

Synthesis and Chemical Behaviour of Thioacylsilanes (Silyl Thioketones). Part 1. Oxidation to S-Oxides, Conversion into Silylated Thiiranes, Silylated Triarylethylenes, and α -Silylated Sulphides

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Trimethylsilyl and triphenylsilyl thioketones have been synthesized by acid catalysed reaction of the corresponding ketones with hydrogen sulphide. Such silylated thioketones have been oxidized to give S-oxides and converted with diaryldiazomethanes into triaryl thiiranes; upon treatment with organolithium nucleophiles they undergo thiophilic addition. The ready desulphurization with triphenylphosphine of silylated thiirans to the corresponding silyl triaryl ethylenes is also reported.

Compounds containing the Si-C-S unit have received increasing attention in recent years. Recently we described in a preliminary note¹ the synthesis and characterization of trimethylsilyl and triphenylsilyl thioketones prepared with a view to their possible use as synthetic equivalents of thioaldehydes and thiocarbonyl anions. Silylated thioketones are, in principle, the intermediates of choice for the preparation of compounds containing the Si-C-S unit owing to the high reactivity of the carbon-sulphur double bond either in nucleophilic or electrophilic additions as well as in cycloaddition reactions.² In this paper we present evidence which demonstrates the great versatility of silylthiones as chemical intermediates.

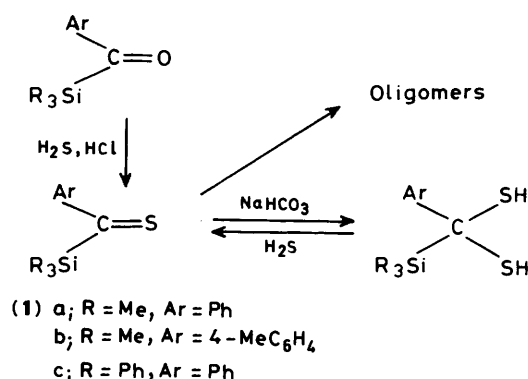
Results and Discussion

Of the various methods we used to prepare thioketones (**1a-c**), the controlled acid-catalysed reaction of acylsilanes (prepared according to the procedure of Brook and Corey³) with hydrogen sulphide was the method that gave the best results. The choice of solvent was of critical importance, diethyl ether proving to be the best among the many tested. Also, the reaction temperature had to be carefully controlled at -20 to -15 °C during the addition of gases. Excessively long reaction times led to the disappearance of the blue colour of the thioketone, probably as a consequence of addition of a second molecule of hydrogen sulphide onto the thioketone itself to give white gem-dithiols; washing of the ethereal solution with saturated aqueous sodium hydrogen carbonate gave back the blue colour of the thioketone. Additional loss of thioketones may be due to loss through oligomerisation with time or during work-up† (see Scheme 1).

Yields in the three cases examined were in the range 65–90%. The chemical stabilities of the trimethylsilyl thioketones (**1a** and **b**) were low and they tended to decompose extensively during isolation. For this reason the thioketones were prepared immediately prior to use‡ and kept in ethereal solution after neutralization with cold aqueous sodium hydrogen carbonate and quick chromatography on Florisil.

† With time, silylated thioketones formed white products whose mass spectra showed the molecular ions corresponding to the dimer. ¹H and ¹³C N.m.r. spectra were in agreement with a symmetric structure not yet completely elucidated.

‡ Solutions of thione (**1a**), stored in sealed ampoules and carefully degassed under high vacuum (10^{-3} Torr), were stored for several days at -20 °C without appreciable decomposition.



Scheme 1.

