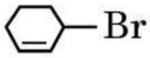
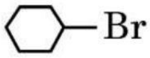
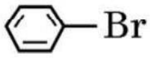
Haloalkanes and Haloarenes

1. The compound which undergoes S_N1 reaction most rapidly is : (2024)

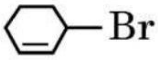
(A) 

(B) 

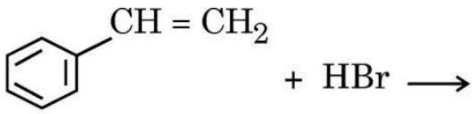
(C) 

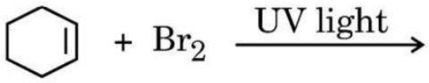
(D) 

Ans.

(A) 

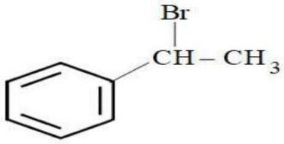
2. Draw the structures of major monohalo products in each of the following reactions : (2024)

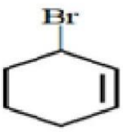
(i) 

(ii) 

Ans.

(i)



(ii) 

3. Give reasons for the following : (2024)

(i) Grignard reagent should be prepared under anhydrous conditions.

Ans. It reacts with water to form alkane.

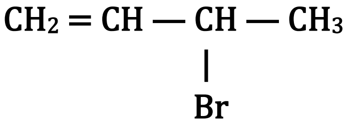
(ii) Alkyl halides give alcohol with aqueous KOH whereas in the presence of alcoholic KOH, alkenes are formed.

Ans. Alcoholic KOH acts as a stronger base than aqueous KOH leads to elimination reaction of alkyl halide. / alkoxide ions in alcoholic KOH acts as a stronger base due to which elimination reaction takes place.

4. Which of the following is an allylic halide ? (2024)

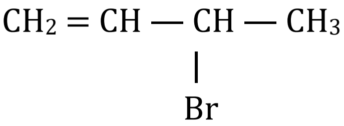
(i) $CH_3 - CH = CH - Br$

(ii)



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

Ans.



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

5. Out of chlorobenzene and 2,4,6-trinitrochlorobenzene, which is more reactive towards nucleophilic substitution and why ? (2024)

Ans. 2,4,6-trinitrochlorobenzene, because of electron withdrawing nature of $-NO_2$ group.

6. Which isomer of C_4H_9Cl has the lowest boiling point ? (2024)

Ans. $(CH_3)_3C\text{-}CI$ / tert-butyl chloride

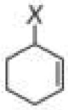
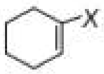
Previous Years' CBSE Board Questions

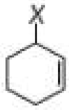
6.1 Classification

MCQ

1. Which one of the following halides contains $C_{sp^2}-X$ bond?
   (a) Allyl halide (b) Alkyl halide
   (c) Benzyl halide (d) Vinyl halide
   (Term I, 2021-22) Ap

VSA (1 mark)

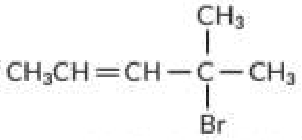
2. Out of  and , which is an example of allylic halide? *(AI 2017)*

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

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

6.2 Nomenclature

VSA (1 mark)

5. Write the IUPAC name of  $CH_3CH=CH-\underset{Br}{\overset{CH_3}{C}}-CH_3$
   (AI 2019, Delhi 2013)

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

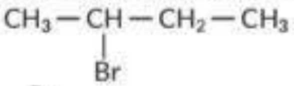
7. Write the structure of 3-bromo-2-methylprop- 1-ene. *(Delhi 2017)* U

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

SA I (2 marks)

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

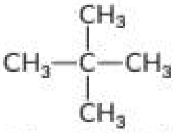
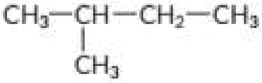
SA II (3 marks)

10. Give the IUPAC names of the following compounds :
    (i)  $CH_3-\underset{Br}{CH}-CH_2-CH_3$
    (ii) 
    (iii) $CH_2=CH-CH_2-Cl$ *(AI 2015C)* Ap

6.4 Methods of Preparation of Haloalkanes

MCQ

11. The synthesis of alkyl flouride is best obtained from
    (a) Free radicals (b) Swarts reaction
    (c) Sandmeyer reaction (d) Finkelstein reaction.
    (2023)

12. Which of the following isomer of pentane (C_5H_{12}) will give three isomeric monochlorides on photochemical chlorination?
    (a)  $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$ (b) $CH_3CH_2CH_2CH_2CH_3$
    (c)  $CH_3-\underset{CH_3}{CH}-CH_2-CH_3$ (d) All of the above.
    (Term I, 2021-22) An

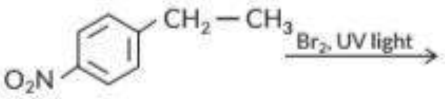
VSA (1 mark)

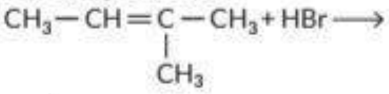
13. How can you convert the following?
    But-1-ene to 1-iodobutane *(NCERT, 1/3, 2020)* An

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

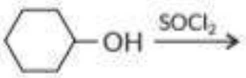
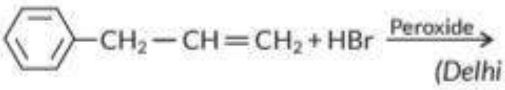
15. Write equation for preparation of 1-iodobutane from 1-chlorobutane. *(1/3, AI 2019)*

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

17. Write the major product in the following :
    
    (1/3, AI 2016)

18. Write the structure of the major product in the following reaction :
     $CH_3-CH=\underset{CH_3}{C}-CH_3+HBr\longrightarrow$
    (1/3, AI 2015)

SA I (2 marks)

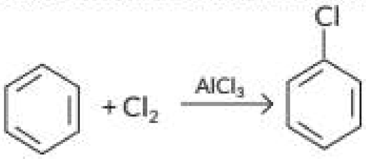
19. Draw the structure of major monohalo product in each of the following reactions :
    (i)  *(NCERT)*
    (ii) 
    (Delhi 2014)

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

6.5 Preparation of Haloarenes

MCQ

21. The species that attacks benzene in following is



(a) Cl^- (b) $AlCl_4^-$ (c) $AlCl_3$ (d) Cl^+

(2023)

6.6 Physical Properties

MCQ

22. Which of the following has highest boiling point?
(a) C_2H_5-F (b) C_2H_5-Cl
(c) C_2H_5-Br (d) C_2H_5-I

(Term I, 2021-22)

23. **Assertion (A) :** Boiling points of alkyl halides decrease in the order *R-I > R-Br > R-Cl > R-F*.
Reason (R) : van der Waals' forces decrease with increase in the size of halogen atom.
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true and R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true. *(2020)*

VSA (1 mark)

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

25. Explain the following :
Alkyl halides, though polar, are immiscible with water. *(NCERT, 1/2, AI 2017C, 1/3, Foreign 2015)*

26. Explain why the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride. *(NCERT, 1/3, Delhi 2016)*

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

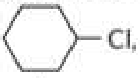
6.7 Chemical Reactions

Nucleophilic Substitution Reactions

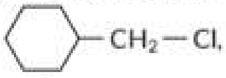
MCQ

28. Which of the following molecules has a chiral centre correctly labelled with an asterisk(*)?
(a) $CH_3C^*HBrCH_3$
(b) $CH_3C^*HClCH_2Br$
(c) $HOCH_2C^*H(OH)CH_2OH$
(d) $CH_3C^*Br_2CH_3$ *(2023)*

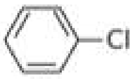
29. Consider the following compounds



I



II

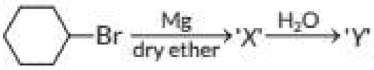


III

the correct order of reactivity towards S_N2 reaction
(a) I > III > II (b) II > III > I
(c) II > I > III (d) III > I > II

(Term I, 2021-22)

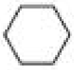
30. In the reaction,

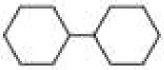


compound 'Y' is

(a)


(b)


(c)


(d)


(Term I, 2021-22) An

31. Enantiomers differ only in
(a) boiling point
(b) rotation of polarised light
(c) melting point
(d) solubility. *(Term I, 2021-22)* R

32. **Assertion (A) :** Chlorobenzene is less reactive towards nucleophilic substitution reaction.
Reason (R) : Nitro group in chlorobenzene increases its reactivity towards nucleophilic substitution reaction.
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true and R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true. *(Term I, 2021-22)* U

33. The reaction given below:

is called
(a) Wurtz reaction (b) Wurtz-Fitting reaction
(c) Fitting reaction (d) None of the above

(2021 C)

