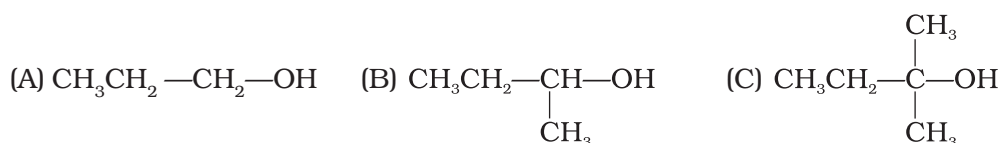


Unit 10

HALOALKANES AND HALOARENES

I. Multiple Choice Questions (Type-I)

1. The order of reactivity of following alcohols with halogen acids is _____.

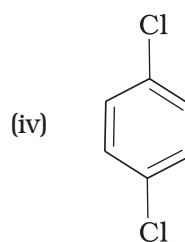
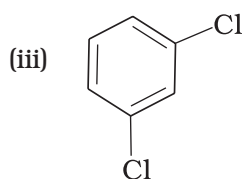
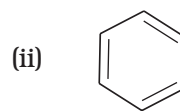
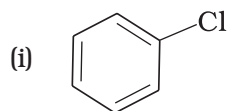
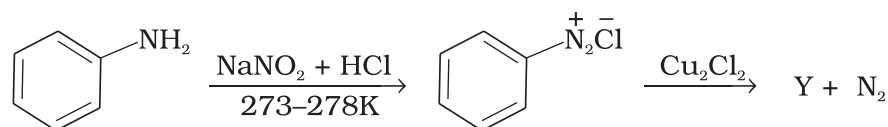


- (i) (A) > (B) > (C)
- (ii) (C) > (B) > (A)
- (iii) (B) > (A) > (C)
- (iv) (A) > (C) > (B)

2. Which of the following alcohols will yield the corresponding alkyl chloride on reaction with concentrated HCl at room temperature?

- (i) $\text{CH}_3\text{CH}_2-\text{CH}_2-\text{OH}$
- (ii) $\text{CH}_3\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{OH}$
- (iii) $\text{CH}_3\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2\text{OH}$
- (iv) $\text{CH}_3\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{OH}$

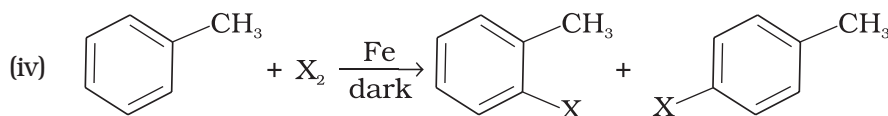
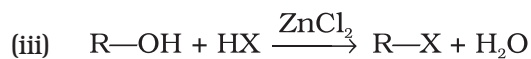
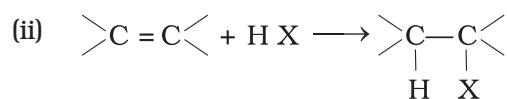
3. Identify the compound Y in the following reaction.



4. Toluene reacts with a halogen in the presence of iron (III) chloride giving ortho and para halo compounds. The reaction is

- Electrophilic elimination reaction
- Electrophilic substitution reaction
- Free radical addition reaction
- Nucleophilic substitution reaction

5. Which of the following is halogen exchange reaction?

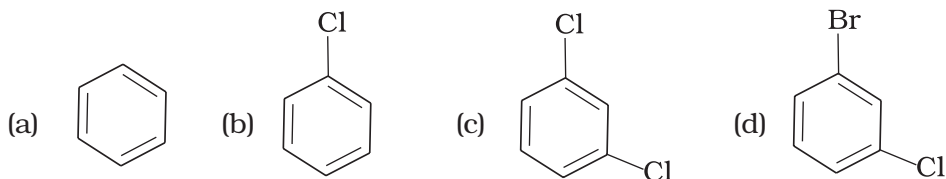


6. Which reagent will you use for the following reaction?



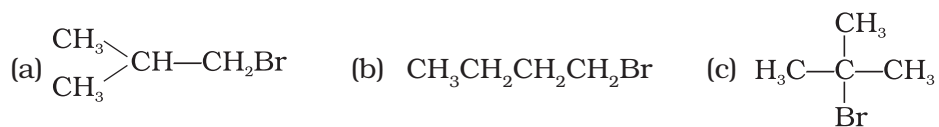
- $\text{Cl}_2/\text{UV light}$
- $\text{NaCl} + \text{H}_2\text{SO}_4$
- Cl_2 gas in dark
- Cl_2 gas in the presence of iron in dark

