Synthesis of Acylsilanes from Amides and Esters, and the Selective Oxidation of α-Silyl Alcohols to Aldehydes

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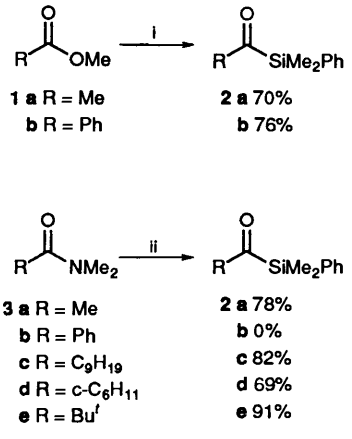
The acylsilanes **2** can easily be made directly from the dimethylamides **3** by treatment with phenyldimethylsilyllithium. They can also be made in two steps from the esters **4** using 2 equiv. of phenyldimethylsilyllithium followed by oxidation of the disilyl alcohols **5** with PDC. The disilyl alcohols **5** can be used as intermediates in the conversion of esters into aldehydes without recourse to hydride reagents, by monodesilylation, using a Brook rearrangement, followed by oxidation and selective removal of the silyl group, using chromium trioxide in DMSO.

Acylsilanes can be prepared in a large number of ways,[1] but one of the most direct seeming methods, the reaction between a carboxylic acid derivative and a silyl nucleophile appears rarely to have been used. In our hands, one known reaction of this type, the reaction between a carboxylic acid chloride and a silyl-cuprate,[2] has not proved to be high yielding, and we speculate that it is rarely used for this reason. Other reactions of this general type[3] have not been well established. We now report a one-step reaction for making acylsilanes from the corresponding amides, and a simple two-step sequence from carboxylic esters, both of which are more convenient starting materials than acid chlorides. We also report some other simple reactions of the intermediates that might have some uses in organic synthesis, including for the first time the selective oxidation of α-silyl alcohols to aldehydes, complementing the known selective oxidation of these substrates to acylsilanes.

We find that phenyldimethylsilyllithium[4] reacts rapidly with esters at −110 °C, there being no need for acid chlorides or silyl-cuprates (Scheme 1). In two cases, with methyl acetate **1a**

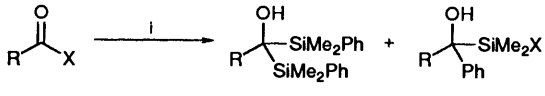


Scheme 1 *Reagents and conditions:* i, 1 equiv. $PhMe_2SiLi$, THF −110 ± 10 °C, 45 min; ii, 1.2 equiv. $PhMe_2SiLi$, THF, −78 °C, 1.5 h

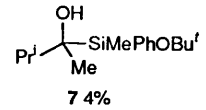
and methyl benzoate **1b**, we had no difficulty in isolating quite good yields of the acylsilanes **2a** and **2b** directly from reactions carried out at −110 °C. However, this level of control did not prove to be general. The two major problems with this procedure are familiar in organometallic reactions with esters. (i) The first limitation is that the silyllithium reagent can react with the first-formed product, the acylsilane, to give the disilyl alcohols **5**. (ii) The method is also limited to esters that are not α,β-unsaturated—with methyl crotonate and methyl cinnamate we obtained mixtures of products, presumably because there is some conjugate attack by the silyllithium reagent, either directly on the α-β-unsaturated ester or on the α,β-unsaturated acylsilane produced from it.

We turned, therefore, to the reaction with the corresponding dimethylamides **3a–e**, which reacted rapidly with phenyldimethylsilyllithium at −78 °C. An aqueous quench at this temperature gave directly good yields of the acylsilanes **2a** and **2c–e**, but not of the benzoylsilane **2b**, where the major product identified was α-dimethylaminobenzyldimethyl(phenyl)silane. It is important that the reaction and quench be carried out at low temperature—when the reaction was carried out at −20 °C, we obtained quite different products, that will be the subject of a separate paper in due course.

Because esters are in many ways more convenient substrates, we returned to their reactions with phenyldimethylsilyllithium. An excess of this reagent gave the 1,1-disilyl alcohols **5** in adequate to good yield (Scheme 2). This class of compound



4 aa R = Me, X = OMe	**5 a** 82%	**6**
ba R = Ph, X = OMe	**b** 0%	
ca R = n-C_9H_{19}, X = OMe	**c** 88%	
da R = c-C_6H_{11}, X = OMe	**d** 63%	**da** 22%
dd R = c-C_6H_{11}, X = OMe	**d** 81%	**dd** 0%
ea R = Bu^t, X = OMe	**e** 71%	
fa R = $Ph(CH_2)_2$, X = OMe	**f** 90%	
ga R = Pr^i, X = OMe	**g** 60%	**ga** 17%
gb R = Pr^i, X = OBu^i	**g** 19%	**gb** 62%
gc R = Pr^i, X = OBu^t	**g** 0%	**gc** 65%
gd R = Pr^i, X = OPh	**g** 77%	**gd** 0%