34. Racemisation occurs in
(a) S_N2 reaction
(b) S_N1 reaction
(c) neither S_N2 nor S_N1 reaction
(d) S_N2 reaction as well as S_N1 reaction. *(2020)* R

35. The conversion of an alkyl halide into an alcohol by aqueous NaOH is classified as
(a) a dehydrohalogenation reaction
(b) a substitution reaction
(c) an addition reaction
(d) a dehydration reaction *(2020)* U

36. Out of the following, the one which is most reactive towards nucleophilic substitution reaction is
(a) $CH_2=CH-Cl$
(b) C_6H_5-Cl
(c) $CH_3CH=CH-Cl$
(d) $CH_3-CH_2-CH_2-Cl$ *(2020 C)*

VSA (1 mark)

Read the passage given below and answer the following questions (Q. No. 37 to 41):

The substitution reaction of alkyl halide mainly occurs by S_N1 or S_N2 mechanism. Whatever mechanism alkyl halides follow for the substitution reaction to occur, the polarity of the carbon halogen bond is responsible for these substitution reactions. The rate of S_N1 reactions are governed by the stability of carbocation whereas for S_N2 reactions steric factor is the deciding factor. If the starting material is a chiral compound, we may end up with an inverted product or racemic mixture depending upon the type of mechanism followed by alkyl halide. Cleavage of ethers with HI is also governed by steric factor and stability of carbocation, which indicates that in organic chemistry, these two major factors help us in deciding the kind of product formed.

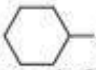
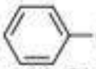
37. Predict the stereochemistry of the product formed if an optically active alkyl halide undergoes substitution reaction by S_N1 mechanism.

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

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

40. Give one use of CHI_3.

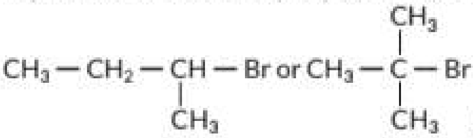
41. Write the structures of the products formed when anisole is treated with HI. *(2020)*

42. Out of  $-CH_2Cl$ and  $-CH_2-Cl$, which will react faster in S_N1 reaction with OH^-? *(One word, 2020)*

43. Why is *t*-butyl bromide more reactive towards S_N1 reaction as compared to *n*-butyl bromide? *(2019)*

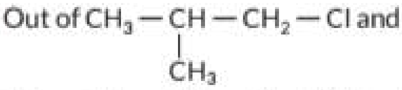
44. Out of chlorobenzene and cyclohexyl chloride, which one is more reactive towards nucleophilic substitution reaction and why? *(2019)*

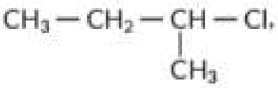
45. Which alkyl halide from the following pair would you expect to react more rapidly by an S_N2 mechanism?



$CH_3-CH_2-\underset{CH_3}{CH}-Br$ or $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br$ *(AI 2019)* An

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

47. Out of  $CH_3-\underset{CH_3}{CH}-CH_2-Cl$ and

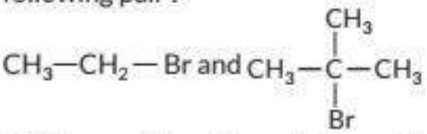
 $CH_3-CH_2-\underset{CH_3}{CH}-Cl$, which is more reactive towards S_N1 reaction and why? *(Delhi 2016)*

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 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 and $CH_3-\underset{Br}{\overset{CH_3}{C}}-CH_3$ *(AI 2015)*

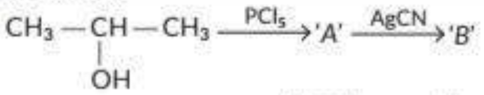
51. Which would undergo S_N2 reaction faster in the following pair and why?
CH_3-CH_2-Br and CH_3-CH_2-I *(Foreign 2015)*

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
(AI 2014, Delhi 2014C)

SA I (2 marks)

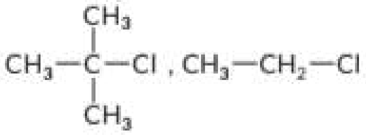
54. (a)  $CH_3-\underset{OH}{CH}-CH_3 \xrightarrow{PCl_5} \text{'A'} \xrightarrow{AgCN} \text{'B'}$

(b) $CH_3CH_2CH_2Cl + KOH \xrightarrow{ethanol} \text{'A'} \xrightarrow{HBr} \text{'B'}$
(2023)

55. Why haloarenes are not reactive towards nucleophilic substitution reaction? Give two reasons. *(2023)*

56. In the following pairs of halogen compounds, which would undergo S_N2 reaction faster?
Given reason in support of your answer.

(i) 

(ii)  $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl$, CH_3-CH_2-Cl *(2021 C)*

57. Write the mechanism of the following S_N1 reaction.
$(CH_3)_3C-Br \xrightarrow{aq.\ NaOH} (CH_3)_3C-OH + NaBr$
(2/3, 2020)

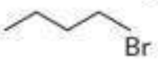
58. Give reasons:
(i) Racemic mixture is optically inactive.
(ii) The presence of nitro group $(-NO_2)$ at *o/p* positions increases the reactivity of haloarenes towards nucleophilic substitution reactions.
(AI 2019, 2/3, Delhi 2015)

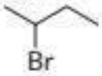
59. Give reasons:
(i) C—Cl bond length in chlorobenzene is shorter than C—Cl bond length in CH_3-Cl.
(ii) S_N1 reactions are accompanied by racemization in optically active alkyl halides.
(2/3, Delhi 2016) Ap

60. How do you convert?
(i) Chlorobenzene to Biphenyl
(ii) 2-Bromobutane to but-2-ene *(2/3, AI 2016)*

61. (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)*

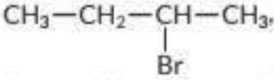
62. (i) Which alkyl halide from the following pair is chiral and undergoes faster S_N2 reaction?

(a) 

(b) 

(ii) Out of S_N1 and S_N2, which reaction occurs with
(a) inversion of configuration
(b) racemisation? *(2/3, Delhi 2014)* An

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



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

$CH_3-CH_2-CH_2-CH_2-Br$

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

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

SA II (3 marks)

65. Write main product formed when
(a) Methyl chloride is treated with NaI/Acetone.
(b) 2,4,6-trinitrochlorobenzene is subjected to hydrolysis.
(c) *n*-Butyl chloride is treated with alcoholic KOH. *(2023)*

66. Give reasons :
(a) Grignard reagent should be prepared under anhydrous conditions,
(b) Alkyl halides are immiscible with water although they are polar, and
(c) Chloroform is stored in dark coloured bottles filled up to the brim. *(2020 C)*

67. (a) Define the following terms :
(i) Enantiomers (ii) Racemic mixture
(b) Why is chlorobenzene resistant to nucleophilic substitution reaction ? *(2019)*

68. (i) Out of $(CH_3)_3C-Br$ and $(CH_3)_3C-I$, which one is more reactive towards S_N1 and why?
(ii) Write the product formed when *p*-nitrochlorobenzene is heated with aqueous NaOH at 443 K followed by acidification.
(iii) Why *dextro* and *laevo*-rotatory isomers of butan-2-ol are difficult to separate by fractional distillation? *(Delhi 2019)*

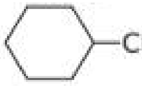
LA (4 marks)

The following questions are case-based questions. Read the case carefully and answer the questions that follow:

69. **Nucleophilic Substitution**

Nucleophilic substitution reaction of haloalkane can be conducted according to both S_N1 and S_N2 mechanisms. S_N1 is a two step reaction while S_N2 is a single step reaction. For any haloalkane which mechanism is followed depends on factors such as structure of haloalkane, properties of leaving group, nucleophilic reagent and solvent.

