The stereochemistry of the vinylogous Peterson elimination
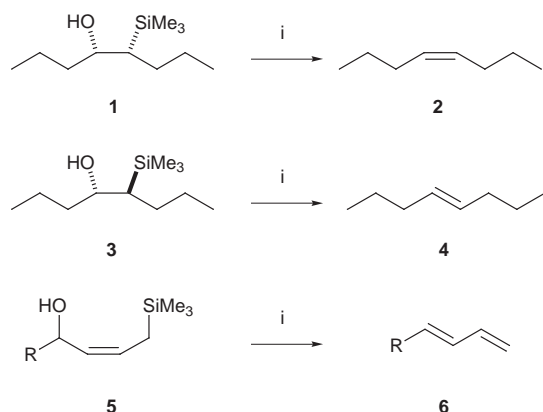
Ian Fleming,* Ian T. Morgan and Achintya K. Sarkar

Department of Chemistry, Lensfield Road, Cambridge, UK CB2 1EW

Base-induced eliminations of the vinylogous β-hydroxysilanes 7, 9, 11 and 12 are stereospecifically *syn*, giving largely the *trans,trans*-diene 8 from 7 and 11, the *cis,trans*-diene 10 from 9, and the *trans,cis*-diene 13 from 12. When a *cis* double bond is produced, it is selectively placed adjacent to the carbon atom that originally carried the hydroxy group. E2′ Reactions with silyl as the electrofugal group and acetate as the nucleofugal group, initiated by fluoride ion, are not stereospecific, but can be highly stereoselective in favour of the *trans,trans*-diene 8 when the carbon substituent at the silicon-bearing end is a cyclohexyl group and the double bond is *cis*, and in favour of the *trans,cis*-diene 13 when the carbon substituent at the silicon-bearing end is a methyl group and the double bond is *trans*. Attempts to use the Peterson reactions to make *o*-quinodimethanes stereospecifically failed, with no evidence of 1,4-elimination from the alcohols 40 and 41. The corresponding E2′ reaction from the esters using fluoride ion on the acetates or formates 46 and 47 gave stereoselectively the *E,E*-quinodimethane 48.

Introduction

The base-catalysed elimination of β-hydroxysilanes, commonly known as the Peterson elimination,[1] **1** ⟶ **2** and **3** ⟶ **4** has been shown by Hudrlik *et al.* to be stereospecifically *syn*.[2] A vinylogous version of this elimination **5** ⟶ **6** has also been observed by Clive,[3] in which he noted the formation selectively of a *trans* double bond for the internal double bond, but the terminal double had no stereochemistry (Scheme 1).
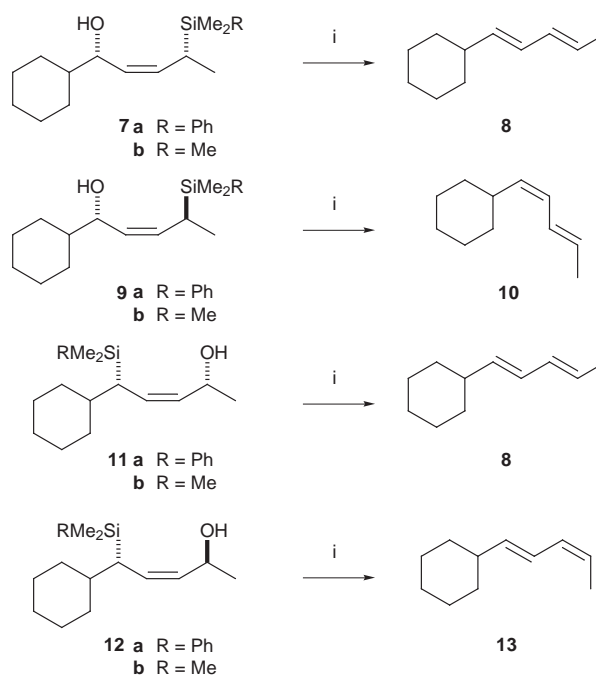

Scheme 1

Scheme 2 *Reagents and conditions*: i, KH, THF, room temperature

We now report the full stereochemistry of this diene synthesis, which is, as expected, and as we reported in a preliminary communication,[4] stereospecifically *syn* (Scheme 2). Thus, the hydroxysilane **7a** gives the *trans,trans*-diene **8**, but its diastereoisomer **9a** gives the *cis,trans*-diene **10**. Similarly, the hydroxysilane **11a** gives the *trans,trans*-diene **8**, but its diastereoisomer **12a** gives the *trans,cis*-diene **13**. More interestingly, the reaction shows a remarkable regioselectivity in those cases where the stereospecificity demands that one of the double bonds be *cis*: the isomer **9a**, having the hydroxy group adjacent to the cyclohexyl group gives largely the *cis,trans*-diene **10**, with the *cis* double bond adjacent to the cyclohexyl group, but the isomer **12a**, with the hydroxy and silyl groups transposed, gives largely the *trans,cis*-diene **13**, with the *cis* double bond adjacent to the methyl group.

Results and discussion

We prepared the hydroxysilanes by adding the anions of the appropriate propargylsilanes (prop-2-ynylsilanes) with a ter-minal triple bond,[5,6] to the complementary aldehydes, and reducing the triple bonds to the *cis* double bonds by hydrogenation. The diastereoisomers were then separated by column chromatography. We also prepared the corresponding trimethylsilyl analogues **7b** and **9b**, but were unable to separate the pair **11b** and **12b**. The reactions were carried out by treating the individual hydroxysilanes with an excess of potassium hydride in THF at room temperature, and the product mixtures analysed by GC, using a capillary column that separated the four stereoisomers, all of which were known.[7] The detailed proportions of the mixtures of dienes, measured by GC and probably accurate to ± 0.1%, are given in Table 1; the diastereoisomeric purity of the starting materials was >95%, as assessed by ^{1}H NMR spectroscopy. The yields were not optimised nor should those given in the table be taken as representative of the efficiency of the reaction, which is generally very clean. The *trans,trans*-diene **8** and both *trans,cis*-dienes **10** and **13** were pure enough for structural assignment by ^{1}H NMR spectroscopy, and we prepared an authentic sample of the

Table 1 Stereospecificity in the vinylogous Peterson eliminations in Scheme 2

Substrate	Total yield	*trans,trans-* 8	*cis,trans-* 10	*trans,cis-* 13	*cis,cis*
7a	37	100	0	0	0
7b	57	100	0	0	0
9a	80	2.3	92.7	5	0
9b	16	1.7	97.2[a]	1.1[a]	0
11a	79	99.6	0	0.4	0
12a	47	2.6	1.9	95.5	0
11b + 12b	87	47.2	0.6[a]	52.2[a]	0.1

Yield (%)

[a] Incorrectly transposed in our preliminary communication.[4]

cis,cis-isomer, which was always a very minor component of the product mixtures, by hydroboration–protodeboronation[8] of the diyne,[9] in order to identify it on the GC trace.

We proved the relative stereochemistry of the starting materials **7a** and **9a** by the sequence of reactions shown in Scheme 3. Hydrogenation of the alkene **7a** gave the saturated
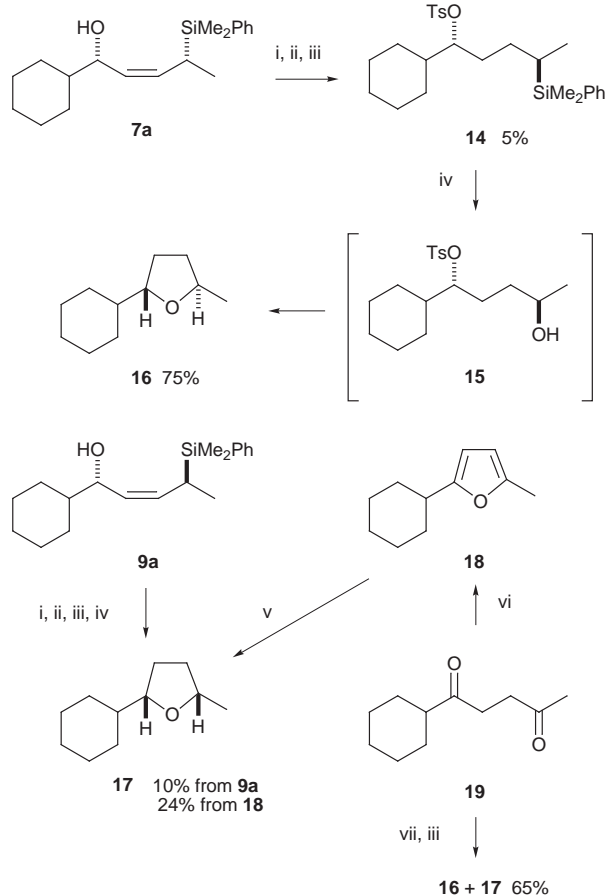

Scheme 3 *Reagents*: i, H₂, Pd/C; ii, BuLi; iii, TsCl; iv, Hg(OAc)₂, AcOOH, AcOH; v, Raney Ni, Pr^iOH; vi, TsOH; vii, NaBH₄

δ-hydroxysilane, although not in good or even reproducible yield. We have frequently had difficulties hydrogenating allylsilanes, and in this case saw some loss of the silyl group, presumably by a retro-hydrosilylation followed by hydrogenation. Tosylation of the alcohol gave the toluene-*p*-sulfonate (tosylate) **14**, and conversion of the phenyldimethylsilyl group into a hydroxy group **14 ⟶ 15**,[10] directly gave the corresponding tetrahydrofuran **16**, for which we can reasonably assume an inversion process at the carbon carrying the tosyloxy group. A similar sequence on the diastereoisomer **9a** gave the tetrahydrofuran **17**. The known tetrahydrofurans **16** and **17** were identified, using NMR spectroscopic and GC comparisons with the

reported data,[11] and by direct comparison with a sample of the *cis*-isomer **17**, prepared stereoselectively by hydrogenation[12] of the known furan **18**.[13] The hydrogenation of furans is well established to lead largely to *cis*-2,5-disubstituted tetrahydrofurans.[14] We also prepared an authentic mixture of the tetrahydrofurans **16** and **17**, in order to be sure that the peak we were seeing on the GC trace was indeed the *trans*-isomer **16**. The route we used was to reduce the diketone **19** with sodium borohydride, and treat the 1:1 mixture of 1,4-diols with toluene-*p*-sulfonyl chloride.

That the elimination process is *syn* stereospecific is hardly surprising, but the selectivity for placing the *cis* double bond at the carbon atom that carried the hydroxy group was unexpected. The pentacoordinate silyl anions **20** and **24**, derived from the diastereoisomers **9a** and **12a**, respectively, are probably intermediates (Scheme 4). These will break down by a
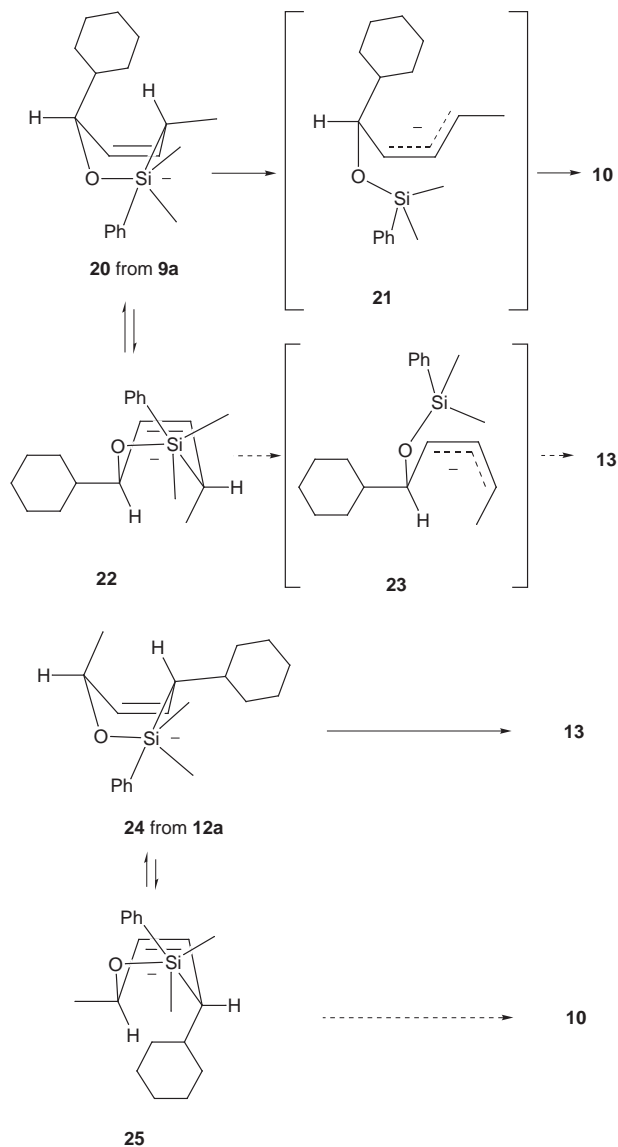
Scheme 4

process that resembles, in outline at least, a retro Diels–Alder reaction. Insofar as the transition structure is boat-like, resembling the structure of the intermediates, it is not obvious why reaction is favoured from the boats **20** and **24**, in which the carbon atoms at the prow adjacent to the oxygen atoms should be the ones to carry the axial substituent, rather than from the alternative boats **22** and 25. However, the retro-cycloaddition is likely, by analogy with the probable mechanism of the Peterson elimination,[1,15] to involve in the transition structure the develop-

ment of a substantial negative charge on the carbon atom from which the silyl group is departing, and it is better to consider the movements involved as the presumed intermediates **20** and **24** change to the products **10** and **13** than it is to look at the structures of the intermediates themselves. As the Si–C bond stretches, the carbon atom becomes trigonal, and rotation must take place about the axis of the developing C=C double bond. Starting from **20**, rotation along the shorter path leads to a sickle-shaped configuration in the allyl anion-like species **21**, and starting from **22** it leads to a U-shaped configuration **23**. The allyl anions **21** and **23** are probably not fully formed intermediates, but they are drawn here as such for clarity of argument. Although the *cis* arrangement is known to be lower in energy than the *trans* in 1-substituted allyl-metal systems,[16] we can be reasonably confident that the sickle-shaped configuration in 1,3-disubstituted allyl-metal systems is lower in energy than the U-shaped configuration. Hence Si–C bond stretching takes place more easily from **20** than from **22**, and a sickle-shaped allyl anion-like configuration **21** is set up more rapidly than the U-shaped ion **23**. Thus the regiochemistry of double bond formation is determined by which of the double bonds in the product is more established in the transition state—since the Si–C bond is probably more stretched than the O–C bond, it is the double bond at this end of the system that comes out *trans*. The other double bond is then forced to adopt the configuration demanded by the stereospecificity of the overall process—*cis* from **9a** and **12a** and *trans* from **7a** and **11a**.

While we were using the *syn* stereospecificity of the vinylogous Peterson elimination to assign relative configurations to some (Z)-4-silylbut-2-enols,[17] we came across a limitation to the stereospecificity—when the silyl group was benzylic, as in the pair of compounds corresponding to **11a** and **12a**, but with a phenyl group in place of the cyclohexyl, both isomers gave the *trans,trans*-diene corresponding to **8**, adding further support to the idea that there is a well developed carbanion intermediate, living long enough in this case to undergo rotation before elimination is consummated. This result is in contrast to the normal Peterson elimination, which is still stereospecifically *syn*, even when the silyl group is benzylic.[18,19] Evidently the greater stabilisation afforded by the extended conjugation present in the anion developing from the vinylogous hydroxysilanes is enough to give it the necessary lifetime for rotation.
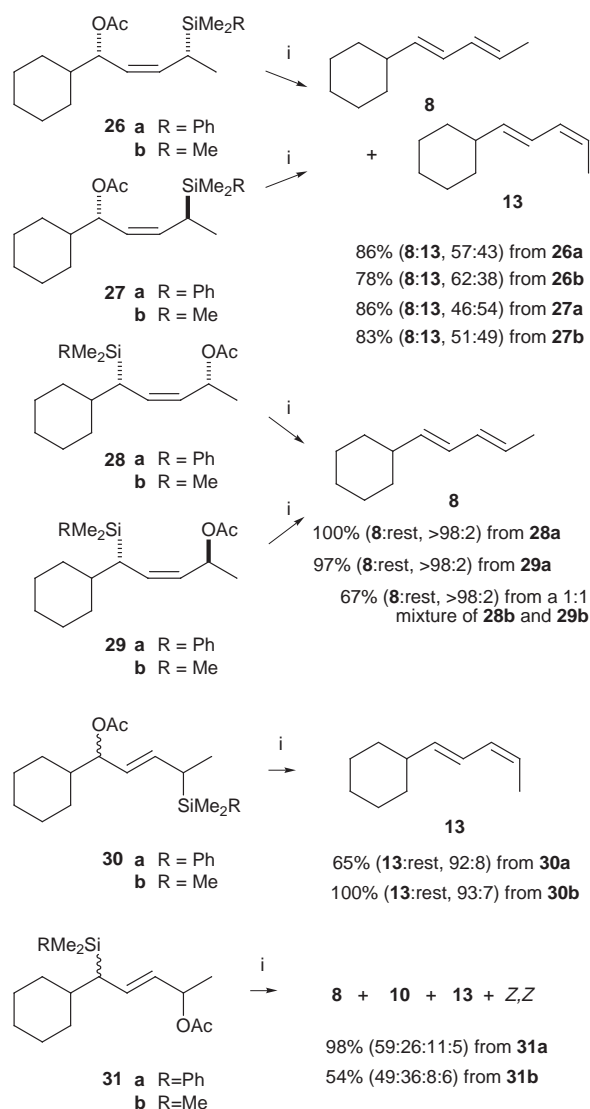
In addition to the Peterson elimination, it is also possible to induce elimination by nucleophilic catalysis if the hydroxy group is first converted into a better nucleofugal group. Thus we have already shown that fluoride ion induces stereospecifically *anti* 1,2-elimination of a silyl group and a vicinal acetate,[20] except that stereospecificity is lost when the silyl group is benzylic, with the reaction becoming merely stereoselective in favour of the formation of a *trans* double bond.[19] We therefore looked at the possibilities for making dienes this way from the acetates of our substrates **7**, **9**, **11** and **12**, and also from their isomers **30** and **31** having a *trans* double bond, hoping that E2′ reactions of this kind might also be stereospecific, or at any rate usefully stereoselective. Eschenmoser's work on decarboxylative E2′ reactions[21] indicated that we were unlikely to succeed, and indeed we stopped when we learned that he had also investigated this possibility with silyl electrofugal groups with disappointing results.[22] Our results are summarised in Scheme 5, with full data in Table 2, where we see that there are some potentially useful patterns, not of stereospecificity but of stereoselectivity. These results were not included in our preliminary communication.

Clearly the reactions are not stereospecific—the acetates **26** give very similar results to their diastereoisomers **27**, and similarly with the pairs of diastereoisomers **28** and **29**. The formation of the *trans,cis*-diene **13** as a sizeable by-product from the acetates **26** and **27** is remarkable. The reaction can be thought of as taking place by way of a transition structure more or less resembling an allylic anion, with the major transi-

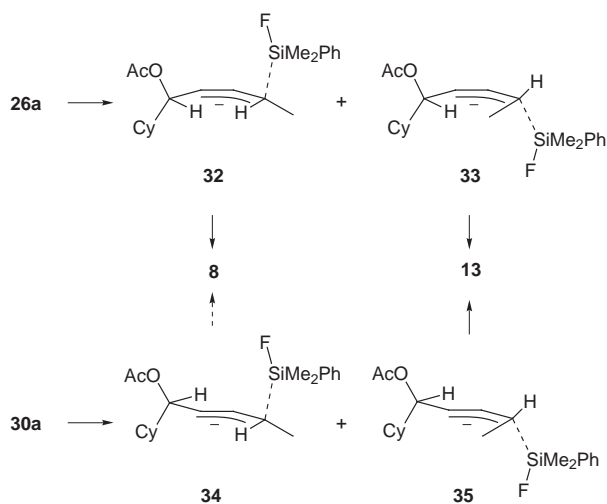**Table 2** Stereoselectivity in the E2′ eliminations in Scheme 5

| Substrate | Yield (%) | | | | |
	Total yield[a]	*trans,trans*-**8**	*cis,trans*-**10**	*trans,cis*-**13**	*cis,cis*
26a	86	56.8	0	43.2	0
26b	78	62.3	0	37.7	0
27a	86	45.5	0.1	54.3	0.1
27b	83	51.3	0.1	48.6	0
28a	100	98.6	1.1	0.3	0
29a	97	98.4	0.9	0.6	0.1
28b + 29b	67[b]	98.8	0.8	0.4	0
30a	65	3.4	0.1	91.7	4.8
30b	100	2.8	0.1	92.7	4.4
31a	98	58.9	25.6	10.9	4.6
31b	54	49.4	36.4	8.3	5.9

[a] Measured by GC, using decalin as an internal standard, except where otherwise stated. [b] Isolated yield.

