

## Synthesis of Salts of a Pentaoxyspirophosphorane Having a P–OH Bond

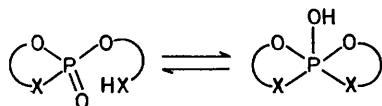
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**Summary** The pentaoxyspirophosphorane (**1**) having a P–OH bond was prepared from the reaction of  $\text{POCl}_3$  with benzoic acid and isolated as its triethylammonium salt: this compound and the corresponding *NN*-dimethylformamidinium salt have also been synthesised from the spirophosphorane (**2**), having a P–H bond, by oxidation with  $\text{Me}_2\text{SO}$ .

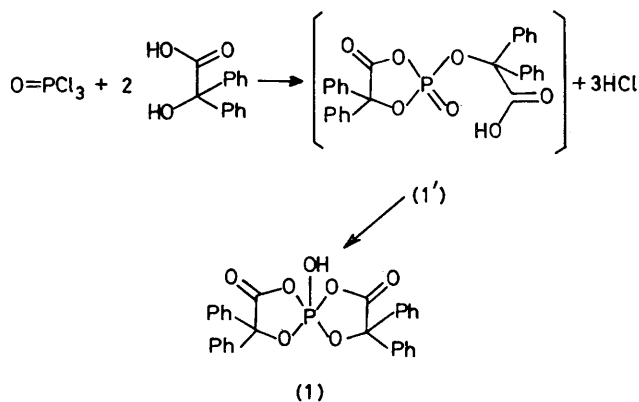
We report the synthesis of a pentaoxyspirophosphorane having a P–OH bond, obtained as its triethylammonium and *NN*-dimethylformamidinium salts.

In previous papers we have postulated that equilibrium (**1**) exists in oxidations, with  $\text{Me}_2\text{SO}$ , of spirophosphoranes having a P–H bond prepared from *o*-biphenols.<sup>1</sup> We obtained a phosphoric ester which exists in equilibrium with the tautomeric pentaoxyspirophosphorane having a P–OH bond, this equilibrium being controlled by base and temperature.<sup>2</sup> Ramirez *et al.* have isolated a crystalline compound which in solution gave an equilibrium mixture of hydroxyphosphorane and phosphate ester.<sup>3</sup>



The tautomeric equilibrium (**1**) might be attainable by the reaction of  $\text{POCl}_3$  with a bidentate ligand. For example reaction with benzoic acid should give the phosphoric ester (**1'**) or the tautomeric phosphorane (**1**) (Scheme 1).

This reaction in benzene solution, in the presence of pyridine, gave a phosphorus-containing compound whose  $^{31}\text{P}$  n.m.r. chemical shift is consistent with the pentaoxyspirophosphorane structure (**1**) ( $\delta -49.75$  p.p.m.)<sup>4</sup> and not with the phosphoric ester structure (**1'**).

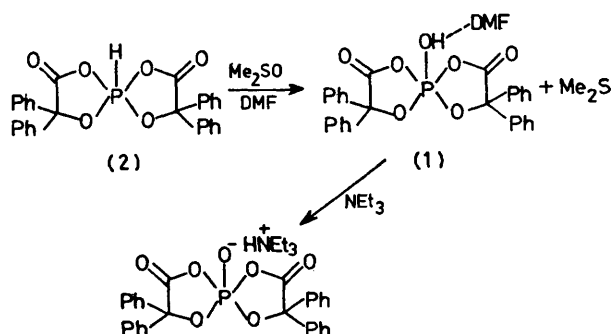


SCHEME 1

A crystalline substance was isolated (40% yield) by addition of 1 equiv. of triethylamine. Elemental analysis and its  $^1\text{H}$  and  $^{31}\text{P}$  n.m.r. [ $\text{CDCl}_3$ ,  $\delta$  ( $^1\text{H}$  rel. to  $\text{Me}_4\text{Si}$ ) 10.9 (s, 1H,  $\text{HNEt}_3$ ), 7.3 (m, 20H, Ph), 2.7 (q, 6H,  $\text{NCH}_2$ ), and 0.9 (t, 9H,  $\text{NCH}_2\text{Me}$ );  $\delta$  ( $^{31}\text{P}$ )  $-48.5$  p.p.m.<sup>4</sup>] and i.r. spectra [ $\nu_{\text{C}=\text{O}}$  1738 ( $\text{CH}_2\text{Cl}_2$ ) and 1735  $\text{cm}^{-1}$  (KBr disc)] are consistent with it being the triethylammonium salt of the phosphorane (**1**). This compound can also be obtained in good yield (60%) by oxidation with  $\text{Me}_2\text{SO}$  (1 equiv.) of the spirophosphorane (**2**), in *NN*-dimethylformamide (DMF) solution at 33 °C, followed by addition of triethylamine (Scheme 2).

The oxidation is complete after *ca.* 10 h. The chief product (> 80%) is the phosphorane (**1**). A phosphoric ester ( $\delta$   $^{31}\text{P}$   $-0.5$  p.p.m.) is also present (20%). From this reaction mixture the triethylammonium salt of (**1**) was prepared by addition of 1 equiv. of triethylamine followed by reprecipitation with ether. Elemental analysis and n.m.r.

data are again consistent with it being the triethylammonium salt of (1).



SCHEME 2. DMF = *NN*-dimethylformamide.

However, without the addition of triethylamine, after evaporation of DMF and the Me<sub>2</sub>S resulting from reduction of Me<sub>2</sub>SO, followed by washing with ether, we obtained a crystalline compound whose <sup>31</sup>P and <sup>1</sup>H n.m.r. spectra [CDCl<sub>3</sub>, δ (<sup>1</sup>H, rel. to Me<sub>4</sub>Si), 10.0 (s, 1H, DMF ··· H), 7.75 (s, 1H, HCONMe<sub>2</sub>), 7.3 (m, 20H, Ph), and 2.8 (d, 6H, NMe<sub>2</sub>); δ (<sup>31</sup>P) - 50.5 p.p.m.<sup>4</sup>] and elemental analysis are consistent with it being a dimethylformamide salt of (1).

Compound (2) was prepared by the general synthetic route for spirophosphoranes containing two α-hydroxy-acid ligands and having a P-H bond<sup>5</sup> [δ (<sup>31</sup>P) - 50.5 p.p.m., *J*<sub>P-H</sub> 923 Hz].

These results show that, with the phosphorane (1), equilibrium (1) is wholly displaced towards the pentacoordinated form. The existence of a DMF salt shows that (1) is a relatively strong acid.

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<sup>1</sup> A. Munoz, M. Gallagher, A. Klaebé, and R. Wolf, *Tetrahedron Letters*, 1976, 673.

<sup>2</sup> C. Bui Cong, A. Munoz, M. Sanchez, and A. Klaebé, *Tetrahedron Letters*, 1977, 1587.

<sup>3</sup> F. Ramirez, M. Nowakowski, and J. Marecek, *J. Amer. Chem. Soc.*, 1977, **99**, 4515.

<sup>4</sup> Shifts upfield of 85% H<sub>3</sub>PO<sub>4</sub> (δ 0 p.p.m.) are denoted negative (*cf.* G. Vael, *Annual Reports on N.M.R. Spectroscopy*, ed. E. F. Mooney, Academic Press, New York, 1973).

<sup>5</sup> M. Koenig, A. Munoz, and R. Wolf, *Bull. Soc. chim. France*, 1971, 4185 and M. Koenig, Thesis, no. 1311, Toulouse, 1972.