

Stannyl-cupration of Acetylenes and the Reaction of the Intermediate Cuprates with Electrophiles as a Synthesis of Substituted Vinylstannanes

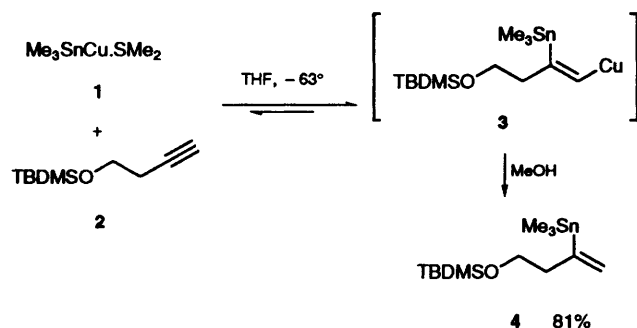
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Stannyl-cupration of acetylenes followed by electrophilic attack with a variety of electrophiles gives *E*-vinylstannanes. These can be used either to form acetylenes, thus achieving overall the addition of an ethynyl group, or to form carbon–carbon bonds in Stille reactions.

The stannyl-cupration of acetylenes was discovered more than 10 years ago, when Piers and his co-workers found that a trimethylstannyl-copper¹ or cuprate² reagent added to acetylenic esters. Since then he,³ and others,^{4–7} have found that stannyl-copper reagents and stannyl-cuprates also add to simple alkyl-substituted acetylenes, where the reaction in Scheme 1 is typical. However, a major limitation of these



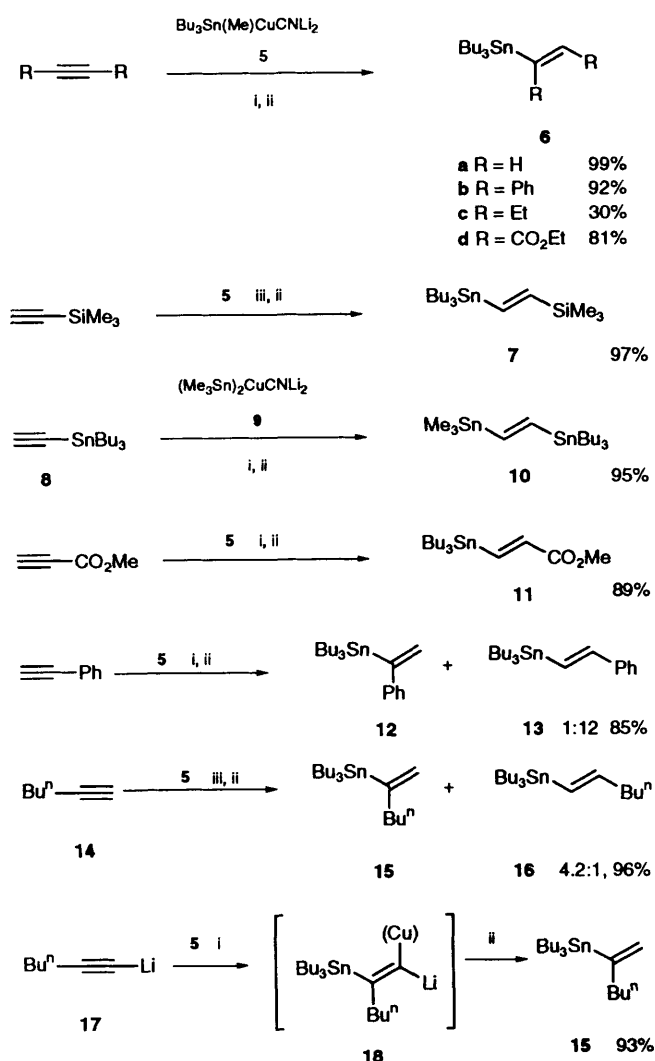
otherwise powerful reactions has been the difficulty in persuading the vinyl-copper or vinyl-cuprate intermediate to react with anything more interesting than a proton. The problem appears to be that the stannyl-cupration step **1** + **2** → **3**, although well to the right at equilibrium, is easily reversible,⁵ and the stannyl-copper reagent itself **1** is more reactive than the vinyl-copper intermediate **3** towards many electrophiles. Stannyl-copper and cuprate reagents are evidently not very basic, with the result that a proton, usually delivered from methanol included in the reaction mixture, is relatively selective for the vinyl-copper intermediate, making the formation of the addition product **4** high-yielding. The only successes in achieving more substantial reactions have been (a) with an acetylenic ester carrying an internal alkyl halide electrophile;^{1,2} (b) with methylation, allylation and prop-2-ynylation, in the presence of HMPA, of an acetylenic ester carrying a β-siloxymethyl substituent treated with a mixed higher-order cyano(thiophenyl)trimethylstannylcuprate reagent;² (c) with methylation, allylation and ethynylation, again in the presence of HMPA, of acetylene itself treated with a triphenylstannyl-copper or cuprate reagent;⁶ and (d) with metal-exchange followed by Stille coupling with an ethynyl bromide or iodide.⁷ It is not clear how general these reactions are. The usual solution to the problem has been to use copper or palladium to catalyse the addition of the tin and another main-group metal, such as boron, aluminium, magnesium or zinc, across the triple bond.^{8,9} The other main-group metal can then be replaced in a second step by a variety of electrophiles.

