

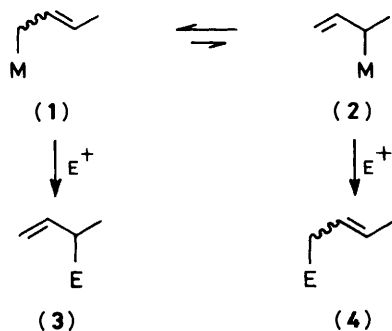
A Synthesis of Allylsilanes in which the Silyl Group is at the More-substituted End of the Allyl Group.†

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The allylsilanes (**8**), (**11**), (**18**)—(**20**), and (**26**), have been made by a three-step sequence from $\alpha\beta$ -unsaturated esters. The steps are conjugate addition of the phenyldimethylsilyl group, lithium aluminium hydride reduction, and selenium-mediated dehydration. The route is versatile and leads regioselectively to allylsilanes, in which the silyl group is at the more-substituted end of the allyl group.

It is well-established that allyl-metal reagents,¹ including allylsilanes,² react with electrophiles with allylic transposition (**1**)→(**3**). It is also well-established that almost all allyl-metal reagents, but not allylsilanes,³ are subject to more or less rapid 1,3-allylic rearrangement (**1**)→(**2**).⁴ The result is that most unsymmetrical allyl metal compounds react with electrophiles at the more-substituted end of the allyl group (**1**)→(**3**),^{1,5}



Scheme 1.

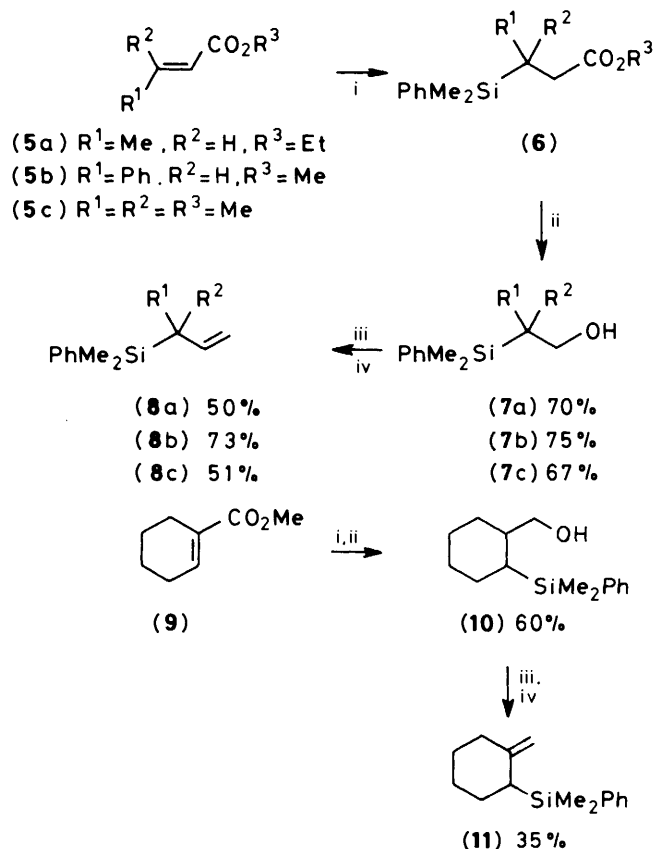
because the metal spends most of its time at the less-substituted end (**1**). Only with large electrophiles (chlorotrimethylsilane,³ for example, and hindered ketones^{1,6}), does the allyl-metal compound react at the less-substituted end, presumably as a result of a reversible 1,3-shift of the metal to the more-substituted position (**1**)→(**2**), followed by attack by the electrophile at the sterically less-crowded end (**2**)→(**4**). Since little can be done to control this pattern, it is generally difficult to persuade an allyl-metal reagent to react at the less-substituted end. Allylsilanes, on the other hand, do not undergo the rapid 1,3-allylic shift (**1**)→(**2**) (temperatures of the order of 500 °C are needed with allyltrimethylsilane itself³), with the result that, almost uniquely, they can be relied upon to react with electrophiles at the opposite end of the allylic fragment to which the silyl group is attached. This has been amply demonstrated in many examples,² but almost always (see, however, ref. 7) with allylsilanes in which the silyl group is at the less-substituted end, and the electrophile is attacking at the more substituted end, precisely the situation which is well-catered for by the more-conventional allyl-metal reagents. Allylsilanes, therefore, ought to be at their most useful when the silyl group is placed at the more-substituted end of the allyl group. However, there are not many methods, and no really general ones, for building allylsilanes of this type,^{7,8} which is why so many of the reactions in the literature are of allylsilanes of the opposite type. The latter are relatively easily made, as mentioned above, by the reaction of unsymmetrical allyl-

Grignard or allyl-lithium reagents with chlorotrimethylsilane,^{3,9,10} as well as by other methods.^{1,11}

In continuation of our pursuit of distinctive and controlled allylsilane syntheses,^{11,12} and of our interest in the unique capabilities of silicon-containing compounds, we now report a general three-step sequence, suitable for the construction of a wide-variety of allylsilanes, and particularly suitable for placing the silyl group regioselectively at the more-substituted end of the allyl fragment.

