STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI-86 (For candidates admitted during the academic year 2019-20 & thereafter)

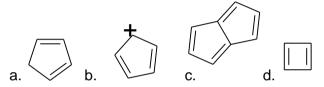
SUBJECT CODE: 19CH/PC/OC14 M.Sc. DEGREE EXAMINATION, NOVEMBER 2022 BRANCH IV- CHEMISTRY FIRST SEMESTER

COURSE: CORE PAPER : ORGANIC CHEMISTRY - I TIME : 3 HOURS SECTION – A

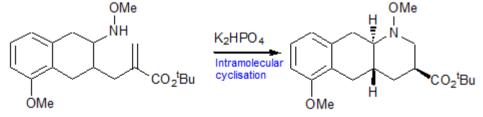
MAX.MARKS : 100 (20x1=20)

Answer all the questions: I Choose the correct answer:

- For the molecule, CH₃-CH=CH-CH(OH)-CH=CH-CH=C(CH₃)₂ the number of all possible stereoisomers is ____.
 a. 16 b. 8. C. 32. D. 4
- 2. Among the following, the non-aromatic compound is



- 3. Which of the following incorrectly describes cis-1,2-dimethylcyclopentane?
 - a. It is a meso compound , b. It contains two asymmetric carbons but achiral c. Its diastereomer is trans-1,2-dimethylcyclopentane, d. It has an enantiomer.
- 4. The gauche conformer of n- butane is dissymmetric (having only C₂) yet n-butane as a whole is optically inactive. The most appropriate reason would be
 - a. At equilibrium, the number of achiral conformations is greater than the number of chiral conformations
 - b. Since the molecule primarily exists in the anti-conformer (which is achiral)
 - c. n-butane exists as a non-resolvable dl-pair
 - d. At equilibrium, every chiral conformation (like gauche) has an energetically degenerate non-superimposable mirror image conformation
- 5. The following cyclisation is a part of a synthesis of quinagolide.

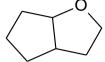


Which of the following statements is true?

- a) The cyclisation is defined as 6-exo-tet and is allowed by Baldwin's rules
- b) The cyclisation is defined as 6-exo-trig and is allowed by Baldwin's rules
- c) The cyclisation is defined as 6-endo-tet and is allowed by Baldwin's rules
- d) The cyclisation is defined as 6-endo-trig and is allowed by Baldwin's rules

II Fill in the blanks:

6. The IUPAC name of the following bicyclic heterocycle is _____



- 7. Stereoisomers which are not mirror images are called _____
- 8. The boat conformation of cyclohexane is less stable than the chair form due to _________ interaction.
- 9. The optical purity of a racemic mixture is _____
- 10. The dihedral angle between the two methyl groups in the gauche-staggered conformation of n-butane is _____.

III State whether true or false:

- 11. Propene adds to HBr forming 2-bromopropane as the major product and 1-bromopropane as the minor product. This is an example of stereoselective reaction.
- 12. Geometrical isomers are diastereomers.
- 13. All the hydrogen atoms in propane are homotopic.
- 14. All dissymmetric molecules are asymmetric.
- 15. In cases of C-H or C-D functionalization appearing in the rate determining step, K_{H}/K_{D} is equal to one.

III Match the following:

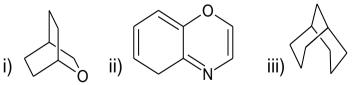
16. Cyclopropenyl anion	a) Non-aromatic
17. Cycloheptane	b) Boat-chair
18. Cyclooctane	c) Pyramidal inversion
19. Cyclooctatetraene	d) Antiaromatic
20. Ethyl methyl amine	e) Twist chair

SECTION – B

(5x8=40)

Answer any five questions:

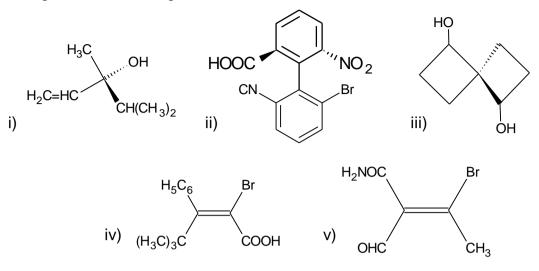
21. a. Explain diatropic and paratropic nature of (4n+2) and 4n systems with suitable examples.b. Write the IUPAC names of



(5+3)



22. a. Assign E/Z or R/S configuration.

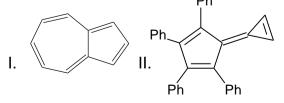


- b. Calculate the ee and the specific rotation of a mixture containing 10g of (+) -2-butanol and 6g of (-)-2-butanol. The specific rotation of enantiomerically pure (+)-2-butanol is $+13.5^{\circ}$. (5+3)
- 23. a. State and explain Cram's rule.b. Compare asymmetry and dissymmetry. (5+3)
- 24. a. Discuss the geometry and account for the ring strain in cyclopentane and cyclobutane.
 b. Draw the most stable conformation of i) Trans-1,4-di-t-buyl cyclohexane, ii) cis-1,3-cyclohexandiol. (5+3)
- 25. a. How do kinetic isotopic effects help in the determination of the mechanism of a reaction? Explain with an apt example.
 - b. State Curtin-Hammett principle.
- 26. a. How is a racemic mixture resolved through diastereomer formation?b. What is meant by a chiral auxiliary? Give two examples.
- 27. a. Elucidate the chemoselectivity of Shapless asymmetric epoxidation.b. Among the cis and trans isomers of 4-t-buyl cyclohexanol, which undergoes oxidation with chromic acid at a faster rate? Why? (5+3)

SECTION – C

Answer any Two questions.

28. a. Discuss the aromaticity of [8], [10] and [12] annulenes.b. The dipole moment of compound I is 1.08D while that of II is 6.3D. Give reason Ph

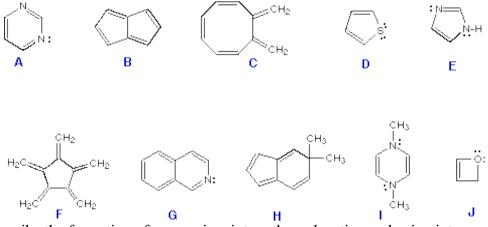


(2x20=40)

(5+3)

(5+3)

- c. What is the criteria for a molecule to exhibit homoaromaticity? Explain with reference to tropylium ion.
- d. Draw the chair conformations of cis and trans decalins and comment on their flexibilities. Comment on their stability and chirality. (4 x 5)
- 29. a. Identify the aromatic compounds among the compounds listed below.



- b. Describe the formation of a racemic mixture through cation and anion intermediates.
- c. Compare the stabilities and discuss the stereochemistry of cis and trans isomers of 1,2 and 1,4 dimethyl cyclohexane.
- d. With suitable examples, explain the importance of trapping of intermediates in deducing the mechanism of an organic reaction.
 (4 x 5)
- 30. a. Write the Taft's equation and explain the terms involved. How is it superior over Hammett's equation?
 - b. Trans-1,2-dimethyl cyclobutane is more stable than its cis isomer while trans-1,3-dimethyl cyclobutane is less stable than its cis isomer. Explain these observations.
 - c. Compare stereospecific and stereoselective reactions with examples.
 - d. Explain atropisomerism exhibited by suitably substituted biphenyls. (4 x 5)
