UNIVERSITY OF RUHUNA
BACHELOR OF SCIENCE (GENERAL) DEGREE LEVEL II (SEMESTER – I)
EXAMINATION JULY/AUGUST – 2023

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

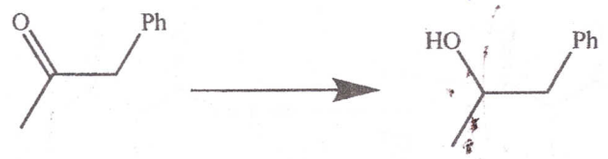
Answer **four (04)** questions only by selecting **at least 01** question from part **A**.

Part A

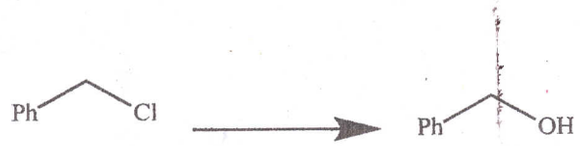
01. Answer **all** parts.

(a) For each of the following reactions, identify the reaction type (oxidation, reduction, substitution, or elimination) and provide the necessary reagents and reaction conditions to carry out the transformations.

(i)

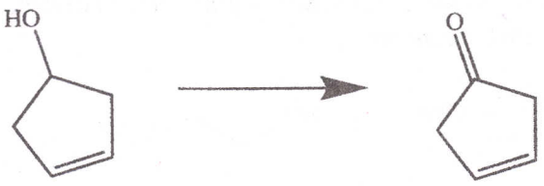


(ii)



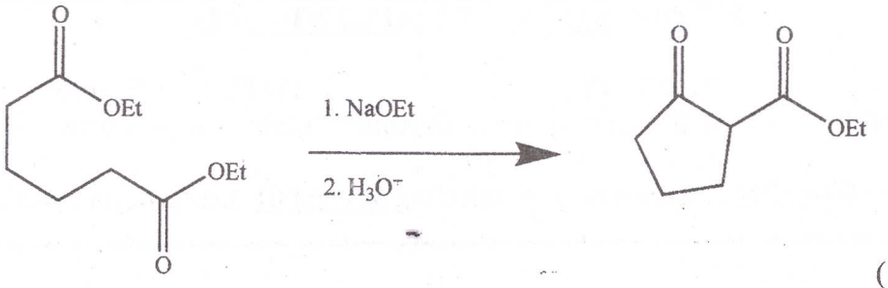
(iii)

(iv)



(24 marks)

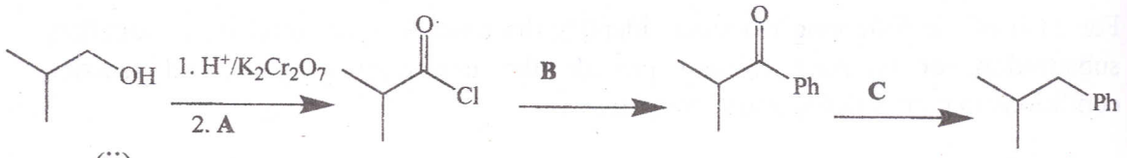
(b) Provide a plausible mechanism for the following transformation.



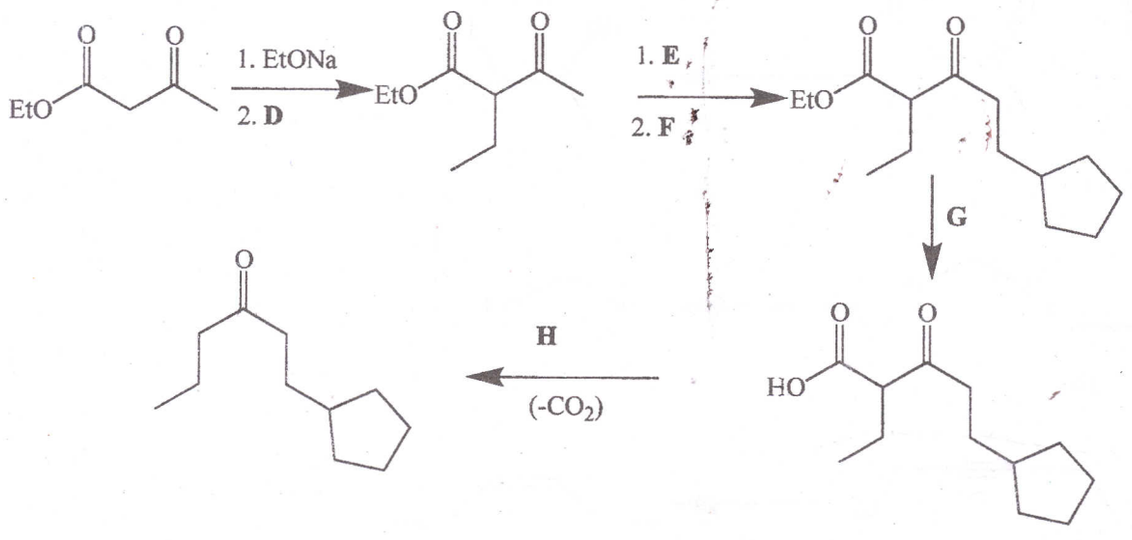
(14 marks)

(c) Fill in the missing reagents and reaction conditions (**A-H**) in each of the following conversions.

