The Stereochemistry of the Reaction of Allylsilanes with Osmium Tetroxide and of the Epoxidation and Methylenation of Allylsilanes

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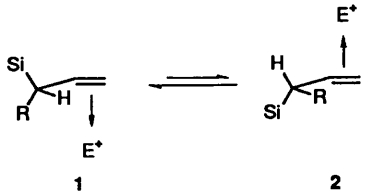
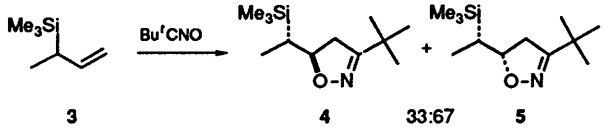
The allylsilanes *E*-**7** react with osmium tetroxide, with *m*-chloroperbenzoic acid and with the Yamamoto methylenating reagent to give the diols **8** and **9**, the epoxides **10** and **11**, and the cyclopropanes **12** and **13**, respectively. The reactions are more selective for the formation of the even-numbered diastereoisomers when the substituent on the stereogenic centre is an isopropyl or phenyl group than when it is a methyl group. The corresponding *Z*-allylsilanes, *Z*-**7**, are even more selective in this sense, giving more of the diol **14** than of **15**, and only the epoxides **16** and the cyclopropanes **18**. The ground-state conformation, as measured by the coupling constants in **24** and **25**, correlates with the diastereoselectivity, as does a simple calculation of the relative energies of the two most appropriate conformations of the starting materials.

Allylsilanes undergo electrophilic substitution reactions regiospecifically in the S_E2' sense,[1] and stereospecifically in an *anti* sense, as shown, principally, by the work of Wetter,[2] Eschenmoser,[3] Kumada,[4] Kitching[5] and ourselves.[6] The stereochemistry of these reactions, like the stereochemistry of those reported in the four papers preceding this, are concisely explained by the general picture **1**, which only needs modification in detail in any particular case in order to take account of



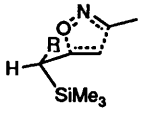
1 **2**

the nature of the electrophile, the preferred angle of attack by the electrophile and the small changes these induce in the optimum dihedral angles along the bond between the trigonal carbon and the stereogenic centre. The detail we address in this paper is the choice of an outside position for the carbon group R, as in the structure **1**, or an inside position, as in the structure **2**. The problem arose, because the clean *anti* stereospecificity in the electrophilic substitution reactions of allylsilanes, explained with a picture like **1**,[4] was in contrast to some observations by Curran[7] and by Vedejs.[8] Curran found that the allylsilane **3** reacted with pivalonitrile oxide to give the isoxazolines **4** and **5**



3 **4** 33:67 **5**

in a 1:2 ratio. The major product **5** is that which corresponds to attack on the allylsilane in the sense **2**. Houk explained this result by pointing out[9] that the carbon–silicon bond and the incoming bond from the oxygen atom of the nitrile oxide will adopt an antiperiplanar arrangement **6**, in which the inside position for the R group causes it to suffer less $A^{1,3}$-strain than it does in a transition state modelled only by the crude drawing **2**. An alternative or additional explanation[8] is that attack on the upper surface of conformation **2**, *cis* to the hydrogen atom, is less hindered than attack on the lower surface of conformation **1**, *cis* to the R group. Vedejs similarly found that the reaction of



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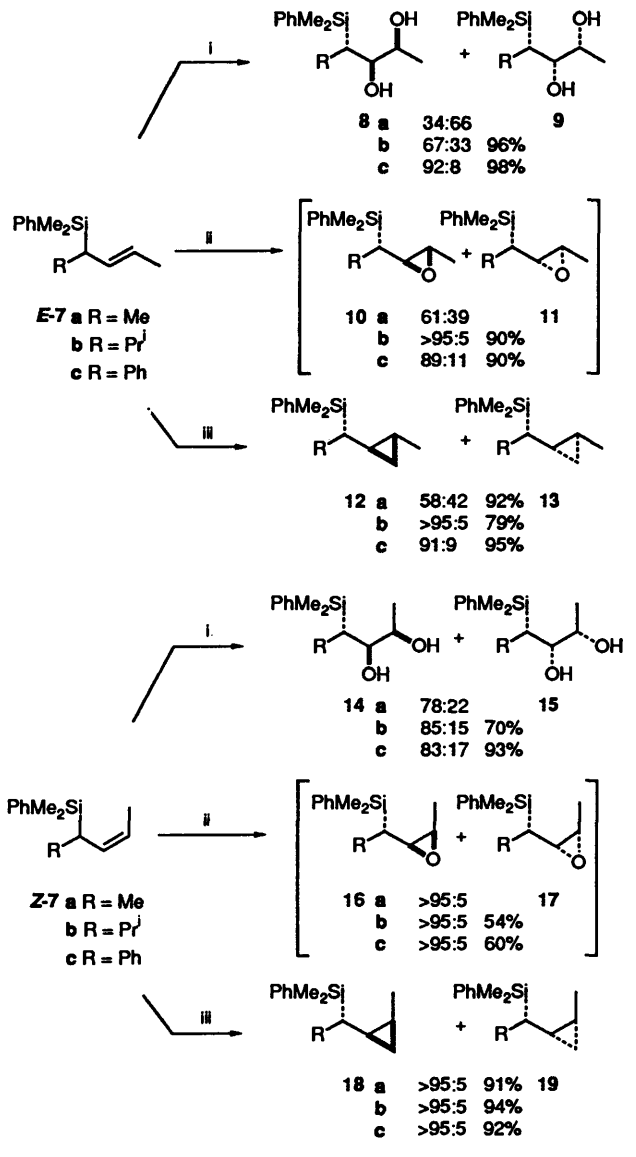
osmium tetroxide on the allylsilane *E*-**7a** gave the diols **8a** and **9a** in a ratio of 1:2, with the diol **9a** as the major product. In Vedejs's and Curran's examples the R group was a methyl group, and the group on the double bond *cis* to the stereogenic centre was only a hydrogen atom, inducing little $A^{1,3}$-strain. When the group *cis* to the stereogenic centre was a methyl group, as in the *Z*-allylsilane *Z*-**7a**, Vedejs found that osmium tetroxide reacted predominantly in the sense **1**, to give the diol **14a**, presumably because the $A^{1,3}$-strain was now more severe. Thus, it seems that the crude model represented by the picture **1** is applicable as long as the $A^{1,3}$-strain is severe enough, as it is in the reactions described in the preceding papers in this series, because, in almost all of them, the group *cis* to the stereogenic centre is, as we have already pointed out, larger than a hydrogen atom. However, it was not easy to guess in which sense allylsilanes would react if the R group were made larger than a methyl group, while leaving the group *cis* to the stereogenic centre as only a hydrogen atom. It might be that increasing the size of the R group would make the lower surface of **1** even more hindered relative to the upper surface of **2**, and the reaction might become even more selective for attack in the sense **2**. Alternatively, the conformation **2**, and even its more exact version **6**, might suffer so much $A^{1,3}$-strain that it would not be significantly populated, and reaction would then take place predominantly in the sense **1**. In this paper, we report in full our results, already reported in a preliminary communication,[10] on the reactions of osmium tetroxide, *m*-chloroperbenzoic acid (MCPBA) and the Yamamoto version of the Simmons–Smith methylenating reagent on allylsilanes having methyl, phenyl and isopropyl groups on the stereogenic centre of both *E*- and *Z*-allylsilanes. In the following paper, we report the related hydroborations of a wider range of allylsilanes. In general, we find for all these reactions that increasing the size of the R group increases the likelihood that reaction will take place in the sense **1**.

