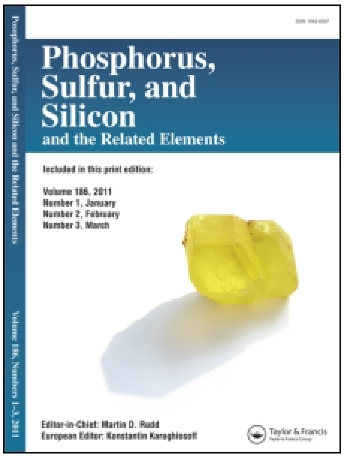

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SYNTHESIS AND ^{17}O NMR SPECTROSCOPY OF A SERIES OF ^{17}O LABELED TRIARYLPHOSPHINE OXIDES

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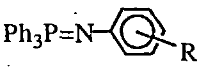
Abstract. A series of nine ^{17}O labeled triarylphosphine oxides [(p-R–$C_6H_4)_3PO$] was synthesized, ^{17}O NMR spectroscopic studies were carried out (toluene solvent / 95 °C and $CDCl_3$ / 60 °C) and the spectrum was fit with two Lorentzian peaks. The chemical shifts range from δ 51.8 to 55.7 in toluene and δ 44.8 to 48.9 in $CDCl_3$, while $^1J_{PO}$ varies from 159.6 to 168.6 Hz in toluene. The data were fit to the Taft DSP and Hammett equations and related to other NMR parameters for this system and the analogous λ^5-phosphazenes [(p-R–$C_6H_4)_3PNPh$]. Using the Taft DSP equation the ^{17}O substituent chemical shifts gave ρ_I and ρ_R with opposite signs which is different from what is observed with the λ^5-phosphazenes. $^1J_{PO}$, on the other hand correlates best with the Hammett σ_p^+ constants. The data are consistent with a triple bond contribution to the PO bonding.

Key Words: Triarylphosphine oxides, O-17 NMR spectroscopy

INTRODUCTION

For a number of years we have been interested in the synthesis and properties of phosphorus and nitrogen compounds, in particular λ^5-phosphazenes ($R_3P{=}N{-}R'$; phosphinimines) and related molecules. We have carried out considerable ^{31}P, ^{15}N and ^{13}C NMR spectroscopic studies of several series of λ^5-phosphazenes, **1-4** [1-8], phosphines **5** and phosphine oxides **6** [7,8]. Using the NMR data along with PRDDO molecular orbital calculations, we described the electronic structure in terms of charge densities and induced dipoles and suggested that pπ-σ* bonding between phosphorus and nitrogen [using a σ* P-C(phenyl) orbital] was an important factor in the PN bonding. Systems **4** and **6** were similar to each other [7,8] in that changes in R resulted in essentially the same changes in the chemical shifts of the substituted ring carbon, but the phosphorus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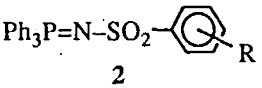
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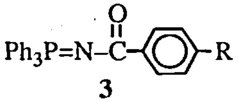
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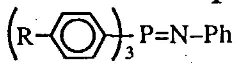
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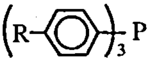
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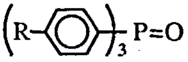
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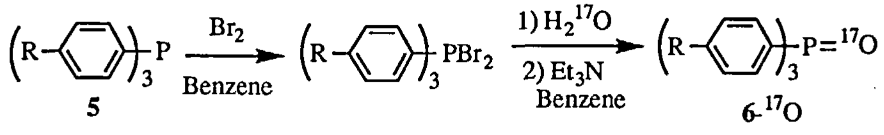
chemical shift in **6** was twice as sensitive as that in **4** to changes in R [7,8]. This, we believe, is the result of the *N*-phenyl ring in **4** being able to delocalize charge. We have now turned to the synthesis of ^{17}O labeled phosphine oxides **6**, for ^{17}O NMR spectroscopic studies, in order to attempt to better understand the bonding in the oxides and how series **6** relates to series **4**. Since the parent **6**, Ar = C_6H_5, had been prepared previously with an ^{17}O label and its ^{17}O NMR parameters reported [9-11], we did not anticipate problems with the synthesis or NMR spectroscopy.

