

## Conjugate Addition of the Phenyl dimethylsilyl Group to $\alpha\beta$ -Unsaturated Carbonyl Compounds Using a Silylzincate in Place of the Silylcuprate

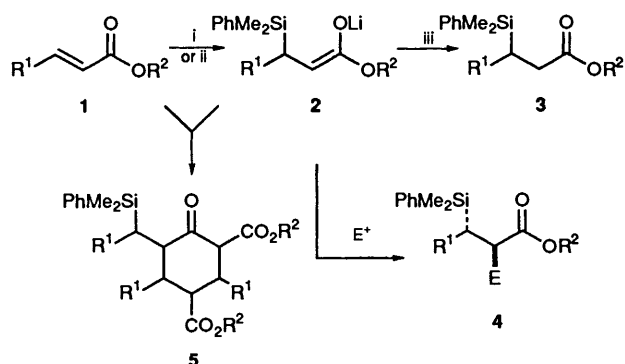
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Lithium phenyl dimethylsilyl(dialkyl)zincates add to a number of  $\alpha\beta$ -unsaturated carbonyl compounds to give, in most cases, higher yields of the conjugate addition product than we had achieved with the corresponding silylcuprate.

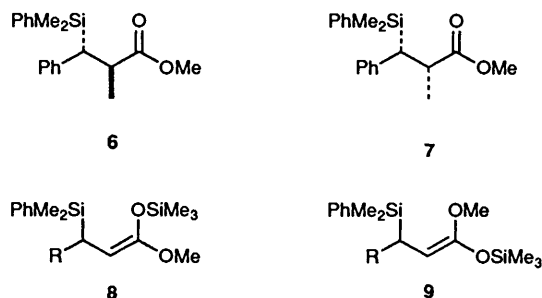
We have used the conjugate addition of lithium bis(phenyl dimethylsilyl)cuprate to  $\alpha\beta$ -unsaturated esters **1** in much of our work in recent years, notably to create enolates **2** that can be protonated to give  $\beta$ -silyl esters **3** (Scheme 1).<sup>1</sup> Alternatively,



**Scheme 1** Reagents: i,  $(\text{PhMe}_2\text{Si})_2\text{CuCN Li}_2$ ; ii,  $\text{PhMe}_2\text{SiZnR}_2 \text{ Li}$ ; iii,  $\text{NH}_4\text{Cl}$

the enolates can be alkylated,<sup>2</sup> or treated with aldehydes<sup>3</sup> to give 2-substituted 3-silyl esters **4** with high levels of stereocontrol. The products of these reactions have been used for the synthesis of allylsilanes,<sup>4</sup> in the total synthesis of natural products,<sup>5</sup> and in the synthesis of compounds used in exploratory mechanistic chemistry.<sup>6</sup> However, the yields of  $\beta$ -silyl esters **3** and **4** are not always high, largely, we believe, because the intermediate enolate **2** can react with one or more molecules of the  $\alpha\beta$ -unsaturated ester **1** to induce oligomerisation. We have occasionally found evidence for this pathway, isolating cyclic products derived from one silyl group and three molecules of ester of general structure **5**.<sup>7</sup> This problem is especially acute when the reaction is carried out on a larger scale, because the higher concentration of reagents makes oligomerisation a more favourable pathway.

We have now found that this problem can be overcome by using a silyl(dialkyl)zincate in place of the cuprate. The inspiration for this work came from Nozaki and his co-workers,<sup>8</sup> who used silylzincates in conjugate addition reactions with  $\alpha\beta$ -unsaturated ketones. Their yields were satisfactory with ketones, but much lower with methyl cinnamate, the only ester they tried. We now find that it is possible easily to get high yields with esters (and amides), and the yields of the  $\beta$ -silyl esters **3** are regularly higher, where comparisons are possible, than we obtained using our cuprate. There is no sign of oligomerisation, the reaction is essentially instantaneous at  $-78^\circ\text{C}$ , there are fewer operations at different temperatures, there is a convenient colour change from red to yellow when the zincate is consumed, and the work-up is easier because copper salts do not have to be removed. Furthermore, the reagent nominally uses only one silyl group compared to the two for the



silylcuprate reagent. Consequently the chromatography is easier because of the smaller proportion of silicon-containing by-products. Although we had developed a mixed cuprate to get over this problem,<sup>7</sup> it rarely gave yields as high as those from the bis-silylcuprate, so the zincate is even more of an improvement in this respect. However, we have not yet completely overcome this problem, because we find that the best overall yields with the zincate need 1.4 equivalents rather than the nominal 1 equivalent.

We prepared the zincate by adding dimethyl(phenyl)silyllithium to a solution of either dimethyl- or diethyl-zinc at  $0^\circ\text{C}$ , and used it at  $-78^\circ\text{C}$ . There appeared to be no significant difference between the dimethyl- and diethyl-zincates when they were compared with the same substrate—our choice of which to use subsequently was governed by the availability of the dialkylzinc reagents. Table 1 records our results with some representative esters. Significantly, allyl cinnamate gave conjugate addition with the zincate, whereas it only gave cinnamic acid with the cuprate.<sup>9</sup> In Table 2, we record our results with cinnamaldehyde, cinnamionitrile, *N,N*-diethylcinnamide, *N*-cinnamoylpyrrolidone and several  $\alpha\beta$ -unsaturated ketones. Only cinnamionitrile<sup>10</sup> and isophorone gave significantly lower yields than we obtained using the silylcuprate reagent. In addition we find that the zincate reacts, like the cuprate, with benzaldehyde to give the  $\alpha$ -silylbenzyl alcohol in 83% yield, and with allylic acetates to give allylsilanes, but it does not react with acetylenes. The reactions with allylic acetates are much slower than with  $\alpha\beta$ -unsaturated carbonyl compounds: with allyl acetate itself the reaction took 2 h at  $-78^\circ\text{C}$  and gave allyldimethyl(phenyl)silane in 88% yield (the cuprate gave 89%), and 1-vinylcyclohexyl acetate gave the allylsilane, 2-dimethyl(phenyl)silylethylidene cyclohexane, in 78% yield (the cuprate gave 93% yield).

