Synthesis of Allylstannanes and Vinylstannanes by the Stannyl-cupration of Allenes

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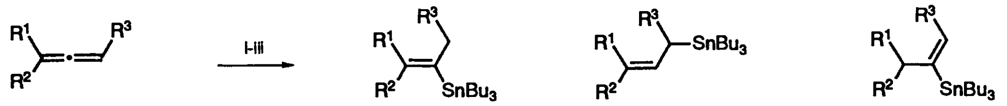
Stannyl-cupration of allenes followed by electrophilic attack gives allyl-and vinyl-stannanes with a variety of substitution patterns. The regiochemistry of the reaction depends upon the temperature at which the intermediate cuprate is quenched with an electrophile. With allene itself, the allylstannane-vinylcuprate 1-(tributylstannylmethyl)vinylcuprate, **5**, is the product of kinetically controlled addition, but the vinylstannane-allylcuprate 2-(tributylstannyl)allylcuprate, **6**, is thermodynamically lower in energy. The equilibration between these isomers begins to take place between −100 and −78 °C.

In earlier papers,[1-4] we reported the synthesis of allylsilanes and vinylsilanes by silyl-cupration of allenes. The reactions usually proceed with a high degree of regiocontrol, which depends upon the substitution pattern of the allene, and in one case at least we showed[4] that it took place with complete *syn* stereospecificity. Other metallo-metallations of unactivated allenes are also known, such as the addition of silicon–magnesium, silicon–aluminium and silicon–zinc to allenes catalysed by copper(I) or palladium.[5] We have also reported briefly the stannyl-cupration of allenes,[3] in which we used Piers' stannyl-copper and stannyl-cuprate reagents, the latter being a lower-order cuprate,[6] and we reported in a preliminary communication[7] the stannyl-cupration of allenes by using other stannyl-cuprate reagents. We now publish the latter work in full. The regiochemistry of the stannyl-cupration of allenes depends upon the nature of the stannyl-cuprate and on the temperature.

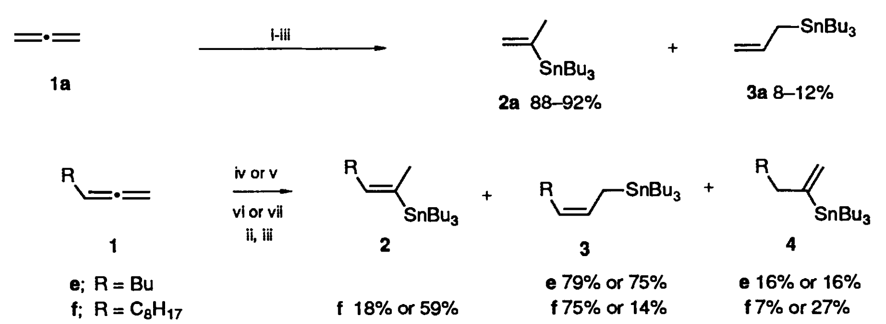
Bis(tributylstannyl)cuprate, prepared at −78 °C from two molar equivalents of tributylstannyllithium (itself prepared from tributyltin chloride and metallic lithium)[8] and one molar equivalent of copper(I) cyanide, and therefore a higher-order cuprate,[6] reacts with allenes **1a–e** (THF; −78 to 0 °C; 1 h) giving, after protonation, either vinylstannanes **2a**, **c**, **d** or allylstannanes **3b**, **c** in good yield (Scheme 1). The stereochemistry of the vinylstannanes **2c** and **2d** is cleanly *E* (transmetallation with butyllithium followed by protonation gives the *Z*-alkenes), presumably as a result of the stannyl-cuprate's attacking the less hindered face of the allene. Phenylallene **1c** gives a mixture of regioisomers, favouring the vinylstannane over the allylstannane (10:1). The formation of allylstannanes **3b** and **3c** shows that the stannyl-cuprate attaches the tin atom to the less substituted end of the allene. The trisubstituted allenes 3-methyl-1-phenylbuta-1,2-diene and 2-methylocta-2,3-diene failed to react with this cuprate.

