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Synthesis of 2-Substituted *O*,*O*-Bis(trimethylsilyl) Alkylphosphonites with Aryl and Heterocyclic Fragments and Their Amino or Amido Derivatives

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ABSTRACT: *Free-radical addition of bis(trimethylsiloxy)phosphine to various functionalized alkenes with aryl and heterocyclic fragments is proposed as a convenient procedure for the synthesis of new 2-substituted alkylphosphonites of corresponding structures. 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 19:345–351, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20431

INTRODUCTION

The reaction of P—H phosphines with organic compounds, containing multiple bonds, provides a convenient synthetic route to functionalized organophosphorus compounds [1]. Recently we have synthesized the new 2-element(Si, Ge, P, Fe) substituted alkylphosphonites with high yields via the radical addition of bis(trimethylsiloxy)phosphine to element(Si, Ge, P, Fe) substituted alkenes [2]. Also the functionalized derivatives of organophosphorus acids containing aryl or heterocyclic fragments and various amino or amido groups have great interest as promising polydentate ligands in a series of catalytic systems and biologically active compounds as organophosphorus biomimetics of amino acids [3,4]. In the present work, we report here the results of the radical addition of bis(trimethylsiloxy)phosphine to styrene, 2-vinylfuran, isomeric vinylpyridines, *N*-vinylcarbazole, *N*-vinyl-2-pyrrolidone, indene, and aryl-substituted acetylenes, resulting in formation of corresponding phosphonites in high yield. Futhermore, amino or amidomethylation of these phosphonites results in the new derivatives of organophosphorus acids containing aryl or heterocyclic fragments and various aminomethyl or amidomethyl moieties.

RESULTS AND DISCUSSION

So the radical addition of bis(trimethylsiloxy)phosphine **A** to functionalized ethylenes with aryl groups or heterocyclic fragments results in 2-substituted ethylphosphonites **1–7** with high yields (cf. [5]). The reaction was initiated by azobis(isobutyronitrile) under thermolytic conditions (100–120°C) (Eq. (1)).

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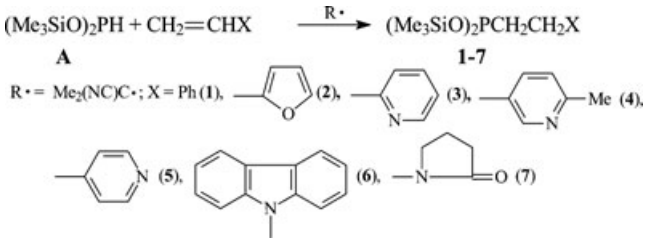
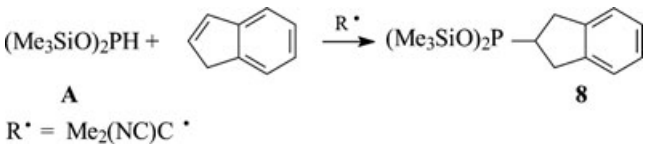


(1)

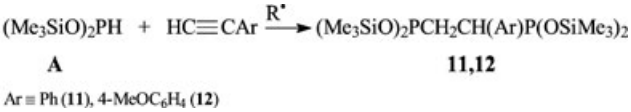
Also the similar addition of phosphine **A** to indene proceeds regioselectively to give indan-2-ylphosphonite **8** in high yield (Eq. (2)).



(2)

Note that even with the excess of phosphine **A** the considerable amount of phosphonites **9, 10** is formed by the reaction with styrene and 2-vinylfuran due to the propagation of the radical process on an another molecule of substituted ethylene. Evidently, formation of phosphonites **9, 10** is due to the chain transfer to the substituted ethylene molecule via intermediate radicals **B** and **C**. So we showed that the reaction of phosphine **A** with styrene at 1:1.7 molar ratio gives phosphonite **9** with 22% yield together with phosphonite **1**. The use of solvents such as bis(trimethylsilyl)amine and toluene reduces the formation of polymeric tars but does not allow preparation of phosphonite **9** in a higher yield under the given conditions. This may be due to high reactivity of the P—H bond in the radical processes [6] (Eq. (3)).