Another solution is the addition of *two* trimethyltin groups across the triple bond, with selective replacement of one or both of them by tin–lithium exchange followed by treatment with carbon electrophiles.¹⁰ A third solution is simply to use a large excess of the stannyl-cupration product to make the yield based on the electrophile high.¹¹

We reported in a preliminary communication¹² that the mixed higher-order cyano(methyl)tributylstannylcuprate **5**^{13,14} was useful, not only for the synthesis of some potentially useful small synthons in the unexceptional reactions shown in Scheme 2, but that it also overcame some of the difficulties referred to above. We now report this work in full, adding some observations about how the products might be useful in synthesis. Since we prepared our preliminary communication, there have been four reports^{15,16} indicating that we have not been alone in finding that stannyl-cupration can be followed by attack with some carbon electrophiles.

Using simple acetylenes, and working up with a proton source in the usual way, we prepared the vinylstannanes shown in Scheme 2. The only complications were that the stannyl-acetylene **8** did not react with the mixed cuprate **5**, but did with the bis(trimethyl)stannylcuprate **9**, and the reaction with hex-1-yne **14** was only moderately regioselective, as expected by analogy with Piers' work. We find that high regioselectivity in the same sense, giving the 2-stannylhex-1-ene **15**, can be achieved, without necessarily committing oneself to a proton electrophile, by carrying out the addition of the stannylcuprate **5** to the corresponding lithium acetylide **17**, with reaction presumably taking place by way of the three times over differentially metallated alkene **18**.

More significantly, we have easily achieved the successive addition of a stannyl-cuprate and carbon and other electrophiles to unactivated acetylenes. Thus, the mixed cuprate **5** reacts with acetylene itself, and the intermediate cuprate reacts well (Scheme 3) with trimethylsilyl chloride, tributyltin chloride, bromine, iodine, methyl iodide, cyclohexenone and ethylene oxide, and moderately well with acetyl chloride and methyl crotonate to give the vinylstannanes **19–27**. We did not use HMPA in any of these reactions. The reaction is not, however, limited to acetylene itself—the mixed cuprate also reacts with hex-1-yne, and the intermediate vinylcuprate can be trapped with iodine, methyl iodide and ethylene oxide to give the vinylstannanes **28–30** (Scheme 4). Phenylacetylene and hex-3-yne also react, and in both cases the intermediate reacts with cyclohexenone and ethylene oxide as representative carbon electrophiles to give the vinylstannanes **31–33**. It is clear that stannylcupration is not limited merely to the addition of tin and a proton across a triple bond, powerful through that reaction is already.¹⁷ We note in particular that we now have easy methods for preparing both (*E*)- and (*Z*)-2-silylvinylstannanes **7** and **19**,

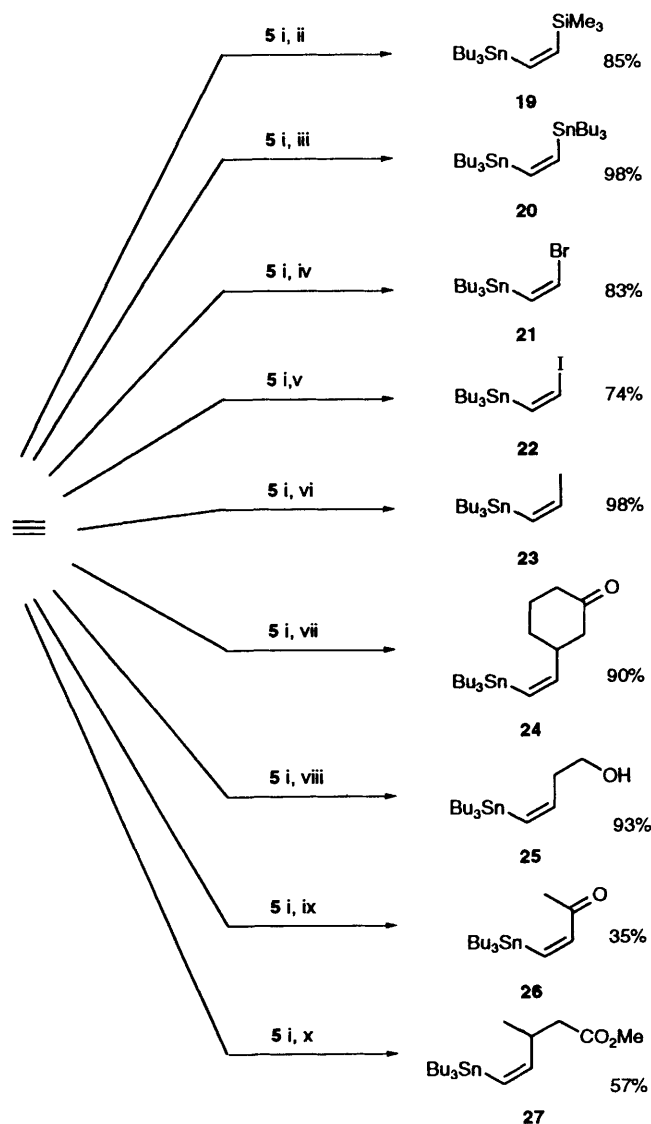


Scheme 2 Reagents and conditions: i, $-78 \rightarrow 0^\circ\text{C}$; ii, NH_4Cl ; iii, -78°C

and (*E*)- and (*Z*)-vinylbisstannanes **10** and **20**. However, since our preliminary communication, we have found that we are not entirely successful with attaching all the carbon electrophiles that worked with acetylene itself to the intermediate derived from substituted acetylenes. Thus, stannylation of either hex-1-yne or hex-3-yne, followed by treatment with cyclohexanone, gave only 3-tributylstannylcyclohexanone. There are, therefore still some problems with this reaction.

