

C 83028

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Name.....

Reg. No.....

SECOND SEMESTER M.A./M.Sc./M.Com. DEGREE EXAMINATION, JUNE 2020

(CBCSS)

Chemistry

CHE 2C 07—REACTION MECHANISM IN ORGANIC CHEMISTRY

(2019 Admissions)

Time : Three Hours

Maximum : 30 Weightage

Section A

Answer any eight questions.

Each question carries a weightage of 1.

1. How does α - and β -substitution affect the reactivity of the substrate and mechanism of the reaction in aliphatic nucleophilic substitutions ?
2. Give an example of an aliphatic electrophilic substitution involving SE_i mechanism.
3. Write down an example of a nucleophilic addition reaction and indicate how the substituents influence the orientation of the incoming group.
4. What are syn eliminations ? Illustrate with a suitable example.
5. Give any two general methods of preparation of benzyne in the context of synthesis.
6. Outline a simple synthesis of cyclopentanone starting from hexanedioic acid.
7. What is a [1, 3]sigmatropic rearrangement ? Illustrate with a suitable example.
8. Illustrate the photochemical Norrish type-II cleavage of an appropriate carbonyl compound.
9. Write down the general method of isolation of alkaloids from plant products.
10. With a suitable example explain a degradative reaction used in the structural elucidation of natural products.

(8 × 1 = 8 weightage)

Section B

Answer any six questions.

Each question carries a weightage of 2.

11. Explain the benzyne mechanism of aromatic nucleophilic substitution. Predict the products obtained in the reaction of o-, p- and m-chlorotoluene with $\text{NaNH}_2/\text{NH}_3$. Justify.
12. Explain major factors affecting the stability and reactivity of carbon radicals.

Turn over

13. Predict the major product obtained in the sodium catalyzed mixed condensation of ethyl benzoate and ethyl acetate. Indicate the mechanism.
14. Write down the mechanism and its evidence for $A_{Ac}2$ ester hydrolysis.
15. What is the structure of the product obtained by the base catalysed condensation of acetone and benzaldehyde? What by-product/s might be formed if an excess of aldehyde is employed?
16. For a [2+2] cycloaddition, thermal reaction is symmetry forbidden while photochemical reaction is symmetry allowed. Explain.
17. Give a brief account of the photoprocesses involving excited alkenes and alkynes, with suitable examples.
18. Indicate any strategy used to make the tricyclic ring system in longifolene synthesis.

(6 × 2 = 12 weightage)

Section C

Answer any two questions.

Each question carries a weightage of 5.

19. Discuss the mechanistic and stereochemical aspects of E1, E1cB and E2 eliminations.
20. A thermal electrocyclic reaction involving $[4n+2]$ π -electrons proceeds with disrotatory motion, and photochemical reaction proceeds with conrotatory motion. Explain using Woodward-Hoffmann rules. Verify by correlation method.
21. Draw the Jablonski diagram and discuss the major unimolecular photophysical processes available to a molecule. Indicate rates and times (approximate) of the events involved.
22. Discuss the structural elucidation of atropine.

(2 × 5 = 10 weightage)