The results with allene itself and with 1,1-dimethylallene are the same as we had observed earlier with Piers' stannyl-cuprate,[3] but the reaction with a differently constituted higher-order cuprate, derived from hexabutylditin and butyllithium,[9] and essentially halide ion-free, gave slightly different results (Scheme 2). In our preliminary communication,[7] we reported that this stannyl-cuprate gave the allylstannane **3a**, but we now find this not to be reproducible. The major product is, in fact, the vinylsilane **2a**, just as it was with the stannyl-cuprate described above and with Piers' reagent; the difference is only that there is a minor amount (8–12%) of the allylstannane present. More recently, Singh and Oehlschlager have reported that several different stannyl-cuprates react with undeca-1,2-diene **1f** to give various proportions of the stannanes **2f** and **3f**.[10] Similar to our observations with the 1,1-disubstituted allene **1b**, they found that the allylstannane **3f** was the major product (75%) with a stannyl-cuprate derived from tributyltin hydride, but they also observed the formation of some of the vinylstannane **2f** (18%) and a little of a regioisomeric vinylstannane, 2-(tributylstannyl)undec-1-ene **4f** (7%). More notably, however, they find that a mixed stannyl-butyl-cuprate gives the two vinylstannanes as the major products (59 and 27%, respectively), with the allylstannane **3f** as the minor one (14%). We find that a mixed stannyl-butyl-cuprate reacts with allene itself and with 1,1-dimethylallene to give results very similar to the corresponding reactions of the bis(tributylstannyl) cuprate, allene giving the vinylstannane **2a** in 94% yield and 1,1-dimethylallene giving the allylstannane **3b** in 96% yield. However, in contrast to Singh and Oehlschlager's result with undeca-1,2-diene **1f**, hepta-1,2-diene **1e** reacts with our bis(tributylstannyl)-cuprate or with the mixed stannyl-butyl-cuprate, both slightly differently constituted from Singh and Oehlschlager's, to give the allylstannane **3e** as the major



1	2	3	4
a; $R^1 = R^2 = R^3 = H$	a 92%		
b; $R^1 = R^2 = Me, R^3 = H$		b 99%	
c; $R^1 = Ph, R^2 = R^3 = H$	c 91%	c 9%	
d; $R^1 = Me, R^2 = H, R^3 = Ph$	d 89%		
e; $R^1 = Bu, R^2 = R^3 = H$		e 80%	e 15%

Scheme 1 *Reagents and conditions:* i, $(Bu_3Sn)_2CuLi$ (from Bu_3SnCl, Li and CuCN); ii, −78 to 0 °C; iii, NH_4Cl



Scheme 2 *Reagents and conditions:* i, $(Bu_3Sn)_2CuLi$ [from $(Bu_3Sn)_2$, BuLi and CuCN]; ii, −78 to 0 °C; iii, MeOH; iv, $(Bu_3Sn)_2CuLi$ (from Bu_3SnH, $LiNPr_2{}^i$ and CuCN); v, $(Bu_3Sn)BuCuLi$ (from Bu_3SnH, $LiNPr_2{}^i$, BuLi and CuCN); vi, $(Bu_3Sn)_2CuLi$ (from Bu_3SnCl, Li and CuCN); vii, $(Bu_3Sn)BuCuLi$ (from Bu_3SnCl, Li, CuCN and BuLi)

product, and the vinylstannane **4e** as the minor one. We conclude, as Singh and Oehlschlager did, that minor changes in the constitution of the cuprate reagents can cause variations in the proportions of the various products in those reactions that do not show a strong inclination towards the production of a single isomer.

One cause of such variation, although not of the results described immediately above, is that the regiochemistry of the reaction can strongly depend upon the temperature: when we treated allene itself (**1a**) with the stannyl-cuprate reagent derived from tributyltin chloride, but at −100 °C instead of at −78 °C, and quenched the intermediate with methanol at −100 °C instead of at 0 °C, we obtained only the allylstannane **7a** (=**3a**) instead of the vinylstannane **8a** (=**2a**). When we treated allene with the same stannyl-cuprate at −100 °C for 1 h, allowed the mixture to warm to 0 °C during 1 h, and quenched it at −100 °C, we obtained only the vinylstannane **8a**; when we repeated the experiment, warming the mixture from −100 °C only to −78 °C, and then quenched it at that temperature, we obtained a mixture of **7a** and **8a** (1:4.5; 98%). Therefore it appears that the intermediate **5** is the kinetic product of stannylcupration, and the intermediate **6** is the thermodynamic product. The slightly different result that we obtained in the reaction between allene itself and the stannyl-cuprate derived from hexabutylditin may indicate that the equilibrium process is a little slower with this reagent. Owing to the low temperature at which the kinetic intermediate **5** starts to rearrange to the thermodynamic intermediate **6**, there is a very limited range of electrophiles that can react with the kinetic product. Bromine was effective, giving the allylstannane **7b**, but amongst carbon electrophiles, only acetyl chloride and methyl propiolate straightforwardly gave the ketone **7d** and the conjugated diene **7k**, respectively. The thermodynamic intermediate **6**, however, reacts with a range of carbon electrophiles. Reactions with acetyl chloride, ethylene oxide, and carbon dioxide were reported in our preliminary communication, giving the products **8d**, **8e** and **8f**, respectively. Since then we have used bromine, allyl bromide, acetaldehyde, acetone and cyclohex-2-enone, giving the products **8b** and **8g–j**. Methyl iodide, however, is anomalous: with any of the three stannyl-cuprates we have tried, we always obtained mixtures of the allylstannane **7c** and the vinylstannane **8c**, with the latter regularly the major product but to an unreproducible degree (ranging from 1:4 to 1:1.5). This result indicates, perhaps, that our simple analysis of kinetic and thermodynamic intermediates is at least incomplete, and is further disturbing because we had wanted to use this route to prepare 2-(tributylstannyl)butene **8c** for our synthesis of ebelactone-a.[11] From the point of view of synthesis, we have been able to solve this problem by making the bromide **8b**, as described above, and treating it directly with lithium dimethylcuprate to give compound **8c** cleanly in an overall yield of 65%. A second anomaly is that, in contrast to the reaction with methyl propiolate, the reaction with diethyl acetylenedicarboxylate gave a mixture of the regioisomers **7l** and **8l** richer in the latter. It seems likely that, in addition to a thermodynamic preference for the formation of the intermediate cuprate **5**, one must also allow for the relative reactivities of both components, **5** and **6**, in the equilibrium, with the intermediate **5** sometimes reacting faster than its isomer. No pattern has emerged yet that allows one to predict when this problem will turn up. The result with methyl propiolate was reproducible, and when we quenched the reaction with deuterium oxide in place of ammonium chloride the product was the appropriately α-deuteriated version of the αβ-unsaturated ester **7k**. These reactions are summarised in Scheme 3.