7. Arrange the following compounds in the increasing order of their densities.



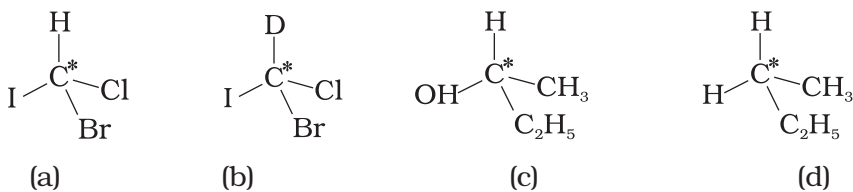
- (i) (a) < (b) < (c) < (d)
 (ii) (a) < (c) < (d) < (b)
 (iii) (d) < (c) < (b) < (a)
 (iv) (b) < (d) < (c) < (a)

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



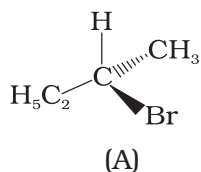
- (i) (b) < (a) < (c)
 (ii) (a) < (b) < (c)
 (iii) (c) < (a) < (b)
 (iv) (c) < (b) < (a)

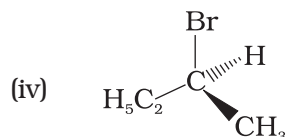
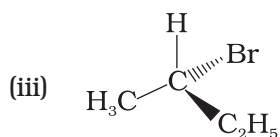
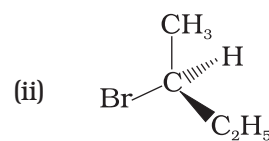
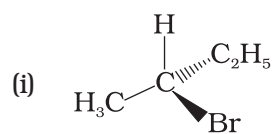
9. In which of the following molecules carbon atom marked with asterisk (*) is asymmetric?



- (i) (a), (b), (c), (d)
 (ii) (a), (b), (c)
 (iii) (b), (c), (d)
 (iv) (a), (c), (d)

10. Which of the following structures is enantiomeric with the molecule (A) given below :





11. Which of the following is an example of *vic*-dihalide?

- (i) Dichloromethane
- (ii) 1,2-dichloroethane
- (iii) Ethylidene chloride
- (iv) Allyl chloride

12. The position of $-Br$ in the compound in $CH_3CH=CHC(Br)(CH_3)_2$ can be classified as _____.

- (i) Allyl
- (ii) Aryl
- (iii) Vinyl
- (iv) Secondary

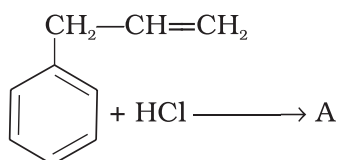
13. Chlorobenzene is formed by reaction of chlorine with benzene in the presence of $AlCl_3$. Which of the following species attacks the benzene ring in this reaction?

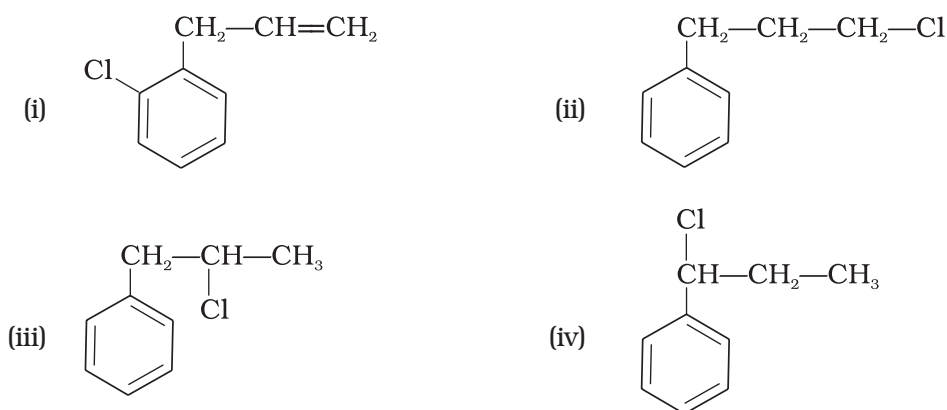
- (i) Cl^-
- (ii) Cl^+
- (iii) $AlCl_3$
- (iv) $[AlCl_4]^-$

14. Ethylidene chloride is a/an _____.

- (i) *vic*-dihalide
- (ii) *gem*-dihalide
- (iii) allylic halide
- (iv) vinylic halide

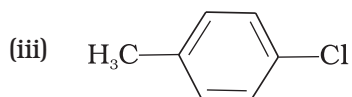
15. What is 'A' in the following reaction?





