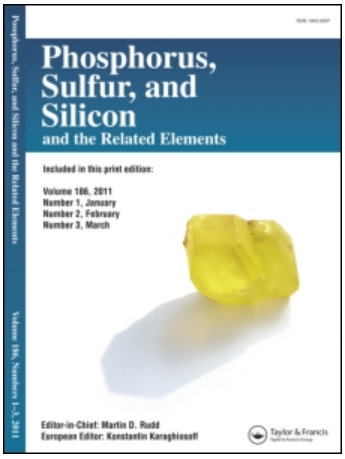

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SYNTHESIS AND NMR SPECTROSCOPIC INVESTIGATION OF PHENYLPHOSPHORYL DERIVATIVES

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SYNTHESIS AND NMR SPECTROSCOPIC INVESTIGATION OF PHENYLPHOSPHORYL DERIVATIVES

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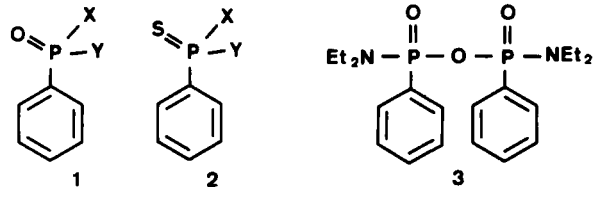
The syntheses of 16 phenyl- (**1** and **3**) and phenylthiophosphoryl (**2**) derivatives are described. The ^{13}C and ^{17}O NMR data sensitively reflect electron density changes in the phosphoryl substituents caused by p^{π}–d^{π} back-donation from *X*/*Y* to *P*. Taft constants σ_I and σ_R^0 were derived for 16 phosphoryl substituents.

INTRODUCTION

In continuation of our studies on ^{13}C, ^{17}O and ^{31}P of some organophosphorus adamantane derivatives[1,2] we were interested to extend such investigations to some phenylphosphonic and -thiophosphonic acid derivatives. The availability of such



1 2 3

	a	b	c	d	e	f	g	h
X	Cl	Br	OMe	OEt	O-i-Pr	OPh	NH-n-Bu	OMe
Y	Cl	Br	OMe	OEt	O-i-Pr	OPh	NH-n-Bu	Cl

	i	k	l	m	n
X	OEt	OPh	OEt	OEt	OMe
Y	Cl	Cl	NH-n-Bu	NEt_2	N

SCHEME 1 Structures of Phenyl- and Phenylthiophosphoryl Derivatives.

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multi-NMR data enabled us to perform a comparative study of phosphorylated benzene vs. adamantane derivatives with respect to the effect of electron distribution changes in the substituents on various chemical shifts and coupling constants.

RESULTS AND DISCUSSION

Synthesis of Phenylphosphoryl Derivatives 1 *and* 3

Phenylphosphonic acid and its dichloride (**1a**) (Aldrich) were used as starting materials. The dibromide **1b** was prepared from the acid by using PBr_3. From **1a** the diesters **1c–1e** were obtained by treatment of **1a** with the respective alkoxide reagents. With LiOPh the dichloride **1a** gave the diphenyl ester **1f** but with phenol in the presence of pyridine only one chlorine atom was exchanged to afford **1k**. Under analogous conditions the chloridate **1i** could be prepared. This compound could be converted to **1l** by treatment with *n*-butylamine or to **1m** with diethylamine. The diamide **1g** could be obtained directly from **1a**. The monoamide **1n** was formed from **1a** and methanol in the presence of a pyrrolidine-pyridine mixture. If, however, **1a** was subjected to a diethylamine-pyridine mixture without any alcohol, the anhydride **3** was isolated.

Synthesis of Phenylthiophosphoryl Derivatives 2

The dichloride **2a** was prepared from dichlorophenylphosphine (Aldrich) with $PSCl_3$ and could be converted to the diester **2c** with NaOMe. However, methanol in pyridine afforded the chloridate **2h**. It should be noted that **2h** is remarkably stable whereas our efforts to prepare **1h** under similar conditions failed.

NMR Spectra of Phenylphosphoryl- and -thiophosphoryl Derivatives 1 *and* 2

All ^{13}C, ^{17}O and ^{31}P chemical shifts as well as $^{13}C—^{31}P$ and $^{17}O—^{31}P$ coupling constants of the compounds **1–3** are collected in Table I.

From these data an interesting evidence about the electronic properties of the phosphoryl substituents can be derived. In previous reports[1,2] on bridgehead-phosphorylated adamantanes we have shown that the chemical shifts of the α carbon [$\delta(^{13}C)$] and the monocoordinated oxygen atom [$\delta(^{17}O)$] as well as the coupling constants between the directly bonded P and α—C nuclei [$^1J_{CP}$] and P and O [$^1J_{OP}$], respectively, respond very sensitively to the electron density in the substituent. This density can be changed by more or less effective p^{π}–d^{π} back-donation from *X* and/or *Y* to the phosphorus atom. The results[1,2] can be summarized as follows (cf. Figures 1 and 2): In the sequence Br—Cl—N—O the ability of *X*/*Y* to undergo this type of back-donation increases, thereby enhancing the electron density at P. The consequences are: (a) the α-carbon is shielded reflecting a decrease in the group electronegativity; (b) the s character in the α—C—P single bond is increased leading to larger one-bond $^{13}C—^{31}P$ coupling constants; (c) there is an increasing 2p electron transfer in the P=O bond towards the oxygen resulting in smaller ^{17}O chemical shifts and (d) smaller $^{17}O—^{31}P$ coupling constants.

