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Name.....................................

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SECOND SEMESTER M.Sc. DEGREE EXAMINATION, JUNE 2015

(CUCSS)

Chemistry

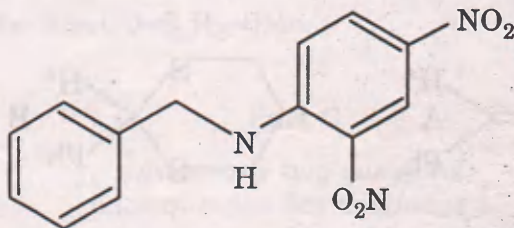## CH 2C 06—ORGANIC CHEMISTRY—II

(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.
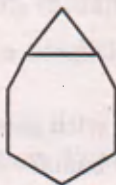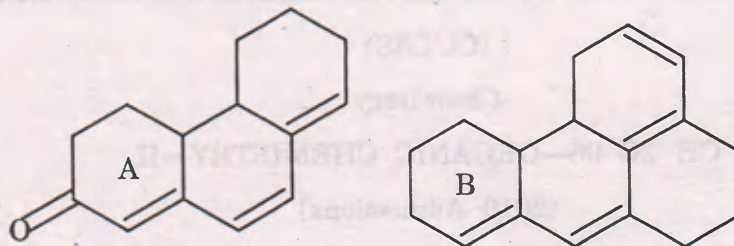

4. Photochlorination of alkanes preferably introduces chlorine at a secondary carbon. Explain, why.

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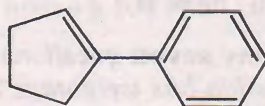

Turn over

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

7. Predict the C = O stretching band position in cm^{-1} 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.
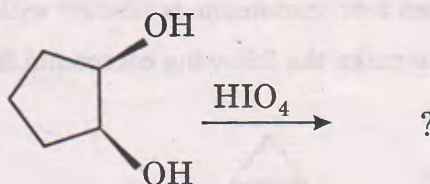
12. Destructive distillation of a natural product with selenium gave phenanthrene. What conclusion regarding its structure can be drawn on this basis?

13. What is Emde degradation ?

14. What are the use of Me$_3$SiCl and DDQ ?

(14 × 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-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 δ 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$_6$H$_4$–OMe.

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

(2 × 4 = 8 weightage)