Results and Discussion

The sequence, as illustrated in Scheme 2, involves the conjugate addition of our silyl-cuprate reagent¹³ to $\alpha\beta$ -unsaturated esters (**5**), reduction of the saturated esters (**6**), and dehydration of the resultant alcohols (**7**) to give the allylsilanes (**8**). It was convenient not to isolate the intermediate ester (**6**), since it was

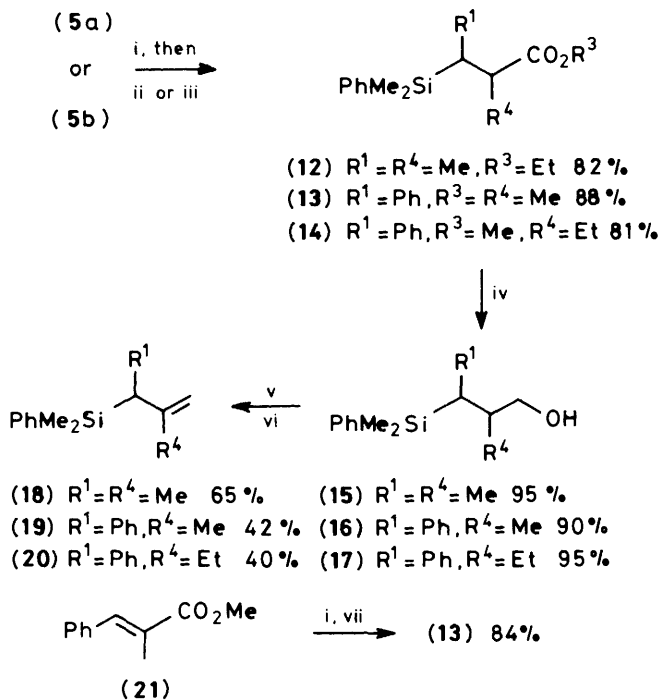


Scheme 2. Reagents: i, $(PhMe_2Si)_2CuLi$; ii, $LiAlH_4$; iii, $o\text{-O}_2NC_6H_4\text{-SeCN}$, Bu^t_3P ; iv, H_2O_2

† No reprints available

always contaminated with by-products produced from the unused phenyldimethylsilyl group. In the preceding paper¹⁴ we describe one way to minimise or remove this problem, but in the work described in this paper, we simply reduced the total crude product to give the alcohol (7), which was easily separated chromatographically from the phenyldimethylsilyl-containing by-products. The dehydration steps, (7)→(8), were notable only in that the selenoxide elimination was slower than in comparable compounds which do not have the silyl group.¹⁵ This observation ties in with an earlier observation we made with respect to sulphoxide-elimination. In that work,¹⁶ we had a silyl group *directly* attached to the carbon atom to which the hydrogen atom undergoing elimination was attached. In that position, the silyl group, a π -electron-withdrawing group, was rate-accelerating. In the present case, the silyl group is one further atom away and is, therefore, part of a silylmethyl substituent. Since the silylmethyl group is a π -donor ($\sigma^+ = -0.6$, for example¹⁷), it should be rate-retarding in its effect on the rate of selenoxide elimination, which it evidently is. The eliminations leading to (8) regularly took several days at room temperature compared with 3–12 h for comparable compounds without silicon.¹⁵

The sequence shown in Scheme 2 is made more versatile by the possibilities shown in Scheme 3, where the conjugate addi-

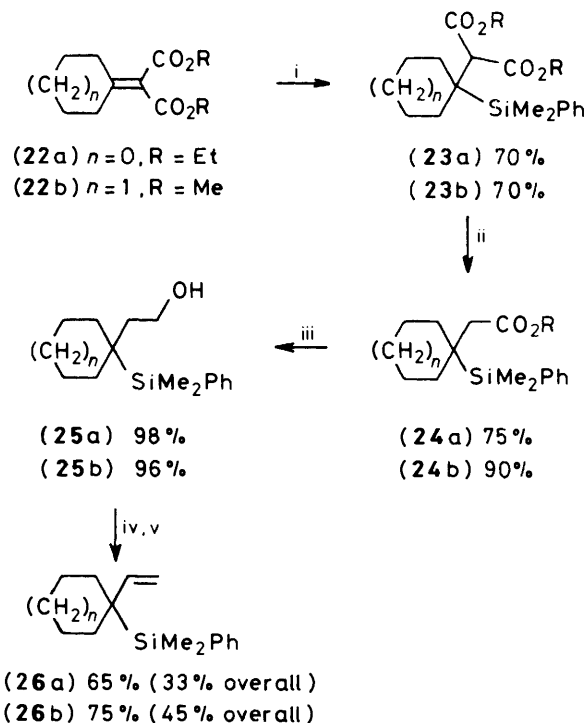


Scheme 3. Reagents: i, $(\text{PhMe}_2\text{Si})_2\text{CuLi}$; ii, MeI; iii, EtI; iv, LiAlH_4 ; v, Bu^n_3P ; $o\text{-O}_2\text{NC}_6\text{H}_4\text{SeCN}$; vi, H_2O_2 ; vii, H_2O

tion step is followed immediately by an alkylation step. This gives overall the 1,2-disubstituted allylsilanes (18)–(20). It is also, of course, possible to have the future 2-substituent built into the starting material, as in the ester (21) which gave the ester (13) on treatment with the silylcuprate reagent. As it happens, the route from (5) to the esters (12), (13), and (14) took place with remarkably high diastereoselectivity, and the alternative route, (21)–(13), gave largely the opposite diastereoisomer. Since this is of no consequence to the work in this paper, we refrain from further comment at this stage, except to note that we are currently pursuing the implications of these observations.

The only cases in which we ran into serious difficulties were those in which we had two substituents on the β -carbon of the $\alpha\beta$ -unsaturated esters (5). Although two methyl groups in that position, (5c), gave us no trouble, a cyclopentane or cyclohexane ring spanning the β -position, caused complete failure in the conjugate addition.

