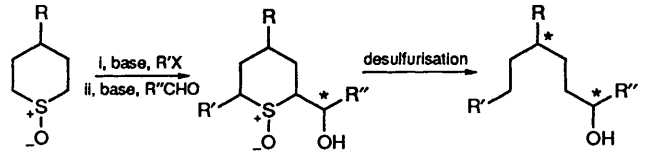
Stereoselective Synthesis using a Thiane Oxide System as a Disposable Template

Richard Armer, Michael J. Begley, Paul J. Cox, Andrew Persad and Nigel S. Simpkins*
Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, UK

Substitution of the thiane oxide **1**, *via* the corresponding α-sulfinyl carbanion, has been explored as a means of obtaining a range of functionalised products in stereoselective fashion. Whereas reaction of the α-sulfinyl carbanion derived from **1** with either MeI, BnBr or Me_3SiCl results in substitution *trans* to the sulfoxide oxygen, *e.g.*, to give **3–5**, acylation occurs in a stereocomplementary fashion to give keto sulfoxide products with the new substitutent *cis* to the sulfoxide oxygen. The change in stereochemical outcome is accompanied by an inversion of the thiane oxide ring conformation, as demonstrated by X-ray crystallography. Subsequent manipulation of the initially obtained products was also examined, *e.g.* involving desulfinylation or thiane ring opening, to give useful products, such as epoxides, in stereoselective fashion.

The use of six-membered ring templates for the stereocontrolled assembly of functionalised products is a well-established strategy in both carbocyclic and heterocyclic synthesis. One particular protocol which has been examined involves building up stereocentres onto a preformed sulfur-containing ring, the sulfur atom of which is subsequently excised, to give acyclic products.[1] Although the recent advances in 'acyclic stereocontrol' have substantially superseded such approaches, we were attracted by the generalised variant shown in Scheme 1 using six-membered sulfoxides (thiane oxides). Sequential regio- and stereo-controlled introduction of substituents around the thiane oxide ring, using sulfoxide carbanion chemistry (*e.g.* alkylation, acylation and aldol type reactions) as shown, followed by sulfur removal, should furnish useful functionalised products.

Our reasons for choosing to explore this apparently outmoded approach were threefold. Firstly, whilst the stereoelectronics of deprotonation and simple methylation of thiane oxide systems have been examined, relatively little synthetic exploration in this area has been carried out, *vide infra*. Secondly, the system promises a high degree of versatility, leading to a wide range of substituted cyclic and acyclic products following desulfurisation. Lastly, and most significantly, the sequence starts from a prochiral sulfoxide; the first step in the sequence involves breaking the symmetry of the molecule by deprotonation. *Consequently, racemic products obtained* via *the route shown in Scheme 1 are potentially available in non-racemic form by the use of a homochiral base in the initial step.*†,[2]



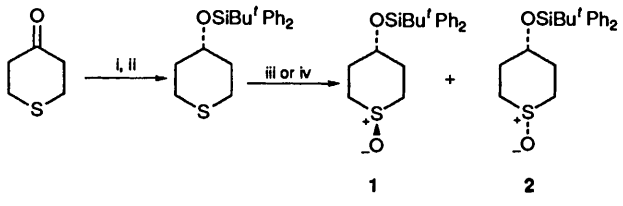
Scheme 1

Previously we described our preliminary explorations of the chemistry of one easily available thiane oxide system,[3,4] and in the present paper we report full details of our work in this area, *including revision of some of our initial stereochemical assignments* in the light of further spectroscopic studies and X-ray structure determinations.

Results and Discussion

The methylation of 4-*tert*-butylthiane oxides, using MeI, has been shown to proceed with good stereoselectivity, alkylation occurring predominantly or exclusively *trans* to the S=O bond.[5] The only other significant results in this area are those of Crumbie *et al.*, who have concentrated their efforts on the rather less well-behaved unsaturated cyclic sulfoxides.[6]

We chose to examine the chemistry of a protected thian-4-ol oxide system (R = OP, P = a suitable protecting group in Scheme 1), since additional functionality on the ring is synthetically attractive. The synthesis of protected hydroxy sulfoxide **1** from thian-4-one proved straightforward (Scheme 2). Sulfide oxidation with Oxone® or MCPBA gives the corresponding sulfoxide as a *ca.* 2–3:1 mixture of diastereoisomers. Subsequent explorations have been conducted using the major crystalline *trans*-isomer **1** rather than the oily *cis* compound **2**.



Scheme 2 *Reagents and conditions:* i, $NaBH_4$ (84%); ii, Bu^tPh_2SiCl, DMF, imidazole (98%); iii, MCPBA (90%) *trans*:*cis* (2:1); iv, Oxone®, MeOH, H_2O (90%) *trans*:*cis* (3:1)

Initially, we examined the reaction of the α-sulfinyl carbanion derived from **1** with the alkylating agents MeI and $PhCH_2Br$, and with Me_3SiCl, to give substituted products **3–5**. In each case the new substituent is introduced *trans* to the S=O bond, in accord with our expectation from previous such alkylations. The assignment of relative configuration of the α-silyl sulfoxides **5** is based on an X-ray structure determination (Fig. 1), which clearly shows the all-equatorial arrangement of substituents around the ring. Comparison of the ^1H NMR of this compound with those of **3** and **4** clearly indicates analogous all-equatorial arrangements for these compounds.

We next examined acylation and carbonyl additions of the sulfoxide **1**, with the ultimate aim of introducing additional

† See preceding paper for full details of the asymmetric transformations of the sulfoxide **1**, using homochiral lithium amide bases.

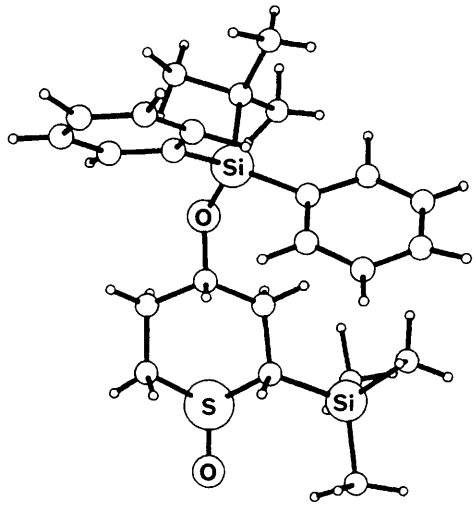


Fig. 1 X-Ray structure of compound **5**

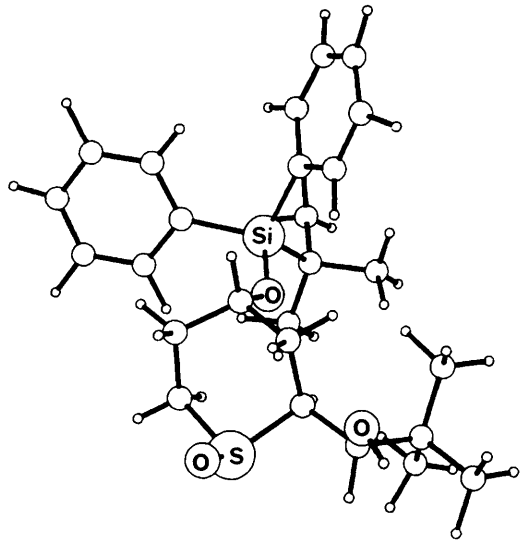
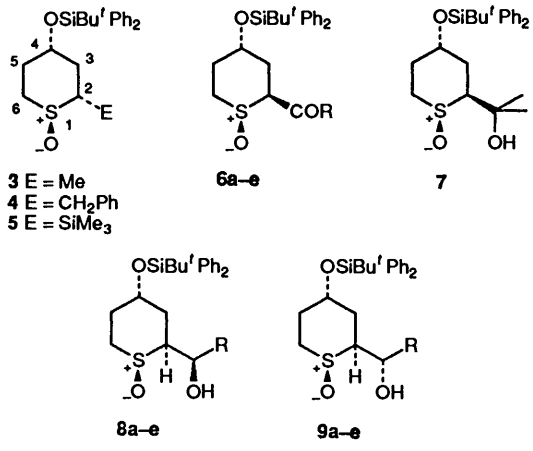


Fig. 2 X-Ray structure of compound **8a**

'off-template' asymmetric centres. The use of carboxylic acid esters as the electrophilic quenching agents results in the formation of single stereoisomeric products **6a–e** in good yield.*[4] Similarly, the use of acetone as electrophile gives a single addition product **7** in 86% yield, in accord with similar experiments involving acyclic sulfoxides,[7] whereas aldehydes, such as Bu^{t}CHO give mixtures of epimeric products, *e.g.* **8a** and **9a**.



