Chiral Sulfur Compounds. Part 25.[1] Diastereoselective 1,2-Additions of Lithiated (+)-(*S*)-*N*-*tert*-Butyldiphenylsilyl-*S*-methyl-*S*-phenylsulfoximine to Ketones

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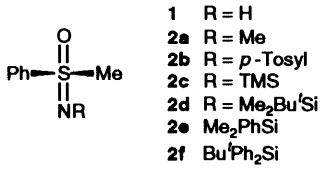
Lithiated (+)-(*S*)-*N*-*tert*-butyldiphenylsilyl-*S*-methyl-*S*-phenylsulfoximine **2f** reacts with prochiral ketones to give a mixture of diastereoisomeric β-hydroxy sulfoximine adducts with a diastereoselection ranging from 79:21 to 98:2 depending upon the steric demand of the ketone. Racemic chiral cyclic ketones react with **2f** to give a mixture of diastereoisomeric β-hydroxy sulfoximine adducts which could be separated by a combination of column chromatography and recrystallization. Thermolysis of the diastereoisomerically pure adducts gave 2-alkylcyclohexanones in high enantiomeric purity. The relative stereochemistries of four of the β-hydroxy sulfoximine adducts have been unequivocally determined from single-crystal X-ray structural analysis. The stereochemical outcome of these 1,2-additions can best be rationalized by invoking competing boat transition states.

Enantiomerically pure (+)-(*S*)- and (−)-(*R*)-*S*-methyl-*S*-phenylsulfoximine **1** are readily available *via* the resolution of racemic **1** with (+)- or (−)-10-camphorsulfonic acid.[2,3] The *N*-methyl,[3,4] *N*-*p*-tosyl[5] and *N*-silyl[6,7] derivatives (**2a–f**) are conveniently prepared from **1** and have been employed in



1 R = H
2a R = Me
2b R = *p*-Tosyl
2c R = TMS
2d R = Me_2Bu^tSi
2e Me_2PhSi
2f Bu^tPh_2Si

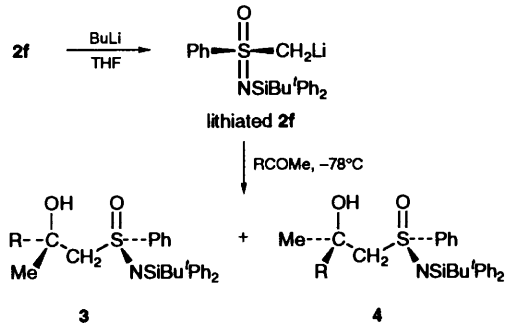
diastereoselective synthesis.[8] In 1982, Johnson[9] and his co-workers reported the condensation of (+)-**2a** with various aldehydes and prochiral ketones. The reaction of lithiated **2a** with phenyl aryl ketones (PhCOR; R = Me, Et, Pr, Bu and c-C_6H_{11}) gave a mixture of two diastereoisomeric β-hydroxy-sulfoximine adducts with modest diastereoselectivity (60:40 to 67:33). These diastereoisomeric adducts could be readily separated by column chromatography and the resulting diastereoisomerically pure adducts could be converted into chiral tertiary alcohols in high antimeric purity (87–100%) by reductive desulfurization with Raney nickel.[9] The reaction of lithiated **2a** with aldehydes also proceeded with modest diastereoselectivity (60:40 to 75:25).[9] In these cases the resolution of the diastereoisomeric adducts was difficult. More recently, Hwang *et al.*[6] and Pyne *et al.*[7] have reported much higher diastereoselectivities employing the *N*-silylated analogues of **2a**. While racemic *N*-trimethylsilyl-*S*-methyl-*S*-phenylsulfoximine **2d** showed a similar diastereoselectivity to **2a** on condensation with aldehydes, the sterically more hindered *tert*-butyldimethylsilyl, methyldiphenylsilyl and *tert*-butyldiphenylsilyl derivatives (**2d–f**) exhibited much improved product diastereoselections. For example, in the reaction of lithiated **2d–f** with pivaldehyde the product diastereoselection increased dramatically from 71:29 for **2c** to 94:6 for **2f**. We now report the synthesis of (+)-(*S*)-*N*-*tert*-butyldiphenylsilyl-*S*-methyl-*S*-phenylsulfoximine **2f** and the diastereoselectivity and stereochemistry of its reactions with prochiral and racemic chiral cyclic ketones.

Table 1 Reaction of lithiated **2f** with ketones (RCOMe)

Entry	R of ketone	Yield (%)	Diastereoselection (3:4)
1	Et	69	80:20
2	Pr^i	43	79:21
3	Ph	65	91:9
4	Bu^t	63*	98:2

Results and Discussion

Reaction of Lithiated (+)-(*S*)-**2f** *with Prochiral Acyclic Ketones.*—Enantiomerically pure (+)-(*S*)-**1** {$[\alpha]_D^{25}$ +35.6, *c* 1.3, acetone (lit.,[2,3] +36.5, *c* 1.2, acetone)} was treated with *tert*-butylchlorodiphenylsilane/imidazole in DMF to give (+)-(*S*)-**2f** ($[\alpha]_D^{26}$ +6.1, *c* 1.5, acetone) in 94% yield. Lithiated (+)-**2f** was prepared in THF and was treated at −78 °C with prochiral methyl ketones (RCOMe) to give a mixture of diastereoisomeric β-hydroxy sulfoximine adducts **3** and **4** as reported in Table 1 (entries 1–4). In each case, the major diastereoisomeric adduct **3**



could be obtained diastereoisomerically pure after purification of the crude reaction mixture by column chromatography or recrystallization. The yields of diastereoisomerically pure **3**, obtained after purification, are reported in Table 1. In each case the product diastereoselectivity was determined on the crude reaction product by ^1H NMR (400 MHz) analysis and is reported in Table 1. From an inspection of Table 1 it is evident, for the reaction of **2f** with ketones (RCOMe), that the diastereoselection increases as the steric bulk of the R group of the ketone increases. The relative (2*S*, S_S) stereochemistry of the major diastereoisomeric adducts **3** (R = Bu^t) and **3** (R = Ph) was determined by single-crystal X-ray structure analysis as

