HALOALKANES AND HALOARENES

FACT/DEFINITION TYPE QUESTIONS

1. Which of the following is a primary halide?

(a) Isopropyl iodide (b) Secondary butyl iodide

(c) Tertiary butyl bromide (d) Neohexyl chloride

2. When two halogen atoms are attached to same carbon atom then it is :

(a) *vic*-dihalide (b) *gem*-dihalide

(c) α, ω -halide (d) α, β -halide

3. Gem-dibromide is

(a) $CH_3CH(Br)CH_2(Br)$ (b) $CH_3CBr_2CH_3$

(c) $CH_2(Br)CH_2CH_2$ (d) CH_2BrCH_2Br

4. How many structural isomers are possible for a compound with molecular formula C_3H_7Cl ?

(a) 2 (b) 5

(c) 7 (d) 9

5. The compound which contains all the four 1°, 2°, 3° and 4° carbon atoms is

(a) 2, 3-dimethyl pentane

(b) 3-chloro-2, 3-dimethylpentane

(c) 2, 3, 4-trimethylpentane

(d) 3, 3-dimethylpentane

6. IUPAC name of $(CH_3)_3CCl$

(a) 3-Chlorobutane

(b) 2-Chloro-2-methylpropane

(c) *t*-butyl chloride

(d) *n*-butyl chloride

7. IUPAC name of

$CH_3CH_2C(Br) = CH — Cl$ is

(a) 2-bromo-1-chloro butene

(b) 1-chloro-2-bromo butene

(c) 3-chloro-2-bromo butene

(d) None of the above

8. The IUPAC name of $CH_2 = CH - CH_2Cl$ is

(a) Allyl chloride (b) 1-chloro-3-propene

(c) Vinyl chloride (d) 3-chloro-1-propene

9. Which of the following halide is 2° ?

(a) Isopropyl chloride (b) Isobutyl chloride

(c) *n*-propyl chloride (d) *n*-butyl chloride

10. Benzene hexachloride is

(a) 1, 2, 3, 4, 5, 6 - hexachlorocyclohexane

(b) 1, 1, 1, 6, 6, 6 - hexachlorocyclohexane

(c) 1, 6 - phenyl - 1, 6 - chlorohexane

(d) 1, 1 - phenyl - 6, 6 -chlorohexane

11. Phosgene is a common name for

(a) phosphoryl chloride

(b) thionyl chloride

(c) carbon dioxide and phosphine

(d) carbonyl chloride

12. C – X bond is strongest in

(a) CH_3Cl (b) CH_3Br

(c) CH_3F (d) CH_3I

13. Which of the following will have the maximum dipole moment?

(a) CH_3F (b) CH_3Cl

(c) CH_3Br (d) CH_3I

14. The decreasing order of boiling points of alkyl halides is

(a) RF > RCl > RBr > RI (b) RBr > RCl > RI > RF

(c) RI > RBr > RCl > RF (d) RCl > RF > RI > RBr

15. $C_3H_8 + Cl_2 \xrightarrow{\text{Light}} C_3H_7Cl + HCl$ is an example of

(a) substitution (b) elimination

(c) addition (d) rearrangement reaction

16. The reaction conditions leading to the best yields of C_2H_5Cl are :

(a) $C_2H_6\ (\text{excess}) + Cl_2 \xrightarrow{\text{UV light}}$

(b) $C_2H_6 + Cl_2 \xrightarrow[\text{room temperature}]{\text{dark}}$

(c) $C_2H_6 + Cl_2\ (\text{excess}) \xrightarrow{\text{UV light}}$

(d) $C_2H_6 + Cl_2 \xrightarrow{\text{UV light}}$

17. Halogenation of alkanes is
(a) a reductive process (b) an oxidative process
(c) an isothermal process (d) an endothermal process

18. Ethylene dichloride can be prepared by adding HCl to
(a) Ethane (b) Ethylene
(c) Acetylene (d) Ethylene glycol

19. In which of the following conversions, phosphorus pentachloride is used as the reagent?
(a) $H_2C=CH_2 \longrightarrow CH_3CH_2Cl$
(b) $CH_3CH_2OH \longrightarrow CH_3CH_2Cl$
(c) $H_3C-O-CH_3 \longrightarrow CH_3Cl$
(d) $CH\equiv CH \longrightarrow CH_2=CHCl$

20. The best method for the conversion of an alcohol into an alkyl chloride is by treating the alcohol with
(a) PCl_5
(b) dry HCl in the presence of anhydrous $ZnCl_2$
(c) $SOCl_2$ in presence of pyridine
(d) None of these

21. Which of the following is liquid at room temperature (b.p. is shown against it) ?
(a) CH_3I 42°C
(b) CH_3Br 3°C
(c) C_2H_5Cl 12°C
(d) CH_3F –78°C

22. The catalyst used in the preparation of an alkyl chloride by the action of dry HCl on an alcohol is
(a) anhydrous $AlCl_3$ (b) $FeCl_3$
(c) anhydrous $ZnCl_2$ (d) Cu

23. Chlorobenzene is prepared commercially by
(a) Raschig process
(b) Wurtz Fittig reaction
(c) Friedel-Craft's reaction
(d) Grignard reaction

24. In the preparation of chlorobenzene from aniline, the most suitable reagent is
(a) Chlorine in the presence of ultraviolet light
(b) Chlorine in the presence of $AlCl_3$
(c) Nitrous acid followed by heating with Cu_2Cl_2
(d) HCl and Cu_2Cl_2

25. Which of the following possesses highest melting point?
(a) Chlorobenzene (b) m-dichlorobenzene
(c) o-dichlorobenzene (d) p-dichlorobenzene

26. Conant Finkelstein reaction for the preparation of alkyl iodide is based upon the fact that
(a) Sodium iodide is soluble in methanol, while sodium chloride is insoluble in methanol
(b) Sodium iodide is soluble in methanol, while NaCl and NaBr are insoluble in methanol
(c) Sodium iodide is insoluble in methanol, while NaCl and NaBr are soluble
(d) The three halogens differ considerably in their electronegativity

27. Silver acetate $+ Br_2 \xrightarrow{CS_2}$. The main product of this reaction is
(a) CH_3-Br (b) CH_3COI
(c) CH_3COOH (d) None of these

28. Which of the following reactions is an example of nucleophilic substitution reaction?
(a) $2RX+2Na \rightarrow R-R+2NaX$
(b) $RX+H_2 \rightarrow RH+HX$
(c) $RX+Mg \rightarrow RMgX$
(d) $RX+KOH \rightarrow ROH+KX$

29. Which one is most reactive towards S_N1 reaction ?
(a) $C_6H_5CH(C_6H_5)Br$
(b) $C_6H_5CH(CH_3)Br$
(c) $C_6H_5C(CH_3)(C_6H_5)Br$
(d) $C_6H_5CH_2Br$

30. A Grignard reagent may be made by reacting magnesium with
(a) Methyl amine (b) Diethyl ether
(c) Ethyl iodide (d) Ethyl alcohol

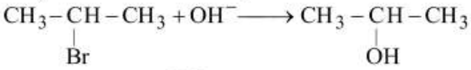
31. Which one of the following halogen compounds is difficult to be hydrolysed by S_N1 mechanism?
(a) Tertiary butyl chloride (b) Isopropyl chloride
(c) Benzyl chloride (d) Chlorobenzene

32. The order of reactivity of the given haloalkanes towards nucleophile is :
(a) RI > RBr > KCl (b) RCl > RBr > RI
(c) RBr > RCl > RI (d) RBr > RI > RCl

33. Most reactive halide towards S_N1 reaction is
(a) *n*-Butyl chloride (b) *sec*-Butyl chloride
(c) *tert*-Butyl chloride (d) Allyl chloride

34. In S_N1 reaction, the recemization takes place. It is due to
(a) inversion of configuration
(b) retention of configuration
(c) conversion of configuration
(d) Both (a) and (b)

35. The order of reactivities of the following alkyl halides for a S_N2 reaction is
(a) RF > RCl > RBr > RI (b) RF > RBr > RCl > RI
(c) RCl > RBr > RF > RI (d) RI > RBr > RCl > RF

36. Which of the following is an example of S_N2 reaction?
(a) $CH_3Br+OH^- \longrightarrow CH_3OH+Br^-$
(b) 
$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3+OH^- \longrightarrow CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$
(c) $CH_3CH_2OH \xrightarrow{-H_2O} CH_2=CH_2$
(d) $(CH_3)_3C-Br+OH^- \longrightarrow (CH_3)_3COH+Br^-$

37. S_N2 mechanism proceeds through intervention of
(a) carbonium ion (b) transition state
(c) free radical (d) carbanion

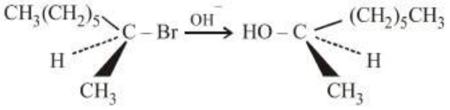
38. Which among MeX, RCH_2X, R_2CHX and R_3CX is most reactive towards S_N2 reaction?
(a) MeX (b) RCH_2X
(c) R_2CHX (d) R_3CX

39. Isopropyl chloride undergoes hydrolysis by
(a) S_N1 mechanism
(b) S_N2 mechanism
(c) S_N1 and S_N2 mechanisms
(d) Neither S_N1 nor S_N2 mechanism

40. Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of
(a) steric hindrance (b) inductive effect
(c) instability (d) insolubility

41. Which of the following is the correct order of decreasing S_N2 reactivity?
(a) $R_2CHX > R_3CX > RCH_2X$
(b) $RCHX > R_3CX > R_2CHX$
(c) $RCH_2X > R_2CHX > R_3CX$
(d) $R_3CX > R_2CHX > RCH_2X$.
(X is a halogen)

42. The reaction is described as



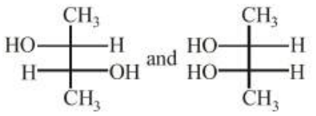
(a) S_E2 (b) S_N1
(c) S_N2 (d) S_N0

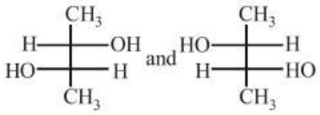
43. Which of the following is an optically active compound ?
(a) 1-Butanol (b) 1-Propanol
(c) 2-Chlorobutane (d) 4-Hydroxyheptane

