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CHEMISTRY

PAPER No. 12: Organic Spectroscopy

MODULE No. 32: Combined problem on UV, IR, ¹H NMR, ¹³C NMR and Mass- Part IV

TABLE OF CONTENTS

1. Learning Outcomes
2. Introduction
3. Problems and their solutions



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1. Learning Outcomes

After studying this module, you shall be able to

- Solve problem related with electronic transitions
- Learn how to differentiate molecule on the basis of IR spectroscopy
- Correlate spectra with structure of compound
- Interpret the spectroscopic data

2. Introduction

The knowledge and concepts of UV-visible, IR, ^1H NMR, ^{13}C NMR and Mass help us in solving problems based on the experimental data. It will help us in analysing the experimental data to elucidate the structure of any organic compound.

While analysing the data the following point must be kept in mind:

- In UV-visible spectroscopy; the types of bonds and electrons plays important role in understanding the electronic transitions.
- UV-visible spectroscopy gives information regarding the presence of conjugation, carbonyl group etc.
- The IR values gives information regarding the functional group present in the molecule
- The ^1H NMR tells us the number and environment of neighbouring hydrogens present.
- The ^{13}C NMR helps in getting the information about the type of carbon atom(s) present in the molecule.
- Mass spectral data gives information about the total mass and fragmentation pattern of the molecule.

By combining all the information one can find the structure of the molecule.

3. Problems and their solutions

Q. 1: A volatile compound with molecular mass 130 contains 73.85% C and 13.5% H. The compound is transparent above 210 m μ in UV region. In its IR region, bands are formed at 2960-2851 (m), 1342 (w) and 1075 cm⁻¹ (s). Only a singlet at 8.95 τ is formed in its NMR spectrum. Find the structural formula of the compound.

A. 1: The compound contains:

$$C = 73.85\%$$

$$H = 13.50\%$$

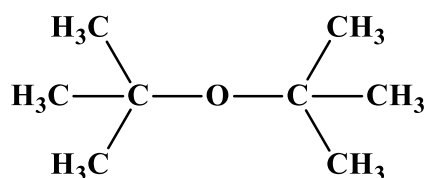
$$O = 100 - (73.85 + 13.85) = 12.3\%$$

From this data, the empirical formula of the compound is C₈H₁₈O.

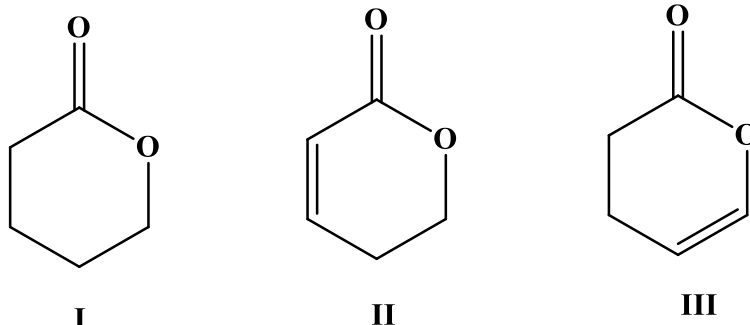
Since, the compound is transparent above 210 m μ in the UV region, it shows the absence of carbonyl group, N containing group and conjugation etc. In the IR region spectrum, there is a most characteristic at 1075 cm⁻¹ (s) for an ether (C-O stretching) in C-O-C group.

The other bands at 2960-2851 (m) and at 1342 cm⁻¹ (w) are for C-H stretching and C-H bending vibrations respectively.

The appearance of only one singlet at the high field 8.95 τ reveals that the alkyl groups in the compound are in exactly similar environments. It is only possible if the structure of the compound is as given below:



Q. 2: The carbonyl stretching absorptions for the following lactones are (1745); (1720); 1760 cm^{-1} . Match the absorptions with the appropriate structure and give a reason for each choice.



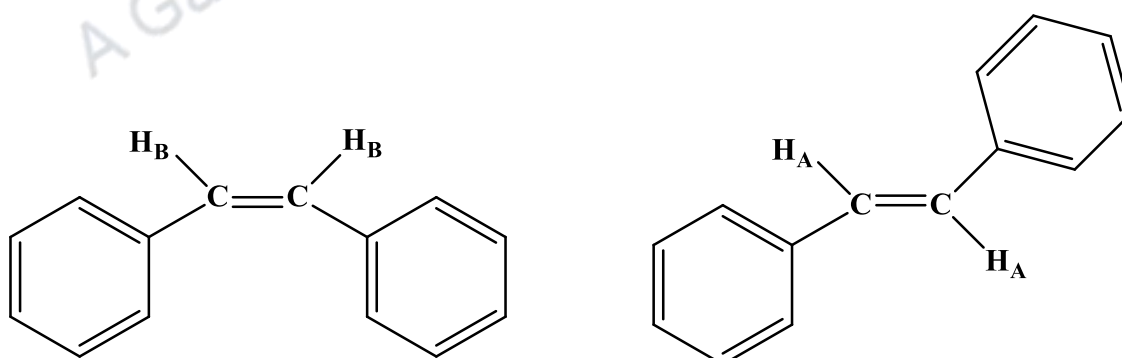
A. 2: The carbonyl stretching absorptions for the following lactones are as follows:

I (1745); II (1720); III 1760 cm^{-1} .