Influences of solvent polarity : In S_N1 reaction, the polarity of the system increases from the reactant to the transition state, because a polar solvent has a greater effect on the transition state than the reactant, thereby reducing activation energy and accelerating the reaction, In S_N2 reaction, the polarity of the system generally does not change from the reactant to the transition state and only charge dispersion occurs. At this time, polar solvent has a great stabilizing effect on Nu^- than the transition state, thereby increasing the activation energy and slow down the reaction rate. For example, the decomposition rate (S_N1) of tertiary chlorobutane at 25°C in water (dielectric constant 79) is 300000 times faster than in ethanol (dielectric constant 24). The reaction rate (S_N2) of 2-Bromopropane and NaOH in ethanol containing 40% water is twice slower than in absolute ethanol. Hence, the level of solvent polarity has influence on both S_N1 and S_N2 reaction, but with different results. Generally speaking weak polar solvent is favourable for S_N2 reaction, while strong polar solvent is favourable for S_N1. Generally speaking the substitution reaction of tertiary haloalkane is based on S_N1 mechanism in solvents with a strong polarity (for example ethanol containing water)

Answer the following questions.
(a) Why racemisation occurs in S_N1?
(b) Why is ethanol less polar than water?
(c) Which one of the following in each pair is more reactive towards S_N2 reaction?
(i) CH_3CH_2-I or CH_3CH_2-Cl
(ii)  or 

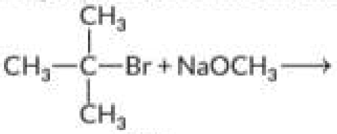
OR

(c) Arrange the following in the increasing order of their reactivity towards S_N1 reactions:
(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane
(ii) 1-Bromo-3-methylbutane, 2-Bromo-2 methylbutane, 2-Bromo-3-methylbutane *(2023)*

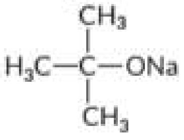
Reaction with Metals, Electrophilic Substitution and Elimination Reactions

MCQ

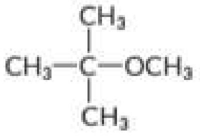
70. Major product formed in the following reaction



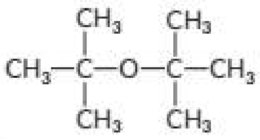
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-Br + NaOCH_3 \longrightarrow$

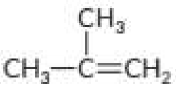
(a) 

$H_3C-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-ONa$

(b) 

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-OCH_3$

(c) 
$CH_3-C(CH_3)_2-O-C(CH_3)_2-CH_3$

(d) 
$CH_3-C(CH_3)=CH_2$

(Term I, 2021-22) An

VSA **(1 mark)**

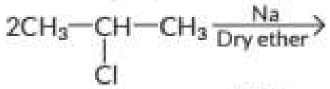
71. Write the major product(s) of the following reaction :

(1/3, 2020)

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

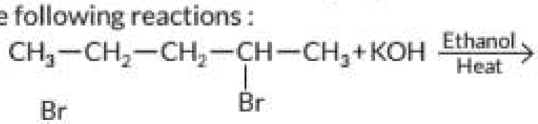
SA I **(2 marks)**

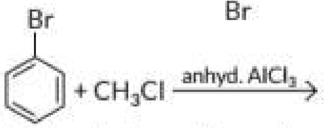
73. Write the major product(s) in the following :

(i) 
$2CH_3-CH(Cl)-CH_3 \xrightarrow[\text{Dry ether}]{\text{Na}}$

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

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

(i) 
$CH_3-CH_2-CH_2-CH(Br)-CH_3 + KOH \xrightarrow[\text{Heat}]{\text{Ethanol}}$

(ii)  *(2/3, AI 2015)*

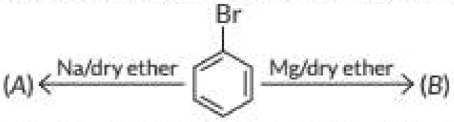
75. Write chemical equations when
   (i) ethyl chloride is treated with aqueous KOH.
   (ii) chlorobenzene is treated with CH_3COCl in presence of anhydrous $AlCl_3$. *(Foreign 2014)*

76. 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)*

SA II **(3 marks)**

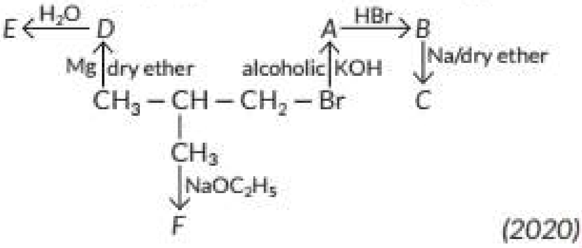
77. (i) Write the structure of major alkene formed by β-elimination of 2, 2, 3-trimethyl-3-bromopentane with sodium ethoxide in ethanol.
   (ii) Which one of the compounds in the following pairs is chiral?

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



(2020) An

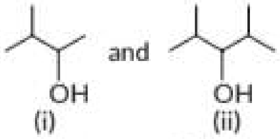
78. Identify A, B, C, D, E and F in the following :



(2020) An

79. Among all the isomers of molecular formula C_4H_9Br, identify
   (a) the one isomer which is optically active.
   (b) the one isomer which is highly reactive towards S_N2.
   (c) the two isomers which give same product on dehydrohalogenation with alcoholic KOH. *(2019)*

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



   (b) Write the structure of the product when chlorobenzene is treated with methyl chloride in the presence of sodium metal and dry ether.
   (c) Write the structure of the alkene formed by dehydrohalogenation of 1-bromo-1-methylcyclohexane with alcoholic KOH. *(2018)*

81. Following compounds are given to you :
   2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane
   (i) Write the compound which is most reactive towards S_N2 reaction.
   (ii) Write the compound which is optically active.
   (iii) Write the compound which is most reactive towards β-elimination reaction. *(Delhi 2017)* U

CBSE Sample Questions

6.4 Methods of Preparation of Haloalkanes

MCQ

1. Major product obtained on reaction of 3-phenylpropene with HBr in presence of organic peroxide is
   (a) 3-phenyl-1-bromopropane
   (b) 1-phenyl-3-bromopropane
   (c) 1-phenyl-2-bromopropane
   (d) 3-phenyl -2- bromopropane. *(Term I, 2021-22)*

2. Alkenes decolourise bromine water in presence of CCl_4 due to formation of
   (a) allyl bromide (b) vinyl bromide
   (c) bromoform (d) vicinal dibromide. *(Term I, 2021-22)*

6.5 Preparation of Haloarenes

MCQ

3. The reaction of toluene with Cl_2 in presence of $FeCl_3$ gives '*X*' while the reaction of toluene with Cl_2 in presence of light gives '*Y*'. Thus '*X*' and '*Y*' are
   (a) *X* = benzyl chloride, *Y* = *o*- and *p*-chlorotoluene
   (b) *X* = *m*-chlorotoluene, *Y* = *p*-chlorotoluene
   (c) *X* = *o*- and *p*-chlorotoluene, *Y* = trichloromethylbenzene
   (d) *X* = benzyl chloride, *Y* = *m*-chlorotoluene.
   (Term I, 2021-22)

6.6 Physical Properties

MCQ

4. Which of the following isomers has the highest melting point?
   (a) 1,2-Dichlorobenzene
   (b) 1,3-Dichlorobenzene
   (c) 1,4-Dichlorobenzene
   (d) All isomers have same melting points.
   (Term I, 2021-22)

6.7 Chemical Properties

MCQ

5. Which one of the following compounds is more reactive towards S_N1 reaction?
   (a) $CH_2{=}CHCH_2Br$
   (b) $C_6H_5CH_2Br$
   (c) $C_6H_5CH(C_6H_5)Br$
   (d) $C_6H_5CH(CH_3)Br$ *(2022-23)*

6. Which of the following is a correct statement for C_2H_5Br?
   (a) It reacts with metallic Na to give ethane.
   (b) It gives nitroethane on heating with aqueous solution of $AgNO_2$.
   (c) It gives C_2H_5OH on boiling with alcoholic potash.
   (d) It forms diethylthioether on heating with alcoholic KSH. *(Term I, 2021-22)*

7. Which reagents are required for one step conversion of chlorobenzene to toluene?
   (a) $CH_3Cl/AlCl_3$
   (b) CH_3Cl, Na, dry ether
   (c) CH_3Cl/Fe dark
   (d) $NaNO_2$/ HCl /0-5°C *(Term I, 2021-22)*

8. Complete the following analogy:
   Same molecular formula but different structures : *A* :: Non superimposable mirror images : *B*
   (a) *A* : Isomers, *B* : Enantiomers
   (b) *A* : Enantiomers, *B* : Racemic mixture
   (c) *A* : Stereoisomers, *B* : Retention
   (d) *A* : Isomers, *B* : Stereoisomers *(2020-21)*

9. Identify *A*, *B*, *C* and *D* :

$$\begin{tikzcd}
 & D & \\
C & C_2H_5Cl \arrow[l, "AgCN"'] \arrow[u, "KCN"'] \arrow[r, "alc.\ KOH"] \arrow[d, "aq.\ KOH"] & A \\
 & B &
\end{tikzcd}$$

   (a) $A = C_2H_4, B = C_2H_5OH, C = C_2H_5NC, D = C_2H_5CN$
   (b) $A = C_2H_5OH, B = C_2H_4, C = C_2H_5CN, D = C_2H_5NC$
   (c) $A = C_2H_4, B = C_2H_5OH, C = C_2H_5CN, D = C_2H_5NC$
   (d) $A = C_2H_5OH, B = C_2H_4, C = C_2H_5NC, D = C_2H_5CN$
   (2020-21)

SA I **(2 marks)**

10. Give reason for the following:
    (a) During the electrophilic substitution reaction of haloarenes, *para*-substituted derivative is the major product.
    (b) The product formed during S_N1 reaction is a racemic mixture.