We are unclear why we have been able to overcome some of the limitations experienced by others, but most probably it is connected with the fact that we, Westmijze,⁶ Quintard, Normant, Parsons¹⁵ and Marino,¹⁶ have all used a cuprate, where the earlier work had most often been carried out using stannyl-copper reagents. It is significant that Piers used a cuprate in the only reactions in which he was able to achieve intermolecular reaction with carbon electrophiles, although in his case he needed HMPA, and still found substantial amounts of protonation.² What is clear is that it is not just the fact that we have usually used a mixed cuprate, for we find that the corresponding dibutylstannylcuprate behaves very similarly in several of these reactions, and we have also found that the carbon ligand can equally well come from butyllithium as from methylolithium.

In view of a report¹⁸ that stannylation of acetylenes does not take place below -35°C , we checked that our solution had not, in fact, warmed up to this temperature before we had added

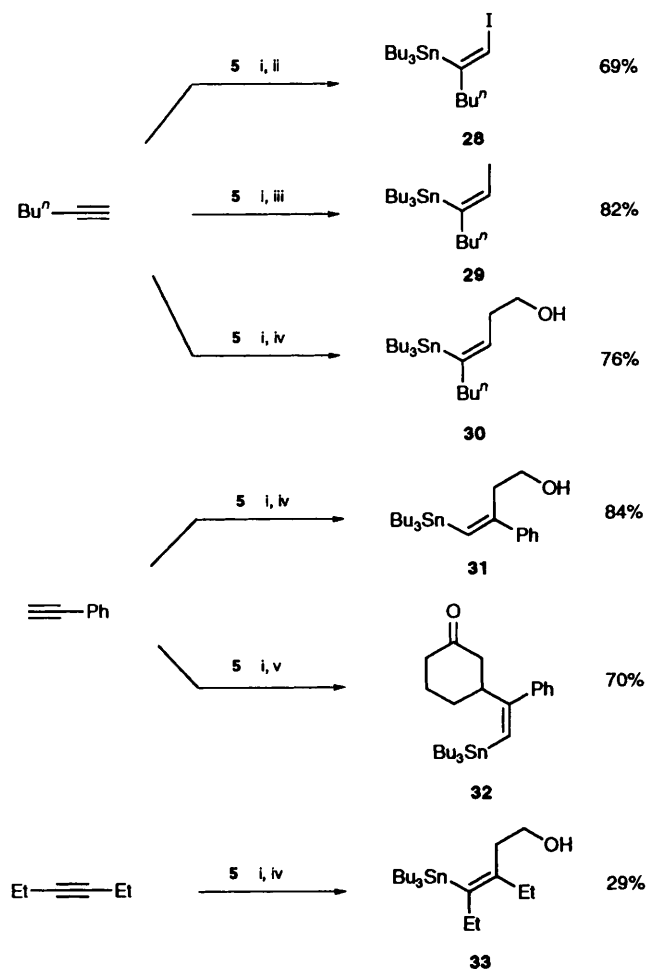


Scheme 3 Reagents and conditions: i, THF, -78°C ; ii, Me_3SiCl , $-78 \rightarrow 0^\circ\text{C}$; iii, Bu_3SnCl , $-78^\circ\text{C} \rightarrow 0^\circ\text{C}$; iv, Br_2 , $-78 \rightarrow 0^\circ\text{C}$; v, I_2 , $-78 \rightarrow 0^\circ\text{C}$; vi, MeI , $-78 \rightarrow 0^\circ\text{C}$; vii, cyclohexanone, $-78 \rightarrow 0^\circ\text{C}$; viii, ethylene oxide, $-78 \rightarrow 0^\circ\text{C}$; ix, AcCl , $-78 \rightarrow 0^\circ\text{C}$; x, $\text{MeCH=CHCO}_2\text{Me}$, $-78 \rightarrow 0^\circ\text{C}$

the electrophile—the temperature in the flask did not rise above -67°C . We conclude that, in our conditions at least, the stannylation must have taken place below this temperature, since the stannylation, if there were any still in the reaction mixture when the electrophile was added, would surely have reacted with most of the electrophiles before it reacted with the acetylene.

Whatever the explanation, it is clear that we have available a wide range of vinylstannanes. Of the many uses that these compounds might be put to, we illustrate two here (Scheme 5) that are based on the work of Corey and Stille.

