

Formation and Partial Characterisation of a Stable Phosphinine 1-Sulphide

David G. Holah, Alan N. Hughes,* and Karen L. Knudsen

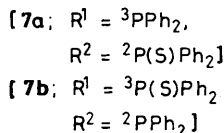
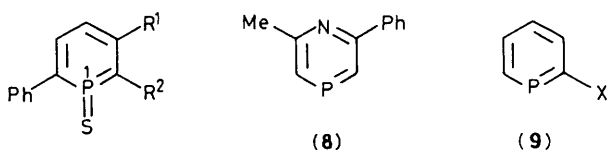
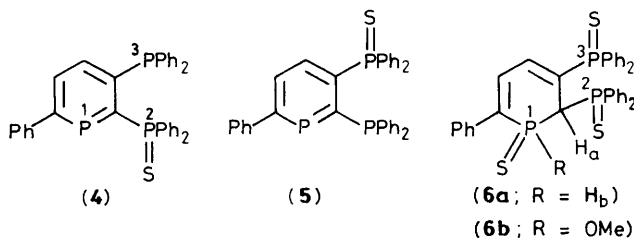
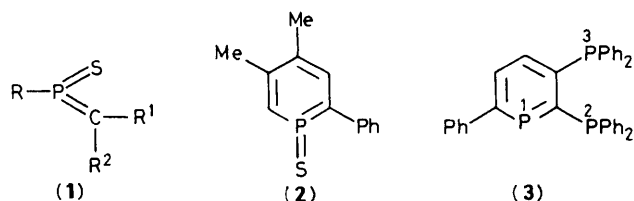
Department of Chemistry, Lakehead University, Thunder Bay, Ontario P7B 5E1, Canada

2,3-Bis(diphenylphosphino)-6-phenyl- λ^3 -phosphinine reacts with sulphur under very mild conditions to give a phosphinine 1-sulphide which survives chromatography on silica gel and for which ^{31}P n.m.r. and mass spectral data have been obtained.

Very few phospho-alkene sulphides (**1**) have been reported and even fewer of these usually highly reactive low-coordination phosphorus systems have been characterised as the free species.¹ A particularly interesting heterocyclic relative of these phospho-alkene sulphides is the phosphinine derivative (**2**) which has been generated² by prolonged heating of the parent λ^3 -phosphinine with sulphur in boiling xylene. While (**2**) has not been unambiguously characterised as the free

species,[†] it has been trapped² in addition reactions with both dienes and dienophiles. We report here the formation and partial characterisation of a stable phosphinine 1-sulphide.

[†] In the reactions, probably leading to the formation of (**2**), a product exhibiting a ^{31}P resonance at δ 145.7 p.p.m. was formed but this could not be isolated or otherwise characterised as (**2**) except by trapping experiments.



As an extension of a study³ of the λ^3 -phosphinine (3), this compound was treated with an excess of sulphur in benzene under reflux (3 h). Chromatography of the reaction mixture on silica gel [dry column, C₆H₆-CHCl₃ (1 : 1) followed by pure CHCl₃] yielded, in order of elution, unreacted sulphur, the monosulphide (4) (68%), the trisulphide (6a) (2%), and traces of unreacted (3). Compounds (4) and (6a) were characterised by microanalyses, ³¹P n.m.r. spectra [for (4): δ (p.p.m.) P¹ 218.5 (dd), P² 45.0 (dd), P³ -11.8 (dd); ²J(P¹P²) 110.5, ³J(P¹P³) 8.5, ³J(P²P³) 45.3 Hz; for (6a): δ (p.p.m.) P¹ 8.6 (t), P² and P³ 38.6 (dd) and 48.9 (dd); ²J(P¹P²) = ³J(P¹P³) 17.1, ³J(P²P³) 4.9 Hz] and, in the case of (6a), a ¹H n.m.r. spectrum [δ 3.28 (m, v.br., 1H, H_a), 7.18 (dm, 1H, H_b), ¹J_{PH} 527 Hz (confirmed by proton-coupled ³¹P measurements); 5.85–8.25 (m, 27H, aromatic/olefinic)]. Mass spectra showed, for (4), *m/z* 572 (*M*⁺), while (6a) has insufficient thermal stability. That (4) rather than (5) was formed is shown by the large two-bond coupling between P¹ and the phosphorus atom bearing the sulphur. Similarly, for (6a), the very small coupling between P² and P³ compared with values observed for (3)³ and (4) suggests that a change in hybridisation has occurred at a carbon atom bearing one of these phosphorus atoms.

