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Synthesis of New Organophosphorus-Substituted Derivatives of Functionalized Propionates and Their Analogues

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ABSTRACT: *Nucleophilic or radical addition of trimethylsilyl esters of trivalent organophosphorus acids to various functionalized acrylates and their cyclic analogues is proposed as convenient methods for the synthesis of new 2-trimethylsiloxycarbonyl-substituted alkylphosphonites and their derivatives under mild conditions. Also the new functionalized derivatives of these phosphonites, including amino, amido, and amino acids fragments as well as certain properties of these compounds, are presented as important precursors of new organophosphorus-substituted derivatives of functionalized propionates and their analogues.* © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:418–428, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20446

INTRODUCTION

Organophosphorus analogues of amino acids containing carboxyl and amino groups as well as heterocyclic and organoelement fragments are of great interest as promising ligands and biologically active compounds [1–4]. Recently, we have found that various derivatives of functionalized organophosphorus acids with aryl, heterocyclic, and organoelement fragments were obtained in high yields via addition of trimethylsilyl esters of trivalent organophosphorus acids to various organic compounds containing multiple bonds [5–7]. In the present work, we report the results of the nucleophilic or radical addition of bis(trimethylsiloxy)phosphine, trimethylsilyl phosphites, and phosphonites to trimethylsilyl acrylate and its various functionalized or cyclic analogues such as γ-crotonolactone, trimethylsilyl esters of 2-(acetylamino)acrylic, itaconic, maleic, acetylenedicarboxylic, cinnamic, 3-(2-furyl)propionic, and 1*H*-indene-2-carboxylic acids. The obtained phosphonites were easily transformed to aminomethyl phosphinates using various methods of aminomethylation thoroughly investigated by us (cf. [8]). These reactions provide a convenient synthetic route to new organophosphorus-substituted derivatives of functionalized propionates and their analogues including fragments of indan, γ-butyrolactone, furan, pyridine, proline, and sarcosine.

RESULTS AND DISCUSSION

In the present work, we showed that the reaction of bis(trimethylsiloxy)phosphine **A** with trimethylsilyl acrylate and its various functionalized or cyclic analogues is a convenient route to functionalized 2-(trimethylsiloxycarbonyl)alkylphosphonites **1–8**. So phosphine **A** in methylene chloride readily reacts with trimethylsilyl or methyl esters of acrylic,

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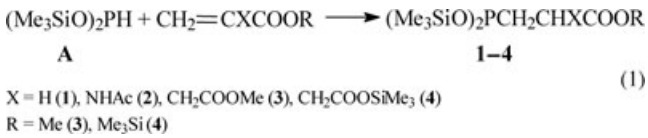
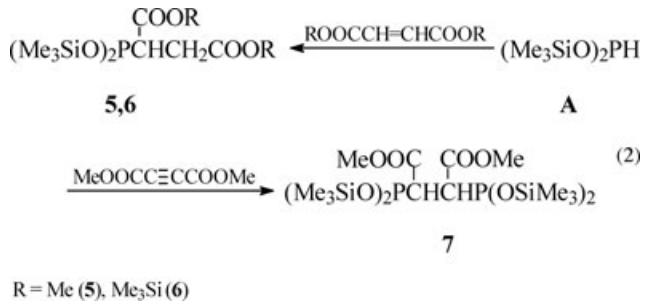
2-(acetylamino)acrylic, and 2-(carboxymethyl)-acrylic (itaconic) acids exclusively by way of 3,4-addition involving the PH fragment to form phosphonites **1–4** in high yield. The phosphonite **2** is a new organophosphorus analogue of aspartic acid (Eq. (1); cf. [9]).



(1)

Under the similar conditions, excess of phosphine **A** readily adds to maleic and acetylenedicarboxylic acid diesters to give phosphonites **5,6**, and bisphosphonite **7**, incorporating a succinic acid fragment (Eq. (2)).

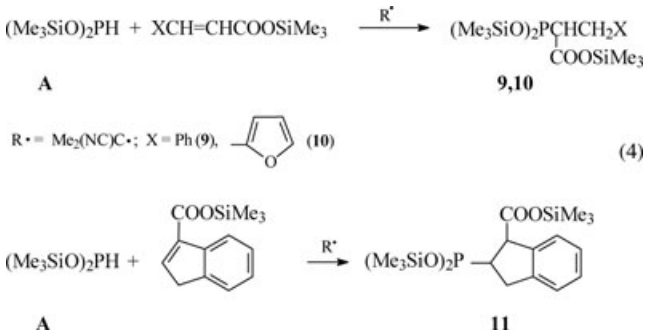


(2)

The functionalized and cyclic analogues of trimethylsilyl acrylate possess the lower activity toward phosphine **A**. So bis(trimethylsiloxy)phosphine **A** slowly adds to γ-crotonolactone at 20°C to form phosphonite **8**, and heating at 100°C is required for the reaction to be completed (Eq. (3)).

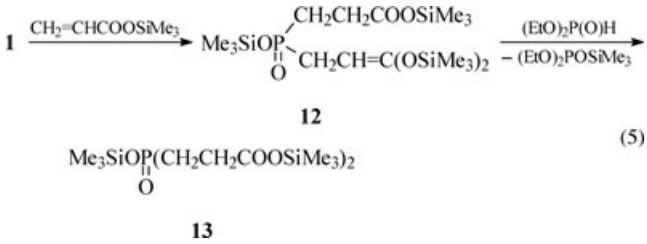
(3)

The addition of phosphine **A** to trimethylsilyl esters of cinnamic, 3-(2-furyl)propionic, and 1*H*-indene-2-carboxylic acids proceeds only in the presence of azobis(isobutyronitrile) at 100–130°C to give phosphonites **9–11** in high yields (Eq. (4); cf. [10]). Note that the influence of phenyl or furyl fragments on the orientation of the addition in these reactions is more preferable (cf. [6]).



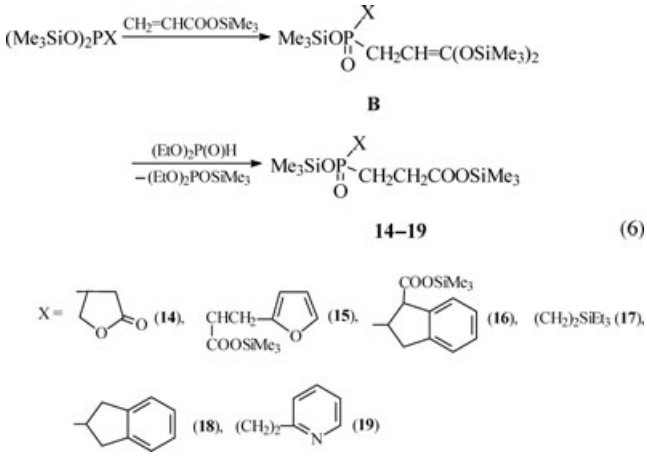
(4)

Phosphonite **1** smoothly reacts with trimethylsilyl acrylate in methylene chloride via 1,4-addition involving the POSi fragment to form corresponding ketene bis(trimethylsilyl) acetal **12** in high yield (cf. [11]), and treatment of acetal **12** with diethyl phosphite yields phosphinate **13** with two propionate fragments (Eq. (5)).



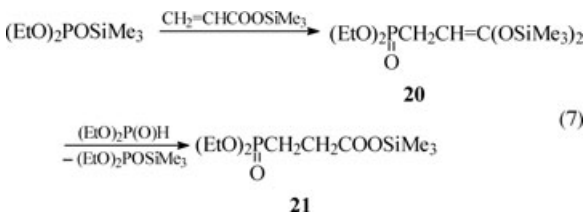
(5)

By a similar way, the functionalized phosphonites with element or heterocyclic fragments [5,6] were transformed by us after the treatment of the intermediate acetals **B** with diethyl phosphite to phosphinates **14–19**, containing sometimes two different fragments with the carboxyl groups (Eq. (6)).