    OR

    (a) Name the suitable alcohol and reagent, from which 2-chloro-2-methyl propane can be prepared.
    (b) Out of the chloromethane and fluoromethane, which one has higher dipole moment and why?
    (2022-23)

11. The following haloalkanes are hydrolysed in presence of *aq.* KOH :
    (i) 2-Chlorobutane
    (ii) 2-Chloro-2-methylpropane
    Which of the above is most likely to give a racemic mixture? Justify your answer. *(2020-21)*

12. With the help of resonating structures explain the effect of presence of nitro group at *ortho*-position in chlorobenzene.

    OR

    Carry out the following conversions in not more than 2 steps :
    (i) Aniline to chlorobenzene
    (ii) 2-Bromopropane to 1-bromopropane *(2020-21)*

SA II **(3 marks)**

13. (a) Identify the major product formed when 2-cyclohexylchloroethane undergoes a dehydrohalogenation reaction. Name the reagent which is used to carry out the reaction.
    (b) Why are haloalkanes more reactive towards nucleophilic substitution reactions than haloarenes and vinylic halides?

    OR

    (a) Name the possible alkenes which will yield 1-chloro-1-methylcyclohexane on their reaction with HCl. Write the reactions involved.
    (b) Allyl chloride is hydrolysed more readily than *n*-propyl chloride. Why? *(2022-23)*

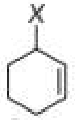
Detailed SOLUTIONS

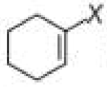
Previous Years' CBSE Board Questions

1. (d) : Vinyl halide contains $C_{sp^2}-X$ bond.

$$\overset{sp^2}{H_2C}=\overset{sp^2}{CH}-Cl$$

Vinyl chloride

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

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

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

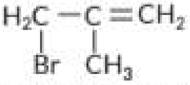
Answer Tips

- Benzylic halide : $Ph-\overset{|}{\underset{|}{C}}-X$

5. 4-Bromo-4-methylpent-2-ene

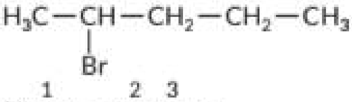
6. $Cl-\overset{4}{C}H_2-\overset{3}{C}H=\overset{2}{C}H-\overset{1}{C}H_2-Br$

1-Bromo-4-chlorobut-2-ene

7. 

$$H_2\underset{Br}{\underset{|}{C}}-\underset{CH_3}{\underset{|}{C}}=CH_2$$

3-Bromo-2-methylprop-1-ene

8. 

$$H_3C-\underset{Br}{\underset{|}{C}H}-CH_2-CH_2-CH_3$$

9. (i) $\overset{1}{C}H_2=\overset{2}{C}H\overset{3}{C}H_2Br$

3-Bromoprop-1-ene

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

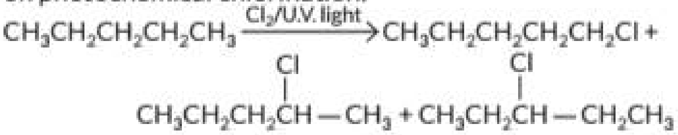
10. (i) 2-Bromobutane (ii) 1,3-Dibromobenzene

(iii) 3-Chloropropene

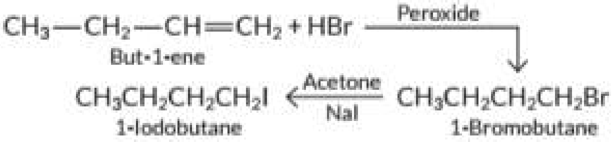
11. (b): Alkyl chloride or bromide when heated with heavy metal fluoride gives alkyl fluoride in a reaction called Swarts reaction.

$$CH_3-Br+AgF\longrightarrow CH_3-F+AgBr$$

12. (b) : *n*-Pentane will give three isomeric monochlorides on photochemical chlorination.



$$CH_3CH_2CH_2CH_2CH_3\xrightarrow{Cl_2/U.V.\ light}CH_3CH_2CH_2CH_2CH_2Cl+$$
$$CH_3CH_2CH_2\overset{Cl}{\overset{|}{C}H}-CH_3+CH_3CH_2\overset{Cl}{\overset{|}{C}H}-CH_2CH_3$$

13. 

$$\underset{\text{But-1-ene}}{CH_3-CH_2-CH=CH_2}+HBr\xrightarrow{Peroxide}\underset{\text{1-Bromobutane}}{CH_3CH_2CH_2CH_2Br}\xrightarrow[NaI]{Acetone}\underset{\text{1-Iodobutane}}{CH_3CH_2CH_2CH_2I}$$

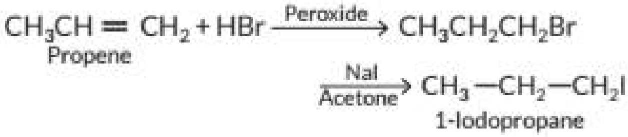
Key Points

- Follow Anti-Markownikoff's path to get the product.

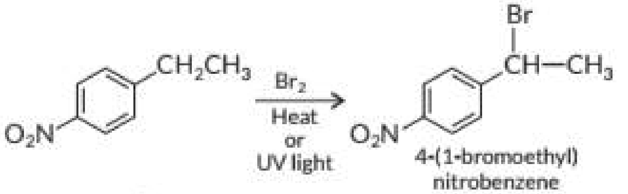
14. Thionyl chloride is preferred because in this reaction alkyl halide is formed along with gases SO_2 and HCl. These two gaseous products are escapable, hence the reaction gives pure alkyl halides.

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

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

16. 

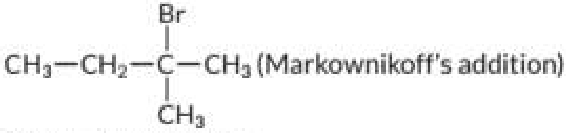
$$\underset{\text{Propene}}{CH_3CH=CH_2}+HBr\xrightarrow{Peroxide}CH_3CH_2CH_2Br\xrightarrow[Acetone]{NaI}\underset{\text{1-Iodopropane}}{CH_3-CH_2-CH_2I}$$

17. 

4-(1-bromoethyl) nitrobenzene

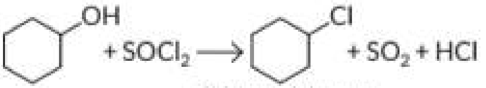
Answer Tips

- Side chain halogenation occurs at high temperature in presence of light and in absence of halogen carriers.

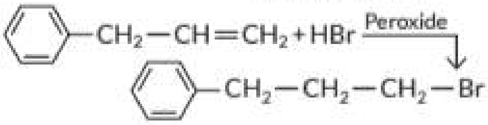
18. 

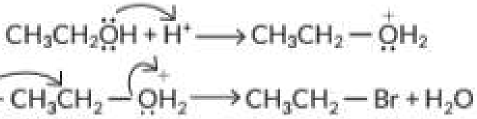
$$CH_3-CH_2-\underset{CH_3}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-CH_3\ \text{(Markownikoff's addition)}$$

2-Bromo-2-methylbutane

19. (i) 

Chlorocyclohexane

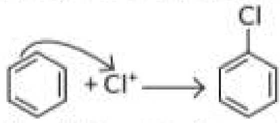
(ii) 

20. 

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

21. (d): 

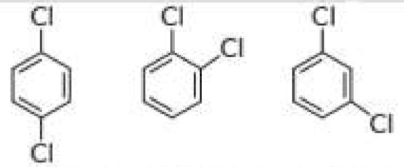
It is an electrophilic substitution reaction. This substitution reaction is initiated by an electrophile Cl^+.



22. (d): C_2H_5-I has highest boiling point due to higher molecular mass.

23. (c): For the same alkyl group, the boiling points of alkyl halides decreases in the order :
$RI > RBr > RCl > RF$. This is because with the increase in size and mass of halogen atom, the magnitude of van der Waals' forces increases.

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



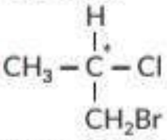
p-isomer *o*-isomer *m*-isomer

25. 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.

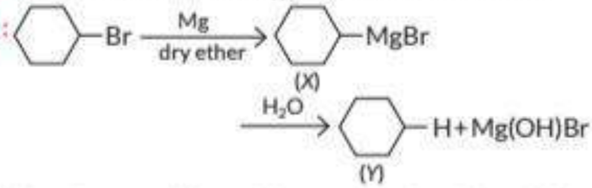
26. There are two reasons :
(i) In case of chlorobenzene, carbon to which chlorine is attached is sp^2-hybridised and is more electronegative than the corresponding carbon in cyclohexyl chloride which is sp^3-hybridised. So the net dipole moment is lower in chlorobenzene.
(ii) In chlorobenzene, C—Cl bond has some double bond character so its bond length is smaller.
Hence, dipole moment of chlorobenzene is smaller than cyclohexyl chloride which has a longer C—Cl single bond.

