

New Methods of Synthesis of Boron, Germanium, and Tin Derivatives of Pentavalent Phosphorus Thioacids

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ABSTRACT: *The reactions of S-trimethylsilyl esters of S-propyl-4-methoxyphenyltrithiophosphonic, bis-(dialkylamido)dithiophosphoric, and S-ethyl-diethyl-amidotrithiophosphoric acids with trialkyl borates, triorganylbromogermanes, trimethyl(isobutylthio)germane, and trialkylchlorostannanes were studied. On the basis of these studies, new methods of synthesizing S-boron, S-germyl, and S-stannyl derivatives of pentavalent phosphorus thioacids were developed. S-Diethylaminomethyl O-isopropyl-4-ethoxyphenyl-dithiophosphonate was obtained by the reaction of the diisopropylboron derivative of the corresponding dithiophosphonic acid with the aminal 6. © 2002 John Wiley & Sons, Inc. Heteroatom Chem 13:27–35, 2002; DOI 10.1002/hc.1103*

INTRODUCTION

There is a considerable interest in main group III and IV element derivatives of pentavalent phosphorus thioacids containing the P(S)SE (E = B, Si, Sn) structural fragment because of their biological activity, their high reactivity, and their use as synthetic intermediates in the preparation of new organothiophosphorus compounds [1–11]. Boron dithiophosphates containing the P(S)SB linkage

have recently been studied. 2-(O,O'-Dialkyl and alkylenedithiophosphato)-1,3,2-dioxaborinanes have been prepared by the reactions of the corresponding dithiophosphoric acids or their ammonium salts with 2-chloro-1,3,2-dioxaborinanes or with trimethylaminoboranes [1,2]. O-Ethyl-S,S'-bis(o-carborane-9-yl)dithiophosphate, -trithiophosphate, and -diphenyldithiophosphinate have also been obtained by addition of elemental sulfur to the corresponding (o-carborane-9-yl)thiophosphite, -dithiophosphite, and -diphenyldithiophosphinite, respectively [3–7]. Organogermyl alkylenedithiophosphates and heterocycles with the P(S)SGe structural fragment were obtained by the reactions of ammonium alkylenedithiophosphonic acids with organogermanium mono- and dichlorides [12–15]. The common methods of synthesizing organotin dithiophosphates, dithiophosphinates, and tetrathiophosphates are usually based on the reactions of the corresponding pentavalent phosphorus thioacids or their salts with organotin halides (also in the presence of β -diketones), oxides, hydroxides, tetraalkyltin, and tributyltin isocyanates [7–9,16–25]. Bis(trimethylstannyl) *tert*-butyltrithiophosphonate was obtained by the reaction of 2,4-bis(*tert*-butyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide with bis(trimethylstannyl)sulfide [26].

Over the past few years, we have been involved in the development of alternate methods of synthesizing boron, germanium, and tin derivatives

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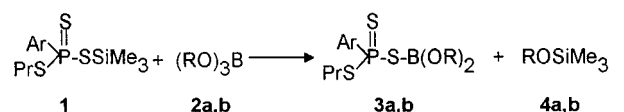
of pentavalent phosphorus thioacids. We have recently developed convenient methods for the synthesis of *S*-(*O,O'*-dialkyl)boron *O,O'*-dialkyldithiophosphates and -aryldithiophosphonates by the reactions of tetraphosphorus decasulfide and 1,3,2,4-dithiadiphosphetane-2,4-disulfides with alkyl borates, *O,O'*-dialkyl dithiophosphoric acids with trialkyl borates promoted by ultrasonic irradiation, and ammonium *O,O'*-dialkyldithiophosphates with fluorodialkyl borates [27–30], which were summarized in a review [31]. *S*-Triphenyl or trialkylgermyl esters of dialkyl dithiophosphoric and tetrathiophosphoric acids, and 4-methoxyphenyldithiophosphonic and -trithiophosphonic acids were easily obtained by the reactions of tetraphosphorus decasulfide and Lawesson's reagent with triphenyl and trialkyl (alkoxy)germanes, and with -(alkylthio)germanes [32–34]. Reactions of tetraphosphorus decasulfide and Lawesson's reagent with trialkyl(alkoxy)stannanes, and with -(alkylthio)stannanes, and bis(trialkylstannyl)sulfide result in *S*-trialkylstannyl dialkyldithiophosphates, *S*-trialkylstannyl tetrathiophosphates, tris(trialkylstannyl) tetrathiophosphates, and *S*-trialkylstannyl 4-methoxyphenyldithiophosphonates and -trithiophosphates, respectively [35–41]. In this article, new methods are presented for synthesizing boron, germanium, and tin derivatives of pentavalent phosphorus thioacids by use of *S*-trimethylsilyl esters of the corresponding pentavalent phosphorus thioacids.

RESULTS AND DISCUSSION

S-Trimethylsilyl esters of dithiophosphoric and tetrathiophosphoric acids are efficient intermediates for the synthesis of useful organothiophosphorus compounds [10,11,42]. The substitution reactions of *S*-trimethylsilyl *O,O'*-dialkyldithiophosphates or *S,S'*-bis(trimethylsilyl) trithiophosphonates with trialkyl-isocyanatostannane and its thioanalogue, trialkyl(*N,N'*-dialkylamino)stannanes, trimethylbenzyl- or 4-vinylbenzylstannanes or trimethylchlorostannane have been reported to result in *S*-trialkylstannyl dithiophosphates and bis(trimethylstannyl) trithiophosphonates [26,43].

Taking into account the rather high reactivity of the S–Si bond, we have studied the reactions of *S*-trimethylsilyl esters of pentavalent phosphorus thioacids with trialkyl borates. However, trialkyl borates possess a low reactivity in the reactions, which proceed with the rupture of the O–B bond. Thus, trialkyl borates do not appear to react with dithiophosphoric acids in the absence of any additives [1]. We have recently

established that tri-isobutyl borate reacts with *O,O'*-dialkyldithiophosphoric acids under the influence of low frequency ultrasonic irradiation (22 kHz, power 130 W) at 25–60°C for 0.5 h to give *S*-(*O,O'*-diisobutyl)boron *O,O'*-dialkyldithiophosphates with the elimination of isobutyl alcohol [29]. In this connection, we expected to observe the same low reactivity of trialkyl borates in the substitution reactions with *S*-trimethylsilyl esters of pentavalent phosphorus thioacids. Indeed, we have now found that the reactions of *S*-trimethylsilyl *S'*-propyl-4-methoxyphenyltrithiophosphonate (**1**) with trialkyl borates (**2a,b**) proceed only under severe conditions (170°C, 6 h) to yield *S*-(*S'*-propyl-4-methoxyphenyltrithiophosphonato) *O,O'*-dialkylborates (**3a,b**) and trimethyl(alkoxy)silanes (**4a,b**) (Reaction 1, Tables 1–5).