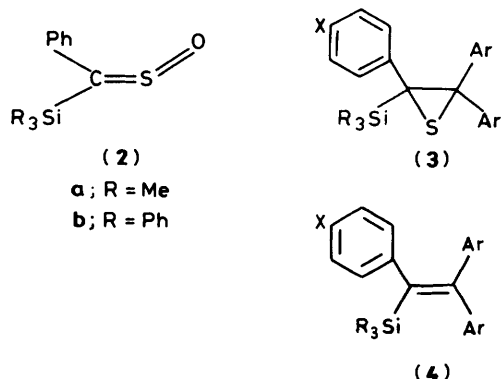
The concentration of the solution of (**1a**) was calculated by assuming that the reaction with di-*p*-tolylidiazomethane leading to the thiirane (**3c**) was quantitative. On this basis we could calculate the molar extinction coefficient in the u.v. spectrum at the λ_{\max} of the $n \rightarrow \pi^*$ transition (see Experimental section). This parameter was used for quantitative purposes. The triphenylsilyl thioketone (**1c**) was stable enough to allow its purification. It is a blue crystalline material (m.p. 98 – 100 °C) which can be recrystallized from diethyl ether and stored in a refrigerator for considerable periods of time.

The thioketones (**1a,c**) could be oxidized to the corresponding S-oxides with *m*-chloroperoxybenzoic acid in very good yields. Not unexpectedly only one of the two possible *Z,E*-diastereoisomers was obtained in both cases. The crude thioketone S-oxides exhibited ¹H and ¹³C n.m.r. spectra which were very clean and typical of a single product. Therefore we could exclude, within the uncertainty of the n.m.r. measurement, the possibility that both *Z/E* isomers were present in the crude isolated material.

Zwanenburg has demonstrated⁴ that lanthanide shift reagents complex with S-oxides at the sulphur-bonded oxygen atom and has applied the LIS technique to the attribution of configurations based on differential shifts of protons situated in the direct environment of the CSO group. In order to establish the geometry of the sulphines obtained in our reaction we applied the LIS effect to the differential shift of the ¹³C signals of the carbon atoms located in close proximity to the sulphur-bonded oxygen.

The ^{13}C n.m.r. spectrum at 75.46 MHz of (2b) showed two signals at 131.3 and 134.1 p.p.m. which, according to off-resonance experiments, could be unambiguously attributed to the two types of quaternary aromatic carbons, namely the C-1 of the three phenyl nuclei bonded to silicon and the C-1 of the phenyl nucleus bonded to the *S*-oxide function (ratio 3:1).

For the *S*-oxide (2b), after addition of $[\text{Yb}(\text{fod})_3]$ the signal at 134.1 p.p.m. showed the greatest downfield shift; for the *S*-oxide (2a) the comparison was made between the signal at -0.5 p.p.m. (Me) and the signal at 133.7 p.p.m. (quaternary carbon of the phenyl group). After addition of the LIS reagent it was the last signal to show the greatest downfield shift. These findings, which are clearly in favour of an *E* configuration for the *S*-oxides (2) are also in agreement with the stereochemical result of the oxidation of silylated thiirans (3),⁵ which was unambiguously shown to be *anti* to the silyl group.



The *S*-oxides (2a,b) are surprisingly stable compared to other non silylated *S*-oxides and α -silyl sulphoxides. They can be stored for long periods of time without appreciable decomposition. This stability can be attributed both to a stabilizing effect of silicon itself and to the rigid geometry of the molecule which does not allow the intramolecular interaction between oxygen and silicon which in open chain α -silyl sulphoxides leads to Pummerer-type rearrangements.⁶

This finding could represent indirect evidence that a *syn* coplanarity of the C-Si and S=O bonds is a necessary condition for the Pummerer rearrangement of α -silylated sulphinyl compounds. Accordingly, the *Z*-*S*-oxide might also be formed from oxidation of the silyl thioketones but have escaped detection owing to a fast rearrangement. On the basis of a careful product analysis we can, however, exclude such a hypothesis since we never found any trace of silylthiono-carboxylic esters.

The reaction between the thioketones (1) and diphenyl-, di-*p*-methoxyphenyl-, and di-*p*-tolyl-diazomethane gave the silylated thiiranes (3a-h) in very good yields (see Table 1). The three-membered ring heterocycles could be oxidized to the corresponding *S*-oxides.⁵ With triphenylphosphine they easily desulphurize to give, in very good to quantitative yields, the silylated olefins (4a-f) (see Table 2).

