

## Asymmetric Dihydroxylation of Vinyl- and Allyl-silanes

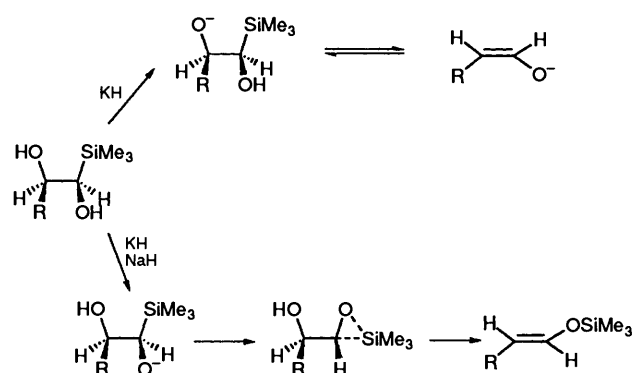
Alan R. Bassindale,\* Peter G. Taylor\* and Youli Xu

Chemistry Department, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK

Allyl- and vinyl-silanes undergo efficient dihydroxylation using the Sharpless AD-mix- $\alpha$  and  $\beta$ -reagents. Thirteen examples are given. The chemical yields were typically 80% or more, but the enantiomeric excesses (ee) are critically dependent on the structure of the alkene. The ee values obtained were greater than 96% for *E*-allyl- and vinyl-silanes but only 50–60% for the *Z*-analogues, and less than 30% for the parent allyl- and vinyl-silanes. A disubstituted vinylsilane required forcing conditions for reaction and gave an ee of 85%. The dihydroxy compounds from allylsilanes can be converted stereoselectively into chiral allyl alcohols. The vinylsilane-derived diols were readily converted into aldehydes by a Peterson reaction, and with a trace of acid acetals are recovered in high yield. For 1-trimethylsilyl-ethane-1,2-diol the cyclic sulfate was made in good yield and gave the 2-silyl-substituted aziridine with PhNH<sub>2</sub> and BuLi.

Allylsilanes<sup>1,2</sup> and vinylsilanes<sup>1,3,4</sup> and their derivatives are versatile reagents in organic synthesis owing to the powerful activating and directing effect of the silyl groups and the ease of removal of the silicon fragment through such reactions as the Peterson reaction<sup>5</sup>  $\beta$ -eliminations<sup>1</sup> and fluorodesilylations.<sup>1,2,6</sup> Our aim in this work was to investigate the dihydroxylation, and in particular the Sharpless asymmetric dihydroxylation,<sup>7</sup> of allyl- and vinyl-silanes and to investigate the synthetic utility of the products. The enantioselectivity of the Sharpless asymmetric dihydroxylation is generally very high (ee > 94%) for *E*-alkenes,<sup>7e</sup> moderate for monosubstituted alkenes (ee 74–97%)<sup>7c,e</sup> but less good for *Z*-alkenes (ee 16–80%).

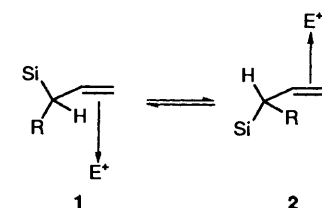
The synthesis of  $\alpha,\beta$ -dihydroxysilanes by acid-catalysed hydrolysis of  $\alpha,\beta$ -epoxysilanes and subsequently by osmium tetroxide-catalysed oxidation of vinylsilanes were first reported by Hudrlik.<sup>8–10</sup> It was also reported<sup>10</sup> that the  $\alpha,\beta$ -dihydroxysilanes undergo elimination reactions with metal hydrides. With KH there was competition between the Brook<sup>11</sup> rearrangement and the Peterson reaction.<sup>5</sup> However, when



NaH was used as the base the Brook rearrangement route was the exclusive route and the silylenol ether was obtained with a high degree of stereoselectivity.

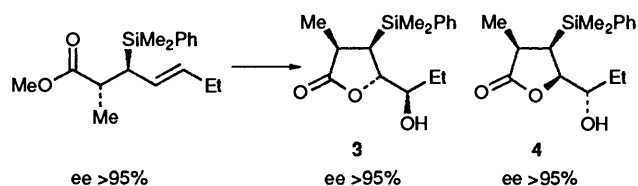
Fleming<sup>12–14</sup> examined the selectivity of dihydroxylation (and other reactions) of racemic *E*- and *Z*-allylsilanes, R(PhMe<sub>2</sub>Si)CHCH=CHR<sup>1</sup> and found some diastereoselectivity, especially for R = Ph, but not as much as for epoxidation or the Yamamoto version of the Simmons–Smith methylating reaction. In general increasing the size of R increased the likelihood that the reaction took place in the sense 1.

Fleming<sup>13,14</sup> also showed that the diols could undergo the



Peterson elimination with NaH, or a related fluoride-ion induced elimination, to give the allyl alcohols in stereoprecise reactions. Other diastereoselective osmylations using OsO<sub>4</sub> of chiral allylsilanes, followed by Peterson elimination have been reported.<sup>15,16</sup>

Procter<sup>17</sup> carried out a 'double asymmetric induction' of two chiral allylsilanes and by using dihydroquinidine 4-chlorobenzoate as catalyst<sup>7b</sup> in the most favourable case obtained ee values as high as 95% with a diastereoselectivity, 3:4, of 91:9.



In the present work a variety of allyl- and vinyl-silanes were subjected to the Sharpless asymmetric hydroxylation reaction using the AD-mix- $\alpha$  and - $\beta$  catalysts.<sup>7e</sup> The aim was to examine the effect of the silyl group on the enantioselectivity of the reaction and to use the resulting diols in synthesis. The effect of substitution at silicon was also examined.<sup>18</sup> We wished to investigate the effect of successively replacing the methyl groups in Me<sub>3</sub>Si by phenyl groups in the hope that there might be some specific interactions with the aromatic ligands that could enhance the enantioselectivity. In view of the strong directive and activating effect of the R<sub>3</sub>Si group and its high steric bulk we were interested to see whether *Z*-vinyl- and allyl-silanes were dihydroxylated with any greater selectivity than their organic counterparts.

When we started the work there were no reports on the asymmetric dihydroxylation of unsaturated silyl compounds and nothing was known about the effect of the bulky silyl substituent on stereoselectivity, but in addition to the work of Procter<sup>17</sup> there have been two very recent and closely related

communications on this topic. The first was by Soderquist<sup>19</sup> who obtained diols from  $\text{CH}_2=\text{CHSiR}_3$  ( $\text{R}_3 = \text{Me}_3, \text{Et}_3$  and  $\text{Pr}^i_3$ ),  $E\text{-BuCH}=\text{CHSiMe}_3$ ,  $Z\text{-BuCH}=\text{CHSiEt}_3$ ,  $\text{CH}_2=\text{CHCH}_2\text{-SiR}_3$  ( $\text{R}_3 = \text{Me}_3$  and  $\text{Pr}^i_3$ ),  $E\text{-BuCH}=\text{CHCH}_2\text{SiMe}_3$  and  $E\text{-Pr}^i\text{CH}=\text{CHCH}_2\text{SiMe}_3$  using AD-mix- $\alpha$  as the hydroxylation agent. The time for completion of the reaction increased as the steric bulk of the  $\text{R}_3\text{Si}$  group increased while the ee decreased from 44% for  $\text{R} = \text{Me}$  to 6% for  $\text{R} = \text{Pr}^i$ . An 89% ee was obtained for dihydroxylation of  $E\text{-BuCH}=\text{CHSiMe}_3$ , and the diol from  $E\text{-Pr}^i\text{CH}=\text{CHCH}_2\text{SiMe}_3$  (ee 68%) was shown to undergo a Peterson elimination with KH in diethyl ether to give the allyl alcohol with an identical ee to the diol. All the other silanes gave diols in which the enantiomeric excesses were much more modest (16–70%).

