Heteroatom Chemistry
Volume 17, Number 7, 2006

Synthesis and Thermal Stability of *S*-Trimethylsilyl Esters of Tetracoordinated Phosphorus Amidothioacids

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Received 22 January 2006

ABSTRACT: *S-(Diethylamino)dimethylsilyl bis-(diethylamido)dithiophosphate* **3** *was obtained by the reaction of tetraphosphorus decasulfide* **1** *with bis-(diethylamino)dimethylsilane* **2a**. *The reactions of Lawesson's reagent* **5** *with* **2a** *and the alkyl homologues of Davy's reagent* **8a,b** *with trimethyl-(diethylamino)silane* **6** *were studied. On the basis of these reactions, methods of synthesizing S-(diethylamino)dimethylsilyl or S-(diethylamino)-diphenylsilyl 4-methoxyphenyl (diethylamido)dithiophosphonates* **7a** *and* **7b** *and S-trimethylsilyl S-alkyl(diethylamido)trithiophosphates* **9a,b** *are described. The optimal reaction conditions and thermal stability of S-trimethylsilyl S-ethyl-(diethylamido)trithiophosphate* **9a** *were defined by differential thermal analyses. Compound* **9a** *have been decomposed to form 2,4-bis(diethylamido)-1,3,2,4-dithiadiphosphetane-2,4-disulfide* **10** *which structure was established by X-ray single crystal diffraction.* © 2006 Wiley Periodicals, Inc. Heteroatom Chem 17:670–675, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20231

INTRODUCTION

Over the past few years, we have been involved in the development of methods of synthesizing *S*-silyl esters of tetracoordinated phosphorus thioacids on the basis of tetraphosphorus decasulfide **1** and 1,3,2,4-dithiadiphosphetane-2,4-disulfides [1–8]. Silanes containing only one dialkylamino group have been reported to react with **1** [9] and 2,4-bis(diethylamido)-1,3,2,4-dithiadiphosphetane-2,4-disulfide **10** [4] to give *S*-silyl diamidodithiophosphates. However, the chemical behavior of silanes containing a few dialkylamino groups remained unknown in the similar reactions. In this article, reactions of **1** and 1,3,2,4-dithiadiphosphetane-2,4-disulfides with diaminosilanes are presented. The thermal stability of *S*-silyl amidotrithiophosphates is defined. The formation and molecular and crystal structure of **10** are described.

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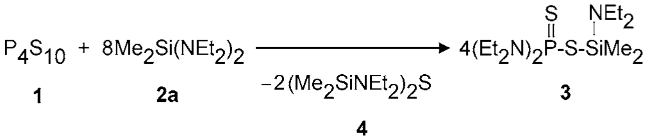
RESULTS AND DISCUSSION

Taking into account the rather high reactivity of aminosilanes [4,9], the formation of the mixtures of monophosphorylated and diphosphorylated silanes could be expected by the use of diaminosilanes in the reaction with **1**. To avoid the formation of the mixtures of organophosphorus products in this reaction, we have defined the optimal conditions of the formation of a monophosphorylated product by differential thermal analysis. It was found that **1** starts to react with bis(diethylamino)dimethylsilane **2a** at 40°C (Table 1). The reaction of 1 with 2a at 40°C for 2 h in CH_2Cl_2 suspension proceeds via the rupture of only one of the N—Si bonds and with the formation of S-(diethylamino)dimethylsilyl bis(diethylamido)dithiophosphate 3 (reaction 1, Tables 2–6).



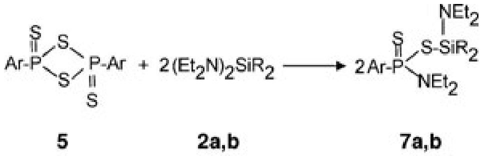
$$\underset{\mathbf{1}}{P_4S_{10}} + \underset{\mathbf{2a}}{8Me_2Si(NEt_2)_2} \xrightarrow[-2(Me_2SiNEt_2)_2S\ (\mathbf{4})]{} \underset{\mathbf{3}}{4(Et_2N)_2\overset{S}{\overset{\|}{P}}\text{-}S\text{-}\overset{NEt_2}{\overset{|}{Si}}Me_2} \qquad (1)$$

