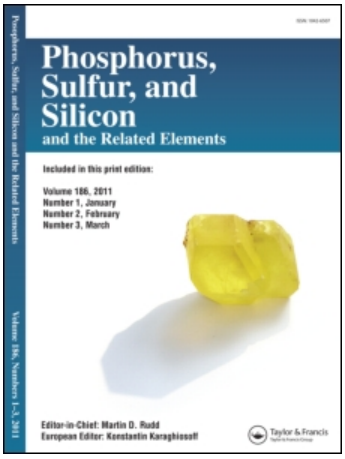


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# SIGMATROPIC-[2,3]-WITTIG REARRANGEMENT OF α-ALLYLIC-HETEROSUBSTITUTED METHYLPHOSPHONATES. REARRANGEMENT IN THE SULFUR SERIES

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# SIGMATROPIC-[2,3]-WITTIG REARRANGEMENT OF α-ALLYLIC-HETEROSUBSTITUTED METHYLPHOSPHONATES. REARRANGEMENT IN THE SULFUR SERIES

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The diisopropyl (allylthiomethyl)phosphonates (variously substituted on the allylic group) are submitted to the [2,3]-sigmatropic rearrangement, via either the carbanions or the sulfonium ylides. Synthetic potentialities are examined, and in particular new (1-mercaptobut-3-enyl)phosphonates are conveniently prepared.

*Key words:* Thia-[2,3]-Wittig sigmatropic rearrangement, (allylthiomethyl)phosphonates, (1-mercaptobut-3-enyl)phosphonates, (1-alkylthiobut-3-enyl)phosphonates, 2-thiolanylphosphonate, allyl-phosphonomethyl-methyl-sulfonium tetrafluoroborates.



## INTRODUCTION

α-Heterosubstituted alkylphosphonates have focused interest, due to their biological activities, as antibacterial, antiviral and herbicidal agents.[1-3] Among phosphonates containing a sulfur functionality, the α-phosphorylated thiols, and their derivatives (sulfides, sulfoxides, or sulfones) have recently been reviewed.[4] Of particular interest for further functional transformations[5] are the scarcely studied (1-mercaptoalkyl)-phosphonates.[4,6,7]

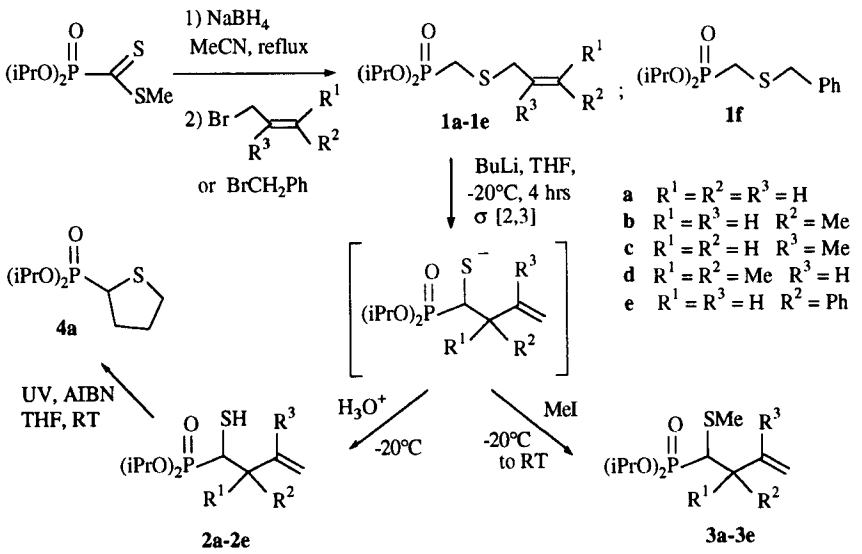
We previously reported a convenient synthesis of diisopropyl and diethyl (mercaptomethyl) phosphonates,[8,9] via the reduction with sodium borohydride of the easy accessible phosphonodithiofomates,[10] and further hydrolysis of the thiolates thus formed. α-Phosphorylated thiols are precursors of various derivatives,[9] in particular of the allylic phosphonomethyl sulfides which are obtained by *in situ* allylation of the corresponding thiolates.[8,9] These allylic phosphonomethyl sulfides may lead to the formation of new carbon-carbon bonds via the well-known [2,3]-sigmatropic rearrangement[11-15] of either the corresponding carbanions (we reported a preliminary example[8]) or sulfonium ylides. Syntheses of (1-hydroxybut-3-enyl)phosphonates have been performed[16] using the oxa-[2,3]-Wittig sigmatropic transposition of α-

phosphono carbanions, and the aza-[2,3]-sigmatropic rearrangement of $\alpha$-phosphono ammonium ylides was also examined.[17] We herein report our results in the sulfur series.

## RESULTS AND DISCUSSION

### *Syntheses of (1-mercaptobut-3-enyl)phosphonates, and S-methyl Derivatives, via the Carbanions obtained from (allylthiomethyl)phosphonates with Butyllithium*

The allylic or benzylic phosphonomethyl sulfides **1a–1f** (Scheme 1) were prepared by reduction of the methyl diisopropoxyphosphinylmethanedithioate and allylation (or benzylation) *in situ*.[8,9] The diisopropyl group was chosen in order to avoid any dealkylation by ionic species, reaction often encountered with diethyl phosphonates.[17,18] Deprotonation of compounds **1a–1e** with a slight excess of butyllithium in THF at −20°C, and subsequent hydrolysis or methylation, afforded thiols **2a–2e** or sulfides **3a–3e** respectively in 70 to 97% yields (Scheme 1). Two diastereoisomers were obtained (in the mentioned ratio) for the crotyl [$\mathbf{2b_1}$:$\mathbf{2b_2}$ (51/49), $\mathbf{3b_1}$:$\mathbf{3b_2}$ (60/40)] derivatives, and for the cinnamyl [$\mathbf{2e_1}$:$\mathbf{2e_2}$ (70/30), $\mathbf{3e_1}$:$\mathbf{3e_2}$ 60/40)] derivatives. The thiol function of the new compounds **2** was identified in IR spectroscopy by the expected[19] two weak $\nu_{SH}$ bands at 2520 and 2560 $cm^{-1}$ (in the neat), and in $^1H$ NMR spectroscopy by the SH signal at ≈1.8 ppm showing a doublet of doublet, with $^3J_{HP}$ ≈ 9.5 Hz and $^3J_{HH}$ ≈ 7 to 10 Hz. Both series of compounds **2** and **3** exhibited in $^{31}P$ NMR spectroscopy a signal at ≈23 ppm, as reported in similar phosphonomethyl sulfides,[6] and in $^{13}C$ NMR spectroscopy a signal for the PCHS group at ≈45 ppm. Moreover, the $^1H$ NMR signal for the PCHS group was found ≈0.3 ppm downfield in the thiols **2**, compared to the sulfides **3**. Benzyl sulfide **1f** did not rearrange when treated with buthyllithium even at +60°C; the corresponding carbanion has been

