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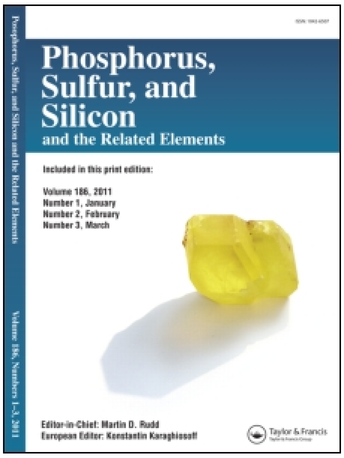

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FORMATION OF SULFINAMIDES AND SULFONAMIDES BEARING THE ORGANO-AMINOMETHYLENE-DIMETHYLPHOSPHINE OXIDE OR SULFIDE GROUP

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FORMATION OF SULFINAMIDES AND SULFONAMIDES BEARING THE ORGANO-AMINOMETHYLENE-DIMETHYLPHOSPHINE OXIDE OR SULFIDE GROUP

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(Received 22 October 1996)

The reaction of N-methyl-N-trimethylsilylaminomethylene-dimethylphosphine oxide **1** and sulfide **2** with various sulfinyl and sulfonyl chlorides furnished, in good yield, a series of phosphorus-containing sulfinamides and sulfonamides, **3–11**, bearing the dimethylphosphoryl and thiophosphoryl group, respectively. All sulfinamides (**3–8**) show a complicated splitting pattern for the ^{1}H-n.m.r. resonances of the $C\underline{H}_2P$-group, due to the presence of a chiral sulfur atom. For the same reason, doubling of the $(C\underline{H}_3)_2P$-proton resonances is observed for **3**, **4**, **7** and **8**. N.m.r. spectra for the sulfonamides **9–11** are in accord with expectation.

N-benzylaminomethylene-dimethylphosphine oxide **12** was allowed to react with chlorosulfonylacetic acid methyl ester in the presence of triethylamine as a base to form the phosphorus-containing sulfonamide **13** in good yield. In the reaction of **5** with air/moisture, by an unknown reaction course, the phosphorus-containing ammonium hydrogen sulfate **14** was formed. X-ray crystal structure determinations were conducted for **10** and **14**. The two independent molecules of **10** are closely similar and show C-N-S-C torsion angles of 89, 83°. In compound **14**, hydrogen bonding links two formula units.

Keywords: Aminomethylene-dimethylphosphine oxide; -sulfide; sulfinamides; sulfonamides; n.m.r. spectra; X-ray crystal structure determinations

INTRODUCTION

During the past few years, phosphorus-containing derivatives of the amino acid glycine have been of special interest because of their importance as plant growth regulators and herbicides[1].

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Few investigations concerning substituted glycines with the N-alkylaminomethylene dimethylphosphine oxide group of type **A** (Fig. 1) have been carried out until now[1–3]. These compounds are readily available by reaction of dimethylphosphine oxide with the corresponding nitrogen-substituted triazines[4].

Whereas reactions of compounds of type **B** (Fig. 1) with various acyl halides were described recently[5], comparable reactions with sulfinyl and sulfonyl chlorides have previously been unknown. In the following, such reactions are described and n.m.r. spectroscopic properties of the reaction products are discussed.

RESULTS AND DISCUSSION

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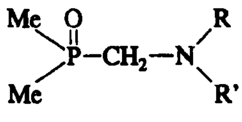
The reaction of sulfinyl chlorides with amines constitutes the principal method for the synthesis of both aliphatic and aromatic sulfinylamides[6–11]. This method has also been used for the synthesis of N,N-dialkylalkane sulfinylamides[12,13]. According to this method, the reaction of **1** and **2** with a number of organosubstituted sulfinyl and sulfonyl chlorides furnished, in good yields, a series of sulfinylamides and sulfonylamides, respectively (Scheme 1).

The n.m.r. spectroscopic investigation of all compounds presented in Scheme 1 revealed some peculiarities.

In the reaction of **1** with the sulfinyl chlorides, ^{t}BuSOCl, ^{1}AdSOCl and 4-Me-C_6H_4SOCl, compounds **3**, **5** and **7** were obtained. Their $\delta(^{31}P)$ values in the n.m.r. spectra (between 41.56 and 41.86 ppm) are very similar. These values are comparable to that of the starting compound **1** ($\delta(P)$ = 44.38 ppm)[1].



R = Me, CH_2Ph

R' = various hydrocarbon groups   R' = $SiMe_3$, H

A   **B**

FIGURE 1 The N-alkylaminomethylene-dimethylphosphine oxide skeleton **A** and its N-trimethylsilylated and N-H derivatives, **B**.

