

[Time: 2 ½ Hours]

Revised course

[Total Marks: 60]

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

- Q. 1 (a) Attempt any **two** of the following: - 8
- The change in the reaction mechanism of a reaction can be explained with Hammett's equation. Justify the statement with a suitable example.
 - Establish the structure-reactivity correlation for the phenomenon shown by *p*-substituted phenols with electron withdrawing groups during their dissociation in water.
 - Explain Grunwald-Winstein equation.
 - Match the columns and justify your answer.

	Acid ionization in water		ρ
I)	C_6H_5COOH	A)	1.20
II)	$C_6H_5CH=COOH$	B)	0.47
III)	$C_6H_5CH_2COOH$	C)	0.49
IV)	$C_6H_5CH_2CH_2COOH$	D)	1.0
		E)	0.21

- (b) Attempt any **one** of the following: - 4
- Establish the equation for the structure-activity relationship for compounds for which Hammett's equation is not applicable.
 - Explain Yukawa-Tsuno Equation.

- Q. 2 (a) Attempt any **two** of the following: - 8
- Describe the various strategies adopted for antibody catalysis in terms of molecular recognition.
 - Discuss the structural features of calixarenes and give any one method of synthesis.
 - What is molecular self-assembly? Explain the process based on hydrogen bonds.
 - Enzymes exhibit the concept of molecular recognition. Justify with suitable example.

- (b) Attempt any **one** of the following: - 4
- Discuss the structural features of cyclodextrins and explain how they act as hosts in the phenomenon of molecular recognition.
 - What are molecular clefts? Explain any one with suitable example.

- Q. 3 (a) Attempt any **two** of the following: - 8
- What is resolution of racemates? Explain resolution of an alcohol through acid succinate.
 - Explain how to calculate optical purity and enantiomeric excess.

- (iii) Discuss chemical transformation involving the chiral centre involving Walden inversion and molecular rearrangement.
- (iv) How does octant rule and axial α -haloketone rule help in ascertaining molecular dissymmetry and chiroptical properties?

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

- (i) Explain resolution through kinetic asymmetric transformation with the help of reaction co-ordinates.
- (ii) Write a note on determination of enantiomeric purity by using chiral solvating agents.

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

- (i) Explain with appropriate reactions stereochemistry involved in reaction of chiral aldehyde with chiral enolates.
- (ii) Give synthesis of α -amino acid by Corey's diastereoselective hydrogenation of cyclic hydrazones.
- (iii) Explain Sharpless enantioselective epoxidation.
- (iv) What is asymmetric amplification? Explain with suitable examples.

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

- (i) What is asymmetric induction? Give structures of three natural product molecules in the chiral pool.
- (ii) Illustrate the reactions enantioselective synthesis using chiral oxazolines.

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

- (a) Explain the parameters: E_s and δ .
- (b) What is Dimroth's equation? Explain its significance.
- (c) What are crown ethers? Discuss their properties.
- (d) Give the two principles governing the stability of synthetic molecular receptors.
- (e) What is cotton effect? How will you use this effect to determine position of functional group in steroids?
- (f) What are quasi-racemates? How does it help in determination of configuration? explain
- (g) Give synthesis of L-DOPA using Knowles's method.
- (h) Explain use of BINOL's in asymmetric transformations.

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