

## A Regiocontrolled and Stereocontrolled Synthesis of Allylsilanes from $\beta$ -Silyl Enolates

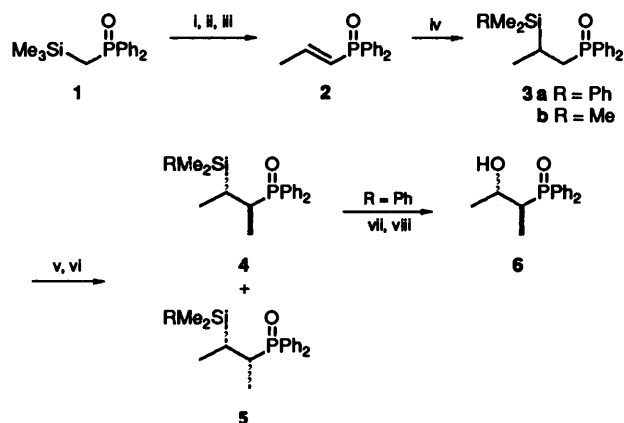
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The  $\alpha$ -lithiated diphenylphosphine oxides **3** react with methyl iodide to give the phosphine oxides **4** and **5** in a ratio of 3–4:1. The corresponding reaction with aldehydes gives all four diastereoisomeric alcohols **7–10**, which are not suitable for the synthesis of allylsilanes by a Wittig–Horner reaction. The  $\beta$ -dimethyl(phenyl)silyl enolates **13–15** and **25–28** react with aldehydes to give aldol products with high diastereoselectivity. The benzyl and allyl ester groups can be cleaved from these aldols to give the acids **16–18** and **29–32**. The acids, in turn, can be induced to undergo decarboxylative elimination stereospecifically either in a *syn* or an *anti* sense to give the allylsilanes **19, 20, 23, 24, 33, 34** and **39–41**. A similar series of reactions can be carried out with the  $\beta$ -trimethylsilyl enolates **45** and **46** giving the allylsilanes **49, 50, 53** and **54**.

The synthesis of allylsilanes from allylic alcohols described in the preceding paper<sup>1</sup> is notable for its good stereocontrol and regiocontrol. The stereogenic centre carrying the silyl group can be set up in either sense, and the placing of the silyl group at either end of an allylic fragment is reasonably, although not always completely controllable. Nevertheless, this route has deficiencies—it is not conducive to the synthesis of allylsilanes with a *Z* double bond, nor does it provide much opportunity for improving the stereochemical purity of the intermediates. The syntheses of allylsilanes described in this paper, some of which have already been published in preliminary form,<sup>2</sup> were designed to overcome these problems. They do so, at the expense of being somewhat more cumbersome. We have, nevertheless, used them frequently in our subsequent and continuing work on allylsilanes,<sup>3,4</sup> where the high level of control that they provide has been invaluable. We have also used the same idea in our synthesis of allylstannanes, which has been published in full.<sup>5</sup>

### Results and Discussion

Our first hope had been to use a Wittig–Horner reaction to make the double bond. Warren's work has established that  $\beta$ -hydroxydiphenylphosphine oxides can often be set up with either diastereoisomeric relationship between the diphenylphosphine oxide group and the hydroxy group; the intermediates are usually crystalline and can be easily purified, and hence either an *E* or a *Z* double bond can be set up in a high

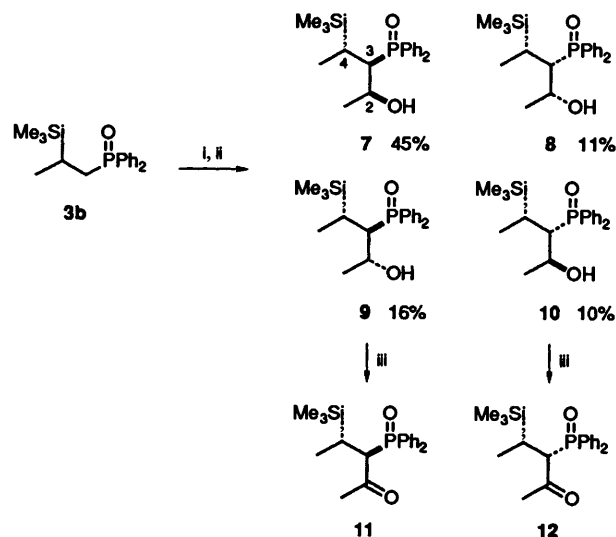


Scheme 1 Reagents: i, BuLi; ii, MeCHO; iii, NaOEt; iv,  $(\text{RMe}_2\text{Si})_2\text{-CuCN Li}_2$ ; v, LDA; vi, MeI; vii,  $\text{BF}_3\cdot 2\text{AcOH}$ ; viii, MCPBA

state of purity by the *syn* stereospecific elimination of these two groups.<sup>6,7</sup>

We first examined the diastereoselectivity of attack by methyl iodide on the anion adjacent to the diphenylphosphine oxide group in the  $\beta$ -silyl phosphine oxides **3** (Scheme 1). In both cases, there was some diastereoselectivity, 78:22 from **3a** and 81:19 from **3b**, in favour of the formation of the *anti* isomer **4**. In the dimethyl(phenyl)silyl series, we established the relative configuration by converting the major product **4** into the known  $\beta$ -hydroxyphosphine oxide **6**,<sup>7</sup> using our two-step procedure for the conversion of dimethyl(phenyl)silyl groups into hydroxys.<sup>8</sup> In spite of the difference between a lithiated phosphine oxide and a lithium enolate, the sense of the diastereoselectivity is in line with our observations on the diastereoselectivity of alkylation of  $\beta$ -silyl enolates,<sup>9</sup> but the degree of selectivity is less.

We next examined the corresponding reactions with acetaldehyde (Scheme 2), which proved to be disappointing.



Scheme 2 Reagents: i, BuLi; ii, MeCHO; iii, PDC

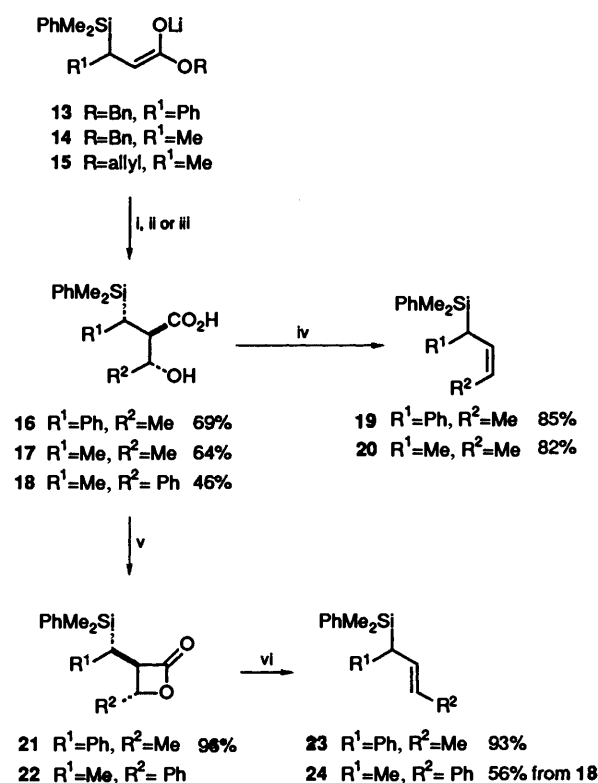
Although the yield of crude material was good, it clearly consisted of a mixture of all four possible diastereoisomers, none of which was especially dominant. In the dimethyl(phenyl)silyl series, we isolated two of these in 28 and 19% yield. In the trimethylsilyl series, we isolated all four and assigned structures **7–10** to them. Two of the alcohols gave the ketone **11** on oxidation, while the other two gave its isomer **12**. We assigned

the relative configurations to these two ketones on the basis that the major pair 7 and 9 which gave the ketone 11 were those from attack on the lithiated phosphine oxide in the same sense as in the reaction with methyl iodide. The overall selectivity in favour of the 3,4 *anti* relationship (7 + 9):(8 + 10) is 74:26, similar to that for methylation. On the assumption that the major products within each pair have the 2,3 *syn* (*erythro*) arrangement that is normal for phosphine oxide reactions, we then assigned all the relative configurations. Obviously, these assignments, especially to 8 and 10, are somewhat tentative, but the important conclusion is not—this reaction is not nearly clean enough stereochemically to be a good candidate for allylsilane synthesis. The overall selectivity in favour of the *syn* arrangement between C-2 and C-3, which is all that matters, is only 68:32, matching Warren's experience when the group adjacent to the nucleophilic carbon is branched.<sup>7</sup> There is also the problem that four isomers have to be separated before the olefin-forming reaction can be carried out. The final blow was that the  $\beta$ -hydroxyphosphine oxides, in preliminary experiments, did not undergo clean elimination on treatment with sodium hydride. There was no evidence in the crude product for the presence of either of the allylsilanes 50 or 54, both of which became available to us, as described below. We surmise that the problem is similar to that which Tsukamoto and Iio discovered with similarly constituted substrates for a conventional Wittig reaction, namely, that the intermediate oxyanion removes the silyl group and the phosphorus group to make allylic silyl ethers.<sup>10</sup> Consistent with this hypothesis, some of the signals appropriate for the trimethylsilyl ether of (*Z*)-pent-3-en-2-ol stood out from the background in the <sup>1</sup>H NMR spectrum of the crude product.

A second possibility was to use Julia coupling, with a phenylsulfonyl group in place of the diphenylphosphine oxide group.<sup>11</sup> This is a useful approach to allylsilanes,<sup>12</sup> but we did not pursue it because it did not meet one of our requirements: it is stereoselective for the formation of *E* double bonds, regardless of the relative stereochemistry of the  $\beta$ -hydroxysulfone, and we needed a synthesis that would allow us to make either *E* or *Z* double bonds at will, especially the latter. Accordingly we returned to the ester group in this position, even though that requires that we sacrifice a carbon-carbon bond in a decarboxylative  $\beta$ -elimination.

We already knew that the aldol reactions between aldehydes and  $\beta$ -silyl enolates made from methyl esters were much better controlled stereochemically than the phosphine oxide reactions above, and that a single diastereoisomer was very much the major product.<sup>13</sup> However, we could not use the methyl esters for allylsilane synthesis, because they gave a lot of retro-aldol reaction when we tried to hydrolyse the  $\beta$ -hydroxy esters with alkali. We have used instead either the benzyl esters or the allyl esters, which can easily be cleaved selectively. These groups are larger than methyl, and might have interfered with the clean diastereoselectivity of the aldol reaction, which is somewhat dependent upon having a small group on the oxygen atom of the enolate.<sup>14</sup> In our experience so far, this has not proved to be a major problem with benzyl or allyl esters, although with larger groups, in preliminary work, we have seen signs of this problem becoming serious.

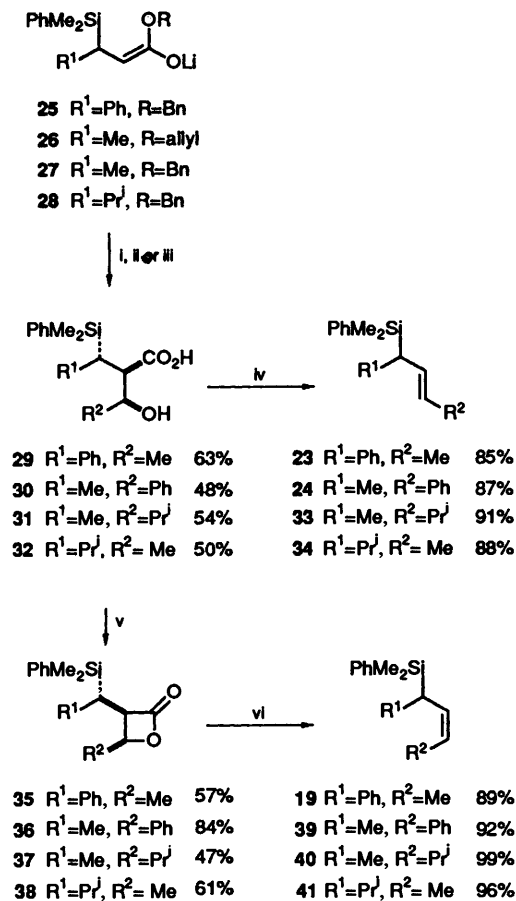
The *E*-enolates 13 and 14, prepared in the usual way by conjugate addition of our silyl-cuprate reagent to benzyl cinnamate and benzyl crotonate, gave very largely single aldol products on treatment with acetaldehyde. The selectivity with respect to the aldol geometry was high ( $\approx 90:10$ ), exactly as it had been for the corresponding methyl esters.<sup>13</sup> Hydrogenolysis of the benzyl esters gave the acids 16 and 17 (Scheme 3). Similarly, conjugate addition of the silyl-cuprate reagent to allyl crotonate gave the enolate 15, which reacted with benzaldehyde to give again very largely a single aldol product. In this case, we



Scheme 3 Reagents: i, R<sup>2</sup>CHO; ii, H<sub>2</sub>, Pd/C; iii, Me<sub>2</sub>CuLi; iv, Me<sub>2</sub>NCH(OMe)<sub>2</sub>; v, PhSO<sub>2</sub>Cl; vi, reflux, collidine

avoided the benzyl ester because we feared that hydrogenolysis would have cleaved the benzyl alcohol group. Treatment of the allyl ester with lithium dimethylcuprate<sup>15</sup> gave the acid 18. The acids 16 and 18 were crystalline, and the acid 17 could be purified by crystallisation of the benzyl isothiuronium salt.  $\beta$ -Hydroxy acids can be induced to undergo decarboxylative elimination either stereospecifically *anti* or stereospecifically *syn*, using reactions developed by Eschenmoser,<sup>16</sup> Nozaki,<sup>17</sup> Mulzer<sup>18</sup> and Adam.<sup>19</sup> Thus the  $\beta$ -hydroxy acids 16 and 17 gave the *cis* allylsilanes 19 and 20, by *anti* elimination, using dimethylformamide dimethyl acetal in refluxing chloroform. Alternatively, treating the acid 16 with benzenesulfonyl chloride gave the  $\beta$ -lactone 21, which gave, in refluxing collidine in an overall *syn* elimination, the *trans* allylsilane 23. Similarly, the acid 18 gave the allylsilane 24, except that in this case the  $\beta$ -lactone 22 was not a detectable intermediate.

