LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FIRST SEMESTER – **APRIL 2022**

PCH 1501 – ORGANIC REACTION MECHANISM AND STEREOCHEMISTRY

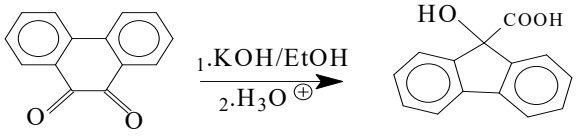
Date: 16-06-2022 Dept. No. Max. : 100 Marks

Time: 01:00-04:00

Part-A

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

1. What is meant by the term "microscopic reversibility"? Give an example.
2. How would you trace the mechanism of acid-catalyzed hydrolysis of an ester?
3. Outline the mechanism of the following transformation.

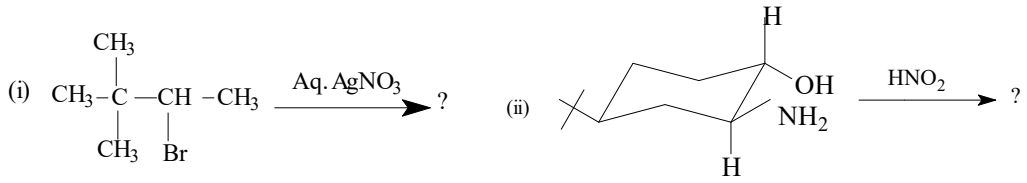


4. What is Cope rearrangement? Give example.
5. Give any two synthetic uses of quinone.
6. Write the mechanism of Clemmenson reduction.
7. What is second asymmetric racemic modification?
8. Predict the sign of Cotton effect for the following.
   (a) trans-2-decalone (b) axial -3-methylcyclohexanone
9. What are the criteria for good resolving agents?
10. Draw the wedge structure for the following:
    (i) 2(*R*),3(*R*)-2,3-dihydroxybutanal (ii) (*R*)-1-bromo-1-chloroethae

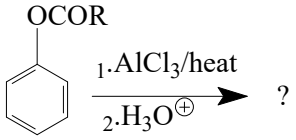
Part-B

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

11. State and explain Hammond postulate with an example.
12. Explain any two non-kinetic methods which are used to determine the reaction mechanism.
13. Write the mechanism of von-Richter reaction and explain its importance in determining the reaction mechanism.
14. Write the mechanism of the following reaction. (2 + 3)

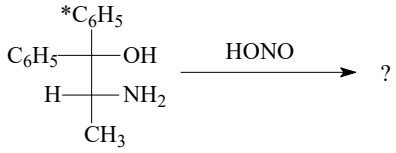


15. Explain the mechanism of Fischer's indole synthesis.
16. Predict the product and write the mechanism of the following reaction.



17. Explain the effect of electron donating and electron withdrawing substituents in Birch reduction with mechanism.
18. What are chiral derivatizing agents (CDAs) in NMR spectral techniques and mention their characteristics?

19. Explain the chemical method of racemisation by anion intermediate formation with suitable example.
20. Discuss the steric course of the acetolysis reaction of 2-phenyl-3-pentyl tosylate & 3-phenyl-2-pentyl tosylate.
21. Explain Curtin-Hammett principle using the following reaction.

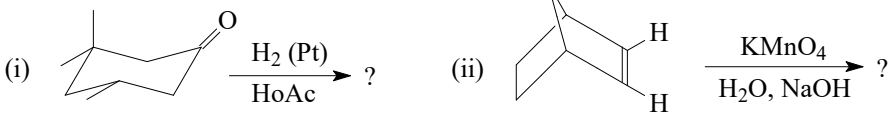


22. Explain the mechanism of the following.
    (a) Reaction of *cis* & *trans*-2-aminocyclohexanol with HONO.
    (b) Reaction of erythro-3-bromo-2-butanol with HBr.

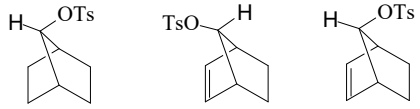
Part-C

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

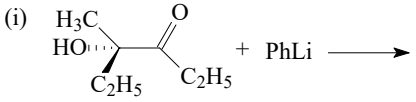
23a. Explain the following methods of determining the reaction mechanism. (3+3)
    (i) Isolation of intermediate (ii) Kinetic isotope effects.
  b. The rate of the diazotization of aniline is $-d[C_6H_5NH_2]/dt = k[C_6H_5NH_2][HNO_2]^2$. Explain the mechanistic implications of the rate law in this reaction. (4)
24. Write the mechanism of the following rearrangements. (5+5)
    (i) Claisen (ii) Wagner-Meerwin
25a. Predict the product with mechanism. (6)



  b. Explain the mechanism of Favorskii rearrangement. (4)
26a. Explain any one application of the following oxidizing agents with mechanism. (3+3)
    (i) HIO_4 (ii) SeO_2
  b. Give any two synthetic applications of OsO_4. (4)
27a. Discuss the pyrolysis reaction of xanthates, acetates, and N-oxides. (5)
  b. Discuss the acetolysis reaction of the following. (5)



28. Apply Cram's or Prelog's rule to predict the major product in each of the following reactions. (5 + 5)



(ii) (*R*)-PhCOCOOCH(C_2H_5)CPh_3 + EtMgBr ⟶

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