# LONG-RANGE <sup>31</sup>P-<sup>1</sup>H SPIN-SPIN COUPLING IN ortho-STYRYLDIPHENYLPHOSPHINE\*

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A detailed examination of the n.m.r. spectrum of the previously reported<sup>1</sup> ortho-styryldiphenylphosphine (I) reveals (Fig. 1) that the proton  $H_A$ , whose assignment<sup>1</sup> is based on the magnitude of the vicinal coupling constant, is subject to an interaction which causes splitting of the signal beyond the multiplicity due to spin-spin coupling within the vinyl group. We consider that this interaction is a long-range spin-spin coupling with <sup>31</sup>P, as coupling of that magnitude  $(1 \cdot 10 \pm$  $0 \cdot 05$  Hz) to one of the aryl protons would be entirely unprecedented.<sup>2</sup> <sup>1</sup>H-{<sup>31</sup>P} spin-decoupling confirmed unequivocally (Fig. 1(b)) that this coupling involves the <sup>31</sup>P nucleus. A small but reproducible line-sharpening was also observed for lines



assigned to  $H_M$  with  ${}^{1}H{-}{}^{\$1}P$  spin-decoupling, indicating a coupling between  $H_M$ and  ${}^{\$1}P$  of c. 0.05–0.10 Hz. While long-range  ${}^{\$1}P{-}^{1}H$  spin-spin coupling in aromatic and unsaturated systems has been investigated in detail,<sup>3</sup> no analogy with the present case has been reported. The stereospecificity of the interaction between  ${}^{\$1}P$  and  $H_M$ , combined with the fact that the coupling path would not normally be considered favourable<sup>3,4</sup> for a relatively strong interaction, makes it possible that a "direct interaction" (i.e. one not involving all the intervening bonds) occurs. A somewhat sterically analogous situation occurs in *ortho*-fluoro-N,N'-dimethylbenzamide, where a  ${}^{19}F{-}1H$  spin-spin coupling across six bonds is involved.<sup>5</sup> It is,

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<sup>1</sup> Bennett, M. A., Nyholm, R. S., and Saxby, J. D., J. organomet. Chem., 1967, 10, 301.

<sup>2</sup> Newsoroff, G. P., and Sternhell, S., Aust. J. Chem., 1968, 21, 747.

<sup>8</sup> Griffin, C. E., and Gordon, M., J. Am. chem. Soc., 1967, **89**, 4427; Martin, D. J., Gordon, M., and Griffin, C. E., *Tetrahedron*, 1967, **23**, 1831; Khaleeluddin, N., and Scott, J. M. W., *Chemy Ind.*, 1966, 1034; Kaplan, F., and Schultz, C. O., *Chem. Commun.*, 1967, 376.

<sup>4</sup> Bothner-By, A. A., and Harris, R. K., J. Am. chem. Soc., 1965, 87, 3451.

<sup>5</sup> Lewin, A. H., J. Am. chem. Soc., 1964, 86, 2303.

Aust. J. Chem., 1968, 21, 2565-7

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however, important to note that the analogous interproton coupling in 1,3-butadienes is highly dependent on substitution and stereochemistry<sup>4</sup> and thus the interaction observed here may be analogous to that in *cis*-tagetone<sup>4</sup> (II), where  $J_{\rm AM} = 0.59$  Hz and  $J_{\rm AX} = 1.59$  Hz.



Fig. 1.—Portion of the <sup>1</sup>H n.m.r. spectrum of o-styryldiphenylphosphine (I) at 60 MHz (5% in CDCl<sub>3</sub>). (a) Normal spectrum; (b) with strong irradiation of the <sup>31</sup>P nucleus.

In the methiodide (III) the signals assigned to the vinyl group give a straightforward AMX spectrum ( $\delta_A$  5.75,  $\delta_M$  5.40,  $\delta_X$  6.51 p.p.m.,  $J_{AM}$  0.9,  $J_{AX}$  16.9, and  $J_{MX}$  10.9 Hz). The widths of the components of signals due to H<sub>A</sub> and H<sub>M</sub> are equal and were estimated to be not more than 0.3 Hz larger than those of genuine singlets at the same resolution. Thus there is no evidence of significant long-range <sup>31</sup>P-<sup>1</sup>H coupling in (III) analogous to that postulated in (I). It is therefore attractive to consider that the origin of the long-range coupling in (I) is connected with direct overlap of the lone pair on the phosphorus with the  $\sigma$ -electrons of H<sub>A</sub>, i.e. a type of hydrogen bonding. However, any significant intramolecular hydrogen bonding would be expected<sup>6</sup> to be associated with a conspicuous downfield shift of the proton involved, while the chemical shift of H<sub>A</sub> in (I) (5.60 p.p.m.) (Fig. 1) is unexceptional (the chemical shift of H<sub>M</sub> in (I) is 5.18 p.p.m. as compared with 5.25 p.p.m.).<sup>7</sup> The chemical shift of H<sub>M</sub> in (I) is 5.18 p.p.m. as compared with 5.25 p.p.m. for the corresponding proton in *ortho*-methylstyrene.<sup>7</sup>

<sup>6</sup> Jackman, L. M., and Sternhell, S., "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry." Ch. 2-2E. (Pergamon: London 1968.)

<sup>7</sup> Gurudata, Stothers, J. B., and Talman, J. D., Can. J. Chem., 1967, 45, 731.

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Clearly, the n.m.r. spectra of 1,3-but adienes substituted at C1 (or C4) with the  $-P(C_6H_5)_2$  group would throw light on the mechanism of this long-range interaction and on the possible analogy with long-range interproton coupling in 1,3-but adienes.<sup>4</sup>

### Experimental

N.m.r. spectra were determined on a Varian HA100 spectrometer as 10% solutions in deuterochloroform, and on a Varian model HA60IL spectrometer as a 5% solution in deuterochloroform. The <sup>1</sup>H–{<sup>81</sup>P} spin-decoupled spectra were obtained with the HA60IL spectrometer operating in the frequency-sweep mode, using a variable crystal oscillator and amplifier<sup>8</sup> at 24.29 MHz to supply the decoupling field.

#### o-Styryldiphenylmethylphosphonium Iodide (III)

o-Styryldiphenylphosphine (1.0 g) and methyl iodide (1.5 g) were allowed to stand in dry ether for c. 24 hr at room temperature.<sup>9</sup> The white precipitate (c. 85% yield) which formed was collected and crystallized from a mixture of acetone and ethanol to give o-*styryldiphenylmethylphosphonium iodide*, m.p. 182° (Found: C, 59.0; H, 4.8; P, 6.8. Calc. for C<sub>21</sub>H<sub>20</sub>PI: C, 58.6; H, 4.7; P, 7.2%). N.m.r.: AMX system for the vinyl protons (3H, see text), doublet  $\delta$  3.14, J(H-C-P) 13 Hz (3H, methyl), and multiplet  $\delta$  7-8 (14H, aromatic protons).

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<sup>8</sup> Long, G. L., and Moritz, A. G., unpublished data.

<sup>9</sup> Morgan, P. W., and Herr, B. C., J. Am. chem. Soc., 1952, 74, 4526; Deacon, G. B., and Jones, R. A., Aust. J. Chem., 1963, 16, 499.