The Regiochemistry of the Protodesilylation of Some Cyclopropylmethylsilanes Derived from Allylsilanes

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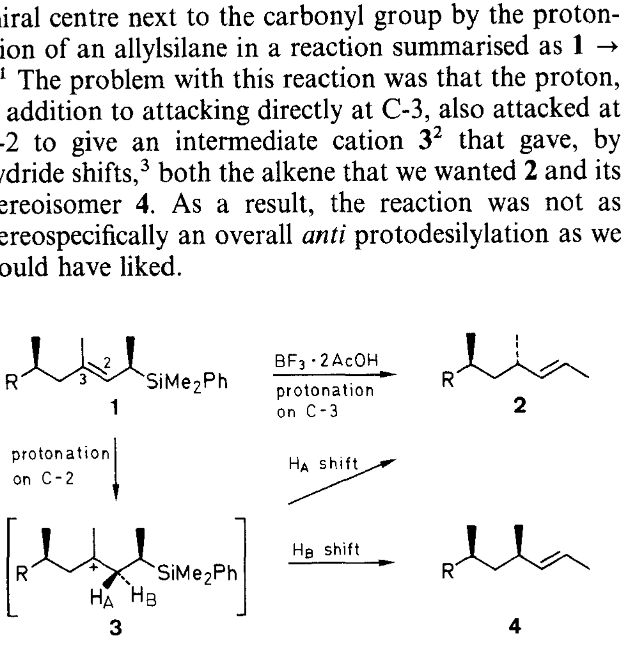
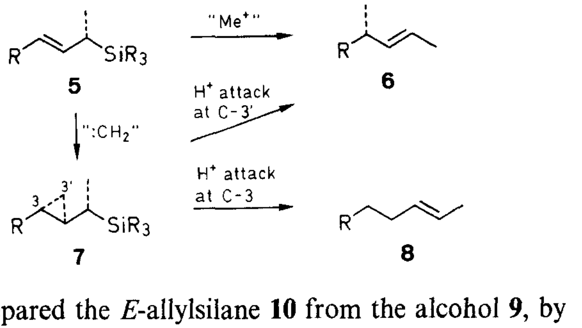
Simmons–Smith type methylenation of allylsilanes, followed by protodesilylation, can be used to achieve overall the S_E2' replacement of the silyl group by a methyl group. The regioselectivity is good for protonation on the methylene carbon of the cyclopropylmethylsilanes **11**, **17**, **20** and **23**, but the low stereoselectivity in the formation of the cyclopropylmethylsilane **26** and its failure to undergo clean protodesilylation make the method of limited use.

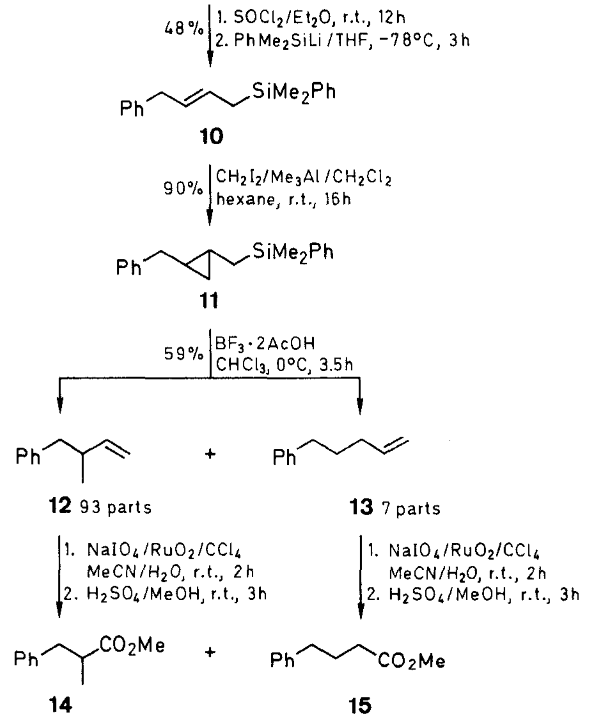
In our work on the synthesis of the Prelog–Djerassi lactone, we controlled the relative stereochemistry of the chiral centre next to the carbonyl group by the protonation of an allylsilane in a reaction summarised as **1** → **2**.[1] The problem with this reaction was that the proton, in addition to attacking directly at C-3, also attacked at C-2 to give an intermediate cation **3**[2] that gave, by hydride shifts,[3] both the alkene that we wanted **2** and its stereoisomer **4**. As a result, the reaction was not as stereospecifically an overall *anti* protodesilylation as we would have liked.



