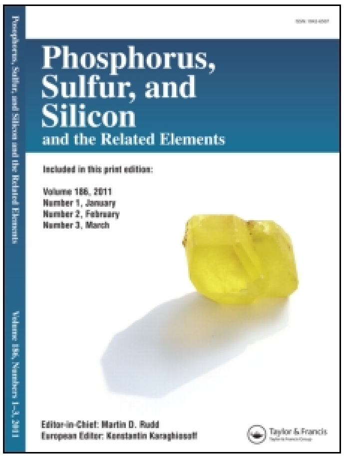

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O-SILYLATION OF SOME UNSATURATED CYCLIC PHOSPHINE OXIDES

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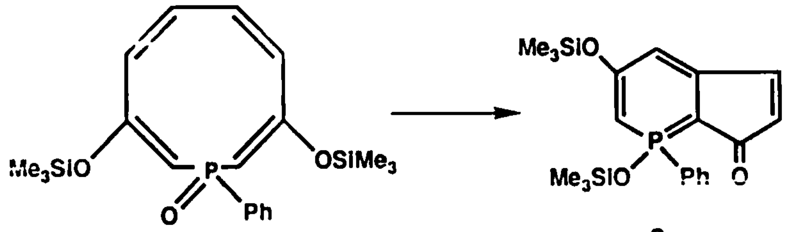
The phosphoryl oxygen of 1,6-dihydrophosphinine oxides is silylated rapidly at room temperature by bis(trimethylsilyl)trifluoroacetamide; the product loses a ring proton to establish the resonance stabilized λ^5-phosphinine ring system. Similar events take place with a 3-keto derivative of a tetrahydrophosphinine oxide, which also undergoes silylation of the keto oxygen. 1,4-Dihydro-1,4-azaphosphinine are silylated to give 1,4-aza-λ^5-phosphinines; their dibenzo derivatives (5,10-dihydrophenophosphazine oxides) require more forcing conditions (triethylsilyl bromide at 100°C) for phosphoryl silylation. These conditions are also effective for silylation of a 3-phospholene oxide.

Key words: 1,6-dihydrophosphinine-1-oxides; O-silyl λ^5-phosphinines; O-silyl 1,4-aza- λ^5-phosphinines; 5,10-dihydrophenophosphazine-10-oxide; 1,4-dihydro-1,4-azaphosphinine-1-oxides; trialkylsilylation

The recently observed[1] rearrangement of silyl enol ether 1 to a P-siloxy phosphorus derivative (**2**) must include a step that amounts to a silylation of oxygen in a tertiary phosphine oxide. The product derives stabilization from the resonance delocalization of the λ^5-phosphinine produced.



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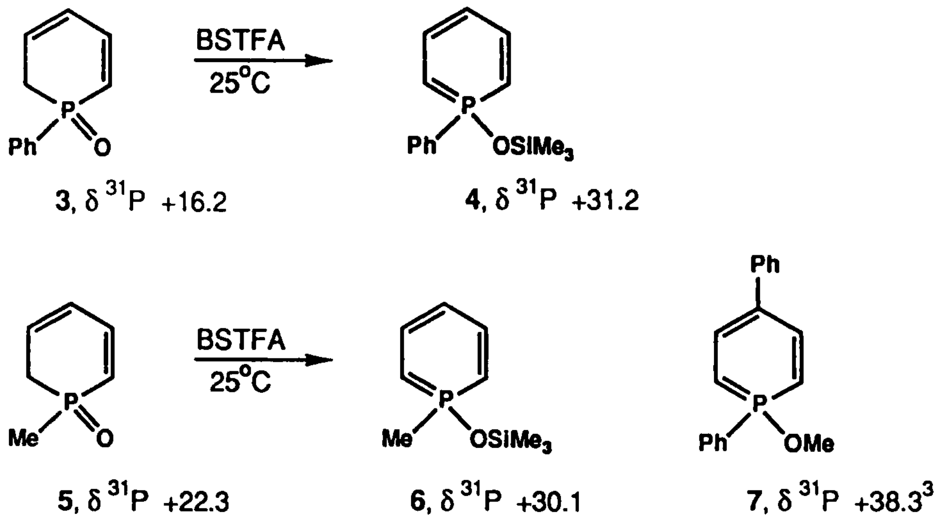
2