The intermediate enolate derived from methyl cinnamate can be alkylated directly with methyl iodide to give the esters **6** and **7** in the same ratio (97:3) as in the corresponding silylcuprate reactions,<sup>2</sup> but in better overall yield (94% instead of 88%). Treating the silylzincate with methyl  $\alpha$ -methylcinnamate and protonating the intermediate enolate gave the same esters in a

**Table 1** Yields of conjugate addition products **3** of silylzincates to  $\alpha\beta$ -unsaturated esters **1**

Identifying letter for compound numbers	R <sup>1</sup>	R <sup>2</sup>	Dialkylzinc	Yield (%)	Yield with cuprate (%)	Reference for cuprate reaction
<b>a</b>	Ph	Me	Me <sub>2</sub> Zn Et <sub>2</sub> Zn	98 99	73	7
<b>b</b>	Ph	Bu <sup>t</sup>	Me <sub>2</sub> Zn	97		
<b>c</b>	Ph	allyl	Et <sub>2</sub> Zn	87	0 <sup>a</sup>	9
<b>d</b>	Me	Me	Et <sub>2</sub> Zn Me <sub>2</sub> Zn	98 93	95	3
<b>e</b>	Pr <sup>i</sup>	Me	Me <sub>2</sub> Zn	69	68	this work
<b>f</b>	-(CH <sub>2</sub> ) <sub>2</sub>		Et <sub>2</sub> Zn	84	very low	29

<sup>a</sup> The only product was cinnamic acid.

**Table 2** Yields of conjugate addition products of silylzincates with other electrophilic alkenes

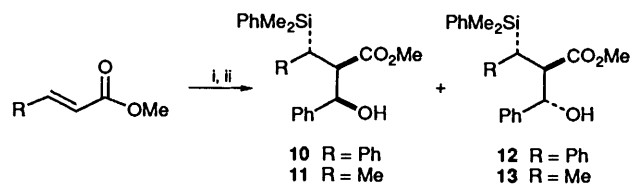
Substrate	Dialkylzinc	Yield (%)	Yield with cuprate (%)	Reference for cuprate reaction
<i>E</i> -PhCH=CHCHO	Me <sub>2</sub> Zn	59	71	1
<i>E</i> -PhCH=CHCN	Me <sub>2</sub> Zn	41	54	10
<i>E</i> -PhCH=CHCONEt <sub>2</sub>	Me <sub>2</sub> Zn	94	99	this work
<i>E</i> -PhCH=CHCON(CH <sub>2</sub> ) <sub>4</sub>	Me <sub>2</sub> Zn	91		
<i>E</i> -PhCH=CHCOMe	Me <sub>2</sub> Zn	92	65	24
<i>E</i> -PhCH=CHCOBu <sup>t</sup>	Me <sub>2</sub> Zn	91		
Cyclohexenone	Me <sub>2</sub> Zn	95	65	1
Isophorone	Me <sub>2</sub> Zn	31	68	1

**Table 3** Yields and diastereoselectivity in conjugate addition of silylzincates to the enone systems **14** and **17**

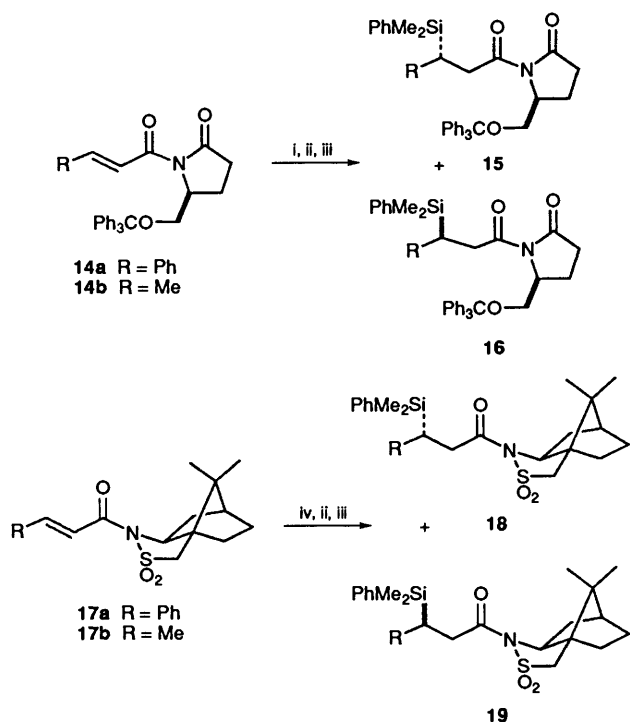
Substrate	Dialkylzinc	Lewis acid (equiv.)	Yield (%)	Ratio <b>15:16</b> or <b>18:19</b>	Yield with cuprate (%)	Ratio <b>15:16</b> or <b>18:19</b> with cuprate	Reference for cuprate reaction
<b>14a</b>	Et <sub>2</sub> Zn	MgBr <sub>2</sub> (6)	80	96:4	72	92:8	14, 20
<b>14a</b>	Me <sub>2</sub> Zn	—	94	75:25			
<b>14a</b>	Et <sub>2</sub> Zn	MgBr <sub>2</sub> (3)	97	92:8			
<b>14a</b>	Et <sub>2</sub> Zn	MgBr <sub>2</sub> (1)	84	83:17			
<b>14a</b>	Me <sub>2</sub> Zn	MgBr <sub>2</sub> (6)	89	93:7			
<b>14b</b>	Et <sub>2</sub> Zn	MgBr <sub>2</sub> (6)	84	76:24	93	89:11	14, 20
<b>17a</b>	Me <sub>2</sub> Zn	EtAlCl <sub>2</sub> (3)	96	86:14	88	90:10	15
<b>17a</b>	Et <sub>2</sub> Zn	EtAlCl <sub>2</sub> (3)	91	84:16			
<b>17a</b>	Me <sub>2</sub> Zn	—	86	55:45			
<b>17b</b>	Et <sub>2</sub> Zn	EtAlCl <sub>2</sub> (3)	85	57:43	89	57:43	15

ratio of 10:90, which is slightly more selective and again in better yield (98%) than the corresponding reaction with the silylcuprate (15:85 and 84%).

