

M.Sc. CHEMISTRY EXAMINATION, 2018

(2nd Semester)

ORGANIC CHEMISTRY

PAPER - VI

Time : Two hours

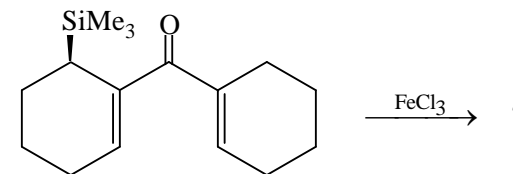
Full Marks : 50

(25 marks for each unit)

Use a separate Answer-script for each unit.

UNIT - 2061

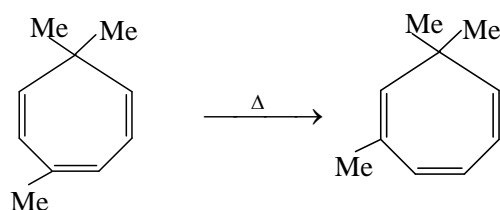
1. Molecules with $(4n + 2)\pi$ electrons respond in electrocyclic reactions *via* disrotation mode under thermal condition. Establish the above statement constructing an appropriate correlation diagram for a suitable example of electrocyclic reaction. 3
2. Answer *any three* : 2×3
 - a) Write the product with proper mechanism. Comment on the stereoselectivity obtained here.



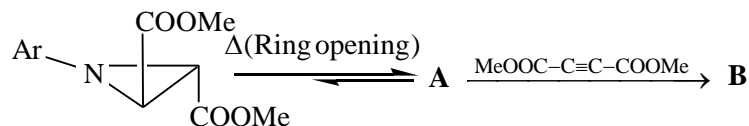
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[2]

- b) Write all the probable intermediates involved in the following transformation.



- c) Give an example of cycloaddition reaction which produces exclusively the *exo*-product between two possible diastereomeric products. State the reason of *exo*-selectivity.
- d) Complete the following sequence of reactions. Comment on the mode of pericyclic reactions involved in each step.

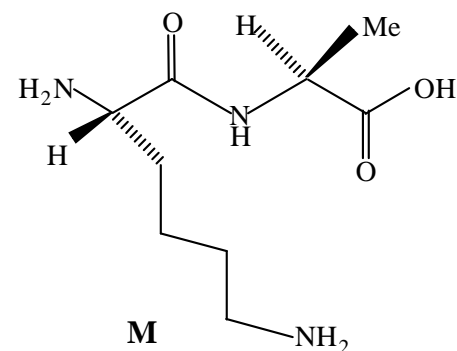


3. Answer *any two* :

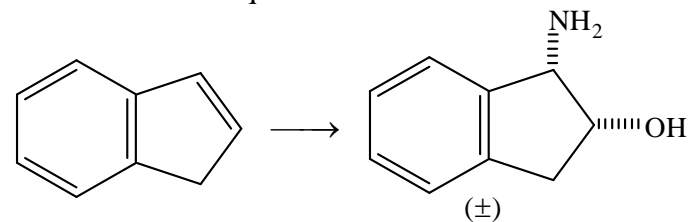
2x2

- a) The values of ρ for the acid dissociation equilibria of substituted benzoic acids, phenylacetic acids and phenylpropionic acids are 1.00, 0.49 and 0.21,

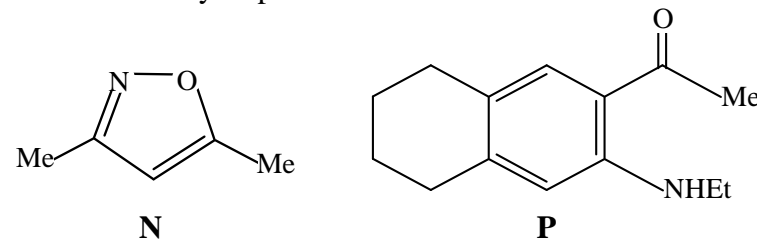
[9]



- d) How can you accomplish the following transformation through the temporary construction of a heterocyclic system? Highlight the stereochemical feature of this sequence.



