



LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

FIRST SEMESTER – APRIL 2024

PCH 1501 – ORGANIC REACTION MECHANISM AND STEREOCHEMISTRY

Date: 15-04-2024

Dept. No.

Max. : 100 Marks

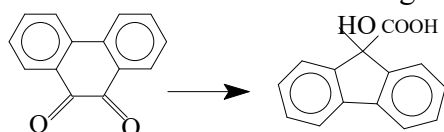
Time: 09:00 AM - 12:00 NOON

Part-A

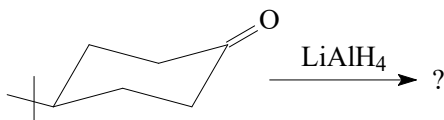
Answer ALL questions.

(10 × 2 = 20)

1. “Sulfonation of benzene follows microscopic reversibility”. Justify.
2. Show the importance of cross-over experiment with an example.
3. Outline the mechanism of the following transformation choosing suitable reagent/s.



4. How would you prove that Claisen rearrangement is an intra-molecular process?
5. Predict the *major*- and *minor*- products and justify.



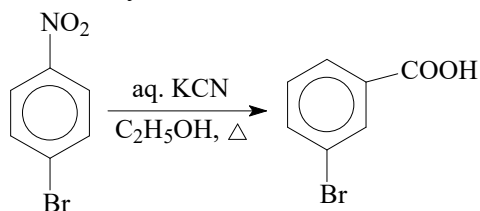
6. What are the criteria for good resolving agents?
7. Write the mechanism of Clemmenson reduction.
8. What is plain curve?
9. Draw the structure of the following:
(i) 2(*R*), 3(*R*)-2,3-dihydroxybutanal (ii) (*R*)-1-bromo-1-chloroethane
10. What is second asymmetric racemic modification?

Part-B

Answer any FOUR questions.

(4 × 10 = 40)

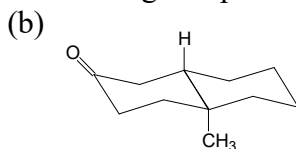
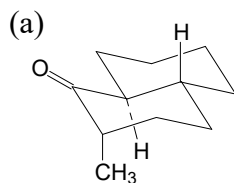
11. State and explain Hammond postulate for the bromination of n-propane that is more selective than chlorination. Illustrate with mechanism and potential diagram.
12. Describe the following methods of determining reaction mechanism with suitable example.
(i) Identification of the products (ii) Kinetic isotope effect (5+5)
13. How would you determine the mechanism of the following reaction? Explain.



14. Write the mechanism of the following rearrangements with suitable examples. (5+5)
(i) Favorskii (ii) Baeyer-Villiger oxidation
15. Illustrate the effects of electron withdrawing and donating substituents on Birch reduction.
16. (a) Discuss the conformational analysis of 1,2 & 1,3-disubstituted cyclohexane. (6)
(b) Explain the following with suitable example:
(i) Bredt's rule (ii) Epimerisation (2 + 2)

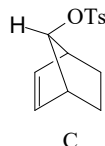
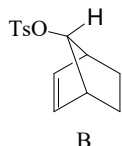
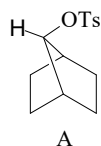
17. Predict the Cotton effect for the following compounds

(5+5)



18. (a) Discuss the steric course of the acetolysis reaction of 2-phenyl-3-pentyl tosylate and 3-phenyl-2-pentyl tosylate. (6)

(b) Discuss the acetolysis reaction of the following. (4)



Part-C

Answer any TWO questions.

(2 × 20= 40)

19. (a) Outline the mechanism of Friedel-Crafts alkylation of toluene and highlight its limitations. (8)

(b) The rate of the diazotization of aniline, $-d[C_6H_5NH_2]/dt = k[C_6H_5NH_2][HNO_2]^2$. (7)

Explain the mechanistic implications of the rate law in this reaction. (7)

(c) Sketch the mechanism for the acid & base-catalyzed hydrolysis of an ester. (5)

20. (a) Illustrate the following rearrangements with plausible mechanism: (6+4+4)

(i) Fries & photo-Fries (ii) Abnormal Claisen (iii) Beckmann

(b) Explain any one synthetic application of the following oxidizing agents with mechanism. (3+3)

(i) HIO_4 (ii) SeO_2

21. (a) Discuss the stereochemistry of allenes and biphenyls. (8)

(b) Predict the course of stereochemistry of the acetolysis reaction of

3-methoxy-2-bromobutane in the presence of silver acetate in acetic acid. (6)

(c) Explain chemical method of racemization by cation intermediate formation. (6)

22. (a) How can the major product in an asymmetric induction reaction be predicted by Cram's rule and prelog's rule with suitable example? (10)

(b) Prove that the rate of racemization is twice the rate of interconversion. (5)

(c) Explain Curtin-Hammett principle using the following reaction. (5)

