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Disilyl Dithiophosphonates in the Synthesis of Open Chain and Cyclic Organothiophosphorus Compounds

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ABSTRACT: O-*(Trimethylsiloxy)alkyl* S-*trimethylsilyl aryldithiophosphonates* **7a–d** *were obtained by the reaction of 2,4-diaryl-1,3,2,4-dithiadiphosphetane-2,4-disulfides* **5a,b** *with disilyl derivatives of glycols* **6a,c** *and salicyl alcohol* **6b**. *The reactions of mixed* O,S-*bis(trimethylsilyl) 2,4-di(3,5-di-tert-butyl-4-hydroxyphenyl)dithiophosphonate* **1** *and* S-*silyl aryldithiophosphonates* **7a,b** *with* S,S-*diethyldithiodiphenylgermane* **2**, *dichlorodiphenylgermane* **8a**, *and dichlorodiphenylstannane* **8b** *were studied. The structure of hexaphenyl-2,4,6,1,3,5-trithiatrigerminane* **11** *was established by X-ray single crystal diffraction.* Heteroatom Chem 15:225–232, 2004; DOI 10.1002/hc.20009

INTRODUCTION

The chemistry of derivatives of tetracoordinated phosphorus thioacids containing a few trimethylsilyl groups have recently been developed [1–7]. Common methods of synthesizing tris(trimethylsilyl) tetrathiophosphate and bis(trimethylsilyl) phenyltrithiophosphonate containing three or two S—$SiMe_3$ fragments were usually based on the reactions of bis (trimethylsilyl)sulfide with tetraphosphorus decasulfide and 2,4-diphenyl-1,3,2,4-dithiadiphosphetane-2,4-disulfide or addition of sulfur to disilyl or trisilyl phosphines [1,2]. In this article, a method is presented for synthesizing new *O*-trimethylsiloxyorganyl *S*-trimethylsilyl aryldithiophosphonates on the basis of the reactions of 2,4-diaryl-1,3,2,4-dithiadiphosphetane-2,4-disulfides with disilyl derivatives of diols. The reactions of *O*,*S*-disilyl aryldithiophosphonates and *O*-trimethylsiloxyorganyl *S*-trimethylsilyl aryldithiophosphonates with *S*,*S*-diethyldithio- and dichlorodiphenylgermanes, and dichlorodiphenylstannane were also studied. The formation and molecular and crystal structure of six-membered 1,3,5-hexaphenyl-2,4,6,1,3,5-trithiatrigerminane are described.

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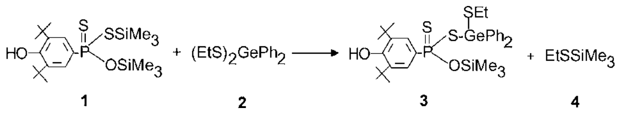
RESULTS AND DISCUSSION

The chemical properties of bis(trimethylsilyl) organyltrithiophosphonates were rather studied. Thus, the substitution reactions of bis(trimethylsilyl) organyltrithiophosphonates with methanol, water, halogens, sulfur chlorides, and dimethyl sulfoxide have been reported to result in trithiophosphonic acids and cyclic anhydrides of perthiophosphonic acids [4–6]. Taking into account the facile occurrence of substitution reactions [4–7], we have tried to extent similar reactions on dithiophosphonates containing both S—SiMe$_3$ and O—SiMe$_3$ fragments. We have recently developed convenient methods for the synthesis of mixed *O*,*S*-bis(trimethylsilyl) esters of aryldithiophosphonic acids by of the reaction of 2,4-diaryl-1,3,2,4-dithiadiphosphetane-2,4-disulfides with disilylated acetamide [3]. *O*,*S*-Disilyl aryldithiophosphonates contain both reactive S—Si and O—Si bonds and two readily leaving trimethylsilyl groups. The formation of linear or cyclic products could be expected by the use of *O*,*S*-disilyl aryldithiophosphonates in the reactions with halides or dialkyldithio derivatives of germanium and tin containing the Ge—S, Ge—Cl, or Sn—Cl bonds.

The reaction of *O*,*S*-bis(trimethylsilyl) 2,4-di(3,5-di-*tert*-butyl-4-hydroxyphenyl)dithiophosphonate **1** with *S*,*S*-diethyldithiodiphenylgermane **2** in anhydrous benzene at 20°C for 4 h has been found to bring about the formation of *O*-trimethylsilyl *S*-(ethylthio)diphenylgermyl 3,5-di-*tert*-butyl-4-hydroxyphenyldithiophosphonate **3** with the elimination of trimethylsilyl(ethylthio)silane **4** (Reaction 1, see Tables 1–5).



(1)

Product **3** was purified by column chromatography. Ethylthiosilane **4** was removed from the reaction mixtures by evaporation at reduced pressure. It was purified by a subsequent distillation. Substitution of only one of the silicon atoms of **1** was confirmed by ^{31}P and ^{1}H NMR spectra of **3** (Tables 2 and 4). The ^{31}P NMR spectrum of *S*-germyl dithiophosphonate **3** in benzene solution (Table 2) shows a singlet at $\delta = 83.9$. This resonance is shifted toward low field in comparison with that **1** ($\delta = 75.6$ [3]). The ^{1}H NMR spectrum of **3** (Table 4) reveals the characteristic resonances of a *O*-trimethylsiloxy group attached to the phosphorus atom. The band of strong intensity in the region of ν 1260 cm^{-1} in the IR spectrum of **3** (Table 3) is due to the CH$_3$(Si) symmetrical deformation vibrations. Two bands in the region of ν 465 and 408 cm^{-1} are assigned to the GePh$_2$ and S—Ge

