

FIRST SEMESTER M.Sc. DEGREE EXAMINATION, DECEMBER 2017

(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. Ninhydrin has a carbon bearing two OH groups and is still stable. Why ?
2. Why is 2-norbornyl carbocation (2-bicyclo-[2.2.1]heptyl cation) is considered by some chemists to be an example of a non-classical carbocation?
3. Draw the stereo structure of the most stable conformer of ethyl 4-*t*-butylcyclohexane-1-carboxylate and justify your choice.
4. Using stereo projections, discuss the stability of chlorohydrin conformers.
5. Draw the projection of *threo*-1, 2-diphenyl-1-(4-chlorophenyl)-2-aminoethanol and state the result of its semipinacolic deamination reaction.
6. Consider *trans*- or *cis*-4-*t*-butylcyclohexanol ; which one would undergo chromic acid oxidation faster and why ?
7. Identify the pro-R and pro-S hydrogens in PhCH₂-OMe.
8. Draw the wedge stereo projection of a chiral allene and label it either R, or S, based on CIP system.
9. If EtMgBr reacted stereoselectively with Ph-CO-Me to form (R)-1-methyl-1-phenylpropan-1-ol in 46% EE, what would be the (R) : (S) isomer ratio of the product mixture ?
10. What is a chiral pool ? Explain with examples.
11. Illustrate the use of diisopinocampheylborane IPC₂BH in asymmetric hydroboration of *cis*-2-butene.
12. How are asymmetric synthesis classified ?

(12 × 1 = 12 weightage)

Turn over

Section B

Answer any **eight** questions.

Each question carries 2 weightage.

13. Explain the nomenclature used to designate the structure of crown ethers. Write the structure respectively of a Na^+ binding crown ether and a K^+ binding crown ether.
14. Write a brief note on the structure and bonding in electron donor-acceptor complexes. These are usually highly colored, why ?
15. Which Hammett parameter, $\sigma_{\text{p-OMe}}$ or $\sigma_{\text{m-OMe}}$, is larger ? Explain in detail.
16. What is the basic tenets of Marcus' theory of unimolecular one electron transfer between a donor and an acceptor ? What are its applications ?
17. Critically analyze the stability of all isomers of 1,2-dimethylcyclohexane.
18. What is 1,3-diaxial interaction in cycloalkanes? What are its consequences on the stability of conformers ?
19. Explain with examples the various factors that affect the conformational stability of acyclic and cyclic compounds.
20. Between *trans*- and *cis*-4-*t*-butylcyclohexyl chlorides; which one would undergo a slower dehydrochlorination in alcoholic potash ? What product would form and why ?
21. Draw the Fischer projection of *d,l* and *meso*-2, 3-dibromobutanes. Comment on their KI catalyzed debromination.
22. Pyrolytic elimination of HO-CO-Me from isomeric 4-*t*-Bu-cyclohex-1-yl-O-COMe, is influenced by conformation. Explain how, using chair conformations.
23. Describe with examples how chirality arises on the basis of molecular shape and overcrowding.
24. Define a chiral auxiliary. Cite an example to illustrate the use of a typical chiral auxiliary in synthesis.

(8 × 2 = 16 weightage)

Section C

Answer any two questions.

Each question carries 4 weightage.

25. Write brief notes on : (a) homoaromaticity, (b) hyperconjugation, (c) influence of delocalized π -electron on pK_a of cyclic organic compounds and (d) MOs of buta-1, 3-diene.
26. Describe briefly the various types of neighbouring group participation and its effect on reactivity.
27. Explain the resolution methods by which enantiomers and diastereomers could be separated.
28. Discuss the mechanism and reagents involved in Sharpless asymmetric epoxidation.

(2 × 4 = 8 weightage)