3 E = Me
4 E = CH_2Ph
5 E = $SiMe_3$

6a–e **7**

8a–e **9a–e**

a, R = Bu^t; **b**, R = Me; **c**, R = Et; **d**, R = Pr^i; **e**, R = Ph

On the basis of our previous results, in which the bulky Ph_2Bu^tSiO group *appeared to be* acting as a conformational lock (thus allowing stereochemical assignment from ^{1}H NMR coupling constants—particularly couplings to 2-H), we initially inferred analogous stereochemical outcomes for the acylations and some of the carbonyl additions as seen in the formation of **3–5**. However, that these initial assignments were incorrect (and that the stereochemistry shown for **6–9** is correct), was amply demonstrated by an X-ray structure determination, carried out on compound **8a** (Fig. 2).

This hydroxy sulfoxide clearly has the new α-substituent *cis* to the S=O bond, and this stereochemical arrangement has resulted in a conformational inversion of the thiane oxide ring, both the silyloxy group at C-4 and the sulfoxide oxygen being axially orientated. The contrasting results for hydroxy sulfoxide **8a**, compared with α-silyl sulfoxide **5**, are highlighted by views of the crystal structures from the side of the thiane oxide ring (Fig. 3), and required a reassessment of the ^{1}H NMR spectra.

The *simultaneous* change in the stereochemical outcome of the quench of the α-sulfinyl carbanion *and* in the ring conformation of the resulting products, results in a deceptively similar appearance of key regions of the ^{1}H NMR spectra for the two series of compounds. In particular, each of the compounds **3–9** has two axial and one equatorial hydrogen α to the sulfoxide group (a key factor in our initial stereochemical misassignment). The key difference in the two series of spectra is the appearance of the 4-H signal, which is axial in compounds **3–5**, and hence shows two, large, H_{ax}–H_{ax} couplings (along with two smaller couplings, usually giving this signal the overall appearance of a triplet of triplets), but which is equatorial in **6–9** and thus, due to the absence of large coupling, appears as a much narrower signal (often a broadened singlet). The appearance of the 4-H signal was, therefore, established as an indicator of ring conformation, allowing simplification of the stereochemical assignment of the thiane oxide products.

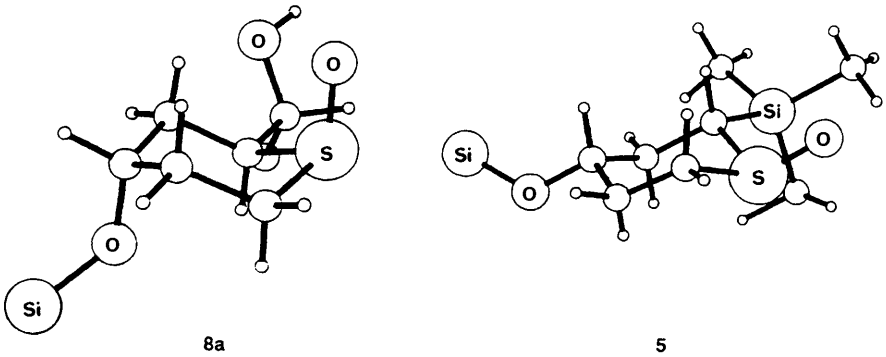
Although we were initially somewhat surprised by the conformational preference of products **6–9**, there appears to be ample precedent for such behaviour, despite the origin of such effects being poorly understood.[8]

It became clear that the additions of the thiane oxide **1** with a range of aldehydes proceed with unpredictable stereochemical results, with at least two diastereoisomeric products always formed, and these belonging to either conformational 'family'.[9] Thus, reaction with benzaldehyde gave two addition products, in one of which 4-H is equatorial, and in the other it is axial. In order to access such addition products as single isomers, in a more stereochemically predictable fashion, we examined the reduction of the keto sulfoxides **6a–e**, using the protocols employed previously by Solladié,[10] to give the two diastereoisomeric hydroxy sulfoxides **8** and **9** (Table 1).

Several points are worth noting from the results given in the Table. Firstly, all the reductions employing $ZnCl_2$ in the reaction mixture proceeded to give only the hydroxy sulfoxide **8**. Secondly, the reactions involving the use of DIBAL alone give more mixed results, with **6a** and **6d** giving only **9**, whereas **6b** and **6c** give mixtures of isomers. In addition, we found that the reduction of **6e** with DIBAL alone did not give acceptable results, perhaps due to retro-aldol type complications.

These reduction results can reasonably be accommodated

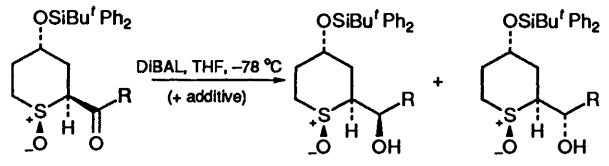
* It is unclear if this is the result of kinetic or thermodynamic control, see accompanying paper for some further comment.



8a 5

Fig. 3 X-Ray structures of compounds **5** and **8a** (the bulk of the silicon protecting group, and the Bu^t group of **8a** have been omitted for clarity)

Table 1

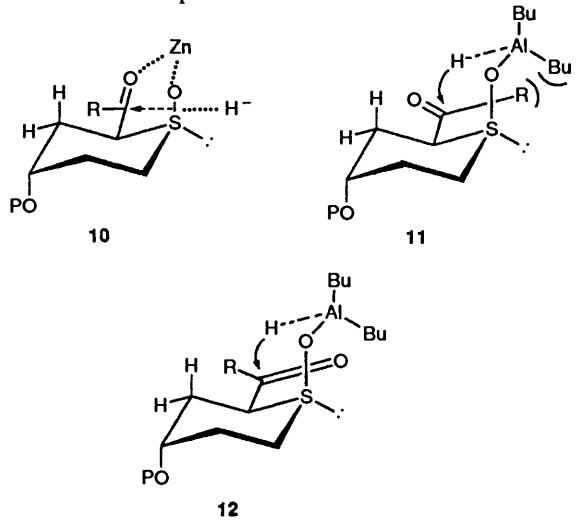


6 8 9

Keto sulfoxide	R	Additive	Yield (%)	8:9
6a	Bu^t	—	88	9 only[a]
6a	Bu^t	$ZnCl_2$	65	8 only[a]
6b	Me	—	57	1.6:1
6b	Me	$ZnCl_2$	67	8 only
6c	Et	—	72	1:1.9
6c	Et	$ZnCl_2$	75	8 only
6d	Pr^i	—	50	9 only
6d	Pr^i	$ZnCl_2$	60	8 only
6e	Ph	—	—	—[b]
6e	Ph	$ZnCl_2$	74	8 only

[a] Indicates other isomer not detected. [b] Reaction unsuccessful.

by the usual transition state models for this type of reduction, which involve either the least sterically hindered approach of the hydride reagent on a $ZnCl_2$-chelated keto sulfoxide, as represented by **10**, or intramolecular hydride delivery as in **11** and **12**.*[11] In the chelated form **10**, the rearside hydride approach shown, which leads to **8**, is clearly less hindered than the alternative trajectory, which would involve substantial interaction with hydrogens on the thiane oxide ring. In addition, this mode of reduction may be assisted by a favourable interaction of the electrophilic Bu$^i_2$AlH reagent with the sulfur lone pair.[11]

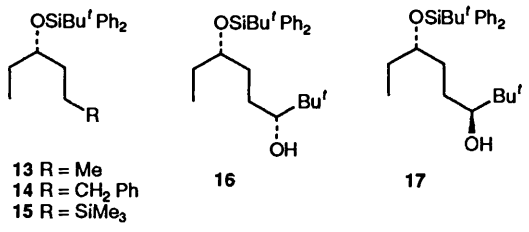


10 11 12

P = SiBu^{t}Ph$_2$

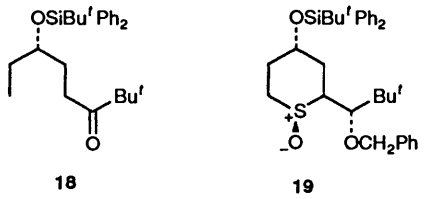
In the reactions involving DIBAL alone we observed high levels of selectivity only with **6a** and **6d**, both of which have fairly bulky alkyl groups attached to the ketone. With the smaller methyl or ethyl ketones, **6b** and **6c**, very little selectivity was seen. The poor selectivity in the latter cases indicates that transition states approximated by **11** and **12** are close in energy. However, when the group R is relatively large, as is the case in **6a** and **6d**, the unfavourable interaction indicated in **11** involving the R group and one of the substituents on aluminium must dominate, leading to the exclusive formation of **9** *via* **12**.