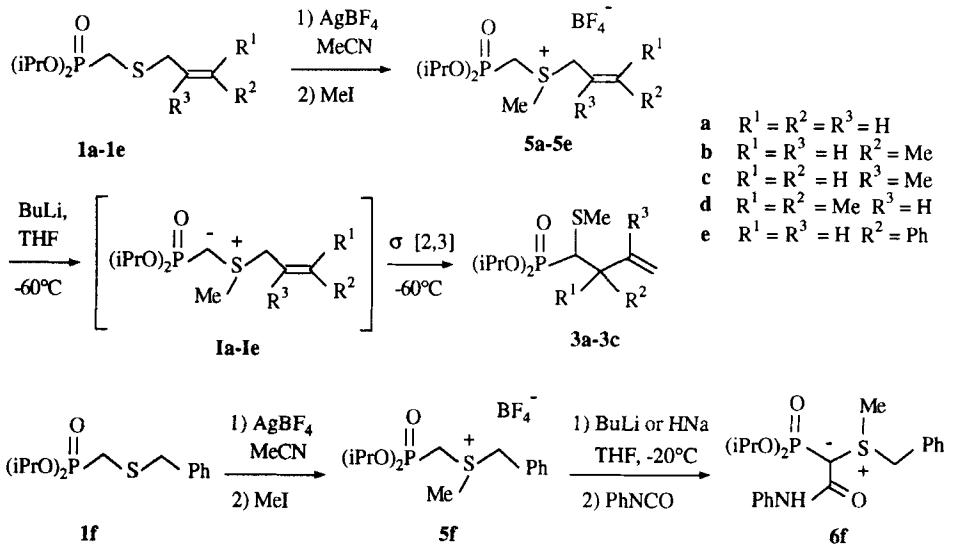



SCHEME 1

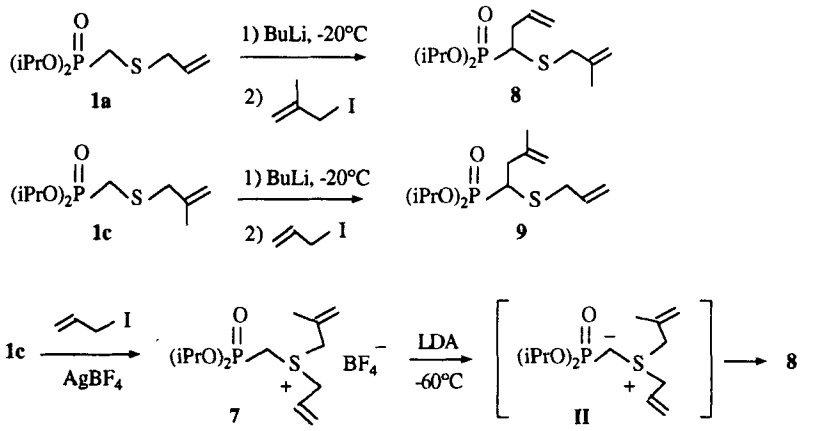
deuterated, but could not be methylated at −20°C. The thiol **2a** underwent cyclisation in THF, at room temperature, in the presence of AIBN and with ultra-violet irradiation (Scheme 1). The resulting diisopropyl 2-thiolanylphosphonate **4a**, thia- and phosphono- analogue of proline, which was not previously described, may present biological interest (similarly 2-pyrrolidinylphosphonate was mentioned as an inhibitor of the angiotensine-converting enzyme[20]).

### *Syntheses and [2,3]-sigmatropic Rearrangement of S-methyl Sulfonium Ylides of (allylthiomethyl)phosphonates*

S-methyl sulfonium tetrafluoborates of (allylthiomethyl)phosphonates **5a–5f** were quantitatively obtained by reaction of the sulfides **1a–1f** with methyl iodide and silver tetrafluoroborate in acetonitrile, at 50°C (Scheme 2). The use of the low nucleophilic tetrafluoroborate anion[21] was recommended owing to the well-known susceptibilities of sulfonium salts towards nucleophilic attack. Crude compounds **5** were obtained as viscous and hygroscopic oils, with 90% yields. They exhibited a characteristic signal in $^{31}P$ NMR spectroscopy at $\delta \approx 11$ ppm (starting material 1:$\delta \approx$ 23 ppm). Deprotonation of the sulfonium salts **5a–5c** with butyllithium at −60°C in THF led to the methyl [α-allylic (phosphonomethyl)] sulfides **3a–3c** via the [2,3]-sigmatropic rearrangement of the reactive, not isolated ylides **Ia–Ic**. From the crotyl substituted sulfonium salt **5b**, the rearranged compound **3b** was obtained as two diasteroisomers $\mathbf{3b_1}$ and $\mathbf{3b_2}$ in the ratio 90/10. This high diastereoselectivity in the [2,3]-sigmatropic rearrangement of ylide **Ib**, as compared to that of the related carbanion issued from **1b**, is in agreement with previously mentioned results in other series.[11,22] With the more crowded prenyl and cinnamyl derivatives **5d** and **5e**, no rearrangement product **3d** or **3e** was obtained, with butyllithium between −60°C and −20°C. Also, the observed failure of [2,3]-sigmatropy from **5f**, with BuLi in THF




SCHEME 2




SCHEME 3

at −20°C, is in concordance with the results of Warren *et al.*[23] concerning some arylthio sulfonium ylides. However, stable intermediate sulfonium ylide **If**, when treated with phenylisocyanate according to a described procedure,[24,25] led to the sulfonium ylide **6f**.

A surprising very high selectivity was observed with the "mixed" sulfonium salt **7**, synthesized from diisopropyl (methallylthiomethyl)phosphonate **1c** and allyl iodide. Deprotonation of **7** with LDA at −60°C led, via the sulfonium ylide **II**, to the sulfide **8** (90% yield), resulting from the migration of the non substituted allyl group only (Scheme 3). The two possibly expected sulfides **8** and **9** have been independently and quantitatively prepared via the carbanions of sulfides **1a** and **1c** respectively, by using butyllithium and adequate allylic halides at −20°C (Scheme 3).

## CONCLUSION

Thia-[2,3]-Wittig sigmatropic rearrangement of carbanions, obtained from the (allylthiomethyl)phosphonates and butyllithium, offers a convenient route to new (1-mercaptobut-3-enyl)phosphonates, and to their alkylated derivatives. The corresponding sulfonium ylides, prepared from the sulfonium salts with butyllithium, also underwent an *in situ* [2,3]-sigmatropic shift (except in the case of crowded derivatives), leading to the same sulfides. It is interesting to remind that, in the oxygen and nitrogen series, the [2,3]-sigmatropic rearrangement was observed respectively with the carbanions of (O-allylic methyl) phosphonates, and with the ylides of (N-allylic methyl)phosphonates. In the sulfur series, the [2,3]-sigmatropy is obtained with both ylides and carbanions. As far as stereochemistry is concerned, it was shown from the (crotylthiomethyl)phosphonate that the diastereoselectivity is different according to the use of a carbanion or an ylide as an intermediate for the sigmatropic rearrangement. Further studies are now in progress to investigate more extensively the possibility of asymmetric induction in these rearrangements and of stereocontrolled formation of $\alpha$-mercapto or $\alpha$-alkylthio alkyphosponates.

## EXPERIMENTAL

*General Methods.* The $^1H$ NMR spectra were recorded with 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 AC 250" spectrometer at 62.89 MHz, in $CDCl_3$ with TMS as internal standard (proton decoupled, $J_{CP}$ given). With a "Bruker WP 80 SY" spectrometer were recorded the $^{31}P$ NMR spectra at 32.44 MHz, the $^{11}B$ NMR spectra at 25.70 MHz and the $^{19}F$ NMR spectra at 75.30 MHz, with $H_3PO_4$, $Et_2O,BF_3$ or $CFCl_3$, respectively, as external standard. Chemical shifts are given in $\delta$ ppm and coupling constants in Hz. Conventional abbreviations were used. The infra-red spectra were recorded with a "Perkin-Elmer 16 PC" spectrometer on the liquid film; $\nu$ are given in $cm^{-1}$, and the following abbreviations are used (s): strong; (vs): very strong; (m): medium; (w): weak, (vw): very weak. Mass spectra were recorded with a "Nermag R 10 10H" spectrometer with electronic impact at 70 eV; m/z and relative abundance are given.

*Syntheses of diisopropyl (allylthiomethyl)phosphonates* **1**. The experimental procedure, and compounds **1a** and **1b** have already been described.[9]

*Diisopropyl (methallylthiomethyl)phosphonate* **1c**. Pale yellow liquid. Yield = 85%. Analysis: $C_{11}H_{23}O_3PS$: calc. %: S 12.03; obs. %: S 12.07. $^1H$ NMR: 1.20 and 1.21 (2d, $J$ = 6.2 12H); 1.67 (s, 3H); 2.42 (d, $J$ = 13.4, 2H); 3.12 (s, 2H); 4.61 (sept d, $J$ = 6.2 and $J$ = 7.6, 2H); 4.74 and 4.77 (2s). $^{13}C$ NMR: 20.5 (s); 24.0 and 24.1 (2d, $J$ = 4.9 and $J$ = 3.8); 24.5 (d, $J$ = 150.8); 40.2 (d, $J$ = 3.9); 71.0 (d, $J$ = 6.8); 114.8 (s); 140.0 (s). $^{31}P$ NMR: 22.7 (s). IR: 3078 (w); 2978 (m); 2934 (m); 2874 (m); 1648 (w); 1552 (m); 1514 (m); 1466 (m); 1452 (m); 1384 (m); 1374 (m); 1254 (s); 1178 (m); 1142 (m); 1108 (m); 1008 (s); 984 (vs); 898 (m); 888 (m); 806 (m); 758 (m); 700 (w). Mass: 266 (19, $M^{+\cdot}$); 204 (12); 203 (10); 182 (11); 181 (16); 180 (9); 165 (8); 97 (35); 96 (87); 95 (100, $(HO)_2P(O)CH_2^+$); 94 (64); 87 (7); 85 (9); 58 (10); 55 (25); 54 (17); 45 (11); 44 (9); 43 (38); 42 (20); 41 (23).

