

# SMART ACHIEVERS

**CHEMISTRY - XII** 

Haloalkanes and Haloarenes PYQs

Date: 23/10/2021

- Q1. Draw the structure of 2-bromopentane
- Q2. Write the IUPAC name of  $CH_3 CH CH_2 CH = CH_2$ .
- Q3. Write the IUPAC name of

$$CH_3$$
 $CH_3CH = CH - C - CH_3$ 
 $Br$ 
 $OCH_3$ .

CM - CH $_3$ 
 $CH - CH_3$ 
 $CH$ 

- Q4. Write the IUPAC name of (CH<sub>3</sub>)<sub>2</sub>CHCH(CI)CH<sub>3</sub>.
- Q5. Write the IUPAC name of the following compound:

- Q6. Write the structure of the following compound: 1-bromo-4-sec-butyl-2-methylbenzene.
- Q7. Write the structure of the following compound: 2-(2-chlorophenyl)-1-iodooctane.
- Q8. Give IUPAC name of the following organic compound:

- Q9. Write the structure of the following compound: 2-(2-Bromophenl)butane.
- Q10. Write the structure of the following compound: 1,4-dibromobut-2-ene.
- Q11. Write the IUPAC name of the following compound: CH, = CHCH, Br.
- Q12. Write the IUPAC name of the following compound:  $CH_2 = C CH_2Br$ .
- Q13. Write the IUPAC name of the following compound: (CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>Br.
- Q14. Write the IUPAC name of the following:

$$CH_3 - C = C - CH_2OH$$
 $CH_3 - Br$ 

Q15. Write the IUPAC name of the following compound:

Q16. State the IUPAC name of the following compound:  $H_3C$  H H H H H H

Q17. Write the IUPAC name of the following compound:  $CH_3CH - CH - CH_3$ .  $CH_3CH - CH_3$ .  $CH_3CH - CH_3$ .

Q18. Write the structure of the compound 1-chloro-4-ethylcylohexane.

Q19. Write the IUPAC name of the following compound:

Q20. Write the structure of the compound: 4-tert-butyl-3-iodoheptane.

Q21. A hydrocarbon C<sub>5</sub>H<sub>12</sub> gives only one monochlorination product. Identify the hydrocarbon.

Q22. Write the structure of the major product in the following reaction:

$$CH_3 - CH = C - CH_3 + HBr \longrightarrow CH_3$$

Q23. Write the major products in the following:

Q24. How do you convert: Propene to 1-iodopropane?

Q25. Write the IUPAC name of  $CICH_2C = CCH_2Br$ .

Q26. Complete the following chemical equation:

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

Q27. What happens when bromine attacks

Q28. Draw the structure of major monohalogen product in the following reaction:

Q29. Draw the structure of major monohalogen product in the following reaction:

Q30. Draw the structure of major monohalogen product formed in the following reaction:

Q31. Which would undergo S<sub>N</sub>1 reaction faster in the following pair:

$$CH_3$$
  $CH_3$   $CH_3$ 

Q32. Which would undergo S<sub>N</sub>2 reaction fater in the following pair and why?

$$\begin{array}{c|cccc} & CH_3 \\ CH_3 - CH_2 - Br & and & CH_3 - C - CH_3 \\ & & Br \end{array}$$

- Q33. Write the structure of an isomer of compound  $C_4H_9Br$  which is most reactive towards  $S_N1$  reaction.
- Q34. Out of CH $_3$  CH $_2$  CI and CH $_3$  CH $_2$  CH $_3$  CH
- Q35. Out of ethyl bromide and ethyl chloride which has higher boiling point and why?
- Q36. Answer the following: Haloalkanes easily dissolve in organic solvents, why?
- Q37. Explain the following: Alkyl halides, though polar, are immiscible with water.
- Q38. Why does p-dichlorobenzene have a higher m.p. than its o- and m-isomers?
- Q39. Why are alkyl halides insoluble in water?
- Q40. Give reason: *n*-Butyl bromide has higher boiling point than *t*-butyl bromide.
- Q41. A solution of KOH hydrolyses CH<sub>3</sub>CHCICH<sub>2</sub>CH<sub>3</sub> and CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CI. Which one of these is more easily hydrolysed?
- Q42. Which will react faster in S<sub>N</sub>1 displacement reaction:
  - 1-Bromobutane or 2-bromobutane and why?
- Q43. Which will react faster in S<sub>N</sub>2 displacement, 1-bromopentane or 2-bromopentane and why?
- Q44. Give a chemical test of distinguish between C<sub>2</sub>H<sub>5</sub>Br and C<sub>6</sub>H<sub>5</sub>Br.
- Q45. Predict the order of reactivity of the following compounds in  $S_N$ 1 reaction.  $C_6H_5CH_2Br$ ,  $C_6H_5C(CH_3)(C_6H_5)Br$ ,  $C_6H_5CH(C_6H_5)Br$ ,  $C_6H_5CH(CH_3)Br$ .
- Q46. Predict the order of rectivity of four isomeric bromobutanes in S<sub>N</sub>1 reaction.
- Q47. Account for the following: Grignard's reagents should be prepared under anhydrous conditions.
- Q48. Which compound in the following pair undergoes faster S<sub>N</sub>1 reaction?

