Desilylation of (*Z*)-α-dimethylphenylsilyl vinyl sulfides with fluoride ion:[1] revised mechanism for phenyl group migration in substrates containing an electron-withdrawing group β to the sulfur

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A detailed investigation of the desilylation of (*Z*)-α-dimethylphenylsilyl vinyl sulfides with fluoride ion has shown that in substrates containing an electron-withdrawing group β to the sulfur, phenyl group migration occurs as a result of a fluoride ion catalyzed retro-Michael reaction.

Introduction

α-Silyl vinyl sulfides [2a–d,3a,b] are intriguing species since they can react both as vinylsilanes and vinyl sulfides.[4a,b] Recently, we synthesized a number of these compounds and investigated their chemistry.[1,5,6] During our study on the protiodesilylation of the α-silyl vinyl sulfides **1** with fluoride ion,[1] we found that desilylation of (*Z*)-α-trimethylsilyl vinyl sulfides **1** (R³ = Me) can be

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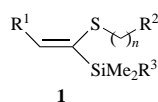
readily achieved to afford, stereoselectively, the corresponding (*Z*)-vinyl sulfides. In contrast, desilylation of compounds **1** (R³ = Ph) gave unexpected results.

In fact, while treatment of **1a** with moist TBAF in boiling THF gave the desilylated (*Z*)-α-vinyl sulfide **2a**, the reaction of the homologous compound **1b** under the same conditions gave **3a**, arising from migration of the phenyl group from the silicon to the adjacent carbon atom (Scheme 1). The different
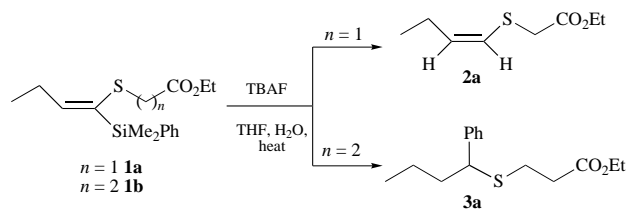
Scheme 1

behaviour of **1a** and **1b** upon desilylation indicates that structural features are crucial for phenyl group migration. According to these preliminary results[1] we attributed the phenyl group migration in **1b** to greater nucleophilicity of its sulfur atom compared with that of **1a**. Thus, compound **1b** can be easily protonated in the β position and this initiates the phenyl group migration.[1] In this paper we report the full details of the desilylation of (*Z*)-α-dimethylphenyl silyl vinyl sulfides and provide a new rationale for the phenyl group migration.

Results and discussion

In order to investigate in detail the desilylation of (*Z*)-α-dimethylphenylsilyl vinyl sulfides **1** we synthesized a variety of compounds **1** [R³ = Ph, R¹ = Et, Prⁱ, *n* = 1, 2, 3 and R² = an electron-withdrawing group (EWG), an electron-donating

Table 1 Synthesis of (*Z*)-α-dimethylphenylsilyl vinyl sulfides **1** (paths A and path B)

1	R¹	*n*	R²	X	Path	Yield (%)[b]
a	Et	1	CO₂Et	I	A	80[a]
b	Et	2	CO₂Et	Cl	A	80[a]
b	Et		CO₂Et		B	80
c	Et	1	CN	Cl	A	89
d	Et	1	COMe	Cl	A	69
e	Et	1	OEt	Cl	A	20[c]
e	Et	1	OEt	Cl		90[d]
f	Et	2	OEt	Cl	A	26
g	Et	1	H	I	A	95[a]
h	Et	2	H	Br	A	90
i	Et	3	H	Br	A	80
j	Et		CN		B	91
k	Et		COMe		B	66
l	Et		CO₂Me		B	92
m	Prⁱ		CO₂Et		B	84
n	Prⁱ		CO₂Me		B	86

[a] Ref 1. [b] The yields were determined after chromatography. [c] Beside **1e** product **5** was obtained in 25% yield. [d] Prepared using triethylamine as the base (see text).

group (EDG) or an alkyl group]. Products **1** were prepared from the corresponding (*Z*)-α-dimethylphenylsilyl enethiols **4**[1] with two different procedures illustrated in Scheme 2 and Table 1.
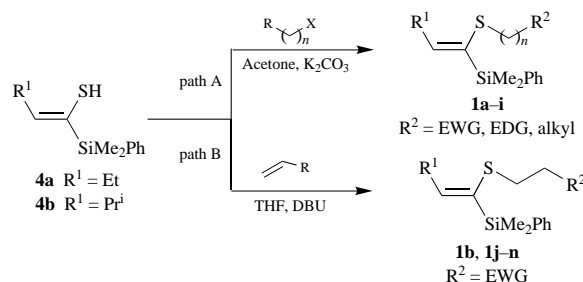
Scheme 2

The full details of the synthesis of (*Z*)-1-[dimethyl(phenyl)-silyl]but-1-enethiol **4a** have been previously reported;[1] the (*Z*)-1-[dimethyl(phenyl)silyl]-3-methylbut-1-enethiol **4b** has been prepared by a similar procedure to that used to prepare **4a** (see Experimental section).

According to path A, products **1a–i** were obtained in a stereoselective manner by reaction of **4** with halides R²(CH₂)ₙX in acetone in the presence of dry K₂CO₃ at room temperature;

Table 2 Protiodesilylation of (Z)-α-dimethylphenylsilyl vinyl sulfides **1**

1	n	R²	**2**	Yield (%)
a	1	CO₂Et	**a**	80[a]
c	1	CN	**c**	72
d	1	COMe	**d**	82[b]
e	1	OEt	**e**	95
f	2	OEt	**f**	98
g	1	H	**g**	46[c]
h	2	H	**h**	98
i	3	H	**i**	75

[a] Compared with an authentic sample (ref. 1). [b] Beside product **2d** a cyclic product **6** was obtained in 18% yield (see Experimental section). [c] Ref. 1.

good yields were generally obtained except in the case of halides containing an ethoxy group in the α- or in a β-position. During the synthesis of **1e** (20% yield), the thioacetal **5** was formed in 25% yield, arising probably by an acid-catalyzed reaction[7] (HCl) of the O,S-thioacetal **1e** with the starting enethiols **4a** (Scheme 3). The structure of product **5** was estab-
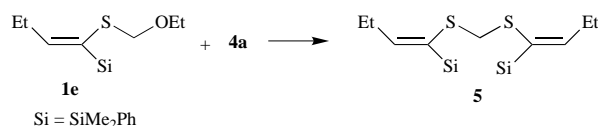

Scheme 3

lished on the basis of analytical and spectral data (see Experimental section). In an effort to improve the yield of products **1e** and **1f**, we allowed **4a** to react with chloromethyl ethyl ether in diethyl ether in the presence of an equimolar amount of triethylamine to give product **1e** (90%) yield; attempted reaction of **4a** with chloroethyl ethyl ether gave, under similar reaction conditions, recovery of **4a**.

By path B (Scheme 2), the enethiols **4** gave a base- (DBU) catalyzed Michael type addition[8] with olefins bearing an electron-withdrawing group, to afford (Z)-α-dimethylphenylsilyl vinyl sulfides **1b**, **1j–n** in very good yields (Table 1).

