## 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
MAX.MARKS : 100
SECTION - A
(20x1=20)

## Answer all the questions:

I Choose the correct answer:

1. For the molecule, $\mathrm{CH}_{3}-\mathrm{CH}=\mathrm{CH}-\mathrm{CH}(\mathrm{OH})-\mathrm{CH}=\mathrm{CH}-\mathrm{CH}=\mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}$ the number of all possible stereoisomers is $\qquad$ _.
a. 16
b. 8 .
C. 32 .
D. 4
2. Among the following, the non-aromatic compound is
a.

b.


C.
d.
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 $\mathrm{C}_{2}$ ) 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 $\qquad$ .

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

## 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

## Answer any five questions:

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

ii)

iii)

22. a. Assign $\mathrm{E} / \mathrm{Z}$ or $\mathrm{R} / \mathrm{S}$ configuration.
i)


iii)


iv)

v)

b. Calculate the ee and the specific rotation of a mixture containing 10 g of $(+)-2$-butanol and 6 g of (-)-2-butanol. The specific rotation of enantiomerically pure (+)-2-butanol is $+13.5^{0}$.
23. a. State and explain Cram's rule.
b. Compare asymmetry and dissymmetry.
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-1,3cyclohexandiol.
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?

## 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 1.08 D while that of II is 6.3 D . Give reason

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.
29. a. Identify the aromatic compounds among the compounds listed below.

A

B

C

D

E

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.
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.
