

**Table II.** Predicted Changes in Directly Bonded  $^{13}\text{C}$ -H Coupling Constant with Deformation of C-C-H Angle

Deformation, deg	$^{13}\text{C}$ -H <sup>a</sup> (aromatic)	$^{13}\text{C}$ -H <sup>b</sup> (olefinic)
+12	-28.4	-44.6
+10	-19.5	-32.5
+8	-12.3	-22.4
+6	-6.9	-14.2
+4	-3.0	-7.8
+2	-0.8	-3.1
0		
-2	-0.8	+1.5
-4	-3.0	+1.5
-6	-6.9	0.0
-8	-12.3	-3.1
-10	-19.5	-7.8
-12	-28.4	-14.2

<sup>a</sup> With C-C-C angle held at 120° and initially sp<sup>2</sup> carbon.

<sup>b</sup> Starting with  $\theta_{12}$  and  $\theta_{23}$  of 122.0 and 116.0° for ethylene; see footnote g, Table I.

remain constant and  $\theta_{12}$  to change by small increments, the data in Table II were generated neglecting the small changes of overlap with  $a_{\text{C}}^2$ .

On going from **14** to **16**, the  $^1J_{^{13}\text{C}-\text{H}}$  change suggests a C=C-H angle decrease of 8°; *i.e.*, the proton moves away from the geminal *tert*-butyl group in **16**. The increase of  $^1J_{^{13}\text{C}-\text{H}}$  of +0.7 Hz on going from **15** to **17** may indicate C=C-H angle decreases of the order of 0.7 or 5.3° such that again the proton moves away from a geminal *tert*-butyl group. Recently  $^1J_{^{13}\text{C}-\text{H}}$ 's in trimethylethylene (**23**) and tri-*tert*-butylethylene (**24**) were reported to be 148.4 and 143.3 Hz, respectively.<sup>12</sup> The value for **23** is only slightly less than that for **15** which may be taken to indicate similar C=C-H angles. Based on the discussion above, the change of  $^1J_{^{13}\text{C}-\text{H}}$  in **24** represents about a 7° decrease in the C=C-H angle from that in **23**. For the cyclic olefins the main effect causing the increase of  $^1J_{^{13}\text{C}-\text{H}}$  in the smaller rings is not steric effects of bulky groups but rehybridization.<sup>8</sup> The trends in deformation of the C=C-H angle predicted here agree qualitatively with what is expected and are of magnitudes which should be detectable by common structure determination methods.

(12) G. J. Abruscato, P. D. Ellis, and T. T. Tidwell, *J. Chem. Soc., Chem. Commun.*, 988 (1972).

(13) NASA Resident Research Associate, 1968-1970.

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## Nuclear Magnetic Resonance of Phosphorus Compounds. VII. Evidence for Steric Effects on the $^{31}\text{P}$ - $^{77}\text{Se}$ Coupling and $^{31}\text{P}$ Chemical Shifts<sup>1</sup>

Sir:

In connection with an investigation of the question of

(1) Previous paper in this series: A. H. Cowley, J. R. Schweiger, and S. L. Manatt, *Chem. Commun.*, 1491 (1970).

$p_{\pi}$ - $d_{\pi}$  bonding involving phosphorus, we have had occasion to synthesize and study the phosphorus nmr spectra of a number of triarylphosphines and triarylphosphine selenides. We wish to report evidence which indicates how the nmr parameters for phosphorus whose local electronic environment is sterically perturbed can deviate from those expected on the basis of observed substituent effect correlations<sup>2</sup> in less crowded molecules.

There are some practical difficulties which deserve mention regarding the  $^{31}\text{P}$  spectra of the triarylphosphines and triarylphosphine selenides which we have studied. Direct determination of the  $^{31}\text{P}$  chemical shifts of these classes of compounds is not easily accomplished because extensive spin-spin coupling between the protons on the aromatic rings and phosphorus smears the nmr spectrum for the latter over a wide band. The direct observation of the  $^{31}\text{P}$ - $^{77}\text{Se}$  coupling in the triarylphosphine selenides, which is exhibited by only 7.5% of the molecules, appeared even more difficult to observe. In addition, many of these compounds possess limited solubility so an increase in concentration was not a possible solution to the signal-to-noise problem. However, taking advantage of proton-noise decoupling<sup>3</sup> along with digital-sweep time averaging<sup>4</sup> and elevated probe temperature, it was possible to make successful measurement of the relevant nmr parameters. Typical spectra are shown in Figure 1.

