

Synthesis of Aldehydes from Phenylthiotrimethylsilylmethane

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Phenylthiotrimethylsilylmethyl-lithium (4) reacts with alkyl halides to give 1-phenylthio-1-trimethylsilylalkanes (5), which can also be prepared by the addition of alkyl-lithium to 1-phenylthio-1-trimethylsilylethene (8), or from bis(phenylthio)acetals (11). The 1-phenylthio-1-trimethylsilylalkanes (5) can be converted into the corresponding aldehyde (15) by oxidation to the sulfoxide (13), thermal rearrangement, and hydrolysis of the resultant *O*-silyl thioacetal (14).

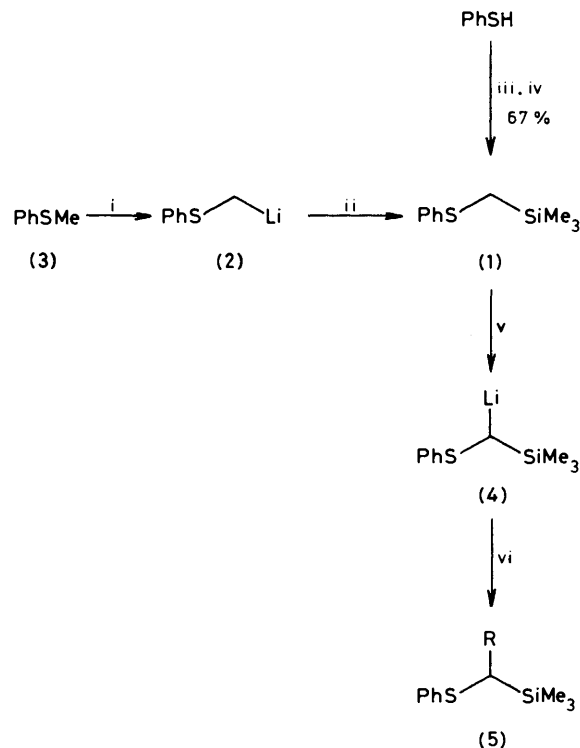
In recent years, much effort has been directed towards umpolung,¹ in particular to the preparation of acyl anion equivalents.² One class of acyl anion equivalent which has found widespread use in organic synthesis is 1,3-dithians.³

Unfortunately, hydrolysis of 1,3-dithians to the corresponding carbonyl compounds has, on occasions, proved difficult, as is borne out by the many methods which have appeared in the literature.⁴ We decided, therefore, to investigate a new acyl anion equivalent which would be easily converted into the carbonyl compound under mild conditions. The system chosen is based on phenylthiotrimethylsilylmethane (1). We have reported some preliminary results⁵⁻⁷; this paper describes the experimental work and adds a few examples.

Cooper⁸ has reported the preparation of phenylthiotrimethylsilylmethane (1). Sodium thiophenoxide was treated with chloromethyltrimethylsilane to give (1) in 67% yield. As phenylthiomethyl-lithium (2) is known,^{9,10} the preparation of the silane (1) was investigated using this anion. The method of Gilman and Webb⁹ was chosen in preference to that of Corey and Seebach¹⁰ on the grounds of cost as the latter method uses equimolar quantities of 1,4-diazabicyclo[2.2.2]octane (DABCO) although it is quicker.¹¹ Thioanisole (3) and *n*-butyl-lithium, as a solution in hexane, were heated in diethyl ether for 15 h, and the resulting anion quenched with chlorotrimethylsilane to give phenylthiotrimethylsilylmethane (1) in 95% yield (Scheme 1). The reaction has been carried out on a molar scale with no difficulty.

Phenylthiotrimethylsilylmethyl-lithium (4) has been prepared previously by Carey and Court¹² from the silane (1) by treatment with *n*-butyl-lithium in tetrahydrofuran (THF). Various solvents were investigated for the generation of (4) from (1). Although the alkyl-lithium (4) was formed in all the solvents tried, the *n*-butyl-lithium-*N,N,N',N'*-tetramethylethylenediamine (TMEDA) complex¹³ in hexane was the one of choice as Carey¹⁴ had noted that the related phenylsulphenyltrimethylsilylmethyl-lithium was not alkylated in THF.¹¹

The results of the alkylation reactions of the anion (4) with alkyl halides are given in Table 2. Primary alkyl iodides or bromides gave high yields of the adducts (5) (Scheme 1). Secondary alkyl halides gave much lower yields, elimination being a major pathway, and large amounts of phenylthiotrimethylsilylmethane (1) were recovered from these reactions. With cyclohexyl bromide, elimination was the only reaction detected. Kocienski obtained similar results for the alkylation of (4) when the reactions were carried out in THF.¹¹ The anion has been treated with other electrophiles and this provides a means of synthesising substituted aldehydes.^{11,15}



Scheme 1. Reagents: i, BuⁿLi, Et₂O, hexane, heat; ii, Me₃SiCl; iii, NaOH, EtOH; iv, Me₃SiCH₂Cl; v, BuⁿLi, TMEDA, hexane; vi, RX

Table 1. Anion formation of phenylthiotrimethylsilylmethane (1) with *n*-butyl lithium as base^a

Solvent	Yield ^b (%) ^c
Hexane/TMEDA	99
Et ₂ O	73
THF	97
DME	96
PhMe	80 ^d

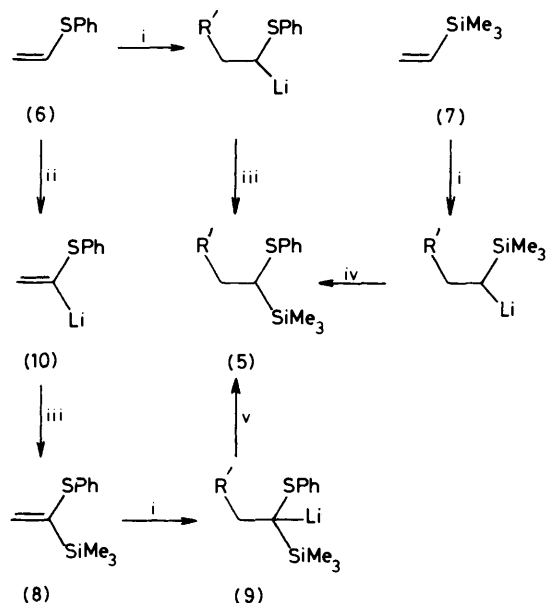
^a The reactions were carried out at 0 °C for 1 h. ^b The reactions were quenched with iodomethane. ^c Isolated yields. ^d The reaction was quenched with chlorotrimethylsilane.

