UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE SPECIAL DEGREE (LEVEL I) SEMESTER- I
EXAMINATION   JULY 2 017

SUBJECT :CHEMISTRY
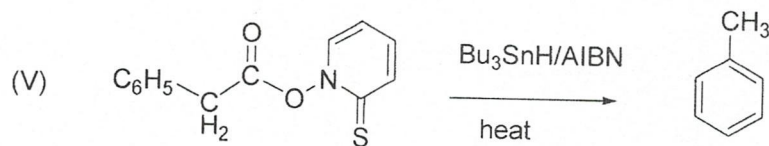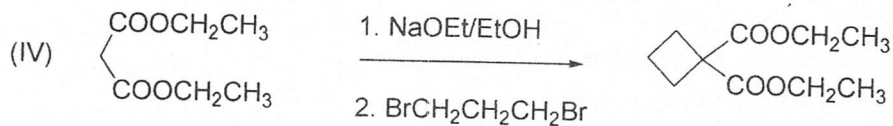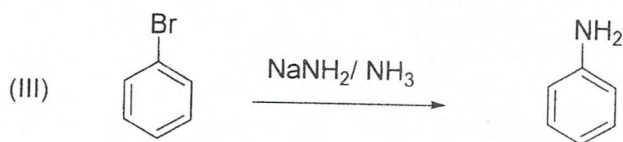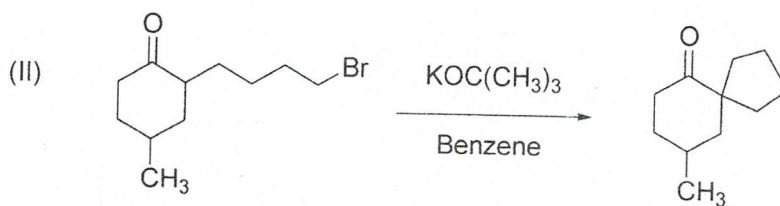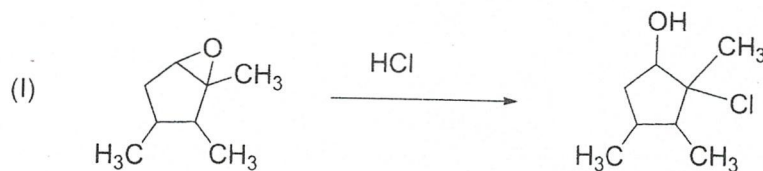
COURSE UNIT : CHE 4123   **TIME :Three (03)** hours

Answer **all** questions.

01. Answer **all** parts

   (a) Consider the following chemical transformations;
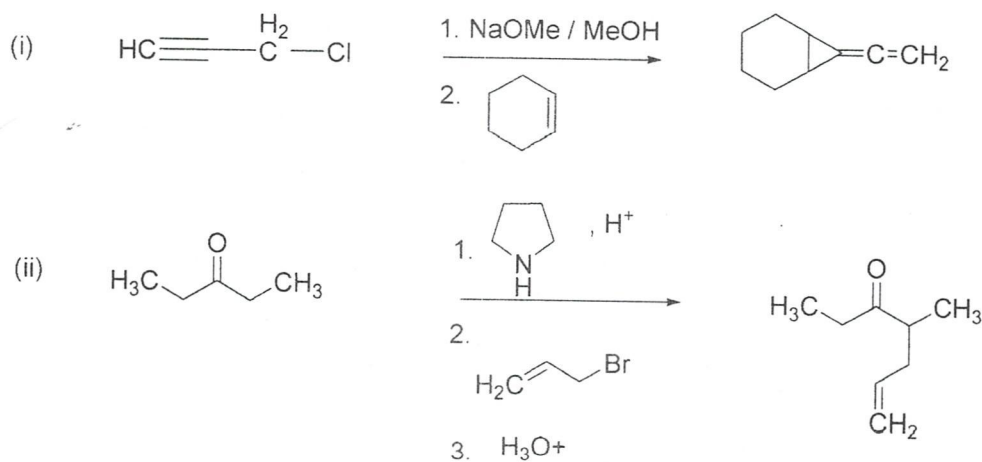
(I)

(II)

(III)

(IV)

(V)

(i) Draw the structure of the intermediate formed in each of those reactions.

