Reaction of the Diphosphene ArP=PAr (Ar = 2,4,6-Bu^t₃C₆H₂) with Sulphur: Isolation and X-Ray Structure of the Diphosphene Monosulphide

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The diphosphene ArP=PAr (Ar = $2,4,6-But_3C_6H_2$) reacts with elemental sulphur to give the stable monosulphide ArP(S)=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 ArP-S-PAr.

Phosphorus(III) compounds with a $p_{\pi}-p_{\pi}$ double bond are of current interest.^{1,2} We have isolated *E*-bis(2,4,6-tri-t-butylphenyl)diphosphene (1) which has a sterically stabilised phosphorus-phosphorus double bond.³ 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), v(P=S) 760 and 740, v(P=P) 624 cm⁻¹; u.v. (CH₂Cl₂), λ_{max} 267 (ϵ 18 300) and 384 nm (6 650); ¹H n.m.r. (CDCl₃) δ 7.49—7.40 (m, 4H, aromatic), 1.68 (s, 18H, *o*-Bu^t), 1.51 (s, 18H, *o*-Bu^t), and 1.34 (s, 18H, *p*-



Scheme 1. i, $1/8 S_8$; ii, $P(NMe_2)_3$; iii, $h\nu$ or heat. Ar = 2,4,6-But₂C₆H₂.

and p'-Bu^t); high resolution mass spectrum m/z 584.3755, C₃₆H₅₈P₂S requires 584.3734]. In triethylamine at 30 °C the ³¹P n.m.r. spectrum (36.3 MHz) of (2) appeared as an AB quartet (¹J_{PP} 629.9 Hz) centred at δ_P (from external 85% H₃PO₄) 255.8 and 247.8 p.p.m., whereas in CDCl₃ a singlet was observed at δ_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, δ_P (CDCl₃) -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 P–S–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.⁴

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

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

[‡] It is interesting that the ³¹P n.m.r. chemical shifts of both of the phosphorus atoms in (2) are almost equal even though their co-ordination numbers are different.



Figure 1. Molecular structure of *trans*-1,2-bis(2,4,6-tri-t-butyl-phenyl)diphosphene 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)².

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: $C_{36}H_{58}P_2S$, M = 584.872, triclinic, space group $P\overline{1}$, a = 14.439(6), b = 13.305(6), c = 10.577(4) Å, $\alpha = 88.03(4)$, $\beta = 106.90(4)$, $\gamma = 107.76(3)^\circ$, U = 1848(1) Å³, Z = 2, $D_c = 1.05$ g cm⁻³. 4520 Reflections with $2\theta \le 44^\circ$ were recorded on a four-circle diffractometer in the dark using graphite-monochromated Mo- K_{χ} radiation. Of these 2834 [with $I > 3\sigma(I)$] were judged as observed. The structure was solved using MULTAN.⁵ Full-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms converged to R 0.049.⁶§

Figure 1 is an ORTEP drawing of (2).⁷ 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].³

An 'azothiobenzene' or alternatively a 'diazene sulphide' was first described by Foffani *et al.*⁸ but was later correctly formulated^{9,10} 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.¹¹

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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.