- Q49. Why (±)-butan-2-ol is optically inactive?
- Q50. What happens when ethyl chloride is treated with aqueous KOH?
- Q51. What happens when CH<sub>3</sub> Br is treated with KCN?
- Q52. Identify the chiral molecule in the following pair.

Q53. Which would undergo S<sub>N</sub>2 reaction fater in the following pair and why?

$$CH_3 - CH_2 - Br$$
 and  $CH_3 - CH_2 - I$ 

- Q54. Which halogen compound in each of the following pairs will react faster in S<sub>N</sub>2 reaction:
  - (a) CH<sub>3</sub>Br or CH<sub>3</sub>I
- (b) (CH<sub>3</sub>)<sub>3</sub>CCI or CH<sub>3</sub>CI.
- Q55. State one use each of DDT and iodoform.
- Q56. Write the balanced equation for the following:
  - (a) When chloroform is oxidised by air.
  - (b) Chloroform reacts with chlorine.
- Q57. Explain why in the pair,  $(CH_3)_3CCI$  and  $CH_3CI$  will react faster in  $S_N2$  reaction with OH?
- Q58. How may methyl bromide be preferentially converted to methyl isocyanide?
- Q59. Why is the following occur: Chloroform is stored in closed dark coloured bottles completely filled so that air is kept out.
- Q60. Explain the following reactions with an example: Friedel-Crafts reaction.
- Q61. Write the IUPAC names of the following compounds:
  - (a)  $CH_2 = CHCH_2Br$

(b) (CCI<sub>3</sub>)<sub>3</sub>CCI

TK. IX

Q62. Complete the following reaction equations:

(a) 
$$CH_3$$
 + HI  $\longrightarrow$  (b)  $CH_3CH_2CH = CH_2 + HBr  $\longrightarrow$$ 

Q63. Complete the following reaction equations:

(a) 
$$\bigcirc$$
 OH + SOCI<sub>2</sub>  $\longrightarrow$  (b)  $\bigcirc$  CH<sub>3</sub>OH + HCI  $\longrightarrow$ 

Q64. Write the mechanism of the following reaction:

Q65. Draw the structure of major monohalo product in each of the following reactions:

(a) 
$$\bigcirc$$
 OH  $\xrightarrow{SOCI_2}$  (b)  $\bigcirc$  CH<sub>2</sub> - CH = CH<sub>2</sub> + HBr  $\xrightarrow{Peroxide}$  Br

### Q66. Explain why

- (a) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?
- (b) alkyl halides, though polar, are immiscible with water?
- Q67. Complete the following reaction equations:

(a) 
$$C_6H_5N_2CI + KI \longrightarrow (b) \stackrel{H}{+}C = C \stackrel{H}{\leftarrow} + Br_2 \stackrel{CCI_4}{\longrightarrow}$$

- Q68. (a) Why is buan-1-ol optically inactive but butan-2-ol is optically active?
  - (b) Although chlorine is an electron withdrawing group, yet it is ortho-, para-directing in electrophilic aromatic substitution reactions. Why?
- Q69. Write the structure of the major product in each of the following reactions:

(a) 
$$CH_3 - CH_2 - CH_2 - CH_3 + KOH \xrightarrow{Ethanol}$$

Br

#### Q70. Give reasons:

- (a) Racemic mixture is iptically inactive.
- MG Pyt. Itd. (b) The presence of nitro group (- NO<sub>2</sub>) at o/p positions increases the reactivity of haloarenes towards nucleophilic substitution reactions
- Q71. Write the major product(s) in the following:

Write the major product(s) in the following:

(a) 
$$2CH_3 - CH - CH_3 \xrightarrow{Na} (b) CH_3 - CH_2 - Br \xrightarrow{AgCN}$$

CI

Give reasons:

#### Q72. Give reasons:

- (a) C CI bond length in chlorobenzene is shorter than C CI bond length in CH<sub>3</sub> CI.
- (b) S<sub>N</sub>1 reactions are accompanied by racemization in optically active alkyl halides.
- Q73. Give reasons for the following:
  - (a) Ethyl iodide undergoes S<sub>N</sub>2 reaction faster than ethyl bromide.
  - (b) C X bond length in halobenzene is smaller than C X bond length in  $CH_3 X$ .
- Q74. Account for the following:
  - (a) The C-CI bond length in chlorobenzene is shorter than that in  $CH_3-CI$ .
  - (b) Chloroform is stored in closed dark brown bottles.
- Q75. Chlorobenzene is extremely less reactive towards a nucleophilic substitution reaction Give two reasons for the same.
- Q76. What are ambident nucleophiles? Explain with an example.