*Diisopropyl (prenylthiomethyl)phosphonate* **1d**. Pale yellow liquid. Yield = 80%. Analysis: $C_{12}H_{25}O_3PS$: calc. %: S 11.43; obs. %: S 11.52. $^1H$ NMR: 1.35 (d, $J$ = 6.2, 12H); 1.69 and 1.75 (2s, 6H); 2.62 (d, $J$ = 13.2, 2H); 3.32 (d, $J$ = 7.8, 2H); 4.76 (sept d, $J \approx 6.2$ and $J \approx 6.2$, 2H); 5.20 (t, $J$ = 7.8, 1H). $^{13}C$ NMR: 17.8 (s); 23.9 and 24.1 (2d, $J$ = 4.5 and $J$ = 3.7); 24.9 (d, $J$ = 151.3); 25.7 (s); 30.8 (d, $J$ = 3.5); 70.9 (d, $J$ = 6.8); 119.7 (s); 136.8 (s). $^{31}P$ NMR: 22.9 (s). IR: 3040 (vw, shoulder); 3000 to 2850 (m); 1665 (w); 1470 (m); 1465 (m); 1380 (m); 1370 (m); 1250 (vs and broad); 1175 (m); 1140 (m); 1100 (m); 1000 and 984 (vs and broad); 925 (w); 805 (w); 730 (m). Mass: 280 (21, $M^{+\cdot}$); 238 (4); 212 (15); 196 (14); 194 (21); 169 (28); 155 (24); 154 (25); 139 (18); 128 (46); 127 (43); 101 (19); 96 (85); 95 (100, $(HO)_2(P(O)CH_2^+$); 94 (53); 69 (40); 68 (29); 43 (33); 42 (33); 41 (48).

*Diisopropyl (cinnamylthio)phosphonate* **1e**. Pale yellow liquid. Yield = 73%. Analysis: $C_{16}H_{25}O_3PS$: calc. %: S 9.76; obs. %: S 9.52. $^1H$ NMR: 1.34 (d, $J$ = 6.2, 12H); 2.63 (d, $J$ = 13.0, 2H); 3.49 (d, $J$ = 7.5, 2H); 4.73 (sept d, $J$ = 6.2 and $J$ = 7.7, 2H); 6.14 (t d, $J$ = 7.5 and $J$ = 15.7, 1H); 6.51 (d, $J$ = 15.7, 1H); 7.2 to 7.4 (m, 5H). $^{13}C$ NMR: 24.1 and 24.2 (2d, $J$ = 5.3 and $J$ = 3.6); 24.3 (d, $J$ = 151.0); 35.2 (d, $J$ = 2.9); 71.2 (d, $J$ = 6.6); 124.7 (s); 126.5, 127.8 and 128.7 (3s); 133.5 (s); 136.6 (s). $^{31}P$ NMR: 22.7 (s). IR: 3060 (w); 3026 (w); 2978 (m); 2934 (m); 1648 (w); 1596 (w); 1578 (w); 1490 (m); 1466 (m); 1450 (m); 1422 (w); 1386 (m); 1374 (m); 1250 (s); 1178 (m); 1142 (m); 1106 (m); 1074 (s); 984 (vs); 888 (w); 786 (m); 752 (w). Mass: 328 (7, $M^{+\cdot}$); 244 (19); 243 (19); 149 (20); 117 (39); 116 (12); 115 (56); 99 (17); 97 (22); 96 (24); 91 (17); 84 (13); 77 (8); 65 (15); 59 (15); 51 (20); 49 (46); 47 (19); 45 (27); 43 (100, $C_3H_7^+$); 41 (57).

*Diisopropyl (benzylthiomethyl)phosphonate* **1f**. Pale yellow liquid. Yield = 79%. Analysis: $C_{14}H_{23}O_3PS$: calc. %: S 10.60; obs. % S 10.66. $^1H$ NMR: 1.33 (d, $J$ = 6.2, 12H); 2.51 (d, $J$ = 13.0, 2H); 3.90 (s, 2H); 4.76 (sept d, $J$ = 6.2 and $J$ = 7.6, 2H); 7.2 to 7.4 (m, 5H). $^{13}C$ NMR: 24.0 and 24.1 (2d, $J$ = 5.1 and $J$ = 3.8); 24.8 (d, $J$ = 151.0); 36.9 (d, $J$ = 3.5); 71.1 (d, $J$ = 6.8); 127.2, 128.5, 129.2 and 137.4 (4s). $^{31}P$ NMR: 22.5 (s). IR: 3030 (w); 3025 (w); 3010 (w); 3000 to 2800 (s); 1605 (w); 1460 (m); 1445 (m); 1440 (m); 1380 (w); 1375 (w); 1240 (s); 1195 (m); 1165 (m); 1100 (m); 1040 (w); ≈1000 (vs and broad); 910 (w); 905 (m); 885 (m); 812 (m); 805 (m); 785 (m); 730 (m); 710 (m). Mass: 302 (10, $M^{+\cdot}$); 218 (5); 217 (14); 139 (29); 123 (15); 97 (100, $(HO)_3PCH_3^+$); 91 (99); 86 (45); 84 (68); 77 (4); 65 (19); 51 (26); 49 (94); 43 (77).

*Procedure A*

*Thia-[2,3]-Wittig sigmatropic rearrangement of the carbanions issued of sulfides* **1** *and butyllithium: syntheses of (1-mercaptobut-3-enyl)phosphonates* **2** *and of (3-methylthiobut-3-enyl) phosphonates* **3**. The allylic phosphonomethyl sulfides **1** (1 mmol) were dissolved in dry THF (10 ml) under $N_2$ and the solution was cooled into a bath at −20°C. Butyllithium (1 mmol, solution 1.32 M in hexane) was

added, and the solution was stirred for 4 hours at −20°C and then either quenched with HCl 5% (10 ml), or alkylated with iodomethane (2 mmol) and stirred for 12 hours at room temperature for complete alkylation. Extraction with ether, washings with brine, drying over $Na_2SO_4$, and evaporation of the solvent under reduced pressure yielded crude thiols **2** or sulfides **3** respectively, which were further purified by column chromatography (silicagel Merck 60 M, eluent:petroleum ether/ethyl acetate 80/20). Attribution of the signals of PCHS and $SCH_2(C{=}C)$ in $^1H$ NMR of compounds **2a**, **2c**, and **3a**, **3c** were performed by 2D ($^1H$-$^{13}C$) NMR, and the $^1H$ NMR and $^{13}C$ NMR published[8] for **2a** are revised.