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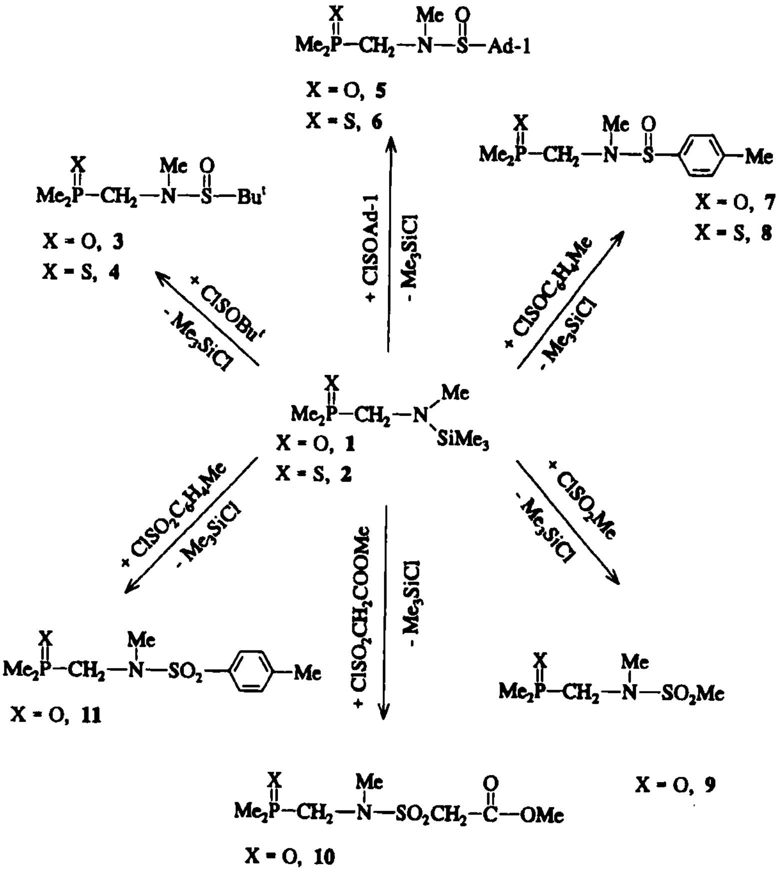

SCHEME 1

The $\delta(^{31}P)$ values of **4**, **6** and **8**, bearing the thiophosphoryl group, lie in the range $\delta(P) = 36.64$ to 37.98 ppm, values almost identical to that of the starting compound **2** ($\delta(P) = 38.85$ ppm)[1].

In general, all ^{31}P-n.m.r. resonances of compounds bearing the thiophosphoryl group (**4**, **6**, **8**) are shifted slightly to higher field, compared to those bearing the phosphoryl group (**3**, **5**, **7**).

Because of the chiral sulfur atom in **3**–**8**, arising from the tetrahedral orientation of groups around sulfur, a complicated splitting pattern for the proton resonances of the CH_2P-group is observed. Each spectrum shows eight signals for this group, due to the AB part of an ABX spectrum. For the same reason, doubling of the $(C\underline{H}_3)_2P$ proton resonance is observed for **3**, **4**, **7** and **8** by ^1H-n.m.r. spectroscopy. Contrary to expectation, this splitting does not occur for

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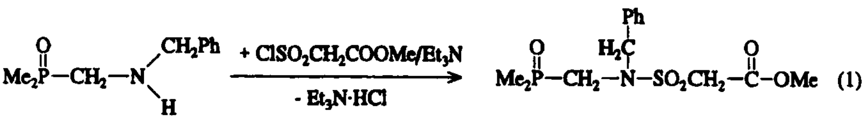
5 and **6**, where only one single resonance is detected for this group. Because the adamantyl group represents the only difference from compounds **3**, **4**, **7** and **8**, the influence of this group, bonded to sulfur, must be responsible for this observation.

Upon reaction of **1** with the sulfonyl chlorides $MeSO_2Cl$, $MeC(:O)OCH_2SO_2Cl$ and $4\text{-}Me\text{-}C_6H_4SO_2Cl$, compounds **9–11** are formed. In these cases, the sulfur atom is achiral. Thus, the ^1H-n.m.r. resonance of the $C\underline{H}_2P$-protons is split, as expected, only into a doublet, due to coupling to ^{31}P. For the same reason, two different ^1H-n.m.r. resonances for the $(C\underline{H}_3)_2P$ protons are not observed for **9–11** (absence of a chiral sulfur atom).

All further n.m.r.-spectroscopic details of **9–11** are comparable to those found for **3–8** (cf. Experimental Part).

In EI-mass spectrometric investigations on **3–11**, the molecular ion could be detected in most cases in low intensity (<1%), except for **6** (20%). Characteristic fragments could be assigned to each compound. For **7**, a characteristic mass spectrum was obtained, using the CI-method. The corresponding EI-spectrum did not exhibit the molecular ion and the small number of fragments was not sufficient to allow an unambiguous characterization.

According to eqn. (1), compound **12** was allowed to react with chlorosulfonylacetic acid methyl ester in the presence of triethylamine as a base. Triethylamine hydrochloride, formed during the reaction, was removed from the reaction mixture by treatment with water.

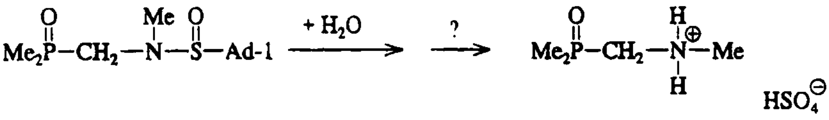


$$\mathrm{Me_2P(O)-CH_2-N(CH_2Ph)H} \xrightarrow[-\,\mathrm{Et_3N\cdot HCl}]{+\,\mathrm{ClSO_2CH_2COOMe/Et_3N}} \mathrm{Me_2P(O)-CH_2-N(CH_2Ph)-SO_2CH_2-C(O)-OMe} \quad (1)$$

12 **13**

Compound **13** was isolated in good yield. Compared to **10**, **13** bears a benzyl group at nitrogen instead of the methyl group. This does not have much influence on the n.m.r.-spectroscopic behaviour. Because the N-silylated derivative of **12** is not available[5], the use of a base (Et_3N) was necessary to form **13**, but this does not affect the yield of the product which was nearly quantitative. Thus, both the N-silylated derivatives **1** and **2** and the non-silylated compound **12** can be employed for the reaction with sulfinyl or sulfonyl chlorides, leading to the same kind of compounds in comparable yields.