In reaction 1, bis(diethylaminodimethylsilyl)-sulfide **4** is formed. It is noteworthy that the ^{31}P resonance of **3** (Table 3) appears in practically the same region as that of *S*-trimethylsilyl bis(diethylamido)dithiophosphate (δ = 83.6 [9]). Both compounds have the same $N_2P(S)S$—Si fragment. The ^1H NMR spectrum of **3** (Table 5) shows two triplets of the methyl protons of the $(CH_3CH_2)_2N$—Si and $[(CH_3CH_2)_2N]_2P$ groups. The chemical ionization spectrum of **3** (Table 6) exhibits the mass peak *m/e* 370 because of its molecular ion $[M + H]^+$.

It is considered of interest to compare the reactivity of silanes containing one and two dialkylamino groups at the silicon atom toward 1,3,2,4-dithiadiphosphetane-2,4-disulfides. We have shown that **2a** is more reactive than that of trimethyl(diethylamino)silane (**6**) in the reaction with Lawesson's reagent **5** (Table 1). The reaction of **5** with **2a** and bis(diethylamino)diphenylsilane **2b** at 20°C for 1–2 h (in CH_2Cl_2 suspension or with no solvent) has been found to bring about the formation of *S*-(diethylamino)dimethylsilyl or *S*-(diethylamino)diphenylsilyl 4-methoxyphenyl(diethylamido)dithiophosphonates **7a** and **7b**, respectively (reaction 2, Tables 2–6).

TABLE 1 Differential Thermal Analysis Data of the Reaction Mixtures; Temperature of the Initial of the Thermal Effect (°C)

1 + **2a**	40
5 + **6**	32
5 + **2a**	10



(2)

Ar = 4-MeOC$_6$H$_4$; R = Me (**2a, 7a**), Ph (**2b, 7b**)

Compounds **7a** and **7b** were isolated in 72% yields. Product **7a** is a colorless crystalline solid. Liquid **7b** was purified by means of a falling-film distillation. The ^{31}P chemical shift values of *S*-dimethylsilyl containing **7a** is shifted to high field ($\delta = 86.9$) with respect to that its diphenylsilyl homologue **7b** ($\delta = 73.0$). The ^1H NMR spectrum of **7a** in CD_3CN solution (Table 5) reveals a triplet at $\delta = 1.24$ for the methyl protons of the $(CH_3CH_2)_2N$—Si group. This resonance is shifted toward high field in comparison with the similar protons of the same group of **3**. The electron impact mass spectra of **7a** and **7b** (Table 6) show the mass peaks *m/e* 404 and 528 of their molecular ions $[M]^{+\bullet}$, respectively.

In continuation of our study, we have managed to involve other 1,3,2,4-dithiadiphosphetane-2,4-disulfides, for example, the alkyl homologues of Davy's reagent **8a**,**b**, in the reaction with monoaminosilane **6** at 50°C for 9 h (reaction 3, Tables 2–6).

(3)

R = Et (**8a, 9a**), Bu-*i* (**8b, 9b**)

S-Trimethylsilyl *S*-alkyl(diethylamido)trithiophosphates **9a,b** containing mixed alkylthio- and dialkylamido substituents were obtained in this reaction as depicted in reaction 3. All of the compounds **9a,b** were purified by use of a falling-film distillations. The ^{31}P resonances of **9a,b** ($\delta = 83$–84) appear in practically the same region as that for *S*-silyl diamidodithiophosphate **3** ($\delta = 83.1$, Table 3). The methylene protons of the two ethyl substituents of the $(CH_3CH_2)_2NP$ group of **9a** in CCl_4 solution (Table 5) resonate as a doublet of quartets. The mass peaks *m/e* 301 in the electron impact mass spectrum of **9a** (Table 6) is due to its molecular ion $[M]^{+\bullet}$.

