C 83713

SECOND SEMESTER M.Sc. DEGREE EXAMINATION, JUNE 2015

(CUCSS)

Chemistry

CH 2C 06—ORGANIC CHEMISTRY—II
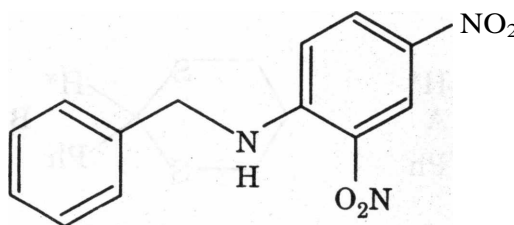
(2010 Admissions)

Time : 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 ?

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.
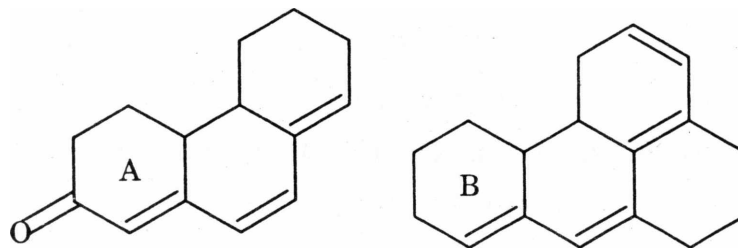

4. Photochlorination of alkanes preferably introduces chlorine at a secondary carbon. Explain, why.

5. Suggest a Pd based method to prepare the compound below.
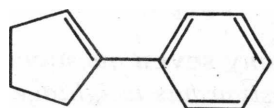

Turn over

6. Calculate the λ_{max}^{Ab} in the UV spectrum of the following compounds :

7. Predict the C = 0 stretching band position in cm⁻ in the IR spectra of Ph-CO-Me and PhO-CO-Me.

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 derivative B can be. Why ?
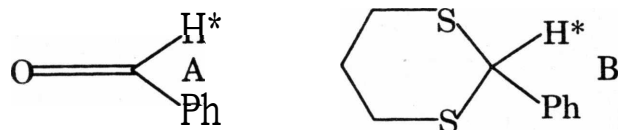
11. Identify the product in the reaction below.
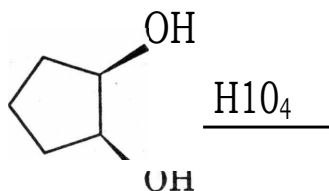
12. Destructive distillation of a natural product with selenium gave phenanthrene. What conclusion regarding its structure can be drawn on this basis?

13. What is Emde degradation ?

14. What are the use of Me_3SiCl and DDQ ?

(14 x 1 = 14 weightage)

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-0 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 5 values of **(i)** the Me hydrogens in ^{1}H **NMR** and (ii) the methyl carbons in ^{13}C **NMR** spectra of p–Me–CO–C$_0$H$_4$–OMe.

(7 **x** 2 = 14 **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 ^{1}H **NMR** spectra.

(ii) Compound C$_8$l1$_{10}$0 exhibits the following spectral data : ^{1}H **NMR :** 5 : 2.4, singlet (3H) ; 3.8, singlet (3H) ; 6.7, double doublet (2H) and 7.00, double doublet (2H). ^{13}C **NMR** 5 : 21 (q) and 57 (q) in addition to peaks above 5 100 ppm. Deduce its structure.

(2 **x** 4 = 8 **weightage**)