Synthesis and Reactivity of Diethyl (Methylthio)(trimethylsilyl)methylphosphonate[1]

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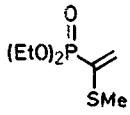
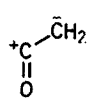
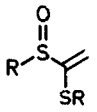
The title compound is obtained in 80% yield by silylation of the lithium salt of diethyl 1-methylthiomethylphosphonate. Other approaches involving sulfenylation of diethyl 1-trimethylsilylmethylphosphonate or the Arbuzov reaction of triethyl phosphite with bromo(methylthio)(trimethylsilyl)methane are less efficient. Aldehydes react with the lithium salt of diethyl (methylthio)(trimethylsilyl)methylphosphonate to give the corresponding 1-methylthioethenylphosphonates in good yields (60–85%) while the reaction with ketones is more complex and Peterson reaction products are formed in very low yields. Methylation, silylation, sulfenylation, and oxidation of the title compound are also described.

In the course of our work[2,3] on the utilization of organic phosphorus and sulphur compounds in synthetic and stereochemical studies we have synthesized[4,5] diethyl 1-methylthioethenylphosphonate (**1a**). This compound is a new Michael acceptor and was successfully used in the total synthesis of dihydrojasmone[4] and α-sulfenylated ketones.[5] It is worthy of note that vinylphosphonate **1a** represents a new acetyl anion equivalent shown below and that its reactivity may be compared with that of the ketene dithioacetal *S*-oxides[6] **2**.



1a





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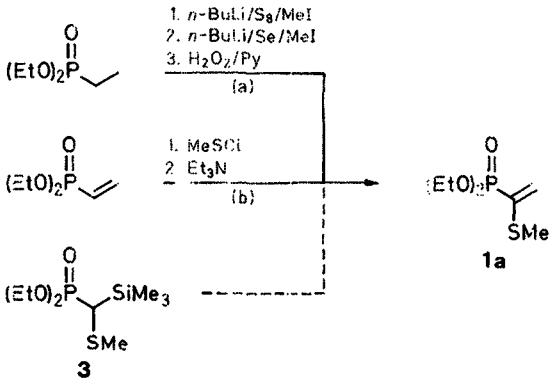
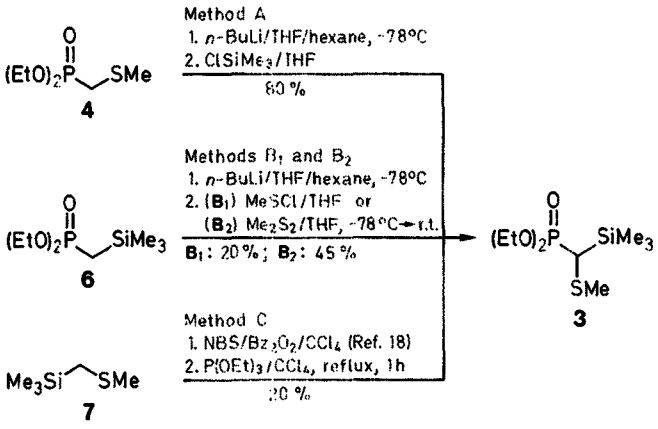
The synthesis of vinylphosphonate **1a** has been accomplished in two ways: (a) consecutive addition of sulfur and selenium to the phosphonate α-carbanion followed by the known selenoxide elimination reaction;[4] (b) addition of methylsulfenyl chloride to diethyl ethenylphosphonate followed by dehydrochlorination.[5] Considering other possible approaches to **1a** and to other sulfur-containing vinylphosphonates in general we turned our attention to diethyl (methylthio)(trimethylsilyl) methylphosphonate (**3**) as a potential starting reagent.



Because of the presence of the trimethylsilyl group in phosphonate 3, the lithio derivative of 3 was expected to undergo the Peterson but not the Horner–Wittig reaction with carbonyl compounds to afford the desired vinylphosphonates. Such a reaction course of α-trimethylsilylphosphonate carbanions is documented in the literature.[7–12] In the present paper, we describe the synthesis of diethyl (methylthio)(trimethylsilyl) methylphosphonate (3), its reaction with aldehydes and ketones, and other aspects of the reactivity of this new reagent.

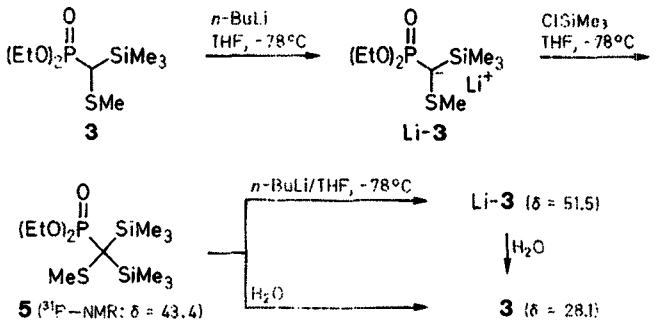
Synthesis and Stability of Diethyl (Methylthio)(trimethylsilyl)methylphosphonate (3)

Compound 3 was obtained in three different ways (Scheme A).



