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Synthesis of New Functionalized Aminomethylphosphonites and Their Derivatives

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ABSTRACT: *The aminomethylation of the several esters of hypophosphorous acid using chloro-, alkoxy-, and amino-substituted methylamines of various structure is proposed as convenient method for the synthesis of new functionalized aminomethylphosphonites and bis(aminomethyl)phosphinates. Also* O,O*-diethyl(pivaloyl)phosphonite is successfully applied in the aminomethylation as a synthetic analog of unstable diethoxyphosphine.* © 2010 Wiley Periodicals, Inc. Heteroatom Chem 21:361–367, 2010; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20620

INTRODUCTION

The numerous organophosphorus compounds including the several PCH_2N fragments are of great interest as polydentate chelating ligands, extragents, and promising biomimetics of amino acids with interesting properties [1–4]. Here, we present convenient methods for obtaining the new functionalized aminomethylphosphonites that are the key substances for synthesis of corresponding organophosphorus compounds with four and five coordinated phosphorus. In order to develop convenient methods for the synthesis of aminomethylphosphonites that were not readily available so far, we undertook a research in the aminomethylation of the several alkyl and trimethylsilyl esters of hypophosphorous acid. Highly reactive PH and POSi fragments along with a sufficiently nucleophilic phosphorus atom make these compounds prospective for the aminomethylation (cf. [5–8]). Also chloro-, alkoxy-, and amino-substituted methylamines were applied as aminomethylating reagents, and three structural types of resulting compounds were obtained depending on the reactivity of starting substances. The synthesized compounds contain the several moieties of various amines, carboxamides, sulfonamides, and amino acids and are promising synthons, ligands, and bioactive substances.

RESULTS AND DISCUSSION

We found that the interaction of bis(trimethylsiloxy)phosphine containing two highly reactive centers PH and POSi with several chloromethylamines and chloromethylamides under mild conditions allowed us to obtain both aminomethylphosphonites and bis(aminomethyl)phosphinates selectively with a good yield. Thus, under equimolar ratio of starting reagents only intermediate phosphonites **A** were observed in the reaction mixture by NMR ^{31}P

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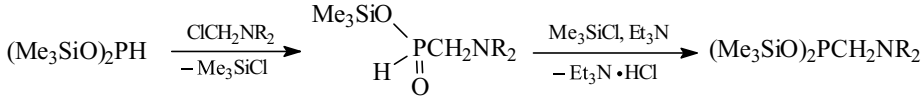
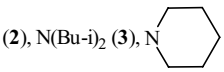
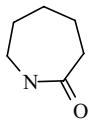
spectroscopy (for R = Et, δ_P 20.2 ppm, $^1J_{PH}$ 582 Hz). Further addition of triethylamine to the reaction mixture resulted in the *N,N*-disubstituted aminomethylphosphonites **1–10** in good yield (Eq. (1)).

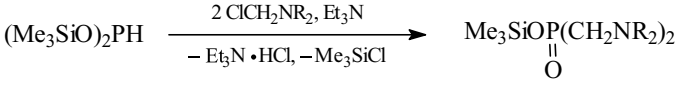


A **1–10**

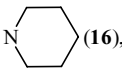
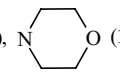
NR_2 = NMe_2 (**1**), NEt_2 (**2**), $N(Bu\text{-}i)_2$ (**3**),  (**4**), N(Me)CHO (**5**), N(Me)Ac (**6**),  (**7**),  (**8**),

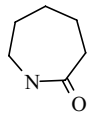
$N(COOEt)CH_2COOEt$ (**9**), $N(Me)SO_2Me$ (**10**). (1)

The conceivable scheme of this process involves the Arbuzov reaction of bis(trimethylsiloxy)phosphine with chloromethylamine or chloromethylamide followed by the silylation of the intermediate phosphonite **A** by trimethylchlorosilane in the presence of triethylamine. This must be the first example for a successful Arbuzov reaction of bis(trimethylsiloxy)phosphine, which was reported to give only a complex mixture of compounds in the reactions with alkyl halides [9]. The application of an excess of chloromethylamine or amide in similar reactions in the presence of triethylamine gave *N,N*-disubstituted bis(aminomethyl)phosphinates **11–23** in high yields (Eq. (2)). All the reported reactions (Eqs. (1), (2)) took place in dichloromethane solution at room temperature.