*Diisopropyl (1-mercaptobut-3-enyl)phosphonate* **2a**. Colourless liquid. Yield: 90%. Analysis: $C_{10}H_{21}O_3PS$: calc. %: S 12.70; obs. %: S 12.91. $^1H$ NMR: 1.35 (d, $J$ = 6.1, 12H); 1.93 (d d, $^3J_{HH}$ = 8.7 and $^3J_{HP}$ = 8.7, 1H, SH); 2.3 (m, 1H of $CH_2$); 2.7 to 2.9 (m, 2H: PCHS and 1H of $CH_2$); 4.77 (sept d, $J$ = 6.1 and $J$ = 7.4, 2H); 5.15 (d, $J \approx 11$, 1H); 5.16 (d, $J \approx 16$, 1H); 5.85 (d d t, $J \approx 11$, $J \approx 16$ and $J \approx 7$, 1H). $^{13}C$ NMR: 24.0 and 24.2 (2d, $J$ = 4.9 and $J$ = 3.4); 34.4 (d, $J$ = 150.6); 36.8 (s); 71.6 and 71.7 (2d, $J$ = 7.2); 118.3 (s); 134.4 (d, $J$ = 13.8). $^{31}P$ NMR: 23.7 (s). IR: 3078 (w); 3020 (w); 2978 (s); 2924 (s); 2852 (s); 2560 and 2520 (w, $\nu_{S-H}$); 1642 (m); 1466 (m); 1450 (m); 1416 (w); 1386 (m); 1374 (m); 1356 (w); 1248 (s); 1178 (m); 1142 (m); 1106 and 986 (s); 916 (m); 896 (m); 818 (w); 768 (m); 738 (w). Mass: 252 (6, $M^+$); 210 (10); 169 (12); 168 (60); 167 (13); 135 (26); 127 (54); 87 (52); 86 (15); 85 (24); 65 (10); 59 (19); 55 (12); 54 (10); 53 (21); 49 (16); 47 (15); 45 (38); 43 (100, $C_3H_7^+$); 41 (63).

*Diisopropyl (1-mercapto-2-methylbut-3-enyl)phosphonate* **2b**. Pale yellow liquid. Yield = 97%. Mixture of two diastereoisomers **2b$_1$** and **2b$_2$** (51/49, estimated on $^{31}P$ NMR). Analysis: $C_{11}H_{23}O_3PS$: calc. %: S 12.03; obs. %: S 12.18. $^1H$ NMR: **2b$_1$**: 1.19 (d, $J$ = 7.0, 3H); 1.34 (d, $J$ = 6.2, 12H); 1.77 (d d, $J \approx 10$ and $J \approx 10$, 1H, S—H); 2.77 (d d d, $J$ = 18.5, $J \approx 10$ and $J \approx 4$, 1H, PCHS); 2.85 to 2.95 (m, 1H); 4.77 (sept d, $J \approx 6.2$ and $J \approx 6.2$, 2H); 5.07 (d, $J$ = 10.5, 1H); 5.08 (d, $J$ = 16.5, 1H); 5.92 (d d d, $J$ = 10.5, $J$ = 16.5 and $J$ = 7.0, 1H). **2b$_2$**: 1.16 (d, $J \approx 6.8$, 3H); 1.35 (d, $J \approx 6$, 12H); 1.79 (d d, $J \approx 10$ and $J \approx 10$, 1H, S—H); 2.77 (d d d, $J$ = 18.5, $J \approx 10$ and $J \approx 4$, 1H, PCHS); 2.85 to 2.95 (m, 1H); 4.79 (sept d, $J \approx 6$ and $J \approx 6$, 2H); 5.10 d, $J \approx 17$, 1H); 5.11 (d, $J \approx 10$, 1H); 5.93 (d d d, $J \approx 17$, $J \approx 10$ and $J \approx 7$, 1H). $^{13}C$ NMR: **2b$_1$**: 18.2 (d, $J$ = 12.8); 24.2 and 24.3 (2d, $J$ = 3.6 and $J$ = 2.7); 37.9 (s); 40.7 (d, $J$ = 149.7); 71.3 and 71.9 (2d, $J$ = 7.4); 116.2 (s); 138.4 (d, $J$ = 3.3). **2b$_2$**: 14.8 (d, $J$ = 2.1); 23.8 and 23.9 (2d, $J$ = 5.8 and $J$ = 3.4); 38.1 (s); 40.2 (d, $J$ = 146.6); 71.4 and 71.9 (2d, $J$ = 7.5); 114.9 (s); 141.23 (d, $J$ = 15.2). $^{31}P$ NMR: **2b$_1$**: 23.1 (s); **2b$_2$**: 22.9 (s). IR: 3082 (w); 2978 (s); 2934 (m); 2874 (m); 2562 and 2520 (w, $\nu_{S-H}$); 1640 (m); 1466 (m); 1454 (m); 1416 (m); 1388 (m); 1374 (w); 1248 (s); 1178 (m); 1142 (m); 1106 (s); ≈986 (vs); 935 (m); 916 (m); 896 (m); 822 (w); 768 (w); 734 (w). Mass: 266 (1, $M^+$); 224 (4); 211 (8); 182 (17); 169 (12); 149 (16); 128 (27); 127 (92); 101 (23); 84 (12); 55 (22); 49 (24); 47 (13); 45 (21); 43 (100, $C_3H_7^+$); 41 (56).

*Diisopropyl (1-mercapto-3-methylbut-3-enyl)phosphonate* **2c**. Colourless liquid. Yield = 77%. Analysis: $C_{11}H_{23}O_3PS$: calc. %: S 12.03; obs. %: S 12.13. $^1H$ NMR: 1.36 (d, $J$ = 6.3, 12H); 1.73 (s, 3H); 1.91 (d d, $J$ = 10.6 and $J$ = 6.7, 1H, S—H); 2.2 to 2.3 (m, 1H of $CH_2$); 2.7 to 2.9 (m, 1H of $CH_2$); 3.0 (m, 1H, PCHS); 4.78 (sept d, $J \approx 6.3$ and $J \approx 6.3$, 2H); 4.83 (s, 1H); 4.91 (s, 1H). $^{13}C$ NMR: 24.3 (s); 23.9 and 24.0 (2d, $J$ = 5.1); 32.6 (d, $J$ = 151.5); 40.2 (≈ s); 71.6 and 71.7 (2d, $J$ = 3.8 and $J$ = 4.2); 114.3 (s); 141.0 (d, $J$ = 15.2). $^{31}P$ NMR: 24.3 (s). IR: 3078 (w); 2978 (s); 2926 (s); 2852 (s); 2560 and 2520 (w, $\nu_{SH}$); 1642 (w); 1466 (m); 1450 (m); 1384 (m); 1374 (m); 1354 (m); 1246 (s); 1178 (m); 1142 (m); 1106 (m); 986 (vs); 936 (w); 916 (w); 896 (w); 888 (w); 822 (w); 768 (m); 738 (w). Mass: 266 (23, $M^+$); 224 (11); 182 (41); 181 (64); 180 (29); 149 (27); 108 (21); 107 (23); 101 (58); 100 (79); 99 (100, $CH_2{=}C(CH_3)CH{=}CHS^+$); 98 (43); 97 (35); 96 (20); 84 (91); 83 (87); 82 (25); 67 (24); 59 (25); 58 (24); 55 (14); 49 (36); 48 (37); 47 (24); 46 (26); 43 (57); 42 (55); 41 (41).

*Diisopropyl (1-mercapto-2,2-dimethylbut-3enyl)phosphonate* **2d**. Colourless liquid. Yield = 66%. Analysis: $C_{12}H_{25}O_3PS$: calc. %: S 11.43; obs. %: S 11.79. $^1H$ NMR: 1.27 and 1.29 (2s, 6H); 1.34 and 1.36 (2d, $J$ = 6.2, 12H); 1.96 (d d, $J \approx 9.5$ and $J \approx 9.5$, 1H, SH); 2.75 (d d, $J$ = 18,0 and $J$ = 9.5, 1H, PCHS); 4.75 (sept d, $J \approx 6.2$ and $J \approx 6.2$, 2H); 5.03 (d, $J \approx 17.5$, 1H); 5.04 (d, $J \approx 10.5$, 1H); 6.00 (d d, $J \approx 17.5$ and $J \approx 10.5$, 1H). $^{13}C$ NMR: 23.7 and 24.0 (2d, $J$ = 4.6 and $J$ = 5.1); 25.8 (d, $J$ = 4.9); 26.1 (d, $J$ = 6.6); 40.3 (s); 45.6 (d, $J$ = 145.1); 71.3 and 72.1 (d, $J$ = 7.5); 112.5 (s); 145.3 (d, $J$ = 7.5). $^{31}P$ NMR: 22.7 (s). IR: 3084 (w); 2977 to 2874 (s); 2560 and 2520 (w, $\nu_{S-H}$); 1639 (m); 1467 (m); 1453 (m); 1414 (w); 1384 (m); 1373 (m); 1244 (s); 1117 (m); 1141 (m); 1106 (m); 985 (vs and broad); 913 (w); 896 (m); 812 (w); 773 (m); 740 (w). Mass: 281 (0.5, $MH^+$); 280 (1.5, $M^+$); 238 (2); 211 (10); 169 (15); 128 (68); 127 (65); 115 (10); 69 (14); 59 (10); 53 (13); 49 (43); 45 (19); 43 (100, $C_3H_7^+$); 42 (10); 41 (80).

