LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FIRST SEMESTER – **NOVEMBER 2023**

PCH 1501 – ORGANIC REACTION MECHANISM AND STEREOCHEMISTRY

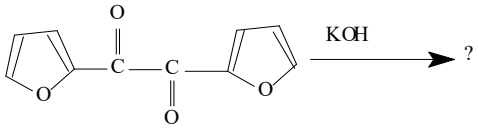
Date: 31-10-2023 Dept. No. Max. : 100 Marks

Time: 01:00 PM - 04:00 PM

Part-A

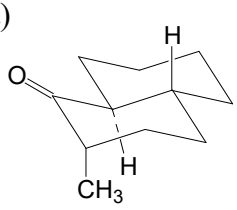
Answer ALL questions. **(10 × 2= 20)**

1. What is meant by thermodynamically controlled and kinetically controlled product? Cite an example.
2. List the informations obtained from the potential energy diagram of S_N1 reaction.
3. Predict the product with mechanism.

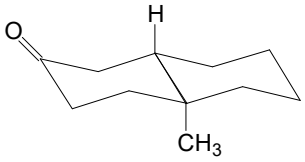


4. What is the use of cross-over experiments? Cite example.
5. Compare the reduction reaction of LAH and NBH.
6. Write the mechanism of Clemmensen reduction?
7. Solvolysis rate of *cis*-4-*t*-butyl cyclohexyl tosylate is greater than that of *trans*-isomer. Justify.
8. What is second order asymmetric racemic modification?
9. Why is *cis*-1,2-dimethylcyclohexane optically inactive at room temperature though the molecule lacks the elements of symmetry?
10. Predict the Cotton effect for the following compounds

a)



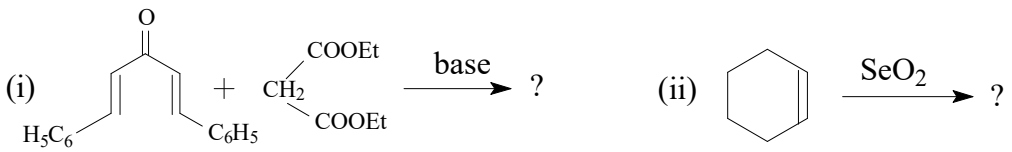
b)



Part-B

Answer any EIGHT questions. **(8 × 5= 40)**

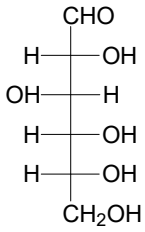
11. State and explain the Hammond postulate with an example.
12. Explain the applications of the following non-kinetic methods of determining the reaction mechanism.
    (i) Isotope labelling study (ii) Trapping of an intermediate
13. Derive Hammett equation.
14. Write and explain Wagner-Meerwein rearrangement using bicyclic system.
15. Explain the mechanism of Fischer-Indole synthesis.
16. Predict the product and give the mechanism of the following reaction. (3+2)

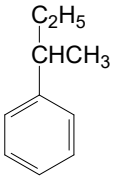


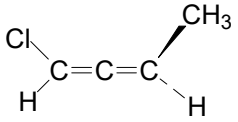
17. Explain the mechanism and effect of substituents of Birch reduction in detail.
18. Explain Curtin-Hammet principle with suitable example.
19. Discuss the steric course of the acetolysis reaction of 2-phenyl-3-pentyl tosylate & 3-phenyl-2-pentyl tosylate.

20. Explain axial haloketone rule with suitable example.
21. Assign R/S notation for the following compounds.

a) b) c)





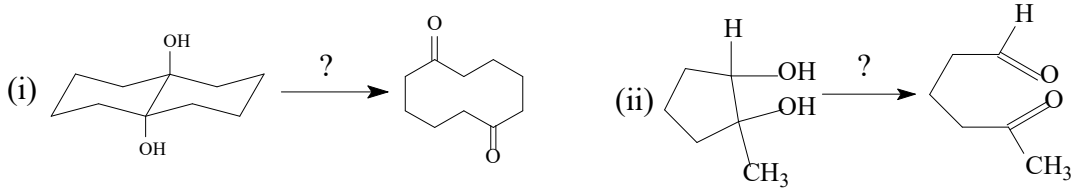


22. Discuss the conformation analysis of 1,2 & 1,3-disubstituted cyclohexane.

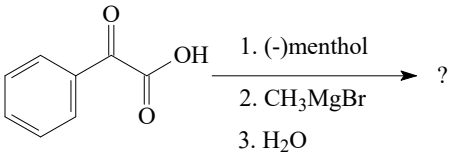
Part-C

Answer any FOUR questions. **(4 × 10 = 40)**

23a. Explain the importance of (i) von-Ritcher reaction and (ii) kinetic isotope effect. (5)
b. The rate of benzoin condensation reaction is $-d[C_6H_5CHO]/dt = k[C_6H_5CHO]^2[CN]$. Explain the mechanistic implications of the rate law in this reaction. (5)
24a. Illustrate the mechanism of abnormal Beckmann and Favorskii rearrangement. (3+3)
b. Write the mechanism of Claisen rearrangement. (4)
25a. Suggest a mechanism for the following conversions using suitable oxidizing agents. (6)



b. Give the structure and use of Chloranil. (4)
26a. Write any one synthetic applications for the following oxidizing agents.
(i) OsO_4 (b) $KMnO_4$
b. Explain the following with suitable example: a) Mutarotation b) Anomeric effect (5 + 5)
27. Discuss the following reaction
a) Reaction of *cis* & *trans* 2-aminocyclohexanol with HONO.
b) Reaction of *erythro*-3-bromo-2-butanol with HBr
28a. Explain the chemical method of racemisation by anion intermediate formation.
b. Apply Prelog rule for the following reaction and predict the product.



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