Chemistry of Silyl Thioketones. Part 5.[1] Synthesis and Properties of Alkyl α-Silyl Thioketones: a Comparison with Aryl Derivatives

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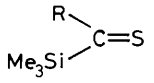
t-Butyl and methyl trimethylsilyl thioketones have been synthesized, and the reactivity towards organometallic compounds, dienes, and oxidation, and the desilylation of the resulting adducts, have been investigated. Where possible, a comparison with aryl trimethylsilyl thioketones has been made.

Our interest in the chemistry of silyl thioketones is due both to the high reactivity of the carbon-sulphur double bond, which makes possible the synthesis of a variety of compounds containing the Si–C–S unit,[2] and to the synthetic equivalence of silicon with an achiral or 'chiral' proton;[3] in the latter case, of course a chiral silicon must be used.[4,5] This synthetic equivalence has not previously been exploited successfully at the silyl thioketone stage.†

In an earlier paper we reported the synthesis and reactivity of aryl silyl thioketones;[6] we now describe two examples of aliphatic thioacylsilanes, namely t-butyl and methyl trimethylsilyl thioketones (**1a,b**), and compare them with the corresponding aryl derivatives.

Results and Discussion

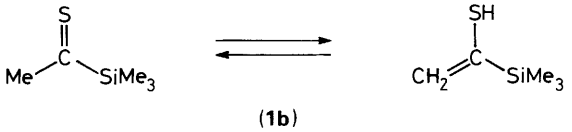
The thiones (**1a,b**) were prepared by the same procedure as used for the aryl derivatives, *i.e.* the acid-catalyzed reaction of acylsilanes with hydrogen sulphide to give the gem-dithiol, followed by alkaline washing of the reaction mixture. In the



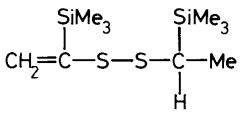
(1)

a; R = Bu^t

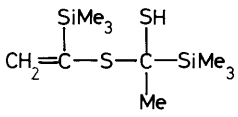
b; R = Me



(1b)



(2)



(3)

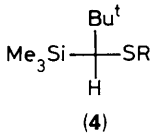
case of (**1b**) the gem-dithiol was formed quantitatively and could be isolated from the solution and characterized prior to the alkaline wash.

The thiones (**1a,b**) show very different stabilities; the t-butyl derivative (**1a**) (obtained in 90% yield) was thermally more stable than the aryl compounds, and no trimers were formed during its preparation or when it was set aside.[1] This stability arises from the steric hindrance exerted on C=S by the t-butyl group; recently thiopivaldehyde has been found to be relatively long-lived in solution[7] compared to other aliphatic derivatives. The thione (**1a**) showed $\lambda_{max.}$ 612 nm. (ε 10) in its u.v. spectrum and two singlets at δ 0.25 ($SiMe_3$) and 1.3 (t-butyl) p.p.m. in its ^1H n.m.r. spectrum. The ^{13}C n.m.r. spectrum showed the thiocarbonyl carbon at 316.02 p.p.m.

The thione (**1b**), however, totally decomposed during the n.m.r. measurement time at room temperature in deuteriochloroform to give the products (**2**) and (**3**) in the ratio 3:1. For this reason it could not be isolated pure but was trapped with 1,3-dienes. Although it has been claimed that methyl thiones have no tendency to exist in the enethiol form,[8] the formation of (**2**) and (**3**) by decomposition of the thione (**1b**) can be rationalized only in terms of a thiophilic and a carbophilic addition, respectively, of the enethiol form to another molecule of the thione. To our knowledge no example of this type of reaction has been reported in the literature.

Structures of (**2**) and (**3**) were assigned on the basis of correct analytical and spectroscopic data. Thus the ^1H n.m.r. spectrum of (**2**) showed signals at δ 0.13 and 0.22 (both s, 2 × $SiMe_3$), 1.31 (d, CH_3), 2.16 (q, CH), and 5.66 and 6.1 (both s, diastereotopic hydrogens of the CH_2). Compound (**3**) showed signals at δ 0.16 and 0.25 (2 × $SiMe_3$) 1.78 (s, Me), 2.3 (s, SH), and 5.97 and 6.43 (diastereotopic hydrogens of the CH_2). The mass spectra of both (**2**) and (**3**) showed the molecular ion at *m/z* 264.

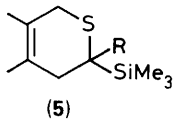
The more stable compound (**1a**) was treated with organolithium reagents; with methyl- and butyl-lithium only the thiophilic addition products (**4a**) and (**4b**) were formed in 60 and 70% yield respectively.



(4)

a; R = Me

b; R = Bu



(5)

a; R = Bu^t

b; R = Me

The bulkiness of the t-butyl group which stabilizes (**1a**) leads to a corresponding reduction in the reactivity of the carbon–sulphur double bond to Diels-Alder cycloadditions. Thus, the reaction between (**1a**) and 2,3-dimethylbuta-1,3-diene took *ca.* 15 days in a refrigerator, affording the adduct (**5a**) in 99% yield. In contrast, the unstable (**1b**) reacted very rapidly *in situ* with the same diene to afford (**5b**) in 30% yield, together with the decomposition products (**2**) and (**3**).

