7-Phosphanorbornene Derivatives as Precursors of Esters and Amides of Two-co-ordinate Thiophosphenous *O*-Acid

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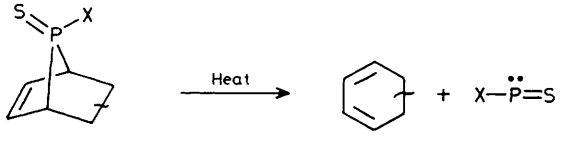
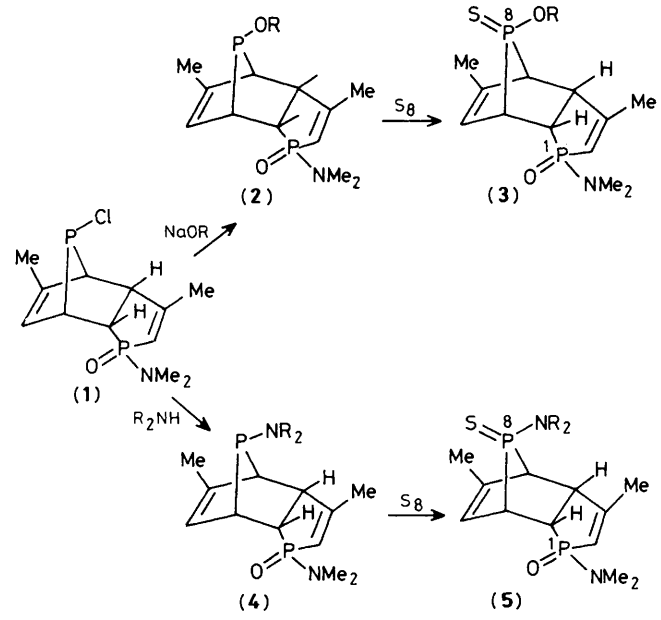
Heating thiophosphinate *O*-esters and thiophosphinamides having the 7-phosphanorbornene framework results in elimination of fragments that are derivatives of thiophosphenous *O*-acid; they are trapped by cycloaddition with 2,3-dimethylbutadiene to form 2,5-dihydrophospholes.

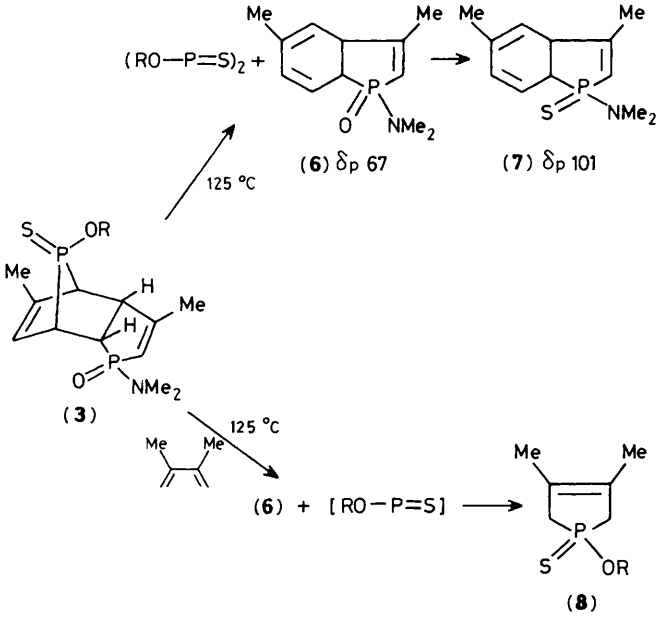
In the rapidly expanding number of isolatable or detectable phosphorus species with low co-ordination number, derivatives of the phosphenous acid (HO–P=O) family are barely represented. An alkyl phosphenite has been detected as a reaction intermediate,[1] and spectral characterisation of the species Cl–P=O and Cl–P=S indicated their formation at very high temperatures.[2] The only stable phosphenous acid derivatives[3] are based on the structure R_2N–P=NR′ which allows large substituents to surround the double bond and prevent dimerisation. We have now obtained evidence from trapping experiments that the previously undescribed thiophosphenous *O*-acid derivatives RO–P=S and R_2N–P=S can be generated in substantial amounts by causing appropriate 7-phosphanorbornene derivatives to undergo retro-cycloaddition reactions (Scheme 1). The technique may be useful for generating other phosphenous acid derivatives as well.