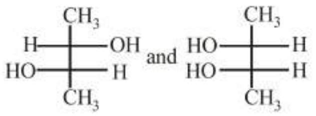
44. An important chemical method to resolve a racemic mixture makes use of the formation of
(a) a meso compound (b) enantiomers
(c) diasteromers (d) racemates

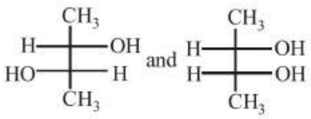
45. The process of separation of a racemic modification into d and ℓ-enantiomers is called
(a) Resolution (b) Dehydration
(c) Revolution (d) Dehydrohalogenation

46. Which of the following pairs of compounds are enantiomers?

(a) 

(b) 

(c) 

(d) 

47. Which of the following will have a mesoisomer also?
(a) 2, 3- Dichloropentane
(b) 2, 3-Dichlorobutane
(c) 2-Chlorobutane
(d) 2-Hydroxypropanoic acid

48. Which of the following compounds is optically active ?
(a) $CH_3CHClCOOH$ (b) $CH_3CH_2CH_2CH_3$
(c) $(CH_3)_2CHOH$ (d) $(CH_3)_3CCl$

49. Racemic compound has
(a) equimolar mixture of enantiomers
(b) 1 : 1 mixture of enantiomer and diastereomer
(c) 1 : 1 mixture of diastereomers
(d) 1 : 2 mixture of enantiomers

50. An organic molecule necessarily shows optical activity if it
(a) contains asymmetric carbon atoms
(b) is non-polar
(c) is non-superimposable on its mirror image
(d) is superimposable on its mirror image

51. Optically active isomers but not mirror images are called
(a) enantiomers (b) mesomers
(c) tautomers (d) diastereomers

52. Which of the following alkyl halides is used as a methylating agent?
(a) C_2H_5Br (b) C_6H_5Cl
(c) CH_3I (d) C_2H_5Cl

53. Mg reacts with RBr best in
(a) $C_2H_5OC_2H_5$ (b) $C_6H_5OCH_3$
(c) $C_6H_5N(CH_3)_2$ (d) Equally in all the three

54. 2-Bromopentane is heated with potassium ethoxide in ethanol. The major product obtained is
(a) 2-ethoxypentane (b) pentene-1
(c) trans-2-pentene (d) cis-pentene-2

55. An alkyl halide reacts with metallic sodium in dry ether. The reaction is known as :
(a) Frankland's reaction (b) Sandmeyer's reaction
(c) Wurtz reaction (d) Kolbe's reaction

56. When 2-bromobutane reacts with alcoholic KOH, the reaction is called
(a) halogenation (b) chlorination
(c) hydrogenation (d) dehydrohalogenation

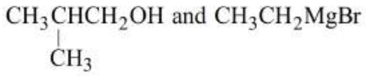
57. An alkyl halide by formation of its Grignard reagent and heating with water yields propane. What is the original alkyl halide ?
(a) Methyl iodide (b) Ethyl iodide
(c) Ethyl bromide (d) Propyl bromide

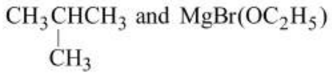
58. An organic compound A (C_4H_9Cl) on reaction with Na/diethyl ether gives a hydrocarbon which on monochlorination gives only one chloro derivative, then A is
(a) tert-butyl chloride (b) sec-butyl chloride
(c) isobutyl chloride (d) n-butyl chloride

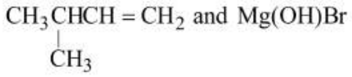
59. Elimination of bromine from 2-bromobutane results in the formation of–

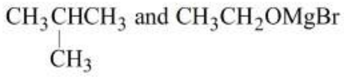
(a) predominantly 2-butyne
(b) predominantly 1-butene
(c) predominantly 2-butene
(d) equimolar mixture of 1 and 2-butene

60. Isobutyl magnesium bromide with dry ether and ethyl alcohol gives :

(a) 
$CH_3\underset{\substack{|\\ CH_3}}{C}HCH_2OH$ and CH_3CH_2MgBr

(b) 
$CH_3\underset{\substack{|\\ CH_3}}{C}HCH_3$ and $MgBr(OC_2H_5)$

(c) 
$CH_3\underset{\substack{|\\ CH_3}}{C}HCH = CH_2$ and $Mg(OH)Br$

(d) 
$CH_3\underset{\substack{|\\ CH_3}}{C}HCH_3$ and CH_3CH_2OMgBr

61. Reactivity order of halides for dehydrohalogenation is

(a) $R-F > R-Cl > R-Br > R-I$
(b) $R-I > R-Br > R-Cl > R-F$
(c) $R-I > R-Cl > R-Br > R-F$
(d) $R-F > R-I > R-Br > R-Cl$

62. Arrange the following alcohols in increasing order of their reactivity towards the reaction with HCl.

$(CH_3)_2CH\text{-}OH\,(1), (CH_3)_3C\text{-}OH\,(2), (C_6H_5)_3C\text{-}OH\,(3)$

(a) $1 < 2 < 3$ (b) $2 < 1 < 3$
(c) $3 < 1 < 2$ (d) $2 < 3 < 1$

63. Which of following can be used as solvent for grignard reagent ?

(a) H_2O (b) C_2H_5OH
(c) CH_3OH (d) $C_2H_5OC_2H_5$

64. Benzene reacts with CH_3Cl in the presence of anhydrous $AlCl_3$ to form :

(a) chlorobenzene (b) benzylchloride
(c) xylene (d) toluene

65. Chlorobenzene reacts with Mg in dry ether to give a compound (A) which further reacts with ethanol to yield

(a) Phenol (b) Benzene
(c) Ethylbenzene (d) Phenyl ether

66. Benzene reacts with n-propyl chloride in the presence of anhydrous $AlCl_3$ to give

(a) 3 – Propyl – 1 – chlorobenzene
(b) n-Propylbenzene
(c) No reaction
(d) Isopropylbenzene

67. Which of the following is the example of Friedal Craft reaction?

(a) $C_6H_6 + CH_3CH_2Cl \xrightarrow{AlCl_3} C_6H_5C_2H_5 + HCl$

(b) $C_6H_5OH + CH_3CH_2Cl \xrightarrow{AlCl_3} C_6H_5C_2H_5 + HOCl$

(c) $C_6H_5Cl + CH_3CH_2Cl \xrightarrow{[AlCl_3]} C_6H_5C_2H_5 + Cl_2$

(d) $C_6H_5CH_3 + CH_3CH_2Cl \xrightarrow{[AlCl_3]} C_6H_5C_2H_5 + CH_3Cl$

68. On sulphonation of C_6H_5Cl

(a) benzene sulphonic acid is formed
(b) metachlorobenzene sulphonic acid is formed
(c) orthochlorobenzene sulphonic acid is formed
(d) ortho and para chlorobenzene sulphonic acids are formed

69. $C-Cl$ bond of chlorobenzene in comparison to $C-Cl$ bond in methyl chloride is

(a) Longer and weaker (b) Shorter and weaker
(c) Shorter and stronger (d) Longer and stronger

70. Which of the following is not used in Friedel-Crafts reaction?

(a) N–Phenyl acetanilide (b) Bromobenzene
(c) Benzene (d) Chlorobenzene

71. Which one of the following is most reactive towards nucleophilic substitution reaction?

(a) $CH_2 = CH - Cl$ (b) C_6H_5Cl
(c) $CH_3CH = CH - Cl$ (d) $ClCH_2 - CH = CH_2$

72. Which one is most reactive towards S_N1 reaction ?

(a) $C_6H_5CH(C_6H_5)Br$
(b) $C_6H_5CH(CH_3)Br$
(c) $C_6H_5C(CH_3)(C_6H_5)Br$
(d) $C_6H_5CH_2Br$

73. Chlorobenzene can be prepared by reacting aniline with :

(a) hydrochloric acid
(b) cuprous chloride
(c) chlorine in presence of anhydrous aluminium chloride
(d) nitrous acid followed by heating with cuprous chloride

74. Aryl halides can not be prepared by the reaction of aryl alcohols with PCl_3, PCl_5 or $SOCl_2$ because

(a) phenols are highly stable compounds.
(b) carbon-oxygen bond in phenols has a partial double bond character.
(c) carbon-oxygen bond is highly polar
(d) all of these

75. Haloarenes are ortho and para directing due to

(a) Resonance in aryl halide
(b) – I effect of halogen atom
(c) + I effect of halogen atom
(d) Both (a) and (b)

76. Chloropicrin is obtained by the reaction of

(a) steam on carbon tetrachloride
(b) nitric acid on chlorobenzene
(c) chlorine on picric acid
(d) nitric acid on chloroform

77. Which of these can be used as moth repellant

(a) Benzene hexachloride (b) Benzal chloride
(c) Hexachloroethane (d) Tetrachloroethane

78. CF_xCl_y [where $x + y = 4$]. These compounds are not used because
(a) these are fluorocarbons
(b) these are difficult to synthesise
(c) they deplete ozone layer
(d) None of the these

79. Freon (dichlorodifluoro methane) is used
(a) as local anaesthetic
(b) for dissolving impurities in metallurgical process
(c) in refrigerator
(d) in printing industry

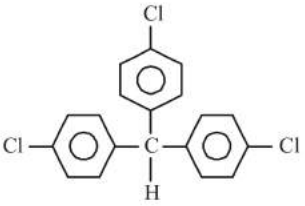
80. Use of chlorofluorocarbons is not encouraged because
(a) They are harmful to the eyes of people that use it
(b) They damage the refrigerators and air conditioners
(c) They eat away the ozone in the atmosphere
(d) They destroy the oxygen layer

81. Which of the following is used in fire extinguishers
(a) CH_4 (b) $CHCl_3$
(c) CH_2Cl_2 (d) CCl_4

82. Solvent which is used in the synthesis of chlorofluorocarbons
(a) iodoform (b) chloroform
(c) carbon tetrachloride (d) methylene chloride

83. Uses of dichloromethane is
(a) paint remover
(b) solvent in drugs manufacturing
(c) metal cleansing and finishing solvent
(d) All of the above