Scheme A

The most efficient approach (Method A) was the reaction of chlorotrimethylsilane with the lithium salt of diethyl methylthiomethylphosphonate (4) which affords 3 in 80% yield. Since fast proton exchange occurs between 3 and the lithiated substrate 4, the optimum ratio of reagents in this synthesis, i.e., 4/*n*-BuLi/$ClSiMe_3$, was found to be 1:1.5:1 by ^{31}P-NMR spectrometry. The use of excess chlorotrimethylsilane in this reaction does not lower the yield of 3 because the product of exhaustive silylation (5) is very water-sensitive; it hydrolyses quantitatively to 3 during the aqueous work-up. An attempt to isolate 5 in pure form was unsuccessful; however, its formation was supported by ^{31}P-NMR spectrometry and by the additional experiments summarized in Scheme B.



Scheme B

The introduction of the methylthio group into phosphonate 6 was carried out by treatment of its lithium salt with either methylsulfenyl chloride (Method B_1) or dimethyl disulfide (Method B_2). By Method B_1, compound 3 was obtained in only 20% yield (whereas a 45% yield of 3 was obtained using Method B_2). The optimum ratio of reagents, i.e., 6/*n*-BuLi/Me_2S_2 was found to be 1:1.5:1 by low-temperature ^{31}P-NMR spectrometry. The use of an excess of dimethyl disulfide in Method B_2 leads to a decrease in yield of 3 and the formation of diethyl bis(methylthio)methyl phosphonate.

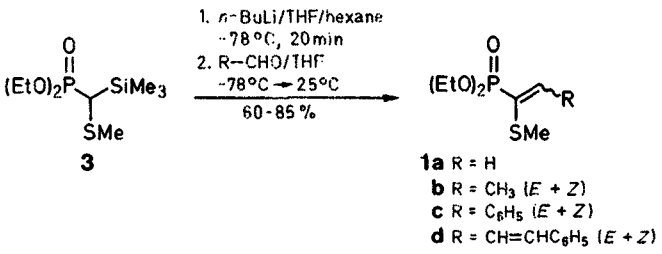
The third approach to 3 (Method C) consisting of the Arbuzov reaction of triethyl phosphite with 1-bromo-1-methylthio-1-trimethylsilylmethane formed *in situ* from (methylthiomethyl)trimethylsilane (7) and *N*-bromosuccinimide afforded the desired product in only 20% yield. Due to the formation of various side-products the yield of 3 could not be increased.

Investigation of the stability of compound 3 under various conditions showed that 3 is stable in a mixture of water and methanol both at room temperature and at the boiling point. Chloroform solutions of 3 may be washed with saturated aqueous sodium or potassium carbonate at room temperature. However, in boiling aqueous sodium carbonate compound 3 was hydrolysed to 4 to an extent of 50% after 2 hours. On treatment with aqueous sodium hydroxide, compound 3 undergoes complete hydrolysis to 4.

The reaction of 3 with butyllithium under standard conditions (−78 °C, THF) results in deprotonation only. The lithio derivative of 3 is sufficiently stable within a wide temperature range from −78 °C to +65 °C; after 48 h storage at room temperature, it still possesses 50% of its initial activity.

Reaction of Diethyl (Methylthio)(trimethylsilyl)methylphosphonate (3) with Aldehydes

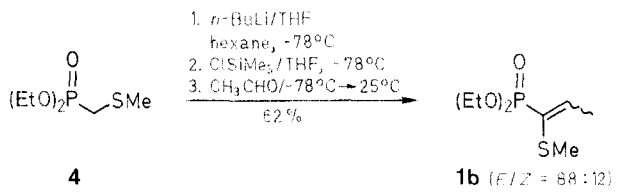
The reaction of the lithium salt of 3 with saturated, α,β-unsaturated, and aromtic aldehydes was found to proceed smoothly at −78 °C affording the corresponding Peterson reaction products 1a–d in 60–85% yields (Scheme C and Table). The reaction is highly stereoselective and gives predominantly or exclusively the *E*-isomers of 1b, c, d. Monitoring each reaction by ^{31}P-NMR spectrometry at −78 °C revealed only the immediate disappearance of the signal of Li-3 ($\delta = 51.5$) and appearance of a new signal corresponding to the alkenylphosphonate formed.



Scheme C

To obtain vinylphosphonate 1a, the lithium salt of 3 was treated with gaseous formaldehyde; the reaction was completed within a short time at −78 °C and 1a was isolated in 60% yield (Method D). A more convenient procedure (Method E) consists of heating a tetrahydrofuran solution of Li-3 with paraformaldehyde for 2 hours to afford 1a also in 60% yield.

In addition, we found that 1-methylthio-1-propenylphosphonate (1b) can be prepared directly from diethyl methylthiomethylphosphonate (4) in 62% yield by successive treatment with butyllithium, chlorotrimethylsilane, and acetaldehyde (Scheme D).

