Heteroatom Chemistry
Volume 23, Number 1, 2012

Synthesis of New Functionalized Mono- and Bisorganophosphorus Acids and Their Derivatives with Unsaturated and Aromatic Fragments

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Received 20 April 2011; revised 14 June 2011

ABSTRACT: *Convenient procedures for the synthesis of functionalized mono- and bisorganophosphorus acids and their derivatives with unsaturated and aromatic fragments, starting from the available derivatives of trivalent phosphorus acids, unsaturated and aromatic aldehydes, and carboxylic acid chlorides, are proposed, and some properties of the new unsaturated organophosphorus compounds are presented.* © 2011 Wiley Periodicals, Inc. Heteroatom Chem 23:32–40, 2012; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20749

INTRODUCTION

The functionalized derivatives of mono- and bis(organophosphorus) acids containing aromatic and heterocyclic fragments with various hydroxy, amino, or amido groups present great interest as promising polydentate ligands and organophosphorus biomimetics of hydroxyl and amino acids and natural pyrophosphates. Various derivatives of substituted hydroxymethylenebisphosphonic acids are good complexones and widely used in medicine [1–3]. Recently, we have proposed convenient procedures for synthesis of a series of organophosphorus derivatives of 2,6-di-tert-butyl-4-methylphenol (ionol) with one, two, or three phosphorus-containing groups [4,5]. These compounds were used by us for the preparation of stable phenoxyl radicals [6] and were interesting as effective antioxidants with the multifunctional mode of action [7]. In this study, we propose the convenient methods for the synthesis of new functionalized mono- and bisphosphinates, including unsaturated and aromatic fragments, starting from the readily accessible unsaturated aldehydes and carboxylic acid chlorides, which were prepared by the procedures in Ref. [8], and trimethylsilyl esters of various trivalent phosphorus acids, which were prepared by us previously as unique organophosphorus synthons [9,10]. In the present study, we found that the unsaturated aldehydes and carboxylic acid chlorides smoothly react with various trimethylsilyl esters of trivalent phosphorus acids under mild conditions to form new functionalized mono- and bisorganophosphorus acids and their derivatives with unsaturated and aromatic fragments, which are of great interest as promising polydentate ligands and effective multifunctional antioxidants.

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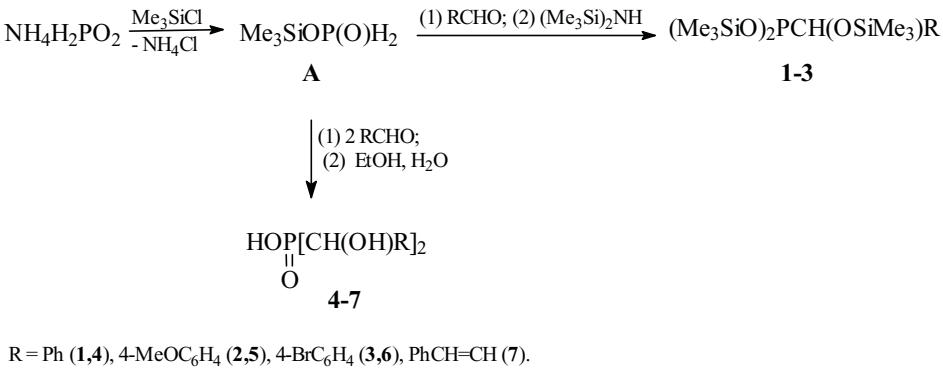
Contract grant sponsor: Russian Foundation for Basic Research.
Contract grant number: 11-03-00402.

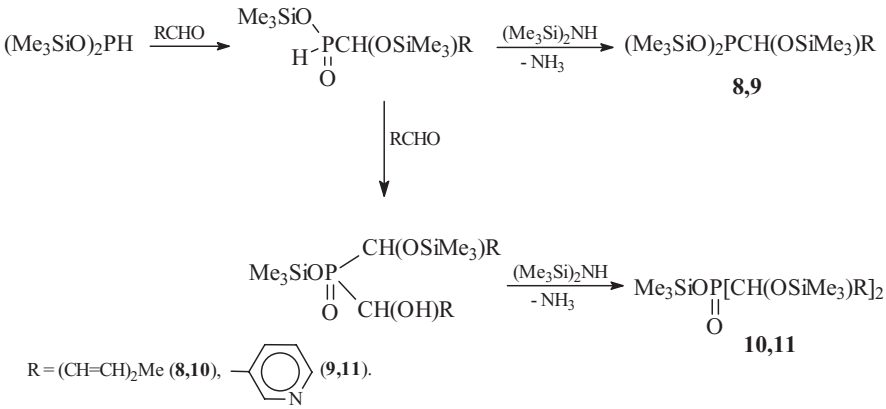
RESULTS AND DISCUSSION

Thus, trimethylsilyl hypophosphite **A** formed in situ from ammonium hypophosphite and chlorotrimethylsilane easily reacts with 1 or 2 equiv of unsaturated and aromatic aldehydes in methylene chloride to give either phosphonites **1–3** or phosphinates **4–7**, depending on the reagents ratio, in quite a high yield. Phosphonites **1–3** were isolated by additional treatment of the reaction mixture with bis(trimethylsilyl)amine, and phosphinic acids **4–7** were recrystallized from aqueous ethanol (Eq. (1)).



