Synthesis of Alkenes *via* the Peterson Reaction

David J. Ager
Department of Chemistry, University of Toledo, 2801 W. Bancroft St., Toledo, Ohio 43606, U.S.A.

The α-phenylthiosilanes (2) have been used to prepare the α-silyl anions (1) by reaction with lithium naphthalenide; subsequent condensation with a carbonyl compound gave the alkene (8) *via* the Peterson reaction. The α-phenylthiosilanes (2) were prepared from *n,n*-bis(phenylthio)acetals (4) by reaction with lithium naphthalenide and chlorotimethylsilane. The *n,n*-bis(phenylthio)acetals (4) were obtained, in turn, from 1,1-bis(phenylthio)acetals (5) by anion formation with butyl-lithium-*N,N,N',N'*-tetramethylethylenediamine complex in hexane followed by reaction with an alkyl halide. The Peterson reaction was also used to prepare vinyl sulphides (9) and vinyl sulphones (13).

The Peterson reaction[1,2] has the following advantages over the traditional Wittig reaction:[3] a volatile by-product (hexamethyl-disiloxane) which is easily removed; rapid condensation between the anion and carbonyl compound when a functionalised alkene is required;[4] and control over the stereochemical outcome of the elimination step.[5] In contrast, the disadvantages of the Peterson reaction are that it is under kinetic control[6] and that the diastereoisomeric β-hydroxy-silanes usually formed have to be separated if just one isomer of the alkene is required. Unlike anions stabilised by phosphorus, α-silyl anions (1) are not generally available by direct deprotonation[7] and less direct methods have to be employed. Although chloromethyltrimethylsilane is commercially available, other α-halogenosilanes are not readily accessible.

α-Silyl anions (1) have been prepared by the addition of an alkyl-lithium to a vinylsilane.[5,8] The alternative methods have been based on substitution of a heteroatom for a metal. Heteroatoms used in this context have been selenium,[9] silicon,[10] and tin.[11] This paper describes the use of sulphur[12] which has the advantage that the precursors are readily available and the transmetallation step is less susceptible to steric effects.

The required α-thiosilanes (2) are available by a variety of routes which are summarised in Scheme 1.[13] The various

methods are: alkylation of an α-thiosilane—this is limited to the cases where R^2 = H or an anion stabilising group,[4,14] and the alkylating agent is a primary alkyl halide; addition of an alkyl-lithium to 1-phenylthio-1-trimethylsilylethene (3), which by necessity includes the methylene group in the compound and limits the two alkyl substituents to being primary; while the last method involves displacement of sulphur for silicon in a bis(phenylthio)acetal (4) *via* the organolithium.[15] These acetals (4) can contain secondary or tertiary alkyl groups if they are prepared by condensation of the corresponding carbonyl compound with thiophenol. An alternative procedure for the preparation of the acetals (4) is to alkylate a 1,1-bis(phenyl-thio)alkane (5). This was the major approach used in this study; the alternatives are discussed elsewhere.[14]

Alkylations of Bis(phenylthio)acetals (5).—Unlike 1,3-di-thianes,[16,17] bis(phenylthio)acetals (5) have not found wide-spread use as acyl anion equivalents because of difficulties encountered while attempting alkylation. Although little success has been achieved by treating the lithium anion derived from (5) with an alkyl halide,[17,18] the required reaction has been accomplished with the sodium anion prepared from (5) by sodium in liquid ammonia.[19,20] Despite this alkylation problem, the lithium anions of bis(phenylthio)acetals have found some synthetic usage. For example, bis(phenylthio)acetals (5) have been deprotonated by butyl-lithium in tetrahydro-furan(THF) and the resultant anion added in a conjugate manner to α,β-unsaturated ketones after cuprate formation.[21] In a similar manner, the acetals (5) were deprotonated with butyl-lithium-*N,N,N',N'*-tetramethylethylenediamine (TMEDA) in THF and condensed with aldehydes and ketones; alkylations, in these studies, were not successful.[22-24]
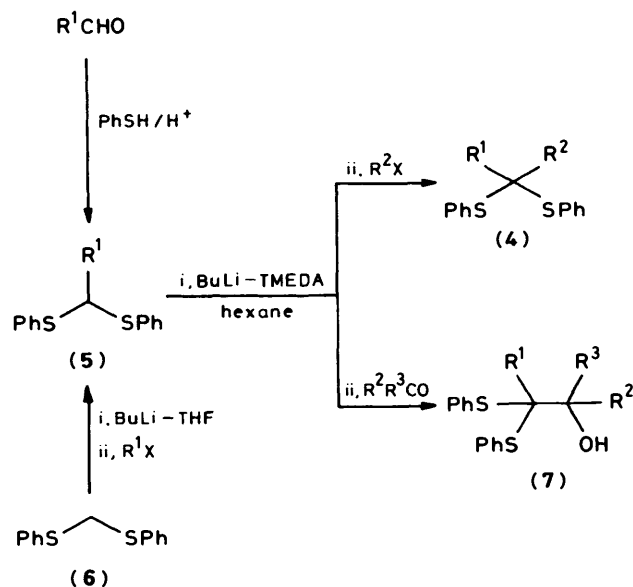
The major problem with the alkylation of (5), therefore, seems not to lie with anion formation but with reaction of the anion with the alkylating agent. It was found that the conditions used for anion formation in a related study[25,26] could also be utilised for bis(phenylthio)acetals, and alkylation did occur.[27]

The starting bis(phenylthio)acetals (5) were prepared by the standard methods of condensation of thiophenol with the appropriate aldehyde[22,26] or by alkylation of bis(phenyl-thio)methane (6) (see Scheme 2).

The alkylations of (5) were carried out by adding the acetal to a butyl-lithium–TMEDA complex in hexane at 0 °C and, after 1 h, the alkyl halide was added to give the ketone derivative (4) in good yield (see Table 1). Under these conditions, very little carbon–sulphur bond cleavage was detected,[28] the major by-product usually being recovered (5). This was not the case, however, when the reaction temperature exceeded 0 °C; reaction of thiophenoxide with the alkyl halide then became an important side reaction. If the temperature was lowered (*e.g.*
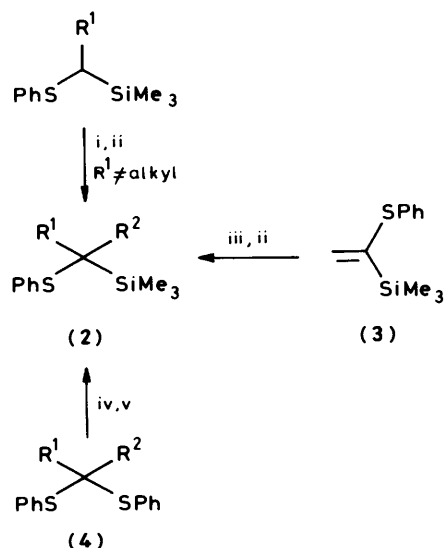
Scheme 1. *Reagents:* i, BuLi; ii, R^2X; iii, R^3Li (R^1 = R^3CH_2); iv, Li naphthalenide; v, Me$_3$SiCl.

R^{1}CHO

PhSH/H$^+$

R^1

PhS ⟍ SPh

(5)

i, BuLi–TMEDA
hexane

ii, R^{2}X

R^1 ⟍ ⟋ R^2
PhS ⟋ ⟍ SPh

(4)

ii, R^{2}R^{3}CO

R^1 ⟍ ⟋ R^3
PhS ⟍ ⟋ ⟍ R^2
PhS ⟋ ⟍ OH

(7)

i, BuLi–THF
ii, R^{1}X

PhS ⟍⟋⟍ SPh

(6)

Scheme 2.

Table 1. Alkylations of bis(phenylthio)acetals (5) with butyl-lithium–TMEDA in hexane.

	Yield of (4) (%) R^1				
R^{2}I	Me	Et	Bu	C$_5$H$_{11}$	Ph[a]
MeI	97	93	91	96	95
EtBr	85	82	78	79	80
EtI	92	89	86	91	87
PrI	90	86	82	89	91
BuBr	78	74	70	77	64
BuI	88	84	79	87	86
C$_{12}$H$_{25}$Br	61	65	61	72	69
CH$_2$=CHCH$_2$Br	91	84	85	85	82
PhCH$_2$Br	63	58	61	56	44

[a] With THF as solvent

Table 2. Reactions of lithium anions derived from acetals (5) with carbonyl compounds.

		Yield of (7) (%) R	
R^1	R^2	Me	Et
Et	H	70	65
Ph	H	50	45
–(CH$_2$)$_5$–		0	0
Me	Me	0	0

−23 °C or −78 °C), anion formation became very slow and yields were drastically decreased. In the case of bis(phenylthio)phenylmethane (5; R = Ph), the alkylation was carried out with THF as solvent because the acetal is solid. Attempts to omit the THF resulted in a 10—20% decrease in the yields through inefficient anion formation.

It seems, therefore, that for the technique described here to be efficient, the acetal (5) and the alkyl halide have to be soluble in hexane. In addition, as the anions derived from (5) were invariably present as a precipitate, the solubility of this anion in the reaction medium may also be a factor. If the alkyl halide was added in THF solution to the suspension of the anion derived from (5) in hexane, the yields were again decreased and the amount of carbon–sulphur bond cleavage increased significantly. Bis(phenylthio)phenylmethane (5; R = Ph), presumably, was a little different because of the presence of the anion-stabilising phenyl group; bis(phenylthio)trimethylsilylmethane (5; R = Me$_3$Si) has been alkylated in THF in a similar manner.[15]

Other shortcomings of this technique are apparent from Table 1. The best yields were obtained with primary alkyl halides. Secondary alkyl halides underwent almost exclusive elimination to the alkene, while the starting acetal (5) was recovered. The medium described above seems to be more basic than when THF was used as a solvent. Although condensation of the anions derived from (5) with aldehydes gave slightly lower yields of the alcohols (7) than had been previously found in THF,[21] the acetal anions acted as bases with enolisable ketones (see Table 2 and Scheme 2) and the thioacetal (5) was recovered (>90%). As THF had to be used as a co-solvent with bis(phenylthio)phenylmethane (1; R = Ph), no adducts were formed, in agreement with Blatcher and Warren.[21]

Anion formation of bis(phenylthio)acetals (1) with butyl-lithium–TMEDA in hexane and subsequent alkylation has the limitations of the acetal and alkyl halide being soluble in hexane and, experimentally, strict temperature control. When a large scale reaction (0.25 mol) was attempted with 1,1-bis(phenylthio)ethane (5; R^1 = Me) and alkylation with iodomethane, the yield of adduct (4; R^1 = R^2 = Me) was reduced to 35% and significant amounts of thioanisole were produced.

In addition to spectroscopic data, representative examples of the acetals (4) were hydrolysed to the corresponding ketones

(see Experimental Section) as further proof of the structure. This alkylation method is, therefore, not general as it is limited to thioacetals and alkylating agents which are soluble in hexane. For our purposes, the method described above was adequate.

Preparation and Reactions of α-Silyl Anions (1).—The bis(phenylthio)acetals (4) were converted into the required α-silyl sulphides (2) by reaction with lithium naphthalenide followed by quenching of the resultant anion with chlorotrimethylsilane (see Scheme 1).

The α-silyl sulphides (2) were readily separated from the reaction by-product, naphthalene, by simple procedures. This was in contrast to reports by other workers.[24–31] The majority of silanes (2) employed in this study were liquid. Evaporation of the solvent, after work-up, resulted in an oil, which, with time, deposited naphthalene crystals. Filtration removed nearly all of this by-product; the final traces were separated out by flash chromatography. Lithium 1-(dimethylamino)naphthalene (LDMAN)[32] was tried with a few selected examples and gave comparable yields to those obtained with naphthalene.

When the α-silyl sulphide (2) was not a liquid, the naphthalene had to be removed by chromatography. The silanes (2) were stable to the conditions of this technique[33] and did not decompose.[29.30] In an attempt to eliminate this tedious step, trial experiments were carried out with a catalytic amount of naphthalene after the method of Screttas.[34] This approach resulted in only a slight decrease (5—10%) in the yields of (2). While bis-silylation was not a problem, the reaction time was increased to about 17 h. If the silicon electrophile was, however, introduced before all of the lithium had reacted, bis-silylation was observed. The efficiency of the method was highly dependent upon the size and quality of the lithium sand. The small amount of naphthalene present in the product (2), however, still had to be removed by chromatography.

This displacement of the phenylthio group was then repeated with the silanes (2) to give the required α-silyl anions (1) (see
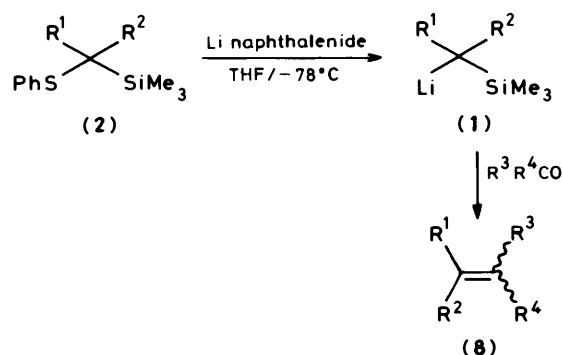
Scheme 3.

Scheme 3). Since the α-thiosilanes (2) are also masked carbonyl compounds,[13,14,26] formation of the α-silyl anion (1) by this method and subsequent condensation with a carbonyl compound gives the retrosynthetic disconnection shown in Scheme 4—the reverse of an oxidative alkene cleavage such as ozonolysis.
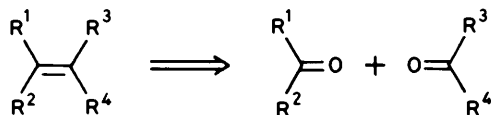
Scheme 4.