### Q77. Write chemical equations when

- (a) methyl chloride is treated with AgNO<sub>2</sub>.
- (b) bromobenzene is treated with CH<sub>3</sub>CI in the presence of anhydrous AICI<sub>3</sub>.

# Q78. Halokanes undergo nucleophilic substitution whereas haloarenes undergo electrophilic substitution. Explain.

Q79. Write the mechanism of the following reaction:

$$n$$
-BuBr + KCN  $\xrightarrow{\text{EtOH, H}_2O}$   $n$ -BuCN

### Q80. Answer the following:

- (a) What is known as a racemic mixture? Give an example.
- (b) Of the two bromoderivatives,  $C_6H_5CH(CH_3)Br$  and  $C_6H_5CH(C_6H_5)Br$ , which one is more reactive in  $S_N1$  substitution reaction and why?
- Q81. (a) Why is sulphuric acid not used during the reaction of alcohols with KI in the conversion of a alcohol to the alkyl iodide?
  - (b) Why are haloarenes less reactive than haloalkanes towards nucleophilic substitution reactions?

# Q82. Which compound in the following couple will react faster in S<sub>N</sub>2 displacement why?

- (a) 1-Bromopentane or 2-bromopentane
- (b) 1-Bromo-2-methylbutane or 2-bromo-2-methylbutane.

# Q83. How would you account for the following:

(a) Griganrd reagents are prepared strictl under anhydrous conditions?

#### Q84. Give reasons for the following observations:

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

# Q85. Suggest a possible reason for the following observations:

- (a) The order of reactivity of haloalkanes is RI > RCI > RBr.
- (b) Neopentyl chloride (CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>CI does not follow S<sub>N</sub>2 mechanism.

Q86. Which one in the following pars undergoes S<sub>N</sub>1 substitution reaction faster and why?

- Q87. (a) Why is it that haloalkanes are more reactive than haloarenes towards nucleophiles.
  - (b) Which one of the following reacts faster in an S<sub>N</sub>1 reaction and why?

Q88. Give one example of each of the following reactions:

- (a) Wurtz reaction.
- (b) Wurtz-Fitting reaction.

Q89. What is Saytzeff rule? Illustrate with suitable example.

Q90. Discuss the mechanism of  $S_N1$  reaction of haloalkanes.

Q91. (a) Why are haloalkanes more reactive towards nucleophilic substitution reactions than haloarenens?

(b) Which one of the following two substances undergoes S<sub>N</sub>1 reaction faster and why?

Q92. How do you convert?

- (a) Chlorobenzene to biphenyl
- (b) 2-bromobutane to but-2-ene.

Q93. Write chemical equations when

- (a) ethyl chloride is treated with aqueous KOH.
- (b) chlorobenzene is treated with CH<sub>3</sub>COCI in presence of anhydrous AlCI<sub>3</sub>.

Q94. How are the following conversions carried out?

- (a) Benzyl chloride to benzyl alcoho.
- (b) Methyl magnesium bromide to methylpropan-2-ol.

Q95. (a) Which alkyl halide from the following pairs would you expect to react more rapidly by an S<sub>N</sub>2 mechanism and why?

$$CH_3 - CH_2 - CH - CH_3$$
 and  $CH_3 - CH_2 - CH_2 - CH_2 - Br$ 

(b) Racemisation occurs in S<sub>N</sub>1 reactions. Why?

Q96. Give the IUPAC mames of the following compounds:

(c) 
$$CH_2 = CH - CH_2 - CH_2$$

Q97. Compute the following reaction equations:

(a) 
$$CH_3 + HI \longrightarrow$$

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

## Q98. Answer the following questions:

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

(c) Which one undergoes S<sub>N</sub>2 substitution reaction faster and why?

$$\sim$$
I or  $\sim$ CI

Q99. Differentiate between  $S_N1$  and  $S_N2$  mechanisms and give examples.

# Q100(a) Write a chemical test to distinguish between:

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

Q101Complete the equation for the following reactions:

(a) 
$$H + HBr \rightarrow (b) CH_3 + HI \rightarrow (c) OH + SOCI_2 \rightarrow$$

Q102Rearrange the compounds of each of the following sets in order of reactivity towards  $S_N^2$  displacement:

- (a) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane.
- (b) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 3-Bromo-2-methylbutane.
- (c) 1-Bromobutane, 2-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane.



# **SMART ACHIEVE**

**CHEMISTRY - XII** 

Haloalkanes and Haloarenes PYQs-Solution

JEVERS LEAR LINE PAR. LINE.

Date: 23/10/2021

**S1.** 
$$H_3C - CH - CH_2 - CH_2 - CH_3$$
.

- 4-Chloropent-1-ene.
- 4-Bromo-4-methylpent-2-ene.
- S4. 2-Chloro-3-methyl butane.
- S5. 3-Chloro-2,2-dimethyl butane.