The presence of a sulphur atom upon P¹ of (6a) suggested the possible intermediacy of a phosphinine 1-sulphide. Accordingly, the reaction of (3) with sulphur in dry benzene under dry N₂ was carried out at room temperature until, after four days, no (3) remained. The reaction mixture then contained (4) (*ca.* 80% by integration) and a phosphinine

1-sulphide (7a) or (7b) (*ca.* 20%). Chromatography [silica gel; C₆H₆-CHCl₃ (1 : 1)] removed unreacted sulphur but (4) could not be separated from the phosphinine sulphide chromatographically or by crystallisation. If the reaction is extended beyond four days, (7a) or (7b) slowly disappears from the mixture to be replaced by (6a). Under similar conditions, pure (4) does not react with sulphur and (4) therefore cannot be an intermediate in the formation of either the phosphinine 1-sulphide or the trisulphide (6a).

That either (7a) or (7b) was indeed formed is clear from the following evidence. The ³¹P n.m.r. spectrum of the mixture showed, in addition to the signals arising from (4), three signals at δ 248.8 (d, *J* 2.4 Hz), 44.4 (d, *J* 37.8 Hz) and -14.8 p.p.m. (dd). The P¹ signal (δ 248.8 p.p.m.) is considerably downfield of the signal due to the ring phosphorus atom of any known λ^3 -phosphinine derivative, including (3),³ other derivatives of (3)³ and (4), with the exception of the azaphosphinine (8) (δ 245.4 p.p.m.).⁴ More significantly, the ring P atom exhibits negligible coupling with the side-chain P atoms. Normally, ²J_{PX} [where X = H, C, or P as in (3) or (4)] for λ^3 -phosphinines of type (9) is large because of the proximity and coplanarity of the phosphorus non-bonding pair and X.⁷ It seems clear that no such non-bonding pair is present and a λ^3 -phosphinine structure for this product (*e.g.* 5) can be ruled out.

Evaporation of a small chromatographic fraction of the product mixture containing no free sulphur yielded a solid for which a mass spectrum (20 eV, 240 °C, direct inlet) showed a strong *M*⁺ peak for (4) at *m/z* 572 and a weak peak at *m/z* 604, the molecular weight of (7a) or (7b). Also, elemental analyses were very close to those which would be expected for a 4 : 1 mixture of (4) and the phosphinine 1-sulphide, a ratio indicated by the ³¹P spectrum.

Similar room temperature reactions of (3) with selenium[‡] yield mixtures, in a 2.5 : 1 ratio, of the selenide analogues of (4) [δ (p.p.m.) P¹ 217.4 (dd), P² 36.9 (dd), P³ -12.6 (dd); ²J(P¹P²) 108.0, ³J(P¹P³) 8.0, ³J(P²P³) 54.0 Hz] and (7a) or (7b) [δ (p.p.m.) P¹ 250.3 (s), P² and P³ 35.7 (d) and -15.7 (d) or *vice versa*, *J* 46.0 Hz]. Mass spectra of the mixture (40 eV, 260–320 °C) showed a clear *M*⁺ cluster (Se isotopes) *ca.* *m/z* 620 for the monoselenide, but only poorly defined very weak peaks *ca.* *m/z* 700 for the diselenide.

While it has not been possible to distinguish (7a) from (7b) on the basis of the above information, there can be little doubt that a phosphinine 1-sulphide of general structure (7) has been formed in these reactions. Confirmation of this comes from the fact that it adds methanol slowly across the ring P–C bond in a manner analogous to that previously observed⁸ for very short-lived phospho-alkene sulphides. Thus, stirring a concentrated mixture of (4) and (7a) or (7b) containing some unreacted sulphur (which can only be removed completely from very small samples of the mixture) with an excess of methanol at room temperature gave, over two days, the methanol adduct (6b) which was characterised spectroscopically [³¹P n.m.r.: δ (p.p.m.) P¹ 78.9 (dd, *J* 13.3 and 24.4 Hz), P² and P³ 49.6 (dd, *J* 4.9 and 24.4 Hz) and 38.6 (dd); ¹H n.m.r.: δ 2.88 (d, OMe, ³J(POMe) 14.5 Hz), 3.72 (m, H_a, v. br.), 6.20–8.25 (m, aromatic/olefinic); insufficient thermal stability for a mass spectrum]. Both the P¹ chemical shift and ³J(POMe) are as expected for a methyl thiophosphinate.⁸ Also, the ³J(P²P³) coupling (4.9 Hz) for (6b) is the same as that observed for (6a) and P² and P³ have almost identical locations in the spectra of (6a) and (6b).

Further work regarding the separation of the phosphinine

‡ We are indebted to a referee for suggesting this reaction.

1-sulphide from (4), its full characterisation, its reactions with dienes and other reagents, and the pathways whereby it and (6a) are formed, is in progress.

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