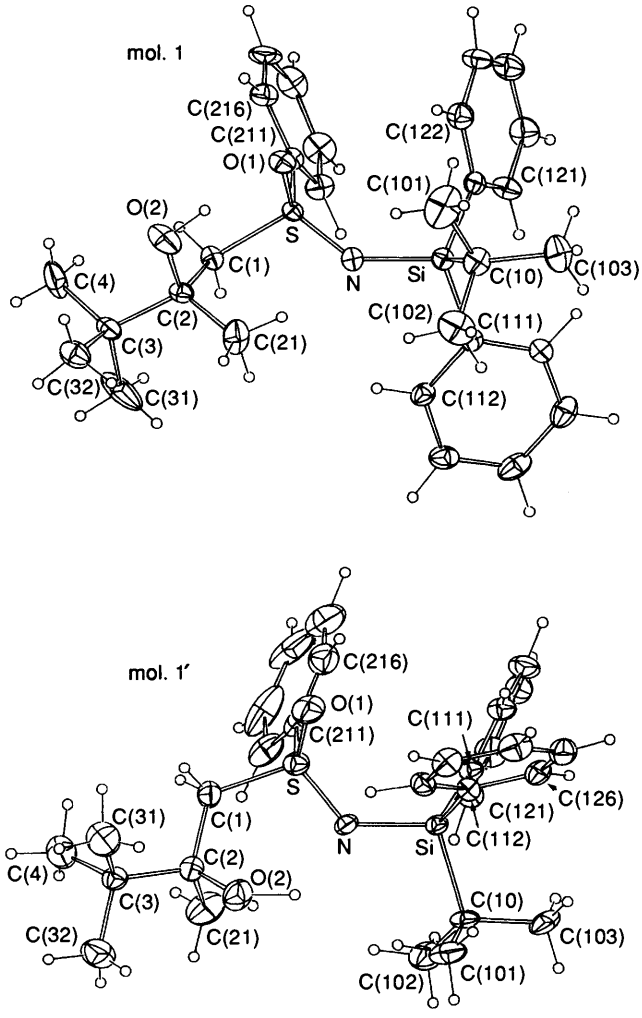


Fig. 1 X-Ray molecular structure of compound **3** (R = Bu^t)

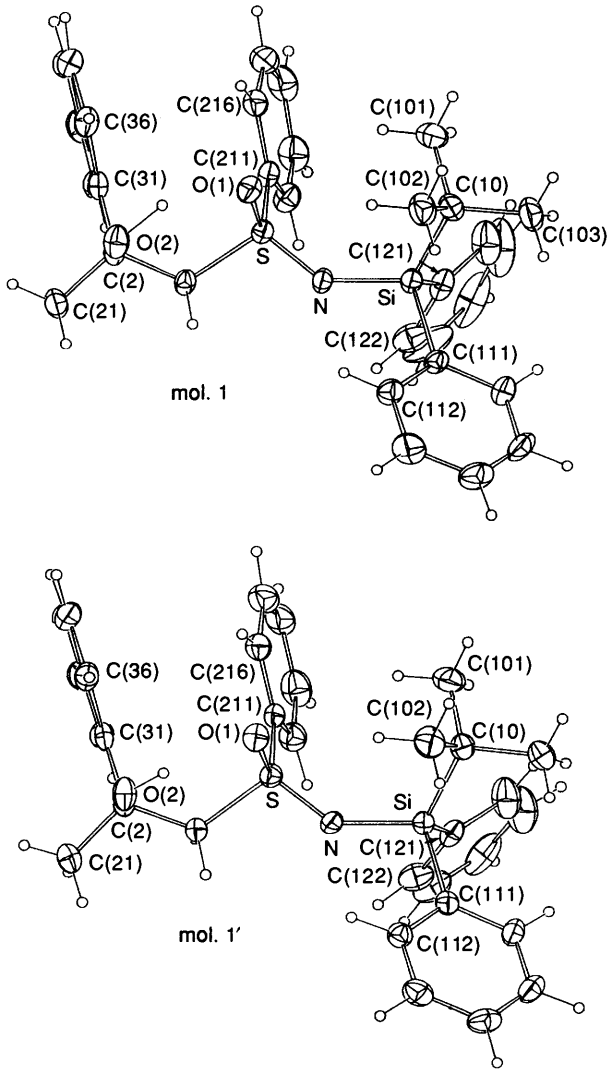
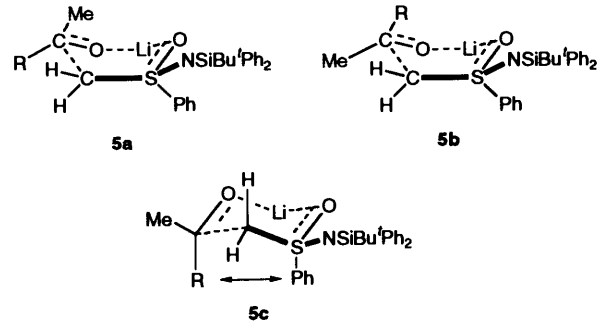


Fig. 2 X-Ray molecular structure of compound **3** (R = Ph)

shown in Figs. 1 and 2. The stereochemical outcome can be readily rationalized by invoking two competing boat transition states **5a** and **5b**. The difference in free energy between **5a** and **5b** and hence the diastereoselectivity, would be expected to increase as the steric demand of the R group of the ketone increases due to an increasing flagpole interaction between R and the sulfoximine oxygen in **5b**. We



believe that the bulky *N-tert*-butyldiphenylsilyl substituent ensures that competing chelated cyclic transition states that involve either chelation of lithium to the sulfoximine nitrogen or chelation of lithium to the sulfoximine oxygen in a chair-like transition state (*e.g.* **5c**) are energetically less favourable due to severe non-bonded steric interactions.[10] We have proposed a similar boat transition state to explain the stereochemical outcome of lithiated *tert*-butyl benzyl sulfoxide with aldehydes and these results have been confirmed by Casey.[11]

Reaction of Lithiated (+)-(S)-**2f** *with Racemic Cyclic Ketones.*—β-Hydroxy sulfoximines are thermally labile and revert to their starting carbonyl compound and sulfoximine upon mild thermolysis.[12] This property has been exploited effectively as a method for the resolution of racemic chiral cyclic ketones. This method, however, relies on the separation of the individual β-hydroxy sulfoximine diastereoisomers which is often difficult or tedious. We were interested in examining if the reaction between lithiated (+)-**2f** with 2 molar equiv. of a racemic chiral cyclic ketone would allow for the kinetic resolution of these ketones and/or enable a more facile separation of the diastereoisomeric β-hydroxy sulfoximine adducts.

Lithiated (+)-**2f** in THF and was treated at −78 °C with 1.3 molar equiv. of the racemic cyclic ketones, 2-methylcyclohexanone, 2-*tert*-butylcyclohexanone and norcamphor, to give a mixture of either three or two diastereoisomeric β-hydroxy sulfoximine adducts as reported in Table 2. In entries 1 and 2, the major diastereoisomeric adduct could be obtained diastereoisomerically pure after purification of the crude reaction mixture by column chromatography and then recrystallization. In the case of the reaction of 2-*tert*-butylcyclohexanone a

Table 2 Reaction of lithiated **2f** with racemic cyclic chiral ketones

Entry	Cyclic ketone	Yield (%)	Diastereoselection (products)
1	2-Methylcyclohexanone	54	56:34:10 (**6a**:**6b**:**6c**)
2	2-*tert*-Butylcyclohexanone	91	64:24:12 (**7a**:**7b**:**7c**)
3	Norcamphor	50	50:50 (**8a**:**8b**)

