MAASAI MARA UNIVERSITY

REGULAR UNIVERSITY EXAMINATIONS
2023/2024 ACADEMIC YEAR
THIRD YEAR SECOND SEMESTER

SCHOOL OF PURE, APPLIED AND HEALTH SCIENCES
BACHELOR OF SCIENCE (BSc.)

COURSE CODE: CHE 3225
UNIT NAME: ANALYTICAL TECHNIQUES IN STRUCTURAL DETERMINATION

DATE: **TIME:**

INSTRUCTIONS TO CANDIDATES

1. Answer question ONE and any other TWO
2. All instructions regarding University examinations apply

This paper consists of 5 printed pages. Please turn over:

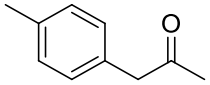
SECTION A

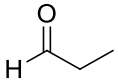
QUESTION ONE (20MARKS)

a) Briefly distinguish between the following spectroscopic terms (4 marks)
   i. Upfield and downfield
   ii. Homotopic hydrogens and enantiotopic hydrogens (use examples)

b) Describe the functions of four main components of an Atomic Absorption Spectroscopy (AAS). (4 marks)

c) Consider the following molecules:

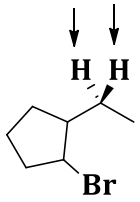
P 

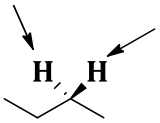
Q 

   i. Determine the number of ^{1}H signals, splitting pattern and abundance. Draw a sketch of ^{1}H NMR spectrum. (For each molecule). (4 marks)
   ii. Determine the number of ^{13}C signals for each molecule. (2 marks)

d) The 1H NMR signal for dimethylsulphoxide-d_6 (C_2D_6SO) appears at 1336 Hz when recorded on a 400-MHz NMR spectrometer. Calculate the chemical shift in ppm? (2 marks)

e) Indicate whether the hydrogens (pointed with arrows) are homotopic, enantiotopic or diastereotopic. Do these hydrogens have same or different chemical shifts? Briefly explain. (4 marks)

i) 

ii) 

SECTION B

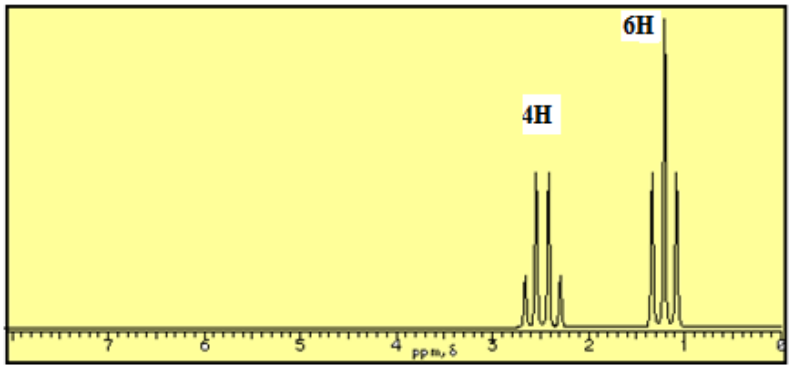
QUESTION TWO (15 MARKS)

a) What information can we learn from a routine DEPT experiment regarding hydrogen or carbon nuclides that we cannot learn form a routine 13C NMR? (2 marks)

b) Propanone and 2-propen-1-ol are constitutional isomers. Show how to distinguish between them by IR spectroscopy. (2 marks)

c) 2,2-dimethylpentane shows an intense peak in the mass spectrum at m/z = 57. Propose a likely structure for this fragmented ion. (3 marks)

