

## The Synthesis of Ketones via $\alpha$ -Silyl Sulphides

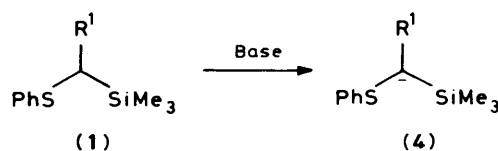
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$\alpha$ -Phenylthiosilanes (**2**) have been prepared by alkylation of the anion (**4**) derived from the 1-phenylthio-1-trimethylsilylalkane (**1**). These anions (**4**) have been prepared by a variety of methods including, direct deprotonation of (**1**), displacement of a phenylthio group by lithium naphthalenide, addition of an alkyl-lithium to 1-phenylthio-1-trimethylsilylethene (**7**), and transmetalation of a tributylstannyl moiety. The formation of an alkyl-lithium by reaction of lithium naphthalenide with a phenyl sulphide provided an additional route to (**2**) from bis(phenylthio)acetals (**8**). An alternative path to the  $\alpha$ -phenylthiosilanes (**2**) was to reduce the corresponding  $\alpha$ -phenylsulphonylsilane (**15**); these, in turn, being readily available from alkylation or silylation of  $\alpha$ -sulphonyl anions. The  $\alpha$ -phenylthiosilanes (**2**) were converted into the *O*-trimethylsilylphenylthioacetal (**18**) by the sila-Pummerer rearrangement, although this was complicated by vinyl sulphide (**20**) formation in certain cases. Subsequent hydrolysis of (**18**) and (**20**) gave the ketone (**3**).

The use of  $\alpha$ -silyl sulphides (**1**) for the synthesis of aldehydes has recently been described.<sup>1,2</sup> The advantages of this system over the use of 1,3-dithianes,<sup>3-5</sup> *i.e.* mild hydrolysis conditions and the ability to prepare other functional groups directly from the masked aldehyde,<sup>6</sup> led us to investigate the use of  $\alpha$ -silyl sulphides (**2**) for the preparation of ketones (**3**).

The first step was, therefore, to deprotonate (**1**) (Scheme 1). This could only be accomplished when R<sup>1</sup> was an anion-stabilising group such as phenyl (*vide infra*), trimethylsilyl,<sup>7</sup> or phenylthio.<sup>7</sup> The key nature of this step in the overall strategy prompted an intensive study into the effects of different bases, solvents, additives, and temperatures.



Scheme 1.

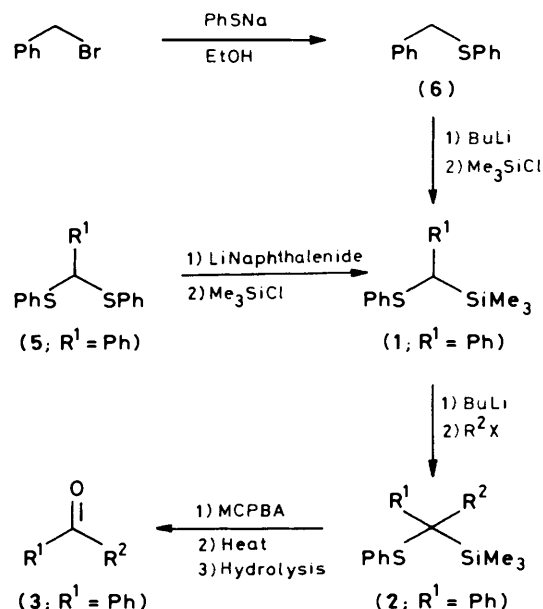
Although the required deprotonation did take place when (**1**; R<sup>1</sup> = Me) was treated with potassium di-isopropylamide<sup>8</sup> (KDA) in THF at  $-80^\circ\text{C}$  for 1 h or with lithium di-isopropylamide (LDA) in HMPA-THF (1:9) at  $0^\circ\text{C}$  for 0.25 h, when treated with iodomethane the yield of (**2**; R<sup>1</sup> = R<sup>2</sup> = Me) was less than 20% in the former case and *ca.* 5% in the latter. A strong base in a polar solvent was required for any reaction with (**1**; R<sup>1</sup> = Me) to be observed. The two primary modes of reaction were then carbon-sulphur or carbon-silicon bond cleavage with deprotonation of a silyl methyl group as a minor pathway. In the two cases where the required anion (**4**) was detected, displacement of the silyl group was still the major reaction pathway. It, therefore, became clear that the use of an  $\alpha$ -silyl sulphide (**1**) as an acyl anion equivalent by direct deprotonation was not a viable possibility without the presence of another anion-stabilising group.

**Preparation of Phenyl Ketones.**—(Phenylthio)phenyl(trimethylsilyl)methane (**1**; R<sup>1</sup> = Ph) was readily deprotonated in high yield by butyl-lithium-TMEDA complex in hexane at  $0^\circ\text{C}$ ;<sup>9</sup> butyl-lithium in THF gave a slightly lower yield. The silane (**1**; R<sup>1</sup> = Ph) has been prepared from bis(phenylthio)phenylmethane (**5**; R<sup>1</sup> = Ph) but for this work an

Table 1. Alkylations of (phenylthio)phenyl(trimethylsilyl)methane (**1**; R<sup>1</sup> = Ph)

R <sup>2</sup> X	Yield (%) of ( <b>2</b> ; R <sup>1</sup> = Ph)	R <sup>2</sup> X	Yield (%) of ( <b>2</b> ; R <sup>1</sup> = Ph)
MeI	94	C <sub>5</sub> H <sub>11</sub> I	61
EtI	85	C <sub>6</sub> H <sub>11</sub> Br	0 <sup>a</sup>
PrI	86	C <sub>12</sub> H <sub>25</sub> Br	64
Pr <sup>t</sup> I	34	CH <sub>2</sub> =CHCH <sub>2</sub> Br	73
BuBr	75	PhCH <sub>2</sub> Br	71
BuI	85		

<sup>a</sup> (Phenylthio)phenyl(trimethylsilyl)methane (**1**; R<sup>1</sup> = Ph) was recovered (92%).



Scheme 2.

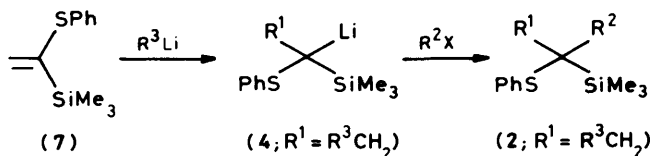
alternative approach was employed (see Scheme 2). Benzyl phenyl sulphide (**6**) was prepared in 95% yield by reaction of sodium thiophenoxide with benzyl bromide. Subsequent anion formation with butyl-lithium-TMEDA complex in THF at

–78 °C and silylation gave the required silane (1; R<sup>1</sup> = Ph) in 89% yield (85% overall).

The anion derived from (phenylthio)phenyl(trimethylsilyl)methane (1; R<sup>1</sup> = Ph) reacted cleanly with primary alkyl halides to give, after aqueous work-up, the adducts (2; R<sup>1</sup> = Ph) (see Scheme 2 and Table 1). As with phenylthiotrimethylsilylmethane<sup>1,2</sup> (1; R<sup>1</sup> = H), alkylation occurred in high yield with primary alkyl iodides and in slightly lower yield with primary alkyl bromides. Some alkylation did occur with secondary acyclic alkyl halides but the major pathway was elimination. When THF was used as the solvent, alkylation occurred with primary alkyl halides but in greatly reduced yield, with the exception of methyl iodide (87%). The adducts (2; R<sup>1</sup> = Ph) were converted into the corresponding carbonyl compounds by the standard procedure of oxidation to the sulphoxide, sila-Pummerer rearrangement, and hydrolysis (see Scheme 2) which is discussed in detail below.

**Preparation of (2) from 1-Phenylthio-1-trimethylsilylethene (7).**—As the required α-thiosilane acyl anion equivalents were not generally available by direct means, alternative methods of preparation were sought. Indeed, at this stage of the investigation, it was not known whether the required anion (4) could be alkylated without unwanted side reactions occurring. The first route to be investigated was the alkylation of the anion (4) obtained by addition of an alkyl-lithium to 1-phenylthio-1-trimethylsilylethene (7),<sup>2</sup> as this method has been successful for the preparation of aldehydes. The slow addition of the alkene (7) to butyl-lithium-TMEDA in ether at 0 °C, followed by quenching the anion with an alkyl halide, gave the required silanes (2) (see Scheme 3 and Table 2).<sup>10</sup> This observation confirmed that the anion (4) was stable and did not undergo secondary reactions.

Although the addition of an alkyl-lithium to the vinylsilane (7) provides a useful route to the α-silyl sulphides (2), it is limited to the presence of an α-methylene group in R<sup>1</sup>. To overcome this

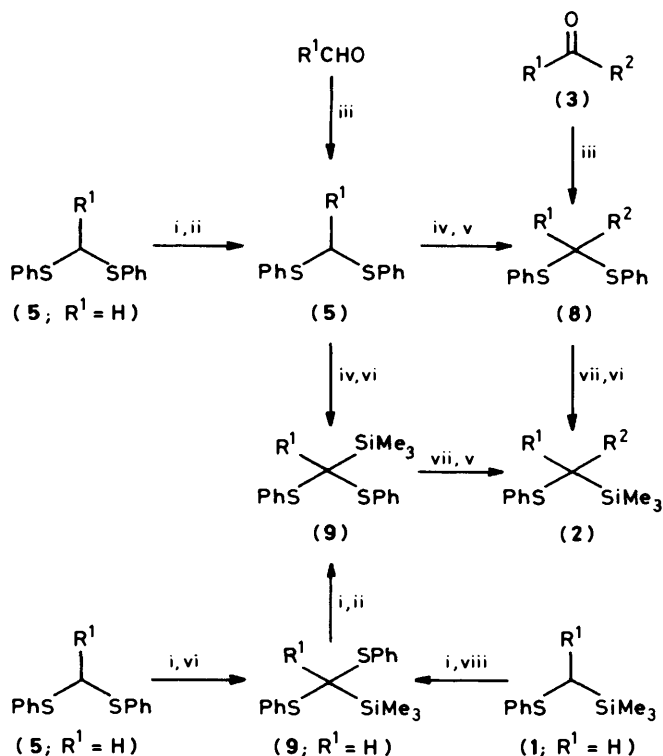


Scheme 3.

Table 2. Preparation of α-silyl sulphides (2) from 1-phenylthio-1-trimethylsilylethene (7) (see Scheme 3)

Alkyl-lithium (R <sup>3</sup> = <sup>a</sup> )	R <sup>2</sup> X	Yield (%) of (2)
Me	MeI	85
Me	EtI	79
Me	BuBr	64
Me	BuI	69
Me	Bu <sup>1</sup> Br	23
Me	C <sub>5</sub> H <sub>11</sub> I	67
Me	C <sub>6</sub> H <sub>11</sub> Br	0
Bu	MeI	82
Bu	EtI	80
Bu	BuBr	70
Bu	BuI	76
Bu <sup>1</sup>	MeI	24
Bu <sup>1</sup>	BuI	18
Ph	MeI	62
Ph	BuI	53

<sup>a</sup> R<sup>1</sup> = R<sup>3</sup>CH<sub>2</sub>.



Scheme 4. Reagents: i, BuLi-THF; ii, R<sup>1</sup>X; iii, PhSH/H<sup>+</sup>; iv, BuLi-TMEDA; v, R<sup>2</sup>X; vi, Me<sub>3</sub>SiCl; vii, LiNaph-THF; viii, PhSCl or PhSSPh

problem and to increase the scope of (2) as ketone equivalents, other methods of preparation were investigated. These methods employ a group which stabilises an α-carbanion but may later be substituted for lithium.

