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The Silylcupration of Acetylenes: a Synthesis of Vinylsilanes †

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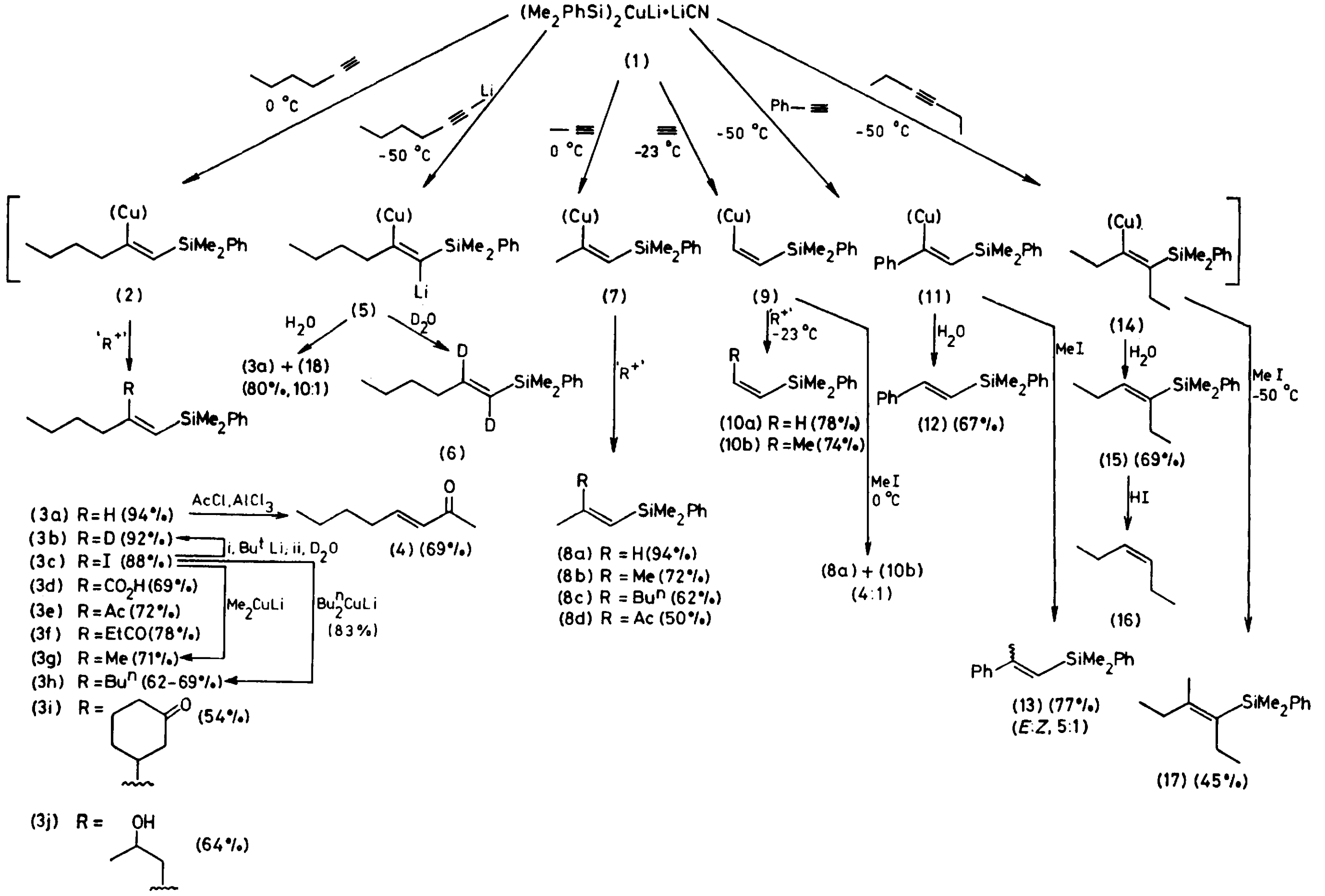
Bis(dimethylphenylsilyl)copper-lithium (1) reacts with hex-1-yne, propyne, acetylene itself, phenylacetylene, and hex-3-yne to give the products of *syn* addition of the dimethylphenylsilyl group and the copper. The resultant vinylcopper reagents react with a variety of electrophiles, such as the proton, iodine, acyl and alkyl halides, enones, and epoxides, to give vinylsilanes. With the terminal alkynes, the silyl group becomes attached with a high level of regioselectivity to the terminal carbon atom, with the result that the final products are 2,2-disubstituted vinylsilanes.

VINYLSILANES now occupy an established place in organic synthesis, because they often react with electrophiles regio- and stereo-specifically,[1] and because their epoxides are masked aldehydes or ketones.[2] However, there are not many ways of preparing 2,2-disubstituted vinylsilanes.[3] In a preliminary communication,[4] we reported that our silylcuprate reagent (1) [5] reacted with terminal acetylenes, and the intermediate vinylcopper compounds (2), (7), and (9) then reacted with the standard electrophiles of organocopper chemistry [6] to give 2,2-disubstituted vinylsilanes (3), (8), and (10). We now report our work in full, and include further examples establishing the scope of this easy vinylsilane synthesis.



Reaction of the Silylcuprate Reagent (1) *with Acetylenes.*—Dimethylphenylsilyl-lithium is easier to make [7] than trimethylsilyl-lithium [8] and we have used it throughout in this work. We have no reason to expect the phenyl group to interfere seriously with the vinylsilane chemistry which one might want to do subsequently. We find that the reagent (1), prepared by mixing 2 mol equiv. of dimethylphenylsilyl-lithium with 1 mol equiv. of copper(I) cyanide, reacts with hex-1-yne to give a vinylcopper species (2). When we quenched this intermediate with water, we obtained only [>99% (by g.l.c. and ^{1}H n.m.r.)] the vinylsilane (3a) in 94% yield based on the acetylene. The silylcuprate reagent (1) had not removed the proton from the hexyne, as alkylcopper reagents do; [9] this was

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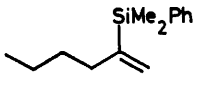
shown by quenching the intermediate (2) with deuterium oxide to give the *mono*-deuteriated vinylsilane (3b). When we deliberately removed the proton from the hexyne with butyl-lithium, the hexynyl-lithium produced still reacted with the silylcuprate reagent (1), although not quite as regioselectively; quenching with water gave the vinylsilane (3a) and its regioisomer (18) in 80% yield in a 10 : 1 ratio. Work-up with deuterium oxide gave a mixture consisting largely of (6), which showed no olefinic signals in the ^{1}H n.m.r. spectrum. The intermediate in this reaction appears therefore to be the vinyl-copper-lithium-silane (5), an extraordinary alkene with three different metals bonded to it.