Attempted desilylation of the thiirane (3a) with an excess of tetraethylammonium fluoride in acetonitrile at room temperature gave triphenylethylene as the result of concomitant desilylation and desulphurization. We did not investigate

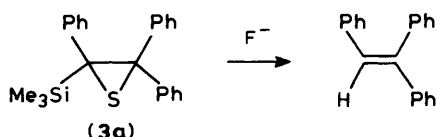


Table 1. 2-Silyl substituted 2,3,3-triarylthiiranes (3)

(3)	R	Ar	X	M.p. (°C)	Cryst'n solvent	Yield (%)
a	Me	Ph	H	108—109	Ethanol	47.5 ^a
b	Me	C ₆ H ₄ OMe- <i>p</i>	H	144—146	Ethanol	59 ^a
c	Me	C ₆ H ₄ Me- <i>p</i>	H	146—147	Ethanol	58 ^b
d	Me	Ph	Me	108—110	Ethanol	48 ^a
e	Me	C ₆ H ₄ OMe- <i>p</i>	Me	124—126	Pentane	52 ^a
f	Ph	Ph	H	174—175	Ethanol	90.5
g	Ph	C ₆ H ₄ OMe- <i>p</i>	H	156—158	Ethanol	92
h	Ph	C ₆ H ₄ Me- <i>p</i>	H	148—149	Ethanol	100

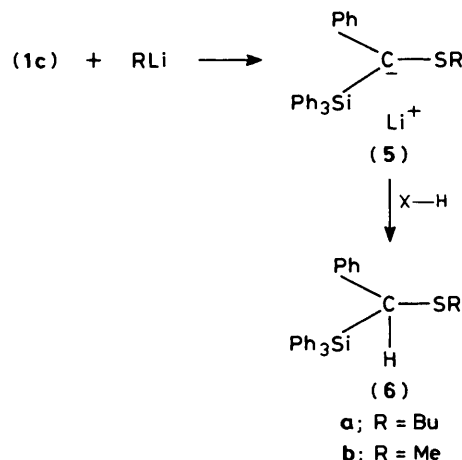
^a Based on the starting ketone. ^b Based on the molar extinction coefficient of the starting thione.

Table 2. 2-Silyl substituted 1,2,2-triarylethenes (4)

(4)	R	Ar	X	M.p. (°C)	Cryst'n solvent	Yield (%)
a	Me	Ph	H	93—94	Methanol	79
b	Me	C ₆ H ₄ OMe- <i>p</i>	H	65—67	Methanol	100
c	Me	C ₆ H ₄ Me- <i>p</i>	H	102—104	Methanol	100
d	Ph	Ph	H	152—153	Methanol	97
e	Ph	C ₆ H ₄ OMe	H	151—152	Ethanol	100
f	Ph	C ₆ H ₄ Me- <i>p</i>	H	134—135	Ethanol	99

further the relative rates of the two reactions, desilylation and desulphurization, promoted by fluoride ion.

It is known that thioketones react with alkyl- or phenyllithiums to give the corresponding alkyl or phenyl sulphides.⁷ The preferential addition of carbanions onto the sulphur rather than onto the carbon atom is a well established characteristic of thioketones and the effect should be enhanced in the case of the silylated thioketones since an α -silyl substituted carbanion (5) is formed (Scheme 2).

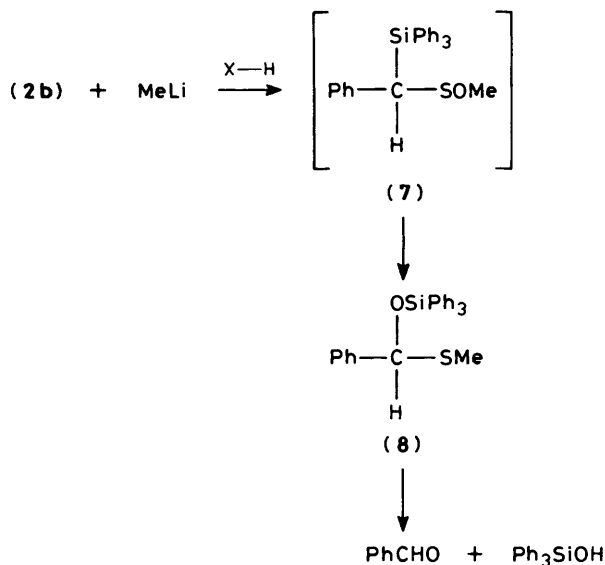


Scheme 2.

