

Synthesis of Allenylsilanes from Propargyl Carbamates†

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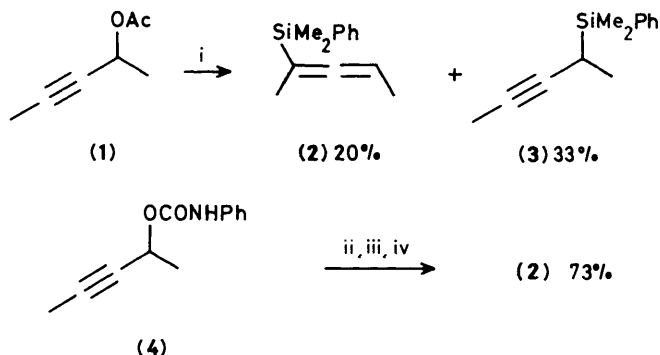
Pent-3-yn-2-yl acetate (1) reacts with dimethyl(phenyl)silyl cuprate reagent to give a mixture of allenylsilane and propargylsilane. The corresponding *N*-phenylcarbamate (4) gives only the allenylsilane. Four other examples of this regioselective reaction are reported. The stereochemistry is largely *syn*.

We reported earlier that tertiary propargyl (propynyl) acetates react stereospecifically *anti* with our silyl cuprate reagent to give allenylsilanes regioselectively.¹ We now report on the corresponding synthesis of allenylsilanes from secondary propargylic alcohol derivatives.

The secondary propargyl acetate (1) reacted with the dimethyl(phenyl)silyl cuprate reagent in tetrahydrofuran (THF) to give a mixture of the allenylsilane (2) and the propargylsilane (3) (Scheme 1). The loss of regioselectivity in

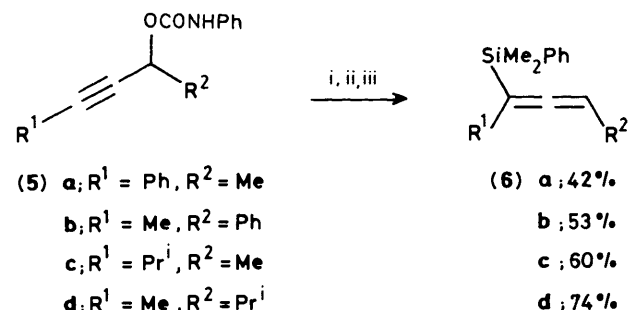
To investigate the stereochemistry of the reaction, we used the carbamate (7) of the propargyl alcohol from our earlier work. It reacted stereospecifically *syn* to give the allenylsilane (8a) and its diastereoisomer (8b) in a ratio of 4:1. It is likely that all our reactions show similar *syn* stereospecificity.

We also tried to use trimethylsilyl-lithium in place of dimethyl(phenyl)silyl-lithium, knowing that in general, the similar, even though hexamethylphosphoric triamide (HMPA) is present in the former.⁴ In this case, however, although the allenylsilane (10) can be prepared from the carbamate (4), the yield is low. This allenylsilane is better prepared starting with

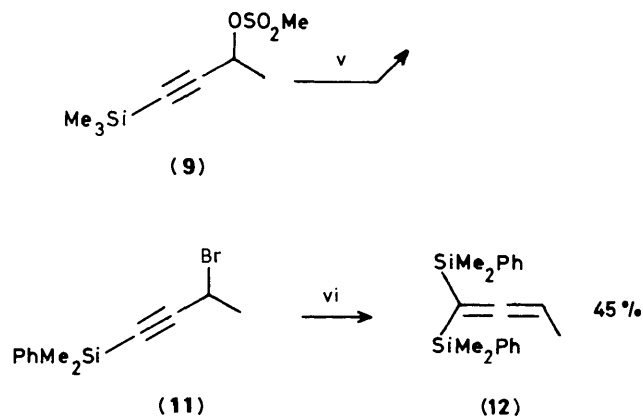
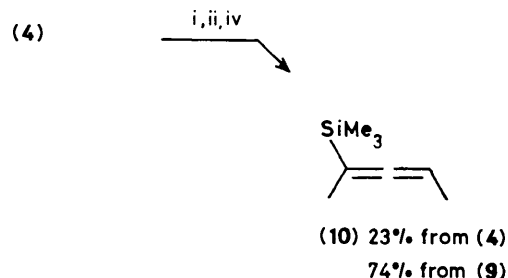
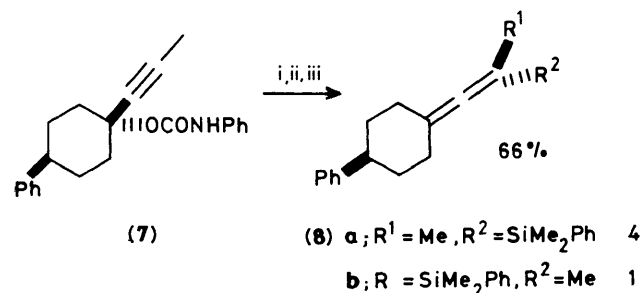


Scheme 1. Reagents: i, $(\text{PhMe}_2\text{Si})_2\text{CuLi}$; ii, MeLi; iii, CuI; iv, PhMe_2SiLi

this reaction is not surprising in view of our earlier finding that unsymmetrical secondary *E*-allyl acetates give mixtures of regioisomeric allylsilanes.² In that work, we largely overcame the loss of regioselectivity by using the *Z*-allyl acetates or the *E*- or *Z*-allyl phenylcarbamates. Thus we turned to the propargyl carbamate (4), which indeed reacted cleanly to give only the allenylsilane (2). (The protocol for this reaction is based on Goering's for the reaction of alkyl-lithium reagents with the copper salts of allylic carbamates.³) We then successfully used this route for the synthesis of the four unsymmetrical allenylsilanes (6) from the propargyl carbamates (5).