We examined briefly the stereochemistry of the enolates produced in the conjugate additions. Although the silylcuprate gives only the *E*-isomers **2**,<sup>3</sup> and hence the *Z*-silyl enol ethers **8** (we are using strict CIP nomenclature here), the silylzincate is less well behaved, giving mixtures of enolate isomers, and hence mixtures of silyl enol ethers **8** and **9**: 50:50 from methyl cinnamate (R=Ph) and 22:78 from methyl crotonate (R=Me). In consequence, the aldol reactions of the enolate mixtures produced by silyl-zincation are less stereoselective than, and reversed in sense from, the aldol reactions of the enolates produced by silyl-cupration. Thus, conjugate addition to methyl cinnamate and trapping with benzaldehyde gave the aldols **10** and **12** (Scheme 2) in a ratio of 81:19, whereas the corresponding reaction with the cuprate gave 9:91. Similarly, conjugate addition to methyl crotonate and trapping with benzaldehyde gave the aldols **11** and **13** in a ratio of 87:13, whereas the corresponding reaction with the cuprate gave 6:94. It appears that the enolates derived from silyl-zincation, although highly stereoselective, are not stereospecific in their aldol reactions, which poses a problem in making the aldols of

**Scheme 2** Reagents: i, PhMe<sub>2</sub>SiZnEt<sub>2</sub> Li; ii, PhCHO

relative stereochemistry **12** and **13**. These are available by silyl-cupration and trapping the *E*-enolate **2** with aldehydes, but the yields are not as good, because of the problems in silyl-cupration discussed above. One solution to this problem might be to make the esters **3** using silyl-zincation to get a high yield, and then to generate the enolate from them with LDA in the presence of HMPA, which Ireland has shown gives lithium *E*-enolates.<sup>11</sup> When we tried this idea briefly, we obtained inconsistent results. In the cinnamate series, the enolate of the ester **3a** prepared using LDA and HMPA, gave mainly (95:5) the aldol product **12** on treatment with benzaldehyde, as expected from the *E*-enolate. This result is nicely in contrast to our earlier result,<sup>3</sup> in which the lithium *Z*-enolate derived from



**Scheme 3** Reagents: i, MgBr<sub>2</sub>; ii, PhMe<sub>2</sub>SiZnEt<sub>2</sub> Li or (PhMe<sub>2</sub>Si)<sub>2</sub>-CuCN Li<sub>2</sub>; iii, NH<sub>4</sub>Cl, H<sub>2</sub>O; iv, EtAlCl<sub>2</sub>

the same ester **3a** gave largely the aldol product **10**. In the hope that DMPU might work as well as HMPA, we repeated the reaction using this co-solvent, but obtained more (69:31) of the aldol product **10** than of its diastereoisomer. In the crotonate series, the enolate derived from **3d** using Ireland's more recently developed<sup>12</sup> conditions gave disappointingly low selectivity (59:41) in favour of the aldol product **13**, and repeating the reaction, but using DMPU in place of HMPA, gave largely (82:18) the aldol product **11**, that we associate with the *Z*-enolate. It appears that this route to aldol products with the relative stereochemistry of **12** and **13** is only occasionally going to work, although we have been able to use it in synthesis on one occasion, when it worked admirably.<sup>13</sup>

Finally, we examined how well the zincates worked when the cinnamoyl and crotonoyl groups were attached to the homochiral auxiliaries that we<sup>14</sup> and Oppolzer<sup>15</sup> have already found work well with the silylcuprate reagent (Scheme 3). Table 3 records our results with the cinnamoyl and crotonoyl derivatives of Koga's chiral auxiliary **14** and Oppolzer's chiral auxiliary **17**. In every case, the major diastereoisomers **15** and **18**, respectively, were the same as we and Oppolzer obtained using the silylcuprate reagent. In some of the reactions the zincate was more stereoselective than the cuprate, but, since these substrates are less apt to give oligomerisation, it did not always give a higher yield than the cuprate. With both chiral auxiliaries, it is still necessary to add a Lewis acid, magnesium bromide with Koga's and ethylaluminium dichloride with Oppolzer's. Without the Lewis acid, the diastereoselectivity was low—evidently the presence of zinc did not suffice to chelate the imide and sultam oxygen atoms. Our conclusion for these substrates is that the zincate is always worth trying as well as the cuprate, because there is no systematic way of telling which will be better, either in yield or in stereoselectivity.

## Experimental

The following starting materials were prepared by the methods cited: allyl 3-phenylpropanoate **1c**,<sup>16</sup> (*E*)-3-methyl 4-methyl-

pent-2-enoate **1e**<sup>17</sup> prepared (84%) by the method of Wadsworth and Emmons,<sup>18</sup> 4,4-dimethyl-1-phenylpent-1-en-3-one,<sup>19</sup> (5*S*)-1-[(*E*)-3'-phenylpropenoyl]-5-triphenylmethoxymethylpyrrolidin-2-one **14a**,<sup>20</sup> (5*S*)-1-[(*E*)-but-2-enoyl]-5-triphenylmethoxymethylpyrrolidin-2-one **14b**,<sup>20</sup> [(*E*)-phenylpropenoyl]-(*7R*)-10,10-dimethyl-5-thia-4-azatricyclo[5.2.10]-decane-5,5-dioxide **17a**,<sup>15</sup> by the method of Oppolzer,<sup>21</sup> (*7R*)-[(*E*)-But-2-enoyl]-10,10-dimethyl-5-thia-4-azatricyclo[5.2.10]-decane-5,5-dioxide **17b**,<sup>21</sup> and *tert*-butyl cinnamate **1b**.<sup>22</sup>

