



Reg. No. :

Name :

Second Semester M.Sc. Degree Examination, August 2016
Branch : Chemistry
CH/CL/CA/CM 222 : ORGANIC CHEMISTRY - II
(2013 Admission Onwards)

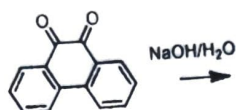
Time : 3 Hours

Max. Marks : 75

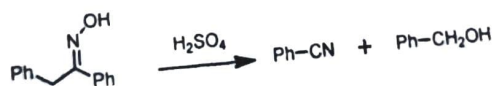
SECTION - A

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

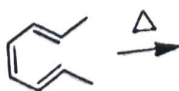
1. a) Predict the product/s in the following reaction.



- 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.

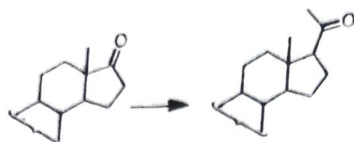


2. a) Cyclooctatetraene despite having alternate single and double bonds, do not show the extended overlap of *p* orbitals and delocalization as it is tub shaped. Explain.
- b) What do you mean by the term antiaromaticity? Give an example each of an aromatic and a nonaromatic [10]-annulene.
- c) Predict the structure of the product with stereochemical details in the following reaction.



P.T.O.

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?

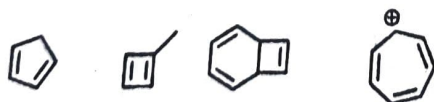


- c) What is Emde degradation? Illustrate with a suitable example.
5. a) The pK_a of *p*-methoxybenzoic acid is 4.49 and that of benzoic acid is 4.19. Calculate σ for *p*-OMe.
 b) What is primary kinetic isotope effect? How does it affect the rate of the reaction?
 c) Give an example for impact of ortho effect on reactions. (2x10=20 Marks)

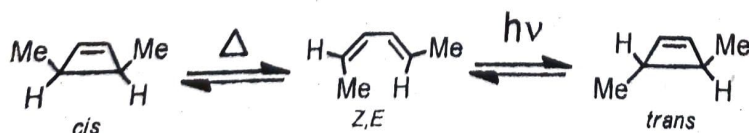
SECTION - B

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:



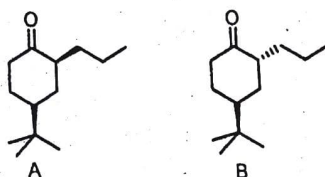


- 8. a) Write a brief note on the photochemical reactions of enes and dienes.
b) Discuss the photoreactions of Vitamin - D.
- 9. a) Explain any two reactions employed in the determination of carbon skeleton of alkaloids.
b) Discuss the structural elucidation of atropine (synthesis NOT required).
- 10. 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)
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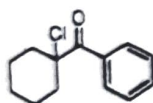
Max. Marks : 75

Time : 3 Hours

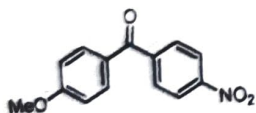
SECTION - A

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

1. a) Illustrate the mechanism of dienone-phenol rearrangement with a suitable example.
- b) The following compound on treatment with NaOH followed by neutralization gave a monocarboxylic acid which did not contain chlorine. Predict the structure of the product.



- c) Write down the structure of the major product obtained, when the following compound is treated with *m*-CPBA.



2. a) The pKa of cyclopentadiene is 15, which is extraordinary for a hydrogen that is bonded to an sp³ carbon. How will you account for this observation?
- b) Give one example each for a 1,3-dipolar cycloaddition and an ene-reaction.
- c) What are mesoionic compounds? Give examples.
3. a) Explain the role of the dye usually used in photochemical generation of singlet oxygen.
- b) Give two photoreactions of dienes.
- c) Illustrate Barton reaction with a suitable example.

P.T.O.