Oxidation of (**5a**) led to the sulphoxide *trans*-(**6**), whose configuration was determined by the l.i.s. effect. On addition of

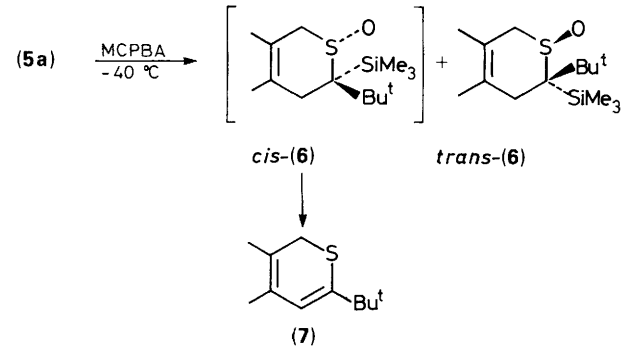
† Unpublished results of our laboratory. See also preceding works of the group.

Table. ^{1}H n.m.r. (300 MHz; $CDCl_3$) chemical shifts (p.p.m.) of 3,4-dimethyl-6-t-butyl-5,6-dihydro-2*H*-thiopyran derivatives (**8**), *trans*-(**11**), *cis*-(**11**) and (**12**)

	(**8**)	*trans*-(**11**)	*cis*-(**11**)	(**12**)
Bu^t	1.00 (s)	1.09 (s)	1.14 (s)	1.2 (s)
Me	3-Me[a] 1.66 (s) 4-Me[a] 1.68 (s)	1.70 (brs)	1.75 (brs)	1.65 (s) 1.70 (s)
5-H_2	2.14 (brs)	2.09 (t)	2.39 (dd)	2.7 (m)
6-H	2.65 (dd)	2.73 (brt)	2.60 (dd)	2.86 (dd)
$CH_2S(0)_{0-2}$	2.80 (d) 3.34 (d)	3.17 (brs)	3.40 (q)	3.19 (d) 3.70 (d)

[a] Attributed by n.O.e.

[$Yb(fod)_3$], the signal at δ 1.33 p.p.m. (Bu^t) showed the greatest downfield shift in comparison with the signal at δ 0.23 p.p.m. (Me_3Si). In addition to (**6**), a small quantity of 6-t-butyl-2*H*-thipyran (**7**) was formed during the oxidation, probably deriving from a Si-Pummerer rearrangement of the *cis* sulphoxide (Scheme 1). Compound (**7**) does not



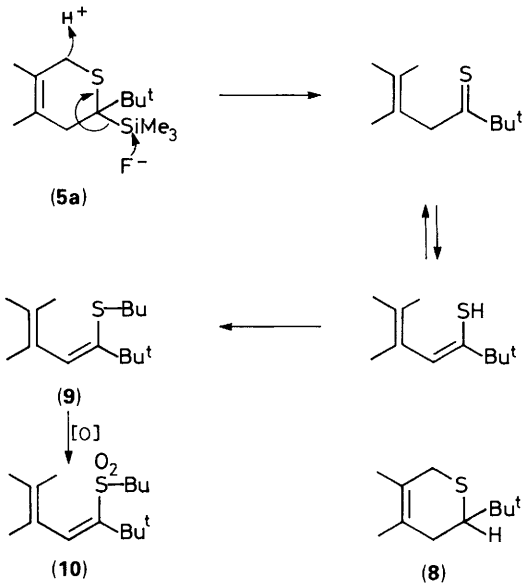
Scheme 1.

derive from *trans*-(**6**), since the latter is stable in deuteriochloroform at 30 °C over a long period. In the aromatic series, the oxidation of silyldihydrothiopyrans gave only 6-aryl-2*H*-thiopyrans,[2] no trace of sulphoxide being isolated.

The differing behaviour of the two α-silyl sulphoxides, *cis*- and *trans*-(**6**), with respect to the Si-Pummerer rearrangement could be related to the rigidity of the rings, caused by the presence of the t-butyl group, which prevents interaction between silicon and oxygen in the *trans*-sulphoxide.

The diene (**7**) is rather unstable and, with time, at room temperature or in solution it becomes green-blue, the ^{1}H n.m.r. signal of the vinylic proton disappearing. Analogous instability was found in open-chain sulphur dienes.[9]

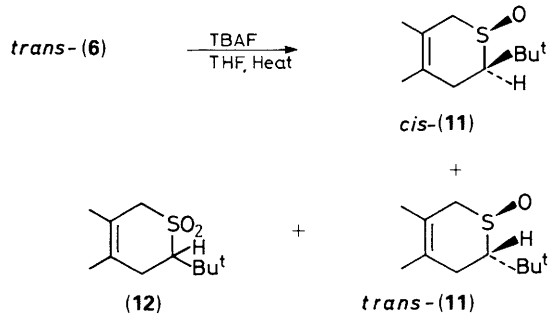
The adducts (**5a,b**) and *trans*-(**6**) were protodesilylated in order to obtain the adducts formally deriving from the cycloaddition of thioaldehydes and dienes. The reaction with the t-butyl derivative (**5a**) occurred only in boiling toluene with TBAF for 12 h, affording 3,4-dimethyl-6-t-butyl-5,6-dihydro-2*H*-thiopyran (**8**) in 30% yield. Surprisingly, (**5b**) could not be desilylated even in boiling toluene for 5 days. In the desilylation of (**5a**), besides the expected product (**8**), an open-chain diene (**9**) containing a butyl residue of the tetrabutylammonium fluoride was found to be the main product (60% yield). The structure of (**9**) was determined on the basis of analytical and spectral evidence (see Experimental section). In particular, the presence of a conjugated diene in the molecule was confirmed by the value of λ_{max} 244 n.m. in the u.v. spectrum which is in agreement with the Woodward-Fieser rules. Product (**9**) was oxidized to the corresponding sulphone (**10**) which was fully characterized. The formation of (**9**) probably proceeds as shown in Scheme 2, namely *via* a fluoride-mediated ring