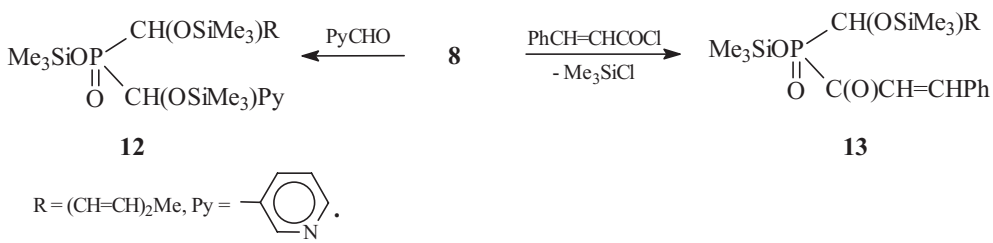
R = Ph (**1,4**), 4-MeOC$_6$H$_4$ (**2,5**), 4-BrC$_6$H$_4$ (**3,6**), PhCH=CH (**7**). (1)

Also, we developed a convenient method of synthesis of the similar phosphonites **8,9** and phosphinates **10,11** using the highly reactive bis(trimethylsiloxy)phosphine (cf. [11]), which readily adds to the carbonyl group of the corresponding aldehydes in methylene chloride to give the compounds **8–11** in high yields (Eq. (2)).



(2)

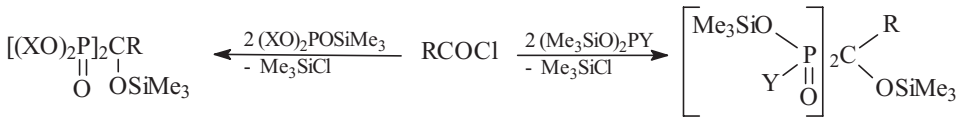
Phosphonite **8** is a suitable synthon for a series of trimethylsiloxymethylphosphinates, including unsaturated fragments and pyridine moieties. Thus, phosphonite **8** adds readily to the carbonyl group of 3-pyridinecarboxaldehyde and reacts smoothly with cinnamoyl chloride via the route of Arbuzov reaction in methylene chloride to form phosphinates **12,13** (Eq. (3)).



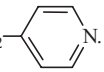
(3)

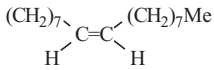
Also, we showed that the reactions of trimethylsilyl esters of trivalent phosphorus acids with readily available unsaturated carboxylic acid chlorides yield the new diphosphorylated trimethylsiloxymethylene

derivatives containing pyridine moieties, and unsaturated and aromatic fragments (cf. [5,12]). As initial compounds, we used accessible trimethylsilyl phosphites and 2-pyridylethylphosphonite that were successfully applied earlier to the synthesis of organophosphorus analogs of amino acids containing amino and carboxyl groups [13]. Therefore, trimethylsilyl phosphites and bis(trimethylsilyl) 2-pyridylethylphosphonite readily react with acid chlorides in methylene chloride to form bisphosphonate **14–18** or bisphosphinates **19–22**, respectively, in high yields (Eq. (4)).

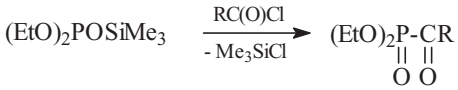


14-18 **19-22**

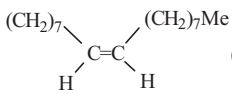
X = Et (**14,15**), Me_3Si (**16-18**); Y = $(CH_2)_2$– 

R = CH=CHMe (**19**), $(CH=CH)_2Me$ (**14,17,20**), CH=CHPh (**16,21**),  (**15,18,22**). (4)

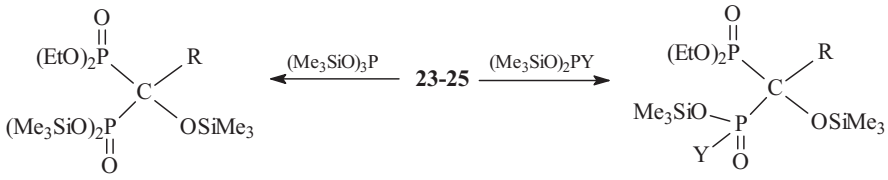
Under similar conditions, the reaction of diethyl trimethylsilyl phosphite with unsaturated carboxylic acid chlorides in 1:1 ratio gives unsaturated keto phosphonates **23–25** in high yields (Eq. (5)).



