

The Reaction of *tert*-Butyldiphenylsilylcuprates with Allenes

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Bis(*tert*-butyldiphenylsilyl)cuprate **1** reacts with allenes to form allyl- and vinyl-silanes. With allene itself the cuprate reagent shows a different regiochemistry from that of bis(phenyldimethylsilyl)cuprate. The regiochemistry can be controlled by choosing an appropriate reaction temperature. The intermediate cuprate **4** resulting from the addition of **1** to allene reacts with a wide variety of electrophiles giving functionalised allylsilanes. Phenylallenes isomerise to acetylenes.

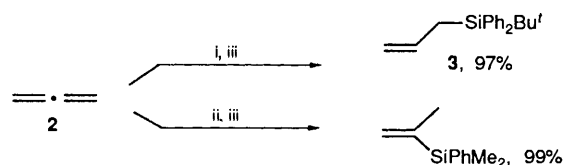
We reported earlier that silylcuprate reagents react with allenes to give either allyl- or vinyl-silanes depending upon the structure of the allene.^{1–3} The intermediate copper species react with electrophiles giving functionalised silylated synthons. Since the silylcuprate reagents are usually nucleophiles, this reaction is formally a nucleophilic attack on an unactivated allene, a type of reaction with very little precedent. Oshima and his co-workers reported⁴ the addition of silicon–magnesium, silicon–aluminium and silicon–zinc bonds to allenes, catalysed by copper(I) or palladium, but the carbocupration of allenes is not known except when activating substituents are present.⁵ In our work, using silylcuprates and allenes, we mostly used bis(phenyldimethylsilyl)cuprate rather than bis(trimethylsilyl)cuprate because phenyldimethylsilyllithium[†] is more easily made than trimethylsilyllithium.[‡] Furthermore, the phenyl group is a functional handle that makes it possible to convert the phenyldimethylsilyl group into a hydroxy group in an oxidative rearrangement.⁸

Recently, we reported⁹ the synthesis and some reactions of two new silyl-nucleophiles: *tert*-butyldiphenylsilyllithium and bis(*tert*-butyldiphenylsilyl)cuprate. The former shows a different pattern of reactivity from trimethyl- and phenyldimethylsilyllithium, giving carbonyl addition on reaction with α,β -unsaturated ketones.⁹ On the other hand, bis(*tert*-butyldiphenylsilyl)cuprate reacts with acyl chlorides,⁹ α,β -unsaturated ketones and esters,⁹ and acetylenes,¹⁰ just as the other silylcuprates react with electrophiles.

We now describe the regiochemistry of the silyl-cupration of allenes using this bulky silyl-cuprate reagent. We found that the *tert*-butyldiphenylsilylcuprate shows some different regioselectivity in its reaction with allenes from that shown by the phenyldimethylsilylcuprate.

Results and Discussion

The reaction of *tert*-butyldiphenylsilylcuprate **1** with allene **2**, at solid CO₂–acetone temperatures, followed by protonation at this temperature, gives the allylsilane **3** in high yield (Scheme 1)



Scheme 1 Reagents and conditions: i, (Bu^tPh₂Si)₂CuLi, THF, 1, –78 °C; ii, (PhMe₂Si)₂CuLi, THF, –78 °C; iii, NH₄Cl, MeOH, –78 °C

[†] Dimethyl(phenyl)silyl chloride and lithium shot in THF.⁶

[‡] Methylolithium and hexamethyldisilane in neat HMPA.⁷

1). This regiochemistry is the opposite of that for the phenyldimethylsilyl analogue. It seems likely that the change of regiochemistry may be a consequence of the steric preference of the bulky *tert*-butyldiphenylsilyl group for the end of the allenic system. In any case, the intermediate vinyl-copper species, formulated as **4**, reacts cleanly with a wide variety of other electrophiles, giving the allylsilanes **5a–i** (Scheme 2).

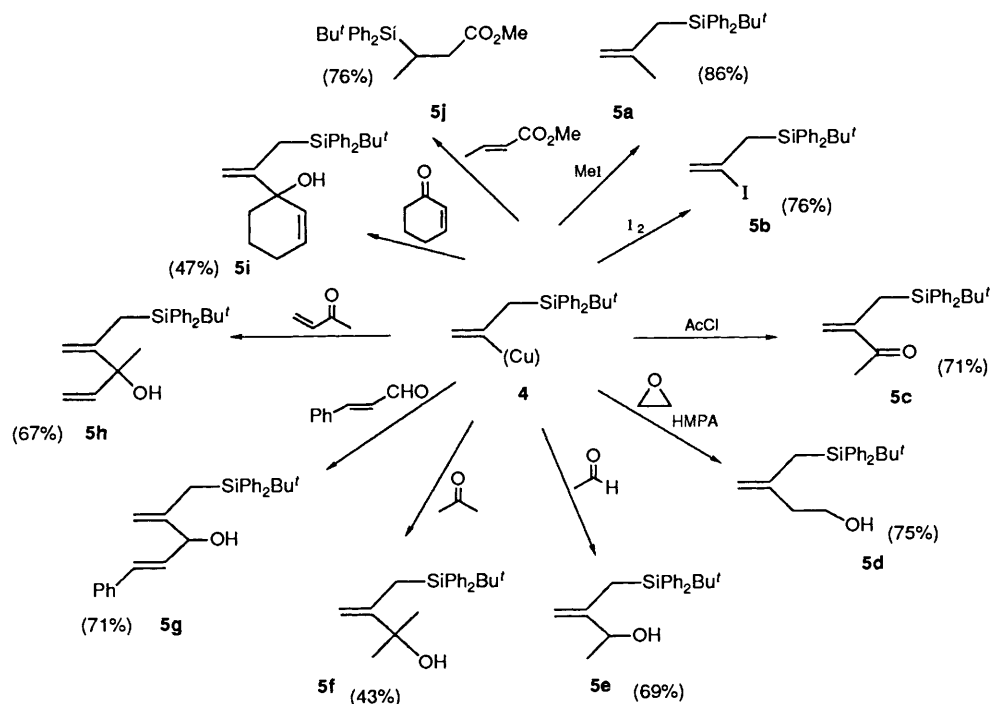
Thus, the present route is an easy entry into the synthesis of diversely substituted allylsilanes. Alkyl halides other than methyl iodide do not give acceptable yields when added to the copper intermediate **4**, but the iodide **5b** can be lithiated by metal–iodine exchange with butyllithium, and the resulting vinylolithium reagent **6** reacts with ethyl bromide to give **7a** in good yield (Scheme 3).

