The Regiochemistry and Stereochemistry of the Hydroboration of Allylsilanes

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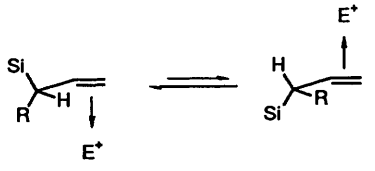
The hydroboration of a wide range of allylsilanes **3** and **5**–**21** is found to be generally regioselective for attachment of the boron to C-3 and hydrogen to C-2 of the allyl unit, and to be generally stereoselective in the sense **1**, with attachment of the boron and the hydrogen *anti* to the silyl group in the most populated conformation. This stereochemistry is opposite in sense to that already known for the hydroboration–oxidation of the corresponding allylic alcohol derivatives. The degree of selectivity, both regio- and stereo-, is found to be greater with 9-BBN and other hindered boranes than with borane itself. Since the boron group and the dimethyl(phenyl)silyl group in the products can be successively converted into hydroxy groups with retention of configuration at both sites, the overall sequence is a stereocontrolled synthesis of 1,3-diols. The diols may be obtained with either relative stereochemistry by the appropriate choice of double bond geometry in the allylsilane, and, because the hydroxy groups are released separately, they may be easily differentiated. The structures and relative stereochemistries of all the products, major and minor, is proved by alternative syntheses and/or conversions into known compounds. The borane intermediates can also be used in carbon–carbon bond-forming reactions. A moderately high level (3:1) of 1,3 induction is found both in nucleophilic attack on the 3-silyl ketone **46** and in the hydroboration of the homoallylsilane **61**.

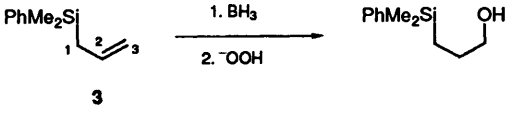
In the preceding paper,[1] we described our work on the reactions of allylsilanes with osmium tetroxide, *m*-chloroperbenzoic acid and a carbenoid-methylenating reagent. These reactions are stereoselective in the general sense **1**, except that, when the



1 **2**

group R on the stereogenic centre is a methyl group and the substituent on the double bond *cis* and vicinal to the stereogenic centre is a hydrogen atom, a substantial proportion of the reaction takes place in the sense **2**. These reagents are somewhat electrophilic in nature and the reactions are cycloadditions. We now describe in full our work on the hydroboration of allylsilanes, already reported in two preliminary communications.[2] We find many similarities between hydroboration and the reactions described in the preceding paper, although the common boranes, at least in their reactivity, can barely be described as electrophilic reagents, and mechanistically their reactions with alkenes can only be described rather loosely as cycloadditions. Thus boranes react more rapidly with less-substituted rather than with more-substituted alkenes, whereas the other reagents react more rapidly with the more-substituted alkenes. Nevertheless, the regioselectivity of hydroboration is clearly that in which the boron atom is the electrophilic component, with the boron attaching itself to the less-substituted carbon of an unsymmetrical alkene. Also, there are positive correlations between the reactivity of an alkene in hydroboration and both the energy of the HOMO and its ionisation potential, and between the regioselectivity and the difference in magnitude of the coefficients in the HOMO of the π-bond.[3] We find, in agreement with these properties, that the hydroboration of allylsilanes is highly regioselective and stereoselective, and is consequently useful in the synthesis of 1,3-diols, since the dimethyl(phenyl)silyl group can be converted with retention of configuration into a hydroxy group.[4,5]

Before we started, several hydroborations had been carried out on the unsubstituted allylsilane **3** (and similar compounds



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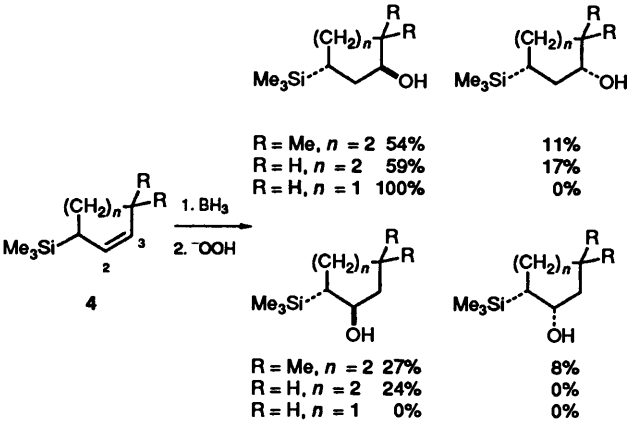
which differ only in the substituents on the silicon atom).[6,7] With one exception, the selectivity for attack by the boron atom at the terminus C-3 was reported to be essentially complete, whereas a simple terminal alkene like but-1-ene is known to give rise to some 7% of attachment of the boron at C-2.[8] Because of that one exception,[7] we too repeated this work and find with the majority that the selectivity is at least 98:2. The allylsilanes **4**, which are monosubstituted at both ends of the double bond,



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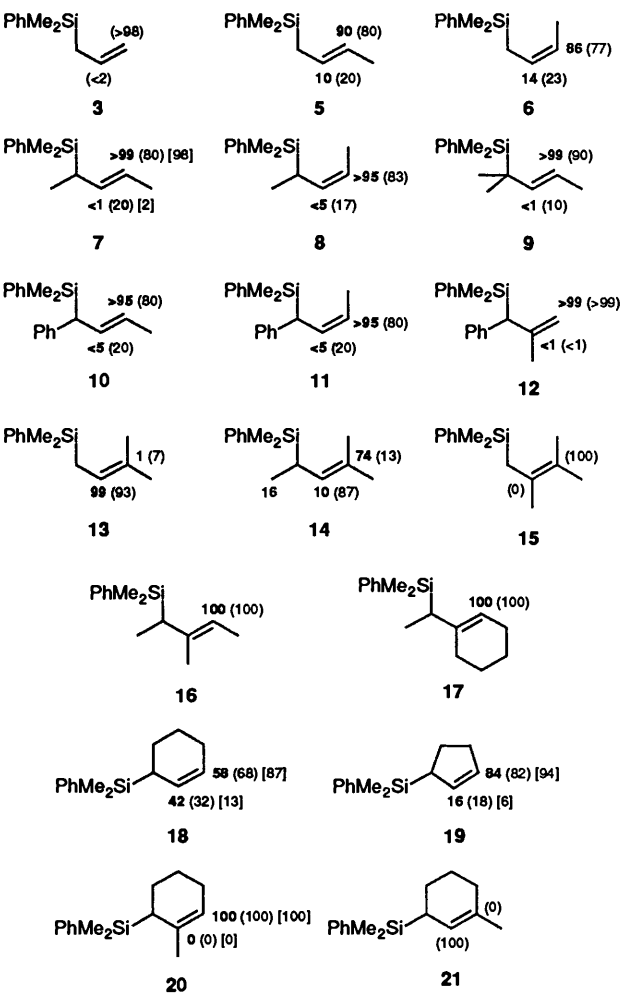
had also been studied by Richer[9] and by Larson.[10] In agreement with the general expectation that the boron atom would attack the more nucleophilic carbon, Richer's allylsilane **4** (R = Me, n = 2) showed some selectivity (65:35) in favour of attachment of the boron at C-3 of the allyl unit, in spite of its having a gem dimethyl group adjacent to it, and Larson's allylsilanes (R = H, n = 1 or 2) understandably show higher selectivity (n = 2, 76:24; n = 1, 100:0). The stereoselectivities were also in favour of attack *anti* to the silyl group (*anti*:*syn* to Si: 81:19; 83:17; 100:0). Larson also found that both the regioselectivity and the stereoselectivity were higher with thexylborane than with borane itself. The only other allylsilanes that had been studied were 4-silacyclopentenes,[11] which have no regiochemistry or stereochemistry with respect to the silyl group. Since we carried out our work, Bryson has shown that allylsilanes are somewhat more reactive in hydroboration than the corresponding alkenes without a silyl group—the allylsilane **15** reacts nine times faster than 2,3-dimethylbut-2-ene with borane.[12]

Results and Discussion

We divide our discussion into four parts: (i) the regioselectivity of the hydroboration, (ii) the stereoselectivity with respect to the stereogenic centre carrying the silyl group, (iii) the proof of structure of the large number of 1,2 and 1,3 silyl alcohols produced in the course of this work, and (iv) the formation of carbon–carbon bonds from the intermediate boranes. Only the first two sections were reported in our preliminary communications, and only for the open-chain allylsilanes **3** and **5**–**14**. The syntheses of most of the allylsilanes used here are described in two later papers in this series.[13]

The Regioselectivity of Hydroboration.—The allylsilanes that we used, to which we have added Bryson's example **15**, are shown in Scheme 1, which illustrates only the regioselectivity for hydroboration. The yields in all these reactions, although not separately quoted for each case, were regularly high. The numbers placed immediately above or below the carbon atoms represent the proportion of attack by the boron atom at that carbon, normalised to 100%. The reactions were carried out with 9-BBN (9-borabicyclo[3.3.1]nonane) (bold numbers) as a small excess in THF at temperatures ranging from room temperature for 4 h to reflux for 48 h, with borane itself (numbers in round brackets), typically at least 3 mol equiv. administered in the form of its THF complex at 0 °C for 1–2 h, or with thexylborane (2,3-dimethylbut-2-ene•BH_3 in tetrahydrofuran) (numbers in square brackets) at 0 °C for 6 h. In each case we oxidised the products to give mixtures of 1,2- and 1,3-silyl alcohols, which we assessed by ^{1}H NMR spectroscopy or gas chromatography, having prepared, in many cases, authentic samples for comparison, as described below. The regioselectivity with borane is, of course, dependent upon the molar excess of borane present, because this influences the relative concentration of the various hydroborating species present. The numbers on the structures in Scheme 1 are not, therefore, to be taken as very reliable. In our experience, the regioselectivities sometimes appear to change from run to run. The numbers given in this paper were mostly reproducible to within ±5%, but occasionally a maverick run took place well outside these limits.

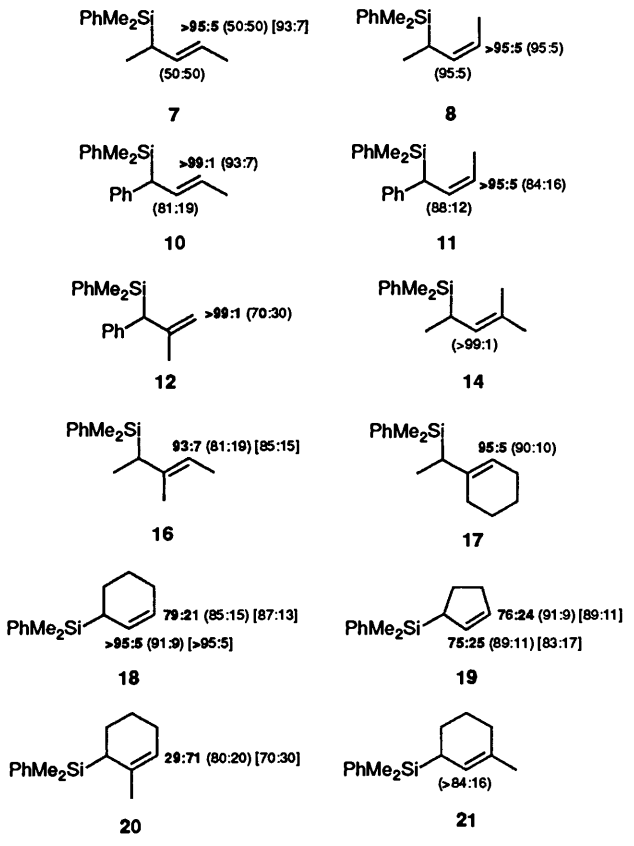
Not surprisingly, the allylsilanes **3**, **12**, **16**, **17** and **20** that are less substituted on C-3 than on C-2 are completely regioselective. More interestingly, there is considerable regioselectivity with the allylsilanes **5**–**11**, **18** and **19** that are monosubstituted at both ends of the double bond, and with the allylsilane **15** that is disubstituted at both ends. It is also clear that the regioselectivity is almost always significantly higher



Scheme 1 Regioselectivity in the hydroboration of allylsilanes with 9-BBN (bold numbers), BH_3–THF (numbers in round brackets) or thexylBH_2 (numbers in square brackets)

with 9-BBN or thexylborane than with borane itself, high enough to be synthetically useful in most cases. The silyl group is evidently having a profound influence in directing the boron atom to C-3 of the allyl unit. Thus, in the series *trans*-but-2-ene, **5**, **7** and **9** reacting with borane itself, the effect of adding a silyl group is to change a ratio of 50:50 to one of 80:20, whereas the subsequent attachment of two methyl groups induces only a small further increase. Our results with the allylsilanes **18** and **19** are similar to Larson's with the corresponding trimethylsilyl compounds, showing that the phenyl group on the silicon is not influencing the results in any serious way.

In one of the allylsilanes that is disubstituted at C-3, **13**, the regioselectivity for both hydroborating agents, with the boron attaching itself to the less substituted carbon atom, C-2, is that which would be expected, without reference to the silyl group, simply from its substitution pattern. In contrast, the other allylsilane that is disubstituted at C-3, **14**, shows strikingly different regioselectivity with the two reagents. With borane it is regioselective for placing the boron at C-2, but with 9-BBN the major product has the boron on the fully substituted carbon, C-3. The reactions with these two allylsilanes are slow. Although the numbers shown on the structures are unlikely to be those of complete thermodynamic control, they are probably not the numbers for purely kinetic control either. Larson found with his allylsilanes that the ratios changed with time, implying that even at room temperature some equilibration is taking place. After 7 days at room temperature, for example, the regioselectivity with trimethylsilylcyclohexene **4** (R = H, n = 2) had



Scheme 2 Stereoselectivity in the hydroboration of allylsilanes, expressed as *anti*:*syn* ratios, with 9-BBN (bold numbers), BH_3–THF (numbers in round brackets) or thexylBH_2 (numbers in square brackets)

increased from 76:24 to 94:6. Thus the presence of a saturated product (16%) having a hydroxy group at the methyl terminus adjacent to the silyl group is understandably the product of a series of hydroborations and retro-hydroborations taking place by way of vinylsilanes. We were unable to detect any product in which the boron atom has found its way to the other methyl termini, although we would have been able to detect very small amounts of the two stereoisomeric alcohols that would have been produced, because we prepared authentic samples of them both. Evidently the successive retro-hydroboration and hydroboration that placed the boron on the carbon atom carrying the silyl group, and allowed it to move on, must have been much faster than the retro-hydroboration of the product having the boron atom on the other fully substituted carbon atom, C-3. This is somewhat surprising in view of how slowly the corresponding hydrometallation and β-elimination processes next to a silyl group are when the metal is a transition metal, as judged by the ease with which a double bond can be moved with a rhodium or iridium catalyst along a carbon chain up to, but no further than, the allylic position with respect to a silyl group.[14]

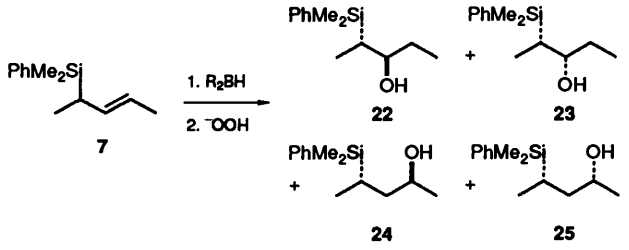
We used the allysilane **7** to test how temperature and other hydroborating agents would affect the regioselectivity. Our results are summarised in column 4 of Table 1 where it is clear that a change of temperature, at least between −25 °C and 0 °C with borane–THF has little effect, and that the different hydroborating agents, even catecholborane at 100 °C, are all more highly regioselective than borane. The very high selectivity by the more electrophilic borane, dibromoborane, supported the idea that there is an electronic component to the regioselectivity. To investigate this possibility, we examined the correlation between the regioselectivity and the difference in the ^{13}C chemical shift of C-2 and C-3. Brown had found a correlation in the hydroboration of some heterocyclic alkenes,[15] but had not extended it to many other alkenes, although it is well established that the ^{13}C chemical shifts are some measure of the electron distribution in a π-bond.[16] Taking hydroboration data[17] from the literature for 18 hydrocarbons and from this work for 8 allylsilanes, and plotting the log of the isomer ratio for hydroboration with borane against the difference in the ^{13}C chemical shift,[18] we found only a poor correlation. The correlation coefficients were 0.79 for the 18 alkenes, 0.89 for the allylsilanes and 0.80 for both series combined. The data are summarised in Table 2 in which each group of compounds is ranked in order of the ^{13}C chemical shift difference. The correlation was worse (0.74 for both series combined) for the results with 9-BBN. These correlations are only good enough to say that there is a general trend for the boron to be placed at the alkene carbon having the smaller chemical shift. They are poor, presumably, because there are steric effects on the reaction that are less important in determining the chemical shifts, and, nor surprisingly, the steric effects appear to be more important with 9-BBN than with borane. We find, from the same source, that a group of styrenes, collected in Table 3, where this is not a factor, show a quite good correlation between the regioselectivity for hydroboration with borane and the chemical shift difference (0.89), just as the same styrenes have been reported to show a good correlation between the regioselectivity and Hammett σ-values. Even more strikingly, we find that the correlation between the regioselectivity and the ^{13}C chemical shift difference becomes very good (0.99) with the same styrenes and monochloroborane, which can reasonably be expected to respond more sensitively than borane itself to electronic effects.

The Stereoselectivity of Hydroboration of Allylsilanes.—In Scheme 2 we collect all the allylsilanes from Scheme 1 that have both a stereogenic centre at the carbon atom carrying the silyl group and a substituent on the double bond, and show on them the stereoselectivity for the formation of the new bond at C-2 and/or C-3 relative to the resident silyl group. The numbers on the structures are the *anti*:*syn* ratios for each regioisomer, with *anti* defined as being attack in the sense **1** and *syn* being defined as attack in the sense **2**. As in Scheme 1, the bold numbers are the results with 9-BBN, the numbers in round brackets are for borane itself and the numbers in square brackets are for thexylborane.

Except for the allylsilane **7**, the open-chain allylsilanes **7**–**16** and the allylsilane **17** with the silyl group on the side chain of a ring all show high stereoselectivity in the *anti* sense with borane, and even higher stereoselectivity with 9-BBN. That the allylsilane **7** should be anomalous is entirely consistent with the results we reported in the preceding paper. This is the one allylsilane that has a relatively small group, the methyl group, on the stereogenic centre and only a hydrogen atom *cis* and vicinal to the stereogenic centre. That this allylsilane should give poor stereoselectivity is, therefore, reasonable. What is more remarkable is that this allylsilane reacts with high stereoselectivity in the *anti* sense, to give largely the alcohol **24**, with all the larger boranes (Table 1, column 6) and especially with 9-BBN.

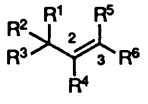
It had been possible to argue for this allylsilane that the upper surface of the conformation **2** was less hindered than the lower surface of conformation **1**, and that a more-hindered reagent would attack more selectively in the sense **2**, as we and Vedejs had argued for its reaction with osmium tetroxide. This seems not to be the explanation, since 9-BBN is clearly a bulkier reagent than borane, as commonly agreed[19] and as we have already commented upon, in connection with the even less good correlation between the ^{13}C chemical shift differences and the regioselectivity of hydroboration with 9-BBN than with

Table 1 Regioselectivity and stereoselectivity in the hydroboration–oxidation of the allylsilane **7**



Hydroborating agent, R_2BH	Conditions	Yield (%)	Regioselectivity, **24** + **25**:**22** + **23**	Stereoselectivity, **22**:**23**	Stereoselectivity, **24**:**25**
BH_3–THF	0 °C, 2 h	80	80:20	50:50	50:50
BH_3–THF	−25 °C, 2 h	86	79:21	50:50	46:54
BH_3–Me_2S	0 °C, 2 h	78	78:22	50:50	47:53
9-BBN	25 °C, 4 h	93	>99:1	—	>95:5
ThexylBH$_2$–THF	−25 °C, 1 h	73	98:2	—	93:7
DicyclohexylBH–THF	25 °C, 2 h	89	99:1	—	>95:5
CatecholBH–THF	100 °C, 4 h	84	94:6	—	93:7
Br_2BH–Me_2S	40 °C, 23 h	66	>99:1	—	95:5

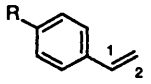
Table 2 Correlation between the difference $\Delta\delta$ in ^{13}C chemical shift for the olefinic carbons of alkenes and the regioselectivity in hydroboration, where $\Delta\delta = \delta_{C-2} - \delta_{C-3}$ and ln(3/2) is the natural logarithm of the ratio of regioisomers having boron attached to C-3 and C-2



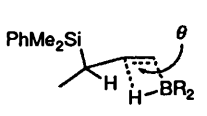
Compound	R^1	R^2	R^3	R^4	R^5	R^6	$\Delta\delta$ ^{13}C	ln(3/2) BH_3	ln(3/2) 9-BBN
Hydrocarbons:									
	H	H	H	H	Me	H	0	0	
	H	H	H	H	H	Me	0	0	
	Et	H	H	H	H	Me	6.9	−0.16	
	Et	H	H	H	H	Me	6.9	0	
	Me	H	H	H	H	Me	9.6	0.04	
	Me	Me	H	H	H	Me	9.6	0.28	
	Me	H	H	H	Me	H	9.6	0.2	
	Me	Me	H	H	Me	H	12.6		6.2
	H	H	H	Me	H	Me	13.3	3.9	6.2
	Me	Me	Me	H	Me	H	18.6	0.32	6.9
	Bu^t	H	H	H	H	H	19.1	2.6	
	Ph	H	H	H	H	H	22	2.2	
	Et	H	H	H	H	H	24	2.8	
	Pr	H	H	H	H	H	24.6	2.7	4.7
	Me	H	H	H	H	H	27	2.6	
	Bu^t	H	H	H	Me	H	29.2	4.6	
	Me	Me	H	H	H	H	34.7	2.7	
	Pr	H	H	Me	H	H	35.1		6.2
	Me	H	H	Me	H	H	38.9	4.6	
	Me	Me	Me	H	H	H	40.8	2.8	5.8
Allylsilanes:									
13	$PhMe_2Si$	H	H	H	Me	Me	−10.1	−2.6	−4.6
14	$PhMe_2Si$	Me	H	H	Me	Me	−0.51	−1.9	2.9
5	$PhMe_2Si$	H	H	H	H	Me	2.49	1.4	2.19
6	$PhMe_2Si$	H	H	H	Me	H	3.8	1.2	1.8
7	$PhMe_2Si$	Me	H	H	H	Me	12.24	1.4	4.6
8	$PhMe_2Si$	Me	H	H	Me	H	13.0	1.6	2.9
3	$PhMe_2Si$	H	H	H	H	H	18.1	3.9	
9	$PhMe_2Si$	Me	Me	H	H	Me	19.07	2.2	4.6

borane. It seems likely here that the relevant transition structures look more like **26** and **27**, respectively, than the oversimplified structures **1** and **2**. As Houk has pointed out for hydroboration in general,[20] with an acute angle θ between the incoming hydrogen atom and the bond between C-2 and C-3, there is little room for a large substituent to be staggered in this sector. In the present example, there is evidently room for a methyl group when borane is the hydroborating agent, but the larger hydroborating agents make the transition structure **26** lower in energy than transition structure **27**. Comparing all the reactions discussed in this and the preceding paper, it is consistent that the nitrile oxide cycloaddition and the osmium

Table 3 Correlation between the difference $\Delta\delta$ in ^{13}C chemical shift for the olefinic carbons of styrenes and the regioselectivity in hydroboration, where $\Delta\delta = \delta_{C-1} - \delta_{C-2}$ and ln(2/1) is the natural logarithm of the ratio of regioisomers having boron attached to C-2 and C-1



R	$\Delta\delta$ ^{13}C	ln(2/1) BH_3	ln(2/1) Cl_2BH
CF_3	19.6	0.66	
NO_2	17.1		0.71
Cl	21.7	0.99	1.9
Br	21.7		1.99
F	22.7		2.09
H	23.8	1.45	2.19
Me	24.5	1.52	2.44
OEt	25.5		2.51
MeO	25.4	2.59	2.63



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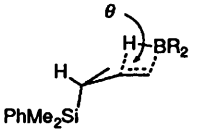

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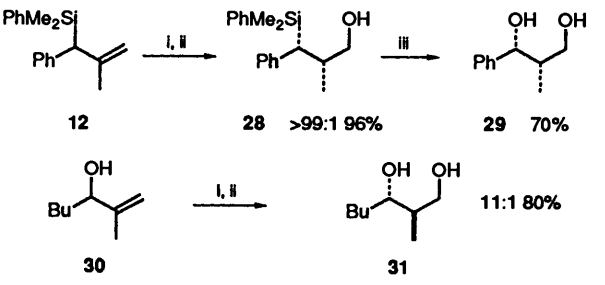
tetroxide reaction, which either do, or may, have obtuse angles θ, are *syn* selective, hydroboration with diborane, with an acute angle θ, but with only a hydrogen atom as the incoming group, is unselective, and epoxidation and methylenation, with acute angles θ, are moderately *anti* selective. The most important point, however, from the point of view of organic synthesis, is that 9-BBN and other larger hydroborating agents are highly stereoselective with most of the open-chain allylsilanes for which there is any relevant stereochemistry.

