

**M. Sc. CHEMISTRY EXAMINATION, 2017**

( 2nd Semester )

**ORGANIC CHEMISTRY****PAPER - VI**

Time : Two hours

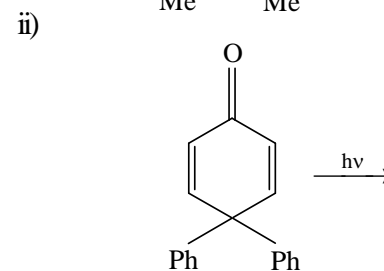
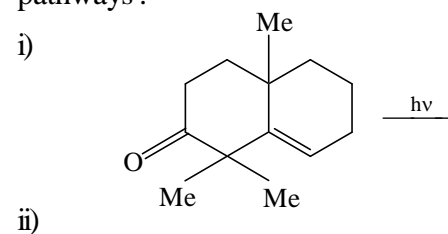
Full Marks : 50

( 25 marks for each unit )

Use a separate answerscript for each unit.

**UNIT - 2061**Answer *any two* of the following questions :

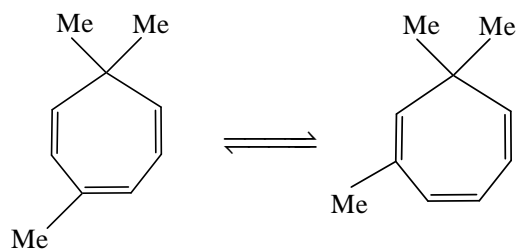
1. a) Draw the orbital correlation diagram for the cycloaddition reaction of two ethylene molecules occurring by supra-supra mode and hence predict whether the process is thermally or photochemically allowed. 3
- b) Write the products of the following reactions and explain their formation by showing appropriate mechanistic pathways :  $1\frac{1}{2} \times 2$



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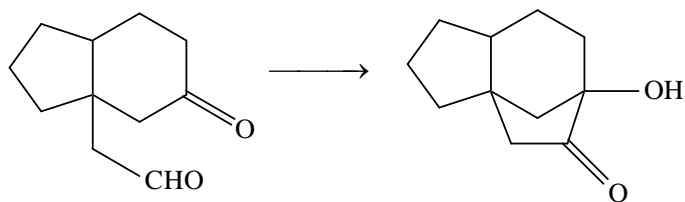
[ 2 ]

- c) Show the steps by which the following equilibration can occur : 1  $\frac{1}{2}$



- d) What is  $\sigma^+$  scale for substituent constants ? For which type of substituents  $\sigma^+$  values differ significantly from  $\sigma$  values ? Explain why. 2

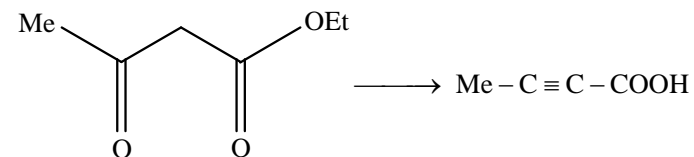
- e) How would you carry out the following transformation ?



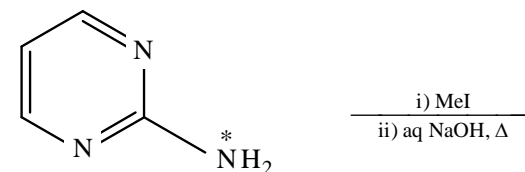
Give a plausible mechanism of the last step of the synthetic route of your choice. 2

[ 11 ]

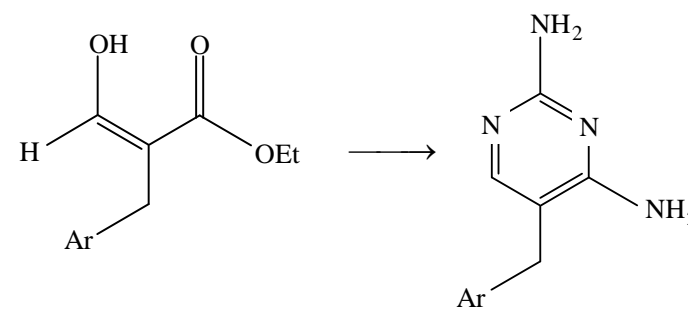
- d) Accomplish the following transformation involving an appropriate heterocyclic intermediate with mechanism(s) of the key step(s). 3