In our earlier work,<sup>13</sup> we had found that the aldol diastereoselectivity shown by the corresponding *Z*-enolates was, if anything, even better. We therefore repeated the work in Scheme 3 with the corresponding *Z*-enolates 25–28, easily available by deprotonation of the corresponding esters with LDA, and we also carried out a few related reactions with different combinations of esters and aldehydes. Our results are shown in Scheme 4, where we made again all four *trans* allylsilanes 23, 24, 33 and 34 that we already knew from the work described in the preceding paper, but now we were able to prepare cleanly the four *cis* isomers 19 and 39–41. To cleave the allyl ester produced by the reaction of the enolate 26 with benzaldehyde we used the silyl-cuprate in place of the more obvious methyl-cuprate. It is noteworthy that in this sequence we had first used the silyl-cuprate to add to the  $\alpha\beta$ -unsaturated ester group of allyl crotonate, and then used it again to take off the allyl ester group. This was the first time in which we had had a substrate, allyl crotonate, having two functional groups both of which were known to react with the silyl-cuprate reagent. Evidently the enone group present in the  $\alpha\beta$ -unsaturated ester is



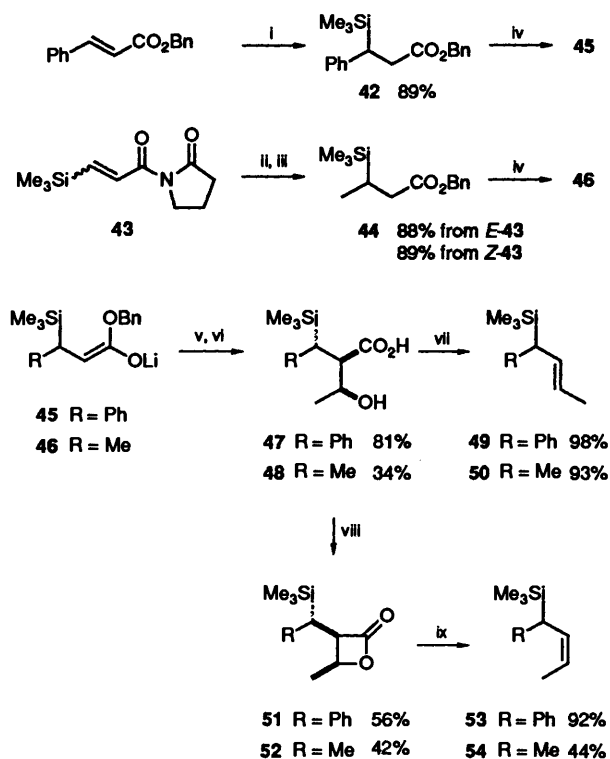
**Scheme 4** Reagents: i, R<sup>2</sup>CHO; ii, H<sub>2</sub>, Pd/C; iii, (PhMe<sub>2</sub>Si)<sub>2</sub>CuCN Li<sub>2</sub>; iv, Me<sub>2</sub>NCH(OMe)<sub>2</sub>; v, PhSO<sub>2</sub>Cl; vi, reflux, collidine

more reactive than the allylic group towards the silyl-cuprate, in contrast to the corresponding reaction with lithium dimethylcuprate, in which the allyl ester is selectively cleaved.<sup>20</sup>

We also carried out two similar sequences using a trimethylsilyl group in place of the dimethyl(phenyl)silyl group, and got comparable results (Scheme 5) except for the yields of the very volatile allylsilanes **50** and **54**. For this work, we prepared the trimethylsilyl-containing ester **42** by adding the bistrimethylsilyl-cuprate reagent, which we already knew added to  $\alpha,\beta$ -unsaturated esters,<sup>21</sup> to benzyl cinnamate. However, since this procedure requires hexamethylphosphoric amide (HMPA), we also developed an alternative synthesis for the ester **44** in which we added lithium dimethylcuprate in the presence of ethylaluminium dichloride to either stereoisomer of the  $\beta$ -silylacryloylpyrrolidone **43**, and then removed the pyrrolidone group with lithium benzyl oxide. More efficiently, we find that the conjugate addition step can be followed immediately by the addition of benzyl alcohol, giving directly the benzyl ester **44** without having to isolate the intermediate pyrrolidone.

The allylsilanes prepared in this work were generally fairly pure with respect to double bond geometry, although in some of the reactions up to ca. 15% of the geometrical isomer was present, either because the carboxylic acid was not as diastereoisomerically pure as it might be or because the decarboxylative elimination was not completely stereospecific, or both. In one case, where we had a particular need to prepare geometrically very pure allylsilanes, we completely separated the geometrical isomers **50** and **54** by chromatography on a silica gel column heavily impregnated with silver nitrate with virtually no losses other than those inevitable with such volatile compounds.

In summary, we have developed an allylsilane synthesis that



**Scheme 5** Reagents: i, (Me<sub>3</sub>Si)<sub>2</sub>CuLi, THF, HMPA; ii, Me<sub>2</sub>CuLi, EtAlCl<sub>2</sub>; iii, BnOLi; iv, LDA; v, MeCHO; vi, H<sub>2</sub>, Pd/C; vii, Me<sub>2</sub>NCH(OMe)<sub>2</sub>; viii, PhSO<sub>2</sub>Cl; ix, reflux, collidine

is suitable for the preparation of unsymmetrical allylsilanes that are secondary at both ends. The synthesis is not particularly short, or high-yielding overall, but it is unique in giving both a high level of control over the double bond geometry and complete control over the regioselectivity. Furthermore, it is amenable to being used for the synthesis of homochiral allylsilanes, since we know how to set up the  $\beta$ -silyl esters, like **42** and **44** and their dimethyl(phenyl)silyl counterparts, with high enantiomeric excesses.<sup>22</sup>

## Experimental

**(E)-Diphenyl(prop-1-enyl)phosphine Oxide 2.**—Butyllithium (1.25 mol dm<sup>-3</sup> solution in hexane; 25 cm<sup>3</sup>) was added to a stirred solution of trimethylsilylmethyl(diphenyl)phosphine oxide **1** (10.35 g) in dry THF (40 cm<sup>3</sup>) under argon at room temp. After 15 min, acetaldehyde (3.0 cm<sup>3</sup>) was added at -78 °C and, after 10 min, the mixture was quenched with saturated aqueous ammonium chloride. The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>), evaporated under reduced pressure and the residue chromatographed (CH<sub>2</sub>Cl<sub>2</sub>-MeOH, 95:5) to give the alkenes as a 1:4 mixture of the *E* and *Z* isomers (4.37 g, 50%) as needles, m.p. 110–114 °C (from Et<sub>2</sub>O-Pr<sup>i</sup><sub>2</sub>O); *R*<sub>f</sub>(Et<sub>2</sub>O) 0.31;  $\delta$ (250 MHz, CDCl<sub>3</sub>) 7.80–7.35 (10 H, m, Ph), 6.80 (1 H, ddq, *J* 13, 40 and 7, CHMe), 6.12 (1 H, ddq, *J* 13, 26 and 1.5, CHP), 2.08 (3 H, ddd, *J* 7, 1.5 and 3, Me of *Z* isomer) and 1.97 (3 H, dt, *J* 6 and 2, Me of *E* isomer); *m/z* 242 (M<sup>+</sup>) and 201 (M - C<sub>3</sub>H<sub>5</sub>). Sodium (20 mg) in dry ethanol (5 cm<sup>3</sup>) and the mixture of phosphine oxides (137 mg) were kept at room temperature for 4 h. The mixture was acidified with hydrochloric acid (2 mol dm<sup>-3</sup> solution; 1 cm<sup>3</sup>) and extracted with dichloromethane. The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated under reduced pressure to give the *E*-alkene (112 mg, 82%) as prisms, m.p. 122–125 °C [from light petroleum (b.p. 40–60 °C)] (lit.,<sup>23</sup> 124–125 °C; *R*<sub>f</sub>(CH<sub>2</sub>Cl<sub>2</sub>-MeOH 19:1) 0.40;  $\nu_{\max}$ (CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 1640 (C=C), 1440 (Ar) and 1185 (P=O);  $\delta$ (250 MHz, CDCl<sub>3</sub>) 8.1–7.2 (10 H,

m, Ph), 6.9–5.9 (2 H, m, HC=CH) and 2.0 (3 H, m, Me) (Found: C, 74.7; H, 6.5; P, 13.0. C<sub>15</sub>H<sub>15</sub>OP requires C, 74.4; H, 6.2; P, 12.8%).

**2-[Dimethyl(phenyl)silyl]propyl(diphenyl)phosphine Oxide 3a.**—Dimethyl(phenyl)syllithium (0.75 mol dm<sup>-3</sup> solution in THF; 2.7 cm<sup>3</sup>) was added to a stirred suspension of copper(I) cyanide (90 mg) in THF (1.3 cm<sup>3</sup>) under argon at 0 °C. After 20 min, the solution was cooled to -78 °C and the phosphine oxide (182 mg) in THF (2.0 cm<sup>3</sup>) was added slowly to it. The mixture was kept at -78 °C for 1 h and then allowed to warm to 0 °C over 3 h. The mixture was quenched with basic aqueous ammonium chloride (pH 8; 5 cm<sup>3</sup>) and extracted with ether (1 × 60 and 2 × 20 cm<sup>3</sup>). The combined extracts were washed with basic aqueous ammonium chloride (3 × 5 cm<sup>3</sup>), dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated under reduced pressure, and the residue was chromatographed (Et<sub>2</sub>O) to give the phosphine oxide (201 mg, 70%); R<sub>f</sub>(CH<sub>2</sub>Cl<sub>2</sub>-MeOH, 19:1) 0.35; ν<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 2950 (CH), 1180 (P=O), 830 and 810 (SiC); δ(CCl<sub>4</sub>) 8.0–7.1 (15 H, m, Ph), 2.25–1.60 (2 H, m, CH<sub>2</sub>P), 1.20–1.05 (4 H, m, CHMe), 0.26 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.24 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); m/z 378 (M<sup>+</sup>), 287 (M - C<sub>7</sub>H<sub>7</sub>) and 243 (M - SiMe<sub>2</sub>Ph).

**Diphenyl(2-trimethylsilylpropyl)phosphine Oxide 3b.**—Methylolithium (1 mol dm<sup>-3</sup> solution in Et<sub>2</sub>O; 2.0 cm<sup>3</sup>) was added to a mixture of hexamethyldisilane (0.5 cm<sup>3</sup>) and HMPA (1.1 cm<sup>3</sup>) at 0 °C under argon. After 20 min, THF (2.0 cm<sup>3</sup>) and copper(I) cyanide (90 mg) were added to the mixture, and stirring was continued for 25 min. The phosphine oxide (245 mg) in THF (3 cm<sup>3</sup>) was added at -78 °C to the mixture which was then kept for 5.5 h. An aqueous work-up, as above, and chromatography (Et<sub>2</sub>O, followed by Et<sub>2</sub>O-MeOH, 97.5:2.5) gave the phosphine oxide (170 mg, 54%) as prisms, m.p. 118–122 °C [from Et<sub>2</sub>O-light petroleum (b.p. 40–60 °C)]; R<sub>f</sub>(Et<sub>2</sub>O) 0.29; ν<sub>max</sub>(CH<sub>2</sub>-Cl<sub>2</sub>)/cm<sup>-1</sup> 2960 (CH), 1185 (P=O), 850 and 835 (SiC); δ(250 MHz, CDCl<sub>3</sub>) 7.82–7.37 (10 H, m, Ph), 2.30 (1 H, ddd, J 2.5, 10 and 15, CH<sub>A</sub>CH<sub>B</sub>P), 2.03 (1 H, dt, J 10 and 15, CH<sub>A</sub>CH<sub>B</sub>P), 1.27–1.02 (1 H, m, CHSi), 1.01 (3 H, d, J 6.8, MeCH) and 0.0 (9 H, s, SiMe<sub>3</sub>); m/z 316 (M<sup>+</sup>), 243 (M - SiMe<sub>3</sub>) and 201 (Ph<sub>2</sub>PO) (Found: C, 68.2; H, 7.9; P, 9.6. C<sub>18</sub>H<sub>25</sub>OPSi requires C, 68.3; H, 8.0; P, 9.8%).

**3-[Dimethyl(phenyl)silyl]butan-2-yl(diphenyl)phosphine Oxide 4a and 5a.**—Butyllithium (1.5 mol dm<sup>-3</sup> solution in hexane; 0.4 cm<sup>3</sup>) was added to diisopropylamine (0.1 cm<sup>3</sup>) in THF (1.0 cm<sup>3</sup>) at 0 °C under argon. After 10 min, the phosphine oxide 3a (140 mg) in THF (2.0 cm<sup>3</sup>) was added at 0 °C to the mixture which was then kept for 30 min. After this, methyl iodide (0.1 cm<sup>3</sup>) was added to the mixture, which was then warmed to room temperature. Aqueous ammonium chloride (2 mol dm<sup>-3</sup> solution; 1.0 cm<sup>3</sup>) was added to the mixture which was then extracted with light petroleum [1 × 45 cm<sup>3</sup> and 1 × 15 cm<sup>3</sup> (b.p. 40–60 °C)]. The combined extracts were washed with water (3 × 3 cm<sup>3</sup>), dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated under reduced pressure. Chromatography (Et<sub>2</sub>O followed by Et<sub>2</sub>O-MeOH, 95:5) of the residue (126 mg) gave the minor (2RS,3SR)-phosphine oxide 5a (24 mg, 17%) as an oil; R<sub>f</sub>(CH<sub>2</sub>Cl<sub>2</sub>) 0.28; ν<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 2970 (CH), 1185 (P=O), 1105, 830 and 810 (SiC); δ(250 MHz, CDCl<sub>3</sub>) 8.15–7.32 (15 H, m, Ph), 2.55 (1 H, m, PCH), 1.57 (1 H, m, CHSi), 1.15 (3 H, dd, J 7 and 18, PCHMe), 1.04 (3 H, d, J 7, SiCHMe), 0.45 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.44 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); m/z 392 (M<sup>+</sup>), 377 (M - Me), 243 (M - C<sub>5</sub>H<sub>13</sub>Si) and 201 (Ph<sub>2</sub>PO); followed (Et<sub>2</sub>O-MeOH, 99:1) by the major (2RS,3RS)-phosphine oxide 4a (86 mg, 59%) as prisms, m.p. 113–114 °C (from Et<sub>2</sub>O); R<sub>f</sub>(CH<sub>2</sub>Cl<sub>2</sub>-MeOH, 19:1) 0.21; ν<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 2970 (CH), 1180 (P=O), 1110, 825 and 805 (SiC); δ(250 MHz, CDCl<sub>3</sub>) 7.75–

7.33 (15 H, m, Ph), 2.49 (1 H, m, CHP), 1.48 (1 H, m, CHSi), 1.24 (3 H, d, J 7, SiCHMe), 1.13 (3 H, dd, J 7 and 18, PCHMe), 0.36 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.29 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); m/z 392 (M<sup>+</sup>), 257 (M - SiMe<sub>2</sub>Ph) and 201 (Ph<sub>2</sub>PO) (Found: C, 73.3; H, 7.6; P, 8.10. C<sub>24</sub>H<sub>29</sub>OPSi requires C, 73.4; H, 7.5; P, 7.9%).

**Diphenyl(3-trimethylsilylbutan-2-yl)phosphine Oxide 4b.**—A similar reaction starting with the phosphine oxide 3b (51 mg) gave the mixture of *silanes* in a ratio of 81:19 (47 mg, 89%) as prisms, m.p. 166–167 °C (from Et<sub>2</sub>O); R<sub>f</sub>(Et<sub>2</sub>O-MeOH, 39:1) 0.39; ν<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 2960 (CH), 1185 (P=O), 1115, 860 and 830 (SiC); δ(250 MHz, CDCl<sub>3</sub>) 7.90–7.35 (10 H, m, Ph), 2.56 (1 H, m, CHP), 1.77 (1 H, m, CHSi), 1.19 (3 H, d, J 7, PCHMe), 1.12 (3 H, d, J 6, SiCHMe), 0.00 (9 H, s, SiMe<sub>3</sub>, major isomer) and -0.04 (9 H, s, SiMe<sub>3</sub>, minor isomer); m/z 330 (M<sup>+</sup>), 257 (M - C<sub>3</sub>H<sub>9</sub>Si), 229 (M - C<sub>5</sub>H<sub>13</sub>Si) and 201 (Ph<sub>2</sub>PO) (Found: C, 68.9; H, 8.1. C<sub>19</sub>H<sub>27</sub>OPSi requires C, 69.0; H, 8.2%).

