Chemistry of Silyl Thioketones. Part 7.[1] Synthesis, Cycloaddition and Oxidation of Cycloalkyl Silyl Thioketones and Desilylation of the Reaction Products

Bianca F. Bonini,[a] Filippo Busi,*[,a] Roland C. de Laet,[a] Germana Mazzanti,[a] Jan-Willem J. F. Thuring,[a] Paolo Zani[a] and Binne Zwanenburg[b]

[a] *Dipartimento di Chimica Organica 'A. Mangini' dell'Universita', Viale Risorgimento n. 4, I-40136 Bologna, Italy*

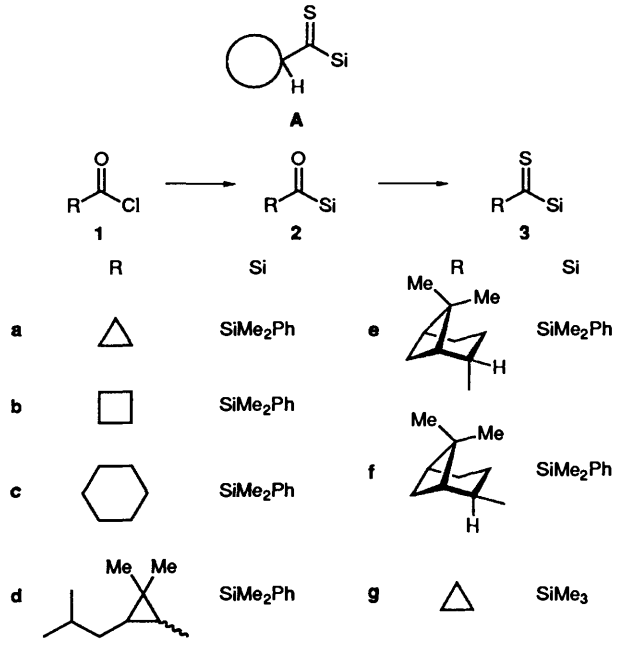
[b] *Department of Organic Chemistry, NSR Center, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands*

Cycloalkyl silyl thioketones **3**, achiral as well as chiral at carbon, have been synthesized by thionation of the corresponding acyl silanes **2**. During thionation of **2a**, **2d** and **2f** unexpected products were observed. Cycloaddition reactions of cycloalkyl silyl thioketones **3** with buta-1,3-diene have been performed. A diastereoisomeric excess (d.e.) of 80% was obtained in the case of chiral thione **3e**. Desilylation of the cycloadducts was only possible at the stage of the corresponding α-silyl sulfones **11**. Oxidation of compounds **3** led to the corresponding (*E*)-silyl sulfines **13** which by stereospecific fluorodesilylation gave (*Z*)-thioaldehyde *S*-oxides **14**. Compound **14e** is the first example of enantiomerically pure mono-substituted sulfine (thioaldehyde *S*-oxide).

Silyl thioketones are interesting compounds because of the high reactivity of the carbon–sulfur double bond in either nucleophilic or electrophilic additions and in cycloaddition reactions, enabling the synthesis of various products containing the Si–C–S unit.[2] Moreover, silyl thioketones can serve as synthetic equivalents of thioaldehydes by performing a proto-desilylation reaction at the stage of the reaction products.[3,4] In earlier papers we reported the synthesis and reactions of aryl[5] and *tert*-alkyl[6] silyl thioketones, and silyl thioketones which are chiral at silicon.[7] In this paper we describe the synthesis and reactions of cycloalkyl silyl thioketones **A**. These substrates will enable the involvement of enethiolization in their chemical behaviour to be established and, in addition, will allow the introduction of a chiral centre at the α-carbon atom or at a more remote position in the cycloalkyl moiety. With these *C*-chiral silyl thioketones, aspects of chirality transfer can be investigated.

Results and Discussion

A series of representative cycloalkyl silyl thioketones **3** was prepared by the sequence of reactions shown in Scheme 1. Since the first synthesis of silyl ketones (acyl silanes) reported by Brook[8] and Corey,[9] many other methods appeared in the literature.[10a,b] One of the most convenient routes involves the use of an acid chloride as starting material. Cyclopropyl trimethylsilyl ketone **2g** was synthesized in 59% yield following a known procedure involving the reaction of acid chloride **1a** with tris(trimethylsilyl)aluminium.[11] This method, however, gave very poor results when applied to other substrates. Therefore, a more generally applicable method was developed utilizing the reaction of an acid chloride with bis(dimethylphenylsilyl)copperlithium[12a,b] at −78 °C. The acid chlorides **1** gave satisfactory yields of silyl ketones **2** (Table 1). Also Mosher's reagent, *i.e.* (*S*)-(−)-α-methoxy-α-(trifluoromethyl)-phenylacetyl chloride could be converted into the corresponding silyl ketone using this silylating agent. The *cis*/*trans* mixture obtained from racemic *cis*/*trans* acid chloride **1d** was separated by chromatography. Enantiomerically pure silyl ketone **2e**, $[\alpha]_D$ + 54 (*c* 1.26 in C_6H_{12}) was obtained from commercially available (1*S*,2*S*)-(−)-*trans*-myrtanol, by first conversion into the acid chloride **1e** and subsequent silylation. The diastereo-



Scheme 1

Table 1 Synthesis of cycloalkyl silyl ketones **2** and thioketones **3**

Entry	Yield (%) 2	3
a	69	85
b	40	95
c	71	82
d	47	—[b]
e	65	77
f	34	—[c]
g	50[a]	75

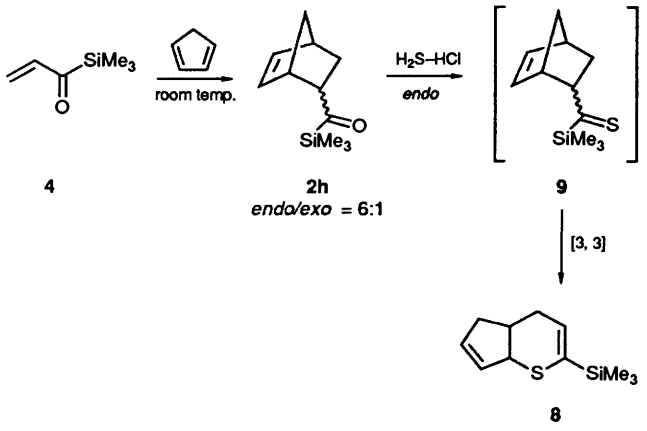
[a] Prepared using $(Me_3Si)_3Al$. [b] A deviant reaction occurs, for details, see Scheme 3. [c] A deviant reaction occurs, for details, see text.

Table 2

Entry	Yield (%) 10[a]	11	12
a	60	90	81
b	63	82	86
c	96	70	82
e	64[b]	64[b]	84[b]
g	40	—	—

[a] Yields based on starting ketone. [b] As diastereomeric mixture (see text).

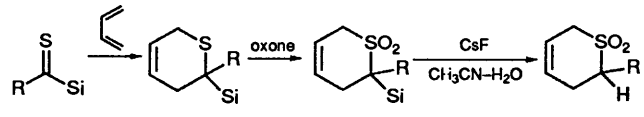
isomeric (1*S*,2*R*)-(−)-*cis*-myrtanol could, in a similar fashion, be converted into the corresponding silyl ketone **2f**. For acyl silane **2h** a different procedure was followed, *viz.* a Diels–Alder reaction of propenoylsilane **4** with cyclopentadiene[13] (Scheme 2). Thionation of silyl ketones **2** was performed in the same



