Tandem Conjugate addition of Silylcuprate and Benzenesulfenyl Chloride to Unsaturated Esters: Stereoselective Preparation of *anti*-3-Dimethylphenylsilyl-2-phenylthio Aldehydes

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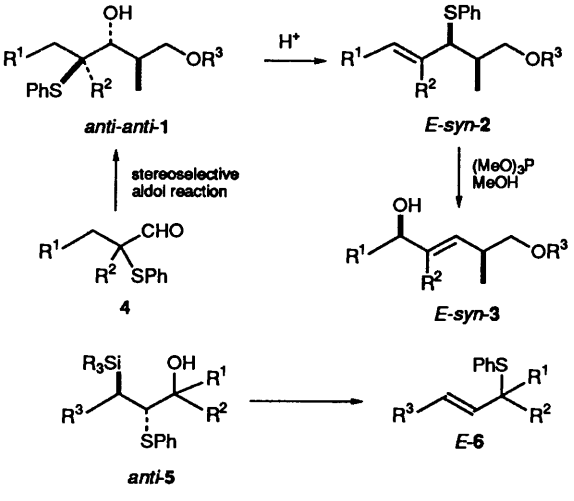
Conjugate addition of dimethylphenylsilylcuprate is successful even to a 2,3-disubstituted acrylate ester and when followed by α-sulfenylation of the trapped silyl enol ether intermediate, reduction and re-oxidation gives, for example, (2*SR*,3*RS*)-(*anti*)-2,5-dimethyl-3-dimethylphenylsilyl-2-phenylthiohexanal as a single diastereoisomer.

We have described[1] how stereospecific [1,2]-phenylthio shifts of β-phenylthio alcohols **1** can be used to prepare allylic alcohols **3** with two stereochemically defined 1,4-related chiral centres *via* the allylic sulfides **2**. The stereocontrolled synthesis of pure *syn* and *anti*[2] alcohols **3** can be achieved only when the three chiral centres in **1** and the geometry of the double bond in **2** are controlled. *syn*- And *anti*-selective† aldol reactions between enolates of propionate esters and 2-phenylthio aldehydes **4** have provided β-phenylthio alcohols **1** with high C(2)–C(3) (*anti* or *syn* aldol)[3] and C(3)–C(4) (Felkin–Anh)[4] diastereo and enantio-selectivity. The stereoselectivity in the rearrangement is affected by the stereochemistry of C(2)–C(3).[1] Thus, *anti,anti*-**1**[5] rearranges to *E-syn*-**2**, which was transformed into *E-syn*-**3**. The rearrangement of *syn,anti*-**1** gives an inseparable *E*- and *Z-anti*-**2** mixture, which would lead to a mixture of *E-anti*- and *E-syn*-**3**.



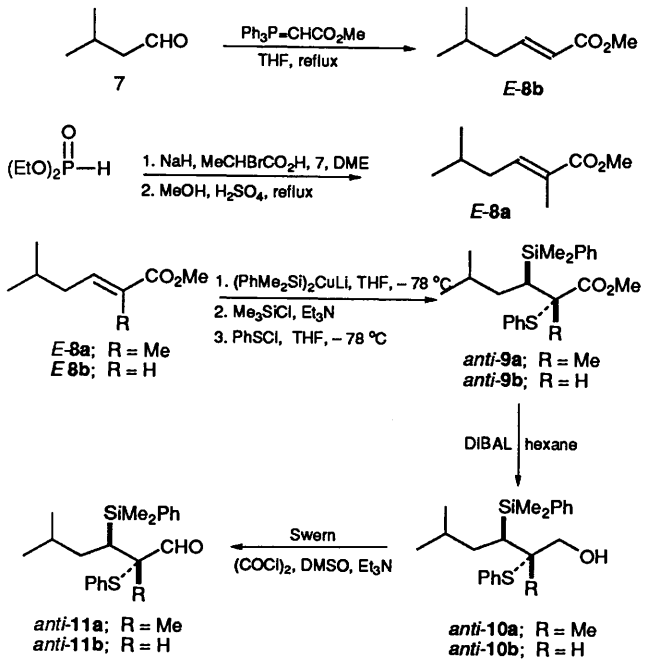
Although an alternative route to *E-anti*-**3** by Ireland–Claisen [3,3] sigmatropic rearrangement has been demonstrated,[1] we are interested in achieving the [1,2]-phenylthio shift of **1** to **2** with total control of the double-bond geometry, in order to extend the aldol methodology. A potentially general and versatile way to do that would be to prepare β-phenylthio-γ-silyl alcohols **5**, as similar compounds are known to rearrange to allyl sulfides *E* (or *Z*)-**6**, *via* [1,2]-phenylthio shift and loss of silicon. The silyl group controls the position and geometry of the double bond and encourages the rearrangement when required ('uphill' migrations).[6] It is necessary to have *anti* related silyl and phenylthio groups in **5** for the rearrangement to give an *E* double bond in the allylic sulfide **6**.