Ar = 4-MeOC₆H₄ (**1**, **3a,b**);

R = Pr-*i* (**2a**, **3b**, **4a**); Bu-*i* (**2b**, **3b**, **4b**)

(1)

Note that trialkyl borates (**2a,b**) take part in reaction 1 via the cleavage of only one O–B bond under the conditions used. Other alkoxy groups remained attached to the boron atom. We believe that the compounds (**3a,b**) are a new type of boron(III) derivative of pentavalent phosphorus thioacids containing the S(C)P(S)SB structural fragment. Alkoxysilanes (**4a,b**) were easily removed from the reaction mixtures by evaporation at reduced pressure (see Experimental). They were purified by a subsequent distillation. Compounds (**3a,b**) are yellow, oily liquids. They are nonvolatile even under reduced pressure, and stable at room temperature. The thermal stabilities of boron trithiophosphonates (**3a,b**) are lower than those of the boron aryldithiophosphonates previously obtained by the treatment of 2,4-diaryl-1,3,2,4-dithiadiphosphetane-2,4-disulfides with alkyl borates [44] or boron dithiophosphates [28,29]. Compound **3a** was isolated by column chromatography, whereas substance **3b** tended to decompose partially when falling-film distillations were used in attempted purification.

The ³¹P NMR spectra of boron trithiophosphonates (**3a,b**) (Table 2) show singlets in the range of δ = 88.1–90.8 in benzene solutions. These resonances are shifted toward low field in comparison with the ³¹P NMR data of initial *S*-trimethylsilyl trithiophosphonate **1** (δ = 69 [40]). Substitution of the silicon atom on the boron atom in the

TABLE 1 Experimental Data and Yields of the Products Obtained

Initial Compounds ^a	Reaction Conditions		Product Yield ^b
	Temp. (°C)	Time (h)	
1 6.0 (17.1); 2a 3.2 (17.0)	170	6	3a 2.2 (31) ^c ; 4a 0.5 (22) ^d
1 6.3 (18.0); 2b 4.1 (17.8)	170	6	3b 7.3 (94) ^e ; 4b 0.8 (31) ^d
5 2.0 (5.0); 6 0.7 (5.1)	20	3	7 0.7 (39) ^f
9a 2.7 (10.5); 10a 4.0 (10.4)	50	2	11a 2.3 (47) ^e 12 0.8 (50) ^d
9b 4.7 (15.1); 10b 3.0 (15.1)	120	3	11b 2.8 (52) ^e /1.5 (28) ^g ; 12 0.9 (39) ^d
13 5.8 (19.3); 14 4.0 (19.4)	170	5	15 4.4 (66) ^e ; 16 0.7 (23) ^d
9b 4.1 (13.1); 17a 2.6 (13.1)	20	5	18a 4.4 (83) ^e /2.2 (42) ^g ; 19 0.9 (64) ^d
9b 6.2 (19.9); 17b 6.5 (20.0)	20	5	18b 9.4 (90) ^e /6.3 (60) ^g ; 19 1.3 (59) ^d

^aBold numbers indicate reactants; values that follow indicate quantity in grams (mmols).

^bBold numbers indicate the products obtained; values that follow indicate the product yield in grams (percentage).

^cYield of product isolated by column chromatography.

^dYield of product isolated by a distillation.

^eYield of crude product.

^fYield of crystalline product.

^gYield of product isolated by a falling-film distillation.

molecules of the derivatives of trithiophosphonic acids was confirmed by the data of ¹H NMR spectra of **3a,b** (Table 4). Although a signal of the trimethylsilyl group [45] is absent in the range of $\delta = 0.05\text{--}0.08$, they reveal the characteristic resonances

of the alkoxy groups at the boron atom. Bands of strong intensity in the region $\nu 1032$ and 1020 cm^{-1} in the IR spectra of **3a,b** (Table 3) are assigned to the C—O(C—O—C) and the O—B valence vibrations, respectively. Valence vibrations of the P=S bond

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

Compounds	bp (°C) ^a	<i>n</i> ²⁰ _D	Molecular Formula (Mol. mass)	Found/Calc. %			³¹ P NMR, δ (C ₆ H ₅)
				E	P	S	
3a^b			C ₁₆ H ₂₈ BO ₃ PS ₃ (406.6)	2.72 ^B 2.66 ^B	7.80 7.63	23.21 23.63	79.0 ^c
3b			C ₁₈ H ₃₂ BO ₃ PS ₃ (434.0)	2.51 ^B 2.49 ^B	7.21 7.14	22.60 22.10	78.1
7	113–115 ^d		C ₁₆ H ₂₈ NO ₂ PS ₂ (361.2)		8.50 8.57	17.38 17.70	102.8 ^e
11a			C ₂₂ H ₂₇ GeN ₂ PS ₂ (486.8)	14.96 ^{Ge} 14.91 ^{Ge}	6.11 6.36	13.55 13.14	88.4
11b	95–100 (0.03) ^f	1.4880	C ₁₁ H ₂₉ GeN ₂ PS ₂ (356.8)	20.04 ^{Ge} 20.35 ^{Ge}	9.07 8.68	17.70 17.92	65.7
15	110–120 (0.03) ^g		C ₉ H ₂₄ GeNPS ₃ (345.7)	21.06 ^{Ge} 21.00 ^{Ge}	8.52 8.96	27.34 27.74	78.3
18a	120–125 (0.03)	1.5500	C ₁₁ H ₂₉ N ₂ PS ₂ Sn (402.9)	29.42 ^{Sn} 29.46 ^{Sn}	8.18 7.69	15.37 15.87	86.8
18b	135–140 (0.03)	1.5290	C ₂₀ H ₄₇ N ₂ PS ₂ Sn (529.1)	22.17 ^{Sn} 22.43 ^{Sn}	6.05 5.85	12.02 12.09	87.7

^aTemperature of thermal element of a falling-film distillation.

^bR_f 0.75 (CHCl₃).