7 4%

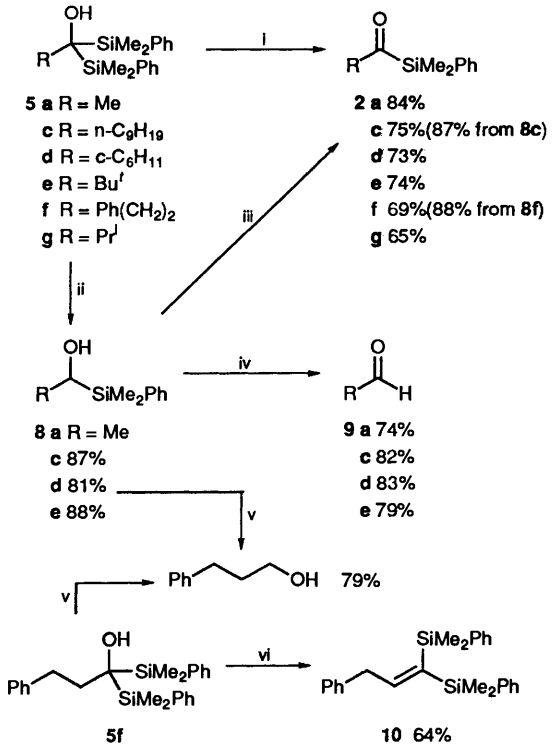
Scheme 2 *Reagents and conditions:* i, 2.4 equiv. $PhMe_2SiLi$, THF, −78 °C, 3 h

can also be prepared, along with acyloin products, by treating esters with trimethylsilyl chloride and sodium[5] or lithium.[6] For our reactions, aimed at making the alcohols **5**, there was no advantage to carrying out the reactions at −110 °C, as we had before when trying to control the reaction to give acylsilanes, and we used instead normal solid CO_2—acetone cooling. When the yields with the methyl esters were only adequate, as with the esters **4da** and **4ga** having a single branch at the α position, the by-products **6da** and **6ga** were easily identifiable as being the result of a 1,2 phenyl shift taking place

before the second equivalent of the silyllithium reagent attacked the intermediate acylsilane. 1,2-Shift of a phenyl group set off by alkoxide attack on an acylsilane is well precedented.[7,8]

In order to minimise this pathway, we considered the possibility that a more-hindered alkoxide might not attack the silyl group as rapidly or extensively as methoxide ion, and might therefore give the acylsilane a longer lifetime. We found instead that the isobutyl ester **4gb** and the *tert*-butyl ester **4gc** gave even more rearrangement, with the latter actually giving none of the disilyl alcohol **5g** and enough rearrangement for us to detect the very minor product **7** of methyl migration as well as the major product **6gc** of phenyl migration. The solution to this problem was to use the phenyl esters **4dd** and **4gd** in place of the alkyl esters. Evidently a lower pK_a in the oxyanion was more important in minimising attack on silicon than adjusting the steric bulk. The phenyl esters **4dd** and **4gd** gave no trace of the rearrangement products, and reasonably good yields of the disilyl alcohols **5d** and **5g**.

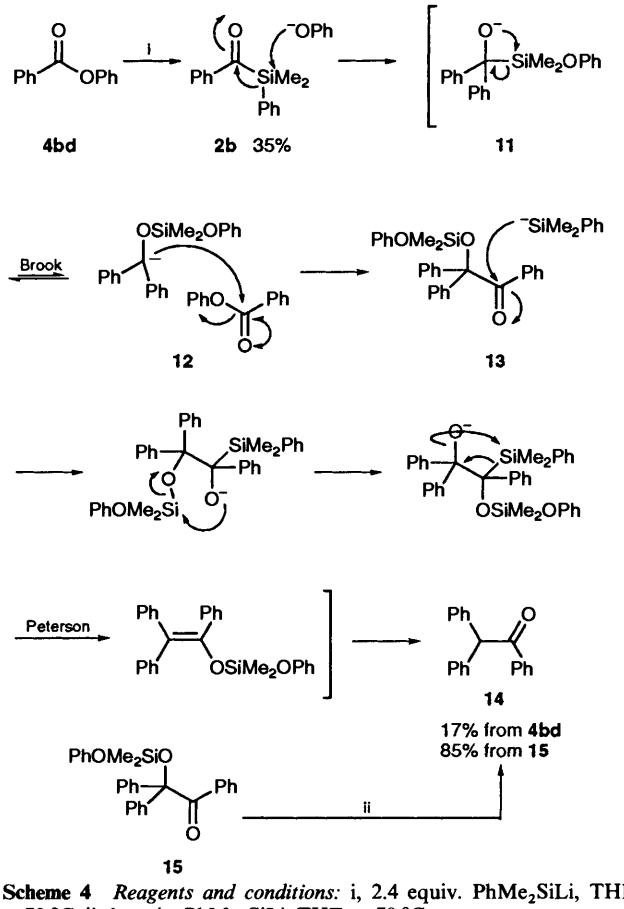
Having obtained good yields of the disilyl alcohols **5**, we find that these can easily be oxidised to the corresponding acylsilanes using pyridinium dichromate (PDC)[9] (Scheme 3),



Scheme 3 *Reagents and conditions:* i, PDC, CH_2Cl_2, room temp.; ii, NaOMe, MeOH, reflux; iii, $(COCl)_2$, DMSO; iv, CrO_3, DMSO, room temp.; v, 10% NaOH, EtOH, reflux; vi, $SOCl_2$, Py, 0 °C

with the two steps **4**→**5**→**2** making a simple synthesis of acylsilanes from esters. 1,1-Disilyl alcohols have also been oxidised to acylsilanes with *tert*-butyl hypochlorite.[10] The disilyl alcohols **5** can also be used to prepare the α-hydroxysilanes **8**, using the well-precedented Brook rearrangement.[7,11] The α-hydroxysilanes **8** can then be used to prepare the acylsilanes **2**, since Ireland has shown that Swern conditions[12] selectively cause the removal of the proton rather than the silyl group.[13] We only carried out this known reaction on two of our α-hydroxysilanes, namely **8c** and **8f**, since this route offered no advantages. There is, however, no method in the literature for oxidising an α-hydroxysilane to an aldehyde, with selective removal of the silyl group rather than the proton. Chromium-based oxidising agents are known to give mixtures of acylsilanes and aldehydes.[14] Thus we found, typically, that the α-hydroxysilane **8f** gave the acylsilane **2f** (17%) and hydrocinnamaldehyde **9f** (64%). We now report that chromium trioxide in DMSO[15] selectively gives the aldehydes **9** from a representative group of α-hydroxysilanes **8**, with no trace (TLC, IR) of the corresponding acylsilanes **2**. The sequence **4**→**5**→**8**→**9** provides a route from esters to aldehydes avoiding hydride reagents. The α-hydroxysilanes **8** can also be converted into the corresponding primary alcohols by carrying out a second, equally well-precedented Brook rearrangement[16] under more vigorous conditions and a longer time, as illustrated by the conversion of **8f** into 3-phenylpropanol. It is, of course, also possible to convert the disilyl alcohol **5f** directly into 3-phenylpropanol under the same conditions, when the overall yield was 79%. This provides a route from esters to alcohols similarly avoiding hydride reagents. Finally the disilyl alcohols **5** can be dehydrated with surprising ease using thionyl chloride, as shown by the conversion of the alcohol **5f** into the vinyldisilane **10**.