Scheme 2

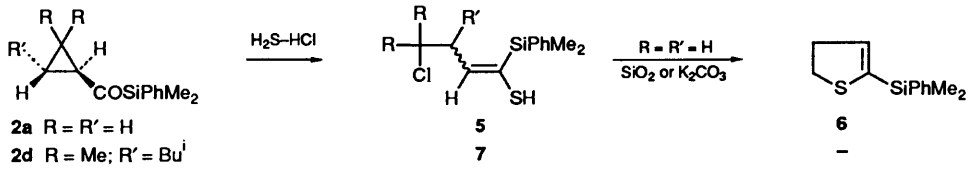
manner as used previously for aromatic[5] and *tert*-alkyl[6] derivatives, *viz.* H_2S–HCl at low temperature (−30 °C) (Scheme 1). The results are collected in Table 1. The products obtained were relatively stable in comparison with methyl silyl thioketone[6] and phenyl silyl thioketones.[5] In particular, cyclopropyl silyl thiones **3a** and **3g** can be stored at −20 °C for several months without noticeable decomposition. It is of importance to mention that the experimental conditions for the thionation reaction of cyclopropyl derivatives are rather critical. When an excess of HCl is used and the temperature exceeds −10 °C, a ring-opening reaction takes place to produce chloro enethiol **5** (Scheme 3) in the case of substrate **2a**. This product cyclizes to 2-(dimethylphenylsilyl)-4,5-dihydrothiophene **6** during chromatography on silica gel or by treatment with base (*e.g.* during alkaline washing). A similar ring enlargement to dihydrofuran derivatives has been reported for the cyclopropyl silyl ketones in the presence of acids.[14] Insurmountable difficulties were encountered with cyclopropyl silyl ketone **2d**. Only chloro enethiol **7** (Scheme 3) was obtained during several thionation attempts. Cyclobutyl silyl thioketone **3b** was too unstable for isolation and, therefore, was subjected to further reaction without further purification (*vide infra*). The cyclohexyl and *trans*-myrtanyl silyl thioketones **3c** and **3e**, enjoy an acceptable stability allowing full characterization. Product **3e** is the first example of an enantiomerically pure silyl thione chiral at carbon, $[\alpha]_D$ −371 (*c* 0.098 in C_6H_{12}). In contrast, to our surprise, the diastereoisomeric *cis*-myrtanyl silyl thioketone **3f** that was expected from thionation of *cis*-myrtanyl silyl ketone **2f** was not formed, but instead the same *trans*-myrtanyl silyl thioketone **3e** was obtained albeit in low yield, as was also confirmed by further reaction of thus obtained thioketone **3e** (see Experimental section). Apparently epimerization has taken place. In order to find out at which stage epimerization occurs, silyl ketone **2f** was treated with HCl. This gave a mixture of **2f** and **2e** besides a mixture of *cis*- and *trans*-myrtanal[15a,b] (see Experimental section). Deviating behaviour during the thionation was also observed for bicyclic substrate **2h**, the ultimate product turned out to be *endo*-tetrahydro-2-trimethylsilylcyclopenta[*b*]thiopyran **8**. The formation of this product can be rationalized by a [3,3]-sigmatropic rearrangement of initially formed thione **9** (Scheme 2). Similarly, a retro-thio-Claisen rearrangement has been observed during thionation of *endo*-2-acetylnorborn-5-ene.[16]

As mentioned in the introduction, thioketones readily undergo [4 + 2] cycloaddition reactions with suitable 1,3-dienes.[3] Thioketones **3** indeed reacted smoothly with buta-1,3-diene at room temperature. The completion of this reaction is indicated by the complete disappearance of the typical blue thione colour. The cycloadducts obtained were fully characterized by correct elemental analysis, exact mass and spectral features (Scheme 4). The yields are collected in Table 2.



Scheme 4 For R/Si = **a**–**g** see Scheme 1

Enantiomerically pure thione **3e** gave a mixture of two diastereoisomeric dihydrothiopyrans **10e** with a d.e. of 80% as deduced from the ^{13}C NMR spectrum (signals at 28.7 and 28.4 ppm) and a ^1H NMR spectrum (400 MHz) of the corresponding sulfone **11e**. It was established that the stereochemistry of the cyclohexane moiety was not affected during the cycloaddition reaction. The same reaction was performed with the thioketone obtained from **2f** and gave exactly the same product **10e** with the same d.e. Cycloaddition of cyclopropyl trimethylsilyl thioketone **3g** was performed with both buta-1,3-diene and cyclopentadiene. In the latter case, cycloaddition gave, at −78 °C as well as at room temperature, a 7:3 mixture of two diastereoisomers (see Experimental section). Direct desilylation of cycloadducts **10** met with severe difficulties. Attempted reactions with TBAF in THF, CsF in CH_3CN all failed leaving the cycloadducts unchanged. This behaviour confirms that protodesilylation of 6-silyldihydrothiopyrans occurs only when the carbon atom adjacent to silicon bears an aryl group.[3,6] In addition, the corresponding sulfones **11**, obtained from cycloadducts **10** by oxidation with oxone (potassium hydrogen persulfate) were subjected to desilylation conditions using CsF in CH_3CN–H_2O at room temperature. In this case protodesilylation could be accomplished in good yields (Table 2) to produce compounds **12** (Scheme 4). These cyclic sulfones are formally derived from a cycloaddition of butadiene with



Scheme 3

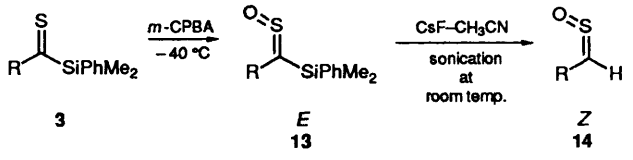
Table 3

Entry	Yield (%) 13[a]	Yield (%) 14[b]	$\delta_H(CDCl_3)$ 14 Z[c]	$\delta_H(CDCl_3)$ 14 E[c]
a	77	27	7.65	8.55
b	64	42	8.30	8.50
c	80	—	—	—
e	21	quantitative	8.08	8.77
g	50	—	—	—

[a] Yields based on starting ketone. [b] After purification by chromatography. [c] Measured at 200 MHz.

thioaldehyde *S*,*S*-dioxide (a sulfene). It should be noted that sulfene when produced by dehydrochlorination of methanesulfonyl chloride and base does not undergo a [4 + 2] cycloaddition reaction.[17] In the case of protodesilylation of *trans*-myrtanol derivative **11e** compound **12e** was obtained with a d.e. of 37% as was deduced from a ^{1}H NMR spectrum (400 MHz). Therefore, protodesilylation of **11e** was poorly stereoselective.

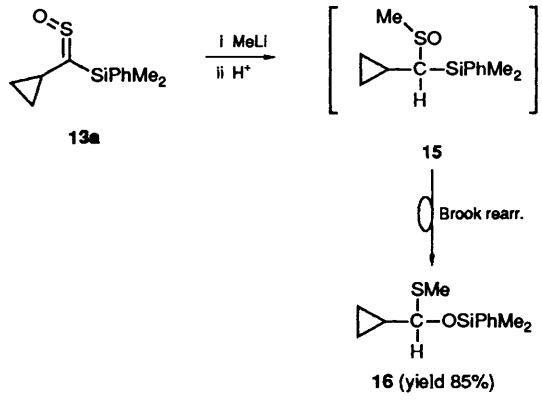
Next, the oxidation of cycloalkyl silyl thioketones **3** was investigated. When performed with *m*-chloroperbenzoic acid, oxidation gave (*E*)-sulfines **13** as the exclusive isomers (Scheme 5), which apparently are the kinetically preferred



Scheme 5

products.[4,5] The yields as estimated by ^{1}H NMR spectroscopy on the crude reaction mixture are quite satisfactory (Table 3). However, during chromatographic purification on silica gel a considerable loss had to be accepted either due to partial protodesilylation in the case of **13c** and **13e** to the corresponding thioaldehyde *S*-oxide or partial decomposition in the case of **13a** and **13b**. It is noteworthy that these sulfines bearing an α-hydrogen atom can be prepared without difficulty. In an early stage of our work on sulfines we had established[18] that enethiolizable thioketones can be oxidized to the corresponding *S*-oxides. Later, this finding was confirmed by Metzner.[19] Protodesilylation of silyl sulfines **13** was accomplished with CsF in CH_3CN–H_2O as reagent of choice, at room temperature. The resulting thioaldehyde *S*-oxides (monosubstituted sulfines) **14** are rather stable and can be separated chromatographically from dimethylphenylsilanol and siloxane. Sulfine **14e**, obtained from myrtanyl silyl sulfine **13e** is, in fact, the first example of an enantiomerically pure thioaldehyde *S*-oxide, $[\alpha]_D$ −39.8 (*c* 1.99 in C_6H_{12}). The assignment of the geometrical configuration of the desilylated sulfines was performed by a careful ^{1}H NMR spectroscopic analysis of the reaction mixture (Table 3). The predominant thioaldehyde *S*-oxide which has a typical lowfield thioaldehyde *S*-oxide proton resonance in the range 7.65–8.35 ppm is assigned *Z*-geometry on the basis of a comparison with NMR spectroscopic data of aromatic[4] and aliphatic[20] monosubstituted sulfines. These results reveal that the replacement of Si by H has taken place with an almost exclusive retention of configuration; in fact, a 98:2 mixture of *Z*- and *E*-isomers was obtained.

It is of interest to study the behaviour of cycloalkyl silyl thioketones towards organometallic reagents, because of the possible involvement of base-promoted enethiolization in these reactions. It should be noted, however, that attempts to deprotonate cyclopropanecarboxylic derivatives[21] lead to the formation of self condensation products. Reaction of substrate **1a** with a variety of organolithium or Grignard reagents led to a complex mixture of self condensation products (it was not possible to fully establish their structures). An exhaustive modification of the experimental conditions did not change the result. In contrast to silyl thioketone **3a**, the corresponding *S*-oxide **13a** (sulfine) reacted with methyllithium to give a unique product (Scheme 6), *viz*. *O*-dimethylphenylsilyl monothioacetal



Scheme 6

16. The formation of this product can be readily explained by assuming an initial attack of MeLi at the sulfine sulfur atom, to give the intermediate **15**, and a subsequent Brook rearrangement. Such silyl–oxygen transfer reactions of α-silyl sulfoxides are frequently encountered. It is remarkable that enethiolization of the sulfine **13a** does not interfere at all.

Experimental

B.p.s and m.p.s are uncorrected. IR spectra were recorded on a Perkin-Elmer 250 grating spectrometer. Routine ^{1}H NMR spectra were recorded with a Varian EM 360 L instrument. Highfield ^{1}H and ^{13}C NMR spectra were obtained with a Varian Gemini 200 and a Bruker 400 spectrometer. Mass spectra were recorded with a V.G. 7070-E spectrometer.

