

Synthesis of New Organophosphorus-substituted Mono- and Bis(trimethylsilyl)amines with PCH_2N Fragments and Their Derivatives

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ABSTRACT: Convenient procedures for the synthesis of new organophosphorus-substituted mono- and bis(trimethylsilyl)amines with PCH_2N moiety are proposed, starting from trimethylsilyl esters of organophosphorus acids, as well as 1,3,5-trialkylhexahydro-1,3,5-triazines and *N*-alkoxymethyl bis(trimethylsilyl)amines as aminomethylating reagents. Certain properties of the resulting compounds are presented. © 2010 Wiley Periodicals, Inc. *Heteroatom Chem* 21:71–77, 2010; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20580

INTRODUCTION

N-Trimethylsilylated amines are widely used in organophosphorus chemistry [1], but the *N*-trimethylsilyl-substituted organophosphorus compounds remained unavailable. At the same time, the latter compounds are the key precursors for various interesting types of new organophospho-

rus compounds including PCH_2NH_2 , $\text{PCH}_2\text{NC(O)}$, and PCH_2NSO_2 fragments, which are also of interest as biologically active compounds and promising ligands [2,3]. In this work, we propose the convenient way for synthesis of new organophosphorus-substituted *N*-trimethylsilylamines and their derivatives such as organophosphorus-substituted amides and sulfonamides of various structures. Starting trimethylsilyl esters of trivalent organophosphorus acids [1], symmetrical trialkylhexahydrotriazines [4], and *N*-alkoxymethyl bis(trimethylsilyl)amines [5–7] were used by us.

RESULTS AND DISCUSSION

Thus an excess of diethyl trimethylsilyl phosphite reacts with symmetrical hexahydrotriazines **A** on heating to 130°C in the presence of zinc chloride as a catalyst forming *N*-trimethylsilylaminomethylphosphonates **1–4** with a good yield. Also the bisphosphonates **5–8** are isolated as the by-products after distillation of the

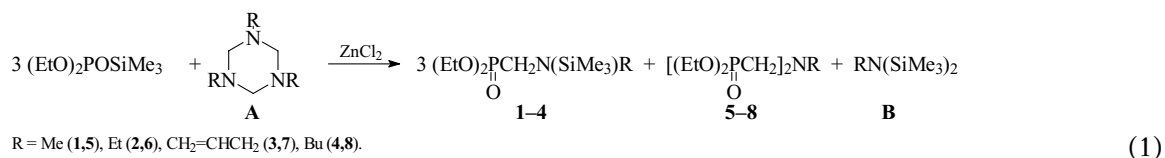
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Contract grant sponsor: Russian Foundation for Basic Research.

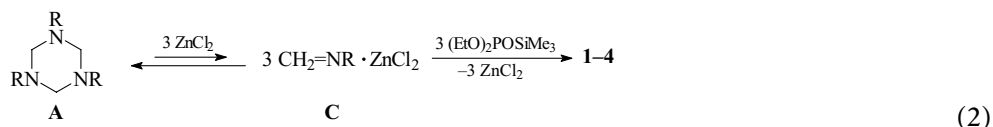
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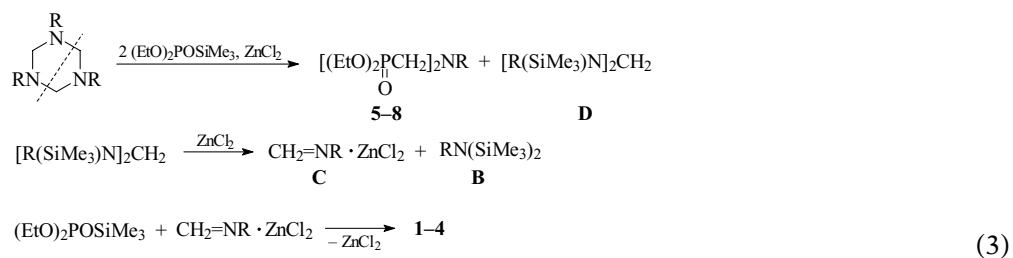
reaction mixture (cf. [8]; Eq. (1)).