**Preparation of (2) from Bis(phenylthio)acetals (8).**—The bis(phenylthio) group lends itself to this type of approach and, as a phenylthio group is also present in the product (2), several alternative methods of preparation are available (see Scheme 4).

Bis(phenylthio)acetals (8) were prepared by alkylation of the corresponding aldehyde derivative (5) after anion formation with butyl-lithium-TMEDA complex in hexane.<sup>11</sup> An alternative method was to condense the ketone with thiophenol in the presence of an acid catalyst.<sup>5,12,13</sup> Although this last method allows branched alkyl groups to be present in the R groups, it was not of great use in this study; this route does lend itself, however, to the synthesis of α-thiosilanes (2) for the preparation of alkenes.<sup>11</sup>

The bis(phenylthio)acetals (8) were treated with lithium naphthalene to produce the α-lithio sulphide which was then silylated to produce (2)<sup>11</sup> (see Table 3). A similar approach was the reaction of 1,1-bis(phenylthio)-1-trimethylsilylalkanes (9) with lithium naphthalene to produce the anion (4), followed by alkylation. Primary alkyl halides gave good yields of (2) by this method when TMEDA or HMPA were also added (see Table 3). Secondary alkyl halides gave very low or no yields of (2); elimination was the major pathway. This type of approach to α-silyl sulphides (2) from bis(phenylthio) acetals (8) has also been used by others.<sup>14,15</sup> The problem of separating the product from naphthalene could be overcome by use of a catalytic amount of naphthalene. These reactions resulted in only a slight decrease in the yields of (2), bis-silylation not being a problem, but the reaction time was increased.<sup>16</sup>

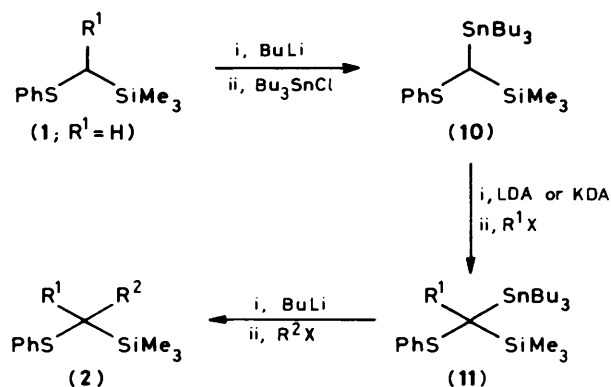
The 1,1-bis(phenylthio)-1-trimethylsilylalkanes (9) were

**Table 3.** Preparation of  $\alpha$ -silyl sulphides (2) by displacement of a phenylthio group (see Scheme 4)

Sulphide		R <sup>2</sup> X	Yield (%) of (2)
R <sup>1</sup>	R <sup>2</sup>		
(8) Me	Me	Me <sub>3</sub> SiCl	76
(8) Me	Et	Me <sub>3</sub> SiCl	71
(8) Me	Bu	Me <sub>3</sub> SiCl	73
(8) Et	Et	Me <sub>3</sub> SiCl	65
(8) Bu	Bu	Me <sub>3</sub> SiCl	61
(8) Ph	Me	Me <sub>3</sub> SiCl	83
(8) Ph	Bu	Me <sub>3</sub> SiCl	64
(9) Me	<sup>a</sup>	MeI	79
(9) Me		BuBr	68
(9) Me		BuI	71
(9) Me		Bu <sup>t</sup> Br	13
(9) Me		C <sub>6</sub> H <sub>11</sub> Br	0 <sup>b</sup>
(9) Bu		MeI	70
(9) Bu		BuBr	59
(9) Bu		BuI	60
(9) Bu		Bu <sup>t</sup> Br	<10 <sup>c</sup>
(9) Bu		C <sub>6</sub> H <sub>11</sub> Br	0
(9) Bu <sup>t</sup>		MeI	64

<sup>a</sup> Not applicable. <sup>b</sup> No product could be detected. <sup>c</sup> Product could only be detected in very small amounts.

readily available by alkylation of the anion derived from bis(phenylthio)trimethylsilylmethane (9; R<sup>1</sup> = H)<sup>7</sup> or by silylation of the anion derived from the bis(phenylthio) acetal (5).<sup>11</sup> The wide variety of methods available for the preparation of  $\alpha$ -silyl sulphides (2) is summarised in Scheme 4. One advantage of this methodology is that branched alkyl chains may be introduced in high yield.

**Scheme 5.**

**Preparation of (2) from Tin Compounds.**—In a manner similar to that just described, a trialkylstannyl group was used to stabilise the  $\alpha$ -anion and then displaced to yield the required anion (7). In these studies the stannyl moiety was tributyltin, solely on the grounds of cost. Phenylthiotributylstannyltrimethylsilylmethane (10) was prepared as previously described<sup>17</sup> (see Scheme 5). Subsequent anion formation with LDA or KDA<sup>8</sup> in THF at  $-78^\circ\text{C}$  followed by an alkyl halide gave the adducts (11). The potassium anions were formed rapidly (0.25 h) and alkylated readily (see Table 4) whereas the analogous lithium anions were formed much more slowly (1 h) and a complexing agent, such as HMPA or TMEDA, had to be added with the alkyl halide to achieve good yields of (11). Deuteriation experiments with LDA and (10) showed that

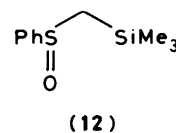
**Table 4.** Preparation of  $\alpha$ -silyl sulphides (2) from phenylthiotributylstannyltrimethylsilylmethane (10)

R <sup>1</sup> X	Base	Yield of (11) (%)	R <sup>2</sup> X	Yield of (2) (%)
MeI	LDA	81	MeI	71
	KDA	89	BuBr	58
BuI	LDA	61	BuI	67
			Bu <sup>t</sup> Br	21
	KDA	78	C <sub>6</sub> H <sub>11</sub> Br	0
			MeI	76
			BuBr	62
Bu <sup>t</sup> Br	LDA	<10 <sup>a</sup>	BuI	63
			Bu <sup>t</sup> Br	<10 <sup>a</sup>
			C <sub>6</sub> H <sub>11</sub> Br	0
Bu <sup>t</sup> Br	KDA	<10 <sup>a</sup>		

<sup>a</sup> Some product could be detected but only in very small amounts.

anion formation was not complete (*ca.* 80%) within 1 h, but longer reaction times or the addition of TMEDA or HMPA during anion formation led to significant amounts of carbon-tin bond cleavage. Neither anion system could be used with secondary alkyl halides; elimination was the major pathway. To prepare the  $\alpha$ -silyl sulphides (2), the tributylstannyl group was displaced with butyl-lithium in THF-hexane (8:1)<sup>18</sup> and the resultant organolithium alkylated. As before, this was best carried out in the presence of TMEDA or HMPA and was restricted to primary alkyl halides—others presumably failing because of the large groups around the anion (see Table 4).

**Preparation of  $\alpha$ -Silyl Sulphones.**—The problems associated with the above methods led us to seek an alternative approach. The obvious method was to try and increase the stability of the anion (4) by oxidising the sulphur atom. It had already been shown that the anion of phenylsulphonyltrimethylsilylmethane (12) could be prepared by treatment of (12) with *n*- or *t*-butyl-



lithium in THF. Although condensation took place with carbonyl compounds, alkylation did not occur.<sup>19</sup> This result was confirmed and when TMEDA or HMPA were used, complex mixtures were obtained. Many problems are associated with the sulphoxide system: sulphoxides react with alkyl-lithiums<sup>20</sup> and the sila-Pummerer rearrangement<sup>2,6</sup> occurs readily. This rearrangement also makes purification extremely difficult. Since a general, simple procedure was the object of this work, sulphones were used instead of the sulphoxides.

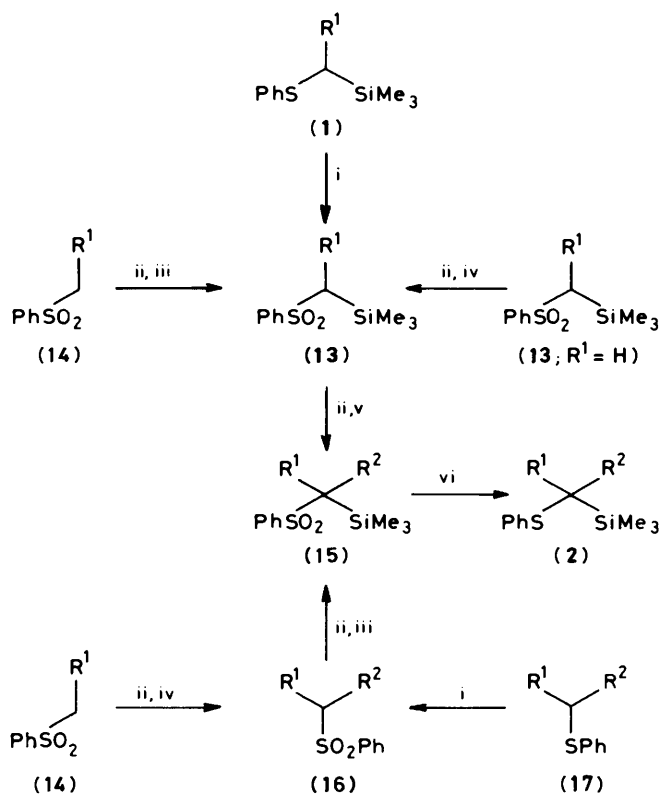
The  $\alpha$ -silyl sulphones (3)<sup>21,22</sup> were obtained in almost quantitative yield by oxidation of the corresponding sulphide (1) with *m*-chloroperbenzoic acid (MCPBA) (2.2 equiv.) in dichloromethane at  $-23^\circ\text{C}$ . This temperature was used to minimise the probability of the sila-Pummerer rearrangement occurring. An alternative procedure was to use sodium periodate in aqueous methanol at  $0^\circ\text{C}$  (see Scheme 6 and Table 5). The required  $\alpha$ -silyl sulphones (13) were also prepared by silylation of the anion derived from the sulphone (14) or by alkylation of phenylsulphonyltrimethylsilylmethyl-lithium (see Scheme 6 and Table 5).

This oxidation allowed facile formation of the required anion with butyl-lithium; subsequent alkylation with a primary alkyl

**Table 5.** Preparation of the sulphones (13)

R <sup>1</sup>	Yield (%) of (13) from		
	(1) <sup>a</sup>	(14)	(13; R <sup>1</sup> = H) <sup>b</sup>
Me	92	93	93
Et	84	90	81
Pr	86	82	77
Bu	88	81	80
Bu <sup>i</sup>	85	72	19 <sup>c</sup>
C <sub>5</sub> H <sub>11</sub>	89	89	76
Ph	93	74	

<sup>a</sup> Yields refer to oxidation with MCPBA. <sup>b</sup> Yields refer to alkylation with R<sup>1</sup>I. <sup>c</sup> The bromide was used in this case.



**Scheme 6.** Reagents: i, MCPBA/CHCl<sub>2</sub>; ii, BuLi/THF; iii, Me<sub>3</sub>SiCl; iv, R<sup>1</sup>X; v, R<sup>2</sup>X; vi, DIBAL-H or LiAlH<sub>4</sub>.

halide gave the adducts (15) in good yield (see Table 6). Again, an alternative is available, but in this case silylation of the anion derived from the disubstituted sulphone (16) did not proceed in high yield. It should be noted, however, that moderate yields were still obtained when one of the alkyl groups was secondary and that cyclic derivatives are accessible by this method (see Table 6). The sulphones (16) were, in turn, obtained by alkylation of the sulphone (16) or by oxidation of the sulphide (17) (see Experimental section).