This observation prompted further study of P=O silylation in some other heterocyclic phosphorus compounds. Normally, phosphoryl oxygen is not very sensitive to this form of electrophilic attack, and it appeared that factors could be introduced with the heterocyclic structure that could lower the energy requirement for this reaction to take place. We have now found that certain types of unsaturated six-membered cyclic phosphine oxides undergo O-silylation under mild conditions; formally, this provides a siloxy phosphonium ion, but an important observation from this study is that in some cases this type of product can undergo a proton loss from an α-carbon. This is particularly likely when a resonance-stabilized λ^5-phosphinine system can develop. These events have led to new types of λ^5-phosphinines; the derivatives are, however, highly reactive to moisture and all attempts to isolate them have resulted in their destruction. The solutions in which they are prepared are suitable for characterization of the species by NMR techniques. O-Silylation of a 3-phospholene oxide and a dihydrophenophosphazine was also accomplished but under more forcing conditions.

Silylation of 1,6-Dihydrophosphinine-1-oxides

The synthesis of the two 1,6-dihydrophosphinines **3** and **5** was reported in a recent publication from this Laboratory.[2] This ring system seemed ideal for an initial examination of the possibility of O-silylation, since the siloxy phosphonium ion first produced might undergo loss of an α-proton to form the λ^5-phosphinine system as suggested from the formation of **2** from the phosphonin oxide **1**. Indeed, the silylation was very rapid and quantitative when performed at room temperature with bis(trimethylsilyl)trifluoroacetamide (BSTFA). The course of the reaction was easily followed by ^{31}P NMR spectroscopy; the products gave signals (Scheme 1) that were appreciably downfield of those of the starting oxides, and were in the range expected for the predicted λ^5-phosphinine structure. Thus, compound **7** has been reported to have a shift of δ +38.3[3] and serves as an appropriate model compound for the new silyl phosphinine derivatives.



3, δ ^{31}P +16.2

4, δ ^{31}P +31.2

5, δ ^{31}P +22.3

6, δ ^{31}P +30.1

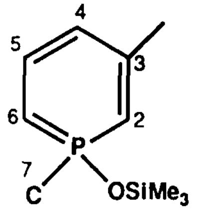
7, δ ^{31}P +38.3[3]

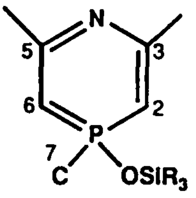
SCHEME 1

The ^{13}C NMR spectra (Table 1) of **4** and **6** completely confirmed the λ^5-phosphinine structure; only three ring carbon signals were observed, all in the sp^2 region, as expected for loss of an α-methylene proton to stabilize an initially formed siloxy phosphonium ion. For both compounds, the carbons α- and γ- to phosphorus were very strongly shielded (δ 81 and 100, respectively), quite in keeping with the presence of high electron density on these positions as called for from the delocalization (shown in resonance hybrid **8**) of the initially formed ylide.

TABLE 1

^{13}C NMR spectra of silylated monocyclic systems in $CDCl_3$



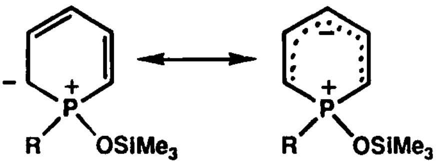


Carbon	**4**	**6**	**10**	**13**[a]	**17**[b]
2	81.0(117.6)	81.1(114.3)	72.2(117.6)	77.0(113.2)	76.2(118)
3	137.2(s)	137.9(s)	163.3(11.0)	163.6(s)	161.8(3.2)
4	100.2(25.3)	100.3(25.3)	93.3(13.2)		
5	137.2(s)	137.9(s)	138.7(4.4)	163.6(s)	161.8(3.2)
6	81.0(117.6)	81.1(114.3)	74.8(116.5)	77.0(113.2)	76.2(113.2)
7	20.3(108.8)	—[c]	20.4(109.9)	19.4(104.4)	

[a] CH_3-$C_{3,5}$ 28.1 (13.2).

