

SECOND SEMESTER M.Sc. DEGREE EXAMINATION, APRIL 2024
(Regular/Improvement/Supplementary)

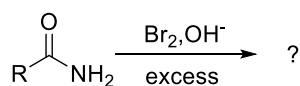
CHEMISTRY
FCHE2C07: REACTION MECHANISM IN ORGANIC CHEMISTRY

Time: 3 Hours

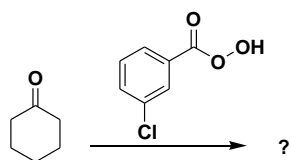
Maximum Weightage: 30

Section A: Short answer questions. Answer any *eight* questions. Each carries 1 weightage.

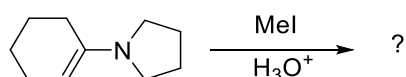
- The rate of elimination reaction of isopropyl bromide is greater in ^tBuOK/DMSO than that in KOH/EtOH. Justify this statement.
- Is it possible to isolate carbocations? Substantiate.
- What are nitrenes? Give any one method of its generation.
- Give any two factors affecting the carbocation stability.
- Enamines from ammonia and primary amines are found to be unstable and are difficult to isolate. Suggest any other method to synthesize them.
- What is Barton reaction? Give an example.
- Both PhCH₂COCH₂Cl and PhCHClCOCH₃ form PhCH₂CH₂COOH when reacted with OH⁻ followed by acidification. Give reason.
- What is dienone-phenol rearrangement reaction? Give an example.
- Complete the following reaction with mechanism.



- Complete the following reaction with mechanism.



- What is Fries rearrangement reaction? Give an example.
- Complete the following reaction with mechanism.



(8 × 1 = 8 weightage)

Section B: Short essay questions. Answer any *four* questions. Each carries 3 weightage.

13. Discuss the ion-pair mechanistic approach of S_N1 reactions.
14. The ratio of the rates of solvolysis of ethyl tosylate and phenylethyl tosylate in CF₃COOH is about 1:3040. Account for the fact.
15. State and illustrate: a) Saytzev's rule; b) Bredt's rule.
16. What do you mean by non-classical carbocations? In what aspect they differ from classical carbocations? Give an example of any non-classical carbocation.
17. What is an intramolecular aldol condensation? Explain by giving examples its utility in synthesis.
18. Discuss Hoffmann-Loeffler-Fretag reaction with example.
19. The Wittig reaction is stereospecific, but not regiospecific. Explain.

(4 × 3 = 12 weightage)

Section C: Essay questions. Answer any *two* questions. Each carries 5 weightage.

20. Discuss the mechanistic and stereochemical aspects of E1, E1cB and E2 elimination reactions.
21. Explain the following reactions with suitable mechanism.
 - a) Perkin reaction
 - b) Knoevenagel reaction
 - c) Reformatsky reaction
 - d) Stobbe condensation reaction.
22. a) What are carbenes? Add a note on the singlet and triplet carbenes and their relative stability. Cite examples of carbene that exist as a stable compound.

b) *Cis*-2-butene on photo-irradiation in presence of diazomethane yields *cis*-1,2-dimethyl cyclopropane stereospecifically. Explain the course of the reaction in presence of large excess of perfluoropropane.
23. Write notes on the following reactions with mechanism.
 - a) Beckmann rearrangement reaction
 - b) Benzidine rearrangement reaction
 - c) Sommelet-Hauser rearrangement reaction
 - d) Pinacol-Pinacolone rearrangement reaction

(2 × 5 = 10 weightage)