Although we had been able to make the acylsilane **2b** directly, we were not able to make the disilyl alcohol **5b** from 2 equiv. of the silyllithium reagent and methyl benzoate. Our hydride-free method for reducing esters to aldehydes or alcohols is not, therefore, applicable to aromatic methyl esters. We had, therefore, had to make the α-hydroxysilane **8b** from benzaldehyde only to oxidise it back to benzaldehyde **9b**. Hoping to overcome this problem in the same way that had worked for the branched esters **4dd** and **4gd**, we tried the reaction of 2 equiv. of the silyllithium reagent on phenyl benzoate **4bd**. This gave the acylsilane **2b** in 35% yield together with an unexpected product in 17% yield, the ketone **14** (Scheme 4), with no sign



Scheme 4 *Reagents and conditions:* i, 2.4 equiv. $PhMe_2SiLi$, THF, −78 °C; ii, 1 equiv. $PhMe_2SiLi$, THF, −78 °C

of the alcohol **5b**. We believe that the ketone **14** arises because phenyl shift takes place **2b** (arrows), and leads to an intermediate **11** that can undergo the Brook rearrangement excep-

tionally easily. The intermediate **12** can then attack another molecule of phenyl benzoate to give the α-hydroxy ketone silyl ether **13**, and the final step is the reduction of this silyl ether. There are precedents for all the steps.[17] We checked that this last step is reasonable by making the silyl ether **15**, which is closely similar to the silyl ether **13**, and showing that it is reduced by the silyllithium reagent to give the ketone **14**. The mechanism involving a Peterson elimination that we illustrate for the reduction of the acyloin ether **13** is only one of several variants. Whatever the mechanism, it suggests that the step illustrated by **15**→**14** might be a simple way to reduce α-hydroxy ketones to ketone silyl enol ethers and hence to ketones in general.

Experimental

Acyldimethyl(phenyl)silanes **2a** *and* **2b** *prepared directly from Methyl Esters* **1a** *and* **1b**.—Dimethyl(phenyl)silyllithium (1.1 mol dm^{-3} in THF; 5.5 cm^3, 6 mmol) was added dropwise to a stirred solution of the ester **1a** or **1b** (6 mmol) in a mixture of dry THF, ether and pentane (60 cm^3, 4:4:1) under argon at −110 ± 10 °C over 20 min. After 45 min at −110 °C, saturated aqueous ammonium chloride (10 cm^3) was added to the mixture, which was then extracted with ether (2 × 60 cm^3). The combined extracts were washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The following compounds were prepared by this method.

Acetyldimethyl(phenyl)silane **2a** (747 mg, 70%), b.p. 65–66 °C/2 mmHg (lit.,[18] 60–63 °C/1.9 mmHg); R_f (hexane–Et_2O, 90:10) 0.22; ν_{max}(film)/cm^{-1} 1635 (C=O), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.57–7.50 (2 H, m, Ph), 7.42–7.34 (3 H, m, Ph), 2.23 (3 H, s, Me) and 0.49 (6 H, s, $SiMe_2$).

Benzoyldimethyl(phenyl)silane[19] **2b** (1.09 g, 76%) after chromatography (SiO_2, hexane–Et_2O, 95:5); R_f (hexane–Et_2O, 90:10) 0.37; ν_{max}(film)/cm^{-1} 1611 (C=O), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.75–7.72 (2 H, m, Ph), 7.60–7.53 (2 H, m, Ph), 7.49–7.32 (6 H, m, Ph) and 0.61 (6 H, s, $SiMe_2$).

Acyldimethyl(phenyl)silanes from N,N-*Dimethylamides*.—Dimethyl(phenyl)silyllithium (1 mol dm^{-3} in THF; 2.4 cm^3) was added dropwise to a stirred solution of the amide **3** (2 mmol) in dry THF (3 cm^3) under argon at −78 °C, and the mixture kept for 1.5 h at −78 °C. Saturated aqueous ammonium chloride (10 cm^3) was added to the mixture, which was then extracted with ether (2 × 50 cm^3). The combined extracts were washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane–Et_2O) to give the acylsilanes. The following compounds were prepared by this method.

Acetyldimethyl(phenyl)silane **2a** (78%) identical (TLC, IR, ^1H NMR) with the sample described above.

Decanoyldimethyl(phenyl)silane[20] **2c** (82%); R_f (hexane–Et_2O, 95:5) 0.28; ν_{max}(film)/cm^{-1} 1635 (C=O), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.55–7.48 (2 H, m, Ph), 7.41–7.33 (3 H, m, Ph), 2.54 (2 H, t, *J* 7.2, CH_2), 1.41 (2 H, m, CH_2), 1.30–1.16 (12 H, m, CH_2), 0.86 (3 H, t, *J* 6.5, Me) and 0.47 (6 H, s, $SiMe_2$).