The regiochemistry of attack by the intermediate **4** on the enones, giving the allylic alcohols **5h** and **5i** is remarkable. The corresponding intermediate derived from the phenyldimethylsilyl reagent is normal in undergoing conjugate addition with cyclohexenone. The reaction with methyl crotonate is also unusual in that the silyl group is transferred, rather than the allylsilane group, giving methyl 3-*tert*-butyldiphenylsilylbutanoate **5j**.

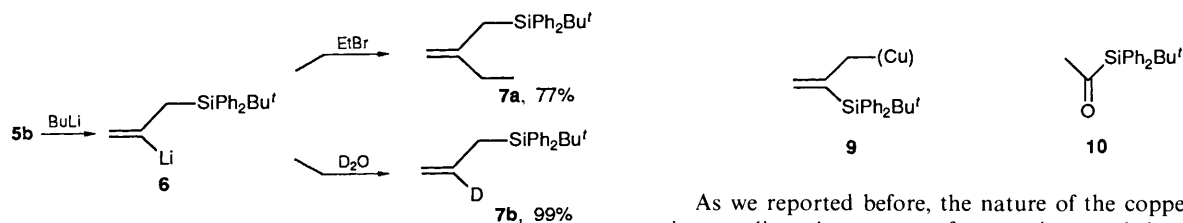
The vinylolithium reagent **6** is regiochemically stable at any temperature between –78 and 0 °C. Deuteriation of **6** gives the allylsilane **7b** in almost quantitative yield at either temperature.

In contrast, the intermediate cuprate **4** is not regiochemically stable. When we carried out the reaction of allene **2** with reagent **1** at the usual solid CO₂–acetone temperature, and then warmed the mixture to 0 °C before quenching it (either at –78 or 0 °C) we obtained the vinylsilane **8**, the regioisomer of **3** (Scheme 4). Presumably, the addition of the silylcuprate **1** is reversible. Thus the overall regiochemistry is easily controlled in either sense by the temperature.

Unfortunately, the presumed allylcopper intermediate **9**, produced by the reaction of **1** with **2** at 0 °C, does not react with electrophiles apart from protons. We checked the reaction of the presumed intermediate **9** with our usual electrophiles, iodine, methyl iodide and acetyl chloride, and in all the experiments only the vinylsilane **8** resulting from protodecupration (96%) was formed. Reaction of **9** with acetyl chloride also gave the acylsilane **10** (75%). Since it is reasonable to expect that the cuprate **9** is a mixed higher-order cuprate, in which the copper has one carbon ligand and one silyl ligand (from the disilylcuprate), it is reasonable that the silyl ligand is selectively transferred to the electrophile. This explains the formation of the acylsilane **10**, since it has already been found¹¹ that mixed cuprates transfer the silyl group rather than the carbon group to electrophiles. As we have pointed out before, this still leaves unexplained the anomalous behaviour of mixed cuprate intermediates such as **4**, in which the carbon group is cleanly



