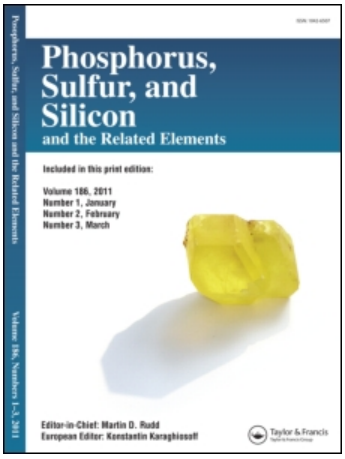

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CATALYZED AMINATION OF DITHIOACID SODIUM SALTS: A ONE POT SYNTHESIS OF α-PHOSPHONOTHIOAMIDES

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An efficient synthesis of α-phosphonothioamides is described, involving thioacylation of primary or secondary amines with α-phosphonodithioacid salts (prepared *in situ*), in the presence of boron trichloride. This method can also be used for the preparation of non-phosphorylated thioamides. In the same conditions and with thiophenol, a dithioacid sodium salt is converted into the S-aryldithioester, while an α-phosphorylated dithioacid sodium salt is reduced into the *bis* (phosphonomethyl) disulfide.

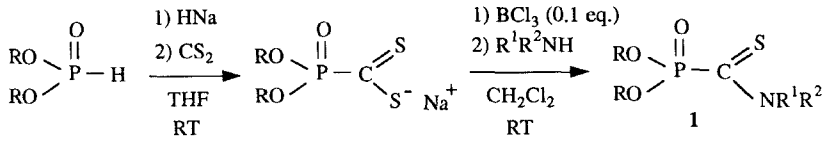
Key words: Thioacylation; α-phosphonothioamides; thioamides; boron trichloride.

There has recently been an increasing interest in the synthesis of α-phosphonothioamides, as precursors of α-substituted methylphosphonate derivatives showing various biological effects (histaminic antagonists, antiinflammation or antihypertension agents, pesticides, antiviral agents).[1] Some α-phosphonothioamides have been obtained: by addition of the dialkylphosphites to isothiocyanates,[1] or by an Arbuzov reaction with triethylphosphite and *N*,*N*-diethyl thiocarbamoyl chloride.[2]

Amination of dithioacids and their salts, and of dithioesters, has been extensively used for a direct preparation of thioamides.[3,4] Recently, two kinds of general thioacylating reagents have been developed: Kato *et al.* prepared and isolated 1-methyl-2-thioacylthiopyridinium salts of aromatic dithioacids[5]; and we previously reported thioacylations *via* *S*-boron dithioesters, which were prepared *in situ* from dithioacids (aliphatic or aromatic) and catecholborane[6] or 9-BBN[7]; they led to the synthesis of thioamides and *S*-aryl dithioesters.

We noticed that the amination of α-phosphonodithioesters suffered limitation due to thiophilic addition of the eliminated thiol on the thiocarbonyl group of the starting dithioester.[8] With α-phosphonodithioacids being unstable and non-isolable,[9] it was of interest to thioacylate their sodium salts, intermediates formed in the synthesis of the α-phosphonodithioesters,[9] by reaction of sodium phosphite with carbon disulfide; thus we did obtain a phosphonothioamide (**1a**), with 20% isolated yield only.

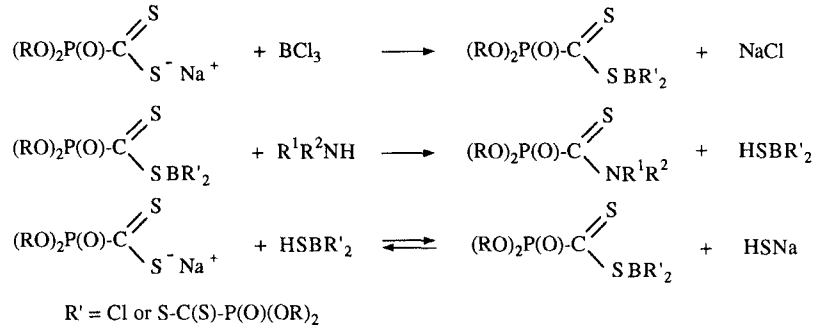
In the course of our investigations concerning thioacylations *via* *S*-boron dithioesters,[6,7] we found that a catalytic amount of boron trichloride (0.1 equivalent) allowed a successful amination of dithioacid sodium salts; thus an efficient synthesis of the α-phosphonothioamides (**1**) was performed, in a one-pot procedure, from the corresponding dithioacid sodium salts prepared *in situ*, and using mild conditions: room temperature, aprotic and inert solvent (methylene chloride) for the amination step (Scheme 1 and Table I). This catalysis may be explained by the following sequence described in Scheme 2, in which a sulfur-substituted boron species such as $HSBR'_2$ would be the effective catalyst. Surprisingly, we observed



