

Enrolment No.:

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M. Sc. Chemistry, III Semester
End-term Examination 2024

Paper Name: Photochemistry and Pericyclic reaction
Time: 2.5 hours

Paper Code: MCHCCO-303
Maximum Marks: 60

Note: This paper has 3 sections A, B, and C, attempt all three sections; *Section A: Answer all the questions; Section B: Answer any 2 out of 4; Section C: Answer all the questions, each question has an internal choice*

Abbreviations Used

CLO- Course Learning Outcome, PLO- Program learning Outcome, BTL- Bloom Taxonomy Level: BT level 1-Remember; BT level 2-Understand; BT level 3-Apply; BT level 4-Analyse; BT level 5-Evaluate, BT level 6-Create

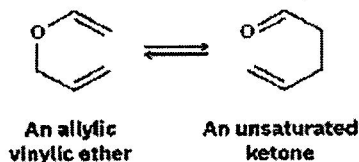
SECTION- A

Attempt all questions

(10*2= 20 Marks)

[BTL] CLO PLO

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|-------------|---|-----|-----|-----|
| A 1. | Give the mechanism of Nazarov reaction. | 1/2 | 1-3 | 1-3 |
| A 2. | Draw FMO diagram of butadiene | 1/2 | 1-3 | 1-3 |
| A 3. | Define photo quenching. | 1/2 | 1-3 | 1-3 |
| A 4. | State Second law of photochemistry | 1/2 | 1-3 | 1-3 |
| A 5. | Predict the stereochemistry of the photochemical cyclisation of a conjugated tetraene | 1/2 | 1-3 | 1-3 |
| A 6. | Giving an example to show how [4+2]- cycloaddition occurs in dipolar compounds | 1/2 | 1-3 | 1-3 |
| A 7. | Define the Quantum yield of a photochemical reaction | 3/4 | 4-5 | 4-5 |
| A 8. | Identify the reaction and draw a curved-arrow mechanism | 3/4 | 4-5 | 4-5 |



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|--------------|---|-----|-----|-----|
| A 9. | What is Flash Photolysis? | 3/4 | 4-5 | 4-5 |
| A 10. | What stereochemistry would you expect for the product of the Diels–Alder reaction between (2E,4E)-2,4-hexadiene and ethylene? What stereochemistry would you expect if (2E,4Z)-2,4-hexadiene were used instead? | 4/5 | 4/5 | 4/5 |

SECTION B

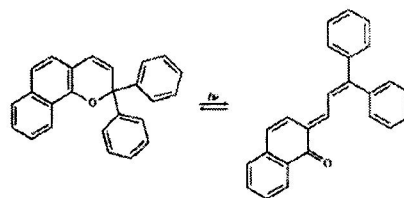
Attempt any two out of the following four questions

(2*10=20 Marks)

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|-------------|--|-----|-----|-----|
| B 1. | With the help of FMO method, explain the mechanism and stereochemistry of electrocyclic reactions under thermal and photochemical conditions | 3/4 | 4-5 | 4-5 |
| B 2. | Plastic photochromic sunglasses are based on the following reversible rearrangement of a dye inside the lenses that occurs when the lenses are exposed to sunlight. The original dye absorbs UV light but not visible light and is thus colorless, while the rearrangement product absorbs visible light and is thus darkened. | 5/6 | 6-7 | 6-7 |

(a) Show the mechanism of the rearrangement.

(b) Why does the rearrangement product absorb at a longer wavelength (visible light) than the original dye (UV)?



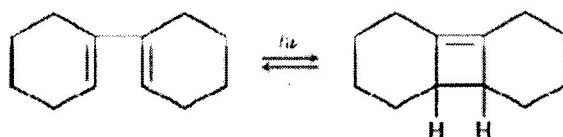
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|------|--|-----|-----|-----|
| B 3. | a) Many aromatic ketones react by hydrogen atom abstraction and the stable products are diols formed by coupling of the resulting α -hydroxybenzyl radicals. Illustrate giving examples | 5/6 | 6-7 | 6-7 |
| | b) Why do cisoid and transoid conformers of 1,3-butadiene display independent photobehavior? | 5/6 | 6-7 | 6-7 |
| B 4. | a) How can Norrish I and Norrish II reactions contribute towards the photolysis of polymers? | 3/4 | 4-5 | 4-5 |
| | b) Organic chemists have found utility in singlet oxygen as a versatile synthetic reagent, justify | | | |

SECTION C

Attempt all questions, each question has an internal choice

(5x5=25 Marks)

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|------|---|-----|-----|-----|
| C 1. | Would you expect the following reaction to proceed in a conrotatory or disrotatory manner? Show the stereochemistry of the cyclobutene product. and explain your answer | 5/6 | 6-7 | 6-7 |
|------|---|-----|-----|-----|



OR

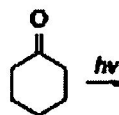
Answer the following question for π -molecular orbitals of 1,3,5,7-octatetraene

- Which are the bonding orbitals and antibonding orbitals?
- Which orbitals are HOMO and LUMO in the ground state and excited state?
- Which orbitals are symmetric and asymmetric with respect to the mirror plane and C2 axis?

- | | | | | |
|------|---|-----|-----|-----|
| C 2. | When irradiated without added substances many aromatic compounds, undergo photoisomerization. Illustrate using xylene as an example | 5/2 | 6-7 | 6-7 |
|------|---|-----|-----|-----|

OR

Give all possible products with the mechanism

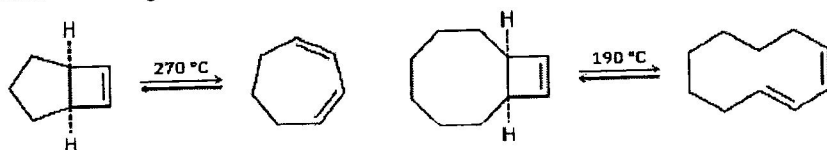


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|------|---|-----|-----|-----|
| C 3. | What are the possible products when dibenzyl ketone is cleaved photolytically | 3/4 | 4-5 | 4-5 |
|------|---|-----|-----|-----|

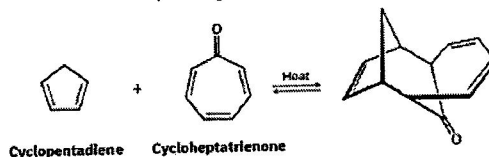
OR

When the compound having a cyclobutene fused to a five-membered ring is heated, (1Z,3Z)-1,3-cycloheptadiene is formed. When the related compound having a cyclobutene fused to an eight-membered ring is heated, however, (1E,3Z)-1,3-	5/6	6-7	6-7
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cyclodecadiene is formed. Explain these results, and suggest a reason why opening of the eight-membered ring occurs at a lower temperature



C 4. 1,3-Cyclopentadiene reacts with cycloheptatrienone to give the product shown. Tell what kind of reaction is involved, and explain the observed result. Is the reaction suprafacial or antarafacial?



OR

What stereochemistry—antarafacial or suprafacial—would you expect to observe in the following reactions?

- (a) A photochemical [1,5] sigmatropic rearrangement
- (b) A thermal [4 + 6] cycloaddition
- (c) A thermal [1,7] sigmatropic rearrangement
- (d) A photochemical [2 + 6] cycloaddition

C 5. What can be done to prevent smog formation?

OR

Explain the formation of PAN (peroxyacetylnitrate) in the environment