(6)

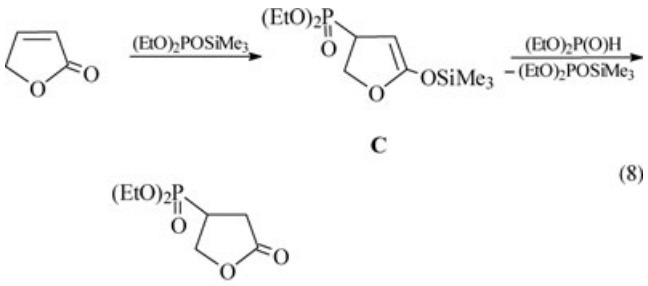
Diethyl trimethylsilyl phosphite adds to trimethylsilyl acrylate only by heating at 120–130°C to give ketene acetal **20** in high yield, which was transformed to phosphonate **21** after the treatment with diethyl phosphite (Eq. (7); cf. [12–14]).



(7)

Also the heating of a mixture of γ-crotonolactone with diethyl phosphite and diethyl trimethylsilyl phosphite at 120°C in the presence of zinc chloride leads to formation of phosphonate **22** in high yield.

Note that under other reaction conditions the starting lactone and the intermediate ketene acetal **C** readily polymerize (Eq. (8)).

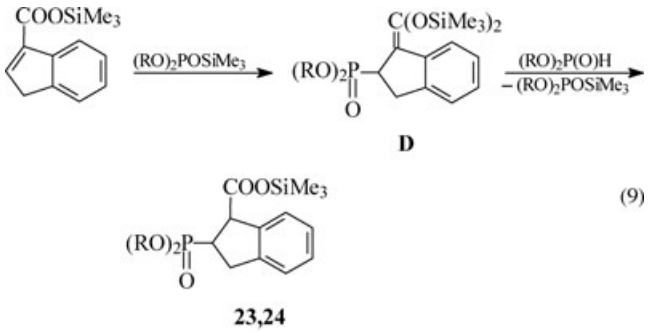


C

(8)

22

Under similar conditions, the reactions of trimethylsilyl esters of phosphorous acid with trimethylsilyl 1*H*-indene-2-carboxylate yield the new phosphonates **23,24** containing fragments of indan-1-carboxylic acid. Apparently, these reactions involve intermediate formation of unstable ketene acetals **D** (Eq. (9)).



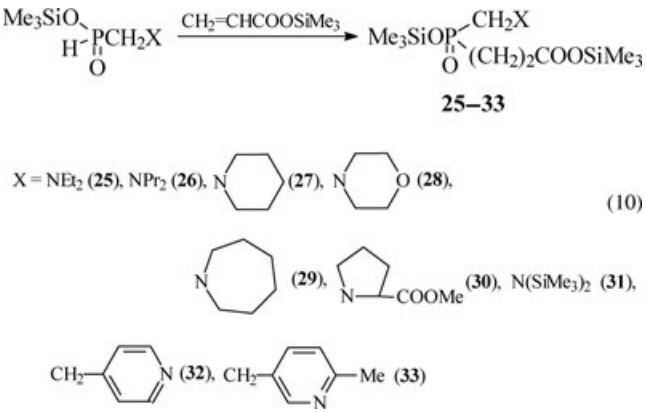
D

(9)

23,24

R = Et (**23**), Me_3Si (**24**)

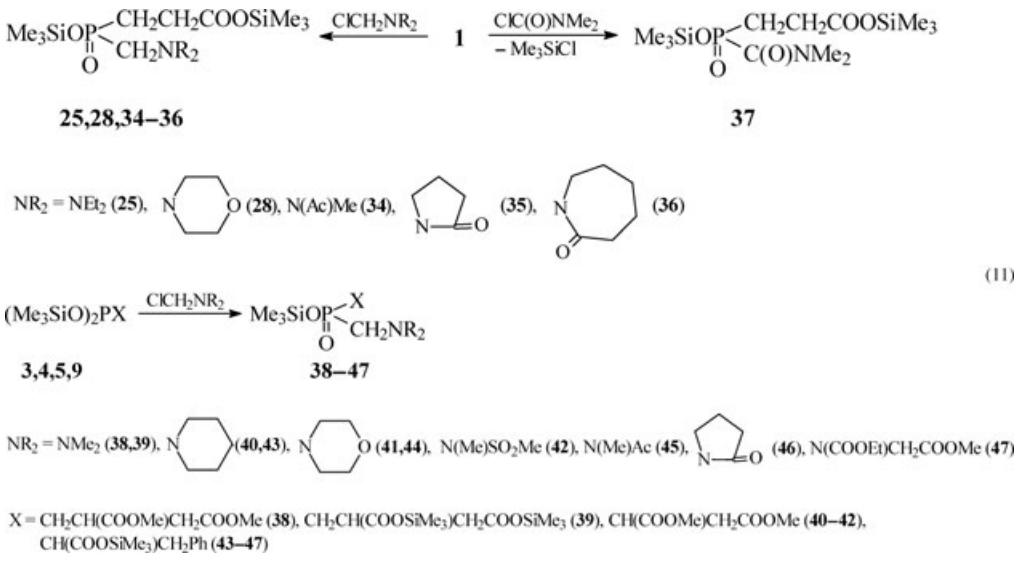
We have developed the methods for synthesis of new phosphinates with propionate, aminomethyl, and pyridine fragments by 2-carboxyethylation of available functionalized phosphonites containing the P(O)H moieties [15]. Thus these phosphonites add to trimethylsilyl acrylate on heating to 140°C in the presence of triethylamine or pyridine to give phosphinates **25–33** in high yield (Eq. (10)).



25–33

(10)

Functionalized phosphonites **1–11** are convenient synthons for preparing various organophosphorus analogues of amino acids and their derivatives with promising properties [3,4]. In the present work, we propose a universal synthetic approach to such compounds on the basis of amino- or amido-methylation of the highly reactive phosphonites **1,3–5,9** with *N*-chloromethylamines, *N*-chloromethylamides, and *N,N*-dimethylcarbamoyl chloride. These reactions proceed under mild conditions in methylene chloride and form phosphinates **25,28,34–47** in high yields (Eq. (11)).



25,28,34–36 **37**

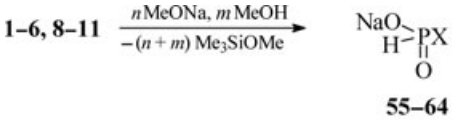
3,4,5,9 **38–47**

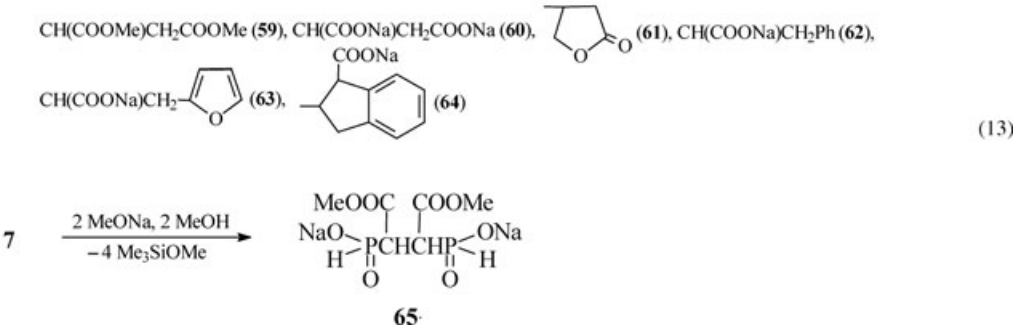
(11)

X = $CH_2CH(COOMe)CH_2COOMe$ (**38**), $CH_2CH(COOSiMe_3)CH_2COOSiMe_3$ (**39**), $CH(COOMe)CH_2COOMe$ (**40–42**), $CH(COOSiMe_3)CH_2Ph$ (**43–47**)

