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Attempted 1,3-Trimethylsilyl Migration in $Me_3Si-P=S=N-R$ System

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ABSTRACT

A dimer of thioxo-N-t-butylimino(trimethylsiloxy)-phosphorane **5** *has been prepared by reaction of tris(trimethylsilyl)phosphine with N-sulfinyl-N-tert-butylamine. The structure of* **5** *has been confirmed by X-ray analysis data. 1-Aza-2-thia-3-phosphaallene* **1**, *thiaphosphaziridine* **3**, *iminophosphine P-sulfide* **4** *are postulated as intermediates of the reaction studied.*

INTRODUCTION

1,3-Trimethylsilyl migration is widely used nowadays for the formation of $-\mathrm{P}=\mathrm{C}<$ and $-\mathrm{P}=\mathrm{S}<$ double bonds [1, 2]. The fact of the matter is that a silyl function at a phosphorus atom tends usually to migrate from it to such elements as N, O, or S, provided that they are double-bonded to the vicinal α-carbon (α-sulfur) atom at phosphorus. Such a migration, in its turn, results in the formation of an energetically more favourable $-\mathrm{P}=\mathrm{C}<$ ($-\mathrm{P}=\mathrm{S}<$) bond together with a strong Si-element bond.

Appel *et al.* [3] appeared to be the first who succeeded in making use of 1,3-migration of a Me_3Si-group in P-trimethylsilyl-1-aza-3-phosphaallene to synthesize N-substituted one-coordinated phosphorus compounds.

By analogy, we expected the similar 1,3-migration of the Me_3Si-group in 1-aza-2-thia-3-phosphaallene **1**, for the synthesis of which we have carried out a condensation of tris(trimethylsilyl)-phosphine with N-sulfinyl-tert-butylamine.

RESULTS AND DISCUSSION

As far as we can gather, the reaction that actually occurred involves 3 steps. The first step is the combination of the starting reagents with elimination of hexamethyldisiloxane to yield 1-aza-2-thia-3-phosphaallene **1**, the Me_3Si-group of which does not migrate, however, from the phosphorus to the nitrogen atom. The second step is the isomerization of **1** into the iminophosphine P-sulfide **4**. Therefore, the reduction of the atom S^{IV} to atom S^{II} in **1** seems to be energetically more favored than the process of 1,3-trimethylsilyl migration from the phosphorus to the nitrogen atom. The last step is the oxidation of the dimer **4** by N-sulfinyl-tert-butylamine with the formation of **5**. When the starting materials were taken in the ratio of 1:1 they did not react in THF solution at room temperature. However they did react at the reflux temperature; the progress of reaction could be monitored by ^{31}P-NMR spectroscopy. However, nearly 0.5 mole of the starting tris(trimethylsilyl)phosphine, according to the ^{31}P-NMR spectra, was found not to have taken part in the reaction. Complete conversion of tris(trimethylsilyl)phosphine into **5** required the ratio of $(Me_3Si)_3P$ to $^tBu-N=S=O$ to be 1:2. In this case, the process of the elimination was shown to be the limiting step of the reaction, while the oxidation step proceeds more quickly than the elimination one. Moreover, the course of the reaction seems to be similar to that of the reaction between N-sulfinyl-2,4-di-tert-butyl-6-methylaniline and lithium (tert-butyl-dimethyl-

