, Delhi 2012C)
84. Answer the following :
(i) What is known as a racemic mixture? Give an example.
(ii) Of the two bromo derivatives, $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$ and $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$, which one is more reactive in $\text{S}_{\text{N}}1$ substitution reaction and why?
(2/3, Delhi 2011)
85. Write the mechanism of the following reaction :

$$n\text{-BuBr} + \text{KCN} \xrightarrow{\text{EtOH}, \text{H}_2\text{O}} n\text{-BuCN}$$

(1/3, Delhi 2011C)
86. How are the following conversions carried out?
(i) Benzyl chloride to benzyl alcohol
(ii) Methyl magnesium bromide to methylpropan-2-ol. (2/3, Delhi 2010)
87. Which compound in the following couple will react faster in $\text{S}_{\text{N}}2$ displacement and why?
(i) 1-Bromopentane or 2-bromopentane
(ii) 1-Bromo-2-methylbutane or 2-bromo-2-methylbutane.
(2/3, Delhi 2010)
88. (a) Why is sulphuric acid not used during the reaction of alcohols with KI in the conversion of an alcohol to the alkyl iodide?
(b) Why are haloarenes less reactive than haloalkanes towards nucleophilic substitution reactions? (Delhi 2010C)
89. How would you account for the following :
(i) Grignard reagents are prepared strictly under anhydrous conditions?
(ii)  undergoes faster $\text{S}_{\text{N}}1$ reaction than ? (Delhi 2010C)
90. Which one in the following pairs of substances undergoes $\text{S}_{\text{N}}2$ substitution reaction faster and why?
(i)  or 
(ii)  or  (Delhi 2009)

91. Which one in the following pairs undergoes S_N1 substitution reaction faster and why?



(AI 2009)

92. Suggest a possible reason for the following observations :

- The order of reactivity of haloalkanes is $RI > RCl > RBr$.
- Neopentyl chloride $(CH_3)_3CCH_2Cl$ does not follow S_N2 mechanism.

(2/3, Delhi 2009C)

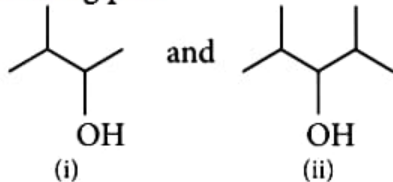
93. Give reasons for the following observations :

- Haloarenes are less reactive than haloalkanes towards nucleophilic substitution reactions.
- The treatment of alkyl chloride with aqueous KOH leads to the formation of alcohol but in the presence of alcoholic KOH, alkene is the major product.

(2/3, AI 2009C)

SA II (3 marks)

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



- Write the structure of the product when chlorobenzene is treated with methyl chloride in the presence of sodium metal and dry ether.
- Write the structure of the alkene formed by dehydrohalogenation of 1-bromo-1-methylcyclohexane with alcoholic KOH.

(2018)

95. Following compounds are given to you:

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

- Write the compound which is most reactive towards S_N2 reaction.

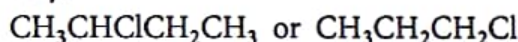
- Write the compound which is optically active.

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

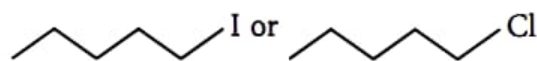
(Delhi 2017)

96. Answer the following questions:

- What is meant by chirality of a compound? Give an example.
- Which one of the following compounds is more easily hydrolysed by KOH and why?



- Which one undergoes S_N2 substitution reaction faster and why?



(AI 2012)

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

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

(AI 2011)

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

- Chlorobenzene and benzyl chloride
 - Chloroform and carbon tetrachloride
- (b) Why is methyl chloride hydrolysed more easily than chlorobenzene?

(Delhi 2011C)

99. Differentiate between S_N1 and S_N2 mechanisms and give examples. (AI 2010)

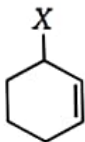
10.7 Polyhalogen Compounds

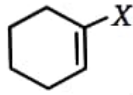
VSA (1 mark)

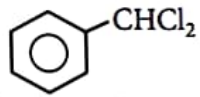
100. State one use each of DDT and iodoform.

