



LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

FIRST SEMESTER – NOVEMBER 2014

CH 1812/1806 - ORGANIC REACTION MECHANISM & STEREOCHEMISTRY

Date : 31/10/2014

Dept. No.

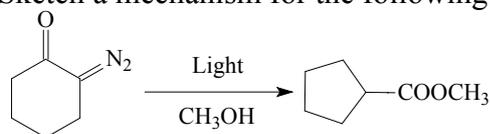
Max. : 100 Marks

Time : 01:00-04:00

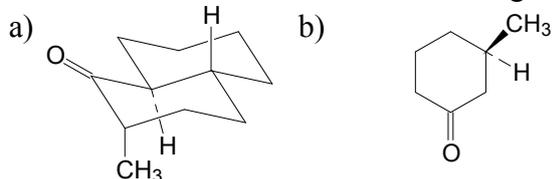
Part-A

Answer all the questions. Each question carries two marks:

1. Define microscopic reversibility with suitable example.
2. What is meant by kinetic isotope effect? How is it classified?
3. What is the stereo chemical use of Beckmann rearrangement reaction?
4. Sketch a mechanism for the following conversion.



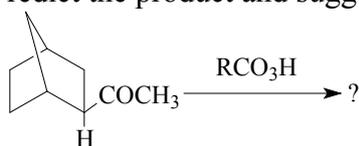
5. Why is excess diazomethane used in Arndt-Eistert synthesis?
6. State axial haloketone rule with an example.
7. What is anomeric equilibrium? Give an example.
8. The pK_a value of *cis*- and *trans*- isomers of 4-*t*-butylcyclohexanecarboxylic acid in 66% aqueous DMF are found to be 8.23 and 7.79 respectively. Account for the difference in acid strength.
9. What is crystallisation induced asymmetric transformation?
10. Predict the Cotton effect for the following compounds



Part-B

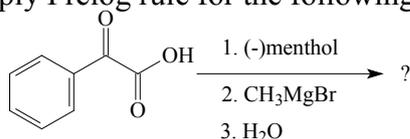
Answer eight questions. Each question carries five marks:

11. Explain the thermodynamic requirements for a chemical reaction to occur.
12. Describe in detail the importance of Marcus theory.
13. Discuss the various steps involved in free radical rearrangement reaction.
14. Prove that the alkyl group does not migrate as a free carbanion in the Wolf rearrangement.
15. Predict the product and suggest the mechanism for the following reaction:



16. Write a mechanism for the conversion of unsubstituted amide into primary amine. Give evidence in favour of the mechanism.
17. What is first order asymmetric transformation?
18. Explain the oxidation reaction mechanism of propene using SeO_2 .
19. Predict the product and explain the reaction of *cis*- and *trans*-2-aminocyclohexanol with HONO.
20. Discuss the pyrolysis reaction of *cis* and *trans*-2-phenylcyclohexylxanthates.

21. Apply Prelog rule for the following reaction and predict the product.



22. Explain stereoselective synthesis with suitable example.

Part-C

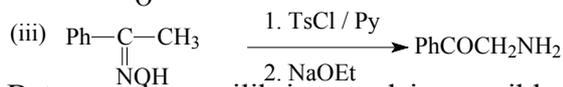
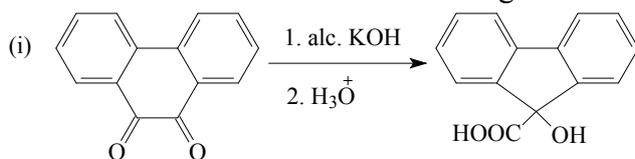
Answer four questions. Each question carries ten marks:

23. Describe any five non kinetic methods for determining the mechanism of organic reactions.

24a. Predict the mechanism of Fischer-Indole synthesis with evidences.

b. What is called semi benzilic acid mechanism? (7+3)

25. Predict the mechanism of the following transformations (4 + 3 + 3)

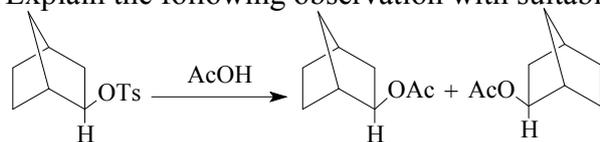


26a. Between the equilibrium and irreversible reactions, the rate of racemisation is twice the rate of interconversion. Justify this statement.

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

27a. Discuss the conformational stability and optical isomerism of 1,2- and 1,3-dimethyl cyclohexane.

b. Explain the following observation with suitable mechanism. (5 + 5)



28. Identify A-E. (5 × 2)