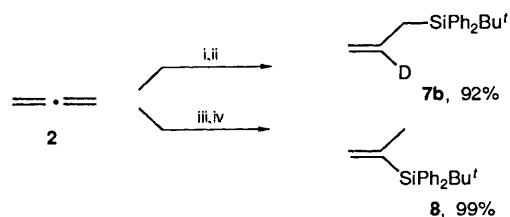
Scheme 2



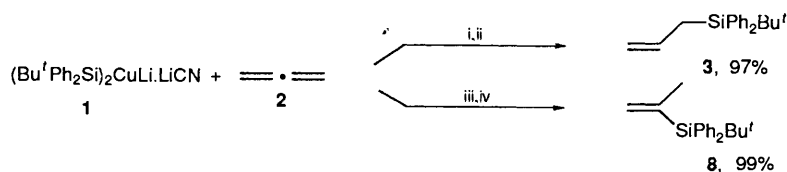
Scheme 3

transferred to electrophiles. We are not able to identify the corresponding silicon product in the analogous reactions of the presumed intermediate **9** with iodine and methyl iodide. We have made an effort to understand why only the protodecupration product **8** is formed in all these reactions. Reaction of allene **1** at -78°C followed by quenching at the same temperature with deuterium oxide, gave the expected deuteriated allylsilane **7b**, whereas the same reaction carried out at 0°C and quenched with deuterium oxide at 0°C gives **8** with no detectable deuterium incorporation (Scheme 5). Evidently the formation of **7b** results from the deuteration of the vinylcopper species **4**, but protodecupration of the allylcopper intermediate **9** must have occurred before quenching with deuterium oxide. We naturally suspected that the THF was the source of the proton, but when the same sequence was carried out in $[\text{}^2\text{H}_8]\text{-THF}$ (tetrahydrofuran), quenching at 0°C with water, again no deuterium was present in the product **8**. The yield was calculated on the amount of allene, and so the allene cannot be the proton source. This leaves only the extra *tert*-butyldiphenylsilyl group, which would be unlikely to supply a proton.

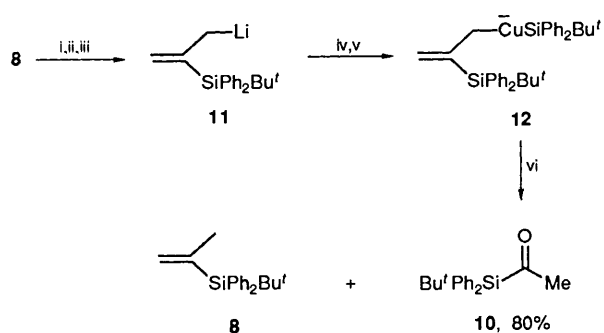
As we reported before, the nature of the copper-containing intermediates is a matter of uncertainty, and the copper intermediates **4** and **9** cannot be as simple as we represent them here. We made the reconstituted cuprate **12** from **8** by way of the allyllithium **11**, to check whether or not it shows the same unexplained reactivity pattern as the presumed intermediate cuprate **9**. We treated the cuprate **12** with methyl iodide and acetyl chloride and got, as before, only the vinylsilane **8**, and with acetyl chloride the acylsilane **10** (Scheme 6). Thus reconstituted cuprate **12** appears to behave in essentially the same way as that produced in the reaction of allene with **1** at 0°C . We still need to find the source of the proton in the reactions of **9** and **12**.



Scheme 5 Reagents and conditions: i, $(\text{Bu}^t\text{Ph}_2\text{Si})_2\text{CuLi}$, -78°C ; ii, D_2O , -78°C ; iii, $(\text{Bu}^t\text{Ph}_2\text{Si})_2\text{CuLi}$, 0°C ; iv, D_2O , 0°C

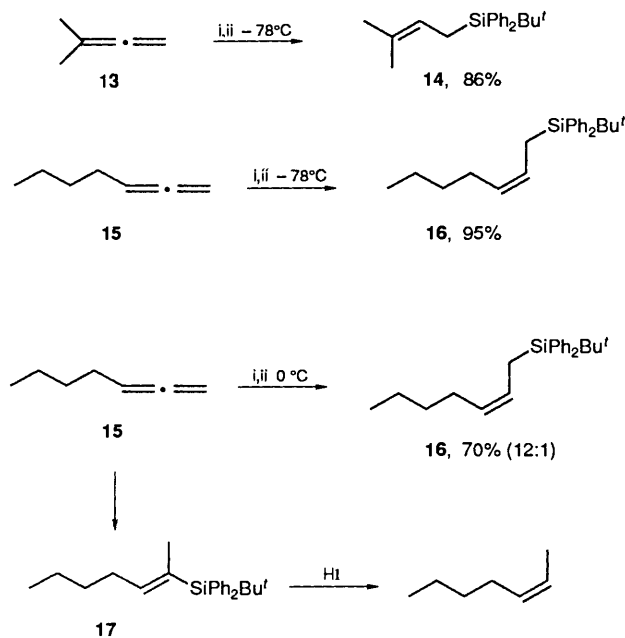


Scheme 4 Reagents and conditions: i, -78°C , 1 h; ii, NH_4Cl , MeOH , -78°C ; iii, $-78 \rightarrow 0^\circ\text{C}$ or $\text{O} \rightarrow -78^\circ\text{C}$ or $-78 \rightarrow 0 \rightarrow -78^\circ\text{C}$; iv, NH_4Cl , MeOH



Scheme 6 Reagents and conditions: i, NBS; ii, Bu_3SnLi ; iii, BuLi ; iv, CNCu ; v, $(\text{Bu}^t\text{Ph}_2\text{Si})_2\text{CuLi}$; vi, MeCOCl

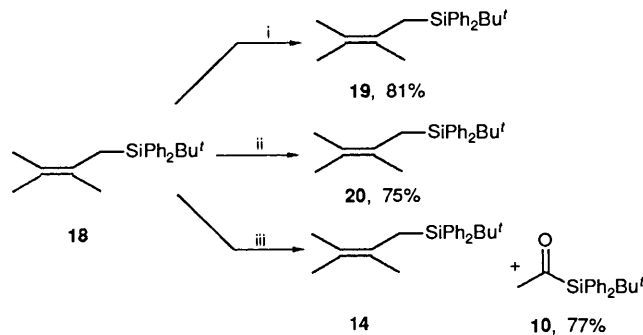
The silylcuprate reagent **1** reacted with alkyl-substituted allenes **13** and **15** at solid CO_2 -acetone temperatures to give allylsilanes **14** and **16** (Scheme 7). The corresponding reaction