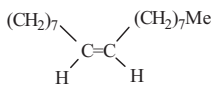
23-25

R = CH=CHMe (**23**), $(CH=CH)_2Me$ (**24**),  (**25**). (5)

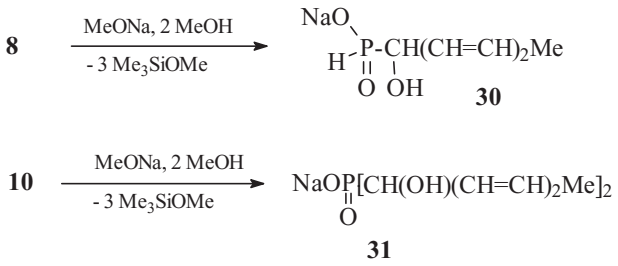
Here, we found a facile route to new derivatives of unsymmetrical trimethylsiloxymethylenebisphosphorus acids containing unsaturated fragments starting from keto phosphonates **23–25**. Tris(trimethylsilyl) phosphite as well as bis(trimethylsilyl) 2-pyridylethylphosphonite readily add to the carbonyl group of keto phosphonates **23–25** with the formation of bisphosphonates **26,27** and phosphonate-phosphinates **28,29**, respectively, in high yields (Eq. (6)).



26,27 **28,29**

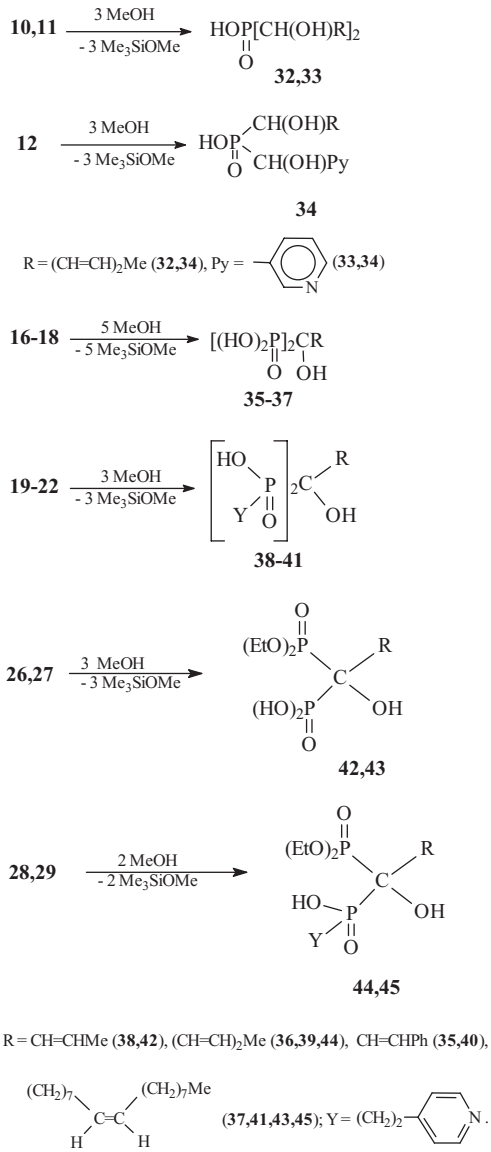
R = CH=CHMe (**26**), $(CH=CH)_2Me$ (**28**),  (**27,29**); Y = $(CH_2)_2$–  (6)

The treatment of phosphonite **8** and phosphinate **10** with dilute sodium methoxide in methanol gave the corresponding sodium salts **30,31** (Eq. (7)).



(7)

The reactions of trimethylsilyl esters of organophosphorus acids **10–12, 16–22**, and **26–29** with an excess methanol gave functionalized mono- and bisorganophosphorus acids **32–45** with unsaturated and aromatic fragments in high yields (Eq. (8)).



(8)

Acids **4–7, 32–34**, and **38–41** are obtained as white or yellow hygroscopic crystals; other acids are thick oils. Yellow crystalline salts **30,31** decompose on heating above 120–130°C without definite melting points. The structures of compounds **1–45** were confirmed by the ^{1}H, ^{13}C, ^{31}P NMR spectra, which show characteristic signals of the PCHOX and PCP fragments, and signals of substituted unsaturated and aromatic fragments (see Tables 1–3). According to the NMR spectra, some compounds are mixtures of stereoisomers. Their ratio was determined from the ^{1}H NMR and ^{31}P spectra. The elemental 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 Bruker Avance-400 spectrometer (400, 100, and 162 MHz, respectively) in $CDCl_3$ (**1–3**, **8–29**), CD_3OD (**4–7, 30–37, 42–45**), or DCOOD (**38–41**) against TMS (^{1}H and ^{13}C) and 85% H_3PO_4 in D_2O (^{31}P). All reactions were performed under dry argon in anhydrous solvents. Starting unsaturated acid chlorides and trimethylsilyl esters of trivalent phosphorus acids were prepared according to the procedures in Ref. [8–10], respectively.