One solution of this problem would be to use an allylsilane with a disubstituted double bond **5**, and to methylate it in the sense (**5** → **6**). Allylsilanes with disubstituted double bonds do not suffer the same problem as allylsilanes like **1** with trisubstituted double bonds, and they react with electrophiles with a high level of *anti* stereospecificity,[4] other things being equal.[5] The problem with the idea of using methylation is that allylsilanes do not react with methyl halides. Two ways round this difficulty suggested themselves: to use phenylthiomethylation[6] followed by desulphurisation, and to use a Simmons–Smith type of reaction (**5** → **7**), followed by protodesilylation (**7** → **6**) of the cyclopropylmethylsilane. Protodesilylations and a few other electrophilic substitution reactions of some simple cyclopropylmethylsilanes were known,[7] but it was not known how selectively the proton would attack the unsubstituted carbon, C-3′, to give the alkene **6**, rather than the substituted carbon, C-3, to give the alternative alkene **8**. It is however known that when one of the substituents on C-3 of the cyclopropane is a carboalkoxy group, protonation on the carbonyl oxygen ensures that the bond to C-3 breaks,[8] and more recently, a few Lewis acids have been found to attack selectively the methylene carbon C-3′ rather than a methine or quaternary carbon C-3.[9] In this paper we briefly address the question of which carbon is attacked by a proton, and show that the level of selectivity in the sense that we want (**5** → **6**) is high. We should mention here that a very preliminary investigation of this problem had led us to believe that the selectivity was not high, and these results, which should now be discounted, did find their way into print.[10]

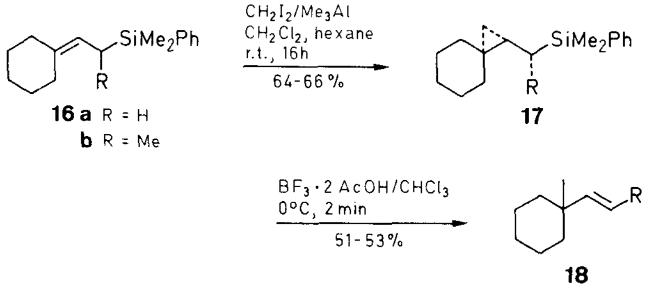


We prepared the *E*-allylsilane **10** from the alcohol **9**, by way of the allyl chlorides, following Smith and her coworkers.[11] When we used our own method,[12] by way of the allylic acetate derived from the alcohol **9**, we obtained the allylsilane **10** as an inconvenient 45:55 mixture of *E* and *Z* isomers. The allylsilane **10** gave the cyclopropylmethylsilane **11** in a version of the Simmons–Smith reaction due to Yamamoto,[13] which we find to be superior to other methods.[14] The protodesilyl-

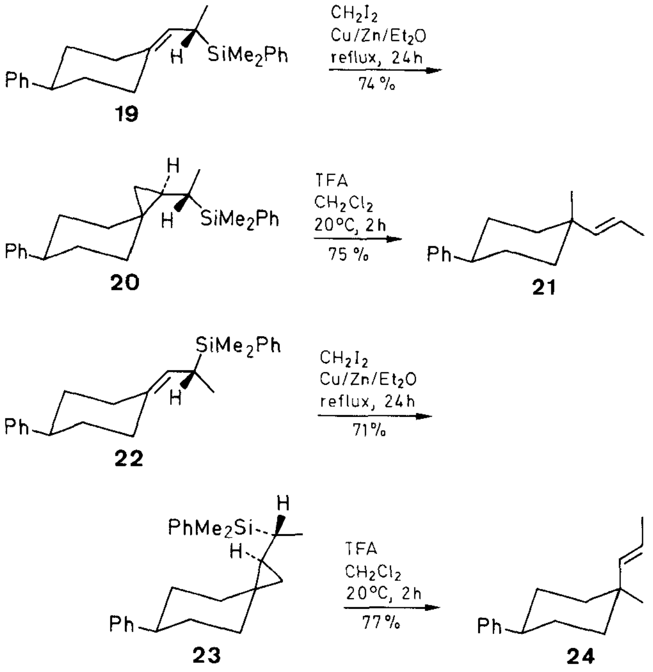


ation of this compound using the boron trifluoride–acetic acid complex[15] took three and a half hours at room temperature to go to completion, and gave a mixture of the alkenes, **12** and **13**. We measured the proportion of these two products by converting them to the methyl esters, **14** and **15**, which were cleanly separable on gas chromatography, and identifiable by comparison with authentic samples. The GC ratio, 93 : 7, was in agreement with an approximate measure taken from the ^{1}H NMR spectrum, showing that the yield in the oxidation and methylation steps was probably very similar for each of the alkenes. The protodesilylation had evidently taken place very largely by proton attack at the less substituted carbon atom, C-3′.