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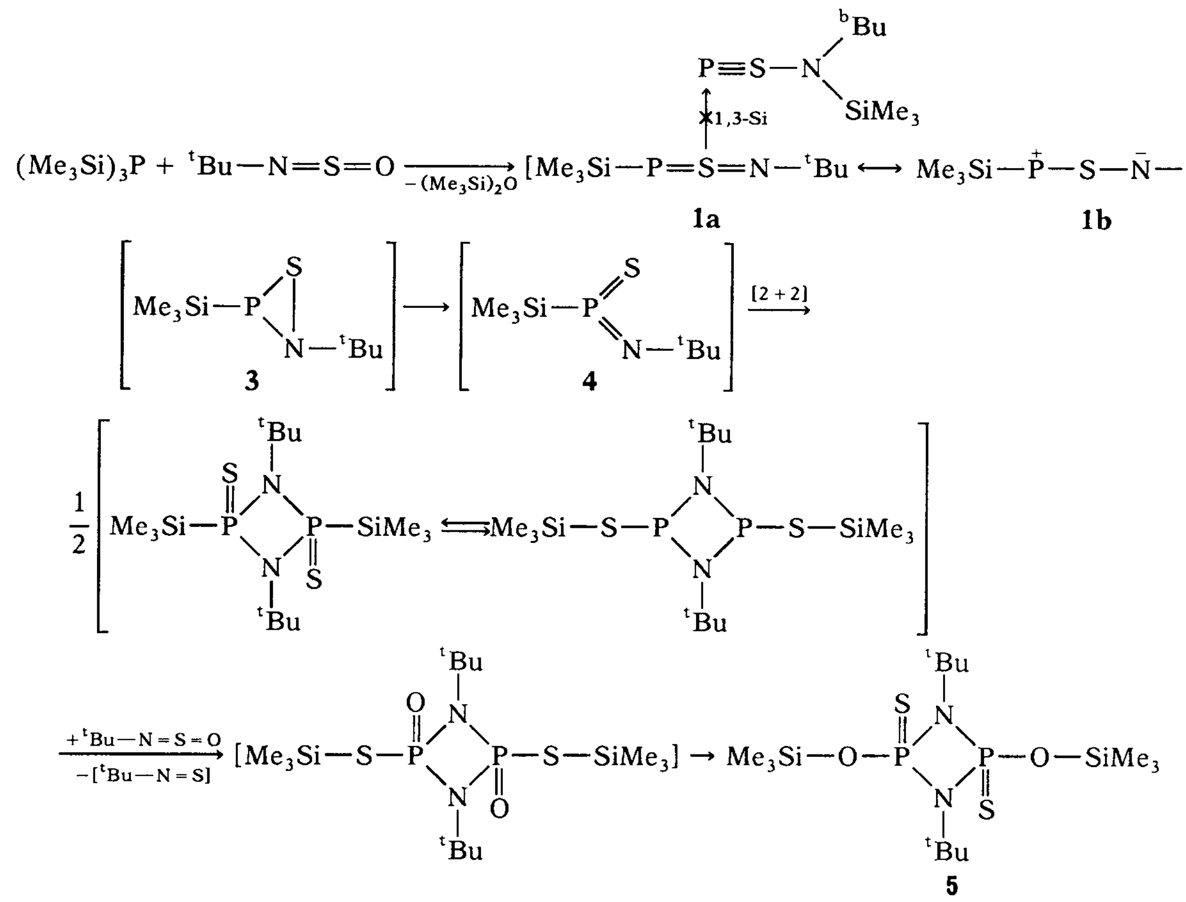


FIGURE 1

silyl) (2,4,6-tri-tert-butylphenyl) phosphide [4]. By analogy with the reaction described in [4], **1** can be considered to be a phosphorus-containing 1,3-dipole **2**, which undergoes intramolecular cyclization to yield thiaphosphaziridine **3**, a reopening of the three-membered ring of which leads to the iminophosphine P-sulfide **4**. Unlike the similar iminophosphine P-sulfide described by Yoshifuji *et al.* [4] that is stabilized by sterically large groups, the intermediate **4** is not sterically protected enough and undergoes dimerization. The dimer **4**, as shown in the Scheme, is oxidized by excess N-sulfinyl-tert-butylamine to give a dimer of thioxo-N-t-butylimino(trimethylsiloxy)phosphorane **5**.

The structure of **5** is in agreement with the results of its elemental and X-ray analyses, and ^{31}P-NMR spectroscopy. Thus, the only signal with a chemical shift δ_P of 45.8 in the ^{31}P-NMR spectrum of 5 is characteristic of compounds containing the 2,4-dithioxo-1,3,2-λ^5, 4λ^5-diazadiphospetidine ring [5].

