



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

**M.Sc. DEGREE EXAMINATION – CHEMISTRY**

**SECOND SEMESTER – NOVEMBER 2016**

**CH 2814 - ORGANIC SUBSTITUTION, ADDITION & ELIMINATION RXNS**

Date: 08-11-2016  
Time: 01:00-04:00

Dept. No.

Max. : 100 Marks

**Part-A**

**Answer ALL questions.**

**(10 × 2= 20)**

1. What is Swain-Scott relationship?
2. Predict the products for the reaction between *m*-dichlorobenzene with  $\text{KNH}_2$  in liq.  $\text{NH}_3$  and mention the intermediate involved.
3. Why is the peroxide effect not observed in the addition of HCl to unsymmetrical olefin?
4. Write the mechanism of Bucherer reaction.
5. The rate of acid-catalyzed hydrolysis of benzamide is -0.298 and the relative electron withdrawing effect of  $-\text{NO}_2$  substituent is + 0.710. Calculate the relative reactivity of nitrobenzamide.
6. What is the role of  $\text{HNO}_3$  in the iodination of benzene?
7. Which among the following is more reactive in the electrophilic substitution reaction with HCl? Crotyl mercuric bromide or *n*-butyl bromide
8. What is Cope reaction? Give an example.
9. The rate of addition of  $\text{Br}_2$  to ethylene increases with  $\text{AlBr}_3$ , and decreases with KBr. Justify.
10. "Stereospecificity of bromination reaction of  $\text{PhCH}=\text{CHCH}_3$  decreases in solvents of high dielectric constant". Account.

**Part-B**

**Answer any EIGHT questions.**

**(8 × 5= 40)**

11. Which of the following compounds have aromatic character and account for your answer? (a)  $\text{C}_4\text{H}_4^{2+}$   
(b)  $\text{C}_7\text{H}_7^+$  (c)  $\text{C}_8\text{H}_8$
12. a) Explain the mechanism of Stork – enamine reaction. (3)  
b) What is meant by *ipso* substitution reaction? Give an example. (2)
13. Discuss the mechanism of Sommelet Hauser reaction. How does it compete with Steven's rearrangement?
14. Discuss the mechanism and stereo chemistry of  $\text{E}_1$  elimination reaction with an example.
15. a) Acid catalysed dehydration of *neopentyl* alcohol yields 2-methyl-2-butene as the major product. Explain.  
b) What is cheletropic reaction? Cite an example. ( $2\frac{1}{2} \times 2$ )
16. Reaction of isobutylene oxide with methanol in acidic medium gives primary alcohol as the major product, while in basic medium it gives tertiary alcohol as the major product. Explain.
17. How does the ability of leaving and incoming nucleophiles decide the formation of products during  $\text{S}_{\text{N}}\text{Ar}$  reactions?
- 18 a. Free radical addition of HBr to 1-bromocyclohexene gives only *cis*-isomer and not *trans*-isomer. Explain. (3+2)  
b. Explain Simon-Smith reaction with suitable example.
19. Explain single electron transfer (SET) mechanism with an example.
20. What is  $\text{E}_i$  reaction? Explain the stereo specificity of  $\text{E}_i$  elimination reaction.
21. Discuss the mechanism of von-Richter reaction. How does the nature of Z group affect the reaction rate?
22. Addition of carbenes to unsymmetrical olefin is non-stereospecific in gas phase. Justify.

**Part-C**

*Answer any FOUR questions.*

**(4 × 10= 40)**

- 23a. Discuss various factors affecting the aliphatic electrophilic substitution reaction mechanisms. **(5)**
- b. Discuss the important features of SE2 reaction mechanism with evidences. **(5)**
- 24a. Write a note on E1-E2-E1cB spectrum. **(4)**
- b. Describe the mechanism and orientation of pyrolytic elimination reaction with an example. **(6)**
- 25a. Write the mechanism and limitations of Friedel-Crafts alkylation reaction. **(5)**
- b. What are the conditions for a compound to undergo 1,2- and 1,4-Michael addition reactions? Give suitable examples. **(5)**
26. Explain the following with evidences:
- a) Ion Pair mechanism    b) Bucherer reaction **(5 + 5)**
- 27a. Prove that the E2 reaction of erythro-1-bromo-1,2-diphenyl propane is stereospecific.
- b. Explain Hofmann degradation reaction with an example. **(5 + 5)**
- 28a. Explain the reactivity of aromatic substrates and solvents in free radical reaction.
- b. Compare the reactivity of alkenes and alkynes towards electrophilic, nucleophilic and free radical addition reactions. **(5 + 5)**

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