LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – **CHEMISTRY**

FIRST SEMESTER – NOVEMBER 2015

CH 1812 - ORGANIC REACTION MECHANISM & STEREOCHEMISTRY

Date : 03/11/2015 Dept. No. Max. : 100 Marks

Time : 01:00-04:00

Part-A

Answer ALL questions. **(10 × 2 = 20)**

1. Give any two electrophilic and nucleophilic reagents.
2. State Hammond's postulate.
3. Give an example for a ring enlargement rearrangement reaction.
4. What are non-1,2-rearrangement reactions?
5. How does a redox reaction take place by a hydrogen transfer?
6. What would be the preferred conformation of trans-1,2-dibromocyclohexane? How does its confirmation change with solvent polarity?
7. The rate of solvolysis of cis-4-t-butylcyclohexyl tosylate is greater than that of trans-isomer. Give reasons.
8. What is second asymmetric racemic modification?
9. Racemization is a thermodynamically favorable process. Justify this statement.
10. What are the criteria for good resolving agents?

Part-B

Answer any EIGHT questions. **(8 × 5 = 40)**

11. How can an isotopic labeling study predict a reaction mechanism? Explain with an example.
12. A prochiral alkene, 3,4-dimethyl-Z-3-heptene, on hydrobromination under two different conditions, namely (a) HBr and (b) HBr/peroxide, forms two diastereomeric products. Suggest a suitable reaction mechanism for the reaction and identify the products.
13. How is migratory aptitude explained in the hydrolysis reaction of bicyclic systems?
14. Describe Fischer indole synthesis. What are the type of rearrangement processes involved in this reaction?
15. Explain the complete mechanism of oxidation of primary alcohol to aldehyde and then to acid by Cr(VI) reagent.

16a. Explain OsO_4 oxidation of cyclohexene. (3)

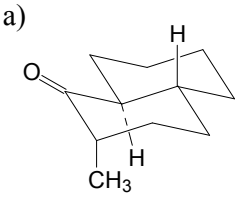
b. What are the [illegible] formed when 2-pentene undergoes ozonolysis? (2)

17. Predict the [illegible] and explain the mechanism of the following reaction:

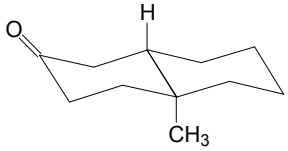
2-butyne $\xrightarrow{ia}$?

18. Define the following terms: a) Circular dichroism b) circular birefringence
19. Predict the stereochemical change of acetolysis of 3-methoxy-2-bromobutane in the presence of silver acetate in acetic acid.
20. Discuss the conformational analysis of 1,2 -disubstituted cyclohexane.
21. Predict the Cotton effect for the following compounds

a)



b)



22. Discuss the acetolysis reaction of *syn* and *anti* 7-norbornyl tosylate.

Part-C

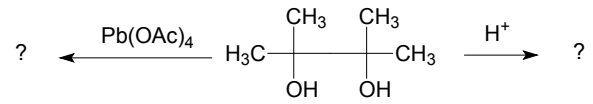
Answer any FOUR questions. **(4 × 10 = 40)**

23a. How are thermodynamically and kinetically controlled products formed in a reaction? Give suitable reasons. (5)

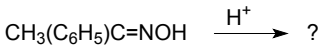
b. According to kinetics, benzoin condensation is a third order reaction. Prove that the reaction mechanism supports it. (5)

24a. Predict the products in the following reactions. (3+3)

a)



b)



b. Discuss carbon boron migration reaction with a suitable example. (4)

25a. How can Ni, Pt and Pd act as oxidizing agents? What type of compounds are involved in these oxidation processes? Explain them with an example. (5)

b. Explain the mechanism of Swern oxidation. (5)

26a. Discuss the steric course of the acetolysis reaction of 2-phenyl-3-pentyl tosylate and 3-phenyl-2-pentyl tosylate. (6)

b. Explain the following with suitable example: (i) Bredt's rule (ii) Epimerization (2+2)

27a. Discuss the stereochemistry of allenes.

b. Predict the course of stereochemistry of the acetolysis reaction of 3-methoxy-2-bromobutane in the presence of silver acetate in acetic acid. (5+5)

28a. Explain mutarotation and anomeric effect with suitable example. (4+4+2)

b. Prove that the rate of racemization is twice the rate of interconversion.

c. Explain the chemical method of racemization through cation intermediate formation.