Addition of alkyl-lithiums to triphenylsilylphenyl thioketone in THF at -78 °C followed by quenching with water or methanol gave a good yield of the sulphides (6). Thus the reaction of a silyl thioketone with organolithium derivatives represents a point of entry into the synthesis of α -silyl- α -mercaptocarbanions, an alternative to the well-known procedure of base-catalysed proton abstraction from α -silyl- α -mercaptomethanes.

Attempted isolation of an α -triphenylsilyl sulphoxide by reaction of the *S*-oxide (**2b**) with methyl-lithium gave only the very unstable α -methylthio- α -triphenylsilyloxytoluene (**8**) which represents the product of thermal rearrangement of the sulphoxide (**7**), in line with the mechanism proposed by Brook.⁶

The product (**8**) was characterized only by i.r. and n.m.r. spectroscopy and gave with time, in solution, benzaldehyde and triphenylsilylanol (Scheme 3).



Scheme 3.

Experimental

All m.p.s are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 257 grating spectrometer. The routine n.m.r. spectra (60 MHz) were obtained with a Varian EM 360 L instrument. ¹³C N.m.r. spectra were recorded at 75.46 MHz (Bruker CXP 300 spectrometer of the High Field n.m.r. Service of CNR in Bologna). Mass spectra were recorded with a JEOL JMS D 100 spectrometer. Phenyl trimethylsilyl ketone and phenyl-triphenylsilyl ketone were obtained by hydrolysis of the related 1,3-dithianes by the methods of Corey *et al.* and Brook *et al.*,³ and *p*-tolyl trimethylsilyl ketone was prepared according to Picard *et al.*⁸ Diphenyldiazomethane,⁹ di-*p*-methoxyphenyldiazomethane and di-*p*-tolylidiazomethane¹⁰ were prepared by oxidation of the corresponding hydrazones with mercury(II) oxide. Diethyl ether was distilled from P₂O₅, benzene from CaH₂, and THF from LiAlH₄ before use. Light petroleum refers to the fraction b.p. 40–70 °C.

Preparation of Thioketones: General Procedure.—Into a solution of the silyl ketones (1 g) in anhydrous ether (30 ml) were bubbled hydrogen chloride and hydrogen sulphide at –20 °C; the solution first turned green, then blue. The reaction was followed by t.l.c. [light petroleum–ether (4:1) as eluant]. After the disappearance of the starting ketone (*ca.* 40 min), the solution was washed under CO₂ with 5% aqueous sodium hydrogen carbonate and with water and then dried (Na₂SO₄).

Trimethylsilyl Phenyl Thioketone (1a) and Trimethylsilyl *p*-Tolyl Thioketone (1b). The ethereal solution was concentrated and chromatographed under CO₂ on Florisil (light petroleum–ether 4:1 as eluant). The blue fraction was collected and concentrated under reduced pressure. The blue oil was too unstable to allow its distillation but was obtained pure on t.l.c.

(1a): Blue oil (yield based on ϵ , 58% calculated as described

below), $\delta_H(CDCl_3)$ 0.4 (9 H, s, SiMe₃) and 6.7–8.2 (5 H, m, ArH); m/z 194 (M^+), 121 ($M^+ - SiMe_3$), and 73 (SiMe₃); λ_{max} (diethyl ether) 678 nm (ϵ 37.3).

(1b): Blue oil, $\delta_H(CDCl_3)$ 0.37 (9 H, s, SiMe₃), 2.33 (3 H, s, Me), and 7.2 and 7.75 (4 H, AB system, J_{AB} 10 Hz).

