LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

SECOND SEMESTER – **APRIL 2016**

CH 2819 – ORGANIC REACTION MECHANISMS & HETEROCYCLICS

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. CH_3Br reacts with NaCN to give CH_3CN, while it gives CH_3NC with AgCN. Why?
2. Write the Swain-Scott equation and mention the terms involved in it.
3. Give the mechanism of Sommelet-Hauser rearrangement.
4. Define isoracemisation process with an example.
5. Predict the pk_a for the following phenols using the appropriate substituent constant, a pk_a for unsubstituted phenol of 9.90 and a ρ value of 2.25.
6. Give any two methods of carbene synthesis.
7. How is double bond formation in elimination reaction stereoselective?
8. Why is alkyne less reactive than alkene toward electrophilic addition reaction?
9. Which is more aromatic- pyrrole or thiophene? Give reasons.
10. Mention the biological importance of pyrimidines.

PART-B

Answer any EIGHT questions. **(8 x 5= 40 marks)**

11. The effect of attacking nucleophile in S_N1 reaction kinetics is negligible. Why?
12. Explain the single electron transfer (SET) mechanism with an example.
13. Methylation of toluene at 0 °C gives a mixture of *o*- & *p*-xylene while at 80 °C it gives mainly m-xylene.
14. Explain the mechanism of nitration of benzene with evidences.
15. Discuss the effect of solvent in substitution reactions.
16. Explain the ion-pair mechanism with evidences.
17. Discuss the mechanism and orientation in pyrolytic elimination with suitable examples.
18. Why does E2 reaction of a *threo* form give *trans* alkene while an *erythro* form gives a *cis* olefin? Explain them with examples.
19. How do conjugated dienes undergo 1,2- and 1,4-nucleophilic addition reactions? Give suitable example.
20. Describe any two free radical addition reactions with examples.
21. Discuss the synthesis of (a) substituted indole and (b) carbazole. (2.5 + 2.5)
22. Compare the structure and properties of chroman and coumarin. (2.5 + 2.5)

PART-C

Answer any FOUR questions. **(4 x 10= 40 marks)**

23. a. Explain bimolecular aliphatic electrophilic substitution (S_E2) reaction with a suitable example. (6)

b. Acetanilide undergoes nitration by Ac_2O-HNO_3 predominantly at the sterically hindered ortho position-Explain. (4)

24. a. Explain the mechanism of von-Ritcher rearrangement with evidences. (5)

b. Between diphenylmethyl bromide and t-butyl bromide which will undergo solvolysis readily and why? (5)

25. Explain the following with evidences: a) Benzyne mechanism b) Bucherer reaction

26. a. Discuss the connection between E1-E2-E1cB reactions. (5)

b. Explain the reactivity of organometallic compounds with alkenes. Give examples. (5)

27. a. What are the products formed when an excess of propylene is added to ethylamine? (4)

b. Discuss the electrophilic substitution reactions in oxazole and thiazole with suitable examples. (6)

28. Describe the synthesis of the following heterocyclic compound derivatives. (4+4+2)

(a) thiamine (b) α-tocopherol (c) luciferin.

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