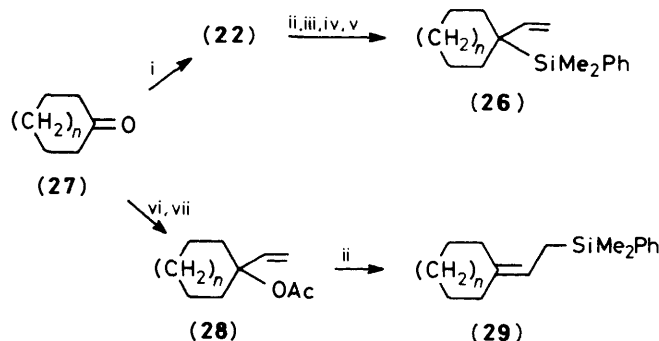
This problem was easily solved by the route shown in Scheme 4, which allowed us to make the allylsilanes (26). The conjugate



Scheme 4. Reagents: i, $(\text{PhMe}_2\text{Si})_2\text{CuLi}$; ii, LiCl, DMSO; iii, LiAlH_4 ; iv, Bu_3^nP ; $o\text{-O}_2\text{NC}_6\text{H}_4\text{SeCN}$; v, H_2O_2

addition steps (22)→(23) were not successful when we used phenyldimethylsilyl-lithium in place of the silyl cuprate reagent.

In summary, 1-substituted and 1,1- and 1,2-disubstituted allylsilanes can now be made, with complete control of regiochemistry. By obvious extensions, which we have not investigated, it should also be possible to make allylsilanes with higher levels of substitution. The route is versatile but not particularly cheap, and is at present useful only on a fairly small scale. It is, however, complementary to a synthesis of allylsilanes, which we introduced earlier.¹¹ As shown in Scheme 5, we can now start



Scheme 5. Reagents: i, $\text{CH}_2(\text{CO}_2\text{R})_2$, TiCl_4 , Py; ii, $(\text{PhMe}_2\text{Si})_2\text{CuLi}$; iii, LiCl, DMSO; iv, Bu_3^nP ; $o\text{-O}_2\text{NC}_6\text{H}_4\text{SeCN}$; v, H_2O_2 ; vi, $\text{CH}_2=\text{CHMgCl}$; vii, Ac_2O , DMAP

with a ketone (**27**; $n = 0$ or 1) and prepare either the allylsilanes (**26**), by the route described in this paper, or the isomeric allylsilanes (**29**), by way of the allylic acetates (**28**) and their reaction with the silyl-cuprate reagent.

Experimental

Light petroleum is the fraction b.p. 60–80 °C.

The Silylcupration Reaction.—Typically the $\alpha\beta$ -unsaturated ester (15 mmol) in dry THF (10 ml) was added dropwise to the cuprate reagent¹⁸ (16 mmol, based on CuCN) at -23 °C and stirring continued for a further 3 h. The solution was then allowed to warm to room temperature and quenched with ammonium chloride solution (25 ml). Light petroleum (75 ml) was added and the organic phase washed with aqueous alkaline ammonium chloride. The organic layer was dried (MgSO₄) and evaporated under reduced pressure. For preparative purposes the crude material was used directly in the next stage, but pure samples of the intermediates were obtained by t.l.c. (light petroleum–ethyl acetate, 10:1, v/v). The following compounds were prepared using this method: *methyl 3-dimethyl(phenyl)silyl-3-phenylpropanoate* (**6b**), an oil, R_F (light petroleum–ethyl acetate, 10:1 v/v) 0.22, v_{\max} (CHCl₃) 1 730 (C=O), 1 600, 1 580, and 1 500 (Ph), 1 255 (SiMe), and 1 120 cm⁻¹ (SiPh); δ (CCl₄) 7.60–6.95 (10 H, m, Ph), 3.50 (3 H, s, OMe), 3.00–2.65 (3 H, m, CHCH₂), and 0.30 and 0.25 (6 H, 2 s, SiMe₂) (Found: M^+ , 298.1369. C₁₈H₂₂O₂Si requires M , 298.1389), m/z 298 (40%, M^+), 135 (100, PhMe₂Si), and 104 (82, PhCHCH₂); *methyl 3-dimethyl(phenyl)silyl-3-methylbutanoate* (**6c**), an oil, R_F (light petroleum–ether, 95:5 v/v) 0.27, v_{\max} (neat) 1 740 (C=O), 1 600 (Ph), 1 250 (SiMe), and 1 115 cm⁻¹ (SiPh); δ (CCl₄) 7.50–7.00 (5 H, m, Ph), 3.50 (3 H, s, OMe), 2.15 (2 H, s, CH₂), 1.05 (6 H, s, CMe₂), and 0.40 (6 H, s, SiMe₂) (Found: M^+ – Me, 235.1163. C₁₄H₂₂O₂Si – Me requires M – Me, 235.1155), m/z 250 (3%, M^+), 235 (13, M – Me), 219 (5, M – OMe), and 135 (100, PhMe₂Si); *methyl 2-dimethyl(phenyl)silylcyclohexanecarboxylate*, an oil, R_F (light petroleum–ethyl acetate, 10:1 v/v) 0.42, v_{\max} (neat) 1 740 (C=O) and 1 255 cm⁻¹ (SiMe); δ (CCl₄) 7.70–7.35 (5 H, m, Ph), 3.65 (3 H, s, OMe), 2.75 (1 H, m, CHCO₂Me), 2.25–1.10 [9 H, m, (CH₂)₄CHSi], and 0.40 (6 H, s, SiMe₂) (Found: M^+ , 276.1548. C₁₆H₂₄O₂Si requires M , 276.1546), m/z 276 (19%, M), 261 (28, M – Me), 199 (50, M – Ph), and 135 (100, PhMe₂Si).