**S7.** 
$$IH_2C - CH - (CH_2)_4 - CH_2$$

**S8.** 
$${}^{1}_{CH_{3}CH} = {}^{3}_{CH_{3}} - {}^{4}_{CH_{3}} - {}^{5}_{CH_{3}}$$
  
 ${}^{1}_{CH_{3}} = {}^{3}_{CH_{3}} - {}^{4}_{CH_{3}} - {}^{5}_{CH_{3}}$   
 ${}^{2}_{CH_{3}} = {}^{3}_{CH_{3}} - {}^{4}_{CH_{3}} - {}^{5}_{CH_{3}}$ 

4-Bromo-3-methylpent-2-ene

**S10.** 
$$H_2C - CH = CH - CH$$

Br

Br

**S12.** 
$$CH_2 = C - CH_2Br$$
  $CH_3$ 

3-Bromo-2-methylpropene

S13.  $H_3C - C - C + CH_2 - Br$   $CH_3$   $CH_3$ 

1-Bromo-2,2-dimethylpropane

**S14.**  ${}^{4}_{CH_3} - {}^{3}_{||} = {}^{2}_{||} - {}^{1}_{CH_2OH}$ .

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

- **\$15.** 2-Bromo-4-chloropentane.
- S16. 1-Bromobut-2-ene.

S17. 
$${}^{4}_{CH_3}$$
  $-{}^{3}_{CH}$   $-{}^{2}_{CH}$   $-{}^{1}_{CH_3}$ .

2-Bromo-3-Chlorobutane

$$\begin{array}{c} {\rm CH_3} \\ {\rm H_3C - C - CH_2CI} \\ {\rm CH_3} \end{array}$$

1-Chloro-2,2-dimethylpropane

#### S22.

$$CH_3 - CH_2 - CH_3 - CH_3$$
 (Markownikny's addition)

2-Bromo-2-methylbutane

S24. 
$$CH_3CH = CH_2 + HBr \xrightarrow{Peroxide} CH_3CH_2CH_2CH_2Br \xrightarrow{Peroxide} CH_3 - CH_2 - CH_2I$$
Propene  $CH_3CH = CH_2 + HBr \xrightarrow{Peroxide} CH_3CH_2CH_2CH_2Br \xrightarrow{Peroxide} CH_3 - CH_2 - CH_2I$ 

**S25.** 
$$CICH_2 - C \equiv C - CH_2 - Br.$$
1-Bromo-4-chlorobut-2-yne

**S27.** 
$$CH_2 - CH - CH_2 - C \equiv CH$$

$$\begin{vmatrix}
& & & \\
& & & \\
& & & \\
Br & & Br
\end{vmatrix}$$

$$+ Br_2 \xrightarrow{\text{Heat}} + HBr$$

+ HI 
$$\longrightarrow$$
  $I$ 

$$CH_3$$
  $CH_3$   $CH_3$ 

**S32.**  $CH_3 - CH_2 - Br$  would undergo  $S_N 2$  reaction faster due to formating of less steric hindrance.

S33.

$$CH_3 - C - Br$$

$$CH_3 - C - Br$$

$$CH_3$$

Tertiary butyl bromide or 2-Bromo-2-methylpropane

**S34.** The S<sub>N</sub>1 reaction proceeds through carbocation formation thus, the compound which forms more stable carbocation will be more reactive.

$$CH_{3}-CH_{2}-CH-CI \xrightarrow{-CI^{-}} CH_{3}-CH_{2}-\overset{+}{C}H$$

$$CH_{3} CH_{3}$$

As,  $2^{\circ}$  carbocation is mre stable than  $1^{\circ}$  carbocation thus, 2-chlorobutane is more reactive towards  $S_N 1$  reaction.

- **S35.** The boiling point of ethyl bromide is higher due to the greater magnitude of the van der Waals forces which depend upon molecular size and mass.
- **S36.** Haloalkanes dissolve in organic solvents because the intermolecular attractions between haloalkanes and organic solvent molecules have the same strength as in the separate haloalkanes and solvent molecules.
- **S37.** Alkyl halides are polar but are insoluble in water because energy required to break the intermolecular H-bond among water molecules is much higher than energy released by water halide interaction.
- **S38.** *p*-Dichlorobenzene has higher melting point than those of *o* and *m*-isomers because it is more symmetrical and packing is better in solid from. Hence, it has stronger intermolecular force of attraction than *o* and *m*-isomers.

$$\begin{array}{c|c}
CI & CI & CI \\
\hline
CI & CI & \hline
CI &$$

- **S39.** Alkyl halides are polar but are insoluble in water because energy required to break the intermolecular H-bond among water molecules is much higher than energy released by water halide interaction.
- **S40.** *n*-Butyl bromide, being a straight chain molecule have strong intermolecular forces whereas *t*-butyl bromide being a branched chain molecule have weaker intermolecular forces due to smaller surface area.