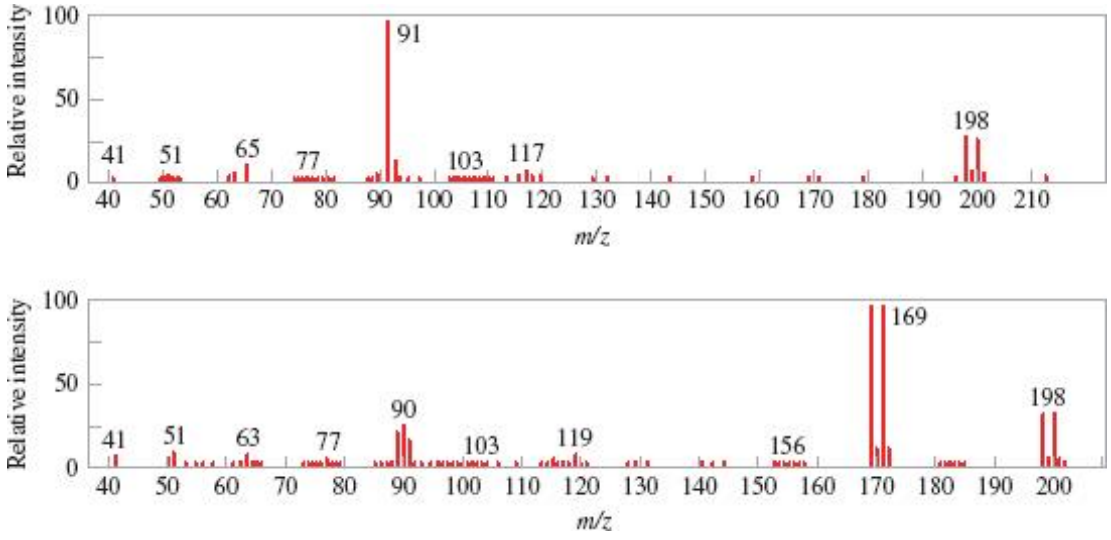
d) Propose a structure for the compound $\mathbf{C_5H_{10}O}$ that exhibits the following ^{1}H NMR spectrum. (4 marks)



e) The spectroscopic techniques MS, IR, UV-Vis and NMR are said to be complementary in structure determination. What structural information does each of these techniques provide? (4 marks)

QUESTION THREE (15 MARKS)

a) 1-bromo-4-propylbenzene and (3-bromopropyl)benzene are constitutional isomers. These two isomers give distinguishable mass spectra shown below. Match the correct isomer to its corresponding mass spectrum. Show your reasoning! (2 marks)



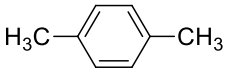
b) Briefly explain the general principles of Fourier transform infrared (FTIR) spectroscopy. (3 marks)

c) Determine the number of 1H NMR signals and splitting pattern (Label each unique carbon with letters A, B, C…..) (6 marks)

(I)

pentan-3-one

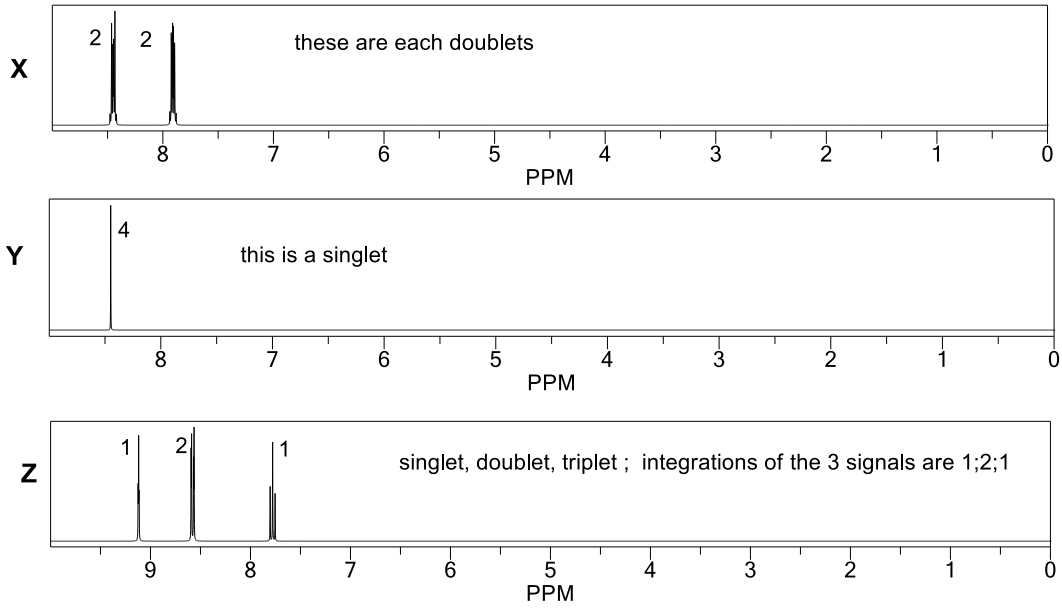
(II)