1-Phenylthio-1-trimethylsilylalkanes (5) may be prepared by the addition of an alkyl-lithium to an appropriately substituted olefin. The alkanes (5) were obtained in good yield when phenylthioethene (6) was added to the alkyl-lithium in

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Table 2. Alkylations of phenylthio-trimethylsilylmethyl-lithium (4)

Alkyl halide	Yield of (5) (%)
MeI	99
EtI	90
Pr ⁿ Br	82
Pr ⁱ I	59
Bu ⁿ Br	84
Bu ^s Br	45
n-C ₅ H ₁₁ Br	82
n-C ₅ H ₁₁ I	86
n-C ₆ H ₁₃ Br	81
n-C ₁₂ H ₂₅ Br	78
PhCH ₂ Br	83
c-C ₆ H ₁₁ Br	0

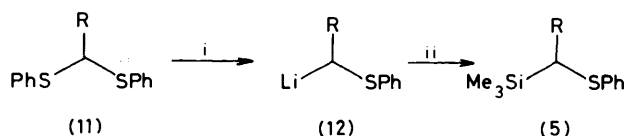
**Scheme 2.** Reagents: i, RLi, TMEDA, Et₂O, 0 °C; ii, BuⁿLi, TMEDA, THF, -90 °C; iii, Me₃SiCl; iv, PhSCl or PhSSPh; v, NH₄Cl, H₂O

diethyl ether at 0 °C in the presence of TMEDA followed by quenching with chlorotrimethylsilane (Scheme 2 and Table 3). Alternatively, reaction of trimethylsilylethene (7) with an alkyl-lithium followed by phenylsulphenyl chloride or diphenyl disulphide gave (5) but this procedure gave lower yields than above. The third possible procedure for the preparation of (5) involves the addition¹⁶ of alkyl-lithiums to 1-phenylthio-1-trimethylsilylethene (8). This reaction has not previously been carried out in satisfactory yield¹⁶ but we found that the slow addition of the olefin (8) to excess of alkyl-lithiums gave the anions (9) in high yields. These reaction conditions ensure that (8) reacts with the alkyl-lithium rather than the addition product (9), and hence drastically reduces the amount of polymeric material formed. Grignard reagents did not add to 1-phenylthio-1-trimethylsilylethene (8) in ether or THF. The starting olefin (8) was prepared by silylation of the vinyl-lithium compound (10), obtained by lithiation of phenylthioethene (6) as described by Cookson and Parsons¹⁷ (Scheme 2).

Finally, 1-phenylthio-1-trimethylsilylalkanes (5) can be prepared by treating bis(phenylthio)acetals (11) with lithium

Table 3. Conversions of olefins into 1-phenylthio-1-trimethylsilylalkanes (5)

Olefin	Alkyl-lithium	Electrophile	Yield of (5) (%)
(6)	MeLi	Me ₃ SiCl	81
(6)	Bu ⁿ Li	Me ₃ SiCl	85
(6)	PhLi	Me ₃ SiCl	73
(7)	MeLi	PhSCl	53
(7)	MeLi	PhSSPh	62
(7)	Bu ⁿ Li	PhSCl	60
(7)	Bu ⁿ Li	PhSSPh	67
(7)	PhLi	PhSCl	51
(7)	PhLi	PhSSPh	55
(8)	MeLi	NH ₄ Cl	89
(8)	Bu ⁿ Li	NH ₄ Cl	85
(8)	PhLi	NH ₄ Cl	78

**Scheme 3.** Reagents: i, Lithium naphthalenide, THF, -78 °C; ii, Me₃SiCl**Table 4.** Preparation of 1-phenylthio-1-trimethylsilylalkanes (5) from bis(phenylthio)acetals (11)

Acetal (11) R	Yield of (5) (%)
H	86
Me	90
Pr ⁿ	82
Pr ⁱ	87
Bu ⁿ	75
Bu ^s	79
n-C ₅ H ₁₁	72
Ph	84

naphthalenide,¹⁸ to give the α -lithio sulphide (12), followed by chlorotrimethylsilane (see Scheme 3 and Table 4). As bis(phenylthio)acetals (11) can be prepared from aldehydes,¹⁹ this reaction provides a method for preparing the alkanes (5) from aldehydes and, thus, provides a means of protecting them. This is not the main use of this method of preparation; it provides a high yielding route to the alkanes (5) when the alkyl group is not derived from a primary alkyl halide. The alkenes (5) have been used to prepare olefins⁷ and this is dealt with elsewhere.