Scheme 2. Reagents: i, BuLi; ii, CuI- Ph_3P ; iii, PhMe_2SiLi



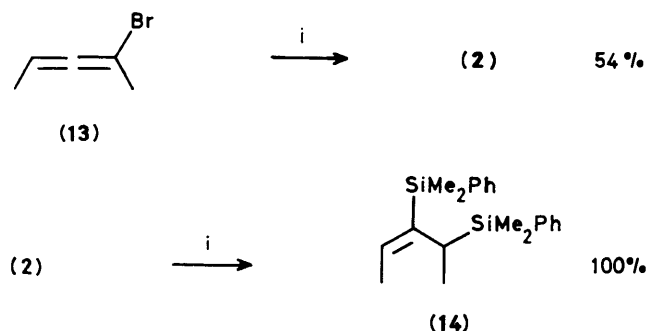
Scheme 3. Reagents: i, BuLi; ii, CuI- Ph_3P ; iii, PhMe_2SiLi ; iv, Me_3SiLi ; v, Me_2CuLi ; vi, $(\text{PhMe}_2\text{Si})_2\text{CuLi}$

† No reprints available.

the silylated propargyl methanesulphonate (9), and treating it with the methyl cuprate reagent. This reaction is similar to those of Westmijze and Vermeer,⁵ who used Grignard derived alkylcopper reagents and trimethylsilylpropargyl methanesulphonates, and is in contrast to those of Brinkmeyer and MacDonald,⁶ who used alkyl-lithium derived alkyl cuprates and trimethylsilylpropargyl acetates, but got only propargyl products and not allenes. We also find that the silyl cuprate reagent shows the same regioselectivity with the propargyl bromide (11) which gave the allenylsilane (12).

Finally, in the hope of preparing propargylsilanes regioselectively, we prepared the allenyl bromide (13) by the method of Vermeer,⁷ and treated it with the dimethyl(phenyl)silyl cuprate reagent. The only product was the allenylsilane (2).

In the course of this work, we encountered a further reaction: the allenylsilanes themselves react with the silylcuprate reagent, so that sometimes by-products were obtained from those reactions in which the silyl cuprate reagent was used. (In the carbamate reactions, the silyl cuprate reagent itself is not used,



Scheme 4. Reagent: i, (PhMe₂Si)₂CuLi

and the by-product is not formed. This is a second advantage to the carbamate route). In one case, we deliberately treated the pure allenylsilane (2) with the silyl cuprate reagent and isolated the *E*-vinylsilane (14) in high yield. We have since investigated the reaction of the silyl cuprate reagent with allenes in general.⁸

Experimental

Pent-3-yn-2-ol.—Propyne was bubbled through dry tetrahydrofuran (THF) (200 ml) while ethylmagnesium bromide (0.50 mol) in THF (300 ml) was added dropwise at room temperature. Acetaldehyde (19.4 g, 0.44 mol) in dry THF (20 ml) was then added under nitrogen at 0 °C and the mixture stirred overnight at room temperature. The mixture was poured into aqueous ammonium chloride (700 ml), extracted with ether, washed with water and brine, dried (MgSO₄), then evaporated under reduced pressure. The residue was distilled to give the alcohol (19.58 g, 53%), b.p. 75–77 °C/59 mmHg; v_{\max} (film) 3 350 (OH) and 2 243 cm⁻¹ (C≡C); δ (CDCl₃) 4.7–4.0 (1 H, m, CHOH) 2.40 (1 H, br s, OH), 1.78 (3 H, d, *J* 2.0 Hz, C≡CMe), and 1.38 (3 H, d, *J* 6.4 Hz, MeCOH).

Pent-3-yn-2-yl Acetate (1).—The above alcohol (1.85 g) and acetic anhydride (4.49 g) were heated together for 1.5 h at 110 °C with stirring. The mixture was poured into ice-cooled aqueous sodium carbonate and was allowed to stand for 15 min with occasional shaking. The mixture was then extracted with ether, washed with aqueous sodium carbonate and brine, dried (MgSO₄), and evaporated under reduced pressure. The residue was distilled to give the acetate (1) (2.29 g, 83%), b.p. 80 °C/20 mmHg; v_{\max} (film) 2 264 (C≡C) and 1 737 cm⁻¹ (C=O); δ (CDCl₃) 5.7–5.3 (1 H, m, CHOAc), 2.07 (3 H s, MeCO), 1.83 (3 H, d, *J* 1.8 Hz, C≡CMe), and 1.45 (3 H, d, *J* 6.9 Hz, MeCOAc).