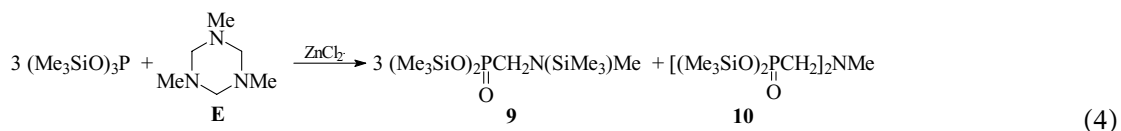
Hence the splitting of triazines **A** proceeds mainly by symmetrical way via formation of highly reactive intermediates **C** following by the addition of trimethylsilyl phosphite (Eq. (2)).



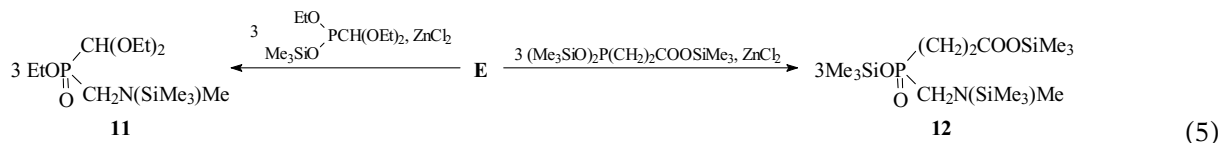
The proposed scheme of the minor unsymmetrical splitting of triazines **A** includes the formation of unstable aminales **D** and bis(trimethylsilyl)amines **B** in the mixture with starting compounds (Eq. (3)). The yields of bisphosphonates **5-8** are about 10–15%.



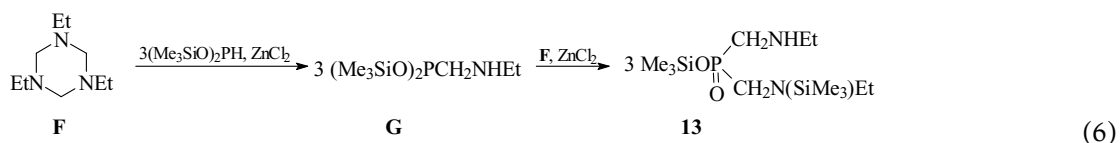
Under the same conditions, tris(trimethylsilyl)phosphite reacts with triazine **E** to form phosphonate **9** and bisphosphonate **10** (Eq. (4)).



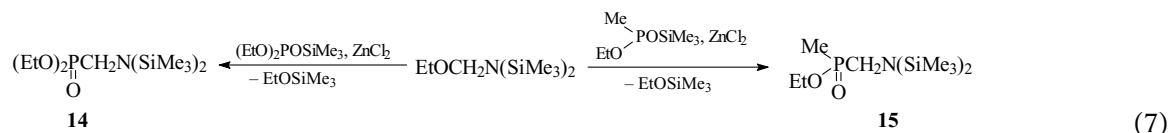
Analogously functionalized phosphonites react with triazine **E** giving only functionalized phosphinates **11,12** with high yields due to the sterical factors (Eq. (5)).



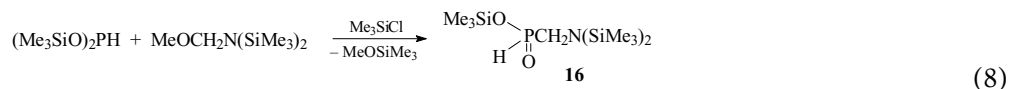
The interaction of triazine **F** even with an excess of bis(trimethylsilyl)phosphine proceeds as double aminomethylation via highly reactive intermediate phosphonite **G**, yielding phosphinate **13** (Eq. (6)).



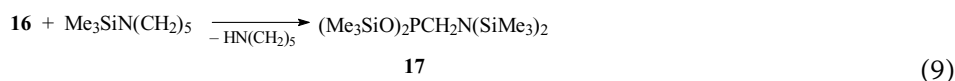
Thus we proposed the convenient methods for preparing *N*-trimethylsilyl-substituted aminomethyl organophosphorus compounds using symmetrical hexahydrotriazines as aminomethylation reagents. The aminomethyl organophosphorus compounds with *N,N*-bis(trimethylsilyl) moiety are synthesized by us using *N*-alkoxymethyl bis(trimethylsilyl)amines as aminomethylating reagents. So the corresponding phosphonate **14** and phosphinite **15** are synthesized through the reaction of *N*-ethoxymethyl bis(trimethylsilyl)amine with trimethylsilyl phosphite and phosphonite under heating to 130°C in the presence of zinc chloride as a catalyst (cf. [6]; Eq. (7)).