Triphenylsilyl Phenyl Thioketone (1c). The ethereal solution was concentrated, and after cooling the blue thioketone was precipitated from the residual solution (85% yield), m.p. 98–100 °C (Found: C, 79.1; H, 5.4; S, 8.4. C₂₅H₂₀SSi requires C, 78.9; H, 5.3; S, 8.4%; $v_{max}(KBr)$ 1 110 (SiPh₃) and 1 215 (C=S) cm⁻¹; $\delta_C(CDCl_3)$ 238.8 (C=S), 151.8, 136.4, 133.7, 131.9, 129.8, 128.8, 128.0, 127.9, and 126.6 (ArC); m/z 380 (M^+), 303 ($M^+ - Ph$), 259 (SiPh₃), 121 (PhC=S), and 105 (SiPh); $\lambda_{max}(CCl_4)$ 692 nm (ϵ 53.0). The molar extinction coefficients of the thioketones (1a) and (1c) were evaluated at the λ_{max} values of 678 nm and 692 nm, respectively. Details for the thioketone (1a) are given below. A freshly prepared solution of di-*p*-tolylidiazomethane in diethyl ether (1 ml, 0.018 35 mmol) was treated with an excess of (1a) in diethyl ether (2 ml). The value of ϵ (37.3 ± 0.9) was determined from the decrease in absorption of the reacted thione ($A = 0.227$). The experiment was repeated several times by varying the internal ratio (1a):dialzo, always using an excess of thione.

A stoichiometric control of the reaction (dialzo:thioketone 1:1) was obtained by measuring the concentration of the same thioketone solution using an excess of dialzo and by measuring the amount of reacted dialzo at the λ_{max} of 530 nm of its absorption spectrum. The results agreed to within an error of ±3%.

The same procedure was used for thioketone (1c) in CCl₄ (ϵ 53.0 ± 1.3).

Phenyltrimethylsilyl Thioketone *S*-Oxide (2a).—A solution of an equimolar amount of *m*-chloroperbenzoic acid in ether was added at –40 °C under nitrogen to the ethereal solution of (1a) obtained from 5 mmol of the corresponding ketone until the disappearance of the blue colour of the thioketone. The solution was washed with 5% aqueous sodium hydrogen carbonate and with water, and then dried and concentrated. Chromatography of the residue on Florisil (light petroleum–ether 9:1 as eluant) afforded (2a) (0.44 g, 42% based on the starting ketone) as a liquid (Found: C, 56.7; H, 6.5; S, 15.0. C₁₀H₁₄OSSi requires C, 57.1; H, 6.7; S, 15.2%; $v_{max}(\text{neat})$ 1 115 (C=SO), 840, and 1 250 (SiMe₃) cm⁻¹; $\delta_H(CDCl_3)$ 0.33 (9 H, s, SiMe₃), 7.1–7.8 (5 H, m, ArH); $\delta_C(CDCl_3)$ 187.7 (CSO), 133.7, 129.2, 128.7, 127.6 (ArC), and –0.5 (SiMe₃). Subsequent addition of [Yb(fod)₃] shifts downfield the lines of C-1 and C-2 of the phenyl ring much more than the line of the SiMe₃ carbon. The maximum observed shift variation for C-1 and C-2 was 2.5 and 1.9 p.p.m., compared with 0.7 p.p.m. observed for the Me₃Si carbon; m/z 210 (M^+), 209 ($M^+ - H$), 195 ($M^+ - Me$), 177 ($M^+ - SH$), 136 ($M^+ - SiMe_3 - H$), 121 (PhC=S), and 105 (PhC=O).

Phenyltriphenylsilyl Thioketone *S*-Oxide (2b).—Under the same reaction conditions as for (2a), starting from (1c) (0.49 g, 1.05 mmol), (2b) (0.3 g, 75%), m.p. 131 °C was obtained from diethyl ether (Found: C, 75.6; H, 5.0; S, 8.1. C₂₅H₂₀OSSi requires C, 75.7; H, 5.1; S, 8.1%; $v_{max}(CS_2)$ 3 070, 3 050, 1 120, 1 110, 760, 740, and 700 cm⁻¹; $\delta_H(CDCl_3)$ 7.0–8.1 (m, ArH); $\delta_C(CDCl_3)$ 183.8 (CSO), 136.4, 134.1, 131.3, 130.5, 129.8, 128.9, 128.5, and 128.2. Subsequent addition of [Yb(fod)₃] shifts the signal at 134.1 p.p.m. (attributed to the quaternary carbon bonded to silicon) downfield, much more than the signal at 131.3 p.p.m. (attributed to the quaternary carbon of the phenyl bonded to the *S*-oxide function). The observed shift variations were respectively 2.0 and 0.5 p.p.m.; m/z 396 (M^+), 380 ($M^+ - O$), 319 ($M^+ - Ph$), 259 (SiPh₃), 242 ($M^+ - 2Ph$), 214 ($M^+ - Ph_2Si$), and 105 (PhSi).