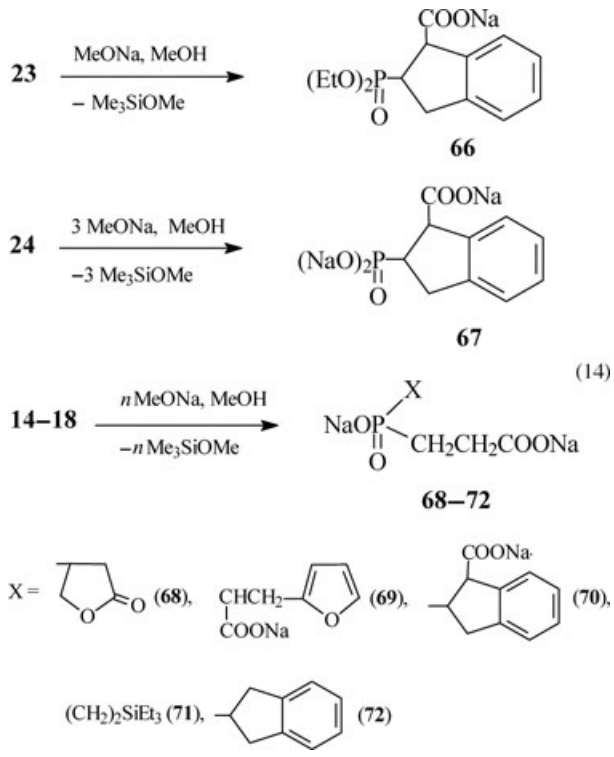
In contrast, the aminomethylation of the phosphonites **8,10,11** with aminals takes place at 120–130°C in the presence of zinc chloride to form functionalized phosphinates including carboxyl and aminomethyl moieties **48–54** (Eq. (12); cf. [8]).

Thus we proposed the convenient synthesis of trimethylsilyl derivatives of new functionalized organophosphorus analogues of amino acids including various amino and carboxyl groups **1–54** (see Tables 1–3). Trimethylsilyl esters of several functionalized organophosphorus acids were useful for obtaining the series of water-soluble acids and their sodium salts (cf. [5–7]). So *O*-trimethylsilyl-substituted phosphonites **1–11** smoothly react with diluted solutions of sodium methylate in methanol, giving stable crystalline sodium salts of functionalized 2-carboxyalkylphosphonous acids **55–65** (see Table 4; Eq. (13)).

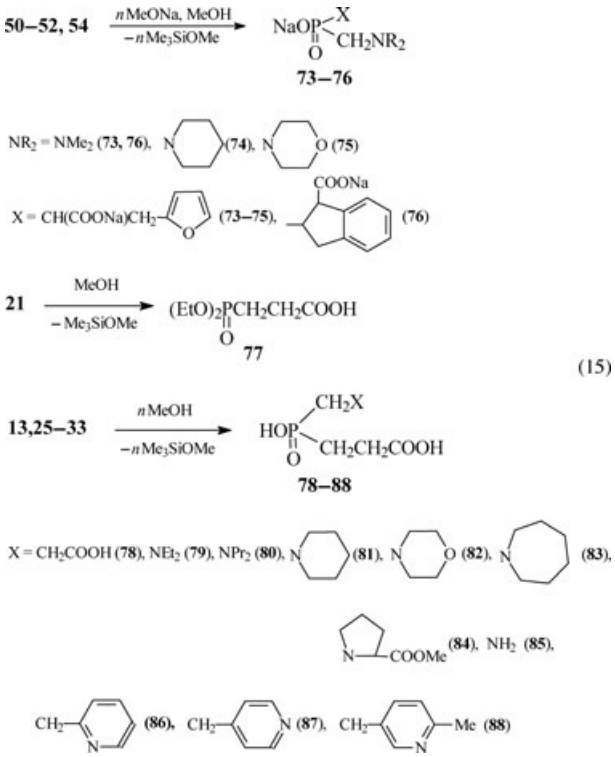




Also the treatment of phosphonates **23,24** and phosphinates **14–18** with diluted solution of sodium methylate in methanol results in formation of water-soluble sodium phosphonates **66,67** and sodium phosphinates **68–76** as white hygroscopic crystals (Eq. (14)).



Also phosphonate **21** and phosphinates **13, 25–33** were easily transformed to corresponding organophosphorus acids **77–88** via treatment with methanol in high yields (Eq. (15)).



Synthesized acids and salts **66–88** are white hygroscopic crystals (acid **77** is thick oil; see Table 5) 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 6.

EXPERIMENTAL

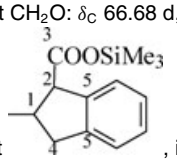
The ^{1}H, ^{13}C, and ^{31}P NMR spectra were registered on the Varian VXR-400 and Bruker Avance-400 spectrometers (400, 100, and 162 MHz, respectively) in $CDCl_3$ (**1–54**) or D_2O and $(CD_3)_2SO$ (**55–88**) against TMS (^{1}H, ^{13}C) and 85% H_3PO_4 in D_2O (^{31}P). All reactions were carried out under dry argon in anhydrous solvents.

*O,O-Bis(trimethylsilyl)-2-(trimethylsiloxycarbonyl)-ethylphosphonite (**1**).* A solution of 6 g of trimethylsilyl acrylate in 20 mL of methylene chloride was added dropwise with stirring and cooling to 10°C to a solution of 9 g of phosphine **A** in 60 mL of methylene chloride. The reaction mixture was kept for 24 h at 20°C, the solvent was then removed, and the residue was distilled in a vacuum to obtain 10.1 g of phosphonite **1**.

Phosphonites **2–7** were prepared similarly.

TABLE 1 Yields, Product Constants, and NMR Spectral Data for the $PC^{1}H_mC^{2}H_nC^{3}$ Fragments[a] (δ, ppm; J, Hz) of Phosphonites **1–11**[a]

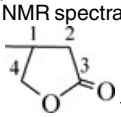
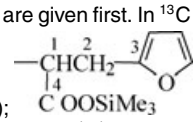
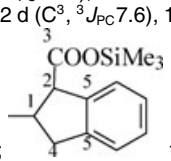
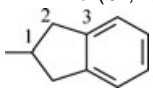
Compound	*Yield (%)*	*Bp (°C) (p, mmHg)*	*$\delta(C^1)$ (d)*	*$^{1}J_{PC}$*	*$\delta(C^2)$ (d)*	*$^{2}J_{PC}$*	*$\delta(C^3)$(d)*	*$^{3}J_{PC}$*	*$\delta(P)$ (s)*
1	68	86 (1)	36.41	25.8	27.74	13.0	173.63	9.0	159.49
2[b]	83	146 (1)	44.16	32.3	49.53	11.6	173.25	5.7	156.87
3	83	126 (1)	42.28	30.2	35.00	11.3	36.21	6.5	155.58
4	81	133 (1)	42.46	30.3	36.82	11.6	38.19	7.2	156.35
5	89	115 (1)	52.02	38.9	27.99	12.1	172.73	7.4	145.55
6	83	127 (1)	53.89	38.2	30.39	14.1	172.72	9.1	146.63
7	74	148 (1)	54.15[c]	16.1	54.15	16.1	169.76[d]	6.6	144.62
			52.75[e]	49.1	52.75	13.0	168.93	<1	146.83
8[f]	74	122 (1)	41.59	24.6	26.90	14.5	176.63	4.6	146.29
9	89	121 (1)	53.31	28.8	34.83	18.1	138.12	7.8	151.52
10	89	126 (1)	46.24	28.9	32.27	15.0	152.44	8.9	144.55
11[g]	87	152 (1)	52.72	29.5	32.16	23.9	172.61	<1	159.38

