Heteroatom Chemistry
Volume 19, Number 5, 2008

Synthesis of 2-Element(Si, Ge, P, Fc)-Substituted *O*,*O*-Bis(trimethylsilyl) Alkylphosphonites and Their Functionalized Derivatives

Andrey A. Prishchenko, Mikhail V. Livantsov, Olga P. Novikova, Ludmila I. Livantsova, and Valery S. Petrosyan

Department of Chemistry, M. V. Lomonosov Moscow State University, Moscow 119991, Russia

Received 26 June 2007; revised 7 April 2008

ABSTRACT: *Addition of bis(trimethylsiloxy)phosphine to element(Si, Ge, P, Fc)-substituted alkenes is proposed as convenient procedures for the synthesis of new 2-element(Si, Ge, P, Fc)-substituted alkylphosphonites. Also the new functionalized derivatives of these phosphonites including various amino and amido groups as well as certain properties of these compounds are presented.* © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:500–505, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20469

INTRODUCTION

Silicon-containing esters of trivalent phosphorus acids are widely used in organophosphorus synthesis as highly reactive synthons, which were successfully added to a variety of unsaturated substances to obtain promising types of organophosphorus compounds [1,2]. Functionalized derivatives of organophosphorus acids containing organoelement fragments and various amino or amido groups present interest as promising ligands in a series of catalytic systems and biologically active compounds as organophosphorus biomimetics of amino acids [3–6]. In the present work, we report here the radical addition of bis(trimethylsiloxy)phosphine to element(Si, Ge, P, Fc)-substituted alkenes, resulting in formation of corresponding phosphonite in high yield. Furthermore, amino- or amidomethylation of these phosphonites is resulting in the new derivatives of organophosphorus acids containing organoelement groups and various aminomethyl or amidomethyl moiety.

RESULTS AND DISCUSSION

So the radical addition of bis(trimethylsiloxy)phosphine **A** to element(Si, Ge, P, Fc)-substituted ethylenes resulting in formation of phosphonites **1–4** in high yields (cf. [7]). The reaction was initiated by azobis(isobutyronitrile) under conditions of its thermolysis (100–120°C) (Eq. (1)).

$$\underset{\mathbf{A}}{(Me_3SiO)_2PH} + CH_2{=}CHE \xrightarrow{R\cdot} \underset{\mathbf{1\text{-}4}}{(Me_3SiO)_2PCH_2CH_2E} \qquad (1)$$

$R\cdot = Me_2(NC)C\cdot$; $E = SiEt_3$ (**1**), $Si(OEt)_3$ (**2**), $GeEt_3$ (**3**), PPh_2 (**4**).

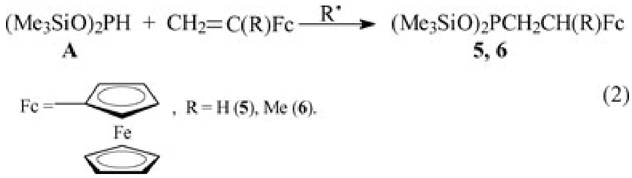
Also the similar addition of phosphine **A** to vinyl- and isopropenyl ferrocenes proceeds regioselectively

---

Correspondence to: Andrey A. Prishchenko; e-mail: aprishchenko@yandex.ru.

Contract grant sponsor: Russian Foundation for Basic Research.
Contract grant number: 08-03-00282.

to give 2-ferrocenyl-substituted alkylphosphonites **5, 6** in high yields (Eq. (2)).



(2)

Under similar conditions, the reaction of an excess of phosphine **A** with methyl(phenyl)divinylsilane provides a mixture of phosphonite **7** and bisphosphonite **8** in equal amounts. Phosphonites **7** and **8** were isolated by distillation in good yields (Eq. (3)).

