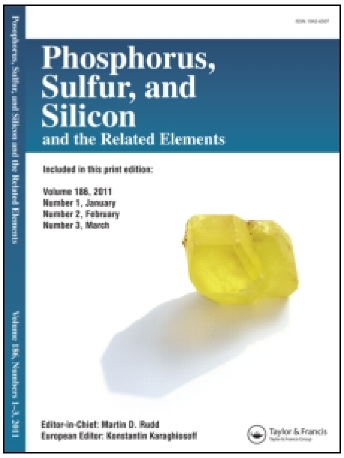

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2,4-N,N'-BIS(DIALKYLAMIDO)-2,4-DITHIOXO-1,3,$2\lambda^5$,$4\lambda^5$-DITHIADIPHOSPHETANES

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2,4-N,N'-BIS(DIALKYLAMIDO)-2,4-DITHIOXO-1,3,2λ^5,4λ^5-DITHIADIPHOSPHETANES

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2,4-N,N'-Bis(dialkylamido)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes were obtained by the interactions of tetraphosphorus decasulfide with sulfenamides. The reactions of amido-1,3,2,4-dithiadiphosphetane-2,4-disulfides obtained with diethyl disulfide, ethylsulfendiethylamide and trimethyl(diethylamino)silane were studied.

Key words: Tetraphosphorus decasulfide, sulfenamides, 2,4-N,N'-bis(dialkylamido)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes.

INTRODUCTION

2,4-Bis(alkyl, aryl, alkylthio and arylthio substituted)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes, in particular Lawesson's and Davy's reagents, are used as thiation agents for organic substances and for the synthesis of organothiophosphorus compounds.[1–4] However, 1,3,2,4-dithiadiphosphetane-2,4-disulfides with amido substituents have received less attention. Thus, tetraphosphorus trisulfide is known to react with bis(dimethylamino)sulfide to give 2,4-N,N'-bis(dimethylamido)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetane, which is obtained as a four- and six-membered ring molecule.[5] In this article a new method is presented for the synthesis of 2,4-N,N'-bis(dialkylamido)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes and their reactions with organic compounds are studied.

RESULTS AND DISCUSSION

We have previously studied the reaction of tetraphosphorus trisulfide with alkylsulfendiethylamides which results in the formation of S-alkyl-N,N'-bis(diethylamido)dithiophosphates and S,S'-dialkyl-N-diethylamidotrithiophosphates.[6] The reactivity of higher phosphorus sulfides in the reaction with sulfenamides remained unknown. We have found that tetraphosphorus decasulfide **1** reacts with alkylsulfendialkylamides **2a–e** to form 2,4-N,N'-bis(dialkylamido)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes **3a, b** (Equation (1) and Table I).

The reaction (1) proceeds in benzene or in the absence of an organic solvent and is accompanied by the formation of dialkyl disulfides **4a–c** and elemental sulfur.

