

Registration No:

Date & Session:



**ST. JOSEPH'S COLLEGE (AUTONOMOUS), BENGALURU -27**  
**M.Sc. ORGANIC CHEMISTRY – III SEMESTER**  
**SEMESTER EXAMINATION: OCTOBER 2022**

(Examination conducted in December 2022)

**OCH 9422 : STEREOCHEMISTRY AND ASYMMETRIC SYNTHESIS**

Time: 2 ½ Hours

Max. Marks: 70

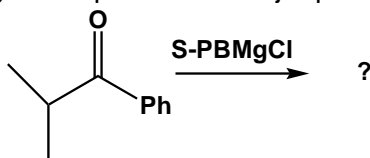
This question paper contains THREE printed pages and THREE parts

**PART-A**

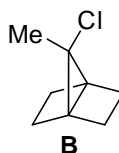
Answer any SIX questions

(6 x 2 =12 Marks)

1. What is 'absolute asymmetric synthesis'? Give an example.
2. Define 'asymmetric amplification' with an example.
3. Draw the structure of *S*-PBMgCl and predict the major product of following reaction.



4. Mention the names of chiroptical properties with brief explanation.
5. Write the IUPAC name of the following compounds.



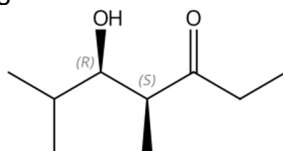
6. How many molecular units are present in [2]catenane and [2]rotaxane?
7. Predict the expected signal in the mass spectrum of C<sub>70</sub> buckminsterfullerene. How many double bonds are present in it?
8. State the mathematical expressions of the Curtin-Hammett equation in terms of the rate constants.

**PART-B**

Answer any FOUR questions

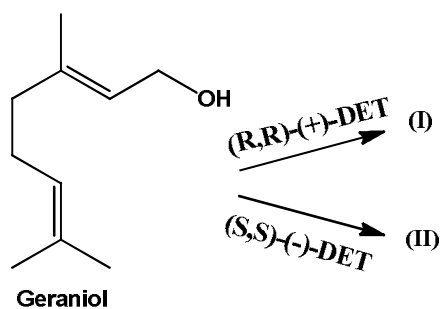
(4 x 12 =48 Marks)

9. (a) Using Zimmerman-Traxler model, discuss the possibilities of forming all the four stereoisomers of the following aldol from suitable enolates.



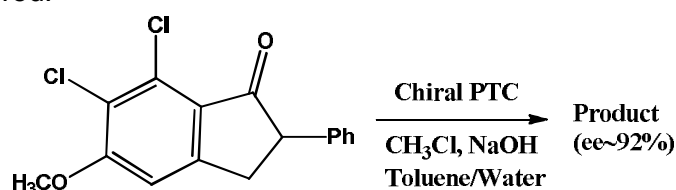
- (b) Explain the general mechanism of Sharpless asymmetric epoxidation with the help of a 10-membered ring metal complex intermediate. Predict the major products of the following Sharpless epoxidation of geraniol.

OCH 9422\_A-22



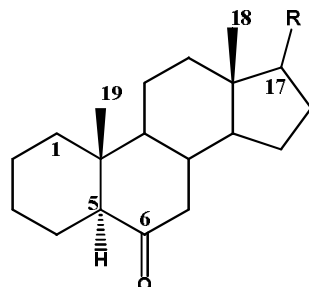
(6+6)

10. (a) Using 4<sup>th</sup> generation stereoselective method, complete the following asymmetric synthesis starting from 2-phenyl indanone derivative and rationalize the high enantiomeric excess observed.

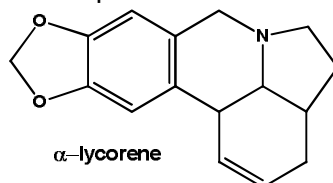


- (b) Explain  $\alpha$ -axial haloketone rule for simple cyclohexanone system. Apply this rule to predict the ORD sign and configuration of trans-1-decalone if its mono  $\alpha$ -axial brominated product exhibits a strong positive Cotton effect. (6+6)

11. (a) Demonstrate Octant rule for simple cyclohexanone system. Predict the ORD sign of 5 $\alpha$ -cholestan-6-one using Octant rule.



- (b) Apply Benzene quadrant rule to predict the Cotton effect of  $\alpha$ -lycorene.



- (c) Discuss the CD spectra and conformational changes of (-)-menthone with change in solvent polarity. (6+3+3)

12. (a) Mention any four methods of directed synthesis for supramolecular compounds. Explain any one of them.

- (b) Draw the structures of tetrahedrane and cubane. Compare their kinetic stabilities.

OCH 9422\_A-22

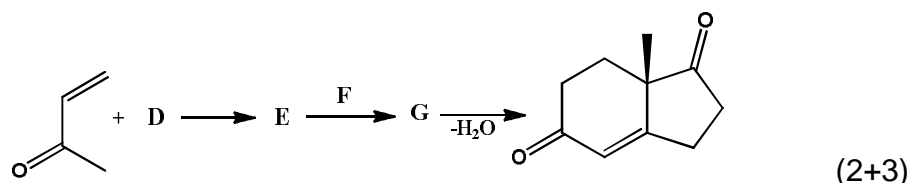
- (c) Draw the *s*-cis and *s*-trans conformation of methyl acetate. Which is the most stable conformation? Explain. (4+4+4)
13. (a) Define the terms racemate and conglomerate. Explain any four methods available for the identification of conglomerates.  
 (b) Mention different methods used for large scale resolution of pharmaceuticals. Explain any one of them with an example. (6+6)
14. (a) Draw the structure of [3.2.1]Propellane, [2.2.2]Propellane and [2.1.1]Propellane. Compare their stabilities with proper justification.  
 (b) Draw an energy profile diagram with the help of following information:  
 (i) A and B are in equilibrium  
 (ii) A is more stable than B  
 (iii) A gives product C; B gives the product D  
 (iv) Activation energy of A is less than that of B.  
 (c) Derive Winstein-Holness equation in terms of the rate constants. (4+4+4)

### PART-C

Answer any TWO questions

(2 x 5 =10 Marks)

15. (a) Using 'exciton chirality method', rationalise the Davydov splitting in the CD spectra of 2 $\alpha$ ,3 $\beta$ -dibenzoyloxy cholestane.  
 (b) Identify the compounds **D**, **E**, **F** and **G** and justify this statement: 'Chiral catalysts can differentiate enantiotopic faces of cyclic 1,3-diketone during enantioselective Robinson annulation'.



16. (a) 'Haptophilic stereocontrol in asymmetric heterogenous catalytic hydrogenation of tetrahydrofluorene derivatives depends on the type of substituent'. Justify this statement.  
 (b). The <sup>13</sup>C- NMR spectra of tetra- (*tert*-butyl)tetrahedrane shows chemical shifts at 9.27, 27.16 and 31.78 ppm. Identify the carbon atoms corresponding to the above chemical shift values. (2+3)
17. Identify the major and minor products for the following reactions. Justify your answer.