The most recent paper on asymmetric dihydroxylations by Sato and Sharpless<sup>20</sup> showed that three  $E$ -allylsilanes could be converted *via* the diols into the corresponding secondary allylic alcohol by the Peterson reaction with overall ee values of 91–94%, using the dihydroquinidine ligand DHQD-PHN as the dihydroxylation catalyst. A trisubstituted allylsilane gave the allyl alcohol with a maximum ee of 48% using the ligand DHQB-CLB. The AD-mix compounds were not as efficient as the other DHQD ligands. It was also observed that the ee of dihydroxylation decreased as Me was replaced by  $\text{Pr}^i$  in  $\text{CH}_2=\text{CHSiR}_3$ . We now report our results against this background of increasing interest in asymmetric diols produced from vinyl- and allyl-silanes.

## Results and Discussion

In this initial investigation we chose to limit the asymmetric dihydroxylation conditions to the use of the commercially available AD-mix- $\alpha$  and - $\beta$  (Aldrich Chemical Co. Inc.). We prepared thirteen different vinyl- and allyl-silanes and dihydroxylated each using both AD-mix- $\alpha$  and - $\beta$ . The enantiomeric excess of each reaction was measured by the use of the chiral shift reagent  $\text{Eu}(\text{hfc})_3$ . This method involved the direct addition of  $\text{Eu}(\text{hfc})_3$  to the diol and integration of selected  $^1\text{H}$  NMR resonances from each enantiomer. In general, in the presence of  $\text{Eu}(\text{hfc})_3$  the CH resonances on the hydroxy-bearing carbon atoms gave isolated, readily recognisable signals and integrations that were reproducible to within 1%. The results obtained compare very favourably with those of the more usual derivatisation to form Mosher's diesters.<sup>19,21,22</sup> The mixture reached equilibrium within 30 min and provided a quick and reliable measure of the enantiomeric excess. To be certain that the method was giving accurate results, racemic diols were prepared in a number of examples and in each case the position and integration of the CHO resonances of the two enantiomers confirmed our interpretation.

The chemical yields, conditions and ee values for the asymmetric dihydroxylation of the allyl- and vinyl-silanes are given in Table 1. The absolute configurations of the diols were not measured, but in each case the diol obtained from AD-mix- $\alpha$  was shown by NMR analysis with  $\text{Eu}(\text{hfc})_3$  to be the enantiomer of the diol obtained from AD-mix- $\beta$ . Although the two AD-mixes are not enantiomeric—the configuration of one of the chiral carbon atoms is the same in each catalyst—they generally have almost exactly equal and opposite effects and that was also observed in this work.

There is at least one example of seven different types of vinyl- or allyl-silanes; unsubstituted vinyl- and allyl-silanes;  $E$ - and  $Z$ -monosubstituted vinyl- and allyl-silanes; and a disubstituted vinylsilane,  $E\text{-Me}_3\text{Si}(\text{Me})\text{C}=\text{CHC}_6\text{H}_{13}$ . There are four unsubstituted vinylsilanes  $\text{Me}_{3-n}\text{Ph}_n\text{SiCH}=\text{CH}_2$  ( $n = 0\text{--}3$ ). We were surprised to find that the ee for dihydroxylation of  $\text{Me}_3\text{-SiCH}=\text{CH}_2$  with either of the two AD-mixes was as low as 34%. As Sharpless has found ee values between 74 and 93% for

monosubstituted alkenes<sup>7c</sup> we repeated the experiment several times and each time found a similar result. Subsequently we discovered that Sharpless<sup>20</sup> and Soderquist<sup>19</sup> found ee values of about 44% for vinyltrimethylsilane. It is not clear why the trimethylsilyl group should lower the ee so significantly but it is now well-established that large substituents on the silicon lower the enantioselectivity even more. We found that as methyl was replaced by phenyl, two possibly related effects were observed. First, the time for reaction increased and the isolated yields decreased considerably. As  $n$  in  $\text{Me}_{3-n}\text{Ph}_n\text{SiCH}=\text{CH}_2$  increased from 0 to 3, the time for reaction with AD-mix- $\beta$  at 0 °C increased from 14 to 96 h while the yield dropped from 80 to 25% (there were no observed by-products. The remainder of the mass balance was accounted for by unchanged vinylsilane). With AD-mix- $\alpha$  there was no reaction with  $\text{Ph}_3\text{SiCH}=\text{CH}_2$  after 96 h and the silane was recovered unchanged. Concomitantly as the number of phenyl groups and the reaction time increased the ee decreased dramatically from 34% with vinyltrimethylsilane to 0% with vinylmethyldiphenylsilane and vinyltriphenylsilane. A similar effect has been noted previously<sup>19,20</sup> as isopropyl groups replaced methyl groups, but the effect on ee and yield was not as marked. In both reports the increased steric effect of the isopropyl group was cited as the most likely cause of the effect. The phenyl group is roughly equivalent to an isopropyl group in size, so it is possible that with the phenyl group both steric and electronic effects militate against efficient asymmetric induction.

The large trimethylsilyl group was not a universally ineffective substituent in asymmetric dihydroxylations. The  $E$ -vinylsilanes (entries 10 and 11) both gave extremely high ee values, >95%, with both AD-mixes. There was effectively no difference between the effect of a phenyl group and a butyl group on the alkene in these examples. The  $E$ -allylsilane shown in entry 4 also gave 95% ee and it appears that the synthetically most useful dihydroxylations of silicon-containing alkenes will start with  $E$ -alkenes.

As with dihydroxylations of non-silylated alkenes<sup>7</sup> the  $Z$ -alkenes gave diols with lower ee than their  $E$ -counterparts.  $Z$ -1-Trimethylsilyloct-1-ene (entry 12) was readily dihydroxylated but the ee was the relatively modest 61%. Sharpless<sup>7c</sup> commented on the 'meso problem' as modelled by the catalyst-substrate interaction mnemonic<sup>7c,e</sup> as a factor in the lower ee values obtained for  $Z$ -alkenes. The hexyl and trimethylsilyl groups should have rather different steric demands and it is not easy to rationalise the low ee value in this case simply by a *meso* effect. Slightly lower ee values were obtained for the  $Z$ -allylsilanes shown in entries 2 and 3. In those examples we varied the length of the hydrocarbon chain attached to the double bond but found it to have no measurable effect on reaction times, chemical yields or ee, which were all about 50%. Once again the difference between vinyl- and allyl-silanes in asymmetric dihydroxylations is insignificant.