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TABLE I

Experimental, physical and analytical data of the products obtained

Initial cpd.		Prod.	Reaction conditions temp. (°C)/time (h)	Yield, (%) of liquid product crude/isolated	Yield, (%) of crystalline product	B.p., °C (mm Hg)	M.p., °C	n_D^{20}	Molecular formula (Mol. mass)	Analytical data Found/Calc., (%) C	H	N	P	S
1	2a[a]	3a	80/0.5	72[b]	9		168-171	1.5167	$C_4H_{12}N_2P_2S_4$	17.53	3.96	9.62	21.60	46.87
									(277.9)	17.27	4.36	10.07	22.29	46.01
1	2b[a]	3a	70/4	60[b]		108 (0.06)			$C_4H_{12}N_2P_2S_4$	17.77	4.49	10.40	22.01	46.39
									(277.9)	17.27	4.36	10.07	22.29	46.01
1	2c	3b	20/12	94[b]/72[c]	10	145 (0.02)[e]	143-145	1.5612	$C_8H_{20}N_2P_2S_4$	28.46	6.10	7.91	17.78	38.82
									(334)	28.74	6.05	8.38	18.54	38.29
1	2d[a]	3b	20/12	94[c]	4	160 (0.04)	145	1.5629	$C_8H_{20}N_2P_2S_4$	28.50	6.44	8.01	18.89	39.46
									(334)	28.74	6.05	8.38	18.54	38.29
1	2e[a]	3b	20/3		34		143		$C_8H_{20}N_2P_2S_4$	28.73	6.12	8.12	18.44	38.27
									(334)	28.74	6.05	8.38	18.54	38.29
3b	4a	5[f]	75/4	28[b]/10[c]		125 (0.02)[e]		1.6272	$C_8H_{20}NPS_4$	32.86	6.56	4.96	11.10	44.50
									(289.0)	33.21	6.99	4.84	10.71	44.24
6	2c[a]	5	20/336	99[b]/55[c]		105 (0.02)[e]		1.6260	$C_8H_{20}NPS_4$	33.13	6.62	4.75	10.62	44.65
									(289.0)	33.21	6.99	4.84	10.71	44.24
3b	2c[a]	7	60/0.25	93[b]					$C_{10}H_{25}N_2PS_3$	39.63	8.10	8.80	10.01	32.18
									(300.1)	39.98	8.41	9.33	10.32	31.96
3b	8	9[g,h]	70/6.5	44[b]					$C_{11}H_{29}N_2PSSi$	42.87	9.14	8.81	10.02	19.95
									(312.2)	42.28	9.38	8.97	9.92	20.48

[a] Solvent for reaction: benzene.

[b] Yield of crude liquid product.

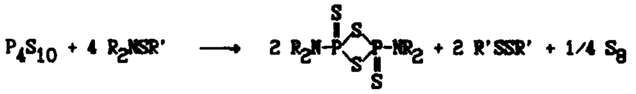
[c] Yield of distilled liquid product.

[e] Temperature of the spiral of the thermal element of thin layer distillation apparatus.

[f] d_4^{20} 1.2291.

[g] Reference 13: b.p. 103 °C (0.001 mm Hg).

[h] Analytical data: Found, %: Si 9.04; Calc., %: 8.97.



(1)

1 2a, R= Me, R'= Et 3a, R = Me 4a, R'= Et
b, R= Me, R'= Pr-i b, R = Et b, R'= Pr-i
c, R= Et, R'= Et c, R'= Bu-i
d, R= Et, R'= Pr-i
e, R= Et, R'= Bu-i

In general the formation of **3** proceeds at room temperature but for the reactivity enhancement we carried out the reaction (1) at 50–70°C. Besides in order to increase yields of **3** we used a 1.5-fold excess of initial sulfenamides **2**. Products **3** are isolated in their crystalline forms only after the elimination of disulfides **4** also formed in the reaction mixtures (by distillation or evaporation under vacuum). However, **3** might be distilled at reduced pressure or isolated by means of thin layer distillation from crude liquid reaction mixtures. After distillation **3** form crystals in benzene solution.

The structure of **3** has been established by IR (Table II), ^1H NMR (Table III), ^{31}P NMR (Table V) spectroscopy and by mass spectral data (Table IV) and microanalyses (Table I). Disulfides **4a–c** were identified by their IR, ^1H NMR and mass spectral data, and by comparing their physical constants with literature data

TABLE II
IR spectral data (cm^{-1}) of the products obtained

Prod.	ν, cm^{-1}
3a[a,b]	1080, 1020 $\nu^c(NC_2)$; 780, 720 ν (NPS as); 680, 640 ν (NPS s, P=S); 555 δ^d (NC_2 s); 495 δ (P◇P); 470 ν (P_xS_x); 405 ν (P_xS_x), δ (NPS).
3b[b]	1165 δ, ρ (CH_3); 1070, 1045 ν (NC_2); 770, 730 ν (NPS as); 672, 625 ν (P=S, NPS s); 560 δ (NC_2 s); 515 δ (P◇P); 463 ν (P_xS_x); 410 ν (P_xS_x), δ (NPS).
5	2975, 2930, 2878 ν (CH_3 as, s; CH_2 as, s); 1170 ν (C-N-C as); 1025 ν (P-N-C as); 694 ν (P=S as, PS_2 as); 660 ν (P-N-C s); 532 ν (PS_2 s, P-SC).
7	1455 δ (CH_3 as; CH_2 as); 1380 δ (CH_3 s); 1208 ω, τ (CH_2); 1020 ν (P-N-C as); 950 ν (NC-C); 810 ρ (CH_2); 625 ν (P=S); 505 δ (CNC).

