UNIVERSITY OF RUHUNA
BACHELOR OF SCIENCE (GENERAL) DEGREE LEVEL II (SEMESTER – I)
EXAMINATION JANUARY – 2022

SUBJECT : CHEMISTRY **TIME** : **Two (02)** hours
COURSE UNIT : CHE 2112 *(Descriptive organic chemistry & Spectroscopy)*

Answer **four (04)** questions only.

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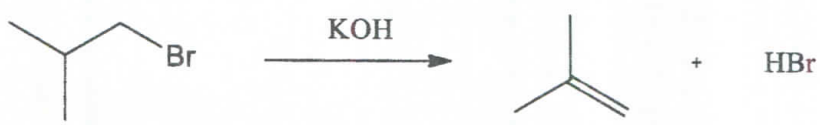
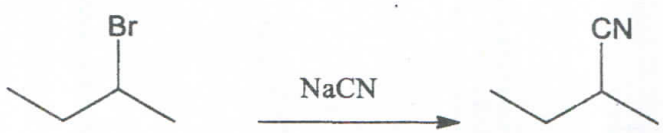
01. Answer **all** parts

(a) Identify the reaction type (addition, elimination, substitution) and draw the reactive intermediate involves in each reaction shown below.

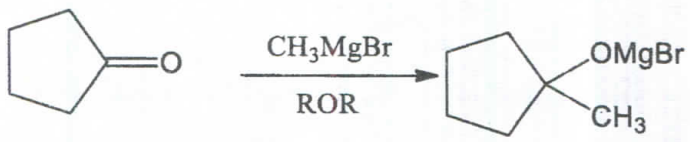
(i)



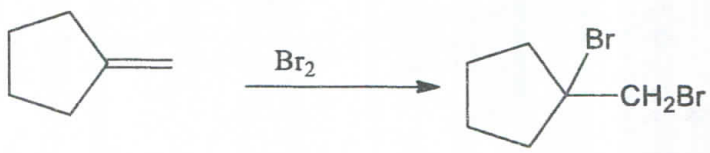
(ii)



(iii)



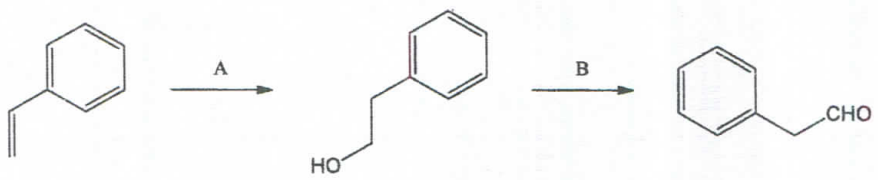
(iv)



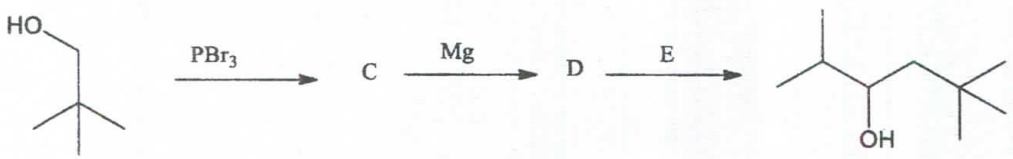
(24 marks)

(b) Fill in the missing reagents or intermediate formed in each of the following conversions.

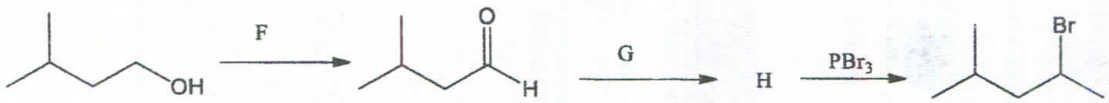
(i)



(ii)

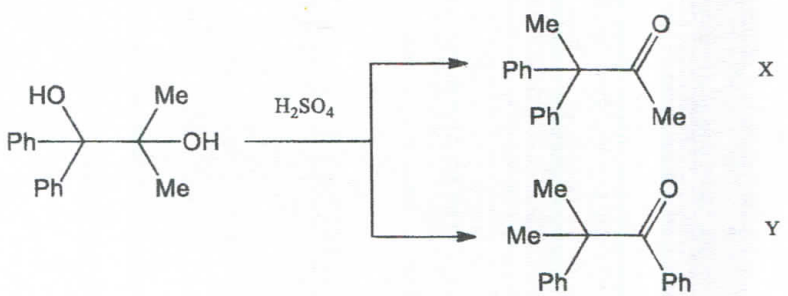


(iii)



(32 marks)

(c) Based on the given pinacol rearrangement of a diol, answer the questions given below.