^cIn CDCl₃.

^dM.p.

^eIn CD₃CN.

^fValues in parentheses in this column indicate pressure (mm/Hg).

^gTemperature of decomposition.

TABLE 3 IR Data of the Products Obtained

Compounds	ν (cm^{-1})
3a	3080, 3010 ν (=C–H, Ar); 2975, 2932, 2875, 2841 ν (CH_3 as, s; CH_2 as, s; CH); 1594, 1570, 1499, 1463 ν (C=C, Ar); 1440, 1410 δ (CH_3 as); 1387, 1375 δ [$(\text{CH}_3)_2\text{C}$ gem s]; 1292 ν (C=C, Ar); 1256 ω , τ (CH_2); 1181, 1100, 1032 ν (C–O), ν (C–O–C); 693 ν (P=S); 646, 623 ν (C–S); 543, 510 ν (P–S, S–B).
3b	3070, 3010 ν (=C–H, Ar); 2965, 2940, 2900, 2880 ν (CH_3 as, s; CH_2 as, s; CH); 1596, 1502, 1470 ν (C=C, Ar); 1420 δ (CH_3 as, s; CH_2); 1380, 1352 δ [$(\text{CH}_3)_2\text{C}$ gem s]; 1260 ω , τ (CH_2); 1031 ν (OC–C); 1020 ν (O–B); 852 ν (S–B); 695 ν (P=S); 625 ν (C–S); 540, 516 ν (P–S).
7^a	3090, 3060, 3030 ν (=C–H, Ar); 1596, 1500, 1470 ν (C=C, Ar); 1390, 1370 δ [$(\text{CH}_3)_2\text{C}$ gem s]; 1300 ν (C=C, Ar); 1250 ω , τ (CH_2); 1182 ν (C–N–C as); 1060 ν (C–N–C as); 958 ν [(OC)–C]; 922 ν [(N)C–C]; 875 ν [P–O(C)]; 678 ν (P=S); 630 ν (C–S); 572 ν (P–S); 530 δ (CNC).
11a	3070, 3050, 3030, 3010, 3000 ν (=C–H, Ar); 2960, 2885, 2800 ν (CH_3 as, s); 1580, 1480 ν (C=C, Ar); 1190 ν (C–N–C as); 1030, 1000 ν (P–N–C as); 695 ν (P=S); 679, 623 ν (P–N–C as); ν (C–S); ν (P–S); δ (C–S); 500 δ (C–N–C); 410 ν (S–Ge).
11b	2970, 2938, 2905, 2878 ν (CH_3 as, s; CH_2 as, s); 1467, 1380 δ (CH_3 as, CH_2); 1259 δ [$\text{CH}_3(\text{Ge})$]; 1180 ν (C–N–C as); 1030, 997 ν (P–N–C as); 950 ν [(N)C–C]; 710 ν (P=S); 535 ν (P–S); 540 δ (CNC); 428 ν (S–Ge).
15	2963, 2935, 2910, 2888 ν (CH_3 as, s; CH_2 as, s); 1465, 1380 δ (CH_3 as, s); 1260 δ [$\text{CH}_3(\text{Ge})$]; 1020 ν (P–N–C as); 700 ν (P=S); 535, 520 ν (P=S); 420 ν (S–Ge).
18a	2970, 2930, 2912, 2873 ν (CH_3 as, s), ν (CH_2 as, s); 1460 δ (CH_3 as); 1030 γ (C–N–C as); 790 ρ (Sn–C); 621 ν (P=S); 535, 509 ν (P–S), γ (Sn–C).
18b	2960, 2926, 2872, 2855 ν (CH_3 as, s; CH_2 as, s); 1460 δ (CH_3 as); 1029 γ (C–N–C as); 792 ρ (Sn–C); 623 ν (P=S); 525 ν (P–S); γ (Sn–C).

^aIn vaseline oil.

were observed in the region ν 695–693 cm^{-1} for **3a,b**. The electron impact mass spectrum of **3b** exhibits the mass peak m/e 406 that may be attributed to its molecular ion $[\text{M}]^+$ (Table 5).

As we can see, reaction 1 resulted in the formation of the organothiophosphorus compounds **3a,b** containing the P(S)SB structural fragment. Substances of this type contain the reactive S–B bond and a readily leaving boryl group. They may be

