Organic Chemistry I

Q. P. Code: 38875

[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 structural reactivity relationship for para-substituted phenols with electrons withdrawing groups during their ionization in aqueous medium.
       (ii) Explain any one deviation from Hammett's straight line relationship.
       (iii) Why is Hammett's equation not applicable for aliphatic and o-substituted compounds? Derive an equation which can correlate structure -- reactivity for such compound.
       (iv) Match the following and justify your answer.

I	Substituent constant σ	A	Reaction constant ρ
II	Negative charge at the reaction centre	B	Between structure and activity.
III	Proportionality constant between log k values and σ is -	C	A measure of the total polar effect exerted by substituent X on the reaction center.
IV	Linear free energy relationships are attempts to develop quantitative relationships	D	Positive sign of magnitude of reaction constant ρ
		E	Between reaction constant and proportionality constant.

       (b)   Attempt any one of the following: -   4
       (i)   Explain Grunwald-Winstein equation.
       (ii) Explain Edward-Ritchie correlation.

Q. 2   (a)   Attempt any two of the following: -   8
       (i)   Explain the molecular recognition and association as exhibited by proteins.
       (ii) What are calixarenes? Give the synthesis and receptor properties of Calixarenes.
       (iii) What is molecular assembly? Explain with the suitable example.
       (iv) Discuss the structural features of molecular cleft derived from Kemp's tri acid for their application as synthetic receptors

       (b)   Attempt any one of the following: -   4
       (i)   Give one method of synthesis of cryptands. Discuss their structural features.
       (ii) Discuss Molecular recognition as shown in enzymes.

Q. 3   (a)   Attempt any two of the following: -   8
       (i)   Explain in details mechanism of racemisation involving carbanions. How is racemates resolved through diastereomers formation?
       (ii) What do you mean by resolution through kinetic asymmetric transformation? Explain resolution through inclusion compounds and describe graphically kinetic method of resolution.
       (iii) How is enzymatic and chromatographic methods useful in determining optical purity and enantiomeric excess in racemates?

(iv) Give an account on 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) Discuss configurational correlation of β-methoxy adipic acid and steroids.

Q. 4 (a) Attempt any **two** of the following: - 8
(i) Explain principles of stereoselectivity. Illustrate enantioselective reaction with the help of energy diagram.
(ii) Explain asymmetric synthesis of aldol involving achiral aldehyde and chiral enolate.
(iii) Elaborate on enantioselective hydroxylation of fumaric acid using OsO_4 based chiral reagent.
(iv) How is chiral oxazolines employed in asymmetric transformation? Explain with reactions.

(b) Attempt any **one** of the following: - 4
(i) Give the mechanism and stereochemistry involved in sharpless enantioselective epoxidation.
(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) What is Es parameter? Discuss its significance.
(b) How is Dimroth's parameter determined?
(c) Discuss the structural features of crown ethers.
(d) State two principals which govern the stability of synthetic molecular receptors.
(e) Explain the effect of circular birefringence.
(f) Give an account on the axial haloketone rule.
(g) Give synthesis of L-DOPA using Knowles's method.
(h) Write a note on asymmetric amplification.

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