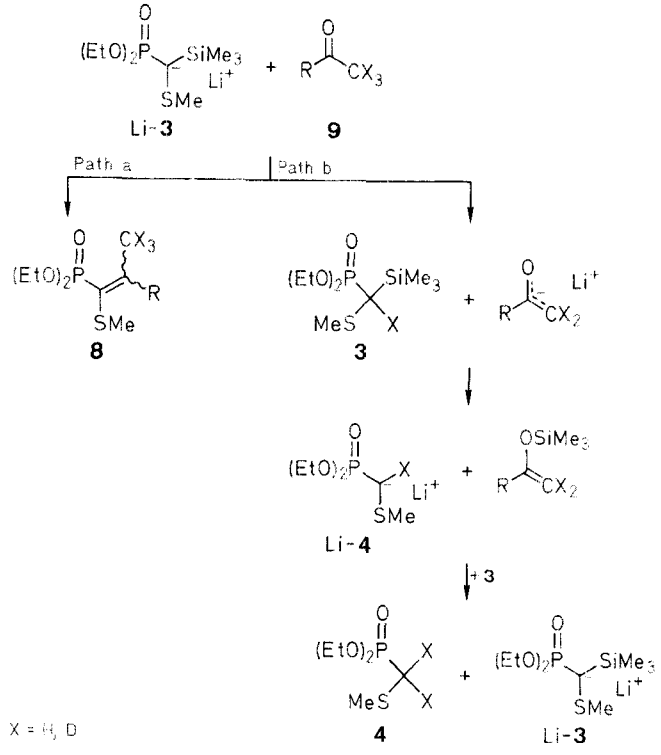


4 **1b** (E/Z = 88:12)

Scheme **D**

Reaction of Diethyl (Methylthio)(trimethylsilyl)methylphosphonate (3) with Ketones

The positive results reported for the Peterson reaction of α-silylated phosphonates,[7,9-11] sulfides,[7,13,14] and sulfoxides[15] with ketones lead us to investigate the reaction of compound **3** with ketones. We found that the treatment of Li-**3** with acetone resulted in the formation of the expected product, diethyl 1-methylthio-2-methyl-2-propenylphosphonate **(8)** in only 5% yield together with the methylthiomethylphosphonate **4** (55%), the starting phosphonate **3** (20%), and unidentified products (20%). Monitoring of the reaction by ^{31}P-NMR spectrometry upon addition of a solution of equimolecular amounts of acetone to the solution of Li-**3** in tetrahydrofuran at −78 °C showed the appearance of three signals at δ = 28.1, 51.5, and 15.5 with an intensity ratio of 35:60:5. These signals correspond to phosphonate **3**, its lithium salt Li-**3**, and vinylphosphonate **8**, respectively. The ^{31}P-NMR spectrum of the reaction mixture recorded at −20 °C showed a new signal at δ = 24.3, due to the presence of the methylthiomethylphosphonate **4** (5%), and the signals of **3** and **8** in a 90:5 ratio. Further increase of the temperature from −20 °C to +25 °C caused a continuous increase in the intensity of the signal of **4** up to 55% at the expense of the signal of **3**. Simultaneously, the spectrum revealed the formation of by-products (20%) and the presence of Li-**3** (15%). Based on these observations, the following main reaction pathways may be proposed (Scheme **E**):

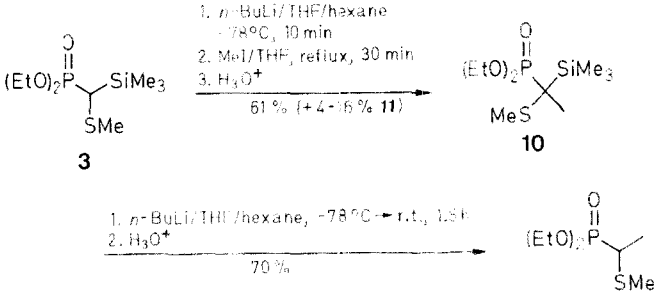


Scheme **E**

The reaction of Li-**3** with ketones **9** may thus proceed by two competitive pathways. The minor, first one (Path a) is the Peterson reaction leading to **8**. The predominant reaction (Path b) involves deprotonation of the enolizable ketone **9** by Li-**3** in the first step, followed by the interaction between the resultant lithium enolate and product **3** resulting in desilylation of **3** to give the lithio derivative Li-**4** and the silyl enolate. This reaction step was confirmed by an independent experiment. In the last step, due to a fast proton exchange between **3** and Li-**4**, methylthiomethylphosphonate **4** and Li-**3** are formed as the final reaction products. In accord with this proposed mechanism, the reaction of Li-**3** with acetone-d_6 gave **4**-1,1-d_2 and vinylphosphonate **8**-d_6 (R = CD_3, X = D) in 45% and 26–35% yield, respectively. The higher yield of **8** observed in this case may be considered to reflect the primary hydrogen isotope effect in this reaction.

Methylation of Diethyl (Methylthio)(trimethylsilyl)methylphosphonate (3)

In contrast to the silylation of Li-**3** and the Peterson reaction with aldehydes (both proceeding at low temperatures), the methylation of Li-**3** with methyl iodide requires more forced conditions (30 min reflux) and gives diethyl 1-methylthio-1-trimethylsilylethylphosphonate **(10)** in 61% yield together with small amounts (4–16%) of diethyl 1-methylthioethylphosphonate **(11)** as a by-product (Scheme **F**).