84. Trichloroacetaldehyde, CCl_3CHO reacts with chlorobenzene in presence of sulphuric acid and produces:

(a)


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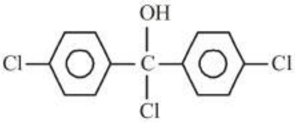

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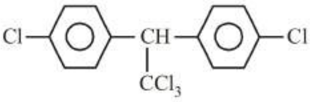
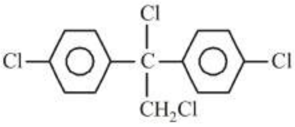


(d)


85. Chloroform on treatment with conc. HNO_3 gives
(a) Chloropicrin (b) Nitromethane
(c) Picric acid (d) Acetylene

86. Which of the following is responsible for depletion of the ozone layer in the upper strata of the atmosphere?
(a) Polyhalogens (b) Ferrocene
(c) Fullerenes (d) Freons

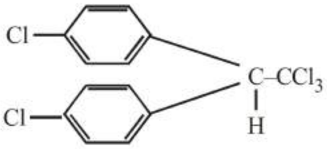
87. Haloforms are trihalogen derivatives of
(a) Ethane (b) Methane
(c) Propane (d) Benzene

88. Which of the following compounds is used as a refrigerant?
(a) Acetone (b) CCl_4
(c) CF_4 (d) CCl_2F_2

89. Chloroform is used as :
(a) Fire extinguisher (b) Industrial solvent
(c) Refrigerant (d) Insecticide

90. $AgNO_3$ does not give precipitate with $CHCl_3$ because
(a) $CHCl_3$ does not ionise in water
(b) $CHCl_3$ does not react with $AgNO_3$
(c) $CHCl_3$ is chemically inert
(d) None of these

91. When chloroform is exposed to light and air, it forms
(a) chlorine gas (b) methyl chloride
(c) phosgene gas (d) carbon tetrachloride

92.


The above structural formula refers to
(a) BHC (b) DNA
(c) DDT (d) RNA

93. If chloroform is left open in air in the presence of sunlight, it gives
(a) carbon tetrachloride (b) carbonyl chloride
(c) mustard gas (d) lewisite

94. Full name of DDT is
(a) 1, 1, 1-trichloro-2, 2-bis(*p*-chlorophenyl) ethane
(b) 1, 1-dichloro-2, 2-diphenyl trimethylethane
(c) 1, 1-dichloro-2, 2-diphenyl trichloroethane
(d) None of these

95. Freon(s) is/are :
(a) $CClF_3$ (b) $CFCl_3$
(c) CCl_2F_2 (d) All of these

96. Freon-12 is commonly used as
(a) insecticide (b) refrigerant
(c) a solvent (d) a fire extinguisher

97. Freon used as refrigerant is
(a) $CF_2{=}CF_2$ (b) CH_2F_2
(c) CCl_2F_2 (d) CF_4

98. Methylene chloride can be used as
(a) paint remover
(b) propellant in aerosols
(c) solvent in manufacturing of drugs
(d) All of these

99. Which of the following are the harmful effects of methylene chloride?
(a) Impaired hearing and vision
(b) Dizziness, nausea and tingling
(c) Skin burning
(d) All of these

STATEMENT TYPE QUESTIONS

100. Read the following statements and choose the correct option.
(i) The general formula of alkyl halides is $C_nH_{2n+1}X$
(ii) The general formula of aryl halides is $C_n H_{n-1} X$
(iii) In alkyl halides halogen atom(s) is attached to sp^2 hybridised carbon atom
(iv) In aryl halides halogen atom(s) is attached to sp^2 hybridised carbon atom.
(a) (i), (ii) and (iii) are correct
(b) (i), (ii) and (iv) are correct
(c) (ii), (iii) and (iv) are correct
(d) (i), (ii), (iii) and (iv) are correct

101. Following statements are given regarding the preparation of aryl halides from toluene. Read the following statements and choose the correct option.
(i) Aryl chlorides and bromides can be easily prepared by this method.
(ii) The ortho and para isomers formed in the reaction can not be separated easily due to small difference in their melting point.
(iii) Reactions with iodine are reversible in nature and require the presence of an oxidising agent.
(iv) Fluoro compounds are not prepared by this method due to low reactivity of fluorine.
(a) (i) and (iii) are correct
(b) (ii) and (iv) are correct
(c) (i), (ii), and (iii) are correct
(d) All statements are correct

102. Read the following statements and choose the correct option.
(i) For the same alkyl group, the boiling points of alkyl halides decreases in the order.
$RI > RBr > RCl > RF$
(ii) With the increases in size and mass of halogen atom, the magnitude of van der Waal's forces increases.
(a) Both statements (i) and (ii) are correct
(b) Statement (i) is correct and (ii) is incorrect
(c) Statement (ii) is correct and (i) is incorrect
(d) Both statement (i) and (ii) are incorrect

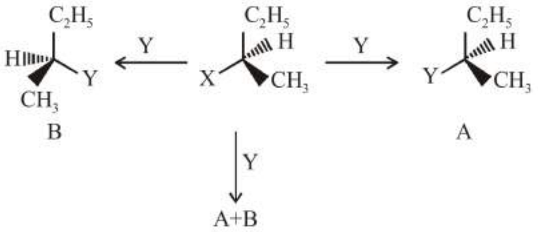
103. Read the following statements and choose the correct answer
(i) The boiling points of isomeric haloalkanes decrease with increase in branching.
(ii) Among isomeric dihalobenzenes the para-isomers have higher melting point than their ortho and meta-isomers.
(iii) The isomeric dihalobenzene have large difference in their boiling and melting points
(iv) The isomeric dihalobenzene have nearly same boiling point.
(a) (i), (ii) and (iii) are correct
(b) (i) and (iii) are correct
(c) (ii) and (iv) are correct
(d) (i), (ii) and (iv) are correct

104. Read the following statements and choose the correct code
(i) S_N2 reactions follows a second order kinetics whereas S_N1 reactions follows the first order kinetics
(ii) S_N1 reactions follows the second order kinetics whereas S_N2 follows the first order kinetics
(iii) S_N2 reactions take place in a single step whereas S_N1 reactions take place in a two steps
(iv) Tertiary alkyl halides are least reactive towards S_N2 reactions but we show high reactivity towards S_N1 reaction.
(a) (ii) and (iv) are correct
(b) (i) and (iii) are correct
(c) (i), (ii) and are correct
(d) (ii), (iii) and (iv) are correct

105. Read the following statements and choose the correct option.
(i) S_N1 reactions are carried out through formation of carbocation as an intermediate.
(ii) S_N1 reactions are two step reactions in which step 1 is fast and irreversible.
(iii) Step 1 involves breaking of C–Br bond which obtain energy through solvation of halide.
(iv) S_N1 reactions are two step reactions in which step 2 is slow and reversible.
(v) Allylic and benzylic halides show high reactivity toward S_N1 reactions.
(a) (i), (iii) and (v) are correct
(b) (ii), (iii) and (v) are correct
(c) (i), (iii) and (iv) are correct
(d) (i), (ii) and (iv) are correct

106. Read the following statements and choose the correct code
(i) S_N2 reaction proceed with complete stereochemical inversion.
(ii) $S_N{}^1$ reaction proceed with recimisation.
(iii) A dextrorotatory compound rotate the plane polarised light to the left.
(iv) A laevorotatory compound rotate the plane polarised light to the right
(a) TFTT (b) TTFF
(c) FFTT (d) TFTF

107.



For the reaction scheme given above some statements are given. Read the statements and choose the correct option.

(i) If (A) is the only compound obtained, the process is called retention of configuration.

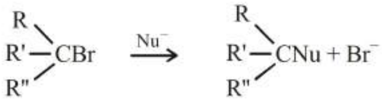
(ii) If (B) is the only compound obtained, the process is called inversion of configuration.

(iii) If a 50 : 50 mixture of the above two is obtained then the process is called racemisation

(iv) The product A + B is optically active

(a) TTTF (b) TFTF
(c) TTFF (d) TFFT

108. Which of the statement(s) is/are true, regarding following reaction?



$$RR'R''CBr \xrightarrow{Nu^-} RR'R''CNu + Br^-$$

(i) The reaction involves the formation of transition state.

(ii) Higher the nucleophilic character of the nucleophile, faster will be the reaction.

(iii) The product is always optically inactive.

(a) (ii) only (b) (ii) and (iii)
(c) (i), (ii) and (iii) (d) Neither (i), (ii) nor (iii)

MATCHING TYPE QUESTIONS

109. Match the columns

Column - I	**Column - II**
(A) $CH_2=CH-CH_2Cl$	(p) Gem-dichloride
(B) $CH_2=CHX$	(q) Vinylic halide
(C) CH_3CHCl_2	(r) Dichloride
(D) CH_2ClCH_2Cl	(s) Allylic halide

(a) A – (r), B – (q), C – (p), D – (s)
(b) A – (q), B – (p), C – (s), D – (r)
(c) A – (s), B – (q), C – (p), D – (r)
(d) A – (r), B – (p), C – (s), D – (q)

110. Match the columns

Column - I	**Column - II**
(A) $C_2H_6 \xrightarrow{Cl_2/UV\ light} C_2H_5Cl$	(p) Finkelstein reaction
(B) $C_6H_5NH_2 \xrightarrow[273-278K]{NaNO_2+HCl/Cu_2Cl_2} C_6H_5Cl$	(q) Free radical substitution
(C) $CH_3Cl + NaI \longrightarrow CH_3I + NaCl$	(r) Swarts reaction
(D) $CH_3-Br + AgF \longrightarrow CH_3F + AgBr$	(s) Sandmeyer's reaction

(a) A – (q), B – (s), C – (p), D – (r)
(b) A – (q), B – (r), C – (p), D – (s)
(c) A – (r), B – (p), C – (s), D – (q)
(d) A – (s), B – (r), C – (p), D – (q)

111. Match the columns

Column - I	**Column - II**
(A) Chloroform	(p) Antiseptic
(B) Iodoform	(q) Insecticide
(C) Trichloromethane	(r) Anesthetic
(D) DDT	(s) Propellant

(a) A – (s), B – (p), C – (r), D – (q)
(b) A – (r), B – (p), C – (s), D – (q)
(c) A – (q), B – (s), C – (p), D – (q)
(d) A – (r), B – (s), C – (p), D – (q)

112. Match the columns.

Column - I **(Haloalkane/arene)**	**Column - II** **(Applications)**
(A) Iodoform	(p) CF_4
(B) BHC	(q) Antiseptic
(C) Freon - 14	(r) Moth repellant
(D) Halothanes	(s) Inhalative anesthetic
(E) p-dichlorobenzene	(t) Termite pesticide

(a) A – (q), B – (s), C – (t), D – (r), E – (p)
(b) A – (q), B – (t), C – (p), D – (s), E – (r)
(c) A – (r), B – (s), C – (q), D – (p), E – (t)
(d) A – (p), B – (r), C – (t), D – (q), E – (s)

113. Match the columns

Column-I	**Column-II**
(A) Chloramphenicol	(p) Goiter
(B) Thyroxine	(q) Surgery
(C) Chloroquine	(r) Typhoid
(D) Halothane	(s) Malaria

(a) A – (q), B – (p), C – (s), D – (r)
(b) A – (r), B – (p), C – (s), D – (q)
(c) A – (s), B – (r), C – (q), D – (p)
(d) A – (p), B – (s), C – (q), D – (r)

ASSERTION-REASON TYPE QUESTIONS

Directions : Each of these questions contain two statements, Assertion and Reason. Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below.