Compound **14** was formed, by an unknown reaction pathway, by exposing a solution of **5** in $CDCl_3$ to moist air for two days (eqn. (2)):



$$Me_2\overset{\overset{O}{\|}}{P}-CH_2-\overset{\overset{Me}{|}}{N}-\overset{\overset{O}{\|}}{S}-Ad\text{-}1 \xrightarrow{+H_2O} \xrightarrow{?} Me_2\overset{\overset{O}{\|}}{P}-CH_2-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N^{\oplus}}}-Me \quad HSO_4^{\ominus} \qquad (2)$$

5 **14**

A small amount of crystals was isolated. The presence of atmospheric moisture probably causes the cleavage of the N-S-bond and leads to the formation of an ammonium cation. The presence of the hydrogensulfate anion was established, but the fate of the adamantyl group was not determined.

The structure of **10** and **14** was proved unambiguously by X-ray crystal structure determinations.

X-ray Crystal Structure Determination of **10** *and* **14**

Compound **10** crystallizes with two independent molecules (Fig. 2), which are, however, very similar; differences in equivalent bond lengths and angles (Table I) are minimal (<1 pm, 1°) and equivalent torsion angles differ by less than 7°. The S-N bond lengths of 162.09, 161.70(13) pm may be compared with the standard value for $C\text{-}SO_2\text{-}NC_2$ systems of 164.2 pm[14]. The conformation about the N-S bond is defined by the torsion angle C3-N1-S1-C5 (absolute values 89.4, 82.8°). The nitrogen atom is slightly pyramidalised; it lies 21 pm out of the plane of its immediate substituents in both molecules.

Compound **14** (Fig. 3) is ionic; the cation shows an extended conformation (torsion angles C2-P-C3-N 179°, P-C3-N-C4 174°). In the anion, the S-OH bond is, as expected, appreciably longer than the other S-O bonds (Table II). Hydrogen bonding (Table III) links two formula units together (Fig. 4), and the hydrophilic groups occupy the regions $y = 0, 0.5, 1$, etc. (Fig. 5).

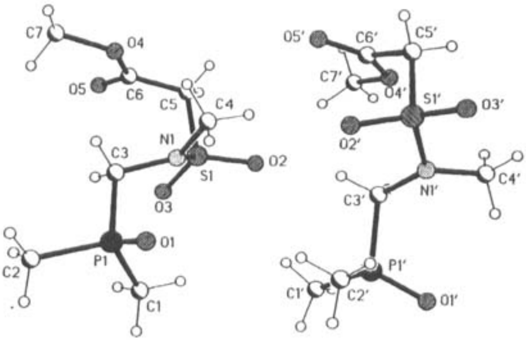


FIGURE 2 The two independent molecules of compound **10** in the crystal. Radii are arbitrary.

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TABLE I Selected bond lengths (pm) and angles (°) for compound **10** (two independent molecules)

P(1)-O(1)	149.05(12)	148.69(13)	P(1)-C(2)	178.5(2)	178.8(2)
P(1)-C(1)	179.0(2)	179.2(2)	P(1)-C(3)	182.4(2)	182.2(2)
S(1)-O(2)	143.34(11)	143.04(12)	S(1)-O(3)	143.48(11)	143.10(11)
S(1)-N(1)	162.09(13)	161.70(13)	S(1)-C(5)	178.2(2)	178.6(2)
N(1)-C(4)	146.5(2)	146.7(2)	N(1)-C(3)	147.2(2)	146.9(2)
O(1)-P(1)-C(2)	113.65(8)	113.81(8)	O(1)-P(1)-C(1)	113.61(8)	113.41(8)
C(2)-P(1)-C(1)	106.18(9)	106.73(10)	O(1)-P(1)-C(3)	112.83(7)	113.10(7)
C(2)-P(1)-C(3)	105.04(7)	104.04(8)	C(1)-P(1)-C(3)	104.69(8)	104.89(8)
O(2)-S(1)-O(3)	119.25(7)	119.85(7)	O(2)-S(1)-N(1)	107.34(7)	107.30(7)
O(3)-S(1)-N(1)	107.16(7)	107.41(7)	O(2)-S(1)-C(5)	105.52(7)	104.97(8)
O(3)-S(1)-C(5)	108.31(7)	107.62(7)	N(1)-S(1)-C(5)	108.95(7)	109.41(8)
C(4)-N(1)-C(3)	115.70(12)	115.74(13)	C(4)-N(1)-S(1)	118.57(10)	118.56(11)
C(3)-N(1)-S(1)	120.27(10)	119.97(10)	N(1)-C(3)-P(1)	108.87(10)	109.92(10)

EXPERIMENTAL

Experimental conditions and instruments used for the n.m.r. spectroscopic and mass spectrometric investigations were identical to those mentioned in ref.[3]. The abbreviation "i.v." relates to a pressure of *ca.* 0.1 Torr.