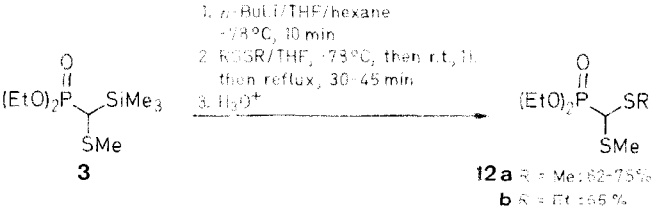


Scheme **F**

Compound **11** is formed from **10** upon treatment with butyllithium as proven by an independent experiment. Thus, the mixture of products **10** and **11**, formed in the first step, on heating in tetrahydrofuran gave **11** in 70% yield.

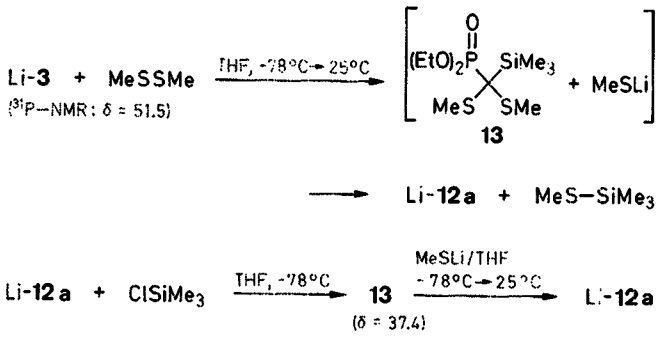
Reaction of Diethyl (Methylthio)(trimethylsilyl)methylphosphonate (3) with Disulfides

The formation of diethyl bis(methylthio)methylphosphonate **(12a)** as a by-product in the synthesis of **3** from **6** and disulfides indicated the possibility to synthesize diethyl bis(alkylthio)methylphosphonates **12** from equimolecular amounts of **3** and disulfides. Indeed, dimethyl and diethyl disulfide were found to react with Li-**3** to give the bis(alkylthio)methylphosphonates **12a** and **12b** in 62–75% and 65% yield, respectively (Scheme **G**).



Scheme **G**

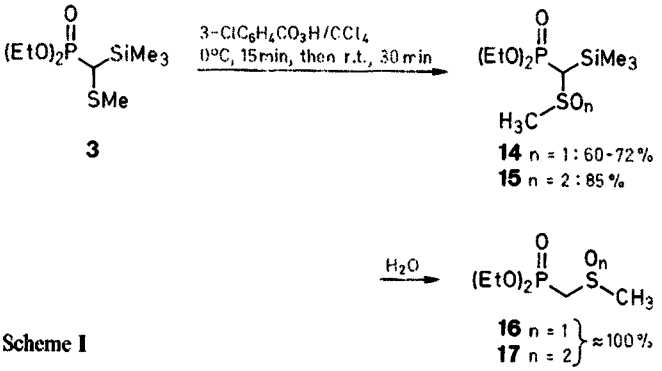
The reaction of Li-3 with dimethyl disulfide was followed by ^{31}P-NMR spectrometry. The results are summarized in Scheme H. Although we were not able to observe the signal of diethyl bis(methylthio)(trimethylsilyl)methylphosphonate **13** due to its fast reaction with lithium methanethiolate, the intermediary formation of **13** in this reaction is supported by the fact that an NMR sample of independently prepared **13** also gave Li-**12a** on treatment with lithium methanethiolate or butyllithium.



Scheme H

Oxidation of Diethyl (Methylthio)(trimethylsilyl)methylphosphonate (3)

Compound **3** was found to be readily oxidized by 3-chloroperoxybenzoic acid. The use of an equimolecular amount of oxidizing agent leads to the corresponding sulfoxide **14** which is contaminated with 13% of the sulfone **15**. The latter was the only product when two molecular equivalents of oxidizing agent were used (Scheme I). Compounds **14** and **15** were characterized by their ^{1}H- and ^{31}P-NMR spectra. Most probably, the sulfoxide **14** is a mixture of two diastereoisomers; however, in the 60 MHz ^{1}H-NMR spectrum these isomers could not be distinguished. Due to sensitivity towards water, usual work-up of **14** and **15** gave the desilylated products, i.e., sulfoxide **16**[16] and sulfone **17**.[17] No attempt was made to isolate compounds **14** and **15**.



Scheme I

Melting and boiling points are uncorrected. Mass spectra were recorded on a LKB 2091 mass spectrometer. ^{1}H-NMR spectra were recorded with Perkin Elmer R-12B (60 MHz) and Tesla BS-487 C (80 MHz) spectrometers using tetramethylsilane (TMS) or hexamethyldisiloxane (HMDSO) as internal standards. ^{13}C-NMR spectra were obtained with a Jeol JNM-C-60 HL spectrometer using TMS as internal standard. ^{31}P-NMR spectra were measured on a Bruker HFX-72 (24.3 MHz) using 85% H_3PO_4 as external standard. The low-temperature ^{31}P-NMR measurements were performed in 10 mm tubes cooled with liquid N_2 or acetone/dry ice.

Commercially available chemicals were purified by distillation or recrystallization immediately before use. All solvents used were purified by standard procedures; THF was distilled from $LiAlH_4$. Silica gel 60 F_{254} plates (Merck) were used for analytic and preparative chromatography. Silica gel (Merck, 70–230 mesh) was used for column chromatography.