Cyclohexylcarbonyldimethyl(phenyl)silane **2d** (69%); R_f (hexane–Et_2O, 90:10) 0.34; ν_{max}(film)/cm^{-1} 1635 (C=O), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.55–7.49 (2 H, m, Ph), 7.43–7.31 (3 H, m, Ph), 2.66 (1 H, m, CH), 1.68–1.52 (5 H, m, CH_2), 1.24–1.05 (5 H, m, CH_2) and 0.47 (6 H, s, $SiMe_2$) (Found: C, 73.1; H, 8.9. $C_{15}H_{22}OSi$ requires C, 73.1; H, 9.0%).

Trimethylacetyldimethyl(phenyl)silane **2e** (91%); R_f (hexane–Et_2O, 95:5) 0.34; ν_{max}(film)/cm^{-1} 1635 (C=O), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.57–7.51 (2 H, m, Ph), 7.41–7.28 (3 H, m, Ph), 0.97 (9 H, s, Me_3C) and 0.49 (6 H, s, $SiMe_2$) (Found: C, 70.8; H, 9.2. $C_{13}H_{20}OSi$ requires C, 70.9; H, 9.2%).

α-*Dimethylaminobenzyldimethylphenylsilane* (28%), from *N*,*N*-dimethylbenzamide, after chromatography on basic alumina (hexane–Et_2O, 80:20); R_f (hexane–Et_2O, 70:30) 0.23; ν_{max}(film)/cm^{-1} 1246 (SiMe) and 1112 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.50–7.44 (2 H, m, Ph), 7.31–7.27 (3 H, m, Ph), 7.21–7.09 (5 H, m, Ph), 2.97 (1 H, s, CH), 2.18 (6 H, s, NMe_2), 0.37 (3 H, s, Me_AMeSi) and 0.01 (3 H, s, Me_AMe_BSi); *m*/*z* 269 (4%, M^+), 254 (2, M − Me) and 134 (100, M − $SiMe_2Ph$) (Found: M^+, 269.1594. $C_{17}H_{23}NSi$ requires *M*, 269.1599).

Preparation of the Disilyl Alcohols **5**.—Dimethyl(phenyl)-silyllithium (1 mol dm^{-3} in THF; 4.4 cm^3, 4.4 mmol) was added dropwise to a stirred solution of the ester **4** (2 mmol) in dry THF (5 cm^3) under argon at −78 °C over 15 min, after which the mixture was stored at the same temperature for 3 h. After addition of aqueous ammonium chloride (5 cm^3) to the mixture it was extracted with ether (2 × 50 cm^3). The combined extracts were washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane–Et_2O) to give the disilyl alcohols. The following disilyl alcohols were made by this method.

1,1-Bis[dimethyl(phenyl)silyl]ethanol[21] **5a** (82% from **4aa**); R_f (hexane–Et_2O, 90:10) 0.22; ν_{max}(film)/cm^{-1} 3560 (OH), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.57–7.50 (4 H, m, Ph), 7.41–7.29 (6 H, m, Ph), 1.28 (3 H, s, Me), 0.22 (6 H, s, $SiMe_2$) and 0.20 (6 H, s, $SiMe_2$).

1,1-*Bis*[*dimethyl*(*phenyl*)*silyl*]*decan*-1-*ol* **5c** (88% from **4ca**); R_f (hexane–Et_2O, 94:6) 0.35; ν_{max}(film)/cm^{-1} 3560 (OH), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.53–7.50 (4 H, m, Ph), 7.38–7.27 (6 H, m, Ph), 1.65–1.59 (2 H, m, CH_2), 1.28–1.11 (14 H, m, CH_2), 0.87 (3 H, t, *J* 6.5, Me), 0.28 (6 H, s, $SiMe_2$) and 0.21 (6 H, s, $SiMe_2$) (Found: C, 73.4; H, 9.8. $C_{26}H_{42}OSi_2$ requires C, 73.2; H, 9.9%).

1,1-*Bis*[*dimethyl*(*phenyl*)*silyl*]*cyclohexanemethanol* **5d** (81% from **4dd**, 63% from **4da**); R_f (hexane–Et_2O, 96:4) 0.27; ν_{max}(film)/cm^{-1} 3560 (OH), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.55–7.50 (4 H, m, Ph), 7.39–7.27 (6 H, m, Ph), 1.66–1.49 (7 H, m, CH_2, CH, OH), 1.06–0.66 (5 H, m, CH_2), 0.43 (6 H, s, $SiMe_2$) and 0.26 (6 H, s, $SiMe_2$) (Found: C, 72.2; H, 8.8. $C_{23}H_{34}OSi_2$ requires C, 72.2; H, 9.0%).

1,1-*Bis*[*dimethyl*(*phenyl*)*silyl*]-2,2-*dimethylpropan*-1-*ol* **5e** (71% from **4ea**); R_f (hexane–Et_2O, 96:4) 0.20; ν_{max}(film)/cm^{-1} 3560 (OH), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.62–7.52 (4 H, m, Ph), 7.36–7.21 (6 H, m, Ph), 1.37 (1 H, br s, OH), 0.88 (9 H, s, Me_3), 0.52 (6 H, s, $SiMe_2$) and 0.32 (6 H, s, $SiMe_2$) (Found: C, 70.4; H, 9.1. $C_{21}H_{32}OSi_2$ requires C, 70.7; H, 9.0%).

