

# Chemistry of silyl thioketones. Part 8.<sup>1</sup> Photo-induced cycloadditions of silyl thioketones with olefins

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Photo-induced cycloadditions of phenyl triphenylsilyl thioketone **1** with electron-poor olefins (acrylonitrile, methyl acrylate and *cis*- and *trans*-1,2-dichloroethene) gave silyl thietanes in a regio- and highly stereoselective manner. In contrast, reaction with vinyl ethers gave thietanes without any regio- or stereo-control. Reaction with  $\alpha$ -methylstyrene and 2,3-dimethylbut-2-ene gave open chain products. Desilylation of silyl thietanes occurs with prevalent inversion of configuration at the carbon bearing the silicon group.

Photochemical cycloadditions of thiones with olefins have received considerable attention in the chemical literature. Various types of thiones, especially aromatic,<sup>2a-d</sup> aliphatic<sup>3a-f</sup> and  $\alpha,\beta$ -unsaturated<sup>4a,b</sup> thioketones have been reported to react with electron-rich and electron-poor olefins. These studies revealed that formation of thietanes *via* the S<sub>1</sub> ( $n-\pi^*$ ) excitation proceeds through a triplet (T<sub>1</sub>) state and the four-membered rings are obtained in a non-stereoselective but regioselective manner in accordance with the occurrence of an intermediate diradical species. Conversely, cyclizations involving the S<sub>2</sub> ( $\pi-\pi^*$ ) excitation were found to be non-regioselective but stereoselective. The reaction of aromatic thioketones *via* S<sub>1</sub> excitation is often accompanied by the formation of 1,4-dithianes.<sup>2b</sup>

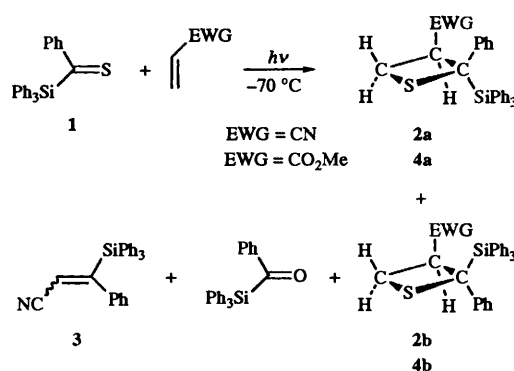
This paper deals with a special type of thioketone, *viz.* silyl thioketone,<sup>1,5</sup> which shows a higher reactivity of the carbon-sulfur double bond in comparison with *e.g.* diaryl thioketones. Moreover, silyl thioketones can serve as synthetic equivalents of thioaldehydes<sup>1,5</sup> by subsequent protodesilylation of the initial products containing the Si-C-S unit. For these reasons, it is of interest to investigate their behaviour in photo-induced cycloadditions with various types of olefins. Such reactions will provide an entry to new types of substituted thietanes.

## Results and discussion

For the purpose of this study, phenyl triphenylsilyl thioketone **1** was selected as the substrate because of its ready availability and good stability. In the spectral region of 300–700 nm this compound displays two absorption bands, *viz.* one at  $\lambda_{\max}$  692 nm (CCl<sub>4</sub>,  $\epsilon \cong 53 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) which is bathochromically shifted in comparison with thiobenzophenone  $\lambda_{\max}$  609 nm (C<sub>6</sub>H<sub>12</sub>,  $\epsilon \cong 180 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), and the other at  $\lambda_{\max}$  362 nm (CCl<sub>4</sub>,  $\epsilon \cong 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). All photochemical experiments were performed using a 125 W high pressure mercury lamp in an argon atmosphere usually at  $-70^\circ\text{C}$  employing the respective olefins as solvent. It is of importance to note that the reaction times ranged from 0.5 to 4 h, which is considerable shorter than those used for other aromatic,<sup>2a-d</sup> aliphatic<sup>3a-f</sup> and  $\alpha,\beta$ -unsaturated<sup>4a,b</sup> thioketones. The yields of the products were estimated by <sup>1</sup>H NMR directly on the crude mixtures which were subsequently purified by chromatography (see Experimental section).

### Photocycloaddition of thioketone **1** with electron-poor olefins

Irradiation of a solution of thioketone **1** in acrylonitrile gave



Scheme 1

a mixture of *c*-2-phenyl-*t*-2-triphenylsilyl- and *t*-2-phenyl-*c*-2-triphenylsilyl-thietanes-*r*-3-carbonitriles **2a** and **2b** in a ratio of 12:1 and a total yield of 80% (Scheme 1). By-products were 3-phenyl-3-triphenylsilylacrylonitrile **3** (13%) and some (5%) acylsilane corresponding to **1**. The structure of the products **2a** and **2b** was assigned on the basis of their spectral features. The mass spectrum was indicative of the regiochemistry as it showed for both products a fragment with  $m/z$  387 corresponding to the loss CH<sub>2</sub>S and no fragment with  $m/z$  362 was observed which would be expected from the elimination of CH(CN)S from the other regioisomer. The <sup>1</sup>H NMR spectrum of **2a** showed the CH<sub>2</sub> protons at  $\delta$  3.25 and 3.1 typical of methylene protons adjacent to a sulfur atom. In addition, the regiochemistry of **2a** was substantiated by measuring the values of <sup>1</sup>J(C,H), the coupling through one bond, and comparing them with the values of structurally related products reported in the literature.<sup>7</sup> Unambiguous proof of the structure of **2a** was obtained from an X-ray diffraction analysis (see Fig. 1) details of which will be published elsewhere. The structure of the minor product **2b** was then deduced by comparison of its spectral characteristics with those of **2a**. The signal at  $\delta$  4.75 for the CHCN proton in **2a** and at  $\delta$  4.6 for **2b** is as expected for a methine proton flanked by two carbon atoms and not as would be expected for a proton with an adjacent sulfur and carbon atom. The above results show that the cycloaddition with acrylonitrile takes place regioselectively with a high degree of stereoselectivity. This reaction was also performed at  $-40$  and  $25^\circ\text{C}$ , however the results were not as good as those described above (see Experimental section).