General Procedure for Preparation of Silylated Thiiranes (3a—h).—An ethereal solution of diaryldiazomethane was dropped at room temperature, under nitrogen and stirring, into an ethereal solution (50 ml) of the silyl thioketone (obtained from 5 mmol of the corresponding ketone) until the disappearance of the colours of the reagents. The solvent was removed under reduced pressure and the crude thiirane was crystallized using a suitable solvent.

(3a): 47.5% (based on the ketone), m.p. 108—110 °C (from ethanol) (Found: C, 75.8; H, 6.8; S, 9.0. $C_{23}H_{24}SSi$ requires C, 76.6; H, 6.7; S, 8.9%); $\delta_H(CDCl_3)$ 0.21 (9 H, s, $SiMe_3$) and 6.8—7.9 (15 H, m, ArH); m/z 360 (M^+), 345 ($M^+ - Me$), 287 ($M^+ - SiMe_3$), and 255 ($M^+ - SiMe_3 - S$).

(3b): 59% (based on the ketone), m.p. 144—146 °C (from ethanol) (Found: C, 71.6; H, 6.7; S, 7.5. $C_{25}H_{28}O_2SSi$ requires C, 71.4; H, 6.7; S, 7.6%); $\delta_H(CDCl_3)$ -0.24 (9 H, s, $SiMe_3$), 3.7 (3 H, s, OMe), 3.8 (3 H, s, OMe), and 6.4—7.6 (13 H, m, ArH); m/z 420 (M^+), 405 ($M^+ - Me$), 389 ($M^+ - OMe$), 373 ($M^+ - MeS$), 347 ($M^+ - SiMe_3$), and 315 ($M^+ - Me_3SiS$).

(3c): 58% (based on the ketone), m.p. 146—147 °C (from ethanol) (Found: C, 77.1; H, 7.3; S, 8.3. $C_{25}H_{28}SSi$ requires C, 77.3; H, 7.3; S, 8.2%); $\delta_H(CDCl_3)$ -0.27 (9 H, s, $SiMe_3$), 2.05 (3 H, s, Me), 2.33 (3 H, s, Me), and 6.6—7.6 (13 H, m, ArH); m/z 388 (M^+), 373 ($M^+ - Me$), and 356 ($M^+ - S$).

(3d): 48% (based on the starting ketone), m.p. 108—110 °C (ethanol) (Found: C, 77.0; H, 7.0; S, 8.6. $C_{24}H_{26}SSi$ requires C, 76.9; H, 7.0; S, 8.6%); $\delta_H(CDCl_3)$ -0.24 (9 H, s, $SiMe_3$), 2.2 (3 H, s, Me), and 6.7—7.9 (14 H, m, ArH); m/z 374 (M^+), 359 ($M^+ - Me$), 342 ($M^+ - S$), 327 ($M^+ - MeS$), 301 ($M^+ - SiMe_3$), and 269 ($M^+ - Me_3SiS$).

(3e): 52% (based on the starting ketone), m.p. 124—126 °C (from pentane) (Found: C, 72.5; H, 7.0; S, 7.0. $C_{26}H_{30}O_2SSi$ requires C, 71.8; H, 6.9; S, 7.4%); $\delta_H(CDCl_3)$ -0.24 (9 H, s, $SiMe_3$), 2.2 (3 H, s, Me), 3.6 (3 H, s, OMe), 3.8 (3 H, s, OMe), and 6.3—7.7 (12 H, m, ArH); m/z 434 (M^+), 419 ($M^+ - Me$), 387 ($M^+ - S - Me$), 361 ($M^+ - SiMe_3$), and 329 ($M^+ - Me_3SiS$).