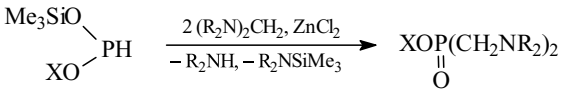


11–23

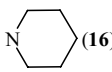
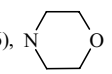
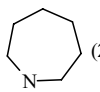
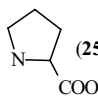
NR_2 = NMe_2 (**11**), NEt_2 (**12**), NBu_2 (**13**), $N(Bu\text{-}i)_2$ (**14**), $N(Am\text{-}i)_2$ (**15**),  (**16**),  (**17**),

N(Me)CHO (**18**), N(Me)Ac (**19**),  (**20**),  (**21**), $N(COOEt)CH_2COOEt$ (**22**), $N(Me)SO_2Me$ (**23**). (2)

Also alkoxy(trimethylsiloxy)phosphines and bis(trimethylsiloxy)phosphine reacted with 2 equivalents of bis(dialkylamino)methanes under heating at 100–130°C in the presence of zinc chloride as a catalyst to give bis(aminomethyl)phosphinates **11–17,24–29** in good yield (Eq. (3)).



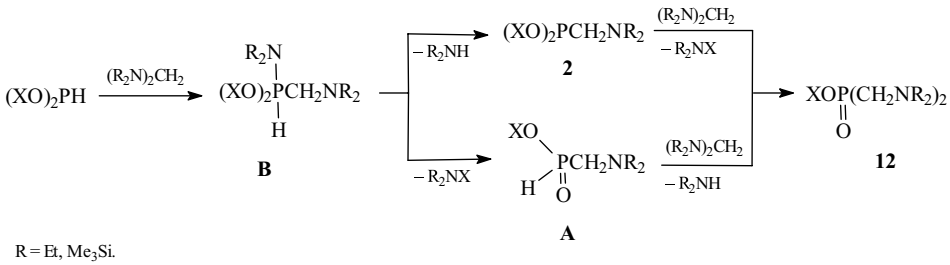
11–17, 24–29

NR_2 = NMe_2 (**11,28**), NEt_2 (**12,26,27,29**), NBu_2 (**13**), $N(Bu\text{-}i)_2$ (**14**), $N(Am\text{-}i)_2$ (**15**),  (**16**),  (**17**),  (**24**),  (**25**);

X = Me_3Si (**11–17,24,25**), Et (**26**), Pr (**27**), Bu (**28,29**). (3)

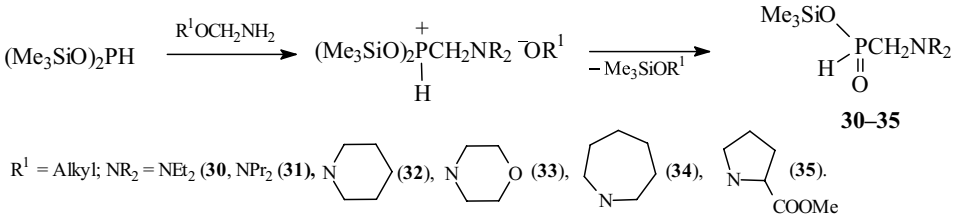
Under equimolar ratio of the starting compounds, this reaction yields a mixture of products. For example, the reaction of bis(trimethylsiloxy)phosphine and bis(diethylamino)methane resulted in a mixture of phosphinate **12**, intermediate phosphonites **2**, **A**, and the starting bis(trimethylsiloxy)phosphine that were detected by NMR ^{31}P spectroscopy. The course of the process suggests that the intermediate complex **B** can be decomposed in two ways giving phosphonites **2** and **A**, respectively. Phosphonites **2** and **A** are more nucleophilic than the starting phosphine and are involved in further aminomethylation to give the same

product, bis(aminomethyl)phosphinate **12** (Eq. (4)).



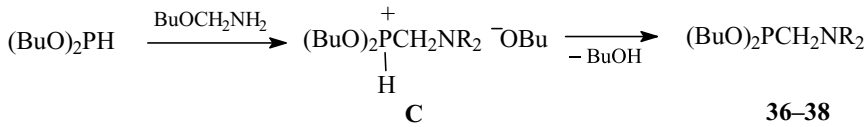
R = Et, Me_3Si. (4)

It should also be noted that the similar reaction of bis(trimethylsiloxy)phosphine with more reactive alkoxymethylamines proceeded under mild conditions and provided new aminomethylphosphonites **30–35** with PH fragments in high yields (Eq. (5)).