Scheme 2.

opening of the silyl adduct (**5a**), leading to an enethiolizable thione which is then alkylated either by TBAF itself or by other species deriving from its decomposition at high temperature.[10]

With the aim of obtaining the desilylated product (**8**) in better yield, desilylation was performed in boiling toluene with several other desilylating agents, *viz.* caesium fluoride, tetraethylammonium fluoride (TEAF), and benzyltrimethylammonium fluoride (BTMAF); however, in all cases (**5a**) was recovered unchanged. Complete desilylation of the corresponding sulphoxide *trans*-(**6**) was achieved with TBAF in boiling THF for 4 h. Under these conditions desilylation was not stereospecific, affording a mixture of the two protodesilylated sulphoxides *cis*- and *trans*-(**11**) in the ratio 1:3, and also an unexpected sulphone (**12**) as a minor product (Scheme 3). Similar results were found using toluene as the solvent.



Scheme 3.

The sulphoxides *cis*- and *trans*-(**11**) could also be obtained in low yields by oxidation of the sulphide (**8**) with *m*-chloroperbenzoic acid at −30 °C. The low yields of the sulphoxides from this oxidation is due, in part, to a further oxidation to the corresponding sulphone (**12**).

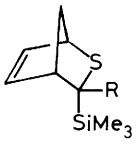
The separation of the two diasteroisomeric sulphoxides (**11**) presented considerable difficulties and only the *cis*-isomer could be obtained in a pure state after thick layer chromatography

(see Experimental section). The *trans*-sulphoxide was always contaminated with the *cis*-isomer. The ^{1}H n.m.r. chemical shifts of (**8**), *trans*-(**11**), *cis*-(**11**), and (**12**) are reported in the Table.

The stereochemistries of the two sulphoxides (**11**) were assigned by the l.i.s. effect with [Yb(fod)$_3$] on the mixture. For the sulphide (**8**), the sulphoxide *cis*-(**11**), and the sulphone (**12**), the 6-H shows a pattern formed by four sharp bands with two apparent coupling constants (*J ca.* 10—12 and *ca.* 4—6 Hz; see Experimental section). This suggests a pseudo-axial position for 6-H *anti* and *gauche* to 5-H and 5-H$_1$, respectively), and a pseudo-equatorial position for the t-butyl group. It follows that in *cis*-(**11**) the sulphoxide oxygen occupies a pseudo-axial position. In the other isomer, *trans*-(**11**), the 6-H signal is a broad triplet (*J ca.* 15 Hz). In this case, more information is necessary to assign the positions of the sulphoxide oxygen and the t-butyl group; we are currently investigating in this direction.

Both (**1a**) and (**1b**) were treated with cyclopentadiene. The reaction with (**1a**) at 5 °C was very slow; after 3 months, the starting thioketone was still present in the reaction mixture. Separation of the unchanged thione by chromatography gave the adduct (**13a**) in 44% yield. Compound (**1b**) was trapped *in situ* with cyclopentadiene and afforded (**13b**) (40% yield). The configuration of both adducts was assigned as Si-*endo* by n.O.e. experiments.

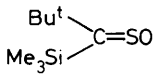
The thione (**1a**) could be oxidized with MCPBA to the corresponding *S*-oxide (**14**), obtained as a mixture of *E*- and *Z*-isomers in 3:2 ratio (89% yield); the geometry of the two



(**13**)

a; R = Bu^t

b; R = Me



(**14**)

thioketone oxides was attributed by the l.i.s. technique with [Yb(fod)$_3$] on the isomeric mixture, observing the differential shifts of the signals of the trimethylsilyl and t-butyl groups (see Experimental section). This behaviour contrasts with that of aryl thioacylsilanes which gave only the *E*-isomer, possibly due to the comparable steric hindrance of the t-butyl and trimethylsilyl groups which leads to an undirected attack of the peracid on the thione group. An attempt to separate the two isomers by chromatography on silica gave only the *E*-isomer, together with hexamethyldisiloxane and other unidentified products deriving from the decomposition of the *Z*-isomer. The formation of hexamethyldisiloxane from the *Z*-isomer can be explained by an interaction between the silicon and the oxygen leading to a siloxy derivative. This behaviour is common to that of other organosilicon compounds in which an oxygen is β-coplanar to silicon.[11]

Conclusions

The results presented here show that the chemical behaviour of alkyl silyl thioketones is similar to that of the aromatic series as far as the cycloaddition with 1,3-dienes and the addition of organometallics are concerned. Differences were found in the oxidation of alkyl silyl thioketones; oxidation of (**1a**) leads to a mixture of *E* and *Z* thioketone oxides whereas oxidation of aryl silyl thiones gives only the *E*-isomer. A remarkable finding is the ability of methyl trimethylsilyl thioketone to tautomerize to the enethiol; this is not found in non-silylated methyl thioketones.

Experimental

M.p.s and chemical shifts are uncorrected. U.v.—visible spectra were measured on a Jasco UVIDEC-650 spectrophotometer. I.r. spectra were recorded on a Perkin-Elmer 257 grating spectrometer. Routine n.m.r. spectra were obtained with a Varian EM 360 L instrument. High field ^{1}H and ^{13}C n.m.r. spectra were obtained at 300 and 75.46 MHz respectively with the Bruker CXP 300 spectrometer of the High Field N.m.r. Spectroscopy Service of CNR in Bologna. Mass spectra were recorded with a V.G. 7070-E spectrometer.