The overall yields for the transformation shown in Scheme 3 are given in Table 3. It should be noted that when no anion stabilising group is present on the α-carbon of the silyl anion (1) then the β-hydroxysilane (9) may be isolated.[2,5] Rather than isolate the intermediate (9), elimination to the alkene (8) was achieved by the addition of (i) hydrochloric acid, (ii) an aqueous solution of sodium acetate and acetic acid, (iii) aqueous sodium hydroxide, (iv) potassium hydride, or (v) sodium hydride. Although one of the by-products, thiophenol, was easily removed by base treatment, the acid method (i) gave the cleanest elimination (the yields given in Table 3 are for this method) and the by-product was removed by a subsequent base wash. For the model compounds used in this study the removal of naphthalene was not always trivial and various techniques had to be employed (see Experimental section). It should be noted, however, that this could be achieved with more

functionalised products by chromatography. An alternative method was to substitute 1-(dimethylamino)naphthalene for naphthalene,[32] which could then be removed by an acid wash; lithium di-t-butylbiphenyl has also been advocated for formation of alkyl-lithiums from phenylthioalkanes.[35] The LDMAN method was used with selected examples and gave yields comparable to the corresponding naphthalene cases; indeed this substitution can also prove useful in the transformation of (4) to (2) if the α-thiosilane and naphthalene are not easily separable. These findings have also been published by other workers.[31] In this case, the use of a catalytic quantity of naphthalene resulted in very low yields of the alkenes. The long reaction times and relative instability of the α-silyl anion may have resulted in proton abstraction from the solvent; certainly the parent silane was detected as a major by-product, while enolisable carbonyl compounds gave large amounts of aldol products.

As the yields in Table 3 of the alkenes (8) show, the condensation proceeded smoothly when only one alkyl group was present in the α-silyl anion [i.e. (1; R^2 = H)]. In our hands, the presence of a second alkyl group excluded condensations with enolisable carbonyl compounds because the anion acted as a base; even with a non-enolisable compound, such as benzaldehyde, the yield was only moderate. α-Silyl anions are more prone to proton abstraction than a phosphorus ylide; this has been demonstrated by a failure to add trimethylsilyl-methylmagnesium chloride to a hindered ketone.[36] Some success has been achieved in this area by other workers.[31]

In this study, no attempt was made to isolate the β-hydroxysilane intermediate (vide supra) and the alkenes (8) were, therefore, isolated as a ca. 1:1 mixture of E- and Z-isomers.

The Peterson reaction was also used to prepare sulphur-substituted alkenes. When an anion-stabilising group is present on the α-carbon atom, the elimination of the β-hydroxysilane is usually so fast that it cannot be isolated. This means that a 1:1 mixture of the E- and Z-isomers is usually formed. Vinyl sulphides (9) were prepared by the route shown in Scheme 5; additional examples to those of Carey[37] for phenyl-thiotrimethylsilylmethyl-lithium (10; R^1 = H) and alkyl-substituted anions are given in Table 4. The displacement of a phenylthio group by lithium naphthalenide for preparation of the anions of type (10) has already been discussed elsewhere[15] but some entries in Table 4 have been included for comparison. In addition to this method, the required anions (10) were generated by deprotonation of the parent silane (12) by treatment with butyl-lithium in either THF or TMEDA[14,26,38] (when R^1 was either hydrogen or an anion stabilising group such as phenyl)[14,39] or by addition of an alkyl-lithium to 1-phenylthio-1-trimethylsilylethene (11).[14,26,40,41] Yields of the vinyl sulphides (4) were good in most cases and condensation even occurred with an enolisable ketone.

Table 3. Preparation of alkenes (8) from α-thiosilanes (2)

		Yield (%) of (8) R^3, R^4							
(2)									
R^1	R^2	H,H	Me,H	Pr,H	Ph,H	Me,Me	Ph,Me	Ph,Ph	-(CH₂)₅-
H	H	a		64	77		83	71	69
Me	H			74	75	51	79	80	47
Bu	H	58	82	78	86	61[b]	76	74	52
Buⁱ	H				32	<20[b]	0		0
Ph	H	62	71	85	76	70	69	59	41
Me	Me			0	47	0			0
-(CH₂)₅-			0	0	38	0			0
Ph	Me			0	<20[b]	0			0

[a] Denotes that the reaction was not carried out   [b] A small amount of product was detected by n.m.r. and g.l.c. but was not isolated

Table 4. Preparation of vinyl sulphides (9) from α-thiosilanes

Anion (10) R¹	Method of preparation[a]	R²	R³	Yield (%) of (9)
H	A	H	H	65 (63[b])
H	A	Me	H	58
H	A	Bu	H	67
H	A	C₅H₁₁	H	63 (71[b])
H	B	C₅H₁₁	H	75
H	A	C₇H₁₅	H	64
H	A	Ph	H	71 (74[b])
H	B	Ph	H	70[15]
H	A	Me	Me	62
H	A	Me	Prⁱ	68
H	A	Me	Ph	63 (69[b])
H	A	Et	Et	71
H	A	—(CH₂)₄—		60
H	A	—(CH₂)₅—		65 (68[b])
H	B	—(CH₂)₅—		61[15]
H	A	Ph	Ph	82 (78[b])
H	B	Ph	Ph	73[15]
Me	B	Bu	H	63
Me	B	Ph	H	64[15]
Et	C	Bu	H	60
Et	C	Ph	H	65
Bu	B	H	H	71[15]
Bu	B	Bu	H	58[15]
Bu	B	Ph	H	66[15]
Bu	B	Ph	Ph	61[15]
Bu	B	—(CH₂)₅—		51[15]
C₅H₁₁	C	Me	H	47
C₅H₁₁	C	Bu	H	52
C₅H₁₁	C	Ph	H	61
C₅H₁₁	C	Ph	Me	43
C₅H₁₁	C	—(CH₂)₅—		50
Ph	A	H	H	71[b]
Ph	A	Bu	H	63[b]
Ph	A	Ph	H	53[b]
Ph	A	—(CH₂)₅—		47[b]
PhCH₂	C	Bu	H	49
PhCH₂	C	Ph	H	51
PhCH₂	C	—(CH₂)₅—		38

[a] Method A: from (12) by treatment with BuLi B: from (4) by treatment with lithium naphthalenide C: from (11) by addition of an alkyl-lithium [b] Yield when hexane–TMEDA was the solvent

Table 5. Preparation of vinyl sulphones (13) from α-sulphonylsilanes (15)

Anion (14) R¹	Carbonyl compound R²	R³	Yield (%) of (13)-solvent THF	DME
H	H	H[a]	87	b
H	Me	H	81	
H	Bu	H	85	89
H	C₅H₁₁	H	73	79
H	Ph	H	79	83
H	Me	Me	75	
H	Et	Et	60	
H	—(CH₂)₄—		51	
H	—(CH₂)₅—		83	86(82[47])
H	Ph	Me	68	
H	Ph	Ph	71	
Me	H	H	64	
Me	Me	H	48	
Me	Bu	H	35	44
Me	Ph	H	74	78
Me	—(CH₂)₅—		32	39
C₅H₁₁	Bu	H	40	42
C₅H₁₁	Ph	H	66	
C₅H₁₁	Me	Me	34	
C₅H₁₁	—(CH₂)₅—		19	23
Ph	H	H	70	
Ph	Bu	H	61	
Ph	Ph	H	82	
Ph	—(CH₂)₅—		23	25
Ph	Ph	Me	65	

[a] As paraformaldehyde [b] This reaction was not carried out

Although the Peterson reaction has been used to prepare many classes of substituted olefin, little attention has been paid to the preparation of vinyl sulphones (13). Until recently, the only examples were 1-methoxyvinyl sulphones.[45] Formation of the anion (14) was achieved by reaction of the α-silyl sulphone (15) with butyl-lithium with THF as solvent at −78 or 0 °C. Subsequent reaction with carbonyl compounds gave the vinyl sulphones in good to moderate yields (see Scheme 6 and Table 5). The anion (14) tended to act as a base when an alkyl group

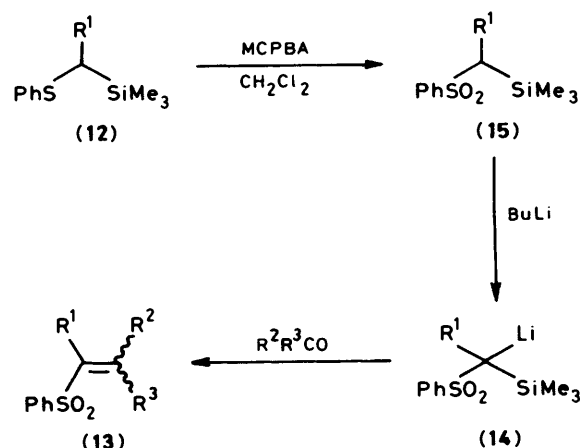

(11)

Scheme 5.

Scheme 6.

Vinyl sulphoxides have been prepared by the Peterson reaction [2,42,43] but because of the problems invoked by the ease of the sila-Pummerer rearrangement [13] and the tendency for alkyl-lithiums to attack the sulphur,[44] this approach was not pursued vigorously.

was present (R¹ ≠ H), a contrast to the sulphide case. Since the original study,[46] it has been shown that this tendency may be decreased by the use of 1,2-dimethoxyethane(DME) as the solvent rather than THF,[47] and low temperatures. Comparative yields of the reaction with the different solvents are given in

Table 5. The yields with the anion derived from phenyl-sulphonyltrimethylsilylmethane (15; R^1 = H) were increased by ca. 10% at best when DME was used; the alkyl substituted cases (15; $R^1 \neq$ H) showed little or no improvement in the yield of the vinyl sulphone (13), the anion still tending to act as a base.

This route to vinyl sulphones, although limited by the tendency of the anion (14) to act as a base, does provide a useful alternative[48-50] for the preparation of these useful synthetic intermediates.[48,49,51] Indeed, the Peterson approach to vinyl sulphones has proven useful to prepare α-silylvinyl sulphones.[52]

In conclusion, the use of phenylthio as a masked anion provides a general method for the preparation of α-silyl anions which can then be treated with a carbonyl compound to give an alkene via the Peterson reaction. Although the route to the α-silyl anion is general, dialkyl substituted α-silyl anions tend to act as bases and hence tetrasubstituted alkenes are not readily accessible by this method.

Compounds with a sulphur and a silicon group attached to the same carbon atom can be used to prepare vinyl sulphides and vinyl sulphones, the best yields being obtained when the anion moiety does not bear an alkyl group. Vinyl sulphides have been hydrolysed to carbonyl compounds[17,37] which, in turn, increases the scope and utility of α-silyl sulphides for the preparation of these compounds.[13,14,26]

Experimental

All melting points are uncorrected. 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. Light petroleum refers to that fraction with b.p. 60—80 °C.

G.l.c. analysis was carried out on a 10% Carbowax 20 M column (6 ft × $\frac{1}{8}$ in, 80—100 mesh, Chromosorb G).

All n.m.r. spectra were recorded at 90 or 220 MHz in CDCl$_3$ solution with SiMe$_4$ as internal standard, unless stated otherwise.

Alkylations of the Bis(phenylthio)acetals (5).—The acetals (5; R = H, Me, Bu, C_5H_{11} and Ph) were prepared as previously described.[26] 1,1-Bis(phenylthio)propane (5; R^1 = Et) was obtained as described by Blatcher and Warren[22] [b.p. 150—155 °C at 0.25 mmHg (lit.,[22] 126—130 °C at 0.1 mm Hg)] and had identical spectroscopic properties. The thioacetal (5) (10 mmol) was added to butyl-lithium (1.4M solution in hexane; 7.5 ml, 10 mmol) and TMEDA (1.5 ml, 1.16 g, 10 mmol) so that the temperature of the reaction mixture did not exceed 0 °C. The mixture was stirred for 0.5 h at 0 °C after which the alkyl halide (11 mol) was added so that the reaction temperature was kept between −5 and 0 °C. After 1 h, the mixture was poured into saturated aqueous ammonium chloride (25 ml) and extracted with ether (2 × 25 ml). The extracts were washed with brine (25 ml), dried (Na$_2$SO$_4$) and evaporated under reduced pressure to give, after column chromatography on silica (250 g; 600 × 30 mm, eluting with light petroleum), the acetals (4). Compounds * prepared by this method were: 1,1-*bis(phenylthio)-1,2-diphenylethane* (4; R^1 = Ph, R^2 = PhCH$_2$) (1.75 g, 44%) as an oil (Found: C, 78.25; H, 5.8. $C_{26}H_{22}S_2$ requires C, 78.35; H, 5.55%); $\nu_{max.}$ (CHCl$_3$) 1 585 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.9—7.0 (20 H, m, Ph's) and 3.25 (2 H, s, CH$_2$); m/z 398.1166 (1%, M^+) ($C_{26}H_{22}S_2$ requires 398.1163), 289 (100, M − PhS), and 110 (100, PhSH); 1,1-*bis(phenylthio)-1-phenylbutane*[53] (4; R^1 = Ph, R^2 = Pr) (3.19 g, 91%) as an oil (Found: C, 75.3; H, 6.1. $C_{22}H_{22}S_2$ requires C, 75.4; H, 6.35%); $\nu_{max.}$ (CHCl$_3$) 1 580 cm^{-1} (Ar C=C);