SCHEME 1

TABLE I
Preparation of phosphonothioamides (**1**)

Compound	R	R^1	R^2	Yield %
1a	$(CH_3)_2CH$	CH_3	CH_3	83
1b	$(CH_3)_2CH$	H	CH_3	57
1c	$(CH_3)_2CH$	H	$(CH_3)_2CH$	57
1d	$(CH_3)_2CH$	H	cyclohexyl	60
1e	$(CH_3)_2CH$		$(CH_2)_4$	80
1f	C_2H_5	CH_3	CH_3	62



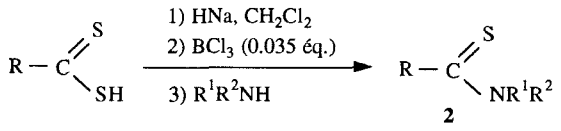
R' = Cl or S-C(S)-P(O)$(OR)_2$

SCHEME 2

a decrease of the isolated yield when a larger quantity of boron trichloride was used (44% to 54% of (**1a**) with 0.33 equivalent).

Non-phosphorylated dithioacids gave the same results (Scheme 3 and Table II): as an example, *N,N*-dimethyl-2-methylpropanethioamide (**2a**) was obtained in very good yield (84 to 92%) from dimethylamine and sodium salt of 2-methylpropanedithioic acid, in the presence of 0.035 equivalent of boron trichloride; without this catalyst, yields of isolated (**2a**) were only 60% from the dithioacid sodium salt, and 34% from the dithioacid itself.

We noticed that thiophenol could be thioacylated with non-phosphorylated dithioacid salt (*R* = *iso*-propyl as an example), leading to the corresponding *S*-phenyl dithioester (**3**) in a moderate yield (Scheme 4). However, α-phosphonodithioacid salt (tested with *R* = *iso*-propyl) could not thioacylate thiols; instead, the *bis*(dialkylphosphonyl)methyl disulfide (**4**) was obtained in fairly good yield, accompanied with the disulfide of the reactant thiol (Scheme 5). This reduction may involve thiophilic additions (as the easy thiophilic addition of soft thiols on thio-



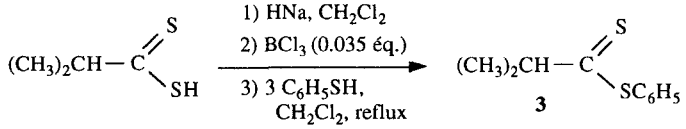
2

SCHEME 3

TABLE II

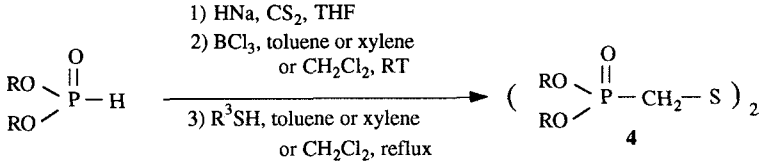
Preparation of thioamides (**2**)

Compound	R	R^1	R^2	Yield %
2a	$(CH_3)_2CH$	CH_3	CH_3	92
2b	$(CH_3)_2CH$	H	H	59
2c	$(CH_3)_2CH$	H	CH_3	85
2d	$(CH_3)_2CH$		$(CH_2)_4$	90



