TECHNICAL UNIVERSITY OF MOMBASA

FACULTY OF APPLIED AND HEALTH SCIENCES

DEPARTMENT OF PURE & APPLIED SCIENCES

UNIVERSITY EXAMINATION FOR:

BACHELOR OF TECHNOLOGY IN APPLIED CHEMISTRY

ACH 4315: ORGANIC SPECTROSCOPY

END OF SEMESTER EXAMINATION

SERIES: DECEMBER Pickyear

TIME: 2HOURS

DATE: Pick Date Dec2016

Instructions to Candidates
You should have the following for this examination
-Answer Booklet, examination pass and student ID
This paper consists of **FIVE** questions. Attempt question ONE (Compulsory) and any other TWO questions.
Do not write on the question paper.

Question ONE

(a) Define the following terms as applied in NMR spectroscopy: **[3 marks]**

  i.   Chemical shift
  ii. Spin-spin coupling constant
  iii. Spin multiplicity

(b) Provide a possible structure of each of the following organic compounds with the given IR and ^{1}H-NMR data clearly indicating how you arrive at your suggestion:

  i. C_3H_8O IR: 3400 cm^{-1} (broad, strong)
                          ^{1}H-NMR: δ 4.9, singlet (1H); δ 4.0, septet (1H); δ 1.1, doublet (6H)
                          [4 marks]

  ii. $C_4H_7ClO_2$ IR: 3000 cm^{-1} (very broad, strong), 1730 cm^{-1} (strong)
                          ^{1}H-NMR: δ 11.6, singlet (1H); δ 4.2, triplet (1H); δ 2.1, quintet (2H);
                          δ 1.1, triplet (3H).
                          [4 marks]

(c) Describe the spectroscopic processes in UV spectroscopy that leads to an absorption spectrum.[**4 marks**]

(d) i. State the two types of molecular vibrations utilized in IR spectroscopy and provide with reason the vibration which will be registered at a higher IR absorption frequency.   [**4 marks**]

ii. State four factors that influence IR absorption frequency by organic molecules.   [**4 marks**]

(e) A molecule ion peak of unknown organic molecule appears at m/z value of 70. If the molecule is known to contain one atom of oxygen:

i. Determine its molecular formula by applying the Rule of Thirteen.   [**3 marks**]

ii. Determine the unsaturation index and provide a probable line bond structure of the molecule.[**4 marks**]

Question TWO

(a) State and explain by making use of relevant examples any two factors that affect chemical shift values for a given proton in a molecule.   [**4 marks**]

(b) State any two factors that influences coupling constant (J) between two coupled nuclei in ^1H NMR spectroscopy.   [**2 marks**]

(c) An organic compound (X) has a molecular formula of C_4H_8O. The ^{13}C-NMR and ^1H-NMR spectra of the compound are given below.