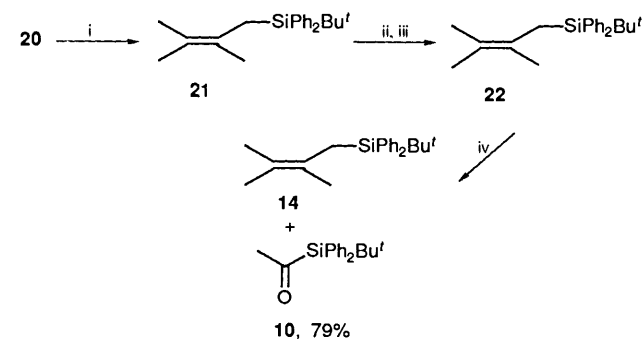
Scheme 7 Reagents and conditions: i, $(\text{Bu}^t\text{Ph}_2\text{Si})_2\text{CuLi}$; ii, NH_4Cl

of the phenyldimethylsilylcuprate reagent with the allene **13** was the same, but with the allene **15** it gave a mixture of the allylsilane and the regioisomer, the vinylsilane, in a 1:4 ratio. We repeated the reaction of the silylcuprate reagent **1** with butylallene **15**, but at 0°C , and obtained two products, the allylsilane **16**, as before, and the vinylsilane **17**, in ratio of 1:12. The result described above is additional evidence of the regiochemical instability of the intermediate, favouring at high temperatures the vinylsilane over the allylsilane. The *E*-geometry of the vinylsilane **17** has been proved by protodesilylation with hydrogen iodide giving the *Z*-alkene. The stereochemistry of the double bond of **16** and **17** is reasonable if the silylcuprate attacks the allene *anti* to the butyl group. The reaction of the intermediate **18**, prepared by silylcupration of 1,1-dimethylallene with iodine or methyl iodide gives cleanly the allylsilanes **19** and **20**, but acetyl chloride reacts with the same intermediate **18** giving the allylsilane **14** and the acylsilane **10**, in which the silyl group has been transferred to the acetyl chloride instead of the carbon ligand (Scheme 8). We also get the same result in the reaction with acetyl chloride of a reconstituted cuprate **22**, prepared from the lithium reagent **21** (Scheme 9).

In contrast to their reactions with the phenyldimethylsilyl-

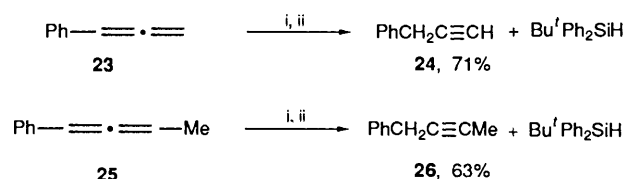


Scheme 8 Reagents: i, MeI ; ii, I_2 ; iii, MeCOCl



Scheme 9 Reagents: i, BuLi ; ii, CNCu ; iii, $\text{Bu}^t\text{Ph}_2\text{SiLi}$; iv, MeCOCl

cuprate, phenylallenes are not suitable substrates for the silylcupration reaction using the new silylcuprate reagent **1**, because they undergo isomerisation to acetylenes. Thus, 1-phenylallene **23** and 3-methyl-1-phenylallene **25** are converted, in not easily reproducible reactions, into benzylacetylene **24** and 1-phenylprop-2-yne **26**, respectively (Scheme 10). The yields quoted are



Scheme 10 Reagents and conditions: i, $(\text{Bu}^t\text{Ph}_2\text{Si})_2\text{CuLi}$, THF, -78°C ; ii, NH_4Cl , MeOH , -78°C

the highest we obtained and were measured, using an internal standard, by GC and the products were identified by ^1H NMR spectroscopy. Although the reagent is basic (*tert*-butylalcohol inactivates it), it is surprising that it induces the isomerisation of the phenylallenes into acetylenes. This type of isomerisation using strong bases,¹² is well known, but usually leads to terminal alkynes.

Trisubstituted allenes fail to react with **1**, whereas they do react with the phenyldimethylsilyl analogue.

Experimental

General.—Ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl under nitrogen in a standard still. All chromatographic and work-up solvents were distilled prior to use. Copper(I) cyanide was dried *in vacuo* over P_2O_5 . All reactions involving organometallic agents were carried out under an atmosphere of dry nitrogen or argon using flame-dried glassware. IR spectra were recorded on a Pye-Unicam SP-1100 and a Mattson Cygnus-100 spectrometers as neat liquid films. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker AC-80 spectrometer, and are reported in ppm (δ) from TMS ($[(\text{CH}_3)_4\text{Si}]$, *J* values are given in Hz. Mass

spectra were obtained from a Hewlett-Packard 5988-A instrument.

The allenes **2** and **13** were bought. The allenes **15** (47%), **23** (51%) and **25** (79%) were prepared by the method of Crabbé.¹³

tert-Butyldiphenylsilyllithium.—*tert*-Butyldiphenylchlorosilane (30 mmol, 7.7 cm³) was stirred with lithium (180 mmol, 1.26 g) in THF (30 cm³) at 0 °C for 4 h. The red-black solution is stable for at least 5 d, at -15 °C. For titration, an aliquot was transferred by syringe into water and the basic solution was titrated against hydrochloric acid (0.1 mol dm⁻³).

