LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FIRST SEMESTER – NOVEMBER 2010

# CH 1806 - ORGANIC REACTION MECHANISM & STEREOCHEMISTRY

Date : 30-10-10 Dept. No. Max. : 100 Marks

Time : 1:00 - 4:00

**PART-A**

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

01. What is peroxide effect? Explain with a reaction mechanism.

02. State and explain the principle of microscopic reversibility.

03. Explain the importance of the reaction between neopentyl iodide and aqueous AgNO**3**.

04. Complete the following reaction with mechanism.



05. Explain the effect of electron withdrawing and releasing groups in direct electron transfer mechanism with example.

06. Predict the product of the following reaction;



07. Why is the following β-ketoacid highly resistant to decarboxylation?



08. Explain Curtin-Hammett principle with an example.

09. How would you resolve optically active alcohols from a racemic mixture?

10. What is epimerization? Give an example.

**PART-B**

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

11. Give an example for α, β, γ and δ-elimination reaction.

12. State and explain the Hammond postulate to the bromination of n-propane.

13. How will you determine the reaction mechanism of hydrolysis of an ester using isotoping labeling method?

14. Write and explain the Steven’s rearrangement.

15. Predict the product and explain the mechanism of the following reaction.



16. Discuss the Gomberg-Bechmann synthesis.

17. Write the mechanism of the following reaction



18. Identify the stereochemistry of the products obtained when   
α-phenyl-β-bromo-β-benzoyl propionic acid is heated with pyridine.

19. Explain the process of racemisation through cation formation with two suitable examples.

20. Assign R/S configuration to the following:

a) b) c)

  

21. Explain the stability of various conformers of disubstituted cyclohexanes with energy.

22. State and explain Octant rule. Draw the octants and predict the sign of Cotton effect to the following compounds.

a) (+)-3-methylcyclohexanone b) 2-bromocyclohexan-4-one carboxylic acid

**PART-C**

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

23. (a) How does crossover experiment is used to determine the reaction mechanism? Explain with example. (4)

(b) Explain the mechanistic implications of rate law for a diazotization of aniline reaction. (6)

24. (a) What is migratory aptitude? Suggest any two methods to determine the migratory aptitude. (4)

(b) Give the products of the following (1+1)



(c) How will you convert the following? Explain with mechanism. (4)



25. (a) Explain the addition-elimination reaction mechanism of a α, β-unsaturated ketone. (4)

(b) Give any two synthetic applications of selenium dioxide. (2)

(c) Write the product with mechanism for the following reaction (4)



26. a) Write the most stable conformations to the following: (6)  
i) ii) iii)

  

b) Explain second order asymmetric transformation with a suitable example.

27. Explain the following:

a) meso-stilbene dichloride possesses a dipole moment 1.27D

b) Threo-3-bromo-2butanol with HBr gives dl product.

c) Trans-4-tert-butyl cyclohexane carboxylic acid in aqueous DMF is more acidic than cis isomer. (3+3+4)

28. a) Explain the axial haloketone rule. What are the uses of this rule? Explain with an example each. (5)

b) Explain the steps involved in the stereochemical synthesis of reserpine.(5)

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