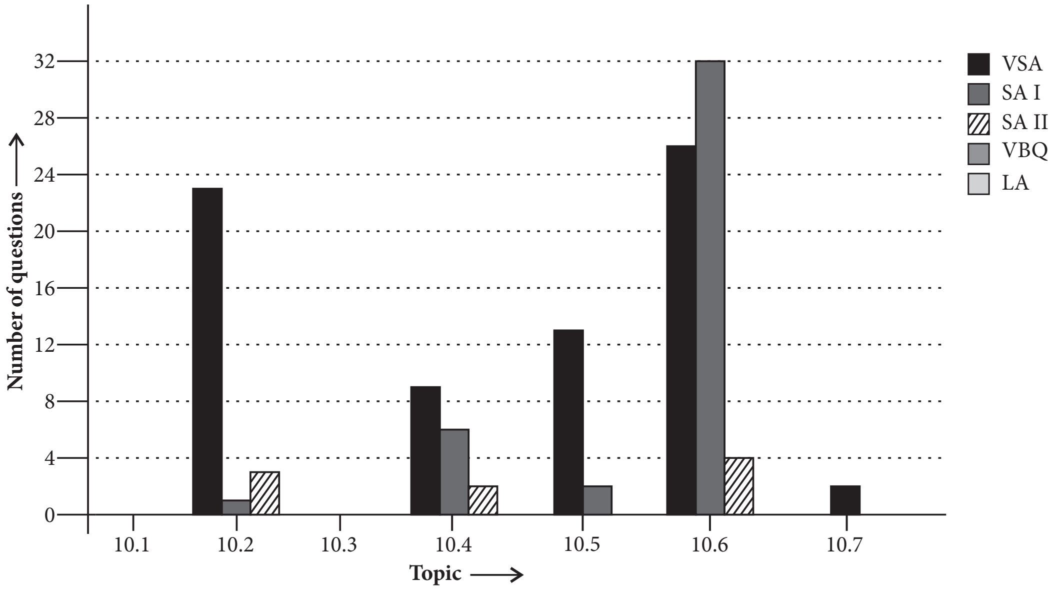
10

Haloalkanes and Haloarenes

- 10.1 Classification
- 10.2 Nomenclature
- 10.3 Nature of C—*X* Bond
- 10.4 Methods of Preparation
- 10.5 Physical Properties
- 10.6 Chemical Reactions
- 10.7 Polyhalogen Compounds

Topicwise Analysis of Last 10 Years' CBSE Board Questions



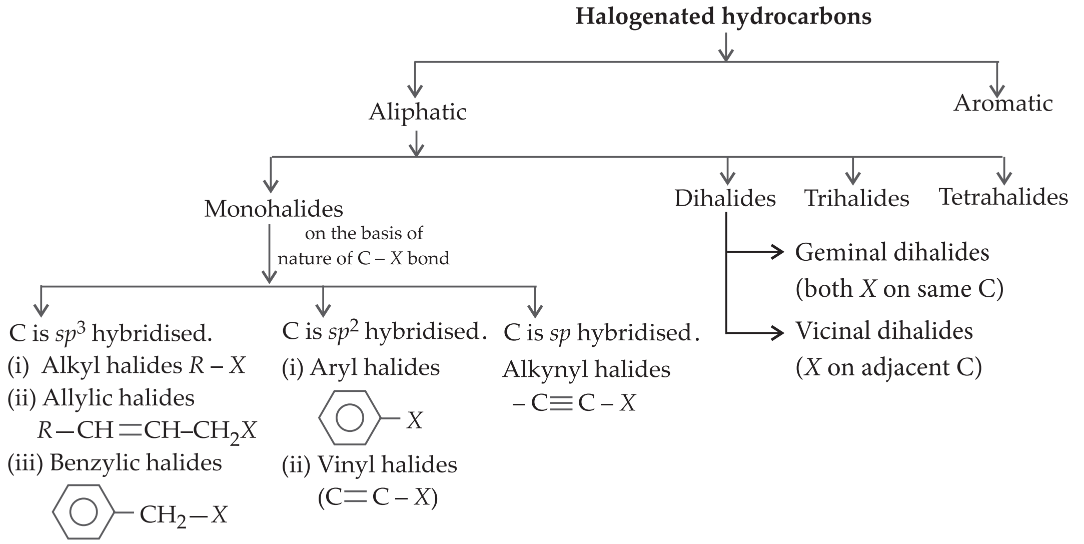
- Maximum total weightage is of *Chemical Reactions.*
- Maximum VSA type questions were asked from *Chemical Reactions.*
- Maximum SA I and SA II type questions were asked from *Chemical Reactions.*

QUICK RECAP

HALOALKANES

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

Classification :



General methods of preparation :

- **From alcohols :** Alkyl halides can be prepared from alcohols in a number of ways :
  - **Action of hydrogen halides :**

$$R\text{–OH} \xrightarrow{\text{HCl/anhyd. ZnCl}_2} R\text{Cl} + H_2O$$

$$R\text{–OH} \xrightarrow[\text{or KBr + conc. }H_2SO_4\text{ reflux}]{\text{HBr/}H_2SO_4\text{ reflux}} R\text{–Br} + H_2O$$

$$R\text{–OH} \xrightarrow[\text{or KI + }H_3PO_4\text{ reflux}]{\text{HI reflux}} R\text{–I} + H_2O$$

- 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 :

  allyl benzyl > tertiary > secondary > primary

  - **Action of phosphorus halides :**

$$R\text{–OH} \xrightarrow{PCl_5} R\text{–Cl} + POCl_3 + HCl$$

$$R\text{–OH} \xrightarrow{PCl_3} R\text{–Cl} + H_3PO_3$$

$$R\text{–OH} \xrightarrow[(P + Br_2)]{PBr_3} R\text{–Br} + H_3PO_3$$

$$R\text{–OH} \xrightarrow[(P + I_2)]{PI_3} R\text{–I} + H_3PO_3$$

  - **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 :**

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

  - 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.*

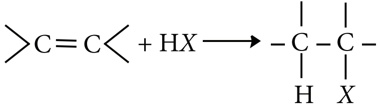
$$2CH_3CH_2Cl + \underset{\text{Mercurous fluoride}}{Hg_2F_2} \longrightarrow 2CH_3CH_2F + \underset{\text{Mercurous chloride}}{Hg_2Cl_2}$$

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

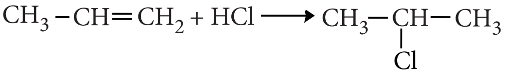
$$R\text{—O—}R + 2HX \longrightarrow 2R - X + H_2O$$

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

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

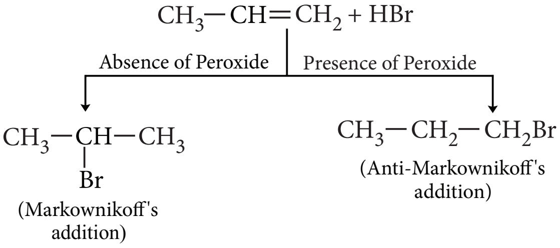


$$>C=C< + HX \longrightarrow -\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{X}{\overset{|}{\underset{|}{C}}}-$$



