OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY
B.Sc. (Industrial Chemistry) Degree Examination **Part III**

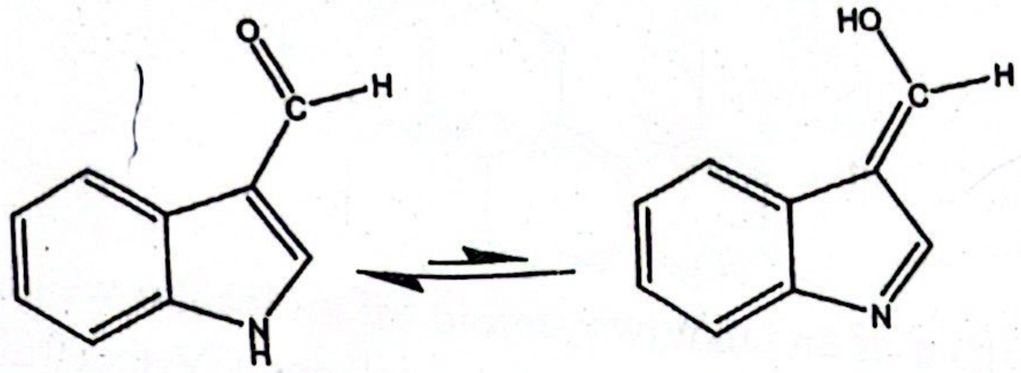
CHM 307 – Application of Spectroscopic Techniques
Harmattan Semester Examination (2023/2024 Session)

Time Allowed: 3 *hours* **Date: 3rd March 2025**

INSTRUCTION: Answer **any TWO** questions in Section **A** and **ALL** questions in Section **B.**

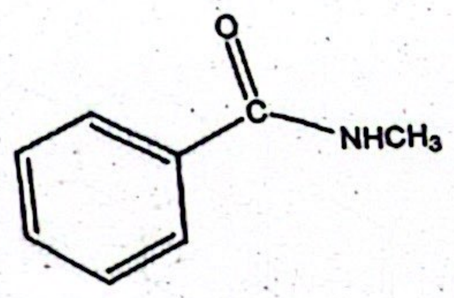
SECTION A: Answer any TWO questions

1(a). Shown below are the structures of indole-3-aldehyde and its enol tautomer. Give the IR absorption frequencies of each that could be used to differentiate them



Indole-3-aldehyde

(b). The IR spectrum of methyl benzamide, shown below, was taken and the following frequencies (average values) were obtained: 3450; 3050; 2980; 2840; 1680; 1610; 1590. Account for the absorption frequencies.



Methyl bezamide

(c). If the amide above is reduced to its corresponding amine, what changes in the IR absorption frequencies would you expect?

2 (a).