3

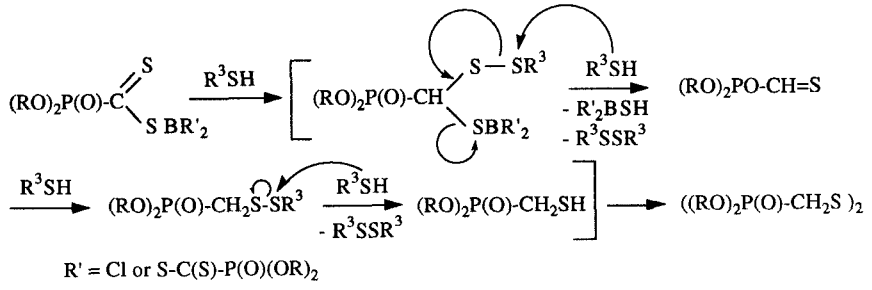
SCHEME 4



4

R = $(CH_3)_2CH$ R^3 = C_6H_5, *m*-CH_3-C_6H_4, CH_3-CH_2-CH_2

SCHEME 5



SCHEME 6

carbonyl functions has already been observed[8,10]), and cleavages of disulfide links (Scheme 6).

We demonstrated that dithioacids salts are convenient to prepare thioamides in

the presence of boron trichloride, at room temperature and in aprotic solvent, especially to synthesize α-phosphonylated thioamides in a one-pot process.

EXPERIMENTAL

The ^1H NMR spectra were recorded with a "Varian EM 360" spectrometer, at 60 MHz using TMS as internal standard; the ^{13}C and ^{31}P NMR spectra were recorded (except other conditions mentioned) with a "Bruker WP 80 SY" spectrometer, at 20.15 MHz for ^{13}C using TMS as internal standard, and at 32.44 MHz for ^{31}P with H_3PO_4 as external standard; chemical shifts are given in δ (ppm). Infra-red spectra were recorded with a "Perkin-Elmer 684" spectrometer (ν of important bands are given in cm^{-1}), and mass spectra were recorded with a "Nermag R 10 10 H" spectrometer in electronic impact at 70 eV (significative m/z and their relative abundance are given).

General procedure for the synthesis of phosphonothioamides (**1**). Under nitrogen a dispersion of HNa (3 mmol) in anhydrous THF (15 ml) was cooled at 0°C; dialkylphosphite (3 mmol) was added, and the reaction mixture was stirred at RT for 3 h. The solution thus obtained was dropped into carbon disulfide (15 mmol) previously cooled at −10°C, and the solution was stirred at RT for 1 h 30. The solvent was then evaporated (under nitrogen, at 12 mmHg and at RT), and CH_2Cl_2 was introduced (30 ml). A solution 1 M in CH_2Cl_2 (Aldrich) of BCl_3 (0.3 mmol) was added directly into the solution at RT, and the mixture stirred at RT for 2 h. Then the solution was saturated with gaseous amine, or liquid amine (9 mmol) was introduced at RT, and the solution was stirred at RT for 20 h. The reaction mixture was poured into water (25 ml) and the aqueous layer was extracted with additional CH_2Cl_2 (3 × 30 ml). Combined organic layers were dried over $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. The crude phosphonothioamide (**1**) was purified by liquid chromatography on silicagel (Merck 60 M, 63 to 200 microns, eluent: petroleum ether/ethyl acetate 60 to 80/20 to 40). Physical aspect, elemental analysis, and spectral data are given for each compound.

Some remarks about spectroscopic studies. For secondary phosphonothioamides (**1b**), (**1c**) and (**1d**), we assumed the *Z* geometry, and the absence of the other isomer: in ^1H NMR of compound (**1b**), the observed doublet of doublet for the N—CH_3 is explained by long range coupling $^4J_{P-C=N-CH}$, as previously demonstrated in similar compounds,[1] and the *Z* isomer of these compounds is known to be more stable.[1] In ^{13}C NMR spectra (with ^1H decoupling) the methyl groups of the dialkylphosphonate appear as four (or sometimes three) close signals; precise chemical shifts of the two doublets has been determined by comparison of the spectra run at 20.15 MHz and 62.896 MHz ("AC Bruker 250 SY" spectrometer) on compound (**1e**); assignments for other compounds have been made by analogy. In Ir spectra we noticed the three characteristic bands of secondary or tertiary thioamides[11]: band "B" at 1440–1520 cm^{-1}, band "C" at 1200–1400 cm^{-1}, band "D" at 1000–1200 cm^{-1}; "no band can rightly be classified as "$\nu_{C=S}$ band", the C—S vibration in thioamide having simple bond character and being probably located in the 600–800 cm^{-1} region"[11]; also were observed the P=O and P—O—R absorptions near 1240 cm^{-1} and 1000 cm^{-1}, respectively.[12] The electron-impact mass spectra showed, besides the molecular ion, the following fragmentations: alkoxy cleavage of the phosphonate group, McLafferty rearrangement (simple and double) with P=O bond of the phosphonate group, cleavage of the P—CS bond, formation of the starting phosphite, in agreement with previously reported results[1]; surprisingly an important peak due to MH^+, and its fragments, were also frequently observed.