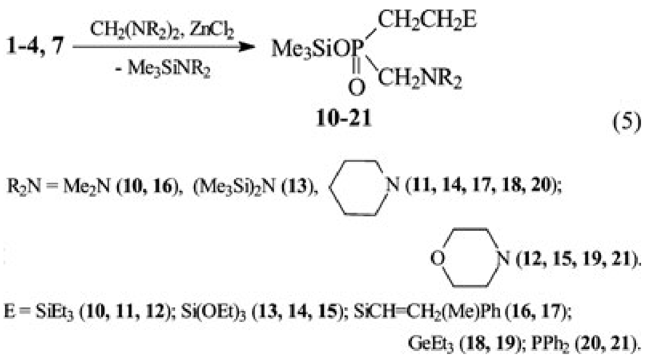
$$\underset{\mathbf{A}}{n\,(Me_3SiO)_2PH} + (CH_2{=}CH)_2Si(Me)Ph \xrightarrow{R\bullet} \underset{\mathbf{7}}{(Me_3SiO)_2PCH_2CH_2SiCH{=}CH_2(Me)Ph} + \underset{\mathbf{8}}{[(Me_3SiO)_2PCH_2CH_2]_2Si(Me)Ph} \quad (3)$$

Note that the similar reaction of an excess of phosphine **A** with phenyldivinylphosphine gives only bisphosphonite **9** (Eq. (4)).

$$\underset{\mathbf{A}}{2\,(Me_3SiO)_2PH} + (CH_2{=}CH)_2PPh \xrightarrow{R\bullet} \underset{\mathbf{9}}{[(Me_3SiO)_2PCH_2CH_2]_2PPh} \quad (4)$$

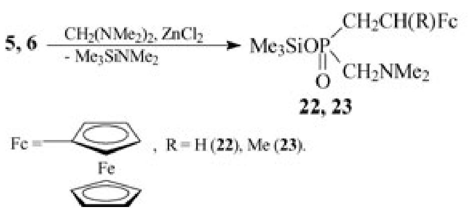
To conclude, we proposed a convenient method to give the new element(Si, Ge, P, Fc)-substituted alkylphosphonites **1–9** (see Table 1), which are the promising synthons in organophosphorus chemistry.

Phosphonites **1–9** were successfully used by us for preparing new derivatives of functionalized organophosphorus acids containing stable organoelement groups and aminomethyl group. The aminomethylation of trimethylsilyl esters of hypophosphorous and phosphorous acids was thoroughly investigated by us in [8]. Now we present the new results of aminomethylation of element(Si, Ge, P, Fc)-substituted alkylphosphonites. Hence, phosphonites **1–4,7** are easily aminomethylated with bis(dialkylamino)methanes at 130°C in the presence of zinc chloride as a catalyst to give corresponding phosphinates (**10–21**) in high yields (Eq. (5)). Note that to obtain phosphinate **13**, it is necessary to use *N*-methoxymethylbis(trimethylsilyl)amine $MeOCH_2N(SiMe)_2$ as an aminomethylating reagent.



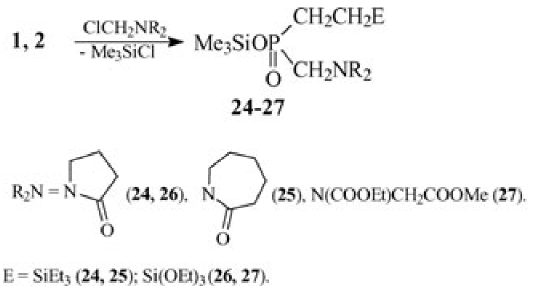
(5)

Ferrocenyl-substituted phosphonites **5, 6** are smoothly aminomethylated with bis(dimethylamino)methane under similar conditions to form phosphinates **22, 23** (Eq. (6)).



(6)

Silicon-substituted phosphonites **1, 2** readily react with various *N*-chloromethylamides in methylene chloride solution by the Arbuzov reaction scheme to form phosphinates **24–27** (Eq. (7)).



(7)

The constants and NMR data of synthesized phosphinates **10–27** are presented in Table 2.

Trimethylsilyl esters of several organophosphorus acids easily react with methanol to obtain a series of water-soluble acids [1]. So treatment of phosphonites **3–9** and phosphinates **16–23** with a dilute solution of sodium methylate in methanol results in formation of water-soluble sodium phosphonites **28–34** and sodium phosphinates **35–42**, respectively (Eq. (8)).