TABLE 1 Experimental Data and Yields of the Products

Initial Compounds[a]		*Reaction Conditions* *Temp. (°C)*	*Time (h)*	*Product Yield*[b]
1 1.0 (2.2);	**2** 0.8 (2.2)	20 5 ml C$_6$H$_6$	4	**3** 0.9 (60)[c]/0.6 (40)[d]; **4** 0.2 (67)[c]
5a 81.2 (209.9);	**6a** 94.3 (402.1)	60–70	8	**7a** 132.7 (76)[c]/98.0 (56)[e]
5b 15.0 (25.0);	**6a** 11.7 (49.9)	20	20	**7b** 12.6 (47)[c]/2.7 (10)[e]
5a 3.5 (8.7);	**6b** 4.6 (17.2)	20	15	**7c** 5.1 (65)[c]/2.5 (32)[e]
5a 15.6 (38.6);	**6c** 19.2 (77.3)	20	14	**7d** 18.7 (53)[c]/11.1 (32)[e]
7a 3.3 (7.6);	**8a** 2.3 (7.7)	20 3 ml C$_6$H$_6$	4	**9a** 3.6 (65)[c]/1.4 (25)[e]
7b 3.6 (6.7);	**8a** 2.0 (6.7)	50 5 ml C$_6$H$_6$	2	**9b** 3.2 (78)[c]/1.3 (32)[d]; **10** 0.9 (60)[f]
7a 5.5 (12.6);	**8b** 4.3 (12.5)	20 10 ml C$_6$H$_6$	4	**9c** 7.2 (85)[c]/1.3 (18)[d]; **10** 0.8 (57)[f]
7b 3.0 (5.6);	**2** 2.0 (5.7)	125	3	**9b** 2.2 (63)[g]; **11** 0.5[g]; **4** 0.8 (53)[f]

[a] Quantity in gram (mmol).
[b] Product yield in gram (percent).
[c] Yield of crude product.
[d] Yield of product isolated by column chromatography.
[e] Yield of product isolated by a falling-film distillation.
[f] Yield of product isolated by a distillation.
[g] Yield of crystalline product.

TABLE 2 Physical, Analytical, and ^{31}P NMR Data of the Products Obtained

	b.p. (°C)[a]	n_D^{20}	*Molecular Formula (Mol. mass)*	*Found/Calc. %*			^{31}*P NMR*, δ *(C$_6$H$_6$)*
				E	*P*	*S*	
3[b]			$C_{31}H_{45}GeO_2PS_3Si$	10.66^{Ge}	4.26	14.55	83.9
			(676.9)	10.72^{Ge}	4.58	14.17	
7a	100 (0.04)[c]	1.5183	$C_{17}H_{33}O_3PS_2Si_2$	12.48^{Si}	6.80		85.7 (6)[d]
			(436.2)	12.83^{Si}	7.10		85.5 (10)[d]
							84.8 (19)[d]
							84.4 (12)[d]
7b	150 (0.03)[c]	1.5280	$C_{24}H_{47}O_3PS_2Si_2$	10.35^{Si}	5.59		87.9 (13)[d]
			(534.3)	10.47^{Si}	5.80		86.8 (11)[d]
							86.5 (58)[d]
							86.1 (100)[d]
7c	100–105 (0.04)[c]		$C_{20}H_{31}O_2PS_2Si_2$	12.72^{Si}	7.01		85.4
			(454.2)	12.32^{Si}	6.82		
7d	95 (0.06)[c]	1.5320	$C_{18}H_{35}O_3PS_3Si_2$	12.36^{Si}	6.74	14.19	85.6
			(450.2)	12.43^{Si}	6.88	14.20	
9a	170 (0.05)[c]	1.5958	$C_{23}H_{25}GeO_3PS_2$	14.47^{Ge}	5.82		100.8 (2)[d]
			(516.8)	14.05^{Ge}	5.99		99.8 (100)[d]
							99.3 (4)[d]
9b	70[e]		$C_{30}H_{39}GeO_3PS_2$	11.74^{Ge}	5.01		103.3 (1)[d]
			(614.9)	11.84^{Ge}	5.04		101.9 (7)[d]
9c	130(0.05)	1.6244	$C_{23}H_{25}O_3PS_2Sn$	20.92^{Sn}	5.17		100.6 (13)[d]
			(562.8)	21.09^{Sn}	5.50		99.8 (18)[d]

[a] *Temperature* of thermal element of a falling-film distillation.
[b] R_f 0.94 (C_6H_6)
[c] Values in parentheses in this column indicate pressure (mm Hg).
[d] The mixture of isomers, values in parentheses in this column indicate the integral intensity ratio (percentage).
[e] m.p. (°C).

