LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FIRST SEMESTER – **APRIL 2014**

CH 1812 - ORGANIC REACTION MECHANISM & STEREOCHEMISTRY

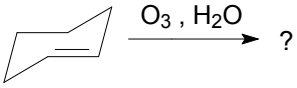
Date : 12/04/2014 Dept. No. Max. : 100 Marks

Time : 09:00-12:00

Part-A

Answer *all* the questions. Each carries *two* marks.

1. What is Chichibabin reaction? Give its mechanism.
2. State and explain Kharaush effect with an example.
3. What is meant by migratory aptitude? Give its order for pinacol-pinacolone rearrangement.
4. Write a rearrangement mechanism involving ring enlargement.
5. Complete the following with mechanism.

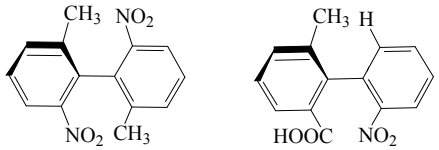


6. Give the mechanism of hydroboration with acetone.
7. Between erythro and threo forms of 1-bromo-1,2-diphenylpropane, which will undergo dehydrohalogenation faster in the presence of a base and why?
8. What are invertomers and epimers? Cite an example each.
9. Write axial haloketone rule with one example.
10. Define circular dichroism and circular birefringence.

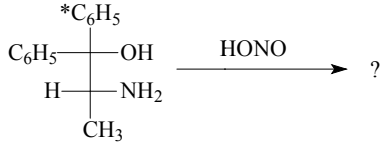
Part-B

Answer any *eight* questions. Each carries *five* marks.

11. State and explain the microscopic reversibility with a suitable example.
12. Explain the secondary kinetic isotope effect with a relevant example.
13. Suggest a suitable method to detect the benzyne intermediate and explain with an example.
14. Explain the mechanism of Wagner-Meerwein rearrangement.
15. Describe the preparation of indole from phenyl hydrazine with mechanism.
16. Explain any one application of the following reagents:
    (a) lithium aluminium hydride and (b) aluminium isopropoxide.
17. Explain the following with a suitable example:
    (a) aromatisation of 6-membered ring and (b) Birch reduction.
18. Predict the major product in an asymmetric induction reaction by Cram's and Prelog's rules with suitable examples.
19. Which of following is more easily resolvable and why?



20. Explain Curtin-Hammett principle using the following reaction:



21. Describe the pyrolysis reaction of xanthates and acetates.
22. Predict cotton effect for (a) (+)-3-methyl cyclohexanone and (b) *trans*-10-methyl-2-decalone.

Part-C

Answer any *four* questions. Each carries *ten* marks

23a. State and explain Hammond postulate with a suitable example. (5+5)

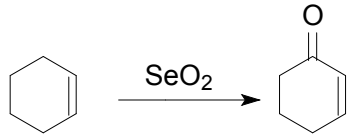
b. Show the formation of intermediate in von-Ritcher rearrangement with mechanism.

24a. Cannizzaro reaction follows second order with respect to substrate and first order with respect to base. Predict the mechanism.

b. Explain Hoffmann and Baeyer-Villiger rearrangements. (5+5)

25a. Explain the mechanism of abnormal Claisen rearrangement.

b. Effect the following conversion and give mechanism.



(5+5)

26a. Write the mechanism for Clemmenson reduction.

b. Explain the following with a suitable example.
(i) absolute asymmetric synthesis and (ii) Walden inversion (5+5)

27a. Discuss the optical isomerism of allenes and biphenyls.

b. Draw the structures of (i) 2(*R*), 3(*R*)-2,3-dihydroxybutanal, (ii) (*R*)-1-bromo-1-chloroethane, and (iii) (*S*)-2-phenyl butane (6+4)

28. Explain the following:
a) First order asymmetric transformation
b) Stereoselective synthesis of Yohimbine. (3+7)