



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

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

SECOND SEMESTER – APRIL 2018

**CH 2819- ORGANIC REACTION MECHANISMS & HETEROCYCLICS**

Date: 17-04-2018  
Time: 01:00-04:00

Dept. No.

Max. : 100 Marks

### Part-A

*Answer ALL questions.*

(10 × 2 = 20)

1. Write Swain-Scott equation and mention the terms involved in it.
2. Give the mechanism of Sommelet-Hauser rearrangement reaction.
3. Write the nitrosation reaction of primary and secondary amines.
4. Predict the  $pK_a$  for the following phenols using the appropriate substituent constant. The  $pK_a$  for unsubstituted phenol is 9.90 and the  $\rho$  value is 2.25.
5. Define isoracemisation process with an example.
6. How is nitrene generated? Write an equation.
7. E1 and S<sub>N</sub>1 reactions are competitive. Justify.
8. Write an example for 1,3-dipolar addition reaction.
9. How is phthalocyanine synthesized?
10. Draw the resonance structures of pyridine.

### Part-B

*Answer any EIGHT questions.*

(8 × 5 = 40)

11. Write the mechanism of sulphonation of benzene and give evidences for the mechanism.
12. Explain concerted mechanism with suitable example.
13. Explain neighbouring group participation reaction with an example.
14. Reaction of 2-buten-1-ol with SOCl<sub>2</sub> forms 3-chloro-1-butene as an exclusive product. Write the mechanism and mention the type of mechanism it follows.
15. 'The effect of attacking nucleophile in S<sub>N</sub>1 reaction kinetics is negligible.' Why?
16. Write the mechanism of von Richter rearrangement.
17. What are E1-E2-E1cB spectrum.
18. Explain the addition of water onto an alkene by Markonikov and anti-Markonikov mechanism.
19. How are free radicals generated? Explain free radical polymerization reaction.
20. Explain any one method of synthesis of imidazole.
21. Discuss the nucleophilic substitution reactions of pyridine.
22. Write the biological importance of carbazole, chroman, uracil and chromone derivatives.

### Part-C

*Answer any FOUR questions.*

(4 × 10 = 40)

- 23a. Explain the reaction mechanism of halogenation of benzene with evidences.
  - b. Acetanilide undergoes nitration by Ac<sub>2</sub>O-HNO<sub>3</sub> predominantly at the sterically hindered ortho position. Explain. (5+5)
- 24a. Explain ion-pair mechanism with evidences.
  - b. Discuss single electron transfer (SET) mechanism with an example. (5+5)
25. Explain the following with evidences: a) Benzyne mechanism b) Bucherer reaction
- 26a. What is pyrolytic elimination reaction? Explain with suitable examples. (5)
  - b. Write short notes on long lived and short lived free radicals. (5)
- 27a. Discuss the addition of carbenes to double bonded compounds. Give suitable examples.
  - b. Write the mechanism of electrophilic and nucleophilic addition reactions. (4+6)
- 28a. Describe a suitable synthetic route for the following compounds. (3+3)

(a) indole

(b) Luciferin

b. Compare the natural existence and stability of pyrimidine, pyridazine and pyrazine derivatives.

(4)

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