LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION - **CHEMISTRY**

FIRST SEMESTER – **NOVEMBER 2013**

CH 1812/1806 - ORGANIC REACTION MECHANISM & STEREOCHEMISTRY

Date : 05/11/2013 Dept. No. Max. : 100 Marks

Time : 1:00 - 4:00

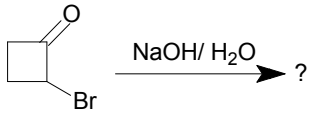
Part-A

Answer all questions. Each question carries two marks.

01. Explain the effect of H_2O_2 in the electrophilic addition of olefins.

02. What is meant by kinetic isotope effect? How are they classified?

03. Complete the following with mechanism and name the rearrangement.



04. How is acyl azide prepared? Show the preparation of urethane from acyl azide.

05. Write the mechanism of Kolbe electrolytic process with a suitable example.

06. What happens when cyclohexene undergoes ozonolysis?

07. Between ephedrine and ψ-ephedrine which is stronger base and why?

08. What are the criteria for good resolving agents?

09. Solvolysis rate of *cis*-4-t-butyl cyclohexyltosylate is greater than that of *trans*-isomer. Explain.

10. What is Cram's cyclic model?

Part-B

Answer eight questions. Each question carries five marks.

11. Give the mechanism of the following reactions:

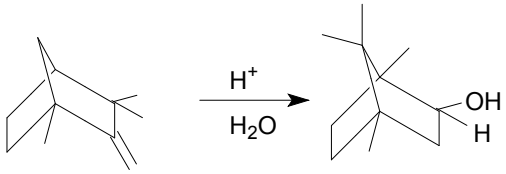
    (i) Chichibabin reaction (ii) γ- elimination

12. How are the following methods used to determine the reaction mechanism? Explain with a suitable example.

    (i) Direct isolation (ii) Raman spectroscopy

13. Explain the microscopic reversibility with suitable example.

14. Explain the mechanism of the following conversion.



15. How do cyclic α-haloketones undergo ring-contraction reaction? Explain the mechanism.

16. Write the mechanism of the following reactions.

    (a) Gomberg-Bachmann synthesis and (b) Fischer-Indole synthesis

17. Explain any one application for the reagents: (a) SeO_2 and (b) OsO_4.

18. Draw the wedge structure for the following:

(a) 2(*R*), 3(*R*)-dihydroxybutanal, (b) (*R*)-1-bromo-1-chloroethane, and

(c) (*S*)-2-phenyl butane.

19. Prove that the rate of racemisation is twice the rate of interconversion in a racemic modification process.

20. Discuss the steric course of the acetolysis reaction of 2-phenyl-3-pentyl tosylate and3-phenyl-2-pentyl tosylate.

21. Discuss the conformation analysis of 1,2 and 1,3-disubstituted cyclohexane.

22. Why the deamination of (Ph)(Ph')(OH)CCH(NH_2)CH_3 does not follow Curtin-Hammet principle? Explain.

Part-C

Answer four questions. Each question carries ten marks

23. Explain the following non-kinetic methods of determining reaction mechanism.

(i) Isolation of intermediates (ii) Addition of suspected intermediate (5 + 5)

24. (a) Explain the mechanistic implications of rate law of diazotization of aniline.

(b) Explain the mechanism of abnormal Claisen rearrangement. (5 + 5)

25. Discuss the following rearrangements with mechanism:

(i) Beckmann rearrangement, (ii) Baeyer-Villiger rearrangement, and

(iii) Cope rearrangement. (4 + 4 + 2)

26. (a) Give the mechanism of the following reactions using LTA.

(i) Oxidation of cyclohexene (ii) Oxidative decarboxylation (2.5 + 2.5)

(b) Explain the mechanism of oxidation of alkane, alcohol and aldehyde using $K_2Cr_2O_7/H_2SO_4$. (5)

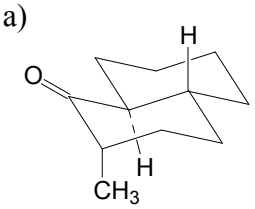
27. Explain the following with example: (a) enantiomeric excess, (b) atropisomerism,

(c) chemical method of racemisation by anion intermediate formation (2 + 3 + 5)

28. (a) Explain Curtin-Hammett principle with suitable example. (6)

b) Predict the Cotton effect for the following compounds. (2 + 1 + 1)

a)



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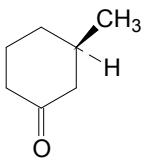

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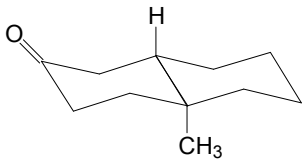

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