[b] CH_3CH_2Si, δ 6.5 and 5.6 (both s).

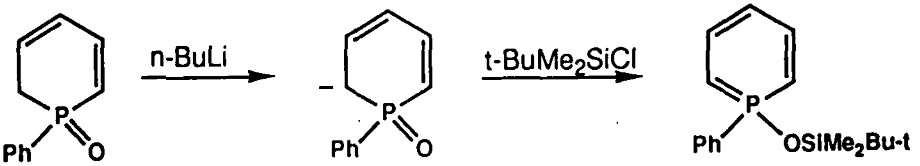
[c] Phenyl *ortho* C, 132.3 (11.0), *meta* C, 127.6 (14.3), *para* C, 130.3 (3.3).



8

The shifts were similar to those found for 1,1-dimethyl-λ^5-phosphinine[4] (α, δ 67.5; γ, δ 94.0). The β-carbons (δ 137) are in the normal sp^2 range, again as seen in the 1,1-dimethyl analog (δ 139.2).

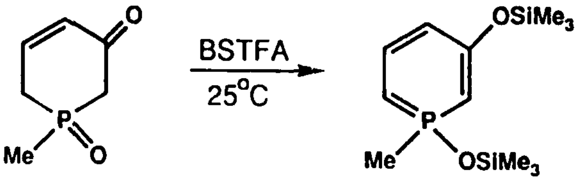
Compounds **4** and **6** were stable in chloroform solution when carefully protected from the atmosphere; attempts to isolate them resulted in hydrolysis. Even the O-*tert*-butyldimethylsilyl derivative **9**, prepared by silylation of the anion of **3**, did not lead to an adequately stabilized structure to allow isolation.



3 **9**

Silylation of a 3-Keto Tetrahydrophosphinine Oxide

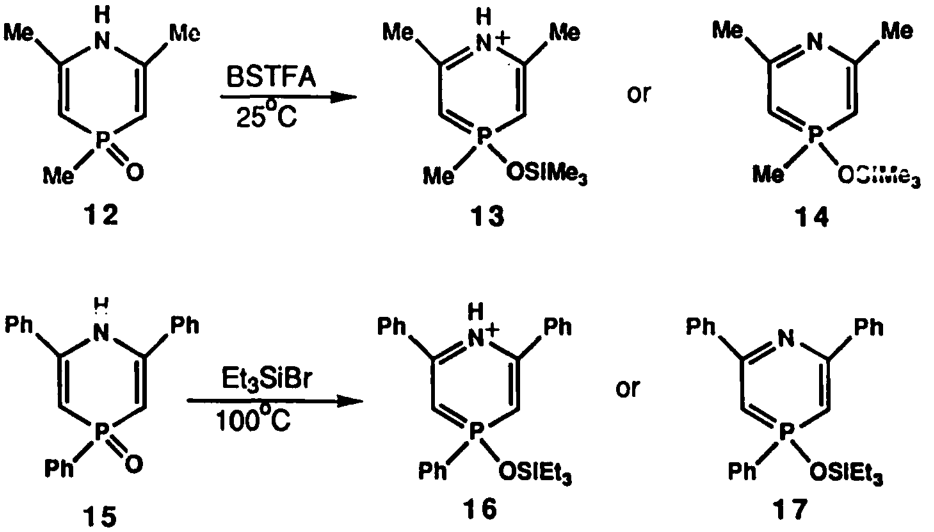
Silylation of the carbonyl oxygen of a 3-keto derivative of a tetrahydrophosphinine oxide should lead to a substituted 1,6-dihydrophosphinine, which might be expected to react further in the manner shown for **3** and **5** to form the λ^5-phosphinine system. This has been realized in the silylation of ketone **10**[5] with BSTFA. Again the reaction was rapid and quantitative, and gave a product whose ^{31}P NMR shift (+36.4) was similar to that of the unsubstituted λ^5-phosphinine **6** (+30.1). The ^{13}C NMR spectrum (Table 1) was conclusive in showing that this ring system had been established; both of the methylene carbons of **10** were converted to sp^2 carbons, and the two carbons *alpha* to phosphorus (C-2, δ 72.2; C-6, δ 74.8), as well as the γ carbon (δ 93.3), showed the expected strong upfield-shifting. It is notable that, in the bicyclic λ^5-phosphinine **2**, C-2 (δ 75.5, J = 121.1 Hz) and C-3 (δ 169.7, J = 14.6 Hz) have quite comparable ^{13}C NMR characteristics to the corresponding carbons in the monocyclic structure **11**.