Chlorobenzene Cyclohexyl chloride

27. *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.

28. (b):

$CH_3-\overset{H}{\underset{CH_2Br}{C^*}}-Cl$ is marked correctly since it is a chiral carbon with four different groups.

29. (c): The correct order of S_N2 reaction is II > I > III.

30. (c):


31. (b): Enantiomers differ only in rotation of polarised light.

32. (b): Chlorobenzene is less reactive towards nucleophilic substitution reaction due to partial double bond character of $C-X$ bond which is very difficult to break.

33. (b): A mixture of an alkyl halide and aryl halide gives an alkylarene when treated with sodium in dry ether. This reaction is called Wurtz - Fitting reaction.

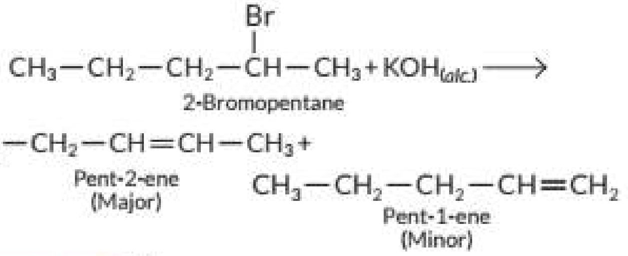
34. (b): S_N1 reactions are accompanied by racemisation.

35. (b): The conversion of an alkyl halide into an alcohol by aqueous NaOH is a substitution reaction.

36. (d): Order of reactivity towards nucleophilic substitution reaction is alkyl halide > vinyl halide > halobenzene.

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

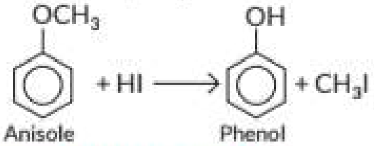
38. Polarimeter is used for measuring the angle by which the plane polarised light is rotated.

39.

$CH_3-CH_2-CH_2-\overset{Br}{CH}-CH_3 + KOH_{(alc)} \longrightarrow$
2-Bromopentane
$CH_3-CH_2-CH=CH-CH_3 +$ $CH_3-CH_2-CH_2-CH=CH_2$
Pent-2-ene (Major) Pent-1-ene (Minor)

Answer Tips

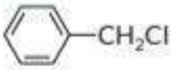
- Apply Saytzeff's rule.
- More substituted alkene will be more stable.

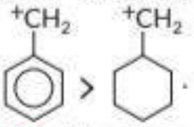
40. Iodoform (CHI_3) is used as a mild antiseptic.

41.


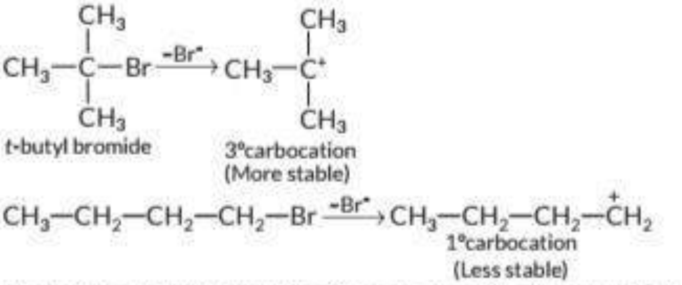
Commonly Made Mistake

- Remember cleavage of phenolic ethers always gives the phenol and the corresponding alkyl halide.

42.  $-CH_2Cl$ will react faster in S_N1 reaction since benzyl carbocation is more stable carbocation than aliphatic primary cyclohexyl carbocation, *i.e.*,



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


$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br \xrightarrow{-Br^-} CH_3-\overset{CH_3}{\underset{CH_3}{C^+}}$
t-butyl bromide 3°carbocation (More stable)
$CH_3-CH_2-CH_2-CH_2-Br \xrightarrow{-Br^-} CH_3-CH_2-CH_2-\overset{+}{C}H_2$
1°carbocation (Less stable)

Therefore, *t*-butyl bromide is more reactive towards S_N1 reaction as compared to *n*-butyl bromide.

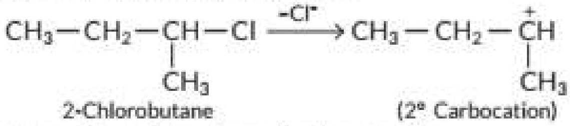
44. Cyclohexyl chloride is more reactive than chlorobenzene towards nucleophilic substitution reaction as it forms a stable 2° carbocation. Aryl halides are extremely

less reactive towards nucleophilic substitution reaction. In aryl halides due to reasonance, $C-X$ bond acquires a partial double bond character, hence $C-X$ bond cleavage is difficult. Also in aryl halide, the carbon atom attached to halogen is sp^2 hybridised, hence the electron pair of $C-X$ bond is more tightly held.

45. 2° alkyl halide *i.e.*, $CH_3-CH_2-\overset{CH_3}{\overset{|}{C}}H-Br$ would undergo S_N2 reaction faster than compared to 3° alkyl halide *i.e.*, $(CH_3)_3CBr$ due to formation of less sterically hindered transition state.

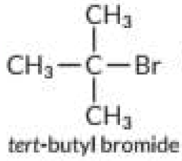
46. Benzyl chloride gets easily hydrolysed by *aq*. NaOH due to formation of stable benzyl carbocation. But due to partial double bond character of $C-Cl$ bond in chlorobenzene, it does not hydrolyse.

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



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

2° carbocation will undergo faster reaction.

48.  $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br$ is an isomer of C_4H_9Br that undergoes

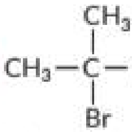
tert-butyl bromide

S_N1 reaction faster due to formation of 3° carbocation.

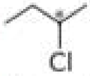
Answer Tips

- It forms 3° carbocation which is most stable.

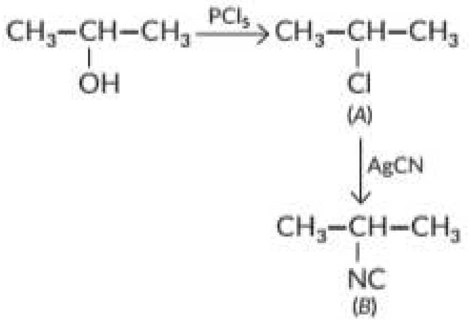
49. CH_3-CH_2-Br would undergo S_N2 reaction faster due to formation of less sterically hindered transition state.

50.  $CH_3-\overset{CH_3}{\underset{Br}{C}}-CH_3$ will undergo S_N1 reaction faster due to the formation of stable 3° carbocation.

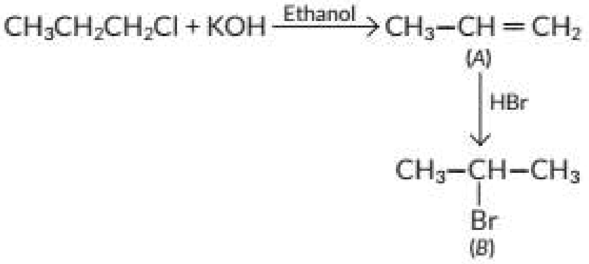
51. Since, I^- is a better leaving group than Br^-, thus, CH_3CH_2I undergoes S_N2 reaction faster than CH_3CH_2Br.

52.  is a chiral molecule.

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

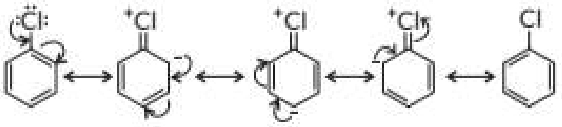
54. (a) 

$$CH_3-\underset{OH}{\underset{|}{C}}H-CH_3 \xrightarrow{PCl_5} \underset{(A)}{CH_3-\underset{Cl}{\underset{|}{C}}H-CH_3} \xrightarrow{AgCN} \underset{(B)}{CH_3-\underset{NC}{\underset{|}{C}}H-CH_3}$$

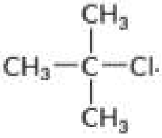
(b) 

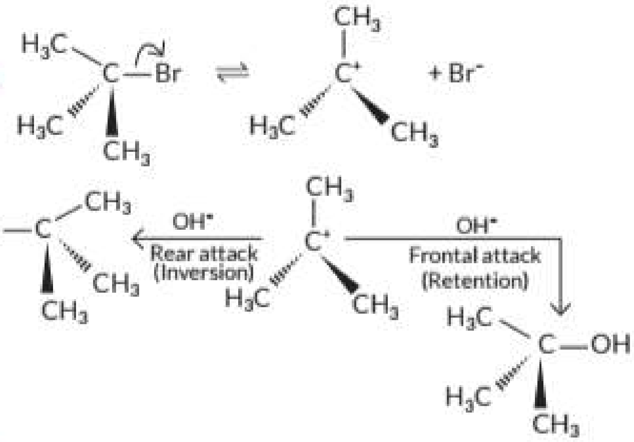
$$CH_3CH_2CH_2Cl + KOH \xrightarrow{\text{Ethanol}} \underset{(A)}{CH_3-CH=CH_2} \xrightarrow{HBr} \underset{(B)}{CH_3-\underset{Br}{\underset{|}{C}}H-CH_3}$$

55. 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.