Results and Discussion

We prepared the six allylsilanes *E*- and *Z*-**7a–c**, by the

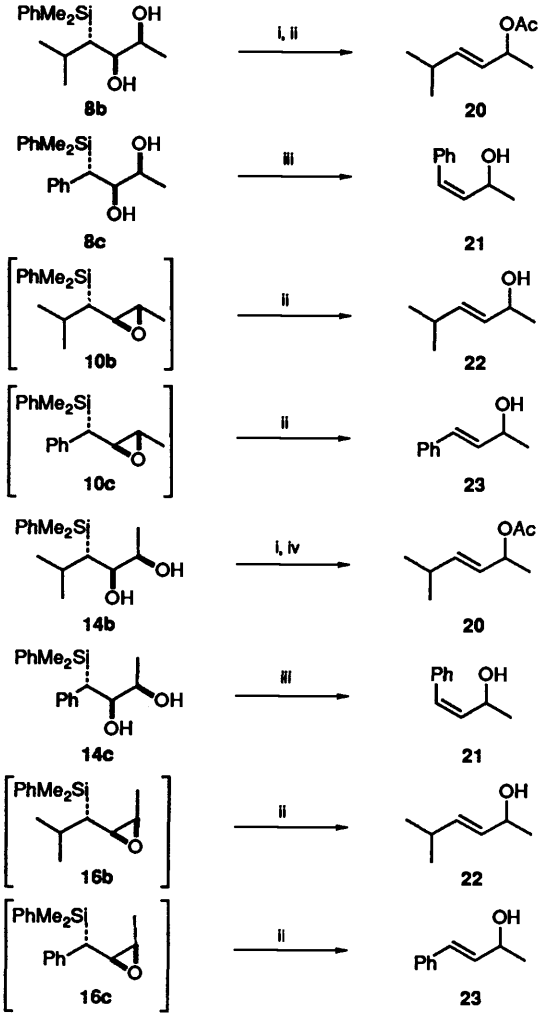
methods described in two papers later in this series.[11,12] We treated each with osmium tetroxide, with MCPBA and with Yamamoto's trimethylaluminium–methylene iodide mixture.[13] In our hands this has given better yields of the cyclopropanes, and, insofar as we have compared them, the same diastereoselectivity as the usual Simmons–Smith reagent. We present our results in Scheme 1, where the products corresponding to



Scheme 1 *Reagents:* i, OsO_4, Py; ii, MCPBA, NaH_2PO_4; iii, Me_3Al, CH_2I_2

attack in the sense **1** are on the left, and the products corresponding to attack in the sense **2** are on the right. The results quoted for the reactions in the **a** series (R = Me) with osmium tetroxide and with MCPBA are those of Vedejs and McClure.[8]

We proved the relative stereochemistry of the diols and the epoxides by the methods illustrated in Scheme 2, where we show only the fate of the major component of each of the mixtures. Thus we converted the mixture of diols **8b** and **9b** into the corresponding mixture of diacetates, which were still present in a ratio of 67:33. We then used the fluoride ion-catalysed elimination of the silyl group and the vicinal acetate group to obtain the known allylic acetates,[11] in which the *E*-isomer **20** was the major component of the 67:33 mixture. Since this process is known to be stereospecifically *anti*,[14] the major diol must have been **8b**. The yield was good enough (~80%) for us to be sure that an inefficient conversion of the major diacetate coupled with a more efficient elimination from the minor diacetate had not misled us. We merely assume that the osmium tetroxide reaction is *syn* stereospecific as usual. It was a little easier to assign configurations to the mixture of diols **8c** and **9c**: sodium hydride induced a Peterson elimination to give directly the known allylic alcohols,[11] in which the *Z*-isomer **21** was the major component. Since this reaction is known to be stereospecifically *syn*,[15] the major diol must have been **8c**. We had been unable to use this simple reaction to prove the stereochemistry of the diol **8b**, because the Peterson elimination did not take place. In all probability in this case, when the silyl group is not benzylic, the oxyanion from the γ-hydroxy group had attacked the silyl group, displacing the phenyl group, as we have found before in a similar situation.[6] The other diols in Scheme 2 similarly gave the allylic alcohols and acetates shown.