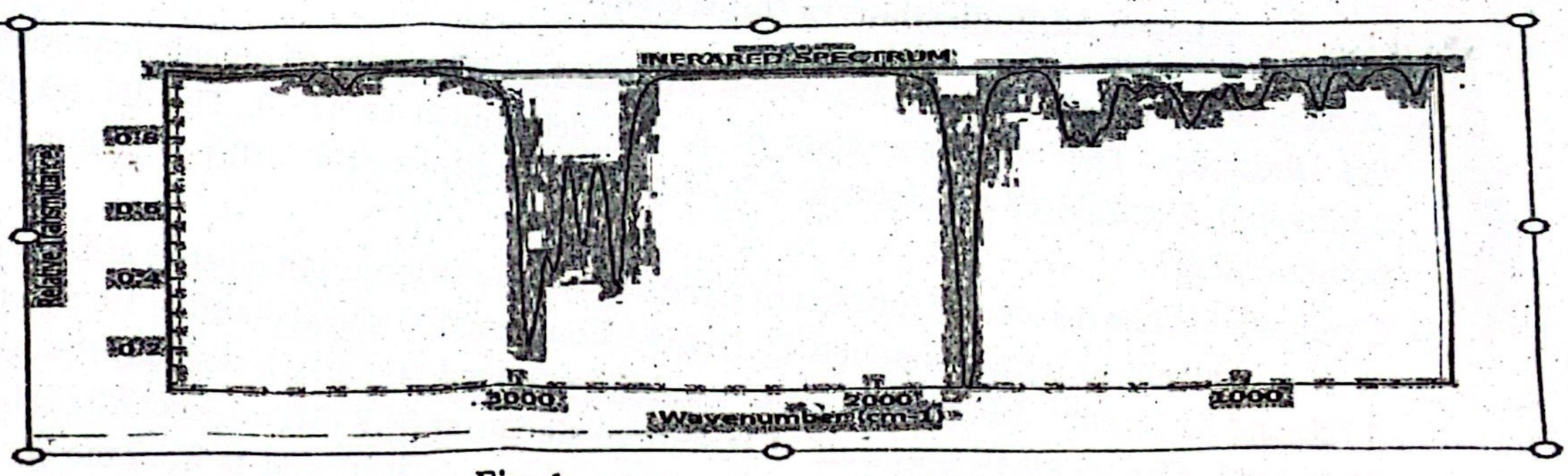
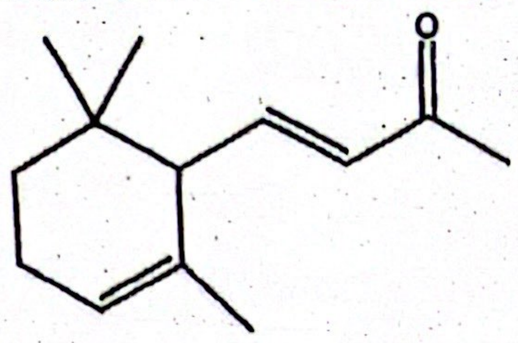


Fig. 1

(i). Which of the underlisted compounds would you expect to give the IR spectrum shown in **Fig, 1**: Butanol; Butane; Butanoic acid; Butanal; Butanone.

(ii). Identify any FOUR stretching absorption frequencies to support your answer

(b). Differentiate between the following pairs of compounds using UV spectroscopic method: (i)



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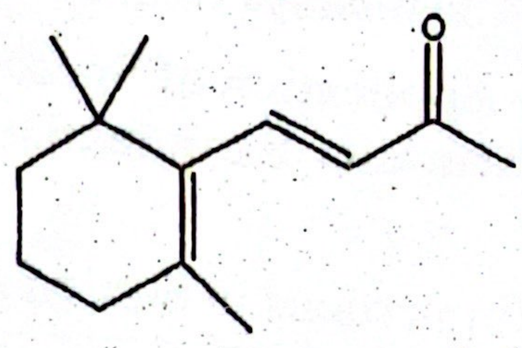
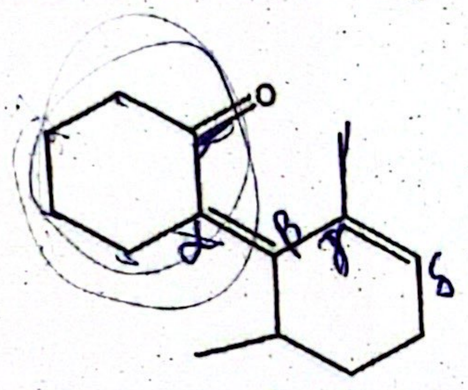


α- ionone β- ionone

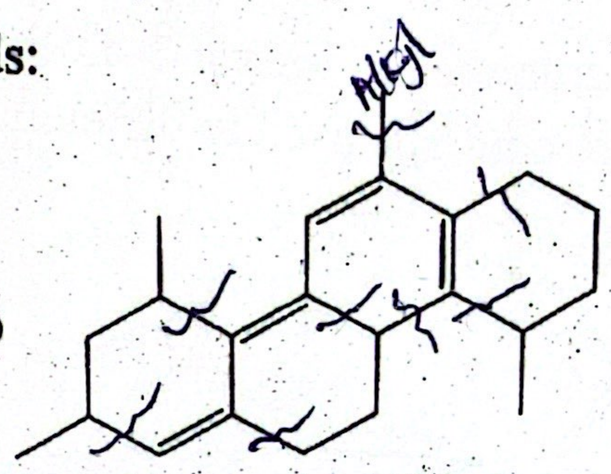
(ii). 1,1,3-trichloro-4,6-dimethylhepta-1,3,5-triene & 1,1,3-trichloro-4,6-dimethylhepta-1,4,6-trien