TABLE I

Chemical shifts (in ppm) and coupling constants (in Hz) of phenylphophoryl- (**1** and **3**) and -thiophosphoryl derivatives (**2**)[a]

	$\delta(^{13}C)$[b]								$\delta(^{17}O)$[c]		$\delta(^{31}P)$[d]
	ipso	ortho	meta	para	α-C[e]	β-C[e]	γ-C[e]	δ-C[e]	P=O	P-O	
1a	133.9 (154.3)	129.9 (13.9)	128.8 (18.3)	134.3 (3.9)	-	-	-	-	160 (195) 60	-	34.3
1b	138.2 (128.4)	129.5 (13.8)	128.8 (18.2)	134.3 (4.1)	-	-	-	-	185 (194) 60	-	1.1
1c	126.5 (189.0)	131.5 (10.0)	128.2 (15.0)	132.4 (2.8)	52.3 (5.6) "	-	-	-	92 (164) 65	36 f 430	21.0
1d	128.0 (188.1)	131.3 (10.0)	128.1 (14.4)	132.0 (3.3)	61.6 (5.6) "	15.9 (6.7) "	-	-	95 (158) 130	69 f 470	18.0
1e	129.3 (186.1)	130.8 (9.4)	127.5 (14.4)	131.2 (3.3)	69.7 (5.6) "	23.3[g] (3.9) 23.0[g] (5.0)	-	-	96 (164) 90	f	16.0
1f	126.5 (192.5)	132.0 (10.5)	128.4 (15.5)	133.0 (2.8)	150.1 (7.2) "	120.3 (4.4) "	129.5 - "	124.4 - "	108 f	f	11.1
1g	133.1 (151.2)	131.4 (9.4)	128.1 (13.4)	131.1 -	40.3 - "	34.1 (6.2) "	19.8 - "	13.6 - "	87 f 250	-	19.4
1k	129.7 (180.6)	131.0 (12.0)	128.6 (17.0)	133.8 (2.8)	149.4 (10.7)	120.6 (5.1)	129.7 -	125.8 -	140 (183) 100	f	24.4
1l	130.9 (172.0)	130.5 (9.4)	127.4 (13.9)	130.6 (2.2)	59.2 (5.5) 39.9 -	15.6 (6.7) 33.1 (6.1)	- 19.0 -	- 12.9 -	90 f 250	ca 70 f vb	22.3
1m	131.5 (174.8	130.8 (9.4)	127.8 (13.9)	130.9 -	59.4 (6.1) 38.4 (5.0)	16.0 (6.7) 13.7 (1.7)	-	-	88 (160) 150	ca 65 f vb	21.7
1n	129.7 (172.2)	130.8 (9.2)	128.0 (13.9)	131.2 (2.0)	50.5 (5.8) 46.0 (4.5)	- 25.8 (8.0)	- -	- -	89 (160) 120	ca 40 f vb	21.4
3[h]	130.5[i] 130.3[i]	130.4[i]	127.7[i]	131.1[i]	38.5 (17.1) "	13.2 - "	-	-	100 (122) 150	ca 130 f vb	15.7 16.2
2a	137.9 (117.9)	129.9 (14.9)	128.6 (17.4)	133.7 (3.5)	-	-	-	-	-	-	74.8
2c	132.0 (151.3)	130.8 (11.2)	128.2 (14.8)	132.2 -	52.9 (5.9) "	-	-	-	-	k	90.6
2h	134.7 (142.6)	130.4 (13.6)	128.4 (16.7)	133.2 (3.4)	53.1 (7.7)	-	-	-	-	k	90.2
2k	134.9 (141.0)	130.5 (12.7)	128.5 (16.6)	133.3 (2.7)	149.6 (11.9)	121.5 (4.9)	129.5 -	125.9 (2.1)	-	k	84.3

[a] Chemical shifts in δ-scale relative to following standards (δ = 0): ^{13}C and ^{1}H, tetramethylsilane (internal); ^{17}O, deuterium oxide (external); ^{31}P, 85% phosphoric acid (external); positive values denote deshielding; in parentheses: coupling constants in Hz, "—" means " < 2Hz".

[b] In $CDCl_3$.

[c] In 1,2-dibromoethane at 343 K; values in parentheses are $^{17}O—^{31}P$ coupling constants; third entries denote estimated line widths at half height in Hz; vb: very broad (> 500 Hz).

[d] In 1,2-dibromoethane at 297 K.

