Generation and Trapping of a Phosphinine Sulphide†

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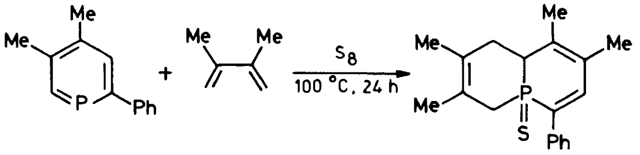
With sulphur at *ca.* 140 °C in xylene, 4,5-dimethyl-2-phenylphosphinine gives a transient *P*-sulphide which reacts with 2,3-dimethylbutadiene as a dienophile through its 1,6 positions and with dimethyl acetylenedicarboxylate as a diene through its 1,4 positions.

Recently the oxidation and sulphurization of some methylenephosphines have been studied and shown to proceed through transient *P*-oxides and *P*-sulphides respectively.[1] In one case, a stable methylenephosphine *P*-selenide has been described.[2] Although the oxidation of phosphinines, either by oxygen or by hydrogen peroxide, has been studied and shown to give 1,4- and 1,2-dihydrophosphinine oxides,[3,4] nothing is known about the sulphurization of phosphinines. In view of the recent results on methylenephosphines, a preliminary study of the reaction of S_8 with 4,5-dimethyl-2-phenylphosphinine (**1**) has been carried out.[5] The reaction of (**1**) with an excess of sulphur in boiling xylene for 5 h produced a major new product, which has a ^{31}P n.m.r. resonance at δ 145.7 p.p.m. (ref. external 85% H_3PO_4, δ +ve for downfield shifts) which cannot be purified by chromatography. Some starting material (**1**) was still present in the crude reaction mixture, as can be seen from the ^{31}P n.m.r. spectrum (δ 185 p.p.m.). When a few drops of 1-methylimidazole were added to the reaction medium as a catalyst,[6] the reaction of (**1**) with S_8 could be performed at a much lower temperature in boiling benzene. Again the product with a ^{31}P n.m.r. resonance at δ 145.7 p.p.m. was transiently produced, but the reaction proceeded further, and gave ultimately two compounds with ^{31}P n.m.r. resonances at δ 46.7 and 46.1 p.p.m. in $CDCl_3$. Obviously these two stable compounds are closely related but, until now, we have been unable to separate them, either by chromatography or crystallization, to establish their formulae unambiguously. In order to get more precise information on the reaction of S_8 with (**1**), we decided to perform the reaction in the presence of trapping reagents. When a stirred mixture of the phosphinine (**1**) (1 equiv.), sulphur (1.5 equiv.), 2,3-dimethylbutadiene (10 equiv.), was heated in a sealed tube at 100 °C for 24 h, the cycloadduct (**2**) was formed in high yield, whereas (**1**) itself does not react with dimethylbutadiene (Scheme 1).



(**1**) (**2**) (85 %)

Scheme 1

This cycloadduct‡ was purified by chromatography on silica gel with toluene. Its empirical formula was established by C, H, P, and S elemental analysis and mass spectroscopy {electron impact, 70 eV: *m/z* 314 (*M*, 53%), 281 (*M* − SH, 46%), and 232 [(**1** + S), 100%]}. It is interesting that the major decomposition pathway of (**2**) in the mass spectrometer is the retro-Diels–Alder reaction leading to the phosphinine sulphide (**3**), which is the most likely intermediate in the formation of (**2**). Similarly, reaction of the phosphinine (**1**) first with sulphur in boiling xylene, then with dimethyl acetylenedicarboxylate at 100 °C, gave the cycloadduct (**4**) in moderate yield (Scheme 2).

