

3. Compound E has the molecular formula $C_4H_{10}O$ with IR absorption at 3400 cm^{-1} and $^1H\text{ NMR}$ spectrum as **Figure 1**. Deduce a structure which you consider as being most consistent with the given spectroscopic details.

- (i) Briefly explain why the methyl protons of an ethyl group appear as a triplet and the methylene protons as a quartet in the $^1H\text{ NMR}$

(ii) What is chemical shift?

3a. How could the following pairs of isomeric compounds be differentiated by mass spectrometry?

- (a) Pentan-2-ol and 2-methylbutan-2-ol
(b) 3-methylbutan-2-one and ~~3-methylbutan-2-ol~~ Pentan-2-one
(c) Butanoic acid and methylpropanoate

b. A compound with molecular formula $C_7H_{14}O$ gives a crystalline precipitate with 2,4-dinitrophenylhydrazine. In the mass spectrum, the following peaks were observed.

m/z	114	85	72	57	29
R.A. (%)	18	22	20	100	70

Write the correct and reasonable structure for the compound proving your line of reasoning by showing the movement of arrows to show how the fragments were formed.

4a. Arrange the following facial isomers of Molybdenum tricarbonyl complexes in their increasing order of carbonyl stretching frequency giving reason(s). $Mo(CO)_3(PCI_3)_3$, $Mo(CO)_3(PMe_3)_3$, $Mo(CO)_3(PF_3)_3$ and $Mo(CO)_3(PhCl)_3$.

b. For the complex 5-exo-anilino-1-4- η -2-methoxycyclohexa-1,3-diene irontricarbonyl [$C_6H_5NH-C_6H_6OMeFe(CO)_3$]: The $^1H\text{ NMR}$ spectrum shows multiplets at 2.90, 1.80, 4.70, 2.20 and singlet at 3.70 ppm. Assign the chemical shift values to the protons.

c. Comment on the following statements concerning electronic spectra:

- (i) $[Fe(bpy)_3]^{+2}$ exhibits metal-ligand charge transfer rather than ligand-metal charge transfer absorption
(ii) $[Co(Br)_6]^{4-}$ displayed two bands at 605 nm and 272 nm while $[Co(Br)_6]^{3-}$ had an absorption band of 253 nm.

Predict the fragmentation pattern and relative atomic mass of the ions fragmented from the complex $Ta_2N_2C_2Cl_3$ using the relative mass abundance of isotopes. [C = 12, Cl = 35.5, N = 14 and Te = 128].



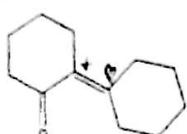
TIME ALLOWED: 2 hours 30 minutes

INSTRUCTION: Answer ALL Questions

1 (a). Give the electronic transition(s) you would expect if the following compounds are exposed to UV light:

- (i) Pyridine. (ii) The compound formed when pyridine is treated with HCl
(iii) 4-chloropenta-2-one. (iv) The compound formed when 4-chloropenta-2-one is treated with NaOH/EtOH.

(b). Using IR spectra only, distinguish between N-methyl ethanamide and N,N-dimethyl ethanamide
(c). Deduce the λ_{max} value of the compound below:



(d). The structure of an acyclic organic compound containing C, H and O only was confirmed as follows:
The UV spectrum of the compound run on 0.32mg per 100 ml of ethanol in a 10 mm cell, gave an absorbance of 1.00 at maximum absorption of 227 nm and molar absorptivity of 30,700. The IR spectrum of the compound, run on a KBr disc, showed significant absorptions at the following frequencies: 2970 – 2890; 1700 and 1620 cm^{-1} but transparent between 1710 and 2890 cm^{-1} .

- (i) Calculate the molar mass of the compound
(ii) Deduce the possible structures for the compound based on the spectra data given.
(iii) If the NMR spectrum of the compound showed a singlet (3H) at 1.5 ppm (downfield of TMS). What is the most probable structure of the compound?

2a. A synthetic organic compound **A** has the molecular formula $C_{11}H_{14}$ and exhibited weak IR absorption at about $\nu_{\text{max}} 1620 \text{ cm}^{-1}$. The ^1H NMR shows signals at δ 1.1 (6H, d, $J=3$ Hz), 2.9 (1H, heptet, $J=3$ Hz), 5.4 (2H, d, $J=5$ Hz), 5.9 (1H, t, $J=5$ Hz), 6.9 (2H, d, $J=10$ Hz) and 7.3 (2H, d, $J=10$ Hz). Ozonolysis of **A** followed by appropriate work up of reaction product gave two compounds **B** and **C** of molecular formulae $C_6H_{12}O$ and CH_2O respectively. Compound **C** was further oxidized and methylated to give compound **D** $C_7H_8O_2$. Compound **D** ^1H NMR shows signals at δ 3.8 (3H, S) and 9.0 (1H, S). Deduce the structural features which you will expect in each of the compounds **A-D** from the data provided, and hence postulate appropriate structures for compounds **A-D**.

(iii) Primary Sources

i. Ammonia ✓ (ii) Ethylene oxide ✓

(iv) The soaps are alkali and ammonium salts of fatty acids containing from 8 to 22 carbon atoms; which are generally mixture of saturated, unsaturated and poly saturated moieties. ✓

Examples of saturated - $\text{CH}_3(\text{CH}_2)_{10}\text{COOM}$ - M = K^+ , Na^+ , NH_4^+ ✓

" " unsaturated - $\text{CH}_3(\text{CH}_2)_n\text{CH}_2\text{Cl} \sim \text{H}(\text{CH}_2)_n$ ✓

(v) Palm oil, Palm Kernel oil, Fish oil, Canola oil, Sunflower seed oil, Olive Oil. (Any two) ✓

(vi) $\text{K}^+ > \text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+}$ OR $\text{Ca}^{2+} < \text{Mg}^{2+} < \text{Na}^+ < \text{K}^+$ ✓

(vii) Chemical Pulping involves digesting / cooking of woodchips in aqueous chemical medium / solution at elevated temperature and pressure. To break down the lignin bonds of the cellulose. ✓

(Viii) Kraft Pulping ✓ sodium sulphide (Na_2S) and sodium hydroxide at 10% concentration ✓

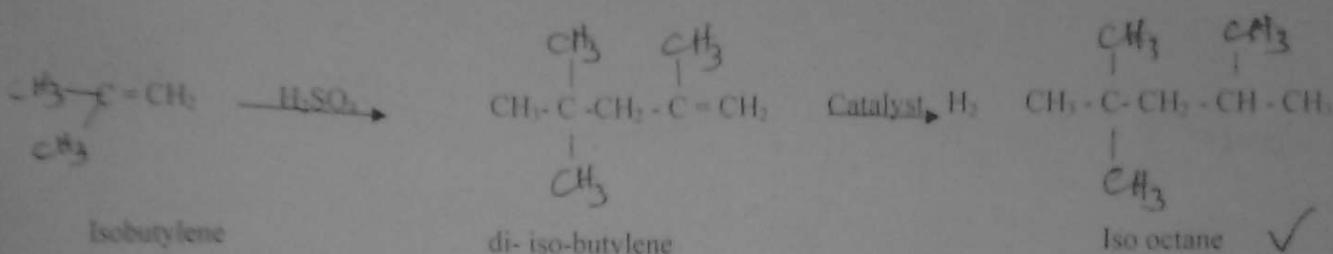
Sulphite Pulping ✓ It uses acid solutions of sulphurous acid (H_2SO_3) and bisulphite (HSO_3^-) ✓

Score $\times \frac{10}{1}$
24

MARKING GUIDE MID SEMESTER TEST CHM 405

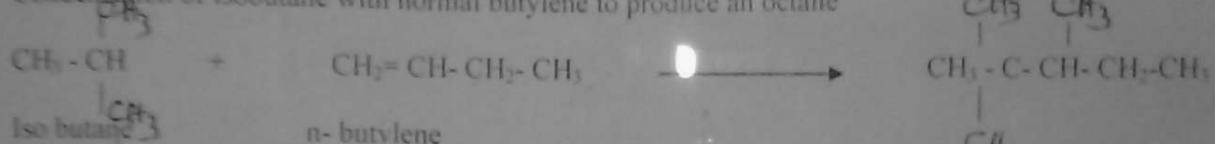
(i) High octane gasoline can be synthesized through (a) Polymerization (b) alkylation (c) Isomerization.

a. Polymerization of isobutylene give di-iso-butylene which on hydrogenation is converted to iso-octane ✓



b. Alkylation ✓

Condensation of isobutane with normal butylene to produce an octane



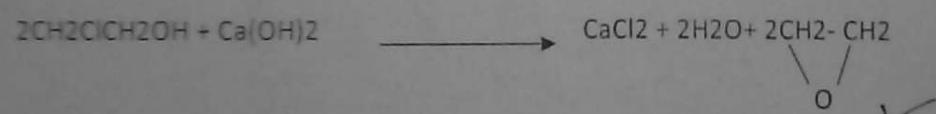
This process can be catalyzed by H_2SO_4 ✓

c. Isomerization. ✓

In the presence of anhydrous aluminum chloride promoted by anhydrous hydrogen chloride, n - butane can be isomerized into iso- butane required for alkylation while n - pentane and n- hexane may be similarly converted to their branched isomers. ✓

(ii) Ethylene Oxide ✓

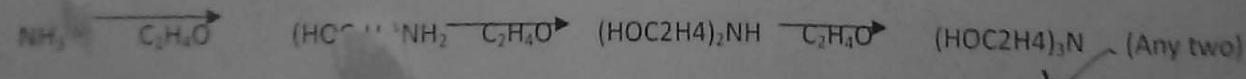
Ethylene reacted with Hypochlorous acid and Base



Ethylene Glycols ✓



Ethanolamine ✓



(ii) Chemical shift is the small spectral shift in the transition frequencies between two such chemically non equivalent nuclei. The chemical shift is the position on the δ scale (in ppm) of proton absorption and is usually measured relative to the single peak of the reference substance, tetramethylsilane (TMS), which has very low shielding.

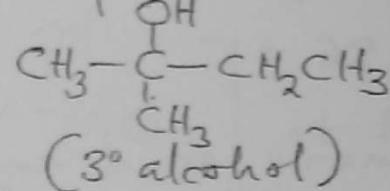
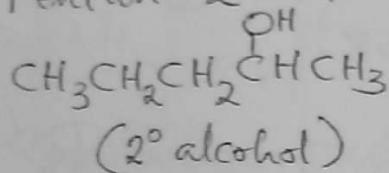
$$\text{Chemical shift, } \delta = \frac{\nu_{\text{obs}} - \nu_{\text{TMS}}}{\nu_{\text{spec}}} \times 10^6$$

ν_{obs} = Observed frequency

ν_{TMS} = reference frequency

ν_{spec} = spectrometer "

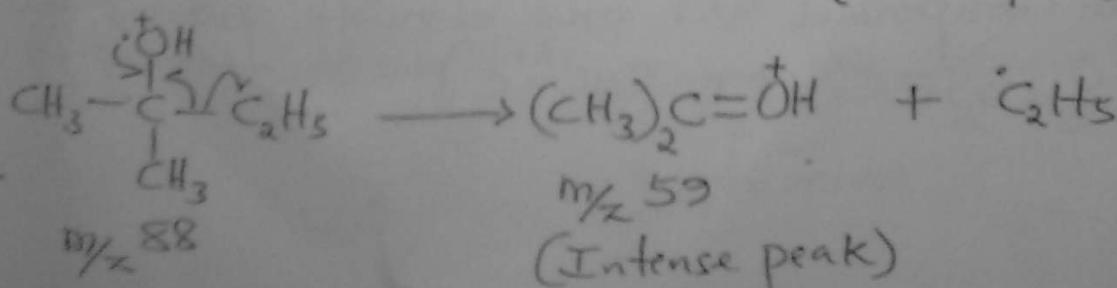
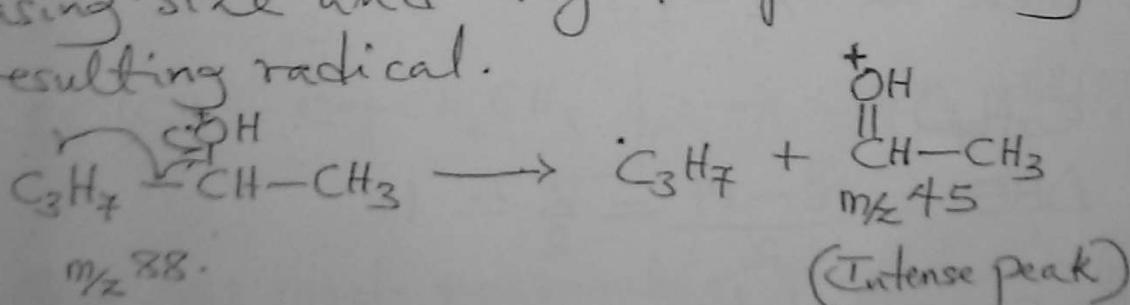
(3) (a) Pentan-2-ol & 2-methylbutan-2-ol.

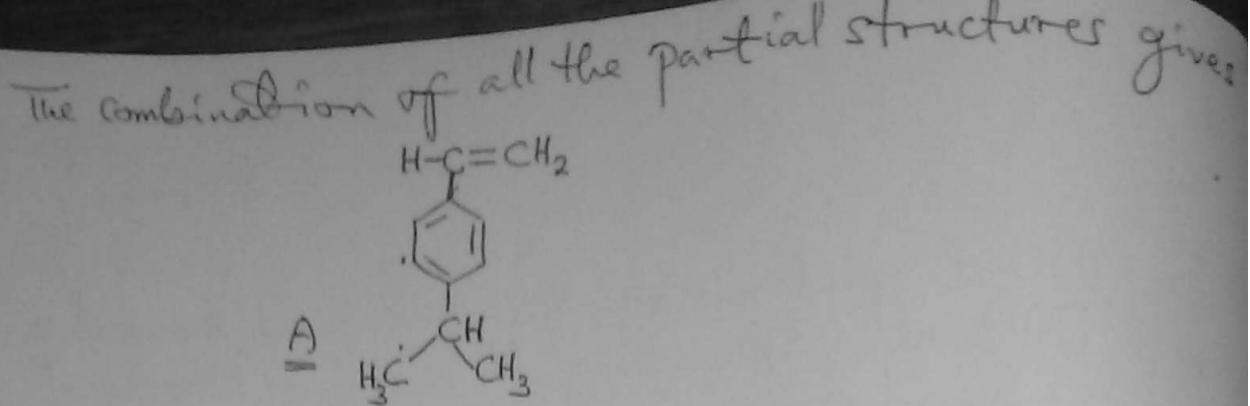


⇒ The intensity of the molecular ion peak in the mass spectrum of a secondary alcohol is usually rather low while it may be entirely absent in the mass spectrum of a tertiary alcohol.

The most important fragmentation pattern for alcohol is the loss of an alkyl group.

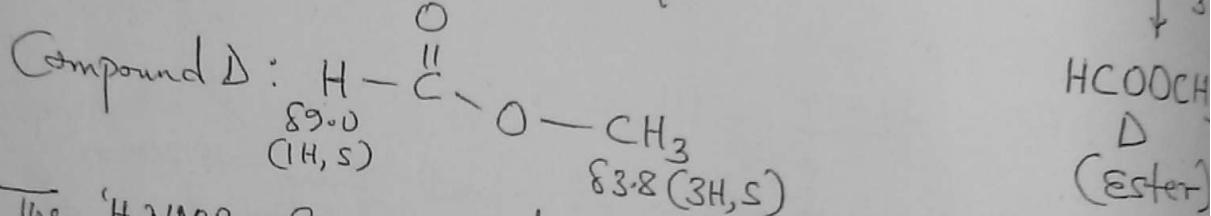
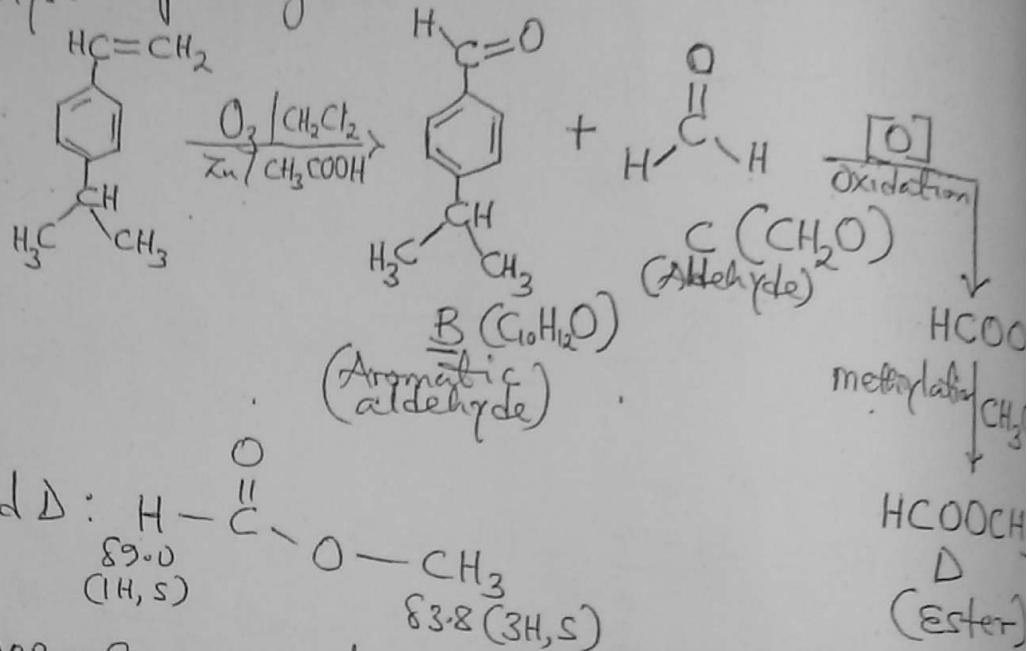
The ease of elimination increases with the increasing size and degree of branching of the resulting radical.



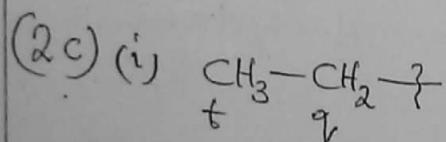


Further analysis:

- Ozonolysis of A gave B & C



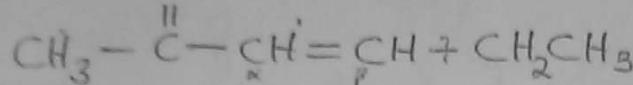
The $^1\text{H NMR}$ of compound D is consisted with the above structure.



The CH_3 protons of an ethyl group appear as a triple and the methylene (CH_2) protons as a quartet in the $^1\text{H NMR}$ due to spin-spin coupling. The CH_3 protons interact with the CH_2 protons and this leads to splitting of the absorption signal. The CH_3 & the CH_2 protons are in different chemical environment. The CH_3 protons split the CH_2 protons by $(3+1)$ peak while the CH_2 split the CH_3 protons by $(2+1)$ peak.

iii) The $^1\text{H NMR}$ spectrum of the compound showed a singlet (3H) at 1.5 ppm suggest a CH_3 - attached to a carbonyl group.

The most probable structure of the compound is



$$\lambda_{\text{max}} = 227\text{nm}$$

$$\text{Parent value} = 215\text{nm}$$

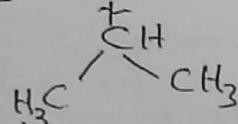
$$\beta\text{-alkyl residue} = \frac{12\text{nm}}{\lambda_{\text{max}} = 227\text{nm}}$$

(Q2) $\text{C}_{11}\text{H}_{14}$

$$\text{DBE} = \frac{24 - 14}{2} = \frac{10}{2} = 5$$

The weak IR absorption at about $\bar{\nu}_{\text{max}} = 1620\text{cm}^{-1}$ suggests a conjugated $\text{C}=\text{C}$ double bond.

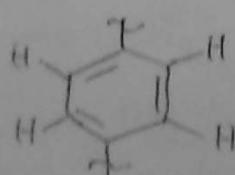
The $^1\text{H NMR}$ signal at $\delta 1.1$ (6H, d, $J = 3\text{Hz}$) suggests two CH_3 - systems attached to a CH -system.



The signal at $\delta 2.9$ (1H, heptet, $J = 3\text{Hz}$) suggests a CH -system attached to two CH_3 -systems. The CH - is then attached to a more deshielding system and this is confirmed by the chemical shift, $\delta 2.9$.

The signal at $\delta 5.4$ (2H, d, $J = 5\text{Hz}$) suggests a CH_2 - of a double bond and the signal at $\delta 5.9$ (1H, t, $J = 5\text{Hz}$) suggest that a CH -system is coupled to the CH_2 -system.

The signals at $\delta 6.9$ (2H, d, $J = 10\text{Hz}$) & $\delta 7.3$ (2H, d, $J = 10\text{Hz}$) suggests aromatic protons on opposite side of the ring.



(i) Mass of the compound = $0.32 \text{ mg} = 0.32 \times 10^{-3} \text{ g}$
 Volume of solution = $100 \text{ ml} = 0.1 \text{ dm}^3$
 Path length, $= 10 \text{ mm} = 1.0 \text{ cm}$.
 Absorbance, $A = 1.00$
 Absorptivity, $\epsilon = 30,700$
 Using Beer-Lambert's law,

$$A = \epsilon b C$$

$$\therefore \text{Concentration, } C = \frac{A}{\epsilon b}$$

$$= \frac{1.00}{30700 \times 1.0}$$

$$= 0.00003257 \text{ mol/dm}^3$$

$$\text{Mass concentration of solution} = \frac{0.32 \times 10^{-3} \text{ g}}{0.10 \text{ dm}^3}$$

$$= 0.0032 \text{ g/dm}^3$$

Concentration in mol/dm^{-3} = concentration in g/dm^{-3}
 Molar mass

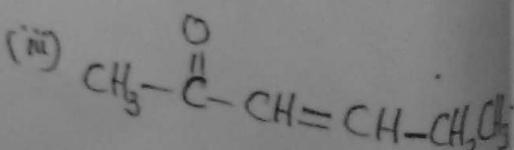
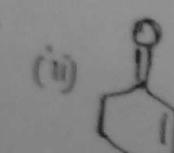
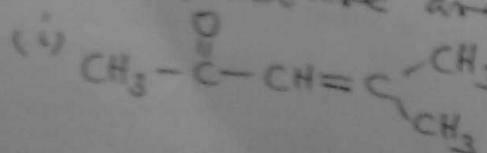
$$\therefore \text{Molar mass} = \frac{\text{Concentration in } \text{g/dm}^{-3}}{\text{Concentration in } \text{mol/dm}^{-3}}$$

$$= \frac{0.0032}{0.00003257}$$

$$= 98.25 \text{ g/mol}^{-1}$$

(ii): The IR band at $2970 - 2890 \text{ cm}^{-1}$ suggests a CH_3 -stretching vibrational frequency.
 The IR band at 1700 cm^{-1} suggests carbonyl, C=O stretching vibrational frequency. The band at 1620 cm^{-1} suggests the vibrational frequency of C=C of an unsaturated carbonyl compound.
 Since the compound is transparent between $1710 - 2890 \text{ cm}^{-1}$ confirmed the fact that the compound is not an aldehyde.

