



LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

FIRST SEMESTER – NOVEMBER 2017

CH 1812 /CH1806- ORGANIC REACTION MECHANISM & STEREOCHEMISTRY

Date: 02-11-2017
Time: 01:00-04:00

Dept. No.

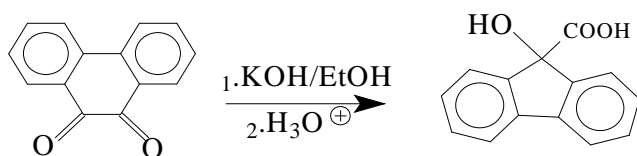
Max. : 100 Marks

Part-A

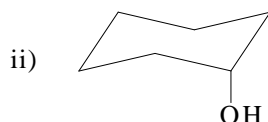
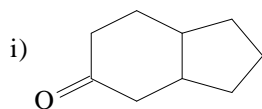
Answer ALL questions.

(10 × 2= 20)

1. State the Hammond postulate.
2. How will you detect the benzyne intermediate? Give an example.
3. Outline the mechanism of the following transformation.



4. What is semi-pinacol rearrangement? Give an example.
5. Give a reaction mechanism in which hydride transfer takes place.
6. Write the mechanism of 1,2-Michael addition with a suitable example.
7. What is Cram's cyclic model?
8. Among the following which will undergo racemisation more readily and why?
i) lactic acid ii) mandelic acid
9. Define the following examples: a) invertomers b) epimers
10. What is axial haloketone rule? Predict the cotton effect for the following compounds.

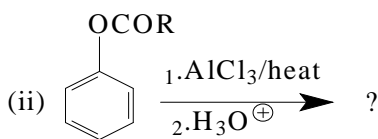
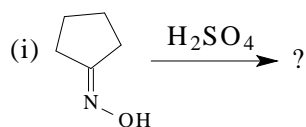


Part-B

Answer any EIGHT questions.

(8 × 5= 40)

11. How are cross-over experiment and isotopic labeling studies used to determine the reaction mechanism? Explain.
12. Explain the concept of microscopic reversibility for the acid catalysed reaction between isobutylene and methanol.
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.
$$\text{RCOOH} + \text{HN}_3 \xrightarrow{\text{H}_2\text{SO}_4} \text{RNH}_2 + \text{CO}_2 + \text{N}_2$$
15. Explain the mechanism of Arndt-Eistert synthesis.
16. Predict the product and suggest a mechanism for the following reactions:



17. Explain the effect of electron donating and electron withdrawing substituents in Birch reduction with mechanism.
18. Explain the Curtin-Hammet principle with a suitable example.

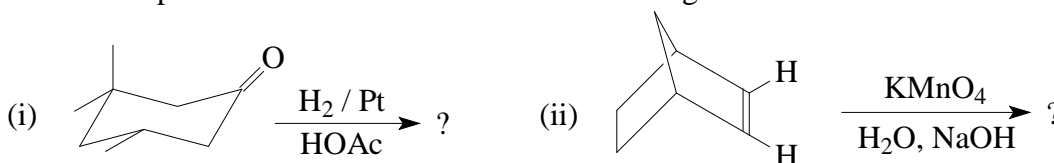
19. Discuss the steric course of the acetolysis reaction of 2-phenyl-3-pentyl tosylate and 3-phenyl-2-pentyl tosylate.
20. Discuss the conformation analyses of 1,2 & 1,3-disubstituted cyclohexanes.
21. Define the following: a) Circular dichroism b) circular birefringence
22. Prove that the rate of racemisation is twice the rate of interconversion in a racemic modification process.

Part-C

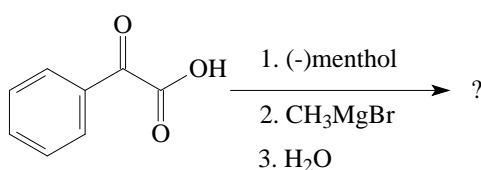
Answer any **FOUR** questions.

(4 × 10= 40)

- 23a. Give the mechanism of the following reactions. (2+2)
- (i) Chichibabin reaction (ii) -elimination reaction
- b. Explain the following methods of determining the reaction mechanism. (3+3)
- (i) Isolation of intermediate (ii) Kinetic isotope effects.
- 24a. The rate law 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. (4)
- b. Predict the product with mechanism for the following reactions. (3+3)



25. Write the mechanism of the following rearrangements: (5+5)
- (i) Favorskii (ii) Wagner-Meerwin
- 26a. Explain any one application of the following oxidizing agents with mechanism. (3+3)
- (i) HIO_4 (ii) SeO_2
- b. Write the mechanism of Wolff-Kishner reduction with a suitable example. (4)
- 27a. Explain the term atropisomerism? Discuss the optical activity of biphenyls.
- b. Discuss the acetolysis reaction of *syn*- and *anti*- 7-norbornyltosylate. (5+5)
- 28a. Discuss the pyrolysis reaction of *cis*- and *trans*-2-phenylcyclohexylxanthates.
- b. Apply Prelog rule for the following reaction and predict the product. (6+4)



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