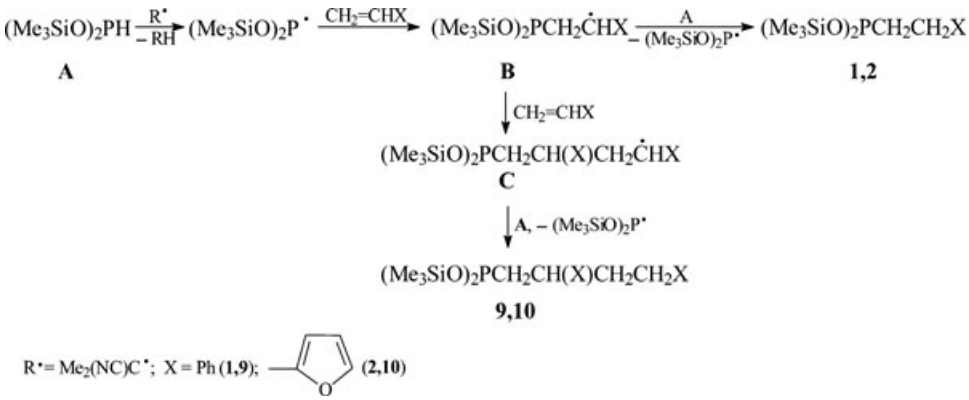
Also we showed that the excess of phosphine **A** reacts with aryl-substituted acetylenes under similar conditions via double regioselective addition to the acetylene fragment to form bisphosphonites **11, 12** (Eq. (4)).



(4)

To conclude, we proposed a convenient method to give the new 2-substituted ethylphosphonites or bisphosphonites with aryl or heterocyclic fragments **1–12** (see Table 1), which are the promising synthons in organophosphorus chemistry.

Phosphonites **1–12** were successfully used by us for preparing new derivatives of functionalized organophosphorus acids containing aryl or heterocyclic fragments. The aminomethylation of element (Si, Ge, P, Fe) substituted alkylphosphonites was thoroughly investigated by us in [2]. Now, we present the new results of aminomethylation of 2-alkylphosphonites with aryl or heterocyclic fragments. Phosphonites **1–9** undergo facile aminomethylation under the action of *N*-chloromethylamines, amides, or aminals, yielding new functionalized phosphinates **13–27**. So phosphonites **1, 7, 9** readily react with various *N*-chloromethylamides in the methylene chloride solution by the Arbuzov reaction scheme to form phosphinates **13–18** (Eq. (5)).

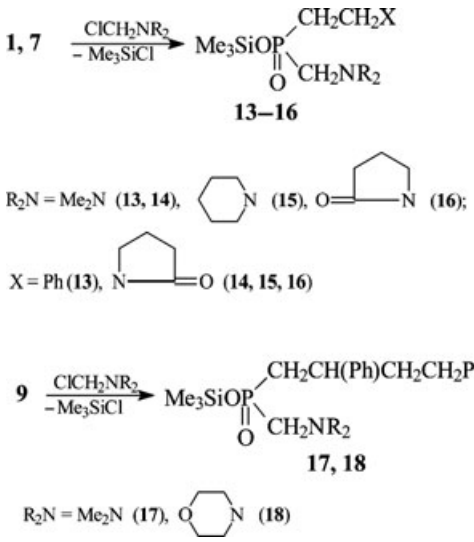


(3)

TABLE 1 Yields, Product Constants, and NMR Spectral Data for the $PC^1H_mC^2H_nC^3$ Fragments[a] (δ, ppm; *J*, Hz) of Phosphonites **1–12**

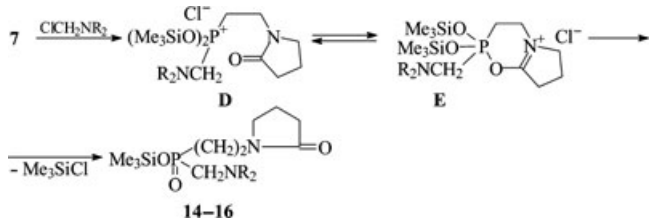
No.	*Yield (%)*	*bp (°C) (p, mm Hg)*	δ (C^1) d	$^1J_{PC}$	δ (C^2) d	$^2J_{PC}$	δ (C^3) d	$^3J_{PC}$	δ (P) s
1	91	83 (0.5)	43.80	25.8	27.93	14.5	143.27	9.3	159.10
2	64	92 (1)	38.97	25.1	19.64	15.1	156.19	10.6	157.22
3	90	114 (1)	41.52	25.6	30.34	13.8	162.80	9.3	159.65
4	89	120 (1)	43.22	26.7	24.56	14.7	134.94	9.1	158.27
5	93	116 (1)	42.09	26.3	26.97	14.5	151.44	9.1	157.52
6	86	185 (1)	39.69	27.2	35.74	13.3	140.21[b]	–	156.87
7	76	133 (2)	39.82	27.1	36.04	16.2	173.07[c]	–	158.24
8	83	126 (1)	46.27	20.3	31.99	19.7	143.06	5.6	155.56
9[d]	22	149 (1)	50.43	28.8	39.84	12.4	146.28	4.5	160.48
10[d]	25	135 (1)	46.09	28.1	33.76	6.9	157.81	4.6	158.33
11[e]	78	133 (0.5)	40.27	31.7	50.72	9.6	139.81	3.1	160.89
12[e]	74	133 (0.5)	39.60	30.0	49.07	11.3	130.75	3.4	164.33

