Q. P. Code: 38874

[Time: 2:30 Hours] [Total Marks: 60]

N. 1. **All** questions are **compulsory**.
B: **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 phenols with electron withdrawing groups during their ionisation in aqueous solution.

(ii) Explain Grunwald-Winstein equation.

(iii) Explain that the Taft equation is a structure-reactivity equation which co-relates only field effects.

(iv) Match the following and justify your answer.

Ionization of acid in water.		ρ
I	X- $C_6H_4CH_2CH_2COOH$	A 1.00
II	$X-C_6H_4COOH$	B 0.49
III	$X-C_6H_4\,CH_2COOH$	C 0.21
IV	$X-C_6H_4\,CH=CHCOOH$	D 0.82
		E 0.47

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

(i) How are Steric Es and Dimroth's E_T parameters determined?

(ii) Explain Yukawa-Tsuno equation.

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

(i) What are Cryptands? Discuss their structural features and give any one method of synthesis of cryptands.

(ii) What are molecular tweezers?. Discuss their salient structural features with an example.

(iii) Explain the strategies employed for antibody catalysis in terms of molecular recognition.

(iv) Discuss with an example the structural requirements of a receptor molecule for its molecular recognition and catalytic property.

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

(i) Give one method of synthesis of crown ethers. Discuss their structural features.

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

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

(i) Explain mechanism of racemisation involving carbanions. How will you resolve the racemates through diastereomer formation?

(ii) What do you understand from resolution through kinetic asymmetric transformation and resolution through inclusion compounds? Explain graphically kinetic method of resolution of diastereomers.

(iii) Specific rotation [α] is highest for an enantiomerically pure compound and with contamination gets lower. Explain with the help of suitable mathematical equation. Also show how optical purity is determined by isotopic dilution method.

(iv) Explain the use of chiral shift reagents and chiral solvating agents in determination of enantiomeric excess.

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

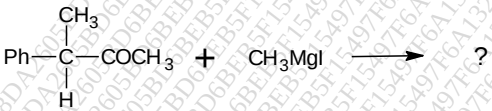
(i) Discuss configurational correlation of β-methoxy adipic acid and steroids

(ii) Explain application of CD and ORD with specific reference to use of plain curves and determination of configurational changes.

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

(i) Explain the principle of stereoselectivity. Illustrate enantioselective reaction with the help of energy diagram.

(ii) What is asymmetric induction? Explain the application of Cram's rule in predicting the products in the following reactions.



(iii) Account for enantioselective hydroxylation of fumaric acid using OsO_4 based chiral reagent.

(iv) What are chiral auxiliaries? Give two examples with structures of chiral auxiliaries? How are they used in asymmetric amplification?

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

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

(ii) Discuss enantioselective alkylation through chiral oxazolines with appropriate reactions.

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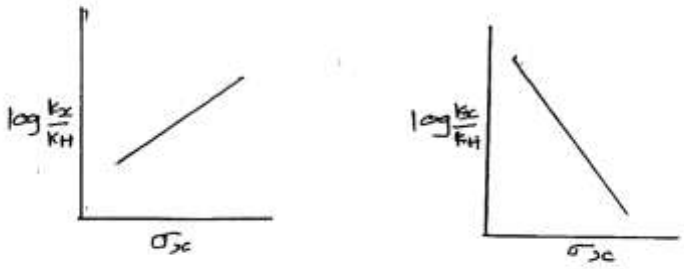
Q. 5 (a) Attempt any **four** of the following: - 12

(a) Explain Edward- Ritchie equation.

(b) Interpret the sign of reaction constant ρ and the charge of the reaction centre for the following Graphs.



(c) Discuss the structural features of cyclodextrins.

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

(e) Elaborate on effects of circular birefringence. Give diagrammatic sketch showing optical rotation due to circular birefringence.

(f) What is racemisation through rotation around bonds? Explain giving a suitable example.

(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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