Silylation of Pent-3-yn-2-yl Acetate (1).—Dimethyl(phenyl)silyl-lithium (0.78M solution in THF; 28.2 ml) was added to a stirred suspension of copper(I) cyanide (986 mg) in dry THF (30 ml) and pentane (30 ml) under nitrogen at –20 °C, and the mixture stirred for 1 h. The acetate (1) (1.15 g) was then added and the mixture was stirred at room temperature for 18 h. The mixture was then poured into aqueous ammonium chloride, extracted with ether, washed with aqueous ammonium chloride, dried (MgSO₄) and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexane and then by distillation to give 2-dimethyl(phenyl)silylpenta-2,3-diene (2) (0.37 g, 20%), b.p. 100 °C/0.08 mmHg (Kugelrohr); v_{\max} (film) 1 940 cm⁻¹ (C=C=C); δ (CDCl₃) 7.7–7.2 (5 H, m, Ph), 5.0–4.6 (1 H, m, CH=C), 1.68 [3 H, d, *J* 1.5 Hz, MeC(Si)=C], 1.60 (3 H, d, *J* 6.0 Hz, MeCH=C), and 0.33 (6 H, s, 2 × SiMe) (Found: *M*⁺, 202.1181. C₁₃H₁₈Si requires *M*, 202.1178); *m/z* 202 (18%, *M*⁺) and 135 (100, PhMe₂Si); and 4-dimethyl(phenyl)silylpent-2-yne (3) (0.60 g, 33%), b.p. 95 °C/0.1 mmHg (Kugelrohr); v_{\max} (film) no acetylene stretch observed; δ (CDCl₃) 7.8–7.3 (5 H, m, Ph), 2.2–1.6 (1 H, m, CHSi), 1.80 (3 H, s, C≡CMe), 1.11 (3 H, d, *J* 6.9 Hz, MeCSi), and 0.35 (6 H, s, 2 × SiMe) (Found: *M*⁺, 202.1179. C₁₃H₁₈Si requires *M*, 202.1178); *m/z* 202 (13%, *M*⁺), and 135 (100, PhMe₂Si).

Pent-3-yn-2-yl N-Phenylcarbamate (4).—Phenyl isocyanate (6.98 g) was added to a solution of pent-3-yn-2-ol (4.48 g) in dry benzene (30 ml) under nitrogen at room temperature and refluxed for 2.5 h. After having been cooled, the mixture was evaporated under reduced pressure. The residue was recrystallised from benzene–hexane to give the carbamate (4) (8.11 g, 75%), m.p. 88–89 °C (Found: C, 71.1; H, 6.35; N, 6.8. C₁₂H₁₃NO₂ requires C, 70.9; H, 6.45; N, 6.9%). v_{\max} (Nujol) 3 300 (NH), 1 690 (C=O), and 1 600 cm⁻¹ (C=C); δ (CDCl₃) 7.6–7.0 (5 H, m, Ph), 6.66 (1 H, br s, NH), 5.52 (1 H, m, CHMe), 1.88 (3 H, d, *J* 2.3 Hz, C≡CMe), and 1.55 (3 H, d, *J* 6.3 Hz, CHMe); *m/z* 203 (8%, *M*⁺), 93 (41, PhNH₂), and 67 (100, *M* – PhNHCO₂).

2-Dimethyl(phenyl)silylpenta-2,3-diene (2).—Methyl-lithium (1.8M solution in ether; 2.6 ml) was added to a solution of the carbamate (4) (0.90 g, 4.43 mmol) in dry THF (15 ml) under nitrogen at –20 °C and stirred for 15 min at 0 °C. The mixture was then transferred to a suspension of copper(I) iodide (844 mg, 4.43 mmol) in THF (10 ml) under nitrogen at –20 °C and stirred for 20 min at room temperature. The mixture was cooled again to –20 °C and dimethyl(phenyl)silyl-lithium (0.76M solution in THF; 5.25 ml) was added. The mixture was stirred for 22 h at room temperature, when it was poured into aqueous ammonium chloride, extracted with ether, washed with aqueous ammonium chloride and brine, dried (MgSO₄), and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexane to give the allenylsilane (2) (0.59 g, 73%).

4-Phenylbut-3-yn-2-ol.—This alcohol was prepared by a modification of the method of Pitman and Olah.⁹ Butyl-lithium (1.6M solution in hexane; 25 ml) was added slowly to a stirred solution of phenylacetylene (4.08 g) in dry ether (30 ml) under nitrogen at 0 °C. The resulting mixture was stirred at 0 °C for 10 min. Acetaldehyde (2.0 g) in dry ether (10 ml) was added dropwise and stirring was continued for 2 h at 0 °C. The reaction mixture was quenched with aqueous ammonium chloride (30 ml), the organic phase was separated and the aqueous layer extracted with ether (2 × 20 ml). The extracts were combined, dried (MgSO₄), and evaporated under reduced pressure. The residue was distilled to give the alcohol (4.26 g, 73%), b.p. 95–97 °C/3.5 mmHg (lit.,⁹ 89–92 °C/3 mmHg); v_{\max} (film) 3 365

(OH) and 2 232 cm^{-1} ($\text{C}\equiv\text{C}$); $\delta(\text{CDCl}_3)$ 7.5—6.9 (5 H, m, Ph), 4.59 (1 H, q, J 7 Hz, CHOH), 2.45 (1 H, s, OH), and 1.53 (3 H, d, J 7 Hz, Me).

