Q. P. Code: 09250

[Time: 2 $\frac{1}{2}$ Hours] **Revised course** **[Total Marks: 60]**

N. B: 1. **All** questions are **compulsory**.
2. Answers to the same question must be written together.
3. **Figures** to the **right** indicate **full marks**.

Q. 1 (a) Attempt any **two** of the following: - 8
(i) The shifts in the rate limiting step within the same overall reaction pathway can be explained using Hammett's equation. Justify the statement with a suitable example.
(ii) Explain the quantitative structure-reactivity relationship for *p*-substituted 2-aryl-2-chloropropanes with electron donating groups during their solvolysis in water.
(iii) Explain the Swain-Scott equation.
(iv) Match the columns and justify your answer.

	Solvent for dissociation of Benzoic Acid		**ρ**
I)	H_2O	**A)**	1.96
II)	50% Alcohol	**B)**	0.50
II)	Alcohol	**C)**	1.60
-	-	**D)**	1.00

(b) Attempt any **one** of the following: - 4
(i) Consider the base-catalysed hydrolysis of *m*- and *p*- hydroxy ethyl benzoates, which of these reactions will proceed faster according to Hammett's equation? Justify your answer.
(ii) Explain the Grunwald-Winstein equation.

Q. 2 (a) Attempt any **two** of the following: - 8
(i) Explain the strategies employed for antibody catalysis in terms of molecular recognition.
(ii) What are cryptands? Discuss their structural features and give any one method of synthesis.
(iii) What are molecular tweezers? Write their structural features and give a suitable example.
(iv) Discuss with a suitable example the structural requirements of a receptor molecule for its molecular recognition and catalytic properties.

(b) Attempt any **one** of the following: - 4
(i) How is molecular recognition exemplified in proteins? Explain with an example.
(ii) What are cyclophanes? Give their structural features.

Q. 3 (a) Attempt any **two** of the following: - 8
(i) What is resolution through kinetic asymmetric transformation? Elaborate on kinetic method of resolution.
(ii) Explain use of NMR spectroscopy method in determination of enantiomeric purity by use of diastereomers.
(iii) Configurational assignment can be done through chemical transformation involving the chiral center. Explain with two suitable reactions.

(iv) What is cotton effect? Discuss cotton effect of 5α – and 5β - nordihydrotestosterone in determining its configuration.

(b) Attempt any **one** of the following: - 4

(i) Explain octant rule with diagrams.

(ii) Describe configurational assignment through Mills' rule for epimeric cyclohex-2-en-1-ols.

Q. 4 (a) Attempt any **two** of the following: - 8

(i) Explain the following terminology with examples.

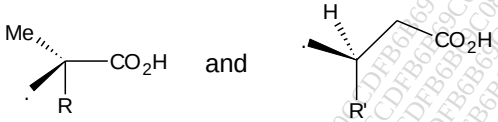
I) Substrate selectivity

II) Product selectivity.

(ii) Illustrate diastereoselective hydrogenation of cyclic hydrazone.

(iii) Syn-hydroxylation with $KMnO_4$, maleic acid and fumaric acid gives meso- and (±)-tartaric acid respectively. Explain with reaction.

(iv) Explain the use of chiral oxazolines in the enantioselective synthesis of



(b) Attempt any **one** of the following: - 4

(i) What are the requirements of an asymmetric synthesis? Give Meerwein-Pondorf-Verley reduction of a prochiral ketone with S-2-butanol.

(ii) Explain asymmetric synthesis of an aldol involving chiral aldehyde and chiral enolate.

Q. 5 Attempt any **four** of the following: - 12

(a) Explain the parameters: E_s and δ.

(b) Explain Edward – Ritchie equation

(c) State the two principles governing the stability of synthetic molecular receptors.

(d) What are cyclodextrins? Give their structural features.

(e) Write a note on resolution through inclusion compound.

(f) Give synthesis of L-DOPA by Knowles's and Monsanto process.

(g) Discuss correlative method for configurational assignment based on NMR spectroscopy.

(h) Give three natural products with structure in chiral pool used for asymmetric synthesis.

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