3(a). Deduce the λ_{max} of the following compounds:

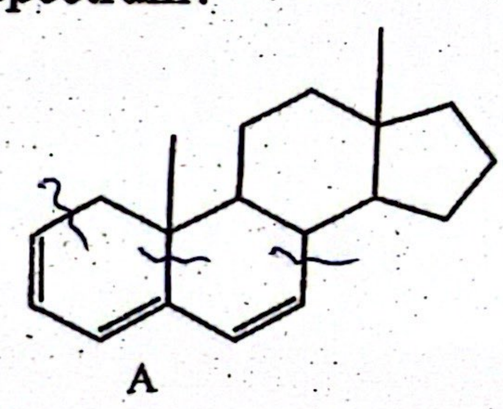
(i)



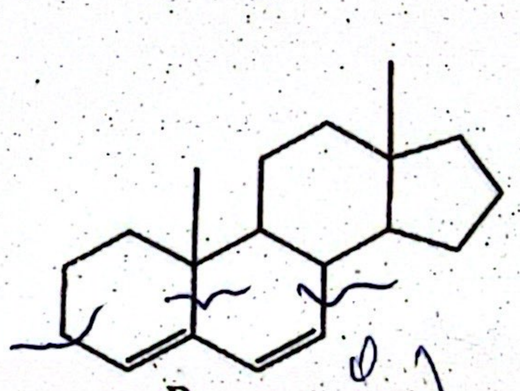
(ii)



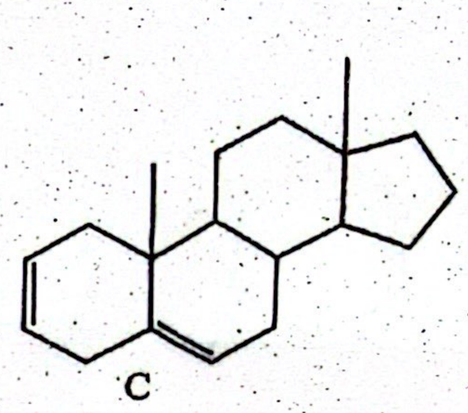
(b). A solution was prepared using 0.0010 g of an unknown steroid (of molecular weight around 255) in a 100 mL of ethanol. Some of this solution was placed in a 1 cm cell and UV spectrum was measured. This solution was found to have λ_{max} of 235 nm and absorbance of 0.74. (i) Compute the value of the molar absorptivity at 235 nm. (ii) Which of the following compounds below might give this spectrum?



A



B



C

SECTION B: Answer ALL questions in this section

4(a). A dichloro compound **A** was obtained as a by-product of a series of organic reactions conducted in the laboratory. The molecular mass of **A** was determined as 113.0. The ^{1}H NMR spectrum of compound **A** exhibited a quintet at δ 2.20 ppm and a triplet at δ 3.70 ppm. Give the structure of compound **A**?

(b). Compound **B** has molecular formula of CH_2O and strong IR absorption bands at 1710 and 2707 cm^{-1}. **B** was oxidized to give compound **C**, CH_2O_2. Compound **C** showed strong IR absorption bands at 1720 and 3250 cm^{-1}. Methylation of **C** yielded compound **D**, $C_2H_4O_2$ with an IR absorption band at 1740 cm^{-1}. The ^{1}H NMR spectrum of **D** showed signals at δ3.8 (3H, s), and 9.0 (1H, s). Deduce the structural features which you would expect in compounds **B**, **C** and **D** from the spectroscopic data provided and postulate appropriate structures for compounds **B**, **C** and **D**.

(c). The ^1H NMR Spectrum of a synthetic organic compound **E** is presented as Figure 1 below. It showed signals for different kinds of hydrogens and the molecular formula of Compound **E** was determined as $C_9H_{18}O$. The IR spectrum of **E** showed a prominent absorption band at 1705 cm^{-1}.