The silylcupration was equally successful with other acetylenes: propyne, acetylene itself, phenylacetylene, and hex-3-yne all gave the corresponding vinylsilanes (8a), (10a), (12), and (15) by silylcupration followed by quenching with water. The *syn*-stereoselectivity in these reactions was clear from the *trans* coupling constants (20 Hz) of the olefinic signals of the vinylsilanes (3a), (8a), and (12), and by the formation of *cis*-hex-3-ene (16) by protodesilylation of the vinylsilane (15), a reaction which is known to go with retention of configuration.[1] The overall result in this case is therefore the *cis*-hydrogenation of the alkyne. In one other case, we checked that the phenyl group did not interfere with the vinylsilane chemistry: the vinylsilane (3a) reacted with acetyl chloride and aluminium chloride to give (*E*)-oct-3-en-2-one (4), with retention of configuration as expected.[1] Only a trace of acetophenone was detectable in the product mixture, showing that the hexenyl group had reacted faster than the phenyl group with the acetyl electrophile.

Reaction of the Vinylcopper Reagents with Electrophiles.—The simple vinylsilanes described above are the same as those which might be produced by hydrosilation. We were therefore more interested in the reactions of the vinylcopper reagents (2), (7), (9), (11), and (14) with other electrophiles than the proton. One precaution needs to be observed when other electrophiles are to be used: any excess of the terminal alkynes provides a source of protons, which can react with the intermediate vinylcopper species. Thus a ten-fold excess of hexyne protonated the intermediate (2) over about five hours at 0 °C, and a ten-fold excess of acetylene itself protonated the intermediate (9) in less than forty minutes.

Some of the standard electrophiles of organocopper chemistry[6] react with the vinylcopper species (2) without difficulty. Thus, iodine, carbon dioxide, acetyl chloride, propionyl chloride, and methyl iodide gave the vinylsilanes (3c—g), respectively. These electrophiles all reacted at 0 °C within three hours or less, a time within which the vinylcopper species had deteriorated only a little. Electrophiles which reacted more slowly could not be used directly in this way, but the addition either of hexamethyl phosphorus(III) triamide or of hexynyl-lithium to the vinyl-copper intermediate (2) activated it, and weaker electrophiles could then be made to react. In this way, butyl iodide, cyclohexenone, and propylene oxide gave the vinylsilanes (3 h—j), respectively. The silylcupration of acetylenes is therefore a powerful method for the synthesis of a variety of functionalised and unfunctionalised vinylsilanes.

Although we have used an excess of the electrophile in all this work, it may sometimes be wise to use only one equivalent, since the excess sometimes reacts with the second (and unused) silyl group to give by-products which are not always easily separated from the vinylsilane. For example, propylene oxide gave the alcohol (19) as a by-product in the preparation of (3j). This alcohol (19) could be prepared in better yield by the direct reaction of the silylcuprate (1) with propylene oxide.



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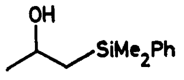

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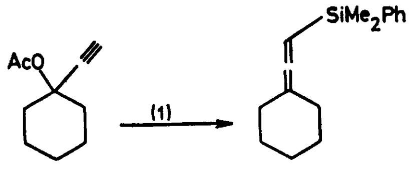

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Stereochemistry of the Vinylsilanes.—In all the reactions, so far, we only observed one stereoisomer in the products. The vinylcopper species (2) is evidently regiostable, and stereoselective in its reactions. This was confirmed when we prepared the (*Z*)-stereoisomer (8c) of (3g) by butylating the vinylcopper intermediate (7). The (*E*)-stereochemistry was assigned to (3g) and the (*Z*) to (8c) on the basis of the similarity of the chemical shifts of the *C*-methyl protons in the n.m.r. spectra to those of the *C*-methyl protons of the vinylsilanes (8a) and (10b), the latter being formed by methylation of the vinylcopper species (9). The vinylsilane (8a) was clearly *trans* and the vinylsilane (10b) *cis*, because the coupling constants for the vinyl hydrogens were 20 and 14 Hz respectively. The dimethylphenylsilyl group evidently causes a methyl group *cis* to it to be shielded slightly relative to a methyl group *trans* to it, and the same trend was evident in the allylic methylene signals of (3g) and (8c). The direction of this effect is the same as that observed by Chan[10] for the influence of a trimethylsilyl group on the *cis*- and *trans*-hydrogens of 1,2-disubstituted vinylsilanes.

The iodovinylsilane (3c) reacted with lithium dimethylcuprate to give (3g). Since this type of reaction usually goes with retention of configuration,[11] the iodosilane (3c) probably has the (*Z*)-configuration. This was confirmed by metallation of (3c) with t-butyl-lithium and quenching with deuterium oxide, which gave the vinylsilane (3b). The reaction of an organocuprate with the iodide (3c) provides another way of synthesising the vinylsilane (3h), since lithium dibutylcuprate reacted

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with (3c) to give (3h) in good yield. The other vinylsilanes (3), not specifically mentioned above, were assigned the (*Z*)-configuration by analogy.