(III)

d) In 2D NMR experiments, what is the general difference between correlation spectroscopy (COSY) and Heteronuclear Multiple Quantum Correlation (HSQC)? (1 mark)

e) The 3 ^{1}H NMR spectra below are for the three dinitrobenzene isomers. Draw the correct compound that corresponds to each of the given spectra X, Y and Z. Give a brief explanation on how you deduced and matched each structure to spectrum. (3 marks)



QUESTION FOUR (15 MARKS)

a) Provide the region(s) of the electromagnetic spectrum utilized in NMR, IR and UV-Vis spectroscopic techniques and what transitions do absorption of these electromagnetic radiations result? (3 marks)

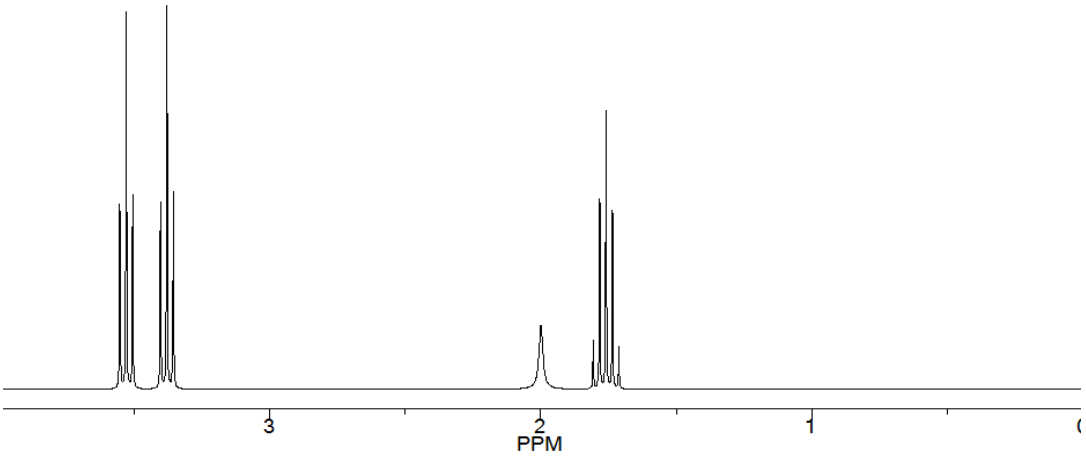
b) Hydrocarbon **B**, C_6H_6, gave an NMR spectrum with two signals: δ 6.55 and δ 3.84, peak area ratio 2:1. When warmed in pyridine for three hours, **B** was quantitatively converted into benzene. Mild hydrogenation of **B** yielded **C**, whose spectra showed the following:

Mass spectrum, mol. Wt. 82; IR spectrum, no double bonds, and NMR spectrum, one broad peak at δ 2.34.

i. Can you suggest the possible structures for compounds **B** and **C**? (4 marks)

ii. When NMR spectrum of B was zoomed in, the upfield signal was a quintet, and the downfield signal was a triplet. How can one account for these multiplicities? (2 marks)

c) Carboxylic acid **P** is treated with $LiAlH_4$ to give a saturated product, compound **Q**. The ^{1}HNMR of the unknown **Q** is shown below. Compounds **P** and **Q** are known to contain at least one chlorine atom. Using the info provided, determine the structures of **P** and **Q**. Show your reasoning! (4 marks)



d) Account for fragments having a *m/z* value of 45 and 55 in the mass spectrum of 2-hexanol by drawing structures of the fragments. (2 marks)

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