TABLE 1 Yields, Product Constants, and NMR Spectral Data for the $PC^1H_2C^2HE$ Fragments[a] (δ, ppm; J, Hz) of Phosphonites **1–9**[a]

No.	*Yield (%)*	*bp(°C) (p (mmHg))*	*$\delta(C^1)d$*	*$^1J_{PC}$*	*$\delta(C^2)d$*	*$^2J_{PC}$*	*$\delta(P)$ s*
1	89	108 (2)	34.92	26.3	1.34	10.1	159.74
2	87	103 (1)	33.91	25.8	1.09	11.9	159.34
3	78	113 (1)	35.67	25.7	3.70 s	–	158.30
4	83	164 (1)	36.44[b]	27.2	18.54[b]	13.3	157.23[b]
5[c]	88	162 (1)	42.10	24.3	20.73	16.2	158.74
6[d]	85	165 (1)	50.98	27.5	27.63	14.7	160.81
7	48	133 (1)	34.01	25.7	4.20	6.8	157.34
8	45	178 (1)	33.58	26.0	3.01	10.8	158.23
9	87	192 (1)	35.75[e]	26.4	17.63[e]	12.2	156.96[e]

[a] In ^1H NMR spectra, the signals of methylene groups of these fragments are multiplets and partially or completely overlap; all signals of the alkyl, vinyl, phenyl, trimethylsilyl, and ferrocenyl fragments are in the standard area.
[b] dd, $^2J_{PC} = 10.7$, $^1J_{PC} = 13.3$, respectively; d, $^3J_{PP} = 22.5$; δ_P (PPh_2) $= -15.17$ d, $^3J_{PP} = 22.5$.
[c,d] Cherry-red liquids; ^{13}C NMR spectrum, δ, ppm (J, Hz): **5**: 89.77 d (C_{Fc}, $^3J_{PC} = 12.2$); **6**: 96.81 d (C_{Fc}, $^3J_{PC} = 7.8$), 22.62 d (Me_{Pr}, $^3J_{PC} = 8.4$).
[e] d.d, $^2J_{PC} = 8.4$, $^1J_{PC} = 15.1$, respectively; d, $^3J_{PP} = 20.0$; δ_P (PPh) $= -20.67$ t, $^3J_{PP} = 20.0$.

TABLE 2 Yields, Product Constants, and NMR Spectral Data for the $PC^1H_2C^2H_2E$ and $PC^3H_2NC^4H_n$ Fragments[a] (δ, ppm; J, Hz) of Phosphinates **10–27**[a]

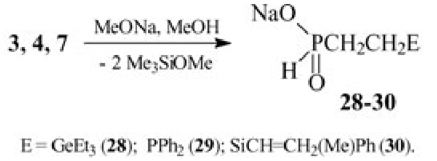
No.	*Yield (%)*	*bp(°C) (p, mmHg)*	*n_D^{20}*	*$\delta(C^1)$ d*	*$^1J_{PC}$*	*$\delta(C^2)$ d*	*$^2J_{PC}$*	*$\delta(C^3)$ d*	*$^1J_{PC}$*	*$\delta(C^4)d$*	*$^3J_{PC}$*	*$\delta(P)$ s*
10	81	115 (1)	1.4575	22.85	91.2	2.74	7	58.25	110.7	47.79	9.1	41.34
11	83	151 (2)	1.4705	23.05	90.2	2.91	7.3	57.91	110.8	56.97	8.4	41.48
12	85	132 (1)	1.4713	23.04	91.9	2.82	7.4	57.30	109.7	56.07	8.9	40.74
13	65	147 (2)	1.4458	22.24	85.5	1.54 s	–	45.26	102.8	–	–	40.78
14	74	146 (1)	1.4502	20.76	93.0	1.23	6.6	57.45	109.6	55.76	9.0	42.87
15	72	152 (1)	1.4498	21.03	95.0	1.45	6.5	56.14	111.4	54.90	8.8	41.80
16	78	141 (1)	1.5019	21.81	91.5	4.84	7.2	57.14	111.9	47.08	10.0	42.99
17	72	189 (2)	1.5085	21.60	91.2	4.78	6.7	56.31	117.7	55.68	8.3	43.32
18	67	160 (1)	1.4755	23.36	89.7	2.71	8.3	56.59	111.1	56.16	8.9	43.63
19	68	152 (1)	1.4785	23.38	90.7	1.94	8.2	56.03	110.8	55.05	9.1	42.35
20	65	208 (1.5)	1.5495	24.91[b]	91.2	19.87[b]	4.6	57.84	113.5	56.31	9.2	41.32[b]
21	68	202 (1)	1.5505	24.43[c]	91.5	19.52[c]	2.6	56.86	112.6	54.83	9.1	39.95[c]
22[d]	75	182 (1)	1.5435	29.04	92.3	21.40 s	–	57.93	113.3	47.13	9.8	40.90
23[e]	72	174 (0.5)	1.5422	36.52	92.2	27.38 s	–	58.95	112.2	47.22	9.4	40.60
				36.36	91.2	27.18 s	–	58.90	112.3	45.38	3.8	40.70
24	82	154 (1)	1.4785	23.54	88.9	2.45	7.4	42.08	101.6	48.11 s	–	39.35
25	78	175 (2)	1.4835	23.53	88.0	2.47	7.4	46.95	101.3	50.71 s	–	40.25
26	73	159 (1)	1.4527	22.84	90.7	1.26	4.2	42.05	102.3	48.69	8.1	39.09
27	69	176 (1)	1.4480	22.21	89.5	2.15	3.5	46.20	105.4	49.20	7.3	39.97