TABLE 3 IR Data of the Products Obtained

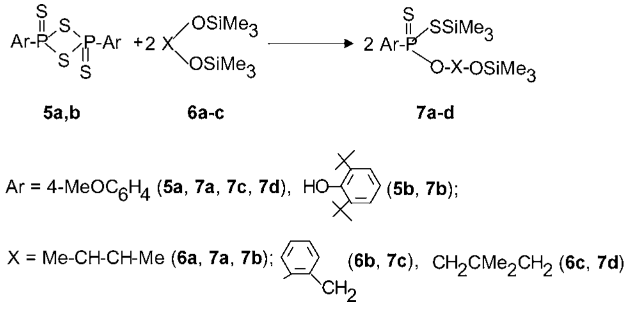
	ν, *cm*$^{-1}$
3	3636 ν (O—H); 3075, 3050 ν (=C—H, Ar); 2966, 2930, 2875 ν (CH$_3$ as, s), ν [CH$_3$(Si) s]; 1585, 1485 ν (C=C, Ar); 1435 δ (CH$_3$ as); 1260 δ [CH$_3$(Si) s]; 1100 ν (P—Ar); 860 ν [P—O(C)]; 695 ν (P=S); 652 ν (C—S); 615 ν (P—S); 465 ν (GePh$_2$); 408 ν (S—Ge).
7a	3075 ν (=C—H, Ar); 2980, 2960, 2900, 2842 ν (CH$_3$ as, s), ν (CH), ν [CH$_3$(Si) s]; 1593, 1500 ν (C=C, Ar); 1255 δ [CH$_3$(Si) s]; 1036 ν [(P)O— C)]; 880 ρ [CH$_3$(Si)], 848 ν [P—O(C)]; 680 ν (P=S); 622, 539, 515 ν (P—S, S-Si).
7b	3635 ν (O—H); 3010 ν (=C—H, Ar); 2965, 2910, 2885 ν (CH$_3$ as, s), ν (CH), ν [CH$_3$(Si) s]; 1588, 1490 ν (C=C, Ar); 1435 δ (CH$_3$ as); 1370 δ (CH$_3$ s); 1258 δ [CH$_3$(Si) s]; 1040 ν [(P)O—C]; 850 ρ [CH$_3$(Si)], ν [P—O(C)]; 665 ν (P=S); 515 ν (P—S, S—Si).
7c	3085, 3012 ν (=C—H, Ar); 2967, 2910, 2844 ν (CH$_3$ as, s; CH$_2$ as, s), ν [CH$_3$(Si) s]; 1600, 1505, 1460 ν (C=C, Ar); 1270, 1260 δ [CH$_3$(Si) s]; 1035, 1020, 1010 ν [(P)O—C], ν [O—C(Ar)]; 855 ρ [CH$_3$(Si)], ν [P—O(C)]; 710 ν (P=S); 625, 580, 535 ν (P—S, S—Si).
7d	3075, 3012 ν (=CH, Ar); 2965, 2910, 2840 ν [CH$_3$(Si) s]; ν (CH$_3$ as, s; CH$_2$ as, s); 1594, 1504 ν (C=C, Ar); 1463 δ (CH$_3$s); 1260 δ [CH$_3$(Si) s]; 1034 ν [(P)O—C)]; 860 ρ [CH$_3$(Si)]; ν [P—O(C)]; 688 ν (P=S); 541 ν (P—S, S—Si).
9a	3073, 3052 ν (=C—H, Ar); 2980, 2932, 2910, 2840 ν (CH$_3$ as, s; CH); 1593, 1500 ν (C=C, Ar); 1030 ν [(P)O—C]; 945 ν (OC—C); 695 ν (P=S); 563, 530, 520 ν (P—S); 465 ν (GePh$_2$ as); 410 ν (S—Ge).
9b[a]	3618 ν (O—H); 3080, 3058 ν (=C—H, Ar); 2965. 2912, 2878 ν (CH$_3$ as, s, CH); 1588, 1488, 1455 ν (C=C, Ar); 1432 δ (CH$_3$ as); 1030 ν [(P)O—C)]; 950 ν (C—CO); 865 ν [P—O(C)]; 695 ν (P=S); 570, 510 ν (P—S); 463 ν (GePh$_2$ as); 412 ν (S—Ge).
9c	3080, 3050 ν (=C—H, Ar); 2980, 2933, 2910, 2845 ν (CH$_3$ as, s; CH); 1594, 1500 ν (C=C, Ar); 1030 cp ν [(P)O—C]; 945 ν (OC—C); 678 ν (P=S); 570, 535 ν (P—S); 450 ν (GePh$_2$ as).

[a] In vaseline oil.

valence vibrations, respectively. The electron impact mass spectrum of **3** (Table 5) exibits the mass peak *m/e* 677 that may be attributed to its molecular ion $[M]^{+\cdot}$. The O—Si bond remained attached to the phosphorus atom of **3**.

Thus, the reaction of mixed *O,S*-disilyl dithiophosphonates **1** with diethyldithiogermane **2** at room temperature proceeds via the rupture of the most reactive S—Si bond and only one of the S—Ge linkages. The reaction stops on the stage of the open chain *S*-germyldithiophosphonate **3** which does not undergo a further transformation to a cyclic compound at room temperature. Nevertheless, **3** seems to be a model of some precursor of the ring-closure reaction.

To obtain the heterocycles we decided to use more reactive bifunctional compounds. For this purpose, disilyl dithiophosphonates **7** were obtained. Disilyl derivatives of glycols **6a,c** and of salicyl alcohol **6b** were found to react with 2,4-diaryl-1,3,2,4-dithiadiphosphetane-2,4-disulfides **5a,b** at 20–70°C for 8–20 h with the rupture of only one O—Si bond and the formation of *O*-(trimethylsiloxy)alkyl *S*-trimethylsilyl aryldithiophosphonates **7a–d** (Reaction 2, Tables 1–5). All compounds **7a–d** were purified by use of a falling-film distillation.



