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## Generation and Trapping of a C-Unsubstituted Methylenephosphine Sulphide

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The synthesis of a 7-phosphabicyclo[2.2.2]octa-2,5-diene *P*-sulphide is described; on thermolysis in boiling toluene, this compound generates Ph–P(S)=CH<sub>2</sub> which can be trapped by methanol, 2,3-dimethylbutadiene, and benzylideneacetophenone.

Whereas numerous studies have been devoted to the synthesis and chemistry of methylenephosphines<sup>1</sup> and methylenephosphine oxides,<sup>2</sup> almost nothing is known about methylenephosphine sulphides. These species have been generated either by direct sulphurization of methylenephosphines<sup>3-5</sup> or by rearrangement of thiophosphorylcarbenes.<sup>6,7</sup> In all cases, the P=C double bonds were sterically crowded and their chemistry was not seriously explored.<sup>‡</sup> In view of this, we decided to synthesise a series of precursors which would, at reasonable temperatures, lead to 'naked' (and thus highly reactive<sup>8</sup>) methylenephosphine sulphides.

Our initial experiments started with the readily available 1,2-dihydrophosphinine oxide (1).<sup>9</sup> This oxide was treated with dimethyl acetylenedicarboxylate in the presence of aluminium trichloride as a catalyst (Scheme 1). After hydrolysis (ice + NH<sub>4</sub>Cl) and evaporation of CH<sub>2</sub>Cl<sub>2</sub>, the organic residue was washed with Et<sub>2</sub>O and chromatographed on a silica gel column with ethyl acetate. The structure of (2) was established by elemental analysis, mass spectrometry {(electron impact, 70 eV, 185 °C): m/z 436 ( $M^+$ , 2.5%) and 266 [M – PhP(O)CH<sub>2</sub>OMe, 100%]} and <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P n.m.r.



Scheme 1. Reagents: i,  $MeO_2CC\equiv CCO_2Me$  (1.5 equiv.),  $AlCl_3$  (5 equiv.),  $CH_2Cl_2$ , reflux, 2.5 h; ii,  $P_4S_{10}$  (0.5 equiv.),  $C_6H_6$ , reflux, 2.5 h.

spectroscopy  $[\delta, +ve \text{ for downfield shifts, ref. external 85%} H_3PO_4: \delta(^{31}P) + 46.2 p.p.m. in CDCl_3]. The corresponding sulphide (3) was obtained by the reaction of freshly purified P_4S_{10} (continuous extraction with CS_2) with (2). After hydrolysis (H_2O + K_2CO_3), the organic residue was recrystallized from acetone–light petroleum or chromatographed on silica gel with toluene–ethyl acetate (80:20) as eluant. The n.m.r. parameters of (3)‡ were closely similar to those of (2)$ 

<sup>&</sup>lt;sup>†</sup> The only reported reactions include the addition of alcohols<sup>4,6,7</sup> and the addition of sulphur.<sup>3</sup> When generated by rearrangement of thiophosphorylcarbenes,<sup>6,7</sup> the reactivity of methylenephosphine sulphides is often masked by the reactivity of their carbene precursors.

 $<sup>\</sup>ddagger$  (3): δ(<sup>31</sup>P) N.m.r. (CH<sub>2</sub>Cl<sub>2</sub>) +58.7 p.p.m.; δ(<sup>13</sup>C) n.m.r. (CDCl<sub>3</sub>) 17.23 [d, *J*(C−P) 3.7 Hz, Me], 19.78 [d, *J*(C−P) 11 Hz, Me], 43.98 [d, <sup>1</sup>*J*(C−P) 85.5 Hz, CH<sub>2</sub>P], 44.34 [d, <sup>2</sup>*J*(C−P) 9.8 Hz, Me−C sp<sup>3</sup>], 51.86 (s, OMe), 52.22 (s, OMe), and 56.83 p.p.m. [d, <sup>1</sup>*J*(C−P) 36.6 Hz, Ph−C−P].



but its mass spectrum did not contain the molecular ion peak, suggesting lower thermal stability. Indeed, (3) decomposed readily in boiling toluene whereas (2) decomposed only around 170 °C [this thermal instability of (3) perhaps explains why the reaction of dimethyl acetylenedicarboxylate with the *P*-sulphide corresponding to (1) leads only to decomposition products]. According to <sup>31</sup>P n.m.r. experiments, the decomposition of (3) was complete in *ca*. 3 h in boiling toluene. The corresponding phthalate (4) was recovered in quantitative yield. When no trapping reagent was added to the reaction medium, the expected phenyl(methylene)phosphine sulphide (5) polymerized [<sup>31</sup>P resonances at +30 (broad), +57, +58, +84.6, and +84.9 p.p.m.].