**(2RS,3RS)-3-Hydroxybutan-2-yl(diphenyl)phosphine Oxide 6.**—The phosphine oxide 4a (34.6 mg) was stirred at room temperature for 16 h in dichloromethane (0.25 cm<sup>3</sup>) containing boron trifluoride-acetic acid (2 drops). Aqueous sodium hydrogen carbonate (saturated solution; 2 cm<sup>3</sup>) and dichloromethane (10 cm<sup>3</sup>) were added to the mixture which was then shaken vigorously. The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated under reduced pressure to give the fluorosilane (29.0 mg, 98%), which was used without further purification. *m*-Chloroperbenzoic acid (65.5 mg) was added to a solution of the fluorosilane and potassium fluoride (15.2 mg) in dimethylformamide (1.5 cm<sup>3</sup>) and the mixture was stirred at room temperature for 6 h. It was then diluted with dichloromethane (2 × 10 cm<sup>3</sup>) and treated consecutively with aqueous sodium iodide (0.1 mol dm<sup>-3</sup> solution; 3 cm<sup>3</sup>), aqueous sodium thiosulfate (0.1 mol dm<sup>-3</sup> solution; 4 cm<sup>3</sup>) and water (4 cm<sup>3</sup>). The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated under reduced pressure to give an oil (56 mg), which was chromatographed (Et<sub>2</sub>O-MeOH, successively 99:1, 97.5:2.5, 95:5 and 90:10) to give the alcohol (10.0 mg, 42%) as plates, m.p. 155–156 °C (from Et<sub>2</sub>O); R<sub>f</sub>(Et<sub>2</sub>O) 0.06; ν<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 3350 (OH), 2950 (CH) and 1155 (P=O); δ(250 MHz, CDCl<sub>3</sub>) 7.90–7.42 (10 H, m, Ph), 4.02 (1 H, ddq, J 9.7, 7.5 and 6.2, CHOH), 2.65 (1 H, d quintet, J 8.7 and 7.5, CHP), 1.25 (3 H, d, J 6.2, MeCHOH) and 1.00 (3 H, dd, J 17.5 and 7.5, MeCHP) matching the spectrum reported for the *threo* isomer, and distinctly different from the *erythro* isomer;<sup>7</sup> m/z 273 (M - OH), 229 (M - MeCHOH), 202 and 201 (Ph<sub>2</sub>PO) (Found: C, 70.0; H, 6.9. C<sub>16</sub>H<sub>19</sub>O<sub>2</sub>P requires C, 70.0; H, 7.0%).

**4-Dimethyl(phenyl)silyl-2-hydroxypentan-3-yl(diphenyl)phosphine Oxides.**—Butyllithium (1.4 mol dm<sup>-3</sup> solution in hexane; 0.35 cm<sup>3</sup>) was added to a mixture of THF (1.0 cm<sup>3</sup>) and diisopropylamine (0.1 cm<sup>3</sup>) at 0 °C under argon. The silane 3a (145 mg) in THF (2.0 cm<sup>3</sup>) was added at 0 °C to the mixture, followed, after 15 min, by acetaldehyde (0.1 cm<sup>3</sup>); the mixture was then kept at 0 °C for 10 min and at room temperature for 45 min. Aqueous ammonium chloride (2 mol dm<sup>-3</sup> solution; 1.0 cm<sup>3</sup>) was added to the mixture and the product was extracted with light petroleum (b.p. 40–60 °C) (45 and 15 cm<sup>3</sup>). The organic layers were washed with water (3 × 3 cm<sup>3</sup>), dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated under reduced pressure to give a yellow oil (139 mg), which was chromatographed (Et<sub>2</sub>O and Et<sub>2</sub>O-MeOH, 98:2) to give successively the major isomer (44 mg, 28%) as an oil; R<sub>f</sub>(Et<sub>2</sub>O) 0.20; ν<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 3400 (OH), 2970 (CH), 1160 (P=O), 1110, 830 and 810 (SiC); δ(250 MHz, CDCl<sub>3</sub>) 7.62–7.28 (15 H, m, Ph), 5.0 (1 H, br, OH), 4.25 (1 H, dq, J 22 and 7, 2-H), 2.46 (1 H, dd, J 11 and 3, 3-H), 1.28 (1 H, br m, 4-H), 1.29 (3 H, s, 5-H), 0.94 (3 H, d, J 7, 1-H), 0.35 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.23 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); m/z 422 (M<sup>+</sup>), 287

(M - SiMe<sub>2</sub>Ph), 243 (287 - C<sub>2</sub>H<sub>6</sub>O) and 201 (Ph<sub>2</sub>PO); and the minor isomer (30 mg, 19%) as prisms, m.p. 175–177 °C (from Et<sub>2</sub>O); *R*<sub>f</sub>(Et<sub>2</sub>O) 0.14; *v*<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 3380 (OH), 2960 (CH), 1175 (P=O), 1110, 830 and 810 (SiC); δ(250 MHz, CDCl<sub>3</sub>) 7.76–7.30 (15 H, m, Ph), 4.29 (1 H, septet, 2-H), 2.53 (1 H, dd, *J* 8 and 5, 3-H), 2.09 (1 H, br, OH), 1.35 (1 H, m, 4-H), 1.26 (3 H, d, *J* 7, 5-H), 1.19 (3 H, d, *J* 7, 1-H), 0.31 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.22 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); *m/z* 422 (M<sup>+</sup>), 287 (M - SiMe<sub>2</sub>Ph), 243 (287 - C<sub>2</sub>H<sub>6</sub>O) and 201 (Ph<sub>2</sub>PO) (Found: C, 71.2; H, 7.4. C<sub>25</sub>H<sub>31</sub>O<sub>2</sub>PSi requires C, 71.1; H, 7.4%).

2-Hydroxy-4-trimethylsilylpentan-3-yl(diphenyl)phosphine

*Oxides 7–10.*—Butyllithium (1.3 mol dm<sup>-3</sup> solution in hexane; 0.3 cm<sup>3</sup>) was added to a stirred mixture of THF (1.0 cm<sup>3</sup>) and diisopropylamine (0.1 cm<sup>3</sup>) at 0 °C under argon. The silane **3b** (91 mg) and acetaldehyde (0.1 cm<sup>3</sup>) were added successively to the mixture, which was then kept at 0 °C for 15 min and at room temp. for 10 min. After this, aqueous ammonium chloride (2 mol dm<sup>-3</sup> solution; 1 cm<sup>3</sup>) and water (1 cm<sup>3</sup>) were added to it and the product extracted with light petroleum (b.p. 40–60 °C) (1 × 50 and 2 × 15 cm<sup>3</sup>). The combined extracts were washed with water (2 × 3 cm<sup>3</sup>), dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated under reduced pressure to give an oil (105.5 mg), which was chromatographed on silica gel (5.1 g) eluting with ether (5 × 5 cm<sup>3</sup>) and ether–methanol (97.5:5) (11 × 5 cm<sup>3</sup>) to give successively the *alcohols 8* (11.2 mg, 11%) as prisms m.p. 161–164 °C [from light petroleum (b.p. 40–60 °C)]; *R*<sub>f</sub>(Et<sub>2</sub>O) 0.38; *v*<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 3380 (OH), 2980 (CH), 1160 (P=O) and 840 (SiC); δ(250 MHz, CDCl<sub>3</sub>) 7.95–7.40 (10 H, m, Ph), 4.18 (1 H, dq, *J* 23.4, 6.7 and 3.4, 2-H), 2.50 (1 H, ddd, *J* 10.8, 3.2 and 1.9, 3-H), 1.15 (1 H, m, 4-H), 1.15 (3 H, d, *J* 6.7, 1-H), 1.10 (3 H, d, *J* 3.9, 5-H) and 0.00 (9 H, s, SiMe<sub>3</sub>); *m/z* 360 (M<sup>+</sup>), 345 (M - Me), 316 (M - C<sub>2</sub>H<sub>4</sub>O), 243 (316 - SiMe<sub>3</sub>) and 201 (Ph<sub>2</sub>PO) (Found: C, 66.8; H, 8.4. C<sub>20</sub>H<sub>29</sub>O<sub>2</sub>PSi requires C, 66.6; H, 8.1%); **10** (10.1 mg, 10%) as prisms, m.p. 141–143 °C [from Et<sub>2</sub>O–light petroleum (b.p. 40–60 °C)]; *R*<sub>f</sub>(Et<sub>2</sub>O) 0.33; *v*<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 3400 (OH), 2950 (CH), 1170 (P=O), 850 and 835 (SiC); δ(250 MHz, CDCl<sub>3</sub>) 7.90–7.40 (10 H, m, Ph), 4.38 (1 H, dq, *J* 6.5, 6.4 and 6.5, 2-H), 2.46 (1 H, dt, *J* 9.3 and 1.5, 3-H), 1.54–1.25 (1 H, m, 4-H), 1.24 (3 H, d, *J* 7.5, 5-H), 1.19 (3 H, d, *J* 6.4, 1-H) and -0.10 (9 H, s, SiMe<sub>3</sub>); *m/z* 360 (M<sup>+</sup>), 345 (M - Me), 316 (M - C<sub>2</sub>H<sub>4</sub>O), 243 (316 - SiMe<sub>3</sub>) and 201 (Ph<sub>2</sub>PO) (Found: C, 66.9; H, 8.2. C<sub>20</sub>H<sub>29</sub>O<sub>2</sub>PSi requires C, 66.6; H, 8.1%); **7** (46.9 mg, 45%) as prisms m.p. 142–144 °C [from Et<sub>2</sub>O–light petroleum (b.p. 40–60 °C)]; *R*<sub>f</sub>(Et<sub>2</sub>O) 0.20; *v*<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 3380 (OH), 2955 (CH), 1160 (P=O) and 835 (SiC); δ(250 MHz, CDCl<sub>3</sub>) 7.93–7.42 (10 H, m, Ph), 4.29 (1 H, dq, *J* 21.4, 6.7 and 2.0, 2-H), 2.64 (1 H, dt, *J* 9.6 and 1.9, 3-H), 1.22 (3 H, d, *J* 7.2, 5-H), 1.20–1.00 (1 H, m, 4-H), 1.08 (3 H, d, *J* 6.7, 1-H) and 0.00 (9 H, s, SiMe<sub>3</sub>); *m/z* 360 (M<sup>+</sup>), 345 (M - Me), 315 (M - C<sub>2</sub>H<sub>5</sub>O), 242 (315 - SiMe<sub>3</sub>) and 201 (Ph<sub>2</sub>PO) (Found: C, 66.5; H, 8.2; P, 8.6. C<sub>20</sub>H<sub>29</sub>O<sub>2</sub>PSi requires C, 66.6; H, 8.1; P, 8.6%); and **9** (16.1 mg, 16%) as prisms m.p. 144–147 °C [from Et<sub>2</sub>O–light petroleum (b.p. 40–60 °C)]; *R*<sub>f</sub>(Et<sub>2</sub>O) 0.13; *v*<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 3380 (OH), 2950 (CH), 1175 (P=O) and 835 (SiC); δ(250 MHz, CDCl<sub>3</sub>) 7.95–7.41 (10 H, m, Ph), 4.32 (1 H, m, 2-H), 2.61 (1 H, ddd, *J* 9.3, 4.2 and 1, 3-H), 1.60 (1 H, br, OH), 1.28 (3 H, d, *J* 6.5, 1-H), 1.22 (3 H, s, 5-H), 1.30–1.05 (1 H, m, 4-H) and -0.03 (9 H, s, SiMe<sub>3</sub>); *m/z* 360 (M<sup>+</sup>), 345 (M - Me), 315 (M - C<sub>2</sub>H<sub>5</sub>O), 243 (316 - SiMe<sub>3</sub>) and 201 (Ph<sub>2</sub>PO) (Found: C, 66.5; H, 8.3; P, 8.7. C<sub>20</sub>H<sub>29</sub>O<sub>2</sub>PSi requires C, 66.6; H, 8.1; P, 8.6%). Treatment of the major phosphine oxide **7** with sodium hydride in DMF gave a crude product in which a few characteristic signals stood out at δ(250 MHz, CDCl<sub>3</sub>) 5.45 (2 H, m, CH=CH), 4.7 (1 H, quintet, *J* 7, CHOSi) and 1.65 (3 H, d, *J* 7, MeCH=CH), appropriate for the trimethylsilyl ether of (*Z*)-pent-3-en-2-ol.

2-Oxo-4-trimethylsilylpentan-3-yl(diphenyl)phosphine Oxide

**11.**—The alcohol **7** (20.8 mg) and pyridinium dichromate (71 mg) were stirred in dichloromethane (0.5 cm<sup>3</sup>) at room temp. for 18 h. The mixture was filtered through silica gel (0.7 g) eluting with ether (8 × 2 cm<sup>3</sup>), after which the filtrate was evaporated under reduced pressure to give the *ketone* (10.8 mg, 52%) as prisms, m.p. 129–131 °C [from Et<sub>2</sub>O–light petroleum (b.p. 40–60 °C)]; *R*<sub>f</sub>(Et<sub>2</sub>O) 0.38; *v*<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 2950 (CH), 1700 (C=O), 1200 (P=O) and 840 (SiC); δ(250 MHz, CDCl<sub>3</sub>) 7.90–7.40 (10 H, m, Ph), 3.61 (1 H, dd, *J* 7.8 and 1.9, 3-H), 2.14 (3 H, s, 1-H), 1.34 (1 H, m, 4-H), 1.34 (3 H, s, 5-H) and -0.06 (9 H, s, SiMe<sub>3</sub>); *m/z* 343 (M - Me), 315 (M - C<sub>2</sub>H<sub>3</sub>O), 285 (M - SiMe<sub>3</sub>), 243 (286 - C<sub>2</sub>H<sub>3</sub>O) and 201 (Ph<sub>2</sub>PO) (Found: C, 67.2; H, 7.7. C<sub>20</sub>H<sub>27</sub>O<sub>2</sub>PSi requires C, 67.0; H, 7.6%).

2-Oxo-4-trimethylsilylpentan-3-yl(diphenyl)phosphine Oxide

**12.**—A similar reaction carried out on the alcohols **8** (20.9 mg) and **10** (10.1 mg) gave the *ketone* (43%) as prisms, m.p. 133–135 °C [from Et<sub>2</sub>O–light petroleum (b.p. 40–60 °C)]; *R*<sub>f</sub>(Et<sub>2</sub>O) 0.38; *v*<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 2960 (CH), 1700 (C=O), 1190 (P=O) and 840 (SiC); δ(250 MHz, CDCl<sub>3</sub>) 8.00–7.40 (10 H, m, Ph), 3.63 (1 H, t, *J* 11.7, 3-H), 1.84 (1 H, m, 4-H), 1.84 (3 H, s, 5-H), 0.96 (3 H, d, *J* 7.5, 5-H) and -0.03 (9 H, s, SiMe<sub>3</sub>); *m/z* 343 (M - Me), 315 (M - C<sub>2</sub>H<sub>3</sub>O), 285 (M - SiMe<sub>3</sub>), 243 (286 - C<sub>2</sub>H<sub>3</sub>O) and 201 (Ph<sub>2</sub>PO) (Found: C, 66.8; H, 7.7. C<sub>20</sub>H<sub>27</sub>O<sub>2</sub>PSi requires C, 67.0; H, 7.6%).