The following starting compounds were synthesized according to methods described in the literature:

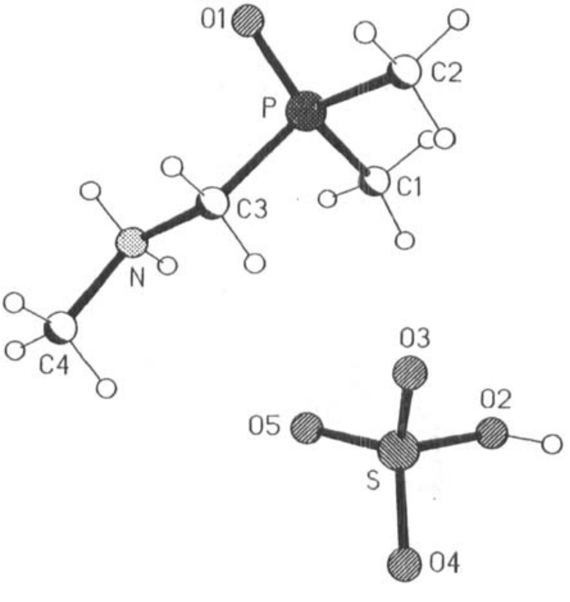

FIGURE 3 The formula unit of compound 14 in the crystal. Radii are arbitrary.

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TABLE II Bond lengths (pm) and angles (°) for compound **14**

P-O(1)	149.4(3)	P-C(1)	177.8(4)
P-C(2)	177.8(4)	P-C(3)	181.0(4)
N-C(4)	148.2(5)	N-C(3)	148.7(5)
S-O(3)	143.1(3)	S-O(4)	143.8(3)
S-O(5)	145.1(3)	S-O(2)	154.8(3)
O(1)-P-C(1)	113.1(2)	O(1)-P-C(2)	113.4(2)
C(1)-P-C(2)	107.4(2)	O(1)-P-C(3)	111.5(2)
C(1)-P-C(3)	107.6(2)	C(2)-P-C(3)	103.2(2)
C(4)-N-C(3)	112.4(3)	N-C(3)-P	113.6(2)
O(3)-S-O(4)	113.5(2)	O(3)-S-O(5)	111.9(2)
O(4)-S-O(5)	113.4(2)	O(3)-S-O(2)	107.7(2)
O(4)-S-O(2)	106.6(2)	O(5)-S-O(2)	102.8(2)

TABLE III Hydrogen bonds in compound **14**

X-H...Y	*Symmetry operator (Y)*	*X...Y (pm)*	*H...Y (pm)*	*X-H...Y (°)*
N-H0A...O4	$x - 1, y, z - 1$	273.7(4)	187	157
N-H0B...O5	$-x + 1, -y, -z + 1$	279.5(4)	192	159
O2-H2...O1	$x + 1, y, z + 1$	252.5(4)	169	170

N-Methyl-N-trimethylsilylaminomethyl-dimethylphosphine oxide, **1**[1]; N-methyl-N-trimethylsilylaminomethyl-dimethylphosphine sulfide, **2**[1]: N-benzylaminomethyl-dimethylphosphine oxide, **12**[1], *tert*.-butylsulfinyl chloride[15]; 1-adamantylsulfinyl chloride[16]; 4-tolylsulfinyl chloride[17]. All the other compounds were commercially available.

General Procedure for the Preparation of Compounds 3–11 (Table IV)

In a 100 ml Schlenk tube, the N-trimethylsilyl-N-methylaminomethyl-dimethylphosphine oxide, **1**, or the sulfide, **2**, was dissolved in 20 ml of dichloromethane. An equimolar amount of the corresponding sulfinyl or sulfonyl chloride, dissolved in 10 ml of dichloromethane, was added dropwise at r.t. within 30 min. The reaction mixture was stirred for 1 h at r.t. Subsequently, the solvent and volatile compounds (Me_3SiCl) were removed i.v., and the remaining colourless solids (or oils) were dried i.v.

Experimental data are presented in Table IV.

Compound 3

^{1}H-n.m.r.: δ = 1.15 [s, $(CH_3)_3C$], 1.48 and 1.50 [2d, $^2J(PH)$ = 12.47 and 12.63 Hz, $(CH_3)_2P$], 2.87 [s, $(CH_3)N$], 3.29 [m, CH_2, [18]],—^{13}C-n.m.r.: δ = 15.51

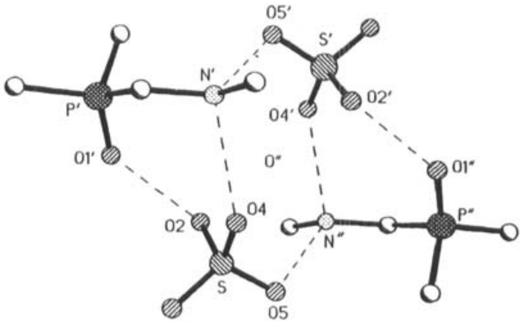

FIGURE 4 Two formula units of compound **14** (H atoms omitted) showing hydrogen bonds as dashed lines (for symmetry operators see text).

and 15.67 [2d, $^1J(PC)$ = 67.92 and 67.17 Hz, $(\mathit{C}H_3)_2P$], 23.29 [s. $(\mathit{C}H_3)_3C$]. 36.97 [s, $(\mathit{C}H_3)N$], 52.98 [d, $^1J(PC)$ = 78.46 Hz, $\mathit{C}H_2P$], 59.20 [s, $(CH_3)_3\mathit{C}$],—^{31}P-n.m.r.: δ = 41.89 [s].—EI-MS: *m/z* (%): 225 (1) $[M]^+$, 210 (1) $[M\text{-}Me]^+$, 168 (70) $[M\text{-}{}^tBu]^+$, 120 (20) $[M\text{-}S(O){}^tBu]^+$, 91 (60) $[Me_2P(O)CH_2]^+$, 77 (40) $[Me_2P(O)]^+$, 57 (24) $[{}^tBu]^+$.