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

- 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. 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

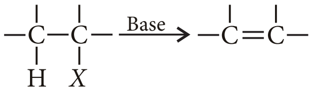
  $CH_3—F > CH_3—Cl > CH_3—Br > CH_3—I$

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

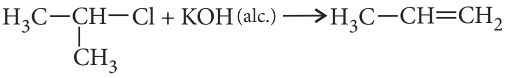
  $R—F > R—Cl > R—Br > R—I$

Chemical properties :

- **Dehydrohalogenation :**

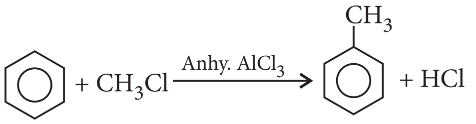


$$-\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{X}{\overset{|}{\underset{|}{C}}}- \xrightarrow{Base} -\overset{|}{C}=\overset{|}{C}-$$



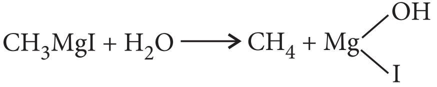
$$H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-Cl + KOH\,(alc.) \longrightarrow H_3C-CH=CH_2$$

- **Friedel Crafts reacton :**



- **Reaction with Mg metal :**

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

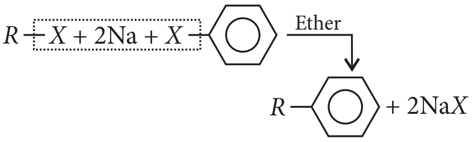


$$CH_3MgI + H_2O \longrightarrow CH_4 + Mg\begin{matrix} OH \\ I \end{matrix}$$

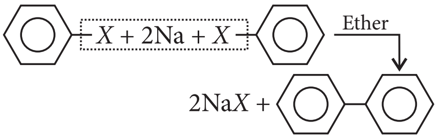
- **Wurtz reaction :**

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

- **Wurtz Fittig reaction :**



- **Fittig reaction :**



- **Reduction of alkyl halides :**

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

HALOARENES

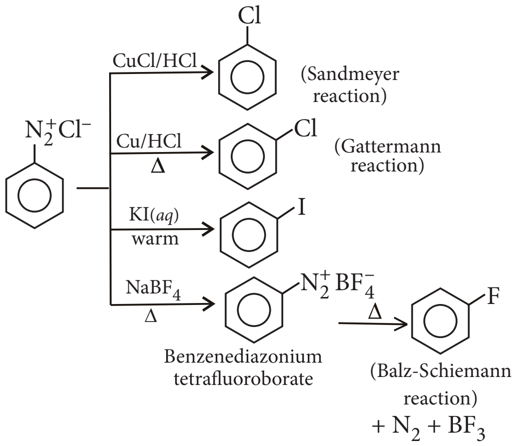
Aryl halides : General formula is ArX, where Ar = aryl group.

General methods of preparation :

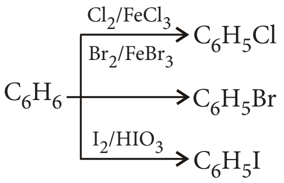
- **By Raschig process :**

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

- **From benzenediazonium salt :**



- **By direct halogenation of benzene :**

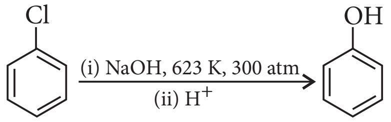


Physical properties :

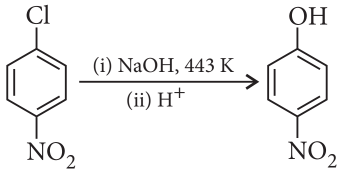
- Aryl halides are colourless stable liquids with pleasant odour.
- These are insoluble in water but readily miscible with organic solvents.
- Most of them are steam volatile, heavier than water.
- Their boiling points are higher than corresponding alkyl halides. The boiling points rise gradually from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

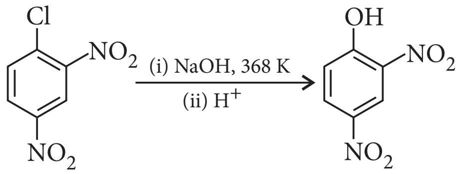
Chemical properties :

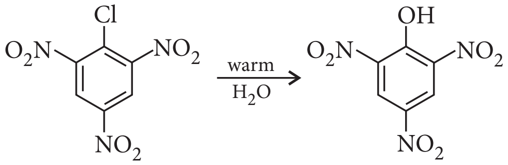
- **Nucleophilic substitution reactions :**



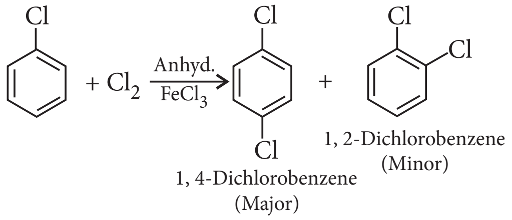
The presence of an electron withdrawing group ($—NO_2$) at *ortho*- and *para*-positions increases the reactivity of haloarenes.







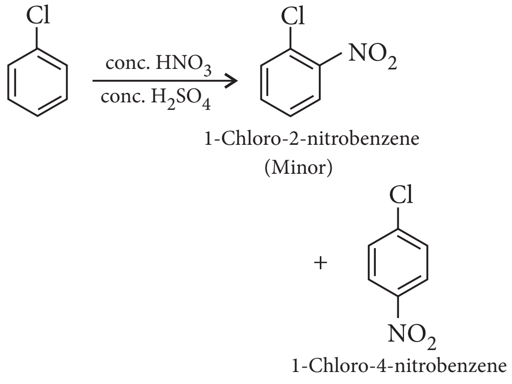
- **Electrophilic substitution reactions :**
  - **Halogenation :**



1, 4-Dichlorobenzene (Major)

1, 2-Dichlorobenzene (Minor)

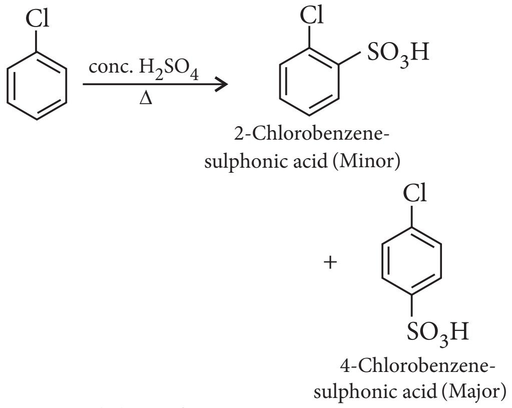
- **Nitration :**



1-Chloro-2-nitrobenzene (Minor)

1-Chloro-4-nitrobenzene (Major)