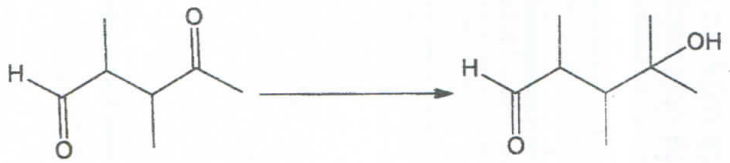
(i) State which product (from X and Y) will be formed from the reaction with explanations.

(ii) Draw the possible mechanism for the product formation mentioned in (i).

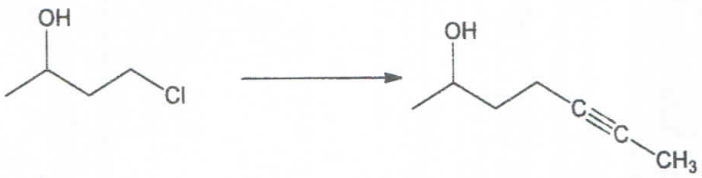
(24 marks)

(d) With necessary chemical reagents and intermediates show how you would carry out following transformations. (Hint: Protecting groups may involve in the reactions)

(i)



(ii)

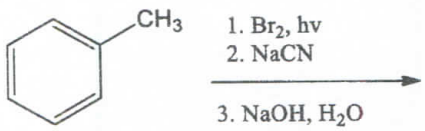


(20 marks)

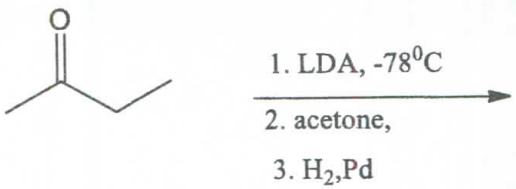
02. Answer **all** parts.

(a) Predict the major product of each of the following reactions

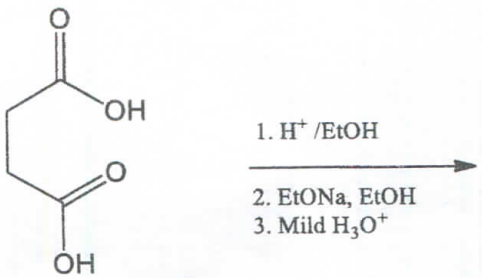
(i)



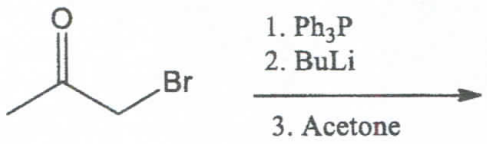
(ii)



(iii)



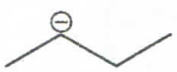
(iv)



(32 marks)

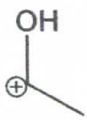
(b) Provide synthetic equivalent for each given synthon.

(i)

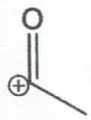


(ii)

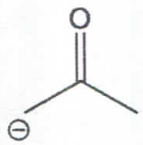
(iii)



(iv)

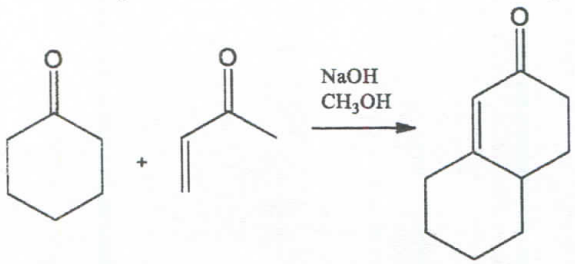


(v)



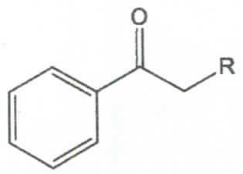
(20 marks)

(c) Provide a complete mechanism for the following transformation.



(18 marks)

(d) Use the following target molecule to answer the questions below.



