Ex/SC/CHEM/PG/CORE/TH/XI-O/2023

M. Sc. Chemistry Examination, 2023

(3rd Semester, CBCS)

PAPER: XI-O

[ORGANIC CHEMISTRY SPECIAL]

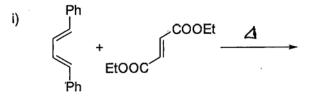
Time: Two Hours Full Marks: 40

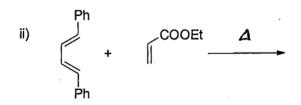
(20 marks for each Unit)

Use a separate answer script for each Unit.

UNIT - O - 3111

- 1. (a) Draw the π -MOs for 1,3,5-hexatriene. Also calculate the energy and lobe coefficients for its HOMO and LUMO.
 - (b) Explain the feasibility of [2+2] cycloaddition reaction under thermal and photochhemical conditions with the help of FMO approach. Can [2+2] cycloaddition reaction take place under thermal conditions? If yes, explain with proper example and orbital diagram.
- 2. Answer any *seven* of the following questions: 2x7
 - (a) Draw the structure of the product(s) in following transformations, showing proper stereochemistry wherever applicable:





(b) Explain the following observation with proper reasoning:

$$X = CH_3$$
 30% 70% $X = OCH_3$ >99% <1%

(c) Arrange the following four stereoisomers of 1-(prop-1-en-l-yloxy)but-2-ene in the order of increasing rates towards Claisen rearrangement, with proper reasoning.

(d) Write the mechanism for the following transformation:

- (iii) Under photochemical condition, 1,3-acyl shift of enamide follows an intermolecular mechanism via radical intermediate.
- (iv) Di-pi-methane rearrangement in the acyclic system occurs through S₁ excited state.
- 4. Carry out the following transformations :

(Answer any *two*)

2x2

- (i) cholesterol \rightarrow testosterone
- (ii) naphthalene → Diels' hydrocarbon
- (iii) cholesterol \rightarrow progesterone
- 5. Write down all the intermediate steps for the following conversion.

[3]

UNIT - O - 3112

3. (a) Write down the product with suitable mechanism for the following reaction.

(b) Write down the probable product(s) with plausible mechanism. (answer *any two*) 2x2

iii)
$$NO_2$$
 hv

- (c) Give evidence in favour of the following statements: Answer *any three*: 2×3
 - (i) Paterno Büchi reaction proceeds through diradical intermediate.
 - (ii) Barton reaction involves a 6-membered cyclic transition state.

(e) Explain the following transformation with proper mechanism:

OSiMe₃
$$\triangle$$
 $\stackrel{H}{\longrightarrow}$ $\stackrel{O}{\longrightarrow}$ $\stackrel{Me_3SiO}{\longrightarrow}$

(f) Write the structure of the product formed in the following reaction. Explain your answer with proper mechanism.

(g) Write proper mechanism for the following transformation:

(h) Write the structure of the product formed when furan reacts with maleic anhydride under thermal condition. Give proper explanation and mechanism.