- 16.** A primary alkyl halide would prefer to undergo _____.
- S_N1 reaction
 - S_N2 reaction
 - α -Elimination
 - Racemisation
- 17.** Which of the following alkyl halides will undergo S_N1 reaction most readily?
- $(CH_3)_3C-F$
 - $(CH_3)_3C-Cl$
 - $(CH_3)_3C-Br$
 - $(CH_3)_3C-I$
- 18.** Which is the correct IUPAC name for $CH_3-\underset{\substack{| \\ C_2H_5}}{CH}-CH_2-Br$?
- 1-Bromo-2-ethylpropane
 - 1-Bromo-2-ethyl-2-methylethane
 - 1-Bromo-2-methylbutane
 - 2-Methyl-1-bromobutane
- 19.** What should be the correct IUPAC name for diethylbromomethane?
- 1-Bromo-1,1-diethylmethane
 - 3-Bromopentane
 - 1-Bromo-1-ethylpropane
 - 1-Bromopentane
- 20.** The reaction of toluene with chlorine in the presence of iron and in the absence of light yields _____.





(iv) Mixture of (ii) and (iii)

21. Chloromethane on treatment with excess of ammonia yields mainly



(iv) Mixture containing all these in equal proportion

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

(i) 2-Bromobutane

(ii) 1-Bromobutane

(iii) 2-Bromopropane

(iv) 2-Bromopropan-2-ol

23. Reaction of $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ with aqueous sodium hydroxide follows _____.

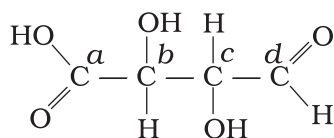
(i) $\text{S}_{\text{N}}1$ mechanism

(ii) $\text{S}_{\text{N}}2$ mechanism

(iii) Any of the above two depending upon the temperature of reaction

(iv) Saytzeff rule

24. Which of the carbon atoms present in the molecule given below are asymmetric?



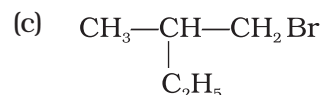
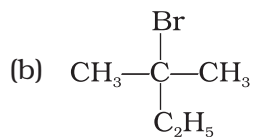
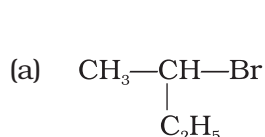
(i) a, b, c, d

(ii) b, c

(iii) a, d

(iv) a, b, c

25. Which of the following compounds will give racemic mixture on nucleophilic substitution by OH^- ion?



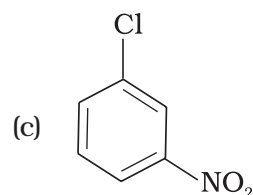
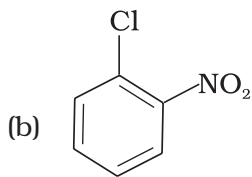
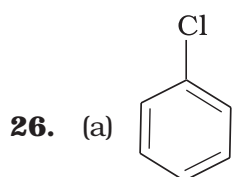
(i) (a)

(ii) (a), (b), (c)

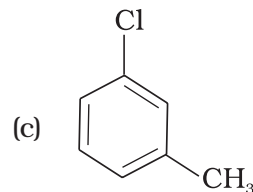
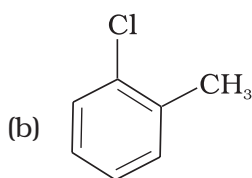
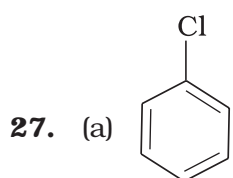
(iii) (b), (c)

(iv) (a), (c)

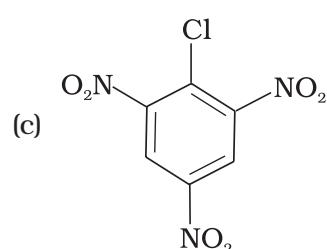
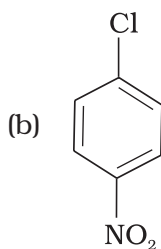
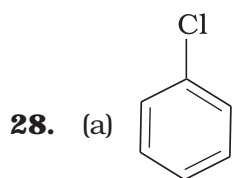
Note : In the questions 26 to 29 arrange the compounds in increasing order of rate of reaction towards nucleophilic substitution.



