

## Reaction of the Diphosphene $\text{ArP}=\text{PAr}$ ( $\text{Ar} = 2,4,6\text{-Bu}^t_3\text{C}_6\text{H}_2$ ) with Sulphur: Isolation and X-Ray Structure of the Diphosphene Monosulphide

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The diphosphene  $\text{ArP}=\text{PAr}$  ( $\text{Ar} = 2,4,6\text{-Bu}^t_3\text{C}_6\text{H}_2$ ) reacts with elemental sulphur to give the stable monosulphide  $\text{ArP}(\text{S})=\text{PAr}$  (**2**) whose structure was confirmed by an X-ray analysis; when treated with hexamethylphosphorous triamide, (**2**) reverts to the starting diphosphene but thermal and photochemical isomerisation of (**2**) gives the thiadiphosphirane  $\text{ArP}-\text{S}-\text{PAr}$ .

Phosphorus(III) compounds with a  $p_\pi-p_\pi$  double bond are of current interest.<sup>1,2</sup> We have isolated *E*-bis(2,4,6-tri-*t*-butylphenyl)diphosphene (**1**) which has a sterically stabilised phosphorus-phosphorus double bond.<sup>3</sup> We report here the reaction of (**1**) with elemental sulphur (1 equiv.) to give a stable diphosphene 1-sulphide (**2**) (Scheme 1).

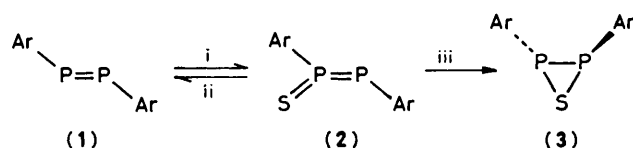
The diphosphene (**1**) (0.0474 mmol) in triethylamine (5 ml)† reacted with elemental sulphur (0.06 mg atom) at room temperature overnight in the dark to give a yellow homogeneous solution. This was chromatographed on silica gel to give bright yellow crystals [67% yield based on (**1**)] of *trans*-1,2-bis-(2,4,6-tri-*t*-butylphenyl)diphosphene 1-sulphide (**2**), m.p. 151.5–152 °C (from pentane) [i.r. (KBr),  $\nu(\text{P}=\text{S})$  760 and 740,  $\nu(\text{P}=\text{P})$  624  $\text{cm}^{-1}$ ; u.v. ( $\text{CH}_2\text{Cl}_2$ ),  $\lambda_{\text{max}}$  267 ( $\epsilon$  18 300) and 384 nm (6 650); <sup>1</sup>H n.m.r. ( $\text{CDCl}_3$ )  $\delta$  7.49–7.40 (m, 4H, aromatic), 1.68 (s, 18H, *o*-Bu<sup>t</sup>), 1.51 (s, 18H, *o*-Bu<sup>t</sup>), and 1.34 (s, 18H, *p*-

and *p'*-Bu<sup>t</sup>); high resolution mass spectrum  $m/z$  584.3755,  $\text{C}_{36}\text{H}_{58}\text{P}_2\text{S}$  requires 584.3734]. In triethylamine at 30 °C the <sup>31</sup>P n.m.r. spectrum (36.3 MHz) of (**2**) appeared as an AB quartet (<sup>1</sup> $J_{\text{PP}}$  629.9 Hz) centred at  $\delta_{\text{P}}$  (from external 85%  $\text{H}_3\text{PO}_4$ ) 255.8 and 247.8 p.p.m., whereas in  $\text{CDCl}_3$  a singlet was observed at  $\delta_{\text{P}}$  255.4 p.p.m. However, at –70 °C the spectrum contained a similar AB quartet ( $J$  633.9 Hz).‡

When (**2**) was heated at 95 °C for 0.5 h or at 50 °C overnight in toluene, the yellow solution became colourless and gave stable *E*-2,3-bis(2,4,6-tri-*t*-butylphenyl)-1,2,3-thiadiphosphirane (**3**) almost quantitatively,  $\delta_{\text{P}}$  ( $\text{CDCl}_3$ ) –65.1 p.p.m. Irradiation of a toluene solution of (**2**) with a medium-pressure mercury lamp (100 W, Pyrex filter) at 0 °C gave (**3**) almost exclusively within 5 min (Scheme 1). The sulphide (**2**) even in the solid state was photochemically isomerised to (**3**). The

thiadiphosphirane (**3**) thus obtained has a  $\text{P}-\text{S}-\text{P}$  ring stabilised by steric protection and is identical with the product of the reaction of 2,4,6-tri-*t*-butylphenylphosphonothioic dichloride with magnesium, a product whose structure has been determined by X-ray crystallography.<sup>4</sup>