(i)



(ii)

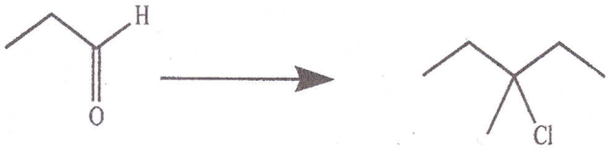


(32 marks)

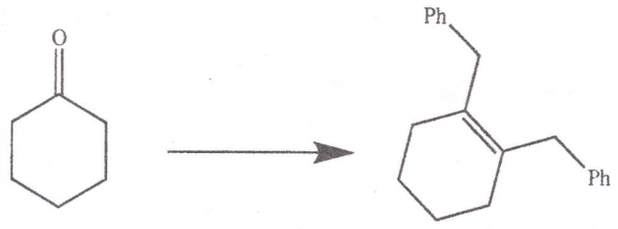
(d) With necessary chemical reagents, reaction conditions and intermediates, show how you would carry out following transformations.

(i)

(ii)



(iii)

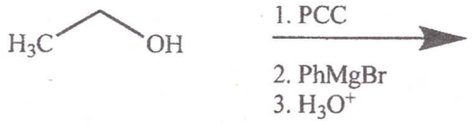


(30 marks)

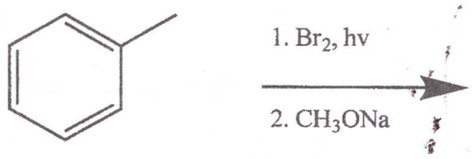
02. Answer **all** parts.

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

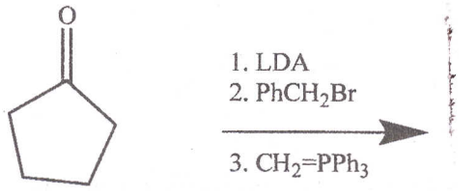
(i)



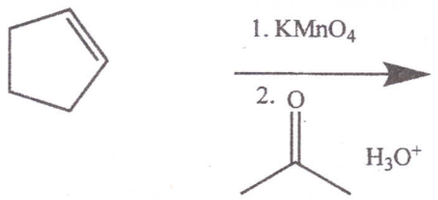
(ii)



(iii)



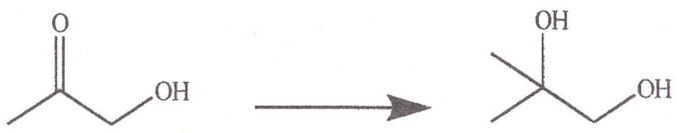
(iv)



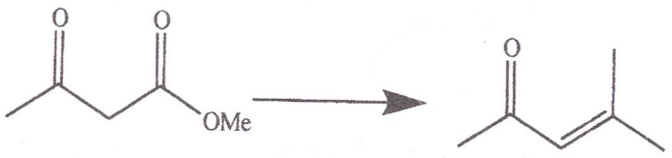
(20 marks)

(b) With necessary chemical reagents, reaction conditions and intermediates show how you would carry out following transformations. (Hint: you may use protecting groups during the synthesis).

(i)



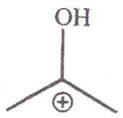
(ii)



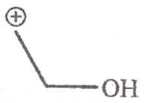
(20 marks)

(c) Provide synthetic equivalent for each of the given synthons.

(i)

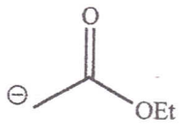


(ii)

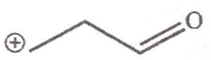


(iii)

(iv)

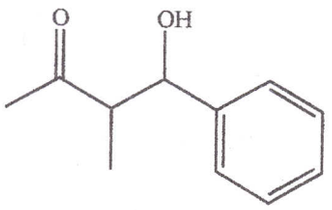


(v)

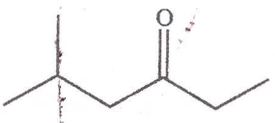


(20 marks)

(d) Use the following target molecules (**A** and **B**) to answer the questions given below.



A



B

(i) Carry out a retrosynthetic analysis for the target molecules **A** and **B**.

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

(40 marks)

Part B

03. Answer **all** parts.

(a) (i) List out five (**05**) applications of Natural Products.