TABLE 2 Experimental Data and Yields of the Products Obtained

Initial Compounds Quantity (g (mmol))	*Reaction Conditions* *Temperature (°C)/ Time (h)*		*Product Yield (g (%))*
1: 4.2 (9.5); **2a**: 15.4 (76.1)	40/2.5	10 mL CH_2Cl_2	**3**: 5.6 (40)[b]
5: 3.5 (8.7); **2a**: 3.5 (17.3)	20/2	10 mL CH_2Cl_2	**7a**: 3.4 (49)[c]
5: 3.0 (7.4); **2b**: 4.9 (15.0)	20/1		**7b**: 5.6 (72)[a]
8a: 22.2 (71.6); **6**: 20.8 (143.3)	50/9		**9a**: 21.3 (49)[b]
8b: 15.8 (42.9); **6**: 12.5 (86.4)	80/10		**9b**: 4.4 (16)[b]

[a] Yield of crude product.
[b] Yield of product isolated by a falling-film distillation.
[c] Yield of crystalline product.

TABLE 3 Physical, Analytical, and ^{31}P NMR Data of the Products Obtained

	n_D^{20}	d_4^{20}	*B.p., °C (mmHg)*[a]	*Molecular Formula (molecular mass)*	*Found/Calcd (%)* *P*	 *S*	 *Si*	*^{31}P NMR, δ (Solvent)*
3	1.5021		160 (0.05)	$C_{14}H_{36}N_3PS_2Si$ (369.3)	8.81/8.39	17.56/17.32	7.94/7.58	83.1 (C_6H_6)
7a			88–89[b]	$C_{17}H_{33}N_2OPS_2Si$ (404.2)	7.53/7.66	15.54/15.82	6.79/6.92	86.9 (MeCN)
7b	1.5325		100 (0.06)	$C_{27}H_{37}N_2OPS_2Si$ (528.3)	5.40/5.86	11.92/12.10	4.87/5.30	73.0 (C_6H_6)
9a	1.5478	1.0639	100 (0.02)	$C_9H_{24}NPS_3Si$ (301.1)	10.59/10.29	32.10/31.85	9.44/9.29	83.3 (CCl_4)
9b	1.5483	1.0133	120 (0.02)	$C_{11}H_{18}NPS_3Si$ (319.0)	10.10/9.71	30.16/30.06	9.57/8.77	84.1 (C_6H_6)

[a] Temperature of thermal element of a falling-film distillation.
[b] M.p.

TABLE 4 IR Data of the Products Obtained (ν, cm^{-1})

3	2980, 2831 $\nu(CH_3$ as, s; CH_2 as, s), $\nu[CH_3(Si)$ s]; 1450, 1480, 1379 $\delta(CH_3$ as); 1254 $\delta[CH_3(Si)$ s]; 1030 ν(C—N—C as); 934 ν(C—C); 825 $\rho[CH_3(Si)]$; 713 ν(P=S); 623, 613, 530, 490, 455 ν(P—S, S—Si)
7a[a]	3090, 3070, 3030 ν(=C—H, Ar); 2970, 2934, 2881, 2840, 2810 $\nu(CH_3$ as, s; CH_2 as, s), $\nu[CH_3(Si)$ s]; 1596, 1498, 1464 ν(C=C, Ar); 1440, 1379 $\delta(CH_3$ as); 1257 $\delta[CH_3(Si)$ s]; 1032 ν(C—N—C as); 933 ν(C—C); 838 $\rho[CH_3(Si)]$; 704 ν(P=S); 610, 535, 523, 445 ν(P—S, S—Si)
7b	3070, 3050, 3010, 3000 ν(=C—H, Ar); 2970, 2935, 2870, 2840 $\nu(CH_3$ as, s; CH_2 as, s), $\nu[CH_3(Si)$ s]; 1590, 1495, 1460 ν(C=C, Ar); 1430, 1380 $\delta(CH_3$ as); 1260 $\delta[CH_3(Si)$ s]; 1032 ν(C—N—C as); 940 ν(C—C); 838 $\rho[CH_3(Si)]$; 697 ν(P=S); 610, 570, 535, 505, 485 ν(P—S, S—Si)
9a	2980, 2935, 2880, 2815 $\nu[CH_3(Si)$ s], $\nu(CH_3$ as, s; CH_2 as, s); 1455 $\delta(CH_3$ as); 1385 $\delta(CH_3$ as); 1260 $\delta[CH_3(Si)$ s]; 1025 ν(C—N—C as); 855 $\rho[CH_3(Si)]$; 665 ν(P=S); 560, 555, 515 ν(P—SC, S—Si)
9b	2965, 2940, 2900, 2875 $\nu[CH_3(Si)$ s], $\nu(CH_3$ as, s; CH_2 as, s); 1465 $\delta(CH_3$ as); 1383, 1370 $\delta[(CH_3)_2C$ gem s]; 1255 $\delta[CH_3(Si)$ s]; 1025 ν(C—N—C as); 855 $\rho[CH_3(Si)]$; 685 ν(P=S); 565, 525 ν(P—SC, S—Si)