EXPERIMENTAL

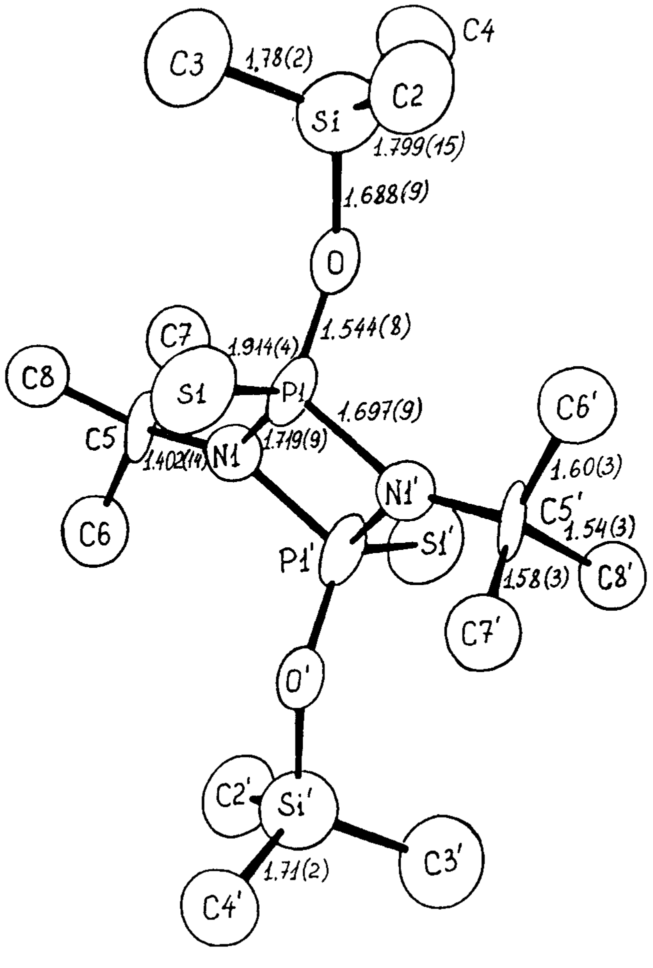
^{31}P-NMR spectra were recorded with a "Bruker M-250" instrument. All experiments were carried out under dry argon in anhydrous THF.

Reaction of Tris(trimethylsilyl)phosphine with N-sulfinyl-tert-butylamine

A mixture of 6.39 g (0.023 mol) of tris(trimethylsilyl)phosphine and 3.04 g (0.025 mol) of N-sulfinyl-N-tert-butylamine [6] in THF (15 ml) was heated at reflux for 3 hours. Since almost half of the taken amount of the starting phosphine had been found unchanged (according to ^{31}P NMR spectroscopy), heating was extended for 3 hours more. The other portion (3.04 g; 0.025 mol) of N-sulfinyl-N-tert-butylamine was then added, and the reaction mixture was boiled for an additional hour. The subsequent distillation of the reaction mixture gave **5** (3.7 g; 65%): b.p. 148–150°C/10^{-4} mm, m.p. 162–164°C. Found C 37.52, H 8.06, N 6.03, P 13.56, S 14.06%. $C_{14}H_{36}N_2O_2P_2S_2Si_2$ requires C 37.66, H 8.07, P 13.90, N 6.27, S 14.34%.

X-ray Structure Determination of 5

A suitable crystal of **5** was obtained by slow recrystallization from benzene. Data were collected at 20 ∓ 2^0 on an Enraf-Nonius CAD-4 diffractometer. The crystal structure was solved and refined using the Enraf-Nonius supplied SDP package. The compound crystallized in the space group $P2_{1/2}$, $a =$



SCHEME 1

9.927(9), b = 12.08(1), c = 10.32(1) Å, β = 93.99(8)°. V = 1235(5) Å^3, Z = 2, D_{calc} = 1.20 g/cm^{-3}, MoK$_\alpha$ radiation (λ = 0.71073 Å) graphite monochromator, μ = 4.40 cm^{-1}, F/000/ = 480. A total of 2304 unique reflections were recorded in the range 3° < $2\theta \le 50°$, of which 544 were considered as observed ($F^2 \ge 3\sigma$). The structure was solved by a direct method. The tert-butyl group is disordered by two positions. Atom $C^6 \div C^8$ was refined isotropically with occupations 2/3, $C^{6.1} \div C^{8.1}$ – 1/3. All other atoms were refined anisotropically. The hydrogen atoms of the SiMe$_3$-group where placed in the calculated positions with B_{iso} = 4 Å^2 and not refined. A non-Poisson weighting scheme was applied with a p-factor equal to 0.07.

The final R factors were R = 0.095, R_w = 0.123, GOF = 2.66.

Supplementary Material Available

Expanded Tables of bond distances, bond angles, refined displacement parameter expressions, positional parameters, and 10 × F_{abs} plus F_{calc}. Ordering information is available from the authors.

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