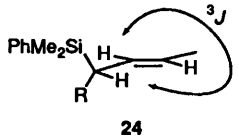
Scheme 2 *Reagents:* i, Ac_2O, Et_3N, DMAP; ii, TBAF, THF; iii, NaH, THF; iv, CsF, DMSO

We did not try seriously to isolate the epoxides shown in Scheme 1, because they underwent desilylative opening too readily. As Vedejs and McClure had, we treated the reaction mixtures directly with fluoride ion to induce the formation of the allylic alcohols shown in Scheme 2. The yields and ratios shown in Scheme 1 are those of the allylic alcohols actually isolated, and the assignments of configuration follow from the *anti* stereospecificity of the opening process. We had no easy way of proving the relative stereochemistry of the cyclopro-

panes shown in Scheme 1. These are assigned merely by analogy, but the assignment is probably reliable, given the extraordinarily close similarity of all the cyclopropanation ratios to those of the corresponding epoxidations.

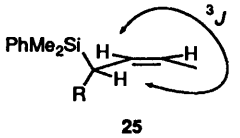
It is not clear, of course, how much of each product in these reactions is produced from each of the conformations **1** and **2**. Thus, at one extreme, implicit in the discussion above, the even-numbered products like **8** could be entirely the result of reaction *anti* to the silyl group in a conformation close to **1**, and the odd-numbered products like **9** could be the result entirely of reaction *anti* to the silyl group in a conformation close to **2**. Our results add some evidence to the general impression from all the work on allylsilanes that this is substantially true. The alternative possibility is that some of each of the odd-numbered products could have come from reaction taking place in a conformation close to **1**, but with attack taking place *syn* to the silyl group. Were this to be a *substantial* pathway, we would have expected the larger R groups studied in this work to lead to larger amounts of the odd-numbered products in the reactions of the **b** and **c** series than in the **a** series. That this is a reasonable expectation is suggested by some work described in an earlier paper in this series on enolate alkylations, where the conformation corresponding to **2** was hardly populated. In that work, with most of the reaction probably taking place in a conformation close to **1**, we found that the larger the R group the less diastereoselective was the attack *anti* to the silyl group, at least in the series methyl > isopropyl > *tert*-butyl.[16] Since this is not what is observed in the results in this paper, we conclude that a larger group than methyl on the stereogenic centre makes the cycloadditions more selective in the sense **1** than in the sense **2**. Evidently, it is energetically more favourable for a large group R to avoid the $A^{1,3}$ interaction in **2** than it is for the R group to avoid the incoming electrophile in **1**. Obviously, the extent to which this is true is affected by the size of the incoming electrophile, and the lower selectivity with osmium tetroxide may reflect this effect.

In most of the discussion above, we have concentrated on the conformations of the starting materials, trusting that the transition structures would have most of the same features, a reasonable assumption given that the reactions are probably exothermic in the stereochemistry-determining step. We also have some evidence from this work that supports this approach. The coupling constant between the hydrogens illustrated in **24** and **25** is some measure of the extent to which this conformation



24

R	^3J
Me	7.5
Pr^i	9.8
Ph	9.8

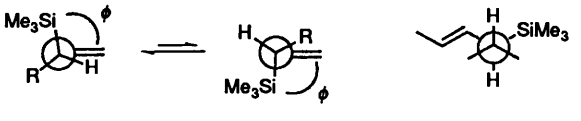


25

R	^3J
Me	10.5
Pr^i	11.4
Ph	11.4

is populated, the higher the coupling constant the more this conformation is populated, as Bothner-By established for alkenes in general.[17] He found that the maximum coupling constant was 11 Hz. When the R group in the *E*-allylsilane is methyl, and the reactions are least selective in the sense **1**, the coupling constant is only 7.5 Hz, indicating that a substantial proportion of the starting material is not in a conformation close to **1**, but is probably in a conformation close to **2**. At the other extreme, when the R group in the *Z*-allylsilane is isopropyl or phenyl, and all three reactions are highly selective in this sense, the coupling constant is 11.4 Hz, which marginally exceeds Bothner-By's maximum. In between, the coupling constants correlate quite well with the degree of diastereoselectivity in ours and Vedejs's reactions. Taking only the osmium tetroxide reactions, the least selective of the reagents and the only one for which a ratio can actually be measured from all six allylsilanes, a plot of the log of the ratio of diastereoisomers to the coupling constants gives a surprisingly good straight line with one anomalous point (the reaction of *E*-**7c**). Excluding this point, the correlation coefficient is 0.9966. It would seem that the conformation of the starting material is not too bad a starting point for picturing the transition structures.

We also estimated the likely difference in energy between the two conformations close to **1** and **2** for each of the six allylsilanes **7**. Hehre and his co-workers have calculated the energies for but-3-en-2-ylsilane **3** (using SiH_3 in place of $SiMe_3$) at the 3-21G* level, and found that conformations close to those of the pictures **1** and **2** were low-energy minima, with that in **1** the global minimum. The difference in energy between these two conformations was calculated to be between 2.1 and 2.5 kJ mol^{-1}.[18] The dihedal angle φ, as defined in **26** and **27** was 108° in both conformations, close to the angle of 107° measured for allylsilane itself.[19] Applying Still's Macromodel, with Cartledge's adjusted parameters[20] applied to the MM2 force field, to the same allylsilane, we simply fixed the dihedral angle φ at a series of values from 0 to 360° and found the structure with minimum energy for each, bunching our points near the minima. We then plotted this energy against the dihedral angle, and found reassuringly a smooth curve, with a difference between the two low-energy conformations of 2.8 kJ mol^{-1}. The lowest energy conformation had φ 112°, with the hydrogen atom tilted a little below the plane of the π-bond, as in **26**. The next higher energy minimum, actually the only other minimum, had a conformation close to **27**, with the angle φ 107°. These



