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Reg. No.....

SECOND SEMESTER M.Sc. DEGREE EXAMINATION, JUNE 2014

(CUCSS)

Chemistry

CH2 C06—ORGANIC CHEMISTRY—II

(2010 Admissions)

me: Three Hours

Maximum: 36 Weightage

Part A

Answer all questions.
Each question carries 1 weightage.

- 1. With an example illustrate the use of PhN≡ N+ as a synthetic intermediate.
- 2. Discuss the structure and formation of triplet and singlet carbenes.
- 3. Write two methods by which arylnitrenes may be obtained.
- 4. What is the ElcB mechanism of nucleophilic aromatic substitution?
- 5. What is Schmidt reaction?
- 6. What are batho, hypso, hypo and hyperchromic shifts of absorption bands in UV-Vis spectroscopy?
- 7. How can a primary amide distinguished from a secondary amide by IR spectroscopy?
- 8. The substitution pattern of disubstituted benzene derivatives can be determined by IR spectroscopy. Explain how.
- 9. Write an example for the use of DDQ as an oxidant.
- 10. Crown ethers are useful in organic synthesis. Explain why and illustrate with examples.
- 11. What would be the product in the following reaction?

12. Li and Na borohydrides are useful in synthesis. Compare their selectivity as reductants.

- 13. S and Se find use in natural product structure elucidation. With an example show how.
- 14. How can the number of active hydrogens in natural products estimated chemically?

 $(14 \times 1 = 14 \text{ weight})$

Part B

Answer any seven questions. Each question carries weightage 2.

- 15. Describe the formation stability and reactivity of carbon free radicals.
- 16. Elucidate the selection rules for 1,3 and 1,5 sigmatropic rearrangements.
- Write the mechanism of Wagner-Meerwin and pinacole-pinacolone rearrangements.
- 18. Discuss the ORD curves of decalones and show how ORD is useful in elucidating structural asp
- 19. With examples, show why IR spectroscopy is a simple tool for the detection of functional grounds.
- 20. What are the major rearrangement-cum-fission reactions seen in EI mass spectroscopy?
- 21. Write examples for the use of (i) Me₃SnH and (ii) Wilkinson catalyst in synthesis.
- 22. Write a brief note photochemical rearrangements.
- 23. How was atropine structure established?
- 24. Write notes on Hoffman and Emde degradations of alkaloids.

 $(7 \times 2 = 14 \text{ weight})$

Part C

Answer any **two** questions.

Each question carries weightage 4.

- 25. Elucidate the selection rules for thermal and photochemical 4n and 4n+2 electrocyclisations.
- 26. Describe the mechanism and application of (i) Peterson reaction; (ii) Favorski rearrangem (iii) Heck reaction and; (iv) Bayer Villiger rearrangement.
- 27. (a) Explain how chemical shift values aid in the structure determination of organic compou
 - (b) Deduce the structure of the compound C_8H_8O which shows : IR : 3010, 2950w, 28 1695, 1510, 1005, 750, 690 cm⁻¹ : ¹H NMR (400 MHz) δ : 3.66, singlet (2H) ; 7.06, multi (3H) ; 7.14, multiplet, (2H) ; 9.71, singlet (1H). Mass spectrum shows an intense peal m/z 91 and 65. ¹³C NMR has peaks at 198, 136, 130, 124, 122 and 50 ppm.
- 28. Write notes on (i) Patterno Buchi reaction and ; (ii) di-pi methane rearrangement ; (iii) Bareaction and (iv) Jablonski diagram.

 $(2 \times 4 = 8 \text{ weight})$