(ii) Write down four (**04**) scope of Natural Product Chemistry.

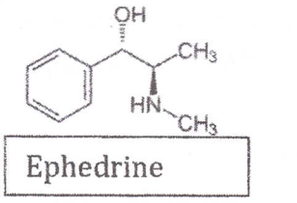
(iii) How does traditional knowledge on medicinal uses of plant relate to drug discovery?

(iv) What is the importance of knowing the target before planning the Natural Products extraction process?

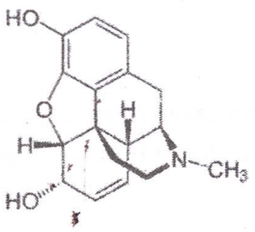
(30 marks)

(b) (i) Name chemical screening method & chromatographic method that can be used to analyze the nature of crude plant extract.

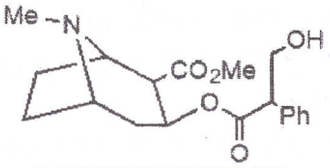
(ii) Consider the structures of the alkaloids given below and, categorize them into Atypical and Typical alkaloids.



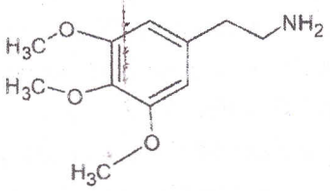
Ephedrine



Morphine

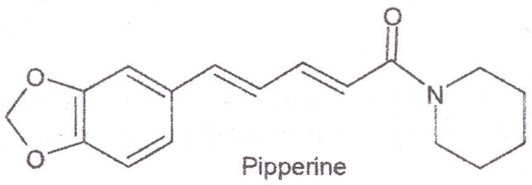


Atropine



Mescaline

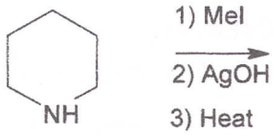
(iii) Piperine is a common alkaloid present in Black Pepper. The structure of piperine is given below:



Pipperine

What are the other isomers possible / available of this compound?

(iv) What are the products that would be formed in the following reaction that is used to determine the ring size of alkaloids? Draw the intermediate(s) formed during the reaction.



(40 marks)

(c) Answer following questions related to terpenes.

(i) What are the categories of terpenoids belong to essential oil?

(ii) Give brief illustration of the steps for extraction of essential oil using the fat absorption method.

(iii) Draw the structure of basic biological unit for the biosynthesis of tepenoids in plants.

(30 marks)

04. Answer **all** parts.

(a) ^{1}H NMR spectroscopy is a powerful technique used in structure elucidation of organic molecules. Briefly explain the following terms used in NMR spectroscopy.

(i) Chemical shift

(ii) Spin-spin coupling

(20 marks)

(b) The ^{1}H NMR spectrum of compound **X** gives a singlet and a doublet at 315 and 1548 Hz, respectively when the spectrum is acquired at 300 MHz NMR spectrometer.

(i) Derive the chemical shifts of the above two peaks.

(ii) What would be the frequency (ν) of the singlet obtained for the compound **X** if this spectrum would be acquired at 500 MHz NMR spectrometer?

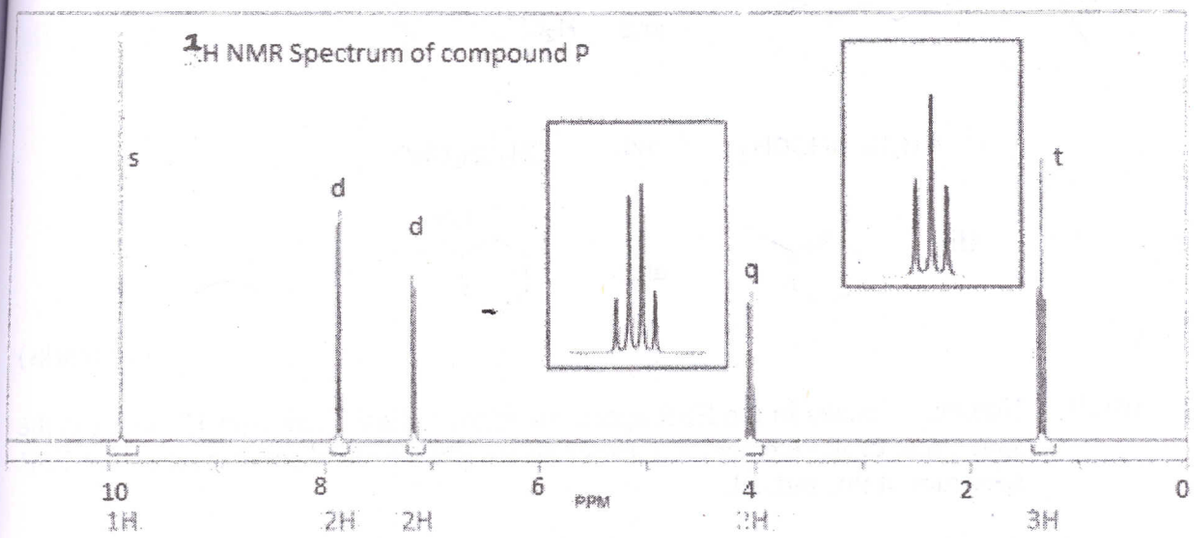
(20 marks)

(c) "A ^{1}H NMR signal can split into either a *triplet* or a *doublet of doublets* due to the effect of two other protons, which are less than three σ-bonds apart." Explain this statement using a suitable stick diagram(s).