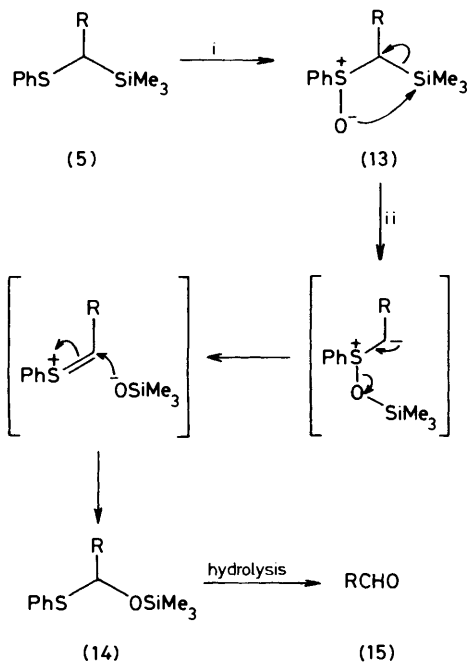
1-Methylthio-1-trimethylsilylalk-3-enes have been prepared by a rearrangement reaction of α -silyl sulphides. These alkenes are masked β,γ -unsaturated aldehyde equivalents.²⁰

The 1-phenylthio-1-trimethylsilylalkanes (5) were converted into the corresponding aldehydes by oxidation at sulphur to give the sulphoxide (13), thermal rearrangement of the sulphoxide (13) to give the *O*-trimethylsilyl phenyl monothioacetal (14) and subsequent hydrolysis. The first step was straightforward and oxidation was achieved using *m*-chloroperoxybenzoic acid (MCPBA) under standard conditions (see Table 5). The rearrangement of the sulphoxides to the *O*-trimethylsilyl monothioacetal has been investigated by Brook,²¹ who proposed the mechanism given in Scheme 4. Vedejs and Mullins²² have also investigated this reaction and

Table 5. Oxidation of 1-phenylthio-1-trimethylsilylalkanes (5), rearrangement to the acetals (14), and subsequent hydrolysis to the aldehydes (15)

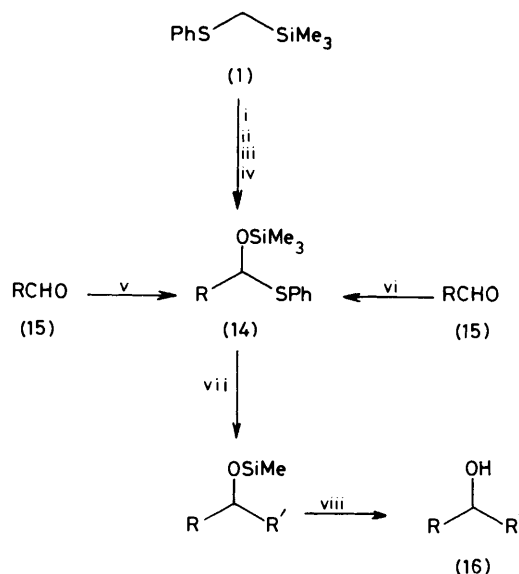
Alkane (5) R	(13) ^a	Yields of (14) ^a (%)	(15) ^b
H	91	89 ^c	<i>d</i>
Me	83	97	<i>d</i>
Et	89	88	<i>d</i>
Pr ⁿ	92	85	70 ^{a,e}
Pr ^s	81	72	55 ^{a,e}
Bu ⁿ	92	83	72 ^{a,e}
Bu ^s	92	83	74 ^{a,e}
n-C ₅ H ₁₁	88	82	68 ^{a,e}
n-C ₆ H ₁₃	91	85	77 ^{a,e}
n-C ₁₂ H ₂₅	96	88	(80 ^a) 71
PhCH ₂	96	92	(85 ^a) 77

^a Yield by n.m.r. ^b Overall yield from (5). ^c The thermal rearrangement was carried out by heating under reflux in carbon tetrachloride. ^d The acetal was not hydrolysed (volatile product). ^e The aldehyde was isolated as its 2,4-dinitrophenylhydrazone derivative. Yields were $\pm 3\%$ those obtained by n.m.r. (see Experimental section).

**Scheme 4.** Reagents: i, MCPBA, CH₂Cl₂; ii, heat

extended the examples covered to substituted sulphoxides (13; R = Me and Ph). The sulphoxides (13) were not characterised, although their formation could be detected by n.m.r. and i.r. spectroscopy, and no attempts were made to isolate them. The crude sulphoxide (13) was heated under reflux in benzene, carbon tetrachloride, or THF for 4 h to give the *O*-trimethylsilyl monothioacetal (14), which was not normally isolated when the carbonyl compound was required but hydrolysed directly to the aldehyde (15) using an established procedure²³ (Scheme 4 and Table 5). The preparation of (14), and hence (15), provides a new route for the preparation of aldehydes. (The rearrangement has been used by Cutting and Parsons to prepare enals from propargyl alcohols.²⁴)

O-Trimethylsilyl monothioacetals (14) have been prepared

**Scheme 5.** Reagents: i, BuⁿLi, TMEDA; ii, RX; iii, MCPBA; iv, heat; v, PhSH,²¹ Me₃SiCl, pyridine; vi, PhSSiMe₃,²² CN⁻; vii, RⁿLi, TMEDA; viii, H₂O**Table 6.** Conversion of *O*-trimethylsilyl phenyl monothioacetals (14) into alcohols

Acetal (14) R	Alkyl-lithium	Yield of alcohol (16) (%)
H	Bu ⁿ Li	87
H	PhLi	85
Me	Bu ⁿ Li	82
Me	PhLi	81
Pr ⁿ	Bu ⁿ Li	84
Pr ⁿ	PhLi	79

previously by Chan²³ and Evans.²⁵ It has been shown²³ that the acetals (14) can be converted into secondary alcohols by reaction with an alkyl-lithium in hexamethylphosphoric triamide (HMPA) or TMEDA, followed by hydrolysis of the resulting trimethylsilyl ether. Thus, the sequence can be adapted for a convenient synthesis of secondary alcohols which does not require isolation of the aldehyde, a great advantage for volatile or unstable aldehydes. For example, *n*-butyl-lithium and phenyl-lithium reacted with the thioacetals (14; R = H, Me, and Prⁿ) in TMEDA to give, after aqueous work-up, the corresponding alcohols (16) (Scheme 5 and Table 6).

The value of phenylthiotrimethylsilylmethane was shown by synthesising undecanal (17), a pheromone produced by the greater wax moth (*Galleria mellonella*),^{26,27} from 1-bromodecane in an overall yield of 51%.