26 a R = Ph
b R = Me

27 a R = Ph
b R = Me

86% (**8**:**13**, 57:43) from **26a**
78% (**8**:**13**, 62:38) from **26b**
86% (**8**:**13**, 46:54) from **27a**
83% (**8**:**13**, 51:49) from **27b**

28 a R = Me
b R = Me

29 a R = Ph
b R = Me

100% (**8**:rest, >98:2) from **28a**
97% (**8**:rest, >98:2) from **29a**
67% (**8**:rest, >98:2) from a 1:1 mixture of **28b** and **29b**

30 a R = Ph
b R = Me

65% (**13**:rest, 92:8) from **30a**
100% (**13**:rest, 93:7) from **30b**

31 a R=Ph
b R=Me

8 + **10** + **13** + Z,Z

98% (59:26:11:5) from **31a**
54% (49:36:8:6) from **31b**

Scheme 5 *Reagents*: i, TBAF, THF, CH₂Cl₂

tion structure being sickle-shaped **32** (from **26a**) with the methyl group 'outside', leading to a *trans* double bond at that end (see Scheme 6). The cyclohexyl group, being larger, will also sit 'outside', and a *trans* double bond develops at that end too as the acetate ion leaves. The formation of the diene **13** seems to imply that removal of the silyl group is quite often taking place with the development of a U-shaped anion **33**, having the methyl group 'inside', in spite of the strain present in such a structure. In contrast, the isomers **28** and **29**, with the silyl and
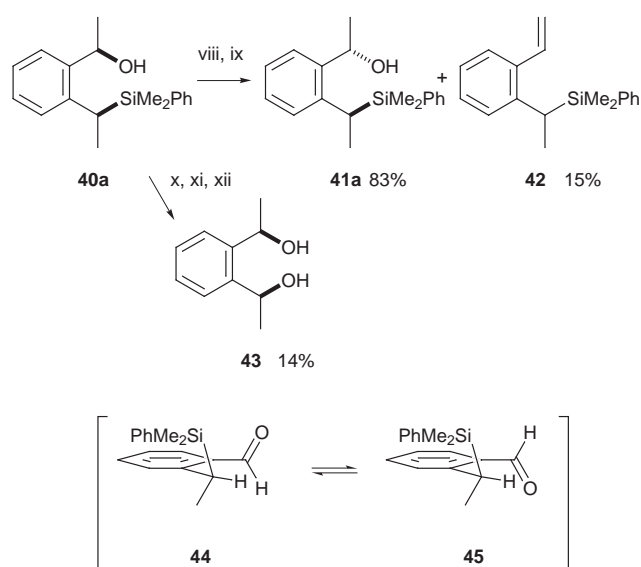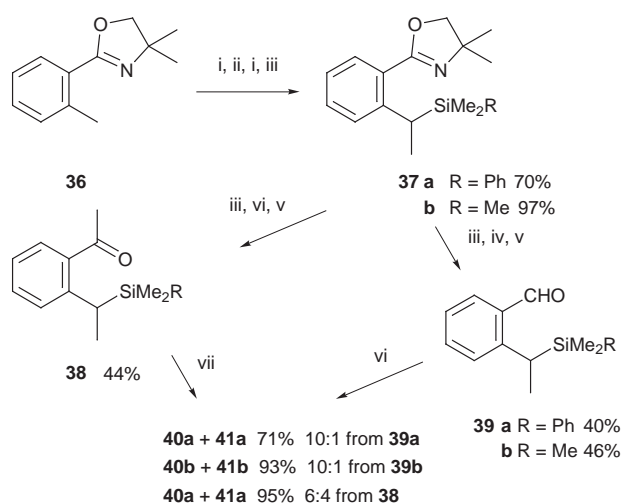
Scheme 6

Scheme 7 *Reagents*: i, BuLi; ii, PhMe₂SiCl or Me₃SiCl; iii, MeI; iv, NaBH₄; v, HCl, H₂O; vi, MeMgI; vii, NaBH₄; viii, EtO₂CN=NCO₂Et, Ph₃P, HCO₂H; ix, K₂CO₃, H₂O, EtOH; x, Ac₂O, Et₃N, DMAP; xi, Hg(OAc)₂, AcOOH, AcOH; xii, NaOH, EtOH

acetoxy groups interchanged, give very little of the *cis,trans*-diene **10**. Presumably a cyclohexyl group 'inside' makes such strain forbiddingly high and so they give the *trans,trans*-diene **8** with high stereoselectivity by way of transition structures like **32**, but with the methyl and cyclohexyl groups interchanged.

We were unable to separate any of the pairs of *trans* allylic alcohols, neither the pair **30** nor the pair **31**, and neither in the phenyldimethylsilyl series **a** nor in the trimethylsilyl series **b**. Nevertheless, the results with the former pairs **30** are of interest, since clearly both diastereoisomers in both series give largely the *trans,cis*-diene **13**. Presumably an allyl anion begins to develop in the sickle-shaped configuration **35**, rather than the W-shaped configuration **34**. Having the methyl group inside, without the penalty of having another substituent *cis* to it as in **33**, is now evidently favoured, as usual for allylic anions.[16] This configuration is then preserved in the *cis* double bond at what had been the silicon-bearing end of the diene **13**. On the other hand, the isomers **31**, with the silyl and acetoxy groups interchanged, do not lead largely to the diene **10** with a *cis* double bond at what had been the silicon-bearing end, although there is a measurable amount of this isomer in the product mixture. Presumably the extra strain in having a cyclohexyl group inside is too much. All these observations lend support to the idea that a degree of allyl anion character develops in the transition structure, just as we believe it does in the Peterson eliminations.

We tried to carry over some of these selectivities, both from the Peterson eliminations and from the E2′ reactions, to the synthesis of *o*-quinodimethanes, with limited success. We were able to prepare the diastereoisomers **40** and **41** by the routes shown in Scheme 7, and to separate the pair in the phenyl-dimethylsilyl series **a**. The Grignard reactions on the aldehydes **39** gave mainly the diastereoisomers **40**, a fine example of a phenylogous Cram's rule with high (10:1) selectivity. We imagine that the small substituent, the hydrogen atom, sits inside, and that the carbonyl group twists, so as to be more or less orthogonal to the benzene ring, minimising steric inter-actions **44** or **45**. Thus the aldehyde group could in principle be oriented with either diastereotopic surface presented to the incoming nucleophile, and it is unclear which ought to be the lower in energy for a Felkin-like rule to operate. Clearly the choice is influenced by the close proximity of the *ortho* stereo-genic centre with three well-differentiated substituents, but it is not obvious how. We proved which isomer was which in the **a** series by converting the acetate of the major alcohol **40a** into the known diol **43**. The reaction, therefore, would seem to have taken place from a conformation **44**, with the nucleophile attacking from behind as drawn. It is tempting to suggest that the carbonyl oxygen is coordinated to the silicon atom. We have never seen any sign of Lewis acid properties in a fully carbon-

substituted silane, and it seems unlikely here. In agreement, the selectivity in the reduction of the ketone **38** was much less (60:40), and the ketone oxygen ought, if anything, to be more Lewis basic. With only limited evidence, we suggest that the reactive conformation for the aldehyde resembles **44**, but with the aldehyde group rotated somewhere between 0 and 90° clock-wise to gain conjugation with the benzene ring, but pushing the hydrogen atom closer to the *ortho* substituent—attack by the nucleophile would then take place from behind and below. This rotation is less favourable with the ketone, because it would bring the methyl group close to the *ortho* substituent. A Mitsunobu reaction on the pure diastereoisomer **40a** using formic acid led to its diastereoisomer **41a** together with some elimination product **42**.

The fluoride-induced reactions were stereoselective for the formation only of the (*E*,*E*)-*o*-quinodimethane **48**, as shown by the isolation of the Diels–Alder adduct **49** (Scheme 8). This is hardly surprising, in view of our results in Scheme 5, with our knowledge that benzylic silanes are not even stereospecific in E2 eliminations,[19] and from similar results of Ito's using a tri-methylammonium ion as the nucleofugal group.[23] The yields were noticeably better when we used the formates **46b** and **47b** in place of the acetates. Unfortunately, treatment of the alcohols **40a** or **41a** with potassium hydride in the presence of dieno-philes, where a stereospecific Peterson elimination might have allowed us to intercept the (*Z*,*E*)-*o*-quinodimethane from the
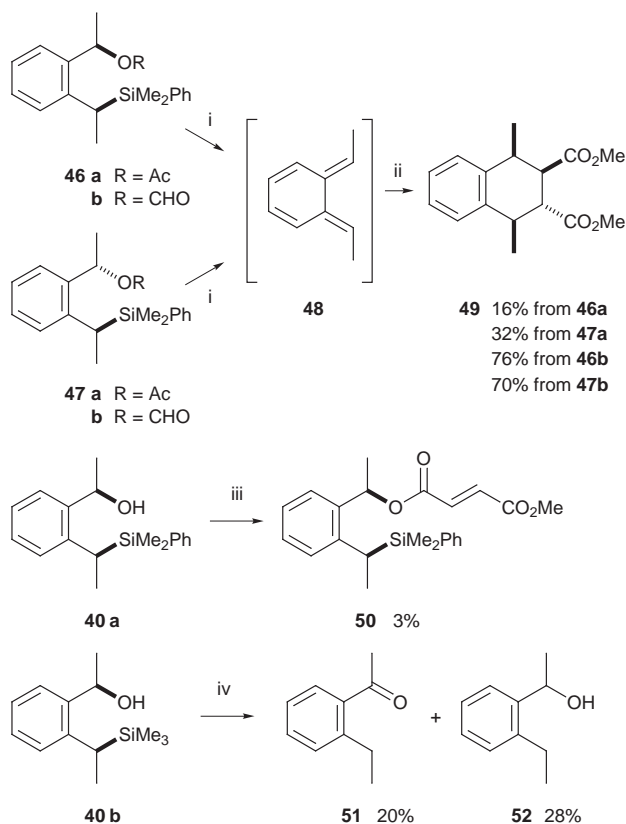
Scheme 8 *Reagents*: i, TBAF, THF; ii, (*E*)-MeO₂CCH=CHCO₂Me; iii, KN(SiMe₃)₂, THF, (*E*)-MeO₂CCH=CHCO₂Me; iv, KH, THF

alcohol **41a**, gave no sign of the Diels–Alder adducts. The only product we were able to identify was the ester **50** from attack by the oxyanion of the alcohol **40a** on the carbonyl group of fumarate when we used lithium hexamethyldisilazide as the base. We were no more successful using a trimethylsilyl group in place of the phenyldimethylsilyl group—a mixture rich in the alcohol **40b** gave low yields of the ketone **51** and of the alcohol **52**, with the latter indicating that the benzylic silyl group can be removed without the concomitant elimination of the oxygen substituent.

Experimental

Gas chromatographs (GC) were obtained using a Carlo Erba Strumentazione 4130 machine with a 25 m, BP5, 5% phenyl-methylsiloxane column, 5 µm film thickness (equivalent to SE54 or SE52 columns), using hydrogen carrier gas (≈ 0.3 m s^{-1}) and flame ionisation detector. Data were collected on a Shimadzu C-R3A chromatopac, and very small peaks were estimated manually from the chromatographs. The usual temperature programme used was 90 °C for 20 min, $+10$ °C min^{-1} gradient to 260 °C.

3-Cyclohexylpropyne

Following Meijer and Vermeer,[6] cyclohexylmagnesium bromide (0.71 mol dm^{-3} in diethyl ether, 465 cm^3) was added to methoxy-allene[24] (21.03 g, 300 mmol) in diethyl ether (300 cm^3) containing suspended copper(I) iodide (5.7 g, 30 mmol) at 10 °C maintaining the temperature in the range 20–30 °C over 30 min. The mixture was allowed to warm to 15 °C over 40 min and sodium cyanide (3 g) and ammonium chloride (60 g) in water (600 cm^3) were added carefully. The aqueous layer was separated and extracted with diethyl ether (250 cm^3). The combined organic layers were washed with brine (250 cm^3), dried (MgSO₄), filtered and evaporated under reduced pressure and the residue (50 cm^3) distilled, to give the alkyne (28.52 g, 78%), bp 145–150 °C (lit.,[6] 45 °C at 12 mmHg); R_f (pentane) 0.4; v_{max}(film)/

cm^{-1} 3280 (≡C-H), 2900, 2840 (CH) and 2100 (C≡C); δ_H(CDCl₃; 250 MHz) 2.06 (2 H, dd, *J* 2.7 and 6.6, CH₂), 1.94 (1 H, t, *J* 2.7, C≡CH), 1.9–1.55 (5 H, m, 5 × CH equatorial), 1.45 (1 H, m, C≡CCH₂C*H*) and 1.35–0.85 (5 H, m, 5 × CH axial); *m/z* 122 (1%, M$^+$), 121 (1, M − H) and 83 (96, C₆H₁₁) (Found: M$^+$, 122.1089. C₉H₁₄ requires *M*, 122.1096).

1-Silylalkynes

Typically, following Rajagopalan and Zweifel,[5] *n*-butyllithium (1.5 mol dm^{-3} in hexane, 150 cm^3) was added dropwise under nitrogen to the alkyne (240 mmol) in THF (100 cm^3) cooled in a dry-ice–acetone bath keeping the internal temperature at −45 °C. After 1 h the chlorosilane (240 mmol) was added dropwise, keeping the internal temperature below −40 °C. The mixture was allowed to warm to 20 °C over 1 h. Water (100 cm^3) was added and the mixture extracted with pentane (100 cm^3). The organic layer was washed with water (3 × 100 cm^3), brine (100 cm^3), dried (MgSO₄) and filtered. Solvents were then removed by distillation (8 inch Vigreux column, atmospheric pressure for low-boiling products) and the residue (50 cm^3) was distilled (2 inch Vigreux column) under nitrogen. The following silylalkynes were prepared by this method.

1-Trimethylsilylbutyne.[25] (63%) Bp 108–117 °C (lit.,[25] 115–116 °C); R_f (hexane) 0.73; v_{max}(film)/cm^{-1} 2950 (CH), 2160 (C≡C) and 1240 (SiMe); δ_H(CCl₄; 90 MHz) 2.15 (2 H, q, *J* 7.2, CH₂), 1.14 (3 H, t, *J* 7.2, CMe) and 0.11 (9 H, s, SiMe₃); *m/z* 126 (13%, M) and 111 (100%, M − Me) (Found: M$^+$, 126.0875. C₇H₁₄Si requires *M*, 126.0865).

1-Dimethyl(phenyl)silylbutyne. (96%) Bp 108–113 °C at 15 mmHg; v_{max}(film)/cm^{-1} 2165 (C≡C), 1245 (SiMe) and 1110 (SiPh); δ_H(CDCl₃; 60 MHz) 7.75–7.55 (2 H, m, SiPh), 7.50–7.25 (3 H, m, SiPh), 2.3 (2 H, q, *J* 7, C*H*₂CH₃), 1.2 (3 H, t, *J* 7, CH₂C*H*₃) and 0.4 (6 H, s, SiMe₂); *m/z* 188 (28%, M$^+$) and 173 (100, M − Me) (Found: M$^+$, 188.1032. C₁₂H₁₆Si requires *M*, 188.1042).

1-Trimethylsilyl-3-cyclohexylpropyne.[6] (91%) Bp 48–50 °C at 5 mmHg; R_f (pentane) 0.36; v_{max}(film)/cm^{-1} 2900, 2840 (CH), 2160 (C≡C) and 1240 (SiMe); δ_H(CDCl₃; 250 MHz) 2.09 (2 H, d, *J* 6.7, CH₂), 1.8–0.8 (11 H, m, CH and CH₂s) and 0.13 (9 H, s, SiMe₃); *m/z* 194 (5%, M$^+$), 179 (100, M − *Me*) and 73 (38, SiMe₃) (Found: M$^+$, 194.1495. C₁₂H₂₂Si requires *M*, 194.1491).

1,3-Bis-silylalkynes

Typically, following Rajagopalan and Zweifel,[5] *tert*-butyllithium (1.7 mol dm^{-3} in hexane, 32.5 cm^3) was added dropwise to tetramethylethylenediamine (TMEDA) (7.5 cm^3, 50 mmol) in THF (50 cm^3) at −70 °C under nitrogen. The 1-silylalkyne (50 mmol) in THF (25 cm^3) was added dropwise, stirred for 15 min and warmed to 0 °C for 1 h. The chlorosilane (50 mmol) was added dropwise at −70 °C, stirred for 15 min and then allowed to warm to 20 °C over 75 min. Water (50 cm^3) was added and the mixture extracted with diethyl ether (2 × 100 cm^3). The combined extracts were washed with water (100 cm^3), brine (100 cm^3), dried (MgSO₄), filtered and solvents evaporated under reduced pressure. The residue was fractionally distilled. The following bis-silylalkynes were prepared by this method.

1,3-Bis(trimethylsilyl)butyne.[26] (71%) Bp 72–73 °C at 24 mmHg; R_f (hexane) 0.34; v_{max}(film)/cm^{-1} 2940, 2840 (CH), 2140 (C≡C) and 1240 (SiMe); δ_H(CDCl₃; 90 MHz) 1.75 (1 H, q, *J* 7, MeC*H*SiC≡), 1.15 (3 H, d, *J* 7, *Me*CH), 0.15 (9 H, s, *Me*₃SiCH) and 0.05 (9 H, s, *Me*₃SiC≡C); *m/z* 198 (25%, M$^+$), 183 (20, M − Me) and 73 (100, Me₃Si) (Found: M$^+$, 198.1255. C₁₀H₂₂Si₂ requires *M*, 198.1260).

1-Trimethylsilyl-3-dimethyl(phenyl)silylbut-1-yne. (70%) Bp 80–89 °C/0.35 mmHg; R_f (hexane) 0.18; v_{max}(film)/cm^{-1} 3040 (ArH), 2940 (CH), 2140 (C≡C), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl₃; 250 MHz) 7.6–7.5 (2 H, m, ArH), 7.4–7.3 (3 H, m, ArH), 1.94 (1 H, q, *J* 7.2, MeCH), 1.12 (3 H, d, *J* 7.2, MeC), 0.38 (6 H, s, SiMe₂) and 0.13 (9 H, s, Me₃Si); *m/z* 260 (14%, M$^+$), 245 (2, M − Me), 172 (8, M − Me − Me₃Si), 135 (100,

PhMe$_2$Si) and 110 (20, M − Me − PhMe$_2$Si) (Found: M$^+$, 260.1416. C$_{15}$H$_{24}$Si$_2$ requires M, 260.1416).