Hence, boiling point of n-butyl bromide is higher than that of t-butyl bromide.

- **S41.** CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>3</sub> hydrolyses easily with KOH because it is secondary halide.
- **S42.** 2-bromobutane will react faster in S<sub>N</sub>1 displacement reaction because it will form more stable secondary carbocation intermediate.
- **S43.** 1-bromopentane is a primary alkyl halide, hence reacts faster in  $S_N 2$  displacement than secondary hailde 2-bromopentane.

- **S44.** C<sub>2</sub>H<sub>5</sub>Br reacts with AgNO<sub>3</sub> to give yellow precipitate of AgBr while C<sub>6</sub>H<sub>5</sub>Br.
- **S45.**  $C_6H_5C(CH_3)(C_6H_5)Br > C_6H_5CH(C_6H_5)Br > C_6H_5CH(CH_3)Br > C_6H_5CH_2Br$ .
- **S46.**  $(CH_3)_3CBr > CH_3CH_2CH CH_3 > (CH_3)_2CHCH_2Br > CH_3CH_2CH_2CH_2Br$ .
- **S47.** Grignard's reagents react with water to form alkanes.

$$R - Mg - X + H_2O \longrightarrow R - H + Mg < X$$

So, they must be prepared under anhydrous conditions.

- **S48.** Tertiary halide CI reacts faster than the secondary halide because ofthe greater stability of *tert*-carbocation.
- **S49.** The (±)-butan-2-ol is optically inactive because it iexist in two enantiometric forms which are non-superimposable mirror images of each other. Both the isomers are present in equal amounts therefore, it does not rotate the plane of polarized light and is optically inactive.

$$\begin{array}{c|c} \mathsf{CH_3} & \mathsf{CH_3} \\ \mathsf{HO} & \mathsf{C}^* \\ \mathsf{HO} & \mathsf{CH_2CH_3} \\ \mathsf{H} & \mathsf{CH_3CH_2} \\ \mathsf{HO} & \mathsf{H} \\ \mathsf{50\%-(+) \ Butan-2-ol} \\ \end{array}$$

\$50. When ethyl chloride is treated with awueous KOH, ethanol is formed,

$$CH_3CH_2CI + KOH(aq) \longrightarrow CH_3CH_2OH + KCI$$

**S51.** CH<sub>3</sub>CN is formed by nucleophilic substitution reaction.

$$CH_3Br + KCN \longrightarrow CH_3CN + KBr$$

- ss2. is a chiral molecule.
- **S53.** Since I $^-$  is a better leaving group than Br $^-$ , thus, CH $_3$ CH $_2$ I undergoes S $_N$ 2 reaction faster than CH $_3$ CH $_2$ Br.
- **S54.** (a)  $CH_3I$  will give faster  $S_N2$  reaction.
  - (b) CH<sub>3</sub>CI will give faster S<sub>N</sub>2 reaction.
- \$55. DDT is used as an insecticide and iodoform is used as a mild antiseptic.
- **S56.** (a)  $2CHCl_3 + O_2 \xrightarrow{Light} 2COCl_2 + 2HCl$  Chloroform Carbonyl chloride

- **S57.** CH<sub>3</sub>Cl will react faster in S<sub>N</sub>2 reaction with OH<sup>-</sup>.
- \$58. KCN is predominantly ionic and provides cyanide ions in solution

$$CH_3Br + KCN \longrightarrow CH_3C \equiv N + KBr$$
  
Methyl cyanide  
bromide

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

$$CH_3Br + AgCn \longrightarrow CH_3N \equiv C + AgBr$$
Methyl isocyanide
bromide

**\$59.** Chloroform when exposed to air and sunlight changes to phosgene which is a poisonous gas.

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

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

**S60.** Haloarenes can undergo both freidal craft alkylation (with alkyl halide) or freidal craft acylation (with acid halide) in presence of Lewis acid catalyst to give a mixture of *o*- and *p*-haloalkyl benzene or *o*- and *p*-haloacylbenzene.

$$\begin{array}{c|c} CI \\ & C \\ \hline \end{array} + CH_3 - C - CI \xrightarrow{Anhyd, AlCI_3} \begin{array}{c} CI \\ \hline \\ 2\text{-Chloroacetophenone} \\ \hline \\ \text{(Minor)} \end{array} + \begin{array}{c} CI \\ \hline \\ \text{CH}_3 \\ \hline \\ \text{4-Chloroacetophenone} \\ \hline \\ \text{(Major)} \end{array}$$

- **S61.** (a)  $CH_2 = CHCH_2Br$ . 3-Bromoprop-1-ene
- (b) 2-(Trichloromethyl)-1,1,12,3,3,3-heptachloropropae

S62. (a) 
$$CH_3 + HI \longrightarrow I$$

(b) 
$$CH_3CH_2CH = CH_2 + HBr \longrightarrow CH_3CH_2 - CH - CH_3$$

Br

S63. (a) 
$$OH + SOCI_2 \longrightarrow CI + SOCI_2 + SOCI_2 \rightarrow Chlorocylohexane$$

