2018

CHEMISTRY (Major)

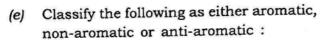
Paper : 1.2

(Organic Chemistry)

Full Marks: 60 Time: 3 hours

The figures in the margin indicate full marks for the questions

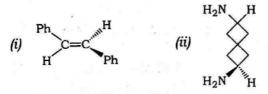
- 1. Answer the following questions (any seven): $1 \times 7 = 7$
 - (a) Draw the structural formula of bicyclo-[2, 2.2]octane.
 - (b) Which of the following compounds has a longer C=C bond length? CH₃—CH=CH₂ and CH₂=CH₂
 - (c) Give one example by which benzyne can be trapped.
 - (d) Why is melting point of p-nitrophenol higher than o-nitrophenol?







Assign the absolute configuration R/S (f) or E/Z to the following:



- Between ethanol and ethanethiol, which *(g)* is stronger acid?
- (h) Give one example of cross-conjugated compound.
- 2. Answer the following questions (any four): $2 \times 4 = 8$
 - (a) What is S_Ni reaction? Write with an example.
 - Write Fischer projection, staggered (b) Sawhorse projection and Newman projection formulae of threo-2,3dichloro-3-phenylpropanoic acid.
 - Why is triplet carbene more stable than (c) singlet carbene? Explain.

(Continued)

(d) What is the major product of the following reaction? Justify your answer and give the name of the reaction:

$$\bigcirc + \bigcirc \stackrel{\text{Cl}}{\longrightarrow} \stackrel{\text{AlCl}_3}{\longrightarrow} ?$$

- (e) Why does acid catalyzed dehydration of neopentyl alcohol yield 2-methyl-2butene as the major product?
- Answer the following questions (any three):
 5×3=15
 - (a) Define dipole moment. How is it related to melting and boiling point? Why is dipole moment of nitrobenzene (μ = 3.95D) higher than nitromethane (μ = 3.60D) although both have same polar group? What is the μ-value of p-dinitrobenzene?

1+1+2+1=5

(b) (i) Arrange the following resonating structures in the order of decreasing stability and give reasonable explanation: 1+2=3

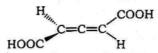
(ii) Explain why 1,3,5-cycloheptatrienyl cation is aromatic but 1,3,5-cycloheptatriene is not.

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(c) Give the evidences for the formation of σ- and π-complexes in electrophilic aromatic substitution. Write the mechanism for the nitration of benzene.

3+2=5

(d) (i) The allene



is optically active although it has no chiral centre. Explain.

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- (ii) How is a racemic mixture different from meso-compound? Give examples to illustrate the differences. 2+1=3
- (e) (i) What happens when pyridine is treated with NaNH₂? Give the mechanism. 2½
 - (ii) Write the mechanism of cyclopropanation of alkene with singlet carbene. 21/2

(Continued)

- **4.** Answer the following questions [either (a) or (b), (c) or (d) and (e) or (f)]: $10\times3=30$
 - (a) (i) What is trigonal hybridization? Write its characteristics. Find the types of hybridization of C_a and C_b in the following by electron pair method: 1+2+2=5

 CH_3 — $^{\Theta}C_aH$ — CH_3 and H_2C_b = CH_2

(ii) What is trans-annular strain? The chair form of methylcyclohexane is less stable when methyl group is in axial position than it is in equatorial position. Explain. Draw the Newman projection for chair form of methyl cyclohexane when methyl group is (i) anti to C_3 and (ii) anti to C_5^{-1} . 1+2+2=5

Or

(b) (i) What is $S_N 1$ reaction? What are the evidences for $S_N 1$ reactions? Why does \rightarrow Br give $S_N 1$ reaction whereas does not give $S_N 1$

reaction?

1+2+2=5

(ii) What do you mean by kinetically controlled and thermodynamically controlled reaction? Give two reactions to justify such reactions.

2+3=5

- (c) (i) The addition of HBr to propene is regioselective. Explain this statement and illustrate the steps involved in the mechanism of the reaction.
 - (ii) What is pK_a ? Between 2-bromopentanoic acid and 3-bromopentanoic acid, which one has higher pK_a value and why? 1+2=3
 - (iii) What are carbanions? How are they different from carbene? Arrange the following carbocations in increasing order of their stabilities: 1+1+1=3



Or

(d) (i) Why does ethoxymethylchloride react with nucleophiles 10⁶ times faster than 1-chlorobutane even though both are primary alkyl chloride? Explain.

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(ii) Write the mechanism for the following conversion:

- (iii) Which one is more reactive towards nucleophiles-acetaldehyde or acetone? Explain. What happens when acetaldehyde is allowed to react with aq. NaOH? Propose a 2+3=5 mechanism.
- (i) Draw and label the E, Z-isomers (e) of 1,2-dichloro-3-ethyl-4-methyl-2pentene.

(ii) Write the structure of meso-tartaric

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1

- acid. Is it optically active? Give the R.S-nomenclature for the two chiral centres in meso-tartaric acid. 1+1+1=3
- configurational and (iii) What are conformational isomers? Draw the possible conformations of n-butane. Arrange the conformations in order of decreasing stability. 2+2+1=5
- (iv) What are the products A and B in the following?

$$CH_3$$
— $C=CH_2$ \xrightarrow{HBr} A $\xrightarrow{\Delta}$ B CH_3 $\xrightarrow{CH_3}$ $\xrightarrow{Peroxide}$ A $\xrightarrow{KOH (aq)}$ B

Or

- (f) (i) Under what conditions E2elimination reaction is synelimination? Discuss a pyrolytic
 syn-elimination reaction with one
 example. 2+2=4
 - (ii) Define carbon-free radicals. How can carbon-free radical be generated? 1+2=3
 - (iii) Distinguish S_N1 reaction from S_N2 reaction.

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