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ISOLATION AND CHARACTERIZATION OF A STABLE DITHIOXOPHOSPHORANE

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A sterically protected dithioxophosphorane, 2,4,6-tri-<u>t</u>-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 <u>et al.³⁾</u> 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-<u>t</u>-butylphenyldithioxophosphorane (<u>1</u>), a stable compound prepared from the reaction of the corresponding phosphine <u>2</u> with disulfur dichloride in the presence of a base.⁴⁾



To a THF solution (tetrahydrofuran, 20 ml) of 2,4,6-tri-<u>t</u>-butylphenylphosphine ($\underline{2}$; 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 <u>1</u>: mp 150 - 151 °C; decomp >160 °C; ³¹P NMR (CDCl₃) δ_p 298.2 ppm from ext. 85% H₃PO₄; ¹H NMR (CDCl₃) 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 C₁₈H₂₉S₂P: M, 340.1448. In the solid state, compound <u>1</u> displays relative stability to atmospheric moisture or oxygen.

The phosphorane $\underline{1}$ could be also obtained from the corresponding primary phosphine sulfide $\underline{3}^{5}$ and elemental sulfur in the presence of a base. However, when the phosphine $\underline{2}$ (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 $\underline{3}$ was observed. On the other hand, addition of one drop of lutidine at room temperature to the resulting $\underline{3}$ in the presence of sulfur gave $\underline{1}$, almost quantitatively, within 3 h. During the transformation of $\underline{3}$ to $\underline{1}$, evolution of hydrogen sulfide was determined by qualitative analysis with copper(II) sulfate. Furthermore, monitoring of this reaction by ${}^{31}P$ NMR suggested the inter-

mediacy of the acid, ArP(S)H(SH). This was confirmed by preparation of the acid, by treatment of $\underline{2}$ 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 (CDCl₃) 16.8 ppm (d, ${}^{1}J_{PH} = 529.8$ Hz); ¹H NMR (CDCl₃) δ 9.15 (1H, d, ${}^{1}J_{PH} = 530.9$ 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 $\underline{4}$ from the phosphonothioic dichloride $\underline{5}$ with magnesium,⁶⁾ however the mechanism of this reaction was not clear. Monitoring of this reaction by ³¹P NMR in THF at -10 °C indicated appearance of the signals due to $\underline{1}$ (δ_p 298 ppm), the diphosphene $\underline{6}$ (δ_p 493 ppm),⁷⁾ the trithiatriphosphorinane $\underline{7}$ (δ_p 91 ppm), and the diphosphene monosulfide $\underline{8}$ (a part of the AB pattern: δ_p 252 and 251 ppm)⁸⁾ at the first stage. Detection of $\underline{1}$ suggests the generation of [phosphinidene sulfide ($\underline{9}$)] which may disproportionate to $\underline{1}$ and [phosphinidene ($\underline{10}$)].⁹⁾ Coupling of $\underline{9}$ and $\underline{10}$ is then thought to give $\underline{8}$ which isomerizes to $\underline{4}$ on warming.⁸⁾ A similar mechanism might be plausible for the formation of the corresponding diphosphene monoxide.¹⁰



References

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