26 **27** **28**

R	ΔE/kJmol^{-1} MM2-82	MM2-updated
E-Me	3.1	2.2
E-Pr^i	4.9	1.9
E-Ph	5.3	8.8
Z-Me	9.0	11.4
Z-Pr^i	11.2	8.8
Z-Ph	14.5	12.1

figures were close enough to Hehre's and to the experimentally determined values to indicate that our simple approach was not likely to be seriously misleading. We then calculated the difference in energy between the two low-energy conformations for each of the six allylsilanes **7**, except that we used a trimethylsilyl group in place of the phenyldimethylsilyl group. The values are listed below the drawings **26** and **27**, both for an older force field (MM2-82) and the modified forcefield. The results confirm our earlier diagnoses, with one anomaly—the isopropyl group appears in the calculations with the modified forcefield to impart a smaller difference to the energy of the two conformations than a methyl group does, in contrast to its influence on the stereochemistry of our reactions. We can only surmise that our calculations are too crude, and that higher level calculations might give better results. The fact that the older force field leads to a better fit with our results supports this

supposition. However, although the numbers for the isopropyl group do not fit our expectation, the conformation we find about the bond between the isopropyl group and the stereogenic centre is revealing. The hydrogen atoms are cleanly *anti* to each other in the lowest energy conformation **28**, with both alternative rotamers more than 10 kJ mol^{-1} higher in energy. The isopropyl group is, therefore, presenting one of its methyl groups towards the double bond most of the time, removing the ambiguity about the orientation of the isopropyl group.

Experimental

Preparation of the Allylsilanes.—The *E*-allylsilanes were prepared by the methods described in a paper later in this series,[11] and the *Z*-allylsilanes were prepared by the methods described in another paper later in this series.[12]

Reactions of the Allylsilanes with Osmium Tetroxide.—Typically, osmium tetroxide (100 mg, 0.39 mmol) in pyridine (2 cm^3) was stirred with the allylsilane (0.34 mmol) for 18 h at room temp. Sodium metabisulfite (100 mg) in water (0.5 cm^3) was added to the mixture which was then stirred for a further 5 h. Water (2 cm^3) was added to the mixture which was then extracted with ether (4 × 10 cm^3). The combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the diols. The following diols were prepared by this method.

(2RS,3SR,4RS)-4-*Dimethyl(phenyl)silyl-5-methyl*-2,3-*diol* **8b** (64%). Separated by preparative TLC (SiO_2, hexane–EtOAc, 1:1); R_f (hexane–EtOAc, 1:1) 0.4; ν_{max}(film)/cm^{-1} 3365 (OH), 1260 (SiMe) and 1163 (SiPh); $\delta(CDCl_3)$ 7.60–7.30 (5 H, m, Ph), 3.82 (1 H, quintet, *J* 6.4, MeC*H*OH), 3.48 (1 H, dd, *J* 6.4 and 4.4, $Me_2CHCHOH$) 2.16 (1 H, d, septet, *J* 2.5 and 7, Me_2CH), 1.87 (2 H, s, OH), 1.16 (1 H, dd, *J* 4.4 and 2.5, CHSi), 1.10 (3 H, d, *J* 7.0, Me_AMe_BCH), 1.06 (3 H, d, *J* 6.4, *Me*CHOH), 0.96 (3 H, d, *J* 7.0, Me_AMe_BCH), 0.43 (3 H, s, $SiMe_AMe_B$) and 0.41 (3 H, s, $SiMe_AMe_B$); *m/z* 221 (11%, M − MeCHOH), 143 (28, M − MeCHOH − PhH) and 135 (100, $SiMe_2Ph$) (Found: M − MeCHOH, 221.1365. $C_{15}H_{26}O_2Si$ requires *M* − MeCHOH, 221.1362) and (2RS,3SR,4SR)-4-dimethyl(phenyl)silyl-5-*methylhexane*-2,3-*diol* **9b** (32%); R_f (hexane–EtOAc, 1:1) 0.5; ν_{max}(film)/cm^{-1} 3395 (OH), 1256 (SiMe) and 1123 (SiPh); $\delta(CDCl_3)$ 7.6–7.3 (5 H, m, Ph), 3.59 (1 H, dd, *J* 8.1 and 2.1, $Me_2CHCHOH$), 3.50 (1 H, dq, *J* 8.1 and 6.1, MeC*H*OH), 2.01 (1 H, d septet, *J* 2.1, and 6.9, Me_2CH), 1.56 (2 H, br s, OH), 1.11 (3 H, d, *J* 6.1, *Me*CHOH), 1.04 (1 H, t, *J* 2.1, CHSi), 0.93 (3 H, d, *J* 6.9, Me_AMe_BCH), 0.91 (3 H, d, *J* 6.9, Me_AMe_BCH) and 0.40 (6 H, s, $SiMe_2$); *m/z* 221 (11%, M − MeCHOH), 143 (17, M − MeCHOH − PhH) and 135 (100, $SiMe_2Ph$) (Found: M − MeCHOH, 221.1377. $C_{15}H_{26}O_2Si$ requires *M* − MeCHOH, 221.1362).

(2RS,3SR,4RS)-4-*Dimethyl(phenyl)silyl-4-phenylbutane*-2,3-*diol* **8c** *and* (2RS,3SR,4SR)-4-*dimethyl(phenyl)silyl-4-phenylbutane*-2,3-*diol* **9c** (98%). R_f (hexane–EtOAc, 1:1) 0.5; ν_{max}(CH_2Cl_2)/cm^{-1} 3535 (OH), 1258 (SiMe) and 1127 (SiPh); $\delta(CDCl_3)$(major isomer) 7.5–7.0 (10 H, m, 2 × Ph), 3.55 (1 H, dd, *J* 7.2 and 4.4, PhCC*H*OH), 3.42 (1 H, dq, *J* 7.2 and 6.2, MeC*H*OH), 2.28 (1 H, d, *J* 4.4, PhC*H*), 1.9 (2 H, br s, OH), 0.92 (3 H, d, *J* 6.2, *Me*CHOH), 0.29 (3 H, s, $SiMe_AMe_B$) and 0.12 (3 H, s, $SiMe_AMe_B$); $\delta(CDCl_3)$(minor isomer) 7.5–7.0 (10 H, m, 2 × Ph), 3.72 (1 H, dd, *J* 3 and 10, PhCC*H*OH), 3.45 (1 H, m, MeC*H*OH), 2.54 (1 H, d, *J* 10, PhC*H*), 0.95 (3 H, d, *J* 7, *Me*CHOH), 0.19 (3 H, s, $SiMe_AMe_B$) and 0.11 (3 H, s, $SiMe_AMe_B$); *m/z* 282 (1%, M − H_2O), 177 (17, M − Ph − H_2O − C_2H_4), 148 (100, $PhMe_2SiCH$) and 135 (100, $SiMe_2Ph$) (Found: M − H_2O, 282.1440. $C_{18}H_{24}O_2Si$ requires *M* − H_2O, 282.1440). The ratio 92:8 was determined by integration of several of the peaks in the ^1H NMR spectrum.