Compounds **1a–n** were desilylated by reaction with TBAF in moist THF at reflux. Normal protiodesilylation occurs with the following: substrates containing an electron-withdrawing group α to the sulfur **1a**, **c**, **d**; substrates containing an electron-donating group α or β to the sulfur **1e**, **f**; and substrates with an alkyl group bonded to the sulfur **1g–i** (Scheme 4). The yield of
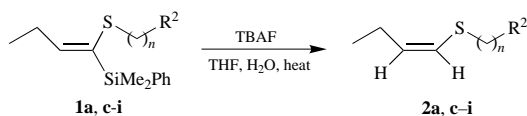
Scheme 4

products **2** were generally good (Table 2) except for **2g** where the product was volatile. Desilylation of **1d** gave, beside product **2d**, a cyclic compound **6** (18%) arising from an intramolecular
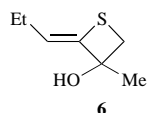

cyclization of the intermediate vinyl anion formed during the desilylation on the carbonyl group. In contrast, the derivatives containing an electron-withdrawing group β to the sulfur **1b**, **j–n**, gave upon treatment with moist TBAF in boiling THF, products **3**, the result of phenyl group migration (Scheme 5, Table 3).

These results clearly show the inadequacy of our previous

Table 3

| **1**	R¹	R²	**3**	Yield (%)
b	Et	CO₂Et	**b**	48[a]
j	Et	CN	**j**	48
k	Et	COMe	**k**	48
l	Et	CO₂Me	**l**	49
m	Prⁱ	CO₂Et	**m**	60
n	Prⁱ	CO₂Me	**n**	48

[a] Ref. 1.
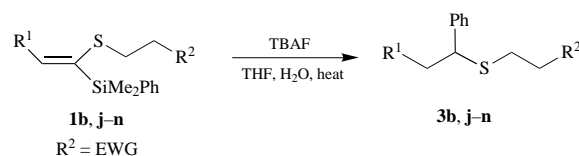
Scheme 5

mechanism.[1] In fact, substrates containing an electron-donating group in a position α or β to the sulfur which would increase the availability of electron density on the sulfur did not favour phenyl group migration. A plausible mechanistic interpretation of the phenyl group migration is outlined in Scheme 6.
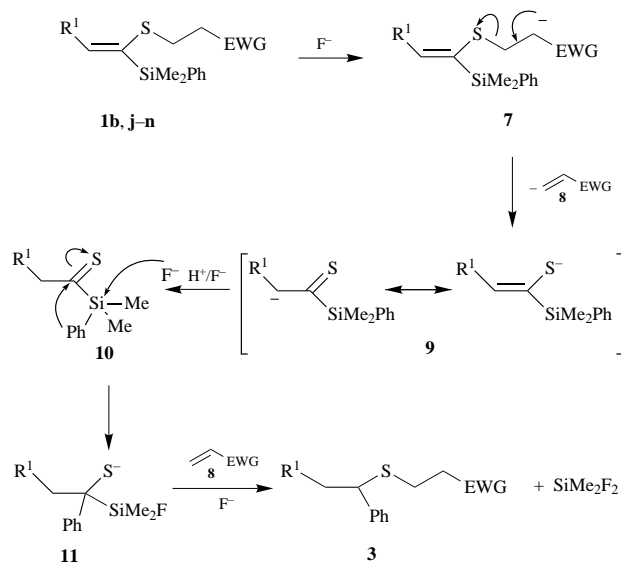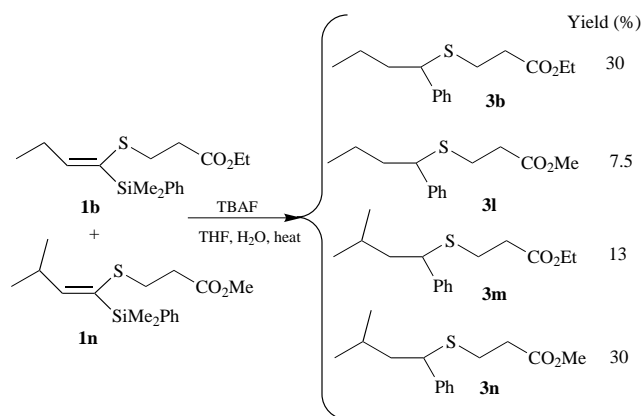

Scheme 6

Substrates **1** containing a hydrogen atom α to an electron-withdrawing group can be easily deprotonated by a base such as TBAF. In fact, TBAF behaves not only as a potent source of nucleophilic fluoride but also as a potent base.[9] If the produced carbanion can undergo a retro-Michael reaction as in the case of the intermediate **7**, extrusion of the olefins **8** takes place to give the enethiolate **9**. The silicon may or may not have a fluoride ion coordinated to it in these stages. The phenyl group in the thione **10** can then migrate from the silicon to the adjacent carbon to give **11**; this by a Michael addition to the olefin **8** affords, after desilylation, product **3**.

To test this hypothesis we desilylated **1b** in the presence of 1 equiv. of methyl acrylate to obtain compounds **3b** and **3l**; these arose from the thiolate **11a** (R¹ = Et) as a result of Michael addition with ethyl acrylate and methyl acrylate, followed by desilylation (Scheme 7). A further proof of the mechanism depicted in Scheme 6 was obtained by desilylation of equimolar amounts of **1b** and **1n** under the usual experimental conditions when four crossed products **3b**, **3l**, **3n** and **3m** were obtained in the yields reported in Scheme 8. These yields were calculated from the ¹H NMR spectrum of the crude mixture by comparison with the ¹H NMR spectra of authentic samples (see
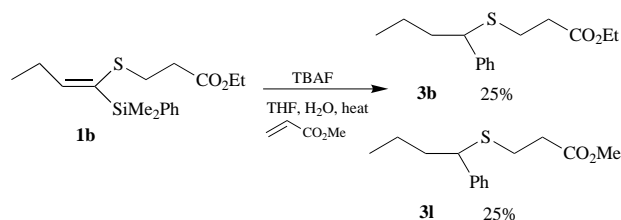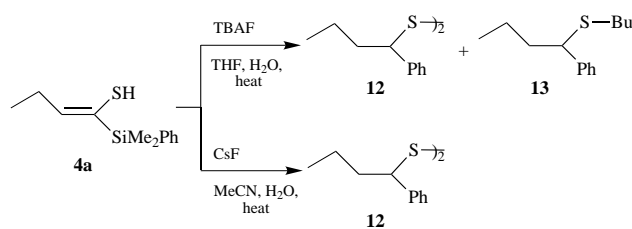
Scheme 7

Scheme 8

Experimental section). The four products arise from the reaction of the two intermediates **11a** (R^1 = Et in Scheme 6) and **11b** (R^1 = Pr^i in Scheme 6) with ethyl acrylate and methyl acrylate which are formed in the retro-Michael reaction stage.

We then examined the desilylation of the enethiol **4a**, which was expected to give the same intermediate **11a**. In fact, treatment of **4a** with TBAF in boiling THF, gave an inseparable mixture of the disulfide **12**, arising from dimerization of the thiolate **11a** followed by desilylation, and of product **13** (Scheme 9). The formation of product **13** is probably the result of alkylation of the thiolate **11a** (R^1 = Et in Scheme 6) either by the TBAF itself or by other species deriving from its decomposition at higher temperature.[10] Product **12** could be obtained pure by performing the desilylation of **4a** with CsF in boiling Me$_3$CN (Scheme 9); its structure was established on the basis of satisfactory analytical and spectral results.