Loss of Stereoselectivity with the Methylation of the Vinylcopper Reagents (9), (11), *and* (14).—The methylation of the vinylcopper reagent (9) gave only the vinylsilane (10b), as described above. However, this was true only if the vinylcopper reagent was prepared and methylated at −23 °C; at 0 °C, it gave largely (4 : 1) the *trans*-isomer (8a). Similarly, the vinylcopper reagent (14) gave a mixture of the (*E*)- and (*Z*)-isomers of (17) when methylation was carried out at −23 °C or above. At 0 °C, the (*Z*)-isomer was the major product (2 : 1), and at −23 °C, the (*E*)- and (*Z*)-isomers were formed in equal amounts. At −50 °C, however, the (*Z*)-isomer was only just detectable. Finally, methylation of the silylcopper reagent (11) gave a mixture of the (*E*)- and (*Z*)-isomers of the vinylsilane (13), but this time the ratio was not noticeably affected by the temperature at which the reaction was carried out. It seems likely that *cis–trans* equilibration of the styrylcopper reagent is particularly fast.[12]

Silylcupration with Opposite Regioselectivity.—The regioselectivity of the silylcupration reaction described above is the opposite of that which might have been expected by analogy with the corresponding carbocupration reaction.[9,12] We found that the regioselectivity could be changed by changing the silylcopper reagent: in particular, a reagent prepared by mixing two equivalents of dimethylphenylsilyl-lithium with one of the copper(I) bromide–dimethyl sulphide complex reacted with hex-1-yne to give mixtures rich in the isomeric vinylsilane (18). The proportions varied from run to run, but were in the region of 1 : 3 in favour of (18). Similarly, a reagent produced by mixing the silyl-lithium with copper(I) cyanide or iodide in a 1 : 1 ratio gave mixtures of (3a) and (18), usually in a ratio of *ca.* 2 : 1, respectively. We were unable to find conditions which gave reliable and high yields of (18).

Silylcupration of a Propargyl Acetate.—Since silylcupration of terminal acetylenes proved to be such an easy reaction, we expected that a propargyl acetate such as (20) would react with the silylcuprate reagent (1), and that the copper and the acetate groups would undergo elimination to give the allenylsilane (21). This proved to be true, but the yield was variable, and the reaction clearly needs more work before we can claim it to be general.

Minimum Conditions under which the Silylcupration Reaction occurs.—In most of the work described above, the silylcupration reaction, *e.g.* (1) ⟶ (2), was carried out at 0 °C, because it was convenient. However, this was certainly much warmer than necessary, as shown by such reactions as (1) ⟶ (14). To find how mild the conditions could be, we treated dec-1-yne with the cuprate (1) at −78 °C for various lengths of time, and looked for unchanged dec-1-yne. We found that reaction was complete after only 20 min. The silylcupration is evidently a very fast reaction indeed.

EXPERIMENTAL

Light petroleum is the fraction of b.p. 40—60 °C.

Dimethylphenylsilyl-lithium.—Dimethylphenylsilyl chloride[13] (1.7 g, 10 mmol) was stirred with lithium (21 mg, 30 mmol, Fison's ' shot ') in tetrahydrofuran (THF) (25 ml) at −8 °C under nitrogen for 36 h. The red solution is stable for several weeks at −20 °C. For calibration, an aliquot was injected into water, and the alkaline solution was titrated against standard hydrochloric acid. Although this measures only the total base present, it proved more reliable than more sophisticated methods. Our success in this work in getting high regioselectivity dated from the time that we adopted this simple method of calibrating the silyl-lithium reagent.

The Silylcuprate Reagent (1).—Dimethylphenylsilyl-lithium (10 mmol) in dry THF (25 ml) was added to copper(I) cyanide (447 mg, 5 mmol, dried at 120 °C for 10 h) at 0 °C under nitrogen and the mixture was stirred for 20 min. It was generally used immediately.

The Silylcupration Reaction Products (2), (5), (7), (9), (11), *and* (14).—Typically the alkyne (4.5 mmol) in THF (1 ml) was added slowly to the silylcuprate (1) (5 mmol, based on CuCN) at 0 °C and the mixture was stirred for 15—20 min at 0 °C. These conditions are certainly too vigorous, as discussed in the text, and as shown by the experiment with dec-1-yne, described below.

(E)-1-*Dimethyl(phenyl)silylhex*-1-*ene* (3a).—The vinylcopper reagent (2) was quenched with saturated ammonium chloride solution (1 ml) and stirred for 5 min at 0 °C. Light petroleum was added and the organic phase was washed with ammonium chloride solution. The organic layer was dried ($MgSO_4$) and evaporated *in vacuo*, and the residue was chromatographed on silica gel [Kieselgel 60 (Merck), 0.063—0.2 mm] to give the *vinylsilane* (3a) (920 mg, 94% based on hexyne), R_F (light petroleum) 0.6 $\nu_{max.}$ (CCl_4) 1 620 (C=C), 1 250 (SiMe), 1 115 (SiPh), and 990 cm^{-1} (*trans*-CH=CH), δ(CCl_4) 7.54—7.14 (5 H, m, Ph), 6.12 (1 H, dt, *J* 20 and 6 Hz, C*H*=CHSi), 5.77br (1 H, d, *J* 20 Hz, CH=C*H*Si), 2.14—2.04 (2 H, m, CH_2CH=CH), 1.64—1.13 (4 H, m, CH_2CH_2), 0.99 (3 H, t, *J* 7 Hz, CH_2*Me*), and 0.38 (6 H, s, $SiMe_2$) (Found: *m/z*, 203.1240. $C_{13}H_{19}Si$ requires *M* − Me, 203.1256), *m/z* 218 (M^+, 5%), 203 (*M* − Me, 35), 162 (15), 161 (30), 145 (10), 135 (40) and 121 (95). This same compound was prepared from the vinyl-lithium-copper species (5) (6 mmol) (prepared at −50 °C for 1 h) by a similar quench with ammonium chloride solution. The yield was 105 mg (80%) and the ^1H n.m.r. spectrum clearly showed the vinylsilane (3a) mixed with the vinylsilane (18): δ(CCl_4) 5.88br (d, *J* 1.6 Hz, C=CH_2) and 0.45 (s, $SiMe_2$); integration of the n.m.r. spectrum showed that (3a) and (18) were present in the ratio *ca.* 10 : 1.