Thus, phenylthiotrimethylsilylmethane (1) can be alkylated in high yield and that the resulting alkanes (5) can be converted into the corresponding aldehydes (or secondary alcohols) under mild conditions.

Experimental

All reactions involving organometallic reagents were carried out under dry nitrogen.

Diethyl ether (ether), 1,2-dimethoxyethane (DME), and

tetrahydrofuran (THF) were freshly distilled from sodium benzophenone just prior to use. Light petroleum refers to that fraction with b.p. 60–80 °C.

Phenylthio-trimethylsilylmethane (1).—Thioanisole (3) (117 ml, 123.8 g, 0.997 mol) was added to *n*-butyl-lithium (720 ml of a 1.4M-solution in hexane, 1.01 mol) in diethyl ether (300 ml) and the resulting solution heated under reflux for 18 h. Chlorotrimethylsilane (150 ml, 128.4 g, 1.18 mol) was added to the precipitated anion (2) and the mixture heated under reflux for 1 h, poured into saturated aqueous ammonium chloride (500 ml), extracted with ether (3 × 500 ml), washed with water (500 ml), dried (Na₂SO₄) and evaporated under reduced pressure to give, after distillation, phenylthio-trimethylsilylmethane (1) (185.8 g, 95%), b.p. 122–123 °C/15 mmHg (lit.,⁸ b.p. 158.5 °C/52 mmHg); ν_{\max} (CCl₄) 1 600 (Ar C=C) and 1 245 cm⁻¹ (SiMe₃); δ (CCl₄; CH₂Cl₂ as internal lock) 7.4 (5 H, br s, Ph), 2.05 (2 H, s, CH₂), and 0.05 (9 H, s, SiMe₃); m/z 196 (23%, M⁺), 109 (11, PhS⁺), and 73 (100, Me₃Si⁺).

Alkylations of Phenylthio-trimethylsilylmethane (1).—*n*-Butyl-lithium (142 ml of a 1.4M-solution in hexane, 20 mmol) was added to the silane (1) (3.92 g, 20 mmol) at 0 °C, and after being stirred for 1 h the alkyl halide (25 mmol) was added. The reaction mixture, after 1 h, was poured into saturated aqueous ammonium chloride (75 ml), extracted with ether (3 × 30 ml), washed with water (50 ml), dried (Na₂SO₄), and evaporated under reduced pressure to give after distillation or column chromatography (SiO₂ eluting with light petroleum) the alkane (5). Compounds prepared by this method were: *2-methyl-1-phenylthio-1-trimethylsilylbutane* (5; R = Buⁿ) (2.27 g, 45%), as diastereoisomers, b.p. 83–85 °C/0.5 mmHg (Found: C, 66.55; H, 9.55. C₁₄H₂₄SSi requires C, 66.6; H, 9.6%); ν_{\max} (CCl₄) 1 600 (Ar C=C), 1 240 cm⁻¹ (SiMe₃); δ (CCl₄; CH₂Cl₂ as internal standard) 7.5–7.1 (5 H, m, Ph), 2.65 (1 H, m, SCHSi), 1.6–1.2 (3 H, m, CH₂ and CH), 1.1 (3 H, two overlapping d, J 7 Hz, CHMe), 0.97 and 0.83 (3 H, two overlapping t, J 7 Hz, CH₂Me), and 0.23 (9 H, s, SiMe₃); m/z 252.136 79 (51%, M⁺) (C₁₄H₂₄SSi requires 252.136 80), 109 (24, PhS⁺), and 73 (100, Me₃Si⁺); *2-methyl-1-phenylthio-1-trimethylsilylpropane* (5; R = Prⁱ) (2.81 g, 59%) (Found: C, 65.5; H, 9.25. C₁₃H₂₂SSi requires C, 65.5; H, 9.3%); R_F (light petroleum) 0.50; ν_{\max} (CCl₄) 1 600 (Ar C=C) and 1 240 cm⁻¹ (SiMe₃); δ (CCl₄; CH₂Cl₂ as internal standard) 7.5–7.0 (5 H, m, Ph), 2.46 (1 H, d, J 3 Hz, SiCHS), 2.15 (1 H, m, CHMe₂), 0.96 (6 H, 2 overlapping d, both J 7 Hz, CHMe₂), and 0.13 (9 H, s, SiMe₃); m/z 238.121 05 (53%, M⁺) (C₁₃H₂₂SSi requires 238.12115), and 73 (100, Me₃Si⁺); *2-phenyl-1-phenylthio-1-trimethylsilylethane* (5; R = PhCH₂) (4.75 g, 83%), b.p. 128–135 °C/0.3 mmHg (Found: C, 71.0; H, 7.6. C₁₇H₂₂SSi requires C, 71.3; H, 7.75%); ν_{\max} (CCl₄) 1 595 (Ar C=C) and 1 240 cm⁻¹ (SiMe₃); δ (CCl₄; CH₂Cl₂ as internal standard) 7.5–7.1 (10 H, m, Ph), 3.2–2.8 (3 H, m, CHCH₂), and 0.20 (9 H, s, SiMe₃); m/z 286.121 11 (40%, M⁺) (C₁₇H₂₂SSi requires 286.121 15), 209 (48, M – Ph), 109 (22, PhS⁺), 77 (51, Ph⁺), and 73 (100, Me₃Si⁺); *1-phenylthio-1-trimethylsilylbutane* (5; R = Prⁿ) (3.90 g, 82%), b.p. 84–86 °C/0.45 mmHg (Found: C, 65.5; H, 9.3. C₁₃H₂₂SSi requires C, 65.5; H, 9.3%); ν_{\max} (CCl₄) 1 600 (Ar C=C) and 1 240 cm⁻¹ (SiMe₃); δ (CCl₄; CH₂Cl₂ as internal standard) 7.5–7.1 (5 H, m, Ph), 2.55 (1 H, t, J 6 Hz, CH), 1.9–1.3 (4 H, m, CH₂'s), 0.95 (3 H, t, J 6 Hz, Me), and 0.23 (9 H, s, SiMe₃); m/z 238.121 14 (58%, M⁺) (C₁₃H₂₂SSi requires 238.121 15), 109 (58, PhS⁺), and 73 (100, Me₃Si⁺); *1-phenylthio-1-trimethylsilylethane* (5; R = Me) (4.16 g, 99%), b.p. 129–132 °C/15 mmHg (lit.,²⁸ b.p. 88–89 °C/1.7 mmHg), ν_{\max} (CCl₄) 1 600 (Ar C=C) and 1 245 cm⁻¹ (SiMe₃); δ (CCl₄;