The one example of a disubstituted vinylsilane (entry 13) was interesting in that it did not react with either AD-mix at the usual 0 °C even after more than one week. However, after a week at 20 °C a chemical yield of about 50% was obtained with ee values of 80 and 85% with AD-mix- $\alpha$  and AD-mix- $\beta$ , respectively.

All of the diols that were prepared are stable under normal conditions and show no tendency to decompose spontaneously in the absence of acid or base. Hudrlik<sup>10</sup> has described the reaction of 1-trimethylsilyl 1,2-diols with bases but there is no information about their reactions with acid. We heated *threo*-1-trimethylsilyloctane-1,2-diol, **5**, under reduced pressure with a trace of acid and obtained an almost quantitative yield of the diastereoisomeric acetals, **6** and **7**. Presumably the acid catalyses elimination of  $\text{Me}_3\text{SiOH}$  to give octanal which, again with acid catalysis, reacts rapidly with the diol to form the cyclic

**Table 1** Asymmetric dihydroxylation of allyl- and vinyl-silane

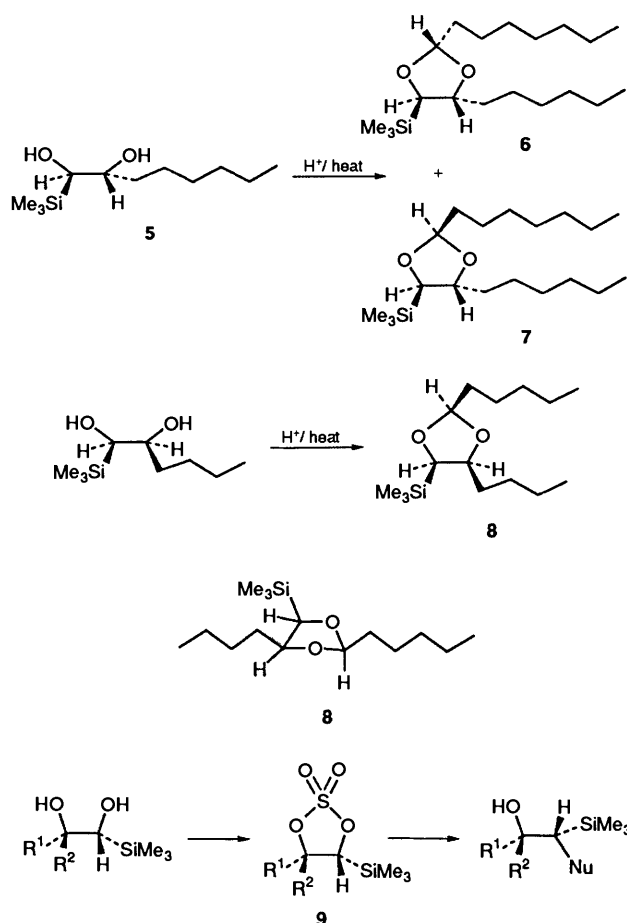
Entry	Allyl- and vinyl-silane	AD-mix- $\beta$ /(DHQD) <sub>2</sub> -PHAL				AD-mix- $\alpha$ /(DHQD) <sub>2</sub> -PHAL			
		ee (%)	T/°C	t/h	yield (%)	ee (%)	T/°C	t/h	yield (%)
1		34	0	14	82	34	0	14	81
2		54	0	24	83	50	0	24	81
3		43	0	24	81	50	0	24	79
4		95	0	28	86	95	0	28	86
5		53	0	24	82	53	0	24	84
6		34	0	14	80	34	0	14	81
7		27	0	48	83	25	0	48	84
8		0	0	62	30	0	0	62	31
9		0	0	96	25	0	0	96	0
10		96	0	24	76	95	0	24	79
11		97	0	28	83	97	0	28	82
12		61	0	26	81	61	0	26	78
13		85	20	168	53	80	20	168	47

acetals. NMR spectroscopy clearly shows the presence of two diastereoisomers in a ratio of about 60:40. No attempt was made to separate the diastereoisomers or identify which was formed in excess.

A similar reaction with *erythro*-1-trimethylsilylhexane-1,2-diol gave a single acetal stereoselectively, which was shown unambiguously by NOE measurements to be the *cis*-isomer, **8**. The all-*cis* configuration of **8** initially seemed surprising but

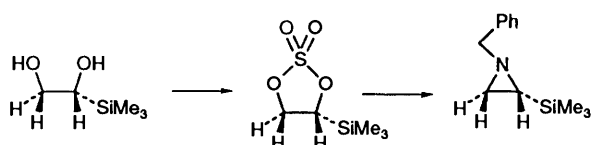
examination of molecular models showed that in this configuration the substituent groups can all adopt pseudo-equatorial conformations, as shown below. Such a relief of steric strain is not possible in the superficially less crowded *cis,trans,trans* configuration.

Sharpless has shown that diols can be transformed readily into the cyclic sulfates that are equivalent in chemistry to epoxides, but more reactive.<sup>23,24</sup> By analogy with the chemistry

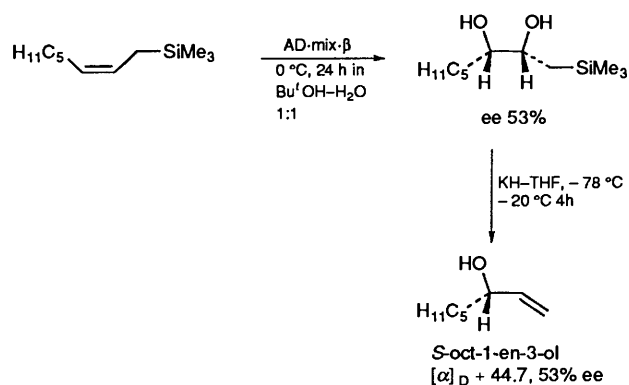


of epoxysilanes<sup>25</sup> the cyclic sulfates **9** should be extremely versatile synthetic intermediates, particularly if they could be prepared as a single enantiomer. To our knowledge chiral silyl epoxides have not been used in synthesis. The cyclic sulfates should undergo facile nucleophilic attack, most likely directed at the silicon-bearing carbon.<sup>25</sup>

We have succeeded in preparing the parent cyclic sulfate, **9** ( $\text{R}^1 = \text{R}^2 = \text{H}$ ), in good yield and converting it into the  $\alpha$ -silylaziridine by reaction with benzylamine, followed by  $\text{BuLi}$ .<sup>26</sup> The isolated yield was only 30%, but the reaction was only carried out once and no attempt has yet been made to optimise the yield. For reasons that elude us at present we have been unable to make any other cyclic sulfates. The published procedure<sup>23</sup> for cyclic sulfate synthesis consists of a one-pot reaction in two stages. The first stage is reaction of the diol with  $\text{SOCl}_2$  to form the cyclic sulfite (as a pair of diastereoisomers) and that is followed by an oxidation using  $\text{NaIO}_4/\text{RuCl}_3$ . We have shown that the reaction stops at the cyclic sulfite stage and these may be isolated, pure, in high yield. The oxidation step for the allyltrimethylsilanes and the *E*- and *Z*-substituted vinylsilanes does not proceed under the published conditions. The same reagents, either in a one-pot procedure or in two separate steps, were completely successful in the high yield synthesis of non-silyl-containing cyclic sulfates as reported.<sup>23</sup> Further investigations are in progress and modified oxidation conditions are being sought.