Possible structures are



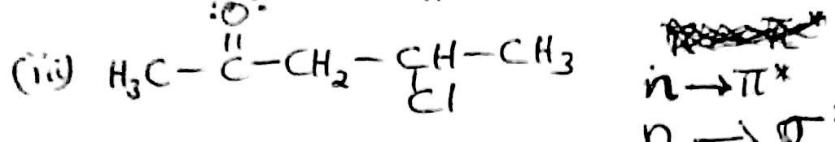
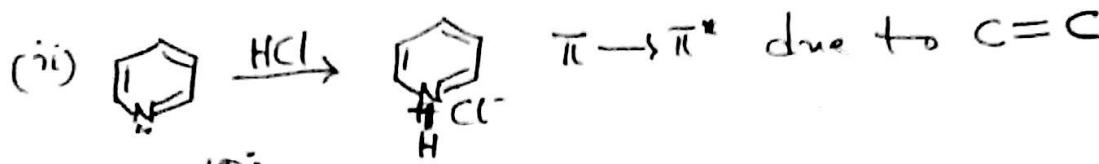
SOLUTIONS TO 2013/2014 EXAM

~~n - σ^* due to the lone pair
on N-atom~~

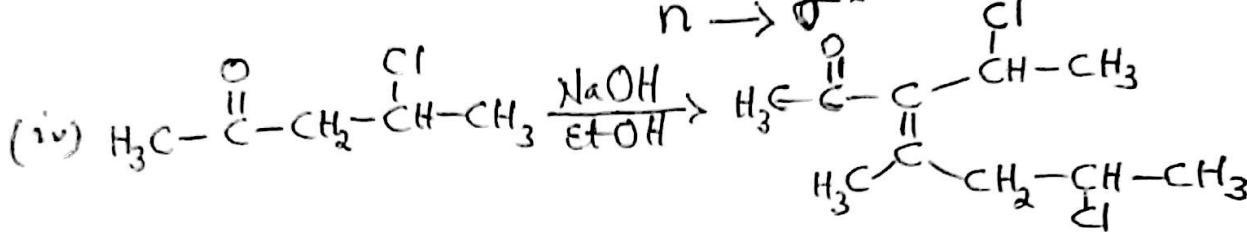
1(a) (i) Pyridine



$\pi \rightarrow \pi^*$ due to $C=C$



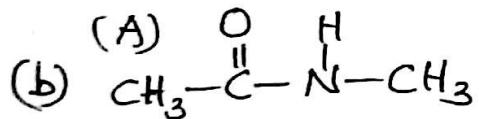
$n \rightarrow \pi^*$



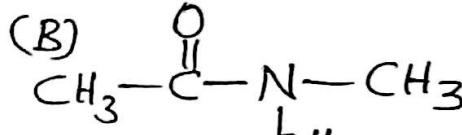
* $\pi \rightarrow \pi^*$ due to $C=C$

* $n \rightarrow \pi^*$ due to the carbonyl group.

* $n \rightarrow \sigma^*$ due to the lone pair on O-atom.



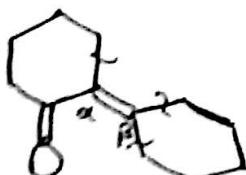
N-methylethanamide



N,N-dimethylethanamide

The IR spectrum of compound A will show ν -H stretching vibrational frequency ($\bar{\nu}=3300\text{cm}^{-1}$) but this is absent in compound B.

(C)



Parent value (α,β -unsaturated six-membered ketone)

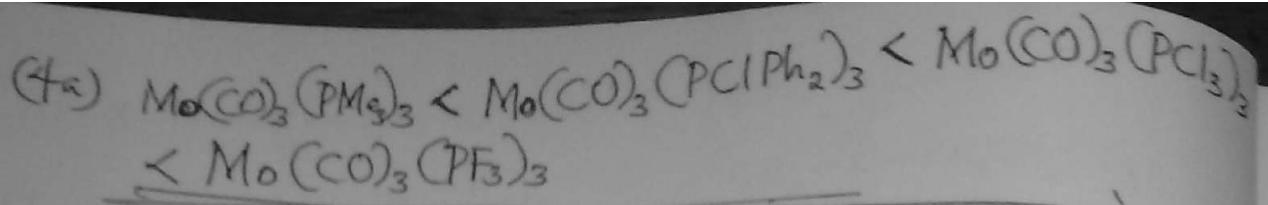
$$= 215\text{nm}$$

$$\alpha\text{-ring residue} = 10\text{nm}$$

$$\beta\text{-ring residue} \times 2 = 24\text{nm}$$

$$\text{Exocyclic double bond} \times 2 = 10\text{nm}$$

$$\lambda_{\max} = \underline{\underline{259\text{nm}}}$$



Increasing order of carbonyl stretching frequency

Reason:

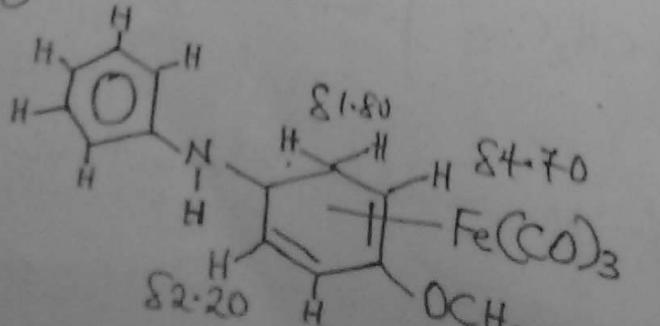
Electron-rich phosphine such as $(\text{PMe}_3)_3$ is a good σ -donor and poor π -acceptor whereas electron-poor phosphines, such as PF_3 , PCl_3 and PClPh_2 are poor σ -donors and good π -acceptors.

PMe_3 is the strongest σ -donor and the weakest π -acceptor due to the high electron-donating ability of the ~~back~~ ~~back~~ ~~back~~ ~~all~~ groups attached to the phosphorus atom.

The PMe_3 will have greater electron density at the Mo metal atom. The greater electron density will result in greater backbonding into the C=O π^* orbitals and thus a lower CO stretching frequency results.

PF_3 is the weakest donor (as a consequence of the highly electronegative fluorine atoms) and the strongest π -acceptor. The fluorine withdraws electron density away from the phosphorus; this results in a net withdrawal of electron density on the Molybdenum, Mo metal atom. Consequently, the metal cannot backdonate effectively into the C=O π^* orbitals and this makes the C-O bonds stronger. Therefore the CO stretching vibration in this complex is the greatest.

(4b)

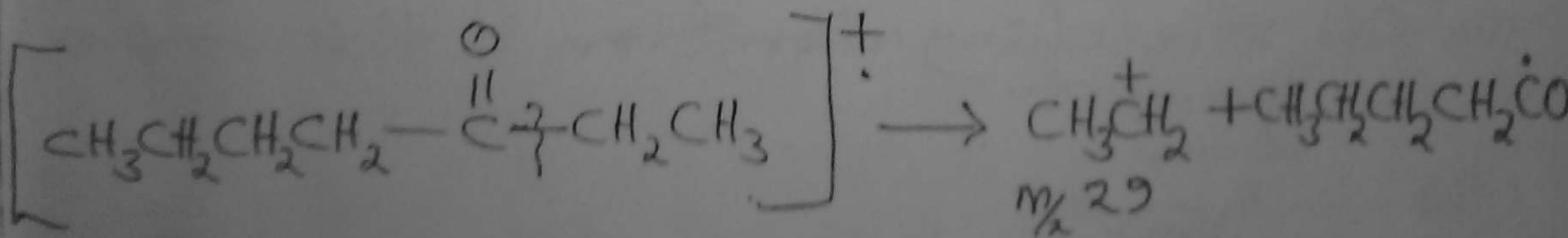
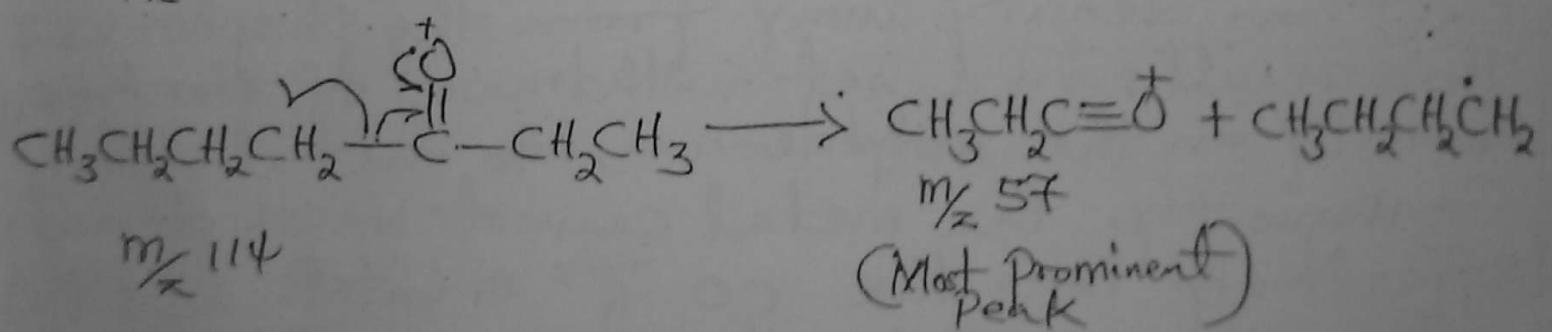
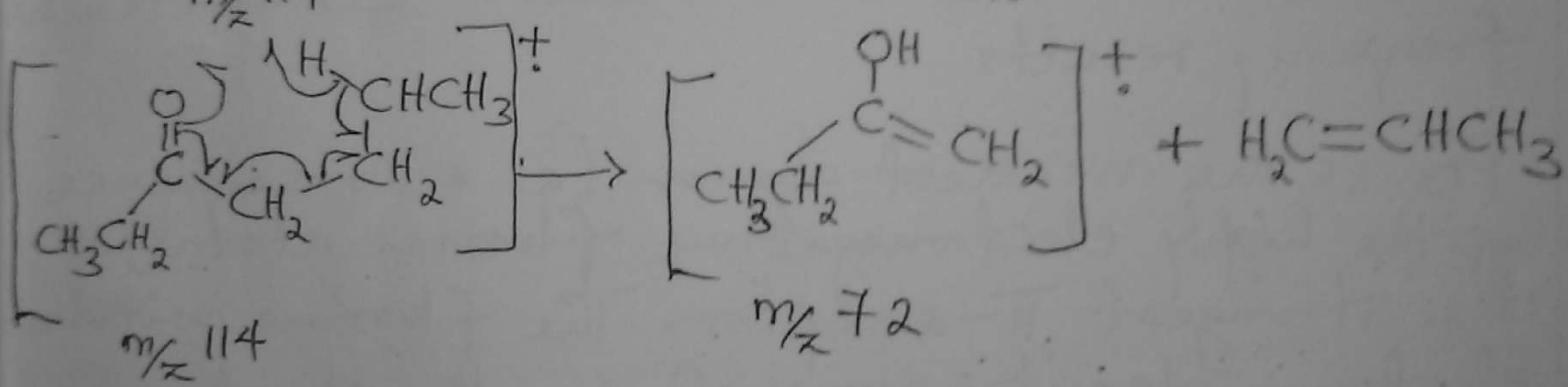
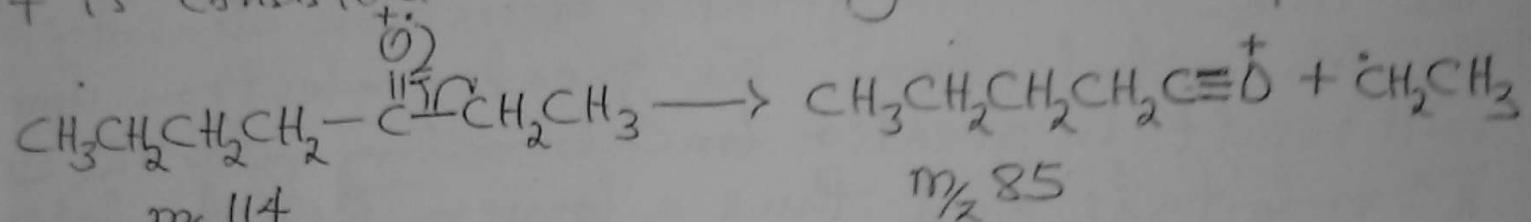


The compound reacts with 2,4-dinitrophenylhydrazine to give a crystalline precipitate. This implies that the compound is an aldehyde or a ketone.

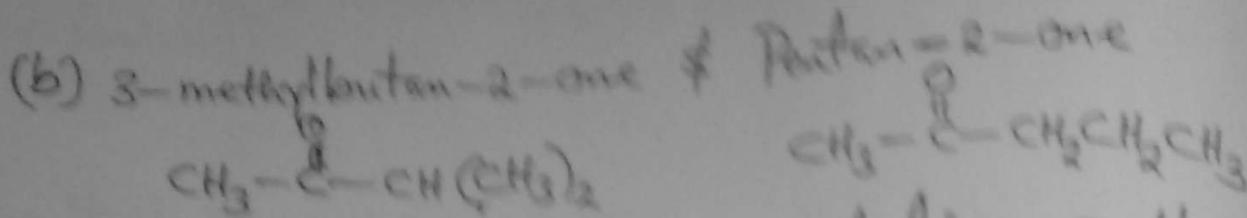
Probable structures:

- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}=\text{CH}_3$
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}=\text{H}$
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}=\text{CH}_2\text{CH}_3$

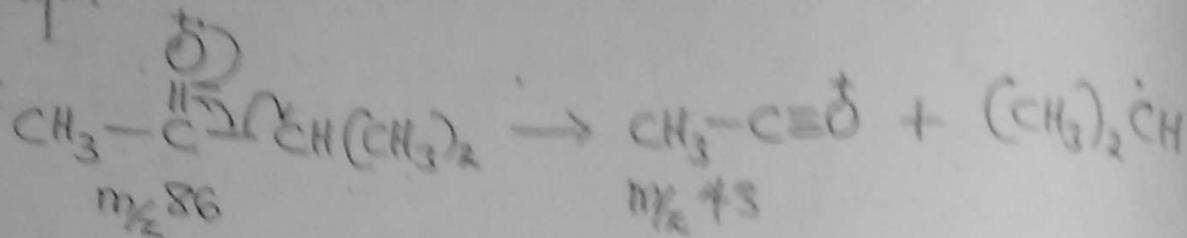
The structure (iii) is the most probable because it is consistent with the given mass spectrum.



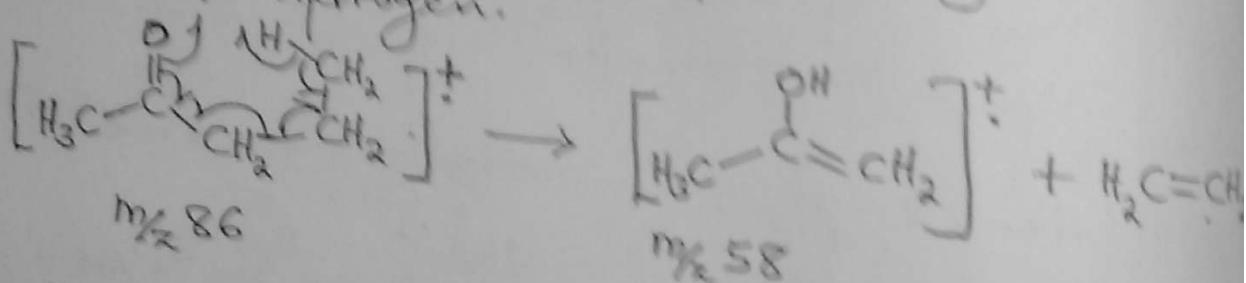
Therefore, the most reasonable structure for the compound is



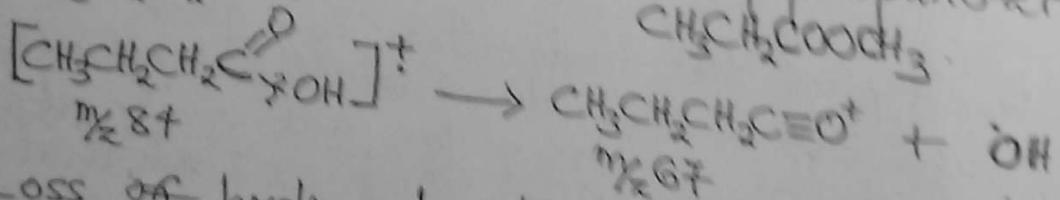
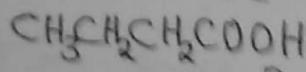
The most important fragmentation pattern is the loss of alkyl group attached to the carbonyl group.



Pentan-2-one also give peak at $m/z 43$ due to formation of the acylium ion. It also give peak due to McLafferty rearrangement because it has γ -hydrogen.



(c) Butanoic acid and methylpropanoate



Loss of hydroxyl radical ($M^{+}-17$) ion is indicated by the presence of carboxylic acid. This is absent in ester.

The ester will show loss of $\text{CH}_3\dot{\text{O}}$ radical + give peak at $m/z 57$.

(3b) $\text{C}_7\text{H}_{14}\text{O}$

$$\Delta \text{BE} = \frac{16-14}{2} = \frac{2}{2} = 1$$

The compound has one double bond.

(c) (i) C-O stretch of the ether $\approx 1120\text{cm}^{-1}$
(ii) C=O stretch of the carboxylic acid
 $\approx 1725\text{cm}^{-1}$

(ii) Aromatic C=C stretch $\approx 1600\text{cm}^{-1}$

(d) $A = 0.52 @ 236\text{nm}$.

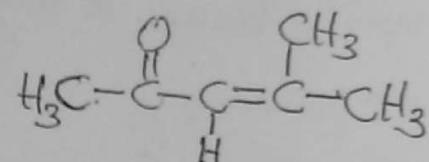
$$l = 1\text{cm}$$

$$\epsilon = 12600$$

$$\therefore A = \epsilon cl$$

$$C = \frac{A}{\epsilon l} = \frac{0.52}{12600 \times 1} = 4.13 \times 10^{-5} \text{M}$$

\therefore Molar mass of



$$= 86\text{g mol}^{-1}$$

$$\begin{aligned} \therefore \text{Conc. in g dm}^{-3} &= \text{Conc. in mol dm}^{-3} \times \text{Molar mass} \\ &= 4.13 \times 10^{-5} \times 86 \\ &= \underline{\underline{3.55 \times 10^{-3} \text{g dm}^{-3}}} \end{aligned}$$

2 (a) Compound A smells like an orange fruit =
Compound A is an ester.

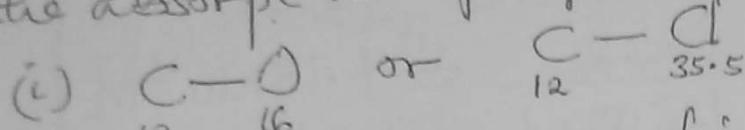
From the Mass spectrum of compound A it can be deduced that the molecular mass of the compound is 158 (M^+).

- The prominent peak ($M^+ 74$) is a characteristic peak of the methyl ester of an aliphatic acid unbranched ~~from the base of the alkyl group~~.
- \Rightarrow The compound is a methyl ester.
- The peak ($M^+ 59$) is due to the loss of the alkyl group from the acyl portion of the molecule.

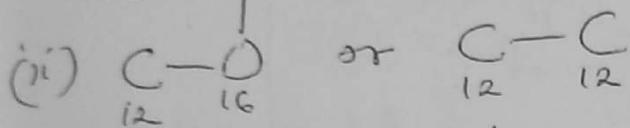
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1(a) Please note the assumption: Same force constants
 Therefore the absorption frequency will depend
 on the masses of the atoms linked by the bond.

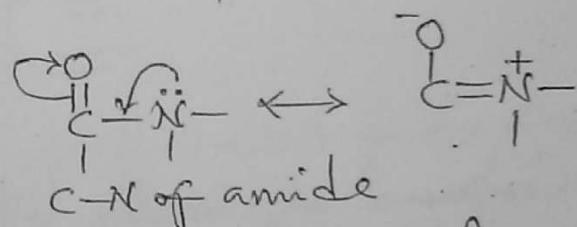
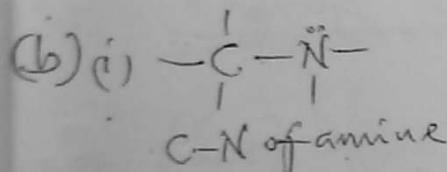
\Rightarrow The smaller the atomic masses, the higher the absorption frequency.



$\Rightarrow C-O$ will have a higher frequency of absorption.



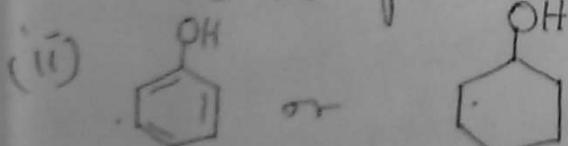
$\Rightarrow C-C$ will have a higher frequency of absorption.



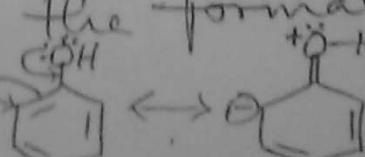
The $C-N$ of amide will absorb at higher frequency because the lone pair in amide is conjugated to the $C=O$ bond & thus, movement of electrons to form stronger $C\equiv N$ bond.

$C-N$ of amine $\approx 1300\text{cm}^{-1}$

$C-N$ of amide $\approx 1500\text{cm}^{-1}$



The $C\equiv O$ stretch of phenol will absorb at a higher frequency due to the formation of stronger $C=O$ bond.





3. (a) How many signals and what signal ratio will you expect each of the following compounds to give in the ^1H NMR spectrum?