(ii) Explain the stability of the intermediate(s) proposed in each case.
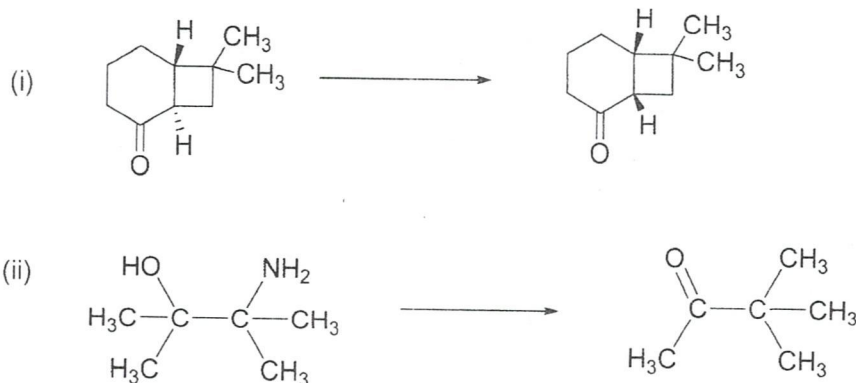
(30 marks)

(b) Give plausible mechanism for the following reactions.

Note: The reactive intermediate of each reaction needs to be highlighted.

(i)

(ii)

(30 marks)

(c) What is the structure of the reactive intermediate(s) required to be generated in order to perform the following transformations? Giving necessary reagents show how you would carry out the transformation through the intermediates you proposed. When there are more than one reagent, indicate the order of adding them.
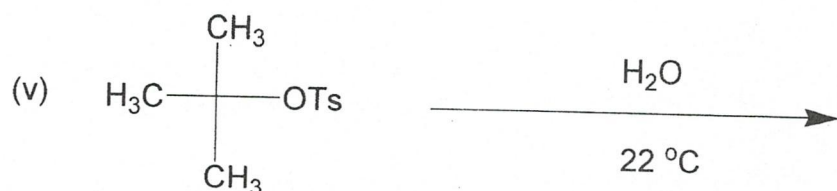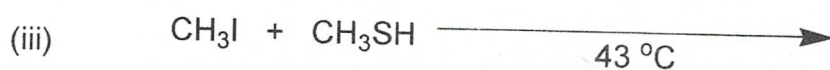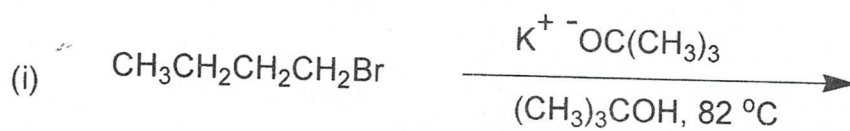
(i)

(ii)

2

(iii)

(iv)
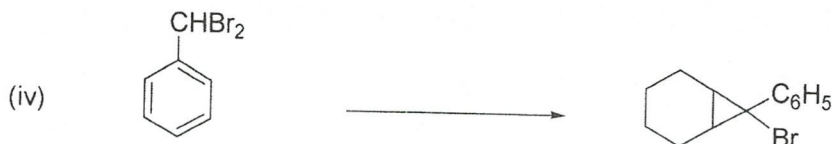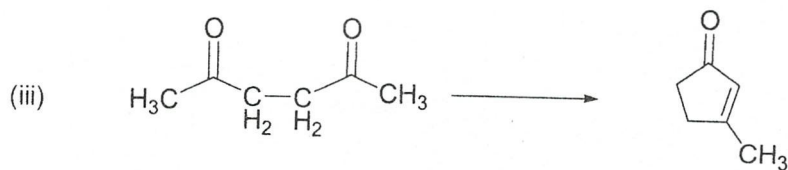
(40 marks)

02. Answer **all** parts.

(a) Predict the major product of each of the following reactions. State whether the reactions are occurring under S_N1, S_N2, E1, or E2 mechanisms.

(i) $CH_3CH_2CH_2CH_2Br$ $\xrightarrow[\text{(CH}_3\text{)}_3\text{COH, 82 °C}]{\text{K}^+ \text{ }^-\text{OC(CH}_3\text{)}_3}$

(ii)

$\xrightarrow[\text{(CH}_3\text{)}_3\text{COH, 82 °C}]{\text{K}^+ \text{ }^-\text{OC(CH}_3\text{)}_3}$

(iii) CH_3I + CH_3SH $\xrightarrow[\text{43 °C}]{}$

(iv)

$\xrightarrow[\text{22 °C}]{\text{H}_2\text{O}}$

(v)

$\xrightarrow[\text{22 °C}]{\text{H}_2\text{O}}$

(25 marks)

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(b) Draw step-by-step reaction mechanisms for the following reactions. You may abbreviate the substituent/s if needed.