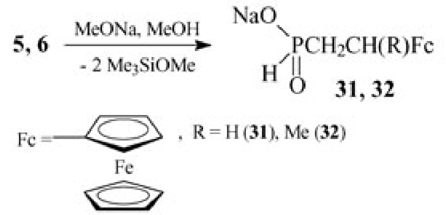
[a] In ^1H NMR spectra, the signals of methylene groups of these fragments are multiplets and partially or completely overlap; all signals of the alkyl, vinyl, phenyl, trimethylsilyl, and ferrocenyl fragments are in the standard area.
[b] dd, $^2J_{PC} = 15.0$, $^1J_{PC} = 14.9$, respectively; d, $^3J_{PP} = 50.5$; δ_P (PPh_2) $= -14.69$ d, $^3J_{PP} = 50.5$.
[c] dd, $^2J_{PC} = 15.2$, $^1J_{PC} = 14.8$, respectively; d, $^3J_{PP} = 49.7$; δ_P (PPh_2) $= -15.18$ d, $^3J_{PP} = 49.7$.
[d,e] Cherry-red liquids; ^{13}C NMR spectrum, δ, ppm (J, Hz): **22**: 87.81 d (C_{Fc}, $^3J_{PC} = 18.2$); **23**, first isomer: 95.65 d (C_{Fc}, $^3J_{PC} = 15.2$), 22.17 d (Me_{Pr}, $^3J_{PC} = 3.0$); **23**, second isomer: 95.53 d (C_{Fc}, $^3J_{PC} = 14.4$), 22.26 d (Me_{Pr}, $^3J_{PC} = 2.8$); ratio of stereoisomers 7:3 (measured by ^{31}P NMR).

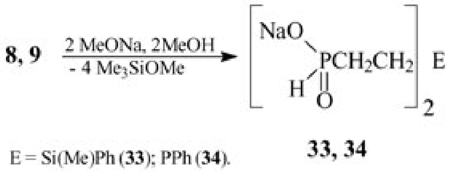
TABLE 3 Yields, Product Constants, and NMR Spectral Data for the $PC^1H_2C^2H_2E$ fragments[a] (δ, ppm; J, Hz) of Sodium Phosphonites **28–34**[a]