*N*-[(*E*)-3'-Phenylpropenoyl]pyrrolidinone.—Butyllithium (1.4 mol dm<sup>-3</sup> solution in hexane; 4 cm<sup>3</sup>, 5.6 mmol), was injected into a stirred solution of pyrrolidinone (0.29 g, 4.0 mmol) in THF (10 cm<sup>3</sup>) at -78 °C under argon, and the resulting red solution stirred at this temperature for 45 min. A solution of cinnamoyl chloride (0.66 g, 4 mmol) in THF (10 cm<sup>3</sup>) was added by cannula and the mixture stirred for 1 h, and then allowed to warm to room temperature. The mixture was quenched with aqueous ammonium chloride (20 cm<sup>3</sup>) and extracted with dichloromethane (2 × 30 cm<sup>3</sup>) and the organic layers were combined and evaporated under reduced pressure. The residue was chromatographed (EtOAc-hexane, 1:1) to give the *imide* (0.61 g, 71%) as an oil; *R*<sub>f</sub>(EtOAc-hexane, 1:1) 0.30; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 1734 (C=O), 1668 (C=O), 1614 (C=C) and 1580 (Ph); *δ*<sub>H</sub>(250 MHz; CDCl<sub>3</sub>) 7.93 (1 H, d, *J* 16, PhCH), 7.82 (1 H, d, *J* 16, CHCO), 7.7–7.3 (5 H, m, Ph), 3.91 (2 H, t, *J* 8, CH<sub>2</sub>CO), 2.64 (2 H, t, *J* 8, CH<sub>2</sub>N) and 2.06 (2 H, qn, *J* 8, CH<sub>2</sub>CH<sub>2</sub>CO); *m/z* 215 (78%, M<sup>+</sup>), 131 (100, M - C<sub>4</sub>H<sub>6</sub>NO), 103 (88, M - C<sub>4</sub>H<sub>6</sub>NO - CO), 84 (10, C<sub>4</sub>H<sub>6</sub>NO) and 77 (60, Ph) (Found: M<sup>+</sup>, 215.0946. C<sub>13</sub>H<sub>13</sub>NO<sub>2</sub> requires *M*, 215.0946) (Found: C, 72.35; H, 6.05; N, 6.2. C<sub>13</sub>H<sub>13</sub>NO<sub>2</sub> requires C, 72.5; H, 6.05; N, 6.5).

*General Procedure for the Silyl-zincation of Substrates.*—Typically, dimethyl(phenyl)silyllithium<sup>23</sup> (0.7 mol dm<sup>-3</sup> solution in THF; 2.3 cm<sup>3</sup>, 1.6 mmol) was added to a stirred solution of either dimethylzinc (2 mol dm<sup>-3</sup> solution in toluene; 0.80 cm<sup>3</sup>, 1.6 mmol) or diethylzinc (1 mol dm<sup>-3</sup> solution in THF; 1.6 cm<sup>3</sup>, 1.6 mmol) in THF (6 cm<sup>3</sup>) at 0 °C under argon. The wine-red solution was stirred at this temperature for 5 min and then brought to -78 °C. The substrate (1.14 mmol) in THF (2 cm<sup>3</sup>) was injected over 1 min. Reaction was instantaneous in all but a few cases, and was accompanied by a paling of the red colour to a light brown. The reaction was quenched with saturated aqueous ammonium chloride (10 cm<sup>3</sup>) (when dimethylzinc was used, the ammonium chloride was added cautiously at first because of violent effervescence). Dilute hydrochloric acid (2 cm<sup>3</sup>) was added to dissolve the zinc salts, and the aqueous layer extracted with ether (2 × 15 cm<sup>3</sup>). The organic layers were combined, washed with brine, dried (MgSO<sub>4</sub>) and evaporated under reduced pressure. The residue was chromatographed (EtOAc-hexane) to give the silylated products. The following compounds were prepared by this method.

Methyl 3-dimethyl(phenyl)silyl-3-phenylpropanoate **7a** (99% using Et<sub>2</sub>Zn, 98% using Me<sub>2</sub>Zn).

*tert*-Butyl 3-dimethyl(phenyl)silyl-3-phenylpropanoate **3b** (97%); *R*<sub>f</sub>(EtOAc-hexane, 1:10) 0.28; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 1726 (C=O), 1602 (Ph), 1252 (SiMe) and 1105 (SiPh); *δ*<sub>H</sub>(250 MHz; CDCl<sub>3</sub>) 7.55–6.85 (10 H, m, 2 × Ph), 2.75–2.35 (3 H, m, SiCH and CH<sub>2</sub>CO), 1.16 (9 H, s, Bu<sup>t</sup>), 0.22 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>) and 0.18 (3 H, s, SiMe<sub>A</sub>Me<sub>B</sub>); *m/z* 358 (10%, M + NH<sub>4</sub><sup>+</sup>), 269 (23, M - Me - C<sub>4</sub>H<sub>8</sub>), 205 (22, M - PhMe<sub>2</sub>Si) and 135 (100, PhMe<sub>2</sub>Si).

Allyl 3-dimethyl(phenyl)silyl-3-phenylpropanoate **3c** (87%); *R*<sub>f</sub>(EtOAc-hexane, 1:10) 0.36; *v*<sub>max</sub>(film)/cm<sup>-1</sup> 1730 (C=O), 1640 (C=C), 1590 (Ph), 1250 (SiMe) and 1110 (SiPh); *δ*<sub>H</sub>(250 MHz; CDCl<sub>3</sub>) 7.5–6.9 (10 H, m, 2 × Ph), 5.70 (1 H, ddt, *J* 17.5,

10 and 6, OCH<sub>2</sub>CH<sub>2</sub>, 5.17–5.03 (2 H, m, CH<sub>A</sub>H<sub>B</sub>CH<sub>C</sub> and CH<sub>A</sub>H<sub>B</sub>CH<sub>C</sub>), 4.40–4.32 (2 H, m, CH<sub>2</sub>O), 2.91–2.62 (3 H, m, SiCH and CH<sub>2</sub>CO), 0.26 (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* 324 (37%, M<sup>+</sup>), 309 (32, M – Me), 247 (41, M – Ph), 267 (43, M – C<sub>3</sub>H<sub>5</sub>O), 239 (62, M – C<sub>3</sub>H<sub>5</sub>O-CO) and 135 (87, PhMe<sub>2</sub>Si) (Found: M<sup>+</sup>, 324.1527. C<sub>20</sub>H<sub>24</sub>O<sub>2</sub>Si requires *M*, 324.1546).