Having developed methods for the stereoselective silylation, alkylation, acylation and (indirectly) hydroxyalkylation of the parent thiane oxide **1**, we were interested in showing that manipulation of the resulting intermediates could be carried out to give either ring-opened or sulfur-free products. We found that the simple alkylated or silylated products **3**–**5** undergo facile desulfurisation to give the acyclic silyl ether derivatives **13**–**15** in good yield (78–94%). Attempts to induce the hydroxy sulfoxides **8** or **9** to react in a similar fashion were much less successful; for example, **8e** and **9e** undergo concomitant hydrogenolysis, to give **14**. Desulfurisation of **8a** or **9a** required very forcing conditions (Raney nickel in refluxing EtOH under a H_2 atmosphere for 2–3 days), and gave poor yields of products (30–50%) such as **16** and **17**. The required secondary



13 R = Me
14 R = CH_2Ph
15 R = $SiMe_3$

16 17



18 19

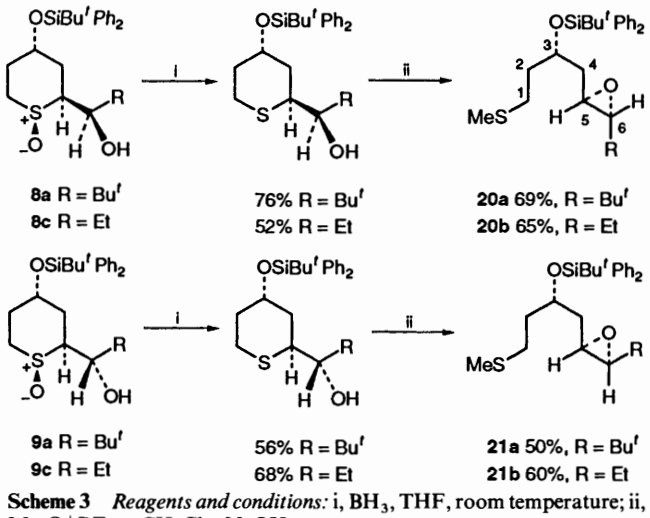
alcohols were accompanied by the corresponding ketone **18** which is presumably the product of Raney nickel-mediated oxidation, as described by Krafft and co-workers.[12] Various protected forms of **9a** were prepared, in order to avoid the unwanted oxidation, but with little success. Interestingly, the benzyl-protected sulfoxide **19** gave the best yield of the desired alcohol **16**, the protecting group being removed during the

* Transition state representations **10**–**12** assume that the conformation assigned for the keto sulfoxides **6** is maintained under the reaction conditions.

desulfinylation, but relatively little of the ketone **18** being formed. A versatile stereocontrolled route to monoprotected 1,4-diols such as **16** and **17** was, therefore, compromised by the unsatisfactory yields of the desulfinylation step. We failed to solve this problem, despite the examination of numerous reaction conditions and alternative reagents.

An alternative method of transforming the hydroxy sulfoxides **8** and **9** into useful products was subsequently developed, involving initial reduction of the sulfoxide group to the corresponding sulfide,[13] followed by treatment with $Me_3O^+BF_4^-$ and then base,[14] to give the epoxide products shown in Scheme 3.

Two examples of each stereochemical series of the hydroxy sulfoxide **8** and **9** were taken through this sequence to give the *trans*-epoxide products **20** or the *cis*-compounds **21**. The stereochemistry shown is that expected from the earlier assignments for the hydroxy sulfoxide precursors, assuming stereospecific epoxide ring formation. The assignments for the epoxides are fully in accord with the observed vicinal coupling constants between hydrogens on the epoxide ring (2.3 and 2.2 Hz for the *trans*-compounds **20a** and **20b** respectively, and 4.5



Scheme 3 *Reagents and conditions:* i, BH_3, THF, room temperature; ii, $Me_3O^+BF_4^-$, CH_2Cl_2; NaOHaq

and 4.3 Hz for the *cis*-compounds **21a** and **21b** respectively).[15] The products are essentially protected forms of epoxides derived from *homoallylic* alcohols, which are not straightforward to prepare in stereoselective fashion. Furthermore, our stereoselective route to this type of epoxy alcohol derivative is quite versatile, and should allow the introduction of additional functionality, or substituents, by further substitution of the thiane oxide ring. We have also shown that the methylthio group present in **20a** can be removed by reaction with Raney nickel to give the expected sulfur-free epoxide.

Finally, it should be noted that the compounds described above are available in non-racemic form, since we have shown that enantioselective substitution of the thiane oxide **1** can be achieved by employing a homochiral lithium amide base for the initial deprotonation.*

Experimental

Melting points for solid products were determined using a Reichert Microscope apparatus, and are uncorrected. IR spectra were recorded on a Philips PU96706, Pye Unicam SP3-100 or Perkin-Elmer 1720 FTIR instrument. NMR spectra were recorded on a Bruker WP80, Bruker AM250, JEOL FX270 or Bruker AM400 machine, with Me_4Si as internal standard. *J* Values are recorded in Hz and multiplicities indicated for ^{13}C NMR were obtained using a DEPT sequence. Mass spectra were recorded on AEI 902 or VG micromass 70E spectrometers. Microanalyses were performed at the microanalytical laboratory at Nottingham University using a Perkin-Elmer 240B elemental analyser. Analytical TLC was performed on Merck precoated silica gel F_{254} plates. Preparative chromatography was carried out on columns of Merck Keiselgel 60 (230–400 mesh). Solvents were purified by standard techniques. The preparation and characterisation of certain of the products mentioned above (**1–3**, **5**, **6a**, **8a**, **13**, **17a** and **20a**) is described in the preceding paper.

Preparation of Benzyl-substituted Thiane Oxide **4**.—A solution of the thiane oxide **1** (0.19 g, 0.51 mmol) in THF (2.0 cm^3) was added to a solution of LDA, prepared by addition of BuLi (0.38 cm^3, 0.6 mmol) to diisopropylamine (0.09 cm^3, 0.6 mmol) in THF (2 cm^3), at −78 °C under an atmosphere of N_2. After 1 h, $PhCH_2Br$ (0.42 cm^3, 3.5 mmol) was added to the reaction mixture which was then stirred at −78 °C for a further 30 min before the aqueous work-up. Flash column chromatography gave the title thiane oxide as a colourless solid (0.165 g, 70%), m.p. 134 °C (Found: C, 72.7; H, 7.5. $C_{28}H_{34}O_2SSi$ requires C, 72.68; H, 7.41%); ν_{max}(KBr)/cm^{-1} 2934, 1603, 1590, 1429, 1108, 1081 and 1053; δ_H(400 MHz; $CDCl_3$) 0.99 (9 H, s), 1.47 (1 H, m, 3-CH_{ax}), 1.75 (1 H, m, 5-CH_{ax}), 1.97 (1 H, m, 3-CH_{eq}), 2.08 (1 H, m, 5-CH_{eq}), 2.48–2.73 (3 H, PhC*H*, 2-CH_{ax}, 6-CH_{ax}), 3.23–3.28 (1 H, m, 6-CH_{eq}), 3.33 (1 H, dd, *J* 13 and 3, PhC*H*), 3.62 (1 H, dddd, *J* 14, 14, 4 and 4) and 7.07–7.54 (15 H, m, Ph); *m/z* 402 (M^+ − Bu^t, 52%), 207 (100), 199 (56) and 91 (33).

Compounds **3**, **5** and **7** were prepared in a similar way; spectroscopic data for non-racemic **3** and **5** compounds can be found in the preceding paper; the hydroxy sulfoxide **7** was obtained in 86% yield as a colourless solid m.p. 36–37 °C (Found: C, 66.9; H, 8.01. $C_{24}H_{34}O_3SSi$ requires C, 66.93; H, 7.96%); ν_{max}(KBr)/cm^{-1} 3368, 2926, 2857, 1590, 1428, 1367, 1113, 1068 and 1027; δ_H(250 MHz, $CDCl_3$) 1.09 (9 H, s), 1.17 (3 H, s), 1.51 (3 H, s), 1.67–1.75 (2 H, m, 3-CH_{eq} and OH), 2.24–2.38 (2 H, m, 3-CH_{ax} and 5-CH_{eq}), 2.77–3.08 (4 H, m, 6-CH_2, 2-CH and 5-CH_{ax}), 4.26 (1 H, br s, 4-CH) and 7.26–7.66 (10 H, m, Ph); *m/z* 430 (M^+ < 1%), 373 (74), 199 (100) and 59 (13) [Found: (M^+ − Bu^t) 373.1262. ($C_{20}H_{25}O_3SiS$) requires *M*, 373.1293].