(2)

As 2,3-bis(trimethoxy)butane **6a** exists in a mixture D,L- and *meso*-forms, the disilyl dithiophosphonates **7a** and **7b** occur as a mixture of isomers too. Compounds **7a** and **7b** contain three asymmetrical atoms. The ^{31}P NMR spectrum of **7a** (Table 2) in benzene solution reveals four singlets at $\delta = 85.7$, 85.5, 84.8, and 84.4 in the integral intensity ratio 6:10:19:12. Four ^{31}P resonances of **7b** ($\delta = 86.1$–87.9) appear in practically the same region as that of **7a** (Table 2). In contrast of this, the ^{31}P NMR spectra of **7c** and **7d** show singlets at $\delta = 85.4$ and 85.6, respectively. The ^{1}H NMR spectrum of **7c** in CCl_4 solution (Table 4) reveals two singlets at $\delta = 0.33$ and 0.45 as

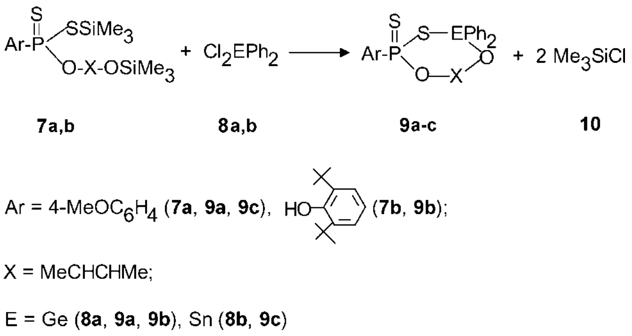
TABLE 4 ^{1}H NMR Data of the Products Obtained

	δ, *J [Hz]*
3[a]	0.33 (s, 9H, $(\underline{CH}_3)_3SiOP$); 1.31 (t, 3H, $\underline{CH}_3CH_2S$, $^3J_{HH}7.2$); 1.56 (s, 18H, $(\underline{CH}_3)_3C$); 2.97 (q, 2H, $CH_3\underline{CH}_2S$, $^3J_{HH}7.2$); 6.98–7.98 (m, 10H, $(C_6\underline{H}_5)_2Ge$; 2H, 2,6-$\underline{H}_2C_6$).
7a[a,b]	0.13–0.25 (m, 9H, $(\underline{CH}_3)_3SiSP$; 9H, $(\underline{CH}_3)_3SiOC$); 0.87–1.64 (m, 3H, $\underline{CH}_3CHOP$ + 3H, $\underline{CH}_3CHOSi$, $^3J_{HH}$ 6.0); 3.35–4.26 (m, 2H, $\underline{CH}$); 3.77–3.92 (m, 3H, $\underline{CH}_3OC_6H_4$); 6.72–7.03 (m, 2H, 3,5-$H_2C_6\underline{CH}_2$, $^3J_{HH}$ 9.0, $^4J_{PH}$ 3.0); 7.92–8.06 (m, 2H, 2,6-$\underline{H}_2C_6H_2$, $^3J_{HH}$ 9.0, $^3J_{PH}$ 15.0).
7b[b,c]	0.03–0.20 (m, 9H, $(\underline{CH}_3)_3SiSP$); 0.28–0.42g(m, 9H, $(\underline{CH}_3)_3SiOC$); 1.05–1.20 (m, 6H, $OCH\underline{CH}_3$ $CH\underline{CH}_3O$); 1.30, 1.37, 1.39, 1.45 (four s, 18H, $(\underline{CH}_3)_3C$); 3.48–3.65 (m, 2H, $O\underline{CHCH}O$); 7.81–7.83 (m, 2H, 2,6-$\underline{H}_2C_6$, $^3J_{PH}15.0$).
7c[a]	0.33 (s, 9H, $(\underline{CH}_3)_3SiSP$); 0.45 (s, 9H, $(\underline{CH}_3)_3SiOC$); 3.82 (s, 3H, $\underline{CH}_3OC_6H_4$); 5.26 (d, 2H, $\underline{CH}_2OP$, $^3J_{HH}$ 9.0); 6.67–7.61 (m, 4H, $C_6\underline{H}_4CH_2$; 2H, 3,5-$H_2C_6\underline{H}_2$; 2H, 2,6-$\underline{H}_2C_6H_2$).
7d[a]	0.11 (s, 9H, $(\underline{CH}_3)_3SiSP$); 0.30 (s, 9H, $(\underline{CH}_3)_3SiOC$); 1.11 (s, 6H, $(\underline{CH}_3)_2C$); 3.67 (s, 2H, $\underline{CH}_2OSi$); 3.82 (s, 3H, 4-$\underline{CH}_3OC_6H_4$); 4.07 (d, 2H, $\underline{CH}_2OP$, $^3J_{PH}6.0$); 6.93 (d. d, 2H, 3,5-$H_2C_6\underline{H}_2$, $^3J_{HH}9.0$,$^4J_{PH}3.5$); 7.76 (d. d, 2H, 2,6-$\underline{H}_2C_6H_2$, $^3J_{HH}9.0$,$^4J_{PH}14.0$).
9a[b,d]	0.76–1.05 (m, 6H, $OCH\underline{CH}_3CH\underline{CH}_3O$); 3.23 (broad s, 3H, $\underline{CH}_3OC_6H_4$); 3.69 (m, 1H, $CH_3\underline{CH}OGe$); 3.99–4.10 (m, 1H, $CH_3\underline{CH}OP$); 6.77 (m, 2H, 3,5-$H_2C_6\underline{H}_2$, $^3J_{HH}$ 9.0, $^4J_{PH}$ 3.0); 6.96–7.15 and 7.54–7.63 (two m, 10H, $Ge(C_6\underline{H}_5)_2$); 7.86 (m, 2H, 2,6-$\underline{H}_2C_6H_2$, $^3J_{HH}$ 9.0, $^3J_{PH}$ 14.5).
9b[b,c]	1.17–1.74 (m, 24H, $\underline{CH}_3$); δ_1 4.21 (m, 1H, $GeO\underline{CH}CH$); δ_2 4.47 (m, 1H, $PO\underline{CH}CH$); δ_1 4.76 (m, 1H, $GeO\underline{CH}CH$); $\delta_{2'}$ 5.00 (m, 1H, $PO\underline{CH}CH$); 5.81 (M, 1H, $\underline{OH}$); 7.46–7.94 (m, 12H, $\underline{H}$ arom.).
9c[b,d]	0.83–1.11 (m, 6H, $OCH\underline{CH}_3CH\underline{CH}_3O$); 3.21 (broad s, 3H, $\underline{CH}_3OC_6H_4$); 3.64–3.76 (m, 1H, $CH_3\underline{CH}OSn$); 3.21–3.24 (m, 1H, $CH_3\underline{CH}OP$); 7.12–7.15 and 7.75 (two m, 10H, $Sn(C_6\underline{H}_5)_2$); 6.60–6.60 (m, 2H, 3,5-$H_2C_6\underline{H}_2$); 7.88 (m, 2H, 2,6-$\underline{H}_2C_6H_2$, $^3J_{HH}$ 9.0).