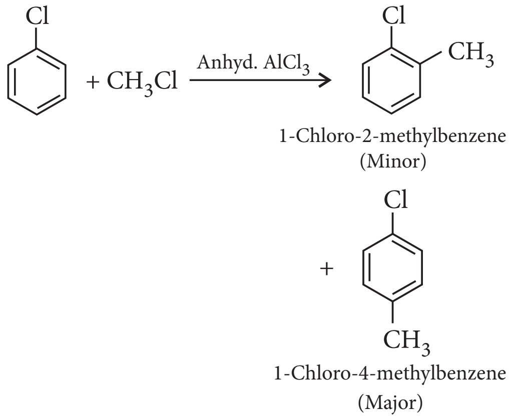
- **Sulphonation :**



2-Chlorobenzene-sulphonic acid (Minor)

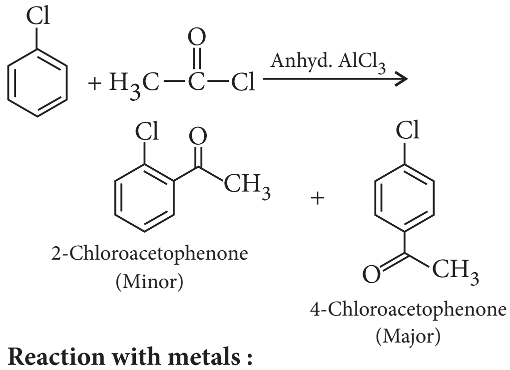
4-Chlorobenzene-sulphonic acid (Major)

- **Friedal-Crafts reaction :**

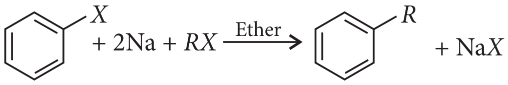


1-Chloro-2-methylbenzene (Minor)

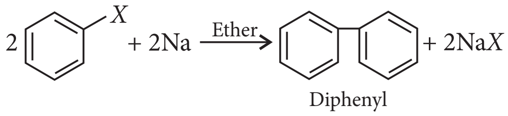
1-Chloro-4-methylbenzene (Major)



- **Reaction with metals :**



- **Fitting 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 : $3° > 2° > 1° > \overset{+}{C}H_3$ (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 T.S., 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.
Configuration is retained but in front attack inversion takes place (racemisation and inversion).	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 which 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.

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 CNS, causes dizziness, fatigue and headache.
Iodoform (CHI_3)	– It is used as an antiseptic in dressing of wounds due to liberation of iodine. – It is used as methylating agent in organic synthesis.	– It has strong smell.
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 greenhouse 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.

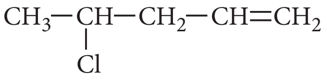
Previous Years' CBSE Board Questions

10.2 Nomenclature

VSA **(1 mark)**

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

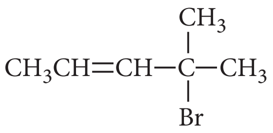
2. Write the IUPAC name of



$CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-CH=CH_2$

(Delhi 2013)

3. Write the IUPAC name of

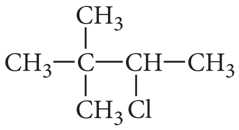


$CH_3CH=CH-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-CH_3$

(Delhi 2013)

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

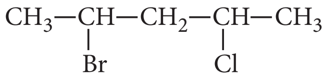
5. Write the IUPAC name of the following compound:



$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\underset{\underset{Cl}{|}}{CH}-CH_3$

(AI 2013)

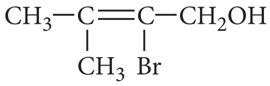
6. Write the IUPAC name of the following compound:



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

(AI 2013)

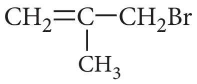
7. Write IUPAC name of the following:



$CH_3-\underset{\underset{CH_3}{|}}{C}=\underset{\underset{Br}{|}}{C}-CH_2OH$

(AI 2013C, 2012C, Foreign 2011)

8. Give the IUPAC name of the following compound:



$CH_2=\underset{\underset{CH_3}{|}}{C}-CH_2Br$

(Delhi 2012, AI 2011)

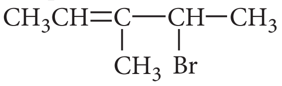
9. Write the IUPAC name of the following compound: $(CH_3)_3CCH_2Br$ *(Delhi 2011)*

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

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

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

13. Give IUPAC name of the following organic compound:



$CH_3CH=\underset{\underset{CH_3}{|}}{C}-\underset{\underset{Br}{|}}{CH}-CH_3$

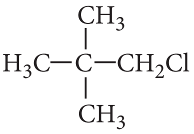
(Delhi 2011C)

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

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

16. Write the structure of the compound: 4-*tert*-butyl-3-iodoheptane *(AI 2010C)*

17. Write the IUPAC name of the following compound:

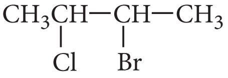


$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2Cl$

(AI 2010C)

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

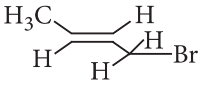
19. Write the IUPAC name of the following compound:



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

(Delhi 2008)

20. State the IUPAC name of the following compound:



21. Write the IUPAC name of $ClCH_2C\equiv CCH_2Br$. *(AI 2008C)*

SA I **(2 marks)**

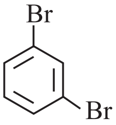
22. Write the IUPAC names of the following compounds:
(i) $CH_2=CHCH_2Br$ (ii) $(CCl_3)_3CCl$ *(AI 2014C)*

SA II (3 marks)

23. Give the IUPAC names of the following compounds :

(i) 

$CH_3-CH(Br)-CH_2-CH_3$

(ii) 

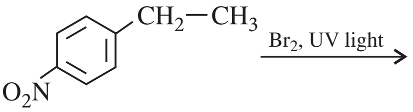
(iii) $CH_2=CH-CH_2-Cl$ *(AI 2015C)*

10.4 Methods of Preparation

VSA (1 mark)

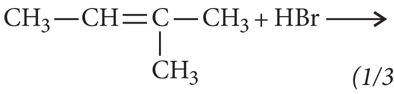
24. How do you convert:
Propene to 1-iodopropane ? *(1/3, AI 2016)*

25. Write the major products in the following :



(1/3, AI 2016)

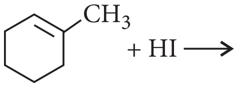
26. Write the structure of the major product in the following reaction :



$CH_3-CH=C(CH_3)-CH_3 + HBr \longrightarrow$ *(1/3, AI 2015)*

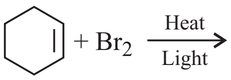
27. A hydrocarbon C_5H_{12} gives only one monochlorination product. Identify the hydrocarbon. *(Delhi 2013C)*

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



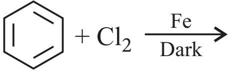
(Delhi 2012C)

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



(Delhi 2012C)

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



(Delhi 2012C)