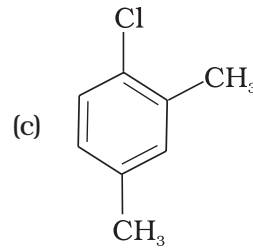
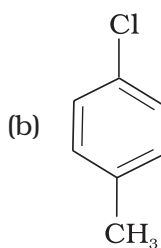
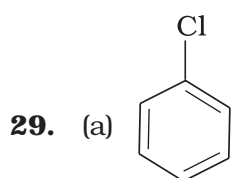
- (i) (a) < (b) < (c)
- (ii) (c) < (b) < (a)
- (iii) (a) < (c) < (b)
- (iv) (c) < (a) < (b)



- (i) (a) < (b) < (c)
- (ii) (a) < (c) < (b)
- (iii) (c) < (b) < (a)
- (iv) (b) < (c) < (a)



- (i) (c) < (b) < (a)
- (ii) (b) < (c) < (a)
- (iii) (a) < (c) < (b)
- (iv) (a) < (b) < (c)



- (i) (a) < (b) < (c)
- (ii) (b) < (a) < (c)
- (iii) (c) < (b) < (a)
- (iv) (a) < (c) < (b)

30. Which is the correct increasing order of boiling points of the following compounds?

1-Iodobutane, 1-Bromobutane, 1-Chlorobutane, Butane

- (i) Butane < 1-Chlorobutane < 1-Bromobutane < 1-Iodobutane
- (ii) 1-Iodobutane < 1-Bromobutane < 1-Chlorobutane < Butane
- (iii) Butane < 1-Iodobutane < 1-Bromobutane < 1-Chlorobutane
- (iv) Butane < 1-Chlorobutane < 1-Iodobutane < 1-Bromobutane

31. Which is the correct increasing order of boiling points of the following compounds?

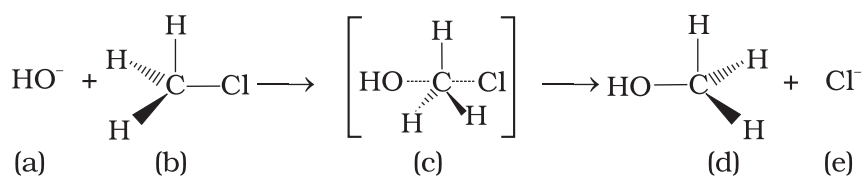
1-Bromoethane, 1-Bromopropane, 1-Bromobutane, Bromobenzene

- (i) Bromobenzene < 1-Bromobutane < 1-Bromopropane < 1-Bromoethane
- (ii) Bromobenzene < 1-Bromoethane < 1-Bromopropane < 1-Bromobutane
- (iii) 1-Bromopropane < 1-Bromobutane < 1-Bromoethane < Bromobenzene
- (iv) 1-Bromoethane < 1-Bromopropane < 1-Bromobutane < Bromobenzene

II. Multiple Choice Questions (Type-II)

Note : In the following questions two or more options may be correct.

Consider the following reaction and answer the questions no. 32-34.



32. Which of the statements are correct about above reaction?

- (i) (a) and (e) both are nucleophiles.
- (ii) In (c) carbon atom is sp^3 hybridised.
- (iii) In (c) carbon atom is sp^2 hybridised.
- (iv) (a) and (e) both are electrophiles.

33. Which of the following statements are correct about this reaction?

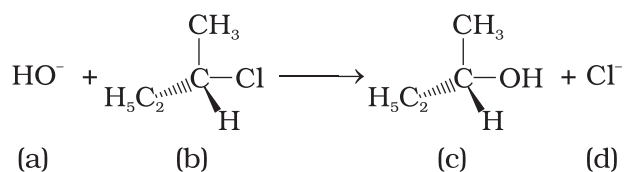
- (i) The given reaction follows S_N2 mechanism.
- (ii) (b) and (d) have opposite configuration.

- (iii) (b) and (d) have same configuration.
- (iv) The given reaction follows S_N1 mechanism.

34. Which of the following statements are correct about the reaction intermediate?

- (i) Intermediate (c) is unstable because in this carbon is attached to 5 atoms.
- (ii) Intermediate (c) is unstable because carbon atom is sp^2 hybridised.
- (iii) Intermediate (c) is stable because carbon atom is sp^2 hybridised.
- (iv) Intermediate (c) is less stable than the reactant (b).