(a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.
(b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion
(c) Assertion is correct, reason is incorrect
(d) Assertion is incorrect, reason is correct.

114. **Assertion :** S_N2 reaction of an optically active aryl halide with an aqueous solution of KOH always gives an alcohol with opposite sign of rotation.
Reason : S_N2 reactions always proceed with inversion of configuration.

115. **Assertion :** Alkylbenzene is not prepared by Friedel-Crafts alkylation of benzene.
Reason : Alkyl halides are less reactive than acyl halides.

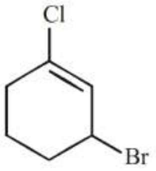
116. **Assertion :** Exposure of ultraviolet rays to human causes the skin cancer, disorder and disrupt the immune system.
Reason : Carbon tetrachloride is released into air it rises to atmosphere and depletes the ozone layer.

117. **Assertion :** $CHCl_3$ is stored in dark bottles.
Reason : $CHCl_3$ is oxidised in dark.

118. **Assertion :** CCl_4 is not a fire extinguisher.
Reason : CCl_4 is insoluble in water.

CRITICAL THINKING TYPE QUESTIONS

119. The IUPAC name of the compound shown below is



(a) 2-bromo-6-chlorocyclohex-1-ene
(b) 6-bromo-2-chlorocyclohexene
(c) 3-bromo-1-chlorocyclohexene
(d) 1-bromo-3-chlorocyclohexene

120. A compound is formed by substitution of two chlorine for two hydrogens in propane. The number of possible isomeric compounds is

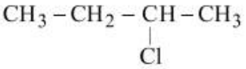
(a) 4 (b) 3
(c) 5 (d) 2

121. Which one of the following is not an allylic halide?

(a) 4-Bromopent-2-ene
(b) 3-Bromo-2-methylbut-1-ene
(c) 1-Bromobut-2-ene
(d) 4-Bromobut-1-ene

122. The catalyst used in the preparation of an alkyl chloride by the action of dry HCl on an alcohol is

(a) Anhydrous $AlCl_3$ (b) $FeCl_3$
(c) Anhydrous $ZnCl_2$ (d) Cu

123. 
$\underset{\displaystyle Cl}{CH_3-CH_2-\underset{|}{CH}-CH_3}$ obtained by chlorination of n-butane, will be

(a) *l*-form (b) *d*-form
(c) Meso form (d) Racemic mixture

124. The number of possible enantiomeric pairs that can be produced during monochlorination of 2-methylbutane is

(a) 2 (b) 3
(c) 4 (d) 1

125. The number of structural and configurational isomers of a bromo compound, C_5H_9Br, formed by the addition of HBr to 2-pentyne respectively are

(a) 1 and 2 (b) 2 and 4
(c) 4 and 2 (d) 2 and 1

126. Which of the following reagent produces pure alkyl halides when heated with alcohols?

(a) PCl_5 (b) PCl_3
(c) $SOCl_2$ (d) dry HCl

127. If C_5H_{12} undergoes reaction with chlorine in the presence of sunlight, only one product is formed, than reactant is

(a) 3, 3-dimethylpropane (b) 2, 3-dimethylpropane
(c) 1, 3-dimethylpropane (d) 2, 2,-dimethylpropane

128. Hydrocarbon $(CH_3)_3CH$ undergoes reaction with Br_2 and Cl_2 in the presence of sunlight, if the reaction with Cl is highly reactive and that with Br is highly selective so no.of possible products respectively is (are)

(a) 2, 2 (b) 2, 1
(c) 1, 2 (d) 1, 1

129. Possible major product formed in the reaction of neopentylalcohol with HCl is

(a) 2 -chloro-2-methylbutane
(b) 2, 2 -dimethyl 1-chloropropane
(c) 2 -chloro -3-methylbutane
(d) 3, chloro -3-methylbutane

130. Fluorobenzene (C_6H_5F) can be synthesized in the laboratory

(a) by direct fluorination of benzene with F_2 gas
(b) by reacting bromobenzene with NaF solution
(c) by heating phenol with HF and KF
(d) from aniline by diazotisation followed by heating the diazonium salt with HBF_4

131. Which chloride is least reactive with the hydrolysis point of view?

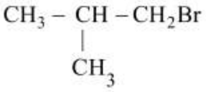
(a) CH_3Cl (b) CH_3CH_2Cl
(c) $(CH_3)_3CCl$ (d) $CH_2=CH-Cl$

132. In a S_N2 substitution reaction of the type

$R-Br+Cl^- \xrightarrow{DMF} R-Cl+Br^-$

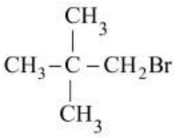
which one of the following has the highest relative rate ?

(a) $CH_3-CH_2-CH_2Br$ (b)



$CH_3-CH(CH_3)-CH_2Br$

(c)



$CH_3-C(CH_3)_2-CH_2Br$

(d) CH_3CH_2Br

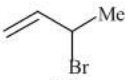
133. Which will undergo S_N2 reaction fastest among the following halogen compounds?

(a) CH_3CH_2F (b) CH_3CH_2Cl

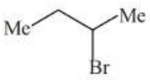
(c) CH_3CH_2Br (d) CH_3CH_2I

134. Consider the following bromides :

(A)



(B)



(C)

The correct order of S_N1 reactivity is

(a) B>C>A (b) B>A>C

(c) C>B>A (d) A>B>C

135. Which one is most reactive towards S_N1 reaction ?

(a) $C_6H_5CH(C_6H_5)Br$

(b) $C_6H_5CH(CH_3)Br$

(c) $C_6H_5C(CH_3)(C_6H_5)Br$

(d) $C_6H_5CH_2Br$

136. Consider the reactions :

(i) $(CH_3)_2CH-CH_2Br \xrightarrow{C_2H_5OH} (CH_3)_2CH-CH_2OC_2H_5+HBr$

(ii) $(CH_3)_2CH-CH_2Br \xrightarrow{C_2H_5O^-} (CH_3)_2CH-CH_2OC_2H_5+Br^-$

The mechanisms of reactions (i) and (ii) are respectively :

(a) S_N1 and S_N2 (b) S_N1 and S_N1

(c) S_N2 and S_N2 (d) S_N2 and S_N1

137. The organic chloro compound, which shows complete stereochemical inversion during a S_N2 reaction, is

(a) $(C_2H_5)_2CHCl$ (b) $(CH_3)_3CCl$

(c) $(CH_3)_2CHCl$ (d) CH_3Cl

138. Under certain conditions an alkyl halide reacts with base to give an alkene and HCl [Elimination Reaction] for example

$R-CH_2-CH_2-Cl \rightarrow R-CH=CH_2+HCl$

The extent of these reactions depends on the structure of alkyl halides (e.g. primary, secondary or tertiary). The relative extent to which such reactions take place is in the order (of haloalkanes) :

(a) Primary < secondary < Tertiary

(b) Primary > Secondary > Tertiary

(c) Primary > Secondary < Tertiary

(d) Primary < Secondary > Tertiary

139. The correct order of reactivity of the halides, ethyl chloride (I) *iso*-propyl chloride (II) and benzyl chloride (III) in S_N1 reaction is

(a) I > II > III (b) III > II > I

(c) II > I > III (d) I > III > II

140. Which of the following represents correct set of ambident nucleophiles?

(a) CN^- and NH_3 (b) CN^-, NO_2

(c) OH^-, RO^- (d) CN^-, OH^-

141. Which of the following statements is correct?

(a) S_N2 reactions of optically active halides are accompanied by inversion of configuration.

(b) S_N1 reactions of optically active halides are accompanied by racemisation.

(c) Carbocation formed in S_N1 reaction is sp^2 hybridized.

(d) All of the above.

142. The replacement of chlorine of chlorobenzene to give phenol requires drastic conditions, but the chlorine of 2, 4-dinitrochlorobenzene is readily replaced since,

(a) nitro groups make the aromatic ring electron rich at ortho/para positions

(b) nitro groups withdraw electrons from the meta position of the aromatic ring

(c) nitro groups donate electrons at meta position

(d) nitro groups withdraw electrons from ortho/para positions of the aromatic ring

143. A set of compounds in which the reactivity of halogen atom in the ascending order is

(a) chlorobenzene, vinyl chloride, chloroethane

(b) chloroethane, chlorobenzene, vinyl chloride

(c) vinyl chloride, chlorobenzene, chloroethane

(d) vinyl chloride, chloroethane, chlorobenzene

144. Aryl halides are extremely less reactive towards nucleophilic substitution than alkylhalides. Which of the following accounts for this ?

(i) Due to resonance in aryl halides.

(ii) In alkyl halides carbon atom in C–X bond is sp^2 hybridised whereas in aryl halides carbon atom in C–X bond is sp^3 hybridized.

(iii) Due to stability of phenyl cation.

