

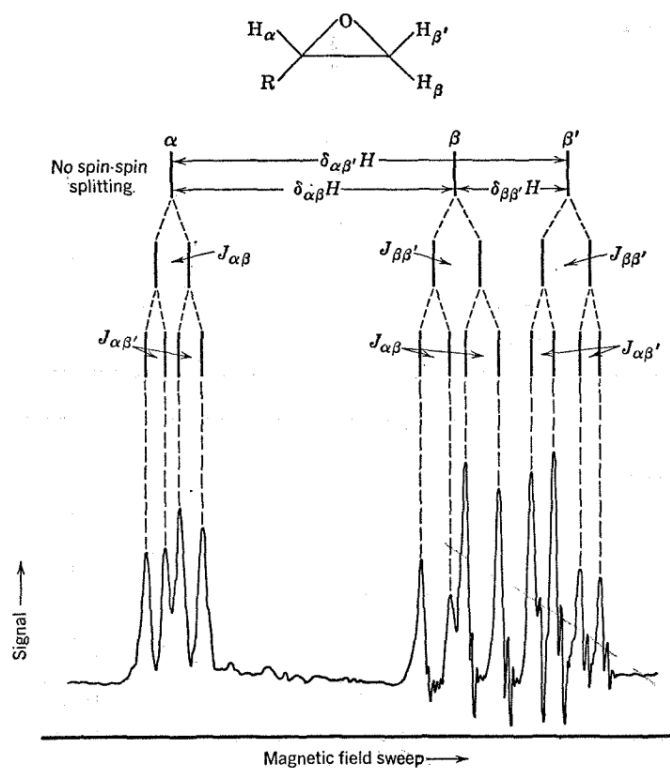
## 3.5: More Complex Spin-Spin Splittings

### a. Styrene Oxide

In general, we shall anticipate that the resonance of a given nucleus will be split into  $(n + 1)$  lines by  $n$  equivalently placed magnetic nuclei with  $I = 1/2$ . The situation is more complex if more than one  $J$  value is involved. Styrene oxide offers a nice example of three nonequivalent protons each coupled to the others with different  $J$ 's. The spectrum of styrene oxide is shown in Fig. 3-6; the ring protons are not coupled to the side-chain protons, so only the latter will be considered. None of the side-chain protons are in equivalent chemical locations since one ( $\alpha$ ) is adjacent to the phenyl ring and the other two are either *cis*( $\beta$ ) or *trans*( $\beta'$ ) to the phenyl ring. In the absence of spin-spin coupling, we would then expect a simple three-line proton spectrum as shown at the top of Fig. 3-6. The  $\alpha$  proton will be coupled unequally to the  $\beta$  protons, and if we assume  $J_{\alpha\beta}$  (*trans*) to be larger than  $J_{\alpha\beta'}$  (*cis*), then four lines of roughly equal height will be observed for the  $\alpha$  proton. The  $\beta$  protons are coupled to each other and in the first-order treatment would be expected to split each other's resonance so as to have four lines of equal strength. As will be shown later, the fact that the chemical shift difference between the  $\beta$  protons ( $\delta\beta\beta'H$ ) is not a great deal larger than the coupling constant ( $J\beta\beta'$ ) means that the lines are not all of equal height and the spacings between the centers of the groups are not  $\delta\beta\beta'H$  but  $\sqrt{J\beta\beta'^2 + (\delta\beta\beta', H)^2}$ . This, however, is a second-order effect which does not change the basic argument. Each line for the  $\beta$  protons will then be split by the coupling between the  $\alpha$  and  $\beta$  protons with different  $J$  values, so that the  $\beta$  protons will give eight lines in all, as is clearly evident from the observed spectrum.