(Delhi 2010)

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. $\text{Cl}-\overset{4}{\text{CH}_2}-\overset{3}{\text{CH}}=\overset{2}{\text{CH}}-\overset{1}{\text{CH}_2}-\text{Br}$
1-Bromo-4-chlorobut-2-ene

5. $\text{H}_2\text{C}-\overset{\text{Br}}{\underset{\text{CH}_3}{\text{C}}}=\text{CH}_2$
3-Bromo-2-methylprop-1-ene

6. $\text{H}_3\text{C}-\overset{\text{Br}}{\underset{\text{Br}}{\text{CH}}}-\text{CH}_2-\text{CH}_2-\text{CH}_3$

7. 4-Chloropent-1-ene
8. 4-Bromo-4-methylpent-2-ene
9. 2-Chloro-3-methylbutane
10. 3-Chloro-2,2-dimethylbutane
11. 2-Bromo-4-chloropentane

12. $\overset{4}{\text{CH}_3}-\overset{3}{\underset{\text{CH}_3}{\text{C}}}=\overset{2}{\underset{\text{Br}}{\text{C}}}-\overset{1}{\text{CH}_2\text{OH}}$
2-Bromo-3-methylbut-2-en-1-ol

13. $\overset{1}{\text{CH}_2}=\overset{2}{\underset{\text{CH}_3}{\text{C}}}-\overset{3}{\text{CH}_2\text{Br}}$
3-Bromo-2-methylpropene

14. $\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}}-\overset{1}{\text{CH}_2}-\text{Br}$
1-Bromo-2,2,2-trimethylpropane

15. $\overset{1}{\text{CH}_2}=\overset{2}{\text{CH}}-\overset{3}{\text{CH}_2\text{Br}}$
3-Bromoprop-1-ene

16. $\text{H}_2\text{C}-\overset{\text{Br}}{\text{CH}}=\text{CH}-\overset{\text{Br}}{\text{CH}_2}$

17. $\text{CH}_3-\overset{\text{Br}}{\underset{\text{C}_6\text{H}_5}{\text{CH}}}-\text{CH}_2-\text{CH}_3$

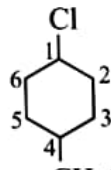
18. $\overset{1}{\text{CH}_3}-\overset{2}{\text{CH}}=\overset{3}{\underset{\text{CH}_3}{\text{C}}}-\overset{4}{\underset{\text{Br}}{\text{CH}}}-\overset{5}{\text{CH}_3}$
4-Bromo-3-methylpent-2-ene

19. $\text{H}_2\text{C}-\overset{\text{Cl}}{\underset{\text{C}_6\text{H}_5}{\text{CH}}}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$

20. $\text{CH}_3-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{Br}}{\underset{\text{C}_6\text{H}_4}{\text{CH}}}}-\text{CH}_3$

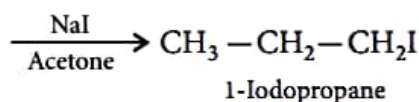
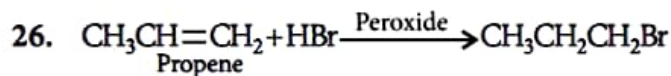
21. $\text{H}_3\text{C}-\text{CH}_2-\overset{\text{I}}{\text{CH}}-\overset{\text{C}(\text{CH}_3)_3}{\text{CH}}-\text{CH}_2-\text{CH}_2-\text{CH}_3$

22. $\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}}-\overset{1}{\text{CH}_2}-\text{Cl}$
1-Chloro-2,2,2-trimethylpropane