δ(CDCl$_3$) 7.8—7.1 (15 H, m, Ph's), 1.9—1.4 (4 H, m, CH$_2$'s), and 0.97 (3 H, t, J 7 Hz, Me); m/z 350.1161 (2%, M^+) ($C_{22}H_{22}S_2$ requires 350.116 29), 241 (100, M − PhS), and 110 (89, PhSH); 1,1-*bis(phenylthio)-1-phenylbut-3-ene* (4; R^1 = Ph, R^2 = CH$_2$CH=CH$_2$) (2.85 g, 82%) as an oil (Found: C, 75.75; H, 5.9. $C_{22}H_{20}S_2$ requires C, 75.8; H, 5.8%); $\nu_{max.}$ (CHCl$_3$) 1 630 (C=C) and 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.1 (15 H, m, Ph's), 6.2—5.8 (1 H, m, CH=C), 5.2—4.8 (2 H, m, C=CH$_2$), and 2.15 (2 H, d J 8 Hz, CH$_2$CH=CH$_2$); m/z 348.100 4 (7%, M^+) ($C_{22}H_{20}S_2$ requires 348.100 64), 239 (100, M − PhS), and 110 (83, PhSH); 1,1-bis(phenylthio)-1-phenylethane (4; R^1 = Ph, R^2 = Me) (3.06 g, 95%) as rhomboids, m.p. 53—55 °C (from light petroleum) (lit.,[28] m.p. 54—55 °C); $\nu_{max.}$ (CHCl$_3$) 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.0 (15 H, m, Ph's) and 1.82 (3 H, s, Me); m/z 322 (4%, M^+), 109 (87, PhS$^+$), and 105 (100, M − C_8H_9); 1,1-*bis(phenylthio)-1-phenylpentane* (4; R^1 = Ph, R^2 = Bu) (2.33 g, 64% from BuBr; 3.13 g, 86% from BuI) as an oil (Found: C, 75.65; H, 6.85. $C_{23}H_{24}S_2$ requires C, 75.8; H, 6.65%); $\nu_{max.}$ (CHCl$_3$) 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.9—7.1 (15 H, m, Ph's), 2.0—1.2 (8 H, m, CH$_2$'s), and 0.97 (3 H, t, J 7 Hz, Me); m/z 255 (100, M − PhS) and 110 (100, PhSH); 1,1-*bis(phenylthio)-1-phenylpropane* (4; R^1 = Ph, R^2 = Et) (2.69 g, 80% from EtBr; 2.92 g, 87% from EtI) as an oil (Found: C, 74.85; H, 5.95. $C_{21}H_{20}S_2$ requires C, 75.0; H, 6.0%); $\nu_{max.}$ (CHCl$_3$) 1 590 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.9—7.1 (15 H, m, Ph's), 1.80 (2 H, q, J 7 Hz, CH$_2$), and 1.01 (3 H, t, J 7 Hz, Me); m/z 336.100 88 (2%, M^+) ($C_{21}H_{20}S_2$ requires 336.100 64), 227 (100, M − PhS), and 109 (85, PhS$^+$); 1,1-*bis(phenylthio)-1-phenyltridecane* (4; R^1 = Ph, R^2 = $C_{12}H_{25}$) (3.28 g, 69%) as an oil (Found: C, 77.95; H, 8.3. $C_{31}H_{40}S_2$ requires C, 78.1; H, 8.5%); $\nu_{max.}$ (CHCl$_3$) 1 585 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.0 (15 H, m, Ph's) and 2.0—0.8 (25 H, m, alkyls); m/z 367 (59%, M − PhS) and 110 (100, PhSH); 2,2-*bis(phenylthio)butane* (4; R^1 = Me, R^2 = Et) (2.55 g, 93% with MeI; 2.33 g, 85% with EtBr; 2.52 g, 92% with EtI) as an oil (Found: C, 69.85; H, 6.5. $C_{16}H_{18}S_2$ requires C, 70.0; H, 6.6%); $\nu_{max.}$ (CHCl$_3$) 1 585 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.7—7.0 (10 H, m, Ph), 1.86 (2 H, q, J 7 Hz, CH$_2$Me), 1.35 (3 H, s, Me), and 1.07 (3 H, t, J 7 Hz, CH$_2$Me); m/z 274.084 70 (4%, M^+) ($C_{16}H_{18}S_2$ requires 274.084 99), 164 (99, M − PhSH), 121 (100, $C_7H_7S^+$), and 109 (100, PhS$^+$); 2,2-*bis(phenylthio)heptane* (4; R^1 = Me, R^2 = C_5H_{11}) (3.03 g, 96%) as an oil (Found: C, 72.3; H, 7.55. $C_{19}H_{24}S_2$ requires C, 72.1; H, 7.65%); $\nu_{max.}$ (CHCl$_3$) 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.1 (10 H, m, Ph's), 1.9—1.2 (8 H, m, CH$_2$'s), 1.37 (3 H, s, Me), and 0.94 (3 H, t, J 7 Hz, CH$_2$Me); m/z 316.132 16 (5%, M^+) ($C_{19}H_{24}S_2$ requires 316.131 94), 207 (100, M − PhS), and 110 (90, PhSH); 2,2-*bis(phenylthio)hexane* (4; R^1 = Me, R^2 = Bu) (2.75 g, 91% with MeI; 2.36 g, 78% with BuBr; 2.66 g, 88% with BuI) as an oil (Found: C, 71.5; H, 7.4. $C_{18}H_{22}S_2$ requires C, 71.5; H, 7.3%); $\nu_{max.}$ (CHCl$_3$) 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.05 (10 H, m, Ph's), 2.0—1.2 (6 H, m, CH$_2$'s), 1.35 (3 H, s, Me), and 0.97 (3 H, t, J 7 Hz, CH$_2$Me); m/z 302.116 44 (6%, M^+) ($C_{18}H_{22}S_2$ requires 302.116 29), 192 (100, M − PhSH), and 109 (100, PhS$^+$); 2,2-*bis(phenylthio)pentane* (4; R^1 = Me, R^2 = Pr) (2.59 g, 90%) as an oil (Found: C, 70.65; H, 6.95. $C_{17}H_{20}S_2$ requires C, 70.8; H, 7.0%); $\nu_{max.}$ (CHCl$_3$) 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.1 (10 H, m, Ph's), 2.0—1.4 (4 H, m, CH$_2$'s), 1.36 (3 H, s, Me), and 0.92 (3 H, t, J 7 Hz, CH$_2$Me); m/z 288.100 91 (4%, M^+) ($C_{17}H_{20}S_2$ requires 288.100 64), 179 (100, M − PhSH), and 110 (92, PhSH); 2,2-*bis(phenylthio)pent-4-ene* [4; R^1 = Me, R^2 = (CH$_2$)$_3$] (2.60 g, 91%) as an oil (Found: C, 71.2; H, 6.45. $C_{17}H_{18}S_2$ requires C, 71.3; H, 6.3%); $\nu_{max.}$ (CHCl$_3$) 1 640 (C=C) and 1 575 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.1 (10 H, m, Ph's), 6.2—5.8 (1 H, m, CH=CH$_2$), 5.2—4.8 (2 H, m, CH=CH$_2$), 2.09 (2 H, m, CH$_2$), and 1.48 (3 H, s, Me); m/z 286.085 30 (8%, M^+) ($C_{17}H_{18}S_2$ requires 286.084 99), 177 (100, M − PhS), and 110 (74, PhSH); 2,2-*bis(phenylthio)-1-phenylbutane* (4; R^1 = Et; R^2 = PhCH$_2$) (2.03 g, 58%) as an oil (Found: C, 75.3; H, 6.25;

---

* Several compounds have been cited in the literature but full spectroscopic data were not included.

$C_{22}H_{22}S_2$ requires C, 75.4; H, 6.3%); $v_{max.}$ (CHCl$_3$) 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.9—7.0 (15 H, m, Ph's), 2.0—1.3 (6 H, m, CH$_2$'s), and 0.93 (3 H, t, J 7 Hz, Me); m/z 241 (100, M − PhS) and 110 (81, PhSH); 2,2-*bis*(*phenylthio*)-1-*phenylheptane* (4; $R^1 = C_5H_{11}$, $R^2 = PhCH_2$) (2.20 g, 56%) as an oil (Found: C, 76.25; H, 7.35. $C_{25}H_{28}S_2$ requires C, 76.5; H, 7.2%); $v_{max.}$ (CHCl$_3$) 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.1 (15 H, m, Ph's), 3.20 (2 H, s, PhCH$_2$), 2.1—1.2 (8 H, m, alkyl CH$_2$'s), and 0.89 (3 H, t, J 7 Hz, Me); m/z 282 (65%, M − PhSH) and 109 (100, PhS$^+$); 2,2-*bis*(*phenylthio*)-1-*phenylhexane* (4; $R^1 = $ Bu; $R^2 = PhCH_2$) (2.31 g, 61%) as an oil (Found: C, 76.0; H, 6.95. $C_{24}H_{26}S_2$ requires C, 76.15; H, 6.9%); $v_{max.}$ (CHCl$_3$) 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.9—7.0 (15 H, m, Ph's), 3.21 (2 H, s, PhCH$_2$), and 2.1—0.7 (9 H, m, alkyls); m/z 269 (51%, M − PhS) and 110 (100, PhSH); 2,2-*bis*(*phenylthio*)-1-*phenylpropane*[53] (4; $R^1 = $ Me, $R^2 = PhCH_2$) (2.12 g, 63%) as rhomboids, m.p. 99—101 °C (from light petroleum) (Found: C, 74.9; H, 5.95. $C_{21}H_{20}S_2$ requires C, 74.9; H, 5.95%); $v_{max.}$ (CHCl$_3$) 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.1 (15 H, m, Ph's), 3.18 (2 H, s, PhCH$_2$), and 1.29 (3 H, s, Me); m/z 227 (64%, M − PhS), 149 [36, M − (PhSH + Ph)], 110 (100, PhSH), and 91 (45, C$_7$H$_7^+$); 2,2-*bis*(*phenylthio*)*propane*[54] (4; $R^1 = R^2 = $ Me) (2.52 g, 97%), as rhomboids, m.p. 54—56 °C (from light petroleum); $v_{max.}$ (CHCl$_3$) 1 585 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.1 (10 H, m, Ph's) and 1.35 (6 H, s, Me's); m/z 260 (2%, M^+), 151 (100, M − PhS), and 110 (97, PhSH); 2,2-*bis*(*phenylthio*)*tetradecane* (4; $R^1 = $ Me, $R^2 = C_{12}H_{25}$) (2.53 g, 61%) as an oil (Found: C, 75.05; H, 9.5. $C_{26}H_{38}S_2$ requires C, 75.3; H, 9.25%); $v_{max.}$ (CHCl$_3$) 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.1 (10 H, m, Ph's), 2.0—1.1 (25 H, m, CH$_2$'s overlaid with a singlet at 1.32, Me) and 0.91 (3 H, t, J 7 Hz, CH$_2$Me); m/z 305 (71%, M − PhS) and 110 (100, PhSH); 3,3-*bis*(*phenylthio*)*heptane* (4; $R^1 = $ Et, $R^2 = $ Bu) (2.47 g, 78% with EtBr; 2.72 g, 86% with EtI; 2.34 g, 74% with BuBr; 2.65 g, 84% with BuI) as an oil (Found: C, 72.15; H, 7.8. $C_{19}H_{24}S_2$ requires C, 72.1; H, 7.65%); $v_{max.}$ (CHCl$_3$) 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.1 (10 H, m, Ph's) and 2.1—0.8 (14 H, m, alkyls); m/z 316.132 10 (4%, M^+) ($C_{19}H_{24}S_2$ requires 316.131 94), 206 (84, M − PhSH), and 109 (100, PhS$^+$); 3,3-*bis*(*phenylthio*)*hexane* (4; $R^1 = $ Me, $R^2 = $ Pr) (3.00 g, 86%) as an oil (Found: C, 71.2; H, 7.55. $C_{18}H_{22}S_2$ requires C, 71.5; H, 7.3%); $v_{max.}$ (CHCl$_3$) 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.1 (10 H, m, Ph's), 2.1—1.4 (8 H, m, CH$_2$'s), and 0.93 (6 H, t, J 7 Hz, Me); m/z 302.116 41 (6%, M^+) ($C_{18}H_{22}S_2$ requires 302.116 29), 193 (100, M − PhS), and 110 (98, PhSH); 3,3-*bis*(*phenylthio*)*hex-5-ene* (4; $R^1 = $ Et, $R^2 = CH_2CH = CH_2$) (2.52 g, 84%) as an oil (Found: C, 72.0; H, 6.85 $C_{18}H_{20}S_2$ requires C, 71.95; H, 6.7%); $v_{max.}$ (CHCl$_3$) 1 645 (C=C) and 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.1 (10 H, m, Ph's), 6.2—5.8 (1 H, m, CH=CH$_2$), 5.2—4.8 (2 H, m, CH=CH$_2$), 2.03 (2 H, m, CH$_2$CH=), 1.58 (2 H, q, J 7 Hz, CH$_2$Me), and 0.95 (3 H, t, J 7 Hz, CH$_2$Me); m/z 300.100 40 (6%, M^+) ($C_{18}H_{20}S_2$ requires 300.100 64), 190 (69, M − PhSH), and 109 (100, PhS$^+$); 3,3-*bis*(*phenylthio*)*octane* (4; $R^1 = C_5H_{11}$; $R^2 = $ Et) (2.61 g, 79% with EtBr; 3.00 g, 91% with EtI) as an oil (Found: C, 72.5; H, 8.05. $C_{20}H_{26}S_2$ requires C, 72.7; H, 7.95%); $v_{max.}$ (CHCl$_3$) 1 575 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.1 (10 H, m, Ph), 2.2—0.8 (16 H, m, alkyls); m/z 221 (62%, M − PhS), and 109 (100, PhS$^+$); 3,3-*bis*(*phenylthio*)*pentadecane* (4; $R^1 = $ Et, $R^2 = C_{12}H_{25}$) (2.78 g, 65%) as an oil (Found: C, 75.4; H, 9.65. $C_{27}H_{40}S_2$ requires C, 75.65; H, 9.4%); $v_{max.}$ (CHCl$_3$) 1 585 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.9—7.1 (10 H, m, Ph's) and 2.2—0.8 (30 H, m, alkyls); m/z 319 (51%, M − PhS) and 110 (100, PhSH); 3,3-*bis*(*phenylthio*)-*pentane* (4; $R^1 = R^2 = $ Et) (2.36 g, 82% with EtBr; 2.56 g, 89% with EtI) as an oil (Found: C, 70.75; H, 6.95. $C_{17}H_{20}S_2$ requires C, 70.8; H, 7.0%); $v_{max.}$ (CHCl$_3$) 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.0 (10 H, m, Ph's), 1.54 (4 H, q, J 7.5 Hz, CH$_2$'s), and 0.95 (6 H, t, J 7.5 Hz, Me's); m/z 288.100 00 (10%, M^+) ($C_{17}H_{20}S_2$ requires 288.100 64), 179 (100, M − PhS), and 110 (44, PhSH);

