



LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

SECOND SEMESTER – APRIL 2016

CH 2814 – ORGANIC SUBSTITUTION, ADDITION & ELIMINATION RXNS

Date: 16-04-2016

Dept. No.

Max. : 100 Marks

Time: 01:00-04:00

PART-A

Answer ALL questions.

(10 x 2= 20 marks)

1. How will you synthesize *m*-bromophenol from benzene?
2. $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Br}$ undergoes $\text{S}_{\text{N}}2$ reaction faster than ethyl bromide-Why?
3. When does Hofmann elimination take place in E2 reaction?
4. Why does the addition of hydrogen bromide by free radical mechanism seem to follow anti-Markovnikoff's rule?
5. CH_3Br reacts with NaCN to give CH_3CN , while it reacts with AgCN to give CH_3NC . Why?
6. Mention any four general characteristics of free radical reactions.
7. Adduce evidences for the formation of σ - and π -complexes in aromatic electrophilic substitution reaction.
8. How is the formation of benzyne intermediate confirmed in aromatic nucleophilic substitution reaction?
9. Write the role of inhibitors in free radical reaction with examples.
10. What is oxymercuration-demercuration reaction? Give an example.

PART-B

Answer any EIGHT questions.

(8 x 5= 40 marks)

11. Discuss the various factors affecting the aliphatic electrophilic substitution reaction mechanisms.
12. Account for the following:
 - i) Mixture of $\text{HNO}_3/\text{H}_2\text{SO}_4$ is used for nitration than HNO_3 alone.
 - ii) Pyrrole is a weaker base than pyridine. (2½+2½)
13. Discuss the mechanism and stereo chemistry of E1 elimination reaction with an example.
14. a. Catalytic hydrogenation of a double bond follows *syn* addition. Explain with an example.
b. What is cheletropic reaction? Cite an example. (3+2)
15. Compare the reactivity of alkenes and alkynes towards electrophilic, nucleophilic and free radical addition reactions.
16. Discuss the mechanism of von-Richter reaction. How does the nature of Z- group affect the reaction rate?
17. Account for the following: (2½ × 2)
 - a) In E2 reaction, a *threo* form gives *trans* alkene while an *erythro* form gives a *cis* olefin.
 - b) Acid catalysed dehydration of *neopentyl* alcohol yields 2-methyl-2-butene as the major product.
18. How are carbenes synthesized? How do they undergo reaction with alkenes and conjugated dienes?

19. How does the ability of leaving and incoming nucleophiles decide the formation of products during S_NAr reactions?
20. Explain the reactivity of aromatic substrates and solvents in free radical reactions.
21. What are the conditions for a compound to undergo Michael 1,2- and 1,4-addition reactions? Give suitable examples.
22. Isobutylene oxide reacts with methanol in acidic medium to give primary alcohol as the major product, whereas in basic medium it gives tertiary alcohol as the major product- Explain.

PART-C

Answer any FOUR questions.

(4 x 10= 40 marks)

23. a) Derive the Hammett equation to correlate the substituent and reaction constant. (6)
b) Write the mechanism and limitations of Friedel-Crafts alkylation reaction. (4)
24. a) Explain the mechanism of Rosenmund von Braun reaction. How do oxidative addition and reductive elimination take place in this reaction? (6)
b) How is amination of 1-butene done? What are the products formed? (4)
25. a) How does hydration of alkenes take place by direct and indirect methods? Give an example for each.
b) Explain the stereochemistry involved in the epoxidation of alkenes.
26. a) Discuss the important features of S_E2 reaction mechanism with evidences.
b) Explain the mechanism of Bucherer-Rosenmund reaction.
27. a) Write the mechanism of Stork–enamine reaction. (3)
b) Explain the Sommelet-Hauser rearrangement with its mechanism. (3)
c) Explain the single electron transfer (SET) mechanism with an example. (4)
28. a) Write a note on E1-E2-E1cB spectrum. (4)
b) Discuss the mechanism and orientation of pyrolytic elimination reaction with an example. (6)

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