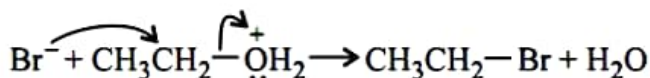
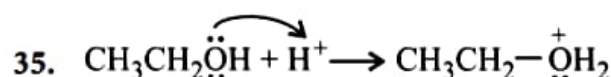
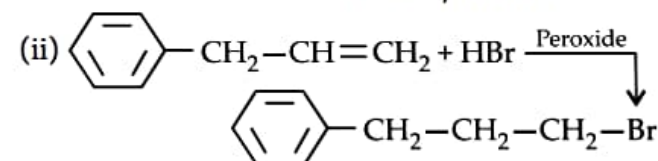
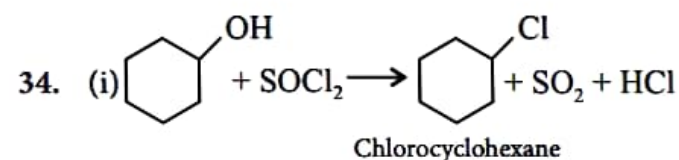
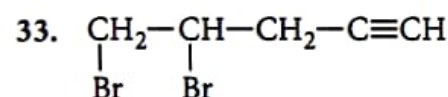
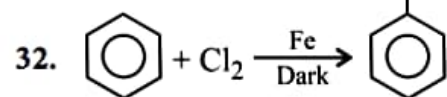
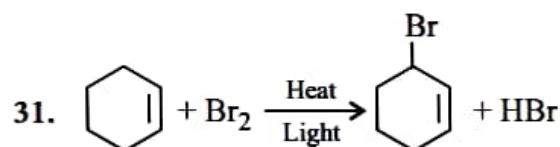
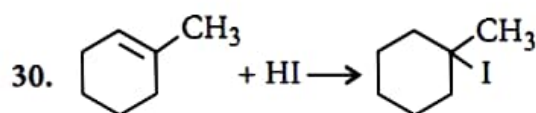
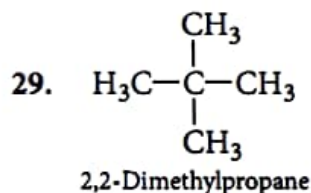
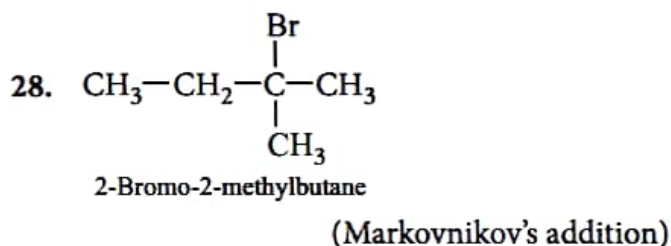
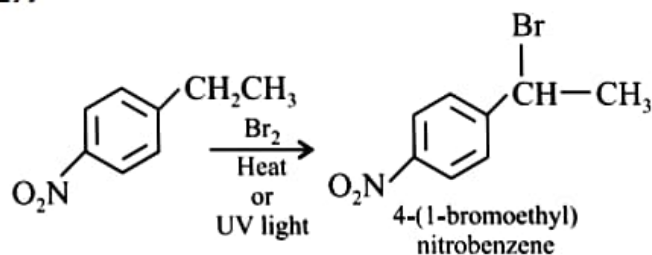
23. 

24. (i) Refer to answer 15.
(ii) 2-(Trichloromethyl)-1,1,1,2,3,3,3-heptachloropropane

25. (i) 2-Bromobutane
(ii) 1,3-Dibromobenzene
(iii) 3-Chloropropene

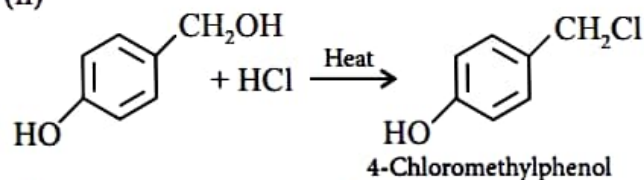


27.

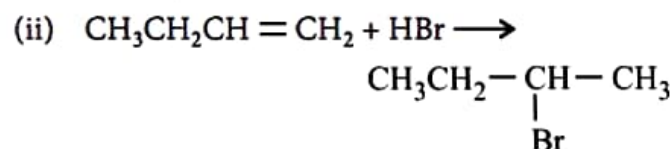


36. (i) Refer to answer 34 (i).

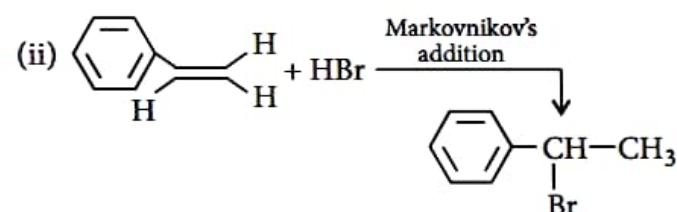
(ii)



37. (i) Refer to answer 30.



38. (i) Refer to answer 30.



(iii) Refer to answer 37(ii).

39. (i) Refer to answer 38(ii).

(ii) Refer to answer 30.

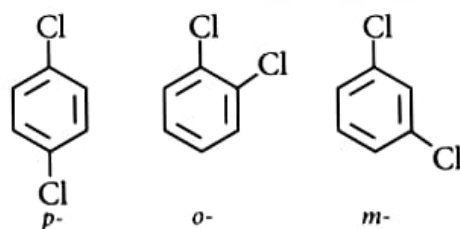
(iii) Refer to answer 34(i).