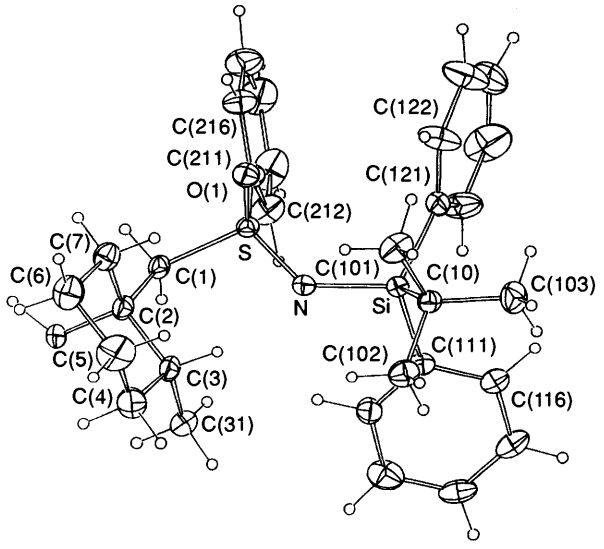
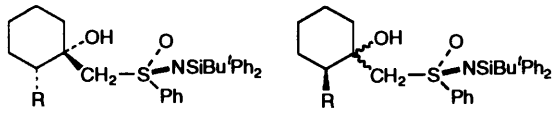


Fig. 3 X-Ray molecular structure of compound **6a**

significant amount of kinetic resolution in favour of the *S* enantiomer of the ketone had evidently occurred. Attempts to increase the extent of this kinetic resolution by treating lithiated **2f** with 2 molar equiv. of the ketone at −78 °C were unsuccessful. The diastereoselectivity of this reaction was identical with that obtained when these reagents were mixed in a 1:1.3 molar ratio.



6a R = Me
7a R = Bu^t

6b,c R = Me
7b,c R = Bu^t

The major diastereoisomeric adducts from (+)-**2f** and 2-methylcyclohexanone and 2-*tert*-butylcyclohexanone were shown to be (1*S*,2*R*,*S*$_S$)-**6a**, and (1*S*,2*S*,*S*$_S$)-**7a**, respectively, from a single-crystal X-ray structure analysis (Figs. 3 and 4). The difference in configurational assignments for C-2 in these adducts is due to a change in priorities of the ligands around C-2 according to the *R*-*S* sequence rules. Consistent with the above results with prochiral ketones, the carbinol carbon in **6a** and **7a** has the *S* stereochemistry. The structural analysis clearly shows that **6a** and **7a** result from equatorial attack of lithiated (+)-**2f** on the carbonyl carbon of the 2-alkylcyclohexanone (Figs. 3 and 4). Equatorial stereoselectivity has been reported for the addition of other hindered nucleophiles to 2-alkylcyclohexanones and other hindered cyclic ketones.[13] Johnson has also observed equatorial stereoselectivity in the reaction of lithiated **2a** with 2-*tert*-butylcyclohexanone.[12] The stereochemistry of **6a** and **7a** is readily rationalized by invoking the boat transition state **9** in which addition of lithiated **2f** occurs in an equatorial sense and *anti* to the equatorial 2-alkyl substituent. In light of the above stereochemical considerations

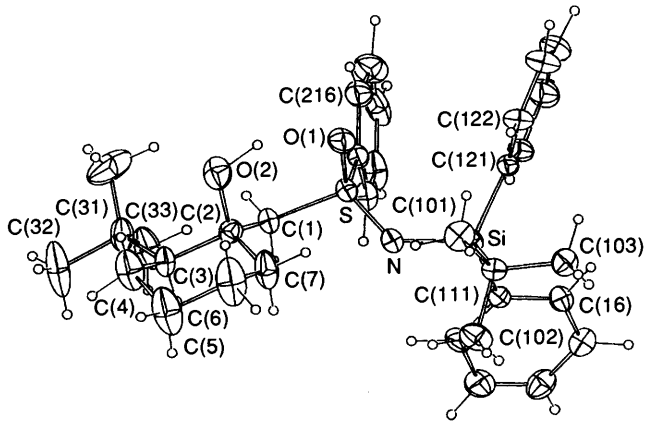
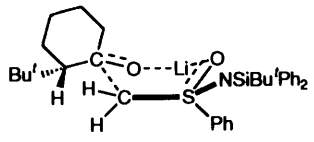


Fig. 4 X-Ray molecular structure of compound **7a**



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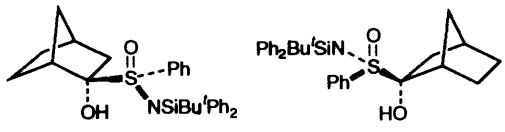
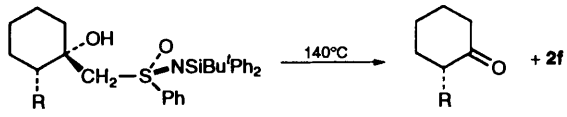
we assume that the minor diastereoisomers **6b**, **c** and **7b**, **c** have the 2*S* and 2*R* stereochemistry, respectively. While the stereochemistry of the two adducts that arise from the addition of lithiated **2f** to norcamphor is not known, we assume they arise from the attack of **2f** from the *exo* face of the ketone and are compounds **8a** and **8b**.[13,14]



8a **8b**

As further proof of the stereochemistry of **6a** and **7a** we have examined the thermolysis of these compounds to give **2f** and the optically active starting 2-alkylcyclohexanones. The diastereoisomerically pure β-hydroxy sulfoximines **6a** and **7a** when heated at *ca.* 140 °C in a Kugelrohr oven on a vacuum line at 1 mmHg for 20 min and collection of the volatile distillate gave the optically active starting 2-alkylcyclohexanones in good yield. In this way (*R*)-(−)-2-methylcyclohexanone **10** ([α]$_D^{28}$ −15.5 (*c* 0.15, MeOH) {lit.,[15] for the (*S*)-(+) enantiomer [α]$_D$ +12.3 (*c* 0.15, MeOH)} and (*S*)-(−)-2-*tert*-butylcyclohexanone **11** {[α]$_D^{23}$ −34.2 (*c* 0.99, MeOH), (lit.,[12] [α]$_D^{24.5}$ −35.4 (*c* 1, MeOH)} were obtained in 80 and 95% yields, respectively.



6a R = Me
7a R = Bu^t

(*R*)-(−)-**10** R = Me
(*S*)-(−)-**11** R = Bu^t

Compared with the reported literature optical rotations for these compounds our samples of (−)-2-*tert*-butylcyclohexanone and (−)-2-methylcyclohexanone are approximately 97 and 100% enantiomerically pure, respectively. This enantiomeric purity is very close to the enantiomeric purity of the starting sulfoximine **1** (98% e.e.). It is noteworthy that the major diastereoisomer from the reaction of lithiated **2a** and racemic 2-*tert*-butylcyclohexanone gave (*R*)-(+)-**11** upon thermolysis.[12]

The suggested transition state for this reaction involved chelation of the lithium cation through the sulfoximine nitrogen atom which is clearly disfavoured in lithiated **2f**.