RESULTS AND DISCUSSION

We have synthesized the series of triarylphosphine oxides **6**-^{17}O with an approximately 10% ^{17}O label and have obtained the ^{17}O NMR spectra, which provided the chemical shifts and ^{17}O–^{31}P coupling constants. The synthesis is presented in Scheme 1. ^{17}O NMR spectra are generally quite broad due to the rapid quadrupolar relaxation [12] and we have found that rather elevated temperatures (95 °C / toluene solvent) and deconvolution using two overlapping Lorentzian bands were required to resolve the spectra into two peaks. However, with $CDCl_3$ solvent at 60 °C several of the compounds showed a single broad peak and resolution into two peaks was not very accurate. It is well known that higher temperatures and lower viscosity solvents help in sharpening up the peaks [12]. Table 1 gives the ^{17}O NMR spectral data for series **6**-^{17}O.

Scheme 1



a: R = $N(CH_3)_2$ c: R = CH_3 e: R = F g: R = CO_2CH_3 i: R = CN
b: R = OCH_3 d: R = H f: R = Cl h: R = CF_3

Analysis of the data for **6**-^{17}O (toluene / 95 °C) provided the following relationships: ^{17}O SCS = $2.93\,\sigma_I - 5.37\,\sigma_R^o$ ($f = 0.160$) and $^1J_{^{17}O-^{31}P} = 3.71\,\sigma_p^+ + 165.9$ ($r = 0.976$) [13]. Perhaps the most interesting aspect of these data is that the Taft DSP treatment of the ^{17}O SCS data gives opposite signs for ρ_I and ρ_R^o which is in marked contrast to the situation with **4** where ρ_I and ρ_R are both negative [7]. Thus the resonance effect in both systems appear similar (similar negative ρ values, –5.37 and –4.65 respectively) while the inductive effect in the two systems is opposite (ρ values of +2.93 and –1.99 respectively). This difference is consistent with a triple bond contribution to the PO bond where electron donation / withdrawal to the oxygen can occur via both inductive and resonance effects through two different pπ- σ* / pπ-dπ orbitals [14]. That is, a substituent such as dimethylamino might donate electrons by a resonance effect onto the oxygen through a π-bond (pπ- σ* or pπ-dπ) while at the same time electron density can be withdrawn from the oxygen (which now has an excess of electron density because of this resonance effect) through the perpendicular π-bond and into the sigma system of the phenyl ring(s). It should be mentioned that the ^{17}O–^{31}P coupling constant correlation with a positive slope

TABLE 1. ^{17}O NMR chemical shifts and coupling constants for series **6**-^{17}O.

Compound	Solvent R =	Chemical Shift (δ) Toluene	^{17}O–^{31}P Coupling Constant (Hz) Toluene	Chemical Shift (δ) $CDCl_3$
6a-^{17}O	$N(CH_3)_2$	54.65	159.6	48.9
6b-^{17}O	OCH_3	54.97	163.1	48.1
6c-^{17}O	CH_3	52.77	163.6	45.4
6d-^{17}O	H	51.90	166.6	44.8
6e-^{17}O	F	55.73	165.9	48.7
6f-^{17}O	Cl	53.89	167.1	46.8
6g-^{17}O	$COOCH_3$	51.84	167.6	46.6
6h-^{17}O	CF_3	52.52	167.1	45.4
6i-^{17}O	CN	52.86	168.6	46.0

also stands in contrast to the negative slope of the corresponding ^{15}N–^{31}P coupling constant in **4** ($^1J_{^{15}N-^{31}P} = -2.15\ \sigma_p + 33.4$ ($r = 0.927$) [7]. This again is consistent with a different type of PO and PN bonding. The chemical shifts in toluene span the range of δ 51.8 to 55.7 and these are deshielded relative to those in $CDCl_3$ which are δ 44.8 to 48.9. As expected, the chemical shifts are to higher field in chloroform [11], in agreement with the observations that more polar or hydrogen bonding solvents shield the oxygen [11], presumably due to the stabilization of greater negative charge on the oxygen. The coupling constants from the $CDCl_3$ experiments at the lower temperature, where they could be measured, however, were much less accurate than those from the toluene experiments. The peaks were broader and so the resolution of the doublets was much poorer and with several compounds single, broad peaks were observed.