40. *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.

41. 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.

42. *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.



43. Refer to answer 41.

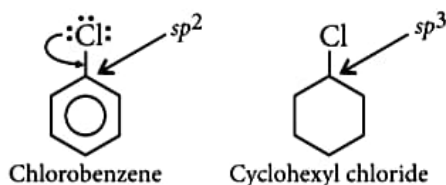
44. Haloalkanes dissolve in organic solvents because the intermolecular attractions between haloalkanes and organic solvent molecules have the same strength as in the separate haloalkanes and solvent molecules.

45. (i) There are two reasons :

(a) 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.

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

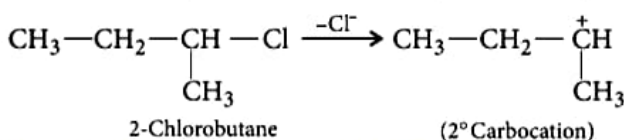
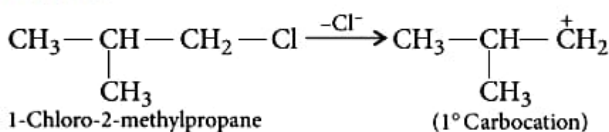
Hence dipole moment is smaller than cyclohexyl chloride which has a longer C—Cl single bond.



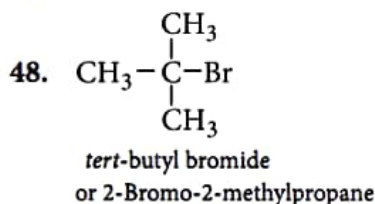
(ii) Refer to answer 41.

46. 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.

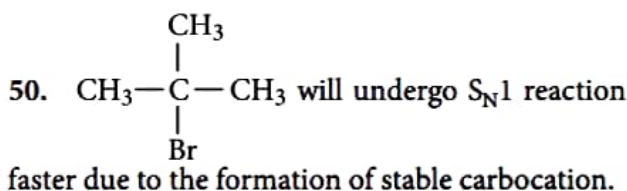
47. The S_N1 reaction proceeds through carbocation formation thus, the compound which forms more stable carbocation will be more reactive.



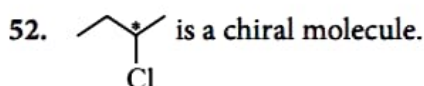
As, 2° carbocation is more stable than 1° carbocation thus, 2-chlorobutane is more reactive towards S_N1 reaction.



49. $\text{CH}_3-\text{CH}_2-\text{Br}$ would undergo S_N2 reaction faster due to formation of less sterically hindered transition state.

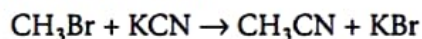


51. Since I^- is a better leaving group than Br^- , thus, $\text{CH}_3\text{CH}_2\text{I}$ undergoes S_N2 reaction faster than $\text{CH}_3\text{CH}_2\text{Br}$.

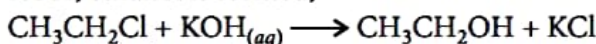


53. (i) CH_3I will give faster S_N2 reaction.
(ii) CH_3Cl will give faster S_N2 reaction.

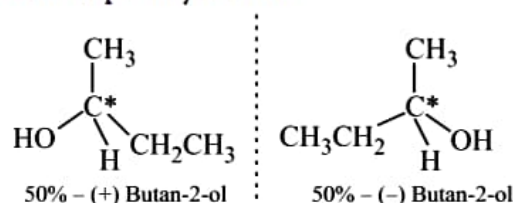
54. CH_3CN is formed by nucleophilic substitution reaction.



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

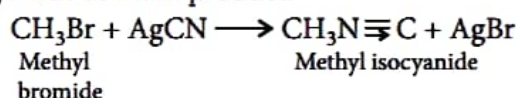


56. (\pm)-Butan-2-ol is optically inactive because it exist in two enantiomeric forms which are non-superimposable mirror images of each other. Both the isomers are present in equal amounts therefore, it does not rotate the plane of polarized light and is optically inactive.