This paper deals with the synthesis of 3-dimethylphenylsilyl-2-phenylthio esters and aldehydes *via* Michael addition of dimethylphenylsilylcuprate to esters followed by α-sulfenylation. Although α,β-substitution prevents conjugated addition of methylcopper reagents to some but not all enoate esters, more reactive copper reagents are expected to add 1,4 to α,β-dialkyl acrylic esters. Thus, dimethylphenylsilylcuprate $(PhMe_2Si)_2$-CuLi,[7] is an effective stereocontrol unit in alkylations of acyclic and cyclic α,β-unsaturated aldehydes, ketones or esters[8,9] with a high degree of diastereoselectivity towards the isomer having the silyl and alkyl groups *anti*. Protonation of the enolate containing the alkyl group gives the other isomer but with somewhat lower diastereoselectivity.[7] We reasoned that Michael addition of this silylcuprate to unsaturated esters, and perhaps even to aldehydes, in tandem with sulfenylation should also give largely the *anti* diastereoisomer of the α-phenylthio-β-silyl carbonyl compound.

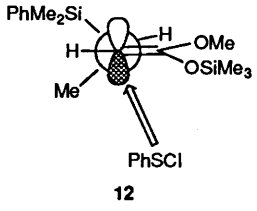
We were interested in the chemistry of one particular series to compare the results with those from the sequence (a) stereoselective aldol reaction, (b) [1,2]-phenylthio migration[1] in the preparation of 2*RS*,5*SR*-(*E*)- and 2*RS*, 5*RS*-(*E*)-2,4,7-trimethyloct-3-ene-1,5-diols from 2,5-dimethyl-2-phenylthiohexanal **4** (R^1 = Bu^i, R^2 = Me).[10] The starting material **8a** was accessible by phosphite-mediated *in situ* carboxyvinylation.[11] Treatment of diethyl phosphite with 3 equiv. of sodium hydride and 2-bromopropionic acid in 1,2-dimethoxyethane at room temperature gave the phosphonate anion, which was treated with 3-methylbutanal **7** at this temperature. Esterification of the resulting acrylic acid with methanol in acidic medium gave **8a**. That this is pure *E* isomer is shown by the chemical shift of the vinylic proton (δ 6.78) in the range[12] 6.5–7.0 ppm. More conventional olefination with ethyl 2-(diethylphosphono)-propionate is also completely *E* selective.[13]

Conjugate addition of the dimethylphenylsilylcuprate to **8a** in THF at low temperature (−78 °C) gave the enolate which was silylated directly with chlorotrimethylsilane. The silyl enol ether was sulfenylated with benzenesulfenyl chloride in THF solution.[14] The crude mixture was chromatographed on a silica column and the α-phenylthio-β-silyl methyl ester *anti*-**9a** was obtained in a 55% yield. NMR spectra of the crude reaction