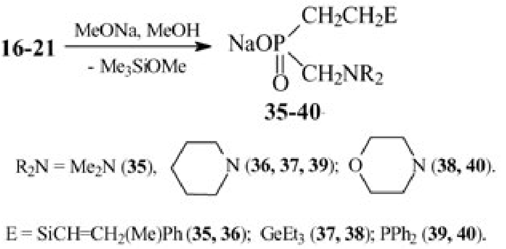
No.	*Yield (%)*	*δ(H) PH, d t*	$^1J_{PH}$	$^3J_{HH}$	*δ(C^1) d*	$^1J_{PC}$	*δ(C^2) d*	$^2J_{PC}$	*δ(P) s*[b]
28	97	6.82	497.2	2.0	26.95	87.2	2.18	5.9	32.13
29	96	6.88 d	508.0	–	28.99[c]	87.5	19.32[c]	<1	27.29[c]
30	96	6.84	495.6	1.6	25.84	88.3	5.23	5.2	30.93
31[d]	94	6.95 d	501.2	–	33.24	88.5	21.72 s	–	27.22
32[d]	95	7.03 d	502.4	–	41.07	89.2	28.22 s	–	25.69
33	94	6.83	499.2	1.8	25.46	88.0	4.33	5.4	31.06
34	93	6.90 d	506.4	–	27.70[e]	86.8	18.47[e]	<1	27.43[e]

[a] In ^{1}H NMR spectra, the signals of methylene groups of these fragments are multiplets and partially or completely overlap; all signals of the alkyl, vinyl, phenyl, and ferrocenyl fragments are in the standard area.
[b] Data of $^{31}P\{^1H\}$ spectra.
[c] dd, $^2J_{PC} = 13.8$, $^1J_{PC} = 10.1$, respectively; d, $^3J_{PP} = 53.7$; δ_P (PPh$_2$) = −15.61 d, $^3J_{PP} = 53.7$.
[d] Orange crystals; ^{13}C NMR spectrum, δ, ppm (J, Hz): **31**: 89.98 d (C$_{Fc}$, $^3J_{PC} = 18.9$); **32**: 87.28 d (C$_{Fc}$, $^3J_{PC} = 15.0$), 22.36 d (Me$_{Pr}$, $^3J_{PC} = 5.3$).
[e] dd, $^2J_{PC} = 10.3$, $^1J_{PC} = 7.9$, respectively; d, $^3J_{PP} = 46.4$; δ_P (PPh) = −19.29 t, $^3J_{PP} = 46.4$.

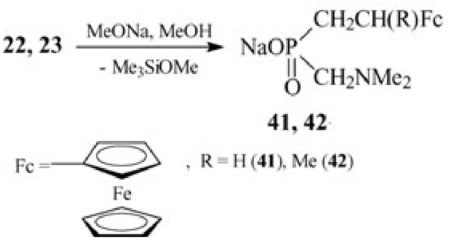








(8)



The synthesized salts are white (**28–30, 33–40**) or orange (**31, 32, 41, 42**) hygroscopic crystals (see Tables 3 and 4) and may be used as water-soluble ligands in promising catalytic complexes as well as biologically active compounds (cf. [9,10]). The elemental analysis data of some synthesized compounds are summarized in Table 5.

EXPERIMENTAL

The ^{1}H, ^{13}C, and ^{31}P NMR spectra were registered on a Varian VXR-400 spectrometer (400, 100, and 162 MHz, respectively) in $CDCl_3$ (**1–27**) or D_2O (**28–42**) against TMS (^{1}H, ^{13}C) and 85% H_3PO_4 in D_2O (^{31}P). All reactions were carried out under dry argon in anhydrous solvents.

*O,O- Bis(trimethylsilyl)2-(triethylsilyl)ethylphosphonite (**1**)*

A mixture of 31 g of bis(trimethylsiloxy)phosphine, 14 g of triethyl(vinyl)silane, and 0.3 g of azobis(isobutyronitrile) was heated to 100°C, and then the temperature was gradually raised to 120°C in 2 h. Distillation of the reaction mixture gave 30.9 g of phosphonite **1**.

Phosphonites **2–9** were prepared similarly.

*O-Trimethylsilyl(dimethylaminomethyl)-2-(triethylsilyl)ethylphosphinate (**10**)*

A mixture of 13.2 g of phosphonite **1**, 5 g of bis(dimethylamino)methane, and 0.1 g of zinc chloride was heated at 110–130°C for 1.5 h and then distilled to obtain 10.2 g of phosphinate **10**.

Phosphinates **11–23** were prepared similarly.