O,O-Bis(trimethylsilyl) phenyl(trimethylsiloxy) methylphosphonite (**1**). A mixture of 8.3 g ammonium hypophosphite, 10.6 g of benzaldehyde, and 26 g of chlorotrimethylsilane in 50 mL of methylene chloride was heated under reflux with stirring for 2 h. Ammonium chloride was filtered off, the solvent was distilled off, and 65 g of bis(trimethylsilyl)amine was added to the residue. The mixture was refluxed until ammonia no longer evolved and then distilled to obtain 26.4 g of phosphonite **1** (see Table 1).

Phosphonites 2 and 3 Were Synthesized by the Same Method

Bis[hydroxy(phenyl)methyl]phosphinic acid (***4***). A mixture of 8.3 g ammonium hypophosphite, 22.4 g of benzaldehyde, and 40 g of chlorotrimethylsilane in 60 mL of methylene chloride was heated under reflux with stirring for 2 h. Ammonium chloride was filtered off and 60 mL ethanol was added to the residue. The mixture was heated to boil, ethanol was distilled off, and the residue was recrystallized from 70% aqueous ethanol. The white crystals that formed were kept in a vacuum (1 mm Hg) to obtain 21.7 g of acid **4**.

Acids **5–7** *Were Prepared by the Same Method*

O,O-Bis(trimethylsilyl) 1-(trimethylsiloxy)-2,4-hexadien-1-ylphosphonite (**8**). A solution of sorbic

TABLE 1 Yields, Product Constants, and NMR Spectral Data (δ, ppm, J, Hz) for the $PC^1H_nC^2C^3C^4C^5$ Fragments of Monophosphorus Compounds **1–13, 23–25,** and **30–34**[a]