(2SR,3SR)-Benzyl 2-[(SR)-Dimethyl(phenyl)silylbenzyl]-3-hydroxybutanoate.—Dimethyl(phenyl)silyllithium (12 mmol) in dry THF was added to copper(i) cyanide (0.54 g, 6 mmol) under nitrogen at 0 °C. Benzyl cinnamate (1.2 g, 5 mmol) in THF (5 cm<sup>3</sup>) was added at -78 °C to the mixture which was then stirred for 2 h. Freshly distilled acetaldehyde (0.26 g, 6 mmol) was then added dropwise at -78 °C to the mixture and, after 1 h, was followed by basic aqueous ammonium chloride (20 cm<sup>3</sup>); the mixture was then allowed to warm to room temp. It was then extracted with ether (3 × 25 cm<sup>3</sup>) and the combined ether extracts were washed with basic aqueous ammonium chloride (3 × 15 cm<sup>3</sup>) and with brine (10 cm<sup>3</sup>), dried (MgSO<sub>4</sub>) and evaporated under reduced pressure. The residue was chromatographed (SiO<sub>2</sub>, hexane–EtOAc, 5:1) to give the *ester* 1.45 g, 70%); *R*<sub>f</sub>(hexane–EtOAc, 10:1) 0.2; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 3450 (OH), 1735 (C=O), 1250 (SiMe) and 1110 (SiPh); δ(CDCl<sub>3</sub>) 7.45–6.96 (15 H, m, 3 × Ph), 4.76 (1 H, d, *J* 12.3, OCH<sub>A</sub>H<sub>B</sub>Ph), 4.61 (1 H, d, *J* 12.3, OCH<sub>A</sub>H<sub>B</sub>Ph), 3.56 (1 H, dq, *J* 2.4 and 6.5, MeCHOH), 3.05 (1 H, d, *J* 12.6, PhCHSi), 2.95 (1 H, dd, *J* 12.6 and 2.4, CHCO), 2.2 (1 H, br s, OH), 0.98 (3 H, d, *J* 6.5, MeCHOH), 0.31 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.07 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); *m/z* 403 (0.1%, M - Me) 373 (14, M - MeCHOH), 238 (33, M - SiMe<sub>2</sub>Ph - MeCHOH), 205 (100, M - Ph - CH<sub>2</sub>Ph - MeCHOH), 135 (82, SiMe<sub>2</sub>Ph) and 91 (90, PhCH<sub>2</sub>) (Found: M<sup>+</sup> - Me, 403.1745. C<sub>26</sub>H<sub>30</sub>O<sub>3</sub>Si requires M - Me, 403.1730).

(2RS,3SR)-Allyl 2-[(SR)-Hydroxybenzyl]-3-dimethyl(phenyl)silylbutanoate.—This was prepared in the same way as the ester above, using allyl crotonate (0.5 g, 4 mmol) to give the *ester* (0.72 g, 49%); *R*<sub>f</sub>(hexane–EtOAc, 5:1) 0.33; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 3450 (OH), 1735 (C=O), 1250 (SiMe) and 1110 (SiPh); δ(CDCl<sub>3</sub>) 7.51–7.15 (10 H, m, 2 × Ph), 5.54–5.34 (1 H, m, CH=CH<sub>2</sub>), 5.05–4.92 (3 H, m, CH=CH<sub>2</sub> and PhCH), 4.10 (2 H, dd, *J* 6 and 13, OCH<sub>2</sub>), 3.61 (1 H, br s, OH), 2.71 (1 H, dd, *J* 4.3 and 9.4, CHCO), 1.61 (1 H, quintet, *J* 7.5, MeCH), 1.18 (3 H, d, *J* 7.5, MeCH), 0.34 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.29 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); *m/z* 353 (5.8%, M - Me) and 135 (100, SiMe<sub>2</sub>Ph) (Found: M<sup>+</sup> - Me, 353.1570. C<sub>22</sub>H<sub>28</sub>O<sub>3</sub>Si requires M - Me, 353.1573).

*Conjugate Addition of the Silyl-cuprate Reagent to αβ-Unsaturated Esters.*—Typically, dimethyl(phenyl)silyllithium

(12 mmol) in dry THF was added to copper(I) cyanide (0.54 g, 6 mmol) under nitrogen at 0 °C. Benzyl cinnamate (1.19 g, 5 mmol) in THF (5 cm<sup>3</sup>) was added to the cuprate reagent at -78 °C and the mixture was stirred for 2 h and then quenched by addition of saturated basic aqueous ammonium chloride (10 cm<sup>3</sup>). After being allowed to warm to room temperature, the mixture was extracted with ether (3 × 25 cm<sup>3</sup>). The combined extracts were washed with basic aqueous ammonium chloride (3 × 10 cm<sup>3</sup>) and brine (10 cm<sup>3</sup>), dried (MgSO<sub>4</sub>) and evaporated under reduced pressure. The residue was chromatographed (hexane-EtOAc, 10:1) to give the β-silyl esters. The following esters were prepared by this method.

**Benzyl 3-dimethyl(phenyl)silyl-3-phenylpropanoate** (89%). B.p. 220 °C/0.3 mmHg; *R<sub>f</sub>*(hexane-EtOAc, 10:1) 0.34; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 1737 (C=O), 1600, 1495, 1451 and 1428 (Ph), 1251 (SiMe) and 1113 (SiPh); *δ*<sub>H</sub>(CDCl<sub>3</sub>) 7.48–6.89 (15 H, m, 3 × Ph), 4.91 (2 H, s, OCH<sub>2</sub>Ph), 2.94–2.67 (3 H, m, CH<sub>2</sub>CHSi), 0.26 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.23 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); *δ*<sub>C</sub>(CDCl<sub>3</sub>) 173.0, 141.7, 136.5, 135.9, 134.2, 129.4, 128.5, 128.2, 128.12, 128.08, 127.9, 127.8, 127.7, 125.1, 66.3, 35.0, 32.5, -4.0 and -5.4; *m/z* 359 (0.3%, M - Me), 269 (5, M - PhCO), 135 (100, Me<sub>2</sub>PhSi) and 91 (5, PhCH<sub>2</sub>) (Found: M<sup>+</sup> - Me, 359.1458. C<sub>24</sub>H<sub>26</sub>O<sub>2</sub>Si requires M - Me, 359.1467).

**Benzyl 3-dimethyl(phenyl)silylbutanoate** (72%). *R<sub>f</sub>*(hexane-EtOAc, 10:1) 0.4; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 1745 (C=O), 1255 (SiMe) and 1115 (SiPh); *δ*(CDCl<sub>3</sub>) 7.58–7.27 (10 H, m, 2 × Ph), 5.07 (2 H, s, OCH<sub>2</sub>Ph), 2.47 (1 H, dd, *J* 4.5 and 15.2, CH<sub>A</sub>CH<sub>B</sub>(CO)), 2.10 (1 H, dd, *J* 10.2 and 15.1, CH<sub>A</sub>CH<sub>B</sub>CO), 1.62–1.27 (1 H, m, CHSi), 0.98 (3 H, d, *J* 7, MeCH) and 0.29 (6 H, s, SiMe<sub>2</sub>); *m/z* 297 (3.3%, M - Me) and 135 (100, SiMe<sub>2</sub>Ph) (Found: M<sup>+</sup> - Me, 297.1327. C<sub>19</sub>H<sub>24</sub>O<sub>2</sub>Si requires M - Me, 297.1311).

**Benzyl-3-dimethyl(phenyl)silyl-4-methylpentanoate** (82%). *R<sub>f</sub>*(hexane-EtOAc, 10:1) 0.4; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 1735 (C=O), 1249 (SiMe) and 1110 (SiPh); *δ*(CDCl<sub>3</sub>) 7.59–7.23 (10 H, m, 2 × Ph), 5.00 (2 H, s, OCH<sub>2</sub>), 2.39 (2 H, dd, *J* 1 and 6.4, CH<sub>2</sub>CO), 1.91 (1 H, m, Me<sub>2</sub>CH), 1.57 (1 H, m, CHSi), 0.91 (3 H, d, *J* 6.4, Me<sub>A</sub>Me<sub>B</sub>CH), 0.83 (3 H, d, *J* 6.4, Me<sub>A</sub>Me<sub>B</sub>CH), 0.33 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.32 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); *m/z* 325 (1.8%, M - Me), 135 (44, SiMe<sub>2</sub>Ph), 92 (92, PhMe) and 91 (100, PhCH<sub>2</sub>) (Found: M<sup>+</sup> - Me, 324.1608. C<sub>21</sub>H<sub>28</sub>O<sub>2</sub>Si requires M - Me, 324.1624).

**Benzyl 3-Phenyl-3-trimethylsilylpropanoate 42.**—Benzyl cinnamate (1.2 g, 5 mmol) in THF (10 cm<sup>3</sup>) was added dropwise slowly with stirring to the bis(trimethylsilyl)cuprate<sup>21</sup> (8 mmol) under nitrogen at -78 °C. The mixture was stirred for 1 h at -78 °C and for 1 h at -23 °C and was then quenched with basic aqueous ammonium chloride (5 cm<sup>3</sup>). An aqueous work-up and chromatography (hexane-EtOAc, 10:1) gave the β-silyl ester (1.4 g, 89%); *R<sub>f</sub>*(hexane-EtOAc, 10:1) 0.34; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 1745 (C=O), 1610, 1500 and 1455 (Ph) and 1255 (SiMe); *δ*(CDCl<sub>3</sub>) 7.35–6.96 (10 H, m, 2 × Ph), 4.97 (2 H, s, OCH<sub>2</sub>), 2.80–2.67 (3 H, m, CHCH<sub>2</sub>CO) and -0.04 (9 H, s, SiMe<sub>3</sub>); *m/z* 297 (5.4%, M - Me), 91 (100, PhCH<sub>2</sub>) and 73 (90, SiMe<sub>3</sub>) (Found: M<sup>+</sup> - Me, 297.1317. C<sub>19</sub>H<sub>24</sub>O<sub>2</sub>Si requires M - Me, 297.1311).

**(E)-3-Trimethylsilylpropenoic Acid.**—Chromium trioxide (48 g, 480 mmol) in sulfuric acid (76 g) and water (190 cm<sup>3</sup>) was added dropwise to a stirred solution of (E)-3-trimethylsilylpropenol<sup>24</sup> (23.5 g, 180 mmol) in acetone (145 cm<sup>3</sup>) at 0 °C. After 6 h at 0 °C the mixture was poured over ice (1000 g) and extracted with ether (4 × 500 cm<sup>3</sup>). The combined extracts were washed with aqueous sodium hydroxide (5%; 4 × 350 cm<sup>3</sup>). The combined aqueous layers were acidified with hydrochloric acid (3 mol dm<sup>-3</sup>) and extracted with dichloromethane (5 × 350 cm<sup>3</sup>). The combined organic layers were dried (MgSO<sub>4</sub>) and evaporated under reduced pressure to give the acid<sup>25</sup> (21.7 g,

84%); *δ*(CDCl<sub>3</sub>) 10.2 (1 H, s, OH), 7.15 (1 H, d, *J* 18, CH<sub>A</sub>=CH<sub>B</sub>), 5.95 (1 H, d, *J* 18, CH<sub>A</sub>=CH<sub>B</sub>) and 0.5 (9 H, s, SiMe<sub>3</sub>).

**Trimethylsilylpropynoic Acid.**—Trimethylsilylethyne<sup>26</sup> (58 g, 0.59 mol) in THF (450 cm<sup>3</sup>) was slowly added with stirring to methylmagnesium bromide (3 mol dm<sup>-3</sup> solution in Et<sub>2</sub>O; 250 cm<sup>3</sup>) under argon at 0 °C. After being stirred at room temp. for 2 h, the mixture was cooled to -23 °C and carbon dioxide (purified by bubbling through concentrated sulfuric acid, paraffin and anhydrous calcium chloride) was bubbled through the solution for 30 min at -23 °C and for 2 h at room temperature. Dilute aqueous hydrochloric acid (1 mole dm<sup>-3</sup>; 550 cm<sup>3</sup>) was slowly added at 0 °C to the mixture, which was then extracted with light petroleum (b.p. 40–60 °C; 6 × 250 cm<sup>3</sup>). The combined extracts were washed with brine, dried (MgSO<sub>4</sub>) and evaporated under reduced pressure to give the acid<sup>27</sup> (56 g, 67%); *v*<sub>max</sub>(film)/cm<sup>-1</sup> 3600–2400 (CO<sub>2</sub>H), 2175 (C=C), 1690 (C=O) and 1255 and 850 (SiMe<sub>3</sub>); *δ*(CDCl<sub>3</sub>) 11.2 (1 H, s, OH) and 0.2 (9 H, s, SiMe<sub>3</sub>).

**(Z)-3-Trimethylsilylpropenoic Acid.**—Trimethylsilylpropynoic acid (18 g, 127 mmol) was stirred in methanol (130 cm<sup>3</sup>) with palladium (10% on BaSO<sub>4</sub>; 1.0 g) and quinoline (30 cm<sup>3</sup>) under hydrogen at room temp. for 7 h when hydrogen (2.8 dm<sup>3</sup>) had been consumed. The catalyst was filtered off and the filtrate concentrated under reduced pressure and then diluted with ether (200 cm<sup>3</sup>). The mixture was washed with aqueous hydrochloric acid (3 mol dm<sup>-3</sup>; 5 × 50 cm<sup>3</sup>) after which the ether layer was dried (MgSO<sub>4</sub>) and evaporated under reduced pressure to give a mixture of acids (13.8 g, 76%) containing the *Z*-acid<sup>28</sup> (76%), the *E*-isomer (4%), saturated acid (9%) and starting material (11%). The mixture of acids was dissolved in hexane (10 cm<sup>3</sup>) and the solution cooled in liquid nitrogen to give long prisms (7.22 g), m.p. 47–54 °C, still contaminated with 6% of the saturated acid; *δ*(CDCl<sub>3</sub>) 12 (1 H, s, OH), 6.75 (1 H, d, 12, CH<sub>A</sub>=CH<sub>B</sub>), 6.55 (1 H, d, 12, CH<sub>A</sub>=CH<sub>B</sub>) and 0.15 (9 H, s, SiMe<sub>3</sub>).