Diethyl ether was distilled from phosphorus pentaoxide and tetrahydrofuran (THF) from $LiAlH_4$ immediately before use. Light petroleum refers to the fraction of b.p. 40—70 °C. All reactions involving silylated thioketones were carried out under nitrogen or argon. New compounds were authenticated with elemental analysis, except for compounds (**1b**), (**3**), (**7**), (**9**), (**13a**,**b**), and (**14**) which degrade rapidly with time; in these cases, accurate mass measurements were performed.

t-Butyl Trimethylsilyl Thioketone (**1a**).—Hydrogen chloride and hydrogen sulphide were bubbled into a solution of t-butyl trimethylsilyl ketone[12] (1 g, 6.35 mmol) in anhydrous ether (40 ml) at −10 °C. The solution turned green and then blue. The reaction was followed by t.l.c. (light petroleum–ether, 10:1 as eluant), a 0.4% solution of 2,4-dinitrophenylhydrazine in 2M HCl being used as developer to give a yellow colour with the starting ketone. After disappearance of the starting ketone (*ca.* 2h), the solution was washed under carbon dioxide with 5% aqueous sodium hydrogen carbonate and with water, and then dried (Na_2SO_4) and concentrated under reduced pressure to give almost pure (**1a**) (0.98 g, 90%). Further purification of (**1a**) by flash chromatography (pentane as eluant) gave a blue *oil* (Found: C, 55.0; H, 10.5; S, 18.3%; M^+, 174.0899. $C_8H_{18}SSi$ requires C, 55.1; H, 10.4; S, 18.4%; *M*, 174.0898); $\lambda_{max.}$(cyclohexane) 612 nm (ε 10.1); $\nu_{max.}$ (CS_2) 2 960, 1 250, 1 100, 930, 845, and 755 cm^{-1}; δ_H($CDCl_3$) 0.28 (9 H, s, $SiMe_3$) and 1.3 (9 H, s, Bu^t); δ_C($CDCl_3$) 316.0 (C=S), 57.1 (*C*Me$_3$), 28.8 (Me), and 2.3 ($SiMe_3$); *m*/*z* 174 (M^+), 173 ($M^+ - H$), 159 ($M^+ - CH_3$), and 101 ($M^+ - SiMe_3$).

Methyl Trimethylsilyl Thioketone (**1b**).—Hydrogen chloride and hydrogen sulphide were bubbled into a solution of methyl trimethylsilyl ketone[13] (0.68 g, 5.86 mmol) in anhydrous ether (50 ml) at −30 °C, until the starting ketone had disappeared. The blue colour of the thione appeared only during the alkaline wash. Owing to its instability it was not possible to obtain any spectra of this thione. The blue solution rapidly became colourless and after chromatography on silica (light petroleum as eluant) afforded two fractions; the first fraction was (**2**) (0.36 g, 47%) as an *oil* (Found: C, 45.6; H, 9.2; S, 24.2%; M^+, 264.0863. $C_{10}H_{24}S_2Si_2$ requires C, 45.4; H, 9.1; S, 24.2%; *M*, 264.0858); $\nu_{max.}$(neat) 2 950, 1 250, and 840 cm^{-1}; δ_H($CDCl_3$) 0.13 (9 H, s, $SiMe_3$), 0.22 (9 H, s, $SiMe_3$), 1.31 (3 H, d, Me), 2.16 (1 H, q, CH), 5.66 (1 H, s, vinyl H), and 6.1 (1 H, s, vinyl H); δ_C($CDCl_3$) −2.96, −1.30, 16.10, 31.05, 118.05, and 145.37; *m*/*z* 264 (M^+), 249 ($M^+ - CH_3$), 230 ($M^+ - H_2S$), 133 (MeCHSSiMe_3), and 73 ($SiMe_3$); the second fraction was (**3**) (0.12 g, 16%) as an *oil* (Found: M^+, 264.0860. $C_{10}H_{24}S_2Si_2$ requires *M*, 264.0858); $\nu_{max.}$(CS_2) 2 950, 2 920, 2 900, 2 850, 1 250, 832, 750, and 690 cm^{-1}; δ_H($CDCl_3$) 0.17 (9 H, s, $SiMe_3$), 0.25 (9 H, s, SiMe), 1.78 (3 H, s, Me), 2.3 (1 H, s, SH), 5.97 (1 H, s, vinyl H), and 6.43 (1 H, s, vinyl H); δ_C($CDCl_3$) −3.93, −1.84,

25.98, 41.24, 126.98, and 143.37; *m/z* 264 (M^+), 249 ($M^+ - CH_3$), 231 ($M^+ - SH$), 133 ($MeCSHSiMe_3$), 132 ($MeCSSiMe_3$), 117 (Me_3SiCS), and 73 ($SiMe_3$).

Repetition of this reaction without the alkaline washing gave 1-trimethylsilylethane-1,1-dithiol as a white solid. This product proved unstable when its recrystallization was attempted, m.p. 115—125 °C; $\nu_{max.}(CCl_4)$ 2 540 cm^{-1} (SH); $\delta_H(CCl_4)$ 0.23 (9 H, s, $SiMe_3$), 1.7 (3 H, s, Me), and 2.17 (2 H, s, SH); thermal decomposition prevented the recording of the e.i. mass spectrum for this compound.