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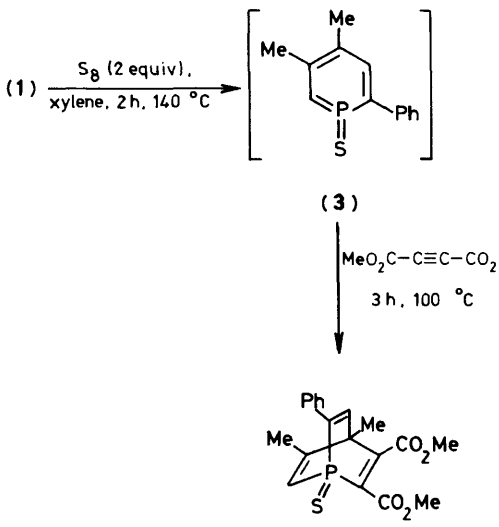
† Formerly phosphorin sulphide; see *Pure Appl. Chem.*, 1983, **55**, 409.

‡ Compound (**2**), m.p. 111—112 °C; δ (^{31}P) n.m.r. (C_6D_6) +20.49 p.p.m.; δ(^1H) n.m.r. ($CDCl_3$) 1.58, 1.71, 1.91, 1.99 (4s, 4 × 3H, 4Me), 2.1—2.7 (m, 5H, 2 × CH_2 and CH–P), 6.50 [d, ^3J(H–P) 31.3 Hz, 1H, =CH], 7.32 (m, 3H, Ph), and 7.69 (m, 2H, Ph *ortho*); δ(^{13}C) n.m.r. ($CDCl_3$) 19.75 (s, Me), 20.05 [d, *J*(C–P) 2.4 Hz, Me], 20.66 (s, Me), 21.02 (s, Me), 35.14 [d, ^2J(C–P) 7.3 Hz, CH_2], 36.29 [d, ^1J(C–P) 63.5 Hz, CH_2–P], 45.74 [d, ^1J(C–P) 61 Hz, CH–P], and 139.25 [d, ^2J(C–P) 3.7 Hz, =CH].



(4) (*Ca.* 48 %)

Scheme 2

It must be stressed that the reaction of (**1**) with dimethyl acetylenedicarboxylate gives only polymeric red compounds[7] which are formed here as by-products. The adduct (**4**)§ can be purified by chromatography on silica gel with toluene–ethyl acetate (80:20) and recrystallization in methanol. Its empirical formula was established by C, H, P, and S elemental analysis and mass spectroscopy [electron impact, 70 eV: m/z 374 (M, 42%) and 178 (100%)]. The formation of (**2**) and (**4**) clearly demonstrates the intermediacy of the phosphinine sulphide (**3**) but, at present, we are unsure whether the ^{31}P n.m.r. signal at δ145.7 p.p.m. can be assigned to it. It may be noted that the only recorded chemical shift for a methylenephosphine *P*-selenide falls in the same range (δ +125.7 p.p.m.).[2] Although (**3**) has not yet been fully characterized, its chemistry appears to be similar to that of the P–W(CO)$_5$ complex of (**1**).[7]

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§ Compound (**4**), m.p. 112—113 °C; δ(^{31}P) n.m.r. ($CDCl_3$) +6.64 p.p.m.; δ(^1H) n.m.r. ($CDCl_3$) 1.82 (s, 3H, Me), 2.07 [dd, ^4J(H–P) *ca.* ^4J(H–H) 1.7 Hz, 3H, Me–C=], 3.78 (s, 3H, OMe), 3.80 (s, 3H, OMe), 6.46 [dd, ^2J(H–P) 23.4 Hz, =CH–P], 6.97 [d, ^3J(H–P) 30.5 Hz, =CH], 7.26—7.54 (m, 5H, Ph); δ(^{13}C) n.m.r. ($CDCl_3$) 18.11 (s, Me), 19.42 [d, J(C–P) 13.4 Hz, Me], 52.34 (s, OMe), 52.52 (s, OMe), 53.10 [d, ^3J(C–P) 33 Hz, Me-*C* sp^3], 140.61 [d, ^1J(C–P) 56.2 Hz, C–P], 146.34 [d, ^1J(C–P) 62.3 Hz, C–P], and 150.67 (s, β-CH); i.r. (CH_2Cl_2), ν(CO) 1730 cm^{-1}.