No.	Yield (%)	Bp, °C, (p, mm Hg), mp, °C	Ratio (%)	$\delta_H(C^1H)$, d	$^2J_{PH}$	$\delta(C^1)$, d	$^1J_{PC}$	$\delta(C^2)$, d	$^2J_{PC}$	$\delta(C^3)$, d	$^3J_{PC}$	$\delta(C^4)$, s	$\delta(C^5)$, s	δ_P, s[b]
1	68	120 (1.5)	100	4.28	< 1	82.72	11.0	139.60	13.0	127.45	5.0	127.67	126.85	140.47
2	59	115 (1)	100	4.15	< 1	82.18	9.0	131.72	13.0	128.5	5.0	113.13	158.77	140.07
3	64	159 (1), 62	100	4.19	< 1	81.77	14.0	138.60	11.0	128.89	4.0	130.60	120.50	139.22
4	78	187	90	5.17	8.0	68.96	106.0	139.06	3.0	128.14	5.0	128.0	127.35	39.31
			10	4.86	8.0	–	–	–	–	–	–	–	–	37.05
5	72	165	85	5.07	8.0	68.50	107.0	130.93	4.0	129.36	4.0	113.56	158.95	38.88
			15	4.75	8.0	–	–	–	–	–	–	–	–	36.96
6	52	162	55	4.87	8.0	69.64	104.0	138.70	< 1	130.14	< 1	130.97	120.74	35.95
			45	5.15	8.0	68.46	106.0	138.33	< 1	130.14	< 1	130.97	120.77	38.10
7	89	153	60	4.76[c]	7.6	69.88	103.9	130.97	10.0	[d]	[d]	[d]	[d]	38.99
			40	4.87[c]	8.0	68.33	104.7	131.03	9.2	[d]	[d]	[d]	[d]	40.18
8	78	111 (1)	100	3.72	6.8	80.82	11.8	130.98	6.7	128.05	11.8	131.28	127.88	142.40
9	87	118 (1)	100	4.13	4.0	79.56	14.0	134.59	9.0	148.57	4.0	134.18[e]	122.34	137.91
10	86	152 (1)	40	4.28[c]	8.8	71.31	115.6	132.78	11.7	[d]	[d]	[d]	[d]	32.88
			30	4.25[c]	8.8	71.15	119.0	132.97	10.1	[d]	[d]	[d]	[d]	31.84
			20	4.49[c]	7.6	70.71	115.6	133.19	10.9	[d]	[d]	[d]	[d]	32.44
			10	4.34[c]	8.2	69.39	113.1	134.15	10.9	[d]	[d]	[d]	[d]	32.74
11	78	167 (1), 69	60	4.37	12.0	69.45	115.0	[d]	[d]	[d]	[d]	[d]	[d]	30.23
			40	4.60,	8.0	68.47	119.0	[d]	[d]	[d]	[d]	[d]	[d]	31.59
				4.71	8.0	68.90	112.0	[d]	[d]	[d]	[d]	[d]	[d]	
12	91	157 (1)	35	4.16[c]	11.2	71.61	115.6	[d]	[d]	[d]	[d]	[d]	[d]	30.95
				4.77[f]	7.6	69.24	114.8	[d]	[d]	[d]	[d]	[d]	[d]	
			30	4.32[c]	8.8	71.25	103.1	[d]	[d]	[d]	[d]	[d]	[d]	32.62
				4.95[f]	6.8	68.73	108.9	[d]	[d]	[d]	[d]	[d]	[d]	
			20	4.21[c]	10.4	70.06	97.2	[d]	[d]	[d]	[d]	[d]	[d]	31.96
				4.84[f]	6.0	69.27	109.8	[d]	[d]	[d]	[d]	[d]	[d]	
			15	4.47[c]	7.6	71.71	117.3	[d]	[d]	[d]	[d]	[d]	[d]	31.71
				4.82[f]	7.6	68.68	118.1	[d]	[d]	[d]	[d]	[d]	[d]	
13	94	oil	60	4.41[c]	8.0	71.10	119.9	132.12	11.7	[d]	[d]	[d]	[d]	15.08
						202.87[g]	105.6	[d]	[d]	148.12	< 1	[d]	[d]	
			40	4.53[c]	8.0	71.23	114.8	134.05	10.9	[d]	[d]	[d]	[d]	15.86
						202.87[g]	108.1	[d]	[d]	147.17	< 1	[d]	[d]	
23	96	oil	100	–	–	197.26	170.9	130.83	64.5	150.10	< 1	18.48	–	– 2.22
24	97	oil	100	–	–	198.12	172.6	126.37	65.4	130.38	< 1	144.34	148.34	– 1.75
25	96	oil	100	–	–	210.40	164.3	[d]	[d]	[d]	[d]	[d]	[d]	– 2.89
30	96	100[h]	100	4.10[c]	12.8	72.71	106.4	130.99	10.9	128.25	3.3	131.25[e]	127.07	26.64
31	97	100[h]	70	4.3	–	71.32	103.9	130.91	9.3	128.03	< 1	131.43	128.03	31.23
			30	4.5 m	–	70.86	105.6	130.61	9.2	127.83	< 1	131.43	127.83	31.52
32	97	101	55	4.56[c]	7.2	68.97	108.1	133.32	< 1	130.84	< 1	129.85	130.84	41.53
			45	4.66[c]	7.2	69.32	105.6	133.22	< 1	130.84	< 1	129.90	130.84	40.51
33	94	204	75	5.56[f]	8.0	70.92	98.0	[d]	[d]	[d]	[d]	[d]	[d]	29.42
			25	5.61[f]	8.0	71.08	98.0	[d]	[d]	[d]	[d]	[d]	[d]	30.80
34	96	120[h]	55	3.73[c]	8.2	70.60	109.0	[c]	–	–		–	–	28.72
				4.43[f]	9.2	68.69	95.5	[c]	–	–		–	–	
			45	3.81[c]	8.2	69.10	110.6	[c]	–	–		–	–	30.47
				4.54[f]	8.4	67.25	97.2	[c]	–	–		–	–	

[a]All signals of alkyl, aryl, trimethylsilyl, and 3-pyridyl groups are in the standard area.
[b]Data of $^{31}P-\{^1H\}$ spectra.
[c]d d, $^3J_{HH}$ for compounds: **7**, 6.8 and 6.0; **10**, 8.8, 8.8; 7.6, and 8.2; **12**, 7.2, 8.8, 10.0, and 7.6; **13**, 8.0 and 8.0; fragment CHPh: 8.02 d and 7.84 d, $^3J_{HH}$16.4; **30**, 6.4 and 6.4, fragment PH: 6.74 dd, $^3J_{PH}$504.4, $^3J_{HH}$1.2; **32**, 7.2 and 7.2;**34**, 8.2 and 8.2.
[d]Overlapping multiplets.
[e]d, $^3J_{PC}$ for compounds: **9**, 4.0; **30**, 4.2.
[f] Fragment CHPy.
[g]Fragment CHPh in ^{13}C NMR spectra: 148.12 s and 147.17 s.
[h]With decomposition.