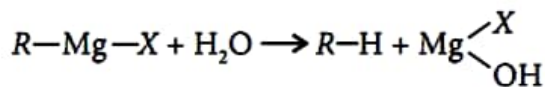


57. Tertiary halide reacts faster than the secondary halide because of the greater stability of tert-carbocation.

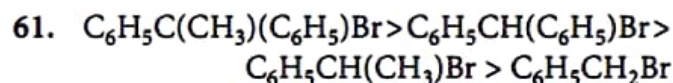
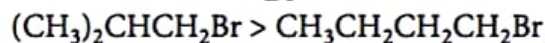
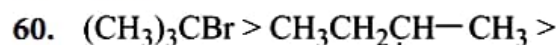
58. AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as main product.



59. Grignard reagents react with water to form alkanes.



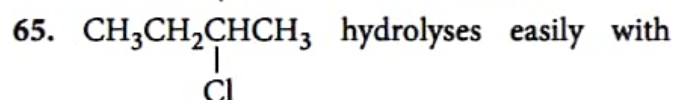
So, they must be prepared under anhydrous conditions.



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

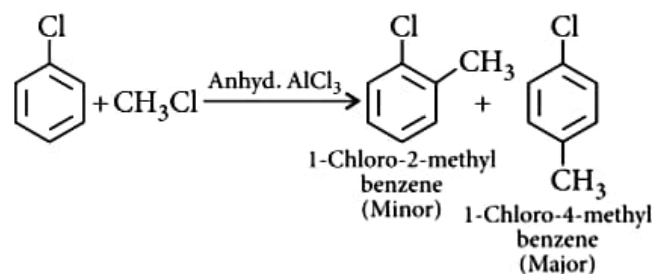
63. 1-Bromopentane is a primary alkyl halide, hence reacts faster in S_N2 displacement than secondary halide 2-bromopentane.

64. 2-Bromobutane will react faster in S_N1 displacement reaction because it will form more stable secondary carbocation intermediate.

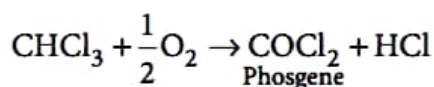


KOH because it is secondary halide.

66. Haloarenes can undergo both Friedel-Craft alkylation (with alkyl halide) or Friedel-Craft acylation (with acid halide) in presence of Lewis acid catalyst to give a mixture of *o*- and *p*-haloalkyl benzene or *o*- and *p*-haloacylbenzene.



67. Chloroform when exposed to air and sunlight changes to phosgene which is a poisonous gas.

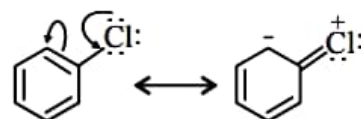


Thus, it is kept in dark coloured bottles to prevent the oxidation.

68. CH_3Cl will react faster in S_N2 reaction with OH^- as CH_3Cl is a primary halide and it will give less sterically hindered transition state.

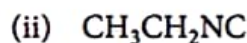
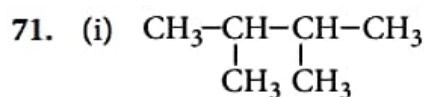
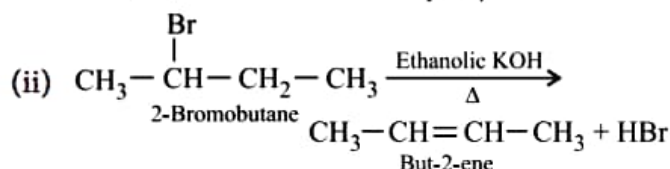
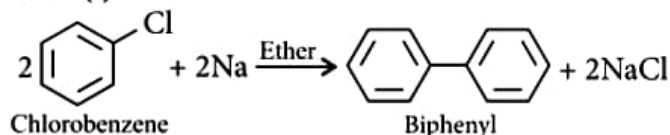
69. (i) In halobenzene $C-X$ bond has partial double bond character due to resonance while CH_3-X bond is single bond.

Thus, bond length of $C-X$ bond in halobenzene is smaller than that in CH_3-X .