In contrast, the cyclic allylsilanes **18**–**20** are not uniformly selective for *anti* attack with 9-BBN. As Larson had found in the reaction between thexylborane and similar allylsilanes, there is evidence that equilibration is taking place during these relatively slow reactions, and we assume that we too, especially with 9-BBN, are getting closer to the thermodynamic ratios than we were with the open-chain allylsilanes. The reaction with the allylsilane **20** and 9-BBN, for example, which is actually *syn* selective, is also a slow reaction (6 h at 64 °C), making it more than probable that this is closer to a thermodynamic result. In these cases borane is more *anti* selective than 9-BBN, presumably because it reacts fast enough (0 °C, 2–4 h) for us to be measuring the kinetic ratios. There is also, with these cyclic systems, the problem that a pseudo-equatorial silyl group is not able to overlap efficiently with the π-bond orbitals, and this may disturb the regular pattern found in the open-chain allylsilanes. The four allylsilanes **16**, **17**, **20**, and **21** are notable because the hydroboration has created three contiguous stereogenic centres with high stereoselectivity.

Finally, we note the contrast (Scheme 3) between the stereochemistry of hydroboration of the allylsilane **12**, which gives only the alcohol **28**, and hence the diol **29**, and of a similar compound **30** having a hydroxy group in place of the silyl and a butyl group in place of the phenyl. With this allyl alcohol, Still and Barrish[21] found selectivity with 9-BBN of 11 : 1 in favour of the diol **31**, in other words with stereochemistry in the opposite sense to that observed by us in the diol **29**. Since the hydroxy group is a π-donor, a σ-acceptor, and not large, and the silyl group is a π-acceptor, a σ-donor, and large, this is perhaps not too surprising.



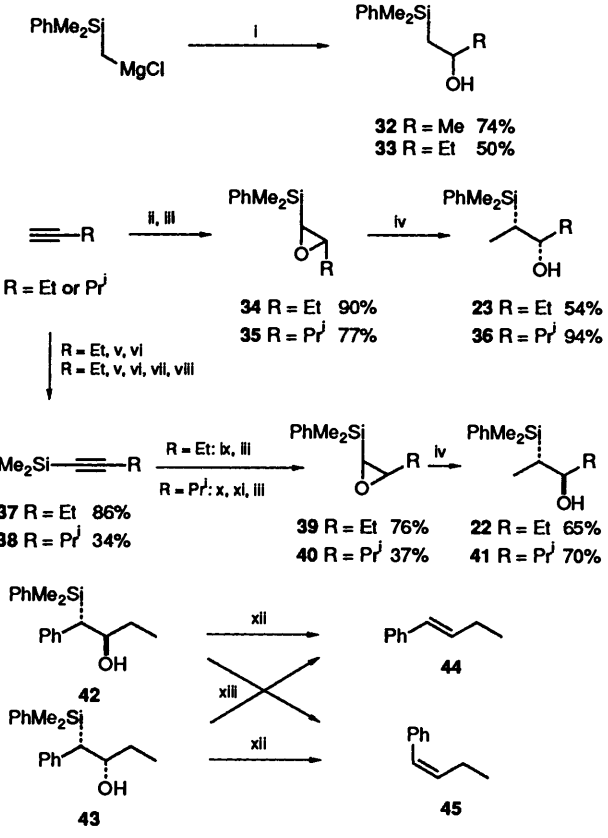
12 **28** >99:1 96% **29** 70%

30 **31** 11:1 80%

Scheme 3 *Reagents:* i, 9-BBN:THF; ii, NaOH, H_2O_2; iii, $Hg(OAc)_2$, AcO_2H

In conclusion, we find that the hydroboration of allylsilanes with 9-BBN, although frequently rather slow, is a regioselective and stereoselective method for setting up 1,3-related silyl alcohols in either stereochemical sense, depending upon the geometry of the double bond in the allylsilane. Since the dimethyl(phenyl)silyl group can be converted into a hydroxy group with retention of configuration, this reaction is also an efficient synthesis of 1,3-diols, as we show in our work proving the structures and stereochemistry of all the products of the reactions summarised in Schemes 1 and 2.

Proof of Structure and Stereochemistry.—We made the product **32** that might have been produced by hydroboration of the allylsilane **3** by adding the dimethyl(phenyl)silylmethyl Grignard reagent to acetaldehyde (Scheme 4). There was no



32 R = Me 74%
33 R = Et 50%

R = Et or Pr^i

34 R = Et 90%
35 R = Pr^i 77%

23 R = Et 54%
36 R = Pr^i 94%

R = Et, v, vi
R = Et, v, vi, vii, viii

R = Et: ix, iii
R = Pr^i: x, xi, iii

37 R = Et 86%
38 R = Pr^i 34%

39 R = Et 76%
40 R = Pr^i 37%

22 R = Et 65%
41 R = Pr^i 70%

42

43

44

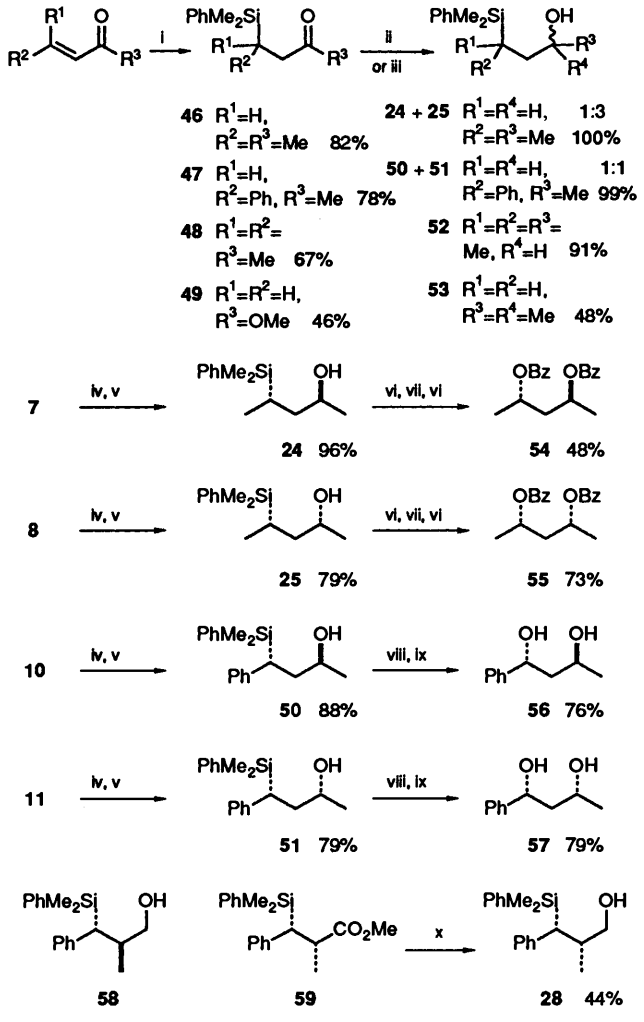
45

Scheme 4 *Reagents*: i, RCHO; ii, $(PhMe_2Si)_2CuLi$; iii, MCPBA; iv, Me_2CuLi; v, BuLi; vi, $PhMe_2SiCl$; vii, BuLi, TMEDA; viii, MeI; ix, H_2, Lindlar; x, Cy_2BH; xi, AcOH; xii, $BF_3{\cdot}OEt_2$; xiii, KH

trace of this product in the hydroboration mixtures. Similarly, we prepared the minor regioisomer **33**, found in the hydroboration of the allylsilanes **5** and **6**, from propionaldehyde. We prepared the minor products **23** and **22** in the

hydroboration of the allylsilanes **7** and **8** by stereospecifically opening the epoxides **34** and **39**, respectively, in reactions based on the work of Hudrlik.[22] We used similar reactions for the products **36** and **41** in the hydroboration of the allylsilane **14**. We were not able to use this sequence to prepare the minor products **42** and **43** from the hydroboration of the allylsilanes **10** and **11**, but we were able to take the 4:1 mixture of alcohols from the hydroboration of the allylsilane **10** through to the mixture of styrenes **44** and **45**, using stereospecific desilylative eliminations, which are also based on the work of Hudrlik.[23] Potassium hydride gave the *E*:*Z* mixture in a ratio of 18:82 and boron trifluoride–diethyl etherate gave the same compounds in a ratio of 81:19, showing that the stereochemistry of the major alcohol **42** was *anti*.

We prepared six of the 3-silyl alcohols **24** and **25** and **50**–**53** from the corresponding 3-silyl ketones **46**–**49**, which were available from the conjugate addition of the silyl-cuprate reagent to the appropriate enones (Scheme 5). The alcohols **24**

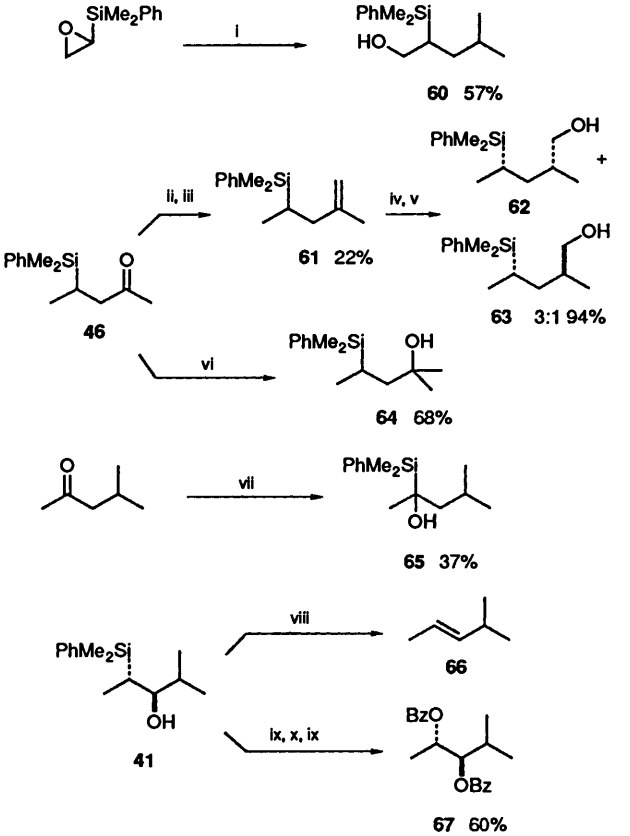


Scheme 5 *Reagents*: i, $(PhMe_2Si)_2CuLi$; ii, $NaBH_4$; iii, MeLi; iv, 9-BBN; v, NaOH, H_2O_2; vi, $(PhCO)_2O$; vii, KBr, AcO_2H; viii, BF_3·2AcOH; ix, AcO_2H; x, $LiAlH_4$

and **25** and **50** and **51** were, of course, mixtures of stereoisomers, of unknown configuration at this stage, the former in a ratio of 27:73 and the latter in a ratio of 50:50. To prove the stereochemistry of the 3-silyl alcohols from the hydroboration of the allylsilanes **7** and **8**, we converted the stereochemically clean products **24**, from the reaction of the former with 9-BBN, and **25**, from the reaction of the latter, into the known[24] dibenzoates **54** and **55**. Similarly, we converted the products **50** and **51** from the hydroboration of the allylsilanes **10** and **11** into the known[25] diols **56** and **57**. With the stereochemistry now identified, we could assign the relative configuration **25** to the major product in the reduction of the ketone **46**. We return to a discussion of the remarkable level of stereoselectivity in this reaction at the end of this paper.

The only alcohol **28** produced from the hydroboration of the allylsilane **12** was clearly different from its known diastereoisomer **58**, of which we had a sample.[26] Nevertheless, we easily prepared an authentic sample by reduction of the ester **59**, of which we also had a sample.[27] We also converted the alcohol **28** into the known diol **29**.[28]

Because we found a minor product **60** in the hydroboration of the allylsilane **14**, we deliberately made all the possible hydroboration products **36**, **41**, **60**, **62**, **63**, **64** and **65** (Scheme 6), in order to know where they might have characteristic

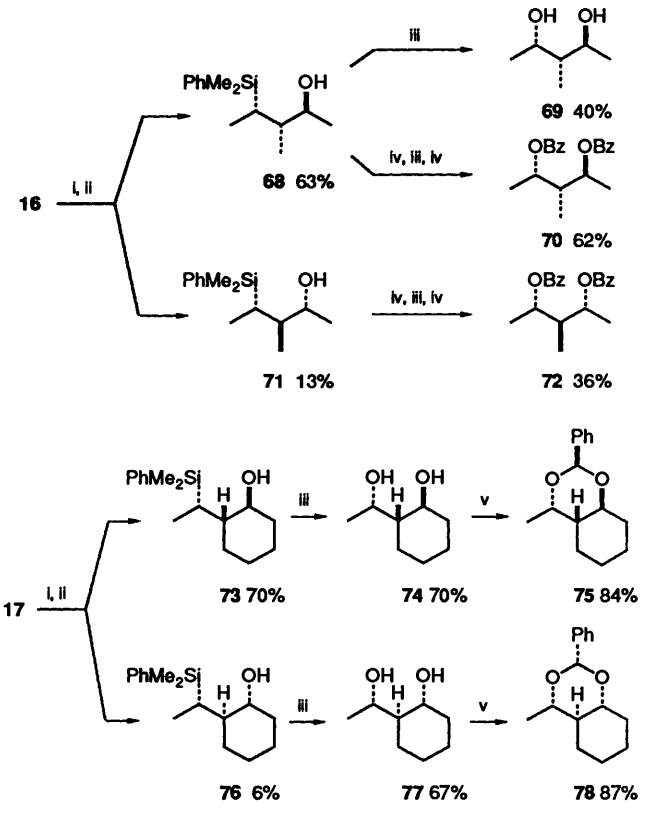


Scheme 6 *Reagents*: i, Me_2CHCH_2MgBr, CuI; ii, Me_3SiCH_2MgCl; iii, AcOH; iv, 9-BBN; v, NaOH, H_2O_2; vi, MeLi; vii, $PhMe_2SiLi$; viii, BF_3·2AcOH, $CDCl_3$; ix, $(PhCO)_2O$; x, KBr, AcO_2H

signals in their ^1H NMR spectra. As it turned out, only the alcohols **36**, **41**, **60** and **64** could be detected in the ^1H NMR spectra of the hydroboration mixtures, with surprisingly no trace of either of the alcohols **62** or **63**. The synthesis of these alcohols was remarkable for the relatively high level of stereocontrol (3:1) in the hydroboration of the homoallylsilane **61**, to which we return at the end of this paper. We also converted the alcohol **41** into the known[29] dibenzoate **67**, not because it proved the stereochemistry, but because this gave us one of our first chances to check that the one-pot method for converting a dimethyl(phenyl)silyl group into a hydroxy group[5] would work when the silyl group was vicinal to a hydroxy group. The older two-pot sequence,[4] involving protic acid as the electrophile for the removal of the phenyl group, was not expected to be suitable for this transformation, because it would induce desilylative elimination, as we confirmed in an NMR experiment using the alcohol **41** and

boron trifluoride–acetic acid in deuteriochloroform, which gave a product with the ^{1}H NMR spectrum of the alkene **66**. In contrast, the one-pot sequence, using bromine as the electrophile in buffered peracetic acid, worked tolerably well on the monobenzoate to give, after benzoylation, the dibenzoate **67**.

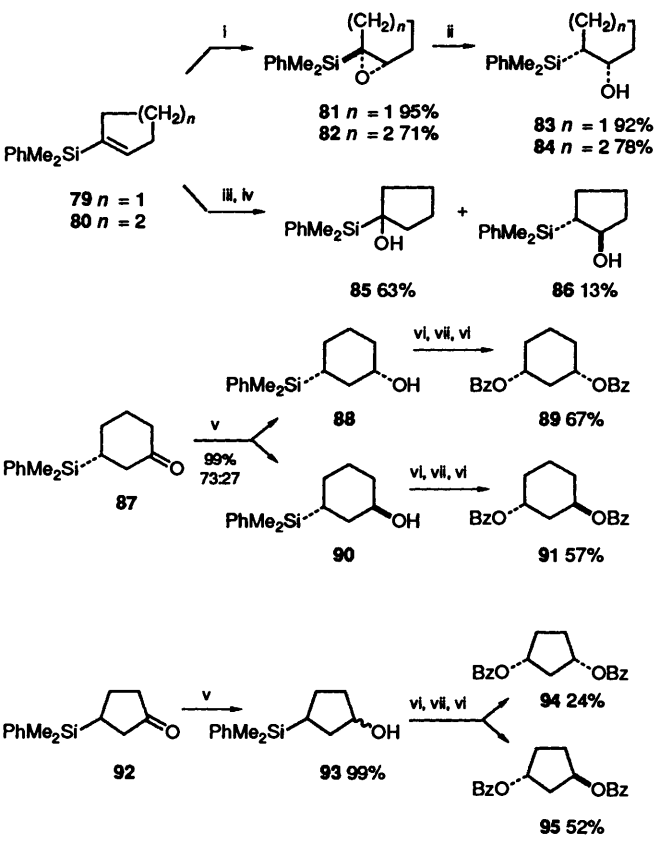
The hydroboration of the allylsilane **16** gave the alcohols **68** and **71** (Scheme 7). The former gave the known[30] diol **69**, but



Scheme 7 *Reagents:* i, BH_3; ii, NaOH, H_2O_2; iii, KBr, AcO_2H; iv, $(PhCO)_2O$; v, $PhCH(OMe)_2$, TsOH

only in low yield, probably because of its water solubility. Successive derivatisation of each hydroxy group as the benzoates gave the dibenzoate **70** in better yield. We used the same procedure to make the dibenzoate **72** derived from the minor product **71**. The ^{1}H NMR spectrum of the dibenzoate **72**, with only two methyl doublets, amongst several other definitive features, was clearly that of a symmetrical molecule, and the former with three methyl doublets was not. The hydroboration of the allylsilane **17** gave the alcohols **73** and **76**, which we identified by converting them into the acetals **75** and **78**, which had already been prepared from the diols **74** and **77**, themselves prepared by hydroboration of the allylic alcohol corresponding to the allylsilane **17**.[31] In that work, it was the diol **77** that was the major product and the diol **74** the minor (in a ratio of 87:13), showing again the sharp difference between allylic alcohols and the corresponding allylsilanes.