CH₂Cl₂ as internal standard) 7.55–7.2 (5 H, m, Ph), 2.72 (1 H, q, J 8 Hz, CH), 1.45 (3 H, d, J 8 Hz, Me), and 0.31 (9 H, s, SiMe₃); m/z 210 (27%, M⁺), 109 (21, PhS⁺), 105 (59, M – PhS), and 73 (100, Me₃Si⁺); *1-phenylthio-1-trimethylsilylheptane* (5; R = *n*-C₆H₁₃) (4.54 g, 81%), b.p. 108–112 °C/0.07 mmHg (Found: C, 68.6; H, 10.0. C₁₆H₂₈SSi requires C, 68.5; H, 10.1%); ν_{\max} (CCl₄) 1 595 (Ar C=C) and 1 240 cm⁻¹ (SiMe₃); δ (CCl₄; CH₂Cl₂ as internal standard) 7.5–7.1 (5 H, m, Ph), 2.53 (1 H, t, J 7 Hz, CH), 1.9–1.1 (10 H, m, CH₂'s), 0.93 (3 H, t, J 7 Hz, Me), and 0.19 (9 H, s, SiMe₃); m/z 280.168 72 (64%, M⁺) (C₁₆H₂₈SSi requires 280.168 70), 109 (47, PhS⁺), and 73 (100, Me₃Si⁺); *1-phenylthio-1-trimethylsilylhexane* (5; R = *n*-C₅H₁₁) (4.36 g, 82% from *n*-C₅H₁₁Br) (4.58 g, 86% from *n*-C₅H₁₁I), b.p. 92–96 °C/0.15 mmHg (Found: C, 67.7; H, 9.95. C₁₅H₂₆SSi requires C, 67.6; H, 9.8%); ν_{\max} (CCl₄) 1 600 (Ar C=C) and 1 240 cm⁻¹ (SiMe₃); δ (CCl₄; CH₂Cl₂ as internal standard) 7.4–7.0 (5 H, m, Ph), 2.50 (1 H, t, J 6 Hz, CH), 1.8–1.1 (8 H, m, CH₂'s), 0.83 (3 H, t, J 6 Hz, Me), and 0.11 (9 H, s, SiMe₃); m/z 266.152 40 (29%, M⁺) (C₁₅H₂₆SSi requires 266.152 45), 109 (57, PhS⁺), and 73 (100, Me₃Si⁺); *1-phenylthio-1-trimethylsilylpentane* (5; R = Buⁿ) (4.23 g, 84%), b.p. 78–82 °C/0.08 mmHg (Found: C, 66.5; H, 9.6. C₁₄H₂₄SSi requires C, 66.6; H, 9.5%); ν_{\max} (CCl₄) 1 600 (Ar C=C) and 1 240 cm⁻¹ (SiMe₃); δ (CCl₄; CH₂Cl₂ as internal standard) 7.5–7.1 (5 H, m, Ph), 2.55 (1 H, t, J 7 Hz, CH), 1.9–1.2 (6 H, m, CH₂'s), 0.93 (3 H, t, J 7 Hz, Me), and 0.23 (9 H, s, SiMe₃); m/z 252.136 83 (45%, M⁺) (C₁₄H₂₄SSi requires 252.136 80), 109 (30, PhS⁺), and 73 (100, Me₃Si⁺); *1-phenylthio-1-trimethylsilylpropane* (5; R = Et) (4.03 g, 90%), b.p. 140–142 °C/15 mmHg (Found: C, 64.3; H, 8.85. C₁₂H₂₀SSi requires C, 64.2; H, 9.0%); ν_{\max} (CCl₄) 1 600 (Ar C=C) and 1 245 cm⁻¹ (SiMe₃); δ (CCl₄; CH₂Cl₂ as internal standard) 7.5–7.1 (5 H, m, Ph), 2.61 (1 H, t, J 7 Hz, CH), 2.0–1.6 (2 H, m, CH₂), 1.18 (3 H, t, J 7 Hz, Me), and 0.30 (9 H, s, SiMe₃); m/z 224.105 47 (70%, M⁺) (C₁₂H₂₀SSi requires 224.105 50), 109 (59, PhS⁺), and 73 (100, Me₃Si⁺); *1-phenylthio-1-trimethylsilyltridecane* (5; R = *n*-C₁₂H₂₅) (5.69 g, 78%) (Found: C, 72.2; H, 11.2. C₂₂H₄₀SSi requires C, 72.45; H, 11.05%); R_F (light petroleum) 0.33; ν_{\max} (CCl₄) 1 600 (Ar C=C) and 1 240 cm⁻¹ (SiMe₃); δ (CCl₄; CH₂Cl₂ as internal standard) 7.5–7.0 (5 H, m, Ph), 2.5–0.8 (24 H, m overlaid with a triplet at 0.91, J 7 Hz, alkyl), and 0.92 (9 H, s, SiMe₃); m/z 364.262 21 (57%, M⁺) (C₂₂H₄₀SSi requires 364.262 00), 109 (70, PhS⁺), and 73 (100, Me₃Si⁺).