$C_8H_{20}NO_2PS$ (225.29) Calc. C 42.65 H 8.94 N 6.21%,
Found C 42.10 H 8.94 N 6.38%.

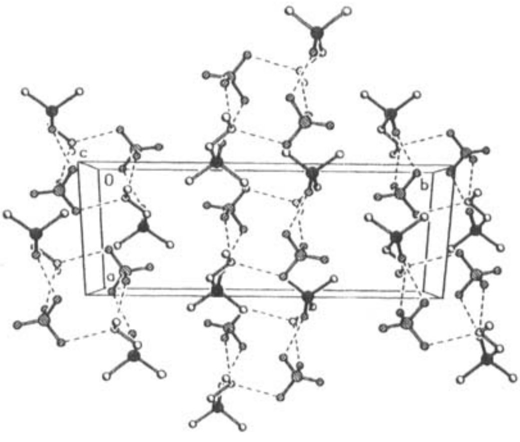

FIGURE 5 Packing diagram of compound **14**. H atoms are omitted for clarity. Hydrogen bonds are shown by dashed lines.

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TABLE IV Experimental data for the preparation of **3–11**

No.	*Starting Compounds g (mmol)*	*Yield: g (%) M.p.: (°C)*	No.	*Starting Compounds g (mmol)*	*Yield: g (%) M.p.: (°C)*
3	1.05 (5.44) **1**; 0.77 (5.44) $ClSOBu^t$	1.13 (92.7) 50	**8**	1.00 (4.78) **2**; 0.83 (4.78) $ClSOC_6H_4Me$-4	1.29 (98.5) 103
4	1.20 (5.74) **2**; 0.81 (5.74) $ClSOBu^t$	1.07 (77.2) 81	**9**	1.25 (6.48) **1**; 0.74 (6.48) $ClSO_2Me$	1.18 (91.5) Oil
5	1.18 (6.11) **1**; 1.34 (6.11) ClSOAd-1	1.78 (95.9) 122	**10**	1.05 (5.44) **1**; 0.94 (5.44) $ClSO_2CH_2COOMe$	1.03 (73.7) 104
6	1.15 (5.50) **2**; 1.20 (5.50) ClSOAd-1	1.25 (71.3) Oil			
7	1.00 (5.18) **1**; 0.90 (5.18) $ClSOC_6H_4Me$-4	1.32 (98.5) 107	**11**	1.60 (8.29) **1**; 1.57 (8.29) $ClSO_2C_6H_4Me$-4	2.13 (93.4) 144

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Compound 4

^{1}H-n.m.r.: δ = 1.19 [s, $(CH_3)_3C$], 1.54 and 1.62 [2d, $^2J(PH)$ = 12.71 and 12.63 Hz, $(CH_3)_2P$], 2.61 [s, $(CH_3)N$], 3.34 [m, CH_2, [18]].—^{31}P-n.m.r.: δ = 37.12 [s].—EI-MS: *m/z* (%): 241 (1) $[M]^+$, 148 (100) $[M\text{-}Me_2P(S)]^+$, 134 (10) $[^tBu\text{-}S(O)N(Me)]^+$, 105 (40) $[^tBuS(O)]^+$, 57 (4) $[^tBu]^+$.

$C_8H_{20}NOPS_2$ (241.35) Calc. C 39.81 H 8.35 N 5.80%,
Found C 39.67 H 8.41 N 5.74%.

Compound 5

^{1}H-n.m.r.: δ = 1.54 [d, $^2J(PH)$ = 12.74 Hz, $(CH_3)_2P$], 1.71–2.24 [m, $C_{10}H_{15}$], 2.96 [s, $(CH_3)N$], 3.35 [m, CH_2, [18]].—^{31}P-n.m.r.: δ = 41.86 [s].—EI-MS: *m/z* (%): 303 (3) $[M]^+$, 168 (4) [M-adamantyl]$^+$, 135 (100) [adamantyl]$^+$, 107 (10) $[Me_2P(S)CH_2]^+$, 93 (15) $[Me_2P(S)]^+$.

$C_{14}H_{26}NO_2PS$ (303.40) Calc. C 55.42 H 8.63 N 4.61 S 10.56%,
Found C 53.78 H 8.57 N 4.14 S 10.47%.

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Compound 6

^{1}H-n.m.r.: δ = 1.43 [d, $^2J(PH)$ = 14.18 Hz, $(C\mathit{H}_3)_2P$], 1.65–2.06 [m, $C_{10}\mathit{H}_{15}$], 2.28 [s, $(C\mathit{H}_3)N$], 3.41 [m, $C\mathit{H}_2$, [18]].—^{31}P-n.m.r.: δ = 37.98 [s].—EI-MS: *m/z* (%): 319 (20) $[M]^+$, 135 (100) $[\text{adamantyl}]^+$, 107 (10) $[Me_2P(S)CH_2]^+$, 93 (20) $[Me_2P(S)]^+$.

$C_{14}H_{26}NOPS_2$ (319.46) Calc. C 52.64 H 8.20 N 4.38 S 20.07%,
Found C 52.34 H 8.24 N 4.17 S 20.22%.