Diisopropyl (N,N-dimethylthiocarbamoyl) phosphonate (**1a**). Pale yellow liquid; Analysis: $C_9H_{20}NO_3PS$: calc. %: C 42.67; H 7.95; S 12.65; obs. %: C 42.25; H 8.34; S 12.76. ^1H NMR (CCl_4): 1.33 and 1.40 (2d, J_{HH} = 6.5 Hz, 12H, $P(OCH(C\underline{H}_3)_2)_2$); 3.41 and 3.61 (2d, J_{HP} = 2 Hz, 6H, $N(C\underline{H}_3)_2$); 4.70 (sept d, $J_{HH} = J_{HP}$ = 6.5 Hz, 2H, $P(OC\underline{H}(CH_3)_2)_2$). ^{13}C NMR ($CDCl_3$): 23.73 and 24.07 (2d, J_{CP} = 6.5 Hz and J_{CP} = 3.4 Hz, $P(OCH(\underline{C}H_3)_2)_2$); 44.09 (d, J_{CP} = 4.6 Hz, NCH_3 *syn* to CS); 44.34 (s, NCH_3 *anti* to CS); 193.88 (d, J_{CP} = 188.8 Hz, CS). ^{31}P NMR ($CDCl_3$): −1.52 (s). Ir (NaCl): 2850 to 3020; 1500; 1380; 1240 (strong); 1045; 990 (strong and broad). Mass: m/z: 253 (49.38) $M^{+\cdot}$; 210 (12.84); 169 (11.48) double McLafferty on $M^{+\cdot}$; 168 (10.49); 152 (8.89); 89 (65.56); 88 (100.00) $C_3H_5OP^{+\cdot}$; 73 (14.94); 44 (26.30) $(CH_3)_2N^+$; 43 (25.93).

Diisopropyl (N-methylthiocarbamoyl) phosphonate (**1b**). Pale yellow crystals; m.p. = 41°C; Analysis: $C_8H_{18}NO_3PS$: calc. %: C 40.15; H 7.58; N 5.85; S 13.40; obs. %: C 39.50; H 7.75; N 5.50; S 13.52. ^1H NMR (CCl_4): 1.33 (d, J_{HH} = 6.5 Hz, 12H, $P(OCH(C\underline{H}_3)_2)_2$); 3.16 (d d, J_{HH} = 5 Hz and J_{HP} = 2 Hz, 3H, NCH_3 *syn* to CS); 4.76 (sept d, $J_{HH} = J_{HP}$ = 6.5 Hz, 2H, $P(OC\underline{H}(CH_3)_2)_2$); 10.2 to 10.6 (s, broad, 1H, NH). ^{13}C NMR ($CDCl_3$): 23.68 and 23.90 (2d, J_{CP} = 3.2 Hz and J_{CP} = 2.9 Hz, $P(OCH(\underline{C}H_3)_2)_2$); 32.31 (d, J_{CP} = 9.4 Hz, NCH_3); 74.10 (d, J_{CP} = 6.6 Hz, $P(O\underline{C}H(CH_3)_2)_2$); 194.83 (d, J_{CP} = 181.8,

CS). ^{31}P NMR ($CDCl_3$): −2.91 (s). Ir (KBr): 3200 (broad); 2850 to 3030; 1520; 1345; 1240 (strong); 1010 (strong and broad, shoulder at 1050). Mass: m/z: 239 (32.98) $M^{+\cdot}$; 155 (13.68) $(HO)_2POCSNHCH_3^{+\cdot}$ double McLafferty rearrangement with P=O from $M^{+\cdot}$; 86 (61.40); 84 (100.00) $C_3HOP^{+\cdot}$; 82 (20.88); 75 (24.39); 74 (40.53) CH_3NHCS^+; 51 (30.53); 49 (89.47) PH_2O^+; 48 (24.21); 47 (31.23); 43 (42.11) $(CH_3)_2CH^+$; 42 (28.42); 41 (25.44).