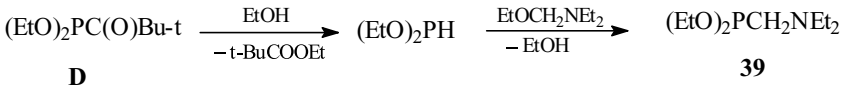
R^1 = Alkyl; NR_2 = NEt_2 (**30**, NPr_2 (**31**), (**32**), (**33**), (**34**), (**35**). (5)

In contrast, dibutoxyphosphine reacted exothermically with *N*-butoxymethyl dialkylamines to give dialkylaminomethylphosphonites **36–38** in good yield (Eq. (6)).



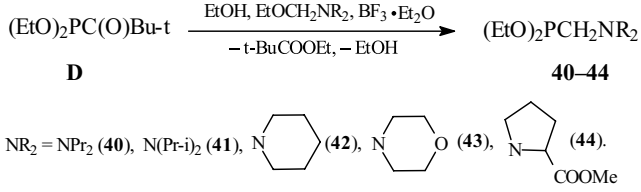
R = Me (**36**), Et (**37**), Pr (**38**). (6)

The suggested scheme of this reaction includes an electrophilic attack of the methylene group of *N*-butoxymethyl dialkylamine on the trivalent phosphorus followed by the destruction of the intermediate complex **C** with butanol being eliminated. However, this method is applicable only to dibuthoxyphosphine due to the unstability of dialkoxyphosphines with less-bulky substituents [10]. We showed that *O*,*O*-diethyl(pivaloyl)phosphonite containing labile P—C bond [11,12] may be successfully applied in the aminomethylation as a synthetic analog of unstable diethoxyphospine. Thus, pivaloylphosphonite **D** reacted exothermically with *N*-ethoxymethyl diethylamine in the presence of ethanol to give phosphonite **39** in good yield. The scheme of this reaction involves the cleavage of the P—C bond of the starting phosphonite by ethanol resulting in diethoxyphosphine (δ_P 169 ppm, $^1J_{PH}$ 200 Hz), which undergoes further aminomethylation similarly to dibutoxyphosphine (Eq. (7)).



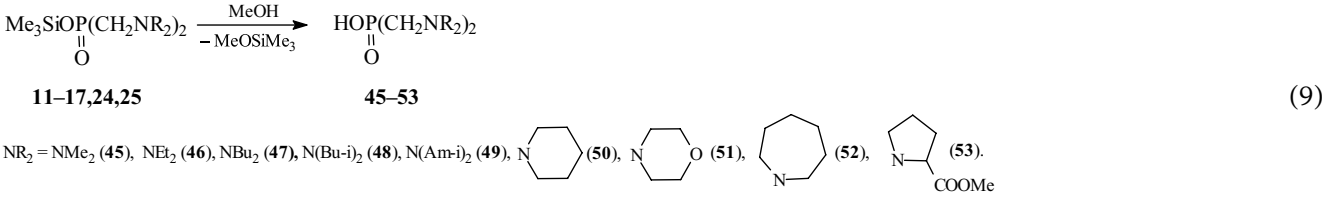
(7)

Ethoxymethylamines with bulky substituents at nitrogen undergo analogous reaction only under heating to 70°C and in the presence of boron trifluoride etherate as a catalyst resulting in phosphonites **40–44** (Eq. (8)).



NR_2 = NPr_2 (**40**), $N(Pr\text{-}i)_2$ (**41**), (**42**), (**43**), (**44**). (8)

Thus, the aminomethylation of the esters of hypophosphorous acid may be successfully applied in the synthesis of several types of functionalized aminomethylphosphonites and bis(aminomethyl)phosphinates. The trimethylsilyl substituted aminomethyl organophosphorus compounds with highly reactive *O*—Si bonds were easily transformed into various aminomethyl organophosphorus derivatives (cf. [13]). So trimethylsilyl containing bis(aminomethyl)phosphinates easily reacted with an excess of methanol forming the water-soluble bis(aminomethyl)phosphinic acids **45–53** (Eq. (9)).