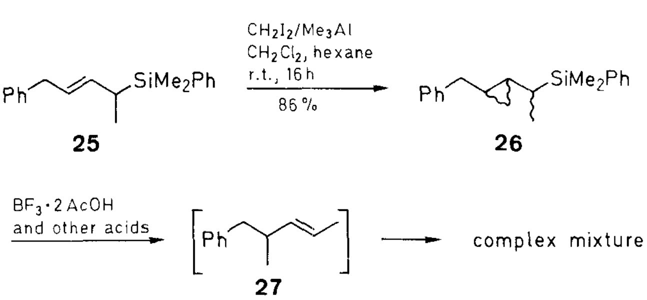
The allylsilane **16a**[12] gave the cyclopropylmethylsilane **17a**, protodesilylation of which took place rapidly at 0 °C in chloroform to give, as far as we could tell (^{1}H NMR), only the alkene **18a**. In particular, the integration of all the olefinic signals to that of the methyl singlet was 1 : 1. Protodesilylation was evidently very selective for proton attack on the methylene carbon over the quaternary carbon.



Methylenation of the allylsilane **16b**[5] gave only one diastereoisomer of the cyclopropylmethylsilane **17b**, as expected,[5] and protodesilylation of this compound in an NMR experiment cleanly gave the appropriate signals for the alkene **18b**. Furthermore, the allylsilanes **19** and **22**[5] each gave a single cyclopropylmethylsilane, **20** and **23**, respectively. Evidently the chiral centre adjacent to the silicon atom is powerful enough, as it is not in most other reactions that we have looked at,[5] to induce methylenation *anti* to the silyl group, overcoming any axial or equatorial preference stemming from the fixed cyclohexane ring conformation. Protodesilylation of these two cyclopropylmethylsilanes cleanly gave the isomeric alkenes **21** and **24**, respectively, to which relative configurations could be assigned with some confidence, by a ^{13}C chemical shift correlation with some similar compounds.[16]



However, in spite of these promising precedents, there is a problem in generalising this method for introducing a methyl group stereoselectively. Although the reactions (**16b** → **17b**, **19** → **20** → **21**, and **22** → **23** → **24**) are stereochemically very well behaved, we already knew from other work, that allylsilanes with an *E*-disubstituted double bond and a methyl group on C-1 do not give good stereochemical control in methylenation and similar reactions.[17] In agreement with this observation, the allylsilane **25**, prepared in three steps from 1-phenyl-3-pentyn-2-ol using our urethane protocol,[18] gave a 58 : 42 mixture of diastereoisomeric cyclopropylmethylsilanes **26**. The ratio was insignificantly changed to 66 : 34 using the method of cyclopropanation involving treatment with Seyferth's reagent[19] followed by reductive debromination. Furthermore, the protodesilyation of this compound, even under carefully monitored conditions that led to incomplete consumption of starting material, gave a complex mixture of alkene products. We presume that the alkene **27** is formed cleanly, by analogy with the work described above, but that this alkene is attacked by the acid at a rate that is comparable to the rate of its formation. The more hindered double bond of the alkenes **18b**, **21** and **24**, presumably protects these products from a similar fate, and the monosubstituted alkenes **12** and **18a** are evidently much less easily protonated than their cyclopropane precursors **11** and **17a**.



We conclude that, at least as developed so far, this method for the introduction of a methyl group onto an allylsilane in two steps, although highly regioselective in a desirable sense, is severely compromised by the lack of stereochemical control in some cases and by the reactivity of the double bond in the product of the protodesilylation reaction.

Light petroleum refers to the fraction bp 60–80 °C. THF was freshly distilled from lithium aluminium hydride under nitrogen.