Corey showed that (*E*)-vinylstannanes can be oxidised to acetylenes with lead tetraacetate,¹⁹ and Pinhey, investigating the mechanism showed that (*Z*)-vinylstannanes were sometimes better in giving fewer by-products.^{20,21} We find that the vinylstannanes **24** and **27** are converted into the acetylenes **34** and **35**, respectively, making the overall reaction the conjugate addition of acetylene to an $\alpha\beta$ -unsaturated ketone or an $\alpha\beta$ -unsaturated ester in two easy steps. This reaction cannot be done directly with ethynylcuprates, although it can with ethynylthallates.²² Less predictably, we also oxidised the



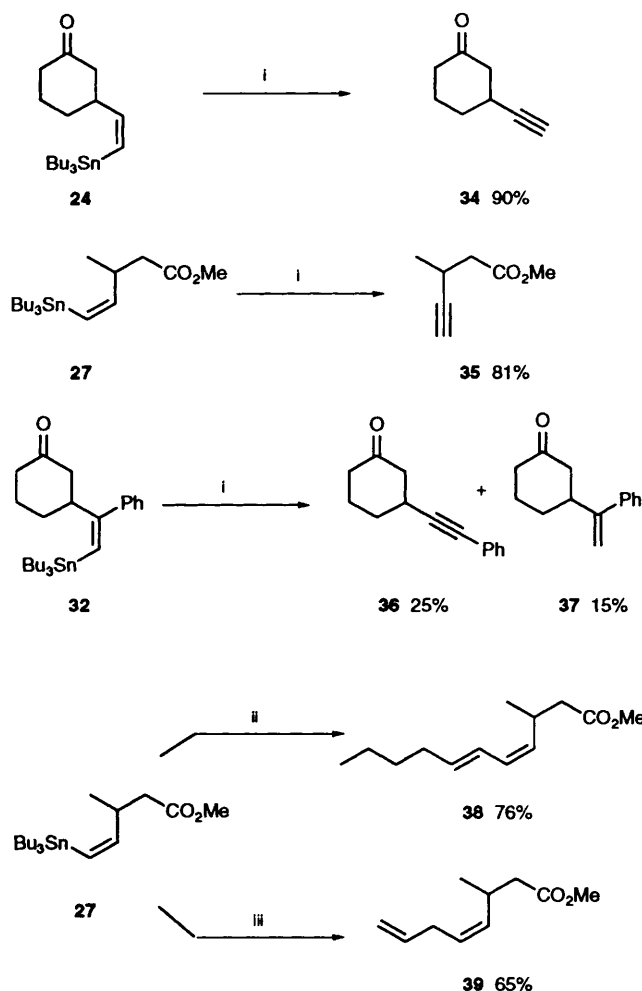
Scheme 4 Reagents and conditions: i, -78°C ; ii, I_2 , $-78 \rightarrow 0^{\circ}\text{C}$; iii, MeI , $-78 \rightarrow 0^{\circ}\text{C}$; iv, ethylene oxide, $-78 \rightarrow 0^{\circ}\text{C}$; v, cyclohexenone, $-78 \rightarrow 0^{\circ}\text{C}$

vinylstannane **32**. Although the yield was not good, the major product **36** suggested that a 1,2 phenyl shift had taken place in the vinyl-lead(IV) intermediate, in a reaction that has precedent,²⁰ with the minor product **37** the result of protodestannylation or protodeplumbation. Stille reactions²³ on the vinylstannane **27** gave the 1,3-diene **38** and the 1,4-diene **39**.

We also direct attention to another use for some of these vinylstannanes, which we have published ourselves.²⁴ When we treated the ketones **24** and **32** and the toluene-*p*-sulfonates of the alcohols **25** and **31** with butyllithium, tin-lithium exchange took place faster than the attack of the butyllithium on the ketone or the primary toluene-*p*-sulfonate group, but the vinylolithium so created did attack those groups making five- and four-membered rings, respectively.

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 Bruker WP-200-5Y or A-80 spectrometer. 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 nitrogen. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl under nitrogen. Chromatographic solvents were distilled prior to use. Alkylolithium reagents were purchased from Aldrich, and copper(I) cyanide from Fluka. The latter was dried in an oven



Scheme 5 Reagents: i, $\text{Pb}(\text{OAc})_4$, MeCN , 20°C , 72–120 h; ii, *E*-1-iodohexene, $\text{PdCl}_2(\text{MeCN})_2$ cat., DMF , 20°C , 96 h; iii, allyl bromide, $\text{PdCl}_2(\text{MeCN})_2$ cat., DMF , 80°C , 20 h

overnight at 120°C . We bought all the acetylenes (Aldrich). Trimethylstannylolithium and tributylstannylolithium were prepared by the established procedures.^{25,26}

Lithium Bis(trimethylstannyl)cuprate.—A solution of trimethylstannylolithium (12 mmol) prepared in THF by the method of Tamborski²⁵ 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 black mixture was stirred at this temperature for 30 min and used immediately.

Lithium Methyl(tributylstannyl)cuprate.—A mixture of tributylstannylolithium (6 mmol), prepared in THF by the method of Still²⁶ (10 cm^3), and methylolithium (1.6 mol dm^{-3} solution in hexane; 3.57 cm^3) was stirred at -78°C for 10 min. Copper(I) cyanide (537 mg, 6 mmol) was then added and the resulting red solution stirred at -78°C for 30 min.

General Procedure for the Stannylcupration of Acetylenes.—Typically, a solution of the acetylene (4 mmol) in THF (4 cm^3) was added dropwise to the tin-cuprate reagent (4 mmol) cooled with a solid carbon dioxide-acetone bath, and the mixture was stirred for 30 min at this temperature. Yields are based on the stannylcuprate reagent used, on the assumption that one of the stannyl groups was transferred.