*Diisopropyl (1-mercapto-2-phenylbut-3-enyl)phosphonate* **2e**. Colourless liquid. Yield = 72%. Mixture of two diastereoisomers **2e$_1$** and **2e$_2$** [70:30, estimated by $^{31}P$ NMR and $^1H$ NMR (SH signals)]. Analysis: $C_{16}H_{25}O_3PS$: calc. %: S 9.76; obs. %: S 10.02. $^1H$ NMR: **2e$_1$**: ≈ 1.3 (2d, $J \approx 6.2$, 12H); 1.98 (d d, $J$ =

8.9 and $J$ = 11.8, 1H, SH); ≈3.1 (m, 1H, PCHS); 4.03 (d d d, $J$ ≈ 8.5, $J$ ≈ 8.5 and $J$ ≈ 4.7, 1H); ≈4.7 (m, 2H); ≈5.16 (≈d, $J$ ≈ 17.1, 1H); ≈5.23 (≈d, $J$ ≈ 10.1, 1H); 6.23 (d d d, $J$ ≈ 17.1, $J$ ≈ 10.1 and $J$ = 8.5, 1H); 7.2 to 7.3 (m, 5H). **2e$_2$**: same signals are observed, except for the SH: 1.81 (d d, $J$ = 8.9 and $J$ = 10.5, 1H). $^{13}$C NMR: **2e$_1$**: ≈ 24.1 (2d, $J$ ≈ 4); 40.8 (d, $J$ = 147.0); 49.9 (s); ≈7.1.7 (d, $J$ ≈ 7.3); 118.2 (s); 126.9, 127.2, ≈ 128.3 and 128.4 (4s); 136.5 (d, $J$ = 5.34). **2e$_2$**: ≈24.1 (2d, $J$ ≈ 4); 40.2 (d, $J$ = 147.9); 51.6 (s); 71.7 (d, $J$ ≈ 7.3); 116.4 (s); around 128 ppm, several signals (aromatic carbons); 139.0 (d, $J$ = 8.9). $^{31}$P NMR: **2e$_1$**: 22.3 (s); **2e$_2$**: 21.8 (s). IR: 3080 (w); 3062 (w); 3028 (m); 2978 (s); 2932 (s); 2874 (m); 2562 and 2520 (w, $\nu_{S-H}$); 1638 (m); 1600 (m), 1584 (m); 1494 (m); 1466 (m); 1454 (m); 1418 (w); 1386 (m); 1374 (m); 1354 (m); 1244 (s); 1178 (m); 1142 (m); 1106 (s); 1074 (s); 988 (vs and broad); 762 (m); 732 (m). Mass: 328 (14, $M^{+\cdot}$); 242 (11); 241 (32); 213 (13); 212 (62); 186 (38); 170 (16); 164 (15); 163 (49); 162 (10); 130 (12); 115 (10); 86 (54); 84 (100, $C_4H_4S^{+\cdot}$); 51 (31); 41 (10).

*Diisopropyl (1-methylthiobut-3-enyl)phosphonate* **3a**. Pale yellow liquid. Yield = 92%. Analysis: $C_{11}H_{23}O_3PS$: calc. %: C 49.60; H 8.70; S 12.03; obs. %: C 49.66; H 8.82; S 11.85. $^1$H NMR: 1.35 (d d, $J$ = 6.2, 12H); 2.26 (s, 3H); ≈2.30 (m, 1H of $CH_2$); ≈2.50 (m, 1H, PCHS); ≈2.70 (m, 1H of $CH_2$); 4.70 (m, 2H); 5.10 (≈ d, $J$ ≈ 10, 1H); 5.15 (≈ d, $J$ ≈ 17, 1H); 5.92 (d d t, $J$ ≈ 17, $J$ ≈ 10 and $J$ = 7, 1H). $^{13}$C NMR: 15.0 (s); 24.0 and 24.3 (2d, $J$ = 5.0 and $J$ = 2.7); 33.1 (s); 41.4 (d, $J$ = 150.1); 71.3 (d, $J$ = 7.1); 117.2 (s); 135.1 (d, $J$ = 13.9). $^{31}$P NMR: 23.5 (s). IR: 3078 (w); 2978 (m); 2926 (m); 2874 (m); 1642 (m); 1468 (m); 1442 (m); 1384 (m); 1374 (m); 1320 (m); 1244 (s); 1178 (m); 1142 (m); 1108 (s); ≈1008 (s); 982 (vs); 936 (m); 914 (m); 896 (m); 886 (w); 882 (w); 768 (m); 740 (w). Mass: 266 (17, $M^{+\cdot}$); 224 (6); 183 (15); 182 (69); 179 (16); 178 (32); 165 (27); 137 (38); 136 (100, $(HO)_2P(O)CH_2CH_2CH{=}CH_2^{+\cdot}$); 101 (26); 85 (18); 61 (27); 59 (17); 55 (68); 53 (34); 45 (18); 43 (66); 41 (53).

*Diisopropyl (1-methylthio-2-methylbut-3-enyl)phosphonate* **3b**. Pale yellow liquid. Yield = 90%. Mixture of two diastereoisomers **3b$_1$** and **3b$_2$** (60:40, estimated by $^1$H NMR on the PCHS signals). Pale yellow liquid. Analysis: $C_{12}H_{25}O_3PS$: calc. %: C 51.40; H 8.98; S 11.43; obs. %: C 51.50; H 8.98; S 11.23. $^1$H NMR: **3b$_1$**: 1.25 (d, $J$ = 6.8, 3H); 1.34 and 1.35 (2d, $J$ = 6.2, 12H); 2.27 (s, 3H); 2.48 (d d, $J$ ≈ 17.7 and $J$ ≈ 3.7, 1H, PCHS); ≈2.8 (m, 1H); 4.79 (sept d, $J$ ≈ 6.2 and $J$ ≈ 7.6, 2H); 5.02 (≈d, $J$ ≈ 10, 1H); 5.04 (d, $J$ ≈ 17); 5.97 (d d d, $J$ = 17, $J$ ≈ 10 and $J$ ≈ 7, 1H). **3b$_2$**: 1.15 (d, $J$ = 6.8, 3H); 1.34 and 1.35 (2d, $J$ ≈ 6.2, 12H); 2.25 (s, 3H); 2.58 (d d, $J$ ≈ 17.7 and $J$ ≈ 3.0, 1H, PCHS); ≈ 2.8 (m); 4.75 (sept d, $J$ ≈ 6.2 and $J$ ≈ 7.6, 2H); 5.09 (d, $J$ ≈ 17, 1H); 5.11 (d, $J$ ≈ 10, 1H); 5.95 (d d d, $J$ ≈ 17, $J$ ≈ 10 and $J$ ≈ 7, 1H). $^{13}$C NMR: **3b$_1$**: 18.1 (s); 19.0 (d, $J$ = 9.1); 23.9 and 24.0 (2d, $J$ = 3.0); 38.1 (s); 49.7 (d, $J$ = 149.6); 71.0 and 71.4 (2d, $J$ = 7.4); 114.9 (s); 139.9 (d, $J$ = 3.6). **3b$_2$**: 15.8 (s); (d, $J$ ≈ 2.9); 24.3 and 24.4 (2d, $J$ ≈ 3); 38.0 (s); 49.7 (d, $J$ = 149.6); 71.4 and 71.5 (2d, $J$ ≈ 7.5); 114.2 (s); 142.1 (d, $J$ ≈ 15.3); $^{31}$P NMR: **3b$_1$**: 23.0 (s); **3b$_2$**: 23.1 (s). IR: 3078 (w); 2978 (s); 2924 (s); 2872 (m); 1640 (m); 1550 (m); 1466 (m); 1452 (m); 1422 (m); 1384 (m); 1374 (m); 1288 (m); 1248 (s); 1178 (m); 1142 (m); 1108 (s); 986 (vs); 936 (m); 914 (m); 896 (m); 888 (m); 830 (w); 770 (m); 744 (m); 704 (w). Mass: 280 (6, $M^{+\cdot}$); 207 (7); 197 (5); 196 (27); 184 (12); 183 (64); 179 (23); 166(7); 165 (11); 151 (13); 150 (99); 149 (29); 143 (45); 142 (48); 141 (71); 115 (15); 99 (6); 96 (2); 56 (39); 45 (100, $SCH^+$); 43 (90); 41 (43).