Table 1. Preparation of Cyclopropylmethylsilanes

Product	Method	Yield (%)	Molecular Formula[a]	IR (film) ν (cm^{-1})	^{1}H NMR (CDCl$_3$/TMS, 90 MHz) δ, J (Hz)	MS (70 eV) m/z (%)
11	A	90	$C_{19}H_{24}Si$ (280.2)	1600, 1580, 1240, 1105	0.2–0.9 (m, 6H, remainder), 0.3 (s, 6H, SiMe$_2$), 2.4 (dd, J = 15 and 7, 1H, PhC$\underline{H}_A$CH$_B$), 2.6 (dd, J = 15 and 6, 1H, PhCH$_A$C$\underline{H}_B$), 7.1–7.7 (m, 10H, 2Ph)	280 (M$^+$, 0.3%), 135 (100)
17a	A	64	$C_{17}H_{26}Si$ (258.2)	1245, 1110	0.35–1.6 (m, 15H, remainder), 0.3 (s, 6H, SiMe$_2$), 7.3–7.7 (m, 5H, Ph)	258 (M$^+$, 5%), 180 (4) and 135 (100)
17b	A B	66 65	$C_{18}H_{28}Si$ (272.2)	1245, 1110	0.29 (s, 3H, Si$\underline{Me}_A$Me$_B$), 0.30 (s, 3H, SiMe$_A\underline{Me}_B$), 0.30–1.70 (m, 13H, remainder), 0.95 (d, J = 7.1, 3H, CH$\underline{Me}$), 7.32–7.35 (m, Ph *m*- and *p*- H's, 3H), 7.48–7.53 (m, 2H, Ph *o*- H's)[b]	272 (M$^+$, 2), 194 (17), 135 (100)
20	B	74	$C_{24}H_{32}Si$ (348.2)	1430, 1255, 1118	−0.08 (m, 1H, cyclopropyl-C$\underline{H}_A$H$_B$), 0.35 (s, 3H, Si$\underline{Me}_A$Me$_B$), 0.36 (s, 3H, SiMe$_A\underline{Me}_B$), 0.40 (m, 1H, cyclopropyl-CH$_A\underline{H}_B$), 0.56 (m, 2H, 2 × CH), 1.02 (d, J = 6.9, 3H, $\underline{Me}$CH), 0.82–1.88 (m, 8H, remainder), 2.45 (tt, J = 11.9 and 3.5, 1H, PhC$\underline{H}$), 7.17–7.58 (m, 10H, 2 × Ph)[b]	348 (M$^+$, 2), 270 (23), 212 (18), 161 (19), 135 (100)
23	B	71	$C_{24}H_{32}Si$ (348.2)	1427, 1250, 1115	0.09 (dd, J = 4.1 and 5, 1H, cyclopropyl-C$\underline{H}_A$H$_B$), 0.32 (dd, J = 4.1 and 8.3, 1H, cyclopropyl-CH$_A\underline{H}_B$), 0.39 (s, 3H, Si$\underline{Me}_A$Me$_B$), 0.41 (s, 3H, SiMe$_A\underline{Me}_B$), 0.67–0.78 (m, 2H, 2 × CH), 0.94 (d, J = 7.1, 3H, $\underline{Me}$CH), 1.03–1.80 (m, 8H, remainder), 2.56 (tt, J = 10.7 and 3.2, 1H, Ph$\underline{H}$), 7.15–7.60 (m, 10H, 2 × Ph)[b]	348 (M$^+$, 8), 270 (12), 212 (10), 161 (13), 135 (100)
26	A B	86[c] 40[d]	$C_{20}H_{26}Si$ (294.2)	1245, 1110	0.0–1.0 (m, 5H, remainder), 0.35 (s, 3H, Si$\underline{Me}_A$Me$_B$), 0.4 (s, 3H, SiMe$_A\underline{Me}_B$), 0.95 (m, 3H, Me), 2.05–2.85 (m, 2H, PhC$\underline{H}_2$), 7.0–7.7 (m, 10H, 2 × Ph)[e]	294 (M$^+$, 7%), 135 (100)

[a] Satisfactory HRMS obtained: m/z ±0.0028.

[b] Spectrum taken at 250 MHz.

[c] 2 Diastereoisomers present in ratio (GC) of 52 : 48, with the major isomer eluting first.

[d] 2 Diastereoisomers present in ratio (GC) of 42 : 58, with the minor isomer eluting first.

[e] Spectrum taken in CCl$_4$.

Table 2. Protodesilylation of Cyclopropylmethylsilanes

Product	Method	Yield (%)	Molecular Formula	IR (film) ν (cm^{-1})	^{1}H NMR (CDCl$_3$/TMS, 250 MHz), δ, J (Hz)	^{13}C NMR (CDCl$_3$/TMS), δ	MS (70 eV) m/z (%)
12 + **13**	A[a]	59			**12:** 1.02 (d, J = 6.5, 3H, Me), 2.45–2.76 (m, 3H, PhC$\underline{H}_2$C$\underline{H}$), 4.92–5.02 (m, 2H, CH=C$\underline{H}_2$), 5.87 (ddd, J = 17.1, 10.4 and 6.5, 1H, C$\underline{H}$=CH$_2$), 7.20–7.66 (m, 5H, Ph) + **13:** 1.78 (quint, J = 7, C-4 CH$_2$)[b]		
18a	A	53			1.25–1.55 [m, 10H, (CH$_2$)$_5$], 0.97 (s, 3H, Me), 4.89–4.98 (m, 2H, CH=C$\underline{H}_2$), 5.79 (dd, J = 18.0 and 10.5, 1H, C$\underline{H}$=CH$_2$)		
18b	A	51	$C_{10}H_{18}$ (138.2)[d]	980	0.88 (s, 3H, Me), 1.2–1.7 [m, 10H, (CH$_2$)$_5$], 1.6 (d, J = 4, 3H, CH=CH$\underline{Me}$), 5.4–5.2 (m, 2H, CH=CH)[c]		
21	B	75	$C_{16}H_{22}$ (214.2)[d]	980	1.06 (s, 3H, Me), 1.67 (d, J = 4.9, 3H, C=CH$\underline{Me}$), 1.21–2.00 (m, 8H, 2 × CH$_2$CH$_2$), 2.44 (m, 1H, PhC$\underline{H}$), 5.36 (dq, J = 15.9 and 4.9, 1H, C=C$\underline{H}$Me), 5.47 (d, J = 15.9, 1H, C$\underline{H}$=CHMe), 7.14–7.33 (m, 5H, Ph)	18.1, 22.3,[e] 29.8, 34.7, 37.8, 44.4, 119.3, 125.8, 126.8, 128.3, 144.2,[e] 147.9	214 (M$^+$, 48), 130 (100), 104 (47), 91 (62)
24	B	77[f]	$C_{16}H_{22}$ (214.2)[d]	980	1.00 (s, 3H, Me), 1.74 (d, J = 4.5, 3H, C=CH$\underline{Me}$), 1.37–1.80 (m, 8H, 2 × CH$_2$CH$_2$), 2.44 (m, 1H, PhC$\underline{H}$), 5.45 (dq, J = 13.2 and 4.5, 1H, C=C$\underline{H}$Me), 5.47 (d, J = 13.2, C$\underline{H}$=CHMe), 7.15–7.33 (m, 5H, Ph)	18.3, 30.4, 31.9,[g] 35.4, 38.8, 44.5, 122.4, 125.8, 126.9, 128.2, 138.8,[g] 147.8	214 (M$^+$, 76), 157 (43), 143 (67), 130 (78), 104 (85), 91 (100)

