

Enrolment No.:

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M. Sc. Chemistry, III Semester
End-term Examination 2023

Paper Name: Photochemistry and Pericyclic reaction
Time: 3 hours

Paper Code: MCHCCO-303
Maximum Marks: 75

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)

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|--------------|--|-----|-----|-----|
| A 1. | What type of following electrocyclic reaction will a molecule with an even number of π -bonds undergo? | 1/2 | 1-3 | 1-3 |
| | a. Conrotatory thermal | | | |
| | b. Conrotatory photochemical | | | |
| | c. Disrotatory thermal | | | |
| | d. Disrotatory photochemical | | | |
| A 2. | Which of the following molecule can act as a photosensitizer? | 1/2 | 1-3 | 1-3 |
| | a. Benzophenone | | | |
| | b. Acetophenone | | | |
| | c. Benzene | | | |
| | d. All of the above | | | |
| 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. | What is a cheletropic reaction? Give an example. | 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. | Give one photochemical reaction, each of the Diazo compounds and Azides | 1/2 | 1-3 | 1-3 |
| A 9. | α,β -Unsaturated ketones with γ hydrogens can undergo hydrogen atom transfer resulting in formation of a dienol, how the mechanism | 1/2 | 1-3 | 1-3 |
| A 10. | What is Flash Photolysis? | 3/4 | 4-5 | 4-5 |

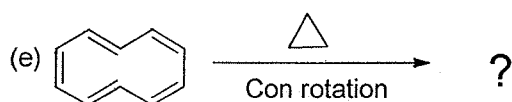
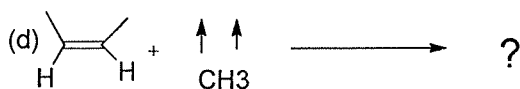
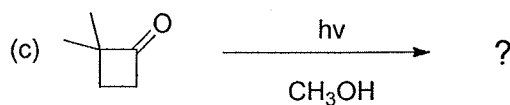
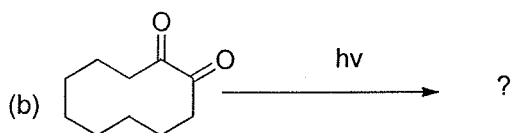
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C

SECTION- B

Attempt any two out of the following four questions

(2*10=20 Marks)

- B 1.** With the help of FMO method, explain the stereochemistry of [3,3] sigma tropic rearrangements under thermal and photochemical conditions 3/4 4-5 4-5
- B 2.** Explain the photochemical rearrangement of 4,4-diphenylcyclohexenone. 5/6 6-7 6-7
- B 3.**
- a. Photoreduction of benzophenone with diphenyl methanol involves a quantum yield of 1 compared to that of 2-propanol which has a quantum yield of 2. Explain. 5/6 6-7 6-7
 - b. Why is the photoreduction of benzophenone derivatives greatly diminished when an ortho alkyl substituent is present? 5/6 6-7 6-7
- B 4.** Complete the following photochemical reactions: 3/4 4-5 4-5



SECTION C

Attempt **all** questions, each question has an internal choice

(7x5=35 Marks)

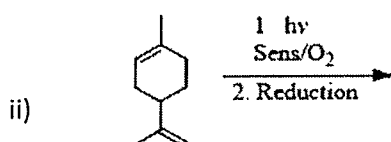
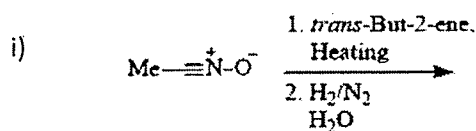
C 1. How does the percent transmittance of a solution vary with (a) increasing concentration and (b) increasing path length? A solution of thickness 2 cm transmitted 40% incident light. Calculate the concentration of solution given that $\epsilon = 6000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$

3/4 4-5 4-5

OR

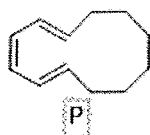
Give the product(s) and support your arguments with suitable mechanisms

5/6 6-7 6-7



C 2. a) What product is formed when triene P undergoes thermal electrocyclic ring closure?
b) What product is formed when triene P undergoes photochemical ring closure? Label each process as conrotatory or disrotatory.

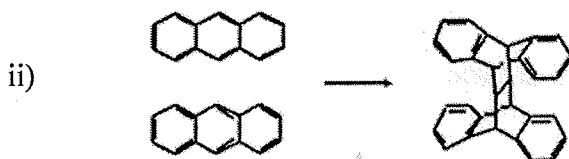
5/6 6-7 6-7



OR

Explain the formation with the mechanism.

5/6 6-7 6-7



C 3. Answer the following question for π -molecular orbitals of 1,3,5-hexatriene,

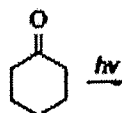
5/2 6-7 6-7

- 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?

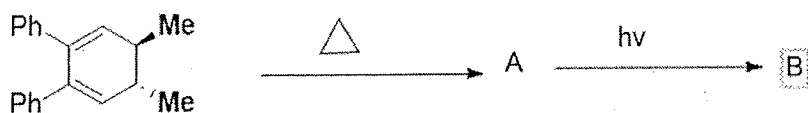
OR

Give all possible products with the mechanism

5/6 6-7 6-7



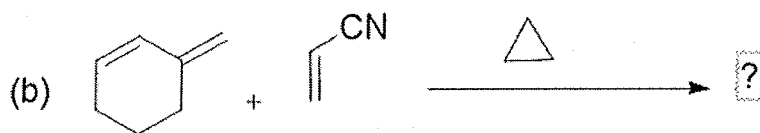
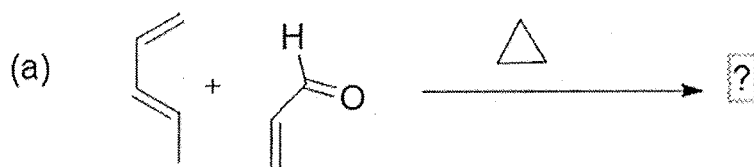
C 4. Identify A and B in the following reaction sequence. Label each process as conrotatory or disrotatory.	3/4	4-5	4-5
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OR

Explain how indoles are synthesized from ortho-iodo aniline using a photochemical route.	5/6	6-7	6-7
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C 5. Predict the product of the following reactions with the stereochemistry	3/4	4-5	4-5
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OR

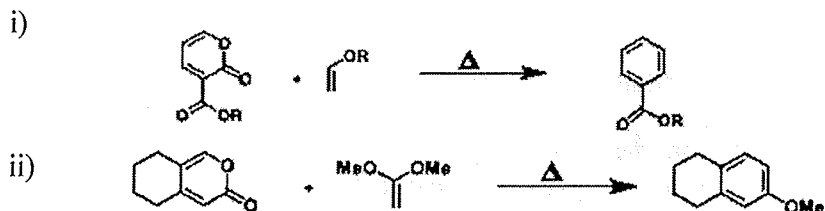
Can trans-stilbene be converted to phenanthrene through photo cyclization reactions? If so, explain how.	5/6	6-7	6-7
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C 6. Explain the following:	3/4	4-5	4-5
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- a. Cope rearrangement.
- b. Claisen rearrangement.

OR

Support the formation of product(s) by a suitable mechanism at each step of the reaction.	5/6	6-7	6-7
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C 7. What is the dominant photochemical reaction of Dibenzyl ketone in the gas phase	5/6	6-7	6-7
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OR

Explain the formation of PAN (peroxyacetylnitrate) in the environment	3/4	4-5	4-5
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