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(**Pages : 2**)

Name..... Reg. No.....

9860

SECOND SEMESTER M.Sc. DEGREE (REGULAR/SUPPLEMENTARY) EXAMINATION, APRIL 2021

(CBCSS)

Chemistry

CHE 2C 07-REACTION MECHANISM IN ORGANIC CHEMISTRY

(2019 Admissions)

Time : Three Hours

0260

Maximum : 30 Weightage

General Instructions

- 1. In cases where choices are provided, students can attend **all** questions in each section.
- 2. The minimum number of questions to be attended from the Section/Part shall remain the same.
- 3. There will be an overall ceiling for each Section / Part that is equivalent to the maximum weightage of the Section / Part.

Section A

Answer any **eight** questions. Each question carries a weightage of 1.

- 1. What are ambident nucleophiles ? Explain with examples.
- 2. In aromatic electrophilic substitution reactions, each hydrogen atom of donor-substituted aromatic compound should be substituted faster than a H atom in benzene and each hydrogen atom of acceptor-substituted aromatic compound should be substituted more slowly than a H atom in benzene. Explain.
- 3. Explain the mechanism of Hofmann elimination, highlighting the stereochemical relationship of the substrate and product.
- 4. Arrange the following in order of stability : CF_2 , : CCl_2 , : CBr_2 and CH_2 . Justify.
- 5. Indicate the mechanism of Dieckmann condensation reaction. Comment on the synthetic utility of this reaction.
- 6. Predict the product in the CN⁻ catalyzed condensation of benzaldehyde and p-dimethylaminobenzaldehyde. Indicate mechanism involved.
- 7. Given the triplet energies of norbornene (70 78), benzophenone (70) and acetophenone (78), predict the products obtained when each of the ketone is irradiated with norbornene.



Turn over

- 8. Write down the mechanism of di-pi methane rearrangement.
- 9. Illustrate Paterno-Büchi reaction with a suitable example.
- 10. Cholesterol undergoes oxidation of side chain under various conditions. Give the structure of two major products formed in these reactions.

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 $(8 \times 1 = 8 \text{ weightage})$

Section B

Answer any **six** questions. Each question carries a weightage of 2.

- 11. Explain the SNAr and SRN1 mechanisms of aromatic nucleophilic substitution with a suitable examples.
- 12. Explain the ion-pair mechanism of nucleophilic aliphatic substitution. Comment on the stereochemical outcome in such reactions.
- 13. Substitution and elimination reactions are often competing reactions. Why? What are the precautions to be taken to get the desired products?
- 14. Briefly discuss the main pathways of generation of carbanions. Comment on their structure and stability.
- 15. Explain Mannich reaction with an appropriate example.
- 16. Predict whether the thermal ring closure of a compound with three conjugated pi-bonds is conrotatory or disrotatory. Explain.
- 17. Explain the following terms : i) photosensitization ; ii) quenching ; and iii) photoenolization.
- 18. Write a brief note on general structure and properties of anthocyanins.

 $(6 \times 2 = 12 \text{ weightage})$

Section C

Answer any **two** questions. Each question carries a weightage of 5.

- 19. Discuss the mechanisms of electrophilic aromatic substitution with special reference to substituent effect on reactivity and orientation in mono and disubstituted benzene rings.
- 20. Discuss the major acid and base catalyzed mechanisms of ester hydrolysis.
- 21. Give one example each of : i) thermally allowed cycloaddition reaction ; and ii) photochemically allowed electrocyclic reaction. Justify the answer by FMO method.
- 22. Discuss the salient features of total synthesis of longifolene.



 $(2 \times 5 = 10 \text{ weightage})$