We prepared the *syn* 2-hydroxysilanes **83** and **84** by regioselective reduction of the epoxides **81** and **82**, in a reaction based on the work of Whitham,[32] and we prepared the *anti* 2-hydroxysilane **86**, in a reaction based on the work of Larson[10] (Scheme 8). We did not prepare an authentic sample of the six-membered analogue of the 2-hydroxysilane **86**, but its ^{1}H NMR spectrum was distinguishable from that of its isomer **84** in having a 10.3 Hz coupling between the protons on C-1 and C-2, and it was unchanged after treatment with sodium hydride in DMF. We prepared authentic samples of the 3-hydroxysilanes **88** and **90** by reduction of the ketone **87**, which was somewhat

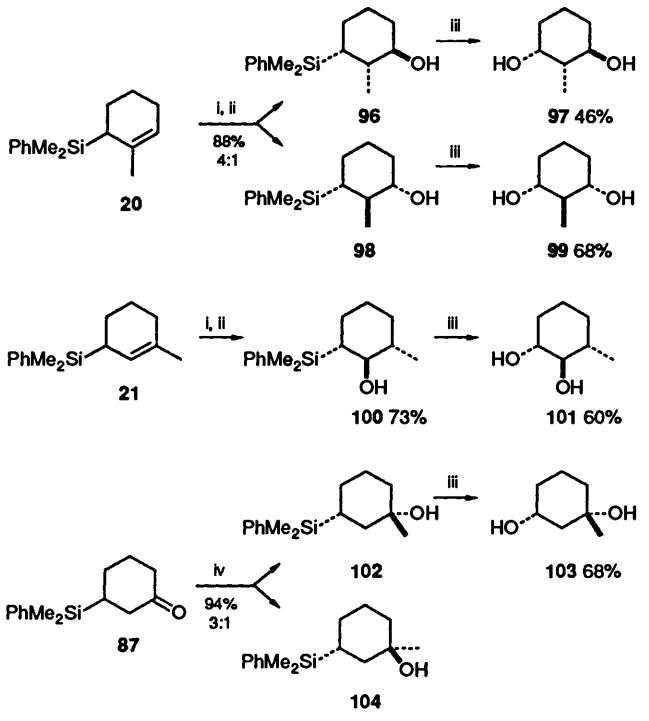


Scheme 8 *Reagents:* i, MCPBA; ii, $LiAlH_4$; iii, BH_3; iv, NaOH, H_2O_2; v, $NaBH_4$; vi, $(PhCO)_2O$; vii, KBr, AcO_2H

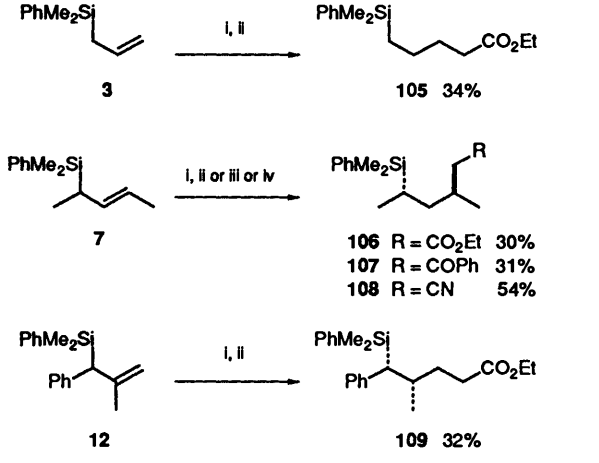
selective, as expected,[33] for the formation of the equatorial alcohol **88**, identifiable from the two diaxial 10 Hz couplings from the proton adjacent to the hydroxy group in this isomer. In addition, we separated these alcohols and converted them into the known[34] dibenzoates **89** and **91**, which we also prepared from the commercially available cyclohexane-1,3-diols. The corresponding alcohols **93** in the five-membered ring were not separable, but the dibenzoates **94** and **95** were. The signals of the methylene protons on C-2 in the ^{1}H NMR spectra were definitive of the relative stereochemistry—the dibenzoate **94** having two one-proton multiplets and the dibenzoate **95** having one two-proton triplet.

The hydroboration of the allylsilane **20** gave the alcohols **96** and **98**, which we converted into the known[35] 1,3-diols **97** and **99** (Scheme 9). If we make the reasonable assumption that the all-*cis* stereochemistry is most unlikely in these products, their ^{1}H and ^{13}C NMR spectra were, from the symmetry of the diol **99**, definitive of their relative stereochemistry. The 2-hydroxysilane **100** was the major product from the hydroboration of the allylsilane **21**. It had in its ^{1}H NMR spectrum a definitive triplet with a coupling constant of 10 Hz for the proton adjacent to the hydroxy group. We also converted it into the known[36] diol **101**. We prepared the alcohols **102** and **104** by treatment of the ketone **87** with the methyl Grignard reagent. Neither stereoisomer was detectable in the mixture from the hydroboration of the allylsilane **21**, but we assigned stereochemistry to them nevertheless by converting the major product **102** into the known[37] diol **103**.

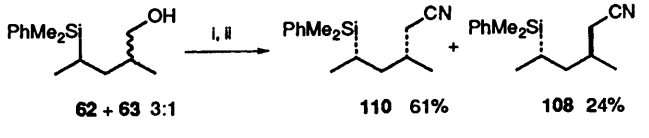
Carbon–Carbon Bond-formation after Hydroboration of the Allylsilanes.—In all the work described above we converted the boranes stereospecifically into alcohols using alkaline hydrogen peroxide. This is not, of course, the only reaction that boranes undergo, and we therefore carried out one representative



Scheme 9 *Reagents:* i, BH_3; ii, NaOH, H_2O_2; iii, KBr, AcO_2H; iv, MeMgCl



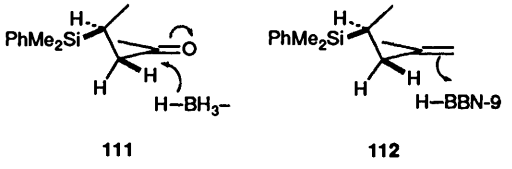
Scheme 10 *Reagents:* i, 9-BBN; ii, $ClCH_2CO_2Et$, $KOC_6H_3Bu^t_2$-2,6; iii, $ClCH_2COPh$, $KOC_6H_3Bu^t_2$-2,6; iv, $ClCH_2CN$; $KOC_6H_3Bu^t_2$-2,6



Scheme 11 *Reagents:* i, TsCl, Et_3N; ii, NaCN, DMSO

reaction of the many possible that would establish a new carbon–carbon bond from the carbon–boron bond of our hydroboration products. Following the work of Brown,[38] we chose the reaction of an α-halogenocarbonyl compound, first with the hydroboration product of the simple allylsilane **3** having no stereochemical features, and then with the two allylsilanes **7** and **12**, for which the hydroboration with 9-BBN cleanly set up stereocentres with 1,3- and 1,2-relationships (Scheme 10). The yields in these reactions were unspectacular, although somewhat better with α-chloroacetonitrile, in the one case **108** that we tried, than with the corresponding ester, as Midland had found.[39] The level of stereocontrol remained high, of course, in all these reactions and the potential for synthesis has therefore been demonstrated.

We were also able to use the nitrile **108** produced by this sequence in order to assign stereochemistry to the products **62** and **63** of the hydroboration–oxidation of the homoallylsilane **61** (Scheme 6). The mixture of alcohols **62** and **63**, present in a ratio of 3:1, gave the nitriles **110** and **108** (Scheme 11), of which the minor proved to be the same as the nitrile prepared with reliable stereochemistry in the hydroboration–α-chloroacetonitrile reaction. The degree of selectivity in this reaction (3:1) is the same as that which we had observed in the reduction of the similarly constituted ketone **46** (3:1), and is remarkably high for a reaction involving 1,3-control of stereochemistry, considering that there is little likelihood of any element of chelation in the delivery of either reagent. Also, the sense of the attack **111** and **112**, giving the alcohols **25** and **62** as the major products, is the same, evidently insensitive as to whether the attack on the double bond is primarily nucleophilic or electrophilic in nature, in contrast to our observations on the effect of a neighbouring stereogenic centre on electrophilic attack on a double bond,[40] which proves to be opposite in sense to Cram's rule for nucleophilic attack. The explanation embedded in the drawings **111** and **112** is that of Evans,[41] who first saw comparably high



levels of 1,3 selectivity in the sense **112** for the hydroboration of some alkenes having large functionalised alkyl groups where we have a silyl group.

Experimental

The synthesis of most of the allylsilanes used in this work is described in two papers later in this series. We prepared the allylsilane **3** (70%) by the method of Topchiev,[42] the allylsilane **12** (54%) by the method of Waterson,[26] and the allylsilane **13**[43] (75%) from 2-methylbut-3-en-2-yl acetate by the method of Marchi.[44]

1-*Dimethyl(phenyl)silylbut-2-yne.*—Butyllithium (1.6 mol dm^{-3} solution in hexane; 2.4 cm^3) was added to a solution of propyne (5 mmol) in THF (30 cm^3) at −20 °C and stirred for 10 min. Iodomethyldimethyl(phenyl)silane[45] (1 g) was added to the slurry and the mixture refluxed for 15 h. Standard aqueous work-up and chromatography (SiO_2, hexane) gave the *prop*-2-*ynylsilane* (0.42 g, 65%); R_f(hexane) 0.2; ν_{max}(film)/cm^{-1} 1260 (SiMe) and 1120 (SiPh); δ_H($CDCl_3$) 7.60–7.30 (5 H, m, Ph), 1.76 (3 H, q, *J* 2.8, Me), 1.63 (2 H, t, *J* 2.8, CH_2) and 0.36 (6 H, s, $SiMe_2$); δ_C($CDCl_3$) 137.9, 133.5, 129.2, 127.7, 75.8, 74.5, 6.2, 3.6 and −3.5; *m/z* 188 (13%, M^+), 173 (10, M − Me) and 135 (100, Me_2PhSi) (Found: M^+, 188.1007. $C_{12}H_{16}Si$ requires *M*, 188.1021).

(Z)-1-*Dimethyl(phenyl)silylbut-2-ene* **6**.—The silylbutyne (1 g, 5.3 mmol) was added to a slurry of dicyclohexylborane (6.4 mmol) in THF (6 cm^3) and the mixture stirred at room temperature for 2 h. Glacial acetic acid (1.08 cm^3) was added to the mixture, which was then stirred at 0 °C for 2 h. Standard aqueous work-up, washing with aqueous sodium hydrogen carbonate and chromatography (SiO_2, hexane) gave the allylsilane[46] (0.9 g, 89%); R_f(hexane) 0.56; ν_{max}(film)/cm^{-1} 1640 (C=C), 1260 (SiMe) and 1125 (SiPh); δ_H($CDCl_3$) 7.50–7.30 (5 H, m, Ph), 5.50–5.30 (2 H, m, CH=CH), 1.71 (2 H, d, *J* 7.3, CH_2), 1.50 (3 H, d, *J* 5.8, Me) and 0.27 (6 H, s, $SiMe_2$);

$\delta_C(CDCl_3)$ 139.0, 133.6, 129.0, 127.7, 125.8, 122.0, 17.2, 12.6 and −3.3; *m/z* 190 (7%, M^+) and 135 (100, Me_2PhSi) (Found: M^+, 190.1173. $C_{12}H_{18}$ requires *M*, 190.1178).

3-*Dimethyl(phenyl)silyl*-1-*methylcyclohex*-1-*ene* **21**.—Silylcupration[44] of 1-methylcyclohex-2-enyl acetate (1.17 g) gave the *allylsilane* (1.17 g, 84%); R_f(hexane) 0.39; ν_{max}(film)/cm^{-1} 1240 (SiMe) and 1110 (SiPh); $\delta_H(CDCl_3)$ 7.55–7.33 (5 H, m, Ph), 5.36 (1 H, m, C=CH), 1.9–1.3 (7 H, m, ring Hs), 1.65 (3 H, d, *J* 0.9, C=CMe), 0.28 (3 H, s, $SiMe_AMe_B$) and 0.26 (3 H, s, $SiMe_AMe_B$); $\delta_C(CDCl_3)$ 138.6, 134.0, 132.9, 128.8, 127.7, 121.1, 30.0, 25.4, 23.5, 23.1, −4.5 and −4.7; *m/z* 230 (4%, M^+) and 135 (100, Me_2PhSi) (Found: M^+, 230.1485). $C_{15}H_{22}Si$ requires *M*, 230.1490).

Hydroboration of the Allylsilanes.—We used the methods developed by Brown and others.[47] The borane–THF complex (Aldrich) (1 mol dm^{-3} solution in THF; 3 mmol) was added to the allylsilane (1 mmol) at 0 °C and generally stirred for 2–4 h. 9-BBN (Aldrich) (0.5 mol dm^{-3} solution in THF; 1.5 mmol) was added to the allylsilane (1 mmol) at room temperature or reflux and stirred for the time stated. Dibromoborane–dimethyl sulfide (Aldrich) (1 mol dm^{-3} solution in dichloromethane; 3 mmol) was added to the allylsilane (1 mmol) and the mixture was refluxed for 23 h. Triethylamine (6 mmol) was added to the mixture which was then oxidised in the standard manner. Thexylborane was prepared by adding iodomethane (1 mmol) dropwise to lithium thexylborohydride (Aldrich or prepared by the method of Brown[48]) (2 mol dm^{-3} solution in THF; 0.5 cm^3) at 0 °C and stirring for 30 min. This solution of thexylborane was added to the allylsilane (0.5 mmol) at −25 °C and stirred for the time stated. Dicyclohexylborane was prepared from cyclohexene (4 mmol) and the borane–THF complex (1 mol dm^{-3} solution in THF; 2 mmol) at 0 °C and stirred for 1 h in a centrifuge tube. The white slurry was centrifuged and the supernatant removed. The residue was washed with THF and the centrifugation process repeated. The allylsilane (1 mmol) was added to the resulting slurry of dicyclohexylborane at 0 °C and stirred for 4 h. Catecholborane (Aldrich) (2 mmol) was added to the allylsilane (1 mmol) and stirred at 100 °C for 4 h.

Oxidation of the Organoboranes.—The organoboranes were oxidised by successive treatment with water, aqueous sodium hydroxide (3 mol dm^{-3}; 1 mol equiv. for each mol equiv. of borane) and 30% hydrogen peroxide (1 equiv. for each B–C bond) and heated at 50 °C for 1 h. The solution was extracted with ether and the extracts were dried (Na_2SO_4) and evaporated under reduced pressure. The residue was generally purified by chromatography. The following alcohols were prepared by these methods:

3-*Dimethyl(phenyl)silylpropan*-1-*ol* (1.07 g, 97%). From the allylsilane **3** (1.0 g) (BH_3·THF, 3 equiv. 0 °C, 2 h); $R_f(CH_2Cl_2)$ 0.31; ν_{max}(film)/cm^{-1} 3400 (OH), 1252 (SiMe) and 1116 (SiPh); $\delta_H(CDCl_3)$ 7.52–7.33 (5 H, m, Ph), 3.57 (1 H, t, *J* 6.7, CH_2CH_2OH), 1.60 (2 H, m, CH_2CH_2OH), 1.34 (1 H, s, OH), 0.74 (2 H, m, $SiCH_2$) and 0.28 (6 H, s, $SiMe_2$); $\delta_C(CDCl_3)$ 139.1, 133.6, 128.9, 127.6, 65.5, 27.1, 11.5 and −3.1; *m/z* 179 (12%, M − Me), 137 (55, MePhSiOH) and 135 (100, Me_2PhSi) (Found: M^+ − Me, 179.0893. $C_{11}H_{18}OSi$ requires *M* − Me, 179.0892).

4-*Dimethyl(phenyl)silylbutan*-2-*ol* (0.41 g, 75%). From the allylsilane **5** (0.5 g (BH_3·THF, 3 equiv., 0 °C, 2 h); $R_f(CH_2Cl_2)$ 0.22; ν_{max}(film)/cm^{-1} 3400 (OH), 1248 (SiMe) and 1222 (SiPh); $\delta_H(CDCl_3)$ 7.6–7.3 (5 H, m, Ph), 3.68 (1 H, sextet, *J* 6.1, CHOH), 1.6–1.3 (2 H, m, CH_2COH), 1.56 (1 H, s, OH), 1.16 (3 H, d, *J* 6.1, Me), 0.91–0.62 (2 H, m, $SiCH_2$) and 0.29 (6 H, s, $SiMe_2$); $\delta_C(CDCl_3)$ 139.2, 133.6, 129.0, 127.8, 70.2, 33.4, 22.8, 11.4, −3.05 and −3.08; *m/z* 193 (4%, M − Me), 137 (100, MePhSiOH) and 135 (55, Me_2PhSi) (Found: M^+ − Me, 193.1046. $C_{12}H_{20}OSi$ requires *M* − Me, 193.1049) together with the alcohol **33** (0.08 g, 19%) identical (^{1}H NMR) with an authentic sample.

(2RS,4RS)-4-*Dimethyl(phenyl)silylpentan*-2-*ol* **24** (0.83 g, 93%). From the allylsilane **7** (0.82 g) (9-BBN, 1.3 equiv., room temp., 2 h) followed by chromatography (SiO_2, hexane–Et_2O, 1:1); R_f(hexane–ether, 1:1) 0.72; ν_{max}(film)/cm^{-1} 3400 (OH), 1249 (SiMe) and 1120 (SiPh); $\delta_H(CDCl_3)$ 7.5–7.3 (5 H, m, Ph), 3.86 (1 H, m, CHOH), 1.42 (2 H, m, CH_2), 1.30 (1 H, br s, OH), 1.10 (3 H, d, *J* 6.1 CHOH*Me*), 0.97–0.90 (4 H, m, SiCH and SiCH*Me*), 0.26 (3 H, s, $SiMe_AMe_B$) and 0.27 (3 H, s, $SiMe_AMe_B$); $\delta_C(CDCl_3)$ 138.1, 133.8, 128.8, 127.6, 66.9, 41.2, 22.4, 16.3, 14.3, −5.0 and −5.3; *m/z* 207 (0.6%, M − Me), 137 (100, MePhSiOH), 135 (90, Me_2PhSi) and 70 (50, C_5H_{10}) (Found: M^+ − Me, 207.1216. $C_{13}H_{22}OSi$ requires *M* − Me, 207.1205).

(2RS,4SR)-4-*Dimethyl(phenyl)silylpentan*-2-*ol* **25** (87.1 mg, 79%). From the allylsilane **8** (101 mg) (9-BBN, 2 equiv., room temp., 4 h) followed by chromatography (SiO_2, CH_2Cl_2); $R_f(CH_2Cl_2)$ 0.30; ν_{max}(film)/cm^{-1} 3350 (OH), 1260 (SiMe) and 1120 (SiPh); $\delta_H(CDCl_3)$ 7.54–7.35 (5 H, m, Ph), 3.90 (1 H, m, CHOH), 1.51 (1 H, t, *J* 10, CH_AH_B), 1.38 (1 H, s, OH), 1.22–1.08 (2 H, m, CH_AH_B and SiCH), 1.18 (3 H, d, *J* 5.8, CHOH*Me*), 0.97 (3 H, d, *J* 6.5, SiCH*Me*) and 0.28 (6 H, s, $SiMe_2$); $\delta_C(CDCl_3)$ 138.1, 133.9, 128.8, 127.6, 64.8, 40.7, 24.1, 14.8, 13.4, −4.9 and −5.0; *m/z* 207 (1%, M − Me), 137 (100, MePhSiOH) and 135 (100, Me_2PhSi) (Found: M^+ − Me, 207.1205. $C_{13}H_{22}OSi$ requires *M* − Me, 207.1205).

2-*Dimethyl(phenyl)silyl*-2-*methylpentan*-3-*ol* (20 mg, 12%). From the allylsilane **9** (166 mg) (BH_3·THF, 3 equiv., 0 °C, 2 h); $R_f(CH_2Cl_2)$ 0.50; ν_{max}(film)/cm^{-1} 3476 (OH), 1248 (SiMe) and 1108 (SiPh); $\delta_H(CDCl_3)$ 7.58–7.29 (5 H, m, Ph), 3.26 (1 H, dd, *J* 10.4 and 1.6, CHOH), 1.50 (2 H, m, CH_2Me), 1.20 (1 H, s, OH), 0.92 (3 H, t, *J* 7.3, CH_2Me), 0.92 (3 H, s, CMe_AMe_B), 0.86 (3 H, s, CMe_AMe_B), 0.34 (3 H, s, $SiMe_AMe_B$) and 0.33 (3 H, s, $SiMe_AMe_B$); $\delta_C(CDCl_3)$ 138.7, 134.6, 128.7, 127.6, 80.2, 27.2, 24.6, 21.1, 18.7, 11.3, −4.0 and −4.1; *m/z* 207 (0.4%, M − Et), 137 (55, MePhSiOH), 135 (80, Me_2PhSi) and 84 (100, M − Me_2PhSi) (Found: M^+ − Et, 207.1216. $C_{14}H_{24}OSi$ requires *M* − Et, 207.1205) together with the alcohol **52** (142 mg, 84%) identical (IR, ^{1}H NMR) with the authentic sample. With 9-BBN, the allylsilane (189 mg) gave only the alcohol **52** (201 mg, 98%).

(1RS,3SR)- *and* (1RS,3RS)-1-*Dimethyl(phenyl)silyl*-1-*phenylbutan*-3-*ols* **50** *and* **51** (80 mg, 75%). In a ratio 93:7 from the allylsilane **10** (100 mg) (BH_3·THF, 3 equiv., 0 °C, 10 h) $R_f(CH_2Cl_2)$ 0.24; identical (^{1}H NMR) with authentic samples, and a mixture of the alcohols **42** and **43** (21 mg, 20%); $R_f(CH_2Cl_2)$ 0.39; $\delta_H(CDCl_3)$ **42** 7.48–7.10 (10 H, m, 2 × Ph), 3.94 (1 H, dt, *J* 6.3 and 7.0, CHOH), 2.40 (1 H, d, *J* 6.3, SiCH), 1.50 (1 H, s, OH), 1.40–1.00 (2 H, m, CH_2), 0.81 (3 H, t, *J* 7.4, Me), 0.33 (3 H, s, $SiMe_AMe_B$) and 0.17 (3 H, s, $SiMe_AMe_B$); the ratio *anti*:*syn* was determined by stirring a portion of the mixture (10 mg) with potassium hydride (200 mg) in THF (2 cm^3) at room temp. for 1 h. Standard aqueous work-up followed by preparative TLC gave 1-phenylbut-1-ene[49] (*E*:*Z* 18:82) as determined by gas chromatography (R_t 4.60 and 5.30 min respectively). Another portion of the mixture (10 mg) was stirred with BF_3·OEt_2 (0.05 cm^3) in dichloromethane (2 cm^3) at 0 °C for 1 h. The solution was quenched with water (2 drops) and dried (Na_2SO_4). The *E*:*Z* ratio in the crude mixture was 81:19.