(b) 
$$HO$$
  $CH_2OH$   $+ HCI$   $Heat$   $HO$   $CH_2CI$ 

**S64.** (a) 
$$CH_3CH_2\overset{\bullet}{OH} + \overset{\bullet}{H}^+ \longrightarrow CH_3CH_2 - \overset{\bullet}{O}H_2$$

(b) 
$$Br + CH_3CH_2 - OH_2CH_2 - Br + H_2O$$

S65. (a) 
$$OH + SOCI_2 \longrightarrow CI + HCI + SOCI_2$$

(b) 
$$CH_2 - CH_2 - CH_2 + HBr \xrightarrow{Peroxide} CH_2 - CH_2 - CH_2 - Br$$

- **S66.** (a) There are two reasons:
  - In case of chlorobenzene, carbon to which chlorine is attached is  $sp^2$  hybridised and is (i) more electronegative than the corresponding carbon in cyclohexyl chloride which is  $sp^3$  hybridised. So the net dipole moment is lower in chlorobenzene.
  - In chlorobenzene C CI bond has some double bond character so its bond length is smaller.

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

(b) Alkyl halides are polar but are insoluble in water because energy required to break the intermolecular H-bond among water molecules is much higher than energy released by water halide interaction.

**S67.** (a) 
$$C_6H_5N_2CI + KI \longrightarrow C_6H_5I + N_2 + KCI$$

**S67.** (a) 
$$C_6H_5N_2CI + KI \longrightarrow C_6H_5I + N_2 + KCI$$
  
(b)  $H \longrightarrow C = C \hookrightarrow H + Br_2 \xrightarrow{CCI_4} CH_2 - CH_2$ 
Br Br

**S68.** (a) Buan-1-ol is achrial, *i.e.*, does not have chiral 'C' atom which is attached to four different groups, therefore, it is optically inactive.

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

$$H \xrightarrow{*} OH \qquad HO \xrightarrow{*} H$$

$$CH_2CH_3 \qquad CH_2CH_3$$

$$d(+) \qquad Butan-2-ol$$

$$CH_2CH_3 \qquad I(-) \qquad Butan-2-ol$$

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

**S69.** (a) 
$$CH_3 - CH_2 - CH = CH - Ch_3$$
 (Saytzeff rule)

- **S70.** (a) Racemic mixture contains equal amount of *d* and *l* forms, hence rotation due to one enantiomer is cancelled by another.
  - (b) The presence of nitro group at *o* and *p*-positions withdraws electrons from the benzene ring and thus, facilitates the attack of the nucleophile on haloarenes. The carbanion thus formed is further stabilised by reasonance.

**S71.** (a) 
$$CH_3 - CH - CH - CH_3$$
 (b)  $CH_3CH_2NC$ .  $CH_3 - CH_3$ 

**S72.** (a) In halobenzene C - X bond has partial double bond character due to resonance while  $CH_3 - X$  bond is single bond.

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

- (b) In S<sub>N</sub>1 reaction carbocation intermediate is formed which is a planar molecule so, an incoming nucleophile can attack from either side and a equilmolar mixture of two components are formed and resulting mixture is optically inactive.
- **S73.** (a) Since  $I^-$  is a better leaving group than  $Br^-$ , thus,  $CH_3CH_2I$  undergoes  $S_N^2$  reaction faster than  $CH_3CH_2Br$ .
  - (b) In halobenzene C X bond has partial double bond character due to resonance while  $CH_3 X$  bond is single bond.

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

**S74.** (a) In halobenzene C — X bond has partial double bond character due to resonance while  $CH_3 - X$  bond is single bond.

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

(b) Chloroform when exposed to air and sunlight changes to phosgene which is a poisonous gas.

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

- **S75.** Haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions due to the following reasons.
  - (a) Resonance effect: In haloarenes the electron pairs on halogen atom are in conjugation with  $\pi$ -electrons of the ring and the following resonating structures are possible.

- C CI bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, are less reactive towards nucleophilic substitution reaction.
- (b) Difference in hybridisation of carbon atom in C X bond.
- **\$76.** A nucleophile which can attack from more than one centres, is known as ambident nucleophile.
  - e.g., ¯C ≡ N: Cyanide ion.

**S77.** (a) 
$$CH_3CI + AgNO_2 \longrightarrow CH_3NO_2 + AgCI$$

(b) 
$$\begin{array}{c} Br \\ + CH_3CI \xrightarrow{Anhyd, AlCl_3} \end{array} \begin{array}{c} Br \\ CH_3 \end{array} + \begin{array}{c} CH_3 \\ CH \end{array}$$

**S78.** In haloarenes – ve charge gets localised on arenes using resonance, therefore they undergo electrophilic substitution.