Typical Procedure for the Preparation of the Keto Sulfoxides **6**.—A solution of the thiane oxide **1** (500 mg, 1.32 mmol) in THF (5 cm^3) was added dropwise to a stirred solution of LDA, prepared by addition of BuLi (1.6 mol dm^{-3} solution in hexanes; 1.02 cm^3, 1.6 mmol) to diisopropylamine (0.23 cm^3, 1.60 mmol) in THF (5 cm^3) at −78 °C under an atmosphere of N_2. After 15 min ethyl isobutyrate (0.64 cm^3, 4.8 mmol) was rapidly added to the mixture which was then stirred at −78 °C, before addition of saturated aqueous NH_4Cl (10 cm^3). The mixture was then extracted with CH_2Cl_2 (3 × 15 cm^3) and the combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The resultant oil was subjected to flash chromatography (EtOAc) to give the keto sulfoxide **6d** as a white crystalline solid (307 mg, 52%), m.p. 102–105 °C (Found: C, 67.6; H, 8.1. $C_{25}H_{34}O_3SSi$ requires C, 67.87; H, 7.69%); ν_{max}(film)/cm^{-1} 3069, 2929, 2856, 1712, 1486, 1110, 1070 and 1043; δ_H(400 MHz; $CDCl_3$) 1.09 (9 H, s), 1.13 and 1.15 (6 H, overlapping d, *J* 7, $CHMe_2$), 1.65 (1 H, dm, *J* 12.6, 3-CH_{eq}), 1.77 (1 H, dm, *J* 12.6, 5-CH_{eq}), 2.34 (1 H, ddm, *J* 12.5 and 12.5, 5-CH_{ax}), 2.41 (1 H, ddd, *J* 12.5, 12.5 and 2.0, 3-CH_{ax}), 2.93 (1 H, ddd, *J* 10.3, 3.3 and 3.3, 6-CH_{eq}), 3.00 (1 H, sept, *J* 7.2, $CHMe_2$), 3.10 (1 H, ddd, *J* 13.6, 13.6 and

* See earlier footnote †.

3.3, 6-CH_{ax}), 4.04 (1 H, dd, *J* 12.3 and 2.6, 2-CH_{ax}), 4.30 (1 H, br s, 4-CH_{eq}), 7.30 (6 H, m, Ph) and 7.60 (4 H, m, Ph); δ_C(100 MHz; $CDCl_3$) 17.7 (CH_3), 19.0 (CH_3) 19,3 (C), 21.8 (CH_2, C-5), 24.7 (CH_2, C-3), 27.1 (CH_3, Bu^t), 38.6 (CH), 42.0 (CH_2, C-6), 60.0 (CH, C-2) 65.4 (CH, C-4), 127.9 (CH), 130.1 (CH), 133.5 (C), 135.5 (CH) and 208.2 (C, C=O); *m/z* (FAB) 443 (M^+ + H, 41%), 199 (34), 197 (34) and 135 (100).

The other keto sulfoxides were prepared by reaction of the thiane oxide **1** with the appropriate ethyl ester in a similar fashion. Data for compound **6a** can be found in the preceding paper.

Reaction with ethyl benzoate gave the keto sulfoxide **6e** as a white foam (472 mg, 74%), m.p. 54–56 °C (Found: C, 70.3; H, 6.9. $C_{28}H_{32}O_3SSi$ requires C, 70.59; H, 6.72%); ν_{max}(film)/cm^{-1} 3070, 2930, 2858, 1682, 1487, 1428, 1110, 1071, 1044 and 1009; δ_H(250 MHz; $CDCl_3$) 1.15 (9 H, s), 1.68 (1 H, br d, *J* 12.8, 3-CH_{eq}), 1.95 (1 H, br d, *J* 15.2, 5-CH_{eq}), 2.36 (1 H, br dd, *J* 14.1 and 14.1, 5-CH_{ax}), 2.64 (1 H, br dd, *J* 12.8, 3-CH_{ax}), 2.95 (1 H, dm, *J* 14.0, 6-CH_{eq}), 3.21 (1 H, ddd, *J* 13.4, 13.4 and 3.0, 6-CH_{ax}), 4.35 (1 H, br s, 4-CH_{eq}), 4.85 (1 H, dd, *J* 12.2 and 2.2, 2-CH_{ax}), 7.30–7.50 (8 H, m, Ph), 7.65 (5 H, m, Ph) and 7.90 (2 H, br d, *J* 10, Ph); δ_C(100 MHz; $CDCl_3$) 19.4 [C,*C*(CH_3)$_3$], 21.9 (CH_2, C-5), 25.7 (CH_2, C-3), 27.1 (CH_3, Bu^t), 42.1 (CH_2, C-6), 57.4 (CH, C-2), 65.7 (CH, C-4), 127.9 (CH, Ph), 128.8 (CH, Ph), 130.1 (CH, Ph), 133.3 (C, Ph), 133.8 (CH, Ph), 135.1 (C, Ph), 135.5 (CH, Ph), 135.6 (CH, Ph) and 194.9 (C, C=O); *m/z* (FAB) 477 (M^+ + H, 100%), 419 (8), 221 (19), 199 (28), 197 (28) and 135 (74).

Reaction with ethyl acetate gave the keto sulfoxide **6b** as a white crystalline solid (302 mg, 73%), m.p. 95–98 °C (Found: C, 66.5; H, 7.45. $C_{23}H_{30}O_3SSi$ requires C, 66.67; H, 7.25%); ν_{max}(film)/cm^{-1} 3071, 2930, 2857, 1715, 1428, 1112 and 1043; δ_H(250 MHz; $CDCl_3$) 1.09 (9 H, s) 1.65 (1 H, br d, *J* 13, 3-CH_{eq}), 1.85 (1 H, br d, *J* 14.7, 5-CH_{eq}), 2.31 (3 H, s, COMe), 2.20–2.50 (2 H, m, 5-CH_{ax} and 3-CH_{ax}), 2.93 (1 H, ddd, *J* 14, 3.2 and 3.2, 6-CH_{eq}), 3.10 (1 H, ddd, *J* 14, 14 and 3.1, 6-CH_{ax}), 3.80 (1 H, dd, *J* 12.5 and 2.6, 2-CH_{ax}, 4.27 (1 H, br s, 4-CH_{eq}), 7.40 (6 H, m, Ph) and 7.62 (4 H, m, Ph); δ_C(100 MHz; $CDCl_3$) 19.3 [s, *C*(CH_3)$_3$], 21.7 (CH_2, C-5), 24.8 (CH_2, C-3), 27.1 (CH_3, Bu^t), 28.6 (CH_3, CO*Me*), 41.7 (CH_2, C-6), 62.5 (CH, C-2), 65.2 (CH, C-4), 127.9 (CH), 130.2 (CH), 133.3 (C), 135.6 (CH) and 202.8 (C, C=O); *m/z* (FAB), 415 (M^+ + H, 86%), 357 (10), 199 (47) and 135 (100).

Reaction with ethyl propionate gave the keto sulfoxide **6c** as a white foam (491 mg, 86%), m.p. 93–95 °C (Found: C, 66.6; H, 7.5. $C_{24}H_{32}O_3SSi$ requires C, 67.28; H, 7.48%); ν_{max}(film)/cm^{-1} 3070, 3048, 2930, 2856, 1714, 1427, 1159, 1112 and 1042; δ_H(250 MHz; $CDCl_3$) 1.07 (3 H, t, *J* 7, $COCH_2CH_3$), 1.08 (9 H, s), 1.61 (1 H, br d, *J* 14.6, 3-CH_{eq}), 1.84 (1 H, br d, *J* 14.6, 5-CH_{eq}), 2.10–2.45 (2 H, m, 3-CH_{ax} and 5-CH_{ax}), 2.52 (1 H, dq, *J* 18.5 and 7.2, C*H*Me), 2.72 (1 H, dq, *J* 18.5 and 7.2, C*H*Me), 2.88 (1 H, ddd, *J* 14, 3.1 and 3.1, 6-CH_{eq}), 3.07 (1 H, ddd, *J* 14, 14 and 3.1, 6-CH_{ax}), 3.81 (1 H, dd, *J* 12.5 and 2.6, 2-CH_{ax}), 4.26 (1 H, br s, 4-CH_{eq}), 7.40 (6 H, m, Ph) and 7.60 (4 H, m, Ph); δ_C(100 MHz; $CDCl_3$) 7.5 (CH_3), 19.4 (C), 21.8 (CH_2), 24.8 (CH_2), 27.2 (CH_3), 34.5 (CH_2), 41.8 (CH_2), 61.7 (CH), 65.3 (CH), 128.0 (CH), 130.2 (CH), 133.4 (C), 135.7 (CH) and 205.4 (C); *m/z* (FAB) 429 (M^+ + H, 100%), 371 (8), 199 (38) and 135 (92).