1-Dimethyl(phenyl)silyl-3-trimethylsilylbutyne. (82%) After flash chromatography (Merck SiO$_2$ 9385, hexane), bp 88–94 °C at 0.6 mmHg; R_f (hexane) 0.18; v_{max}(film)/cm^{-1} 3060, 2880 (CH), 2240 (C≡C), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.67 (2 H, m, SiPh), 7.40–7.32 (3 H, m, SiPh), 1.77 (1 H, q, J 7.2, MeCHSi), 1.19 (3 H, d, J 7.2, MeCHSi), 0.37 (6 H, s, SiMe$_2$Ph) and 0.09 (9 H, s, SiMe$_3$); m/z 260 (21%, M$^+$), 245 (8, M − Me), 172 (11, M − Me − SiMe$_3$) and 135 (100, SiMe$_2$Ph) (Found: C, 68.99; H, 9.26; M$^+$, 260.1400. C$_{15}$H$_{24}$Si$_2$ requires C, 69.15; H, 9.26%; M, 260.1416). In one preparation of this compound, an excess of *tert*-butyllithium and chlorotrimethylsilane were used, giving the disilylacetylene and 1-*dimethyl(phenyl)-silyl*-1,3-*bis(trimethylsilyl)buta*-1,2-*diene*; R_f (hexane) 0.46; v_{max}(film)/cm^{-1} 3060, 2940, 2840 (CH), 1890 (C=C=C), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 60 MHz) 7.55–7.40 (2 H, m, SiPh), 7.35–7.25 (3 H, m, SiPh), 1.70 (3 H, s, CMe), 0.45 (6 H, s, SiMe$_2$Ph), 0.15 [9 H, s, Me$_2$(Ph)SiCSiMe$_3$] and 0.10 (9 H, s, MeCSiMe$_3$); m/z 332 (33%, M$^+$), 317 (6, M − Me), 244 (13, M − Me − SiMe$_3$), 229 (17, M − 2Me − SiMe$_3$), 182 (100, M − Me − PhSiMe$_2$) and 135 (78, PhSiMe$_2$) (Found: M$^+$, 332.1819. C$_{18}$H$_{32}$Si$_3$ requires M, 332.1812).

1,3-Bis[dimethyl(phenyl)silyl]butyne. (100%), v_{max}(film)/cm^{-1} 3060, 2960 (CH), 2150 (C≡C), 1250 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.65–7.54 (4 H, m, SiPh), 7.43–7.31 (6 H, m, SiPh), 2.02 (1 H, q, J 7.2, MeCH), 1.18 (3 H, d, J 7.2, MeCH), 0.40 (6 H, s, PhSiMe$_2$C≡C) and 0.39 (6 H, s, PhSiMe$_2$CH); m/z 322 (12%, M$^+$), 307 (1, M − Me), 172 (35, M − Me − PhSiMe$_2$) and 135 (100, PhSiMe$_2$) (Found: M$^+$, 322.1590. C$_{20}$H$_{26}$Si$_2$ requires M, 322.1573).

1,3-Bis(trimethylsilyl)-3-cyclohexylpropyne. (60%) Bp 74–88 °C at 0.3 mmHg (lit.,[5] 76–78 °C at 0.3 mmHg), still contaminated with the allene; chromatography (Merck SiO$_2$ 9385, hexane) gave the pure propargylsilane; R_f (hexane) 0.44; v_{max}(film)/cm^{-1} 2920, 2840 (CH), 2140 (C≡C) and 1240 (SiMe); δ_H(CDCl$_3$; 250 MHz) 1.8–1.0 (11 H, m, CH and CH$_2$s), 1.65 (1 H, d, J 4.2, SiCH), 0.12 (9 H, s, Me$_3$SiCH) and 0.10 (9 H, s, Me$_3$SiC≡C); m/z 266 (25%, M$^+$), 251 (10, M − Me), 178 (55, M − Me − Me$_3$Si) and 73 (100, Me$_3$Si) (Found: M$^+$, 266.1886. C$_{15}$H$_{30}$Si$_2$ requires M, 266.1886).

1-Trimethylsilyl-3-cyclohexyl-3-dimethyl(phenyl)silylpropyne. (83%) R_f (Hexane) 0.21; v_{max}(film)/cm^{-1} 3060, 2900, 2840 (CH), 2140 (C≡C), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.65–7.55 (2 H, m, Ph), 7.4–7.35 (3 H, m, Ph), 1.9 (1 H, d, J 3.8, SiCH), 1.7–1.1 (11 H, m, cyclohexyl CH and CH$_2$s), 0.43 (3 H, s, SiMe$_A$Me$_B$) and 0.42 (3 H, s, SiMe$_A$Me$_B$) and 0.17 (9 H, s, SiMe$_3$); m/z 328 (10%, M$^+$), 178 (20, M − Me − Me$_2$SiPh), 135 (100, Me$_2$SiPh) and 73 (35, SiMe$_3$) (Found: M$^+$, 328.2049. C$_{20}$H$_{32}$Si$_2$ requires M, 328.2043).

Synthesis of propargylsilanes

Typically, following Schmid and Arens[27] and Rajagopalan and Zweifel,[5] silver nitrate (27.5 mmol) in water (12 cm^3) and ethanol (35 cm^3) was added in four equal portions 15 min apart to a solution of bis-silylalkyne (20 mmol) in ethanol (40 cm^3) at 0–5 °C, and the mixture stirred for 15 min. Potassium cyanide (8.95 g, 137.5 mmol) in water (16 cm^3) was added, producing heavy precipitation, and the mixture allowed to warm to 20 °C and stirred for 2 h. Water (50 cm^3) was added and the mixture extracted with pentane (2 × 100 cm^3). The combined extracts were washed with water (3 × 50 cm^3), brine (50 cm^3), dried (MgSO$_4$) and filtered. Solvents were removed by distillation (8 inch Vigreux column for low-boiling products), and the residue (20 cm^3) fractionally distilled under nitrogen, giving the propargylsilanes. The following propargylsilanes were prepared by this method.

3-Trimethylsilylbutyne.[28] [62% From the 1,3-bis(trimethylsilyl)alkyne; 21% from 1-dimethyl(phenyl)silyl-3-trimethylsilylbut-1-yne] bp 97–105 °C and ≈ 60–70 °C (distillation was

erratic) contaminated with hexamethyldisiloxane in the preparation from the 1,3-bis(trimethylsilyl)alkyne; R_f (hexane) 0.4; v_{max}(film)/cm^{-1} 3300 (≡CH), 2940 (CH), 2100 (C≡C) and 1240 (SiMe); δ_H(CDCl$_3$; 90 MHz) 1.9 (1 H, d, J 3, =CH), 1.65 (1 H, dq, J 3 and 6, MeCH), 1.15 (3 H, d, J 6, MeC) and 0.1 (9 H, s, Me$_3$Si) with a singlet due to hexamethyldisiloxane at δ 0.09; R_f (hexane) 0.43; δ_H(CDCl$_3$; 250 MHz) 1.96 (1 H, d, J 2.8, C≡CH), 1.65 (1 H, dq, J 2.8 and 7.3, MeCH), 1.17 (3 H, d, J 7.2, MeCH) and 0.08 (9 H, s, SiMe$_3$); m/z 126 (14%, M$^+$), 111 (20, M − Me) and 73 (100, SiMe$_3$) (Found: M$^+$, 126.0860. C$_7$H$_{14}$Si requires M, 126.0865).

3-Dimethyl(phenyl)silylbutyne. [98% From 1-trimethylsilyl-butyne; 67% from the 1-dimethyl(phenyl)silylalkyne], bp 100–105 °C (18 mmHg); R_f (hexane) 0.18; v_{max}(film)/cm^{-1} 3300 (≡CH), 3060 (ArH), 2940 (CH), 2080 (C≡C), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz), 7.65–7.5 (2 H, m, ArH), 7.45–7.3 (3 H, m, ArH), 2.0 (1 H, d, J 2.7, ≡CH), 1.9 (1 H, dq, J 2.7 and 7.2, MeCH), 1.16 (3 H, d, J 7.2, MeC) and 0.4 (6 H, s, Me$_2$SiPh); m/z 188 (20%, M$^+$), 173 (10, M − Me) and 135 (100, Me$_2$PhSi) (Found: M$^+$, 188.1014. C$_{12}$H$_{16}$Si requires M, 188.1022).

3-Cyclohexyl-3-trimethylsilylpropyne.[5] (71%) Bp *ca*. 110 °C at 19 mmHg; R_f (hexane) 0.42; v_{max}(film)/cm^{-1} 3300 (≡CH), 2905, 2840 (CH), 2080 (C≡C), 1440 (CH$_2$) and 1240 (SiMe); δ_H(CDCl$_3$; 250 MHz) 2.01 (1 H, d, J 2.9, C≡CH), 1.61 (1 H, dd, J 2.9 and 3.9, SiCH), 1.9–1.0 (11 H, m, cyclohexyl CH and CH$_2$s) and 0.10 (9 H, s, SiMe$_3$); m/z 194 (1.5%, M$^+$), 179 (12, M − Me) and 73 (100, Me$_3$Si) (Found: M$^+$, 194.1482. C$_{12}$H$_{22}$Si requires M, 194.1490).

3-Cyclohexyl-3-dimethyl(phenyl)silylpropyne. (55%) R_f (Hexane) 0.20; v_{max}(film)/cm^{-1} 3300 (≡CH), 3040, 2920, 2840 (CH), 2080 (C≡C), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.65–7.5 (2 H, m, Ph), 7.4–7.3 (3 H, m, Ph), 2.08 (1 H, d, J 2.7, C≡CH), 1.7 (1 H, br t, J ≈ 2.7, SiCH), 1.7–0.9 (11 H, m, cyclohexyl CH and CH$_2$s) and 0.43 (6 H, 2 × s, just resolved diastereotopic SiMe$_2$); m/z 256 (10%, M$^+$) and 135 (100, Me$_2$SiPh) (Found: M$^+$, 256.1644. C$_{17}$H$_{24}$Si requires M, 256.1648).

Synthesis of 4-silylpentyn-2-ols

Method A

Typically, *n*-butyllithium (1.5 mol dm^{-3} in hexane, 8 cm^3) was added dropwise under nitrogen to the 3-silylalkyne (10.5 mmol) in diethyl ether (25 cm^3) at 0 °C and stirred for 75 min. The aldehyde (12 mmol) in diethyl ether (5 cm^3) was added dropwise and stirred for 30 min. Saturated aqueous ammonium chloride (10 cm^3) and water (5 cm^3) were added, and the organic layer was separated. The aqueous layer was extracted with diethyl ether (2 × 20 cm^3), and the combined organic layers were washed with water (20 cm^3), brine (20 cm^3), dried (MgSO$_4$), filtered and evaporated under reduced pressure. The following alcohols were prepared by this method.

1-Cyclohexyl-4-trimethylsilylpent-2-ynol. (87%) R_f (Hexane–EtOAc, 6:1) 0.35; v_{max}(film)/cm^{-1} 3350 (br OH), 2910, 2840 (CH), 2200 (C≡C), 1440 (CH$_2$) and 1240 (SiMe); δ_H(CDCl$_3$; 250 MHz) 4.15 (1 H, m, CHOH), 1.8–0.8 (13 H, m, CH, CH$_2$s and OH), 1.14 (3 H, d, J 7.7, CMe) and 0.06 (9 H, s, SiMe$_3$); m/z 238 (0.1%, M$^+$), 236 (1, M − 2H), 126 (30, C$_7$H$_{14}$Si) and 73 (100, Me$_3$Si) (Found: M − 2, 236.1590. C$_{14}$H$_{24}$OSi requires M − 2, 236.1596).

1-Cyclohexyl-4-dimethyl(phenyl)silylpent-2-ynol. (47%) R_f (Hexane–EtOAc, 6:1) 0.24; v_{max}(film)/cm^{-1} 3400 (br OH), 3060, 2920, 2840 (CH), 2200 (C≡C), 1440 (CH$_2$), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 80 MHz) 7.7–7.2 (5 H, m, PhSi), 4.1 (1 H, dd, J 1.9 and 4.9, CHOH), 2.2–0.8 (13 H, m, OH, CH and CH$_2$s), 1.15 (3 H, d, J 7.2, CMe) and 0.4 (6 H, s, SiMe$_2$); m/z 300 (0.5%, M$^+$), 298.1738 (10, M − 2H), 188 (40, C$_{12}$H$_{16}$Si) and 135 (100, PhMe$_2$Si) (Found: M$^+$, 300.1888. C$_{19}$H$_{28}$OSi requires M, 300.1910). We assigned tentative structures to two by-products 1,5-*dicyclohexyl*-2-*methyl*-2-*dimethyl(phenyl)silylpent*-3-*yn*-1,5-

diol (9%); R_f (hexane–EtOAc, 85:15) 0.12; ν_{max}(film)/cm^{-1} 3400 (br OH), 3060, 2910, 2840 (CH), 2200 (C≡C), 1440 (CH$_2$), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.65–7.55 (2 H, m, PhSi), 7.4–7.3 (3 H, m, PhSi), 4.18 (1 H, d, J 5.75, C≡CCHOH), 3.2 (1 H, br s, SiCCHOH), 2.1–1.10 (22 H, m, 2 × c-C$_6$H$_{11}$), 1.1 (3 H, s, CMe), 0.46 (3 H, s, SiMe$_A$Me$_B$) and 0.44 (3 H, s, SiMe$_A$Me$_B$); *m/z* 394 (0.5%, M − H$_2$O), 177 (40, C$_{12}$H$_{17}$O) and 135 (100, PhMe$_2$Si) (Found: M − H$_2$O, 394.2679. C$_{26}$H$_{40}$O$_2$Si requires M − H$_2$O, 394.2692) and a mixture of (*E*)- and (*Z*)-1,5-*dicyclohexylpent-4-en-2-ynols* (0.7%); R_f (hexane) 0.31; ν_{max}(CDCl$_3$)/cm^{-1} 3600 (OH), 2900, 2840 (CH), 2200 (C≡C), 1440 (CH$_2$), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 5.67 and 5.49 (total of 1 H, 2 × d, $J \approx$ 1.4, C=CH of each isomer), 4.31 and 4.23 (total of 1 H, d, J 5.7 and 5.8, respectively, CHOH of each isomer), 2.6–2.3 and 2.3–2.1 (total of 1 H, m, cyclohexyl CHCH=C of each isomer), 1.80 and 1.78 (total of 3 H, d, J 1.5, Me of each isomer) and 1.8–0.8 (21 H, m, 10 × CH$_2$ and cyclohexyl CHCHOH); *m/z* 260 (20%, M$^+$) and 177 (100, C$_{12}$H$_{17}$O) (Found: M$^+$, 260.2143. C$_{18}$H$_{28}$O requires M, 260.2140).

5-Cyclohexyl-5-trimethylsilylpent-3-yn-2-ol. (49%) R_f (Hexane–EtOAc, 4:1) 0.36; ν_{max}(film)/cm^{-1} 3350 (br OH), 2920, 2840 (CH), 2200 (C≡C), 1440 (CH$_2$) and 1240 (SiMe); δ_H(CDCl$_3$; 400 MHz) 4.54 (1 H, dq, J 1.9 and 6.5, CHOH), 1.8–1.0 (13 H, m, OH, CH and 5 × CH$_2$), 1.42 (3 H, d, J 6.5, CMe) and 0.08 (9 H, s, SiMe$_3$); δ_C(CDCl$_3$; 400 MHz) 84.6 (*C*≡C), 85.2 (C≡*C*), 58.7 (CO), 37.8 (*M*eC), 27.5 (cyclohexyl *C*), 26.6, 26.5, 26.0 (CH$_2$s), 25.2 (SiCH) and −1.8 (SiMe$_3$); *m/z* 238 (0.1%, M$^+$), 223 (0.3, M − Me), 221 (0.8, M − OH), 194 (3, M − C$_2$H$_4$O), 179 (20, M − C$_2$H$_4$O − OH), 148 (20, M − OH − Me$_3$Si) and 73 (100, SiMe$_3$) (Found: M$^+$, 238.1750. C$_{14}$H$_{26}$OSi requires M, 238.1753).

5-Cyclohexyl-5-dimethyl(phenyl)silylpent-3-yn-2-ol. (51%) R_f (Hexane–EtOAc, 9:1) 0.16; ν_{max}(film)/cm^{-1} 3350 (br OH), 3060, 2905, 2840 (CH), 2200 (C≡C), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.60–7.55 (2 H, m, SiPh), 7.40–7.30 (3 H, m, SiPh), 4.53 (1 H, dq, J 2.0 and 6.5, MeCHOH), 2.0–1.0 (13 H, m, c-C$_6$H$_{11}$, SiCH and OH), 1.41 (3 H, d, J 6.5, *M*eCHOH) and 0.41 (6 H, s, SiMe$_2$); *m/z* 285 (0.1%, M − Me), 282 (0.4, M − H$_2$O) and 135 (100, SiMe$_2$Ph) (Found: M − Me, 285.1697. C$_{19}$H$_{28}$OSi requires M − Me, 285.1719).

Method B

Following Hommes and co-workers,[28] *n*-butyllithium (1.5 mol dm^{-3} in hexane, 100 cm^3, 150 mmol) was added dropwise over 6 min to a solution of but-1-yne (3.29 g, 60.9 mmol) in THF (50 cm^3) below −30 °C under nitrogen and warmed slowly to 30 °C for 4 h, forming a yellow suspension of the dianion. The mixture was cooled to −20 °C, chlorodimethyl(phenyl)silane (11 g, 61 mmol) in THF (30 cm^3) was added slowly over 10 min and the mixture was warmed to 10 °C. TLC (Hexane) indicated incomplete reaction, so more chlorodimethyl(phenyl)silane (4 g) in THF (10 cm^3) was added, whereupon the yellow suspension dissolved. Cyclohexanecarbaldehyde (6.83 g, 61 mmol) in THF (30 cm^3) was added over 5 min between 15 and 30 °C and the mixture stirred for a further 15 min. Aqueous ammonium chloride (saturated, 20 cm^3) and water (20 cm^3) were added and left to stand at room temperature for 3 days. The organic layer was separated and the aqueous layer re-extracted with diethyl ether (100 cm^3). The combined organic layers were washed with water (100 cm^3), brine (200 cm^3), dried (MgSO$_4$), filtered, evaporated under reduced pressure and the residue flash chromatographed (2 × , Merck SiO$_2$ 9385, hexane–EtOAc, 9:1) giving 1-cyclohexyl-4-dimethyl(phenyl)silylpent-2-ynol (0.98 g, 6%) and butyl(dimethyl) (phenyl)silane[29] (10.7 g), suggesting that too large an excess of *n*-butyllithium had been used.

Synthesis of the (*Z*)-4-silylpentenols

Palladium (5% on BaSO$_4$, 0.24 g) and quinoline (0.24 g) in methanol (4 cm^3) were exposed to an atmosphere of hydrogen for 15 min. The alcohol (7.9 mmol) in methanol (16 cm^3) was added and the mixture stirred under hydrogen for 3.5 h. The mixture was filtered through Celite, washing with methanol and the solvents evaporated. The residue was separated by dry column chromatography[30] (SiO$_2$ Merck 7736, hexane–EtOAc, 19:1) into samples enriched in each of the two diastereoisomers and the enriched samples were then resolved completely by flash chromatography (Merck SiO$_2$ 9385, hexane–EtOAc, 19:1) to give the alcohols and 1,2,3,4-tetrahydroquinoline; R_f (hexane–EtOAc, 9:1) 0.20 (quinoline itself has R_f 0.07) identified from its ^{1}H NMR spectrum; δ_H(CDCl$_3$; 250 MHz) 7.00–6.93 (2 H, m, ArH *m*- to N), 6.61 (1 H, t, J 7.7, ArH *p*- to N), 6.47 (1 H, d, J 7.8, ArH *o*- to N), 3.30 (2 H, t, J 5.5, ArNHCH_2CH$_2$), 2.77 (2 H, t, J 6.4, ArCH_2CH$_2$) and 2.00–1.89 (2 H, m, NHCH$_2$CH_2CH$_2$Ar).[31] The following pairs of alcohols were prepared in this way.