2,2-*Dimethyl*-1-*trimethylsilylpropyl Methyl Sulphide* (**4a**).—Methyl-lithium (4.7 mmol) in hexane was added to a solution of (**1a**) (0.69 g, 3.96 mmol) in anhydrous THF (50 ml) at −78 °C under nitrogen. After being stirred for 20 min, the reaction mixture was allowed to warm to 0 °C, when it was quenched with saturated aqueous ammonium chloride, and the aqueous layer extracted with ether. The organic layer was dried and concentrated. Purification by chromatography (pentane as eluant) afforded (**4a**) (0.46 g, 61%) as an *oil* (Found: C, 56.5; H, 11.6; S, 16.9%; M^+, 190.1213. $C_9H_{22}SSi$ requires C, 56.8; H, 11.7; S, 16.9%; *M*, 190.1212); $\delta_H(CDCl_3)$ 0.18 (9 H, s, $SiMe_3$), 1.08 (9 H, s, Bu^t), 1.38 (1 H, s, CH), and 2.16 (3 H, s, Me); *m/z* 190 (M^+), 174 ($M^+ - CH_3$), 73 ($SiMe_3$), and 57 (Bu^t).

Butyl 2,2-*Dimethyl*-1-*trimethylsilylpropyl Sulphide* (**4b**).—The procedure as given for (**4a**) was followed using butyl-lithium instead of methyl-lithium. Purification by chromatography (pentane as eluant) afforded (**4b**) (69%) as an *oil* (Found: C, 61.9; H, 12.2; S, 13.7%; M^+, 232.1675. $C_{12}H_{28}SSi$ requires C, 62.0; H, 12.1; S, 13.8%; *M*, 232.1681); $\delta_H(CDCl_3)$ 0.12 (9 H, s, $SiMe_3$), 0.87 (3 H, t, Me), 1.01 (9 H, s, Bu^t), 1.3—1.6 (4 H, m, CH_2CH_2), 1.47 (1 H, s, CH), and 2.35—2.65 (2 H, m, CH_2S); *m/z* 232 (M^+), 217 ($M^+ - CH_3$), 175 ($M^+ - Bu^t$), and 73 ($SiMe_3$).

3,4-*Dimethyl*-6-*t*-*butyl*-6-*trimethylsilyl*-5,6-*dihydro*-2H-*thiopyran* (**5a**).—A solution of (**1a**) (0.6 g, 3.45 mmol) and 2,3-dimethylbuta-1,3-diene (1.9 ml, 17 mmol) in ether (5 ml) was kept in the refrigerator for 15 days, during which the blue colour of the thioketone disappeared. The solvent and the excess diene were removed under reduced pressure to give the adduct (**5a**) (0.88 g, 99%). Further purification by flash chromatography (light petroleum–ethyl acetate, 20:1 as eluant) gave (**5a**) as an *oil* (Found: C, 65.5; H, 11.0; S, 12.4%; M^+, 256.1675. $C_{14}H_{28}SSi$ requires C, 65.6; H, 11.0; S, 12.5%; *M*, 256.1681); $\delta_H(CDCl_3)$ 0.15 (9 H, s, $SiMe_3$), 1.03 (9 H, s, Bu^t), 1.77 (6 H, br s, Me), 2.27 (2 H, br s, CH_2), and 2.9 (2 H, br s, CH_2S); *m/z* 256 (M^+), 199 ($M^+ - Bu^t$), 73 ($SiMe_3$), and 57 (Bu^t).

3,4,6-*Trimethyl*-6-*trimethylsilyl*-5,6-*dihydro*-2H-*thiopyran* (**5b**).—2,3-Dimethylbuta-1,3-diene was added to (**1b**) in ether [prepared from methyl trimethylsilyl ketone (0.62 g, 5.3 mmol)] until the blue colour of the thioketone disappeared. After evaporation of the solvent, chromatography of the mixture on silica gel plates (light petroleum as eluant) gave (**5b**) as the lower fraction (0.22 g, 25%), (**3**) as the middle fraction (0.06 g, 5%), and (**2**) as the higher fraction (0.28 g, 20%). (**5b**) was an *oil* (Found: C, 61.4; H, 10.4; S, 14.8%; M^+, 214.1207. $C_{11}H_{22}SSi$ requires C, 61.6; H, 10.3; S, 14.9%; *M*, 214.1212); $\delta_H(CDCl_3)$ 0.08 (9 H, s, $SiMe_3$), 1.31 (3 H, s, Me), 1.70 (6 H, br s, MeC=), and 2.16—3.36 (4 H, m, CH_2); *m/z* 214 (M^+), 199 ($M^+ - CH_3$), 141 ($M^+ - SiMe_3$), 109 ($M^+ - SiMe_3S$), 108 ($M^+ - SiMe_3SH$), and 73 ($SiMe_3$).