(3f): 90.5%, m.p. 174—175 °C (from ethanol) (Found: C, 83.6; H, 5.5; S, 5.9. $C_{38}H_{30}SSi$ requires C, 83.5; H, 5.5; S, 5.9%); m/z 546 (M^+), 514 ($M^+ - S$), and 259 ($SiPh_3$).

(3g): 92%, m.p. 156—158 °C (from ethanol) (Found: C, 79.3; H, 5.6; S, 5.3. $C_{40}H_{34}O_2SSi$ requires C, 79.2; H, 5.6; S, 5.3%); $\delta_H(CDCl_3)$ 3.56 (3 H, s, OMe), 3.68 (3 H, s, OMe), and 6.16—8.5 (28 H, m, ArH); m/z 606 (M^+), 574 ($M^+ - S$), and 259 ($SiPh_3$).

(3h): 100%, m.p. 148—149 °C (from ethanol) (Found: C, 83.7; H, 6.1; S, 5.6. $C_{40}H_{34}SSi$ requires C, 83.57; H, 5.96; S, 5.58%).

General Procedure for Preparation of Silylated Olefins.—A solution of thiirane (1 mmol) and triphenylphosphine (1 mmol) in benzene (50 ml) was refluxed for 4 h. The solvent was removed and the residue chromatographed (preparative t.l.c., elution with benzene) to give as the higher R_F fraction, the olefin and as the lower R_F fraction, triphenylphosphine sulphide.

(4a): 79%, m.p. 93—94 °C (from methanol) (Found: C, 82.8; H, 7.4. $C_{23}H_{24}Si$ requires C, 84.1; H, 7.4%); $\delta_H(CDCl_3)$ -0.20 (9 H, s, $SiMe_3$) and 6.7—7.7 (15 H, m, ArH); m/z 328 (M^+), 313 ($M^+ - Me$).

(4b): 100%, m.p. 65—67 °C (from methanol) (Found: C, 76.3; H, 7.0. $C_{25}H_{28}O_2Si$ requires C, 77.3; H, 7.3%); $\delta_H(CDCl_3)$ 0.0 (9 H, s, $SiMe_3$), 3.9 (3 H, s, OMe), 4.1 (3 H, s, OMe), and 6.7—7.6 (13 H, m, ArH); m/z 388 (M^+), 373 ($M^+ - Me$), 358 ($M^+ - 2Me$), and 315 ($M^+ - SiMe_3$).

(4c): 100%, m.p. 102—104 °C (from methanol) (Found: C, 83.3; H, 7.9. $C_{23}H_{28}Si$ requires C, 84.2; H, 7.9%); $\delta_H(CDCl_3)$ -0.22 (9 H, s, $SiMe_3$), 2.12 (3 H, s, Me), 2.35 (3 H, s, Me), and 6.36—7.7 (13 H, m, ArH); m/z 356 (M^+) and 341 ($M^+ - Me$).

(4d): 97%, m.p. 152—153 °C (from methanol) (Found: C, 88.9; H, 6.0. $C_{38}H_{30}Si$ requires C, 88.7; H, 5.9%); $\delta_H(CDCl_3)$ 6.3—8.0 (m, ArH); m/z 514 (M^+), 437 ($M^+ - Ph$), and 259 ($SiPh_3$).

(4e): 100%, m.p. 151—152 °C (from ethanol) (Found: C, 83.3; H, 6.0. $C_{40}H_{34}O_2Si$ requires C, 83.6; H, 6.0%); $\delta_H(CDCl_3)$ 3.58 (3 H, s, OMe), 3.65 (3 H, s, OMe), and 6.0—8.0 (28 H, m, ArH); m/z 574 (M^+), 559 ($M^+ - Me$), and 259 ($SiPh_3$).