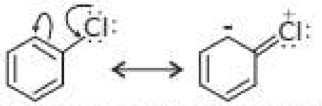
$C-Cl$ bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, haloarenes are less reactive towards nucleophilic substitution reaction.
(ii) In haloarenes, halogen is attached to sp^2-hybridised carbon while in haloalkanes, halogen is attached to sp^3-hybridised carbon.

56. (i) Since, I^- is a better leaving group than Cl^-, therefore  will react faster than  in S_N2 reactions.
(ii) Reactivity in S_N2 reactions depends upon steric hindrance. Since, 1° alkyl halides experience less steric hindrance than 3° alkyl halides, therefore $CH_3-CH_2\,Cl$ will react faster than  $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl$.

57. 

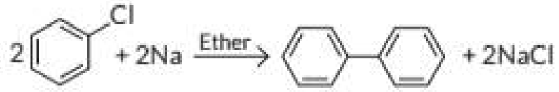
58. (i) Racemic mixture contains equal amount of *d*- and *l*-forms, hence rotation due to one enantiomer is cancelled by another.
(ii) The presence of nitro group at *o*-and *p*-positions withdraws electrons from the benzene ring and thus, facilitates the attack of the nucleophile on haloarenes. The carbanion thus formed is further stabilised by resonance.

59. (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.



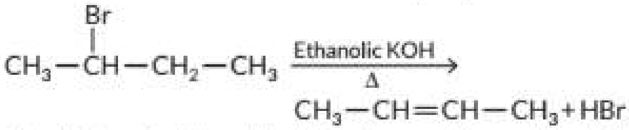
(ii) In S_N1 reaction carbocation intermediate is formed which is a planar molecule so, an incoming nucleophile can attack from either side and an equimolar mixture of two components are formed and resulting mixture is optically inactive.

60. (i)



Chlorobenzene Biphenyl

(ii)



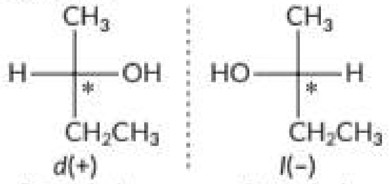
$$CH_3-\overset{\overset{\large Br}{|}}{C}H-CH_2-CH_3 \xrightarrow[\Delta]{\text{Ethanolic KOH}} CH_3-CH=CH-CH_3+HBr$$

61. (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.

$$\underset{\text{Butan-1-ol}}{CH_3-CH_2-CH_2-CH_2OH}$$

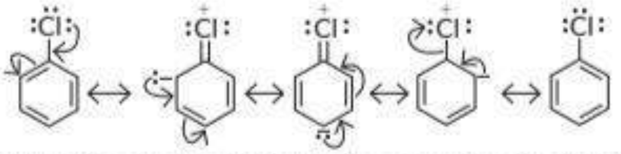
(Optically inactive)
(No chiral carbon)

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

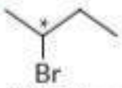


d(+) Butan-2-ol *l*(−) Butan-2-ol

(ii)



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

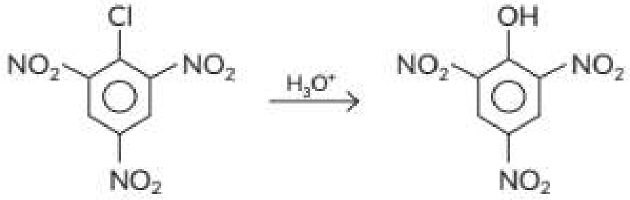
62. (i) (a)  Br undergoes faster S_N2 reaction.
(b)  is chiral.
(ii) (a) S_N2 reaction occurs with inversion of configuration.
(b) S_N1 reaction occurs with racemisation.

63. (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) 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.

64. A nucleophile which can attack from more than one centres, is known as ambident nucleophile,
e.g., $^-\ddot{C}\equiv N:$, cyanide ion.
$R-X+AgCN \rightarrow R-NC+AgX$; $R-X+KCN \rightarrow R-CN+KX$

65. (a) $CH_3Cl+NaI \xrightarrow{\text{Acetone}} \underset{\text{Iodomethane}}{CH_3I}+NaCl$

(b) 

Picric acid

(c) $H_3C-CH_2-CH_2-CH_2-Cl \xrightarrow{\text{alc. KOH}} \underset{\text{But-1-ene}}{H_3C-CH_2-CH=CH_2}$

66. (a) Grignard reagents react with water to form alkanes.

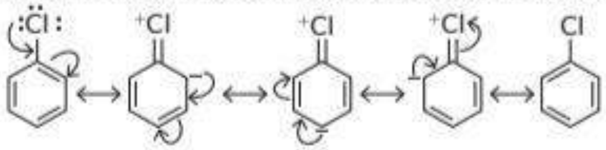
$$R-Mg-X+H_2O \longrightarrow R-H+Mg\begin{smallmatrix}X\\OH\end{smallmatrix}$$

So, they must be prepared under anhydrous conditions.
(b) 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.
(c) Chloroform when exposed to air and sunlight changes to phosgene which is a poisonous gas.

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

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

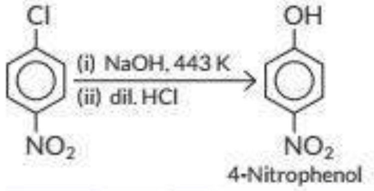
67. (a) (i) The stereoisomers related to each other as non-superimposable mirror images are called enantiomers.
(ii) A mixture containing two enantiomers in equal proportions will have zero optical rotation as the rotation due to one isomer will be cancelled by the rotation due to other isomer. Such a mixture is known as racemic mixture.
(b) Haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions due to the following reasons.
(i) Resonance effect : In haloarenes, the electron pairs on halogen atom are in conjugation with π-electrons of the ring and the following resonating structures are possible.



C—Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, are less reactive towards nucleophilic substitution reaction.
(ii) In halorenes, halogen is attached to sp^2-hybridised carbon while in haloalkanes, halogen is attached to sp^3-hybridised carbon.

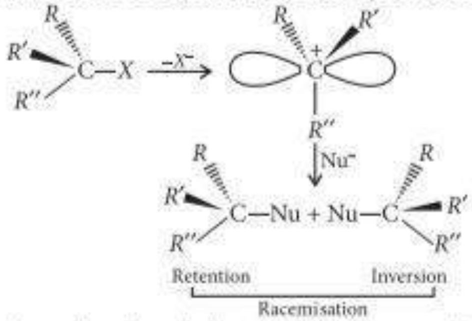
68. (i) $(CH_3)_3C-I$ is more reactive because C—I bond has the minimum bond dissociation enthalpy.

(ii)

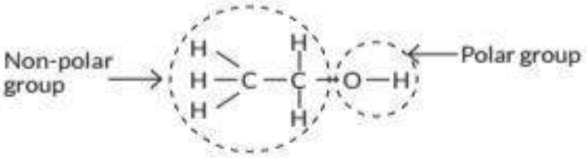


(iii) *Dextro* and *laevo*-rotatory isomers of butan-2-ol are difficult to separate by fractional distillation because they have almost same boiling point.

69. (a) Carbonium ion intermediate produced in the course of S_N1 reaction has a planar structure. It can be attacked by the nucleophilic reagent from either side to give two isomers *d* and *l* if the starting alkyl halide is asymmetric.
Thus, a racemic mixture is obtained due to formation of equal amount of *d* and *l* forms and optical activity is lost.



(b) In water, two hydrogen atoms are attached to one oxygen atom. The bonds are attached in such a way that the dipoles of oxygen –hydrogen bonds add constructively. Due to the difference in electronegativity of oxygen and hydrogen, water molecule is much more polar.
In ethanol, one of the hydrogen atom is replaced by a hydrocarbon group which is non-polar in nature. Due to the low polarity of the hydrocarbon group, ethanol is less polar than water.



(c) (i) As iodide is a better leaving group than chloride because of its large size, therefore, CH_3CH_2I undergoes S_N2 reaction faster than CH_3CH_2Cl.