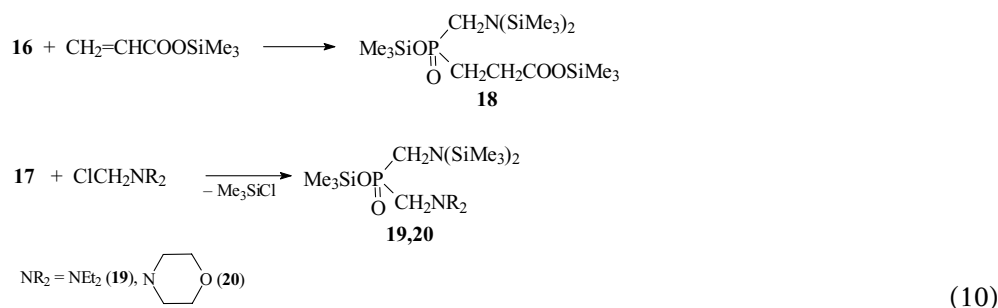
Also we found that of bis(trimethylsiloxy)phosphine reacts with *N*-methoxymethyl bis(trimethylsilyl)amine at 120°C in the presence of trimethylchlorosilane as a catalyst, resulting in formation of phosphonite **16** in high yield (Eq. (8)).



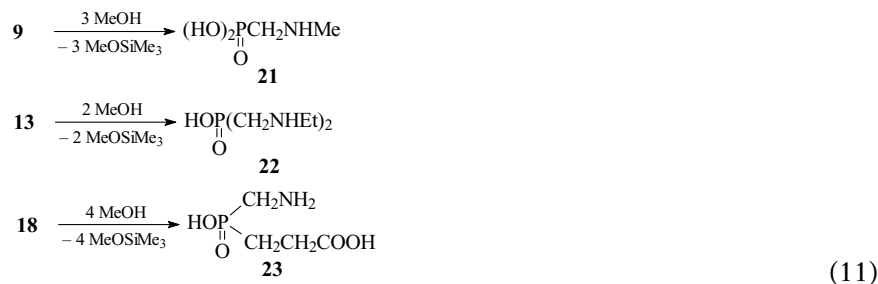
Treatment of phosphonite **16** with excess *N*-trimethylsilylpiperidine readily produces phosphonite **17** with a tricoordinated phosphorus atom (cf. [9]; Eq. (9)).



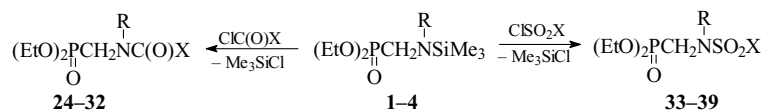
Previously unavailable phosphonites **16,17** are the key precursors for various organophosphorus compounds with a PCH₂N(SiMe₃)₂ fragment such as the unsymmetrical phosphinates **18–20**. Thus phosphonite **16** smoothly adds to trimethylsilyl acrylate to give phosphinate **18**, and phosphonite **17** is easily aminomethylated with substituted chloromethylamines, yielding phosphinates **19,20** (Eq. (10)).



Mono- and bis-*N*-trimethylsilyl-substituted aminomethyl organophosphorus compounds with highly reactive N–Si bonds are easily transformed into various aminomethyl organophosphorus derivatives. So trimethylsilyl-containing phosphonate **9** and phosphinates **13** and **18** easily reacted with methanol to obtain the water-soluble organophosphorus acids **21–23** (Eq. (11)).



In the present work, we have developed the convenient methods for preparing novel organophosphorus-substituted amides containing $\text{PCH}_2\text{NC(O)}$ and PCH_2NSO_2 fragments. It was found by us that easily available *N*-trimethylsilyl aminomethylphosphonates **1–4** are convenient synthons for preparing promising phosphorus-containing carboxamides and sulfonamides. Thus *N*-trimethylsilylamines **1–4** easily react with various carboxylic acid chlorides and substituted sulfonyl chlorides in methylene chloride to form functionalized phosphonates **24–39** in high yields (cf. [10]; Eq. (12)).