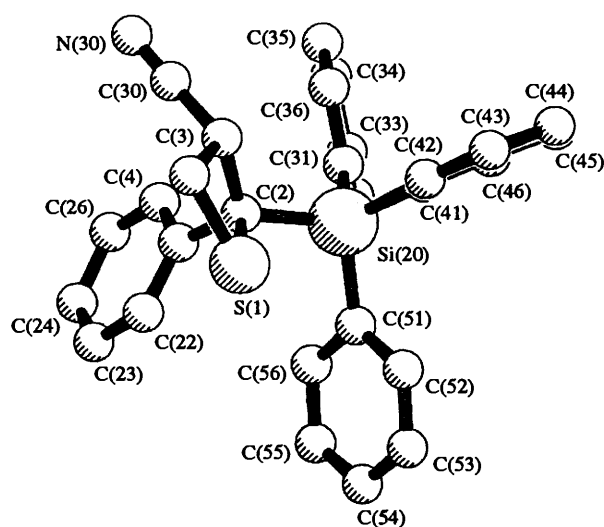
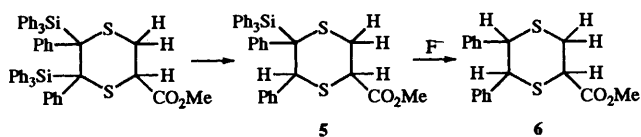
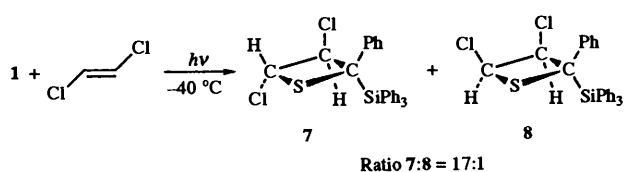


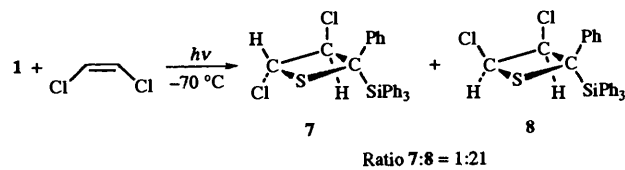
Fig. 1



Scheme 2



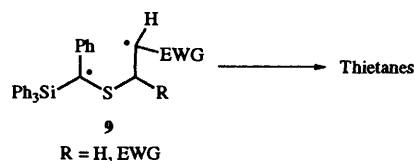
Ratio 7:8 = 17:1



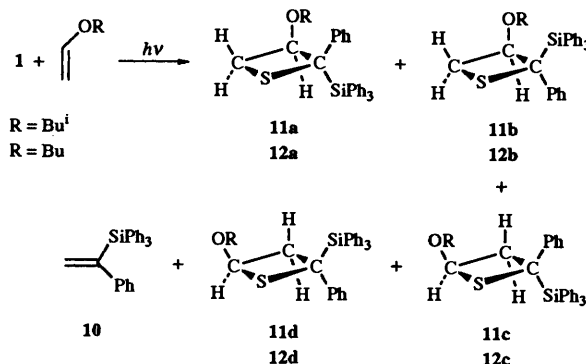
Ratio 7:8 = 1:21

Scheme 3

The reaction of thioether **1** with methyl acrylate at  $-70\text{ }^{\circ}\text{C}$  gave a mixture of diastereoisomeric products **4a** and **4b** in a ratio of 12:1 and a total yield of 80%. The structures of these products were established in essentially the same manner as described for **2a** and **2b**, thereby strongly relying on a comparison with the spectra of these compounds (see Experimental section). In addition to **4a** and **4b** a minor by-product (2%) was isolated to which structure **5** was assigned. The molecular formula  $\text{C}_{36}\text{H}_{32}\text{O}_2\text{S}_2\text{Si}$  indicated that two thiones had reacted with one olefin molecule. The  $^1\text{H}$  NMR spectrum showed signals for the methine protons  $\text{CHPh}$  and  $\text{CH}(\text{CO}_2\text{CH}_3)$  at  $\delta$  4.3 and 4.0, respectively. In the  $^{13}\text{C}$  NMR spectrum (DEPT experiment) the carbon signals for  $\text{CHPh}$  and  $\text{CH}(\text{CO}_2\text{CH}_3)$  appeared at  $\delta$  27.16 and 46.52, respectively. Additional information on this structure, as far as the regiochemistry is concerned, was obtained by protodesilylation of product **5** with  $\text{CsF}$  in acetonitrile to give compound **6** in 41% yield. The  $^1\text{H}$  NMR spectrum of compound **6** showed the  $\text{CH}(\text{CO}_2\text{CH}_3)$  signal as a triplet at  $\delta$  4.3, two double doublets at  $\delta$  3.03 and 3.3 for  $\text{CH}_2$  protons and the resonance of the two  $\text{CHPh}$  protons as a singlet at  $\delta$  3.8. Product **5** is unstable which



Scheme 4



Scheme 5

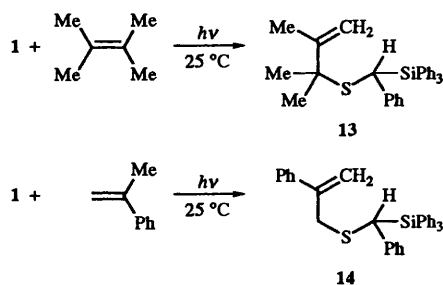
hampers chromatographic purification. The 1,4-dithiane **5** was preponderant when the photocyclization was carried out at ambient temperature. This product **5** is probably the result of a partial desilylation of the initial (2 + 1) adduct of **1** and the olefin (Scheme 2).

The photo-induced cyclization was also studied with *trans*- and *cis*-dichloroethene. With the *trans* olefin cycloadduct **7** was obtained along with diastereoisomeric product **8** in a ratio of 17:1 and a total yield of 70%. When the same reaction was performed with the *cis* olefin the same products were obtained, *viz.* **7** and **8**, but now in a ratio of 1:21 and again a total yield of 70% (Scheme 3). The structures of products **7** and **8** were established on the basis of the spectral characteristics. The  $^1\text{H}$  NMR spectrum of **7** showed two doublets at  $\delta$  6.55 and 5.35 with  $J_{\text{AB}}$  8.3 Hz, whereas product **8** displayed two doublets at  $\delta$  6.05 and 5.45 with  $J_{\text{AB}}$  6.0 Hz. Similar NMR patterns were reported by Ohno *et al.*<sup>2d</sup> for the corresponding cycloadducts of dichloroethene with thiobenzophenone. The result with the isomeric dichloroethenes reveals that the cycloaddition presents a high degree of stereospecificity. By analogy with products **2a** and **4a** we assume that, due to steric reasons, the triphenylsilyl group and the chlorine, at the C-3 in **7** and **8**, have a *trans* relationship.

