LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FIRST SEMESTER – NOVEMBER 2016

CH 1806 / CH 1812 - ORGANIC REACTION MECHANISM & STEREOCHEMISTRY

Date: 02-11-2016 Dept. No. Max. : 100 Marks

Time: 01:00-04:00

Part-A

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

1. State Hammond postulate.
2. What are non-1,2-rearrangement reactions?
3. What would be the preferred conformation of trans-1,2-dibromocyclohexane? How does its confirmation change with solvent polarity?
4. What is second asymmetric racemic modification?
5. Mention the criteria for good resolving agents.
6. What are the differences between an intermediate and a transition state?
7. Write a rearrangement reaction that involves a ring contraction.
8. Define the following with suitable example. (a) invertomers (b) epimers.
9. What is anancomeric effect? Give an example.
10. Define plane curve and mention its significance.

Part-B

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

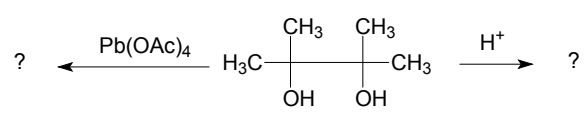
11. A prochiral alkene, 3,4-dimethyl-Z-3-heptene, on hydrobromination under two different conditions, namely (a) HBr and (b) HBr/peroxide, forms two diastereomeric products. Suggest a suitable reaction mechanism for the reaction and identify the products.
12. Describe Fischer indole synthesis. What are the types of rearrangement processes involved in this reaction?
13. a) Explain OsO_4 oxidation of cyclohexene. (3)
    b) What are the products formed when 2-pentene undergoes ozonolysis? (2)
14. Define the following: a) Circular dichroism b) circular birefringence (2½x2)
15. Discuss the conformation analysis of 1,2 & 1,3-disubstituted cyclohexane.
16. Discuss the acetolysis reaction of syn and anti 7-norbornyltosylate.
17. How are thermodynamically and kinetically controlled products formed in a reaction? Give suitable reasons.
18. Explain the mechanism of following reactions.
    (a) Benzil-benzilic acid rearrangement (b) Favorskii rearrangement
19. How is neighbouring group participation of phenyl, methyl and hydride groups compared in Wagner Meerwin rearrangement reactions?
20. Prove that the rate of racemisation is twice the rate of interconversion in a racemic modification process.
21. Predict the product and explain the reaction of *cis*- and *trans*-2-aminocyclohexanol with HONO.
22. Explain the pyrolysis reaction of xanthates and acetates.

Part-C

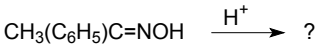
Answer any FOUR questions. **(4 × 10= 40)**

23a. Predict the products in the following reactions. (3+3)

i)



ii)



b. Explain the mechanism of Ardnt-eistert synthesis with an example. (4)

24a. 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) Epimerisation (2 + 2)

25 a. Explain mutarotation and anomeric effect with suitable example. (4)

b. Discuss the stereochemistry of the reaction of racemic and meso stilbene dichloride with hot pyridine.

. (4)

c. Explain chemical method of racemisation by cation intermediate formation. (2)

26. Predict suitable product(s) and explain the reaction mechanism of the following. (5+5)

(a) Baeyer Villiger oxidation of 2-pentanone.

(b) Neber rearrangement of acetophenone O-tosyl oxime.

27 a. Explain the mechanism of reduction reaction of ethene using $[(Ph_3P)_3RhCl]$. (5)

b. Explain Curtin-Hammett principle with suitable example. (5)

28 a. How can the major product in an asymmetric induction reaction be predicted by Cram's and prelog's rules with suitable example. (7)

b. Draw the structure of the following: (3)

(i) 2(*R*), 3(*R*)-2,3-dihydroxybutanal

(ii) (*R*)-1-bromo-1-chloroethane

(iii) (*S*)-2-phenyl butane

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