We also demonstrated that chiral secondary alcohols could be prepared in high optical and chemical yield by the  $\text{KH}$ -induced Peterson elimination reaction on the diols obtained from asymmetric dihydroxylation of *E*-allylsilanes. Our results in this area were essentially identical to those of Sharpless and Soderquist and confirmed that the absolute configuration of the diols derived from allylsilanes is that predicted by the Sharpless mnemonic. The *Z*-allylsilane shown in entry 5 (Table 1) was subjected to the following series of reactions<sup>20</sup> and, assuming that the dihydroxylation is *cis*, confirms the configuration of the diol to be the *2S,3S*-configuration. The *3S*-configuration of the secondary alcohol was confirmed by comparison of its positive rotation of  $+44.7$  with that of an authentic sample of *S*-oct-1-en-3-ol.<sup>27</sup>



So far we have been unable to confirm the absolute configuration of the diols derived from vinylsilanes for want of reactions that can be used unambiguously to convert those diols into compounds of known configuration. Work is in progress to find other ways of determining their configurations, but we have no reason to believe that the Sharpless mnemonic will not be followed.

In summary, we have examined the asymmetric dihydroxylation of seven different classes of silyl-substituted alkenes and made a preliminary study of some of the potential uses of the silyl-substituted vicinal diols. The compounds show promise and if the cyclic sulfate synthesis can be made general then new and useful chiral, silicon-containing reagents will be readily available.

## Experimental

NMR spectra were recorded as solutions in deuterated chloroform on a JEOL EX400 NMR spectrometer ( $J$  values are given in Hz). Infrared spectra were obtained as Nujol mulls or thin films using sodium chloride plates on a Nicolet 205 FT-IR spectrometer. Mass spectra were run on a VG20-250 quadrupole instrument equipped with an Ion Tech fast atom bombardment (FAB) gun. Enantiomeric excesses were determined by  $^1\text{H}$  NMR spectroscopy using the chiral europium shift reagent  $[\text{Eu}(\text{hfc})_3]$  in chloroform solution. All of the silyl diols were prepared by the Sharpless asymmetric dihydroxylation method.<sup>7e</sup> A typical procedure was as follows, a 25  $\text{cm}^3$  round bottomed flask, equipped with magnetic stirrer, was charged with *tert*-butyl alcohol (5  $\text{cm}^3$ ), water (5  $\text{cm}^3$ ), and  $\text{AD-mix-}\alpha$  or  $\text{AD-mix-}\beta$  (1.4 g). Stirring at room temperature produced two clear phases; the lower aqueous phase appeared bright yellow.

Methanesulfonamide (95 mg, 1 equiv. based on 1 mmol of olefin) was added at this point only if the olefin was trisubstituted or 1,2-disubstituted. No methanesulfonamide was added for terminal olefins. The mixture was cooled to  $0^\circ\text{C}$  and

some of the dissolved salts precipitated. Olefin (1 mmol) was added at once, and the heterogeneous slurry was stirred vigorously at 0 °C for 24 h. While the mixture was stirred at 0 °C, solid sodium sulfite (1.5 g) was added and the mixture was allowed to warm to room temperature and stirred for 30–60 min. Methylene dichloride (10 cm<sup>3</sup>) was added to the reaction mixture, and after separation of the layers, the aqueous phase was further extracted with the organic solvent (3.5 cm<sup>3</sup>) and when methanesulfonamide was used, the combined organic layers were washed with 2 mol dm<sup>-3</sup> KOH. The combined organic extracts were dried (MgSO<sub>4</sub>) and concentrated to give the diol and the ligand. This crude product was purified by flash chromatography on silica gel, CH<sub>2</sub>Cl<sub>2</sub>–Et<sub>2</sub>O, 3:2 (the ligand does not elute in this solvent system) to afford 1,2-silyl diol in 80% or more yield. The above procedure was used for all alkenes except 2-trimethylsilylnonane-2,3-diol which was made at room temperature over 7 days instead of the normal 0 °C for about 24 h.

The following data refer to reaction with AD-mix-β. The physical properties of the products from reaction with AD-mix-α were identical apart from the ee which is given in Table 1.

**3-Trimethylsilylpropane-1,2-diol.** The title compound (122 mg, 82% yield, 34% ee) was prepared from allyltrimethylsilane (114 mg) and AD-mix-β. The reaction mixture was kept at 0 °C for 14 h and worked up in the usual way. The product was separated by preparative TLC (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>–Et<sub>2</sub>O, 3:2); *R<sub>f</sub>* (CH<sub>2</sub>Cl<sub>2</sub>–Et<sub>2</sub>O, 3:2) 0.57; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 3340 br (OH), 2954, 1249 (SiMe), 1117, 1083, 864 and 840; *δ*<sub>H</sub>(CDCl<sub>3</sub>) 0.05 (9 H, s, SiMe<sub>3</sub>), 0.71 (1 H<sup>a</sup>, dd, *J* 14, *J* 8, CH<sub>2</sub>-Si), 0.81 (1 H<sup>b</sup>, dd, *J* 15, *J* 8, CH<sub>2</sub>-Si), 2.35 (2 H, br, OH), 3.34 (1 H<sup>a</sup>, dd, *J* 11, *J* 8, CH<sub>2</sub>OH), 3.60 (1 H<sup>b</sup>, dd, *J* 11, *J* 3, CH<sub>2</sub>OH) and 3.87 (1 H, m, CHO); *m/z* (FAB) 147 (13.5%, M – H), 115 (8, M – H<sub>2</sub>O – CH<sub>3</sub>), 102 (100, M – H<sub>2</sub>O – CHO) and 73 (44%, SiMe<sub>3</sub>).