(9)

Therefore, we developed convenient methods for the synthesis of previously unavailable aminomethylphosphonites and bis(aminomethyl)phosphinates that might be applied as polydentate ligands and as precursors for the synthesis of biologically active compounds.

The structures of functionalized aminomethylphosphonites and their derivatives were confirmed by the ^{1}H, ^{13}C, and ^{31}P NMR spectra, which indicated the characteristic signals of the $PC^{1}H_2NC^{2}H_n$ fragments (see Tables 1–3). The element analysis data of synthesized compounds are summarized in Table 4.

EXPERIMENTAL

The ^{1}H, ^{13}C, and ^{31}P NMR spectra were registered on a Varian VXR-400 and Bruker Avance-400 spectrometer (400, 100, and 162 MHz, respectively) in C_6D_6, $CDCl_3$ (**1–44**), or CD_3OD, D_2O (**45–53**). All reactions were carried out under dry argon in anhydrous solvents. The starting compounds were prepared as described in [9–12,14–17].

O,O-Bis(trimethylsilyl) dimethylaminomethylphosphonite (**1**). To a solution of 7.2 g of bis(trimethylsiloxy)phosphine in 30 mL of methylene chloride, a solution of 3.2 g of *N*-chloromethyl dimethylamine in 35 mL of methylene chloride was added dropwise under stirring at 20°C. The mixture was stirred for 1 h, 3.6 g of triethylamine was added under stirring, and the mixture was left for 2 h. The solvent was distilled off in a vacuum, 150 mL of pentane was added to the residue, and the mixture was filtrated. The solvent was distilled off in a vacuum, and the residue was distilled to give 6 g phosphonite **1**.

The phosphonites **2–10** were obtained analogously.

O-Trimethylsilylbis(dimethylaminomethyl)phosphinate (**11**). To a solution of 7.6 g of bis(trimethylsiloxy)phosphine and 3.7 g of triethylamine in 40 mL of diethyl ether, a solution of 6.7 g of *N*-(chloromethyl) dimethylamine in 50 mL of methylene chloride was added dropwise under stirring at 20°C. The mixture was stirred for 1 h, then the solvent was removed, and 150 mL of diethyl ether was added to residue. The mixture was filtrated, the solvent was distilled off, and the residue was distilled in a vacuum to give 7.7 g of phosphinate **11**.

The phosphinates **12–23** were obtained analogously.

O-Ethyl bis(diethylaminomethyl)phosphinate (**26**). A mixture of 6 g of ethoxy (trimethylsiloxy)phosphine, 13.7 g of bis (diethylamino)-methane, and 0.2 g of zinc chloride was heated at 100°C for 1.5 h, and then distilled in a vacuum to give 7.5 g of phosphinate **26**.

The phosphinates **17,24,25,27–29** were prepared similarly.

O-Trimethylsilyl diethylaminomethylphosphonite (**30**). To a solution of 17.9 g of bis(trimethylsiloxy)phosphine in 50 mL of methylene chloride, a solution of 6.8 g of *N*-butoxymethyl diethylamine in 10 mL of methylene chloride was added dropwise under stirring at 10°C. The mixture was heated to reflux, the solvent was removed, and the residue was distilled in a vacuum. Phosphonite **30**, 6.7 g was obtained.

The phosphonites **31–35** were prepared similarly.

O,O-Dibutyl dimethylaminomethylphosphonite (**36**). A mixture of 6.5 g of dibutoxyphosphine and 5.4 g of *N*-butoxymethyl dimethylamine was left for 3 h and then distilled in a vacuum to obtain 7.3 g of phosphonite **36**.

Phosphonites **37,38** were prepared similarly.