Lithium Bis(tert-butyldiphenylsilyl)cuprate 1.—A THF solution of *tert*-butyldiphenylsilyllithium (12 mmol), prepared as before, was added by syringe to a stirred suspension of copper(I) cyanide (6 mmol, 537 mg) in THF (10 cm³) at 0 °C. The resulting black mixture was stirred for 30 min. It was used immediately.

General Procedure for the Silylcupration of Allenes.—Typically, the allene (5 mmol) in THF (5 cm³) was added dropwise to the *tert*-butyldiphenylsilylcuprate reagent **1** (5.5 mmol), cooled with a solid CO₂-acetone bath, and the mixture stirred under nitrogen for 1 h. Yields are based on the allene.

The Preparation of the Lithium Reagents 6 and 21.—Butyllithium (1.6 mol dm⁻³ solution in hexane; 3.5 cm³) was added dropwise to the vinyl iodide, **5b** or **20**, in THF (5 cm³) at solid CO₂-acetone temperatures, and the mixture stirred under nitrogen for 1 h.

Preparation of the Cuprate Reagent 22.—The lithium reagent **21** (2 mmol) and copper(I) cyanide (2 mmol) were stirred together at solid CO₂-acetone temperatures for 15 min, the silyllithium reagent **1** (2 mmol) was then added, and the mixture stirred for a further 30 min.

Preparation of the Lithium Reagent 11.—The vinylsilane **8** (1.40 g, 5 mmol) and *N*-bromosuccinimide (NBS) (0.89 g, 5 mmol) were refluxed in carbon tetrachloride (10 cm³) for 12 h with a catalytic amount of benzyl peroxide. Filtration, evaporation and chromatography (SiO₂, hexane) gave 3-bromo-2-*tert*-butyldiphenylsilylpropene (1.54 g, 86%) (Found: C, 63.2; H, 6.5. C₁₉H₂₃BrSi requires C, 63.5; H, 6.4%; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1600, 1230 and 1130; $\delta_{\text{H}}(\text{CDCl}_3)$ 7.8–7.5 (4 H, m), 7.5–7.2 (6 H, m), 6.4 (1 H, m), 5.9 (1 H, m), 4.05 (2 H, br s) and 1.15 (27 H, s); m/z 303, 301 (M – Bu⁺, 19%), 263 (100), 261 (98), 223 (24) and 181 (28). The above allyl bromide (1.1 g, 3 mmol) in THF (5 cm³) was added slowly to a solution of tributylstannylithium¹⁴ (1.2 mol dm⁻³ solution in THF prepared from tributyltin chloride; 1.5 cm³) at 0 °C and the mixture stirred for 1 h; it was then warmed to room temperature and stirred for a further 1 h. Work-up and chromatography (SiO₂, hexane) gave 2-*tert*-butyldiphenylsilyl-3-tributylstannylpropene (1.53 g, 91%), $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1580, 1200 and 1120; $\delta_{\text{H}}(\text{CDCl}_3)$ 7.6–7.4 (4 H, m), 7.4–7.2 (6 H, m), 5.7 (1 H, m), 5.4 (1 H, d, *J* 1.3), 1.9 (2 H, br s), 1.4–0.5 (27 H, m) and 1.1 (9 H, s); $\delta_{\text{C}}(\text{CDCl}_3)$ 146.50, 136.50, 135.04, 129.00, 126.08, 97.05, 29.09, 28.90, 27.49, 20.00, 19.92, 14.00 and 9.95. Butyllithium (1.6 mol dm⁻³ solution in hexane; 0.7 cm³) was added dropwise to the above allylstannane (1 mmol) in ether (2 cm³) at 0 °C and the mixture stirred for 30 min.

Preparation of the Cuprate Reagent 12.—The allyllithium reagent **11** (1 mmol) was added to a solution of CuCN (0.045 g,

0.5 mmol) in THF (2 cm³) at solid CO₂-acetone temperature, and the black solution stirred for 30 min.

Protonation of the Organometallic Intermediates.—Methanol (3 cm³) saturated with ammonium chloride was added at low temperature to the still cold solution following the silylcupration or the halogen-metal exchange, as appropriate: the mixture was allowed to warm to 0 °C and stirred for 10 min. Aqueous work-up using ether, drying (MgSO₄), and chromatography (SiO₂, hexane) gave the following compounds.

3-*tert*-Butyl(diphenyl)silylpropene **3** (97%) (Found: C, 81.6; H, 8.5. C₁₉H₂₄Si requires C, 81.4; H, 8.6%; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1650, 1620, 1460, 1030, 850 and 810; $\delta_{\text{H}}(\text{CDCl}_3)$ 7.8–7.6 (4 H, m), 7.5–7.3 (6 H, m), 6.2–5.5 (1 H, m), 5.15–4.7 (2 H, m), 2.2 (2 H, d, *J* 4) and 1.05 (9 H, s); $\delta_{\text{C}}(\text{CDCl}_3)$ 135.98, 134.58, 134.45, 129.05, 127.51, 114.50, 27.89, 18.83 and 18.46; m/z 280 (M⁺, 6%), 239 (60, 223 (97), 197 (42), 181 (32), 145 (35), 135 (100) and 105 (42). When the reaction mixture was warmed to 0 °C and quenched at either 0 °C or at -78 °C, the product was vinylsilane **8**.

