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Reductions of Phosphonodithioformates : Syntheses of α-Phosphonyl Thiols and Hemidithioacetals.

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Abstract : The phosphonodithioformates appeared versatile precursors to the (mercaptomethyl)phosphonates and derivatives, through sodium borohydride reduction in acetonitrile heated under reflux. By contrast, when the reduction was performed at room temperature with sodium borohydride, the (mercapto-alkylthio-methyl)phosphonates were exclusively obtained ; reduction with BH_3-Me_2S (BMS) or with lithium diisopropylaminoborohydride also led to these hemidithioacetals. The aforementioned products of reduction were characterized by the syntheses of various derivatives. In particular, S-phosphonyl trithiocarbonates, N-phenyl imidodithiocarbonate and dithiocarbamate were prepared.

Key-words : Phosphonodithioformates ; (mercaptomethyl)phosphonates ; (mercapto-alkylthio-methyl)phosphonates; S-phosphonyl trithiocarbonates ; S-phosphonyl N-phenyl imidodithiocarbonates ; S-phosphonyl dithiocarbamates ; reduction ; sodium borohydride ; lithium diisopropylaminoborohydride ; borane-dimethylsulfide complex.

Phosphonate esters have recently received increased interest as analogues of biological phosphates [1] and their syntheses are reviewed.[2] In particular, phosphonates $(RO)_2P(O)R'$ which contain a functionality (oxygen or nitrogen group) in the R' chain offer wide applications in biochemistry and medicine,[3-5] as potential antiviral and antibacterial agents, or antihistaminics and pesticides. Some α-functionalized methylphosphonates including a sulfur group are synthesized [3,6,7,8] and used for further transformations,[6] but their biological activity has been tested only occasionaly.[8] We investigated and report here the reduction of phosphonodithioformates, which appear to give new and easy access to the (mercaptomethyl)phosphonates, and we also describe a synthesis of the corresponding (mercapto-alkylthio-methyl)phosphonates. These compounds could be versatile precursors to different α-substituted methylphosphonate derivatives, potential complexing agents or enzyme inhibitors, of biological interest.

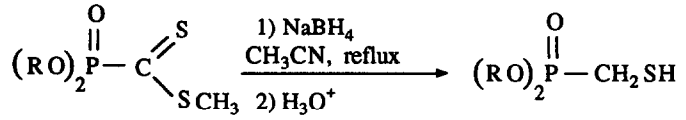
Some α-(mercaptomethyl)phosphonates are known. Diethyl (mercaptomethyl)phosphonate is obtained by reaction of elemental sulfur with lithium diethyl methylphosphonate carbanion.[9] An alternative approach to diethyl (mercaptomethyl)phosphonate is the alkylation of the tetramethylammonium salt of thiolacetic acid with (iodomethyl)phosphonate, the resulting thiolacetate being subjected to alkaline hydrolysis.[9] More recently, a new synthetic route to diethyl (mercaptomethyl)phosphonate was developed.[10] This multistep method involves the preparation (and further hydrolysis) of the acetylated thiol, by condensation of triethylphosphite and S-bromomethyl thiolacetate, the latter being obtained from paraformaldehyde and thiolacetic acid, and subsequent treatment with phosphorus tribromide. Also some α-phosphonyl secondary thiols [9] and α-phosphonyl tertiary thiols [11-14] are described. Besides this, one α-phosphonyl hemidithioacetal has been

prepared [9] by condensation of elemental sulfur on metallated diethyl (methylthiomethyl)phosphonate, followed by acid hydrolysis, half of the starting material being recovered.

The preparation of a thiol by the reduction with sodium borohydride of an aromatic dithioester has been mentioned in the literature, although the thiol was isolated in low yield (~ 16 %),[15] while a hemidithioacetal has been prepared (~ 40 % after distillation) with the same reductive reagent and an aliphatic dithioester.[16] Besides this, a convenient conversion of the unphosphorylated dithioesters into the corresponding thiols, through reduction with borane-dimethylsulfide complex (BMS), has been described by our group.[17] In a preliminary note [18] we reported that the easily accessible phosphonodithioformates [19] were suitable precursors of α-phosphonyl thiols *via* the selective reduction of the dithioesters. To complete this result, we have shown that it is possible to stop this reduction at the hemidithioacetal step. We have also compared the reductions of the phosphonodithioformates by three different reagents : sodium borohydride, BMS and lithium diisopropylaminoborohydride. In addition, some new functionalized phosphonates were prepared from the obtained reduction products : α-phosphonyl thiols or hemidithioacetals.

Synthesis and characterization of the (mercaptomethyl)phosphonates.

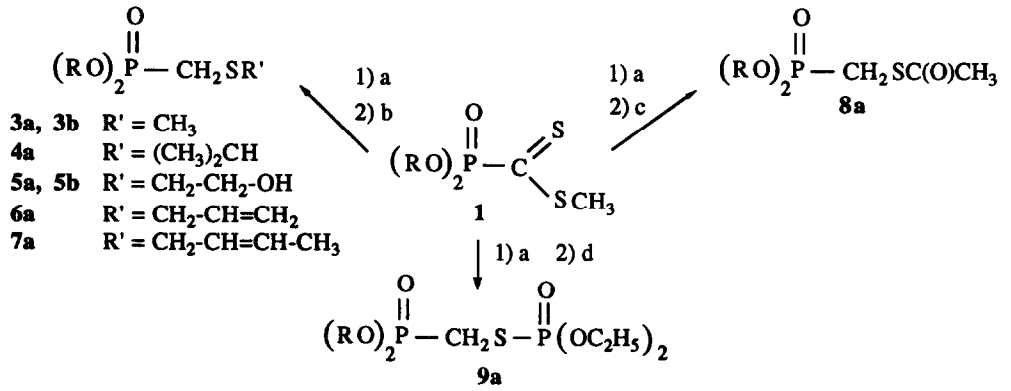
Phosphonodithioformate **1a** or **1b** was prepared according to the known procedure.[19] (Mercaptomethyl)phosphonate **2a** or **2b** was obtained by treatment of dithioformate **1a** or **1b** with an excess of sodium borohydride, in acetonitrile heated under reflux, followed by acidic hydrolysis (Scheme 1). Crude diisopropyl (mercaptomethyl)phosphonate **2a** was obtained in a nearly quantitative yield with a purity up to 95 %. Surprisingly, diethyl (mercaptomethyl)phosphonate **2b** needed purification by basic extraction, and was isolated in only 61 % yield. Greater reactivity, already observed,[20] of the phosphonyl substituted by ethoxy groups, could explain a lesser selectivity of the reduction. These thiols **2** were partly oxidized by column chromatography on silica gel.



