Reg. No.					



CHH/ACH/OCH/CAH 452

Second Semester M.Sc. Degree Examination, September/October 2022 CHEMISTRY/APPLIED CHEMISTRY/ORGANIC CHEMISTRY/ANALYTICAL CHEMISTRY

Advanced Organic Chemistry (CBCS: 2016-17 Syllabus) (Freshers and Repeaters)

Time: 3 Hours Max. Marks: 70

Note: i) Answer **all** sub-questions from Part – **A** and **any four** questions from Part – **B**.

ii) Figures to the **right** indicate marks.

PART - A

Answer all the following sub-questions.

 $(2 \times 9 = 18)$

- 1. a) The –NH₂ group is o, p-directing group but it gives meta-substitution during nitration. Comment on this.
 - b) What is $S_{\rm E}$ i reaction? Outline the mechanism taking suitable example.
 - c) Outline the mechanism with comment.

d) Predict the product and give reasons for its formation.

e) Complete the following reaction with necessary comments.

f) The migration of phenyl group in radical A is faster than in B. Offer explanations.

- g) Outline the mechanism of acid catalyzed transesterification of methyl acetate with ethanol.
- h) Predict the major product formed in the following.

i) Predict the product(s) and indicate the stereochemistry for the following reaction.

$$+Br-Br \xrightarrow{MeOH} ?$$

- 2. a) Explain aromatic electrophilic substitution reaction taking suitable example.
 - b) Predict the products and offer an explanation for their formation.

$$\begin{array}{c}
\text{OH} \\
\hline
\Delta
\end{array}$$
?

- c) Discuss the mechanisms for the following rearrangements. (4+3+6)
 - i) Fries Rearrangement
 - ii) Smiles Rearrangement.
- 3. a) Discuss the mechanisms of $S_{\rm E}1$ and $S_{\rm E}2$ reactions taking suitable examples.
 - b) Predict the product for the following and outline its mechanism.

c) Identify the reagents, conditions and discuss the following conversions. (4+3+6)



- 4. a) Explain the xanthate pyrolysis with suitable examples.
 - b) What are the experimental evidences in support of existence of free radicals in organic reactions? Give an account of free radical reactions.
 - c) When treated with EtOK/EtOH, the threo isomer of MeCHDCH(Br)Me loses HBr but the erythro isomer loses DBr on similar treatment. Explain this observation. (3+6+4)
- 5. a) Discuss the factors which affect the rate of elimination reactions.
 - b) Write a note on Hofmann degradations.
 - c) Predict the structures of A and B and outline the mechanism for the following: (6+4+3)

$$\begin{array}{c|c}
 & \text{NBS [1Eq.]} \\
 & \xrightarrow{\text{AIBN}} A \xrightarrow{\text{KOH}} B
\end{array}$$

- 6. a) Outline the mechanisms for $A_{AC}2$ and $A_{AL}1$ ester hydrolysis. Discuss the evidences to support these mechanisms.
 - b) Predict the products and explain their formation for the following reactions.

$$? \xleftarrow{\text{dil.H}_2\text{SO}_4} \qquad \xrightarrow{\text{1) B}_2\text{H}_6, \text{ THF}} ?$$

- c) Explain the preparation of the following from cyclopentene.
 - i) cis-Cyclopentane-1, 2-diol
 - ii) trans-Cyclopentane-1, 2-diol.

(5+4+4)

- 7. a) Discuss the mechanisms for the following reactions.
 - i) Knoevenagel condensations
 - ii) Perkin reaction.
 - b) Suggest the suitable products in the following reactions and propose the mechanisms.

1) Br
$$CH_3$$
 i) Mg, THF ii) aq. NH₄CI ?

2) CN NH_3 ?

c) Write a note on Michael addition reactions.

(6+4+3)