[a] In CCl_4.
[b] The mixture of isomers.
[c] In $CDCl_3$.
[d] In C_6D_6.

a result of the methyl protons of two $SiMe_3$ groups at the oxygen and the sulfur atoms, respectively, in the integral intensity ratio 1:1. It is noteworthy that a doublet at $\delta = 5.25$ ($^3J_{PH} = 9.0$) is attributed to the protons of the $\underline{CH_2}OP$ group. Therefore, disilylated salicyl alcohol **6b** reacts with Lawesson's reagent **1a** via the cleavage of the most reactive O—Si bond of the CH_2O—Si fragment under mild conditions used, with another O—Si bond being in the ArO—Si fragment. Strong bands in the region of ν 855–844 cm^{-1} in the IR spectra of **7a–d** (Table 3) are due to the mutual ρ $CH_3(Si)$ deformation vibrations and P—O(C) valence vibrations. The $CH_3(Si)$ symmetrical deformation vibrations appear in the region of ν 1260–1255 cm^{-1}. The electron impact and chemical ionization mass spectra of **7a** and **7b** show the mass peaks *m/e* 436 and 535 of their molecular ions $[M]^{+\cdot}$ and $[M + H]^+$, respectively.

Disilyl dithiophosphonates **7** containing both silylthio- and siloxy groups were used as intermediates for the synthesis of cyclic organothiophosphorus compounds. We have shown that disilyl dithiophosphonates **7a,b** react with dichlorodiphenylgermane **8a** and dichlorodiphenylstannane **8b** in anhydrous benzene at 20–50°C for 2–4 h with the formation of 2-(aryl)-2-thioxo-4,4-diphenyl-6,7-dimethyl-1,5,3,2,4-dioxathiaphosphagermepanes **9a,b** and 2-(4-methoxyphenyl)-2-thioxo-4,4-diphenyl-6,7-dimethyl-1,5,3,2,4-dioxathiaphosphastannepane **9c**, respectively (Reaction 3, Tables 1–5).



(3)

Note that dichlorogermane **8a** and dichlorostannane **8b** take part in the reaction 3 via the cleavage both Ge—Cl or Sn—Cl bonds under the conditions used. Trimethylchlorosilane **10** was also isolated from the reaction mixtures. Compounds **9a** and **9c** were purified by a falling-film distillation, whereas substance **9b** was isolated by column chromatography. Phosphagermepanes **9a,b** and phosphastannepane **9c** are a new type of germanium and tin cyclic derivatives of tetracoordinated phosphorus thioacids. Phosphacycles **9a–c** were formed as the mixtures of isomers. The ^{31}P NMR spectrum of **9a** in benzene solution (Table 2) shows three main singlets at $\delta = 100.8$, 99.8, and 99.3 in the integral intensity ratio 2:100:4. A similar picture was observed in the case of **9b** (see Table 2). Two singlets ($\delta = 100.6$ and 99.8 in the integral intensity ratio 13:18) were observed in the ^{31}P NMR spectrum of **9c**. The ^1H NMR spectra of phosphacycles **9a–c** have complicated appearance (Table 4). Two multiplets situated in the regions of $\delta = 6.95$–7.15 and 7.54–7.63 were assigned to the protons of two phenyl groups of the $(C_6\underline{H_5})_2Ge$ fragment of **9a**. Strong bands in the region of ν 465–463 and 450 cm^{-1} in the IR spectra of **9a–c** (Table 3) are due to the asymmetrical valence vibrations of the $GePh_2$ and $SnPh_2$ bonds, respectively. The chemical ionization spectrum of **9a** (Table 5) exhibits the mass peak *m/e* 519 because of its molecular ion $[M + H]^+$.

Along with spectral data, the structure of phosphacycles **9** was confirmed by cryoscopy. Molecular weight determinations in anhydrous benzene of phosphagermepane **9b** (found 604.7, calculated 614.9) and phosphastannepane **9c** (found 564.6, calculated 562.8) reveal that they do not form dimeric or polymeric associations.