Scheme 9

Conclusion

In summary, we have examined the desilylation of (Z)-α-dimethylphenylsilyl vinyl sulfides **1** with fluoride ion and rationalized the migration of the phenyl group from the silicon to the adjacent carbon atom in substrates containing an electron-withdrawing group β to the sulfur. Substrates containing an electron-withdrawing group α to the sulfur, or an electron-donating group α or β to the sulfur or an alkyl chain bonded to the sulfur gave compounds arising from normal protiodesilylation.

Experimental

Bps and mps are uncorrected. ^{1}H NMR and ^{13}C NMR spectra

were recorded with Varian Gemini 200 or 300 MHz spectrometers as solutions in CDCl$_3$: chemical shifts (δ) are given in ppm relative to tetramethylsilane TMS. J Values are given in Hz. ^{13}C NMR spectra assignments were made by DEPT experiments. Mass spectra were obtained using a VG 7070-E (EI, 70 eV) spectrometer. IR spectra were recorded on a Perkin-Elmer model 257 grating spectrometer. Reactions were conducted in oven-dried (120 °C) glassware under a positive argon atmosphere. Transfer of anhydrous solvents or mixtures was accomplished with oven-dried syringes. THF was distilled from sodium benzophenone just prior to use and stored under argon. Et$_2$O was distilled from phosphorus pentoxide. The reactions were monitored by TLC performed on silica gel plates (Baker-flex IB2-F). Column chromatography was performed with Merck silica gel 60 (70–230 mesh) and preparative thick layer chromatography was carried out on glass plates using a 1-mm layer of Merck silica gel 60 Pf$_{254}$ or aluminium oxide F$_{254}$. Light petroleum refers to the fraction with bp 40–60 °C. Because of the small scale used in the preparations, new compounds which were oily products have been characterized by accurate mass measurements. All chemicals were used as obtained or purified by distillation as needed. Sodium hydrogen carbonate 99% was purchased from Carlo Erba Reagenti; hydrogen chloride was purchased from Praxair (Belgium).

3-Methylbutanoyl(dimethyl)phenylsilane

3-Methylbutanoyl chloride (1.20 g, 1.22 cm^3, 10.0 mmol) in anhydrous THF (3 cm^3), was added slowly to lithium bis-[dimethyl(phenyl)silyl]cuprate[11] (10.0 mmol) at −78 °C under argon. The mixture was stirred at −78 °C for 1 h and then allowed to warm to 0 °C at which temperature it was stirred for 1 h. The mixture was then treated with saturated aqueous ammonium chloride to quench the reaction and extracted with diethyl ether. The extract was dried and concentrated under reduced pressure. Chromatography of the residue on silica gel column [light petroleum–diethyl ether (10:1) as eluent] gave, as the higher R_F fraction, a product arising from the silylcuprate and as the lower R_F fraction the acylsilane (1.6 g, 73%) as a yellow oil (Found: M$^+$, 220.1379. C$_{13}$H$_{20}$OSi requires M, 220.1283); ν_{max}(CCl$_4$)/cm^{-1} 1650 (CO), 1430, 1110 (SiPh) and 1250 (SiMe$_2$); δ_H(CDCl$_3$) 0.45 (6H, s, SiMe$_2$), 0.85 (6H, d, J 6.6, CH$_3$), 2.2 (2H, m, CH), 2.50 (2H, d, J 6.7, CH$_2$CO), 7.45–7.50 (3H, m, ArH) and 7.58–7.62 (2H, m, ArH); δ_C(CDCl$_3$) −4.86 (SiMe$_2$), 22.54 (2CH$_3$), 22.86 (CH), 57.58 (CH$_2$CO), 128.01, 129.71, 133.85 (ArCH), 139.15 (ArC) and 246.51 (CO); m/z (EI) 220 (M$^+$), 163 [M$^+$ − (CH$_3$)$_2$CHCH$_2$] and 135 (SiMe$_2$Ph).

(Z)-1-[Dimethyl(phenyl)silyl]-3-methylbut-1-enethiol 4b

Hydrogen chloride and hydrogen sulfide were bubbled into a solution of 3-methylbutanoyl(dimethyl)phenylsilane (0.35 g, 1.59 mmol) in diethyl ether (70 cm^3) at −20 °C, until the starting ketone had disappeared [TLC with light petroleum–diethyl ether (10:1) as eluent]. After the mixture has been allowed to warm to room temperature it was treated with solid sodium hydrogen carbonate until evolution of carbon dioxide ceased; it was then left overnight. Filtration and concentration of the mixture under reduced pressure gave the pure (Z)-enethiol **4b** as an oil (0.35 g, 1.48 mmol, 93%) (Found: M$^+$, 236.1059. C$_{13}$H$_{20}$SSi requires M, 236.1055); ν_{max}(CCl$_4$)/cm^{-1} 2540 (SH), 1430, 1110 (SiPh), 1250 and 890 (SiMe$_2$); δ_H(CDCl$_3$) 0.45 (6H, s, SiMe$_2$), 1.05 (6H, d, J 10.0, 2CH$_3$), 2.40 (1H, s, SH), 2.65–2.85 (1H, m, CH), 5.80 (1H, d, J 9.0, vinylic H), 7.40 (3H, m, ArH) and 7.70 (2H, m, ArH); δ_C(CDCl$_3$) −3.16 (SiMe$_2$), 21.82 (2CH$_3$), 29.89 (CH), 125.24 (C), 127.94, 129.44, 134.18 (ArCH), 136.57 (C) and 147.52 (vinylic CH); m/z (EI) 236 (M$^+$), 221 (M$^+$ − CH$_3$), 187 (M$^+$ − H$_2$S), 158 (M$^+$ − C$_6$H$_6$), 143 (M$^+$ − C$_7$H$_9$) and 135 (SiMe$_2$Ph).

Synthesis of (Z)-α-silyl vinyl sulfides 1: general method (Path A). To a solution of (Z)-α-silyl enethiol **4** (1.0 mmol) in acetone (4 cm^3), solid oven-dried K$_2$CO$_3$ (1.3 mmol) and the halide (1.1

mmol) were added. The mixture was stirred at room temperature until the starting enethiol had disappeared. The mixture was then diluted with water and extracted with diethyl ether. The extract was dried and concentrated to give the title product. In some cases the product was purified by chromatography on silica [light petroleum–diethyl ether (10:1) as eluent].

(*Z*)-{1-[Dimethyl(phenyl)silyl]but-1-enylsulfanyl}acetonitrile 1c. Yield 89% as an oil (Found: M⁺, 261.1012. $C_{14}H_{19}NSSi$ requires M, 261.1007); $\nu_{max}(CCl_4)/cm^{-1}$ 2242 (CN), 1426 (SiPh), 1248 (SiMe₂) and 1109 (SiPh); $\delta_H(CDCl_3)$ 0.50 (6H, s, SiMe₂), 1.05 (3H, t, J 7.5, CH₃), 2.55 (2H, m, CH₂), 2.85 (2H, s, CH₂CN), 6.65 (1H, t, J 6.9, vinylic H), 7.38 (3H, m, ArH) and 7.60 (2H, m, ArH); $\delta_C(CDCl_3)$ −2.90 (SiMe₂), 13.50 (CH₃), 19.55, 24.45 (CH₂), 116.65 (CN), 128.01, 129.58, 133.93 (ArCH), 135.10 (ArC), 136.90 (vinylic C) and 158.73 (vinylic CH); *m/z* (EI) 261 (M⁺), 260 (M⁺ − 1), 246 (M⁺ − CH₃), 221 (M⁺ − CH₂CN) and 135 (SiMe₂Ph).