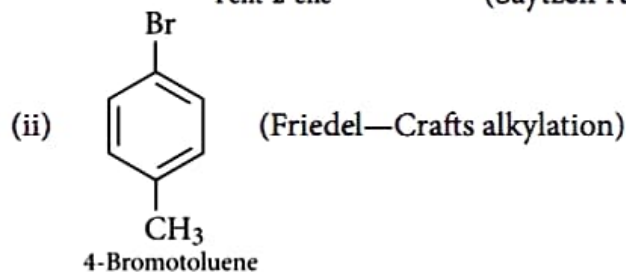
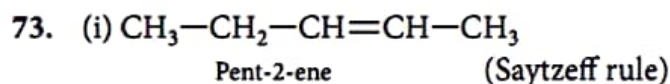
(ii) In S_N1 reaction carbocation intermediate is formed which is a planar molecule so, an incoming nucleophile can attack from either side and a equimolar mixture of two components are formed and resulting mixture is optically inactive.

70. (i)

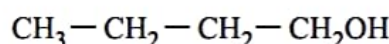


72. (i) Racemic mixture contains equal amount of *d*- and *l*-forms, hence rotation due to one enantiomer is cancelled by another.

(ii) 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.

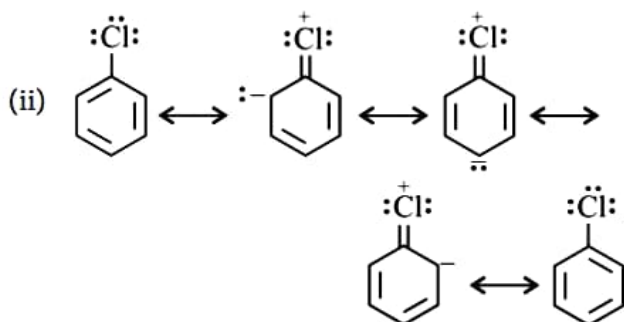
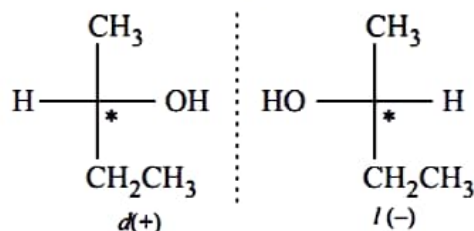


74. (i) Butan-1-ol is achiral, *i.e.*, does not have chiral 'C' atom which is attached to four different groups, therefore, it is optically inactive.



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

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



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.

75. (i) (a) Br undergoes faster S_N2 reaction.

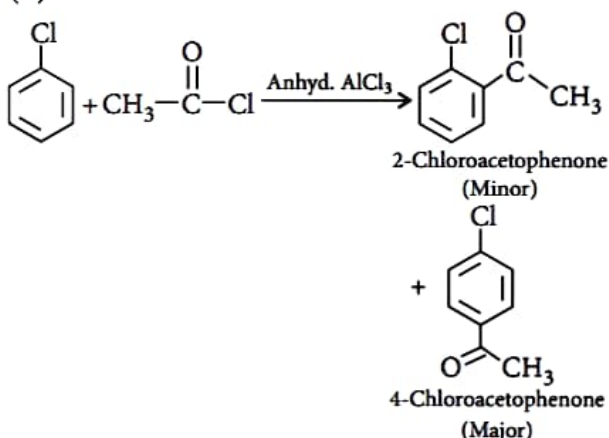
(b) is chiral.

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

(b) S_N1 reaction occurs with racemisation.

76. (i) Refer to answer 55.

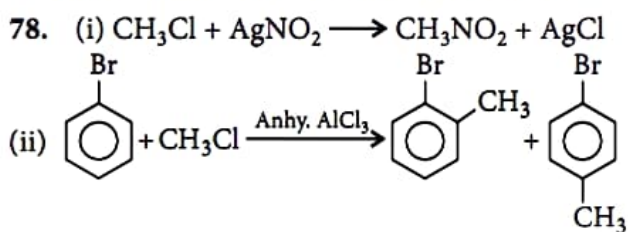
(ii)



77. (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.

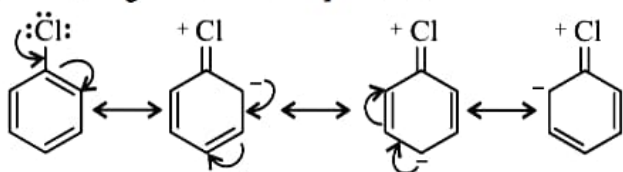
(ii) Carbocations are formed in S_N1 reaction which are planar species, thus, racemisation occurs.



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

80. 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 haloarenes, halogen is attached to sp^2 -hybridised carbon while in haloalkanes, halogen is attached to sp^3 -hybridised carbon.

81. (i) Refer to answer 69(i).

(ii) Refer to answer 77.