Compound 7

^{1}H-n.m.r.: δ = 1.20 and 1.35 [2d, $^2J(PH)$ = 12.59 and 12.54 Hz, $(C\mathit{H}_3)_2P$], 2.27 [s, $(C\mathit{H}_3)N$], 2.77 [s, $C_6H_4C\mathit{H}_3$], 2.91–3.21 [m, $C\mathit{H}_2$, [18]], 7.18 and 7.39 [2d, $^3J(HH)$ = 7.90 and 8.22 Hz, $C_6\mathit{H}_4$].—^{13}C-n.m.r.: δ = 14.99 [d, $^1J(PC)$ = 69.06 Hz, $(\mathit{C}H_3)_2P$], 21.13 [s, $C_6H_4\mathit{C}H_3$], 36.93 [s, $(\mathit{C}H_3)N$], 49.85 [d, $^1J(PC)$ = 79.24 Hz, $\mathit{C}H_2$], 125.41, 129.48, 139.41 and 141.84 [4s, C_6H_4].—^{31}P-n.m.r.: δ = 41.56 [s].—CI-MS: *m/z* (%): pos. CI (NH_3): 277 (10) $[M + NH_4]^+$, 260 (100) $[M + H]^+$, 120 (60) $[Me_2P(O)CH_2N(Me)]^+$; neg. CI (NH_3): 259 (1) $[M]^-$, 139 (100) $[MeC_6H_4S(O)]^-$, 123 (20) $[MeC_6H_4S]^-$.

$C_{11}H_{18}NO_2PS$ (259.30) Calc. C 50.95 H 7.00 N 5.40 S 12.36%,
Found C 49.42 H 7.02 N 5.39 S 11.74%.

Compound 8

^{1}H-n.m.r.: δ = 1.58 and 1.64 [2d, $^2J(PH)$ = 12.88 and 12.54 Hz, $(C\mathit{H}_3)_2P$], 2.35 [s, $(C\mathit{H}_3)N$], 2.80 [s, $C_6H_4C\mathit{H}_3$], 3.28–3.61 [m, $C\mathit{H}_2$, [18]], 7.27 and 7.51 [2d, $^3J(HH)$ = 8.58 and 8.26 Hz, $C_6\mathit{H}_4$].—^{13}C-n.m.r.: δ = 19.63 [d, $^1J(PC)$ = 53.41 Hz, $(\mathit{C}H_3)_2P$], 21.33 [s, $C_6H_4\mathit{C}H_3$], 36.71 [s, $(\mathit{C}H_3)N$], 54.53 [d, $^1J(PC)$ = 63.67 Hz, $\mathit{C}H_2$], 125.69, 129.76, 139.50 and 142.14 [4s, C_6H_4].—^{31}P-n.m.r.: δ = 36.64 [s].—EI-MS: *m/z* (%): 275 (1) $[M]^+$, 232 (20) $[M\text{-}CH_2N(Me)]^+$, 182 (40) $[M\text{-}Me_2P(S)]^+$, 139 (100) $[MeC_6H_4S(O)]^+$, 93 (30) $[Me_2P(S)]^+$, 77 (24) $[N(Me)S(O)]^+$.

$C_{11}H_{18}NOPS_2$ (275.36) Calc. C 47.98 H 6.59 N 5.09 S 23.29%,
Found C 46.58 H 6.68 N 5.17 S 23.12%.

Compound 9

^{1}H-n.m.r.: δ = 1.53 [d, $^2J(PH)$ = 12.48 Hz, $(C\mathit{H}_3)_2P$], 2.77 [s, $(C\mathit{H}_3)N$], 3.01 [s, $C\mathit{H}_3S$], 3.39 [d, $^2J(PH)$ = 4.75 Hz, $C\mathit{H}_2$].—^{13}C-n.m.r.: δ = 14.75 [d, $^1J(PC)$ = 69.01 Hz, $(\mathit{C}H_3)_2P$], 34.21 [s, $\mathit{C}H_3S$], 37.37 [s, $(\mathit{C}H_3)N$], 50.20 [d, $^1J(PC)$ =

78.78 Hz, CH_2].—^{31}P-n.m.r.: δ = 44.46 [s].—EI-MS: *m/z* (%): 199 (<1) $[M]^+$, 122 (100) $[M-Me_2P(O)]^+$, 120 (80) $[M-SO_2Me]^+$, 77 (80) $[N(Me)S(O)]^+$.

$C_5H_{14}NO_3PS$ (199.20)	Calc.	C 30.15	H 7.08	N 7.03	S 16.09%,
	Found	C 29.56	H 6.96	N 6.97	S 16.22%.

Compound 10

^{1}H-n.m.r.: δ = 1.56 [d, $^2J(PH)$ = 12.72 Hz, $(CH_3)_2P$], 3.15 [s, $(CH_3)N$], 3.55 [d, $^2J(PH)$ = 4.83 Hz, CH_2], 3.76 [s, $(CH_3)O$], 4.03 [s, CH_2S].—^{13}C-n.m.r.: δ = 14.81 [d, $^1J(PC)$ = 68.63 Hz, $(CH_3)_2P$], 37.47 [s, $(CH_3)N$], 51.31 [d, $^1J(PC)$ = 76.65 Hz, CH_2P], 53.21 [s, CH_2S], 65.79 [s, CH_3O], 163.64 [s, $C(:O)$].—^{31}P-n.m.r.: δ = 43.80 [s].—EI-MS: *m/z* (%): 257 (<1) $[M]^+$, 226 (8) $[M-MeO]^+$, 184 (4) $[M-MeOC(O)CH_2]^+$, 180 (60) $[M-Me_2P(O)]^+$, 137 (14) $[MeOC(O)CH_2SO_2]^+$, 120 (100) $[Me_2P(O)CH_2N(Me)]^+$, 77 (18) $[Me_2P(O)]^+$, 44 (22) $[CO_2]^+$.