[a] In vaseline oil.

TABLE 5 ^1H NMR Data of the Products Obtained (δ, J (Hz), in CCl_4)

3[a]	0.12 (s, 6H, $(\underline{CH_3})_2Si$); 1.00 (t, 6H, $(\underline{CH_3}CH_2)_2NSi$, $^3J_{HH} = 7.0$); 1.19 (t, 12H, $[(\underline{CH_3}CH_2)_2N]_2P$, $^3J_{HH} = 7.0$); 2.81 (q, 4H, $(CH_3\underline{CH_2})_2NSi$, $^3J_{HH} = 7.0$); 3.24 (d, q, 8H, $[(CH_3\underline{CH_2})_2NP$, $^3J_{HH} = 7.0$, $^3J_{PH} = 13.0$)
7a[b]	0.03 (s, 6H, $(\underline{CH_3})_2Si$); 0.97 (t, 6H, $(\underline{CH_3}CH_2)_2NP$, $^3J_{HH} = 6.8$); 1.24 (t, 6H, $(\underline{CH_3}CH_2)_2NSi$, $^3J_{HH} = 6.8$); 2.95 (q, 4H, $(CH_3\underline{CH_2})_2NSi$, $^3J_{HH} = 6.8$); 3.14 (d, q, 4H, $(CH_3\underline{CH_2})_2NP$, $^3J_{HH} = 6.8$, $^3J_{PH} = 12.9$); 6.86 (d, d, 2H, 3,5-H_2C_6 ${}_2\underline{H}$ $^3J_{HH} = 9.1$, $^4J_{PH} = 1.5$); 7.99 (d, d, 2,6-$\underline{H_2}C_6H_2$, $^3J_{HH} = 9.1$, $^3J_{PH} = 13.0$)
7b[a]	1.13 (t, 6H, $(\underline{CH_3}CH_2)_2NP$, $^3J_{HH} = 7.0$); 1.24 (t, 6H, $(\underline{CH_3}CH_2)$ N_2Si, $^3J_{HH} = 7.0$); 3.00 (q, 4H, $(CH_3\underline{CH_2})_2NSi$, $^3J_{HH} = 7.0$,); 3.08 (d, q, 4H, $(CH_3\underline{CH_2})_2NP$, $J_{HH} = 7.0$, $^3J_{PH} = 15.0$); 6.78 (d, d, 3,5-$H_2C_6\underline{H_2}$, $^3J_{HH} = 9.0$, $^4J_{PH} = 3.0$); 7.11–7.45 and 7.53–7.92 (m, m, 10H, $(C_6\underline{H_5})Si$); 8.08 (d, d, 2H, 2,6-$\underline{H_2}C_6H_2$, $^3J_{HH} = 9.0$, $^3J_{PH} = 13.0$)
9a	0.53 (s, 9H, $(\underline{CH_3})_3Si$); 1.17 (t, 6H, $(\underline{CH_3}CH_2)_2NP$, $^3J_{HH} = 7.0$); 1.40 (t, 3H, $\underline{CH_3}CH_2S$, $^3J_{HH} = 7.5$); 2.95 (d, q, 2H, $CH_3\underline{CH_2}SP$, $^3J_{HH} = 7.5$, $^3J_{PH} = 15.0$); 3.36 (d, q, 4H, $(CH_3\underline{CH_2})_2NP$, $^3J_{HH} = 7.0$, $^3J_{PH} = 14.0$)
9b	0.56 (s, 9H, $(\underline{CH_3})_3Si$); 1.06 (t, 6H, $(\underline{CH_3})_2CHCH_2S$, $^3J_{HH} = 7.0$); 1.17 (t, 6H, $(\underline{CH_3}CH_2)_2NP$, $^3J_{HH} = 7.0$); 2.82 (d, d, 2H, $(CH_2)_2CH\underline{CH_2}SP$, $^3J_{HH} = 7.0$, $^3J_{PH} = 15.0$); 3.42 (d, q, 4H, $(CH_3\underline{CH_2})_2NP$, $^3J_{HH} = 7.0$, $^3J_{PH} = 14.0$)