**(E)-1-(3-Trimethylsilylacryloyl)-2-pyrrolidone E-43.**—Oxalyl chloride (0.9 cm<sup>3</sup>) was added dropwise to a stirred solution of the *E*-acid (1.20 g, 8.3 mmol) in dry dichloromethane (7 cm<sup>3</sup>) under argon at 0 °C. After 2 h the solvent and excess of reagent were evaporated off under reduced pressure and the residue was dissolved in dry toluene (20 cm<sup>3</sup>). 2-Pyrrolidone (0.64 g, 7.5 mmol) in dry toluene (30 cm<sup>3</sup>) was stirred under argon at room temp. with sodium hydride (50% dispersion in oil; 0.4 g) for 1 h. The acid chloride solution was added slowly and the mixture stirred at room temp. for 2 h. Water (30 cm<sup>3</sup>) was added dropwise to the mixture, which was then extracted with toluene (3 × 30 cm<sup>3</sup>). The combined extracts were dried (MgSO<sub>4</sub>) and evaporated under reduced pressure. The residue (1.45 g) was flash chromatographed (hexane-Et<sub>2</sub>O, 9:1) to give the imide (1.39 g, 88%) as needles, m.p. 37.5–38.5 °C (from hexane); *R<sub>f</sub>*(hexane-Et<sub>2</sub>O, 4:1) 0.08; *v*<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 1745 (NC=O), 1680 (C=CC=O), 1600 (C=C), 1255 and 855 (SiMe<sub>3</sub>) and 1000 (E CH=CH); *δ*(CDCl<sub>3</sub>) 7.57 (1 H, d, *J* 18.6, COCH=CH), 7.34 (1 H, d, *J* 18.6, CH=CHSi), 3.83 (2 H, t, *J* 7.1, NCH<sub>2</sub>), 2.58 (2 H, t, *J* 8.0, COCH<sub>2</sub>), 2.03 (2 H, tt, *J* 8.0 and 7.1, CH<sub>2</sub>) and 0.12 (9 H, s, SiMe<sub>3</sub>); *m/z* 211 (10%, M<sup>+</sup>), 196 (50, M - Me), and 138 (100, M - SiMe<sub>3</sub>) (Found: M<sup>+</sup>, 211.1033. C<sub>10</sub>H<sub>17</sub>NO<sub>2</sub>Si requires M, 211.1029) (Found: C, 57.0; H, 8.3; N, 6.5. C<sub>10</sub>H<sub>17</sub>NO<sub>2</sub>Si requires C, 56.9; H, 8.1; N, 6.6%).

**(Z)-1-(3-Trimethylsilylacryloyl)-2-pyrrolidone Z-43.**—Similarly, the *Z*-acid (7.20 g, 50 mmol) gave the imide (5.89 g, 61%); *v*<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/cm<sup>-1</sup> 1725 (NC=O), 1665 (C=CC=O), 1585 (C=C), 1235 and 845 (SiMe<sub>3</sub>) and 660 (Z CH=CH); *δ*(CDCl<sub>3</sub>) 7.65 (1 H, d, *J* 4.3, COCH=), 6.58 (1 H, d, *J* 4.3, SiCH=), 3.84 (2 H, t,

*J* 7.1, NCH<sub>2</sub>), 2.60 (2 H, t, *J* 8.0, COCH<sub>2</sub>), 2.05 (2 H, tt, *J* 8.0 and 7.1, CH<sub>2</sub>) and 0.15 (9 H, s, SiMe<sub>3</sub>); *m/z* 211 (40%, M<sup>+</sup>), 196 (100, M - Me) and 138 (80, M - Me<sub>3</sub>Si) (Found: M<sup>+</sup>, 211.1024. C<sub>10</sub>H<sub>17</sub>NO<sub>2</sub>Si requires *M*, 211.1029).

**1-(3-Trimethylsilylbutanoyl)-2-pyrrolidone.**—Methylolithium (1.5 mol dm<sup>-3</sup> solution in Et<sub>2</sub>O; 20 cm<sup>3</sup>) was added dropwise to a stirred mixture of copper(I) iodide (5.33 g, 28 mmol) and ether (36 cm<sup>3</sup>) under argon at -20 °C until a clear solution was obtained. After 20 min the solution was cooled to -78 °C and ethylaluminium dichloride (1 mol dm<sup>-3</sup> solution in hexane; 28 cm<sup>3</sup>) was added dropwise. After 20 min a solution of the *Z*-imide (3.10 g, 14.7 mmol) in dry ether (30 cm<sup>3</sup>) was added slowly. After 2 h at -10 °C, the mixture was quenched with saturated aqueous ammonium chloride (100 cm<sup>3</sup>), and extracted with ether (5 × 60 cm<sup>3</sup>). The combined extracts were washed with aqueous ammonia (pH 8; 2 × 100 cm<sup>3</sup>), dried (MgSO<sub>4</sub>) and evaporated under reduced pressure to give the *imide* (3.17 g, 95%); *v*<sub>max</sub>(film)/cm<sup>-1</sup> 1750 (C=O), 1700 (C=O), 1240 and 840 (SiMe<sub>3</sub>); δ(CDCl<sub>3</sub>) 3.82 (2 H, dt, *J* 2.1 and 7.2, NCH<sub>2</sub>), 2.99 (1 H, dd, *J* 3.7 and 15.9, COCH<sub>A</sub>H<sub>B</sub>CHSi), 2.61 (1 H, dd, *J* 11 and 15.9, COCH<sub>A</sub>H<sub>B</sub>CHSi), 2.57 (2 H, t, *J* 8.2, COCH<sub>2</sub>), 2.00 (2 H, tt, 8.2 and 7.2, CH<sub>2</sub>), 1.2 (1 H, m, CHSi), 0.92 (3 H, d, *J* 7.3, Me) and -0.02 (9 H, s, SiMe<sub>3</sub>); *m/z* 227 (10%, M<sup>+</sup>), 212 (83, M - Me) and 73 (100, SiMe<sub>3</sub>) (Found: M<sup>+</sup>, 227.1348. C<sub>11</sub>H<sub>21</sub>NO<sub>2</sub>Si requires *M*, 227.1342). The *E*-imide, by the same procedure, gave an identical product (94%).

**Benzyl 3-Trimethylsilylbutanoate 44.**—*Method A.* Butyllithium (1.6 mol dm<sup>-3</sup> solution in hexane; 43 cm<sup>3</sup>) was added dropwise to a stirred solution of benzyl alcohol (11 cm<sup>3</sup>) in dry THF (54 cm<sup>3</sup>) under argon at -10 °C. After 10 min the imide (5.1 g, 22.5 mmol) in dry THF (50 cm<sup>3</sup>) was added. A white precipitate appeared after 1 or 2 h. After 22 h at room temp. the mixture was diluted with water (100 cm<sup>3</sup>) and extracted with light petroleum (b.p. 40–60 °C; 3 × 100 cm<sup>3</sup>). The organic layer was dried (MgSO<sub>4</sub>), evaporated under reduced pressure and the residue flash chromatographed (hexane–Et<sub>2</sub>O, 9:1) to give the *ester* (5.3 g, 94%); *v*<sub>max</sub>(film)/cm<sup>-1</sup> 1745 (C=O), 1500 (Ph), 1260 and 840 (SiMe<sub>3</sub>), 1220 and 1160 (C–O) and 760 and 710 (Ph); δ(CDCl<sub>3</sub>) 7.3–7.4 (5 H, m, Ph), 5.1 (2 H, s, CH<sub>2</sub>Ph), 2.45 (1 H, dd, *J* 4.2 and 15.1, COCH<sub>A</sub>H<sub>B</sub>CHSi), 2.11 (1 H, dd, *J* 11 and 15.1, COCH<sub>A</sub>H<sub>B</sub>CHSi), 1.3–1.2 (1 H, m, CHSi), 0.95 (3 H, d, *J* 7.2, Me) and -0.03 (9 H, s, SiMe<sub>3</sub>); *m/z* 250 (15%, M<sup>+</sup>) and 235 (100, M - Me) (Found: M<sup>+</sup>, 250.1380. C<sub>14</sub>H<sub>22</sub>O<sub>2</sub>Si requires *M*, 250.1389) (Found: C, 67.0; H, 8.8. C<sub>14</sub>H<sub>22</sub>O<sub>2</sub>Si requires C, 67.2; H, 8.9%).

*Method B.* Methylolithium (1.4 mol dm<sup>-3</sup> solution in Et<sub>2</sub>O; 80 cm<sup>3</sup>) was added dropwise with stirring to copper(I) iodide (10.7 g, 56 mmol) in ether (20 cm<sup>3</sup>) under argon at -20 °C until a clear solution was obtained. The solution was cooled to -78 °C and ethylaluminium dichloride (1 mol dm<sup>-3</sup> solution in hexane; 56 cm<sup>3</sup>) was added to it. After 20 min, the *E*-imide (6.0 g, 28 mmol) in ether (60 cm<sup>3</sup>) was added slowly, and the mixture warmed to -10 °C and kept for 2 h. After this, benzyl alcohol (14.5 cm<sup>3</sup>, 140 mmol) was added slowly to it and the suspension stirred at room temp. for 15 h. The mixture was then diluted with water (100 cm<sup>3</sup>) and extracted with ether (3 × 100 cm<sup>3</sup>). The combined extracts were washed with aqueous ammonia (pH 9; 2 × 100 cm<sup>3</sup>) and brine (100 cm<sup>3</sup>), dried (MgSO<sub>4</sub>), and evaporated under reduced pressure. The residue was chromatographed (hexane–Et<sub>2</sub>O, 9:1) to give the *ester* (6.1 g, 86%) identical (<sup>1</sup>H NMR, TLC) with the sample above.

**The Aldol Reactions of the β-Silyl Esters.**—Typically, butyllithium (1.5 mol dm<sup>-3</sup> solution in hexane; 3 cm<sup>3</sup>) was added dropwise to a stirred solution of diisopropylamine (0.75 cm<sup>3</sup>, 5 mmol) in THF (10 cm<sup>3</sup>) at -20 °C and after 30 min this mixture

was cooled to -78 °C. The ester (4 mmol) in THF (4 cm<sup>3</sup>) was then added dropwise to the cooled solution. After 20 min, freshly distilled aldehyde (5 mmol) was also added dropwise to the mixture, which was then stirred for 1 h. After this the solution was quenched with saturated aqueous ammonium chloride (10 cm<sup>3</sup>) and allowed to warm to room temperature. The mixture was then diluted with ether (50 cm<sup>3</sup>). The ether layer was separated, washed with brine, dried (MgSO<sub>4</sub>) and evaporated under reduced pressure and the residue chromatographed (hexane–EtOAc, 5:1) to give the β-hydroxy esters. The following esters were prepared by this method.

**Benzyl (2RS,3SR)-2-[(RS)-α-dimethyl(phenyl)silylbenzyl]-3-hydroxybutanoate (82%).** *R*<sub>f</sub>(hexane–EtOAc, 10:1) 0.25; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 3470 (OH), 1740 (C=O), 1250 (SiMe) and 1110 (SiPh); δ(CDCl<sub>3</sub>) 7.43–6.89 (15 H, m, 3 × Ph), 4.85 (2 H, s, OCH<sub>2</sub>Ph), 3.83 (1 H, m, MeCHOH), 3.31 (1 H, dd, *J* 12.3 and 4.9, CHCO<sub>2</sub>Bn), 2.72 (1 H, d, *J* 12.3, PhCHSi), 1.58 (1 H, br s, OH), 0.99 (3 H, d, *J* 6.4, MeCH), 0.19 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.14 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); *m/z* 373 (0.53%, M - MeCHOH), 205 (100, M - MeCHOH - Ph - PhCH<sub>2</sub>) and 135 (95, SiMe<sub>2</sub>Ph) (Found: M<sup>+</sup> - MeCHOH, 373.1592. C<sub>26</sub>H<sub>30</sub>O<sub>3</sub>Si requires *M* - MeCHOH, 373.1623).

**Allyl (2RS,3SR)-2-[(RS)-α-hydroxybenzyl]-3-dimethyl(phenyl)silylbutanoate (58%).** From allyl 3-dimethyl(phenyl)silylbutanoate;<sup>4</sup> *R*<sub>f</sub>(hexane–EtOAc, 5:1) 0.36; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 3500 (OH), 1740 (C=O), 1255 (SiMe) and 1115 (SiPh); δ(CDCl<sub>3</sub>) 7.64–7.18 (10 H, m, 2 × Ph), 5.59–5.52 (1 H, m, CH=CH<sub>2</sub>), 5.07–4.96 (2 H, m, CH=CH<sub>2</sub>), 4.75 (1 H, d, *J* 9.7, PhCH), 4.21 (2 H, dt, *J* 5.7 and 1.3, OCH<sub>2</sub>), 2.93 (1 H, dd, *J* 3.7 and 9.7, CHCO), 1.84 (1 H, br s, OH), 1.75–1.63 (1 H, m, CHSi), 1.16 (3 H, d, *J* 7.7, MeCH), 0.42 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.36 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); *m/z* 291 (1%, M - Ph) and 135 (100, SiMe<sub>2</sub>Ph) (Found: M<sup>+</sup> - Ph, 291.1418. C<sub>22</sub>H<sub>28</sub>O<sub>3</sub>Si requires *M* - Ph, 291.1416).

**Benzyl (2RS, 3SR)-2-[(SR)-1-dimethyl(phenyl)silyl-ethyl]-3-hydroxy-4-methylpentanoate (59%).** *R*<sub>f</sub>(hexane–EtOAc, 5:1) 0.45; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 3550 (OH), 1740 (C=O), 1260 (SiMe) and 1120 (SiPh); δ(CDCl<sub>3</sub>) 7.57–7.22 (10 H, m, 2 × Ph), 5.03 (2 H, s, OCH<sub>2</sub>Ph), 3.60 (1 H, dd, *J* 2.5 and 10, CHOH), 2.70 (1 H, dd, *J* 3.4 and 10, CHCO), 1.60–1.47 (1 H, m, MeCH), 1.08 (3 H, d, *J* 7.6, MeCH), 1.06–0.86 (1 H, m, Me<sub>2</sub>CH), 0.83 (3 H, d, *J* 6.8, Me<sub>A</sub>Me<sub>B</sub>CH), 0.71 (3 H, d, *J* 6.8, Me<sub>A</sub>Me<sub>B</sub>CH), 0.34 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.30 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); *m/z* 369 (3.4%, M - Me), 135 (32, SiMe<sub>2</sub>Ph) and 91 (100, PhCH<sub>2</sub>) (Found: M<sup>+</sup> - Me, 369.1891. C<sub>23</sub>H<sub>32</sub>O<sub>3</sub>Si requires *M* - Me, 369.1886).

**Benzyl (2RS,3SR)-3-dimethyl(phenyl)silyl-2-[(SR)-1-hydroxyethyl]-4-methylpentanoate (56%).** *R*<sub>f</sub>(hexane–EtOAc, 5:1) 0.3; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 3500 (OH), 1738 (C=O), 1265 (SiMe) and 1120 (SiPh); δ(CDCl<sub>3</sub>) 7.60–7.28 (10 H, m, 2 × Ph), 5.04 (2 H, s, CH<sub>2</sub>Ph), 3.81 (1 H, m, CHOH), 2.65 (1 H, dd, *J* 8.3 and 3, CHCO), 2.01 (1 H, m, Me<sub>2</sub>CH), 1.58 (1 H, t, *J* 3, CHSi), 1.5 (1 H, br s, OH), 1.10 (3 H, d, *J* 6.1, MeCHOH), 0.88 (3 H, d, *J* 6.9, Me<sub>A</sub>Me<sub>B</sub>CH), 0.80 (3 H, d, *J* 6.9, Me<sub>A</sub>Me<sub>B</sub>CH), 0.41 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.37 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); *m/z* 369 (2.1%, M - Me), 135 (39, SiMe<sub>2</sub>Ph) and 91 (100, PhCH<sub>2</sub>) (Found: M<sup>+</sup> - Me, 369.1873. C<sub>22</sub>H<sub>29</sub>O<sub>3</sub>Si requires *M*, 369.1886).