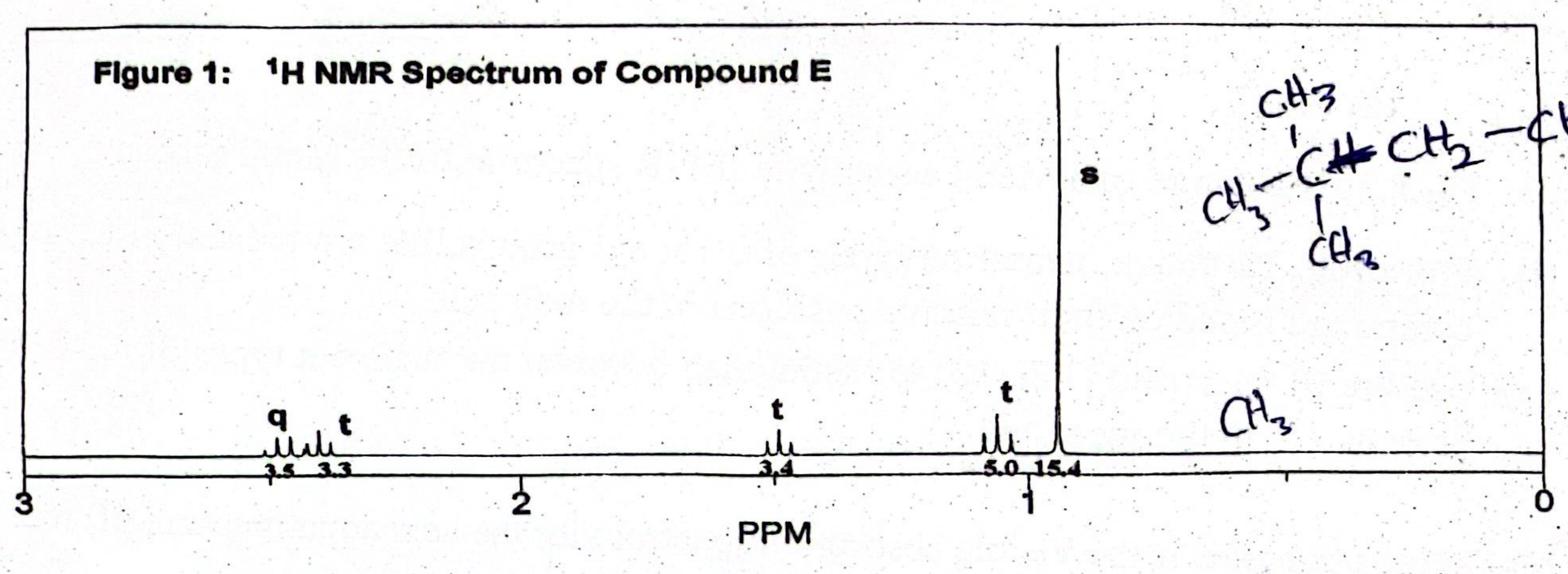
(i) Determine the integral height per hydrogen in compound **E**

(ii) Determine the number of different kinds of hydrogens in **E**

(iii) Calculate the number of each kind of hydrogens in the molecule and deduce the structural features that corresponds to each kind of hydrogens in compound **E**

(iv) Propose a structure for compound **E**, that is consistent with the exhibited structural features.

