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ISOLATION AND CHARACTERIZATION OF A STABLE DITHIOXOPHOSPHORANE

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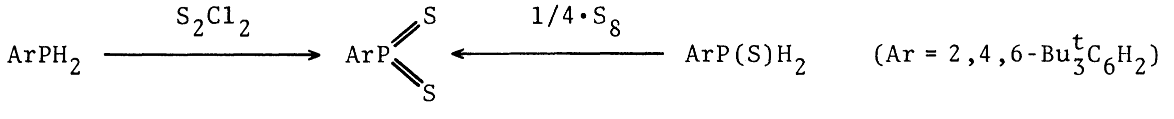
A sterically protected dithioxophosphorane, 2,4,6-tri-*t*-butylphenyldithioxophosphorane, has been isolated and characterized for the first time as a stable compound.

Dithioxophosphoranes have long been speculated as reactive intermediates.[1] Even Lawesson's reagent is thought to be reactive in its monomeric form.[2] Furthermore, Cadogan *et al.*[3] have recently reported on monomeric metaphosphonates, which are known to be important biological species.

We now wish to report the isolation and characterization of 2,4,6-tri-*t*-butylphenyldithioxophosphorane (1), a stable compound prepared from the reaction of the corresponding phosphine 2 with disulfur dichloride in the presence of a base.[4]

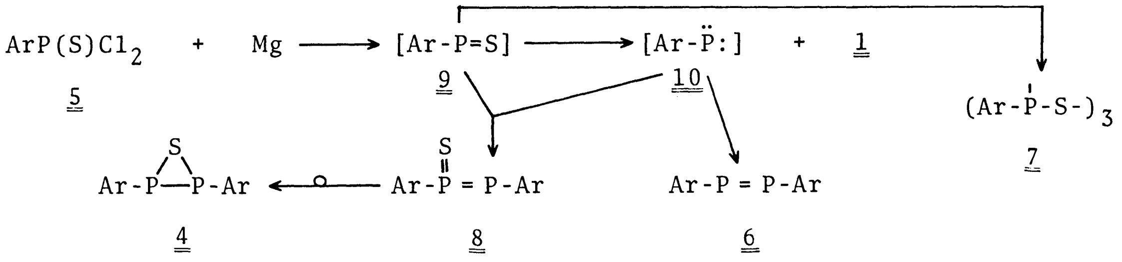


2 1 3

To a THF solution (tetrahydrofuran, 20 ml) of 2,4,6-tri-*t*-butylphenylphosphine (2; 121.5 mg, 0.437 mmol) and 2,6-lutidine (0.12 ml, 1.0 mmol) was added a 2 M solution of disulfur dichloride in THF (0.5 mmol) at 0 °C and the resulting solution was stirred for 30 min. Evaporation followed by removal of insoluble materials by addition of pentane and filtration afforded a yellow powder of the dithioxophosphorane 1: mp 150 - 151 °C; decomp >160 °C; ^{31}P NMR (CDCl$_3$) δ_P 298.2 ppm from ext. 85% H$_3$PO$_4$; ^{1}H NMR (CDCl$_3$) δ 7.51 (2H, d, $^4J_{PH} = 6.6$ Hz, arom.), 1.76 (18H, d, $^5J_{PH} = 1.1$ Hz, o-Bu^t), and 1.31 (9H, s, p-Bu^t); IR (KBr) ν_{PS} 660 cm^{-1}; mol wt (benzene) 336; UV (hexane) λ_{max} (ε) 243 (8530) and 328 nm (2530). Found: m/e 340.1478. Calcd for C$_{18}$H$_{29}$S$_2$P: M, 340.1448. In the solid state, compound 1 displays relative stability to atmospheric moisture or oxygen.

The phosphorane 1 could be also obtained from the corresponding primary phosphine sulfide 3[5] and elemental sulfur in the presence of a base. However, when the phosphine 2 (107.1 mg, 0.385 mmol) was allowed to react with elemental sulfur (60.4 mg, 1.89 mg-atom) in benzene (5 ml) at room temperature for 1 week, only formation of the phosphine sulfide 3 was observed. On the other hand, addition of one drop of lutidine at room temperature to the resulting 3 in the presence of sulfur gave 1, almost quantitatively, within 3 h. During the transformation of 3 to 1, evolution of hydrogen sulfide was determined by qualitative analysis with copper(II) sulfate. Furthermore, monitoring of this reaction by ^{31}P NMR suggested the intermediacy of the acid, ArP(S)H(SH). This was confirmed by preparation of the acid, by treatment of 2 with 2 equiv. of sulfur in toluene at 0 °C in the presence of a trace of lutidine for 10 d, and comparison of the δ_P values which were found to be identical [mp 106 - 109 °C; δ_P ($CDCl_3$) 16.8 ppm (d, $^1J_{PH} = 529.8$ Hz); ^1H NMR ($CDCl_3$) δ 9.15 (1H, d, $^1J_{PH} = 530.9$ Hz, PH), 7.44 (2H, d, J = 5.3 Hz, arom.), 4.05 (1H, bs, SH), 1.67 (18H, d, J = 0.7 Hz, o-Bu^t), and 1.31 (9H, s, p-Bu^t); $\nu_{PH,SH} = 2480$ (w), 2310 (b,w) and ν_{PS} 610 cm^{-1}].

We recently reported on the formation of a very stable thiadiphosphirane 4 from the phosphonothioic dichloride 5 with magnesium,6) however the mechanism of this reaction was not clear. Monitoring of this reaction by ^{31}P NMR in THF at -10 °C indicated appearance of the signals due to 1 (δ_P 298 ppm), the diphosphene 6 (δ_P 493 ppm),7) the trithiatriphosphorinane 7 (δ_P 91 ppm), and the diphosphene monosulfide 8 (a part of the AB pattern: δ_P 252 and 251 ppm)8) at the first stage. Detection of 1 suggests the generation of [phosphinidene sulfide (9)] which may disproportionate to 1 and [phosphinidene (10)].9) Coupling of 9 and 10 is then thought to give 8 which isomerizes to 4 on warming.8) A similar mechanism might be plausible for the formation of the corresponding diphosphene monoxide.10)



References

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2) H. Z. Lecher, R. A. Greenwood, K. C. Whitehouse, and T. H. Chao, J. Am. Chem. Soc., 78, 5018 (1956).
3) S. Bracher, J. I. G. Cadogan, I. Gosney, and S. Yaslak, J. Chem. Soc., Chem. Commun., 1983, 857.
4) Very recently Appel et al. analyzed the X-ray structure of 1 which has independently prepared from bis(trimethylsilyl)-2,4,6-tri-t-butylphenylphosphine and S_2Cl_2: R. Appel, F. Knoch, and H. Kunze, Angew. Chem., 95, in press (1983).
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9) We reserve the postulation of generation of phosphinidene (or phosphinidenoid) type of reaction intermediates (9 and 10) to further investigation.
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