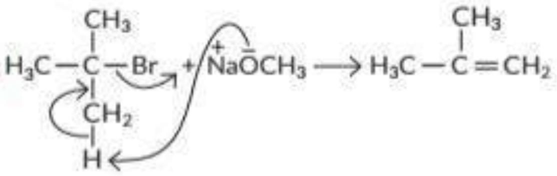
(ii)  CH_2Cl is a primary halide and therefore, undergoes S_N2 reaction faster than the secondary halide  Cl.

OR

(c) (i) The reactivity order toward S_N1 is 2-bromo-2-methylbutene > 2-bromopentane > 1-bromopentane as the reactivity order of S_N1 reaction is 3° > 2° > 1°.

(ii) The reactivity order is 2-bromo-2-methylbutane > 2-bromo-3-methylbutane > 1-bromo-3-methylbutane as the stability order of carbocation and reactivity order of S_N1 reaction is 3° > 2° > 1°.

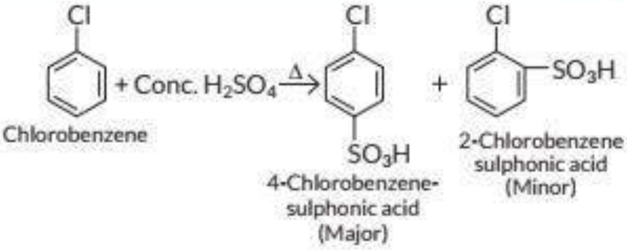
70. (d):



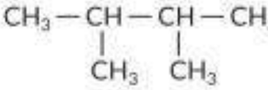
Concept Applied

- With strong bases like $CH_3CH_2O^-$, *t*-butyl bromide undergoes elimination rather than substitution.

71.



72. 2-Bromo-2-methylbutane will give fastest elimination reaction because it is a *tert*-halide and *tert*-halides prefer elimination reaction.

73. (i)  $CH_3-\underset{CH_3}{\underset{|}{C}H}-\underset{CH_3}{\underset{|}{C}H}-CH_3$ (ii) CH_3CH_2NC

Commonly Made Mistake

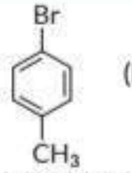
- Remember, Alkyl halide $\xrightarrow{\text{Alc. KCN}}$ Alkyl cyanide
  $\xrightarrow{\text{Alc. AgCN}}$ Alkyl isocyanide

74. (i) $CH_3-CH_2-CH=CH-CH_3$ (Saytzeff rule)
Pent-2-ene

Commonly Made Mistake

- Remember, Alkyl halide $\xrightarrow{aq.\ \text{KOH}}$ Alcohol
  $\xrightarrow{alc.\ \text{KOH}}$ Alkene

(ii)



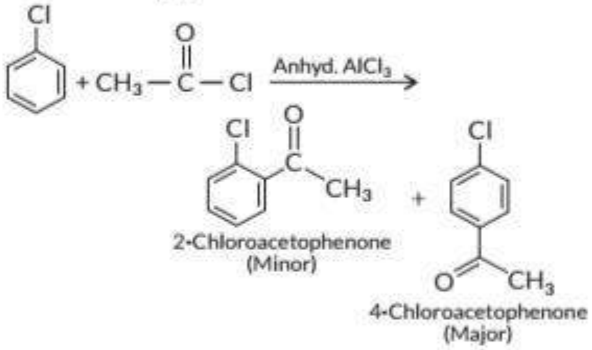
4-Bromotoluene

(Friedel–Crafts alkylation)

75. (i) When ethyl chloride is treated with aqueous KOH, ethanol is formed,

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

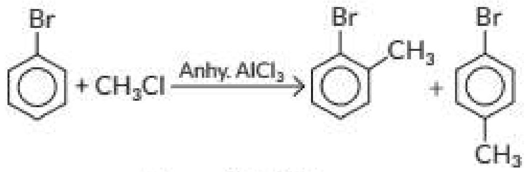
(ii)

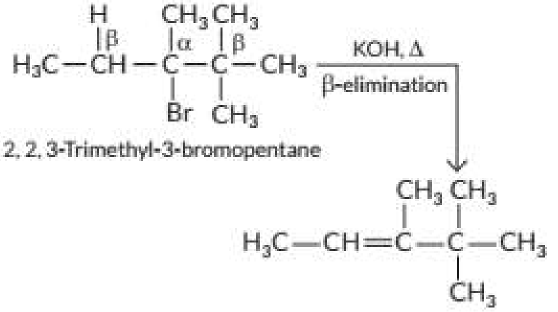


76. (i) $CH_3Cl + AgNO_2 \longrightarrow CH_3NO_2 + AgCl$

Commonly Made Mistake

- Remember, Alkyl halide $\xrightarrow{\text{KNO}_2}$ Alkyl nitrite
  $\xrightarrow{\text{AgNO}_2}$ Nitroalkane

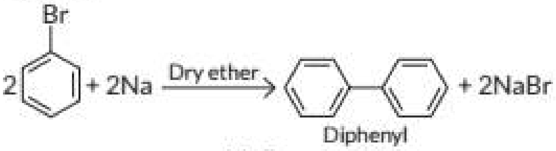
(ii) 

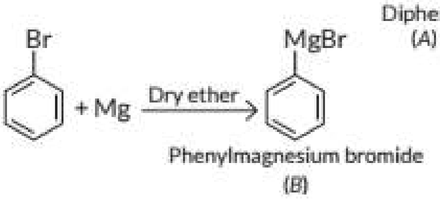
77. (i) 

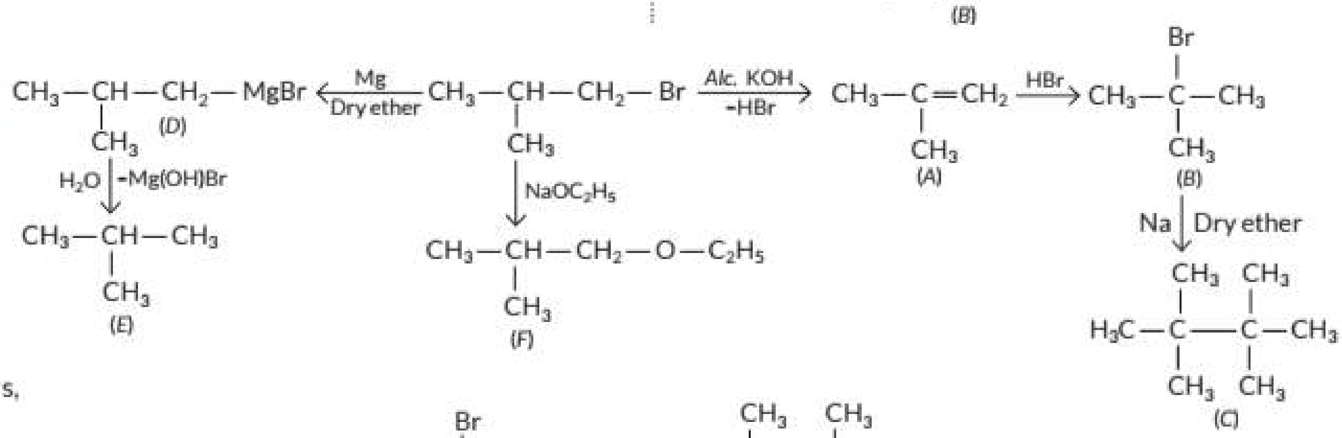
Answer Tips

- H is available only on one β-carbon only one product will be formed.

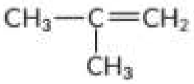
(ii) 

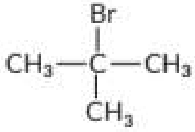
(iii) 

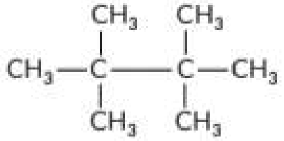


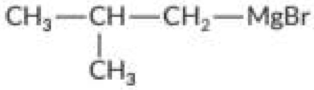
78. 