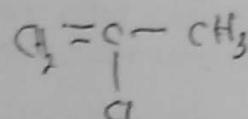
i. para-dimethylbenzene

ii. 2-chloropropene

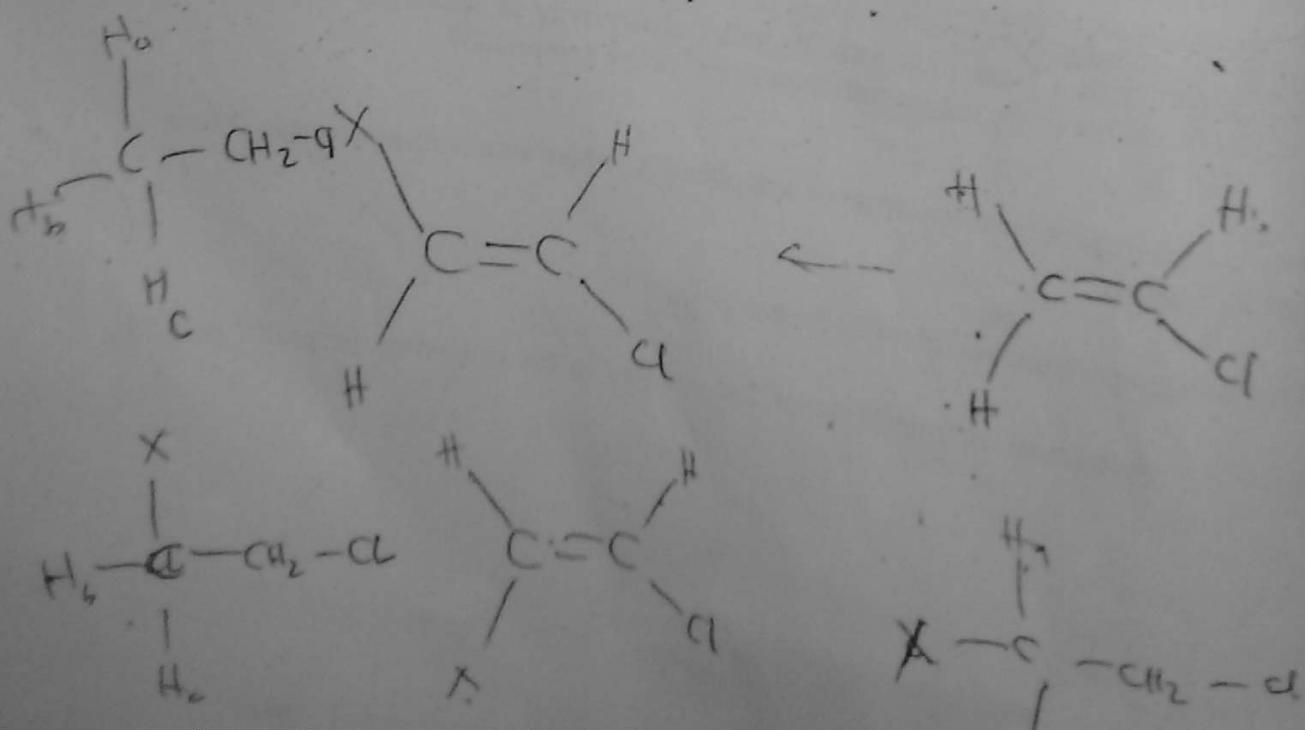
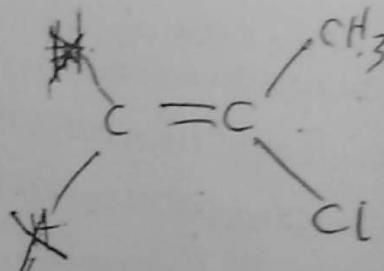
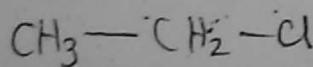
(b) A compound M containing only carbon, hydrogen and oxygen is found to contain 58.80% C and 9.87% H. The mass spectrum of this compound shows a weak $(\text{M}+\text{H})^+$ peak at m/z 103. The IR spectrum of this compound shows a strong absorption band at 1741 cm^{-1} and the ^1H NMR analysis shows the following signals: a triplet integrating as 3 protons at δ 1.0, a singlet integrating as 2 protons at δ 1.7, a triplet integrating as 2 protons at δ 2.3 and a singlet integrating as 3 protons at δ 3.7.

(i) Determine the molecular formula of compound M

(ii) Showing your reasoning, propose a structure for compound M



J_{CH_3}



Obafemi Awolowo University, Ile-Ife, Nigeria

Department of Chemistry

B.Sc. Degree Mid-Semester Examination 2012/2013 Academic Session

CHM 307: Application of Spectroscopic Methods

Date: 11th May 2013

Time Allowed: 45 minutes

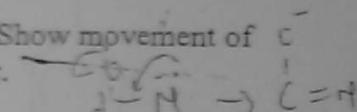
Instruction: Attempt ALL questions

- 1 (a) Assuming the force constants are the same, which of the absorption bands below will occur at higher frequency? And state your reason(s).

- (i) A C=O stretch or a C-Cl stretch
(ii) A C-O stretch or a C-C stretch

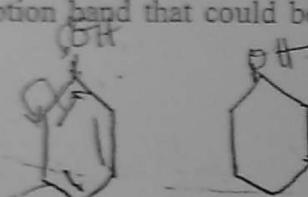
$$\nu = \frac{f}{2\pi} \sqrt{\frac{k}{\mu}}$$

- (b) Which of the absorption bands below will occur at higher frequency? Show movement of electrons on partial structures where applicable to support your answer.



- (i) The C-N stretch of an amine or C-N stretch of an amide
(ii) The C-O stretch of phenol or the C-O stretch of cyclohexanol

- (c) For each of the following pairs of compounds, give one absorption band that could be used to distinguish between them;



- (i) $\text{CH}_3(\text{CH}_2)_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$
(ii) $\text{CH}_3(\text{CH}_2)_2\text{OOOH}$ and $\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{OH}$
(iii) Cyclohexene and benzene

- (d) A solution of 4-methyl-2-penten-2-one in ethanol showed an absorbance of 0.52 at 236 nm in a cell with a 1 cm light path. Its molar absorptivity in ethanol at that wavelength was 12,600. What is the concentration in g/dm³ of the compound?

2. The electron-impact mass spectrum of compound A, which smells like an orange fruit is presented below.

- (a) Interpret the spectrum and identify the compound

- (b) Show the mechanism of fragmentation that resulted in the following ion peaks; m/z 59, 74, and 87.

$$\lambda = ccl \cdot \frac{m}{v}$$
$$\left(\frac{1.56}{12,600 \times 1} \right) m$$

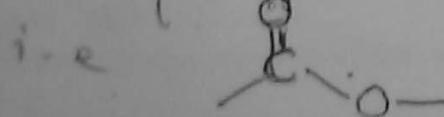
i) \Rightarrow The weak $(M+H)^+$ peak at $m/z 103$ in the mass spectrum is a characteristic of methyl esters.

Important Notice: Work out the DBE of the compound from the Molecular formula, $C_5H_{10}O_2$ before you proceed.

$$\begin{aligned} \text{DBE} &= \frac{(2a+2) - \cancel{(b-d)}}{2} \\ &= \frac{(2(5)+2) - (10-0)}{2} \\ &= \frac{(10+2) - 10}{2} \\ &= \frac{12 - 10}{2} \\ &= \frac{2}{2} \\ &= 1. \end{aligned}$$

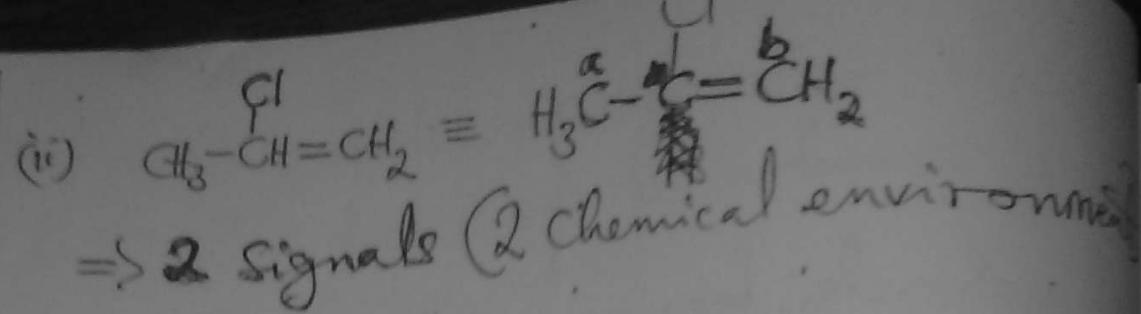
The $\text{DBE} = 1$ means the presence of a π -system in the compound i.e. $C=O$ or $C=C$ or the presence of a cyclic compound.

* The IR spectrum of the compound shows a strong absorption band at 1741cm^{-1} suggests the carbonyl of an ester.

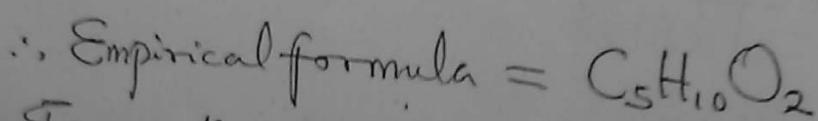


* In the $^1\text{H NMR}$ analysis;

- The signal showing a triplet integrating as 3 protons at 81.0 suggests a CH_3 attached to a CH_2 -system i.e. CH_3-CH_2-



(b) Element:	C	H	O
% Composition:	58.80	9.87	31.33
Atomic Mass	12	1	16
	<u>58.80</u>	<u>9.87</u>	<u>31.33</u>
	12	1	16
Ratio:	<u>$\frac{4.9}{1.96}$</u>	<u>$\frac{9.87}{1.96}$</u>	<u>$\frac{1.96}{1.96}$</u>
	2.50	5.03	1.00
	$2\frac{1}{2}$	5.0	1.0
$\times 2$	$\frac{5}{2}$	5.0	1.0
	5	10	2



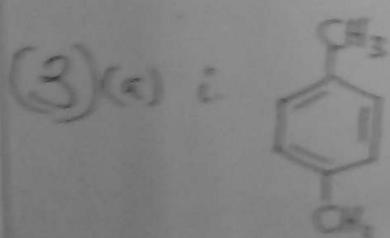
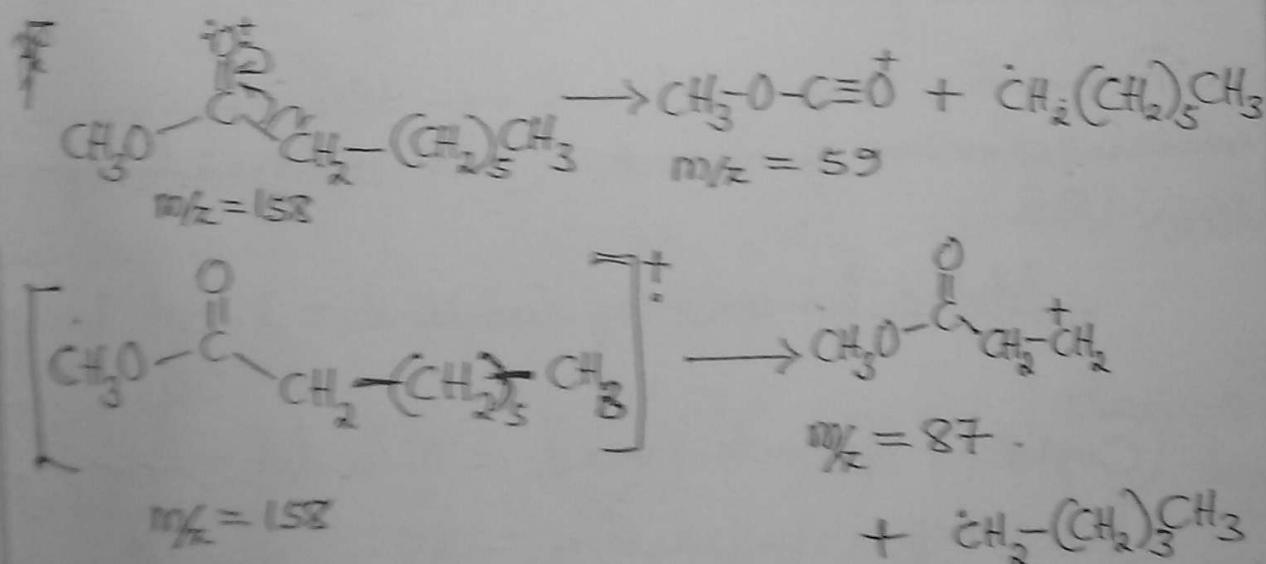
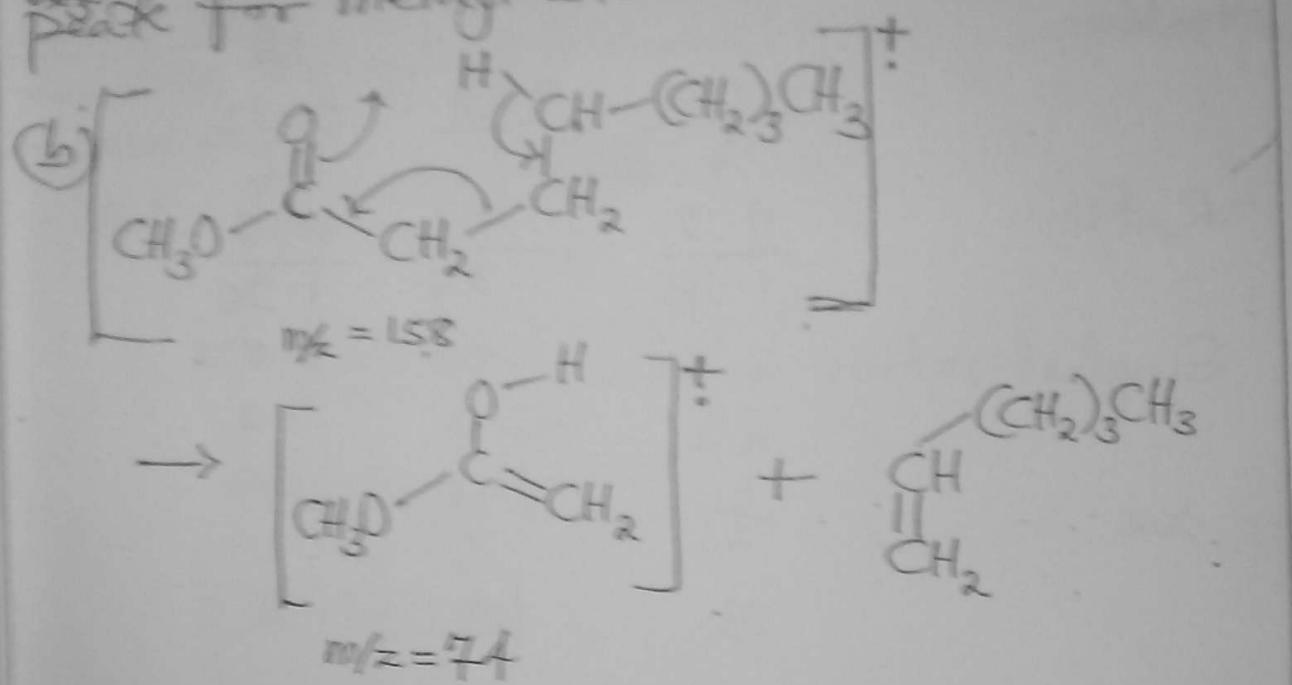
\therefore From the Mass spectrum of the compound which shows a weak $(M+H)^+$ peak at $m/z 103$.

\therefore Molecular mass of Compound = $103 - 1$

$$\begin{aligned} \text{Empirical formula mass} &= 102 \\ ((5 \times 12) + (10 \times 1) + (2 \times 16))_n &= \text{Molecular mass} \\ (60 + 10 + 32)_n &= 102 \\ 102n &= 102 \end{aligned}$$

\therefore Molecular formula of Compound M is $\text{C}_5\text{H}_{10}\text{O}_2$

ester molecule, leaving a fragment $\text{CH}_3\text{-O}-\text{C}\equiv\delta$. This peak (m/z 59), though less intense than the acetonium ion peak, is a useful diagnostic peak for methyl esters.



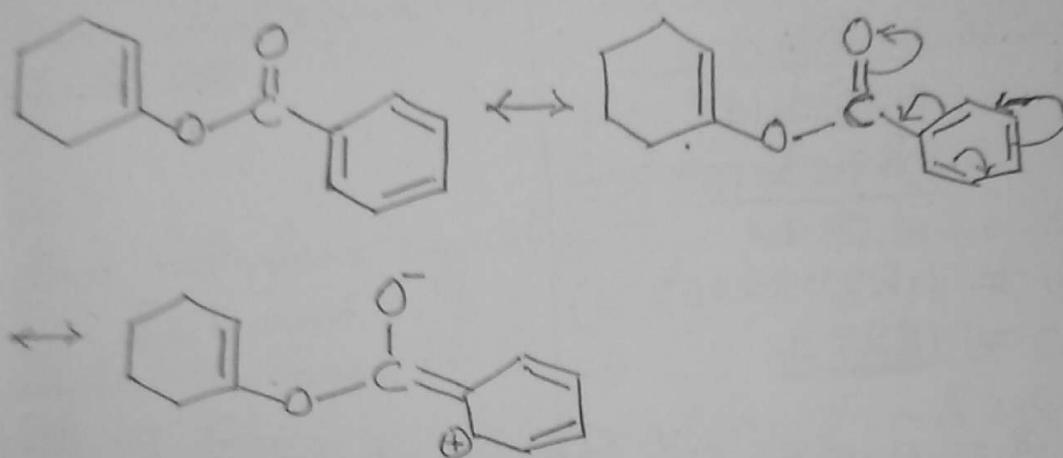
Two signals (6H singlet & 4H doublet or doublet).

$\delta_{7.2}$ $\delta_{7.8}$

2011/2012 TEST SOLUTIONS

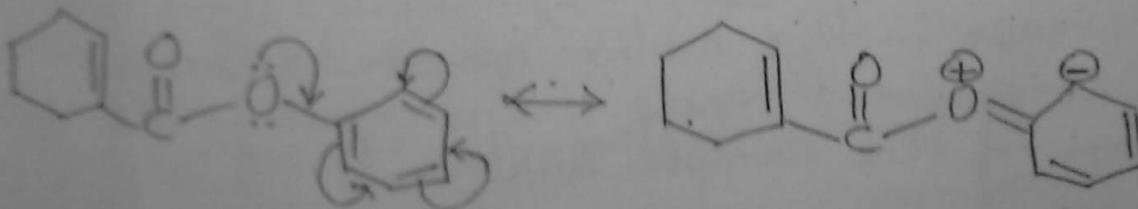
1. The frequency shifts are brought about by structural changes in the molecule, thus in structures (a) and (b), factors such as meso-meric (or resonance) effect, inductive and conjugation effects affect the carbonyl vibrational frequency.

For compound (a)

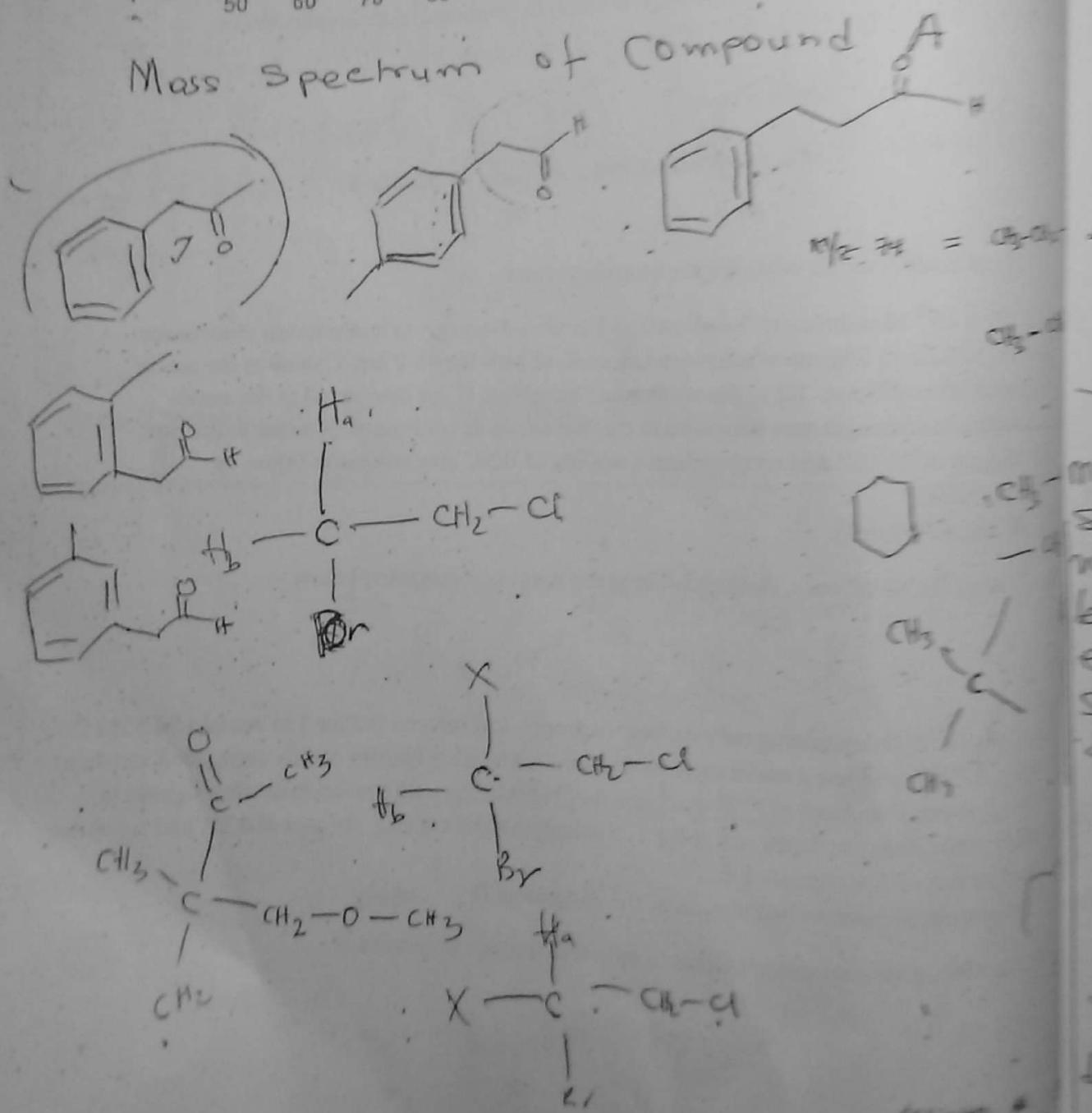
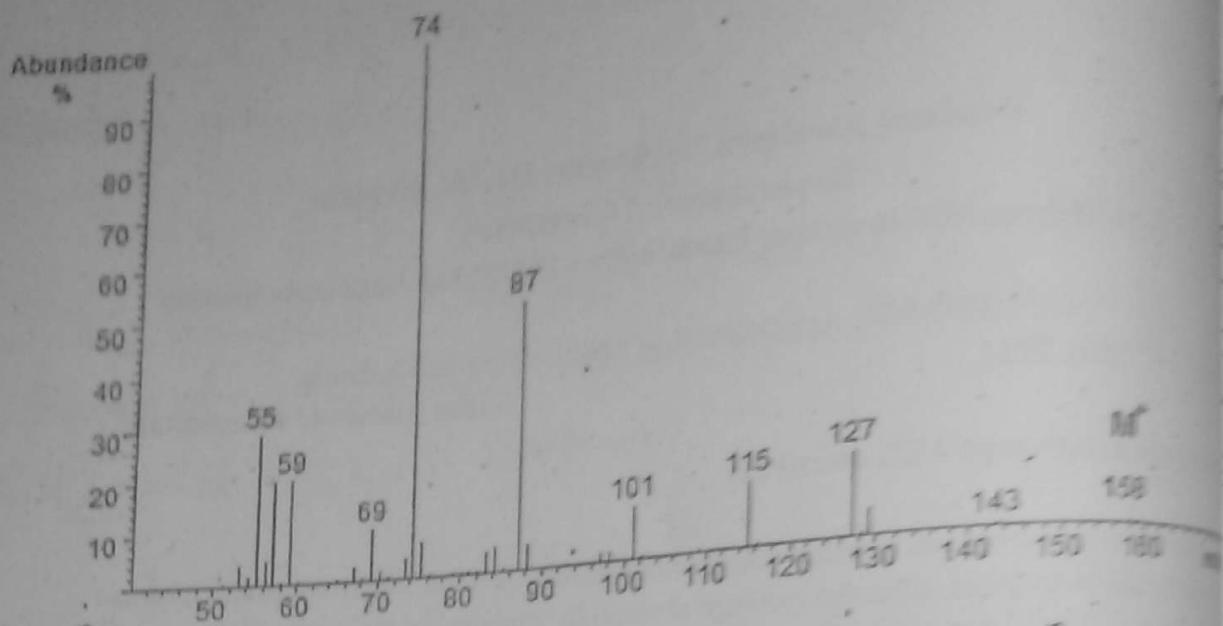


The C=O frequency shift is attributed to the mesomeric (or resonance) effect, thus any substituent that enhances the mesomeric shift will decrease the bond order of the C=O bond and lead to lower C=O frequency, extended conjugation with phenyl ring does so.