[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, trimethylsilyl, aryl, and heterocyclic fragments are in the standard area.
[b]s, NC^3.
[c]s, NC═O.
[d]Fragments $PC^1H_2C^2H(C^3)C^4H_2C^5H_2C^6$, ^{13}C NMR spectra, δ (ppm), *J* (Hz): **9**: 40.23 d (C^4, $^3J_{PC}$ 7.4), 34.0 s (C^5); 142.39 s (C^6); **10**: 32.43 d (C^4, $^3J_{PC}$ 12.6), 25.35 s (C^5); 155.39 s (C^6).
[e]Fragments $P^1C^1H_2C^2H(C^3)P^2$, ^{13}C NMR spectrum, δ (ppm) (*J* (Hz): **11**: 40.27 dd (C^1, $^1J_{PC}$ 31.7, $^2J_{PC}$ 15.5), 50.72 dd (C^2, $^1J_{PC}$ 30.3, $^2J_{PC}$ 9.6), 139.81 dd (C^3, $^2J_{PC}$ 9.1, $^3J_{PC}$ 3.1); ^{31}P NMR spectrum: 160.89 d (P^1, $^3J_{PP}$7.0), 148.84 d (P^2, $^3J_{PP}$7.0); **12**: ^{13}C NMR spectrum, δ (ppm) (*J*, Hz): 39.60 dd (C^1, $^1J_{PC}$ 30.0, $^2J_{PC}$ 14.9), 49.07 dd (C^2, $^1J_{PC}$ 27.6, $^2J_{PC}$ 11.3), 130.75 dd (C^3, $^2J_{PC}$ 9.0, $^3J_{PC}$ 3.4), 55.02 s (OCH_3), 157.85 s (OC_{Ar}); ^{31}P NMR spectrum: 164.33 d (P^1, $^3J_{PP}$ 8.4), 151.46 d (P^2, $^3J_{PP}$ 8.4).



(5)

Note that phosphonite **7** easily reacts with various *N*-chloromethylamines (amides) with initial formation of viscous oils or crystals, presumably phosphonium and immonium salts **D** and **E**. Several singlets of intermediates **D** and **E** in the reaction mixtures were observed in ^{31}P NMR spectra at 44.7, 46.5, 47.8, and 49.7 ppm in the ratio 30:30:15:25. These intermediates, when heated, decompose to trimethylchlorosilane and unsymmetrical phosphinates **14–16**. The unusual stability of the intermediates is undoubtedly connected with the reversible formation of cyclic immonium salt **E** (cf. [7, 8]); Eq. (6)).



(6)

On the other hand, phosphonites **2–6** are smoothly aminomethylated with bis(dialkylamino)-methanes at 130°C in the presence of zinc chloride as a catalyst to give corresponding phosphinates **19–25** in high yield (Eq. (7)).

(7)

TABLE 2 Yields, Product Constants, and NMR Spectral Data for the $PC^1H_mC^2H_nC^3$ and $PC^4H_2NC^5H_n$ Fragments[a] (δ, ppm; J, Hz) of Phosphinates **13–27**