TABLE 4 Yields, Product Constants, and NMR Spectral Data for the $PC^1H_2C^2H_2E$ and $PC^3H_2NC^4H_n$ Fragments[a] (δ, ppm; *J*, Hz) of Sodium Phosphinates **35–42**[a]

No.	Yield (%)	$\delta(C^1)$d	$^1J_{PC}$	$\delta(C^2)$d	$^2J_{PC}$	$\delta(C^3)$d	$^1J_{PC}$	$\delta(C^4)$d	$^3J_{PC}$	$\delta(P)$ s
35[b]	95	24.30	89.7	6.27	6.4	58.06	99.4	47.27	7.9	37.95
36[b]	93	25.01	88.5	6.57	6.6	57.83	98.6	56.19	7.0	38.66
37	95	26.69	87.5	4.26	5.4	57.77	98.3	56.38	7.1	38.62
38	96	25.53	88.2	3.45	5.2	57.38	102.2	55.58	8.1	38.82
39	95	28.08[c]	92.6	21.57[c]	<1	59.27	105.2	56.80	4.9	34.09[c]
40	95	27.81[d]	89.7	21.79[d]	<1	58.78	103.3	55.60	7.5	34.16[d]
41[e]	95	31.59	89.7	22.49 s	–	58.94	100.9	47.33	8.0	36.44
42[e]	93	39.73	88.5	28.37 s	–	60.22	101.0	47.55	8.0	35.01

[a] The salts **35–42** are very hydroscopic crystals; therefore, their melting points were not measured. In ^1H NMR spectra, the signals of methylene groups of these fragments are multiplets and partially or completely overlap; all signals of the alkyl, vinyl, phenyl, and ferrocenyl fragments are in the standard area.

[b] ^1H NMR spectrum, δ, ppm (*J*, Hz): **35**: 4.49 d (C^3H_2, $^2J_{PH} = 9.2$), 2.23 c (C^4H_3); **36**: 3.50 d (C^3H_2, $^2J_{PH} = 9.2$); 2.42 t (C^4H_2, $^2J_{HH} = 5.2$).

[c] dd, $^2J_{PC} = 12.1$, $^1J_{PC} = 11.8$, respectively; d, $^3J_{PP} = 47.1$; δ_P (PPh_2) = – 14.43 d, $^3J_{PP} = 47.1$.

[d] d. d, $^2J_{PC} = 12.5$, $^1J_{PC} = 12.1$, respectively; d, $^3J_{PP} = 48.4$; δ_P (PPh_2) = – 14.97 d, $^3J_{PP} = 48.4$.

[e] Orange crystals; ^{13}C NMR spectrum, δ, ppm (*J*, Hz): **41**: 90.46 d (C_{Fc}, $^3J_{PC} = 18.6$); **42**: 98.04 d (C_{Fc}, $^3J_{PC} = 14.9$), 22.84 c (Me_{Pr}).

TABLE 5 Elemental Analyses Data of Synthesized Compounds[a]

