Register Number:
DATE:

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

End Semester Examination, February, 2022

III Semester M.Sc. Organic Chemistry

OCH 9419 – Stereochemistry and Asymmetric Synthesis

Time: 2½ hours Max. Marks: 70

Note: This question paper has 4 pages and 3 sections

PART A

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

1. Calculate the *ee*, given percentage of the major and minor enantiomers of the optically active sample is 99% and 1% respectively.
2. Name two reagents used for the synthesis of equatorial alcohols from cyclohexanones.
3. What is stereoselectivity? Give an example of a stereoselective reaction.
4. Define 'Circularly polarized luminescence'.
5. What structural features are desirable for resolving agent of amino acids? Give one example.
6. Mention any two methods of separation of enantiomer via crystallization.
7. Mention any two criteria for the selection of a chemical bond for the supramolecular preorganization of the macrocyclic precursors.
8. How many double bonds are present in C_{60} buckminsterfullerene? Are they conjugated?

PART B

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

9. a) What is 'sector rule'? How is benzene sector rule applied to predict the CD of α-lycorene?

   b) With the help of a circular projection diagram, explain the emergence of elliptically polarized ray due to circular dichroism. (6+6)

10. a) With the help of a detailed diagram, explain the variation of chiroptical properties of (-) methone by varying the solvent polarity.

    b) Using Cram's open chain model, predict the product when

    i) CH_3MgI adds to $PhCH(CH_3)CHO$

    ii) $LiAlH_4$ adds to $PhCH(CH_3)COCH_3$

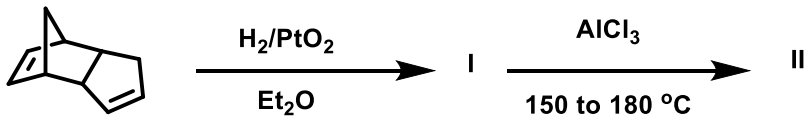
    (6+6)

11. a) Give the major product formed when acetophenone is treated with alpine borane; clearly illustrating the favored and disfavored transition states.

    b) With a suitable mechanism, illustrate the use of (±) diethyl tartarate (DET) in asymmetric epoxidation. (6+6)

12. (a) Compare the stability between two conformers of *trans*-2-halocyclohexanol. What would be the product when it is treated with a base? Justify.

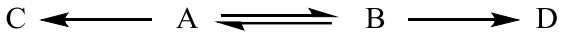
    (b) What are **I** and **II**? Mention the nature of ^{1}H-NMR spectra of **II.**



    . (6+6)

13. (a) State the mathematical expressions of the Winstein Holness and the Curtin-Hammett equation in terms of the rate constants.

    (b) Calculate the product ratio of the following hypothetical reaction.



Given

$k_c = 1 \times 10^{-2}$ sec^{-1}

$k_d = 3 \times 10^{-2}$ sec^{-1}

K = 1

(c) Unsubstituted tetrahedrane has not been synthesized yet, however substituted tetrahedranes are synthetically feasible. Explain. Mention how many minimum substitutions is/are required to synthesize a stable tetrahedrane. (2+4+6)

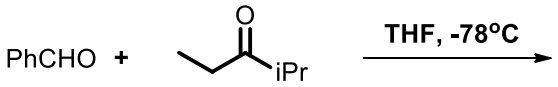
14. (a) Explain any three applications of Buckminsterfullerene.

(b) In the case of resolutions, does it matter whether one uses enantiomerically pure resolving agents? Explain with an example. (6+6)

PART C

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

15. Predict the major and minor products of the following reaction with the help of a suitable transition state: (5)



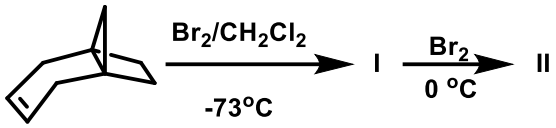
16. Mention the product formed when glucose is treated with (a) MeOH/H^+, (b) acetone, $CuSO_4/H^+$ and (c) phenyl hydrazine. Justify the results. (5)

17. a) Which chiroptical tool is best suited to measure the chiroptical properties of a chromophore that exhibits:

i) emission in the excited state

ii) helical secondary structures in solution.

(b) Predict **I** and **II**. Justify your answer.



(2+3)

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