The following alcohols were prepared by the same general method but using the following proportions: acetylene (1.15—2.0 equiv.), butyl-lithium (1.1 equiv.), and aldehyde (1.0 equiv.).

1-Phenylbut-2-yn-1-ol (18.83 g, 86%), b.p. 93—94 °C/0.25 mmHg (lit.,¹⁰ 110 °C/0.8 mmHg); v_{max} (film) 3 350 (OH) and 2 235 cm^{-1} ($\text{C}\equiv\text{C}$); $\delta(\text{CDCl}_3)$ 7.5—7.0 (5 H, m, Ph), 5.25 (1 H, q, J 2 Hz, PhCHOH), 4.03 (1 H, s, OH), and 1.80 (3 H, d, J 2 Hz, Me).

2-Methylhex-4-yn-3-ol (3.50 g, 69%), b.p. 65—68 °C/16 mmHg; v_{max} (film) 3 421 (OH) and 2 220 cm^{-1} ($\text{C}\equiv\text{C}$); $\delta(\text{CDCl}_3)$ 4.10 (1 H, dq, J 5.5 and 2.1 Hz, CHOH), 2.9 (1 H, s, OH), 2.3—1.5 (1 H, m, Me_2CH), 1.82 (3 H, d, J 2.1 Hz, $\text{MeC}\equiv\text{C}$), and 0.96 and 0.94 (3 H each, d, J 6.6 Hz, Me_2CH) (Found: M^+ — H, 111.0805. $\text{C}_7\text{H}_{11}\text{O}$ requires M — H, 111.0800); m/z 111 (2%, M^+ — H), 97 (24, M^+ — Me), and 69 (100, M^+ — Prⁱ).

5-Methylhex-3-yn-2-ol (6.44 g, 81%), b.p. 64—65 °C/18 mmHg; v_{max} (film) 3 349 (OH) and 2 246 cm^{-1} ($\text{C}\equiv\text{C}$); $\delta(\text{CDCl}_3)$ 4.46 (1 H, qd, J 6.5 and 1.7 Hz, CHOH), 2.52 (1 H, septet d, J 6.8 and 1.7 Hz, Me_2CH), and 1.11 (6 H, d, J 6.8 Hz, Me_2CH) (Found: M^+ — H, 111.0808. $\text{C}_7\text{H}_{11}\text{O}$ requires M — H, 111.0800); m/z 111 (2%, M^+ — H), 97 (100, M^+ — Me) and 69 (92, M — Prⁱ).

4-Phenylbut-3-yn-2-yl N-Phenylcarbamate (5a).—Phenyl isocyanate (4.0 g, 34 mmol) was added to a solution of 4-phenylbut-3-ynol (4.87 g, 33 mmol) and triethylamine (4.0 g, 40 mmol) in dry dichloromethane (30 ml) under nitrogen at room temperature. After 3 h, the mixture was filtered and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexane—ether (5:1, v/v) to give the carbamate (5a) (7.25 g, 82%) as needles, m.p. 64—65 °C (from hexane) (Found: C, 77.3; H, 5.65; N, 5.3. $\text{C}_{17}\text{H}_{15}\text{NO}_2$ requires C, 77.0; H, 5.65; N, 5.3%); R_F [hexane—ether (5:1 v/v)] 0.4; v_{max} (CH_2Cl_2) 3 410 (NH), 2 254 ($\text{C}\equiv\text{C}$), and 1 731 cm^{-1} ($\text{C}=\text{O}$); $\delta(\text{CDCl}_3)$ 7.6—6.9 (10 H, m, 2 × Ph), 6.68 (1 H, s, NH), 5.75 (1 H, q, J 6.6 Hz, CHOR), and 1.64 (3 H, d, J 6.6 Hz, Me); m/z 265 (3%, M^+), 129 (100, M^+ — PhNHCO_2), and 93 (16, PhNH_2).

The following carbamates were prepared by the same method:

1-Phenylbut-2-yn-1-yl N-phenylcarbamate (5b) (2.31 g, 87%) as needles, m.p. 98—99 °C (from hexane) (Found: C, 76.9; H, 5.75; N, 5.3. $\text{C}_{17}\text{H}_{15}\text{NO}_2$ requires C, 77.0; H, 5.65; N, 5.3%); R_F [hexane—ether (5:1 v/v)] 0.4; v_{max} (CH_2Cl_2) 3 407 (NH), 2 256 ($\text{C}\equiv\text{C}$), and 1 728 cm^{-1} ($\text{C}=\text{O}$); $\delta(\text{CDCl}_3)$ 7.7—6.9 (10 H, m, 2 × Ph), 6.66 (1 H, s, NH), 6.48 (1 H, q, J 2.2 Hz, PhCH), and 1.92 (3 H, d, J 2.2 Hz, Me); m/z 262 (5%, M^+), 221 (26, M^+ — CO_2), and 129 (100, M^+ — PhNHCO_2).