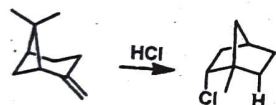
4. a) Explain the method of isolation of alkaloids from plant products.
 b) What are the functions of secondary metabolites in plants?
 c) Sterols are nor-triterpenoids. Explain.
5. a) What is F strain? Give an example.
 b) State Hammett equation and explain the terms involved.
 c) Give an example to illustrate the importance of steric effects in reactions.

(2×10=20 Mar

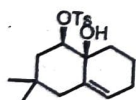
SECTION - B

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

6. a) Suggest a plausible mechanism for the following reaction. Explain.



- b) The following compound undergoes $\text{BF}_3 \cdot \text{OEt}_2$ catalysed rearrangement. Predict the major product. Indicate mechanism. Justify.



7. a) Illustrate the stereochemical outcome of electrocyclic reactions using appropriate examples.
 b) Predict whether the following compounds are aromatic, non-aromatic or antiaromatic. Justify the answer



8. a) Discuss the photochemistry of acyclic ketones.
 b) Write a detailed note on di- π -methane rearrangement.

9. a) Discuss the mevalonic acid pathway of biosynthesis of terpenes in plants.
b) Outline the synthesis of testosterone.
10. a) What is bond angle strain? Discuss how it affects the rate of reactions.
b) Write a detailed note on phase transfer catalysis.

(5×5=25 Marks)

SECTION - C

Answer any three questions. Each question carries 10 marks.

11. Give a detailed account of rearrangements involving electron deficient carbon atoms.
12. Discuss the FO analysis of electrocyclic reactions of 4 electron and 6 electron systems.
13. Write a note on :
a) Photoreactions of carbonyl compounds
b) Photochemistry of vision.
14. a) Outline the synthesis of progesterone.
b) What are the general chemical methods used for the structural elucidation of alkaloids?
15. Write a note on the common methods of determining organic reaction mechanisms.

(3×10=30 Marks)



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E – 5203

Reg. No. :

Name :

Second Semester M.Sc. Degree Examination, October 2018
Branch : CHEMISTRY
CH/CL/CA/CM 222 : Organic Chemistry – II
(2013-2015 Admissions)

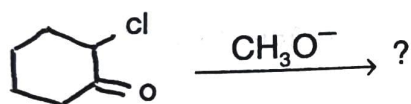
Time : 3 Hours

Max. Marks : 75

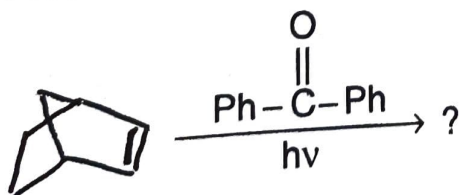
SECTION – A

Answer any two sub-questions among a-c from each question.
Each sub-question carries 2 marks :

1. a) What is Dienone-phenol rearrangement ? How is it carried out ?
b) Outline the mechanism of Curtius rearrangement.
c) Predict the product in the following reaction. Give mechanism.



2. a) What are non-benzenoid aromatic compounds ? Give suitable examples.
b) Write a brief note on mesoionic compounds.
c) What is oxy-Cope rearrangement ? Mention its importance.
3. a) Benzophenone is a very good triplet sensitizer. Explain how.
b) Predict the products when singlet oxygen reacts with :
 - i) anthracene
 - ii) furan.
- c) Predict the product in the following reaction. Outline the mechanism.



P.T.O.



4. a) What are monoterpenes ? Give any two examples.
b) What are alkaloids ? Explain.
c) Explain the Von Braun method of degradation used in structure elucidation.
5. a) What is meant by kinetic control of reactions ?
b) Explain the principle of microscopic reversibility.
c) Explain the term 'Hammond postulate'.