The reaction of dimethylallene **1b** with our usual higher-order cuprate, quenching at −78 °C with methyl iodide, acetyl chloride, ethylene oxide, or cyclohex-2-enone, gave only the allylstannanes **9a–d** (Scheme 4), just as we had found when using Piers' reagent.[3] The last of these results is new since our preliminary communication.

Experimental

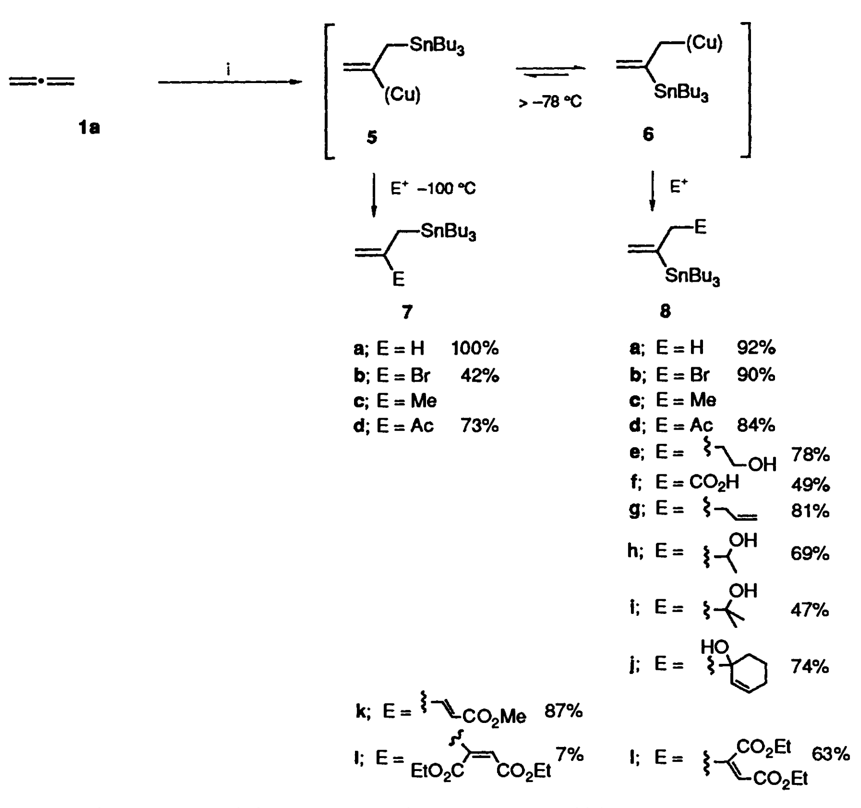
IR spectra were recorded on Pye-Unicam SP-1100 and Mattson Cygnus-100 spectrometers as films. ^1H NMR and ^{13}C NMR spectra were taken on a Brucker WP-200-5Y or A-80 spectrometer. *J*-Values are given in Hz. Mass spectra were obtained on a Hewlett-Packard 5988-A instrument. Capillary gas chromatographic analyses were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a FID detector.

All reactions were carried out under argon. Diethyl ether and tetrahydrofuran (THF) were freshly distilled from lithium aluminium hydride. Chromatographic solvents were distilled prior to use. Alkyllithium reagents were purchased from Aldrich, and copper(I) cyanide from Fluka. The latter was dried in an oven overnight at 120 °C.