Protonation of the Cuprate Intermediates.—The reaction mixture was warmed to 0°C during 1 h, and saturated aqueous

ammonium chloride was added to it. Extract with diethyl ether, drying (MgSO₄) and chromatography gave the following compounds: **6a–d**, **7**, **10–13**, **15** and **16**. Compounds **6a** (99%),²⁷ **6b** (92%),²⁸ **11** (89%),²⁹ **12** (78%),⁹ **13** (7%),⁹ **15** (78%)³⁰ and **16** (18%)²⁸ have been described previously. The following new compounds were prepared by this method.

(E)-3-Tributylstannylhex-3-ene **6c** (30%). *R_f* (hexane) 0.52; ν_{\max} (film)/cm⁻¹ 1670; δ_{H} (CDCl₃) 5.47 (1 H, tt, *J* 7 and 1.3), 2.45–1.95 (4 H, m) and 1.7–0.7 (33 H, m); δ_{C} (CDCl₃) 145, 142, 29, 27, 17, 16, 13.5 and 8.5; *m/z* 317 (28%, M – Bu), 261 (24), 235 (3) and 121 (100).

Diethyl (E)-2-tributylstannylbut-2-ene-1,4-dioate **6d** (81%). *R_f* (hexane–EtOAc, 7:1) 0.32; ν_{\max} (film)/cm⁻¹ 1715, 1710, 1640 and 1210; δ_{H} (CDCl₃) 6.8 (1 H, s, ³*J*_{Sn–Hcis} 81.5), 4.25 (2 H, q, *J* 7.7), 4.2 (2 H, q, *J* 7.7) and 1.6–0.7 (33 H, m); δ_{C} (CDCl₃) 167.5, 165, 151, 146.5, 61, 60.5, 29, 27, 14, 13.5 and 12; *m/z* 417 (20%, M – OEt), 405 (100, M – Bu), 361 (10, M – Bu–OEt) and 291 (15) (Found: C, 51.9; H, 8.4. C₂₀H₃₈O₄Sn requires C, 52.1; H, 8.3%).

(E)-1-Tributylstannyl-2-trimethylsilylethylene **7** (97%). *R_f* (hexane) 0.68; ν_{\max} (film)/cm⁻¹ 1650, 1250, 840 and 690; δ_{H} (CDCl₃) 7.05 (1 H, d, *J* 22.7, ²*J*_{Sn–Hgem} 104), 6.6 (1 H, d, *J* 22.7, ³*J*_{Sn–Hcis} 101), 1.6–0.7 (27 H, m) and 0.1 (9 H, s); δ_{C} (CDCl₃) 155, 150, 29.5, 27.5, 14, 9 and –1.5; *m/z* 375 (7%, M – Me), 333 (100, M – Bu), 291 (69) and 235 (4) (Found: C, 52.2; H, 9.6. C₁₇H₃₄SnSi requires C, 52.45; H, 9.8%).

(E)-1-Tributylstannyl-2-trimethylstannylethylene **10** (95%). *R_f* (hexane) 0.68; ν_{\max} (film)/cm⁻¹ 960; δ_{H} (CDCl₃) 7.3 (2 H, s), 1.8–0.7 (27 H, m) and 0.15 (9 H, s); δ_{C} (CDCl₃) 155, 154, 28, 27, 17, 13.5 and –1; *m/z* 425 (8%, M – Bu), 368 (5) and 235 (24).

Alkylation of the Cuprate Intermediates.—Methyl iodide (3 mmol) was added dropwise to the appropriate stannylcupration mixture (2 mmol) at –78 °C. The mixture was stirred at this temperature for 1 h and then at 0 °C for 3 h. Aqueous work-up using diethyl ether and chromatography gave the following vinylstannanes.

(Z)-1-Tributylstannylpropene **23** (98%). *R_f* (hexane) 0.76; ν_{\max} (film)/cm⁻¹ 1650 and 685; δ_{H} (CDCl₃) 6.6 (1 H, dq, *J* 12.3 and 6.15), 5.8 (1 H, dq, *J* 12.3 and 1.5), 1.8 (3 H, dd, *J* 6.15 and 1.5) and 1.6–0.7 (27 H, m); δ_{C} (CDCl₃) 143, 129, 29, 27, 22, 14 and 9; *m/z* 275 (73%, M – Bu), 219 (93) and 161 (100) (Found: C, 54.45; H, 9.7. C₁₅H₃₂Sn requires C, 54.4; H, 9.7%).

(Z)-3-Tributylstannylhept-2-ene **29** (82%). *R_f* (hexane) 0.64; δ_{H} (CDCl₃) 6.1 (1 H, qt, *J* 6.6 and 1, ³*J*_{Sn–Htrans} 144), 2.2 (2 H, br t, *J* 7), 1.7 (3 H, br d, *J* 6.6) and 1.7–0.7 (34 H, m); δ_{C} (CDCl₃) 145, 134, 40.5, 33, 29, 27, 23, 20, 13.5 and 9; *m/z* 331 (43%, M – Bu), 275 (31), 235 (3) and 121 (100) (Found: C, 58.9; H, 10.45. C₁₉H₄₀Sn requires C, 58.9; H, 10.4%).