10 **11**

Silylation of the 1,4-Dihydro-1,4-azaphosphinine-1-oxide System

When the silylation was applied to an aza-substituted compound (**12**), an O-silyl derivative was again formed. As before, the reaction was rapid and quantitative, and accompanied by a pronounced downfield shift of the ^{31}P NMR signal to +30.5, in the range already established for the O-silyl λ^5-phosphinines. O-Silylation of such compounds could be followed by loss of hydrogen from nitrogen to form a λ^5-azaphosphinine (**14**); we have assigned the ^{13}C NMR spectrum (Table 1) on this basis, but there is no direct proof that this event has occurred. The carbons α- to



12 **13** **14**

15 **16** **17**

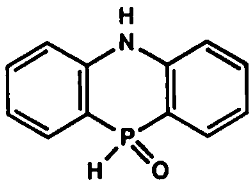
SCHEME 2

phosphorus had the characteristic upfield shift (δ 77.0, from 91.4 in the starting enamine **12**) expected for the resonance-delocalized ylide structure. The products of such silylations have a new substitution pattern for the 1,4-aza-λ^5-phosphinine system; derivatives with two alkyl or aryl groups on P have been reported,[5] but the silylation products appear to be the first of the series to have an oxygen substituent on phosphorus. Sensitivity to water has again prevented their isolation.

The silylation of 2,4,6-triphenyl-1,4-dihydro-1,4-azaphosphinine (**15**) at room temperature with BSTFA was incomplete. However, silylation could be effected with Et_3SiBr; this was carried out at 25°C for 10 min, followed by heating at 100°C in a closed tube. It was found that treatment of the initial product (presumably **16**) with BSTFA to remove protons gave a distillable product, which is presumed to be **17**.

Silylation of the 5,10-Dihydrophenophosphazine-10-oxide System

The BSTFA silylation technique was applied to representatives of the readily available[7] family of dibenzo derivatives of the 1,4-dihydro-1,4-azaphosphinine ring system, but this type of compound proved to be much more difficult to silylate. The simple conditions used for the other ring systems had no effect on the 5,10-dihydrophenophosphazine derivatives **18** and **19**.[8]



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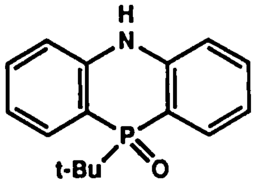

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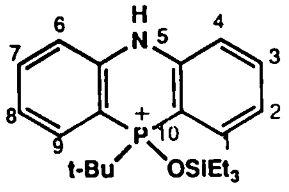

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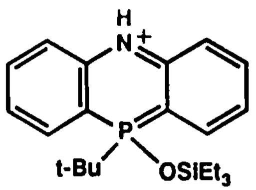
However, it was discovered that silylation of **19** could be effected with triethylsilyl bromide in CH_2Cl_2 when the reaction was conducted at room temperature and then in a closed tube at 100°C. The ^{31}P NMR shift of the product obtained from tertiary phosphine oxide **19** (with δ 31) was δ 46.5; its ^{13}C NMR spectrum was also obtained and showed a distinct difference from the spectrum of the starting oxide at the carbons attached to the P-function [in **19**, δ 107.6 (J 91.4 Hz); in **20**, δ 95.8 (J 94.7 Hz)]. In this product, loss of H from N might be retarded since the establishment of a λ^5-azaphosphinine would require disruption of the benzene resonance system. We have therefore chosen to represent the O-silylation product as **20**, rather than as **21** or **22**, but there is no experimental evidence supporting this suggestion.