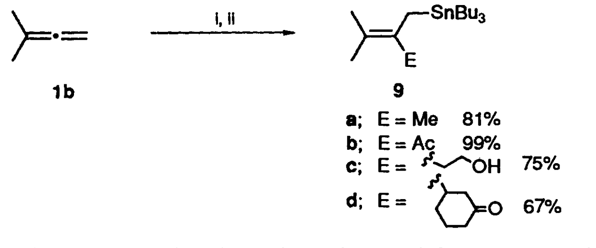
We bought the allenes **1a** and **1b** (Aldrich). The allenes **1c** (51%), **1d** (79%) and **1e** (butylallene) (47%) were prepared by the method of Crabbé.[12] Tributylstannyllithium with lithium chloride[8] and halide ion-free tributylstannyllithium[9] were prepared by the established procedures.

Lithium Bis(tributylstannyl)cuprate.—A solution of tributylstannyllithium (12 mmol) prepared in THF according to the Tamborski[8] or Still[9] procedure was added by syringe to a stirred suspension of copper(I) cyanide (6 mmol, 537 mg) in THF (10 cm^3) at −78 °C. The resulting green-black mixture was stirred at this temperature for an additional period of 30 min and was then used immediately.

Lithium Butyl(tributylstannyl)cuprate.—A mixture of tributylstannyllithium (6 mmol), prepared as before in THF (10 cm^3), and butyllithium (3.75 cm^3 of a 1.6 mol dm^{-3} solution in



Scheme 3 *Reagents and conditions:* i, $(Bu_3Sn)_2CuLi$ (from Bu_3SnCl, Li and Cu(CN), −100 °C



Scheme 4 *Reagents and conditions:* i, $(Bu_2Sn)_2CuLi$ (from Bu_3SnCl, Li and CuCN), −78 °C; ii, MeI, AcCl, ethylene oxide or cyclohex-2-enone, −78 °C to 0 °C

hexane) was stirred at −78 °C for 10 min. Copper(I) cyanide (537 mg, 6 mmol) was then added and the resulting black solution was stirred at −78 °C for a further 30 min.

General Procedure for the Stannyl-cupration of Allenes.—Typically, a solution of the allene (4 mmol) in THF (4 cm^3) was added dropwise to the tin-cuprate reagent (4.4 mmol) cooled with a solid CO_2/acetone-bath, and the mixture was stirred for 30 min at this temperature. Yields are based on the stannyl-cuprate reagent used, on the assumption that one of the stannyl groups is transferred.

Protonation of the Cuprate Intermediates.—The reaction mixture was warmed to 0 °C during 1 h, and saturated aq. ammonium chloride was added. Extraction (Et_2O), drying ($MgSO_4$), and chromatography gave the following compounds: **2a**, **2c**, **2d**, **3b**, **3c**, **3e** and **4e**. Compounds **2a** (92%) and **3b** (99%) have been described previously.[3] (E)-1-*Phenyl-2-(tributylstannyl)propene* **2c** (91%); R_f(hexane) 0.32; ν_{max}(film)/cm^{-1} 1635, 1595, 1490 and 700; $\delta_H(CDCl_3)$ 7.3–7.0 (5 H, m), 6.55 (1 H, q, J 2), 2.05 (3 H, d, J 2) and 1.65–0.7 (27 H, m); $\delta_C(CDCl_3)$ 136, 132, 130, 128, 127, 125, 29, 27, 20.5, 14 and 9.5; m/z 409 (6%, M + 1), 351 (100, M − Bu), 331 (13) and 291 (70) (Found: C, 62.1; H, 9.1. $C_{21}H_{36}Sn$ requires C, 61.94; H, 8.91%).

(Z)-1-Phenyl-3-(tributylstannyl)propene **3c** (9%) R_f(hexane) 0.38; ν_{max}(film)/cm^{-1} 1630, 1585, 1490, 750 and 590; $\delta_H(CDCl_3)$ 7.3–7.0 (5 H, m), 6.05–5.5 (2 H, m), 1.85 (2 H, dd, J 7 and 2) and 1.6–0.7 (27 H, m); m/z 409 (7%, M^+), 351 (100, M − Bu) and 291 (60).

(E)-1-*Phenyl-2-(tributylstannyl)but-2-ene* **2d** (89%); ν_{max}(film)/cm^{-1} 1635, 1560, 1450 and 690; $\delta_H(CDCl_3)$ 7.4–7.05 (5 H, m), 5.8 (1 H, qt, J 8 and 1), 3.6 (2 H, br s), 1.85 (3 H, d, J 8) and 1.6–0.6 (27 H, m); m/z 422 (1%, M^+), 365 (100, M − Bu) and 291 (93) (Found: C, 62.9; H, 9.2. $C_{22}H_{38}Sn$ requires C, 62.7; H, 9.1%).