† The *syn* and *anti* convention suggested by Masamune (see refs. 2 and 5) is used: the carbon chain is drawn in its most extended form and compounds **2** and **3** are *syn* if Me and PhS or OH are on the same side and *anti* if they are on opposite sides. For compound **1** the first *syn* or *anti* refers to the relationship of OH and PhS in the 2,3 positions and the second to the PhS and Me in the 3,4 positions.



mixture exhibited no trace of the *syn* isomer nor was this isomer detectable by chromatography. The high diastereoselectivity of sulfenylation can be explained if the electrophile (PhSCl) attacks the less hindered face of the Houk conformation **12** of the silyl enol ether.[15] We also examined 1,4-addition of the silylcuprate to the α,β-unsaturated ester **8b**, easily made in good yield by a Wittig reaction between methoxycarbonylmethylenetriphenylphosphorane[16] and 3-methylbutanal **7** in refluxing THF.[17] When a similar conjugate addition was attempted with **8b**, an inseparable mixture of *anti*-**10b** and methyl 3-dimethylphenylsilyl-5-methylhexanoate was obtained. Reduction of the ester *anti*-**9a** with DIBAL gave the primary alcohol *anti*-**10a**, whose oxidation (Swern)[18] gave aldehyde *anti*-**11a**. Similarly, the mixture of *anti*-**9b** and the non-sulfenylated ester was reduced with DIBAL and the primary alcohol *anti*-**10b** was isolated. Further oxidation (Swern)[18] gave aldehyde *anti*-**11b**.



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In order to extend this methodology, we applied it to an α,β-unsaturated aldehyde, 2-methylhex-2-enal. This enal was easily made by aldol condensation of propionaldehyde (NaOH) but attempts to prepare 2,5-dimethylhex-2-enal by $TiCl_4$-mediated condensation of the trimethylsilyl enol ether of propionaldehyde with 3-methylbutanal failed. Similarly, $ZnBr_2$- or $TiCl_4$-mediated alkylidenation of this silyl enol ether with α-chlorobutyl phenyl sulfide always failed to provide 2,5-dimethylhex-2-enal.[19] Conjugate addition of lithium dimethylphenylsilylcuprate to 2-methylhex-2-enal was attempted in different solvents (pentane and diethyl ether have been reported as the best solvents for conjugate addition of copper reagents to α,β-unsaturated aldehydes and THF is considered the worst)[20] and, after quenching the enolate with chlorotrimethylsilane, sulfenylation was attempted with THF solutions of benzenesulfenyl chloride. Traces of the α-phenylthio-β-silyl aldehyde could be detected by ^1H NMR as part of a complex mixture of products. Attempts to purify the product by distillation or chromatographic methods were unsuccessful.

Experimental

General experimental details have been published in this journal.[21]