Table. Diethyl 1-Methylthio-1-alkenylphosphonates **1a–d** Prepared

Product	Yield (%)	*E*/*Z* (Method)	n_D^{20}	Molecular Formula[a] or Lit. n_D^{20}	MS (70 eV) *m*/*z* (%)	^{1}H-NMR (CDCl$_3$/TMS) δ, *J*(Hz)	^{13}C-NMR (CDCl$_3$/TMS) δ, *J*(Hz)	^{31}P-NMR δ(solvent)
1a	60	–	1.4850	1.4854[5]	210 (M$^+$, 63)	1.32 (t, 6H, $^3J_{H,H}$ = 7.3, 2OCH$_2$CH$_3$); 2.30 (s, 3H, SCH$_3$); 4.05 (dq, 4H, $^3J_{P,H}$ = 7.3, 2OCH$_2$CH$_3$); 5.60 (d, 1H, $^3J_{P,H}$ = 43.3, *trans*-C=CH); 6.12 (d, 1H, $^3J_{P,H}$ = 22.7, *cis*-C=CH)	12.73 (d, ^3J = 7.8, OCH$_2$CH$_3$); 14.16 (d, ^3J = 7.8, SCH$_3$); 60.62 (d, ^2J = 5.9, OCH$_2$CH$_3$); 119.81 (d, ^2J = 7.8); =CH$_2$); 135.02 (d, ^1J = 179.7, P–C)	12.8 (CCl$_4$)
1b	85	100/0 (D) 88/12 (F)	1.4800	$C_8H_{17}O_3PS$ (224.3)	224 (M$^+$, 74)	1.33 (t, 6H, $^3J_{H,H}$ = 7.5, 2OCH$_2$CH$_3$); 2.00 (dd, 3H, $^2J_{H,H}$ = 7.0, $^4J_{H,P}$ = 3.0, CHCH$_3$); 2.30 (s, 3H, SCH$_3$); 4.10 (dq, 4H, $^3J_{H,P}$ = 7.5, 2OCH$_2$CH$_3$); 7.08 (dq, 1H, $^3J_{H,H}$ = 7.0, $^3J_{H,P}$ = 18.5, CHCH$_3$)	13.48 (s, CHCH$_3$); 14.37 (d, ^3J = 7.3, OCH$_2$CH$_3$); 15.43 (s, SCH$_3$); 60.18 (d, ^2J = 7.3, OCH$_2$CH$_3$); 124.3 (d, $^1J_{P,C}$ = 190.4, P–C); 147.0 (d, ^2J = 14.6, CHCH$_3$)	15.6 (CDCl$_3$)
1c	83	100/0	1.5590	oil[8]	286 (M$^+$, 58)	1.30 (t, 6H, $^3J_{H,H}$ = 7.5, 2OCH$_2$CH$_3$); 2.43 (s, 3H, SCH$_3$); 4.11 (dq, 4H, $^3J_{H,P}$ = 7.5, 2OCH$_2$CH$_3$); 7.15–8.00 (m, 6H, C$_6$H$_5$CH)[b]	14.23 (d, ^3J = 5.8, OCH$_2$CH$_3$); 15.21 (d, ^3J = 3.9, SCH$_3$); 60.36 (d, ^2J = 5.8, OCH$_2$CH$_3$); 123.06 (d, ^1J = 183.6, P–C); 126.18, 127.09, 128.26, 132.2, 133.59 (m, C$_6$H$_5$); 142.88 (d, ^2J = 13.6, =CH)	16.2 (CDCl$_3$)
1d	81	85/15	1.6055	$C_{15}H_{21}O_3PS$ (312.4)	312 (M$^+$, 48)	1.35 (t, 6H, $^3J_{H,H}$ = 7.5, 2OCH$_2$CH$_3$); 2.42 (s, 3H, SCH$_3$); 4.16 (dq, 4H, $^3J_{H,P}$ = 7.5, 2OCH$_2$CH$_3$); 6.76–7.87 (m, 8H, =HC–CH=CHC$_6$H$_5$	14.68 (d, ^3J = 3.9, OCH$_2$CH$_3$); 16.63 (s, SCH$_3$); 60.68 (d, ^2J = 5.8, OCH$_2$CH$_3$); 122.67 (d, ^1J = 195.3, P–C); 121.63, 122.80, 125.79, 127.10, 134.50, 139.30 (m, C$_6$H$_5$, P–C=CH); 146.84 (d, ^2J = 20.6, P–C=CH)	16.5 (CDCl$_3$)

[a] Satisfactory microanalyses: C ±0.3, H ±0.3, P ±0.1, S ±0.3.

[b] Measured without solvent with TMS as internal standard.

All reactions with butyllithium were performed under an argon atmosphere.

Diethyl (Methylthio)(trimethylsilyl)methylphosphonate (3):

Method A: A 1.35 M solution of *n*-BuLi in hexane (60 mL, 81 mmol) is added dropwise to a stirred solution of diethyl 1-methylthiomethylphosphonate (**4**; 15.84 g, 81 mmol) in dry THF (300 mL) at −78 °C over a period of 15 min. Then, a solution of $ClSiMe_3$ (4.34 g, 40 mmol) in THF (40 mL) is added and stirring is continued for 15 min. A 0.35 M solution of *n*-BuLi in hexane (30 mL, 40.5 mmol) is added dropwise at −78 °C, followed after 15 min by a solution of $ClSiMe_3$ (4.34 g, 40 mmol) in THF (40 mL) at −78 °C. Then, the mixture is slowly warmed to room temperature, then evaporated. The crude product is dissolved in pentane (200 mL), and this solution is washed with H_2O (2 × 100 mL), dried ($MgSO_4$), and evaporated. The residue is distilled in vacuum to give **3** as a colorless liquid; yield: 17.2 g (80%); bp 66 °C/0.15 mbar; n_D^{20} 1.4694.