For Compound (b)



This is an example of a phenyl ester, the non-bonding electrons are partly drawn into the



Obafemi Awolowo University, Ile-Ife, Nigeria
 Department of Chemistry
 B.Sc. Degree Mid-Semester Examination 2011/2012 Academic Session

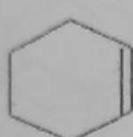
CHM 307: Application of Spectroscopic Methods

Time Allowed: 45 minutes

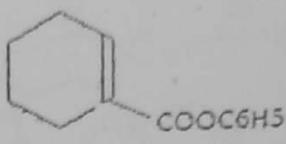
Date: 11th May 2012

Instruction: Attempt ALL questions

1. With the aid of structures together with movements of electrons, where necessary, discuss briefly the factors that affect the carbonyl absorption bands in the molecules below:



(a)



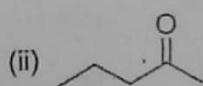
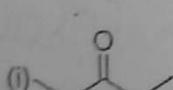
(b)

Then predict an IR value for each carbonyl band.

2. A 0.205×10^{-4} M solution of 3,4-dimethyl-3-penten-2-one gives a maximum absorbance reading of 0.75 at 350 nm when placed in a cell of path length 2 cm. Calculate the molar absorptivity coefficient (ϵ) at the maximum absorption. If the compound at the same maximum wavelength was subjected to another round of analysis with molar extinction coefficient of 25 000 and an absorbance reading of 0.53, give comment(s) on its concentration.

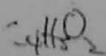
(Path length = 2 cm).

3. a) Using ^1H NMR only, distinguish between the two compounds below.

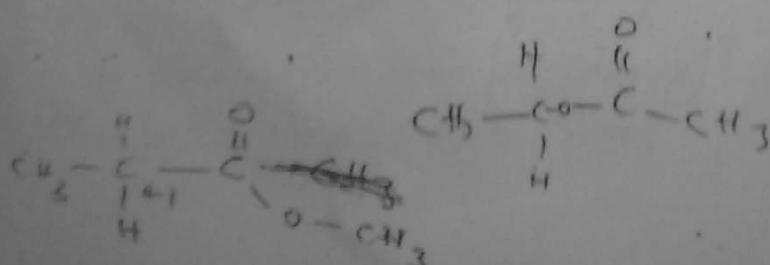


- b) A compound H containing only carbon, hydrogen and oxygen is found to contain 54.53% C and 9.15% H and has a molar mass of 88 g mol^{-1} . The IR spectrum of this compound shows a strong absorption band at 1741 cm^{-1} and the ^1H NMR data shows the following signals: a triplet integrating as 3 protons at δ 1.1, a singlet integrating as 3 protons at δ 2.1 and a quartet integrating as 2 protons at δ 4.1.

(i) Determine the molecular formula of the compound H



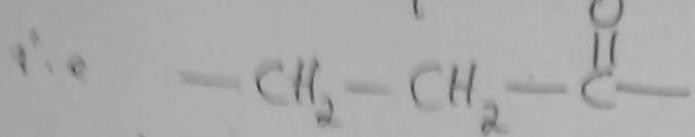
(ii) Showing your reasoning, propose a structure for the compound H



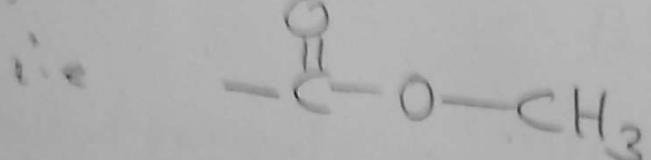
— The sextet integrating as 2 protons at δ 3.7 suggests a CH_2 sandwiched between CH_3 and CH_2 connected to an electron-releasing group.



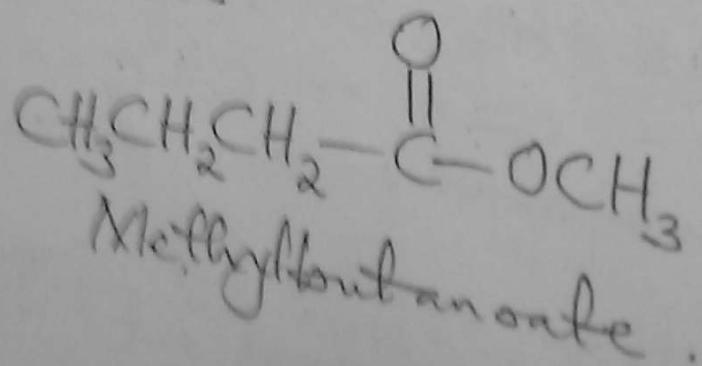
— The triplet integrating as 2 protons at δ 3.7 suggests a CH_2 sandwiched between CH_3 and C=O systems.



— The singlet integrating as 3 protons at δ 3.7 suggests a CH_3- connected to a highly electronegative element such as oxygen.



Therefore, the proposed structure for compound M is:



$$\text{Molecular formula} = (\text{C}_2\text{H}_4\text{O})_2 \\ = \text{C}_4\text{H}_8\text{O}_2$$

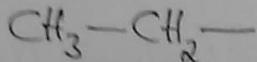
$$\text{(ii) Double bond equivalent} = \frac{(2a+2)-(b-d)}{2} \\ = \frac{(8+2)-(8-0)}{2} \\ = \frac{10-8}{2} \\ = 1$$

This DBE implies that there is only one double bond in the compound, $\text{C}_4\text{H}_8\text{O}_2$. i.e either $\text{C}=\text{O}$ or $\text{C}=\text{C}$

* The IR band at 1741cm^{-1} suggest the carbonyl (CO) of an ester.



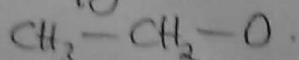
* The triplet at $\delta 1.1$ integrating as 3 p suggests a CH_3- attached to a CH_2-



* The Singlet at $\delta 2.1$ integrating as 3 p suggests a CH_3- attached to a carbonyl group



* The quartet at $\delta 4.1$ integrating as 2 p suggests a CH_2- attached to an electronegative element such as oxygen & it is attached to a CH_3- .



Therefore, proposed structure: $\begin{array}{c} \text{CH}_3-\text{C} \end{array} \begin{array}{c} \text{O} \\ \parallel \end{array} \begin{array}{c} \text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3. \end{array}$

ring, and their conjugation with $C=O$ is con-
sequently diminished. The ^{negative} inductive (-I) effect
of oxygen becomes dominant, and $C=O$ moves
to higher frequency.

The IR value of structure (b) is therefore
expected to be higher than that of struc-
(a) at $\approx 1730\text{cm}^{-1}$ and 1670cm^{-1} respectively

2. $A = 0.75, C = 0.205 \times 10^{-4}\text{M}, l = 2\text{cm}, \epsilon = ?$

$$A = \epsilon Cl \quad (\text{Beer-Lambert's law}).$$

$$\begin{aligned} \therefore \epsilon &= \frac{A}{Cl} \\ &= \frac{0.75}{0.205 \times 10^{-4} \times 2} \\ &= \frac{0.75 \times 10^4}{0.41} \\ &= 1.8293 \times 10^4 \\ &= \underline{\underline{18293}} \end{aligned}$$

(b) New $A = 0.53, \epsilon = 25000, l = 2, C = ?$

$$A = 25000 \times C \times 2$$

$$0.53 = 50000C$$

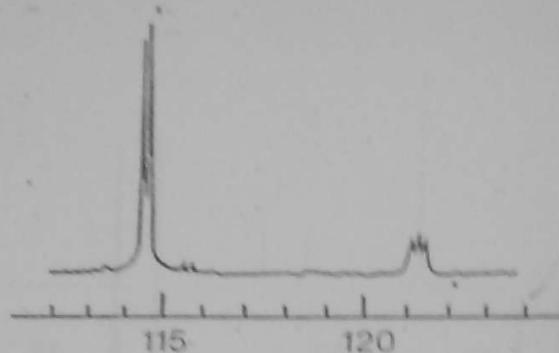
$$\therefore C = \frac{0.53}{50000}$$

$$C = 0.106 \times 10^{-4}\text{M} \equiv \frac{1}{2} \text{ of initial concentration}$$

Since $A = \epsilon Cl \rightarrow$ Beer-Lambert's law.
and $C \propto \frac{1}{\epsilon}$

This shows that Beer-Lambert's law is observed i.e. increase in the molar ~~concentration~~ extinction coefficient leads to decrease in the concentration of the sample analyzed.

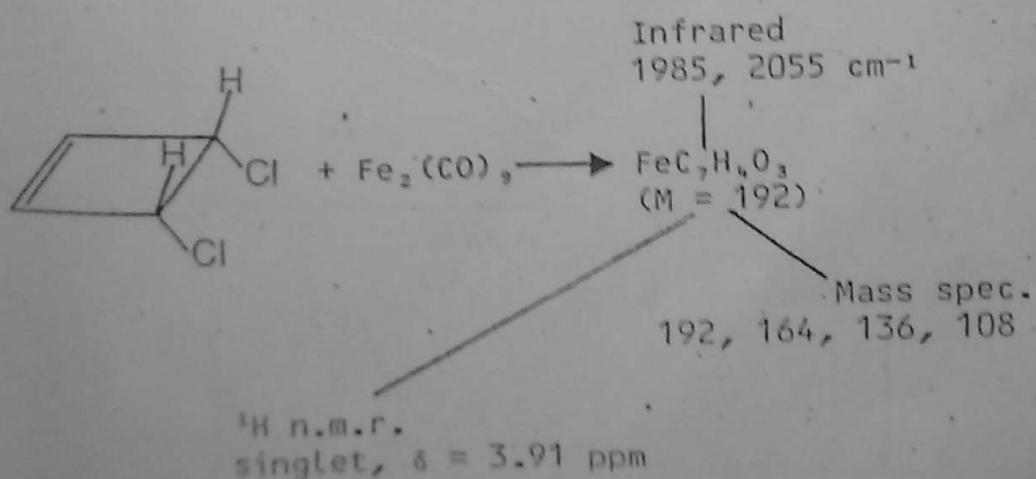
5a. The compound $[(C_3H_7)_4N]_2C_6H_5SiF_5$ can be formulated as a double salt, $[(C_3H_7)_4N]^+[(C_3H_7)_4N][C_6H_5SiF_5]$ or as a six-coordinate complex of silicon $[(C_3H_7)_4N]_2[C_6H_5SiF_5]$. The ^{19}F n. m. r. spectrum of the compound in dichloromethane at $-28^\circ C$ is shown below:



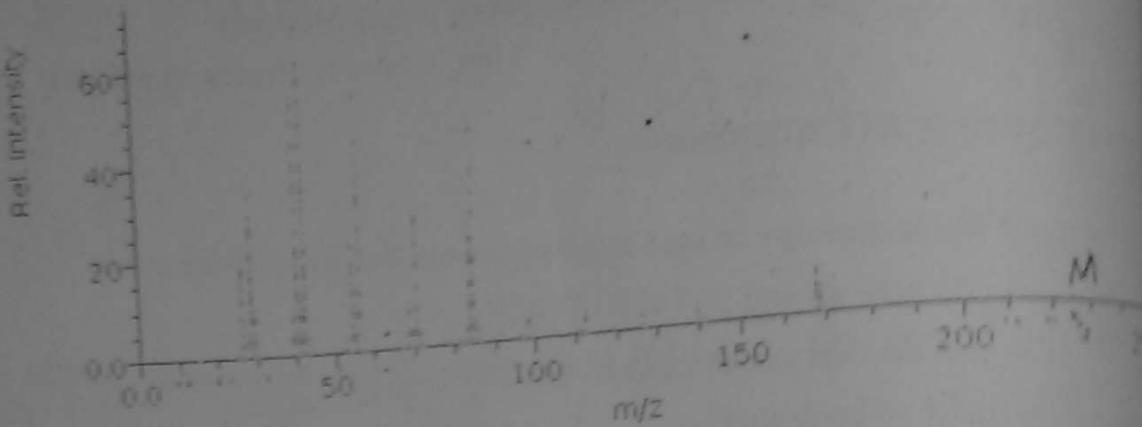
Chemical shift - ppm upfield of $CFCl_3$

Which formulation does this indicate?

5b. Reaction of Cis-3,4-dichlorocyclobutane with an excess of $Fe_2(CO)_9$ in isopentane at $30^\circ C$ produces a pale yellow compound $FeC_7H_4O_3$. The infrared spectrum shows two strong bands at 1985 and 2055 cm^{-1} and the 1H n. m. r. spectrum consists of a single sharp line at $\delta = 3.91$ ppm. The mass spectrum gives peaks at 192 , 164 , 136 , and 108 . Deduce the structure of the product [Fe = 56, C = 12, O = 16, H = 1]



c. Compound A represented by an electron-impact spectrum below is a non-polar compound



Obafemi Awolowo University, Ile-Ife, Nigeria

Department of Chemistry

B.Sc. Degree Harmattan Semester Examination 2011/2012

CHM 307: Application of Spectroscopic Methods

Time Allowed: 2 hours 30 minutes

Date: June 2012

Instruction: Attempt ALL questions

1 a. (i) How could IR spectroscopy be used to distinguish between the following pair of compounds: (a) $(CH_3)_3N$ and (b) $CH_3NHCH_2CH_3$

(ii) How does the O-H stretch in the IR spectrum of a carboxylic acid differ from the O-H stretch of an alcohol?

(iii) Sodium borohydride can be used to reduce cyclohexanone to cyclohexanol. How could one use IR to determine if all starting material had been consumed?

b. (i) Define Beer's and Lambert's Laws.

(ii) What would be the expected λ_{max} values for the following compounds: (a) 2-Chloro-3-methyl-cyclopent-2-ene-1-one (b) $\text{H}_3\text{C}-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{OCH}_3$ -3-penten-2-one?

2. During a visit to the Central Science Laboratory at Obafemi Awolowo University, a student approached you with an unknown compound L, which she found to give a positive iodoform test i.e. on reaction with iodine in the presence of a base. She also presented you with the spectra data for compound L as shown in attached figures

i) Showing your reasoning, propose the structure of this unknown compound

ii) Give the correct systematic name for compound L

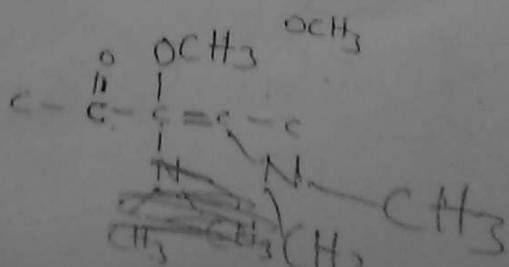
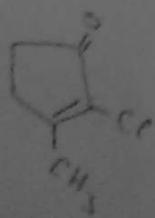
iii) Where will be most likely point of a nucleophilic attack in compound L?

3 a. (i) What is the difference between electron impact (EI) technique and direct inlet probe (DIP) technique?

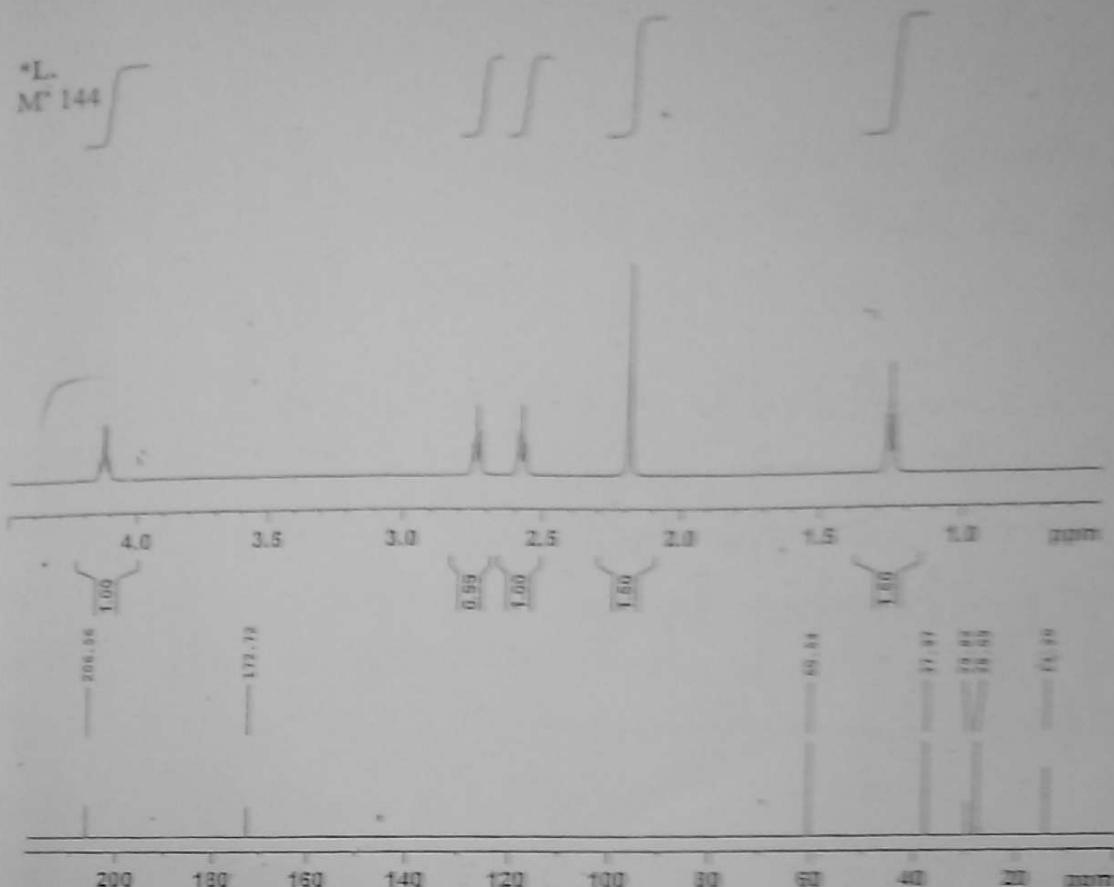
(ii) What is the advantage of using chemical ionization (CI) technique in mass spectrometry?

b. (i) What are the conditions that a molecule must fulfill to undergo McLafferty rearrangement?

(ii) Account for the following peaks in the mass spectrum of butanoic acid; m/z 43, 60 and 71. The mechanism of fragmentation that resulted in each peak must be clearly shown.