*Diisopropyl (1-methylthio-3-methylbut-3-enyl)phosphonate* **3c**. Pale yellow liquid. Yield = 80%. Analysis: $C_{12}H_{25}O_3PS$: calc. %: C 51.40; H 8.98; S 11.43; obs. %: C 51.40; H 9.04; S 11.28. $^1$H NMR: 1.35 and 1.36 (2d, $J$ ≈ 6.2, 12H); 1.77 (s, 3H); 2.26 (s, 3H); 2.30 (m, 1H of $CH_2$); 2.67 (m, 2H, PCHS and 1H of $CH_2$); 4.77 (sept d, $J$ ≈ 6.2 and $J$ ≈ 6.2, 2H); 4.85 and 4.90 (≈ 2s, 2H). $^{13}$C NMR: 14.9 (s); 21.6 (s); 24.0 and 24.3 (2d, $J$ = 3.0); 36.6 (s); 39.1 (d, $J$ = 151.5); 71.3 and 71.4 (2d, $J$ = 7.4 and $J$ = 7.2); 113.5 (s); 141.5 (d, $J$ ≈ 14.6). $^{31}$P NMR: 24.0 (s). IR: 3076 (w); 2978 (s); 2926 (m); 2872 (m); 2854 (m); 1650 (m); 1466 (m); 1450 (m); 1384 (m); 1374 (m); 1322 (m); 1244 (s); 1178 (m); 1142 (m); 1106 (s); 982 (vs); 888 (s); 840 (w); 808 (w); 768 (m); 740 (w). Mass: 280 (16, $M^{+\cdot}$); 196 (14); 192 (13); 183 (8); 179 (13); 151 (32); 150 (100, $(HO)_3PCHCH_2C(CH_3){=}CH_2^{+\cdot}$); 149 (35); 143 (8); 141 (20); 123 (8); 115 (22); 109 (8); 99 (16); 85 (9); 69 (60); 68 (15); 67 (46); 65 (19); 61 (11); 59 (11); 43 (37); 41 (37).

*Diisopropyl (1-methylthio-2,2-dimethylbut-3-enyl)phosphonate* **3d**. Pale liquid yellow. Yield = 71%. Analysis: $C_{13}H_{27}O_3PS$: calc. %: C 53.03: H 9.24; S 10.89; obs. %: C 53.27; H 9.26; S 10.89. $^1$H NMR: 1.27 and 1.28 (2s, 6H); 1.34 and 1.35 (2d, $J$ ≈ 6.2, 12H); 2.25 (≈ s, 3H); 2.30 (d, $J$ = 18.0, PCHS); 4.79 (sept d, $J$ = 6.2 and $J$ = 7.3, 2H); 4.99 (≈d, $J$ ≈ 10.7, 1H); 5.02 (≈d, $J$ ≈ 17.4, 1H); 6.07 (d d, $J$ = 17.4 and $J$ = 10.7, 1H). $^{13}$C NMR: 19.9 (≈s); 23.8, 24.0, 24.4 and 24.5 (4d, $J$ = 6.3, $J$ = 5.3, $J$ = 3.5 and $J$ = 2.8); 26.0 (d, $J$ = 5.7); 26.1 (d, $J$ = 5.4); 40.9 (s); 55.7 (d, $J$ = 146.7, PCHS); 71.1 and 71.6 (2d, $J$ = 7.6 and $J$ = 7.7); 111.5 (s); 146.3 (d, $J$ = 7.7). $^{31}$P NMR: 23.2 (s). IR: 3084 (w); 2976 (s); 2926 (s); 2874 (m); 1636 (m); 1466 (m); 1452 (m); 1414 (m); 1384 (m); 1374 (m); 1316 (m); 1244 (s); 1176 (m); 1140 (m); 1106 (s); 1078 (m); 980 (vs); 936 (m); 912 (m); 894 (m); 886 (m); 822 (w); 776 (w);

744 (m); 702 (w). Mass: 294 (7, $M^{+\cdot}$); 293 (12); 292 (12); 240 (13); 234 (29); 227 (16); 221 (61); 194 (21); 182 (63); 181 (34); 163 (13); 142 (53); 141 (16); 127 (11); 124 (13); 113 (10); 99 (14); 96 (14); 95 (32); 83 (28); 82 (40); 81 (48); 79 (39); 77 (19); 73 (12); 69 (36); 67 (36); 65 (20); 61 (21); 59 (34); 55 (28); 53 (23); 43 (65); 41 (100, $C_3H_5^+$).

*Diisopropyl (1-methylthio-2-phenylbut-3-enyl)phosphonate* **3e**. Pale yellow liquid, Yield = 76%. Mixture of two diastereoisomers $\mathbf{3e_1}$ and $\mathbf{3e_2}$ (60:40, estimated by $^1H$ NMR on the $SCH_3$ signals). Analysis: $C_{17}H_{27}O_3PS$: calc. %: S 9.36; obs. %: S 9.11. $^1H$ NMR: $\mathbf{3e_1}$: 1.30 (d, $J \approx 6.2$, 12H); 1.97 (s, 3H); 2.83 (d d, $J = 18.0$ and $J = 4.5$, 1H, PCHS); 4.05 (d d d, $J \approx 8.7$, $J \approx 8.7$ and $J \approx 4.5$, 1H); ≈4.71 (m, 2H); ≈5.11 (d, $J \approx 17$, 1H); ≈5.17 (d, $J \approx 10.1$, 1H); ≈6.26 (d d d, $J \approx 17$, $J \approx 10.1$ and $J = 8.7$, 1H); 7.2 to 7.4 (m, 5H). $\mathbf{3e_2}$: 1.31 (d, $J \approx 6.2$, 12H); 2.21 (s, 3H); 2.91 (d d, $J = 16.9$ and $J = 6.6$, 1H, PCHS); 3.91 (d d d, $J \approx 8.1$, $J \approx 8.1$ and $J \approx 7.0$, 1H); ≈4.71 (m, 2H); ≈5.11 (d, $J \approx 17$, 1H); ≈5.17 (d, $J \approx 10.1$, 1H); ≈6.28 (d d d, $J \approx 17$, $J \approx 10.1$ and $J \approx 8.1$, 1H); 7.2 to 7.4 (m, 5H). $^{13}C$ NMR: $\mathbf{3e_1}$: 17.6 (s); around 24.0 (2d, $J = 2.5$ to 3.0); 49.1 (s); 49.8 (d, $J = 148.2$); 71.4 (d, $J = 7.8$); 117.4 (s); 126.8 to 128.9, several signals (aromatic carbons); 137.3 (d, $J = 4.5$). $\mathbf{3e_2}$: same signals are observed, except for the $\underline{C}{=}{=}CH_2$ signal at 143.0 (d, $J = 12.6$). $^{31}P$ NMR: $\mathbf{3e_1}$ and $\mathbf{3e_2}$: one signal only at 22.0 (s). IR: 3062 (w); 3028 (w); 2978 (s); 2924 (m); 2872 (m); 1676 (w); 1654 (w); 1636 (w); 1600 (m); 1560 (w); 1540 (w); 1494 (m); 1466 (m); 1454 (m); 1420 (m); 1384 (m); 1374 (m); 1318 (w); 1244 (s); 1178 (s); 1142 (m); 1106 (s); 1072 (m); 986 (vs); 918 (m); 888 (m); 810 (w); 762 (m); 740 (m); 700 (m). Mass: 342 (1, $M^{+\cdot}$); 294 (12); 293 (23); 292 (46); 249 (19); 212 (16); 211 (46); 185 (13); 184 (8); 183 (100, $(HO)_3PCCC_6H_5^+$); 131 (16); 130 (14); 129 (24); 128 (19); 123 (10); 117 (39); 115 (26); 114 (18); 91 (28); 86 (25); 84 (43); 83 (13); 81 (9); 77 (24); 73 (11); 71 (13); 69 (16); 65 (11); 59 (18); 57 (16).

