LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION - **CHEMISTRY**

FIRST SEMESTER – NOVEMBER 2011

CH 1806 - ORGANIC REACTION MECHANISM & STEREOCHEMISTRY

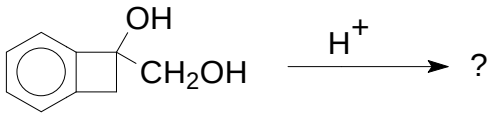
Date : 01-11-2011 Dept. No. Max. : 100 Marks

Time : 1:00 - 4:00

PART-A

Answer ***all*** questions. (10 × 2 = 20 marks)

01. How will you detect the formation of intermediate in Riemer-Tiemann reaction?
02. What is cross over experiment? Explain its importance in determining reaction mechanism.
03. Write and explain the Benzil-Benzillic acid rearrangement.
04. What happens when acetyl chloride reacts with diazomethane in acid medium?
05. $NaBH_4$ is less powerful but more selective reducing agent. Justify this statement with an example.
06. Predict the major product and suggest a mechanism of the following reaction.



07. What happens when erythro 3-bromo-2-butanol react with HBr? Identify the stereochemistry of the product formed.
08. 'trans 4-t-butyl cyclohexane carboxylic acid is more acidic than cis isomer in 66% aq. DMF'. Why?
09. State and explain Prelog's rule with an example.
10. What is first order asymmetric transformation? Give an example.

PART-B

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

11. Compare the kinetically controlled and thermodynamically controlled product formation with potential energy diagram for a suitable reaction.
12. How will you determine the mechanism of hydrolysis of methylacetate reaction.
13. How does the kinetic observation used in determining the reaction mechanism?
14. Explain the Wagner-Meerwein rearrangement with mechanism.
15. Discuss any two important applications of pinacol-pinacolone rearrangement.

16. Explain the role of DDQ in aromatization reaction.

17. Explain the following with mechanism.

    a) dehydro elimination b) dehydrogenation of amines

18. How does α-phenyl-β-bromo-β-benzoyl propionic acid react with pyridine? Explain the stereochemistry involved in the reaction.

19. Explain the following:
    a) Observed dipole moment for 1,2-dibromoethane is 1 D.
    b) meso-stilbene dichloride does not react with pyridine at 200°C.

20. Explain the conformation of n-butane, $C_2 - C_3$ rotation.

21. How will you determine the configuration of
    a) (–) mandelic acid with respect to (+) lactic acid.
    b) (–) lactic acid with respect to (+) tartaric acid.

22. Discuss the conformational analysis of 1,2-disubstituted cyclohexane.

PART-C

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

23. (a) How will you determine the mechanism for the conversion of p-chloronitrobenzene into m- chlorobenzoic acid? (5)

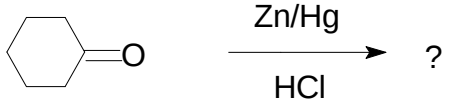
    (b) Suggest a method to detect the intermediate of Hofmann rearrangement and explain with mechanism. (5)

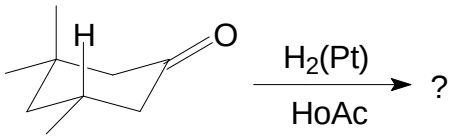
24. Explain the following rearrangements:

    (i) Baeyer-Villiger (ii) Steven's (5+5)

25. (a) Give the applications of Selenium dioxide and Osmium tetroxide with one example for each. (4)

    (b) Identify the products with mechanism. (3+3)

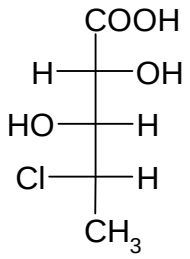
(i) 

(ii) 

26. a) Explain absolute asymmetric synthesis with a suitable example.

b) Assign R/S configuration to the following:

a)



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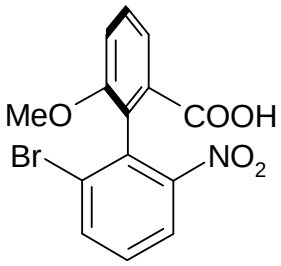

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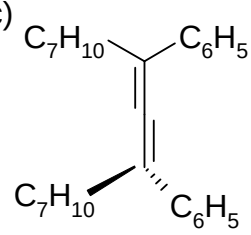

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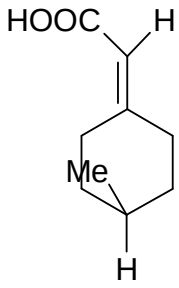

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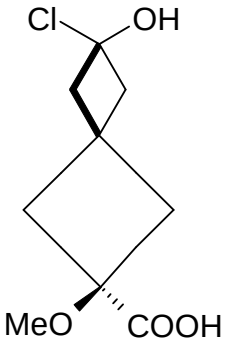

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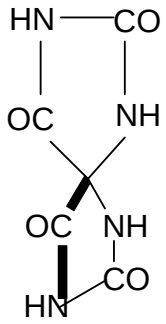

27. a) Explain Octant rule with a suitable example.

b) Predict the Cotton effect by the sign of the most occupied octant in the following compounds:

(i) trans-10-methyl-2-decalone

(ii) cholestan-6-one

28. a) How would you make racemic modifications? Explain thermal racemisation and racemization by cation formation.

b) Explain all the steps involved in the stereochemical synthesis of yohimbine.

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