



LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

FIRST SEMESTER – APRIL 2017

CH 1806- ORGANIC REACTION MECHANISM & STEREOCHEMISTRY

Date: 02-05-2017
Time: 09:00-12:00

Dept. No.

Max. : 100 Marks

Part-A

Answer ALL questions.

(10 × 2 = 20)

1. Write the Baldwin's rules for ring closure reactions.
2. What are the differences between an intermediate and a transition state?
3. How is a cyclic carbocation formed?
4. Write a rearrangement reaction that involves a ring contraction.
5. How is an addition-elimination process sometimes considered as a redox process?
6. Define the following terms: a) invertomers b) epimers
7. Which among the following undergoes racemisation more readily, lactic acid or mandelic acid? Account for your choice
8. What is an anomeric effect? Give an example.
9. What is plain curve?
10. Predict the Cotton effect for the following compounds.

Part-B

Answer any EIGHT questions.

(8 × 5 = 40)

11. How are thermodynamically and kinetically controlled products formed in a reaction? Give suitable reasons.
12. According to the kinetics, benzoin condensation is a third order reaction. Prove that the reaction mechanism supports it.
13. Explain the mechanism of the following reactions.
a) Benzil-benzilic acid rearrangement b) Favorskii rearrangement
14. The following reaction first undergoes an oxidation to form A, which later undergoes a rearrangement reaction to form the final product. Identify A and explain the mechanism of reaction.

15. How is neighbouring group participation of phenyl, methyl and hydride groups compared in Wagner Meerwin rearrangement reactions?
16. Explain the complete mechanism of oxidation of primary alcohol to aldehyde and then to acid by Cr(VI) reagent.
17. Prove that rate of racemization is twice the rate of interconversion in a racemic modification process.
18. Explain the chemical method of racemization through anion intermediate formation with a suitable example.
19. Predict the product and explain the reaction of *cis*- and *trans*-2-aminocyclohexanol with HONO.
20. Discuss the solvolysis reactions of 2-phenyl-3-pentyltosylate and 3-phenyl-2-pentyltosylate with acetic acid.
21. Explain the pyrolysis reaction of xanthates and acetates.
22. Explain the Curtin-Hammett principle using the following reaction.

Part-C

Answer any FOUR questions.

(4 × 10 = 40)

23. How do cross over experiments and trapping of intermediate decide the reaction mechanism. Explain them with suitable examples. (5+5)
24. Predict suitable product(s) and explain the reaction mechanism of the following.
 - (a) Baeyer-Villiger oxidation of 2-pentanone
 - (b) Neber rearrangement of acetophenone O-tosyloxime (5+5)
25. Explain the mechanism of the following reactions. (3+4+3)
 - (a) Periodic acid oxidation of 1,2-dihydroxycyclohexane to form 1,6-hexane dialdehyde
 - (b) SeO₂ oxidation of toluene to form benzyl alcohol
 - (c) Oppenauer oxidation of isopropanol to form acetone
- 26a. Explain the mechanism of reduction of ethene using [(Ph₃P)₃RhCl].
- b. How is Prelog rule used in predicting the stereochemistry of the product? (5+5)
- 27a. Discuss the conformational stability and optical isomerism of 1,2- and 1,3-dimethyl cyclohexane.
- b. Explain the following observation with a suitable mechanism: (5+5)

- 28a. How is the major product in an asymmetric induction reaction predicted by Cram's rule and prelog's rule? Give a suitable example.
- b. Draw the structures of the following:
 - (i) 2(*R*), 3(*R*)-2,3-dihydroxybutanal
 - (ii) (*R*)-1-bromo-1-chloroethane
 - (iii) (*S*)-2-phenylbutane (7+3)

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