2-*tert*-Butyl(diphenyl)silylpropene **8** (99%) (Found: C, 81.2; H, 8.5. C₁₉H₂₄Si requires C, 81.4; H, 8.6%; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1640, 1610, 1460, 1020 and 900; $\delta_{\text{H}}(\text{CDCl}_3)$ 7.80–7.60 (4 H, m), 7.60–7.20 (6 H, m), 6.00–5.80 (1 H, m), 5.60–5.40 (1 H, m), 2.00 (3 H, br s) and 1.20 (9 H, s); $\delta_{\text{C}}(\text{CDCl}_3)$ 142.50, 136.20, 131.50, 129.00, 127.75, 127.60, 28.60, 25.20 and 18.30; m/z 280 (M⁺, 3%), 223 (100), 197 (31), 183 (27) and 105 (25). Quenching with deuterium oxide in place of ammonium chloride, at 0 °C, omitting the ammonia gave the vinylsilane **8** (99%) as the sole product.

3-*tert*-Butyl(diphenyl)silyl-2-deuteriopropene **7b** (92%) (Quenching with deuterium oxide in place of methanol, at -78 °C, and omitting the ammonia) (Found: C, 81.3; H, 9.1. C₁₉H₂₃DSi requires C, 81.1; H, 8.95%; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2230 and 980; $\delta_{\text{H}}(\text{CDCl}_3)$ 7.80–7.40 (4 H, m), 7.40–7.10 (6 H, m), 5.60 (1 H, m), 5.20 (1 H, m), 2.40 (2 H, s) and 1.20 (9 H, s). The same product was obtained when the lithium reagent **6** was quenched with deuterium oxide.

1-*tert*-Butyl(diphenyl)silyl-3-methylbut-2-ene **14** (86%) (Found: C, 81.9; H, 9.2. C₂₁H₂₈Si requires C, 81.7; H, 9.1%; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1640, 1080 and 820; $\delta_{\text{H}}(\text{CDCl}_3)$ 7.70–7.40 (4 H, m), 7.40–7.00 (6 H, m), 5.00 (1 H, t, *J* 5), 1.90 (2 H, d, *J* 5), 1.50 (3 H, s), 1.30 (3 H, s) and 1.00 (9 H, s); m/z 308 (8%, M⁺), 293 (2), 251 (4), 239 (100), 231 (7) and 197 (3).

(*Z*)-1-*tert*-Butyl(diphenyl)silylhept-2-ene **16** (95%) (Found: C, 82.3; H, 9.5. C₂₃H₃₂Si requires C, 82.1; H, 9.6%; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1650, 1090 and 700; $\delta_{\text{H}}(\text{CDCl}_3)$ 7.80–7.60 (4 H, m), 7.60–7.20 (6 H, m), 5.60–5.00 (2 H, m), 2.10 (2 H, d, *J* 4), 2.00–1.70 (2 H, m), 1.50–1.00 (4 H, m), 1.10 (9 H, s) and 0.90 (3 H, t, *J* 7); m/z 336 (M⁺, 2%), 279 (29), 259 (38), 239 (100), 179 (7) and 135 (8). When the silyl-cupration of allene **15** was carried out at 0 °C the allylsilane **16** and the vinylsilane **17** were formed (70%) in a ratio (1:12).

(*E*)-2-*tert*-Butyl(diphenyl)silylhept-2-ene **17** (Found: C, 82.0; H, 9.55. C₂₃H₃₂Si requires C, 82.1; H, 9.6%; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1660, 1090 and 820; $\delta_{\text{H}}(\text{CDCl}_3)$ 7.80–7.50 (4 H, m), 7.50–7.20 (6 H, m), 6.20–5.80 (1 H, td, *J* 5, 2), 2.40–2.00 (2 H, m), 1.90 (3 H, d, *J* 2), 1.40–1.20 (4 H, m), 1.10 (9 H, s), 0.90 (3 H, t, *J* 7); m/z 336 (M⁺, 5%), 221 (4), 279 (29), 259 (100), 239 (21) and 179 (3).

Methylation of the Cuprate Intermediates.—Methyl iodide (3 mmol) was added dropwise to the silylcupration mixture (2 mmol) and stirred at solid CO₂-acetone temperatures for 1 h and then at 0 °C for 1 h. Aqueous work-up using ether, and chromatography (SiO₂, hexane) gave the following compounds 3-*tert*-butyl(diphenyl)silyl-2-methylpropene **5a** (86%) (Found: C, 81.5; H, 8.9. C₂₀H₂₆Si requires C, 81.6; H, 8.9%; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1680, 1090, 1020 and 900; $\delta_{\text{H}}(\text{CDCl}_3)$ 7.80–7.50 (4 H, m), 7.50–7.20 (6 H, m), 4.60 (2 H, s), 2.20 (2 H, s),

1.40 (3 H, s) and 1.05 (9 H, s); m/z 294 (M^+ , 6%), 237 (100), 135 (89) and 105 (28).

1-*tert*-Butyl(diphenyl)silyl-2,3-dimethylbut-2-ene **19** (81%) (Found: C, 81.8; H, 9.6. $C_{22}H_{30}Si$ requires C, 81.9; H, 9.4%); $\nu_{max}(\text{film})/\text{cm}^{-1}$ 1630 and 1070; $\delta_H(\text{CDCl}_3)$ 7.80–7.50 (4 H, m), 7.50–7.10 (6 H, m), 2.20 (2 H, s), 1.40 (3 H, s), 1.30 (3 H, s), 1.20 (9 H, s) and 1.00 (3 H, s); m/z 322 (M^+ , 1%), 307 (6), 265 (31), 245 (24) and 239 (100).