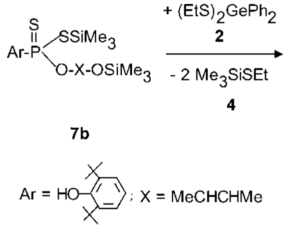
It is considered of interest to compare the reactivity of germanes containing the Ge—Cl and Ge—S bonds toward disilyl dithiophosphonates **7**. We have shown that dichlorodiphenylgermane **8a** is more reactive than that of *S,S*-diethyldithiodiphenylgermane **2**. Thus, the optimal conditions of reaction of disilyl dithiophosphonate **7b** with **2** were defined by the differential thermal analysis. It was

TABLE 5 Mass Spectral Data of the Products Obtained

	i-C_4H_{10}, *m/e* (I_{relt}, %)
3[a]	600 $[M - Ph]^{+\cdot}$ (2).
7a[a]	436 $[M]^{+\cdot}$ (7); 289 $[M - 5\,Me]^{+\cdot}$ (10); 257 $[M - 5\,Me - S]^{+\cdot}$ (100).
7a[b]	349 $[M + H - Me_3Si - O]^+$ (10).
7b[b]	535 $[M + H]^+$ (5); 505 $[M + H - 2\,Me]^+$ (3); 359 $[M + H - 3\,Me - CHMeOSiMe_3]^+$ (100).
7c[a]	350 $[M - Me - O - SiMe_3]^{+\cdot}$ (5); 349 $[M - S - SiMe_3]^{+\cdot}$ (4); 334 $[M - S - Me - SiMe_3]^{+\cdot}$ (8).
7d[b]	347 $[M + 2\,H - S - SiMe_3]^{+\cdot}$(7); 331 $[M + H - Me - S - SiMe_3]^{+\cdot}$(7).
9a[a]	259 $[M - Me - O - GePh_2]^{+\cdot}$ (100).
9a[b]	519 $[M + H]^+$ (30); 396 $[M + H - MeO - Ph]^+$ (9).
9b[b]	341 $[M + H - Ph_2Ge - S - O]^+$(2).
9c[a]	344 $[M - 2\,Ph - MeO - 2\,H]^{+\cdot}$ (5).
9c[b]	395 $[M + 2\,H - 2\,Ph - Me]^+$ (16).

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

found that this reaction started at 107°C. To complete the reaction it was carried out at 125°C for 3 h with the formation of the same crystalline phosphagermepane **9b** (as a mixture of isomers) (Reaction 4, Tables 1–5). Physical and spectral data of **9b** from reaction 4 were identical with those of **9b** from reaction 3.



(4)

Dithiaphosphagermetanes and dithiadiphosphadigermolanes containing the P—S—Ge endocyclic fragment have been reported to be rather thermal unstable substances [8,9]. Thus, 2-(4-methoxyphenyl)-4,4-dimethyl-2-thio-1,3,2,4-dithiaphosphagermetane undergoes thermal transformations into monomeric dimethylgermanium sulfide and 4-methoxyphenylphosphonic anhydride in accordance with the β-destruction. These monomeric units form corresponding dimers and trimers [8]. The formation of similar secondary products could be expected in the case of phosphagermepanes **9**. To verify this idea the thermal stability of phosphagermepane **9b** was studied by differential thermal analysis. It was found that **9b** starts to decompose at 155°C and results in the formation of 1,3,5-hexaphenyl-2,4,6,1,3,5-trithiatrigerminane **11**.

It should be emphasized that [10] and other cyclic organylgermanium sulfides were earlier obtained [11–14]. Tetra(methylgermanium) hexasulfide has been shown by X-ray crystallography to have an adamantane-type structure [12]. However, the molecular structure of the trimer of diphenylgermanium sulfide remained unknown. The molecular and crystal structure of **11** was established by X-ray single crystal diffraction (Fig. 1). The selected bond distances, bond angles, and torsion angles of **11** are listed in Table 6. Inspection proves that **11** exists in the most thermodynamically stable *trans*-chair conformation.

We assume that **9b** decomposes via β-elimination [10] to give unstable monomeric diphenylgermanium sulfide and 4-methoxyphenyl methathiophosphonate and some nonidentified by-products. The trimerization of these intermediates leads to **11** and 2,4,6-tris(4-methoxyphenyl)-1,3,5,2,4,6-trioxatriphosphinane 2,4,6-trisulfide [15].

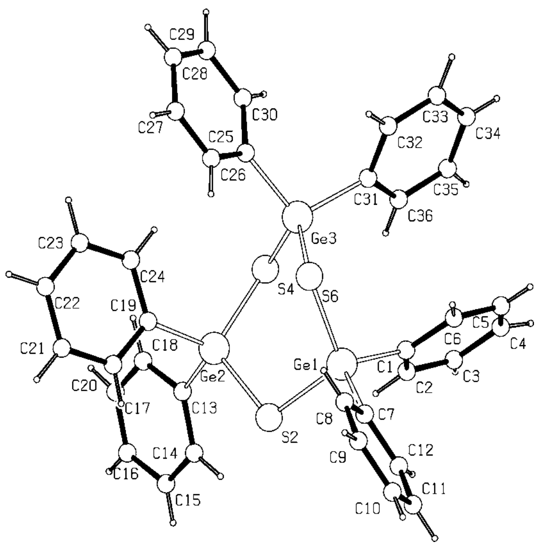
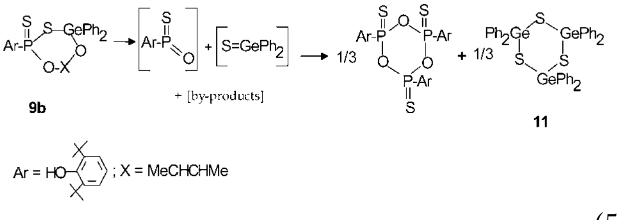


FIGURE 1 Molecular structure of **11**.