(i) Carryout a retrosynthetic analysis for the target molecule.

(ii) Provide a detailed synthetic scheme for the synthesis of the target molecule based on the retrosynthetic analysis proposed in (i).

(30 marks)

03. Answer **all** parts

(a) (i) List four main uses of Natural products in human life.

(ii) Why Natural Product Chemistry is important in the field of science (list **four** reasons)?

(iii) State what is the most used extraction method for volatile oil extraction in natural product chemistry.

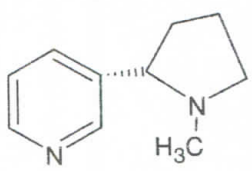
(iv) If your target is to isolate almost all bioactive compounds from a medicinal plant, out of gradient and isocratic extraction methods what is the most suitable?

(30 marks)

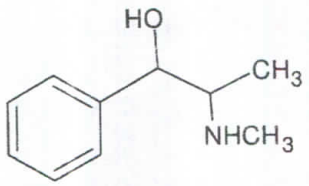
(b) (i) Which property of an alkaloid is important in the isolation of them from a plant?

(ii) State why alkaloids are important to human being?

(iii) Structures of Ephedrine and Nicotine are given below. Giving reasons, categorize each into alkaloid amine / true alkaloid.

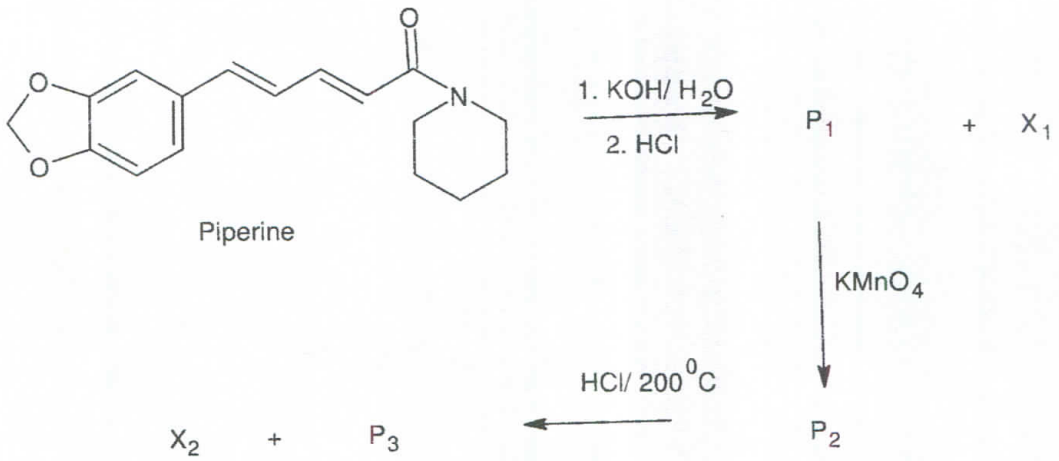


Nicotine



Ephedrine

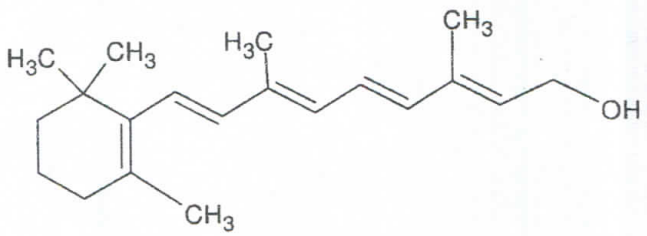
(iv) Degradation and oxidation reactions are important in the structure elucidation process of Natural Products. The following reactions have been carried out in the structure elucidation process of piperine.



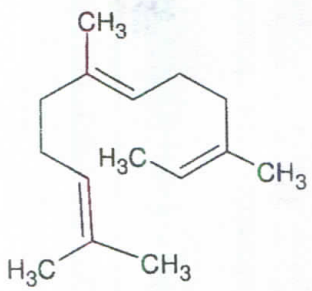
Draw the structures of **P_1, P_2** and **P_3.**

(40 marks)

(c) (i) Highlighting the connection points (appropriate carbons), show whether following compounds obey with isoprene rule.