[a] Reference 5.
[b] In vaseline oil.
[c] Valence vibrations.
[d] Deformation vibrations.

TABLE III

^{1}H NMR spectral data of the products obtained

Prod.	δ, ppm, J, Hz
$\underline{3a}^{a}$	δ_1 2.75 (d, 12H, $\underline{CH_3}$NP, $^3J_{P-H}$ 5.6); δ_2 2.77 (d, 12H, $\underline{CH_3}$NP, $^3J_{P-H}$ 5.6).
$\underline{3b}^{a}$	1.34 (t, 12H, $\underline{CH_3}CH_2$N, $^3J_{H-H}$ 7.2); 3.15 (dq, 8H, $CH_3\underline{CH_2}$NP, $^3J_{H-H}$ 7.2, $^3J_{P-H}$ 7.1).
$\underline{5}^{b}$	1.12 (t, 3H, $\underline{CH_3}CH_2$SS, $^3J_{H-H}$ 7.5); 1.31 (t, 6H, $\underline{CH_3}CH_2$N, $^3J_{H-H}$ 7.2); 1.38 (t, 3H, $\underline{CH_3}CH_2$SP, $^3J_{H-H}$ 7.5); 2.47-3.50 (m, 6H, $CH_3\underline{CH_2}$SS, $CH_3\underline{CH_2}$SP, $CH_3\underline{CH_2}$NP).
$\underline{7}^{b}$	1.23 (t, 3H, $\underline{CH_3}CH_2$SS, $^3J_{H-H}$ 7.2), 1.40 (t, 12H, $\underline{CH_3}CH_2$N, $^3J_{H-H}$ 7.2); 2.63 (q, 2H, $CH_3\underline{CH_2}$SS, $^3J_{H-H}$ 7.2); 2.97 (dq, 8H, $CH_3\underline{CH_2}$NP, $^3J_{H-H}$ 7.2, $^3J_{P-H}$ 15.0).

[a] In CD_3CN.

[b] In CCl_4.

TABLE IV

Mass spectral data of the products obtained

Prod.	i-C_4H_{10}, m/e (I_{rel}, %)
$\underline{3a}^{a}$	139 $[0.5\ M]^{+\cdot}$ (55), 107 $[0.5\ M - S]^{+\cdot}$ (27), 44 $[0.5\ M - P - 2S]^{+\cdot}$ (100).
$\underline{3b}^{a}$	334 $[M]^{+\cdot}$ (20), 167 $[0.5\ M]^{+\cdot}$ (50).
$\underline{3b}^{b}$	335.006295 $[M + H]^{+}$ (45), 168.0071 $[0.5\ M + H]^{+}$ (20).
$\underline{5}^{a}$	196 $[M - SEt - S]^{+\cdot}$ (20).
$\underline{5}^{b}$	258 $[M + H - S]^{+}$ (31), 218 $[M + H - Et_2N]^{+}$ (10), 125 $[M - Et_2N - SEt - S]^{+}$ (50).
$\underline{7}^{a}$	155 $[M - 4Et - 2S]^{+\cdot}$ (100).
$\underline{7}^{b}$	186 $[M + H - 4Et]^{+}$ (65).

[a] Electron impact, 70 eV.

[b] Chemical ionization, 100 eV.