TABLE 4 ^1H NMR Data of the Products Obtained

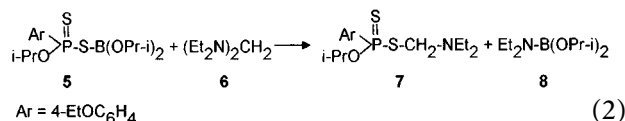
Compounds	δ , $J(\text{Hz})$
3a^a	1.00 (t, 3H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{SP}$, $^3J_{\text{HH}}$ 7.0); 1.02 (d, 12H, $[(\text{CH}_3)_2\text{CHO}]_2\text{B}$, $^3J_{\text{HH}}$ 7.0); 1.21–1.97 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{SP}$; 1H, $(\text{CH}_3)_2\text{CHO}$); 2.23 (d. t, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{SP}$, $^3J_{\text{HH}}$ 7.0, $^3J_{\text{PH}}$ 15.5); 3.84 (s, 3H, $\text{CH}_3\text{OC}_6\text{H}_4$); 6.92 (d. d, 2H, 3,5- $\text{H}_2\text{C}_6\text{H}_2$, $^3J_{\text{HH}}$ 9.0, $^4J_{\text{PH}}$ 3.0); 7.76 (d. d, 2H, 2,6- $\text{H}_2\text{C}_6\text{H}_2$, $^3J_{\text{HH}}$ 9.0, $^3J_{\text{PH}}$ 14.0).
3b^a	0.91 (t, 12H, $[(\text{CH}_3)_2\text{CHCH}_2\text{O}]_2\text{B}$, $^3J_{\text{HH}}$ 7.0); 0.92 (t, 3H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{SP}$, $^3J_{\text{HH}}$ 7.0); 1.35–2.08 (m, 2H, $[(\text{CH}_3)_2\text{CHCH}_2\text{O}]_2\text{B}$; 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{SP}$); 2.92 (d. t, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{SP}$, $^3J_{\text{HH}}$ 7.0, $^3J_{\text{PH}}$ 15.0); 3.57 (d, 4H, $[(\text{CH}_3)_2\text{CHCH}_2\text{O}]_2\text{B}$, $^3J_{\text{HH}}$ 7.0); 3.85 (s, 3H, $\text{CH}_3\text{OC}_6\text{H}_4$); 6.92 (d. d, 2H, 3,5- $\text{H}_2\text{C}_6\text{H}_2$, $^3J_{\text{HH}}$ 9.0, $^4J_{\text{PH}}$ 3.0); 7.85 (d. d, 2H, 2,6- $\text{H}_2\text{C}_6\text{H}_2$, $^3J_{\text{HH}}$ 9.0, $^3J_{\text{PH}}$ 14.0).
7^b	1.11 (d, 6H, $(\text{CH}_3)_2\text{CHOP}$, $^3J_{\text{HH}}$ 6.0); 1.25 (t, 6H, $(\text{CH}_3\text{CH}_2)_2\text{N}$, $^3J_{\text{HH}}$ 6.8); 1.34 (t, 3H, $\text{CH}_3\text{CH}_2\text{OC}_6\text{H}_4$, $^3J_{\text{HH}}$ 6.8); 3.02 (q, 4H, $(\text{CH}_3\text{CH}_2)_2\text{N}$, $^3J_{\text{HH}}$ 6.8); 3.04–3.14 (m, 2H, $\text{CH}_3\text{CH}_2\text{OC}_6\text{H}_4$, $^3J_{\text{HH}}$ 6.8; 1H, CH_2SP); 5.40–6.10 (m, 1H, $(\text{CH}_3)_2\text{CHOP}$); 6.84 (d. d, 2H, 3,5- $\text{H}_2\text{C}_6\text{H}_2$, $^3J_{\text{HH}}$ 8.3, $^4J_{\text{PH}}$ 2.3); 7.96 (d. d, 2H, 2,6- $\text{H}_2\text{C}_6\text{H}_2$, $^3J_{\text{HH}}$ 8.3, $^3J_{\text{PH}}$ 13.0).
11a^a	2.62 (d, 12H, $[(\text{CH}_3)_2\text{N}]_2\text{P}$, $^3J_{\text{HH}}$ 14.0); 7.26–7.58 and 7.62–7.93 (two m, 15H, $(\text{C}_6\text{H}_5)_3\text{Ge}$).
11b^a	0.78 (s, 9H, $(\text{CH}_3)_3\text{Ge}$); 1.04 (t, 12H, $[(\text{CH}_3\text{CH}_2)_2\text{P}$, $^3J_{\text{HH}}$ 7.0); 3.05 (d. q, 8H, $[(\text{CH}_3\text{CH}_2)_2\text{N}]_2\text{P}$, $^3J_{\text{HH}}$ 7.0, $^3J_{\text{PH}}$ 13.0).
18a^c	0.67 (s, 9H, $(\text{CH}_3)_3\text{Si}$); 1.18 (t, 12H, $(\text{CH}_3\text{CH}_2)_2\text{NP}$, $^3J_{\text{HH}}$ 6.5); 3.20 (d. q, 8H, $(\text{CH}_3\text{CH}_2)_2\text{NP}$, $^3J_{\text{HH}}$ 6.5; $^3J_{\text{PH}}$ 13.0).
18b^c	0.84–1.97 (m, 27H, $(\text{C}_4\text{H}_9)_3\text{Sn}$ + 12H, $(\text{CH}_3\text{CH}_2)_2\text{NP}$); 3.21 (d. q, 8H, $(\text{CH}_3\text{CH}_2)_2\text{NP}$, $^3J_{\text{HH}}$ 6.5; $^3J_{\text{PH}}$ 13.0).

^aIn CDCl_3 .

^bIn CD_3CN .

^cIn CCl_4 .

used as efficient intermediates for the synthesis of organothiophosphorus compounds. Thus, 2-(*O,O'*-dipropyldithiophosphato)-1,3,2-dioxaborinane has been reported to react with dibutyl oxide in a molar ratio of 2:1 in benzene at room temperature, with the rupture of the S–B bond to give the corresponding bis(dithiophosphato) dibutyltin and bis(1,3,2-dioxaborinane) oxide [1]. Moreover, we have previously shown that *S*-trimethylsilyl dialkyltetrathiophosphates and trimethyldialkylaminosilanes [46]. We have now found that the reaction of *S*-(*O*-isopropyl-4-ethoxyphenyldithiophosphonato) *O,O'*-di-isopropyl borate **5** with bis(diethylamino)methane (**6**) gives *S*-diethylaminomethyl *O*-isopropyl-4-ethoxyphenyldithiophosphonate **7** and *O,O'*-di-iso-butyl-diethylaminoborate **8** (Reaction 2, Tables 1–5).

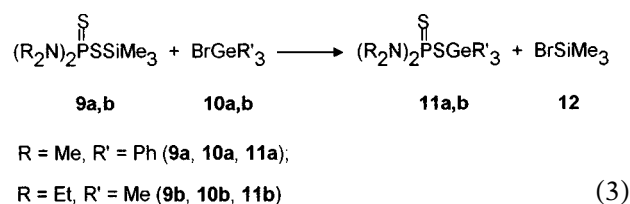


Reaction 2 is exothermic and occurs at room temperature for 3 hours. Compound **7** is a white crystalline solid. The ^{31}P NMR spectral signal of **7** reveals a significant change ($\delta = 101.8$) with respect to **5** ($\delta = 83.0$). It should be noted that the ^{31}P nuclei of the corresponding dialkylaminomethyl tetrathiophosphates are reported to resonate in practically the same region ($\delta = 98.5\text{--}101$ [44]) as observed in **7**. The attachment of the diethylaminomethyl group to the sulfur atom of **7** was confirmed by IR, ^1H NMR, and mass spectroscopy (Tables 3–5). Bands in the region of ν 922 and 530 cm^{-1} in the IR spectra of **7** (Table 3) are due to the (N)C–C valence vibrations and the CNC deformation vibrations, respectively. The mass peak m/e 362 observed in the chemical ionization mass spectrum of **7** is due to its molecular ion $[\text{M} + \text{H}]^+$.

Aminoborate **8** was removed from the reaction mixture by vacuum distillation. The electron impact mass spectrum of the volatile liquid, collected in a liquid nitrogen cooled trap from the crude reaction mixture of reaction 2, shows the mass peak m/e 201 that can be attributed to the molecular ion $[\text{M}]^+$ of aminoborate (**8**) (calculated molecular mass of **8** is 201.1).