Acetylation of the Cuprate Intermediate.—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 (Z)-4-tributylstannylbut-3-en-2-one **26** (35%). *R_f* (hexane–Et₂O, 20:1) 0.3; ν_{\max} (film)/cm⁻¹(CCl₄) 1675, 1650 and 685; δ_{H} (CCl₄) 7.05 (1 H, d, *J* 13), 6.7 (1 H, d, *J* 13), 2.05 (3 H, s) and 1.6–0.7 (27 H, m); *m/z* 303 (60%, M – Bu), 235 (60) and 179 (100).

Halogenation of the Cuprate Intermediates.—Bromine or iodine (2.2 mmol) was added to the stannylcupration mixture (2 mmol) at –78 °C and stirred at –78 °C for 15 min and then warmed to 0 °C. Aqueous work-up as before gave the following vinyl bromines.

(Z)-2-Bromo-1-tributylstannylethylene **21** (83%). *R_f* (pentane) 0.79; ν_{\max} (film)/cm⁻¹ 1650 and 680; δ_{H} (CDCl₃) 7.15 (1 H, d, *J* 8, ³*J*_{Sn–Htrans} 99), 6.9 (1 H, d, *J* 8, ²*J*_{Sn–Hgem} 56) and 1.6–0.7 (27 H, m); δ_{C} (CDCl₃) 137, 123, 29, 27, 13 and 9; *m/z* 339 (5%, M – Bu), 313 (100), 257 (14) and 199 (7).

(Z)-2-Iodo-1-tributylstannylethylene **22** (74%). *R_f* (hexane) 0.65; ν_{\max} (film)/cm⁻¹ 1650 and 690; δ_{H} (CDCl₃) 7.65 (1 H, d, *J* 8), 7.35 (1 H, d, *J* 8) and 1.7–0.7 (27 H, m); δ_{C} (CDCl₃) 148.98, 29, 27, 13.5 and 10; *m/z* 317 (0.5%, M – I) (Found: C, 38.3; H, 6.75. C₁₄H₂₉ISn requires C, 38.0; H, 6.6%).

(Z)-1-Iodo-2-tributylstannylhex-1-ene **28** (69%). *R_f* (hexane) 0.63; δ_{H} (CDCl₃) 6.75 (1 H, t, *J* 1), 2.2 (2 H, br t, *J* 7, ³*J*_{Sn–Htrans} 106.7) and 1.8–0.7 (34 H, m); *m/z* 373 (15%, M – I), 316 (15, M – I – Bu), 235 (8) and 121 (100).

Reaction of the Cuprate Intermediates 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. The usual work-up gave the following alcohols.

(Z)-4-Tributylstannylbut-3-en-1-ol **25** (93%). *R_f* (pentane–EtOAc, 10:1) 0.4; ν_{\max} (film)/cm⁻¹ 3610, 3350, 1600, 1050 and 700; δ_{H} (CDCl₃) 6.55 (1 H, dt, *J* 12 and 6.7, ³*J*_{Sn–Htrans} 136), 6.9 (1 H, dt, *J* 12 and 1, ²*J*_{Sn–Hgem} 58.6), 3.7 (2 H, t, *J* 6.7), 2.3 (2 H, qd, *J* 6.7 and 1) and 1.6–0.7 (28 H, m); δ_{C} (CDCl₃) 145, 132, 62, 40, 29, 27, 13.5 and 10; *m/z* 305 (100%, M – Bu), 291 (71), 235 (9) and 71 (34) (Found: 53.25; H, 9.5. C₁₆H₃₄OSn requires C, 53.2; H, 9.5%).

(Z)-4-Tributylstannylbut-3-en-1-ol **30** (76%). *R_f* (hexane–EtOAc, 10:1) 0.31; ν_{\max} (film)/cm⁻¹ 3610, 3320, 1615, 1045 and 860; δ_{H} (CDCl₃) 6.0 (1 H, tt, *J* 7.2 and 1.3, ³*J*_{Sn–Htrans} 133.3), 3.63 (2 H, t, *J* 6.6), 2.5–2.1 (5 H, m) and 1.7–0.7 (34 H, m); δ_{C} (CDCl₃) 148, 135.5, 62, 40.5, 38, 33, 29, 27, 22, 14, 13.5 and 10; *m/z* 418 (1%, M⁺), 361 (100, M – Bu) and 291 (78) (Found: C, 57.7; H, 10.2. C₂₀H₄₂OSn requires C, 57.6; H, 10.15%).

(Z)-3-Ethyl-4-tributylstannylhex-3-en-1-ol **33** (29%). *R_f* (pentane–EtOAc, 10:1) 0.35; ν_{\max} (film)/cm⁻¹ 3600, 3420 and 1025; δ_{H} (CDCl₃) 3.7 (2 H, t, *J* 8), 2.9 (1 H, br s) and 2.2–0.6 (39 H, m); *m/z* 418 (10%, M⁺), 327 (7), 235 (20) and 179 (100).

(Z)-3-Phenyl-4-tributylstannylbut-3-en-1-ol **31** (84%). *R_f* (hexane–EtOAc, 8:3) 0.36; ν_{\max} (film)/cm⁻¹ 3600, 3450, 1670, 1580, 1050 and 860; δ_{H} (CDCl₃) 7.45–7.2 (5 H, m), 6.25 (1 H, s, ²*J*_{Sn–Hgem} 61.34), 3.6 (2 H, t, *J* 6.7), 2.8 (2 H, t, *J* 6.7) and 1.7–0.7 (28 H, m); δ_{C} (CDCl₃) 154, 143.5, 132, 128, 127, 126, 61.5, 42, 29, 27, 14.5 and 10.5; *m/z* 351 (11%, M – Bu–CH₂OH), 291 (45), 235 (87) and 177 (100) (Found: C, 60.65; H, 9.1. C₂₂H₃₈OSn requires C, 60.4; H, 8.8%).