(iv) Due to possible repulsion there are less chances of nucleophile to approach electron rich arenes.

(a) (i), (ii) and (iv) (b) (i), (ii) and (iii)

(c) (i) and (iv) (d) (ii), (iii) and (iv)

145. The organic compound used as feedstock in the synthesis of chlorofluorocarbons is

(a) CH_2Cl_2 (b) $CHCl_3$

(c) CH_3Cl (d) CCl_4

146. CCl_4 is well known fire extinguisher. However after using it to extinguish fire, the room should be well ventilated. This is because

(a) It is flammable at higher temperatures

(b) It is toxic

(c) It produces phosgene by reaction with water vapour at higher temperatures

(d) It is corrosive

147. In which part of the atmosphere, does the freon remain unchanged ?

(a) Stratosphere (b) Troposphere

(c) Mesosphere (d) Thermosphere

148. Natural ozone layer is unbalanced due to

(a) cloudiness of poisonous gases

(b) presence of rain in the atmosphere

(c) initiation of radical chain by freon

(d) All of the above

149. Exposure of CCl_4 causes

(a) Liver cancer in human

(b) Damage to nerve cells

(c) Coma, unconsciousness

(d) All of these

150. Chloroform cannot be prepared from which of the following?

(a) CH_3OH (b) C_2H_5OH

(c) CH_3CHO (d) $(CH_3)_2CO$

151. Which one of the following has antiseptic property?

(a) Dichloromethane (b) Trifluoromethane

(c) Triiodomethane (d) Tetrachloromethane

152. Chronic chloroform exposure may cause damage to liver and kidney, due to the formation of

(a) phosgene (b) methylene chloride

(c) methyl chloride (d) carbon tetrachloride

153. The spatial arrangement of four groups around a central carbon atom is tetrahedral and if all the substituents attached to that a carbon are different. Such a carbon is called ______.

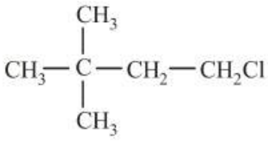
(a) asymmetric carbon (b) stereocentre

(c) chiral (d) All of these

HINTS AND SOLUTIONS

FACT/DEFINITION TYPE QUESTIONS

1. (d) Neohexyl chloride is a primary halide as in it Cl-atom is attached to a primary carbon.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_2Cl$$

2. (b)

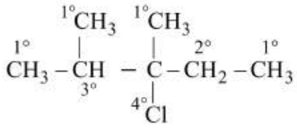
$$\begin{array}{c} CHCl_2 \\ | \\ CH_3 \end{array} \qquad \begin{array}{c} CH_2Cl \\ | \\ CH_2Cl \end{array}$$

(*gem*-dihalide) (*vic*-dihalide)

3. (b) Gem-dihalides are those in which two halogen atoms are attached on the same carbon atom.

4. (a)

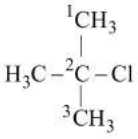
5. (b)



$$\overset{1^\circ}{CH_3}-\underset{3^\circ}{\overset{1^\circ CH_3}{CH}}-\underset{4^\circ Cl}{\overset{1^\circ CH_3}{C}}-\overset{2^\circ}{CH_2}-\overset{1^\circ}{CH_3}$$

3-chloro-2-3-dimethylpentane

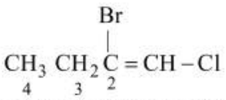
6. (b)



$$H_3C-\underset{^3CH_3}{\overset{^1CH_3}{^2C}}-Cl$$

IUPAC name : 2-Chloro-2-methylpropane.

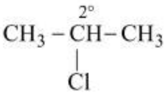
7. (a)



$$\underset{4}{CH_3}\ \underset{3}{CH_2}\ \underset{2}{\overset{Br}{C}}=CH-Cl$$

2 - bromo - 1 - chloro but - 1 - ene

8. (d) $CH_2=CH-CH_2Cl$
(3–chloro–1–propene)



9. (a) Isopropyl chloride $CH_3-\underset{Cl}{\overset{2^\circ}{CH}}-CH_3$ chlorine atom is attached to 2° carbon atom.

10. (a) 11. (d)

12. (c) Because of the small size of F, the C–F bond is strongest in CH_3F.

13. (b) CH_3Cl has higher dipole moment than CH_3F due to *much longer* C–Cl bond length than the C–F bond. The much longer bond length of the C–C bond outweighs the effect produced by lower electronegativity of Cl than that of F.

14. (c) For the same alkyl group, the boiling points of alkyl halides decrease 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 Waal's forces increases.

15. (a)

16. (a) $C_2H_6 + Cl_2 \xrightarrow{\text{UV light}} C_2H_5Cl+HCl$

17. (b)

18. (d) Ethylene dichloride can be prepared by adding HCl to ethylene glycol ($CH_2OH.\ CH_2OH$).

19. (b) When ethyl alcohol is treated with PCl_5, then ethyl chloride is formed.

$$CH_3CH_2-OH + PCl_5 \xrightarrow[\Delta]{} CH_3CH_2-Cl+HCl+POCl_3$$

20. (c) The best method for the conversion of an alcohol into an alkyl chloride is reaction of the alcohol with thionyl chloride ($SOCl_2$) in the presence of pyridine.

$$R-OH+SOCl_2 \xrightarrow{\text{Pyridine}} RCl+SO_2\uparrow+HCl\uparrow$$

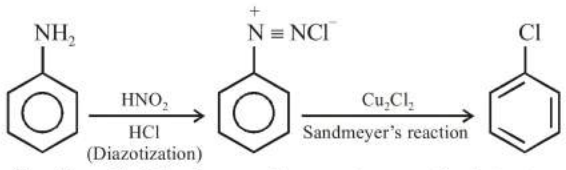
SO_2 and HCl being gases escape leaving behind pure alkyl halide.

21. (a) Boiling point of CH_3I is 42°C which indicates that it is liquid at room temperature. CH_3I is larger molecule so it has stronger vander Waal's force of attraction than others.

22. (c) In preparation of an alkyl chloride by the action of dry HCl, the catalyst generally used is anhydrous $ZnCl_2$.

23. (a)

24. (c)



25. (d) Para-di-chlorobenzene has most symmetrical structure than others. It is found as crystalline lattice form, therefore, it has highest melting point (52°C) due to symmetrical structure.

Para-chlorobenzene

26. **(b)** $$\underset{\substack{\text{Soluble in}\\(CH_3OH,\ Me_2CO)}}{R-X + NaI} \xrightarrow{\text{acetone}} R-I + \underset{\substack{\text{Insoluble in}\\(CH_3OH,\ Me_2CO)}}{NaX\downarrow}$$

(where X = Cl or Br)

27. **(a)** $CH_3COOAg + Br_2 \xrightarrow{CS_2} CH_3Br + AgBr + CO_2$

28. **(d)** In **nucleophilic substitution,** a nucleophile provides an electron pair to the substrate and the leaving group departs with an electron pair.

$Nu{:} + R{-}X \longrightarrow R{-}Nu + X{:}^{\ominus}$

These are usually written as S_N (S stands for substitution and N for nucleophilic) and are common in aliphatic compounds especially in alkyl halides and acyl halides.

29. **(c)** S_N1 reactions involve the formation of carbocations, hence higher the stability of carbocation, more will be reactivity of the parent alkyl halide. Thus tertiary carbocation formed from (c) is stabilized by two phenyl groups and one methyl group, hence most stable.

30. **(c)** $CH_3CH_2I + Mg \xrightarrow[\text{Ether}]{\text{Dry}} \underset{\text{Ethyl magnesium iodide}}{CH_3CH_2MgI}$

31. **(d)** Chlorobenzene does not undergo hydrolysis by S_N1 mechanism because in this halogen is present on sp^2 hybridised carbon atom, such halogens are relatively inert.

32. **(a)** For a given alkyl group, the order of reactivity is

$$\underline{R-I > R-Br > R-Cl > R-F}$$

increasing bond energy

decreasing halogen reactivity.

This order depends on the carbon-halogen bond energy; the carbon-fluorine bond energy is maximum and thus fluorides are least reactive while carbon-iodine bond energy is minimum hence iodides are most reactive.

33. **(c)** More stable the carbocation, more reactive will be the parent alkyl halide towards S_N1 reaction.

3° > Benzyl > Allyl > 2° > 1° > methyl

34. **(d)** S_N1 reaction involves carbocation which are planar (sp^2 hybridised) and thus can be attacked on either face of the carbon.

35. **(d)** Weaker the C–X bond, greater is the reactivity.

36. **(a)** Only 1° alkyl halides (i.e. CH_3Br) undergo S_N2 reaction.

37. **(b)**

38. **(a)** 1° Alkyl halides (having least steric hindrance at α-carbon atom) are most reactive towards S_N2 reaction.

39. **(c)** Isopropyl chloride, being 2° alkyl halides, can undergo S_N1 as well as S_N2 mechanism.

40. **(b)** Due to steric hindrance tertiary alkyl halide do not react by S_N2 mechanism they react by S_N1 mechanism. S_N2 mechanisam is followed in case of primary and secondary alkyl halides of

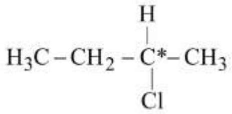
$$CH_3-X > CH_3-CH_2X > (CH_3)_2-CH.X > (CH_3)_3-C-X$$

41. **(c)** In S_N2 mechanism transition state is pentavalent. Thus bulky alkyl group will be sterically hindered and smaller alkyl group will favour the S_N2 mechanism. So the decreasing order of reactivity of alkyl halides is

$RCH_2X > R_2CHX > R_3CX$

42. **(c)** Inversion in configuration occurs in S_N2 reactions.

43. **(c)**



$$H_3C-CH_2-\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C^*}}-CH_3$$

The compound containing a chiral carbon atom i.e., (a carbon atom which is attached to four different atoms is known as a chiral carbon atom) is optically active.

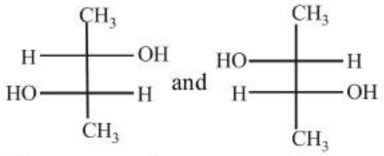
A s

2-chlorobutane contains a chiral C* atom hence it is optically active.

44. **(c)** Diastereomers since they have different melting points, boiling points, solubilities etc.