To further quantify the enantiomeric purity of (−)-2-*tert*-butylcyclohexanone it was reduced with $LiAlH_4$ to (−)-2-*tert*-butylcyclohexanol in 92% yield as a mixture (56:44) of *cis* and *trans* isomers. Treatment of this mixture with 2 molar equiv. of (*R*)-(+)-methoxy(trifluoromethyl)phenylacetyl chloride (MTPAC)[17] in dichloromethane and in the presence pyridine and a small amount of 4-dimethylaminopyridine at room temperature afforded the corresponding methoxy(trifluoromethyl)phenylacetate (MTPA) ester of the *trans* alcohol, the isomeric *cis* isomer failed to give the corresponding ester probably due to steric hindrance of the axial hydroxy group. Similar treatment of a mixture of racemic *cis*- and *trans*-2-*tert*-butylcyclohexanol with (MTPAC) provided the corresponding MTPA esters of the *trans* alcohol as a 1:1 mixture of two diastereoisomers. From an examination of the ^1H NMR spectrum of the crude MTPA esters the enantiomeric purity of *trans*-2-*tert*-butylcyclohexanol was determined to be 96%. This result is in accord with the optical rotation of **11** and the optical purity of **1**.

In summary, we have shown that the sulfoximine **2f** can be obtained in high enantiomeric purity and that it reacts with methyl alkyl ketones to give carbinol products in which the major diastereoisomeric adducts have the 2*S*, S_S stereochemistry. Lithiated **2f** added to racemic 2-alkylcyclohexanones to give three diastereoisomeric adducts, the major diastereoisomer having the *S*-configuration at the tertiary carbinol centre. These adducts can be separated and used to resolve 2-methyl- and 2-*tert*-butylcyclohexanone. The stereochemical outcome of these reactions can be rationalized by invoking a chelated boat transition state that involves coordination of lithium with the sulfoximine oxygen. Thus, the diastereoselectivity of the 1,2-additions of lithiated sulfoxides and sulfoximines to carbonyl compounds can be dramatically improved when sterically hindered versions of these compounds are employed.[1,11,18]

Experimental

General Methods.—M.p.s were determined on a Reichert hot-stage apparatus and are uncorrected. IR spectra were recorded on a Bio Rad Fourier Transform Infrared Spectrophotometer model FTS-7 as mulls in Nujol unless otherwise stated. NMR spectra were recorded on a JEOL FX 90Q Fourier Transform NMR Spectrometer (90 MHz for ^1H) or a Varian Unity 400 Fourier Transform NMR spectrometer (400 MHz for ^1H) in $CDCl_3$ solution. Low resolution mass were recorded on a Vacuum Generator V.G. Quattro triple quadrupole mass spectrometer. Microanalyses were performed by the Australian National University Services Unit, Canberra or the Queensland University Chemistry Department, Queensland. The chromatography adsorbent used was silica gel (0.063–0.2 mm, Merck). Optical rotations were recorded on a Jasco model DIP-370 digital polarimeter.

(+)-(S)-N-tert-*Butyldiphenylsilyl*-S-*methyl*-S-*phenylsulfoximine* **2f**.—To a solution of (*S*)-(+)-**1** (2.82 g, 0.018 mol) and imidazole (3.1 g, 0.045 mol) in dry DMF (12 cm^3) at 0 °C was added *tert*-butylchlorodiphenylsilane (5 g, 0.018 mol, 4.73 cm^3). The reaction mixture was warmed to room temperature and stirred overnight. Water (10 cm^3) was added to the mixture which was then stirred for a further 30 min before it was extracted with dichloromethane. The extract was dried ($MgSO_4$) and evaporated and the crude product was purified by column chromatography on silica gel with 2% ethyl acetate–hexane as eluent to yield an oil (6.74 g, 94%); $[\alpha]_D^{26}$ 6.1 (*c* 1.50, acetone); δ_H(400 MHz) 7.93–7.71 (m, 6 H), 7.55–7.20 (m, 9 H), 2.85 (s, 3 H) and 1.09 (s, 9 H); δ_C(100 MHz) 135.51, 132.0, 128.91, 128.75, 127.32, 126.84, 48.96, 27.13 and 19.32; *m*/*z* (CI positive) 394 (M + H, 20%), 339 (100), 316 (100), 256 (20) and 199 (37).

(2S,S_S)-2-*Methyl*-1-(N-tert-*butyldiphenylsilyl*-S-*phenylsulfonimidoyl*)*butan*-2-*ol* **3** (R = Et) *and* (2R,S_S) **4** (R = Et).—To a solution of (+)-(*S*)-**2f** (0.4 g, 1 mmol) in dry THF (3 cm^3) was added 1.25 equiv. of butyllithium (1.6 mol dm^{-3} in hexane; 1.25 mmol, 0.78 cm^3) at 0 °C. The reaction mixture was stirred for 20 min and then cooled to −78 °C. To this solution was added ethyl methyl ketone (0.094 g, 1.3 mmol, 0.12 cm^3) and the mixture was stirred for 40 min. The reaction was quenched by the addition of 10% aqueous NH_4Cl (5 cm^3) to the mixture at −78 °C after which the whole was extracted with dichloromethane (2 × 30 cm^3). The organic layer was dried ($MgSO_4$) and evaporated and the crude product was purified by column chromatography on silica gel using 10% ethyl acetate–hexane as eluent to give **3** (R = Et) (69%). This product crystallized from hexane as a white solid, m.p. 86.5–87 °C (Found: C, 69.5; H, 7.5; N, 3.2. Calc. for $C_{27}H_{35}NO_2SSi$: C, 69.63; H, 7.57; N, 3.01%); δ_H(400 MHz) (major) 7.70–7.61 (m, 4 H), 7.55–7.50 (m, 2 H), 7.37–7.29 (m, 4 H), 7.24–7.21 (m, 3 H), 7.16–7.12 (m, 2 H), 3.35 (d, *J* 14, 1 H), 3.17 (d, *J* 14, 1 H), 1.93 (q, *J* 7.2, 2 H), 1.21 (s, 3 H), 1.08 (s, 9 H) and 0.93 (t, *J* 7.2, 3 H); δ_C(100 MHz) 144.2, 135.7, 135.6, 135.3, 134.9, 131.9, 128.9, 128.8, 128.5, 127.3, 127.0, 73.0, 67.1, 34.3, 27.1, 26.8, 19.2 and 8.04; ν_{max}(film)/cm^{-1} 3382s, 3030s, 2969s, 2858m, 1959w, 1427m, 1258s and 1149s; *m*/*z* (FAB, positive) 466 (M + H, 30%), 408 (20), 378 (10), 338 (80), 304 (30), 244 (45), 229 (50), 213 (70), 199 (100), 167 (60) and 135 (100); $[\alpha]_D^{22}$ 79 (*c* 0.63, $CHCl_3$).

