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-copper[1] or cuprate[2] 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
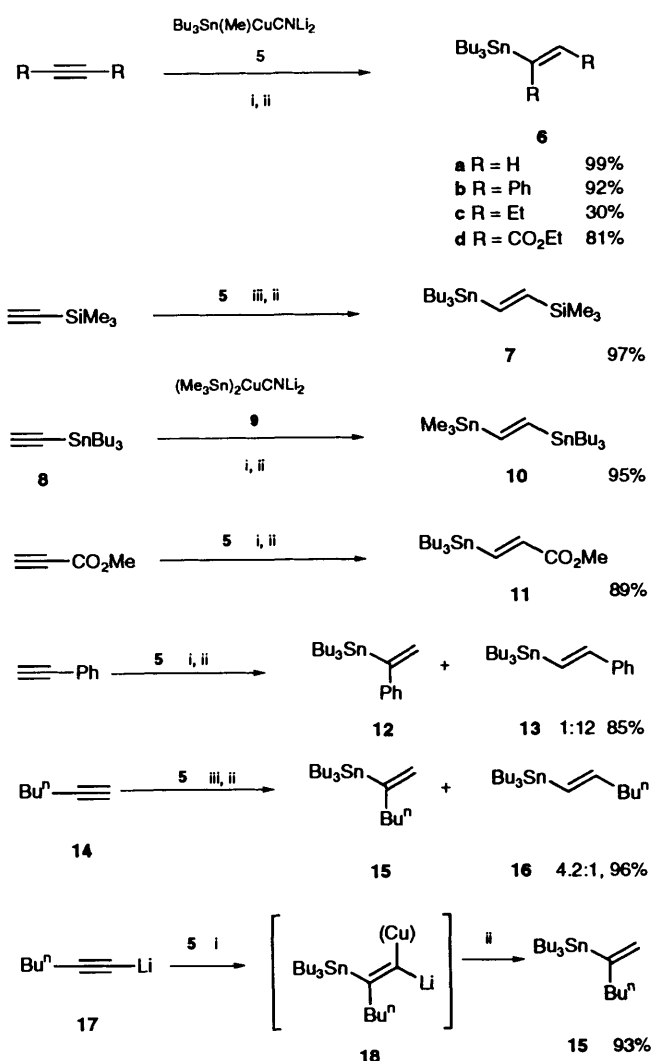

Scheme 1
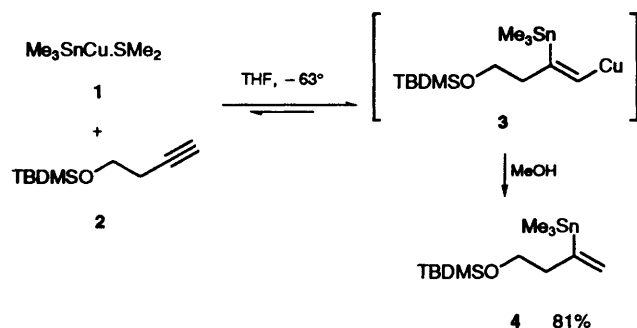
otherwise powerful reactions has been the difficulty in persuading the vinyl-copper or vinyl-cuprate intermediate to react with anything more interesting than a proton. The problem appears to be that the stannyl-cupration step **1** + **2**——→**3**, although well to the right at equilibrium, is easily 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 communication[12] 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-silylvinylstannes **7** and **19**,