[a] This reaction took 3.5 h, not 2 min.

[b] The integration of this signal relative to the rest of the spectrum was consistent with the 93 : 7 ratio of **12** to **13**.

[c] Spectrum 90 MHz.

[d] Satisfactory HRMS obtained: m/z ±0.0005.

[e] These signals allow the assignment of the relative configuration to **21**, since they are consistent with an axial methyl group.[16]

[f] A minor byproduct (4%) was also isolated and assigned the structure 1-(1-methylpropyl)-4-phenylcyclohexene as a mixture of diastereoisomers. HRMS: (m/z), $C_{16}H_{22}$, 214.1722 (M$^+$); found: 214.1724. MS (70 eV): m/z (%) = 214 (M$^+$, 52), 157 (38), 143 (35), 130 (48), 129 (54), 104 (100). IR (film) ν = 1600, 1496, 768, 715 cm^{-1}; ^{1}H NMR(CDCl$_3$/TMS): δ = 1.1–2.45 (m, 9H, remainder), 0.83 (t, J = 6.6 Hz, 3H, CH$_2\underline{Me}$), 0.99 (d, J = 4 Hz, 3H, CH$\underline{Me}$), 2.82 (m, 1H, PhC$\underline{H}$), 5.45 (m, 1H, C=CH), 7.14–7.36 (m, 5H, Ph).

[g] These signals allow the assignment of the relative configuration to **24**, since they are consistent with an equatorial methyl group.[16]

CH_2Cl_2 was distilled from phosphorus pentoxide under nitrogen. Et_2O was distilled from phosphorus pentoxide, and was stored over sodium wire. All other solvents were distilled before use. Ammonium chloride solution was adjusted to pH 8 by the addition of aqueous ammonia. Column chromatography was carried out using Merck Kieselgel 60 (70–230, or 230–400 mesh ASTM). TLC was performed on plates coated with Kieselgel 60 PF_{254}. For preparative TLC the plates were coated to a thickness of 1 mm. Melting points were measured using a Buchi 510 apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1310 grating spectrophotometer. ^1H NMR spectra were recorded on Varian EM 390 (90 MHz) and Bruker WM-250 (250 MHz) spectrometers. Chemical shifts are measured relative to TMS, CH_2Cl_2, or $CHCl_3$. Mass spectra were recorded on AEI MS 902 or AEI MS 30 spectrometers using EI at 70 eV.

The known allylsilanes **16a**,[12] **19**,[5] and **22**[5] were prepared as already described.

(*E*)-1-[Dimethyl(phenyl)silyl]-4-phenylbut-2-ene (10):

(E)-1-Chloro-4-phenylbut-2-ene:

The allyl alcohol **9**[20] (0.87 g, 5.23 mmol) in dry Et_2O (1 mL) was added dropwise to a stirred solution of $SOCl_2$ (0.73 mL, 10 mmol) in dry Et_2O (10 mL) at 0 °C and the mixture kept at r.t. overnight. Light petroleum (100 mL) was added and the solution washed with aq $NaHCO_3$ solution (20 mL) and brine (20 mL), dried ($MgSO_4$), and evaporated under vacuum. The residue was distilled (Kugelrohr, oven temperature 70–80 °C, 1 Torr) to give the allyl chloride; yield: 0.61 g (70 %) as a 5:1 mixture of regioisomers.

HRMS: (*m/z*), $C_{10}H_{11}Cl$, calc.: 166.0549 (M^+); found: 166.0559.

MS (EI): *m/z* (%) = 166 (M^+, 17), 311 (M – Cl, 39), 117 (M – CH_2Cl, 50), 91 (C_7H_7, 100), 77 (Ph, 25).