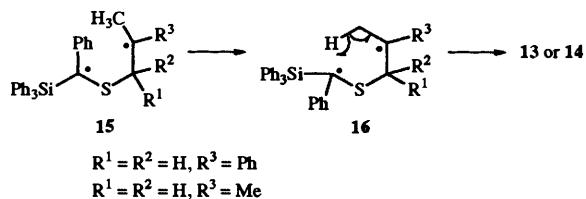
It is suggested that the thietane formation with these electron-poor olefins proceeds *via* an  $\text{S}_1$  excitation involving a 1,4-diradical species as the initial intermediate. In the present case the more stable biradical **9** prevails, thus explaining the observed regioselectivity. Ring closure is governed by steric effects; the preponderant product is the one with the least hindrance of the bulky triphenylsilyl group and the adjacent electron-withdrawing group. The result is an almost exclusive preference of these groups for a *trans* relationship (Scheme 4).

#### Photocycloaddition of thioether **1** with electron-rich olefins

Reactions of thione **1** with isobutyl vinyl ether, butyl vinyl ether, 2,3-dimethylbut-2-ene and  $\alpha$ -methylstyrene were investigated. With both vinyl ethers similar products were obtained as is depicted in Scheme 5. In fact, a mixture of all four stereo and regio thietane isomers was obtained, indicating that this cycloaddition is neither regio- nor stereo-selective. The NMR spectra of the crude reaction mixture in both cases showed four



Scheme 6



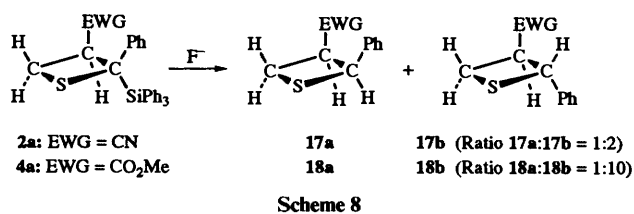
Scheme 7

triplets typical of the *CHOR* methine proton ( $R = \text{Bu}^1$  58%,  $R = \text{Bu}$  57%). The product mixture obtained from isobutyl vinyl ether could not be separated and the composition was deduced from an NMR analysis (see Experimental section). For butyl vinyl ether one cycloadduct could be separated from the crude product mixture, the structure of which has not yet been deduced. In both cases 1-phenyl-1-triphenylsilylene **10** was isolated as a major by-product in about 30% yield. Its identity was established by a comparison with an authentic sample;<sup>8</sup> it probably arises from a degradation of either **11c/11d** or **12c/12d**.

Reaction of **1** with 2,3-dimethylbut-2-ene and  $\alpha$ -methylstyrene gave at ambient and at low temperature ( $-40^\circ\text{C}$ ,  $-70^\circ\text{C}$ ) products **13** and **14** in 30 and 85% yield, respectively (Scheme 6). The structures of these products were deduced essentially on the basis of an  $^1\text{H}$  NMR analysis (see Experimental section). The formation of **13** and **14** can be explained by assuming the intermediacy of 1,4-diradical **15** which undergoes an intramolecular hydrogen shift. Apparently, a methyl group adjacent to a carbon radical can give this reaction *via* a six-membered ring transition state **16** (Scheme 7). A similar ene product was isolated during the irradiation of adamantane-thione and  $\alpha$ -methylstyrene.<sup>3a</sup>

#### Protodesilylation experiments

In principle, silyl thioketones may serve as synthetic equivalents of thioaldehydes<sup>1-5</sup>. For this purpose the stereochemistry of the protodesilylation of cycloadducts **2a** and **4a** was investigated. Reaction of product **2a** with either TBAF in  $\text{THF-H}_2\text{O}$  or CsF in  $\text{DMSO-H}_2\text{O}$  for 24 h at room temperature leads to a mixture of desilylated products, *viz.* *trans*- and *cis*-2-phenylthietane-3-carbonitrile **17b** and **17a**, respectively. With the first mentioned reagent the product ratio amounted to 2:1 and for the latter to 1.5:1 (Scheme 8). The stereochemical configuration of the isomers **17a** and **17b** was established by NOE experiments performed on the mixture of the two isomers. Saturation of the phenyl resonance produced a significant increase in the intensity of the geminal proton signal (6.80%) at  $\delta$  5.15 and in the intensity of the *CHCN* proton signal (8.75%) at  $\delta$  4.05 of the *trans* isomer **17b**, and only an increase of the intensity of the geminal proton signal (3.3%) at  $\delta$  4.95 of the *cis* isomer **17a**. Protodesilylation of thietane **4a** with CsF in  $\text{DMSO-H}_2\text{O}$  at room temperature produced a 1:10 mixture of *cis* and *trans* isomers **18a** and **18b** (Scheme 8). The structural assignment was



Scheme 8

similarly based on NOE experiments (see Experimental section).

The protodesilylation reactions with **2a** and **4a** takes place with predominant inversion of configuration at the C-2 atom. This stereochemical result does not imply that inversion is the nature of the event, but is probably due to the fact that in this way the less crowded product is obtained.

#### Experimental

Bps, and mps, are uncorrected.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded with a Varian Gemini 200 spectrometer as solutions in  $\text{CDCl}_3$ ; chemical shifts ( $\delta$ ) are given in ppm relative to tetramethylsilane (TMS). *J* Values are given in Hz.  $^{13}\text{C}$  NMR spectral assignments were made by DEPT. NMR 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 ( $120^\circ\text{C}$ ) glassware under a positive argon atmosphere. Transfer of anhydrous solvents or mixtures was accomplished with oven-dried syringes. Tetrahydrofuran (THF) was distilled from sodium benzophenone just prior to use and stored under argon. 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 10 mm layer of Merck silica gel 60  $\text{Pf}_{254}$  or aluminium oxide  $\text{F}_{254}$ . Light petroleum refers to the fraction with bp,  $40\text{--}60^\circ\text{C}$ . In the characterization of the new compounds, elemental analysis has been performed on crystalline products. Oily products, because of the small scale used for the preparation, have been characterized by accurate mass measurements.