Methyl (E)-2,5-*Dimethylhex*-2-*enoate* **8a**.—A solution of 2-bromopropionic acid (2.4 g, 15.5 mmol) in 1,2-dimethoxyethane (15 cm^3) was added dropwise to a suspension of sodium hydride in mineral oil (60%; 2.2 g, 55 mmol) and diethyl phosphite (2 cm^3, 15.5 mmol) in 1,2-dimethoxyethane (50 cm^3). The mixture was stirred until hydrogen gas evolution ceased after which a solution of 3-methylbutyraldehyde (1.3 g, 15.5 mmol) in 1,2-dimethoxyethane (2 cm^3) was added to it. The mixture was stirred for 1 h at room temperature after which the reaction was quenched with ethanol (2.5 cm^3) and the solution poured into water (250 cm^3). The strongly basic solution was washed with diethyl ether (2 × 25 cm^3) to remove the mineral oil, acidified with concentrated hydrochloric acid to pH 4 and extracted with diethyl ether (3 × 150 cm^3). The organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure. Distillation of the residue gave (E)-2,5-*dimethylhex*-2-*enoic acid* (1.8 g, 81%) as a colourless oil, b.p. 135–140 °C/30 mmHg; ν_{max}(film)/cm^{-1} 3300–2800 (OH), 1680 (CO) and 1620 (C=C); $\delta_H(CDCl_3)$ 11.5–11.0 (1 H, br s, CO_2H), 6.97 (1 H, t, *J* 7.6,* CH=C), 2.08 (2 H, dd, *J* 7.1, 7.6, CH_2C=C), 1.82 (3 H, s, MeC=C), 1.79–1.71 (1 H, m, Me_2CH) and 0.92 (6 H, d, *J* 6.6, Me_2CH) (Found: M^+, 142.0992. $C_8H_{14}O_2$ requires *M*, 142.0990); *m*/*z* 142 (36%, M^+), 100 (100, M − C_2H_2O), 87 (33, $C_4H_7O_2$) and 82 (35, M − $MeCO_2H$). A mixture of this acid (1.7 g, 12 mmol), methanol (6 cm^3, 148 mmol) and concentrated sulfuric acid (0.15 cm^3) was refluxed for 4 h. After cooling, the mixture was diluted with water (7 cm^3) and extracted with diethyl ether (3 × 120 cm^3). The combined extracts were washed with saturated aqueous sodium carbonate, dried ($MgSO_4$) and evaporated under reduced pressure to give an oil. Distillation of this gave the unsaturated ester **8a** previously described[12] but not characterised (1.4 g, 77%), b.p. 85–87 °C/10 mmHg; ν_{max}(film)/cm^{-1} 1700 (CO) and 1640 (C=C); $\delta_H(CDCl_3)$ 6.78 (1 H, t, *J* 7.6, CH=C), 3.72 (3 H, s, CO_2Me), 2.05 (2 H, t, *J* 7.5, CH_2CHC=C), 1.81 (3 H, s, *Me*C=CH), 1.79–1.68 (1 H, m, Me_2CH), and 0.92 (6 H, d, *J* 6.6, Me_2CH); $\delta_C(CDCl_3)$ 12.27 (*Me*C=CH), 22.26 (Me_2CH), 28.13 (Me_2CH), 37.55 (CH_2CH=C), 51.41 (CO_2Me), 127.80 (CH=*C*), 141.40 (*C*H=C) and 168.46 (CO_2Me) (Found: M^+, 156.1153. $C_9H_{16}O_2$ requires *M*, 156.4567); *m*/*z* 156 (25%, M^+), 114 (100, M − C_2H_2O) and 100 (80, M − Me − C_2H_2O).

Methyl (E)-5-*Methylhex*-2-*enoate* **8b**.—Methyl bromoacetate (5.3 g, 34.6 mmol) in dry toluene (20 cm^3) was added dropwise to a stirred solution of triphenylphosphine (9.5 g, 36.3 mmol) in toluene (20 cm^3). The mixture was stirred for 1 h, left overnight and then filtered and washed with toluene to give methoxycarbonylmethyltriphenylphosphonium bromide (11.5 g, 80%) as a solid, m.p. 160–162 °C (lit.,[16] 163 °C). The bromide (5 g, 12 mmol) was dissolved in dichloromethane (20 cm^3) and 10% aqueous sodium carbonate (15 cm^3) was added to the solution. The mixture was stirred for 20 min after which the organic phase was separated and the aqueous layer extracted with dichloromethane (2 × 120 cm^3). The combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure. Recrystallization of the residue from ethyl acetate

* Throughout *J* values are recorded in Hz.