Oxidation of 3,4-*Dimethyl*-6-*t*-*butyl*-6-*trimethylsilyl*-5,6-*dihydro*-2H-*thiopyran* (**5a**).—To a solution of (**5a**) (0.37 g, 1.44 mmol) in ether (20 ml) was added *m*-chloroperbenzoic acid (1.44 mmol) in ether (10 ml) at −30 °C. The reaction was followed by t.l.c. (light petroleum–ethyl acetate, 7:3 as eluant) which showed the formation of two products, one at higher R_F (**7**) and one at lower R_F *trans*-(**6**). After 2 h the solution was washed with aqueous sodium hydrogen carbonate, dried, and concentrated under reduced pressure at low temperature. An n.m.r. spectrum of the residue confirmed the presence of the sulphoxide *trans*-(**6**) and the diene (**7**) in the ratio 7:3. The mixture was chromatographed on silica gel plates using light petroleum–ethyl acetate, 7:3 as eluant. The higher fraction gave (**7**) (57 mg, 22%) as an unstable *oil* (Found: M^+, 182.1133. $C_{11}H_{18}S$ requires *M*, 182.1129); $\lambda_{max.}$ 310 nm (calc. according to Woodward-Fieser rules: 305 nm); $\nu_{max.}$(neat) 2 960, 2 900, 2 860, 1 455, 1 360, 1 250, 1 110, 830, and 730 cm^{-1}; $\delta_H(CDCl_3)$ 1.18 (9 H, s, $SiMe_3$), 1.8 (6 H, br s, Me), 3.13 (2 H, s, CH_2), and 5.9 (1 H, s, vinylic H); *m/z* 182 (M^+), 167 ($M^+ - CH_3$), and 152 ($M^+ - 2\,CH_3$). The lower fraction gave *trans*-(**6**) (180 mg, 46%), m.p. 83—85 °C (from pentane) (Found: C, 61.6; H, 10.3; S, 11.6%; M^+, 272.1629; $C_{14}H_{28}OSSi$ requires C, 61.7; H, 10.4; S, 11.8%; *M*, 272.1630); $\nu_{max.}(CS_2)$ 1 050 (SO), 1 250, and 840 cm^{-1} ($SiMe_3$); $\delta_H(CDCl_3)$ 0.23 (9 H, s, $SiMe_3$), 1.33 (9 H, s, Bu^t), 1.78 (6 H, br s, Me), 2.1—3.1 (2 H, m, CH_2), and 3.4 (2 H, br s, CH_2SO); *m/z* 272 (M^+), 256 ($M^+ - O$), 215 ($M^+ - Bu^t$), 73 ($SiMe_3$), and 57 (Bu^t). Subsequent addition of [Yb(fod)$_3$] shifts the Bu^t signal at δ 1.33 p.p.m. downfield, much more than the $SiMe_3$ signal at δ 0.23. The maximum observed shift variations were respectively 24 and 12 Hz at 60 MHz. A solution of *trans*-(**6**) in deuteriochloroform was kept at 30 °C for 65 h. No trace of the diene (**7**) was observed in the n.m.r. spectrum.

Desilylation of (**5a**).— To a solution of (**5a**) (0.71 g, 2.76 mmol) in toluene (6 ml) and water (two drops) was added tetrabutylammonium fluoride (TBAF) in THF (1M, 2.76 mmol). The mixture was refluxed until the starting material had disappeared (16 h). After cooling, the mixture was quenched with water and extracted with ether. The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure and the residue chromatographed on silica gel plates (pentane as eluant). The higher fraction gave (**9**) (0.35 g, 53%) as an *oil* (Found: M^+, 240.1912. $C_{15}H_{28}S$ requires *M*, 240.1912); $\lambda_{max.}$ 250 nm (cyclohexane) (Calc. according to Woodward-Fieser rules 265 nm); $\nu_{max.}$ (CS_2) 2 960, 2 920, 2 860, 1 360, 1 215, and 760 cm^{-1}; $\delta_H(CDCl_3$; 300 MHz) 0.85 (3 H, t, Me), 1.15 (9 H, s, Bu^t), 1.31 (2 H, m, CH_2), 1.44 (2 H, m, CH_2), 1.63 (3 H, s, Me), 1.67 (3 H, s, Me), 1.84 (3 H, s, Me), 2.49 (2 H, t, CH_2S), and 6.33 (1 H, s, CH); $\delta_C(CDCl_3)$ 13.64 (q), 17.51 (q), 20.04 (q), 21.68 (q), 22.08 (t), 29.65 [q, $(CH_3)_3C$], 31.68 (t), 33.85 (t, CH_2S), 38.84 [s, $C(CH_3)_3$], 126.24 (s), 127.99 (s), 130.70 (d, CH), and 145.65 (s, =C–S); *m/z* 240 (M^+), 225 ($M^+ - CH_3$), 183 ($M^+ - Bu^t$), 153 ($M^+ - Bu^t - CH_3$), and 127 ($M^+ - Bu^t - Bu$). The lower fraction gave (**8**) (0.16 g, 31%) as an *oil* (Found: C, 71.5; H, 11.0; S, 17.3%; M^+, 184.1281. $C_{11}H_{20}S$ requires C, 71.7; H, 10.9; S, 17.4%; *M*, 184.1286); $\nu_{max.}$ (CS_2) 2 960, 2 900, 2 800, 1 365, 1 270, 1 240, and 1 050 cm^{-1}; $\delta_H(CDCl_3$; 300 MHz) 1.00 (9 H, s, Bu^t), 1.66 (3 H, s, Me), 1.68 (3 H, s, Me), 2.14 (2 H, br s, CH_2), 2.65 (1 H, dd, *J* 10 and 6 Hz, CH), 2.80 (1 H, d, *J* 16.5 Hz, CH*H*S), and 3.34 (1 H, d, *J* 16.5 Hz, C*H*HS). Saturation of the signal at δ 3.34 p.p.m. produced a significant increase in the intensity of the methyl signal at δ 1.66 which can therefore be assigned to the 3-methyl group (closer to the CH_2S group). Saturation of the signal at δ 2.80 p.p.m. produced no significant increase of the same signal at δ 1.66 p.p.m. Saturation of the signal of the CH_2 at δ 2.14 p.p.m. enhanced the resonance of the 4-methyl at δ 1.68; $\delta_C(CDCl_3)$ 19.21, 20.42, 27.60, 33.57, 34.35, 34.59, 51.77, 123.46, and 127.83; *m/z* 184 (M^+), 127 ($M^+ - Bu^t$), and 57 (Bu^t).