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

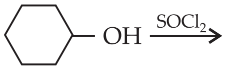
32. Complete the following chemical equation :

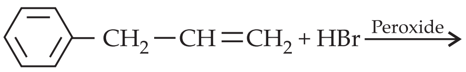
$CH_3CH_2CH=CH_2 + HBr \xrightarrow{\text{Peroxide}} \ldots$

(1/2, Delhi 2008)

SA I (2 marks)

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

(i) 

(ii) 

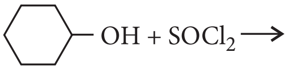
(Delhi 2014)

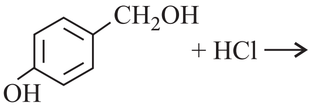
34. Write the mechanism of the following reaction :

$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$

(AI 2014)

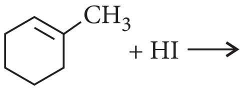
35. Complete the following reaction equations :

(i) 

(ii) 

(Delhi 2009)

36. Complete the following reaction equations :

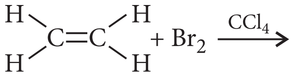
(i) 

(ii) $CH_3CH_2CH=CH_2 + HBr \longrightarrow$

(AI 2009)

37. Complete the following reaction equation :

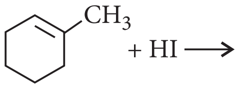
(i) $C_6H_5N_2Cl + KI \longrightarrow$

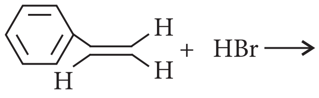
(ii) 

(Delhi, AI 2008)

SA II (3 marks)

38. Compute the following reaction equations:

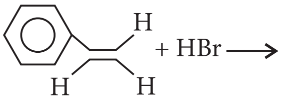
(i) 

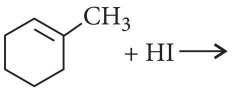
(ii) 

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

(Foreign 2011)

39. Complete the equation for the following reactions :

(i) 

(ii) 

(iii) 

(Delhi 2011C)

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.p. 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, AI2010C)*

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

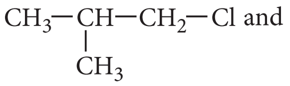
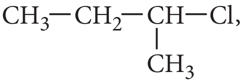
45. Out of ethyl bromide and ethyl chloride which has higher boiling point and why? *(1/3, AI 2007)*

SA I (2 marks)

46. 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)*

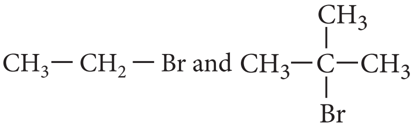
10.6 Chemical Reactions

VSA (1 mark)

47. Out of  $CH_3-\underset{CH_3}{CH}-CH_2-Cl$ and  $CH_3-CH_2-\underset{CH_3}{CH}-Cl$, which is more reactive towards S_N1 reaction and why? *(Delhi 2016)*

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

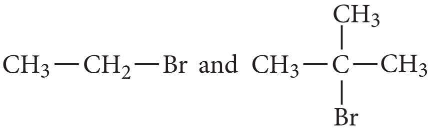
49. Which would undergo S_N2 reaction faster in the following pair and why?



$$CH_3-CH_2-Br \text{ and } CH_3-\underset{Br}{\overset{CH_3}{C}}-CH_3$$

(Delhi 2015)

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

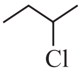


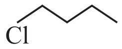
$$CH_3-CH_2-Br \text{ and } CH_3-\underset{Br}{\overset{CH_3}{C}}-CH_3$$

(AI 2015)

51. 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)*

52. Identify the chiral molecule in the following pair:





(AI 2014)

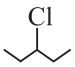
53. Which halogen compound in each of the following pairs will react faster in S_N2 reaction:
(i) CH_3Br or CH_3I
(ii) $(CH_3)_3CCl$ or CH_3Cl
(Delhi 2014C, AI 2014)

54. What happens when CH_3-Br 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?

 and 

(Delhi 2013, 2013C, 2012C)

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.
$C_6H_5CH_2Br$, $C_6H_5C(CH_3)(C_6H_5)Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$
(Delhi 2012C)

62. Give a chemical test of 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 reactions 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)

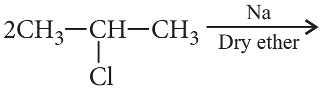
68. Explain why in the pair, $(CH_3)_3CCl$ and CH_3Cl will react faster in S_N2 reaction with OH^-? *(1/3, AI 2010C)*

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) 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)

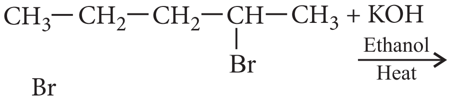
71. Write the major product(s) in the following :

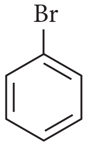
(i) 
$2CH_3-\underset{Cl}{\underset{|}{C}H}-CH_3 \xrightarrow[\text{Dry ether}]{\text{Na}}$

(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 :

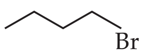
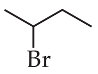
(i) 
$CH_3—CH_2—CH_2—\underset{Br}{\underset{|}{C}H}—CH_3 + KOH \xrightarrow[\text{Heat}]{\text{Ethanol}}$

(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)

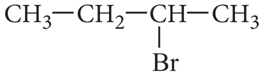
75. (i) Which alkyl halide from the following pair is chiral and undergoes faster S_N2 reaction?

(a)  (b) 

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



$CH_3-CH_2-\underset{\displaystyle Br}{\underset{|}{C}H}-CH_3$

$CH_3-CH_2-CH_2-CH_2-Br$

(ii) Racemisation occurs in S_N1 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 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)*

82. 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)*

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 bromoderivatives, $C_6H_5CH(CH_3)Br$ and $C_6H_5CH(C_6H_5)Br$, which one is more reactive in S_N1 substitution reaction and why? *(2/3, Delhi 2011)*

85. Write the mechanism of the following reaction :

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

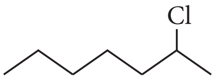
(1/3, Delhi, 2011C)

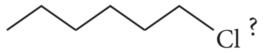
86. How are the following conversions carried out?
(i) Benzyl chloride to benzyl alcohol,
(ii) Methyl magnesium bromide to methylpropan-2-ol. *(2/3, Delhi 2010)*

87. Which compound in the following couple will react faster in S_N2 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 ?

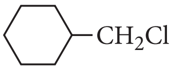
(ii) 

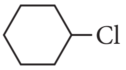
undergoes faster S_N1 reaction than 

?

(Delhi 2010C)

90. Which one in the following pairs of substances undergoes S_N2 substitution reaction faster and why?

(i) 

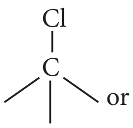
or 

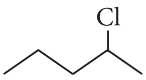
(ii) 

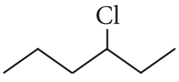
or 

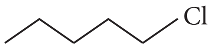
(Delhi 2009)

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

(i) 

or 

(ii) 

or 

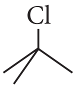
(AI 2009)

92. Suggest a possible reason for the following observations :
(i) The order of reactivity of haloalkanes is $RI > RCl > RBr$.

