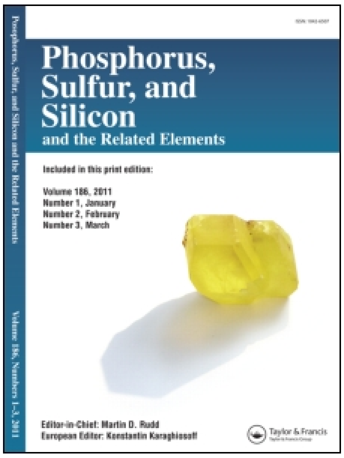

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REACTION OF (SILYLAMINO)PHOSPHINES WITH CARBON DISULFIDE[1]

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The (silylamino)phosphines $Me_3SiN(R)PMe_2$ (**1**: R = $SiMe_3$; **2**: R = Me) react smoothly with CS_2 to yield the zwitterions $Me_3SiN(R)P^+Me_2CS_2^-$ (**3**: R = $SiMe_3$; **4**: R = Me) as red solids. No cleavage of or insertion into P—N or Si—N bonds is observed in these reactions. Compound **3** reacts with MeI to yield the *S*-methylated phosphonium salt $[(Me_3Si)_2NP^+Me_2C(S)SMe]I^-$ (**5**). Upon heating, **5** readily evolves Me_3SiI to give the thioester-substituted phosphoranimine $Me_3SiN{=}PMe_2C(S)SMe$ (**6**) as a distillable red liquid.

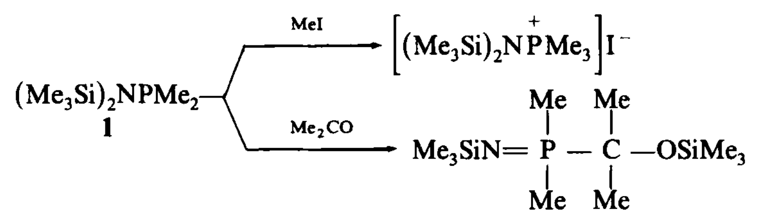
INTRODUCTION

Simple organophosphines typically react with carbon disulfide to form zwitterionic products (eq 1)[2]. With some aminophosphines, however, CS_2 and similar small molecules may insert into the P—N bond. For example, a novel, formally 7-coordinate, product has been reported by Paine and coworkers (eq 2)[3].

$$R_3P + CS_2 \rightarrow R_3\overset{+}{P}\text{—}C\begin{smallmatrix}S\\S\end{smallmatrix}^{-} \qquad (1)$$

$$(Me_2N)_3P + CS_2 \rightarrow (Me_2NCS_2)_3P \qquad (2)$$

(Silylamino)phosphines such as $(Me_3Si)_2NPMe_2$ (**1**) undergo a variety of interesting and often synthetically useful reactions with electrophilic organic reagents.[4,5] With alkyl halides, phosphonium salts (eq 3) are formed but, more commonly, Si—N bond cleavage occurs leading to rearranged products (eq 4).



(3)

(4)

In contrast to these results, we report here that neither P—N insertion nor Si—N cleavage occurs in the reactions of CS_2 with (silylamino)phosphine **1** and the related compound $Me_3SiN(Me)PMe_2$ (**2**).

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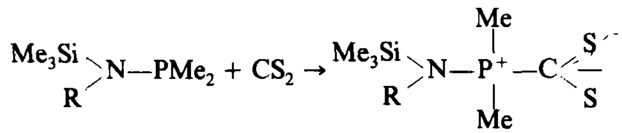
RESULTS AND DISCUSSION

When the (silylamino)phosphines **1** and **2** are treated with CS_2 at 0°C in CH_2Cl_2 solution, exothermic reactions ensue with the production of a very dark red color. When the solvent is removed, in each case, a red solid remains. These products are identified as the zwitterions **3** and **4** (eq 5) by NMR spectroscopy and by the derivative chemistry of **1** as described below. Both the ^1H and ^{13}C NMR spectra of **3** contain only a single Me_3Si resonance,

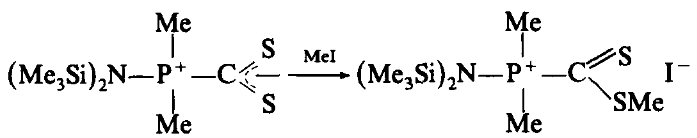
 (5)

1: R = $SiMe_3$ **3**: R = $SiMe_3$

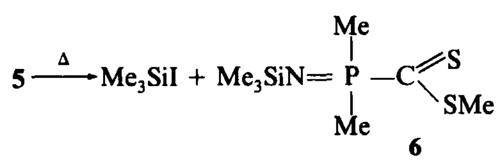
2: R = Me **4**: R = Me

indicating equivalence of the two silyl groups on nitrogen with no migration of silicon to the sulfur anion. The presence of the phosphonium-like center is confirmed by the large J_{PC} (65.4 Hz) and J_{PCH} (11.9 Hz) values observed for the PMe_2 moiety.[6] Moreover, heating these zwitterions at about 90°C under vacuum results in dissociation by the reverse of eq 5 to give the starting phosphines.

Addition of methyl iodide to a CH_2Cl_2 solution of **3** results in methylation of the sulfur anion (eq 6), yielding the phosphonium salt **5**. The SMe group gives rise to a new doublet (δ 2.85, $^4J_{PH} = 0.7$ Hz) in the ^1H NMR spectrum. After solvent removal, heating of the red solid **5** to its melting temperature (ca. 80°C) under vacuum causes elimination of Me_3SiI (eq 7). Distillation then affords the *P*-dithiomethoxycarbonyl substituted

 (6)

3 **5**

 (7)

6

phosphoranimine **6** as a red-violet liquid. Compound **6** is fully characterized by ^1H, ^{13}C, and ^{31}P NMR as well as elemental analysis. The PCS_2Me chromophore exhibits an intense λ_{max} at 358 nm in the visible spectrum.