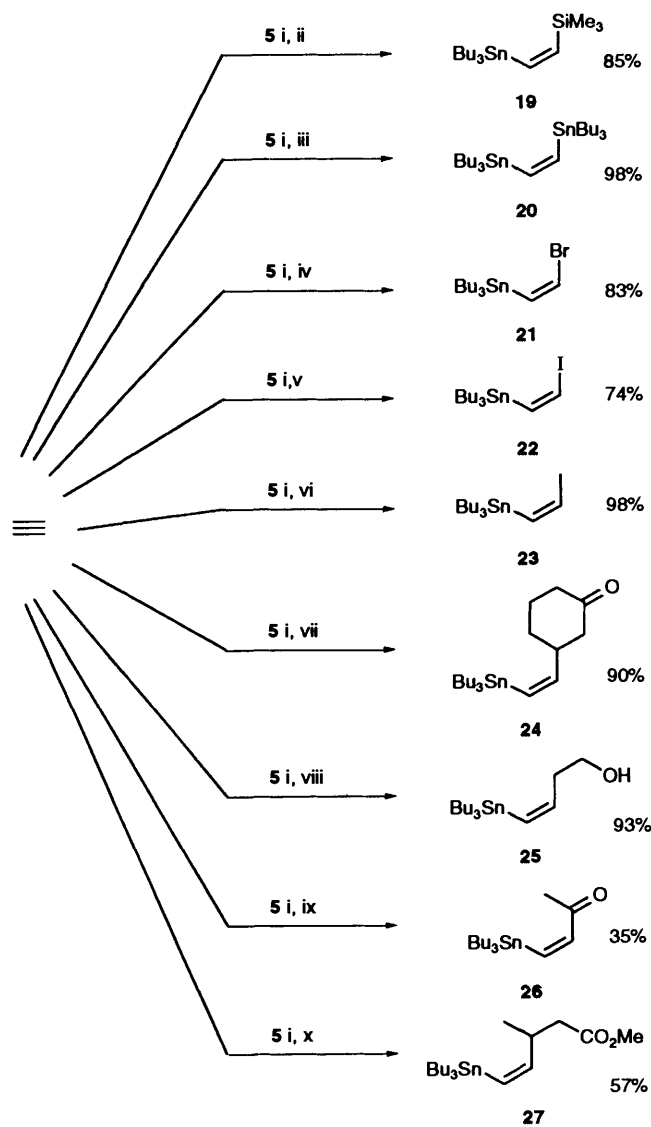**Scheme 2** *Reagents and conditions:* i, −78 ⟶ 0 °C; ii, NH₄Cl; iii, −78 °C

and (*E*)- and (*Z*)-vinylbisstannanes **10** and **20**. However, since our preliminary communication, we have found that we are not intirely successful with attaching all the carbon electrophiles that worked with acetylene itself to the intermediate derived from substituted acetylenes. Thus, stannylcupration of either hex-1-yne or hex-3-yne, followed by treatment with cyclohexenone, 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, Parsons[15] 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 bistributylstannylcuprate 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 methyllithium.

In view of a report[18] that stannylcupration 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
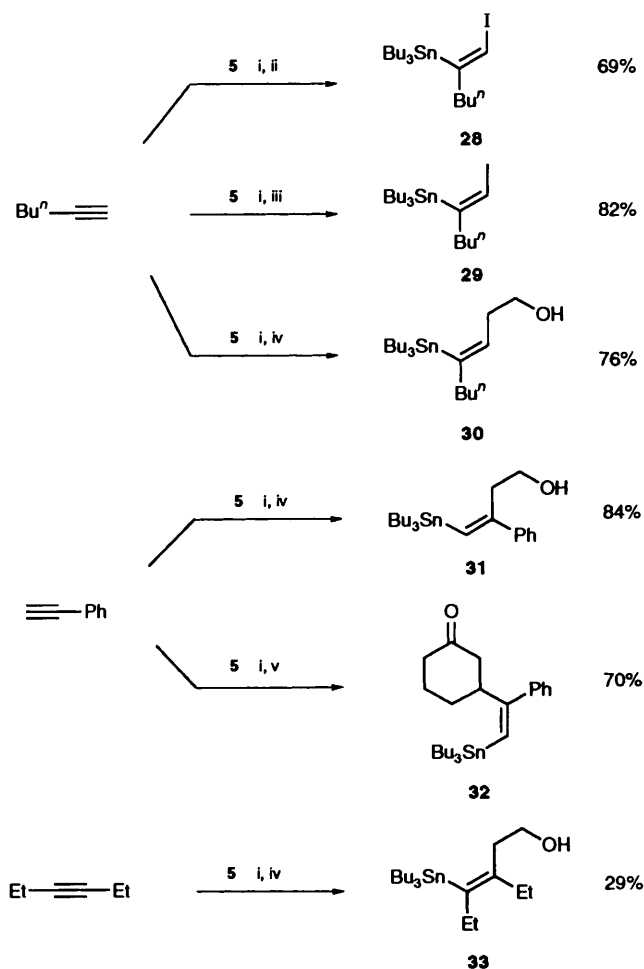