Preparation of Alkanes (5) from Phenylthioethene (6).—Phenylthioethene (6) (1.36 g, 10 mmol) in ether (50 ml) was added to the alkyl-lithium (20 mmol) and TMEDA (3.02 ml, 2.32 g, 20 mmol) in ether (30 ml) at 0 °C during 1.5 h. The reaction mixture was stirred for 1 h at 0 °C and chlorotrimethylsilane (3.17 ml, 2.71 g, 25 mmol) added. The mixture was poured into saturated aqueous ammonium chloride (75 ml), extracted with ether (3 × 25 ml), washed with water (30 ml), dried (Na₂SO₄), and evaporated under reduced pressure to give, after distillation or column chromatography, the alkane (5). Compounds prepared by this method were: *2-phenyl-1-phenylthio-1-trimethylsilylethane* (5; R = PhCH₂) (73%); *1-phenylthio-1-trimethylsilylhexane* (5; R = *n*-C₅H₁₁) (85%); and *1-phenylthio-1-trimethylsilylpropane* (5; R = Et) (81%). All compounds were identical with those prepared above (n.m.r., i.r., t.l.c., b.p.).

Preparation of Alkanes (5) from Trimethylsilylethene (7).—Trimethylsilylethene (7) (1.00 g, 10 mmol) in ether (50 ml) was added to the alkyl-lithium (20 mmol) and TMEDA (3.02 ml, 2.32 g, 20 mmol) in ether (30 ml) at 0 °C during 1.5 h. The reaction mixture was stirred for 1 h at 0 °C and phenyl-

sulphenyl chloride²⁹ (3.60 g, 25 mmol) or diphenyl disulphide (5.45 g, 25 mmol) in ether (15 ml) was added. The mixture was poured into saturated aqueous ammonium chloride (75 ml), extracted with ether (3 × 25 ml), washed with 2.5M-aqueous sodium hydroxide solution (30 ml) and water (30 ml), dried (Na₂SO₄) and evaporated under reduced pressure to give, after distillation or column chromatography, the alkane (5). Compounds prepared by this method were: 2-phenyl-1-phenylthio-1-trimethylsilylethane (5; R = PhCH₂) (51% from PhSCl; 55% from Ph₂S₂); 1-phenylthio-1-trimethylsilylhexane (5; R = n-C₅H₁₁) (60% from Ph₂S₂); and 1-phenylthio-1-trimethylsilylpropane (5; R = Et) (53% from PhSCl; 62% from Ph₂S₂). All compounds were identical with those prepared above (n.m.r., i.r., t.l.c., b.p.).

1-Phenylthio-1-trimethylsilylethane (8).—Phenylthioethene (6) (13.6 g, 0.1 mol) in THF (40 ml) was added to n-butyl-lithium (72 ml of a 1.4M-solution in hexane, 0.1 mol) in TMEDA (15.1 ml, 11.6 g, 0.1 mol) in THF (150 ml) at -90 °C at such a rate that the temperature was lower than -80 °C. When the addition was complete, the mixture was stirred for 1 h at -90 °C. Chlorotrimethylsilane (15.2 ml, 13.0 g, 0.12 mol) was added and the solution left to warm to room temperature. The reaction mixture was poured into saturated aqueous ammonium chloride (300 ml), extracted with ether (3 × 150 ml), washed with water (100 ml), dried (Na₂SO₄) and evaporated under reduced pressure to give, after distillation, the olefin (8) (17.1 g, 82%), b.p. 130–134 °C/15 mmHg (lit.,³⁰ 45 °C/0.025 mmHg); ν_{\max} (CCl₄) 1 590 (ArC=C) and 1 250 cm⁻¹ (SiMe₃); δ (CCl₄, Me₂CO as internal standard) 7.3–7.0 (5 H, m, Ph), 5.40 and 5.20 (2 H, 2 s, CH₂), and 0.10 (9 H, s, SiMe₃); m/z 208 (86%, M⁺), 134 (64, M - Me₃SiH), and 73 (100, Me₃Si⁺).

Preparation of Alkanes (5) from 1-Phenylthio-1-trimethylsilylethane (8).—1-Phenylthio-1-trimethylsilylethane (8) (1.35 g, 10 mmol) in ether (50 ml) was added to the alkyl lithium (20 mmol) and TMEDA (3.02 ml, 2.32 g, 20 mmol) in ether (30 ml) at 0 °C during 1.5 h. The reaction mixture was stirred for 1 h at 0 °C, poured into saturated aqueous ammonium chloride (75 ml), extracted with ether (3 × 25 ml), washed with water (30 ml), dried (Na₂SO₄) and evaporated under reduced pressure to give, after distillation or column chromatography, the alkane (5). Compounds prepared by this method were: 2-phenyl-1-phenylthio-1-trimethylsilylethane (5; R = PhCH₂) (78%); 1-phenylthio-1-trimethylsilylhexane (5; R = n-C₅H₁₁) (85%); and 1-phenylthio-1-trimethylsilylpropane (5; R = Et) (89%).

Synthesis of Bis(phenylthio)acetals (11).—The aldehyde (0.1 mol), thiophenol (25.6 ml, 27.5 g, 0.25 mol), toluene-*p*-sulphonic acid monohydrate (0.5 g), and benzene (200 ml) were heated under reflux in a Dean-Stark apparatus until no more water separated (ca. 8 h). The mixture was cooled, poured into 2M-aqueous sodium hydroxide (500 ml) and the organic layer separated. The aqueous phase was extracted with ether (2 × 100 ml). The combined organic phase was washed with 2M-aqueous sodium hydroxide (150 ml) and saturated aqueous sodium chloride (150 ml), dried (Na₂SO₄), and evaporated under reduced pressure to give the bisthioacetal (11). Compounds prepared by this method were: 1,1-bis(phenylthio)butane (11; R = Prⁿ) (27.0 g, 98.5%), b.p. 149–153 °C/0.1 mmHg (lit.,³¹ 145–155 °C/0.1 mmHg); ν_{\max} (CCl₄) 1 590 cm⁻¹ (ArC=C); δ (CCl₄) 7.6–7.1 (10 H, m, Ph), 4.39 (1 H, t, J 7 Hz, CH), 2.0–1.4 (4 H, m, CH₂'s), and 0.86 (3 H, t, J 7 Hz, Me); m/z 274 (50%, M⁺), 165 (40, M - SPh), 123 (100, PhSCH₂), and 110 (100, PhSH); 1,1-bis(phenylthio)ethane³² (11; R = Me) (18.0 g, 73%), b.p.