(E)-1-*Dimethyl(phenyl)silyl*[2-^{2}H]*hex*-1-*ene* (3b).—The vinylcopper species (2) was quenched with ^2H_2O (0.5 ml) and the mixture worked up as above to give the *deuteriated silane* (3b) (905 mg, 92%), identical to (3a) (n.m.r., t.l.c.) except for δ 5.77br (s), 2.22 (t, *J* 7 Hz), and the absence of the signal at 6.12 (Found: *m/z*, 204.1318. $C_{13}H_{18}DSi$ requires *M* − Me, 204.1319). The same compound was prepared from the vinyl iodide (3c) (172 mg, 0.5 mmol) by reaction first with t-butyl-lithium (1 mmol in pentane) in ether (5 ml) at −78 °C for 30 min, and then quenching with ^2H_2O. The product (98 mg, 89%) was identical with that above (n.m.r. and, i.r. spectra t.l.c.).

(Z)-1-*Dimethyl(phenyl)silyl*-2-*iodohex*-1-*ene* (3c).—Iodine (14.93 g, 58.8 mmol) was added in portions (2 g) to a solution

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of (2) (28 mmol based on hexyne) at 0 °C and the mixture stirred for 2 h. Quenching with saturated ammonium chloride and work-up as before gave the *iodide* (3c) (8.6 g, 88%), R_F (light petroleum) 0.7, $\nu_{max.}$ (CCl_4) 1.600 (C=C), 1 250, and 1 115 cm^{-1}, δ(CCl_4) 7.64—7.22 (5 H, m, Ph), 6.52 (1 H, s, C=CHSi), 2.62 (2 H, t, *J* 7 Hz, $CH_2CI=C$), 1.78—1.20 (4 H, m, CH_2CH_2), 0.98 (3 H, t, *J* 7 Hz, CH_2*Me*), and 0.52 (6 H, s, $SiMe_2$) (Found: *m/z*, 217.1403. $C_{14}H_{21}Si$ requires *M* − I, 217.1413) *m/z* 329 (M^+, 5%), 217 (*M* − I, 100), 216 (20), and 201 (10).

(Z)-2-*Butyl*-3-*dimethyl(phenyl)silylacrylic Acid* (3d).—Solid carbon dioxide (in excess) was added to the vinylcopper species (2) (0.7 mmol based on hexyne) and the mixture was stirred for 1 h. Work-up as before but with extraction into potassium carbonate solution, acidification with hydrochloric acid, extraction with ether, and chromatography eluting with light petroleum–ether (4 : 1 v/v) gave the *acid* (3d) (126 mg, 69%), R_F (light petroleum–ether, 4 : 1 v/v) 0.4, $\nu_{max.}$ (CCl_4) 1 690 (CO), 1 245, and 1 115 cm^{-1}, δ(CCl_4) 12.13 (1 H, s, OH), 7.6—7.2 (5 H, m, Ph), 6.21br (1 H, s, C=CHSi), 2.45br (2 H, t, *J* 7 Hz, $CH_2C=C$), 1.74—1.22 (4 H, m, CH_2CH_2), 1.01 (3 H, t, *J* 7 Hz, CH_2*Me*), and 0.48 (6 H, s, $SiMe_2$) (Found: *m/z*, 247.1158. $C_{14}H_{19}O_2Si$ requires *M* − Me, 247.1154), *m/z* 248 (20%), 247 (100), 185 (66), 137 (60), 135 (16), and 129 (25).

(Z)-2-*Butyl*-1-*dimethyl(phenyl)silylbut*-1-*ene*-3-*one* (3e).—Acetyl chloride (495 mg, 7 mmol) was added to the vinylcopper species (2) (3.2 mmol) at 0 °C and the mixture was kept for 3 h. Aqueous work-up as before and chromatography eluting with light petroleum–ether 19 : 1 vv) gave the *ketone* (3e) (0.56 g, 72%), R_F (light petroleum–ether, 19 : 1 v/v) 0.3, $\nu_{max.}$ (CCl_4) 1 695 (CO), 1 580 (C=C), 1 248, and 1 112 cm^{-1}, δ(CCl_4) 7.7—7.1 (5 H, m, Ph), 5.9 (1 H, s, C=CHSi), 2.6—0.7 (9 H, m, Bu), 2.1 (3 H, s, COMe), and 0.4 (6 H, s, $SiMe_2$) (Found: M^+, 260.1626. $C_{16}H_{24}OSi$ requires *M*, 260.1596), *m/z* 260 (M^+, 0.2%), 245 (30, *M* − Me), 183 (25, *M* − Ph), and 135 (100, Me_2PhSi).

(Z)-2-*Butyl*-1-*dimethyl(phenyl)silylpent*-1-*en*-3-*one* (3f).—Propionyl chloride (2.8 ml, 32 mmol) in THF (10 ml) was added to the vinylcopper reagent (2) (15 mmol) and the mixture was kept at 0 °C for 3 h. Work-up, and chromatography as above, gave the *ketone* (3f) (3.2 g, 78%) b.p. 170 °C at 0.1 mmHg, R_F (light petroleum–ether, 20 : 1 v/v) 0.5, $\nu_{max.}$ (CCl_4) 1 690, 1 245, and 1 110 cm^{-1}, δ(CCl_4) 7.6—7.16 (5 H, m, Ph), 5.84br (1 H, s, C=CHSi), 2.62—2.26 (4 H, m, CH_2CO and $CH_2C=C$), 1.63—1.25 (4 H, m, CH_2CH_2), 1.12—0.84 (6 H, m, 2 × CH_2*Me*), and 0.38 (6 H, s, $SiMe_2$) (Found: *m/z*, 259.1523. $C_{16}H_{23}OSi$ requires *M* − Me, 259.1518), *m/z* 260 (16%), 259 (100), 231 (15), 217 (55), 198 (20), and 197 (93).