(*Z*)-{1-[Dimethyl(phenyl)silyl]but-1-enylsulfanyl}propan-2-one 1d. Chromatography on silica gel of the crude reaction mixture, using light petroleum–diethyl ether (8:1) as eluent, gave the title product as oil (70%) (Found: M⁺, 278.1158. $C_{15}H_{22}$-OSSi requires M, 278.1161); $\nu_{max}(CCl_4)/cm^{-1}$ 1720 (CO), 1440 (SiPh), 1240 (SiMe₂) and 1110 (SiPh); $\delta_H(CDCl_3)$ 0.45 (6H, s, SiMe₂), 1.00 (3H, t, J 7.5, CH₃), 2.00 (3H, s, COCH₃), 2.40 (2H, m, CH₂), 3.10 (2H, s, CH₂CO), 6.35 (1H, t, J 6.8, vinylic H), 7.35 (3H, m, ArH) and 7.65 (2H, m, ArH); $\delta_C(CDCl_3)$ −2.49 (SiMe₂), 13.41 (CH₃), 24.32 (CH₂), 27.96 (CH₃), 44.57 (SCH₂), 127.82, 129.25, 133.98 (ArCH), 131.15 (ArC), 137.62 (vinylic C), 154.73 (vinylic CH) and 203.18 (CO); *m/z* (EI) 278 (M⁺), 263 (M⁺ − CH₃) and 135 (SiMe₂Ph).

(*Z*)-1-[Dimethyl(phenyl)silyl]-1-ethoxymethylsulfanylbut-1-ene 1e. Chromatography on alumina of the crude product, using light petroleum–diethyl ether (20:1) as eluent, gave as the higher R_F fraction product **5** as an oil (25%) (Found: M⁺, 456.1792. $C_{25}H_{36}S_2Si_2$ requires M, 456.1797); $\nu_{max}(CCl_4)/cm^{-1}$ 1430, 1110 (SiPh) and 1250 (SiMe₂); $\delta_H(CDCl_3)$ 0.40 (12H, s, 2 SiMe₂), 1.00 (6H, t, J 7.5, 2 CH₃), 2.40 (4H, m, 2CH₂), 3.4 (2H, s, SCH₂S), 6.30 (2H, t, J 6.8, 2 vinylic H), 7.4 (6H, m, ArH) and 7.6 (4H, m, ArH); $\delta_C(CDCl_3)$ −2.35 (SiMe₂), 13.39 (CH₃), 24.37, 40.03 (CH₂), 127.74, 129.10, 134.00 (ArCH), 132.72 (ArC), 137.86 (vinylic C) and 153.77 (vinylic CH); *m/z* (EI) 456 (M⁺), 221 (CH₃CH₂CHCSSiMe₂Ph), 144 (CH₃CH₂-CHCSCH₂SC), 135 (SiMe₂Ph) and 91 (C₇H₇); as the second R_F fraction the title product as an oil (20%) (Found: M⁺, 280.1315. $C_{15}H_{24}$OSSi requires M, 280.1317); $\nu_{max}(CCl_4)/cm^{-1}$ 1080, 1140 (C-O-C), 1430, 1110 (SiPh) and 1250 (SiMe₂); $\delta_H(CDCl_3)$ 0.45 (6H, s, SiMe₂), 1.05 (3H, t, J 7.6, CH₃), 1.15 (3H, t, J 7.1, CH₃), 2.45 (2H, m, CH₂), 3.5 (2H, q, J 7.1, OCH₂), 4.45 (2H, s, CH₂O), 6.35 (1H, t, J 6.8, vinylic H), 7.35 (3H, m, ArH) and 7.65 (2H, m, ArH); $\delta_C(CDCl_3)$ −2.55 (SiMe₂), 13.39, 14.70 (CH₃), 24.32, 63.99, 75.91 (CH₂), 127.68, 129.06, 134.08 (ArCH), 131.89 (ArC), 139.00 (vinylic C) and 152.42 (vinylic CH); *m/z* (EI) 280 (M⁺), 221 (M⁺ − CH₂OC₂H₅) and 135 (SiMe₂Ph).

Improved procedure for 1e. To a solution of (*Z*)-1-[dimethyl-(phenyl)silyl]but-1-enethiol (0.13 g, 0.59 mmol) in anhydrous diethyl ether (3 cm³), chloromethyl ethyl ether (0.065 g, 0.07 cm³, 0.7 mmol) and triethylamine (0.07 g, 0.1 cm³, 0.7 mmol) were added. The mixture was stirred at room temperature until the starting enethiol had disappeared [TLC light petroleum–diethyl ether (20:1) as eluent, 10 min.]. The mixture was then diluted with water and extracted with diethyl ether. The organic layer was dried and concentrated to give the title product as an oil (1.15 g, 0.53 mmol, 90%). Use of an excess of chloromethyl ethyl ether and triethylamine gave the title product in quantitative yield.

(*Z*)-1-[Dimethyl(phenyl)silyl]-1-(2′-ethoxyethylsulfanyl)but-1-ene 1f. Chromatography on silica gel of the crude product, using light petroleum–diethyl ether (10:1) as eluent, gave the title product as an oil (26%) (Found: M⁺, 294.1478. $C_{16}H_{26}$OSSi

requires M, 294.1474); $\nu_{max}(CCl_4)/cm^{-1}$ 1430, 1110 (SiPh), 1248 (SiMe₂) and 1150–1070 (C-O-C); $\delta_H(CDCl_3)$ 0.45 (6H, s, SiMe₂), 1.05 (3H, t, J 7.6, CH₃), 1.15 (3H, t, J 7.1, CH₃), 2.45 (2H, m, CH₂), 2.62 (2H, t, J 7.2, SCH₂), 3.30 (2H, t, J 7.2, CH₂), 3.34 (2H, q, J 7.1, CH₂O), 6.3 (1H, t, J 6.8, vinylic H), 7.35 (3H, m, ArH) and 7.45 (2H, m, ArH); $\delta_C(CDCl_3)$ −2.37 (SiMe₂), 13.37, 15.11 (CH₃), 24.22, 33.64, 66.05, 69.66 (CH₂), 127.73, 129.07, 133.95 (ArCH), 132.20 (ArC), 138.60 (vinylic C) and 152.90 (vinylic CH); *m/z* (EI) 294 (M⁺), 249 (M⁺ − OC₂H₅), 221 (M⁺ − CH₂CH₂OC₂H₅), 179 (221 − C₃H₆) and 135 (SiMe₂Ph).

A reaction performed using triethylamine as a base in diethyl ether with the (*Z*)-enethiol **4a** gave recovery of starting material.