1a R = $(CH_3)_2CH$ **2a** R = $(CH_3)_2CH$
1b R = C_2H_5 **2b** R = C_2H_5

Scheme 1

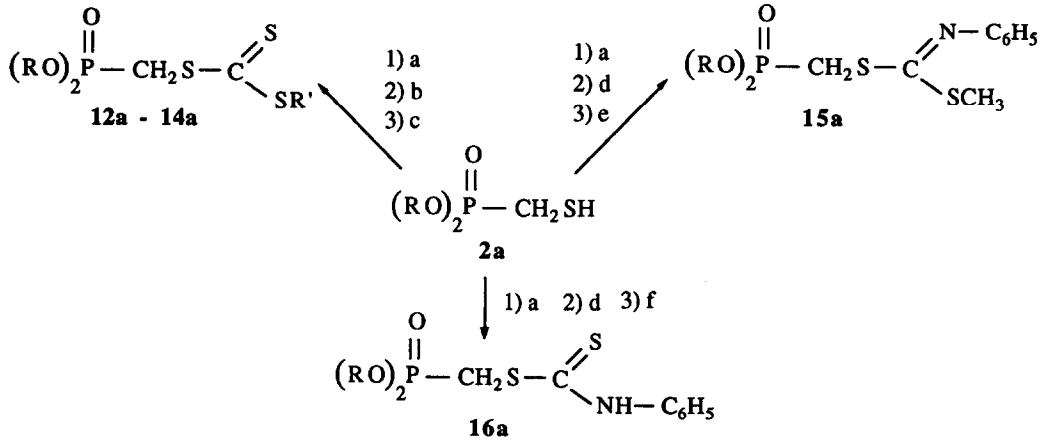
(Mercaptomethyl)phosphonate **2a** (or **2b**) has been characterized more completely by alkylations, allylations,[21] acylation and phosphonylation, leading to the derivatives **3** to **9** (Scheme 2). Reaction of thiol **2a** with diiodomethane led us to compound **10a** $[(CH_3)_2CHO)_2P(O)CH_2S]_2CH_2$, and we achieved the conversion of sulfide **4a** into the corresponding sulfoxide **11a** with sodium periodate in acetone.[22] Although Mikolajczyk *et al.* reported that the best yield and purity are obtained when the thiol is isolated and then alkylated under phase-transfer catalytic conditions,[9] with all tested electrophilic reagents we obtained here satisfactory results by treatment *in situ* of the thiolates resulting from the reduction.



R = $(CH_3)_2CH$ or R = C_2H_5 a : $NaBH_4$, CH_3CN, reflux ; b : R'X : CH_3I or $(CH_3)_2CHBr$ or $HO\text{-}CH_2\text{-}CH_2Br$ or $CH_2{=}CH\text{-}CH_2Br$ or $CH_3\text{-}CH{=}CH\text{-}CH_2Br$; c : $CH_3C(O)Cl$; d : $(C_2H_5)_2P(O)Cl$

Scheme 2

The dialkyl (mercaptomethyl)phosphonates appeared useful in the synthesis of the unknown trithiocarbonates or N-phenyl dithiocarbamates or N-phenyl imidodithiocarbonates, all of them substituted by α-phosphinylmethyl group. Thus, we found that deprotonation of compound **2a** with sodium hydride in THF, condensation of the thiolate with carbon disulfide, and methylation or allylation, actually produced compounds **12a-14a**. Similarly, condensation of the thiolate with phenyl isothiocyanate and further alkylation or hydrolysis afforded N-phenyl imidodithiocarbonate **15a** or dithiocarbamate **16a** respectively (Scheme 3).



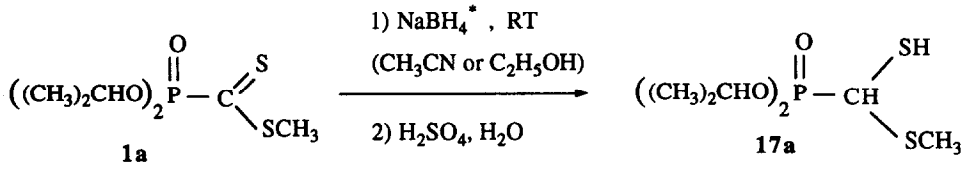
R = $(CH_3)_2CH$ a : HNa, THF ; b : CS_2 ; c : R'X : CH_3I or $Br\text{-}CH_2\text{-}CH{=}CH_2$ or $Br\text{-}CH_2\text{-}CH{=}CH\text{-}CH_3$ d : $C_6H_5\text{-}N{=}C{=}S$; e : CH_3I (HMPA) ; f : H_3O^+

Scheme 3

Synthesis and characterization of the α-phosphonyl hemidithioacetals [(mercapto-alkylthio-methyl)phosphonates].

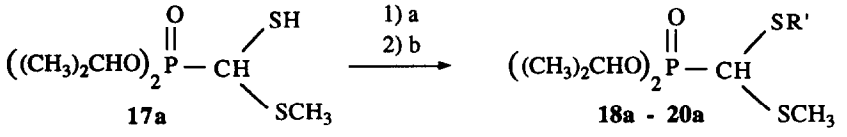
In our group,[7] some phosphonyl hemidithioacetals have already been obtained as by-products in the synthesis of the phosphonyl dithioacetals disulfides $(RO)_2P(O)CH(SR)(SSR')$, through treatment of the phosphonodithioformates with various mercaptans, in the presence of triethylamine and when the reaction was performed at room temperature ; we suggested that cleavage of the S-S bond of the dithioacetal disulfide led to the thiolate anion, precursor of the dithioacetal. Besides this, some of their alkyl derivatives, *i.e.* the phosphonyl dithioacetals, have been prepared ; their first general synthesis was achieved by reaction of trialkylphosphites with the chloro-dialkylthio-methanes, or the chloro-*bis*-phenylthio analogues,[23] and also with N,N,N-trimethylformamidinium ethylenedithioacetal for the synthesis of cyclic dithioacetals.[23] More recently, some phosphonyl dithioacetals have been prepared conveniently in our group [24,25] by thiophilic addition of organolithium (one equivalent) or Grignard reagents (in large excess) to phosphonodithioesters.

We previously noticed that the conversion of the phosphonodithioformates **1** into the phosphonyl thiols **2** with sodium borohydride required heating. However, when these reductions were effected at room temperature, in various solvents, and even with an excess of reductive agent, we conveniently obtained the phosphonyl hemidithioacetals. Thus, S-methyl (diisopropoxyphosphinyl)methanedithioate **1a** was reduced with sodium borohydride, in acetonitrile or in ethanol at room temperature, into diisopropyl (mercapto-methylthio-methyl)phosphonate **17a** with a 90 to 95 % yield (Scheme 4). A recently discovered reagent, lithium diisopropylaminoborohydride, [26] also reduced phosphonodithioformate **1a** into hemidithioacetal **17a**, in THF or in methylene chloride, at room temperature as well as heated under reflux (Scheme 4). This hemidithioacetal could not be easily purified (considerable loss of material occurred through distillation or column chromatography on silica gel). Crude product **17a** was analyzed by spectroscopic methods and fully characterized through preparation of some derivatives : compounds **18a** to **20a** obtained by alkylation, allylation or acylation (Scheme 5).