R = Me (**24–26**, **33–36**), Et (**27,28,37**), $\text{CH}_2=\text{CHCH}_2$ (**29–31**, **38**), Bu (**32,39**);

X = Me (**33,37–39**), $\triangle$ (**30,32**), *t*-Bu (**29**), 2- FC_6H_4 (**24,31**), 3- FC_6H_4 (**28**), 2- ClC_6H_4 (**25**), 4- ClC_6H_4 (**35**), 2- BrC_6H_4 (**27**), 4- BrC_6H_4 (**36**),

4- IC_6H_4 (**26**), 4- MeC_6H_4 (**34**).

(12)

TABLE 1 Yields, Products Constants, and NMR Spectral Data (δ , ppm; J , Hz) for the $\text{PC}^1\text{H}_2\text{NC}^2$ Fragments^a of Amines **1–23**

Compound	Yield (%)	Bp (°C) (p, mmHg) (mp (°C))	n_D^{20}	$\delta(\text{H})$ C^1H_2 d	$^2J_{\text{PH}}$	$\delta(\text{C}^1)$ d	$^1J_{\text{PC}}$	$\delta(\text{C}^2)$	δ_P , s ^b
1	71	70 (1)	1.4375	2.96	7.5	47.64	157.6	36.47 s	23.51
2	75	102 (1)	1.4390	3.08	7.1	42.89	157.4	41.91 s	26.15
3	78	103 (1)	1.4505	3.06	6.8	42.69	156.6	50.20 s	23.93
4	80	104 (1)	1.4435	3.09	6.8	43.27	154.9	47.56 s	23.92
5	12	154 (1)	1.4520	2.97	9.6	53.93 ^c	157.4	42.26 t ^d	21.59
6	15	155 (1)	1.4482	3.12	9.2	50.09 ^c	156.3	51.03 t ^d	22.22
7	10	158 (1)	1.4580	3.16	9.6	50.05 ^c	156.8	60.05 t ^d	22.00
8	10	168 (1.5)	1.4500	3.13	9.2	50.60 ^c	155.3	56.92 t ^d	22.30
9	76	98 (1)	1.4332	2.82	7.6	48.25	165.4	35.85 s	7.35
10	13	157 (1)	1.4392	3.01	9.2	56.08 ^c	161.7	45.75 t ^d	4.38
11	82	132 (1.5)	1.4358	3.0–3.3	–	47.48	97.9	36.89 s	36.86
12	78	145 (1.5)	1.4375	2.79	5.6	51.88	107.6	36.53 s	40.03
13	54	125 (1)	1.4515	2.81	11.1	47.97	105.7	46.08 s	39.84
				2.83	10.4	47.97	105.7	45.93 s	
14	78	87 (0.5)	1.4420	3.12	9.2	46.21	159.5	–	26.40
15^e	74	102 (1)	1.4572	2.8–2.9	–	45.03	106.4	–	48.92
16	59	105 (2)	^f	2.9–3.1	–	46.73	106.2	–	24.21
17	81	102 (1)	^f	2.88	9.6	56.64	23.1	–	151.90
18	87	140 (1)	1.4558	1.6–2.0	–	45.93	105.2	–	38.55
19	85	140 (1)	1.4568	2.2–2.7	–	41.05	106.3	–	35.24
20	82	147 (1)	1.4678	2.2–2.6	–	43.36	104.8	–	34.77
21	94	(169)	–	3.68	12.4	45.76	138.2	34.84 d	6.62
22	95	(58)	–	2.96	10.4	45.79	99.9	45.24 d	16.64
23	85	(168)	–	3.04	9.6	37.57	90.9	–	29.45

