



17/16PCH1MC01- ORGANIC REACTION MECHANISM AND STEREOCHEMISTRY

Date: 25-04-2018  
Time: 09:00-12:00

Dept. No.

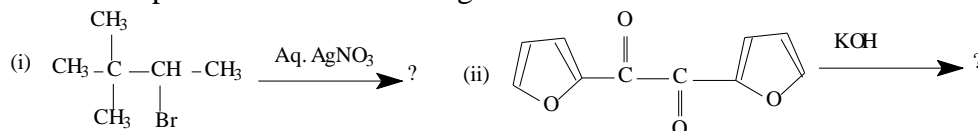
Max. : 100 Marks

Part-A

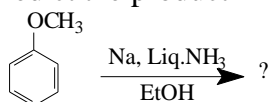
Answer ALL questions.

(10 × 2 = 20)

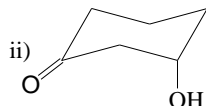
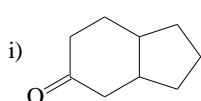
1. What are the conditions favoured for thermodynamically controlled chemical reactions?
2. Draw the potential energy diagram for the nucleophilic substitution of chloride by hydroxyl group in *tert*-butyl chloride. Label  $\Delta G^\circ$ ,  $\Delta G^\ddagger$ , transition states and intermediates.
3. Predict the products in the following:



4. Write a rearrangement reaction which follows ring contraction.
5. Predict the product in the following reaction with mechanism.



6. What is Bouveault-Blanc reduction?
7. Base induced dehydrohalogenation reaction of erythro-1-bromo-1,2-diphenylpropane undergoes much slower rate than its threo isomer. Why?
8. Compare the conformational stabilities of diastereomers using general substituents.
9. Define the following terms with an example for each: a) invertomers b) epimers
10. Predict the Cotton effect for the following compounds.



Part-B

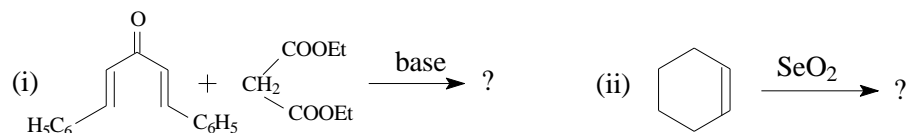
Answer any EIGHT questions.

(8 × 5 = 40)

11. State and explain the Hammond postulates with examples.
- 12a. How is isotopic labeling study used to determine the mechanism of acid or base catalysed hydrolysis of an ester? (3)
  - b. How will you detect the formation of benzyne intermediate in an organic reaction? (2)
- 13a. What is an anomeric equilibrium? Give an example.
  - b. The  $pK_a$  values of *cis*- and *trans*- isomer of 4-*t*-butylcyclohexanecarboxylic acid in 66 % aqueous DMF are found to be 8.23 and 7.79 respectively. Account for the difference in acid strength.
- 14a. How would you convert 1,7,7'-trimethyl bicyclo[2,2,1<sup>1-4</sup>]heptan-2-ol into 2,2'-dimethyl-3-methylidene bicyclo [2,2,1<sup>1-4</sup>] heptane? (3)
  - b. Write the mechanism of benzidine rearrangement. (2)

15. Explain the mechanism of Fischer-indole synthesis.

16. Predict the product and give the mechanism for the following reaction. (3+2)



17. Write the mechanism of Wolff-Kishner and Clemmensen's reduction with a suitable example.

(3+2)

18. Prove that rate of racemisation is twice the rate of interconversion in a racemic modification process.

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

20. 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.

21. Predict the product and explain the reaction of *cis*- and *trans*-2-aminocyclohexanol with HONO.

22. Discuss the solvolysis reactions of 2-phenyl-3-pentyl tosylate and 3-phenyl-2-pentyl tosylate with acetic acid.

### Part-C

Answer any **FOUR** questions.

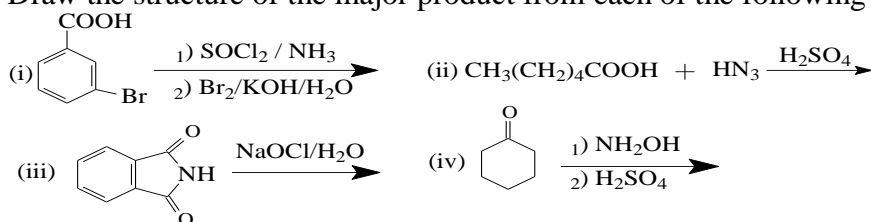
(4 × 10= 40)

23a. Explain the importance of various kinetic isotope effects in determining the reaction mechanism.

(5)

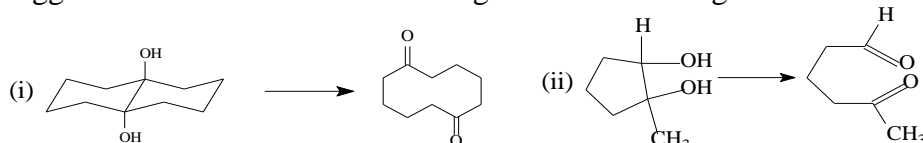
b. The rate of benzoin condensation reaction,  $-d[\text{C}_6\text{H}_5\text{CHO}]/dt = k[\text{C}_6\text{H}_5\text{CHO}]^2 [\text{CN}^-]$ . Explain the mechanistic implications of the rate law in this reaction. (5)

24a. Draw the structure of the major product from each of the following reactions. (4)



b. Explain the mechanism of *ortho*-Claisen and *para*-Claisen rearrangement. (6)

25a. Suggest a mechanism of the following conversions using suitable oxidizing agents. (6)



b. Give any one use of DDQ in organic synthesis. Give its mechanism. (4)

26a. Compare the selectivity of LAH and NBH with any two examples for each. (4)

b. Explain Curtin Hammett principle with suitable example.

27a. Explain the pyrolysis reaction of xanthates and acetates.

b. Discuss the solvolysis reactions of 2-phenyl-3-pentyl tosylate and 3-phenyl-2-pentyl tosylate in acetic acid. (5+5)

28a. How can the major product in an asymmetric induction reaction be predicted by Cram's rule and Prelog's with suitable example?

b. Draw the structure for the following:

(i) 2(*R*), 3(*R*)-2,3-dihydroxybutanal (ii) (*R*)-1-bromo-1-chloroethane

(iii) (*S*)-2-phenyl butane (5+5)

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