in water–ethanol (10:1) followed by rhodium(I)-catalyzed[4] coupling to 1 produced 13[12e] in modest yield (30%). The stereochemical integrity of the trisubstituted double bond in the both 12 and 13 is preserved, as evidenced by the ^{13}C NMR spectrum.[12d,12e]

In summary, an enantioselective synthesis of a lophotoxin intermediate has been described. The problems of conducting the carbometalation reaction on oxygenated substrates have been identified, and a general solution has been developed. Work in progress has indicated that substituted furyl nucleophiles undergo rhodium(I)-catalyzed coupling to 1 without interference by the carboxylate on the furan or by the lactone carbonyl group.[17]

Acknowledgment is made to the National Science Foundation (CHE-84-03495) for support of this work. NSF Grant CHE-81-00240 supported the purchase of the 300-MHz NMR spectrometer.

Supplementary Material Available: Experimental details for the coupling reactions leading to 12 and 13 (1 page). Ordering information is given on any current masthead page.

---

(16) Gilman, H.; Burtner, R. R. *J. Am. Chem. Soc.* **1949**, *71*, 1213–1215.

(17) A reviewer suggested that the cross-coupling might be performed directly on the vinylzirconium intermediate and a furyl halide. This approach was examined in a model study. 4-[(*tert*-Butyldimethylsilyl)-oxy]-dec-1-yne was subjected to the carbometalation reaction followed by Pd(0)- or Ni(0)-catalyzed coupling with iodo- or bromobenzene to give 4-[(*tert*-butyldimethylsilyl)oxy]-2-methyl-1-phenyl-dec-1-ene and 4-[(*tert*-butyldimethylsilyl)oxy]-2-methyldec-1-ene in 20% and 30% yield, respectively. The hydrocarbon which results from adventitious protonation is not recyclable. See: Negishi, E.-i.; Okukado, N.; King, A. O.; Horn, D. E. V.; Spiegel, B. I. *J. Am. Chem. Soc.* **1978**, *100*, 2254–2256.

Marcus A. Tius,* Sanjay Trehan
Department of Chemistry
University of Hawaii
Honolulu, Hawaii 96822

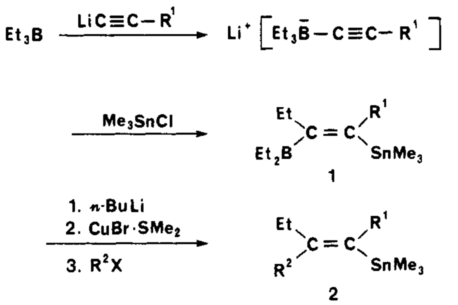
Received October 21, 1985

Regio- and Stereoselective Synthesis of Trisubstituted Vinylstannanes

Summary: The selective transformation of the alkenylborane moiety of 1 to alkenylcopper followed by coupling with alkyl halides afforded trisubstituted vinylstannanes with high regio- and stereoselectivity.

Sir: The trialkyltin chloride induced intramolecular transfer reaction of lithium 1-alkynyltrialkylborates was found to be stereoselective with the resulting olefinic intermediate 1 having the migrating alkyl group trans to the trialkyltin group[1–3] (Scheme I). Subsequent protonolysis, oxidation, or iodination afforded the corresponding (*Z*)-alkenes, ketones, or alkynes, respectively.[3] We have adopted these reactions for the synthesis of three straight-chain insect sex pheromones.[3] Interestingly, reactions of 1 with alkynylstannanes have also been observed.[2b] However, the olefinic intermediate 1 constructed with both boron and tin substituents has not been fully explored for other synthetic applications. We believe that this bifunctional intermediate could provide many synthetic opportunities and wish to report our recent findings in this area.

Scheme I



Scheme II

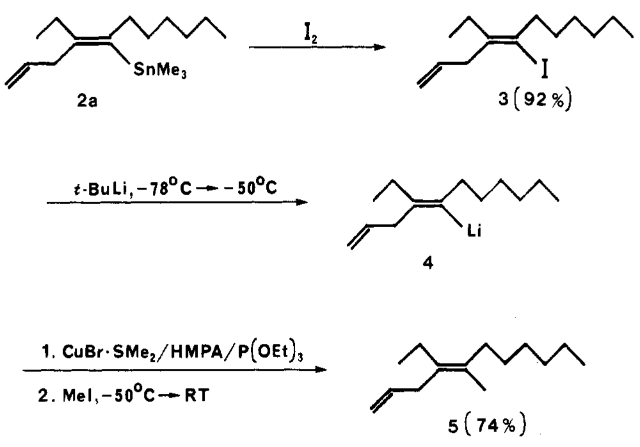


Table I. Preparation of Trisubstituted Vinylstannanes

vinylstannane	R^1	R^2 [a]	isolated yield,[b] %
2a	n-C$_6$H$_{13}$	H$_2$C=CHCH$_2$	80
2b	n-C$_6$H$_{13}$	CH$_3$	70
2c	CH$_2$CH$_2$CH$_2$Cl	H$_2$C=CHCH$_2$	75
2d	C$_6$H$_5$	H$_2$C=CHCH$_2$	58
2e	CH$_2$SiMe$_3$	H$_2$C=CHCH$_2$	61

[a] R^{2}X = allyl bromide or methyl iodide. [b] The isolated products have been fully characterized by IR and ^{1}H and ^{13}C NMR (JEOL GX-270, 270 MHz in ^{1}H) spectroscopy and satisfactory carbon (±0.22%) and hydrogen (±0.21%) composition determined by combustion analysis.

