

FIRST SEMESTER M.Sc. DEGREE EXAMINATION, DECEMBER 2014

(CSS)

Chemistry

CH 1C 03—ORGANIC CHEMISTRY—I

Three Hours

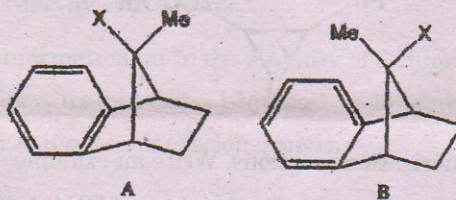
Maximum : 36 Weightage

Section A

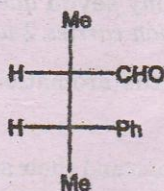
Answer all questions.

Each question carries 1 weightage.

- Between [18] and [10] annulenes, which one is more aromatic and why ?
- Which one of the following two compounds would hydrolyse faster and why ?



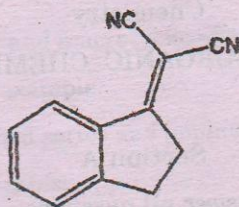
- Assign R or S stereo descriptors for the chiral carbons in the following compound. Then draw the projection of its diastereomer.



- Using a Fischer projection of phenylacetaldehyde, identify its pro-R and pro-S hydrogens.
- With an example, show the use of $(\text{Ph-CHMe})_2\text{NLi}$ as a chiral catalyst.
- Write the structure of a camphor based chiral auxiliary. What is its use ?
- Identify the most stable conformation of methyl 4-*t*-butylcyclohexane-1-carboxylate and explain your answer.

Turn over

8. Illustrate how the HCl elimination reaction of menthyl and neomenthyl chlorides differ and why?
9. Write a scheme to obtain the following compound by condensation.



10. What is the mechanism of MPV reduction?
11. How can the following compound be obtained from PhCHO?



12. Which are the major polymerization reactions. Write an example each.
13. What are the major differences between the structure of DNA and RNA?
14. How can rayon be manufactured?

(14 × 1 = 14 weight)

Section B

Answer any seven questions.
Each question carries 2 weightage.

15. On the basis of MO theory discuss the aromaticity of benzene and the antiaromaticity of cyclobutadiene.
16. Explain the Hammett and Taft equations and their significance in the study of organic reactions.
17. With suitable examples, explain the terms enantiotopicity, homotopicity, and diastereotopicity.
18. Exemplify with appropriate examples the use of chiral auxiliaries in asymmetric synthesis.
19. Discuss the Felkin-Ahn model of Cram's rule in predicting the stereoselective course of the reaction of Grignard reagents with chiral aldehydes.
20. Discuss the effect of conformation on S_N1 and S_N2 reactions of axial and equatorial leaving groups in flexible and rigid cyclohexanes.

21. Describe the conformers and their stability of (a) *n*-butane ; (b) Ethylene glycol ; and (c) Acetaldehyde.
22. What are the most common mechanisms of ester hydrolysis ? What are their evidences ?
23. How can glutathione be synthesized ?

(7 × 2 = 14 weightage)

Section C

*Answer any two questions.
Each question carries 4 weightage*

24. Explain how Huckel MO theory and the Perturbation theory can be applied to $[4n + 2]$ delocalized planar π systems and thus account for their aromaticity.
25. Write brief notes on (a) Curtin-Hammett principle ; (b) Formation and detection of reactive intermediates in organic reactions ; and (c) Electronic substituent effects in S_N1 and S_N2 reactivity.
26. Comment on the conformation and stability of decalins, adamantane and the three isomeric 1-t-butyl-2-, -3- and -4-methylcyclohexanes.
27. Discuss the effect of conformation on (i) the stability of dichlorocyclohexanes ; (ii) the rate of HBr elimination reaction of erythro and threo-1-bromo-1, 2-diphenylpropane ; and (iii) semipinacolic deamination of *cis*- and *trans*-2-aminocyclohexanols.

(2 × 4 = 8 weightage)