

Time : 2 ½ Hours

Marks : 60

NB : (1) Answer all questions.

(2) Figures to the right indicate full marks.

(3) Answers to the same question must be written together.

- Q. 1 a) Answer any **two** of the following.
- "The shifts in rate limiting step within the same overall reaction pathway can be explained by using Hammett's equation." Justify with suitable example. 04
 - Explain Yukawa-Tsuno equation. 04
 - Discuss the upward deviation from Hammett's equation with a suitable example. 04
 - Explain quantitative structure reactivity relationship for *p*-substituted phenols and electron withdrawing groups during their ionization in aqueous solution. 04
- b) Answer any **one** of the following.
- Why and what is the sign of σ for *m*-methoxy and *p*-methoxy groups? How will the rate of base catalyzed hydrolysis of ethyl benzoate be influenced by the presence of these groups? 04
 - Explain Grunwald - Winstein equation. 04
- Q. 2 a) Answer any **two** of the following.
- What are crown ethers? Discuss their properties and structural features. 04
 - What is molecular self - assembly? Write a note on molecular necklaces. 04
 - What are molecular clefts? Discuss the properties of two dimensional molecular clefts. 04
 - What are rotaxanes? Explain their structural features. 04
- b) Answer any **one** of the following.
- Discuss the structural features of calixarenes and give one method of their synthesis. 04
 - Explain the organization and recognition exhibited by enzymes for their catalytic activity with a suitable example. 04
- Q. 3 a) Answer any **two** of the following.
- Discuss resolution of conglomerates with suitable examples. 04
 - Discuss the principle in the use of chiral shift reagents [CSR] in NMR for determination of enantiomeric composition. Give two examples of CSR. 04
 - Explain any two chemical correlative methods used in determination of configuration. Give one example of each. 04
 - Give informative note on circular dichroism. 04
- b) Answer any **one** of the following.
- Explain in details resolution of racemates through formation of diastereomers. Give one example each of resolving agents used to resolve acids and bases. 04
 - Explain any two empirical rules for correlative configurational assignment based on optical rotation. 04
- Q. 4 a) Answer any **two** of the following.
- What is asymmetric induction? Give structures of three natural product molecules in the chiral pool. 04
 - Give synthesis of L-DOPA by Knowles method. 04
 - With suitable examples, describe Felkin-Anh model. 04
 - Discuss the use of chiral BINOLs in asymmetric transformations. 04
- b) Answer any **one** of the following.
- Discuss substrate controlled asymmetric induction with suitable example. 04
 - Give an account of Sharpless epoxidation. 04

- Q. 5 Answer any **four** of the following.
- a) Explain Edward-Ritchie correlations used for nucleophilicity scale. 03
 - b) Discuss the Solvatochromism Z-scale. 03
 - c) Write a note on synthetic molecular receptors. 03
 - d) How is molecular recognition exemplified by proteins? Explain with example. 03
 - e) Discuss the use of chiral stationary phase in determination of enantiomeric composition by chromatographic method. 03
 - f) How will you use Cotton effect to determine position of functional group in steroids? 03
 - g) With a suitable example, discuss the use of chiral auxiliary in asymmetric Diels-Alder reaction. 03
 - h) What is asymmetric amplification? Explain with suitable examples. 03
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