Objectives

After completing this section, you should be able to

1. explain how multiple coupling can give rise to complex-looking $^1$H NMR spectra.
2. predict the splitting pattern expected in the $^1$H NMR spectrum of an organic compound in which multiple coupling is possible.
3. interpret $^1$H NMR spectra in which multiple coupling is evident.

Key Terms

Make certain that you can define, and use in context, the key term below.

- tree diagram

Study Notes

We saw the effects of spin-spin coupling on the appearance of a $^1$H NMR signal. These effects can be further complicated when that signal is coupled to several different protons. For example, BrCH$_2$CH$_2$CH$_2$Cl would produce three signals. The hydrogens at C$_1$ and C$_3$ would each be triplets because of coupling to the two hydrogens on C$_2$. However, the hydrogen on C$_2$ “sees” two different sets of neighbouring hydrogens, and would therefore produce a triplet of triplets.

Another effect that can complicate a spectrum is the “closeness” of signals. If signals accidently overlap they can be difficult to identify. In the example above, we expected a triplet of triplets. However, if the coupling is identical (or almost identical) between the hydrogens on C$_2$ and the hydrogens on both C$_1$ and C$_3$, one would observe a quintet in the $^1$H NMR spectrum. [You can try this yourself by drawing a tree diagram of a triplet of triplets assuming, first, different coupling constants, and then, identical coupling constants.] Keep this point in mind when interpreting real $^1$H NMR spectra.

Also, when multiplets are well separated, they form patterns. However, when multiplets approach each other in the spectrum they sometimes become distorted. Usually, the inner peaks become larger than the outer peaks. Note the following examples:

- two multiplet NMR signals brought closer together become distorted

Aromatic ring protons quite commonly have overlapping signals and multiplet distortions. Sometimes you cannot distinguish between individual signals, and one or more messy multiplets often appear in the aromatic region.

It is much easier to rationalize the observed $^1$H NMR spectrum of a known compound than it is to determine the structure of an unknown compound from its $^1$H NMR spectrum. However, rationalizations can be a useful learning technique as you try to improve your proficiency in spectral interpretation. Remember that when a chemist tries to interpret the $^1$H NMR spectrum of an unknown compound, he or she usually has additional information available to
make the task easier. For example, the chemist will almost certainly have an infrared spectrum of the compound and possibly a mass spectrum too. Details of how the compound was synthesized may be available, together with some indication of its chemical properties, its physical properties, or both.

In examinations, you will be given a range of information (IR, MS, UV data and empirical formulae) to aid you with your structural determination using $^1$H NMR spectroscopy. For example, you may be asked to determine the structure of C$_6$H$_{12}$O given the following spectra:

**Infrared spectrum:** 3000 cm$^{-1}$ and 1720 cm$^{-1}$ absorptions are both strong

<table>
<thead>
<tr>
<th>$^1$H NMR</th>
<th>δ (ppm)</th>
<th>Protons</th>
<th>Multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.87</td>
<td>6</td>
<td>doublet</td>
<td></td>
</tr>
<tr>
<td>1.72</td>
<td>1</td>
<td>broad multiplet</td>
<td></td>
</tr>
<tr>
<td>2.00</td>
<td>3</td>
<td>singlet</td>
<td></td>
</tr>
<tr>
<td>2.18</td>
<td>2</td>
<td>doublet</td>
<td></td>
</tr>
</tbody>
</table>

To answer this question, you note that the infrared spectrum of C$_6$H$_{12}$O shows $\ce{\sf{C-H}}$ stretching (3000 cm$^{-1}$) and $\ce{\sf{C-O}}$ stretching (1720 cm$^{-1}$). Now you have to piece together the information from the $^1$H NMR spectrum. Notice the singlet with three protons at 2.00 ppm. This signal indicates a methyl group that is not coupled to other protons. It could possibly mean the presence of a methyl ketone functional group.

methyl ketone group

The signal at 1.72 ppm is a broad multiplet, suggesting that a carbon with a single proton is beside carbons with several different protons.

lone proton on carbon

The doublet signal at 2.18 ppm implies that a $\ce{\sf{-CH2-}}$ group is attached to a carbon having only one proton.

carbon with two hydrogens attached to carbon with one hydrogen

The six protons showing a doublet at 0.87 ppm indicate two equivalent methyl groups attached to a carbon with one proton.

carbon with one proton and two methyl groups

Whenever you see a signal in the 0.7-1.3 ppm range that is a multiplet of three protons (3, 6, 9) it is most likely caused by equivalent methyl groups.