[a]All signals of alkyl, aryl, furyl, and trimethylsilyl groups are in the standard area. The ^{1}H NMR signals of the protons of the groups $C^{1}H_mC^{2}H_nC^{3}$ are multiplets. According to the NMR spectra, compound **7** is a mixture of two stereoisomers. Their ratio was determined from the ^{1}H NMR and ^{31}P NMR spectra as 60:40. The spectral parameters of the major isomer are given first. Fragments COOR in ^{13}C NMR spectra, d, $^{3}J_{PC}$, **3**: 174.65, 4.8, and 171.50 s; **4**: 175.07, 5.9, and 171.90 s; d, $^{2}J_{PC}$, **5**: 170.57, 6.4; **6**: 170.29, 6.6; **9**: 172.44, 11.1; **10**: 172.62, 9.1.
[b]Fragment NHC(O)Me. In ^{1}H NMR spectra: 1.82 s (Me), 7.22 d (NH, $^{3}J_{HH}$ 7.6). In ^{13}C NMR spectra, s: 22.73 (Me), 169.43 [C(O)N]].
[c]t, $^{1}J_{PC} = {}^{2}J_{PC}$.
[d]t, $^{2}J_{PC} = {}^{3}J_{PC}$.
[e]d. d.
[f] Fragment CH_2O: δ_C 66.68 d, $^{2}J_{PC}$ 16.8.
[g]Fragment 

, in ^{13}C NMR spectra: 32.16 d (C^4, $^{2}J_{PC}$ 23.9), 144.84 d (C^5, $^{3}J_{PC}$ 9.4), 141.73 d (C^5, $^{3}J_{PC}$4.2).

TABLE 2 Yields, Product Constants, and NMR Spectral Data for the $PC^1H_2C^2H_2C^3(O)$ Fragments[a] (δ, ppm; J, Hz) of Phosphinates **12–19, 32, 33** and Phosphonates **20–24**

Compound	*Yield (%)*	*Bp (°C) (p, mmHg)*	n_D^{20}	$\delta(C^1)d$	$^1J_{PC}$	$\delta(C^2)d$	$^2J_{PC}$	$\delta(C^3)d$	$^3J_{PC}$	$\delta(P)s$
12	64	155 (2)	1.4455	25.77	94.4	28.73	<1	172.54	14.4	43.86
				24.64[b]	93.6	72.68	9.2	152.63	11.7	
13	88	135 (1)	1.4480	25.68	94.1	28.68	3.0	172.54	14.9	43.46
14	81	186 (1)	1.4610	23.12	95.8	27.90	3.9	171.22	14.4	39.67
				23.25	95.8	27.43	<1	171.20	11.1	39.84
15	76	178 (1)	1.4640	23.27	96.4	27.50	<1	171.64	17.0	38.53
				22.52	95.8	27.28	<1	171.63	18.3	39.30
16	83	197 (1)	1.4969	23.80	93.6	27.81	<1	[c]	–	44.21
				23.46	94.1	27.88	<1	[c]	–	44.17
17	80	163 (2)	1.4522	24.51	91.5	28.83	<1	172.76	13.8	44.04
18	82	178 (1)	1.4932	22.13	93.0	27.63	1.2	171.90	15.3	45.43
19	86	187 (1)	1.4817	25.72	92.5	28.81	2.5	172.62	15.2	42.45
				29.73[d]	92.9	30.67	3.0	160.78	14.3	
20	74	95 (1)	1.4375	23.97[b]	141.9	72.75	10.3	152.70	13.8	27.09
21	78	104 (2)	1.4310	21.16	143.2	29.35	4.0	172.27	17.9	27.82
22	64	155 (1)	1.4565	30.98	151.6	27.93	4.2	174.16	12.3	23.37
23	83	173 (1)	1.4888	36.52	147.2	52.35	<1	171.29	5.8	28.75
24	86	165 (1)	1.4771	38.35	152.9	52.94	5.8	171.63	9.3	11.09
32	81	192 (2)	1.4869	25.27	92.6	28.73	<1	172.66	14.6	41.32
				30.78[d]	92.0	27.56	<1	150.09	21.6	
33	88	185 (1)	1.4811	24.32	93.7	27.56	<1	171.53	15.0	41.78
				30.86[d]	92.0	24.14	<1	132.31	15.0	

[a]All signals of alkyl, trimethylsilyl, aryl, and heterocyclic groups are in the standard area. The ^1H NMR signals of the protons of the groups $C^1H_2C^2H_2C^3(O)$ are multiplets. According to the NMR spectra, compounds **14–16** are mixtures of two stereoisomers. Their ratio was determined from the ^1H NMR and ^{31}P NMR spectra as 60:40 for **14,16** and as 55:45 for **15**. The spectral parameters of the major isomer are given first. In ^{13}C NMR spectra, fragments:  for **14**, δ_C, 33.87 d (C^1, $^1J_{PC}$97.6), 27.03 s (C^2), 171.21 d (C^3, $^3J_{PC}$11.5), 65.75 s (C^5);  for **15**, first isomer, 37.09 d (C^1, $^1J_{PC}$93.2), 32.82 s (C^2), 148.92 d (C^3, $^3J_{PC}$7.6), 170.30 d (C^4, $^2J_{PC}$16.5), second isomer, 38.07 d (C^1, $^1J_{PC}$93.1), 33.26 s (C^2), 148.92 d (C^3, $^3J_{PC}$5.4), 170.22 d (C^4, $^2J_{PC}$16.7);  for **16**, first isomer, 39.42 d (C^1, $^1J_{PC}$93.2), 52.17 s (C^2), 32.13 s (C^4), 141.26 d (C^5, $^3J_{PC}$6.8) and 138.80 d (C^5, $^3J_{PC}$7.1), second isomer, 39.70 d (C^1, $^1J_{PC}$96.6), 51.68 d (C^2, $^2J_{PC}$6.4), 31.69 s (C^4), 141.96 d (C^5, $^3J_{PC}$ 6.4) and 138.99 d (C^5, $^3J_{PC}$6.4), 171.68–172.05 m (C^3) for two isomers; for **23**, 36.52 d (C^1, $^1J_{PC}$147.2), 52.35 s (C^2), 32.16 s (C^4), 140.97 d (C^5, $^3J_{PC}$10.8), and 138.75 d (C^5, $^3J_{PC}$9.9), 171.29 d (C^3, $^3J_{PC}$5.8); for **24**, 38.35 d (C^1, $^1J_{PC}$152.9); 52.94 d (C^2, $^2J_{PC}$5.8), 32.84 s (C^4), 141.44 d (C^5, $^3J_{PC}$7.7) and 139.13 d (C^5, $^3J_{PC}$7.4), 171.63 d (C^3, $^3J_{PC}$9.3); $C^1H_2C^2H_2Si$ for **17**, 24.47 d (C^1, $^1J_{PC}$91.6); 2.60 d (C^2, $^2J_{PC}$7.4);  for **18**, 37.33 d (C^1, $^1J_{PC}$98.6); 32.80 s and 32.82 s (C^2), 140.90 s (C^3); CH_2O for **22**, 66.28 s.

[b]Fragment $PC^1H_2C^2H{=}C^3$.

[c]171.68–172.05 m, two C=O groups from two stereoisomers.

[d]Fragment $PC^1H_2C^2H_2C^3_{Py}$.

*O,O-Bis(trimethylsilyl)-2-oxotetrahydrofur-4-ylphosphonite (**8**).* A solution of 12.4 g of γ-crotonolactone in 20 mL of methylene chloride was added dropwise with stirring to a solution of 37 g of phosphine **A** in 50 mL of methylene chloride. The resulting mixture was stirred for 1 h, the solvent was removed by distillation, and the residue was heated for 1 h at 100°C and then distilled to obtain 32 g phosphonite **8**.

