

M. Sc. (CHEMISTRY) EXAMINATION, 2023

(2nd Semester, CBCS)

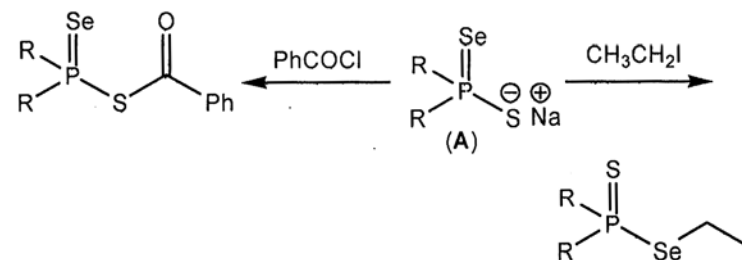
ORGANIC CHEMISTRY**PAPER – VI**

Time : Two hours

Full Marks : 40

(20 marks for each unit)**Use a separate answer script for each Unit.****UNIT – 2061**

1. With the help of correlation diagram show that disrotatory electrocyclic ring closure is not allowed under thermal condition for a $4n$ electronic system. 3
2. The following compound (A) undergoes Se-C bond formation in presence of ethyl iodide. However, it undergoes S-C bond formation with benzoyl chloride. Explain the reason. 1

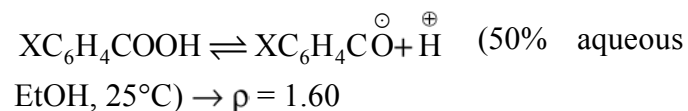


3. Answer **any three** of the following questions: 2×3
 - a) The following equilibrium has the reaction constant (ρ) equal to 1.60 in 50% aqueous EtOH medium.

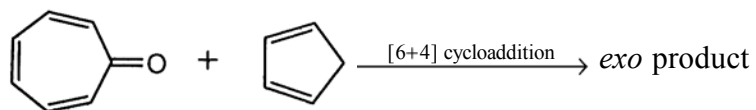
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[2]

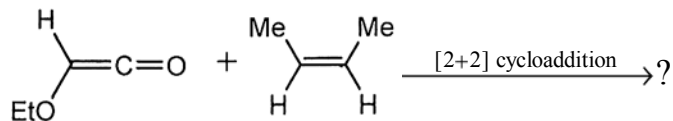
The value of “ ρ ” has been observed to be increased with increasing the percentage of EtOH in the reaction medium. Explain the reason of this observation.



- b) It has been found that in the dissociation of phenylacetic acids, σ_m is identical with σ_m° in case of *m*-OMe substituent. However, *p*-OMe shows different σ_p and σ_p° values. Justify the statement.
- c) Why do we get negative values for the substituent constants (σ) of electron donating groups?
- d) In the [6+4] cycloaddition reaction of tropone with cyclopentadiene, we get the *exo* product exclusively. The *endo* product does not form at all. Explain this observation.



- e) Write down the structure of the product of the following reaction with proper justification.

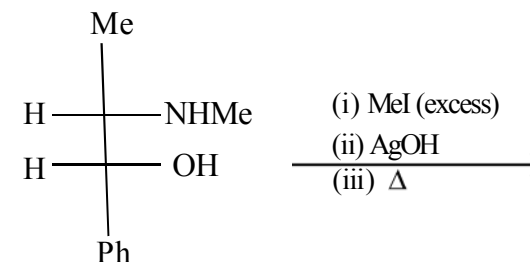


[7]

- d) How can you effect the following conversion? Show all the intermediate products. Mechanism is not required. 1 $\frac{1}{2}$



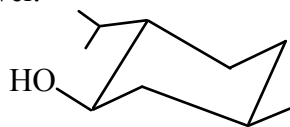
- e) Predict the product of the following reaction with mechanistic and stereochemical explanations. 1



[6]

b)

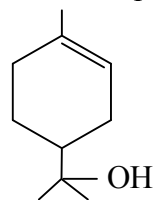
The relative order of rates of reaction of (+)-neomenthol, (+)-neoisomenthol, (+)-isomenthol and (–)-menthol with 3, 5-dinitrobenzoyl chloride was found to be 1.0, 3.1, 12.3 and 16.5, respectively. If **E** be the conformation of (–)-menthol, then draw conformations of the other three on the basis of outcome of the above mentioned experiment. Justify your answer.