(i)

Hoveyda-Grubs II catalyst

Toluene, Δ

(ii)

NBS

CCl_4

(iii)

H^+
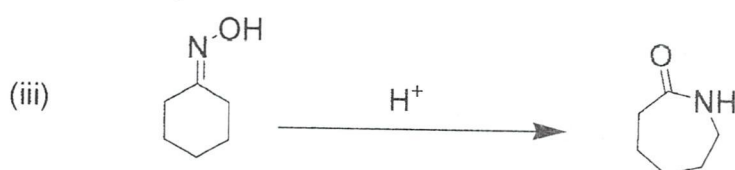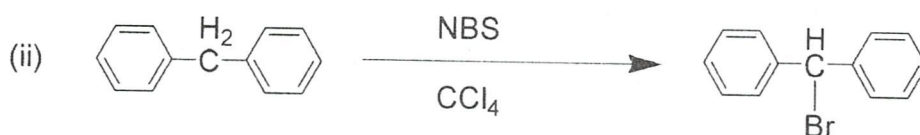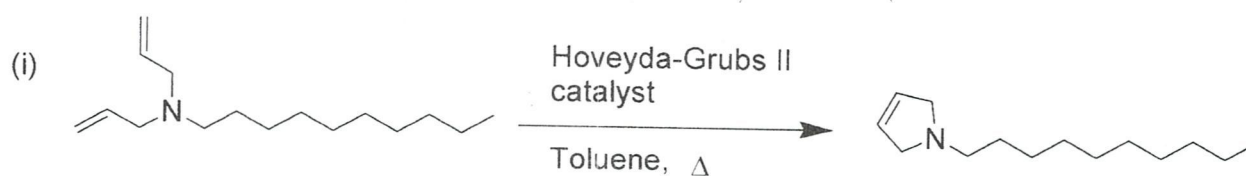
(45 marks)

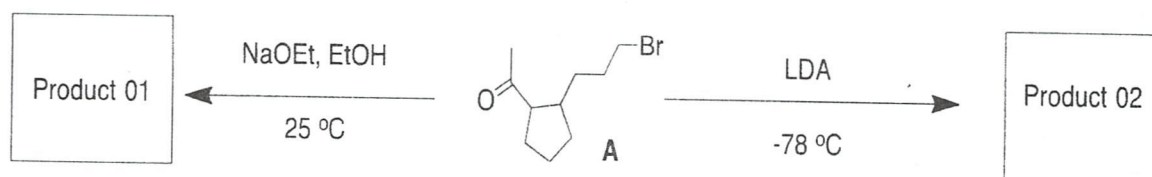(c) Consider the given chemical transformations of the compound A below.

Product 01

NaOEt, EtOH
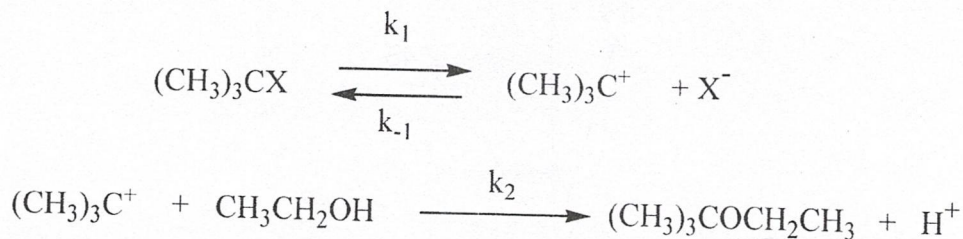
25 °C

A

LDA

-78 °C

Product 02

(i)   Draw the structures of the major compound produced from each reaction.
(ii) Rationalize your answer to part (i).
(iii) Outline the mechanisms for the formation of product 01 and product 02.