1,1-*Bis*[*dimethyl*(*phenyl*)*silyl*]-3-*phenylpropan*-1-*ol* **5f** (90% from **4fa**); R_f (hexane–Et_2O, 90:10) 0.30; ν_{max}(film)/cm^{-1} 3560 (OH), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.66–7.54 (4 H, m, Ph), 7.41–7.31 (6 H, m, Ph), 7.24–7.10 (3 H, m, Ph), 6.93–6.90 (2 H, m, Ph), 2.51–2.45 (2 H, m, PhCH_2), 2.00–1.92 (2 H, m, CH_2), 0.36 (6 H, s, $SiMe_2$) and 0.29 (6 H, s, $SiMe_2$) (Found: C, 74.1; H, 8.1. $C_{25}H_{32}OSi_2$ requires, C, 74.2; H, 8.0%).

2-*Methyl*-1,1-*bis*[*dimethyl*(*phenyl*)*silyl*]*propan*-1-*ol* **5g** (60% from **4ga**, 19% from **4gb**, 0% from **4gc**, and 77% from **4gd**); R_f (hexane–Et_2O, 96:4) 0.27; ν_{max}(film)/cm^{-1} 3560 (OH), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.58–7.51 (4 H, m, Ph), 7.40–7.26 (6 H, m, Ph), 1.93 (1 H, septet, *J* 7, CH), 1.12 (1 H, br s, OH), 0.85 (6 H, d, *J* 7, Me_2CH), 0.44 (6 H, s, $SiMe_2$) and 0.28 (6 H, s, $SiMe_2$) (Found: C, 69.9; H, 8.7. $C_{20}H_{30}OSi_2$ requires C, 70.1; H, 8.8%).

The following by-products were also obtained from some of these reactions.

1-*Dimethyl*(*methoxy*)*silyl*-1-*phenylcyclohexylmethanol* **6da** (22% from **4da**); R_f (hexane–Et_2O, 90:10) 0.21; ν_{max}(film)/cm^{-1} 3560 (OH), 1250 (SiMe) and 1090 (SiO); δ_H(250 MHz; $CDCl_3$) 7.36–7.24 (4 H, m, Ph), 7.13 (1 H, m, Ph), 3.40 (3 H, s, OMe),

2.10–1.90 (2 H, m, CH_2), 1.80 (1 H, m, CH), 1.64–1.55 (2 H, m, CH_2), 1.39–1.21 (2 H, m, CH_2), 1.19–0.91 (4 H, m, CH_2), 0.12 (3 H, s, Me_AMe_BSi) and −0.15 (3 H, s, Me_AMe_BSi) (Found: C, 69.2; H, 9.5. $C_{16}H_{26}O_2Si$ requires C, 69.0; H, 9.4%).

1-*Dimethylmethoxysilyl*-2-*methyl*-1-*phenylpropan*-1-*ol* **6ga** (17% from **4ga**); R_f (hexane–Et_2O, 90:10) 0.21; ν_{max}(film)/cm^{-1} 3560 (OH), 1250 (SiMe) and 1090 (SiO); δ_H(250 MHz; $CDCl_3$) 7.33–7.25 (4 H, m, Ph), 7.14 (1 H, m, Ph), 3.41 (3 H, s, OMe), 2.37 (1 H, septet, *J* 6.8, CH), 1.94 (1 H, br s, OH), 1.12 (3 H, d, *J* 6.8, Me_AMe_BCH), 0.61 (3 H, d, *J* 6.8, Me_AMe_BCH), 0.12 (3 H, s, Me_AMe_BSi) and −0.15 (3 H, s, Me_AMe_BSi) (Found: C, 65.3; H, 9.3. $C_{13}H_{22}O_2Si$ requires C, 65.5; H, 9.3%).

1-*Dimethyl*(2-*methylpropoxy*)*silyl*-2-*methyl*-1-*phenylpropan*-1-*ol* **6gb** (62% from **4gb**); R_f (hexane–Et_2O, 90:10) 0.31; ν_{max}(film)/cm^{-1} 3560 (OH), 1250 (SiMe) and 1090 (SiO); δ_H(250 MHz; $CDCl_3$) 7.32–7.24 (4 H, m, Ph), 7.13 (1 H, m, Ph), 3.34 (2 H, d, *J* 6.3, OCH_2), 2.33 (1 H, septet, *J* 6.8, Me_2CH), 1.73 (1 H, septet, *J* 6.7, OCH_2CHMe_2), 1.13 (3 H, d, *J* 6.8, Me_AMe_BCH), 0.86 (6 H, d, *J* 6.7, OCH_2CHMe_2), 0.61 (3 H, d, *J* 6.8, Me_AMe_BCH), 0.14 (3 H, s, Me_AMe_BSi) and −0.21 (3 H, s, Me_AMe_BSi) (Found: C, 68.4; H, 10.1. $C_{16}H_{28}O_2Si$ requires C, 68.5; H, 10.1%).

1-*Dimethyl*(tert-*butoxy*)*silyl*-2-*methyl*-1-*phenylpropan*-1-*ol* **6gc** (65% from **4gc**); R_f (hexane–Et_2O, 90:10) 0.33 ν_{max}(film)/cm^{-1} 3560 (OH), 1250 (SiMe) and 1060 (SiO); δ_H(250 MHz; $CDCl_3$) 7.32–7.23 (4 H, m, Ph), 7.10 (1 H, m, Ph), 2.50 (1 H, br s, OH), 2.33 (1 H, septet, *J* 6.8, Me_2CH), 1.27 (9 H, s, CMe_3), 1.10 (3 H, d, *J* 6.8, Me_AMe_BCH), 0.60 (3 H, d, *J* 6.8, Me_AMe_BCH), 0.20 (3 H, s, Me_AMe_BSi) and −0.24 (3 H, s, Me_AMe_BSi) (Found: C, 68.4; H, 10.0. $C_{16}H_{28}O_2Si$ requires C, 68.5; H, 10.1%).

