

- 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) Give an account of Grunwald-Winstein equation.
 - (ii) Explain the phenomenon shown by p-substituted 2-chloro-2-phenyl propane containing electron donating groups during its solvolysis. How can structure-reactivity be established for such compounds ?
 - (iii) The Taft equation is a structure - reactivity equation which correlates only field effects. Explain.
 - (iv) Match the following and justify your answer :-

(A) Ionisation of p-substituted phenols with electron withdrawing groups	(1) Negative σ_x magnitudes
(B) Acid catalysed hydrolysis of m- and p- substituted ethyl benzoates	(2) Show straight line with σ_x^- values.
(C) Negatively charged reaction centre	(3) Insensitive towards substituents effect.
(D) Electron donating groups	(4) Positive sign of magnitude of reaction const ρ .
- (b) Attempt any one of the following :- 4
- (i) Give an account of Yukawa - Tsuno equation.
 - (ii) Discuss any one example where deviation from linear Hammett plots helps in detection of change of mechanism.
2. (a) Attempt any two of the following :- 8
- (i) Explain the organization and recognition as exhibited by enzymes for their catalytic activity with example.
 - (ii) What are molecular tweezers ? Discuss their salient structural features with examples.
 - (iii) What are cyclophanes ? Give different types of cyclophanes.
 - (iv) Explain the strategies employed for antibody catalysis in terms of molecular recognition. 4
- (b) Attempt any one of the following :-
- (i) Give synthesis and receptor properties of cryptands.
 - (ii) What are molecular clefts ? Discuss the properties of two dimensional molecular clefts.

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

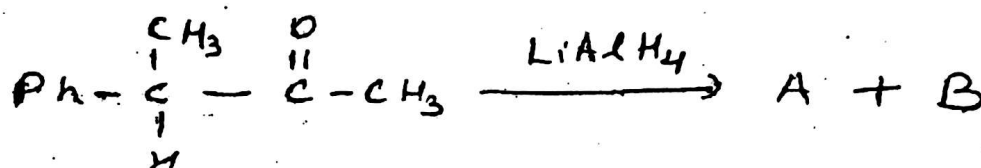
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- (i) Illustrate with examples the principle in the use of chiral shift reagents for determination of enantiotopic composition using NMR spectroscopy.
- (ii) Explain axial α -haloketone rule and give two applications.
- (iii) Explain any two empirical rules for correlative configurational assignment based on optical rotation.
- (iv) Discuss the resolution of racemate through kinetic asymmetric transformation.

(b) Attempt any one of the following :-

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- (i) Complete the following reaction, draw Newmann projection of the products and indicate which isomer predominates.

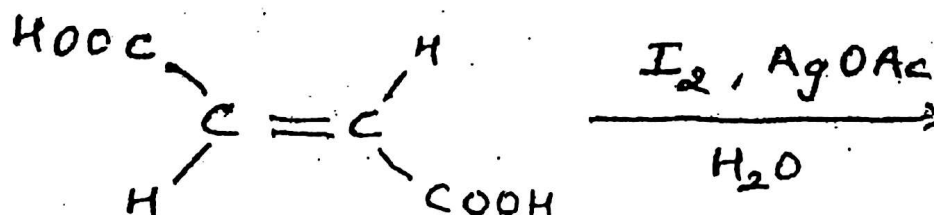


- (ii) Explain any two applications of octant rule.

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

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- (i) Explain 1, 2-asymmetric induction in addition of RMgX to carbonyl compounds.
- (ii) Complete the following reaction, name the reaction involved and give its mechanism.



- (iii) Give an account of sharpless epoxidation of allylic alcohols.
- (iv) Explain asymmetric synthesis of an aldol involving chiral aldehyde and achiral enolate.

(b) Attempt any one of the following :-

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- (i) Discuss the use of chiral borane reagents for asymmetric reduction of prochiral carbonyl compounds.
- (ii) Illustrate with suitable examples, how asymmetric Diels-Alder reaction can be achieved effectively?

5. Attempt any four of the following :-

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- (a) Explain Swain-Scott equation used for determination of nucleophilicity scale.
 - (b) How is steric parameter E_s determined ? Explain.
 - (c) Explain the concept of molecular self-assembly.
 - (d) What are cyclodextrins ? Discuss their structural features.
 - (e) Write informative note on circular birefringence.
 - (f) Explain method of quasi-racemate for configurational assignment.
 - (g) Give synthesis of L-DOPA by Monsanto process.
 - (h) What is chiral pool strategy in asymmetric synthesis ? Explain with one example.
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