Scheme 3 *Reagents and conditions:* i, THF, −78 °C; ii, Me₃SiCl, −78 ⟶ 0 °C; iii, Bu₃SnCl, −78° ⟶ 0 °C; iv, Br₂, −78 ⟶ 0 °C, v, I₂, −78 ⟶ 0 °C; vi, MeI, −78 ⟶ 0 °C; vii, cyclohexenone, −78 ⟶ 0 °C; viii, ethylene oxide, −78 ⟶ 0 °C; ix, AcCl, −78 ⟶ 0 °C; x, MeCH=CHCO₂Me. −78 ⟶ 0 °C

the electrophile—the temperature in the flask did not rise above −67 °C. We conclude that, in our conditions at least, the stannylcupration must have taken place below this temperature, since the stannylcuprate, 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 αβ-unsaturated ketone or an αβ-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 ⟶ 0 °C; iii, MeI, −78 ⟶ 0 °C; iv, ethylene oxide, −78 ⟶ 0 °C; v, cyclohexenone, −78 ⟶ 0 °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 reactions[23] 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 buyllithium on the ketone or the primary toluene-*p*-sulfonate group, but the vinyllithium 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. ^{1}H 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. Alkylithium reagents were purchased from Aldrich, and copper(I) cyanide from Fluka. The latter was dried in an oven
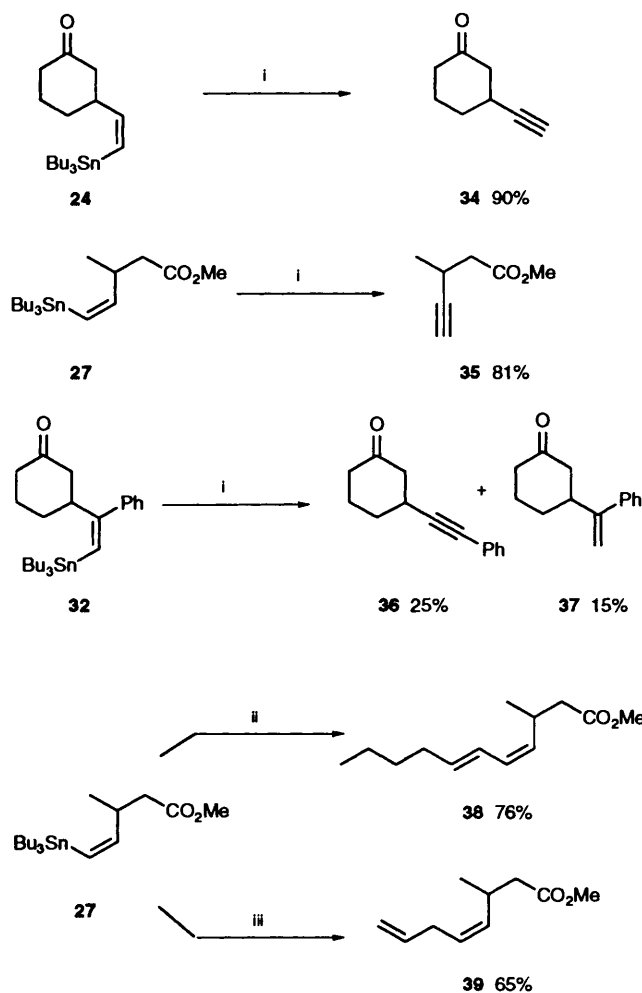
Scheme 5 *Reagents:* i, Pb(OAc)$_4$, MeCN, 20 °C, 72–120 h; ii, *E*-1-iodohexene, PdCl$_2$(MeCN)$_2$ cat., DMF, 20 °C, 96 h; iii, allyl bromide, PdCl$_2$(MeCN)$_2$ cat., DMF, 80 °C, 20 h

overnight at 120 °C. We bought all the acetylenes (Aldrich). Trimethylstannyllithium and tributylstannyllithium were prepared by the established procedures.[25,26]

Lithium Bis(trimethylstannyl)cuprate.—A solution of trimethylstannyllithium (12 mmol) prepared in THF by the method of Tamborski[25] 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 tributylstannyllithium (6 mmol), prepared in THF by the method of Still[26] (10 cm^3), and methyllithium (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 stanylcuprate 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 ($MgSO_4$) 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(CDCl$_3$) 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(CDCl$_3$) 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(CDCl$_3$) 6.8 (1 H, s, $^3J_{Sn-Hcis}$ 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(CDCl$_3$) 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. $C_{20}H_{38}O_4Sn$ 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(CDCl$_3$) 7.05 (1 H, d, J 22.7, $^2J_{Sn-Hgem}$ 104), 6.6 (1 H, d, J 22.7, $^3J_{Sn-Hcis}$ 101), 1.6–0.7 (27 H, m) and 0.1 (9 H, s); δ_C(CDCl$_3$) 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. $C_{17}H_{34}SnSi$ 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(CDCl$_3$) 7.3 (2 H, s), 1.8–0.7 (27 H, m) and 0.15 (9 H, s); δ_C(CDCl$_3$) 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(CDCl$_3$) 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(CDCl$_3$) 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. $C_{15}H_{32}Sn$ requires C, 54.4; H, 9.7%).