Figure 1: ^1H NMR Spectrum of Compound E

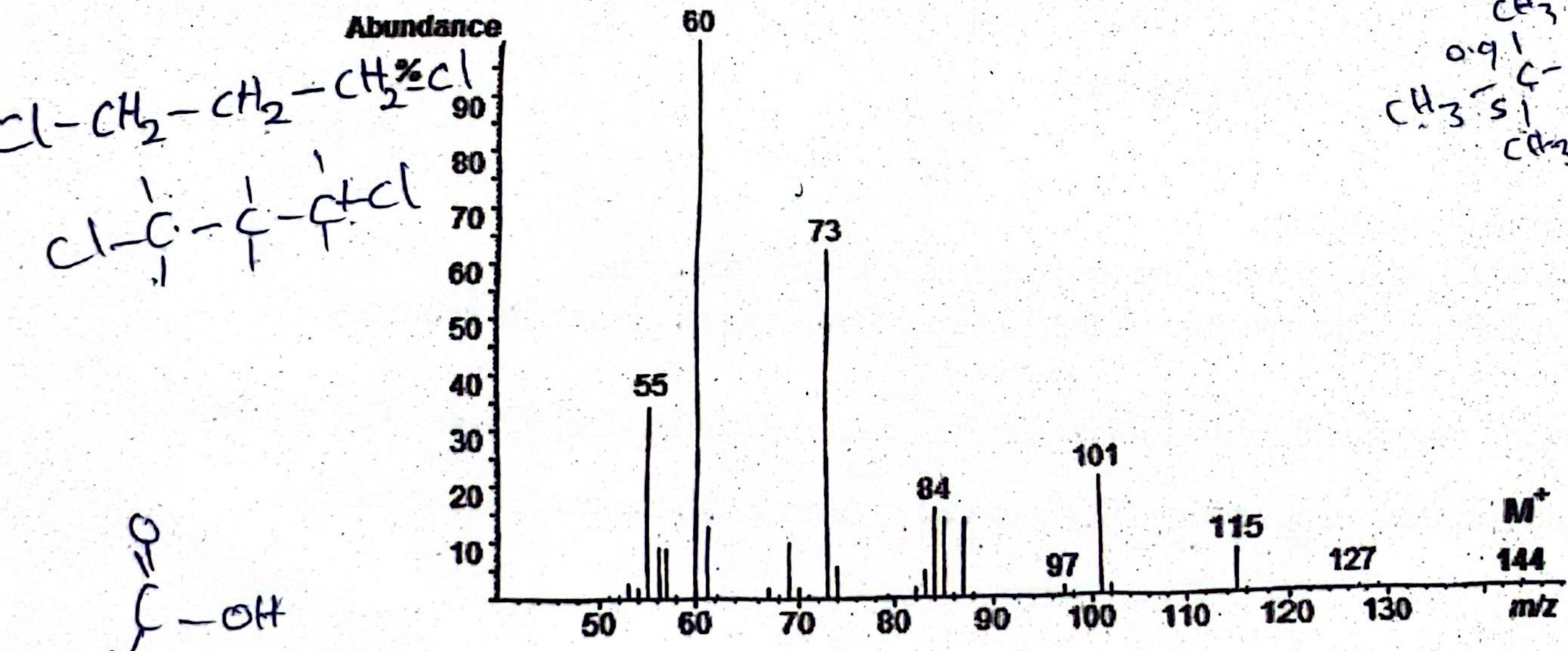


5(a). Account for the following peaks in the mass spectrum of 2-pentanone by showing the mechanism of fragmentation that resulted in each peak; m/z 43, 58 and 71

(b). The mass spectrum of a non-volatile compound **A** which can react with an aliphatic alcohol to produce a fruity volatile compound is presented below.

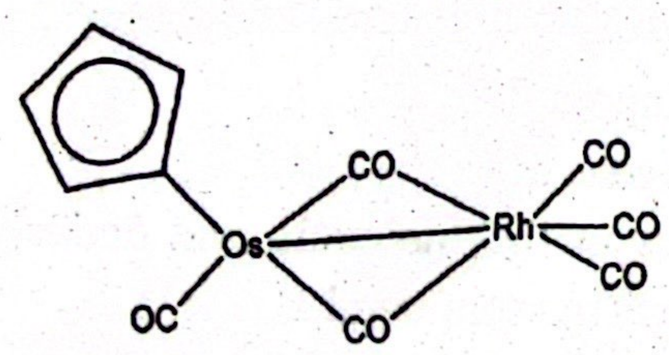
(i) Interpret the spectrum and determine the structure and name of the compound.

(ii) Show the mechanism of fragmentation that resulted in the following ion peaks; m/z 60 and 127 in the mass spectrum of compound A.