(2RS,3RS,4SR)-4-*Dimethyl(phenyl)silyl-5-methylhexane*-2,3-*diol* **14b** (60%). Separated by preparative TLC (SiO_2, hexane–EtOAc, 1:1); R_f (hexane–EtOAc, 1:1) 0.5; ν_{max}(film)/cm^{-1} 3420 (OH), 1255 (SiMe) and 1110 (SiPh); $\delta(CDCl_3)$ 7.58–7.30 (5 H, m, Ph), 3.80–3.68 (2 H, m, MeC*H*CH), 1.94 (1 H, d septet, *J* 2.4 and 7, Me_2CH), 1.68 (1 H, d, *J* 4.7, OH), 1.52 (1 H, d, *J* 5.6, OH), 1.28 (1 H, dd, *J* 5.9 and 2.4, CHSi), 1.09 (3 H, d, *J* 6.2, *Me*CH), 0.93 (3 H, d, *J* 7, Me_AMe_BCH), 0.91 (3 H, d, *J* 7, Me_AMe_BCH), 0.42 (3 H, s, $SiMe_AMe_B$) and 0.40 (3 H, s, $SiMe_AMe_B$); *m/z* 221 (1.5%, M − MeCHOH), 143 (12, M − MeCHOH − PhH) and 135 (100, $SiMe_2Ph$) (Found: M − MeCHOH, 221.1380. $C_{15}H_{26}O_2Si$ requires *M* − MeCHOH, 221.1362) and (2RS,3RS,4RS)-4-*dimethyl(phenyl)silyl-5-methyl-4-hexane*-2,3-*diol* **15b** (10%); R_f (hexane–EtOAc, 1:1) 0.4; $\delta(CDCl_3)$ 7.54–7.32 (5 H, m, Ph), 3.8–3.7 (2 H, m, MeC*H*CHOH), 2.35–2.2 (1 H, m, Me_2CH), 1.61 (2 H, br s, OH), 1.2 (1 H, m, CHSi), 1.10 (3 H, d, *J* 7.1, Me_AMe_BCH), 0.99 (3 H, d, *J* 7.1, Me_AMe_BCH), 0.93 (3 H, d, *J* 6.1, *Me*CHOH), 0.41 (3 H, s, $SiMe_AMe_B$) and 0.38 (3 H, s, $SiMe_AMe_B$).

(2RS,3RS,4SR)-4-*Dimethyl(phenyl)silyl-4-phenylbutane*-2,3-*diol* **14c** *and* (2RS,3RS,4RS)-4-*dimethyl(phenyl)silyl-4-phenylbutane*-2,3-*diol* **15c** (93%); R_f (hexane–EtOAc, 1:1) 0.45; ν_{max}(film)/cm^{-1} 3425 (OH), 1247 (SiMe) and 1108 (SiPh); $\delta(CDCl_3)$(major isomer) 7.52–7.12 (10 H, m, 2 × Ph), 3.96 (1 H, dd, *J* 6.1 and 6.6, PhCC*H*OH), 3.61 (1 H, quintet, *J* 6, MeC*H*OH), 2.56 (1 H, d, *J* 6.6, PhC*H*), 1.77 (1 H, br s, OH), 1.59 (1 H, br s, OH), 1.01 (3 H, d, *J* 6.2, *Me*CHOH), 0.37 (3 H, s, $SiMe_AMe_B$) and 0.16 (3 H, s, $SiMe_AMe_B$); $\delta(CDCl_3)$(minor isomer) 7.5–7.1 (10 H, m, 2 × Ph), 4.2 (1 H, dd, *J* 3 and 11, PhCC*H*OH), 3.55 (1 H, m, MeC*H*OH), 2.39 (1 H, d, *J* 11, PhC*H*), 0.28 (3 H, s, $SiMe_AMe_B$) and 0.20 (3 H, s, $SiMe_AMe_B$); *m/z* 267 (1%, M − Me − H_2O), 177 (15, M − Ph − H_2O − C_2H_4), 148 (45, $PhMe_2SiCH$) and 135 (100, $SiMe_2Ph$) (Found: M − Me − H_2O, 267.1225. $C_{18}H_{24}O_2Si$ requires *M* − Me − H_2O, 267.1205). The ratio 83:17 was determined by integration of several of the peaks in the ^1H NMR spectrum.