(30 marks)

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03. Answer **all** parts

(a) Nucleophilic substitution of tertiary butyl halides with ethanol which proceeds via an S_N1 mechanism is given below.

$$(CH_3)_3CX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (CH_3)_3C^+ \; + X^-$$

$$(CH_3)_3C^+ \; + \; CH_3CH_2OH \xrightarrow{k_2} (CH_3)_3COCH_2CH_3 \; + \; H^+$$

(i) Show that the rate of the reaction can be given by the following equation.

$$-\frac{d[RX]}{dt} = \frac{k_1 k_2 [R'OH]\,[RX]}{k_{-1}[X^-] + k_2[R'OH]}$$

where $R'OH = CH_3CH_2OH$ and $RX = (CH_3)_3CX$.

(20 marks)

(ii) If the reaction is carried out with excess alcohol to keep [R'OH] constant, the reaction becomes pseudo-first order with a simple form of the rate equation

$$-\frac{d[RX]}{dt} = k_{obs}[RX]$$
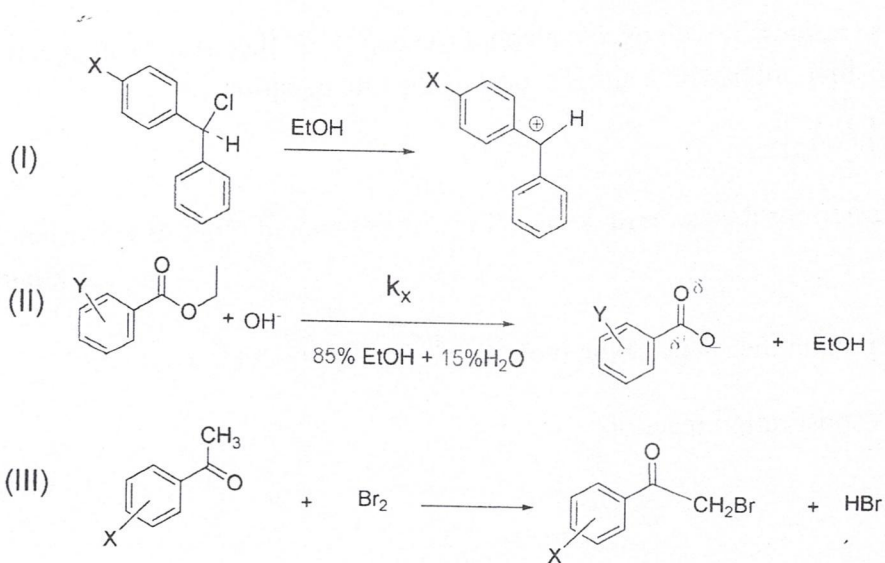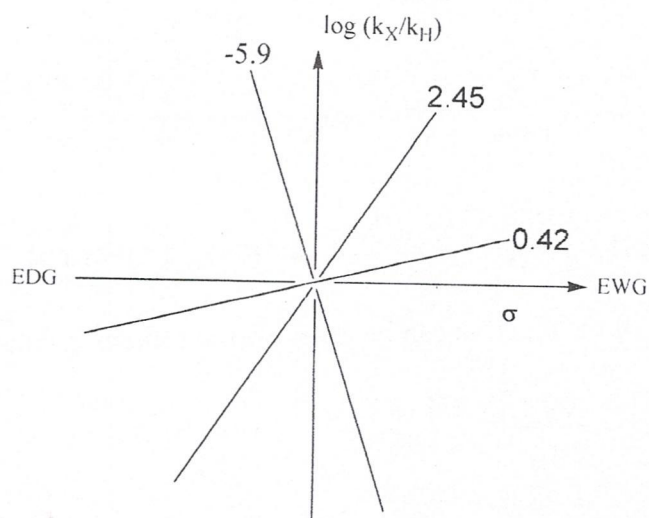
Deduce an expression for the k_{obs} with k_2' ($k_2[R'OH] = k_2'$) and all other rate constants.

(10 marks)

(iii) Giving reasons predict the shape of the plot of $\ln \dfrac{[RX]_0}{[RX]_t}$ vs t which would be observed for this substitution reaction.
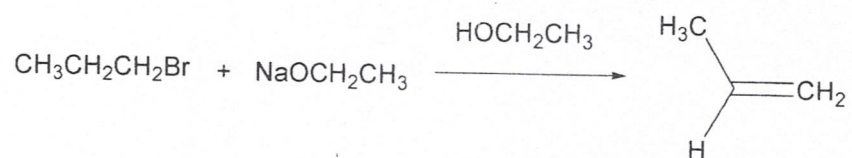
(15 marks)

(b) Giving reasons assign the ρ values indicated below in the Hammett plots to each of the following reactions.