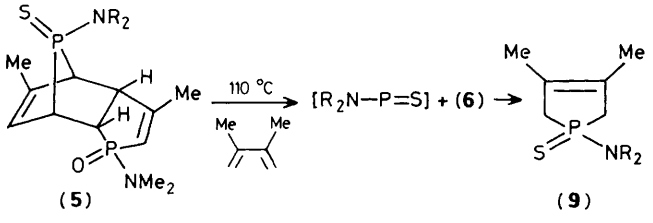
Scheme 1. X = OR or NR_2.



Scheme 2



Scheme 3



Scheme 4

The dimers of phosphole oxides constitute a ready source of the 7-phosphanorbornene system; with phosphorus in the phosphinamide state, a method is available[4] for preparing the versatile phosphinous chloride structure (from the phosphinamide, with $HSiCl_3$–pyridine), and this has made possible the synthesis (Scheme 2) of the thiophosphinate *O*-esters and thiophosphinamides necessary as generators of the phosphenous acid derivatives. Displacement of Cl from (**1**) by NaOR proceeds with complete retention of stereochemistry;[5] amines give a mixture with the product with retained stereochemistry predominating,[4] but sulphur addition gives a chromatographically separable mixture of thiophosphinamides. Sulphur addition was effected with (**2**) and (**4**) (plus its isomer) in benzene at room temperature for 3—6 days (80—90% yield). ^{31}P N.m.r. spectral data for the products are given in Table 1; satisfactory C, H, and P analyses were obtained.

The retro-cycloaddition of the thiophosphinates (**3**) occurred in toluene at 125 °C in a sealed tube, and was complete after 16 h. In the absence of a trapping agent, the eliminated fragment appeared to dimerise to a species capable of replacing O by S at the phosphinamide function in the co-product (**6**) (Scheme 3); this reaction resembles that between the Lawesson reagent $(ArPS_2)_2$ and phosphoryl groups. In the presence of 2,3-dimethylbutadiene as a trapping agent,[6] however, the fragment was intercepted and the diene product then had structure (**6**). Of more importance was the high-yield (80—90% by ^{31}P n.m.r. measurements) formation of the 2,5-dihydrophosphole derivative (**8**), which after chromatography was isolated in 37% yield from the ester (**3a**), and 28% from the ester (**3b**). Some properties are given in Table 2. The thiophosphinamides (**5**) were decomposed similarly (110 °C in toluene, 4 h), providing the dihydrophosphole derivatives (**9**) when dimethylbutadiene was present (Scheme 4).

In support of the concerted nature of the elimination of the phosphorus bridge from (**3**) and (**5**), and of the lack of direct involvement of the trapping agent in the elimination step, the rates of decomposition of (**3**) and (**5**) were the same with and without the diene present.

Table 1. Data for thiophosphinic acid derivatives (**3**) and (**5**).

Compound	OR or NR_2	M.p., *t*/°C	^{31}P Data[a] P-1	P-8	$^3J_{PP}$ /Hz
(**3a**)	OCH_2CCl_3	154—156	65.2	122.0	39.0
(**3b**)	OPh	167—169	62.6	117.3	38.0
(**5a**)	NMe_2	163—164	62.5	125.0	34.2
(**5b**)	$N[CH_2]_4CH_2$	161—163[b]	64.2	120.8	34.2
(**5c**)	NEt_2	145—146	62.7	122.8	34.2

[a] Proton decoupled Fourier-transform mode with JEOL FX-90Q, in $CDCl_3$. All shifts are in p.p.m., positive and downfield of 85% H_3PO_4. [b] Decomp.

Table 2. Spectral data for the dihydrophosphole derivatives (**8**) and (**9**).

Compound	OR or NR_2	^{31}P N.m.r.[a] δ	Mass spectrum[b] Formula	M_r	M^+, *m/z*
(**8a**)	OCH_2CCl_3	114.1	$C_8H_{12}Cl_3OPS$	291.9414	291.9412
(**8b**)	OPh	108.5	$C_{12}H_{15}OP$	238.0582	238.0584
(**9a**)	NMe_2	84.1[c]	—	—	—
(**9b**)	$N[CH_2]_4CH_2$	81.0	$C_{11}H_{20}NPS$	229.1055	229.1054
(**9c**)	NEt_2	79.6[c]	—	—	—

[a] See footnote a, Table 1. [b] Obtained with an AEI MS-902 Spectrometer, Research Triangle Mass Spectrometry Center, Research Triangle Park, N.C. [c] Previously reported in ref. 7.

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