TABLE 1 Yields, Products Constants, and NMR Spectral Data (δ, ppm, J, Hz) for the $PC^1H_2NC^2H_n$ Fragments[a] of Aminomethylphosphonites **1–10,36–44**

No.	*Yield (%)*	*Bp (°C) (p, mmHg)*	*δ(H) C^1H_2 d*	*$^2J_{PH}$*	*$\delta(C^1)$ d*	*$^1J_{PC}$*	*$\delta(C^2)$ d*	*$^3J_{PC}$*	*δ(C═O) s*	*δ_P s[b]*
1	65	48 (1)	2.40	9.0	72.15	17.5	48.26	7.8	–	153.17
2	61	65 (1)	[c]	–	66.42	16.0	49.61	6.6	–	152.54
3	60	95 (1)	2.54	8.6	69.21	17.3	66.28	6.8	–	154.48
4	51	77 (1)	2.35	9.2	71.77	17.1	57.29	7.9	–	152.66
5	72	107 (2)	2.81	12.2	58.90	25.8	31.85	4.2	162.14	143.51
			3.23	9.6	54.93	29.1	35.89	3.0	161.58	149.95
6	42	93 (1)	3.11	11.3	58.54	28.0	38.21	1.9	168.70	149.51
			3.37	9.0	60.76	25.4	35.31	4.4	169.07	153.52
7	42	102 (1)	[c]	–	53.42	27.0	31.74	<1	173.27	151.96
8	68	126 (1)	3.44	8.8	59.24	28.6	51.18	<1	174.04	151.13
9	52	130 (2)	3.47	9.6	58.66	26.1	50.58	<1	169.31	149.40
			3.38	10.1	58.28	25.7	50.52	<1	169.31	148.47
10	87	126 (1)	2.75	9.2	58.90	28.4	36.59	4.2	–	145.72
36	85	85 (1)	2.62	7.6	65.19	9.4	48.59	7.4	–	172.93
37	81	95 (1)	2.71	7.7	59.56	7.3	49.57	7.1	–	173.12
38	85	99 (1)	2.72	8.1	60.92	6.3	57.52	7.2	–	175.01
39	88	56 (1)	2.73	7.7	59.45	7.1	49.53	6.9	–	173.67
40	75	62 (1)	2.76	7.7	59.07	6.7	57.00	6.9	–	174.47
41	67	57 (1)	2.81	8.5	51.48	3.0	49.78	4.8	–	176.09
42	73	64 (1)	2.65	6.9	64.86	8.6	57.97	8.1	–	171.83
43	78	68 (1)	2.60	6.5	64.20	9.1	56.92	7.7	–	170.78
44	66	103 (1)	[c]	–	58.58	9.9	66.85	9.3	173.52	170.43

[a]All signals of alkyl and trimethylsilyl fragments are in the standard area. According to the NMR spectra, the compounds **5,6,9** are the mixtures of two stereoisomers. Their ratio was determined from the ^1H, ^{31}P NMR spectra. The spectral parameters of the major isomer are given first, their ratio for compounds: **5**, 60 : 40; **6**, 55 : 45; **9**, 70 : 30. In ^1H NMR spectra, fragments of compounds, s: NCHO of **5**, 7.89 and 7.86; $NCH_2C(O)$ of **9**, 4.15 and 4.05. In ^{13}C NMR spectra, fragments of compounds: NC(O) of **9**, 156.51 s and 156.15 s; NCH_2 of **44**, 54.86 d, $^3J_{PC}$ 5.0.
[b]Data of ^{31}P $\{^1H\}$ spectra.
[c]Overlapping multiplets.

TABLE 2 Yields, Products Constants, and NMR Spectral Data (δ, ppm, J, Hz) for the $PC^1H_2NC^2H_n$ Fragments[a] of Bis(aminomethyl)phosphinates **11–29, 45–53**

No.	*Yield (%)*	*Bp (°C) (p, mmHg) (mp (°C))*	*n_D^{20}*	*δ (C^1) d*	*$^1J_{PC}$*	*δ (C^2) d*	*$^3J_{PC}$*	*δ (C═O) s*	*δ_P s[b]*
11	85	73 (1)	1.4445	57.18	114.2	47.85	8.7	–	37.85
12	90	92 (7)	1.4510	51.80	112.8	48.52	8.1	–	40.09
13	88	162 (1)	1.4504	53.28	103.7	55.04	6.9	–	41.88
14	91	134 (1)	1.4490	54.83	104.9	65.39	7.2	–	39.17
15	89	168 (1)	1.4520	55.13	104.4	53.79	8.0	–	40.54
16	86	137 (1)	1.4740	57.02	114.0	56.91	8.9	–	40.03
17	89	143 (1) (44)	–	56.51	114.8	55.83	9.0	–	37.80
18	68	198 (1)	1.4905	44.13	98.8	35.51	<1	162.45	30.15
				48.51	98.3	31.53	<1	162.59	30.32
19	40	175 (1)	1.4830	47.37	97.9	37.47	<1	169.72	34.61
				50.68	94.7	37.82	<1	169.91	35.16
20	42	182 (1)	1.4935	42.78	100.2	30.24	<1	173.98[c]	33.86
21	49	210 (1)	1.4905	46.83	103.2	49.74	<1	174.68	34.07
22	37	196 (2)	1.4594	46.72	104.3	49.53	<1	169.57	30.19