* or $Li^+ (CH_3)_2CHNBH_3^-$ (THF) RT 2) HCl, H_2O

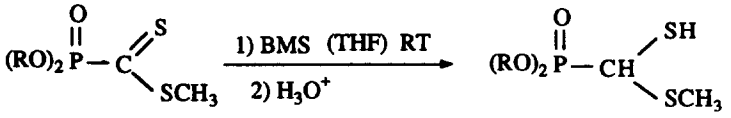
Scheme 4



a : ^nBuLi, THF, O°C ; b : R'X : CH_3I or Br-CH_2-CH=CH_2 or $CH_3C(O)Cl$

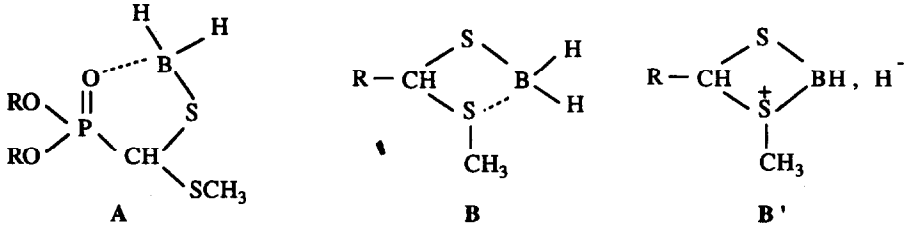
Scheme 5

It is worth comparing these reductions with those obtained with the Lewis-acidic boranes. We have previously reported a convenient conversion of the dithioester function into the thiol function [17] by means of borane-dimethylsulfide complex (BMS) in toluene heated under reflux ; at room temperature, this reaction is very much slower (two days were required instead of four hours), but the reduction process cannot be stopped at the stage of the hemidithioacetal.[17] In the phosphorylated series, we found that phosphonodithioformates **1a** and **1b**, with BMS at room temperature in THF, led conveniently and with a nearly quantitative yield (90 %) to hemidithioacetals **17a** and **17b** (Scheme 6). Excess BMS and heating (in refluxed THF or toluene) did not allow the formation of the thiols, the hemidithioacetals still being isolated. In order to explain this different reactivity, we suggest an intermediate **A** in which the electron deficient boron atom may coordinate to the P=O group ; this stabilization can prevent further elimination of CH_3SBH_2 leading possibly to the thioaldehyde $(RO)_2P(O)CH{=}S$, which is then reduced into the thiol. From the unphosphorylated dithioester, we previously considered [17] an intermediate **B** or **B'** involving coordination of the boron atom with the sulfur atom of the alkylthio group (Scheme 7).



1a R = $(CH_3)_2CH$ **17a** R = $(CH_3)_2CH$
1b R = C_2H_5 **17b** R = C_2H_5

Scheme 6



A **B** **B'**

Scheme 7

The described methods of reduction of dialkyl phosphonyl dithioformates offer convenient alternative routes for the syntheses of α-phosphonyl derivatives like thiols, sulfides, hemidithioacetals and acetals, trithiocarbonates, dithiocarbamates and N-aryl imidodithiocarbonates, compounds of currently potential interest.

EXPERIMENTAL

General methods.

The ^1H NMR spectra were recorded with a "Varian EM 360" spectrometer at 60 MHz in CCl_4, or a "Bruker AC 250" spectrometer at 250.13 MHz in $CDCl_3$, using TMS as internal standard. The ^{13}C NMR

spectra were recorded with a "Bruker WP 80 SY" spectrometer at 20.15 MHz or a "Bruker AC 250" spectrometer at 62.89 MHz, in $CDCl_3$, with TMS as internal standard (proton decoupled, J_{CP} given). The ^{31}P NMR spectra were recorded with a "Bruker WP 80 SY" spectrometer at 32.44 MHz with H_3PO_4 as external standard. Chemical shifts are given in δ (ppm), and coupling constants in cps. The infra-red spectra were recorded with a "Perkin-Elmer 684" or a "Perkin-Elmer 16 PC" spectrometer (significant ν are given in cm^{-1}). Mass spectra were recorded with a "Nermag R 10 10 H" spectrometer in electronic impact at 70 ev (the molecular ion and the most abundant ion are reported).

Synthesis of the (mercaptomethyl)phosphonate 2a.

Dithioester **1a** (2 mmol), prepared according to the known procedure,[19] was dissolved in acetonitrile (20ml) under N_2 ; a solution (2ml) of $NaBH_4$ (4 to 8 mmol) in NaOH 1N and CH_3OH was added dropwise, and the mixture was stirred and heated under reflux for 2 to 4 hours. After cooling, HCl 2N (15 ml) was added under N_2. The solution was stirred at room temperature during 15 mn. Then it was extracted with CH_2Cl_2 (3 x 15 ml) ; the organic layer was washed with water (3 x 10 ml), dried over Na_2SO_4, and the solvent was removed under reduced pressure. Crude thiol **2a** was obtained as an oil and used without further purification (an analytical sample was obtained by purification through basic extraction).

Diisopropyl (mercaptomethyl)phosphonate 2a : Pale yellow oil.[18] Yield = 90 %, purity > 95 %. Analysis : $C_7H_{17}O_3PS$: calc. % : S 15.10 ; obs. % : S 15.50. ^1H NMR, ^{13}C NMR and ^{31}P NMR described.[18] Mass : 212 (7.28) $M^{+\cdot}$; 128 (100.00) double Mc Lafferty $(HO)_2P(O)CH_2SH^{+\cdot}$. IR (film NaCl) : ~ 2500 (w) SH ; 1240 (s) ν P=O ; ~ 1000 (vs) ν P-O-C.

Synthesis of the (mercaptomethyl)phosphonate 2b.

Dithioester **1b** (2.1 mmol), prepared according to the described method,[19] was dissolved in acetonitrile (20 ml) under N_2. A solution (3 ml) of $NaBH_4$ (8 mmol) in NaOH 1N and CH_3OH was added dropwise. Immediate decoloration occurred, and the mixture was stirred under reflux for 4 hours. After cooling, NaOH 1N (20 ml) was added, and the mixture was extracted with CH_2Cl_2 (30 ml). Then the aqueous layer was separated and acidified with HCl 5 % (40 ml), and the mixture was stirred at room temperature for 1 hour. This aqueous phase was extracted with CH_2Cl_2 (3 x 20 ml) ; the organic layer was washed with water, dried over Na_2SO_4, and the solvent was removed under reduced pressure. Thiol **2b** was obtained as an oil.

