Objectives

After completing this section, you should be able to

1. determine whether an unknown compound contains an aromatic ring by inspection of its infrared spectrum, given a table of characteristic infrared absorptions.
2. state the approximate chemical shift of aryl protons in a proton NMR spectrum.
3. explain why signals resulting from the presence of aryl protons are found downfield from those caused by vinylic protons in a proton NMR spectrum.
4. propose possible structures for an unknown aromatic compound, given its proton NMR spectrum, other spectroscopic data (such as a $^{13}$C NMR or infrared spectrum), or both.

Key Terms

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

- ring current

Study Notes

It is not necessary that you memorize detailed spectroscopic data. In the laboratory, on assignments and when writing examinations, you will be provided with a table of characteristic infrared absorptions to assist you in interpreting infrared spectra.

The important points to note about the proton NMR of aromatic compounds are the approximate chemical shifts of such protons and the complex splitting pattern that is sometimes observed. You are advised not to spend too long trying to understand why the signal for an aryl proton is found downfield from the signal for a vinylic proton. In general, we want you to be able to interpret NMR spectra, and leave the underlying theory for subsequent chemistry courses.

The chemical shifts of aromatic protons

Some protons resonate much further downfield than can be accounted for simply by the deshielding effect of nearby electronegative atoms. Vinylic protons (those directly bonded to an alkene carbon) and aromatic (benzylic) protons are dramatic examples.
We'll consider the aromatic proton first. Recall that in benzene and many other aromatic structures, a sextet of p-electrons is delocalized around the ring. When the molecule is exposed to \( B_0 \), these p-electrons begin to circulate in a ring current, generating their own induced magnetic field that opposes \( B_0 \). In this case, however, the induced field of the p-electrons does not shield the benzylic protons from \( B_0 \) as you might expect—rather, it causes the protons to experience a stronger magnetic field in the direction of \( B_0 \)—in other words, it adds to \( B_0 \) rather than subtracting from it.

To understand how this happens, we need to understand the concept of **diamagnetic anisotropy** (anisotropy means ‘non-uniformity’). So far, we have been picturing magnetic fields as being oriented in a uniform direction. This is only true over a small area. If we step back and take a wider view, however, we see that the lines of force in a magnetic field are actually anisotropic. They start in the ‘north’ direction, then loop around like a snake biting its own tail.

If we are at point A in the figure above, we feel a magnetic field pointing in a northerly direction. If we are at point B, however, we feel a field pointing to the south.

In the induced field generated by the aromatic ring current, the benzylic protons are at the equivalent of ‘point B’—this means that the induced current in this region of space is oriented in the same direction as \( B_0 \).
In total, the benzylic protons are subjected to three magnetic fields: the applied field ($B_0$) and the induced field from the p-electrons pointing in one direction, and the induced field of the non-aromatic electrons pointing in the opposite (shielding) direction. The end result is that benzylic protons, due to the anisotropy of the induced field generated by the ring current, appear to be highly deshielded. Their chemical shift is far downfield, in the 6.5-8 ppm region.

**Characteristic NMR Absorption of Benzene Derivatives**

Hydrogens directly attached to an arene ring show up about 7-9 PPM in the NMR. **This is called the aromatic region.** Hydrogen environments directly bonded to an arene ring show up about 2.5 PPM.

**Charateristic IR Absorption of Benzene Derivatives**

Arenes have absorption bands in the 650-900 cm$^{-1}$ region due to bending of the C–H bond out of the plane of the ring. The exact placement of these absorptions can indicate the pattern of substitution on a benzene ring. However, this is beyond the scope of introductory organic chemistry. Arenes also possess a characteristic absorption at about 3030-3100 cm$^{-1}$ as a result of the aromatic C–H stretch. It is somewhat higher than the alkyl C–H stretch (2850–2960 cm$^{-1}$), but falls in the same region as olefinic compounds. Two bands (1500 and 1660 cm$^{-1}$) caused by C=C in plane vibrations are the most useful for characterization as they are intense and are likely observed.

In aromatic compounds, each band in the spectrum can be assigned:
• C–H stretch from 3100-3000 cm\(^{-1}\)
• overtones, weak, from 2000-1665 cm\(^{-1}\)
• C–C stretch (in-ring) from 1600-1585 cm\(^{-1}\)
• C–C stretch (in-ring) from 1500-1400 cm\(^{-1}\)
• C–H "oop" from 900-675 cm\(^{-1}\)

Note that this is at slightly higher frequency than is the –C–H stretch in alkanes. This is a very useful tool for interpreting IR spectra. Only alkenes and aromatics show a C–H stretch slightly higher than 3000 cm\(^{-1}\).

Figure 6. Infrared Spectrum of Toluene

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