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# SECOND SEMESTER M.Sc. DEGREE EXAMINATION, JUNE 2015

(CUCSS)

Chemistry

### CH 2C 06—ORGANIC CHEMISTRY—II

(2010 Admissions)

me: Three Hours

Maximum: 36 Weightage

#### Part A

Answer all questions.

Each question has weightage 1.

1. How can the following compound be obtained by an aromatic nucleophilic substitution?

$$\bigcap_{H} \bigcap_{O_2N}^{NO_2}$$

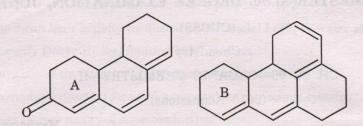
- 2. What product(s) would arise when 3-bromotoluene is reacted with sodamide in liquid ammonia?
- 3. Carbene reactivity can be used to make the following compound from cycloheptene. Explain how.



- 4. Photochlorination of alkanes preferably introduces chlorine at a secondary carbon. Explain, why.
- 5. Suggest a Pd based method to prepare the compound below.

Turn over

6. Calculate the  $\lambda_{max}^{\phantom{max}Ab}$  in the UV spectrum of the following compounds :



- 7. Predict the C = O stretching band position in cm<sup>-1</sup> in the IR spectra of Ph-CO-Me and PhO-CO-M
- 8. How can one detect nitro and cyano groups by IR?
- 9. What reactions do peroxy acids undergo with (i) ketones and (ii) alkenes?
- 10. The hydrogen H\* in benzaldehyde A cannot be removed by a base whereas that in its derivati B can be. Why?

$$0 \longrightarrow \begin{pmatrix} H^* \\ A \\ Ph \end{pmatrix} \qquad \begin{pmatrix} S \\ Ph \end{pmatrix} B$$

11. Identify the product in the reaction below.

- 12. Destructive distillation of a natural product with selenium gave phenanthrene. What conclusive regarding its structure can be drawn on this basis?
- 13. What is Emde degradation?
- 14. What are the use of Me<sub>3</sub>SiCl and DDQ?

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

## Part B

Answer any seven questions. Each question has weightage 2.

- 15. Explain Bredt's rule.
- 16. What is the mechanism of (i) Sommlet Hauser; and (ii) Cope rearrangements?

- 17. Discuss the Woodward and Prevost methods of alkene hydroxylation using cyclohexene as an example.
- 18. How does solvent polarity affect the various UV absorption bands of ketones? Explain with an energy diagram.
- 19. Discuss how C = O stretching IR bands are affected by (i) hydrogen bonding; and (ii) bond order.
- 20. What chemical methods are available to estimate the number of (i) methoxy MeO; and (ii) acetoxy Me-CO-O groups in natural products?
- 21. Explain how ester and amide bonds can be formed by the use of dicyclohexyl carbodimide.
- 22. The photochemical reaction of 3, 3-dimethylpenta-1, 4-diene leads to a cyclopropane derivative. Which is it? How does it form? What is the mechanism?
- 23. How can the structure of flavones be established?
- 24. Predict the chemical shift  $\delta$  values of (i) the Me hydrogens in <sup>1</sup>H NMR and (ii) the methyl carbons in <sup>13</sup>C NMR spectra of p-Me-CO-C<sub>6</sub>H<sub>4</sub>-OMe.

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

#### Part C

### Answer any **two** questions. Each question has weightage 4.

- 25. Establish selection rules to predict the stereochemical course of four and six electron electrocyclic ring closing—opening reactions.
- 26. Explain the mechanism of Barton reaction and Patterno-Buchi reaction.
- 27. Heck reaction and Suzuki coupling are valuable C-C bond forming reactions. Establish this with suitable examples. Write the reaction conditions, the reagents required and the mechanism of these reactions.
- 28. (i) Discuss the use of coupling constant J values in Hz in obtaining stereochemical information based on <sup>1</sup>H NMR spectra.
  - (ii) Compound  $C_8H_{10}O$  exhibits the following spectral data:  $^1H$  NMR:  $\delta$ : 2.4, singlet (3H); 3.8, singlet (3H); 6.7, double doublet (2H) and 7.00, double doublet (2H).  $^{13}C$  NMR  $\delta$ : 21 (q) and 57 (q) in addition to peaks above  $\delta$  100 ppm. Deduce its structure.

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