TABLE 2 Yields, Product Constants, and NMR Spectral Data (δ, ppm, J, Hz) for the $P_2C^1C^2C^3C^4$ and $PC^5C^6C^7_{Py}$ Fragments of Bisphosphoryl Compounds **14–22, 35–41**[a]

No	*Yield, %*	*Ratio (%)*	$\delta(C^1)$ *t*	$^1J_{PC}$	$\delta(C^2)$, *t*	$^2J_{PC}$	$\delta(C^3)$ *t*	$^3J_{PC}$	$\delta(C^4)$, *s*	$\delta(C^5)$, *d*	$^2J_{PC}$	$\delta(C^6)$, *s*	$\delta(C^7)$,	$^3J_{PC}$	δ_P, *s*[b]
14	96	100	78.53	155.9	132.63	10.1	124.26	5.9	130.36	–	–	–	–	–	15.59
15	97	100	78.53	155.9	23.33	5.0	*c*	*c*	*c*	–	–	–	–	–	19.16
16	96	100	79.03	162.6	130.37	10.0	126.34	5.8	136.22	–	–	–	–	–	− 2.58
17	96	100	78.30	162.6	131.01	10.9	126.69	5.9	130.28	–	–	–	–	–	− 2.46
18	97	100	77.89	164.6	23.37	5.9	*c*	*c*	*c*	–	–	–	–	–	1.80
19	94	75	80.81	101.4	124.91	< 1	122.62	6.7	18.03	30.52	93.0	26.56	149.70	15.9	39.00
		15	–	–	–	–	–	–	–	–	–	–	–	–	37.84[d], 41.01[d]
		10	–	–	–	–	–	–	–	–	–	–	–	–	37.32
20	93	70	81.29	101.8	133.84	9.7	130.21	< 1	131.42	30.65	93.1	26.72	149.81	16.2	38.93
		20	–	–	–	–	–	–	–	–	–	–	–	–	37.76[d], 41.26[d]
		10	–	–	–	–	–	–	–	–	–	–	–	–	37.63
21	91	65	81.74	100.2	132.80	9.6	128.26	< 1	135.28	30.59	93.1	26.93	148.57	15.1	38.72
		25	–	–	–	–	–	–	–	–	–	–	–	–	37.40[d], 40.88[d]
		10	–	–	–	–	–	–	–	–	–	–	–	–	36.88
22	95	65	80.96	101.4	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	148.55	15.1	42.23
		20	–	–	–	–	–	–	–	–	–	–	–	–	40.27[d], 44.37[d]
		15	–	–	–	–	–	–	–	–	–	–	–	–	40.51
35	98	100	75.79	149.2	130.96	10.0	123.47	< 1	136.57	–	–	–	–	–	16.12
36	97	100	75.25	149.6	131.35	< 1	129.58	< 1	131.07	–	–	–	–	–	16.27
37	96	100	73.18	147.1	23.30	< 1	*c*	*c*	*c*	–	–	–	–	–	20.35
38	96	100	77.99	95.3	129.09	9.8	123.15	< 1	16.98	25.35	93.2	27.61	164.00	15.7	43.74
39	98	100	78.35	94.8	132.27	5.4	129.89	< 1	131.68	26.56	93.2	27.66	164.05	14.1	43.32
40	97	100	74.49	94.3	126.79	9.8	124.29	< 1	130.93	25.35	93.2	27.61	158.92	16.3	38.04
41	96	100	71.28	94.3	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	159.49	14.3	42.29

[a]The compounds **14–22** and **35–37** are the thick oils. The melting points for crystalline compounds, °C: **38**, 96; **39**, 110; **40**, 111; **41**, 85.
All signals of alkyl, trimethylsilyl, aryl, and 4-pyridyl fragments are in the standard area. Fragment $C^2H = C^3HPh$ for compounds: **16**, 6.47 d t (C^2H, $^3J_{HH}$15.8, $^3J_{PH}$5.2), 6.19 d t (C^3H, $^3J_{HH}$15.8, $^4J_{PH}$6.2); **35**, 6.95 d t (C^2H, $^3J_{HH}$15.4, $^3J_{PH}$4.8), 6.67 d t (C^3H, $^3J_{HH}$15.4, $^4J_{PH}$< 1); **40**, 6.45 d t and 6.61 d t ($^3J_{PH} = ^4J_{PH}$ 4.4, $^3J_{HH}$16.4).
[b]Data of $^{31}P–\{^1H\}$ spectra.
[c]Overlapping multiplets.
[d]d, $^2J_{PP}$ for compounds: **19**, 43.6; **20**, 43.6, **21**, 40.7;**22**, 47.6.