Diethyl (mercaptomethyl)phosphonate 2b : Pale yellow oil.[9] Yield = 61 %. ^1H NMR and ^{31}P NMR described.[9] ^{13}C NMR (62.89 MHz) : 16.51, d, J = 5.4 ; 17.71, d, J = 151.0 ; 63.08, d, J = 6.8. Mass : 184 (28.13) $M^{+\cdot}$; 47 (100.00) CH_2SH^+ . IR (film NaCl) : ~ 2540 (w) ν SH ; 1240 (s) ν P=O ; ~ 1030 (vs and broad) ν P-O-C.

Characterization of (mercaptomethyl)phosphonates 2 : derivatives 3 to 11.

The thiolate of thiol **2** was prepared from the dithioester **1** (2.2 mmol) as described above in acetonitrile. Then the solution was cooled to 0°C and this thiolate was treated *in situ* with *ca* one equivalent (2.2 mmol) of the appropriate reactive (scheme 2), except for the synthesis of compound **10a** (1.1 mmol of CH_2I_2), and the reaction mixture was stirred at room temperature for ~ 20 hours. Usual work-up (extraction with ether (30 ml), washings with water (3 x 20 ml), drying over Na_2SO_4), and purification with column chromatography (silica gel Merck 60 M, eluent : petroleum ether / ethyl acetate) yielded pure compounds **3** to **10**.

Diisopropyl (methylthiomethyl)phosphonate 3a : Colorless liquid. Yield = 71 %. Analysis : $C_8H_{19}O_3PS$: calc. % : C 42.46, H 8.46, O 21.21, P 13.68 ; obs. % : C 42.16, H 8.26, O 21.06, P 13.74. ^1H NMR (250 MHz) : 1.35 and 1.355, 2 d, J_{HH} = 6.2, 12H ; 2.29, ~ s, 3H ; 2.65, d, J_{HP} ~ 12.9, 2H ; 4.77, sept d, J_{HH} = 6.2 and J_{HP} = 7.7, 2H. ^{13}C NMR (20.15 MHz) : 17.41, d, J = 2.9 ; 24.01 and 24.22, 2 d, J = 3.1 and J = 2.0 ; 28.65, d, J = 151.5 ; 71.13, d, J = 7.2. ^{31}P NMR : 22.41, s. Mass : 226 (18.05) $M^{+\cdot}$; 96 (100.00) $(HO)_2P(O)CH_3^{+\cdot}$. IR (film NaCl) : 1245 (vs) ν P=O ; 1100 (s) ; 990 (vs, broad) ν P-O-C.

Diethyl (methylthiomethyl)phosphonate 3b : Colorless liquid.[9] Yield = 68 %. ^1H NMR and ^{31}P NMR described.[9] ^{13}C NMR (20.15 MHz) : 16.46, d, J = 5.9 ; 17.34, d, J = 2.8 ; 27.57, d, J = 150.6 ; 62.65, d, J = 6.7. Mass : 198 (31.03) $M^{+\cdot}$; 152 (100.00) $(C_2H_5O)_2P(O)CH_3^{+\cdot}$. IR (film NaCl) : 1245 (m) ν P=O ; 1020 (s) ν P-O-C.

Diisopropyl (isopropylthiomethyl)phosphonate 4a : Colorless liquid. Yield = 67 %. Analysis : $C_{10}H_{23}O_3PS$: calc. % : C 47.22, S 12.60 ; obs. % : C 47.30, S 12.75. ^1H NMR (250 MHz, $CDCl_3$) : 1.26, d, J_{HH} = 6.7, 6H ; 1.34 and 1.35, 2d, J_{HH} = 6.2, 12H ; 2.72, d, J_{HP} = 14.5, 2H ; 3.17, sept, J_{HH} = 6.7, 1H ; 4.75, sept d, J_{HH} ~ 6.2 and J_{HP} ~ 7.5, 2H. ^{13}C NMR (20.15 MHz) : 22.89, s ; 23.94 and 24.15, 2 d, J = 3.0 and J = 1.4 ; 25.31, d, J = 150.6 ; 36.12, d, J = 4.6 ; 71.03, d, J = 6.8. ^{31}P NMR : 22.52, s. Mass : 254 (100.00) $M^{+\cdot}$. IR (film NaCl) : 1260 (s) ν P=O ; 1175 (m) ; ~ 1000 (vs) ν P-O-C.

Diisopropyl [(isopropylsulfinyl)methyl]phosphonate 11a : Sulfoxide **11a** has been prepared from sulfide **4a** according the known procedure (periodate in acetone) [22]. Pale yellow liquid. Yield = 97 % from **4a**. $C_{10}H_{23}O_4PS$: calc. % : S 11.86 ; obs. % : S 12.00. ^1H NMR (250 MHz, $CDCl_3$) : 1.31, d, J_{HH} = 6.8, 6H ; 1.37, d, J_{HH} = 6.1, 12H ; 3.02, $d_{(AB)}$ d, $J_{(AB)}$ = 14.6 and J_{HP} = 16.8, 1H, P(O)C$\underline{H}_2$S(O) ; 3.08, sept, J_{HH} = 6.8, 1H ; 3.18, $d_{(AB)}$ d, $J_{(AB)}$ = 14.6 and J_{HP} = 29.3, 1H, P(O)C$\underline{H}_2$S(O) ; 4.77, sept d, J_{HH} = 6.1 and J_{HP} = 7.8, 2H. ^{13}C NMR (62.89 MHz) : 12.57, s and 16.8, s, S(O)CH($\underline{C}H_3$)$_2$; 23.96, d, J = 1.8 and 24.06, d, J = 4.0, [($\underline{C}H_3$)$_2$CHO]$_2$P ; 47.00, d, J = 140.9, P(O)$\underline{C}H_2$S ; 50.92, d, J = 5.6, S(O)$\underline{C}$H(CH$_3$)$_2$; 72.01, d, J = 6.4 and 72.07, d, J = 6.7, [(CH$_3$)$_2\underline{C}$HO]$_2$P. ^{31}P NMR : 15.37, s. Mass : 270 (31.74) $M^{+\cdot}$; 143 (100.00) $(HO)_2P(O)CH_2S(O)^+$. IR (film NaCl) : 1250 (s) ν P=O ; 1050 (s) ν SO ; 1000 (vs) ν P-O-C.

Diisopropyl [(2-hydroxyethyl)thiomethyl]phosphonate 5a : Colorless liquid. Yield = 86 %. Analysis : $C_9H_{21}O_4PS$: calc. % : S 12.51 ; obs. % : S 12.60. ^1H NMR (60 MHz) : 1.35, d, J_{HH} = 6.5, 12H ; 2.71, d, J_{HP} = 13.0, 2H ; 2.71, t, J_{HH} ~ 6.0, 2H ; 3.80, t, J_{HH} ~ 6.0, 2H ; ~ 3.8, s, broad, 1H ; 4.73, sept d, J_{HH} ~ J_{HP} ~ 6.5, 2H. ^{13}C NMR (20.15 MHz) : 23.98 and 24.11, 2 d, J = 3.1 and J = 2.1 ; 26.34, d, J = 151.5 ; 36.87, d, J = 2.2 ; 61.50, s ; 71.58, d, J = 6.9. ^{31}P NMR : 23.12, s. Mass : 256 (5.77) $M^{+\cdot}$; 43 (100.00) $(CH_3)_2CH^+$. IR(film NaCl) : 3650 to 3050 (s and broad) ν OH ; 1230 (s) ν P=O ; 1000 (s and broad) ν P-O-C and ν C-O.