5-Methylhex-3-yn-2-yl N-phenylcarbamate (5c) (3.01 g, 90%) as an amorphous solid, m.p. 55—56 °C, R_F [hexane—ether (5:1 v/v)] 0.3; v_{max} (Nujol) 3 326 (NH), 2 249 ($\text{C}\equiv\text{C}$), and 1 700 cm^{-1} ($\text{C}=\text{O}$); $\delta(\text{CDCl}_3)$ 7.5—6.9 (5 H, m, Ph), 6.65 (1 H, s, NH), 5.51 (1 H, qd, J 6.6 and 1.8 Hz, CHOR), 2.58 (1 H, septet d, J 6.8 and 1.8 Hz, Me_2CH), 1.51 (3 H, d, J 6.6 Hz, MeCOR), and 1.16 (6 H, d, J 6.8 Hz, Me_2CH) (Found: M^+ , 231.1252. $\text{C}_{14}\text{H}_{17}\text{NO}_2$ requires M , 231.1259); m/z 231 (16%, M^+), 95 (31, M^+ — PhNHCO_2), 93 (39, PhNH_2), and 55 (100, C_4H_7).

2-Methylhex-4-yn-3-yl N-phenylcarbamate (5d) (0.76 g, 74%) as a viscous oil, R_F [hexane—ether (5:1 v/v)] 0.3; v_{max} (film) 3 320 (NH), 2 237 ($\text{C}\equiv\text{C}$), and 1 704 cm^{-1} ($\text{C}=\text{O}$); $\delta(\text{CDCl}_3)$ 7.5—6.9 (5 H, m, Ph), 6.62 (1 H, s, NH), 5.23 (1 H, dq, J 5.5 and 2.2 Hz, CHOR), 1.98 (1 H, septet d, J 6.7 and 5.5 Hz, Me_2CH), 1.86 (3 H, d, J 2.2 Hz, $\text{MeC}\equiv\text{C}$), and 1.04 and 1.01 (3 H each, d, J 6.7 Hz, Me_2CH) (Found: M^+ , 231.1264. $\text{C}_{14}\text{H}_{17}\text{NO}_2$ requires M , 231.1259); m/z 231 (41%, M^+), 144 (36, M^+ — CO_2 — C_3H_7), 95 (100, M^+ — PhNHCO_2), and 93 (89, PhNH_2).

1-Dimethyl(phenyl)silyl-1-phenylbuta-1,2-diene (6a).—Butyl-lithium (1.6M solution in hexane; 0.63 ml) was added to a stirred solution of the carbamate (5a) (0.265 g, 1.0 mmol) in dry THF (10 ml) under nitrogen at 0 °C. After 2 min, the mixture was transferred to a stirred slurry of copper(i) iodide (0.190 g, 1.0 mmol) and triphenylphosphine (0.524 g, 2.0 mmol) in dry ether (3 ml). The mixture was stirred for 15 min, then dimethyl(phenyl)silyl-lithium (0.95M solution in THF; 1.05 ml) was added and stirring was continued at 0 °C for 3 h. The mixture was quenched with aqueous ammonium chloride (15 ml), the organic phase separated and the aqueous layer extracted with ether (10 ml). The extracts were combined, dried (MgSO_4), and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexane to give the silane (6a) (0.11 g, 42%) as an oil, R_F (hexane) 0.25; v_{max} (film) 1 933 ($\text{C}=\text{C}=\text{C}$), 1 242 (SiMe), and 1 102 cm^{-1} (SiPh); $\delta(\text{CDCl}_3)$ 7.7—7.0 (10 H, m, 2 × Ph), 5.18 (1 H, q, J 6.9 Hz, $\text{MeCH}=\text{C}$), 1.75 (3 H, d, J 6.9 Hz, $\text{MeC}=\text{C}$), and 0.46 (6 H, s, 2 × SiMe) (Found: M^+ , 264.1336. $\text{C}_{18}\text{H}_{20}\text{Si}$ requires M , 264.1334); m/z 264 (16%, M^+) and 135 (100, PhMe_2Si).

The following allenylsilanes were prepared by the same method.

3-Dimethyl(phenyl)silyl-1-phenylbuta-1,2-diene (6b) (0.14 g, 53%) as an oil, R_F (hexane) 0.25; v_{max} (film) 1 927 ($\text{C}=\text{C}=\text{C}$), 1 244 (SiMe), and 1 105 cm^{-1} (SiPh); $\delta(\text{CDCl}_3)$ 7.7—6.9 (10 H, m, 2 × Ph), 5.88 (1 H, q, J 2.9 Hz, $\text{PhCH}=\text{C}$), 1.78 (3 H, d, J 2.9 Hz, $\text{MeC}=\text{C}$), and 0.42 and 0.41 (3 H each, s, 2 × SiMe) (Found: M^+ , 264.1344. $\text{C}_{18}\text{H}_{20}\text{Si}$ requires M , 264.1334); m/z 264 (7%, M^+) and 135 (100, PhMe_2Si).

3-Dimethyl(phenyl)silyl-2-methylhexa-3,4-diene (6c) (0.14 g, 60%) as an oil, R_F (hexane) 0.45; v_{max} (film) 1 934 ($\text{C}=\text{C}=\text{C}$), 1 241 (SiMe), and 1 103 cm^{-1} (SiPh); $\delta(\text{CDCl}_3)$ 7.6—7.3 (5 H, m, Ph), 4.87 (1 H, qd, J 6.8 and 1.8 Hz, $\text{C}=\text{CHMe}$), 2.14 (1 H, septet d, J 6.7 and 1.8 Hz, Me_2CH), 1.63 (3 H, d, J 6.8 Hz, $\text{MeC}=\text{C}$), 0.96 and 0.95 (3 H each, d, J 6.8 Hz, Me_2CH), and 0.36 (6 H, s, 2 × SiMe) (Found: M^+ , 230.1498. $\text{C}_{15}\text{H}_{22}\text{Si}$ requires M , 230.1490); m/z 230 (3%, M^+), 162 (7, M^+ — Me — C_3H_7), and 135 (100, PhMe_2Si).