(E)-1-*Dimethyl(phenyl)silyl*-2-*methylhex*-1-*ene* (3g).—Methyl iodide (0.2 ml, 3.2 mmol) in THF (2 ml) was added to the vinylcopper reagent (2) (0.8 mmol) and the mixture was kept at 0 °C for 40 min. Work-up as in the preparation of (3a) gave the *vinylsilane* (3g) (130 mg, 71%), R_F (light petroleum) 0.6, $\nu_{max.}$ (CCl_4) 1 615 (C=C), 1 250, and 1 115 cm^{-1}, δ(CCl_4) 7.56—7.14 (5 H, m, Ph), 5.33 (1 H, s, C=CHSi), 2.14 (2 H, t, *J* 7 Hz, $CH_2C=C$), 1.72 (3 H, s, MeC=C), 1.6—1.14 (4 H, m, CH_2CH_2), 0.98 (3 H, t, *J* 7 Hz, CH_2*Me*), and 0.38 (6 H, s, $SiMe_2$) (Found: *m/z*, 217.1423. $C_{14}H_{21}Si$ requires *M* − Me, 217.1412), *m/z* 217 (54%), 190 (40), 148 (38), 135 (100), and 121 (37).

2-*Butyl*-1-*dimethyl(phenyl)silylhex*-1-*ene* (3h).—*Method A*. Hexamethylphosphorus triamide (1 ml, 5.5 mmol) in THF (1 ml) was added to the vinylcopper reagent (2) (2.7 mmol) at −23 °C. After 2 min, n-butyl iodide (0.62 ml, 5.4 mmol) in THF (2 ml) was added and the mixture was kept at −23 °C for 60 min and at −8 °C for 16 h. Quenching at 0 °C, and work-up as before, gave the *vinylsilane* (3h) (460 mg, 62%), R_F (light petroleum) 0.6, $\nu_{max.}$ (CCl_4) 1 610 (C=C), 1 250, and 1 115 cm^{-1}, δ(CCl_4) 7.61—7.18 (5 H, m, Ph), 5.37br (1 H, s, C=CHSi), 2.29—1.91 (4 H, m, allylic CH_2), 1.6—1.11 (8 H, m, 2 × CH_2CH_2), 1.11—0.72 (6 H, m, 2 × CH_2*Me*), and 0.39 (6 H, s, $SiMe_2$) (Found: M^+, 274.2118. $C_{18}H_{30}Si$ requires *M*, 274.2116), *m/z* 274 (4%, M^+), 259 (25), 232 (15), 212 (100), 203 (14), 190 (38), and 188 (20).

Method B. n-Butyl-lithium (2.8 ml of a 1.72M-solution in hexane) was added to hex-1-yne (4.0 mmol) in THF (2 ml) at −78 °C and this solution was then added to the vinylcopper reagent (2) (4.9 mmol) at −78 °C. After 5 min, n-butyl iodide (7.2 mmol) in THF (2 ml) was added, and after a further 30 min the mixture was brought slowly to −8 °C and kept at this temperature for 40 h. Finally, after 1 h at room temperature, the mixture was worked up as before to give the same vinylsilane (3h) (0.83 g, 67%) (t.l.c. and n.m.r., i.r., and mass spectra) (Found: M^+, 274.2117).

Method C. n-Butyl-lithium (4 ml of a 1.62M-solution in hexane) was added to a suspension of copper(I) cyanide (585 mg) in dry ether (15 ml) under nitrogen at 0 °C. The vinyl iodide (3c) (1.73 g) in dry ether (20 ml) was added dropwise and the mixture was kept at 0 °C for 1 h. Work-up as before gave the same vinylsilane (3h) (1.14 g, 83%).

3-[(Z)-1-*Dimethyl(phenyl)silylhex*-1-*en*-2-*yl*]*cyclohexanone* (3i).—Hexamethylphosphorus triamide (1 ml, 5.5 mmol) in THF (1 ml) was added to the vinylcopper reagent (2) (2.7 mmol) at −23 °C. After 2 min, cyclohex-2-enone (0.53 ml, 5.4 mmol) in THF (2 ml) was added and the mixture was kept at −23 °C for 80 min. Work-up as before and chromatography, eluting with light petroleum–ether (7 : 3 v/v), gave the *ketone* (3i) (460 mg, 54%), R_F (light petroleum–ether, 7 : 3 v/v) 0.4, $\nu_{max.}$ (CCl_4) 1 720 (CO), 1 605 (C=C), 1 250, and 1 115 cm^{-1}, δ(CCl_4) 7.58—7.14 (5 H, m, Ph), 5.38br (1 H, s, C=CHS), 2.8—1.74 (7 H, m), 1.72—1.4 (8 H, m), 0.95 (3 H, t, *J* 7 Hz, CH_2*Me*), and 0.36 (6 H, s, $SiMe_2$) (Found: M^+, 314.2051. $C_{20}H_{30}OSi$ requires *M*, 314.2066) *m/z* 314 (18%, M^+), 299 (49), 272 (65), 259 (100), and 257 (50).

(Z)-4-*Butyl*-5-*dimethyl(phenyl)silylpent*-4-*en*-2-*ol* (3j).—Hexynyl-lithium (3.85 mmol), prepared as described for (3h) (method B) above, was added to the vinylcopper reagent (2) (3.85 mmol) at −78 °C. After 5 min, propylene oxide (0.54 ml, 7.7 mmol) in THF (1 ml) was added and after 20 min at −78 °C, the mixture was kept at −8 °C for 68 h. Work-up and chromatography, eluting with light petroleum–ether (5 : 1 v/v) gave the *alcohol* (3j) (680 mg, 64%), R_F (light petroleum–ether, 5 : 1 v/v) 0.4, $\nu_{max.}$ (CCl_4) 3 580 (OH), 1 610 (C=C), 1 250, and 1 115 cm^{-1}, δ(CCl_4) 7.64—7.2 (5 H, m, Ph), 5.56br (1 H, s, C=CHSi), 4.02—3.60 (1 H, m, C*H*OH), 2.33—2.0 (4 H, m, 2 × allylic CH_2), 1.67—1.18 (5 H, m, CH_2CH_2 and OH), 1.16—0.92 (6 H, m, CH*Me* and CH_2*Me*), and 0.43 (6 H, s, $SiMe_2$) (Found: *m/z* 261.1696. $C_{16}H_{25}OSi$ requires *M* − Me, 261.167 4), *m/z* 261 (34%), 243 (27), 137 (51), and 135 (100). The chromatography also gave 1-dimethyl(phenyl)silylpropan-2-ol (19), identical with a sample prepared as described below.

