

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

1. (a) Attempt any two of the following :- 8
- (i) Why is Hammett's equation not applicable for aliphatic and o - substituted compounds ? Derive an equation which can correlate structure - reactivity for such compounds.
 - (ii) Explain any one deviation from Hammett's straight line relationship.
 - (iii) Give an account of the phenomenon shown by p-substituted phenols with strong electron - withdrawing groups. How the structure reactivity can be established for such compounds ?
 - (iv) Match the following and justify your answer :-

Acid ionisation	ρ
(a) $X-C_6H_4COOH$	(i) 0.49
(b) $X-C_6H_4CH_2COOH$	(ii) 0.21
(c) $X-C_6H_4CH_2CH_2COOH$	(iii) 0.47
(d) $X-C_6H_4CH=CHCOOH$	(iv) 1.00
- (b) Attempt any one of the following :- 4
- (i) Explain Grunwald - Winstein equation.
 - (ii) How are the following parameters determined ?
 - (1) Steric parameter E_s .
 - (2) Dimroth's E_T parameter.
2. (a) Attempt any two of the following :- 8
- (i) Explain the molecular recognition and association as exhibited by proteins.
 - (ii) Discuss the structural features of molecular cleft derived from Kemp's triacid for their applications as synthetic receptors.
 - (iii) What are cyclophanes ? Discuss the structure of any one type of cyclophane.
 - (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) What are calixarenes ? Give the synthesis and receptor properties of calixarenes.
 - (ii) Define molecular self-assembly. Explain the process based on hydrogen bonds.

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3. Attempt any two of the following :-

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- (i) Explain Octant rule with one example.
- (ii) Phenyl sec-butyl ketone undergoes racemisation easily with aq. NaOH solution, lactic acid does so much less readily whereas atrolactic acid does not racemise at all. Explain.
- (iii) Explain chemical correlation of configuration by methods :-
 - (1) Without involving the chiral centre.
 - (2) Involving the chiral centre.
- (iv) Explain any two applications of CD and ORD curves with cotton effects.

(b) Attempt any one of the following :-

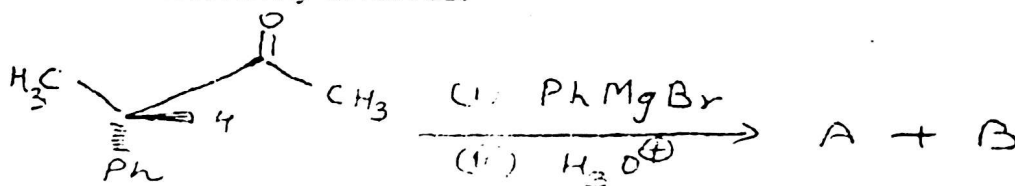
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- (i) Explain axial α -haloketone rule and give its applications.
- (ii) Illustrate the principle in the use of lanthanide shift reagents for determination of enantiotopic composition by NMR spectroscopy.

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

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- (i) Explain asymmetric synthesis of an aldol involving chiral aldehyde and chiral enolate.
- (ii) Complete the following reaction; indicate the type of reaction and the stereoselectivity involved.



- (iii) Give an account of enantioselective hydroxylation of fumaric acid using OsO₄ based chiral reagent.
- (iv) What are chiral auxiliaries? How are they used in asymmetric amplification?

(b) Attempt any one of the following :-

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- (i) What are the requirements of an asymmetric synthesis? Give Meerwein-Ponndorf-Verley reduction of a prochiral ketone with S-2-butanol.
- (ii) Explain mechanism and stereochemistry of sharpless epoxidation of allylic alcohols.

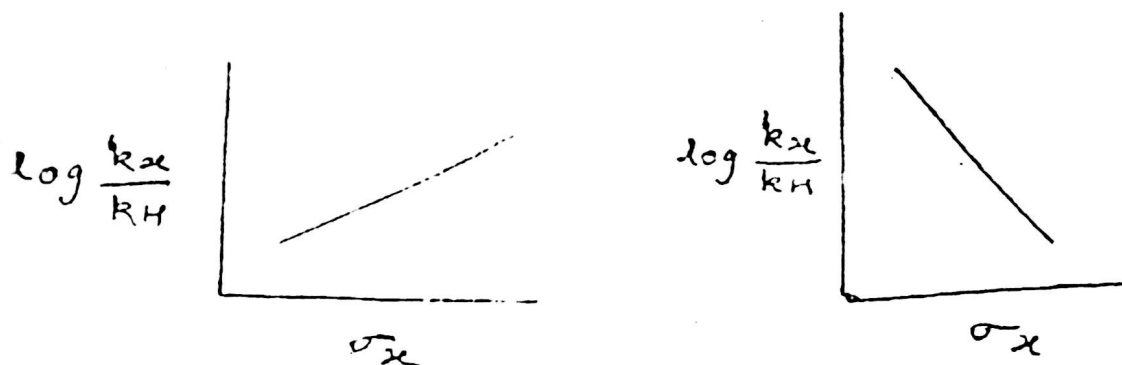
5. Attempt any four of the following :-

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- (a) Explain Edward and Ritchie correlations used for nucleophilicity scale.

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- (b) Interpret the sign of reaction constant ρ and the charge on the reaction centre from the following graphs.



- (c) Discuss the structural features of cyclodextrins.
 (d) Write a note on synthetic molecular receptors.
 (e) Discuss the principle of resolution of racemate by chemical method.
 (f) How is optical purity and enantiomeric excess calculated ?
 (g) Give synthesis of L-DOPA by Monsanto process.
 (h) Complete the following reactions: name the reaction and stereoselectivity involved.