There are two reports of the ^{17}O NMR spectral parameters of triphenylphosphine oxide, **6d**, in the literature. In the first, $CDCl_3$ solvent, 30 °C, δ is given as 43.3 and $^1J_{PO}$ as 160 ± 2.4 Hz [10] and in the other, CD_3CN solvent, 70 °C, δ is given as 47.7 and $^1J_{PO}$ as 153.9 Hz [9]. While the chemical shifts seem to agree reasonably well with those obtained here, the coupling constants do not. A reasonable explanation for the differences, particularly in the latter study at 70 °C [9], is that with two broad overlapping peaks, peak fitting is required. This can be seen in Figure 1 (**6b**-^{17}O, R = OCH_3, toluene solvent, 95 °C) where the doublet is only partially resolved and the fitted peaks show a greater separation (larger coupling constant) than the peak maxima from the original spectrum.

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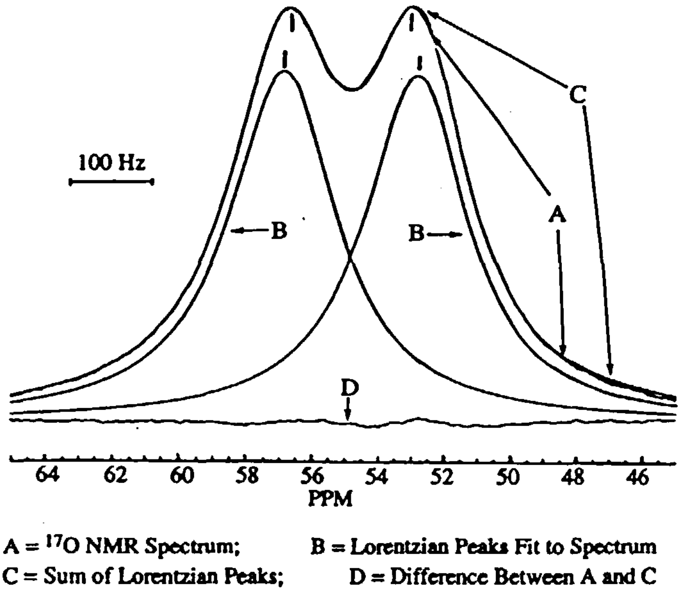

FIGURE 1. ^{17}O NMR spectrum of tris(*p*-methoxyphenyl)phosphine oxide-^{17}O (6b-^{17}O, toluene solvent / 95 °C)

REFERENCES AND NOTES

1. M. POMERANTZ, B. T. ZIEMNICKA, Z. M. MERCHANT, W.-N. CHOU, W. B. PERKINS, and S. BITTNER, *J. Org. Chem.*, **50,** 1757 (1985).
2. M. POMERANTZ, D. S. MARYNICK, K. RAJESHWAR, W.-N. CHOU, L. THROCKMORTON, E. W. TSAI, P. C. Y. CHEN and T. CAIN, *J. Org. Chem.*, **51**, 1223 (1986).
3. M. POMERANTZ, W.-N. CHOU, M. K. WITCZAK, and C. G. SMITH, *J. Org. Chem.*, **52**, 159 (1987).
4. M. POMERANTZ, W.-N. CHOU, M. K. WITCZAK, and C. G. SMITH, *Phosphorus and Sulfur*, **30,** 799 (1987).
5. W.-N. CHOU, M. POMERANTZ, and M. K. WITCZAK, *J. Org. Chem.*, **55**, 716 (1990).
6. M. POMERANTZ and W.-N. CHOU, *Phosphorus, Sulfur and Silicon,* **51/52**, 241 (1990).
7. W.-N. CHOU and M. POMERANTZ, *J. Org. Chem.*, **56**, 2762 (1991), .
8. M. POMERANTZ, in *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*, edited by L. D. Quin and J. G. Verkade (VCH Publishers, New York, 1994), Chap. 10, pp 115-128.
9. L. D. QUIN, J. SZEWCZYK, K. LINEHAN and D. L. HARRIS, *Magn. Reson. Chem.*, **25**, 271 (1987).
10. R. D. SAMMONS, P. A. FREY, K. BRUZIK, and M.-D. TSAI, *J. Am. Chem. Soc.*, **105**, 5455 (1983).
11. S. A. EVANS JR., in *^{17}O NMR Spectroscopy in Organic Chemistry*, edited by D. W. Boykin (CRC Press, Boca Raton, FL, 1991), Chapter 10.
12. L. G. BUTLER, in *^{17}O NMR Spectroscopy in Organic Chemistry*, edited by D. W. Boykin (CRC Press, Boca Raton, FL, 1991), Chapter 1.
13. SCS = Substituent Chemical Shift; *f* = SD / rms.
14. D. G. GILHEANY, *Chem. Rev.*, **94**, 1339 (1994), and references cited therein.