2-[*Methyl*(*phenyl*)-tert-*butoxysilyl*]-3-*methylbutan*-2-*ol* **7** (4% from **4gc**); R_f (hexane–Et_2O, 90:10) 0.22; ν_{max}(film)/cm^{-1} 3560 (OH), 1250 (SiMe), 1110 (SiPh) and 1040 (SiO); δ_H(250 MHz; $CDCl_3$) 7.69–7.62 (2 H, m, Ph), 7.41–7.27 (3 H, m, Ph), 1.71 (1 H, septet, *J* 6.8, Me_2CH), 1.23 (9 H, s, CMe_3), 1.10 (3 H, s, Me), 0.88 (3 H, d, *J* 6.8, Me_AMe_BCH), 0.74 (3 H, d, *J* 6.8, Me_AMe_BCH) and 0.56 (3 H, s, SiMe) (Found: C, 68.6; H, 10.1. $C_{16}H_{28}O_2Si$ requires C, 68.5; H, 10.1%).

Oxidation of α-Silyl Alcohols to Acylsilanes **2**.—*Method A, from the disilyl alcohols* **5**. Pyridinium dichromate (677 mg, 1.8 mmol) was stirred with the disilyl alcohol (1.2 mmol) in dry dichloromethane (3 cm^3) at room temperature for 6–12 h. The mixture was diluted with ether (10 cm^3), filtered through a pad of silica gel (5 cm × 2 cm) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane–Et_2O) to give the acylsilanes.

Method B, by Swern oxidation of the α-hydroxysilanes **8**. Dimethyl sulfoxide (0.09 cm^3, 1.22 mmol) in dichloromethane (1 cm^3) was added dropwise to a stirred solution of oxalyl chloride (0.53 cm^3, 0.61 mmol) in dichloromethane (0.5 cm^3) at −60 °C and the mixture kept for 5 min at the same temperature. The alcohol **6** (0.55 mmol) in dichloromethane (1 cm^3) was added dropwise over 5 min to the mixture, which was then stirred for 15 min. After this, triethylamine (0.3 cm^3, 2.5 mmol) was added to the mixture, which was then allowed to warm to room temperature. It was then poured into water and extracted with ether (2 × 20 cm^3). The combined extracts were washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure, and the residue chromatographed (SiO_2, hexane–Et_2O) to give the acylsilanes. The following compounds were prepared by either or both of these methods.

Acetyldimethyl(phenyl)silane **2a** (Method A, 84%) identical (TLC, IR, ^1H NMR) with the sample described above.

Decanoyldimethyl(phenyl)silane **2c** (Method A, 75%; Method B 87%) identical (TLC, IR, ^1H NMR) with the sample described above.

Cyclohexylcarbonyldimethyl(*phenyl*)*silane* **2d** (Method A, 73%) identical (TLC, IR, ^1H NMR) with the sample described above.

Trimethylacetyldimethyl(*phenyl*)*silane* **2e** (Method A, 75%) identical (TLC, IR, ^1H NMR) with the sample described above.

3-*Phenylpropionyldimethyl*(*phenyl*)*silane* **2f** (Method A, 69%; Method B, 88%); R_f (hexane–Et_2O, 96:4) 0.24; ν_{max}(film)/cm^{-1} 1640 (C=O), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.53–7.49 (2 H, m, Ph), 7.41–7.35 (3 H, m, Ph), 7.23–7.18 (3 H, m, Ph), 7.15–7.05 (2 H, m, Ph), 2.91–2.85 (2 H, m, $PhCH_2$), 2.78–2.72 (2 H, m, CH_2) and 0.46 (6 H, s, $SiMe_2$) (Found: C, 75.9; H, 7.7, $C_{17}H_{20}OSi$ requires C, 76.1; H, 7.5%).

2-*Methylpropionoyldimethyl*(*phenyl*)*silane* **2g** (Method A, 65%); R_f (hexane–Et_2O, 96:4) 0.26; ν_{max}(film)/cm^{-1} 1635 (C=O), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.57–7.47 (2 H, m, Ph), 7.41–7.30 (3 H, m, Ph), 2.89 (1 H, septet, *J* 7, CH), 0.90 (6 H, d, *J* 7, Me_2CH) and 0.49 (6 H, s, $SiMe_2$) (Found: C, 69.5; H, 8.8. $C_{12}H_{18}OSi$ requires C, 69.8; H, 8.8%).

1-*Dimethyl*(*phenyl*)*silyl*-1-*phenylmethanol* **8b**—Dimethyl(phenyl)silyllithium (1 mol dm^{-1} in THF; 2.3 cm^3) was added dropwise to a stirred solution of benzaldehyde (212 mg, 2 mmol) in dry THF (5 cm^3) under argon at −78 °C over 15 min, after which the mixture was stored at the same temperature for 3 h. After this, saturated aqueous NH_4Cl (5 cm^3) was added to the mixture which was then extracted with ether (2 × 50 cm^3). The combined extracts were washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane–Et_2O, 90:10) to give the hydroxysilane[22] (375 mg, 77%); R_f (hexane–Et_2O, 85:15) 0.27; ν_{max}(film)/cm^{-1} 3420 (OH), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.49–7.47 (2 H, m, Ph), 7.40–7.33 (3 H, m, Ph), 7.28–7.24 (2 H, m, Ph), 7.17 (1 H, m, Ph), 7.14–7.07 (2 H, m, Ph), 4.70 (1 H, s, CH), 1.84 (1 H, br s, OH), 0.31 (3 H, s, $SiMe_AMe_B$) and 0.29 (3 H, s, $SiMe_AMe_B$).