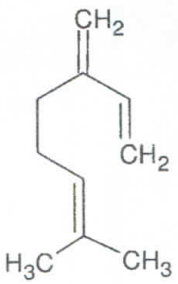


(I)

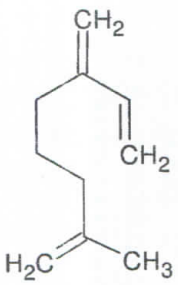


(II)

(ii) Two structures (**A** or **B**) given below, can be suggested for the structure of mycene. How can the results of ozonolysis be used to confirm the real structure? Note: draw the appropriate structures.



(A)



(B)

(30 marks)

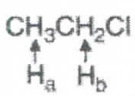
04. Answer **all** parts

(a) The chemical shift is one of the important parameters in NMR spectroscopy, which plays a major role in structure elucidation.

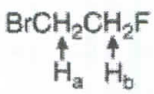
(i) Define the term chemical shift used in NMR spectroscopy.

(10 marks)

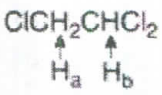
(ii) Giving reasons, indicate which hydrogen (H_a or H_b) will have higher chemical shift value in the molecules **A**, **B** and **C?**



A



B



C

(15 marks)

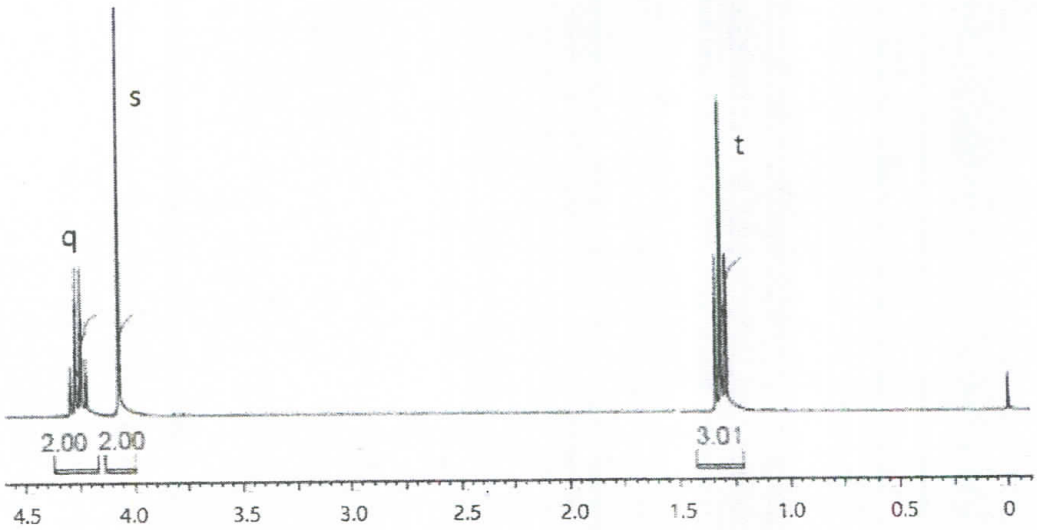
(iii) If you have been provided with ^1H NMR spectra of the above three molecules (**A**, **B** and **C**), how would you assign these three molecules for the given spectra? **Note:** assume that the halogen does not contribute for spin-spin coupling.

(15 marks)

(b) In a magnetic field, the loosely held π-electrons in alkenes and alkynes affect their ^1H NMR chemical shifts. In ^1H NMR spectra, chemical shifts of alkenyl protons are observed around 4.5-6 ppm while the chemical shifts of alkynyl protons are observed around 2.5 ppm. Briefly describe this effect.

(20 marks)

(c) The ^1H NMR spectrum below is shown for the molecule **P** with the molecular formula of $C_4H_7O_2Cl$. It shows an infrared absorption peak at 1740 cm^{-1}. Giving reasons, propose a plausible structure for the molecule **P**. (Integration ratio of the three NMR peaks are 3:2:2)



(40 marks)

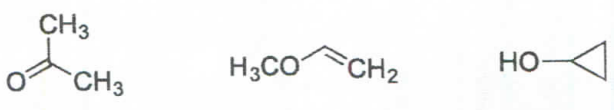
05. Answer **all** parts

(a) (i) Explain how you would calculate degrees of vibrations of linear and non-linear molecules theoretically.

(ii) "Theoretical number of vibrations is seldom observed". Give **five** reasons to support this statement.