82. (i) Refer to answer 51.

(ii) Refer to answer 69(i).

83. In haloarenes $-ve$ charge gets localised on arenes using resonance, therefore they undergo electrophilic substitution.

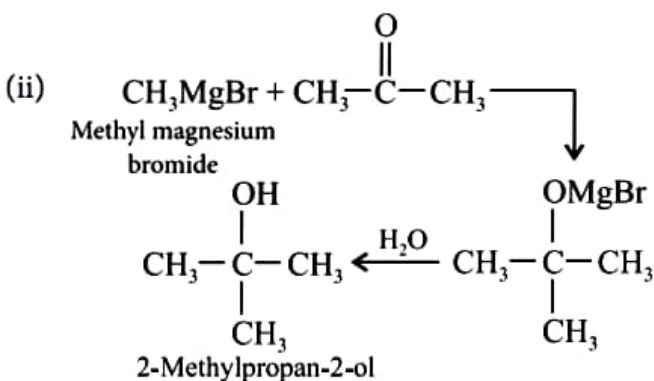
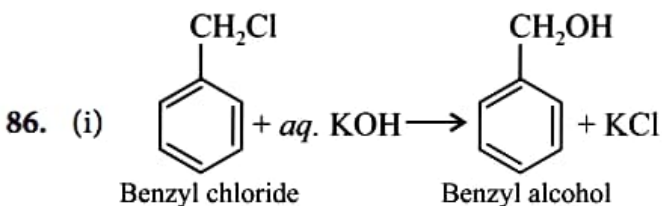
Haloalkanes have electrophilic carbon centre due to polarity of $\text{C} \rightarrow \text{X}$ bond.

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

$$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_3 \\ | \\ \text{OH} \end{array}$$

(ii) Of the two bromo derivatives, $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$ is more reactive than $\text{C}_6\text{H}_5(\text{CH}_3)\text{Br}$ for $\text{S}_\text{N}1$ reaction because its carbocation is resonance stabilised by two phenyl groups.


$$\begin{array}{c}
 \text{CH}_2\text{CH}_2\text{CH}_3 \\
 | \\
 \text{K}^+\text{CN}^- + \text{C}-\text{Br} \longrightarrow \text{NC}-\overset{\delta}{\text{C}}-\overset{\delta}{\text{C}}-\text{Br} \\
 \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
 | \\
 \text{CH}_2\text{CH}_2\text{CH}_3 \\
 | \\
 \text{NC}-\text{C} \\
 \text{H} \quad \text{H} \\
 \text{n-Butyl cyanide}
 \end{array}$$




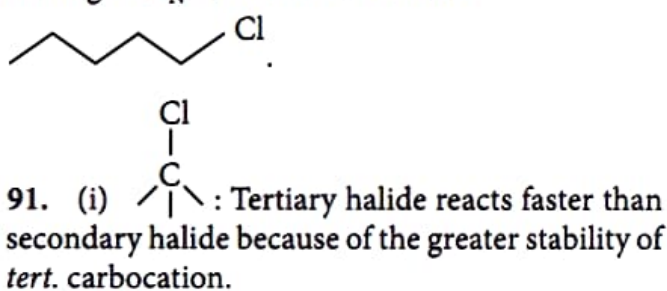
(b) 1-Bromo-2-methylbutane, as it is a primary alkyl halide.



88. (a) H_2SO_4 is an oxidant. KI reacts with H_2SO_4 and gives HI and H_2SO_4 oxidises HI to I_2 .
 $2\text{KI} + \text{H}_2\text{SO}_4 \rightarrow 2\text{KHSO}_4 + 2\text{HI}$
 $2\text{HI} + \text{H}_2\text{SO}_4 \rightarrow 2\text{H}_2\text{O} + \text{I}_2 + \text{SO}_2$

This is why sulphuric acid is not used during the reaction of alcohols with KI.

(ii)  undergoes faster S_N1 reaction as it is a secondary halide and give more stable carbocation than primary halide.

(ii) As iodide is a better leaving group because of its large size, therefore,  I undergoes S_N2 reaction faster than



(ii)  reacts faster than  because of greater stability of secondary carbocation than primary.

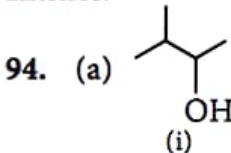
92. (i) Among the various halides with same alkyl group the order of reactivity is $RI > RBr > RCl$.