5

$\log (k_X/k_H)$

-5.9

2.45

-0.42

EDG ————————————————→ EWG

σ

(I)

X—⬡—CHCl(H) attached to phenyl →[EtOH] X—⬡—CH⊕(H) attached to phenyl

(II)

Y—⬡—C(=O)—O—ethyl + OH⁻ →[k_x] [85% EtOH + 15%H_2O] Y—⬡—C(=O^δ)—O^δ⁻ + EtOH

(III)

X—⬡—C(CH₃)=O + Br₂ → X—⬡—C(=O)—CH₂Br + HBr

(30 marks)

(C) The kinetic isotope effect (KIE) observed for the following elimination reaction is
$k_H/k_D = 6.7$.

$CH_3CH_2CH_2Br$ + $NaOCH_2CH_3$ →[$HOCH_2CH_3$] (H₃C)(H)C=CH₂

Explaining with suitable structures determine the elimination mechanism involved in this reaction.
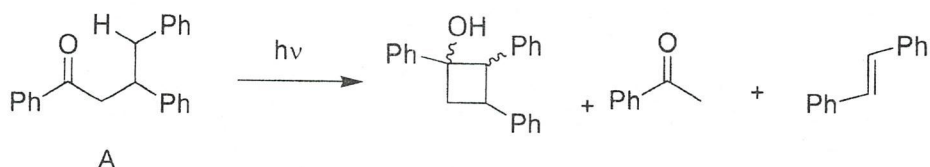
(25 marks)

04. Answer **all** parts

(a) The quantum yield for the conversion of benzophenone to the dimeric reduction product is 2.0 in the solvent 2-propanol. Giving suitable chemical reactions explain this.
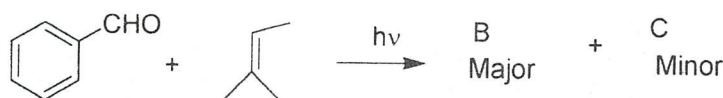
(20 marks)

(b) On irradiation of compound **A**, the products shown below are formed. Propose a suitable mechanism for this transformation.

(20 marks)

(c) Consider the following photochemical reaction and answer the questions given below.

(i) What is the spin multiplicity of the reactive excited state of the carbonyl compound in this reaction?

(ii) Which orbtials of the carbonyl group are involved in the electronic transition in the photochemical process?

(iii) Give the structures of the free radical intermediate(s) involved in this reaction.

(iv) Give the structure of the photoproducts **B** and **C**.

(v) Which property of the intermediates play the key role in the formation of the major product in this reaction?

(vi) If this photochemical reaction is carried out in the presence of atmospheric oxygen, what result would you expect?

(36 marks)

(d) Indicating whether each of the following reactions is electrocyclic, cycloaddition or rearrangement, give the structure of the product(s).
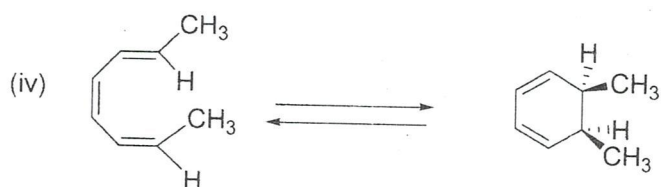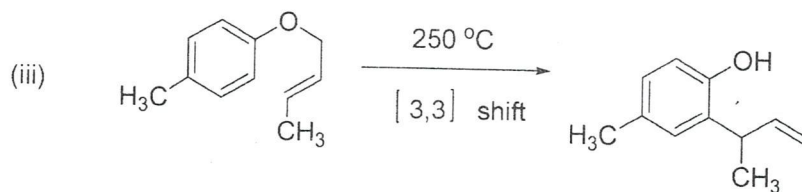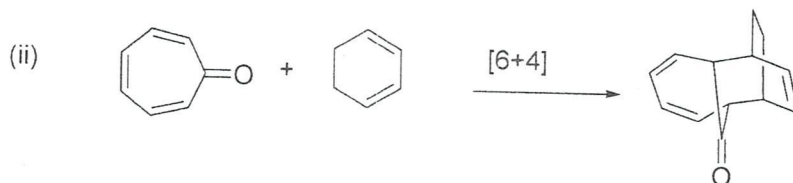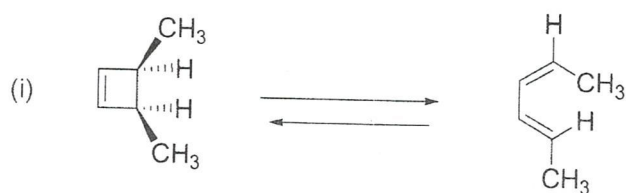

(i)

7

(ii)

$\xrightarrow{h\nu}$?

