LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

FIRST SEMESTER – NOVEMBER 2009

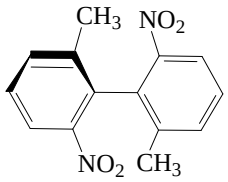
CH 1806 - ORGANIC REACTION MECHANISM & STEREOCHEMISTRY

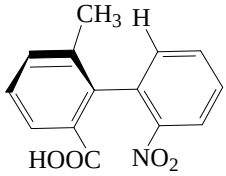
Date & Time: 04/11/2009 / 1:00 - 4:00 Dept. No. Max. : 100 Marks

PART-A

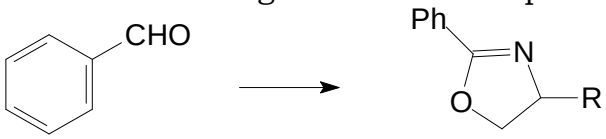
*Answer **ALL** questions.* (10 × 2 = 20)

01. Which of following is easily resolvable and why?





02. Explain why the conductivity of boric acid in (–) 2,3-butanediol is more than the meso isomer?
03. In *trans*-1,2-dibromocyclohexane the relative population of *a,a*- and *e,e*-conformers in liquid state is 65% and 35% respectively, whereas in gaseous state 95% and 5% respectively.Explain.
04. Why neomenthyl chloride reacts faster with NaOEt than menthyl chloride?
05. Between erythro and threo form of 1-bromo-1, 2-diphenylpropane, which of the two would undergo dehydrohalogenation faster in the presence of a base. Explain why?
06. Explain the mechanism in oxidative decarboxylation reactions.
07. Explain memory effect in rearrangement reactions with an example.
08. Explain the mechanism of insertion of methylene group using diazomethane
09. Is Benzidine rearrangement inter or intramolecuar? Justify your answer.
10. How would you effect the following conversion? Explain with mechanism.



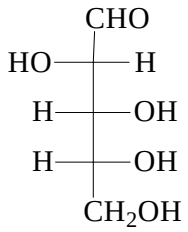
PART-B

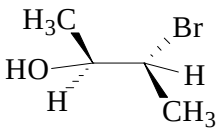
*Answer **any eight** questions.* (8 × 5 = 40)

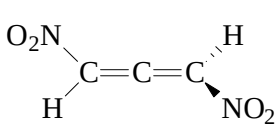
11. Discuss the steric course of the acetolysis reaction of 2-phenyl-3-pentyl tosylate and 3-phenyl-2-pentyl tosylate.
12. Discuss the reactivity *racemic* and *meso* stilbene dichloride with hot pyridine.
13. Prove that the rate of racemisation is twice the rate of interconversion in a racemic modification process.
14. Explain the stereic course of the pyrolysis reaction of diastereomers of 3-phenyl-2-butyl xanthates.
15. Explain the following with suitable example.
    a) absolute asymmetric synthesis
    b) chemical method of racemisation by anion formation

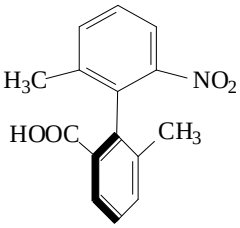
16. Assign R & S configuration for the following.

a) b) c) d)









17. How is isotopic labeling technique helpful in determining reaction mechanism? Explain with any two examples.
18. How does the kinetics study in chain and parallel reactions help to design the reaction mechanism? Explain with suitable examples.
19. What are the characteristics of Hofmann rearrangement? How is the mechanism of rearrangement confirmed?
20. Explain Stevens rearrangement. What are the different mechanisms which explain this rearrangement?
21. What are the types of organic redox reactions? Explain with an example for each.
22. 'Metal reduction is the most powerful method to reduce benzene derivatives'. Substantiate this statement with suitable examples.

PART-C

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

23. a) Explain the term 'memory effect' with a suitable example
    b) Write reaction of *erythro*-3-bromo-2-butanol with HBr
    c) Write the conformations of *cis* and *trans* decalines and discuss their stability.
24. Explain the following.
    a) atropisomerism
    b) asymmetric destruction
    c) ephedrine is weaker base than ψ-ephedrine.
25. Discuss the stereochemical synthesis of reserpine.
26. a) How do isotopic labeling and stereochemistry help in predicting suitable reaction mechanisms? Explain with two suitable examples.
    b) How is the mechanism of von-Ritcher rearrangement modified? Give the evidences for this mechanism.
27. a) Explain the mechanism of Arndt-Eistert synthesis. Mention any one evidence for the mechanism.
    b) What are the importances of Lossen and Schmidt rearrangements in Organic synthesis? Explain with mechanism.
28. a) Write the mechanism of reaction for the conversion of R_3B into R_3C-OH. What are the evidences for this mechanism?
    b) Explain the mechanism of oxidative cleavage of alkyl groups from benzene rings with suitable examples.

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