^aAll signals of alkyl and trimethylsilyl fragments are in the standard area. In ^1H NMR spectra the signals of the diastereotopic protons of methylene groups C^1H_2 of **11,15,18–20** are characteristic ABX multiplets, $\delta(\text{H}_\text{A})$, $\delta(\text{H}_\text{B})$, $^2J(\text{H}_\text{A}\text{H}_\text{B})$, $^2J(\text{PH}_\text{A})$, $^2J(\text{PH}_\text{B})$ for compounds: **11**, 3.23, 3.09, 15.6, <1, 5.6; **18**, 3.00, 2.94, 16.0, 2.0, 7.6; **19**, 3.08, 2.86, 16.0, 1.8, 6.6; **20**, 3.12, 2.91, 16.2, 1.5, 6.4; fragment $\text{H}_\text{M}\text{PCH}_\text{A}\text{H}_\text{B}\text{N}$ of compound **16**: $\delta(\text{H}_\text{M})$ ddd, $^1J(\text{PH}_\text{M})$ 528.4, $^3J(\text{H}_\text{A}\text{H}_\text{M})$ 2.8, $^3J(\text{H}_\text{B}\text{H}_\text{M})$ 1.6, $\delta(\text{H}_\text{A})$ 3.04, $\delta(\text{H}_\text{B})$ 2.94, $^2J(\text{H}_\text{A}\text{H}_\text{B})$ 16.4, $^2J(\text{PH}_\text{A})$ 8.4, $^2J(\text{PH}_\text{B})$ 6.4, $^3J(\text{H}_\text{M}\text{H}_\text{A})$ 2.8, $^3J(\text{H}_\text{M}\text{H}_\text{B})$ 1.6. In ^{13}C NMR spectra fragment $\text{PC}^1\text{H}_2\text{C}^2\text{H}_2\text{C}^3(\text{O})$ of compounds, $\delta(\text{C}^1)$, $^1J_{\text{PC}}$; $\delta(\text{C}^2)$, $^2J_{\text{PC}}$; $\delta(\text{C}^3)$, $^3J_{\text{PC}}$: **12**, 24.49, 93.4; 29.92, 3.0; 172.77, 15.2; **18**, 24.32, 86.3; 28.95, 3.0; 172.61, 13.6; **23**, 24.42, 97.1; 27.01, 3.1; 177.31, 13.8.

^bData of ^{31}P { ^1H } spectra.

^cdd, $^3J_{\text{PC}}$ for compounds: **5**, 10.4; **6**, 7.6; **7**, 7.8; **8**, 7.1; **10**, 9.4.

^d $^3J_{\text{PC}}$ for compounds: **5**, 7.9; **6**, 8.0; **7**, 8.6; **8**, 8.4; **10**, 7.9; **21**, 7.5; **22**, 12.1.

^eFragment PCH_3 for compound **15**: δ_H 1.08 d, $^2J_{\text{PH}}$ 12.8; δ_C 11.76 d, $^1J_{\text{PC}}$ 84.9.

^fThe compounds **16** and **17** are air-sensitive.

TABLE 2 Yields, Products Constants, and NMR Spectral Data (δ , ppm; J , Hz) for the PC¹H₂N(C²)C³(O) Fragments^a of Amides **24–32**

Compound	Yield (%)	Bp (°C) (p, mmHg)	n_D^{20}	δ (H) C ¹ H ₂ d	² J _{PH}	δ (C ¹) d	¹ J _{PC}	δ (C ²) s	δ (C ³) s	δ_P (b), s ^c
24	82	170 (1)	1.4978	3.53	11.6	41.79	155.0	37.61	168.29	19.35 (95)
				—	—	—	—	—	—	18.19 (5)
25	81	194 (1)	1.5160	3.57	11.6	41.04	154.3	36.17	166.96	18.95 (90)
				2.76	10.0	45.40	157.3	32.82	167.32 ^d	18.00 (10)
26	85	210 (1)	1.5578	3.71	11.2	42.19	153.5	38.19	169.18	19.50 (95)
				—	—	—	—	—	—	18.24 (5)
27	83	202 (1)	1.5109	3.62	10.0	37.72	155.0	42.91	167.65	19.21 (83)
				3.60	9.6	42.92	159.0	39.75	166.65	18.27 (17)
28	79	183 (1)	1.4902	^e	^e	38.52	155.2	43.51	168.86	19.67 (95)
				—	—	—	—	—	—	18.42 (5)
29	78	119 (0.5)	1.4635	3.57	11.2	40.55	154.8	50.40	176.70	21.03 (98)
				—	—	—	—	—	—	20.22 (2)
30	84	138 (2)	1.4785	3.32	10.8	39.53	155.8	49.23	172.12	19.68 (79)
				^e	^e	41.36	159.4	47.61	171.92	18.65 (21)
31	81	162 (1)	1.5035	^e	^e	38.42	155.4	51.11	166.10	19.23 (83)
				^e	^e	43.01	157.9	46.93	166.00	18.33 (17)
32	86	145 (1)	1.4680	3.41	11.2	39.82	155.3	46.96	171.62	19.83 (85)
				3.43	9.0	42.48	159.3	45.73	171.74	18.60 (15)

^aAll signals of alkyl and aryl groups are in the standard area. In the ¹³C NMR spectra fragments CHal for compounds: **24**, 161.24 d, ¹J_{CF} 246.7; **25**, 129.03 s and 128.96 s; **26**, 95.33 s; **27**, 117.99 s and 117.86 s; **28**, 161.48 d ¹J_{CF} 246.1; **31**, 157.52 d ¹J_{CF} 246.8.