Preparation of α-Hydroxysilanes **8** *from Disilyl Alcohols* **5**.—Sodium methoxide (2 mol dm^{-3} in methanol; 5 cm^3) and the disilyl alcohol **5** (1.2 mmol) were refluxed in methanol (1 cm^3) for 2 h (**8c**) or 40 min (**8d** and **8f**). The mixture was poured into saturated aqueous ammonium chloride (10 cm^3) and extracted with ether (2 × 20 cm^3). The combined extracts were washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane–Et_2O) to give the hydroxysilanes. The following compounds were prepared by this method.

1-Dimethyl(phenyl)silyldecan-1-ol[23] **8c** (87%); R_f (hexane–Et_2O, 90:10) 0.19; ν_{max}(film)/cm^{-1} 3420 (OH), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.59–7.49 (2 H, m, Ph), 7.41–7.29 (3 H, m, Ph), 3.52–3.46 (1 H, m, CH), 1.51–1.41 (3 H, m, CH_2 and OH), 1.31–1.15 (14 H, m, CH_2), 0.86 (3 H, t, *J* 6.8, Me), 0.33 (3 H, s, $SiMe_AMe_B$) and 0.32 (3 H, s, $SiMe_AMe_B$).

1-Dimethyl(phenyl)silylcyclohexanemethanol[22] **8d** (81%); R_f (hexane–Et_2O, 85:15) 0.20; ν_{max}(film)/cm^{-1} 3450 (OH), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.60–7.53 (2 H, m, Ph), 7.40–7.28 (3 H, m, Ph), 3.34 (1 H, d, *J* 5.9, CH), 1.85–1.46 (6 H, m, CH_2, CH), 1.29–0.94 (6 H, m, CH_2, OH), 0.37 (3 H, s, $SiMe_AMe_B$) and 0.36 (3 H, s, $SiMe_AMe_B$).

1-*Dimethyl*(*phenyl*)*silyl*-3-*phenylpropan*-1-*ol* **8f** (88%); R_f (hexane–EtOAc, 80:20) 0.29; ν_{max}(film)/cm^{-1} 3420 (OH), 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.61–7.52 (2 H, m, Ph), 7.41–7.33 (3 H, m, Ph), 7.30–7.24 (3 H, m, Ph), 7.20–7.14 (2 H, m, Ph), 3.52 (1 H, t, *J* 7.5, CH), 2.90 (1 H, td *J* 7.1 and 14, $PhCH_AH_B$), 2.60 (1 H, td, *J* 8.0 and 14, $PhCH_AH_B$), 1.90–1.77 (2 H, m, CH_2), 0.33 (3 H, s, $SiMe_AMe_B$) and 0.32 (3 H, s, $SiMe_AMe_B$) (Found: M^+ − Me, 255.1207. $C_{17}H_{22}OSi$ requires *M* − Me, 255.1205).

PDC Oxidation of 1-*Dimethyl*(*phenyl*)*silyl*-3-*phenylpropan*-1-*ol* **8f**.—Pyridinium dichromate (124 mg, 0.33 mmol) and the alcohol (60 mg, 0.22 mmol) were stirred in dry dichloromethane (1 cm^3) at 0 °C for 3 h at room temperature. The mixture was then diluted with ether (10 cm^3), filtered through a small pad of silica gel (5 cm × 2 cm) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane–Et_2O, 98:2) to give the acylsilane **2f** (10 mg, 17%), identical (TLC, IR, ^1H NMR) with the sample described above, and the aldehyde **9f** (18 mg, 64%); R_f (hexane–Et_2O, 90:10) 0.24; ν_{max}(film)/cm^{-1} 1710 (C=O); δ_H(250 MHz; $CDCl_3$) 9.82 (1 H, s, CHO), 7.38–7.26 (2 H, m, Ph), 7.24–7.16 (3 H, m, Ph), 2.95 (2 H, t, *J* 7.4, CH_2) and 2.80 (2 H, t, *J* 7.4, CH_2).

Oxidation of the α-*Hydroxysilanes* **8** *to the Aldehydes* **9**.—Chromium trioxide (1 mol dm^{-3} in dry DMSO; 2.4 cm^2) and the alcohol (1.2 mmol) were stirred in dry DMSO (1 cm^3) at 25 °C for 12–18 h. The mixture was diluted with water (5 cm^3) and extracted with ether (2 × 20 cm^3). The combined extracts were washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane–Et_2O) to give the aldehyde. The following compounds were prepared by this method.

Benzaldehyde **9b** (75%); R_f (hexane–Et_2O, 95:5) 0.34; ν_{max}(film)/cm^{-1} 1690 (C=O); δ_H(250 MHz; $CDCl_3$) 10.0 (1 H, s, CHO), 7.90–7.84 (2 H, m, Ph) and 7.66–7.43 (3 H, m, Ph).

Decanal **9c** (82%); R_f (hexane–Et_2O, 95:5) 0.34; ν_{max}(film)/cm^{-1} 1720 (C=O); δ_H(250 MHz; $CDCl_3$) 9.66 (1 H, t, *J* 1.8, CHO), 2.41 (2 H, dt, *J* 1.8 and 13.2, CH_2), 1.63–1.50 (2 H, m, CH_2), 1.26–1.10 (12 H, m, CH_2) and 0.86 (3 H, t, *J* 6.8, Me).

Cyclohexanecarbaldehyde **9d** (83%); R_f (hexane–Et_2O, 95:5) 0.30; ν_{max}(film)/cm^{-1} 1710 (C=O); δ_H(250 MHz; $CDCl_3$) 9.60 (1 H, d, *J* 1.2, CHO), 2.23 (1 H, m, CH), 1.93–1.49 (5 H, m, CH_2) and 1.41–1.16 (5 H, m, CH_2).