			Calcd. (%)		Found (%)	
No.	Empirical Formula	Formula Weight	C	H	C	H
10	$C_{14}H_{36}NO_2PSi_2$	337.58	49.81	10.75	49.52	10.60
11	$C_{17}H_{40}NO_2PSi_2$	377.64	54.07	10.68	53.86	10.59
12	$C_{16}H_{38}NO_3PSi_2$	379.62	50.62	10.09	50.49	9.97
13	$C_{18}H_{48}NO_5PSi_4$	501.90	43.08	9.64	42.83	9.57
14	$C_{17}H_{40}NO_5PSi_2$	425.66	47.97	9.47	47.75	9.39
15	$C_{16}H_{38}NO_6PSi_2$	427.63	44.94	8.96	44.72	8.81
24	$C_{16}H_{36}NO_3PSi_2$	377.60	50.90	9.61	50.95	9.54
25	$C_{18}H_{40}NO_3PSi_2$	405.65	53.30	9.94	53.04	9.98
26	$C_{16}H_{36}NO_6PSi_2$	425.61	45.15	8.52	44.96	8.43
27	$C_{18}H_{40}NO_9PSi_2$	501.66	43.10	8.04	42.93	7.89
28	$C_8H_{20}GeNaO_2P$	284.80	34.97	7.37	34.72	7.49
29	$C_{14}H_{15}NaO_2P_2$	300.21	56.01	5.04	55.87	5.12
30	$C_{11}H_{16}NaO_2PSi$	262.30	50.37	6.15	50.26	6.09
31	$C_{12}H_{14}FeNaO_2P$	300.05	48.04	4.70	47.89	4.75
32	$C_{13}H_{16}FeNaO_2P$	314.08	49.71	5.14	49.52	5.22
33	$C_{11}H_{18}Na_2O_4P_2Si$	350.28	37.72	5.18	37.59	5.10
34	$C_{10}H_{15}Na_2O_4P_3$	338.13	35.52	4.47	35.30	4.59
35	$C_{14}H_{23}NNaO_2PSi$	319.39	52.65	7.26	52.57	7.12
36	$C_{17}H_{27}NNaO_2PSi$	359.46	56.80	7.57	56.64	7.49
37	$C_{14}H_{31}GeNNaO_2P$	371.95	45.21	8.40	45.02	8.52
38	$C_{13}H_{29}GeNNaO_3P$	373.92	41.76	7.88	41.65	7.82
39	$C_{20}H_{26}NNaO_2P_2$	397.38	60.45	6.60	60.26	6.69
40	$C_{19}H_{24}NNaO_3P_2$	399.35	57.15	6.06	56.83	6.16
41	$C_{15}H_{21}FeNNaO_2P$	357.16	50.45	5.93	50.28	6.02
42	$C_{16}H_{23}FeNNaO_2P$	371.19	51.77	6.24	51.49	6.14

[a] The other compounds are unstable in the air atmosphere; therefore, these substances were analyzed as their sodium salts.

*O-Trimethylsilyl(2-oxopyrrolidino)methyl-2-(triethylsilyl)ethylphosphinate (**24**)*

A solution of 2.6 g of *N*-chloromethylpyrrolidone-2 in 10 mL of methylene chloride was added dropwise to a solution of 6.6 g of **1** in 15 mL of methylene chloride. The resulting mixture was heated to boiling, the solvent was removed, and the residue was distilled in a vacuum to obtain 5.8 g of phosphinate **24**.

Phosphinates **25–27** were prepared similarly.

*Sodium 2-(triethylgermyl)ethylphosphonite (**28**)*

A solution of 4 g of phosphonite **3** in 5 mL of diethyl ether was added with stirring at 10°C to a solution of 0.55 g of sodium methylate in 30 mL of methanol. The reaction mixture was heated to boiling, the solvent was distilled off, and the residue was subjected to vacuum (1 mmHg) for 1 h to give 2.7 g of salt **28**.

The salts **29–42** were prepared similarly.

REFERENCES

[1] Wozniak, L.; Chojnowski, J. Tetrahedron 1989, 45, 2465–2524.

[2] Prishchenko, A. A.; Livantsov, M. V.; Minko, S. V.; Petrosyan, V. S. Zh Obsh Khim 1992, 62, 1430–1432 (in Russian).

[3] Voronkov, M. G.; Dyakov, V. M. Silatranes; Nauka: Novosibirsk, USSR, 1978.

[4] Lutsenko, I. F. Pure Appl Chem 1972, 30, 409–425.

[5] Lesbre, M.; Mazerolles, P.; Satge, J. The Organic Compounds of Germanium; Academic Press: London, 1971.

[6] Jemilev, U. M.; Porodko, N. R.; Kozlova, E. V. Metal Complex Catalysis in Organic Synthesis; Khimiya: Moscow, 1999.

[7] Voronkov, M. G.; Marmur, L. Z.; Dolgov, O. N.; Pestunovich, V. A.; Pokrovskii, E. I.; Popel, Yu. I. Zh Obsh Khim 1971, 41, 1987–1991 (in Russian).

[8] Prishchenko, A. A.; Livantsov, M. V.; Petrosyan, V. S. Zh Obsh Khim 1994, 64, 1316–1330 (in Russian).

[9] Kukhar, V. P.; Hudson, H. R. Aminophosphonic and Aminophosphinic Acids. Chemistry and Biological Activity; Wiley: New York, 2000.

[10] Kolodiazhnyi, O. I. Usp Khim 2006, 75, 254–282 (in Russian).