Data for the Hydroxy Sulfoxides **8**, *from DIBAL–*$ZnCl_2$ *Reduction.*—The reductions of the keto sulfoxides **6**, employing $ZnCl_2$ as additive, were conducted as described in the preceding paper (which includes data for **8a**), to furnish the hydroxy sulfoxides **8** as single epimers (by examination of the crude mixtures by TLC and NMR).

The hydroxy sulfoxide **8b** was obtained as a white crystalline solid (53 mg, 67%), m.p. 122–128 °C (Found: C, 66.4; H, 7.9. $C_{23}H_{32}O_3SSi$ requires C, 66.30; H, 7.74%); ν_{max}(film)/cm^{-1} 3362, 3011, 2928, 2856, 1487, 1108, 1071 and 1009; δ_H(250 MHz; $CDCl_3$ after D_2O exchange) 1.10 (9 H, s), 1.15 (3 H, d, *J* 6.4), 1.68 (2 H, m, 3-CH_{eq} and 5-CH_{eq}), 2.30 (2 H, coincident ddm, *J* 14 and 14, 3-CH_{ax} and 5-CH_{ax}), 2.80–2.92 (2 H, m, 6-CH_{eq} and 2-CH_{ax}), 3.08 (1 H, td, *J* 14, 14 and 3.3, 6-CH_{ax}), 4.27 (1 H, br s, 4-CH_{eq}), 4.46 (1 H, qd, *J* 6.4 and 2.2, C*H*OH), 7.35 (6 H, m, Ph) and 7.55 (4 H, m, Ph); δ_C(68 MHz; $CDCl_3$) 19.4 (C), 20.0 (CH_3), 22.15 (CH_2), 22.2 (CH_2), 27.0 (CH_3), 41.1 (CH_2), 53.2 (CH), 65.2 (CH), 69.8 (CH), 127.8 (CH), 130.0 (CH), 133.3 (C) and 135.5 (CH); *m/z* (FAB) 417 (M^+ + H, 95%), 359 (12), 199 (36), 135 (57) and 55 (100).

The hydroxy sulfoxide **8c** was obtained as a white foam (277 mg, 75%), m.p. 45–47 °C (Found: C, 66.8; H, 8.0. $C_{24}H_{34}O_3SSi$ requires C, 66.93; H, 7.96%); ν_{max}(film)/cm^{-1} 3384, 3071, 2929, 2856, 1427, 1112 and 1026; δ_H(270 MHz; $CDCl_3$), 0.87 (3 H, t, *J* 7.2), 101 (9 H, s), 1.16–1.29 (2 H, m, CH_2Me), 1.65 (2 H, m, 3-CH_{eq} and 5-CH_{eq}), 2.23 (2 H, coincident ddm, 5-CH_{ax} and 3-CH_{ax}, *J* 13.3), 2.81 (2 H, m, 6-CH_{eq} and 2-CH_{ax}), 3.10 (1 H, ddd, *J* 13.9, 13.9 and 3.3, 6-CH_{ax}), 3.50 (1 H, br s, OH), 4.11 (1 H, br tm, *J* 6.3, C*H*OH), 4.20 (1 H, br s, 4-CH_{eq}), 7.35 (6 H, m, Ph) and 7.55 (4 H, m, Ph); δ_C(100 MHz; $CDCl_3$), 10.1 (CH_3), 19.3 (C), 22.2 (CH_2), 22.4 (CH_2), 26.8 (CH_2), 27.1 (CH_3), 41.2 (CH_2), 51.6 (CH), 65.4 (CH), 75.6 (CH), 127.9 (CH), 130.05 (CH), 133.4 (C) and 135.6 (CH); *m/z* (FAB) 431 (M^+ + H, 51%), 295 (17), 199 (35), 135 (100) and 57 (62).

The hydroxy sulfoxide **8d** was obtained as a white crystalline solid (40 mg, 60%), m.p. 103–106 °C (Found: C, 67.3; H, 8.5. $C_{25}H_{36}O_3SSi$ requires: C, 67.52; H, 8.16%); ν_{max}($CHCl_3$)/cm^{-1} 3392, 2993, 2931, 2858, 1463, 1112 and 999; δ_H(250 MHz; $CDCl_3$—after D_2O exchange) 0.84 (3 H, d, *J* 6.7), 1.00 (3 H, d, *J* 6.7), 1.09 (9 H, s), 1.63 (3 H, m, 5-CH_{eq}, 3-CH_{eq} and C*H*Me_2), 2.20–2.40 (2 H, m, 5-CH_{ax} and 3-CH_{ax}), 2.82 (1 H, ddd, *J* 14.2, 3.3 and 3.3, 6-CH_{eq}), 3.00–3.20 (2 H, m, 6-CH_{ax} and 2-CH), 3.83 (1 H, dd, *J* 8.8 and 1.6, C*H*OH), 4.29 (1 H, br s, 4-CH_{eq}), 7.43 (6 H, m, Ph) and 7.64 (4 H, m, Ph); δ_C(100 MHz; $CDCl_3$) 18.7 (CH_3), 18.9 (CH_3), 19.2 (C), 22.0 (CH_2), 22.7 (CH_2), 27.10 (CH_3), 30.4 (CH_2), 41.2 (CH_2), 49.8 (CH), 65.4 (CH), 79.65 (CH), 127.85 (CH), 130.1 (CH), 133.4 (C) and 135.6 (CH); *m/z* (FAB) 445 (M^+ + H, 99%), 427 (8), 387 (10), 199 (48) and 135 (100).

The hydroxy sulfoxide **8e** was obtained as a white foam (75 mg, 74%), m.p. 48–51 °C (Found: C, 70.1; H, 7.0. $C_{28}H_{34}O_3SSi$ requires C, 70.25; H, 7.16%); ν_{max}(film)/cm^{-1} 3515, 3070, 2931, 2858, 1487, 1110, 1070 and 1045; δ_H($CDCl_3$; 250 MHz) 0.91 (9 H, s), 1.71 (1 H, dm, *J* 14, 5-CH_{eq}), 1.95–2.15 (3 H, m, 3-CH_2 and 5-CH_{ax}), 3.00 (1 H, ddd, *J* 14.1, 3.5 and 3.5, 6-CH_{eq}), 3.14 (1 H, br s, OH), 3.55–3.70 (2 H, m, 2-CH_{ax} and 6-CH_{ax}), 4.03 (1 H, br s, 4-CH_{eq}), 5.91 (1 H, s, C*H*OH) and 7.10–7.60 (15 H, m); δ_C(100 MHz; $CDCl_3$) 19.1 (C), 26.9 (CH_3), 29.6 (CH_2), 31.5 (CH_2), 47.6 (CH_2), 61.3 (CH_2), 64.4 (CH), 67.05 (CH), 125.7 (CH), 127.7 (CH), 127.8 (CH), 128.5 (CH), 130.0 (CH), 132.7 (C), 135.5 (CH) and 139.3 (C); *m/z* (FAB) 479 (M^+ + H, 28%), 461 (28), 199 (44) and 130 (100).