^bAccording to the NMR spectra, the amides **24–32** are mixtures of two stereoisomers. Their ratio was determined from the ¹H and ³¹P NMR spectra. The spectral parameters of the major isomer are given first; for compounds **24**, **26**, **28**, **29** there are only ³¹P NMR spectral parameters for minor isomers due to its low contents.

^cData of ³¹P {¹H} spectra.

^dd, ³J_{PC} 3.5.

^eOverlapping multiplets.

TABLE 3 Yields, Products Constants, and NMR Spectral Data (δ , ppm; J , Hz) for the PC¹H₂N(C²)SO₂C³ Fragments^a of Sulfonamides **33–39**

Compound	Yield (%)	Bp (°C) (p, mmHg) (mp (°C))	n_D^{20}	δ (H) d	² J _{PH}	δ (C ¹) d	¹ J _{PC}	δ (C ²) s	δ (C ³) s	δ_P , s ^b
33	74	184 (4)	1.4559	3.22	10.0	44.08	160.0	35.35	35.52	18.46
34	75	195 (1)	1.5100	3.16	11.2	44.78	163.7	36.11	143.30	17.93
35	70	188 (0.5) (53)	—	3.14	11.2	44.58	163.5	35.90	138.80	17.56
36	72	241 (1) (65)	—	3.33	11.6	45.09	163.7	36.42	135.31	17.68
37	78	182 (4)	1.4518	3.34	9.2	40.62	159.4	42.51	38.48	19.13
38	73	162 (1)	1.4642	3.42	8.8	40.08	159.0	49.55	39.14	19.14
39	78	166 (1)	1.4569	3.29	8.8	40.89	157.4	47.06	38.15	19.19

^aAll signals of alkyl and aryl groups are in the standard area. The ¹H NMR spectra fragment NMe, s for compounds: **33**, 2.74; **34**, 2.68; **35**, 2.64; **36**, 2.86; fragment SO₂Me, s for compounds: **33**, 2.63; **37**, 2.67, **38**, 2.80, **39**, 2.61. Fragment Me_{Ar}, s; **34**: δ_H 2.22, δ_C 20.92. In the ¹³C NMR spectra, fragment CHal, s for compounds: **35**, 134.35; **36**, 127.99.

^bData of ³¹P {¹H} spectra.

The novel organophosphorus-substituted amines **5–8**, **21–23**, and amides **24–39** present interest as promising ligands and biologically active compounds. The structures of organophosphorus-substituted amines and amides **1–39** were confirmed by the ¹H, ¹³C, and ³¹P NMR spectra, which show characteristic signals of the PC¹H₂NC², PC¹H₂N(C²)C³(O), and PC¹H₂N(C²)SO₂C³ fragments (see Tables 1–3). The elemental analysis data

of synthesized compounds are summarized in Table 4.

EXPERIMENTAL

The ¹H, ¹³C, and ³¹P NMR spectra were registered on the Varian VXR-400 and Bruker Avance-400 spectrometer (400, 100, and 162 MHz, respectively) in CDCl₃ (**1–20,24–39**) or D₂O (**21–23**) against TMS