$C_9H_{23}PSSiO_3$	calc	C 39.97	H 8.87	P 11.45	S 11.86	
(270.4)	found	40.18	8.78	11.15	12.20	

MS (70 eV): *m/z* (%) = 270 (M^+, 41).

^{1}H-NMR (without solvent/TMS): δ = 0.18 [s, 9 H, $Si(CH_3)_3$]; 1.28 (t, 6 H, $2OCH_2C\underline{H}_3$, $^3J_{H,H}$ = 7.2 Hz); 2.01 (d, 1 H, PCH, $^2J_{H,P}$ = 16.0 Hz); 2.29 (s, 3 H, SCH_3); 4.10 (dq, 4 H, $2OC\underline{H}_2CH_3$, $^3J_{H,H}$ = 7.2 Hz).

^{13}C-NMR ($CDCl_3$): δ = 3.37 [s, $Si(CH_3)_3$]; 14.68 (d, ^3J = 7.8 Hz, $OCH_2\underline{C}H_3$); 17.54 (s, SCH_3); 27.87 (d, ^2J = 134.8 Hz, PCH); 60.69 (d, ^2J = 7.8 Hz, $O\underline{C}H_2CH_3$).

^{31}P-NMR ($CDCl_3$): δ = 28.5.

Method B_2: A 1.35 M solution of *n*-BuLi in hexane (8.2 mL, 11 mmol) is added to a stirred solution of diethyl trimethylsilylmethylphosphonate (**6**; 2.24 g, 10 mmol) in dry THF (80 mL) at −78 °C over a period of 10 min. Then, a solution of dimethyl disulfide (0.47 g, 5 mmol) in THF (20 mL) is added, stirring at −78 °C is continued for 10 min, a solution of *n*-BuLi (as above) is added dropwise, stirring at −78 °C is continued for 10 min, a solution of dimethyl disulfide (0.47 g, 5 mmol) in THF (10 mL) is added, and stirring at −78 °C is continued for 10 min. The mixture is then allowed to slowly warm to room temperature, the solvent is evaporated, and the residue is dissolved in CH_2Cl_2 (70 mL). This solution is washed with H_2O (2–3 × 40 mL), dried ($MgSO_4$), and evaporated. The residue is distilled in vacuum to afford **3**; yield: 1.21 g (45%).

Method B_1: The procedure of Method B_2 is followed with the modification that methylsulfenyl chloride (MeSCl; 0.83 g, 10 mmol) is used in place of dimethyl disulfide for the sulfenylation of Li-**6**; yield of **3**: 0.83 g (20%).

Method C: A solution of *1-Methylthioethenylphosphonate* is prepared according to Lit.[18] by heating to reflux a mixture of (methylthiomethyl)trimethylsilane (**7**; 1.34 g, 10 mmol), NBS (1.96 g, 11 mmol), CCl_4 (10 mL), and dibenzoyl peroxide (484 mg, 2 mmol) for 1 h. The solution is allowed to cool to 25 °C and $P(OEt)_3$ (1.66 g, 10 mmol) is added with stirring. The mixture is then heated to reflux for 1 h, the solvent is evaporated at reduced pressure, and the residue is column-chromatographed on silica gel using benzene/acetone gradient as eluent to give **3** as an oil; yield: 0.54 g (20%).

Diethyl 1-Methylthioethenylphosphonates 1a–d; General Procedures:

Method D (for phosphonates **1b, c, d**; Scheme C): A 1.35 M solution of *n*-BuLi in hexane (8.2 mL, 11 mmol) is added to a stirred solution of diethyl (methylthio)(trimethylsilyl)methylphosphonate (**3**; 2.7 g; 10 mmol) in dry THF (50 mL) at −78 °C. Stirring is continued for 20 min and a solution of the aldehyde (10 mmol) in THF (20 mL) is added. The mixture is then slowly warmed to room temperature, the solvents are removed, and the residue is dissolved in $CHCl_3$ (100 mL). This solution is washed with saturated aq. NH_4Cl (2 × 50 mL) and with H_2O (2 × 50 mL), dried ($MgSO_4$), and evaporated to afford the crude product **1b, c, d** which is purified by column chromatography on silica gel (benzene/acetone gradient as eluent) (Table).

Method E (for phosphonate **1a**; Scheme C): Compound **1a** is prepared according to the Method D from **3** and gaseous formaldehyde generated by thermal decomposition of paraformaldehyde. When paraformaldehyde is employed instead of gaseous formaldehyde the mixture has to be heated to reflux for 2 h after the addition of paraformaldehyde; yield in both cases: 60% (Table).