No	Yield (%)	bp (°C) (p, mm Hg)	n_D^{20} (mp, °C)	$\delta(C^1)$ d	$^1J_{PC}$	$\delta(C^2)$ s	$\delta(C^3)$ d	$^3J_{PC}$	$\delta(C^4)$ d	$^1J_{PC}$	$\delta(C^5)$ d	$^3J_{PC}$	$\delta(P)$ s
13	86	125 (2)	1.4935	30.95	91.4	28.62[a]	142.05	13.9	59.27	112.1	47.75	9.6	38.69
14	71	160 (2)	1.4805	27.35	90.7	36.56	173.54[b]	–	59.01	113.7	47.70	7.5	37.45
15	75	185 (2)	1.4885	23.65	90.4	36.77	173.52[b]	–	58.88	113.5	56.85	9.3	37.24
16	73	192 (2)	1.4948	27.84	88.0	36.46	173.75[b]	–	43.25	104.5	174.08[b]	–	34.78
17	89	191 (2)	1.5239	[c]	–	–	–	–	59.73	112.3	47.64	6.1	37.59
				[c]	–	–	–	–	59.18	111.7	47.40	7.8	38.79
18	74	194 (0.5)	1.5250	[c]	–	–	–	–	58.46	112.0	55.84	8.6	38.18
				[c]	–	–	–	–	58.65	111.6	55.74	11.3	36.98
19	83	118 (1)	1.4720	26.05	93.1	19.83	153.39	16.4	57.67	113.7	46.60	10.0	39.32
20	78	158 (1)	(42)	26.77	93.1	20.37	154.04	16.4	57.79	113.8	56.03	9.2	39.81
21	86	152 (1)	1.4848	26.33	93.7	19.99	153.45	16.0	56.85	112.7	54.60	9.1	38.59
22	95	178 (1)	1.5009	28.31	92.9	29.83	160.11	14.6	57.95	113.3	56.03	9.1	40.51
23	90	190 (2)	(45)	29.59	92.4	24.40	132.74	14.3	57.34	112.4	54.88	9.1	38.84
24	93	184 (1)	(39)	28.89	93.4	27.21	149.38	18.6	57.74	113.5	55.22	9.1	38.64
25	83	197 (1)	1.5117	27.33	89.3	35.86	138.81[d]	–	58.38	115.0	46.72	10.0	38.04
26	74	141 (1)	1.5068	35.54	97.9	31.63	140.53	9.1	56.66	112.1	46.51	9.7	41.55
						32.23	140.70	9.1			46.61	10.5	
27[e]	70	187 (1)	1.5131	36.14	96.7	31.75	140.78	8.9	42.50	101.0	35.29 s	–	38.81
						32.80	140.93	8.6			161.65[b]	–	
				35.91	96.1	32.04	140.33	8.8	46.89	99.5	35.29 s	–	38.26
						32.47	140.46	8.4			162.12[b]	–	

[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, trimethylsilyl, aryl, and heterocyclic fragments are in the standard area. For **13**: δ (C^2) 28.62 d ($^2J_{PC}$ 3.7). Compounds **17, 18**, and **27** are mixtures of two stereoisomers; note that the two $C^2H_2C^3$ and C^5H_2 groups in compounds **26** and **27**, which contain asymmetric phosphorus centers are nonequivalent and give different signals in the ^{13}C NMR spectra for each isomer. The ratio of stereoisomers was measured by ^{31}P NMR.

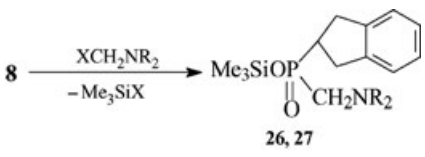
[b]s, NC=O.

[c]The signals of the C^1–C^8 carbon atoms of the fragments $PC^1H_2C^2H(C^3)C^6H_2C^7H_2C^8$ in the ^{13}C NMR spectra of diastereomers of **17** and **18** are overlapping singlets and doublets at 30–40 and 140–145 ppm. The ratio of stereoisomers, 65:35 (**17**); 85:15 (**18**).

[d]s. NC^3.

[e] 1H NMR spectrum: first isomer (75%): 7.78 s (CHO), 2.87 s (C^5H_3); second isomer (25%): 7.72 s (CHO), 2.77 s (C^5H_3).

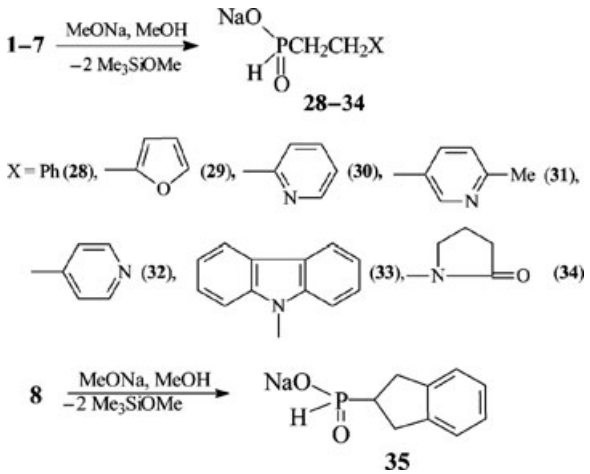
Note that to obtain indanylphosphonites **26, 27** it may be used as aminomethylating reagents both bis(dimethylamino)methane and *N*-chloromethyl-*N*-methylformamide. So, phosphonite **8** undergoes facile aminomethylation giving phosphinates **26, 27**, containing the bicyclic indane fragments in high yields (Eq. (8)).