- e) Predict the product and explain with mechanism. 2  $\frac{1}{2}$

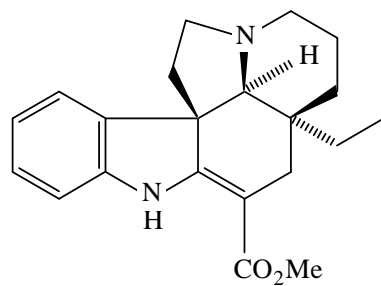


- f) Suggest reagents for each step of the following transformation (no mechanism is needed) 1  $\frac{1}{2}$

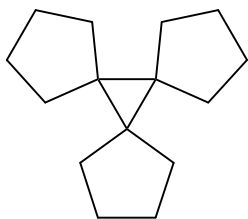


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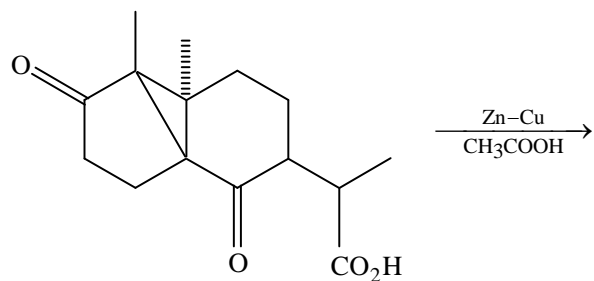
- ii) The following compound readily undergoes thermal racemisation. 1  $\frac{1}{2}$



- b) Outline a synthesis of the following compound involving photochemical reaction in one of the steps. 1



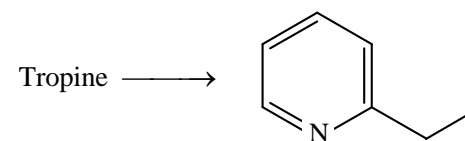
- c) Predict the product of the following reaction and give a plausible mechanism. 1  $\frac{1}{2}$



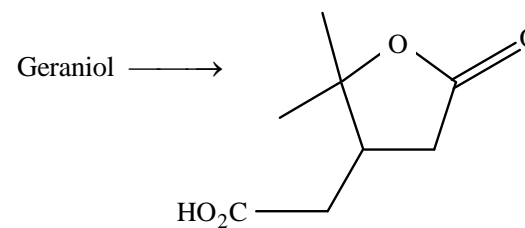
[ 9 ]

- b) Carry out the following transformations. (No mechanism is required) 2+2

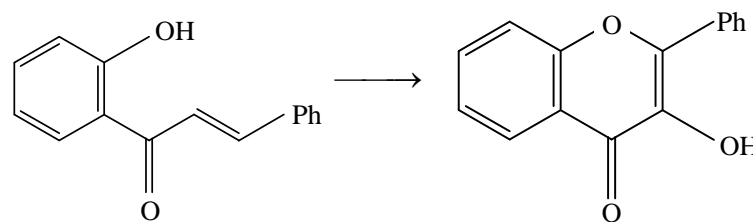
i)



ii)



- c) How can you effect the following conversion? Suggest plausible mechanism. 1

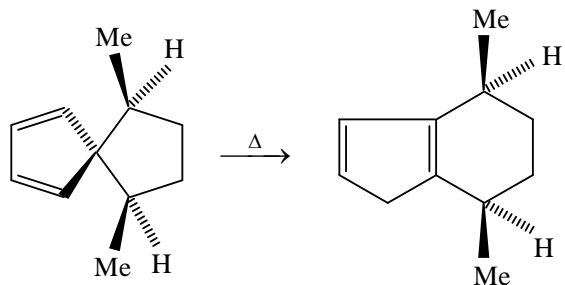


- d) Mention the reaction which indicated that  $\alpha$ -pinene contains a six-membered ring. 1  $\frac{1}{2}$