*Diisopropyl (*N-*isopropylthiocarbamoyl) phosphonate* (**1c**). Pale yellow crystals, m.p. = 56–57°C; Analysis: $C_{10}H_{22}NO_3PS$: calc. %: C 44.92; H 8.29; N 5.23; S 11.99; obs. %: C 44.96; H 8.49; N 5.07; S 12.08. ^1H NMR (CCl_4): 1.33 (d, J_{HH} = 6.5 Hz, 18H, $P(OCH(C\underline{H}_3)_2)_2$ and $NHCH(C\underline{H}_3)_2$); 4.65 (sept d, $J_{HH} = J_{HP}$ = 6.5 Hz, 3H, $P(OC\underline{H}(CH_3)_2)_2$ and $NHC\underline{H}(CH_3)_2$); 9.5 to 10.6 (s, broad, 1H, NH). ^{13}C NMR ($CDCl_3$): 21.57 (s, $NHCH(\underline{C}H_3)_2$); 24.33 and 24.55 (2d, J_{CP} = 3.6 Hz and J_{CP} = 3.2 Hz, $P(OCH(\underline{C}H_3)_2)_2$); 47.40 (d, J_{CP} = 7.7 Hz, $N\underline{C}H(CH_3)_2$); 74.82 (d, J_{CP} = 7.0 Hz, $P(O\underline{C}H(CH_3)_2)_2$); 194.15 (d, J_{CP} = 180.7 Hz, CS). ^{31}P NMR ($CDCl_3$): −2.94 (s). Ir (KBr): 3180 (strong and broad); 2850 to 3020; 1520 (strong); 1240 (strong); 1040; 1000 (strong and broad). Mass: m/z = 268 (50.08) MH^+; 267 (100.00) $M^{+\cdot}$; 226 (20.18) McLafferty with P=O from MH^+; 225 (14.81) McLafferty with P=O from $M^{+\cdot}$; 183 (61.52) double McLafferty from MH^+; 182 (48.01) double McLafferty from $M^{+\cdot}$; 150 (36.89); 149 (23.83); 100 (59.45); 58 (89.04); 43 (55.17).

*Diisopropyl (*N-*cyclohexylthiocarbamoyl) phosphonate* (**1d**). Pale yellow crystals, m.p. = 82–83°C; Analysis: $C_{13}H_{26}NO_3PS$: calc. %: C 50.79; H 8.52; N 4.55; S 10.43; obs. %: C 50.34; H 8.56; N 4.61; S 10.26. ^1H NMR (CCl_4): 1.32 (d, J_{HH} = 6.5 Hz, 12H, $P(OCH(C\underline{H}_3)_2)_2$); 1.0 to 2.2 (m, 10H, $(CH_2)_5$ of the cycle); 4.0 to 5.0 (m, 3H, NCH of the cycle and $P(OC\underline{H}(CH_3)_2)_2$); 9.3 to 10.0 (s, broad, 1H, NH). ^{13}C NMR ($CDCl_3$): 23.67 and 23.87 (2d, J_{CP} = 4.2 Hz and J_{CP} = 3.8 Hz, $P(OCH(\underline{C}H_3)_2)_2$); 24.56 (s, C^3 and C^5 of the cycle); 25.43 (s, C^4 of the cycle); 31.02 (s, C^2 and C^6 of the cycle); 53.54 (d, J_{CP} = 7.5 Hz, NCH); 74,09 (d, J_{CP} = 6.8 Hz, $P(O\underline{C}H(CH_3)_2)_2$); 193.24 (d, J_{CP} = 181.3 Hz, CS). ^{31}P NMR ($CDCl_3$): −2.88 (s). Ir (KBr): 3170 (strong and broad); 2850 to 3040; 1515 (strong); 1370; 1230 (strong); 1045 and 990 (strong and broad). Mass: m/z: 308 (17.25) MH^+; 307 (75.63) $M^{+\cdot}$; 264 (25.71); 223 (42.35) double McLafferty with P=O of $M^{+\cdot}$; 222 (100.00) McLafferty with P=O of ion at m/z = 164; 190 (21.55); 142 (54.88); 98 (90.77) C_6H_{11}-NH^+; 83 (75.56) $C_6H_{11}^+$; 55 (43.40); 43 (34.28).