(*Z*)-1-[Dimethyl(phenyl)silyl]-1-ethylsulfanylbut-1-ene 1h. Yield 90% as an oil (Found: M⁺, 250.1216. $C_{14}H_{22}$SSi requires M, 250.121 15); $\nu_{max}(CCl_4)/cm^{-1}$ 1430 (SiPh), 1250 (SiMe₂) and 1100 (SiPh); $\delta_H(CDCl_3)$ 0.50 (6H, s, SiMe₂), 1.03 (3H, t, J 7.4, CH₃), 1.06 (3H, t, J 7.5, 2CH₃), 2.45 (4H, m, 2CH₂), 6.30 (1H, t, J 6.5, vinylic H), 7.38 (3H, m, ArH) and 7.60 (2H, m, ArH); $\delta_C(CDCl_3)$ −2.30 (SiMe₂), 13.39, 14.81 (CH₃), 24.14, 28.42 (CH₂), 127.66, 128.99, 133.93 (ArCH), 132.80 (ArC), 138.05 (vinylic C) and 152.194 (vinylic CH); *m/z* (EI) 250 (M⁺), 221 (M⁺ − C₂H₅) and 135 (SiMe₂Ph).

(*Z*)-1-[Dimethyl(phenyl)silyl]-1-propylsulfanylbut-1-ene 1i. Yield 80% as an oil (Found: M⁺, 264.1362. $C_{15}H_{24}$SSi requires M, 264.1368); $\nu_{max}(CCl_4)/cm^{-1}$ 1426 (SiPh), 1246 (SiMe₂) and 1108 (SiPh); $\delta_H(CDCl_3)$ 0.40 (6H, s, SiMe₂), 0.80 (3H, t, J 7.3, CH₃), 1.00 (3H, t, J 7.6, CH₃), 1.40 (2H, m, CH₂), 2.40 (4H, m, 2CH₂), 6.25 (1H, t, J 6.7, vinylic H), 7.35 (3H, m, ArH) and 7.65 (2H, m, ArH); $\delta_C(CDCl_3)$ −2.32 (SiMe₂), 13.24, 13.36 (CH₃), 23.22, 24.12, 36.37 (CH₂), 127.61, 128.93, 133.87 (ArCH), 134.60 (ArC), 138.22 (vinylic C) and 152.03 (vinylic CH); *m/z* (EI) 264 (M⁺), 221 (M⁺ − C₃H₇) and 135 (SiMe₂-Ph).

Synthesis of (*Z*)-α-silyl vinyl sulfides 1: general method (Path B)
To a solution of (*Z*)-α-silyl enethiol (1.0 mmol) in THF (5 cm³), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (1.1 mmol) and the olefin (1.1 mmol) were added. The mixture was stirred at room temperature until the starting enethiol had disappeared. The mixture was then treated with water and extracted with diethyl ether. The extract was dried and concentrated to give the title product. All the yields were calculated on the crude products. The crude products were used for further reactions without purification. In some cases the products were purified by chromatography on silica [light petroleum–diethyl ether (10:1) as eluent] for the complete characterization analysis.

3-{(*Z*)-[1-Dimethyl(phenyl)silyl]but-1-enylsulfanyl}propionitrile 1j. Yield 91% as an oil (Found: M⁺, 275.1168. $C_{15}H_{21}$NSSi requires M, 275.1164); $\nu_{max}(CCl_4)/cm^{-1}$ 2248 (CN), 1426, 1109 (SiPh) and 1248 (SiMe₂); $\delta_H(CDCl_3)$ 0.45 (6H, s, SiMe₂), 1.05 (3H, t, J 7.6, CH₃), 2.15 (2H, t, J 7.2, CH₂), 2.45 (2H, m, CH₂), 2.55 (2H, t, J 7.2, CH₂), 6.45 (1H, t, J 6.8, vinylic H), 7.35 (3H, m, ArH) and 7.65 (2H, m, ArH); $\delta_C(CDCl_3)$ −2.68 (SiMe₂), 13.38 (CH₃), 18.22, 24.34, 29.36 (CH₂), 118.20 (CN), 128.01, 129.50, 133.81 (ArCH), 131.12 (ArC), 137.65 (vinylic C) and 155.03 (vinylic CH); *m/z* (EI) 275 (M⁺), 260 (M⁺ − CH₃), 246 (M⁺ − C₂H₅), 221 (M⁺ − CH₂CH₂CN) and 135 (SiMe₂Ph).

4-{(*Z*)-1-[Dimethyl(phenyl)silyl]but-1-enylsulfanyl}butan-2-one 1k. Chromatography on silica gel of the crude product using light petroleum–diethyl ether (10:1) as eluent, gave the title product as an oil (66%) (Found: M⁺, 292.1319. $C_{16}H_{24}$OSSi requires M, 292.1317); $\nu_{max}(CCl_4)/cm^{-1}$ 1725 (COMe), 1430, 1110 (SiPh) and 1250 (SiMe₂); $\delta_H(CDCl_3)$ 0.45 (6H, s, SiMe₂), 1.00 (3H, t, J 7.6, CH₃), 1.95 (3H, s, COCH₃), 2.3–2.4 (4H, m, 2CH₂), 2.6 (2H, t, J 7.2, CH₂), 6.3 (1H, t, J 6.7, vinylic H), 7.35 (3H, m, ArH) and 7.65 (2H, m, ArH); $\delta_C(CDCl_3)$ −2.55 (SiMe₂), 13.38 (CH₃), 24.21, 27.98 (CH₂), 29.68 (COCH₃), 43.68 (CH₂), 127.74, 129.11, 133.90 (ArCH), 132.46 (ArC),

138.02 (vinylic C), 152.85 (vinylic CH) and 206.74 (CO); m/z (EI) 292 (M^+), 277 ($M^+ - CH_3$), 221 ($M^+ - CH_2CH_2COMe$), 189 ($M^+ - SCH_2CH_2COMe$) and 135 ($SiMe_2Ph$).

Ethyl 3-{(Z)-1-[dimethyl(phenyl)silyl]but-1-enylsulfanyl}propionate 1b. Yield 80%, the product was compared with an authentic sample.[1]

Methyl 3-{(Z)-1-[dimethyl(phenyl)silyl]but-1-enylsulfanyl}propionate 1l. Yield 92% as an oil (Found: M^+, 308.1264. $C_{16}H_{24}O_2SSi$ requires M, 308.1266); $v_{max}(CCl_4)/cm^{-1}$ 1745 (CO_2Me), 1435, 1115 (SiPh) and 1250 ($SiMe_2$); $\delta_H(CDCl_3)$ 0.40 (6H, s, $SiMe_2$), 0.95 (3H, t, J 7.6, CH_3), 2.29 (2H, t, J 7.1, CH_2), 2.38 (2H, m, CH_2), 2.62 (2H, t, J 7.7, CH_2), 3.60 (3H, s, OCH_3), 6.30 (1H, t, J 6.6, vinylic H), 7.30 (3H, m, ArH) and 7.55 (2H, m, ArH); $\delta_C(CDCl_3)$ −2.48 ($SiMe_2$), 13.37 (CH_3), 24.23, 29.03, 34.50 (CH_2), 51.60 (OCH_3), 127.76, 129.11, 133.90 (ArCH), 131.93 (ArC), 137.92 (vinylic C), 153.67 (vinylic CH) and 172.28 (CO); m/z (EI) 308 (M^+), 222 ($M^+ - CHCH_2CO_2Me$) and 135 ($SiMe_2Ph$).