IR (film): ν = 1640 (C=C), 1600 cm^{-1} (Ph).

^1H NMR ($CDCl_3$, 90 MHz): δ = 3.15 (d, *J* = 6 Hz, 2 H, $PhC\underline{H}_2$), 3.8 (d, *J* = 6 Hz, 2 H, CH_2Cl), 5.4 (dt, *J* = 15 and 16 Hz, 1 H, $C\underline{H}_A = CH_B$), 5.7 (dt, *J* = 15 and 16 Hz, 1 H, $CH_A = C\underline{H}_B$, 7.1–7.5 (m, 5 H, Ph).

(E)-1-[Dimethyl(phenyl)silyl]-4-phenylbut-2-ene **(10)**:

[Dimethyl(phenyl)silyl]lithium[21] (3 mL of a 1.4 M solution in THF, 4.2 mmol) was added dropwise to a stirred solution of the allyl chloride (0.55 g, 3.3 mmol) in dry THF (3 mL) at – 78 °C under nitrogen. After 3 h, the solution was warmed to r.t. and the reaction quenched with aq NH_4Cl solution (100 mL). Hexane (150 mL) was added, the organic layer was washed with brine (20 mL), dried ($MgSO_4$) and evaporated under vacuum, and the residue chromatographed (silica gel, hexane); yield: 0.61 g (69 %); R_f 0.17 (hexane).

HRMS: (*m/z*), $C_{18}H_{22}Si$, calc.: 266.1443 (M^+); found: 266.1467.

MS (EI): *m/z* (%) = 266 (M^+, 0.16), 188 (M-PhH, 12), 135 ($PhMe_2Si$, 100).

IR (film): ν = 1240 (SiMe), 1110 cm^{-1} (SiPh).

^1H NMR ($CDCl_3$, 90 MHz): δ = 0.3 (s, 6 H, $SiMe_2$), 1.7 (d, *J* = 6 Hz, 2 H, $SiCH_2$), 3.3 (d, *J* = 6 Hz, 2 H, $PhC\underline{H}_2$), 5.45 (m, 2 H, CH =CH), 7.1–7.6 (m, 10 H, 2 Ph).

Dimethyl(phenyl)(1-methyl-2-cyclohexylidenylethyl)silane (16b):

1-Propynylcyclohexyl acetate[22] (4.82 g, 26.8 mmol) in MeOH (200 mL) was stirred with Lindlar's catalyst [0.4 g, 5 % Pd on $BaSO_4$, poisoned with quinoline (0.8 g)] under hydrogen at r.t. and atmospheric pressure. When one molar equivalent of hydrogen was taken up, the mixture was filtered through Celite and evaporated under vacuum. The residue was taken up in Et_2O and washed successively with 1 M hydrochloric acid, aq $NaHCO_3$ solution and brine, dried ($MgSO_4$), and evaporated under vacuum. The crude (*Z*)-1-propenylcyclohexyl acetate (2.0 g, 11 mmol) in dry THF (20 mL) was added to a stirred solution of the bisdimethyl(phenyl)silyl cuprate reagent[5] (13 mmol) in dry THF (13 mL) at – 78 °C under nitrogen. After 1 h, the mixture was warmed to 0 °C over 3 h, poured into basic NH_4Cl solution (20 mL) and brine (10 mL), dried ($MgSO_4$), and evaporated, and the residue chromatographed (silica gel, hexane); yield: 2.04 g (61 %); R_f 0.4 (hexane).

HRMS: (*m/z*), $C_{17}H_{26}Si$, calc.: 258.1826 (M^+); found: 258.1828.

MS (EI): *m/z* (%) = 258 (M^+, 4), 135 ($PhMe_2Si$, 100).

IR (film): ν = 1250 (SiMe) and 1110 cm^{-1} (SiPh).

^1H NMR ($CDCl_3$, 250 MHz): δ = 1.00–2.10 (m, 11 H, remainder), 0.25 (s, 3 H, $Si\underline{Me}_AMe_B$), 0.27 (s, 3 H, $SiMe_A\underline{Me}_B$), 1.00 (d, *J* = 7.2 Hz, 3 H, $CH\underline{Me}$), 4.88 (d, *J* = 11.0 Hz, 1 H, C=CH), 7.31–7.38 (m, 3 H, Ph *m*- and *p*-H's), 7.46–7.50 (m, 2 H, Ph *o*-H's).

(*E*)-2-[Dimethyl(phenyl)silyl]-5-phenylpent-3-ene (25):

1-Phenyl-3-propyn-2-yl N-Phenylurethane:

Et_3N (3.1 mL, 22 mmol) and phenylisocyanate (2.4 mL, 22 mmol) were added to a stirred solution of 1-phenyl-3-pentyn-2-ol[23] (3.2 g, 20 mmol) in dry CH_2Cl_2 (20 mL), with cooling. After 5 h at r.t., Et_2O (200 mL) was added and the solution washed with aq $NaHCO_3$ solution (20 mL) and brine (20 mL), dried ($MgSO_4$) and evaporated under vacuum. The residue was chromatographed (silica gel, light petroleum/EtOAc, 10:1) to give the urethane; yield: 5.33 g (95 %); mp 87.5–88 °C.