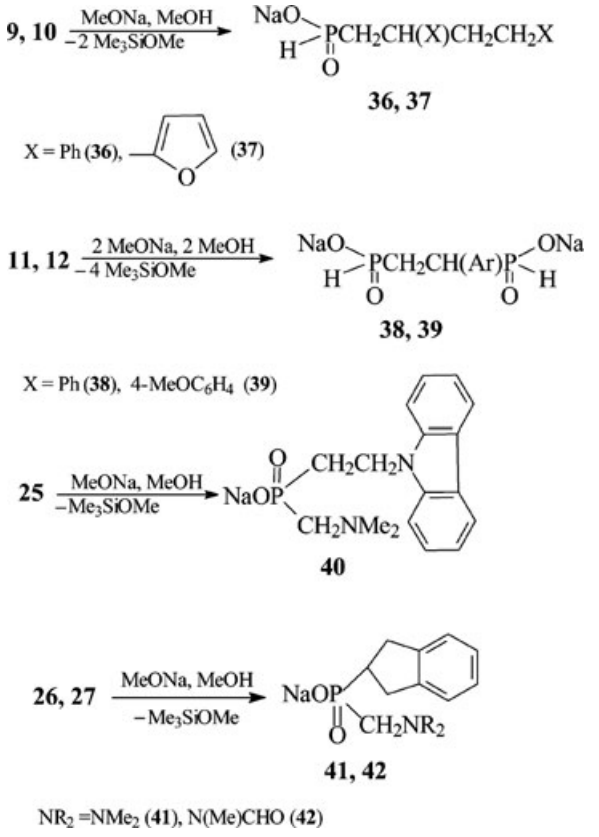


NR_2 =NMe_2 (**26**), N(Me)CHO (**27**); X= Cl, NR_2

(8)

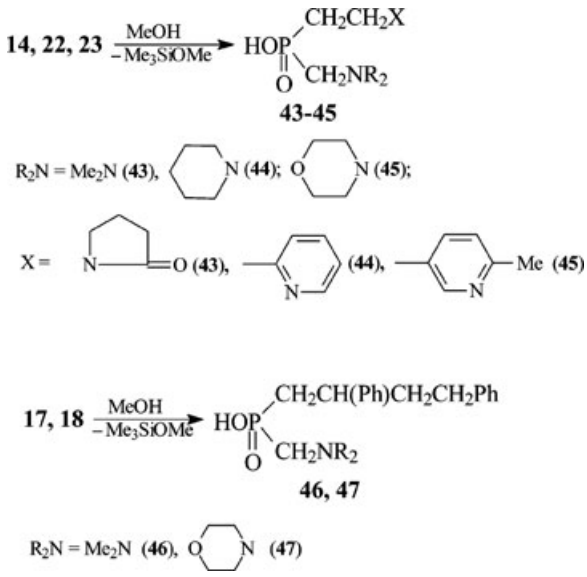
The constants and NMR data of synthesized phosphinates **13–27** are presented in Table 2. Trimethylsilyl esters of several organophosphorus acids easily react with methanol to give a series of water-soluble acids (cf. [2]). So treatment of phosphonites **1–12** and phosphinates **25–27** with a diluted solution of sodium methylate in methanol results in water-soluble sodium phosphonites **28–39** and sodium phosphinates **40–42**, respectively (Eq. (9)).





(9)

Also the phosphinates **14, 17, 18, 22, 23** were easily transformed to corresponding phosphinic acids **43–47** in high yields (Eq. (10)).



(10)

Synthesized salts **28–42** and acids **43–47** are white 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. [3,4]). The elemental analysis data of some synthesized compounds are summarized in Table 5.