(4f): 99%, m.p. 134—135 °C (from ethanol) (Found: C, 88.7; H, 6.3. $C_{40}H_{34}Si$ requires C, 88.5; H, 6.3%); $\delta_H(CDCl_3)$ 2.06 (3 H, s, Me), 2.18 (3 H, s, Me), and 6.5—8.0 (28 H, m, ArH); m/z 542 (M^+) and 259 ($SiPh_3$).

Desilylation of 2-Trimethylsilyl-2,3,3-triphenylthiirane.—To a solution of (3a) (0.105 g, 0.29 mmol) in acetonitrile (5 ml), a solution of tetraethylammonium fluoride (0.091 g, 0.49 mmol) in acetonitrile (5 ml) was added. After 12 h the solution was quenched with water, extracted with ether, and the extract dried (Na_2SO_4) and evaporated; chromatography of the residue (preparative t.l.c.) and elution with pentane gave, as the higher R_F fraction, triphenylethylene (0.05 g, 67.6%), compared with an authentic sample.¹¹

Butyl α -Triphenylsilylbenzyl Sulphide (6a).—Buthyl-lithium (0.29 mmol) in hexane was added to a solution of triphenylsilylphenyl thioketone (0.1 g, 0.26 mmol) in THF (10 ml) at -78 °C under nitrogen. After being stirred for 1 h the reaction mixture was allowed to warm to room temperature. Stirring was continued for 15 min after which a saturated aqueous NH_4Cl solution was carefully added and the aqueous layer extracted with ether. The extract was evaporated to give almost pure (6a) (0.11 g, 95%), m.p. 94—95 °C (from methanol) (Found: C, 79.3; H, 6.8; S, 7.3. $C_{29}H_{30}SSi$ requires C, 79.4; H, 6.9; S, 7.3%); $v_{max}(CS_2)$ 3 070, 3 050, 3 020, 2 950, 2 920, 2 860, 1 210, 1 190, 1 110 (s), 1 030, 1 000, 905, 800, 760s, 735s, and 700 cm^{-1} ; $\delta_H(CDCl_3)$ 0.5—1.83 (7 H, m, CH_2CH_2Me), 2.06—2.66 (2 H, m, SCH_2), 4.0 (1 H, s, CH), and 6.83—8.33 (20 H, m, ArH); m/z 438 (M^+), 381 ($M^+ - Bu$), 349 ($M^+ - SBu$), and 259 ($SiPh_3$).

Methyl α -Triphenylsilylbenzyl Sulphide (6b).—This product was obtained in 65% yield by the same procedure as for (6a) using MeLi instead of BuLi; m.p. 143—144 °C (from methanol) (Found: C, 78.6; H, 6.15; S, 8.1. $C_{26}H_{24}SSi$ requires C, 78.7; H, 6.1; S, 8.1%); $\delta_H(CDCl_3)$ 1.92 (3 H, s, SMe), 3.92 (1 H, s, CH), 7.1 (5 H, s, ArH), and 7.23—7.83 (15 H, m, ArH); m/z 396 (M^+), 381 ($M^+ - Me$), and 259 ($SiPh_3$).

Reaction of Phenyl Triphenylsilyl Thioketone S-Oxide (2b) with Methyl-lithium.—Methyl-lithium (0.45 mmol) in hexane was added to a solution of the S-oxide (2b) (0.15 g, 0.38 mmol) in anhydrous ether at -78 °C under nitrogen. The mixture was stirred for 30 min and then warmed to 0 °C. Saturated aqueous NH_4Cl (10 ml) was added to it and the organic layer separated and dried (Na_2SO_4).

The ethereal solution was concentrated under reduced pressure to afford an oily residue (0.117 g, 75.1%) which was too unstable to be purified and to which, on the basis of its i.r. and n.m.r. spectra, the structure of α -methylthio- α -triphenylsilyloxytoluene (8) was assigned; $v_{max}(CS_2)$ 1 120, 1 060, 900, 760, 745, 710, and 700 cm^{-1} ; $\delta_H(CDCl_3)$ 1.83 (3 H, s, SMe), 6.08 (1 H, s, CH), and 7.0—8.1 (20 H, m, ArH).

After 1 h the product decomposed spontaneously, giving quantitatively benzaldehyde and triphenylsilylanol.

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