*Diisopropyl (*N,N-*tetramethylenethiocarbamoyl) phosphonate* (**1e**). Pale yellow liquid; Analysis: $C_{11}H_{22}NO_3PS$: calc. %: S 11.47; obs. %: S 11.59. ^1H NMR (CCl_4): 1.31 and 1.36 (2d, J_{HH} = 6.5 Hz, 12H, $P(OCH(C\underline{H}_3)_2)_2$); 1.8 to 2.2 (m, 4H, CH_2 on C^2 and C^3 of the cycle); 3.5 to 4.2 (m, 4H, CH_2 on C^1 and C^4 of the cycle); 4.65 (sept d, $J_{HH} = J_{HP}$ = 6.5 Hz, $P(OC\underline{H}(CH_3)_2)_2$). ^{13}C NMR ($CDCl_3$, TMS, DEPT, recorded with a "AC Bruker 250 SY" spectrometer at 62,896 MHz): 23.24 (s, C^2 of the cycle, *syn* to CS); 23.53 and 23.87 (2d, J_{CP} = 6.1 Hz and J_{CP} = 3.5 Hz, $P(OCH(\underline{C}H_3)_2)_2$); 26.40 (s, C^3 of the cycle, *anti* to CS); 53.04 (d, J_{CP} = 1.5 Hz, C^1 of the cycle, *syn* to CS); 54.24 (d, J_{CP} = 6.7 Hz, C^4 *anti* to CS); 73.07 (d, J_{CP} = 7.5 Hz, $P(O\underline{C}H(CH_3)_2)_2$); 189.37 (d, J_{CP} = 189.1 Hz, CS). ^{31}P NMR ($CDCl_3$): −2,14 (s). Ir (NaCl): 2870 to 2900; 1440 (strong and broad, shoulder at 1465); 1240 (strong); 1050; 1000 (strong and broad). Mass: m/z: 279 (30.85) $M^{+\cdot}$; 195 (26.42) double McLafferty with P=O of $M^{+\cdot}$; 194 (24.84); 115 (23.23); 114 (25.00); 70 (100.00) $C_4H_8N^+$.

*Diethyl (*N,N-*dimethylthiocarbamoyl) phosphonate* (**1f**). Pale yellow liquid; Analysis: $C_7H_{16}NO_3PS$: calc. %: S 14.23; obs. %: S 14.30. ^1H NMR (CCl_4): 1.38 (t, J_{HH} = 7 Hz, 6H, $(C\underline{H}_3CH_2O)_2P$); 3.41 and 3.65 (2d, J_{HP} = 2 Hz, 6H, $N(CH_3)_2$); 4.18 (qd d, $J_{HH} = J_{HP}$ = 7 Hz, 4H, $(CH_3C\underline{H}_2O)_2P$). ^{13}C NMR ($CDCl_3$): 16.15 and 16.30 (2d, J_{CP} = 3.9 Hz and J_{CP} = 2.1 Hz, $(\underline{C}H_3CH_2O)_2P$); 43.81 and 44.13 (2d, J_{CP} = 7.0 Hz and J_{CP} = 3.8 Hz, $N(CH_3)_2$ *syn* and *anti* to CS); 64.14 and 64.23 (2d, J_{CP} = 5.4 Hz and J_{CP} = 2.0 Hz, $(CH_3\underline{C}H_2O)_2P$); 192.40 (d, J_{CP} = 187.6, CS). ^{31}P NMR ($CDCl_3$): −0,66 (s). Ir (NaCl): 2850 to 3020; 1505; 1380; 1240 (strong); 1060; 1020 (strong and broad). Mass: m/z: 226 (20.73) MH^+; 225 (46.47) $M^{+\cdot}$; 192 (17.26); 89 (25.95); 88 (100.00) $C_3H_5OP^{+\cdot}$; 84 (36.00); 73 (22.90); 49 (99.66) H_2OP^+; 48 (22.06); 47 (40.91); 45 (20.09).