(ii) Neopentyl chloride $(CH_3)_3CCH_2Cl$ does not follow S_N2 mechanism.
(2/3, Delhi 2009C)

93. Give reasons for the following observations :
(i) Haloarenes are less reactive than haloalkanes towards nucleophilic substitution reactions.
(ii) 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)

94. (i) Why is it that haloalkanes are more reactive than haloarenes towards nucleophiles.
(ii) Which one of the following reacts faster in an S_N1 reaction and why?



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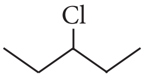
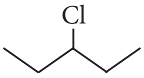


(Delhi 2008)

95. (i) Why are haloalkanes more reactive towards nucleophilic substitution reactions than haloarenes?
(ii) Which one of the following two substances undergoes S_N1 reaction faster and why?



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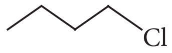


(AI 2008)

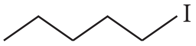
96. Discuss the mechanism of S_N1 reaction of haloalkanes. *(Delhi 2008C)*

97. What is Saytzeff rule? Illustrate with suitable example. *(2/5, AI 2007)*

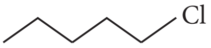
98. Give one example of each of the following reactions :
(i) Wurtz reaction
(ii) Wurtz-Fittig reaction. *(2/5, Delhi 2007)*

SA II (3 marks)

99. 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)

100. 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)

101. (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)*

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

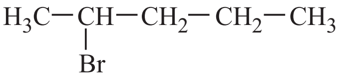
10.7 Polyhalogen Compounds

VSA (1 mark)

103. State one use each of DDT and iodoform.
(Delhi 2010)

104. Write the balanced equation for the following:
(i) When chloroform is oxidised by air.
(ii) Chloroform reacts with chlorine.
(2/5, Delhi 2007)

Detailed Solutions

1. 
$H_3C-\underset{Br}{CH}-CH_2-CH_2-CH_3$

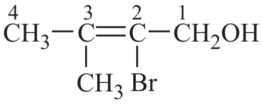
2. 4-Chloropent-1-ene

3. 4-Bromo-4-methylpent-2-ene

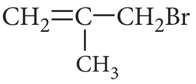
4. 2-Chloro-3-methyl butane

5. 3-Chloro-2,2-dimethyl butane

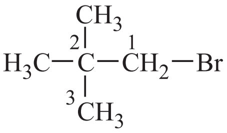
6. 2-Bromo-4-chloropentane

7. 
$\overset{4}{C}H_3-\overset{3}{\underset{CH_3}{C}}=\overset{2}{\underset{Br}{C}}-\overset{1}{C}H_2OH$

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

8. 
$CH_2=\underset{CH_3}{C}-CH_2Br$

3-Bromo-2-methylpropene

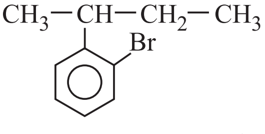
9. 
$H_3C-\overset{\overset{CH_3}{2|}}{\underset{\underset{^3CH_3}{|}}{C}}-\overset{1}{C}H_2-Br$

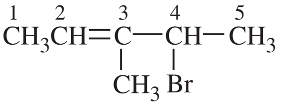
1-Bromo-2,2-dimethylpropane

10. $CH_2=CHCH_2Br$

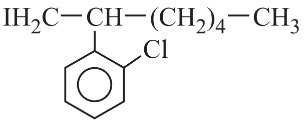
3-Bromoprop-1-ene

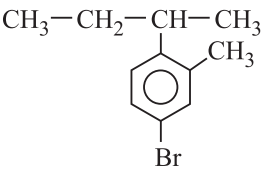
11. 
$H_2\underset{Br}{C}-CH=CH-\underset{Br}{C}H_2$

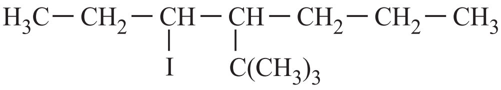
12. 

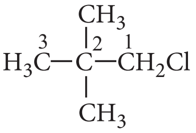
13. 
$\overset{1}{C}H_3\overset{2}{C}H=\overset{3}{\underset{CH_3}{C}}-\overset{4}{\underset{Br}{C}H}-\overset{5}{C}H_3$

4-Bromo-3-methylpent-2-ene

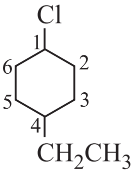
14. 

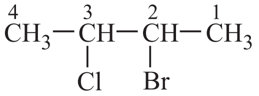
15. 

16. 
$H_3C-CH_2-\underset{I}{CH}-\underset{C(CH_3)_3}{CH}-CH_2-CH_2-CH_3$

17. 
$\overset{3}{H_3C}-\overset{\overset{CH_3}{|2}}{\underset{\underset{CH_3}{|}}{C}}-\overset{1}{C}H_2Cl$

1-Chloro-2,2-dimethylpropane

18. 

19. 
$\overset{4}{C}H_3-\overset{3}{\underset{Cl}{C}H}-\overset{2}{\underset{Br}{C}H}-\overset{1}{C}H_3$

2-Bromo-3-chlorobutane

20. 1-Bromobut-2-ene

21. $Cl\overset{4}{C}H_2-\overset{3}{C}\equiv\overset{2}{C}-\overset{1}{C}H_2-Br$

1-Bromo-4-chlorobut-2-yne

22. (i) *Refer to answer 10.*

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

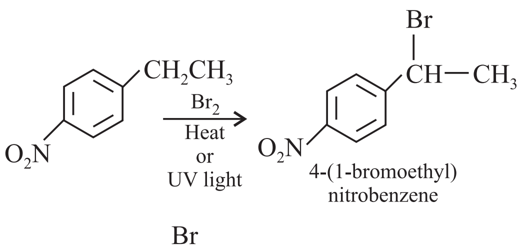
23. (i) 2-Bromobutane

(ii) 1,3-Dibromobenzene

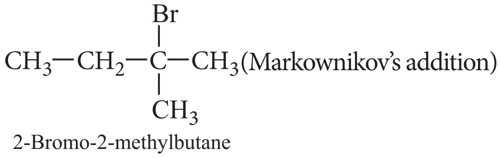
(iii) 3-Chloropropene

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

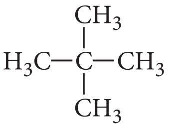
$$\xrightarrow[\text{Acetone}]{\text{NaI}}\underset{\text{1-Iodopropane}}{CH_3-CH_2-CH_2I}$$

25. 

4-(1-bromoethyl) nitrobenzene

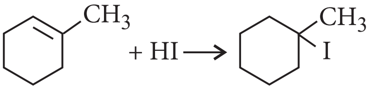
26. 
$CH_3-CH_2-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$(Markownikov's addition)

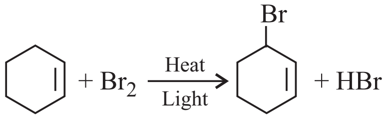
2-Bromo-2-methylbutane

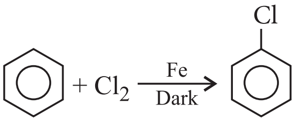
27. 