Typical Procedure for the Reduction of the Keto Sulfoxides **6** *with DIBAL.*—To a stirred solution of the β-keto sulfoxide **6a** (70 mg) in THF (4 cm^3) at −78 °C under an atmosphere of N_2 was added DIBAL (1 mol dm^{-3} in hexanes; 0.15 cm^3, 0.15 mmol) dropwise. After the mixture had been stirred for a further 15 min the reaction was quenched by addition of MeOH (5 cm^3) at −78 °C. Evaporation of the solvent under reduced pressure gave a solid which was subjected to column chromatography (EtOAc) to give the hydroxy sulfoxide **9a** as a white crystalline solid (61 mg, 88%), m.p. 43–45 °C;

ν_{max}(film)/cm^{-1} 3319, 3070, 2931, 2858, 1428, 1112, 1068 and 1022; δ_H(270 MHz; $CDCl_3$) 0.92 (9 H, s), 1.00 (9 H, s), 1.40 (1 H, br d, *J* 14.5, 5-CH_{eq}), 1.52 (1 H, dd, *J* 14.5 and 2.1, 3-CH_{eq}), 2.20 (1 H, br dd, *J* 14.3 and 14.3, 5-CH_{ax}), 2.48 (1 H, br dd, *J* 14.2 and 14.2, 3-CH_{ax}), 2.72 (1 H, ddd, *J* 14.3, 3 and 3, 6-CH_{eq}), 2.90 (1 H, ddd, *J* 14.3, 14.3 and 3.3, 6-CH_{ax}), 3.12 [2 H, m, 2-CH_{ax} and C*H*(OH)Bu^t], 3.95 (1 H, br s, OH), 4.15 (1 H, br s, 4-CH_{eq}), 7.35 (6 H, m, Ph) and 7.55 (4 H, m, Ph); δ_C(100 MHz; $CDCl_3$) 19.2 (C), 22.2 (CH_2, C-3), 26.5 (CH_3), 27.0 (CH_3), 30.1 (CH_2, C-5), 36.2 (C), 40.5 (CH_2, C-6), 49.5 (CH, C-2), 66.1 (CH, C-4), 82.8 (CH, CHOH), 127.8 (CH, Ph), 130.0 (CH, Ph), 133.5 (C, Ph) and 135.6 (CH, Ph); *m/z* (FAB) 459 (M^+ + H, 28%), 441 (9), 199 (28), 135 (67) and 57 (100). The other DIBAL reductions were carried out in a similar way, to give the hydroxy sulfoxides indicated in the Table.

The keto sulfoxide **6b** (80 mg) furnished a crude mixture of epimeric sulfoxides which was subjected to column chromatography (EtOAc) to give firstly **8b** (28 mg, 35%) identical with that obtained from the DIBAL–$ZnCl_2$ reaction, described above, followed by **9b** as a white crystalline solid (17 mg, 22%), m.p. 102–105 °C (Found: C, 66.35; H, 7.9. $C_{23}H_{32}O_3SSi$ requires, C, 66.30; H, 7.74%); ν_{max}(film)/cm^{-1} 3376, 3018, 2929, 2857, 1487, 1216, 1110, 1071 and 1010; δ_H(250 MHz; $CDCl_3$—after D_2O exchange) 1.08 (9 H, s), 1.25 (3 H, d *J* 6.6), 1.48 (1 H, br d, *J* 14.4, 5-CH_{eq}), 1.64 (1 H, br d, *J* 14.4, 3-CH_{eq}), 2.08–2.32 (2 H, m, 5-H_{ax} and 3-H_{ax}), 2.80–2.31 (3 H, br m, 6-CH_2 and 2-CH_{ax}), 3.83 (1 H, quint, *J* 6.6, C*H*OH), 4.18 (1 H, br s, 4-CH_{eq}), 7.40 (6 H, m, Ph) and 7.55 (4 H, m, Ph); δ_C(68 MHz; $CDCl_3$) 19.2 (C), 21.2 (CH_3), 22.1 (CH_2), 26.7 (CH_2), 27.0 (CH_3), 56.6 (CH), 65.3 (CH), 65.8 (CH_2), 67.3 (CH), 127.8 (CH), 130.1 (CH), 133.4 (C) and 135.6 (CH); *m/z* (FAB) 417 (M^+ + H, 66%), 359 (10), 199 (43), 135 (61) and 55 (100).

The keto sulfoxide **6c** (205 mg) furnished a crude mixture of epimeric sulfoxides which was subjected to column chromatography (EtOAc) to give first **8c** (51 mg, 25%) identical with that obtained from the DIBAL–$ZnCl_2$ reaction, described above, followed by **9c** as a white powder (98 mg, 47%), m.p. 149–151 °C (Found: C, 67.0; H, 8.0. $C_{24}H_{34}O_3SSi$ requires C, 66.98; H, 7.91); ν_{max}(film)/cm^{-1} 3323, 3070, 3051, 2931, 2857, 1426, 1266, 1112 and 1020; δ_H(270 MHz; $CDCl_3$) 0.90 (3 H, t, *J* 7.6), 1.00 (9 H, s), 1.51 (4 H, br m, CH_2CH$_3$, 3-CH_{eq} and 5-CH_{eq}), 2.12–2.33 (2 H, m, 5-H_{ax} and 3-H_{ax}), 2.86–3.05 (3 H, m, 2-CH_{ax} and 6-CH_2), 3.52 (1 H, m, C*H*OH), 3.65 (1 H, br s, OH), 4.12 (1 H, br s, 4-CH_{eq}), 7.35 (6 H, m) and 7.55 (4 H, m); δ_C(100 MHz; $CDCl_3$) 9.4 (CH_3), 19.25 (C), 22.2 (CH_2), 26.8 (CH_2), 27.0 (CH_3), 27.3 (CH_2), 40.1 (CH_2), 54.6 (CH), 65.5 (CH), 72.05 (CH), 127.8 (CH), 130.0 (CH), 133.5 (C) and 135.6 (CH); *m/z* (FAB) 431 (M^+ + H, 97%), 373 (6), 295 (21), 199 (30) and 135 (100).

The hydroxy sulfoxide **9d** was obtained as a white crystalline solid (33 mg, 50%), m.p. 165–168 °C (Found: C, 67.1; H, 8.4. $C_{25}H_{36}O_3SSi$ requires C, 67.52; H, 8.16); ν_{max}($CHCl_3$)/cm^{-1} 3339, 2992, 2932, 2859, 1369, 1113 and 999; δ_H(250 MHz; $CDCl_3$) 0.96 and 0.97 (6 H, overlapping d, *J* 6.7, CH*Me*$_2$), 1.08 (9 H, s), 1.48 (1 H, br d, *J* 14.2, 5-CH_{eq}), 1.51 (1 H, br d, *J* 14.2, 3-CH_{eq}), 1.85 (1 H, m, C*H*Me$_2$), 2.15–2.40 (2 H, m, 3-CH_{ax} and 5-CH_{ax}), 2.80–3.20 (3 H, m, 6-CH_2 and 2-CH_{ax}), 3.47 (1 H, br t, *J* 7, C*H*OH), 4.22 (1 H, br s, 4-CH_{eq}), 7.37 (6 H, m) and 7.63 (4 H, m); δ_C(68 MHz; $CDCl_3$) 19.2 (CH_3), 19.7 (C), 21.0 (CH_3), 22.1 (CH_2), 27.0 (CH_3), 30.2 (CH), 27.3 (CH_2), 40.1 (CH_2), 52.3 (CH), 60.4 (CH_2), 65.5 (CH), 76.1 (CH), 127.8 (CH), 130.0 (CH), 133.4 (C) and 135.6 (CH); *m/z* (FAB) 445 (M^+ + H, 100%), 427 (9), 387 (10), 199 (41) and 135 (94).

Desulfinylation of Compounds **3–5**, **8a**, **9a** *and* **19**.—The experimental procedure used for the desulfinylation of compound **3**, and data for the silyl ether **13**, is given in the preceding paper. The sulfoxides **4** and **5** were allowed to react in an identical fashion to give **14** and **15**, respectively.

Silyl ether **14** was obtained as a colourless oil (Found: C, 80.9; H, 9.0. $C_{28}H_{36}OSi$ requires C, 80.71; H, 8.71%); ν_{max}(film)/cm^{-1} 2930, 2856, 1600, 1588, 1427, 1110 and 1050; δ_H(270 MHz; $CDCl_3$) 0.76 (3 H, t, *J* 7), 1.04 (9 H, s), 1.42–1.62 (6 H, m), 2.44 (2 H, t, *J* 7), 3.68 (1 H, m) and 7.05–7.67 (15 H, m); δ_C(68 MHz; $CDCl_3$) 9.4 (CH_3), 19.5 (C), 26.6 (CH_2), 27.2 (CH_3), 29.0 (CH_2), 35.3 (CH_2), 36.0 (CH_2), 74.2 (CH), 125.6 (CH), 127.5 (CH), 128.3 (CH), 128.4 (CH), 129.5 (CH), 134.8 (C), 136.0 (CH) and 142.7 (C); *m/z* 359 (M^+ − Bu^t, 71%), 199 (100), 91 (36) and 77 (17).

The silane **15** was obtained as a colourless oil; ν_{max}(film)/cm^{-1} 2960, 2932, 2859, 1590, 1428, 1110, 1039 and 1007; δ_H(250 MHz; $CDCl_3$) 0.11 (9 H, s), 0.29–0.39 (2 H, m, $SiCH_2$), 0.79 (3 H, t, *J* 7.5), 1.06 (9 H, s), 1.26–1.46 (4 H, m), 3.62 (1 H, m, CHOSi) and 7.32–7.70 (10 H, m, Ph); δ_C(68 MHz; $CDCl_3$) −1.89 (CH_3), 9.1 (CH_3), 11.0 (CH_2), 19.4 (C), 27.1 (CH_3), 27.9 (CH_2), 29.5 (CH_2), 76.2 (CH), 127.4 (CH), 129.3 (CH), 135.0 (C) and 136.0 (CH); *m/z* 271 (100%), 199 (19) and 73 (33).