The  $\alpha$ -silyl sulphones (15) were converted into the required  $\alpha$ -silyl sulphides (2) by standard procedures. The two reducing agents used were di-isobutylaluminium hydride (Dibal-H) and lithium aluminium hydride; the reactions proceeded smoothly in contrast to some previous sulphone reductions in the literature.<sup>23-25</sup> This could have been due to the  $\alpha$ -carbon atom being fully substituted so that an anion could not form. The

**Table 6.** Preparation of the sulphones (15)

R <sup>1</sup>	R <sup>2</sup>	X <sup>a</sup>	Yield (%) of (15)	
			from (13)	from (16)
Me	Me	I	91	68
Me	Bu	Br	74	62
Me	Bu	I	77	62
Bu	Me	I	82	62
Bu	Et	Br	71	57
Bu	Et	I	73	57
Bu	Bu	Br	69	50
Bu	Bu	I	74	50
Bu	Bu <sup>s</sup>	Br	15 <sup>b</sup>	49
Bu	C <sub>6</sub> H <sub>11</sub>	Br	0	<sup>c</sup>
Ph	Me	I	84	60
Ph	Bu	I	63	48
	-(CH <sub>2</sub> ) <sub>5</sub> -	<sup>c</sup>	<sup>c</sup>	67

<sup>a</sup> For the method from (15). <sup>b</sup> This yield is approximate as the product was not obtained pure by this method. <sup>c</sup> Not applicable.

**Table 7.** Reductions of the sulphones (15) to sulphides (2)

Sulphone (15)		Yield (%) of (2) <sup>a</sup>
R <sup>1</sup>	R <sup>2</sup>	
Me	Me	78 (81) <sup>b</sup>
Me	Bu	73 (79) <sup>b</sup>
Et	Bu	81
Bu	Bu	82 (86) <sup>b</sup>
Ph	Me	85 (79) <sup>b</sup>
Ph	Bu	77

<sup>a</sup> With LiAlH<sub>4</sub> as reductant. <sup>b</sup> With Dibal-H as reductant.

reduction was also clean in that no products of a sila-Pummerer rearrangement were detected, reduction of any intermediate sulphoxide presumably being faster than rearrangement. Representative examples for the conversion of sulphone (15) into sulphide (2) are given in Table 7.

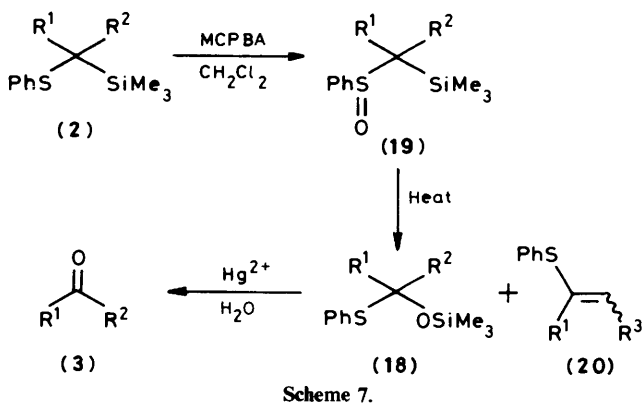
Attempts were made to add an alkyl-lithium to oxidised forms of the alkene (7). Addition to 1-phenylsulphonyl-1-trimethylsilylethene would have led directly to the sulphoxide (2) which could have given the sila-Pummerer product (18) without isolation. This transformation could not, however, be achieved under a wide variety of conditions; a complex mixture was invariably the result. In a similar vein, addition of any alkyl-lithium to 1-phenylsulphonyl-1-trimethylsilylethene gave only moderate yields (<50%) of the adduct. This was also the case when phenylsulphonylethene was the alkene, a complex mixture being the result. This approach of adding an alkyl-lithium to a substituted olefin is, therefore, only high yielding in the sulphide (7) case.

**Conversion of (2) into Ketones.**—The  $\alpha$ -silyl sulphides (2) were converted into the ketones (3) in a manner similar to that previously described for aldehydes.<sup>1,2,6</sup> The sulphide (2) was oxidised to the sulphoxide (19) with one equivalent of MCPBA. The sila-Pummerer rearrangement was carried out by heating (19) in THF or carbon tetrachloride. The product of the rearrangement was the required *O*-trimethylsilylphenylthioacetal (18) for the phenyl ketones (R<sup>1</sup> = Ph).<sup>26</sup> When both of the groups in the sulphoxide (19) were alkyl, a side reaction was observed; the formation of the vinyl sulphide (20) became a significant factor particularly if one of the alkyl chains was branched. The vinyl sulphide (20) can arise in these cases by deprotonation competing with silanoxide attack in the intermediate sulphur-ylide.<sup>6,26,27</sup> To date, the formation of this

**Table 8.** Conversion of the  $\alpha$ -silyl sulphides (2) to the ketones (3)

(2)		Yield (%) of (3)
R <sup>1</sup>	R <sup>2</sup>	
Me	Me	51 <sup>a</sup>
Me	Et	58 <sup>a</sup>
Me	Bu	63 <sup>a</sup>
Et	Et	52 <sup>a</sup>
Bu	Bu	66 (69) <sup>a</sup>
Bu	Bu <sup>i</sup>	48 (42) <sup>a</sup>
Ph	Me	82 (83) <sup>a</sup>
Ph	Et	74 (78) <sup>a</sup>
Ph	Pr <sup>i</sup>	53
Ph	Bu	75
Ph	CH <sub>2</sub> Ph	69
Ph	CH <sub>2</sub> CH=CH <sub>2</sub>	72 <sup>b</sup>

<sup>a</sup> Isolated as the 2,4-dinitrophenylhydrazone. <sup>b</sup> The double bond moved into conjugation during hydrolysis.



unwanted product has not been overcome. Although the *O*-silylthioacetals (18) are useful synthetic intermediates, the overall loss in yield due to the formation of the vinyl sulphide (20) led us to adopt a more general approach for the conversion of the sulphoxide (19) into ketone (3). The acetals (18) have been hydrolysed by acid and base or in the presence of a metal ion such as copper, silver, or mercury.<sup>1,6,28,29</sup> This last observation and the fact that vinyl sulphides can be hydrolysed with mercury(II) catalysis, led to the adoption of the method of hydrolysis of the mixture of (18) and (20) in aqueous acetonitrile or THF.<sup>5</sup> Ketones bearing a substituted alkyl chain have been prepared by this hydrolysis procedure but in these cases the vinyl sulphide was the major product of the rearrangement reaction. The example of (2; R = Ph, R<sup>1</sup> = CH<sub>2</sub>CH=CH<sub>2</sub>) which had been prepared from an allyl halide gave a comparable yield of the carbonyl compounds but the double bond moved into conjugation during the hydrolysis.

The overall procedure, therefore, was to carry out the oxidation, thermal rearrangement, and hydrolysis without isolation of the intermediates. Representative examples are given in Table 8. It should be noted that volatile ketones were isolated as their 2,4-dinitrophenylhydrazone derivatives.

Various methods, therefore, exist for the preparation of  $\alpha$ -silyl sulphides (2) which may then be converted into the ketone (3). Indirect methods have to be used to prepare the anion (4) unless an anion-stabilising group is present in the silane (1). The Pummerer rearrangement is not as clean for the conversion of sulphoxides (19) into ketones, steric and electronic factors

playing a major role, but this can be overcome by use of mercury(II) assisted hydrolysis of the product mixture.

### Experimental

All m.p.s are uncorrected. Reactions involving organometallic reagents were carried out under dry nitrogen. Tetrahydrofuran (THF) and ether were freshly distilled from sodium-benzophenone. Light petroleum refers to that fraction with b.p. 60–80 °C. All n.m.r. spectra were recorded at 90 or 220 MHz in CDCl<sub>3</sub> solution with CH<sub>2</sub>Cl<sub>2</sub> as internal standard, unless otherwise stated.

**Preparation of (Phenylthio)phenyl(trimethylsilyl)methane (1; R<sup>1</sup> = Ph).**—Butyl-lithium (1.4M solution in hexane; 14 ml, 20 mmol) was added to benzyl phenyl sulphide<sup>30</sup> (6) (4.00 g, 20 mmol) in THF (50 ml) at 0 °C. The mixture was stirred at this temperature for 1 h after which chlorotrimethylsilane (2.87 ml, 2.44 g, 22.5 mmol) was added and the mixture allowed to warm to room temperature. The reaction mixture was poured into saturated aqueous ammonium chloride (50 ml), extracted with ether (3 × 30 ml), washed with saturated aqueous sodium chloride (50 ml), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated under reduced pressure to give, after column chromatography, (phenylthio)phenyl(trimethylsilyl)methane<sup>2</sup> (1; R<sup>1</sup> = Ph) (4.84 g, 89%) as an oil (Found: C, 70.75; H, 7.15. C<sub>16</sub>H<sub>20</sub>SSi requires C, 70.5; H, 7.4%;  $\nu_{\max}$ (CHCl<sub>3</sub>) 1 590 (Ar C=C) and 1 260 cm<sup>-1</sup> (SiMe<sub>3</sub>);  $\delta$  7.7–7.0 (10 H, m, Ph), 3.83 (1 H, s, CH), and 0.2 (9 H, s, SiMe<sub>3</sub>).