Compounds (**12**)–(**14**) were also prepared using the same silylcupration conditions, although for these after the 3 h period of stirring at -23 °C the appropriate alkyl iodide [methyl iodide for (**12**) and (**13**), ethyl iodide for (**14**)] (60 mmol) was added dropwise. Stirring was continued for 1 h at -23 °C and the reaction was worked up in the usual way. For preparative purposes the crude material was used directly in the next stage, but pure samples of the intermediates were obtained by flash column chromatography¹⁹ on silica (250 g) eluting with light petroleum–ethyl acetate (15:1 v/v). *Ethyl (2RS,3RS)-3-dimethyl(phenyl)silyl-2-methylbutanoate* (**12**) (as mainly one diastereoisomer) an oil (82%), R_F (light petroleum–ethyl acetate, 10:1 v/v) 0.35, v_{\max} (CHCl₃) 1 730 (C=O), and 1 115 cm⁻¹ (SiPh); δ (CCl₄) 7.65–7.30 (5 H, m, Ph), 4.05 (2 H, q, J 8 Hz, CH₂CH₃), 2.55 (1 H, dq, J 6 and 8 Hz, CHCO₂Et), 1.50 (1 H, dq, J 6 and 8 Hz, CHSi), 1.25 (3 H, t, J 8 Hz, CH₂CH₃), 1.05 and 0.95 (3 H each, d, J 8 Hz, CH₃CSi and CH₃CCO), and 0.35 (6 H, s, SiMe₂) (Found: M^+ , 264.1559. C₁₅H₂₄O₂Si requires M^+ , 264.1559), m/z 264 (15%, M^+), 249 (25, M – Me), and 135 (100, PhMe₂Si).

Methyl (2RS,3RS)-3-dimethyl(phenyl)silyl-2-methyl-3-phenylpropanoate (**13**) (as mainly one diastereoisomer, 97%),²⁰ an oil (88%), R_F (light petroleum–ethyl acetate, 10:1 v/v) 0.29, v_{\max} (CHCl₃) 1 730 (C=O), 1 600, 1 580, and 1 500 (Ph), and

1 255 cm⁻¹ (SiMe); δ (CCl₄) 7.55–6.85 (10 H, m, Ph), 3.40 (3 H, s, OMe), 2.95 (1 H, dq, J 7 and 12 Hz, CHCH₃), 2.55 (1 H, d, J 12 Hz, PhCH), 1.00 (3 H, d, J 7 Hz, CCH₃), and 0.25 and 0.15 (6 H, 2 s, SiMe₂) (Found: M^+ , 312.1549. C₁₉H₂₄O₂Si requires M , 312.1546), m/z 312 (12%, M), 297 (12, M – Me), and 135 (100, PhMe₂Si).

Methyl (2RS,3RS)-3-dimethyl(phenyl)silyl-2-ethyl-3-phenylpropanoate (**14**) (as mainly one diastereoisomer) an oil (81%), R_F (light petroleum–ethyl acetate, 3:1 v/v) 0.49, v_{\max} (neat) 1 740 (C=O), 1 600, 1 580, and 1 500 cm⁻¹ (Ph); δ (CCl₄) 7.65–6.85 (10 H, m, Ph), 3.40 (3 H, s, OMe), 2.85 (1 H, m, CHCO₂Me), 2.65 (1 H, d, J 11 Hz, PhCH), 1.45 (2 H, m, CH₂CH₃), 0.80 (3 H, t, J 7 Hz), and 0.35 and 0.20 (6 H, 2 s, SiMe₂) (Found: M^+ , 326.1696. C₂₀H₂₆O₂Si requires M , 326.1702), m/z 326 (19%, M^+), 297 (40, M – Et), 135 (78, PhMe₂Si), and 131 (100, PhC₄H₇).

The alternative method of preparing (**13**) used the normal silyl cupration conditions with (**21**) as the starting material. The product obtained in 84% was a 1:5 mixture of methyl (2RS,3RS)-3-dimethyl(phenyl)silyl-2-methyl-3-phenylpropanoate and methyl (2RS,3SR)-3-dimethyl(phenyl)silyl-2-methyl-3-phenylpropanoate,²⁰ R_F (light petroleum–ethyl acetate, 10:1 v/v) 0.31, v_{\max} (neat) 1 730 (CO), 1 600, and 1 500 cm⁻¹ (Ph); δ (CCl₄) 7.65–6.90 (5 H, m, Ph), 3.35 (3 H, s, OMe), 3.00 (1 H, dq, J 7 and 11 Hz, CHMe), 2.55 (1 H, d, J 11 Hz, PhCH), 1.10 (3 H, d, J 7 Hz, MeC), and 0.35 and 0.10 (6 H, 2 s, SiMe₂) (Found: M^+ , 312.1547. C₁₉H₂₄O₂Si requires M , 312.1545), m/z 312 (17%, M^+), 297 (20, M – Me), and 135 (100, PhMe₂Si).