We conclude, therefore, that the reaction of CS_2 with (silylamino)phosphines occurs via simple zwitterion formation without any accompanying P—N or Si—N bond cleavage reactions.[7] Furthermore, the MeI reaction and decomposition of the resulting phosphonium salt (eqs 6, 7) demonstrate the feasibility of preparing new thioester-functionalized organophosphorus compounds from (silylamino)phosphines.

EXPERIMENTAL

Materials and General Procedures. Reagent grade CS_2 and MeI were used as received from commercial sources. Methylene chloride was distilled from CaH_2 prior to use. (Silylamino)phosphines **1** and **2** were prepared according to the literature procedures.[6,8] Proton NMR spectra were recorded on a Varian EM-390 spectrometer; ^{13}C and ^{31}P NMR, both with ^1H decoupling, were obtained in the FT mode on a JEOL FX-60 instrument. Infrared and UV-visible spectra were obtained on Beckman IR-4250 and UV-5230 spectrophotometers, respectively. Elemental analysis was performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Preparation of Zwitterions **3** *and* **4**. In a typical experiment, phosphine **1** (ca. 15 mmol) was dissolved in CH_2Cl_2 (15 mL) in a 25-mL flask equipped with a magnetic stirrer and an adapter with a N_2 inlet side arm and a rubber septum. Carbon disulfide (15 mmol) was then added via syringe to the stirred phosphine solution at 0°C. The reaction appeared to be complete almost instantaneously. Solvent evaporation left **3** as a red solid. ^1H NMR: δ 0.41 ($SiMe_3$), 2.08 (J_{PH} = 11.9 Hz, PMe_2). ^{13}C NMR: δ 4.68 (J_{PC} = 2.0 Hz, $SiMe_3$), 17.90 (J_{PC} = 65.4 Hz, PMe_2), 242.64 (J_{PC} = 55.7 Hz, CS_2). ^{31}P NMR: δ 29.01. Compound **4** was prepared in a similar fashion. ^1H NMR: δ 0.29 ($SiMe_3$), 2.02 (J_{PH} = 12.0 Hz, PMe_2), 2.74 (J_{PH} = 13.8 Hz, NMe). ^{13}C NMR: δ 0.58 ($SiMe_3$), 13.90 (J_{PC} = 66.4 Hz, PMe_2), 32.91 (J_{PC} = 2.9 Hz, NMe), 239.56 (J_{PC} = 56.6 Hz, CS_2).

Preparation of phosphonium salt **5** *and phosphoranimine* **6**. A solution of the zwitterion **3** (15 mmol) in CH_2Cl_2 (15 mL) was prepared as described above. Methyl iodide (15 mmol) was then added via syringe to the stirred solution of **3** at 0°C. The formation of **5** in the solution was confirmed by its ^1H NMR spectrum: δ 0.44 ($SiMe_3$), 2.49 (J_{PH} = 12.5 Hz, PMe_2), 2.85 (J_{PH} = 0.7 Hz, SMe). The solvent was removed from the crude reaction mixture containing phosphonium salt **5** and the flask was attached to a fractional distillation assembly. Upon heating the flask to ca. 80°C, the solid material liquified and compound **6** distilled as a red-violet liquid (bp 48–49°C/0.01 mm, 59% yield). ^1H NMR: δ 0.01 (J_{PH} = 0.4 Hz, $SiMe_3$), 1.61 (J_{PH} = 12.9 Hz, PMe_2), 2.60 (J_{PH} = 0.9 Hz, SMe). ^{13}C NMR: δ 3.22 (J_{PC} = 2.9 Hz, $SiMe_3$), 19.10 (J_{PC} = 74.2 Hz, PMe_2), 19.30 (SMe), 245.96 (J_{PC} = 69.3 Hz, CS_2). ^{31}P NMR: δ 10.54. IR (cm^{-1}): 2960s, 2947s, 2913s, 2898m, 1400s, 1350–1230 vs, br, 1080s, 940s, 918s, 862s, 851s, 830s, 817s, 748s, 730s, 675s, 642m, 563w, 493m, 477m, 358s, 345s. UV-visible (nm): 358vs, 542w, 529w. Anal. Calcd: C 35.12; H, 7.58. Found: C, 35.29; H. 7.76. Samples of **6** which were cooled to −196°C and then warmed to room temperature contained a yellowish precipitate (presumably sulfur).

ACKNOWLEDGMENT

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REFERENCES AND NOTES

1. Taken in part from: D. W. Morton, Ph.D. Dissertation, Texas Christian University, Fort Worth, TX 1981.
2. J. Emsley and D. Hall, "The Chemistry of Phosphorus", Halsted Press: New York, 1976.
3. R. W. Light, L. D. Hutchins, R. T. Paine, and C. F. Campana, *Inorg. Chem.*, **19**, 3597 (1980).
4. D. W. Morton and R. H. Neilson, *Organometallics*, **1**, 289 (1982).
5. D. W. Morton and R. H. Neilson, *Organometallics*, **1**, 623 (1982).
6. J. C. Wilburn and R. H. Neilson, *Inorg. Chem.*, **18**, 347 (1979).
7. An analogous compound, $(Me_3Si)_2NPH_2CS_2$, has been reported but little characterization data was given. E. Niecke and R. Ruger, *Angew, Chem., Int. Ed. Engl.* **21**, 62 (1982).
8. R. H. Neilson and P. Wisian-Neilson, *Inorg. Chem.*, **21**, 3568 (1982).