LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FIRST SEMESTER – **NOVEMBER 2022**

PCH 1501 – ORGANIC REACTION MECHANISM AND STEREOCHEMISTRY

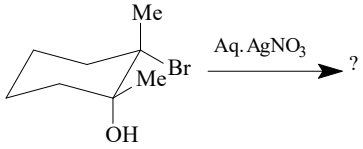
Date: 23-11-2022 Dept. No. Max. : 100 Marks

Time: 01:00 PM - 04:00 PM

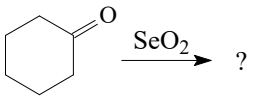
Part - A

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

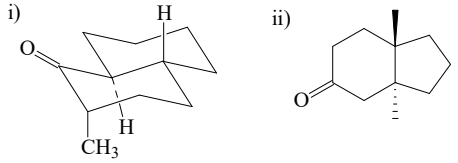
1. State and explain peroxide effect with an example.
2. Show the formation and detection of a nitrene intermediate.
3. How will you justify that Claisen rearrangement is an intramolecular?
4. Predict the product and give its mechanism.



5. Predict the product and give its mechanism.



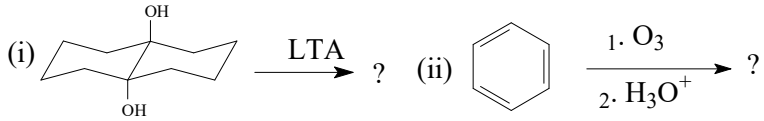
6. What is MPV reduction? Give an example.
7. What is first order asymmetric racemic modification?
8. Define enantiomeric excess. What is its percentage value for active and racemic products?
9. What is 2-alkyl ketone rule?
10. Apply octant rule and predict the Cotton effect for the following.



Part-B

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

11. State and explain microscopic reversibility in sulphonation of benzene.
12. Explain Hammond postulate for the reaction of halogenation of alkane.
13. Write any one example for a ring-contraction and a ring expansion of pinacol-pinacolone rearrangement.
14. Write the mechanism of (i) Favorskii and (ii) Wolf rearrangement. **(3+2)**
15. Write the mechanism of the following conversions using suitable reagents. **(2+3)**

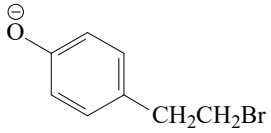


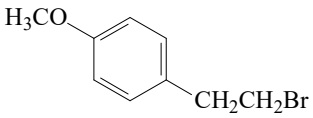
16. Explain the mechanism of any one synthetic application for the following reagents.
    (i) CrO_3 (ii) DIBAL-H **(2+3)**

17. Compare the mechanism of any one synthetic application for the following reagents:

(i) Zn/Hg in HCl (ii) H_2N-NH_2/NaOH **(3+2)**

18. Explain the chemical method of racemisation by anion intermediate formation with suitable example.
19. The ethanolysis of conjugate base of 2-(*p*-hydroxyphenyl)ethyl bromide is about 10^6 times faster than that of the corresponding *p*-methoxy compound. Explain Why?





20. Prove that rate of racemisation is twice the rate of interconversion in a racemic modification process with suitable example.
21. When but-2-en-1-ol is treated with $SOCl_2$ in ethereal solution, 3-chlorobut-1-ene is formed in quantitative yield, whereas but-1-en-3-ol is treated with $SOCl_2$ in ether solution forms 3-chlorobut-1-ene as the only product. Explain.
22. Explain Curtin-Hammett principle using suitable example.

Part-C

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

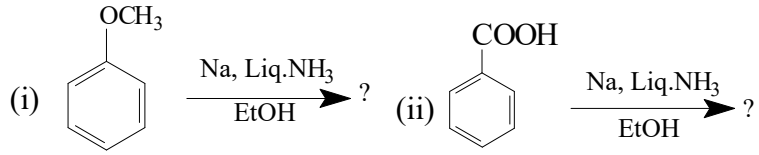
23a. Outline the mechanistic implications of rate law for the reaction iodination of acetone in an alkaline medium. **(6)**

b. How would you detect benzyne intermediate? Explain with an example. **(4)**

24. Discuss the mechanism of the following rearrangements: **(5+5)**
(i) Hofmann (ii) Fries

25a. How is azyl azide prepared? Mention any two of its synthetic applications. **(4)**

b. Predict the product with mechanism. **(3+3)**



26a. Write the mechanism of McFadyen-Stevens reduction. **(4)**

b. Predict the product and explain the reaction of *cis*- and *trans*-2-aminocyclohexanol with HONO. **(6)**

27a. Discuss the pyrolysis reaction of xanthates, acetates, and N-oxides. **(5)**

b. Explain the influence of steric assistance in the solvolysis reaction of diastereomers of 4-*t*-butylcyclohexyl tosylate using Curtin Hammett principle**.** **(5)**

28a. Explain Absolute asymmetric synthesis with suitable example. **(4)**

b. How the major product in an asymmetric induction reaction can be predicted by Cram's rule and Prelog's with suitable example. **(3 + 3)**

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