13.10 SOLVING STRUCTURE PROBLEMS WITH SPECTROSCOPY

You are now ready to use what you know about IR, NMR, and mass spectrometry to solve some problems that require more than one of these techniques. Study Problems 13.7 and 13.8 illustrate the techniques involved. Although no single method works in every case, the following suggestions should prove useful.

1. From the mass spectrum determine, if possible, the molecular mass.
2. If an elemental analysis is given, calculate the molecular formula and determine the unsaturation number.
3. Look for evidence in both the IR and NMR spectra for any functional groups that are consistent with the molecular formula: OH groups, alkenes, and so on. Write down any structural fragments indicated by the spectra.
4. Use the $^{13}$C NMR spectrum and, if possible, the proton NMR spectrum, to determine the number of nonequivalent sets of carbons or protons (or both). If the proton NMR spectrum is complex, this may not be possible, but you should be able to set some limits.
5. Apply the suggestions in both Sec. 13.3F and Sec. 13.4C to complete your analysis by NMR. Be sure to write out partial structures and all possible complete structures that are consistent with your spectra. As you write out partial structures, notice how many carbons are unaccounted for; different partial structures may have carbons in common. Decide between possible structures by asking what features of the different spectra would be expected for each, and look for those features; it is sometimes easy to overlook some feature of a spectrum that will decide between structures.
6. Finally, rationalize all spectra for consistency with the proposed structure.

### Study Problem 13.7

Propose a structure for the compound with the IR, NMR, and EI mass spectra shown in Fig. 13.24 on p. 631.

**Solution** The EI mass spectrum of this compound shows a pair of peaks at $m/z = 90$ and 92, with the latter peak about one-third the size of the former. This pattern indicates the presence of chlorine. Furthermore, the base peak at $m/z = 55$ corresponds to a loss of Cl (35 and 37 mass units, respectively). Let’s adopt the hypothesis that this is a chlorine-containing compound with molecular mass of 90 (for the $^{35}$Cl isotope). In the IR spectrum, the peak at 1642 cm$^{-1}$ suggests a C==C stretch, and, in the NMR spectrum, there is a complex signal in the vinylic proton region. Evidently this compound is a chlorine-containing alkene.

In the NMR spectrum, the total integral is 43,996 units; the vinylic protons at δ 5–6 account for $(6667 + 12007) = 18,674$ units, or 42% of the integral. The quintet at δ 4.6 accounts for 5768 units, or 13% of the integral. The doublet at δ 1.6 accounts for 44% of the total integral. The...
integrals of the three sets of resonances are (in order from highest δ) in the ratio of about 3:1:3, to the nearest whole numbers. The integral suggests some multiple of seven protons. If the compound has seven protons (7 mass units) and one chlorine (35 mass units), then the remaining 48 mass units can be accounted for by four carbons, two of which are part of an alkene double bond. A possible molecular formula is then C₄H₇Cl. (Would 14 protons be a likely possibility? Why or why not?)

The unsaturation number for this formula is 1. Hence, the molecule contains only one double bond. Because the NMR integral indicates three vinylic protons, the molecule must contain a —CH=CH₂ group. In the IR spectrum, the peaks at 930 and 990 cm⁻¹ are consistent with such a group, although the former peak is at somewhat higher wavenumber than is usual for this type of alkene. The three-proton doublet at δ 1.6 suggests a methyl group adjacent to a CH group.

