

D 33395

(Pages : 3)

Name.....

Reg. No.....

FIRST SEMESTER M.Sc. DEGREE EXAMINATION, FEBRUARY 2013

(CUCSS)

Chemistry

CH 1C 03—ORGANIC CHEMISTRY—I

(2010 Admissions)

Time : Three Hours

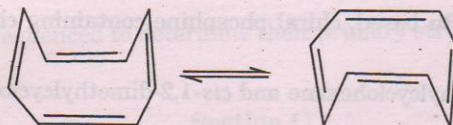
Maximum : 36 Weightage

Section A

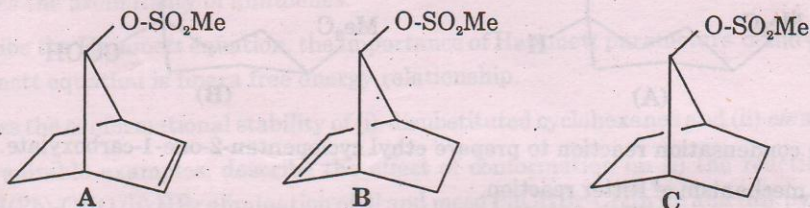
Answer all questions.

Each question carries 1 weightage.

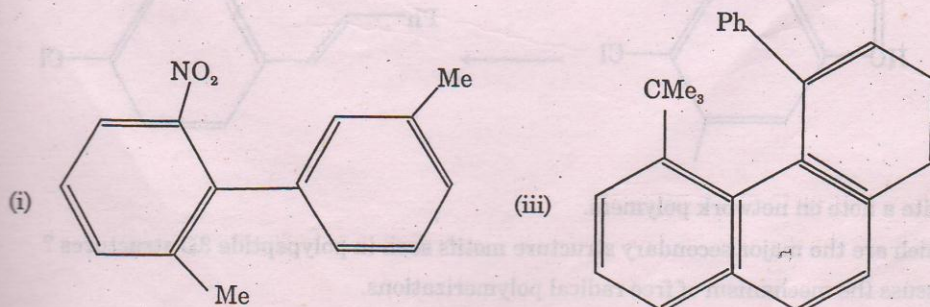
1. The flipping of cyclooctatetraene as shown below from one tub shape to the other has a fairly high energy barrier of $13.7 \text{ kcal mol}^{-1}$. Why ?



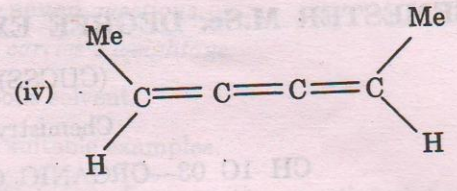
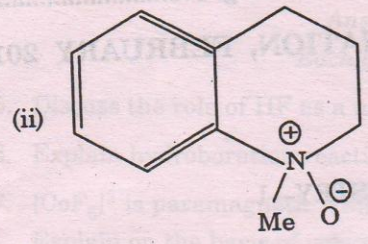
2. Which one among the following would solvolyze the fastest ?



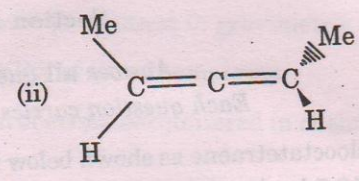
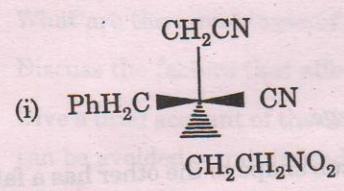
3. Which one(s) among the following compounds is/are chiral ? Why ?



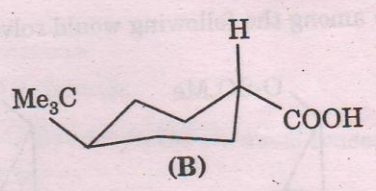
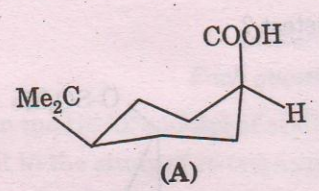
Turn over



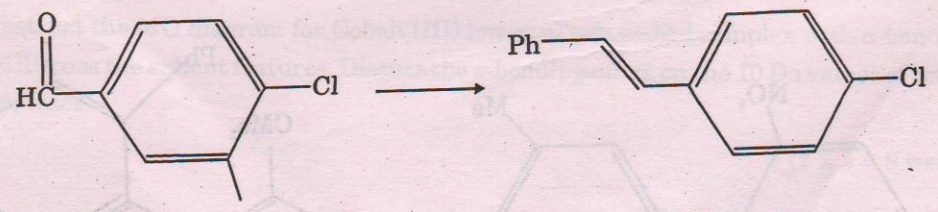
4. Assign R or S configurational notation to the following compounds.



- Explain the Felkin-Ahn model for the Cram's rule. Use structural diagram.
- Write the structure of a Ru based, chiral phosphine containing chiral catalyst and suggest application.
- Between *trans* -1,2-dimethylcyclohexane and *cis*-1,2-dimethylcyclohexane, which is more stable and why?
- Which among A and B would esterify faster and why?



- Suggest a condensation reaction to prepare ethyl cyclopentan-2-one-1-carboxylate.
- Write the mechanism of Ritter reaction.
- Suggest a method for the following conversion in one step.



- Write a note on network polymers.
- Which are the major secondary structure motifs seen in polypeptide 3D structures?
- Discuss the mechanism of free radical polymerizations.

(14 × 1 = 14 weight)

Section B

Answer any seven questions.

Each question carries 2 weightage.

15. Discuss the effect of delocalization of electrons on the pK_a values of organic compounds.
16. Explain the use of isotope labeling in elucidating organic reaction mechanisms.
17. Discuss the (i) chirality of sulfur compounds and (ii) chirality due to helical shape.
18. Write a brief note on the stereoisomerism of aldoximes and ketoximes.
19. Discuss the use of α -amino acids as a chiral pool in the asymmetric synthesis of benzodiazepines.
20. What are chiral reagents? Using typical examples, illustrate their use in asymmetric synthesis.
21. Discuss the conformation of 2-bromocyclohexanone, *cis* and *trans*-2,6-dibromocyclohexanones and 2-bromo-4,4-dimethylcyclohexanones.
22. Illustrate the conformational effect on the hydrolysis of esters of cyclohexane carboxylic acids.
23. Discuss the mechanism of benzoin condensation and Ritter reaction.
24. How can peptides be sequenced to determine their primary structure?

(7 × 2 = 14 weightage)

Section C

Answer any two questions.

Each question carries 4 weightage.

25. Discuss the aromaticity of annulenes.
26. Describe the Hammett equation, the importance of Hammett parameters σ and ρ and explain why Hammett equation is linear free energy relationship.
27. Discuss the conformational stability of (i) disubstituted cyclohexanes and (ii) *cis* and *trans*-decalins.
28. With suitable examples, describe the effect of conformation on (i) the reaction of MeMgBr on MeCH(Ph)-CHO (ii) HBr elimination of *dl* and *meso* PhCHBr-CHBrPh and (iii) pyrolytic elimination of Ac-OH from cyclohexyl acetates.

(2 × 4 = 8 weightage)