Reaction of the Cuprate Intermediate with αβ-Unsaturated Ketones and Esters.—A solution of cyclohex-2-enone (2.5 mmol) or methyl crotonate (3 mmol) in THF (5 cm³) was added to the stannylcupration mixture (2 mmol) at –78 °C, and the mixture was stirred for 1 h and then warmed and kept at 0 °C for 3 h. Aqueous work-up and chromatography gave the following ketone and esters.

(Z)-3-(1-Tributylstannylethenyl)cyclohexanone **24** (90%). *R_f* (hexane–EtOAc, 10:1) 0.5; ν_{\max} (film)/cm⁻¹ 1715, 1600 and 720; δ_{H} (CDCl₃) 6.3 (1 H, dd, *J* 12.3 and 8, ³*J*_{Sn–Htrans} 154.6), 5.7 (1 H, d, *J* 12.3, ²*J*_{Sn–Hgem} 58.7), 2.2 (4 H, m) and 2.05–0.7 (32 H, m); δ_{C} (CDCl₃) 209, 150.5, 128, 48, 47, 40.5, 31.5, 29, 27, 25, 13 and 10; *m/z* 415 (10%, M⁺), 357 (99, M – Bu) and 291 (100) (Found: C, 58.3; H, 9.35. C₂₀H₃₈OSn requires C, 58.1; H, 9.3%).

Methyl(Z)-3-methyl-5-tributylstannylpent-4-enoate **27** (57%). *R_f* (hexane–EtOAc, 20:1) 0.28; ν_{\max} (film)/cm⁻¹ 1730, 1210 and 1150; δ_{H} (CDCl₃) 6.3 (1 H, dd, *J* 12.4 and 9, ³*J*_{Sn–Htrans} 133.3), 5.75 (1 H, d, *J* 12.4, ²*J*_{Sn–Hgem} 69.3), 3.7 (3 H, s), 2.7–2.2 (3 H, m) and 1.7–0.7 (30 H, m); δ_{C} (CDCl₃) 172, 152, 128, 51, 41.5, 38.5, 29, 27, 21, 13.5 and 10; *m/z* 419 (37%, M⁺ + 1), 361 (41%, M – Bu), 291 (7) and 235 (28) (Found: C, 54.9; H, 9.35. C₁₉H₃₈O₂Sn requires C, 54.7; H, 9.2%).

(Z)-3-(2-Phenyl-1-tributylstannylethenyl)cyclohexanone **32** (70%). *R_f* (hexane–EtOAc, 11:1) 0.43; ν_{\max} (film)/cm⁻¹ 1715 and 1580; δ_{H} (CDCl₃) 7.4–7.0 (5 H, m), 5.7 (1 H, s, ²*J*_{Sn–Hgem} 66) and

2.8–0.8 (36 H, m); $\delta_c(\text{CDCl}_3)$ 210, 161, 143, 130, 128, 127.5, 126.5, 50, 47, 41, 31, 29, 27, 25.5, 13.5 and 10; m/z 433 (92%, M – Bu), 376 (1) and 291 (1) (Found: C, 64.1; H, 8.75. $\text{C}_{26}\text{H}_{42}\text{OSn}$ requires C, 63.8; H, 8.65%).

Reaction of the Cuprate Intermediates with Tributyltin Chloride and Trimethylsilyl Chloride.—Tributyltin chloride (2.5 mmol) or trimethylsilyl chloride (2.5 mmol) was added to the stannylcupration mixture (2 mmol) at -78°C and 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 the following vinylstannanes.

(Z)-1-Tributylstannyl-2-trimethylsilylethylene 19 (85%). R_f (hexane) 0.79; $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1650, 1250, 860 and 690; $\delta_H(\text{CDCl}_3)$ 7.15 (1 H, d, J 12), 6.95 (1 H, d, J 12), 1.6–0.7 (27 H, m) and 0.15 (9 H, s); $\delta_c(\text{CDCl}_3)$ 154, 151, 29, 27, 14, 9 and -0.5 ; m/z 333 (80, M – Bu), 277 (42) and 235 (8) (Found: C, 52.3; H, 9.65. C_{17}SiSn requires C, 52.45; H, 9.8%).

(Z)-1,2-Bis(tributylstannyl)ethylene 20 (98%). R_f (hexane) 0.7; $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 1650 and 685; $\delta_H(\text{CDCl}_3)$ 7.3 (2 H, s) and 1.7–0.7 (54 H, m); $\delta_c(\text{CDCl}_3)$ 154, 29, 27, 13.5 and 9; m/z 608 (15%, M^+) and 291 (100) (Found: C, 51.65; H, 9.4. $\text{C}_{26}\text{H}_{56}\text{Sn}_2$ requires C, 51.5; H, 9.3%).