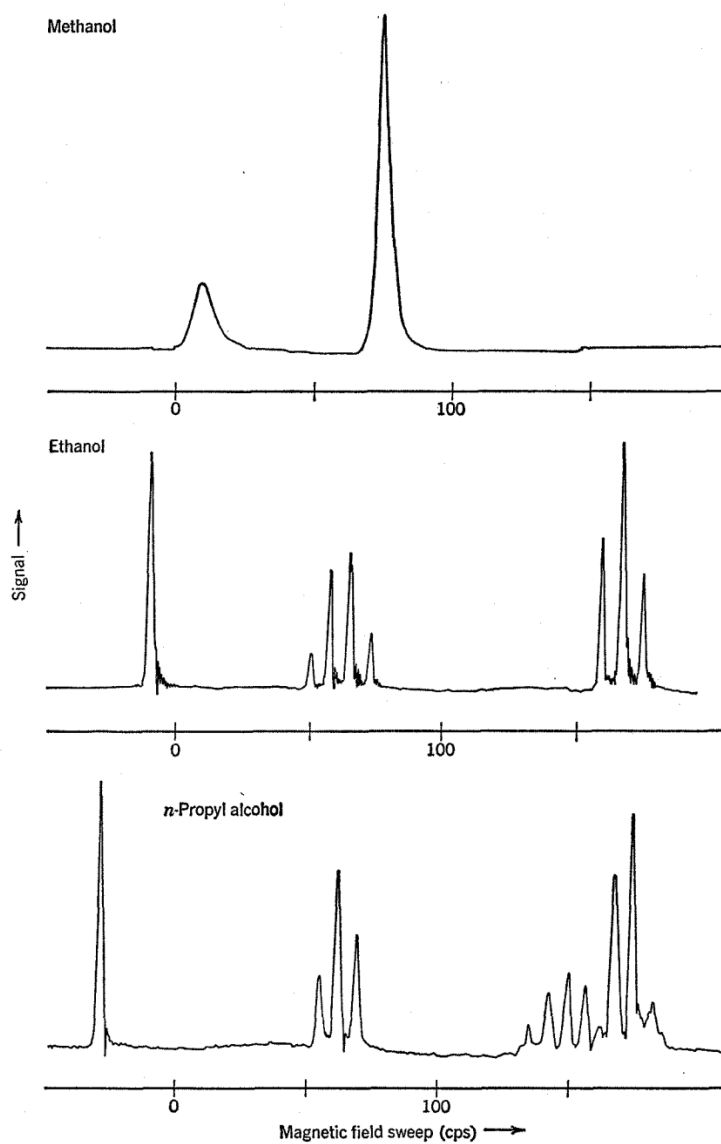
### b. Aliphatic Alcohols

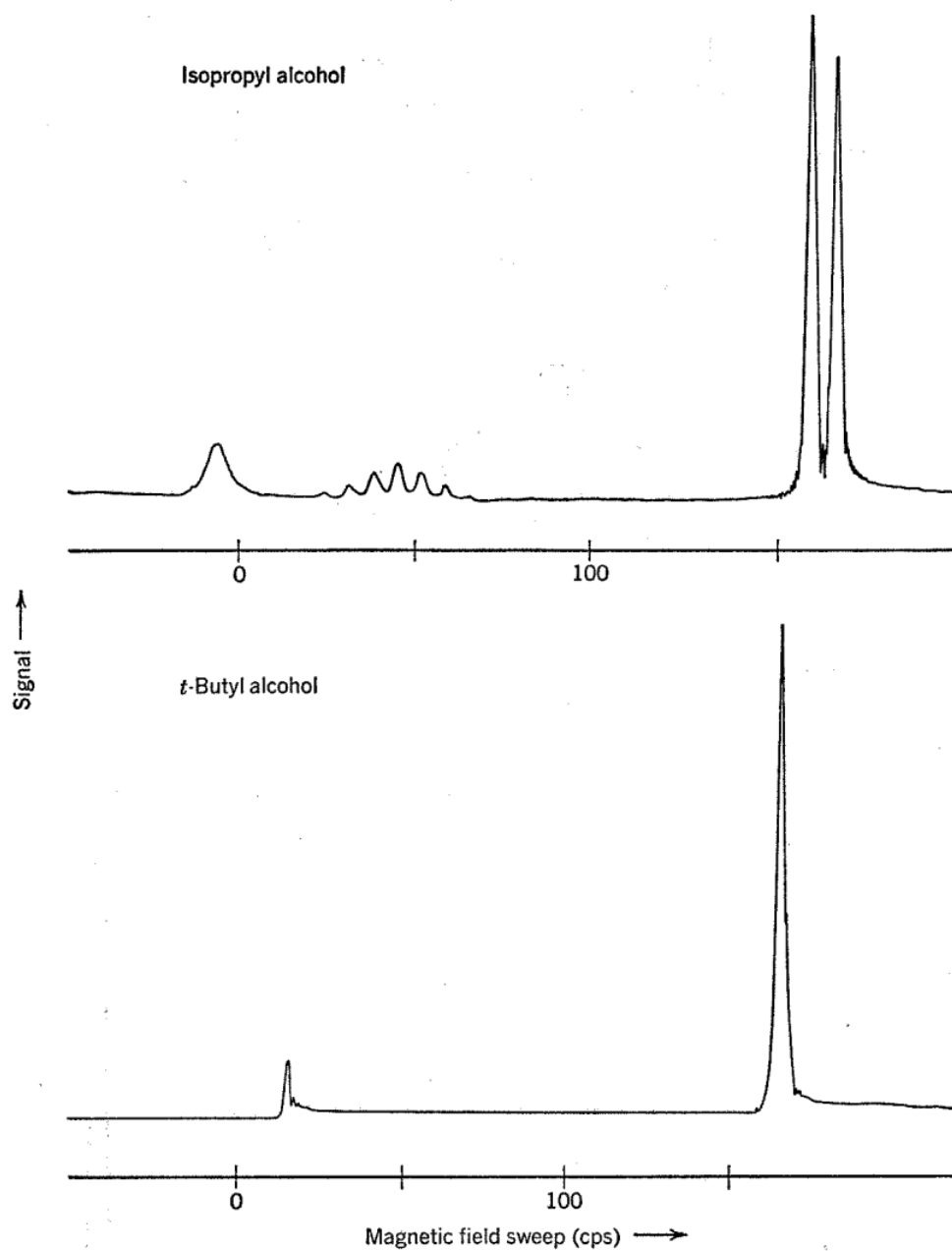
Nuclear spin-spin coupling and chemical-shift data are extremely useful for structural investigations. As an example, we may consider high resolution NMR spectra of a number of simple aliphatic alcohols (Fig. 3-7). The signal strengths, line positions, and degrees of spin-spin splitting permit each alcohol to be identified unambiguously. Thus, isopropyl alcohol shows an O-H proton resonance, an  $\alpha$ -proton resonance split into seven, and the resonance of six  $\beta$  