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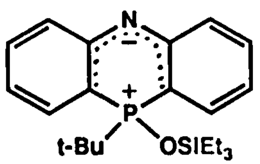
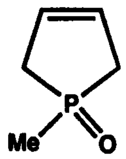


22

Silylation of 1-Methyl-3-phospholene-1-oxide

Clear evidence for the O-silylation of 1-methyl-3-phospholene-1-oxide (**23**) by Et_3SiBr at 100°C (closed tube) was obtained from the ^{31}P NMR spectrum of the reaction product. There was a pronounced downfield shift, from δ +64.6[9] to δ +101. The milder reaction with BSTFA was not effective with this heterocyclic system since no feature of the ring system could assist in stabilization of the product. The product was highly reactive and was not further characterized, but may be tentatively represented by **24**.



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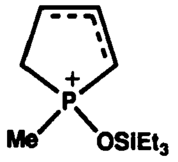

24

EXPERIMENTAL

General. Phosphorus compounds used as starting materials were available from previous studies, as follows: **3** and **5**, ref. 2; **10**, ref. 5; **12** and **15**, ref. 6; **18** and **19**, ref. 8, **23**, ref. 9. Proton-decoupled ^{31}P NMR spectra were obtained on a JEOL 90Q Spectrometer at 36.2 MHz or a Varian XL300 Spectrometer at 121.43 MHz; shifts are referenced to external 85% H_3PO_4, with positive shifts downfield. Proton-decoupled ^{13}C NMR spectra were obtained on the same instruments.

O-Silylations with BSTFA. This reagent (0.48 g, 1.86 mmol) was added to room-temperature solutions of the phosphine oxides in 0.5 mL of $CDCl_3$ as follows: **5**, 0.01 g (0.781 mmol); **3**, 0.025 g (0.132 mmol); **10**, 0.096 g (0.666 mmol); **12**, 0.0566 g (0.36 mmol). The solutions rapidly became dark brown. Their ^{13}C NMR (Table 1) and ^{31}P NMR spectra (in text) were recorded without delay as the products were sensitive to moisture.

O-Silylation with tert-Butyldimethylsilyl Chloride. Oxide **3** (0.1 g, 0.526 mmol) in 5 mL of THF at −78°C (under nitrogen) was treated with 0.3 mL of 2.6 M *n*-butyllithium in hexane. To the red solution was added 0.0793 g (0.526 mmol) of *t*-butyldimethylsilyl chloride in 1 mL of THF. The solution was allowed to warm to room temperature and then stirred for 1 hr. The solvent was evaporated and the residue of **9** taken up in $CDCl_3$ for determination of the ^{31}P NMR shift (δ +31.5).

O-Silylation with Triethylsilyl Bromide. Aza derivatives **15** (100 mg) or **19** (100 mg) were added to 10 mL of dry CH_2Cl_2 in a Schlenk tube, and treated with a 20% excess of triethylsilyl bromide. The solution was stirred for 15 min at room temperature, and then heated to 100°C in a closed tube. After a brief period (10–15 min), the solution was cooled, the solvent was evaporated, finally at 0.5 mm Hg, and the residue taken up in $CDCl_3$ for spectral measurements. The product from **19** was treated with BSTFA to scavenge protons and distilled in a Kugelrohr apparatus at about 300°C (0.5 mm Hg). ^{13}C NMR: **17** (from **15**) (Table 1), **20** (from **19**) C-1,9 (129.1, s), C-2,8 or C-4,6 (121, J = 10.1), C-3,7 (135.4, s), C-4,6 or C-2,8 (119.4, s), C-4a,5a (144.2, J = 5.7), C-9a,10a (95.8, J = 94.7), C*Me*$_3$ (23.6, s), Me_3*C* (37.4, J = 80.7), *CH*$_3$CH$_2$Si (7.0 and 7.8); ^{31}P NMR: **17**, δ +31.8; **20**, δ +46.5.

The same procedure was applied to 1-methyl-3-phospholene-1-oxide (**23**). The product was only characterized by ^{31}P NMR because of its high reactivity; δ ^{31}P ($CDCl_3$) +101.

ACKNOWLEDGEMENT

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