Compound **4** (R = Et): δ_H(400 MHz) (in part) 3.375 (d, *J* 13.6) and 3.075 (d, *J* 13.6).

(2S,S_S)-1-(N-tert-*Butyldiphenylsilyl*-S-*phenylsulfonimidoyl*)-2,3-*dimethylbutan*-2-*ol* **3** (R = Pr^i) *and* (2R,S_S) **4** (R = Pr^i).—The title compound was prepared by the method described for the synthesis of **3** (R = Et) except that isopropyl methyl ketone was used instead of ethyl methyl ketone, gave **3** (R = Pr^i) as a white solid (43%), m.p. 83–84 °C (Found: C, 70.25; H, 7.6; N, 2.8. Calc. for $C_{28}H_{37}NO_2SSi$: C, 70.10; H, 7.77; N, 2.92%); δ_H(400 MHz) 7.67–7.61 (m, 4 H), 7.52–7.50 (m, 2 H), 7.35–7.29 (m, 4 H), 7.24–7.20 (m, 3 H), 7.14–7.12 (m, 2 H), 3.33 (d, *J* 14, 1 H), 3.26 (d, *J* 14, 1 H), 2.43 (m, 1 H), 1.12 (s, 3 H), 1.08 (s, 9 H), 0.985 (d, *J* 6.8, 3 H) and 0.918 (d, *J* 6.8, 3 H); δ_C(100 MHz) 144.5, 135.8, 135.7, 135.4, 135.0, 132.0, 129.1, 128.9, 128.6, 127.4, 127.1, 75.4, 66.0, 36.9, 27.2, 22.6, 19.3, 18.2 and 16.5; ν_{max}(film)/cm^{-1} 3358s, 3030s, 2964s, 2858m, 1427m, 1258s and 1148s; *m*/*z* (FAB, positive) 480 (M + H, 15%), 466 (10), 378 (10), 338 (50), 244 (65), 229 (65), 312 (70), 199 (100) and 167 (80); $[\alpha]_D^{22}$ 69.1 (*c* 0.78, $CHCl_3$).

Compound **4** (R = Pr^i): δ_H(400 MHz) (in part) 3.360 (d, *J* 13.6), 3.091 (d, *J* 14).

(2S,S_S)-1-(N-tert-*Butyldiphenylsilyl*-S-*phenylsulfonimidoyl*)-2-*phenylpropan*-2-*ol* **3** (R = Ph) *and* (2R,S_S) **4** (R = Ph).—The title compound was prepared by the method described for the synthesis of **3** (R = Et) except that methyl phenyl ketone was used instead of ethyl methyl ketone and gave **3** (R = Ph) as white crystals (65%), m.p. 102–103 °C (Found: C, 72.1; H, 7.3; N, 2.55. Calc. for $C_{31}H_{35}NO_2SSi$: C, 72.47; H, 6.87; N, 2.73%); δ_H(400 MHz) 7.62–7.60 (m, 2 H), 7.43–7.41 (m, 2 H), 7.36–7.23 (m, 9 H), 7.16–7.14 (m, 5 H), 7.07 (m, 2 H), 3.78 (d, *J* 14.4, 1 H), 3.57 (d, *J* 14.4, 1 H), 1.45 (s, 3 H) and 1.03 (s, 9 H); δ_C(22.5 MHz) 144.7, 143.7, 135.7, 131.6, 129.0, 128.9, 128.3, 128.0, 127.4, 127.2, 127.0, 126.7, 125.0, 73.4, 69.3, 32.3, 27.1 and 19.2; ν_{max}(film)/cm^{-1} 3449s, 3323m, 3068s, 2959s, 2857s, 1958m, 1426m, 1264s and 1109s; *m*/*z* (FAB, positive) 514 (M + H,

5%), 461 (5), 369 (30), 277 (10), 211 (100), 192 (100) and 115 (100); $[\alpha]_D^{23}$ 36.8 (*c* 0.74, $CHCl_3$).

Compound **4** (R = Ph): δ_H(400 MHz) (in part) 3.79 (d, *J* 17.2) and 3.35 (d, *J* 17.2).

(2S,S_S)-1-(N-tert-*Butyldiphenylsilyl*-S-*phenylsulfonimidoyl*)-2,3,3-*trimethylbutan*-2-*ol* **3** (R = Bu^t) *and* (2R,S_S) **4** (R = Bu^t).—The title compound, prepared by the method described for the synthesis of **3** (R = Et) except that butyl methyl ketone was used instead of ethyl methyl ketone, was purified by recrystallization of the crude product from hexane to give **3** (R = Bu^t) as white crystals (63%), m.p. 128–130 °C (Found: C, 70.3; H, 8.1; N, 2.8. Calc. for $C_{29}H_{39}NO_2SSi$: C, 70.54; H, 7.96; N, 2.84%); δ_H(400 MHz) 7.74–7.69 (m, 4 H), 7.62–7.60 (m, 2 H), 7.43–7.19 (m, 9 H), 3.38 (d, *J* 14, 1 H), 3.31 (d, *J* 14, 1 H), 1.28 (s, 3 H), 1.08 (s, 9 H) and 0.84 (s, 9 H); δ_C(22.4 MHz) 144.5, 135.7, 131.9, 129.0, 128.9, 128.6, 127.4, 127.2, 127.1, 75.2, 65.7, 38.7, 27.3, 24.7, 22.4 and 19.4; ν_{max}(film)/cm^{-1} 3378s, 3070s, 2960s, 2858s, 1960w, 1473s, 1274s, 1157s and 1107m; *m*/*z* (FAB, positive) 494 (M + H, 5%), 461 (5), 211 (100) and 137 (100); $[\alpha]_D^{22}$ 49.4 (*c* 0.9, $CHCl_3$).

Compound **4** (R = Bu^t): δ_H(400 MHz) (in part) 3.41 (d, *J* 13.6) and 3.09 (d, *J* 13.6).

(1S,2R,S_S)-2-*Methyl*-1-(N-tert-*butyldiphenylsilyl*-S-*phenylsulfonimidoylmethyl*)*cyclohexanol* **6a** *and* (1R,2R*, S_S) **6b**, **c**.—The title compound was prepared by the method described for the synthesis of **3** (R = Et) except that 2-methylcyclohexanone was used instead of methyl phenyl ketone and gave a mixture of **6a–c** in 54% yield after recrystallization of the crude reaction mixture. Further recrystallization gave pure **6a** as white crystals, m.p. 140–141 °C (Found: C, 71.55; H, 8.1; N, 2.7. $C_{30}H_{39}NO_2SSi$ requires C, 71.24; H, 7.77; N, 2.77%); δ_H(400 MHz) 7.69–7.64 (m, 4 H), 7.57–7.55 (m, 2 H), 7.40–7.22 (m, 7 H), 7.16 (m, 2 H), 3.51 (d, *J* 14, 1 H), 3.25 (d, *J* 14, 1 H), 2.16–2.08 (m, 1 H), 1.86–1.14 (m, 9 H), 1.07 (s, 9 H) and 0.92 (d, *J* 6.8, 3 H); δ_C(22.5 MHz) 135.7, 131.9, 129.0, 128.9, 128.6, 127.4, 127.1, 127.0, 73.4, 67.6, 39.2, 36.4, 30.2, 27.3, 23.8, 21.7, 19.4 and 14.8; ν_{max}(film)/cm^{-1} 3485s, 3363s, 3030s, 2933s, 2859s, 1959w, 1426m, 1259s and 1139s; *m*/*z* (FAB, positive) 506 (M + H, 10%), 452 (10), 302 (15), 211 (90), 199 (100) and 167 (100); $[\alpha]_D^{22}$ 56.6 (*c* 1.16, $CHCl_3$).