*Synthesis of diisopropyl 2-thiolanylphosphonate* **4a**. Under $N_2$, compound **2a** (1 mmol) was dissolved in dry THF (100 ml), and a catalytic amount of azoisobutyronitrile was added. The mixture was stirred and irradiated with UV ("Hanovia" lamp, 50 Hz, 125 Watts, 2A) for 2.5 hours. Then the solvent was evaporated at reduced pressure, and the residue was extracted with ether. The organic layer was washed with water, dried over $Na_2SO_4$, and the ether was evaporated. Crude product was purified by column chromatography (silicagel Merck 60 M, eluent:cyclohexane/ethyl acetate:90/10). Pure **4a** was obtained as a pale yellow liquid, with 76% yield. Analysis: $C_{10}H_{21}O_3PS$: calc. %: S 12.70; obs. %: S 12.16 $^1H$ NMR: 1.33 and 1.64 (2d, $J \approx 6.2$, 12H); 1.9 to 2.3 (m, 4H); 2.90 (d d, $^3J_{HH} \approx 7.2$ and $^3J_{HH} \approx 5.6$, 2H); 3.40 (d t, $^2J_{HP} \approx 15.5$ and $^3J_{HH} \approx 6.2$, 1H, PCHS); 4.77 (sept d, $J \approx 6.2$ and $J \approx 6.2$, 2H). $^{13}C$ NMR: 24.0 and 24.3 (2d, $J = 2.2$ and $J = 3.2$); 31.4 (d, $^2J_{CP} = 8.9$); 32.1 (d, $^3J_{CP} = 2.5$); 33.2 (d, $^3J_{CP} = 3.0$); 41.6 (d, $^1J_{CP} = 156.2$); 71.2 and 71.3 (2d, $J = 7.1$ and $J = 7.2$). $^{31}P$ NMR: 24.8 (s). IR: 2976 (vs); 2964 (vs); 2868 (s); 1466 (m); 1442 (m); 1384 (s); 1374 (s); 1308 (m); 1248 (vs); 1178 (s); 1142 (s); 1108 (vs); 982 (vs); 896 (s); 884 (s); 856 (m); 822 (m); 770 (m); 736 (m); 700 (w). Mass: 252 (30, $M^{+\cdot}$); 169 (11); 168 (100, double McLafferty transposition); 167 (62); 166 (5); 109 (12); 88 (7); 87 (68); 86 (7); 85 (11); 44 (14); 42 (16).

*Procedure B*

*Preparation of the sulfonium salts* **5**. $AgBF_4$ (2.6 mmol, 1.4 eq.) was added under $N_2$ to the sulfide **1** (1.87 mmol) and the mixture was stirred in the dark. After decolourization, methyl iodide (2.6 mmol) and then dry acetonitrile (3 ml) were introduced. The mixture was warmed at 50°C for 3 hours (or kept at room temperature for 6–12 hours) for compounds **5a**–**5c** and **5f**, and heated at 50°C for 5 hours for compounds **5d** and **5e**. The solution was filtered, the solvent was evaporated under reduced pressure at room temperature, and the crude sulfonium salts, not very stable, were used without further purification. Their characterization has been mainly done by $^{31}P$ NMR spectroscopy.

*Allyl-diisopropylphosphonomethyl-methyl-sulfonium tetrafluoroborate* **5a**. $^1H$ NMR: 1.39 and 1.40 (2d, $J = 6.2$, 12H); 3.03 (s, 3H); 3.68 (d, $J = 14.5$, 2H); 4.23 (d d, $J_{AB} \approx 12.8$ and $J \approx 7$, 1H); 4.29 (d, d, $J_{AB} \approx 12.8$ and $J \approx 7$, 1H); 4.85 (sept d, $J = 6.2$ and $J = 6.2$, 2H); 5.75 (≈d, $J \approx 10.9$, 1H); 5.80 (≈d, $J \approx 14.1$, 1H); 5.8 to 6.0 (m, 1H). $^{13}C$ NMR: 23.8 and 24.0 (2d, $J = 5.0$ and $J = 4.1$); 24.1 (d, $J = 3.1$); 33.3 (d, $J = 143.5$); 45.4 (d, $J = 5.0$); 74.9 and 75.0 (d, $J = 6.7$); 122.4 (s); 128.9 (s). $^{31}P$ NMR: 11.1 (s). $^{11}B$ NMR: −0.8 (s). $^{19}F$ NMR: −150.0 (s).

*Crotyl-diisopropylphosphonomethyl-methyl-sulfonium tetrafluoroborate* **5b**. $^1H$ NMR: 1.39 and 1.40 (2d, $J = 6.1$, 12H); 1.84 (d, $J = 6.6$, 3H); 2.99 (s, 3H); 3.62 (d, $J = 15.0$, 2H); 4.21 (d, $J = 8.0$, 2H); 4.85 (sept d, $J = 6.3$ and $J = 6.3$, 2H); 5.51 (d t, $J = 15.2$ and $J = 8.0$, 1H); 6.25 (d qd, $J = 15.2$ and $J = 6.6$, 1H). $^{31}P$ NMR: 11.7 (s).

*Diisopropylphosphonomethyl-methylallyl-methyl-sulfonium tetrafluoroborate* **5c**. $^{31}P$ NMR: 11.4 (s).

*Diisopropylphosphonomethyl-methyl-prenyl-sulfonium tetrafluoroborate* **5d**. $^{31}P$ NMR: 11.6 (s).

*Cinnamyl-diisopropylphosphonomethyl-methyl-sulfonium tetrafluoroborate* **5e**. $^{31}P$ NMR: 11.3 (s).

*Benzyl-diisopropyl-methyl-sulfonium tetrafluoroborate* **5f**. $^{31}P$ NMR: 11.4 (s).

*Procedure C*

*Preparation and [2,3]-sigmatropic rearrangement of the ylides of the sulfonium salts* **5**. To a solution of the sulfonium salts **5** (1.87 mmol), prepared according to procedure B, in dry THF (3 ml) was added dropwise at −60°C and under $N_2$ a solution of BuLi (1.87 mmol in hexane). The mixture was stirred for 2 hours at −60°C, and then quenched with 1 ml acidic MeOH (5% HCl, ph = 3). Extraction with ether, washing with brine, and evaporation of the solvent led crude sulfides **3a**–**3e** which were purified by column chromatography (silicagel Merck 60 M, petroleum ether/ethyl acetate 80/20). Compounds **3** are already described above. The not separated crotyl $\mathbf{3b_1}$ and $\mathbf{3b_2}$ derivatives were obtained in the ratio 90/10. No product **3d** or **3e** or **3f** has been obtained, even when rising the temperature to −20°C.