**erythro-1-Trimethylsilylhexane-2,3-diol.** The title compound (158 mg, 83% yield, 54% ee) was prepared from 1-trimethylsilylhex-2-ene (156 mg) and AD-mix-β (1.4 g). The reaction mixture was kept at 0 °C for 24 h and then worked up in the usual way; *R<sub>f</sub>* (CH<sub>2</sub>Cl<sub>2</sub>–Et<sub>2</sub>O, 3:2) 0.75; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 3382 br (OH), 2957 (CH<sub>3</sub>), 2935 (=CH<sub>2</sub>), 1249 (SiMe), 863 and 840; *δ*<sub>H</sub>(CDCl<sub>3</sub>) 0.06 (9 H, s, SiMe<sub>3</sub>), 0.66 (1 H<sup>a</sup>, dd, *J* 14, *J* 4, CH<sub>2</sub>-Si), 0.81 (1 H<sup>b</sup>, dd, *J* 15, *J* 10, CH<sub>2</sub>-Si), 0.95 (3 H, t, CH<sub>3</sub>-C), 1.40 (2 H, m, CH<sub>2</sub>), 1.34 [1 H<sup>a</sup>, m, CH<sub>2</sub>-(COH)], 1.53 [1 H<sup>b</sup>, m, CH<sub>2</sub>-(COH)], 1.81 (2 H, br, OH), 3.56 (1 H, m, CH-C-Si) and 3.79 (1 H, m, CH-C<sub>3</sub>H<sub>7</sub>); *m/z* (FAB) 189 (4%, M – H), 157 (20, M – CH<sub>3</sub> – H<sub>2</sub>O), 117 [20, M – CH<sub>3</sub>(CH<sub>2</sub>)CHOH] and 73 (100, SiMe<sub>3</sub>) (Found: C, 56.5, H, 11.6. C<sub>9</sub>H<sub>22</sub>O<sub>2</sub>Si requires C, 56.79, H, 11.65%).

**erythro-1-Trimethylsilylnonane-2,3-diol.** The title compound (186 mg, 81% yield, 43% ee) was prepared from 1-trimethylsilylnon-2-ene (198 mg) and AD-mix-β (1.4 g). The reaction mixture was kept at 0 °C for 24 h and then worked up in the usual way; *R<sub>f</sub>* (CH<sub>2</sub>Cl<sub>2</sub>–Et<sub>2</sub>O, 3:2) 0.81; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 3399 br (OH), 2955, 2928, 2873, 2859, 1248 (SiMe), 862 and 840; *δ*<sub>H</sub>(CDCl<sub>3</sub>) 0.06 (9 H, s, SiMe<sub>3</sub>), 0.66 (1 H<sup>a</sup>, dd, *J* 15, *J* 4, CH<sub>2</sub>-Si), 0.80 (1 H<sup>b</sup>, dd, *J* 16, *J* 10, CH<sub>2</sub>-Si), 0.88 (3 H, t, CH<sub>3</sub>), 1.39 [10 H, m (CH<sub>2</sub>)<sub>5</sub>], 1.87 (2 H, br, OH), 3.53 [1 H, m, C<sub>6</sub>-CH(OH)] and 3.79 (1 H, m, CH-C-Si); *m/z* (FAB) 231 (3%, M – H), 199 (37, M – H<sub>2</sub>O – CH<sub>3</sub>), 125 (26, M + H – H<sub>2</sub>O – CH<sub>3</sub> – SiMe<sub>3</sub>) and 73 (100, SiMe<sub>3</sub>) (Found: C, 63.8, H, 9.1. C<sub>12</sub>H<sub>28</sub>O<sub>2</sub>Si requires: C, 64.24, H, 8.98%).

**threo-1-Phenyl-3-trimethylsilylpropane-1,2-diol.** The title compound (193 mg, 86% yield, 95% ee) was prepared from 1-phenyl-3-trimethylsilylprop-1-ene (190 mg) and AD-mix-β (1.4 g). The reaction mixture was kept at 0 °C for 28 h and then worked up in the usual way; *R<sub>f</sub>* (CH<sub>2</sub>Cl<sub>2</sub>–Et<sub>2</sub>O, 3:2) 0.81; *v*<sub>max</sub>(Nujol)/cm<sup>-1</sup> 3382 br (OH), 1246 (SiMe), 1073, 1055, 863 and 842; *δ*<sub>H</sub>(CDCl<sub>3</sub>) 0.01 (9 H, s, SiMe<sub>3</sub>), 0.56 (1 H<sup>a</sup>, dd, *J* 15, *J* 3, CH<sub>2</sub>-Si), 0.75 (1 H<sup>b</sup>, dd, *J* 14, *J* 11, CH<sub>2</sub>-Si), 2.33 (1 H, br,

OH), 2.65 (1 H, br, OH), 3.85 (1 H, m, CH-C-Si), 4.37 (1 H, d, *J* 6, CH-Ph) and 7.33 (5 H, m, Ph); *m/z* (FAB) 223 (2%, M – H), 207 (8, M – H<sub>2</sub>O + H<sup>+</sup>), 191 (10, M – H<sub>2</sub>O – CH<sub>3</sub>), 117 (87, M – PhCHOH) and 73 (80, SiMe<sub>3</sub>) (Found: C, 64.5, H, 8.7. C<sub>12</sub>H<sub>20</sub>O<sub>2</sub>Si requires C, 64.24, H, 8.89%).

**erythro-1-Trimethylsilyloctane-2,3-diol.** The title compound (181 mg, 82% yield, 53% ee) was prepared from 1-trimethylsilyloct-2-ene (184 mg) and AD-mix-β (1.4 g). The reaction mixture was kept at 0 °C for 24 h and then worked up in the usual way; *R<sub>f</sub>* (CH<sub>2</sub>Cl<sub>2</sub>–Et<sub>2</sub>O, 3:2) 0.81; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 3407 br (OH), 2956, 2931.8, 2874, 2861, 1248 (SiMe), 1052, 1034, 862 and 841; *δ*<sub>H</sub>(CDCl<sub>3</sub>) 0.06 (9 H, s, SiMe<sub>3</sub>), 0.66 (1 H<sup>a</sup>, dd, *J* 15, *J* 4, CH<sub>2</sub>-Si), 0.80 (1 H<sup>b</sup>, dd, *J* 15, *J* 11, CH<sub>2</sub>-Si), 0.89 (3 H, t, CH<sub>3</sub>), 1.38 [8 H, m, (CH<sub>2</sub>)<sub>4</sub>], 1.84 (2 H, br, OH), 3.54 (1 H, m, C<sub>5</sub>-CH) and 3.79 (1 H, m, CH-C-Si); *m/z* (FAB) 217 (3%, M – H<sup>+</sup>), 199 (14, M – H<sub>2</sub>O – H<sup>+</sup>), 185 (23, M – H<sub>2</sub>O – CH<sub>3</sub>), 147 (20, M – C<sub>5</sub>H<sub>11</sub>), 111 (28, C<sub>5</sub>H<sub>11</sub>COC) and 73 (100, SiMe<sub>3</sub>) (Found: C, 60.65, H, 11.95. C<sub>11</sub>H<sub>26</sub>O<sub>2</sub>Si requires C, 60.49, H, 12.00%).

**1-Trimethylsilylethane-1,2-diol.** The title compound (107 mg, 80% yield, 34% ee) was prepared from vinyltrimethylsilane (100 mg) and AD-mix-β (1.4 g). The reaction mixture was kept at 0 °C for 14 h and then worked up in the usual way; *R<sub>f</sub>* (CH<sub>2</sub>Cl<sub>2</sub>–Et<sub>2</sub>O, 3:2) 0.51; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 3368 br (OH), 2957, 1250 (SiMe), 1066, 882 and 840; *δ*<sub>H</sub>(CDCl<sub>3</sub>) 0.07 (9 H, s, SiMe<sub>3</sub>), 2.26 (2 H, br, OH), 3.46 (1 H, m, CH-Si) and 3.73 (2 H, m, CH<sub>2</sub>); *m/z* (FAB) 135 (12%, M + H<sup>+</sup>), 117 (23, M – H<sub>2</sub>O) and 73 (100, SiMe<sub>3</sub>); *m/z* (FAB) 135 (M + H<sup>+</sup>), 117 (M – OH<sup>-</sup>) and 73 (SiMe<sub>3</sub>).