TABLE 3 Yields, Product Constants, and NMR Spectral Data for the $HPC^1H_mC^2H_nC^3$ Fragments[a] (δ, ppm; J, Hz) of Sodium Phosphonites **28–39**[a]

No	*Yield (%)*	*δ(H) PH, dt*	*$^1J_{PH}$*	*$^3J_{HH}$*	*δ(C¹) d*	*$^1J_{PC}$*	*δ(C²) s*	*δ(C³) d*	*$^3J_{PC}$*	*δ(P) s*[b]
28	97	7.02	510.7	2.6	31.25	87.1	27.40	141.12	16.9	24.10
29	94	6.88	508.0	2.0	29.71	89.4	20.17	155.55	15.5	26.15
30	96	6.93	505.6	<1	31.55	88.4	29.39	160.46	16.7	34.74
31	98	6.94	507.2	<1	30.49	89.7	23.12	133.81	15.9	24.75
32	95	6.90	506.4	<1	31.81	88.5	26.97	152.65	15.7	25.55
33	95	6.90	510.6	1.8	31.46	84.8	36.70	140.14[c]	–	21.92
34	97	6.94	510.0	2.0	29.56	86.5	36.55	177.89[d]	–	22.30
35	97	6.83[e]	500.7	2.2	38.84	94.5	32.19	142.66	9.1	32.81
36[f]	95	6.78	506.9	2.9	40.37	87.7	39.97	145.26	7.1	22.21
37[f]	93	6.74	510.0	2.4	36.33	89.5	33.18	156.88	6.7	23.53

[a]The salts **28–37** 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, aryl, and heterocyclic fragments are in the standard area. Salt **38**, yield 98%; fragment $P^1C^1H_2C^2H(C^3)P^2$; ^1H NMR spectrum: 6.65 d (P^1H, $^1J_{PH}$ 516.3), 6.78 dd (P^2H, $^1J_{PH}$ 515.5, $^3J_{HH}$ 2.4). ^{13}C NMR spectrum: 29.66 d (C^1, $^1J_{PC}$ 89.5); 43.04 d (C^2, $^1J_{PC}$ 82.9); 136.4–134.4 m (C^3), ^1P NMR spectrum: 29.06 dd (P^1, $^1J_{PH}$ 516.3, $^3J_{PP}$ 55.6), 23.56 dd (P^2, $^1J_{PH}$ 515.5, $^3J_{PP}$ 55.6). Salt **39**, yield 96%; fragment $P^1C^1H_2C^2H(C^3)P$; ^1H NMR spectrum: 6.52 d (P^1H, $^1J_{PH}$ 519.4), 6.81 dd (P^2H, $^1J_{PH}$ 522.1, $^3J_{HH}$ 2.6). ^{13}C NMR spectrum: 30.05 d (C^1, $^1J_{PC}$ 90.3); 41.89 d (C^2, $^1J_{PC}$ 83.7); 135.1–135.3 m (C^3), 54.92 s (OCH_3), 158.01 s (OC_{Ar}), ^1P NMR spectrum: 35.83 dd (P^1, $^1J_{PH}$ 519.4, $^3J_{PP}$ 57.1), 29.55 dd (P^2, $^1J_{PH}$ 522.1, $^3J_{PP}$ 57.1).

[b]Data of $^{31}P\{^1H\}$ spectra.

[c]s, NC^3.

[d]s, NC═O.

[e]dd.

[f] Fragments $PC^1H_2C^2H(C^3)C^4H_2C^5H_2C^6$, ^{13}C NMR spectra: **36**: 37.87 d (C^4, $^3J_{PC}$ 6.7), 33.92 s (C^5), 142.89 s (C^6); **37**: 33.74 d (C^4, $^3J_{PC}$ 11.3), 25.14 s (C^5), 155.58 s (C^6).

TABLE 4 Yields, Product Constants, and NMR Spectral Data for the $PC^1H_mC^2H_nC^3$ and $PC^4H_2NC^5H_n$ Fragments[a] (δ, ppm; J, Hz) of Sodium Phosphinates **40–42**[a] and Phosphinic Acids **43–47**

No	*Yield (%)*	*Mp (°C)*	δ_H, C^4H_2	$^2J_{PH}$	δ (C^1) d	$^1J_{PC}$	δ(C^2) s	δ(C^3) d	$^3J_{PC}$	δ(C^4) d	$^1J_{PC}$	δ(C^5) d	$^3J_{PC}$	δ(P) s
40	94	–	2.11	8.8	30.97	87.0	37.58	140.07[b]	–	59.21	110.4	47.93	7.8	32.61
41	95	–	2.35[c]	–	37.71	96.6	33.08	142.89	9.9	57.46	99.1	46.84	4.2	37.83
42[d]	95	–	7.71[d]	–	37.20	96.4	33.09	142.70	9.3	43.67	94.2	36.56 s	–	35.86
			7.91[d]	–	37.69	97.6	33.09	142.39	8.6	43.52	94.4	36.62 s	–	36.30
43	97	145	3.05	7.3	29.95	95.2	35.30	173.89[b]	–	58.07	90.2	47.59 s	–	27.26
44	96	162	3.17	7.6	31.74	97.1	27.38	153.13	15.2	55.25	81.9	55.87 s	–	26.04
45	96	194	2.97	8.4	31.76	93.7	24.75	136.81	15.1	56.56	89.7	54.47	5.9	29.37
46[e]	96	[f]	2.45	5.6	39.07	76.8	39.73	145.40	4.7	56.50	79.7	44.78	3.9	21.97
47[e]	95	58	2.61	6.4	39.92	85.6	40.35	144.67	4.5	56.40	80.4	53.99	4.2	24.23