**Alkylations of (Phenylthio)phenyltrimethylsilylmethane (1; R<sup>1</sup> = Ph).**—Butyl-lithium (1.4M solution in hexane; 7 ml, 10 mmol) was added to the silane (1; R<sup>1</sup> = Ph) (2.72 g, 10 mmol) and TMEDA (1.88 ml, 1.45 g, 12.5 mmol) at 0 °C. After 1 h the alkyl halide (10 mmol) was added. The reaction was quenched when the mixture was poured into saturated aqueous ammonium chloride (25 ml). The mixture was extracted with ether (3 × 25 ml) and the combined extract washed with 2M hydrochloric acid (30 ml) and saturated aqueous sodium chloride (30 ml), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated under reduced pressure to give, after column chromatography, the alkylated silane (2; R<sup>1</sup> = Ph). Compounds prepared by this method were: 1,2-diphenyl-1-phenylthio-1-trimethylsilylethane (2; R<sup>1</sup> = Ph, R<sup>2</sup> = PhCH<sub>2</sub>) (2.57 g, 71%) as a viscous oil (Found: C, 76.45; H, 7.0. C<sub>23</sub>H<sub>26</sub>SSi requires C, 76.2; H, 7.2%;  $\nu_{\max}$ (CHCl<sub>3</sub>) 1 585 (Ar C=C) and 1 250 cm<sup>-1</sup> (SiMe<sub>3</sub>);  $\delta$  7.9–7.0 (1 H, m, Ph), 3.90 (2 H, s, CH<sub>2</sub>), and 0.20 (9 H, s, SiMe<sub>3</sub>);  $m/z$  362 (3%, M<sup>+</sup>), 110 (71, PhSH), 91 (65, C<sub>7</sub>H<sub>7</sub><sup>+</sup>), and 73 (100, Me<sub>3</sub>Si<sup>+</sup>); 2-methyl-1-phenyl-1-phenylthio-1-trimethylsilylpropane (2; R<sup>1</sup> = Ph, R<sup>2</sup> = Pr<sup>i</sup>) (1.07 g, 34%) as an oil (Found: C, 76.5; H, 8.5. C<sub>19</sub>H<sub>26</sub>SSi requires C, 76.35; H, 8.35%;  $\nu_{\max}$ (CHCl<sub>3</sub>) 1 585 (Ar C=C) and 1 250 cm<sup>-1</sup> (SiMe<sub>3</sub>);  $\delta$  7.8–7.0 (10 H, m, Ph), 2.5–0.8 (7 H, m, alkyls), and 0.21 (9 H, s, SiMe<sub>3</sub>);  $m/z$  314.1530 (M<sup>+</sup>, 8%) (C<sub>19</sub>H<sub>26</sub>SSi requires 314.1525), 109 (43, PhS<sup>+</sup>), 77 (29, Ph<sup>+</sup>), and 73 (100, Me<sub>3</sub>Si<sup>+</sup>); 1-phenyl-1-phenylthio-1-trimethylsilylbutane (2; R<sup>1</sup> = Ph, R<sup>2</sup> = Pr) as an oil (2.70 g, 86%) (Found: C, 76.6; H, 8.14. C<sub>19</sub>H<sub>26</sub>SSi requires C, 76.35; H, 8.35%;  $\nu_{\max}$ (thin film) 1 590 (Ar C=C) and 1 255 cm<sup>-1</sup> (SiMe<sub>3</sub>);  $\delta$  7.8–7.0 (10 H, m, Ph), 2.2 (2 H, t, J 7 Hz, SCCH<sub>2</sub>), 1.4–0.9 (5 H, m, CH<sub>2</sub>CH<sub>2</sub>Me), and 0.15 (9 H, s, SiMe<sub>3</sub>);  $m/z$  314.1538 (7%, M<sup>+</sup>) (C<sub>19</sub>H<sub>26</sub>SSi requires 314.1525), 109 (50, PhS<sup>+</sup>), and 73 (100, Me<sub>3</sub>Si<sup>+</sup>); 1-phenyl-1-phenylthio-1-trimethylsilylbut-3-ene (2; R<sup>1</sup> = Ph, R<sup>2</sup> = allyl) (2.28 g, 73%) as an oil (Found: C, 72.8; H, 7.75. C<sub>19</sub>H<sub>24</sub>SSi requires C, 73.0; H, 7.7%;  $\nu_{\max}$ (CHCl<sub>3</sub>) 1 660 (C=C), 1 590 (Ar C=C) and 1 260 cm<sup>-1</sup> (SiMe<sub>3</sub>);  $\delta$  7.9–7.0 (10 H, m, Ph), 6.5–5.9 (1 H, m, -CH<sub>2</sub>CH=CH<sub>2</sub>), 5.4–5.0 (2 H, m, CH=CH<sub>2</sub>), 3.0 (2 H, m, CH<sub>2</sub>CH=CH<sub>2</sub>), and 0.25 (9 H, s, SiMe<sub>3</sub>);  $m/z$  312.1379 (12%, M<sup>+</sup>) (C<sub>19</sub>H<sub>24</sub>SSi requires 312.1368), 110 (69, PhSH) and 73

(100,  $\text{Me}_3\text{Si}^+$ ); 1-phenyl-1-phenylthio-1-trimethylsilylethane (**2**;  $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{Me}$ ) as a viscous oil (2.69 g, 95%) (Found: C, 70.9; H, 7.95.  $\text{C}_{17}\text{H}_{22}\text{SSi}$  requires C, 71.25; H, 7.75%);  $\nu_{\text{max.}}(\text{CHCl}_3)$  1 585 (Ar C=C) and 1 255  $\text{cm}^{-1}$  ( $\text{SiMe}_3$ );  $\delta$  7.8—7.0 (10 H, m, Ph), 1.72 (3 H, s, CMe), and 0.18 (9 H, s,  $\text{SiMe}_3$ );  $m/z$  286.1222 (21%,  $M^+$ ) ( $\text{C}_{17}\text{H}_{22}\text{SSi}$  requires 286.1212), 109 (41,  $\text{PhS}^+$ ), and 73 (100,  $\text{Me}_3\text{Si}^+$ ); 1-phenyl-1-phenylthio-1-trimethylsilylhexane (**2**;  $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{C}_5\text{H}_{11}$ ) as an oil (2.09 g, 61%) (Found: C, 73.4; H, 9.05.  $\text{C}_{21}\text{H}_{30}\text{SSi}$  requires C, 73.6; H, 8.8%);  $\nu_{\text{max.}}(\text{CHCl}_3)$  1 590 (Ar C=C) and 1 250  $\text{cm}^{-1}$  ( $\text{SiMe}_3$ );  $\delta$  7.9—7.0 (10 H, m, Ph), 2.4—0.8 (11 H, m, alkyls), and 0.20 (9 H, s,  $\text{SiMe}_3$ );  $m/z$  342 (6%,  $M^+$ ), 109 (22,  $\text{PhS}^+$ ), and 73 (100,  $\text{Me}_3\text{Si}^+$ ); 1-phenyl-1-phenylthio-1-trimethylsilylpentane (**2**;  $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{Bu}$ ) as an oil (2.46 g, 75% from BuBr; 2.79 g, 85% from BuI) (Found: C, 73.2; H, 8.45.  $\text{C}_{20}\text{H}_{28}\text{SSi}$  requires C, 73.1; H, 8.6%);  $\nu_{\text{max.}}(\text{CHCl}_3)$  1 590 (Ar C=C) and 1 255  $\text{cm}^{-1}$  ( $\text{SiMe}_3$ );  $\delta$  7.8—7.0 (10 H, m, Ph), 2.30 (2 H, t,  $J$  8 Hz,  $\text{SCCH}_2$ ), 2.1—0.8 (7 H, m, Pr), and 0.18 (9 H, s,  $\text{SiMe}_3$ );  $m/z$  328.1703 (12%,  $M^+$ ) ( $\text{C}_{20}\text{H}_{28}\text{SSi}$  requires 328.1681), 109 (64,  $\text{PhS}^+$ ), 77 (39,  $\text{Ph}^+$ ), and 73 (100,  $\text{Me}_3\text{Si}^+$ ); 1-phenyl-1-phenylthio-1-trimethylsilylpropane (**2**;  $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{Et}$ ) as an oil (2.55 g, 85%) (Found: C, 71.95; H, 7.9.  $\text{C}_{18}\text{H}_{24}\text{SSi}$  requires C, 71.95; H, 8.05%);  $\nu_{\text{max.}}(\text{CHCl}_3)$  1 585 (Ar C=C) and 1 250  $\text{cm}^{-1}$  ( $\text{SiMe}_3$ );  $\delta$  7.8—7.0 (10 H, m, Ph), 2.23 (2 H, q,  $J$  7.5 Hz,  $\text{CH}_2\text{Me}$ ), 1.05 (3 H, t,  $J$  7.5 Hz,  $\text{CH}_2\text{Me}$ ), and 0.20 (9 H, s,  $\text{SiMe}_3$ );  $m/z$  300.1378 (14%,  $M^+$ ) ( $\text{C}_{18}\text{H}_{24}\text{SSi}$  requires 300.1388), 109 (52,  $\text{PhS}^+$ ), 77 (51,  $\text{Ph}^+$ ), and 73 (100,  $\text{Me}_3\text{Si}^+$ ); and 1-phenyl-1-phenylthio-1-trimethylsilyltridecane (**2**;  $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{C}_{12}\text{H}_{25}$ ) as an oil (2.82 g, 64%) (Found: C, 76.45; H, 9.1.  $\text{C}_{28}\text{H}_{44}\text{SSi}$  requires C, 76.3; H, 10.05%);  $\nu_{\text{max.}}(\text{CHCl}_3)$  1 590 (Ar C=C) and 1 250  $\text{cm}^{-1}$  ( $\text{SiMe}_3$ );  $\delta$  7.8—7.0 (10 H, m, Ph), 2.2—0.8 (25 H, m, alkyls), and 0.20 (9 H, s,  $\text{SiMe}_3$ );  $m/z$  440 (2%,  $M^+$ ), 110 (35,  $\text{PhSH}$ ), and 73 (100,  $\text{Me}_3\text{Si}^+$ ).

**Additions to 1-Phenylthio-1-trimethylsilylethane (7).**—The alkene (**7**)<sup>2</sup> (1.35 g, 10 mmol) in ether (25 ml) was added to the alkyl-lithium (12 mmol) and TMEDA (2.27 ml, 1.74 g, 15 mmol) in ether (15 ml) at 0 °C over 1.5 h. The reaction mixture was stirred for 1 h at 0 °C after which the alkyl halide (12 ml) was added and the whole warmed to room temperature; it was then poured into saturated aqueous ammonium chloride (50 ml), extracted with ether (3 × 25 ml), and the combined ether extracts washed with saturated aqueous sodium chloride (25 ml), dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated under reduced pressure to give, after distillation or column chromatography, the adduct (**2**). Compounds prepared by this method were: 2,2-dimethyl-4-phenylthio-4-trimethylsilyloctane (**2**;  $\text{R}^1 = \text{Bu}^i\text{CH}_2$ ,  $\text{R}^2 = \text{Bu}$ ) as an oil (0.58 g, 18%);  $\nu_{\text{max.}}(\text{CHCl}_3)$  1 585 (Ar C=C) and 1 250  $\text{cm}^{-1}$  ( $\text{SiMe}_3$ );  $\delta$  7.8—7.0 (5 H, m, Ph), 2.0—0.8 (20 H, m overlaid with singlets at 1.21 and 1.17, alkyls), and 0.13 (9 H, s,  $\text{SiMe}_3$ );  $m/z$  322.2169 (21%,  $M^+$ ) ( $\text{C}_{19}\text{H}_{34}\text{SSi}$  requires 322.2151), 109 (48,  $\text{PhS}^+$ ), and 73 (100,  $\text{Me}_3\text{Si}^+$ ); 4,4-dimethyl-2-phenylthio-2-trimethylsilylpentane (**2**;  $\text{R}^1 = \text{Bu}^i\text{CH}_2$ ,  $\text{R}^2 = \text{Me}$ ) as an oil (0.67 g, 24%);  $\nu_{\text{max.}}(\text{CHCl}_3)$  1 580 (Ar C=C) and 1 250  $\text{cm}^{-1}$  ( $\text{SiMe}_3$ );  $\delta$  7.7—7.1 (5 H, m, Ph), 1.23 (2 H, s,  $\text{CH}_2$ ), 1.15 (9 H, s, CMe<sub>3</sub>), 1.05 (3 H, s, CMe), and 0.08 (9 H, s,  $\text{SiMe}_3$ );  $m/z$  280.1704 ( $M^+$ , 31%) ( $\text{C}_{16}\text{H}_{28}\text{SSi}$  requires 280.1681), 109 (20,  $\text{PhS}^+$ ), and 73 (100,  $\text{Me}_3\text{Si}^+$ ); 4-methyl-3-phenylthio-3-trimethylsilylhexane (**2**;  $\text{R}^1 = \text{Et}$ ,  $\text{R}^2 = \text{Bu}^i$ ) as an oil (0.64 g, 23%);  $\nu_{\text{max.}}(\text{CHCl}_3)$  1 590 (Ar C=C) and 1 250  $\text{cm}^{-1}$  ( $\text{SiMe}_3$ );  $\delta$  7.6—7.0 (5 H, m, Ph), 1.7—0.7 (14 H, m, alkyls), and 0.05 (9 H, s,  $\text{SiMe}_3$ );  $m/z$  280.1710 (28%,  $M^+$ ) ( $\text{C}_{16}\text{H}_{28}\text{SSi}$  requires 280.1681), 109 (54,  $\text{PhS}^+$ ), and 73 (100,  $\text{Me}_3\text{Si}^+$ ); 1-phenyl-2-phenylthio-2-trimethylsilylhexane (**2**;  $\text{R}^1 = \text{PhCH}_2$ ;  $\text{R}^2 = \text{Bu}$ ) as a viscous oil (1.81 g, 53%) (Found: C, 73.9; H, 8.55.  $\text{C}_{21}\text{H}_{30}\text{SSi}$  requires C, 73.6; H, 8.8%);  $\nu_{\text{max.}}(\text{CHCl}_3)$  1 590 (Ar C=C) and 1 250  $\text{cm}^{-1}$  ( $\text{SiMe}_3$ );  $\delta$  7.9—7.0 (10 H, m, Ph), 4.40 (2 H, s,  $\text{PhCH}_2$ ), 1.8—1.0 (6 H, m,  $\text{CH}_2$ 's), 0.82 (3 H, t,  $J$  8 Hz,