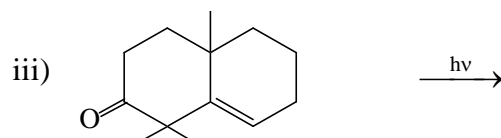
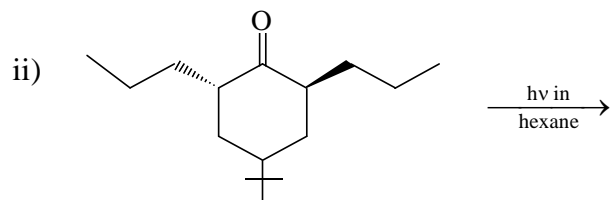
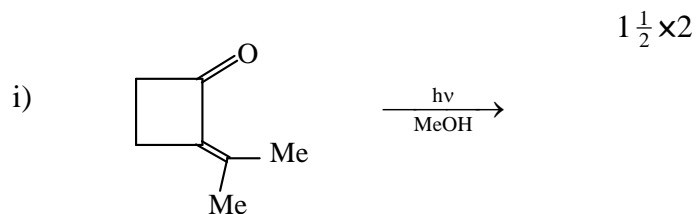
- e) Suggest a method for the synthesis of the compound **N** and delineate the scheme for the conversion of **N** to **P** with due emphasis to the mechanistic aspect of the key step.



3 $\frac{1}{2}$

[4]

b) With appropriate mechanism show the outcome of the following photochemical reactions (any *two*) :

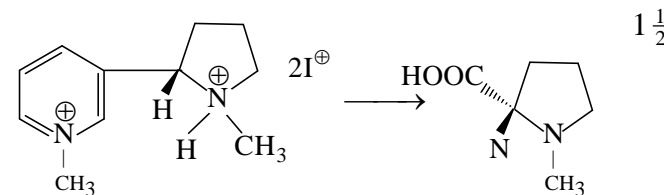


c) Discuss the importance of sensitizer in photochemistry. Explain with an example what criteria should be fulfilled by the compound to become a sensitizer. $1+1$

d) How do you accomplish the following transformation? Explain with mechanism. $1\frac{1}{2}$

[7]

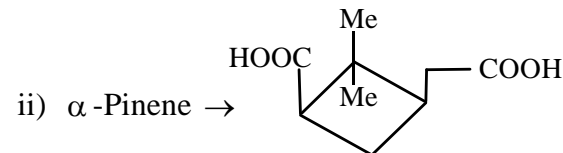
d) Carry out the following transformation. Suggest plausible mechanistic interpretation for the first step. $1\frac{1}{2}$



e) How can you effect the following conversions ?

(Mechanism is not required) $1\frac{1}{2} + 1$

i) Tropine \rightarrow cycloheptatriene



f) i) How was the epimeric carbon of (-) - ephedrine and (+) - ψ - ephedrine, having the same gross structure $PhCH(OH)CH(Me)NHMe$, determined chemically ? 1

ii) What happens when either of the two above mentioned alkaloids is heated with concentrated hydrochloric acid ? Give plausible mechanistic explanation. 1

6. a) How can you synthesize the compound **I** starting from the racemic variety of a naturally occurring α -amino $1\frac{1}{2}$

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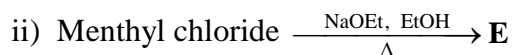
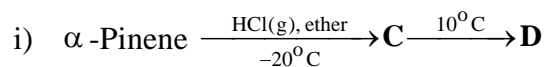
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UNIT - 2062

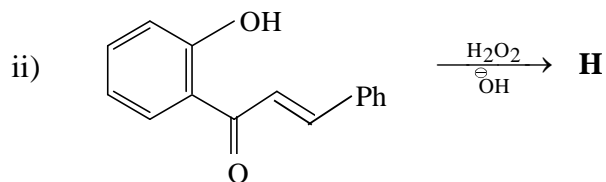
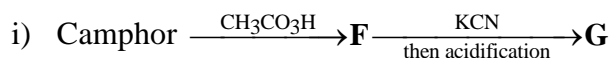
5. a) How can you distinguish the following pairs of compounds by ^1H NMR spectroscopy? Justify your answer. $1\frac{1}{2} + \frac{1}{2}$

- i) Geranial and neral
- ii) Coumarin and 7-hydroxycoumarin

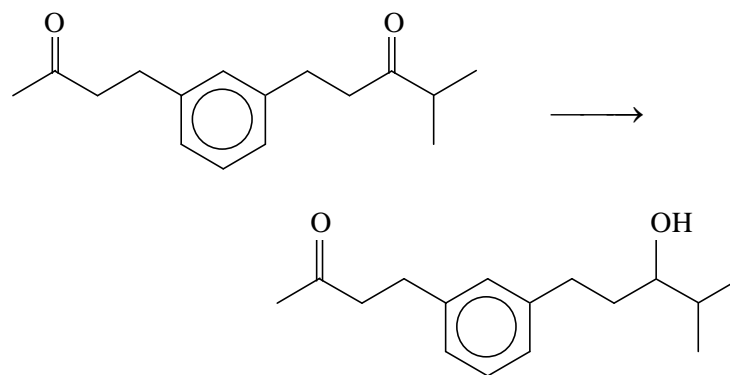
b) Identify the products **C**, **D** and **E** of the following reactions. Provide appropriate mechanistic and stereochemical explanations for their formation, as necessary. $1\frac{1}{2} + 1$