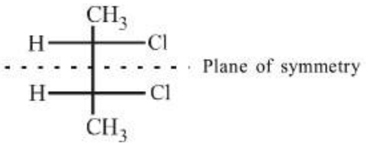
45. **(a)**

46. **(b)** Compound which are mirror image of each other and are non superimposable are termed as enantiomers.



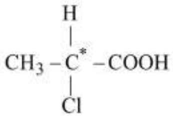
These are enantiomers

47. **(b)** The compound has two similar assymmetric C-atoms. It has plane of symmetry and exist in meso form.



Meso - 2, 3 dichlorobutane

48. **(a)** Compounds having chiral carbon atom are optically active.



$$CH_3-\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C^*}}-COOH$$

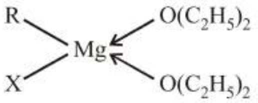
(* is chiral carbon atom)

49. **(a)** A mixture of equal amounts of the two enantiomers is called a racemic mixture.

50. **(c)** **51.** **(d)**

52. **(c)** C_2H_5Br and C_2H_5Cl are ethylating agents, while C_6H_5Cl is inert.

53. **(a)** Although all the three compounds can be used for preparing Grignard reagents, diethyl ether is considered as the best because it provides electron pairs to Mg of the reagent fully for coordination, in case of $C_6H_5OCH_3$ and $C_6H_5N(CH_3)_2$ electron pair on O and N are partialy delocalised over the benzene and hence are less available for coordination with Mg.



54. **(c)** Potassium ethoxide is a strong base, and 2-bromopentane is a 2° bromide, so elimination raction predominates

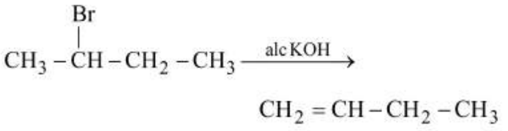
$$CH_3CH(Br)CH_2CH_2CH_3 \xrightarrow{OC_2H_5^-} \underset{\text{Pentene - 2(major) } trans}{CH_3CH=CHCH_2CH_3} + \underset{\text{Pentene-1(minor) } cis}{CH_2=CHCH_2CH_2CH_3}$$

Since *trans*- alkene is more stable than *cis*. Thus *trans*-pentene -2 is the main product.

55. **(c)** Wurtz reaction : It involves the interaction of two molecules of an alkyl halide (preferably bromide or iodide) with metalic sodium in presence of dry ether to form symmetrical alkanes containing double the number of carbon atoms present in the alkyl halide. For example,

$$\underset{\text{Alkyl halide}}{R-X} + 2Na + X-R \xrightarrow{\text{Dry ether}} \underset{\text{Alkane}}{R-R} + 2NaX$$

56. **(d)**

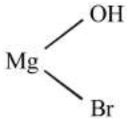


$$CH_3-\overset{\overset{\large Br}{|}}{C}H-CH_2-CH_3 \xrightarrow{\text{alc KOH}} CH_2=CH-CH_2-CH_3$$

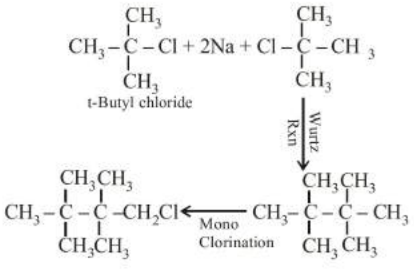
In this reaction both hydrogen and halogen atom has been removed so it is known as dehydro halogenation reaction.

57. **(d)** $\underset{\text{(Propyl Bromide)}}{CH_3CH_2CH_2Br} + Mg \longrightarrow CH_3CH_2CH_2MgBr$

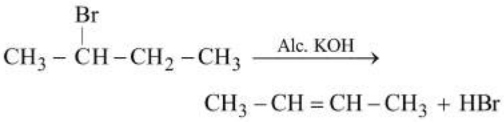
$CH_3CH_2CH_2MgBr + H_2O \longrightarrow CH_3CH_2CH_3 +$



58. **(a)**



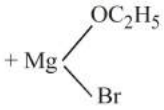
59. **(c)**



$$CH_3-\overset{\overset{\large Br}{|}}{C}H-CH_2-CH_3 \xrightarrow{\text{Alc. KOH}} CH_3-CH=CH-CH_3 + HBr$$

The formation of 2-butene is in accordance to **Saytzeff's rule**. The more substituted alkene is formed in major quantity.

60. **(b)** $(CH_3)_2CHCH_2MgBr \xrightarrow{C_2H_5OH} (CH_3)_2CHCH_3$



61. **(b)** The order of atomic size of halogens decrease in the order I > Br > Cl > F. On moving down a group atomic size increases. Further the bond length of C-X bond decreases in the order

$C-I > C-Br > C-Cl > C-F$

and hence the bond dissociation energy decreases in the order

$R-F > R-Cl > R-Br > R-I$

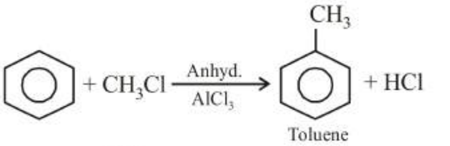
hence R – I being a weakest bond break most easily.

hence R – I is most reactive.

62. **(a)** Alkylhalide formation in the reaction of alcohol with HCl undergoes S_N1 reaction in which formation of the carbocation as intermediate occurs. Stability of carbocation is greatest for $(C_6H_5)_3C^+$ due to resonance effect, and stability of tertiary carbocation is greater than the secondary carbocation hence the option (a) shows the correct order.

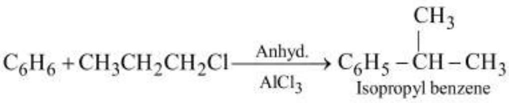
63. **(d)** Except (d) all contain abstractable proton

64. **(d)**



65. **(b)** $C_6H_5Cl \xrightarrow{Mg} C_6H_5MgBr \xrightarrow{CH_3CH_2OH} C_6H_6 + CH_3CH_2OMgBr$

66. **(d)**

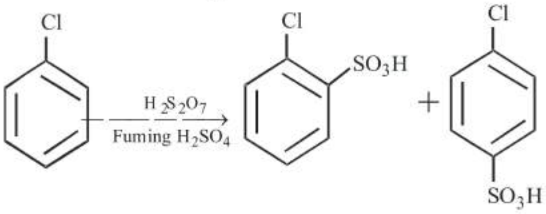


$$C_6H_6 + CH_3CH_2CH_2Cl \xrightarrow[AlCl_3]{\text{Anhyd.}} \underset{\text{Isopropyl benzene}}{C_6H_5-\overset{\overset{\large CH_3}{|}}{C}H-CH_3}$$

67. **(a)** Friedel-Craft's reaction is mainly applied on benzene.

$C_6H_6 + CH_3CH_2Cl \xrightarrow{AlCl_3} C_6H_5C_2H_5 + HCl$

68. **(d)** On sulphonation of chlorobenzene, ortho and para chlorobenzene is formed because – Cl group is para and ortho directing.



69. **(c)** Due to resonance in chlorobenzene.

70. **(a)** N-Phenylacetanilide, $C_6H_5N(C_6H_5)COCH_3$, precipitates out to a complex with anhydrous $AlCl_3$.

71. **(d)** More the stability of the carbocation, higher will be the reactivity of the parent chloride. Allyl chloride > Vinyl chloride > Chlorobenzene

72. **(c)** S_N1 reactions involve the formation of carbocations, hence higher the stability of carbocation, more will be reactivity of the parent alkyl halide. Thus tertiary carbocation formed from (c) is stabilized by two phenyl groups and one methyl group, hence most stable.

73. **(d)** $C_6H_5NH_2 \xrightarrow[HCl]{HONO} C_6H_5N_2Cl \xrightarrow{CuCl} C_6H_5Cl$

74. **(b)** This method is not applicable for the preparation of aryl halides because the C–O bond in phenol has a partial double bond character and is difficult to break being stronger than a single bond.

75. **(d)** Due to resonance, the electron density increases more at ortho- and para-positions than at meta-positions. Further, the halogen atom because of its – I effect has some tendency to withdraw electrons from the benzene ring. As a result, the ring gets somewhat deactivated as compared to benzene and hence the electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene.

76. **(d)** Chloropicrin is nitrochloroform. It is obtained by the nitration of chloroform with HNO_3.

$$\underset{\text{Chloroform}}{HCCl_3} \xrightarrow{HNO_3} \underset{\text{Chloropicrin}}{O_2NCCl_3}$$

Chloropicrin is a liquids, poisonous and used as an insecticide and a war gas

77. **(c)** 78. **(c)**

79. **(c)** Freon (CCl_2F_2) is an odourless, non-corrosive, non toxic gas which is stable even at high temperatures and pressures. It has low b.p. low specific heat and can be easily liquified by applying pressure at room temperature. It is therefore, widely used as refrigerant (cooling agent) in refrigerators and air conditioners.

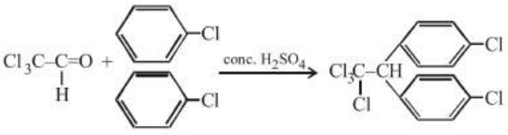
80. **(c)** Chlorofluorocarbon is used in air-conditioners and in domestic refrigerators for cooling purposes. Its main drawback is this, it is responsible for ozone depletion.

81. **(d)** Its vapours are non-inflammable (*i.e.* do not catch fire). Hence used as fire extinguishers under the name pyrene.

82. **(c)** Tetrachloromethane (carbon tetrachloride) is also used as feedstock in the synthesis of chlorofluorocarbon and other pharmaceutical manufacturing and general solvents etc.

83. **(d)** Dichloromethane is widely used as solvent as a paint remover, as a propellant in aerosols and as a process solvent in the manufacture of drugs. It is also used as a metal cleaning and finishing solvent.