Compound **6b**: δ_H(400 MHz) (in part) 3.42 (d, *J* 14), 3.14 (d, *J* 14); **6c**: δ_H(400 MHz) (in part) 3.55 (d, *J* 13.6) and 2.96 (d, *J* 13.6).

(1S,2S,S_S)-2-tert-*Butyl*-1-(N-tert-*butyldiphenylsilyl*-S-*phenylsulfonimidoylmethyl*)*cyclohexanol* **7a** *and* (1R,2R*, S_S) **7b**, **c**.—The title compound, prepared by the method described for the synthesis of **3** (R = Et) except that 2-*tert*-butylcyclohexanone was used instead of ethyl methyl ketone, gave **7a–c** (91%) after column chromatography. Recrystallization gave pure **7a** as white crystals, m.p. 124–125 °C (Found: C, 72.5; H, 8.3; N, 2.9. $C_{33}H_{46}NO_2SSi$ requires C, 72.21; H, 8.45; N, 2.55%); δ_H(400 MHz) 7.71–7.63 (m, 4 H), 7.59–7.57 (m, 2 H), 7.38–7.23 (m, 6 H), 7.21–7.15 (m, 3 H), 3.88 (d, *J* 14, 1 H), 3.35 (d, *J* 14, 1 H), 2.34–2.26 (m, 1 H), 1.78–1.12 (m, 8 H), 1.07 (s, 9 H) and 0.996 (s, 9 H); δ_C(100 MHz) 145.4, 135.7, 135.67, 135.6, 135.3, 131.9, 129.0, 128.9, 128.6, 127.4, 127.2, 126.9, 75.3, 69.8, 52.8, 38.5, 34.7, 31.8, 27.2, 24.8, 24.7, 21.7 and 19.4; ν_{max}/cm^{-1} 3472s, 3069m, 1959w, 1296s, 1141s and 1110s; *m*/*z* (CI, positive) 549 (M + H, 25%), 378 (20), 338 (100), 318 (30), 302 (30), 262 (55), 244 (50) and 199 (100); $[\alpha]_D^{24}$ 45.1 (*c* 0.9, $CHCl_3$).

Compound **7b**: δ_H(400 MHz) (in part) 4.02 (*J* 13.6), 3.11 (d, *J* 13.6); **7c**: δ_H(400 MHz) (in part) 3.70 (d, *J* 14.4) and 3.54 (d, *J* 14.4).

(1R*,2S*,4R*,S_S)-2-(N-tert-*Butyldiphenylsilyl*-S-*phenylsulfonimidoylmethyl*)*bicyclo*[2.2.1]*heptan*-2-*ol* **8**.—The title compound was prepared by the method described for the synthesis of **3** (R = Et) except that norcamphor was used instead of methyl phenyl ketone and gave **8** as a mixture of two isomers in 50% yield as white solid, m.p. 141–142 °C (Found: C, 71.8; H, 7.6; N, 2.7. $C_{30}H_{37}NO_2SSi$ requires C, 71.53; H, 7.40; N, 2.78%); δ_H(400 MHz) 7.64–7.57 (m, 4 H), 7.50–7.48 (m, 2 H), 7.36–7.24 (m, 4 H), 7.22–7.18 (m, 3 H), 7.17–7.10 (m, 2 H), 5.84 (s, 1 H), 3.46 (d, *J* 14, 1 H), 3.24 (d, *J* 14, 1 H), 2.35–2.29 (m, 1 H), 2.25–2.15 (m, 2 H), 1.59–1.22 (m, 7 H) and 1.09 (s, 9 H); isomer **2** 5.79 (s, 1 H), 3.44 (d, *J* 14), 3.22 (d, *J* 14) and 1.08 (s, 9 H); δ_C(100 MHz) (on mixture of both isomers) (144.1, 143.95), (135.8, 135.6), (135.2, 135.0), (134.8, 134.7), (132.04, 132.01), 129.0, (128.91, 128.89), 128.6, 127.4, 127.1, 127.09, 127.07, (79.0, 78.4), (68.3, 66.8), (47.8, 47.3), (45.3, 44.5), (38.6, 37.9), (37.7, 36.9), (28.6, 28.3), (27.2, 27.1), (21.9, 21.3) and (19.3, 19.2); ν_{max}/cm^{-1} 3346s, 3059m, 1959w, 1254s, 1155s and 1101m; *m*/*z* (CI, positive), 504 (M + H, 10%), 446 (20), 428 (10), 368 (30), 338 (100), 244 (80), 199 (100) and 125 (100).

(−)-2-*Methylcyclohexanone*.—Solid **6a** (0.54 g) in a small round bottom flask (25 cm^3) was heated in a Kugelrohr oven at 135 °C on a vacuum line (1 mmHg) for 20 min. The ketone (0.18 g, 80%) was obtained in the cooled collector; $[\alpha]_D^{28}$ −15.4 (*c* 0.15, MeOH).

(−)-2-tert-*Butylcyclohexanone*.—The title compound was prepared by the method described above by heating **7a**. The ketone was obtained in 95% yield as an oil; $[\alpha]_D^{23}$ −34.2 (*c* 0.985, MeOH); δ_H(400 MHz) 2.32–1.43 (m, 9 H) and 0.992 (s, 9 H); ν_{max}(film)/cm^{-1} 1710s, 1440s, 1363s and 1125s.

cis *and* trans 2-tert-*Butylcyclohexanol*.—To a solution of (−)-2-*tert*-butylcyclohexanone (0.1 g, 0.65 mmol) in dry ether (1.5 cm^3) at 0 °C was added 3 cm^3 of a 0.175 mol dm^{-3} solution of lithium aluminium hydride in ether (0.02 g in 3 cm^3 of ether) under a N_2 atmosphere. After 2 h the reaction mixture was warmed to room temperature and stirring was continued for a further 20 min. The slurry was then filtered and the filtrate was washed with saturated aqueous NaCl, dried ($MgSO_4$) and the ether was removed on a water-bath to provide an oil (0.092 g, 92%); δ_H(400 MHz) 4.25 (s, 1 H), 3.49 (m, 1 H), 1.96–0.82 (m, 9 H), 0.998 (s, Bu^t of *cis*), 0.953 (s, Bu^t of *trans*) (*cis*:*trans* = 56:44); ν_{max}/cm^{-1} 3325s, 1340s, 1081s, 850s.