3-Phenylpropanal **9f** (79%); R_f (hexane–Et_2O, 90:10) 0.24; ν_{max}(film)/cm^{-1} 1710 (C=O); δ_H(250 MHz; $CDCl_3$) 9.82 (1 H, s, CHO), 7.38–7.26 (2 H, m, Ph), 7.24–7.16 (3 H, m, Ph), 2.95 (2 H, t, *J* 7.4, CH_2) and 2.80 (2 H, t, *J* 7.4, CH_2).

3-*Phenylpropan*-1-*ol*.—Sodium hydroxide (10% aqueous solution; 1 cm^3) and the disilyl alcohol **5f** or the monosilyl alcohol **8f** (0.5 mmol) were refluxed in ethanol (10 cm^3) for 22 h. The mixture was poured into saturated aqueous ammonium chloride (10 cm^3) and extracted with ethyl acetate (2 × 20 cm^3). The combined extracts were washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane–EtOAc, 80:20) to give 3-phenylpropanol (54 mg, 79% in both cases); R_f (hexane–EtOAc, 70:30) 0.18; ν_{max}(film)/cm^{-1} 3320 (OH); δ_H(400 MHz; $CDCl_3$) 7.31–7.27 (2 H, m, Ph), 7.21–7.17 (3 H, m, Ph), 3.67 (2 H, t, *J* 6.5, CH_2), 2.71 (2 H, t, *J* 7.6, CH_2), 1.93–1.85 (2 H, m, CH_2) and 1.57 (1 H, s, OH).

1,1-*Bis*[*dimethyl*(*phenyl*)*silyl*]-3-*phenylprop*-1-*ene* **10**.—Thionyl chloride (0.28 cm^3, 0.38 mmol) was added dropwise to the disilyl alcohol **5f** (130 mg, 0.32 mmol) in dichloromethane (1 cm^3) and dry pyridine (0.62 cm^3, 0.77 mmol) at 0 °C. After 5 min at 0 °C, water (2 cm^3) was added to the mixture, which was then extracted with ether (2 × 20 cm^3). The combined extracts were washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane) to give the *vinyldisilane* **10** (79 mg, 64%); R_f (hexane–Et_2O, 99:1) 0.29; ν_{max}(film)/cm^{-1} 1250 (SiMe) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.56–7.49 (4 H, m, Ph), 7.39–7.32 (6 H, m, Ph), 7.27–7.20 (3 H, m, Ph), 6.99–6.94 (3 H, m, Ph, CH), 3.45 (2 H, d, *J* 6.8, CH_2), 0.40 (6 H, s, 2 × $SiMe_AMe_B$) and 0.31 (6 H, s, 2 × $SiMe_AMe_B$) (Found: C, 77.6; H, 7.8. $C_{25}H_{30}Si_2$ requires C, 77.7; H, 7.8%).

Reaction of Dimethyl(*phenyl*)*silyllithium with Phenyl Benzoate*.—Dimethyl(phenyl)silyllithium (1 mol dm^{-3} in THF; 4.4 cm^3) was added dropwise to a stirred solution of the ester **4bd** (396 mg, 2 mmol) in dry THF (5 cm^3) under argon at −78 °C over 15 min and the mixture kept at the same temperature for 4 h. Saturated aqueous ammonium chloride (5 cm^3) was added to the mixture, which was then extracted with ether (2 × 50 cm^3). The combined extracts were washed with aqueous sodium hydroxide and brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was triturated with hexane to give 1,2,2-triphenylethanone **14** (94 mg, 17%) as needles, m.p. 131–132 °C (from EtOH) (lit.,[24] 136 °C); R_f (hexane–Et_2O, 90:10) 0.33; ν_{max}(film)/cm^{-1} 1680 (C=O); δ_H(250 MHz; $CDCl_3$) 8.01–7.90 (2 H, m, Ph), 7.50–7.21 (13 H, m, Ph) and 6.03 (1 H, s, CH). The remaining oil was chromatographed (SiO_2, hexane–Et_2O, 95:5) to give benzoyldimethyl(phenyl)-silane **2b** (168 mg, 35%).

Reaction of Dimethyl(*phenyl*)*silyllithium with the Silyl Ether* **15**.—The silyl ether **15** was prepared by adding dimethyl(phenyl)silyl chloride (0.40 cm^3, 2.5 mmol) dropwise to a stirred solution of the 2-hydroxy-2,2-diphenylacetophenone[25] (576 mg, 2 mmol) and imidazole (340 mg, 5 mmol) in dry DMF (4 cm^3) under argon at 0 °C over 10 min. After being stirred overnight at room temperature, the mixture was poured into aqueous sodium hydrogen carbonate (5 cm^3) and extracted with hexane (2 × 30 cm^3). The combined extracts were washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane–Et_2O, 98:2) to give the silyl ether (785 mg, 93%); R_f (hexane–Et_2O, 96:4) 0.24; ν_{max}(film)/cm^{-1} 1660 (C=O), 1250 (SiMe), 1110 (SiPh) and 1070 (SiO); δ_H(250 MHz; $CDCl_3$) 7.89–7.86 (2 H, m, Ph), 7.44–7.32 (2 H, m, Ph), 7.31–7.09 (16 H, m, Ph) and −0.05 (6 H, s, $SiMe_2$). Dimethyl(phenyl)silyllithium (1 mol dm^{-3} in THF; 0.48 cm^3) was added dropwise to a stirred solution of the silyl ether (182 mg, 0.43 mmol) in dry THF (0.5 cm^3) under argon at −78 °C over 5 min. After 1 h at −78 °C, saturated aqueous ammonium chloride (5 cm^3) was added to the mixture which was then extracted with ether (2 × 20 cm^3). The combined extracts were washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was triturated with hexane to give the ketone **14** (99 mg, 85%) as needles, m.p. 131–132 °C (from EtOH), identical (TLC, IR, ^1H NMR, m.p.) with the sample prepared from phenyl benzoate.

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