In the lactone III, the conjugation of the C-C double bond with carbonyl group resulting in an increase in the double bond character of the carbonyl group and consequently an increase in the carbonyl frequency occurs as compared to the saturated lactone (I).

Q. 3: How will you distinguish between cis and trans- stilbenes on the basis of PMR spectroscopy?

A. 3: Cis and trans stilbenes can be distinguished from their respective chemical shift values.



In trans-stilbene, a planar structure, each of the two olefinic protons (H_A) is deshielded by both aromatic rings while in the cis-stilbene each hydrogen (H_B) is deshielded by only one

adjacent aromatic ring. H_A 's, therefore, appear at a low field than H_B 's (7.0 δ and 6.05 δ ppm respectively).

Q. 4: Why aren't all proton magnetic resonance signals found at the same frequency? After all they all arise from the magnetic properties of the same nucleus, namely H.

A. 4: The resonance condition $\Delta E = h\nu$ is satisfied when $\Delta E = \gamma B$ where B is the value of the magnetic field at the H nucleus being observed. B can be regarded as having three components: B_0 the external applied magnetic field; B_1 the field due to electrons circulating near the nucleus being observed; this is called the chemical shift δ ; and B_2 the local magnetic field due to other magnetic nuclei (e.g. other H nuclei) near the observed H nucleus; this is called J or spin-spin coupling. So in general differently situated H nuclei resonate at different ν values.

Q. 5: How many different chemical shifts do you expect for H nuclei in the following molecules? Where there is more than one chemical shift expected what will be the relative intensities of the different signals?



A. 5: In CH_4 , all H nuclei are equivalent since the molecule has a regular tetrahedral shape. Equivalent protons have the same chemical shift and do not give rise to J splitting. Only one chemical shift is expected. In CH_3CH_3 the argument is the same as for CH_4 and only one shift is expected. A useful test for magnetic and chemical equivalence is to replace mentally the hydrogens in question by a Cl atom. If you get the same compound then the nuclei are equivalent. Thus ClCH_2CH_3 is the same compound as $\text{CH}_3\text{CH}_2\text{Cl}$. In $\text{CH}_3\text{CH}_2\text{CH}_3$, the two terminal CH_3 groups are magnetically and chemically equivalent and so their hydrogen atoms will all have the same chemical shift. The central CH_2 group is different and will give a resonance signal at a different chemical shift. So two different chemical shifts are expected. Their relative intensities will have the same ratio as the number of H nuclei in the different environments, that is 6:2 or 3:1. $\text{H}_2\text{C}=\text{CH}_2$ All H nuclei in this planar molecule are

equivalent. Try the Cl substitution test. Only one chemical shift is expected. $\text{H}_2\text{C}=\text{CHBr}$ Each H nucleus in this planar molecule is different! Try the Cl replacement test – you get three different molecules. So three chemical shifts are expected with intensities in the ratio 1:1:1. 3.

Q. 6: What spin-spin coupling patterns do you expect for each distinct set of H nuclei in the following molecules. CH_3CHCl_2 , $\text{CH}_3\text{CHClCH}_3$, $\text{CH}_3\text{OCH}_2\text{CH}_3$?

A. 6: In CH_3CHCl_2 , there are two different chemical shifts for the H nuclei in this compound. The $n+1$ rule tells us that for the CH_3 group the single H nucleus in the adjacent CHCl_2 group will split its signal into a 1:1 doublet (2 equal peaks). For the CHCl_2 group the 3 protons in the adjacent CH_3 group will split its signal into a quartet: four peaks of relative intensities 1:3:3:1. The total intensities of the two signals will be in the ratio 3:1. In $\text{CH}_3\text{CHClCH}_3$ for the CHCl group the 6 equivalent H nuclei in the two adjacent and equivalent CH_3 groups will give rise to a 7 peak signal (a septet). For the two equivalent CH_3 groups the single H nucleus in the CHCl group will give rise to an equal doublet signal. The total intensities of the two signals will be in the ratio of 1:6. In $\text{CH}_3\text{OCH}_2\text{CH}_3$, the ether oxygen with its bonds means that the magnetic effects of the sets of H nuclei on the two sides of the ether O are not transmitted through it. Thus the 3 H nuclei in the CH_3O group give rise to one unsplit signal. For the OCH_2CH_3 group we expect a 1:3:3:1 quartet for the CH_2 group and a 1:2:1 triplet for the CH_3 group. Total intensities for the 3 signals will be in the ratio 3:2:3.