[e] Carbon atoms of the *X*/*Y* substituents; positions are denoted relative to the *X* and *Y* atoms, respectively; first entry corresponds to *X*, second to *Y*; "means that the first and the second entry are identical.

[f] Not observed.

[g] Diastereotopic methyl within each isopropyl group.

[h] The first entry corresponds to the major diastereomer (ca 60%), the second to the minor diastereomer (ca 40%).

[i] The $^{13}C—^{31}P$ coupling constants cannot be determined confidently since the ^{13}C signals overlap and represent X-parts of ABX subspectra (cf. ref. 1).

[k] Not measured.

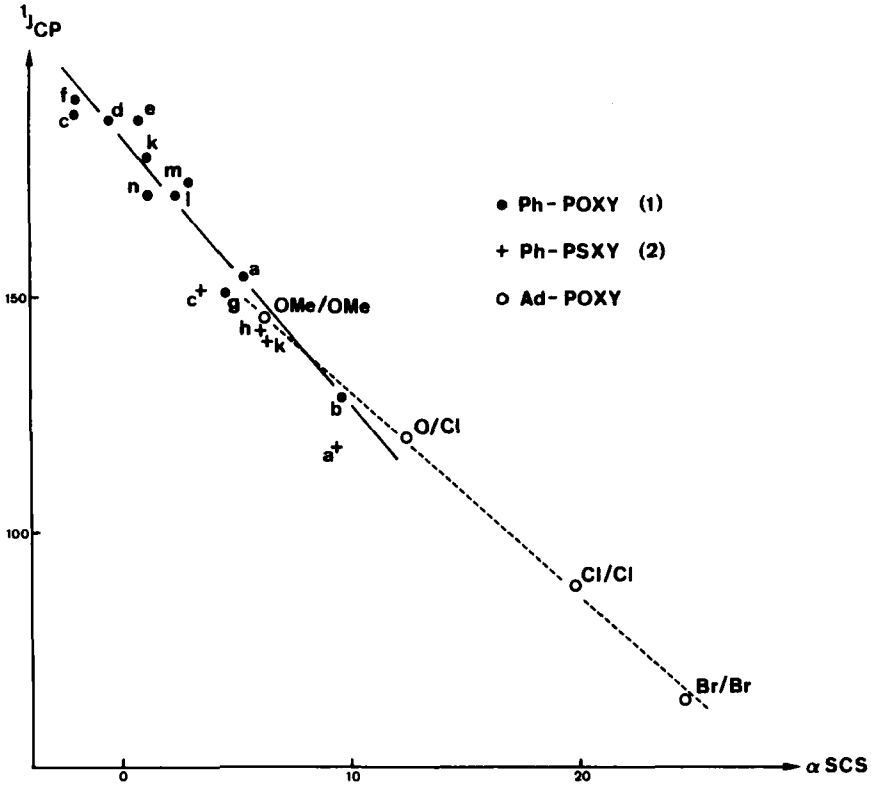

FIGURE 1 One-bond $^{13}C—^{31}P$ coupling constants ($^1J_{CP}$) plotted against substituent effects on α carbon chemical shifts (αSCS); data for 1-adamantylphosphoryl derivatives taken from ref. 1.

In the present study we want to extend this investigation with special emphasis on the contribution of the phenyl group which, in contrast to 1-adamantyl,[1,2] can participate in the electron density changes.

As can be seen from Figure 1 and Figure 2 the tendencies in the phenyl- (**1**) and 1-adamantylphosphoryl compounds[1,2] are qualitatively the same, and this holds even for the thiophosphoryl derivatives **2**. Thus, we conclude that the physical origin of the changes in these parameters, namely the electron density variations within the POXY group, is the same for both the 1-adamantyl and phenyl compounds. It is apparent, however, that the ranges of most NMR parameter variations are clearly smaller for **1** than for adamantyl analogues (Table II), i.e. the δ- and J-values respond less sensitively in the aromatic system. A plausible explanation is the participation of the aromatic π-system as indicated by the mesomeric forms in Figure 3, "diluting" the effects of back-donation.

This interpretation is supported by the substituent effects on the methine carbon chemical shifts of **1** and **2**. It is well-known[3] that in monosubstituted benzenes a linear relationship exists between the meta- and para-carbon chemical shifts and the Taft constants σ_I and σ_R^0 (dual-substituent parameter (dsp) approach); these constants describe the inductive and mesomeric properties of the substituents,