(Continued)

*O,O-Diethyl diethylaminomethylphosphonite (**39**)*. A mixture of 5.7 g of *O,O*-diethyl pivaloylphosphonite, 4.3 g of *N*-ethoxymethyl dimethylamine, and 2 mL of ethanol was left for 3 h. Then the mixture was distilled in a vacuum to obtain 5.0 g of phosphonite **39**.

The phosphonites **40–44** were obtained similarly via heating of the mixtures at 70°C for

TABLE 2 Continued

No.	*Yield (%)*	*Bp (°C) (p, mmHg) (mp (°C))*	n_D^{20}	δ $(C^1)d$	$^1J_{PC}$	δ $(C^2)d$	$^3J_{PC}$	δ (C═O) s	$\delta_P s^b$
				46.44	100.4	49.73	<1	169.57	30.73
23	86	210 (2)	1.4808	47.10	107.4	34.17	<1	–	28.86
24	81	149 (1)	1.4865	55.88	113.0	57.89	7.7	–	39.01
25	93	183 (0.5)	1.4810	52.25	111.8	66.20[d]	11.7	173.63	38.58
26	79	88 (1)	1.4557	50.77	110.0	48.60	7.8	–	43.40
27	92	118 (1)	1.4570	50.73	109.1	48.63	7.8	–	49.33
28	93	81 (1)	1.4530	55.85	111.3	47.81	10.1	–	47.21
29	91	125 (1)	1.4575	50.79	110.3	48.65	7.8	–	47.64
45	95	(126)	–	57.09	99.5	45.39	5.8	–	25.52
46	92	(119)	–	57.47	100.1	47.49	5.9	–	22.18
47	95	oil	–	51.86	99.9	53.08	6.1	–	23.21
48	93	oil	–	54.40	101.8	64.57	5.2	–	25.45
49	93	oil	–	53.91	103.6	53.45	6.9	–	27.20
50	91	(188)	–	57.60	99.6	55.53	6.4	–	23.25
51	96	(204)	–	57.79	100.8	55.01	6.4	–	21.25
52	96	(79)	–	58.52	96.9	58.68	4.3	–	19.03
53	97	oil	–	52.73	100.7	65.63[d]	8.6	171.70	22.01

[a]All signals of alkyl and trimethylsilyl fragments are in the standard area. According to the NMR spectra, the compounds **18,19,22** are the mixtures of two stereoisomers. The spectral parameters of the major isomer isomer are given first; their ratio for compounds: **18**, 65 : 35; **19**, 80 : 20; **22**, 70 : 30. In ^{1}H NMR spectra, fragment C^1H_2 of compounds, d: **23**, 3.23, $^2J_{PH}$ 7.2; **45**, 2.71, $^2J_{PH}$ 9.6; **48**, 3.10, $^2J_{PH}$ 7.8; **51**, 2.80, $^2J_{PH}$ 9.6; the signals of the diastereotopic protons of methylene groups C^1H_2 of **25** and **53** are characteristic ABX multiplets δ (H_A), δ (H_B), $^2J(H_AH_B)$, $^2J(PH_A)$, $^2J(PH_B)$ for compounds: **25**, 3.18, 2.68, 14.8, 10.4, 7.7; **53**, 2.79, 2.60, 14.2, 11.2, 9.2; the signals of fragment C^1H_2 for other compounds are in the overlapping multiplets. In ^{1}H NMR spectra, fragment NCHO of compound **18**, s, 7.85 and 7.87. In ^{13}C NMR spectra, fragments of compounds, s: NC(O) of **22**, 156.36 and 156.04; NCH_2 of **25**, 54.90 and **53**, 54.44.
[b]Data of ^{31}P {^{1}H} spectra.
[c]d, $^3J_{PC}$, 2.1.
[d]Fragment NCHC(O), for compounds, δ_H: **25**, overlapping multiplets, **53**, 3.60 dd, $^3J_{HH}$ 8.4, and 5.2.