The functionalised sulfoxides **8a**, **9a** and **19** were desulfinylated using a similar procedure, except that the reactions were conducted under an atmosphere of hydrogen. Raney nickel reaction of **8a** gave **17** as a colourless oil (20 mg, 50%), ν_{max}(film)/cm^{-1} 3434, 2960, 2859, 1590, 1472, 1428, 1111, 1059 and 1012; δ_H(250 MHz; $CDCl_3$) 0.78 (12 H, m), 1.06 (9 H, s), 1.32–1.74 (7 H, m, one D_2O exch.), 2.97 (1 H, dd, *J* 1.05 and 1.6), 3.70 (1 H, m) and 7.34–7.71 (10 H, m); δ_C(68 MHz; $CDCl_3$) 9.4 (CH_3), 19.5 (C), 25.8 (CH_3), 27.2 (CH_3), 27.4 (C), 29.4 (CH_2), 33.3 (CH_2), 35.0 (CH_2), 74.7 (CH), 80.2 (CH), 127.5 (CH), 129.6 (CH), 134.7 (C) and 136.1 (CH); *m/z* 355 (M^+ − Bu^t, 2%), 199 (77) and 83 (100).

Raney nickel reaction of **19** gave first, the undesired ketone **18** as a colourless solid (7 mg, 19%); ν_{max}($CHCl_3$)/cm^{-1} 2932, 2857, 1700, 1463, 1364 and 1111; δ_H(270 MHz; $CDCl_3$) 1.09 (18 H, s, 2 × Bu^t), 1.48 (3 H, m), 1.69 (4 H, m), 2.32 (1 H, m), 2.55 (1 H, m) 3.71 (1 H, m), 7.33 (6 H, m) and 7.63 (4 H, m); δ_C(68 MHz; $CDCl_3$) 19.4 (C, *C*Me$_3$), 25.7 (CH_3), 26.4 (CH_3, C*Me*$_3$), 27.15 (CH_3, C*Me*$_3$), 29.5 (CH_2), 32.2 (CH_2), 44.3 (C, *C*Me$_3$), 74.0 (CH), 127.4 (CH, Ph), 129.5 (CH, Ph), 133.5 (C, Ph), 135.9 (CH, Ph) and 216.5 (C, C=O); *m/z* (FAB) 411 (M^+ + H, 1%), 353 (22), 199 (91), 135 (62) and 57 (100); followed by the desired alcohol **16** as a colourless solid (18 mg, 49%); ν_{max}(film)/cm^{-1} 3440, 3071, 2959, 2831, 2858, 1428 and 1111; δ_H(250 MHz; $CDCl_3$) 0.82 (9 H, s), 1.05 (9 H, s), 1.13–1.78 (10 H, m, one D_2O exch.), 3.03 (1 H, dd *J* 10.5 and 1.8, C*H*OH), 3.72 (1 H, quint, *J* 5.4, CHOSi), 7.39 (6 H, m) and 7.68 (4 H, m); δ_C(68 MHz; $CDCl_3$) 9.5 (CH_3), 19.4 (C, *C*Me$_3$), 25.6 (CH_3, C*Me*$_3$), 26.5 (CH_2), 27.05 (CH_3, C*Me*$_3$), 29.2 (CH_2), 32.9 (CH_2), 34.9 (C, *C*Me$_3$), 74.5 (CH, CHOH), 80.3 (CH, CHOSi), 127.4 (CH, Ph), 129.4 (CH, Ph), 134.64 (C, Ph) and 135.92 (CH, Ph); *m/z* (FAB) 413 (M^+ + H, 3%), 355 (3), 199 (87), 139 (92), 83 (100) and 69 (100).

Data for Conversions into Epoxides **20** *and* **21**.—Single epimers of the β-hydroxy sulfoxides were converted into epoxides as indicated in Scheme 3 by the method described (for **8a** ⟶ **20a**) in the preceding paper (which includes data for **20a**).

The hydroxy sulfoxide **8c** was reduced to give the corresponding sulfide as a colourless oil (192 mg, 52%); ν_{max}(film)/cm^{-1} 3448, 3070, 3048, 2959, 2931, 2857, 1427, 1111 and 1055; δ_H(270 MHz; $CDCl_3$) 0.95 (3 H, t, *J* 7.6), 1.09 (9 H, s), 1.40–1.70 (4 H, br m) 1.73 (1 H, br s, OH), 1.87 (2 H, dm, *J* 13.5), 2.40 (1 H, ddd, *J* 13.2, 3.6 and 3.6), 3.32

(1 H, ddd, *J* 13.5, 13.5 and 2.6), 3.48 (2 H, m), 4.22 (1 H, br s), 7.39 (6 H, m) and 7.65 (4 H, m); *m/z* (FAB) 415 (M^+ + H, 1%), 397 (18), 357 (14), 199 (35) and 135 (100). This was then reacted to give the epoxide **20b** as a colourless oil (123 mg, 65%); ν_{max}(film)/cm^{-1} 3070, 3048, 2953, 2930, 2857, 1472, 1428 and 1111; δ_H(250 MHz; $CDCl_3$), 0.92 (3 H, t, *J* 7.4, 8-CH_3), 1.07 (9 H, s), 1.42–1.53 (2 H, m, 7-CH_2), 1.65 (2 H, t, *J* 6, 2-CH_2), 1.75–1.83 (2 H, m, 4-CH_2), 1.95 (3 H, s, SMe), 2.40–2.50 (3 H, m, 1-CH_2 and 6-CH), 2.66 (1 H, ddd, *J* 5.9, 5.9 and 2.2, 5-CH), 4.04 (1 H, quint, *J* 5.8, 3-CH), 7.41 (6 H, m, Ph) and 7.69 (4 H, m, Ph); δ_C(68 MHz; $CDCl_3$) 9.7 (CH_3, C-8), 15.2 (CH_3, SMe), 19.4 (C, *C*Me_3), 24.9 (CH_2, C-7), 27.0 (CH_3, C*Me*$_3$), 29.65 (CH_2, C-4), 36.5 (CH_2, C-2), 39.3 (CH_2, C-1), 55.1 (CH, C-6), 59.8 (CH, C-5), 70.7 (CH, C-3), 127.6 (CH, Ph), 129.7 (CH, Ph), 133.8 (C, Ph) and 135.8 (CH, Ph); *m/z* (FAB) 429 (M^+ + H, 14%), 371 (5), 287 (16), 267 (15), 199 (45), 135 (59), 89 (81) and 77 (100) [Found (EI): M^+ − Bu^t, 371.1513. $C_{21}H_{27}O_2SSi$ requires *M*, 371.1501].

The hydroxy sulfoxide **9a** was reduced to give the corresponding sulfide as a colourless oil (162 mg, 56%), ν_{max}(film)/cm^{-1} 3461, 3071, 3049, 2955, 2858, 1472, 1112 and 1068; δ_H(270 MHz; $CDCl_3$), 0.94 (9 H, s), 1.09 (9 H, s), 1.80–2.00 (4 H, m), 2.02 (1 H, br s, OH), 2.43 (1 H, ddd, *J* 14, 4.2 and 4.2), 2.90 (1 H, d *J* 2.3), 3.21 (1 H, ddd, *J* 14, 14 and 3), 3.59 (1 H, br d, *J* 9.9), 4.14 (1 H, br s) 7.35 (6 H, m) and 7.65 (4 H, m); *m/z* (FAB) 443 (M^+ + H, 2%), 385 (36), 199 (75), 135 (100) and 57 (100).