4,4-*bis*(*phenylthio*)*nonane* (4; $R^1 = C_5H_{11}$, $R^2 = $ Pr) (3.06 g, 89%) as an oil (Found: C, 73.0; H, 8.45. $C_{21}H_{28}S_2$ requires C, 73.2; H, 8.2%); $v_{max.}$ (CHCl$_3$) 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.1 (10 H, m, Ph's) and 2.1—0.8 (18 H, m, alkyls); m/z 344.163 54 (2%, M^+) $C_{21}H_{28}S_2$ requires 344.163 24), 235 (100, M − PhS), and 110 (79, PhSH); 4,4-*bis*(*phenylthio*)*non-1-ene* (4; $R^1 = C_5H_{11}$, $R^2 = CH_2CH$=CH$_2$) (2.91 g, 85%) as an oil (Found: C, 73.4; H, 7.4. $C_{21}H_{26}S_2$ requires C, 73.6; H, 7.65%); $v_{max.}$ (CHCl$_3$) 1 640 (C=C) and 1 575 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.9—7.1 (10 H, m, Ph's), 6.2—5.8 (1 H, m, CH=CH$_2$), 5.2—4.8 (2 H, m, CH=CH_2), and 2.3—0.7 (13 H, m, CH$_2$'s and Me); m/z 342.147 97 (8%, M^+) ($C_{21}H_{26}S_2$ requires 342.147 59), 233 (48, M − PhS), and 110 (100, PhSH); 4,4-*bis*(*phenylthio*)*octane* (4; $R^1 = $ Bu; $R^2 = $ Pr) (2.71 g, 82%) as an oil (Found: C, 72.4; H, 8.2. $C_{20}H_{26}S_2$ requires C, 72.65; H, 7.95%); $v_{max.}$ (CHCl$_3$) 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.0 (10 H, m, Ph's), 2.2—1.2 (12 H, m, CH$_2$'s), and 0.91 (6 H, t, J 7 Hz, Me's); m/z 330.147 91 (7%, M^+) ($C_{20}H_{26}S_2$ requires 330.147 59), 221 (64, M − PhS), and 109 (100, PhS$^+$); 4,4-*bis*(*phenylthio*)*oct-1-ene* (4; $R^1 = $ Bu; $R^2 = CH_2CH$=CH$_2$) (2.79 g, 85%) as an oil (Found: C, 72.95; H, 7.65. $C_{20}H_{42}S_2$ requires C, 73.1; H, 7.35%); $v_{max.}$ (CHCl$_3$) 1 635 (C=C) and 1 590 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.0 (10 H, m, Ph's), 6.2—5.8 (1 H, m, CH=CH$_2$), 5.2—4.8 (2 H, m, CH=CH_2), and 2.5—0.7 (11 H, m, CH$_2$'s and Me); m/z 328.132 59 (3%, M^+) ($C_{20}H_{24}S_2$ requires 328.131 94), 219 (50, M − PhS), and 110 (100, PhSH); 5,5-*bis*(*phenylthio*)*decane* (4; $R^1 = C_5H_{11}$; $R^2 = $ Bu) (2.76 g, 77% with BuBr; 3.12 g, 87% with BuI) as an oil (Found: C, 73.55; H, 8.55. $C_{22}H_{30}S_2$ requires C, 73.7; H, 8.4%); $v_{max.}$ (CHCl$_3$) 1 590 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.9—7.0 (10 H, m, Ph's) and 2.2—0.7 (20 H, m, alkyls); m/z 358.179 01 (4%, M^+) ($C_{22}H_{30}S_2$ requires 358.178 89), 248 (67, M − PhSH), and 109 (100, PhSH); 5,5-*bis*(*phenylthio*)*heptadecane* (4; $R^1 = $ Bu; $R^2 = C_{12}H_{25}$) as an oil (Found: C, 75.9; H, 10.0. $C_{29}H_{44}S_2$ requires C, 76.25; H, 9.7%); $v_{max.}$ (CHCl$_3$) 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.9—7.0 (10 H, m, Ph) and 2.3—0.6 (34 H, m, alkyls); m/z 347 (22%, M − PhS) and 110 (100, PhSH); 5,5-*bis*(*phenylthio*)*nonane* (4; $R^1 = R^2 = $ Bu) (2.41 g, 70% with BuBr; 2.72 g, 79% with BuI) as an oil, $v_{max.}$ (CHCl$_3$) 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.9—7.1 (10 H, m, Ph's) and 2.1—0.7 (18 H, m, alkyls); m/z 235 (61%, M − PhS) and 110 (100, PhSH); and 6,6-*bis*(*phenylthio*)*octadecane*[20] (4; $R^1 = C_5H_{11}$; $R^2 = C_{12}H_{25}$) (3.38 g, 72%) as an oil; $v_{max.}$ (CHCl$_3$) 1 590 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.9—7.1 (10 H, m, Ph's) and 2.2—0.6 (36 H, m, alkyls); m/z 361 (93%, M − PhS) and 110 (100, PhSH).

Reaction of the Bis(phenylthio)acetals (5) *with Aldehydes.*—The reaction was carried out as described above except that the anion was quenched with the appropriate carbonyl compound. Compounds prepared by this method were 2,2-bis(phenylthio)-1-phenylbutan-1-ol[22] (7; $R^1 = $ Et, $R^2 = $ Ph, $R^3 = $ H) (1.65 g, 45%) as an oil; $v_{max.}$ (CHCl$_3$) 3 500br (OH) and 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.1 (15 H, m, Ph's), 4.73 (1 H, br s, CHOH), 3.25 (1 H, s, exch. in D$_2$O), 1.53 (2 H, m, CH_2Me), and 1.08 (3 H, t, J 8 Hz, CH$_2$Me); m/z 259 (40%, M − PhCHOH), 256 (100, M − PhSH), and 110 (100, PhSH); 2,2-bis(phenylthio)-1-phenylpropan-1-ol (7; $R^1 = $ Me, $R^2 = $ Ph, $R^3 = $ H) (1.76 g, 50%) as rhomboids, m.p. 135—137 °C (lit.[22] m.p. 137—138 °C); $v_{max.}$ (CHCl$_3$) 3 500br (OH) and 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.1 (15 H, m, Ph's), 4.71 (1 H, br s, CHOH), 3.5 (1 H, s, exch. in D$_2$O), and 1.13 (3 H, s, Me); m/z 245 (90%, M − PhCHOH), 243 (100, M − PhS), and 110 (100, PhSH); 2,2-bis(phenylthio)pentan-3-ol[22] (7; $R^1 = $ Me, $R^2 = $ Et, $R^3 = $ H) (2.13 g, 70%) as an oil; $v_{max.}$ (CHCl$_3$) 3 500br (OH) and 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.0 (10 H, m, Ph's), 3.45 (1 H, dd, J 3.9 Hz, CH$_2$CHOH), 3.05 (1 H, br s, exch. in D$_2$O), 2.1—1.4 (2 H, m, CH$_2$), 1.23 (3 H, s, CMe), and 1.04 (3 H, t, J 7 Hz, CH$_2$Me); m/z 304 (4%, M^+), 245 (10, M − EtCHOH), 185 (100, M − PhS), and 110 (44, PhSH); and 3,3-bis(phenylthio)hexan-

4-ol[22] (7; $R^1 = R^2 = Et$, $R^3 = H$) (2.07 g, 65%) as an oil; $v_{max.}$ (CHCl$_3$) 3 500br (OH) and 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.0 (10 H, m, Ph's), 3.55 (1 H, dd, J 3, 4 Hz, CH$_2$CHOH), 2.80 (1 H, br s, exch. in D$_2$O), 2.0—1.3 (4 H, m, CH$_2$'s), and 1.02 (6 H, t, J 7 Hz, Me's); m/z 318 (3%, M^+) 259 (11, M − EtCHOH), 209 (100, M − PhS), and 110 (40, PhSH).

Hydrolysis of the Acetals (4).—The thioacetals (4; $R^1 = Et$, $R^2 = Bu$) and (4; $R^1 = R^2 = Bu$) (10 mmol) were hydrolysed in the presence of mercury(II) oxide and boron trifluoride (after the method of Vedejs and Fuchs[55]) and copper(II) chloride[56] to give the ketones heptan-3-one [72% with mercury(II), 78% with copper(II)], b.p. 143—150 °C (bath temperature, bulb-to-bulb, lit.,[57] 146—149 °C); $v_{max.}$ (film) 1 740 cm^{-1} (C=O); δ(CDCl$_3$) 2.6—2.1 (4 H, m, COCH$_2$'s) and 2.0—0.7 (10 H, m, Et's) and nonan-5-one [78% with mercury(II), 79% with copper(II)], b.p. 183—190 °C (bath temperature, bulb-to-bulb, lit.,[57] 186—187 °C); $v_{max.}$ (film) 1 735 cm^{-1} (C=O); δ(CDCl$_3$) 2.40 (4 H, t, J 7 Hz, COCH$_2$'s) and 2.0—0.7 (14 H, m, Pr's). The 2,4-dinitrophenylhydrazones were prepared by reaction of the thioacetal with the hydrazone in acidic methanol.[53,58] Thioacetals used for this procedure were (4; $R^1 = R^2 = Me$) to give the hydrazone, m.p. 125—126 °C (lit.,[58] 126 °C) and (4; $R^1 = R^2 = Et$), hydrazone m.p. 156—157 °C (lit.,[58] m.p. 156 °C).

Preparation of the α-Thiosilanes (12).—Phenylthiotrimethyl-silylmethane (12; $R = H$), 1-phenylthio-1-trimethylsilylethane (12; $R = Me$), 1-phenylthio-1-trimethylsilylpentane (12; $R = Bu$), and phenyl(phenylthio)(trimethylsilyl)methane (12; $R = Ph$) were prepared as previously described.[26] 2,2-*Dimethyl-1-phenylthio-1-trimethylsilylpropane* (12, $R = Bu^t$) (Found: C, 66.4; H, 9.45. C$_{14}$H$_{24}$SSi requires C, 66.6; H, 9.6%); $v_{max.}$ (CCl$_4$) 1 590 (Ar C=C) and 1 250 cm^{-1} (SiMe$_3$); δ(CCl$_4$, CH$_2$Cl$_2$ as internal standard) 7.7—7.1 (5 H, m, Ph), 2.20 (1 H, 2, CH), 0.90 (9 H, s, CMe$_3$), and 0.12 (9 H, s, SiMe$_3$); m/z 252 (7%, M^+), 109 (35, PhS$^+$) and 73 (100, Me$_3$Si$^+$) was prepared as an oil (74% yield) by reaction of 1,1-*bis(phenylthio)-2,2-dimethylpropane* (5; $R^1 = Bu^t$), rhomboids, m.p. 67—69 °C (light petroleum) (Found: C, 71.0; H, 6.65. C$_{17}$H$_{20}$S$_2$ requires C, 70.8; H, 7.0%); $v_{max.}$ (CHCl$_3$) 1 585 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.23 (10 H, br s, Ph), 4.26 (1 H, s, CH), and 1.21 (9 H, s, CMe$_3$); m/z 179 (80%, M − PhS) and 110 (100, PhSH), in turn prepared from 2,2-dimethylpropanal and thiophenol in the presence of an acid catalyst,[22] with lithium naphthalenide and chlorotrimethyl-silane.[12,26]

Preparation of the α-Thiosilanes (2).—This last method was also used for the the preparation of 1-*phenylthio-1-trimethyl-silylcyclohexane* [2; R, $R^1 = -(CH_2)_5-$] (80%) (Found: C, 67.9; H, 9.35. C$_{15}$H$_{24}$SSi requires C, 68.1; H, 9.15%); $v_{max.}$ (CCl$_4$) 1 590 (Ar C=C) and 1 245 cm^{-1} (SiMe$_3$); δ(CCl$_4$, CH$_2$Cl$_2$ as internal standard) 7.8—7.3 (5 H, m, Ph), 2.1—1.2 (10 H, m, CH$_2$'s), and 0.01 (9 H, s, SiMe$_3$); m/z 264.1389 (4% M^+) (C$_{15}$H$_{24}$SSi requires 264.1368), 155 (60, M − PhS), 110 (54, PhSH), and 73 (100, Me$_3$Si$^+$) from 1,1-bis(phenylthio)cyclohexane (4; R, $R^1 = -(CH_2)_5-$, m.p. 75—77 °C (light petroleum)*; $v_{max.}$ (CHCl$_3$) 1 585 cm^{-1} (Ar C=C); δ(CDCl$_3$, SiMe$_4$ as internal standard) 7.9—7.3 (10 H, m, Ph) and 2.0—1.2 (10 H, m, CH$_2$'s); m/z 300 (2%, M^+), 191 (85, M − PhS), and 109 (100, PhS$^+$) in turn prepared from cyclohexanone; 2-*phenylthio-2-trimethylsilylpropane* (2; $R^1 = R^2 = Me$) (76%) (Found: C, 63.95; H, 8.95. C$_{12}$H$_{20}$SSi requires C, 64.2; H, 9.0%); $v_{max.}$ (CCl$_4$) 1 590 (Ar C=C) and 1 250 cm^{-1} (SiMe$_3$); δ(CCl$_4$, CH$_2$Cl$_2$ as internal standard) 7.7—7.1 (5 H, m, Ph), 1.07 (5 H, s,

CMe's), and 0.10 (9 H, s, SiMe$_3$); m/z 224.106 13 (5%, M^+) (C$_{12}$H$_{20}$SSi requires 224.105 50), 115 (73, M − PhS), 109 (58, PhS$^+$), and 73 (100, Me$_3$Si$^+$) from 2,2-bis(phenylthio)propane (4; $R^1 = R^2 = Me$) (*vide supra*) and 1-*phenyl-1-phenylthio-1-trimethylsilylethane* (2; $R^1 = Ph$, $R^2 = Me$) (83%) (Found: C, 71.0; H, 7.9. C$_{17}$H$_{22}$SSi requires C, 71.3; H, 7.75%); $v_{max.}$ (CHCl$_3$) 1 590 (Ar C=C) and 1 250 cm^{-1} (SiMe$_3$); δ (CDCl$_3$, CH$_2$Cl$_2$ as internal standard), 7.9—7.1 (10 H, m, Ph's), 1.68 (3 H, s, CMe), and 0.12 (9 H, s, SiMe$_3$); m/z 286.122 27 (8%, M^+) (C$_{17}$H$_{22}$SSi requires 286.121 15), 177 (58, M − PhS), 109 (41, PhS$^+$), and 73 (100, Me$_3$Si$^+$) from 1,1-bis(phenylthio)-1-phenylethane (4; $R^1 = Ph$, $R^2 = Me$).

The bis(thioacetal) (4) (10 mmol), lithium sand[60] (139 mg, 20 mmol), naphthalene (10 mg), and THF (25 ml) were stirred at 0 °C until all of the lithium had disappeared. Chlorotrimethyl-silane (1.52 ml, 1.30 g, 12 mmol) was added and after 1 h, saturated aqueous ammonium chloride (25 ml) was added. The mixture was extracted with ether (3 × 25 ml), washed with 2M sodium hydroxide (25 ml) and saturated aqueous sodium chloride (25 ml), dried (Na$_2$SO$_4$), and evaporated under reduced pressure to give, after chromatography, the α-silyl sulphide (2). Compounds prepared by this method were: 1-phenylthio-1-trimethylsilylcyclohexane [2; R^1, $R^2 = -(CH_2)_5-$] (1.87 g, 71%), 2,2-dimethyl-1-phenylthio-1-trimethylsilyl-propane (12; $R = Bu^t$) (1.59 g, 63%) and phenyl(phenylthio)-trimethylsilylmethane (12; $R = Ph$)(1.81 g, 67%) and were identical with those prepared previously.