| ^{13}C NMR of compound X | ^1H NMR of compound X |
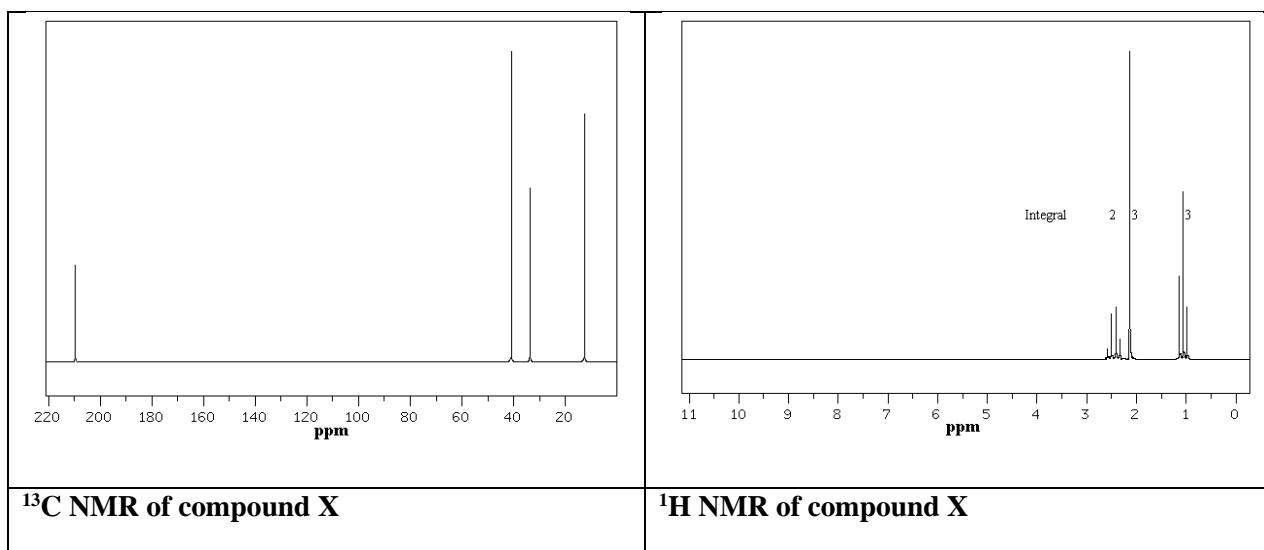
(i) Determine the double bond equivalence of the compound.   [**1 mark**]

(ii) If the compound has a strong IR absorption peak of ≈ 1700 cm^{-1}, suggest two possible classes of organic compounds which the compound may belong.   [**2 marks**]

(iii) State the multiplicity of the protons signal that appear in the low field region of ^1H NMR spectrum of the compound.   [**2 marks**]

(iv) Based on the unsauration index, IR data, ^{13}C NMR and ^{1}H NMR spectra, provide line bond structure of the compound (X) clearly accounting for the pieces of information obtained from each spectral data. **[9 marks]**

**Question THREE**

(a) Differentiate between the following pairs of terms as applied in UV spectroscopy.   **[4 marks]**

  i.   Hypsochromic shift and bathochromic shift
  ii.   Hyperchromic effect and hypochromic effect

 (b) Provide the mathematical expression of Beer-Lambert's law and explain why relatively dilute solutions are used in UV quantitative analysis.   **[3 marks]**
(c) Explain why broad absorption peaks are usually observed in UV spectra.   **[3 mark]**
(d) Calculate the expected λ max for the following pair of organic molecules by applying Woodward-Fieser rules and state with reason if it is possible to differentiate them by making use of UV spectroscopy.
                    [10 Marks]

i.

A   B

ii.

X

Y
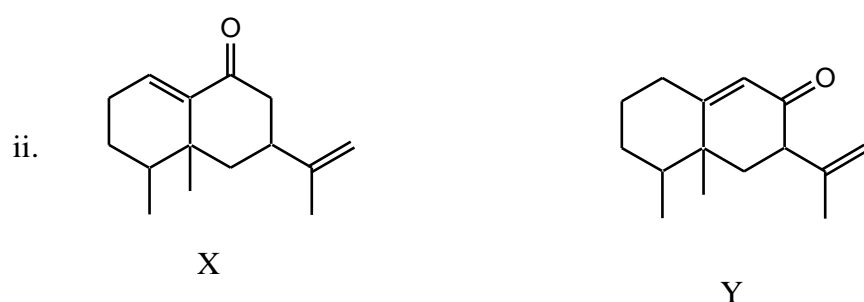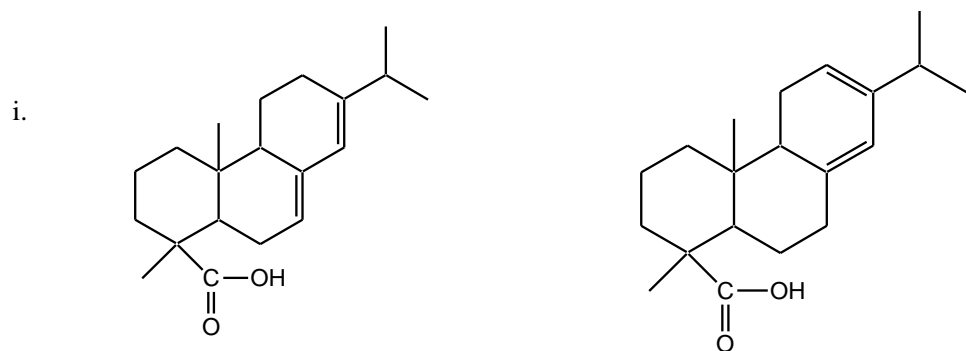
Question FOUR