**1-Dimethylphenylsilylethane-1,2-diol.** The title compound (163 mg, 83% yield, 27% ee) was prepared from vinyl dimethylphenylsilane (162 mg) and AD-mix-β (1.4 g). The reaction mixture was kept at 0 °C for 48 h and then worked up in the usual way; *R<sub>f</sub>* (CH<sub>2</sub>Cl<sub>2</sub>–Et<sub>2</sub>O, 3:2) 0.73; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 3367 br (OH), 1251 (SiMe), 1113 (SiPh), 877, 834, 817, 785, 734 and 700; *δ*<sub>H</sub>(CDCl<sub>3</sub>) 0.37 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>), 0.38 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>), 2.07 (2 H, br, OH), 3.64–3.76 (3 H, m, CH<sub>2</sub>CH) and 7.37–7.62 (5 H, m, SiPh); *m/z* (FAB) 393 (2%, M<sub>2</sub>H<sup>+</sup>), 197 (3, MH<sup>+</sup>), 195 (5 M – H<sup>+</sup>), 193 (6 M – 3 H<sup>+</sup>), 135 (100, SiMe<sub>2</sub>Ph) (Found: C, 61.35, H, 8.15. C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>Si requires C, 61.18, H, 8.21%).

**1-Diphenylmethylsilylethane-1,2-diol.** The title compound (80 mg, 30% yield, 0% ee) was prepared from vinyl diphenylmethylsilane (258 mg) and AD-mix-β (1.4 g). The reaction mixture was kept at 0 °C for 62 h and then worked up in the usual way; *R<sub>f</sub>* (CH<sub>2</sub>Cl<sub>2</sub>–Et<sub>2</sub>O, 3:2), 0.62; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 3375 br (OH), 1428, 1250 (SiMe), 1114 (SiPh), 791–733 and 699; *δ*<sub>H</sub>(CDCl<sub>3</sub>) 0.64 (3 H, s, SiMe), 2.11 (2 H, br, OH), 3.79 (2 H, dd, *J* 9, *J* 4, CH<sub>2</sub>-C), 4.05 (1 H, dd, *J* 8, *J* 4, CH-Si) and 7.36–7.45 (10 H, m, Ph); *m/z* (FAB) 257 (4%, M – H<sup>+</sup>), 255 (5, M – 2 H<sup>+</sup>), 241 (2, M – OH) and 197 (82, SiPh<sub>2</sub>Me).

**1-Triphenylsilylethane-1,2-diol.** The title compound (80 mg, 25% yield, 0% ee) was prepared from vinyltriphenylsilane (286 mg) and AD-mix-β (1.4 g). The reaction mixture was kept at 0 °C for 96 h and then worked up in the usual way; *R<sub>f</sub>* (CH<sub>2</sub>Cl<sub>2</sub>–Et<sub>2</sub>O, 3:2) 0.5; *v*<sub>max</sub>(Nujol)/cm<sup>-1</sup> 3354 br (OH), 1428, 1377, 1110 (SiPh) and 700; *δ*<sub>H</sub>(CDCl<sub>3</sub>) 2.12 (2 H, br, OH), 3.92 (2 H, d, *J* 6, CH<sub>2</sub>-C), 4.36 (1 H, t, CH-Si) and 7.35–7.66 (15 H, m, Ph); *m/z* 319 (6%, M – H<sup>+</sup>) and 259 [81, Si(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>] (Found: C, 74.85, H, 6.3. C<sub>20</sub>H<sub>20</sub>O<sub>2</sub>Si requires C, 74.96, H, 6.29%).

**threo-1-Trimethylsilylhexane-1,2-diol.** The title compound (160 mg, 76% yield, 96% ee) was prepared from *E*-1-trimethylsilylhex-1-ene (156 mg) and AD-mix-β (1.4 g). The reaction mixture was kept at 0 °C for 24 h and worked up in the usual way; *R<sub>f</sub>* (CH<sub>2</sub>Cl<sub>2</sub>–Et<sub>2</sub>O, 3:2) 0.74; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 3390 br (OH), 2958, 2934, 1249 (SiMe), 858 and 840; *δ*<sub>H</sub>(CDCl<sub>3</sub>) 0.09 (9 H, s, SiMe<sub>3</sub>), 0.91 (3 H, t, CH<sub>3</sub>), 1.31–1.59 (6 H, m, CH<sub>2</sub>), 1.85 (1 H, br, OH), 2.03 (1 H, br, OH), 3.17 (1 H, d, *J* 6, CH-Si) and

3.67 (1 H, m, CH-C<sub>4</sub>); *m/z* (FAB) 189 (3%, M - H<sup>+</sup>), 173 (17, M - OH<sup>-</sup>), 133 (28, M - C<sub>4</sub>H<sub>9</sub>) and 73 (100, SiMe<sub>3</sub>) (Found: C, 55.25, H, 11.15. C<sub>9</sub>H<sub>22</sub>O<sub>2</sub>Si requires C, 56.79, H, 11.65%).

*threo*-1-Trimethylsilyl-2-phenylethane-1,2-diol. The title compound (175 mg, 83% yield, 97% ee) was prepared from *E*-trimethylsilylstyrene (176 mg) and AD-mix-β (1.4 g). The reaction mixture was kept at 0 °C for 28 h and worked up in the usual way; *R*<sub>f</sub> (CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O, 3:2) 0.82; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 3324 br (OH), 1250 (SiMe), 843 and 700; *δ*<sub>H</sub>(CDCl<sub>3</sub>) 0.10 (9 H, s, SiMe<sub>3</sub>), 3.49 (1 H, d, *J* 7, CH-Si), 4.73 (1 H, d, *J* 7, CHPh) and 7.28-7.37 (5 H, m, Ph); *m/z* (FAB) 209 (1%, M - H<sup>+</sup>), 207 (2, M - 3 H<sup>+</sup>), 193 (35, M - OH<sup>-</sup>), 103 [15, M - PhCH(OH)] and 73 (100, SiMe<sub>3</sub>) (Found: C, 62.25, H, 8.65. C<sub>11</sub>H<sub>18</sub>O<sub>2</sub>Si requires C, 62.81, H, 8.62%).