1-(2-tert-*Butyl*)*cyclohexyl*-(S)-α-*methoxy*-α-(*trifluoromethyl*)*phenylacetate*.—To a solution of 2-*tert*-butylcyclohexanol (16 mg, 0.1 mmol) in dry dichloromethane (0.5 cm^3) at 0 °C was added pyridine (3 drops) and dimethylaminopyridine (2 crystals). Then (*R*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (MTPAC; 0.15 mmol, 28 mm^3) was added with a microsyringe. The solution was warmed to room temperature and stirring was continued under N_2 for 10 days. The mixture was then extracted with ether (2 × 15 cm^3) and extract washed with 5% of HCl (10 cm^3), water (10 cm^3), 10% aqueous NaOH (10 cm^3) and then water (10 cm^3). The extract was dried ($MgSO_4$) and evaporated. Purification was carried out on a preparative TLC plate to afford the title compound (18 mg, 47%); δ_H(400 MHz) (major diastereoisomer) 7.58–7.56 (m, 2 H), 7.38–7.36 (m, 3 H), 4.91 (dt, *J* 4, 10, 1 H), 3.624 (q, *J* 1.2, 3 H), 2.17–0.83 (m, 9 H), 0.633 (s, 9 H); minor diastereoisomer: 4.97 (dt, *J* 4, 10, 1 H), 3.44 (q, *J* 1.2), 0.827 (s, 3 H); *m*/*z* [CI (NH_3), positive] 390 (M + NH_4^+, 100).

Structure Determinations.—Unique room-temperature diffractometer data sets ($T \sim 295$ K; monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å; $2\theta/\theta$ scan mode) yielded N independent reflections, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full matrix/large block least-squares

Table 3 Selected geometrical parameters for **3** (R = Ph, Bu^t), **6a**, **7a**

Compd./R/mol	3/Ph/1,2	3/Bu^t/1,2	6a	7a
(a) Distances (Å)				
Si(1)–C(10)	1.892(9), 1.891(9)	1.88(1), 1.92(1)	1.898(5)	1.907(6)
Si(1)–C(111)	1.882(8), 1.850(9)	1.88(1), 1.87(1)	1.868(5)	1.865(6)
Si(1)–C(121)	1.861(9), 1.88(1)	1.84(1), 1.87(1)	1.880(5)	1.878(6)
Si(1)–N(1)	1.704(6), 1.726(7)	1.72(1), 1.72(1)	1.716(4)	1.719(5)
N(1)–S(1)	1.497(7), 1.483(7)	1.45(1), 1.535(9)	1.494(4)	1.487(5)
S(1)–O(1)	1.448(6), 1.460(6)	1.484(8), 1.47(1)	1.448(4)	1.432(5)
S(1)–C(211)	1.794(8), 1.760(9)	1.77(1), 1.77(1)	1.785(5)	1.800(6)
S(1)–C(1)	1.798(8), 1.792(8)	1.78(1), 1.77(2)	1.794(5)	1.795(6)
C(1)–C(2)	1.56(2), 1.56(1)	1.55(2), 1.52(2)	1.550(7)	1.502(9)
C(2)–O(2)	1.40(1), 1.42(1)	1.43(1), 1.41(1)	1.427(6)	1.440(9)
O(1)···O(2)	2.740(8), 2.737(8)	2.83(1), —	2.858(5)	2.814(7)
(b) Angles (°)				
N(1)–Si(1)–C(10)	112.8(7), 112.6(4)	110.0(6), 106.6(6)	108.1(2)	107.4(3)
N(1)–Si(1)–C(111)	104.4(3), 104.1(4)	107.0(4), 110.4(5)	105.0(2)	106.2(3)
N(1)–Si(1)–C(121)	107.9(4), 106.6(4)	109.0(4), 108.7(5)	112.0(2)	112.5(3)
C(10)–Si(1)–C(111)	108.3(4), 109.6(4)	107.5(5), 113.7(4)	108.7(2)	109.9(3)
C(10)–Si(1)–C(121)	113.3(4), 115.4(4)	113.1(4), 109.1(5)	113.3(2)	112.5(3)
C(111)–Si(1)–C(121)	109.8(4), 107.9(4)	110.1(5), 108.7(6)	109.3(2)	108.1(3)
Si(1)–N(1)–S(1)	139.9(5), 141.9(5)	140.4(4), 128.7(7)	133.8(3)	131.2(3)
N(1)–S(1)–O(1)	120.2(4), 118.0(4)	120.8(5), 118.0(6)	120.2(2)	121.1(3)
N(1)–S(1)–C(211)	110.8(4), 112.6(4)	111.5(6), 110.9(5)	111.0(2)	111.2(3)
N(1)–S(1)–C(1)	105.2(4), 104.3(4)	109.5(4), 108.2(6)	108.3(2)	109.4(3)
O(1)–S(1)–C(211)	106.7(4), 107.2(4)	104.4(4), 105.3(7)	106.5(2)	106.4(3)
O(1)–S(1)–C(1)	108.4(4), 108.3(4)	106.5(5), 109.7(6)	108.6(2)	106.3(3)
C(211)–S(1)–C(1)	104.5(4), 105.7(4)	102.5(5), 103.9(7)	100.4(2)	100.4(3)
S(1)–C(1)–C(2)	115.2(6), 115.8(6)	117.2(7), 123(1)	120.9(4)	117.6(4)
C(1)–C(2)–O(2)	109.0(7), 109.9(6)	107.8(7), 110(1)	104.0(4)	107.5(5)
(c) Torsion angles (°)*				
N–Si–111–112	−23.3(8), −20.6(7)	−17.5(9), −75.2(10)	−8.1(5)	−17.9(6)
N–Si–121–122	−52.2(8), −40.6(8)	62.6(10), 16.3(10)	74.8(6)	88.1(6)
N–Si–10–101	−61.7(7), −68.1(8)	−51(1), −71.5(11)	−53.4(4)	−49.7(5)
S–N–Si–10	33.5(8), 31.2(9)	91.7(9), −175.7(5)	98.9(4)	118.8(4)
S–N–Si–111	150.9(7), 149.8(7)	−151.8(9), −52.3(7)	−145.2(4)	−123.7(4)
S–N–Si–121	−92.4(8), −96.3(8)	−32.8(10), 66.9(7)	−26.6(4)	−5.7(5)
Si–N–S–O(1)	−68.4(8), −71.7(9)	−61.6(11), −49.4(8)	−59.7(4)	−62.8(5)
Si–N–S–1	169.2(6), 168.2(7)	174.1(8), −174.7(5)	174.7(3)	173.1(4)
Si–N–S–211	56.8(8), 54.1(9)	61.5(10), 72.1(9)	65.4(4)	63.2(5)
O(1)–S–1–2	28.0(7), 30.1(7)	−52.2(8), −122.2(9)	−59.9(4)	−46.0(6)
N–S–1–2	157.8(6), 156.5(6)	80.1(9), 7.8(10)	72.3(4)	86.4(5)
211–S–1–2	−85.5(6), −84.5(7)	−161.5(8), 125.7(9)	−171.3(4)	−156.6(5)
O(2)–2–1–S	−61.4(8), −59.8(8)	63.4(11), 42.9(11)	−174.1(3)	66.8(6)
O(1)–S–211–212	173.8(7), 175.2(6)	164.6(9), −158.8(11)	167.8(5)	177.7(5)
N–S–211–212	41.32(8), 43.8(8)	32.5(10), 72.5(14)	35.3(5)	43.9(6)