Oxidation of (**9**).—*m*-Chloroperbenzoic acid (1.25 mmol) in ether (15 ml) was added to a solution of (**9**) (0.15 g, 0.625 mmol)

at 0 °C in ether (15 ml). After 3 days in the refrigerator, the solution was washed with aqueous sodium hydrogen carbonate and water, dried (Na_2SO_4), and concentrated under reduced pressure. Chromatography of the residue on silica (light petroleum–ethyl acetate, 2:1 as eluant) gave *sulphone* (**10**) (0.092 g, 54%), m.p. 119—121 °C (from MeOH) (Found: C, 66.2; H, 10.5; S, 11.6%; M^+, 272.1815. $C_{15}H_{28}O_2S$ requires C, 66.1; H, 10.4; S, 11.8%; *M*, 272.1810); $\nu_{max.}(CS_2)$ 1 315 and 1 135 cm^{-1} (SO_2); $\delta_H(CDCl_3)$, 0.93 (3 H, t, Me), 1.0—2.2 (4 H, m, CH_2CH_2), 1.4 (9 H, s, Bu^t), 1.7 (6 H, br s, 2 × Me), 1.83 (3 H, br s, Me), 3.0 (2 H, t, CH_2SO_2), and 6.8 (1 H, br s, CH); *m/z* 272 (M^+), 150 ($M^+ - SO_2 - C_3H_7$), 135 ($M^+ - SO_2Bu$), and 57(Bu^t).

Attempted Desilylation of (**5b**).—Compound (**5b**) (0.22g, 1 mmol) was subjected to the same desilylation conditions as (**5a**). After 4 days at reflux and subsequent work-up starting (**5b**) (0.215 g) was recovered.

Desilylation of trans-(**6**).—To a solution of *trans*-(**6**) (0.134 g, 0.34 mmol) in THF (10 ml) and water (2 drops) was added TBAF in THF (1M; 0.34 mmol), and the mixture was refluxed until the starting sulphoxide had been consumed. After cooling, the mixture was quenched with water and extracted with ether. The organic layer was dried (Na_2SO_4), concentrated under reduced pressure, and the residue was chromatographed on silica gel plates (light petroleum–ethyl acetate, 7:3 as eluant). The higher fraction gave the *sulphone* (**12**) (0.019 g, 18%), m.p. 76—78 °C (pentane) (Found: C, 61.0; H, 9.1; S, 14.9%; M^+, 216.1190. $C_{11}H_{20}O_2S$ requires C, 61.1; H, 9.3; S, 14.8%; *M*, 216.1184); $\nu_{max.}(CS_2)$ 1 320 and 1 125 cm^{-1} (SO_2); $\delta_H(CDCl_3$; 300 MHz) 1.2 (9 H, s, Bu^t), 1.65 (3 H, s, Me), 1.70 (3 H, s, Me), 2.7 (2 H, m, CH_2), 2.86 (1 H, dd, *J* 12 and 4Hz, CH), 3.19 (1 H, d, *J* 18Hz, $CHHSO_2$), and 3.7 (1 H, d, *J* 18 Hz, $CHHSO_2$); *m/z* 216 (M^+), 199 (M^+ − OH), 170($M^+ - O - 2CH_3$), 152 ($M^+ - SO_2$), 82 (C_6H_{10}), and 57 (Bu^t).

The lower fraction gave a mixture (0.026 g, 26%) of the two sulphoxides *trans*-(**11**) and *cis*-(**11**) in ratio 2.5:1. These two sulphoxides were compared with those obtained by oxidation of the sulphide (**8**).

Oxidation of (**8**).—*m*-Chloroperbenzoic acid (0.16 mmol) in ether (15 ml) was added at −30 °C to a solution of (**8**) (0.3 g, 0.16 mmol) in ether (15 ml). After 1.3 h, the solution was washed with aqueous sodium hydrogen carbonate and water, dried (Na_2SO_4), and concentrated under reduced pressure. Chromatography of the residue on silica gel plates (ethyl acetate–light petroleum, 3:7 as eluant) gave as the higher fraction the sulphone (**12**) (0.04 g, 12%), identical in all respects with that obtained from the desilylation of *trans*-(**6**). The lower fraction was a mixture of the two sulphoxides *trans*-(**11**) and *cis*-(**11**) (0.18 g, 55%) in ratio 0.9:1. Repeated elutions on silica gel plates (ethyl acetate–light petroleum, 7:3) afforded pure only the *sulphoxide cis*-(**11**), m.p. 64—66 °C (from pentane) (Found: C, 66.1; H, 10.0; S, 15.8%; M^+, 200.1236. $C_{11}H_{20}OS$ requires C, 66.0; H, 10.1; S, 16.0%; *M*, 200.1235); $\nu_{max.}(CS_2)$ 1 050 cm^{-1} (SO); $\delta_H(CDCl_3$; 300 MHz) 1.14 (9 H, s, Bu^t), 1.75 (6 H, br s, Me), 2.39 (2 H, dd, CH_2), 2.60 (1 H, dd, *J* 10 and 5 Hz, CH), and 3.4 (2 H, d, CH_2SO); *m/z* 200 (M^+), 183 (M^+ − OH), 151 (M^+ − SOH), 82 (C_6H_{10}), and 57 (Bu^t). The lower fraction gave unresolved *trans*-(**11**) and *cis*-(**11**) as a mixture in the ratio 3:1. Subtracting the signals of the *cis* sulphoxide from the n.m.r. (300 MHz) spectrum of the mixture the following signals could be assigned to the *trans* sulphoxide; δ_H 1.09 (9 H, s, Bu^t), 1.70 (6 H, br s, Me), 2.09 (2 H, t, CH_2), 2.73 (1 H, br t, line separation 15 Hz, CH), 3.17 (2 H, br s, CH_2SO). Addition of [Yb(fod)$_3$] to the mixture of the two sulphoxides in deuteriochloroform shifted the t-butyl group signal at δ 1.14 much more downfield than the signal at δ 1.09. The maximum observed shift variations were respectively 15 and 9 Hz at 300 MHz.