Routine UV-VIS spectra were obtained with a Jasco Uvidec-650 spectrometer. GC analyses were run on a Varian 3700 gas chromatograph equipped with a flame ionization detector and fitted to a Varian 4270 electronic integrator. Optical rotations were measured at *ca.* 20 °C on a Jasco DIP-360 Digital Polarimeter. $[\alpha]_D$ Values are given in units of 10^{-1} deg cm^2 g^{-1}. Preparative thick layer chromatography was carried out on glass plates using a 10 mm layer of Merk silica gel 60 PF 254.

Diethyl ether was distilled from phosphorus pentoxide and THF from sodium. Light petroleum refers to the fraction of b.p. 40–70 °C. All reactions involving organolithium derivatives and silylated thioketones were carried out under argon. All ^{1}H NMR and ^{13}C NMR spectra, if not specified, were performed at 200 MHz and at 50.3 MHz, respectively. In the characterization of the new compounds, elemental analysis has been performed for crystalline products. Oily products, because of the small scale used for the preparation, have been characterized by accurate mass measurements.

General Method for the Synthesis of Cycloalkyl Dimethylphenylsilyl Ketones **2**.—The acyl chloride (4.2 mmol) in anhydrous THF (2 cm^3) was added slowly to the bis(dimethylphenylsilyl)copper lithium[12a] (4.2 mmol based on CuCN) at −78 °C under argon. The mixture was stirred for 1 h at −78 °C, then was allowed to warm to 0 °C. The reaction was followed by GC and after 30 min at 0 °C the amount of ketone was generally

stabilized. The mixture was quenched with saturated aqueous ammonium chloride, and extracted with diethyl ether. The organic layer was dried and concentrated under reduced pressure and the residue was chromatographed on silica usually with light petroleum–diethyl ether, 9:1 as eluent. The higher R_f fraction was a product arising from the silylcuprate. The lower R_f fraction was ketone **2**.

Cyclopropyl dimethylphenylsilyl ketone **2a**. Yield 69%; oil (Found: M^+, 204.0973. $C_{12}H_{16}OSi$ requires *M*, 204.0970); $\nu_{max}(CCl_4)/cm^{-1}$ 1620 (C=O); λ_{max}(cyclohexane)/nm 367 (ε 689); $\delta_H(CDCl_3)$ 0.5 (6 H, s, $SiMe_2$), 0.8 (2 H, m), 1.0 (2 H, m), 2.4 (1 H, m, CH) and 7.3–7.7 (5 H, m, ArH); $\delta_C(CDCl_3)$ −4.9 ($SiMe_2$), 11.1 (CH_2), 25.4 (CH), 128.1, 129.8 and 134.1 (ArC) and 244.9 (C=O); *m/z* (EI) 204 (M^+), 203 ($M^+ - 1$), 189 ($M^+ - CH_3$), 176 ($M^+ - CO$) and 135 ($SiPhMe_2^+$).

Cyclobutyl dimethylphenylsilyl ketone **2b**. Yield 40%; oil (Found: M^+, 218.1121. $C_{13}H_{18}OSi$ requires *M* 218.1127); $\nu_{max}(CCl_4)/cm^{-1}$ 1630 (C=O); $\delta_H(CDCl_3)$ 0.50 (6 H, s, $SiMe_2$), 1.6–2.3 (6 H, m, CH_2), 3.5 (1 H, m, CH) and 7.3–7.7 (5 H, m, ArH); *m/z* (EI) 218 (M^+), 217 ($M^+ - 1$), 203 ($M^+ - CH_3$), 190 ($M^+ - CO$), 163 ($M^+ - C_4H_7$) and 135 ($SiPhMe_2^+$).

Cyclohexyl dimethylphenylsilyl ketone **2c**. Yield 71%; oil (Found: M^+, 246.1443. $C_{15}H_{22}OSi$ requires *M*, 246.1440); $\nu_{max}(C_2Cl_4)/cm^{-1}$ 1635 (C=O); $\delta_H(CDCl_3)$ 0.45 (6 H, s, $SiMe_2$), 1.0–1.9 (10 H, m, CH_2), 2.65 (1 H, m, CH) and 7.3–7.7 (5 H, m, ArH); *m/z* (EI) 246 (M^+), 245 ($M^+ - 1$), 231 ($M^+ - CH_3$), 163 ($M^+ - C_6H_{11}$) and 135 ($SiPhMe_2^+$).

Preparation of (±)-cis *and* trans-3-*isobutyl*-2,2-*dimethylcyclopropyl dimethylphenylsilyl ketone* **2d**. To a solution of (±)-*cis* and *trans* mixture of chrysanthemic acid[22] (5 g, 30 mmol) in ethanol (30 cm^3), 10% Pd/C (0.21 g, 0.2 mmol) was added. Hydrogen (2.5 atm) was introduced for 6 h. The mixture was filtered and the solvent evaporated at reduced pressure to give (±)-*cis*- and *trans*-2,2-dimethyl-3-isobutylcyclopropanecarboxylic acid (2.6 g, 52% yield, lit.[23]). The product was used without further purification for the next step. To a solution of (±)-*cis*- and *trans*-2,2-dimethyl-3-isobutylcyclopropanecarboxylic acid (2.6 g, 15 mmol) in diethyl ether (30 cm^3), was added $SOCl_2$ (2.1 cm^3, 30 mmol) slowly. The reaction mixture was refluxed for 1 h and stirred for 8 h at room temp. Diethyl ether and the excess of $SOCl_2$ were distilled off and subsequent distillation of the residue at reduced pressure (14 mmHg) gave (±)-*cis*- and *trans*-3-isobutyl-2,2-dimethylcyclopropanecarbonyl chloride (2.3 g, 79% yield, b.p. 80–85 °C, lit.[24]). This mixture was used for the synthesis of the corresponding acylsilane **2d** (see General procedure). The mixture of the two isomers was separated by preparative TLC (benzene–light petroleum 1:1, as eluent). The higher R_f fraction was the *cis*-**2d** isomer: oil; 13% (Found: M^+, 288.1913. $C_{18}H_{28}OSi$ requires *M*, 288.1909); $\nu_{max}(CCl_4)/cm^{-1}$ 1615 (C=O); $\delta_H(CDCl_3)$ 0.48 and 0.52 (6 H, 2s, $SiMe_2$), 0.87 (6 H, d, *J* 6.8, CH_3), 1.09 and 1.12 (6 H, 2s, CH_3), 1.0–1.8 (4 H, m), 2.39 (1 H, d, *J* 10, CHCO) and 7.3–7.7 (5 H, m, ArH); *m/z* (EI) 288 (M^+), 273 ($M^+ - CH_3$), 245 ($M^+ - C_3H_7$) and 135 ($SiPhMe_2^+$). The lower R_f fraction was the *trans*-**2d** isomer: oil; 34% (Found: M^+, 288.1907. $C_{18}H_{28}OSi$ requires *M*, 288.1909); $\nu_{max}(CCl_4)/cm^{-1}$ 1610 (C=O); $\delta_H(CDCl_3)$ 0.54 and 0.57 (6 H, 2s, $SiMe_2$), 0.90 (6 H, d, *J* 6.5, $2CH_3$), 1.00 and 1.13 (6 H, 2s, CH_3), 1.18–1.40 (2 H, m), 1.50–1.68 (1 H, m), 1.68–1.76 (1 H, m), 2.14 (1 H, d, *J* 6.0, CHCO) and 7.3–7.7 (5 H, m, ArH); $\delta_C(CDCl_3)$ −5.12 and −4.86 ($SiMe_2$), 20.42, 21.79, 22.50 and 22.65 (CH_3), 28.72 and 33.65 (CH), 34.49 (C), 37.69 (CH_2), 48.51 (CH), 128.50, 130.14 and 134.53 (ArCH), 135.44 (ArC) and 244.52 (C=O), assignments were made by DEPT; *m/z* (EI) 288 (M^+), 273 ($M^+ - CH_3$), 245 ($M^+ - C_3H_7$) and 135 ($SiPhMe_2^+$).

(1S,2S,5S)-(+)-6,6-*Dimethylbicyclo*[3.1.1]*heptan*-2-*yl dimethylphenylsilyl ketone* **2e**. From the corresponding acid chloride[25] ketone **2e** was obtained in 65% yield (based on starting acid) after chromatography (light petroleum–diethyl ether, 9:1 as eluent); oil (Found: M^+, 286.1750. $C_{18}H_{26}OSi$ requires *M*, 286.1753); $[\alpha]_D$ +54 (*c* 1.26 in C_6H_{12}); $\nu_{max}(CCl_4)/cm^{-1}$ 1638 (C=O); λ_{max}(cyclohexane)/nm 371 (ε 572); λ_{max}(cyclohexane) fluorescence/nm 420; $\delta_H(CDCl_3)$ 0.44 and 0.45 (6 H, 2s, $SiMe_2$), 0.72 (3 H, s, CH_3), 1.10 (3 H, s, CH_3), 1.15 (1 H, d, *J* 9.9), 1.20–1.30 (1 H, m), 1.66–2.30 (6 H, m), 3.27 (1 H, br t, CHCO) and 7.3–7.6 (5 H, m, ArH); *m/z* (EI) 286 (M^+), 163 ($COSiPhMe_2^+$) and 135 ($SiPhMe_2^+$).