Synthesis of Alkenes (8) *from α-Silyl Anions: General Pro-cedure*.—The 1-phenylthio-1-trimethylsilylalkane (2) (0.01 mol) in THF (10 ml) was added to a solution of lithium naphthalenide [from lithium (0.14 g, 0.02 mol) and naphthalene (2.56 g, 0.02 mol)[34,61,62]] in THF (50 ml) at − 78 °C. After 0.5 h, the carbonyl compound (0.01 mol) in THF (5 ml) was added and allowed to warm slowly to room temperature. 2M-Hydrochloric acid (50 ml) (or another reagent for carrying out the elimination of the β-hydroxysilane—see text) was added and the mixture stirred overnight. The mixture was poured into saturated aqueous ammonium chloride (50 ml), extracted with ether (3 × 50 ml), and the extract washed with 2M sodium hydroxide (2 × 40 ml) and saturated sodium chloride (50 ml), and dried (Na$_2$SO$_4$). Isolation depended upon the olefin being prepared. Isomer ratios were determined by n.m.r. and g.l.c.[63] analysis.

Low Boiling Alkenes. The reaction was carried out as described above but the work-up was carried out by adding 2M sodium hydroxide (75 ml) stirring the mixture at room temperature for 0.25 h warming the reaction flask; the product was condensed with a solid CO$_2$–acetone condenser. Attempts to remove the THF by dilution with tetralin, copious washing with water, and subsequent distillation resulted in the alkene being contaminated with THF. The best general method of purifying the alkenes was found to be by converting them into their dibromides and then distilling, recrystallising, or washing these; subsequent reaction with zinc in an alcoholic solvent regenerated the olefin.[64] Although ethanol was the usual choice of alcohol, the use of butanol was found to be advantageous for the hexenes. Fractional redistillation with tetralin chaser afforded the alkene. This method was used to prepare hex-1-ene (8; $R^1 = Bu$, $R^2 = R^3 = R^4 = H$) (0.49 g, 58%), b.p. 62—63 °C (lit.,[57] 64 °C), n.m.r. and i.r. identical with literature;[65–67] hex-2-ene (8; $R^1 = Pr$, $R^3 = Me$, $R^2 = R^4 = H$ or $R^3 = H$, $R^4 = Me$) (0.62 g, 74%), b.p. 66—68 °C (lit.,[57] 67—69 °C) as a 1:1 mixture of *E*- and *Z*-isomers (by n.m.r.†), i.r. and n.m.r. identical with literature;[65,66] 2-methylbut-2-ene (8; $R^1 = R^3 = R^4 =

---

* Previously reported as a viscous oil.[59]

† These were obtained prior to purification

Me, R^2 = H) (0.36 g, 51%), b.p. 34—39 °C (lit.,[57] b.p. 35—38 °C), i.r. and n.m.r. identical with literature;[65,66] and pent-1-ene (8; R^1 = Pr, R^2 = R^3 = R^4 = H) (0.45 g, 64%), b.p. 28—32 °C (lit.,[57] 29.9—30.1 °C), n.m.r. identical with literature.[65,66]

Other alkenes. The reaction was carried out as described above and the alkene was isolated by fractional distillation (yield was ±8% of that determined by g.c. analysis of the crude reaction mixture). Compounds prepared by this method were benzylidenecyclohexane [8; R^1 = Ph, R^2 = H, R^3, R^4 = –(CH$_2$)$_5$–] [0.71 g, 41% from (2; R^1 = Ph, R^2 = H) and 0.65 g, 38% from (2; R^1, R^2 = –(CH$_2$)$_5$–], b.p. 110—115 °C/3 mmHg (lit.,[68] 83 °C/1 mmHg), identical with a sample (t.l.c., n.m.r., i.r.) prepared by the literature procedure;[69] 3,3-dimethyl-1-phenyl-but-1-ene (8; R^1 = Bu^t, R^2 = H, R^3 or R^4 = Ph, R^4 or R^3 = H) (0.51 g, 32%) as an oil and a *ca.* 1:1 mixture of *E*- and *Z*-isomers, identical with literature;[70] 1,1-diphenylethene (8; R^1 = R^2 = H, R^3 = R^4 = Ph) (1.28 g, 71%, 78% when isolated as the dibromide), b.p. 138—146 °C (bath temperature)/15 mmHg (lit.,[57] 270—271 °C), i.r. and n.m.r. identical with literature;[64,65] 1,2-diphenylethene (8; R^1 = R^3 or R^4 = Ph; R^2 = R^4 or R^3 = H) (1.37 g, 76%; 84% when isolated as the dibromide) as a 1:1 mixture of the *E*- and *Z*- isomers which were separated by p.l.c. (cyclohexane), and gave i.r. and n.m.r. spectra identical with the literature;[65,66] 1,1-diphenylhex-1-ene[71] (8; R^1 = Bu, R^2 = H, R^3 = R^4 = Ph) as an oil (1.75 g, 74%); 1,1-diphenylprop-1-ene[72,73] (8; R^1 = Me, R^2 = H, R^3 = R^4 = Ph) as plates (1.55 g, 80%) b.p. 95—105 °C (bath temperature)/0.8 mmHg (lit.,[68] 98—100 °C/1 mmHg), m.p. 50—51 °C (EtOH) (lit.,[68] m.p. 52 °C); 1,2-diphenylprop-1-ene (8; R^1 = Ph, R^2 = H, R^3 or R^4 = Ph, R^4 or R^3 = Me), isolated as the *E*-isomer (1.34 g, 69%), by treatment of the isomeric mixture with warm hydrogen bromide in acetic acid, m.p. 79—80 °C (EtOH) (lit.,[74] 81—82 °C), which gave spectra identical with the literature;[75] ethylidenecyclohexane [8; R^1 = Me, R^2 = H, R^3, R^4 = –(CH$_2$)$_5$–] as an oil (0.52 g, 47%), b.p. 85—95 °C (bath temperature)/15 mmHg (lit.,[68] b.p. 79—81 °C/10 mmHg) identical with an authentic sample[76] (n.m.r., i.r.); hept-2-ene (8; R^1 = Bu, R^2 = H, R^3 or R^4 = Me, R^4 or R^3 = H) and a 1:1 mixture of *E*-and *Z*-isomers (0.80 g, 82%), b.p. 93—105 °C (bath temperature) (lit.,[57] 98 °C);[65,66,77] methylenecyclohexane [8; R^1 = R^2 = H; R^3, R^4 = –(CH$_2$)$_5$–] (0.66 g, 69%), b.p. 95—105 °C (lit.,[78] b.p. 100—102 °C), identical with a sample (n.m.r., i.r., b.p.) prepared by a Wittig reaction;[79] 2-methylhept-2-ene[80] (8; R^1 = Bu, R^2 = H, R^3 = R^4 = Me) (0.68 g, 61%), b.p. 90—100 °C (bath temperature) (lit.,[67,81] b.p. 94.4—94.6 °C); 1-methyl-1-phenylethene (8; R^1 = R^2 = H, R^3 = Ph, R^4 = Me) (0.88 g, 83%), b.p. 52—60 °C/15 mmHg (lit.,[57] 165—169 °C) with spectra identical with the literature;[65,66] 2-methyl-1-phenylprop-1-ene (8; R^1 = Ph, R^2 = H, R^3 = R^4 = Me), [0.92 g, 70% from (12; R = Ph) and 0.62 g, 47% from (2; R^1 = R^2 = Me)], b.p. 64—72 °C (bath temperature)/15 mmHg (lit.,[68] 76—77 °C/11 mmHg) with spectra identical to literature;[82] non-4-ene (8; R^1 = Bu, R^2 = H, R^3 or R^4 = Pr, R^4 or R^3 = H) as a 1:1 mixture of *E*- and *Z*-isomers (0.98 g, 78%), b.p. 42—50 °C (bath temperature)/15 mmHg, [lit.,[68] 44—46 °C/12 mmHg (*E*-isomer) and 124.7 °C/400 mmHg (*Z*-isomer)] and gave spectra identical with the literature;[83] pentylidenecyclohexane [8; R^1 = Bu, R^2 = H, R^3, R^4 = –(CH$_2$)$_5$–] as an oil (0.78 g, 52%);[84] 1-phenylbut-1-ene (8; R^1 = Ph, R^2 = H, R^3 or R^4 = Pr, R^4 or R^3 = H) as a 1:1 mixture of *E*- and *Z*-isomers (1.24 g, 85%) and gave spectra identical with the literature;[85] 2-phenylbut-2-ene (8; R^1 = Me, R^2 = H, R^3 or R^4 = Ph, R^4 or R^3 = Me) as a 1:1 mixture of *E*- and *Z*-isomers (1.04 g, 79%), separated by p.l.c. (cyclohexane) which gave spectra identical with the literature;[86,87] phenylethene (8; R^1 = Ph, R^2 = R^3 = R^4 = H) [0.80 g, 77% from (12; R = H); 0.65 g, 62% from (2; R^1 = Ph, R^2 = H)], b.p. 143—150 °C (bath temperature) (lit.,[57] 145—146 °C), spectra identical with the

literature;[65,66] 2-phenylhept-2-ene (8; R^1 = Bu, R^2 = H; R^3 or R^4 = Ph, R^4 or R^3 = Me) as a 1:1 mixture of *E*- and *Z*-isomers (1.32 g, 76%) spectra identical with an authentic sample prepared by a Wittig reaction;[79] 1-phenylhex-1-ene (8; R^1 = Bu, R^2 = R^3 or R^4 = H, R^4 or R^3 = Ph) (1.38 g, 86%) as a 1:1 mixture of *E*- and *Z*-isomers, spectra identical with the literature;[88] 1-phenylprop-1-ene (8; R^1 = Ph, R^2 = R^3 or R^4 = H, R^4 or R^3 = Me) as a 1:1 mixture of *E*- and *Z*-isomers [0.89 g, 75% from (12; R = Me) and 0.84 g, 71% from (12; R = Ph)];[57,65,66] and 1,1,2-triphenylethene (8; R^1 = R^3 = R^4 = Ph, R^2 = H) (1.51 g, 59%), m.p. 71—72 °C (EtOH) (lit.,[68] 72—73 °C), identical (m.p., mixed m.p., n.m.r., i.r.) with an authentic sample.[89]

Preparations of Vinyl Sulphides (9).—*Method A* Butyl-lithium (1.4M solution in hexane; 7.15 ml, 10 mmol) was added to phenylthiotrimethylsilylmethane[26] (12; R = H) (1.96 g, 10 mmol) in THF (25 ml) at 0 °C. After 0.5 h, the carbonyl compound (10 mmol) was added. The mixture was allowed to warm to room temperature overnight, poured into saturated aqueous ammonium chloride (50 ml) and extracted with ether (3 × 25 ml). The combined extracts were washed with 2M-aqueous sodium hydroxide (30 ml), saturated aqueous sodium chloride (30 ml), dried (Na$_2$SO$_4$), and evaporated under reduced pressure to give, after column chromatography, the vinyl sulphide (9). Compounds prepared by this method were: 2,3-*dimethyl*-1-*phenylthiobut*-1-*ene* (9; R^1 = H, R^2 or R^3 = Me, R^3 or R^2 = Pr^i)(1.31 g, 68%) as an oil (Found: C, 75.1; H, 8.35. C$_{12}$H$_{16}$S requires C, 74.9; H, 8.4%); ν$_{max.}$ (CHCl$_3$) 1 600 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.15 (5 H, br s, Ph), 5.90 and 5.75 (1 H, 2 br s, ratio *ca* 1:1, CH=), 2.5—2.0 (1 H, m, CHCO), 1.75 (3 H, br s, COMe), and 1.0 (6 H, 2 overlapping d, J 8 Hz, CHMe$_2$); m/z 192 (16%, M^+) and 109 (100, PhS$^+$); 2,2-diphenyl-1-phenyl-thioethene (9; R^1 = H, R^2 = R^3 = Ph) (2.36 g, 82%) as rhomboids, m.p. 71—73 °C (light petroleum) (lit.,[37] 71—73 °C), ν$_{max.}$ (CHCl$_3$) 1 595 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.35 and 7.15 (15 H, 2 br s, Ph's) and 6.74 (1 H, s, CH=C); 2-*ethyl*-1-*phenylthiobut*-1-*ene* (9; R^1 = H, R^2 = R^3 = Et) (1.36 g, 71%) as an oil (Found: C, 75.1; H, 8.3. C$_{12}$H$_{16}$S requires C, 74.9; H, 8.4%); ν$_{max.}$ (CHCl$_3$) 1 595 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.1 (5 H, br s, Ph), 5.8 (1 H, br s, CH=C), 2.25 (4 H, q, J 8 Hz, CH$_2$'s), and 1.0 (6 H, 2 overlapping t, J 8 Hz, Me's); m/z 192 (15%, M^+), 109 (100, PhS$^+$); 2-methyl-1-phenylthioprop-1-ene[90] (9; R^1 = H, R^2 = R^3 = Me) (1.02 g, 62%) as an oil, n.m.r. identical with the literature;[91] phenylthioethene (9; R^1 = R^2 = R^3 = H), identical with an authentic sample;[26] 1-phenylthiohept-1-ene (9; R^1 = H, R^2 or R^3 = C$_5$H$_{11}$, R^3 or R^2 = H) (1.30 g, 63%) as an oil, spectra identical with the literature;[92,93] 1-phenylthiohex-1-ene (9; R^1 = H, R^2 or R^3 = Bu, R^3 or R^2 = H) (1.29 g, 67%) as an oil comprising a 1:1 mixture of isomers, identical with the literature;[94,95] (phenylthiomethylene)cyclohexane (9; R^1 = H, R^2, R^3 = –(CH$_2$)$_5$–) (1.33 g, 65%) which gave spectra identical with the literature;[37] (phenylthiomethylene)cyclopentane [9; R^1 = H, R^2, R^3 = –(CH$_2$)$_4$–] (1.14 g, 60%) which gave spectra identical with the literature;[22] 1-phenylthionon-1-ene[96] (9; R^1 = H, R^2 or R^3 = C$_7$H$_{15}$; R^3 or R^2 = H) as an oil (Found: C, 76.6; H, 9.2. C$_{15}$H$_{22}$S requires C, 76.9; H, 9.45%); ν$_{max.}$ (CHCl$_3$) 1 590 (Ar C=C) cm^{-1}; δ(CDCl$_3$) 7.4—7.0 (5 H, m, Ph), 6.1—5.7 (2 H, m, CH=CH), and 2.3—0.7 (15 H, m, alkyl); 1-phenylthio-2-phenylethene (9; R^1 = H, R^2 or R^3 = Ph, R^3 or R^2 = H) (1.51 g, 71%) identical with the literature;[37,97] 1-phenylthio-2-phenylprop-1-ene[98,99] (9; R^1 = H, R^2 or R^3 = Ph, R^3 or R^2 = Me) (1.42 g, 63%) as an oil, ν$_{max.}$ (CHCl$_3$) 1 595 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.9—6.9 (10 H, m, Ph's), 6.55 and 6.17 (1 H, m's, CH=C), and 2.08 (3 H, br s, C=CMe); and 1-phenylthiopro-1-ene (9; R^1 = H, R^2 or R^3 = Me, R^3 or R^2 = H) (0.87 g, 58%) identical with the literature.[97]