1-*Dimethyl(phenyl)silylpropan*-2-*ol* (19).—Propylene oxide (4.6 mmol) in THF (1 ml) was added to the silylcopper reagent (1) (1.15 mmol) under nitrogen and the mixture was kept at 0 °C for 6 h. Aqueous work-up and column chromatography (Et_2O) gave the *alcohol* (19) (152 mg, 68%),

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R_F (Et_2O) 0.74, $\nu_{max.}$ (CCl_4) 3 690s and 3 700—3 000 (OH), 1 250 ($SiMe_2$), and 1 117 cm^{-1} (SiPh), δ(CCl_4) 7.4—6.8 (5 H, m, Ph), 3.6 (1 H, sextuplet, *J* 6 Hz, C*H*OH), 2.2br (1 H, s, OH), 0.95 (3 H, d, *J* 6 Hz, *Me*CHOH), 0.89 (2 H, d, *J* 6 Hz, CH_2Si), and 0.15 (6 H, s, $SiMe_2$) (Found: *m/z*, 193.1057. $C_{11}H_{17}OSi$ requires *M* − H 193.1048), *m/z* 194 (6%, M^+), 193 (16, *M* − H), 137 (100, $PhMeSiOH^+$), and 135 (91, Me_2PhSi^+).

(E)-*Oct-3-en-2-one* (4).—Acetyl chloride (0.07 ml, 1 mmol), the vinylsilane (3a) (105 mg, 0.48 mmol) and aluminium trichloride (133 mg, 1 mmol) were stirred in dichloromethane (10 ml) at 0 °C for 30 min. The mixture was diluted with dichloromethane, washed with sodium hydrogencarbonate solution, and dried ($MgSO_4$), and the product was chromatographed eluting with light petroleum–dichoromethane (3 : 2 v/v) to give the ketone [14] (4) (42 mg, 69%), R_F (light petroleum–ether, 4 : 1 v/v) 0.2, $\nu_{max.}$ (CCl_4) 1 680 (CO) and 1 630 cm^{-1} (C=C), δ(CCl_4) 6.63 (1 H, dt, *J* 16 and 7 Hz, CH_2C*H*=CH), 5.94 (1 H, d, *J* 16 Hz, CH=C*H*CO), 2.32—2.0 (2 H, m, CH_2CH=CH), 2.11 (3 H, s, COMe), 1.65—1.1 (4 H, m, CH_2CH_2), and 0.92 (3 H, t, *J* 6 Hz, CH_2*Me*) (Found: M^+, 126.1051. $C_8H_{14}O$ requires *M*, 126.1045), *m/z* 126 (36%), 111 (100), and 97 (75). Acetophenone was detected to an extent of *ca.* 5% (t.l.c., ^{1}H n.m.r.).

(E)-1-*Dimethyl(phenyl)silylprop*-1-*ene* (8a).—The vinylcopper reagent (7) (4.35 mmol) was quenched with ammonium chloride solution as described in the preparation of (3a) and gave the *vinylsilane* (8a) (700 mg, 94%), R_F (light petroleum) 0.7, $\nu_{max.}$ (CCl_4) 1 625 (C=C), 1 250, 1 115, and 990 cm^{-1} (*trans*-CH=CH), δ(CCl_4) 7.63—7.23 (5 H, m, Ph), 6.19 (1 H, dq, *J* 20 and 6 Hz, MeC*H*=CH), 5.81 (1 H, dq, *J* 20 and 1.5 Hz, CH=C*H*Si), 1.92 (3 H, dd, *J* 6 and 1.5 Hz, *Me*CH=CH), and 0.41 (6 H, s, $SiMe_2$) (Found: M^+, 176.0989. $C_{11}H_{16}Si$ requires *M*, 176.1021), *m/z* 176 (20%, M^+), 162 (15), 161 (96), 135 (28), and 121 (100). The same vinylsilane (8a) was produced when the vinylcopper reagent (9) was treated with methyl iodide at 0 °C for 30 min. Integration of the ^{1}H n.m.r. signals indicated that (8a) was present to the extent of 80% of the mixture, and (10b) was 20% of the mixture.

1-*Dimethyl(phenyl)silyl*-2-*methylprop*-1-*ene* (7b).—Methyl iodide (0.89 ml, 1.62 mmol) was added to the vinylcopper reagent (7) (5.7 mmol) and the mixture was kept at 0 °C for 30 min. Work-up gave the *vinylsilane* (8b) (0.78 g, 72%), b.p. 68—70 °C at 0.05 mmHg, R_F (light petroleum) 0.65, $\nu_{max.}$ (CCl_4) 1 620 (C=C), 1 248, and 1 112 cm^{-1}, δ(CCl_4) 7.7—7.1 (5 H, m, Ph), 5.4br (1 H, s, C=CHSi), 1.97 (3 H, s, Me *trans* to Si), 1.79 (3 H, s, Me *cis* to Si), and 0.4 (6 H, s, $SiMe_2$) (Found: M^+, 190.1197. $C_{12}H_{18}Si$ requires *M*, 190.1178), *m/z* 190 (25%), 175 (59, *M* − Me), and 135 (100, Me_2PhSi).

(Z)-1-*Dimethyl(phenyl)silyl*-2-*methylhex*-1-*ene* (8c).—Hexynyl-lithium (17.8 mmol) was added to the vinylcopper reagent (7) (17.6 mmol) at −78 °C. After 5 min, n-butyl iodide (4.05 ml, 35.6 mmol) was added and the mixture was kept at −8 °C for 5 h. Work-up gave the *vinylsilane* (8c) (2.55 g, 62%), b.p. 95 °C at 0.2 mmHg, R_F (light petroleum) 0.7, $\nu_{max.}$ (CCl_4) 1 615 (C=C), 1 250, and 1 115 cm^{-1}, δ(CCl_4) 7.64—7.2 (5 H, m, Ph), 5.42 (1 H, q, *J* 1 Hz, C=CHSi), 2.08br (2 H, t, *J* 8 Hz, CH_2C=C), 1.91 (3 H, d, *J* 1 Hz, MeC=C), 1.51—1.05 (4 H, m, CH_2CH_2), 0.87 (3 H, t, CH_2*Me*), and 0.40 (6 H, s, $SiMe_2$) (Found: M^+, 232.1628. $C_{15}H_{24}Si$ requires *M*, 232.1647), *m/z* 232 (5%, M^+), 217 (35) 190 (30), 148 (28), 135 (100), and 121 (40).

