

**LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034**

M.Sc. DEGREE EXAMINATION – CHEMISTRY

FIRST SEMESTER – NOVEMBER 2007

AD 14

**CH 1806 - ORGANIC REACTION MECHANISM & STEREOCHEMISTRY**

Date : 25/10/2007  
Time : 1:00 - 4:00

Dept. No.

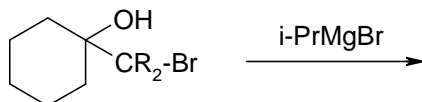
Max. : 100 Marks

**PART - A**

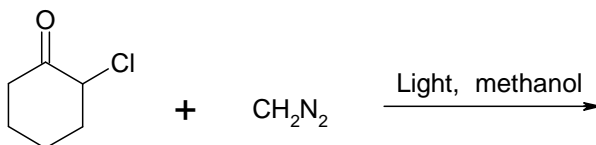
Answer **ALL** questions

(10 × 2 = 20 marks)

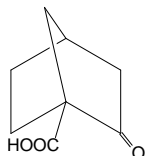
01. Identify the product obtained in the following:



02. Explain the formation of the product in the following:



03. Is Benzidine rearrangement inter or intramolecular? Explain.
04. How is stereochemical studies useful in determining the mechanism of a chemical reaction? Explain with an example.
05. What happens when a mixture of 1,3-cyclohexadiene and chloranil is reduced with platinum? Give its mechanism.
06. Which of the following is more acidic and why?  
*e,a*-4-*t*-butylcyclohexane carboxylic acid & *e,e*-4-*t*-butylcyclohexane carboxylic acid
07. Between epedrine and  $\psi$ -ephedrine, which is stronger base and why?
08. Explain why the following keto acid will not undergo decarboxylation reaction.



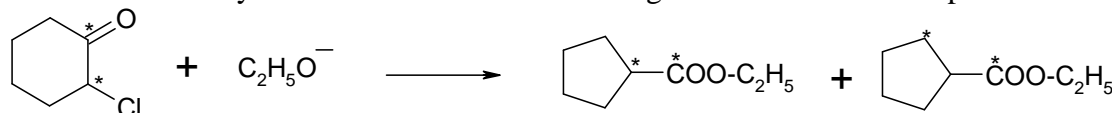
09. Define the following and give examples  
a) invertomers                      b) epimers
10. Explain axial haloketone rule with one example.

**PART - B**

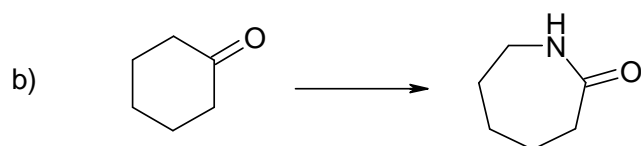
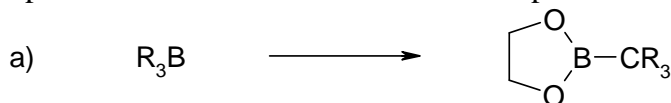
Answer any **EIGHT** questions

(8 × 5 = 40 marks)

11. How would you effect the following conversion? Explain with mechanism.

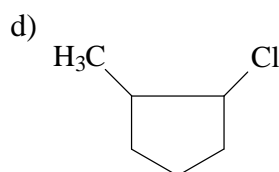
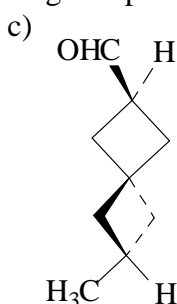
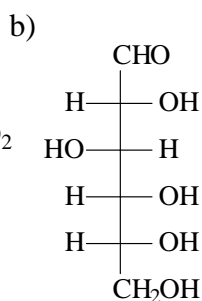
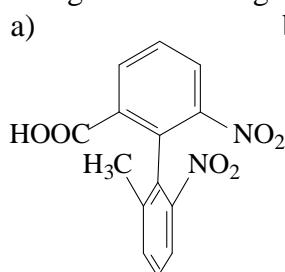


12. Explain with mechanism the formation of product in the following:



13. 'The diazotization of aniline in moderately concentrated acid has been found to be second order in nitrous acid'. Derive the rate law and explain with mechanism.

14. How is Crossover experiment technique useful in determining the mechanism of a chemical reaction? Explain with two suitable examples.
15. Explain the mechanism of oxidation of olefins using Baeyer's reagent and peracids. How are the stereochemistry of the products identified?
16. How is hydride transfer reaction mechanism useful in identifying the products in oxidation-reduction reactions? Explain with two suitable examples.
17. Explain the pyrolysis reaction of cis and trans-2-phenylcyclohexyl xanthates.
18. Explain Curtin-Hammett principle with suitable example.
19. What is first and second order asymmetric transformation?
20. What is atropisomerism? Explain the optical isomerism in 6,6'-dinitridiphenic acid.
21. Assign R & S configuration for the following compounds



22. Predict cotton effect for the following
- a) (+)-3-methyl cyclohexanone      b) trans -10-methyl-2-decalone

### **PART - C**

Answer any **FOUR** questions

( 4 × 10 = 40 marks)

23. a) Explain the mechanistic implications from rate laws with two suitable examples.  
b) What are consecutive reactions? Derive the kinetics for nitration on aromatic substrates with excess nitric acid and explain the mechanism.
24. Explain the mechanism of the following rearrangements with suitable examples.
- a) Neber rearrangement  
b) Curtius rearrangement  
c) Benzil-benzilic acid rearrangement
25. Explain the following with suitable mechanism in oxidation-reduction reactions.
- a) Direct electron transfer reaction  
b) Formation of ester intermediate  
c) Displacement reaction
26. a) Discuss the optical isomerism of allenes and biphenyls.  
b) Write the conformations of cis and trans decalines and discuss about their stability.
27. Explain the following with suitable example.
- a) absolute asymmetric synthesis  
b) chemical method of racemisation by anion formation  
c) Assymmetric destruction
28. Explain the steps involved in the stereoselective synthesis of Yohimbine.

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