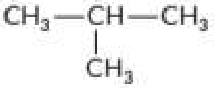
Thus,

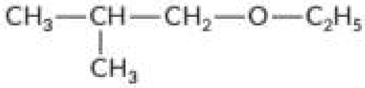
A: 
$CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2$

B: 
$CH_3-\overset{Br}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$

C: 
$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$

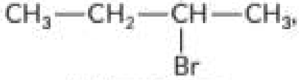
D: 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-MgBr$

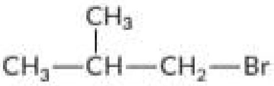
E: 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_3$

F: 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-O-C_2H_5$

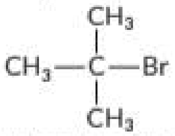
79. The isomers of molecular formula C_4H_9Br are

$CH_3CH_2CH_2CH_2Br$,
1-Bromobutane


$CH_3-CH_2-\underset{Br}{\underset{|}{\overset{*}{C}H}}-CH_3,$
2-Bromobutane
(optically active)


$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-Br$
1-Bromo-2-methyl propane

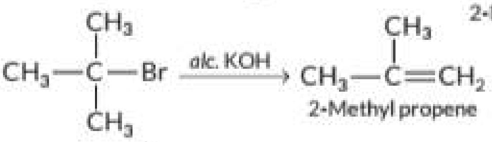
and

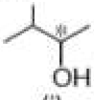

$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-Br$
2-Bromo-2-methyl propane

(a) 2-Bromopropane is optically active.

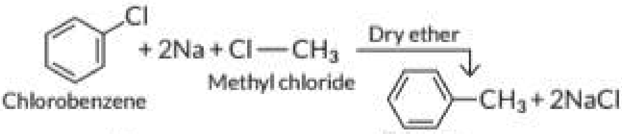
(b) 1-Bromobutane is highly reactive towards S_N2 reaction as 1° alkyl halides are less sterically hindered.

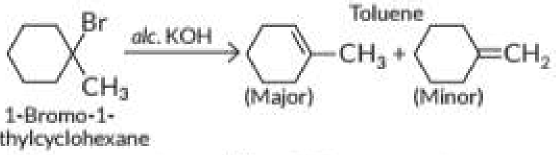
(c) 
$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-Br \xrightarrow{alc.\ KOH} CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2$
2-Methyl propene


$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-Br \xrightarrow{alc.\ KOH} CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2$
2-Methyl propene

80. (a) 

is a chiral molecule.
(i)

(b) 

(c) 

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

CBSE Sample Questions

1. (b): 1-Phenyl-3-bromopropane is formed.

$$(C_6H_5)CH_2CH=CH_2 + HBr \xrightarrow{Peroxide} (C_6H_5)CH_2CH_2CH_2Br \quad (0.77)$$

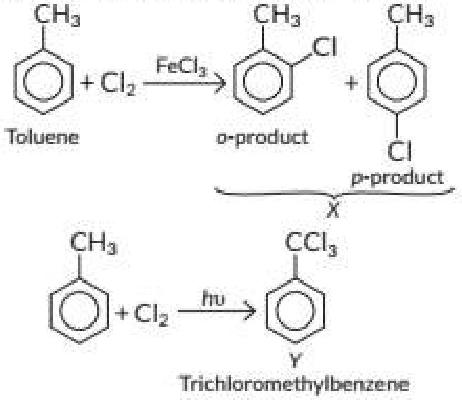
(Anti-Markownikoff addition)

2. (d): Vicinal dibromide is formed.


$$R-CH=CH_2 + Br_2 \xrightarrow{CCl_4} BrCH_2-\overset{R}{\overset{|}{C}HBr} \quad (0.77)$$

3. (c): The reaction of toluene with Cl_2 in presence of $FeCl_3$ is electrophilic substitution reaction forming

o-chlorotoluene and *p*-chlorotoluene. Reaction taking place in the presence of light gives 'Y', *via* free radical mechanism forming trichloromethylbenzene.



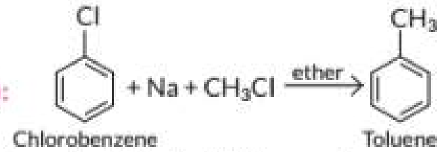
Thus 'X' and 'Y' are, X = *ortho* and *para*-chlorotoluene, Y = trichloromethylbenzene. **(0.77)**

4. (c): 1,4-Dichlorobenzene has higher melting point because *para* isomers are more symmetric than *ortho* and *meta* isomers. **(0.77)**

5. (c): $[C_6H_5CH(C_6H_5)Br] \longrightarrow [C_6H_5\overset{+}{C}H(C_6H_5)]$
Here, carbocation formed is more stable through resonance with two benzene ring. **(1)**

6. (b) : C_2H_5Br gives nitroethane on heating with aqueous solution of $AgNO_2$. C_2H_5Br reacts with metallic Na to give butane · C_2H_5Br gives ethene on boiling with alcoholic potash and forms C_2H_5SH (thiol) on heating with alcoholic KSH. **(0.77)**

7. (b):



This is also called Wurtz-Fittig reaction. **(0.77)**

8. (a): A : Isomers, B : Enantiomer
Isomers have same molecular formula but different structure and enantiomers are non-superimposable mirror images. **(1)**

9. (a):

$$\begin{tikzcd}
 & \underset{(D)}{C_2H_5CN} & \\
\underset{(C)}{C_2H_5NC} & C_2H_5Cl \arrow[l, "AgCN"'] \arrow[r, "alc.\ KOH"] \arrow[u, "KCN"'] \arrow[d, "aq.\ KOH"] & \underset{(A)}{C_2H_4} \\
 & \underset{(B)}{C_2H_5OH} &
\end{tikzcd}$$

(1)

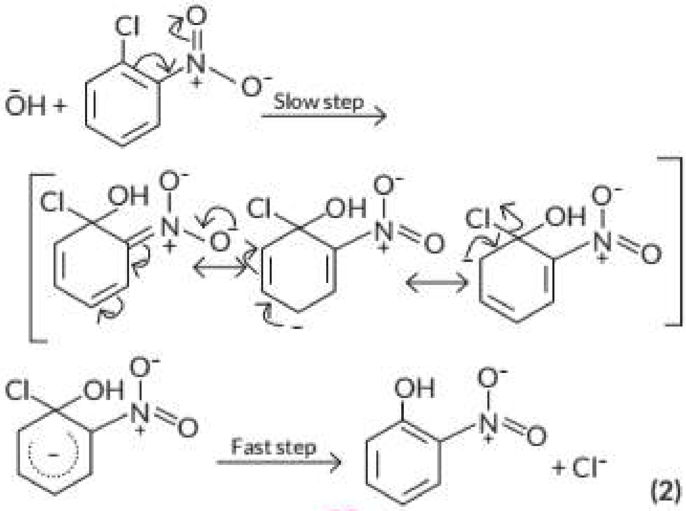
10. (a) At the *ortho* position, higher steric hindrance is present, hence *para* isomer is usually predominant and is obtained in the major amount. **(1)**
(b) During the S_N1 mechanism, intermediate carbocation formed is sp^2 hybridized and planar in nature. This allows the attack of nucleophile from either side of the plane resulting in a racemic mixture. **(1)**

OR

(a) *tert*-Butyl alcohol or 2-methyl propan-2-ol reacts with Lucas reagent (mixture of conc. HCl and $ZnCl_2$) to form 2-chloro-2-methylpropane through S_N1 mechanism. **(1)**
(b) Chloromethane have higher dipole moment and due to smaller size of fluorine, the dipole moment of flouromethane is comparatively lesser. **(1)**

11. Racemic mixture will be given by 2-chlorobutane as it is an optically active compound. **(1)**
When 2-chlorobutane undergoes S_N1 reaction, both front and rear attack are possible, resulting in a racemic mixture. **(1)**

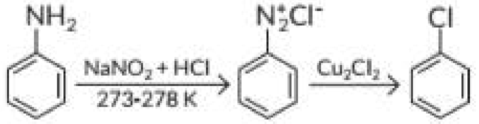
12. Nitro group at *ortho* position withdraws the electron density from benzene ring and thus facilitates the attack of the nucleophile on haloarene.



(2)

OR

(i)



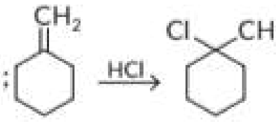
(1)

(ii) $CH_3CH(Br)CH_3 \xrightarrow{alc.\ KOH} CH_3CH{=}CH_2 \xrightarrow{HBr,\ organic\ peroxide} CH_3CH_2CH_2Br$ **(1)**

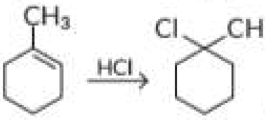
13. (a) The major product formed when 2-cyclohexylchloroethane undergoes dehydrohalogenation reaction is 1-cyclohexylethene. The reagent which is used to carry out the reaction is ethanolic KOH. **(2)**
(b) Haloalkanes are more reactive than haloarenes and vinylic halides because of the presence of partial double bond character of C-X bond in haloarenes and vinylic halides. Hence, they do not undergo nucleophilic reactions easily. **(1)**

OR

(a) (i) Methylenecyclohexane;



(ii) 1-Methylcyclohexene;



(2)

(b) Allyl chloride shows high reactivity as the carbocation formed in the first step is stabilised by resonance while no such stabilisation of carbocation exists in the case of *n*-propyl chloride. **(1)**