In continuation of a study of the reactivity of the S–Si bond of *S*-trimethylsilyl esters of pentavalent phosphorus thioacids, we have tried to extend these substitution reactions to derivatives of main group IV elements, containing labile X–E bonds (X = Cl, Br, S; E = Ge, Sn). Taking into account the facile

occurrence of the substitution reactions of disilyl trithiophosphonates with chlorostannanes [26], we have involved in a corresponding manner bromogermanes in the reactions with silyl esters of pentavalent phosphorus thioacids. Thus, the reactions of *S*-trimethylsilyl bis(dialkylamido)dithiophosphates (**9a,b**) with triphenyl and trimethylbromogermanes (**10a,b**) have been found to bring about the formation of *S*-triphenyl and *S*-trimethylgermyl bis(dialkylamido)dithiophosphates (**11a,b**) and trimethylbromosilane (**12**) (Reaction 3, Tables 1–5).



The reaction of *S*-trimethylsilyl diamidodithiophosphate (**9a**) with triphenylbromogermane (**10a**) proceeds in anhydrous benzene at 50°C for 2 h. In contrast to this, trimethylbromogermane (**10b**) reacts with *S*-trimethylsilyl bis(diethylamido)dithiophosphate (**9b**) only at 120°C for 3 h. *S*-Germyl diamidodithiophosphates (**11a,b**) are a new type of germanium derivatives of pentavalent phosphorus thioacids. *S*-Triphenylgermyl derivative **11a** was obtained as a semisolid. It is nonvolatile in a high vacuum and tended to decompose when column chromatography (silica gel with benzene as an eluant) was used in an attempted purification. We have managed to isolate the *S*-trimethylgermyl derivative **11b** in distillate form by means of a falling-film distillation. Trimethylbromosilane (**12**) was evaporated from the reaction mixtures under vacuum and purified by a subsequent distillation.

The ^{31}P NMR spectrum of **11a** in benzene solution (Table 2) reveals a singlet at δ 88.4. As we can see, the ^{31}P NMR spectral signal of **11a** shows no significant change with respect to **9a** ($\delta = 89.9$ [47]). Broad bands of medium intensities in the region of ν 428–410 cm^{-1} in the IR spectra of **11a,b** (Table 3) are due to the S–Ge valence vibrations. Bands in the range of ν 710–690 cm^{-1} are assigned to the P=S valence vibrations. These bands appear in practically the same region as those for **9a,b** (ν (P=S) 727–692 cm^{-1} [47]). The ^1H NMR spectrum of **11b** in CDCl_3 solution shows a low field shift of the singlet of the trimethylgermyl group ($\delta = 0.78$) with respect to the isostructural **9b** ($\delta = 0.78$ in CH_2Cl_2 solution [47]). The electron impact mass spectrum of **11b** (Table 5) exhibits the mass peaks m/e 357, 342, and 325 due to its molecular ions $[\text{M}]^+$, $[\text{M} - \text{Me}]^+$, and $[\text{M} - \text{S}]^+$, respectively. The phenyl and sulfur

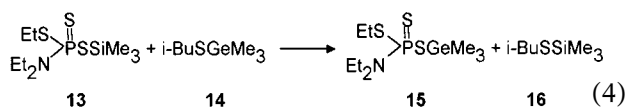
TABLE 5 Mass Spectral Data of the Products Obtained

Compounds	<i>i</i> -C ₄ H ₁₀ , <i>m/e</i> (<i>I</i> _{rel} , %)
3a^a	406 [M] ⁺ (1); 288 [M - 2i - PrO] ⁺ (3)
3a^b	364 [M + H - Pr] ⁺ (2); 348 [M + H - 2i - PrO] ⁺ (2)
7^b	362 [M + H] ⁺ (4)
11a^a	410 [M - Ph] ⁺ (1); 378 [M - Ph - S] ⁺ (2); 301 [M - 2Ph - S] ⁺ (12); 333 [M - 2Ph] ⁺ (1); 224 [M - 3Ph - S] ⁺ (2)
11a^b	444 [M + H - NMe ₂] ⁺ (16); 412 [M + H - NMe ₂ - S] ⁺ (1)
11b^a	357 [M] ⁺ (7); 342 [M - Me] ⁺ (5); 325 [M - S] ⁺ (33); 328 [M - Et] ⁺ (2); 327 [M - 2Me] ⁺ (12); 312 [M - 3Me] ⁺ (16); 299 [M - 2 Et] ⁺ (10)
15^b	301 [M] ⁺ (1); 285 [M + Et - S] ⁺ (2); 274 [M - Et ₂ N] ⁺ (2); 270 [M - Et - Me - S] ⁺ (2); 256 [M - 2Et - S] ⁺ (43)
15^a	275 [M + H - Et ₂ N] ⁺ (3); 257 [M + H - 2Et - S] ⁺ (3); 241 [M + H - 3 Me - Et - S] ⁺ (2)
18a^a	403 [M] ⁺ (3); 388 [M - Me] ⁺ (75); 374 [M - Et] ⁺ (9); 373 [M - 2Me] ⁺ (4); 371 [M - S] ⁺ (5); 358 [M - 3 Me] ⁺ (2); 356 [M - S - Me] ⁺ (2); 239 [M - SnMe ₃] ⁺ (2); 164 [M - 2Et ₂ N - PS ₂] ⁺ (17)
18a^b	359 [M + H - 3Me] ⁺ (6)
18b^a	529 [M] ⁺ (1); 497 [M - S] ⁺ (1); 472 [M - Bu] ⁺ (4); 239 [M - SnBu ₃] ⁺ (1); 290 [M - (Et ₂ N) ₂ PS ₂] ⁺ (15)
18b^b	530 [M + H] ⁺ (2); 498 [M + H - S] ⁺ (3); 416 [M + H - 2Bu] ⁺ (1); 360 [M + 2H - 3Bu] ⁺ (3)

^aElectron impact, 70 eV.^bChemical ionization, 100 eV.

fragments are split out from the molecule of **11a** under the conditions of the recording of the mass spectra. Thus, the mass peaks *m/e* 410, 378, and 301 in the electron impact mass spectrum of **11a** are due to ions [M - Ph]⁺, [M - Ph - S]⁺, and [M - 2Ph - S]⁺, respectively.