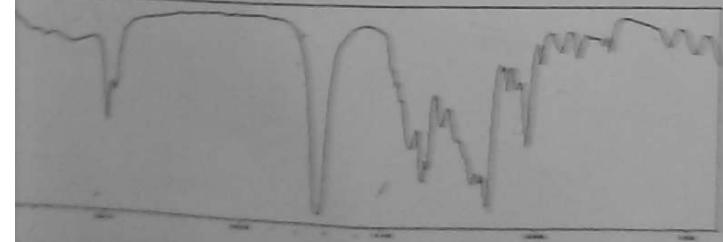


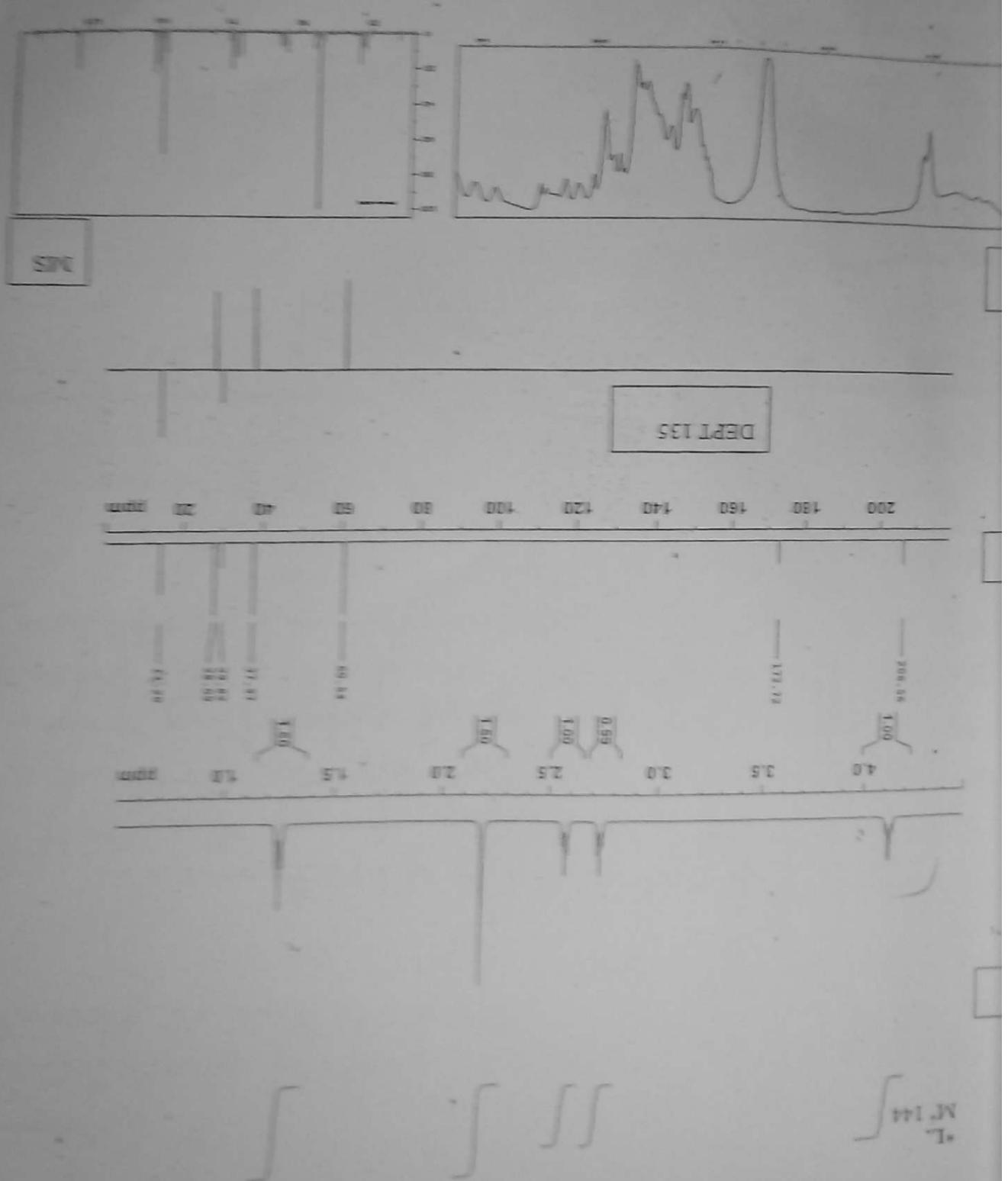
¹³C
M⁺ 144



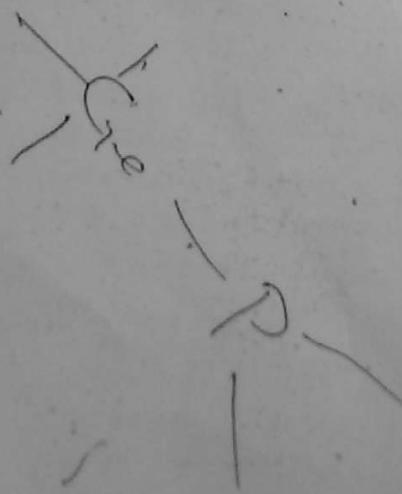
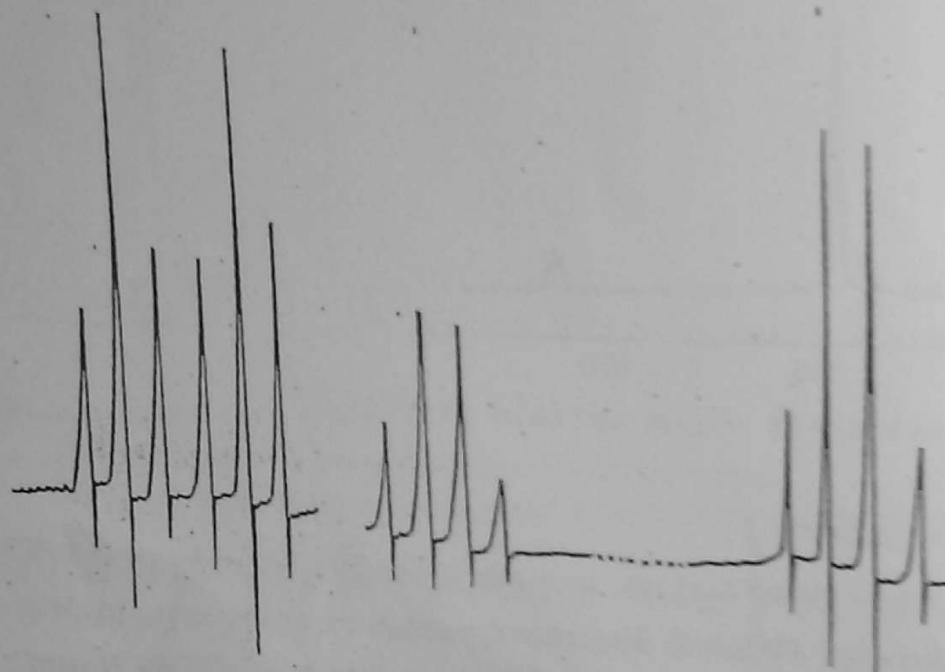
DEPT 135

MS





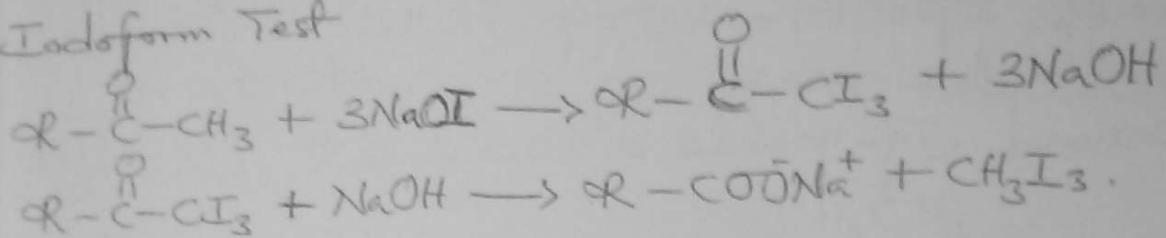
5c. The proton n. m. r. spectrum of GePH₃ is shown below. Deduce the structure of the compound. (Both ³¹P and ¹H have a spin of $\frac{1}{2}$ and essentially 100 % natural abundance. Coupling constants between P and H are often very large) Justify your suggested assignments.



2.(i) Compound L tests positive to iodoform test implies that compound L is a methyl ketone i.e. $\text{CH}_3-\overset{\text{O}}{\underset{\text{R}}{\text{C}}}-\text{R}'$ or a methyl alcohol i.e.

$$\text{CH}_3-\overset{\text{OH}}{\underset{\text{R}}{\text{C}}}-\text{R}'$$

Iodoform Test



* The proton no. integration gives a total of 12 protons present in the compound

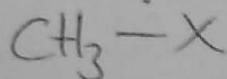
i.e. 1.00 : 0.99 : 1.00 : 1.50 : 1.50

$\times 2$ 2 : 2 : 2 : 3 : 3

¹H NMR

- The triplet at $\delta 1.3$ represents a CH_3 attached to a CH_2- attached to a more electron-withdrawing group: $\text{CH}_3-\text{CH}_2-X$

- The 3H singlet at $\delta 2.2$ indicates a CH_3 -system attached to more electron-withdrawing group.



\Rightarrow Interpret others yourself.

¹³C NMR \Rightarrow CO carbon is above $\delta 200$.

DEPT \Rightarrow shows 3 CH_2 systems & 2 CH_3 system which corresponds to the NMR spectrum.

\Rightarrow The IR spectrum also shows a CO absorption at around 1700cm^{-1} .

(b)(i). The Beer's law states that the absorption of light is directly proportional to the number of absorbing molecules.

The Lambert's law states that fraction of the incident light absorbed is independent of the source i.e $A = ECl$ (Beer-Lambert's law)

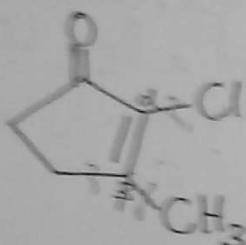
where A = absorbance

E = Molar absorptivity Coefficient or molar extinction coefficient

C = Concentration in mol dm⁻³

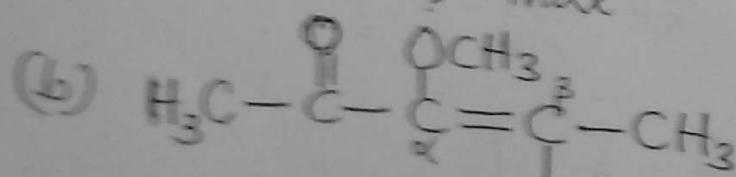
l = Path length in cm.

(ii) (a).



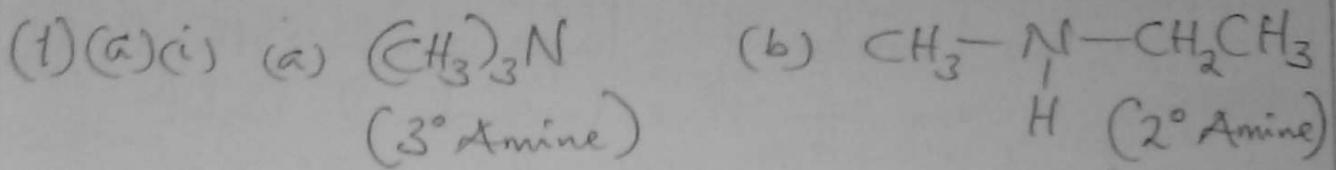
Base value (5-membered ring cyclic) = 202 nm
 α -Cl = 15 nm

β -alkyl residue = $2 \times 12 \text{ nm} = \frac{24 \text{ nm}}{241 \text{ nm}}$



Base value (α, β -Unsubstituted ketone) = 215 nm
 α -alkoxy residue (-OCH₃) = 35 nm
 β -alkyl residue (-CH₃) = 12 nm
 β -amino residue (-N(CH₃)₂) = 95 nm
 λ_{\max} = 357 nm

2011/2012 EXAMINATION SOLUTION

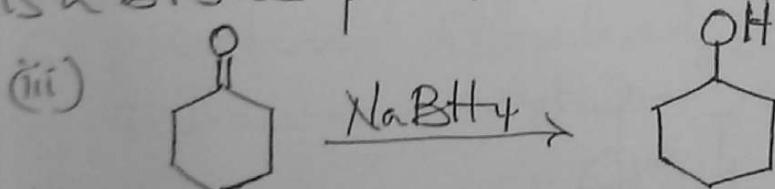


Compound (b) will show a N-H stretching vibration at $\approx 3500\text{cm}^{-1}$. This is absent in compound (a).

(ii) The O-H stretching vibrations in carboxylic acids differ from the O-H stretch of an alcohol by the presence of a very broad band extending from 3400 to 2400cm^{-1} and also the presence of a carbonyl absorption ($\approx 1725\text{cm}^{-1}$).

NOTE:

The free O-H stretch of alcohol is sharp peak at $3670 - 3610\text{cm}^{-1}$. This band appears in combination with the hydrogen-bonded O-H peak when the alcohol is dissolved in a solvent. The hydrogen bonded O-H band is a broad peak at $3400 - 3300\text{cm}^{-1}$.

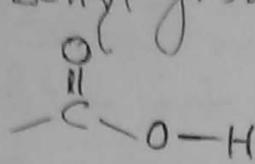


The starting material (cyclohexanone) has a carbonyl absorption at about 1720cm^{-1} while the product formed as free O-H stretch at about 3600cm^{-1} . Therefore, the absence of the carbonyl absorption indicates that all the starting material had been consumed.

compound; $C=O$, or $C=C$ or cyclic compound. Since the compound does not absorb significantly in the UV, the compound is not conjugated.

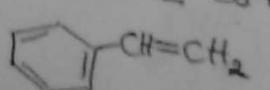
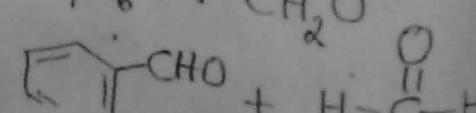
- The IR band at 2985cm^{-1} suggests the $C-H$ stretching vibration of a CH_3- group, i.e. $C-H$ stretching vibration of sp^3 .

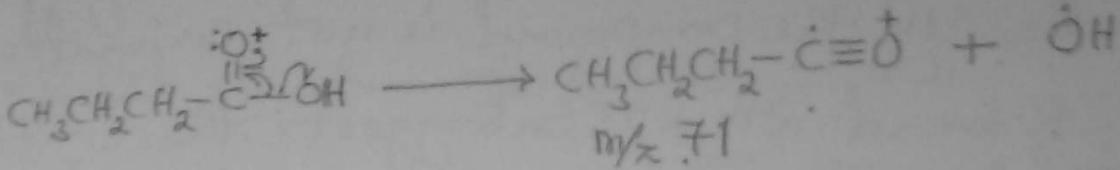
- Strong IR band at 1701cm^{-1} suggests the carbonyl group of a saturated carboxylic acid.



- The strong IR band at 1220cm^{-1} suggests the $C-O$ stretching vibration of a saturated carboxylic acid.

- The integration ratios: $\frac{18}{3} : \frac{2.1}{3} : \frac{6.0}{3} : \frac{9}{3}$
 $= 6 : 2 : 2 : 3$

- (b) Compound B consumes two moles of Cl_2 to give compound C. Suggests that compound B is either an alkyne or a diene.
- Compound B + $\text{H}_2 \xrightarrow{\text{Pt}}$ C_8H_8 (D)
 - Possible structure of D: 
 - Compound D + $\text{O}_3 \xrightarrow{(\text{CH}_3)_2\text{S}}$ $\text{C}_7\text{H}_6\text{O} + \text{CH}_2\text{O}$




c. The molecular ion, M^+ is very weak, m/z 226
 * The peak at m/z 57 is due to the formation of butyl carbocation. $\text{CH}_3\text{CH}_2\text{CH}_2\dot{\text{C}}\text{H}_2^+$ m/z 57

* The peak at m/z 85 is due to a cleavage that gives hexyl carbocation.

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\dot{\text{C}}\text{H}_2$$

m/z 85

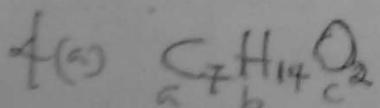
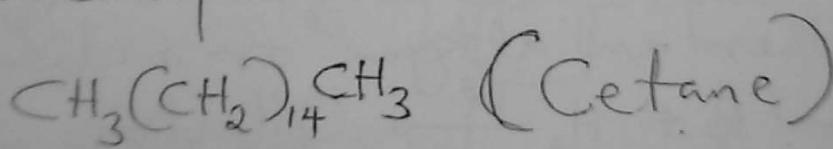
* m/z 141 is due to formation of $\text{CH}_3\text{CH}_2\text{CH}_2\dot{\text{C}}\text{H}_2(\text{CH}_2)_5\dot{\text{C}}\text{H}_2$ m/z 141

* m/z 169 $\text{CH}_3(\text{CH}_2)_8-\dot{\text{C}}\text{H}_2-\text{CH}_2=\dot{\text{C}}\text{H}_2$ m/z 169

\rightarrow The compound is a saturated alkane.

* The peak at m/z 169 was due to the loss of butyl radical, $\text{CH}_3\text{CH}_2\text{CH}_2\dot{\text{C}}\text{H}_2$

\therefore The compound is



$$\text{Double bond equivalent (DBE)} = \frac{(2a+2)-(b-d)}{2}$$

$$\text{DBE} = \frac{(14+2)-(14-0)}{2} = \frac{16-14}{2} = \frac{2}{2} = 1$$

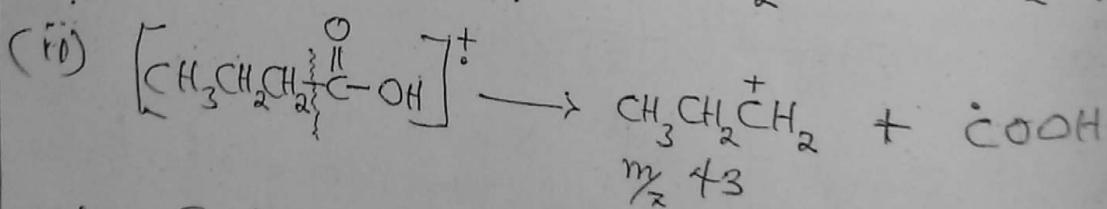
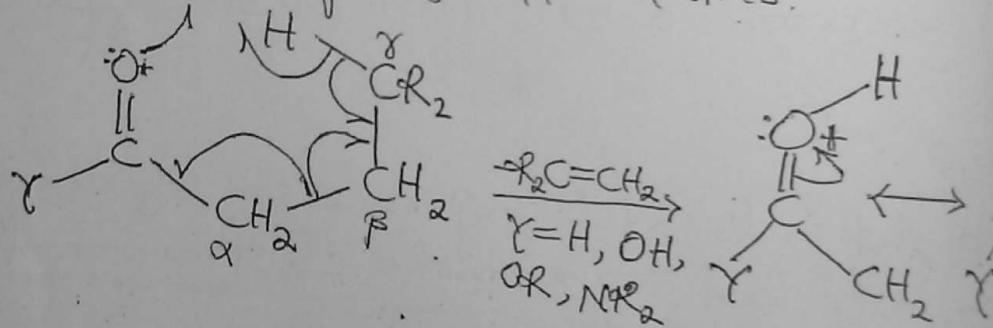
The DBE = 1 suggests a π -system in the

3. (a) (i) ~~Electron ionization~~ technique used in spectrometry depends on ionization carried out by bombarding the molecule by a beam of electron generated by heating a filament at 70eV to give the molecular ion.

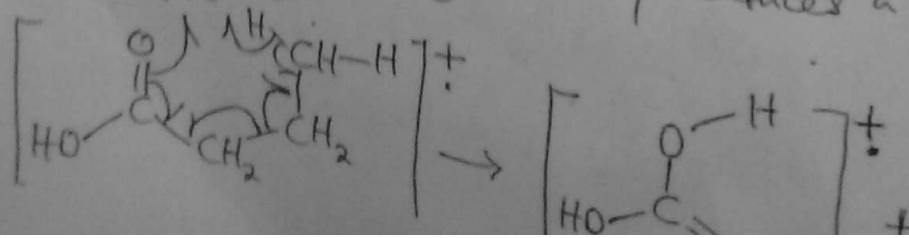
Direct Insertion probe (DIP) does not ionize the sample. Samples are introduced directly into the mass spectrometer. It is for less volatile compounds but thermally stable.

(ii) Chemical ionization (CI) technique in mass spectrometry is used to determine the molecular mass of an unknown compound. It yields a prominent $[M + H]^+$.

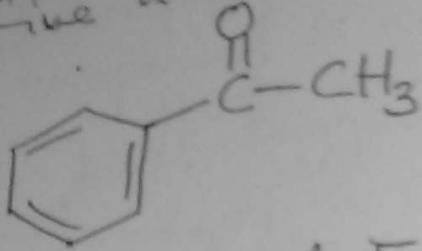
(b) (i) Appropriately located heteroatoms
(ii) Presence of π -electron system
(iii) Presence of γ -H atoms.



Note: Butanoic acid is an acid containing 3 hydrogens. The principal pathway for formation is the McHafferty rearrangement. In the case, this arrangement produces a prominent peak at m/z 60.

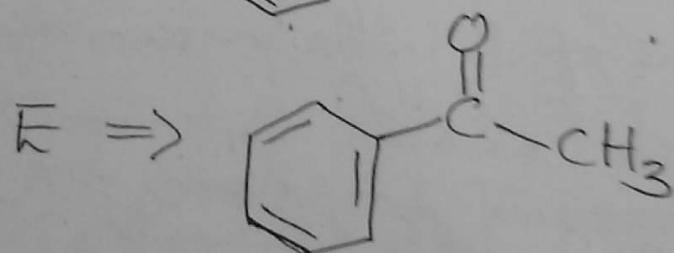
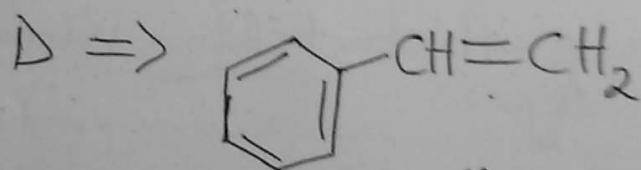
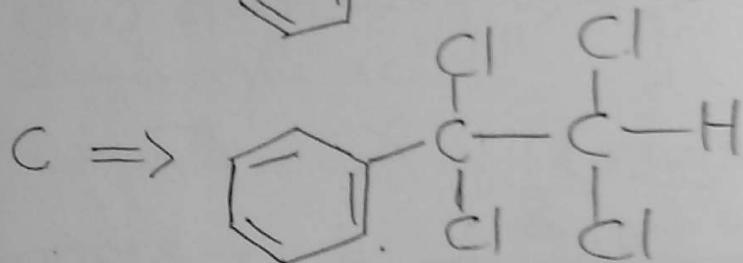
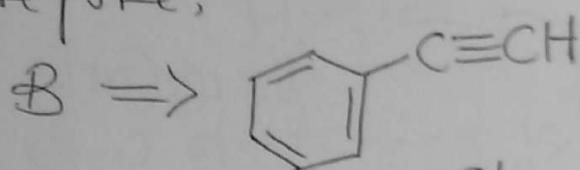


and the multiplet (5H) at $\delta = 7.2$ ppm
confirms the five aromatic protons.
Hence, E is

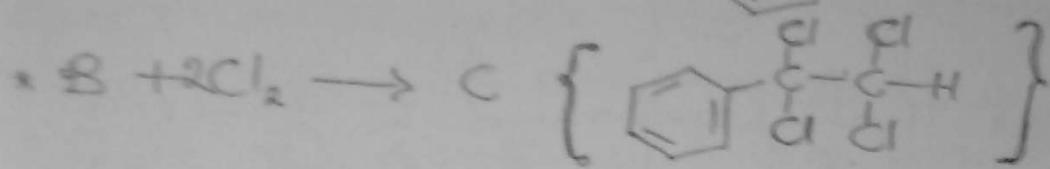


\Rightarrow The fact that Compound E gives a positive iodoform test further confirms the structure. This is a test for a methyl ketone.

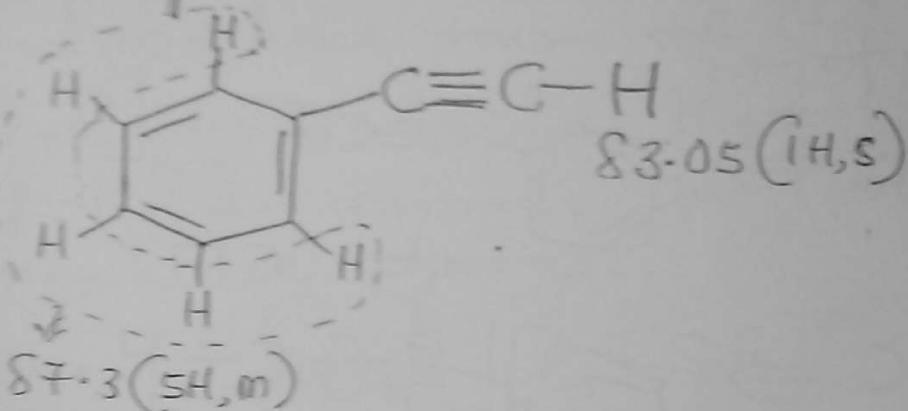
Therefore,



* Possible structure of B: 

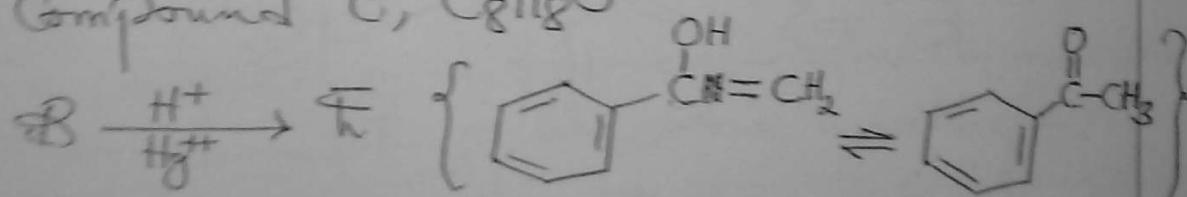


* The 1H -NMR of B confirms the above structure of B.