(see Experimental). The formation of elemental sulfur in this reaction was confirmed by the electron impact mass spectral analysis of the reaction mixture of **1** with **2a** indicating the mass peaks m/e (I_{rel}, %): 256 $[S_8]^{+\cdot}$ (15), 224 $[S_7]^{+\cdot}$ (5), 192 $[S_6]^{+\cdot}$ (15), 160 $[S_5]^{+\cdot}$ (20), 128 $[S_4]^{+\cdot}$ (25), 96 $[S_3]^{+\cdot}$ (27) and 64 $[S_2]^{+\cdot}$ (100). The electron impact and the chemical ionization mass spectra of **3b** in its liquid distilled form exhibit the mass peaks 334 and 167, and 334.99715 and 168.0071 respectively, which may be attributed to the ions $[M]^{+\cdot}$, $[0.5\ M]^{+\cdot}$, $[M + H]^{+}$ and $[0.5\ M + H]^{+}$ respectively of **3b**. The electron impact mass spectrum of **3a** in its crystalline

TABLE V

^{31}P NMR spectral data of the products obtained[a]

Initial cpd.		Prod.	δ, ppm (I_{rel})[b]
1	2a	3a[c]	99.7 (44), 98.9 (194), 98.1 (27), 97.5 (55), 94.6 (18).
1	2b	3a[c]	116.5 (2), 104.4 (7), 95.0 (30), 93.8 (8), 83.4 (5), 73.0 (8).
1	2c	3b[d]	94.8 (129), 93.1 (99), 91.3 (40), 83.9 (38), 20.3 (22).
1	2d	3b[d]	95.1 (128), 94.0 (21), 92.0 (24), 90.8 (20), 83.9 (18).
1	2e	3b[c]	105.5 (5), 101.2 (4), 97.8 (28), 96.3 (30), 95.0 (5), 94.3 (19), 90.7 (4), 75.7 (8), 66.8 (7), 51.2 (3).
3b	4a	5[d]	98.9
6	2c	5[d]	98.7
3b	2c	7[c]	97.0
3b	8	9[c,e]	83.6

[a] In liquid form (in benzene solution).

[b] Integral intensity.

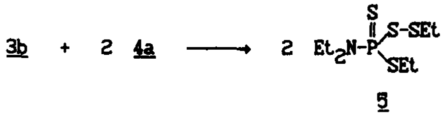
[c] In liquid crude form.

[d] In liquid distilled form.

[e] Reference 12: δ_P (CCl_4) 83.6 ppm.

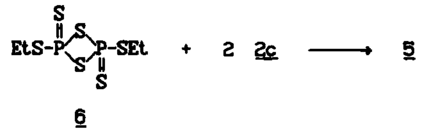
form also indicates the mass peak m/e 139 which is the monomeric unit of **3a** (see Table IV). In the ^1H NMR spectrum of crystalline **3b** (in the solution of CD_3CN) the $\underline{CH_2}CH_2N$ protons appear as a triplet in the region of δ 1.34 ppm with $^3J_{H-H}$ 7.2 Hz (12 H), while the $CH_3\underline{CH_2}NP$ protons appear as a doublet of quartets at δ 3.15 ppm with $^3J_{H-H}$ 7.2 Hz and $^3J_{P-H}$ 7.1 Hz (8 H). The ^{31}P NMR spectrum of crystalline **3a** (MeCN) reveals resonances at δ_P 117.5 and 53.9 ppm the ratio 5:1. Its ^{31}P NMR spectrum in the solution in $PhNO_2$ shows a signal at δ_P 116 ppm. The ^{31}P NMR spectrum of the solution of $PhNO_2$ of crystalline **3b** has the same signal (δ_P 116 ppm). However, the ^{31}P NMR spectra of **3a** and **3b** in their liquid forms neat or in the solutions in anhydrous benzene (in their distilled liquid forms or in the crude reaction mixtures of **1** with **2a–e**) reveal a few signals in the region of δ_P 83–99 ppm (see Table V). The ^{31}P NMR spectra of liquid **3b** reveal large intensity resonances at δ_P 94.8 ppm (for the reaction of **1** and **2c**), at δ_P 95.1 ppm (for the reaction of **1** with **2d**) and at δ_P 96.3 ppm (for the reaction of **1** with **2e**) along with a few weak intensity signals (Table V). The large intensity ^{31}P NMR signal with δ_P 95.0 ppm in the case of the reaction of **1** with dimethylamido derivative **2b** was observed in the liquid reaction mixture as well. These signals may be attributed to cis- and trans-isomers[7] for four-, six- and eight-membered cyclic molecules[8] and, perhaps, to monomeric units, R_2NPS_2, of **3** similar to the ^{31}P NMR spectra of other 1,3,2,4-dithiadiphosphetane-2,4-disulfides.[7,8]