protons split into a doublet. In the examples shown, the  $\alpha$  hydrogens do not appear to be coupled to the hydroxyl protons, although there are only three bonds (H-C-O-H) separating them. The lack of this expected spin-spin splitting is a consequence of rapid intermolecular chemical exchange of the hydroxyl protons, as will be described later.



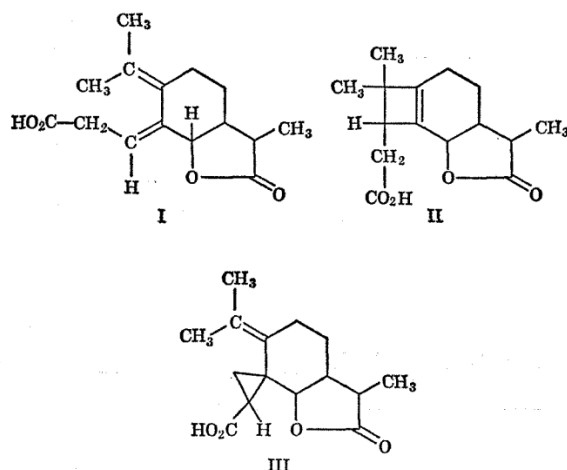
**Fig. 3-6.** Proton NMR spectra of styrene oxide at 40 Mc illustrating interaction between three nonequivalent protons. The resonance of the phenyl protons is off scale on the left.