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

**\$79.** Normal butyl bromide will give S<sub>N</sub>2 reaction:

$$K^{+}CN^{-} + CH_{3}CH_{2}CH_{2}CH_{2}Br \longrightarrow CH_{3}CH_{2}CH_{2}CH_{2}CN + KBr$$
 $n$ -Butyl cyanide

S80. (a) An equimolar mixture of a pair of enantiomers is called racemic mixture. A racemic mixture is optically inactive due to external compensation.

- (b) Of the two bromoderivatives,  $C_6H_5CH(CH_3)Br$  and  $C_6H_5CH(C_6H_5)Br$ , The  $C_6H_5CH(C_6H_5)Br$  is more reactive than  $C_6H_5CH(CH_3)Br$  for  $S_N1$  reaction because its carbocation is reasonance stabilised by two phenyl groups.
- **S81.** (a)  $H_2SO_4$  is an oxidant. KI reacts with  $H_2SO_4$  and give HI and  $H_2SO_4$  oxidises HI to  $I_2$ .

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

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

- (b) Haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions due to the following reasons.
  - (i) **Resonance effect:** In haloarenes the electron pairs on halogen atom are in conjugation with  $\pi$ -electrons of the ring and the following resonating structures are possible.

C — CI bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, are less reactive towards nucleophilic substitution reaction.

(ii) Difference in hybridisation of carbon atom in C - X bond.

- **\$82.** (a) 1-Bromopentane, as it is a primary alkyl halide.
  - (b) 1-Bromo-2-methylbutane, as it is a primary alkyl halide.
- **S83.** (a) Grignard's reagents react with water to form alkanes.

$$R - Mg - X + H_2O \longrightarrow R - H + Mg < X$$

So, they must be prepared under anhydrous conditions.

- **S84.** (a) Haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions due to the following reasons.
  - (i) **Resonance effect:** In haloarenes the electron pairs on halogen atom are in conjugation with  $\pi$ -electrons of the ring and the following resonating structures are possible.

C — CI bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, are less reactive towards nucleophilic substitution reaction.

- (ii) Difference in hybridisation of carbon atom in C X bond.
- (b) In aqueous solution, KOH is almost completely involved to give OH<sup>-</sup> ion which being a getter nucleophile gives a substitution reaction on alkyl halides to form alcohol. But an alcoholic solution of KOH containing alkoxide (RO–) ions which being a much stronger base than OH<sup>-</sup> ion preferentially snatches a H<sup>+</sup> ion from an alkyl chloride to form alkenes.
- **S85.** (a) Among the various halides with same alkyl group the order of reactivity is RI > RBr > RCI. Due to increasing bond strength of C I, C Br and C CI the reactivity decreases.
  - (b) Neopentyl chloride being a primary halide reacts slowly through S<sub>N</sub>1 and the carbon carrying halogen is sterically more hindered. Hence, it does not follow S<sub>N</sub>2 mechanism.

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

- **S87.** (a) Haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions due to the following reasons.
  - (i) **Resonance effect:** In haloarenes the electron pairs on halogen atom are in conjugation with  $\pi$ -electrons of the ring and the following resonating structures are possible.

C — CI bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, are less reactive towards nucleophilic substitution reaction.

- (ii) Difference in hybridisation of carbon atom in C X bond.
- (b) ertiary halide CI reacts faster than the secondary halide because ofthe greater stability of *tert*-carbocation.
- **S88.** (a) Wurtz reaction: It converts alkyl halide into higher alkane in presence of sodium metal and dry ether.

$${
m CH_3CI}$$
 + 2Na +  ${
m CH_3CI}$   $\xrightarrow{
m Ether}$  2NaCl +  ${
m C_2H_6}$  Chloromethane

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

$$\begin{array}{c|c} CI & CH_3 \\ \hline & + 2Na + CH_3CI \xrightarrow{Ether} & + 2NaCI \\ \hline \\ Chloromethane & Toluene \\ \hline \\ (Methyl benzene) \end{array}$$

**S89.** Saytzeff rule: In elimination reaction alkene having the lasser number of hydrogen on the double bonded carbon atom is formed. This generalisation is known as Saytzeff rule for example.

$$CH_{3}-CH_{2}-CHBr-CH_{3} \xrightarrow{alc. KOH} CH_{3}-CH_{2}-CH=CH-CH_{3}$$

$$CH_{3}-CH_{2}-CH=CH-CH_{3}$$

$$CH_{3}-CH_{2}-CH=CH_{2}-CH=CH_{2}$$

$$CH_{3}-CH_{2}-CH=CH_{2}$$

$$CH_{3}-CH_{2}-CH=CH_{2}$$

$$CH_{3}-CH_{2}-CH=CH_{2}$$

$$CH_{3}-CH=CH_{3}$$

$$CH_{3}-CH=$$

**S90.** In S<sub>N</sub>1 mechanism of substitution reaction, the rate of reaction depends upon the concentration of only one reactant. It is two steps reactant.