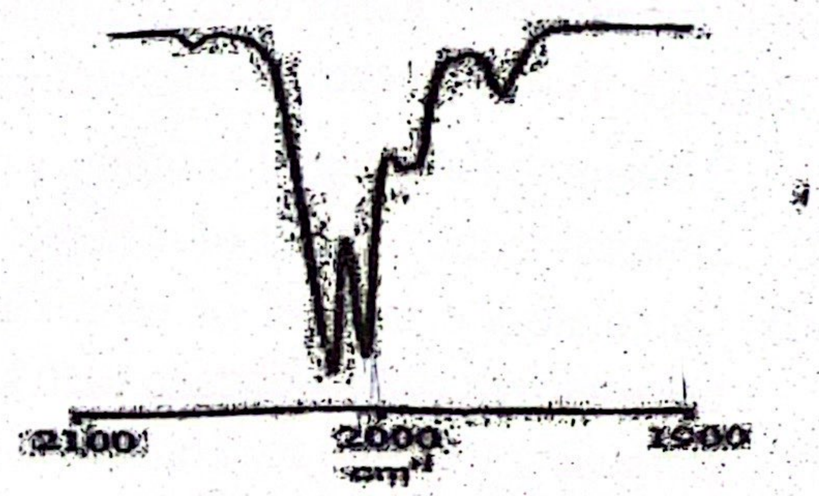


Mass spectrum of compound A

6(a).



(a)



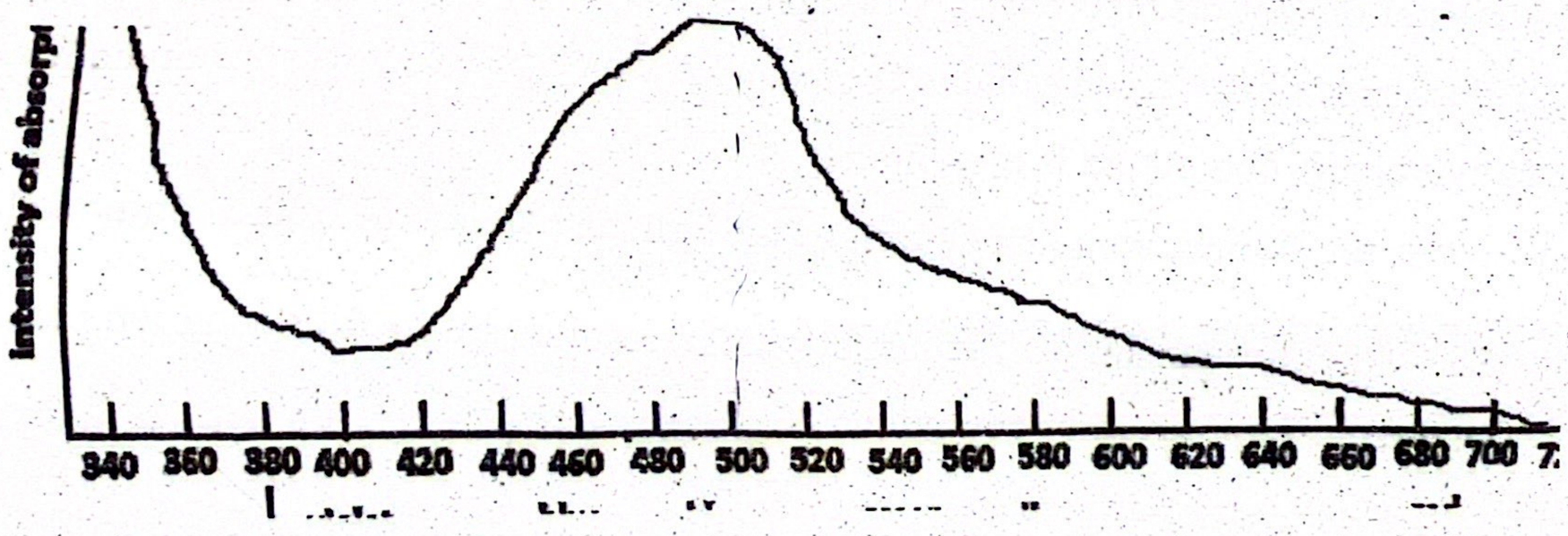
(b)

Fig 1. (a) Structure of a Metal carbonyl. (b) IR spectrum of the Metal carbonyl.

(i). From **Fig. 1a** above, name the types of carbonyl groups that are present in the organometallic compound based on their relative positions in the molecule

(ii). Use the IR spectrum (Fig. 1b) to distinguish between the different types of the carbonyl groups present in the molecule.