In the para-substituted triphenylphosphines and phosphine selenides,  $^{31}\text{P}$ -chemical shifts correlate linearly with the electronegativity of the substituents<sup>2</sup> with full complement of electrons (*i.e.*, other than H-), but in the case of the *o*-methyl derivatives, we have found substantially upfield  $^{31}\text{P}$  chemical shifts as illustrated in Figure 1 and summarized in Table I. The

**Table I.** Phosphorus-31 Chemical Shifts and  $^{31}\text{P}$ - $^{77}\text{Se}$  Couplings for Some Triphenylphosphines and Phosphine Selenides<sup>a</sup>

Substituent on aryl ring	$\text{R}_3\text{PSe}$		$\text{R}_3\text{P}$ $\delta$ , ppm
	$J_{\text{P-Se}}$ , Hz	$\delta$ , ppm	
<i>p</i> -Cl	752.8	+2.21	+3.11
H	735.4	0.00	0.00
<i>p</i> -CH <sub>3</sub>	723.5	+1.61	+2.47
<i>p</i> -OCH <sub>3</sub>	719.3	+3.82	+4.61
<i>o</i> -CH <sub>3</sub>	708.0	+7.57	+24.62
<i>m</i> -CH <sub>3</sub>	726.3	-0.16	-0.19

<sup>a</sup>  $\delta(\text{Ph}_3\text{P}) - \delta(\text{Ph}_3\text{P=Se}) = 43.02$  ppm.

electronic effect of *o*-methyl as a part of the aromatic substituent is not expected to be much different from that of *p*-methyl unless steric factors are important.<sup>5</sup> As appears to be the case for  $^{13}\text{C}$  chemical shifts,<sup>6</sup> these

(2) R. P. Pinnell, C. A. Megerle, and S. L. Manatt, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 13, 1971, Abstract INOR 39.

(3) R. R. Ernst, *J. Chem. Phys.*, **45**, 3845 (1966).

(4) The system for  $^{31}\text{P}$  which was used is a modification of that described previously: M. A. Cooper, H. Weber, and S. L. Manatt, *J. Amer. Chem. Soc.*, **93**, 2369 (1971).

(5) See, for example, R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1966; P. C. Lauterbur, *Ann. N. Y. Acad. Sci.*, **70**, 841 (1958); and J. B. Stothers, *Quart. Rev., Chem. Soc.*, **19**, 144 (1965).

(6) D. M. Grant and B. V. Cheney, *J. Amer. Chem. Soc.*, **89**, 5315 (1967).