Reactions of the Allylsilanes with m-*Chloroperoxybenzoic Acid.*—Typically, *m*-chloroperoxybenzoic acid (87 mg, 0.5 mmol) was stirred with the allylsilane (0.37 mmol) and a suspension of disodium hydrogen phosphate (71 mg, 0.5 mmol) in dry dichloromethane (1 cm^3) at 0 °C for 2 h. The mixture was diluted with ether (5 cm^3), filtered, and evaporated under reduced pressure. The residue in ether (10 cm^3) was washed with saturated aqueous sodium hydrogen carbonate (5 cm^3) and brine (5 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give the silyl epoxide. The crude epoxide in THF (1 cm^3) was stirred at room temp. for 15 h with tetrabutylammonium fluoride (TBAF) (1.0 mol dm^{-3} solution in THF; 0.5 cm^3). The mixture was filtered through silica gel, washing with dichloromethane, and then evaporated under reduced pressure to give the allylic alcohols, all of which were distinctively recognisable (TLC, ^1H NMR) as the starting materials used for the synthesis of some of the allylsilanes.[11] The ratios of isomers were determined by integration of appropriate signals in the ^1H NMR spectra. Ratios quoted as >95:5 mean that we were unable to detect the signals of the isomers, even though we knew in every case where to look for them. The only compound we had not made in the earlier work, the *Z*-isomer of **22**, is described below.

5-Methylhex-3-yn-2-yl Benzoate.—5-Methylhex-3-yn-2-ol[11] (0.56 g, 5 mmol), triethylamine (0.5 g, 5 mmol), DMAP (0.05 g, 0.4 mmol) and benzoic anhydride (1.13 g, 5 mmol) were kept in dichloromethane (6 cm^3) at room temperature for 20 h. The mixture was then diluted with ether (20 cm^3) washed with aqueous hydrochloric acid (2 mol dm^{-3}; 20 cm^3), aqueous sodium hydrogen carbonate (20 cm^3) and brine (10 cm^3), dried

($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane–Et_2O, 20:1) to give the *benzoate* (0.902 g, 84%); R_f (hexane–Et_2O, 20:1) 0.3; ν_{max}(film)/cm^{-1} 2258 (C≡C) and 1724 (C=O); δ($CDCl_3$) 8.05 (2 H, m, *o*-Ph), 7.7–7.2 (3 H, m, *m*- and *p*-Ph), 5.7 (1 H, dq, *J* 1.8 and 6.6, C*H*OBz), 2.58 (1 H, d septet, *J* 1.8 and 6.8, Me_2CH), 1.57 (3 H, d, *J* 6.6, *Me*CHOBz) and 1.16 (6 H, d, *J* 6.8, Me_2CH); *m/z* 216 (13%, M^+), 105 (100, PhCO) and 77 (41, Ph) (Found: M^+, 216.1158. $C_{14}H_{16}O_2$ requires *M*, 216.1150).

(Z)-5-*Methylhex*-3-*en*-2-*yl Benzoate*.—The benzoate (0.72 g) was stirred in methanol (15 cm^3) with palladium (5% on $BaSO_4$; 0.1 g) and treated with quinoline (0.3 g) under hydrogen for 1.5 h. The catalyst was filtered off and the filtrate evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane–Et_2O, 20:1) to give the *benzoate* (0.68 g, 94%); R_f (hexane–Et_2O, 20:1) 0.37; ν_{max}(film)/cm^{-1} 1718 (C=O); δ($CDCl_3$) 8.05 (2 H, m, *o*-Ph), 7.7–7.2 (3 H, m, *m*- and *p*-Ph), 5.92 (1 H, d quintet, *J* 1.4 and 6.3, C*H*OBz), 5.6–5.1 (2 H, m, CH=CH), 2.76 (1 H, d septet, *J* 2.0 and 6.6, Me_2CH), 1.41 (3 H, d, *J* 6.3, *Me*CHOBz), 0.99 (3 H, d, *J* 6.6, Me_AMe_BCH) and 0.98 (3 H, d, *J* 6.6, Me_A*Me*$_B$CH); *m/z* 218 (3%, M^+), 175 (2, M – Pr^i), 105 (100, PhCO) and 77 (26, Ph) (Found: M^+, 218.1324. $C_{14}H_{18}O_2$ requires *M*, 218.1306).

(Z)-5-*Methylhex*-3-*en*-2-*ol*.—The benzoate (0.218 g, 1 mmol) in ether (2 cm^3) was stirred with lithium aluminium hydride (2 mmol) in ether (2 cm^3) under nitrogen at room temp. for 2 h. Aqueous ammonium chloride (0.5 cm^3) was added at 0 °C to the mixture, which was then filtered through Celite, washing with ethyl acetate. The filtrate was washed with brine (5 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give an equimolar mixture of benzyl alcohol and the *alcohol*; δ($CDCl_3$) 7.35 (5 H, s, *Ph*CH_2OH), 5.3–5.2 (2 H, m, CH=CH), 4.6 (2 H, s, PhCH_2OH), 4.7–4.55 (1 H, m, MeC*H*OH), 2.7–2.0 (2 H, m, Me_2CH and OH), 1.2 (3 H, d, *J* 7, *Me*CHOH), 0.97 (3 H, d, *J* 7, Me_AMe_BCH) and 0.94 (3 H, d, *J* 7, Me_A*Me*$_B$CH).

Cyclopropanation of the Allylsilanes.—Typically, trimethylaluminium (2 mol dm^{-3} solution in hexane; 0.37 cm^3) was added to the allylsilane (0.37 mmol) and diiodomethane (200 mg, 0.74 mmol) in dry dichloromethane (1 cm^3) under nitrogen at room temperature and the mixture stirred for 3 h. Dichloromethane (10 cm^3) and water (0.5 cm^3) were added to the mixture, after which the organic layer was separated, washed with brine (5 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane) to give the mixture of cyclopropanes. The following cyclopropanes were prepared by this method.

(1RS,2RS)-2-[(1′SR)-*Dimethyl*(*phenyl*)*silylethyl*]-1-*methylcyclopropane* **12a** *and* (1RS,2RS)-2-[(1′RS)-*dimethyl*(*phenyl*)*silylethyl*]-1-*methylcyclopropane* **13a** (92%). R_f (hexane) 0.45; ν_{max}(film)/cm^{-1} 1259 (SiMe) and 1125 (SiPh); δ($CDCl_3$) 7.6–7.2 (5 H, m, Ph), 1.1–0.9 (6 H, 4 × d, Me), 0.33 (6 H, s, $SiMe_2$, major isomer), 0.32 (3 H, s, Si$Me_A$$Me_B$, minor isomer), 0.31 (3 H, s, $SiMe_A$*Me*$_B$, minor isomer) and 0.5–0.0 (5 H, m, remainder); *m/z* 218 (3%, M^+), 135 (100, $SiMe_2Ph$) and 82 (12, M – $PhMe_2SiH$) (Found: M^+, 218.1495. $C_{14}H_{22}Si$ requires *M*, 218.1491).