Preparation of thioamides (**2**). The dithioacid (2 mmol) was added to a suspension of HNa (2 mmol) in anhydrous CH_2Cl_2 (15 ml) and under nitrogen (dithioacids were prepared by condensation of CS_2 on a Grignard reagent, and hydrolysis[13,14]). Then 0.070 mmol of BCl_3 was added, and the procedure was continued as described for the synthesis of phosphonothioamides (**1**), with 15 h reaction time after the addition of the amine. Physical aspect, and analytical and spectroscopic data for thioamides (**2**) have already been reported.[6,7]

Preparation of S-*phenyl 2-methylpropanedithioate* (**3**). The sodium salt of 2-methylpropanedithioic acid was prepared from the dithioacid (2 mmol) and HNa (2 mmol) in CH_2Cl_2. A solution (CH_2Cl_2) of BCl_3 (0.070 mmol) was added, and the mixture was stirred at RT during 2 h; then thiophenol (6 mmol) was added, and the reaction mixture was refluxed during 24 h. After cooling, the mixture was

decanted; the aqueous layer was extracted twice with CH_2Cl_2, and the combined organic layers were washed with NaOH 1N, then with water, dried over $MgSO_4$, filtered, and the solvent was removed. The crude dithioester was purified by liquid column chromatography on silicagel Merck 60, 63 to 200 microns, eluent: pentane). Yield = 30%. This dithioester (**3**) has already been described.[6]

Preparation of bis (diisopropylphosphonyl) methyl disulfide (**4**). The sodium salt of (diisopropylphosphono) dithiocarboxylic acid (3 mmol) was prepared as described for the synthesis of compounds (**1**), from diisopropylphosphite, HNa, and CS_2. Then THF was replaced by either CH_2Cl_2, or toluene, or xylene; a solution of BCl_3 (0.3 mmol) was added and the mixture was stirred during 2 h at RT. The thiol (9 mmol) was added (thiophenol, or 3-methylthiophenol, or propanethiol). The reaction mixture was refluxed during 24 h; after cooling the mixture was poured into water, the aqueous layer was extracted with CH_2Cl_2; the combined organic layers were washed with water, dried over $MgSO_4$, and the solvent was evaporated. Crude material was purified by column liquid chromatography on silicagel Merck 60, 63 to 200 microns, eluent: petroleum ether/ethyl acetate 80/20. Compound (**4**) was obtained as a colorless liquid, with a yield of 45 to 50%. Analysis: $C_{14}H_{32}O_6P_2S_2$: calc. %: S 15.17; obs. %: S 15.49. ^{1}H NMR (CCl_4): 1.30 (d, J_{HH} = 6.5 Hz, 24H, $((C\underline{H}_3)_2CHO)_2P$, twice); 3.13 (d, J_{HP} = 14 Hz, 4H, $(CH_2S)_2$); 4.60 (sept d, J_{HH} = J_{HP} = 6.5 Hz, 4H, $((CH_3)_2C\underline{H}O)_2P$, twice). ^{13}C NMR ($CDCl_3$): 24.07 (d, J_{CP} = 4.1 Hz, $((\underline{C}H_3)_2CHO)_2P$, twice); 35.60 (d d, $^1J_{CP}$ = 145.2 Hz and $^4J_{CP}$ = 2.2 Hz, $(PCH_2S)_2$; 71.43 (d, J_{CP} = 6.75 Hz, $((CH_3)_2\underline{C}HO)_2P$, twice). ^{31}P NMR: +20.15 (s). Mass: m/z: 423 (27.34) MH^+; 422 (28.24) $M^{+\cdot}$; 339 (13.83); 279 (14.90); 237 (20.03); 212 (39.59); 211 (19.23); 210 (23.29); 191 (33.74); 170 (24.13); 139 (22.94); 128 (36.38); 97 (12.97). The disulfide $(R^3S)_2$ (R^3 = phenyl, or 3-methylphenyl, or propyl) was also isolated.

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