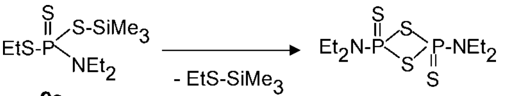
[a] In $CDCl_3$.
[b] In CD_3CN.

TABLE 6 Mass Spectral Data of the Products Obtained; i-C_4H_{10}, m/e (I_{rel}, %)

3[a]	354 $[M-Me]^{+\bullet}$ (1); 297 $[M-NEt_2]^{+\bullet}$ (20)
3[b]	371 $[M+2H]^{+}$ (1); 341 $[M+H-Et]^{+}$ (2)
7a[a]	404 $[M]^{+\bullet}$ (1)
7a[b]	348 $[M+2H-2Et]^{+}$ (13); 261 $[M+H-2NEt_2]^{+}$ (10)
7b[a]	528 $[M]^{+\bullet}$ (3); 496 $[M-S]^{+\bullet}$ (2)
7b[b]	459 $[M+3H-NEt_2]^{+}$ (1); 275 $[M+H-Si(NEt_2)Ph_2]^{+}$ (2)
9a[a]	301 $[M]^{+\bullet}$ (10); 269 $[M-S]^{+\bullet}$ (10)
9a[b]	274 $[M+2H-Et]^{+}$ (22); 241 $[M+H-Et-S]^{+}$ (50)
9b[a]	274 $[M-3Me]^{+\bullet}$ (75), 242 $[M-3Me-S]^{+\bullet}$ (72)
9b[b]	259 $[M+H-Et-S]^{+}$ (10)

[a] Electron impact, 70 eV.
[b] Chemical ionization, 100 eV.

S-Trimethylsilyl diamidodithiophosphates have been reported to be rather thermal unstable substances [9]. They undergo transformations into bis(diamidothiophosphoryl)sulfides and bis (trimethylsilyl)sulfide by heating or in prolonged storing at room temperature. Therefore, it is considered of interest to study thermal stability of *S*-silyl amidotrithiophosphates **9** containing the $RS(R_2N)P(S)S$—Si structural fragment by differential thermal analysis. It was found that **9a** starts to decompose at 99°C. Nevertheless, we have shown that **9a** have partially been decomposed even at room temperature for 6 months to form crystalline 2,4-bis(diethylamido)-1,3,2,4-dithiadiphosphetane-2,4-disulfide **10** (reaction 4). Trimethyl(ethylthio)silane **11** was also obtained in reaction 4. The physical and spectral data of **10** were identical with literature ones [4].



9a **11** **10** (4)

It should be noted that 1,3,2,4-dithiadiphosphetane-2,4-disulfides containing the dialkylamido groups on the phosphorus atom have remained little known. Thus, the first representative of these compounds, namely 2,4-bis(dimethylamido)-1,3,2,4-dithiadiphosphetane-2,4-disulfide **12**, was earlier obtained by the reaction of tetraphosphorus trisulfide (P_4S_3) with thiobis(diethylamine) [10]. The crystal and molecular structure of **12** was previously studied [10]. It was interest to elucidate how the length of alkyl substituents on the nitrogen atom affect on the structural parameters of 2,4-bis(dialkylamido)-1,3,2,4-dithiadiphosphetane-2,4-disulfides. That is why we decided to study the molecular and crystal structure of **10** by X-ray single crystal diffraction (Table 7, Fig. 1). It was found that **10** was crystallized in trans-configuration. The comparative P—S and P═S bond lengths and S—P—S and P—S—P bond angles of **10** and its dimethylamido analogue **12** are listed in Table 7. Inspection of Table 7 proves that when the Me_2N-group was exchanged with the Et_2N-group, the P—S and P═S bond distances were decreased from 2.122(1) to 2.1081(12) Å (P—S) and from 1.926(1) to 1.9207(11) Å (P═S). It is noteworthy that the S—P—S bond angle is decreased (from 93.14(3) to 92.76(3)°) while the P—S—P bond angle is increased (from 86.86(3) to 87.24(3)°). Thus, when the size of alkyl substituents on the nitrogen atom is increased, the endocyclic angles magnitudes of dithiadiphosphetane ring posses a tendency to equalize. It seems to lead to the increasing