gave the ylide (3.8 g, 95%) as a solid, m.p. 160–162 °C (lit.,[16] 162–163 °C). A mixture of the ylide (17 g, 51 mmol) and 3-methylbutyraldehyde (3 g, 35 mmol) in dry THF (175 cm^3) was refluxed under argon for 18 h. The solvent was evaporated and distillation of the residue gave the unsaturated ester [17] **8b** (3.7 g, 75%) as the pure *E* isomer without chromatography, as an oil, b.p. 95–100 °C/26 mmHg; $\delta_H(CDCl_3)$ 6.93 (1 H, dt, *J* 7.5, 15.5, CH_2CH=CH), 5.80 (1 H, d, *J* 15.5, CH=C*H*CO_2Me), 3.71 (3 H, s, CO_2Me), 2.08 (2 H, dd, *J* 7, 7.5, CH_2CH=CH), 1.74 (1 H, m, Me_2CH) and 0.90 (6 H, d, *J* 6.6, Me_2CH) (Found: M^+, 142.1000. $C_8H_{14}O_2$ requires *M*, 142.0990); *m*/*z* 142 (5%, M^+), 111 (22, M – MeO), 100 (100, M – C_2H_2O) and 87 (38, $C_4H_7O_2$).

Methyl (2SR,3RS)-3-*Dimethylphenylsilyl*-2,5-*dimethyl*-2-*phenylthiohexanoate* **9a**.—A mixture of dimethylphenylchlorosilane (4 cm^3), lithium shot (*ca.* 0.8 g) and dry THF (24 cm^3) was stirred under nitrogen at 0 °C for 4 h and left overnight at 0 °C. The resulting red solution of dimethylphenylsilyllithium was titrated as described by Whitesides.[7] Dimethylphenylsilyllithium (1.05 mol dm^{-3} solution in THF; 4.7 mmol, 4.5 cm^3) was added to a stirred suspension of copper(I) cyanide (0.2 g, 2.2 mmol) in dry THF (0.5 cm^3) under nitrogen at 0 °C. After 20 min, the mixture was cooled to −78 °C and a solution of the ester **8a** (0.325 g, 2.1 mmol) in dry THF (2 cm^3) was added dropwise to it. After 3 h, chlorotrimethylsilane (2 cm^3, 15.8 mmol), followed by triethylamine (2.2 cm^3, 15.8 mmol) were added to the mixture which was then warmed to room temperature and stirred for an additional 1 h. Benzenesulfenyl chloride solution was prepared from sulfuryl chloride (0.14 cm^3, 1.78 mmol) and diphenyl disulfide (0.38 g, 1.74 mmol) in dry THF (5 cm^3) containing dry pyridine (2 drops), the mixture being stirred for 2 h under nitrogen at room temperature and used without further distillation. The enol silane solution was recooled to −78 °C and a solution of benzenesulfenyl chloride in THF was added to it. The mixture was allowed to warm to room temperature and then quenched with saturated aqueous ammonium chloride (5 cm^3) and diluted with light petroleum (b.p. 30–40 °C). The crude mixture was filtered through Celite and extracted with light petroleum (b.p. 30–40 °C; 3 × 25 cm^3). The combined organic extracts were washed with aqueous ammonium chloride (2 × 20 cm^3) and brine (2 × 20 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. Flash column chromatography of the residue on silica gel eluting with light petroleum (b.p. 30–40 °C)–ethyl acetate (15:1), gave the *ester* **9a** (0.46 g, 55%) as an oil, R_F [light petroleum (b.p. 30–40 °C)–ethyl acetate (15:1)] 0.6; ν_{max}(film)/cm^{-1} 1710 (CO) and 1595 (PhS); $\delta_H(CDCl_3)$ 7.55–7.27 (10 H, m, Ph and PhS), 3.45 (3 H, s, CO_2Me), 2.06 (1 H, m, CHSi), 1.88–1.77 (1 H, m, CH_AH_BCHSi), 1.55–1.43 (2 H, m, Me_2CH and CH_AH_BCHSi), 1.41 (3 H, s, *Me*CSPh), 0.75 and 0.72 (6 H, 2 d, *J* 6.4, Me_2CH), 0.33 and 0.19 (6 H, 2 s, $SiMe_2Ph$); $\delta_C(CDCl_3)$ −2.42 and −0.78 (Me_2Si), 20.66 and 21.13 (Me_2CH), 23.88 (*Me*CSPh), 27.46 (CHSi), 29.3 (Me_2CH), 36.55 (Me_2CHCH_2), 51.67 (CO_2Me), 60.90 (*C*SPh), 127.63, 128.54, 128.87, 129.31, 134.10 and 137.14 (Ar), 131.78 (Ar*C*-S), 139.05 (Ar*C*-Si) and 173.5 (*C*O_2Me) (Found: M^+ – Me, 385.1656. $C_{22}H_{29}O_2SSi$ requires M – CH_3, 385.1650); *m*/*z* 385 (1%, M^+ – Me), 291 (48, M – PhS), 135 (98, $PhMe_2Si$) and 125 (100, M – PhS – $PhMe_2Si$ – Me_2).