Synthesis of β -Ethyne Ketones and β -Ethyne Esters.—A solution of the vinylstannanes **24**, **27** or **32** (0.5 mmol) in dry acetonitrile (5 cm^3) was treated with lead tetraacetate (0.232 g, 0.52 mmol) at room temperature. The reaction mixture became homogeneous after being stirred for 3 min and then began to form a brown precipitate. After the reaction mixture had been stirred at room temperature for 24 h TLC analysis (hexane–EtOAc, 10:1) showed the absence of starting material. The mixture was filtered and concentrated under reduced pressure, and the residue chromatographed to give the following ketones.

3-Ethyne cyclohexanone 34 (90%).³¹ R_f [hexane–ACOEt (10:1)] 0.2; $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 3300, 2110 and 1715; $\delta_H(\text{CDCl}_3)$ 2.85 (1 H, m), 2.6–2.25 (4 H, m), 2.2 (1 H, d, J 3), 2.1–1.7 (4 H, m); $\delta_c(\text{CDCl}_3)$ 209, 85, 70.5, 47, 41, 31, 30 and 24; m/z 122 (100%, M^+).

Methyl 3-methylpent-5-ynoate 35 (85%). $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 3300, 2950, 2920, 2100, 1715, 1730, 1450 and 660; $\delta_H(\text{CDCl}_3)$ 3.70 (3 H, s) and 2.93 (1 H, m), 2.48 (2 H, dd, J 3.6 and 4.75), 2.07 (1 H, d, J 2.3) and 1.24 (3 H, d, J 6.7); m/z 127 (100%, $\text{M} + 1$) (Found: C, 66.5; H, 7.9. $\text{C}_7\text{H}_{10}\text{O}_2$ requires C, 66.6; H, 8.0%).

3-(2-Phenylethynyl)cyclohexanone 36 (25%). R_f (hexane–EtOAc, 10:1) 0.3; $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 2240, 2210 and 1710; $\delta_H(\text{CDCl}_3)$ 7.4–7.2 (5 H, m), 3.3–3.0 (1 H, m) and 2.75–1.7 (8 H, m); $\delta_c(\text{CDCl}_3)$ 205, 138, 129.5, 30.5, 29, 27, 22, 21, 17, 13.5 and 10; m/z 199 (100%, $\text{M}^+ + 1$), 157 (48) and 115 (5) (Found: C, 85.05; H, 7.25. $\text{C}_{26}\text{H}_{42}\text{OSn}$ requires C, 84.8; H, 7.1%) and **3-(1-phenylethenyl)cyclohexanone 37** (35%). R_f (hexane–EtOAc, 10:1) 0.2; $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 1715; $\delta_H(\text{CDCl}_3)$ 7.3 (5 H, s), 5.25 (1 H, br s), 5.05 (1 H, br s), 3.1–2.8 (1 H, m) and 2.6–1.5 (8 H, m); m/z 201 (100%, $\text{M}^+ + 1$), 183 (28), 125 (9) and 97 (84).

Palladium-catalysed Coupling Reactions of 27 with Vinyl and Allyl Halides.—The allyl or vinyl halide⁸ (0.23 mmol) was added to palladium chloride–acetonitrile complex (1 mg, 2 mol %)³² in DMF (1 cm^3), followed by the organotin reagent **27** (0.23 mmol) and of (*E*)-1-iodohexene³³ or allyl bromide (0.23 mmol). The mixture was stirred at 20°C for 4 days or at 80°C for 20 h, respectively. The reactions were monitored by TLC analysis until the starting materials were consumed. Aqueous ammonium hydroxide (10%; 1 cm^3) was added to the mixture which was then stirred for several minutes. The product was extracted with pentane and the extract washed with water, dried (MgSO_4) and concentrated under reduced pressure; the residue was chromatographed to give the following esters.

Methyl (E,E)-3-methylundeca-4,6-dienoate 38 (76%); $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 3020, 2940, 2900, 2850, 1735, 1545, 1010, 980 and 950; $\delta_H(\text{CDCl}_3)$ 6.4–5.0 (4 H, m), 3.64 (3 H, s), 3.15 (1 H, m), 2.28 (2 H, d, J 7.2), 2.07 (2 H, br q, J 6.8) and 1.35 (4 H, m), 1.03 (3 H, d, J 6.6) and 0.90 (3 H, t, J 7.5); m/z 210 (33%, M^+), 179 (7, M – OMe) 168 (40), 136 (30), 107 (100) and 93 (90) (Found: C, 74.4; H, 10.65. $\text{C}_{13}\text{H}_{22}\text{O}_2$ requires C, 74.2; H, 10.5%).

Methyl (Z)-3-methylocta-4,7-dienoate 39 (65%); $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 3080, 3010, 2960, 1735, 1635, 1170, 1005, 910 and 750; $\delta_H(\text{CDCl}_3)$ 6.10–4.90 (5 H, m), 3.64 (3 H, s), 3.0 (1 H, m), 2.82 (2 H, t, J 6.6 with fine couplings), 2.17 (2 H, d, J 7.2) and 1.0 (3 H, d, J 6.6); $\delta_c(\text{CDCl}_3)$ 172.85, 136.9, 134.9, 127.6, 114.75, 51.6, 41.85, 31.6, 29 and 20.85; m/z 168 (5%, M^+), 153 (2, M – Me) 127 (11), 108 (18), 95 (40) and 79 (100) (Found: C, 71.7; H, 9.7. $\text{C}_{10}\text{H}_{16}\text{O}_2$ requires C, 71.4; H, 9.6%).

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