

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

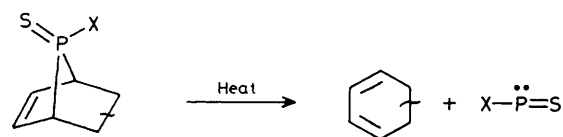
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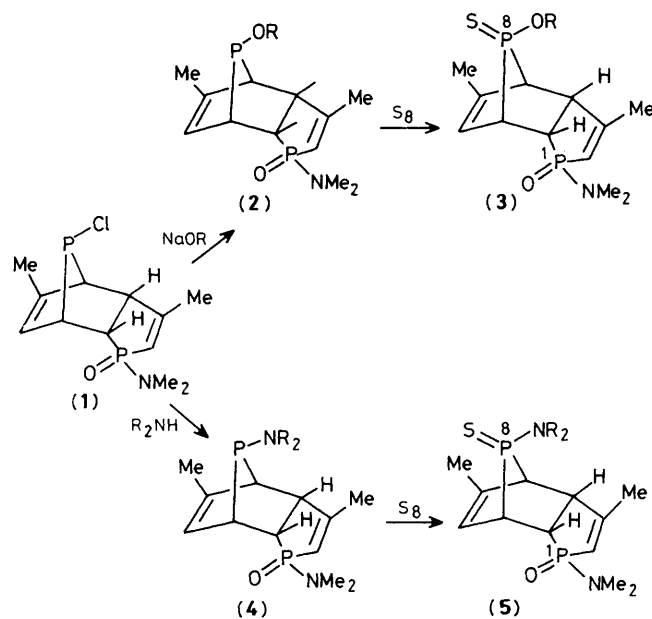
Heating thiophosphinate *O*-esters and thiophosphinamides having the 7-phosphanorbornene framework results in elimination of fragments that are derivatives of thiophosphenous *O*-acid; they are trapped by cycloaddition with 2,3-dimethylbutadiene to form 2,5-dihydrophospholes.

In the rapidly expanding number of isolatable or detectable phosphorus species with low co-ordination number, derivatives of the phosphinous acid ($\text{HO}-\text{P}=\text{O}$) family are barely represented. An alkyl phosphenite has been detected as a reaction intermediate,¹ and spectral characterisation of the species $\text{Cl}-\text{P}=\text{O}$ and $\text{Cl}-\text{P}=\text{S}$ indicated their formation at very high temperatures.² The only stable phosphinous acid derivatives³ are based on the structure $\text{R}_2\text{N}-\text{P}=\text{NR}'$ 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 $\text{RO}-\text{P}=\text{S}$ and $\text{R}_2\text{N}-\text{P}=\text{S}$ can be generated in

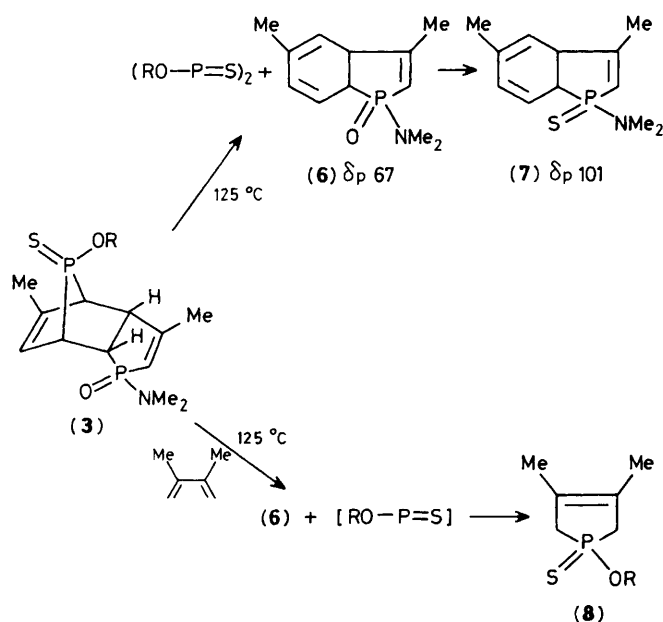
substantial amounts by causing appropriate 7-phosphanorbornene derivatives to undergo retro-cycloaddition reactions (Scheme 1). The technique may be useful for generating other phosphinous acid derivatives as well.



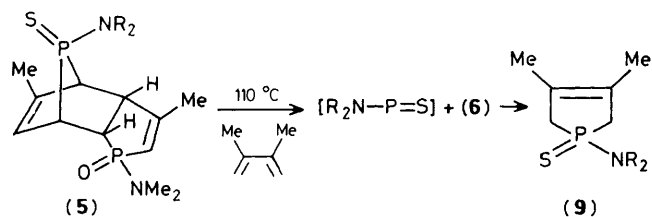
Scheme 1. X = OR or NR₂.



Scheme 2



Scheme 3



Scheme 4

The dimers of phosphole oxides constitute a ready source of the 7-phosphanorborene system; with phosphorus in the phosphinamide state, a method is available⁴ for preparing the versatile phosphinous chloride structure (from the phos-

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	³ J _{PP} /Hz
(3a)	OCH ₂ CCl 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] ₄ CH 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 CDCl₃. All shifts are in p.p.m., positive and downfield of 85% H₃PO₄. ^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 ₂ CCl ₃	114.1	C ₈ H ₁₂ Cl ₃ OPS	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] ₄ CH 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.

phinamide, with HSiCl₃-pyridine), and this has made possible the synthesis (Scheme 2) of the thiophosphinate *O*-esters and thiophosphinamides necessary as generators of the phosphinous 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). ³¹P 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 (ArPS₂)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 ³¹P 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.

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References

- 1 C. J. R. Fookes, M. J. Gallagher, and H. Honegger, *J. Chem. Soc., Chem. Commun.*, 1978, 324.
 - 2 M. Binnewies, B. Solouki, H. Bock, R. Becherer, and R. Ahlrichs, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 731.
 - 3 E. Niecke and W. Flick, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 585.
 - 4 L. D. Quin and J. Szewczyk, *J. Chem. Soc., Chem. Commun.*, 1984, 1551.
 - 5 L. D. Quin and G. Keglevich, *J. Chem. Soc., Perkin Trans. 2*, in the press.
 - 6 C.C. Santini, J. Fischer, F. Mathey, and A. Mitschler, *J. Am. Chem. Soc.*, 1980, **102**, 5809.
 - 7 L. D. Quin and J. Szewczyk, *Phosphorus Sulfur*, 1984, **21**, 161.
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