$\text{CH}_2\text{Me}$ ), and 0.06 (9 H, s,  $\text{SiMe}_3$ );  $m/z$  342.1853 (10%,  $M^+$ ) ( $\text{C}_{21}\text{H}_{30}\text{SSi}$  requires 342.1838), 109 (41,  $\text{PhS}^+$ ), 91 (25,  $\text{C}_7\text{H}_7^+$ ), and 73 (100,  $\text{Me}_3\text{Si}^+$ ); 1-phenyl-2-phenylthio-2-trimethylsilylpropane (**2**;  $\text{R}^1 = \text{PhCH}_2$ ,  $\text{R}^2 = \text{Me}$ ) as a viscous oil (1.86 g, 62%) (Found: C, 72.1; H, 7.9.  $\text{C}_{18}\text{H}_{24}\text{SSi}$  requires C, 71.95; H, 8.05%);  $\nu_{\text{max.}}(\text{CHCl}_3)$  1 590 (Ar C=C) and 1 250  $\text{cm}^{-1}$  ( $\text{SiMe}_3$ );  $\delta$  7.8—7.0 (10 H, m, Ph), 4.38 (2 H, s,  $\text{PhCH}_2$ ), 1.13 (3 H, s, CMe), and 0.21 (9 H, s,  $\text{SiMe}_3$ );  $m/z$  300.1391 (17%,  $M^+$ ) ( $\text{C}_{18}\text{H}_{24}\text{SSi}$  requires 300.1368), 109 (32,  $\text{PhS}^+$ ), 91 (40,  $\text{C}_7\text{H}_7^+$ ), and 73 (100,  $\text{Me}_3\text{Si}^+$ ); 2-phenylthio-2-trimethylsilylbutane (**2**;  $\text{R}^1 = \text{Et}$ ,  $\text{R}^2 = \text{Me}$ ) as an oil (2.02 g, 85%) (Found: C, 65.3; H, 9.55.  $\text{C}_{13}\text{H}_{22}\text{SSi}$  requires C, 65.5; H, 9.3%);  $\nu_{\text{max.}}(\text{CHCl}_3)$  1 590 (Ar C=C) and 1 250  $\text{cm}^{-1}$  ( $\text{SiMe}_3$ );  $\delta$  7.6—7.0 (5 H, m, Ph), 1.25 (2 H, q,  $J$  8 Hz,  $\text{CH}_2$ ), 0.90 (3 H, t,  $J$  8 Hz,  $\text{CH}_2\text{Me}$ ), and 0.04 (9 H, s,  $\text{SiMe}_3$ );  $m/z$  238.1264 (61%,  $M^+$ ) ( $\text{C}_{13}\text{H}_{22}\text{SSi}$  requires 238.1212), 109 (45,  $\text{PhS}^+$ ), and 73 (100,  $\text{Me}_3\text{Si}^+$ ); 5-phenylthio-5-trimethylsilyldecane (**2**;  $\text{R}^1 = \text{C}_5\text{H}_{11}$ ,  $\text{R}^2 = \text{Bu}$ ) as an oil (2.25 g, 70% with BuBr; 2.45 g, 76% with BuI) (Found: C, 71.0; H, 10.75.  $\text{C}_{19}\text{H}_{34}\text{SSi}$  requires C, 70.75; H, 10.6%);  $\nu_{\text{max.}}(\text{CHCl}_3)$  1 580 (Ar C=C) and 1 245  $\text{cm}^{-1}$  ( $\text{SiMe}_3$ );  $\delta$  7.8—7.0 (5 H, m, Ph), 2.3—0.8 (20 H, m, alkyls), and 0.05 (9 H, s,  $\text{SiMe}_3$ );  $m/z$  322.2203 (31%,  $M^+$ ) ( $\text{C}_{19}\text{H}_{34}\text{SSi}$  requires 322.2151), 109 (41,  $\text{PhS}^+$ ), and 73 (100,  $\text{Me}_3\text{Si}^+$ ); 2-phenylthio-2-trimethylsilylheptane (**2**;  $\text{R}^1 = \text{C}_5\text{H}_{11}$ ,  $\text{R}^2 = \text{Me}$ ) as an oil (2.30 g, 82%), b.p. 124—130 °C/1 mmHg (Found: C, 68.4; H, 10.2.  $\text{C}_{16}\text{H}_{28}\text{SSi}$  requires C, 68.5; H, 10.05%);  $\nu_{\text{max.}}(\text{CHCl}_3)$  1 590 (Ar C=C) and 1 250  $\text{cm}^{-1}$  ( $\text{SiMe}_3$ );  $\delta$  7.6—7.1 (5 H, m, Ph), 1.9—1.0 (11 H, m overlaid with a singlet at 1.03,  $\text{CH}_2$ 's and SCMe), 0.85 (3 H, t,  $J$  7.5 Hz,  $\text{CH}_2\text{Me}$ ), and 0.04 (9 H, s,  $\text{SiMe}_3$ );  $m/z$  280.1714 (52%,  $M^+$ ) ( $\text{C}_{16}\text{H}_{28}\text{SSi}$  requires 280.1681), 109 (52,  $\text{PhS}^+$ ), and 73 (100,  $\text{Me}_3\text{Si}^+$ ); 3-phenylthio-3-trimethylsilylheptane (**2**;  $\text{R}^1 = \text{Et}$ ,  $\text{R}^2 = \text{Bu}$ ) as an oil (1.79 g, 64% with BuBr; 1.93 g, 69% with BuI) (Found: C, 68.6; H, 9.8.  $\text{C}_{16}\text{H}_{28}\text{SSi}$  requires C, 68.5; H, 10.05%);  $\nu_{\text{max.}}(\text{CHCl}_3)$  1 590 (Ar C=C) and 1 250  $\text{cm}^{-1}$  ( $\text{SiMe}_3$ );  $\delta$  7.6—7.0 (5 H, m, Ph), 2.0—0.7 (14 H, m, alkyls), and 0.06 (9 H, s,  $\text{SiMe}_3$ );  $m/z$  280.1700 ( $M^+$ , 38%) ( $\text{C}_{16}\text{H}_{28}\text{SSi}$  requires 280.1681), 109 (21,  $\text{PhS}^+$ ), and 73 (100,  $\text{Me}_3\text{Si}^+$ ); 3-phenylthio-3-trimethylsilyloctane (**2**;  $\text{R}^1 = \text{Et}$ ,  $\text{R}^2 = \text{C}_5\text{H}_{11}$ ) as an oil (1.97 g, 67% with  $\text{C}_5\text{H}_{11}\text{I}$ ; 2.35 g, 80% with EtI) (Found: C, 69.15; H, 10.4.  $\text{C}_{17}\text{H}_{30}\text{SSi}$  requires C, 69.3; H, 10.25%);  $\nu_{\text{max.}}(\text{CHCl}_3)$  1 590 (Ar C=C) and 1 250  $\text{cm}^{-1}$  ( $\text{SiMe}_3$ );  $\delta$  7.6—7.0 (5 H, m, Ph), 1.9—0.7 (16 H, m, alkyls), and 0.04 (9 H, s,  $\text{SiMe}_3$ );  $m/z$  294.1861 (48%,  $M^+$ ) ( $\text{C}_{17}\text{H}_{30}\text{SSi}$  requires 294.1838), 109 (41,  $\text{PhS}^+$ ), and 73 (100,  $\text{Me}_3\text{Si}^+$ ); and 3-phenylthio-3-trimethylsilylpentane (**2**;  $\text{R}^1 = \text{R}^2 = \text{Et}$ ) as an oil (1.99 g, 79%) (Found: C, 66.9; H, 9.45.  $\text{C}_{14}\text{H}_{24}\text{SSi}$  requires C, 66.6; H, 9.6%);  $\nu_{\text{max.}}(\text{CHCl}_3)$  1 590 (Ar C=C) and 1 250  $\text{cm}^{-1}$  ( $\text{SiMe}_3$ );  $\delta$  7.6—7.0 (5 H, m, Ph), 1.4 (4 H, m,  $\text{CH}_2$ 's), 0.9 (6 H, m,  $\text{CH}_2\text{Me}$ ), and 0.04 (9 H, s,  $\text{SiMe}_3$ );  $m/z$  252.1386 (60%,  $M^+$ ) ( $\text{C}_{14}\text{H}_{24}\text{SSi}$  requires 252.1368), 109 (31,  $\text{PhS}^+$ ), and 73 (100,  $\text{Me}_3\text{Si}^+$ ).

**Preparation of the Silanes (2) from the Bis(phenylthio) Acetal.** (**8**).—These reactions were carried out as previously described.<sup>11</sup> Compounds prepared similarly were: 1-phenyl-1-phenylthio-1-trimethylsilylethane (**2**;  $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{Me}$ ) (76%), identical with the sample prepared above (i.r., n.m.r., t.l.c.);<sup>11</sup> 1-phenyl-1-phenylthio-1-trimethylsilylpentane (**2**;  $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{Bu}$ ) (64%) identical with the sample prepared above (i.r., n.m.r., t.l.c.); 2-phenylthio-2-trimethylsilylbutane (**2**;  $\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = \text{Et}$ ) (71%) identical with the sample prepared above (i.r., n.m.r., t.l.c.); 2-phenylthio-2-trimethylsilylhexane (**2**;  $\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = \text{Bu}$ ) as an oil (1.90 g, 73%) (Found: C, 69.3; H, 7.8.  $\text{C}_{15}\text{H}_{20}\text{SSi}$  requires C, 69.15; H, 7.75%);  $\nu_{\text{max.}}(\text{CHCl}_3)$  1 585 (Ar C=C) and 1 250  $\text{cm}^{-1}$  ( $\text{SiMe}_3$ );  $\delta$  7.7—7.1 (5 H, m, Ph), 1.8—0.8 (12 H, m overlaid with a s at 1.1, alkyls), and 0.05 (9 H, s,  $\text{SiMe}_3$ );  $m/z$  260.1100 ( $M^+$ , 47%) ( $\text{C}_{15}\text{H}_{20}\text{SSi}$  requires 260.1055), 109 (24,  $\text{PhS}^+$ ), and 73 (100,  $\text{Me}_3\text{Si}^+$ ); 5-phenylthio-5-trimethylsilyl-nonane (**2**;  $\text{R}^1 = \text{R}^2 = \text{Bu}$ ) as an oil (1.88 g, 61%) (Found:

C, 69.9; H, 10.8.  $C_{18}H_{32}SSi$  requires C, 70.05; H, 10.5%;  $\nu_{\max}(\text{CHCl}_3)$  1 590 (Ar C=C) and 1 250  $\text{cm}^{-1}$  (SiMe<sub>3</sub>);  $\delta$  7.7—7.0 (5 H, m, Ph), 2.0—0.7 (18 H, m, alkyls), and 0.06 (9 H, s, SiMe<sub>3</sub>);  $m/z$  308.2006 ( $M^+$ , 39%) ( $C_{18}H_{32}SSi$  requires 308.1994), 109 (63, PhS<sup>+</sup>), and 73 (100, Me<sub>3</sub>Si<sup>+</sup>); 3-phenylthio-3-trimethylsilylpentane (**2**; R<sup>1</sup> = R<sup>2</sup> = Et) (65%) and 2-phenylthio-2-trimethylsilylpropane<sup>11</sup> (**2**; R<sup>1</sup> = R<sup>2</sup> = Me) both identical with samples prepared previously (t.l.c., i.r., n.m.r.).