(Z)-3-*Tributylstannylhept*-2-*ene* 29 (82%). R_f (hexane) 0.64; δ_H(CDCl$_3$) 6.1 (1 H, qt, J 6.6 and 1, $^3J_{Sn-Htrans}$ 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(CDCl$_3$) 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. $C_{19}H_{40}Sn$ 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–Et$_2$O, 20:1) 0.3; ν_{max}(film)/cm^{-1}(CCl$_4$) 1675, 1650 and 685; δ_H(CCl$_4$) 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(CDCl$_3$) 7.15 (1 H, d, J 8, $^3J_{Sn-Htrans}$ 99), 6.9 (1 H, d, J 8, $^2J_{Sn-Hgem}$ 56) and 1.6–0.7 (27 H, m); δ_C(CDCl$_3$) 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(CDCl$_3$) 7.65 (1 H, d, J 8), 7.35 (1 H, d, J 8) and 1.7–0.7 (27 H, m); δ_C(CDCl$_3$) 148.98, 29, 27, 13.5 and 10; m/z 317 (0.5%, M − I) (Found: C, 38.3; H, 6.75. $C_{14}H_{29}ISn$ requires C, 38.0; H, 6.6%).

(Z)-1-*Iodo*-2-*tributylstannylhex*-1-*ene* 28 (69%). R_f (hexane) 0.63; δ_H(CDCl$_3$) 6.75 (1 H, t, J 1), 2.2 (2 H, br t, J 7, $^3J_{Sn-Htrans}$ 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 wih 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(CDCl$_3$) 6.55 (1 H, dt, J 12 and 6.7, $^3J_{Sn-Htrans}$ 136), 6.9 (1 H, dt, J 12 and 1, $^2J_{Sn-Hgem}$ 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(CDCl$_3$) 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. $C_{16}H_{34}OSn$ requires C, 53.2; H, 9.5%).

(Z)-4-*Tributylstannyloct*-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(CDCl$_3$) 6.0 (1 H, tt, J 7.2 and 1.3, $^3J_{Sn-Htrans}$ 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(CDCl$_3$) 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. $C_{20}H_{42}OSn$ 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(CDCl$_3$), 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(CDCl$_3$) 7.45–7.2 (5 H, m), 6.25 (1 H, s, $^2J_{Sn-Hgem}$ 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(CDCl$_3$) 154, 143.5, 132, 128, 127, 126, 61.5, 42, 29, 27, 14.5 and 10.5; m/z 351 (11%, M − Bu-CH$_2$OH), 291 (45), 235 (87) and 177 (100) (Found: C, 60.65; H, 9.1. $C_{22}H_{38}OSn$ requires C, 60.4; H, 8.8%).

Reaction of the Cuprate Intermediate with α,β-*Unsaturated Ketones and Esters.*—A solution of cyclohex-2-enone (2.5 mmol) or methyl crotonate (3 mmol) in THF (5 cm^3) 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(CDCl$_3$) 6.3 (1 H, dd, J 12.3 and 8, $^3J_{Sn-Htrans}$ 154.6), 5.7 (1 H, d, J 12.3, $^2J_{Sn-Hgem}$ 58.7), 2.2 (4 H, m) and 2.05–0.7 (32 H, m); δ_C(CDCl$_3$) 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. $C_{20}H_{38}OSn$ 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(CDCl$_3$) 6.3 (1 H, dd, J 12.4 and 9, $^3J_{Sn-Htrans}$ 133.3), 5.75 (1 H, d, J 12.4, $^2J_{Sn-Hgem}$ 69.3), 3.7 (3 H, s), 2.7–2.2 (3 H, m) and 1.7–0.7 (30 H, m); δ_C(CDCl$_3$) 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. $C_{19}H_{38}O_2Sn$ 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(CDCl$_3$) 7.4–7.0 (5 H, m), 5.7 (1 H, s, $^2J_{Sn-Hgem}$ 66) and

2.8–0.8 (36 H, m); δ_C(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. C$_{26}$H$_{42}$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; ν_{max}(film)/cm^{-1} 1650, 1250, 860 and 690; δ_H(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); δ_C(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; ν_{max}(film)/cm^{-1} 1650 and 685; δ_H(CDCl$_3$) 7.3 (2 H, s) and 1.7–0.7 (54 H, m); δ_C(CDCl$_3$) 154, 29, 27, 13.5 and 9; m/z 608 (15%, M$^+$) and 291 (100) (Found: C, 51.65; H, 9.4. C$_{26}$H$_{56}$Sn$_2$ requires C, 51.5; H, 9.3%).