(24 marks)

(b) Consider the three isomers of molecular formula C_3H_6O given below. Explain how you would use IR spectroscopy to distinguish these three molecules. Identify one characteristic IR absorption for each isomer and state it's features.



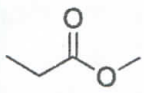
A **B** **C**

(12 marks)

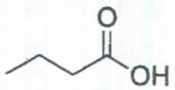
(c) IR spectrum for a compound with the molecular formula $C_4H_8O_2$ is given below.

(i) ***Giving reasons*** suggest which isomer given below best corresponds with the given IR spectrum.

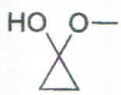
(ii) Assign **four** signals to the corresponding vibrations of the molecule you suggested.



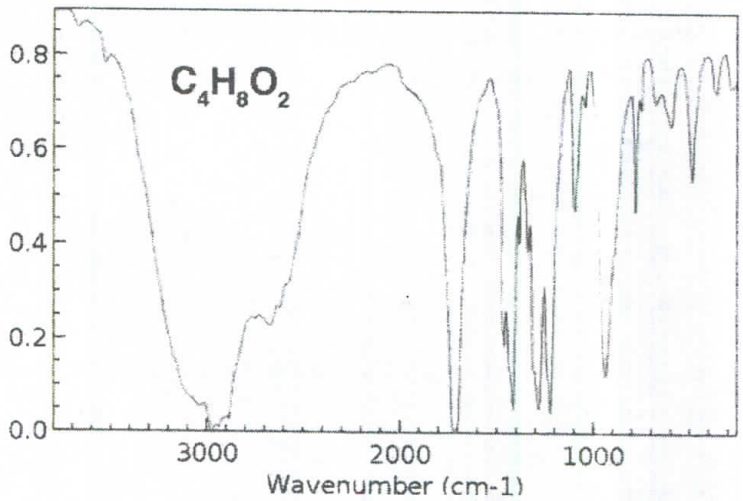
A



B



C



(28 marks)

(d) (i) The ESR spectrum of a radical with a single magnetic nucleus is split into four lines of equal intensity. What is the spin of the nucleus?

(ii) Predict and draw the expected ESR spectrum of methoxymethyl radical ($CH_3OCH_2\bullet$). Clearly explain how the hyperfine splitting pattern is predicted in your spectrum. (I value of H is ½).

(36 marks)

06. Answer **all** parts

(a) The molar absorptivity of 2,5-dimethyl-2,4-hexadiene in methanol is 13,100 L mol^{-1} cm^{-1}.

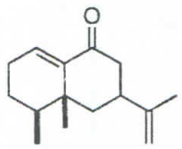
(i) Assuming the path length as 1.00 cm, calculate the required concentration of this diene in methanol to give an absorbance of 1.6.

(ii) What concentration of this diene in methanol would give a 25% transmittance?

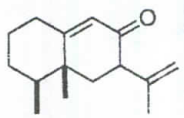
(16 marks)

(b) Eremophilone and *allo*-eremophilone are isomers. Using Woodward-Fieser rules estimate the λ max value expected for the lowest energy $\pi \rightarrow \pi^*$ electronic transition. Can you distinguish them by UV-Visible spectroscopy?

(Base value for six membered ring or acyclic enone = 215 nm; increment value for double bond extending conjugation = 30 nm; alkyl groups or ring residues at α, β, γ, and higher positions = 10, 12, 18 respectively; exocyclic double bond = 5 nm.)



Eremophilone



Allo-eremophilone

(20 marks)

(c) Electron impact ionization (EI) is a technique used to ionize the sample in a mass spectrometer.

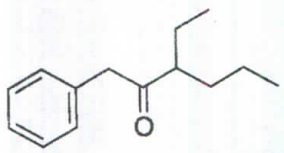
(i) Briefly explain the above ionization technique.

(ii) Name **three** other common ionization techniques used in mass spectrometry.

(24 marks)

(d) The following compound generates the fragments with m/z values given below during its mass spectrometric analysis.

m/z = 85
m/z = 91
m/z = 113
m/z = 119
m/z = 162
m/z = 176



m/z = 204

(i) Draw **four** fragmental structures match with the given m/z values.

(ii) Give a plausible mechanism for the formation of each fragment you proposed in part (i).

(40 marks)

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