(Z)-1-*(Tributylstannyl)hept-2-ene* **3e** (80%); R_f(hexane) 0.58; ν_{max}(film)/cm^{-1} 2960, 1640 and 700; $\delta_H(CDCl_3)$ 5.6–5.15 (2 H, m), 2.15–1.85 (4 H, m) and 1.7–0.7 (34 H, m); $\delta_C(CDCl_3)$ 128, 124.5, 32, 29, 27, 22.6, 14, 13.6, 10.4 and 9.2; m/z 388 (1%, M^+), 331 (3, M − Bu), 291 (37), 235 (63) and 179 (100) (Found: C, 59.2; H, 10.6. $C_{19}H_{40}Sn$ requires C, 58.9; H, 10.4%).

2-(Tributylstannyl)hept-1-ene **4e** (15%); R_f(hexane) 0.52; ν_{max}(film)/cm^{-1} 1640 and 905; $\delta_H(CDCl_3)$ 5.25 (1 H, m), 4.75 (1 H, m), 2.0 (2 H, br t, J 7.5) and 1.7–0.7 (34 H, m); m/z 331 (49%, M − Bu), 275 (30), 219 (55), 179 (38) and 121 (100).

Reaction of allenes **1a**, **1b** and **1e** with the mixed butyl-(tributylstannyl)cuprate gave the same products, with only slight differences in yields: **2a** (94%), **3b** (96%) and a mixture of **3e** and **4e** (91%) in the ratio 4.5:1, respectively. When the allene **1a** was treated with bis(tributylstannyl)cuprate, prepared instead from hexabutylditin with butyllithium and copper(I) cyanide, under the same conditions as described above, a mixture of products **2a** (88–92%) and **3a**[13] was obtained; these were not separated but the allylstannane was identified by the following extra signals in the ^1H NMR spectrum: $\delta(CDCl_3)$ 5.9 (1 H, m), 4.95–4.65 (1 H, m), 1.8 (2 H, d, J 8) and 1.6–0.8 (27 H, m). When the stannylcupration of allene **1a** was carried out at −100 °C following the general procedure described above [bis(tributylstannyl)cuprate from Bu_3SnCl, Li and CuCN] and quenching with methanol at −100 °C, **3a**[13] (= **7a**) (100%) was obtained as the only product. When allene **1a** was treated with the same cuprate at −100 °C, the mixture allowed to warm to 0 °C, and then quenched either at 0 °C or at −100 °C, only compound **2a** (=**8a**) (92%) was produced. Warming of the reaction mixture from −100 to −78 °C and quenching with methanol at −78 °C gave a mixture of compounds **7a** and **8a** (98%; 1:4.5).

Alkylation of the Cuprate Intermediates.—Methyl iodide (3 mmol) was added dropwise to the stannylcupration mixture (2 mmol) at −78 °C and the mixture was stirred at this temperature for 1 h then at 0 °C for 3 h. Aqueous work-up, using diethyl ether, and chromatography then gave a mixture of compounds **7c** and **8c** (typically 91%, in variable ratios) and **9a** (81%).[3] Allyl bromide (3 mmol) was added slowly to the stannylcupration mixture obtained from allene **1a** (2 mmol) at −78 °C and the mixture was stirred at −78 °C for 1 h, and then warmed to 0 °C and stirred for an additional hour. Work-up and chromatography gave compound **8g** (81%).[3]

Acetylation of the Cuprate Intermediates.—Acetyl chloride (2.5 mmol) was added to the stannylcupration mixture (2 mmol) at −78 °C. The mixture was allowed to warm to 0 °C during 1 h. Work-up and chromatography gave the ketones **8d** and **9b**. 4-(*Tributylstannyl*)*pent*-4-*en*-2-*one* **8d** (84%); ν_{max}(film)/cm^{-1} 1715, 1650 and 880; δ_H(CDCl$_3$) 5.7 (1 H, m), 5.25 (1 H, m), 3.3 (2 H, br s), 2.1 (3 H, s) and 1.6–0.7 (27 H, m); *m*/*z* 403 (13%, M + 29), 375 (3, M + 1), 317 (100, M − Bu) and 291 (70) (Found: C, 54.9; H, 9.4. $C_{17}H_{34}OSn$ requires C, 54.7; H, 9.2%).

4-*Methyl*-3-(*tributylstannylmethyl*)*pent*-3-*en*-2-*one* **9b** (99%); ν_{max}(film)/cm^{-1} 1685 and 1660; δ_H(CDCl$_3$) 2.15 (3 H, s), 1.9 (2 H, br s), 1.75 (3 H, s), 1.65 (3 H, s) and 1.6–0.7 (27 H, m); δ_C(CDCl$_3$) 197, 138, 129.5, 30.5, 29, 27, 22, 21, 17, 13.5 and 10; *m*/*z* 431 (6%, M + 29), 403 (7, M + 1), 345 (100, M − Bu) and 291 (77%) (Found: C, 57.1; H, 9.5. $C_{19}H_{38}OSn$ requires C, 56.9; H, 9.55%).