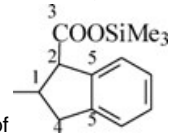
*O,O-Bis(trimethylsilyl)-1-trimethylsiloxycarbonyl-2-phenylethylphosphonite(**9**).* A mixture of 13.5 g of phosphine **A**, 14.2 g of trimethylsilyl cinnamate, and 0.2 g of azobis(isobutyronitrile) was heated at 100–130°C for 1.5 h and then distilled in a vacuum to obtain 24.6 g of phosphonite **9**.

Phosphonites **10,11** were prepared similarly.

*O-Trimethylsilyl-2-(trimethylsiloxycarbonyl)ethyl-3,3-bis(trimethylsiloxy)propen-2-ylphosphinate (**12**).* A solution of 5.1 g of trimethylsilyl acrylate in 15 mL of methylene chloride was added dropwise with stirring and cooling to 10°C to a solution of 8.9 g of phosphonite **1** in 50 mL of methylene chloride.

TABLE 3 Yields, Product Constants, and NMR Spectral Data for the $PC^1H_mC^2H_nC^3$ and $PC^4H_2NFragments^a$ (δ, ppm; J, Hz) of Aminomethyl Phosphinates **25–31, 34–54**

Compound	*Yield (%)*	*Bp (°C) (p, mmHg)*	n_D^{20} *(Mp, °C)*	$\delta(C^1)$ *d*	$^1J_{PC}$	$\delta(C^1)$*s*	$\delta(C^3)$*d*	$^3J_{PC}$	$\delta(C^4)$*d*	$^1J_{PC}$	δ(P)*s*
25	81	126 (2)	1.4485	24.43	93.4	28.99	172.84	15.0	53.58	116.3	39.49
26	86	151 (4)	1.4510	24.33	89.7	28.89	172.74	15.3	54.77	115.3	39.52
27	86	175 (4)	1.4610	25.65	88.0	28.61	172.47	15.5	58.82	114.5	40.05
28	83	167 (3)	(52)	24.29	95.3	28.78[b]	172.71	15.3	58.43	113.7	39.50
29	86	152 (1)	1.4650	24.35	93.5	28.96	172.83	15.2	58.10	115.2	39.41
30	79	180 (2)	1.4655	27.95	99.3	28.96	172.19	15.7	54.29	124.3	41.09
				28.01	97.6	28.90	172.05	15.8	54.21	122.4	39.06
31	87	140 (1)	1.4558	24.32	86.3	28.95[b]	172.61	13.6	45.93	105.2	38.55
34	74	151 (2)	1.4595	25.12	91.6	28.69	172.72	16.4	47.03	103.8	37.51
35	78	181 (1)	1.4710	23.52	93.1	27.42	171.68	16.9	42.01	105.2	37.35
36	81	192(1)	1.4708	24.78	91.5	28.72	172.71	16.2	47.71	104.5	37.74
37	87	152 (1)	1.4581	25.31	103.6	29.14	172.48	15.7	169.13[c]	156.5	23.46
38	89	141 (1)	1.4590	29.04	93.4	34.73[b]	35.22	5.1	58.27	115.3	37.89
				28.66	93.2	34.98	35.27	5.4	58.70	115.1	37.97
39	81	157 (1)	1.4510	28.72	93.4	36.40[b]	37.14	3.9	59.09	114.8	38.72
				29.07	93.6	36.58	37.60	4.0	58.66	115.0	38.57
40	74	160 (1)	1.4652	41.07	79.7	29.02	171.47	15.5	56.74	121.4	31.90
				43.72	79.7	30.58	171.09	16.2	56.35	118.3	32.11
41	78	165 (1)	1.4535	40.97	80.4	28.88	171.47	15.7	56.21	122.1	31.25
				43.89	80.6	30.65	171.30	17.0	55.84	119.2	31.08
42	80	205 (2)	1.4680	41.81	79.9	28.76	170.90	15.2	47.92	114.9	28.55
				42.98	80.7	30.06	170.64	16.7	47.15	112.8	29.02
43	83	175 (1)	1.4965	42.80	88.5	36.09	137.63	6.2	57.47	114.8	36.51
				44.24	88.0	36.19	137.35	3.6	56.65	113.8	37.48
44	85	181 (1)	(45)	42.79	89.0	35.94	137.38	6.2	56.78	113.2	35.99
				44.12	88.7	36.08	137.01	4.0	56.14	112.6	36.80
45	80	206 (3)	1.4972	43.20	86.7	36.15	136.56	6.0	46.21	101.3	34.92
				43.86	87.0	35.90	136.12	3.4	45.55	102.5	33.87
46	85	193 (1)	1.4981	42.95	86.8	36.01	136.42	7.3	42.01	102.5	34.10
				43.88	87.7	35.89	136.13	4.2	41.75	104.0	33.02
47	78	204 (1)	1.4850	42.17	88.0	36.12	136.25	7.2	46.35	103.7	35.16
				43.20	87.3	35.70	136.10	4.6	45.71	104.6	33.93
48	68	162 (1)	1.4635	33.85	98.9	28.08	174.62	10.4	57.34	118.1	36.01
				33.97	99.5	28.15	174.82	12.3	57.48	117.7	36.81
49	69	195 (1)	(65)	33.88	100.0	28.07	174.40	9.3	56.27	121.8	34.91
				33.61	97.2	27.96	174.69	9.3	56.39	115.5	35.67
50	74	143 (2)	1.4665	34.88	92.0	32.22	149.49	8.8	56.09	117.2	34.16
				37.34	91.2	33.13	149.27	6.7	55.80	116.5	34.49
51	72	175 (1)	1.4755	35.34	91.8	32.64	149.85	8.0	56.07	116.8	34.66
				37.75	91.4	33.70	149.73	6.2	55.77	116.7	34.84
52	78	183 (2)	1.4750	35.36	92.7	32.59	149.77	7.8	55.97	116.1	34.00
				37.81	92.2	33.74	149.53	6.9	55.41	111.0	34.02
53	78	186 (1)	1.4702	35.20	91.1	32.81	149.88	7.8	53.35	116.1	34.44
				37.61	90.9	33.57	149.61	6.9	53.09	115.5	34.86
54	81	186 (1)	(67)	38.89	96.0	53.23	171.86	<1	57.64	113.1	41.14
				38.54	96.5	51.83	171.92	<1	57.54	113.6	39.85

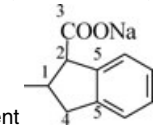
[a]All signals of alkyl, trimethylsilyl, aryl, and heterocyclic fragments are in the standard area: the signals of these fragments are multiplets and partially or completely overlap. The signals of the diastereotopic protons of the methylene groups C^4H_2 of **25–31, 34–36, 38–54** are characteristic ABX multiplets in the range 2–3 ppm. In the spectra of the stereoisomers of phosphinates **30, 38–54**, the signals of these protons partially overlap. According to the NMR spectra, compounds **30, 38–54** are mixtures of two stereoisomers. Their ratio was determined from the ^{1}H NMR and ^{31}P NMR spectra as 55:45 for **39,53**; 60:40 for **30,38,40,42,48,50,52,54**; 65:35 for **41,49,51**; 70:30 for **43–47**. The spectral parameters of the major isomer are given first. In ^{13}C NMR spectra, fragments COOR, δ_C, **30**: 173.39 s, and 173.25 s; **38**: 170.83 s, 172.99 d, $^3J_{PC}$5.8, and 173.10 d, $^3J_{PC}$5.9, 170.90 s; **39**: 171.49 s, 173.61 d, $^3J_{PC}$4.2 and 171.43 s, 173.46 d, $^3J_{PC}$5.1; **40**: 168.94 s, and 169.11 s; **41**: 168.87 s, and 169.19 s; **42**: 168.15 s, and 168.13 s; **43**: 171.58 d, $^2J_{PC}$17.5, and 171.65 d, $^2J_{PC}$16.3; **44**: 171.50 d, $^2J_{PC}$17.3 (the signals of the stereoisomers coincide); **45**: 171.31 d, $^2J_{PC}$18.7, and 171.13 d, $^2J_{PC}$18.7; **46**: 171.28 d, $^2J_{PC}$17.7, and 171.05 d, $^2J_{PC}$17.9; **47**: 171.19 d, $^2J_{PC}$18.4, and 170.95 d, $^2J_{PC}$18.6, 169.81 s (COOMe for two stereoisomers); **50**: 170.18 d, $^2J_{PC}$16.5, and 170.27 d, $^2J_{PC}$16.9; **51**: 170.68 d, $^2J_{PC}$16.5, and 170.79 d, $^2J_{PC}$16.5; **52**: 170.72 d, $^2J_{PC}$16.5, and 170.76 d, $^2J_{PC}$16.7; **53**: 170.74 d, $^2J_{PC}$13.8, and 170.90 d, $^2J_{PC}$15.9, 169.88 s, and 169.83 s (COOEt); fragment NC(O), δ_C, **34**: 169.58 s; **35**: 174.17 s; **36**: 174.52 s; **45**: 169.88 s and 170.0 s; **46**: 174.0 d, $^3J_{PC}$2.7, and 173.93 d, $^3J_{PC}$3.1; **47**: 156.14 s, and 156.2 s; fragment $CH_2OC(O)$, δ_C, **48**: 66.73 s; **49**: 66.80 s; fragment of 