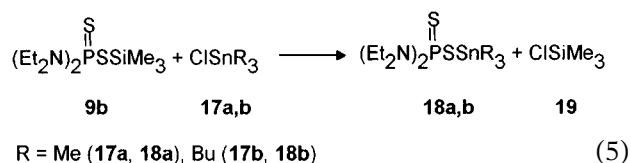
Thus, the Br-Ge bond possesses a rather high reactivity in the substitution reactions with *S*-trimethylsilyl esters of pentavalent phosphorus thioacids. However, when the bromine atom was exchanged on the alkylthio group, we encountered difficulties owing to the low reactivity of the alkylthiogermanes. Thus, the reaction of *S*-trimethylsilyl *S'*-ethyldiethylamidotrithiophosphate (**13**) with trimethyl(isobutylthio)germane (**14**) proceeds only at 170°C for 5 h to give *S*-trimethylgermyl *S'*-ethyldiethylamidotrithiophosphate (**15**) and trimethyl(isobutylthio)silane (**16**) (Reaction 4, Tables 1–5).



S-Germyl derivatives of pentavalent phosphorus thioacids including the S(N)P(S)S-Ge structural fragment remained unknown before our work. Low reactivity of (isobutylthio)germane (**14**) is mainly determined by the rather strong S-Ge bond. The *S*-germyl amidotrithiophosphate **15** formed in reaction 4 was obtained in 66% yield. Compound **15** containing the P-S, P-N, and P-S-Ge bonds tended to partially decompose when a falling-film distillation was used at the temperature of the thermal element of the apparatus, 110–120°C (0.03 mm Hg). Trimethyl(isobutylthio)silane (**16**) was isolated by distillation.

The ³¹P NMR chemical shift value of **15** is shifted to high field ($\delta = 78.3$) with respect to **13** ($\delta = 88.3$). Bands of valence vibrations of the S-Ge bond of **15** appeared at ν 420 cm⁻¹ similarly to **11a,b**. The IR spectrum of **15** also reveals a bond of the P=S valence vibrations (ν 700 cm⁻¹) in the same region as that for **11a,b** (ν (P=S) 710–690 cm⁻¹). The electron impact mass spectrum of **15** (Table 5) exhibits the mass peak *m/e* 301 of its molecular ion [M]⁺. The mass peaks *m/e* 285 and 274 were also observed in the electron impact mass spectrum of **15**, those being attributed to the ions [M - Et - S]⁺ and [M - Et₂N]⁺, respectively.

Taking into account the results of the reactions of *S*-trimethylsilyl diamidodithiophosphates (**9a,b**) with bromogermanes (**10a,b**) (Reaction 3), we developed a convenient method of synthesizing the corresponding *S*-trialkylstannyl diamidodithiophosphates. The reactions of **9b** with trialkylchlorostannane (**17a,b**) at room temperature for 5 h brought about the formation of *S*-trialkylsilyl bis(diethylamido)dithiophosphates (**18a,b**) (Reaction 5, Tables 1–5).



Compounds **18a,b** containing the new N₂P(S)S-Sn structural fragment were formed as oily liquids in high yields (83–90%). They were purified by use of a falling-film distillation. Trimethylchlorosilane **19** was also isolated when the crude reaction mixtures were evaporated under vacuum with use of a trap cooled by liquid nitrogen.

In the case of *S*-trialkylstannyl diamidodithiophosphates (**18a,b**), their ³¹P signals in benzene solutions are shifted to lower field ($\delta = 86.8$ and 87.7, respectively) in comparison with that of **9b** ($\delta = 83.6$

[40]). Thus, an observed tendency of the low field shift of the ^{31}P resonances of the isostructural diamidodithiophosphoric derivatives of the group 14 elements increases when passing from the top to the bottom of this group. This effect indicates a bidentate coordination of the diamidodithiophosphato ligands with the tin atom similar to the chelating behavior of dithiophosphato ligands with the tin atom [48–50]. Broad bands at ν 623–621 cm^{-1} in the IR spectra of **18a,b** (Table 3) are assigned to the P=S valence vibrations, showing a shift to lower frequency with respect to **9b** (ν (P=S) 680 cm^{-1}) that also suggests a chelating behavior of the diamidodithiophosphato ligands. The mass peaks m/e 403 and 529 were observed by examination of the electron impact mass spectrum of **18a** and **18b**, respectively; these may be attributed to their molecular ions (Table 5). This method provides important information about the fragmentation of these molecules. Thus, the mass peaks of ions formed via the rupture of the S–Sn bond of **18a,b** were established in their mass spectra. We have observed the mass peak m/e 239 in the electron impact mass spectra of both **18a** and **18b** that may be attributed to the ions $[\text{M} - \text{SnMe}_3]^+$ and $[\text{M} - \text{SnBu}_3]^+$.

Thus, the above substitution reactions of *S*-silyl esters of pentavalent phosphorus thioacids with trialkyl borates, germanium and tin halides, and alkylmercaptides have a fundamental significance as they lead to new types of boron, germanium, and tin derivatives of pentavalent phosphorus thioacids containing the P(S)SE (E = B, Ge, Sn) structural fragment. Besides, the reactions studied are of interest from the point of view of preparative organophosphorus chemistry. A series of main group element derivatives of pentavalent phosphorus thioacids, which may be prepared on the basis of the approach developed here, is in progress.

EXPERIMENTAL

General Data

The ^{31}P NMR spectra were recorded with a Bruker MSL 400 (162 MHz) instrument in CDCl_3 , C_6H_6 , or CD_3CN with 85% H_3PO_4 as an external reference. The ^1H NMR spectra were taken on a Bruker MSL-400 (400 MHz) spectrometer and a Varian T-60 (60 MHz) spectrometer in CDCl_3 , CD_3CN , or CCl_4 with $(\text{Me}_3\text{Si})_2\text{O}$ 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.

S-(*S*'-Propyl-4-methoxyphenyltrithiophosphonato) *O,O'*-diisopropylborate (**3a**). The mixture of **1** (6.0 g, 17.1 mmol) and **2a** (3.2 g, 17.0 mmol) was stirred at 170°C for 6 h under dry argon. The mixture was evaporated at reduced pressure (0.5 mm Hg) at 40°C for 1 h and under a higher vacuum (0.03 mm Hg) at 40°C for 1 h with use of a trap cooled by liquid nitrogen. The residue was chromatographed on a silica gel column with CHCl_3 as eluant to yield 2.2 g (31%) of pure **3a** (see Tables 1–5). Distillation of the contents of the liquid nitrogen trap gave pure trimethyl(isopropoxy)silane **4a** (0.5 g, 22%), b.p. 87–88°C, n_D^{20} 1.3789 (cf. lit. [51]: b.p. 87°C, n_D^{20} 1.3782).

