



LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

FIRST SEMESTER – NOVEMBER 2016

16PCH1MC01 - ORGANIC REACTION MECHANISM AND STEREOCHEMISTRY

Date: 02-11-2016

Dept. No.

Max. : 100 Marks

Time: 01:00-04:00

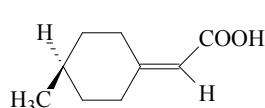
Part-A

Answer ALL questions.

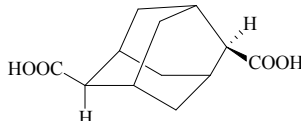
(10 × 2 = 20)

1. Bring out the difference between kinetically controlled and thermodynamically controlled reactions.
2. How is insertion reaction carried out using nitrene intermediate?
3. What is Dakin's reaction?
4. Identify the product formed when benzylmethyl ketone undergoes Baeyer Villiger rearrangement.
5. Write the mechanism of ozonolysis of 1,4-diphenyl-2-pentene.
6. Give the mechanism of McFadyen-Stevens reduction reaction.
7. Assign R/S notation for the following compounds.

a)

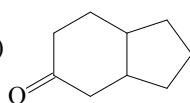


b)

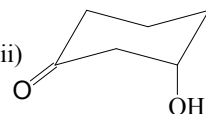


8. Prove that the addition of bromine to trans -2-butene is a stereospecific reaction.
9. What are the conditions for chirality in biphenyl derivatives?
10. Predict cotton effect for the following cyclic ketone derivatives.

i)



ii)



Part-B

Answer any EIGHT questions.

(8 × 5 = 40)

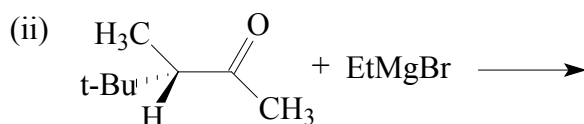
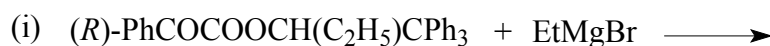
11. Compare the structure and stability of carbocation with that of carbanion.
12. Write (a) Baldwin's rules for ring closure reactions and (b) the Hammond postulate. **(3+2)**
13. What are the products formed when 2,3-diphenyl-2,3-butanediol undergoes pinacol-pinacolone rearrangement reaction. Write the mechanism of reaction and give explanation.
14. How will you compare the mechanisms of Beckmann and Neber rearrangements?
15. Prepare the following.
(a) 2-phenylethyl amine by Hofmann rearrangement reaction.
(b) Methyl acetamide by Schmidt rearrangement reaction.
16. Predict the product(s) and explain the mechanism of the following reaction.
(a) SeO₂ oxidation of phenylbenzyl ketone (b) Swern oxidation of 2-butanol.
17. Explain the use of Mosher method in the determination of enantiomer ratios based on diastereotopicity.
18. Define the following with suitable example: (i) Bredt's rule (ii) Epimerisation **(2.5 + 2.5)**
19. Prove that the rate of racemisation is twice the rate of interconversion.
20. Explain the following with suitable examples. (i) 2-alkylketone effect (ii) Anomeric effect
21. Discuss the steric course of the acetolysis reaction of 2-phenyl-3-pentyl tosylate and 3-phenyl-2-pentyl tosylate.
22. Explain absolute asymmetric synthesis with suitable examples.

Part-C

Answer any **FOUR** questions.

(4 × 10 = 40)

- 23 a. What is the methodology adopted to determine kinetically the reaction mechanism of complex reactions? Give an example. (5)
- b. How is trapping of intermediate useful to determine the reaction mechanism? Explain with an example. (5)
- 24 a. How is isotopic labeling study useful to follow the Favorskii rearrangement in cyclic systems? (5)
- b. What is memory effect? Explain it with a suitable example. (5)
- 25 a. Predict the products formed when 2-pentene is subjected to (i) hydroboration-oxidation (ii) oxymercuration-reduction. Write the mechanism of each reaction. (3+3)
- b. Compare non-aqueous MnO_2 oxidation with CrO_3 oxidation of alcohols to form aldehydes. (4)
- 26a. Give the mechanism of Wolff Kishner reduction reaction with a suitable example. (3)
- b. Apply Cram's or Prelog's rule to predict the major product in each of the following reactions. (4 + 3)



- 27a. Write a short note on the optical isomerism of allenes and spiranes. (5)
- b. Explain the stereospecific pyrolysis reactions of cis- & trans -2-phenylcyclohexanes. (5)
- 28a. Draw the structure of the following: (i) 2(R), 3(R)-2,3-dihydroxybutanal (ii) (S)-2-phenyl butane (3)
- b. Explain chemical method of racemisation by cation intermediate formation. (3)
- c. Explain the following observation with a suitable mechanism: (4)