(1RS,2RS)-2-[(1′SR)-1-*Dimethyl*(*phenyl*)*silyl*-2-*methylpropyl*]-1-*methylcyclopropane* **12b** (79%). R_f (hexane) 0.45; ν_{max}(film)/cm^{-1} 1261 (SiMe) and 1123 (SiPh); δ($CDCl_3$) 7.6–7.3 (5 H, m, Ph), 1.92 (1 H, d, septet, *J* 3.2 and 6.7, Me_2CH), 0.96 (6 H, d, *J* 6.7, Me_2CH), 0.89 (3 H, d, *J* 6.9, *Me*CH), 0.36 (3 H, s, Si$Me_A$$Me_B$), 0.35 (3 H, s, $SiMe_A$*Me*$_B$) and 1.1–0.8 and 0.4–0.0 (5 H, m, remainder); *m/z* 203 (6%, M – Pr), 135 (100, $SiMe_2Ph$) and 110 (23, M – $PhMe_2SiH$) (Found: M – Pr, 203.1260. $C_{16}H_{26}Si$ requires M – Pr, 203.1256).

(1RS,2RS)-2-[(1′RS)-*Dimethyl*(*phenyl*)*silylbenzyl*]-1-*methylcyclopropane* **12c** *and* (1RS,2RS)-2-[(1′SR)-*dimethyl*(*phenyl*)*silylbenzyl*]-1-*methylcyclopropane* **13c** (95%). R_f (hexane) 0.35; ν_{max}(film)/cm^{-1} 1257 (SiMe) and 1126 (SiPh); δ($CDCl_3$) (major isomer) 7.4:6.8 (10 H, m, 2 × Ph), 1.52 (1 H, d, *J* 10.9, PhC*H*), 0.94 (3 H, d, *J* 6, *Me*CH), 0.8 (1 H, m, cyclopropane CH), 0.5 (1 H, m, cyclopropane CH), 0.28 (3 H, s, Si$Me_A$$Me_B$), 0.26 (3 H, s, $SiMe_A$*Me*$_B$), 0.16 (1 H, dt, *J* 7.9 and 4.7, CH_AH_B) and 0.06 (1 H, dt, *J* 8.3 and 4.7, CH_AH_B); δ($CDCl_3$) (minor isomer) 0.95 (3 H, d, *J* 5, *Me*CH), 0.25 (3 H, s, Si$Me_A$$Me_B$) and 0.24 (3 H, s, $SiMe_A$*Me*$_B$); *m/z* 280 (1%, M^+), 144 (8, M – $PhMe_2SiH$) and 135 (100, $SiMe_2Ph$) (Found: M^+, 280.1627. $C_{19}H_{24}Si$ requires *M*, 280.1647). The ratio 92:8 was determined by integration of the SiMe peaks in the ^1H NMR spectrum.

(1RS,2SR)-2-[(1′RS)-*Dimethyl*(*phenyl*)*silylethyl*]*cyclopropane* (1-*methyl* **18a** (91%). R_f (hexane) 0.45; ν_{max}(film)/cm^{-1} 1245 (SiMe) and 1110 (SiPh); δ($CDCl_3$) 7.55–7.31 (5 H, m, Ph), 0.99 (3 H, d, *J* 7.3, *Me*CHSi), 0.82 (3 H, d, *J* 2.4, *Me*CH), 0.9–0.4 and −0.36 to −0.42 (5 H, m, remainder), 0.318 (3 H, s, Si$Me_A$$Me_B$) and 0.311 (3 H, s, $SiMe_A$*Me*$_B$); *m/z* 218 (2%, M^+), 135 (100, $SiMe_2Ph$) and 82 (12, M – $PhMe_2SiH$) (Found: M^+, 218.1496. $C_{14}H_{22}Si$ requires *M*, 218.1491). The allylsilane *Z*-**7a** used in this preparation was an 84:16 mixture with *E*-**7a**. GC (5 m, BP5 capillary column, 5% polymethylphenylsiloxane, 120 °C, N_2 carrier) of the products gave a major peak after 1290 s, and showed only three products in a ratio of 84.3:9.3:6.4. The minor pair of products had retention times identical with those of the cyclopropanes **12a** and **13a** prepared from *E*-**7a**.

(1RS,2SR)-2-[(1′RS)-1-*Dimethyl*(*phenyl*)*silyl*-2-*methylpropyl*]-1-*methylcyclopropane* **18b** (94%). R_f (hexane) 0.45; T_r (5% methylphenylsiloxane, 180 °C) 270 s; ν_{max}(film)/cm^{-1} 1248 (SiMe) and 1110 (SiPh); δ($CDCl_3$) 7.55–7.30 (5 H, m, Ph), 1.94 (1 H, d septet, *J* 3.3 and 6.9, Me_2CH), 0.94 (3 H, d, *J* 6.9, Me_AMe_BCH), 0.98 (3 H, d, *J* 6.9, Me_A*Me*$_B$CH), 0.74 (3 H, br s, *Me*CH), 0.36 (3 H, s, Si$Me_A$$Me_B$), 0.34 (3 H, s, $SiMe_A$*Me*$_B$) and 0.88–0.5 and 0.2 to −0.19 (5 H, m, remainder); *m/z* 246 (2.5%, M^+) and 135 (100, $SiMe_2Ph$) (Found: M^+, 246.1803. $C_{16}H_{26}Si$ requires *M*, 246.1803).