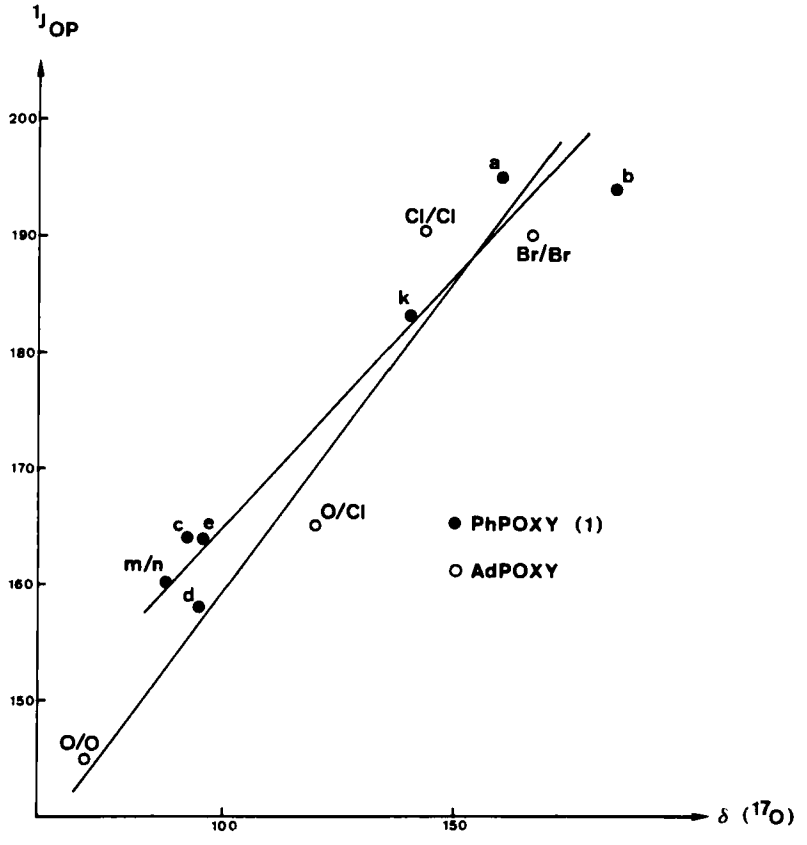

FIGURE 2 One-bond $^{17}O—^{31}P$ coupling constants ($^1J_{OP}$) plotted against ^{17}O chemical shifts $\delta(^{17}O)$; data for 1-adamantylphosphoryl derivatives taken from ref. 2.

TABLE II

NMR Parameter Ranges

	PhPOXY	1-AdPOXY[1,2]
$\Delta\delta(^{13}C)^a$	12 ppm	19 ppm
$\Delta\delta(^{17}O)$	93 ppm	95 ppm
$\Delta^1J_{CP}{}^b$	33 %	57 %
$\Delta^1J_{OP}{}^b$	18 %	ca 30 %

[a] Ipso carbon in **1** and ^{13}C carbon in the adamantane derivatives

[b] Percentage relative to the largest ^1J-value in each case

respectively. Hehre et al.[4] suggested the relations (1) and (2), standard deviations in brackets:

$$\delta(\text{meta-C}) = 1.54\sigma_I - 1.61\sigma_R^0 \quad \langle 0.54 \rangle \tag{1}$$

$$\delta(\text{para-C}) = 3.98\sigma_I + 19.79\sigma_R^0 \quad \langle 0.17 \rangle \tag{2}$$

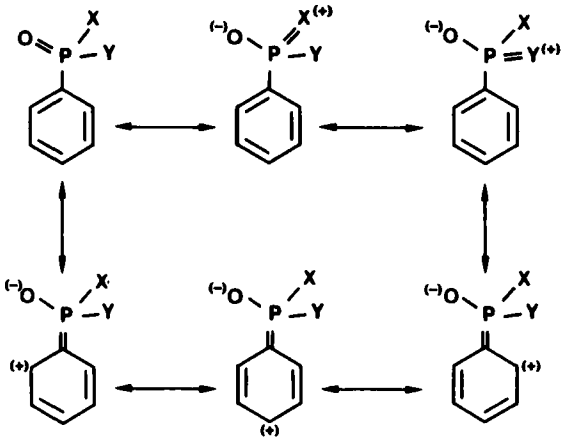

FIGURE 3 Mesomeric Structures of 1.

TABLE III

Taft constants σ_I and σ_R^0 of POXY and PSXY substituents, calculated using equations (1) and (2).

	I	0 R
$POCl_2$	+0.70	+0.18
	+0.65[a]	+0.17[a]
$POBr_2$	+0.70	+0.18
$PO(OMe)_2$	+0.30	+0.16
$PO(OEt)_2$	+0.23	+0.16
	+0.06[a]	+0.16[a]
$PO(O-i-Pr)_2$	−0.13	+0.19
$PO(OPh)_2$	+0.43	+0.17
$PO(NH-n-Bu)_2$	+0.19	+0.12
POCl(OPh)	+0.58	+0.18
PO(OEt)(NH − n − Bu)	−0.21	+0.17
$PO(OEt)(NEt_2)$	+0.02	+0.14
PO(OMe)(pyr)[b]	+0.14	+0.13
PO(NH − n − Bu)(OP)[c]	−0.03	+0.16
$PSCl_2$	+0.57	+0.17
	+0.43[a]	+0.17[a]
$PS(OMe)_2$	+0.29	+0.15
$PSCl(OMe)_2$	+0.44	+0.17
$PSCl(OPh)_2$	+0.50	+0.17

[a] Data from ref. 5 for comparison
[b] pyr ≡ pyrrolidino (NC_4H_8)
[c] Anhydride **3**

Using the equations (1) and (2) Taft constants can be derived for POXY and PSXY substituents (Table III).