(E)-1-*Dimethyl(phenyl)silyl*-2-*methylbut*-1-*en*-3-*one* (8d).—Acetyl chloride (0.45 ml, 7 mmol) was added to the vinylcopper reagent (7) (3.2 mmol) and the mixture was kept at 0 °C for 3 h. Work-up as in the preparation of (3e) gave the *ketone* (8d) (0.65 g, 50%), b.p 148–150 °C at 0.05 mmHg, R_F (light petroleum–ether, 19 : 1 v/v) 0.3, $\nu_{max.}$ (CCl_4) 1 679 (CO), 1 600 (C=C), 1 250, and 1 113 cm^{-1}, δ(CCl_4) 7.7—7.1 (5 H, m, Ph), 6.6br (1 H, s, C=CHSi), 2.3 (3 H, s, COMe), 1.7br (3 H, s, MeC=C), and 0.4 (6 H, s, $SiMe_2$) (Found: M^+, 218.1128. $C_{13}H_{18}OSi$ requires *M*, 218.1128), *m/z* 218 (2%, M^+), 203 (48, *M* − Me), and 135 (100, Me_2PhSi).

Dimethyl(phenyl)(vinyl)silane (10a).—Quenching the vinylcopper reagent (9) (2.2 mmol) with ammonium chloride solution as in the preparation of (3a) gave the vinylsilane [15] (10a) (280 mg, 78%) R_F (light petroleum) 0.7, $\nu_{max.}$ 1 600 (C=C), 1 250, and 1 115 cm^{-1}, δ(CCl_4) 7.87—7.34 (5 H, m, Ph), 6.75—5.79 (3 H, m, CH=CH_2), and 0.59 (6 H, s, $SiMe_2$) (Found: M^+, 162.0866. $C_{10}H_{14}Si$ requires *M*, 162.0864), *m/z* 162 (30%, M^+), 147 (72), 135 (22), 121 (50), and 69 (100).

(Z)-1-*Dimethyl(phenyl)silylprop*-1-*ene* (10b).—Methyl iodide (0.3 ml, 4.8 mmol) was added to the vinylcopper reagent (9) (2.4 mmol, prepared at −23 °C for 30 s, and used immediately) at −23 °C and then allowed to come to 0 °C over 30 min. Work-up gave the *vinylsilane* (10b) (290 mg, 74%), R_F (light petroleum) 0.7, $\nu_{max.}$ (CCl_4) 1 610 (C=C), 1 250 and 1 115 cm^{-1}, δ(CCl_4) 7.66—7.2 (5 H, m, Ph), 6.54 (1 H, dq, *J* 14 and 7 Hz, MeC*H*=CH), 5.66 (1 H, dq, *J* 14 and 1.5 Hz, CH=C*H*Si), 1.76 (3 H, dd, *J* 7 and 1.5 Hz, *Me*CH), and 0.44 (6 H, s, $SiMe_2$) (Found: M^+, 176.1033. $C_{11}H_{16}Si$ requires *M*, 176.1025), *m/z* 176 (28%, M^+), 161 (100), 135 (36), and 121 (60). This product was the minor component when the methylation was carried out on the vinylcopper reagent (9) prepared at 0 °C, as described under the preparation of its isomer (8a) above.

(E)-2-*Dimethyl(phenyl)silylstyrene* (12).—Quenching of the vinylcopper reagent (11) (1.5 mmol, prepared at −50 °C during 30 min) at −50 °C with ammonium chloride as in the preparation of (3a) gave the vinylsilane [16] (12) (250 mg, 67%), R_F (light petroleum–ether, 95 : 5 v/v) 0.6, $\nu_{max.}$ (CCl_4) 1 606 (C=C) and 1 573 (Ph), 1 248, and 1 113 cm^{-1}, δ(CCl_4) 7.8—6.9 (10 H, m, 2 × Ph), 6.96 (1 H, d, *J* 19.5 Hz, PhC*H*=C), 6.46 (1 H, d, *J* 19.5 Hz, C=CHSi), and 0.40 (6 H, s, $SiMe_2$) (Found: M^+, 238.1163. $C_{16}H_{18}Si$ requires *M*, 238.1178).

(E)- *and* (Z)-1-*dimethyl(phenyl)silyl*-2-*phenylprop*-1-*ene* (13).—Methyl iodide (0.41 ml) was added to the vinylcopper reagent (11) (2.66 mmol, prepared at −50 °C) and the mixture was kept at various temperatures for several hours. Whether the reaction was performed at −78 °C or at 0 °C, the products, isolated by column chromatography eluting with light petroleum—ether 19 : 1 v/v), were always a mixture of the *E*- and *Z*-isomers of the *vinylsilane* (13) (485 mg, 77%, typically) in a ratio of *ca.* 5 : 1 (^{1}H n.m.r.), b.p. 142—145 °C at 0.05 mmHg, R_F (light petroleum–ether, 19 : 1 v/v) 0.55, $\nu_{max.}$ (CCl_4) 1 599 (C=C and Ar), 1 574 and 1 494 (Ar), 1 253 ($SiMe_2$), and 1 114 cm^{-1} (SiPh), δ(CCl_4) 7.7—6.9 (10 H, m, 2 × Ph), 5.9br (*E*-isomer) and 5.4 (*Z*-isomer) (1 H, s and q, *J* 2 Hz, respectively, C=CHSi), 2.0br (*E*-isomer) and 2.1 (*Z*-isomer) (3 H, s and d, *J* 2 Hz, respectively, C=CMe), and 0.4 (6 H, s, $SiMe_2$) (Found: M^+, 252.1329. $C_{17}H_{20}Si$ requires *M*, 252.1335) *m/z* 252 (34%, M^+), 237 (29, *M* − Me), 159 (100, *M* − Me − PhH), and 135 (53, $PhMe_2Si$).