Using trial and error, and with the above observations, you should come up with the correct structure.
4-methyl-2-pentanone

**Complex coupling**

In all of the examples of spin-spin coupling that we have seen so far, the observed splitting has resulted from the coupling of one set of hydrogens to *just one* neighboring set of hydrogens. When a set of hydrogens is coupled to *two or more* sets of nonequivalent neighbors, the result is a phenomenon called *complex coupling*. A good illustration is provided by the $^1$H-NMR spectrum of methyl acrylate:

First, let's first consider the $H_c$ signal, which is centered at 6.21 ppm. Here is a closer look:

\[ \begin{align*}
  ^3J_{ac} &= 17.4 \text{ Hz} \\
  ^3J_{ah} &= 10.5 \text{ Hz} \\
  ^2J_{bc} &= 1.5 \text{ Hz}
\end{align*} \]
With this enlargement, it becomes evident that the Hc signal is actually composed of four sub-peaks. Why is this? Hc is coupled to both Ha and Hb, but with two different coupling constants. Once again, a splitting diagram (or tree diagram) can help us to understand what we are seeing. Ha is trans to Hc across the double bond, and splits the Hc signal into a doublet with a coupling constant of $^{3}J_{ac} = 17.4$ Hz. In addition, each of these Hc doublet sub-peaks is split again by Hb (geminal coupling) into two more doublets, each with a much smaller coupling constant of $^{2}J_{bc} = 1.5$ Hz.

The result of this ‘double splitting’ is a pattern referred to as a **doublet of doublets**, abbreviated ‘dd’.

The signal for Ha at 5.95 ppm is also a doublet of doublets, with coupling constants $^{3}J_{ac} = 17.4$ Hz and $^{3}J_{ab} = 10.5$ Hz.
The signal for $H_b$ at 5.64 ppm is split into a doublet by $H_a$, a cis coupling with $^3J_{ab} = 10.4$ Hz. Each of the resulting sub-peaks is split again by $H_c$, with the same geminal coupling constant $^2J_{bc} = 1.5$ Hz that we saw previously when we looked at the $H_c$ signal. The overall result is again a doublet of doublets, this time with the two `sub-doublets` spaced slightly closer due to the smaller coupling constant for the cis interaction. Here is a blow-up of the actual $H_b$ signal:

Example 13.12.1

Construct a splitting diagram for the $H_b$ signal in the $^1H$-NMR spectrum of methyl acrylate. Show the chemical shift value for each sub-peak, expressed in Hz (assume that the resonance frequency of TMS is exactly 300 MHz).

Solution

When constructing a splitting diagram to analyze complex coupling patterns, it is usually easier to show the larger splitting first, followed by the finer splitting (although the reverse would give the same end result).

When a proton is coupled to two different neighboring proton sets with identical or very close coupling constants, the splitting pattern that emerges often appears to follow the simple `$n + 1` rule` of non-complex splitting. In the spectrum of
1,1,3-trichloropropane, for example, we would expect the signal for $H_b$ to be split into a triplet by $H_a$, and again into doublets by $H_c$, resulting in a 'triplet of doublets'.

$H_a$ and $H_c$ are not equivalent (their chemical shifts are different), but it turns out that $3J_{ab}$ is very close to $3J_{bc}$. If we perform a splitting diagram analysis for $H_b$, we see that, due to the overlap of sub-peaks, the signal appears to be a quartet, and for all intents and purposes follows the $n + 1$ rule.

For similar reasons, the $H_c$ peak in the spectrum of 2-pentanone appears as a sextet, split by the five combined $H_b$ and $H_d$ protons. Technically, this 'sextet' could be considered to be a 'triplet of quartets' with overlapping sub-peaks.
Example 13.12.2

What splitting pattern would you expect for the signal corresponding to $H_b$ in the molecule below? Assume that $J_{ab} \sim J_{bc}$.

Draw a splitting diagram for this signal, and determine the relative integration values of each subpeak.