#### Materials

Phenyl triphenylsilyl thioketone **1** was obtained from the corresponding ketone<sup>9</sup> as previously described<sup>6</sup> and used after crystallization. Acrylonitrile, methyl acrylate, 2,3-dimethylbut-2-ene,  $\alpha$ -methylstyrene, *cis*-1,2-dichloroethene and *trans*-1,2-dichloroethene (Aldrich) were distilled before use. Butyl vinyl ether and isobutyl vinyl ether (Aldrich) were heated at reflux over sodium and distilled under an argon atmosphere, before use.

#### Standard irradiation techniques

The preparative irradiations were carried out using a 125 W high-pressure mercury lamp. All irradiations were carried out under an argon atmosphere at different temperatures in a Pyrex reactor. The solutions were deoxygenated by passage through dry argon for about 45 min. The olefins were used as the solvent. The irradiation was continued until the blue colour of the starting material faded; the unchanged olefins were recovered under reduced pressure.

#### *c*-2-Phenyl-*t*-2-triphenylsilyl- and *t*-2-phenyl-*c*-2-triphenylsilylthietane-*r*-3-carbonitrile **2a**, **2b**

A solution of thioketone **1** (0.380 g, 1 mmol) in acrylonitrile (30  $\text{cm}^3$ ) was irradiated at  $-70^\circ\text{C}$ , following the standard irradiation techniques, for 2.5 h. An NMR spectrum of the

Table 1

|                               | $^1J(\text{C,H})/\text{Hz}$                |                               |
|-------------------------------|--|-------------------------------|
|                               | Carbon $\alpha$                            | Carbon $\beta$                |
| Thietane                      | 146.5                                      | 134.6                         |
| Corrective coefficient for CN | 10   | 10                            |
| Measured values               | 154  | 143                           |
|                               | Signal at $\delta$ 3.05 (CH <sub>2</sub> ) | Signal at $\delta$ 4.8 (CHCN) |

reaction mixture showed the presence of the adducts in about 80% yield. Column chromatography on silica gel, using light petroleum–dichloromethane (1:1) as eluent, yielded from the highest  $R_f$  fraction benzoyltriphenylsilane (18.2 mg, 5%); from the second fraction 3-phenyl-3-triphenylsilylacrylonitrile **3** (50.3 mg, 13%) as a white crystalline product, mp 175 °C (from methanol) (Found: C, 90.2; H, 5.9; N, 3.9.  $\text{C}_{27}\text{H}_{21}\text{NSi}$  requires C, 90.21; H, 5.89; N, 3.90%);  $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$  2220 (CN) and 1430 and 1110 (SiPh);  $\delta_{\text{H}}(\text{CDCl}_3)$  5.9 (1 H, s, vinylic-H) and 7.0–8.0 (20 H, m, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  111.79 (vinylic-CH), 116.26 (CN), 127.40, 128.21, 128.52, 130.39, 136.40 (ArCH), 131.27, 139.41 (ArC) and 166.421 (vinylic-C);  $m/z$  (EI) 387 ( $\text{M}^+$ ) and 259 (SiPh<sub>3</sub>); from the third fraction the adduct **2b** (21.6 mg, 5%) as a white crystalline product mp, 185–187 °C (from methanol) (Found: C, 82.95; H, 5.7; N, 3.6; S, 7.9.  $\text{C}_{28}\text{H}_{23}\text{NSSi}$  requires C, 82.93; H, 5.72; N, 3.64; S, 7.89%);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2240 (CN) and 1430 and 1110 (SiPh);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.9 (2 H, m,  $J$  10.0, CH<sub>2</sub>), 4.5 (1 H, t,  $J$  10.0, CH) and 6.8–7.8 (20 H, m, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  24.95 (CH<sub>2</sub>), 38.01 (CH), 47.72 (C), 119.38 (CN), 126.64, 127.69, 128.09, 130.17, 136.41, 137.70 (ArCH) and 131.70 and 145.64 (ArC);  $m/z$  (EI) 433 ( $\text{M}^+$ ), 387 ( $\text{M}^+ - \text{CH}_2\text{S}$ ) and 259 (SiPh<sub>3</sub>); and from the lowest  $R_f$  fraction the major adduct **2a** (258 mg, 60%) as a white crystalline product mp 104–105 °C (from methanol) (Found: C, 82.9; H, 5.75; N, 3.6; S, 7.9.  $\text{C}_{28}\text{H}_{23}\text{NSSi}$  requires C, 82.93; H, 5.72; N, 3.64; S, 7.89%);  $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$  2240 (CN) and 1430 and 1110 (SiPh);  $\delta_{\text{H}}(\text{CDCl}_3)$  3.1 (1 H, t,  $J$  9.10, CH<sub>2</sub>), 3.2 (1 H, dd,  $J_1$  6.30,  $J_2$  9.40, CH<sub>2</sub>), 4.8 (1 H, dd,  $J_1$  6.30,  $J_2$  8.82, CH) and 7.1–7.8 (20 H, m, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  25.17 (CH<sub>2</sub>), 37.12 (CH), 119.05 (CN), 127.64, 128.15, 129.21, 130.51, 132.72, 137.29 (ArCH) and 142.15 and 145.82 (ArC);  $m/z$  (EI) 433 ( $\text{M}^+$ ), 387 ( $\text{M}^+ - \text{CH}_2\text{S}$ ), 312 ( $\text{M}^+ - \text{PhCS}$ ) and 259 (SiPh<sub>3</sub>).

The reaction was performed under the same conditions, but changing the reaction temperature. At –40 °C, the adducts were obtained in about 70% yield and chromatography yielded **2a** in 35% yield. At 10 °C the adducts were obtained in about 55% yield, along with 25% of the trimer of **1**. At room temperature the adducts were obtained in about 30% yield, along with 35% of the trimer of **1** and 20% of benzoyltriphenylsilane.

