LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION - CHEMISTRY

SECONDSEMESTER - APRIL 2017

CH 2819- ORGANIC REACTION MECHANISMS & HETEROCYCLICS

Date: 06-05-2017 Dept. No. Max.: 100 Marks

Time: 09:00-12:00

Part-A

Answer ALL questions.

 $(10 \times 2 = 20)$

- 1. Which of the following species will exhibit aromatic character?
 - a) cycloheptatrienyl anion b) cyclooctatetraene c) [14] Annulene
- 2. Write Grunwald-Winstein relationship and mention the terms involved in it.
- 3. Define isoracemisation process with an example.
- 4. Between diphenylmethyl bromide and t-butyl bromide which will undergo solvolysis very readily and why?
- 5. Give the mechanism of Sommelet-Hauser rearrangement.
- 6. How is carbene generated? Mention its stability with the substituents.
- 7. Compare E1 and E2 reactions.
- 8. What type of addition reaction takes place when HBr reacts with 2-pentene in presence of benzoperoxide?
- 9. Draw the structure of phthalocyanine.
- 10. How is uracil synthesized?

Part-B

Answer any EIGHT questions.

 $(8 \times 5 = 40)$

- 11. Methylation of toluene at 0 °C gives a mixture of *o-&p*-xylene while at 80 °C it gives mainly m-xylene. Justify.
- 12. Explain benzyne mechanism with an example.
- 13. 'The effect of attacking nucleophile in S_N1 reaction kinetics is negligible.' Why?
- 14. Explain the reaction mechanism of nitration of benzene with evidences.
- 15. Discuss the effect of solvent in substitution reactions.
- 16. Explain Bucherer reaction with example.
- 17. Explain E1-E2-E1cB spectrum
- 18. Describe any one method each of direct and indirect method of addition of water molecule to C-C double bond.
- 19. Explain free radical addition reaction with suitable example. How is it different from free radical polymerization?

- 20. Explain Fischer indole synthesis.
- 21. Discuss the nucleophilic substitution reactions of pyridine.
- 22. Compare the structure of chroman and chromone for synthesis and biological properties.

Part-C

Answer any FOUR questions.

 $(4 \times 10 = 40)$

- 23 a. Explain bimolecular aliphatic electrophilic substitution(S_E2) reaction with suitable example.
 - b. Acetanilide undergoes nitration by Ac₂O-HNO₃ predominantly at the sterically hindered ortho position. Explain. (5+5)
- 24a. Explain the mechanism of von Ritcher rearrangement with evidences.
 - b. Give the mechanism for Wohl-Ziegler bromination reaction.

(5+5)

- 25. Explain the following with evidences:
 - a) single electron transfer (SET) mechanism
- b) ion-pair mechanism

(5+5)

- 26a. How does E1 reaction compete with S_N1 reaction? Explain with suitable examples.
 - b. Discuss the 1,2- and 1,4-nucleophilic addition reactions in conjugated alkenes? Give suitable examples. (5)
- 27a. Describe catalytic hydrogenation reactions of alkenes with suitable examples. (4)
 - b. Why are Heterocyclic compounds less aromatic than benzene derivatives? Mention the heterocyclic compounds that undergo addition reactions. (4+2)
- 28 a. Explain a synthetic route for the following compounds.

(4+2)

- (a) carbazole (b) Luciferin.
- b. What are the biological importances of pyrimidine and chromone derivatives? (4)

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