The α,β -unsaturated diesters (**22a**) and (**22b**) gave, under normal silyl cupration conditions, the following compounds after flash column chromatography: *diethyl 2-[1-(dimethylphenylsilyl)cyclopentyl]malonate* (**23a**) an oil (70%), R_F (light petroleum–ethyl acetate, 3:1 v/v) 0.54, v_{\max} (neat) 1 730 and 1 760 cm⁻¹ (CO); δ (CCl₄) 7.65–7.25 (5 H, m, Ph), 4.05 [4 H, q, J 7 Hz, (CO₂CH₂)₂], 3.30 [1 H, s, CH(CO₂Et)₂], 2.10–1.20 [8 H, m, (CH₂)₄], 1.25 [6 H, t, J 7 Hz, (CO₂CCH₃)₂], and 0.35 (6 H, s, SiMe₂) (Found: M^+ – Me, 347.1666. C₂₀H₃₀O₄Si – Me requires M – Me, 347.1678), m/z 347 (0.5%, M – Me), 289 (48, M – CO₂Et), 135 (44, PhMe₂Si), and 109 (100, C₇H₈CHCO); *dimethyl 2-[1-(dimethylphenylsilyl)cyclohexyl]malonate* (**23b**) as plates (70%), m.p. 101–103 °C (from light petroleum) (Found: C, 65.4; H, 8.25. C₁₉H₂₈O₄Si requires C, 65.5; H, 8.10%), R_F (light petroleum–ethyl acetate, 10:1 v/v) 0.23, v_{\max} (Nujol mull) 1 735 cm⁻¹ (CO); δ (CCl₄) 7.65–7.20 (5 H, m, Ph), 3.90 [1 H, s, CH(CO)₂], 3.60 [6 H, s, (OMe)₂] 2.00–1.25 [10 H, m, (CH₂)₅], 0.35 (6 H, s, SiMe₂), m/z 348 (2%, M), 135 (40, PhMe₂Si), and 123 (100, C₆H₁₀CHCO).

The Dealkoxycarbonylation Reaction.—Following the method of Krapcho,²¹ typically the diester (2 mmol) in DMSO (8 ml), containing lithium chloride (4 mmol) and water (4 mmol) was refluxed for 45 min. After cooling, water (15 ml) was added and the reaction mixture extracted with ether (4 × 10 ml). The combined organic fractions were washed with water and brine, dried (Na₂SO₄), and the solvent removed under reduced pressure. The following compounds were obtained by t.l.c. (light petroleum–ethyl acetate, 10:1 v/v). *Ethyl (1-phenyldimethylsilylcyclopentyl)acetate* (**24a**) an oil (75%), R_F (light petroleum–ethyl acetate, 10:1 v/v) 0.45, v_{\max} (neat) 1 730 (CO), 1 260 (SiMe), and 1 120 cm⁻¹ (SiPh); δ (CCl₄) 7.65–7.30 (5 H, m, Ph), 4.05 (2 H, q, J 7 Hz, OCH₂), 2.25 (2 H, s, CH₂CO₂Et), 1.90–1.40 [8 H, m, (CH₂)₄], 1.25 (3 H, t, J 7 Hz, OCH₂CH₃), and 0.40 (6 H, s, SiMe₂) (Found: M^+ , 290.1709. C₁₇H₂₆O₂Si requires M , 290.1702), m/z 290 (8%, M) and 135 (100, PhMe₂Si); *methyl (1-phenyldimethylsilylcyclohexyl)acetate* (**24b**) an oil (90%), R_F (light petroleum–ethyl acetate, 10:1 v/v) 0.43, v_{\max} (neat) 1 735 cm⁻¹ (CO); δ (CCl₄) 7.65–7.25 (5 H, m, Ph), 3.50 (3 H, s, OMe), 2.40 (2 H, s, CH₂CO), 1.80–1.25 [10 H, m, (CH₂)₅], and 0.35 (6

H, s, SiMe₂) (Found: M^+ , 290.1700. C₁₇H₂₆O₂Si requires M , 290.1702), m/z 290 (13%, M^+) and 135 (100, PhMe₂Si).

The Ester to Alcohol Reduction.—Typically the crude silylcupration product (15 mmol) in dry ether (60 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (750 mg) in dry ether (60 ml) at room temperature under nitrogen. Stirring was continued for 1 h and saturated aqueous ammonium chloride was added dropwise until a separate aqueous phase formed. The organic layer was decanted off and the remaining reaction mixture extracted with more ether. The combined organic extracts were dried (MgSO₄) and evaporated under reduced pressure. Siloxane was removed by flash column chromatography¹⁹ on silica (250 g) eluting with light petroleum–ethyl acetate (15:1 v/v) and then the alcohol was collected by eluting with ethyl acetate. The following compounds were prepared using this method, with yields based on the α,β -unsaturated ester (%) and on the silyl ester [%]. 3-Dimethyl(phenyl)silylbutan-1-ol (**7a**), an oil (70%), R_F (light petroleum–ethyl acetate, 3:1 v/v) 0.27, v_{\max} (neat) 3 300 (OH), 1 250 (SiMe), and 1 105 cm⁻¹ (SiPh); δ (CCl₄) 7.65–7.35 (5 H, m, Ph), 3.70–3.45 (2 H, m, CH₂OH), 2.15 (1 H, br s, OH), 1.95–1.05 (3 H, m, CHCH₂), 1.00 (3 H, d, J 2 Hz, CMe), and 0.30 (6 H, s, SiMe₂) (Found: M^+ – Me, 193.1058. C₁₂H₂₀OSi – Me requires M – Me, 193.1049), m/z 193 (5%, M – Me), 137 (100, PhMeSiOH), and 135 (63, PhMe₂Si).

3-Dimethyl(phenyl)silyl-3-phenylpropan-1-ol (**7b**) an oil (75%), R_F (light petroleum–ethyl acetate, 5:1 v/v) 0.20, v_{\max} (neat) 3 320 (OH), 1 600, 1 580, and 1 500 (Ph), 1 255 (SiMe), and 1 120 cm⁻¹ (SiPh); δ (CCl₄) 7.60–6.95 (10 H, m, Ph), 3.65–3.25 (2 H, m, CH₂OH), 2.50 (1 H, t, J 8 Hz, PhCH), 2.15–1.85 (2 H, m, PhCCH₂), 1.90 (1 H, s, OH), and 0.35 and 0.30 (6 H, 2 s, SiMe₂) (Found: M^+ , 270.1450. C₁₇H₂₂OSi requires M , 270.1432), m/z 270 (0.06%, M^+), 255, M – Me), 135 (58, PhMe₂Si), and 118 (100, PhCHCH₂CH₂).