The reaction with methanol led to the thiophosphinate (6) which was purified by chromatography on silica gel with toluene–ethyl acetate (90:10) as eluant and characterized by <sup>31</sup>P [ $\delta$ (<sup>31</sup>P) +89.6 p.p.m. in CH<sub>2</sub>Cl<sub>2</sub>] and <sup>1</sup>H n.m.r. spectroscopy { $\delta$ (<sup>1</sup>H) 2.0 [d, 3H, <sup>2</sup>J(H–P) 13.4 Hz, MeP], 3.57 [d, 3H, <sup>3</sup>J(H–P) 13.4 Hz, OMe], 7.55 (m, 3H, Ph), and 7.95 (m, 2H, Ph *ortho*) in CDCl<sub>3</sub>}.

The reaction with 2,3-dimethylbutadiene led to the tetrahydrophosphinine (7) which was chromatographed twice with toluene–Et<sub>2</sub>O (95:5) as eluant after partial removal of (4) by precipitation in hexane. Compound (7) was mainly characterized by <sup>31</sup>P [ $\delta$ (<sup>31</sup>P) +29.8 p.p.m. in CH<sub>2</sub>Cl<sub>2</sub>] and <sup>13</sup>C n.m.r. spectroscopy { $\delta$ (<sup>13</sup>C) 20.05 [d, *J*(C–P) 2.4 Hz, Me], 21.54 [d, *J*(C–P) 11 Hz, Me], 28.93 [d, <sup>2</sup>*J*(C–P) 6.1 Hz, CH<sub>2</sub>], 29.14 [d, <sup>1</sup>*J*(C–P) 53.7 Hz, CH<sub>2</sub>P], 37.29 [d, <sup>1</sup>*J*(C–P) 52.5 Hz, CH<sub>2</sub>P], 120.92 [d, *J*(C–P) 7.3 Hz, Me–C=], and 128.07 [d, *J*(C–P) 12.2 Hz, Me–C=] in CDCl<sub>3</sub>}.

The reaction with benzylideneacetophenone led to the tetrahydro-1,2-oxaphosphinine (8) as a mixture of two isomers [ $\delta$ (<sup>31</sup>P) +82.57 p.p.m. for (8a) and +80.7 p.p.m. for (8b) in CH<sub>2</sub>Cl<sub>2</sub>]. The crude product was purified by chromatography with hexane–Et<sub>2</sub>O (80:20) as eluant. Compound (8a) eluted first, followed by (8b). Only the more abundant (8b) was fully characterized mainly by <sup>1</sup>H and <sup>13</sup>C n.m.r. spectroscopy { $\delta$ (<sup>13</sup>C) 38.44 [d, <sup>2</sup>*J*(C–P) 6.1 Hz, *C*HPh], 38.80 [d,

<sup>1</sup>*J*(C–P) 62.3 Hz, CH<sub>2</sub>P], 106.75 [d, <sup>3</sup>*J*(C–P) 9.8 Hz, HC=], and 150.46 [d, <sup>2</sup>*J*(C–P) 11 Hz, Ph–C–O] in CDCl<sub>3</sub>}. The PhC*H* protons of (**8a**) and (**8b**) appear respectively at  $\delta$  4.45 and 3.60 in CDCl<sub>3</sub>. This result suggests that (**8b**) would be the less hindered isomer with *cis* (Ph)C–H and P–Ph bonds.

Since it has never been possible to perform Diels-Alder reactions with methylenephosphine oxides up to now,<sup>2</sup> the most noteworthy among this series of results is the successful condensation of (5) with dimethylbutadiene. We cannot decide yet whether this success reflects the low steric hindrance of the P=C double bond in (5) or an intrinsically higher reactivity of the P=C double bond in -P(S)=C < vs. -P(O)=C < systems.

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