Methyl 3-dimethyl(phenyl)silylbutanoate<sup>3</sup> **3d** (98% using diethylzinc, 93% using dimethylzinc).

Methyl (3RS)-3-dimethyl(phenyl)silyl-4-methylpentanoate **3e** (69%); *R<sub>f</sub>*(hexane–CH<sub>2</sub>Cl<sub>2</sub>, 1:1) 0.38; *v*<sub>max</sub>(film)/cm<sup>–1</sup> 1740 (C=O), 1250 (SiMe) and 1110 (SiPh); *δ*<sub>H</sub>(250 MHz; CDCl<sub>3</sub>) 7.53–7.27 (5 H, m, Ph), 3.55 (3 H, s, OMe), 2.36 (1 H, d, *J* 8.0, CH<sub>A</sub>H<sub>B</sub>CO), 2.35 (1 H, d, *J* 8.0, CH<sub>A</sub>H<sub>B</sub>CO), 1.93–1.87 (1 H, m, CHMe<sub>2</sub>), 1.54–1.47 (1 H, m, SiCH), 0.90 (3 H, d, *J* 6.9, CHMe<sub>A</sub>Me<sub>B</sub>), 0.83 (3 H, d, *J* 6.9, CHMe<sub>A</sub>Me<sub>B</sub>) and 0.32 (6 H, s, SiMe<sub>2</sub>); *m/z* 264 (4%, M<sup>+</sup>), 249 (66, M – Me), 221 (73, M – COMe) and 135 (100, PhMe<sub>2</sub>Si) (Found: M<sup>+</sup>, 264.1524. C<sub>15</sub>H<sub>24</sub>O<sub>2</sub>Si requires *M*, 264.1546).

3-Dimethyl(phenyl)silyl-*δ*-valerolactone **3f** (84%); *R<sub>f</sub>*(EtOAc–hexane, 1:2) 0.28; *v*<sub>max</sub>(film)/cm<sup>–1</sup> 1730 (C=O), 1250 (SiMe) and 1110 (SiPh); *δ*<sub>H</sub>(250 MHz; CDCl<sub>3</sub>) 7.5–7.3 (5 H, m, Ph), 4.33 (1 H, ddd, *J* 4.3, 5 and 11.1, CH<sub>A</sub>H<sub>B</sub>O), 4.23 (1 H, ddd, *J* 4.2, 9.6 and 11.2, CH<sub>A</sub>H<sub>B</sub>O), 2.56 (1 H, ddd, *J* 1.5, 5.7 and 17.4, CHSi), 2.26 (1 H, dd, *J* 12.6 and 17.4, CH<sub>A</sub>H<sub>B</sub>CO), 1.9–1.3 (3 H, m, CH<sub>A</sub>H<sub>B</sub>CO and CH<sub>2</sub>CH<sub>2</sub>O) and 0.32 (6 H, s, SiMe<sub>2</sub>); *m/z* 234 (17%, M<sup>+</sup>), 219 (1, M – Me) and 135 (100, PhMe<sub>2</sub>Si) (Found: M<sup>+</sup>, 234.1073. C<sub>13</sub>H<sub>18</sub>O<sub>2</sub>Si requires *M*, 234.1076).

3-Dimethyl(phenyl)silyl-3-phenylpropanal<sup>1</sup> (59%).

3-Dimethyl(phenyl)silyl-3-phenyl-2-propionitrile (41%); *R<sub>f</sub>*(EtOAc–hexane, 1:10) 0.28; *v*<sub>max</sub>(film)/cm<sup>–1</sup> 2248 (CN), 1602 (Ph), 1256 (SiMe) and 1112 (SiPh); *δ*<sub>H</sub>(250 MHz; CDCl<sub>3</sub>) 7.45–6.85 (10 H, m, 2 × Ph), 2.75–2.45 (3 H, m, SiCH and CH<sub>2</sub>CN) and 0.26 (6 H, s, SiMe<sub>2</sub>); *m/z* 265 (30%, M<sup>+</sup>), 250 (2, M – Me) and 135 (100, PhMe<sub>2</sub>Si) (Found: M<sup>+</sup>, 265.1290. C<sub>17</sub>H<sub>19</sub>NSi requires *M*, 265.1287).

*N,N*-Diethyl-3-dimethyl(phenyl)silyl-3-phenylpropionamide (94%); *R<sub>f</sub>*(EtOAc–light petroleum, 1:2) 0.28; *v*<sub>max</sub>(film)/cm<sup>–1</sup> 1693 (C=O), 1256 (SiMe) and 1112 (SiPh); *δ*<sub>H</sub>(250 MHz; CDCl<sub>3</sub>) 7.6–6.85 (10 H, m, 2 × Ph), 3.29–3.08 (4 H, m, CH<sub>2</sub>NCH<sub>2</sub>), 3.01 (1 H, dd, *J* 5 and 9.6, CHSi), 2.75 (1 H, dd, *J* 9.6 and 15.6, CH<sub>A</sub>CH<sub>B</sub>CO), 2.54 (1 H, dd, *J* 5 and 15.6, CH<sub>A</sub>CH<sub>B</sub>CO), 1.02 (3 H, t, *J* 7.1, CH<sub>2</sub>Me), 0.92 (3 H, t, *J* 7.1, CH<sub>2</sub>Me), 0.23 (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* 339 (75%, M<sup>+</sup>), 324 (10, M – Me), 310 (14, M – Et), 262 (5, M – Ph) and 135 (100, PhMe<sub>2</sub>Si) (Found: M<sup>+</sup>, 339.2032. C<sub>21</sub>H<sub>29</sub>NOSi requires *M*, 339.2018).