3-dimethyl(phenyl)silyl-3-methylbutan-1-ol (**7c**) an oil (67%), R_F (Et₂O) 0.61, v_{\max} (neat) 3 360 (OH) and 1 255 cm⁻¹ (SiMe); δ (CCl₄) 7.75–7.30 (5 H, m, Ph), 3.70 (2 H, t, J 8 Hz, CH₂O), 3.20 (1 H, br s, OH), 1.70 (2 H, t, J 8 Hz, CCH₂C), 1.10 (6 H, s, CMe₂), and 0.50 (6 H, s, SiMe₂) (Found: M^+ – Me, 207.1205. C₁₃H₂₂OSi – Me requires M – Me, 207.1205), m/z 207 (1%, M – Me), 152 (12, PhMeSiOH), 137 (100, PhMeSiOH), and 135 (99, PhMe₂Si).

2-Dimethyl(phenyl)silylcyclohexanemethanol (**10**) an oil (60%), R_F (light petroleum–ethyl acetate, 3:1 v/v) 0.28, v_{\max} (CHCl₃) 3 300 (OH) and 1 250 cm⁻¹ (SiMe); δ (CCl₄) 7.60–7.25 (5 H, m, Ph), 3.55 (2 H, d, J 7 Hz, CH₂O), 2.05–0.70 [10 H, m, CH(CH₂)₄CH], and 0.30 and 0.25 (6 H, 2 s, SiMe₂) (Found: M^+ – Me, 233.1355. C₁₅H₂₄OSi – Me requires M – Me, 233.1358); m/z 233 (1.7%, M – Me), 137 (100, PhMeSiOH), and 135 (69, PhMe₂Si); 3-dimethyl(phenyl)silyl-2-methylbutan-1-ol (**15**) an oil (78%) [95%], R_F (light petroleum–ethyl acetate, 3:1 v/v) 0.31, v_{\max} (CHCl₃) 3 360 (OH), 1 255 (SiMe), and 1 120 cm⁻¹ (SiPh); δ (CCl₄) 7.70–7.35 (5 H, m, Ph), 3.45 (2 H, 2 d, J 7 and 8 Hz, CH₂O), 2.50 (1 H, s, OH), 1.95 (1 H, dtq, J 4, 8, and 8 Hz, CHCO), 1.35 (1 H, dq, J 4 and 8 Hz, CHSi), 1.05 and 0.85 (3 H each, d, J 8 Hz, CH₃CSi and CH₃CCO), and 0.40 (6 H, s, SiMe₂) (Found: M^+ – Me, 207.1189. C₁₃H₂₂OSi – Me requires M – Me 207.1205), m/z 207 (3, M – Me), 137 (75, PhMeSiOH), 135 (75, PhMe₂Si), and 70 [100, CH₃CHCH(CH₂)CH₃].

3-Dimethyl(phenyl)silyl-2-methyl-3-phenylpropan-1-ol (**16**) an oil (79%) [90%], R_F (light petroleum–ethyl acetate 1:1 v/v) 0.37, v_{\max} (CHCl₃) 3 450 (OH), 1 600, 1 580, and 1 500 (Ph), 1 255 (SiMe), and 1 115 cm⁻¹ (SiPh); δ (CCl₄) 7.75–7.10 (10 H, m, Ph), 3.45 (2 H, m, CH₂O), 2.55 (1 H, d, J 8 Hz, PhCH), 2.25 (1 H, m, PhCC H), 1.80 (1 H, br s, OH), 0.95 (3 H, d, J 6 Hz, CCH₃), and 0.50 and 0.25 (6 H, 2 s, SiMe₂) (Found: M^+ – Me, 269.1372.

C₁₈H₂₄OSiMe requires M – Me, 269.1361), m/z 269 (1%, M – Me), 135 (92, PhMe₂Si), 132 (95, M – PhMe₂SiOH), and 117 (100, PhCHCH₂).

3-Dimethyl(phenyl)silyl-2-ethyl-3-phenylpropan-1-ol (**17**) an oil 77% [95%], R_F (light petroleum–ethyl acetate, 3:1 v/v) 0.35, v_{\max} (neat) 3 360 (OH), 1 600, 1 580 and 1 500 (Ph), 1 260 (SiMe), and 1 130 cm⁻¹ (SiPh); δ (CCl₄) 7.60–6.95 (10 H, m, Ph), 3.45 (2 H, d, J 4 Hz, CH₂O), 2.50 (1 H, d, J 9 Hz, PhCH), 1.95 (1 H, m, PhCH H), 1.80 (1 H, br s, OH), 1.30 (2 H, m, CH₂CH₃), 0.80 (3 H, t, J 7 Hz, CMe), and 0.35 and 0.05 (6 H, 2 s, SiMe₂) (Found: M^+ – Me, 283.1522. C₁₉H₂₆OSi – Me requires M – Me, 283.1518), m/z 283 (0.3%, M – Me), 146 (95, M – PhMe₂-SiOH), 135 (98, PhMe₂Si), and 117 (100, PhC₃H₄).

2-[1-(Dimethylphenylsilyl)cyclopentyl]ethanol (**25a**) an oil (52%) [98%], R_F (light petroleum–ethyl acetate, 3:1 v/v) 0.32, v_{\max} (neat) 3 300 (OH), 1 255 (SiMe), and 1 115 cm⁻¹ (SiPh); δ (CCl₄) 7.75–7.30 (5 H, m, Ph), 3.55 (2 H, t, J 8 Hz, CH₂O), 3.25 (1 H, br s, OH), 1.90–1.40 [10 H, m, (CH₂)₄CCH₂], and 0.40 (6 H, s, SiMe₂) (Found: M^+ – Me, 233.1345. C₁₅H₂₄OSi – Me requires M – Me 233.1362), m/z 233 (0.8%, M – Me), 137 (100, PhMe₃SiOH), and 135 (98, PhMe₂Si).