Ethyl 3-{(Z)-1-[dimethyl(phenyl)silyl]-3-methylbut-1-enylsulfanyl}propionate 1m. Yield 84% as an oil (Found: M^+, 336.1573. $C_{18}H_{28}O_2SSi$ requires M, 336.1579); $v_{max}(CCl_4)/cm^{-1}$ 1740 (CO_2Et), 1435, 1115 (SiPh) and 1250 ($SiMe_2$); $\delta_H(CDCl_3)$ 0.45 (6H, s, $SiMe_2$), 1.00 (6H, d, J 6.7, $2CH_3$), 1.20 (3H, t, J 7.3, CH_3), 2.30 (2H, t, J 7.5, CH_2), 2.60 (2H, t, J 7.5, CH_2), 3.15 (1H, m, CH), 4.09 (2H, q, J 7.3, OCH_2), 6.15 (1H, d, J 8.9, vinylic H), 7.35 (3H, m, ArH) and 7.55 (2H, m, ArH); $\delta_C(CDCl_3)$ −2.27 ($SiMe_2$), 14.16 (CH_3), 22.22 ($2CH_3$), 29.11 (CH_2), 29.60 (CH), 34.81 (CH_2), 60.41 (OCH_2), 127.76, 129.08, 133.84 (ArCH), 129.72 (ArC), 138.13 (vinylic C), 159.15 (vinylic CH) and 171.78 (CO); m/z (EI) 336 (M^+), 235 ($M^+ - CH_2CH_2-CO_2Et$) and 135 ($SiMe_2Ph$).

Methyl 3-{(Z)-1-[dimethyl(phenyl)silyl]-3-methylbut-1-enylsulfanyl}propionate 1n. Yield 86% as an oil (Found: M^+, 322.1426. $C_{17}H_{26}O_2SSi$ requires M, 322.1423); $v_{max}(CCl_4)/cm^{-1}$ 1750 (CO_2Me), 1435, 1115 (SiPh) and 1250 ($SiMe_2$); $\delta_H(CDCl_3)$ 0.45 (6H, s, $SiMe_2$), 1.00 (6H, d, J 6.6, $2CH_3$), 2.30 (2H, t, J 7.4, CH_2), 2.65 (2H, t, J 7.4, CH_2), 3.20 (1H, m, CH), 3.62 (3H, s, OCH_3), 6.20 (1H, d, J 9.1, vinylic H), 7.35 (3H, m, ArH) and 7.65 (2H, m, ArH); $\delta_C(CDCl_3)$ −2.30 ($SiMe_2$), 22.18 (2 CH_3), 29.04 (CH_2), 29.58 (CH), 34.55 (CH_2), 51.49 (OCH_3), 127.74, 129.05, 133.81 (ArCH), 129.85 (ArC), 138.06 (vinylic C), 159.13 (vinylic CH) and 172.13 (CO); m/z (EI) 322 (M^+), 235 ($M^+ - CH_2CH_2CO_2Me$) and 135 ($SiMe_2Ph$).

General procedure for the desilylation of (Z)-α-dimethylphenylsilyl vinyl sulfides 1

A solution of tetrabutylammonium fluoride (TBAF) in THF (1.0 M; 1.1 mmol) was added to a solution of (Z)-α-silyl vinyl sulfides (1 mmol) in moist THF (6 cm³). The reaction mixture was stirred at reflux temperature until the starting α-silyl vinyl sulfide had disappeared after which it was diluted with saturated aqueous ammonium chloride to quench the reaction and extracted with diethyl ether. The extract was washed several times with water and then dried and concentrated under reduced pressure. The crude product was purified by preparative thick layer chromatography to give, as the higher R_F fraction, a product arising from the $SiMe_2Ph$ moiety and, as the lower R_F fraction, the desilylated product.

[(Z)-But-1-enylsulfanyl]acetonitrile 2c. Chromatography on silica gel of the crude product, using light petroleum–diethyl ether (10:1) as eluent, gave the title product as an oil (72%) (Found: M^+, 127.0459. C_6H_9NS requires M, 127.0456); $v_{max}(CCl_4)/cm^{-1}$ 2260 (CN); $\delta_H(CDCl_3)$ 1.05 (3H, t, J 7.5, CH_3), 2.25 (2H, m, CH_2), 3.4 (2H, s, CH_2CN), 5.94 (1H, dt, J_1 9.2, J_2 6.9, vinylic H) and 6.02 (1H, dt, J_1 9.2, J_2 1.1, vinylic H); $\delta_C(CDCl_3)$ 13.44 (CH_3), 18.92, 22.65 (CH_2), 117.15 (CN) and 119.30 and 137.88 (vinylic CH); m/z (EI) 127 (M^+) and 112 ($M^+ - CH_3$).

[(Z)-But-1-enylsulfanyl]propan-2-one 2d. A mixture of two products was obtained as shown by the ^1H NMR spectrum of the crude reaction mixture: the title product (δ_H 5.60–5.73 and 5.79–5.85) (82%) and a cyclic product 6 (δ_H 5.60) (18%). Since the cyclic product 6 was found to be rather unstable on silica it was characterized in the crude mixture: $v_{max}(CCl_4)/cm^{-1}$ 3500 br (OH); $\delta_H(CDCl_3)$ 0.95 (3H, t, J 7.6, CH_3), 1.50 (3H, s, CH_3), 1.85 (2H, m, CH_2), 3.05–3.30 (2H, dd, J 10, CH_2) and 5.60 (1H, t, J 7.2, vinylic H); $\delta_C(CDCl_3)$ 13.44 (CH_3), 21.13 (CH_2), 26.81 (CH_3), 29.80 (C), 41.65 (CH_2S), 118.57 (vinylic CH) and 144.80 (vinylic C); m/z (EI) 144 (M^+), 129 ($M^+ - CH_3$) and 101 ($M^+ - COCH_3$). Chromatography on silica gel of the crude product, using light petroleum–dichloromethane (2:1) as eluent, gave as the higher R_F fraction, a product arising from the $SiMe_2Ph$ moiety and, as the second R_F fraction, the desilylated product as an oil (65%) (Found: M^+, 144.0612. $C_7H_{12}OS$ requires M, 144.0609); $v_{max}(CCl_4)/cm^{-1}$ 1715 ($COCH_3$); $\delta_H(CDCl_3)$ 1.05 (3H, t, J 7.6, CH_3), 2.15 (2H, m, CH_2), 2.3 (3H, s, $COCH_3$), 3.35 (2H, s, SCH_2CO), 5.60–5.73 (1H, dt, J_1 9.3, J_2 6.9, vinylic H) and 5.79–5.85 (1H, dt, J_1 9.3, J_2 1.2, vinylic H); $\delta_C(CDCl_3)$ 13.47 (CH_3), 22.46 (CH_2), 27.66 (CH_3), 43.46 (SCH_2CO), 121.68 and 133.87 (vinylic CH) and 203.42 (CO); m/z (EI) 144 (M^+), 101 ($M^+ - COMe$), 87 ($M^+ - CH_2COMe$), 55 ($M^+ - SCH_2COMe$) and 43 (COMe).

(Z)-1-Ethoxymethylsulfanylbut-1-ene 2e. Yield 95% as an oil (Found: M^+, 146.0762. $C_7H_{14}OS$ requires M, 146.0765); $v_{max}(CCl_4)/cm^{-1}$ 1070 (C-O-C); $\delta_H(CDCl_3)$ 1.0 (3H, t, J 7.5, CH_3), 1.2 (3H, t, J 7.0, CH_3), 2.15 (2H, m, CH_2), 3.6 (2H, q, J 7.0, OCH_2), 4.75 (2H, s, SCH_2O), 5.65 (1H, dt, J_1 9.3, J_2 7.1, vinylic H) and 6.05 (1H, dt, J_1 9.3, J_2 1.4, vinylic H); $\delta_C(CDCl_3)$ 13.41, 14.71 (CH_3), 22.61 (CH_2), 63.79 (OCH_2), 74.33 (SCH_2O) and 122.37 and 132.35 (vinylic CH); m/z (EI) 146 (M^+), 101 ($M^+ - OEt$), 87 ($M^+ - CH_2OEt$), 59 (CH_2OEt), 45 (OEt) and 40 (C_3H_4). Because of its high volatility, an attempt to purify this product lowered its yield.