A quantitative evaluation using these equations may be problematic;[3] cf. e.g. literature data[5] for **1a**, **1d** and **2a** in Table 3. Nevertheless, the tendencies of the σ_I and σ_R^0 constants are significant.

The electron-withdrawing ability decreases in the sequence:

$$POCl_2 \approx POBr_2 > POCl(OR) > PO(OR)_2$$

and

$$PSCl_2 > PSCl(OR) > PS(OR)_2$$

This is opposite to the electronegativities of X and Y and consistent with our interpretation of the δ- and J-variations (*vide supra*).

The mesomeric effect of all phosphoryl substituents is more or less uniform ($\sigma_R^0 = 0.12$–0.19) and indicates that they are mesomerically electron-withdrawing and as such comparable to the nitro group.[6] Thus, our interpretation of the mesomeric participation of the phenyl group (Figure 3, Table II) is confirmed.

^{31}P chemical shifts in **1** behave in a similar manner to the adamantyl analogues and are not very characteristic,[1] e.g. the $\delta(^{31}P)$-values increase when going from **1f** (X/Y = OPh/OPh: 11.1) to **1k** (X/Y = OPh/Cl: 24.4) and **1a** (X/Y = Cl/Cl: 34.3). On the other hand, the ^{31}P chemical shifts decrease in an analogous series of the thio compounds: **2c** (X/Y = OMe/OMe: 90.6), **2h** (X/Y = OMe/Cl: 90.2) and **2a** (X/Y = Cl/Cl: 74.8).

Attempts to monitor the ^{33}S chemical shifts of 2 failed; apparently the signals are extremely broad (> 2 kHz). A measurement of the smaller and more symmetrical $PSCl_3$ was not successful either. Hitherto, line widths for sulfur nuclei in organic molecules below 1 kHz have been reported mainly for tetracoordinated sulfur atoms, e.g. in sulfones, sulfoximides etc.[7] Exceptions are only a few very small molecules like CS_2.[8]

^1H chemical shifts of the phenyl groups in **1** and **2** are close to each other and often difficult to identify even at 400 MHz. Since they are not very informative we refrain from a detailed analysis and report them in the Experimental Part.

EXPERIMENTAL

Melting points are uncorrected. Silica gel was used for column chromatography and elution was performed by petrol ether (PE)-acetone mixtures. IR spectra were measured on a Perkin-Elmer 1310 or Beckman Akkulab 10 instrument as a thin film or using KBr pellets. NMR spectra were recorded on the following spectrometers: ^1H, Varian T-60 (60 MHz) and Bruker AM-400 (400 MHz); ^{13}C, Bruker AM-400 (100.6 MHz); ^{17}O, Bruker AM-400 (54.2 MHz); ^{31}P, Bruker AM-400 (161.9 MHz); for details see captions of Table I. Mass spectra were measured on Varian MAT CH-5 and CH-7 instruments. Mass spectral data are in m/e units, relative intensities in parentheses.

Syntheses. Compound **1a** is commercially available, **1b**[9] and **2a**[10] were prepared according to known procedures. The yields refer to isolated material and were not optimized.

Dimethyl phenylphosphonate (**1c**). A solution of **1a** (1 ml, 7 mmol) in dry MeOH (20 ml) was stirred with NaOMe (17 mmol) for 3 h at room temperature. The reaction mixture was treated with water (20 ml) and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and evaporated. The residue was purified on silica gel and elution with PE/-acetone (1 : 1) afforded **1c** as a colourless oil (1 g, 77%). IR (cm^{-1}): 3060, 2960, 1595, 1440, 1255 (P=O), 1180, 1130, 1055/1030 (C—O), 830/790 (P—O); ^1H NMR ($CDCl_3$, δ): 3.73 (*d*, 6 H, $^3J_{PH}$ = 11.0 Hz), 7.3–7.63 (*m*, 3 H), 7.6–7.8 (*m*, 1 H), 7.8–8.0 (*m*, 1 H); MS: 187 ($M^+ + 1$, 6), 186 (M^+, 73), 185 (81), 156 ($M^+ - CH_2O$, 39), 155 ($M^+ - CH_3O$, 30), 141 ($PhPO_2H^+$, 62), 91 ($PhCH_2^+$, 100), 77 (Ph^+, 79), 51 (77).