TABLE 4 Elemental Analyses Data of Compounds

Compound	Empirical Formula	Formula Weight	Calcd. (%)		Found (%)	
			C	H	C	H
1	C ₉ H ₂₄ NO ₃ PSi	253.36	42.67	9.55	42.54	9.43
2	C ₁₀ H ₂₆ NO ₃ PSi	267.39	44.92	9.80	44.78	9.69
3	C ₁₁ H ₂₆ NO ₃ PSi	279.40	47.29	9.38	47.12	9.33
4	C ₁₂ H ₃₀ NO ₃ PSi	295.44	48.78	10.24	48.69	10.16
5	C ₁₁ H ₂₇ NO ₆ P ₂	331.24	39.89	8.21	39.74	8.15
6	C ₁₂ H ₂₉ NO ₆ P ₂	345.27	41.74	8.47	41.59	8.40
7	C ₁₃ H ₂₉ NO ₆ P ₂	357.32	43.70	8.18	43.54	8.03
8	C ₁₄ H ₃₃ NO ₆ P ₂	373.36	45.03	8.91	44.90	8.78
9	C ₁₁ H ₃₂ NO ₃ PSi ₃	341.61	38.68	9.44	38.52	9.26
10	C ₁₅ H ₄₃ NO ₆ P ₂ Si ₄	507.81	35.48	8.53	35.28	8.42
11	C ₁₂ H ₃₀ NO ₄ PSi	311.44	46.28	9.71	46.03	9.64
12	C ₁₄ H ₃₆ NO ₄ PSi ₃	397.67	42.28	9.12	42.12	9.06
13	C ₁₂ H ₃₃ N ₂ O ₂ PSi ₂	324.54	44.41	10.25	44.29	10.04
14	C ₁₁ H ₃₀ NO ₃ PSi ₂	311.51	42.41	9.71	42.26	9.66
15	C ₁₀ H ₂₈ NO ₂ PSi ₂	281.48	42.67	10.03	42.55	9.98
16	C ₁₀ H ₃₀ NO ₂ PSi ₃	311.58	38.55	9.71	38.26	9.57
17	C ₁₃ H ₃₈ NO ₂ PSi ₄	383.75	40.69	9.98	40.50	9.83
18	C ₁₆ H ₄₂ NO ₄ PSi ₄	455.83	42.16	9.29	41.97	9.07
19	C ₁₅ H ₄₁ N ₂ O ₂ PSi ₃	396.73	45.41	10.42	45.12	10.39
20	C ₁₅ H ₃₉ N ₂ O ₃ PSi ₃	410.71	43.86	9.57	43.64	9.66
21	C ₂ H ₈ NO ₃ P	125.06	19.21	6.44	19.03	6.49
22	C ₆ H ₁₇ N ₂ O ₂ P	180.19	39.99	9.51	39.75	9.39
23	C ₄ H ₁₀ NO ₄ P	167.10	28.75	6.03	28.64	6.08
24	C ₁₃ H ₁₉ FNO ₄ P	303.27	51.48	6.31	51.26	6.23
25	C ₁₃ H ₁₉ ClNO ₄ P	319.72	48.83	5.99	48.69	5.90
26	C ₁₃ H ₁₉ INO ₄ P	411.17	37.97	4.66	37.69	4.52
27	C ₁₄ H ₂₁ BrNO ₄ P	378.20	44.46	5.60	44.28	5.48
28	C ₁₄ H ₂₁ FNO ₄ P	317.30	52.99	6.67	52.87	6.59
29	C ₁₃ H ₂₆ NO ₄ P	291.33	53.59	9.00	53.35	8.74
30	C ₁₂ H ₂₂ NO ₄ P	275.28	52.36	8.05	52.23	7.94
31	C ₁₅ H ₂₁ FNO ₄ P	329.31	54.71	6.43	54.62	6.30
32	C ₁₃ H ₂₆ NO ₄ P	291.33	53.59	9.00	53.40	8.83
33	C ₇ H ₁₈ NO ₅ PS	259.27	32.43	7.00	32.28	6.87
34	C ₁₃ H ₂₂ NO ₅ PS	335.37	46.56	6.61	46.40	6.52
35	C ₁₂ H ₁₉ ClNO ₅ PS	355.79	40.51	5.38	40.40	5.26
36	C ₁₂ H ₁₉ BrNO ₅ PS	400.24	36.01	4.78	35.87	4.64
37	C ₈ H ₂₀ NO ₅ PS	273.30	35.16	7.38	34.97	7.29
38	C ₉ H ₂₀ NO ₅ PS	285.31	37.89	7.07	37.68	6.97
39	C ₁₀ H ₂₄ NO ₅ PS	301.35	39.86	8.03	39.69	7.92

(¹H and ¹³C) and 85% H₃PO₄ in D₂O (³¹P). All reactions were carried out under dry argon in anhydrous solvents. The starting trimethylsilyl esters of trivalent organophosphorus acids and aminomethylating reagents were prepared as described in [4,5,11].