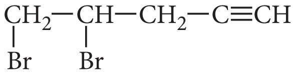
$H_3C-C(CH_3)_2-CH_3$

2,2-Dimethylpropane

28. 

29. 

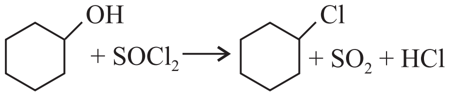
30. 

31. 

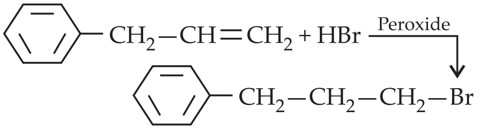
$\underset{Br}{CH_2}-\underset{Br}{CH}-CH_2-C\equiv CH$

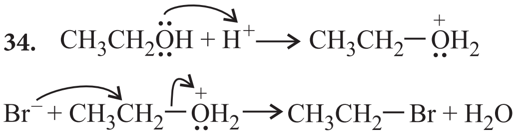
32. $CH_3CH_2CH=CH_2 + HBr \xrightarrow[\text{Anti Markownikoff's addition}]{\text{Peroxide}} CH_3CH_2CH_2CH_2Br$

1-Bromobutane

33. (i) 

Chlorocyclohexane

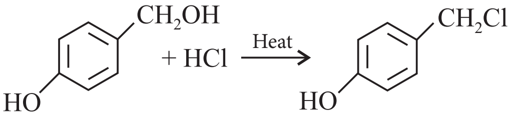
(ii) 

34. 

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

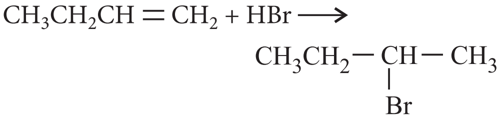
$Br^- + CH_3CH_2-\overset{+}{\ddot{O}}H_2 \longrightarrow CH_3CH_2-Br + H_2O$

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

(ii) 

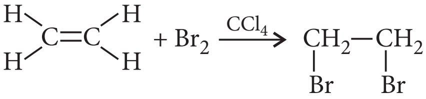
4-Chloromethylphenol

36. (i) *Refer to answer 28.*

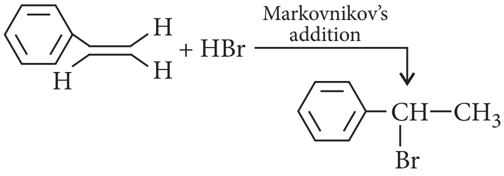
(ii) 

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

37. (i) $C_6H_5N_2Cl + KI \longrightarrow C_6H_5I + N_2 + KCl$

(ii) 

38. (i) *Refer to answer 28.*

(ii) 

(iii) *Refer to answer 36 (ii).*

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

(ii) *Refer to answer 28.*

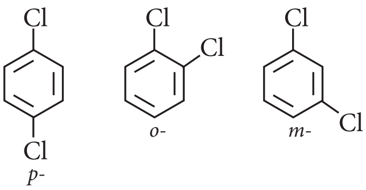
(iii) *Refer to answer 33(i).*

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 force 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.

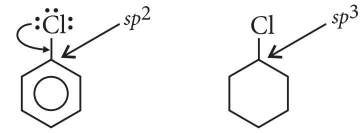
45. The boiling point of ethyl bromide is higher due to the greater magnitude of the van der Waals forces which depend upon molecular size and mass.

46. (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.

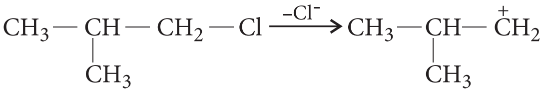
Hence dipole moment is smaller than cyclohexyl chloride which has a longer C—Cl single bond.



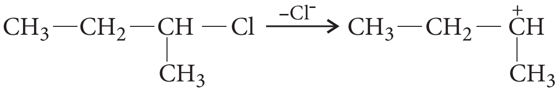
Chlorobenzene Cyclohexyl chloride

(ii) *Refer to answer 41.*

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

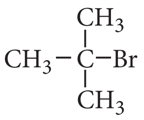


$$\underset{\text{1-Chloro-2-methylpropane}}{\mathrm{CH_3-}\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{CH}}\mathrm{-CH_2-Cl}} \xrightarrow{-\mathrm{Cl^-}} \underset{(1°\ \text{Carbocation})}{\mathrm{CH_3-}\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{CH}}\mathrm{-}\overset{+}{\mathrm{C}}\mathrm{H_2}}$$



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

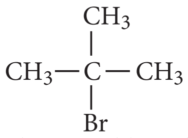
As, 2° carbocation is more stable than 1° carbocation thus, 2-chlorobutane is more reactive towards S_N1 reaction.

48. 

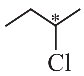
$$\mathrm{CH_3-}\overset{\overset{\mathrm{CH_3}}{|}}{\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{C}}}\mathrm{-Br}$$

Tertiary butyl bromide
or 2-Bromo-2-methylpropane

49. $CH_3—CH_2—Br$ would undergo S_N2 reaction faster due to formating of less steric hindrance.

50.  $\mathrm{CH_3-}\overset{\overset{\mathrm{CH_3}}{|}}{\underset{\underset{\mathrm{Br}}{|}}{\mathrm{C}}}\mathrm{-CH_3}$ will undergo S_N1 reaction faster due to stable carbocation.

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

52.  is a chiral molecule.

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

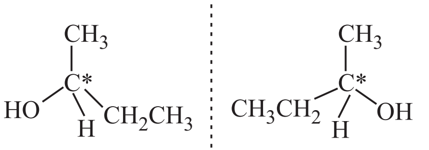
54. CH_3CN is formed by nucleophilic substitution reaction.

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

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

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

56. The (±)-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.



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

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

58. KCN is predominantly ionic and provides cyanide ions in solution

$$\underset{\substack{\text{Methyl}\\ \text{bromide}}}{CH_3Br} + KCN \longrightarrow \underset{\text{Methyl cyanide}}{CH_3C\equiv N} + KBr$$

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

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

59. Grignard reagents react with water to form alkanes.

$$R\text{—}Mg\text{—}X + H_2O \longrightarrow R\text{—}H + Mg\begin{matrix}\diagup X\\ \diagdown OH\end{matrix}$$

So, they must be prepared under anhydrous conditions.

60. 