(1*RS*,4*SR*,2*Z*)-1-Cyclohexyl-4-dimethyl(phenyl)silylpent-2-enol 7a. (33%) Separated after reduction; R_f (hexane–EtOAc, 9:1) 0.25; ν_{max}(film)/cm^{-1} 3400 (br OH), 3060, 2990, 2910, 2840 (CH), 1630 (C=C), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.55–7.45 (2 H, m, SiPh), 7.40–7.30 (3 H, m, SiPh), 5.30 (1 H, t, J 11, SiCHCH=CH), 5.12 (1 H, t, J 10, CH=CH-CHOH), 3.71 (1 H, dd, J 7.3 and 9.2, CHOH), 2.05 (1 H, dd, J 7.1 and 11.6, CHSi), 1.9–0.8 (12 H, m, c-C$_6$H$_{11}$ and OH), 1.05 (3 H, d, J 7.1, CH*M*e), 0.32 (3 H, s, SiMe$_A$Me$_B$) and 0.29 (3 H, s, SiMe$_A$Me$_B$); *m/z* 284 (0.3%, M − H$_2$O), 219 (1.5, M − C$_6$H$_{11}$), 150 (50, C$_{11}$H$_{18}$) and 135 (100, Me$_2$SiPh) (Found: M − H$_2$O, 284.1956. C$_{19}$H$_{30}$OSi requires M − H$_2$O, 284.1960).

(1*RS*,4*RS*,2*Z*)-1-Cyclohexyl-4-dimethyl(phenyl)silylpent-2-enol 9a. (27%) Separated after reduction; R_f (hexane–EtOAc, 9:1) 0.16; ν_{max}(film)/cm^{-1} 3400 (br OH), 3060, 2990, 2905, 2840 (CH), 1630 (C=C), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.51–7.47 (2 H, m, SiPh), 7.39–7.33 (3 H, m, SiPh), 5.50–5.29 (2 H, m, CH=CH), 3.99 (1 H, dd, J 6.0 and 8.0, CHOH), 2.23 (1 H, m, SiCH), 1.78–0.82 (12 H, m, c-C$_6$H$_{11}$ and OH), 1.05 (3 H, d, J 7.1, CH*M*e), 0.30 (3 H, s, SiMe$_a$Me$_B$) and 0.28 (3 H, s, SiMe$_A$Me$_B$); *m/z* 284 (0.2%, M − H$_2$O), 219 (1, M − C$_6$H$_{11}$), 150 (50, C$_{11}$H$_{18}$) and 135 (100, Me$_2$SiPh) (Found: M − H$_2$O, 284.1964. C$_{19}$H$_{30}$OSi requires M − H$_2$O, 284.1960).

(1*RS*,4*SR*,2*Z*)-1-Cyclohexyl-4-trimethylsilylpent-2-enol 7b. (14%) Separated after reduction; R_f (hexane–EtOAc, 9:1) 0.28; ν_{max}(CDCl$_3$)/cm^{-1} 3600 (br OH), 2900, 2840 (CH), 1620 (C=C) and 1240 (SiMe), δ_H(CDCl$_3$; 250 MHz) 5.32 (1 H, t, J 11.1, SiCHCH=CH), 5.21 (1 H, dd, J 8.9 and 11.0, CH=CHCHOH), 4.03 (1 H, dd, J 7.5 and 7.4, CHOH), 1.96–0.87 (12 H, m, c-C$_6$H$_{11}$ and OH), 1.84 (1 H, qd, 7.2 and 10.9, SiCHMe), 1.00 (3 H, d, J 7.1, CH*M*e) and −0.02 (9 H, s, SiMe$_3$); *m/z* 222 (0.2%, M − H$_2$O), 150 (20, C$_{11}$H$_{18}$), 83 (100, C$_6$H$_{11}$), 73 (40, SiMe$_3$) and 68 (50, C$_5$H$_8$) (Found: M − H$_2$O, 222.1810. C$_{14}$H$_{28}$OSi requires M − H$_2$O, 222.1804).

(1*RS*,4*RS*,2*Z*)-1-Cyclohexyl-4-trimethylsilylpent-2-enol 9b. (16%) Separated after reduction; R_f (hexane–EtOAc, 9:1) 0.21; ν_{max}(CDCl$_3$)/cm^{-1} 3600 (br OH), 2900, 2840 (CH), 1620 (C=C) and 1240 (SiMe); δ_H(CDCl$_3$; 250 MHz) 5.45–5.30 (2 H, m, CH=CH), 4.08 (1 H, dd, J 6.6 and 7.7, CHOH), 1.99–0.85 (12 H, m, c-C$_6$H$_{11}$ and OH), 1.94 (1 H, qd, J 7.1 and 11.0, SiCHMe), 1.02 (3 H, d, J 7.1, CH*M*e) and −0.04 (9 H, s, SiMe$_3$); *m/z* 222 (0.1%, M − H$_2$O), 150 (50, C$_{11}$H$_{18}$), 83 (40, C$_6$H$_{11}$), 73 (90, SiMe$_3$) and 68 (100, C$_5$H$_8$) (Found: M − H$_2$O, 222.1804. C$_{14}$H$_{28}$OSi requires M − H$_2$O, 222.1804).

(2*SR*,5*RS*,3*Z*)-5-Cyclohexyl-5-dimethyl(phenyl)silylpent-3-en-2-ol 11a. (35%) Separated after reduction; R_f (hexane–EtOAc, 9:1) 0.20; ν_{max}(film)/cm^{-1} 3330 (br OH), 3060, 2905, 2840 (CH), 1630 (C=C), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.54–7.46 (2 H, m, SiPh), 7.42–7.33 (3 H, m, SiPh), 5.39–5.19 (2 H, m, CH=CH), 4.09 (1 H, m, CHOH), 1.97 (1 H, dd, J 5.1 and 11.6, SiCH), 1.72–1.49 (6 H, m, 5 × CH equatorial and OH), 1.31–0.97 (6 H, m, 5 × CH axial and cyclohexyl CH), 1.04 (3 H, d, J 6.3, *M*eCHOH), 0.38 (3 H, s,

SiMe_AMeB) and 0.34 (3 H, s, SiMe_AMe$_B$); m/z 284 (0.2%, M − H_2O), 150 (100, $C_{11}H_{18}$) and 135 (80, Me_2SiPh) (Found: M − H_2O, 284.1962. $C_{19}H_{30}OSi$ requires M − H_2O, 284.1960).

(2RS,5RS,3Z)-5-Cyclohexyl-5-dimethyl(phenyl)silylpent-3-en-3-ol 12a. (36%) R_f (Hexane–EtOAc, 9:1) 0.16; v_{max}(film)/cm^{-1} 3330 (br OH), 3060, 2905, 2840 (CH), 1630 (C=C), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.48–7.43 (2 H, m, SiPh), 7.36–7.29 (3 H, m, SiPh), 5.41–5.36 (2 H, m, CH=CH), 4.37 (1 H, m, CHOH), 2.05 (1 H, m, SiCH), 1.70–1.49 (6 H, m, 5 × CH equatorial and OH), 1.25–0.91 (6 H, m, 5 × CH axial and cyclohexyl CH), 0.93 (3 H, d, J 6.2, Me CHOH), 0.31 (3 H, s, SiMe_AMe$_B$) and 0.28 (3 H, s, SiMe_AMe$_B$); m/z 284 (0.5%, M − H_2O), 150 (80, $C_{11}H_{18}$) and 135 (100, Me_2SiPh) (Found: M − H_2O, 284.1942. $C_{19}H_{30}OSi$ requires M − H_2O, 284.1960).

5-Cyclohexyl-5-trimethylsilylpent-3-en-2-ol. (71%) As a 50:50 mixture of diastereoisomers **11b** and **12b**; R_f (hexane–EtOAc, 6:1) 0.25; v_{max}(film)/cm^{-1} 3350 (br OH), 2910, 2840 (CH), 1630 (C=C), 1440 (CH$_2$) and 1240 (SiMe); δ_H(CDCl$_3$; 250 MHz) 5.5–5.3 (2 H, m, CH=CH), 4.55 (1 H, m, CHOH), 1.8–0.9 (13 H, m, OH, CH, CH$_2$s), 1.2 (3 H, d, J 6.2, CMe) and 0.02 and −0.02 (total of 9 H, s, SiMe$_3$ of each diastereoisomer); m/z 209 (0.5%, M − C_2H_7), 150 (40, $C_{11}H_{18}$) and 73 (50, Me$_3$Si) (Found: M − C_2H_7, 209.1342. $C_{14}H_{28}OSi$ requires M − C_2H_7, 209.1361).

Synthesis of the (E)-4-silylpentenols

Typically, the alkyne (1 mmol) in THF (3 cm^3) was added to lithium aluminium hydride (0.11 g, 3 mmol) slurried in THF (4 cm^3) at 0 °C under nitrogen. Methanol (1 drop) was added and the mixture was refluxed for 2.5 h. Methanol (1 drop) was again added and the mixture refluxed for a further 2.5 h. Methanol (1 cm^3) was carefully added, followed by ethyl acetate (10 cm^3) and water (5 cm^3). The mixture was filtered through sand, washing with ethyl acetate. The organic layer was washed with brine (10 cm^3), dried (MgSO$_4$), filtered and evaporated under reduced pressure, and the residue was flash chromatographed (Merck SiO$_2$ 9385, hexane–EtOAc, 9:1). The following 4-silylpent-2-enols were prepared in this way, contaminated with the corresponding allene.

(2E)-1-Cyclohexyl-4-dimethyl(phenyl)silylpent-2-enol. (46%) As a 56:44 mixture of diastereoisomers contaminated with the starting acetylene (15%); R_f (hexane–EtOAc, 9:1) 0.16; v_{max}(CDCl$_3$)/cm^{-1} 3600 (OH), 3060, 3000, 2900, 2840 (CH), 1640 (C=C), 1420 (CH$_2$), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.5–7.4 (2 H, m, Ph), 7.4–7.3 (3 H, m, Ph), 5.63 and 5.58 (total of 1 H, ddd, J 0.6, 7.2 and 15.5, CH=CHOH of one diastereoisomer and J 0.6, 7.9 and 15.5, CH=CHOH of the other diastereoisomer, respectively), 5.22 and 5.20 (total of 1 H, ddd, J 1.2, 7.8 and 15.5, C=CHOH of one diastereoisomer, J 1.5, 7.9 and 15.5 of the other diastereoisomer, respectively), 3.7 (1 H, br t, J 7.1, CHOH), 1.9–0.7 (13 H, m, SiCH, OH and c-C$_6$H$_{11}$), 1.07 (minor) and 1.05 (major) (total of 3 H, d, J 7.2, CMe of each diastereoisomer) and 0.27 (6 H, s, Me$_2$Si) (the ratio of diastereoisomers was measured by integration of the methyl doublets at δ 1.05 and 1.07); m/z 284 (10%, M − H_2O), 219 (20, $C_{13}H_{19}OSi$), 150 (55, $C_{11}H_{18}$) and 135 (100, PhMe$_2$Si) (Found: M − H_2O, 284.1941. $C_{19}H_{30}OSi$ requires M − H_2O, 284.1961), together with 1-*cyclohexyl-4-dimethyl(phenyl)silylpenta*-1,2-*diene* (0.04 g, 14%); R_f (hexane–EtOAc, 9:1) 0.64; v_{max}(CDCl$_3$)/cm^{-1} 3060, 3000, 2900, 2840 (CH), 1945 (C=C=C), 1420 (CH$_2$), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.55–7.48 (2 H, m, Ph), 7.38–7.32 (3 H, m, Ph), 5.20 (1 H, m, C=CH), 5.09 (1 H, m, C=CH), 1.90 (1 H, m, cyclohexyl CH), 1.8–1.5 (5 H, m, CH$_2$s), 1.5–1.3 (6 H, m, CH$_2$s and SiCH), 1.024 and 1.018 (total of 3 H, 2 × d, J 7.3, CMe of each diastereoisomer) and 0.29 and 0.28 (total of 6 H, s, Me$_2$Si of each diastereoisomer) (the signal at δ 0.28 is just resolved into two for the diastereotopic methyl groups; the diastereoisomer ratio is 50:50); m/z 284 (5%, M$^+$) and 135

(100, PhMe$_2$Si) (Found: M$^+$, 284.1971. $C_{19}H_{28}Si$ requires M, 284.1961), and the starting acetylene (15%).

(2E)-1-Cyclohexyl-4-trimethylsilylpent-2-enol. (28%) Contaminated with the starting acetylene (20%); R_f (hexane–EtOAc, 19:1) 0.10; v_{max}(film)/cm^{-1} 3360 (br OH), 2950, 2920, 2850 (CH), 1650 (C=C) and 1240 (SiMe); δ_H(CDCl$_3$; 250 MHz) 5.72 and 5.61 (total of 1 H, 2 × dd, J 7.7 and 16.2; and 8.6 and 6.2, respectively, for each diastereoisomer, SiCHCH=CH-CHOH), 5.27 (1 H, m, SiCHCH=CHCHOH), 3.75 (1 H, t, J 7.1, CHOH), 1.9–0.8 (13 H, m, c-C$_6$H$_{11}$, SiCH and OH), 1.045 and 1.038 (total of 1 H, 2 × d, J 7.2, CHMe of each diastereoisomer) and −0.04 (9 H, s, SiMe$_3$); m/z 222 (1%, M − H_2O), 207 (0.3, M − H_2O − Me), 150 (34, $C_{11}H_{18}$) and 73 (100, SiMe$_3$) (Found: M − H_2O, 222.1791. $C_{14}H_{28}OSi$ requires M − H_2O, 222.1803).

(3E)-5-Cyclohexyl-5-dimethyl(phenyl)silylpent-3-en-2-ol. (46%) As an approximately 50:50 mixture of diastereoisomers; R_f (hexane–EtOAc, 9:1) 0.09; v_{max}(film)/cm^{-1} 3350 (br OH), 3060, 3040, 2950, 2905, 2840 (CH), 1650 (C=C), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.48–7.42 (2 H, m, SiPh), 7.37–7.29 (3 H, m, SiPh), 5.48 (1 H, m, C=CH), 5.19 (1 H, m, C=CH), 1.67–0.94 (12 H, m, c-C$_6$H$_{11}$ and OH), 1.17 (3 H, d, J 6.4, CMe) and 0.32, 0.29 and 0.26 (total of 6 H, 3 × s, the peak at δ 0.29 is two of the four diastereotopic SiMe groups); m/z 284 (0.3%, M − H_2O), 150 (80, $C_{11}H_{18}$) and 135 (100, Ph SiMe$_2$) (Found: M − H_2O, 284.1967. $C_{19}H_{30}OSi$ requires M − H_2O, 284.1961), together with 1-*cyclohexyl-1-dimethyl(phenyl)silylpenta*-2,3-*diene* (4%), as a mixture of diastereoisomers; R_f (hexane–EtOAc, 9:1) 0.65; v_{max}(CDCl$_3$)/cm^{-1} 3060, 2950, 2840 (CH), 1950 (C=C=C), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.55–7.48 (2 H, m, SiPh), 7.37–7.31 (3 H, m, SiPh), 5.02–4.88 (2 H, m, HC=C=CH), 1.73–0.84 (11 H, m, c-C$_6$H$_{11}$), 1.61 and 1.60 (total of 1 H, 2 × d, J 6.7 and 6.6, respectively, SiCH of each diastereoisomer), 1.51 and 1.49 (total of 3 H, 2 × d, J 6.6 and 6.5 respectively, CMe of each diastereoisomer) and 0.324 and 0.317 (total of 6 H, 2 × s, SiMe$_2$ of each diastereoisomer); m/z 284 (4%, M$^+$), 269 (1, M − Me), 201 (5, M − C_6H_{11}) and 135 (100, PhSiMe$_2$) (Found: M$^+$, 284.1960. $C_{19}H_{28}Si$ requires M, 284.1961).

(3E)-5-Cyclohexyl-5-trimethylsilylpent-3-en-2-ol. (33%) As an approximately 50:50 mixture of diastereoisomers; R_f (hexane–EtOAc, 4:1) 0.32; v_{max}(film)/cm^{-1} 3300 (br OH), 2900, 2840 (CH), 1640 (C=C) and 1240 (SiMe); δ_H(CDCl$_3$; 250 MHz) 5.50 (1 H, m, C=CH), 5.30 (1 H, m, C=CH), 4.25 (1 H, m, CHOH), 1.8–0.8 (13 H, m, OH, SiCH and c-C$_6$H$_{11}$), 1.25 and 1.24 (total of 3 H, 2 × d, J 6.2 and 6.3, CHMe of each diastereoisomer) and −0.01 and −0.03 (total of 9 H, 2 × s, SiMe$_3$ of each diastereoisomer); m/z 195 (1%, M − C_3H_9), 150 (40, $C_{11}H_{18}$) and 73 (80, SiMe$_3$) (Found: M − C_3H_9, 195.1201. $C_{14}H_{28}OSi$ requires M − C_3H_9, 195.1205), and 1-*cyclohexyl-1-trimethylsilyl-penta*-2,3-*diene* (23%) as a 63:37 mixture of diastereoisomers; R_f (hexane–EtOAc, 4:1) 0.71; v_{max}(film)/cm^{-1} 2910, 2840 (C–H), 1950 and 1930 (C=C=C) and 1240 (SiMe); δ_H(CDCl$_3$; 250 MHz) 5.0–4.9 (2 H, m, C=C=CH), 1.8–0.8 (12 H, m, SiCH and c-C$_6$H$_{11}$), 1.63 and 1.62 (total of 3 H, 2 × d, J 6.8, CHMe of each diastereoisomer) and 0.03 (major) and 0.02 (minor) (total of 9 H, 2 × s, SiMe$_3$ of each diastereoisomer); m/z 222 (10%, M$^+$), 207 (5, M − Me) and 73 (100, SiMe$_3$) (Found: M$^+$, 222.1806. $C_{14}H_{26}Si$ requires M, 222.1804).

Synthesis of the 4-silylpent-2-enyl acetates

Typically, following Höfle and Steglich,[32] N,N-dimethyl-4-aminopyridine (DMAP) (5 mg), distilled acetic anhydride (50 mg) and triethylamine (50 mg) were stirred with the allylic alcohol (0.4 mmol) in diethyl ether (5 cm^3) at 20 °C for 1–18 h. The solution was washed with water (5 cm^3) and the organic layer evaporated under reduced pressure, and the residue was chromatographed (Merck SiO$_2$ 9385, hexane–EtOAc, 9:1). The following acetates were prepared by this method.

(1*RS*,4*SR*,2*Z*)-1-Cyclohexyl-4-dimethyl(phenyl)silylpent-2-enyl acetate 26a. (94%) R_f (Hexane–EtOAc, 9:1) 0.46; ν_{max}(film)/cm^{-1} 3060, 3000, 2920, 2840 (CH), 1725 (C=O), 1635 (C=C), 1230 (C–O) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.51–7.47 (2 H, m, SiPh), 7.35–7.32 (3 H, m, SiPh), 5.43 (1 H, dd, *J* 7.4 and 9.3, C*H*OAc), 5.38 (1 H, dd, *J* 10.4 and 11.5, C*H*=CH-CHOAc), 5.23 (1 H, dd, *J* 9.5 and 10.4, CH=C*H*CHOAc), 2.17 (1 H, qd, *J* 7.1 and 11.6, SiC*H*), 1.99 (3 H, s, COMe), 1.73–0.9 (11 H, m, c-C$_6$H$_{11}$), 0.95 (3 H, d, *J* 7.2, CH*Me*), 0.23 (3 H, s, SiMe$_A$Me$_B$) and 0.22 (3 H, s, SiMe$_A$Me$_B$); *m/z* 284 (0.5%, M − HOAc), 269 (0.01, M − HOAc − Me), 150 (50, C$_{11}$H$_{18}$), 135 (80, Me$_2$SiPh) and 68 (100, C$_5$H$_8$) (Found: M − AcOH, 284.1960. C$_{21}$H$_{32}$O$_2$Si requires *M* − AcOH, 284.1960).

