



Reg. No. :

Name :

Second Semester M.Sc. Degree Examination, August 2016

Branch : Chemistry

CH/CL/CA/CM 222 : ORGANIC CHEMISTRY – II

(2013 Admission Onwards)

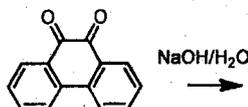
Time : 3 Hours

Max. Marks : 75

SECTION – A

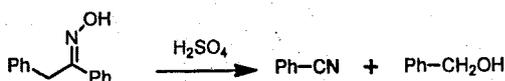
Answer **any two** sub-questions among (a – c) from **each** question. **Each** sub-question carries **2** marks.

1. a) Predict the product/s in the following reaction.



b) Write down the structure of the product obtained in Baeyer-Villiger oxidation of cyclohexylmethyl ketone. Explain.

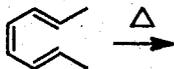
c) Suggest a plausible mechanism for the following reaction.



2. a) Cyclooctatetraene despite having alternate single and double bonds, do not show the extended overlap of *p* orbitals and delocalization as it is tub shaped. Explain.

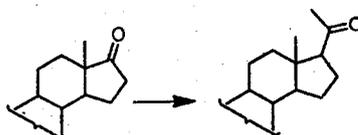
b) What do you mean by the term antiaromaticity? Give an example each of an aromatic and a nonaromatic [10]-annulene.

c) Predict the structure of the product with stereochemical details in the following reaction.





3. a) Norbornene gives an oxetane on photolysis with benzophenone, while it undergoes dimerisation in acetone. Explain.
 b) Give a synthetic application of Barton reaction.
 c) What are the common reactions of singlet oxygen with 1,3-dienes?
4. a) What are secondary metabolites? Give examples.
 b) How will you effect the following conversion?

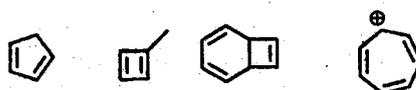


- c) What is Emde degradation? Illustrate with a suitable example.
5. a) The pK_a of *p*-methoxybenzoic acid is 4.49 and that of benzoic acid is 4.19. Calculate σ' for *p*-OMe.
 b) What is primary kinetic isotope effect? How does it affect the rate of the reaction?
 c) Give an example for impact of ortho effect on reactions. **(2×10=20 Marks)**

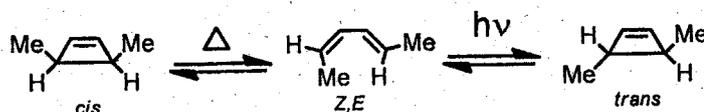
SECTION - B

Answer either (a) or (b) of each question. Each question carries 5 marks.

6. a) Discuss Wagner Meerwein and Pinnacol rearrangements and explain the effect of migrative aptitude on product formation.
 b) a) What is Demjanov rearrangement? Give a an application of this reaction in ring expansion.
 b) Show that Sommet-Hauser rearrangement involves a 2,3-sigmatropic rearrangement step.
7. a) Classify the following compounds into aromatic, non-aromatic and antiaromatic. Justify.



- b) Rationalise the modes of ring opening and ring closure in the following reactions:



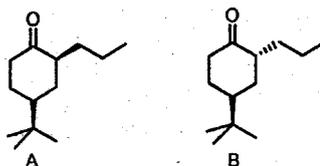


8. a) Write a brief note on the photochemical reactions of enes and dienes.
b) Discuss the photoreactions of Vitamin – D.
9. a) Explain any two reactions employed in the determination of carbon skeleton of alkaloids.
b) Discuss the structural elucidation of atropine (synthesis NOT required).
10. a) Give a brief account of kinetic and thermodynamic control of reactions.
b) Discuss the Hammett equation and its applications. **(5×5=25 Marks)**

SECTION – C

Answer any three questions. Each question carries 10 marks.

11. Write a detailed account on the rearrangements involving an electron deficient nitrogen.
12. a) Show that 2+2 additions are photochemically allowed and thermally forbidden.
b) Write a brief note on di- π -methane rearrangement.
13. On photolysis, compound A undergoes primarily Norrish II chemistry, but B undergoes primarily Norrish I chemistry.



- a) Draw the expected major products for both Norrish Type I and Norrish Type II reactions of A.
- b) Draw the expected major products for both Norrish Type I and Norrish Type II reactions of B.
- c) Explain why A undergoes primarily Norrish II and why B undergoes primarily Norrish I chemistry.
14. Discuss the biosynthesis of lanostetol starting from squalene.
15. Write brief notes on the following :
- a) Hammond postulate.
b) Principle of microscopic reversibility.
c) Isotope labelling.
d) Crossover experiments. **(3×10=30 Marks)**