Methyl (2SR,3RS)-3-*Dimethylphenylsilyl*-5-*methyl*-2-*phenylthiohexanoate* **9b**.—In the same way, dimethylphenylsilyllithium (0.85 mol dm^{-3} solution in THF; 5.95 mmol, 7 cm^3), copper(I) cyanide (0.3 g, 3.4 mmol), the ester **8b** (0.4 g, 2.8 mmol), trimethylchlorosilane (3 cm^3, 25.9 mmol), triethylamine (3.5 cm^3, 25.9 mmol), and the benzenesulfenyl chloride solution in THF [prepared from diphenyl disulfide (0.58 g, 2.7 mmol), sulfuryl chloride (0.22 cm^3, 2.76 mmol) in dry THF (10 cm^3) containing two drops of pyridine], gave a 3.5:1 mixture of the ester **9b** (0.51 g, 47%) and methyl 3-dimethylphenylsilyl-5-methylhexanoate (0.10 g, 13%). This mixture could not be separated by TLC; R_F [light petroleum (b.p. 30–40 °C)–ethyl acetate (15:1)] 0.56; ν_{max}(film)/cm^{-1} 1710 (CO) and 1595 (PhS); $\delta_H(CDCl_3)$ (peaks marked ^{A} belong to the minor product) 7.59–7.16 (10 H, m, Ph and PhS), 4.12 (d, *J* 5.8, C*H*SPh), 3.54^A and 3.49 (3 H, 2 s, CO_2Me), 2.32^A (m, $CH_AH_BCO_2Me$), 2.18^A (m, $CH_AH_BCO_2Me$), 2.09 and 1.75^A (dt and m, *J* 1.4, 6.8, CHSi), 1.70–1.14 (3 H, Me_2CHCH_2), 0.81^A and 0.74 (6 H, 2 d, *J* 5.8, 6.2, Me_2CH), 0.43,^{A} 0.28,^{A} 0.38 and 0.28 (12 H, 4 s, $SiMe_2Ph$).