(Z)-1-(2′-Ethoxyethylsulfanyl)but-1-ene 2f. Yield 98% as an oil (Found: M^+, 160.0926. $C_8H_{16}OS$ requires M, 160.0922); $v_{max}(CCl_4)/cm^{-1}$ 1070 (C-O-C); $\delta_H(CDCl_3)$ 1.0 (3H, t, J 7.6, CH_3), 1.2 (3H, t, J 7.0, CH_3), 2.1 (2H, m, CH_2), 2.8 (2H, t, J 7.0, CH_2), 3.52 (2H, q, J 7.0, CH_2O), 3.60 (2H, t, J 6.9, OCH_2), 5.55 (1H, dt, J_1 9.4, J_2 7.0, vinylic H) and 5.9 (1H, dt, J_1 9.43, J_2 1.4, vinylic H); $\delta_C(CDCl_3)$ 13.44, 15.12 (CH_3), 22.42, 33.13 (CH_2), 66.41, 70.18 (OCH_2) and 123.92, 131.70 (vinylic CH); m/z (EI) 160 (M^+), 101 ($M^+ - CH_2CH_2OEt$), 73 (CH_2CH_2OEt), 59 (CH_2OEt), 45 (OEt) and 40 (C_3H_4). Because of its high volatility, an attempt to purify this product lowered its yield.

(Z)-1-Ethylsulfanylbut-1-ene 2h. Yield 98% as an oil (Found: M^+, 116.0657. $C_6H_{12}S$ requires M, 116.0660); $\delta_H(CDCl_3)$ 0.9 (3H, t, J 7.4, CH_3), 1.24 (3H, t, J 7.2, CH_3), 2.1 (2H, m, CH_2), 2.65 (2H, q, J 7.4, CH_2), 5.53 (1H, dt, J_1 10, J_2 6.9, vinylic H) and 5.85 (1H, dt, J_1 10, J_2 1.4, vinylic H); m/z (EI) 116 (M^+), 87 ($M^+ - C_2H_5$), 73 (87 − CH_2) and 40 (C_3H_4). Because of its high volatility, an attempt to purify this product lowered the yield.

(Z)-1-Propylsulfanylbut-1-ene 2i. Yield 75% as an oil (Found: M^+, 130.0812. $C_7H_{14}S$ requires M, 130.0816); $\delta_H(CDCl_3)$ 0.95 (6H, 2t, $2CH_3$), 1.7 (2H, m, CH_2), 2.1 (2H, m, CH_2), 2.6 (2H, t, J 7.7, SCH_2), 5.5 (1H, dt, J_1 9.3, J_2 7.1, vinylic H) and 5.84 (1H, dt, J_1 9.3, J_2 1.4, vinylic H); m/z (EI) 130 (M^+), 87 ($M^+ - C_3H_7$) and 40 (C_3H_4). Because of its high volatility, an attempt to purify this product lowered its yield.

3-(1′-Phenylbutylsulfanyl)propionitrile 3j. Chromatography on silica gel of the crude product, using light petroleum–ethyl acetate (7:1) as eluent, gave the title product as an oil (48%) (Found: M^+, 219.1085. $C_{13}H_{17}NS$ requires M, 219.1082); $v_{max}(CCl_4)/cm^{-1}$ 2248 (CN); $\delta_H(CDCl_3)$ 0.9 (3H, t, J 7.3, CH_3), 1.3 (2H, m, CH_2), 1.8 (2H, m, CH_2), 2.45 (2H, t, J 7.4, CH_2CN), 2.55 (2H, t, J 7.4, CH_2S), 3.90 (1H, dd, J 7.8, CHPh) and 7.3 (5H, m, ArCH); $\delta_C(CDCl_3)$ 13.76 (CH_3), 18.66, 20.81, 26.58, 38.47 (CH_2), 50.01 (CH), 118.43 (CN), 127.56, 127.86, 128.76 (ArCH) and 142.04 (ArC); m/z (EI) 219 (M^+), 176 ($M^+ - CH_2CH_2CH_3$), 133 ($M^+ - SCH_2CH_2CN$) and 91 (C_7H_7).

4-(1′-Phenylbutylsulfanyl)butan-2-one 3k. Chromatography on silica gel of the crude product, using light petroleum–ethyl acetate (8:1) as eluent, gave the title compound as an oil (48%) (Found: M^+, 236.1233. $C_{14}H_{20}OS$ requires M, 236.1235); $\nu_{max}(CCl_4)/cm^{-1}$ 1735 (COCH₃); $\delta_H(CDCl_3)$ 0.85 (3H, t, J 8.7, CH₃), 1.25 (2H, m, CH₂), 1.80 (2H, m, CH₂), 2.00 (3H, s, COCH₃), 2.48 (4H, m, 2CH₂), 3.75 (1H, dd, J 7.7, CH) and 7.15–7.3 (5H, m, ArH); $\delta_C(CDCl_3)$ 13.72 (CH₃), 20.78, 24.86 (CH₂), 29.91 (CH₃CO), 38.50, 43.38 (CH₂), 50.01 (CHPh), 127.05, 127.77, 128.44 (ArCH), 142.74 (ArC) and 206.93 (CO); m/z (EI) 236 (M^+), 193 ($M^+ - COCH_3$), 165 ($M^+ - CH_2CH_2$-COMe), 133 ($M^+ - SCH_2CH_2CO_2Me$) and 91 (C_7H_7).

Methyl 3-(1′-phenylbutylsulfanyl)propionate 3l. Chromatography on silica gel of the crude product, using light petroleum–dichloromethane (1:1) as eluent, gave the title compound as an oil (49%) (Found: M^+, 252.1186. $C_{14}H_{20}O_2S$ requires M, 252.1184); $\nu_{max}(CCl_4)/cm^{-1}$ 1745 (CO₂Me); $\delta_H(CDCl_3)$ 0.85 (3H, t, J 7.5, CH₃), 1.3 (2H, m, CH₂), 1.8 (2H, m, CH₂), 2.5 (4H, m, 2CH₂), 3.6 (3H, s, OCH₃), 3.8 (1H, dd, J 10.7, CH) and 7.25 (5H, m, ArH); $\delta_C(CDCl_3)$ 13.68 (CH₃), 20.71, 25.84, 34.32, 38.50 (CH₂), 49.58 (CHPh), 51.60 (CH₃), 127.02, 127.74, 128.40 (ArCH), 142.52 (ArC) and 172.28 (CO); m/z (EI) 252 (M^+), 209 ($M^+ - CH_2CH_2CH_3$), 165 ($M^+ - CH_2CH_2CO_2Me$), 133 ($M^+ - SCH_2CH_2CO_2Me$) and 91 (C_7H_7).