**Preparation of 1,1-Bis(phenylthio)-1-trimethylsilylalkanes (9).**—1,1-Bis(phenylthio)-1-trimethylsilyl ethane (**9**; R<sup>1</sup> = Me) and 1,1-bis(phenylthio)-1-(trimethylsilyl)pentane (**9**; R<sup>1</sup> = Bu) were prepared as previously described.<sup>7</sup> Also prepared similarly were 1,1-bis(phenylthio)-3-methyl-1-(trimethylsilyl)butane (**9**; R<sup>1</sup> = Bu<sup>1</sup>) (0.65 g, 18%) as an oil (Found: C, 66.45; H, 7.9.  $C_{20}H_{28}S_2Si$  requires C, 66.6; H, 7.8%;  $\nu_{\max}(\text{CHCl}_3)$  1 590 (Ar C=C) and 1 250  $\text{cm}^{-1}$  (SiMe<sub>3</sub>);  $\delta$  7.6—7.1 (10 H, m, Ph), 2.68 (2 H, d, J 8 Hz, CH<sub>2</sub>CHMe<sub>2</sub>), 1.65 (1 H, m, CHMe<sub>2</sub>), 0.90 (6 H, d, J 8 Hz, CHMe<sub>2</sub>), and 0.03 (9 H, s, SiMe<sub>3</sub>);  $m/z$  360 (16%,  $M^+$ ), 109 (24, PhS<sup>+</sup>), and 73 (100, Me<sub>3</sub>Si<sup>+</sup>).

The above compounds (**9**; R<sup>1</sup> = Me or Bu) were also prepared by silylation of the anion derived from the bis-thioacetal (**5**) by the method previously described for alkylations.<sup>11</sup>

**Preparation of the Silanes (2) from 1,1-Bis(phenylthio)-1-trimethylsilylalkanes (9).**—The 1,1-bis(phenylthio)-1-trimethylsilylalkane (**9**) (10 mmol) was treated with lithium naphthalene (20 mmol) to give the anion (**7**) as previously reported.<sup>7</sup> The alkyl halide (12 mmol) in TMEDA (2 ml) was added after 2 h, and the reaction mixture warmed to room temperature overnight. The mixture was poured into saturated aqueous ammonium chloride (50 ml), extracted with ether (3 × 30 ml), and the combined extracts washed with 2M-aqueous sodium hydroxide (2 × 25 ml) and saturated aqueous sodium chloride (30 ml), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated under reduced pressure to give, after column chromatography, the silanes (**2**). Compounds prepared by this method were: 3-methyl-2-phenylthio-2-trimethylsilylpentane (**2**; R<sup>1</sup> = Me, R<sup>2</sup> = Bu<sup>a</sup>) as an oil [0.35 g, 13% from (**9**; R<sup>1</sup> = Me); 1.70 g, 64% from (**9**; R<sup>1</sup> = Bu<sup>1</sup>)] (Found: C, 67.4; H, 10.0.  $C_{15}H_{26}SSi$  requires C, 67.6; H, 9.85%;  $\nu_{\max}(\text{CHCl}_3)$  1 590 (Ar C=C) and 1 255  $\text{cm}^{-1}$  (SiMe<sub>3</sub>);  $\delta$  7.6—7.0 (5 H, m, Ph), 1.8—0.7 (12 H, m, alkyls), and 0.07 (9 H, s, SiMe<sub>3</sub>);  $m/z$  266.1539 (42%,  $M^+$ ) ( $C_{15}H_{26}SSi$  requires 266.1525), 109 (36, PhS<sup>+</sup>), and 73 (100, Me<sub>3</sub>Si<sup>+</sup>); 2-phenylthio-2-trimethylsilylhexane (**2**; R<sup>1</sup> = Me, R<sup>2</sup> = Bu) (1.81 g, 68% with BuBr; 1.89 g, 71% with BuI and 1.86 g, 70% with MeI); 5-phenylthio-5-trimethylsilylnonane (**2**; R<sup>1</sup> = R<sup>2</sup> = Bu) (1.82 g, 59% with BuBr; 1.85 g, 60% with BuI); and 2-phenylthio-2-trimethylsilylpropane (**2**; R<sup>1</sup> = R<sup>2</sup> = Me) (1.77 g, 79%), all identical with the samples previously prepared.

**Preparation of Phenylthiotributylstannyltrimethylsilylmethane (10).**—Butyl-lithium (1.4M solution in hexane; 36 ml, 50 mmol) was added to phenylthiotrimethylsilylmethane (**1**; R<sup>1</sup> = H) (9.8 g, 50 mmol) in THF (100 ml) at 0 °C. The mixture was stirred for 0.5 h at this temperature after which tributyltin chloride (14.9 ml, 17.9 g, 55 mmol) was added. The mixture warmed to room temperature overnight, was poured into saturated aqueous ammonium chloride (350 ml), extracted with ether (3 × 100 ml), and the combined extracts washed with saturated aqueous sodium chloride (150 ml), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated under reduced pressure to give, after column chromatography (SiO<sub>2</sub>; 500 g; 1 100 × 30 mm, eluting with light petroleum), the stannane (**10**) as an oil (20.6 g, 85%) (Found: C, 54.8; H, 8.7.  $C_{22}H_{42}SSiSn$  requires C, 54.55; H, 8.55%;  $\nu_{\max}(\text{CHCl}_3)$  1 590 (Ar C=C) and 1 250  $\text{cm}^{-1}$  (SiMe<sub>3</sub>);  $\delta$  7.5—7.0 (5 H, m, Ph), 2.10

(1 H, s, CHSSiSn), 1.9—0.7 (27 H, m, SnBu<sub>3</sub>), and 0.15 (9 H, s, SiMe<sub>3</sub>);  $m/z$  484 (6%,  $M^+$ ) and 73 (100, Me<sub>3</sub>Si<sup>+</sup>).

**Alkylations of Phenylthiotributylstannyltrimethylsilylmethane (10).**—Butyl-lithium (1.4M solution in hexane; 7 ml, 10 mmol) was added to di-isopropylamine (1.40 ml, 1.01 g, 10 mmol) and potassium t-butoxide (1.12 g, 10 mmol) in THF (25 ml) at -78 °C.<sup>8</sup> After 5 min, the stannane (**10**) (4.84 g, 10 mmol) in THF (5 ml) was added and after a further 0.25 h, the alkyl halide (10 mmol). The reaction mixture was warmed to room temperature overnight, poured into saturated aqueous ammonium chloride (50 ml), extracted with ether (3 × 30 ml), and the combined extracts washed with saturated aqueous sodium chloride (30 ml), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated under reduced pressure to give, after column chromatography, the adducts (**11**). Compounds prepared by this method were: 1-phenylthio-1-tributylstannyl-1-trimethylsilylethane (**11**; R<sup>1</sup> = Me) as an oil (4.46 g, 89%) (Found: C, 55.7; H, 9.1.  $C_{23}H_{44}SSiSn$  requires C, 55.3; H, 8.9%;  $\nu_{\max}(\text{CHCl}_3)$  1 585 (Ar C=C) and 1 260  $\text{cm}^{-1}$  (SiMe<sub>3</sub>);  $\delta$  7.6—7.1 (5 H, m, Ph), 2.0—0.6 (30 H, m, overlaid with a s at 1.28, CMe and SnBu<sub>3</sub>), and 0.19 (9 H, br s, SiMe<sub>3</sub>);  $m/z$  498 (2%,  $M^+$ ), 110 (45, PhSH), and 73 (100, Me<sub>3</sub>Si<sup>+</sup>); and 1-phenylthio-1-tributylstannyl-1-trimethylsilylpentane (**11**; R<sup>1</sup> = Bu) as an oil (4.21 g, 78%) (Found: C, 58.0; H, 9.7.  $C_{26}H_{50}SSiSn$  requires C, 57.65; H, 9.3%;  $\nu_{\max}(\text{CHCl}_3)$  1 580 (Ar C=C) and 1 260  $\text{cm}^{-1}$  (SiMe<sub>3</sub>);  $\delta$  7.6—7.0 (5 H, m, Ph), 2.0—0.7 (36 H, m, butyls), and 0.11 (9 H, br s, SiMe<sub>3</sub>);  $m/z$  540 (1%,  $M^+$ ) and 73 (100, Me<sub>3</sub>Si<sup>+</sup>).

Alkylations with LDA were carried out in a similar manner but the alkyl halide was added in TMEDA or HMPA (4 ml).

**The Silanes (2) from the Stannanes (11).**—Butyl-lithium (1.4M solution in hexane; 7 ml, 10 mmol) was added to the stannane (**11**) (10 mmol) in THF (55 ml) at 0 °C. After 1.5 h the alkyl halide (10 mmol) in TMEDA or HMPA (4 ml) was added. The reaction mixture was stirred for a further 12 h, poured into saturated aqueous ammonium chloride (150 ml), extracted with ether (3 × 50 ml), washed with saturated aqueous sodium chloride (2 × 50 ml), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated under reduced pressure, to give, after column chromatography, the silanes (**2**). Compounds prepared by this method were: 3-methyl-2-phenylthio-2-trimethylsilylpentane (**2**; R<sup>1</sup> = Me, R<sup>2</sup> = Bu<sup>a</sup>) (0.56 g, 21%); 2-phenylthio-2-trimethylsilylhexane (**2**; R<sup>1</sup> = Me, R<sup>2</sup> = Bu) (1.56 g, 58% with BuBr; 1.80 g, 67% with BuI and 2.02 g, 76% with MeI); 4-phenylthio-4-trimethylsilylnonane (**2**; R<sup>1</sup> = R<sup>2</sup> = Bu) (1.92 g, 62% with BuBr and 1.93 g, 63% with BuI); and 2-phenylthio-2-trimethylsilylpropane (**2**; R<sup>1</sup> = R<sup>2</sup> = Me) (1.61 g, 71%), all identical with samples prepared above (t.l.c., i.r., n.m.r.).

**Preparation of Phenylsulphonyltrimethylsilylmethane (13; R<sup>1</sup> = H).**—Phenylthiotrimethylsilylmethane (**1**; R<sup>1</sup> = H) (9.8 g, 50 mmol) in dry dichloromethane (50 ml) was added to *m*-chloroperbenzoic acid (19.0 g, 110 mmol) in dichloromethane (500 ml) at -23 °C over 1 h. After being stirred overnight at this temperature, the mixture was poured into 2M-aqueous sodium hydroxide (250 ml). The organic layer was separated, washed with saturated aqueous sodium hydrogen carbonate (150 ml) and saturated aqueous sodium chloride (100 ml), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated under reduced pressure to give the sulphone (**13**; R<sup>1</sup> = H) as an oil (11.3 g, 99%) (Found: C, 52.65; H, 7.15.  $C_{10}H_{16}O_2SSi$  requires C, 52.6; H, 7.05%;  $\nu_{\max}(\text{CHCl}_3)$  1 260 (SiMe<sub>3</sub>), 1 310, and 1 160  $\text{cm}^{-1}$  (SO<sub>2</sub>);  $\delta$  7.9—7.3 (5 H, m, Ph), 2.60 (2 H, s, CH<sub>2</sub>), and 0.11 (9 H, s, SiMe<sub>3</sub>);  $m/z$  228 (6%,  $M^+$ ) 77 (94, Ph<sup>+</sup>), and 73 (100, Me<sub>3</sub>Si<sup>+</sup>).