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

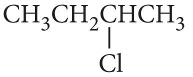
$$(CH_3)_2CHCH_2Br > CH_3CH_2CH_2CH_2Br$$

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

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

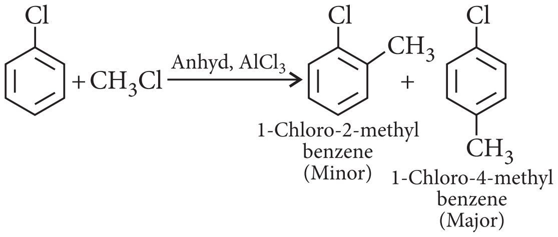
63. 1-Bromopentane is a primary alkyl halide, hence reacts faster in S_N2 displacement than secondary halide 2-bromopentane.

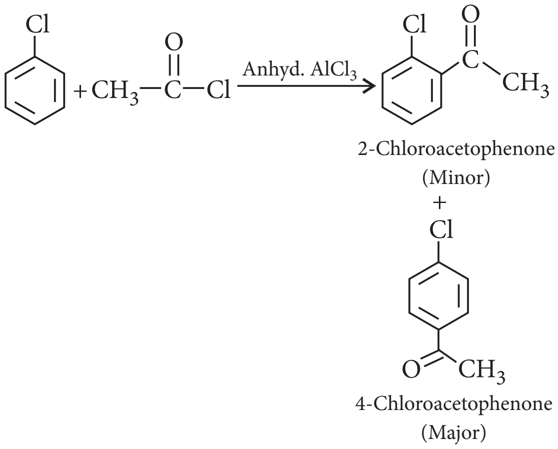
64. 2-Bromobutane will react faster in S_N1 displacement reaction because it will form more stable secondary carbocation intermediate.

65. 

$CH_3CH_2\underset{\substack{|\\ Cl}}{C}HCH_3$ hydrolyses easily with KOH because it is secondary halide.

66. Haloarenes can undergo both freidal craft alkylation (with alkyl halide) or freidal 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.

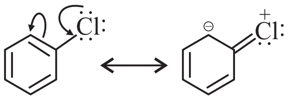
$$CHCl_3 + \frac{1}{2}O_2 \rightarrow COCl_2 + HCl$$

It is kept in dark coloured bottles to prevent the oxidation.

68. CH_3Cl will react faster in S_N2 reaction with OH^-.

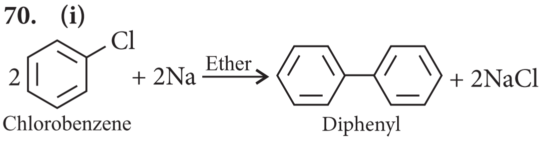
69. (i) In halobenzene C—*X* bond has partial double bond character due to resonance while CH_3—*X* bond is single bond.

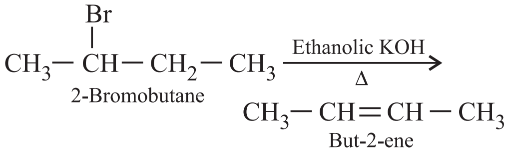
Thus bond length of C—*X* bond in halobenzene is smaller than that in CH_3—*X*.



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

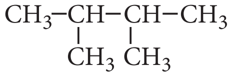
70. **(i)**



(ii) 

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

2-Bromobutane

71. (i) 

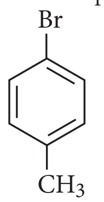
$CH_3-\underset{\substack{|\\ CH_3}}{C}H-\underset{\substack{|\\ CH_3}}{C}H-CH_3$

(ii) CH_3CH_2NC

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.

73. (i) $\underset{\text{Pent-2-ene}}{CH_3-CH_2-CH=CH-CH_3}$ (Saytzeff rule)

(ii)  (Friedel—Crafts alkylation)

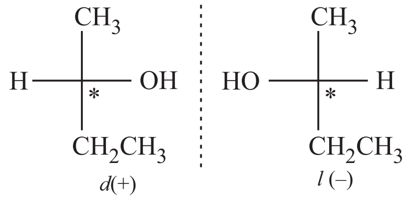
4-Bromotoluene

74. (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.

$$CH_3-CH_2-CH_2-CH_2OH$$

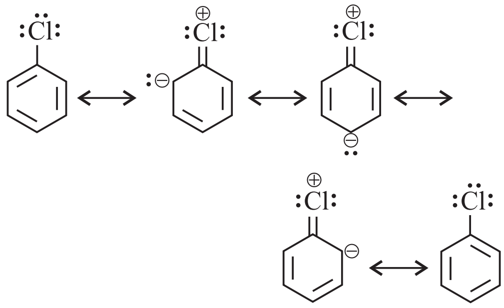
Butan-1-ol
(Optically inactive)
(No chiral carbon)

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

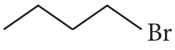


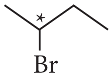
Butan-2-ol

(ii)



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

75. (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.

76. (i) *Refer to answer 55.*

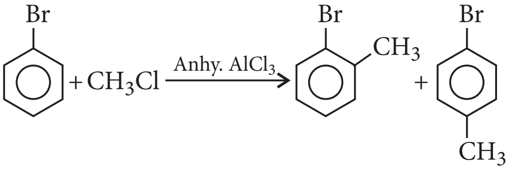
(ii) *Refer to answer 66.*

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.

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

(ii)

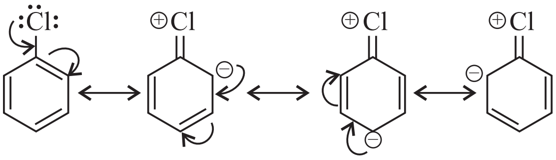


79. A nucleophile which can attack from more than one centres, is known as ambident nucleophile.

e.g., $^{-}\ddot{C}\equiv N\colon$ 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) Difference in hybridisation of carbon atom in C—*X* bond.

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

(ii) *Refer to answer 67.*

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 $C \rightarrow X$ 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.

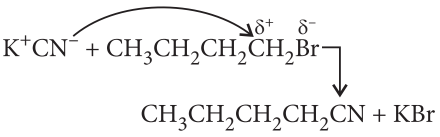
Example :

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

Butan-2-ol

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

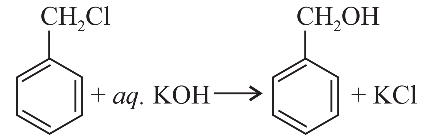
85. Normal butyl bromide will give S_N2 reaction :



$$K^+CN^- + CH_3CH_2CH_2\overset{\delta^+}{C}H_2\overset{\delta^-}{Br} \longrightarrow CH_3CH_2CH_2CH_2CN + KBr$$

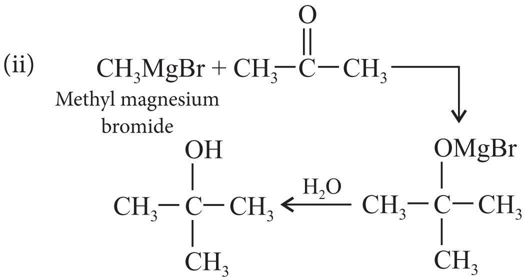
n-Butyl cyanide

86. (i)



Benzyl chloride Benzyl alcohol

(ii)



$$CH_3MgBr + CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow CH_3-\underset{CH_3}{\overset{OMgBr}{C}}-CH_3 \xrightarrow{H_2O} CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_3$$

2-Methylpropan-2-ol

87. (i) 1-Bromopentane, as it is a primary alkyl halide.