* The IR absorption band at 3300cm^{-1} further confirms the structure because it depicts the C-H stretching vibration of terminal alkyne.

* Acid hydrolysis of B in the presence of Hg^{2+} gives Compound E, C_8H_8O



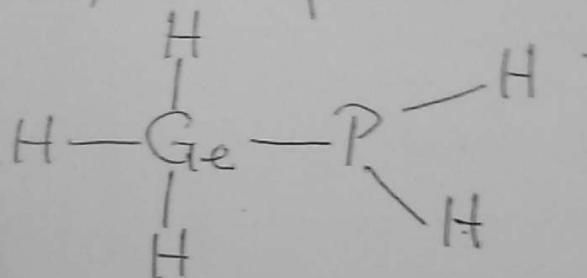
* The IR spectrum of E shows a band at 1690cm^{-1} \Rightarrow carbonyl group (CO) conjugated to the ring, and the band at 770cm^{-1} is the C-H bending vibrations of the aromatic protons.

1H -NMR ~~show~~ for E shows 3H singlet @ $\delta = 2.6$

(5C)

- The spectrum shown indicates two different environments each consisting of two identical signals.
- Ge belongs to group 4, hence, it has four valence electrons while P belongs to group 5, hence it has a valency of 3 or 5.
- P is more electronegative than Ge. Therefore, the protons on P will resonate more down-field than the ones on Ge.
- The hydrogen atoms attached to the more electronegative atom resonate more down field.

Hence, the possible structure is

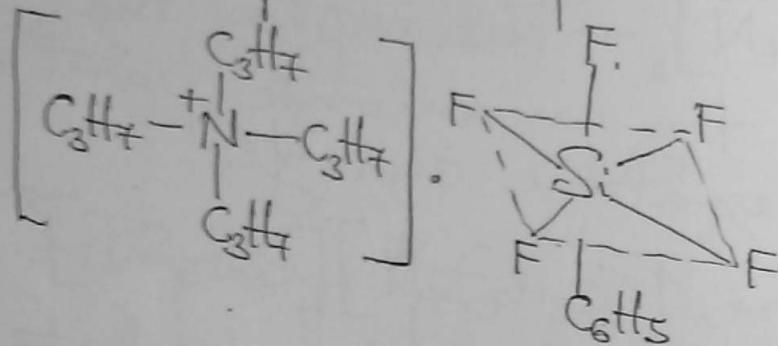


- The 2H on P splits the 3H on Ge by triplet and the 3H on Ge split the 2H on P by quartet.
- The P splits then further to double triplet & double quartet.
- The P will split them again into triplet and quartet.

→ We have two environments (i.e. if in the same plane are equal & will with the one on top (axial position) and the one on top will also interact with them.

The 4 fluorine atoms on the equatorial plane are the same.

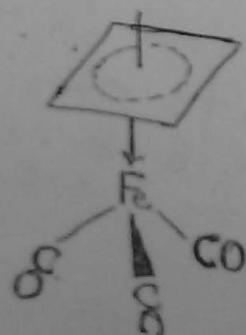
Therefore, we have 2 different fluorine atoms in different environments, the one at the axial position & the ones on the equatorial plane.



(5b) - The strong IR bands at 1985 and 2055cm^{-1} suggests the presence of terminal CO in the product.

The ^1H NMR which gave a sharp line at $\delta = 3.91\text{ ppm}$ suggests that the 4 protons in the product are in the same environment.

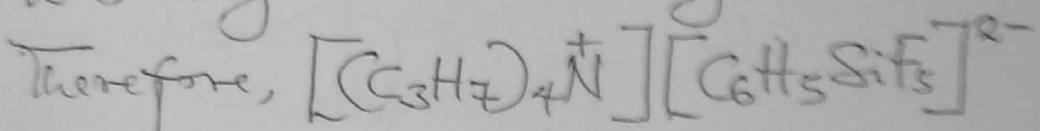
The structure of the product is



(5)(a) The two signals seen in the ^{19}F nmr spectrum suggests fluorine atoms in two different environments.

- Since the compound is a double salt, it has a positive charge and a negative charge.

- The $(\text{C}_3\text{H}_7)_4\text{N}^+$ looks like Li^+ (ammonium ion) and we have two of it i.e $[(\text{C}_3\text{H}_7)_4\text{N}^+]_2$ - This implies that it is joined to an anionic part bearing two negative charges.

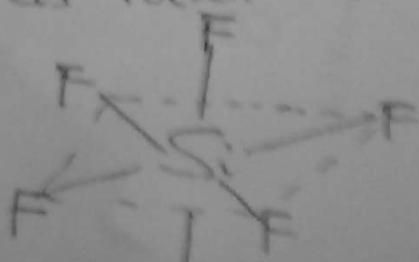


→ Nitrogen, N, cannot extend its covalent character beyond 4 since it is a period 2 element, hence the compound cannot be formulated as $(\text{C}_3\text{H}_7)_4\text{NF} \cdot (\text{C}_3\text{H}_7)_4\text{N} [\text{C}_6\text{H}_5\text{SiF}_5]$ because N cannot have 5 bonds.

→ In this compound, the fluorine atoms are in completely different environment and they cannot split one another.

→ The electronegativity of the atoms affect their position in the nmr spectrum.

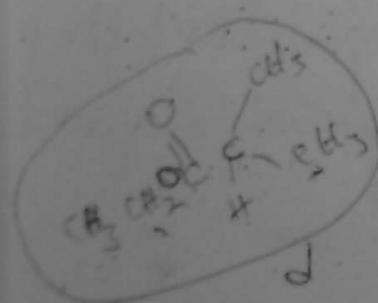
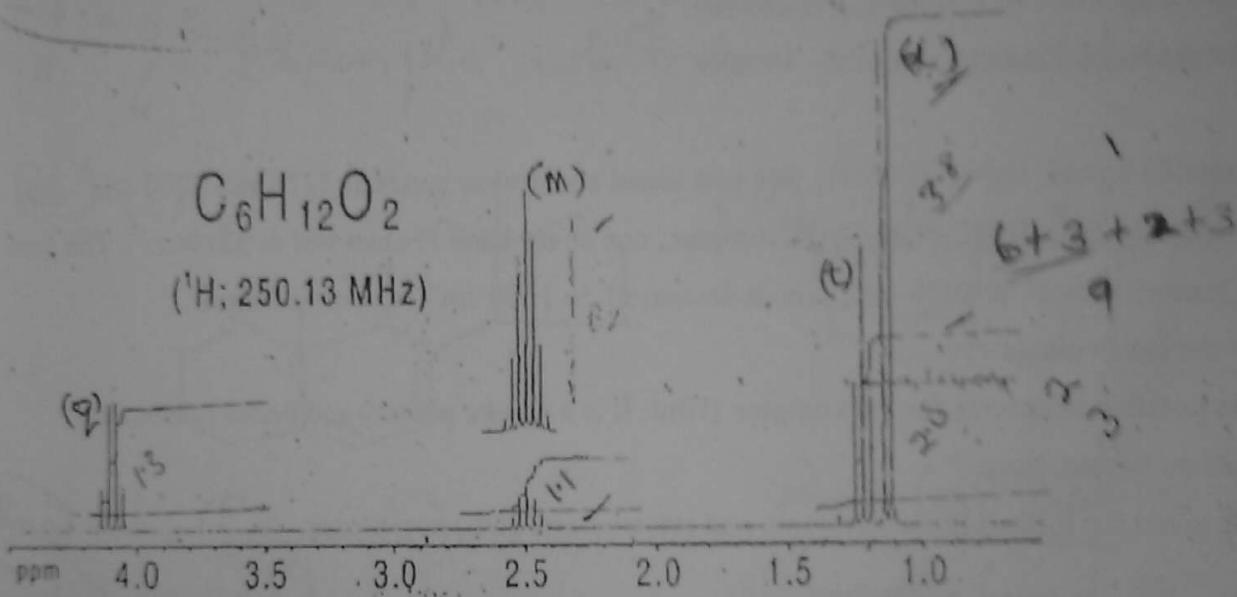
→ Si can extend its coordination number from 4 to 6 because it is in period 3 and that is why this structure is possible.



Compound B

Q3b

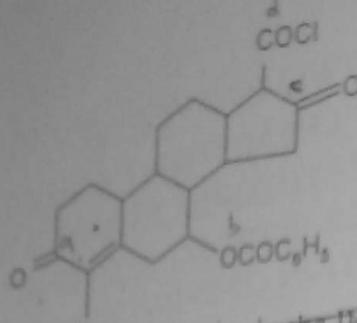
Figure 1



d	3.8 H	3.8	d	3H	8	1.01
t	2.0 2.3	2.0	t	2H	~	1.25
m	2.5 1.1	1.1	m	3H	~	2.5
q	4.0 1.3	1.3	q	3H	~	4.0

6
10 0.6
0.7 3H 6H 1H
1H

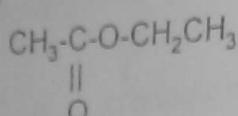
2b. Consider this structure



吸收 at
1710 - 1720 cm⁻¹
due to carbonyl
C=O bond.

- i) List the approximate carbonyl absorption frequencies in the IR and the specific bonds that are responsible for the stated absorption frequencies (2 mks)
- ii) In not more than 2 sentences, state how and why the absorption frequencies differ from that of the carbonyl group in propanone (4 mks)

3a. Predict the proton NMR spectrum of



Indicate the approximate chemical shift and multiplicity for each type of hydrogen. 3 mks

3b. Compound B has molecular formula C₆H₁₂O₂ with IR absorption at 1718 cm⁻¹ and proton NMR spectrum shown in Figure 1. Deduce the structure of B and account for the spectroscopic data provided. 7 mks

4a(i) State the problem associated with the recognition of the molecular ion peak in the mass spectrum of an organic compound. 2 mks

4a(ii) What is the significance of the molecular ion peak in the elucidation of the structure of an organic compound? 2 mks

b. Briefly explain the following terms:

i) Mass spectrum is an intensity vs m/z plot representing a chemical analysis

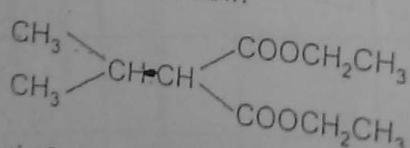
ii) Base peak tallest peak on a mass spectrum

iii) McLafferty rearrangement (give specific example to explain this) 2 mks each

is a retro fragmentation of a molecule of a carbonyl compound containing at least one gamma hydrogen

SECTION B

Examine the structure of a diester D shown below:



List the approximate diagnostic frequencies in the IR at which you would expect the

to absorb.

2mks

(i) It would have sp^2 C-H stretch
on sp C-H stretch
absorption at 1710 - 1720 due to C=O

80

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
 DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE
 B.Sc (CHEMISTRY) DEGREE EXAMINATION PART III
 HARMATTAN SEMESTER, 2010/2011 SESSION
 CHM 307 - APPLICATION OF SPECTROSCOPIC TECHNIQUES



Instructions:

Time allowed: 2½ hrs

Attempt all Questions.

Answer the two sections in separate booklets.

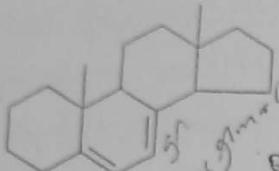
Indicate your Department, registration number on the front cover of every answer booklet used.

SECTION A

State Lambert's/ Beer's law of UV-Vis absorption (equation only) and define each of the parameters in the equation. 2 mks

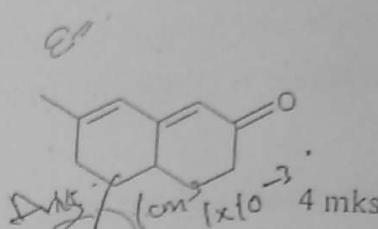
Calculate the wavelength of maximum absorption (λ_{\max}) for each of the following structures:

i)



$C \text{ mol/gm}^{-1}$
 0.0023
molar mass

ii)

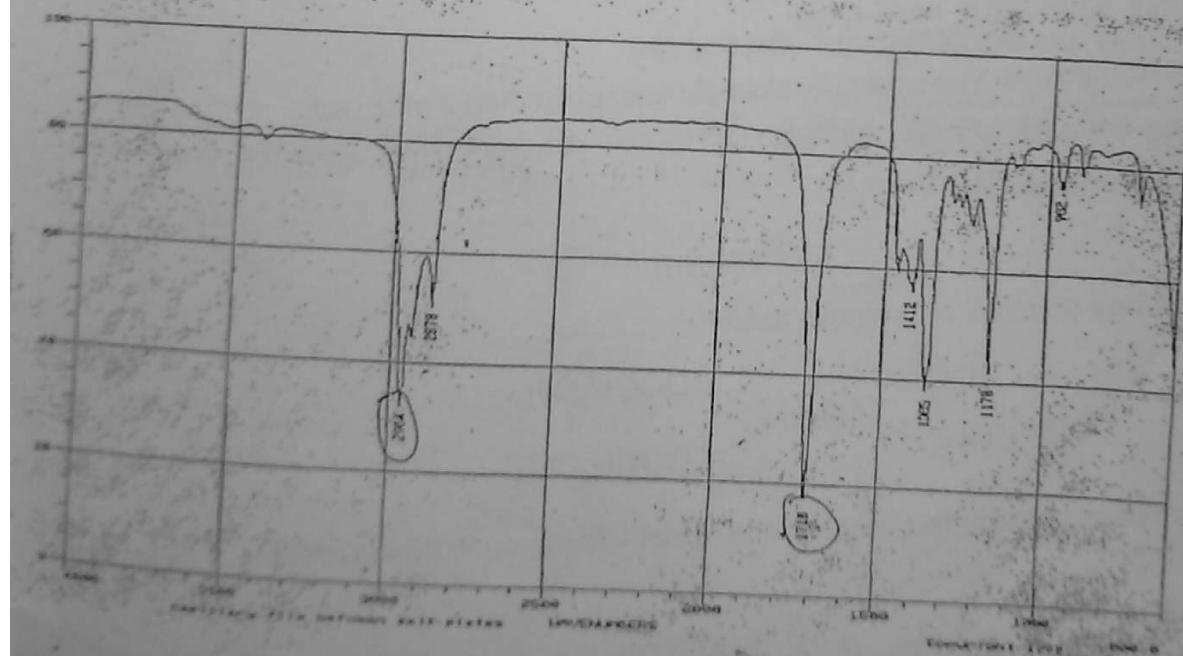


4 mks

A solution of 0.0023 g of 3,4-dimethyl-3-penten-2-one in 1 liter of ethanol gives maximum absorbance of 0.695 at 249 nm when placed in a cell of path length 2.0 cm. Calculate the molar absorptivity of 3,4-dimethyl-3-penten-2-one at the maximum absorption. 4 mks

a. Compound A has the molecular formula $C_5H_{10}O$ and IR spectrum as shown below:

Account for the spectroscopic details provided and deduce the possible structure(s) of A. 4 mks



$$\begin{aligned} l &= 1 \text{ dm}^3 \\ M &= \text{cm}^3 \\ L &= 1000 \text{ cm}^3 \end{aligned}$$

$\delta_{CH} = 1$ 1718 cm^{-1} indicates C=O Sharp bands at
 $\delta_{H_{10}O} = 5$ 2964 cm^{-1} shows $\text{sp}_3\text{C}-\text{H}$ stretch
 $\text{CH}_3\text{CH}_2\text{C}\text{H}_2\text{CH}_3$ $2890 - 2980$
 might indicate a ketone → presence of C=O als

2010/2011 EXAMINATION SOLUTIONS

1. (a) $A = ECl$

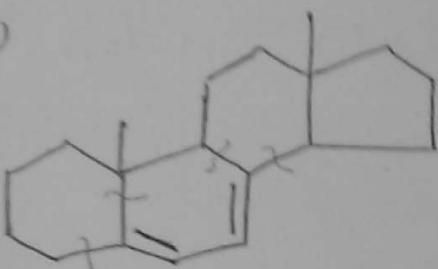
where A is the absorbance.

E is the molar absorptivity coefficient or molar extinction coefficient

l is the path length in cm

C is the concentration of the sample solution in mol dm⁻³.

(b) (i)

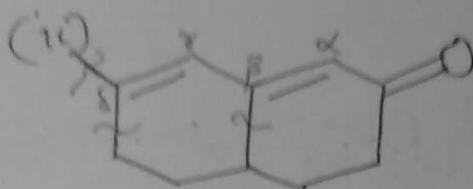


Base value (homocyclic ring) = 253 nm

+ alkyl substituents (5 nm) = 20 nm

Exocyclic bond = 5 nm

$$\lambda_{\max} = \underline{278 \text{ nm}}$$



Base ($\alpha\beta$ -unsat'd ketone) = 215 nm

Exocyclic bond = 5 nm

β -ring residue = +12 nm

δ -ring residues = $2 \times 18 = 36 \text{ nm}$

Double bond ext. = 30 nm

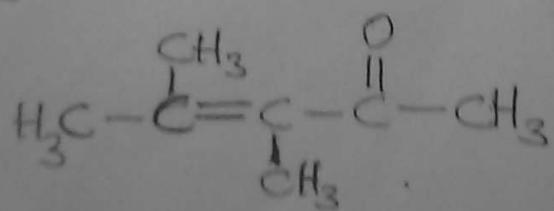
$$\lambda_{\max} = \underline{298 \text{ nm}}$$

(c) m = 0.0023 g

Volume, V = 1 L = 1 dm³

A = 0.695 @ $\lambda = 249 \text{ nm}$

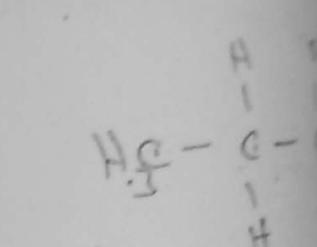
l = 2.0 cm



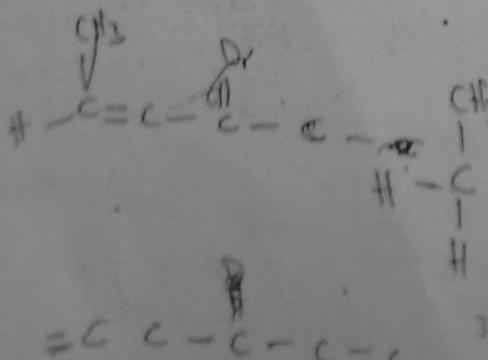
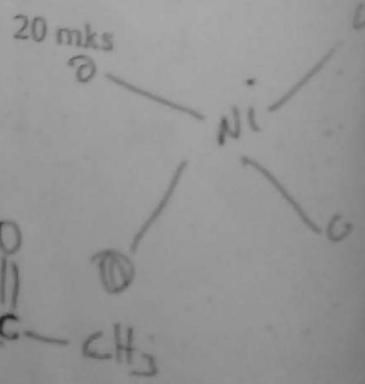
Molar mass, M = $(7 \times 12) + (12 \times 1) + 16$
 $= 84 + 12 + 16$
 $= 112 \text{ g mol}^{-1}$

- ii) Indicate the number of different nmr signals that should be obtained for the structure, together with the multiplicity that would be expected for each different set of hydrogen atoms.
- b) Predict the fragmentation pattern of 2-methyl-3-pentanol upon electron impact showing only major characteristic peaks. 5 mks
- c) A compound E with molecular formula $C_7H_{17}O$ has an IR absorption peak at 1685 cm^{-1} . It gives a positive iodoform test and decolourises bromine in CCl_4 . In addition, ozonolysis of E gives two products:
- propose three structures for E
 - Calculate λ_{max} for each structure
 - identify the structure of E if its λ_{max} is 249 nm .
 - give the products of ozonolysis of E. 10 mks
- 6a. The oxamide ligand, $H_2NCOCONH_2$, has two broad absorption bands at 3370 and 3200 cm^{-1} coordination to form $[Ni(C_2H_2N_2O_2)]^{2-}$ complex, one sharp band is observed at 3310 cm^{-1} . The ligand showed a band at 1650 cm^{-1} which decreased to 1600 cm^{-1} in complexation.
- Assign the bands above
 - Propose possible structures for the complex (Hint: It is a square planar) and hence reasonably conclude on the structure.
- b) You are given the following isoelectronic and isostructural (OL) complexes

Complex	$\nu_{CO}\text{ (cm}^{-1}\text{)}$
$Mn(CO)_6^+$	2090
$Cr(CO)_6$	1970
$V(CO)_6^-$	1860

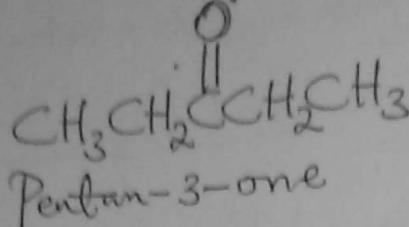


Comment on the bonding in these complexes

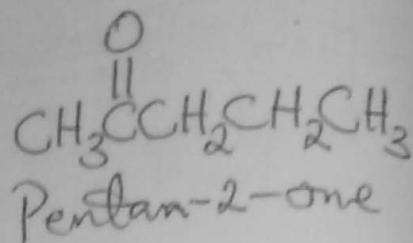


E

Therefore, from the ^{IR} spectrum given, the structures of A are

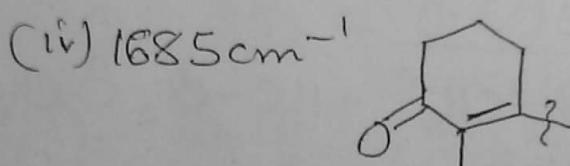
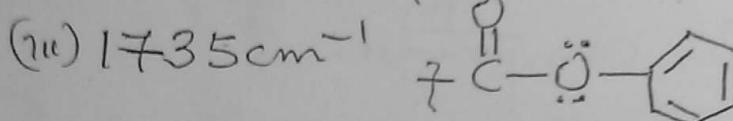
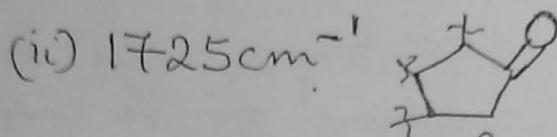
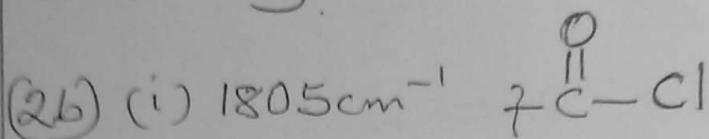


Pentan-3-one

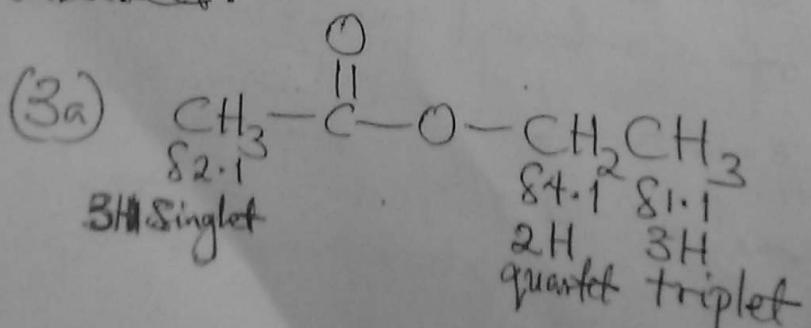


Pentan-2-one

Note: The compound is not an aldehyde. It is confirmed from the absence of IR bands at 2810 and 2740cm^{-1} due to C-H stretching vibration of aldehyde.