The regiochemistry of the adduct **2a** was elucidated by measuring the values of  $^1J(\text{C,H})$ , the coupling through one bond, and comparing them with the values of similar products reported in the literature.<sup>6</sup> The  $^1J(\text{C,H})$  coupling constant was measured from the  $^{13}\text{C}$  satellites in the proton spectra, and was used to provide empirical correlations with structural features. The data available in the literature for thietanes, the corrective coefficient for the presence of the CN substituent and the measured values are collected in Table 1.

#### Methyl *c*-2-phenyl-*t*-2-triphenylsilyl- and *t*-2-phenyl-*c*-2-triphenylsilyl-thietane-*r*-3-carboxylate **4a**, **4b**

A solution of thioketone **1** (0.380 g, 1 mmol) in methyl acrylate (30 cm<sup>3</sup>) was irradiated at –70 °C, following the standard irradiation techniques, for 2 h. An NMR spectrum of the

reaction mixture showed the presence of the adducts in about 80% yield. Column chromatography on silica gel, using light petroleum–dichloromethane (1:1) as eluent, yielded from the highest  $R_f$  fraction the trimer of **1**<sup>10</sup> (34.2 mg, 9.0%); from the second fraction benzoyltriphenylsilane (25.5 mg, 7%); from the third fraction adduct **4b** (23.3 mg, 5%) as a white crystalline product, mp 135–136 °C (from methanol) (Found: C, 85.7; H, 6.4; S, 7.9.  $\text{C}_{29}\text{H}_{26}\text{O}_2\text{SSi}$  requires C, 85.68; H, 6.45; S, 7.87%);  $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$  1750 (CO<sub>2</sub>Me) and 1430 and 1110 (SiPh);  $\delta_{\text{H}}(\text{CDCl}_3)$  3.0 (2 H, m,  $J$  10.0, CH<sub>2</sub>), 3.3 (3 H, s, OCH<sub>3</sub>), 4.5 (1 H, t,  $J$  10.0, CH) and 7.1–7.7 (20 H, m, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  23.86 (CH<sub>2</sub>), 49.20 (C), 51.62 (OCH<sub>3</sub>), 53.34 (CH), 125.81, 127.34, 127.59, 129.53, 137.64 (ArCH), 133.52, 147.95 (ArC) and 172.76 (CO);  $m/z$  (EI) 466 ( $\text{M}^+$ ), 345 ( $\text{M}^+ - \text{PhCS}$ ) and 259 (SiPh<sub>3</sub>); from the fourth fraction adduct **4a** (270.3 mg, 58%) as a white crystalline product, mp 145–146 °C (from methanol) (Found: C, 85.65; H, 6.5; S, 7.9.  $\text{C}_{29}\text{H}_{26}\text{O}_2\text{SSi}$  requires C, 85.68; H, 6.45; S, 7.87%);  $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$  1740 (CO<sub>2</sub>Me) and 1430 and 1110 (SiPh);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.6 (1 H, t,  $J$  9.1, CH<sub>2</sub>), 3.3 (1 H, dd,  $J_1$  5.9,  $J_2$  9.2, CH<sub>2</sub>), 3.3 (3 H, s, OCH<sub>3</sub>), 4.6 (1 H, dd,  $J_1$  5.9,  $J_2$  8.8, CH) and 7.0–7.7 (20 H, m, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  21.87 (CH<sub>2</sub>), 45.65 (C), 51.07 (OCH<sub>3</sub>), 51.72 (CH), 126.74, 128.24, 128.75, 130.41, 137.62, 137.76 (ArCH), 138.17, 141.20 (ArC) and 171.95 (CO);  $m/z$  (EI) 466 ( $\text{M}^+$ ), 380 ( $\text{M}^+ - \text{methyl acrylate}$ ), 345 ( $\text{M}^+ - \text{PhCS}$ ) and 259 (SiPh<sub>3</sub>); and from the lowest  $R_f$  fraction the partially desilylated 2:1 adduct **5** (11.8 mg, 2%) as a white crystalline product, mp 162–163 °C (from MeCN) (Found: C, 81.8; H, 6.1; S, 12.1.  $\text{C}_{36}\text{H}_{32}\text{O}_2\text{S}_2\text{Si}$  requires C, 81.79; H, 6.11; S, 12.11%);  $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$  1740 (CO<sub>2</sub>Me) and 1430 and 1110 (SiPh);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.9 (2 H, m,  $J$  7.5, CH<sub>2</sub>), 3.6 (3 H, s, OCH<sub>3</sub>), 4.0 (1 H, dd,  $J_1$  7.5,  $J_2$  10.0, CH), 4.3 (1 H, s, CH) and 6.8–7.7 (25 H, m, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  27.16 (CH), 27.91 (CH<sub>2</sub>), 46.52 (CH), 52.11 (OCH<sub>3</sub>), 126.02, 127.96, 128.02, 128.21, 129.81, 129.94, 130.24, 136.72, 136.81 (ArCH), 135.52, 136.21, 137.35 (ArC) and 173.16 (CO);  $m/z$  (EI) 586 ( $\text{M}^+ - 2\text{H}$ ), 570 ( $\text{M}^+ - \text{H}_2\text{O}$ ), 466 ( $\text{M}^+ - \text{methyl acrylate}$ ) and 259 (SiPh<sub>3</sub>).

The reaction was performed under the same conditions, but changing the temperature. At –40 °C the yield of the adducts was 70% and, after chromatography, **4b** was isolated in 20% yield and **5** in 12% yield. Product **5** (25%) was the main product obtained by performing the reaction at room temperature (25 °C), and **4a** was isolated in 16% yield. The structure of product **5** was also elucidated by means of a desilylation reaction.

#### Protodesilylation of product **5**

To a solution of adduct **5** (70 mg, 0.12 mmol) in MeCN (4 cm<sup>3</sup>) were added solid CsF (36 mg, 0.24 mmol) and 1 drop of water. The mixture was stirred at room temperature for 24 h [the reaction was followed by TLC, light petroleum–dichloromethane (1:1) as eluent] and then extracted with CHCl<sub>3</sub> (10 cm<sup>3</sup>). The organic layer was washed with water, dried, concentrated and then analysed by NMR.