[a]The salts **40–42** are very hygroscopic crystals; therefore, their melting points were not measured. In ^1H NMR spectra, the signals of methylene groups of these fragments are usually multiplets and partially or completely overlap; all signals of the alkyl, aryl, and heterocyclyc fragments are in the standard area.
[b]s: NC^3 (**40**), NC═O (**43**).
[c]s, NMe_2.
[d]Compound **42** is a mixture of two stereoisomers in ratio 55:45 (measured by ^1H and ^{31}P NMR); in ^1H NMR spectrum signals of C^4H_2 groups are multiplets; the fragments NCHO were given, δ_C (C═O) 165.36 s and 164.51 s respectively.
[e]^{13}C NMR spectra for fragments $PC^1H_2C^2H(C^3)C^6H_2C^7H_2C^8$: **46**: 39.61 d ($C^6$, $^3J_{PC}$ 8.2), 32.68 s (C^7), 142.38 s (C^8); **47**: 40.06 d (C^6, $^3J_{PC}$ 12.4), 33.49 s (C^7), 141.86 s (C^8).
[f] Viscous oil.

EXPERIMENTAL

The ^1H, ^{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(**28–47**) against TMS (^1H, ^{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-phenylethylphosphonite (**1**) and O,O-bis(trimethylsilyl)-2,4-diphenylbutylphosphonite (**9**)*

(*a*) A mixture of 23 g of bis(trimethylsilyloxy)-phosphine, 10.4 g of styrene, and 0.3 g of azobis(isobutyronitrile) was heated to 100°C, and then within 2 h the temperature was gradually raised to 130°C. The resulting mixture was distilled in a vacuum to give 28.6 g of phosphonite **1**.

(*b*) A mixture of 12.6 g of bis(trimethylsiloxy)-phosphine, 10.4 g of styrene, 0.3 g of azobis(isobutyronitrile), 20 mL of bis(trimethylsilyl)-amine, and 10 mL of toluene was heated to 100°C. After that the temperature was raised to 120°C over a period of 1 h, vacuum distillation of the resulting mixture gave two fractions with bp 80–130°C (2 mm) and 150–180°C (2 mm). Repeated distillation of the first fraction gave 10 g (32%) of phosphonite **1**, and repeated distillation of the second fraction gave 4.5 g (22%) of phosphonite **9**.

Phosphonites **2–8** and **10–12** were prepared similarly.

*O-Trimethylsilyl Dimethylaminomethyl-(2-phenylethyl)phosphinate (**13**)*

A solution of 1 g of (chloromethyl)dimethylamine in 10 mL of methylene chloride was added dropwise with stirring to a solution of 3.5 g of phosphonite **1** in 10 mL of methylene chloride. The mixture was heated to the boil, the solvent was removed, and the residue was distilled in a vacuum to give 2.8 g of phosphinate **13**.

Phosphinates **14–18, 27** were prepared similarly.

*O-Trimethylsilyl[2-(2-furyl)ethyl](dimethylaminomethyl)phosphinate (**19**)*

A mixture of 7 g of phosphonite **2**, 2.8 g of bis(dimethylamino)methane, and 0.1 g of zinc chloride was heated at 130°C for 1 h and then distilled to obtain 5.5 g of phosphinate **19**.

Phosphinates **20–26** were prepared similarly.

*Sodium 2-Phenylethylphosphonite (**28**)*

A solution of 7.3 g of phosphonite **1** in 10 mL of diethyl ether was added at 10°C with cooling and stirring to 30 mL of methanol, followed by a solution of 1.25 g of sodium methylate in 27 mL of methanol. The mixture was heated to the boil, the solvent was removed, and the residue was kept in a vacuum (1 mm) for 1 h to obtain 4.3 g of salt **28** as colorless hygroscopic crystals.