TABLE 7 Selected Bond Lengths (Å) and Bond Angles (°)

	10	**12**[a]
S(2)—P(1)	2.1081(12)	2.122(1)
S(2)—P(1)	2.1389(10)	2.122(1)
P(1)—N(1)	1.635(2)	1.633(3)
P(1)—S(1)	1.9207(11)	1.926(1)
N(1)—C(3)	1.465(4)	
N(1)—C(1)	1.493(3)	
C(1)—C(2)	1.511(4)	
C(3)—C(4)	1.470(4)	
P(1)—S(2)—P(1)	87.24(3)	86.86(3)
N(1)—P(1)—S(1)	114.13(9)	
N(1)—P(1)—S(2)	107.10(9)	
S(1)—P(1)—S(2)	116.96(4)	
N(1)—P(1)—S(2)	110.56(9)	
S(1)—P(1)—S(2)	113.32(5)	
S(2)—P(1)—S(2)	92.76(3)	93.14(3)
C(3)—N(1)—C(1)	115.2(2)	
C(3)—N(1)—P(1)	121.48(18)	
C(1)—N(1)—P(1)	120.21(18)	
N(1)—C(1)—C(2)	111.0(2)	
N(1)—C(3)—C(4)	115.1(2)	

[a] Data from [10].

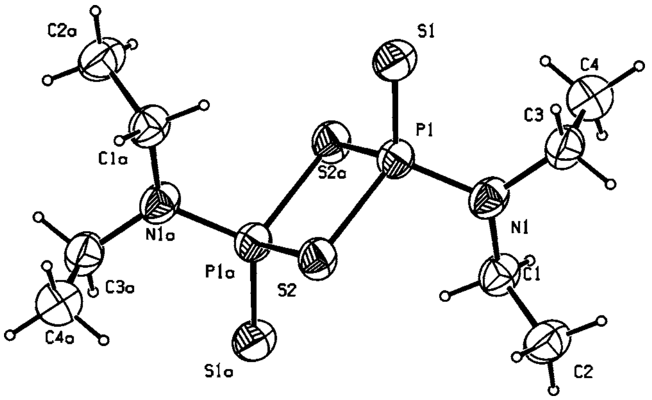


FIGURE 1 Molecular structure of **10**.

of torsion strain of plane four-member ring of 2,4-bis(dialkylamido)-1,3,2,4-dithiadiphosphetane-2,4-disulfides.

EXPERIMENTAL

General Data

The ^{31}P NMR spectra were recorded with a Bruker CXP-100 (36.47 MHz) instrument in CCl_4, C_6H_6, and MeCN with 85% H_3PO_4 as an external reference. The ^{1}H NMR spectra were taken on a Bruker WM-250 (250 MHz) spectrometer and a Varian T-60 (60 MHz) spectrometer in CCl_4, $CDCl_3$, or CD_3CN with $(Me_3Si)_2O$ as an internal reference. The IR spectra were obtained in KBr pellets with a Bruker Vector-22 infrared spectrophotometer. Mass spectra (EI, 70 eV; CI, 100 eV) were determined on an M 80 B Hitachi chromatomass spectrometer. Differential thermal analyses were performed on a Setaram thermoanalyzer TG, DTG, DTA equipped with nonserial heating furnace employing the DTA rate.

