Synthesis of a Triethylammonium Salt of a Spirophosphorane containing a P–SH Bond

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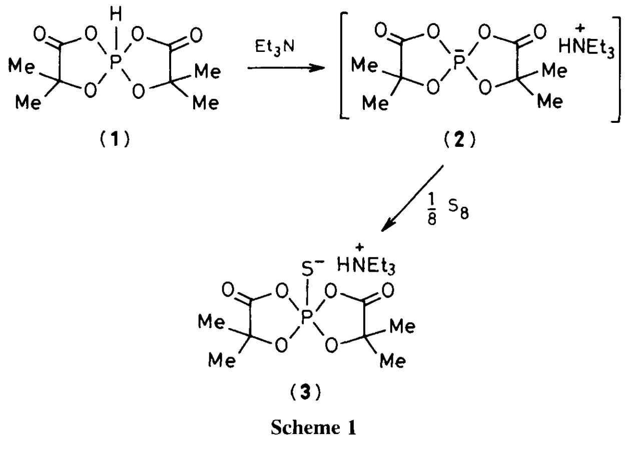
The triethylammonium salt of the phosphoranethiolate (**3**) has been isolated from the reaction of elemental sulphur with the conjugate base of the parent hydridophosphorane; its structure has been established by elemental analysis and n.m.r. (^{31}P, ^{1}H, ^{13}C) and i.r. spectroscopy.

We report the synthesis of a triethylammonium salt of the first phosphoranethiolate.

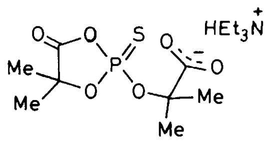
In previous papers, we have reported physicochemical results and the isolation and crystalline structure of some hydroxyphosphoranes and their corresponding salts.[1] We also established equilibria connecting hydridophosphoranes and their conjugate bases, the phosphoranide anions.[2,3] These latter show nucleophilic properties towards various electrophiles (CS_2, PhN_3, MeI, $PhCH_2Br$, *etc.*).[3] The phosphoranide (**2**), generated by the reaction of triethylamine with the hydridophosphorane (**1**), gives, with CS_2 an anionic adduct exhibiting a P–CS_2^- bond.[3,4] Replacing carbon disulphide by elemental sulphur, we would expect to obtain the corresponding phosphorane with a P–S$^-$ bond (Scheme 1).



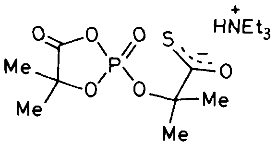
Scheme 1

In fact, sulphur (0.32 g) reacts with a mixture of the hydridophosphorane (**1**) (1.88 g, 0.01 mol) and triethylamine (1.52 g, 0.015 mol) in methylene chloride at room temperature to give a crystalline compound whose ^{31}P n.m.r. spectrum (CH_2Cl_2) exhibits a singlet at −4.3 p.p.m. Its ^{1}H n.m.r. spectrum and elemental analysis are consistent with the triethylammonium salt (**3**), or the isomeric compounds with a tetraco-ordinated phosphorus atom (**4**) and (**5**) [^{1}H n.m.r. ($CDCl_3$, 60 MHz): 9.07 (s, *H*–N, 1H) 3.33 (q, N–CH_2, 6H) 1.6 (s, CH_3–C–O–P) 1.4 (t, N–CH_2–CH_3) (s + t = 21H); a satisfactory elemental analysis was obtained].

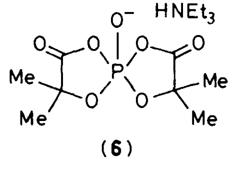
The thioxo compound (**4**) was discarded as the ^{31}P n.m.r. signal of the parent thioxophosphoric ester is between + 50 and + 80 p.p.m.[5] We also eliminated the phosphoric ester (**5**), and assigned the phosphoranethiolate (**3**), by the following arguments. (i) The i.r. spectra of the sulphuration product of the phosphoranide (**2**) and the homologous hydroxyphosphorane (**6**), are analogous: we observed the characteristic absorption band of a carbonyl group included in a 5-oxo-1,3,2-dioxaphospholane ring[1] [ν(C=O) 1735 cm^{-1}, KBr disk or (and) CH_2Cl_2 solution]. We did not observe a ν(C=O) band at



(**4**)



(**5**)



(**6**)

lower frequencies which would correspond to the thiocarboxylate or carboxylate group of the open forms (**4**) or (**5**).[6] (ii) The ^{13}C n.m.r. spectra of the sulphur compound (**3**) and of the oxophosphorane (**6**), are also similar. They show two doublets, resulting from coupling, $J(^{13}C–O–^{31}P)$: 173.31, $J[^{13}C(:O)–O–^{31}P]$ 9.76 Hz (**3**); 173.15, $J[^{13}C(:O)–O–^{31}P]$ 12.69 Hz (**6**); 77.52, $J[^{13}C(Me)–O–^{31}P]$ 4.88 Hz (**3**); 77.83, $J[^{13}C(Me)–O–^{31}P]$ 4.88 Hz (**6**) [in$(CD_3)_2SO$]. These results allow us to reject definitively any open form like (**4**) or (**5**), whose carbon atoms $^{13}C(:O)–O–P$ and $^{13}C(Me)–O–P$ must exhibit two signal groups whether they belong to a 5-oxo-1,3,2-dioxaphospholane ring or to the open chains $P–O–CMe_2–CO_2^-$ or $P–O–CMe_2–CSO^-$.

In conclusion, we have synthesised the triethylammonium salt of a phosphoranethiolate which represents a good model for thiophosphorane intermediates in nucleophilic reactions involving thioxophosphoric esters. The ^{31}P n.m.r. spectrum of this compound shows a variation of only 1 p.p.m. between + 25 °C and −60 °C. Therefore, over this temperature range, the equilibrium phosphoranethiolate $\rightleftharpoons$ thioxophosphoric ester is wholly displaced towards the pentaco-ordinated form. We can also conclude that the spirophosphoranic structure, shown to exist in solution, is also present in the solid state, as the i.r. spectra in solution and KBr disk are similar.

The n.m.r. spectra were recorded on Perkin Elmer R 32 with Fourier transform (36.435 MHz) (^{31}P), Bruker WH 60 (15.08 MHz, ^{13}C), and Varian T 60 (60 MHz, ^{1}H) spectrometers. We thank M. M. Tran and Dall'ava for their technical help.

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