84. **(c)**



DDT

85. **(a)** $Cl_3C-\boxed{H+HO}-NO_2 \longrightarrow \underset{\text{Chloropicrin (used as an insecticide)}}{Cl_3C-NO_2}$

86. **(d)** Chlorofluorocarbons, e.g. CF_2Cl_2, CHF_2Cl_2, HCF_2CHCl_2. These are non-inflammable colourless and stable upto 550ºC. These are emitted as propellants in aerosol spray, cans refrigerators, fire fighting reagents etc. They are chemically inert and hence do not react with any substance with which they come in contact and therefore float through the atmosphere and as a result enter the stratosphere. There they absorb UV-rays and due to this they produce free atomic chlorine which results decomposition of ozone which cause depletion of ozone layer.

87. **(b)** Haloform compounds with the formula CHX_3, where X is a halogen atom.
Haloforms are trihalogen derivatives of methane.
Example : Chloroform $CHCl_3$.

88. **(d)** Under ordinary conditions freon is a gas. Its boiling point is –29.8°C. It can easily be liquified. It is chemically intert. It is used in air-conditioning and in domestic refrigerations for cooling purposes (as refrigerant)

89. **(b)** Chloroform ($CHCl_3$) is used as industrial solvent.

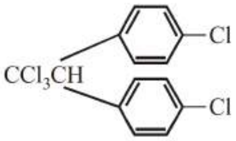
90. **(a)** Chloroform is an organic compound which does not ionise in water. Since it can not provide Cl^-, therefore, it is not precipitated with $AgNO_3$.

91. **(c)** When chloroform is exposed to light it is oxidised to a poisonous gas known as phosgene.

$$2CHCl_3 + 2O_2 \longrightarrow 2COCl_2 + Cl_2$$

92. **(c)** 93. **(b)**

94. **(a)**



(DDT)

95. **(d)** Freons are chlorofluorocarbons.
$\therefore$ $CClF_3$, $CFCl_3$ and CCl_2F_2, all are freons.

96. **(b)**

97. **(c)** Freons are chlorofluorocarbon.

98. **(d)** 99. **(d)**

STATEMENT TYPE QUESTIONS

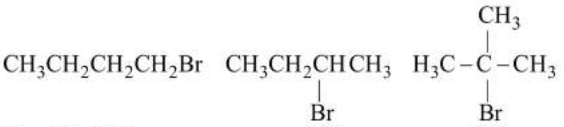
100. **(b)** In alkyl halides halogen atom(s) is attached to sp^3 hybridised carbon atom.

101. (a) Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysis like iron or iron (III) chloride.

The ortho and para isomers can be easily separated due to large difference in their melting points. Reactions with iodine are reversible in nature and require the presence of an oxidising agent (HNO_3, HIO_4) to oxidise the HI formed during iodination. Fluoro compounds are not prepared by this method due to high reactivity of fluorine.

102. (a)

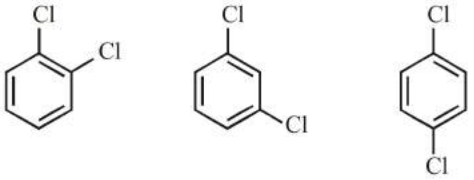
103. (d) The boiling points of isomeric haloalkanes decrease with increase in branching. For example, 2-bromo-2-methylpropane has the lowest boiling point among the three isomers.



$$CH_3CH_2CH_2CH_2Br \quad CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 \quad H_3C-\underset{\displaystyle Br}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3$$

b.p./K 375 364 346

Boiling points of isomeric dihalobenzenes are very nearly the same. However, the para-isomers are high melting as compared to their ortho and meta-isomers. It is due to symmetry of para-isomers that fits in crystal lattice better as compared to ortho- and meta-isomers.



b.p/K	453	446	448
m.p.K	256	249	323

104. (b) S_N2 reaction follow a 2nd order kinetic ie the rate depends upon the concentration of both the reactants, where in S_N1 reactions rate depends only upon the concentration of only one reactants.

The order of reactivity order of alkyl halides for S_N2 reaction $3° > 2° > 1°$ and for S_N1 reactions $3° < 2° < 1°$

105. (a) In S_N1 reactions step 1 is slow and reversible and the slowest step is the rate determining step

106. (b) If the compound rotates the plane polarised light to the right, i.e., clockwise direction, it is called dextrorotatory (Greek for right rotating) or the d-form and is indicated by placing a positive(+) sign before the degree of rotation. If the light is rotated towards left (anticlockwise direction), the compound is said to be laevorotatory or the l-form and a negative (–) sign is placed before the degree of rotation.

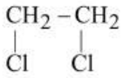
107. (a) If a 50 : 50 mixture of the (A) and (B) is obtained then the process is called racemisation and the product is optically inactive, as one isomer will rotate light in the direction opposite to another.

108. (d) *tert*-Alkyl halides undergo S_N1 reactions, hence they involve the formation of quite stable carbocations, and not the transition state. In S_N1 reactions, the nucleophile is not involved in rate determining (first) step, hence its stronger or weaker nature does not influence the reaction rate. In S_N1, the product has more percentage of the inverted configuration than the retained configuration, i.e. only partial racemization takes place, hence the product will be having some optical activity.

MATCHING TYPE QUESTIONS

109. (c) In allylic halides hydrogen atom is bonded to sp^3 hybridized carbon atom. Whereas in vinylic halide, hydrogen atom is bonded to sp^2 hybridized carbon atom.

CH_3CHCl_2
Ethylidene chloride
(gem-dihalide)



$$\underset{\displaystyle Cl}{\underset{|}{CH_2}}-\underset{\displaystyle Cl}{\underset{|}{CH_2}}$$

Ethylene dichloride (vic-dihalide)

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

$$R-X + NaI \longrightarrow R-I + NaX$$

$X = Cl, Br$

NaCl or NaBr thus formed is precipitated in dry acetone.

It facilitates the forword reaction according to le chatelier's principle. The synthesis of alkyl fluorides is best accomplished by heating an alkyl chloride/bromide in the presence of a metallic fluoride such as AgF, Hg_2F_2, CoF_2 or SbF_3. The reaction is termed as Swarts reaction.

$$H_3C-Br + AgF \longrightarrow H_3C-F + AgBr$$

111. (b) **112. (b)**

113. (b) Chloramphenicol, produced by soil microorganism is very effective for the treatment of typhoid fever. Our body produces iodine containing hormone thyroxine, the deficiency of which causes a disease called goiter. Synthetic halogen compounds, viz chloroquine is used for the treatment of malaria; halothane is used as an anaesthetic during surgery. Certain fully fluorinated compounds are being considered as potential blood substitutes in surgery.

ASSERTION-REASON TYPE QUESTIONS

114. (d) **Assertion** is false, because aryl halides do not undergo nucleophilic substitution under ordinary conditions. This is due to resonance, because of which the carbon–chlorine bond acquires partial double bond character, hence it becomes shorter and stronger and thus cannot be replaced by nucleophiles. However **Reason** is true.

115. (c) Alkyl halides give polyalkylation products.

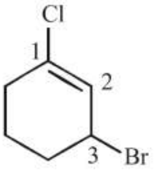
116. (b) Carbon tetrachloride rises to atmosphere and deplete the ozone layer. This depletion of ozone layer increases exposure of UV rays to human being which lead to increase of skin cancer, eye diseases and disorder with discruption of the immune system.

117. (c) $CHCl_3$ is stored in dark bottles to prevent oxidation of $CHCl_3$ in presence of sunlight.

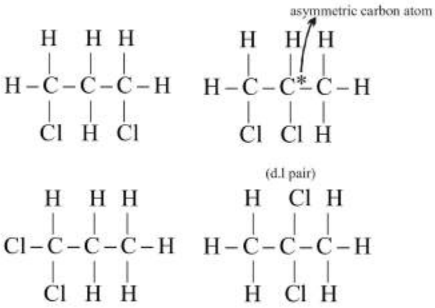
118. (d) CCl_4 is used as a fire extinguisher. The dense, non combustible vapours cover the burning substance and prevents the availability of oxygen around burning material.

CRITICAL THINKING TYPE QUESTIONS

119. (c)



120. (c) The compound is $C_3H_6Cl_2$ and the number of possible isomeric compunds is 5



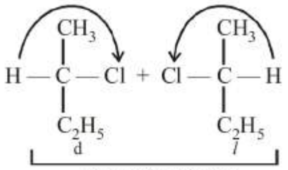
121. (d) 4-Bromobut-l-ene is not an allylic halide

$\underset{\text{4–Bromobut–1–ene}}{BrH_2C-CH_2-CH=CH_2}$

122. (c) Primary and secondary alkyl chlorides are prepared from the respective alcohols by using HCl gas and anhydrous $ZnCl_2$ (Groove's process).

123. (d) Chlorination of n-butane taken place via free radical formation i.e., $Cl_2 \xrightarrow{h\nu} Cl^{\bullet} + Cl^{\bullet}$

$CH_3-CH_2-CH_2-CH_3 \xrightarrow{Cl_2/h\nu}$

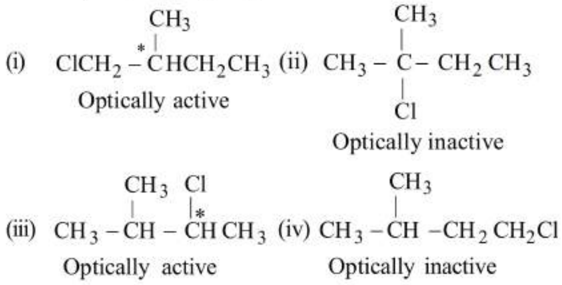


Racemic mixture

50% d form + 50% *l* form

$Cl^{\bullet}$ may attack on either side and give a racemic mixture of 2 chloro butane which contain 50% d form and 50% *l*-form.

124. (d) First draw possible different structures obtained on monochlorination of 2-methylbutane, $CH_3CH(CH_3)CH_2CH_3$.



Thus structures (i) and (iii) are optically active, each has one chiral carbon; so each structure will give one enantiomeric pair; thus total enantiomeric pairs will be two.

125. (b) Addition of HBr of 2-pentyne gives two structural isomers (I) and (II)

$$CH_3-C\equiv C-CH_2CH_3 \xrightarrow{HBr}$$

$$\underset{(I)}{CH_3C(Br)=CHCH_2CH_3} + \underset{(II)}{CH_3CH=C(Br)CH_2CH_3}$$

Each one of these will exist as a pair of geometrical isomers. Thus, there are two structural and four configurational isomers.

