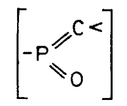
Methylenethioxophosphoranes and 1,2-λ^5-Thiaphosphirans

By Edgar Niecke* and Dirk-A. Wildbredt

(*Fakultät für Chemie der Universität Bielefeld, D-*4800 *Bielefeld, W. Bielefeld, W. Germany*)

Summary The synthesis of methylenethioxophosphoranes and the [1+2] cycloaddition of sulphur to the ylidic P–C bond is described.

In contrast with the labile methyleneoxophosphoranes (**1**)[1] and the methyleneiminophosphoranes (**2**),[2] which are stable as monomers, the isoelectronic bismethylenephosphoranes are unstable towards formation of the phosphirans (**3**).[3] With the higher atomic number analogues the cyclic form would prevail for the still unknown C–P–Si system (**6**)† and at least be favoured energetically for the C–P–P system, as indicated by the existence of diphosphirans (**5**).[4] On the other hand, we have now found that sulphur‡ again forms the ylidic species (**4**), analogous to the oxides.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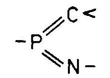
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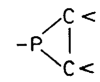
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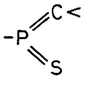
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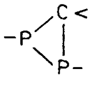
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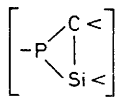
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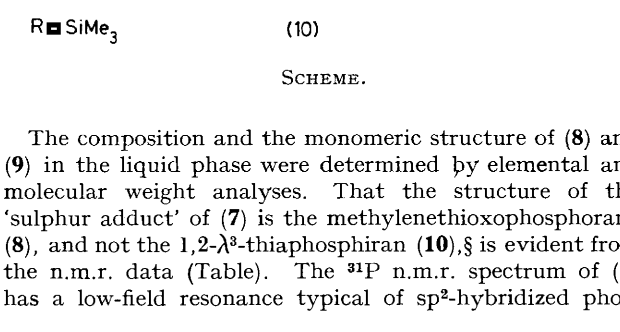
Bis(trimethylsilyl)aminotrimethylsilylmethylenephosphine[3] (**7**) (20 mmol) and sulphur (20 mmol) yielded, after 1 h in 20 ml refluxing benzene, a crude product, containing (**8**) in 90% yield; distillation *in vacuo* gave the methylenethioxophosphorane at 75—77 °C (0·1 Torr) as a water-sensitive, yellow liquid [yield 2·8 g (40%)]. The by-product of the reaction is the as yet unknown λ^5-thiaphosphiran heterocycle (**9**) formed by the [1 + 2] cycloaddition of sulphur to the species (**8**) (Scheme). We also formed this compound quantitatively by the reaction of (**7**) with 2 equiv. of sulphur.



Scheme.

The composition and the monomeric structure of (**8**) and (**9**) in the liquid phase were determined by elemental and molecular weight analyses. That the structure of the 'sulphur adduct' of (**7**) is the methylenethioxophosphorane (**8**), and not the 1,2-λ^3-thiaphosphiran (**10**),§ is evident from the n.m.r. data (Table). The ^{31}P n.m.r. spectrum of (**8**) has a low-field resonance typical of sp^2-hybridized phos-

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† The ylidic species would assume co-ordination number 3 on silicon.

‡ The methyleneselenophosphorane [δ ^{31}P 172·4 p.p.m.; δ ^{13}C P=*C* 110·7 p.p.m. ($^1J_{CP}$ 70·4 Hz); δ ^1H: P=C*H* 5·54 ($^2J_{HP}$ 23·0 Hz)], which is formed analogously from (**7**) and selenium, has not yet been isolated in the pure form.

§ Whether (**10**) is formed as an intermediate cannot as yet be excluded from our hypothesis.

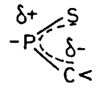
phorus. Substitution of iminonitrogen in (**2**) by sulphur deshields the ^{31}P nucleus by about 100 p.p.m., which is also observed when comparing the di-iminophosphoranes with iminothioxophosphoranes.[5] The ^{13}C-{^{1}H} n.m.r. shift of the methylene carbon resonance is consistent with values observed for the iminomethylenephosphoranes (**2**).[2] The change in hybridisation of phosphorus and the methylene carbon and the formation of the 1,2-λ^{5}-thiaphosphiran system (**9**) causes the expected high-field shift of the ^{31}P and ^{13}C n.m.r. resonances[6] (Table). The reduction of the P–C coupling constant agrees with the changes in hybridisation. The low value of 28·2 Hz reflects the unusual bonding properties of the strained phosphorus-ring system.

Table. ^{31}P, ^{1}H, ^{13}C, and ^{29}Si n.m.r. data for compounds (**8**) and (**9**).[a]

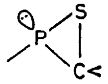
	(**8**)	(**9**)
δ (^{31}P)	185·4	6·2
δ (^{1}H) (J_{HP})		
PCSiMe$_3$	0·26 (0·7)	0·21 (0·6)
PNSiMe$_3$	0·25 (0·2)	0·34 (0·2)
PCH	4·47 (19·5)	2·10 (12·2)
δ (^{13}C) (J_{CP})		
PCSiC_3	0·3 (7·3)	−1·6 (3·0)
PNSiC$_3$	2·5 (2·5)	3·0 (3·4)
PC	97·6 (92·2)	27·2 (28·2)
δ (^{29}Si) (J_{SiP})		
PCSi	−6·4 (10·0)	12·1 (1·9)
PNSi	10·7 (5·2)	3·9 (4·3)

[a] 30% solution in CDCl$_3$, 85% H$_3$PO$_4$ as external standard for ^{31}P and Me$_4$Si as internal standard for ^{1}H, ^{13}C, and ^{29}Si, 30 °C; δ in p.p.m., J in Hz.

Further experiments on weakening the stabilisation in the 'homoallyl anion' system (A) by varying the substituents in (**8**) to stabilize the 1,2-λ^{3}-thiaphosphiran form (B) are in progress.



(A)



(B)

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