

(2 ½ Hours)

[Total Marks :60]

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

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

- (i) Explain the phenomenon shown by p-substituted phenols containing electron-withdrawing groups during their ionisation. Establish the structure-reactivity relationship for such compounds.
- (ii) Discuss concave upward deviation from Hammett's equation with a suitable example.
- (iii) Explain Grunwald-Winstein equation.
- (iv) Match the following:-
- | | |
|--|---|
| (I) Negative value of ρ | (A) Ionisation of benzoic acid |
| (II) Reference reaction used in Hammett's equation | (B) p-substituted 2-aryl-2-chloropropanes. |
| (III) Acid catalysed hydrolysis of m- and p-substituted ethyl benzoates. | (C) Disappearance of negative charge from reaction centre |
| (IV) Straight-line plot with σ_x^+ values | (D) Insensitive towards the influence of substituents. |
| | (E) Nucleophilic substitution of methyl iodide by water |

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(b) Attempt any one of the following:-

- (i) Explain Yukawa-Tsuno equation.
- (ii) How are E_s and δ parameters determined? Discuss their physical significance.

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

- (i) Explain the strategies employed for antibody catalysis in terms of molecular recognition.
- (ii) What are molecular clefts? Discuss the properties of two dimensional clefts.
- (iii) What is molecular self-assembly? Write a brief note on molecular necklaces.
- (iv) What are cyclophanes? Discuss their structural features.

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(b) Attempt any one of the following:-

- (i) Give any one method of synthesis of crown ethers. Discuss their structural features.
- (ii) Discuss molecular recognition as shown in enzymes.

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3. (a) Answer any two of the following:-

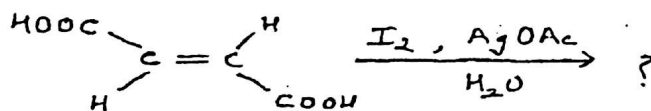
- (i) Explain chemical method of correlation of configuration involving the chiral centre.
- (ii) What is racemisation? Explain its mechanism involving formation of carbanion.
- (iii) How is optical purity of a chiral compound determined by
 - (I) Isotopic dilution method
 - (II) Chromatographic method?
- (iv) What is circular birefringence? How is it used in calculation of specific rotation?

(b) Answer any one of the following:-

- (i) Explain axial α -haloketone rule. How is it useful in determination of absolute configuration of (-) trans-1-decalone
- (ii) Explain the following rules for configurational assignment.
 - (I) Distance rule
 - (II) Rule of optical superposition

4. (a) Answer any two of the following:-

- (i) What is chiral pool strategy in asymmetric synthesis? Explain it with two examples.
- (ii) Explain mechanism and stereochemistry of Sharpless epoxidation of allylic alcohols.
- (iii) Illustrate the use of chiral BINOL in asymmetric transformation.
- (iv) Complete the following reaction, name the reaction involved and give its mechanism



(b) Answer any one of the following:-

- (i) Give synthesis of α -amino acid by Corey's diastereoselective hydrogenation of cyclic hydrazones.
- (ii) Explain asymmetric synthesis of aldol involving achiral aldehyde and chiral enolate.

5. Attempt any four of the following:-

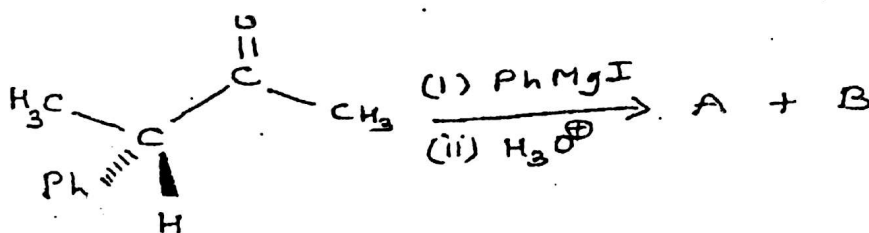
(a) In the following reaction substituent x was varied between electron donating and electron withdrawing. Using σ_x values, what sign of ρ value is expected for equilibrium? Should the reaction be more or less sensitive to x compared to their effect on the dissociation of benzoic acid? Explain.



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- (b) Explain Dimorth's E_T parameter.
 (c) What are rotaxanes? Discuss their structure.
 (d) State the two principles which govern the stability of synthetic molecular receptors.
 (e) Explain octant rule.
 (f) Discuss correlative method for configurational assignment based on NMR spectroscopy.
 (g) Complete the following reaction, predict which product will be the major product and why?



- (h) Give the use of chiral oxazolines in asymmetric transformations.
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