

FIRST SEMESTER M.Sc. DEGREE EXAMINATION, DECEMBER 2016

(CUCSS)

Chemistry

CH 1C 03—STRUCTURE AND REACTIVITY OF ORGANIC COMPOUNDS

(2015 Admissions)

Time : Three Hours

Maximum : 36 Weightage

Section A

*Answer all questions.**Each question carries 1 weightage.*

1. For a **halohydrocarbon, 7-chlorocyclo—1, 3, 5-heptatriene** is unusual in the it ionizes to give chloride ions in water. Why ?
2. The Hammett acidity function H_0 of conc. sulfuric acid is **(—)12**. Explain the meaning of this value, keeping in mind that the acid species present in conc. sulfuric acid is $H_3SO_4^+$.
3. Using (a) Newman and (b) saw-horse projections, draw the gauche conformer of n-butane.
4. Explain with examples, how dipole interaction affects conformational stability of molecules.
5. How would conformation affect the **KI** catalyzed **debromination** of **meso-2, 3-dibromobutane** ?
6. Draw the stable conformations of **cis-decalin**, **trans-decalin** and **adamantane**. Explain.
7. What are **E-** and **Z-cyclooctenes** ? Comment on their **chirality**.
8. Draw the Fischer, Newman and saw-horse projections of **(2R, 3S)-3-bromobutan-2-ol**.
9. Which **one(s)** among **Ph-CH₂-S-C₆H₄-CHO**, **Ph-CH₂-SO-C₆H₄-CHO** and **Ph-CH₂-SO₂-C₆H₄-CHO** is/are chiral and why ?
10. Explain the term asymmetric synthesis and its significance.
11. Why do carbohydrates serve as a useful chiral pool ? Explain.
12. What is **BINAL-H** ? What is its synthetic use ?

(12 x 1 = 12 weightage)

Section B

*Answer any **eighth** questions.**Each question carries 2 weightage.*

13. Write the structure of 12-crown-4 and **dibenzo-18-crown-6**. What are their uses ? Which ion would form a host-guest complex with each of these ?
14. Based upon **Huckel** method, discuss the MOs of **allyl** radical.

Turn over

15. Illustrate with examples the **anchimeric** assistance offered by **alkene** π -systems in substitution reactions of cyclic compounds.
16. Explain how **Bell-Evans-Polanyi** principle relates thermodynamics and reaction kinetics in a closely similar set of reactions. How does it help in the study of reaction mechanisms ?
17. Discuss the conformational preferences of **cyclohexanone** and its **α -brominated** derivatives.
18. Explain the nomenclature used to describe the various conformations of 1, **2-dichloroethane** as it rotates about its central bond. Draw a diagram relating the torsional angle between the chlorines and the energy change.
19. Describe the use of biased systems in the study of the effect of conformation on **reactivities** of cyclic molecules.
20. In **cyclohexyl** carboxylic acids, explain the effect of the axial or equatorial orientation of the **COOH** on the rate of **esterification**.
21. Comment on the effect of conformation on the oxidation of axial and equatorial **cyclohexanols**.
22. How does conformation influence the rate of reaction and product structure in the E2 elimination of **4-t-butylcyclohexyl tosylates**.
23. Explain the E and Z nomenclature used in the **stereochemical** designation of **alkenes**.
24. Discuss the **Felkin-Anh** model for Cram's rule as applied to the asymmetric reaction of a **Grignard** reagent with an aldehyde having a α -chiral center.

(8 x 2 = 16 **weightage**)

Section C

Answer any two questions.

*Each question carries 4 **weightage**.*

25. Write an account of (i) aromatic **annulenes** and (ii) cyclic cationic and anionic aromatic systems.
26. State and explain the Hammett equation and the parameters involved. Discuss its significance in understanding reaction mechanisms.
27. Comment on the optical activity of all **dimethylcyclohexane** isomers in solution.
28. Explain the asymmetric synthesis of **(S)-(-)-iposenol** using amino acid chiral pool.

(2 x 4 = 8 **weightage**)