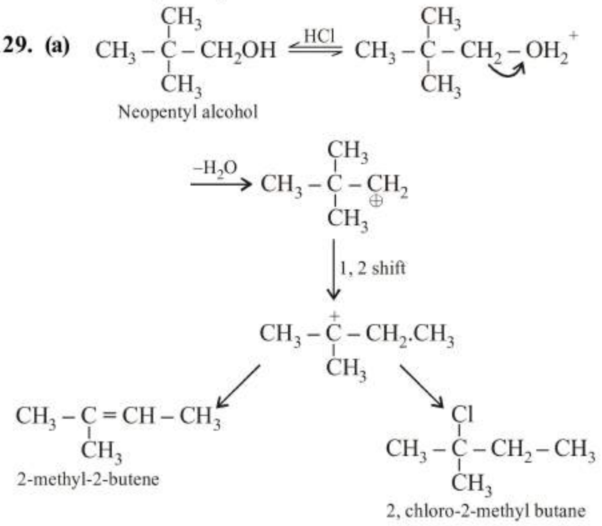
126. (c) Thionyl chloride is preferred because the other two products formed in the reaction are escapable gases. Hence the reaction gives pure alkyl halides

$$ROH + SOCl_2 \longrightarrow R{-}Cl + SO_2\uparrow + HCl\uparrow$$

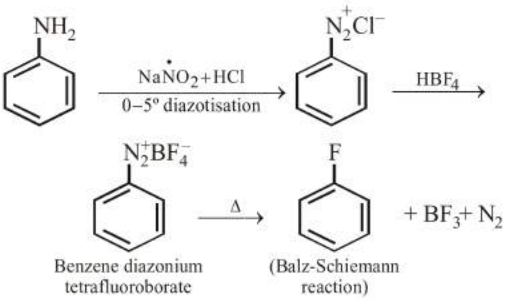
127. (d) This compound have only one type of hydrogen available.

128. (b) Chlorine atom is highly reactive so it will react with all type of hydrogen available while the Br atom is highly selective so it will react with that hydrogen which give the highly stabilize tertiary alkyl radical so only one product is formed.

129. (a)



130. (d)



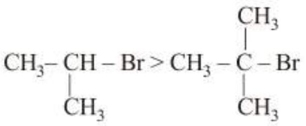
131. (d) $CH_2 = CH - Cl$
(Vinyl Chloride)

The halogen atom in vinyl chloride is not reactive as in other alkyl halides. The non-reactivity of chlorine atom is due to resonance stabilisation. The *ℓ.p.* on Cl-atom can participate in delocalisation (Resonance) to give two canonical structure.


$$CH_2 = CH - \ddot{C}l \longrightarrow \overset{\ominus}{C}H_2 - CH = \overset{+}{C}l:$$

132. (d) The rate of S_N2 substitution reaction is maximum in case of CH_3CH_2Br because S_N2 mechanism is followed in case of primary and secondary halides i.e., S_N2 reaction is favoured by small groups on the carbon atom attached to halogens so

$CH_3\,CH_2\,Br > CH_3\,CH_2\,CH_2\,Br >$


$$CH_3-\underset{\displaystyle CH_3}{CH}-Br > CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-Br$$

133. (d) Smaller the R group reactivity will be higher towards S_N2 reaction. For alkyl halides containing similar alkyl group better will be the leaving group, more facile is the nucleophilic substitution reaction.

Amongst the halide ions, the order in which the leaving groups depart follows the sequence :

$$I^- > Br^- > Cl^- > F^-$$

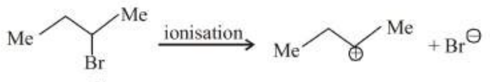
It is because of this reason that the order of reactivity of haloalkanes follows the sequence :

iodoalkanes > bromoalkanes > chloroalkanes > fluoroalkanes

134. (a)

(A)

(B)



(C)

Since S_N1 reactions involve the formation of carbocation as intermediate in the rate determining step, more is the stability of carbocation higher will be the reactivity of alkyl halides towards S_N1 route. Now we know that stability of carbocations follows the order : $3° > 2° > 1°$, so S_N1 reactivity should also follow the same order.

$3° > 2° > 1° >$ Methyl **(S_N1 reactivity)**

135. (c) S_N1 reactions involve the formation of carbocations, order of stability of carbocation is $3° > 2° > 1°$ hence higher the stability of carbocation, more will be the reactivity of the parent alkyl halide. Moreover the tertiary carbocation formed from (c) is stabilized by two phenyl groups.

136. (a) A strong nucleophile favours the S_N2 reaction and a weak nucleophile favours the S_N1 reaction.

First reaction is S_N1 reaction because C_2H_5OH is used as solvent which is a weak nucleophile.

Second reaction is S_N2 reaction because $C_2H_5O^-$ is strong nucleophile.

137. (d) S_N2 reaction is favoured by small groups on the carbon atom attached to halogen.

So, the order of reactivity is

$$CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl > (C_2H_5)_2CHCl$$

S_N2 reaction is shown to maximum extent by primary halides. The only primary halides given is CH_3Cl so the correct answer is (d).

138. (a) Primary halide < Secondary halide < Tertiary halide.

139. (b) Since S_N1 reaction involve the formation of carbocation as intermediate in the rate determining step. More stable the carbocation, more is the reactivity of the halide toward S_N1 route. As we know that the stability of the carbocations decreases in the order :

Benzyl 2° > 1°.

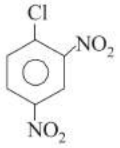
Hence the correct order of stability is

III > II > I

140. (b) Cyanides and nitrites possess two nucleophilic centres and are called ambident nucleophiles. Actually cyanide group is a nucleophile in two different ways $[^{\ominus}C \equiv N \leftrightarrow :C = N^{\ominus}]$. Similarly nitrite ion also represents an ambident nucleophile with two different points of linkage $[^{-}O-\ddot{N}=O]$. The linkage through oxygen results in alkyl nitrites while through nitrogen atom, it leads to nitroalkanes.

141. (d) In case of optically active alkyl halides, the product formed as a result of S_N2 mechanism has the inverted configuration as compared to the reactant. This is because the nucleophile attaches itself on the side opposite to the one where the halogen atom is present. In case of optically active alkyl halides, S_N1 reactions are accompanied by racemisation. The carbocation formed in the slow step being sp^2 hybridised is planar (achiral).

142. (d) —NO_2 group is electron attractive group, so it is able to deactivate the benzene ring.

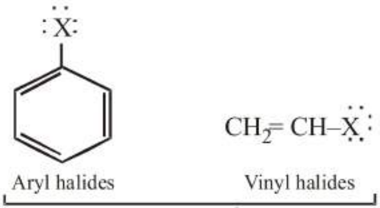


hence withdrawl of electrons from ortho and para position cause easy removal of –Cl atom due to development of +ve charge on o- and p positions.

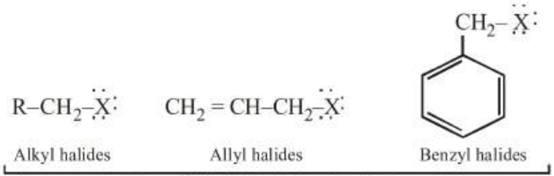
143. (a) On the same basis as above

$CH_3CH_2Cl > CH_2=CHCl > C_6H_5Cl$

144. (c) The carbon-halogen bonds of aryl halides are both shorter and stronger (due to possibility of resonance) than the carbon-halogen bonds of R–X and in this respect as well as in their chemical behaviour, they resemble vinyl halides ($CH_2=CHX$) more than alkyl halides.



Halogen attached to C is sp^2 hybridised C, C–X bond is shorter and stronger because of partial double bond character due to delocalisation of electrons on halogens



Halogen attached to sp^3 hybridised C. Delocalisation of electrons on halogen is not possible, hence C–X bond does not acquire double bond character, hence it is weaker and reactive.

145. (d) $3CCl_4 + 2SbF_5 \xrightarrow{SbCl_5} 2SbCl_3 + \underset{\text{freon–12}}{3CCl_2F_2}$

$CCl_4 + 2H \xrightarrow{C,FeCl_3} 2HCl + CCl_2F_2$

146. (c) Carbon tetrachloride vapours react with steam above 500° C to from phosgene, a poisonous gas.

$CCl_4 + H_2O \xrightarrow{500°C} \underset{\text{phosgene}}{COCl_2} + 2HCl$

147. (a) In stratosphere, freon is able to initiate radical chain reaction that can upset the natural ozone balance.

148. (c) In stratosphere freon is able, to initiate radical chain reactions that can upset the natural ozone balance.

149. (d) Exposure of carbon tetrachloride causes liver cancer in humans. The most common effects are dizziness, light headedness, nausea and vomiting which cause permanent damage to nerve cells. In severe cases, these effects can lead rapidly to stupor, coma, unconsciousness or death.

150. (a) $\underset{\text{Ethanol}}{CH_3CH_2OH} + Cl_2 \xrightarrow{\text{oxidation}} \underset{\text{Ethanal}}{CH_3CHO} + 2HCl$

$\underset{\text{Ethanal}}{CH_3CHO} + 3Cl_2 \longrightarrow \underset{\text{Chloral}}{CCl_3CHO} + 3HCl$

$2CCl_3CHO + Ca(OH)_2 \longrightarrow$

$\underset{\text{Chloroform}}{2CHCl_3} + \underset{\text{Cal. formate}}{(HCOO)_2Ca}$

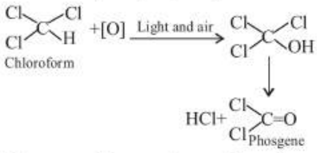
$\underset{\text{Acetone}}{CH_3COCH_3} + 3Cl_2 \longrightarrow \underset{\text{Trichloroacetone}}{CCl_3COCH_3} + 3HCl$

$2CCl_3CO.CH_3 + Ca(OH)_2 \longrightarrow$

$2CHCl_3 + (CH_3COO)_2Ca$

151. (c) Triiodomethane (CHI_3) when comes in contact with organic matter decomposes easily to free iodine which has antiseptic property.

152. (a)



Phosgene is an extremely poisonous gas.

153. (d)