 $2\frac{1}{2}$ **E**c) How could you achieve synthesis of **F** starting from

- i) two acyclic molecules bearing five carbon atoms or less,
- ii) an acyclic natural product

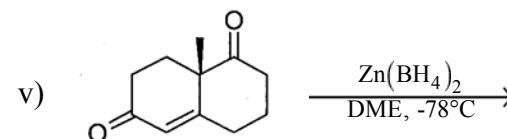
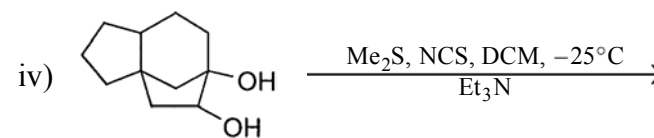
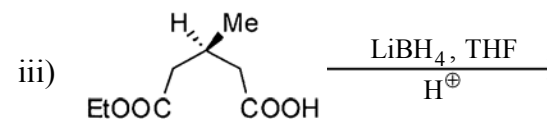
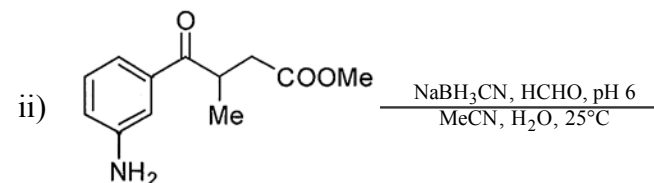
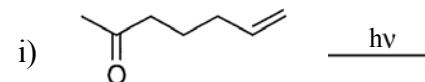
and iii) a cyclic natural product.

Show the intermediate steps. Mechanism is not needed.

 $1 + \frac{1}{2} + \frac{1}{2}$ **F**

[3]

4. a) Predict the product(s) of the following reactions and justify your answer with probable mechanism (answer any **three**). 2×3

b) Answer **any two** of the following questions : 2×2

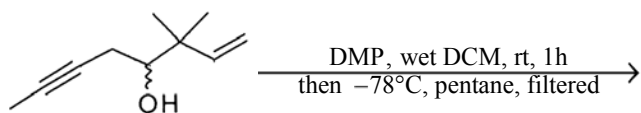
- i) *cis*-2-Propyl-4-*t*-butylcyclohexanone undergoes cleavage to 4-*t*-butylcyclohexanone on photolysis. The *trans* isomer does not undergo fragmentation directly, but is converted to the *cis* isomer which then fragments. The *trans* → *cis* isomerization is quenched by 1, 3-pentadiene, but the photo

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[4]

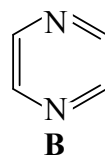
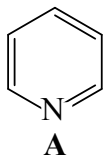
fragmentation is not. Give an explanation of this pronounced stereochemical effect.

- ii) What is Photoenolisation? Explain with a suitable example.
- iii) Schematically show how you prepare Dress-Martin periodinane (DMP) reagent from *o*-iodobenzoic acid (no mechanism required). Discuss the mechanism involved in the oxidation of the following compound.

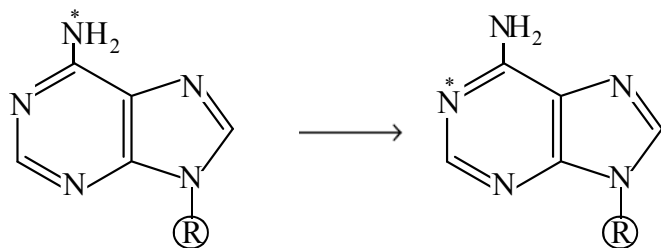


UNIT – 2062

5. a) Which one of the following compounds is more basic and why? 1 $\frac{1}{2}$

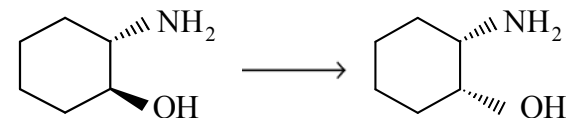


- b) Suggest the reagents and propose the mechanism for the key step of the following transformation. 1 $\frac{1}{2}$ + 2

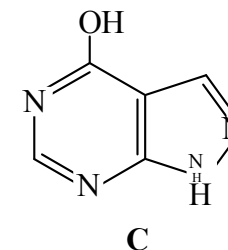


[5]

- c) Accomplish the following conversion through temporary construction of a suitable heterocyclic intermediate and account for the salient feature of this conversion. 2+1



- d) Suggest a scheme for the synthesis of the following compound **C** starting from non-heterocyclic precursor (only suggest the steps with reagents, no mechanism is needed). 2



6. a) Depict schematically biosynthesis of the following enantiopure lactone **D** starting from acetyl coenzyme A. **A**. Show all the intermediate steps. 3