(1*RS*,4*SR*,2*Z*)-1-Cyclohexyl-4-trimethylsilylpent-2-enyl acetate 26b. (87%) R_f (Hexane–EtOAc, 9:1) 0.56; ν_{max}(film)/cm^{-1} 2905, 2840 (CH), 1720 (C=O), 1630 (C=C) and 1235 (C–O); δ_H(CDCl$_3$; 250 MHz) 5.45–5.34 (2 H, m, C*H*=CHC*H*OAc), 5.21 (1 H, dd, *J* 9.8 and 10.6, CH=C*H*CHOAc), 2.00 (3 H, s, COMe), 1.95 (1 H, qd, *J* 7.2 and 12.1, SiC*H*Me), 1.89–0.83 (11 H, m, c-C$_6$H$_{11}$), 0.99 (3 H, d, *J* 7.2, CH*Me*) and −0.08 (9 H, s, SiMe$_3$); *m/z* 267 (0.3%, M − Me), 150 (80, C$_{11}$H$_{18}$), 83 (100, C$_6$H$_{11}$) and 73 (50, SiMe$_3$) (Found: M − Me, 267.1767. C$_{16}$H$_{30}$O$_2$Si requires *M* − Me, 267.1780).

(1*RS*,4*RS*,2*Z*)-1-Cyclohexyl-4-dimethyl(phenyl)silylpent-2-enyl acetate 27a. (93%) R_f (Hexane–EtOAc, 9:1) 0.44; ν_{max}(film)/cm^{-1} 3060, 3000, 2910, 2840 (CH), 1725 (C=O), 1635 (C=C), 1230 (C–O) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.50–7.45 (2 H, m, SiPh), 7.36–7.30 (3 H, m, SiPh), 5.42–5.19 (3 H, m, C*H*OAc and CH=CH), 2.29 (1 H, qd, *J* 7.1 and 11.8, SiC*H*), 1.99 (3 H, s, COMe), 1.69–0.9 (11 H, m, c-C$_6$H$_{11}$), 1.00 (3 H, d, *J* 7.1, CH*Me*), 0.27 (3 H, s, SiMe$_A$Me$_B$) and 0.26 (3 H, s, SiMe$_A$Me$_B$); *m/z* 284 (0.5%, M − HOAc), 269 (0.02, M − HOAc − Me), 150 (60, C$_{11}$H$_{18}$) and 135 (100, Me$_2$SiPh) (Found: M − AcOH, 284.1959. C$_{21}$H$_{32}$O$_2$Si requires *M* − AcOH, 284.1960).

(1*RS*,4*RS*,2*Z*)-1-Cyclohexyl-4-trimethylsilylpent-2-enyl acetate 27b. (84%) R_f (Hexane–EtOAc, 9:1) 0.52; ν_{max}(film)/cm^{-1} 2905, 2840 (CH), 1730 (C=O), 1635 (C=C) and 1235 (C–O); δ_H(CDCl$_3$; 250 MHz) 5.48–5.23 (3 H, m, C*H*=CHCHOAc), 2.01 (3 H, s, COMe), 1.74–0.86 (12 H, m, c-C$_6$H$_{11}$ and SiCH), 0.99 (3 H, d, *J* 7.1, CH*Me*) and −0.04 (9 H, s, SiMe$_3$); *m/z* 223 (2.5%, M − OAc), 150 (80, C$_{11}$H$_{18}$), 135 (18, C$_{10}$H$_{15}$), 73 (80, SiMe$_3$) and 68 (100, C$_5$H$_8$) (Found: M − OAc, 223.1872. C$_{16}$H$_{30}$O$_2$Si requires *M* − OAc, 223.1882).

(2*SR*,5*RS*,3*Z*)-5-Cyclohexyl-5-dimethyl(phenyl)silylpent-3-en-2-yl acetate 28a. (54%) R_f (Hexane–EtOAc, 9:1) 0.45; ν_{max}(film)/cm^{-1} 3060, 3000, 2905, 2840 (CH), 1720 (C=O), 1630 (C=C), 1240 (C–O) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.55–7.45 (2 H, m, SiPh), 7.37–7.30 (3 H, m, SiPh), 5.60 (1 H, m, C*H*OAc), 5.53–5.36 (2 H, m, CH=CH), 2.06 (1 H, m, SiCH), 1.96 (3 H, s, COMe), 1.73–1.35 (6 H, m, 5 × CH equatorial and cyclohexyl CH), 1.24 (3 H, d, *J* 6.1, *Me*CHOAc), 1.22–0.79 (5 H, m, 5 × CH axial), 0.28 (3 H, s, SiMe$_A$Me$_B$) and 0.25 (3 H, s, SiMe$_A$Me$_B$); *m/z* 284 (1.2%, M − AcOH), 150 (60, C$_{11}$H$_{18}$), 135 (70, Me$_2$SiPh) and 68 (100, C$_5$H$_8$) (Found: M − AcOH, 284.1973. C$_{21}$H$_{32}$O$_2$Si requires *M* − AcOH, 284.1960).

(2*RS*,5*RS*,3*Z*)-5-Cyclohexyl-5-dimethyl(phenyl)silylpent-3-en-2-yl acetate 29a. (96%) R_f (Hexane–EtOAc, 9:1) 0.46; ν_{max}(film)/cm^{-1} 3060, 3000, 2905, 2840 (CH), 1720 (C=O), 1630 (C=C), 1240 (C–O) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.55–7.43 (2 H, m, SiPh), 7.39–7.28 (3 H, m, SiPh), 5.55–5.28 (3 H, m, C*H*=CHC*H*OAc), 2.13 (1 H, dd, *J* 5.0 and 12.1, SiCH), 1.98 (3 H, s, COMe), 1.76–1.38 (6 H, m, 5 × CH equatorial and cyclohexyl CH), 0.91 (3 H, d, *J* 6.1, *Me*CHOAc), 1.34–0.84 (5 H, m, 5 × CH axial), 0.32 (3 H, s, SiMe$_A$Me$_B$) and 0.29 (3 H, s, SiMe$_A$Me$_B$); *m/z* 284 (1.2%, M − AcOH), 150 (60, C$_{11}$H$_{18}$), 135 (100, Me$_2$SiPh) and 68 (99, C$_5$H$_8$) (Found: M − AcOH, 284.1967. C$_{21}$H$_{32}$O$_2$Si requires *M* − AcOH, 284.1960).

(3*Z*)-5-Cyclohexyl-5-trimethylsilylpent-3-en-2-yl acetate 28b and 29b. (85%) As a 47:53 mixture of diastereoisomers; R_f (hexane–EtOAc, 4:1) 0.48; ν_{max}(film)/cm^{-1} 3000, 2910, 2840 (CH), 1725 (C=O), 1630 (C=C) and 1240 (C–O); δ_H(CDCl$_3$; 250 MHz) 5.55 (1 H, m, C*H*OAc), 5.5–5.4 (2 H, m, CH=CH), 2.00 and 1.99 (total of 3 H, 2 × s, COMe of each diastereoisomer), 2.0–0.8 (12 H, m, c-C$_6$H$_{11}$CHSi), 1.25 (3 H, d, *J* 6.2, CH*Me*) and −0.01 (minor) and −0.03 (major) (total of 9 H, 2 × s, SiMe$_3$ of each diastereoisomer); *m/z* 237 (0.2%, M − 3Me), 222 (2.5, M − HOAc), 209 (2, M − Me$_3$Si), 150 (95, C$_{11}$H$_{18}$), 73 (90, SiMe$_3$) and 68 (100, C$_5$H$_8$) (Found: M − 3Me, 237.1298. C$_{16}$H$_{30}$O$_2$Si requires *M* − 3Me, 237.1310).

(2*E*)-1-Cyclohexyl-4-dimethyl(phenyl)silylpent-2-enyl acetate 30a. (65%) As a 56:44 mixture of diastereoisomers; R_f (hexane–EtOAc, 9:1); ν_{max}(CDCl$_3$)/cm^{-1} 3060, 3020, 2920, 2840 (CH), 1730 (C=O), 1650 (C=C), 1240 (C–O) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.55–7.4 (2 H, m, Ph), 7.4–7.25 (3 H, m, Ph), 5.73 and 5.69 (total of 1 H, 2 × dd, *J* 7.5 and 15.2, C*H*=CHCHOAc of each diastereoisomer), 5.10 (1 H, ddd, *J* 1.4, 8.2 and 15.2, CH=C*H*CHOAc), 4.95 (1 H, dd, *J* 7.2 and 8.2, C*H*OAc), 2.01 (major) and 2.00 (minor) (total of 3 H, 2 × s, COMe of each diastereoisomer), 1.9–0.8 (11 H, c-C$_6$H$_{11}$), 1.03 (total of 3 H, 2 × d, *J* 7.2, CH*Me* of each diastereoisomer) and 0.25–0.24 (four peaks) (total of 6 H, 4 × s, diastereotopic SiMe$_2$ of each diastereoisomer); *m/z* 284 (3%, M − AcOH), 150 (80, C$_{11}$H$_{18}$) and 135 (100, PhSiMe$_2$) (Found: M − AcOH, 284.1965. C$_{21}$H$_{32}$O$_2$Si requires *M* − AcOH, 284.1960).

(2*E*)-1-Cyclohexyl-4-trimethylsilylpent-2-enyl acetate 30b. (93%) As a 50:50 mixture of diastereoisomers; R_f (hexane–EtOAc, 19:1) 0.37; ν_{max}(CDCl$_3$)/cm^{-1} 2940, 2860 (CH), 1720 (C=O), 1650 (C=C) and 1250 (C–O); δ_H(CDCl$_3$; 250 MHz) 5.77 and 5.72 (total of 1 H, 2 × dd, *J* 7.3 and 15.2; and 7.8 and 15.0, respectively, SiCHC*H*=CH of each diastereoisomer), 5.15 (1 H, m, CH=C*H*CHOAc), 4.98 (1 H, br t, *J* ≈ 8, CH=CHC*H*OAc), 2.01 (3 H, s, COMe), 1.74–1.42 (6 H, m, SiCH and CH$_A$H$_B$ equatorial), 1.28–0.83 (6 H, m, cyclohexyl CH and CH$_A$H$_B$ axial), 1.03 (3 H, d, *J* 7.2, CH*Me*) and −0.05 (9 H, s, SiMe$_3$); *m/z* 239 (0.2%, M − MeCO), 222 (4, M − HOAc), 150 (80, C$_{11}$H$_{18}$), 73 (90, SiMe$_3$) and 68 (100, C$_5$H$_8$) (Found: M − Ac, 239.1829. C$_{16}$H$_{30}$O$_2$Si requires *M* − Ac, 239.1831).

(3*E*)-5-Cyclohexyl-5-dimethyl(phenyl)silylpent-3-en-2-yl acetate 31a. (89%) As an approximately 50:50 mixture of diastereoisomers; R_f (hexane–EtOAc, 9:1) 0.44; ν_{max}(film)/cm^{-1} 3060, 2905, 2840 (CH), 1730 (C=O), 1650 (C=C), 1240 (O–CO) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.48–7.42 (2 H, m, SiPh), 7.36–7.30 (3 H, m, SiPh), 5.70–5.52 (1 H, m, C*H*=CHCHMeOAc of each diastereoisomer), 5.37–5.10 (2 H, m, CH=C*H*CH-MeOAc), 2.00 (3 H, s, Ac), 1.25 and 1.20 (total of 3 H, 2 × d, *J* 6.3, CH*Me* of each diastereoisomer), 1.77–0.82 (12 H, m, c-C$_6$H$_{11}$ and SiCH), 0.28, 0.26 and 0.25 (total of 6 H, 3 × s, the peak at δ 0.28 is a coalescence of two signals from the four diastereotopic SiMe groups); *m/z* 329 (0.02%, M − Me), 300 (0.7, M − CO$_2$), 285 (3, M − OAc), 150 (60, C$_{11}$H$_{18}$) and 135 (100, PhSiMe$_2$) (Found: M − Me, 329.1928. C$_{21}$H$_{32}$O$_2$Si requires *M* − Me, 329.1937).

(3*E*)-5-Cyclohexyl-5-trimethylsilylpent-3-en-2-yl acetate 31b. (85%) As an approximately 50:50 mixture of diastereoisomers; R_f (hexane–EtOAc, 9:1) 0.45; ν_{max}(CDCl$_3$)/cm^{-1} 2920, 2840 (CH), 1710 (C=O), 1650 (C=C) and 1240 (O–CO); δ_H(CDCl$_3$; 250 MHz) 5.60 (1 H, m, C*H*=CHCHMeOAc), 5.4–5.1 (2 H, m, CH=C*H*CHMeOAc), 2.01 and 2.00 (total of 3 H, 2 × s, COMe of each diastereoisomer), 1.28 and 1.27 (total of 3 H, 2 × d, *J* 6.3 and 6.2, respectively, CH*Me* for each diastereoisomer), 1.8–0.7 (12 H, m, c-C$_6$H$_{11}$ and SiCH) and −0.03 (9 H, s, SiMe$_3$); *m/z* 238 (1%, M − C$_2$H$_4$O), 223 (1, M − OAc), 222 (2, M − HOAc), 150 (38, C$_{11}$H$_{18}$) and 73 (80, SiMe$_3$) (Found: M − MeCHO, 238.1738. C$_{16}$H$_{30}$O$_2$Si requires *M* − MeCHO, 238.1753).

1-Cyclohexyl-4-trimethylsilylpent-2-ynyl acetate. (49%) As a 50:50 mixture of diastereoisomers; R_f (hexane–EtOAc, 9:1), (hexane–EtOAc, 19:1) 0.32; ν_{max}(film)/cm^{-1} 2900, 2830 (CH),

2190 (C≡C), 1725 (C=O), 1240 (SiMe) and 1220 (C–O); δ_H(CDCl$_3$; 250 MHz) 5.22 (1 H, m, CHOH), 2.04 (3 H, s, COMe), 1.8–1.5 (6 H, m, SiCH and five equatorial CH_AH$_B$), 1.4–1.0 (6 H, m, cyclohexyl CH and 5 axial CH$_A$H$_B$), 1.129 and 1.127 (total of 3 H, 2 × d, J 7.29, CHMe of each diastereoisomer) and 0.049 and 0.047 (total of 9 H, 2 × s, SiMe$_3$ of each diastereoisomer); m/z 265 (2%, M − Me), 238 (5, M − C$_2$H$_2$O), 148 (8, C$_{11}$H$_{16}$) and 73 (100, SiMe$_3$) (Found: M − Me, 265.1605. C$_{16}$H$_{28}$O$_2$Si requires M − Me, 265.1624).

1-Cyclohexylpenta-1,3-diyne

Following Sonnet and Heath,[8,33] n-butyllithium (1.5 mol dm^{-3} in hexane, 7.4 cm^3) was added dropwise under nitrogen to ethynylcyclohexane[9] (1.08 g, 10 mmol) in THF (16 cm^3) at 0 °C. The solution was then cooled to −70 °C and bromine (1.76 g, 0.57 cm^3, 11 mmol) was added dropwise over 10 min. The mixture was allowed to warm to 20 °C and then water (20 cm^3) was added, and the mixture extracted with pentane (2 × 20 cm^3) and the combined organic layers were washed with water (10 cm^3), dried (K$_2$CO$_3$), and evaporated under reduced pressure (CARE: bromoacetylenes are potentially explosive) to a residual volume (2 cm^3). Distilled n-propylamine (10 cm^3), methanol (6 cm^3), propyne (0.8 g) in cold methanol (5 cm^3), copper(I) chloride (0.02 g) and hydroxylamine hydrochloride (0.03 g) were added and the mixture stirred for 45 min at −40 °C. Water (20 cm^3) was added and the mixture was extracted with pentane (2 × 20 cm^3). The combined extracts were washed with water (10 cm^3), aqueous hydrochloric acid (2 mol dm^{-3}, 10 cm^3), water (10 cm^3), dried (MgSO$_4$) and evaporated under reduced pressure. The residue was distilled to give the *diacetylene* (0.53 g, 36%), bp (Kugelrohr) 88 °C at 2.4 mmHg; ν_{max}(film)/cm^{-1} 2905, 2815 (CH) and 1440 (CH$_2$); δ_H(CDCl$_3$; 250 MHz) 2.40 (1 H, m, CHC≡C-C≡CMe), 1.9 (3 H, d, J 1.1, CHC≡C-C≡CMe) and 1.85–1.2 (10 H, m, 5 × CH$_2$); m/z 146 (100%, M$^+$) and 131 (60, M − Me) (Found: M$^+$, 146.1104. C$_{11}$H$_{14}$ requires M, 146.1096).

(1Z,3Z)-1-Cyclohexylpenta-1-diene

Following Sonnet and Heath,[8] cyclohexene (1.47 cm^3, 14.5 mmol) was stirred under nitrogen with borane (1 mol dm^{-3} in THF, 7.25 cm^3) at 0–5 °C for 1 h. The diyne (0.53 g, 3.63 mmol) in THF (2 cm^3) was added, the mixture allowed to warm to 20 °C and stirred for 5 h. Acetic acid (glacial, 1.82 cm^3) was added dropwise and the solution was heated to 60–65 °C for 5 h. The solution was cooled to −5 °C and aqueous sodium hydroxide (6 mol dm^{-3}, 6.16 cm^3) was added, followed by aqueous hydrogen peroxide (100 vol, 1.9 cm^3, 17 mmol). The solution was heated to 30–40 °C for 30 min, cooled to 20 °C and water (25 cm^3) was added. The mixture was extracted with pentane (2 × 15 cm^3), the combined extracts were washed with water (25 cm^3), brine (25 cm^3), dried (K$_2$CO$_3$), and evaporated under reduced pressure. The residue was flash chromatographed (Merck SiO$_2$ 9385, hexane) and then Kugelrohr distilled to give the (Z,Z)-diene[7] (0.08 g, 15%); R_f (hexane) 0.5; t_R (GC) 15.7 min; ν_{max}(CDCl$_3$)/cm^{-1} 2900, 2840 (CH) and 1430 (CH$_2$); δ_H(CDCl$_3$; 400 MHz) 6.29 (1 H, t, J 11.5, MeCH=CH), 6.16 (1 H, dd, J 10.9 and 11.5, MeCH=CH-CH), 5.51 (1 H, m, MeCH), 5.29 (1 H, d, J ≈ 10, MeCH=CH-CH=CH), 2.43 (1 H, m, cyclohexyl CH), 1.73 (3 H, dd, J 1.7 and 7.1, Me) and 1.7–1.0 (10 H, m, 5 × CH$_2$); δ_C(CDCl$_3$; 400 MHz) 137.92, 125.95, 124.76, 121.39 (CH=CH-CH=CH), 40.69 (cyclohexyl CH), 33.24, 26.03, 25.91 (CH$_2$s) and 13.11 (Me); m/z 150 (43%, M$^+$), 135 (10, M − Me), 68 (100, C$_5$H$_8$) and 67 (74, C$_5$H$_7$) (Found: M$^+$, 150.1407. C$_{11}$H$_{18}$ requires M, 150.1408).

Vinylogous Peterson reactions

Potassium hydride (20% suspension in oil, 96 mg) was washed with pentane (3 × 4 cm^3) under nitrogen and THF (2 cm^3) was added. The allyl alcohol (84.3 mg, 0.28 mmol) was added in THF (1.5 cm^3) and the mixture stirred at room temperature for

3 h. TLC showed that the reaction was complete, and water (6 cm^3) and diethyl ether (6 cm^3) were added. The aqueous layer was extracted with diethyl ether (6 cm^3) and the combined organic layers were washed with brine (6 cm^3), dried (MgSO$_4$), and evaporated. The residue was dissolved in pentane (2 cm^3), filtered through silica, washing with pentane and evaporated. The following dienes were made by this method.