**Alkylations of Phenylsulphonyltrimethylsilylmethane (13; R<sup>1</sup> = H).**—Butyl-lithium (1.4M solution in hexane; 14.2 ml, 20

mmol) was added to the sulphone (13;  $R^1 = H$ ) (4.56 g, 20 mmol) in THF (50 ml) at 0 °C. After 0.5 h, the alkyl halide (21 mmol) was added and after a further 1 h, the mixture was poured into saturated aqueous ammonium chloride (100 ml), extracted with dichloromethane (3 × 50 ml), and the combined extracts washed with saturated aqueous sodium chloride (50 ml), dried ( $Na_2SO_4$ ), and evaporated under reduced pressure to give, after column chromatography ( $SiO_2$ ; 250 g; 600 × 300 mm, eluting with dichloromethane), the adducts (15). Compounds prepared by this method were: 1-phenylsulphonyl-1-trimethylsilylbutane (13;  $R^1 = Pr$ ) as an oil (4.17 g, 77%) (Found: C, 58.0; H, 8.45.  $C_{13}H_{22}O_2SSi$  requires C, 57.75; H, 8.2%;  $\nu_{max}(\text{CHCl}_3)$  1 580 (Ar C=C), 1 310 ( $SO_2$ ), 1 260 ( $SiMe_3$ ), and 1 160  $cm^{-1}$  ( $SO_2$ );  $\delta$  8.0—7.1 (5 H, m, Ph), 2.49 (1 H, t,  $J$  8 Hz, SiCH), 1.3—1.0 (4 H, m,  $CH_2$ 's), 0.8 (3 H, t,  $J$  8 Hz,  $CH_2Me$ ), and 0.18 (9 H, s,  $SiMe_3$ );  $m/z$  270 ( $M^+$ , 3%) and 73 (100,  $Me_3Si^+$ ); 1-phenylsulphonyl-1-trimethylsilylethane (13;  $R^1 = Me$ ) as an oil (4.50 g, 93%) (Found: C, 54.75; H, 7.6.  $C_{11}H_{18}O_2SSi$  requires C, 54.5; H, 7.5%;  $\nu_{max}(\text{CHCl}_3)$  1 320 ( $SO_2$ ), 1 250 ( $SiMe_3$ ), and 1 160  $cm^{-1}$  ( $SO_2$ );  $\delta$  7.9—7.2 (5 H, m, Ph), 2.26 (1 H, q,  $J$  7.5 Hz,  $CHMe$ ), 0.97 (3 H, d,  $J$  7.5 Hz,  $CHMe$ ), and 0.21 (9 H, s,  $SiMe_3$ );  $m/z$  242 ( $M^+$ , 16%), 77 (35,  $Ph^+$ ), and 73 (100,  $Me_3Si^+$ ); 1-phenylsulphonyl-1-trimethylsilylhexane (13;  $R^1 = C_5H_{11}$ ) as an oil (4.54 g, 76%) (Found: C, 60.15; H, 9.05.  $C_{15}H_{26}O_2SSi$  requires C, 60.35; H, 8.8%;  $\nu_{max}(\text{CHCl}_3)$  1 310 ( $SO_2$ ), 1 255 ( $SiMe_3$ ), and 1 160  $cm^{-1}$  ( $SO_2$ );  $\delta$  8.0—7.2 (5 H, m, Ph), 2.47 (1 H, t,  $J$  8 Hz,  $CHCH_2$ ), 1.55 (2 H, t,  $J$  8 Hz,  $CHCH_2$ ), 1.2—0.8 (4 H, m,  $CH_2CH_2Me$ ), 0.70 (3 H, t,  $J$  8 Hz,  $CH_2Me$ ), and 0.20 (9 H, s,  $SiMe_3$ );  $m/z$  298 ( $M^+$ , 4%), and 73 (100,  $Me_3Si^+$ ); 1-phenylsulphonyl-1-trimethylsilylpentane (13;  $R^1 = Bu$ ) as an oil (4.53 g, 80%) (Found: C, 59.2; H, 8.7.  $C_{14}H_{24}O_2SSi$  requires C, 59.1; H, 8.5%;  $\nu_{max}(\text{CHCl}_3)$  1 580 (Ar C=C), 1 320 ( $SO_2$ ), 1 260 ( $SiMe_3$ ), and 1 160  $cm^{-1}$  ( $SO_2$ );  $\delta$  8.0—7.1 (5 H, m, Ph), 2.45 (1 H, t,  $J$  8 Hz,  $CHCH_2$ ), 1.6—0.8 (6 H, m,  $CH_2CH_2CH_2Me$ ), and 0.19 (9 H, s,  $SiMe_3$ );  $m/z$  284 ( $M^+$ , 10%), 77 (19,  $Ph^+$ ), and 73 (100,  $Me_3Si^+$ ); and 1-phenylsulphonyl-1-trimethylsilylpropane (13;  $R^1 = Et$ ) as an oil (4.16 g, 81%) (Found: C, 56.0; H, 8.0.  $C_{12}H_{20}O_2SSi$  requires C, 56.2; H, 7.85%;  $\nu_{max}(\text{CHCl}_3)$  1 310 ( $SO_2$ ), 1 255 ( $SiMe_3$ ), and 1 160  $cm^{-1}$  ( $SO_2$ );  $\delta$  7.9—7.1 (5 H, m, Ph), 2.48 (1 H, t,  $J$  8 Hz,  $CHCH_2$ ), 1.51 (2 H, m,  $CHCH_2$ ), 0.91 (3 H, t,  $J$  8 Hz,  $CH_2Me$ ), and 0.15 (9 H, s,  $SiMe_3$ );  $m/z$  256 ( $M^+$ , 8%) and 73 (100,  $Me_3Si^+$ ). 2-Methyl-1-phenylsulphonyl-1-trimethylsilylbutane (13;  $R^1 = Bu^*$ ) was also prepared by this method (1.03 g, 19%) but was extremely difficult to purify.

**Preparation of the Silanes (13) by Silylation of the Sulphones (14).**—Butyl-lithium (1.4M solution in hexane; 14.2 ml, 20 mmol) was added to the sulphone (14) (20 mmol) (prepared by MCPBA oxidation of the corresponding sulphide, in turn prepared from sodium thiophenoxide and the alkyl halide) in THF (50 ml) at 0 °C. After 0.5 h, chlorotrimethylsilane (2.81 ml, 2.39 g, 22 mmol) was added. The reaction mixture was stirred for 1 h, poured into saturated aqueous ammonium chloride (50 ml), extracted with dichloromethane (3 × 50 ml), and the combined extracts washed with saturated aqueous sodium chloride (50 ml), dried ( $Na_2SO_4$ ) and evaporated under reduced pressure to give, after column chromatography, the  $\alpha$ -silyl sulphone (13). Compounds prepared by this method were: 2-methyl-1-phenylsulphonyl-1-trimethylsilylbutane (13;  $R^1 = Bu^*$ ) as an oil (4.10 g, 72%) (Found: C, 59.05; H, 8.6.  $C_{14}H_{24}O_2SSi$  requires C, 59.1; H, 8.5%;  $\nu_{max}(\text{CHCl}_3)$  1 590 (Ar C=C), 1 310 ( $SO_2$ ), 1 250 ( $SiMe_3$ ), and 1 160  $cm^{-1}$  ( $SO_2$ );  $\delta$  7.9—7.1 (5 H, m, Ph), 2.57 (1 H, m,  $SO_2CH$ ), 1.8—0.7 (9 H, m, alkyls), and 0.19 (9 H, s,  $SiMe_3$ );  $m/z$  284 (21%,  $M^+$ ) and 73 (100,  $Me_3Si^+$ ); phenyl(phenylsulphonyl)trimethylsilylmethane (13;  $R^1 = Ph$ ), as rhomboids, m.p. 87—89 °C (from EtOH) (4.52 g, 74%) (Found: C, 63.0; H, 6.75.  $C_{16}H_{20}O_2SSi$  requires C,

63.1; H, 6.6%;  $\nu_{max}(\text{CHCl}_3)$  1 590 (Ar C=C), 1 320 ( $SO_2$ ), 1 260 ( $SiMe_3$ ), and 1 160  $cm^{-1}$  ( $SO_2$ );  $\delta$  8.0—7.0 (10 H, m, Ph), 3.74 (1 H, s, CH), and 0.21 (9 H, s,  $SiMe_3$ );  $m/z$  304 (82%,  $M^+$ ), 91 (88,  $C_7H_7^+$ ), and 73 (100,  $Me_3Si^+$ ); 1-phenylsulphonyl-1-trimethylsilylbutane (13;  $R^1 = Pr$ ) (4.45 g, 82%); 1-phenylsulphonyl-1-trimethylsilylethane (13;  $R^1 = Pr$ ) (4.52 g, 93%); 1-phenylsulphonyl-1-trimethylsilylhexane (13;  $R^1 = C_5H_{11}$ ) (5.27 g, 89%); 1-phenylsulphonyl-1-trimethylsilylpentane (13;  $R^1 = Bu$ ) (4.57 g, 81%); and 1-phenylsulphonyl-1-trimethylsilylpropane (13;  $R^1 = Et$ ) (4.58 g, 90%), all identical with the samples prepared above (t.l.c., n.m.r., i.r.).

**Preparation of the  $\alpha$ -Silyl Sulphones (13) from the  $\alpha$ -Silyl Sulphides (1).**—The oxidation was carried out as described for phenylthio(trimethylsilyl)methane (1;  $R^1 = H$ ) above to give the sulphones (13) in the yield given in Table 5. All compounds were identical with those prepared by the alternative routes (t.l.c., i.r., n.m.r.).