(1RS,2SR)-1-*Dimethyl(phenyl)silyl*-2-*methyl*-1-*phenylpropan*-3-*ol* **28** *and* (1RS,2RS)-1-*dimethyl(phenyl)silyl*-2-*methyl*-1-*phenylpropan*-3-*ol* **58**.[26] In a ratio of 70:30 from the allylsilane **12** (BH_3·THF, 3 equiv., 0 °C, 2 h) identical (^{1}H NMR) with authentic samples. With 9-BBN, the allylsilane

(154 mg, 9-BBN, 2 equiv., room temp., 2 h) gave only the alcohol **58** (158 mg, 97%).

1-*Dimethyl(phenyl)silyl*-3-*methylbutan*-2-*ol* (72 mg, 70%). From the allylsilane **13** (0.1 g) (BH_3·THF, 3 equiv., 0 °C, 2 h); $R_f(CH_2Cl_2)$ 0.18; ν_{max}(film)/cm^{-1} 3400 (OH), 1250 (SiMe) and 1123 (SiPh); $\delta_H(CDCl_3)$ 7.57–7.34 (5 H, m, Ph), 3.56 (1 H, dt, *J* 9.1 and 4.8, C*H*OH), 1.58 (1 H, d septet, *J* 4.8 and 6.8, C*H*Me_2), 1.27 (1 H, s, OH), 1.01 (3 H, d, *J* 4.8, CH*Me*$_A$Me$_B$), 0.99 (3 H, d, *J* 9.1, CHMe$_A$*Me*$_B$) and 0.35 (6 H, s, $SiMe_2$); $\delta_C(CDCl_3)$ 139.4, 133.5, 128.8, 127.7, 74.3, 35.9, 21.4, 18.5, 16.0, −2.2 and −2.5; *m*/*z* 207 (5%, M − Me), 137 (70, MePhSiOH) and 135 (100, Me_2PhSi) (Found: M^+ − Me, 207.1203. $C_{13}H_{22}OSi$ requires *M* − Me, 207.1205) together with the alcohol **53** (5 mg, 5%) identical (IR, ^1H NMR) with an authentic sample.

(2RS,3RS,4RS)-2-*Dimethyl(phenyl)silyl*-3-*methylpentan*-4-*ol* **68** (683 mg, 63%) *and* (2RS,3SR,4SR)-2-*dimethyl(phenyl)silyl*-3-*methylpentan*-4-*ol* **71** (139 mg, 13%). As an 81:19 mixture from the allylsilane **16** (1.0 g) (BH_3·THF, 3 equiv., 0 °C, 4 h) separated by chromatography (SiO_2, hexane–EtOAc, 3:1); **68** R_f(hexane–EtOAc, 3:1) 0.43; ν_{max}(film)/cm^{-1} 3350 (OH), 1245 (SiMe) and 1105 (SiPh); $\delta_H(CDCl_3)$ 7.55–7.31 (5 H, m, Ph), 3.59 (1 H, dq, *J* 6.3 and 6.2, C*H*OH), 1.57 (1 H, m, CHC*H*MeCH), 1.22 (1 H, m, CHSi), 1.07 (1 H, s, OH), 1.05 (3 H, d, *J* 6.2, CHOH*Me*), 1.00 (3 H, d, *J* 7.5, CHCH*Me*CH), 0.83 (3 H, d, *J* 7.0, SiCH*Me*), 0.33 (3 H, s, Si*Me*$_A$Me$_B$) and 0.30 (3 H, s, SiMe$_A$*Me*$_B$); $\delta_C(CDCl_3)$ 140.1, 133.8, 128.7, 127.7, 69.7, 44.2, 23.3, 20.2, 15.1, 13.3, −2.6 and −2.8; *m*/*z* 191 (1.2%, M − C_2H_5O), 137 (70, MePhSiOH) and 135 (100, Me_2PhSi) (Found: M^+ − C_2H_5O, 191.1253. $C_{14}H_{24}OSi$ requires *M* − C_2H_5O, 191.1256); **71** R_f(hexane–EtOAc, 3:1) 0.37; ν_{max}(film)/cm^{-1} 3380 (OH), 1245 (SiMe) and 1110 (SiPh); $\delta_H(CDCl_3)$ 7.55–7.31 (5 H, m, Ph), 3.58 (1 H, dq, *J* 8.2 and 6.2, C*H*OH), 1.57 (1 H, dqd, *J* 8.2, 7.0 and 2.6, CHC*H*MeCH), 1.46 (1 H, qd, *J* 7.6 and 2.6, SiCH), 1.37 (1 H, s, OH), 1.12 (3 H, d, *J* 6.2, CHOH*Me*), 0.92 (3 H, d, *J* 7.6, SiCH*Me*), 0.74 (3 H, d, *J* 7.0, CHCH*Me*CH) and 0.30 (6 H, s, $SiMe_2$); $\delta_C(CDCl_3)$ 139.0, 133.9, 128.8, 127.7, 69.9, 40.5, 21.3, 19.5, 13.1, 8.3, −3.7 and −3.9; *m*/*z* 191 (1.7%, M − C_2H_5O), 137 (40, MePhSiOH), 135 (100, Me_2PhSi) and 84 (65, C_5H_8O) (Found: M^+ − C_2H_5O, 191.1254. $C_{14}H_{24}OSi$ requires *M* − C_2H_5O, 191.1256).

(1RS,1′RS,2′RS)-2-(1-*Dimethyl(phenyl)silylethyl*)*cyclohexanol* **73** *and* (1RS,1′SR,2′SR)-2-(1-*Dimethyl(phenyl)silylethyl*)*cyclohexanol* **76**. As a 9:1 mixture from the allylsilane **17** (378 mg) (BH_3·THF, 3 equiv., 0 °C, 90 min) separated by chromatography (SiO_2, CH_2Cl_2); **73** (284 mg, 70%) $R_f(CH_2Cl_2)$ 0.37; ν_{max}(film)/cm^{-1} 3400 (OH), 1242 (SiMe) and 1116 (SiPh); $\delta_H(CDCl_3)$ 7.56–7.31 (5 H, m, Ph), 3.15 (1 H, td, *J* 9.7 and 4.5, C*H*OH), 1.85 (11 H, m, ring Hs, SiCH and OH), 1.03 (3 H, d, *J* 7.6, SiCH*Me*), 0.33 (3 H, s, Si*Me*$_A$Me$_B$) and 0.31 (3 H, s, SiMe$_A$*Me*$_B$); $\delta_C(CDCl_3)$ 140.1, 133.8, 128.6, 127.6, 72.1, 49.6, 36.3, 30.1, 26.1, 25.0, 22.1, 12.9, −2.6 and −2.9; *m*/*z* 247 (1.5%, M − Me), 137 (100, MePhSiOH), 135 (80, Me_2PhSi) and 110 (80, M − $Me_2PhSiOH$) (Found: M^+ − Me, 247.1533. $C_{16}H_{26}OSi$ requires *M* − Me, 247.1518); **76** (24 mg, 6%); $R_f(CH_2Cl_2)$ 0.29; ν_{max}(film)/cm^{-1} 3350 (OH), 1251 (SiMe) and 1112 (SiPh); $\delta_H(CDCl_3)$ 7.54–7.31 (5 H, m, Ph), 3.42 (1 H, td, *J* 9.8 and 4.3, C*H*OH), 2.0–1.0 (11 H, m, ring Hs, SiCH and OH), 0.93 (3 H, d, *J* 7.6, SiCH*Me*), 0.30 (3 H, s, Si*Me*$_A$Me$_B$) and 0.29 (3 H, s, SiMe$_A$*Me*$_B$); $\delta_C(CDCl_3)$ 139.1, 133.9, 128.7, 127.6, 70.6, 45.8, 36.0, 27.4, 26.0, 25.2, 18.4, 8.3, −3.6 and −3.7; *m*/*z* 247 (1%, M − Me), 137 (80, MePhSiOH) and 135 (100, Me_2PhSi) (Found: M^+ − Me, 247.1529. $C_{16}H_{26}OSi$ requires *M* − Me, 247.1518).

(1RS,2RS)-2-*Dimethyl(phenyl)silylcyclohexanol*. From the allylsilane **18** (218 mg) (BH_3·THF, 3 equiv., 2 h, 0 °C) followed by chromatography (SiO_2, CH_2Cl_2) of the 3:29:10:58 mixture of the alcohols **84**, this compound, **88** and **90** (226 mg, 96%); $R_f(CH_2Cl_2)$ 0.52; $\nu_{max}(CDCl_3)$ 3700 (OH), 1245 (SiMe) and 1105 (SiPh); $\delta_H(CDCl_3)$ 7.59–7.32 (5 H, m, Ph), 3.41 (1 H, td, *J* 10.3 and 4.1, C*H*OH), 2.0–0.8 (10 H, m, ring Hs and OH), 0.35 (3 H, s, Si*Me*$_A$Me$_B$) and 0.34 (3 H, s, SiMe$_A$*Me*$_B$); $\delta_C(CDCl_3)$ 138.0, 134.0, 127.7, 72.9, 37.7, 34.7, 26.6 (2), 25.0, −3.5 and −3.7; *m*/*z* 216 (3%, M − H_2O), 137 (100, MePhSiOH) and 135 (70, Me_2PhSi) (Found: M^+ − H_2O, 216.1320. $C_{14}H_{22}OSi$ requires *M* − H_2O, 216.1334). Treatment of this alcohol with sodium hydride in DMF did not give cyclohexene. The other components of the mixture were identified by the presence of characteristic peaks identifiable from the ^1H NMR spectra of authentic compounds.

(1RS,2SR,3RS)-3-*Dimethyl(phenyl)silyl*-2-*methylcyclohexanol* **96** *and* (1RS,2SR,3SR)-3-*dimethyl(phenyl)silyl*-2-*methylcyclohexanol* **98**. As a 4:1 mixture (250 mg, 88%) from the allylsilane **20** (263 mg) (BH_3·THF, 3 equiv., 0 °C, 2 h) separated by preparative TLC; **96** $R_f(CH_2Cl_2$–Et_2O, 4:1) 0.79; ν_{max}(film)/cm^{-1} 3650 (OH), 1260 (SiMe) and 1120 (SiPh); $\delta_H(CDCl_3)$ 7.52–7.31 (5 H, m, Ph), 3.61 (1 H, m, br 8.8, C*H*OH), 1.84–1.42 (9 H, m, ring Hs and OH), 0.90 (3 H, d, *J* 7.3, Me) and 0.28 (6 H, s, $SiMe_2$); $\delta_C(CDCl_3)$ 138.9, 133.8, 128.7, 127.6, 71.9, 36.3, 27.9, 23.0, 21.5, 21.2, 15.2, −3.5 and −3.7; *m*/*z* 248 (2%, M^+), 137 (30, MePhSiOH) and 135 (100, Me_2PhSi) (Found: M^+, 248.1589. $C_{15}H_{24}OSi$ requires *M*, 248.1596): **98**: $R_f(CH_2Cl_2$: Et_2O, 4:1) 0.65; ν_{max}(film)/cm^{-1} 3340 (OH), 1245 (SiMe) and 1110 (SiPh); $\delta_H(CDCl_3)$ 7.52–7.31 (5 H, m, Ph), 3.07 (1 H, dt, *J* 4.2 and 10, C*H*OH), 2.0–1.0 (7 H, m, ring Hs), 1.46 (1 H, s, OH), 0.95 (3 H, d, *J* 6.4, Me), 0.70 (1 H, ddd, *J* 9.6, 8.4 and 2.4, SiCH), 0.32 (3 H, s, Si*Me*$_A$Me$_B$) and 0.28 (3 H, s, SiMe$_A$*Me*$_B$); *m*/*z* 171 (2%, M − Ph), 170 (2, M − C_6H_6), 137 (50, MePhSiOH) and 135 (100, Me_2PhSi) (Found: M^+ − Ph, 171.1206. $C_{15}H_{24}OSi$ requires *M* − Ph, 171.1205).

(1RS,2RS,6SR)-2-*Dimethyl(phenyl)silyl*-6-*methylcyclohexanol* **100** (373 mg, 73%). From the allylsilane **21** (473 mg) (BH_3·THF, 3 equiv., 0 °C, 2 h) followed by preparative TLC; $R_f(CH_2Cl_2)$ 0.61; ν_{max}(film)/cm^{-1} 3462 (OH), 1245 (SiMe) and 1105 (SiPh); $\delta_H(CDCl_3)$ 7.58–7.34 (5 H, m, Ph), 3.00 (1 H, t, *J* 10, C*H*OH), 1.80–0.90 (9 H, m, ring Hs and OH), 0.94 (3 H, d, *J* 6.4, Me), 0.36 (3 H, s, Si*Me*$_A$Me$_B$) and 0.35 (3 H, s, SiMe$_A$*Me*$_B$); $\delta_C(CDCl_3)$ 139.1, 134.0, 128.8, 127.8, 78.7, 41.9, 34.4, 34.0, 27.4, 27.3, 18.7, −3.4 and −3.7; *m*/*z* 233 (1%, M − Me), 137 (100, MePhSiOH), 135 (95, Me_2PhSi) and 96 (30, M − MePhSiOH) (Found: M^+ − Me, 233.1356. $C_{15}H_{24}OSi$ requires *M* − Me, 233.1361).

(2RS,4SR)- *and* (2RS,4RS)-4-*Dimethyl(phenyl)silyl*-2-*methylpentan*-1-*ol* **62** *and* **63** (91 mg, 94%). From the homoallylic silane **61** (91 mg) (9-BBN, 2 equiv., room temp., 2 h) as an inseparable 3:1 mixture; $R_f(CH_2Cl_2)$ 0.35; ν_{max}(film)/cm^{-1} 3300 (OH), 1250 (SiMe) and 1110 (SiPh); $\delta_H(CDCl_3)$ 7.50–7.47 (2 H, *o*-Hs SiPh), 7.35–7.32 (3 H, m, *m*- and *p*-Hs SiPh), 3.50 (1 H, dd, *J* 10.6 and 4.4, CH_AH_BO, major isomer), 3.40 (1 H, d, *J* 1.6, CH_AH_BO, minor isomer), 3.38 (1 H, d, *J* 1.6, CH_AH_BO, minor isomer), 3.30 (1 H, dd, *J* 10.6 and 6.6, CH_AH_BO, major isomer), 1.80–1.20 (4 H, m, C*H*CH_2O, CH_2 and O*H*), 0.94 (4 H, s, SiCHMe), 0.87 (3 H, d, *J* 6.7, *Me*CHCHO, major isomer), 0.81 (3 H, d, *J* 6.6, *Me*CHCHO, minor isomer), 0.25 (3 H, s, Si*Me*$_A$Me$_B$) and 0.24 (3 H, s, SiMe$_A$*Me*$_B$); $\delta_C(CDCl_3)$ 138.4, 133.8, 128.8, 127.6, 69.1 (major), 67.0 (minor), 35.4 (major), 34.4 (minor), 33.5 (major), 33.2 (minor), 18.0 (major), 16.5 (major), 15.5 (minor), 15.3 (minor), 14.7 (major), 13.5 (minor), −4.9 (major), −5.1 (minor) and −5.2 (major); *m*/*z* 205 (1.5%, M − C_2H_5) and 135 (100, Me_2PhSi) (Found: M^+ − C_2H_5, 205.1045. $C_{14}H_{24}OSi$ requires *M* − C_2H_5, 205.1049). The ratio of isomers was determined by integration of several signals in the ^{13}C NMR spectrum.

1-*Dimethyl(phenyl)silylcyclopentanol* **85** (340 mg, 63%) *and*

(1RS,2RS)-2-*dimethyl(phenyl)silylcyclopentanol* **86** (70 mg, 13%). From the vinylsilane **79** (496 mg) (BH_3·THF, 3 equiv., 0 °C, 4 h) as an 84:16 mixture (533 mg, 99%) separated by chromatography (SiO_2, CH_2Cl_2); **85** R_f(CH_2Cl_2) 0.51; ν_{max}(film)/cm^{-1} 3560 (OH), 3440 (OH), 1250 (SiMe) and 1112 (SiPh); δ_H($CDCl_3$) 7.60–7.33 (5 H, m, Ph), 1.86–1.60 (8 H, m, ring Hs), 0.8 (1 H, s, OH) and 0.35 (6 H, s, $SiMe_2$); δ_C($CDCl_3$) 136.9, 134.3, 129.2, 127.8, 74.9, 37.6, 23.7 and −5.7; *m/z* 219 (0.5%, M − H), 205 (1, M − Me), 137 (40, MePhSiOH) and 135 (100, Me_2PhSi) (Found: M^+ − 219.1204. $C_{13}H_{20}OSi$ requires *M* − H, 219.1205); **86** R_f(CH_2Cl_2) 0.38; ν_{max}(film)/cm^{-1} 3530 (OH), 3300 (OH), 1590 (Ph), 1250 (SiMe) and 1110 (SiPh); δ_H($CDCl_3$) 7.55–7.33 (5 H, m, Ph), 4.18 (1 H, m, CHOH), 1.94–1.30 (7 H, m, ring Hs and OH), 1.19 (1 H, dt, *J* 5.4 and 9.0, SiCH), 0.30 (3 H, s, $SiMe_AMe_B$) and 0.29 (3 H, s, $SiMe_A*Me*_B$); δ_C($CDCl_3$) 138.2, 133.8, 129.0, 127.8, 76.1, 37.0, 35.4, 26.8, 24.1, −4.2 and −4.6; *m/z* 220 (0.2%, M^+), 137 (100, MePhSiOH) and 135 (90, Me_2PhSi) (Found: M^+, 220.1278. $C_{13}H_{20}OSi$ requires *M*, 220.1283). The ratio of isomers was determined by integration of the $SiMe_2$ signals in the ^1H NMR spectrum.

1-*Dimethyl(phenyl)silyl*-1,2-*epoxyethane*.—Dimethylvinyl(phenyl)silane[50] (1.84 g), *m*-chloroperbenzoic acid (5 g) and disodium orthophosphate (3.66 g) were stirred in dichloromethane (30 cm^3) at 0 °C for 18 h. Standard aqueous work-up and chromatography (SiO_2, CH_2Cl_2) gave the epoxide (0.7 g, 35%); R_f(CH_2Cl_2) 0.5; ν_{max}(film)/cm^{-1} 1592 (Ph), 1255 (SiMe) and 1221 (SiPh); δ_H($CDCl_3$) 7.58–7.37 (5 H, m, Ph), 2.93 (1 H, t, *J* 5.6, SiCH), 2.55 (1 H, dd, *J* 5.6 and 4.0, CH_AH_B), 2.38 (1 H, dd, *J* 5.6 and 4.0, CH_AH_B), 0.35 (3 H, s, $SiMe_AMe_B$) and 0.30 (3 H, s, $SiMe_A*Me*_B$).

1-*Dimethyl(phenyl)silylpropan*-2-*ol* **32**.—Chloromethyldimethyl(phenyl)silane[45] (2 g) in ether (5 cm^3) was added dropwise to magnesium turnings (0.27 g) in ether (5 cm^3) and refluxed for 2 h. Acetaldehyde (0.32 g) in ether (5 cm^3) was added to the mixture which was then stirred at room temperature for 4 h. Standard aqueous work-up and chromatography [SiO_2, Et_2O–light petroleum (b.p. 40–60 °C) 1:1] gave the alcohol[50] (1.01 g, 74%); R_f[Et_2O–light petroleum (b.p. 40–60 °C), 1:1] 0.38; ν_{max}(film)/cm^{-1} 3350 (OH), 1250 (SiMe) and 1113 (SiPh); δ_H($CDCl_3$) 7.70–7.30 (5 H, m, Ph), 4.01 (1 H, sextet, *J* 6.1, CHOH), 1.57 (1 H, s, OH), 1.21 (3 H, d, *J* 6.1, Me), 1.15 (2 H, dd, *J* 1.7 and 6.1, $SiCH_2$) and 0.38 (6 H, s, $SiMe_2$); δ_C($CDCl_3$) 139.0, 133.4, 128.8, 127.7, 65.9, 27.8, 26.6, −2.3 and −2.4; *m/z* 179 (2.5%, M − Me), 137 (100, MePhSiOH) and 135 (25, Me_2PhSi) (Found: M^+ − Me, 179.0886. $C_{11}H_{18}OSi$ requires *M* − Me, 179.0892).

1-*Dimethyl(phenyl)silylbutan*-2-*ol* **33**.—This was prepared in the same way, using propionaldehyde (0.63 g), to give the *alcohol* (1.1 g, 50%); R_f(hexane) 0.33; ν_{max}(film)/cm^{-1} 3400 (OH), 1251 (SiMe) and 1114 (SiPh); δ_H($CDCl_3$) 7.60–7.30 (5 H, m, Ph), 3.81 (1 H, m, OH), 3.75 (1 H, quintet, *J* 6.6, CHOH), 1.40 (2 H, m, CH_2Me), 1.11 (2 H, d, *J* 6.6, $SiCH_2$) and 0.38 (6 H, s, $SiMe_2$); δ_C($CDCl_3$) 139.3, 133.4, 128.8, 127.7, 71.0, 33.4, 25.0, 9.8, −2.2 and −2.4; *m/z* 193 (2%, M − Me), 137 (100, MePhSiOH) and 135 (55, Me_2PhSi) (Found: M^+ − Me, 193.1038. $C_{12}H_{20}OSi$ requires *M* − Me, 193.1048).

(1RS,2RS)-1-*Dimethyl(phenyl)silyl*-1,2-*epoxybutane* **34**.—*m*-Chloroperbenzoic acid (775 mg) in dichloromethane (10 cm^3) was stirred with the (*E*)-1-dimethyl(phenyl)silylbut-1-ene[50] (540 mg) in dichloromethane (10 cm^3) at 0 °C for 2 h. The solution was washed with aqueous sodium sulfite (10 cm^3), dried (Na_2SO_4) and evaporated under reduced pressure. Chromatography (SiO_2, CH_2Cl_2) to give the *epoxide* (0.40 g, 69%); R_f (CH_2Cl_2) 0.67; ν_{max}(film)/cm^{-1} 1259 (SiMe) and 1121 (SiPh); δ_H($CDCl_3$) 7.7–7.3 (5 H, m, Ph), 2.78 (1 H, dt, *J* 3.5 and 5.3, CH_2CHO), 2.16 (1 H, d, *J* 3.5, SiCH), 1.61 (2 H, m, CH_2), 1.02 (3 H, t, *J* 6.8, Me), 0.33 (3 H, s, $SiMe_AMe_B$) and 0.32 (3 H, s, $SiMe_A*Me*_B$); *m/z* 191 (18%, M − Me), 137 (32, MePhSiOH) and 135 (100, Me_2PhSi) (Found: M^+ − Me, 191.0892. $C_{12}H_{18}OSi$ requires *M* − Me, 191.0891).

