# LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

# M.Sc. DEGREE EXAMINATION – CHEMISTRY SECOND SEMESTER – NOVEMBER 2016

## CH 2819 - ORGANIC REACTION MECHANISMS & HETEROCYCLICS

Date: 08-11-2016	Dont No	Max.: 100 Marks
Date: 06-11-2010	Dept. No.	max. 100 marks
Time: 01:00-04:00		

#### Part-A

# Answer ALL questions.

 $(10 \times 2 = 20)$ 

- 1. Neopentyl halide is very un-reactive towards nucleophilic substitution. Justify?
- 2. Reactions of *o-* & *m-*dichlorobenzene with KNH<sub>2</sub> in liq. NH<sub>3</sub> form identical product. Account.
- 3. Define isoracemisation process with an example.
- 4. Predict the product for the reaction of CH<sub>3</sub>-Br with a) AgCN and b) NaCN
- 5. What is Grunwalt-Winstein relationship? Mention its significances.
- 6. How does carbene undergo insertion reaction?
- 7. What is pyrolytic elimination reaction? Give an example.
- 8. Why is 1,2-Micheal addition preferred in  $\alpha,\beta$ -unsaturated carbonyl compounds?
- 9. What type of heterocyclic compound is present in phthalocyanine? Draw its structure.
- 10. Write the synthesis of uric acid.

#### Part-B

## Answer any EIGHT questions.

 $(8\times 5=40)$ 

- 11. Discuss the effect of solvent in nucleophilic substitution reactions.
- 12. Predict the product and justify your answer.

$$A \stackrel{1.TsCl}{\longleftarrow} 2. \text{ LiBr / Acetone} \qquad \begin{array}{c} & & \text{HBr} \\ \hline & \text{CH}_2\text{OH} \end{array} \longrightarrow B$$

- 13. Explain neighbouring group participation using 2-norbornyl system as an example.
- 14. a) Discuss the mechanism of Stork–enamine reaction.

(3)

b) What is meant by ipso substitution reaction? Give an example.

(2)

- 15. Discuss various factors affecting the aliphatic electrophilic substitution reaction mechanisms.
- 16. Which of the following compounds have aromatic character and account for your answer? (a)  $C_4H_4^{2+}$  (b)  $C_7H_7^{+}$  (c)  $C_8H_8$
- 17. Compare E1 and E2 reactions with suitable examples.
- 18. How is carbene generated? Describe its rearrangement and addition reactions.
- 19. What is the speciality of addition of ammonia to alkenes? Describe the complete reaction.
- 20. How is free radical addition reaction different from ionic type? Explain with suitable examples.
- 21. Describe the general synthesis of (a) pyridine and (b) pyrimidine.

 $(2\frac{1}{2} + 2\frac{1}{2})$ 

22. How does electrophilic substitution take place in pyrrole? Give examples.

# Part-C $(4 \times 10 = 40)$ Answer any FOUR questions. 23. Explain the following with evidences: a) Benzyne mechanism b) von Ritcher rearrangement 24 a. How is amination of 1-butene carried out? What are the products formed? b. Explain ion-pair mechanism with evidences. 25 a. Diphenylmethyl bromide undergoes solvolysis faster than t-butyl bromide. Justify this statement. b. Explain the mechanism of Bucherer reaction with evidences. 26 a. Explain E1-E2-E1cB spectrum. **(5)** b. Compare the reactivity of alkenes and alkynes towards electrophilic, nucleophilic and free radical reactions. **(5)** 27 a. How does cycloaddition reaction take place in alkenes? Give suitable examples **(4)** b. Explain the synthesis of following compounds. (i) uracil (ii) carbazole (3+3)

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How are the following derivatives of heterocyclic compounds synthesized?

(b)  $\alpha$ -tocopherol

(a) thiamine

(5+5)