Chromatography on silica preparative TLC of the concentrate, using light petroleum–dichloromethane (2:1) as eluent, gave from the highest  $R_f$  fraction the adduct **6** (16 mg, 41%) as an oil,  $\delta_{\text{H}}(\text{CDCl}_3)$  3.03 (1 H, dd,  $J_1$  14.0,  $J_2$  3.5, CH<sub>2</sub>), 3.30 (1 H, dd,  $J_1$  14.0,  $J_2$  5.9, CH<sub>2</sub>), 3.71 (3 H, s, OCH<sub>3</sub>), 3.78 (2 H, s, CHPh), 4.05 (1 H, dd,  $J_1$  3.5,  $J_2$  5.9, CHCO<sub>2</sub>CH<sub>3</sub>) and 7.3–7.6 (10 H, m, ArCH);  $m/z$  (EI) 208 ( $\text{M}^+ - \text{PhCHS}$ ), 148 (208 – HCO<sub>2</sub>CH<sub>3</sub>) and 115 (148 – SH).

#### *r*-2,*t*-3-Dichloro-*t*-4-phenyl-*c*-4-triphenylsilylthietane **7**

A solution of thioketone **1** (0.200 g, 0.53 mmol) in *trans*-1,2-dichloroethene (20 cm<sup>3</sup>) was irradiated at –40 °C, following the standard irradiation techniques, for 2 h. The unchanged olefin was distilled off under reduced pressure. An NMR

spectrum of the recovered olefin showed that there was no isomerization and an NMR spectrum of the crude product mixture showed the presence of two adducts in 70% yield: the ratio between the two products **7** and **8** was 17:1. Chromatography on aluminium oxide preparative TLC, using light petroleum–dichloromethane (4:1) as eluent, gave from the highest  $R_f$  fraction adduct **7** (101 mg, 40%) as a white crystalline product, mp 128–130 °C (from methanol) (Found: C, 85.7; H, 5.85; S, 8.5.  $C_{27}H_{22}Cl_2SSi$  requires C, 85.68; H, 5.86; S, 8.45%);  $\nu_{max}(CCl_4)/cm^{-1}$  1430 and 1110 (SiPh);  $\delta_H(CDCl_3)$  5.35 (1 H, d,  $J$  8.3, CH), 5.65 (1 H, d,  $J$  8.3, CH) and 7.2–7.6 (20 H, m, ArH);  $\delta_C(CDCl_3)$  53.85 (C), 64.66 (CH), 65.64 (CH), 127.36, 127.73, 127.95, 130.39, 131.27, 137.22 (ArCH) and 137.57 and 134.94 (ArC);  $m/z$  (EI) 476 ( $M^+$ ), 441 ( $M^+ - Cl$ ) and 259 (SiPh<sub>3</sub>); from the second fraction the adduct **8** (15 mg, 5%) as a white crystalline product, mp 162–164 °C (from methanol) (Found: C, 85.7; H, 5.8; S, 8.5.  $C_{27}H_{22}Cl_2SSi$  requires C, 85.68; H, 5.86; S, 8.45%);  $\nu_{max}(CCl_4)/cm^{-1}$  1430 and 1110 (SiPh);  $\delta_H(CDCl_3)$  5.45 (1 H, d,  $J$  6.0, CH), 6.05 (1 H, d,  $J$  6.0, CH) and 7.2–7.6 (20 H, m, ArH);  $\delta_C(CDCl_3)$  57.00 (C), 61.20 (CH), 67.58 (CH), 127.23, 128.24, 130.61, 131.59, 137.44 (ArCH) and 129.85 and 136.20 (ArC);  $m/z$  (EI) 441 ( $M^+ - Cl$ ) and 259 (SiPh<sub>3</sub>); from the third fraction the trimer of **1** (16 mg, 8%) and from the lowest  $R_f$  fraction benzoyltriphenylsilane (19.3 mg, 10%).

#### *r*-2-,*c*-3-Dichloro-*c*-4-phenyl-*t*-4-triphenylsilylthietane **8**

A solution of thioketone **1** (0.200 g, 0.53 mmol) in *cis*-1,2-dichloroethene (20 cm<sup>3</sup>) was irradiated at –70 °C, following the standard irradiation techniques, for 30 min. The unchanged olefin was distilled off under reduced pressure. An NMR spectrum of the recovered olefin showed that there was no isomerization and an NMR spectrum of the crude product mixture showed the presence of two adducts in 70% yield: the ratio between the two products **7** and **8** was 1:21. Chromatography on aluminium oxide preparative TLC, using light petroleum–dichloromethane (4:1) as eluent, gave from the highest  $R_f$  fraction the adduct **7** (7.5 mg, 3%); from the second fraction the adduct **8** (160 mg, 63%); from the third fraction the trimer of **1** (12 mg, 6%); and from the lowest  $R_f$  fraction benzoyltriphenylsilane (19.4 mg, 10%).

#### Reaction of thioketone **1** with isobutyl vinyl ether

A solution of thioketone **1** (0.200 g, 0.53 mmol) in isobutyl vinyl ether (20 cm<sup>3</sup>) was irradiated at –70 °C, following the standard irradiation techniques, for 4 h. An NMR spectrum of the reaction mixture showed the presence of four adducts **11a–d** in 58% yield and of 1-phenyl-1-triphenylsilylethene **10** in 30% yield. Chromatography on aluminium oxide preparative TLC, using light petroleum–dichloromethane (3:1) as eluent, gave from the highest  $R_f$  fraction 1-phenyl-1-triphenylsilylethene **10**<sup>8</sup> (57.5 mg, 30%) as a white crystalline product, mp 146–148 °C (from methanol);  $\delta_H(CDCl_3)$  5.70 (1 H, d,  $J$  2.7 vinylic-CH), 6.3 (1 H, d,  $J$  2.7, vinylic-CH) and 7.15–7.65 (20 H, m, ArH);  $\delta_C(CDCl_3)$  134.06 (vinylic-CH), 126.80, 127.52, 127.89, 128.21, 129.61, 136.47 (ArCH), 134.17, 147.21 (Ar-C) and 143.88 (vinylic-C);  $m/z$  (EI) 362 ( $M^+$ ) and 259 (SiPh<sub>3</sub>); from the second fraction a mixture of adducts **11a–d** (63.6 mg, total yield 25%) [the four products could not be separated and the relative structures were not assigned. Their ratio was calculated as from the integration of the CH resonances 2:3:1:3 at  $\delta_H(CDCl_3)$  4.50, 4.72, 5.11 and 5.49 respectively;  $m/z$  (EI) 480 ( $M^+$ ) and 259 (SiPh<sub>3</sub>)]; and from the lower  $R_f$  fraction benzoyltriphenylsilane (19.3 mg, 10%).