$C_7H_{16}NO_5PS$ (257.24)	Calc.	C 32.68	H 6.27	N 5.44	S 12.46%,
	Found	C 31.98	H 6.31	N 5.42	S 11.78%.

Compound 11

^{1}H-n.m.r.: δ = 1.59 [d, $^2J(PH)$ = 12.71 Hz, $(CH_3)_2P$], 2.39 [s, $C_6H_4CH_3$], 2.88 [s, $(CH_3)N$], 3.22 [d, $^2J(PH)$ = 6.29 Hz, CH_2], 7.25–7.62 [2m, C_6H_4].—^{13}C-n.m.r.: δ = 14.90 [d, $^1J(PC)$ = 69.14 Hz, $(CH_3)_2P$], 21.49 [s, $C_6H_4CH_3$], 37.69 [s, $(CH_3)N$], 50.57 [d, $^1J(PC)$ = 78.83 Hz. CH_2], 127.56, 129.90, 132.55 and 144.17 [4s, C_6H_4].—^{31}P-n.m.r.: δ = 43.82 [s].—EI-MS: *m/z* (%): 259 (<1) $[M-O]^+$, 198 (56) $[M-Me_2P(O)]^+$, 155 (100) $[M-C_6H_4SO_2]^+$, 120 (100) $[Me_2P(O)CH_2N(Me)]^+$, 91 (78) $[Me_2P(O)CH_2$ or $C_6H_4Me]^+$, 77 (24) $[Me_2P(O)]^+$.

$C_{11}H_{18}NO_3PS$ (275.30)	Calc.	C 47.99	H 6.59	N 5.09	S 11.65%,
	Found	C 47.05	H 6.55	N 4.91	S 11.75%.

Compound 13

To a stirred and cooled (0°C) solution of 0.94 g (4.77 mmol) **12** and 0.49 g (4.77 mmol) of triethylamine in 20 ml of dichloromethane, a solution of 0.83 g (4.77 mmol) of chlorosulfonylacetic acid methyl ester in 10 ml of dichloromethane was added dropwise (20 min). Stirring was continued for 1 h at r.t. Subsequently, the reaction solution was washed with two 50 ml-portions of water. The organic layer was separated and dried over Na_2SO_4. After filtration, the solvent was

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removed i.v. The remaining oil could not be crystallized by cooling to $-30°C$. Yield: 1.45 g (91.4%). ^{1}H-n.m.r.: δ = 1.58 [d. $^2J(PH)$ = 12.72 Hz, $(CH_3)_2P$], 3.71 [d, $^2J(PH)$ = 3.72 Hz, CH_2P], 3.80 [s, CH_3O], 4.19 [s, CH_2S], 4.82 [s, $CH_2C_6H_5$], 7.37–7.47 [m, C_6H_5].—^{13}C-n.m.r.: δ = 15.59 [d, $^1J(PC)$ = 67.08 Hz, $(CH_3)_2P$], 47.74 [d, $^1J(PC)$ = 73.89 Hz, CH_2P], 52.78 [s, CH_3O], 53.25 [s, CH_2S], 56.95 [s, $CH_2C_6H_5$], 128.39, 128.56 and 128.84 [3s, C_6H_5], 134.42 [s, ipso-C_6H_5], 163.80 [s, $C(:O)$].—^{31}P-n.m.r.: δ = 42.18 [s].—EI-MS: *m/z* (%): 333 (<1) $[M]^+$, 302 (4) $[M\text{-}MeO]^+$, 256 (4) $[M\text{-}Me_2P(O)]^+$, 196 (60) $[M\text{-}SO_2CH_2C(O)OMe]^+$, 91 (100) $[Me_2P(O)CH_2]^+$, 77 (10) $[Me_2P(O)$ or $C_6H_5]^+$.

$C_{13}H_{20}NO_5PS$ (333.34) Calc. C 46.84 H 6.05 N 4.20 S 9.62%,
Found C 46.49 H 5.99 N 4.31 S 9.60%

Compound 14

A solution of **5** in $CDCl_3$ was stored in an open n.m.r. tube at r.t. for two days. The solvent evaporated slowly, and crystals were formed, suitable for an X-ray crystal structure determination. ^{1}H-n.m.r.: δ = 1.59 [d, $^2J(PH)$ = 12.11 Hz, $(CH_3)_2P$], 2.88 [m, CH_3N], 3.29 [m, CH_2], 9.85 [m, H_2N^+].—^{31}P-n.m.r.: δ = 42.95 [s]. $C_4H_{14}NO_5PS$ (219.19).

Crystal structure analyses of compounds 10 *and* 14

Crystal data are presented in Table V, Data collection: Data were collected with Mo K_α radiation on a Siemens P4 diffractometer equipped with an LT-2 low temperature device. Scan type ω. Cell constants were refined from setting angles of ca. 60 reflections to $2\Theta_{max}$ 25°. *Structure solution*: Direct methods. *Structure refinement*: Anisotropic refinement on F^2, (program SHELXL-93). H atoms as rigid groups (methyl, OH) or with a riding model, weighting schemes $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $3P = (2F_c^2 + F_o^2)$, and a and b are constants optimised by the program. Final atomic coordinates are given in Tables VI and VII, with selected molecular dimensions in Tables I and II.