(1S,2R,5S)-(−)-6,6-*Dimethylbicyclo*[3.1.1]*heptan*-2-*yl dimethylphenylsilyl ketone* **2f**. Oxidation of *cis*-myrtanol (0.812 g, 5.3 mmol) using Sharpless' method[26] gave the corresponding acid (0.83 g, 93%). From the corresponding acid chloride prepared according to the procedure used for the *trans* derivative,[25] ketone **2f** was obtained in 34% yield (based on starting acid) after chromatography (light petroleum–CH_2Cl_2, 5:1 as eluent); oil (Found: M^+, 286.1756. $C_{18}H_{26}OSi$ requires *M*, 286.1753); $[\alpha]_D$ −19.5 (*c* 2.05 in C_6H_{12}); $\nu_{max}(CCl_4)/cm^{-1}$ 1635 (C=O); $\delta_H(CDCl_3)$ 0.45 (3 H, s, CH_3), 0.48 and 0.50 (6 H, 2s, $SiMe_2$), 0.95 (3 H, s, CH_3), 1.6–2.6 (8 H, m), 3.0 (1 H, m, CHCO) and 7.25–7.7 (5 H, m, ArH); *m/z* (EI) 286 (M^+), 163 ($COSiPhMe_2^+$) and 135 ($SiPhMe_2^+$). The low yield of this reaction is probably due to the instability of **2f**. In fact, after one month at −20 °C **2f** was decomposed to a mixture of the *cis*–*trans* myrtanal in a ratio 1:10, as was deduced from the ^1H NMR signals[15b] of the aldehydic protons at 9.6 ppm (*cis*) and 9.75 ppm (*trans*).

endo- *and* exo-*Bicyclo*[2.2.1]*hept*-5-*en*-2-*yl trimethylsilyl ketone* **2h**. A mixture of trimethylsilylprop-2-en-1-one[27] **4** (0.5 g, 3.9 mmol) and freshly distilled cyclopentadiene (1 cm^3) was stirred at room temperature for 2 h. Chromatography by preparative TLC (light petroleum–diethyl ether, 30:1 as eluent) of the product mixture gave **2h** in a ratio *endo*/*exo* 6:1. The higher R_f fraction was *exo*-**2h**: oil (0.14 g, 11%) (Found: M^+, 194.1133. $C_{11}H_{18}OSi$ requires *M*, 194.1127); $\nu_{max}(CCl_4)/cm^{-1}$ 1637 (C=O) and 1261 ($SiMe_3$); $\delta_H(CDCl_3)$ 0.20 (9 H, s, $SiMe_3$), 1.0–1.4 (2 H, m, CH_2), 1.85 (2 H, m, CH_2), 2.75 (1 H, br q), 2.85 (1 H, br s), 2.95 (1 H, br s) and 6.15 (2 H, m, vinylic-H); $\delta_C(CDCl_3)$ −2.99 ($SiMe_3$), 26.79 (CH_2), 41.68 (CH), 43.33 (CH), 45.41 (CH_2), 55.53 (CH), 135.94 and 138.56 (vinylic-CH), assignments were made by DEPT; *m/z* (EI) 194 (M^+), 166 ($M^+ - CO$) and 73 ($SiMe_3^+$).

The lower R_f fraction was *endo*-**2h**: oil (0.85 g, 68%) (Found: M^+, 194.1132. $C_{11}H_{18}OSi$ requires *M*, 194.1127); $\nu_{max}(CCl_4)/cm^{-1}$ 1633 (C=O) and 1249 ($SiMe_3$); $\delta_H(CDCl_3)$ 0.11 (9 H, s, $SiMe_3$), 1.2–1.6 (4 H, m, CH_2), 2.77 (1 H, br s, CH), 3.2–3.3 (2 H, m, CH), 5.77 (1 H, m, vinylic-H) and 5.97 (1 H, m, vinylic-H); $\delta_C(CDCl_3)$ −3.08 ($SiMe_3$), 25.22 (CH_2), 42.33 (CH), 44.47 (CH), 49.40 (CH_2), 57.11 (CH), 131.45 and 136.92 (vinylic-CH) and 246.94 (CO), assignments were made by DEPT; *m/z* (EI) 194 (M^+), 179 ($M^+ - CH_3$), 166 ($M^+ - CO$) and 73 ($SiMe_3^+$).

General Method for the Synthesis of Cycloalkyl Dimethylphenylsilyl Thioketones **3**.—Hydrogen chloride and hydrogen sulfide were bubbled into a solution of the acyl silane (0.1 mmol) in anhydrous diethyl ether (30 cm^3) at −30 °C, until the starting ketone had disappeared by TLC (light petroleum–diethyl ether, 9:1 as eluent). The solution was then washed, under carbon dioxide, with 5% aqueous sodium hydrogen carbonate and with water, dried (Na_2SO_4), concentrated under reduced pressure and chromatographed (light petroleum–diethyl ether, 9:1 as eluent). The blue fraction was collected. In some cases the blue colour of the thione appeared only during the alkaline wash.

Cyclopropyl dimethylphenylsilyl thioketone **3a**. Yield 85% (from **2a**); blue violet oil (Found: M^+, 220.0748. $C_{12}H_{16}SSi$ requires *M*, 220.0742); $\nu_{max}(CS_2)/cm^{-1}$ 1250 ($SiMe_2$), 1220 (C=S) and 1110 (SiPh); $\delta_H(CDCl_3)$ 0.55 (6 H, s, $SiMe_2$), 1.18 (2 H, m),

1.48 (2 H, m), 3.65 (1 H, m, CH) and 7.3–7.7 (5 H, m, ArH); $\delta_C(CDCl_3)$ – 2.80 ($SiMe_2$), 20.84 (CH_2), 38.04 (CH), 128.19, 129.75, 134.31 and 136.24 (ArC) and 303.89 (C=S); *m/z* (EI) 220 (M^+), 205 ($M^+ - CH_3$), 192 ($M^+ - C_2H_4$) and 135 ($SiPhMe_2^+$).

Cyclobutyl dimethylphenylsilyl thioketone **3b**. Starting from **2b** (0.2 g, 0.92 mmol) after chromatography, **3b** (0.2 g, 95%, 0.85 mmol) was obtained as a blue oil. Owing to its instability it was not possible to obtain any spectra. The title compound **3b** was used immediately after preparation for further reactions.

Cyclohexyl dimethylphenylsilyl thioketone **3c**. Yield 82%; blue oil (Found: M^+, 262.1205. $C_{15}H_{22}SSi$ requires *M*, 262.1211); $\nu_{max}(CS_2)/cm^{-1}$ 1245 ($SiMe_2$), 1210 (C=S) and 1110 (SiPh); $\delta_H(CDCl_3)$ 0.55 (6 H, s, $SiMe_2$), 1.0–2.0 (10 H, m, CH_2), 3.75 (1 H, m, CH) and 7.25–7.7 (5 H, m, ArH); *m/z* (EI) 262 (M^+), 179 ($M^+ - C_6H_{11}$) and 135 ($SiPhMe_2^+$).

(1S,2S,5S)-(−)-6,6-*Dimethylbicyclo*[3.1.1]*heptan-2-yl dimethylphenylsilyl thioketone* **3e**. Yield 77%; blue oil (Found: M^+, 302.1530. $C_{18}H_{26}SSi$ requires *M*, 302.1524); $[\alpha]_D$ – 372 (*c* 0.098 in C_6H_{12}); $\nu_{max}(CCl_4)/cm^{-1}$ 1110 (SiPh); $\delta_H(CDCl_3)$ 0.45 and 0.49 (6 H, 2s, $SiMe_2$), 0.68 and 1.08 (6 H, 2s, CH_3), 1.1–2.6 (8 H, m), 4.28 (1 H, br t, CH) and 7.2–7.6 (5 H, m, ArH); $\delta_C(CDCl_3)$ −2.30 and −2.00 ($SiMe_2$), 18.16, 19.56, 21.95, 23.97, 26.44, 39.70, 44.07, 59.92 (CH_3, CH_2 and CH), 128.00, 129.60, 134.07 and 134.33 (ArC); *m/z* (EI) 302 (M^+), 179 ($M^+ - C_9H_{15}$) and 135 ($SiPhMe_2^+$).

Cyclopropyl trimethylsilyl thioketone **3g**. Yield 75% (Found: M^+, 158.0586. $C_7H_{14}SSi$ requires *M*, 158.0585); $\nu_{max}(CS_2)/cm^{-1}$ 1245 ($SiMe_3$) and 1220 (C=S); $\delta_H(CDCl_3)$ 0.20 (9 H, s, $SiMe_3$), 1.11–1.23 (2 H, m), 1.37–1.46 (2 H, m) and 3.61–3.76 (1 H, m, CH); $\delta_C(CDCl_3)$ – 1.69 ($SiMe_3$), 20.47 (CH_2), 37.14 (CH) and 307.14 (C=S); *m/z* (EI) 158 (M^+), 143 ($M^+ - CH_3$), 85 ($M^+ - SiMe_3$) and 73 ($SiMe_3^+$).