$C_{18}H_{19}NO_2$	calc.	C 77.40	H 6.13	N 5.01
(279.1)	found	77.55	6.12	4.95

HRMS: (*m/z*), $C_{18}H_{19}NO_2$, calc.: 279.1250 (M^+); found: 279.1239.

IR (Nujol mull): ν = 3300 (NH), 1700 (C=O), 1600 cm^{-1} (Ph).

^1H NMR ($CDCl_3$, 60 MHz): δ = 1.8 (d, *J* = 2 Hz, 3 H, Me), 3.05 (d, *J* = 6 Hz, 2 H, $PhC\underline{H}_2$), 5.45 (m, 1 H, CHO), 6.5 (br s, 1 H, NH), 6.9–7.3 (m, 10 H, 2 Ph).

(Z)-1-Phenyl-3-propen-2-yl N-Phenylurethane:

The propargyl urethane (1.4 g, 5 mmol) was reduced using hydrogen and Lindlar's catalyst [5 % Pd on $BaSO_4$ (0.13 g), quinoline (0.21 g) and EtOH (50 mL)] to give an oil which was purified by flash chromatographed (light petroleum/EtOAc, 10:1) to give the *Z*-allyl urethane as a yellow oil; yield: 1.32 g (94 %).

HRMS: (*m/z*), $C_{18}H_{21}NO_2$, calc.: 281.1415 (M^+); found: 281.1428

IR (film): ν = 3400 and 3320 (NH), 1700 (C=O), 1600 cm^{-1} (Ph).

^1H NMR ($CDCl_3$, 60 MHz): δ = 1.5 (d, *J* = 6 Hz, 3 H, Me), 2.9 and 3.1 (dd, *J* = 13 and 7 Hz, 1 H each, $PhC\underline{H}_2$), 5.2–5.9 (m, 3 H, OCHCH=CH), 6.65 (br s, 1 H, NH), 6.8–7.3 (m, 10 H, 2 Ph).

(E)-2-[Dimethyl(phenyl)silyl]-5-phenylpent-3-ene:

BuLi (4.45 mL of a 1.48 M solution in hexane) was added dropwise to a stirred solution of the allyl urethane (1.82 g, 6.58 mmol) in dry THF (100 mL) at – 78 °C under nitrogen. The solution was warmed to 0 °C, cannulated into a flask containing Ph_3P (3.45 g, 13.16 mmol) and copper(I) iodide (1.25 g, 6.58 mmol), and stirred ~ 1 h in dry Et_2O (33 mL) at 0 °C under nitrogen until all the solids were dissolved. [Dimethyl(phenyl)silyl]lithium[21] (7.83 mL of 0.84 M solution in THF) was added dropwise at 0 °C and the mixture kept for 3 h before being quenched with aq NH_4Cl solution. Hexane (100 mL) was added and the solution washed with basic NH_4Cl solution (20 mL) and brine (20 mL), dried ($MgSO_4$) and evaporated under vacuum. The residue was flash chromatogaphed (light petroleum) to give the allylsilane; yield: 1.27 g (69 %); R_f 0.2 (hexane).

HRMS: (*m/z*), $C_{19}H_{24}Si$, calc.: 265.1413 (M^+–Me); found: 265.1399.

IR (film): ν = 1605 (Ph), 975 cm^{-1} (*trans* CH=CH).

^1H NMR ($CDCl_3$, 90 MHz): δ = 0.2 (s, 6 H, $SiMe_2$), 1.05 (d, *J* = 7 Hz, 3 H, Me), 1.8 (quint, *J* = 7 Hz, 1 H, CHSi), 3.3 (d, *J* = 6 Hz, 2 H, $PhCH_2$), 5.3 (dt, *J* = 15 and 6 Hz, 1 H, $BnC\underline{H}$), 5.6 (dd, *J* = 15 and 6 Hz, 1 H, $C\underline{H}CHSi$), 7.1–7.6 (m, 10 H, 2 Ph).

Preparation of Cyclopropylmethylsilanes; General Procedure:

Method A: Me_3Al (3.3 mL of a 2 M solution in hexane, 6.6 mmol) was added dropwise to a stirred solution of the allylsilane (3.3 mmol) and CH_2I_2 (0.53 mL, 6.6 mmol) in dry CH_2Cl_2 (13 mL) at 0 °C under nitrogen. After 16 h at r.t., H_2O (0.36 mL, 20 mmol) was added dropwise at – 23 °C, followed by Et_3N (1 mL). The resulting mixture was stirred for 0.5 h at 0 °C, filtered through Celite and evaporated under vacuum. The resulting oil was taken up in Et_2O (20 mL), washed with brine (10 mL), dried ($MgSO_4$), and evaporated under vacuum, and the residue chromatographed on a column (silica gel, hexane). The products were all colourless oils.