Halogenation of the Silylcupration Products.—Iodine (1.5 mmol for 1 mmol) in two portions was added to the cuprate at solid CO_2 -acetone temperatures. The reaction mixture was kept at these temperatures for 1 h after which it was allowed to warm to 0 °C and kept for 1 h. Work-up and chromatography (SiO_2 , hexane) gave the following compounds.

3-*tert*-Butyl(diphenyl)silyl-2-iodopropene **5b** (76%) (Found: C, 56.4; H, 5.6. $C_{19}H_{23}ISi$ requires C, 56.15; H, 5.7%); $\nu_{max}(\text{film})/\text{cm}^{-1}$ 1600, 1120, 1020 and 960; $\delta_H(\text{CDCl}_3)$ 7.80–7.50 (4 H, m), 7.50–7.20 (6 H, m), 5.60–5.40 (2 H, m), 2.90 (2 H, s) and 1.05 (9 H, s); m/z 406 (M^+ , 1%), 349 (22), 309 (100), 279 (11) and 135 (30).

1-*tert*-Butyl(diphenyl)silyl-2-iodo-3-methylbut-2-ene **20** (75%) (Found: C, 58.4; H, 6.1. $C_{21}H_{27}ISi$ requires C, 58.1; H, 6.3%); $\nu_{max}(\text{film})/\text{cm}^{-1}$ 1620 and 1090; $\delta_H(\text{CDCl}_3)$ 7.80–7.40 (4 H, m), 7.40–7.10 (6 H, m), 2.90 (2 H, s), 1.60 (3 H, s), 1.50 (3 H, s) and 1.30 (9 H, s); m/z 434 (M^+ , 2%), 377 (47), 307 (23), 289 (25), 239 (100) and 229 (27).

Acetylation of the Intermediates.—Acetyl chloride (2.25 mmol) was added to the silylcupration mixture (1.5 mmol) as in the reactions above to give the following compounds.

3-*tert*-Butyl(diphenyl)silylmethylbut-3-en-2-one **5c** (71%) (Found: C, 78.2; H, 8.15. $C_{21}H_{26}OSi$ requires C, 78.2; H, 8.1%); $\nu_{max}(\text{film})/\text{cm}^{-1}$ 1690, 1610, 1120 and 880; δ_H 7.80–7.40 (4 H, m), 7.40–7.20 (6 H, m), 5.60 (1 H, m), 5.30 (1 H, m), 2.40 (2 H, s), 1.90 (3 H, s) and 1.05 (9 H, s); m/z 322 (M^+ , 1%), 307 (12), 199 (100) and 135 (30).

tert-Butyldiphenylsilyl methyl ketone **10** (77%), b.p. 84 °C/12 mmHg (lit.,⁹ 88 °C/15 mm).

3-*tert*-Butyl(diphenyl)silylmethylbut-3-en-1-ol **5d**.—Hexamethylphosphoric triamide (HMPA) (3 mmol) in THF (1 cm^3) at solid CO_2 -acetone temperatures, was added to the silylcupration mixture (3 mmol) and kept for 5 min; then ethylene oxide (6 mmol) was then added to it. After 30 min, the mixture was warmed to 0 °C and kept for 10 h before work-up, which gave the allylsilane (75%) (Found: C, 77.9; H, 8.8. $C_{21}H_{28}OSi$ requires C, 77.7; H, 8.7%); $\nu_{max}(\text{film})/\text{cm}^{-1}$ 3350, 1630, 1110, 1030 and 1000; $\delta_H(\text{CDCl}_3)$ 7.80–7.60 (4 H, m), 7.60–7.20 (6 H, m), 4.70 (2 H, m), 3.40 (2 H, t, *J* 6), 2.15 (2 H, s), 1.70 (1 H, br s), 1.90–1.60 (2 H, m) and 1.05 (9 H, s); m/z 324 (M^+ , 1%), 267 (18), 249 (21), 225 (10), 199 (100) and 135 (60).

Reactions of the Cuprate Intermediate 4 with Oxo Compounds.—Acetaldehyde, acetone, cinnamaldehyde, methyl vinylketone or cyclohexenone (4.5 mmol) in THF (1 cm^3) was added to the cuprate reagent **4** (3 mmol) at solid CO_2 -acetone temperatures. The mixture was kept for 2 h and then allowed to warm to 0 °C. After being stirred for 1 h at this temperature, aqueous work-up and chromatography (SiO_2 , Et_2O -hexane) gave the following compounds.

3-*tert*-Butyl(diphenyl)silylmethylbut-3-en-2-ol **5e** (69%) (Found: C, 77.7; H, 8.6. $C_{21}H_{28}OSi$ requires C, 77.7; H, 8.7%); $\nu_{max}(\text{film})/\text{cm}^{-1}$ 3600, 3200, 1630, 1110, 1080 and 870; $\delta_H(\text{CDCl}_3)$ 7.60–7.30 (4 H, m), 7.30–7.10 (6 H, m), 6.0 (1 H, m), 5.80 (1 H, m), 3.50 (1 H, q, *J* 7), 2.30 (2 H, s), 1.60 (1 H, br s), 1.10 (9 H, s) and 0.9 (3 H, d, *J* 7); $\delta_C(\text{CDCl}_3)$ 144, 137, 135, 133, 128, 66, 48 and 29; m/z 267 ($M - \text{Bu}^t$, 26%), 199 (100), 181 (10), 135 (4) and 105 (10).