*erythro*-1-Trimethylsilyloctane-1,2-diol. The title compound (177 mg, 81% yield, 61% ee) was prepared from *Z*-1-trimethylsilyloct-1-ene (184 mg) and AD-mix-β (1.4 g). The reaction mixture was kept at 0 °C for 26 h and worked up in the usual way; *R*<sub>f</sub> (CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O, 3:2) 0.80; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 3441 br (OH), 2955, 2928, 2859, 2124 (SiMe) and 839; *δ*<sub>H</sub>(CDCl<sub>3</sub>) 0.11 (9 H, s, SiMe<sub>3</sub>), 0.88 (3 H, t, CH<sub>3</sub>), 1.21-1.63 (10 H, m, CH<sub>2</sub>), 2.18 (2 H, br, OH), 4.32 (1 H, d, *J* 4, CH-Si) and 3.78-3.82 (1 H, m, CH-C<sub>6</sub>); *m/z* (FAB) 217 (1%, M - H<sup>+</sup>), (42, M - OH) and 73 (100, SiMe<sub>3</sub>) (Found: C, 60.0, H, 11.75. C<sub>11</sub>H<sub>26</sub>O<sub>2</sub>Si requires C, 60.49, H, 12.0%).

*2*-Trimethylsilylnonane-2,3-diol. The title compound (123 mg, 53% yield, 85% ee) was prepared from *E*-2-trimethylsilylnon-2-ene (198 mg) and AD-mix-β (1.4 g). The reaction mixture was kept at 20 °C for 168 h and worked up in the usual way; *R*<sub>f</sub> (CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O, 3:2) 0.83; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 3439 br (OH), 2956, 2928, 2859, 1249 (SiMe) and 839; *δ*<sub>H</sub>(CDCl<sub>3</sub>) 0.10 (9 H, s, SiMe<sub>3</sub>), 0.88 (3 H, t, CH<sub>3</sub>), 1.18 (3 H, s, CH<sub>3</sub>), 1.22-1.56 (10 H, m, CH<sub>2</sub>), 2.06 (2 H, br, OH) and 3.42 (1 H, dd, *J* 10, *J* 2); *m/z* (FAB) 231 (3%, M - H<sup>+</sup>), 215 (64%, M - HO<sup>-</sup>), 199 (6, M - H<sub>2</sub>O - CH<sub>3</sub>), 143 (29, M - C<sub>6</sub>H<sub>13</sub> - 4 H<sup>+</sup>), 91 (80%, SiMe<sub>3</sub> + H<sub>2</sub>O) and 73 (100%, SiMe<sub>3</sub>) (Found: C, 62.9, H, 11.85. C<sub>12</sub>H<sub>26</sub>O<sub>2</sub>Si requires C, 62.01, H, 12.14%).

*1*-Trimethylsilylethane-1,2-diyl Sulfite.—All apparatus was thoroughly dried in a hot (> 120 °C) oven at least 24 h before use. A mixture of 1-trimethylsilylethane-1,2-diol (3 g, 22.4 mmol), dried ether (60 cm<sup>3</sup>) and dried pyridine (3.52 g, 44.5 mmol) were cooled under nitrogen in an ice bath. Distilled thionyl chloride (2.79 g) was dissolved in dried ether (20 cm<sup>3</sup>) and added to the mixture slowly with a syringe and with rapid stirring. The mixture was stirred for about 30 min then filtered under nitrogen. The filtrate was washed with 5% aqueous sodium hydrogen carbonate to remove the excess of SOCl<sub>2</sub>, followed by saturated aqueous sodium chloride dried (MgSO<sub>4</sub>) and concentrated. The corresponding cyclic sulfite was obtained in good yield (2.94 g, 73%); *v*<sub>max</sub>(film)/cm<sup>-1</sup> 1255 (SiMe), 1208 (SO), 931, 845, 748 and 662; *δ*<sub>H</sub>(CDCl<sub>3</sub>) isomer a, 0.17 (9 H, s, SiMe<sub>3</sub>), 3.81 (1 H, dd, *J*<sub>gem</sub> 7.36, *J*<sub>trans</sub> 12.72, CH<sub>2</sub>), 4.39 (1 H, dd, *J*<sub>cis</sub> 6.84, *J*<sub>trans</sub> 12.72, CH) and 4.72 (1 H, dd, *J*<sub>cis</sub> 6.84, *J*<sub>gem</sub> 7.36, CH<sub>2</sub>); *δ*<sub>H</sub>(CDCl<sub>3</sub>) - 3.98 (SiMe<sub>3</sub>), 68.62 (CH) and 72.23 (CH<sub>2</sub>); isomer b, 0.15 (9 H, s, SiMe<sub>3</sub>), 3.79 (1 H, dd, *J*<sub>trans</sub> 13.2, *J*<sub>cis</sub> 6.36, CH), 4.33 (1 H, dd, *J*<sub>gem</sub> 8.8, *J*<sub>trans</sub> 13.2, CH<sub>2</sub>) and 4.56 (1 H, dd, *J*<sub>cis</sub> 6.36, *J*<sub>gem</sub> 8.8, CH<sub>2</sub>); *δ*<sub>C</sub> - 3.98 (SiMe<sub>3</sub>), 68.51 (CH<sub>2</sub>) and 76.43 (CH).

*1*-Trimethylsilylethane-1,2-diyl Sulfate.—1-Trimethylsilylethane-1,2-diyl sulfite (2.85 g, 15.82 mmol), carbon tetrachloride (16 cm<sup>3</sup>), acetonitrile (16 cm<sup>3</sup>), water (24 cm<sup>3</sup>), sodium periodate (5.06 g) and RuCl<sub>3</sub>·3H<sub>2</sub>O (2.53 mg) were placed in a 250 cm<sup>3</sup> flask. The mixture was stirred vigorously for 1 h at 0 °C and then the temperature was allowed to rise to room temperature and stirring continued for another hour. The

mixture was then diluted with ether (130 cm<sup>3</sup>) and the two phases were separated. The organic layer was washed with water (5 cm<sup>3</sup>), saturated aqueous NaHCO<sub>3</sub> (2-3 cm<sup>3</sup>) and brine (5 cm<sup>3</sup>). After drying over MgSO<sub>4</sub>, the solution was filtered through a pad of silica gel. The filtrate was concentrated to give the crude sulfate (2.2 g, 71% yield). *v*<sub>max</sub>(film)/cm<sup>-1</sup> 1381 (SO<sub>2</sub>), 1257 (SiMe), 1206 (SO<sub>2</sub>), 956, 848, 823 and 791; *δ*<sub>C</sub>(CDCl<sub>3</sub>) - 4.31 (SiMe<sub>3</sub>), 72.57 (CH<sub>2</sub>) and 77.84 (CH); *δ*<sub>H</sub>(CDCl<sub>3</sub>) 0.10 (9 H, s, SiMe<sub>3</sub>), 4.48 (1 H, m, CH) and 4.62 (2 H, m, CH<sub>2</sub>).