Diethyl [(2-hydroxyethyl)thiomethyl]phosphonate 5b : Colorless liquid. Yield = 58 %. Analysis : $C_7H_{17}O_4PS$: calc. % : C 36.83, H 7.50, S 14.04 ; obs. % : C 36.90, H 7.69, S 14.30. ^1H NMR (60 MHz) : 1.33, t, J_{HH} = 6.5, 6H ; 2.67, d, J_{HP} = 13.0, 2H ; 2.72, t, J_{HH} = 6, 2H ; 3.68, t, J_{HH} = 6, 2H ; ~ 3.7, s, 1H ; 4.12, qd d, J_{HH} = J_{HP} = 6.5, 4H. ^{13}C NMR (20.15 MHz) : 16.47, d, J = 5.8 ; 25.33, d, J = 150.9 ; 37.03, s ; 61.46, s ; 63.01, d, J = 6.85. ^{31}P NMR : 25.28, s. Mass : 228 (81.74) $M^{+\cdot}$; 151 (100.00) $(C_2H_5O)_2P(O)CH_2^+$. IR (film NaCl) : 3600 to 3000 (s and broad) ν OH ; 1235 (s and broad) ν P=O ; 1040 (s) ν C-O ; 1020 (s) ν P-O-C.

Diisopropyl (allylthiomethyl)phosphonate 6a : Colorless liquid. Yield = 77 %. Analysis : $C_{10}H_{21}O_3PS$: calc. % : C 47.59, H 8.38 ; obs. % : C 47.08, H 8.49. ^1H NMR (250 MHz) : 1.34, d, J_{HH} = 6.2, 6H and

1.35, d, J_{HH} = 6.2, 6H ; 2.60, d, J_{HP} = 13.3, 2H ; 3.30, d, J_{HH} = 7.3, 2H ; 4.75, sept d, J_{HH} ~ 6.2 and J_{HP} ~ 7.7, 2H ; 5.16, ~ d, $J_{HH\ cis}$ ~ 10.5, 1H ; 5.165, ~ d, $J_{HH\ trans}$ ~ 16.3, 1H ; 5.75, t d d, J_{HH} ~ 7.3, $J_{HH\ cis}$ ~ 10.5, and $J_{HH\ trans}$ ~ 16.3, 1H. ^{13}C NMR (62.89 MHz) : 24.02 and 24.12, 2 d, J = 4.9 and J = 3.8 ; 24.24, d, J = 151.3 ; 35.61, d, J = 3.4 ; 71.09, d, J = 6.85 ; 118.34, s ; 133.14, s. ^{31}P NMR : 22.68, s. Mass : 252 (52.33) $M^{+\cdot}$; 96 (100.00) $(HO)_2P(O)CH_3^{+\cdot}$. IR (film NaCl) : 3080 (w) ν H_2C= ; 1630 (w) ν C=C ; 1250 (s) ν P=O ; ~ 1000 (s and broad) ν P-O-C.

Diisopropyl (crotylthiomethyl)phosphonate 7a : Pale yellow liquid. Yield = 71 %. Analysis : $C_{11}H_{23}O_3PS$: calc. % : C 49.60, H 8.70 ; obs. % : C 49.52, H 8.97. ^1H NMR (250 MHz) : 1.33 and 1.34, 2 d, J_{HH} = 6.2, 12H ; 1.72, ~ d, $^3J_{HH}$ = 6.3, 3H ; 2.59, d, J_{HP} = 13.1, 2H ; 3.25, ~ d, $^3J_{HH}$ = 7.2, 2H ; 4.75, sept d, J_{HH} ~ 6.2 and J_{HP} ~ 7.7, 2H ; 5.39, ~ d t, $J_{HH\ trans}$ = 15.1, $^3J_{HH}$ = 7.2, 1H ; 5.60, d qd, $J_{HH\ trans}$ = 15.1, J_{HH} = 6.3, 1H. ^{13}C NMR (62.89 MHz) : 17.66, s ; 24.00 and 24.12, 2 d, J = 4.9 and J = 3.9 ; 24.25, d, J = 151.3 ; 34.86, d, J = 3.5 ; 70.96, d, J = 6.9 ; 126.12, s ; 129.55, s. ^{31}P NMR : 22.94. Mass : 266 (100.00) $M^{+\cdot}$. IR (film NaCl) : 3020 (m) ν H-C= ; 1250 (s) ν P=O ; 1000 (vs) ν P-O-C.

Diisopropyl (acylthiomethyl)phosphonate 8a : Colorless liquid. Yield = 65 %. Analysis : $C_9H_{19}O_3PS$: calc. % : S 12.61 ; obs. % : S 12.73. ^1H NMR (60 MHz) : 1.32, d, J_{HH} = 6.5, 12H ; 2.35, s, 3H ; 3.13, d, J_{HP} ~ 14.0, 2H ; 4.70, sept d, J_{HH} ~ J_{HP} ~ 6.5. ^{13}C NMR (20.15 MHz) : 23.56, d, J = 152.3 ; 23.87 and 24.07, 2 d, J = 3.0 and J = 2.0 ; 29.99, s ; 71.48, d, J = 6.6 ; 193.03, d, J = 4.7. ^{31}P NMR : 20.43, s. Mass : 254 (66.15) $M^{+\cdot}$; 43 (100.00) $(CH_3)_2CH^+$. IR (film NaCl) : 1700 (s) ν C=O ; 1250 (s) ν P=O ; ~ 1000 (vs and broad) ν P-O-C.

O,O-diethyl S-[(diisopropyloxyphosphinyl)methyl]phosphorothioate 9a : Colorless liquid. Yield = 80 %. Analysis : $C_{11}H_{26}O_6P_2S$: calc. % : S 9.20 ; obs. % : S 9.51. ^1H NMR (60 MHz) : 1.33, t, J_{HH} ~ 6 and 1.33, d J_{HH} ~ 6.5, 18H ; 2.96, d d, $^2J_{HP}$ = 14.0 and $^3J_{HP}$ = 10.0, 2H ; 4.16, qd d, $^3J_{HH}$ ~ 6 and $^3J_{HP}$ = 8, 4H ; 4.70, sept d, $^3J_{HH}$ ~ $^3J_{HP}$ ~ 6.5, 2H. ^{13}C NMR (20.15 MHz) : 16.04, d, $^3J_{CP}$ = 6.9 ; 24.02, d, $^3J_{CP}$ = 3.4 ; 24.55, d d, $^1J_{CP}$ = 149.3 and $^2J_{CP}$ = 3.1 ; 64.02, d, $^2J_{CP}$ = 5.7 ; 71.75, d, $^2J_{CP}$ = 6.6. ^{31}P NMR : 19.58, d, $^3J_{PP}$ = 32, P-CH_2 ; 25.75, d, $^3J_{PP}$ = 32, P-S. Mass : 348 (3.26) $M^{+\cdot}$; 264 (100.00) double Mc Lafferty from $M^{+\cdot}$. IR (film NaCl) : 1250 (s) ν P=O ; 1100 (s) and 1135 (s and broad) ν P-O-C ; 1010 to 960 (s) ν P-O-C.