*N*-[3-Dimethyl(phenyl)silyl-3-phenylpropanoyl]pyrrolidine (91%); *R<sub>f</sub>*(EtOAc–hexane, 2:3) 0.34; *v*<sub>max</sub>(film)/cm<sup>–1</sup> 1740 (C=O), 1700 (C=O), 1610 (Ph), 1260 (SiMe) and 1120 (SiPh); *δ*<sub>H</sub>(250 MHz; CDCl<sub>3</sub>) 7.5–6.9 (10 H, m, 2 × Ph), 3.7–3.4 (3 H, m, SiCH and CH<sub>2</sub>N), 3.15 (1 H, dd, *J* 18 and 5, CHCH<sub>A</sub>CH<sub>B</sub>), 3.0 (1 H, dd, *J* 18 and 5, CHCH<sub>A</sub>CH<sub>B</sub>), 2.5 (2 H, t, *J* 8, CH<sub>2</sub>CO), 1.9 (2 H, quintet, *J* 7, CH<sub>2</sub>CH<sub>2</sub>CO), 0.28 (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* 351 (2%, M<sup>+</sup>), 274 (15, M – Ph), 267 (2, M – C<sub>4</sub>H<sub>9</sub>NO) and 216 (100, M – PhMe<sub>2</sub>Si) (Found: M<sup>+</sup>, 351.1639. C<sub>21</sub>H<sub>25</sub>NO<sub>2</sub>Si requires *M*, 351.1654).

4-Dimethyl(phenyl)silyl-4-phenylbutan-2-one<sup>24</sup> (92%).

1-Dimethyl(phenyl)silyl-4,4-dimethyl-1-phenylpentan-3-one (91%); *R<sub>f</sub>*(EtOAc–hexane, 1:10) 0.41; *v*<sub>max</sub>(film)/cm<sup>–1</sup> 1695 (C=O), 1245 (SiMe) and 1110 (SiPh); *δ*<sub>H</sub>(250 MHz; CDCl<sub>3</sub>) 7.5–6.8 (10 H, m, 2 × Ph), 3.07 (1 H, dd, *J* 4 and 7, CH<sub>A</sub>CH<sub>B</sub>CO), 2.96 (1 H, dd, *J* 1.2 and 4, CH<sub>A</sub>CH<sub>B</sub>CO), 2.62 (1 H, dd, *J* 1.2 and 7, CHSi), 0.97 (9 H, s, Bu<sup>t</sup>), 0.23 (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* 324 (7%, M<sup>+</sup>), 309 (10, M – Me), 267 (100, M – C<sub>4</sub>H<sub>9</sub>), 189 (58, M – PhMe<sub>2</sub>Si) and 135 (100, PhMe<sub>2</sub>Si) (Found: M<sup>+</sup>, 324.1902. C<sub>21</sub>H<sub>28</sub>O<sub>2</sub>Si requires *M*, 324.1909).

3-Dimethyl(phenyl)silylcyclohexanone<sup>1</sup> (95%).

3-Dimethyl(phenyl)silyl-3,5,5-trimethylcyclohexanone (31%) as prisms, m.p. 59–60 °C (lit.,<sup>1</sup> 60 °C).

1-Dimethyl(phenyl)silyl-1-phenylmethanol<sup>25</sup> (83%).

(2-Cyclohexylideneethyl)dimethyl(phenyl)silane from 1-vinylcyclohexyl acetate.<sup>26</sup> Reaction was slow at –78 °C but complete in 30 min at room temperature. Work-up gave the allylsilane<sup>27</sup> (78%).

Allyl(dimethyl)(phenyl)silane from allyl acetate. Reaction was slow. After 2 h at –78 °C, the reaction was quenched. Work-up gave the allylsilane<sup>28</sup> (88%). A similar reaction using the silylcuprate gave the same compound (89%).

Methyl(2RS,3RS)-3-dimethyl(phenyl)silyl-2-methyl-3-phenylpropanoate<sup>2,4</sup> **6** from methyl cinnamate (0.232 g, 1.43 mmol), but methyl iodide (0.86 cm<sup>3</sup>, 14.3 mmol) was added before the aqueous quench and the mixture stirred for 3 h at –78 °C to give the diastereoisomeric esters in a ratio (6:7) of 97:3 (0.421 g, 94%).

Methyl(2RS,3SR)-3-dimethyl(phenyl)silyl-2-methyl-3-phenylpropanoate<sup>2,4</sup> **7** from methyl *α*-methylcinnamate (0.252 g, 1.43 mmol) as a mixture in a ratio (6:7) of 10:90 (0.439 g, 98%).

(*Z*)- and (*E*)-Dimethyl(phenyl)silyl-1-methoxy-3-phenyl-1-trimethylsilyloxypropene **8** and **9** (R = Ph).—The silylzincate (1.4 mmol) was prepared from diethylzinc as before. Methyl cinnamate (0.162 g, 1.0 mmol) in THF (1 cm<sup>3</sup>) was slowly injected at –78 °C followed by chlorotrimethylsilane (0.31 cm<sup>3</sup>, 2.5 mmol). The solution was brought to room temperature and stirred at this temperature for 1.5 h. Pentane (15 cm<sup>3</sup>) was added, the solution filtered through Celite and evaporated under reduced pressure. More pentane (15 cm<sup>3</sup>) was added and again the solution was filtered through Celite and evaporated under reduced pressure to give the mixture of silyl enol ethers.<sup>2</sup> The ratio of isomers (50:50) was measured from the methoxy singlets at *δ* 3.60 and 3.55 in the <sup>1</sup>H NMR spectrum.

(*Z*)- and (*E*)-Dimethyl(phenyl)silyl-1-methoxy-1-trimethylsilyloxybutene **8** and **9** (R = Me). Similarly the silylzincate and methyl crotonate gave the mixture of silyl enol ethers.<sup>3</sup> The ratio of isomers (22:78) was measured from the methoxy singlets at *δ* 3.49 and 3.40 in the <sup>1</sup>H NMR spectrum.