Diethyl phenylphosphonate (**1d**). The dichloride **1a** (14 mmol) in abs. ethanol (50 ml) was gradually added to a NaOEt-solution (from 0.8 g Na in 25 ml EtOH) followed by stirring overnight at room temperature, then heated under reflux for 2 hrs. Water was added to the reaction mixture, and after the usual work-up, distillation (b.p. 109°/1–2 Torr) and chromatographic purification with PE/acetone

(1 : 1) gave **1d** as a yellow liquid (330 mg, 12%). IR (cm^{-1}): 3060, 2990, 1595, 1440, 1250 (P=O), 1130, 1050/1025 (C—O), 970, 800/750 (P—O); ^1H NMR ($CDCl_3$, δ): 1.33 (*t*, 6 H), 4.10 (*quint*, 4 H), 7.38–7.60 (*m*, 3 H), 7.60–7.83 (*m*, 1 H), 7.83–8.00 (*m*, 1 H); MS: 214 (M^+, 31), 213 (7), 186 ($M^+ - C_2H_4$, 14), 159 (43), 158 ($M^+ - C_4H_8$, 99), 142 (61), 141 ($PhPO_2H^+$, 90), 105 (40), 94 ($C_6H_6O^+$, 37), 78 (59), 77 (Ph^+, 100), 51 (43)

Di-isopropyl phenylphosphonate (**1e**). LiO – i – Pr was prepared by treatment of Li metal (0.32 g, 45 mmol) in dry ether with isopropanol (2.3 ml, 30 mmol). After 20 min **1a** (4 ml, 28 mmol) was gradually added followed by stirring of the reaction mixture for 3 h at room temperature and addition of an ether–water mixture. Work-up as usual and purification on silica gel with PE–acetone (2 : 1) gave **1e** as a yellow liquid (1.15 g, 18%); IR (cm^{-1}): 3060, 2980, 1595, 1440, 1385/1375, 1255 (P=O), 1175, 1130, 1105, 1010/980 (C—O), 775/750 (P—O); ^1H NMR ($CDCl_3$, δ): 1.25 (*d*, 6 H), 1.35 (*d*, 6 H), 4.70 (*m*, 2 H), 7.35–7.60 (*m*, 3 H), 7.60–7.82 (*m*, 1 H), 7.82–8.0 (*m*, 1 H); MS: 242 (M^+, 5), 201 ($M^+ - C_3H_5$, 17), 183 (13), 159 ($PhPO_3H_3^+$, 100), 141 ($PhPO_2H^+$, 54), 77 (Ph^+, 35), 43 (37).

Diphenyl phenylphosphonate (**1f**). LiOPh was prepared by adding phenol (2.8 g, 30 mmol) in dry ether (25 ml) to Li metal (0.32 g, 45 mmol) under nitrogen atmosphere. A solution of **1a** (3.5 ml, 25 ml) in dry ether (30 ml) was added portionswise during 1.5 h under cooling with dry ice–acetone to −60°C. The product was purified on silica gel with PE–acetone (3 : 1). The viscous residue was recrystallized from *n*-hexane to give **1f** as white needles, m.p. 72–74°C (1.8 g, 24%). IR (cm^{-1}): 3010, 1570, 1470, 1245 (P=O), 1190/1165 (C—O), 1120, 910 (P—O); ^1H NMR ($CDCl_3$, δ): 6.90–7.30 (*m*, 10 H), 7.30–7.55 (*m*, 3 H), 7.80–7.95 (*m*, 1 H), 7.95–8.10 (*m*, 1 H); MS: 311 ($M^+ + 1$, 9), 310 (M^+, 45), 309 ($M^+ - 1$, 45), 217 ($M^+ - OPh$, 40), 170 (Ph_2O^+, 29), 77 (Ph^+, 100), 51 (21).

P-Phenyl-N,N'-di-n-butylphosphonic diamide (**1g**). The dichloride **1a** (3 ml, 21 mmol) in ether (25 ml) was added gradually to *n*-butylamine (8.4 ml, 84 mmol) in dry ether (25 ml) followed by stirring for 30 min at room temperature. After filtration of the precipitate the filtrate was evaporated. The yellowish crude product was purified on silica gel with PE–acetone (3 : 1) and recrystallized from *n*-hexane, m.p. 54°C (2.3 g, 41%). IR (KBr, cm^{-1}): 3170 (NH), 2920, 2890, 2830, 1425, 1165 (P=O); ^1H NMR ($CDCl_3$, δ): 0.70–1.0 (*m*, 6 H), 1.05–1.7 (*m*, 8 H), 2.45–3.15 (*m*, 6 H), 7.30–7.55, (*m*, 3 H), 7.65–8.0 (*m*, 2 H); MS: 268 (M^+, 17), 225 ($M^+ - C_3H_7$, 58), 197 (25), 196 ($M^+ - C_4H_{10}N$, 100), 154 ($PhPON_2H_2^+$, 16), 140 ($PhOPNH_2^+$, 49), 77 (Ph^+, 18), 72 ($C_4H_{10}N^+$, 31).