Full details of the structure determinations have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference numbers 405764 (**10**) and 405765 (**14**).

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TABLE V Crystal Data for Compounds **10** and **14**

Compound	**10**	**14**
Formula	$C_7H_{16}NO_5PS$	$C_4H_{14}NO_5PS$
M_r	257.24	219.19
Crystal habit	Colourless prism	Colourless needle
Crystal size (mm)	0.85 × 0.45 × 0.45	1.0 × 0.15 × 0.05
Space group	$P2_1/c$	$P2_1/n$
Temperature (°C)	−100	−100
Cell constants:		
a (pm)	1247.98(10)	769.5(4)
b (pm)	1128.04(10)	1816.2(9)
c (pm)	1781.0(2)	774.4(4)
β (°)	106.478(6)	117.29(3)
V (nm^3)	2.4043(4)	0.9618(9)
Z	8	4
D_x ($Mg\ m^{-3}$)	1.421	1.514
$F(000)$	1088	464
μ (mm^{-1})	0.40	0.49
$2\Theta_{max}$ (°)	55	50
No. of reflections:		
measured	5552	1842
independent	5511	1667
R_{int}	0.007	0.03
$wR(F^2$, all refl.)	0.0913	0.1132
$R(F, F > 4\sigma(F))$	0.0323	0.047
No. of parameters	280	113
S	1.00	0.92
Max. Δ/σ	0.001	<0.001
Max. $\Delta\rho$ ($e\ nm^{-3}$)	519	400

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TABLE VI Atom coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for compound **10**

	x	*y*	*z*	*U(eq)*
P(1)	9303.4(3)	10367.5(4)	3818.4(2)	20.0(1)
S(1)	6707.3(3)	9512.0(3)	2067.7(2)	18.9(1)
O(1)	10024.4(10)	9298.8(10)	4048.5(7)	29.1(3)
O(2)	6239.0(9)	8371.7(10)	2139.2(7)	27.8(3)
O(3)	6317.5(9)	10530.6(10)	2395.4(7)	26.7(3)
O(4)	8061.1(9)	10658.8(10)	883.5(7)	27.0(3)
O(5)	6571.2(10)	11828.2(10)	780.2(8)	33.9(3)
N(1)	8043.4(10)	9421.5(11)	2471.0(7)	20.1(3)
C(1)	8128.0(14)	10387(2)	4206.2(10)	33.0(4)
C(2)	10026.4(14)	11731.6(15)	4110.8(10)	31.0(4)
C(3)	8700.0(12)	10495.2(13)	2761.4(8)	19.9(3)
C(4)	8658.2(13)	8444.3(15)	2242.4(10)	29.2(4)
C(5)	6454.1(12)	9749.6(13)	1042.7(8)	21.1(3)
C(6)	7005.0(13)	10869.4(14)	874.8(9)	23.2(3)
C(7)	8679(2)	11675(2)	735.9(14)	45.2(5)
P(1′)	6726.4(3)	5920.3(4)	3918.3(2)	24.6(1)
S(1′)	8050.0(3)	4508.4(3)	2345.0(2)	21.4(1)
O(1′)	6283.4(10)	4935.4(12)	4298.6(7)	31.7(3)
O(2′)	8683.3(9)	5576.2(10)	2555.2(7)	28.3(3)
O(3′)	8594.0(10)	3383.5(10)	2514.5(7)	32.2(3)
O(4′)	5686.9(9)	5403.4(11)	1005.2(7)	31.4(3)
O(5′)	7078.0(10)	6502.5(12)	808.9(8)	36.8(3)
N(1′)	7062.7(11)	4535.9(11)	2768.3(8)	23.3(3)
C(1′)	6052(2)	7311(2)	3946.7(11)	36.6(4)
C(2′)	8195.1(15)	6166(2)	4331.8(11)	41.3(5)
C(3′)	6548.7(13)	5668.9(14)	2879.7(9)	22.7(3)
C(4′)	6352(2)	3484(2)	2712.0(13)	39.9(5)
C(5′)	7452.3(14)	4519.0(14)	1307.6(10)	26.9(3)
C(6′)	6742.0(14)	5593.4(15)	1011.7(9)	25.2(3)
C(7′)	4917.6(15)	6380(2)	739.1(12)	41.3(5)

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TABLE VII Atom coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$for compound **14**

	x	*y*	*z*	*U(eq)*
P	4688.6(14)	1344.8(6)	1221.3(14)	16.4(3)
N	2390(4)	926(2)	2944(4)	17.2(7)
O(1)	3120(4)	1235(2)	−812(4)	24.3(7)
C(1)	6278(6)	575(2)	2141(6)	22.3(9)
C(2)	6169(6)	2132(2)	1499(6)	25.7(10)
C(3)	3671(5)	1527(2)	2873(5)	18.7(9)
C(4)	1751(6)	1053(2)	4457(6)	26.1(10)
S	8196.6(14)	1044.3(5)	7701.4(14)	18.4(3)
O(2)	9824(4)	614(2)	7489(5)	37.1(8)
O(3)	7885(5)	1719(2)	6648(5)	45.1(9)
O(4)	8863(4)	1148(2)	9749(4)	42.1(9)
O(5)	6527(4)	554.2(14)	6804(4)	27.0(7)

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