04

[Time: 2½ Hours] [Marks:60]

Please check whether you have got the right question paper.

N.B: 1. **All** questions are **compulsory**.

- 2. **Figures** to the **right** indicate **full** marks.
- 1. A Answer any two of the following:
 - a) Explain primary and secondary kinetic isotope effect, using suitable **04** examples.
 - b) Explain the use of the following techniques as mechanistic evidence: 04
 - i) Isotopic Labelling
 - ii) Cross over experiment
 - c) Write a note on Curtin Hammett principle. 04
 - d) With the help of a potential energy diagram, explain kinetic vs. thermodynamically controlled products using sulphonation of naphthalene as an example.
 - B) Answer any one of the following:
 - a) Comment on the role of solvent in determining the strength of a base. **04**
 - b) Arrange the following in decreasing order of acidity and justify your answer:
 - phenol, o-nitrophenol, m-nitrophenol, p-nitrophenol.
- 2. A) Answer any two of the following:
 - a) Write a note on:
 - i) Walden Inversion
 - ii) Ion-pair effect

Which of the above compounds undergoes nucleophilic substitution with OH most readily? Justify your choice and give the mechanism of the reaction.

- c) Explain the mechanism of S_N reactions involving neighbouring group participation by aryl rings.
- d) Draw the Frost-Musulin diagram of cyclooctatetraene and show the distribution of electrons in MO s. Comment on its aromaticity.
- B) Answer **any one** of the following:
 - a) Give the A_{AL}¹ mechanism for ester hydrolysis. Which type of substrates undergo this mechanism?
 - b) Explain the aromaticity of: 04
 - i) Pyridine
 - ii) Ferrocene

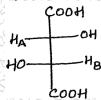
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2

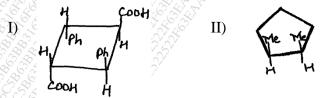
- 3. A) Answer any two of the following:
 - a) Explain the optical activity of trans cyclooctene and assign configurational descriptor to the following compound:



- b) i) Explain the elongated tetrahedron approach with suitable example. **04**
 - ii) Draw the structure of the following compounds:
 - i) S BINOL
 - ii) S-2-nitro-6'-methoxybiphenyl-6-carboxylic acid.
- c) i) Define constitutionally unsymmetrical molecule. Give an example. **04**
 - ii) Write the structure of a molecule with a pseudoasymmetric center and assign its configurational descriptor.
- d) Define homotopic ligand. Identify the relationship between H_A and H_B in the following compound and explain the symmetry criteria employed to determine the topicity of H_A and H_B .



- B) Answer any one of the following:
 - a) Explain S_n axis with suitable example. Label the elements of symmetry in the following examples:



- b) Explain the enantiomerism in the following compounds with suitable **04** examples:
 - i) Quaternary phosphonium compounds
 - ii) Silanes

3

- 4. A) Attempt any two of the following:
 - a) Predict the products in the following reactions:

04

i)
$$H_3C - C = C - CH_3 = \frac{1) O_3}{2) H_2/Pd}$$

b) Complete the following reaction, name it and give its mechanism: 04

c) Complete the following reactions and name them:

d) What is Collins reagent? Give two applications. 04

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4

B) Attempt any one of the following:-

a) Complete the following reactions and give the mechanism of any one:

i)
$$CF_3COOOH$$

b) Complete the following equations:

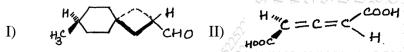
5. Answer **any four** of the following questions:

- A) Explain Hammond's postulate.
- B) Explain the characteristics of specific acid catalysis. Illustrate using a suitable example.
- C) What are ambident nucleophiles? Give two examples.
- D) Explain: [10]-Annulene is not aromatic.

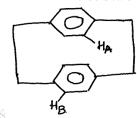
12

5

E) Assign configurational descriptors to the following molecules.



- F) i) Explain chiral axis with a suitable example.
 - ii) Identify the topic relationship between H_A and H_B in the following compound.



- G) Give the synthetic applications of LiAlH₄.
- H) What is Swern oxidation? Give two applications.