2-Dimethyl(phenyl)silyl-5-methylhexa-2,3-diene (6d) (0.17 g, 74%), R_F (hexane) 0.45; v_{max} (film) 1 941 ($\text{C}=\text{C}=\text{C}$), 1 242 (SiMe), and 1 104 cm^{-1} (SiPh); $\delta(\text{CDCl}_3)$ 7.6—7.3 (5 H, m, Ph), 4.82 (1 H, dq, J 5.7 and 2.9 Hz, $\text{Pr}^i\text{CH}=\text{C}$), 2.27 (1 H, septet d, J 6.7 and 5.7 Hz, Me_2CH), 1.66 (3 H, d, J 2.9 Hz, $\text{MeC}=\text{C}$), 0.98 (6 H, d, J 6.7 Hz, Me_2CH), and 0.35 (6 H, s, 2 × SiMe) (Found: M^+ , 230.1490. $\text{C}_{15}\text{H}_{22}\text{Si}$ requires M , 230.1490); m/z 230 (5%, M^+), 215 (7, M^+ — Me), and 135 (100, PhMe_2Si).

trans-4-Phenyl-1-prop-1-ynylcyclohexyl N-Phenylcarbamate (7).—trans-4-Phenyl-1-prop-1-ynylcyclohexanol¹ (0.725 g), triethylamine (0.50 g), and 4-dimethylaminopyridine (0.05 g) were dissolved in dry dichloromethane (5 ml) and phenyl isocyanate (0.50 g) was added. The mixture was left under nitrogen for 200 h and then evaporated under reduced pressure. Column chromatography of the mixture on silica gel eluting with hexane—ethyl acetate (10:1, v/v) gave the carbamate (7) (0.993 g, 88%) as prisms, m.p. 158—159 °C (from CCl_4) (Found: C, 79.1; H, 6.90; N, 4.3. $\text{C}_{22}\text{H}_{23}\text{NO}_2$ requires C, 79.3; H, 6.90; N, 4.2%); R_F [hexane—ethyl acetate (5:1 v/v)] 0.20; v_{max} (CH_2Cl_2) 3 421 (NH), 2 228 ($\text{C}\equiv\text{C}$), and 1 734 cm^{-1} ($\text{C}=\text{O}$); $\delta(\text{CDCl}_3)$ 7.7—6.9 (10 H, m, 2 × Ph), 6.56 (1 H, s, NH), 1.95 (3 H, s, $\text{MeC}\equiv\text{C}$), and 2.8—1.4 (9 H, m, remainder); m/z 333 (1%, M^+), 197 (41, M^+ — PhNHCO_2), 119 (40, PhNCO), and 93 (100, PhNH_2).

Silylation of the Carbamate (7).—The carbamate (7) was silylated by the same method as the carbamate (5a) except that the initial deprotonation was carried out at —78 °C. The reaction gave a 4:1 mixture of the allenylsilanes (8a) and (8b) in

66% yield. *trans*-1-Dimethyl(phenyl)silyl-1-methyl-3,3-(3-phenylpentamethylene)allene (**8a**) had $\delta_c(\text{CDCl}_3)$ 203.0, 147.2, 138.8, 133.8, 128.8, 128.3, 127.7, 126.9, 126.0, 95.1, 88.3, 44.2, 35.1, 31.0, 16.6, and -3.0 . *cis*-1-dimethyl(phenyl)silyl-1-methyl-3,3-(3-phenylpentamethylene)allene (**8b**) had $\delta_c(\text{CDCl}_3)$ 202.9, 147.1, 133.9, 128.9, 128.3, 127.7, 126.8, 125.9, 94.8, 88.5, 44.2, 34.9, 31.3, 16.1, and -2.9 . The spectra of both allenylsilanes were identical with our earlier spectra.¹

4-Trimethylsilylbut-3-yn-2-ol.—Trimethylsilylethyne (5.64 g, 58 mmol) in dry THF (15 ml) was added to a solution of ethylmagnesium bromide (76 mmol) in THF (45 ml) under nitrogen during which the temperature was maintained at below 20 °C with occasional cooling. The mixture was stirred for 30 min at room temperature, then acetaldehyde (3.96 g, 90 mmol) in dry THF (10 ml) was added and stirring was continued for 17 h. Aqueous work-up and distillation gave the title alcohol (7.15 g, 87%), b.p. 83–85 °C/13 mmHg; v_{max} (film) 3 350 (OH) and 2 160 cm^{-1} (C=C); $\delta(\text{CDCl}_3)$ 4.57 (1 H, q, *J* 7.2 Hz, CHOH), 2.03 (1 H br s, OH), 1.43 (3 H, d, *J* 7.2 Hz, MeCOH), and 0.17 (9 H, s, 3 × SiMe).