(1RS,2SR)-2-[(1′SR)-*Dimethyl*(*phenyl*)*silylbenzyl*]-1-*methylcyclopropane* **18c** (92%). R_f (hexane) 0.35; T_r (5% methylphenylsiloxane, 180 °C) 517 s; ν_{max}(film)/cm^{-1} 1245 (SiMe) and 1112 (SiPh); δ($CDCl_3$) 7.4–6.9 (10 H, m, 2 × Ph), 1.93 (1 H, d, *J* 11, PhCH), 0.87 (3 H, d, *J* 5, *Me*CH), 0.28 (3 H, s, Si$Me_A$$Me_B$), 0.25 (3 H, s, $SiMe_A$*Me*$_B$) and 1.2–0.6 and −0.45 to −0.49 (4 H, m, remainder); *m/z* 280 (4.3%, M^+), 144 (20, M – $PhMe_2SiH$) and 135 (100, $SiMe_2Ph$) (Found: M^+, 280.1667. $C_{19}H_{24}Si$ requires *M*, 280.1647).

Conversion of the Diols into the Diacetates.—Typically, the silyl diol (25 mg), triethylamine (30 mg), DMAP (5 mg) and acetic anhydride (30 mg) were kept in dry dichloromethane (2 cm^3) at room temperature for 15 h under nitrogen. The solvent was evaporated under reduced pressure and the residue dissolved in ether (10 cm^3). The ether solution was washed with hydrochloric acid (1 mol dm^{-3}; 5 cm^3), saturated aqueous sodium hydrogen carbonate (5 cm^3) and brine (5 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give the diacetates. The following diacetates were prepared by this method.

(2RS,3SR,4RS)-2,3-*Diacetoxy*-4-*dimethyl*(*phenyl*)*silyl*-5-*methylhexane* (*diacetate from* **8b**) (84%). R_f (CH_2Cl_2) 0.2; ν_{max}(film)/cm^{-1} 1740 (C=O); δ($CDCl_3$) (major isomer) 7.6–7.3 (5 H, m, Ph), 5.18 (1 H, dd, *J* 7.1 and 3.6, PrCC*H*OAc), 5.04 (1 H, quintet, *J* 7.1, MeC*H*OAc), 2.17 (1 H, d septet, *J* 2.3 and 6.3, Me_2CH), 2.00 (3 H, s, MeCO), 1.93 (3 H, s, MeCO), 1.25 (1 H, dd, *J* 2.3 and 3.6, CHSi), 1.07 (6 H, d, *J* 6.3, Me_2CH), 0.91

(3 H, d, *J* 7.1, *Me*CHOAc), 0.39 (3 H, s, Si*Me*$_A$Me$_B$) and 0.36 (3 H, s, SiMe$_A$*Me*$_B$); δ($CDCl_3$) (minor isomer) 7.6–7.3 (5 H, m, Ph), 5.27 (1 H, dd, *J* 8.1 and 2.2, PrCC*H*OAc), 4.87 (1 H, dq, *J* 8.1 and 6.4, MeC*H*OAc), 2.0 (1 H, m, Me_2CH), 1.15 (3 H, d, *J* 6.4, *Me*CHOAc), 0.99 (3 H, d, *J* 6.8, *Me*$_A$Me$_B$CH), 0.91 (3 H, d, *J* 6.8, Me$_A$*Me*$_B$CH), 0.44 (3 H, s, Si*Me*$_A$Me$_B$) and 0.42 (3 H, s, SiMe$_A$*Me*$_B$); *m/z* 290 (1%, M^+ – AcOH), 135 ($PhMe_2Si$), 117 (100, $C_5H_9O_3$) and 114 (88, M – $PhMe_2Si$ – $AcOCH_2CO$) (Found: M – AcOH, 290.1686. $C_{19}H_{30}O_4Si$ requires M – AcOH, 290.1702).

(2RS,3RS,4SR)-2,3-*Diacetoxy*-4-*dimethyl*(*phenyl*)*silyl*-5-*methylhexane* (*diacetate from* **14b**) (77%). R_f (CH_2Cl_2) 0.2; ν_{max}(film)/cm^{-1} 1735 (C=O), 1265 (SiMe) and 1120 (SiPh); δ(CD_3SOCD_3) 7.6–7.2 (5 H, m, Ph), 5.13 (1 H, m, C*H*OAc), 4.7 (1 H, m, C*H*OAc), 1.91 (3 H, s, MeCO), 1.85 (3 H, s, MeCO), 1.85 (1 H, m, Me_2CH), 1.20 (1 H, m, CHSi), 0.95 (3 H, d, *J* 6, *Me*CHOAc), 0.8 (3 H, d, *J* 7, *Me*$_A$Me$_B$CH), 0.7 (3 H, d, *J* 7, Me$_A$*Me*$_B$CH) and 0.25 (6 H, s, $SiMe_2$).

Fluoride-induced Elimination.—Typically, the diacetate (10 mg) was heated with caesium fluoride (5 mg) in [$^2H_6$]-dimethyl sulfoxide (0.5 cm^3) in an NMR tube at 60 °C for 6 h. The clean ^{1}H NMR spectra indentified the (*E*)-5-methylhex-3-en-2-yl acetate as the major product with the *Z*-isomer as the minor, in ratios that matched the ratios of isomers in the starting diols. Both acetates were known from the synthetic work.[11]

Peterson Elimination.—Typically, the mixture of diols (80 mg, 0.26 mmol) was stirred with sodium hydride (21 mg, 0.9 mmol) in dry THF (3 cm^3) at room temperature for 15 h under nitrogen. Saturated aqueous ammonium chloride (3 cm^3) was added to the mixture which was then extracted with ether (3 × 10 cm^3). The extracts were combined, dried ($MgSO_4$) and evaporated under reduced pressure to give the mixture of 4-phenylbut-3-en-2-ols, identical (^{1}H NMR) with the samples prepared in the synthetic work,[11] in ratios that matched the ratios of isomers in the starting diols, and with the *Z*-isomer as the major product in both cases.

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