(1RS,2RS)-2-*Dimethyl(phenyl)silylpentan*-3-*ol* **23**.—Following Hudrlik,[22] the epoxide **34** (49 mg, 0.23 mmol) in ether (1 cm^3) was stirred with lithium dimethylcuprate (0.35 mmol) at −15 °C for 4 h. Standard aqueous work-up and preparative TLC (CH_2Cl_2) gave the *alcohol* (26 mg, 54%); R_f(CH_2Cl_2) 0.33; ν_{max}(film)/cm^{-1} 3400 (OH), 1245 (SiMe) and 1121 (SiPh); δ_H($CDCl_3$) 7.5–7.3 (5 H, m, Ph), 3.52 (1 H, ddd, *J* 3, 6 and 10, CHOH), 1.56–1.49 (1 H, m, SiCH), 1.25 (2 H, m, CH_2), 0.94 (3 H, t, *J* 7.2, CH_2Me), 0.33 (3 H, s, $SiMe_AMe_B$) and 0.32 (3 H, s, $SiMe_A*Me*_B$); *m/z* 204 (0.3%, MH_2O), 137 (100, MePhSiOH) and 135 (35, Me_2PhSi)(Found: M^+ −H_2O, 204.1335. $C_{13}H_{22}OSi$ requires *M* −H_2O, 204.1334).

(E)-1-*Dimethyl(phenyl)silyl*-3-*methylbut*-1-*ene*.—1-Bromo-3-methylbuta-1,2-diene[51] (7.8 g) was stirred with a slurry of lithium aluminium hydride (1 g) in freshly distilled 2-(2-ethoxy)ethanol (20 cm^3) at room temperature overnight. The isopropylacetylene, thus generated, was stirred with the silylcuprate reagent[50] (15 mmol) at −20 °C for 1 h. Standard aqueous work-up and chromatography (SiO_2, hexane) gave the *vinylsilane* (2.36 g, 77%); R_f(hexane) 0.66; ν_{max}(film)/cm^{-1} 1610 (C=C), 1260 (SiMe) and 1115 (SiPh); δ_H($CDCl_3$) 7.56–7.32 (5 H, m, Ph), 6.11 (1 H, dd, *J* 5.8 and 18.7, SiCH), 5.70 (1 H, dd, *J* 1.3 and 18.7, SiCHCH), 2.30 (1 H, m, $CHMe_2$), 1.01 (6 H, d, *J* 6.8, $CHMe_2$) and 0.32 (6 H, s, $SiMe_2$); δ_C($CDCl_3$) 156.0, 139.5, 133.9, 128.8, 127.7, 123.4, 34.4, 21.8 and −2.4; *m/z* 204 (4%, M^+), 189 (60, M − Me), 161 (70, M − C_3H_7) and 135 (100, Me_2PhSi) (Found: M^+, 204.1316. $C_{13}H_{20}Si$ requires *M*, 204.1334).

(1RS,2RS)-1-*Dimethyl(phenyl)silyl*-3-*methyl*-1,2-*epoxybutane* **35**.—This was prepared in the same way as the epoxide **39** from (*E*)-1-dimethyl(phenyl)silyl-3-methylbut-1-ene (740 mg) to give the *epoxide* (688 mg, 86%); R_f[light petroleum (b.p. 30–40 °C)–Et_2O, 10:1] 0.78; ν_{max}(film)/cm^{-1} 1262 (SiMe) and 1130 (SiPh); δ_H($CDCl_3$) 7.58–7.32 (5 H, m, Ph), 2.57 (1 H, dd, *J* 3.5 and 6.9, SiCHCH), 2.20 (1 H, d, *J* 3.5, SiCH), 1.03 (3 H, d, *J* 6.7, $CHMe_AMe_B$) and 0.89 (23 H, d, *J* 6.7, $CHMe_A*Me*_B$), 0.33 (3 H, s, $SiMe_AMe_B$) and 0.29 (3 H, s, $SiMe_A*Me*_B$); δ_C($CDCl_3$) 136.4, 133.7, 129.5, 127.9, 61.7, 49.9, 32.3, 19.4, 18.3, −5.1 and −5.2; *m/z* 205 (18%, M^+ − Me), 137 (30, MePhSiOH) and 135 (100, Me_2PhSi) (Found: M^+ − Me, 205.1030. $C_{13}H_{20}OSi$ requires *M* − Me, 205.1049).

(1RS,2RS)-2-*Dimethyl(phenyl)silyl*-4-*methylpentan*-3-*ol* **36**.—This was prepared in the same way as the alcohol **22** from the epoxide (307 mg), to give the *alcohol* (309 mg, 94%); R_f(CH_2Cl_2) 0.65; ν_{max}(film)/cm^{-1} 3600 (OH), 1260 (SiMe) and 1120 (SiPh); δ_H($CDCl_3$) 7.60–7.32 (5 H, m, Ph), 3.30 (1 H, dd, *J* 9.0 and 3.5, CHOH), 1.80 (1 H, d, septet, *J* 11.2 and 5.6, $CHMe_2$), 1.21 (1 H, m, SiCH), 0.92 (3 H, d, *J* 5.6, $CHMe_AMe_B$) and 0.89 (3 H, d, *J* 5.6, $CHMe_A*Me*_B$), 0.80 (3 H, d, *J* 6.8, $SiCHMe$), 0.36 (3 H, s, $SiMe_AMe_B$) and 0.34 (3 H, s, $SiMe_A*Me*_B$); δ_C($CDCl_3$) 139.6, 133.9, 128.6, 127.6, 80.1, 30.2, 25.0, 20.1, 14.3, 12.8, −3.2 and −3.1; *m/z* 193 (0.6%, M^+ − C_3H_7), 137 (100, MePhSiOH) and 135 (80, Me_2PhSi) (Found: M^+ − C_3H_7, 193.1051. $C_{14}H_{24}OSi$ requires *M* −C_3H_7, 193.1049).

1-*Dimethyl(phenyl)silylbut*-1-*yne* **37**.—Butyllithium (1.6 mol dm^{-3} solution in hexane; 33 cm^3) was stirred with but-1-yne (4.2 cm^3) in THF (50 cm^3) at 0 °C for 30 min. Chlorodimethyl(phenyl)silane (7.5 cm^3) was added to the mixture which was

then refluxed for 18 h. Standard aqueous work-up and distillation gave the *silane* (8.13 g, 86%); b.p. 116–118 °C/17 mmHg; ν_{max}(film)/cm^{-1} 2190 (C≡C), 1250 (SiMe) and 1120 (SiPh); δ_H($CDCl_3$) 7.7–7.3 (5 H, m, Ph), 2.30 (2 H, q, *J* 7, C*H*$_2$Me), 1.18 (3 H, t, *J* 7, CH$_2$*Me*) and 0.40 (6 H, s, SiMe$_2$); δ_C($CDCl_3$) 137.6, 133.6, 129.2, 127.8, 110.8, 81.4, 13.7 and −0.7; *m*/*z* 188 (27%, M$^+$) and 173 (100, M − Me) (Found: M$^+$, 188.1024. $C_{12}H_{16}Si$ requires *M*, 188.1021).

(*Z*)-*Dimethyl*(*phenyl*)*silylbut*-1-*ene*.—The butynylsilane **37** (1.5 g) in methanol (10 cm^3) was stirred with palladium (10% on $BaSO_4$; 0.15 g) and quinoline (4.5 cm^3) under hydrogen at 1 atm for 3 h. The catalyst was filtered off and the filtrate evaporated under reduced pressure. Chromatography (SiO_2, hexane) gave the *vinylsilane* (1.2 g, 80%); R_f(hexane) 0.43; ν_{max}(film)/cm^{-1} 1600 (C=C), 1250 (SiMe) and 1120 (SiPh); δ_H($CDCl_3$) 7.7–7.3 (5 H, m, Ph), 6.46 (1 H, dt, *J* 7 and 15, SiCH=C*H*), 5.62 (1 H, dt, *J* 15 and 1.1, SiC*H*=CH), 2.10 (2 H, dqd, *J* 1.1, 7 and 7.4, C*H*$_2$Me), 0.95 (3 H, t, *J* 7, CH$_2$*Me*) and 0.40 (6 H, s, SiMe$_2$); δ_C($CDCl_3$) 152.7, 139.9, 133.9, 129.0, 128.0, 126.2, 27.4, 14.2 and −0.3; *m*/*z* 190 (47%, M$^+$) and 175 (100, M − Me) (Found: M$^+$, 190.1169. $C_{12}H_{18}Si$ requires *M*, 190.1178).

1-*Dimethyl*(*phenyl*)*silyl*-3-*methylbut*-1-*yne* **38**.—Following Corey,[52] butyllithium (0.3 mol dm^{-3} solution in ether; 50 cm^3) was added to TMEDA (2.3 cm^3) at −15 °C and this was followed by the addition of the butynylsilane **37** (2 g). After the mixture had been stirred at −15 °C for 4 h methyl iodide (3 cm^3) was added to it and stirring continued at −15 °C for a further 6 h. Standard aqueous work-up and chromatography [SiO_2, light petroleum (b.p. 40–60 °C)] gave the *ethynylsilane* (0.85 g, 40%); R_f[light petroleum (b.p. 40–60 °C)] 0.30; ν_{max}(film)/cm^{-1} 2160 (C≡C), 1248 (SiMe) and 1115 (SiPh); δ_H($CDCl_3$) 7.66–7.34 (5 H, m, Ph), 2.66 (1 H, septet, *J* 6.9, C*H*Me$_2$), 1.20 (6 H, d, *J* 6.9, CH*Me*$_2$) and 0.38 (6 H, s, SiMe$_2$); δ_C($CDCl_3$) 137.9, 133.7, 129.2, 127.8, 115.1, 80.8, 22.9, 21.6 and −0.5; *m*/*z* 202 (13%, M$^+$) and 135 (100, Me$_2$PhSi) (Found: M$^+$, 202.1186. $C_{13}H_{18}Si$ requires *M*, 202.1178).

(*Z*)-1-*Dimethyl*(*phenyl*)*silyl*-3-*methylbut*-1-*ene*.—The ethynylsilane **38** (0.2 g) in THF (0.5 cm^3) was stirred with a slurry of dicyclohexylborane (1.5 mmol) in THF at room temp. for 2 h. Glacial acetic acid (0.12 cm^3) was added to the mixture which was then stirred for a further 2 h. The mixture was diluted with water (5 cm^3) and the organic layer washed with aqueous sodium hydrogen carbonate (20 cm^3), dried (Na_2SO_4) and evaporated under reduced pressure. Chromatography [SiO_2, light petroleum (b.p. 30–40 °C)] gave the *vinylsilane* (92 mg, 46%); R_f[light petroleum (b.p. 30–40 °C)] 0.78; ν_{max}(film)/cm^{-1} 1605 (C=C), 1260 (SiMe) and 1125 (SiPh); δ_H($CDCl_3$) 7.56–7.31 (5 H, m, Ph), 6.19 (1 H, dd, *J* 10.1 and 13.8, SiCH=C*H*), 5.48 (1 H, d, *J* 13.8, SiCH), 2.37 (1 H, d septet, *J* 13.8 and 6.6, C*H*Me$_2$), 0.87 (6 H, d, *J* 6.6, CH*Me*$_2$) and 0.36 (6 H, s, SiMe$_2$); *m*/*z* 204 (3%, M$^+$), 189 (40, M − Me), 161 (65, M − C_3H_7) and 135 (100, Me$_2$PhSi) (Found: M$^+$, 204.1337. $C_{13}H_{20}Si$ requires *M*, 204.1334).

(1RS,2SR)-1-*Dimethyl*(*phenyl*)*silyl*-1,2-*epoxybutane* **39**.—This was prepared in the same way as the epoxide **34** from (*Z*)-1-dimethyl(phenyl)silylbutene (0.6 g) to give the *epoxide* (0.62 g, 95%); R_f (light petroleum–Et_2O, 19:1) 0.25; ν_{max}(film)/cm^{-1} 1260 (SiMe) and 1120 (SiPh); δ_H($CDCl_3$) 7.7–7.3 (5 H, m, Ph), 3.10 (1 H, dt, *J* 5 and 5, CH$_2$C*H*O), 2.40 (1 H, d, *J* 5, SiCH), 1.41 (2 H, m, CH$_2$), 0.98 (3 H, t, *J* 7, CH$_2$*Me*) and 0.40 (6 H, s, SiMe$_2$); *m*/*z* 191 (12%, M − Me) and 135 (100, Me$_2$PhSi) (Found: M$^+$ − Me, 191.0891. $C_{12}H_{18}OSi$ requires *M* − Me, 191.0891).

(1RS,2SR)-2-*Dimethyl*(*phenyl*)*silylpentan*-3-*ol* **22**.—This was prepared in the same way as the alcohol **23** from the epoxide **39** (65 mg, 0.32 mmol) with lithium dimethylcuprate (0.47 mmol) to give the *alcohol* (46 mg, 65%); R_f(CH_2Cl_2) 0.33; ν_{max}(film)/cm^{-1} 3300 (OH), 1248 (SiMe) and 1121 (SiPh); δ_H($CDCl_3$) 7.6–7.3 (5 H, m, Ph), 3.67 (1 H, dt, *J* 6 and 3, C*H*OH), 1.48 (2 H, m, CH$_2$), 1.17 (1 H, br s, OH), 1.08 (1 H, dt, *J* 3 and 7, SiCH), 0.97 (3 H, d, *J* 7.1, SiCH*Me*), 0.86 (3 H, t, *J* 7.4, CH$_2$*Me*), 0.33 (3 H, s, Si*Me*$_A$Me$_B$) and 0.32 (3 H, s, SiMe$_A$*Me*$_B$); *m*/*z* 204 (0.17%, M − H_2O), 137 (100, MePhSiOH), 135 (60, Me$_2$PhSi) and 70 (40, C_5H_{10}) (Found: M$^+$ − H_2O, 204.1353. $C_{13}H_{22}OSi$ requires *M* − H_2O, 204.1334).

(1RS,2SR)-1-*Dimethyl*(*phenyl*)*silyl*-3-*methyl*-1,2-*epoxybutane* **40**.—This was prepared in the same way as the epoxide **34** from (*Z*)-1-dimethyl(phenyl)silyl-3-methylbutene (190 mg) to give the *epoxide* (165 mg, 81%); R_f(CH_2Cl_2) 0.68; ν_{max}(film)/cm^{-1} 1262 (SiMe) and 1130 (SiPh); δ_H($CDCl_3$) 7.59–7.35 (5 H, m, Ph), 2.79 (1 H, dd, *J* 5.1 and 9.1, SiCHC*H*), 2.43 (1 H, d, *J* 5.1, SiCH), 1.24 (1 H, br m, C*H*Me$_2$), 1.02 (3 H, d, *J* 6.7, CH*Me*$_A$Me$_B$), 0.85 (3 H, d, *J* 6.7, CHMe$_A$*Me*$_B$), 0.40 (3 H, s, Si*Me*$_A$Me$_B$) and 0.38 (3 H, s, SiMe$_A$*Me*$_B$); *m*/*z* 205 (11%, M − Me), 137 (30, MePhSiOH) and 135 (100, Me$_2$PhSi) (Found: M$^+$ − Me, 205.1065. $C_{13}H_{20}OSi$ requires *M* − Me, 205.1049).

(3RS,2SR)-2-*Dimethyl*(*phenyl*)*silyl*-4-*methylpentan*-3-*ol* **41**.—This was prepared in the same way as the alcohol **22** from the epoxide **40** (165 mg), except that 50 h were required for complete reaction, to give the *alcohol* (125 mg, 70%); R_f(CH_2Cl_2) 0.52; ν_{max}(film)/cm^{-1} 3500 (OH), 1260 (SiMe) and 1125 (SiPh); δ_H($CDCl_3$) 7.57–7.32 (5 H, m, Ph), 3.29 (1 H, dd, *J* 8.6 and 2.9, C*H*OH), 1.74 (2 H, m, C*H*Me$_2$), 1.22 (1 H, m, SiCH), 0.95 (3 H, d, *J* 6.6, CH*Me*$_A$Me$_B$), 0.92 (3 H, d, *J* 6.6, CHMe$_A$*Me*$_B$), 0.79 (3 H, d, *J* 6.7, SiCH*Me*) and 0.33 (6 H, s, SiMe$_2$); δ_C($CDCl_3$) 138.8, 134.0, 128.9, 127.8, 78.4, 31.7, 23.3, 19.4, 19.1, 7.3, −3.92 and −3.94; *m*/*z* 218 (0.2%, M − H_2O), 137 (55, MePhSiOH) and 135 (100, Me$_2$PhSi) (Found: M$^+$ − H_2O, 218.1492. $C_{14}H_{24}OSi$ requires *M* − H_2O, 218.1492).

Reduction of the Silyl Ketone **46**.—The silyl ketone (229 mg) was stirred with sodium borohydride (300 mg) in methanol (5 cm^3) at 0 °C for 30 min. Standard aqueous work-up gave a 23:77 mixture of the alcohols **24** and **25** (225 mg, 97%). The ratio of the isomers was determined by integration of the CHOH*Me* signals in the ^{1}H NMR spectrum.

(1RS,3SR)- *and* (1RS,3RS)-1-*Dimethyl*(*phenyl*)*silyl*-1-*phenylbutan*-3-*ol* **50** *and* **51**.—Sodium borohydride (0.5 g) in ethanol (5 cm^3) was stirred with the ketone **47**[53] (1.03 g) at 0 °C for 2 h. Standard aqueous work-up gave a 1:1 mixture (1.03 g, 100%) of the *alcohols*; **50** R_f(CH_2Cl_2) 0.24; ν_{max}(film)/cm^{-1} 3200 (OH), 1600 (Ph), 1500 (Ph), 1260 (SiMe) and 1125 (SiPh); δ_H($CDCl_3$) 7.4–6.9 (10 H, m, 2 × Ph), 3.62 (1 H, m, C*H*OH), 2.26 (1 H, dd, *J* 12.5 and 3.0, SiCH), 2.10 (1 H, dt, *J* 12.5 and 5, C*H*$_A$H$_B$), 1.68 (1 H, ddd, *J* 12.5, 7.9 and 3.0, CH$_A$*H*$_B$), 1.30 (1 H, br s, OH), 1.05 (3 H, d, *J* 6.2, CH*Me*), 0.25 (3 H, s, Si*Me*$_A$Me$_B$) and 0.17 (3 H, s, SiMe$_A$*Me*$_B$); δ_C($CDCl_3$) 142.2, 137.1, 134.1, 129.2, 128.3, 127.8, 127.6, 124.8, 67.9, 38.9, 33.9, 22.3, −4.0 and −5.5; *m*/*z* 269 (0.5%, M$^+$ − Me), 135 (100, Me$_2$PhSi), 130 (90, PhC_4H_7) and 117 (100, PhC_3H_4) (Found: M$^+$ − Me, 269.1363. $C_{18}H_{24}OSi$ requires *M* − Me, 269.1362); **51** R_f(CH_2Cl_2) 0.28; ν_{max}(film)/cm^{-1} 3300 (OH), 1600 (Ph), 1495 (Ph), 1245 (SiMe) and 1125 (SiPh); δ_H($CDCl_3$) 7.4–6.9 (10 H, m, 2 × Ph), 3.56 (1 H, dqd, *J* 9.6, 6.2 and 2.8, C*H*OH), 2.57 (1 H, dd, *J* 12.8 and 3.2, SiCH), 1.89 (1 H, ddd, *J* 14.3, 12.8 and 2.8, C*H*$_A$H$_B$), 1.67 (1 H, ddd, *J* 14.3, 9.6 and 3.2, CH$_A$*H*$_B$), 1.30 (1 H, br s, OH), 1.07 (3 H, d, *J* 6.2, CH*Me*), 0.24 (3 H, s, Si*Me*$_A$Me$_B$) and 0.18 (3 H, s, SiMe$_A$*Me*$_B$); δ_C($CDCl_3$) 142.2, 137.2, 134.1, 129.0, 128.1,

128.0, 127.6, 124.7, 65.5, 38.5, 32.3, 23.9, −4.0 and −5.3; *m/z* 269 (0.2%, M^+ − Me), 137 (20, MePhSiOH), 135 (98, Me_2PhSi), 130 (90, PhC_4H_7) and 117 (100, PhC_3H_4) (Found: M^+ − Me, 269.1381. $C_{18}H_{24}OSi$ requires *M* − Me, 269.1362). The ratio of isomers was determined by integration of the $SiCHCH_2$ signals in the ^1H NMR spectrum.

2-Dimethyl(phenyl)silyl-2-methylpentan-4-ol **52**.—Sodium borohydride (0.25 g) was stirred with the ketone **48**[53] (0.36 g) in methanol (10 cm^3) at 0 °C for 15 min, quenched with dilute hydrochloric acid (20 cm^3) and extracted with ether (2 × 30 cm^3). The extracts were washed with aqueous sodium hydrogen carbonate (30 cm^3), dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by chromatography (SiO_2, CH_2Cl_2) to give the *alcohol* (0.33 g, 91%); $R_f(CH_2Cl_2)$ 0.23; ν_{max}(film)/cm^{-1} 3400 (OH), 1250 (SiMe) and 1120 (SiPh); $\delta_H(CDCl_3)$ 7.54–7.31 (5 H, m, Ph), 3.96 (1 H, m, C*H*OH), 1.46 (1 H, dd, *J* 14.5 and 7.2, CH_AH_B), 1.37 (1 H, dd, *J* 14.5 and 3.8, CH_AH_B), 1.22 (1 H, s, OH), 1.12 (3 H, d, *J* 6.2, CHOH*Me*), 1.02 (3 H, s, CMe_AMe_B), 0.96 (3 H, s, CMe_AMe_B) and 0.29 (6 H, s, $SiMe_2$); $\delta_C(CDCl_3)$ 137.5, 134.5, 128.7, 127.4, 64.9, 47.4, 26.0, 23.6, 23.3, 19.5, −5.88 and −5.89; *m/z* 221 (0.03%, M − Me), 137 (60, MePhSiOH), 135 (100, Me_2PhSi) and 84 (99, M − $Me_2PhSiOH$) (Found: M^+ − Me, 221.1372. $C_{14}H_{24}OSi$ requires *M* − Me, 221.1362).