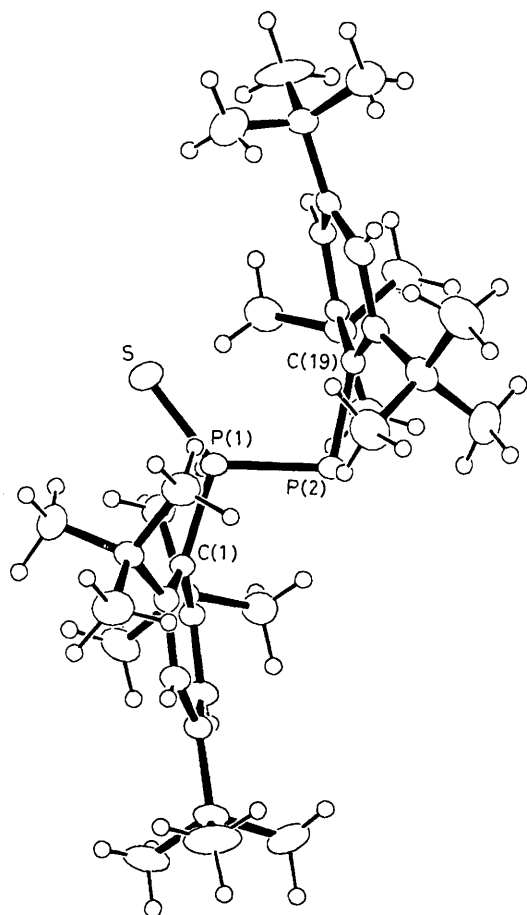
When (**2**) reacted with a large excess of hexamethylphosphorous triamide in benzene at room temperature in the dark



Scheme 1. i, 1/8 S<sub>8</sub>; ii, P(NMe<sub>2</sub>)<sub>3</sub>; iii,  $h\nu$  or heat. Ar = 2,4,6-Bu<sup>t</sup><sub>3</sub>C<sub>6</sub>H<sub>2</sub>.

† No reaction was observed in the absence of triethylamine even under more severe conditions.

‡ It is interesting that the <sup>31</sup>P n.m.r. chemical shifts of both of the phosphorus atoms in (**2**) are almost equal even though their coordination numbers are different.



**Figure 1.** Molecular structure of *trans*-1,2-bis(2,4,6-tri-*t*-butylphenyl)diphosphine 1-sulphide (**2**). Selected bond distances and bond angles: P(1)–P(2) 2.054(2), P(1)–S 1.931(2), P(2)–C(19) 1.863(5), P(1)–C(1) 1.841(5) Å; P(2)–P(1)–S 129.0(1), P(2)–P(1)–C(1) 106.1(1), C(1)–P(1)–S 124.9(1), P(1)–P(2)–C(19) 99.9(1)°.

for 2 h, the initial yellow solution turned orange and gave (**1**) in almost quantitative yield (Scheme 1). The desulphurisation of (**3**) did not proceed even under severe conditions.

The structure of (**2**) was established unambiguously by a single crystal *X*-ray analysis.

*Crystal data:* C<sub>36</sub>H<sub>58</sub>P<sub>2</sub>S, *M* = 584.872, triclinic, space group  $P\bar{1}$ , *a* = 14.439(6), *b* = 13.305(6), *c* = 10.577(4) Å,  $\alpha$  = 88.03(4),  $\beta$  = 106.90(4),  $\gamma$  = 107.76(3)°, *U* = 1848(1) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.05 g cm<sup>-3</sup>. 4520 Reflections with  $2\theta \leq 44^\circ$  were recorded on a four-circle diffractometer in the dark using graphite-monochromated Mo-*K*<sub>α</sub> radiation. Of these 2834 [with  $I > 3\sigma(I)$ ] were judged as observed. The structure was solved using MULTAN.<sup>5</sup> Full-matrix least-squares refinement

with anisotropic temperature factors for non-hydrogen atoms converged to *R* 0.049.<sup>6§</sup>

Figure 1 is an ORTEP drawing of (**2**).<sup>7</sup> The molecule (**2**) has an approximate two-fold axis vertical to the P–P bond and is roughly in the same conformation as that of (**1**) except for the sulphur atom and the *p*-*t*-butyl groups. The C(1), P(1), S, P(2), and C(19) atoms are coplanar within 0.07 Å and the four *o*-*t*-butyl groups lie above and below this plane. The *trans* oriented benzene rings make an average angle of 77.9° with this plane. It is interesting that the P–P bond distance in (**2**) is only slightly longer (by 0.02 Å) than that in (**1**) [2.034(2) Å].<sup>8</sup>

An 'azothiobenzene' or alternatively a 'diazene sulphide' was first described by Foffani *et al.*<sup>8</sup> but was later correctly formulated<sup>9,10</sup> as bis(phenylimino)sulphur(IV). Compound (**2**) is a phosphorus analogue of a true 'azothio' compound and also a sulphur analogue of the diphosphene 1-oxide which we recently reported.<sup>11</sup>

This work was supported in part by Science Research Grant-in-Aids from the Ministry of Education, Science, and Culture of Japan. We thank the Crystallographic Research Centre, Institute for Protein Research, Osaka University, for computer calculations.

Received, 21st March 1983; Com. 357

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§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.