**Benzyl (2RS,3SR)-3-hydroxy-2-[(RS)-α-trimethylsilylbenzyl]-butanoate (85%).** As needles, m.p. 111–112 °C (from hexane); *R*<sub>f</sub>(hexane–EtOAc, 5:1) 0.2; *v*<sub>max</sub>(CCl<sub>4</sub>)/cm<sup>-1</sup> 3500 (OH), 1730 (C=O) and 1250 (SiMe); δ(CDCl<sub>3</sub>) 7.41–7.00 (10 H, m, 2 × Ph), 5.22 (1 H, d, *J* 12.4, OCH<sub>A</sub>H<sub>B</sub>Ph), 5.15 (1 H, d, *J* 12.4, OCH<sub>A</sub>H<sub>B</sub>Ph), 3.88 (1 H, dq, *J* 6.4 and 4.8, MeCH), 3.32 (1 H, dd, *J* 12.4 and 4.8, CHCO), 2.49 (1 H, d, *J* 12.3, CHSi), 1.61 (1 H, br s, OH), 1.04 (3 H, d, *J* 6.4, MeCH) and -0.12 (9 H, s, SiMe<sub>3</sub>); *m/z* 341 (3%, M - Me), 131 (100, M - OH - SiMe<sub>3</sub> - CO<sub>2</sub>-Bn), 91 (95, PhCH<sub>2</sub>) and 73 (49, SiMe<sub>3</sub>) (Found: M<sup>+</sup> - Me, 341.1531. C<sub>21</sub>H<sub>28</sub>O<sub>3</sub>Si requires *M* - Me, 341.1523) (Found: C, 70.9; H, 7.9. C<sub>21</sub>H<sub>28</sub>O<sub>3</sub>Si requires C, 70.7; H, 7.9%).



*Benzyl* (2RS,3SR,1'SR)-3-hydroxy-2-(1-trimethylsilylethyl)-butanoate (78%). Acetaldehyde added at  $-98^{\circ}\text{C}$ ;  $\nu_{\text{max}}$ (film)/ $\text{cm}^{-1}$  3440 (OH), 1735, 1500 (Ar), 1460 (OH) 1250 and 835 (SiMe<sub>3</sub>), 1160 (C=O) and 760 and 700 (Ph);  $\delta$ (CDCl<sub>3</sub>) 7.4–7.3 (5 H, m, Ph), 5.12 (1 H, d, *J* not reliably measurable, PhCH<sub>2</sub>CH<sub>2</sub>O), 5.09 (1 H, d, *J* not reliably measurable, PhCH<sub>2</sub>CH<sub>2</sub>O), 4.09 (1 H, dq, *J* 7.2 and 6.2, CHOH), 2.59 (1 H, t, *J* 7.2, CHCO), 2.13 (1 H, s, OH), 1.27 (1 H, dq, *J* 7.2 and 7.5, SiCH), 1.17 (3 H, d, *J* 6.2, MeCHOH), 0.98 (3 H, d, *J* 7.5, SiCMe) and  $-0.01$  (9 H, s, Me<sub>3</sub>Si); *m/z* 279 (15%, M – Me), 250 (15, M – MeCHO), 249 (70, M – MeCHOH), 187 (30, M – OBn), 159 (65, M – CO<sub>2</sub>Bn) and 73 (100, SiMe<sub>3</sub>) (Found: M<sup>+</sup> – Me, 279.1405. C<sub>16</sub>H<sub>26</sub>O<sub>3</sub>Si requires M – Me, 279.1416).

*Hydrogenolysis of Benzyl Esters.*—Typically, the benzyl ester (2–3 mmol) was stirred with 10% palladium on charcoal (100 mg) in methanol (10 cm<sup>3</sup>) under hydrogen at room temp. and pressure for 4–5 h, monitoring the reaction by TLC. The mixture was filtered and the filtrate evaporated under reduced pressure. The residue in ether (20 cm<sup>3</sup>) was washed with aqueous sodium hydroxide (5%; 3 × 10 cm). The combined alkaline extracts were acidified with concentrated hydrochloric acid at 0°C, and the resultant suspension extracted with dichloromethane (3 × 20 cm<sup>3</sup>). The organic extracts were washed with brine (10 cm<sup>3</sup>), dried (MgSO<sub>4</sub>) and evaporated under reduced pressure to give the hydroxy acid. The following acids were prepared by this method.

(2RS,3RS)-2-[(RS)- $\alpha$ -Dimethyl(phenyl)silylbenzyl]-3-hydroxybutanoic acid **16** (99%). As needles, m.p. 138–140°C (from hexane); *R<sub>f</sub>*(hexane–EtOAc, 1:1) 0.28 (streak);  $\nu_{\text{max}}$ (CCl<sub>4</sub>)/ $\text{cm}^{-1}$  3500–3000 (OH), 1705 (C=O), 1245 (SiMe) and 1110 (SiPh);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 7.4–6.86 (10 H, m, 2 × Ph), 3.62 (1 H, q, *J* 6.5, MeCHOH), 2.89 (2 H, s, CHCHSi), 1.13 (3 H, d, *J* 6.5, MeCH) and 0.26 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.23 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>) 179.8, 139.7, 136.5, 134.5, 129.2, 128.8, 128.4, 127.5, 125.4, 65.4, 51.9, 35.7, 21.5,  $-2.9$  and  $-4.1$ ; *m/z* 310 (3.4%, M – H<sub>2</sub>O) and 135 (100, SiMe<sub>2</sub>Ph) (Found: M<sup>+</sup> – Me, 313.1287. C<sub>19</sub>H<sub>24</sub>O<sub>3</sub>Si requires M – Me, 313.1260) (Found: M<sup>+</sup> – H<sub>2</sub>O, 310.1401. C<sub>19</sub>H<sub>24</sub>O<sub>3</sub>Si requires M – H<sub>2</sub>O, 310.1389) (Found: C, 69.3; H, 7.5. C<sub>19</sub>H<sub>24</sub>O<sub>3</sub>Si requires C, 69.5; H, 7.35%).

(2RS,3SR)-3-[Dimethyl(phenyl)silyl]-2-[1'(RS)-hydroxyethyl]butanoic acid **17**. Directly from benzyl crotonate (10.75 mmol) and acetaldehyde (3 cm<sup>3</sup>) without purification of the intermediate before the hydrogenolysis. The crude acid was purified further by recrystallisation of the *S*-benzyl isothiuronium salt<sup>29</sup> and regeneration of the free acid (1.8 g, 64%); *R<sub>f</sub>*(hexane–EtOAc, 1:1) 0.23;  $\nu_{\text{max}}$ (film)/ $\text{cm}^{-1}$  3400 (OH), 3300–2400 (CO<sub>2</sub>H), 1700 (CO), 1250 (SiMe) and 1120 (SiPh);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 7.54–7.32 (5 H, m, Ph), 4.03 (1 H, dq, *J* 3.6 and 6.5, CHOH), 2.31 (1 H, dd, *J* 9.2 and 3.6, CHCO), 1.56 (1 H, m, SiCH), 1.20 (3 H, d, *J* 6.5, MeCHOH), 1.07 (3 H, d, *J* 7.5, MeCHSi), 0.34 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.32 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); *m/z* 251 (3%, M – Me), 233 (15, M – Me – H<sub>2</sub>O), 137 (50, MePhSiOH) and 135 (100, Me<sub>2</sub>PhSi) (Found: M<sup>+</sup> – Me, 251.1096. C<sub>14</sub>H<sub>22</sub>O<sub>3</sub>Si requires M – Me, 251.2001).

(2RS,3SR)-2-[(RS)- $\alpha$ -Dimethyl(phenyl)silylbenzyl]-3-hydroxybutanoic acid **29** (77%). As needles, m.p. 163–165°C (from hexane); *R<sub>f</sub>*(hexane–EtOAc, 1:1) 0.28 (streak);  $\nu_{\text{max}}$ (CCl<sub>4</sub>)/ $\text{cm}^{-1}$  3500–3000 (OH), 1700 (C=O), 1245 (SiMe) and 1110 (SiPh);  $\delta$ (CDCl<sub>3</sub>) 7.37–6.85 (10 H, m, 2 × Ph), 3.85 (1 H, dq, *J* 4.8 and 6.4, CHOH), 3.26 (1 H, dd, *J* 12.2 and 4.7, CHCO), 2.64 (1 H, d, *J* 12.2, CHSi), 1.06 (3 H, d, *J* 6.4, MeCH), 0.26 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.17 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>) 175.8, 139.9, 136.7, 134.4, 128.9, 128.6, 128.0, 127.3, 125.0, 67.2, 51.5, 35.9, 16.7,  $-3.3$  and  $-3.7$ ; *m/z* 295 (1.6%, M – Me – H<sub>2</sub>O) and 135 (100, SiMe<sub>2</sub>Ph) (Found: M<sup>+</sup> – Me – H<sub>2</sub>O, 295.1169. C<sub>19</sub>H<sub>24</sub>O<sub>3</sub>Si requires M – Me – H<sub>2</sub>O, 295.1154) (Found: C, 69.3; H, 7.35. C<sub>19</sub>H<sub>24</sub>O<sub>3</sub>Si requires C, 69.5; H, 7.35%).

(2RS,3SR)-2-[(SR)-1-Dimethyl(phenyl)silylethyl]-3-hydroxy-4-methylpentanoic acid **31** (92%). *R<sub>f</sub>*(hexane–EtOAc, 1:1) 0.25;  $\nu_{\text{max}}$ (film)/ $\text{cm}^{-1}$  3500–3000 (OH), 1720 (C=O), 1260 (SiMe) and 1115 (SiPh);  $\delta$ (CDCl<sub>3</sub>) 7.58–7.31 (5 H, m, Ph), 3.60 (1 H, dd, *J* 2.6 and 10.1, CHOH), 2.67 (1 H, dd, *J* 3.1 and 10.1, CHCO), 1.70–1.48 (2 H, m, CHSi and Me<sub>2</sub>CH), 1.13 (3 H, d, *J* 7.6, MeCHSi), 0.88 (3 H, d, *J* 6.8, Me<sub>A</sub>Me<sub>B</sub>CH) and 0.73 (3 H, d, *J* 6.8, Me<sub>A</sub>Me<sub>B</sub>CH), 0.36 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.32 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); *m/z* 279 (8%, M – Me), 261 (6, M – Me – H<sub>2</sub>O) and 135 (100, SiMe<sub>2</sub>Ph) (Found: M<sup>+</sup> – Me, 279.1442. C<sub>16</sub>H<sub>26</sub>O<sub>3</sub>Si requires M – Me, 279.1416).

(2RS,3SR)-2-[(SR)-3-Dimethyl(phenyl)silyl-1-hydroxyethyl]-4-methylpentanoic acid **32** (90%). *R<sub>f</sub>*(hexane–EtOAc, 1:1) 0.25 (streak);  $\nu_{\text{max}}$ (film)/ $\text{cm}^{-1}$  3500–3000 (OH), 1700 (C=O), 1245 (SiMe) and 1108 (SiPh);  $\delta$ (CDCl<sub>3</sub>) 7.59–7.56 (2 H, m, *o*-ArH), 7.34–7.30 (3 H, m, *m*- and *p*-ArH), 3.84 (1 H, dq, *J* 8 and 6.1, MeCHOH), 2.66 (1 H, dd, *J* 8 and 2.8, CHCO), 2.07 (1 H, m, Me<sub>2</sub>CH), 1.59 (1 H, t, *J* 3, CHSi), 1.21 (3 H, d, *J* 6.1, MeCHOH), 0.94 (3 H, d, *J* 6.7, Me<sub>A</sub>Me<sub>B</sub>CH), 0.88 (3 H, d, *J* 6.7, Me<sub>A</sub>Me<sub>B</sub>CH), 0.41 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.40 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); *m/z* 261 (3%, M – Me – H<sub>2</sub>O) and 135 (100, SiMe<sub>2</sub>Ph) (Found: M<sup>+</sup> – Me – H<sub>2</sub>O, 261.1310. C<sub>16</sub>H<sub>26</sub>O<sub>3</sub>Si requires M – Me – H<sub>2</sub>O, 261.1311).

(2RS,3SR)-3-Hydroxy-2-[(RS)- $\alpha$ -trimethylsilylbenzyl]butanoic acid **47** (95%). As needles, m.p. 158–159°C (from hexane); *R<sub>f</sub>*(hexane–EtOAc, 1:1) 0.25 (streak);  $\nu_{\text{max}}$ (CCl<sub>4</sub>)/ $\text{cm}^{-1}$  3310 (OH), 1690 (C=O) and 1240 (SiMe);  $\delta$ (CDCl<sub>3</sub>) 7.28–7.02 (5 H, m, Ph), 3.93 (1 H, dq, *J* 6.3 and 4.7, MeCH), 3.32 (1 H, dd, *J* 12.4 and 4.7, CHCO), 2.45 (1 H, d, *J* 12.3, CHSi), 1.11 (3 H, d, *J* 6.3, MeCH) and  $-0.06$  (9 H, s, SiMe<sub>3</sub>); *m/z* 248 (2%, M – H<sub>2</sub>O), 131 (38, M – H<sub>2</sub>O – CO<sub>2</sub> – SiMe<sub>3</sub>) and 73 (100, SiMe<sub>3</sub>) (Found: M<sup>+</sup> – H<sub>2</sub>O, 248.1219. C<sub>14</sub>H<sub>22</sub>O<sub>3</sub>Si requires M – H<sub>2</sub>O, 248.1232) (Found: C, 63.4; H, 8.25. C<sub>14</sub>H<sub>22</sub>O<sub>3</sub>Si requires C, 63.1; H, 8.3%).

(2RS,3SR,1'SR)-3-Hydroxy-2-(1-trimethylsilylethyl)butanoic acid **48** (89%).  $\nu_{\text{max}}$ (film)/ $\text{cm}^{-1}$  3700–2400 (COOH), 3450 (OH), 1705 (C=O), 1250 and 835 (SiMe<sub>3</sub>) and 1160 (C=O);  $\delta$ (CDCl<sub>3</sub>) 6.8 (1 H, s, OH), 4.05 (1 H, dq, *J* 7.5 and 6.0, CHOH), 2.5 (1 H, t, *J* 7.5, CHCO<sub>2</sub>), 1.2 (3 H, d, *J* 6.0, MeCHOH), 0.95 (3 H, d, *J* 6.0, CH<sub>3</sub>CHSi) and 0.0 (9 H, s, SiMe<sub>3</sub>); *m/z* 189 (46%, M – Me), 171 (67, M – Me – H<sub>2</sub>O), 159 (31, M – CO<sub>2</sub>H), 143 (59, M – OH – CO<sub>2</sub>), 127 (32, M – Me – CO<sub>2</sub>) and 73 (100, SiMe<sub>3</sub>) (Found: M<sup>+</sup> – Me, 189.0941. C<sub>9</sub>H<sub>20</sub>O<sub>3</sub>Si requires M – Me, 189.0947).