The δ 4.6 absorption accounts for one proton, and its coupling constant (J = 6.6 Hz) matches that of the absorption at δ 1.6. The splitting and chemical shift of the δ 4.6 absorption fit the partial structure

\[
\text{Cl} \\
\text{H}_3\text{C} \text{—CH—CH—}
\]

With a molecular mass of 90 and three vinylic protons, the only possible complete structure is

\[
\delta 1.60 \quad \text{H}_3\text{C} \text{—CH—CH=CH}_2 \quad \delta 5.0-5.3 \\
\delta 4.60
\]

Study Problem 13.8

A compound C₈H₁₈O₂ with a strong, broad infrared absorption at 3293 cm⁻¹ has the following proton NMR spectrum:

δ 1.22 (12H, s); δ 1.57 (4H, s); δ 1.96 (2H, s)

(The resonance at δ 1.96 disappears when the sample is shaken with D₂O.) The proton-decoupled ¹³C NMR spectrum of this compound consists of three lines, with the following chemical shifts and DEPT data (in parentheses) for attached protons:

δ 29.4 (3), δ 37.8 (2), δ 70.5 (0)

Identify the compound.

Solution The IR spectrum indicates the presence of an alcohol, and the disappearance of the δ 1.96 NMR absorption after the D₂O shake (Secs. 13.6 and 13.7D) provides confirmation. Furthermore, because this absorption integrates for two protons, and because the formula contains two oxygens, the compound is a diol. Because the proton NMR spectrum contains no α-hydrogen absorptions in the δ 3–4 region, both alcohols must be tertiary. The proton NMR indicates only three chemically nonequivalent sets of hydrogens, and the ¹³C NMR indicates only three chemically nonequivalent sets of carbons, one of which must be the two α-carbons of the tertiary alcohol groups. The DEPT data confirm that one set of carbons indeed has no attached protons, as expected for a
Figure 13.24  Proton NMR, IR, and EI mass spectra for Study Problem 13.7. The red number over each expanded resonance in the NMR spectrum is the value of the integral in arbitrary units.
tertiary alcohol, and the chemical shift is consistent with that expected for the $\alpha$-carbon of an alcohol. The presence of only three nonequivalent sets of protons and three nonequivalent sets of carbons requires a structure of considerable symmetry. The only structure that fits these data is

$$\text{CH}_3 - C - CH_2 - CH_2 - C - CH_3$$

$$\text{OH} \quad \text{OH}$$

2,5-dimethyl-2,5-hexanediol

### PROBLEMS

13.33 (a) Tell why each of the following structures is inconsistent with the data in Study Problem 13.7.

\begin{align*}
\text{trans-1-chloro-2-butene} & \quad \text{2-chloro-1-butene} \\
A & \quad B
\end{align*}

(b) Although we did not have to analyze the vinylic proton resonances in detail to determine the structure at the end of Study Problem 13.7, it is interesting to consider these resonances further. First, justify the assignments given at the end of the Study Problem for the resonances of the vinylic protons. Then notice in the NMR spectrum (Fig. 13.24) that the $==CH_2$ proton resonances do not split each other detectably (Table 13.3, geminal protons). Next, draw out the structure of this compound to show the stereochemical relationships of the $==CH_2$ protons to the other vinylic proton. Which resonances in the $\delta 5.0–5.3$ region go with which $==CH_2$ proton? How do you know? (Hint: See Fig. 13.15, p. 615.)

13.34 Tell why each of the following structures is not consistent with the spectroscopic data in Study Problem 13.8.

\begin{align*}
\text{A} & \quad \text{B}
\end{align*}

### 13.11 THE NMR SPECTROMETER

The basic components of an NMR spectrometer are shown in Fig. 13.25. An NMR instrument requires, first, a strong magnetic field to establish the tiny energy differences between nuclear spin states. Early NMR instruments employed electromagnets or permanent magnets that generated fields in the range of 7,000–23,000 gauss. Modern instruments utilize large solenoids—essentially doughnut-shaped wire coils—fabricated of superconducting wire. Current flowing in the coil generates the magnetic field. In a superconducting wire, electric current, once established, persists indefinitely and flows without electrical resistance. Superconducting solenoids are required because the electric current required for large magnetic fields would generate far too much resistance (and therefore heat) in a conventional, nonsuperconducting solenoid. Most metals that exhibit superconductivity do so only at very low temperatures. Because liquid helium is used to maintain these low temperatures, the solenoid is housed in an