M. Sc. (Chemistry) Examination, 2022

(2nd Semester, CBCS)

Organic Chemistry

Paper – VI

Time : Two hours Full Marks : 40

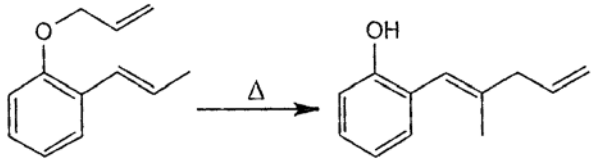
Use a separate answer script for each Unit.

UNIT – 2061

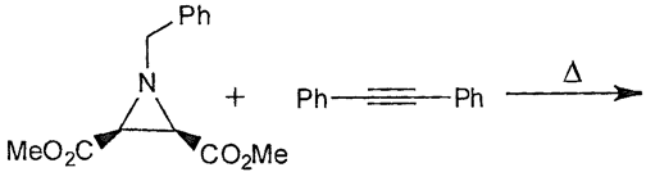
1. Answer ***any two*** : $2\frac{1}{2}+2\frac{1}{2}$

   a) Under photochemical condition, 4n electronic systems follow disrotatory electrocyclic ring closure. Justify the statement by constructing the appropriate correlation diagram.

   b) Give possible mechanism for the following reaction.



   c) Write down the product of the following reaction with probable mechanism.



2. Answer ***any one*** : 2

a) In dissociation of benzoic acid, the value of reaction constant has been observed to change with changing the solvent of the reaction medium as below. Justify this observation.

i) $XC_6H_4COOH \rightleftharpoons XC_6H_4COO^{\ominus} + H^{\oplus}$

$(H_2O,\ 25°C) \rightarrow \rho = 1.00$

ii) $XC_6H_4COOH \rightleftharpoons XC_6H_4COO^{\ominus} + H^{\oplus}$

$(50\%\text{ aq. EtOH},\ 25°C) \rightarrow \rho = 1.60$

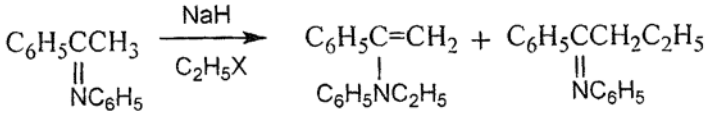
iii) $XC_6H_4COOH \rightleftharpoons XC_6H_4COO^{\ominus} + H^{\oplus}$

$(EtOH,\ 25°C) \rightarrow \rho = 1.96$

b) Why do NH_2 and NMe_2 show negative σ_m values? Explain.

3. Answer ***all*** the questions : $1\frac{1}{2} + 1\frac{1}{2}$

a) During NaH mediated ethylation of the following imine the product selectivity varies with the variation of ethylating agents as shown below:

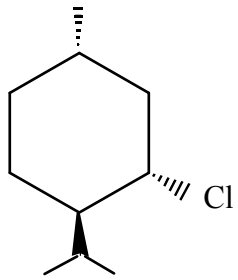


C_2H_5I	0.1	:	1
$(C_2H_5)_2SO_4$	1.2	:	1

Explain the reason of such selectivity.

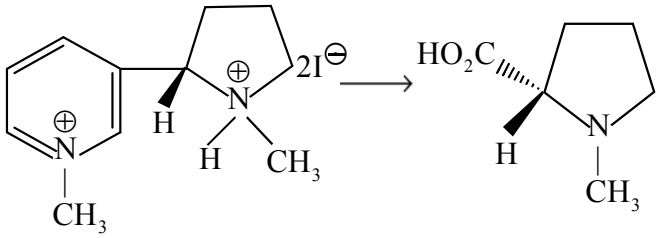
e) Predict the major product(s) formed by the catalytic hydrogenation (H_2-Pt) of 1-phenylpropane-1, 2-dione in presence of methylamine in mehanol. Discuss the stereochemical control involved. $1\frac{1}{2}$

f) Identify the product(s) formed when the following enantiomerically pure molecule **C** is heated with sodium ethoxide in ethanol (mechanism is not required). Draw that conformation of **C** through which the reaction actually proceeds. 1

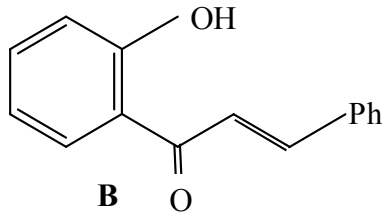


C

b) Carry out the following transformation. Mechanistically explain role of all the reagents used in the first step. $1\frac{1}{2}$



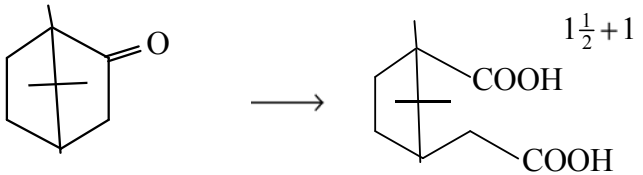
c) What happens when the following molecule **B** is treated with alkaline hydrogen peroxide? Propose plausible mechanism to explain your answer. $1\frac{1}{2}$