The product **3b** was obtained similarly (see Tables 1–5).

S-(1-*N,N*-Diethylaminomethyl) *O*-isopropyl-4-ethoxyphenyldithiophosphonate (**7**). Compound **6** (0.7 g, 5.1 mmol) was added dropwise under dry argon with stirring at 20°C to 2.0 g (5.0 mmol) of **5**. After the exothermic period (up to 35°C) of the reaction had been completed, the stirring of the reaction mixture was continued for 3 h at 20°C. The mixture was evaporated at reduced pressure (0.05 mm Hg) at 40°C for 2 h with use of a liquid nitrogen trap. The residue was crystalline. The crystalline solid was washed with benzene, and dried at reduced pressure (0.06 mm Hg) at 40°C for 2 h. The yield of **7** was 0.7 g (39%) (see Tables 1–5).

S-Trimethylgermyl bis(diethylamido)dithiophosphate (**11a**). The mixture of **9b** (4.7 g, 57.1 mmol) and **10b** (3.0 g, 15.1 mmol) was stirred at 120°C for 3 h. The mixture was evaporated at reduced pressure (0.5 mm Hg) at 40°C for 0.5 h and under a higher vacuum (0.06 mm Hg) at 40°C for 2.5 h with use of a trap cooled by liquid nitrogen and gave 2.8 g (52%) of crude **11b**. Product **11b** (1.5 g, 28%) was isolated from the residue by means of a falling-film distillation (see Tables 1–5). Distillation of the contents of the liquid nitrogen trap gave pure trimethylbromosilane (**12**) (0.9 g, 39%), b.p. 80–81°C, n_D^{20} 1.4205 (cf. lit. [51]: b.p. 80°C, n_D^{20} 1.4211).

The product **11a** was obtained similarly (see Tables 1–5) and trimethylbromosilane (**12**) (0.8 g, 50%) was also isolated from the volatile fractions.

S-Trimethylgermyl *S*'-ethyldiethylamidotrithiophosphate (**15**). The mixture of **13** (5.8 g, 19.3 mmol) and **14** (4.0 g, 19.4 mmol) was stirred at 170°C for 5 h. The mixture was evaporated at reduced pressure (0.03 mm Hg) at 40°C for 2 h with use of a liquid nitrogen trap and gave 4.4 g (66%)

of crude **15** (see Tables 1–5). Distillation of the contents of the liquid nitrogen trap gave pure trimethyl(isobutylthio)silane **16** (0.7 g, 23%), b.p. 165–166°C, n_D^{20} 1.4511. Mass spectrum (CI) m/e 162 [M + H]⁺ (1%).

S-Trimethylstannyl bis(diethylamido)dithiophosphate (**18a**). Compound **17a** (2.6 g, 13.1 mmol) was added dropwise under dry argon with stirring at 20°C to 4.1 g (13.1 mmol) of **9b**, and stirring of the reaction mixture was continued for 5 h at 20°C. The mixture was filtered. The filtrate was evaporated at reduced pressure (0.5 mm Hg) at 40°C for 1 h and under a higher vacuum (0.07 mm Hg) at 40°C for 0.5 h with use of a trap cooled by liquid nitrogen and gave 4.4 g (83%) of crude **18a**. Product **18a** (2.2 g, 42%) was isolated from the residue by means of a falling-film distillation (see Tables 1–5). Distillation of the contents of the liquid nitrogen trap gave pure trimethylchlorosilane (**19**) (0.9 g, 64%), b.p. 57°C, n_D^{20} 1.3890 (cf. lit. [51]: b.p. 57.5°C, n_D^{20} 1.3885).

The product **18b** was obtained similarly (see Tables 1–5) and trimethylchlorosilane (**19**) (0.9 g, 64%) was also isolated from the volatile fractions.