(2SR,3RS)-3-*Dimethylphenylsilyl*-2,5-*dimethyl*-2-*phenylthiohexan*-1-*ol* **10a**.—DIBAL (1 mol dm^{-3} solution in hexane; 5 mmol, 5 cm^3) was added dropwise to a solution of the ester **9a** (0.88 g, 2.2 mmol) in dry hexane (15 cm^3) under a nitrogen atmosphere at −78 °C. The mixture was stirred for 2.5 h and then quenched with saturated aqueous ammonium chloride (10 cm^3) and allowed to come to room temperature. It was then extracted with hexane and the organic extracts were washed with brine (2 × 20 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. Column chromatography of the residue on silica eluting with light petroleum [b.p. 30–40 °C)–ethyl acetate (10:1)] gave the *alcohol* **10a** (0.61 g, 75%), as an oil R_F [light petroleum (b.p. 30–40 °C)–ethyl acetate (10:1)] 0.45; ν_{max}(film)/cm^{-1} 3600–3000 (OH) and 1580 (ArH); $\delta_H(CDCl_3)$ 7.57–7.26 (10 H, m, Ph and PhS), 3.30–3.07 (2 H, m, CH_2OH), 2.62 (1 H, br s, OH), 1.79 and 1.73 (1 H, dd, *J* 2.2, 8.8, CH_2CHSi), 1.55–1.41 (3 H, m, $CHCH_2$CHSi), 0.95 (3 H, s, *Me*CSPh), 0.86 and 0.71 (6 H, 2 d, *J* 6.3, Me_2CH) and 0.44 and 0.41 (6 H, 2 s, $SiMe_2$). When D_2O was added to the solution, the signal at 3.30–3.07 became 3.2 (2 H, 2 d, *J* 10.9, CH_ACH_BOH) and the signal at 2.62 disappeared; $\delta_C(CDCl_3)$ −0.98 and −0.36 (MeSi), 21.66 (*Me*CSPh), 22.05 and 22.94 (Me_2CH), 28.78 (Me_2CH), 30.40 (CHSi), 36.75 (Me_2CHCH_2), 62.38 (*C*SPh), 66.29 (CH_2OH), 127.76, 128.63, 128.86, 128.93, 133.97 and 137.63 (Ar), 131.06 (Ar*C*-S) and 140.03 (Ar*C*-Si) (Found: M^+ – PhSH, 262.1755. $C_{16}H_{26}OSi$ requires *M* – C_6H_6S, 262.1746); *m*/*z* 262 (1%, M^+ – PhSH), 135 (100, $PhMe_2Si^+$) and 110 (35, PhSH).

(2SR,3RS)-3-*Dimethylphenylsilyl*-5-*methyl*-2-*phenylthiohexan*-1-*ol* **10b**.—In the same way, the 3.5:1 mixture of the ester **9b** and methyl 3-dimethylphenylsily-5-methylhexanoate (1.6 g) and DIBAL (1 mol dm^{-3} solution in hexane; 10 mmol, 10 cm^3) gave the alcohol **10b** (1.14 g, 78%) as an oil, R_F [light petroleum (b.p. 30–40 °C)–ethyl acetate (10:1)] 0.5; ν_{max}(film)/cm^{-1} 3600–3000 (OH) and 1580 (ArH); $\delta_H(CDCl_3)$ 7.55–7.18 (10 H, m, Ph and PhS), 3.67 (1 H, dd, *J* 7.3, 11.1, CH_ACH_BOH), 3.54 (1 H, dd, *J* 6.4, 11.1, CH_ACH_BOH), 3.33 (1 H, dt, *J* 2.9, 6.8, C*H*SPh), 1.77 (1 H, br s, OH), 1.6 (1 H, dt, *J* 2.9, 6.9, C*H*Si), 1.55–1.44 (1 H, m, Me_2CH), 1.38 (2 H, dd, *J* 6.9, 12, $CHCH_2$), 0.82 and 0.76 (6 H, 2 d, *J* 6.3, Me_2CH) and 0.41 and 0.38 (6 H, 2 s, $SiMe_2Ph$); $\delta_C(CDCl_3)$ −2.78 and −0.78 (MeSi), 22.59 and 22.82 (Me_2CH), 24.82 (Me_2CH), 27.8 (CHSi), 36.25 ($CHCH_2$), 54.1 (*C*HSPh), 64.24 (CH_2OH), 126.66, 127.84, 127.97, 130.87 and 134.81 (Ar*C*), 135.81 (Ar*C*-S) and 138.77 (Ar*C*-Si) (Found: M^+ – MeO, 327.1608. $C_{20}H_{27}SSi$ requires *M* – CH_3O, 327.1596); *m*/*z* 327 (1%, M^+ – MeO), 135 (80, $PhMe_2Si$), 110 (18, PhSH) and 55 (100, C_3H_6O).

