LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FIRST SEMESTER – **NOVEMBER 2019**

PCH 1501/17/18PCH1MC01 – ORGANIC REACTION MECHANISM AND STEREOCHEMISTRY

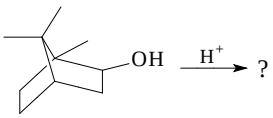
Date: 30-10-2019 Dept. No. Max. : 100 Marks

Time: 01:00-04:00

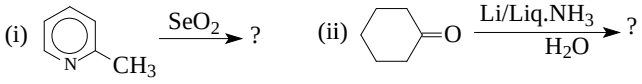
Part-A

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

1. State the possible thermodynamic conditions for chemical reactions.
2. The bromination of toluene using bromine in aqueous acetic acid takes place 605 times faster than does the same reaction of benzene. The product ratio is 32.9% *ortho*-, 0.3% *meta*- and 68.8% *para*-bromotoluene. Calculate the partial rate factors for the reaction.
3. Give an example for Cope and oxy-Cope rearrangement.
4. Identify the product and write the mechanism for the following reaction.



5. What is McFadyen-Stevens reduction? Write its mechanism.
6. Predict the product of the following reactions:



7. Mention the conditions for a good resolving agent in asymmetric transformations.
8. Give an example for each of the following stereoheterotopic terms.

   a) Re / Si face b) ProR / ProS
9. Prove that the rate of racemization is twice the rate of interconversion.
10. Explain the 2-alkylketone rule with a suitable example.

Part-B

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

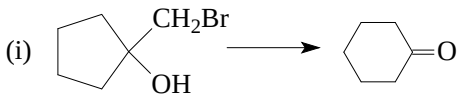
11. Hydrobromination of 1,3-butadiene at 40˚C gives 80% of 1,4-addition product whereas at -80˚C, it gives 80% of 1,2-addition product- Justify.

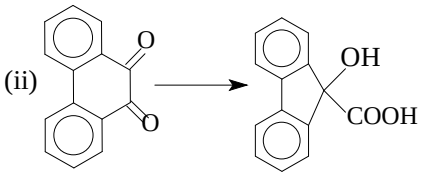
12a. Iodination of acetone in alkaline medium follows second order kinetics. Predict the mechanism of this reaction. (3)

b. Hammett equation is not applicable to aliphatic and *ortho*-substituted compounds. Why? (2)

13. Determine the mechanism of an acid-catalyzed and base-catalyzed hydrolysis of methyl acetate by isotopic labeling studies.

14. Identify the suitable reagents for the following conversions and write the mechanism for the same.



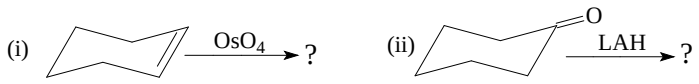


15. Discuss the salient features of Claisen and abnormal Claisen rearrangement with mechanism.

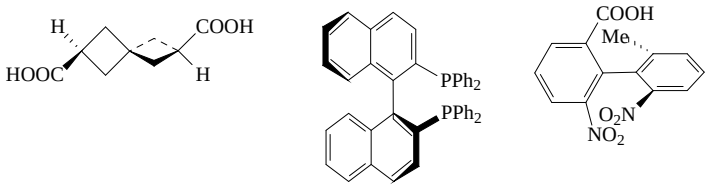
16. Explain the mechanism of the following with a suitable example for each.

(i) Hydride transfer reaction (ii) Displacement reaction

17. Predict the product(s) of the following reactions with their mechanisms.

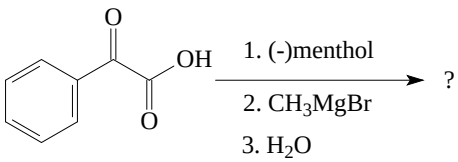


18. What is atropisomerism? Classify the following compounds as axial/plane/ helical chirality.



19. Explain the use of chiral derivatizing agents (CDAs) in NMR spectral techniques and mention their characteristics.

20. Apply Prelog rule for the following reaction and predict the product.



21. Discuss the molecular elimination reactions with suitable examples.

22. Explain the chemical method of racemisation by anion intermediate formation with a suitable example.

Part-C

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

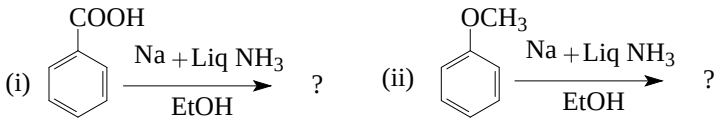
23a. Discuss the quantitative correlations of substituent effects by deriving Hammett equation.

b. The rate of diazotization of aniline is, $-d[C_6H_5NH_2]/dt \alpha [C_6H_5NH_2] [HNO_2]^2$. Explain the mechanistic implications of the rate law in this reaction. **(6+4)**

24a. Write the mechanism of Arndt-Eistert synthesis.

b. Show the formation of reaction intermediate in Hofmann rearrangement and how it is converted into urethane. **(4+6)**

25a. Identify the product(s) and outline the mechanism of the following reactions with product ratio.

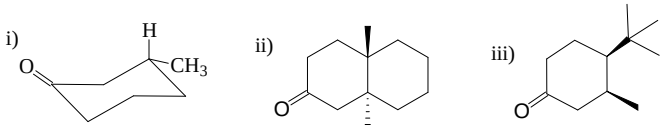


b. Explain the electron transfer mechanism of Clemmensen reduction with a suitable example. **(6+4)**

26a. Write any one example for ring-contraction and ring-expansion of pinacol-pinacolone rearrangement.

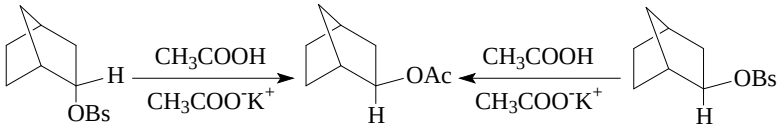
b. Explain the influence of steric assistance in the solvolysis reaction of diastereomers of 4-t-butylcyclohexyl tosylate. **(5+5)**

27a. Apply octant rule and predict the cotton effect for the following compounds.



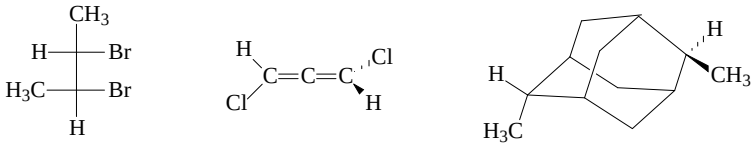
b. Explain Curtin-Hammett principle with a suitable example. **(6 + 4)**

28 a. Discuss the stereochemistry of the following reactions with suitable mechanisms. **(5)**



b. (i) Ethanolysis of conjugate base of 2-(*p*-hydroxyphenyl)ethyl bromide is about 10^6 times faster than that of the corresponding *p*-methoxy compound. Justify. **(2)**

(ii) Assign R / S notation for the following compounds. **(3)**



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