Acetyl chloride was similarly added to the product of stannylcupration of allene **1a** at −100 °C, and the mixture was kept at −100 °C for 1.5 h before quenching with methanol at −100 °C to give 3-(*tributylstannylmethyl*)*but*-3-*en*-2-*one* **7d** (73%); ν_{max}(film)/cm^{-1} 1675, 1650 and 900; δ_H(CDCl$_3$) 5.6 (1 H, m), 5.5 (1 H, m), 2.2 (3 H, s), 1.75 (2 H, br s) and 1.6–0.7 (27 H, m); *m*/*z* 403 (4%, M + 29), 375 (3, M + 1), 317 (100, M − Bu) and 291 (63) (Found: C, 55.1; H, 9.5. $C_{17}H_{34}OSn$ requires C, 54.7; H, 9.2%).

Halogenation of the Cuprate Intermediates.—Bromine (2.2 mmol) was added dropwise to the stannylcupration mixture (2 mmol) at −78 °C and stirred at −78 °C for 15 min then warmed to 0 °C. Aqueous work-up as before gave 3-bromo-2-(tributylstannyl)prop-1-ene **8b** (90%); δ_H(CDCl$_3$) 5.95 (1 H, m), 5.55 (1 H, d, *J* 2), 4.05 (2 H, br s) and 1.7–0.7 (27 H, m); δ_C(CDCl$_3$) 142, 123, 38.5, 29.5, 27, 13.5 and 9; *m*/*z* 410 and 412 (2%, M$^+$), 353 and 355 (6, M − Bu), 291 (10), 177 (100) and 121 (90).

Similar stannylcupration of allene **1a** was carried out at −100 °C followed by addition of bromine at −100 °C and the mixture was stirred for 1 h. Quenching with methanol and work-up as usual gave 2-*bromo*-3-(*tributylstannyl*)*prop*-1-*ene* **7b** (42%); ν_{max}(film)/cm^{-1} 2960, 1635 and 910; δ_H(CDCl$_3$) 5.6 (1 H, m), 5.35 (1 H, m), 2.25 (2 H, s) and 1.7–0.7 (27 H, m); *m*/*z* 410 and 412 (5%, M$^+$), 353 and 355 (13, M − Bu), 291 (40), 235 (60) and 177 (100) (Found: C, 44.0; H, 7.8. $C_{15}H_{31}BrSn$ requires C, 43.9; H, 7.6%).

Reaction of the Cuprate Intermediate with Ethylene Oxide.—Ethylene oxide (4 mmol) was added to the stannylcupration mixture (2 mmol) at −78 °C and the mixture was stirred for 1 h, warmed to 0 °C, and kept for 5 h before the usual work-up, which gave compounds **8e** and **9c**. 4-(*Tributylstannyl*)*pent*-4-*en*-1-*ol* **8e** (78%); ν_{max}(film)/cm^{-1} 3340, 1630, 1070 and 910; δ_H(CDCl$_3$) 5.7 (1 H, m), 5.1 (1 H, m), 3.55 (2 H, t, *J* 7), 2.3 (2 H, br t, *J* 7), 2.1 (1 H, br s), 1.85 (2 H, m) and 1.7–0.7 (27 H, m); δ_C(CDCl$_3$) 148, 125, 62, 37, 32, 29, 27, 13 and 9; *m*/*z* 377 (1%, M + 1), 319 (100, M − Bu) and 291 (76) (Found: C, 54.7; H, 9.9. $C_{17}H_{36}OSn$ requires C, 54.4; H, 9.7%).

4-*Methyl*-3-(*tributylstannylmethyl*)*pent*-3-*en*-1-*ol* **9c** (75%); ν_{max}(film)/cm^{-1} 3340, 1640 and 1080; δ_H(CDCl$_3$) 3.45 (2 H, t, *J* 7), 2.15 (2 H, t, *J* 7), 2.0 (1 H, br s), 1.85 (2 H, s), 1.7 (3 H, s), 1.6 (3 H, s) and 1.6–0.6 (27 H, m); *m*/*z* 347 (52%, M − Bu), 316 (10, M − Bu − CH$_2$OH), 291 (24) and 177 (100) (Found: C, 56.5; H, 10.1. $C_{19}H_{40}OSn$ requires C, 56.6; H, 9.99%).

Reaction of the Cuprate Intermediate with Carbon Dioxide.—Carbon dioxide (excess) was added to the still cold solution (−78 °C) following the stannylcupration of allene **1a** (2 mmol). The mixture was allowed to warm to 0 °C during 1 h, and then stirred at 0 °C for a further 1 h. Work-up as usual gave 3-(tributylstannyl)but-3-enoic acid **8f** (49%); ν_{max}(film)/cm^{-1} 3300–2550, 1700 and 1630; δ_H(CDCl$_3$) 8.5 (1 H, br s), 5.8 (1 H, m), 5.3 (1 H, m), 3.05 (2 H, br s) and 1.7–0.6 (27 H, m); *m*/*z* 319 (20%, M − Bu), 291 (92) and 235 (100).