(1E,3E)-1-Cyclohexylpenta-1,3-diene[7,34] **8.** (37% From **7**); R_f (hexane–EtOAc, 9 : 1) 0.73; t_R (GC) 16.5 min; ν_{max}(CDCl$_3$)/cm^{-1} 3000, 2905, 2840 (CH), 1620 (C=C) and 1440 (CH$_2$); δ_H(CDCl$_3$; 250 MHz) 6.06–5.88 (2 H, m, MeCH=CH-CH=CH), 5.57 (1 H, qd, J 6.9 and 13.9, MeCH=CH-CH=CH), 5.50 (1 H, dd, J 6.8 and 14.4, MeCH=CH-CH=CH), 2.00 (1 H, m, cyclohexyl CH), 1.72 (3 H, d, J 6.4, Me); δ_C(CDCl$_3$; 400 MHz) 138.10, 131.96, 127.63, 126.86 (CH-CH-CH=CH), 40.64 (cyclohexyl CH), 32.98, 26.19, 26.06 (CH$_2$s) and 18.04 (Me); m/z 150 (33%, M$^+$), 135 (7, M − Me) and 68 (100, C$_5$H$_8$) (Found: M$^+$, 150.1395. C$_{11}$H$_{18}$ requires M, 150.1408).

(1Z,3E)-1-Cyclohexylpenta-1,3-diene[7,34] **10.** (80% From **9**); t_R (GC) 14.4 min; ν_{max}(CDCl$_3$)/cm^{-1} 2990, 2900, 2840 (CH), 1650 (C=C) and 1430 (CH$_2$); δ_H(CDCl$_3$; 250 MHz) 6.33 (1 H, t, J 13.6, MeCH=CH-CH=CH), 5.84 (1 H, t, J 10.9, MeCH=CH-CH=CH), 5.66 (1 H, qd, J 6.8 and 14.5, MeCH=CH-CH=CH), 5.13 (1 H, t, J 10.1, MeCH=CH-CH=CH), 2.40 (1 H, m, cyclohexyl CH), 1.77 (3 H, dd, J 1.5 and 6.8, Me) and 1.4–0.8 (10 H, m, 5 × CH$_2$); δ_C(CDCl$_3$; 400 MHz) 135.90, 128.99, 127.21, 126.58 (CH=CH-CH=CH), 36.75 (cyclohexyl CH), 33.34, 26.02, 25.92 (CH$_2$s) and 18.26 (Me); m/z 150 (30%, M$^+$), 135 (50, M − Me) and 68 (100, C$_5$H$_8$) (Found: M$^+$, 150.1395. C$_{11}$H$_{18}$ requires M, 150.1409).

(1E,3Z)-1-Cyclohexylpenta-1,3-diene[7,35] **13.** (19.5 mg, 47% From **12**); t_R (GC) 16.9 min; ν_{max}(CDCl$_3$)/cm^{-1} 3000, 2905, 2840 (CH), 1645 (C=C) and 1440 (CH$_2$); δ_H(CDCl$_3$; 250 MHz) 6.29 (1 H, dd, J 10.9 and 15.2, MeCH=CH-CH=CH), 5.95 (1 H, qt, J 1.6 and 10.8, MeCH=CH-CH=CH), 5.61 (1 H, dd, J 7.0 and 15.2, MeCH=CH-CH=CH), 5.37 (1 H, qd, J 7.1 and 10.7, MeCH=CH-CH=CH), 2.00 (1 H, m, cyclohexyl CH), 1.73 (3 H, dd, J 1.6 and 7.1, Me) and 1.8–1.0 (10 H, m, 5 × CH$_2$); δ_C(CDCl$_3$; 400 MHz) 140.31, 129.69, 123.96, 122.62 (CH=CH-CH=CH), 40.94 (cyclohexyl CH), 32.88, 26.09, 25.96 (CH$_2$s) and 13.22 (Me); m/z 150 (29%, M$^+$), 135 (5%, M − Me) and 68 (100, C$_5$H$_8$) (Found: M$^+$, 150.1397. C$_{11}$H$_{18}$ requires M, 150.1408).

Dienes by E2′ reactions

Typically, the acetate (65 µmol) was stirred with tetrabutylammonium fluoride (1 mol dm^{-3} in THF, 0.26 cm^3) in dichloromethane (0.43 cm^3) containing a mixture of *cis*- and *trans*-decalin (0.2 mol dm^{-3} as internal standard for GC) for 4 h. Water (5 cm^3) was added and the mixture extracted with pentane (2 × 10 cm^3). The extracts were washed with brine (5 cm^3), and an aliquot was filtered through silica gel and analysed by GC; t_R (GC) 5.38 (*cis*-decalin, typically 26%), 6.79 (*trans*-decalin, typically 31%) and the dienes (typically 40%). The identity of the main component in those cases giving the (*E*,*Z*)-diene **13** was confirmed by evaporation of the pentane filtrate and analysis (^{1}H NMR, CDCl$_3$; 250 MHz) of the residue (≈10 mg).

trans-2-Cyclohexyl-5-methyltetrahydrofuran 16

The (*RS*,*SR*)-alcohol **7** (300 mg, 1 mmol) was hydrogenated over palladium on charcoal (5%, 40 mg) in methanol (4 cm^3) for 20 h. The mixture was filtered through Celite, washing with methanol, evaporated and flash chromatographed (Merck SiO$_2$ 9385, hexane–EtOAc, 19 : 1), giving the (*SR*,*SR*)-*alcohol* (120 mg) R_f (hexane–EtOAc, 19 : 1) 0.23; contaminated with 1-cyclohexylpentanol, identified by comparison with an authentic sample; R_f (hexane–EtOAc, 9 : 1) 0.21; ν_{max}(film)/cm^{-1} 3350, 2920, 2860 (CH) and 1450 (CH$_2$); δ_H(CDCl$_3$; 250 MHz) 3.34 (1 H, m, CHOH), 1.87–0.81 (18 H, m, CH$_2$, cyclohexyl CH and OH) and 0.89 (3 H, t, J 7, CH$_3$); m/z 169 (1%, M − H), 152 (6,

M − H$_2$O), 113 (44, M − C$_4$H$_9$), 95 (96, M − C$_4$H$_9$ − H$_2$O), 87 (63, M − C$_6$H$_{11}$) and 69 (100, M − C$_6$H$_{11}$ − H$_2$O) (Found: M − H, 169.1583. C$_{11}$H$_{22}$O requires M − H, 169.1592). n-Butyllithium (1.5 mol dm^{-3} in hexane, 0.3 cm^3) was added dropwise to the alcohol (120 mg) in diethyl ether (3 cm^3) at room temperature and stirred for 5 min, and the mixture was then stirred with toluene-p-sulfonyl chloride (0.15 g, 0.8 mmol) in diethyl ether (3 cm^3) for 3 h. DMAP (70 mg, 0.6 mmol) in THF (1 cm^3) was added dropwise, the mixture stirred, filtered though Celite, washing with diethyl ether, evaporated and the residue triturated with diethyl ether. The supernatant was filtered through a plug of silica, washing with diethyl ether, evaporated and flash chromatographed, giving the *tosylate* **14** (27 mg). Mercury(II) acetate (96 mg, 0.30 mmol) was added to the tosylate (68 mg, 0.15 mmol) in peracetic acid (30% in AcOH, 1 cm^3) and stirred at room temperature for 3 h. Diethyl ether (20 cm^3) was added and the mixture washed with aqueous sodium thiosulfate (1 mol dm^{-3}, 10 cm^3), water (10 cm^3), aqueous sodium hydrogen carbonate (saturated, 10 cm^3), dried (K$_2$CO$_3$), and evaporated. NMR Analysis of the residue showed that it consisted of a mixture of 1-cyclohexylpentyl toluene-p-sulfonate, the unreacted tosylate **14** and *trans*-2-cyclohexyl-5-methyltetrahydrofuran[11] **16** in the approximate molar ratio 5:4:12, respectively. Analysis (GC) showed the *cis*- and *trans*-tetrahydrofurans in the ratio 1:11, respectively.

cis-2-Cyclohexyl-5-methyltetrahydrofuran 17
The (*SR*,*SR*)-alcohol **9** (645.5 mg, 2.14 mmol) in methanol (6 cm^3) was hydrogenated similarly to give the saturated (*RS*,*SR*)-alcohol (108.9 mg); R_f (hexane–EtOAc, 19:1) 0.23; again contaminated with 1-cyclohexylpentanol. The toluene-p-sulfonate (35.5 mg), contaminated with the same by-product, was prepared similarly from the saturated alcohol (91.6 mg). The tosylate (72 mg, 0.16 mmol) and mercury(II) acetate (76 mg, 0.24 mmol) in peracetic acid (1.1 cm^3 of a 30% solution in glacial acetic acid) similarly gave a residue (50 mg), which consisted (^{1}H NMR) of the tosylate of the by-product, the unreacted tosylate of **9** and *cis*-2-cyclohexyl-5-methyl-tetrahydrofuran[11] in the approximate molar ratio 2:1:2, respectively. Analysis (GC) showed the *cis*- and *trans*-tetra-hydrofurans in the ration 4.9:1, respectively.

1-Cyclohexylvinyl trimethylsilyl ether
Following Paterson,[36] n-butyllithium (1.5 mol dm^{-3} in hexane, 30 cm^3) was added to diisopropylamine in THF (120 cm^3) at −78 °C under nitrogen. Cyclohexyl methyl ketone (5.42 g, 43 mmol) in THF (5 cm^3) was added dropwise to lithium diisopropylamide (52 mmol) over 10 min and stirred for 1 h. Chlorotrimethylsilane (9.3 cm^3, 73 mmol) was added dropwise over 5 min and the solution allowed to warm to room temperature over 1 h. Solvent was evaporated and pentane (50 cm^3) added. The solution was filtered, evaporated and the residue distilled under reduced pressure, giving the silyl enol ether[37] (6.11 g, 72%), bp 93–98 °C at 0.2 mmHg; v_{max}(film)/cm^{-1} 3120, 2930, 2860 (CH), 1620 (C=C) and 1250 (SiMe); δ_H(CDCl$_3$; 250 MHz) 3.99 (1 H, d, J 0.8, C=CH$_A$H$_B$), 3.96 (1 H, d, J 0.8, C=CH$_A$H$_B$), 1.83–1.70 (6 H, m, CH), 1.48–1.11 (5 H, m, CH) and 0.18 (9 H, m, SiMe$_3$); m/z 198 (11%, M$^+$), 183 (15, M − Me), 83 (25, C$_6$H$_{11}$) and 73 (100, SiMe$_3$) (Found: M$^+$, 198.1426. C$_{11}$H$_{22}$OSi requires M, 198.1442).

1-Cyclohexylpentane-1,4-dione
Following Yoshikoshi,[38] tin tetrachloride (3.45 cm^3, 30 mmol), 2-nitropropene (3.0 cm^3, 34.5 mmol) and the silyl enol ether (5.94 g, 30 mmol) were stirred in dichloromethane (75 cm^3) at −78 °C under nitrogen for 20 min and allowed to warm to 10 °C over 3 h. Water (42 cm^3) was added, stirring vigorously at reflux for 2 h, and the mixture cooled. The aqueous layer was extracted with dichloromethane (15 cm^3) and the combined organic layers washed with water (2 × 25 cm^3), brine (25 cm^3),

dried (MgSO$_4$), and evaporated and the residue distilled under reduced pressure, to give the diketone[39] (3.21 g, 59%), bp 93–94 °C at 1.3 mmHg; R_f (hexane–EtOAc, 6:1) 0.15; v_{max}(film)/cm^{-1} 2920, 2860 (CH) and 1700 (C=O); δ_H(CDCl$_3$; 250 MHz) 6.49 (4 H, s, COCH$_2$CH$_2$CO), 2.35 [1 H, tt, J 3.4 and 11.4, (CH$_2$)$_2$CHCO], 2.15 (3 H, s, MeCO), 1.91–1.57 (5 H, m, CH equatorial) and 1.41–1.11 (5 H, m, CH axial); m/z 182 (8%, M$^+$), 139 (4, M − MeCO), 111 (10, c-C$_6$H$_{11}$CO), 99 (100, M − C$_6$H$_{11}$), 83 (65, C$_6$H$_{11}$) and 71 (10, MeCOCH$_2$CH$_2$) (Found: M$^+$, 182.1320. C$_{11}$H$_{18}$O$_2$ requires M, 182.1307).

2-Cyclohexyl-5-methylfuran 18
Toluene-p-sulfonic acid (70 mg) and 1-cyclohexylpentane-1,4-dione (0.64 g, 3.5 mmol) were refluxed in benzene (100 cm^3) with a Soxhlet extractor containing molecular sieves (4 Å) for 1 h. The solvent was evaporated and the residue was dissolved in diethyl ether (50 cm^3), washed with aqueous sodium hydrogen carbonate (saturated, 20 cm^3), dried (K$_2$CO$_3$), filtered through silica and evaporated, giving the furan[13] (0.53 g, 91%); R_f (hexane–EtOAc, 6:1) 0.67; t_R (GC) 17.54 min; v_{max}(film)/cm^{-1} 3120, 2940, 2860 (CH), 1620 and 1570 (furan); δ_H(CDCl$_3$; 250 MHz) 5.83 (1 H, dd, J 1.0 and 3.1, furan 3-H), 5.80 (1 H, d, J 3.1, furan 4-H), 2.5 [1 H, m, ArCH(CH$_2$)$_2$], 2.24 (3 H, d, J 0.5, CH$_3$), 2.02–1.82 [2 H, m, ArCH(CH$_A$H$_B$)$_2$], 1.78–1.58 (3 H, m, equatorial CH) and 1.43–1.17 [5 H, m, axial CH and ArCH(CH$_A$H$_B$)$_2$]; m/z 164 (56%, M$^+$) and 121 (100, M − MeCO) (Found: M$^+$, 164.1212. C$_{11}$H$_{14}$O requires M, 164.1201).

Authentic sample of cis-2-cyclohexyl-5-methyltetrahydrofuran 17
Following le Noble,[12] Raney nickel (2 g) was washed with iso-propanol (3 × 5 cm^3) and slurried in isopropanol (5 cm^3) at room temperature under nitrogen. The furan **18** (0.5 g, 3 mmol) in isopropanol (10 cm^3) was added, stirred for 15 h, the mixture filtered through Celite, evaporated and analysed by ^{1}H NMR spectroscopy. The reaction was 60% complete so the procedure was repeated for a further 19 h and worked up as before, giving the *cis*-tetrahydrofuran[11] **17** (120 mg, 24%); v_{max}(film)/cm^{-1} 2970, 2920 and 2860 (CH); δ_H(CDCl$_3$; 250 MHz) 3.91 (1 H, sextet, J 6.2, OCHMe), 3.49 (1 H, q, J 7.1, OCHC$_6$H$_{11}$), 1.95–0.72 (15 H, m, CH$_2$) and 1.19 (3 H, d, J 6.1, OCHMe); m/z 168 (2%, M$^+$), 167 (23, M − H), 149 (20, M − H − H$_2$O) and 55 (100, C$_4$H$_7$) (Found: M − H, 167.1436. C$_{11}$H$_{20}$O requires M − H, 167.1436). GC Analysis gave peaks at t_R 17.1 (**17**, 94.0%), 17.5 (**18**, 2.4%) and 18.0 min (**16**, 3.6%).

2-{2-[Dimethyl(phenyl)silylmethyl]phenyl}-4,4-dimethyl-oxazoline †
Following Ito[40] and Meyers,[41] n-butyllithium (1.5 mol dm^{-3} in hexane, 18.5 cm^3) was added dropwise under nitrogen at 0 °C to a solution of 2-(2-methylphenyl)-4,4-dimethyloxazoline[42] **36** (4.74 g, 25.1 mmol) in diethyl ether (100 cm^3) and stirred for 30 min. Chlorodimethyl(phenyl)silane (5.55 g, 30 mmol) was added dropwise and the mixture was stirred for 2 h and then allowed to warm to room temperature. The solution was washed with water (2 × 100 cm^3), brine (100 cm^3), dried (K$_2$CO$_3$), evaporated and distilled to give the *oxazoline* (6.55 g, 81%), bp 148–160 °C at 0.4 mmHg; R_f (hexane–EtOAc, 9:1) 0.27; v_{max}(film)/cm^{-1} 3050, 3010, 2960, 2880 (CH), 1630 (C=N), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.76 (1 H, dd, J 1.5 and 7.8, ArH o- to C=N), 7.52–7.47 (2 H, m, SiPh), 7.36–7.32 (3 H, m, SiPh), 7.23 (1 H, dt, J 1.5 and 7.5, ArH p- to C=N), 7.10 (1 H, dt, J 1.3 and 7.5, ArH p- to CH$_2$Si), 6.96 (1 H, dd, J 1.1 and 7.7, ArH o- to CH$_2$Si), 3.97 (2 H, s, CH$_2$O), 2.98 (2 H, s, ArCH$_2$Si), 1.43 (6 H, s, CMe$_2$) and 0.20 (6 H, s, SiMe$_2$); m/z 323 (10%, M$^+$), 322 (10, M − H), 308 (30, M − Me), 246 (10, M − Ph) and 135 (100, PhMe$_2$Si) (Found: M$^+$, 323.1709. C$_{20}$H$_{25}$NOSi requires M, 323.1705).

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† The correct IUPAC name for oxazoline is 4,5-dihydrooxazole.

2-{2-[1-Dimethyl(phenyl)silylethyl]phenyl}-4,4-dimethyl-oxazoline 37a

n-Butyllithium (1.5 mol dm^{-3} in hexane, 0.45 cm^3) was added dropwise under nitrogen at 0 °C to the oxazoline (210 mg, 0.65 mmol) in diethyl ether (5 cm^3) and stirred for 1 h. Methyl iodide (98 mg, 0.69 mmol) was then added and the mixture stirred for 1 h. A similar work-up and flash chromatography (Merck SiO$_2$ 9385, hexane–EtOAc, 19:1) gave the *oxazoline* (180 mg, 86%); R_f (hexane–EtOAc, 9:1) 0.27; ν_{max}(film)/cm^{-1} 3060, 3040, 3010, 2960, 2920, 2880, 2860 (CH), 1630 (C=N), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.80 (1 H, dd, *J* 1.4 and 7.8, Ar*H o*- to C=N), 7.76–7.71 (2 H, m, SiPh), 7.55–7.30 (4 H, m, SiPh and Ar*H p*- to C=N), 7.23–7.09 (2 H, m, Ar*H o*- and *p*- to MeCHSi), 4.02 (1 H, d, *J* 8.0, C*H*$_A$H$_B$), 4.01 (1 H, d, *J* 8.0, CH$_A$*H*$_B$), 3.95 (1 H, q, *J* 7.4, C*H*Me), 1.41 (3 H, s, C*Me*$_A$Me$_B$), 1.39 (3 H, s, CMe$_A$*Me*$_B$), 1.34 (3 H, d, *J* 7.4, CH*Me*), 0.25 (3 H, s, Si*Me*$_A$Me$_B$) and 0.16 (3 H, s, SiMe$_A$*Me*$_B$); *m/z* 337 (10%, M$^+$), 336 (10, M − H), 322 (5, M − Me) and 135 (100, PhMe$_2$Si) (Found: M$^+$, 337.1846. C$_{21}$H$_{27}$NOSi requires *M*, 337.1862).