The IR ~~of~~ of the carbonyl absorption depends on various factors such as electronic, ring strain and conjugation are involved. Hence, the absorption frequencies are raised or lowered depending on the factors involved.



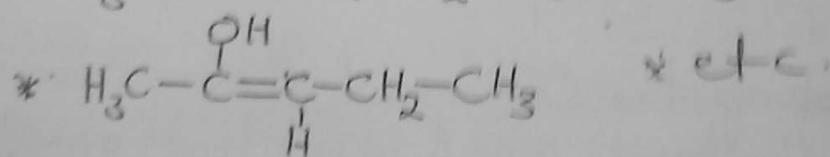
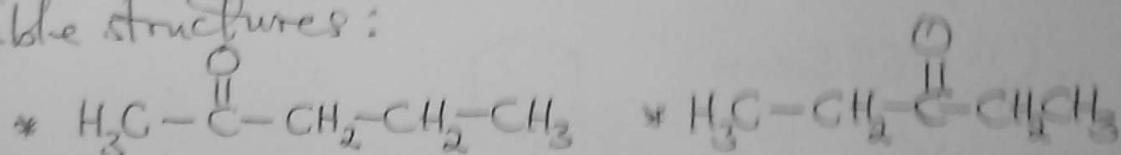
(2) $\text{C}_5\text{H}_{10}\text{O}$ \Rightarrow The molecular formula suggests a ketone, aldehyde, ether or alcohol.

Double bond equivalent, DBE = $\frac{(2a+2)-(b-d)}{2}$

$$= \frac{2(5)+2-10}{2}$$
$$= \frac{12-10}{2}$$
$$= \frac{2}{2}$$
$$= 1.$$

The DBE = 1 indicates one $\text{C}=\text{O}$ bond or $\text{C}=\text{C}$ in the compound or the compound may be a cyclic compound.

Possible structures:



\Rightarrow The sharp IR band at 1718cm^{-1} indicates the presence of carbonyl functional group, C=O in the compound (i.e. CO of a Ketone).

\Rightarrow The IR band at 2964cm^{-1} suggests the C-H stretching vibration of sp^3 carbon.

$$\text{Number of moles, } n = \frac{m}{M}$$
$$= \frac{0.0023\text{ g}}{112\text{ g mol}^{-1}}$$
$$= 2.05 \times 10^{-5} \text{ mol}$$

∴ Concentration of solution,

$$C = \frac{\text{Number of moles of solute}}{\text{Volume of solution}}$$

$$C = \frac{2.05 \times 10^{-5} \text{ mol}}{1.0 \text{ dm}^3}$$

$$C = 2.05 \times 10^{-5} \text{ mol dm}^{-3}$$

i) Using $A = \epsilon Cl$

$$\therefore \epsilon = \frac{A}{Cl}$$

$$\epsilon = \frac{0.695}{2.05 \times 10^{-5} \times 2}$$

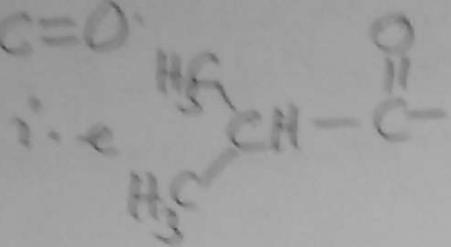
$$\epsilon = \frac{0.695}{5.10 \times 10^{-5}}$$

$$\epsilon = 0.136 \times 10^5$$

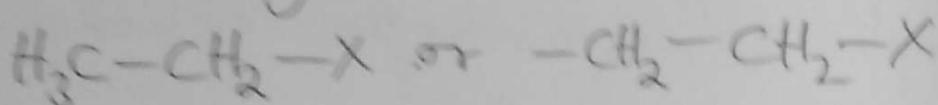
$$\epsilon = 1.36 \times 10^4$$

$$\underline{\epsilon = 13,600}$$

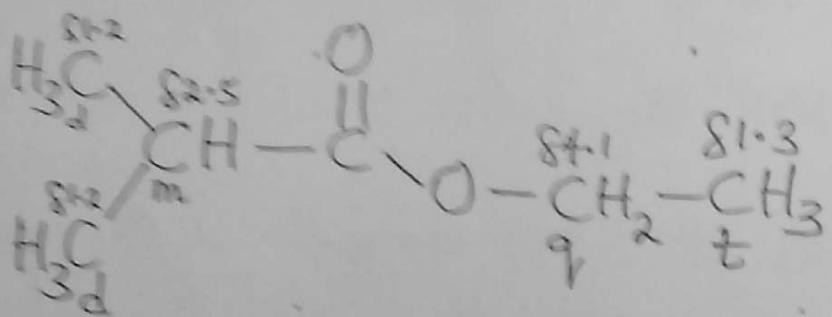
- The multiplet (m) at 82.5 suggests a -CH₂ attached to two CH₃ or CH₂ & the CH is attached to a C=O.



- The triplet (t) at 81.3 suggest a -CH₂ attached to more electronegative element.



Therefore, putting all these information together, the possible structure of X is



The structure is consistent with the 4 chemical environments seen on the ¹H-NMR spectrum in fig. 1.

(3b) The molecular formula, $C_6H_{12}O_2$ suggests a carboxylic acid, acetal, ketal, ester, diol, dicarbonyl compound, hydroxyketone or hydroxyaldehyde.

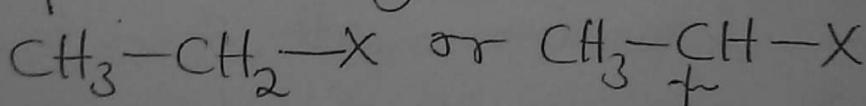
- The IR absorption at 1718cm^{-1} confirms the presence of C=O , therefore the possible compounds narrowed down to carboxylic acid, ester & dicarbonyl compound.

$$-\text{DBE} = \frac{14 - 12}{2} = \frac{2}{2} = 1$$

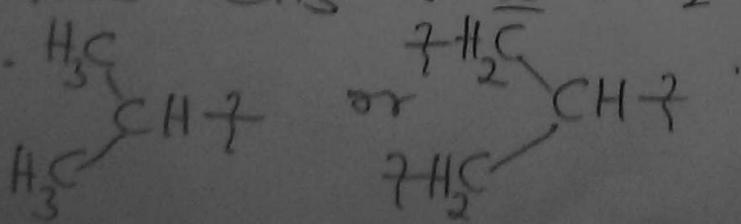
This suggests a carboxylic acid or ester.

- The $^1\text{H-NMR}$ suggests 4 chemical environments.

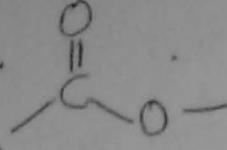
- The quartet (q) at 84.1 suggests a CH_3 attached to either CH or CH_2 which is attached to highly electronegative element.



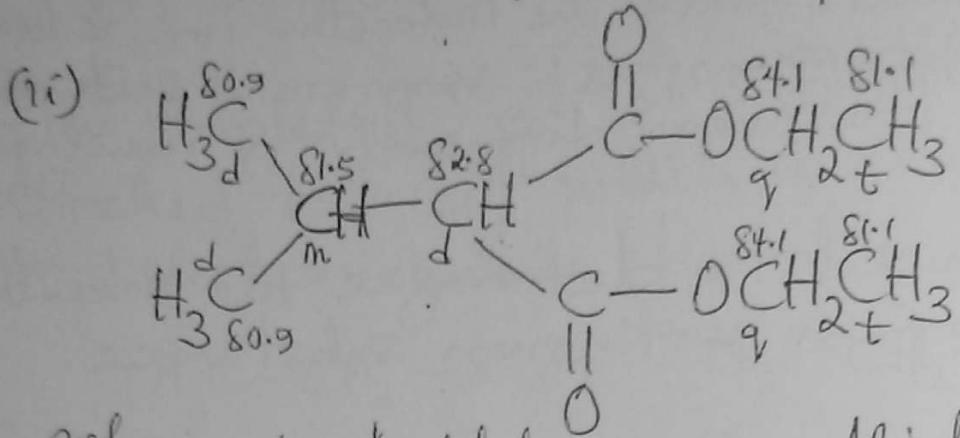
- The doublet (d) at 81.2 suggests a CH_3 or CH_2 system attached to a carbon bearing only one proton. This signal is more pronounced, this may be due to two CH_3 or 2 CH_2 attached to CH .



(5)(a). 1740cm^{-1} due to CO of ester.

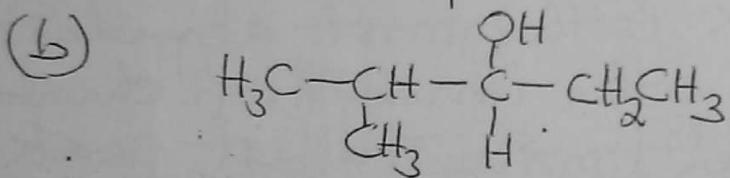


* $\approx 2985\text{cm}^{-1}$ due to C-H stretching
vibration of sp^3 carbon.

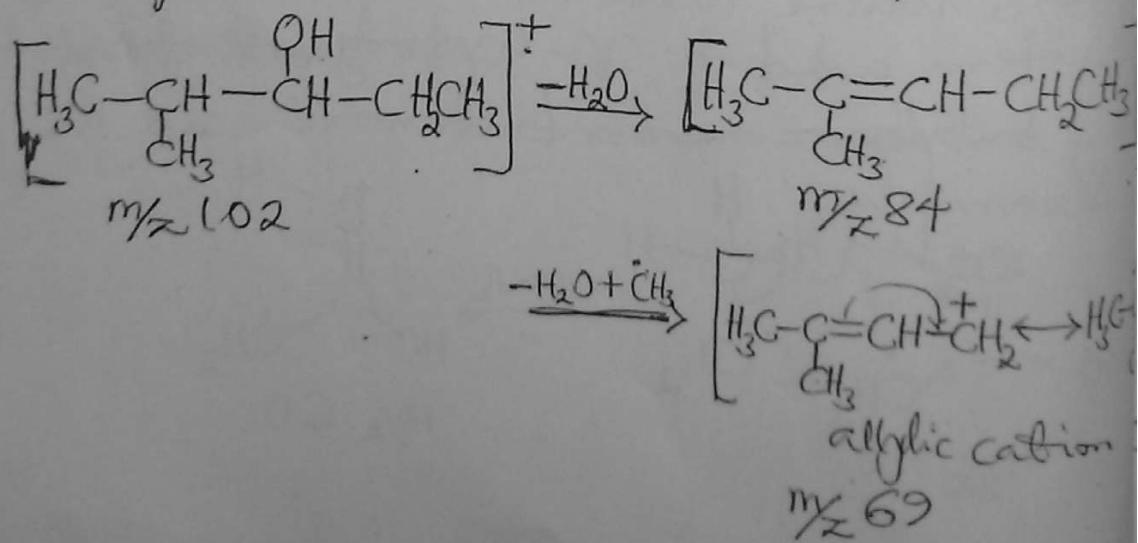


where d = doublet
q = quartet
t = triplet

m = multiplet.



Note: The most common ~~example~~ fragmentation of alcohol is the loss of water, which occurs so readily that the molecular ion is often weak or absent. The peak corresponding to loss of water.



f(a)(i) The problem associated with the recognition of the molecular ion peak in the mass spectrum of an organic compound is the intensity of the peak obtained. Since the molecular ion is heavy sometimes it appear as a very small peak, ~~that~~ such that it is very difficult to identify.

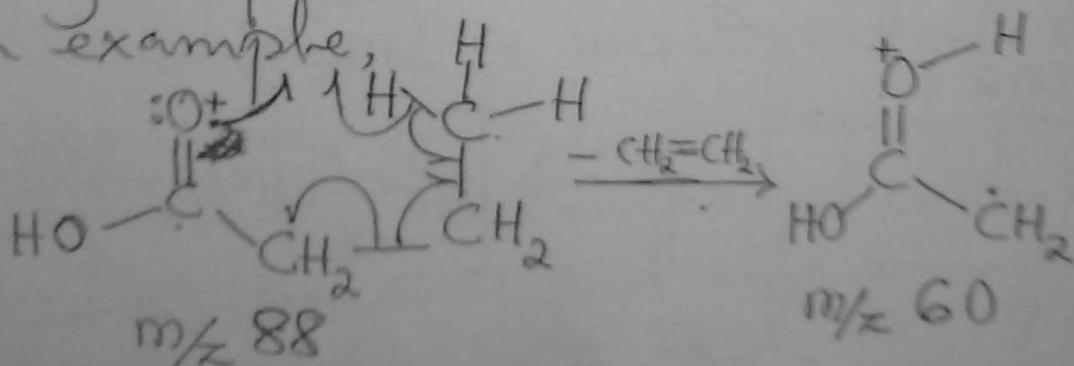
(ii) It is used to determine the molecular weight of an unknown substance.

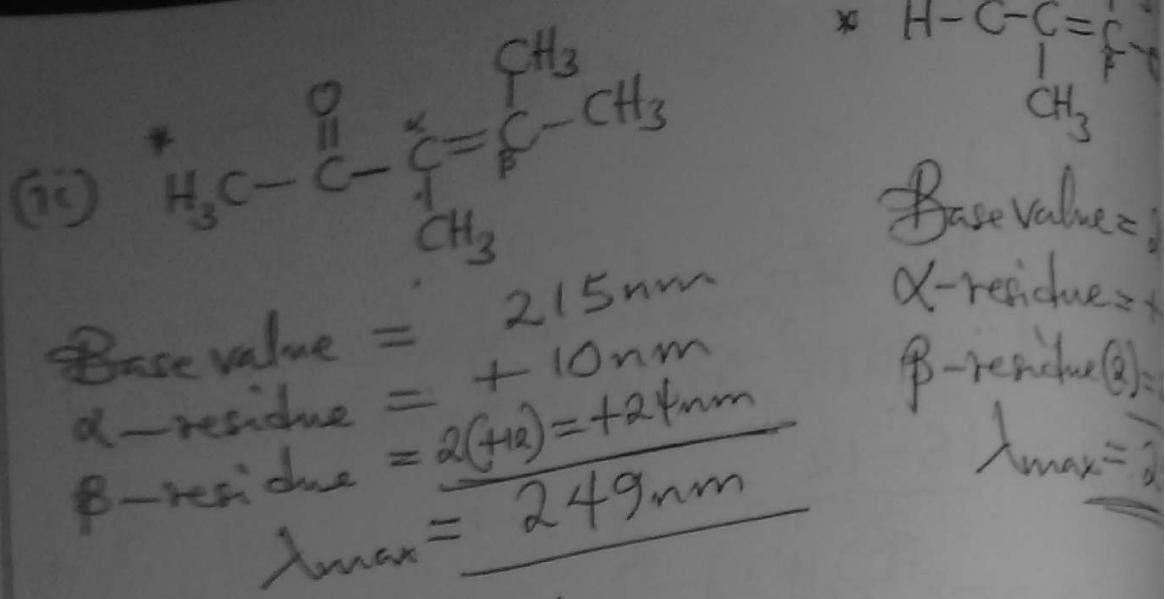
(b) (i) The mass spectrum is a plot of ion abundance versus m/z ratio.

(ii) Base peak is the most abundant ion formed in the ionization chamber which gives rise to the tallest peak in the mass spectrum.

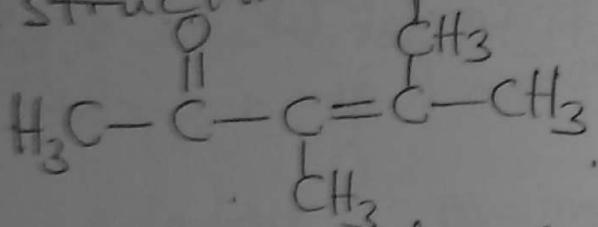
(iii) McLafferty rearrangement

This is a rearrangement that occurs in compound where there is an heteroatom, π -system and a γ -hydrogen atom. Using ~~butyloxene~~ butanoic acid as an example,

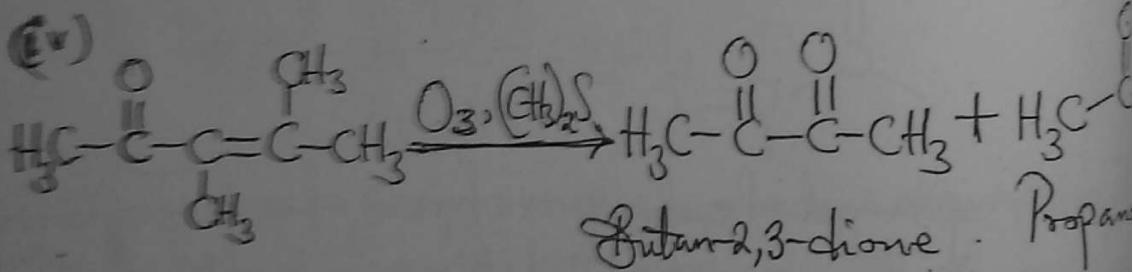




(v) The structure of E is

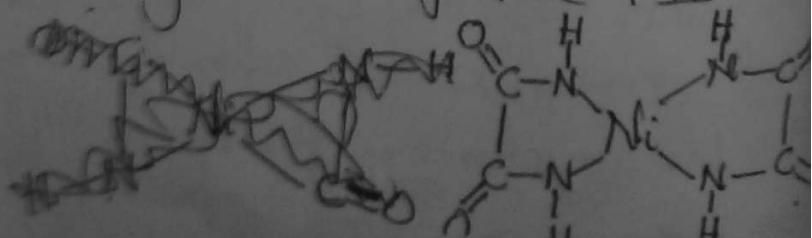


3,4-dimethyl-3-penten-2-one.



(6) (a) Ni is the central atom and it has a coordination number of 4.

$[\text{Ni}(\text{C}_2\text{H}_5\text{N}_2\text{O}_2)]^{2-}$ comes from L_2X salt
 Ni shows a range of oxidation state from (-I) to (+IV) but its chemistry is predominantly that of the +II state.



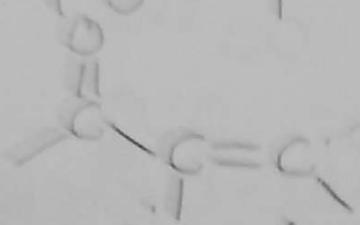
(b) C_8H_{10}

The molecular formula suggests a carbonyl compound, ether, alcohol or hemiacetal.

$$\text{DBE} = \frac{18 - 12}{2} = \frac{4}{2} = 2$$

The DBE suggests the presence of two conjugated systems. It could be an α, β -unsaturated carbonyl compound or a cyclic unsaturated ketone.

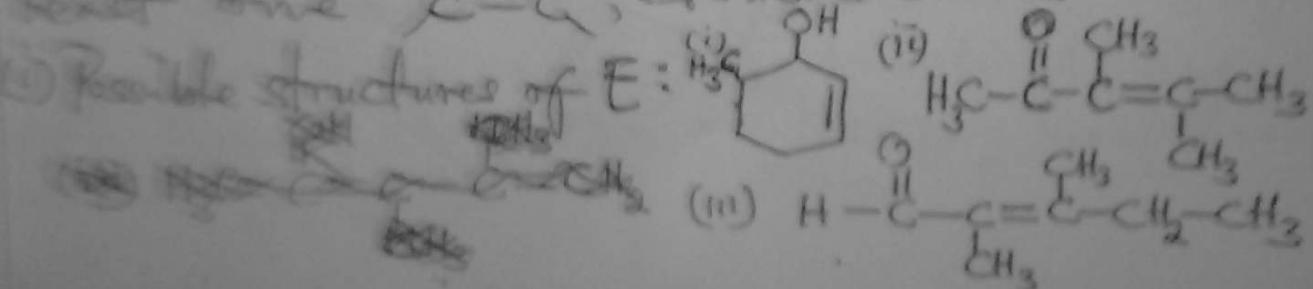
The IR absorption at 1685cm^{-1} suggests carbonyl group, & conjugated to C=C .

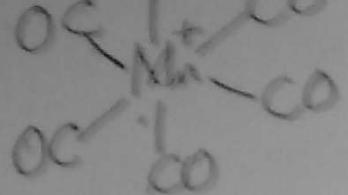


The compound test positive to iodoform test \Rightarrow the compound has a methyl group attached to C=O i.e. methyl ketone or methyl alcohol, $\text{CH}_3-\overset{\text{I}}{\underset{\text{I}}{\text{C}}}-\text{OH}$

The compound decolorises bromine in CCl_4 \Rightarrow the compound is unsaturated.

Izonysis of the compound gives two products \Rightarrow the compound contain at least one C=C , double bond.

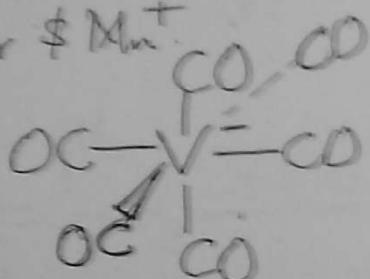




Mn forms this complex with +1 oxidation state.

* $\text{V}(\text{CO})_6^- \Rightarrow \text{V}^- \text{ --- } 4s^2 3d^3$

Vanadium, V obtained six valence electrons through the gain of one electron, V⁺. V⁻ with six valence electrons combines with six molecules of CO, each donating electrons to form hexacarbonovanadate (I)⁻, in which V has 18 electrons and is isoelectronic with both Cr & Mn⁺.



V forms this complex with -1 oxidation state.

Comment on the IR band

* It is observed that the carbonyl absorption increases with increasing electropositivity of the central specie.