O,O-Diethyl *N*-methyl-*N*-trimethylsilylamino-methylphosphonate (**1**). A mixture of 22.2 g of diethyl trimethylsilyl phosphite, 3.9 g of 1,3,5-trimethylhexahydrotriazine, and 0.2 g of zinc chloride was heated at 130°C for 1 h and then distilled to give 16.3 g of phosphonate **1**. Repeated distillation of the high-boiling fraction gave 1.2 g of *N*-methyl-*N*,*N*-bis(diethoxyphosphorylmethyl)amine

5. Phosphonates **2–4,9**, phosphinates **11–13**, and bisphosphonates **6–8,10** were prepared similarly.

O,O-Diethyl *N,N*-bis(trimethylsilyl)aminomethylphosphonate (**14**). A mixture of 12 g of diethyl trimethylsilyl phosphite, 10 g of *N*-ethoxymethylbis(trimethylsilyl)amine, and 0.2 g of zinc chloride was heated at 120–140°C with distillation of ethoxy(trimethyl)silane for 2 h, and then distilled in a vacuum to give 11.1 g of phosphonate **14**.

Phosphinate **15** and phosphonite **16** were obtained analogously.

O,O-Bis(trimethylsilyl) *N,N*-bis(trimethylsilyl)-aminomethylphosphonite (**17**). A mixture of 6.2 g of phosphonite **16**, 4.7 g of *N*-trimethylsilylpiperidine,

and 0.1 g of zinc chloride was heated at 120–130°C for 2 h, and then distilled in a vacuum to give 6.2 g of phosphonite **17**.

O-Trimethylsilyl *N,N*-bis(trimethylsilyl)amino-methyl 2-(trimethylsiloxy-carbonyl)ethylphosphinate (**18**). To a solution of 4.7 g of phosphonite **16** in 5 mL of methylene chloride, 3.5 g of trimethylsilyl acrylate and 2 mL of pyridine were added. Then the solvent was distilled off, and the residue was heated at 100°C for 1 h and then distilled in a vacuum to give 6 g of phosphinate **18**.

O-Trimethylsilyl *N,N*-bis(trimethylsilyl)amino-methyl *N,N*-diethylaminomethylphosphinate (**19**). To a solution of 5.8 g of phosphonite **17** in 20 mL of methylene chloride, a solution of 1.8 g of *N*-(chloromethyl)diethylamine in 20 mL of methylene chloride was added dropwise with stirring at 0°C. The reaction mixture was heated to room temperature and then to the boil, and the solvent was distilled off. The residue was distilled in a vacuum to give 5.1 g of phosphinate **19**.

Phosphinate **20** was obtained analogously.

N-Methyl aminomethylphosphonic acid (**21**). To a solution of 10.9 g of phosphonate **9** in 10 mL of diethyl ether was added dropwise with stirring at 10°C in 30 mL of methanol. The resulting mixture was heated to boil, the solvent was distilled off in a vacuum, and the residue was kept in a vacuum (1 mmHg) for 1 h to give 3.8 g of acid **21** as colorless hydroscopic crystals.

The acids **22** and **23** were obtained similarly.

O,O-Diethyl *N*-allyl-*N*-pivaloylaminomethylphosphonate (**29**). To a solution of 11 g of phosphonate **3** in 20 mL of methylene chloride, a solution of 4.5 g of pivaloyl chloride in 10 mL of methylene chloride was added dropwise with stirring at 10°C. The mixture was heated to reflux, the solvent was removed, and the residue was distilled in a vacuum. Phosphonate **29**, 8.5 g was obtained.

The amides **24–28** and **30–32** were prepared similarly.

O,O-Diethyl *N*-methyl-*N*-(methylsulfonyl)aminomethylphosphonate (**33**). To a solution of 1 g of methanesulfonyl chloride in 5 mL of methylene chloride was added dropwise with stirring and cooling at 10°C to a solution of 2 g of phosphonate **1** in 5 mL of methylene chloride. The mixture was heated to the boil, the solvent was removed, and the residue was distilled in a vacuum to obtain 1.7 g of phosphonate **33**.

The sulfonamides **34–39** were obtained analogously.

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