It seemed of interest to study the reactivity of products **3** obtained. Reactions of **3a** with ammonia, dimethylamine, bis(dimethylamino)sulfide and tributylphosphine were previously studied.[5] Besides it was of interest to examine the influence of disulfides **4** and sulfenamides **2** on the stability of products **3** formed. As was shown in the reaction of **1** with **2** (Equation (1)) it was accompanied by the formation of disulfides **4**. Such 1,3,2,4-dithiadiphosphetane-2,4-disulfides as Lawesson's and Davy's-like reagents are known to react with dialkyl disulfides to give S,S-alkyl-S′-alkyl arylphosphonotrithiolothionoates and S,S′-dialkyl-S,S″-alkyltetrathiolothionophosphates respectively with P—S—S—Alk bonds.[9,10] Considering these results we assumed that the reaction of **3** with dialkyl disulfides results in thionophosphates with the S—S thiol bond as well. In fact we have found that **3b** reacts with diethyl disulfide **4a** to give S-ethyl-S′,S′-ethyl-N-diethylamido trithiolothionophosphate **5** (Equation (2), Tables I–V).



(2)

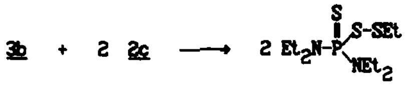
It is remarkable that the reaction (2) proceeds only when heated to 75°C for 4 h unlike reaction (1) (20°C). The product **5** involves the S—S bridge bond. The product **5** obtained is a stable compound and does not decompose in the course of vacuum thin layer distillation. It should be noted that the stability of **5** exceeds that of tetrathiolothionophosphate obtained in the reaction of tetraphosphorus decasulfide or the ethyl homologue of Davy's reagent with **4a**.[10] In order to corroborate the structure of **5** formed in the reaction (2) we carried out the counter-reaction of 2,4-bis(ethylthio)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetane **6** with sulfenamide **2c** (Equation (3)).



(3)

As expected this counter-reaction (Equation (3)) of **6** with **2c** at 20° in anhydrous benzene brought about the same product **5** (Tables I–V). Its physical and spectral data were identical to those of product **5** obtained in the course of the reaction of **3b** with **4a** (Equation (2), Tables I–V). It is noteworthy that the yield of **5** (99%) (Equation (3)) was higher than that in the first case (28%) (Equation (2), Table I).

Thus, we have shown that sulfenamide **2c** can open the 1,3,2.4-dithiadiphosphetane ring of **6**. We assumed that sulfenamides could react with other 1,3,2.4-dithiadiphosphetane-2,4-disulfides, e.g. **3**. Besides it was of interest to investigate the behavior of an excess of sulfenamides **2** as regards initial products **3** formed in the reaction mixture of **1** with **2** (Equation (1)) which might involve complications in the course of the reaction (1) and bring about the formation of some secondary products. In this case the formation of thionophosphates with the S—S thiol bond could be expected in the reaction of **3** and **2** as well. In fact, S,S-ethyl-bis(N-diethylamido)dithiolothionophosphate **7** was obtained in the reaction of crystalline **3b** with **2c** (Equation (4), Tables I–V).

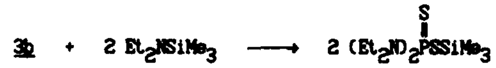


$$\mathbf{3b} + 2\ \mathbf{2c} \longrightarrow 2\ Et_2N\text{-}\overset{\overset{S}{\|}}{P}(S\text{-}SEt)(NEt_2) \qquad (4)$$

7

But this reaction (Equation (4)) proceeds only when heated at 60°C in benzene solution.