Methyl (2RS,3RS)-3-Dimethyl(phenyl)silyl-2-[(RS)-1-hydroxybenzyl]-3-phenylpropanoate **10** and Methyl (2RS,3RS)-3-Dimethyl(phenyl)silyl-2-[(SR)-1-hydroxybenzyl]-3-phenylpropanoate **12**.—*Method A*. The silylzincate (1.0 mmol) was prepared from diethylzinc as before. Methyl cinnamate (0.116 g, 0.72 mmol) in THF (1 cm<sup>3</sup>) was slowly injected at –78 °C followed by benzaldehyde (0.15 g, 1.43 mmol) in THF (1.5 cm<sup>3</sup>) and the solution stirred for 4 h at –78 °C before quenching with aqueous ammonium chloride, followed by work up and chromatography (EtOAc–hexane, 1:4) as usual. The esters **3** **10** and **12** (0.280 g, 97%) were present in a ratio of 81:19, as determined by integration (<sup>1</sup>H NMR) of the methoxy singlets at *δ* 3.22 and 3.04, respectively.

*Method B*. The same aldol products were prepared from the ester **3a**. Butyllithium (1.6 mol dm<sup>–3</sup> solution in hexane; 0.52 cm<sup>3</sup>, 0.8 mmol) was added at –78 °C to diisopropylamine (0.10 cm<sup>3</sup>, 0.68 mmol) in THF (10 cm<sup>3</sup>) and the mixture stirred at 0 °C for 40 min. The solution was cooled to –78 °C, HMPA (1.20 cm<sup>3</sup>, 7.2 mmol) was injected, followed by the ester **3a** (0.130 g, 0.44 mmol) in THF (2 cm<sup>3</sup>) dropwise. The solution was stirred for 1.5 h, benzaldehyde (0.060 g, 0.56 mmol) in THF (2 cm<sup>3</sup>) was injected and the solution stirred for 3 h. The mixture was quenched at –78 °C with aqueous ammonium chloride, worked up and chromatographed (EtOAc–hexane, 1:4) as usual to give a mixture of the esters **10** and **12** (0.106 g, 60%), in a ratio of 5:95. A similar sequence on half the scale, but using DMPU (0.44 cm<sup>3</sup>) in place of HMPA, gave the esters **10** and **12** (0.038 g, 43%), in a ratio of 69:31.

*Methyl (2RS,3SR)-3-Dimethyl(phenyl)silyl-2-[(RS)-1-hydroxybenzyl]butanoate 11 and Methyl (2RS,3SR)-3-Dimethyl(phenyl)silyl-2-[(SR)-1-hydroxybenzyl]butanoate 13.*—Method A. In a similar sequence to that described above, silyl-zincation of methyl crotonate (0.072 g, 0.72 mmol) quenching with benzaldehyde (0.097 g, 0.92 mmol) gave the esters **11** and **13** (0.232 g, 95%) in a ratio of 87:13, as determined by integration (<sup>1</sup>H NMR) of the methoxy singlets at  $\delta$  3.33 and 3.15, respectively.

*Method B.* Sodium bis(trimethylsilyl)amide (1.0 mol dm<sup>-3</sup> solution in THF; 1.9 cm<sup>3</sup>, 1.9 mmol) was added to a solution of lithium chloride (0.32 g, 7.5 mmol) in THF (12 cm<sup>3</sup>) at -78 °C, followed by freshly distilled HMPA (3.5 cm<sup>3</sup>, distilled from CaH<sub>2</sub>). After 5 min, ester **3d** (0.254 g, 0.93 mmol) in THF (2 cm<sup>3</sup>) was added dropwise over 2 min. The solution was stirred for 0.5 h and freshly distilled benzaldehyde (0.12 g, 1.1 mmol, distilled from CaCl<sub>2</sub>) in THF (1 cm<sup>3</sup>) was injected. The solution was stirred for 2 h at -78 °C and then brought to 0 °C. The mixture was quenched with aqueous ammonium chloride, worked up and chromatographed (EtOAc–light petroleum, 1:10) in the usual way to give recovered starting ester (0.056 g) and a mixture of the esters **11** and **13** (0.266 g, 78%, 96% based on ester consumed) in a ratio of 41:59. A similar sequence to that described above in the cinnamate series, but using DMPU in place of HMPA, gave the esters **11** and **13** (65%) in a ratio of 82:18.

(5S)-1-[(3'R and 3'S)-3'-Dimethyl(phenyl)silyl-3'-phenylpropionyl]-5-triphenylmethoxymethylpyrrolidin-2-ones **15a** and **16a**, and (5S)-1-[(3'S and 3'R)-3'-Dimethyl(phenyl)silylbutanoyl]-5-triphenylmethoxymethylpyrrolidin-2-ones **15b** and **16b**.—Typically, a pre-mixed solution of the imide **14** (0.12 mmol) and magnesium bromide (0.13 g, 0.71 mmol) in dry THF (4 cm<sup>3</sup>) was added dropwise over 10 min to a prepared solution of the silylzincate (0.20 mmol) in THF (4 cm<sup>3</sup>) at -78 °C under an argon atmosphere. Reaction was instantaneous. The mixture was worked up in the usual way to give a mixture of the pyrrolidones **15** and **16**. The ratio **15a**:**16a** of 96:4 was determined by integration (<sup>1</sup>H NMR) of the SiMe singlets at  $\delta$  0.39 and 0.27 (from **15a**) and 0.28 and 0.26 (from **16a**), respectively, and the ratio **15b**:**16b** of 76:24 was determined by integration (<sup>1</sup>H NMR) of the MeCH doublets at  $\delta$  0.94 (from **15b**) and 1.02 (from **16b**), respectively. The other data in Table 3 were acquired similarly.