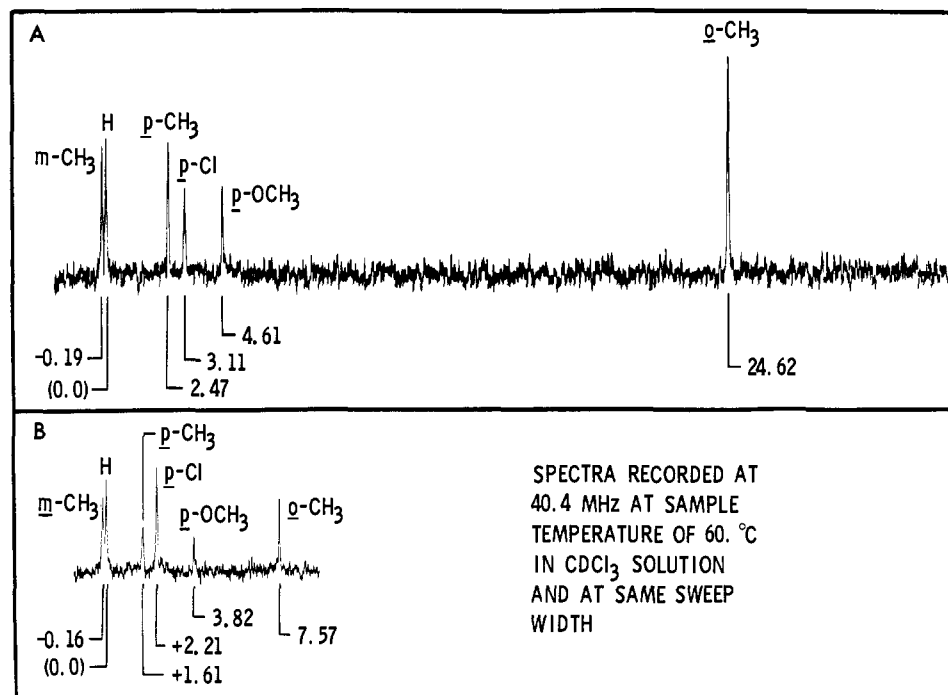


Figure 1. Proton noise decoupled phosphorus-31 nmr of mixtures of triphenylphosphines (A) and phosphine selenides (B). Chemical shifts given in ppm relative to -H compound.

observed changes could not be due to anisotropy effects because of three additional C-C bonds in the vicinity of phosphorus but probably stem from a combination of two effects—steric polarization of the phosphorus valence electrons and changes in the extent of  $\pi$  bonding between the aromatic ring and the phosphorus orbitals. The latter no doubt involve modulation of the occupancies of the p and d orbitals of phosphorus.<sup>7</sup> Thus, it appears that the carbon  $\pi$  orbitals in the aromatic ring have more efficient interaction with <sup>31</sup>P orbitals in the phosphines than in the phosphine selenides.

For the triarylphosphine selenide, a linear correlation of directly bonded <sup>31</sup>P-<sup>77</sup>Se coupling with substituent constants appears to exist.<sup>2</sup> The *o*-methyl compound, however, has a coupling whose magnitude is some 15 Hz less than expected and we attribute this diminution to a steric origin. The question of the detailed mechanism for this effect is open but significant rehybridization of both <sup>31</sup>P and <sup>77</sup>Se orbitals might be involved. Perhaps, the extent of change of <sup>77</sup>Se bonding orbitals could be sorted out from <sup>77</sup>Se chemical shift measurements. The direction of the observed change could be significant relative to the absolute sign of the coupling constant. In the cases of the directly bonded <sup>13</sup>C-<sup>1</sup>H<sup>8,9</sup> and <sup>13</sup>C-<sup>19</sup>F<sup>9</sup> couplings the direction of change precipitated by steric effects appears to be in the absolute negative direction. Thus, if the rehybridization and possible orbital polarization terms responsible for the observed changes in coupling constant are the same for

the <sup>31</sup>P-<sup>77</sup>Se coupling, this coupling would appear to be positive in absolute sign (negative *J* but positive *K*).<sup>10</sup>

(10) This conclusion is supported from the fact that the sign of the <sup>31</sup>P-<sup>77</sup>Se coupling (*i.e.*, *K*) has been reported from double resonance experiments to be positive for (CH<sub>3</sub>)<sub>2</sub>PSeMe and (CH<sub>3</sub>)<sub>2</sub>PSSeMe: W. McFarlan and J. N. Hash, *Chem. Commun.*, 913 (1969).

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## Solvent Effects in Organic Chemistry. XVI. An Enormous Alkyl Substituent Effect in Solution<sup>1</sup>

Sir:

In fluorosulfuric acid (HSO<sub>3</sub>F) at -52° the heats of protonation of CH<sub>3</sub>SH and H<sub>2</sub>S are -19.2 and -5.3 kcal/mol, respectively. The difference (13.9 ± 1.2 kcal/mol) is almost exactly the same as has been reported for their proton affinities (PA) in the gas phase (16 ± 6 kcal/mol).<sup>2</sup> This would represent a 10<sup>15</sup>-fold substituent effect for a methyl group if converted into rates or equilibrium constants at this temperature and is many orders of magnitude greater than any such effect reported previously for a direct thermodynamic measurement in solution. Similarly, large substituent effects are also found for the solution protonation of

(1) Supported by National Science Foundation Grant GP-6550X.

(2) (a) M. S. Haney and J. H. Franklin, *J. Phys. Chem.*, **73**, 4328 (1969); (b) J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968).

(7) See, for example, the discussion of <sup>31</sup>P chemical shifts by M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Top. Phosphorus Chem.*, **5**, 153 (1967).

(8) K. L. Servis, W. P. Weber, and A. K. Willard, *J. Phys. Chem.*, **74**, 3960 (1970).

(9) S. L. Manatt, M. A. Cooper, C. W. Mallory, and F. B. Mallory, *J. Amer. Chem. Soc.*, **95**, 975 (1973).