135–136 °C/0.3 mmHg; ν_{\max} (CCl₄) 1 590 cm⁻¹ (ArC=C); δ (CCl₄) 7.4–7.0 (10 H, m, Ph), 4.40 (1 H, q, J 7 Hz, CH), and 1.51 (3 H, d, J 7 Hz, Me); m/z 246 (35%, M⁺), 137 (100, M - PhS), and 110 (74, PhSH); 1,1-bis(phenylthio)hexane (11; R = n-C₅H₁₁) (28.2 g, 93%), b.p. 168–174 °C/0.025 mmHg (Found: C, 71.3; H, 7.1. C₁₈H₂₂S₂ requires C, 71.5; H, 7.3%); ν_{\max} (CCl₄) 1 590 cm⁻¹ (ArC=C); δ (CCl₄) 7.5–7.0 (10 H, m, Ph), 4.31 (1 H, t, J 7 Hz, CH), 1.9–1.1 (8 H, m, CH₂'s), and 0.84 (3 H, t, J 7 Hz, Me); m/z 302.115 99 (26%, M⁺) (C₁₈H₂₂S₂ requires 302.116 29), 193 (70, M - SPh), and 109 (100, PhS⁺); 1,1-bis(phenylthio)pentane (11; R = Buⁿ) (27.9 g, 97%), b.p. 158–164 °C/0.1 mmHg (lit.,³¹ b.p. 150–160 °C/0.05–0.1 mmHg); ν_{\max} (CCl₄) 1 590 cm⁻¹ (ArC=C); δ (CCl₄) 7.7–7.1 (10 H, m, Ph), 4.45 (1 H, t, J 7 Hz, CH), 2.2–1.0 (6 H, m, CH₂'s), and 0.93 (3 H, t, J 7 Hz, Me); m/z 288 (19%, M⁺) and 179 (100, M - PhS); bis(phenylthio)phenylmethane (11; R = Ph) (30.7 g, 99%) as needles, m.p. 51–52 °C [from light petroleum (b.p. 40–60 °C)₂ (lit.,³³ m.p. 52–53 °C)]; ν_{\max} (CCl₄) 1 590 cm⁻¹ (ArC=C); δ (CDCl₃) 7.7–7.0 (15 H, m, Ph) and 5.45 (1 H, s, CH); m/z 308 (2%, M⁺), 199 (70, M - SPh), and 109 (100, PhS⁺); 2-methyl-1,1-bis(phenylthio)butane (11; R = Buⁿ) (26.2 g, 91%), b.p. 152–156 °C/0.2 mmHg (Found: C, 71.0; H, 7.1. C₁₇H₂₀S₂ requires C, 70.8; H, 7.0%); ν_{\max} (CCl₄) 1 590 cm⁻¹ (ArC=C); δ (CCl₄) 7.5–7.0 (10 H, m, Ph), 4.38 (1 H, d, J 3.5 Hz, CHS₂), 2.09 (1 H, m, CHMeEt), 1.70 (2 H, m, CH₂), 1.12 (3 H, d, J 7 Hz, CHMe), and 0.84 (3 H, t, J 7 Hz, CH₂Me); m/z 288.100 59 (52%, M⁺) (C₁₇H₂₀S₂ requires 288.100 64), 179 (80, M - SPh), and 109 (100, PhS⁺); 2-methyl-1,1-bis(phenylthio)propane³¹ (11; R = Prⁿ) (26.8 g, 98%), b.p. 143–148 °C/0.4 mmHg, ν_{\max} (CCl₄) 1 590 cm⁻¹ (ArC=C); δ (CCl₄) 7.5–7.1 (10 H, m, Ph), 4.40 (1 H, d, J 3.5 Hz, CHS₂), 2.20 (1 H, m, CHMe₂), and 1.14 (6 H, d, J 7 Hz, CHMe₂); m/z 274 (60%, M⁺) and 165 (100, M - PhS). Bis(phenylthio)methane (11; R = H) was prepared by the literature method¹⁰ (m.p. 40 °C).

Preparation of Alkanes (5) from Bis(phenylthio)acetals (11).—The bis(phenylthio)acetal (11) (10 mmol) in THF (10 ml) was added to a solution of lithium naphthalenide¹⁸ (prepared from 140 mg lithium and 2.56 g naphthalene; 20 mmol) in THF (50 ml) at -78 °C. After being stirred for 0.5 h, the reaction was quenched with chlorotrimethylsilane (3.17 ml, 2.71 g, 25 mmol), poured into saturated aqueous ammonium chloride (75 ml), extracted with ether (3 × 30 ml), washed with 2.5M-aqueous sodium hydroxide (30 ml) and saturated aqueous sodium chloride (30 ml), dried (Na₂SO₄), filtered and evaporated under reduced pressure to give, after distillation or column chromatography (SiO₂ eluting with light petroleum), the alkanes (5). Compounds prepared by this method were: 2-methyl-1-phenylthio-1-trimethylsilylbutane (5; R = Buⁿ) (79%); 2-methyl-1-phenylthio-1-trimethylsilylpropane (5; R = Prⁿ) (87%); phenyl(phenylthio)trimethylsilylmethane (5; R = Ph) (84%); 1-phenylthio-1-trimethylsilylbutane (5; R = Prⁿ) (82%); 1-phenylthio-1-trimethylsilylethane (5; R = Me) (90%); 1-phenylthio-1-trimethylsilylhexane (5; R = n-C₅H₁₁) (72%); 1-phenylthio-1-trimethylsilylpentane (5; R = Buⁿ) (75%); phenylthiotrimethylsilylmethane (1) or (5; R = H) (86%). All compounds were identical with those prepared above (n.m.r., i.r., t.l.c., b.p.).