4-Dimethyl(phenyl)silyl-2-methylbutan-2-ol **53**.—Methyllithium (2.7 mol dm^{-3} solution in hexane; 0.6 cm^3) was stirred with the ester **49**[54] (0.1 g) in ether (5 cm^3) at room temp. for 2 h. Standard aqueous work-up and preparative TLC (CH_2Cl_2) gave the *alcohol* (48 mg, 48%); $R_f(CH_2Cl_2)$ 0.18; ν_{max}(film)/cm^{-1} 3300 (OH), 1247 (SiMe) and 1121 (SiPh); $\delta_H(CDCl_3)$ 7.60–7.30 (5 H, m, Ph), 1.80–1.20 (1 H, br s, OH), 1.45 (2 H, m, $SiCH_2CH_2$), 1.19 (6 H, s, CMe_2), 0.75 (2 H, m, $SiCH_2$) and 0.28 (6 H, s, $SiMe_2$); *m/z* (8%, M − Me), 137 (92, MePhSiOH) and 135 (100, Me_2PhSi) (Found: M^+ − Me, 207.1208. $C_{13}H_{22}OSi$ requires *M* − Me, 207.1205).

Benzoylation of Alcohols.—Typically, the alcohol (1 mmol) was stirred with benzoic anhydride (1.2 mmol) and DMAP (0.3 mmol) in triethylamine (1.7 mmol) at room temperature for 3–4 h. A standard aqueous work-up and chromatography (SiO_2, CH_2Cl_2) gave the benzoates.

Conversion of the Phenyldimethylsilyl Group into a Hydroxy Group.—*Method A*. Boron trifluoride-acetic acid complex (1.2 mmol) was stirred with the silane (1 mmol) in dichloromethane (5 cm^3) for 3 h. Aqueous sodium hydrogen carbonate was added to the mixture which was then extracted with ether. The extracts were washed with brine, dried (Na_2SO_4) and evaporated under reduced pressure. Peracetic acid (15% solution in acetic acid; 4 cm^3) was added to the residue and the solution cooled to 0 °C. Triethylamine (1.4 mmol) was added to the mixture which was then stirred at room temp. for 18 h. After addition of ether the organic layer was washed with aqueous sodium thiosulfate and aqueous sodium hydrogen carbonate, dried (Na_2SO_4) and evaporated under reduced pressure. The residue was generally purified by chromatography.

Method B. Potassium bromide (1.2 mmol) and anhydrous sodium acetate (3.1 mmol) were added to the silane (1 mmol) in glacial acetic acid (2.5 cm^3) after which peracetic acid (15% solution in acetic acid; 2.5 cm^3) was added dropwise to the mixture. Further sodium acetate (0.77 g) and peracetic acid (7.7 cm^3) were added and the resulting turbid mixture was stirred at room temperature for 18 h and then at 35 °C for 1 h. The solvent was evaporated under reduced pressure and ether (50 cm^3) added to the residue. The solution was filtered and evaporated under reduced pressure and chromatography of the residue gave the alcohol.

Method C. Mercuric acetate (1.5 mmol) was added to a solution of the silane (1 mmol) in peracetic acid (15% solution in acetic acid; 11 cm^3) and the mixture stirred at room temp. for 3 h. A similar work-up to that of method B gave the alcohol.

The following compounds were prepared either by this method of benzoylation or/and one of these methods of silyl-to-hydroxy conversion.

(2RS,3SR)-2-*Methyl*-1-*phenylpropane*-1,3-*diol* **29**[28] (86 mg, 70%). From the silyl alcohol **28** (210 mg) by method C; $R_f(Et_2O)$ 0.45; ν_{max}(film)/cm^{-1} 3300 (OH); $\delta_H(CDCl_3)$ 7.46–7.22 (5 H, m, Ph), 4.94 (1 H, d, *J* 3.9, PhC*H*OH), 3.66 (2 H, m, CH_2OH), 2.50 (2 H, s, 2 × OH), 2.07 (1 H, m, C*H*Me) and 0.85 (3 H, d, *J* 7.1, CH*Me*).

(2RS,4RS)-4-*Dimethyl(phenyl)silylpentan*-2-*yl benzoate* (0.25 g, 85%). By benzoylation of the alcohol **24** (0.2 g); $R_f(CH_2Cl_2)$ 0.72; ν_{max}(film)/cm^{-1} 1700 (C=O), 1275 (SiMe) and 1120 (SiPh); $\delta_H(CDCl_3)$ 8.1–7.3 (10 H, m, 2 × Ph), 5.22 (2 H, dd, *J* 6.0 and 6.1, C*H*OH), 1.60 (2 H, m, CH_2), 1.28 (3 H, d, *J* 6.2, CHOH*Me*), 1.20–1.01 (1 H, br m, SiCH), 1.03 (3 H, s, SiCH*Me*), 0.27 (3 H, s, $SiMe_AMe_B$) and 0.26 (3 H, s, $SiMe_AMe_B$); *m/z* 311 (0.6%, M − Me) and 135 (100, Me_2PhSi) (Found: M^+ − Me, 311.1451. $C_{20}H_{26}O_2Si$ requires *M* − Me, 311.1467).

(2RS,4RS)-*Pentane*-2,4-*diol monobenzoate* (0.24 g, 74%). From the benzoate (0.57 g) of the silane **24** by method B with preparative TLC (hexane–Et_2O, 1:1); R_f(hexane–ether, 1:1) 0.40; ν_{max}(film)/cm^{-1} 3400 (OH), 1700 (C=O), 1600 (Ph) and 1580 (Ph); $\delta_H(CDCl_3)$ 8.1–7.4 (5 H, m, Ph), 5.42 (1 H, m, C*H*OBz), 3.77 (1 H, m, C*H*OH), 3.02 (1 H, s, OH), 1.72 (2 H, m, CH_2), 1.39 (3 H, d, *J* 6.2, *Me*CHOBz) and 1.18 (3 H, d, *J* 6.2, CHOH*Me*); *m/z* 193 (1%, M − Me) and 105 (100, PhCO) (Found: M^+ − Me, 193.0876. $C_{12}H_{16}O_3$ requires *M* − Me, 193.0864).

(2RS,4RS)-*Pentane*-2,4-*diyl dibenzoate* **54**[24] (48%). By benzoylation of the alcohol, derived from the benzoate of the silyl compound **24**, identical (IR, ^1H NMR) with a sample prepared (91%) from an authentic sample of (2*RS*,4*RS*)-pentane-2,4-diol, kindly provided by Dr Alethea Tabor; $R_f(CH_2Cl_2)$ 0.60; ν_{max}(film)/cm^{-1} 1750 (C=O); $\delta_H(CDCl_3)$ 8.0–7.3 (10 H, m, 2 × Ph), 5.31 (2 H, sextet, *J* 6.3, 2 × C*H*OBz), 2.09 (2 H, t, *J* 6.3, CH_2) and 1.41 (6 H, d, *J* 6.3, 2 × CH*Me*); $\delta_C(CDCl_3)$ 165.9, 132.7, 130.6, 129.5, 128.2, 68.4, 42.4 and 20.5; *m/z* 190 (6%, M − $PhCO_2H$) and 105 (100, PhCO) (Found: M^+ − $PhCO_2H$, 190.1022. $C_{19}H_{20}O_4$ requires *M* − $PhCO_2H$, 190.0994).

(2RS,4SR)-4-*Dimethyl(phenyl)silylpentan*-2-*yl benzoate* (156 mg, 82%). By benzoylation of the alcohol **25** (130.4 mg); $R_f(CH_2Cl_2)$ 0.75; ν_{max}(film)/cm^{-1} 1705 (CO), 1280 (SiMe) and 1120 (SiPh); $\delta_H(CDCl_3)$ 8.02–7.97 (2 H, m, *o*-Hs PhCO), 7.50–7.30 (8 H, m, *m*- and *p*-Hs PhCO and SiPh), 5.29 (1 H, m, CHO), 1.88 (1 H, m, CH_AH_B), 1.31 (1 H, m, CH_AH_B), 1.28 (3 H, d, *J* 6.2, CHOBz*Me*), 0.98 (4 H, m, SiCHMe), 0.27 (3 H, s, $SiMe_AMe_B$) and 0.25 (3 H, s, $SiMe_AMe_B$); *m/z* 311 (1%, M − Me) and 135 (100, Me_2PhSi) (Found: M^+ − Me, 311.1471. $C_{20}H_{26}O_2Si$ requires *M* − Me, 311.1467).

(2RS,4SR)-*Pentane*-2,4-*diol monobenzoate* (83 mg, 90%). From the benzoate (144 mg) of the silane **25** by method B; $R_f(CH_2Cl_2)$ 0.20; ν_{max}(film)/cm^{-1} 3400 (OH), 1710 (CO), 1604 (Ph), 1585 (Ph) and 1490 (Ph); $\delta_H(CDCl_3)$ 8.06–8.00 (2 H, m, *m*-Hs Ph), 7.58–7.51 (1 H, m, *p*-H Ph), 7.47–7.39 (2 H, m, *o*-Hs Ph), 5.28 (1 H, m, C*H*OBz), 3.97 (1 H, m, C*H*OH), 1.85 (1 H, s, OH), 2.01 (1 H, dt, *J* 14.2 and 7.7, CH_AH_B), 1.71 (1 H, dt, *J* 14.2 and 5.2, CH_AH_B), 1.39 (3 H, d, *J* 6.3, *Me*CHOBz) and 1.23 (3 H, d, *J* 6.2, CHOH*Me*); *m/z* 209 (0.1%, M + H), 193 (1 M − Me), 105 (100, PhCO) and 186 (70, M − $PhCO_2H$) (Found: M^+ + H, 209.1159. $C_{12}H_{16}O_3$ requires *M* + H, 209.1177).

(2RS,4SR)-*Pentane*-2,4-*diyl dibenzoate* **55**[24] (62 mg, 99%). By

benzoylation of the alcohol (42 mg) derived from the benzoate of the silyl compound **25**; $R_f(CH_2Cl_2)$ 0.42; ν_{max}(film)/cm^{-1} 1710 (CO), 1603 (Ph), 1585 (Ph) and 1490 (Ph); $\delta_H(CDCl_3)$ 8.05–8.00 (4 H, m, *o*-Hs Ph), 7.56–7.49 (2 H, *m*- and *p*-Hs Ph), 7.43–7.36 (4 H, m, *m*-Hs Ph), 5.32 (2 H, m, CHO), 2.33 (2 H, dt, *J* 14.2 and 7.2, CH_AH_B), 1.90 (2 H, dt, *J* 14.2 and 5.7, CH_AH_B) and 1.40 (6 H, d, *J* 6.3, 2 × Me); $\delta_C(CDCl_3)$ 166.0, 132.8, 130.5, 129.5, 128.3, 66.8, 42.0 and 20.3; *m/z* 207 (1.1%, M − PhCO), 190 (8, M − $PhCO_2H$) and 105 (100, PhCO) (Found: M^+ − PhCO, 207.1014. $C_{19}H_{20}O_4$ requires *M* − PhCO, 207.1021).

(1RS,3SR)-1-*Phenylbutane*-1,3-*diol* **56**[25] (341 mg, 76%). From the alcohol **50** (733 mg) by method A; needles, m.p. 78 °C (from Et_2O–hexane); R_f(ether) 0.43; ν_{max}(film)/cm^{-1} 3320 (OH), 1603 (Ph) and 1492 (Ph); $\delta_H(CDCl_3)$ 7.33–7.23 (5 H, m, Ph), 4.86 (1 H, dd, *J* 9.8 and 3.4, PhC*H*OH), 4.09 (1 H, m, C*H*OHMe), 3.75 (2 H, s, 2 × OH), 1.87–1.65 (2 H, m, CH_2) and 1.17 (3 H, d, *J* 6.2, CHOH*Me*); $\delta_C(CDCl_3)$ 144.4, 128.3, 127.4, 125.6, 74.9, 68.6, 46.7 and 23.8; *m/z* 166 (6%, M^+), 148 (30, M − H_2O), 133, (10, M − H_2O − Me), 107 (100, $PhCH_2O$) and 105 (70, PhCO) (Found: M^+, 166.1003. $C_{10}H_{14}O_2$ requires *M*, 166.0994) (Found: C, 72.0; H, 8.50. $C_{10}H_{14}O_2$ requires C, 72.3; H, 8.50%).

(1RS,3RS)-1-*Phenylbutane*-1,3-*diol* **57**[25] (115 mg, 79%). From the alcohol **51** (250 mg) by method A; prisms, m.p. 62–63 °C (from Et_2O–hexane); R_f(ether) 0.42; ν_{max}(film)/cm^{-1} 3600 (OH), 3470 (OH), 1603 (Ph) and 1492 (Ph); $\delta_H(CDCl_3)$ 7.38–7.22 (5 H, m, Ph), 5.05 (1 H, dd, *J* 7.2 and 4.1, C*H*OHPh), 4.06 (1 H, m, C*H*OHMe), 2.20 (2 H, s, 2 × OH), 1.88 (2 H, m, CH_2) and 1.24 (3 H, d, *J* 6.2, CHOH*Me*); $\delta_C(CDCl_3)$ 144.6, 128.4, 127.2, 125.6, 71.6, 65.3, 46.3 and 23.4; *m/z* 166 (5%, M^+), 148 (20, M − H_2O), 133 (5, M − H_2O − Me), 107 (100, $PhCH_2O$) and 105 (55, PhCO) (Found: M^+, 166.0992. $C_{10}H_{14}O_2$ requires *M*, 166.0994) (Found: C, 72.1; H, 8.5. $C_{10}H_{14}O_2$ requires C, 72.3; H, 8.50%).

(2RS,3SR)-2-*Dimethyl*(*phenyl*)*silyl*-4-*methylpentan*-3-*yl benzoate* (0.90 g, 87%). By benzoylation of the alcohol **41** (0.72 g); $R_f(CH_2Cl_2)$ 0.65; ν_{max}(film)/cm^{-1} 1710 (CO), 1600 (Ph), 1580 (Ph), 1280 (SiMe) and 1123 (SiPh); $\delta_H(CDCl_3)$ 8.01–7.98 (2 H, m, *o*-Hs COPh), 7.57–7.42 (5 H, m, *o*-Hs SiPh and *m*- and *p*-Hs COPh), 7.38–7.25 (3 H, m, *m*- and *p*-Hs SiPh), 5.18 (1 H, dd, *J* 7.2 and 4.7, CHO), 2.03 (1 H, m, C*H*Me_2), 1.46 (1 H, dq, *J* 4.7 and 7.4, SiCH), 1.09 (3 H, d, *J* 7.4, SiCH*Me*), 0.91 (3 H, d, *J* 6.7, CHMe_AMe_B), 0.84 (3 H, d, *J* 6.7, CHMe_AMe_B), 0.34 (3 H, s, SiMe_AMe_B) and 0.28 (3 H, s, SiMe_AMe_B); $\delta_C(CDCl_3)$ 166.1, 138.1, 133.8, 132.6, 130.8, 129.6, 128.9, 128.3, 127.7, 80.0, 31.0, 22.8, 19.7, 18.2, 9.5, −3.8 and −4.5; *m/z* 297 (18%, M − C_3H_7), 241 (60, MePhSiOCOPh), 179 (100, $Me_2SiOCOPh$), 135 (60, Me_2PhSi) and 105 (70, PhCO) (Found: M − C_3H_7, 297.1304. $C_{21}H_{28}O_2Si$ requires *M* − C_3H_7, 297.1311).

(2RS,3SR)-4-*Methylpentane*-2,3-*diyl dibenzoate* **67**[29] (54 mg, 60%). From the benzoate (95 mg) of the alcohol **41** using method B followed by benzoylation; $R_f(CH_2Cl_2)$ 0.75; ν_{max}(film)/cm^{-1} 1710 (CO), 1600 (Ph), 1580 (Ph) and 1490 (Ph); $\delta_H(CDCl_3)$ 8.15–7.85 (4 H, m, *o*-Hs Ph), 7.60–7.30 (6 H, m, *m*- and *p*-Hs Ph), 5.44 (1 H, dq, *J* 5 and 6, MeC*H*O), 5.29 (1 H, dd, *J* 5 and 7, Pr^{i}C*H*O), 2.08 (1 H, octet, *J* 7, Me_2CH), 1.41 (3 H, d, *J* 6, *Me*CHO), 1.05 (3 H, d, *J* 7, CHMe_AMe_B) and 1.02 (3 H, d, *J* 7, CHMe_AMe_B); $\delta_C(CDCl_3)$ 166.0, 165.7, 133.0, 132.9, 130.24, 130.22, 129.64, 129.60, 128.4, 128.3, 79.0, 70.3, 29.3, 19.1, 18.0 and 14.95.

(2RS,4RS)-3-*Methylpentane*-2,4-*diol* **69**[30] (61 mg, 40%). From the alcohol **68** (307 mg) by method C; $R_f(Et_2O)$ 0.40; ν_{max}(film)/cm^{-1} 3300 (OH); $\delta_H(CDCl_3)$ 4.10 (1 H, dq, *J* 2.7 and 6.5, C*H*OH), 3.85 (1 H, quintet, *J* 6.5, C*H*OH), 2.85 (2 H, s, 2 × OH), 1.57 (1 H, d quintet, *J* 2.7 and 7.1, CHOHMe), 1.22 (3 H, d, *J* 6.3, CHOH*Me*), 1.18 (3 H, d, *J* 6.4, CHOH*Me*) and 0.87 (3 H, d, *J* 7.1, CHCH*Me*CH); *m/z* 103 (0.1%, M − Me), 82 (6, M − $2H_2O$) and 57 (100, C_4H_9) (Found: M^+ − Me, 104.0759. $C_6H_{14}O_2$ requires *M* − Me, 103.0759).

(2RS,4RS)-3-*Methylpentane*-2,4-*diyl dibenzoate* **70** (136 mg, 84%). By benzoylation of the diol (59 mg) for 18 h; $R_f(CH_2Cl_2)$ 0.42; ν_{max}(film)/cm^{-1} 1710 (CO), 1603 (Ph), 1585 (Ph) and 1490 (Ph); $\delta_H(CDCl_3)$ 8.00–7.94 (4 H, m, *o*-Hs Ph), 7.56–7.46 (2 H, m, *p*-Hs Ph), 7.42–7.31 (4 H, m, *m*-Hs Ph), 5.39 (1 H, dq, *J* 3.7 and 6.4, Me_ACH_AO), 5.20 (1 H, quintet, *J* 6.5, Me_BCH_BO), 2.11 (1 H, d quintet, *J* 3.7 and 7.0, C*H*Me), 1.40 (3 H, d, *J* 6.5, Me_BCH_BO), 1.37 (3 H, d, *J* 6.4, Me_ACH_AO) and 1.17 (3 H, d, *J* 7.0, CH*Me*); $\delta_C(CDCl_3)$ 165.9, 165.8, 132.8, 132.7, 130.7, 130.6, 129.5, 128.3, 128.2, 72.2, 70.7, 42.8, 18.2, 17.4 and 10.3; *m/z* 221 (0.2%, M − PhCO), 204 (12, M − $PhCO_2H$) and 105 (100, PhCO) (Found: M^+ − PhCO, 221.1158. $C_{20}H_{22}O_4$ requires *M* − PhCO, 221.1177). The same dibenzoate (568 mg, 62%) was made from the alcohol **68** (665 mg) by benzoylation, silyl-to-hydroxy conversion by method B, benzoylation and chromatography (SiO_2, CH_2Cl_2).

(2RS,3SR,4SR)-3-*Methylpentan*-2,4-*diyl dibenzoate* **72** (65 mg, 36%). From the alcohol **71** (125 mg) by benzoylation, silyl-to-hydroxy conversion by method B, benzoylation and chromatography (SiO_2, CH_2Cl_2); $R_f(CH_2Cl_2)$; ν_{max}(film)/cm^{-1} 1715 (CO), 1603 (Ph) and 1585 (Ph); $\delta_H(CDCl_3)$ 8.10–8.04 (4 H, m, *o*-Hs Ph), 7.59–7.53 (2 H, m, *p*-Hs Ph), 7.48–7.41 (4 H, m, *m*-Hs Ph), 5.29 (2 H, quintet, *J* 6.4, CHO), 2.36 (1 H, m, C*H*Me), 1.34 (6 H, d, *J* 6.4, CHOBz*Me*) and 1.08 (3 H, d, *J* 7.0, CH*Me*); $\delta_C(CDCl_3)$ 165.6, 132.9, 130.5, 129.5, 128.4, 71.8, 41.7, 16.4 and 10.5; *m/z* 204 (5%, M − $PhCO_2H$) and 105 (100, PhCO) (Found: M^+ − $PhCO_2H$, 204.1145. $C_{20}H_{22}O_4$ requires *M* − $PhCO_2H$, 204.1150).

(1RS,1′RS,2SR)-2-(1-*Hydroxyethyl*)*cyclohexanol* **74**[31] (83.7 mg, 70%). From the alcohol **73** (217 mg) by method C and chromatography (SiO_2, Et_2O); $R_f(Et_2O)$ 0.25; $\nu_{max}(CDCl_3)$ 3450 (OH); $\delta_H(CDCl_3)$ 3.92 (1 H, dq, *J* 2.6 and 6.6, C*H*OHMe), 3.77 (2 H, s, 2 × OH), 3.63 (1 H, dt, *J* 4.3 and 10.0, $CH_2CHOHCH$), 1.95 (1 H, m, ring Hs), 1.72–1.46 (4 H, m, ring Hs), 1.30–1.10 (2 H, m, ring Hs), 1.19 (3 H, d, *J* 6.6, CHOH*Me*) and 1.00–0.89 (1 H, m, ring H); $\delta_C(CDCl_3)$ 71.3, 70.4, 49.5, 35.4, 26.6, 25.4, 24.4 and 18.0; *m/z* 129 (1.4%, M − Me), 126 (10, M − H_2O), 111 (10, M − H_2O − Me), 108 (20, M − 2 × H_2O) and 82 (100, C_6H_{12}) (Found: M^+ − Me, 129.0910. $C_8H_{16}O_2$ requires *M* − Me, 129.0916).