Phenyl phenylphosphonochloridate (**1k**).[11] The dichloride **1a** (11 ml, 77 mmol) in dry ether (60 ml) was gradually added to phenol (7.24 g, 77 mmol) in dry ether (60 ml) in the presence of pyridine (6.3 ml, 77 mmol) and stirred at 10–15°C for 1 h. The reaction mixture was left to stand overnight at room temperature and then stirred at 0°C for 1 h. The precipitate was filtered off and the ether solution evaporated followed by distillation of the crude product (b.p. 110°C/10^{-3} Torr) to give **1k** as a colourless liquid (10 g, 51%). IR (cm^{-1}): 3070, 1590, 1490, 1440, 1275 (P=O), 1190/1160 (C—O), 1125, 940/910 (P—O); ^1H NMR ($CDCl_3$, δ): 7.0–7.75 (*m*, 8 H), 7.75–8.0 (*m*, 1 H), 8.0–8.2 (*m*, 1 H); MS: 254/252 (M^+, 18/52), 253/251 ($M^+ - 1$, 26/62), 217 ($M^+ - Cl$, 10), 215 (14), 170 ($Ph - O - Ph^+$, 38), 161/159 ($PhPOCl^+$, 11/35), 77 (Ph^+, 100), 51 (43).

Ethyl phenylphosphonochloridate (**1i**). A solution of **1a** (11 ml, 77 mmol) in dry ether (50 ml) was treated with equimolar quantities of an ethanol (4.5 ml) and pyridine (6.3 ml) in ether (50 ml) for 10 min with stirring under nitrogen. After precipitation of the hydrochloride more ether was added and after rapid filtration the solution was used immediately for further reactions.

Ethyl P-phenyl-N-n-butylaminophosphinate (**1l**). A solution of *n*-butylamine (6 ml, 60 mmol) in dry ether (50 ml) was added stepwise to a freshly prepared solution of **1i** in ether under nitrogen. After stirring for 30 min the precipitate was filtered off. The filtrate was evaporated and the residue purified on silica gel with PE–acetone (3 : 1) to give **1l** as a pale yellow liquid (2.1 g, 31%). IR (cm^{-1}): 3220 (NH), 2960, 2930, 2870, 1595, 1440, 1225/1210 (P=O), 1135, 1035 (C—O), 955, 770/750 (P—O); ^1H NMR ($CDCl_3$, δ): 0.70–1.0 (*m*, 3 H), 1.05–1.60 (*m*, 7 H), 2.50–3.15 (*m*, 3 H), 4.10 (*quint*, 2 H), 7.35–7.60 (*m*, 3 H), 7.60–8.00 (*m*, 2 H); MS: 241 (M^+, 13), 240 ($M^+ - 1$, 6), 199 (12), 198 ($M^+ - C_2H_5N$, 90), 170 (15), 169 ($M^+ - C_4H_{10}N$, 27), 141 ($PhPO_2H^+$, 100), 105 ($PhC_2H_4^+$, 7), 94 ($PhOH^+$, 8), 77 (Ph^+, 57), 72 ($C_4H_{10}N^+$, 18), 51 (17).

Ethyl P-phenyl-N,N-diethylaminophosphinate (**1m**). To a stirred solution of diethylamine (6.4 ml, 60 mmol) in dry ether (50 ml) a solution of freshly prepared **1i** in ether was added under nitrogen. The reaction mixture was filtered after 30 min, then the filtrate was evaporated and purified on silica gel with PE/acetone (3 : 1) to give **1m** as a pale yellow liquid (3.1 g, 45%). IR (cm^{-1}): 3060, 2980, 2930, 2900, 2870, 1595, 1440, 1380, 1235/1205 (P=O), 1120, 1040/1025 (C—O), 950, 790/750 (P—O); ^1H NMR

($CDCl_3$, δ): 1.05 (*t*, 6 H), 1.37 (*t*, 3 H), 3.05 (*q*, 2 H), 3.18 (*q*, 2 H), 4.10 (*m*, 2 H), 7.30–7.55 (*m*, 3 H), 7.55–7.95 (*m*, 2 H); MS: 241 (M^+, 9), 226 ($M^+ - CH_3$, 67), 198 ($M^+ - NC_2H_5$, 13), 169 ($M^+ - N(C_2H_5)_2$, 21), 141 ($PhPO_2H^+$, 100), 105 ($PhC_2H_4^+$, 5), 94 ($PhOH^+$, 4), 77 (Ph^+, 59), 72 ($N(C_2H_5)_2^+$, 72), 58 (37).

Methyl phenylpyrrolidinophosphinate (**1n**). The dichloride **1a** (3 ml, 21 mmol) was mixed with dry ether (35 ml) containing dry pyridine (4 ml) and then treated with methanol (0.85 ml, 21 mmol) in ether (20 ml). Then pyrrolidine (0.85 ml, 10 mmol) in dry ether (8 ml) was added under argon. The reaction mixture was stirred for 44 h, water was added and the aqueous layer extracted with ether. The combined organic layers were dried over $MgSO_4$ and evaporated to give a crude oil which, after purification on silica gel with PE/acetone (2 : 1), gave **1n** as a yellow liquid. IR (cm^{-1}): 3060, 2960, 2880, 1595, 1440, 1235 (P=O), 1130, 1040 (C—O), 805/755 (P—O); ^1H NMR ($CDCl_3$, δ): 1.85 (*m*, 4 H), 3.13 (*m*, 4 H), 3.45 (*d*, 3 H, $^3J_{PH}$ = 11.0 Hz), 7.30–7.55 (*m*, 3 H), 7.55–7.90 (*m*, 2 H); MS: 225 (M^+, 7), 224 ($M^+ - 1$, 7), 155 ($PhPO_2CH_3^+$, 28), 77 (Ph^+, 27), 70 ($NC_4H_8^+$, 100).