This was then allowed to react to give the epoxide **21a** as a colourless oil (52 mg, 50%); ν_{max}(film)/cm^{-1} 3071, 3049, 2958, 2950, 2857, 1428, 1111 and 1079; δ_H(250 MHz; $CDCl_3$), 0.91 (9 H, s, Bu^t), 1.06 (9 H, s, Bu^t), 1.70–1.90 (4 H, m, 2-CH_2 and 4-CH_2), 1.97 (3 H, s, SMe), 2.51 (2 H, m, 1-CH_2), 2.55 (1 H, d, *J* 4.5, 6-CH), 2.76 (1 H, m, 5-CH), 4.03 (1 H, m, 3-CH), 7.40 (6 H, m, Ph) and 7.67 (4 H, m, Ph); δ_C(68 MHz; $CDCl_3$), 15.2 (CH_3, SMe), 19.4 (C, *C*Me_3), 27.0 (CH_3, C*Me*$_3$), 27.6 (CH_3, C*Me*$_3$), 29.5 (CH_2, C-2), 31.4 (C, *C*Me_3), 35.7 (CH_2, C-4), 36.4 (CH_2, C-1), 55.6 (CH, C-6), 64.7 (CH, C-5), 71.9 (CH, C-3), 127.6 (CH, Ph), 129.7 (CH, Ph), 134.0 (C, Ph) and 135.9 (CH, Ph); *m/z* (FAB) 457 (M^+ + H, 46%), 399 (7), 329 (54), 199 (70), 135 (99) and 61 (100) [Found (EI) M^+ − Bu^t, 399.1816. $C_{23}H_{31}O_2SSi$ requires *M*, 399.1814].

The hydroxy sulfoxide **9c** was reduced to give the corresponding sulfide as a colourless oil (141 mg, 68%); ν_{max}(film)/cm^{-1} 3440, 3070, 3049, 2959, 2931, 2857, 1427, 1111 and 1063; δ_H(270 MHz; $CDCl_3$) 0.91 (3 H, t, *J* 7.2), 1.08 (9 H, s), 1.20–1.50 (2 H, m), 1.70–1.90 (4 H, m) 2.04 (1 H, br s, OH), 2.48 (1 H, ddd, *J* 13.2, 5.6 and 3.6), 3.06 (1 H, br dd, *J* 10.5 and 10.5), 3.29 (2 H, m), 4.06 (1 H, br s), 7.35 (6 H, m) and 7.63 (4 H, m); *m/z* (FAB) 415 (M^+ + H, 4%), 397 (1), 357 (55), 199 (85) and 135 (100).

This was then allowed to react to give the epoxide **21b** as a colourless oil (81 mg, 60%); ν_{max}(film)/cm^{-1} 3071, 3049, 2963, 2931, 2857, 1428, 1111 and 1075; δ_H(250 MHz; $CDCl_3$) 0.95 (3 H, t, *J* 7.5, 8-CH_3), 1.06 (9 H, s, Bu^t), 1.27–1.41 (2 H, m, 7-CH_2), 1.58–1.85 (4 H, m, 2-CH_2 and 4-CH_2), 1.96 (3 H, s, SMe), 2.44–2.52 (2 H, m, 1-CH_2), 2.77 (1 H, dm, *J* 4.3, 6-CH), 2.91 (1 H, dm, *J* 4.3, 5-CH), 4.05 (1 H, m, 3-CH), 7.41 (6 H, m, Ph) and 7.68 (4 H, m, Ph); δ_C(68 MHz; $CDCl_3$) 10.6 (CH_3, C-8), 15.3 (CH_3, SMe), 19.4 (C, *C*Bu^t), 21.1 (CH_2, C-7), 27.0 (CH_3, C*Me*$_3$), 29.5 (CH_2, C-2), 34.9 (CH_2, C-4), 36.5 (CH_2, C-1), 54.1 (CH, C-6), 58.0 (CH, C-5), 70.8 (CH, C-3), 127.6 (CH, Ph), 129.7 (CH, Ph), 133.85 (C, Ph) and 135.9 (CH, Ph); *m/z* (FAB) 429 (M^+ + H, 55%), 371 (20), 287 (25), 267 (25), 199 (87), 135 (97) and 61 (100) [Found (EI): M^+ − Bu^t, 371.1450. $C_{21}H_{27}O_2SSi$ requires *M*, 371.1501].

Desulfurisation of the Epoxide **20a**.—Raney Nickel (*ca.* 0.5 g excess) was added to a stirred solution of the epoxide (36 mg, 0.08 mmol) in ethanol (5 cm^3) which was then heated at reflux for 20 h under an atmosphere of H_2. The suspension was then cooled, filtered through Celite and evaporated under reduced pressure. Purification of the residue by column chromatography (2% EtOAc in light petroleum) gave the product as a colourless oil (26 mg, 79%); ν_{max}(film)/cm^{-1} 3071, 2959, 2931, 2858, 1428 and 1111; δ_H(250 MHz; $CDCl_3$) 0.79 (3 H, t, *J* 7.5), 0.86 (9 H, s), 1.07 (9 H, s), 1.51 (2 H, m), 1.62 (2 H, ddd, *J* 6, 6 and 2.1), 2.29 (1 H, d, *J* 2.4), 2.87 (1 H, ddd, *J* 6, 6 and 2.4), 3.82 (1 H, quint, *J* 6), 7.38 (6 H, m) and 7.71 (4 H, m); δ_C(68 MHz; $CDCl_3$) 9.2 (CH_3), 19.4 (C), 25.7 (CH_3), 27.0 (CH_3), 29.7 (CH_2), 30.7 (C), 38.7 (CH_2), 52.4 (CH), 66.8 (CH), 72.7 (CH), 127.5 (CH), 129.5 (CH), 134.2 (C) and 135.9 (CH); *m/z* (FAB) 353 (M^+ + H, 5%), 297 (18), 283 (98), 225 (64), 199 (76) and 135 (100).

Crystallographic Analysis of Compounds **5** *and* **8a**.—*Crystal data.* Compound **5**: $C_{24}H_{36}O_2S_1Si_2$, *M*, 444.71. Orthorhombic, a = 10.059(2), b = 19.059(3), c = 27.459(3) Å, U = 5264.10 Å^3, Z = 8, D_c = 1.12 g cm^{-3}, F(000) = 1920, space group *Pbca*, Cu-Kα radiation, λ = 1.541 78 Å, μ(Cu-Kα) = 20.12 cm^{-1}.

Compound **8a** $C_{26}H_{38}O_3S_1Si_1$, *M*, 458.68. Triclinic, a = 7.635(1), b = 12.662(1), c = 14.853(1) Å, α = 72.62(1)°, β = 77.84(1)°, γ = 80.34(1)°, U = 1331.10 Å^3, Z = 2, D_c = 1.14 g cm^{-3}, F(000) = 496, space group $P\bar{1}$, Cu-Kα radiation, λ = 1.541 78 Å, μ(Cu-Kα) = 16.37 cm^{-1}.

Crystals of approximate dimensions 0.6 × 0.5 × 0.4 mm for **5** and 0.6 × 0.4 × 0.4 mm for **8a** were mounted on an Enraf-Nonius CAD4 diffractometer and 25 reflections were used to determine accurate lattice parameters. Intensity data were collected using an $\omega/2\theta$ scan for 1° < θ < 76°. Totals of 5491 **5** and 5553 **8a** independent reflections were measured of which 3358 and 4471 respectively had $I > 3\sigma(I)$ and were considered observed and used in the subsequent refinement. Periodic measurement of standard reflections throughout data collection demonstrated their stability. The data were corrected for Lorentz and polarisation factors but no absorption corrections were made. Crystallographic calculations were performed using the CRYSTALS[16] system of programs. The structures were solved by direct methods using the MULTAN[17] program. Least squares refinement including anisotropic thermal parameters for non-hydrogen atoms and isotropic refinement of hydrogen atoms located in a difference Fourier synthesis terminated at R 0.0450 (R_w 0.0574) for **5** and at R 0.0506 (R_w 0.0605) for **8a**. For both structures final difference maps showed peaks of 0.4 e Å^{-3} close to sulfur and silicon but no other features in excess of 0.2 e Å^{-3} outside the immediate vicinity of these heavy atoms.

The resulting molecular structures are illustrated in Fig. 1 and Fig. 2 which clearly reveal the expected conformation of **5** with all three substituents of the thiane oxide ring equatorial and the inversion of **8a** with both sulfoxide oxygen and silyloxy group at C-4 axial. The chair conformation of this ring in each structure is illustrated in Fig. 3. The inversion takes place with surprisingly little disturbance to the ring geometry with the bond lengths and angles about sulfur and the remaining ring atoms showing no significant differences between the two structures. In **5** the thiane–oxide ring is slightly over-puckered from an ideal chair with the sulfur and contiguous atoms furthest from the mean plane. In **8a** the axial sulfoxide has slightly flattened this ring close to the ideal chair conformation. In **8a** the alcoholic OH forms an intermolecular hydrogen bond with a sulfoxide oxygen. The geometric data for both structures are otherwise unexceptional. Fractional atomic coordinates, thermal parameters, bond lengths and bond angles have all

been deposited with the Cambridge Crystallographic Data Centre.*

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* For details, see *J. Chem. Soc., Perkin Trans. 1*, 1993, Issue 1, Instructions for Authors (1993).

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