St. Joseph's College (Autonomous), Bengaluru – 27

End Semester Examination, November, 2020

III Semester M.Sc. Chemistry

OCH 9419 – Stereochemistry and Asymmetric Synthesis

Time: 2½ hours   Max. Marks: 70

Note: This question paper has 3 pages and 3 sections

PART A

Answer any SIX of the following: 6 X 2 = 12

1. Calculate the percentage of the major and minor enantiomers, given *ee* of the optically active sample is 98%.
2. What is meant by 'anisotropic emission'?
3. Give any two applications of optical rotatory dispersion (ORD) and circular dichroism (CD).
4. What is stereoselectivity? Give an example of a stereoselective reaction.
5. Mention any two criteria for a "perfectly good" commercial resolution method?
6. What is topological isomerism?
7. What is the preferred conformation of 3,3-dimethylbutanal? Explain.
8. Mention any two conditions under which the Winstein-Holness equation and the Curtin-Hammett principle are applicable.

PART B

Answer any FOUR of the following: 4 X 12 = 48

9. a) Explain diastereoselection in cyclic systems, illustrating the formation of axial and equatorial alcohols from cyclic ketones using appropriate reagents.
   b) What is 'helicity rule'? Give any two applications of this rule.   (6+6)

10. a) With the help of a circular projection diagram, explain the emergence of elliptically polarized ray due to circular dichroism.
b) With the help of a detailed diagram, explain the variation of chiroptical properties of (-) methone by varying the solvent polarity. (6+6)

11. (a) With a suitable mechanism, illustrate the use of (±) diethyl tartarate (DET) in asymmetric epoxidation.
(b) Using Zimmerman-Traxler model, give the major and minor products formed in the following reaction in the 'unlike mode'.
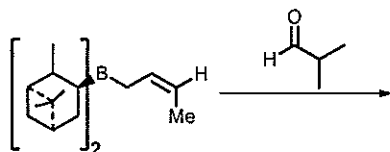
(6+6)

12. (a) Explain the terms racemate and conglomerate. Give any four methods available for the identification of conglomerates.
(b) Write down any four desirable characteristics of a good resolving agent. Provide one example each for acidic and basic resolving agents for amino acids. (6+6)

13. (a) Predict the products when I and II undergo E2 elimination reaction, and compare their reactivities with appropriate justification.

I   II
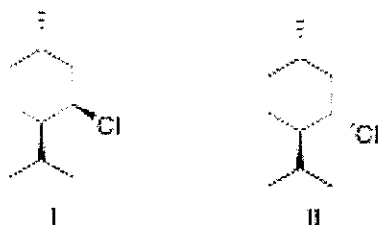
(b) When trans-2-bromocyclohexanol is treated with alkali, only the trans-diaxial conformer leads to the formation of epoxide, whereas the trans-diequatorial conformer remains unreactive. Explain. (6+6)

14. (a) What do you mean by $\pi-\pi$ stacking interaction? Explain with an example how $\pi-\pi$ stacking interactions could be useful for the preorganization of the macrocyclic precursors in the synthesis of catenane.
(b) Why is the Z conformer of methyl formate more stable than the E conformer? (6+6)
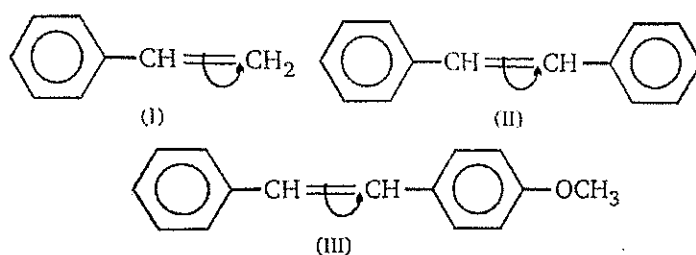
PART C

Answer any TWO of the following: 2 X 5 = 10

15. a) In a nucleophilic addition reaction, name the model which most suitably predicts the major product of the following substrates:
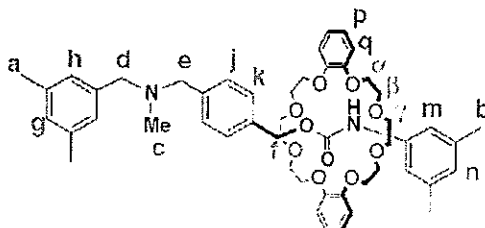

A   B
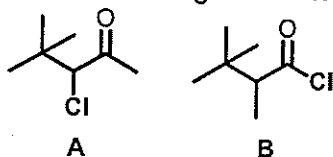
(b) What is the order of rotation barrier about the C=C bond? Give rationale.
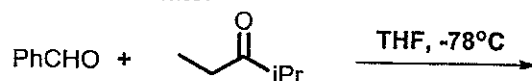

(I)   (II)

(III)

(2+3)

16. Why is the position of the macrocycle locked for rotaxane shown below? What changes would you expect on addition of trichloroacetic acid? Explain. In case there is a structural change, how can you get it back to the original structure?

(5)

17. Predict the major and minor products of the following reaction with the help of a suitable transition state:

PhCHO +   [structure] $\xrightarrow{\text{THF, -78°C}}$

(5)

----------End of questions----------

OCH 9419_A _20