Answer Q. No. 35 and 36 on the basis of the following reaction.



35. Which of the following statements are correct about the mechanism of this reaction?

- (i) A carbocation will be formed as an intermediate in the reaction.
- (ii) OH^- will attach the substrate (b) from one side and Cl^- will leave it simultaneously from other side.
- (iii) An unstable intermediate will be formed in which OH^- and Cl^- will be attached by weak bonds.
- (iv) Reaction proceeds through S_N1 mechanism.

36. Which of the following statements are correct about the kinetics of this reaction?

- (i) The rate of reaction depends on the concentration of only (b).
- (ii) The rate of reaction depends on concentration of both (a) and (b).
- (iii) Molecularity of reaction is one.
- (iv) Molecularity of reaction is two.

37. Haloalkanes contain halogen atom (s) attached to the sp^3 hybridised carbon atom of an alkyl group. Identify haloalkane from the following compounds.

- (i) 2-Bromopentane
- (ii) Vinyl chloride (chloroethene)
- (iii) 2-chloroacetophenone
- (iv) Trichloromethane

38. Ethylene chloride and ethylidene chloride are isomers. Identify the correct statements.

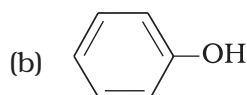
- (i) Both the compounds form same product on treatment with alcoholic KOH.
- (ii) Both the compounds form same product on treatment with aq. NaOH.
- (iii) Both the compounds form same product on reduction.
- (iv) Both the compounds are optically active.

- 39.** Which of the following compounds are *gem*-dihalides?
- Ethylidene chloride
 - Ethylene dichloride
 - Methylene chloride
 - Benzyl chloride
- 40.** Which of the following are secondary bromides?
- $(\text{CH}_3)_2\text{CHBr}$
 - $(\text{CH}_3)_3\text{CCH}_2\text{Br}$
 - $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CH}_3$
 - $(\text{CH}_3)_2\text{CBrCH}_2\text{CH}_3$
- 41.** Which of the following compounds can be classified as aryl halides?
- $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{CH}(\text{CH}_3)_2$
 - $p\text{-CH}_3\text{CHCl}(\text{C}_6\text{H}_4)\text{CH}_2\text{CH}_3$
 - $o\text{-BrH}_2\text{C-C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$
 - $\text{C}_6\text{H}_5\text{-Cl}$
- 42.** Alkyl halides are prepared from alcohols by treating with
- $\text{HCl} + \text{ZnCl}_2$
 - Red P + Br_2
 - $\text{H}_2\text{SO}_4 + \text{KI}$
 - All the above
- 43.** Alkyl fluorides are synthesised by heating an alkyl chloride/bromide in presence of _____ or _____.
- CaF_2
 - CoF_2
 - Hg_2F_2
 - NaF

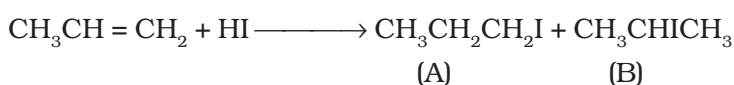
III. Short Answer Type

- 44.** Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysts. But why does preparation of aryl iodides requires presence of an oxidising agent?
- 45.** Out of *o*- and *p*-dibromobenzene which one has higher melting point and why?
- 46.** Which of the compounds will react faster in $\text{S}_{\text{N}}1$ reaction with the OH^- ion?
 $\text{CH}_3\text{—CH}_2\text{—Cl}$ or $\text{C}_6\text{H}_5\text{—CH}_2\text{—Cl}$
- 47.** Why iodoform has appreciable antiseptic property?

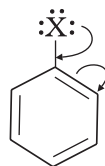
48. Haloarenes are less reactive than haloalkanes and haloalkenes. Explain.
49. Discuss the role of Lewis acids in the preparation of aryl bromides and chlorides in the dark.
50. Which of the following compounds (a) and (b) will not react with a mixture of NaBr and H₂SO₄. Explain why?



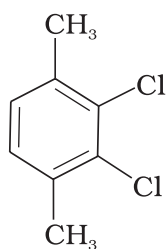
51. Which of the products will be major product in the reaction given below? Explain.



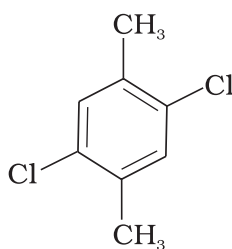
52. Why is the solubility of haloalkanes in water very low?
53. Draw other resonance structures related to the following structure and find out whether the functional group present in the molecule is ortho, para directing or meta directing.