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

88. (i) H_2SO_4 is an oxidant. KI reacts with H_2SO_4 and give HI and H_2SO_4 oxidises HI to I_2.

$2KI + H_2SO_4 \rightarrow 2KHSO_4 + 2HI$

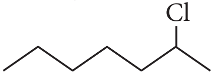
$2HI + H_2SO_4 \rightarrow 2H_2O + I_2 + SO_2$

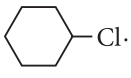
Thus HI will not be available for reaction with alcohol to form alkyl iodide.

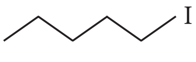
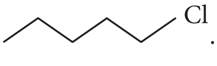
This is why sulphuric acid is not used during the reaction of alcohols with KI.

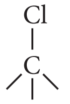
(ii) *Refer to answer 80.*

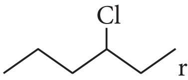
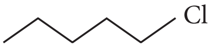
89. (i) *Refer to answer 59.*

(ii)  undergoes faster S_N1 reaction.

90. (i)  is primary halide and therefore, undergoes S_N2 reaction faster than the secondary halide .

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

91. (i)  : Tertiary halide reacts faster than secondary halide because of the greater stability of *tert.* carbocation.

(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 *R*I > *R*Br > *R*Cl.

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.

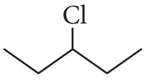
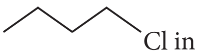
93. (i) *Refer to answer 80.*

(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.

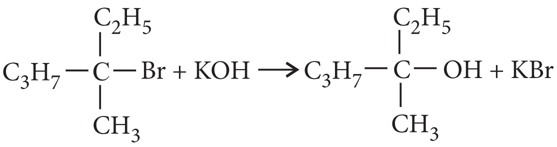
94. (i) *Refer to answer 80.*

(ii) *Refer to answer 57.*

95. (i) *Refer to answer 80.*

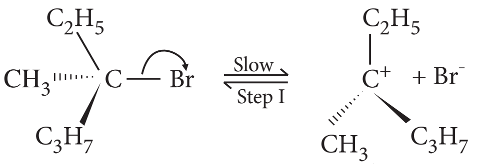
(ii) Due to greater stability of 2° carbocation over 1° carbocation,  will react faster than  in S_N1 reaction.

96. In S_N1 mechanism of substitution reaction, the rate of reaction depends upon the concentration of only one reactant. It is two steps reactants.

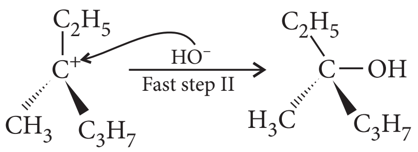


$$C_3H_7-\underset{CH_3}{\overset{C_2H_5}{C}}-Br + KOH \longrightarrow C_3H_7-\underset{CH_3}{\overset{C_2H_5}{C}}-OH + KBr$$

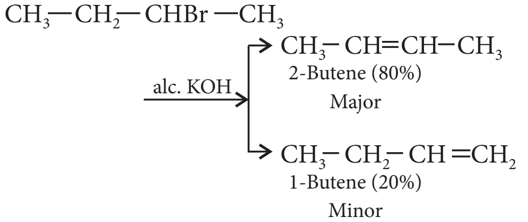
Mechanism :



Carbocation



97. Saytzeff rule : In elimination reaction alkene having the lesser number of hydrogen on the double bonded carbon atom is formed. This generalisation is known as Saytzeff rule for example.

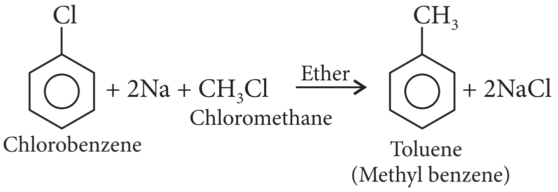


$$CH_3-CH_2-CHBr-CH_3 \xrightarrow{\text{alc. KOH}} \underset{\text{2-Butene (80\%) Major}}{CH_3-CH=CH-CH_3} + \underset{\text{1-Butene (20\%) Minor}}{CH_3-CH_2-CH=CH_2}$$

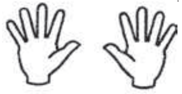
98. (i) **Wurtz reaction :** It converts alkyl halide into higher alkane in presence of sodium metal and dry ether.

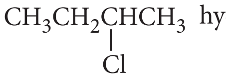
$$\underset{\text{Chloromethane}}{CH_3Cl} + 2Na + CH_3Cl \xrightarrow{\text{Ether}} 2NaCl + \underset{\text{Ethane}}{C_2H_6}$$

(ii) **Wurtz-Fittig reaction :** It converts aryl halide into alkyl arenes in presence of sodium metal and ether.



99. (i) **Chiral object :** An object which has no plane of symmetry (cannot be divided into two identical halves) is called chiral (Greek; Chiral-Hand) or dissymmetric or asymmetric. A Chiral object is not superimposable on its mirror image.
e.g., left and right hand of a person are mirror images of each other and are not superimposable.



(ii)  $CH_3CH_2\underset{\underset{Cl}{|}}{C}HCH_3$ 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  .

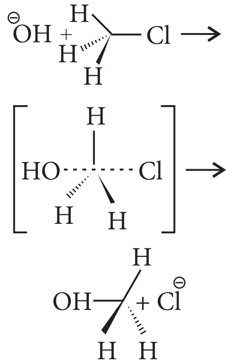
100. (i) 1-Bromopentane > 2-Bromopentane > 2-Bromo-2-methylbutane.

(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

101. (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.

102.

	S_N1 mechanism	S_N2 mechanism
1.	It is two step process, carbocation interme-diate is formed.	It is single step process. No intermediate is formed.
2.	It obeys 1st order kientics. Rate = k [Reactant]	It obeys 2nd order kinetics. Rate = k[Reactant] [Nuclephile]
3.	Order of reactivity 3° > 2° > 1°.	Order of reactivity 1° > 2° > 3°.
4.	Optically inactive product is formed (racemic mixture).	Inversion of configuration takes place.
5.	*e.g.,* $(CH_3)_3CBr + OH^-$ 2-Bromo-2-methyl propane ↓ $(CH_3)_3COH + Br^-$ 2-Methylpropan-2-ol	*e.g.,* 

103. (ii) DDT is used as an insecticide and iodoform is used as a mild antiseptic.

104. (i) $\underset{\text{Chloroform}}{2CHCl_3 + O_2} \xrightarrow{\text{Light}} \underset{\text{Carbonyl chloride}}{2COCl_2} + 2HCl$

(ii) $\underset{\text{Chloroform}}{CHCl_3} + Cl_2 \longrightarrow \underset{\text{Carbon tetrachloride}}{CCl_4} + HCl$