(5)

Thus, dithiophosphonates containing O—SiMe$_3$ and S—SiMe$_3$ groups obtained on the basis of **5a,b** are efficient intermediates for the synthesis of open chain and cyclic organothiophosphorus compounds with the P—S—Ge or P—S—Sn fragments.

EXPERIMENTAL

General Data

^{31}P NMR spectra were recorded with a Bruker MSL 400 (162 MHz) instrument in C_6H_6 with 85% H_3PO_4 as an external reference. The ^{1}H NMR spectra were taken on a Bruker MSL-400 (400 MHz) spectrometer and a Varian T-60 (60 MHz) spectrometer in $CDCl_3$ or CCl_4 with $(Me_3Si)_2O$ as an internal reference. The IR spectra were obtained in KBr pellets with an UR-20 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. Molecular weight determination of

TABLE 6 Selected Bond Lengths (Å), Bond Angles (°), and Torsion Angles, (°) in **11**

Bond lengths			
Ge1—S2	2.2310(9)	Ge2—C13	1.945(3)
Ge1—S6	2.2166(9)	Ge2—C19	1.945(3)
Ge1—C1	1.938(3)	Ge3—S4	2.2416(9)
Ge1—C7	1.935(3)	Ge3—S6	2.2217(8)
Ge2—S2	2.2208(9)	Ge3—C25	1.939(3)
Ge2—S4	2.2184(9)	Ge3—C31	1.938(3)
Bond Angles			
S2—Ge1—S6	110.65(3)	C13—Ge2—C19	106.8(1)
S2—Ge1—C1	112.9(1)	S4—Ge3—S6	112.74(3)
S2—Ge1—C7	103.40(9)	S4—Ge3—C25	114.79(9)
S6—Ge1—C1	111.14(9)	S4—Ge3—C31	103.37(9)
S6—Ge1—C7	105.95(9)	S6—Ge3—C25	103.68(9)
C1—Ge1—C7	112.3(1)	S6—Ge3—C31	114.78(9)
S2—Ge2—S4	112.72(3)	C25—Ge3—C31	107.7(1)
S2—Ge2—C13	105.07(9)	Ge1—S2—Ge2	105.48(4)
S2—Ge2—C19	112.87(9)	Ge2—S4—Ge3	107.03(3)
S4—Ge2—C13	107.26(9)	Ge1—S6—Ge3	103.58(3)
S4—Ge2—C19	111.6(1)		
Torsion Angles			
S6—Ge1—S2—Ge2	40.35(4)	S4—Ge2—C13—C14	121.9(4)
C1—Ge1—S2—Ge2	−84.9(1)	S4—Ge2—C13—C18	−63.7(3)
C7—Ge1—S2—Ge2	153.41(9)	C19—Ge2—C13—C14	−118.3(3)
S2—Ge1—S6—Ge3	−77.04(4)	C19—Ge2—C13—C18	56.1(3)
C1—Ge1—S6—Ge3	49.3(1)	S2—Ge2—C19—C20	−48.7(3)
C7—Ge1—S6—Ge3	171.54(9)	S2—Ge2—C19—C24	139.8(2)
S2—Ge1—C1—C2	−0.4(0.3)	S4—Ge2—C19—C20	−176.8(2)
S2—Ge1—C1—C6	−179.2(2)	S4—Ge2—C19—C24	11.6(3)
S6—Ge1—C1—C2	−125.5(2)	C13—Ge2—C19—C20	66.3(3)
S6—Ge1—C1—C6	55.8(3)	C13—Ge2—C19—C24	−105.3(3)
C7—Ge1—C1—C2	116.0(3)	S6—Ge3—S4—Ge2	28.40(5)
C7—Ge1—C1—C6	−62.7(3)	C25—Ge3—S4—Ge2	−90.0(1)
S2—Ge1—C7—C8	−97.6(3)	C31—Ge3—S4—Ge2	152.92(9)
S2—Ge1—C7—C12	78.2(2)	S4—Ge3—S6—Ge1	36.46(4)
S6—Ge1—C7—C8	18.9(3)	C25—Ge3—S6—Ge1	161.21(9)
S6—Ge1—C7—C12	−165.4(2)	C31—Ge3—S6—Ge1	−81.6(1)
C1—Ge1—C7—C8	140.4(3)	S4—Ge3—C25—C26	104.9(3)
C1—Ge1—C7—C12	−43.9(3)	S6—Ge3—C25—C26	−18.5(3)
S4—Ge2—S2—Ge1	31.27(4)	S6—Ge3—C25—C30	160.5(2)
C13—Ge2—S2—Ge1	147.7(1)	C31—Ge3—C25—C26	−140.5(3)
C19—Ge2—S2—Ge1	−96.4(1)	C31—Ge3—C25—C30	38.5(3)
S2—Ge2—S4—Ge3	−67.92(4)	S4—Ge3—C31—C32	157.2(2)
C13—Ge2—S4—Ge3	176.9(1)	S4—Ge3—C31—C36	−21.2(3)
C19—Ge2—S4—Ge3	60.3(1)	S6—Ge3—C31—C32	−79.6(3)
S2—Ge2—C13—C14	1.8(3)	S6—Ge3—C31—C36	102.0(3)
S2—Ge2—C13—C18	176.2(2)		

compounds obtained were carried out on a nonserial cryoscope with Beckman thermometer.