(Diisopropyl) (2,4-dithiapentamethylene)diphosphonate 10a : Pale yellow liquid. Yield = 87 %. Analysis : $C_{15}H_{34}O_6P_2S_2$: calc. % : C 41.28, S 14.69 ; obs. % : C 41.51, S 15.00. ^1H NMR (250 MHz) : 1.30, d, J_{HH} ~ 6.1 and 1.31, d, J_{HH} ~ 6.1, 24H ; 2.77, d, J_{HP} = 12.8, 4H ; 4.05, s, 2H ; 4.73, sept d, J_{HH} ~ 6.1 and J_{HP} ~ 7.6, 4H. ^{13}C NMR (62.89 MHz) : 23.86, d, J = 151.3 ; 23.98, d, J = 5.1 and 24.08, d, J = 3.8 ; 37.74, t, J ~ 3.0 ; 71.24, d, J = 6.7. ^{31}P NMR : 22.03, s. Mass : 436 (6.9) $M^{+\cdot}$; 97 (100.00) $P(OH)_3CH_3^+$. IR (film NaCl) : 1245 (s and broad) ν P=O ; ~ 1000 (s and broad) ; ν P-O-C.

Synthesis of trithiocarbonates 12a-14a.

Diisopropyl (mercaptomethyl)phosphonate **2a** (2 mmol), dissolved in dry THF (1 ml), was added to a stirred suspension of HNa (2 mmol) in dry THF (15 ml) at room temperature, and the reaction mixture was stirred for 1 hour. Then carbon disulfide (2.2 mmol) was added at -5°C, and the reaction mixture was stirred for 2 hours, allowing the temperature to raise to 20°C. Then methyl iodide, or allyl bromide, or crotyl bromide (2.2 mmol) was added and allowed to react at room temperature for 20 hours. Then the reaction mixture was poured into a stirred mixture of ether (20 ml) and water saturated with NH_4Cl (20 ml). The organic layer was washed

with brine (2 x 20 ml), dried over Na_2SO_4, and the solvent was removed under reduced pressure. Crude compounds **12a**, **13a** or **14a** was purified by column chromatography (silica gel Merck 60 M, eluent : cyclohexane / ethylacetate).

*Methyl and [(diisopropoxyphosphinyl)methyl] trithiocarbonate **12a*** : Orange liquid. Yield = 90 % from **2a**. Analysis : $C_9H_{19}O_3PS_3$: calc. % : C 35.74, H 6.33, S 31.80 ; obs. % : C 35.95, H 6.15, S 32.07. ^1H NMR (250 MHz) : 1.32, d, J_{HH} ~ 6 and 1.34, d, J_{HH} ~ 6, 12H ; 2.79, s, 3H ; 3.80, d, $^2J_{HP}$ = 14.3, 2H ; 4.74, sept d, $^3J_{HH}$ ~ 6 and $^3J_{HP}$ ~ 7.7, 2H. ^{13}C NMR (62.89 MHz) : 20.65, s ; 23.98, d, J = 5.1 and 24.10, d, J = 3.8 ; 31.31, d, J = 147.1 ; 71.94, d, J = 6.6 ; 222.92, d, $^3J_{CP}$ = 9.6, C=S. ^{31}P NMR : 18.61, s. Mass : 302 (10.98) $M^{+\cdot}$; 45 (100.00) SCH^+. IR (film NaCl) : 1255 (s) ν P=O ; ~ 1000 (vs) ν P-O-C.

*Allyl and [(diisopropoxyphosphinyl)methyl] trithiocarbonate **13a*** : Orange liquid. Yield = 80 % from **2a**. Analysis : $C_{11}H_{21}O_3PS_3$: calc. % : C 40.22, H 6.44, S 29.28 ; obs. % : C 40.34, H 6.51, S 29.52. ^1H NMR (250 MHz) : 1.32, d, J_{HH} ~ 6 and 1.34, d, J_{HH} ~ 6, 12H ; 3.78, d, $^2J_{HP}$ = 14.3, 2H ; 4.06, d d, $^3J_{HH}$ = 6.9 and $^4J_{HH}$ ~ 1.2, 2H ; 4.73, sept d, $^3J_{HH}$ ~ 6 and $^3J_{HP}$ = 7.6, 2H ; 5.20, ~ d, J_{cis} = 10.0, 1H ; 5.33, d t, J_{trans} = 17.0 and $^4J_{HH}$ ~ 1.2, 1H ; 5.86, d d t , J_{trans} = 17.0, J_{cis} = 10.0 and $^3J_{HH}$ = 6.9, 1H. ^{13}C NMR (62.89 MHz) : 23.99, d, J = 4.7 and 24.10, d, J = 3.7 ; 31.25, d, J = 147.2 ; 40.23, s ; 71.94, d, J = 6.9 ; 119.96, s ; 130.73, s ; 221.28, d, $^3J_{CP}$ = 9.0, C=S. ^{31}P NMR : 18.56, s. Mass : 328 (4.62) $M^{+\cdot}$; 41 (100.00) CH_2=CH-CH_2^+. IR (film NaCl) : 3080 (w) and 3040 (w) ν H_2C= ; 1635 (m) ν C=C ; 1250 (s and broad) ν P=O ; ~ 1000 (vs and broad) ν P-O-C.

*Crotyl and [(diisopropoxyphosphinyl)methyl] trithiocarbonate **14a*** : Orange liquid. Yield = 72 % from **2a**. Analysis : $C_{12}H_{23}O_3PS_3$: calc. % : S 28.08 ; obs. % : S 27.75. ^1H NMR (250 MHz) : 1.32, d, J_{HH} ~ 6 and 1.34, d, J_{HH} ~ 6, 12H ; 1.69, d, $^3J_{HH}$ ~ 6.5, 3H ; 3.77, d, $^2J_{HP}$ = 14.3, 2H ; 4.01, d d, $^3J_{HH}$ = 7.1 and $^4J_{HH}$ ~ 1.2, 2H ; 4.73, sept d, $^3J_{HH}$ ~ 6 and $^3J_{HP}$ = 7.6, 2H ; 5.50, d t, J_{trans} = 15.0 and $^3J_{HH}$ = 7.1, 1H ; 5.78, d qd t, J_{trans} = 15.0, $^3J_{HH}$ ~ 6.5 and $^4J_{HH}$ ~ 1.2, 1H. ^{13}C NMR (62.89 MHz) : 17.90, s ; 24.00, d, J = 5.0 and 24.12, d, J = 3.8 ; 31.17, d, J = 147.2 ; 40.00, s ; 71.91, d, J = 6.7 ; 123.19, s ; 131.80, s ; 221.70, d, J = 8.8, C=S. ^{31}P NMR : 18.69, s. Mass : 342 (5.68) $M^{+\cdot}$; 43 (100.00) $(CH_3)_2CH^+$. IR (film NaCl) : 3024 (w) ν HC= ; 1664 (w) ν C=C ; 1256 (s) ν P=O ; 988 (s and broad) ν P-O-C.