Synthesis of β-Ethynyl Ketones and β-Ethynyl Esters.—A solution of the vinylstannes **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-*Ethynylcyclohexanone* **34** (90%).[31] R_f [hexane–ACOEt (10:1)] 0.2; ν_{max}(CCl$_4$)/cm^{-1} 3300, 2110 and 1715; δ_H(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); δ_C(CDCl$_3$) 209, 85, 70.5, 47, 41, 31, 30 and 24; m/z 122 (100%, M$^+$).

Methyl 3-*methylpent-5-ynoate* **35** (85%). ν_{max}(CCl$_4$)/cm^{-1} 3300, 2950, 2920, 2100, 1715, 1730, 1450 and 660; δ_H(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%, M + 1) (Found: C, 66.5; H, 7.9. C$_7$H$_{10}$O$_2$ requires C, 66.6; H, 8.0%).

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

Palladium-catalysed Coupling Reactions of **27** *with Vinyl and Allyl Halides.*—The allyl or vinyl halide[8] (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-iodohexene[33] 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%); ν_{max}-(CCl$_4$)/cm^{-1} 3020, 2940, 2900, 2850, 1735, 1545, 1010, 980 and 950; δ_H(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. C$_{13}$H$_{22}$O$_2$ requires C, 74.2; H, 10.5%).

Methyl (Z)-3-*methylocta*-4,7-*dienoate* **39** (65%); ν_{max}(CCl$_4$)/cm^{-1} 3080, 3010, 2960, 1735, 1635, 1170, 1005, 910 and 750; δ_H(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); δ_C(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. C$_{10}$H$_{16}$O$_2$ requires C, 71.4; H, 9.6%).

Acknowledgements

References

1 E. Piers, J. M. Chong and H. E. Morton, *Tetrahedron Lett.*, 1981, **22**, 4905 and *Tetrahedron*, 1989, **45**, 363.
2 E. Piers and R. D. Tillyer, *J. Org. Chem.*, 1988, **53**, 5366.
3 E. Piers and J. M. Chong, *Can. J. Chem.*, 1988, **66**, 1425.
4 B. H. Lipshutz, S. Sharma and D. C. Reuter, *Tetrahedron Lett.*, 1990, **31**, 7253; R. Aksela and A. C. Oehlschlager, *Tetrahedron*, 1991, **47**, 1163.
5 S. D. Cox and F. Wudl, *Organometallics*, 1983, **2**, 184; M. W. Hutzinger, R. D. Singer and A. C. Oehlschlager, *J. Am. Chem. Soc.*, 1990, **112**, 9397.
6 H. Westmijze, K. Ruitenberg, J. Meyer and P. Vermeer, *Tetrahedron Lett.*, 1982, **23**, 2797.
7 P. A. Magriotis, M. E. Scott and K. D. Kim, *Tetrahedron Lett.*, 1991, **32**, 6085.
8 K. Nozaki, K. Wakamatsu, T. Nonaka, W. Tückmantel, K. Oshima and K. Utimoto, *Tetrahedron Lett.*, 1986, **27**, 2007; J. Hibino, S. Matsubara, Y. Morizawa, K. Oshima and H. Nozaki, *Tetrahedron Lett.*, 1984, **25**, 2151; T. Nonaka, Y. Okuda, S. Matsubara, K. Oshima, K. Utimoto and H. Nozaki, *J. Org. Chem.*, 1986, **51**, 4716; S. Sharma and A. C. Oehlschlager, *Tetrahedron Lett.*, 1986, **27**, 6161; *Tetrahedron Lett.*, 1988, **29**, 261; *J. Org. Chem.*, 1989, **54**, 5064; see also R. Aksela and A. C. Oehlschlager, *Tetrahedron*, 1991, **47**, 1163.
9 S. Matsubara, J. Hibino, Y. Morizawa, K. Oshima and H. Nozaki, *J. Organomet. Chem.*, 1985, **285**, 163.
10 G. Zweifel and W. Leong, *J. Am. Chem. Soc.*, 1987, **109**, 6409; see also T. N. Mitchell, A. Amamria, H. Killing and D. Rutschow, *J. Organomet. Chem.*, 1986, **304**, 257; E. Piers and R. T. Skerlj, *J. Chem. Soc., Chem. Commun.*, 1987, 1025.
11 J. P. Marino and J. K. Long, *J. Am. Chem. Soc.*, 1988, **110**, 7916.
12 A. Barbero, P. Cuadrado, I. Fleming, A. M. González and F. J. Pulido, *J. Chem. Soc., Chem. Commun.*, 1992, 351.
13 I. Fleming, M. Rowley, P. Cuadrado, A. M. González-Nogal and F. J. Pulido, *Tetrahedron*, 1989, **45**, 413; A. Barbero, P. Cuadrado, I. Fleming, A. M. González and F. J. Pulido, *J. Chem. Soc., Chem. Commun.*, 1990, 1030.
14 S. Sharma and A. C. Oehlschlager, *J. Org. Chem.*, 1991, **56**, 770.
15 I. Beaudet, J.-L. Parrain and J.-P. Quintard, *Tetrahedron Lett.*, 1991, **32**, 6333; I. Marek, A. Alexakis and J.-F. Normant, *Tetrahedron Lett.*, 1991, **32**, 6337; K. I. Booker-Milburn, G. D. Heffernan and P. J. Parsons, *J. Chem. Soc., Chem. Commun.*, 1992, 350.
16 J. P. Marino, M. V. M. Emonds, P. J. Stengel, A. R. M. Oliveira, F. Simonelli and J. T. B. Ferreira, *Tetrahedron Lett.*, 1992, **33**, 49.
17 E. Piers and V. Karunaratne, *J. Org. Chem.*, 1983, **48**, 1774, *J. Chem. Soc., Chem. Commun.*, 1983, 935 and 1984, 959, and *Can. J. Chem.*, 1984, **62**, 629; E. Piers and B. W. A. Yeung, *J. Org. Chem.*, 1984, **49**, 4567; E. Piers, R. Friesen and B. A. Keay, *J. Chem. Soc., Chem. Commun.*, 1985, 809; E. Piers and R. D. Tillyer, *J. Chem. Soc., Perkin Trans. 1*, 1989, 2124; E. Piers and A. V. Gavai, *J. Org. Chem.*, 1990, **55**, 2374 and 2380; I. Fleming and M. Taddei, *Synthesis*, 1985, 898 and 899; M. Taddei and A. Mann, *Tetrahedron Lett.*, 1986, **27**, 2913.
18 R. D. Singer, M. W. Hutzinger and A. C. Oehlschlager, *J. Org. Chem.*, 1991, **56**, 4933.