Problems Encountered During Thionation of the Cyclopropyl Derivatives.—*2-Dimethylphenylsilyl-4,5-dihydrothiophene* **6**. Thionation of **2a** (0.1 g, 0.33 mmol) using H_2S–HCl was performed with an excess of HCl (too high speed of bubbling of the two gases). The solution remained colourless even when the starting ketone had disappeared. The solvents were evaporated under reduced pressure to give crude 4-chloro-1-dimethylphenylsilylbutene-1-thiol **5** (0.086 g, 69%) as an oil; $\nu_{max}(CCl_4)/cm^{-1}$ 2550 (SH); δ_H(60 MHz; $CDCl_3$) 0.35 (6 H, s, $SiMe_2$), 2.4–2.8 (3 H, m, SH and CH_2), 3.4–3.8 (2 H, m, CH_2Cl) and 7.1–7.6 (5 H, m, ArH). This product was chromatographed on preparative TLC (light petroleum–diethyl ether, 3:1 as eluent) and gave the title compound **6** (0.028 g, 35%) (Found: M^+, 220.0749. $C_{12}H_{16}SSi$ requires *M*, 220.0742); $\nu_{max}(CS_2)/cm^{-1}$ 1430–1110 (SiPh) and 1300 ($SiMe_2$); $\delta_H(CDCl_3)$ 0.5 (6 H, s, $SiMe_2$), 2.7 (2 H, td, J_1 7.5, J_2 < 4, CH_2), 3.2 (2 H, t, *J* 7.5, CH_2), 5.8 (1 H, t, *J* < 4, vinyl H) and 7.2–7.5 (5 H, m, ArH); *m/z* (EI) 220 (M^+), 205 ($M^+ - CH_3$), 159 ($M^+ - C_2H_5S$) and 135 ($SiPhMe_2^+$). Product **6** was obtained also in 65% yield by alkaline treatment (NaH–THF) of the crude reaction mixture.

1-*Dimethylphenylsilyl-3-(1-chloroisopropyl)-5-methylhex-1-ene-1-thiol* **7**. Thionation of *trans*-**2d** (0.1 g, 0.35 mmol) was also performed at −50 °C. The solution remained colourless also when the starting ketone had disappeared (TLC). The solution was washed with 5% aqueous sodium hydrogen carbonate and with water, dried and concentrated under reduced pressure to give the title compound **7** (0.07 g, 60%) as a pure product (Found: M^+, 340.1457. $C_{18}H_{29}ClSSi$ requires *M*, 340.1448); $\nu_{max}(CCl_4)/cm^{-1}$ 2560 (SH); $\delta_H(CDCl_3)$ 0.48 (6 H, s, $SiMe_2$), 0.95 (6 H, br d, CH_3), 1.0–1.7 (3 H, m, CH_2 and CH), 1.52 (3 H, s, CH_3), 1.6 (3 H, s, CH_3), 2.45 (1 H, s, SH), 2.8 (1 H, br t, *J* 10, CH), 5.85 (1 H, d, *J* 10, vinylic-H) and 7.3–7.6 (5 H, m, ArH); $\delta_C(CDCl_3)$ −3.41, −3.30 ($SiMe_2$), 21.79, 24.14, 25.93, 30.26, 31.48, 39.69, 50.25 (CH_3, CH_2 and CH), 74.03 (CCl), 128.17, 129.72, 131.78, 134.28, 136.41 and 141.44 (ArC, vinylic-C); *m/z* (EI) 340 (M^+), 304 (M^+ – HCl), 262 ($M^+ - C_6H_6SiPhMe_2^+$) and 135 ($SiPhMe_2^+$). Attempts to cyclize **7** to the dihydrothiophene in the presence of K_2CO_3 or by chromatography led to an unidentified mixture of products.

Problems Encountered During Thionation of endo-*Bicyclo*[2.2.1]*hept-5-en-2-yl Trimethylsilyl Ketone* **2h**.—*4,4a,5,7a-Tetrahydro-2-trimethylsilylcyclopenta*[b]*thiopyran* **8**. The thionation of **2h** (0.15 g, 0.77 mmol) was performed at −20 °C. The solution became pale blue. The reaction was followed by TLC (light petroleum–diethyl ether, 30:1 as eluent). When the starting ketone disappeared only one product was present on TLC. After the usual work-up the colourless solution was concentrated and the residue purified by preparative thick layer chromatography (light petroleum as eluent) to afford product **8** (0.08 g, 50%), oil (Found: M^+, 210.0906. $C_{11}H_{18}SSi$ requires *M*, 210.0898); $\nu_{max}(CCl_4)/cm^{-1}$ 1240 ($SiMe_3$); $\delta_H(CDCl_3)$ 0.10 (9 H, s, $SiMe_3$), 2.0–2.35 (3 H, m), 2.4–2.6 (1 H, m), 2.7–2.95 (1 H, m), 4.05 (1 H, bd, *J* 8.6), 5.45 (1 H, m, vinylic-H), 5.67 (1 H, m, vinylic-H) and 6.45 (1 H, t, *J* 5.6, vinylic-H); $\delta_C(CDCl_3)$ −2.28 ($SiMe_3$), 31.70 and 39.15 (CH_2), 39.62 and 51.02 (CH), 131.25, 132.83, 137.6 (vinylic-CH) and 140.62 (vinylic-C); assignments were made by DEPT; *m/z* (EI) 210 (M^+), 195 ($M^+ - CH_3$) and 73 ($SiMe_3^+$).

Isomerization of (1S,2R,5S)-(−)-6,6-*dimethylbicyclo*[3.1.1]-*heptan-2-yl dimethylphenylsilyl ketone* **2f** *under thionation conditions*. Thionation of **2f** performed as for the compound **2e** gave a product identical with thioketone **3e** (yield 45%). Cycloaddition of this thioketone with buta-1,3-diene gave cycloadduct **10e** with a d.e. of 79%. In order to establish whether isomerization took place at the stage of acylsilane **2f** or at the stage of the corresponding thioketone, acylsilane **2f**, dissolved in diethyl ether, was treated with HCl gas at 0 °C. Quenching after 30 min with 5% aqueous sodium hydrogen carbonate gave a mixture of **2f**–**2e**, 2:1 and a trace of *cis*- and *trans*-myrtanal. Quenching after 5 h gave complete decomposition of **2f** to the *trans*- and *cis*-myrtanal.[15a,b]

General Procedure for Cycloadditions with Dienes.—The thiones **3** were subjected to cycloaddition immediately after partial evaporation of the chromatographic solvents to a small volume (1–2 cm^3). Usually some diethyl ether (3–5 cm^3) was added and an excess of buta-1,3-diene was bubbled through the blue solution at room temperature. Slowly the blue colour of the thione disappeared. The solvent was removed under reduced pressure and the residue gave the cycloadduct as the only product. In some cases the yields of cycloadducts were calculated on the starting ketone.

6-*Cyclopropyl-6-dimethylphenylsilyl-5,6-dihydro-2H-thiopyran* **10a**. Compound **10a** (0.27 g, 60%) was obtained from **3a** (0.37 g, 1.7 mmol) after chromatography (light petroleum–CH_2Cl_2, 5:1 as eluent), oil (Found: M^+, 274.1206. $C_{16}H_{22}SSi$ requires *M*, 274.1211); $\delta_H(CDCl_3)$ 0.05–0.50 (4 H, m, CH_2), 0.40 (6 H, s, $SiMe_2$), 1.0 (1 H, m, CH), 1.62 (1 H, br d, *J* 17.5), 2.37 (1 H, br d, *J* 17.5), 2.80 (1 H, br d, *J* 17.5), 3.38 (1 H, br d, *J* 17.5), 5.8 (2 H, m, vinylic-H) and 7.2–7.7 (5 H, m, ArH); *m/z* (EI) 274 (M^+) and 135 ($SiPhMe_2^+$).

6-*Cyclobutyl-6-dimethylphenylsilyl-5,6-dihydro-2H-thiopyran* **10b**. Product **10b** (0.10 g, 63%) was obtained from **2b** (0.12 g, 0.55 mmol) after thick layer chromatography (pentane as eluent), oil (Found: M^+, 288.1372. $C_{17}H_{24}SSi$ requires *M*, 288.1368); $\nu_{max}(CS_2)/cm^{-1}$ 1250 ($SiMe_2$) and 1110 (SiPh); $\delta_H(CDCl_3)$ 0.4 (6 H, s, $SiMe_2$), 1.5–3.2 (11 H, m), 5.8 (2 H, m, vinylic-H) and 7.2–7.8 (5 H, m, ArH); *m/z* (EI) 288 (M^+) and 135 ($SiPhMe_2^+$).