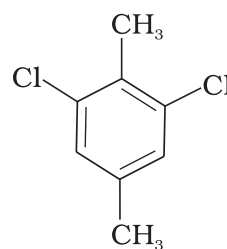
54. Classify the following compounds as primary, secondary and tertiary halides.
- (i) 1-Bromobut-2-ene (ii) 4-Bromopent-2-ene
- (iii) 2-Bromo-2-methylpropane
55. Compound 'A' with molecular formula C₄H₉Br is treated with aq. KOH solution. The rate of this reaction depends upon the concentration of the compound 'A' only. When another optically active isomer 'B' of this compound was treated with aq. KOH solution, the rate of reaction was found to be dependent on concentration of compound and KOH both.
- (i) Write down the structural formula of both compounds 'A' and 'B'.
- (ii) Out of these two compounds, which one will be converted to the product with inverted configuration.
56. Write the structures and names of the compounds formed when compound 'A' with molecular formula, C₇H₈ is treated with Cl₂ in the presence of FeCl₃.
57. Identify the products A and B formed in the following reaction :
- (a) CH₃—CH₂—CH=CH—CH₃+HCl → A + B
58. Which of the following compounds will have the highest melting point and why?



(I)

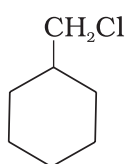


(II)

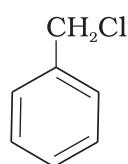


(III)

- 59.** Write down the structure and IUPAC name for neo-pentylbromide.
- 60.** A hydrocarbon of molecular mass 72 g mol^{-1} gives a single monochloro derivative and two dichloro derivatives on photo chlorination. Give the structure of the hydrocarbon.
- 61.** Name the alkene which will yield 1-chloro-1-methylcyclohexane by its reaction with HCl. Write the reactions involved.
- 62.** Which of the following haloalkanes reacts with aqueous KOH most easily? Explain giving reason.
- 1-Bromobutane
 - 2-Bromobutane
 - 2-Bromo-2-methylpropane
 - 2-Chlorobutane
- 63.** Why can aryl halides not be prepared by reaction of phenol with HCl in the presence of ZnCl_2 ?
- 64.** Which of the following compounds would undergo $\text{S}_{\text{N}}1$ reaction faster and why?



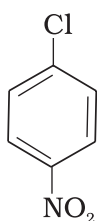
(A)



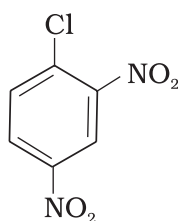
(B)

- 65.** Allyl chloride is hydrolysed more readily than *n*-propyl chloride. Why?
- 66.** Why is it necessary to avoid even traces of moisture during the use of a Grignard reagent?
- 67.** How do polar solvents help in the first step in $\text{S}_{\text{N}}1$ mechanism?
- 68.** Write a test to detect the presence of double bond in a molecule.
- 69.** Diphenyls are potential threat to the environment. How are these produced from arylhalides?

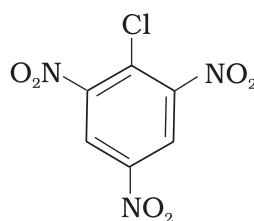
70. What are the IUPAC names of the insecticide DDT and benzenehexachloride? Why is their use banned in India and other countries?
71. Elimination reactions (especially β -elimination) are as common as the nucleophilic substitution reaction in case of alkyl halides. Specify the reagents used in both cases.
72. How will you obtain monobromobenzene from aniline?
73. Aryl halides are extremely less reactive towards nucleophilic substitution. Predict and explain the order of reactivity of the following compounds towards nucleophilic substitution:



(I)



(II)



(III)

74. *tert*-Butylbromide reacts with aq. NaOH by S_N1 mechanism while *n*-butylbromide reacts by S_N2 mechanism. Why?
75. Predict the major product formed when HCl is added to isobutylene. Explain the mechanism involved.
76. Discuss the nature of C–X bond in the haloarenes.
77. How can you obtain iodoethane from ethanol when no other iodine containing reagent except NaI is available in the laboratory?
78. Cyanide ion acts as an ambident nucleophile. From which end it acts as a stronger nucleophile in aqueous medium? Give reason for your answer.

IV. Matching Type

Note : Match the items given in Column I and Column II in the following questions.