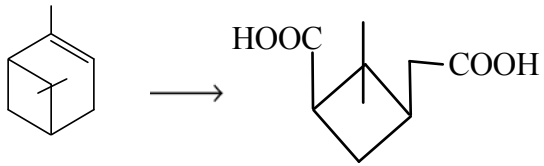
B

d) How do you accomplish the following transformations? $1\frac{1}{2}+1$

i)



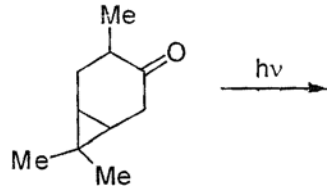
ii)



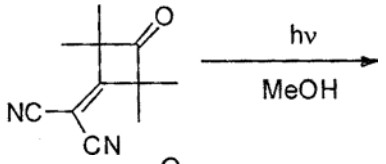
b) Cite a reaction which shows negative reaction constant (ρ). Explain the reason of negative value of ρ.

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

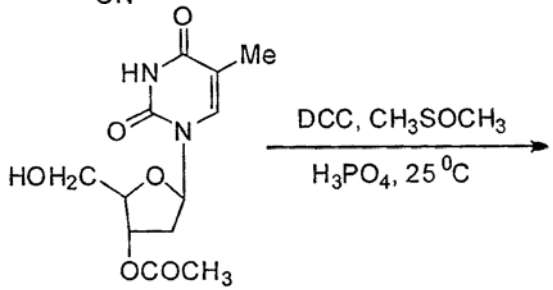
i)



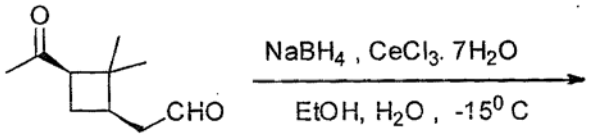
ii)



iii)

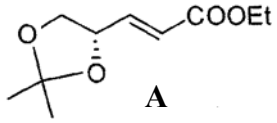


iv)



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

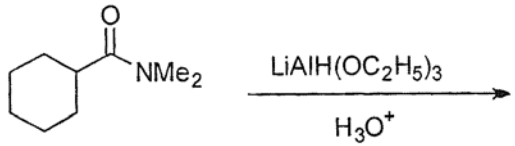
i) How can you prepare DIBAL-H? Discuss with mechanism the role of solvent in the reduction of an ester (**A**) with DIBAL-H.



A

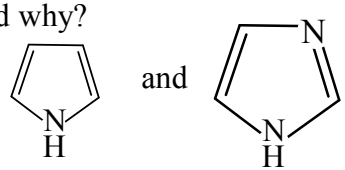
ii) What is the importance of photosensitizer in photochemistry? What criteria should be fulfilled by a compound to become sensitizer? Explain with an example.

iii) Predict the product of the following reaction and explain with probable mechanism.

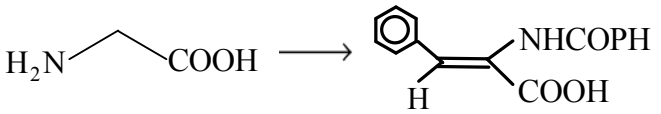


UNIT – 2062

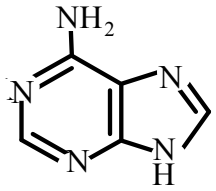
5. a) Which one of the following compounds is a stronger base and why? $1\frac{1}{2}$

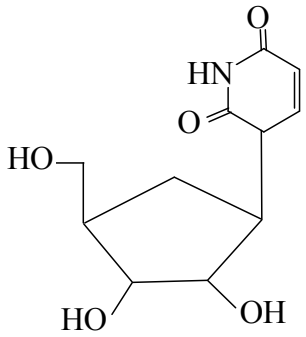


b) Accomplish the following transformation through temporary construction of a heterocyclic intermediate. Highlight the mechanistic feature of the salient step. 2+2



c) Design the schemes for the syntheses of the following compounds from non-heterocyclic precursors (only mention the steps with reagents, no mechanism is needed). $3+1\frac{1}{2}$

i) 

ii) 

6. a) Given below are the chemical shift values of the underlined methyl and methylene protons of two isomers having gross structure $(CH_3)_2C=CHCH_2\underline{CH_2}C(\underline{CH_3})=CHCHO$

Isomer	^{1}H-NMR Chemical Shifts	
	CH_3	CH_2
I	δ 1·98	δ 2·58
II	δ 2·16	δ 2·24

Predict the structures of isomer I and II with appropriate justification. 2