Alternative method. Butyl-lithium (1.4M solution in hexane;

7.1 ml, 10 mmol) was added to the silane (**12**; R = H or Ph) (10 mmol) in TMEDA (1.89 ml, 1.45 g, 12.5 mmol) at 0 °C. After being stirred for 1 h, the carbonyl compound (10 mmol) was added. The mixture was stirred for a further 1 h, poured into saturated aqueous ammonium chloride (50 ml), extracted with ether (3 × 30 ml), and the combined extract washed with saturated aqueous sodium chloride (50 ml), dried (Na_2SO_4), and evaporated under reduced pressure to give, after column chromatography, the vinyl sulphide (**9**). Compounds prepared by this method were: 2,2-diphenyl-1-phenylthioethene (**9**; R^1 = H, $R^2 = R^3$ = Ph) (2.25 g, 78%); phenylthioethene (**9**; R^1 = $R^2 = R^3$ = H) (0.86 g, 63%); 1-phenylthiohept-1-ene (**9**; R^1 = H, R^2 or R^3 = C_5H_{11}, R^3 or R^2 = H) (1.45 g, 71%); (phenylthiomethylene)cyclohexane [**9**; R^1 = H, R^2, R^3 = –$(CH_2)_5$–] (1.31 g, 68%); 1-phenylthio-2-phenylethene (**9**; R^1 = H, R^2 or R^3 = Ph, R^3 or R^2 = H) (1.57 g, 74%) and 1-phenylthio-2-phenylprop-1-ene (**9**; R^1 = H, R^2 or R^3 = Ph, R^3 or R^2 = Me) (1.99 g, 69%); all identical (n.m.r., i.r., t.l.c.) with the samples prepared above. Also prepared by this method were: 1,2-diphenyl-1-phenylthioethene (**9**; R^1 = Ph, R^2 or R^3 = Ph, R^3 or R^2 = H) (1.53 g, 53%), identical with an authentic sample;[100] 1-phenyl-1-phenylthioethene (**9**; R^1 = Ph, R^2 = R^3 = H) (1.51 g, 71%), m.p. 51—53 °C (light petroleum) (lit.,[101] 53—54 °C) which gave spectra identical with the literature;[102] 1-*phenyl*-1-*phenylthiohex*-1-*ene* (**9**; R^1 = Ph, R^2 or R^3 = Bu, R^3 or R^2 = H) (1.69 g, 63%) as an oil (Found: C, 80.8; H, 7.3. $C_{18}H_{20}S$ requires C, 80.55; H, 7.5%; $v_{max.}$ (CHCl$_3$) 1 680 (C=C) and 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.7—7.0 (10 H, m, Ph's), 6.8 (1 H, m, CH=C), and 2.4—0.8 (9 H, m, alkyls); m/z 268 (50%, M^+) and 77 (100, Ph$^+$); and *phenyl*(*phenylthiomethylene*)*cyclohexane* [**9**; R^1 = Ph, R^2, R^3 = –$(CH_2)_5$–] (1.32 g, 47%) as a waxy solid (Found: C, 81.45; H, 6.9. $C_{19}H_{20}S$ requires C, 81.4; H, 7.2%); $v_{max.}$ (CHCl$_3$) 1 590 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—6.9 (10 H, m, Ph's) and 2.6—1.2 (10 H, m, CH$_2$'s); m/z 280 (6%, M^+) and 77 (100, Ph$^+$).

Method B. Formation of the required anions (**10**) and subsequent condensation with a carbonyl compound was carried out as previously described.[15] Compounds prepared by this method were: 2,2-diphenyl-1-phenylthioethene (**9**; R^1 = H, $R^2 = R^3$ = Ph)(2.10 g, 73%[15]) identical with the sample prepared by method A; 1,1-*diphenyl*-2-*phenylthiohex*-1-*ene* (**9**; R^1 = Bu, $R^2 = R^3$ = Ph) (2.10 g, 61%[15]) as an oil (Found: C, 83.3; H, 7.25. $C_{24}H_{24}S$ requires C, 83.7; H, 7.0%); $v_{max.}$ (CHCl$_3$) 1 585 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—6.9 (15 H, m, Ph's) and 2.6—0.9 (9 H, m, alkyls); m/z 344 (11%, M^+) and 77 (100, Ph$^+$); 5-*phenylthiodec*-5-*ene* (**9**; R^1 = Bu, R^2 or R^3 = Bu, R^3 or R^2 = H) (1.44 g, 58%[15]) as an oil (Found: C, 77.6; H, 9.5. $C_{16}H_{24}S$ requires C, 77.35; H, 9.7%); $v_{max.}$ (CHCl$_3$) 1 600 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.2 (5 H, br s, Ph), 6.9—6.5 (1 H, m, CH=C), and 2.8—0.8 (18 H, m, alkyls); m/z 248 (3%, M^+) and 109 (31, PhS$^+$); 1-phenylthiohept-1-ene (**9**; R^1 = H, R^2 or R^3 = C_5H_{11}, R^3 or R^2 = H) (1.55 g, 75%), identical with the sample prepared by method A; 2-*phenylthiohept*-2-*ene* (**9**; R^1 = Me, R^2 or R^3 = Bu, R^3 or R^2 = H) (1.30 g, 63%) as an oil (Found: C, 75.65; H, 8.65. $C_{13}H_{18}S$ requires C, 75.7; H, 8.8%); $v_{max.}$ (CHCl$_3$) 1 660 (C=C) and 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.1 (5 H, br s, Ph), 6.4—5.9 (1 H, m, CH=C), and 2.5—0.8 (12 H, m overlaid with a br s at 2.1, alkyls); m/z 206 (82%, M^+) and 109 (100, PhS$^+$); 2-phenylthiohex-1-ene (**9**; R^1 = Bu, $R^2 = R^3$ = H) (1.36 g, 71%[15]) identical to an authentic sample;[97] (phenylthiomethylene)cyclohexane [**9**; R^1 = H, R^2, R^3 = –$(CH_2)_5$–] (1.24 g, 61%[15]) identical to that prepared by method A; (1-*phenylthiopentylidene*)*cyclohexane* [**9**; R^1 = Bu, R^2, R^3 = –$(CH_2)_5$–] (1.33 g, 51%[15]) as an oil (Found: C, 78.2; H, 9.55. $C_{17}H_{24}S$ requires C, 78.4; H, 9.3%); $v_{max.}$ (CHCl$_3$) 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.6—7.0 (5 H, m, Ph) and 2.8—0.8 (19 H, m, alkyls); m/z 260 (21%, M^+) and 109 (100, PhS$^+$); 1-phenylthio-2-phenylethene (**9**; R^1 = H, R^2 or R^3 = Ph, R^3 or R^2 = H) (1.48

g, 70%[15]), identical with that prepared by method A and 2-*phenylthio*-1-*phenylhex*-1-*ene* (**9**; R^1 = Bu, R^2 or R^3 or R^3 = Ph, R^3 or R^2 = H) (1.77 g, 66%[15]) as an oil (Found: C, 80.2; H, 7.2. $C_{18}H_{20}S$ requires C, 80.55; H, 7.5%); $v_{max.}$ (CHCl$_3$) 1 590 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.7—7.0 (10 H, m, Ph's) 6.9—6.7 (1 H, m, CH=C), and 2.6—0.9 (9 H, m, alkyls); m/z 268 (16%, M^+).

Method C. 1-Phenylthio-1-trimethylsilylethene[26] (**11**) (1.35 g, 10 mmol) in ether (50 ml) was added to the alkyl-lithium (12.5 mmol) and TMEDA (2.27 ml, 1.74 g, 15 mmol) in ether (10 ml) at 0 °C over 2 h. The reaction mixture was stirred for 0.5 h at 0 °C and the carbonyl compound (12.5 mmol) added. After warming 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_2SO_4), and evaporated under reduced pressure to give, after column chromatography, the vinyl sulphide (**9**). Compounds prepared by this method were: 1,3-diphenyl-2-phenylthioprop-1-ene (**9**; R^1 = PhCH$_2$, R^2 or R^3 = Ph, R^3 or R^2 = H) (1.54 g, 51%) which gave spectra identical with the literature;[59] (1-*phenylthiohexylidene*)*cyclo*-*hexane* [**9**; R^1 = C_5H_{11}, R^2, R^3 = –$(CH_2)_5$–] (1.37 g, 50%) as an oil (Found: C, 78.9; H, 9.3. $C_{18}H_{26}S$ requires C, 78.8; H, 9.55%); $v_{max.}$ (CHCl$_3$) 1 590 cm^{-1}(Ar C=C); δ(CDCl$_3$) 7.7—7.0 (5 H, m, Ph) and 2.9—0.8 (21 H, m, alkyls); 3-*phenylthio-oct*-3-*ene* (**9**; R^1 = Et, R^2 or R^3 = Bu, R^3 or R^2 = H)(1.32 g, 60%) as an oil (Found: C, 76.65; H, 8.9. $C_{14}H_{20}S$ requires C, 76.3; H, 9.15%); $v_{max.}$ (CHCl$_3$) 1 670 (C=C) and 1 590 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.4—7.0 (5 H, m, Ph), 6.2—5.8 (1 H, m, CH=C), and 2.8—0.7 (14 H, m, alkyls); m/z 220 (28%, M^+); 3-*phenylthio-oct*-2-*ene* (**9**; R^1 = C_5H_{11}, R^2 or R^3 = Me, R^3 or R^2 = H) (1.03 g, 47%) as an oil (Found: C, 76.0; H, 9.3. $C_{14}H_{20}S$ requires C, 76.3; H, 9.15%); $v_{max.}$ (CHCl$_3$) 1 585 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.6—7.1 (5 H, m, Ph), 6.1—5.9 (1 H, m, CH=C), and 2.8—0.8 (14 H, m overlaid with a br s at 1.8, alkyls); m/z 220 (49%, M^+) and 109 (100, PhS$^+$); 2-phenylthio-1-phenylbut-1-ene[23,103] (**9**; R^1 = Et, R^2 or R^3 = Ph, R^3 or R^2 = H) (1.56 g, 65%) as an oil; (1-*phenylthio*-2-*phenylethylidene*)*cyclohexane* [**9**; R^1 = PhCH$_2$, R^2, R^3 = –$(CH_2)_5$–] (1.12 g, 38%) as an oil (Found: C, 81.9; H, 7.7. $C_{20}H_{22}S$ requires C, 81.6; H, 7.5%); $v_{max.}$ (CHCl$_3$) 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—6.9 (10 H, m, Ph's), 3.9—3.7 (2 H, 2 br s, PhC*H*$_2$C=), and 2.8—1.4 (10 H, m, CH$_2$'s); m/z 294 (16, M^+) and 91 (100, C$_7$H$_7$$^+$); 2-*phenylthio*-1-*phenylhept*-2-*ene* (**9**; R^1 = PhCH$_2$, R^2 or R^3 = Bu, R^3 or R^2 = H) (1.38 g, 49%) as an oil (Found: C, 80.9; H, 7.9. $C_{19}H_{22}S$ requires C, 80.8; H 7.85%); $v_{max.}$ 1 585 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.7—7.1 (10 H, m, Ph's), 7.1—6.9 (1 H, m, CH=C), 3.8—3.6 (2 H, 2s, PhC*H*$_2$C=), and 2.6—1.0 (9 H, m, alkyls); m/z 282 (21%, M^+) and 91 (100, C$_7$H$_7$$^+$); 2-*phenylthio*-1-*phenylhept*-1-*ene* (**9**; R^1 = C_5H_{11}, R^2 or R^3 = Ph, R^3 or R^2 = H) (1.72 g, 61%) as an oil (Found: C, 81.0; H, 7.6. $C_{19}H_{22}S$ requires C, 80.8; H, 7.85%); $v_{max.}$ (CHCl$_3$) 1 590 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.6—7.1 (10 H, m, Ph's), 6.9—6.7 (1 H, m, CH=C), and 2.8—0.9 (11 H, m, alkyls); m/z 282 (21%, M^+); 3-*phenylthio*-2-*phenyloct*-2-*ene* (**9**; R^1 = C_5H_{11}, R^2 or R^3 = Ph, R^3 or R^2 = Me) (1.28 g, 43%) as an oil (Found: C, 81.15; H, 7.9. $C_{20}H_{24}S$ requires C, 81.0; H, 8.15%); $v_{max.}$ (CHCl$_3$) 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.8—7.0 (10 H, m, Ph's) and 2.8—0.9 (14 H, m overlaid with a br s at 1.7, alkyls); m/z 296 (52%, M^+) and 109 (100, PhS$^+$) and 6-*phenylthioundec*-5-*ene* (**9**; R^1 = C_5H_{11}, R^2 or R^3 = Bu, R^3 or R^2 = H) (1.36 g, 52%) as an oil (Found: C, 77.7; H, 9.75. $C_{17}H_{26}S$ requires C, 77.8; H, 10.0%); $v_{max.}$ 1 650 (C=C) and 1 580 cm^{-1} (Ar C=C); δ(CDCl$_3$) 7.3 (5 H, br s, Ph), 6.6—6.4 (1 H, m, CH=C), and 2.8—0.8 (20 H, m, alkyls).