19 E. J. Corey and R. H. Wollenberg, *J. Am. Chem. Soc.*, 1974, **96**, 5581; M. Shibasaki, Y. Torizawa and S. Ikegami, *Tetrahedron Lett.*, 1982, **23**, 4607.

20 M. G. Moloney and J. T. Pinhey, *J. Chem. Soc., Perkin Trans. 1*, 1988, 2847; M. G. Moloney, J. T. Pinhey and M. J. Stoermer, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2645.

21 J. T. Pinhey and M. J. Stoermer, *J. Chem. Soc., Perkin Trans. 1*, 1991, 2455.

22 I. E. Marko and F. Rebierre, *Tetrahedron Lett.*, 1992, **33**, 1763.

23 J. K. Stille and B. L. Groh, *J. Am. Chem. Soc.*, 1987, **109**, 813.

24 A. Barbero, P. Cuadrado, A. M. González, F. J. Pulido, R. Rubio and I. Fleming, *Tetrahedron Lett.*, 1992, **33**, 5841.

25 C. Tamborski, F. E. Ford and E. J. Sotoski, *J. Org. Chem.*, 1963, **28**, 237.

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

27 D. Seyferth and F. G. A. Stone, *J. Am. Chem. Soc.*, 1957, **79**, 515.

28 A. Barbero, P. Cuadrado, I. Fleming, A. M. González and F. J. Pulido, *J. Chem. Res.*, 1990, (*S*), 291.

29 D. E. Seitz and S. H. Lee, *Tetrahedron Lett.*, 1981, **22**, 4909.

30 K. Ritter, *Synthesis*, 1989, 218.

31 E. J. Corey and R. H. Wollenberg, *J. Am. Chem. Soc.*, 1974, **96**, 5582.

32 J. R. Doyle, P. E. Slade and H. B. Jonassen, *Inorg. Synth.*, 1960, **6**, 218.

33 G. Zweifel and C. C. Whitney, *J. Am. Chem. Soc.*, 1967, **89**, 2753.