54, δ_C: first isomer, 32.10 s (C^4), 141.25 d (C^5, $^3J_{PC}$7.1) and 139.39 d (C^5, $^3J_{PC}$6.1), second isomer, 31.85 s (C^4), 141.56 d (C^5, $^3J_{PC}$6.9) and 139.14 d (C^5, $^3J_{PC}$7.1).
[b]d, $^2J_{PC}$, **28**: 3.1; **31**: 3.0; **38**: 3.8; **39**: 4.2.
[c]Fragment $PC(O)NMe_2$, two nonequivalent Me groups: δ_H 3.08 s and 2.50 s; δ_C 36.16 s and 34.57 s.

TABLE 4 Yields, Product Constants, and NMR Spectral Data for the $HPC^1H_mC^2H_nC^3$ Fragments[a] (δ, ppm; J, Hz) of Sodium Phosphonites **55–65**[a]

Compound	*Yield (%)*	*δ(H) PH, d*	*$^1J_{PH}$*	*$^3J_{HH}$*	*$\delta(C^1)d$*	*$^1J_{PC}$*	*$\delta(C^2)s$*	*$\delta(C^3)d$*	*$^3J_{PC}$*	*$\delta(P)$ s[b]*
55	97	6.95	510.2	<1	30.78	86.7	91.97	181.74	11.5	27.57
56	96	6.96	517.6	<1	32.33	88.2	47.41	176.90	12.1	21.98
57	94	7.02[c]	515.2	1.8	33.58	88.1	36.51	36.99	8.3	21.81
58	96	6.94[c]	509.2	1.6	34.95	89.3	41.04	42.57	11.4	25.58
59	97	7.07	514.1	<1	44.57	92.5	26.75	177.83	10.7	22.86
60	95	6.98	506.7	<1	43.29	91.6	27.14	177.57	11.2	26.48
61	96	6.90[d]	521.2	1.6	36.13	92.7	28.63	181.11	10.6	24.13
62	97	6.82	518.8	<1	45.17	84.3	33.77	136.62	6.2	36.40
63	95	6.84	515.6	<1	40.24	86.4	34.29	151.48	7.3	24.89
64	97	7.12[d]	527.2	4.0	43.95	98.9	55.05	180.44	4.6	31.74
65	97	7.17	522.4	<1	47.26	88.7	[e]	175.13	12.0	29.02

[a]The salts **55–65** are very hygroscopic crystals; therefore, their melting points were not measured. In ^{1}H NMR spectra, all signals of the alkyl, aryl, and furyl fragments are in the standard area; the signals of these fragments are multiplets and partially or completely overlap. In ^{13}C NMR spectrum, fragment NC(O) of **56**; δ_C 171.78 s; fragments COOR, δ_C, d, **57**: 177.32, $^3J_{PC}$9.1, and 174.86 s; **58**: 183.57, $^3J_{PC}$7.8, and 181.32 s;



59: 175.49, $^2J_{PC}$4.5; **60**: 175.74, $^2J_{PC}$5.2; **62**: 177.05, $^2J_{PC}$17.5; **63**: 180.04, $^2J_{PC}$17.5; fragment CH_2O of **61**, δ_C 68.99 s; fragment of **64**, δ_C: 55.05 d (C^2, $^2J_{PC}$ 9.5); 32.84 s (C^4); 143.48 d (C^5, $^3J_{PC}$13.5), and 144.78 d (C^5, $^3J_{PC}$11.8).
[b]Data of $^{31}P\{^1H\}$ spectra.
[c]d. t.
[d]d. d.
[e]$C^1 = C^2$.

The reaction mixture was kept for 24 h at 20°C, the solvent was then removed, and the residue was distilled in a vacuum to obtain 8 g of phosphinate **12**.

*O-Trimethylsilyl-bis[2-(trimethylsiloxycarbonyl)-ethyl]phosphinate (**13**).* A mixture of 5 g of phosphinate **12** and 2.8 g of diethyl phosphite was heated at 100°C for 1 h and then distilled in a vacuum to obtain 3.8 g of phosphinate **13**.

Phosphinate **21** was prepared similarly.

*O-Trimethylsilyl-2-(trimethylsiloxycarbonyl)ethyl-[2-(2-furyl)-1-(trimethylsiloxycarbonyl)ethyl]phosphinate (**15**).* A solution of 2.5 g of trimethylsilyl acrylate in 5 mL of methylene chloride was added with stirring to a solution of 7.3 g of phosphonite **10** in 10 mL of methylene chloride. The reaction mixture was refluxed for 30 min, and then a solution of 2.4 g of diethyl phosphite in 5 mL of methylene chloride was added. The solvent was removed, and the residue was heated to 120°C, and then distilled to obtain 6.5 g phosphinate **15**.

Phosphinates **14,16–19** was prepared similarly.

*O,O-Diethyl 3,3-bis(trimethylsiloxy)propen-2-ylphosphonate (**20**).* A mixture of 5.9 g of diethyl trimethylsilyl phosphite and 3.1 g of trimethylsilyl acrylate was heated at 100–120°C for 2 h and then distilled to give 5.8 g of phosphonate **20**.

*Diethyl 2-oxotetrahydrofur-4-ylphosphonate (**22**).* A mixture of 6.5 g of γ-crotonolactone, 20 g of diethyl trimethylsilyl phosphite, 10 g of diethyl phosphite, and 0.1 g of zinc chloride was heated at 100–120°C for 2 h and then distilled to give 10.9 g of phosphonate **22**.

Phosphonates **23,24** were prepared similarly.

*O-Trimethylsilyl-diethylaminomethyl-(trimethylsiloxycarbonyl)ethylphosphinate (**25**).* (*a*) A mixture of 6.7 g of *O*-trimethylsilyl diethylaminomethylphosphonite [15], 6.2 g trimethylsilyl acrylate, and 3 mL of pyridine was heated at 110°C for 2 h and then distilled to obtain 8.9 g of phosphinate **25**.

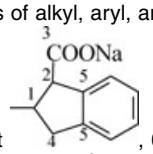
Phosphinates **26–33** were prepared similarly.

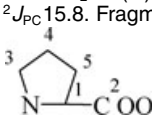
(*b*) A solution of 3 g of *N*-chloromethyldiethylamine in 15 mL of methylene chloride was added dropwise with stirring to a solution of 9 g of phosphonite **1** in 20 mL of methylene chloride. The mixture was heated to the boil, the solvent was distilled, and residue was distilled in a vacuum to give 7.7 g of phosphinate **25** (yield 85%).