Preparations of Vinyl Sulphones (**13**).—Butyl-lithium (1.4M solution in hexane; 7.15 ml, 10 mmol) was added to the α-silyl sulphone (**15**) [prepared by oxidation of the corresponding sulphide (**12**) with 2 equiv. of *m*-chloroperbenzoic

acid [13,14,46] (10 mmol) in THF (or DME) (15 ml) at 0 °C. After 0.5 h, the carbonyl compound (10 mmol) was added and mixture warmed to room temperature overnight. The reaction mixture was poured into saturated aqueous ammonium chloride (50 ml), extracted with ether (3 × 30 ml), and the extract washed with saturated aqueous sodium chloride (30 ml), dried (Na$_2$SO$_4$), and evaporated under reduced pressure to give, after column chromatography, the vinyl sulphone (13). Compounds prepared by this method were: 1,2-diphenyl-1-phenylsulphonylethene (13; R^1 = Ph, R^2 or R^3 = Ph, R^3 or R^2 = H) (2.62 g, 82%) which gave spectra identical with the literature;[104,105] 2,2-diphenyl-1-phenylsulphonylethene (13; R^1 = H, R^2 = R^3 = Ph) (2.27 g, 71%) as rhomboids, m.p. 113—114 °C (EtOH) (lit.,[106] m.p. 114—115 °C), spectra identical to literature;[105] 1,2-diphenyl-1-phenylsulphonylprop-1-ene (13; R^1 = Ph, R^2 or R^3 = Ph, R^3 or R^2 = Me) (2.17 g, 65%) as a waxy solid (Found: C, 75.25; H, 5.7. C$_{21}$H$_{18}$O$_2$S requires C, 75.4; H, 5.4%); ν$_{max.}$ (CHCl$_3$) 1 620 (C=C), 1 320, and 1 160 cm^{-1} (SO$_2$); δ(CDCl$_3$) 8.3—6.9 (15 H, m, Ph's) and 1.98 (3 H, 2 s, Me); m/z 77 (100%, Ph$^+$); 2-ethyl-1-phenylsulphonylbut-1-ene (13; R^1 = H, R^2 = R^3 = Et) (1.34 g, 60%) as an oil (Found: C, 64.0; H, 7.5. C$_{12}$H$_{16}$O$_2$S requires C, 64.25; H, 7.2%), ν$_{max.}$ (CHCl$_3$) 1 620 (C=C), 1 320 and 1 160 cm^{-1} (SO$_2$); δ(CDCl$_3$) 8.2—6.9 (6 H, m, Ph and CH=C) and 1.7—0.8 (10 H, m, alkyls); m/z 224 (4%, M$^+$) and 77 (100, Ph$^+$); 2-methyl-3-phenyl-sulphonyloct-2-ene (13; R^1 = C$_5$H$_{11}$, R^2 = R^3 = Me) (0.90 g, 34%) as an oil (Found: C, 67.95; H, 8.5. C$_{15}$H$_{22}$O$_2$S requires C, 67.6; H, 8.3%); ν$_{max.}$ (CHCl$_3$) 1 625 (C=C), 1 320, and 1 160 cm^{-1} (SO$_2$); δ(CDCl$_3$) 8.2—6.9 (5 H, m, Ph), 2.8—0.8 (17, m, alkyls); 2-methyl-1-phenylsulphonylprop-1-ene (13; R^1 = H, R^2 = R^3 = Me) (1.47 g, 75%) identical with an authentic sample;[106] 2-phenylsulphonylbut-2-ene (13; R^1 = Me, R^2 or R^3 = Me, R^3 or R^2 = H) (0.94 g, 48%) identical properties to literature;[105,107] phenylsulphonylethene (13; R^1 = R^2 = R^3 = H) (1.46 g, 87%), m.p. 67—68 °C (EtOH) (lit.,[108] 66.5—68 °C), spectra identical with the literature;[109] (1-phenylsulphonylethylidene)cyclohexane [13; R^1 = Me, R^2, R^3 = –(CH$_2$)$_5$–] (0.80 g, 32%; 0.98 g, 39% with DME as solvent) as an oil (Found: C, 67.6; H, 7.45. C$_{14}$H$_{18}$O$_2$S requires C, 67.2; H, 7.25%); ν$_{max.}$ (CHCl$_3$) 1 620 (C=C), 1 320, and 1 160 cm^{-1} (SO$_2$); δ(CDCl$_3$) 8.2—7.2 (5 H, m, Ph) and 2.8—1.2 (13 H, m overlaid with s at 1.75, alkyls); m/z 250 (8%, M$^+$) and 77 (100, Ph$^+$); 1-phenylsulphonylhept-1-ene[110] (13; R^1 = H, R^2 or R^3 = C$_5$H$_{11}$, R^3 or R^2 = H) (1.74 g, 73%; 1.88 g, 79% with DME as solvent) as an oil; ν$_{max.}$ (CHCl$_3$) 1 620 (C=C), 1 320, and 1 160 cm^{-2} (SO$_2$) δ(CDCl$_3$) 8.2—7.2 (5 H, m, Ph), 6.0—5.2 (2 H, m, CH=CH), and 2.5—0.8 (11 H, m, alkyls); m/z no M$^+$, 125 (37%), 84 (100, C$_6$H$_{12}^+$) and 77 (52, Ph$^+$); 1-phenylsulphonylhex-1-ene (13; R^1 = H, R^2 or R^3 = Bu, R^3 or R^2 = H) (1.90 g, 85%; 1.99 g, 89% with DME as solvent) as an oil (Found: C, 64.55; H, 7.2. C$_{12}$H$_{16}$O$_2$S requires C, 64.25; H, 7.2%); ν$_{max.}$ (CHCl$_3$) 1 625 (C=C) 1 320, and 1 160 cm^{-1} (SO$_2$); δ(CDCl$_3$) 8.2—7.2 (5 H, m, Ph), 6.0—5.1 (2 H, m, CH–CH), and 2.5—0.8 (9 H, m, alkyls); m/z, no M$^+$, 77 (100, Ph$^+$); (1-phenylsulphonylhexenyl)cyclohexane [13; R^1 = C$_5$H$_{11}$, R^2, R^3 = –(CH$_2$)$_5$–] (0.58 g, 19%; 0.70 g, 23% with DME as solvent) as an oil (Found: C, 70.9; H, 8.6. C$_{18}$H$_{26}$O$_2$S requires C, 70.55; H, 8.55%); ν$_{max.}$ (CHCl$_3$) 1 615 (C=C) 1 320, and 1 160 cm^{-1} (SO$_2$); δ(CDCl$_3$) 8.0—7.2 (5 H, m, Ph) and 2.9—0.8 (21 H, m, alkyls); (phenylsulphonyl-methylene)cyclohexane[47] [13; R^1 = H, R^2, R^3 = –(CH$_2$)$_5$–] (1.96 g, 83%; 2.03 g, 86% with DME as solvent) as an oil (Found: C, 66.3; H, 6.5. Calc. for C$_{13}$H$_{16}$O$_2$S: C, 66.1; H, 6.8%); ν$_{max.}$ (CHCl$_3$) 1 625 (C=C) 1 320 and 1 160 (SO$_2$) cm^{-1}; δ(CDCl$_3$) 8.1—7.3 (5 H, m, Ph), 5.2 (1 H, br s, CH=C), and 2.5—1.3 (10 H, m, CH$_2$'s); m/z 236 (1%, M$^+$) and 77 (100, Ph$^+$); (phenylsulphonylmethylene)cyclopentane [13; R^1 = H; R^2, R^3 = –(CH$_2$)$_4$–] (1.13 g, 51%) as an oil (Found: C, 65.0; H, 6.5. C$_{12}$H$_{14}$O$_2$S requires C, 64.8; H, 6.35%); ν$_{max.}$ (CHCl$_3$) 1 620

(C=C), 1 320, and 1 160 cm^{-1} (SO$_2$); δ(CDCl$_3$) 8.2—7.3 (5 H, m, Ph), 5.3 (1 H, s, CH=C), and 2.6—1.3 (8 H, m, CH$_2$'s); m/z 222 (2%, M$^+$) and 77 (100, Ph$^+$); 1-phenylsulphonyl-1-phenylethene (13; R^1 = Ph, R^2 = R^3 = H) (1.71 g, 70%) identical with an authentic sample prepared by oxidation of the sulphide (9; R^1 = Ph, R^2 = R^3 = H);[111] 1-phenylsulphonyl-2-phenylethene (13; R^1 = H, R^2 or R^3 = Ph, R^3 or R^2 = H) (1.93 g, 79%; 2.03 g, 83% with DME as solvent), identical properties to literature;[105,112,113] 2-phenylsulphonyl-1-phenylhept-1-ene (13; R^1 = C$_5$H$_{11}$, R^2 or R^3 = Ph, R^3 or R^2 = H) (2.07 g, 66%) as an oil (Found: C, 72.65; H, 6.9. C$_{19}$H$_{22}$O$_2$S requires C, 72.6; H, 7.05%); ν$_{max.}$ (CHCl$_3$) 1 620 (C=C), 1 320, and 1 160 cm^{-1} (SO$_2$) δ(CDCl$_3$) 8.2—7.2 (10 H, m, Ph's), 6.8—6.5 (1 H, m, CH=C), and 2.6—0.9 (11 H, m, alkyls); m/z 77 (100%, Ph$^+$); 1-phenylsulphonyl-1-phenylhex-1-ene (13; R^1 = Ph, R^2 or R^3 = Bu, R^3 or R^2 = H) (1.83 g, 61%) as an oil (Found: C, 71.7; H, 6.9. C$_{18}$H$_{20}$O$_2$S requires C, 72.0; H, 6.7%); ν$_{max.}$ (CHCl$_3$) 1 625 (C=C), 1 320, and 1 160 cm^{-1} (SO$_2$); δ(CDCl$_3$), 8.3—7.2 (10 H, m, Ph's), 6.7—6.5 (1 H, m, CH=C), and 2.8—0.9 (9 H, m, alkyls); m/z 300 (2%, M$^+$) and 77 (100, Ph$^+$); [(phenylsulphonyl)phenyl-methylene]cyclohexane [13; R^1 = Ph, R^2, R^3 = –(CH$_2$)$_5$–] (0.72 g, 23%; 0.68 g, 25% with DME as solvent) as a waxy solid (Found: C, 73.3; H, 6.8. C$_{19}$H$_{20}$O$_2$S requires C, 73.05; H, 6.45%); ν$_{max.}$ 1 615 (C=C), 1 325, and 1 160 cm^{-1} (SO$_2$); δ(CDCl$_3$) 8.3—7.1 (10 H, m, Ph's) and 2.7—1.4 (10 H, m, CH$_2$'s); 1-phenylsulphonyl-2-phenylprop-1-ene (13; R^1 = H, R^2 or R^3 = Ph, R^3 or R^2 = Me) (1.75 g, 68%) which gave spectra identical to the literature;[105] 2-phenylsulphonyl-1-phenylprop-1-ene (13; R^1 = Me, R^2 or R^3 = Ph, R^3 or R^2 = H) (1.91 g, 74%; 2.01 g, 78% with DME as solvent) which gave spectra identical with the literature;[114,115] 1-phenylsulphonyl-prop-1-ene (13; R^1 = H, R^2 or R^3 = Me, R^3 or R^2 = H) (1.47 g, 81%) which gave spectra identical with the literature;[105,107,108] 2-phenylsulphonylpropene (13; R^1 = Me, R^2 = R^3 = H) (1.16 g, 64%) identical with an authentic sample prepared from the sulphide (9; R^1 = Me, R^2 = R^3 = H);[116] and 6-phenylsulphonylundec-5-ene (13; R^1 = C$_5$H$_{11}$, R^2 or R^3 = Bu, R^3 or R^2 = H) (1.18 g, 40%; 1.23 g, 42% with DME as solvent) as an oil (Found: C, 69.6; H, 8.6. C$_{17}$H$_{26}$O$_2$S requires C, 69.35; H, 8.9%); ν$_{max.}$ (CHCl$_3$) 1 620 (C=C), 1 320, and 1 160 cm^{-1} (SO$_2$); δ(CDCl$_3$) 8.2—7.0 (5 H, m, Ph), 6.4—6.2 (1 H, m, CH=C), and 2.7—0.75 (20 H, m, alkyls).

References

1 D. J. Peterson, J. Org. Chem., 1968, 33, 780.

2 D. J. Ager, Synthesis, 1984, 384; E. W. Colvin, 'Silicon in Organic Synthesis,' Butterworths, London, 1981, pp. 142ff and references cited therein.

3 A. W. Johnson 'Ylid Chemistry,' Academic Press, New York, 1966; M. Schlosser, Top. Stereochem., 1970, 5, 1.

4 For example see S. L. Hartzell, D. F. Sullivan, and M. W. Rathke, Tetrahedron Lett., 1974, 1403; K. Taguchi, K. Shimoji, H. Yamamoto, and H. Nozaki, Bull. Chem. Soc., Jpn., 1974, 47, 2529.

5 P. F. Hudrlik and D. Peterson, Tetrahedron. Lett., 1974, 1133; J. Am. Chem. Soc., 1975, 97, 1464; P. F. Hudrlik, D. Peterson, and R. J. Rona, J. Org. Chem., 1975, 40, 2263.

6 G. L. Larson, J. A. Prieto, and A. Hernandez, Tetrahedron Lett., 1981, 22, 1575.

7 D. J. Peterson, J. Organomet. Chem., 1967, 9, 373.

8 L. F. Cason and H. G. Brooks, J. Org. Chem., 1954, 19, 1278; J. Am. Chem. Soc., 1952, 74, 4582; J. E. Mulvaney and Z. G. Gardlung, J. Org. Chem., 1965, 30, 917. See also G. R. Buell, R. Corriu, C. Guerin, and L. Spialter, J. Am. Chem. Soc., 1970, 92, 7424.