3-exo-*t-Butyl*-3-endo-*trimethylsilyl*-2-*thiabicyclo*[2.2.1]*hept*-5-*ene* (**13a**).—Cyclopentadiene (7.3 mmol) was added to t-butyl trimethylsilyl thioketone (**1a**) (0.64 g, 3.66 mmol) in ether (5 ml). After 3 months in the refrigerator the blue colour of (**1a**) was still present. Chromatography of the reaction mixture (pentane as eluant) afforded the unchanged thione (0.13 g, 21%) and the adduct (**13a**) (0.4 g, 44%) as an *oil* (Found: M^+, 240.1367. $C_{13}H_{24}SSi$ requires *M*, 240.1368); $\delta_H(CDCl_3$; 300 MHz) 0.17 (9 H, s, $SiMe_3$), 1.12 (9 H, s, Bu^t), 1.45 (1 H, m, CH_2), 2.07 (1 H, m, CH_2), 3.24 (1 H, m, CH), 3.94 (1 H, m, CH), 6.09 (1 H, m, vinyl H), and 6.21 (1 H, m, vinyl H). Saturation of the $SiMe_3$ resonance at δ 0.17 p.p.m. produced a significant (16%) increase in the intensity of the vinylic proton signal at δ 6.09 p.p.m., which can therefore be assigned to 5-H which is closer to the $SiMe_3$ group. A minor enhancement (10%) was found for the signal at δ 6.21 p.p.m. which was assigned to 6-H. The observation of a significant n.O.e. in both vinylic protons indicates an *endo* position for $SiMe_3$ group. Saturation of the t-butyl resonance at δ 1.12 p.p.m. caused no significant increase in the intensity of the vinylic proton signals; *m/z* 240 (M^+), 225 ($M^+ - CH_3$), 183 ($M^+ - Bu^t$), 174 ($Bu^tCSSiMe_3$), 73 ($SiMe_3$), and 60 (C_5H_6).

3-exo-*Methyl*-3-endo-*trimethylsilyl*-2-*thiabicyclo*[2.2.1]*hept*-5-*ene* (**13b**).—Cyclopentadiene was added to an ethereal solution of (**1b**) [prepared from methyl trimethylsilyl ketone (0.92 g, 7.9 mmol)] until the disappearance of the blue colour of the thione (within a few minutes). The solvent was evaporated and the residue was chromatographed on silica (light petroleum as eluant), to afford as the first fraction (**2**) (0.56 g, 30%), then (**3**) (0.1 g, 5%), and as the last fraction (**13b**) (0.45 g, 40%) as an *oil* (Found: M^+, 198.0890. $C_{10}H_{18}SSi$ requires *M*, 198.0899); $\delta_H(CDCl_3)$ 0.0 (9 H, s, $SiMe_3$) 1.50 (3 H, s, Me) 1.52 (1 H, m, CH_2), 1.83 (1 H, m, CH_2), 2.95 (1 H, br s, CH), 4.02 (1 H, br s, CH), 5.85 (1 H, m, vinyl H), and 6.10 (1 H, m, vinyl H); *m/z* 198 (M^+), 164 ($M^+ - H_2S$), 117 ($SiMe_3CS$), 73 ($SiMe_3$), and 59 (CH_3CS). The *endo* position for the trimethylsilyl group was assigned by n.O.e. experiments following the same procedure as described for (**13a**).

t-Butyl Trimethylsilyl Thioketone S-*Oxide* (**14**).—An equimolar proportion of *m*-chloroperbenzoic acid in ether was added at −40 °C under nitrogen to a solution of (**1a**) (1.71 g, 9.9 mmol) in ether (50 ml). After being stirred for 1.3 h at −40 °C, the mixture was warmed to room temperature and washed with aqueous sodium hydrogen carbonate and water, dried (Na_2SO_4), and concentrated under reduced pressure. The n.m.r. spectrum revealed the presence of the two thioketone oxides *E*- and *Z*-(**14**) in the ratio 3:2, $\nu_{max.}(CS_2)$ 1 140 (CSO), 1 250, and 840 ($SiMe_3$) cm^{-1}; $\delta_H(CDCl_3)$ 0.29 (9 H, s, $SiMe_3$), 0.39 (9 H, s, $SiMe_3$), 1.31 (9 H, s, Bu^t), and 1.45 (9 H, s, Bu^t). Subsequent addition of [Yb(fod)$_3$] shifted the signal at δ 0.39 much more than the signal at δ 0.29 p.p.m. ($SiMe_3$), and the signal at δ 1.45 much more than the signal at δ 1.31 p.p.m. (Bu^t). The observed shift variations were respectively 56 and 20 Hz for the $SiMe_3$ group and 44 and 34 Hz for the t-butyl group at 60 MHz. An attempt to separate the two compounds by flash chromatography (light petroleum–ethyl ether, 1:1 as eluant) afforded pure only the *E*-isomer as an *oil* (Found: M^+, 190.0849. $C_8H_{18}OSSi$ requires *M*, 190.0848); $\delta_H(CDCl_3)$ 0.29 (9 H, s, $SiMe_3$) and 1.45 (9 H, s, Bu^t); *m/z* 190 (M^+), 175 ($M^+ - CH_3$), and 85 (Bu^tCO).

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