X-ray Crystallography

Cell parameters and intensities of 1763 independent reflections (1521 with $I \geq 2\ \sigma$) of crystal of **10** were measured on an Enraf-Nonius CAD-4 four-circle diffractometer at −129°C with graphite monochromatized Mo Kα radiation, $\lambda = 0.71073$ Å, employing the $\omega/2\Theta$ technique, $\Theta \leq 26.26°$. Data were corrected for the absorption effect (μMo 8.12 cm^{-1}). The structure was solved by a direct method using the SIR program [11] and refined by the full-matrix least-squares using SHELXL97 program [12]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated position with thermal parameters 30% larger than the atom to which they attached. The final residuals were $R = 0.048$, $R_w = 0.083$ for 1212 reflections with $F^2 > 2\sigma(I)$. Crystal data for **10**: $C_{12}H_{30}N_2P_2S_4$ monoclinic, space group $P2_1/n$, $a = 7.940(2)$ Å, $b = 12.435(4)$ Å, $c = 7.970(3)$ Å, $\beta = 100.40(2)°$, $V = 774.0(4)$ Å^3, $d_{calc} = 1.68$ g/cm^3, $Z = 2$. All calculations were performed using WinGX program [13]. Cell parameters, data collection, and data reduction were performed on Alpha Station 200 computer using MoLEN program [14]. All figures were made using the program PLATON [15]. (CCDC 254401 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223336033; or e-mail: deposit@ccdc.cam.ac.uk)

S-(Diethylamino)dimethylsilyl bis(diethylamido)-dithiophosphate **3**. Compound **1** (4.2 g, 9.5 mmol) was added portionwise under dry argon with stirring at 20°C to the solution of 15.4 g (76.1 mmol) of **2a** in 10 mL of anhydrous CH_2Cl_2. The mixture was refluxed for 2.5 h and then filtered. The filtrate was evaporated at reduced pressure (0.5 and 0.06 mmHg) at 40°C for 3.5 h. The residue was stored at ∼20°C for 2 days. The precipitate formed was filtered off. Product **3** (5.6 g, 40%) was isolated from the filtrate by means of a falling-film distillation (see Tables 2–6).

S-(Diethylamino)dimethylsilyl 4-methoxyphenyl-(diethylamido)dithiophosphonate **7a**. Compound **7a** (3.5 g, 8.7 mmol) was added portionwise under dry argon with stirring at 20°C to the solution of 3.5 g (17.3 mmol) of **2a** in 10 mL of anhydrous CH_2Cl_2, and stirring was continued for 2 h at 20°C. The mixture was filtered. The filtrate was evaporated under vacuum (0.5 and 0.07 mmHg) at 40°C for 2 h. The residue was stored at ∼20°C for 1 week. The crystalline precipitate of **7a** was isolated from the liquid residue by filtration in three portions with overall yield of 3.4 g (49%) (see Tables 2–6).

S-Trimethylsilyl S-Ethyl(diethylamido)trithiophosphate **9a**. Compound **8a** (22.2 g, 71.6 mmol) was added portionwise under dry argon with stirring at 20°C to the solution of 20.8 g (143.3 mmol) of **6**, and stirring was continued for 9 h at 50°C. The mixture was filtered. The filtrate was evaporated at reduced pressure (0.1 and 0.02 mmHg) at 40–50°C for 2 h. Product **9a** (21.3 g, 49%) was isolated from the residue by means of a falling-film distillation (see Tables 2–6).

The products **7b** and **9b** were obtained in a similar manner (see Tables 2–6).

2,4-Bis(diethylamido)-1,3,2,4-dithiadiphosphetane-2,4-disulfide **10**. Compound **9a** (7.0 g, 23.2 mmol) was stored in a sealed ampoule at ~20°C for 6 months. The crystalline precipitate of **10** (1.2 g, 31%) that was formed was filtered, washed with anhydrous CH_2Cl_2, and dried under vacuum (0.02 mmHg) at 40°C for 2 h with the use of a trap cooled by liquid nitrogen, m.p. 143°C (cf. [4]: m.p. 143–145°C). Distillation of the contents of the liquid nitrogen trap gave **11** (1.0 g, 32%), b.p. 128–130°C, $n_D^{20} = 1.4509$ (cf. [16]: b.p. 130°C, $n_D^{20} = 1.4512$).

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