(7R)-N-[(3'R)-3'-Dimethyl(phenyl)silyl-3'-phenylpropanoyl]-10,10-dimethyl-5-thia-4-azatricyclo[5.2.10]decane-5,5-dioxides **18a** and **19a**, and (7R)-N-[(3'S and 3'R)-3'-Dimethyl(phenyl)silylbutanoyl]-10,10-dimethyl-5-thia-4-azatricyclo[5.2.10]decane-5,5-dioxides **18b** and **19b**.—Typically, a pre-mixed solution of the sultam **17** (0.12 mmol) and ethylaluminium dichloride (1 mol dm<sup>-3</sup> hexane solution; 0.36 cm<sup>3</sup>, 0.36 mmol) in dry THF (4 cm<sup>3</sup>) was added dropwise over 10 min to a prepared solution of the silylzincate (0.20 mmol) in THF (4 cm<sup>3</sup>) at -78 °C under an argon atmosphere. Reaction was instantaneous. The mixture was worked up in the usual way to give a mixture of the sultams **18** and **19**. The sultams **18a** and **19a** are known,<sup>15</sup> but spectroscopic data were not reported. The sultams **18a** and **19a** have:  $R_f$ (EtOAc–hexane, 1:3) 0.38 (major) and 0.43 (minor);  $\nu_{\max}$ (CDCl<sub>3</sub>)/cm<sup>-1</sup> 1680 (C=O), 1600 (Ph), 1330 (SO<sub>2</sub>) and 1170 (SO<sub>2</sub>-N);  $\delta_H$ (250 MHz; CDCl<sub>3</sub>) 3'R-isomer: 7.5–6.8 (10 H, m, 2 × Ph), 3.72 (1 H, dd, *J* 4.5 and 7.5, CHN), 3.47 (1 H, d, *J* 14, CH<sub>A</sub>CH<sub>B</sub>S), 3.37 (1 H, d, *J* 14, CH<sub>A</sub>CH<sub>B</sub>S), 3.24 (1 H, dd, *J* 5 and 17.5, CH<sub>A</sub>CH<sub>B</sub>CO), 3.02 (1 H, dd, *J* 11.5 and 17.5, CH<sub>A</sub>CH<sub>B</sub>CO), 2.0–1.2 (8 H, m, CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub> and CHSi), 1.09 (3 H, s, CMe<sub>A</sub>Me<sub>B</sub>), 0.92 (3 H, s, CMe<sub>A</sub>Me<sub>B</sub>) and 0.28 (3 H, s, SiMe<sub>2</sub>); with the 3'S-isomer showing distinctive signals at: 3.43 (1 H, d, *J* 14, CH<sub>A</sub>CH<sub>B</sub>S), 3.35 (1 H, d, *J* 14, CH<sub>A</sub>CH<sub>B</sub>S), 2.96 (1 H, dd, *J* 11 and 15.6, CH<sub>A</sub>CH<sub>B</sub>CO), 2.74 (1 H, dd, *J* 4

and 15.7, CH<sub>A</sub>CH<sub>B</sub>CO), 0.88 (3 H, s, CMe<sub>A</sub>Me<sub>B</sub>), 0.85 (3 H, s, CMe<sub>A</sub>Me<sub>B</sub>) and 0.22 (3 H, s, SiMe<sub>2</sub>). The sultams **18b** and **19b** are new:  $R_f$ (EtOAc–hexane, 1:3) 0.35 (for both isomers;  $\nu_{\max}$ (CDCl<sub>3</sub>)/cm<sup>-1</sup> 1680 (C=O), 1330 (SO<sub>2</sub>), 1245 (SiMe), 1160 (SO<sub>2</sub>-N) and 1110 (SiPh);  $\delta_H$ (250 MHz; CDCl<sub>3</sub>) 3'S-isomer: 7.55–7.30 (5 H, m, Ph), 3.89–3.82 (1 H, m, CHN), 3.47 (1 H, d, *J* 13.8, CH<sub>A</sub>CH<sub>B</sub>S), 3.42 (1 H, d, *J* 14, CH<sub>A</sub>CH<sub>B</sub>S), 2.87 (1 H, dd, *J* 4.3 and 15.9, CH<sub>A</sub>CH<sub>B</sub>CO), 2.49 (1 H, dd, *J* 10.5 and 15.9, CH<sub>A</sub>CH<sub>B</sub>CO), 2.13–1.27 (7 H, m, CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>), 1.72–1.58 (1 H, m, CHSi), 1.14 (3 H, s, CMe<sub>A</sub>Me<sub>B</sub>) and 0.30 (6 H, s, SiMe<sub>2</sub>); distinctive signals of the 3'R isomer: 3.49 (1 H, d, *J* 13.8, CH<sub>A</sub>CH<sub>B</sub>S), 2.71 (1 H, dd, *J* 4.7 and 15.9, CH<sub>A</sub>CH<sub>B</sub>CO), 2.65 (1 H, dd, *J* 10 and 15.9, CH<sub>A</sub>CH<sub>B</sub>CO), 1.16 (3 H, s, CMe<sub>A</sub>Me<sub>B</sub>); *m/z* 419 (13%, M<sup>+</sup>), 404 (19, M – Me), 355 (7, M – SO<sub>2</sub>), 342 (10, M – Ph), 284 (3, M – PhMe<sub>2</sub>Si), 205 (11, M – C<sub>10</sub>H<sub>16</sub>NO<sub>2</sub>S) and 135 (100, PhMe<sub>2</sub>Si) (Found: M<sup>+</sup>, 419.1976. C<sub>22</sub>H<sub>33</sub>NO<sub>3</sub>SSi requires M, 419.1951). The ratio **18a**:**19a** of 86:14 was determined by integration (<sup>1</sup>H NMR) of the CH<sub>A</sub>H<sub>B</sub>CO double doublets at  $\delta$  3.24 (from **18a**) and 2.74 (from **19a**), respectively, and the ratio **18b**:**19b** of 57:43 was determined by integration of the CH<sub>A</sub>H<sub>B</sub>SO<sub>2</sub> doublets at  $\delta$  3.47 (from **18b**) and 3.49 (from **19b**), respectively. The other data in Table 3 were acquired similarly.

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