Name:

Enrolment No:



UPES

End Semester Examination, May 2023

Course: Photochemistry and Pericyclic Reactions

Semester: II

Program: MSc. Hons. Chemistry

Course Code: CHEM7021P

Time: 03 hrs.

Max. Marks: 100

Instructions:

SECTION A (5Qx4M=20Marks)

S. No.		Marks	СО
Q 1	Draw the π molecular orbital diagram of 1,3,5-hexatriene and identify the number of nodes present in ψ_3 and ψ_5 molecular orbitals.	4	CO1
Q2	Differentiate between radiative and non-radiative processes. What is the origin of these processes in a π system.	4	CO2
Q3	Identify the HOMO and LUMO for ground state and first excited state of 1,3-butadiene.	4	CO2
Q4	Differentiate between α - and β - cleavage in Norrish Type reactions. Also mention the products that are formed in the primary step of these reactions.	4	CO3
Q5	What are the LUMO in the ground state for the following molecules? Explain with the help of a diagram. a. b. +	4	CO2
	SECTION B (4Qx10M= 40 Marks)		
Q6	Diagrammatically explain the π molecular orbitals in 2,4-pentadienyl system. Can this system be formed from ethylene and trienyl residues? Explain with reasons.	10	СОЗ
Q7	Explain the following with a Jablonski Diagram a. Radiative and Non-radiative process b. Phosphorescence c. Intersystem crossing d. Internal conversion e. Photoluminescence	10	CO1

Q8	a. What is the difference between a concerted and a stepwise pericyclic reaction?b. How do pericyclic reactions obey the conservation of orbital symmetry?	10	СОЗ
Q9	What is a sigmatropic rearrangement? Give examples. Also explain how it is different from an electrocyclic and cycloaddition reaction?	10	CO2
	OR		
	What are the factors that influence the quantum yield of a		
	photochemical reaction, and how can they be improved? Give examples		CO2
	of reactions with very high quantum yield.		
	SECTION-C (2Qx20M=40 Marks)		
Q 10	Identify the final products in the following Norrish-type reactions.		
	O II		
	a. $\xrightarrow{\beta}$ $\xrightarrow{h\nu}$		
	b. \xrightarrow{hv}		
	$ \begin{array}{c c} C. & Ph \\ Me \end{array} $ $ \begin{array}{c c} C & CH_3 & \xrightarrow{h\nu} $	4+4+4+4+4	СОЗ
	$ \begin{array}{cccc} d. & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & $		
	$e. \qquad \underbrace{\qquad \qquad \qquad }_{hv}$		

Q11	Answer the following: a. What is the importance of a photosensitizer in photochemistry? What are the criteria for a compound to behave like a photosensitizer? b. Comment on the singlet and triplet states of a carbonyl group. c. Give the mechanism of 1,5-sigmatropic shift in the 'ene' reaction.	5+5+5+5	CO2
	d. Sketch the pi molecular orbitals of the allyl system. Give electron occupancy in allyl carbanion, allyl free radical and allyl carbanion. OR		
	Answer the following:		
	 a. Draw molecular orbitals of allyl system using the linear combination of molecular orbital of one ethylene molecule and one <i>p</i>-atomic orbital. Also identify the HOMO and LUMO for this system. b. What are the different products obtained for β-cleavage in cyclopropyl ketones and α, β-epoxy ketones 	10+10	CO2