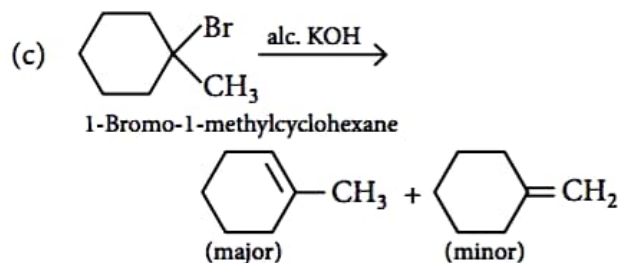
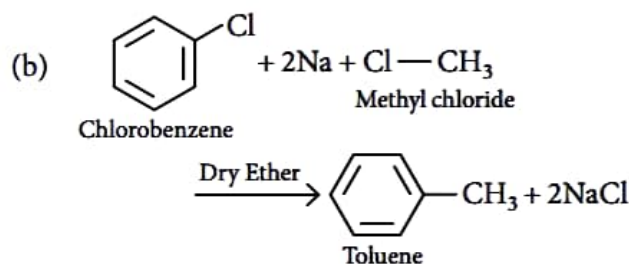
Due to increasing bond strength of C—I, C—Br and C—Cl the reactivity decreases.

(ii) Neopentyl chloride being a primary halide reacts slowly through S_N1 and the carbon carrying halogen is sterically more hindered. Hence it does not follow S_N2 mechanism.

93. (i) Refer to answer 80.

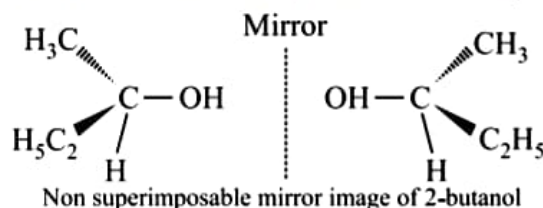
(ii) In aqueous solution, KOH is almost completely involved to give OH^- ion which being a better nucleophile gives a substitution reaction on alkyl halides to form alcohol. But an alcoholic solution of KOH containing alkoxide (RO^-) ions which being a much stronger base than OH^- ion preferentially snatches a H^+ ion from an alkyl chloride to form alkenes.





95. (i) 1-Bromopentane
(ii) 2-Bromopentane
(iii) 2-Bromo-2-methylbutane

96. (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.



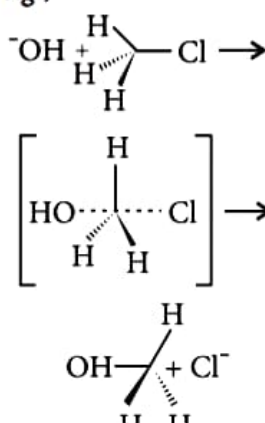
- (ii) Refer to answer 65.
(iii) Refer to answer 90.
97. (i) 1-Bromopentane > 2-Bromopentane > 2-Bromo-2-methylbutane.
(ii) 1-Bromo-3-methylbutane > 3-Bromo-2-methylbutane > 2-Bromo-2-methylbutane
(iii) 1-Bromobutane > 1-Bromo-2-methylbutane > 1-Bromo-2,2-dimethylpropane

98. (a) (i) Benzyl chloride gives white precipitate 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 $\text{C}_6\text{H}_5\text{Cl}$ as chlorobenzene has partial double bond character between C—Cl bond which is difficult to break.

99.

	$\text{S}_{\text{N}}1$ mechanism	$\text{S}_{\text{N}}2$ mechanism
1.	It is two step process, carbocation intermediate is formed.	It is single step process. No intermediate is formed.
2.	It obeys 1 st order kinetics. Rate = k [Reactant]	It obeys 2 nd order kinetics. Rate = k [Reactant] [Nucleophile]
3.	Order of reactivity $3^\circ > 2^\circ > 1^\circ$.	Order of reactivity $1^\circ > 2^\circ > 3^\circ$.
4.	Optically inactive product is formed (racemic mixture).	Inversion of configuration takes place.
5.	e.g., $(\text{CH}_3)_3\text{CBr} + \text{OH}^-$ 2-Bromo-2-methylpropane \downarrow $(\text{CH}_3)_3\text{COH} + \text{Br}^-$ 2-Methylpropan-2-ol	e.g., 

100. DDT is used as an insecticide and iodoform is used as a mild antiseptic.