Conversion of Alkanes (5) into Aldehydes (15).—*m*-Chloroperoxybenzoic acid (2.03 g of 85% peracid, 10 mmol) in dichloromethane (50 ml) was added to the alkane (5) (10.0 mmol) in dichloromethane (50 ml), under nitrogen at -23 °C, during 1.5 h. The reaction mixture was allowed to warm to room temperature during 1 h and poured into saturated aqueous sodium hydrogen carbonate (50 ml). The organic

layer was separated, washed with saturated aqueous sodium chloride (25 ml), dried (Na_2SO_4), evaporated under reduced pressure, taken up in benzene (or THF or carbon tetrachloride) (75 ml), and heated under reflux for 4 h. The solution was evaporated under reduced pressure, dissolved in THF (50 ml), stirred with 2M-aqueous hydrochloric acid (50 ml) for 4 h, poured into saturated aqueous sodium chloride (75 ml), and extracted with ether (3×50 ml). The extracts were washed with 2M-aqueous sodium hydroxide (2×50 ml) and saturated aqueous sodium chloride (50 ml), dried (Na_2SO_4) and evaporated under reduced pressure to give the aldehydes (15) which were characterised by n.m.r. and i.r. comparison with authentic samples and isolation of the 2,4-dinitrophenylhydrazones,³⁴ identical with authentic samples. Yields are given in Table 5.

Conversion of Alkanes (5) into Alcohols (16).—The alkanes (5) (10.0 mmol) were converted into the *O*-trimethylsilyl phenyl monothioacetal (14) as described above. The crude acetal (14) was dissolved in THF (25 ml) and TMEDA (25 ml), cooled to 0 °C and the alkyl-lithium (10.0 mmol as a solution in hexane or ether) was added during 0.5 h. After 1 h, the mixture was poured into saturated aqueous sodium chloride (150 ml) and extracted with ether (3×100 ml). The extracts were washed with 2M-hydrochloric acid (2×75 ml), saturated aqueous sodium hydrogen carbonate (50 ml), and aqueous sodium chloride (50 ml), dried (Na_2SO_4) and evaporated under reduced pressure to give, after short-path distillation, the alcohols, identical with authentic commercial samples (i.r., n.m.r. and b.p.). The yields are given in Table 6.

Synthesis of Undecanal (17).—*n*-Butyl-lithium (14 ml of a 1.4M-solution in hexane, 20 mmol) was added to phenylthio-trimethylsilane (1) (3.92 g, 20 mmol) in THF (100 ml) at 0 °C and the mixture stirred for 0.5 h. 1-Bromodecane (4.2 ml, 4.48 g, 20 mmol) was added and, after 2 h, the reaction was poured into saturated aqueous ammonium chloride (150 ml) and extracted with ether (3×100 ml). The extracts were washed with water (75 ml), dried (Na_2SO_4), evaporated under reduced pressure to give 1-phenylthio-1-trimethylsilylundecane (5; R = $n\text{-C}_{10}\text{H}_{21}$) after column chromatography (silica gel; 250 g; 600×30 mm, eluting with light petroleum), as an oil (4.64 g, 69%) (Found: C, 71.2; H, 10.65. $\text{C}_{20}\text{H}_{36}\text{SSi}$ requires C, 71.4; H, 10.8%; R_F (light petroleum) 0.25; ν_{max} (CCl_4) 1 595 (Ar C=C) and 1 240 cm^{-1} (SiMe_3); δ (CCl_4 ; CH_2Cl_2 as internal standard) 7.5—7.1 (5 H, m, Ph), 2.5—0.8 (22 H, m, overlaid with a triplet at 0.90, J 7 Hz, alkyl H), and 0.17 (9 H, s, SiMe_3); m/z 336.230 52 (47%, M^+) ($\text{C}_{20}\text{H}_{36}\text{SSi}$ requires 336.230 70), 109 (24, PhS^+), and 73 (100, Me_3Si^+).

MCPBA (2.74 g of 85% peracid, 13.5 mmol) in dichloromethane (50 ml) was added during 1.5 h to the alkane (5; R = $n\text{-C}_{10}\text{H}_{21}$) (4.50 g, 13.4 mmol) in dichloromethane (50 ml) at -28 °C. After being allowed to warm to room temperature during 1 h, the reaction mixture was poured into saturated aqueous sodium hydrogen carbonate (50 ml). The organic layer was separated, washed with saturated aqueous sodium chloride (25 ml), dried (Na_2SO_4), evaporated under reduced pressure to give an oil which was dissolved in THF (50 ml), and heated under reflux for 4 h. The solution was cooled and stirred for 10 h with 2M-hydrochloric acid (50 ml), poured into saturated aqueous sodium chloride (50 ml), and extracted with ether (3×50 ml). The extracts were washed with 2M-sodium hydroxide solution (2×50 ml) and saturated aqueous sodium chloride (50 ml), dried (Na_2SO_4), evaporated under reduced pressure and distilled to give undecanal [1.54 g, 74%, 51% from (1)] as an oil, b.p. 112—116 °C/15 mmHg

(bulb to bulb) (lit.,³⁵ b.p. 116—117 °C/18 mmHg); ν_{max} (CCl_4) 2 700 (CHO) and 1 730 cm^{-1} (CHO); δ (CDCl_3) 9.80 (1 H, t, J 1 Hz, CHO), 2.43 (2 H, m, CH_2CHO), and 2.0—0.6 (19 H, m, overlaid with a triplet at 0.88, J 7 Hz, remaining CH_2 's and Me). 2,4-Dinitrophenylhydrazone³⁴ had m.p. 103—104 °C (EtOH), identical with an authentic sample (m.p., m.m.p., t.l.c.).

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