* Except for oxygen atoms, unique non-hydrogen atoms are denoted by symbol and carbon atoms by number.

refinement without absorption correction after solution of the structures by direct methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms (x,y,z, U_{iso})$_H$, being included constrained at estimated values. Conventional residuals R,R_w on $|F|$ are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\ \sigma^4(I_{diff})$ being used. Neutral atom complex scattering factors were employed, chiralities being adopted from the chemistry. Computation used the XTAL 3.0 program system implemented by S. R. Hall.[19] Material deposited comprises atom coordinates and thermal parameters, molecular non-hydrogen geometries, and structure factor amplitudes; pertitent results are given in the Figures and Table 3.

Crystal/Refinement Data.—**3** (R = Ph). $C_{31}H_{35}NO_2SSi$, M = 513.8. Triclinic, space group $P\bar{1}$ (C_1, No. 1), a = 15.516(6), b = 9.860(4), c = 9.491(7) Å, α = 90.59(5), β = 97.22(5), γ = 95.28(3)°, V = 1434 Å^3, D_c (Z = 2) = 1.19 g cm^{-3}; F(000) = 548, μ_{Mo} = 1.2 cm^{-1}; specimen: 0.29 × 0.35 × 0.52 mm; $2\theta_{max}$ = 50°; N = 4962, N_o = 4288; R = 0.065, R_w = 0.070.

3 (R = Bu^t). $C_{29}H_{39}NO_2SSi$, M = 493.8. Triclinic, space group $P\bar{1}$, a = 13.18(2), b = 12.25(1), c = 10.52(1) Å, α = 66.36(8), β = 84.84(8), γ = 65.03(7)°, V = 1404 Å^3, D_c (Z = 2) = 1.17 g cm^{-3}; F(000) = 532, μ_{Mo} = 1.5 cm^{-1}; specimen: 0.55 × 0.22 × 0.45 mm; $2\theta_{max}$ = 46°; N = 3902, N_o = 3422; R = 0.066, R_w = 0.070.

6a. $C_{30}H_{39}NO_2SSi$, M = 505.8. Orthorhombic, space group $P2_12_12_1$ (D_2^4, No. 19), a = 20.574(4), b = 16.162(5), c = 8.689(7) Å, V = 2889 Å^3, D_c (Z = 4) = 1.16 g cm^{-3}; F(000) = 1088, μ_{Mo} = 1.4 cm^{-1}; specimen: 0.45 × 0.32 × 0.42 mm; $2\theta_{max}$ = 50°; N = 2887, N_o = 2327; R = 0.049, R_w = 0.053.

7a. $C_{33}H_{45}NO_2SSi$, M = 547.9. Orthorhombic, space group $P2_12_12_1$, a = 21.697(9), b = 14.257(9), c = 10.284(7) Å, V = 3181 Å^3, D_c (Z = 4) = 1.14 g cm^{-3}; F(000) = 1184, μ_{Mo} = 1.7 cm^{-1}; specimen: 0.48 × 0.35 × 0.80 mm; $2\theta_{max}$ = 50°; N = 2797, N_o = 2060; R = 0.051, R_w = 0.055.

Abnormal Features/Variations in Procedure.—For both compounds **3** (R = Ph, Bu^t), despite being substantial specimens, diffracted rather weakly with wide line widths and rather high residuals not improved by remeasurement of the

data. Both crystallize in space group $P1$ with some pseudo-symmetry, the two independent molecules of the phenyl derivative having a displaced two-fold rotational relationship, while the packing in the *tert*-butyl adduct is quasi-centrosymmetric, so much so that the structure was initially 'solved' in space group $P\bar{1}$ and the non-centrosymmetric perturbation then introduced.

In all four compounds, the locations of the hydroxyl hydrogen atoms were established from difference maps. A gaussian absorption correction was applied to the data of **7a** ($A^*_{min,max}$ = 1.05, 1.08). The common spine of the four species is numbered as shown, with the sequence C(10, 111, 121) in projection down N(1)–Si(1) set clockwise, and the torsion angle N–Si–C(n1)–C(n2) acute; the S-phenyl ring has the O–S–C(1)–C(2) torsion *trans*.

Structural Commentary.—The results of the room-temperature single-crystal X-ray studies are consistent with the above connectivities and stoichiometries; all crystallize in chiral space groups, *i.e.* the single crystal subjected to the X-ray study in each case is enantiomerically pure, with the chirality of the enantiomorph chosen according to that of **2f** and the relative stereochemistry of the remainder following from the structural results. Geometrical parameters for the molecular cores are summarized in Table 3; generally they are as expected, being comparable with values determined in earlier studies on related systems[20] (but see below). In the two derivatives **3** (R = Ph, Bu^t), two independent molecules comprise the asymmetric unit of the structure, pseudosymmetry being particularly evident in the structure of **3** (R = Ph) for which the geometrical parameters, where they differ at all significantly, do so only trivially, remaining generally comparable with values found in **6a** and **7a** also. For the Bu^t analogue, however, the geometries of the two independent molecules differ significantly, being rotamers about the N–Si bond with significant effect on the associated S–N–Si angles, the value for the primed molecule [128.7(7)°] being significantly less than that of the other molecule and those of the phenyl analogue. Concomitantly, the N–S distance is increased, with suggestions of small but consistent associated diminution in the N–S–X angles, while more pronounced angular changes are observed about the silicon atom, presumably a consequence of changes in steric interactions. The disposition of O(2) is more variable across the series, being disposed at the less conjugated extreme of the molecular spine, and it is not clear to what extent its disposition may be a consequence of intra- *vs.* inter-molecular contacts/interactions. Nevertheless, location of the hydroxyl hydrogen atom from difference maps in all cases, suggests a significant interaction with the sulfoxide oxygen is possible [see O(1)···O(2), Table 3; in the primed molecule of **3** (R = Bu^t) N···O(2) is 2.87(1) Å]. Moreover, in **6a** an intermolecular hydrogen bond may be postulated [O, H(2)···O(1)] ($1\frac{1}{2} - x$, $1 - y$, $\frac{1}{2} + z$) 2.858(5), 1.8 (est.) Å, while in the primed molecule of **3** (R = Bu^t) H(2)···N (intramolecular) is 2.3 (est.) Å.

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