*Synthesis of N-phenyl imidodithiocarbonate **15a**.*

Diisopropyl (mercaptomethyl)phosphonate **2a** (2 mmol) dissolved in dry THF (1 ml) was added to a stirred suspension of HNa (2 mmol) in dry THF (10 ml) under N_2 at room temperature. The mixture was stirred for 1 hour at room temperature. Then the solution was cooled at 0°C and phenyl isothiocyanate (2 mmol) was added, and the reaction mixture was stirred for 12 hours at room temperature. After cooling at 0°C, HMPA (2.5 mmol) and then methyliodide (4 mmol) were added, and the reaction mixture was stirred for 12 hours at room temperature. The obtained yellow solution was diluted with water (15 ml) and extracted with ether (2 x 20 ml). The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. Crude product (yellow oil) was purified by column chromatography (silica gel Merck 60 M, eluent : cyclohexane / ethylacetate 90 / 10).

*Methyl and [(diisopropyloxyphosphinyl)methyl] N-phenyl imidodithiocarbonate **15a*** : Pale yellow liquid. Yield = 70 % from **2a**. Analysis : $C_{15}H_{24}NO_3PS_2$: calc.% : S 17.74 ; obs. % : S 17.74. ^1H NMR (250 MHz) : 1.34, d, J_{HH} = 6.4, 12H ; 2.50, s, 3H ; 3.50, d, J = 13.3, 2H ; 4.75, sept d, $^3J_{HH}$ ~ $^3J_{HP}$ ~ 6.4, 2H ; 6.85, d, J ~ 7.8, 2H ; 7.09, t, J ~ 7.8, 1H ; 7.31, t, J ~ 7.8, 2H. ^{13}C NMR (62.89 MHz) : 14.91, s ; 24.05, d, J = 4.8

and 24.15, d, J = 3.8 ; 25.95, d, J = 148.9 ; 71.69, d, J = 6.7 ; 120.34, s ; 124.26, s ; 129.11, s ; 149.30, s ; 160.39, J = 6.0, C=N. ^{31}P NMR : 20.04, s. Mass : 361 (1.08) $M^{+\cdot}$; 43 (100.00) $(CH_3)_2CH^+$. IR (film NaCl) : 1574 (vs) ν C=N ; 1254 (s) ν P=O ; 986 (vs) ν P-O-C.

Synthesis of N-phenyl dithiocarbamate 16a.

The reaction of diisopropyl (mercaptomethyl)phosphonate **2a** (2 mmol) with phenyl isothiocyanate (2 mmol) in THF (10 ml) was done according to the procedure described above for preparation of compound **15a**. Then the reaction mixture was hydrolyzed at room temperature with a saturated aqueous solution of NH_4Cl containing 5 % HCl, and was stirred at room temperature for 1 hour. Extraction with ether (2 x 20 ml), washings with brine, drying over Na_2SO_4 and evaporation of the solvent under reduced pressure, led compound **16a** as a yellow oil, which was purified by column chromatography on silica gel (Merck 60 M, eluent : cyclohexane / ethylacetate 90 / 10), and the crystals thus obtained were washed with pentane.

N-phenyl S-[(diisopropyloxyphosphinyl)methyl] dithiocarbamate 16a : Pale yellow crystals. Mp. = 89°C. Yield = 60 % from **2a**. Analysis : $C_{14}H_{22}NO_3PS_2$: calc.% : S 18.45 ; obs. % : S 18.62. ^1H NMR (250 MHz) : 1.35, d, J = 6.2, 12H ; 3.52, d, J = 12.7, 2H ; 4.79, sept d, J_{HH} = 6.2 and J_{HP} = 7.5, 2H ; 7.24, ~t, J = 7.0, 1H ; 7.37, ~t, J = 8.0, 2H ; 7.65, ~s, broad, 2H ; ~10.8, ~s, very broad, 1H. ^{13}C NMR (62.89 MHz) : 23.96, d, J = 5.3 and 24.09, d, J = 4.2 ; 30.89, d, J = 148.8 ; 72.46, d, J = 7.0 ; 124.97, s ; 127.49, s ; 128.96, s ; 130.06, s ; 136.63, s ; 181.58, s, C=S. ^{31}P NMR : 21.08, s. Mass : 347 (0.64) $M^{+\cdot}$; 135 (100.00) $C_6H_5NCS^{+\cdot}$. IR (film NaCl) : 3424 (m) ν NH ; 1232 (vs) ν P=O ; 994 (vs) ν P-O-C.

Synthesis of (mercapto-alkylthio-methyl)phosphonate 17.

Procedure with $NaBH_4$. To the solution of dithioester **1a** [19] (2 mmol) in acetonitrile or in ethanol (20 ml), and under N_2, was added dropwise a solution (2 ml) of $NaBH_4$ (8 mmol) in NaOH 1N and CH_3OH ; the reaction mixture was stirred for 2 to 4 hours at room temperature. Ether (20 ml) and then H_2SO_4 2N (15 ml) were added under N_2 at 20°C. The mixture was filtered, and extracted with additional ether (3 x 15 ml) ; the organic layer was washed with brine (3 x 10 ml), dried over Na_2SO_4, and the solvent was removed under reduced pressure. Hemidithioacetal **17a** was obtained with ~ 90 % yield and purity up to 90 %.

Procedure with Li^+ $(CH_3)_2CHNBH_3^-$. A solution of lithium diisopropylaminoborohydride (1.34 M) in THF was prepared under N_2 according to the known procedure,[26] from diisopropylamine, borane-Me_2S complex (solution 12M in Me_2S), and ^nBuLi (solution ~ 2M in ether). This solution of lithium diisopropylaminoborohydride (4.6 ml, 6 mmol) was added dropwise, under N_2, to a solution of dithioester **1a** [19] (2 mmol) in THF (20 ml), and the reaction mixture was stirred at room temperature for 3 hours. Then the solution was cooled to 0°C, and HCl 2N (20 ml) was added under N_2, and stirring was continued for 20 hours at room temperature. The reaction mixture was extracted with ether (3 x 15 ml) ; the organic layer was washed with brine (3 x 15 ml), dried over Na_2SO_4, and the solvent was removed under reduced pressure. Compound **17a** was obtained ~ 95 % pure in a nearly quantitative yield.