79. Match the the compounds given in Column I with the effects given in Column II.

Column I

- (i) Chloramphenicol
(ii) Thyroxine
(iii) Chloroquine
(iv) Chloroform

Column II

- (a) Malaria
(b) Anaesthetic
(c) Typhoid fever
(d) Goiter
(e) Blood substituent

80. Match the items of Column I and Column II.

Column I

- (i) S_N1 reaction
- (ii) Chemicals in fire extinguisher
- (iii) Bromination of alkenes
- (iv) Alkylidene halides
- (v) Elimination of HX from alkylhalide

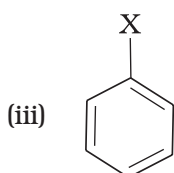
Column II

- (a) *vic*-dibromides
- (b) *gem*-dihalides
- (c) Racemisation
- (d) Saytzeff rule
- (e) Chlorobromocarbons

81. Match the structures of compounds given in Column I with the classes of compounds given in Column II.

Column I

- (i) $\text{CH}_3-\underset{\text{X}}{\text{CH}}-\text{CH}_3$
- (ii) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{X}$



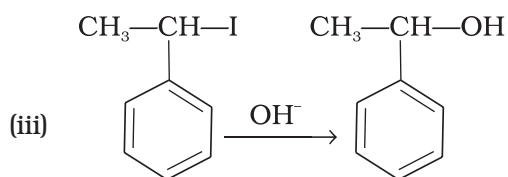
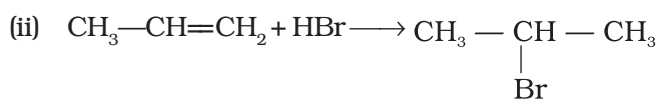
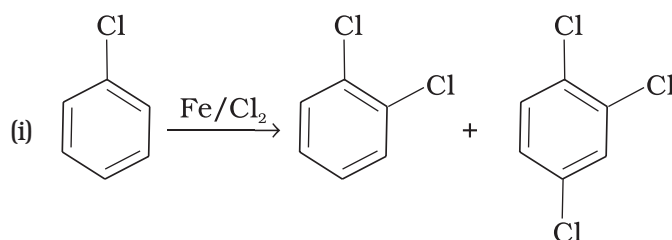
- (iv) $\text{CH}_2=\text{CH}-\text{X}$

Column II

- (a) Aryl halide
- (b) Alkyl halide
- (c) Vinyl halide
- (d) Allyl halide

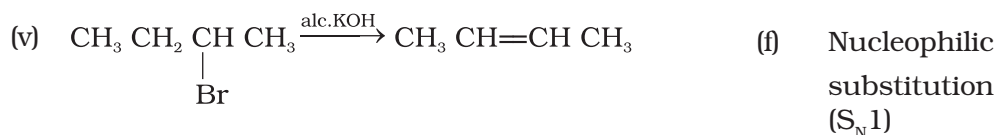
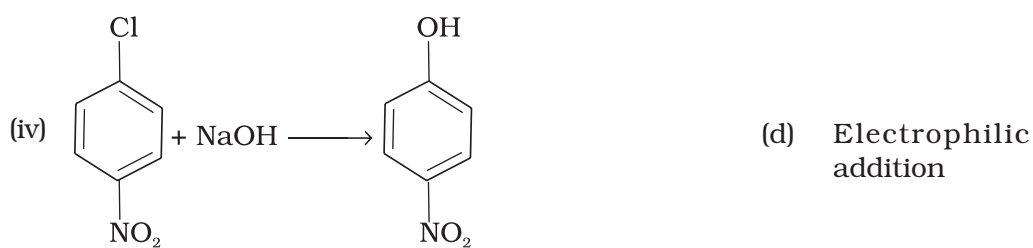
82. Match the reactions given in Column I with the types of reactions given in Column II.