TABLE 3 Yields, Product Constants, and NMR Spectral Data (δ, ppm, J, Hz) for the $(EtO)_2P^1(O)C^1(P^2)C^2C^3$ and $PC^4C^5C^6_{Py}$ Fragments of Compounds of Unsymmetrical Structures **26–29,** and **42–45** [a,b]

No.	*Yield (%)*	*Ratio (%)*	δ (C^1) d d	$^1J(P^1C^1)$	$^2J(P^2C^1)$	δ (C^2), d d	^1J (P^1C^2)	$^2J(P^2C^2)$	δ (C^3) s	δ (C^6), d	$^3J_{PC}$	$\delta(P^1)$	$\delta(P^2)$	$^2J_{PP}$
26	97	100	77.86	154.2	166.7	127.67	10.1	10.1	126.09	–	–	16.47	− 1.99	32.1
27	96	100	77.92	154.2	167.5	[c]	[c]	[c]	[c]	–	–	19.80	0.92	36.7
28	96	80	80.02	153.8	104.4	132.80	10.1	9.2	123.63	149.91[d]	16.0	16.57	38.15	36.7
		20	–	–	–	–	–	–	–	–	–	16.70	36.45	27.5
29	98	70	79.77	159.2	103.00	[c]	[c]	[c]	[c]	148.61[d]	15.9	19.31	39.56	39.0
		30	–	–	–	–	–	–	–	–	–	19.59	43.15	52.8
42	97	100	75.30	153.3	153.3	128.22	9.7	9.7	124.01	–	–	17.81	14.85	28.8
43	96	100	73.92	151.3	151.3	22.56	< 1	[c]	[c]	–	–	21.73	18.37	41.3
44	98	100	78.53	149.2	93.0	[c]	[c]	[c]	[c]	162.98[d]	13.4	19.65	35.01	16.7
45	97	100	76.04	150.8	96.3	22.57	< 1	[c]	[c]	162.77[d]	13.4	23.88	39.22	36.8

[a]All signals of alkyl, trimethylsilyl, aryl, and 4-pyridyl fragments are in the standard area. In ^{13}C NMR spectra for compounds: **28**, 27.10 d (C^4, $^1J_{PC}$ 94.7), 27.03 d (C^5, $^2J_{PC}$ 3.4); **44**, 27.62 d (C^4, $^1J_{PC}$ 93.0), 28.86 s (C^5).
[b]Data of $^{31}P\text{-}\{^1H\}$ spectra.
[c]Overlapping multiplets.
[d]d, $^3J_{PC}$: **28**, 16.0; **29**, 15.9; **44**, 13.4; **45**, 13.4.

TABLE 4 Elemental Analyses Data of Compounds **4–7,10–45**[a]

			Calcd. (%)		Found (%)	
No.	*Empirical Formula*	*Formula Weight*	*C*	*H*	*C*	*H*
4	$C_{14}H_{15}O_4P$	278.25	60.43	5.43	60.09	5.49
5	$C_{16}H_{19}O_6P$	338.30	56.81	5.66	56.69	5.72
6	$C_{14}H_{13}Br_2O_4P$	436.03	38.56	3.00	38.40	2.91
7	$C_{18}H_{19}O_4P$	330.32	65.45	5.78	65.23	5.69
10	$C_{21}H_{43}O_4PSi_3$	474.80	53.12	9.13	52.98	9.03
11	$C_{21}H_{37}N_2O_4PSi_3$	496.78	50.78	7.51	50.59	7.42
12	$C_{21}H_{40}NO_4PSi_3$	485.79	51.92	8.30	51.81	8.23
13	$C_{21}H_{33}O_4PSi_2$	436.63	57.77	7.62	57.65	7.57
14	$C_{17}H_{36}O_7P_2Si$	442.51	46.14	8.20	45.96	8.11
15	$C_{29}H_{62}O_7P_2Si$	612.85	56.84	10.20	56.68	10.12
16	$C_{24}H_{52}O_7P_2Si_3$	655.05	44.01	8.00	43.89	7.91
17	$C_{21}H_{52}O_7P_2Si_5$	619.02	40.75	8.47	40.61	8.40
18	$C_{33}H_{78}O_7P_2Si_5$	789.36	50.21	9.96	50.03	9.88
19	$C_{27}H_{48}N_2O_5P_2Si_3$	626.90	51.73	7.72	51.52	7.65
20	$C_{29}H_{50}N_2O_5P_2Si_3$	652.94	53.35	7.72	53.23	7.64
21	$C_{32}H_{50}N_2O_5P_2Si_3$	688.97	55.79	7.32	55.65	7.26
22	$C_{41}H_{76}N_2O_5P_2Si_3$	823.27	59.82	9.30	59.68	9.22
23	$C_8H_{15}O_4P$	206.18	46.60	7.33	46.49	7.26
24	$C_{10}H_{17}O_4P$	232.21	51.72	7.38	51.57	7.29
25	$C_{22}H_{43}O_4P$	402.55	65.64	10.77	65.52	10.68
26	$C_{17}H_{42}O_7P_2Si_3$	504.73	40.46	8.39	40.30	8.28
27	$C_{31}H_{70}O_7P_2Si_3$	701.10	53.11	10.06	52.96	10.01
28	$C_{23}H_{43}NO_6P_2Si_2$	547.72	50.44	7.91	50.23	7.83
29	$C_{35}H_{69}NO_6P_2Si_2$	718.07	58.54	9.69	58.42	9.59
30	$C_6H_{10}NaO_3P$	184.11	39.15	5.47	39.01	5.40
31	$C_{12}H_{18}NaO_4P$	280.23	51.43	6.47	51.28	6.42
32	$C_{12}H_{19}O_4P$	258.25	55.81	7.42	55.66	7.38
33	$C_{12}H_{13}N_2O_4P$	280.23	51.44	4.68	51.26	4.72
34	$C_{12}H_{16}NO_4P$	269.24	53.53	5.99	53.41	5.87
35	$C_9H_{12}O_7P_2$	294.14	36.75	4.11	36.64	4.07
36	$C_6H_{12}O_7P_2$	258.11	27.92	4.68	27.78	4.59
37	$C_{18}H_{38}O_7P_2$	428.45	50.46	8.94	50.26	8.86
38	$C_{18}H_{24}N_2O_5P_2$	410.35	52.69	5.89	52.54	5.78
39	$C_{20}H_{26}N_2O_5P_2$	436.39	55.05	6.01	54.91	6.09
40	$C_{23}H_{26}N_2O_5P_2$	472.42	58.48	5.55	58.40	5.59
41	$C_{32}H_{52}N_2O_5P_2$	606.72	65.35	8.64	63.20	8.58
42	$C_8H_{18}O_7P_2$	288.18	33.34	6.29	33.15	6.22
43	$C_{22}H_{46}O_7P_2$	484.55	54.53	9.57	54.40	9.52
44	$C_{17}H_{27}NO_6P_2$	403.36	50.62	6.75	50.49	6.70
45	$C_{29}H_{53}NO_6P_2$	573.70	60.71	9.31	60.59	9.26