Ethyl 3-(1′-phenyl-3′-methylbutylsulfanyl)propionate 3m. Chromatography on silica gel of the crude product, using light petroleum–ethyl acetate (10:1) as eluent, gave the title compound as an oil (60%) (Found: M^+, 280.1495. $C_{16}H_{24}O_2S$ requires M, 280.1497); $\nu_{max}(CCl_4)/cm^{-1}$ 1740 (CO₂Et); $\delta_H(CDCl_3)$ 0.85 (6H, dd, J 4.0, 2CH₃), 1.20 (3H, t, J 7.2, CH₃), 1.5 (1H, m, CH), 1.7 (2H, m, CH₂), 2.30–2.55 (4H, m, 2CH₂), 3.85 (1H, dd, J 7.1, CHPh), 4.1 (2H, q, J 7.2, OCH₂) and 7.2–7.35 (5H, m, ArCH); $\delta_C(CDCl_3)$ 14.12, 21.94, 22.71 (CH₃), 25.62 (CH), 25.80, 34.50, 45.32 (CH₂), 47.64 (CHPh), 60.48 (CH₂O), 127.02, 127.73, 128.43 (ArCH), 142.60 (ArC) and 172.10 (CO); m/z (EI) 280 (M^+), 223 [$M^+ - CH_2CH(CH_3)_2$], 179 ($M^+ - CH_2CH_2CO_2Et$), 147 ($M^+ - SCH_2CH_2CO_2Et$) and 91 (C_7H_7).

Methyl 3-(1′-phenyl-3′-methybutylsulfanyl)propionate 3n. Chromatography on silica gel of the crude product, using light petroleum–diethyl ether (20:1) as eluent, gave the title compound as an oil (48%) (Found: M^+, 266.1348. $C_{15}H_{22}O_2S$ requires M, 266.13405); $\nu_{max}(CCl_4)/cm^{-1}$ 1745 (CO₂Me); $\delta_H(CDCl_3)$ 0.90 (6H, dd, J 7.1, 2CH₃), 1.50 (1H, m, CH), 1.70 (2H, m, CH₂), 2.42 (2H, m, CH₂), 2.55 (2H, m, CH₂), 3.65 (3H, s, OMe), 3.90 (1H, dd, J 9.5, CHPh) and 7.2–7.35 (5H, m, ArCH); $\delta_C(CDCl_3)$ 21.98, 22.74 (CH₃), 25.70 (CH), 25.84 (CH₂), 34.37 (CH₂S), 45.40 (CH₂CO), 47.81 (CHPh), 51.68 (CH₃O), 127.08, 127.78, 128.48 (ArCH), 142.64 (ArC) and 172.36 (CO); m/z (EI) 266 (M^+), 209 [$M^+ - CH_2CH(CH_3)_2$], 179 ($M^+ - CH_2CH_2CO_2Me$), 147 ($M^+ - SCH_2CH_2CO_2Me$) and 91 (C_7H_7).

Desilylation of product 1b in the presence of methyl acrylate

To a solution of the ester **1b** (80 mg, 0.25 mmol) in moist THF (3 cm³) were added a solution of tetrabutylammonium fluoride (TBAF) in THF (1.0 M; 0.32 cm³, 0.32 mmol) and methyl acrylate (0.022 cm³, 21.5 mg, 0.25 mmol). The reaction mixture was stirred at reflux temperature for 4 h after which it was diluted with saturated aqueous ammonium chloride and extracted with diethyl ether. The extract was washed several times with water and then dried and concentrated under reduced pressure. Chromatography on silica gel of the crude reaction mixture, using light petroleum–diethyl ether (30:1) as eluent, gave as the higher R_F fraction, a product arising from the SiMe₂Ph moiety, as the second R_F fraction, product **3b** (16.6 mg, 0.0625 mmol, 25%) and, as the lower R_F, fraction product **3l** (15.7 mg, 0.0625 mmol, 25%). Both products were compared with authentic samples.

Desilylation of an equimolar mixture of 1b and 1n

To a solution of the ester **1b** (80 mg, 0.25 mmol) and the ester **1n** (80 mg, 0.25 mmol) in moist THF (6 cm³) was added a solution of tetrabutylammonium fluoride (TBAF) in THF (1.0 M; 0.64 cm³, 0.64 mmol). The reaction mixture was stirred at reflux temperature for 5 h after which it was diluted with saturated aqueous ammonium chloride and extracted with diethyl ether. The extract was washed several times with water and then dried and concentrated under reduced pressure. Chromatography on silica gel of the crude reaction mixture, using light petroleum–benzene (2:1) as eluent, gave as the higher R_F fraction, a product arising from the SiMe₂Ph moiety and as the lower R_F fraction a mixture of four products (80% overall yield) in a ratio of **3b**:**3l**:**3n**:**3m** = 37:9.5:37:16. The four products were compared with authentic samples and the ratio of the products was estimated by ¹H NMR spectrometry.

Desilylation of (Z)-1-[dimethyl(phenyl)silyl]but-1-enethiol 4a [1]

A solution of tetrabutylammonium fluoride (TBAF) in THF (1.0 M; 1.2 cm³, 1.2 mmol) was added to a solution of (Z)-1-[dimethyl(phenyl)silyl]but-1-enethiol **4a** (0.2 g, 0.9 mmol) in moist THF (6 cm³). The reaction mixture was stirred at reflux temperature for 2 h after which it was diluted with saturated aqueous ammonium chloride and extracted with diethyl ether. The organic layer was washed several times with water and then dried and concentrated under reduced pressure. Chromatography on silica gel of the crude reaction mixture, using light petroleum as eluent, gave as the higher R_F fraction, a product arising from the SiMe₂Ph moiety. The lower R_F fraction was a mixture of products **12** and **13** as evidenced by the ¹H NMR and GC–MS spectra. All the attempts at further separation of products **12** and **13** failed. For this reason we prepared product **12** pure by desilylating **4a** (0.170 g, 0.77 mmol) in moist acetonitrile (3 cm³) in the presence of solid CsF (0.23 g, 1.5 mmol). The reaction mixture was stirred at reflux temperature for 4 h after which it was quenched with water and extracted with diethyl ether. The organic layer was washed several times with water and then dried and concentrated under reduced pressure. Chromatography on silica gel of the crude reaction mixture, using light petroleum as eluent, gave as the higher R_F fraction, a product arising from the SiMe₂Ph moiety and, as the lower R_F fraction, product **12** (55%) as an oil (Found: M^+, 330.1472. $C_{20}H_{26}S_2$ requires M, 330.1476); $\nu_{max}(CCl_4)/cm^{-1}$; $\delta_H(CDCl_3)$ 0.85 (3H, t, J 7.0, CH₃), 1.15 (2H, m, CH₂), 1.8 (2H, m, CH₂), 3.30 (1H, dd, J 8.0, CHPh) and 7.2–7.4 (5H, m, ArCH); $\delta_C(CDCl_3)$ 13.72 (CH₃), 20.78, 36.73 (CH₂), 55.07 (CHPh), 127.23, 128.27, 128.34 (ArCH) and 139.18 (ArC); m/z (EI) 330 (M^+), 198 ($M^+ - C_3H_7CPh$), 133 (CH₃CH₂CH₂-CHPh), 117 (133 − CH₂) and 91 (C_7H_7). The structure of product **13** was tentatively assigned on the basis of its mass spectrum: m/z (GC-MS, EI) 222 (M^+), 179 ($M^+ - C_3H_7$), 133 (CH₃CH₂CH₂CHPh), 117 (133-CH₂) and 91 (C_7H_7).

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