6-*Cyclohexyl*-6-*dimethylphenylsilyl*-5,6-*dihydro*-2H-*thiopyran* **10c**. Compound **10c** (0.24 g, 96%) was obtained from **2c** (0.2 g, 0.8 mmol) as a pure product, m.p. 43–44 °C (from CH_2Cl_2–pentane) (Found: C, 72.9; H, 9.3; S, 10.7. $C_{17}H_{24}O_2SSi$ requires: C, 72.1; H, 8.9; S, 10.1%); $\delta_H(CDCl_3)$ 0.45 (6 H, s, $SiMe_2$), 0.8–1.8 (10 H, m, CH_2), 2.0–3.2 (5 H, m, CH_2 and CH), 5.8 (2 H, m, vinylic-H) and 7.2–7.8 (5 H, m, ArH); *m/z* (EI) 316 (M^+), 262 ($M^+ - C_4H_6$), 148 ($M^+ - SHSiPhMe_2$) and 135 ($SiPhMe_2^+$).

6-(1S,2S,5S)-(−)-6,6-*Dimethylbicyclo*[3.1.1]*heptan*-2-*yl*-6-*dimethylphenylsilyl*-5,6-*dihydro*-2H-*thiopyran* **10e**. Product **10e** (0.16 g, 64%) was obtained as a mixture of two diastereoisomers from ketone **2e** (0.20 g, 0.71 mmol); oil (Found: M^+, 356.2014. $C_{22}H_{32}SSi$ requires *M*, 356.1994); $[\alpha]_D$ − 8 (*c* 1.625 in C_6H_{12}); d.e. 78% determined from the intensity of ^{13}C NMR signals at δ_C 28.37 and 28.71; $\nu_{max}(CCl_4)/cm^{-1}$ 1110 (SiPh); $\delta_H(CDCl_3)$ main isomer 0.42 and 0.46 (6H, 2s, $SiMe_2$), 0.57 and 1.14 (6 H, 2s, CH_3), 1.4–1.8 (6 H, m), 1.9–2.15 (2 H, m), 2.2–2.6 (3 H, m), 2.75–3.2 (2 H, m, CH_2S), 5.7–5.9 (2 H, m, vinylic-H) and 7.2–7.7 (5 H, m, ArH); $\delta_C(CDCl_3)$ −2.40 and −2.07 ($SiMe_2$), 19.12, 19.40, 23.73, 24.31, 25.03, 26.68, 28.37, 37.44, 39.48, 40.11, 40.28, 43.26 (CH_3, CH_2, CH and C), 124.49, 127.45, 127.75, 128.97, 135.02 and 138.92 (vinylic-CH and ArC); *m/z* (EI) 356 (M^+), 302 ($M^+ - C_4H_6$) and 135 ($SiPhMe_2^+$).

6-*Cyclopropyl*-6-*trimethylsilyl*-5,6-*dihydro*-2H-*thiopyran* **10g**. Adduct **10g** (42 mg, 40%) was obtained from ketone **2g** (72 mg, 0.5 mmol) after thick layer chromatography (pentane as eluent); oil (Found: M^+, 212.1042. $C_{11}H_{20}SSi$ requires *M*, 212.1055); $\nu_{max}(CCl_4)/cm^{-1}$ 1240 ($SiMe_3$); $\delta_H(CDCl_3)$ 0.10 (9 H, s, $SiMe_3$), 0.15–0.58 (4 H, m, cyclopropyl-CH_2), 1.0–1.3 (1 H, m, cyclopropyl-CH), 1.65 (1 H, dm), 2.25 (1 H, dm), 2.80 (1 H, dm), 3.4 (1 H, dm) and 5.7–5.9 (2 H, m, vinylic-H); *m/z* (EI) 212 (M^+), 197 ($M^+ - CH_3$) and 73 ($SiMe_3^+$).

endo- *and* exo-3-*Cyclopropyl*-3-*trimethylsilyl*-2-*thiabicyclo*-[2.2.1]*hept*-5-*ene*.—To a diethyl ether (10 cm^3) solution of thioketone **3g** (prepared from ketone **2g**, 72 mg, 0.50 mmol) freshly distilled cyclopentadiene (1 cm^3) was added at room temperature. The blue colour of the thioketone disappeared almost instantaneously. The solvent was removed under reduced pressure affording the title compound (55 mg, 49%) after thick layer chromatography (pentane as eluent) as a 7:3 mixture of the two diastereoisomers; oil (Found: M^+, 224.1061. $C_{12}H_{20}SSi$ requires *M*, 224.1055); $\nu_{max}(CCl_4)/cm^{-1}$ 1240 ($SiMe_3$); $\delta_H(CDCl_3)$ major and minor isomer 0.10 and 0.20 (9 H, 2s, $SiMe_3$), −0.20–+1.15 (5 H, m, CH_2 and CH), 1.4 (1 H, 2m), 1.64 and 2.08 (1 H, 2m), 3.15 and 3.4 (1 H, 2m), 3.92 (1 H, 2m), 5.9 and 6.2 (2 H, 2m, vinylic-H); *m/z* (EI) 224 (M^+), 209 ($M^+ - CH_3$) and 73 ($SiMe_3^+$). The same reaction was also performed at −78 °C; the ratio of the two diastereoisomers remained unchanged.

General Procedure for the Oxidation of the Adducts **10** *to the Corresponding Sulfones* **11**.—The adducts **10** (0.5 mmol) were dissolved in methanol (5 cm^3) and cooled to 0 °C. Then a solution of oxone ($KHSO_5$, 1.5 mmol) in water (2 cm^3) was added. The mixture was stirred for 30 min at 0 °C and 4 h at room temperature, diluted with water and extracted with chloroform. The organic layer was washed with water, dried and concentrated under reduced pressure to give the sulfone as a solid. These sulfones were purified by thick layer chromatography (light petroleum–ethyl acetate, 7:3 as eluent) and crystallized from CH_2Cl_2–pentane.

6-*Cyclopropyl*-6-*dimethylphenylsilyl*-5,6-*dihydro*-2H-*thiopyran* S,S-*dioxide* **11a**. Yield 90%, m.p. 98–100 °C (Found: C, 62.9; H, 7.4; S, 10.3. $C_{16}H_{22}O_2SSi$ requires: C, 62.7; H, 7.2; S, 10.4%); $\nu_{max}(CS_2)/cm^{-1}$ 1305 and 1120 (SO_2); $\delta_H(CDCl_3)$ 0.50 (4 H, m, cyclopropyl-CH_2), 0.65 (6 H, 2s, $SiMe_2$), 1.5 (1 H, m, cyclopropyl-CH), 1.75 (1 H, br d, *J* 18), 2.8 (1 H, br d, *J* 18), 3.25 (1 H, br dd, *J* 15), 3.9 (1 H, br d, *J* 15), 5.65 (2 H, dm, vinylic-H) and 7.3–7.7 (5 H, m, ArH); *m/z* (EI) 306 (M^+), 291 ($M^+ - CH_3$), 274 ($M^+ - O_2$), 229 ($M^+ - C_6H_5$), 135 ($SiPhMe_2^+$) and 107 ($M^+ - SO_2SiPhMe_2$).

6-*Cyclobutyl*-6-*dimethylphenylsilyl*-5,6-*dihydro*-2H-*thiopyran* S,S-*dioxide* **11b**. Yield 82%, m.p. 38–40 °C (Found: C, 64.2; H, 7.1; S, 9.4. $C_{17}H_{24}O_2SSi$ requires: C, 63.7; H, 7.6; S, 10.0%); $\nu_{max}(CS_2)/cm^{-1}$ 1300 and 1115 (SO_2); $\delta_H(CDCl_3)$ 0.55 (3 H, 2s, $SiMe_2$), 1.45–2.3 (6 H, m), 2.6–2.95 (2 H, m), 2.95–3.4 (3 H, m), 5.4 and 5.85 (2 H, 2m, vinylic-H) and 7.2–7.65 (5 H, m, ArH); *m/z* (EI) 320 (M^+), 305 ($M^+ - CH_3$), 292 ($M^+ - C_2H_4$), 243 ($M^+ - C_6H_5$), 135 ($SiPhMe_2^+$) and 121 ($M^+ - SO_2SiPhMe_2$).

6-*Cyclohexyl*-6-*dimethylphenylsilyl*-5,6-*dihydro*-2H-*thiopyran* S,S-*dioxide* **11c**. Yield 70%, m.p. 130–132 °C (Found: C, 65.0; H, 8.9; S, 9.5. $C_{19}H_{28}O_2SSi$ requires: C, 65.5; H, 8.1; S, 9.2%); $\nu_{max}(CCl_4)/cm^{-1}$ 1300 and 1120 (SO_2); $\delta_H(CDCl_3)$ 0.70 (6 H, 2s, $SiMe_2$), 0.75–1.85 (10 H, m, cyclohexane-CH_2), 2.5 (1 H, br d), 2.7 (1 H, dd), 3.05 (1 H, br d), 3.35 (1 H, br d), 3.8 (1 H, br d), 5.55 and 5.75 (2 H, 2m, vinylic-H) and 7.3–7.7 (5 H, m, ArH); *m/z* (EI) 348 (M^+), 333 ($M^+ - CH_3$), 271 ($M^+ - C_6H_5$), 149 ($M^+ - SO_2SiPhMe_2$) and 135 ($SiPhMe_2^+$).