Procedure with the complex BH_3-Me_2S (BMS). The dithioester **1a** or **1b** [19] (10 mmol) was dissolved in dry THF (60 ml) under N_2, and a solution of BMS (10 M in Me_2S, 14 mmol) was added. The mixture was stirred at room temperature, and decoloration was observed after 3 hours. The solution was cooled to 0°C, and HCl 2N (20 ml) was added. The mixture was stirred for 20 hours at room temperature, and then was extracted with ether (3 x 15 ml). The organic layer was washed with brine (3 x 15 ml), dried over Na_2SO_4, and the

solvent was removed under diminished pressure. The crude hemidithioacetal **17a** or **17b** was obtained in ~ 90 % yield with purity ~ 95 %.

Diisopropyl (mercapto-methylthio-methyl)phosphonate 17a : Pale yellow liquid.[7] ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and Mass are described.[7]. IR (film NaCl) : 2500 (w) ν SH ; 1240 (s and broad) ; ν P=O ; ~ 1030 (vs and broad) ν P-O-C.

Diethyl (mercapto-methylthio-methyl)phosphonate 17b : Pale yellow liquid.[9] ^{1}H NMR and ^{31}P NMR are described.[9] ^{13}C NMR (20.15 MHZ) : 14.80, d, J = 4 ; 16.45, d, J = 6 ; 38.23, d, J = 156.5 ; 64.06, d, J = 7. Mass : 230 (53.85) $M^{+\cdot}$; 45 (100.00) CSH^+. IR (film NaCl) : 2500 (w) ν SH ; 1240 (s) ν P=O ; ~ 1000 (vs and broad) ν P-O-C.

Characterization of (mercapto-alkylthio-methyl)phosphonate 17a : Dervatives 18a to 20a .

Crude compound **17a** (2 mmol) prepared as described above, was dissolved in dry THF, and a solution 2,25 M of ^{n}BuLi (0.9 ml, 2 mmol) was added dropwise at -15°C under N_2. After stirring for 1 hour at -15°C, alkyl halide or acyl halide (scheme 5) (2.1 mmol) was added at 0°C, and the mixture was allowed to stand at room temperature for 20 hours. Usual work-up (extraction with ether (3 x 15 ml), washings with brine (3 x 15 ml), drying over Na_2SO_4, evaporation of the solvent under diminished pressure) led compound **18a** or **19a** or **20a**, then purified by column chromatography (silica gel Merck 60 M, eluent : petroleum ether / ethyl acetate).

Diisopropyl [(bis-methylthio)methyl)]phosphonate 18a : Pale yellow liquid.[24] Yield = 67 %. ^{1}H NMR described.[24] ^{13}C NMR (62.89 MHz) : 14.52, d, J = 4.3 ; 23.85, d, J = 5.9 and 24.28, d, J = 3.4 ; 47.65, d, J = 156.4 ; 72.33, d, J = 7.3. ^{31}P NMR : 17.64, s. Mass : 272 (12.75) $M^{+\cdot}$; 107 (100.00) $CH(SCH_3)_2^+$ and $P(O)CHSCH_3^+$. IR (film NaCl) : 1245 (vs) ν P=O ; ~ 1000 (vs and broad) ν P-O-C.

Diisopropyl (allylthio-methylthio-methyl)phosphonate 19a : Pale yellow liquid. Yield = 52 %. ^{1}H NMR (250 MHz) : 1.37, d, J_{HH} = 6.2, 12H ; 2.28, s, 3H ; 3.31, d $_{(AB)}$ d t, $^2J_{HH}$ = 13.6, $^3J_{HH}$ = 6.4 and $^4J_{HH}$ ~ 1.3, 1H, SCH_2 ; 3.41, d $_{(AB)}$ d , $^2J_{HH}$ = 13.6, $^3J_{HH}$ = 8.2, 1H, SCH_2 ; 3.65, d, $^2J_{HP}$ ~ 17.0, 1H, $PCHS_2$; 4.80, sept d, $^3J_{HH}$ ~ 6.2 and $^3J_{HP}$ ~ 9.7, 2H ; 5.17, d d, $^3J_{cis}$ ~ 12 and $^4J_{HH}$ ~ 1.3, 1H ; 5.18, d d , $^3J_{trans}$ ~ 15 and $^4J_{HH}$ ~ 1.3, 1H ; 5.78, d d d d, $^3J_{trans}$ ~ 15, $^3J_{cis}$ ~ 12, $^3J_{HH}$ = 8.2 and $^3J_{HH}$ = 6.4, 1H. ^{13}C NMR (62.89 MHz) : 14.10, d, J = 2.7 ; 23.81, d, J = 3.6 ; 23.87, d, J = 3.7 ; 24.22, d, J = 5.2 ; 24.27, d, J = 3.7 ; 34.16, d, J = 5.5, 43.88, d, J = 157.7 ; 72.20, d, J = 7.3 and 72.31, d, J = 7.6 ; 118.63, s ; 132.93, s. ^{31}P NMR : 18.27, s. Mass : 298 (2.88) $M^{+\cdot}$; 41 (100.00) CH_2-CH_2=CH^+. IR (film NaCl) : 3075 (w) ν H_2C= ; 1630 (m) ν C=C ; 1250 (s) ν P=O ; 1000 (vs) ν P-O-C.

Diisopropyl (acylthio-methylthio-methyl)phosphonate 20a : Colorless liquid. Yield = 73 %. Analysis : $C_{10}H_{21}O_4PS_2$: calc. % : C 39.98, H 7.04, S 21.35 ; obs. % : C 39.98, H 6.76, S 21.43. ^{1}H NMR (250 MHz) : 1.35, d, J_{HH} ~ 6.2 and 1.37, d, J_{HH} ~ 6.2, 12H ; 2.27, s, 3H ; 2.42, s, 3H ; 4.70, d, $^2J_{HP}$ ~ 17.5, 1H, $PCHS_2$; ~ 4.77, ~ sept d, $^3J_{HH}$ ~ 6.2 and $^3J_{HP}$ ~ 7.6, 2H. ^{13}C NMR (62.89 MHz) : 15.39, d, J = 4.5 ; 23.70, d, J = 3.5 ; 23.79, d, J = 3.5 ; 24.09, d, J = 3.3 ; 24.19, d, J = 3.5 ; 30.07, s ; 42.55, d, J = 159.0 ; 72.44, d, J = 7.1 and 72.62, d, J = 7.05 ; 192.4, d, J = 5.1. ^{31}P NMR : 16.10, s. Mass : 300 (23.21) $M^{+\cdot}$; 173 (100.00) $(HO)_2P(O)CH(S)SCH_3^+$. IR (film NaCl) : 1700 (s) ν C=O ; 1250 (s) ν P=O ; 1000 (vs and broad) ν P-O-C.

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