(2SR,3RS)-3-*Dimethylphenylsilyl*-2,5-*dimethyl*-2-*phenylthiohexanal* **11a**.—A solution of DMSO (0.24 cm^3, 3.4 mmol) in CH_2Cl_2 (0.8 cm^3) was added dropwise to a stirred solution of oxalyl chloride (0.14 cm^3, 1.55 mmol) in dry CH_2Cl_2 (4 cm^3) at −60 °C under argon. After 10 min, a solution of the alcohol **10a** (0.54 g, 1.48 mmol) in CH_2Cl_2 (1.5 cm^3) was slowly added to the

mixture which was then stirred for 20 min at this temperature. Triethylamine (1 cm^3, 7.4 mmol) was then added to the mixture which was then left to warm to room temperature (*ca.* 0.5 h) before being quenched with water (8 cm^3). The aqueous layer was re-extracted with additional dichloromethane (3 × 15 cm^3) and the combined organic extracts were successively washed with 1% HCl (5 cm^3), water (5 cm^3), 5% aq. Na_2CO_3 (5 cm^3) and water (5 cm^3), dried ($MgSO_4$) and then evaporated under reduced pressure. Flash column chromatography of the residue on silica, eluting with light petroleum (b.p. 30–40 °C)–ethyl acetate (14:1), gave the *aldehyde* **11a** (0.50 g, 90%), m.p. 63–65 °C [from light petroleum (b.p. 30–40 °C)]; R_F [light petroleum (b.p. 30–40 °C)–ethyl acetate (14:1)] 0.58; ν_{max}(film)/cm^{-1} 1700 (CHO) and 1570 (Ph); δ_H($CDCl_3$) 9.01 (1 H, s, CHO), 7.50–7.22 (10 H, m, ArH), 1.94 and 1.88 (1 H, 2 d, *J* 8, CHSi), 1.59–1.43 (3 H, m, Me_2CHCH_2), 1.15 (3 H, s, *Me*CSPh), 0.81 (6 H, d, *J* 6.2, Me_2CH), and 0.38 and 0.31 (6 H, 2 s, $SiMe_2Ph$); δ_C($CDCl_3$) −1.97 and −0.99 (MeSi), 16.51 (*Me*CSPh), 21.47 and 23.41 (Me_2CH), 27.81 (Me_2CH), 28.08 (CHSi), 35.15 ($CHCH_2$), 66.75 (*C*SPh), 127.87, 128.71, 129.38, 129.45, 134.04, 137.59 (Ar*C*), 129.8 (Ar*C*-S), 137.77 (Ar*C*-Si) and 190.02 (CHO) (Found: M^+ − Me, 355.1545. $C_{21}H_{27}OSSi$ requires *M* − CH_3, 355.1545); *m*/*z* 355 (1%, M^+ − Me), 261 (37, M − PhS) and 135 (100, $PhMe_2Si$).

(2SR,3RS)-3-*Dimethylphenylsilyl*-5-*methyl*-2-*phenylthiohexanal* **11b**.—In the same way, the alcohol **10b** (0.4 g, 1.1 mmol), oxalyl chloride (0.11 cm^3, 1.2 mmol), DMSO (0.2 cm^3, 2.6 mmol) and triethylamine (0.8 cm^3, 5.6 mmol) gave the aldehyde **11b** (0.34 g, 85%) as an oil, R_F [light petroleum (b.p. 30–40 °C)–ethyl acetate (15:1)] 0.4; ν_{max}(film)/cm^{-1} 1700 (CHO) and 1580 (Ph); δ_H($CDCl_3$) 9.37 (1 H, d, *J* 4.3, CHO), 7.56–7.15 (10 H, m, Ph and PhS), 3.53 (1 H, dd, *J* 4.4, 5, C*H*SPh), 1.61–1.34 (3 H, m, Me_2CHCH_2), 0.85 and 0.77 (6 H, 2 d, *J* 6, Me_2CH) and 0.43 and 0.40 (6 H, 2 s, $SiMe_2Ph$) (Found: M^+, 356.1653. $C_{21}H_{28}OSiS$ requires *M*, 356.1623); *m*/*z* 356 (1%, M^+ + 1), 247 (13, M + 1 − PhS), 135 (100, $SiMe_2Ph$) and 110 (25, PhSH).

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