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FIRST SEMESTER M.A./M.Sc./M.Com. DEGREE EXAMINATION DECEMBER 2019

(CBCSS)

Chemistry

CHE 1C 03—STRUCTURE AND REACTIVITY OF ORGANIC COMPOUNDS (2019 Admissions)

Time: Three Hours

Maximum: 30 Weightage

Section A

Answer any **eight** questions.

Each question carries a weightage of 1.

- 1. Z, Z, E, Z, E-[10]Annulene is not aromatic, while its oxygen bridged analogue connecting carbons 1 and 6 is aromatic. Explain.
- 2. Differentiate between non aromatic and anti-aromatic compounds. Give examples.
- 3. Give an example of neighboring group participation involving a sigma bond.
- 4. trans-l,2-Dibromocyclohexane prefers a diaxial conformation in hexane and diequatorial conformation in chloroform. Account for the observation.
- 5. Draw the preferred conformation of cis-1,3-dihydroxycyclohexane. Justify.
- 6. Write down the structure of meso-2, 3-dibromobutane. Predict the product obtained when it is treated with KI.
- 7. Draw the Fischer and Newman projection formulae of (R)-2-chlorobutane.
- 8. A stereoselective reaction gives a mixture of enantiomers in the ratio 85: 15. Calculate the enantiomeric excess in the transformation.
- 9. What is a 'chiral pool' in asymmetric synthesis? Give 2 examples.
- 10. Which strategy will you employ to achieve asymmetric synthesis in a Diels Alder reaction. Why? $(8\times 1=8\ \text{weightage})$

Turn over

Section B

Answer any six questions.

Each question carries a weightage of 2.

11. Comment on the aromaticity of azulene (structure given below). How will you account for the fact that azulene has a dipole moment of 1.08 D. Draw resonance structures as a basis for assigning the direction to the dipole.

- 12. The pKa values corresponding to the first and second ionization of maleic acid and fumaric acid are 2.0, 3.0 and 6.3,4.5 respectively. Account for this observation.
- 13. Illustrate the use of isotope effect in the study of reaction mechanisms.
- 14. Draw the preferred conformations of the ethyl ester of cis- and trans-4-(tert-butyl) cyclohexane carboxylic acid. Which of these will undergo base catalyzed hydrolysis faster?
- 15. Menthyl chloride and neomenthyl chloride have the structures shown below. One of these stereoisomers undergoes elimination on treatment with sodium ethoxide in ethanol much more readily than the other. Which reacts faster and why?

16. Assign R/S descriptors for the following compounds:

- 17. Explain substrate controlled asymmetric synthesis. Give an example.
- 18. Illustrate Sharpless asymmetric epoxidation with an appropriate example.

 $(6 \times 2 = 12 \text{ weightage})$

Section C

Answer any two questions. Each question carries a weightage of 5.

- 19. Explain the Huckel concept of aromaticity. Draw the MO diagram for frontier orbitals of 1,3-butadiene.
- 20. Write a brief note on linear free energy relationships. The pKa of p-methoxybenzoic acid is 4.49 and that of benzoic acid is 4.19. Calculate the value of σ for p-MeO.
- 21. Write a note on the major factors affecting the conformational stability of organic compounds.
- 22. What is Cram's rule? Using appropriate example illustrate its application in predicting the stereochemical outcome in nucleophilic additions to carbonyl groups. Indicate whether product predicted by Cram's rule will be same as that predicted by Felkin-Anh model under identical conditions.

 $(2 \times 5 = 10 \text{ weightage})$