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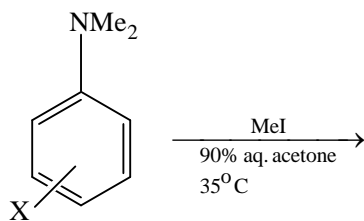
[ 6 ]

ii)

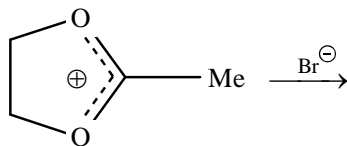
b) What will be the sign of  $\rho$  value of the following reaction?

Explain.

1



c) Applying HSAB principle predict the product of the following reaction :

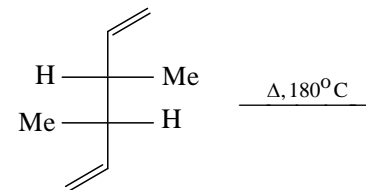
 $\frac{1}{2}$ 

d) Predict the products of the following reactions and explain their formation through involvement of pericyclic reactions.

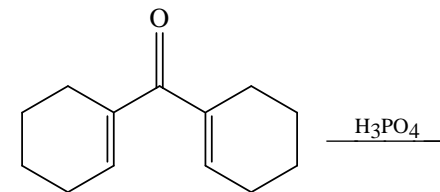
 $1\frac{1}{2} \times 3$ 

[ 7 ]

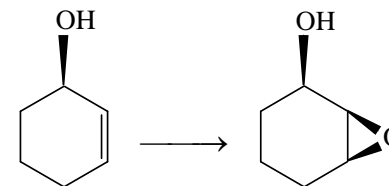
ii)



iii)



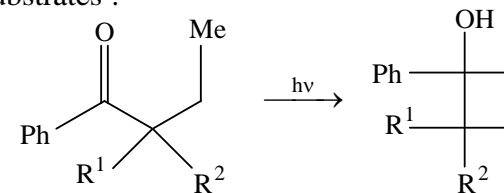
e) How would you carry out the following transformation ?



Give proper explanation for your answer.

1

f) How would you explain the gradual increase of the percentage of cyclization product from the following substrates ?

 $1\frac{1}{2}$ Substituents $\text{R}^1 = \text{R}^2 = \text{H}$  $\text{R}^1 = \text{H}, \text{R}^2 = \text{Me}$  $\text{R}^1 = \text{R}^2 = \text{Me}$ Cyclization

10%

29%

89%

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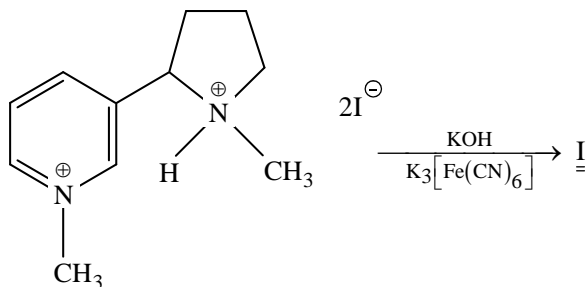
[ 8 ]

- g) Applying Woodward-Hoffmann rule show that the thermal ring opening of cyclobutene will be a conrotatory process. 1

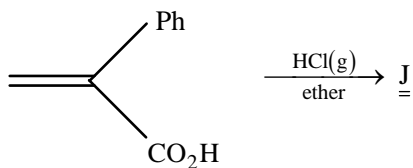
### UNIT - 2062

4. a) Identify the products I and J of the following reactions. Suggest appropriate mechanistic interpretations for their formations. 1+1

i)

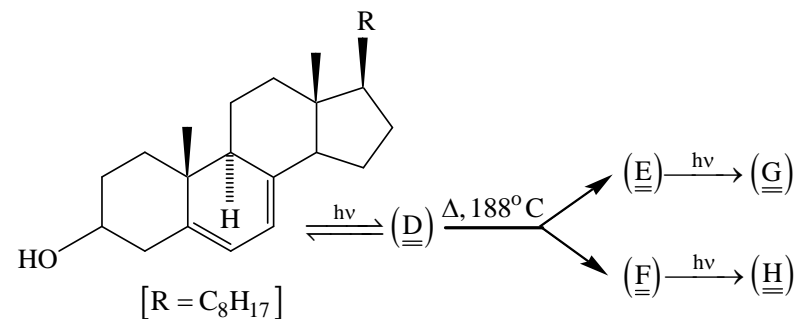


ii)