Method F (One-pot Synthesis from **4**): Solutions of *n*-BuLi (1.35 M) in hexane (15.5 mL, 21 mmol), $ClSiMe_3$ (1.09 g, 10 mmol) in THF (20 mL), *n*-BuLi (11 mmol) in hexane, and $ClSiMe_3$ (1.09 g, 10 mmol) in THF (20 mL) are added in this order, with 15 min intervals, to a stirred solution of diethyl methylthiomethylphosphonate (**4**; 3.96 g, 20 mmol) in THF (100 mL) at −78 °C. Then, a solution of the aldehyde (20 mmol) in THF (20 mL) is added, and the mixture is stirred for 20 min at −78 °C. After slow warming to room temperature, the mixture is worked up as in Method D. Compound **1b** may be obtained in this manner from acetaldehyde; yield: 62%; bp 48 °C/0.005 mbar.

Reaction of Li-3 with Ketones:

A 1.35 M solution of *n*-BuLi in hexane (8.2 mL, 11 mmol) is added to a stirred solution of diethyl (methylthio)(trimethylsilyl)methylphosphonate (**3**; 2.7 g, 10 mmol) in dry THF (50 mL) at −78 °C and stirring is continued for 20 min at −78 °C. Then, a solution of the ketone **9** (10 mmol) in THF (20 mL) is added. The mixture is then slowly warmed to room temperature and stirred for 4 h. The solvents are removed and the residue is dissolved in $CHCl_3$ (100 mL). This solution is washed with saturated aqueous NH_4Cl (2 × 50 mL) and with H_2O (2 × 50 mL), dried ($MgSO_4$), and evaporated to afford a mixture containing the starting phoshonate **3**, *diethyl methylthiomethylphosphonate* (**4**), and the *diethyl 1-methylthio-1-alkenylphosphonate* **8**.

MS, ^{1}H-, and ^{31}P-spectra of compounds **3** and **4** thus obtained were in good accord with the spectra of authentic samples.

Compound **8a** (X = D, R = CD_3); yield: 26–35% (based on ^{31}P-NMR spectrum).

MS (70 eV): *m/z* (%) = 244 (34), 83 (100).

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.25 (t, 6 H, $^3J_{H,H}$ = 6.5 Hz; $2OCH_2C\underline{H}_3$); 2.55 (s, 3 H, SCH_3); 4.50 (m, 4 H, $2OC\underline{H}_2CH_3$).

^{31}P-NMR ($CDCl_3$): δ = 16.5.

Compound **8b** (X = H, R = Ph); yield: 12% (based on ^{31}P-NMR spectrum).

MS (70 eV): *m/z* (%) = 300 (M^+, 1); 197 (100).

^{1}H-NMR ($CDCl_3$/HMDSO): δ = 1.10 (t, 6 H, $^3J_{H,H}$ = 7.0 Hz, $2OCH_2C\underline{H}_3$); 1.35 (s, 3 H, $C\underline{H}_3$); 2.02 (s, 3 H, SCH_3). 3.91 (dq, 4 H, $^3J_{H,H}$ = 7.0 Hz; $^3J_{H,P}$ = 8.0 Hz; $2OC\underline{H}_2CH_3$); 7.90–7.95 (m, 5 H_{arom}).

^{31}P-NMR ($CDCl_3$): δ = 17.0.

Diethyl 1-Methylthio-1-trimethylsilylethylphosphonate (10):

A 1.2 M solution of *n*-BuLi in hexane (2.3 mL, 2.7 mmol) is added at −78 °C to a stirred solution of diethyl (methylthio)(trimethylsilyl)methylphosphonate (**3**; 0.67 g, 2.5 mmol) in dry THF (30 mL) and stirring at −78 °C is continued for 10 min. Then, a solution of freshly distilled MeI (0.38 g, 2.7 mmol) in THF (10 mL) is added dropwise, the mixture is slowly warmed to room temperature, and then refluxed for 30 min. The solvents are evaporated and the residue is dissolved in CH_2Cl_2 (40 mL). This solution is washed with 5% aq. $Na_2S_2O_3$ (10 mL) and with H_2O (2 × 10 mL), dried ($MgSO_4$), and evaporated. The crude product is chromatographed on 20 × 20 cm silica gel plates (Merck) (eluent: benzene/acetone, 1.5:1) to afford the pure product **10**; yield: 0.43 g (61%); n_D^{20} 1.4690.

$C_{10}H_{25}O_3PSSi$	calc.	C 42.23	H 8.86	
(284.4)	found	42.35	8.90	

MS (70 eV): *m/z* (%) = 284 (M^+, 20).

^{1}H-NMR (CCl_4): δ = 0.13 [s, 9 H, $Si(CH_3)_3$]; 1.31 (t, 6 H, $^3J_{H,H}$ = 7.0 Hz, $2OCH_2C\underline{H}_3$); 1.49 (d, 3 H, $^3J_{H,H}$ = 8.0 Hz, CH_3); 2.17 (s, 3 H, SCH_3); 4.11 (dq, 4 H, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,P}$ = 14.0 Hz, $2OC\underline{H}_2CH_3$).

^{31}P-NMR ($CDCl_3$): δ = 29.8.