Phosphinates **28** (yield 86%) and **34–47** were obtained analogously.

TABLE 5 Yields, Product Constants, and NMR Spectral Data for the $PC^1H_mC^2H_nC^3$ and $PC^4H_2NFragments^a$ (δ, ppm; J, Hz) of Sodium Phosphonates **66,67**, Sodium Phosphinates **68–76**, Phosphonic and Phosphinic Acids **77–88**[a]

Compound	*Yield (%)*	*Mp (°C)*	*δ(C¹)d*	*¹J_PC*	*δ(C²)d*	*²J_PC*	*δ(C³)*	*³J_PC*	*δ(C⁴)d*	*¹J_PC*	*δ(P)s*
66	97	–	36.80	142.0	54.04	6.1	174.96	5.9	–	–	32.08
67	96	–	41.83	133.8	56.72	6.3	183.47	5.4	–	–	21.46
68	94	–	33.12	95.2	28.01	<1	174.64	7.8	–	–	35.37
			24.05[b]	90.8	26.93	3.1	179.07	14.9			
69	96	–	38.54	92.4	35.26	<1	152.45	6.3	–	–	31.44
			26.78[b]	88.7	29.72	4.0	182.12	15.2			
70	97	–	42.89	95.4	55.41	11.9	183.06	5.7	–	–	42.03
			26.54 [b]	88.7	31.04	6.4	180.05	15.4			
71	95	–	24.59	92.6	2.45	7.2	–	–	–	–	39.98
			23.62[b]	90.5	29.03	<1	178.64	14.3			
72	98	–	33.65	98.1	34.05	<1	143.94	9.8	–	–	39.05
			26.34 [b]	89.8	30.89	6.1	180.94	15.7			
73	96	–	38.70	86.3	34.96	<1	152.60	6.9	56.78	104.7	32.86
74	95	–	39.77	86.0	35.37	<1	152.70	6.1	56.59	101.1	32.57
75	97	–	39.27	87.1	35.26	<1	152.59	6.2	56.23	103.7	32.50
76	97	–	42.04	94.8	55.41	12.5	181.87	4.9	57.39	100.3	37.64
77	96	Oil	20.39	144.2	26.75	<1	173.74	18.2	–	–	28.61
78[c]	96	159	23.32	92.2	26.40	<1	176.36	15.0	–	–	57.15
79	97	185	28.72	98.8	29.68	7.5	180.00	14.6	53.22	84.5	26.85
80	96	145	28.82	99.2	29.71	8.6	179.93	15.2	54.14	83.7	26.76
81	98	220	26.36	99.0	27.24	3.9	177.49	14.1	55.21	83.6	31.37
82	96	167	27.05	99.3	27.91	3.4	178.18	14.4	56.18	82.5	30.88
83	98	198	27.38	99.1	28.36	3.1	178.48	14.9	56.75	81.76	26.79
84	95	152	26.97	99.8	29.04	3.6	176.82	15.0	52.98	89.4	25.42
85	95	168	24.42	97.1	27.01	3.1	177.31	13.8	37.57	90.9	29.45
86	95	Oil	28.32	88.5	27.60	<1	156.65	13.7	–	–	38.16
			24.95[b]	92.6	26.67	<1	177.51	15.1			
87	96	89	29.31	93.0	27.72	<1	164.36	14.7	–	–	39.04
			25.80[b]	92.0	28.92	<1	174.74	15.1			
88	97	168	30.06	89.7	25.03	<1	139.51	15.2	–	–	39.27
			24.96[b]	91.4	27.64	<1	177.89	15.2			

[a]The salts **66–76** are very hygroscopic crystals; therefore, their melting points were not measured. All signals of alkyl, aryl, and heterocyclic fragments are in the standard area. In ^1H NMR, the signals of presented fragments are multiplets. Fragment 

, **66**, δ_C, 32.78 s (C^4), 141.64 d, $^3J_{PC}$9.1 and 143.49 d, $^3J_{PC}$9.7 (C^5); **67**, δ_H, 4.11 d. d (C^2H, $^3J_{PH}$16.0, $^3J_{HH}$7.2), δ_C 35.03 s (C^4), 143.93 d, $^3J_{PC}$7.6 and 144.31 d, $^3J_{PC}$7.6 (C^5); **70**, δ_H, 4.09 d. d (C^2H, $^3J_{PH}$16.2, $^3J_{HH}$7.6), δ_C 32.17 s (C^4), 140.02 d, $^3J_{PC}$6.7 and 142.91 d, $^3J_{PC}$6.8 (C^5); **76**, δ_H, 4.06 d. d (C^2H, $^3J_{PH}$15.6, $^3J_{HH}$7.2), δ_C 32.58 s (C^4), 142.90 d, $^3J_{PC}$6.6 and 142.97 d, $^3J_{PC}$7.2 (C^5). Fragment $CH_2OC(O)$ of **68**, δ_C66.28 s. Fragment COONa, δ_C, **69**: 179.95 d, $^2J_{PC}$14.8; **73**: 180.43 d, $^2J_{PC}$15.2; **74**: 180.51 d, $^2J_{PC}$15.3; **75**: 180.47 d, $^2J_{PC}$15.8. Fragment PCH_2N, δ_H, d ($^2J_{PH}$), **76**: 2.56 (8.4), **79**: 3.07 (8.4), **80**: 3.11 (8.0), **81**: 3.20 (8.2), **82**: 3.21 (8.4), **85**: 3.55 (7.8). Fragment 

of **84**, δ_H, 3.67 d. d (C^1H, $^3J_{HHA}$8.6, $^3J_{HHB}$6.4), δ_C 66.64 d (C^1, $^3J_{PC}$ 8.9), 171.65 s (C^2), 54.92 d (C^3, $^3J_{PC}$2.8), 23.59 s (C^4), 27.54 s (C^5).
[b]Fragment $PC^1H_2C^2H_2C^3(O)$
[c]cf. [16].

*O-Trimethylsilyl diethylaminomethyl 2-oxotetrahydrofur-4-ylphosphinate (***48***).* A mixture of 6 g of phosphonite **8**, 2.7 g of bis(dimethylamino)methane, and 0.1 g of zinc chloride was heated at 110–120°C for 1.5 h and then distilled to obtain 3.9 g of phosphinate **48**.

Phosphinates **49–54** were prepared similarly.

*Sodium 2,3-bis(methoxycarbonyl)propylphosphonite (***57***).* A solution of 14.7 g of phosphonite **3** in 10 mL of ether was added with stirring at 10°C to a solution of 2.2 g of sodium methylate in 50 mL of methanol. The resulting mixture was heated to the boil, the solvent was removed, and the residue was kept in a vacuum (1 mmHg) for 1 h to give 9.3 g of salt **57** as colorless hygroscopic crystals.

The salts **55,56,58–76** were obtained similarly.