Mechanism:

$$C_2H_5$$
 $CH_3$ 
 $CH_3$ 
 $CH_5$ 
 $CH_6$ 
 $CH_7$ 
 $CH_7$ 

- Haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions due to the following reasons.
  - Resonance effect: In haloarenes the electron pairs on halogen atom are in conjugation (i) with  $\pi$ -electrons of the ring and the following resonating structures are possible.

C — CI bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, are less reactive towards nucleophilic substitution reaction.

- Difference in hybridisation of carbon atom in C X bond.
- (b) Due to greater stability of 2° carbocation over 1° carbocation, will react faster than  $\nearrow \bigcirc$  CI in S<sub>N</sub>1 reaction.

(a) 
$$2 + 2Na \xrightarrow{Ether} Diphenyl$$
 +  $2KC$ 

$$-$$
 CH  $-$  CH $_2$   $-$  CH $_3$   $-$  Ethanolic KOF $_4$ 

$$CH_3 - CH = CH - CH_3$$

When ethyl chloride is treated with awueous KOH, ethanol is formed,

$$CH_3CH_2CI + KOH(aq) \longrightarrow CH_3CH_2OH + KCI$$

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

(Major)

**S94.** (a) 
$$CH_2CI$$
  $CH_2OH$  +  $aq$ .  $KOH$   $\longrightarrow$   $Benzyl chloride$   $Benzyl alcohol$ 

(b) 
$$CH_3MgBr + CH_3 - C - CH_3 \longrightarrow CH_3 - C - CH$$

- 1-Bromobutane is 1° alkyl halide while 2-bromobutane is 2° alkyl halide. Due to steric **S95.** (a) hindrance in 2° alkyl halides, 1° alkyl halide will react faster than 2° alkyl halide in  $S_{\scriptscriptstyle N}2$ reaction.
  - Carbocations are formed in  $S_N 1$  reaction which are planar species, thus, racemisation occurs.
- 2-Bromobutane. **S96.** (a) 1,3-Dibromobenzene. 3-Chloropropene. (b)

S97. (a) 
$$CH_3 + HI \longrightarrow I$$

(b) 
$$H + HBr \xrightarrow{\text{Markovnikov's}} CH - CH_3$$

(c) 
$$CH_3CH_2CH = CH_2 + HBr \longrightarrow CH_3CH_2 - CH - CH_3$$

| Br

**S98.** (a) Chiral object: An object which has no plane of symmetry (cannot be divided into two identical halves) is called chiral (Greek; Chiral-Handd) or dissymmetric or asymmetric. A Chiral object is not superimposable on its mirror image.

e.g., left and right hand of a person are mirror images of each other and are not superimposable.



- (b)  $CH_3CH_2CHCH_3$  hydrolyses easily with KOH because it is secondary halide.

S99.		S <sub>N</sub> 1 mechanisms	S <sub>N</sub> 2 mechanisms
	1.	It is two step process, carbocation intermediate is formed.	lit is single step process. No intermediate is formed.
	2.	It obeys 1 <sup>st</sup> order kinetics. Rate = <i>k</i> [Reactant]	<ol> <li>It obeys 2<sup>nd</sup> order kinetics.</li> <li>Rate = k [Reactant] [Nuclephile]</li> </ol>
	3.	Order of reactivity: 3° > 2° > 1°.	3. Order of reactivity : 1° > 2° > 3°.
	4.	Optically inactive product is formed (racemic mixture).	4. Inversion of configuration takes place.
	5.	e.g., $(CH_3)_3CBr + OH^-$ 2-Bromo-2-methylpropane $\downarrow$ $(CH_3)_3COH + Br^-$ 2-Methylpropane-2-ol	5. e.g., $\Theta$ $H$ $C$ $C$ $C$ $A$

- **S100**(a) (i) Benzyl chloride gives white precipiate with AgNO<sub>3</sub> solution while chlorobenzene does not.
  - (ii)  $CHCl_3$  with aniline in presence of alc. KOH gives foul smelling isocyanides whereas  $CCl_4$  does not.
  - (b)  $CH_3CI$  is hydrolysed easily than  $C_6H_5CI$  as chlorobenzene has partial double bond character between C CI bond which is difficult to break.

S101 (a) 
$$H$$
 + HBr  $A$  Markovnikov's addition  $H$  - CH - CH<sub>3</sub> Br

(b) 
$$CH_3 + HI \longrightarrow I$$

(c) 
$$OH + SOCI_2 \longrightarrow CI + SO_2 + HCI$$

Chlorocylohexane

- **\$102**(a) 1-Bromopentane > 2-Bromopentane > 2-Bromo-2-methylbutane.
  - (b) 1-Bromo-3-methylbutane > 3-Bromo-2-methylbutane > 2-Bromo-2-methylbutane.
  - (c) 1-Bromobutane > 1-Bromo-2-methylbutane > 1-Bromo-2,2-dimethylpropane.