Solution

In many cases, it is difficult to fully analyze a complex splitting pattern. In the spectrum of toluene, for example, if we consider only 3-bond coupling we would expect the signal for $H_b$ to be a doublet, $H_d$ a triplet, and $H_c$ a triplet.
In practice, however, all three aromatic proton groups have very similar chemical shifts and their signals overlap substantially, making such detailed analysis difficult. In this case, we would refer to the aromatic part of the spectrum as a multiplet.

When we start trying to analyze complex splitting patterns in larger molecules, we gain an appreciation for why scientists are willing to pay large sums of money (hundreds of thousands of dollars) for higher-field NMR instruments. Quite simply, the stronger our magnet is, the more resolution we get in our spectrum. In a 100 MHz instrument (with a magnet of approximately 2.4 Tesla field strength), the 12 ppm frequency 'window' in which we can observe proton signals is 1200 Hz wide. In a 500 MHz (~12 Tesla) instrument, however, the window is 6000 Hz - five times wider. In this sense, NMR instruments are like digital cameras and HDTVs: better resolution means more information and clearer pictures (and higher price tags!)

Exercises

1. Given the information below, draw the structures of compounds A through D.
   a. An unknown compound A was prepared as follows:

   3-chloro-2-(chloromethyl)propene

   Mass spectrum:

   base peak \( m/e = 39 \)
   parent peak \( m/e = 54 \)
\( ^1H \) NMR spectrum:

<table>
<thead>
<tr>
<th>( \delta ) (ppm)</th>
<th>Relative Area</th>
<th>Multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>2</td>
<td>triplet</td>
</tr>
<tr>
<td>5.4</td>
<td>1</td>
<td>quintet</td>
</tr>
</tbody>
</table>

b. Unknown compound \( B \) has the molecular formula \( C_7H_6O_2 \).

Infrared spectrum:

3200 cm\(^{-1}\) (broad) and 1747 cm\(^{-1}\) (strong) absorptions

\( ^1H \) NMR spectrum:

<table>
<thead>
<tr>
<th>( \delta ) (ppm)</th>
<th>Protons</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.9</td>
<td>2</td>
</tr>
<tr>
<td>7.4</td>
<td>2</td>
</tr>
<tr>
<td>9.8</td>
<td>1</td>
</tr>
<tr>
<td>10.9</td>
<td>1</td>
</tr>
</tbody>
</table>

**Hint:** Aromatic ring currents deshield all proton signals just outside the ring.

c. Unknown compound \( C \) shows no evidence of unsaturation and contains only carbon and hydrogen.

Mass spectrum:

parent peak \( m/e = 68 \)

\( ^1H \) NMR spectrum:

<table>
<thead>
<tr>
<th>( \delta ) (ppm)</th>
<th>Relative Area</th>
<th>Multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.84</td>
<td>3</td>
<td>triplet</td>
</tr>
<tr>
<td>2.45</td>
<td>1</td>
<td>septet</td>
</tr>
</tbody>
</table>

**Hint:** Think three dimensionally!

d. Unknown compound \( D \) (\( C_{15}H_{14}O \)) has the following spectral properties.

Infrared spectrum:

3010 cm\(^{-1}\) (medium)
1715 cm\(^{-1}\) (strong)
1610 cm\(^{-1}\) (strong)
1500 cm\(^{-1}\) (strong)

\(^1\)H NMR spectrum:

<table>
<thead>
<tr>
<th>δ (ppm)</th>
<th>Relative Area</th>
<th>Multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.00</td>
<td>2</td>
<td>triplet</td>
</tr>
<tr>
<td>3.07</td>
<td>2</td>
<td>triplet</td>
</tr>
<tr>
<td>7.1-7.9</td>
<td>10</td>
<td>Multiplets</td>
</tr>
</tbody>
</table>

Answers
1. a. methylenecyclopropane
   b. 4-hydroxybenzaldehyde
   c. bicyclo(1.1.1)pentane
   d. 1,4-diphenyl-1-butanone

Questions
Q13.12.1

In the following molecule, the C2 is coupled with both the vinyl, C1, and the alkyl C3. Draw the splitting tree diagram.

![Molecule Diagram]

Solutions
S13.12.1
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