P-Phenyl-N,N-diethylphosphonamidic acid, anhydride (**3**). Under an argon atmosphere **1a** (3 ml, 21 mmol) in dry ether (25 ml) was treated with diethylamine (4.2 ml, 40 mmol) and pyridine (3.6 ml, 45 mmol) in dry ether (25 ml). Then 10 ml pyridine were added and the reaction mixture stirred for 2 hrs. Usual work-up and recrystallization from CH_2Cl_2-hexane gave **3** as colourless needles which liquify rapidly on air. Column chromatography using PE/acetone (3 : 1) afforded 3 as a pale yellow oil (0.3 g, 7.5%). IR (cm^{-1}): 3060, 2980, 1595, 1440, 1380, 1250 (P=O), 1210, 1180, 1125, 1035, 950/910 (P—O—P); ^1H NMR ($CDCl_3$, δ): 1.10 and 1.00 (2*t*, each 6 H), 3.15 (*m*, 8 H), 7.35–7.60 (*m*, 6 H), 7.60–8.05 (*m*, 4 H); MS: 408 (M^+, 9), 337 (19), 336 ($M^+ - NEt_2$, 16), 196 ($PhPONEt_2^+$, 60), 86 (14), 84 (22), 72 (NEt_2^+, 100).

Dimethyl phenylthiophosphonate (**2c**). A solution of **2a** (3.9 ml, 25 mmol) in abs. MeOH (5 ml) was treated as described for **1c** and worked up as usual to give **2c** as a colourless liquid (3.6 g, 71%). IR (cm^{-1}): 3050, 3010, 2950, 2850, 1590, 1440, 1180, 1120, 1055/1025 (C—O), 820/800 (P—O), 625 (P=S); ^1H NMR ($CDCl_3$, δ): 3.73 (*d*, 6 H, $^3J_{PH}$ = 13.5 Hz), 7.30–7.60 (*m*, 3 H), 7.70–7.85 (*m*, 1 H), 7.85–8.05 (*m*, 1 H); MS: 202 (M^+, 92), 172 ($M^+ - OCH_2$, 32), 171 ($M^+ - OCH_3$, 11), 139 ($PhPS^+$, 100), 109 (PhS^+, 56), 93 ($PO_2(CH_3)_2^+$, 48), 77 (Ph^+, 38), 63 (PS^+, 20), 51 (54).

Methyl phenylthiophosphonochloridate (**2h**). The dichloride **2a** (3.9 g, 25 mmol) was mixed with dry ether (5 ml), then gradually treated with a mixture of abs. MEOH (1 ml) and pyridine (2.1 ml, 26 mmol) in 5 ml dry ether. The mixture was stirred overnight and the precipitate filtered off. Usual work-up gave a colourless liquid (4.2 g, 82%). IR (cm^{-1}): 3060, 2950, 1590, 1440, 1120, 1030 (C—O), 815 (P—O), 685/655 (P=S); ^1H NMR ($CDCl_3$, δ): 3.98 (*d*, 3 H, $^3J_{PH}$ = 16.0 Hz), 7.30–7.70 (*m*, 3 H), 7.80–8.00 (*m*, 1 H), 8.00–8.25 (*m*, 1 H); MS: 208/206 (M^+, 14/40), 178/176 ($M^+ - OCH_2$, 9/24), 171 ($M^+ - Cl$, 14), 145/143 ($PhPCl^+$, 9/28), 139 ($C_6H_4PS^+$, 10), 109 (PhS^+, 17), 77 (Ph^+, 30), 63 (PS^+, 15), 50 (CH_3Cl^+, 100).

Phenyl phenylthiophosphonochloridate (**2k**). The dichloride **2a** (3.9 ml, 25 mmol) in dry ether (5 ml) was added portionwise to a mixture of phenol (2.35 g, 25 mmol) and 2.1 ml pyridine in dry ether (5 ml) during 2 h at room temperature. Then the mixture was stirred for 1 h under reflux and poured into ice-cold water. Usual work-up afforded **2k** as a colourless oil (3.6 g, 54%). IR (cm^{-1}): 3060, 1590, 1480, 1440, 1185/1155 (C—O), 1120, 925/900 (P—O), 685/665 (P=S); ^1H NMR ($CDCl_3$, δ): 7.00–7.75 (*m*, 3 H), 7.75–8.15 (*m*, 1 H), 8.15–8.35 (*m*, 1 H); MS: 270/268 (M^+, 5/12), 233 ($M^+ - Cl$, 2), 159 (12), 145/143 ($PhPCl^+$, 7/20), 139 ($C_6H_4PS^+$, 41), 109 (PhS^+, 100), 77 (Ph^+, 74), 63 (PS^+, 40), 51 (77).

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