(2SR,3RS)-3-Dimethyl(phenyl)silyl-2-[(RS)- $\alpha$ -hydroxybenzyl]butanoic Acid **18**.—Methyl lithium 1.5 mol dm<sup>-3</sup> solution in ether; 6 mmol, 4 cm<sup>3</sup>) was added slowly under nitrogen to copper(I) iodide (0.57 g, 3 mmol) in dry ether (5 cm<sup>3</sup>) at  $-10^{\circ}\text{C}$ . (2RS,3SR)-Allyl 3-dimethyl(phenyl)silyl-2-[(SR)-hydroxybenzyl]butanoate (0.3 g, 0.8 mmol) in ether (1 cm<sup>3</sup>) was added to the mixture, which was then kept for 1 h at 0°C. Aqueous hydrochloric acid (3 mol dm<sup>-3</sup>; 5 cm<sup>3</sup>) and ether (10 cm<sup>3</sup>) were then added to the mixture and subsequently filtered through Celite. The filtrate was extracted with aqueous sodium hydroxide (5%; 3 × 5 cm<sup>3</sup>). The combined aqueous layers were acidified and extracted with dichloromethane (3 × 15 cm<sup>3</sup>). The organic layer was washed with brine, dried (MgSO<sub>4</sub>) and evaporated under reduced pressure to give the acid (0.25 g, 93%) as needles, m.p. 70–72°C (from hexane); *R<sub>f</sub>*(hexane–EtOAc, 1:1) 0.3;  $\nu_{\text{max}}$ (CCl<sub>4</sub>)/ $\text{cm}^{-1}$  3510 and 3250 (OH), 1250 (SiMe) and 1105 (SiPh);  $\delta$ (CDCl<sub>3</sub>) 7.50–7.13 (10 H, m, 2 × Ph), 4.91 (1 H, d, *J* 5, PhCH), 2.74 (1 H, dd, *J* 5 and 7.7, CHCO), 1.46 (1 H, quintet, *J* 7.6, CHSi), 1.13 (3 H, d, *J* 7.5, MeCH), 0.35 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.29 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); *m/z* 266 (0.9%, M – H<sub>2</sub>O – CO<sub>2</sub>) and 135 (100, SiMe<sub>2</sub>Ph) (Found: M<sup>+</sup> – H<sub>2</sub>O – CO<sub>2</sub>, 266.1489. C<sub>19</sub>H<sub>24</sub>O<sub>3</sub>Si requires M – H<sub>2</sub>O – CO<sub>2</sub>, 266.1591).



(2RS,3SR)-3-Dimethyl(phenyl)silyl-2-[(RS)- $\alpha$ -hydroxybenzyl]butanoic Acid **30**.—Allyl (2RS,3SR)-3-dimethyl(phenyl)silyl-2-[(RS)- $\alpha$ -hydroxybenzyl]butanoate (0.73 g, 2 mmol) in THF (2 cm<sup>3</sup>) was added to the dimethyl(phenyl)silylcuprate reagent (3 mmol) under nitrogen and kept at 0 °C for 1 h and at room temp. overnight. A similar work-up to that above gave the acid (0.54 g, 83%);  $R_f$ (hexane–EtOAc, 1:1) 0.3 (streak);  $\nu_{\max}$ (film)/cm<sup>-1</sup> 3200 (OH), 1705 (C=O), 1247 (SiMe) and 1112 (SiPh);  $\delta$ (CDCl<sub>3</sub>) 7.60–7.17 (10 H, m, 2 × Ph), 4.71 (1 H, d, *J* 9.7, PhCH), 2.89 (1 H, dd, *J* 3.3 and 9.7, CHCO), 1.69–1.58 (1 H, m, MeCH), 1.13 (3 H, d, *J* 7.6, MeCH), 0.39 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.34 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); *m/z* 313 (3.3%, M – Me) and 135 (100, SiMe<sub>2</sub>Ph) (Found: M<sup>+</sup> – Me, 313.1255. C<sub>19</sub>H<sub>24</sub>O<sub>3</sub>Si requires *M* – Me, 313.1260).

*Decarboxylative Elimination using Dimethylformamide Dimethyl Acetal*.—Typically, *N,N*-dimethylformamide dimethyl acetal (0.72 g, 6 mmol) and the  $\beta$ -hydroxy acid (1 mmol) were refluxed in dry chloroform (20 cm<sup>3</sup>) for 5 h. The solvent was removed under reduced pressure and the residue flash column chromatographed (hexane) to give the allylsilane. The following allylsilanes were prepared by this method.

(Z)-1-Dimethyl(phenyl)silyl-1-phenylbut-2-ene **19** (85% from **16**).  $R_f$ (hexane–EtOAc, 20:1) 0.5;  $\nu_{\max}$ (film)/cm<sup>-1</sup> 1600, 1495 and 1460 (Ph), 1255 (SiMe) and 1105 (SiPh);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 7.39–6.93 (10 H, m, 2 × Ph), 5.79 (1 H, ddq, *J* 11.4, 10.8 and 1.8, CHCH=), 5.48 (1 H, dq, *J* 10.8 and 6.7, MeCH=), 3.45 (1 H, d, *J* 11.4, PhCH), 1.47 (3 H, dd, *J* 6.7 and 1.8, MeCH), 0.26 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.23 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>) 142.5, 137.1, 134.3, 129.4, 129.0, 128.1, 127.4 (×2), 124.5, 122.3, 37.2, 12.9, –4.4 and –4.8; *m/z* 266 (7.8%, M<sup>+</sup>) and 135 (100, SiMe<sub>2</sub>Ph) (Found: M<sup>+</sup>, 266.1481. C<sub>18</sub>H<sub>22</sub>Si requires *M*, 266.1491).

(Z)-2-Dimethyl(phenyl)silylpent-3-ene **20** (82%).  $R_f$ (hexane) 0.45;  $\nu_{\max}$ (film)/cm<sup>-1</sup> 1646 (C=C), 1248 (SiMe) and 1110 (SiPh);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 7.52–7.29 (5 H, m, Ph), 5.30 (1 H, dq, *J* 10.7 and 6.6, CH=CHMe), 5.18 (1 H, tq, *J* 10.7 and 1.6, CH=CHMe), 2.07 (1 H, dq, *J* 10.7 and 7.1, SiCH), 1.45 (3 H, dd, *J* 6.6 and 1.6, CH=CHMe), 0.99 (3 H, d, *J* 7.1, SiCHMe), 0.26 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.25 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>) 138.0, 134.0, 133.6, 128.8, 127.5, 120.6, 21.2, 15.2, 13.1, –4.7 and –5.5; *m/z* 204 (1.5%, M<sup>+</sup>) and 135 (100, Me<sub>2</sub>PhSi) (Found: M<sup>+</sup>, 204.1326. C<sub>13</sub>H<sub>20</sub>Si requires *M*, 204.1334).

(E)-1-Dimethyl(phenyl)silyl-1-phenylbut-2-ene **23** (85% from **29**).  $R_f$ (hexane–EtOAc, 20:1) 0.5;  $\nu_{\max}$ (film)/cm<sup>-1</sup> 1610, 1495 and 1440 (Ph), 1250 (SiMe) and 1110 (SiPh);  $\delta$ (CDCl<sub>3</sub>) 7.38–6.88 (10 H, m, 2 × Ph), 5.73 (1 H, ddq, *J* 15.9, 9.8 and 1.5, CHCH=), 5.32 (1 H, ddq, *J* 0.9, 15 and 6.4, MeCH=), 3.05 (1 H, d, *J* 9.8, PhCH), 1.66 (3 H, dd, *J* 6.6 and 1.3, MeCH), 0.24 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.21 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); *m/z* 266 (4.7%, M<sup>+</sup>) and 135 (100, SiMe<sub>2</sub>Ph) (Found: M<sup>+</sup>, 266.1486. C<sub>18</sub>H<sub>22</sub>Si requires *M*, 266.1491), identical (TLC and <sup>1</sup>H NMR) with the sample described in the preceding paper.<sup>1</sup>

(E)-3-Dimethyl(phenyl)silyl-1-phenylbut-1-ene **24** (87%).  $R_f$ (hexane–EtOAc, 20:1) 0.6;  $\nu_{\max}$ (film)/cm<sup>-1</sup> 1635, 1605 and 1428 (Ph), 1248 (SiMe) and 1110 (SiPh);  $\delta$ (CDCl<sub>3</sub>) 7.55–7.15 (10 H, m, 2 × Ph), 6.28 (1 H, dd, *J* 6.9 and 16, PhCH=CH), 6.18 (1 H, d, *J* 16, PhCH=CH), 2.02 (1 H, m, MeCH), 1.17 (3 H, d, *J* 7.2, MeCH), 0.328 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.324 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); *m/z* 266 (2.7%, M<sup>+</sup>) and 135 (100, SiMe<sub>2</sub>Ph) (Found: M<sup>+</sup>, 266.1480. C<sub>18</sub>H<sub>22</sub>Si requires *M*, 266.1491), identical (<sup>1</sup>H NMR) with the sample described in the preceding paper.<sup>1</sup>

(E)-5-Dimethyl(phenyl)silyl-2-methylhex-3-ene **33** (91%).  $R_f$ (hexane–EtOAc, 20:1) 0.5;  $\delta$ (CDCl<sub>3</sub>) 7.47–7.20 (5 H, m, Ph), 5.30 (1 H, ddd, *J* 0.9, 7.5 and 15.3, CH=CHCHMe<sub>2</sub>), 5.11 (1 H, ddd, *J* 1, 6.7 and 15.3, CH=CHCHMe<sub>2</sub>), 2.20 (1 H, m, MeCH), 1.68 (1 H, quintet, *J* 7.3, CHSi), 0.98 (3 H, d, *J* 7.3, MeCH), 0.90

(6 H, d, *J* 6.7, Me<sub>2</sub>CH), 0.21 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.209 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>), identical (<sup>1</sup>H NMR) with the sample described in the preceding paper.<sup>1</sup>

(E)-4-Dimethyl(phenyl)silyl-5-methylhex-2-ene **34** (88%).  $R_f$ (hexane–EtOAc, 20:1) 0.57;  $\nu_{\max}$ (film)/cm<sup>-1</sup> 1245 (SiMe) and 1105 (SiPh);  $\delta$ (CDCl<sub>3</sub>) 7.51–7.47 (2 H, m, *o*-ArH), 7.36–7.31 (3 H, m, *m*- and *p*-ArH), 5.31–5.17 (2 H, m, CH=CH), 1.83–1.76 (1 H, m, MeCH), 1.67 (3 H, d, *J* 4.9, MeCH=CH), 1.58 (1 H, dd, *J* 4.9 and 10, CHSi), 0.82 (6 H, d, *J* 6.8, Me<sub>2</sub>CH), 0.29 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.25 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); *m/z* 232 (2.7%, M<sup>+</sup>) and 135 (100, SiMe<sub>2</sub>Ph) (Found: M<sup>+</sup>, 232.1666. C<sub>15</sub>H<sub>24</sub>Si requires *M*, 232.1647), identical (<sup>1</sup>H NMR) with the sample described in the preceding paper.<sup>1</sup>

(E)-1-Phenyl-1-trimethylsilylbut-2-ene **49** (98%).  $R_f$ (hexane–EtOAc, 20:1) 0.6;  $\nu_{\max}$ (film)/cm<sup>-1</sup> 1617, 1505 and 1450 (Ph), and 1255 (SiMe);  $\delta$ (CDCl<sub>3</sub>) 7.27–7.02 (5 H, m, Ph), 5.79 (1 H, ddq, *J* 15, 9.9 and 1, MeCH=CH), 5.40 (1 H, ddq, *J* 15, 1 and 6.4, MeCH=CH), 2.87 (1 H, d, *J* 9.9, PhCH), 1.7 (3 H, dd, *J* 7 and 1, MeCH) and –0.05 (9 H, s, SiMe<sub>3</sub>); *m/z* 204 (5.8%, M<sup>+</sup>), 131 (23, M – SiMe<sub>3</sub>) and 73 (100, SiMe<sub>3</sub>) (Found: M<sup>+</sup>, 204.1334. C<sub>13</sub>H<sub>20</sub>Si requires *M*, 204.1334).

(E)-4-Trimethylsilylpent-2-ene **50**.—Dimethylformamide dimethyl acetal (3.0 cm<sup>3</sup>) and the acid **48** (0.80 g, 3.9 mmol) were refluxed in dry chloroform (80 cm<sup>3</sup>) under argon for 2 h. The solvent was partially removed by careful fractional distillation, and the residue was flash chromatographed (pentane), the solvent being removed by careful fractional distillation, to give a mixture of *E*-allylsilane<sup>31</sup> and *Z*-allylsilane (0.52 g, 93%) in a ratio of 90:10;  $\delta$ (CDCl<sub>3</sub>) 5.47 (1 H, ddq, *J* 15.1, 7.7 and 1.4, SiCHCH=), 5.21 (1 H, ddq, *J* 15.1, 1.2 and 6.2, MeCH=), 1.66 (3 H, dt, *J* 6.2 and 1.2, MeCH=), 1.5–1.45 (1 H, m, *J* 6, SiCH), 1.01 (3 H, d, *J* 7.2, MeCHSi) and –0.04 (9 H, s, SiMe<sub>3</sub>). The pure *E*- and *Z*-allylsilanes could be completely separated by flash chromatography (SiO<sub>2</sub>–AgNO<sub>3</sub>, 4:1; pentane).

*Preparation of the  $\beta$ -Lactones*.—Typically, benzenesulfonyl chloride (0.35 g, 2 mmol) was added to a suspension of the  $\beta$ -hydroxy acid (0.33 g, 1 mmol) in anhydrous pyridine (7 cm<sup>3</sup>) at 0 °C. The mixture was shaken well, sealed and kept in the refrigerator overnight. The mixture was poured onto crushed ice (25 g) and extracted with ether (3 × 20 cm<sup>3</sup>). The combined ethereal extracts were washed with aqueous hydrochloric acid (1 mol dm<sup>-3</sup>; 10 cm<sup>3</sup>), saturated aqueous sodium hydrogen carbonate (10 cm<sup>3</sup>) and brine (10 cm<sup>3</sup>), dried (MgSO<sub>4</sub>) and evaporated under reduced pressure. The residue was flash chromatographed (hexane–EtOAc, 10:1), to give the lactone. The following  $\beta$ -lactones were prepared by this method.

(2RS,3RS)-2-[(RS)- $\alpha$ -Dimethyl(phenyl)silylbenzyl]-3-methylpropan-3-olide **21** (96%).  $R_f$ (hexane–EtOAc, 10:1) 0.28;  $\nu_{\max}$ (film)/cm<sup>-1</sup> 1810 (C=O), 1600, 1490, 1460 (Ph), 1250 (SiMe) and 1110 (SiPh);  $\delta$ (CDCl<sub>3</sub>) 7.43–6.76 (10 H, m, 2 × Ph), 4.15 (1 H, dq, *J* 6.1 and 4, MeCH), 3.51 (1 H, dd, *J* 12 and 4, CHCO), 2.70 (1 H, d, *J* 12, PhCH), 1.26 (3 H, d, *J* 6.1, MeCH), 0.46 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.19 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); *m/z* 295 (1.27%, M – Me) and 135 (100, SiMe<sub>2</sub>Ph) (Found: M<sup>+</sup> – Me, 295.1145. C<sub>19</sub>H<sub>22</sub>O<sub>2</sub>Si requires *M* – Me, 295.1155).