6(b). The spectrum below is the Visible absorption spectrum for the hexaaquatitanium(III) ion, $[Ti(H_2O)_6]^{3+}$



Wavelenth (nm)

(i). Interpret the spectrum.

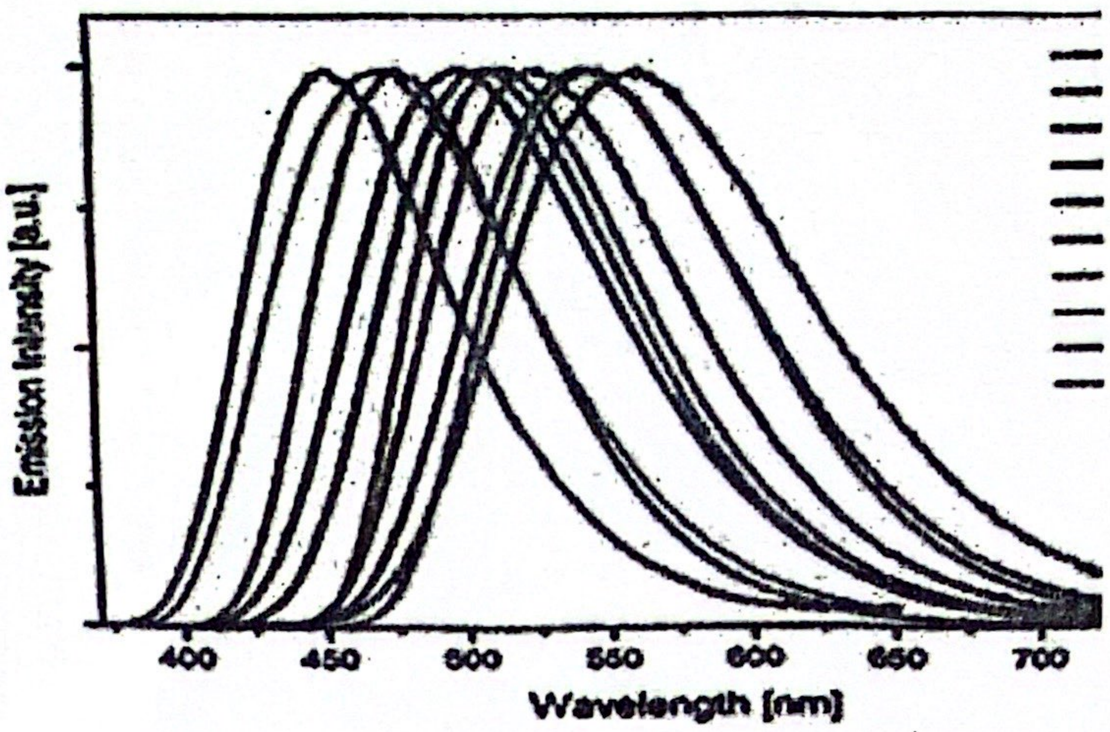
(ii). What is the name given to the transition seen in this spectrum..

(iii). Draw the probable structure of the Titanium complex and predict its geometry

(c). The following compound exhibit ionization isomerism: $[Cr(NH_3)_5Br]SO_4$ and $[Cr\{NH_3)_5SO_4]Br$.

How would Infrared spectroscopy (IR) help you to distinguish the two compounds?

(d).



The series of spectra above was taken for some copper (I) complexes in an experiment.

(i). What type of transition gave rise to these spectra in the Cu^{I} complex?

(ii). Explain your answer in (I), using the electronic configuration of copper.

21 Sc $-4s^2\ 3d^1$
22 Ti $-4s^2\ 3d^2$
23 V $-4s^2\ 3d^3$
24 Cr $-4s^1\ 3d^5$
25 Mn $-4s^2\ 3d^5$
26 Fe $-4s^2\ 3d^6$
27 Co $-4s^2\ 3d^7$
28 Ni $-4s^2\ 3d^8$
29 Cu $-4s^1\ 3d^{10}$
30 Zn $4s^2\ 3d^{10}$

$d^1\ d^4\ d^6\ d^9$ = 1 broad band octahedral
$d^2\ d^3\ d^7\ d^8$ = 3 broad band octahedral

ΔM
O.r
ML

5