#### Reaction of thioketone **1** with butyl vinyl ether

A solution of thioketone **1** (0.200 g, 0.53 mmol) in butyl vinyl ether (20 cm<sup>3</sup>) was irradiated at –70 °C, following the standard

irradiation techniques, for 4 h. An NMR spectrum of the reaction mixture showed the presence of four adducts **12a–d** in 57% yield and of 1-phenyl-1-triphenylsilylethene **10** in 30% yield. The ratio of the four adducts was calculated as 3:1:2:3 from the integration of the CH triplet resonances at  $\delta_H(CDCl_3)$  4.55, 4.70, 5.05 and 5.51 respectively. Chromatography on aluminium oxide preparative TLC, using light petroleum–dichloromethane (3:1) as eluent, gave from the highest  $R_f$  fraction 1-phenyl-1-triphenylsilylethene **10** (57.8 mg, 30%); from the second fraction one of the adducts **12a–d** (25.4 mg, 10%) as a white crystalline product, mp 162–164 °C (from methanol) (Found: C, 85.3; H, 7.4; S, 7.35.  $C_{31}H_{32}OSSi$  requires C, 85.28; H, 7.39; S, 7.33%);  $\delta_H(CDCl_3)$  0.85 (3 H, t, CH<sub>3</sub>), 1.35 (2 H, m), 3.2 (4 H, m), 5.05 (1 H, t,  $J$  7.5, CH) and 7.2–7.8 (20 H, m, ArH);  $\delta_C(CDCl_3)$  13.87 (CH<sub>3</sub>), 19.33 (CH<sub>2</sub>), 31.65 (CH<sub>2</sub>), 35.74 (CH<sub>2</sub>), 56.28 (C), 67.89 (OCH<sub>2</sub>), 76.82 (CH), 125.76, 126.59, 127.51, 129.65, 131.32, 137.18 (ArCH) and 132.88, 138.14 (ArC);  $m/z$  (EI) 480 ( $M^+$ ), 362 ( $M^+ - SCHOR$ ) and 259 (SiPh<sub>3</sub>); and from the lowest  $R_f$  fraction benzoyltriphenylsilane (19.3 mg, 10%). Only one of the four isomer was isolated. In a second experiment the ratio between the four adducts **12a–d** was found to be 1.2:1:1:1.4.

#### 1,1,2-Trimethylallyl phenyl(triphenylsilyl)methyl sulfide **13**

A solution of thioketone **1** (0.100 g, 0.26 mmol) in 2,3-dimethylbut-2-ene (15 cm<sup>3</sup>) was irradiated at 25 °C for 4 h, following the standard irradiation techniques. An NMR spectrum of the reaction mixture showed the presence of the title compound **13** in 45% yield. Chromatography on silica preparative TLC, using light petroleum–dichloromethane (1:1) as eluent, gave from the highest  $R_f$  fraction product **13** (36.2 mg, 30%) as an oil,  $\nu_{max}(CCl_4)/cm^{-1}$  1430 and 1110 (SiPh);  $\delta_H(CDCl_3)$  1.1 (3 H, s, CH<sub>3</sub>), 1.2 (3 H, s, CH<sub>3</sub>), 1.6 (3 H, s, CH<sub>3</sub>), 3.8 (1 H, s, CH), 4.7 (1 H, s, CH), 4.9 (1 H, s, CH) and 7.2–7.5 (20 H, m, ArH);  $\delta_C(CDCl_3)$  19.61 (CH<sub>3</sub>), 27.60 (CH<sub>3</sub>), 28.23 (CH<sub>3</sub>), 36.13 (CH), 53.14 (C), 112.01 (vinylic-CH<sub>2</sub>), 125.44, 127.62, 128.68, 128.82, 134.65, 136.74 (ArCH), 133.27, 147.77 (ArC) and 142.74 (vinylic-C);  $m/z$  (EI) 396 ( $M^+ - 68$ ), 381 ( $M^+ - 2,3$ -dimethylbut-2-ene) and 259 (SiPh<sub>3</sub>); from the second fraction the trimer of **1** (9.9 mg, 10%); from the third fraction benzoyltriphenylsilane (28.4 mg, 30%); and from the lowest  $R_f$  fraction triphenylsilanol (9.5 mg, 10%). The reaction was also performed at –70 °C with the same results.

#### 2-Phenylallyl phenyl(triphenylsilyl)methyl sulfide **14**

A solution of thioketone **1** (0.100 g, 0.26 mmol) in  $\alpha$ -methylstyrene (15 cm<sup>3</sup>) was irradiated at –20 °C for 2 h, following the standard irradiation techniques. An NMR spectrum of the reaction mixture showed the presence of the title compound **14** in 90% yield. Chromatography on silica preparative TLC, using light petroleum–dichloromethane (1:1) as eluent, gave from the highest  $R_f$  fraction product **14** (110 mg, 85%) as a white crystalline product, mp 245 °C (from methanol) (Found: C, 86.8; H, 6.4; S, 6.8.  $C_{34}H_{30}SSi$  requires C, 86.77; H, 6.43; S, 6.80%);  $\nu_{max}$  1430 and 1110 (SiPh);  $\delta_H(CDCl_3)$  3.4 (2 H, dd,  $J_1$  13.8,  $J_2$  28.6, CH<sub>2</sub>), 4.0 (1 H, s, CH), 4.9 (1 H, s, vinylic-H), 5.50 (1 H, s, vinylic-H) and 7.0–7.6 (25 H, m, ArH);  $\delta_C(CDCl_3)$  34.91 (CH), 36.09 (CH<sub>2</sub>), 115.92 (vinylic-CH<sub>2</sub>), 125.92, 126.60, 127.55, 127.90, 128.34, 129.66, 130.04, 136.52 (ArCH), 139.18, 139.37, 142.33 (ArC) and 129.60 (vinylic-C);  $m/z$  (EI) 380 ( $M^+ - \alpha$ -methylstyrene), 259 (SiPh<sub>3</sub>) and 118 ( $\alpha$ -methylstyrene) and from the second fraction benzoyltriphenylsilane (8.5 mg, 9%).

