 LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

SECOND SEMESTER – APRIL 2012

# CH 2814 / 2808 - ORGANIC SUBSTITUTION, ADDITION & ELIMINATION RXNS

Date : 17-04-2012 Dept. No. Max. : 100 Marks

Time : 9:00 - 12:00

**PART – A**

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

01. Which of the following compounds are aromatic?

(i) cyclobutadiene (ii) cyclopentadienylcation

(iii) cyclooctatetraene (iv) cycloheptatrienyl anion

02. Hammett equation is not applicable to aliphatic reactions and *ortho*-product. Why?

03. How would you prove that the transition state in SN2 reaction must be linear? Explain.

04. What are the evidences for SN1’ mechanism with benzene diazonium salts?

05. State and explain Zaitsev’s rule with an example.

06. Identify the stereochemistry of the products obtained on the dehydrobromination of different conformers of 1,2-dibromo-1,2-diphenylpropane.

07. Give any two examples for each long-lived and short-lived free radicals.

08. Give the products of the following. 

09. How does selenoxide undergo thermal syn elimination in the formation of α,β-unsaturated ketone?

10. Explain the mechanism of hydroboration-oxidation reaction with a suitable example.

**PART – B**

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

11. What is ipso substitution? Explain with mechanism.

12. What is partial rate factor? Explain its importance in ArSE reactions with a suitable example.

13. Explain the following electrophilic substitution reaction mechanism with any one example.

(i) Direct amination (ii) Insertion by nitrenes

14. What are ambident nucleophiles? Explain their role in reactions with suitable examples.

15. How does the presence of a neighbouring group enhance the rate of nucleophilic substitution reaction? Explain with typical examples.

16. Explain the mechanism of Bucherer reaction taking β-naphthol as an example.

17. Explain (1) syn elimination with atleast three suitable examples and (2) the mechanism of addition of HBr to 3,3,3-trichloropropene.

18. How many stereoisomers are possible for 1,2,3,4,5,6-hexachlorocyclohexane? Which one will undergo (1) fastest and (2) slowest dehydrochlorination? Why?

19. Explain the factors influencing the different types of free radicals.

20. How is ESR spectroscopy used to detect short-lived free radical? Explain.

21. How does the stereochemistry of the products differ on the hydroxylation of 2-butene using (1) alkaline KMnO4 and (2) perbenzoic acid? Explain.

22. Explain the following:  
a) meso-2,3-dibromobutane reacts faster with iodide ion than dl isomer.  
b) gauche conformation of ethylene glycol is more stabler than anti form.

**PART – C**

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

23. a) Discuss the orientation and reactivity of aniline towards bromination.

b) Explain the mechanism of SE2 reaction with an example.

24. Explain the following:

(i) 3-phenyl-3-methylbutan-1-al with ditertiarybutylperoxide.

(ii) Photolytic cleavage of 5-methyl-2-hexanone

25. (a)How is benzyne formed? What are the evidences for the benzyne mechanism?

(b)‘Acetolysis of both 4-methoxy-1-pentylbrosylate and 5-methoxy-2-pentylbrosylate give the same mixture of products’. Explain.

26. (a)What is ‘product spread’ in allylicnucleophilic substitution reactions? Explain.

(b)Explain the stereochemistry of the product obtained in the rearrangement reaction of 2-amino-1-anisyl-1-phenyl propanol reacts with nitrous acid

27. (a)‘Menthyl chloride undergoes dehydrochlorination at a slower rate comparing neomenthyl chloride’. Why? Identify the products obtained and explain.

(b)‘Dehydrohalogenation of 2-fluorohexane mainly gives Hofmann product while 2-iodohexane gives Zaitsev’s product as major’. Justify this statement and explain.

28. (a)Explain the stereochemistry of the products obtained on hydration of   
cis- and trans-2-pentene with (1) water in the presence of an acid and   
(2) Oxymercuration-demercuration methods.

(b) Arrange the following alkenes in their decreasing order of stereoselectivity of anti-addition of Br2 and explain your answer.

MeCH=CHMe, PhCH=CHMe, PhC(Me)=CHMe

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