Column I

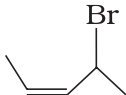
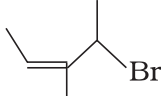
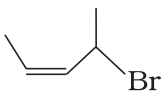



Column II

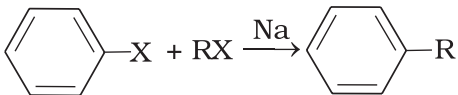
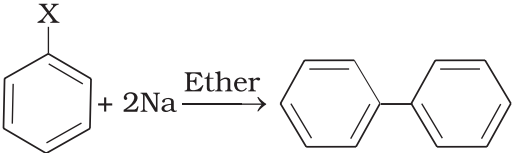
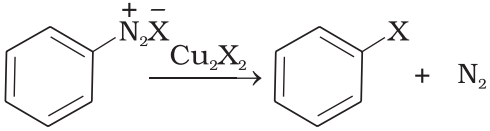
- (a) Nucleophilic aromatic substitution
- (b) Electrophilic aromatic substitution
- (c) Saytzeff elimination



83. Match the structures given in Column I with the names in Column II.

Column I	Column II
(i) 	(a) 4-Bromopent-2-ene
(ii) 	(b) 4-Bromo-3-methylpent-2-ene
(iii) 	(c) 1-Bromo-2-methylbut-2-ene
(iv) 	(d) 1-Bromo-2-methylpent-2-ene

84. Match the reactions given in Column I with the names given in Column II.

Column I	Column II
(i) 	(a) Fittig reaction
(ii) $2 \text{C}_6\text{H}_5\text{X} + 2\text{Na} \xrightarrow{\text{Ether}} \text{C}_6\text{H}_5\text{C}_6\text{H}_5 + 2\text{NaX}$ 	(b) Wurtz Fittig reaction
(iii) 	(c) Finkelstein reaction
(iv) $\text{C}_2\text{H}_5\text{Cl} + \text{NaI} \xrightarrow{\text{dry acetone}} \text{C}_2\text{H}_5\text{I} + \text{NaCl}$	(d) Sandmeyer reaction

V. Assertion and Reason Type

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (i) Assertion and reason both are correct and reason is correct explanation of assertion.
 - (ii) Assertion and reason both are wrong statements.
 - (iii) Assertion is correct but reason is wrong statement.
 - (iv) Assertion is wrong but reason is correct statement.
 - (v) Assertion and reason both are correct statements but reason is not correct explanation of assertion.
- 85. Assertion :** Phosphorus chlorides (tri and penta) are preferred over thionyl chloride for the preparation of alkyl chlorides from alcohols.
Reason : Phosphorus chlorides give pure alkyl halides.
- 86. Assertion :** The boiling points of alkyl halides decrease in the order :
 $RI > RBr > RCl > RF$
Reason : The boiling points of alkyl chlorides, bromides and iodides are considerably higher than that of the hydrocarbon of comparable molecular mass.
- 87. Assertion :** KCN reacts with methyl chloride to give methyl isocyanide
Reason : CN^- is an ambident nucleophile.
- 88. Assertion :** *tert*-Butyl bromide undergoes Wurtz reaction to give 2, 2, 3, 3-tetramethylbutane.
Reason : In Wurtz reaction, alkyl halides react with sodium in dry ether to give hydrocarbon containing double the number of carbon atoms present in the halide.
- 89. Assertion :** Presence of a nitro group at ortho or para position increases the reactivity of haloarenes towards nucleophilic substitution.
Reason : Nitro group, being an electron withdrawing group decreases the electron density over the benzene ring.
- 90. Assertion :** In monohaloarenes, further electrophilic substitution occurs at ortho and para positions.
Reason : Halogen atom is a ring deactivator.
- 91. Assertion :** Aryl iodides can be prepared by reaction of arenes with iodine in the presence of an oxidising agent.
Reason : Oxidising agent oxidises I_2 into HI.
- 92. Assertion :** It is difficult to replace chlorine by $-OH$ in chlorobenzene in comparison to that in chloroethane.
Reason : Chlorine-carbon (C—Cl) bond in chlorobenzene has a partial double bond character due to resonance.

- 93. Assertion** : Hydrolysis of (-)-2-bromooctane proceeds with inversion of configuration.
Reason : This reaction proceeds through the formation of a carbocation.
- 94. Assertion** : Nitration of chlorobenzene leads to the formation of *m*-nitrochlorobenzene
Reason : $-\text{NO}_2$ group is a *m*-directing group.

VI. Long Answer Type

- 95.** Some alkylhalides undergo substitution whereas some undergo elimination reaction on treatment with bases. Discuss the structural features of alkyl halides with the help of examples which are responsible for this difference.
- 96.** Some halogen containing compounds are useful in daily life. Some compounds of this class are responsible for exposure of flora and fauna to more and more of UV light which causes destruction to a great extent. Name the class of these halocompounds. In your opinion, what should be done to minimise harmful effects of these compounds.
- 97.** Why are aryl halides less reactive towards nucleophilic substitution reactions than alkyl halides? How can we enhance the reactivity of aryl halides?