(20 marks)

(d) The ^{1}H NMR spectrum of compound **P** ($C_9H_{10}O_2$) is shown below. Giving reasons, propose a plausible chemical structure for the compound **P**. (Integrations of the NMR peaks are given under the spectrum).

(25 marks)



(e) Explain how NMR spectroscopy can be used to distinguish between phosphorous acid (H_3PO_3) and phosphoric acid (H_3PO_4). (**Note:** I=½ for both ^1H and ^{31}P).

(15 marks)

05. Answer **all** parts.

(a) Arrange the following three molecules (**A**, **B**, and **C**) in ascending order of the C-H stretching vibration indicated by an arrow. Provide a brief explanation for the observed change in stretching frequencies in the order you suggested.

A $CH_3-CH_2-CH_2-CH_2-C\equiv C-H$

B $CH_3-CH_2-CH_2-CH_2-CH=CH-H$

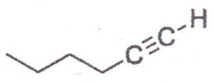
C $CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-H$

(20 marks)

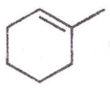
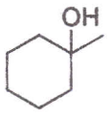
(b) A very dilute solution of ethanol in carbon tetrachloride (CCl_4) shows a sharp IR band at 3580 cm^{-1}. As the solution is made more concentrated, a new (broad) band appears between 3250 - 3350 cm^{-1}. On further concertation, the sharp band disappears, and it is entirely replaced by the broad band. Briefly explain the reason for this observation.

(20 marks)

(c) Explain how you would distinguish following pairs of molecules by using IR spectroscopy. Clearly mention the characteristic peaks you use with their functional group assignments.

(i)  and 

(ii) $H_2C{=}CHOCH_3$ and CH_3CH_2CHO

(iii)  and 

(30 marks)

(d) (i) Number of peaks in the ESR spectrum of the radical $(MH_3)^{\bullet}$ is 12. What is the spin value of the element M? Describe the peak pattern you expect in the ESR spectrum of this radical.

(ii) Calculate and compare the number of lines in the ESR spectra of the radicals XH_2 and X_2H_2 if the nuclear spin of X and H are 5/2, and ½, respectively.

(30 marks)

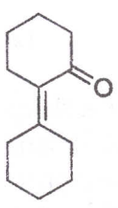
06. Answer **all** parts.

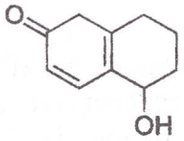
(a) Explain how doubling the concentration of a specific absorbing sample affects absorbance (A) and molar absorptivity (ε).

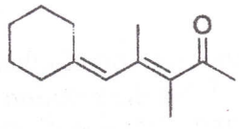
(10 marks)

(b) Showing your calculations, predict the wavelength of maximum absorption (λ_{max}) for the following three molecules using Woodward-Fieser rules.

(Note: Base value for 6 membered ring or acyclic enone: 215 nm, increment values; double bond extending conjugation: 30 nm, alkyl groups or ring residues: α, β, γ and higher: 10, 12, 18 nm, exocyclic double bond: 5 nm. homoanular diene system: 39 nm)

(i) 

(ii) 

(iii) 

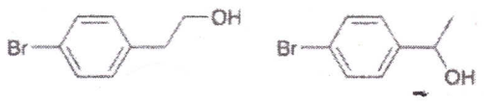
(30 marks)

(c) Briefly explain the Electron Impact ionization (EI) technique used to ionize a sample in a mass spectrometer.

(20 Marks)

(d) The following two isomers were each subjected to mass spectrometric analysis. Some of the significant peaks from each of the two spectra are given below.

Data set **X**, m/z = 202, 200, 187, 185, 159, 157, 121
Data set **Y**, m/z = 202, 200, 171, 169, 121



A B

(i) Draw the structures for the fragments with m/z values of 185/187, 169/171, 157/159, and 121. Show the charged atoms in those fragments.

(ii) Giving reasons, match each mass spectrometry data sets (**X**, **Y**) to one of the two alcohol isomers (**A**, **B**) given above.

(iii) Write mechanisms for the formation of the proposed fragments with m/z values of 185/187 and 169/171 in (d) (ii).

(40 marks)

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