6-(1S,2S,5S)-(+)-6,6-*Dimethyl*-*bicyclo*[3.1.1]*heptan*-2-*yl*-6-*dimethylphenylsilyl*-5,6-*dihydro*-2H-*thiopyran* S,S-*dioxide* **11e**. Yield 70% as a mixture of two diastereoisomers; m.p. 78–80 °C (Found: C, 68.1; H, 8.5; S, 8.3%; M^+, 388.1894. $C_{22}H_{32}O_2SSi$ requires: C, 68.0; H, 8.3; S, 8.2%; *M*, 388.1892); $[\alpha]_D$ + 6.7 (*c* 1.63 in acetone); d.e. 81% calculated from the integrals of 400 MHz ^1H NMR signals at δ_H 5.40, 5.60 and 5.75, 5.85; $\nu_{max}(CCl_4)/cm^{-1}$ 1305 and 1120 (SO_2); δ_H(400 MHz; $CDCl_3$) main isomer 0.55 (3 H, s, CH_3), 0.60 (6 H, 2s, $SiMe_2$), 1.1 (3 H, s, CH_3), 1.5 (1 H, d, *J* 10.4, CH_2[1H]), 1.75 (4 H, m, CH, CH_2[1H] and CH_2[2H]), 2.1 (2 H, m, CH_2[1H] and CH_2[1H]), 2.25 (1 H, m, CH), 2.6 (1 H, m, CH next to $CSiPhMe_2$), 2.75–3.0 (2 H, br dd, CH_2), 3.2–3.6 (2 H, br dd, CH_2S), 5.4 and 5.75 (2 H, 2m, vinylic-H) and 7.25–7.75 (5 H, m, ArH); δ_C(100.614 MHz; $CDCl_3$) −0.479 and 0.175 ($SiMe_2$), 19.225 (CH_3), 19.459, 24.389 and 25.054 (CH_2), 26.912 (CH_3), 33.372 (CH_2 next to $CSiPhMe_2$), 39.187 and 39.839 (CH), 40.598 (C), 43.673 (CH), 52.752 (CH_2SO_2), 59.722 (CSO_2), 120.019 and 126.834 (vinylic-CH), 127.649, 129.640, 135.116 (ArCH), 136.942 (ArC); assignments were made by DEPT and 2D Heterocorrelated sequences; *m/z* (EI) 388 (M^+), 373 ($M^+ - CH_3$), 189 ($M^+ - SO_2SiPhMe_2$) and 135 ($SiPhMe_2^+$).

General Procedure for the Protodesilylation of Silylsulfones **11** *to Compounds* **12**.—The adducts **11** (0.5 mmol) were dissolved in acetonitrile (1 cm^3). To this solution solid CsF (0.5 mmol) and 1 drop of water was added. The mixture was stirred at room temperature for 4 to 24 h (the reaction was followed by TLC, light petroleum–ethyl acetate 7:3 as eluent). The reaction mixture was extracted with diethyl ether and washed with water. The organic layer was dried and concentrated. The residue was separated by preparative thick layer chromatography (light petroleum–ethyl acetate, 7:3 as eluent). The higher R_f fraction was tetramethyldiphenyldisiloxane, the lower R_f fraction (visible only at I_2 vapour) was product **12**.

6-*Cyclopropyl*-5,6-*dihydro*-2H-*thiopyran* S,S-*dioxide* **12a**. Yield 81%, oil; $\nu_{max}(CS_2)/cm^{-1}$ 1315 and 1125 (SO_2); $\delta_H(CDCl_3)$ 0.25 (1 H, m), 0.75 (3 H, m), 1.15 (1 H, m), 2.35 (1 H, m, $CHSO_2$), 2.75 (2 H, m, CH_2), 3.65 (2 H, br s, CH_2SO_2) and 5.6 and 5.85 (2 H, 2m, vinylic-H); *m/z* (EI) 173 ($M^+ + 1$), 108 ($M^+ - SO_2$), 107 ($M^+ - SO_2H$), 93 ($M^+ - SO_2H - CH_2$) and 79 ($M^+ - SO_2H - CH_2 - CH_2$).

6-*Cyclobutyl*-5,6-*dihydro*-2H-*thiopyran* S,S-*dioxide* **12b**. Yield 86%, oil (Found: M^+, 186.0721. $C_9H_{14}O_2S$ requires *M*, 186.0714); $\nu_{max}(CCl_4)/cm^{-1}$ 1320 and 1126 (SO_2); $\delta_H(CDCl_3)$ 1.7–3.2 (10 H, m), 3.65 (2 H, qm, CH_2SO_2) and 5.65 and 5.85

(2 H, 2 m, vinylic-H); *m/z* (EI) 186 (M^+), 121 ($M^+ - SO_2H$), 107 ($M^+ - SO_2H - CH_2$), 93 ($M^+ - SO_2H - CH_2 - CH_2$) and 79 ($M^+ - SO_2H - CH_2 - CH_2 - CH_2$).

6-*Cyclohexyl*-5,6-*dihydro*-2H-*thiopyran* S,S-*dioxide* **12c**. Yield 82%, m.p. 122–124 °C (from CH_2Cl_2–pentane) (Found: C, 62.1; H, 8.8; S, 14.3. $C_{11}H_{18}O_2S$ requires: C, 61.6; H, 8.5; S, 14.9%); $\nu_{max}(CCl_4)/cm^{-1}$ 1320 and 1125 (SO_2); $\delta_H(CDCl_3)$ 1.0–3.0 (13 H, m), 3.35–3.8 (3 H, m, CH_2SO_2 and $CHSO_2$) and 5.55 and 5.85 (2 H, 2 m, vinylic-H); *m/z* (EI) 214 (M^+), 149 ($M^+ - SO_2H$), 135 ($M^+ - SO_2H - CH_2$) and 121 ($M^+ - SO_2H - CH_2 - CH_2$).

6-(1S,2S,5S)-(−)-6,6-*Dimethylbicyclo*[3.1.1]*heptan*-2-*yl*-5,6-*dihydro*-2H-*thiopyran* S,S-*dioxide* **12e**. Yield 84%, oil (Found: M^+, 254.1348. $C_{14}H_{22}O_2S$ requires *M*, 254.1340); $[\alpha]_D$ − 27.9 (*c* 1.07 in $CHCl_3$); d.e. 37% calculated from the integrals of 400 MHz ^1H NMR signals at δ_H 1.35 and 1.45; $\nu_{max}(CCl_4)/cm^{-1}$ 1319 and 1126 (SO_2); δ_H(400 MHz; $CDCl_3$) main isomer 0.89 (3 H, s, CH_3), 1.22 (3 H, s, CH_3), 1.36 (1 H, d, *J* 9.2), 1.6–1.9 (5 H, m), 2.1 (2 H, m), 2.5–2.6 (1 H, m), 2.6–3.2 (2 H, m), 3.4–3.6 (1 H, m, CH_2SO_2), 3.7–3.8 (1 H, m, CH_2SO_2) and 5.6 and 5.8 (2 H, 2m, vinylic-H); δ_C(100.614 MHz; $CDCl_3$) main isomer 20.060 (CH_3), 21.013 and 23.904 (CH_2), 26.754 (CH_3), 28.672 and 29.666 (CH_2), 31.103, 39.618 and 41.857 (CH), 52.181 (CH_2SO_2), 62.264 ($CHSO_2$), 119.012 and 127.834 (vinylic-CH); assignments were made by DEPT; *m/z* (EI) 254 (M^+), 199 ($M^+ - C_4H_7$) and 188 ($M^+ - H_2SO_2$).

General Procedure for the Oxidation of Cycloalkyl Dimethylphenylsilyl Thioketones **3** *to the Corresponding Sulfines* **13**.—A solution of an equimolecular amount of *m*-chloroperbenzoic acid (2 mmol) in diethyl ether was added at −30 °C under argon to the ethereal solution of **3**, obtained from the corresponding ketone **2** (2 mmol), until the disappearance of the thioketone colour. The solution was washed with 5% aqueous sodium hydrogen carbonate and with water, dried and concentrated to give the sulfines **13**, which were not further purified. Attempted chromatography on silica gave in some cases (cyclohexyl and myrtanyl derivatives) partial protodesilylation to the corresponding thioaldehyde *S*-oxides and in other cases (cyclopropyl and cyclobutyl derivatives) partial decomposition.

(E)-*Cyclopropyl dimethylphenylsilyl thioketone* S-*oxide* **13a**. Crude product yield 77% (from **2a**); oil (Found: M^+, 236.0673. $C_{12}H_{16}OSSi$ requires *M*, 236.0691); $\nu_{max}(CCl_4)/cm^{-1}$ 1135 (CSO); δ_H(60 MHz; $CDCl_3$) 0.5 (6 H, s, $SiMe_2$), 0.9–1.2 (4 H, m, CH_2), 2.2–2.8 (1 H, m, CH) and 7.2–7.8 (5 H, m, ArH); δ_H(200 MHz; CD_3CN) 0.6 (6 H, s, $SiMe_2$), 1.0–1.25 (4 H, m, CH_2), 2.4–2.7 (1 H, m, CH) and 7.4–7.8 (5 H, m, ArH); *m/z* (EI) 236 (M^+), 221 ($M^+ - CH_3$) and 135 ($SiPhMe_2^+$). Attempted purification by thick layer chromatography gave a complex mixture of protodesilylated products and diphenyltetramethyldisiloxane.