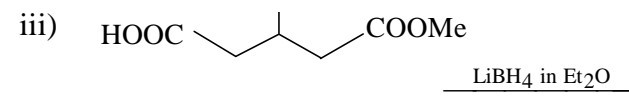
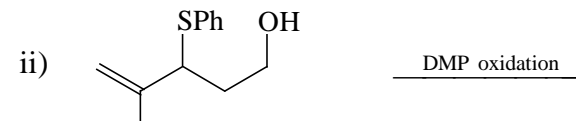
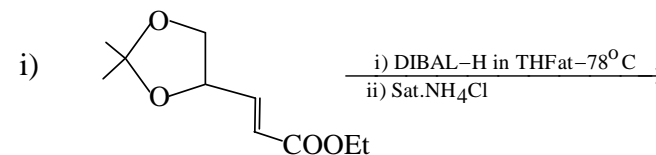
c) Predict the products **F**, **G** and **H** of the following reactions (no mechanism is required). $1 + \frac{1}{2}$



[5]



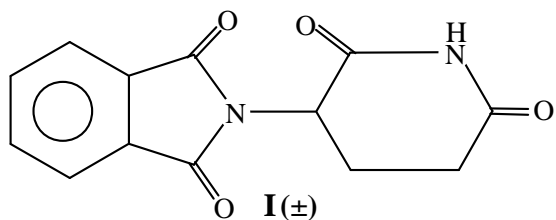
e) Predict the product(s) and explain with mechanism (any two): $\frac{1}{2} \times 2$



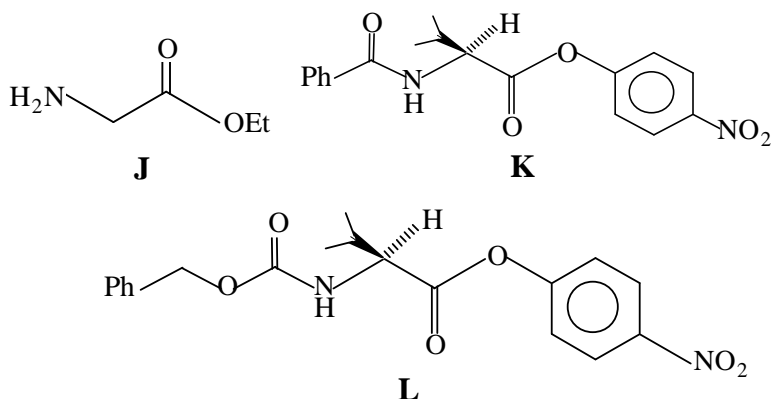
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[8]

acid (only suggest the steps with reagents, no mechanism is needed) ? 2



- b) When the compound **J** reacts with the compound **K** and **L** separately, the extent of racemization in the product is more in case of **K** than that of **L**. Suggest an explanation for this observation. 2

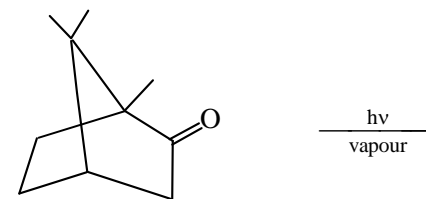


- c) Design a scheme for the synthesis of the following dipeptide **M** starting from appropriate α -amino acids using Staudinger Ligation in one of the steps (only suggest the steps with reagents, no mechanism is needed). 3 $\frac{1}{2}$

[3]

respectively in water at 25°C. Again substituted cinnamic acids show ρ value of 0.47 for the similar type of equilibrium under the identical condition. State the reason behind such type of variations of the ρ values.

- b) $-\text{NH}_2$ and $-\text{NMe}_2$ show negative σ_m values in spite of their $-I$ effects. Explain the reason with proper justification.
- c) $-\text{OCH}_3$, $-\text{NH}_2$ and $-\text{NMe}_2$ show significant deviations in the correlation of $\log K$ vs σ for dissociation of substituted phenylacetic acids in water at 25°C – state the reason. Which type of σ values should be considered for the above functional groups in order to get better correlation ?
4. a) How would you prove that Norrish Type-I cleavage reaction is a reversible process ? Mechanistically predict the product(s) of the following photochemical reaction. 1+1 $\frac{1}{2}$



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