Reaction of the Cuprate Intermediate with Aldehydes and Ketones.—A solution of acetaldehyde, acetone (6 mmol) or cyclohex-2-enone (2.5 mmol) in THF (5 cm^3) was added to the stannylcupration mixture (2 mmol) at solid CO$_2$/acetone temperature, and the mixture was stirred for 1 h. The mixture was warmed and then kept at 0 °C for 3 h. Aqueous work-up and chromatography gave compounds **8h–j** and **9d**. Compound **8j** (74%) has been previously described.[3] 4-(*Tributylstannyl*)-*pent*-4-*en*-2-*ol* **8h** (69%); ν_{max}(film)/cm^{-1} 3520, 3460, 1045 and 900; δ_H(CDCl$_3$) 5.8 (1 H, m), 5.3 (1 H, d, *J* 2), 3.7 (1 H, br q, *J* 8), 2.3 (2 H, m), 1.8 (1 H, br s), 1.6–0.7 (27 H, m) and 1.3 (3 H, d, *J* 8); δ_C(CDCl$_3$) 147, 130, 65, 52, 29, 27, 22, 14 and 9.5; *m*/*z* 319 (100%, M − Bu), 301 (7, M − Bu − 18), 251 (59), 177 (72) and 137 (89) (Found: C, 54.2; H, 9.4. $C_{17}H_{36}OSn$ requires C, 54.4; H, 9.7%).

2-*Methyl*-4-(*tributylstannyl*)*pent*-4-*en*-2-*ol* **8i** (47%); ν_{max}(film)/cm^{-1} 3605, 3400, 1100 and 915; δ_H(CDCl$_3$) 5.8 (1 H, m), 5.35 (1 H, d, *J* 2.5), 2.35 (2 H, br s), 1.7–0.7 (28 H, m) and 1.25 (6 H, s); δ_C(CDCl$_3$) 149.5, 129, 71, 57, 31, 29, 27, 13 and 10; *m*/*z* 333 (58%, M − Bu), 315 (100, M − Bu − 18) and 177 (70) (Found: C, 55.15; H, 9.6. $C_{18}H_{38}OSn$ requires C, 55.55; H, 9.8%).

3-[2-Methyl-1-(tributylstannylmethyl)prop-1-enyl]cyclohexanone **9d** (67%); ν_{max}(film)/cm^{-1} 1715; δ_H(CDCl$_3$) 2.2–1.8 (5 H, m), 1.7 (2 H, s), 1.6 (3 H, s), 1.55 (3 H, s) and 1.7–0.7 (31 H, m); δ_C(CDCl$_3$) 203, 138.5, 119, 47.5, 39, 34.5, 29, 28, 27, 25.5, 25, 16.5, 13.5 and 8.5; *m*/*z* 456 (24%, M$^+$), 399 (89, M − Bu) and 291 (100).

Reaction of the Cuprate Intermediate with Acetylenic Esters.—A solution of methyl propiolate or diethyl acetylenedicarboxylate (2.5 mmol) in THF (2.5 cm^3) was added dropwise to the stannylcupration mixture (2 mmol) prepared from allene **1a** at −78 °C. The mixture was stirred for 1 h at −78 °C and then kept at 0 °C for 4 h; work-up as usual and chromatography gave products **7k**, **7l** and **8l**. *Methyl*(E)-4-(*tributylstannylmethyl*)-*penta*-2,4-*dienoate* **7k** (87%); ν_{max}(film)/cm^{-1} 1720, 1625, 1595, 995 and 875; δ_H(CDCl$_3$) 7.3 (1 H, d, *J* 18), 5.75 (1 H, d, *J* 18), 5.15 (2 H, s), 3.7 (3 H, s), 1.9 (2 H, s) and 1.7–0.6 (27 H, m); δ_C(CDCl$_3$) 165, 147.5, 145, 119.5, 117.5, 51.5, 29, 27, 19, 13.5 and 10; *m*/*z* 359 (6%, M − Bu), 291 (32), 235 (76) and 179 (100) (Found: C, 54.8; H, 8.7. $C_{19}H_{36}O_2Sn$ requires C, 55.0; H, 8.75%). Quenching of the same reaction with deuterium oxide gave the appropriately deuteriated product, methyl(*E*)-2-deuterio-4-(tributylstannylmethyl)penta-2,4-dienoate (51%) with an identical ^{1}H NMR spectrum except for a broad singlet at δ 7.35 and no signal at δ 5.75; *m/z* 417 (7%, M^+), 360 (6, M − Bu), 291 (33), 235 (70) and 179 (100).