2-[2-(1-Trimethylsilylethyl)phenyl]-4,4-dimethyloxazoline 37b

2-[2-(Trimethylsilylmethyl)phenyl]-4,4-dimethyloxazoline[40] (6.25 g, 24 mmol) was methylated similarly to give the *oxazoline* **37b**; R_f (hexane–EtOAc, 9:1) 0.34; ν_{max}(film)/cm^{-1} 3070, 2960, 2900 (CH), 1640 (C=N) and 1240 (SiMe); δ_H(CDCl$_3$; 250 MHz) 7.64 (1 H, dd, *J* 1.4 and 7.8, Ar*H o*- to C=N), 7.32 (1 H, dt, *J* 1.4 and 7.5, Ar*H p*- to C=N), 7.16 (1 H, dd, *J* 1.1 and 7.9, Ar*H o*- to CHSi), 7.07 (1 H, dt, *J* 1.1 and 7.5, Ar*H p*- to CHSi), 4.02 (2 H, s, CH$_2$), 3.50 (1 H, q, *J* 7.4, C*H*Me), 1.36 (3 H, d, *J* CH*Me*), 1.37 (3 H, s, C*Me*$_A$Me$_B$), 1.36 (3 H, s, CMe$_A$*Me*$_B$) and −0.10 (SiMe$_3$); *m/z* 275 (9%, M$^+$), 274 (15, M − H), 260 (17, M − Me) and 73 (100, SiMe$_3$) (Found: M$^+$, 275.1688. C$_{16}$H$_{25}$NOSi requires *M*, 275.1705).

1-{2-[1-Dimethyl(phenyl)silylethyl]phenyl}ethan-1-one 38

Following Ito,[40] the oxazoline (1.72 g, 5.1 mmol) and methyl iodide (0.5 cm^3) were refluxed in nitromethane (2 cm^3) for 20.5 h. The solvent and excess methyl iodide were removed under reduced pressure heating to 70 °C. Methylmagnesium iodide (2.47 mol dm^{-3} in Et$_2$O, 2.9 cm^3) was added to the residue in THF (50 cm^3) and stirred for 15 min. Water (30 cm^3) was added, and the mixture extracted with diethyl ether (2 × 30 cm^3). The aqueous layer was diluted with water (120 cm^3) and extracted with diethyl ether (90 cm^3). The combined extracts were washed with water (60 cm^3), brine (60 cm^3), dried (K$_2$CO$_3$), and evaporated to give the crude aminal (1.22 g, 64%), which was stirred in ethanol (10 cm^3) with aqueous hydrochloric acid (3 mol dm^{-3}, 2 cm^3) for 1.5 h and then diluted with water (25 cm^3). The mixture was extracted with diethyl ether (3 × 25 cm^3) and the combined extracts washed with water (25 cm^3), brine (25 cm^3), dried (K$_2$CO$_3$), evaporated and flash chromatographed (SiO$_2$ Merck 9385, hexane–EtOAc, 19:1) to give unreacted aminal (0.54 g, 44%), R_f (SiO$_2$, hexane–EtOAc, 19:1) 0.52; and the *ketone* (0.3 g, 32%); R_f (SiO$_2$ hexane–EtOAc, 19:1) 0.26; ν_{max}(film)/cm^{-1} 3060, 2960, 2880 (CH), 1680 (C=O), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$, 250 MHz) 7.53 (1 H, dd, *J* 1.5, and 8.0, Ar*H o*- to COMe), 7.39 (6 H, m, SiPh and Ar*H p*- to COMe), 7.16–7.09 (2 H, m, Ar*H m*- to COMe), 3.59 (1 H, q, *J* 7.3, C*H*Me), 2.31 (3 H, s, COMe), 1.32 (3 H, d, *J* 7.3, CH*Me*), 0.23 (3 H, s, Si*Me*$_A$Me$_B$) and 0.14 (3 H, s, SiMe$_A$*Me*$_B$); *m/z* 282 (10%, *M*$^+$), 267 (30, *M* − Me), 163 (60, C$_{10}$H$_{15}$Si), and 135 (100, PhMe$_2$Si) (Found: M$^+$, 282.1460. C$_{18}$H$_{22}$OSi requires *M*, 282.1439). Hydrolysis of the recovered aminal was repeated, giving more of the ketone (0.34 g, total yield 44%).

2-[1-Dimethyl(phenyl)silylethyl]benzaldehyde 39a

The oxazoline (7.17 g, 20.2 mmol) and methyl iodide (3.8 cm^3) were again refluxed in acetonitrile (30 cm^3) for 72 h. Most of the solvent and excess reagent were evaporated off under reduced pressure to leave the oxazolinium salt. Following Nordin,[43]

sodium borohydride (1.52 g, 40 mmol) was stirred with the salt in ethanol (100 cm^3) for 18 h at room temperature. Aqueous hydrochloric acid (3 mol dm^{-3}, 4 cm^3) was added until the mixture was neutral (indicator paper) and water (100 cm^3) was added. The mixture was extracted with diethyl ether (2 × 100 cm^3) and the combined extracts washed with water (2 × 100 cm^3), brine (100 cm^3), dried (K$_2$CO$_3$), and evaporated. Analysis (^{1}H NMR spectroscopy) of the residue showed incomplete hydrolysis, so aqueous hydrochloric acid (3 mol dm^{-3}, 8 cm^3) was added to a solution of the oil in ethanol (20 cm^3), and the mixture stirred for 3.5 h. The same work-up then gave the *aldehyde* (2.27 g, 42%); R_f (hexane–EtOAc, 20:1) 0.24; ν_{max}(film)/cm^{-1} 3060, 2950, 2860 (CH), 2720 (aldehyde CH), 1690 (C=O), 1600, 1570 (aromatic), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 10.06 (1 H, s, CHO), 7.71 (1 H, dd, *J* 1.5 and 7.7, Ar*H o*- to CHO), 7.48 (1 H, dt, *J* 1.5 and 7.6, Ar*H p*- to CHO), 7.42–7.30 (5 H, m, SiPh), 7.27 (1 H, t, *J* 7.5, Ar*H p*- to MeCH-Si), 7.17 (1 H, d, *J* 7.9, Ar*H o*- to CHSi), 3.92 (1 H, q, *J* 7.3, C*H*Me), 1.4 (3 H, d, *J* 7.3, CH*Me*), 0.29 (3 H, s, Si*Me*$_A$Me$_B$) and 0.21 (3 H, s, SiMe$_A$*Me*$_B$); *m/z* 286 (1%, M + H$_2$O), 271 (6, M + H$_2$O − Me), 268 (15, M$^+$), 253 (1, M − Me), 163 (25, C$_{10}$H$_{15}$Si) and 135 (100, PhMe$_2$Si) (Found: M$^+$, 268.1265. C$_{17}$H$_{20}$OSi requires *M*, 268.1283).

2-[2-(1-Trimethylsilylethyl)phenyl]-3,4,4-trimethyloxazolinium iodide

The oxazoline **37b** and methyl iodide (4.5 cm^3, 72 mmol) were similarly refluxed in acetonitrile (30 cm^3) for 4 h, kept at room temperature for 18 h, and refluxed again for 5 h, when TLC analysis showed no remaining starting material. Work-up gave the *oxazolinium salt* (4.49 g, 47%) as a pale lemon-yellow powder, mp 150 °C (decomp.); ν_{max}(Nujol)cm^{-1} 2990, 2940, 2860 (CH), 1650 (C=N$^+$) and 1250 (SiMe); δ_H(CDCl$_3$; 250 MHz) 8.19 (1 H, d, *J* 8, Ar*H o*- to C=N$^+$), 7.58 (1 H, t, *J* 8, Ar*H p*- to C=N$^+$), 7.34 (1 H, t, *J* 8, Ar*H p*- to CSi), 7.26 (1 H, d, *J* 8, Ar*H o*- to CSi), 5.35 (1 H, d, *J* 9.4, C*H*$_A$H$_B$), 5.06 (1 H, d, *J* 9.4, CH$_A$*H*$_B$), 3.32 (3 H, s, MeN$^+$), 1.92 (3 H, s, C*Me*$_A$Me$_B$), 1.88 (1 H, q, *J* 7.3, C*H*Me), 1.80 (3 H, s, CMe$_A$*Me*$_B$), 1.43 (3 H, d, *J* 7.3, CH*Me*) and −0.08 (9 H, s, SiMe$_3$); *m/z* 417 (8%, M$^+$), 290 (11, M − I), 260 (6, M − I − 2 × Me), 234 (30, M − C$_4$H$_8$) and 73 (100, SiMe$_3$) (Found: M$^+$, 417.0967. C$_{17}$H$_{28}$INOSi requires *M*, 417.0985).

2-(1-Trimethylsilylethyl)benzaldehyde 39b

Sodium borohydride (0.78 g, 20.6 mmol) was stirred with the oxazolinium salt (4.29 g, 10.3 mmol) in ethanol (50 cm^3) at room temperature for 5 h. A similar work-up to that used for the aldehyde **39a** gave the *aldehyde* (0.97 g, 46% from the salt); R_f (hexane–EtOAc, 19:1) 0.39; ν_{max}(film)/cm^{-1} 3080, 2970, 2880 (CH), 2740 (OC–H), 1690 (C=O), 1600, 1570 (aromatic) and 1250 (SiMe); δ_H(CDCl$_3$; 250 MHz) 10.22 (1 H, s, CHO), 7.74 (1 H, dd, *J* 1.6 and 8.0, Ar*H o*- to CHO), 7.49 (1 H, dt, *J* 1.5 and 8.0, Ar*H p*- to CHO), 7.27–7.20 (2 H, m, Ar*H m*- to CHO), 3.63 (1 H, q, *J* 7.4, C*H*Me), 1.40 (3 H, d, *J* 7.4, CH*Me*) and −0.08 (9 H, s, SiMe$_3$); *m/z* 206 (32%, M$^+$), 191 (18, M − Me) and 73 (100, SiMe$_3$) (Found: M$^+$, 206.1118. C$_{12}$H$_{18}$OSi requires *M*, 206.1127).

(1*RS*)-1-{2-(1*SR*)-1-Dimethyl(phenyl)silylethyl]phenyl}ethanol 40a and (1*RS*)-1-{2-[(1*RS*)-1-dimethyl(phenyl)silylethyl]-phenyl}ethanol 41a

Method A. Methylmagnesium iodide (2.47 mol dm^{-3} in Et$_2$O, 0.76 cm^3) was added dropwise to the aldehyde **39a** (485 mg, 1.81 mmol) in diethyl ether (20 cm^3) at 0 °C under nitrogen and stirred for 3 min. Aqueous ammonium chloride (3 mol dm^{-3}, 5 cm^3) and water (5 cm^3) were added and the organic layer was separated. The aqueous layer was extracted with diethyl ether (20 cm^3) and the combined organic layers washed with water (20 cm^3), brine (20 cm^3), dried (K$_2$CO$_3$) and evaporated. The residue was flash chromatographed (Merck SiO$_2$ 9385, hexane–

EtOAc, 19:1) giving the faster eluting (RS,SR)-*alcohol* **40a** (350 mg, 68%); R_f (hexane–EtOAc, 9:1) 0.16; ν_{max}(film)/cm[1] 3560, 3420 (OH), 3060, 3020, 2960, 2860 (CH), 1600, 1580 (aromatic), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.41–7.06 (9 H, m, Ar*H*), 4.62 (1 H, q, *J* 6.4, MeC*H*OH), 2.55 (1 H, q, *J* 7.4, MeC*H*Si), 1.44 (3 H, d, *J* 7.4, *Me*CHSi), 1.26 (3 H, d, *J* 6.4, *Me*CHOH), 0.44 (3 H, s, Si*Me*$_A$Me$_B$) and 0.24 (3 H, s, Si*Me*$_A$*Me*$_B$); *m/z* 269 (0.13%, M − Me), 267 (0.3, M − OH), 251 (0.4, M − Me − H$_2$O), 135 (70, PhMe$_2$Si), 132 (100, C$_{10}$H$_{12}$) and 117 (80, C$_9$H$_9^+$) (Found: M − Me, 269.1376. C$_{18}$H$_{24}$OSi requires *M* − Me, 269.1362) and the slower eluting (RS,RS)-*alcohol* **41a** (17.7 mg, 3.4%); R_f (hexane–EtOAc, 9:1) 0.09; ν_{max}(film)/cm^{-1} 3560, 3420 (OH), 3060, 3020, 2960, 2860 (CH), 1600, 1580 (aromatic), 1240 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.37–7.05 (9 H, m, Ar*H*), 4.88 (1 H, q, *J* 6.5, MeC*H*OH), 2.84 (1 H, q, *J* 7.4, MeC*H*Si), 1.39 (3 H, d, *J* 7.5, *Me*CHSi), 1.24 (3 H, d, *J* 6.5, *Me*CHOH), 0.34 (3 H, s, Si*Me*$_A$Me$_B$) and 0.21 (3 H, s, Si*Me*$_A$*Me*$_B$); *m/z* 269 (0.1%, M − Me), 267 (1.8, M − OH), 251 (0.5, M − Me − H$_2$O), 135 (70, PhMe$_2$Si), 132 (100, C$_{10}$H$_{12}$) and 117 (70, C$_9$H$_9$) (Found: M − OH, 267.1553. C$_{18}$H$_{24}$OSi requires *M* − OH, 267.1569).

Method B. Sodium borohydride (0.07 g, 2 mmol) was stirred with the ketone (0.23 g, 0.82 mmol) in ethanol (5 cm^3) at room temperature for 17 h. Aqueous hydrochloric acid (1.1 mol dm^{-3}, 1 cm^3) was added until neutral, water (10 cm^3) was added and the mixture extracted with diethyl ether (3 × 10 cm^3). The extracts were washed with water (10 cm^3), brine (10 cm^3), dried (K$_2$CO$_3$), and evaporated. The diastereoisomeric alcohols **40a** (130 mg, 56%) and **41a** (90 mg, 39%) were isolated by flash chromatography as above. A similar reduction using sodium bis(2-methoxyethoxy)aluminium hydride (Red-Al) in diethyl ether at 0 °C for 10 min gave the alcohols **40a** (177 mg, 53%) and **41a** (137 mg, 41%).

1-[2-(1-Trimethylsilylethyl)phenyl]ethanol 40b

Methylmagnesium iodide (2.4 mol dm^{-3} in Et$_2$O, 2 cm^3) and the aldehyde **39b** (0.94 g, 4.56 mmol) were stirred in diethyl ether (50 cm^3) for 3 min. A similar work-up to that used for the alcohols **40a** gave a mixture of diastereoisomers rich (10:1, ^{1}H NMR spectroscopy) in the isomer **40b** (0.93 g, 93%); R_f (hexane–EtOAc, 19:1) 0.05; ν_{max}(film)/cm^{-1} 3400 (br OH), 3060, 3030, 2960, 2940, 2900, 2870 (CH), 1600, 1580 (aromatic) and 1250 (SiMe); δ_H(CDCl$_3$; 250 MHz) 7.52 (1 H, dd, *J* 1.7 and 7.4, Ar*H o*- to CHOH), 7.26–7.03 (3 H, m, Ar*H m*- and *p*- to CHOH), 5.15 (1 H, q, *J* 6.3, MeC*H*OH), 2.36 (1 H, q, *J* 7.4, MeC*H*Si), 1.7 (1 H, br s, OH), 1.42 (3 H, d, *J* 6.3, *Me*CHOH), 1.35 (3 H, d, *J* 7.4, *Me*CHSi) and −0.03 (9 H, s, SiMe$_3$); *m/z* 205 (4%, M − OH), 204 (4, M − H$_2$O), 189 (5, M − H$_2$O − Me), 132 (50, C$_{10}$H$_{12}$), 117 (70, C$_9$H$_9$) and 73 (100, SiMe$_3$) (Found: M − H$_2$O, 204.1343. C$_{13}$H$_{22}$OSi requires *M* − H$_2$O, 204.1334). The minor diastereoisomer **41b** had signals at δ_H(CDCl$_3$; 250 MHz) 7.44 (1 H, dd, *J* 2.1 and 8.4, Ar*H o*- to CHOH), 7.22–7.08 (3 H, m, Ar*H m*- and *p*- to CHOH), 5.14 (1 H, q, *J* 6.4, MeC*H*OH), 2.59 (1 H, q, *J* 7.4, MeC*H*Si), 1.9 (1 H, br s, CHO*H*), 1.51 (3 H, d, *J* 6.4, *Me*CHOH), 1.37 (3 H, d, *J* 7.4, *Me*CHSi) and −0.02 (9 H, s, SiMe$_3$).

(1*RS*)-1-{(1*SR*)-2-[1-Dimethyl(phenyl)silylethyl]phenyl}ethyl formate 46b

Following Höfle and Steglich,[32] DMAP (6 mg), formic acetic anhydride[44] (0.1 cm^3) and triethylamine (0.1 cm^3) were added sequentially to a solution of the alcohol **40a** (128 mg, 0.45 mmol) in diethyl ether (5 cm^3) at 0 °C under nitrogen and the reaction followed by TLC. After 15 min, the solvent was removed under reduced pressure and the residue was flash chromatographed (Merck SiO$_2$ 9385, hexane–EtOAc, 19:1) to give the *ester* (122 mg, 87%); R_f (hexane–EtOAc, 19:1) 0.41; ν_{max}(film)/cm^{-1} 3070, 3030, 2960, 2930, 2870 (CH), 1720 (C=O), 1600 (aromatic), 1250 (SiMe), 1180 (formate C−O) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.93 (1 H, s, OCHO), 7.43–7.27

(6 H, m, Ar*H*), 7.24–7.11 (2 H, m, Ar*H*), 6.99 (1 H, m, Ar*H*), 6.13 (1 H, q, *J* 6.4, MeC*H*O), 2.52 (1 H, q, *J* 7.4, MeC*H*Si), 1.47 (3 H, d, *J* 6.4, *Me*CHO), 1.36 (3 H, d, *J* 7.4, *Me*CHSi) 0.32 (3 H, s, Si*Me*$_A$Me$_B$) and 0.21 (3 H, s, Si*Me*$_A$*Me*$_B$); *m/z* 268 (0.6%, M − CO$_2$), 267 (1.0 M − HCO$_2$), 266 (1.8, M − HCO$_2$H), 251 (1.2, M − HCO$_2$H − Me), 135 (60, PhMe$_2$Si), 132 (100, C$_{10}$H$_{12}$) and 117 (55, C$_9$H$_9$) (Found: M − HCO$_2$H, 266.1481. C$_{19}$H$_{24}$-O$_2$Si requires *M* − HCO$_2$H, 266.1491).

(1*RS*)-1-{2-[(1*SR*)-1-Trimethylsilylethyl]phenyl}ethyl formate

The alcohol **40b** (10:1 diastereoisomeric mixture) (0.11 g, 0.5 mmol) similarly gave the *formate* (0.11 g, 89%); as a 10:1 mixture of diastereoisomers; R_f (hexane–EtOAc, 9:1) 0.49; ν_{max}(film)/cm^{-1} 3060, 3030, 2960, 2880 (CH), 1720 (C=O), 1600 (aromatic), 1250 (SiMe) and 1170 (formate C−O); δ_H(CDCl$_3$; 250 MHz) 8.11 (1 H, s, OCHO), 7.43 (1 H, dd, *J* 1.5 and 7.6, Ar*H o*- to MeCHOCHO), 7.26–7.05 (3 H, m, Ar*H m*- and *p*- to MeCHOCHO), 6.28 (1 H, q, *J* 6.4, MeC*H*OCHO), 2.33 (1 H, q, *J* 7.4, SiC*H*Me), 1.50 (3 H, d, *J* 6.4, *Me*CHOCHO), 1.35 (3 H, d, *J* 7.4, SiCH*Me*) and −0.04 (9 H, s, SiMe$_3$); *m/z* 250 (0.6%, M$^+$), 206 (0.4, M − CO$_2$), 205 (1, M − HCO$_2$), 204 (0.6, M − HCO$_2$H), 189 (7, M − HCO$_2$H − Me), 132 (100, C$_{10}$H$_{12}$), 117 (80, C$_9$H$_9$) and 73 (60, SiMe$_3$) (Found: M$^+$, 250.1394. C$_{14}$H$_{22}$O$_2$Si requires *M*, 250.1389).