X-Ray Crystallography

Crystal cell data of **11** were measured on an Enraf-Nonius CAD-4 four circle diffractometer fitted with graphite monochromatized Mo K_α radiation, $\lambda = 0.7103$ Å, employing the $\omega/2\Theta$ technique to $\Theta \leq 27°$. From 4806 reflections measured, 3667 were assumed as observed applying the conditions $I \geq 3\sigma(I)$. The final disagreement indices are $R = 0.023$, $R_w = 0.030$ for 3797 independent reflections. Crystal data for **11**: monoclinic, space group $P2_1/n$, at –150°C $a = 11.825(2)$, $b = 21.025(4)$, $c = 13.233(2)$ Å, $\beta = 94.95(2)°$, $V = 3277.5(1)$Å^3, $d_{\text{Calc}} = 1.57$ g/cm^3, $Z = 4$. The structure was solved by the direct method, using the SIR program [16]. All calculations were carried out on an Alpha Station 200 computer, using MolEN programs [17]. Drawings were plotted, using a PLATON program [18]. (CCDC 228694 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 1223 336033; or deposit@ccdc.cam.ac.uk.)

*O-Trimethylsilyl-S-(ethylthio)diphenylgermyl-3,5-di-tert-butyl-4-hydroxyphenyldithiophosphonate (**3**)*

Compound **1** (1.0 g, 2.2 mmol) was added dropwise under dry argon with stirring at 20°C to the suspension of 0.8 g (2.3 mmol) of **2** in 5 ml of anhydrous benzene, and stirring was continued for 4 h at 20°C. The mixture was evaporated at reduced pressure (0.5 and then 0.03 mm Hg) at 40°C for 2 h with use of a trap cooled by liquid nitrogen and gave 0.9 g (60%) of crude **3**. Crude **3** was chromatographed on a silica-gel column with anhydrous benzene as eluant to yield 0.6 g (40%) of pure **3** (see Tables 1–5). Distillation of the contents of the liquid nitrogen trap gave **4** (0.2 g, 67%), b.p. 128–130°C, n_D^{20} 1.4509 (cf. lit. [19]: b.p. 130°C, n_D^{20} 1.4512).

*O-(1,2-Dimethyl-2-(trimethylsiloxy)ethyl-S-Trimethylsilyl-4-Methoxyphenyldithiophosphonate (**7a**)*

The mixture of **6a** (94.3 g, 402.1 mmol) and **5a** (81.2 g, 209.9 mmol) was stirred at 60–70°C for 8 h under dry argon. The mixture was evaporated at reduced pressure (0.1 mm Hg) at 40°C for 1 h and under a higher vacuum (0.07 mm Hg) at 40°C for 1 h and gave 132.7 g (76%) of crude **7a**. Product **7a** (98.0 g, 56%) was isolated from the residue by means of a falling-film distillation (see Tables 1–5).

The products **7b,c** were obtained in a similar manner (see Tables 1–5).

*2-3,5-Di-tert-butyl-4-hydroxyphenyl 2-Thioxo-4,4-diphenyl-6,7-dimethyl-1,5,3,2,4-dioxathiaphosphagermepane (**9b**)*

Compound **8a** (2.0 g, 6.7 mmol) was added dropwise under dry argon with stirring at 20°C to 3.6 g (6.7 mmol) of **7b** in 5 ml of anhydrous benzene, and stirring was continued for 2 h at 50°C. The mixture was filtered. The filtrate was evaporated at reduced pressure (0.5 and 0.03 mm Hg) at 40°C with use of a trap cooled by liquid nitrogen and gave 3.2 g (78%) of crude **9b** (the mixture of isomers). Liquid **9b** was chromatographed on a silica-gel column with anhydrous CH_2Cl_2 as eluant to yield 1.3 g (32%) of **9b** (R_f 0.82 and 0.96, Silufol UV-254, CH_2Cl_2) that was crystallized by removing the eluant under reduced pressure (see Tables 1–5). Distillation of the contents of the liquid nitrogen trap gave **10** (0.9 g, 60%), b.p. 56–57°C, n_D^{20} 1.3892 (cf. lit. [19]: b.p. 57.7°C, n_D^{20} 1.3885).

The products **9a** and **9c** were obtained in a similar manner (see Tables 1–5).

*1,3,5-Hexaphenyl-2,4,6,1,3,5-trithiatrigerminane (**11**)*

The mixture of **7b** (3.0 g, 5.6 mmol) and **2** (2.0 g, 5.7 mmol) was stirred at 125°C for 3 h under dry argon. The mixture was stored at ~20°C for 1 month. The precipitate formed was filtered, washed with anhydrous diethyl ether, dried under vacuum (0.5 mm Hg) for 2 h, and gave 2.2 g (63%) of **9b**, m.p. 72°C. The compound **9b** was heated at 155–160°C for 2 h to yield crystalline **11** (0.2 g). Distillation of filtrate gave **4** (0.8 g, 53%), b.p. 132–133 °C, n_D^{20} 1.4503.

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