2-[1-(Phenyldimethylsilyl)cyclohexyl]ethanol (**25b**) an oil (61%) [96%], R_F (light petroleum–ethyl acetate, 3:1 v/v) 0.29, v_{\max} (neat) 3 300 cm⁻¹ (OH); δ (CCl₄) 7.65–7.25 (5 H, m, Ph), 3.50 (2 H, t, J 8 Hz, CH₂O), 2.20 (1 H, s, OH), 1.80 (2 H, t, J 8 Hz, CH₂CO), 1.70–1.35 [10 H, m, (CH₂)₅], 0.35 (6 H, s, SiMe₂) (Found: M^+ – Me, 247.1530. C₁₆H₂₆OSi – Me requires M – Me, 247.1518), m/z 247 (0.2%, M – Me), 137 (70, PhMeSiOH), and 135 (100, PhMe₂Si).

The Allylsilanes by Alcohol Dehydration.—The dehydrations were carried out using the method of Grieco *et al.*¹⁵ Typically tri-*n*-butylphosphine (6 mmol) was added over 5 min to a stirred solution of the alcohol (5 mmol) and *o*-nitrophenylselenocyanate²² (6 mmol) in dry THF (50 ml) at room temperature under nitrogen. Stirring was continued for a further 1 h. The solvent was removed under reduced pressure and the crude selenoxide redissolved in dichloromethane (50 ml) containing pyridine (10 mmol). Hydrogen peroxide (50 mmol, 100 vol) was added over 10 min at 0 °C and after the solution had been allowed to warm to room temperature stirring was continued for 24 h. Water (50 ml) was added and the organic layer washed with aqueous sodium hydrogencarbonate (25 ml), aqueous copper sulphate (25 ml), and brine (25 ml), and then dried (Na₂SO₄) and the solvent removed under reduced pressure. The following compounds were obtained after flash column chromatography on silica (250 g) eluting with light petroleum–ethyl acetate (10:1 v/v).

3-Dimethyl(phenyl)silylbut-1-ene (**8a**) an oil (50%) b.p. 48–52 °C/0.2 mmHg, R_F (light petroleum–ethyl acetate, 10:1 v/v) 0.65, v_{\max} (neat) 1 635 (C=C), 1 600, and 1 500 (Ph), 1 260 (SiMe), and 1 120 cm⁻¹ (SiPh); δ (CCl₄) 7.65–7.35 (5 H, m, Ph), 5.95 (1 H, ddd, J 17, 12 and 8 Hz, HC=CH_AH_B), 4.95 (1 H, ddd, J 12, 2 and 2 Hz, HC=CH_AH_B), 4.90 (1 H, ddd, J 17, 2 and 2 Hz, HC=CH_AH_B), 1.95 (1 H, m, CHSi), 1.15 (3 H, d, J 8 Hz, CCH₃), and 0.40 (6 H, s, SiMe₂) (Found: M^+ , 190.1176. C₁₂H₁₈Si requires M , 190.1177), m/z 190 (0.6%, M^+), and 135 (100, PhMe₂Si).

3-Dimethyl(phenyl)silyl-3-phenylprop-1-ene (**8b**) an oil (73%), R_F (light petroleum–ethyl acetate, 10:1 v/v) 0.65, v_{\max} (neat) 1 630 (C=C), 1 600, 1 580 and 1 500 (Ph), and 1 255 cm⁻¹ (SiMe); δ (CCl₄) 7.75–6.95 (10 H, m, Ph), 6.25 (1 H, ddd, J 9, 10 and 16 Hz, HC=CH_AH_B), 5.05 (1 H, dd, J 1 and 9 Hz, HC=CH_AH_B), 4.95 (1 H, dd, J 1 and 16 Hz, HC=CH_AH_B), 3.25 (1 H, d, J 10 Hz, PhCH), and 0.45 and 0.40 (6 H, 2 s, SiMe₂) (Found: M^+ , 252.1318. C₁₇H₂₀Si requires M , 252.1334), m/z 252 (6%, M^+) and 135 (100, PhMe₂Si).

3-Dimethyl(phenyl)silyl-3-methylbut-1-ene (**8c**) an oil (51%) b.p. 58–65 °C/0.2 mmHg, R_F (light petroleum–ethyl acetate,

10:1 v/v) 0.63, v_{\max} (neat) 1 635 (C=C), 1 600 and 1 500 (Ph), 1 260 (SiMe), and 1 120 cm^{-1} (SiPh); $\delta(\text{CCl}_4)$ 7.65–7.30 (5 H, m, Ph), 5.85 (1 H, dd, J_{11} and 17 Hz, $\text{HC}=\text{CH}_2$), 4.90 (1 H, dd, J_{11} and 2 Hz, $\text{HC}=\text{CH}_A\text{H}_B$), 4.75 (1 H, dd, J_{17} and 2 Hz, $\text{HC}=\text{CH}_A\text{H}_B$), 1.05 (6 H, s, CMe_2), and 0.30 (6 H, s, SiMe_2) (Found: M^+ , 204.1325. $\text{C}_{13}\text{H}_{20}\text{Si}$ requires M , 204.1335), m/z 204 (0.3%, M^+) and 135 (100, PhMe_2Si).