9 W. Dumont and A. Krief, Angew. Chem., Int. Ed. Engl., 1976, 15, 161.

10 H. Sakurai, K-i. Nishiwaki, and M. Kira, Tetrahedron Lett., 1973, 4193.

11 D. E. Seitz and A. Zapata, Tetrahedron Lett., 1980, 21, 3451.

12 Preliminary communication: D. J. Ager, Tetrahedron Lett., 1981, 22, 2923.

13 D. J. Ager, Chem. Soc. Rev., 1982, 11, 493.

14 D. J. Ager, *J. Chem. Soc., Perkin Trans. 1*, following paper.
15 D. J. Ager, *J. Org. Chem.*, 1984, **49**, 168.
16 D. Seebach, *Synthesis*, 1969, 17.
17 B.-T. Gröbel and D. Seebach, *Synthesis*, 1977, 357.
18 E. J. Corey and D. Seebach, *J. Org. Chem.*, 1966, **31**, 4097.
19 A. Fröling and J. F. Arens, *Recl. Trav. Chim.*, 1962, **81**, 1009.
20 G. Schill and C. Merkel, *Synthesis*, 1975, 387.
21 T. Mukaiyama, K. Narasaka, and M. Furusato, *J. Am. Chem. Soc.*, 1974, **94**, 8641.
22 P. Blatcher and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1074.
23 P. Blatcher, J. I. Grayson, and S. Warren, *J. Chem. Soc., Chem. Commun.*, 1976, 547.
24 P. Blatcher and S. Warren, *J. Chem. Soc., Chem. Commun.*, 1976, 1055.
25 D. J. Ager and R. C. Cookson, *Tetrahedron Lett.*, 1980, **21**, 1677.
26 D. J. Ager, *J. Chem. Soc., Perkin Trans. 1*, 1983, 1131.
27 D. J. Ager, *Tetrahedron Lett.*, 1980, **21**, 4763.
28 W. E. Truce and F. E. Roberts, *J. Org. Chem.*, 1963, **28**, 96 and references cited therein.
29 L. A. Paquette, K. A. Horn, and G. J. Wells, *Tetrahedron Lett.*, 1982, **23**, 259.
30 L. A. Paquette, G. J. Wells, and K. A. Horn, *Tetrahedron*, 1983, **39**, 913.
31 T. Cohen, J. P. Sherbine, J. R. Matz, R. R. Hutchings, B. M. McHenry, and P. R. Wiley, *J. Am. Chem. Soc.*, 1984, **106**, 3245.
32 T. Cohen and J. R. Matz, *Synth. Commun.*, 1980, **10**, 311.
33 P. J. Kocienski, *Tetrahedron Lett.*, 1981, **22**, 1559.
34 C. G. Screttas and M. Micha-Screttas, *J. Org. Chem.*, 1978, **43**, 1064 and C. G. Screttas and M. Micha-Screttas, *J. Org. Chem.*, 1979, **44**, 713.
35 C. Rucker, *Tetrahedron Lett.*, 1984, **25**, 4349.
36 A. B. Smith and P. J. Jerris, *J. Am. Chem. Soc.*, 1981, **103**, 194.
37 F. A. Carey and A. S. Court, *J. Org. Chem.*, 1972, **37**, 939.
38 D. J. Ager, *Tetrahedron Lett.*, 1981, **22**, 2803.
39 D. J. Ager, *Tetrahedron Lett.*, 1980, **21**, 4759.
40 D. J. Ager, *Tetrahedron Lett.*, 1981, **22**, 587.
41 D. J. Ager, *Tetrahedron Lett.*, 1983, **24**, 95.
42 F. A. Carey and O. Hernández, *J. Org. Chem.*, 1973, **38**, 2670.
43 A. G. Brook and D. G. Anderson, *Can. J. Chem.*, 1968, **46**, 2115.
44 E. Block, 'Reactions of Organosulphur Compounds,' Academic Press, New York, 1978.
45 K. Schank and F. Schroeder, *Justus Liebigs Ann. Chem.*, 1977, 1676.
46 D. J. Ager, *J. Chem. Soc., Chem. Commun.*, 1984, 486.
47 S. V. Ley and N. S. Simpkins, *J. Chem. Soc., Chem. Commun.*, 1983, 1281.
48 T. Durst in 'Comprehensive Organic Chemistry,' vol. 3., ed. D. H. R. Barton and W. D. Ollis, Pergamon, Oxford, 1979, pp. 197ff.
49 P. D. Magnus, *Tetrahedron*, 1977, **33**, 2019.
50 *e. g.* J. C. Philips and M. Oku, *J. Am. Chem. Soc.*, 1972, **94**, 1012; J. C. Philips and M. Oku, *J. Org. Chem.*, 1972, **37**, 4479; G. H. Posner and D. J. Brunelle, *Tetrahedron Lett.*, 1973, 935; M. Julia and J.-M. Paris, *Tetrahedron Lett.*, 1973, 4833; S. Fatutta and A. Risaliti, *J. Chem. Soc., Perkin Trans. 1*, 1974, 2387; J.-L. Fabre, M. Julia, and J.-N. Verpeaux, *Tetrahedron Lett.*, 1982, **23**, 2469; J. Bremner, J. Julia, M. Launay, and J.-P. Stacino, *Tetrahedron Lett.*, 1982, **23**, 3265; S. G. Pyne, D. C. Spellmeyer, S. Chen, and P. L. Fuchs, *J. Am. Chem. Soc.*, 1982, **104**, 5728; J. J. Eisch, J. E. Galle, and L. E. Hallenbeck, *J. Org. Chem.*, 1982, **47**, 1608; L. A. Paquette and G. D. Crouse, *J. Org. Chem.*, 1983, **48**, 141 and references cited therein.
51 *e. g.* G. Cardillo, D. Savoia, and A. Umani-Ronchi, *Synthesis*, 1975, 453; M. Mikolajczyk, S. Grzejszczak, W. Midura, and A. Zatorski, *Synthesis*, 1975, 278; W. E. Truce and M. J. Lusch, *J. Org. Chem.*, 1978, **43**, 2262; V. Fiandanese, G. Marchese, and F. Naso, *Tetrahedron Lett.*, 1978, 5131; Y. Ueno, H. Setoi, and M. Okawara, *Chem. Lett.*, 1979, 47; W. Böll, *Liebigs Ann. Chem.*, 1979, 1665; J. Hershberger and G. A. Russell, *Synthesis*, 1980, 475 and references cited therein.
52 M. Isobe, Y. Ichikawa, and T. Goto, *Tetrahedron Lett.*, 1981, **22**, 4287.
53 Y-C. Liu and T. I. Chang, *Hua Hsueh Hsueh Pao*, 1964, **30**, 197 (*Chem. Abstr.*, 1964, **61**, 8217e).
54 B. Wladislaw, P. R. Olivato, and O. Sala, *J. Chem. Soc. B*, 1971, 2037 and references cited therein.
55 E. Vedjs and P. L. Fuchs, *J. Org. Chem.*, 1971, **36**, 366.
56 K. Naraska, T. Sakashita, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 3724; see also reference 2 and papers cited therein.
57 Aldrich catalogue, 1984—85.
58 W. J. Criddle and C. P. Ellis in 'Qualitative Organic Chemical Analysis,' Butterworths, London 1967.
59 B. S. Ong, *Tetrahedron Lett.*, 1980, **21**, 4225.
60 L. F. Fieser and M. Fieser, 'Reagents for Organic Synthesis,' Wiley, New York, 1967, vol. 1, p. 570.
61 T. Cohen, W. M. Daniewski, and R. B. Weisenfeld, *Tetrahedron Lett.*, 1978, 4665; T. Cohen and R. B. Weisenfeld, *J. Org. Chem.*, 1979, **44**, 3601; T. Cohen and J. R. Matz, *J. Am. Chem. Soc.*, 1980, **102**, 6900.
62 D. J. Ager, *J. Organomet. Chem.*, 1983, **241**, 139.
63 W. E. Falconer and L. G. Walker, *J. Chromatog. Sci.*, 1971, **9**, 184.
64 D. E. Ames and R. E. Bowman, *J. Chem. Soc.*, 1951, 1079.
65 Aldrich Catalogue of Infrared Spectra, Aldrich Chemical Company, 1975.
66 Aldrich Catalogue of N.M.R. Spectra, Aldrich Chemical Company, 1974.
67 A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, 1961, **83**, 231.
68 'Dictionary of Organic Compounds,' 5th edn., Chapman and Hall, New York, 1982.
69 I. Elphimoff-Felkin and P. Sarada, *Org. Synth.*, 1977, **56**, 101; I. Elphimoff-Felkin and P. Sarada, *Tetrahedron Lett.*, 1972, 725.
70 E. V. Dehmlow and S. Barahona-Naranjo, *J. Chem. Res.*, 1981, (*S*), 142; (*M*) 1748.
71 M. T. Reetz and W. Stephan, *Angew. Chem., Int. Edn. Engl.*, 1977, **16**, 44.
72 E. J. Corey and G. T. Kwiatkowski, *J. Am. Chem. Soc.*, 1966, **88**, 5652.
73 H. A. Bruson and H. L. Plant, *J. Org. Chem.*, 1967, **32**, 3356.
74 M. Chaykovsky and E. J. Corey, *J. Org. Chem.*, 1960, **28**, 254.
75 M. Feldman, S. Danishefsky, and R. Levine, *J. Org. Chem.*, 1966, **31**, 4322.
76 G. W. Kabalka, D. T. C. Yang, and J. D. Baker, *J. Org. Chem.*, 1976, **41**, 574.
77 D. Savoia, C. Trombini, and A. Umani-Ronchi, *J. Chem. Soc., Perkin Trans. 1*, 1977, 123.
78 A. C. Cope and E. Ciganek, *Org. Synth.*, 1963, Coll. Vol. 4, 612.
79 G. Wittig and U. Schoellkopf, *Org. Synth.*, 1960, **40**, 66.
80 J. Barluenga, M. Yus, J. M. Concellon, and P. Bernard, *J. Chem. Res.* 1980, (*S*), 41; (*M*), 0677.
81 F. J. Soday and C. E. Boord, *J. Am. Chem. Soc.*, 1933, **55**, 3296.
82 L. Hevesi, J. B. Nagy, A. Krief, and E. G. Derouane, *Org. Magn. Reson.*, 1977, **10**, 14; U. Vogeli, D. Herz, and W. von Philipsborn, *Org. Magn. Reson.*, 1980, **13**, 200.
83 K. J. Kolonko and R. H. Shapiro, *J. Org. Chem.*, 1978, **43**, 1404.
84 M. Montury and J. Gore, *Tetrahedron Lett.*, 1980, **21**, 51.
85 M. T. H. Liu, G. E. Palmer, and N. H. Chishti, *J. Chem. Soc., Perkin Trans. 2*, 1981, 53.
86 K. B. Sharpless, M. W. Young, and R. F. Lauer, *Tetrahedron Lett.*, 1973, 1979 and references cited therein.
87 'Standard Spectra,' Sadtler Labs., Philadelphia.
88 H. Adkins and W. Zartman, *Org. Synth.*, 1943, Coll. Vol. 2, 606.
89 W. M. Moore and D. G. Peters, *J. Am. Chem. Soc.*, 1975, **97**, 139.
90 W. Ando, H. Higuchi, and T. Migita, *J. Org. Chem.*, 1977, **42**, 3365.
91 T. Aida, D. N. Harpp, and T. H. Chan, *Tetrahedron Lett.*, 1980, **21**, 3247.
92 G. H. Posner and P-W. Tang, *J. Org. Chem.*, 1978, **43**, 4131.
93 B. M. Trost and Y. Tanigawa, *J. Am. Chem. Soc.*, 1979, **101**, 4743.
94 H. Neumann and D. Seebach, *Chem. Ber.*, 1978, **111**, 2785.
96 S.-I. Murahashi, M. Yamamura, K.-i. Yanagisawa, N. Mita, and K. Kondo, *J. Org. Chem.*, 1979, **44**, 2408.
96 T. Shono, Y. Matsumura, and S. Kashimura, *Tetrahedron Lett.*, 1980, **21**, 1545.
97 S. H. Groen, R. M. Kellogg, J. Buter, and H. Wynberg, *J. Org. Chem.*, 1967, **33**, 2218 and references cited therein.
98 T. Mukaiyama, S. Fukuyama, and T. Kumamoto, *Tetrahedron Lett.*, 1968, 3787.
99 W. N. Weringa, *Tetrahedron Lett.*, 1969, 273.
100 E. Campaigne and J. R. Leal, *J. Am. Chem. Soc.*, 1954, **76**, 1272.
101 R. F. Brookes, J. E. Cranham, D. Greenwood, and H. A. Stevenson, *J. Sci. Food Agric.*, 1957, **8**, 561.
102 A. Behzadi and L. N. Owen, *J. Chem. Soc., Perkin Trans. 1*, 1974, 2287.
103 M. Sato, K. Takai, H. Oshima, and H. Nozaki, *Tetrahedron Lett.*, 1981, **22**, 1609.
104 R. P. Redman, P. J. Thomas, and C. J. M. Stirling, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1135.
105 A. Bongini and D. Savoia, *Org. Magn. Reson.*, 1977, **9**, 175 and references cited therein.
106 W. E. Truce and C. T. Goralski, *J. Org. Chem.*, 1970, **35**, 4220.

107 C. Y. Meyers and I. Sataty, *Tetrahedron Lett.*, 1972, 4323, and references cited therein.
108 W. E. Parham, F. D. Blake, and D. R. Theisson, *J. Org. Chem.*, 1962, **27**, 2415.
109 P. Carlier, Y. Gelas-Mialhe, and R. Vessiere, *Can. J. Chem.*, 1977, **55**, 3190.
110 E. I. Vasil'eva and R. Kh. Friedlind, *Izv. Akad. Nauk. SSSR Otd. Khim. Nauk.*, 1961, 1049 (*Chem. Abstr.*, 1961, **55**, 27008a).
111 J. R. Shelton and K. E. Davis, *Int. J. Sulfur Chem.*, 1973, **3**, 205.
112 W. E. Truce and C. T. Goralski, *J. Org. Chem.*, 1971, **36**, 2536.

113 M. Asscher and D. Vofsi, *J. Chem. Soc.*, 1964, 4962.
114 P. O. Ellingsen and K. Undheim, *Acta. Chem. Scand., Ser. B.*, 1979, **33**, 528.
115 K. Ankner, B. Lamm, and J. Simonet, *Acta. Chem. Scand., Ser. B*, 1977, **31**, 742.
116 N. K. Kul'brovskaya, E.P. Gracheva, and M. F. Shostakovskii, *Zh. Obshch. Khim.*, 1960, **30**, 81 (*Chem. Abstr.*, 1960, **54**, 20949h).