(iii)

$\xrightarrow{h\nu}$?
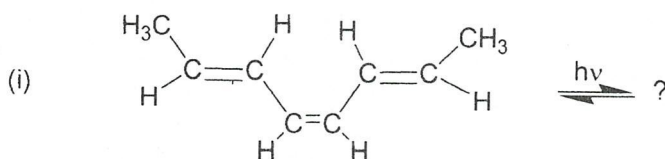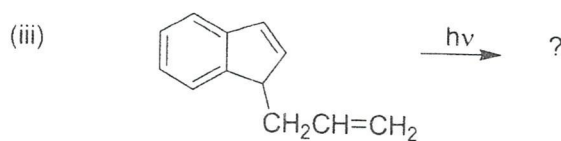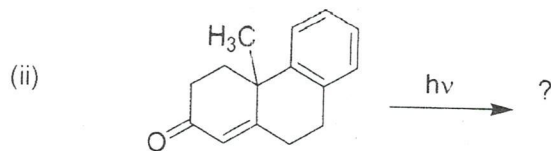
(08x 3 marks)

05. Answer **all** parts

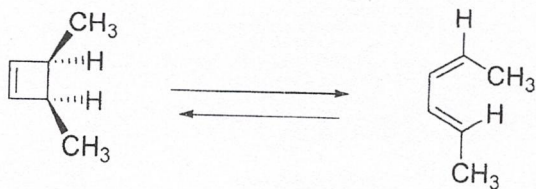(a) Classify the following reactions as electrocyclic, cycloaddition or sigmatropic reactions.

(i)

(ii)

$\xrightarrow{[6+4]}$

(iii)

$\xrightarrow[\ [3,3]\ \text{shift}\ ]{250\ ^{\circ}\text{C}}$
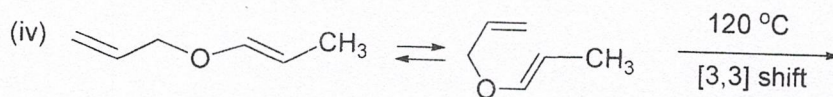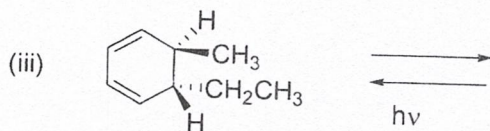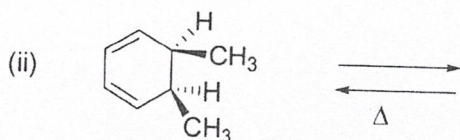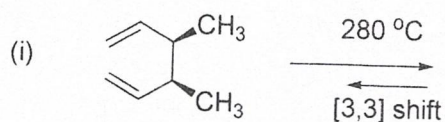
(iv)

(20 marks)

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(b) Using an orbital correlation diagram determine whether the following transformation is thermally allowed or photochemically allowed process.

(35 marks)

(c) Write down the products of the following pericyclic reactions with their correct stereochemistry.

(i)

  280 °C → [3,3] shift

(ii)

  ⇌ Δ

(iii)

  ⇌ hν

(iv)

  120 °C [3,3] shift

(v)

  +   [4+2] 40 °C
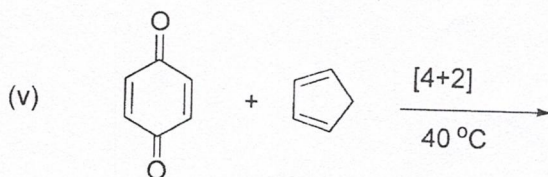
(25 marks)

d) The ^{1}HNMR spectrum of cyclopentadiene at room temperature showed only one(1) peak at $\delta = 4$ ppm. When the temperature was decreased to -50 °C there were three (3) peaks in the spectrum. Explain this observation.

(20 marks)

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