Method B: Zinc powder (2.7 g, 42 mmol) and copper(I) chloride (0.43 g, 42 mmol) were refluxed in Et_2O (20 mL) for 0.5 h. CH_2I_2 (4.32 g, 16 mmol) and the allylsilane (8 mmol) were added and the mixture refluxed for 24 h. The mixture was filtered, washed with aq NH_4Cl solution (10 mL), the ether layer dried ($MgSO_4$), and evaporated under vacuum, and the residue chromatographed on a column (silica gel, hexane). The products were all colourless oils.

Protodesilylation of Cyclopropylmethylsilanes; General Procedure:
Method A: $BF_3 \cdot 2AcOH$ (0.13 mL, 40% boron trifluoride) was added to the cyclopropylmethylsilane (1.2 mmol) in dry $CHCl_3$ (2 mL) at 0 °C. The resulting mixture was shaken vigorously for 2 min, and then poured into aq $NaHCO_3$ solution (10 mL). The organic layer was washed with brine (2 mL), dried ($MgSO_4$), and evaporated, to give a mixture of the alkene and dimethyl(phenyl)silyl fluoride [$\delta = 0.48$ (d, $J = 7.4$ Hz, 6H), 7.25–7.4 (m, 2H), 7.56–7.6 (m, 3H)], which were separated by preparative TLC. The products **12**,[24] **13**,[25] and **18a**[26] are known compounds.

Method B: TFA (2 mL, 26 mmol) was added to a solution of the cyclopropylmethylsilane (0.12 mmol) in CH_2Cl_2 (4 mL) and the mixture kept at 20 °C for 2 h. The mixture was poured into aq $NaHCO_3$ solution (10 mL, 5%), the organic phase dried ($MgSO_4$), and evaporated, and the residue purified by preparative TLC.

Conversion of the Alkenes 12 and 13 into the Esters 14 and 15:
Following the procedure of Sharpless,[27] $NaIO_4$ (0.132 g, 0.615 mmol) and RuO_2 (0.4 mg, 0.003 mmol) were added to a stirred biphasic mixture of the alkenes **12** and **13** (approximately 0.15 mmol) in CCl_4 (0.3 mL), MeCN (0.3 mL), and H_2O (0.45 mL), and the mixture stirred vigorously for 2 h at r.t. CH_2Cl_2 (1.5 mL) was added, and the aqueous phase extracted with CH_2Cl_2 (3 × 1 mL). The combined organic fractions were dried ($MgSO_4$) and evaporated. H_2SO_4 (1 drop) was added to a solution of the crude products (which showed no signals in the olefinic region in the ^1H NMR spectrum) in dry MeOH (5 mL). After 3 h, Et_2O (30 mL) was added, the solution was washed with aq $NaHCO_3$ solution (10 mL) and brine (10 mL), dried ($MgSO_4$), and evaporated. GC of the residue showed the esters to be present in a 93:7 ratio (the relevant peaks overlapping with co-injected, authentic esters). The residue was also purified by preparative TLC (light petroleum/EtOAc, 5:1) collecting a broad band around R_f 0.45. The ^1H NMR spectrum of this material showed it to be predominantly methyl 2-methyl-3-phenylpropionate (**14**),[28] the signals of methyl 4-phenylbutyrate (**15**)[29] being hidden.

Authentic Samples of the Esters 14 and 15:
The ester **15** was made by esterification of commercially available 4-phenylbutyric acid (0.13 g), as above; yield: 0.11 g (78%).

^1H NMR ($CDCl_3$, 90 MHz): $\delta = 1.8–2.8$ (m, 6H, remainder), 3.65 (s, 3H, OMe), 7.2–7.5 (m, 5H, Ph).

The ester **14** was prepared by hydrogenation of methyl α-methylcinnamate (0.36 g) using 10% Pd on $BaSO_4$ in MeOH; yield: 0.35 g (96%)

^1H NMR ($CDCl_3$, 90 MHz): $\delta = 1.2$ (d, $J = 7$ Hz, 3H, Me), 2.6–3.2 (m, 3H, CH_2CH), 3.65 (s, 3H, OMe), 7.1–7.5 (m, 5H, Ph).

Protodesilylation of the Allylsilane 26:
Protodesilylation of this silane was not a satisfactory reaction using either TFA or $BF_3 \cdot 2AcOH$. For example, using the latter acid, as above, on a 52:48 isomeric mixture, and quenching after 15 min, the reaction was incomplete, GC analysis of the recovered silane from this reaction showed that the slow-eluting isomer reacted preferentially (virtually none was recovered). The olefinic products were a complex mixture of isomers (^1H NMR).

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