#### *cis*- and *trans*-2-Phenylthietane-3-carbonitrile **17a**, **17b**

To a solution of the adduct **2a** (90 mg, 0.2 mmol) in THF (3 cm<sup>3</sup>) were added a solution of tetrabutylammonium fluoride (TBAF) in THF (1.1 mol dm<sup>-3</sup>; 0.3 mmol) and a drop of water.

The mixture was stirred at room temperature for 24 h [the reaction was followed by TLC, light petroleum–dichloromethane (1:1) as eluent]. The reaction mixture was extracted with diethyl ether and the organic layer was washed with water, dried, concentrated and analysed by NMR. A ratio of 2:1 of the *trans* **17b** to *cis* **17a** desilylated isomer was found. Chromatography on silica preparative TLC, using light petroleum–dichloromethane (1:1) as eluent, gave from the higher  $R_f$  fraction *trans*-desilylated isomer **17b** (17.5 mg, 50%) as an oil (Found:  $M^+$ , 175.0448.  $C_{10}H_9NS$  requires  $M$ , 175.0456);  $\delta_H$ ( $CDCl_3$ ) 3.18 (1 H, t,  $J$  9.15,  $CH_2$ ), 3.65 (1 H, dd,  $J_1$  9.15,  $J_2$  9.76,  $CH_2$ ), 4.05 (1 H, dt,  $J_1$  9.15,  $J_2$  9.76,  $CHCN$ ), 5.15 (1 H, d,  $J$  9.76,  $CHPh$ ) and 7.35–7.80 (5 H, m, ArH);  $m/z$  (EI) 175 ( $M^+$ ), 129 ( $M^+ - CH_2S$ ), 122 (PhCHS) and 121 (PhCS) and from second fraction the *cis*-desilylated isomer **17a** (8.7 mg, 25%) as an oil (Found:  $M^+$ , 175.0446.  $C_{10}H_9NS$  requires  $M$ , 175.0456);  $\delta_H$ ( $CDCl_3$ ) 3.50 (2 H, m,  $J$  7.9,  $CH_2$ ), 4.43 (1 H, dt,  $J_1$  6.1,  $J_2$  9.8,  $CHCN$ ), 4.95 (1 H, d,  $J$  8.54,  $CHPh$ ) and 7.3–7.7 (5 H, m, ArH);  $m/z$  (EI) 175 ( $M^+$ ), 129 ( $M^+ - CH_2S$ ), 122 (PhCHS) and 121 (PhCS). The  $^{13}C$  NMR spectra was measured on the mixture of the two isomers:  $\delta_C$ ( $CDCl_3$ ) 29.660, 34.105 ( $CH_2$ ), 36.234, 36.325, 44.904, 48.462 (CH), 117.88, 118.332 (CN), 127.08, 129.09, 130.27 (ArCH) and 136.51 (ArC). The configuration of the adducts was elucidated from NOE experiments performed on the mixture of the two isomers: saturation of the phenyl resonance at  $\delta$  7.2–7.8 produced a significant increase in the intensity of the geminal proton signal (9.6%) at  $\delta$  5.15 and in the intensity of the  $CHCN$  proton signal (12.4%) at  $\delta$  4.05 of the *trans* isomer **17b**; however, only a increase in the intensity of the geminal proton signal (4.7%) at  $\delta$  4.95 of the *cis* isomer **17a** was observed. Desilylation of **2a** with  $CsF$   $DMSO-H_2O$  led in 24 h to a mixture 1.5:1 of *trans* **17b** and *cis* **17a** 2-phenylthietane-3-carbonitrile.

#### Methyl *cis*- and *trans*-2-phenylthietane-3-carboxylate **18a**, **18b**

To solution of the adduct **4a** (180 mg, 0.4 mmol) in  $DMSO$  (4  $cm^3$ ) were added solid  $CsF$  (120 mg, 0.8 mmol) and 1 drop of water. The mixture was stirred at room temperature for 24 h [the reaction was followed by TLC, light petroleum–dichloromethane (1:1) as eluent]. The reaction mixture was extracted with diethyl ether and the organic layer was washed with water, dried, concentrated and analysed by NMR. A ratio of 10:1 of the *trans* **18b** and *cis* **18a** desilylated isomer was found. An attempted separation of the product mixture, by chromatography on silica preparative TLC, gave only decomposition products. For this reason an NMR analysis was performed on the crude reaction mixture: methyl *trans*-2-phenylthietane-3-carboxylate **18b**  $\delta_H$ ( $CDCl_3$ ) 3.10 (1 H, t,  $CH_2$ ), 3.50–3.80 (1 H, m,  $CH_2$ ), 3.7 (3 H, s,  $OCH_3$ ), 4.05 (1 H, q,  $CHCO_2Me$ ), 5.12 (1 H, d,  $CHPh$ ) and 7.1–7.7 (5 H, m, ArH);

$\delta_H$ ( $C_6D_6$ ) 2.65 (1 H, t,  $CH_2$ ), 3.15 (3 H, s,  $OCH_3$ ), 3.30 (1 H, q,  $CH_2$ ), 3.75 (1 H, q,  $CHCO_2Me$ ), 5.05 (1 H, d,  $CHPh$ ) and 7.1–8.0 (5 H, m, ArH); methyl *cis*-2-phenylthietane-3-carboxylate **18a**  $\delta_H$ ( $CDCl_3$ ) 3.20 (3 H, s,  $OCH_3$ ), 4.20 (1 H, t,  $CHCO_2Me$ ), 4.90 (1 H, d,  $CHPh$ ) and 7.1–7.7 (5 H, m, ArH). The configuration of the adducts was elucidated from NOE experiments performed on the mixture of the two isomers: saturation of the phenyl resonance at  $\delta$  7.2–7.8 produced an increase in the intensity of the geminal proton signals but only in the intensity of the  $CHCO_2Me$  proton signal (8.5%) at  $\delta$  4.05 of the *trans* isomer **18b**. The reaction was also performed using  $TBAF-THF$ , but the starting material was recovered unchanged.

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