The fragmentation reaction of **3** may be extended to silyl derivatives, e.g. silylamines. We have previously shown that Davy's and Lawesson's-like reagents react with trialkylsilyl and stannyl derivatives to form S-trialkylsilyl and stannyl esters of phosphorus (IV) thioacids.[11,12] The formation of silyldiamidodithiophosphates could be assumed in the reaction of **3** with silylamines. Indeed, we have found that trimethyl(dimethylamido)silane **8** opens the 1,3,2.4-dithiadiphosphetane ring of **3b** with the formation of S-trimethylsilyl N,N′-bis(diethylamido)dithiophosphate **9** at 60–70°C for 6.5 h (Equation (5), Tables I and V).



$$\mathbf{3b} + 2\ Et_2NSiMe_3 \longrightarrow 2\ (Et_2N)_2\overset{\overset{S}{\|}}{P}SSiMe_3 \qquad (5)$$

8 9

It should be emphasized that **9** was previously obtained in the reaction of phosphorus sulfide **1** with silylamine **8**.[12,13] Physical and spectral data of **9** (Equation (5)) were identical to literature data of **9**.[12,13] However, **9** decomposes during distillation. The mechanism of the reaction of phosphorus sulfide **1** with silylamine **8** has previously been discussed by Roesky and Remmers.[13] We assumed that during the initial steps of the destruction process of phosphorus sulfide **1** when affected by silylamine **8**[12,13] some intermediates similar to products **3** in their dimer or trimer forms may be formed. Thus, the interaction of **3b** with **8** (Equation (5)) may serve as a model reaction of some intermediate processes of degradation of **1** when affected by **8** and the formation of **9**.[12,13]

Thus, we have developed a new method of synthesis of bis(amido)-1,3,2,4-dithiadiphosphetane-2,4-disulfides and studied their reactivity with organic and organosilicon compounds.

EXPERIMENTAL

^{31}P NMR spectra were recorded with a Bruker MSL-400 (162 MHz) spectrometer in C_6H_6 and CCl_4 and with a non-serial NMR KGU-4 (10.2 MHz) (neat) spectrometer, reference external H_3PO_4 (85%). ^1H NMR spectra were run on a Varian T-60 (60 MHz) spectrometer and on a Bruker WM-250 (250 MHz) spectrometer in CD_3CN. IR spectra were obtained in a KBr pellet with an UR-20 infrared spectrophotometer. Mass spectra (electron impact, 70 eV; chemical ionization, 100 eV) were obtained on a Finnigan MAT 212 mass spectrometer and on a M 80 B Hitachi chromato mass spectrometer.

2,4-N,N'-Bis(dimethylamido)-2,4-dithioxo-1,3,2λ⁵,4λ⁵-dithiadiphosphetane. **3a**. *Typical Procedure.* Compound **1** (4.6 g, 10.4 mmol) was added portionwise to a stirred solution of **2a** (6.5 g, 61.8 mmol) in 10 mL of anhydrous benzene at 20°C. The mixture was refluxed for 0.5 h and then filtered. The filtrate was evaporated at reduced pressure (10 and 0.02 mm Hg) at 40–50°C for 3 h to give a crude liquid **3a** (4.2 g, 72%). The residue was diluted by 20 mL anhydrous benzene and the solution was kept at ~20°C for a month. The crystalline precipitate of **3a** (0.5 g, 9%) which had formed was filtered, washed with benzene, and dried under vacuum (0.02 mm Hg), m.p. 168–171°C (see Tables I–V). Product **4a** (2.0 g, 80%) was distilled from the distillate, b.p. 155°C, n_D^{20} 1.5074. Mass spectrum (electron impact 70 eV), m/e (I_{rel}, %): 122 $[M]^{+\cdot}$ (100) (Reference 14: b.p. 153.5°C, n_D^{20} 1.5070).

Similarly **1** (7.0 g, 15.8 mmol) and **2b** (11.2 g, 94.0 mmol) (reaction conditions: 70°C, 4 h) produced crude **3a** (4.4 g, 60%) which was distilled (Table I).