(10×2=20 Marks)

SECTION - B

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

6. a) Write a brief note on hydroperoxide and borane rearrangements.
b) Outline the mechanisms of the following rearrangements :
i) Von-Richter
ii) Orton.
7. a) What is retro Diels-Alder reaction ? Discuss its synthetic utility.
b) Write briefly on :
i) 1,3-dipolar cycloadditions
ii) fluxional molecules.
8. a) Write briefly on :
i) sensitization and quenching
ii) photochemistry of vision.
b) Draw and explain Jablonski diagram.
9. a) Discuss the methods available for the extraction of chemical constituents in plants.
b) Outline the synthesis of progesterone. (Specify reagents and conditions in each step).
10. a) What are phase transfer catalysts ? Comment on their applications.
b) Comment on secondary kinetic isotopic effect.

(5×5=25 Marks)



SECTION - C

Answer any three questions. Each question carries 10 marks :

11. What is Hammett equation ? Give the quantitative treatment. Comment on the application of Hammett equation.
12. Discuss the mechanism with evidences in favour of the following rearrangements :
 - i) Wolf
 - ii) Beckmann
 - iii) Wagner-Meerwein
 - iv) Hofmann-Martius.
13. Discuss the photoreactions of carbonyl compounds, enes and dienes.
14. How is correlation diagram approach useful in analysing electrocyclic conversion of butadiene to cyclobutene and hexatriene to cyclohexadiene ? Explain.
15. Describe the structure elucidation of β -carotene.

(3x10=30 Marks)



Q. No. :

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Branch : CHEMISTRY

CH/CL/CA/CM 222 : Organic Chemistry - II
(2016 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) What is von-Richter rearrangement ? How is it carried out ?
b) Outline the mechanism of Smiles rearrangement.
c) Mention the applications of Stevens rearrangement.
2. a) What are cyclic carbocations ? Give suitable examples.
b) Write a brief note on retro Diels-Alder reactions.
c) How do you synthesise heterocyclic compounds using 1, 3-dipolar cycloadditions ?
3. a) Explain the terms 'F strain' and 'bond angle strain'.
b) What is Taft equation ? Explain.
c) Discuss the term 'special salt effects' in nucleophilic substitution reactions.
4. a) Comment on the effect of benzophenone in the photochemical reactions of butadiene. Predict the product/s formed.
b) Distinguish between fluorescence and chemiluminescence.
c) Outline the mechanism of photo Fries rearrangement.
5. a) Outline the Emde method of degradation used in structure determination.
b) Explain the method of extraction of alkaloids using supercritical fluids.
c) Describe the uses of colour reactions and spray reagents for the characterisation of alkaloids and flavanoids.

(10x2=20 Marks)

SECTION - B

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

6. a) What are phase transfer catalysts ? Discuss the applications.
b) Describe the solvent polarity parameters Y, Z and E. Mention their applications.



7. a) Discuss the mechanism and importance of Fischer – Hepp rearrangement in organic chemistry.
- b) Outline the mechanism of the following rearrangements :
 - i) Bamberger
 - ii) Dienone-phenol.
8. a) Write briefly on :
 - i) Intramolecular Diels-Alder reactions
 - ii) Chelotropic reactions.
- b) Explain the terms aromaticity, antiaromaticity and homoaromaticity with suitable examples.
9. a) What is Jablonski diagram ? Explain.
- b) Write briefly on photosynthesis.
10. a) Describe the biosynthesis of sterols from squalene.
- b) Outline the synthesis of quercetin.

(5×5=25 Marks)

SECTION – C

Answer **any three** questions. **Each** question carries **10** marks.

11. Explain Hammett equation. Comment on the application of Hammett equation.
12. Outline the mechanism of the following rearrangements :
 - i) Benzilic acid
 - ii) Beckmann
 - iii) Wagner-Meerwein
 - iv) Demjanov.
13. i) Describe the Norrish type I and II reaction of Ketones.
- ii) Explain the mechanism of Paterno-Buchi reaction.
14. How is F.O. approach useful in analysing electrocyclic and cycloaddition reactions ? Explain.
15. Describe the structure elucidation of atropine.

(3×10=30 Marks)