3-*tert*-Butyl(diphenyl)silylmethyl-2-methylbut-3-en-2-ol **5f** (43%) (Found: C, 78.1; H, 9.0. $C_{22}H_{30}OSi$ requires C, 78.05; H, 8.9%); $\nu_{max}(\text{film})/\text{cm}^{-1}$ 3300, 1620, 1200 and 1090; $\delta_H(\text{CDCl}_3)$ 7.80–7.40 (4 H, m), 7.40–7.10 (6 H, m), 6.10 (1 H, m), 5.80 (1 H, m), 2.30 (2 H, s), 1.50 (1 H, br s), 1.20 (6 H, s) and 1.1 (9 H, s); m/z 281 ($M - \text{Bu}^t$, 8%), 199 (100), 181 (12), 135 (8) and 105 (10).

4-*tert*-Butyl(diphenyl)silylmethyl-1-phenylpenta-1,4-dien-3-ol **5g** (71%) (Found: C, 81.4; H, 7.8. $C_{28}H_{32}OSi$ requires C, 81.5; H, 7.8%); $\nu_{max}(\text{film})/\text{cm}^{-1}$ 3500, 1620, 1150 and 1050; $\delta_H(\text{CDCl}_3)$ 7.80–7.50 (4 H, m), 7.50–7.10 (6 H, m), 7.10 (5 H, s), 6.20 (2 H, m), 6.10 (1 H, m), 5.90 (1 H, m), 4.10 (1 H, m), 2.60 (2 H, s), 1.80 (1 H, br s) and 1.30 (9 H, s); $\delta_C(\text{CDCl}_3)$ 143, 138, 137, 133, 132, 130, 129, 128.8, 128, 126.5, 71, 46, 29 and 19; m/z 355 ($M - \text{Bu}^t$, 40%), 311 (12), 277 (15), 199 (100), 135 (87) and 105 (38).

2-*tert*-Butyl(diphenyl)silylmethyl-3-methylpenta-1,4-dien-3-ol **5h** (67%) (Found: C, 78.6; H, 8.8. $C_{22}H_{30}OSi$ requires C, 78.8; H, 8.6%); $\nu_{max}(\text{film})/\text{cm}^{-1}$ 3500, 1620, 1610, 1100 and 990; $\delta_H(\text{CDCl}_3)$ 7.80–7.40 (4 H, m), 7.40–7.10 (6 H, m), 6.20 (1 H, m), 5.80 (1 H, d, *J* 2), 5.50–4.80 (3 H, m), 2.80 (1 H, s), 2.40 (1 H, br s), 1.20 (3 H, s) and 1.10 (9 H, s); m/z 293 ($M - \text{Bu}^t$, 6%), 199 (100), 163 (4) and 105 (30).

1-(3-*tert*-Butyldiphenylsilylprop-1-en-2-yl)cyclohex-2-enol **5i** (47%) (Found: C, 79.9; H, 8.5. $C_{25}H_{32}OSi$ requires C, 79.7; H, 8.6%); $\nu_{max}(\text{film})/\text{cm}^{-1}$ 3400, 1640, 1100 and 1080; $\delta_H(\text{CDCl}_3)$ 7.80–7.30 (4 H, m), 7.30–7.00 (6 H, m), 6.20 (1 H, m), 5.80 (1 H, d, *J* 1), 5.40 (2 H, m), 2.40 (2 H, s), 2.40–0.80 (7 H, m) and 1.10 (9 H, s); m/z 376 (M^+ , 1%), 336 (2), 319 ($M - \text{Bu}^t$, 8), 279 (90), 199 (100) and 135 (40).

Methyl 3-*tert*-butyldiphenylsilylbutanoate **5j** (76%), b.p. 90 °C/12 mmHg (lit.,⁹ 96 °C/20 mmHg).

2-*tert*-Butyldiphenylsilylbutanoate-1-ene **7a**.—Ethyl bromide (3 mmol) was added dropwise to the lithium reagent **6** (2 mmol) and stirred at solid CO_2 -acetate temperatures for 1 h and then at 0 °C for 1 h. Aqueous work-up using ether, and chromatography gave the allylsilane **7a** (77%) (Found: C, 82.0; H, 9.2. $C_{21}H_{28}Si$ requires C, 81.7; H, 9.1%); $\nu_{max}(\text{film})/\text{cm}^{-1}$ 1670, 1090 and 910; $\delta_H(\text{CDCl}_3)$ 7.80–7.40 (4 H, m), 7.40–7.10 (6 H, m), 4.80 (2 H, br s), 2.30 (2 H, q, *J* 7), 2.20 (2 H, s), 1.30 (9 H, s) and 1.00 (3 H, t, *J* 7); m/z 308 (M^+ , 2%), 279 (40), 251 (84), 239 (70), 135 (100) and 105 (19).

Protodesilylation of the Vinylsilane 17.—The vinylsilane (1.4 mmol) and hydriodic acid (0.12 cm^3) was stirred in benzene (1 cm^3) at room temperature for 1 h. Work-up gave (*Z*)-hept-2-ene.

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