(E)-*Cyclobutyl dimethylphenylsilyl thioketone* S-*oxide* **13b**. Yield 64% (from **2b**); oil (Found: M^+, 250.0839. $C_{13}H_{18}OSSi$ requires *M*, 250.0847); $\nu_{max}(CCl_4)/cm^{-1}$ 1112 (CSO); $\delta_H(CDCl_3)$ 0.5 (6 H, s, $SiMe_2$), 1.6–2.4 (6 H, m, CH_2), 3.95 (1 H, m, CH) and 7.2–7.7 (5 H, m, ArH); *m/z* (EI) 250 (M^+), 234 ($M^+ - O$) and 135 ($SiPhMe_2^+$).

(E)-*Cyclohexyl dimethylphenylsilyl thioketone* S-*oxide* **13c**. Yield 80% (from **2c**); oil (Found: M^+, 278.1173. $C_{15}H_{22}OSSi$ requires *M*, 278.1161); $\nu_{max}(CS_2)/cm^{-1}$ 1240 ($SiMe_2$) and 1110 (CSO); $\delta_H(CDCl_3)$ 0.55 (6 H, s, $SiMe_2$), 1.0–1.9 (10 H, m, CH_2), 3.3 (1 H, quintet, CH) and 7.3–7.7 (5 H, m, ArH); $\delta_C(CDCl_3)$ −2.32 ($SiMe_2$), 25.31, 26.05, 30.90 (CH_2), 42.22 (CH), 128.17, 130.08, 134.07 (ArCH), 135.02 (ArC) and 199.23 (C=SO); *m/z* (EI) 278 (M^+), 260 ($M^+ - H_2O$) and 135 ($SiPhMe_2^+$). Thick layer chromatography of the crude product gave a mixture of sulfine **13c** and of the corresponding thioaldehyde **14c** which was present in about 20% yield.

(E)-(1S,2S,5S)-(−)-6,6-*Dimethylbicyclo*[3.1.1]*heptan*-2-*yl dimethylphenylsilyl thioketone* S-*oxide* **13e**. Yield 21% (from **2e**) after chromatography on Florisil (light petroleum–diethyl ether, 9:1 as eluent), oil (Found: M^+, 318.1467. $C_{18}H_{26}OSSi$ requires *M*, 318.1474); $[\alpha]_D$ − 20.2 (*c* 1.35 in C_6H_{12}); $\nu_{max}(CCl_4)/cm^{-1}$ 1125 (CSO); $\delta_H(CDCl_3)$ 0.5 and 0.52 (6 H, 2s, $SiMe_2$), 0.8 and 1.1 (6 H, 2s, CH_3), 1.55 (1 H, d, *J* 10), 1.6–2.1 (7 H, m), 3.95 (1 H, m, CH) and 7.3–7.6 (5 H, m, ArH); *m/z* (EI) 318 (M^+), 301 ($M^+ - OH$) and 135 ($SiPhMe_2^+$).

(E)-*Cyclopropyl trimethylsilyl thioketone* S-*oxide* **13g**. Yield 50% (from **3a**); oil (Found: M^+, 174.0542. $C_7H_{14}OSSi$ requires *M*, 174.0535); $\nu_{max}(CCl_4)/cm^{-1}$ 1245 ($SiMe_3$) and 1130 (C=SO); $\delta_H(CDCl_3)$ 0.20 (9 H, s, $SiMe_3$), 1.08–1.30 (4 H, m, CH_2) and 2.40–2.59 (1 H, m, CH).

General Procedure for the Desilylation of Silylsulfines **13** *to the Corresponding Thioaldehyde* S-*Oxides* **14**.—An equimolar amount of solid CsF was added to a solution of **13** (0.5 mmol) in CH_3CN (5 cm^3) containing a drop of water at room temperature. This mixture was sonicated until the disappearance of the silylsulfine (TLC, about 10–15 min). In the case of the cyclopropyl derivative a characteristic smell of garlic was noticed. The mixture was quenched with water and extracted with diethyl ether. The organic layer was dried, concentrated and separated by preparative thick layer chromatography. The higher R_f fraction was tetramethyldiphenyldisiloxane, the middle R_f fraction was the thioaldehyde *S*-oxide **13** and the lower R_f fraction was silanol.

(Z)-*Cyclopropanecarbothioaldehyde* S-*oxide* **14a**. Yield 27% after purification (light petroleum–diethyl ether, 8:2 as eluent); oil (Found: M^+, 102.0147. C_4H_6OS requires *M*, 102.0139); $\nu_{max}(CCl_4)/cm^{-1}$ 1123 (C=SO); $\delta_H(CDCl_3)$ 0.9 (2 H, m), 1.25 (2 H, m), 2.8 (1 H, m) and 7.65 (1 H, d, *J* 10.5, CH=SO); $\delta_C(CDCl_3)$ 11.37, 11.91 (CH_2 and CH) and 183.27 (CH=SO); *m/z* (EI) 103 ($M^+ + 1$), 102 (M^+), 85 ($M^+ - OH$), 69 ($M^+ - SH$) and 54 ($C_4H_6^+$). Another doublet was present at 8.55 ppm (*E*-isomer) in the ^1H NMR spectrum with an integrated area of less than 2% of that of the 7.65 ppm doublet.

(Z)-*Cyclohexanecarbothioaldehyde* S-*oxide* **14c**. Yield 60% after purification (light petroleum–ethyl acetate, 7:3 as eluent); oil (Found: M^+, 144.0597. $C_7H_{12}OS$ requires *M*, 144.0609); $\nu_{max}(CS_2)/cm^{-1}$ 1115 (C=SO); δ_HCDCl_3) 1.2–1.95 (10 H, m, CH_2), 3.5 (1 H, m, CH) and 8.3 (1 H, d, *J* 10, CH=SO); *m/z* (EI) 144 (M^+), 127 ($M^+ - OH$) and 95 ($M^+ - SOH$). Another doublet was present at 8.95 ppm (*E*-isomer) with an integrated area of less than 2% of that of the 8.3 ppm doublet.

(Z)-(1S,2S,5S)-(−)-6,6-*Dimethylbicyclo*[3.1.1]*heptane*-2-*carbothioaldehyde* S-*oxide* **14e**. Quantitative yield after purification (light petroleum-diethyl ether, 9:1 as eluent), oil (Found: M^+, 184.0929. $C_{10}H_{16}OS$ requires *M*, 184.0922); $[\alpha]_D$ − 39.8 (*c* 1.99 in C_6H_{12}); $\nu_{max}(CCl_4)/cm^{-1}$ 1131 (C=SO); $\delta_H(CDCl_3)$ 0.9 (3 H, s, CH_3), 1.2 (3 H, s, CH_3), 1.4 (1 H, d, *J* 10), 1.7–2.0 (6 H, m), 2.1 (1 H, m), 4.1 (1 H, m, CH) and 8.08 (1 H, d, *J* 10.1, CH=SO); $\delta_C(CDCl_3)$ 20.07, 20.34, 23.49, 23.87, 26.31, 29.52, 33.11, 40.01, 44.80 (CH_3, CH_2, CH) and 183.17 (CH=SO); *m/z* (EI) 184 (M^+), 167 ($M^+ - OH$) and 135 ($M^+ - SOH$). Another doublet at 8.77 ppm (*E*-isomer) in the ^1H NMR spectrum had an area less than 2% of that of the 8.08 ppm doublet.

1-*Methylthio*-1-*dimethylphenylsiloxy*-1-*cyclopropylmethane* **16**.—Methylithium (1.6 mol dm^{-3} in hexane; 0.38 cm^3, 0.61 mmol) was added to a solution of cyclopropyl dimethylphenylsilyl thioketone *S*-oxide **13a** (0.12 g, 0.51 mmol) in anhydrous diethyl ether at −78 °C under argon. The mixture was stirred for 1 h and then warmed to 0 °C. Saturated aqueous NH_4Cl was added and the organic layer separated and dried. The ethereal solution was concentrated under reduced pressure and afforded

the title compound **16** (0.11 g, 85%). This product was too unstable to be purified by chromatography; $\nu_{max}(CCl_4)/cm^{-1}$ 1252 ($SiMe_2$) and 1119 (SiPh); $\delta_H(CDCl_3)$ 0.2–0.6 (4 H, m, CH_2), 0.46 (6 H, s, $SiMe_2$), 1.1–1.2 (1 H, m, CH), 2.1 (3 H, s, SCH_3), 4.3 (1 H, d, *J* 7, CHS) and 7.3–7.7 (5 H, m, ArH); $\delta_C(CDCl_3)$ selected signal 81.93 (SCH_3); *m/z* (EI) 205 ($M^+ -$ SMe) and 135 ($SiMe_2Ph^+$).

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