(1SR,1′RS,2RS)-2-(*Hydroxyethyl*)*cyclohexanol* **77**[31] (8.1 mg, 67%). From the alcohol **76** (22 mg) by method C and chromatography (SiO_2, Et_2O); $R_f(Et_2O)$ 0.28; ν_{max}(film)/cm^{-1} 3300 (OH); $\delta_H(CDCl_3)$ 3.78 (1 H, dq, *J* 8.5 and 6.2, CHOHMe), 3.53 (1 H, dt, *J* 4.2 and 9.7, $CH_2CHOHCH$), 3.44 (2 H, s, 2 × OH), 1.94 (1 H, m, ring H), 1.66 (3 H, m, ring Hs), 1.40–1.10 (4 H, m, ring Hs), 1.19 (3 H, d, *J* 6.2, Me) and 0.82 (1 H, m, ring H); $\delta_C(CDCl_3)$ 76.6, 74.1, 50.7, 35.6, 27.4, 25.3, 24.6 and 21.7; *m/z* 126 (2.3%, M − H_2O), 111 (7, M − H_2O − Me), 108 (12, M − 2 × H_2O), 82 (70, C_6H_{12}) and 67 (100, C_5H_7) (Found: M^+ − H_2O, 126.1052. $C_8H_{16}O_2$ requires *M* − H_2O, 126.1045).

(1RS,3SR)-*Cyclohexane*-1,3-*diyl dibenzoate* **89** (177 mg, 67%). From the alcohol **88** (191 mg) by benzoylation, silyl-to-hydroxy conversion by method B and benzoylation; needles, m.p. 122–123 °C (from MeOH) (lit.[34] 124 °C); $R_f(CH_2Cl_2)$ 0.48; ν_{max}(film)/cm^{-1} 1717 (CO), 1603 (Ph), 1587 (Ph) and 1493 (Ph); $\delta_H(CDCl_3)$ 8.04–8.00 (4 H, m, *o*-Hs), 7.57–7.50 (2 H, m, *p*-Hs), 7.42–7.36 (4 H, m, *m*-Hs), 5.12 (2 H, br m, C*H*OBz), 2.11–1.46 (8 H, m, ring Hs); $\delta_C(CDCl_3)$ 165.6, 132.7, 130.3, 129.4, 128.1, 70.6, 36.5, 30.6 and 19.4; *m/z* 245 (0.8%, M − Ph), 202 (3, M − $PhCO_2H$), 105 (100, PhCO) and 80 (70, M − 2 × $PhCO_2H$) (Found: C, 74.6; H, 6.30. $C_{20}H_{20}O_4$ requires C, 74.1; H, 6.2%).

(1RS,3RS)-*Cyclohexane*-1,3-*diyl dibenzoate* **91** (60 mg, 57%). From the alcohol **90** (75 mg) by standard benzoylation, silyl-to-hydroxy conversion by method B, standard benzoylation and

chromatography (SiO_2, CH_2Cl_2); needles, m.p. 60–62 °C (from methanol) (lit.,[34] 68 °C); R_f(CH_2Cl_2) 0.33; ν_{max}(CH_2Cl_2)/cm^{-1} 1706 (CO), 1603, 1586 and 1492 (Ph); δ_H($CDCl_3$) 8.08–8.04 (4 H, m, *o*-Hs), 7.59–7.52 (2 H, m, *p*-Hs), 7.47–7.40 (4 H, m, *m*-Hs), 5.45 (2 H, br m, C*H*OBz), 2.13 (2 H, t, *J* 5.6, ring Hs), 1.95–1.63 (6 H, m, ring Hs); δ_C($CDCl_3$) 165.8, 132.9, 130.5, 128.3, 70.5, 35.8, 30.3 and 19.4; *m/z* 219 (0.13%, M − PhCO), 202 (6, M − $PhCO_2H$), 105 (100, PhCO) and 80 (70, M − 2 × $PhCO_2H$) (Found: M$^+$ − PhCO, 219.1024. $C_{20}H_{20}O_4$ requires *M* − PhCO, 219.1021) (Found: C, 74.2; H, 6.20. $C_{20}H_{20}O_4$ requires C, 74.1; H, 6.20%).

(1RS,3SR)-*Cyclopentane*-1,3-*diyl dibenzoate* **94** (0.15 g, 24%) *and* (1RS,3RS)-*cyclopentane*-1,3-*diol dibenzoate* **95** (0.33 g, 52%). By benzoylation of the 72:28 mixture of alcohols **93** (0.46 g), silyl-to-hydroxy conversion by method B, benzoylation and chromatography (SiO_2, CH_2Cl_2); **94** R_f(CH_2Cl_2) 0.20; ν_{max}(film)/cm^{-1} 1710 (CO), 1605 (Ph), 1585 (Ph) and 1495 (Ph); δ_H($CDCl_3$) 8.04–8.00 (4 H, m, *o*-Hs Ph), 7.57–7.55 (2 H, m, *p*-Hs Ph), 7.40–7.33 (4 H, m, *m*-Hs Ph), 5.49 (2 H, m, CHO), 2.41 (1 H, dt, *J* 15.5 and 6.4, CHOCH_AH$_B$CHO), 2.23 (1 H, dm, *J* 15.5 with fine coupling, CHOCH$_A$CH_BCHO) and 2.15 (4 H, d, *J* 2.4, CH_2CH_2); δ_C($CDCl_3$) 166.0, 132.7, 130.3, 19.4, 128.1, 75.5, 39.2 and 31.1; *m/z* 205 (0.3%, M − PhCO), 188 (10, M − $PhCO_2H$), 105 (100, PhCO), 77 (40, Ph) and 66 (35, C_5H_6) Found: M$^+$ − PhCO, 205.0854. $C_{19}H_{18}O_4$ requires *M* − PhCO, 205.0865); **95** R_f(CH_2Cl_2) 0.4; ν_{max}(film)/cm^{-1} 1715 (CO); δ_H($CDCl_3$) 8.04–8.00 (4 H, *o*-Hs Ph), 7.59–7.52 (2 H, m, *p*-Hs Ph), 7.46 (4 H, m, *m*-Hs Ph), 5.59 (2 H, m, CHO), 2.36 (2 H, t, *J* 5.1, CHOBzCH_2CHOBz) and 2.30–1.95 (4 H, m, CH_2CH_2); δ_C($CDCl_3$) 166.2, 133.0, 130.4, 129.6, 128.4, 75.8, 39.7 and 30.8; *m/z* 310 (0.5%, M$^+$), 205 (2 M − PhCO), 188 (12, M − $PhCO_2H$), 105 (100, PhCO), 77 (35, Ph) and 66 (40, C_5H_6) (Found: M$^+$, 310.1214. $C_{19}H_{18}O_4$ requires *M*, 310.1205).

(1RS,3RS)-2-*Methylcyclohexane*-1,3-*diol* **97**[35] (25 mg, 46%). From the alcohol **96** (104 mg) by method C; R_f(Et_2O) 0.26; ν_{max}(film)/cm^{-1} 3620 (OH) and 3460 (OH); δ_H($CDCl_3$) 3.94 (1 H, m, C*H*OH), 3.61 (1 H, dt, *J* 4.2 and 9.7, C*H*OH), 2.0–1.2 (9 H, m, ring Hs and 2 × OH) and 1.08 (3 H, d, *J* 6.9, Me); δ_C($CDCl_3$) 71.6, 71.5, 43.5, 34.3, 32.4, 19.0 and 13.9; *m/z* 112 (45%, M − H_2O), 97 (40, M − H_2O − Me) and 68 (100, C_5H_8) (Found: M$^+$ − H_2O, 112.0898. $C_7H_{14}O_2$ requires *M* − H_2O, 112.0888).

(1RS,2SR,3SR)-2-*Methylcyclohexane*-1,3-*diol* **99**[35] (30 mg, 61%). From the alcohol **98** (95 mg) by method C; R_f(Et_2O) 0.15; ν_{max}(film)/cm^{-1} 3600 (OH) and 3450 (OH); δ_H($CDCl_3$) 3.28 (2 H, dt, *J* 3.9 and 8.6, 2 × C*H*OH), 1.94 (2 H, s, 2 × OH), 1.9–1.2 (7 H, m, ring Hs) and 1.10 (3 H, d, *J* 6.5, Me); δ_C($CDCl_3$) 73.8, 46.5, 33.4, 19.5 and 14.1; *m/z* 122 (7.4%, M − H_2O), 97 (4, M − H_2O − Me), 94 (25, M − 2H_2O) and 68 (100, C_5H_8) (Found: M$^+$ − H_2O, 112.0895. $C_7H_{14}O_2$ requires *M* − H_2O, 112.0888).

(1RS,2RS,3SR)-3-*Methylcyclohexane*-1,2-*diol* **101**[36] (79 mg, 60%). From the alcohol **100** (253 mg) by method B and chromatography (SiO_2, Et_2O–Me_2CO, 1:1); R_f(Et_2O) 0.26; ν_{max}(film)/cm^{-1} 3500 (OH); δ_H($CDCl_3$) 3.36 (1 H, ddd, *J* 4.6, 8.8 and 10.8. C*H*OH), 3.02 (2 H, s, 2 × OH), 2.92 (1 H, t, *J* 9.4, C*H*OH), 2.0–1.0 (7 H, m, ring Hs) and 1.01 (3 H, d, *J* 6.4, Me); δ_C($CDCl_3$) 71.5, 67.2, 47.5, 37.7, 34.7, 31.6 and 19.9; *m/z* 130 (0.7%, M$^+$), 112 (7, M − H_2O) and 97 (100, M − H_2O − Me) (Found: M$^+$, 130.0997. $C_7H_{14}O_2$ requires *M*, 130.0994).

(1RS,3SR)-1-*Methylcyclohexane*-1,3-*diol* **103**[37] (79 mg, 68%). From the alcohol **102** (222 mg) by method B; R_f(Et_2O) 0.13; δ_H($CDCl_3$) 3.87 (1 H, tt, *J* 10.9 and 4.3, C*H*OH), 2.70 (2 H, s, OH), 2.0–1.0 (8 H, m, ring Hs), 1.21 (3 H, s, Me); δ_C($CDCl_3$) 81.1, 75.1, 37.6, 33.2, 32.9, 23.3 and 18.1.

2-*Dimethyl*(*phenyl*)*silyl*-4-*methylpentan*-1-*ol* **60**.—Isobutylmagnesium bromide (1 mol dm^{-3} solution in ether; 11 cm^3) was added to a slurry of copper(I) iodide (0.42 g) in ether (5 cm^3) at −30 °C. After 2 min the solution was warmed to 0 °C, 1-dimethyl(phenyl)silyl-1,2-epoxyethane (0.66 g) in ether (10 cm^3) added and the mixture stirred for 6 h. Standard aqueous work-up and chromatography (SiO_2, CH_2Cl_2) of the residue gave the *alcohol* (0.5 g, 57%); R_f(CH_2Cl_2); ν_{max}(film)/cm^{-1} 3350 (OH), 1248 (SiMe) and 1110 (SiPh); δ_H($CDCl_3$) 7.55–7.34 (5 H, m, Ph), 3.74 (1 H, dd, *J* 10.6 and 4.6, CH_AH$_B$OH), 3.64 (1 H, dd, *J* 10.6 and 5.7, CH$_A$$H_B$OH), 1.61 (1 H, m, Me_2C*H*), 1.40–1.15 (3 H, m, CH_2 and SiCH), 1.27 (1 H, s, OH), 0.85 (3 H, d, *J* 6.6, CH*Me*$_A$Me$_A$), 0.80 (3 H, d, *J* 6.6, CHMe$_A$*Me*$_A$) and 0.32 (6 H, s, $SiMe_2$); δ_C($CDCl_3$) 138.5, 133.9, 128.9, 127.8, 64.1, 36.6, 27.3, 26.7, 23.4, 21.8, −3.7 and −3.9; *m/z* 221 (0.1%, M − Me), 218 (0.1 M − H_2O), 137 (100, MePhSiOH) and 135 (35, Me_2PhSi) (Found: M$^+$ − Me, 221.1365. $C_{14}H_{24}$OSi requires *M* − Me, 221.1362).

4-*Dimethyl*(*phenyl*)*silyl*-2-*methylpent*-1-*ene* **61**.—The ketone **46** (1.2 g) was refluxed for 2 h with the Grignard reagent derived from chloromethyltrimethylsilane (2.45 g) and magnesium (0.5 g) in THF (30 cm^3). Standard aqueous work-up gave crude alcohol which was added to acetic acid (6 cm^3) and water (2 cm^3) and stirred at room temp. for 90 min. Standard aqueous work-up and chromatography (SiO_2, hexane) gave the *homoallylic silane* (0.26 g, 22%); R_f(hexane) 0.54; ν_{max}(film)/cm^{-1} 1635 (C=C), 1240 (SiMe) and 1105 (SiPh); δ_H($CDCl_3$) 7.5–7.3 (5 H, m, Ph), 4.70 (1 H, m, C=CH_AH$_B$), 4.61 (1 H, m, C=CH$_A$$H_B$), 2.15 (1 H, dd, *J* 13.9 and 3, SiCH_AH$_B$), 1.75 (1 H, ddd, *J* 13.9, 11.9 and 0.6, SiCH$_A$$H_B$), 1.63 (3 H, d, *J* 0.6, C=CMe), 1.06 (1 H, m, SiCH), 0.85 (3 H, d, *J* 7.2, SiCH*Me*) and 0.27 (6 H, s, $SiMe_2$); δ_C($CDCl_3$) 144.9, 138.4, 134.0, 128.9, 127.7, 111.1, 40.0, 21.5, 16.6, 13.5, −4.9 and −5.0; *m/z* 218 (5%, M$^+$) and 135 (100, Me_2PhSi) (Found: M$^+$, 218.1503. $C_{14}H_{22}$Si requires *M*, 218.1490).

4-*Dimethyl*(*phenyl*)*silyl*-2-*methylpentan*-2-*ol* **64**.—Methyllithium (2.2 mol dm^{-3} solution in ether; 3.5 cm^3) was stirred with the ketone **46**[53] (0.35 g, 1.57 mmol) in ether (10 cm^3) at 0 °C for 4 h. Standard aqueous work-up and chromatography (SiO_2, Et_2O–light petroleum, 1:1) gave the *alcohol* (0.25 g, 68%); R_f(Et_2O–light petroleum, 1:1) 0.45; ν_{max}(film)/cm^{-1} 3380 (OH), 1248 (SiMe) and 1111 (SiPh); δ_H($CDCl_3$) 7.53–7.32 (5 H, m, Ph), 1.65 (1 H, m, CH_AH$_B$), 1.25 (1 H, m, CH$_A$$H_B$), 1.20 (1 H, br s, OH), 1.15 (6 H, s, CMe_2), 1.06 (4 H, s, SiCHMe) and 0.26 (6 H, s, $SiMe_2$); δ_C($CDCl_3$) 138.1, 133.8, 128.7, 127.5, 72.3, 44.8, 29.6, 29.3, 16.5 and 14.8; *m/z* 218 (1.8%, M − H_2O), 137 (40, MePhSiOH) and 135 (100, $SiMe_2$Ph) (Found: M$^+$ − H_2O, 218.1481. $C_{14}H_{24}$OSi requires *M* − H_2O, 218.1490).

2-*Dimethyl*(*phenyl*)*silyl*-4-*methylpentan*-2-*ol* **65**.—4-Methylpentan-2-one (1.06 cm^3) and dimethyl(phenyl)silyllithium (0.94 mol dm^{-3} solution in THF; 10 cm^3) were stirred at 0 °C for 15 min. Standard aqueous work-up and chromatography (SiO_2, hexane:EtOAc, 10:1) of the residue gave the *alcohol* (0.7 g, 37%); R_f(hexane–EtOAc, 10:1) 0.55; ν_{max}(film)/cm^{-1} 3580 (OH), 3480 (OH), 1245 (SiMe) and 1110 (SiPh); δ_H($CDCl_3$) 7.59–7.34 (5 H, m, Ph), 1.87 (1 H, m, C*H*Me_2), 1.41 (2 H, m, CH_2), 1.21 (3 H, s, SiCMe), 0.94 (3 H, d, *J* 6.6, CH*Me*$_A$Me$_B$) and 0.87 (3 H, d, *J* 6.6, CHMe$_A$*Me*$_B$), 0.35 (3 H, s, Si*Me*$_A$Me$_B$) and 0.34 (3 H, s, SiMe$_A$*Me*$_B$); δ_C($CDCl_3$) 136.6, 134.5, 129.2, 127.7, 67.1, 47.3, 25.2, 24.8, 24.7, 23.4 and −5.7; *m/z* 236 (0.25%, M$^+$), 221 (1, M − Me), 137 (80, MePhSiOH) and 135 (100, Me_2PhSi) (Found: M$^+$, 236.1615. $C_{14}H_{24}$OSi requires *M*, 236.1597).

(1RS,3SR,5RS,6SR)-5-*Methyl*-3-*phenyl*-2,4-*dioxabicyclo*-[4.4.0]*decane* **75**.—The diol **74** (22.1 mg, 0.14 mmol), benzaldehyde dimethyl acetal (0.046 cm^3, 0.31 mmol) and

toluene-*p*-sulfonic acid (5 mg) were stirred in toluene (0.2 cm^3) at 50 °C for 3 h. Saturated aqueous sodium hydrogen carbonate (10 cm^3) was added to the mixture which was then extracted with ether (3 × 5 cm^3). The extracts were dried (Na_2SO_4) and evaporated under reduced pressure. Chromatography (SiO_2, hexane–ethyl acetate 5:1) of the residue gave the acetal[31] (28.4 mg, 84%); R_f(hexane–EtOAc, 5:1) 0.49; ν_{max}(film)/cm^{-1} only CH above 1500; δ_H($CDCl_3$) 7.51–7.29 (5 H, m, Ph), 5.86 (1 H, s, PhC*H*), 4.26 (1 H, quintet, *J* 7.0, MeC*H*O), 3.76 (1 H, dt, *J* 4.4 and 10.4, CHC*H*OCH), 2.08–0.96 (9 H, m, ring Hs) and 1.38 (3 H, d, *J* 7.0, Me); δ_C($CDCl_3$) 139.1, 128.6, 128.3, 126.2, 94.1, 74.8, 72.5, 43.8, 32.2, 26.7, 25.7, 24.6 and 13.1; *m/z* 232 (44%, M^+), 231 (49, M − H), 107 (90, $PhCH_2O$) and 105 (100, PhCO) (Found: M^+, 232.1449. $C_{15}H_{20}O_2$ requires *M*, 232.1463).

(1RS,3SR,5SR,6SR)-5-*Methyl*-3-*phenyl*-2,4-*dioxabicyclo*-[4.4.0]*decane* **78**.—Similarly, the diol **77** (6.2 mg) gave the acetal[31] (7.3 mg, 77%); R_f(hexane–EtOAc, 5:1) 0.44; ν_{max}(film)/cm^{-1} only CH above 1500; δ_H($CDCl_3$) 7.53–7.29 (5 H, m, Ph), 5.62 (1 H, s, PhC*H*), 3.63 (1 H, dq, *J* 9.6 and 6.2, MeC*H*O), 3.45 (1 H, td, *J* 10.1 and 3.8, CHC*H*OCH), 2.02–0.85 (9 H, m, ring Hs) and 1.27 (3 H, d, *J* 6.2, Me); *m/z* 232 (37%, M^+), 231 (47, M − H), 155 (10, M − Ph), 107 (100, Me_2PhSi) and 105 (45, PhCO) (Found: M^+, 232.1452. $C_{15}H_{20}O_2$ requires *M*, 232.1463).

1-*Dimethyl*(*phenyl*)*silylcyclopent*-1-*ene* **79**.—Chlorodimethyl(phenyl)silane (3 cm^3), sodium (1.09 g) and 1-chlorocyclopent-1-ene (1.56 g) were stirred in ether (20 cm^3) at room temperature for 4 h and then refluxed for 17 h. Standard aqueous work-up gave the *vinylsilane* (2.09 g, 69%); R_f(hexane) 0.62; ν_{max}(film)/cm^{-1} 1592 (Ph), 1252 (SiMe) and 1112 (SiPh); δ_H($CDCl_3$) 7.53–7.32 (5 H, m, Ph), 6.06 (1 H, m, C=CH), 2.41–2.34 (4 H, m, ring Hs), 1.82 (2 H, quintet, *J* 7.5, C=CCH_2CH_2) and 0.35 (6 H, s, $SiMe_2$); δ_C($CDCl_3$) 142.6, 142.4, 138.8, 133.8, 128.8, 127.7, 36.0, 35.0, 24.1 and −3.0; *m/z* 202 (52%, M^+), 187 (100, M − Me), 159 (35, M − C_3H_7) and 135 (40, Me_2PhSi) (Found: M^+, 202.1175. $C_{13}H_{18}Si$ requires *M*, 202.1178).

1-*Dimethyl*(*phenyl*)*silylcyclohex*-1-*ene* **80**.—1-Chlorocyclohex-1-ene[55] (1.77 g), sodium wire (1.09 g) and chlorodimethyl(phenyl)silane (3 cm^3) were stirred in ether (20 cm^3) at room temp. for 18 h. Ethanol (10 cm^3) was carefully added to the mixture followed by aqueous ammonium chloride (10 cm^3). The mixture was then filtered through Celite and extracted with hexane. The extracts were dried (Na_2SO_4) and evaporated under reduced pressure. Chromatography (SiO_2, hexane) gave the *vinylsilane* (1.57 g, 48%); R_f(hexane) 0.7; ν_{max}(film)/cm^{-1} 1615 (C=C), 1247 (SiMe) and 1112 (SiPh); δ_H($CDCl_3$) 7.52–7.33 (5 H, m, Ph), 6.06 (1 H, m, C=CH), 2.09–1.99 (4 H, m, ring Hs), 1.61–1.43 (4 H, m, ring Hs) and 0.31 (6 H, s, $SiMe_2$); δ_C($CDCl_3$) 138.8, 137.8, 136.7, 133.9, 128.7, 127.6, 26.9, 26.8, 22.9, 22.4 and −3.6; *m/z* 216 (47%, M^+), 201 (55, M − Me), 135 (100, Me_2PhSi) and 121 (40, MePhSiH) (Found: M^+, 216.1341. $C_{14}H_{20}Si$ requires *M*, 216.1336).