(2RS,3SR)-2-[(RS)- $\alpha$ -Dimethyl(phenyl)silylbenzyl]-3-methylpropan-3-olide **35** (57%). As needles, m.p. 62–63 °C (from hexane);  $R_f$ (hexane–EtOAc, 10:1) 0.28;  $\nu_{\max}$ (CCl<sub>4</sub>)/cm<sup>-1</sup> 1820 (C=O), 1600, 1495, 1450 (Ph), 1250 (SiMe) and 1110 (SiPh);  $\delta$ (CDCl<sub>3</sub>) 7.43–6.72 (10 H, m, 2 × Ph), 4.53 (1 H quintet, *J* 6.2, MeCH), 4.10 (1 H, dd, *J* 13.5 and 6.2, CHCO), 2.79 (1 H, d, *J* 13.6, PhCH), 1.07 (3 H, d, 6.3, MeCH), 0.51 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.15 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); *m/z* 310 (3.1%, M<sup>+</sup>), 295 (15, M – Me) and 135 (100, SiMe<sub>2</sub>Ph) (Found: M<sup>+</sup>, 310.1386. C<sub>19</sub>H<sub>22</sub>O<sub>2</sub>Si requires *M*, 310.1389).

(2RS,3RS)-2-[(SR)-1-Dimethyl(phenyl)silylethyl]-3-phenylpropan-3-olide **36** (84%).  $R_f$ (hexane-EtOAc, 10:1) 0.3;  $\nu_{\max}$ (film)/ $\text{cm}^{-1}$  1830 (C=O), 1250 (SiMe) and 1107 (SiPh);  $\delta$ ( $\text{CDCl}_3$ ) 7.55–7.32 (10 H, m, 2  $\times$  Ph), 5.50 (1 H, d,  $J$  6.3, PhCH), 3.69 (1 H, dd,  $J$  3.6 and 12.7, CHCO), 1.18–1.05 (1 H, m, MeCH), 0.46 (3 H, d,  $J$  7.1, MeCH), 0.46 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.34 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>);  $m/z$  295 (4.8%, M – Me) and 135 (100, SiMe<sub>2</sub>Ph) (Found:  $M^+$  – Me, 295.1150. C<sub>19</sub>H<sub>22</sub>O<sub>2</sub>Si requires  $M$  – Me, 295.1154).

(2RS,3SR)-2-[(SR)-1-Dimethyl(phenyl)silylethyl]-3-isopropylpropan-3-olide **37** (47%).  $R_f$ (hexane-EtOAc, 10:1) 0.37;  $\nu_{\max}$ (film)/ $\text{cm}^{-1}$  1810 (C=O), 1250 (SiMe) and 1120 (SiPh);  $\delta$ ( $\text{CDCl}_3$ ) 7.50–7.33 (5 H, m, Ph), 4.21 (1 H, t,  $J$  6.5, CHO), 3.44 (1 H, dd,  $J$  6.3 and 11, CHCO), 2.05–1.96 (1 H, m, Me<sub>2</sub>CH), 1.44 (1 H, dq,  $J$  13 and 6.6, MeCH), 1.04 (3 H, d,  $J$  6.6, Me<sub>A</sub>Me<sub>B</sub>CH) and 1.00 (3 H, d,  $J$  6.6, Me<sub>A</sub>Me<sub>B</sub>CH), 0.90 (3 H, d,  $J$  7, MeCHSi), 0.46 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.41 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>);  $m/z$  276 (1.6%,  $M^+$ ), 261 (8, M – Me) and 135 (100, SiMe<sub>2</sub>Ph) (Found:  $M^+$ , 276.1557. C<sub>16</sub>H<sub>24</sub>O<sub>2</sub>Si requires  $M$ , 276.1545).

(2RS,3SR)-2-[(SR)-1-Dimethyl(phenyl)silyl-2-methylpropyl]-3-methylpropan-3-olide **38** (61%).  $R_f$ (hexane-EtOAc, 10:1) 0.32;  $\nu_{\max}$ (film)/ $\text{cm}^{-1}$  1810 (C=O), 1250 (SiMe) and 1110 (SiPh);  $\delta$ ( $\text{CDCl}_3$ ) 7.59–7.54 (2 H, m, *o*-ArH), 7.37–7.32 (3 H, m, *m*- and *p*-ArH), 4.70 (1 H, quintet,  $J$  6.2, CHO), 3.84 (1 H, dd,  $J$  9.9 and 6.2, CHCO), 1.74 (1 H, d septet,  $J$  2.8 and 6.9, Me<sub>2</sub>CH), 1.50 (1 H, dd,  $J$  10 and 2.7, CHSi), 1.40 (3 H, d,  $J$  6.2, MeCH), 0.83 (3 H, d,  $J$  7, Me<sub>A</sub>Me<sub>B</sub>CH), 0.79 (3 H, d,  $J$  7, Me<sub>A</sub>Me<sub>B</sub>CH), 0.50 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.45 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>);  $m/z$  276 (5.2%,  $M^+$ ), 261 (9, M – Me), 233 (37, M – Me – CO) and 135 (100, SiMe<sub>2</sub>Ph) (Found:  $M^+$ , 276.1551. C<sub>16</sub>H<sub>24</sub>O<sub>2</sub>Si requires  $M$ , 276.1546).

Only the allylsilane **24** was isolated (56% yield) during the  $\beta$ -lactonisation of the acid **18** by this method.

(2RS,3SR)-3-Methyl-2-[(RS)- $\alpha$ -trimethylsilylbenzyl]propan-3-olide **51** (56%).  $R_f$ (hexane-EtOAc, 10:1) 0.3;  $\nu_{\max}$ (film)/ $\text{cm}^{-1}$  1810 (C=O), 1598, 1495 and 1450 (Ph) and 1258 (SiMe);  $\delta$ ( $\text{CDCl}_3$ ) 7.25–6.94 (5 H, m, Ph), 4.65 (1 H, quintet,  $J$  6.2, MeCH), 4.30 (1 H, dd,  $J$  13.5 and 6, CHCO), 2.65 (1 H, d, 13.5, PhCH), 1.14 (3 H, d,  $J$  6.4, MeCH) and 0.029 (9 H, s, SiMe<sub>3</sub>);  $m/z$  233 (4.5%, M – Me) and 73 (100, SiMe<sub>3</sub>) (Found:  $M^+$  – Me, 233.0990. C<sub>14</sub>H<sub>20</sub>O<sub>2</sub>Si requires  $M$  – Me, 233.0998).

(2RS,3SR,1'SR)-3-Methyl-2-(1-trimethylsilylethyl)propan-3-olide **52** (42%). As a mixture (85:15) of two diastereoisomers;  $\nu_{\max}$ (film)/ $\text{cm}^{-1}$  1820 (C=O), 1290 (C–O), 1240 and 830 (SiMe<sub>3</sub>);  $\delta$ ( $\text{CDCl}_3$ ) 4.70 (1 H, q, 6.2, HCO), 3.48 (1 H, dd,  $J$  6.2 and 12.5, HCC=O), 1.45 (3 H, d,  $J$  6.2, MeCHO), 1.25–1.15 (1 H, m, SiCH), 0.86 (3 H, d,  $J$  7.2, Me) and 0.06 (9 H, s, SiMe<sub>3</sub>);  $m/z$  186 (37%,  $M^+$ ), 171 (45, M – Me) and 73 (100, SiMe<sub>3</sub>) (Found:  $M^+$ , 186.1079. C<sub>9</sub>H<sub>18</sub>O<sub>2</sub>Si requires  $M$ , 186.1076). The minor diastereoisomer gave recognisable signals at  $\delta$  4.4, 3.2 (dd,  $J$  6 and 7.5), 1.5 (d,  $J$  6.1), 1.2, 1.0 (d,  $J$  7.3) and 0.0.

**Pyrolysis of the  $\beta$ -Lactones.**—Typically, the  $\beta$ -lactone (0.15 g, 0.48 mmol) in 2,4,6-collidine (4 cm<sup>3</sup>) was refluxed for 4–5 h under nitrogen. The solution was then diluted with ether (20 cm<sup>3</sup>), washed with aqueous hydrochloric acid (3  $\times$  10 cm<sup>3</sup>, 1 mol dm<sup>-3</sup>), saturated aqueous sodium hydrogen carbonate (10 cm<sup>3</sup>) and brine (10 cm<sup>3</sup>), dried (MgSO<sub>4</sub>) and evaporated under reduced pressure. The residue was chromatographed (hexane) to give the allylsilane. The following allylsilanes were prepared by this method.

(E)-1-Dimethyl(phenyl)silyl-1-phenylbut-2-ene **23** (93% from **21**). Identical (<sup>1</sup>H NMR) with the compound described above and in the preceding paper.<sup>1</sup>

(Z)-1-Dimethyl(phenyl)silyl-1-phenylbut-2-ene **19** (89% from **35**). Identical (<sup>1</sup>H NMR) with the sample described above.

(Z)-3-Dimethyl(phenyl)silyl-1-phenylbut-1-ene **39** (92%).  $R_f$ (hexane-EtOAc, 20:1) 0.6;  $\nu_{\max}$ (film)/ $\text{cm}^{-1}$  1640, 1605, 1495

and 1427 (Ph), 1247 (SiMe) and 1110 (SiPh);  $\delta$ ( $\text{CDCl}_3$ ) 7.50–7.15 (10 H, m, 2  $\times$  Ph), 6.33 (1 H, d,  $J$  11.6, PhCH=CH), 5.49 (1 H, t,  $J$  11.8, PhCH=CH), 2.57 (1 H, dq,  $J$  11.6 and 7.1, MeCH), 1.08 (3 H, d,  $J$  7, MeCH), 0.28 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.26 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>);  $m/z$  266 (10.9%,  $M^+$ ) and 135 (100, SiMe<sub>2</sub>Ph) (Found:  $M^+$ , 266.1498. C<sub>18</sub>H<sub>22</sub>Si requires  $M$ , 266.1491).

(Z)-5-Dimethyl(phenyl)silyl-2-methylhex-3-ene **40** (99%).  $R_f$ (hexane-EtOAc, 20:1) 0.5;  $\nu_{\max}$ (film)/ $\text{cm}^{-1}$  1245 (SiMe) and 1110 (SiPh);  $\delta$ ( $\text{CDCl}_3$ ) 7.52–7.31 (5 H, m, Ph), 5.20–4.90 (2 H, m, CH=CH), 2.44 (1 H, m, Me<sub>2</sub>CH), 2.05 (1 H, m, CHSi), 0.99 (3 H, d,  $J$  7.1, MeCHSi), 0.89 (3 H, d,  $J$  6.6, Me<sub>A</sub>Me<sub>B</sub>CH), 0.77 (3 H, d,  $J$  6.6, Me<sub>A</sub>Me<sub>B</sub>CH), 0.27 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.26 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>);  $m/z$  232 (11%,  $M^+$ ) and 135 (100, SiMe<sub>2</sub>Ph) (Found:  $M^+$ , 232.1652. C<sub>15</sub>H<sub>24</sub>Si requires  $M$ , 232.1647).

(Z)-4-Dimethyl(phenyl)silyl-5-methylhex-2-ene **41** (96%).  $R_f$ (hexane-EtOAc, 20:1) 0.57;  $\nu_{\max}$ (film)/ $\text{cm}^{-1}$  1250 (SiMe) and 1115 (SiPh);  $\delta$ ( $\text{CDCl}_3$ ) 7.60–7.20 (5 H, m, Ph), 5.48 (1 H, dq,  $J$  10.9 and 6.5, MeCH=CH), 5.33 (1 H, ddq,  $J$  11.5, 10.9 and 1.5, MeCH=CH), 1.99 (1 H, dd,  $J$  11.5 and 5.1, CHSi), 1.84 (1 H, d septet,  $J$  5.1 and 6.6, Me<sub>2</sub>CH), 1.43 (3 H, dd,  $J$  6.5 and 1.5, MeCH=CH), 0.82 (6 H, d,  $J$  6.6, Me<sub>2</sub>CH), 0.30 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.26 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>);  $m/z$  232 (1.8%,  $M^+$ ) and 135 (100, SiMe<sub>2</sub>Ph) (Found:  $M^+$ , 232.1652. C<sub>15</sub>H<sub>24</sub>Si requires  $M$ , 232.1647).

(Z)-1-Phenyl-1-trimethylsilylbut-2-ene<sup>30</sup> **53** (92%).  $R_f$ (hexane-EtOAc, 20:1) 0.6;  $\nu_{\max}$ (film)/ $\text{cm}^{-1}$  1615, 1600 and 1485 (Ph) and 1250 (SiMe);  $\delta$ ( $\text{CDCl}_3$ ) 7.26–7.06 (5 H, m, Ph), 5.86 (1 H, ddq,  $J$  11.5, 10.6 and 1.8, MeCH=CH), 5.51 (1 H, dq,  $J$  10.6 and 7, MeCH=CH), 3.28 (1 H, d,  $J$  11.5, PhCH), 1.63 (3 H, dd,  $J$  6.9 and 1.8, MeCH) and –0.05 (9 H, s, SiMe<sub>3</sub>);  $m/z$  204 (8.9%,  $M^+$ ), 131 (12, M – SiMe<sub>3</sub>) and 73 (100, SiMe<sub>3</sub>) (Found:  $M^+$ , 204.1329. C<sub>13</sub>H<sub>20</sub>Si requires  $M$ , 204.1334).

(Z)-4-Trimethylsilylpent-2-ene **54**.—The lactone (0.63 g, 3.4 mmol) was refluxed in collidine (9 cm<sup>3</sup>) under argon for 5 h with an efficient condenser. The mixture was diluted with ether (30 cm<sup>3</sup>) and washed with aqueous hydrochloric acid (3 mol dm<sup>-3</sup>, 5  $\times$  20 cm<sup>3</sup>), aqueous sodium hydrogen carbonate and brine until neutral. The organic layer was dried (MgSO<sub>4</sub>) and the solvent partially removed by fractional distillation. The residue was flash chromatographed (pentane) the solvent being fractionally distilled to give a mixture of the *Z*-allylsilane<sup>32</sup> and the *E*-allylsilane<sup>31</sup> (0.21 g, 44%) in a ratio of 82:18;  $\nu_{\max}$ ( $\text{CHCl}_3$ )/ $\text{cm}^{-1}$  1650 (C=C), 1250 and 845 (SiMe<sub>3</sub>);  $\delta$ ( $\text{CDCl}_3$ ) 5.4–5.1 (2 H, m, CH=CH), 1.87 (1 H, dq,  $J$  10.5 and 7.2, CHSi), 1.56 (3 H, dd,  $J$  6.4 and 1.3, MeCH=), 1.01 (3 H, d,  $J$  7.15, MeCHSi) and –0.05 (9 H, s, SiMe<sub>3</sub>).

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