*Preparation of the diisopropyl [1-(benzyl-methyl-sulfanylidene)-2-phenylamino-2-oxo-ethyl] phosphonate* **6f**. A solution in dry THF (5 ml) of the sulfonium salt **5f** (2 mmol), prepared according to procedure B, was added to a suspension of HNa (2 mmol) in dry THF (5 ml) under $N_2$ at −20°C, and the mixture was stirred at −20°C for 20 mn. Then phenyl isocyanate (2 mmol) was added at −20°C, and the mixture was stirred for 24 hours, allowing the temperature to rise to +20°C. The dark solution thus obtained was dropped into a mixture of saturated aqueous $NH_4Cl$ and ether/pentane (70/30). The organic layer was washed with brine and dried over $Na_2SO_4$. The solvent was evaporated under reduced pressure. Several column chromatographies (silicagel Merck 60 M, eluent:cyclohexane/ethylacetate 80/20 to 40/60) yielded compound **6f** as a yellow oil. Yield = 42%. $^1$H NMR: 1.12, 1.23, 1.25 and 1.30, (4d, $J$ = 6.0, 12H); 2.88 (s, 3H); 4.3 and 4.4 (2 sept d, $J$ = 6.2 and $J$ = 8.2, 2H); 4.75 (s, 2H); 6.97 (t, $J \approx$ 7.4, 1H); 7.29 (t, $J \approx$ 7.4, 2H); 7.38 (s, 5H); 7.54 (d, $J \approx$ 7.4, 2H); 9.78 (s, 1H). $^{13}$C NMR: 24.0 to 26.3 (several signals, $(\underline{C}H_3)_2CH$, $CH_3S^+$ and $C^-$); 49.4 (s); 69.8 and 70.0 (2d, $J$ = 5.5 and $J$ = 5.6); 119.5 (s); 122.1 (s); 128.8 (s); 129.1 (s); 129.3 (s); 130.6 (s); 130.9 (s); 140.2 (s); 167.5 (d, $J$ = 20.7). $^{31}$P NMR: 24.0 (s).

*Syntheses of compounds* **7**, **8** *and* **9**. The sulfonium salt **7** was prepared according to procedure B by reacting compound **1b** with allyl iodide in the presence of $AgBF_4$. The corresponding "mixed" ylide **II**, prepared with the salt **7** and 1.1 equivalent of LDA in THF, and submitted to the [2,3]-sigmatropic rearrangement according to procedure C, led to the sulfide **8** only. Sulfides **8** and **9** were independently prepared with compounds **1a** and **1b** respectively, butyllithium, and the appropriate allylic halides at −20°C, according to procedure *A*.

*Allyl-diisopropylphosphonomethyl-methallyl-sulfonium tetrafluoroborate* **7**. Viscous yellow liquid. Yield: ≈90% (crude material). $^1$H NMR: 1.39 and 1.40 (2d, $J$ = 6.2, 12H); 1.92 (s, 3H); 3.60 (d d, $J_{AB}$ = 15 and $J_{HP}$ = 14, 1H of $PCH_2S$); 3.68 (d d, $J_{AB}$ = 15 and $J_{HP}$ = 14, 1H of $PCH_2S$); 4.19 (d, $J_{AB} \approx$ 11.6, 1H, $CH_2$ of methallyl) and 4.36 (d, $J_{AB}$ = 11.6, 1H, $CH_2$ of methallyl); 4.27 (m, 1H, $CH_2$ of allyl) and 4.40 (m, 1H, $CH_2$ of allyl); 4.83 (sept d, $J$ = 6.2 and $J$ = 7.3, 2H); 5.37 (≈s, 1H, methallyl) and 5.47 (≈s, 1H, methallyl); 5.7 to 6.0 (m, 3H, allyl). $^{31}$P NMR: 10.9 (s).

*Diisopropyl (1-methallylthiobut-3-enyl)phosphonate* **8**. Pale yellow liquid. Yield = 80%. Analysis: $C_{14}H_{27}O_3PS$: calc. %: S 10.46; obs. %: 10.56. $^1$H NMR: 1.34 and 1.35 (2d, $J$ = 6.2, 12H); 1.82 (s, 3H); 2.2 to 2.4 (m, 1H of $CH_2$ of allyl); ≈2.5 to 2.7 (m, 2H, PCHS and 1H of $CH_2$ of allyl); 3.14 (d, $J$ = 13.2, 1H of $CH_2$ of methallyl); 3.52 (≈d, $J$ = 13.2, 1H of $CH_2$ of methallyl, by 2D ($^1$H-$^{13}$C) NMR); 4.78 (sept d, $J$ = 6.2 and $J$ = 7.3, 2H); 4.87 (≈s, 2H); 5.08 (≈d, $J \approx$ 10, 1H); 5.12 (≈d, $J \approx$ 17, 1H); 5.87 (d d t, $J \approx$ 17, $J \approx$ 10 and $J$ = 7.5, 1H). $^{13}$C NMR: 20.8 (s); 24.0 to 24.4 (m); 34.0 (s, $CH_2$ of allyl); 38.6 (d, $J$ = 151.0); 40.0 (s, $CH_2$ of methallyl); 70.9 and 71.5 (2d, $J$ = 7.2); 114.7 (s, $\underline{C}H_2{=}C$ of methallyl by 2D ($^1$H-$^{13}$C)NMR); 117.2 (s, $\underline{C}H_2{=}C$ of allyl); 135.2 (d, $J \approx$ 13.3, allyl); 140.7 (s, methallyl). $^{31}$P NMR: 23.9 (s). IR: 3078 (w); 3028 (w); 2978 (s); 2934 (m); 2874 (m); 1642 (w, $\nu$ C=C of allyl); 1558 (w); 1466 (m); 1454 (m); 1440 (m); 1384 (m); 1374 (m); 1318 (w); 1252 (s); 1178 (s); 1142 (m); 1108 (s); 982 (vs); 912 (m); 896 (m); 824 (w); $\nu$C=C of the methallyl is not seen. Mass: 306 (27, $M^+$); 305 (13); 221 (17); 216 (19); 215 (100); 201 (17); 177 (19); 136 (77); 135 (12); 96 (13); 87 (11); 85 (26); 55 (30); 43 (14); 41 (16).

*Diisopropyl (1-allylthio-3-methylbut-3-enyl)phophonate* **9**. Pale yellow liquid. Yield = 80%. Analysis: $C_{14}H_{27}O_3PS$: calc. %: S 10.46; obs. %: S 11.19. $^1$H NMR: 1.34 and 1.37 (2d, $J$ = 6.3, 12H); 1.72 (s, 3H); ≈2.25 (m, 1H, $CH_2$ of allyl, by 2D); 2.6 to 2.8 (m, 2H, PCHS and 1H of $CH_2$ of allyl); 3.21 (d d, $J \approx$ 13.3 and $J$ = 6.0, 1H, $CH_2$ of methallyl); 3.60 (d d, $J \approx$ 13.3 and $J$ = 8.6, 1H, $CH_2$ of methallyl); 4.80 (sept d, $J$ = 6.3 and $J$ = 7.3, 2H); 4.81 (≈s, 1H) and 4.87 (≈s, 1H); 5.13 (≈d, $J \approx$ 10, 1H); 5.17 (≈d, $J \approx$ 17, 1H); 5.78 (d d d d, $J \approx$ 17, $J \approx$ 10, $J \approx$ 8.5 and $J \approx$ 6.0, 1H). $^{13}$C NMR: 21.7 (s); 24.0 to 24.4 (m); 35.2 (s, $CH_2$ of methallyl); 36.1 (d, $J$ = 152.5); 37.5 (s, $CH_2$ of allyl); 71.0 (2d, $J$ = 7.2); 113.7 (s, $\underline{C}H_2{=}C$ of methallyl by 2D ($^1$H-$^{13}$C) NMR); 118.1 (s, $\underline{C}H_2{=}C$ of allyl by 2D ($^1$H-$^{13}$C) NMR); 133.7 (s, allyl); 141.4 (d, $J \approx$ 14.8 methallyl). $^{31}$P NMR: 24.4 (s). IR: 3078 (w); 3028 (w); 2978 (s); 2934 (m); 2874 (m); 2362 (w); 1652 (w, $\nu$ C=C of methallyl); 1634 (w, $\nu$C=C of allyl); 1558 (w); 1540 (w); 1506 (m); 1466 (m); 1452 (m); 1384 (m); 1374 (m); 1252 (s); 1178 (s); 1142 (m); 1108 (s); 1008 (s); 982 (vs); 920 (m); 888 (m); 838 (w); 808 (w). Mass: 306 (1, $M^+$); 234 (11); 151 (15); 150 (41); 99 (17); 91 (9); 85 (20); 81 (17); 69 (24); 68 (9); 67 (17); 65 (17); 59 (12); 55 (16); 53 (18); 45 (21); 43 (100, $C_3H_7^+$); 42 (10); 41 (90).

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