2-Dimethyl(phenyl)silyl(methylene)cyclohexane (11) an oil (35%), R_F (light petroleum–ethyl acetate, 10:1 v/v) 0.65, v_{\max} (CHCl_3) 1 625 (C=C), 1 250 (SiMe), and 1 115 cm^{-1} (SiPh); $\delta(\text{CCl}_4)$ 7.65–7.25 (5 H, m, Ph), 4.60 and 4.50 (2 H, 2 br s, $=\text{CH}_2$), 2.20–0.70 [9 H, m, $(\text{CH}_2)_4\text{CH}$], and 0.40 and 0.35 (6 H, 2 s, SiMe_2) (Found: M^+ , 230.1490. $\text{C}_{15}\text{H}_{22}\text{Si}$ requires M , 230.1491), m/z 230 (3.4%, M^+) and 135 (100, PhMe_2Si).

3-Dimethyl(phenyl)silyl-2-methylbut-1-ene (18) an oil (65%), R_F (light petroleum–ethyl acetate, 10:1 v/v) 0.68; $\delta(\text{CCl}_4)$ 7.55–7.15 (5 H, m, Ph), 4.60 and 4.45 (2 H, 2 br s, $=\text{CH}_2$), 1.90 (1 H, m, CHSi), 1.65 (3 H, s, $\text{CH}_3\text{C}=\text{C}$), 1.20 (3 H, d, J 6 Hz, CH_3CSi), and 0.40 (6 H, s, SiMe_2) (Found: M^+ , 204.1334. $\text{C}_{13}\text{H}_{20}\text{Si}$ requires M , 204.1335), m/z 204 (2%, M^+) and 135 (100, PhMe_2Si).

3-Dimethyl(phenyl)silyl-2-methyl-3-phenylpropene (19) an oil (42%), R_F (light petroleum–ethyl acetate, 10:1 v/v) 0.59, v_{\max} (CHCl_3) 1 630 (C=C), and 1 600 and 1 580 cm^{-1} (Ph); $\delta(\text{CCl}_4)$ 7.55–6.95 (10 H, m, Ph), 4.85 and 4.80 (2 H, 2 br s, $=\text{CH}_2$), 3.05 (1 H, s, PhCH), 0.65 (3 H, s, CMe), and 0.35 and 0.30 (6 H, 2 s, SiMe_2) (Found: M^+ , 266.1487. $\text{C}_{18}\text{H}_{22}\text{Si}$ requires M , 266.1487), m/z 266 (10%, M^+) and 135 (100, PhMe_2Si).

3-Dimethyl(phenyl)silyl-2-ethyl-3-phenylprop-1-ene (20) an oil (40%), R_F (light petroleum–ethyl acetate, 10:1 v/v) 0.60, v_{\max} (neat) 1 640 (C=C), 1 600, 1 580, and 1 500 cm^{-1} (Ph); $\delta(\text{CCl}_4)$ 7.55–6.90 (10 H, m, Ph), 4.90 (2 H, m, $=\text{CH}_2$), 3.05 (1 H, s, PhCH), 1.95 (2 H, q, J 8 Hz, CH_2CH_3), 0.95 (3 H, t, J 8 Hz, CMe), and 0.40 and 0.30 (6 H, 2 s, SiMe_2) (Found: M^+ , 280.1643. $\text{C}_{19}\text{H}_{24}\text{Si}$ requires M , 280.1647), m/z 280 (11%, M^+) and 135 (100, PhMe_2Si).

1-Dimethyl(phenyl)silylcyclopentylethene (26a) an oil (65%), R_F (light petroleum–ethyl acetate, 10:1 v/v) 0.68, v_{\max} (neat) 1 625 (C=C), 1 250 (SiMe), and 1 120 cm^{-1} (SiPh); $\delta(\text{CCl}_4)$ 7.55–7.20 (5 H, m, Ph), 5.65 (1 H, dd, J_{11} and 18 Hz, $\text{HC}=\text{CH}_2$), 4.85 (1 H, dd, J_{11} and 2 Hz, $\text{HC}=\text{CH}_A\text{H}_B$), 4.65 (1 H, dd, J_2 and 11 Hz, $\text{HC}=\text{CH}_A\text{H}_B$), 1.75–1.30 [8 H, m, $(\text{CH}_2)_4$], and 0.20 (6 H, s, SiMe_2) (Found: M^+ , 230.1495. $\text{C}_{15}\text{H}_{22}\text{Si}$ requires M , 230.1490), m/z 230 (0.6%, M^+) and 135 (100, PhMe_2Si).

1-Dimethyl(phenyl)silylcyclohexylethene (26b) an oil (75%), R_F (light petroleum–ethyl acetate, 10:1 v/v) 0.68, v_{\max} (neat) 1 635 (C=C) and 1 260 cm^{-1} (SiMe); $\delta(\text{CCl}_4)$ 7.50–7.20 (5 H, m, Ph), 5.50 (1 H, dd, J_{11} and 18 Hz, $\text{HC}=\text{CH}_2$), 5.05 (1 H, dd, J_{11} and 2 Hz, $\text{HC}=\text{CH}_A\text{H}_B$), 4.70 (1 H, dd, J_{18} and 2 Hz, $\text{HC}=\text{CH}_A\text{H}_B$), 1.80–1.20 [10 H, m, $(\text{CH}_2)_5$], and 0.20 (6 H, s, SiMe_2) (Found: M^+ , 244.1639. $\text{C}_{16}\text{H}_{24}\text{Si}$ requires M , 244.1648), m/z 244 (0.6%, M^+) and 135 (100, PhMe_2Si).

Acknowledgements

We thank the S.E.R.C. for a maintenance award (D. W.) and Danny Levin for first carrying out the sequence (5c)→(8c).²³

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Received 16th September 1983; Paper 3/1627