2,4-N,N'-Bis(diethylamido)-2,4-dithioxo-1,3,2λ⁵,4λ⁵-dithiadiphosphetane. **3b**. *Typical Procedure.* Compound **1** (10.0 g, 22.5 mmol) was added portionwise to a stirred **2c** (18.0 g, 135 mmol) at 20°C for 2 h and stirring was continued for 10 h at 20°C. The mixture was filtered. The filtrate was evaporated under vacuum (10 and 0.02 mm Hg) at 40–50°C for 2 h. The distillation of the residue by means of thin layer distillation apparatus gave liquid **3b** (10.8 g, 72%) (Table I) which was diluted by 50 mL anhydrous benzene and the solution was kept at ~20°C for a month. The crystalline precipitate of **3b** (0.6 g, 4%) which had formed was filtered, washed with benzene, and dried under vacuum (0.02 mm Hg) for 3 h at 40°C, m.p. 143–145°C (see Tables I–V). Product **4a** (4.1 g, 75%) was isolated from the distillate.

Similarly **1** (10.0 g, 22.5 mmol) and **2d** (19.9 g, 135.5 mmol) in 20 mL anhydrous benzene resulted in distilled liquid **3b** (14.2 g, 94%) and crystalline **3b** (0.6 g, 4%) (Table I), and **4b** (2.8 g, 42%), b.p. 173–174°C, n_D^{20} 1.4952. Mass spectrum (electron impact, 70 eV), m/e (I_{rel}, %): 150 $[M]^{+\cdot}$ (100) (Reference 14: b.p. 176°C, n_D^{20} 1.4948).

Similarly **1** (9.4 g, 21.2 mmol) and **2e** (22.5 g, 127.0 mmol) in 15 mL anhydrous benzene produced crystalline **3b** (4.8 g, 34%) (Table I), and **4c** (6.2 g, 83%), b.p. 70°C (0.06 mm Hg), n_D^{20} 1.4946 (Reference 14: b.p. 85°C (3 mm Hg), n_D^{20} 1.4940).

S-Ethyl-S,S'-ethyl-N-diethylamido trithiolothionophosphate **5**.

a. The mixture of **3b** (17.3 g, 51.8 mmol) and **4a** (12.7 g, 10.4 mmol) was stirred at 75°C for 4 h. The mixture was filtered. The filtrate was evaporated under vacuum (0.1 and 0.02 mm Hg) at 40–50°C for 2 h to give crude **5** (8.4 g, 28%). The distillation of the residue by means of thin layer distillation apparatus gave **5** (2.9 g, 10%) (see Tables I–V).

b. Compound **6** (12.0 g, 38.5 mmol) was added portionwise with stirring at 20°C to the solution of **2c** (10.2 g, 76.7 mmol) in 15 mL anhydrous benzene. The mixture was kept at ~20°C for two weeks. The solid **6** disappeared. The mixture was evaporated at reduced pressure (0.1 and 0.02 mm Hg) at 50°C for 2 h to give crude **5** (21.9 g, 99%). Product **5** was isolated from the residue by means of thin layer distillation (Table I).

S,S-Ethyl-N,N'-bis(diethylamido)dithiolothionophosphate **7**. Solid **3b** (4.5 g, 13.5 mmol) was added portionwise with stirring at 20°C to the solution of **2c** (3.6 g, 27.1 mmol) in 10 mL anhydrous benzene. The mixture was heated at 60°C for 15 min. Solid **3b** disappeared. The mixture was evaporated at reduced pressure (0.1 and 0.02 mm Hg) at 40°C for 2 h. The residue was diluted by 10 mL anhydrous benzene and refluxed for 1 h over absorbent carbon (1 g). The mixture was filtered. The solvent was removed under vacuum (0.02 mm Hg) and gave crude **7** (7.5 g, 93%) (Tables I–V).

S-Trimethylsilyl N,N'-bis(diethylamido)dithiophosphate **9**. The mixture of **3b** (8.6 g, 25.8 mmol) and **8** (7.5 g, 51.7 mmol) was stirred at 60–70°C for 6.5 h. The mixture was filtered. The filtrate was evaporated at reduced pressure (0.1 and 0.02 mm Hg) at 50°C for 2 h and gave crude **9** (7.0 g, 44%). The ^{31}P NMR spectrum (C_6H_6): δ_P 83.3 ppm. Mass spectrum (chemical ionization, 100 eV), m/e (I_{rel}, %): 313 $[M + H]^+$ (10). (Reference 12: the ^{31}P NMR spectrum (CH_2Cl_2): δ_P 83.6 ppm).

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