

- N.B. :** (1) All questions are compulsory.
 (2) Figures to the right indicate full marks.

1. (a) Attempt any two of the following :-

- (i) Establish a quantitative structure reactivity relationship for p-substituted phenols with electron withdrawing groups during their ionisation in aqueous solution.
- (ii) Why and what is the sign of σ_{m-OCH_3} and σ_{p-OCH_3} groups. How will the rate of base catalysed hydrolysis of ethyl benzoate be influenced by the presence of these groups.
- (iii) "The change in the reaction mechanism can be explained by Hammett's equation". Explain this statement with a suitable example.
- (iv) Match the following and justify the answers :-

Ionisation of acids in water	ρ
(I) C_6H_5COOH	(A) 0.49
(II) $C_6H_5CH=CHCOOH$	(B) 1.00
(III) $C_6H_5CH_2CH_2COOH$	(C) 0.47
(IV) $C_6H_5CH_2COOH$	(D) 0.22
	(E) 1.30

(b) Attempt any one of the following :-

- (i) Establish linear free energy relationship for the compounds for which Hammett's equation is not applicable.
- (ii) Explain Grunwald-Winstein equation.

2. (a) Attempt any two of the following :

- (i) What are Cryptands ? Discuss their structural features and give any one method of synthesis of cryptands.
- (ii) Discuss with suitable example the structural requirements of a receptor molecule for its molecular recognition and catalytic properties.
- (iii) Explain the strategies employed for antibody catalysis in terms of molecular recognition.
- (iv) What is molecular self assembly ? Explain with a suitable example.

(b) Attempt any one of the following :

- (i) What are cyclophanes ? Give their structural features.
- (ii) What are molecular clefts ? Discuss the properties of two dimensional molecular clefts.

3. (a) Attempt any **two** of the following : 8
- (i) What is racemisation ? Explain its mechanism involving formation of carbanion.
 - (ii) How is optical purity of a chiral compound established by
 - (I) Isotopic dilution method
 - (II) Enzymatic method
 - (iii) Explain chemical method of correlation of configuration involving the chiral centre.
 - (iv) Explain axial- α -haloketone rule with a suitable example. 4
- (b) Attempt any **one** of the following :
- (i) Discuss resolution of diastereomers through asymmetric transformation using kinetic method.
 - (ii) Explain correlative method of configurational assignment using NMR spectroscopy. 8
4. (a) Attempt any **two** of the following :- 8
- (i) What is chiral pool strategy in asymmetric synthesis? Explain giving two examples.
 - (ii) Give the synthesis of α -amino acid by Corey's diastereoselective hydrogenation of cyclic hydrazones.
 - (iii) Explain mechanism and stereochemistry of Sharpless epoxidation of allylic alcohols.
 - (iv) Illustrate the use of BINOL in asymmetric transformation. 4
- (b) Attempt any **one** of the following :- 4
- (i) Explain asymmetric synthesis of aldol involving achiral aldehyde and chiral enolate.
 - (ii) Discuss the use of chiral auxiliary in asymmetric Diel's-Alder reaction with a suitable example.
5. Attempt any **four** of the following :- 12
- (a) Explain Edward-Ritchie equation.
 - (b) What is Es parameter ? Discuss its significance.
 - (c) State the two principles governing the stability of synthetic molecular receptors.
 - (d) What are cyclodextrins ? Give their characteristic features.
 - (e) Give the use of chiral oxazolines in asymmetric transformation.
 - (f) Give synthesis of L-DOPA by Knowles's method.
 - (g) What are ORD curves ? Give one application of ORD curves.
 - (h) Explain the use of Lanthanide shift reagents in determination of enantiomers and diastereomeric compositions.