Q. P. Code: 38876

[Time: 2 1/2 Hours] [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) Establish a quantitative structure reactivity relationship for *p*-substituent 2-chloro-2-phenyl propane with electron withdrawing groups during its solvolysis.

(ii) "The change in the reaction mechanism can be explained by Hammett's equation". Explain the statement with a suitable example.

(iii) Establish Linear free energy relationship for the compounds for which Hammett's equation is not applicable.

(iv) Match the following and justify your answer.

I	Concave upward deviation in Hammetts plot indicates	A	Change in rate limiting step
II	Positive charge near reaction centre is *decreased* in rate-limiting step	B	Positive charge at the reaction center in the transition state of the rate-limiting step.
III	Negative ρ is diagnostic	C	Negative charge at the reaction centre in the transition state of the rate-limiting step.
IV	Concave downward deviation in Hammetts plot indicates	D	Change in reaction mechanism.
		E	Positive ρ value

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

(i) Discuss concave upward deviation from Hammett's equation with a suitable example.

(ii) Give an account of Yukawa- Tsuno equation.

Q. 2 (a) Attempt any **two** of the following: - 8

(i) What are cyclophanes? Discuss their structural features.

(ii) What are molecular self-assembly? Write a brief note on molecular necklaces.

(iii) Explain the organisation and recognition as exhibited by enzymes for their catalytic activity with example.

(iv) Explain the strategy employed for anti-body catalysis in terms of molecular recognition.

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

(i) What are rotaxanes? Discuss their structures.

(ii) What are molecular clefts? Discuss the property of two dimensional molecular clefts.

Q. 3 (a) Attempt any **two** of the following: - 8

(i) What is racemisation? Discuss racemisation involving mechanism through carbonium ions and through stable symmetrical intermediate.

(ii) Explain in details resolution of racemates through formation of diastereomers. Give one example each of resolving agents used to resolve acids and bases.

(iii) How are enzymatic and chromatographic methods useful in determining optical purity and enantiomeric excess in racemates?

(iv) Discuss in details about octant rule.

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

(i) How is CD and ORD along with cotton effect used in determination of configuration and study of conformational changes?

(ii) Explain correlation method applied for configurational assignment using chemical transformation involving the chiral center.

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

(i) What is chiral pool strategy in asymmetric synthesis? Explain giving two examples.

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

(iii) Discuss the use of chiral auxiliaries in asymmetric reaction involving prochiral carbonyl compounds and also on olefins.

(iv) How is chiral oxazolines employed in asymmetric transformation? Explain with reactions.

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

(i) Explain mechanism and stereochemistry of Sharpless enantioselective epoxidation of allylic alcohols.

(ii) What is asymmetric induction? Elaborate with reaction showing 1,2 asymmetric induction representing addition of nucleophile to a carbonyl compound and application of Cram's rule.

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

(a) Explain steric parameter Es with its significance.

(b) Explain Edward-Ritchie correlations used for nucleophilicity scale.

(c) Write a note on synthetic molecular receptors.

(d) Discuss the structural features of calixarenes and give one method of synthesis.

(e) Explain how NMR spectroscopy is helpful in determination of stereochemistry of diastereomers and in distinguishing enantiomers.

(f) Write a note on axial haloketone rule.

(g) Give synthesis of L-DOPA using Knowles's method.

(h) Give synthesis of α-amino acid via diastereoselective hydrogenation of cyclic hydrazones.

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