[a]Phosphonites **1–3,8,9** are extremely readily oxidized and hydrolyzed, and therefore they were analyzed in the form of the corresponding derivatives **4–6, 10,11**.

aldehyde 18.3 g in 50 mL of methylene chloride was added with stirring to a solution of 52 g of bis(trimethylsiloxy)phosphine in 100 mL methylene chloride, cooled to 0°C. The mixture was stirred for 0.5 h, then the solvent was distilled off, and 100 g bis(trimethylsilyl)amine was added to the residue. The mixture was refluxed until ammonia no longer evolved and then distilled to obtain 56 g of phosphonite **8**.

Compounds **9–11** *Were Prepared Similarly*

O-Trimethylsilyl[pyrid-3-yl(trimethylsiloxy)methyl] (1-trimethylsiloxy-2,4-hexadien-1-yl)phosphinate (**12**). 3-Pyridinecarboxaldehyde, 3.2 g, was added with stirring to a solution of 11.3 g of phosphonite **8** in 40 mL of methylene chloride, cooled to 10°C. The mixture was stirred for 0.5 h, the solvent was then distilled off, the residue was distilled to obtain 13.3 g of phosphinate **12**.

Phosphinate **13** *Was Prepared Similarly*

O,O,O,O-Tetraethyl (1,3-pentadien-1-yl)trimethylsiloxymethylenebisphosphonate (**14**). A solution of sorbinoyl chloride, 6 g, in 15 mL of methylene chloride was added with stirring and cooling to 10°C to a solution of 21 g of diethyl trimethylsilyl phosphite in 20 mL of methylene chloride. The mixture was stirred for 0.5 h and heated to reflux; then the solvent was distilled off and the residue was kept in a vacuum (0.5 mm Hg) for 1 h at 30°C. Bisphosphonate **14** was obtained as a thick oil, a yield of 19.5 g.

Compounds **15–29** *Were Prepared Similarly*

Sodium (1-hydroxy-2,4-hexadien-1-yl)phosphonite (**30**). A solution of 15.2 g of phosphonite **8** in 20 mL of diethyl ether was added with stirring and cooled at 10°C to a solution of 2.16 g of sodium methylate in 30 mL of methanol. The resulting mixture was heated to a boil, the solvent was removed in a vacuum, and the residue was kept in a vacuum (1 mm Hg) for 1 h to obtain 7.1 g of salt **30** as yellow hygroscopic crystals.

Salt **31** *Was Obtained Similarly*

Bis(1-hydroxy-2,4-hexadien-1-yl)phosphinic acid (**32**). Phospinate **10**, 18 g, was added with stirring to 60 mL of methanol cooled to 10°C. The mixture was heated to boiling and then was distilled off; the residue was kept in a vacuum (1 mm Hg) for 1 h to obtain 9.5 g of acid **32**. Acids **33–45** were prepared similarly.

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