4-Trimethylsilylbut-3-yn-2-yl Methanesulphonate (9).—Methanesulphonyl chloride (5.95 g) was added to a solution of the above alcohol (5.68 g) and triethylamine (6.06 g) in dichloromethane (80 ml) at -50 °C and the mixture was then warmed to 0 °C with stirring. After 1 h, the mixture was poured into ice-water, extracted with dichloromethane, washed with 3% hydrochloric acid, aqueous sodium hydrogen carbonate and brine, dried (MgSO₄), and evaporated under reduced pressure to give the methanesulphonate (**9**) (8.80 g, 100%); v_{max} (film) 2 170 (C=C) and 1 360 and 1 180 cm^{-1} (SO₂); $\delta(\text{CDCl}_3)$ 5.30 (1 H, q, *J* 7.0 Hz, CHOMs), 3.15 (3 H, s, MeSO₂), 1.63 (3 H, d, *J* 7.0 Hz, MeCOMs), and 0.20 (9 H, s, 3 × SiMe).

2-Trimethylsilylpenta-2,3-diene (10).—Methyl-lithium (1.6M solution in ether; 44 ml) was added to a stirred slurry of copper(I) iodide (6.70 g) in dry THF (80 ml) under nitrogen at 0 °C and the mixture was stirred for 30 min, then cooled to -78 °C. The methanesulphonate (**9**) (8.60 g) in dry THF (20 ml) was added and the mixture stirred at -78 °C for 1.5 h. The reaction was quenched with aqueous ammonium chloride at -78 °C. The normal work-up and distillation gave the allenylsilane^{5,6} (**10**) (3.64 g, 74%), b.p. 64–65 °C/43 mmHg; v_{max} (film) 1 930 cm^{-1} (C=C=C); $\delta(\text{CDCl}_3)$ 4.78 (1 H, m, C=CH), 1.70 [3 H, d, *J* 2.7 Hz, MeC(Si)=C], 1.65 (3 H, d, *J* 7.2 Hz, C=CMe), and 0.08 (9 H, s, SiMe₃) (Found: M^+ , 140.1017. C₈H₁₆Si requires M , 140.1021); m/z 140 (18%, M^+), 125 (10, $M^+ - \text{Me}$), 97 (21, $M^+ - \text{C}_3\text{H}_7$), and 73 (100, Me₃Si).

The allenylsilane (**10**) was also prepared from the carbamate (**4**) in 23% yield, by the method described for the preparation of the allenylsilane (**2**) except that trimethylsilyl-lithium¹¹ was added.

Dimethyl(phenyl)silylacetylene.—Butylmagnesium chloride (0.14 mol) [1-chlorobutane (12.7 g) and magnesium (3.3 g)] in THF (50 ml) was added dropwise, over 45 min, to an ice-cooled, stirred solution of acetylene in dry THF (50 ml) through which dry acetylene was bubbled. After the Grignard reagent addition was complete, stirring was continued, with acetylene bubbling through the mixture, for 30 min. The solution was then put under a nitrogen atmosphere. Chlorodimethyl(phenyl)silane (17.0 g) in dry THF (10 ml) was added over 15 min and the mixture was then heated under reflux for 1 h. The excess of Grignard reagent was carefully quenched with aqueous ammonium chloride (100 ml), the organic layer separated and the aqueous layer extracted with pentane (2 × 50 ml). The combined extracts were washed with water (5 × 100 ml), dried

(MgSO₄), and evaporated under reduced pressure. The residue was distilled to give the acetylene¹² (11.98 g, 75%), b.p. 81–82 °C/17 mmHg; v_{max} (film) 3 264 (C≡CH), 2 024 (C≡C), 1 248 (SiMe), and 1 111 cm^{-1} (SiPh); $\delta(\text{CDCl}_3)$ 8.0–7.3 (5 H, m, Ph), 2.94 (1 H, s, C≡CH), and 0.80 (6 H, s, 2 × SiMe).

4-Dimethyl(phenyl)silylbut-3-yn-2-ol.—This alcohol was prepared by the method described for the preparation of 4-phenylbut-3-yn-2-ol (5.26 g, 86%), b.p. 102–104 °C/0.2 mmHg; v_{max} (film) 3 400 (OH) and 2 120 cm^{-1} (C=C); $\delta(\text{CDCl}_3)$ 7.9–7.2 (5 H, m, Ph), 4.64 (1 H, q, *J* 7 Hz, CHOH), 1.92 (1 H, s, OH), 1.57 (3 H, d, *J* 7 Hz, MeCOH), and 0.53 (6 H, s, 2 × SiMe) (Found: M^+ , 204.0952. C₁₂H₁₆OSi requires M , 204.0970); m/z 204 (1%, M^+) and 161 (100, $M^+ - \text{C}_2\text{H}_5\text{O}$).