TABLE 3 Yields, Products Constants, and NMR Spectral Data (δ, ppm, J, Hz) for the $HPC^1H_2NC^2H_n$ Fragments[a] of Aminomethylphosphonites **30–35**

No.	*Yield (%)*	*Bp (°C) (p, mmHg)*	n_D^{20}	δ (H) HP d t	$^1J_{PH}$	$^3J_{HH}$	δ $(C^1)d$	$^1J_{PC}$	δ $(C^2)d$	$^3J_{PC}$	$\delta_P dt$	$^1J_{PH}$	$^2J_{PH}$
30	68	80 (2)	1.4401	7.12	538.9	2.1	54.21	117.5	48.92	8.4	22.95	538.9	9.1
31	72	96 (2)	1.4429	7.16	538.0	2.1	55.33	117.1	57.86	8.1	23.08	538.0	9.0
32	75	91 (1)	1.4633	7.18	541.7	2.0	59.73	115.3	56.70	9.5	20.36	541.7	9.7
33	80	102 (2)	1.4688	7.05	545.1	2.0	59.08	113.9	55.72	9.6	17.21	545.1	10.0
34	78	115 (2)	1.4615	7.03	538.4	2.1	58.82	115.1	57.57	7.8	19.38	538.4	8.5
35	83	142 (2)	1.4690	7.15[b]	548.7	1.6[b]	54.38	114.3	66.18[c]	12.4	17.71[d]	548.7	11.2[d]

[a]All signals of alkyl and trimethylsilyl fragments are in the standard area. In ^{1}H NMR spectra, fragments $PC^1H_2NC^2H_m$ of compounds **30–32,34** look as overlapping multiplets. In ^{1}H NMR spectrum, fragment PC^1H_2N of compound **33**: 2.32 dd, $^2J_{HH}$ 10.0, $^3J_{HH}$ 2.0. In ^{13}C NMR spectrum, fragment NCH_2 of compound **35**: 54.67 d, $^3J_{PC}$ 2.8.
[b]In ^{1}H NMR spectrum, fragment $H_MPCH_AH_BN$ of compound **35**: δ (H_M) 7.15 ddd, $^1J(PH_M)$ 548.7, $^3J(H_AH_M)$ 1.6, $^3J(H_BH_M)$ 3.2, δ (H_A) 3.01, δ (H_B) 2.71, $^2J(H_AH_B)$ 14.8, $^2J(PH_A)$ 11.2, $^2J(PH_B)$ 9.2, $^3J(H_MH_A)$ 1.6, $^3J(H_MH_B)$ 3.2.
[c]In NMR spectra, fragment NCHC(O): δ_C (C═O) 173.21 s, δ_H (CH) 3.24 dd, $^3J_{HH}$ 7.2 and 5.6.
[d]In ^{31}P NMR spectrum, ddd, $^2J_{PH}$ 11.2 and 9.2.

0.5 h in the presence of 0.1 g of boron trifluoride etherate.

*Bis(dimethylaminomethyl)phosphinic acid (***45***).* The solution of 4.8 g of phosphinate **11** in 10 mL of diethyl ether was added dropwise under stirring at 10°C to 20 mL of methanol. The resulting mixture was heated to a boil, the solvent was distilled off in a vacuum, and the residue was kept in a vacuum (1 mmHg) for 1 h to give 3.3 g of acid **45** as colorless hydroscopic crystals.

The acids **46–53** were obtained similarly.