(a) Define the following terms as applied in IR Spectroscopy. **[3 marks]**
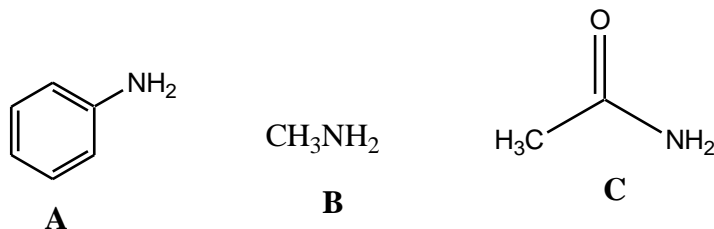   i.   Overtones
   ii.   Combination bands
   iii.   Fingerprint region

(b) Outline the effect of IR radiation on organic molecules state the type of information which can be deduced to help in structure elucidation. **[3 marks]**
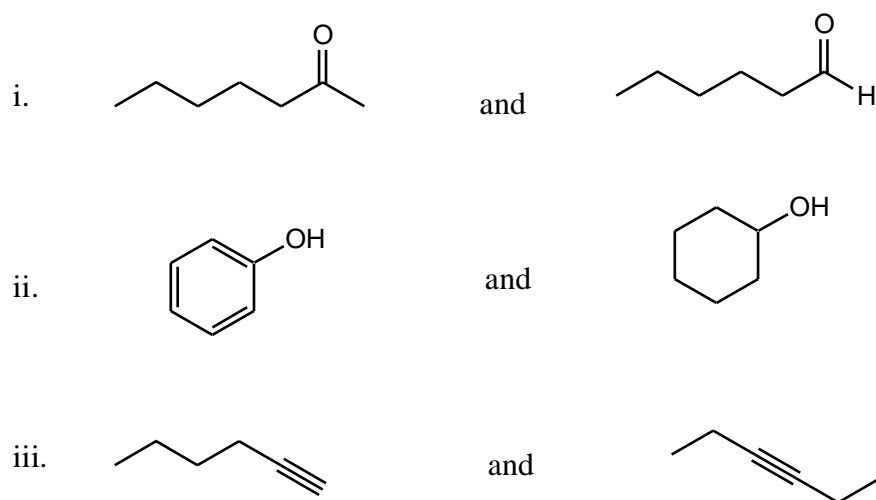
(c) Arrange the following molecules in the increasing order of ν N-H stretch in IR spectroscopy and justify your answer. **[5 marks]**

A   CH₃NH₂   H₃C—C(=O)—NH₂
                B   C

(d) Explain how you can make use of IR spectroscopy to differentiate between the following pairs of molecules. **[9 marks]**

i.   and

ii.   and

iii.   and

Question FIVE

(a) Define the following terms as applied in mass spectrometry. **[4 marks]**

   i.   Mass spectrum
   ii.   Base peak
   iii.   Molecular ion
   iv.   Metastable ion

(b) Describe the following rules as applied in mass spectrometry.   [**6 marks**]

    i.   Nitrogen rule
   ii.   Bromine and Chlorine rule

(c) The figure below id the MS spectrum of dipropylamine. Propose mechanism of fragmentation for the molecule to account for the signal registered at m/z of 101, 100, 72, 58 and 30.   [**10 marks**]