LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FIRSTSEMESTER – APRIL 2018

CH 1812/CH1806 - ORGANIC REACTION MECHANISM & STEREOCHEMISTRY

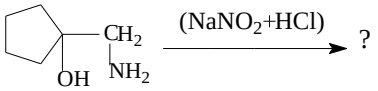
Date: 25-04-2018 Dept. No. Max. : 100 Marks

Time: 09:00-12:00

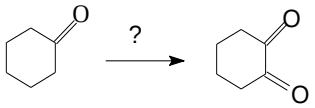
Part-A

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

1. What is meant by microscopic reversibility?
2. What is cross-over experiment? Give an example.
3. Predict the product with mechanism.



4. What is Cope rearrangement?
5. Give the mechanism of the following conversion using a suitable reagent.

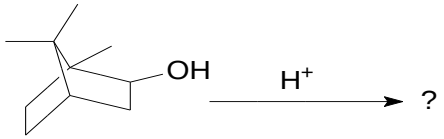


6. What is Wolff-Kishner reduction?
7. Explain why cis-1,2-dimethylcyclohexane is optically inactive at room temperature even though the molecule lacks any elements of symmetry?
8. State axial haloketone rule with an example.
9. "2,3-Pentadiene does not possess any chiral carbon but is resolvable into its enantiomers" Account.
10. Define the following: a) racemic conglomerate b) quasi racemate.

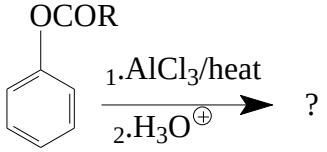
Part-B

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

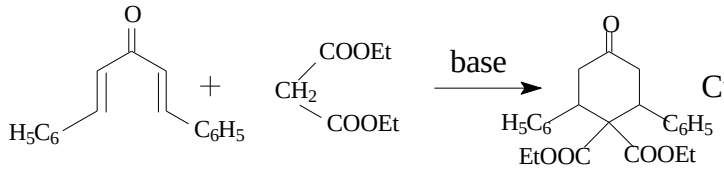
11. State and explain Hammond postulates with a suitable example.
12. Explain any one kinetic method which is used to determine the reaction mechanism.
13. Write the mechanism of von-Ritcher rearrangement.
14. Identify the product in the following reaction with its mechanism.



15. Explain the mechanism of Fischer-indole synthesis.
16. Predict the product and suggest a mechanism for the following reaction:



17. Give the mechanism for the following transformation.

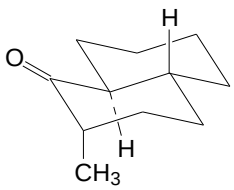


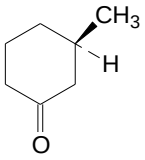
18. Explain Curtin-Hammet principle with a suitable example.

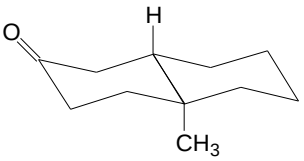
19. Discuss the steric course of the acetolysis reaction of 2-phenyl-3-pentyl tosylate & 3-phenyl-2-pentyl tosylate.

20. Discuss the conformation analyses of 1,2 & 1,3-disubstituted cyclohexanes.

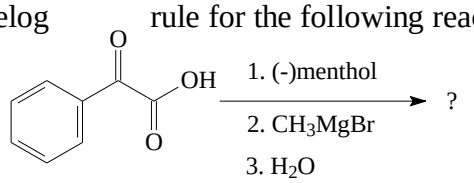
21. Predict the Cotton effect for the following compounds

a) 

b) 

c) 

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



Part-C

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

23a. Explain the following methods of determining the reaction mechanism. (3+3)

(i) Isolation of intermediates (ii) Kinetic isotope effects.

b. Explain the limitations of Hammet equation. (4)

24a. Give the mechanism of pinacol-pinacolone rearrangement. Explain its applications.

b. Outline the mechanism of Arndt-Eistert synthesis. (6+4)

25. Write the mechanism of the following rearrangements:

(i) Baeyer-Villiger (ii) Hoffmann (5+5)

26a. Explain any one application of the following oxidizing agents with mechanism.

(i) DMSO-DCCD (ii) OsO_4 (3+3)

b. Explain the effect of substituents on Birch reduction. (4)

27a. Explain the following with a suitable example.

i) mutarotation ii) anomeric effect

b. Discuss the reactivity of *racemic* and *meso*-stilbene dichloride with hot pyridine.

(3+3+4)

28. Explain the following

i) Pyrolysis reaction of xanthates.

ii) First order asymmetric transformation

iii) Chemical method of racemisation by cation intermediate formation (4+2+4)

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