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SECOND SEMESTER M.Sc. DEGREE EXAMINATION, MAY-2017

(Regular/Supplementary/Improvement)

(CUCSS - PG)

CC15PCH2C07- REACTION MECHANISM IN ORGANIC CHEMISTRY

(Chemistry)

(2015 Admission Onwards)

Time: Three Hours

Maximum: 36 Weightage

Section A

(Answer all questions. Each question carries 1 weightage)

1. Write the stepwise mechanism of the reaction and give its nomenclature

$$\begin{array}{c|c} & & & \\ &$$

- 2. Explain the methods of detection of carbenes.
- 3. Give the structures of A and B

4. Write the structure of the product in the following transformation

5. How are the following terpenes classified? How many isoprene units do they contain?

6. Give the product of the following reaction and state the name reaction involved

7. Write the product and its stereochemistry for the reaction

8. Give an example of Norrish Type I and II Cleavage reactions

9. Identify the products and explain the selectivity in their formation

- 10. How will you recognize whether an aromatic nucleophilic substitution follow a SNAr or benzyne mechanism?
- 11. What structural changes occur to a molecule that undergoes Ritter reaction? State the reaction conditions.
- 12. What is meant by SNⁱ mechanism?

 $(12 \times 1 = 12 \text{ weightage})$

Section B

(Answer any eight questions. Each question carries 2 weightage)

13. What is Simmon-Smith reaction? Write the mechanism showing the role of the metal ion. Write the product structure (with the stereochemistry) when the following compounds reacts with Zn/Cu couple and CH₂I₂.

14. Draw the mechanism and explain the stereochemistry of the pericyclic reactions.

a)
$$1.Ph \longrightarrow N^+ O^{\text{H}_3\text{C}} \longrightarrow Ph$$
 $CH_2 \longrightarrow Ph$ CH_2

15. Complete the equations and write the mechanisms of each step of the reactions.

a)
$$C_2H_5ONa$$
 ? C_2H_5OH ?

- 16 Explain the mechanism
 - a. Pyrolytic elimination of esters of acetic acid
 - b. Baston reaction

17 Account for the contrasting results in the following reactions

a)
$$\begin{array}{c} \text{OH} \\ \text{1. SO}_3/\text{Oleum} \\ \text{1hr, 160 °C} \\ \text{2. NaOH/H}_2\text{O} \end{array} ? \qquad \text{b)} \\ \begin{array}{c} \text{H}_3\text{C} \\ \text{CH}_3 \\ \text{H}_2\text{SO}_4 \end{array} ? \\ \text{CH}_3 \\ \text{CH}_3$$

- 19 What is di-pi methane rearrangement? Give two mechanisms proposed for this reaction. Give two examples to demonstrate the stereo-specificity of the reaction.
- 20 Which name reactions are involved and what reaction condition is needed for the following conversions? Draw the mechanisms of these steps.

- 21 Discuss aliphatic electrophilic substitution mechanisms and their stereochemistry with one example each. How do the mechanisms depend on the substrate structure, leaving group and solvents
- 22 Provide a synthesis that will selectively convert 1,3,5trimethoxy benzene to 2,6 dibromo1,3,5 trimethoxy benzene. Show all of the key intermediates and furnish all of the important reagents.
- 23 Provide the best mechanism showing all the arrow pushing

24 How is testosterone synthesized? Give a detailed account.

 $(8 \times 2 = 16 \text{ weightage})$

Section C

(Answer any two questions. Each question carries 4 weightage)

25 a) Identify structures of A, B and C and write the mechanisms of each of the steps. By FMO method, establish whether the conversion of B to C is thermally allowed.

$$\frac{\text{CH}_2\text{N}_2}{\text{Ether}} \quad \text{A} \qquad \frac{\text{hv}}{\text{B}} \qquad \frac{\text{hv}}{[2+2] \text{cycloaddition}} \quad \text{C}$$

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(Turn Over)

- b) Using FMO method, show that [4+4] cycloaddition of butadiene is forbidden under thermal condition.
- c) Explain why endo products are preferred in Dieles-Alder reaction. Also give the method of predicting the structure of the diastereoisomerformed in this reaction.

- 26 a) Write notes on 1)Jablonskidiagrm2) photochemical polymerization and degradation of polymers
 - b) Write down the mechanism and describe the stereochemistry of each product.

- 27 Give total synthesis of reserpine.
- 28 a) Present a brief account of how aliphatic nucleophilic substitution mechanisms are affected by the structure of the substrate, nature of nucleophile and the strength of bonding of a leaving group.
 - b) What is the white solid obtained when aniline is added to a brominating mixture in an aqueous acidic medium? How is the amino group removed from this molecule? Give a method of synthesis of parabromoaniline. (2 \times 4 = 8 weightage)

Provide the best mechanism showing all the arrow pushing of

 $(8 \times 2 = 16 \text{ weightage})$

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(Answer any new questions teach question carries a weightage)

a) Identify structures of A, B and C and write the mechanisms of each of the steps. By FMC
method, retabilish whether the conversion of B to C is thermally allowed.

CH₂N₂ A hv B hv C (2 + 2) cyclonddition