(1*RS*)-1-{(1*RS*)-2-[1-Dimethyl(phenyl)silylethyl]phenyl}ethyl formate 47b

Following Bose,[45] triphenylphosphine (186 mg, 0.71 mmol), formic acid (33 mg, 0.71 mmol), the alcohol **40a** (100 mg, 0.352 mmol) and diethyl azodicarboxylate (DEAD) (124 mg, 0.71 mmol) were stirred in THF at room temperature under nitrogen for 21 h. The solvent was evaporated off without heating, and the residue flash chromatographed (Merck SiO$_2$ 9385, hexane–EtOAc, 19:1), giving 2-[1-*dimethyl*(*phenyl*)*silylethyl*]*styrene* **42** (14 mg, 15%); R_f (hexane–EtOAc, 9:1) 0.61; ν_{max}(CDCl$_3$)/cm^{-1} 3080, 3060, 3020, 2960, 2940, 2880 (CH), 1620 (C=C), 1600 (aromatic), 1250 (SiMe) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.42–7.26 (6 H, m, SiPh and Ar*H o*- to C=C), 7.17 (1 H, dt, *J* 1.6 and 7.5, Ar*H p*- to C=C), 7.07 (1 H, dt, *J* 1.3 and 7.3, Ar*H p*- to MeCHSi), 6.95 (1 H, dd, *J* 1.4 and 7.5, Ar*H o*- to MeCHSi), 6.88 (1 H, dd, *J* 10.9 and 17.3, ArC*H*=CH$_2$), 5.46 (1 H, dd, *J* 1.6 and 17.3, ArCH=C*H*$_A$H$_B$ *trans*- to hydrogen), 5.17 (1 H, dd, *J* 1.6 and 10.9, ArCH=CH$_A$*H*$_B$ *cis* to hydrogen), 2.74 (1 H, q, *J* 7.4, C*H*Me), 1.32 (3 H, d, *J* 7.4, CH*Me*), 0.25 (3 H, s, Si*Me*$_A$Me$_B$) and 0.16 (3 H, s, Si*Me*$_A$*Me*$_B$); *m/z* 266 (5%, M$^+$), 251 (0.1, M − Me) and 135 (100, PhMe$_2$Si) (Found: M$^+$, 266.1502. C$_{18}$H$_{22}$Si requires *M*, 266.1490) and the *ester* **47b** (91 mg, 83%); R_f (hexane–EtOAc, 9:1) 0.37; ν_{max}(film)/cm^{-1} 3070, 3030, 2960, 2930, 2870 (CH), 1720 (C=O), 1600 (aromatic), 1250 (SiMe), 1180 (format C−O) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.97 (1 H, s, OCHO), 7.41–7.07 (9 H, m, Ar*H*), 6.11 (1 H, q, *J* 6.5, MeC*H*O), 2.76 (1 H, q, *J* 7.4, MeC*H*Si), 1.40 (3 H, d, *J* 7.4, *Me*CHSi), 1.21 (3 H, d, *J* 6.5, *Me*CHO), 0.37 (3 H, s, Si*Me*$_A$Me$_B$) and 0.24 (3 H, s, Si*Me*$_A$*Me*$_B$); *m/z* 268 (0.6%, M − CO$_2$), 2.67 (1.3, M − OCHO), 266 (1.4, M − HCO$_2$H), 251 (0.5, M − HCO$_2$H − Me), 135 (80, PhMe$_2$Si), 132 (100, C$_{10}$H$_{12}$) and 117 (60, C$_9$H$_9$) (Found: M − OCHO, 267.1553. C$_{19}$H$_{24}$O$_2$Si requires *M* − OCHO, 267.1569).

(1*RS*)-1-{2-[(1*RS*)-1-Trimethylsilylethyl]phenyl}ethyl formate

The alcohol **40b** (10:1 mixture) (0.20 g, 0.9 mmol) similarly gave 2-(1-*trimethylsilylethyl*)*styrene* (7 mg, 4%); R_f (hexane–EtOAc, 19:1) 0.63; ν_{max}(CDCl$_3$)/cm^{-1} 2960, 2940 (CH), 1620 (C=C) and 1250 (SiMe); δ_H(CDCl$_3$; 250 MHz) 7.41 (1 H, d, *J* 7.4, Ar*H o*- to C=C), 7.21 (1 H, t, *J* 8.1, Ar*H p*- to C=C), 7.10–7.04 (2 H, m, Ar*H m*- to C=C), 6.98 (1 H, dd, *J* 10.8 and 17.3, ArC*H*=CH$_2$), 5.54 (1 H, dd, *J* 1.6 and 17.3, ArCH=C*H*$_A$H$_B$ *trans* to hydrogen), 5.23 (1 H, dd, *J* 1.6 and 10.8, ArCH=CH$_A$*H*$_B$ *cis* to hydrogen), 2.54 (1 H, q, *J* 7.4, C*H*Me), 1.35 (3 H, d, *J* 7.4, CH*Me*) and −0.07 (9 H, s, SiMe$_3$); *m/z* 204 (15%, M$^+$), 189 (4,

M − Me) and 73 (100, SiMe$_3$) (Found: M$^+$, 204.1342. C$_{13}$H$_{20}$Si requires M, 204.1334), and the *ester* (168 mg, 75%) consisting of both diastereoisomers in a ratio of 1:3; R_f (hexane–EtOAc, 19:1) 0.29, (hexane–EtOAc, 9:1) 0.49; v_{max}(film)/cm^{-1} 3060, 3030, 2960, 2870 (CH), 1710 (C=O), 1600 (aromatic), 1250 (SiMe) and 1180 (formate C–O); δ_H(CDCl$_3$; 250 MHz) signals from the minor diastereoisomer (described above) were accompanied by those from the major diastereoisomer: 8.04 (1 H, s, OCHO), 7.43 (1 H, m, Ar*H o*- to COCHO), 7.25 (1 H, m, Ar*H p*- to COCHO), 7.17–7.10 (2 H, m, Ar*H m*- to COCHO), 6.30 (1 H, q, J 6.5, MeC*H*OCHO), 2.52 (1 H, q, J 7.4, SiC*H*Me), 1.59 (3 H, d, J 6.5, *Me*CHOCHO), 1.37 (3 H, d, J 7.4, *Me*CHSi) and −0.01 (9 H, SiMe$_3$); m/z 250 (0.3%, M$^+$), 205 (1, M − HCO$_2$), 189 (7, M − HCO$_2$H − Me), 132 (100, C$_{10}$H$_{12}$), 117 (97, C$_9$H$_9$) and 73 (94, SiMe$_3$) (Found: M$^+$, 250.1391. C$_{14}$H$_{22}$O$_2$Si requires M, 250.1389). Hydrolysis of this mixture gave a 1:3 mixture of the alcohols rich in **41b**.

(1*RS*)-1-{2-[(1*SR*)-1-Dimethyl(phenyl)silylethyl]phenyl}ethyl acetate 46a

Following Höfle and Steglich, as described above for the allylic acetates **26**–**31**, the faster eluting alcohol **40a** (55 mg, 0.19 mmol) gave the *ester* **46a** (60 mg, 96%); R_f (hexane–EtOAc, 9:1) 0.32; v_{max}(film)/cm^{-1} 3060, 3020, 2960, 2930, 2870 (CH), 1730 (C=O), 1600, 1580 (aromatic), 1250 (C–O) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.43–7.25 (6 H, m, Ar*H*), 7.20–7.09 (2 H, m, Ar*H*), 6.95 (1 H, m, Ar*H*), 6.05 (1 H, q, J 6.4, MeC*H*O), 2.54 (1 H, q, J 7.4, MeC*H*Si), 2.05 (3 H, s, MeCO), 1.41 (3 H, d, J 6.4, *Me*CHO), 1.32 (3 H, d, J 7.4, *Me*CHSi), 0.29 (3 H, s, Si*Me$_A$*Me$_B$) and 0.19 (3 H, s, SiMe$_A$*Me$_B$*); m/z 267 (0.6%, M − OAc), 266 (0.6, M − HOAc), 251 (0.4, M − HOAc − Me), 135 (40, PhMe$_2$Si), 132 (100, C$_{10}$H$_{12}$) and 117 (60, C$_9$H$_9$$^+$) (Found: M − AcOH, 266.1494. C$_{20}$H$_{26}$O$_2$Si requires M − AcOH, 266.1491).

(1*RS*)-1-{2-[(1*RS*)-1-Dimethyl(phenyl)silylethyl]phenyl}ethyl acetate 47a

Similarly the slower eluting alcohol **41a** gave the *ester* **47a** (87%); R_f (hexane–EtOAc, 9:1) 0.32; v_{max}(film)/cm^{-1} 3060, 3040, 2960, 2880 (CH), 1730 (C=O), 1600, 1580 (aromatic), 1250 (C–O) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.62–7.00 (9 H, m, Ar*H*), 5.99 (1 H, q, J 6.5, MeC*H*O), 2.74 (1 H, q, J 7.4, MeC*H*Si), 1.98 (3 H, s, MeCO), 1.38 (3 H, d, J 7.4, *Me*CHSi), 1.18 (3 H, d, J 6.5, *Me*CHO), 0.34 (3 H, s, Si*Me$_A$*Me$_B$) and 0.22 (3 H, s, SiMe$_A$*Me$_B$*); m/z 267 (0.8%, M − OAc), 266 (0.8, M − HOAc), 251 (0.4, M − HOAc − Me), 135 (60, PhMe$_2$Si), 132 (100, C$_{10}$H$_{12}$) and 117 (50, C$_9$H$_9$) (Found: M − AcOH, 266.1486. C$_{20}$H$_{26}$O$_2$Si requires M − AcOH, 266.1491).

1-[2-(1-Trimethylsilylethyl)phenyl]ethyl acetate

Similarly the 10:1 diastereoisomeric mixture of alcohols rich in **40b** (90 mg, 0.41 mmol) gave the *acetates* (91 mg, 85%); R_f (hexane–EtOAc, 9:1) 0.41; v_{max}(film)/cm^{-1} 3060, 3030, 2960, 2870 (CH), 1740 (C=O), 1600 (aromatic) and 1250 (C–O); δ_H(CDCl$_3$) 7.41 (1 H, dd, J 1.5 and 7.7, Ar*H o*- to CHOAc), 7.25–7.06 (3 H, m, Ar*H m*- and *p*- to CHOAc), 6.14 (1 H, q, J 6.4, MeC*H*OAc), 2.35 (1 H, q, J 7.4, MeC*H*Si), 2.09 (3 H, s, MeCO), 1.46 (3 H, d, J 6.4, *Me*CHOAc), 1.34 (3 H, d, J 7.4, *Me*CHSi) and −0.04 (9 H, s, SiMe$_3$); m/z 205 (0.5%, M − OAc), 204 (0.5, M − HOAc), 189 (2.5, M − HOAc − Me), 132 (78, C$_{10}$H$_{12}$), 117 (100, C$_9$H$_9$) and 73 (60, SiMe$_3$) (Found: M − OAc, 205.1397. C$_{15}$H$_{24}$O$_2$Si requires M − OAc, 205.1412).

(1*RS*)-1-{2-[(1*SR*)-1-Hydroxyethyl]phenyl}ethyl acetate

Mercuric acetate (613 mg, 1.93 mmol) and the ester **46a** (0.25 g, 0.77 mmol) were stirred in peracetic acid (32 wt% in AcOH, containing 1% sulfuric acid, 5 cm^3) at room temperature for 4 h. Diethyl ether (70 cm^3) and aqueous sodium thiosulfate (1 mol dm^{-3}, 25 cm^3) were added, and the aqueous layer discarded. The organic layer was washed with water (20 cm^3), aqueous

sodium hydrogen carbonate (saturated, 20 cm^3) and dried (MgSO$_4$), evaporated and flash chromatographed (Merck SiO$_2$, 9385, hexane–EtOAc, 19:1, then diethyl ether) to give the ester (40 mg, 16%) and the *alcohol* (37 mg, 23%); R_f (hexane–EtOAc, 4:1) 0.12; v_{max}(film)/cm^{-1} 3440 (br OH), 3060, 2970, 2920, 2850 (CH), 1730 (C=O) and 1250 (C–O); δ_H(CDCl$_3$; 250 MHz) 7.64 (1 H, m, Ar*H o*- to CHOAc), 7.48 (1 H, m, Ar*H o*- to CHOH), 7.42–7.24 (2 H, m, Ar*H p*- to CHOAc and *p*- to CHOH), 6.13 (1 H, q, J 6.6, MeC*H*OAc), 5.30 (1 H, q, J 6.5, MeC*H*OH), 3.3 (1 H, br s, OH), 2.02 (3 H, s, MeCO), 1.53 (3 H, d, J 6.6, *Me*CHOAc) and 1.51 (3 H, d, J 6.5, *Me*CHOH); m/z 191 (1%, M − OH), 190 (1, M − H$_2$O), 175 (1, M − H$_2$O − Me), 166 (0.02, M − H$_2$C=C=O), 163 (2, M − CO$_2$ − H), 148 (78, M − AcOH), 133 (100, M − AcOH − Me) and 105 (38, PhC=O$^+$) (Found: M − H$_2$C=C=O, 166.1010 and M − AcOH, 148.0877. C$_{12}$H$_{16}$O$_3$ requires M − H$_2$C=C=O, 166.0994 and M − AcOH, 148.0888).

(1*RS*)-1-{2-[(1*SR*)-1-Hydroxethyl]phenyl}ethanol 43

Sodium hydroxide (10 mol dm^{-3}, 1 cm^3) was stirred with the alcohol (37 mg, 0.18 mmol) in ethanol (2 cm^3) at room temperature for 5 min. Diethyl ether (15 cm^3) and water (5 cm^3) were added, the aqueous layer was extracted with diethyl ether (5 cm^3). The combined ethereal layers were dried (K$_2$CO$_3$) and evaporated. The residue was diluted with diethyl ether (20 cm^3), washed with water (2 × 5 cm^3), dried again (K$_2$CO$_3$) and evaporated, giving the diol as needles, mp 96–103 °C (from Et$_2$O) (lit.,^{46} 105 °C, compared with 74 °C for the diastereoisomer); v_{max}(CDCl$_3$)/cm^{-1} 3600, 3400 (OH), 3070, 2960, 2920, 2860 (CH), 1610 and 1580 (Ar); δ_H(CDCl$_3$; 250 MHz) 5.73–7.43 (2 H, m, Ar*H o*- to each CHOH), 7.36–7.24 (2 H, m, Ar*H p*- to each CHOH), 5.15 (2 H, q, J 6.3, 2 × MeC*H*OH), 1.50 (6 H, d, J 6.3, 2 × *Me*CHOH) and 1.25 (2 H, br s, 2 × OH); m/z 148 (39%, M − H$_2$O), 133 (100, M − H$_2$O − Me), 115 (7, M − Me − 2 × H$_2$O), 105 (31, PhC≡O$^+$) and 77 (19, Ph$^+$) (Found: M − H$_2$O, 148.0893. C$_{10}$H$_{14}$O$_2$ requires M − H$_2$O, 148.0845).

1-{2-[1-Dimethyl(phenyl)silylethyl]phenyl}ethyl methyl fumarate 50

Lithium hexamethyldisilazide (1 mol dm^{-3} in THF, 1.1 cm^3) was stirred with the alcohol **40a** (340 mg, 1 mmol) and dimethyl fumarate in THF (10 cm^3) at room temperature for 120 h. Work-up and chromatography (Merck SiO$_2$ 9385, hexane–EtOAc, 19:1) gave the starting alcohol (21%) dimethyl fumarate and the *ester* **50** (11.5 mg, 3%); R_f (hexane–EtOAc, 9:1) 0.17; v_{max}(film)/cm^{-1} 3070, 2960, 2940, 2860 (CH), 1725 (C=O), 1645 (C=C), 1250 (C–O) and 1110 (SiPh); δ_H(CDCl$_3$; 250 MHz) 7.41–6.91 (9 H, m, Ar*H*), 6.85 (2 H, s, CH=CH), 6.09 (1 H, q, J 6.3, MeC*H*O), 3.82 (3 H, s, OMe), 2.52 (1 H, q, J 7.4, MeC*H*Si), 1.45 (3 H, d, J 6.3, *Me*CHO), 1.34 (3 H, d, J 7.4, *Me*CHSi), 0.29 (3 H, s, Si*Me$_A$*Me$_B$) and 0.18 (3 H, s, SiMe$_A$*Me$_B$*); m/z 267 (1%, C$_{18}$H$_{23}$Si), 135 (50, PhMe$_2$Si), 132 (100, C$_{10}$H$_{12}$) and 117 (50, C$_9$H$_9$) (Found: M − MeO$_2$CCH=CHCO$_2$, 267.1579. C$_{23}$H$_{28}$O$_4$Si requires M − MeO$_2$CCH=CHCO$_2$, 267.1569).

Dimethyl (1*RS*,2*RS*,3*RS*,4*SR*)-1,4-dimethyl-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylate 49

Dimethyl fumarate (81 mg, 0.56 mmol) and tetrabutylammonium fluoride (TBAF) (1 mol dm^{-3} in THF, 0.56 cm^3, 0.56 mmol) and the ester **46b** (87.1 mg, 0.28 mmol) were stirred in THF (3 cm^3) at room temperature for 16 h. Solvents were evaporated and the residue triturated with diethyl ether (3 × 4 cm^3). The supernatant was filtered through a plug of cotton wool, washing with diethyl ether, evaporated and flash chromatographed (Merck SiO$_2$ 9385, hexane–EtOAc, 19:1) to give the adduct (59.1 mg, 76%) as needles, mp 77–79 °C (from hexane) lit.,^{23} 77–79 °C from hexane); R_f (hexane–EtOAc, 9:1) 0.16.

1-(2-Ethylphenyl)ethan-1-one 51 and 1-(1-hydroxethyl)-2-ethyl-benzene 52

Potassium hydride (20% suspension in oil, 140 mg, 0.7 mmol) was washed under nitrogen with pentane (3 × 4 cm^3) and slurried in THF (1 cm^3). Alcohol **40b** (10∶1 diastereoisomeric mixture) (122.3 mg, 0.55 mmol) in THF (2 cm^3) was added and the mixture stirred at room temperature for 2 h. Work-up and flash chromatography (Merck SiO$_2$ 9385, hexane–EtOAc, 19∶1) gave the ketone[47] **51** (16 mg, 20%); R_f (hexane–EtOAc, 9∶1) 0.62; v_{max}(CDCl$_3$)/cm^{-1} 3070, 3040, 2970, 2940, 2870, 2860 (CH), 1680 (C=O), 1600 and 1570 (aromatic); δ_H(CDCl$_3$; 250 MHz) 7.62 (1 H, d, J 8, ArH o- to COMe), 7.40 (1 H, t, J 8, ArH p- to COMe), 7.35–7.21 (2 H, m, ArH m- to COMe), 2.87 (2 H, q, J 7.4, CH_2Me), 2.57 (3 H, s, COMe) and 1.21 (3 H, t, J 7.4, CH$_2$$Me$); m/z 148 (33%, M$^+$), 133 (100, M − Me) and 105 (35, M − Ac) (Found: M$^+$, 148.0680. C$_{10}$H$_{12}$O requires M, 148.0688), and the alcohol[48] **52** (23.3 mg, 28%); R_f (hexane–EtOAc, 9∶1) 0.35; v_{max}(film)/cm^{-1} 3350 (br OH), 3070, 3040, 2980, 2940, 2880 (CH) and 1605 (aromatic); δ_H(CDCl$_3$; 250 MHz) 7.52 (1 H, m, ArH o- to CHOH), 7.28–7.14 (3 H, m, ArH m- and p- to CHOH), 5.18 (1 H, q, J 6.4, MeCHOH), 2.69 (2 H, q, J 7.6, CH_2Me), 1.80 (1 H, br s, OH), 1.49 (3 H, d, J 6.4, MeCHOH) and 1.24 (3 H, t, J 7.6, CH$_2$$Me$); m/z 150 (1%, M$^+$), 135 (40, M − Me), 132 (80, M − H$_2$O) and 117 (100, M − H$_2$O − Me) (Found: M$^+$, 150.1056. C$_{10}$H$_{14}$O requires M, 150.1044).

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