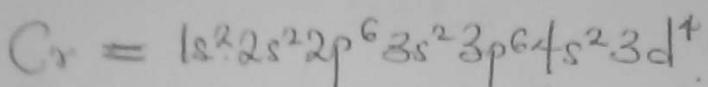
$$\text{i.e. } \text{Mn}^+ > \text{Cr} > \text{V}^-$$

* Therefore, electropositivity of the central affect the carbonyl absorption frequency.

* The terminal carbonyls of Mn⁺ absorb at higher frequency (2030 cm^{-1}), than that of

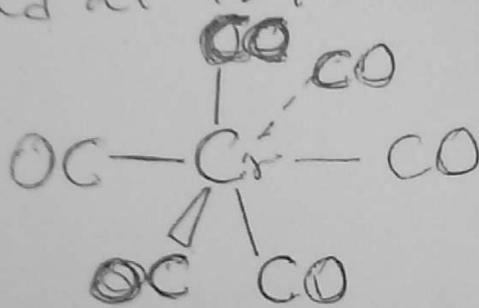
* The IR bands at 3370 & 3200cm^{-1} are due to the N-H stretching frequencies.

(66) $\text{Cr}(\text{CO})_6$



Cr^0 has six valence electrons which combines with six molecules of CO, each donating two electrons, to afford Cr hexacarbonyl $[\text{Cr}(\text{CO})_6]$, in which Cr has 18 valence electrons and is isoelectronic to krypton (Kr).

The band at 1970cm^{-1} suggests terminal CO.



Cr forms six coordinate complex with zero oxidation state.

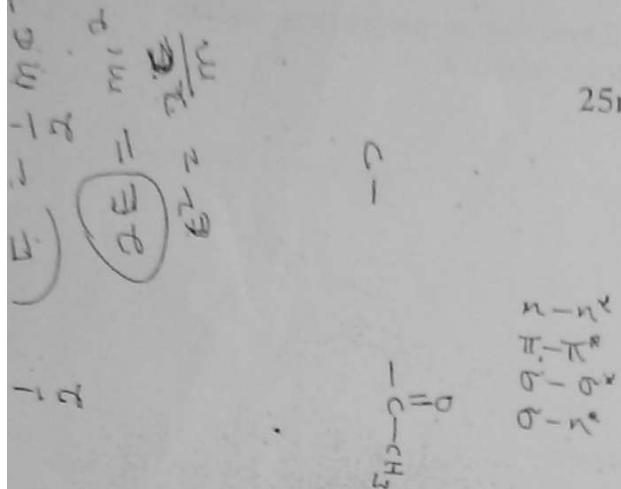


In this complex, Manganese, being the central atom carries positive charge and it is isoelectronic to Cr. Therefore, Mn^+ has six valence electrons which combines with six molecules of CO, each donating two electrons to afford Manganese(I)hexacarbonyl, in which Mn has 18 valence electrons, hence satisfying the eighteen electron rule.

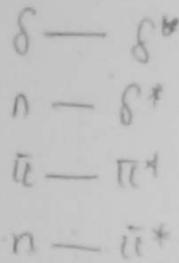
Predict the main features of the IR and UV spectra of B.In doing so, list the diagnostic parameters: ν_{max} for IR and λ_{max} for UV. Also indicate the specific bond structural features which are responsible for the stated parameters.

1c (i). A solution of 0.0015 g of benzophenone ($C_{13}H_{10}O$) in 1 liter of ethanol has maximum absorbance reading of 0.154 in a 1 cm cell at $\lambda_{\text{max}} = 253 \text{ nm}$. Calculate absorptivity of benzophenone

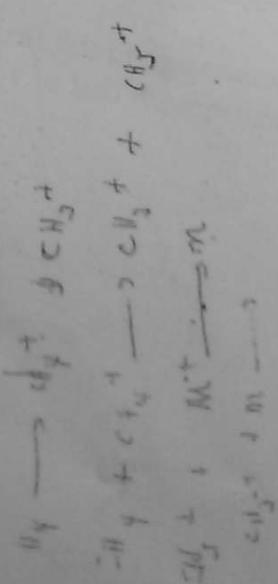
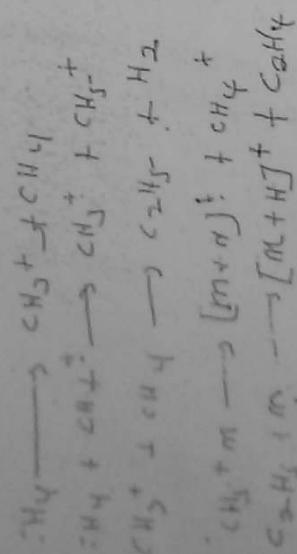
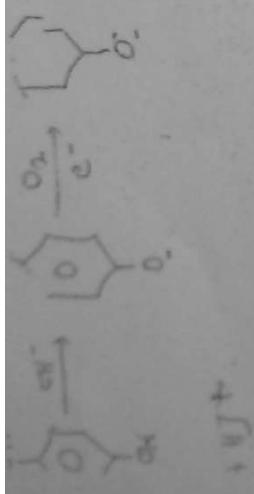
1c(ii) Summarize the four types of electronic excitation for most organic molecules



25marks



Efect
It also have the other fragmental structures for dir by
there is a change to form meta stable ion



CHM 307: Application of spectroscopic techniques

Mid-semester test – May 2011

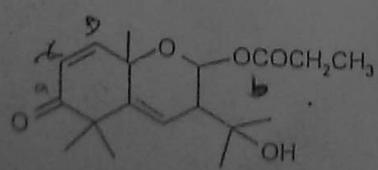
Instructions: Answer all questions

Write your name and registration number on your answer booklet

Compound A has the molecular formula $C_5H_{10}O$ and IR spectrum as shown below. Account for the spectroscopic details provided and deduce the possible structure(s) of A.



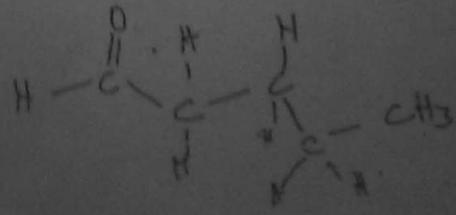
A natural product B has been assigned the structure shown below (by means of chemical correlation of its structure with that of a known compound).



$$a = 1628$$

$$b = 1725$$

$$c = e = 1620 //$$



absorb at a high frequency of 1970cm^{-1}
while the least electropositive V⁻ carbonyl
absorb at 1860cm^{-1} .

$$A = 0.154 \text{ ; } l = 1\text{cm}$$

$$\epsilon = ?$$

Using $A = \epsilon cl$

$$\epsilon = \frac{A}{cl}$$

$$\epsilon = \frac{0.154}{8.72 \times 10^{-6} \times 1}$$

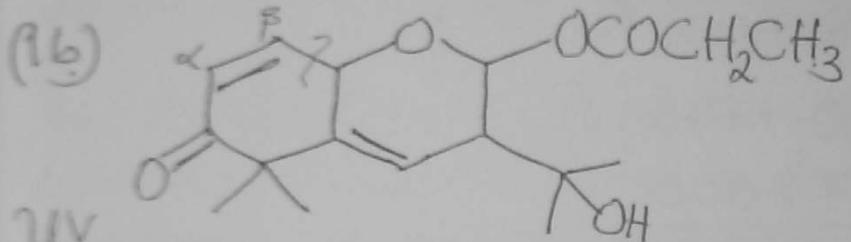
$$\epsilon = 0.177 \times 10^6$$

$$\epsilon = \underline{\underline{177000}}$$



2010/2011 TEST SOLUTION

(1) Check solution to 2a of 2010/2011 Examination.



UV

Base value (α, β -Unsaturated Ketone) = 215 nm

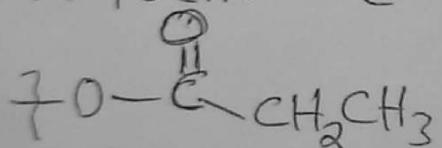
β -residue = +12 nm

Exocyclic bond = +5 nm

$$\lambda_{\text{max}} = \underline{\underline{232 \text{ nm}}}$$

IR: $\bar{\nu}_{\text{CO}} \approx 1685 \text{ cm}^{-1}$ (The CO is in conjugation with the C=C in the ring).

$\bar{\nu}_{\text{CO}} \approx 1740 \text{ cm}^{-1}$ (CO of an ester)



$\bar{\nu}_{\text{OH}} \approx 3500 \text{ cm}^{-1}$ (free OH group of an alcohol).

~~(e)~~ (E) $m = 0.0015 \text{ g}$

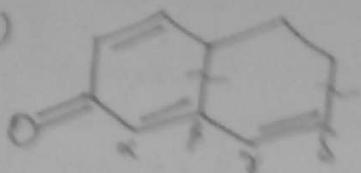
$$M_{\text{C}_4\text{H}_7\text{O}} = (13 \times 12) + (10 \times 1) + 16 = 172 \text{ g mol}^{-1}$$

$$\therefore n = \frac{m}{M} = \frac{0.0015 \text{ g}}{172 \text{ g mol}^{-1}} = 8.72 \times 10^{-6} \text{ mol}$$

$$\therefore \text{Concentration, } C = 8.72 \times 10^{-6} \text{ mol dm}^{-3}$$

SOLUTIONS TO TUTORIAL QUESTIONS

1. (i)



Parent value ($\alpha\beta$ -Unsaturated six ring Ketone) = 215nm

$$= +12\text{nm}$$

β -ring residue

$$= +18\text{nm}$$

δ -ring residue

$$= +5\text{nm}$$

One exocyclic double bond

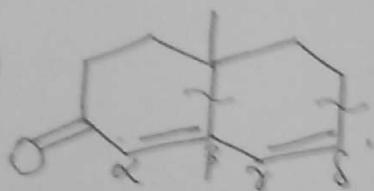
$$= +30\text{nm}$$

Double bond extension

$$\lambda_{\max} = \underline{\underline{280\text{nm}}}$$

λ_{\max}

(ii)



Parent value = 215nm

$$\beta\text{-ring residue} = +12\text{nm}$$

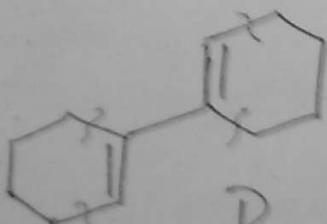
$$\delta\text{-ring residue} = +18\text{nm}$$

$$\text{Double bond extension} = +30\text{nm}$$

$$\text{Exocyclic double bond} = +5\text{nm}$$

$$\lambda_{\max} = \underline{\underline{280\text{nm}}}$$

(iii)



Parent Value = 215nm

$$\delta\text{-ring residue} = +5\text{nm} = 20\text{nm}$$

$$\lambda_{\max} = \underline{\underline{235\text{nm}}}$$

2. $A = 0.735$; $l = 2\text{cm}$; $\epsilon = 21,000$, $c = ?$

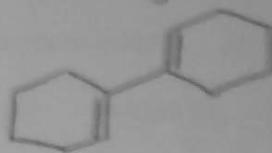
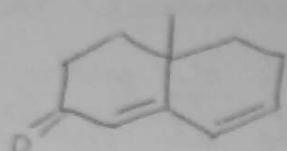
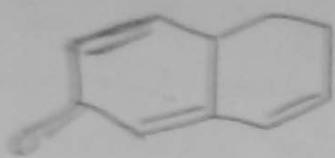
$A = \epsilon cl$ (Beer-Lambert law)

$$\therefore c = \frac{A}{\epsilon l} = \frac{0.735}{21,000 \times 2} = \underline{\underline{1.75 \times 10^{-5} \text{ mol/dm}^3}}$$

4. A 1.64 mg of an organic compound, molar mass 482, was made to 10cm^3 of solution. 1cm^3 of the solution, diluted to 5cm^3 , gave an absorbance of 0.84 at λ_{max} of 227 nm using a cell of 1 cm path length. Use these results to calculate the molar extinction coefficient of the compound.
5. 2.05×10^{-5} M solution of 3,4-dimethyl-3-penten-2-one gives a maximum absorbance reading of 0.695 at 249 nm when placed in a cell of path length 2 cm. Calculate the molar absorptivity at the maximum absorption.
6. A compound with molecular formula $\text{C}_8\text{H}_{12}\text{O}$ has an IR band at 1686 cm^{-1} , it decolorises bromine in CCl_4 and gives a positive iodoform test. Ozonolysis of the compound gives one product only. It has λ_{max} 238 nm. Propose a structure for the compound.
7. In an attempt to determine the UV spectrum of a naturally occurring compound, having a molar mass of 428, a student weighed out 4.1 mg of this compound and made it to the mark in 5 mL standard flask. 2 mL of the solution were pipetted and diluted to 10 mL, a trial run showed that the solution was too concentrated, hence, he diluted 1 mL of the new solution to 5 mL. If this final solution gave an absorbance of 0.84 at a wavelength with λ_{max} of 219 nm calculate the molar extinction coefficient of the compound. Take L to be 1 cm.

UV-VIS Spectroscopy Tutorial Questions.

Calculate $\lambda_{\text{max}}^{\text{start}}$ (UV) for the following compounds:



The UV Spectrum of a solution of 1,3-butadiene was determined and the following data obtained:
 Absorbance reading (maximum) = 0.735

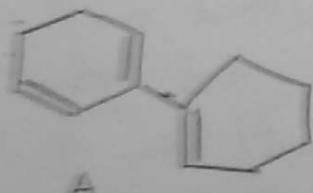
$$\lambda_{\text{max}} = 217 \text{ nm}$$

$$\text{Path length of cell} = 2 \text{ cm}$$

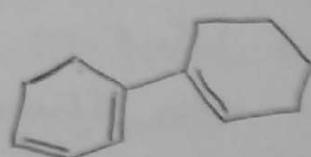
$$\text{Molar extinction coefficient} (E_{\text{max}}) = 21,000$$

Calculate the concentration of the butadiene solution

The λ_{max} for compounds A through I were measured and the following values obtained:



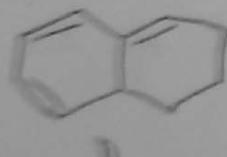
A



B



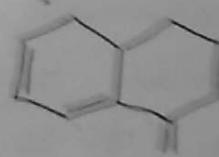
C



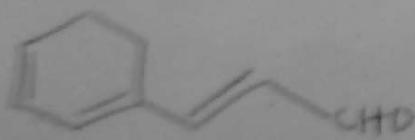
D



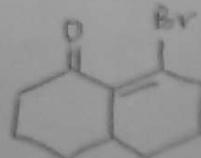
E



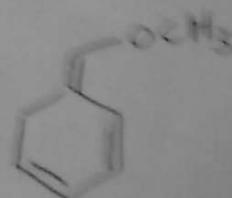
F



G



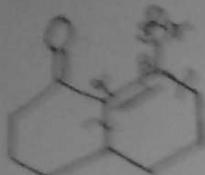
H



I

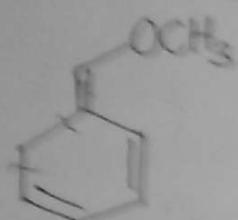
312, 298, 304, 305, 285, 342, 254, 272, and 308. Assign each λ_{max} to lettered compounds.

H



Parent value = 215nm
 α -alkyl residue = +10nm
 β -alkyl residue = +12nm
 Br @ β -position = +30nm
Exocyclic ring = +5nm
 $\lambda_{max} = \underline{272\text{nm}}$

I



Parent value = 253nm
 Double bond extension = +30nm
Exocyclic bond = +5nm
Methoxy Substituent = +6nm
2 ring residue = +10nm
 $\lambda_{max} = \underline{304\text{nm}}$

$$4. m = 1.6\text{mg} = 1.6 \times 10^{-3}\text{g}; M = 482\text{gmol}^{-1}$$

$$\therefore n = \frac{m}{M} = \frac{1.6 \times 10^{-3}\text{g}}{482\text{gmol}^{-1}} = 3.402 \times 10^{-6}\text{mol.}$$

$$\begin{aligned} \text{Conc. of } 10\text{cm}^3 \text{ solution} &= \frac{3.402 \times 10^{-6}}{10} \times 1000 \\ &= 3.402 \times 10^{-4}\text{mol/l} \end{aligned}$$

Using dilution principle,

$$C_1 = 3.402 \times 10^{-4}\text{M}; V_1 = 1\text{cm}^3$$

$$C_2 = ? ; V_2 = 5\text{cm}^3$$

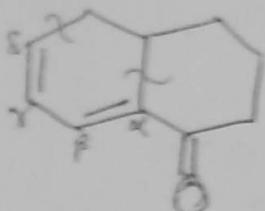
E



Parent value = 253 nm
 Double bond ext. = +30 nm
 α -ring residue = +10 nm
 β -alkyl residue = +5 nm

$$\lambda_{\max} = \underline{\underline{298 \text{ nm}}}$$

F



Parent value = 215 nm
 α -residue = +10 nm
 δ -residue = +19 nm
 Double bond ext. = +30 nm
 Exocyclic bond = +5 nm
 Homodiene component = +39 nm

$$\lambda_{\max} = \underline{\underline{318 \text{ nm}}}$$

G

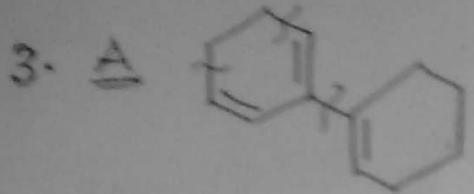


Parent value (χ_2 -unsat. aldehyde) = 207 nm
 γ -residue = +17 nm
 δ -residue = +19 nm

2 double bond extension = +60 nm

Homodiene component = +39 nm

$$\lambda_{\max} = \underline{\underline{342 \text{ nm}}}$$

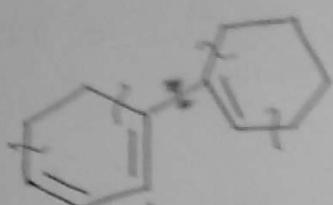


$$\text{Parent value (Homoannular diene)} = 253\text{nm}$$

$$\text{3 ring residue} = 3 \times 5\text{nm} = 15\text{nm}$$

$$\lambda_{\max} = \underline{\underline{268\text{nm}}}$$

B



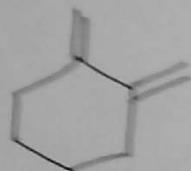
$$\text{Parent value} = 253\text{nm}$$

$$\text{Double bond extension} = +30\text{nm}$$

$$+ \text{ring residue} = +5\text{nm} = +20\text{nm}$$

$$\lambda_{\max} = \underline{\underline{303\text{nm}}}$$

C



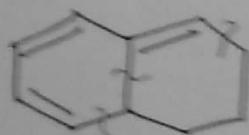
$$\text{Parent value} = 215\text{nm}$$

$$2 \text{ exocyclic bonds} = 10\text{nm}$$

$$2 \text{ ring residue} = \underline{\underline{10\text{nm}}}$$

$$\lambda_{\max} = \underline{\underline{235\text{nm}}}$$

D



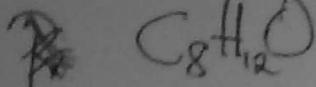
$$\text{Parent value} = 253\text{nm}$$

$$\text{Double bond ext.} = +30\text{nm}$$

$$\text{Exocyclic bond} = +5\text{nm}$$

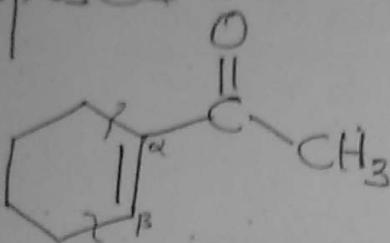
$$3 \text{ ring residue} = +15\text{nm}$$

$$\lambda_{\max} = \underline{\underline{303\text{nm}}}$$



$$\text{DBE} = \frac{18 - 12}{2} = \frac{6}{2} = 3$$

The proposed structure is



$$\text{Parent value} = 215 \text{ nm}$$

$$\alpha\text{-residue} = +10 \text{ nm}$$

$$\beta\text{-residue} = +12 \text{ nm}$$

$$\lambda_{\max} = 237 \text{ nm}$$

$$(7) M = 728; m = 4.1 \times 10^{-3} \text{ g};$$

$$n = \frac{m}{M} = \frac{4.1 \times 10^{-3} \text{ g}}{728 \text{ g mol}^{-1}} = 9.579 \times 10^{-6} \text{ mol}$$

$$C_1 = \frac{9.579 \times 10^{-6}}{5 \times 10^{-3}} = 1.916 \times 10^{-3} \text{ M}$$

$$V_1 = 2 \text{ ml}; V_2 = 10 \text{ ml}; C_2 = ?$$

$$\Rightarrow C_2 = \frac{C_1 V_1}{V_2} = \frac{1.916 \times 10^{-3} \times 2}{10} = 3.832 \times 10^{-4} \text{ M}$$

$$\Rightarrow C'_1 = 3.832 \times 10^{-4} \text{ M}; V'_1 = 1 \text{ ml}; C'_2 = ?; V'_2 = 5 \text{ ml}$$

$$\therefore C'_2 = \frac{3.832 \times 10^{-4} \times 1}{5} = 7.664 \times 10^{-5} \text{ M}$$

$$A = 0.84; l = 1 \text{ cm}; \epsilon = ?$$

$$A = \epsilon C l$$

$$\therefore \epsilon = \frac{A}{C l} = \frac{0.84}{7.664 \times 10^{-5} \times 1} = 10960.33$$

$$\Rightarrow GV_1 = C_2 V_2$$

$$C_2 = \frac{GV_1}{V_2} = \frac{3.402 \times 10^{-4} \times 1}{5}$$

$$C_2 = 6.805 \times 10^{-5} M$$

$$A = 0.84 @ \lambda_{\max} = 227 \text{ nm}$$

$$l = 1 \text{ cm}; \epsilon = ?$$

Using Beer-Lambert's law,

$$A = \epsilon Cl$$

$$\therefore \epsilon = \frac{A}{Cl} = \frac{0.84}{6.805 \times 10^{-5} \times 1}$$

$$\epsilon = 12343.86 \approx \underline{12000}$$

(5) $C = 2.05 \times 10^{-5} M; A = 0.695 @ \lambda_{\max} = 249 \text{ nm}$

$$l = 2 \text{ cm}; \epsilon = ?$$

$$A = \epsilon Cl; \epsilon = \frac{A}{Cl} = \frac{0.693}{2.05 \times 10^{-5} \times 2}$$

$$\epsilon = 16951.22$$

$$\epsilon \approx \underline{17000}$$

- (6) The IR band at 1686 cm^{-1} suggests a carbonyl (CO) in conjugation with a $\text{C}=\text{C}$ double bond (Conjugated ketone).
The compound is said to be unsaturated because it decolorises Br_2 in CCl_4 .
It may be a methyl ketone because it gives positive iodoform test.
Ozonolysis gives only one product \Rightarrow the compound is a ring or symmetrical.