1-*Dimethyl*(*phenyl*)*silyl*-1,2-*epoxycyclopentane* **81**.—Standard epoxidation of the vinylsilane **79** (1.0 g) with MCPBA (2.4 g) after standard aqueous work-up gave the *epoxysilane* (1.02 g, 95%); R_f(CH_2Cl_2) 0.70; ν_{max}(film)/cm^{-1} 1252 (SiMe) and 1112 (SiPh); δ_H($CDCl_3$) 7.58–7.34 (5 H, m, Ph), 3.31 (1 H, s, CHO), 2.1–1.3 (6 H, m, ring Hs), 0.37 (3 H, s, $SiMe_AMe_B$) and 0.33 (3 H, s, $SiMe_AMe_B$); δ_C($CDCl_3$) 136.4, 133.9, 129.3, 127.8, 61.4, 59.4, 28.9, 28.0, 18.6, −4.8 and −4.9; *m/z* 218 (10%, M^+), 137 (70, MePhSiOH) and 135 (100, Me_2PhSi) (Found: M^+, 218.1120. $C_{13}H_{18}OSi$ requires *M*, 218.1127).

1-*Dimethyl*(*phenyl*)*silyl*-1,2-*epoxycyclohexane* **82**.—The vinylsilane **80** (1.43 g), MCPBA (3.2 g) and disodium hydrogen phosphate (2.54 g) were stirred in dichloromethane (20 cm^3) at 0 °C for 18 h. Standard reductive aqueous work-up gave the *epoxide* (1.09 g, 71%); R_f(CH_2Cl_2) 0.74; ν_{max}(film)/cm^{-1} 1250 (SiMe) and 1113 (SiPh); δ_H($CDCl_3$) 7.56–7.33 (5 H, m, Ph), 2.98 (1 H, dd, *J* 1.1 and 3.3, CHO), 2.05–1.10 (8 H, m, ring Hs), 0.32 (3 H, s, $SiMe_AMe_B$) and 0.28 (3 H, s, $SiMe_AMe_B$); δ_C($CDCl_3$) 136.2, 134.1, 129.3, 127.8, 55.2, 53.6, 25.8, 19.9, 19.4, −5.7 and −5.9; *m/z* 232 (6%, M^+), 231 (11, M − H), 217 (20, M − Me), 156 (50, M − C_6H_4), 137 (85, MePhSiOH) and 135 (100, Me_2PhSi) (Found: M^+ − H, 231.1218. $C_{14}H_{20}OSi$ requires *M* − H, 231.1205).

(1RS,2SR)-2-*Dimethyl*(*phenyl*)*silylcyclopentanol* **83**.—The epoxide **81** (0.84 g) was refluxed with lithium aluminium hydride (0.3 g) in ether (10 cm^3) for 4 h. Water (20 cm^3) was cautiously added dropwise to the mixture, which was then extracted with dichloromethane. The extracts were dried (Na_2SO_4) and evaporated under reduced pressure to give the *alcohol* (0.78 g, 92%); ν_{max}(film)/cm^{-1} 3580 (OH) 3440 (OH), 1243 (SiMe) and 1110 (SiPh); δ_H($CDCl_3$) 7.60–7.33 (5 H, m, Ph), 4.43 (1 H, td, *J* 4.8 and 1.7, CHO), 1.80, 1.56 (6 H, m, ring H), 1.22 (1 H, td, *J* 10.0 and 4.8, SiCH), 1.2 (1 H, s, OH), 0.38 (3 H, s, $SiMe_AMe_B$) and 0.34 (3 H, s, $SiMe_AMe_B$); δ_C($CDCl_3$) 139.8, 133.8, 128.6, 127.7, 76.6, 37.6, 34.8, 25.9, 24.3, −2.7 and −3.1; *m/z* 205 (0.3%, M − Me), 137 (100, MePhSiOH) and 135 (62, Me_2PhSi) (Found: M^+ − Me, 205.1030. $C_{13}H_{20}OSi$ requires *M* − Me, 205.1049).

(1RS,2SR)-2-*Dimethyl*(*phenyl*)*silylcyclohexanol* **84**.—The epoxide **82** (0.98 g) was reduced similarly to give the *alcohol* (0.77 g, 78%); R_f(CH_2Cl_2) 0.63; ν_{max}(film)/cm^{-1} 3580 (OH), 3450 (OH), 1248 (SiMe) and 1110 (SiPh); δ_H($CDCl_3$) 7.56–7.32 (5 H, m, Ph), 4.03 (1 H, m, bw 10 Hz, C*H*OH), 1.7–0.9 (10 H, m, ring Hs and OH), 0.32 (3 H, s, $SiMe_AMe_B$) and 0.31 (3 H, s, $SiMe_AMe_B$); δ_C($CDCl_3$) 138.8, 133.9, 128.8, 127.7, 67.8, 34.8, 31.5, 27.3, 21.4, 20.3, −3.9 and −4.0; *m/z* 216 (3%, M − H_2O), 137 (100, MePhSiOH) and 135 (60, Me_2PhSi) (Found: M^+ − H_2O, 216.1351. $C_{14}H_{22}OSi$ requires *M* − H_2O, 216.1334).

(1RS,3SR)- *and* (1RS,3RS)-3-*Dimethyl*(*phenyl*)*silylcyclohexanol* **88** *and* **90**.—Sodium borohydride (0.5 g) was stirred with the ketone **87**[53] (1.07 g) in methanol (30 cm^3) at 0 °C for 30 min. Standard aqueous work-up gave a 73:27 mixture (1.07 g, 99%) of the 1RS,3SR- and 1RS,3RS-*alcohols*, separated by chromatography (SiO_2, CH_2Cl_2); **88** R_f(CH_2Cl_2) 0.23; ν_{max}(film)/cm^{-1} 3350 (OH), 1245 (SiMe) and 1110 (SiPh); δ_H($CDCl_3$) 7.50–7.32 (5 H, m, Ph), 3.50 (1 H, tt, *J* 10.7 and 4.4, C*H*OH), 2.0–0.8 (9 H, complex m, other ring Hs), 1.40 (1 H, br s, OH) and 0.25 (6 H, s, $SiMe_2$); δ_C($CDCl_3$) 137.8, 133.8, 128.8, 127.6, 71.9, 36.4, 35.9, 26.5, 26.0, 24.0, −5.3 and −5.4; *m/z* 219 (1%, M − Me), 137 (100, MePhSiOH) and 135 (90, Me_2PhSi) (Found: M^+ − Me, 219.1198. $C_{14}H_{22}OSi$ requires *M* − Me, 219.1205); **90** R_f(CH_2Cl_2) 0.31; ν_{max}(film)/cm^{-1} 3350 (OH), 1245 (SiMe) and 1105 (SiPh); δ_H($CDCl_3$) 7.52–7.31 (5 H, m, Ph), 4.00 (1 H, quintet, *J* 2.9, C*H*OH), 1.75–1.06 (10 H, m, ring Hs and OH) and 0.24 (6 H, s, $SiMe_2$); δ_C($CDCl_3$) 138.0, 133.9, 128.8, 127.6, 65.9, 33.5, 32.7, 26.6, 21.0, 18.0, −5.22 and −5.26; *m/z* 216 (1%, M − H_2O), 156 (2%, M − C_6H_6), 137 (60, MePhSiOH) and 135 (100, Me_2PhSi) (Found: M^+ − H_2O, 216.1350. $C_{14}H_{22}OSi$ requires *M* − H_2O, 216.1334). The ratio of isomers was determined by integration of the $SiMe_2$ signals in the ^1H NMR spectrum.

(1RS,3SR)- *and* (1RS,3RS)-3-*Dimethyl*(*phenyl*)*silylcyclopentanol* **93**.—Similar reduction of the ketone **92**[53] (0.9 g) gave an inseparable 1:3 mixture (0.9 g, 99%) of the cis- and trans-

alcohols; $R_f(CH_2Cl_2)$ 0.3; ν_{max}(film)/cm^{-1} 3330 (OH), 1248 (SiMe) and 1110 (SiPh); $\delta_H(CDCl_3)$ 7.50–7.30 (5 H, m, Ph), 4.40 (1 H, m, C*H*OH), 2.00–1.20 (8 H, m, ring Hs and OH), 0.26 (6 H, s, $SiMe_2$, minor isomer) and 0.25 (6 H, s, $SiMe_2$, major isomer); $\delta_C(CDCl_3)$ 138.5 (major), 138.2 (minor), 133.7 (minor), 133.6 (major), 128.7, 127.5, 74.3 (major), 74.0 (minor), 37.7 (minor), 37.5 (major), 36.4 (major), 36.0 (minor), 25.6 (minor), 25.3 (major), 23.7 (major), 22.0 (minor), −4.6 (minor), −4.7 (minor), −4.7 (major) and −4.8 (major); *m/z* 205 (0.8%, M − Me), 137 (100, MePhSiOH) and 135 (90, Me_2PhSi) (Found: M$^+$ − Me, 205.1067. $C_{13}H_{20}OSi$ requires *M* − Me, 205.1049). The ratio of isomers was determined by integration of the $SiMe_2$ signals in the ^{1}H NMR spectrum and several signals in the ^{13}C NMR spectrum.

(1RS,3SR)-*and*(1RS,3RS)-3-*Dimethyl*(*phenyl*)*silyl*-1-*methylcyclohexanol* **102** *and* **104**.—Methylmagnesium chloride (3 mol dm^{-3} solution in THF; 7 cm^3) was stirred with the ketone **87**[53] (1 g, 4.3 mmol) in THF (2 cm^3) at 0 °C for 1 h. Standard aqueous work-up gave a 3:1 mixture of the *alcohols* (1 g, 94%) separated by chromatography (SiO_2, CH_2Cl_2); **102** $R_f(CH_2Cl_2)$ 0.42; ν_{max}(film)/cm^{-1} 3400 (OH), 1240 (SiMe) and 1107 (SiPh); $\delta_H(CDCl_3)$ 7.50–7.33 (5 H, m, Ph), 1.70–0.80 (9 H, m, ring Hs), 1.38 (1 H, s, OH), 1.16 (3 H, s, Me) and 0.24 (6 H, s, $SiMe_2$); $\delta_C(CDCl_3)$ 138.0, 134.0, 128.8, 127.7, 68.7, 39.4, 38.5, 31.6, 26.1, 22.9, 20.0, −5.1 and −5.2; *m/z* 248 (5%, M$^+$), 230 (2, M − Me), 137 (40, MePhSiOH) and 135 (100, Me_2PhSi) (Found: M$^+$, 248.1619. $C_{15}H_{24}OSi$ requires *M*, 248.1596); **104** $R_f(CH_2Cl_2)$ 0.26; ν_{max}(film)/cm^{-1} 3350 (OH), 1245 (SiMe) and 1105 (SiPh); $\delta_H(CDCl_3)$ 7.50–7.31 (5 H, m, Ph), 1.7–0.8 (9 H, m, ring Hs), 1.60 (1 H, s, OH), 1.21 (3 H, s, Me) and 0.24 (6 H, s, SiMe2); $\delta_C(CDCl_3)$ 137.8, 133.8, 128.8, 127.6, 71.1, 41.2, 40.6, 26.4, 25.5, 23.0, −5.3 and −5.4; *m/z* 248 (0.1%, M$^+$), 230 (1, M − Me), 137 (80, MePhSiOH) and 135 (100, Me_2PhSi) (Found: M$^+$, 248.1599. $C_{15}H_{24}OSi$ requires *M*, 248.1596). The ratio of the isomers was determined by integration of the CMe signal in the ^{1}H NMR spectrum.

Ethyl 5-*Dimethyl*(*phenyl*)*silylpentanoate* **105**.—9-BBN (0.5 mol dm^{-3} solution in THF; 7 cm^3) was added to the allylsilane **3** (0.58 g, 3.3 mmol) and the mixture stirred at room temp. for 2 h. Ethyl bromoacetate (0.37 cm^3, 0.35 mmol) and potassium *tert*-butoxide (1 mol dm^{-3} solution in *tert*-butyl alcohol; 3.5 cm^3) were added in succession at 0 °C and stirred for 30 min. Standard oxidation (NaOAc, H_2O_2), aqueous work-up and chromatography (SiO_2, CH_2Cl_2) of the residue gave the *ester* (0.32 g, 34%); $R_f(CH_2Cl_2)$ 0.80; ν_{max}(film)/cm^{-1} 1735 (C=O), 1250 (SiMe) and 1115 (SiPh); $\delta_H(CDCl_3)$ 7.51–7.32 (5 H, m, Ph), 4.10 (2 H, q, *J* 7.1, CH_2Me), 2.26 (2 H, t, *J* 7.4, CH_2CO), 1.64 (2 H, m, CH_2CH$_2$CO), 1.34 (2 H, m, SiCH$_2$CH_2), 1.22 (3 H, t, *J* 7.1, Me), 0.76 (2 H, m, $SiCH_2$) and 0.25 (6 H, s, $SiMe_2$); $\delta_C(CDCl_3)$ 173.8, 139.4, 133.5, 128.8, 127.7, 60.1, 34.0, 28.7, 23.5, 15.4, 14.2 and −3.1; *m/z* 264 (0.1%, M$^+$), 259 (1, M − Me), 235 (1, Me − Et) and 135 (100, Me_2PhSi) (Found: M$^+$, 264.1527. $C_{15}H_{24}O_2Si$ requires *M*, 264.1546).

Ethyl (3RS,5SR)-5-*Dimethyl*(*phenyl*)*silyl*-3-*methylhexanoate* **106**.—9-BBN (0.5 mol dm^{-3} solution in THF; 7 cm^3) was added to the allylsilane **7** (436 mg) and the mixture stirred at room temp. for 4 h. 2,6-Di-*tert*-butylphenol (1 mol dm^{-3} solution in THF; 3.5 cm^3) and potassium *tert*-butoxide (1 mol dm^{-3} solution in *tert*-butyl alcohol; 3.5 cm^3) were added in succession to the mixture which was then stirred for 30 min. Ethyl bromoacetate (0.7 g) in THF (1.5 cm^3) was added to the mixture which was then stirred for a further 4 h. The borane was oxidised (sodium acetate, H_2O_2, 25 °C, 1 h) and the mixture extracted with ether. The extracts were dried (Na_2SO_4) and evaporated under reduced pressure. Chromatography (SiO_2, hexane, to eliminate the phenol and then hexane–EtOAc, 5:1) gave the *silyl ester* (145 mg, 30%); R_f(hexane–EtOAc, 5:1) 0.69; ν_{max}(film)/cm^{-1} 1740 (C=O), 1248 (SiMe) and 1110 (SiPh); $\delta_H(CDCl_3)$ 7.52–7.30 (5 H, m, Ph), 4.10 (2 H, q, *J* 7.0, OCH_2), 2.2–2.0 (2 H, m, CH_2CO), 1.30–1.10 (3 H, m, SiCHCH_2C*H*), 1.24 (3 H, t, *J* 7.0, CH_2*Me*), 0.95 (4 H, s, SiCHMe), 0.80 (3 H, d, *J* 6.0, CH*Me*) and 0.25 (6 H, s, $SiMe_2$); $\delta_C(CDCl_3)$ 173.2, 138.3, 133.9, 128.8, 127.6, 60.0, 42.9, 38.2, 32.1, 27.8, 18.3, 15.9, 15.2, 14.2, 13.4, −5.0 and −5.2; *m/z* 292 (6%, M$^+$), 277 (10, M − Me), 249 (60, M − Me − CO), 135 (100, Me_2PhSi) and 69 (40, C_5H_9) (Found: M$^+$, 292.1839. $C_{17}H_{28}O_2Si$ requires *M*, 292.1859).

(3RS,5SR)-5-*Dimethyl*(*phenyl*)*silyl*-3-*methyl*-1-*phenylhexan*-1-*one* **107**.—Hydroboration and further reactions as in the preparation of the ester **106** but using phenacyl bromide in place of ethyl bromoacetate gave the *silyl ketone* (215 mg, 31%); R_f(hexane–EtOAc, 5:1) 0.56; ν_{max}(film)/cm^{-1} 1680 (C=O), 1600 (Ph), 1585 (Ph), 1248 (SiMe) and 1110 (SiPh); $\delta_H(CDCl_3)$ 7.97–7.91 (2 H, m, *o*-Hs PhCO), 7.58–7.33 (8 H, m, *m*- and *p*-Hs PhCO and SiPh), 2.80 (2 H, m, CH_2CO), 2.31 (1 H, m, CH_2CHMeCH$_2$), 1.25 (2 H, m, SiCHCH_2), 0.98 (1 H, m, SiCH), 0.94 (3 H, s, SiCH*Me*), 0.88 (3 H, d, *J* 6.6, CH_2CH*Me*CH$_2$) and 0.25 (6 H, s, $SiMe_2$); $\delta_C(CDCl_3)$ 200.2, 138.4, 137.5, 133.9, 132.8, 128.8, 128.5, 128.0, 127.6, 46.9, 38.8, 27.1, 18.6, 16.0, 13.4, −5.0 and −5.2; *m/z* 324 (0.7%, M$^+$), 319 (2, M − Me), 281 (60, M − Me − CO) and 135 (100, Me_2PhSi) (Found: M$^+$, 324.1910. $C_{21}H_{28}OSi$ requires *M*, 324.1910).

(3RS,5SR)-5-*Dimethyl*(*phenyl*)*silyl*-3-*methylhexanonitrile* **108**.—Hydroboration and further reactions as in the preparation of the ester **106** but using chloroacetonitrile in place of ethyl bromoacetate gave the *nitrile* (0.24 g, 55%); $R_f(CH_2Cl_2)$ 0.70; ν_{max}(film)/cm^{-1} 2250 (C≡N), 1250 (SiMe) and 1112 (SiPh); $\delta_H(CDCl_3)$ 7.49–7.32 (5 H, m, Ph), 2.19 (1 H, dd, *J* 16.6 and 6.6, CH_AH$_B$CN), 2.17 (1 H, dd, *J* 16.6 and 6.6, CH$_A$$H_B$CN), 1.93 (1 H, octet, *J* 6.6, C*H*CH$_2$CN), 1.26 (2 H, m, SiCHCH_2), 0.95 (3 H, d, *J* 6.6, CH*Me*CH$_2$CN), 0.91 (4 H, s, SiCHMe), 0.26 (3 H, s, SiMe_AMe$_B$) and 0.25 (3 H, s, SiMe$_A$$Me_B$); $\delta_C(CDCl_3)$ 137.1, 133.9, 129.0, 127.8, 119.0, 37.9, 28.2, 25.4, 18.1, 16.2, 13.6, −4.9 and −5.2; *m/z* 245 (1.6%, M$^+$), 230 (12, M − Me) and 135 (100, Me_2PhSi) (Found: M$^+$, 245.1605. $C_{15}H_{23}NSi$ requires *M*, 245.1600).

Ethyl (4RS,5SR)-5-*Dimethyl*(*phenyl*)*silyl*-4-*methyl*-5-*phenylpentanoate* **109**.—This was prepared in the same way as the ester **106** from the allylsilane **12** (162 mg) to give the *ester* (69 mg, 32%); $R_f(CH_2Cl_2)$ 0.56; ν_{max}(film)/cm^{-1} 1730 (CO), 1590 (Ph), 1250 (SiMe) and 1115 (SiPh); $\delta_H(CDCl_3)$ 7.46–6.95 (10 H, m, 2 × Ph), 4.00 (2 H, q, *J* 7.1, OCH_2Me), 2.11 (5 H, m, SiCH and CH_2CH_2CO), 1.67 (1 H, m, SiCHC*H*), 1.17 (3 H, t, *J* 7.1, OCH_2*Me*), 0.29 (3 H, s, SiMe_AMe$_B$) and 0.04 (3 H, s, SiMe$_A$$Me_B$); $\delta_C(CDCl_3)$ 173.8, 143.2, 139.2, 133.9, 128.7, 128.1, 127.6, 124.7, 60.1, 43.8, 34.3, 31.4, 31.2, 20.0, 14.1, −1.3 and −4.0; *m/z* 354 (5%, M$^+$), 277 (5, M − Ph), 235 (60, M − Ph − CH_2CO) and 135 (100, Me_2PhSi) (Found: M$^+$, 354.2025. $C_{22}H_{30}O_2Si$ requires *M*, 354.2015).

(2RS,4SR)- *and* (2RS,4RS)-4-*Dimethyl*(*phenyl*)*silyl*-2-*methylhexanonitrile* **108** *and* **110**.—The 3:1 mixture of the alcohols **62** and **63** (158 mg) and toluene-*p*-sulfonyl chloride (192 mg) were stirred in triethylamine (3 cm^3) at room temp. for 3 h. Standard aqueous work-up and chromatography (SiO_2, CH_2Cl_2) gave a mixture of tosylates (244 mg, 93%), R_f (CH_2Cl_2) 0.70, which was stirred with sodium cyanide (60 mg) in DMSO (1 cm^3) at 70 °C for 3 h. Standard aqueous work-up and chromatography (SiO_2, CH_2Cl_2) gave a 1:3 mixture of the

nitriles (135 mg, 91%); $R_f(CH_2Cl_2)$0.67; **110**: $\delta_H(CDCl_3)$ 7.51–7.34 (5 H, m, Ph), 2.30 (1 H, dd, *J* 16.5 and 4.4, CH_AH_BCN), 2.09 (1 H, dd, *J* 16.6 and 7.2, CH_AH_BCN), 1.95 (1 H, m, $CHCH_2CN$), 1.50–1.10 (2 H, m, $SiCHCH_2$), 1.03 (3 H, d, *J* 6.7, Me), 0.90 (4 H, m, SiCHMe), 0.28 (3 H, s, $SiMe_AMe_B$) and 0.27 (3 H, s, $SiMe_AMe_B$). The peaks of the minor isomer also present were the same as those of the nitrile **108** prepared from the homoallylsilane **61**. The ratio of isomers was determined by integration of the CH_2CN signals in the ^1H NMR spectrum.

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