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

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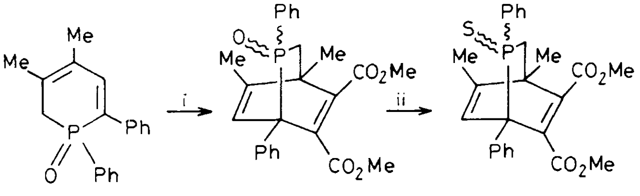
The synthesis of a 7-phosphabicyclo[2.2.2]octa-2,5-diene *P*-sulphide is described; on thermolysis in boiling toluene, this compound generates Ph–P(S)=CH_2 which can be trapped by methanol, 2,3-dimethylbutadiene, and benzylideneacetophenone.

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



(**1**) (**2**) (80%) (**3**) (72%)

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.

Our initial experiments started with the readily available 1,2-dihydrophosphinine oxide (**1**).[9] This oxide was treated with dimethyl acetylenedicarboxylate in the presence of aluminium trichloride as a catalyst (Scheme 1). After hydrolysis (ice + NH_4Cl) and evaporation of CH_2Cl_2, the organic residue was washed with Et_2O 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_2OMe, 100%]} and ^1H, ^{13}C, and ^{31}P n.m.r. spectroscopy [δ, +ve for downfield shifts, ref. external 85% H_3PO_4 : δ(^{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**)

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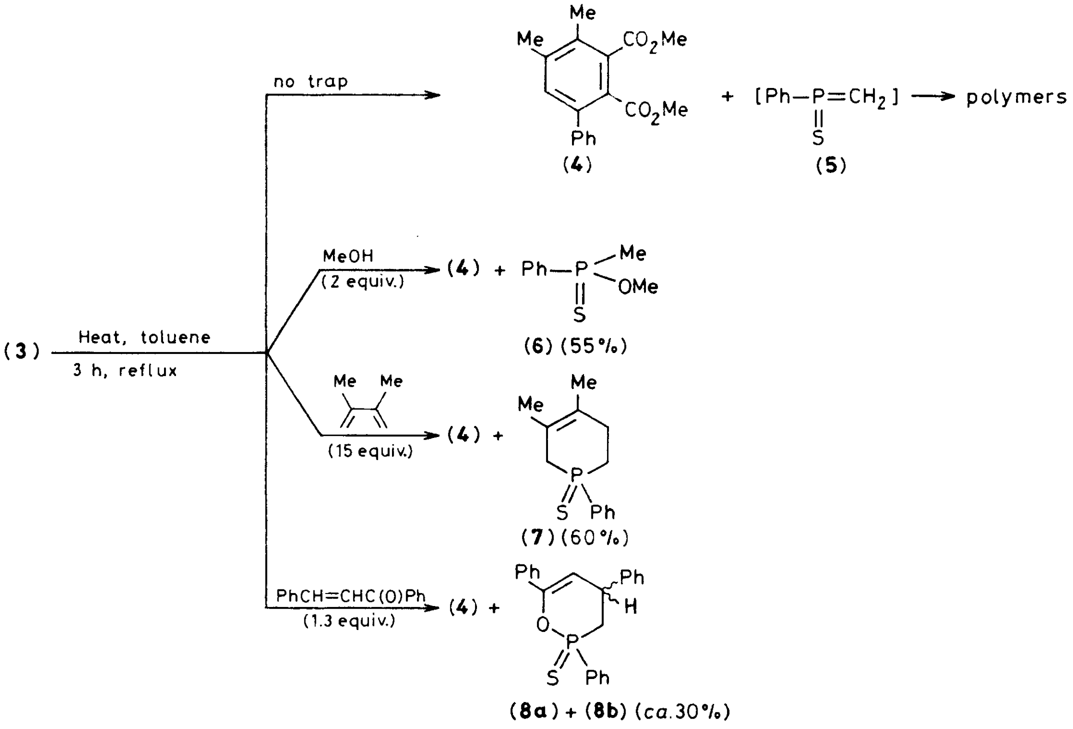
† The only reported reactions include the addition of alcohols[4,6,7] and the addition of sulphur.[3] When generated by rearrangement of thiophosphorylcarbenes,[6,7] the reactivity of methylenephosphine sulphides is often masked by the reactivity of their carbene precursors.

‡ (**3**) : δ(^{31}P) N.m.r. (CH_2Cl_2) +58.7 p.p.m.; δ(^{13}C) n.m.r. ($CDCl_3$) 17.23 [d, *J*(C–P) 3.7 Hz, Me], 19.78 [d, *J*(C–P) 11 Hz, Me], 43.98 [d, ^1J(C–P) 85.5 Hz, CH_2P], 44.34 [d, ^2J(C–P) 9.8 Hz, Me–*C* sp^3], 51.86 (s, OMe), 52.22 (s, OMe), and 56.83 p.p.m. [d, ^1J(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 ^{31}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 [^{31}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 ^{31}P [$\delta(^{31}P)$ +89.6 p.p.m. in CH_2Cl_2] and ^{1}H n.m.r. spectroscopy {$\delta(^1H)$ 2.0 [d, 3H, ^2J(H–P) 13.4 Hz, MeP], 3.57 [d, 3H, ^3J(H–P) 13.4 Hz, OMe], 7.55 (m, 3H, Ph), and 7.95 (m, 2H, Ph *ortho*) in $CDCl_3$}.

The reaction with 2,3-dimethylbutadiene led to the tetrahydrophosphinine (**7**) which was chromatographed twice with toluene–Et_2O (95 : 5) as eluant after partial removal of (**4**) by precipitation in hexane. Compound (**7**) was mainly characterized by ^{31}P [$\delta(^{31}P)$ +29.8 p.p.m. in CH_2Cl_2] and ^{13}C n.m.r. spectroscopy {$\delta(^{13}C)$ 20.05 [d, *J*(C–P) 2.4 Hz, Me], 21.54 [d, *J*(C–P) 11 Hz, Me], 28.93 [d, ^2J(C–P) 6.1 Hz, CH_2], 29.14 [d, ^1J(C–P) 53.7 Hz, CH_2P], 37.29 [d, ^1J(C–P) 52.5 Hz, CH_2P], 120.92 [d, *J*(C–P) 7.3 Hz, Me–*C*=], and 128.07 [d, *J*(C–P) 12.2 Hz, Me–*C*=] in $CDCl_3$}.

The reaction with benzylideneacetophenone led to the tetrahydro-1,2-oxaphosphinine (**8**) as a mixture of two isomers [$\delta(^{31}P)$ +82.57 p.p.m. for (**8a**) and +80.7 p.p.m. for (**8b**) in CH_2Cl_2]. The crude product was purified by chromatography with hexane–Et_2O (80 : 20) as eluant. Compound (**8a**) eluted first, followed by (**8b**). Only the more abundant (**8b**) was fully characterized mainly by ^{1}H and ^{13}C n.m.r. spectroscopy {$\delta(^{13}C)$ 38.44 [d, ^2J(C–P) 6.1 Hz, *C*HPh], 38.80 [d, ^1J(C–P) 62.3 Hz, CH_2P], 106.75 [d, ^3J(C–P) 9.8 Hz, HC=], and 150.46 [d, ^2J(C–P) 11 Hz, Ph–*C*–O] in $CDCl_3$}. The PhC*H* protons of (**8a**) and (**8b**) appear respectively at δ 4.45 and 3.60 in $CDCl_3$. 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,[2] 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 $-P(S)=C\langle$ *vs.* $-P(O)=C\langle$ systems.

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