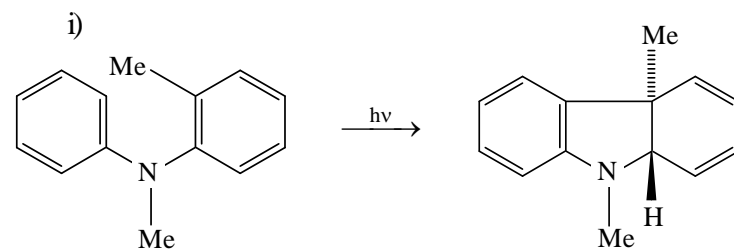


[ 5 ]

- d) Discuss how the Roberts and Moreland treatment .....  $\sigma_1$  values of substituents in the benzene system. 2
- e) What do you mean by quantum yield? Comment on the quantum yield of the photochemical reaction of benzophenone in isopropanol. 2
- f) Write the structures of the compounds D–H in the following reaction sequence and mechanistically explain their formation. 2½



3. a) Delineate a possible pathway for each of the following reactions: ½×2



[ Turn over

[ 10 ]

e) Justify whether the following statement is correct or not.  
 “3,5 - Dinitrobenzoyl chloride reacts with (+) –  
 neomenthol with a faster rate compared to (+) –  
 neoisomenthol.” 2

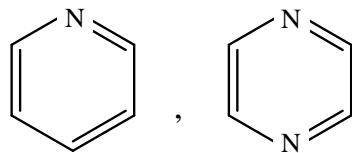
f) Which one between D – (–) – ephedrine and L – (+) –  
 ephedrine is more basic ? Give justification.  $\frac{1}{2}$

5. a) DCC acts better in combination with HOAt than with  
 HOBt to obtain an amide linkage between the reaction of  
 a carboxylic acid and a primary amine – why ?  $1\frac{1}{2}$

b) Design a scheme for the synthesis of the following  
 tripeptide using NCA (N-Carboxamic anhydride)  
 method.

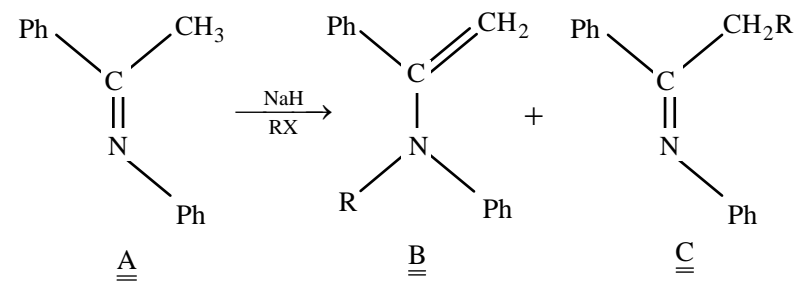
Phe – Val – Ala 3

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



[ 3 ]

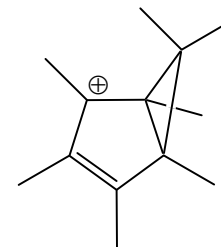
f) Explain the results (ratio of the products) of the following  
 reactions with the help of HSAB principle. 1



RX	<u>B</u> : <u>C</u>
EtI	0.1 : 1
Et <sub>2</sub> SO <sub>4</sub>	1.2 : 1
Et <sub>3</sub> O <sup>+</sup> BF <sub>4</sub> <sup>−</sup>	22 : 1

2. a) How would you account for the following observations ?

i) The following cation containing seven methyl groups  
 in apparently different environments shows a sharp  
 15-proton singlet and two 3-proton singlets in its  
<sup>1</sup>H NMR spectrum. 2



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