REFERENCES

- [1] Singh, B. P.; Mehrotra, R. K.; Srivastava, G. Phosphorus Sulfur Silicon Relat Elem 1991, 60, 147–158.
- [2] Chaturvedi, A.; Nagar, P. N.; Srivastava, G. Phosphorus Sulfur Silicon Relat Elem 1994, 90, 229–233.
- [3] Balema, V. P.; Rys, E. G.; Godovikov, N. N.; Kabachnik, M. I. Izv Akad Nauk, Ser Khim 1990, 2857–2859.
- [4] Balema, V. P.; Rys, E. G.; Godovikov, N. N. Izv Akad Nauk, Ser Khim 1992, 459–461.
- [5] Balema, V. P.; Rys, E. G.; Godovikov, N. N.; Polyakov, A. V.; Struchkov, Yu. T. Izv Akad Nauk, Ser Khim 1992, 180–186.
- [6] Godovikov, N. N.; Balema, V. P.; Rys, E. G. Usp Khimii (Russ) 1997, 66, 1125–1140 and references therein.
- [7] Lefferts, J. L.; Molloy, K. C.; Zuckerman, J. J.; Haiduc, I.; Guta, C.; Ruce, D. Inorg Chem 1980, 19, 1662–1672.
- [8] Singh, B. P.; Srivastava, G.; Mehrotra, R. C. J Organomet Chem 1979, 171, 35–41 and references therein.
- [9] Spiridonov, Yu. Ya.; Shcheglov, Yu. V.; Spiridonova, G. S.; Mitishchev, A. I.; Khokhlov, P. S.; Bliznyuk, N. K. USSR Patent 292683, 1971; Bull Izobr Russ 1971, No. 5.
- [10] Cherkasov, R. A.; Kuttyrev, G. A. Usp Khimii (Russ) 1983, 53, 1675–1708.
- [11] Cherkasov, R. A.; Kuttyrev, G. A.; Pudovik, A. N. Tetrahedron 1985, 41, 2567–2624.
- [12] Rao, R. J. Phosphorus Sulfur Silicon Relat Elem 1990, 53, 203–209.
- [13] Drake, J. E.; Mislankar, A. G.; Ratnani R. Can J Chem 1994, 72, 1830–1838.
- [14] Barrau, J.; El Amine, M.; Rima, G.; Satgé, J. Can J Chem 1986, 64, 615–620.
- [15] Barrau, J.; Rima, G.; Satgé, J. Phosphorus Sulfur Silicon Relat Elem 1995, 107, 99–105.
- [16] Baker, D. R. USA Patent 3992425, 1976; Chem Abstr 1977, 86, 90031.
- [17] Cray, R. A.; Hyzak D. L. USA Patent 4652298, 1987.
- [18] McDermott, J. P.; Springfield, N. J. USA Patent 2786812, 1957; Chem Abstr 1957, 51, 10892f-n.
- [19] Rao, R. J.; Srivastava, G.; Mehrotra, R. C. J Organomet Chem 1983, 258, 155–161.
- [20] Rao, R. J.; Srivastava, G.; Mehrotra, R. C.; Saraswat, B. S.; Mason, J. Polyhedron 1984, 3, 485–490.
- [21] Rao, R. J.; Srivastava, G.; Mehrotra, R. C. Phosphorus Sulfur Silicon Relat Elem 1985, 25, 183–191.
- [22] Lefferts, J. L.; Molloy, K. C.; Zuckerman, J. J.; Haiduc, I.; Guta, C.; Ruse, D. Inorg Chem 1980, 19, 2861–2868.
- [23] Parulekar, C. S.; Jain, V. K.; Kesavadas, T. Phosphorus Sulfur Silicon Relat Elem 1989, 46, 145–151.
- [24] Chaturvedi, A.; Nagar, P. N.; Srivastava, G. Phosphorus Sulfur Silicon Relat Elem 1992, 70, 303–315.
- [25] Kuttyrev, G. A.; Kakurina, V. P.; Cherkasov, R. A. USSR Patent 631519; Bull Izobr Russ 1978, No. 41.
- [26] Hahn, J.; Nataniel, T. Z Anorg Allg Chem 1986, 543, 7–21.
- [27] Nizamov, I. S.; Sergeenko, G. G.; Batyeva, E. S.; Pudovik, A. N. Zh Obshch Khim 1996, 66, 520.
- [28] Nizamov, I. S.; Sergeenko, G. G.; Batyeva, E. S.; Azancheev, N. M.; Al'fonsov, V. A. Heteroatom Chem 2000, 11, 102–106.
- [29] Nizamov, I. S.; Sergeenko, G. G.; Batyeva, E. S.; Azancheev, N. M.; Al'fonsov, V. A. Phosphorus Sulfur Silicon Relat Elem 2000, 158, 157–166.
- [30] Nizamov, I. S.; Sergeenko, G. G.; Batyeva, E. S.; Azancheev, N. M.; Al'fonsov, V. A. Main Group Chem 2000, 3, 129–138.
- [31] Nizamov, I. S.; Batyeva, E. S. Main Group Chem 2000, 3, 117–127.
- [32] Nizamov, I. S.; Kuznetsov, V. A.; Batyeva, E. S. Phosphorus Sulfur Silicon Relat Elem 1994, 88, 67–73.
- [33] Nizamov, I. S.; Kuznetsov, V. A.; Batyeva, E. S. USSR Patent 2059645, 1994; Bull Izobr Russ 1996, No. 3.
- [34] Nizamov, I. S.; Kuznetsov, V. A.; Batyeva, E. S. USSR Patent 2059644, 1994; Bull Izobr Russ 1996, No. 3.
- [35] Nizamov, I. S.; Kuznetsov, V. A.; Al'fonsov, V. A.; Batyeva, E. S.; Pudovik, A. N. USSR Patent 1735299; Bull Izobr Russ 1992, No. 19.
- [36] Nizamov, I. S.; Kuznetsov, V. A.; Al'fonsov, V. A.; Batyeva, E. S.; Pudovik, A. N. Zh Obshch Khim 1992, 62, 1665–1666.
- [37] Nizamov, I. S.; Kuznetsov, V. A.; Al'fonsov, V. A.; Batyeva, E. S. Izv Akad Nauk, Ser Khim 1992, 2457–2458.
- [38] Nizamov, I. S.; Kuznetsov, V. A.; Batyeva, E. S.; Al'fonsov, V. A.; Pudovik, A. N. Heteroatom Chem 1993, 4, 379–382.
- [39] Nizamov, I. S.; Kuznetsov, V. A.; Batyeva, E. S. Russ Patent 2005723; Bull Izobr Russ 1994, No. 1.
- [40] Nizamov, I. S.; Kuznetsov, V. A.; Batyeva, E. S.; Al'fonsov, V. A.; Pudovik, A. N. Heteroatom Chem 1994, 5, 107–111.
- [41] Nizamov, I.; Al'metkina, L.; Kuznetsov, V. XIIth International Conference on Phosphorus Chemistry, Toulouse, 1992, pp. 1–12; Abstracts of Posters.

- [42] Nizamov, I. S.; Popovich, A. E.; Batyeva, E. S.; Alfonsov, V. A. *Heteroatom Chem* 2000, 11, 276–280.
- [43] Kutyrev, G. A.; Lygin, A. V.; Kapura, A. A.; Cherkasov, R. A.; Pudovik, A. N. *Organo-metallic Compounds of Non-transition Metals in Synthesis and Catalysis*, Perm, 1983, p. 59; Abstracts of Vsesoyz Soveshch Russ.
- [44] Nizamov, I.; Alfonsov, V.; Batyeva, E. *Phosphorus Sulfur Silicon Relat Elem* 1996, 109–110, 453–456.
- [45] Raman, I. R. *NMR Spectroscopy of Si, Ge, Sn and Pb Organic Compounds*; Licht, K.; Reich, P. (Eds.); VEB Deutscher Verlag der Wissenschaften: Berlin, 1971; p. 623.
- [46] Nizamov, I. S.; Kuznetsov, V. A.; Batyeva, E. S. *Phosphorus Sulfur Silicon Relat Elem* 1994, 90, 249–257.
- [47] Roesky, H. W.; Remmers, G. *Z Anorg Allg Chem* 1977, 431, 221–226.
- [48] Haiduc, I. *Rev Inorg Chem* 1981, 3, 353–370.
- [49] Silvestru, C.; Haiduc, I. *Coord Chem Rev* 1996, 147, 117–146.
- [50] Glidwell, C. *Inorg Chim Acta* 1977, 25, 159–163.
- [51] Bažant, V.; Chvalovský, V.; Rathouský, J. *Organosilicon Compounds*; Publishing House of the Czechoslovak Academy of Sciences: Prague, 1965; Vol. 2, parts 1 & 2.