TABLE 5 Elemental Analyses Data of Synthesized Compounds[a]

			Calcd. (%)		Found (%)	
No	*Empirical Formula*	*Formula Weight*	*C*	*H*	*C*	*H*
13	$C_{14}H_{26}NO_2PSi$	299.43	56.15	8.75	55.94	8.58
14	$C_{12}H_{27}N_2O_3PSi$	306.46	47.03	8.88	46.90	8.74
15	$C_{15}H_{31}N_2O_3PSi$	346.48	52.00	9.02	51.83	8.84
16	$C_{14}H_{27}N_2O_4PSi$	346.49	48.53	7.86	48.31	7.68
17	$C_{22}H_{34}NO_2PSi$	403.58	65.47	8.49	65.09	8.57
18	$C_{24}H_{36}NO_3PSi$	445.62	64.69	8.14	64.32	8.01
19	$C_{12}H_{24}NO_3PSi$	289.38	49.81	8.36	49.52	8.20
20	$C_{14}H_{28}NO_3PSi$	317.43	52.97	8.89	52.72	8.78
21	$C_{13}H_{26}NO_4PSi$	319.41	48.88	8.21	48.59	8.07
22	$C_{16}H_{29}N_2O_2PSi$	340.48	56.44	8.59	56.12	8.45
23	$C_{16}H_{29}N_2O_3PSi$	356.47	53.91	8.20	53.78	8.05
24	$C_{15}H_{27}N_2O_3PSi$	342.45	52.61	7.95	52.49	7.82
25	$C_{20}H_{29}N_2O_2PSi$	388.52	61.83	7.52	61.67	7.41
26	$C_{15}H_{26}NO_2PSi$	311.43	57.85	8.42	57.64	8.28
27	$C_{15}H_{24}NO_3PSi$	325.42	55.37	7.43	50.29	7.23
28	$C_8H_{10}NaO_2P$	192.13	50.01	5.25	49.83	5.30
29	$C_6H_8NaO_3P$	182.09	39.58	4.43	39.34	4.59
30	$C_7H_9NNaO_2P$	193.12	43.54	4.70	43.42	4.78
31	$C_8H_{11}NNaO_2P$	207.15	46.39	5.35	46.26	5.42
32	$C_7H_9NNaO_2P$	193.12	43.54	4.70	43.48	4.74
33	$C_{14}H_{13}NNaO_2P$	281.22	59.79	4.66	59.58	4.81
34	$C_6H_{11}NNaO_3P$	199.13	36.19	5.57	35.97	5.64
35	$C_9H_{10}NaO_2P$	204.14	52.95	4.94	52.68	5.03
36	$C_{16}H_{18}NaO_2P$	296.28	64.86	6.12	64.72	6.16
37	$C_{12}H_{14}NaO_4P$	276.20	52.18	5.11	51.87	5.19
38	$C_8H_{10}Na_2O_4P_2$	278.10	34.55	3.62	34.43	3.69
39	$C_9H_{12}Na_2O_5P_2$	308.12	35.08	3.92	34.94	3.98
40	$C_{17}H_{20}N_2NaO_2P$	338.32	60.35	5.96	60.07	6.09
41	$C_{12}H_{17}NNaO_2P$	261.23	55.17	6.54	54.94	6.65
42	$C_{12}H_{15}NNaO_3P$	275.22	52.37	5.49	52.02	5.57
43	$C_9H_{19}N_2O_3P$	234.23	46.15	8.18	45.93	8.07
44	$C_{13}H_{21}N_2O_2P$	268.30	58.20	7.89	57.98	7.76
45	$C_{13}H_{21}N_2O_3P$	284.29	54.92	7.45	54.84	7.37
46	$C_{19}H_{26}NO_2P$	331.40	68.86	7.91	68.49	7.81
47	$C_{21}H_{28}NO_3P$	373.44	67.54	7.56	67.18	7.47

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

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

*Dimethylaminomethyl-2-[N-(2-oxopyrrolidino)]-ethylphosphinic Acid (**43**)*

To a solution of 5.4 g of phosphinate **14** in 15 mL of diethyl ether, 25 mL of methanol was added with stirring. The resulting mixture was refluxed for 10 min, the solvent was removed, and the residue was kept in a vacuum (1 mm). Four grams of acid **43**, was obtained as colorless hydroscopic crystals.

The acids **44–47** were prepared similarly.

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