TABLE 4 Elemental Analyses Data of Compounds[a]

No.	Empirical Formula	Formula weight	Calcd. (%)		Found (%)	
			C	H	C	H
11	$C_9H_{25}N_2O_2PSi$	252.37	42.84	9.99	42.86	10.12
12	$C_{13}H_{33}N_2O_2PSi$	308.48	50.62	10.78	50.48	10.64
13	$C_{21}H_{49}N_2O_2PSi$	420.70	59.95	11.74	59.81	11.62
14	$C_{21}H_{49}N_2O_2PSi$	420.70	59.95	11.74	59.78	11.65
15	$C_{25}H_{57}N_2O_2PSi$	476.80	62.98	12.05	62.72	11.96
16	$C_{15}H_{33}N_2O_2PSi$	332.50	54.19	10.00	54.02	9.89
17	$C_{13}H_{29}N_2O_4PSi$	336.45	46.41	8.69	46.26	8.58
18	$C_9H_{21}N_2O_4PSi$	280.34	38.56	7.55	38.46	7.37
19	$C_{11}H_{25}N_2O_4PSi$	308.40	42.84	8.17	42.59	8.29
20	$C_{13}H_{25}N_2O_4PSi$	332.42	46.97	7.58	46.69	7.39
21	$C_{17}H_{33}N_2O_4PSi$	388.51	52.55	8.56	52.26	8.47
22	$C_{19}H_{37}N_2O_{10}PSi$	512.56	44.52	7.28	44.39	7.03
23	$C_9H_{25}N_2O_6PS_2Si$	380.50	28.41	6.62	28.26	6.49
24	$C_{17}H_{37}N_2O_2PSi$	360.55	56.63	10.34	56.49	10.23
25	$C_{17}H_{33}N_2O_6PSi$	420.51	48.55	7.91	48.23	7.80
26	$C_{12}H_{29}N_2O_2P$	264.35	54.52	11.06	54.67	11.23
27	$C_{13}H_{31}N_2O_2P$	278.36	56.09	11.22	55.92	11.15
28	$C_{10}H_{25}N_2O_2P$	236.28	50.83	10.67	50.68	10.54
29	$C_{14}H_{33}N_2O_2P$	292.39	57.51	11.38	57.40	11.26
30	$C_8H_{22}NO_2PSi$	223.33	43.02	9.93	43.15	10.02
31	$C_{10}H_{26}NO_2PSi$	251.38	47.78	10.43	47.59	10.34
32	$C_9H_{22}NO_2PSi$	235.34	45.93	9.42	45.74	9.26
33	$C_8H_{20}NO_3PSi$	237.31	40.49	8.50	40.28	8.45
34	$C_{10}H_{24}NO_2PSi$	249.37	48.17	9.70	47.99	9.59
35	$C_{10}H_{22}NO_4PSi$	279.35	42.99	7.94	42.73	7.89
36	$C_{11}H_{26}NO_2P$	235.31	56.15	11.14	55.92	10.88
37	$C_{13}H_{30}NO_2P$	263.36	59.29	11.48	59.15	11.62
38	$C_{15}H_{34}NO_2P$	291.41	61.83	11.76	61.69	12.04
39	$C_9H_{22}NO_2P$	207.26	52.16	10.70	52.03	10.61
40	$C_{11}H_{26}NO_2P$	235.31	56.15	11.14	56.23	11.20
41	$C_{11}H_{26}NO_2P$	235.31	56.15	11.14	55.97	11.03
42	$C_{10}H_{22}NO_2P$	219.27	54.78	10.11	54.63	10.01
43	$C_9H_{20}NO_3P$	221.24	48.86	9.10	48.69	9.03
44	$C_{11}H_{22}NO_4P$	263.28	50.18	8.42	50.32	8.36
45	$C_6H_{17}N_2O_2P$	180.19	40.00	9.51	36.61	9.60
46	$C_{10}H_{25}N_2O_2P$	236.30	50.83	10.66	50.45	10.85
47	$C_{18}H_{41}N_2O_2P$	348.52	62.03	11.86	61.89	11.74
48	$C_{18}H_{41}N_2O_2P$	348.52	62.03	11.86	61.78	11.68
49	$C_{22}H_{49}N_2O_2P$	404.62	65.30	12.21	64.97	12.05
50	$C_{12}H_{25}N_2O_2P$	260.32	55.37	9.68	55.72	9.72
51	$C_{10}H_{21}N_2O_4P$	264.26	45.45	8.01	45.55	8.28
52	$C_{14}H_{29}N_2O_2P$	288.37	58.31	10.14	58.03	9.98
53	$C_{14}H_{25}N_2O_6P$	348.33	48.27	7.23	48.03	7.16

[a]The compounds **1–10** are very unstable in an air atmosphere; therefore, these substances were analyzed as their derivatives, corresponding phosphinates.

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