2-Bromo-4-dimethyl(phenyl)silylbut-3-yne (11).—Butyllithium (1.6M solution in hexane; 1.88 ml) was added to a stirred solution of the above alcohol (0.612 g, 3.0 mmol) in dry THF (10 ml) under nitrogen -78 °C. After 1 min, methanesulphonyl chloride (3.46 g, 3.0 mmol) was added. The mixture was stirred for 2 min at -78 °C then transferred to a stirred slurry of copper(I) bromide (0.517 g, 3.6 mmol) and lithium bromide (0.313 g, 3.6 mmol) in dry THF (30 ml) at room temperature. After having been stirred for 3 h, the mixture was poured into aqueous ammonium chloride (50 ml), the organic phase separated and the aqueous layer extracted with pentane (2 × 20 ml). The combined organic extracts were washed with water (5 × 50 ml), dried (K₂CO₃), and evaporated under reduced pressure to give the bromide (**11**) (0.795 g, 98%) as an oil, R_F (hexane) 0.22; v_{max} (film) 2 192 cm^{-1} (C=C); $\delta(\text{CDCl}_3)$ 7.9–7.2 (5 H, m, Ph), 4.72 (1 H, q, *J* 7 Hz, CHBr), 1.03 (3 H, d, *J* 7 Hz, MeCBr), and 0.55 (6 H, s, 2 × SiMe) (Found: $M^+ - \text{Me}$ 250.9882. C₁₁H₁₂BrSi requires $M - \text{Me}$, 250.9891); m/z 251 (7%, $M^+ - \text{Me}$), 223 (100, $M^+ - \text{C}_3\text{H}_7$), 187 (60, $M^+ - \text{Br}$), and 159 (100, $M^+ - \text{Br} - \text{C}_2\text{H}_4$).

1,1-Bis[dimethyl(phenyl)silyl]buta-1,2-diene (12).—Dimethyl(phenyl)silyl-lithium (1.05M solution in THF; 2.86 ml) was added to a stirred suspension of copper(I) cyanide (0.134 g) in dry ether (15 ml) under nitrogen at 0 °C. After 15 min, the propargyl bromide (**11**) (0.267 g) was added and the mixture was stirred at 0 °C for 3 h. Standard aqueous work-up and column chromatography on silica gel eluting with hexane, gave the disilane (**12**) (0.144 g, 45%) as an inseparable mixture with tetramethyldiphenyldisilane, R_F (hexane) 0.35; v_{max} (film) 1 896 cm^{-1} (C=C=C); $\delta(\text{CDCl}_3)$ 7.8–7.1 (5 H, m, Ph), 4.63 (1 H, q, *J* 7 Hz, MeCH=C), 1.72 (3 H, d, *J* 7 Hz, MeC=C), and 0.4–0.3 (12 H, m, 4 × SiMe) (Found: M^+ , 322.1587. C₂₀H₂₄Si₂ requires M , 322.1583); m/z 322 (1%, M^+) and 135 (100, PhMe₂Si).

2-Bromopenta-2,3-diene (13).—This allenyl bromide was prepared from pent-3-yn-2-ol by the method described for preparation of the bromide (**11**). The crude product was purified by distillation to give the bromide (**13**) (2.534 g, 48%) as a 9:1 mixture with 2-bromopent-3-yne, b.p. 55–60 °C/48 mmHg, v_{max} (film) 1 950 cm^{-1} (C=C=C); $\delta(\text{CDCl}_3)$ 4.54 (1 H, qq, *J* 4 and 2 Hz, MeCH=C), 1.82 (3 H, d, *J* 4 Hz, MeCH=C), and 1.75 (3 H, d, *J* 2 Hz, MeCBr=C) [2-bromopent-3-yne; $\delta(\text{CDCl}_3)$ 5.15 (1 H, qq, *J* 7 and 3 Hz, CHBr), 2.15 (3 H, d, *J* 3 Hz, MeC=C), and 1.61 (3 H, d, *J* 7 Hz, MeCBr)].

2-Dimethyl(phenyl)silylpenta-2,3-diene (2).—Dimethyl(phenyl)silyl-lithium (1.0M solution in THF; 3.0 ml) was added to a stirred suspension of copper(I) iodide (0.286 g) in dry ether (10 ml) under nitrogen at 0 °C. After 15 min, the allenyl bromide (**13**) (0.147 g) was added and the stirring was continued for 2 h at 0 °C. The standard aqueous work-up and column chromatography

graphy on silica gel eluting with hexane gave the allenylsilane (**2**) (0.110 g, 54%).

(E)-3,4-Bis[*dimethyl(phenyl)silyl*]pent-2-ene (**14**).—The allenylsilane (**2**) (150 mg, 0.74 mmol) was added to a solution of the lithium(dimethylphenylsilyl)cuprate reagent [0.89 mmol based on copper(i) cyanide] in dry THF (7 ml) under nitrogen at -78°C and the mixture was stirred for 1 h. The mixture was quenched with aqueous ammonium chloride at -78°C . Work-up and distillation gave the *bis-silylpentene* (**14**) (250 mg, 100%), b.p. $135^{\circ}\text{C}/0.05\text{ mmHg}$ (Kugelrohr); ν_{max} (film) 1600 cm^{-1} (Ph); $\delta(\text{CDCl}_3)$ 7.7–7.2 (10 H, m, $2 \times \text{Ph}$), 5.90 (1 H, q, J 7 Hz, $\text{CH}=\text{C}$), 2.27 (1 H, q, J 7.5 Hz, CHSi), 1.61 (3 H, d, J 7 Hz, $\text{MeCH}=\text{C}$), 1.13 (3 H, d, J 7.5 Hz, MeCHSi), and 0.28 (12 H, m, $4 \times \text{SiMe}$) (Found: M^+ , 338.1884. $\text{C}_{21}\text{H}_{30}\text{Si}_2$ requires M , 338.1886); m/z 338 (3%, M^+) and 135 (100, PhMe_2Si).

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