### c. Methyl Photosantonate

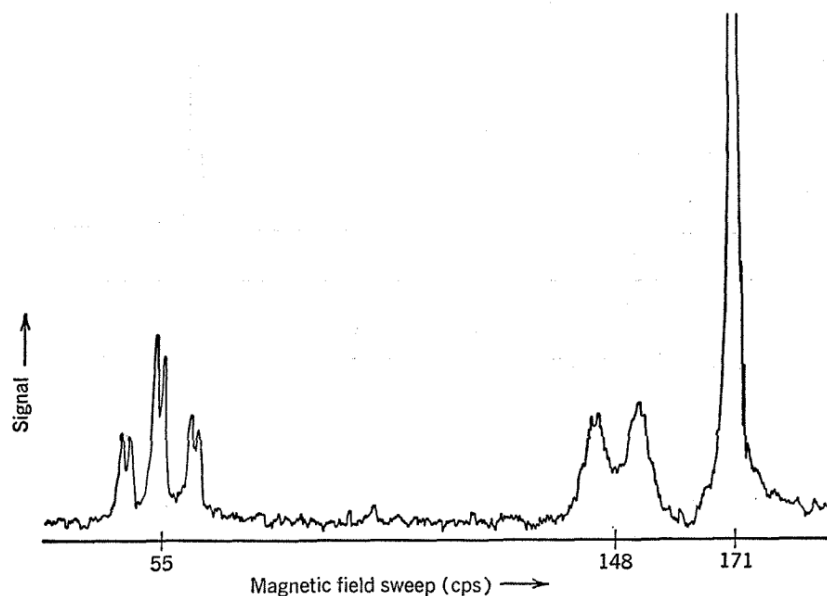




**Fig. 3-7.** Proton resonance spectra of some aliphatic alcohols at 40 Mc.



The nuclear resonance spectrum of methyl photosantonate has been shown by van Tamelen<sup>3</sup> to be decisive in distinguishing among three rather closely related proposed structures for photosantonate. An extraordinarily clear spectrum of the methyl ester at 60 Mc is shown in Fig. 3-8. The group of lines centered on 55 cps is in the vinyl hydrogen region and provides a telling argument in favor of structure I over structures II and III which have no vinyl hydrogens. Furthermore, the vinyl hydrogen resonance is split into three principal lines as would suggest the grouping  $-\text{CH}_2-\text{CH}=\text{C}-$ . This assignment is corroborated by the two principal lines centered on 216 cps which are in about the right place for a methylene group attached on one side to a carbomethoxy and on the other to a double bond. The spacing of these lines is identical with that observed for the vinyl hydrogen.



**Fig. 3-8.** Proton NMR spectrum of methyl photosantonate at 60 Mc in  $\text{CCl}_4$ .

The slight doubling of the anticipated principal three-two pattern of the vinyl and methylene protons is invariant with the applied magnetic field and hence is the result of spin-spin coupling. Apparently, the side-chain  $-\text{CH}_2-$  and  $-\text{CH}=\text{C}-$  protons are coupled to the  $\text{CH}-\text{O}-$  proton with just sufficiently different  $J$  values to lead to only barely perceptible fine structure for the components of the 148-cps doublet.

3 E. E. van Tamelen, S. H. Levin, G. Brenner, J. Wolinsky, and P. Aldrich, *J. Am. Chem. Soc.*, 80, 501 (1958), and private communication.

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