Diethyl 2-[2-(tributylstannyl)prop-2-enyl]butenedioate **8l** (63%); R_f[hexane–EtOAc (7:1)] 0.38; ν_{max}(film)/cm^{-1} 1725, 1650, 1245, 1190, 1120 and 880; δ_H(CDCl$_3$)/cm^{-1} 6.25 (1 H, t, *J* 2), 5.75 (1 H, m), 5.35 (1 H, d, *J* 1.5), 4.2 (2 H, q, *J* 7.5), 4.25 (2 H, q, *J* 7.5), 2.3 (2 H, d, *J* 2) and 1.7–0.7 (33 H, m); δ_C(CDCl$_3$) 166, 165, 150, 146, 129.5, 126, 62, 60.5, 43, 29, 27, 14, 13.5 and 9.5; *m/z* 503 (10%, M + 1), 457 (50, M − 45), 445 (30, M − Bu) and 291 (100) (Found: C, 55.0; H, 8.6. $C_{23}H_{42}O_4Sn$ requires C, 55.1; H, 8.45%).

Diethyl 2-[1-(tributylstannylmethyl)vinyl]butenedioate **7l** (7%); R_f[hexane–EtOAc (7:1)] 0.31; ν_{max}(film)/cm^{-1} 1710, 1635, 1220 and 870; δ_H(CDCl$_3$) 6.5 (1 H, s), 5.5 (1 H, m), 5.2 (1 H, m), 4.3 (2 H, q, *J* 7.5), 4.2 (2 H, q, *J* 7.5), 2.0 (2 H, br s) and 1.6–0.7 (33 H, m); δ_C(CDCl$_3$) 167, 166, 150, 146, 127, 114, 63, 61, 29, 27, 15, 14, 12 and 10; *m/z* 503 (7%, M + 1), 445 (80, M − Bu) and 291 (100).

2-(*Tributylstannyl*)*but*-1-*ene* **8c**.—Allene **1a** (5 mmol) was added from a balloon to the lithium butyl(tributylstannyl)cuprate (4 mmol) prepared from hexabutylditin, butyllithium, copper(I) cyanide and butyllithium at −78 °C as described before. After 30 min at −78 °C, bromine (4.4 mmol) was added and the mixture was allowed to warm to 0 °C. A solution of lithium dimethylcuprate (4.4 mmol) in THF (4 cm^3) was then added quickly to the mixture at 0 °C and the mixture was stirred for 2 h. Aqueous work-up (Et$_2$O, aq. NH$_4$Cl), drying (MgSO$_4$), and chromatography in pentane gave the vinylstannane **8c** (65%).[3]

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References

1 I. Fleming and F. J. Pulido, *J. Chem. Soc., Chem. Commun.*, 1986, 1010.

2 P. Cuadrado, A. M. Gonzalez, F. J. Pulido and I. Fleming, *Tetrahedron Lett.*, 1988, **29**, 1825.

3 I. Fleming, M. Rowley, P. Cuadrado, A. M. González-Nogal and F. J. Pulido, *Tetrahedron*, 1989, **45**, 413.

4 I. Fleming, Y. Landais and P. R. Raithby, *J. Chem. Soc., Perkin Trans. 1*, 1991, 715.

5 Y. Morizawa, H. Oda, K. Oshima and H. Nozaki, *Tetrahedron Lett.*, 1984, **25**, 1163; see also T. N. Mitchell, H. Killing, R. Dicke and R. Wickenkamp, *J. Chem. Soc., Chem. Commun.*, 1985, 354.

6 E. Piers, H. E. Morton and J. M. Chong, *Can. J. Chem.*, 1987, **65**, 78; S. Sharma and A. C. Oehlschlager have characterised this and other stannyl-cuprates, *J. Org. Chem.*, 1991, **56**, 770; see also R. D. Singer, M. W. Hutzinger and A. C. Oehlschlager, *J. Org. Chem.*, 1991, **56**, 4933.

7 A. Barbero, P. Cuadrado, I. Fleming, A. M. González and F. J. Pulido, *J. Chem. Soc., Chem. Commun.*, 1990, 1030.

8 C. Tamborski, F. E. Ford and E. J. Soloski, *J. Org. Chem.*, 1963, **28**, 237.

9 W. C. Still, *J. Am. Chem. Soc.*, 1977, **99**, 4836.

10 S. M. Singh and A. C. Oehlschlager, *Can. J. Chem.*, 1991, in the press.

11 I. Fleming, *Pure Appl. Chem.*, 1990, **62**, 1879.

12 J. L. Luche, E. Barreiro, J. M. Dollat and P. Crabbé, *Tetrahedron Lett.*, 1975, 4615; P. Rona and P. Crabbé, *J. Am. Chem. Soc.*, 1968, **90**, 4733; 1969, **91**, 3289.

13 D. Seyferth and M. A. Weiner, *J. Org. Chem.*, 1961, **26**, 4797.

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