(E)-3-*Dimethyl(phenyl)silylhex*-3-*ene* (15).—The vinylcopper species (14) (1.43 mmol, prepared at 0 °C) was quenched with ammonium chloride solution as in the preparation of (3a) to give the *vinylsilane* (15) (230 mg, 69%), R_F (light petroleum–ether, 19 : 1 v/v) 0.65, $\nu_{max.}$ (CCl_4) 1 610

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(C=C), 1 247 ($SiMe_2$), and 1 109 cm^{-1} (SiPh), $\delta(CCl_4)$ 7.74—7.21 (5 H, m, Ph), 5.83 (1 H, t, *J* 7 Hz, C=C*H*CH_2), 2.21 (4 H, m, CH_2C=CCH_2), 1.08 and 0.92 (3 H each, t, 7.5 and 6.5, respectively, 2 × *Me*CH_2), and 0.41 (6 H, s, $SiMe_2$) (Found: M^+, 218.1498. $C_{14}H_{22}Si$ requires *M*, 218.1491), *m/z* 218 (26%, M^+), 203 (38, *M* − Me), 189 (13, *M* − Et), and 135 (100, $PhMe_2Si$).

(E)-3-*Dimethyl(phenyl)silyl*-4-*methylhex*-3-*ene* (17).—The vinylcopper species (14) (2.2 mmol, prepared at −50 °C for 30 min) and methyl iodide (1 ml) were kept at −50 °C for 2.5 h and then allowed to warm to room temperature over 1 h. Aqueous work-up and t.l.c. (light petroleum–ether, 49 : 1 v/v) gave the *vinylsilane* (17) (104 mg, 45%), R_F (light petroleum–ether, 49 : 1 v/v) 0.85, ν_{max} (CCl_4) 1 610 (C=C), 1 250, and 1 107 cm^{-1}, $\delta(CCl_4)$ 7.5—7.0 (5 H, m, Ph), 2.05br (4 H, q, *J* 7 Hz, CH_2C=CCH_2), 1.5, (3 H, s, MeC=C), 0.9 and 0.8 (3 H each, t, *J* 7 Hz, 2 × *Me*CH_2), and 0.25 (6 H, s, $SiMe_2$) (Found: M^+, 232.1645. $C_{15}H_{24}Si$ requires *M*, 232.1647), *m/z* 232 (33%, M^+), 217 (26, *M* − Me), 203 (11, *M* − Et), 154 (19, *M* − PhH), and 135 (100, $PhMe_2Si$). When the reaction was carried out at higher temperatures (see text) the signal of the *C*-methyl group of the *Z*-isomer could clearly be seen at δ 1.6.

Protodesilylation of the Vinylsilane (15).—The vinylsilane (15) (109 mg) and hydroiodic acid (0.04 ml) were kept in toluene (1 ml) following Utimoto *et al.*[17] After 5 min the i.r. spectrum of the mixture showed signals at 1 660, 1 410, 1 380, 1 075, 902, 840, 800, and 690 cm^{-1} not present in the starting material but characteristic for (Z)-hex-3-ene.[18] There was no sign of the strong signal at 950 cm^{-1}, which would have been characteristic for the *E*-isomer.[19]

1,1-*Pentamethylene*-3-*dimethyl(phenyl)silylallene* (21).—1-Ethynylcyclohexyl acetate [20] (20) (0.33 g, 2 mmol) in THF was added to the cuprate (4 mmol) in THF (30 ml) with stirring under nitrogen at 0 °C and the mixture was kept for 22 h. The mixture was filtered through silica gel, the solvent was removed *in vacuo*, and the residue was distilled to give the *allene* (21) (0.37 g, contaminated with tetramethyldiphenylsiloxane). The yield was variable. The compound had b.p. 80—82 °C at 0.2 mmHg, $\nu_{max.}$ (film) 1 945 (C=C=C) and 1 250 cm^{-1}, $\delta(CCl_4)$ 7.7—7.1 (5 H, m, Ph), 4.85 (1 H, quintet, *J* 3 Hz, =CHSi), 2.20 (4 H, m, 2 × allylic CH_2), 1.50 (6 H, m, other CH_2's), and 0.32 (6 H, s, $SiMe_2$) (Found: M^+, 242.1494. $C_{16}H_{22}Si$ requires *M*, 242.1491), *m/z* 163 (30%), 161 (41), 159 (100), 137 (42), and 135 (75).

The Silylcupration of Dec-1-*yne*.—Dec-1-yne (0.39 ml, 296 mg, 2.35 mmol) was added dropwise to a stirred solution of the silyl-cuprate reagent (2.35 mmol) in dry THF under nitrogen at −78 °C. After 20 min, the mixture was quenched with water (10 ml) and stirred for 1 h at −78 °C and then allowed to warm gradually to room temperature. Work-up and distillation gave (E)-1-*Dimethyl(phenyl)silyldec*-1-*ene* (502 mg, 78%), b.p. 135—140 °C at 0.4 mmHg, R_F (light petroleum–ether, 19 : 1 v/v) 0.7, $\nu_{max.}$ (CCl_4) 1 618 (C=C), and 1 428 cm^{-1} ($SiMe_2$), $\delta(CCl_4)$ 7.9—7.4 (5 H, m, Ph), 6.4 (1 H, dt, *J* 19 and 5 Hz, CH_2C*H*=CH), 5.9 (1 H, d, *J* 19 Hz, SiC*H*=CH), 2.6—2.2 (2 H, m, CH_2CH=CH), 1.9—1.2 (12 H, m, 6 × CH_2), 1.05 (3 H, t, *J* 5 Hz, Me), and 0.6 (6 H, s, $SiMe_2$) (Found: M^+, 274.2114. $C_{18}H_{30}Si$ requires *M*, 274.2117), *m/z* 274 (39%, M^+), 259 (100, *M* − Me), and 135 (70, $PhMe_2Si$). Work-up earlier than 20 min showed the presence of unchanged acetylene.

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