*1*-Benzyl-2-trimethylsilylaziridine.—All apparatus was completely dried (> 120 °C, 24 h) before use. Benzylamine (0.55 g, 5.1 mmol) was added slowly under nitrogen to 1-trimethylsilylethane-1,2-diyl sulfate (0.5 g, 2.548 mmol) in dried THF (25 cm<sup>3</sup>) and the mixture stirred for 24 h at room temperature. The solution was cooled to -78 °C and 2.5 mol dm<sup>-3</sup> BuLi solution in hexane (1.24 cm<sup>3</sup>, 3.1 mmol) was added and stirring continued for another 2 h. The resulting solution was diluted with dried ether (50 cm<sup>3</sup>), filtered on a pad of silica gel and concentrated. The product was purified by chromatography on silica gel to give pure product (110 mg, 30% yield). *v*<sub>max</sub>(film)/cm<sup>-1</sup> 3031, 2956, 2924, 1496, 1454, 1247, 1027, 1012, 854, 839, 752, 730 and 698; *δ*<sub>H</sub>(CDCl<sub>3</sub>) - 0.12 (9 H, s, SiMe<sub>3</sub>), 0.50 (1 H, dd, *J* 4.6, *J* 7.4, CH), 1.46 (1 H, d, *J* 8, CH<sub>2</sub>), 1.72 (1 H, d, *J* 4.8, CH<sub>2</sub>), 2.89 (1 H, d, *J* 13.2, CH<sub>2</sub>-Ph), 3.86 (1 H, d, *J* 13.2, CH<sub>2</sub>-Ph) and 7.21-7.32 (5 H, m, Ph); *δ*<sub>C</sub> - 3.19 (SiMe<sub>3</sub>), 28.57 (CH), 31.83 (CH<sub>2</sub>), 67.56 (CH<sub>2</sub>-Ph), 126.87, 128.11, 128.20 and 139.7 (Ph); *m/z* 205 (3%, M), 204 (8, M - H<sup>+</sup>), 190 (11, M - CH<sub>3</sub>), 114 (100, M - CH<sub>2</sub>-Ph), 91 (58, CH<sub>2</sub> - Ph), 86 (46, HCSiMe<sub>3</sub>) and 73 (70, SiMe<sub>3</sub>).

*1*-Trimethylsilyloctane-1,2-diol.—Water (31.4 cm<sup>3</sup>) and 1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> (17.4 cm<sup>3</sup>) were added to a solution of 1-trimethylsilyl-1,2-epoxyoctane (4.0 g, 9.98 mmol) in THF (31.4 cm<sup>3</sup>). The mixture was stirred for 3 h at 0 °C, then at room temperature for 2 h. After the addition of saturated aqueous NaHCO<sub>3</sub> (50 cm<sup>3</sup>), the solution was stirred for 30 min, and the combined ethereal extracts were washed with water, dried (MgSO<sub>4</sub>), concentrated and chromatographed on Florisil (85 g). Elution with light petroleum (b.p. 40-60 °C) removed unchanged epoxide and a small amount of octanol, further elution with methylene dichloride and with 10% ether in CH<sub>2</sub>Cl<sub>2</sub> gave 1-trimethylsilyloctane-1,2-diol the physical properties of which were identical with those of the compound prepared by the osmium tetroxide route.

*Decomposition of threo*-1-Trimethylsilyloctane-1,2-diol.—*threo*-1-Trimethylsilyloctane-1,2-diol from the epoxide-opening reaction was heated under reduced pressure (0.02 mmHg) to 60-65 °C for 30 min. The resulting product was a mixture of acetals 6 and 7 (95% yield); *m/z* 328 (3%, M), 313 (8, M - CH<sub>3</sub>), 229 (19, M - C<sub>7</sub>H<sub>15</sub>), 200 (12, M - C<sub>7</sub>H<sub>15</sub> - CHO), 185 (24%, M - C<sub>7</sub>H<sub>15</sub> - CHO - CH<sub>3</sub>), 157 (20), 129 (100) and 73 (71, SiMe<sub>3</sub>); *v*<sub>max</sub>(film)/cm<sup>-1</sup> 2956, 2928, 1467, 1459, 1250 (SiMe), 1116, 867 and 841; *δ*<sub>H</sub>(CDCl<sub>3</sub>) isomer-1 (60%) 0.08 (9 H, s, SiMe<sub>3</sub>), 0.86 (6 H, t, CH<sub>3</sub>), 1.28-1.62 [22 H, m, (CH<sub>2</sub>)<sub>5</sub>, (CH<sub>2</sub>)<sub>6</sub>], 3.08 (1 H, d, *J* 9.28, CH-Si), 3.78-3.82 (1 H, m, CH-C<sub>6</sub>), 4.75 (1 H, t, CH-O<sub>2</sub>); isomer-2 (40%) 0.05 (9 H, s, SiMe<sub>3</sub>), 0.087 (6 H, t, CH<sub>3</sub>), 1.28-1.62 [22 H, m, (CH<sub>2</sub>)<sub>5</sub>, (CH<sub>2</sub>)<sub>6</sub>], 3.08 (1 H, d, *J* 9.28, CH-Si), 3.78-3.83 (1 H, m, CH-C<sub>6</sub>) and 4.86 (1 H, t, CH-O<sub>2</sub>) (Found: C, 68.9; H, 12.1. C<sub>19</sub>H<sub>40</sub>O<sub>2</sub>Si requires C, 69.45; H, 12.27%).

*Decomposition of erythro*-1-trimethylsilyloctane-1,2-diol. *erythro*-1-Trimethylsilyloctane-1,2-diol from the epoxide ring-opening reaction was heated under 0.03 mmHg to about 40 °C for 30 min. The product acetal was passed through a column which was packed with silica gel and eluted with dichloro-

methane-hexane (1 : 1)  $R_f$  0.95. The product yield was 85%,  $m/z$  271 (7%,  $M^+ - H$ ), 257 (6,  $M^+ - CH_3$ ), 201 (5,  $C_5H_{11}$ ), 157 (41), 143 (17), 129 (100), 73 (75,  $SiMe_3$ );  $\nu_{max}(film)/cm^{-1}$  3645, 3583, 2957, 2860, 1467, 1408, 1251 ( $SiMe$ ), 1199, 1114 and 842;  $\delta_H(CDCl_3)$  0.12 (9 H, s,  $SiMe_3$ ), 0.87–0.92 (6 H, t,  $CH_3$ ), 1.27–1.66 (20 H, m,  $CH_2$ ), 3.47 (1 H, d,  $J$  7.2,  $CH-Si$ ), 4.13 (1 H, ddd,  $J_1$  10.2,  $J_2$  7.2,  $J_3$  3,  $OCHCH_2^-$ ) and 4.78 (1 H, t,  $O_2CH$ );  $\delta_C(CDCl_3)$  –2.30 (3 C, s,  $SiMe_3$ ), 13.98 (1 C, s,  $CH_3$ ), 14.02 (1 C, s,  $CH_3$ ), 22.58 (2 C, s,  $CH_2$ ), 23.67 (1 C, s,  $CH_2$ ), 28.68 (1 C, s,  $CH_2$ ), 31.81 (1 C, s,  $CH_2$ ), 34.04 (1 C, s,  $CH_2$ ), 34.52 (1 C, s,  $CH_2$ ), 74.48 (1 C, s,  $CH-Si$ ), 78.87 (1 C, s,  $OCH$ ) and 105.46 (1 C, s,  $O_2CH$ ) (Found: C, 66.25, H, 11.8.  $C_{15}H_{32}O_2Si$  requires C, 66.11, H, 11.84%).

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