*Diethylaminomethyl 2-carboxyethylphosphinic acid (***79***).* A solution of 8 g of phosphinate **25** in

TABLE 6 Elemental Analyses Data of Synthesized Compounds[a]

			Calcd. (%)		Found (%)	
Compound	*Empirical Formula*	*Formula Weight*	*C*	*H*	*C*	*H*
12	$C_{18}H_{43}O_6PSi_4$	498.85	43.34	8.89	43.05	8.52
13	$C_{15}H_{35}O_6PSi_3$	426.74	42.22	8.27	41.94	8.09
14	$C_{13}H_{27}O_6PSi_2$	366.50	42.60	7.43	42.28	7.26
15	$C_{19}H_{37}O_7PSi_3$	492.73	46.32	7.57	46.03	7.49
16	$C_{22}H_{39}O_6PSi_3$	514.78	51.33	7.64	51.15	7.58
17	$C_{17}H_{41}O_4PSi_3$	424.73	48.08	9.73	47.92	9.64
18	$C_{18}H_{31}O_4PSi_2$	398.58	54.24	7.84	53.99	7.75
19	$C_{16}H_{30}NO_4PSi_2$	387.55	49.59	7.80	49.28	7.67
20	$C_{13}H_{31}O_5PSi_2$	354.60	44.04	8.81	43.69	8.70
21	$C_{10}H_{23}O_5PSi$	282.34	42.54	8.21	42.38	8.29
22	$C_8H_{15}O_5P$	222.18	43.25	6.81	42.92	6.74
23	$C_{17}H_{27}O_5PSi$	370.44	55.12	7.35	54.89	7.26
24	$C_{19}H_{35}O_5PSi_3$	458.72	49.75	7.69	49.57	7.62
25	$C_{14}H_{34}NO_4PSi_2$	367.70	45.74	9.32	45.59	9.12
26	$C_{16}H_{38}NO_4PSi_2$	395.63	48.58	9.68	48.40	9.57
27	$C_{15}H_{34}NO_4PSi_2$	379.51	47.46	9.03	47.21	8.87
28	$C_{14}H_{32}NO_5PSi_2$	381.66	44.07	8.45	43.86	8.28
29	$C_{16}H_{36}NO_4PSi_2$	393.61	48.82	9.22	48.68	9.14
30	$C_{16}H_{34}NO_6PSi_2$	423.60	45.37	8.09	45.22	8.03
31	$C_{16}H_{42}NO_4PSi_4$	455.83	42.16	9.29	41.97	9.07
32	$C_{16}H_{30}NO_4PSi_2$	387.55	49.59	7.80	49.26	7.62
33	$C_{17}H_{32}NO_4PSi_2$	401.58	50.85	8.03	50.70	7.91
34	$C_{13}H_{30}NO_5PSi_2$	367.52	42.48	8.23	42.26	8.09
35	$C_{14}H_{30}NO_5PSi_2$	379.53	44.30	7.97	44.12	7.83
36	$C_{16}H_{34}NO_5PSi_2$	407.58	47.15	8.41	46.95	8.29
37	$C_{12}H_{28}NO_5PSi_2$	353.49	40.77	7.98	40.63	7.86
38	$C_{13}H_{28}NO_6PSi$	353.43	44.19	7.98	43.97	7.89
39	$C_{17}H_{40}NO_6PSi$	469.75	43.47	8.58	43.28	8.49
40	$C_{15}H_{30}NO_6PSi$	379.48	47.48	7.97	47.26	7.86
41	$C_{14}H_{28}NO_7PSi$	381.45	44.08	7.40	43.92	7.26
42	$C_{12}H_{26}NO_8PSSi$	403.49	35.72	6.50	35.59	6.40
43	$C_{21}H_{38}NO_4PSi_2$	455.41	55.35	8.41	55.12	8.26
44	$C_{20}H_{36}NO_5PSi_2$	457.50	52.49	7.93	52.31	7.82
45	$C_{19}H_{34}NO_5PSi_2$	443.91	51.44	7.72	51.28	7.64
46	$C_{20}H_{34}NO_5PSi_2$	455.71	52.72	7.52	52.58	7.41
47	$C_{22}H_{38}NO_8PSi_2$	531.94	49.69	7.20	49.52	7.03
48	$C_{10}H_{22}NO_4PSi$	279.35	43.00	7.94	42.83	7.89
49	$C_{12}H_{24}NO_5PSi$	321.39	44.86	7.53	44.59	7.38
50	$C_{16}H_{32}NO_5PSi_2$	405.58	47.38	7.95	47.05	7.81
51	$C_{19}H_{36}NO_5PSi_2$	445.64	51.21	8.14	51.03	8.06
52	$C_{18}H_{34}NO_6PSi_2$	447.62	48.30	7.66	47.98	7.52
53	$C_{19}H_{36}NO_7PSi_2$	477.64	47.78	7.60	47.69	7.53
54	$C_{19}H_{34}NO_4PSi_2$	427.63	53.37	8.01	53.12	8.06
55	$C_3H_5Na_2O_4P$	182.02	19.79	2.77	19.60	2.80
56	$C_5H_8NNa_2O_5P$	239.08	25.12	3.37	24.93	3.50
57	$C_7H_{12}NaO_6P$	246.13	34.16	4.91	33.97	4.98
58	$C_5H_6Na_3O_6P$	262.05	22.92	2.31	22.68	2.26
59	$C_6H_{10}NaO_6P$	232.11	31.05	4.34	30.87	4.28
60	$C_4H_4Na_3O_6P$	248.01	19.37	1.62	19.20	1.65
61	$C_4H_6NaO_4P$	172.05	27.92	3.52	27.59	3.65
62	$C_9H_9Na_2O_4P$	258.12	41.88	3.51	41.72	3.47
63	$C_7H_7Na_2O_5P$	248.09	33.89	2.85	33.68	3.03
64	$C_{10}H_9Na_2O_4P$	270.13	44.46	3.36	44.28	3.43
65	$C_6H_{10}Na_2O_8P_2$	318.08	22.66	3.17	22.52	3.23
66	$C_{14}H_{18}NaO_5P$	320.25	52.51	5.66	52.33	5.59
67	$C_{10}H_8Na_3O_5P$	308.11	38.98	2.62	38.83	2.67
68	$C_7H_9Na_2O_6P$	266.10	31.60	3.41	31.49	3.34

(Continued)

TABLE 6 Continued

Compound	Empirical Formula	Formula Weight	Calcd. (%)		Found (%)	
			C	*H*	*C*	*H*
69	$C_{10}H_{10}Na_3O_7P$	342.13	35.11	2.95	34.97	3.01
70	$C_{13}H_{12}Na_3O_6P$	364.17	42.88	3.32	42.65	3.26
71	$C_{11}H_{23}Na_2O_4PSi$	324.34	40.74	7.15	40.59	7.09
72	$C_{12}H_{13}Na_2O_4P$	298.18	48.34	4.39	48.23	4.30
73	$C_{10}H_{14}NNa_2O_5P$	305.18	39.36	4.62	39.23	4.55
74	$C_{13}H_{18}NNa_2O_5P$	345.24	45.23	5.25	44.98	5.12
75	$C_{12}H_{16}NNa_2O_6P$	347.21	41.51	4.65	41.29	4.68
76	$C_{13}H_{16}NNa_2O_4P$	327.23	47.72	4.93	47.61	4.98
77	$C_7H_{15}O_5P$	210.29	40.00	7.19	39.75	7.24
78	$C_6H_{11}O_6P$	210.13	34.30	5.28	34.20	5.30
79	$C_8H_{18}NO_4P$	223.12	43.08	8.13	42.86	8.10
80	$C_{10}H_{22}NO_6P$	251.08	47.80	8.83	47.67	8.61
81	$C_9H_{18}NO_4P$	235.28	45.95	7.71	45.71	7.65
82	$C_8H_{16}NO_5P$	237.21	40.51	6.80	40.39	6.82
83	$C_{10}H_{20}NO_4P$	249.25	48.19	8.09	47.94	7.93
84	$C_{10}H_{18}NO_6P$	279.23	43.01	6.50	42.81	6.45
85	$C_4H_{10}NO_4P$	167.10	28.75	6.03	28.64	6.08
86	$C_{10}H_{14}NO_4P$	243.21	49.38	5.80	49.23	5.64
87	$C_{10}H_{14}NO_4P$	243.21	49.38	5.80	49.12	5.59
88	$C_{11}H_{16}NO_4P$	257.24	51.36	6.27	51.06	6.03

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

20 mL of diethyl ether was added dropwise with stirring at 10°C to 30 mL of methanol. The resulting mixture was heated to boil, the solvent was distilled in a vacuum, and the residue was kept in a vacuum (1 mmHg) for 1 h to give 4.7 g of acid **79** as colorless hygroscopic crystals.

The acids **77,78,80–88** were obtained similarly.

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