**Alkylations of the Sulphones (13).**—Butyl-lithium (1.4M solution in hexane; 7.1 ml, 10 mmol) was added to the sulphone (13) (10 mmol) in THF (30 ml) at 0 °C. After 1 h the alkyl halide (11 mmol) was added and the solution stirred overnight. The reaction mixture was poured into saturated aqueous ammonium chloride (50 ml), extracted with dichloromethane (3 × 50 ml), washed with saturated aqueous sodium chloride (50 ml), dried ( $Na_2SO_4$ ), and evaporated under reduced pressure to give, after column chromatography, the adducts (13). Compounds prepared by this method were: 1-phenyl-1-phenylsulphonyl-1-trimethylsilylethane (13;  $R^1 = Ph$ ,  $R^2 = Me$ ) (2.69 g, 84%) as a viscous oil (Found: C, 63.85; H, 7.2.  $C_{17}H_{22}O_2SSi$  requires C, 64.1; H, 6.95%;  $\nu_{max}(\text{CHCl}_3)$  1 600 (Ar C=C), 1 320 ( $SO_2$ ), 1 255 ( $SiMe_3$ ), and 1 160  $cm^{-1}$  ( $SO_2$ );  $\delta$  7.8—7.1 (10 H, m, Ph), 1.45 (3 H, s,  $CMe$ ), and 0.10 (9 H, s,  $SiMe_3$ );  $m/z$  318 (17%,  $M^+$ ) and 73 (100,  $Me_3Si^+$ ); 1-phenyl-1-phenylsulphonyl-1-trimethylsilylpentane (15;  $R^1 = Ph$ ,  $R^2 = Bu$ ) as an oil (2.29 g, 63%) (Found: C, 66.4; H, 7.95.  $C_{20}H_{28}O_2SSi$  requires C, 66.6; H, 7.85%;  $\nu_{max}(\text{CHCl}_3)$  1 595 (Ar C=C), 1 310 ( $SO_2$ ), 1 260 ( $SiMe_3$ ), and 1 160  $cm^{-1}$  ( $SO_2$ );  $\delta$  7.9—7.0 (10 H, m, Ph), 2.0—0.8 (9 H, m, alkyls), and 0.13 (9 H, s,  $SiMe_3$ );  $m/z$  360 (6%,  $M^+$ ) and 73 (100,  $Me_3Si^+$ ); 3-phenylsulphonyl-3-trimethylsilylheptane (15;  $R^1 = Bu$ ,  $R^2 = Et$ ) as an oil (2.22 g, 71% with EtBr; 2.26 g, 73% with EtI) (Found: C, 61.5; H, 8.95.  $C_{16}H_{28}O_2SSi$  requires C, 61.5; H, 9.05%;  $\nu_{max}(\text{CHCl}_3)$  1 320 ( $SO_2$ ), 1 250 ( $SiMe_3$ ), and 1 150  $cm^{-1}$  ( $SO_2$ );  $\delta$  7.9—7.0 (5 H, m, Ph), 2.1—0.8 (14 H, m, alkyls), and 0.21 (9 H, s,  $SiMe_3$ );  $m/z$  312 (16%,  $M^+$ ) and 73 (100,  $Me_3Si^+$ ); 2-phenylsulphonyl-2-trimethylsilylhexane (15;  $R^1 = Me$ ,  $R^2 = Bu$ ) as an oil (2.22 g, 74% with BuBr; 2.30 g, 77% with BuI and 2.43 g, 82% with MeI) (Found: C, 60.5; H, 8.95.  $C_{15}H_{26}O_2SSi$  requires C, 60.35; H, 8.8%;  $\nu_{max}(\text{CHCl}_3)$  1 320 ( $SO_2$ ), 1 260 ( $SiMe_3$ ), and 1 155  $cm^{-1}$  ( $SO_2$ );  $\delta$  7.9—7.0 (5 H, m, Ph), 2.1—0.8 (12 H, m overlaid with a singlet at 1.11, alkyls), and 0.13 (9 H, s,  $SiMe_3$ );  $m/z$  298 (7%,  $M^+$ ), and 73 (100,  $Me_3Si^+$ ); 5-phenylsulphonyl-5-trimethylsilylnonane (15;  $R^1 = R^2 = Bu$ ) as an oil (2.36 g, 69% with BuBr; 2.52 g, 74% with BuI) (Found: C, 63.2; H, 9.8.  $C_{18}H_{32}O_2SSi$  requires C, 63.5; H, 9.45%;  $\nu_{max}(\text{CHCl}_3)$  1 315 ( $SO_2$ ), 1 260 ( $SiMe_3$ ), and 1 160  $cm^{-1}$  ( $SO_2$ );  $\delta$  7.9—7.2 (5 H, m, Ph), 2.1—0.8 (18 H, m, alkyls), and 0.09 (9 H, s,  $SiMe_3$ );  $m/z$  340 (21%,  $M^+$ ) and 73 (100,  $Me_3Si^+$ ); and 2-phenylsulphonyl-2-trimethylsilylpropane (15;  $R^1 = R^2 = Me$ ) as an oil (2.31 g, 91%) (Found: C, 56.1; H, 8.0.  $C_{12}H_{20}O_2SSi$  requires C, 56.2; H, 7.85%;  $\nu_{max}(\text{CHCl}_3)$  1 580 (Ar C=C), 1 320 ( $SO_2$ ), 1 260 ( $SiMe_3$ ), and 1 160  $cm^{-1}$  ( $SO_2$ );  $\delta$  7.8—7.0 (5 H, m, Ph), 1.01 (6 H, s,  $CMe_2$ ), and 0.10 (9 H, s,  $SiMe_3$ );  $m/z$  256 (31%,  $M^+$ ), and 73 (100,  $Me_3Si^+$ ).

**Silylations of Sulphones (16).**—This was carried out in a manner analogous to that described for (14) above except that



the silyl chloride was added 1 h after the butyl-lithium. Compounds prepared by this method were: 3-methyl-4-phenylsulphonyl-4-trimethylsilyloctane (**15**;  $R^1 = \text{Bu}$ ,  $R^2 = \text{Bu}^i$ ) as an oil (34 g, 49%) (Found: C, 63.25; H, 9.6.  $\text{C}_{18}\text{H}_{32}\text{O}_2\text{SSi}$  requires C, 63.5; H, 9.45%);  $\nu_{\text{max}}$  ( $\text{CHCl}_3$ ) 1 320 ( $\text{SO}_2$ ), 1 260 ( $\text{SiMe}_3$ ), and 1 160  $\text{cm}^{-1}$  ( $\text{SO}_2$ );  $\delta$  7.8–7.0 (5 H, m, Ph), 2.1–0.7 (18 H, m, alkyls), and 0.12 (9 H, s,  $\text{SiMe}_3$ );  $m/z$  340 (16%,  $M^+$ ) and 73 (100,  $\text{Me}_3\text{Si}^+$ ); 1-phenyl-1-phenylsulphonyl-1-trimethylsilylethane (**15**;  $R^1 = \text{Ph}$ ,  $R^2 = \text{Me}$ ) (3.83 g, 60%) and 1-phenyl-1-phenylsulphonyl-1-trimethylsilylpentane (**15**;  $R^1 = \text{Ph}$ ,  $R^2 = \text{Bu}$ ) (3.48 g, 48%), both identical with the samples prepared above (t.l.c., i.r., n.m.r.); 1-phenylsulphonyl-1-trimethylsilylcyclohexane [**15**;  $R^1, R^2 = -(\text{CH}_2)_5-$ ] as an oil (3.98 g, 67%) (Found: C, 61.0; H, 7.95.  $\text{C}_{15}\text{H}_{24}\text{O}_2\text{SSi}$  requires C, 60.75; H, 8.15%);  $\nu_{\text{max}}$  ( $\text{CHCl}_3$ ) 1 320 ( $\text{SO}_2$ ), 1 260 ( $\text{SiMe}_3$ ), and 1 160  $\text{cm}^{-1}$  ( $\text{SO}_2$ );  $\delta$  7.8–7.0 (5 H, m, Ph), 2.3–1.1 (10 H, m,  $\text{CH}_2$ 's), and 0.15 (9 H, s,  $\text{SiMe}_3$ );  $m/z$  296 (61%,  $M^+$ ) and 73 (100,  $\text{Me}_3\text{Si}^+$ ); 3-phenylsulphonyl-3-trimethylsilylheptane (**15**;  $R^1 = \text{Bu}$ ,  $R^2 = \text{Et}$ ) (3.56 g, 57%), 2-phenylsulphonyl-2-trimethylsilylhexane (**15**;  $R^1 = \text{Me}$ ,  $R^2 = \text{Bu}$ ) (3.71 g, 62%), 5-phenylsulphonyl-5-trimethylsilylnonane (**15**;  $R^1 = R^2 = \text{Bu}$ ) (3.42 g, 50%), and 2-phenylsulphonyl-2-trimethylsilylpropane (**15**;  $R^1 = R^2 = \text{Me}$ ) (3.50 g, 68%), all identical with the samples prepared above (i.r., n.m.r., t.l.c.).

**Reductions of Sulphones (15) to Sulphides (2).**<sup>25</sup>—With lithium aluminium hydride. The sulphone (**15**) (10 mmol) in THF (10 ml) was added to lithium aluminium hydride (2.85 g, 75 mmol) in THF (100 ml) at 65 °C. After being heated under reflux for 1–2 h, the mixture was cooled to 0 °C and saturated aqueous ammonium chloride (250 ml) added. The mixture was extracted with ether (3 × 150 ml), and the combined extracts washed with saturated aqueous sodium chloride (150 ml), dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated under reduced pressure; the residue was column chromatographed or distilled to give the sulphide (**2**). Compounds prepared by this method were: 1-phenyl-1-phenylthio-1-trimethylsilylethane (**2**;  $R^1 = \text{Ph}$ ,  $R^2 = \text{Me}$ ) (2.41 g, 85%), 1-phenyl-1-phenylthio-1-trimethylsilylpentane (**2**;  $R^1 = \text{Ph}$ ,  $R^2 = \text{Bu}$ ) (2.50 g, 77%), 3-phenylthio-3-trimethylsilylheptane (**2**;  $R^1 = \text{Et}$ ,  $R^2 = \text{Bu}$ ) (2.28 g, 81%), 2-phenylthio-2-trimethylsilylhexane (**2**;  $R^1 = \text{Me}$ ,  $R^2 = \text{Bu}$ ) (1.95 g, 73%), 5-phenylthio-5-trimethylsilylnonane (**2**;  $R^1 = R^2 = \text{Bu}$ ) (2.54 g, 82%), and 2-phenylthio-2-trimethylsilylpropane (**2**;  $R^1 = R^2 = \text{Me}$ ) (1.76 g, 78%); all identical with the samples prepared above (i.r., n.m.r., and t.l.c.).

With di-isobutylaluminium hydride. The sulphone (**15**) (10 mmol) in THF (10 ml) was added to di-isobutylaluminium hydride (1.5M solution in toluene; 26.7 ml, 40 mmol) in toluene (25 ml) over 0.25 h. The mixture was heated under reflux for 48 h, cooled, and saturated aqueous ammonium chloride (50 ml) added and the organic layer separated. The aqueous layer was extracted with ether (3 × 50 ml). The combined extracts were washed with saturated aqueous sodium chloride (50 ml), dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated under reduced pressure to give, after column chromatography, the sulphides (**2**). Compounds prepared by this method were: 1-phenyl-1-phenylthio-1-trimethylsilylethane (**2**;  $R^1 = \text{Ph}$ ,  $R^2 = \text{Me}$ ) (2.24 g, 79%), 2-phenylthio-2-trimethylsilylhexane (**2**;  $R^1 = \text{Me}$ ,  $R^2 = \text{Bu}$ ) (2.10 g, 79%), 5-phenylthio-5-trimethylsilylnonane (**2**;  $R^1 = R^2 = \text{Bu}$ ) (2.67 g, 86%), and 2-phenylthio-2-trimethylsilylpropane (**2**;  $R^1 = R^2 = \text{Me}$ ) (1.80 g, 81%); all identical with the samples prepared above (i.r., n.m.r., and t.l.c.).

**Conversion of  $\alpha$ -Silyl Sulphides (2) into the Ketones (3).**—MCPBA (85% peracid; 2.0 g, 10 mmol) in dichloromethane (50 ml) was added to the  $\alpha$ -silyl sulphide (**2**) (10 mmol) in

dichloromethane (30 ml) at –23 °C over 1.5 h. The mixture was allowed to warm to room temperature over 1 h and then poured into saturated aqueous sodium hydrogen carbonate (250 ml). The organic layer was separated, washed with saturated aqueous sodium chloride (50 ml), dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated under reduced pressure to give an oil which was dissolved in THF (50 ml). This solution was heated under reflux for 4 h, cooled to room temperature, and stirred for 17 h with 1M-aqueous mercury(II) acetate (100 ml). The reaction mixture was filtered, extracted with ether (3 × 75 ml), and the combined extract washed with 1M-aqueous sodium hydroxide (50 ml) and saturated aqueous sodium chloride (50 ml), dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated under reduced pressure; either the ketones (**3**) were obtained after bulb-to-bulb distillation or the 2,4-dinitrophenylhydrazone by reaction of the products with 2,4-dinitrophenylhydrazine.<sup>31</sup> The latter had physical properties identical with those of authentic samples<sup>31–33</sup> (see Table 8).

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