Diethyl 1-Methylthioethylphosphonate (11):

A 1.2 M solution of *n*-BuLi in hexane (0.6 mL, 0.72 mmol) is added dropwise at −78 °C to a stirred solution of diethyl 1-methylthio-1-trimethylsilylethylphosphonate (**10**; 0.2 g, 0.7 mmol) in THF (8 mL). The mixture is allowed to warm to room temperature, then heated to reflux for 1.5 h, allowed to cool, and neutralized with 5% aq. HCl. The organic phase is evaporated and the residue is dissolved in CH_2Cl_2 (30 mL). This solution is washed with H_2O (2 × 15 mL), dried ($MgSO_4$), and evaporated to afford the crude product **11** which is purified by TLC; yield: 0.1 g (70%); n_D^{20} 1.4632 (Lit.[19] n_D^{23} 1.4620). The spectrometric data of compound **11** thus obtained are identical with those reported.[19]

Diethyl Bis(alkylthio)methylphosphonates 12; General Procedure:
A 1.2 M solution of *n*-BuLi in Et_2O (1.75 mL, 2.1 mmol) is added dropwise at −78 °C to a stirred solution of diethyl (methylthio)(trimethylsilyl)methylphosphonate (**3**; 0.54 g, 2 mmol) in dry THF (40 mL) and stirring is continued for 10 min. A solution of the dialkyl disulfide (2 mmol) in THF (10 mL) is added dropwise. The mixture is allowed to warm, stirred at room temperature for 1 h, and then heated to reflux for 30 min (**12a**) or 45 min (**12b**). The solvents are evaporated and the residue is dissolved in $CHCl_3$ (50 mL). This solution is washed with H_2O (2 × 25 mL), dried ($MgSO_4$), and evaporated. The crude product **12** thus obtained is purified by column chromatography on silica gel (benzene/acetone gradient as eluent).

Diethyl Bis(methylthio)methylphosphonate (**12a**); yield: 62–75%; n_D^{20} 1.5196 (Lit.[20] n_D^{20} 1.5196).

Diethyl (Ethylthio)(methylthio)methylphosphonate (**12b**); yield: 65%; n_D^{20} 1.4950 (Lit.[20] n_D^{20} 1.4950).

The spectrometric data of compounds **12a** and **12b** thus obtained are identical with those reported.[20]

Diethyl Methylsulfinylmethylphosphonate (16):
3-Chloroperoxybenzoic acid (0.18 g, 1 mmol) is added in a few portions to a stirred solution of phosphonate **3** (0.27 g, 1 mmol) in CCl_4 (20 mL) at 0 °C and stirring is continued at 0 °C for 15 min and at room temperature for 30 min. The resultant mixture contains *diethyl (methylsulfinyl)(trimethylsilyl)methylphosphonate* (**14**; 60–72% yield) and sulfone **15** (13% yield) (according to ^{1}H- and ^{31}P-NMR analysis). For hydrolysis of **14**, the CCl_4 solution is washed with H_2O (2 × 20 mL). It is then dried ($MgSO_4$) and evaporated. The residue is column chromatographed on silica gel to give the pure sulfoxide **16**; yield: 0.17 g (100%, based on crude **14**); n_D^{20} 1.4759 (Lit.[16] n_D^{20} 1.4766). The spectrometric data of product **16** thus obtained are identical with those reported.[16]

Sulfoxide **14**:

^{1}H-NMR (CCl_4/HMDSO): δ = 0.33 [s, 9H, $Si(CH_3)_3$]; 1.32 (t, 6H, $^3J_{H,H}$ = 7.2 Hz, $2OCH_2C\underline{H}_3$); 2.90 [s, 3H, $S(O)CH_3$]; 3.64 (d, 1H, $^2J_{H,P}$ = 16.0 Hz, PCH); 4.20 (dq, 4H, $^3J_{H,P}$ = 7.0 Hz, $2OC\underline{H}_2CH_3$).

^{31}P-NMR (CCl_4): δ = 16.5.

Diethyl Methylsulfonylmethylphosphonate (17):
3-Chloroperoxybenzoic acid (0.35 g, 2 mmol) is added in a few portions to a stirred solution of phosphonate **3**, (0.27 g, 1 mmol) in CCl_4 (20 mL) at 0 °C. The mixture is allowed to warm to room temperature and stirring is continued for 1 h. The CCl_4 solution of the crude sulfone **15** thus obtained (85% yield) is hydrolysed by shaking with H_2O (2 × 10 mL). The organic phase is dried, evaporated, and the residue is purified by column chromatography on silica gel (benzene/acetone gradient as eluent) to give the product **17**; yield: 0.256 g (100%, based on crude **15**); mp 95–96 °C (Lit.[17] mp 96 °C).

Sulfoxide **15**:

^{1}H-NMR (CD_3OD/HMDSO): δ = 0.02 [s, 9H, $Si(CH_3)_3$]; 1.30 (t, 6H, $^3J_{H,H}$ = 6.5 Hz, $2OCH_2C\underline{H}_3$); 3.13 (s, 3H, SO_2CH_3); 3.97 (d, 1H, $^2J_{H,P}$ = 18.0 Hz, PCH); 4.12 (dq, 4H, $^3J_{H,H}$ = 6.5 Hz, $^3J_{H,P}$ = 9.0 Hz; $OC\underline{H}_2CH_3$).

^{31}P-NMR (CCl_4): δ = 12.4.

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