It has been shown that both alkenylboranes and alkenylstannanes can be converted to alkenylcopper derivatives by first treating with an alkyllithium reagent followed by adding the resulting solution to a copper(I) species.[4,5] We found that the dialkylborane moiety of 1 could be selectively reacted with an alkyllithium reagent without interference from the adjacent trimethyltin group.[6] The resulting alkenylcopper derivative was then coupled with allyl bromide or methyl iodide to form the corresponding trisubstituted vinylstannane 2 (Scheme I).

The products summarized in Table I were found to contain only one stereoisomer (>98%) as indicated by the ^{1}H and ^{13}C NMR spectra (270 MHz in ^{1}H). Protonolysis of the trisubstituted vinyltin **2b** with 4 N hydrochloric acid produced (*Z*)-3-methyl-3-decene. We have also prepared (*E*)-3-methyl-3-decene by Normant's procedure[7] and have

---

(1) Hooz, J.; Mortimer, R. *Tetrahedron Lett.* **1976**, 805–808.

(2) (a) Zweifel, G.; Backlund, S. J. *J. Organomet. Chem.* **1978**, *156*, 159–170. (b) Wrackmeyer, B.; Bihlmayer, C.; Schilling, M. *Chem. Ber.* **1983**, *116*, 3182–3191.

(3) Wang, K. K.; Chu, K.-H. *J. Org. Chem.* **1984**, *49*, 5175–5178.

(4) (a) Yamamoto, Y.; Yatagai, H.; Maruyama, K.; Sonoda, A.; Murahashi, S.-I. *J. Am. Chem. Soc.* **1977**, *99*, 5652–5656. (b) Campbell, J. B., Jr.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 549–550.

(5) Piers, E.; Yeung, B. W. A. *J. Org. Chem.* **1984**, *49*, 4567–4569.

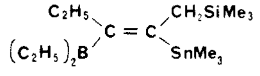
(6) The selective reaction of the alkenylborane moiety has also been observed previously with the less nucleophilic (thiomethoxymethyl)lithium.[1]

0022-3263/86/1951-0767$01.50/0 © 1986 American Chemical Society

compared the ^{1}H and ^{13}C NMR spectra of these two isomers. The *Z* isomer was free from contamination of the *E* isomer. The reaction sequence outlined in Scheme I thus provides a highly regio- and stereoselective pathway to trisubstituted vinylstannanes. Despite increasing synthetic applications of vinylstannanes[8] and the development of many methods toward disubstituted species,[9] a general method for the trisubstituted compounds from simple nonconjugated acetylenes has not been reported previously.

We have converted **2a** to the tetrasubstituted olefin **5** by the procedure outlined in Scheme II. The vinyllithium **4** was obtained by first treating **2a** with iodine[10] followed by reacting the isolated vinyl iodide **3** with 2.5 equiv of *tert*-butyllithium.[11] Attempts to convert **2a** to **4** by transmetalation with *n*-butyllithium failed. This is perhaps not surprising, because other *cis*-vinylstannanes have been found to be very unreactive toward *n*-butyllithium even at room temperature.[12] Direct treatment of **4** with methyl iodide resulted in the formation of **3** again, presumably through metal–halogen exchange. This problem was circumvented by first converting **4** to the corresponding vinylcopper species followed by coupling with methyl iodide to afford **5**. Its structural isomer, (*E*)-3-methyl-4-(2-propenyl)-3-decene (**6**), was also obtained by starting from **2b** followed by treating with allyl bromide (overall yield 48%). The ^{13}C NMR spectra showed that they were free from the presence of each other.[13] The ability to vary all four substituents on the double bond makes the procedure outlined in Schemes I and II a versatile method for preparing a variety of tetrasubstituted olefins.

It is also worth noting that compounds similar to **2c** have been utilized as donor–acceptor conjunctive reagents for the construction of carbocyclic structures.[5] The intermediate **1e** bearing boron, tin, and silicon functionalities is especially of interest to us. It has three reactive sites and their different reactivities could be sequentially exploited. This could allow pulling various fragments together and then transforming them into a complex chemical structure. We are now actively exploring in this direction and the result will be reported later.



1e

The following procedure for the preparation of **2a** is representative. The intermediate **1a** (10 mmol) was prepared as described previously.[1] The reaction flask was cooled to −80 °C and charged with 4.10 mL of *n*-butyllithium (2.44 M in hexane, 10 mmol). After 15 min, the reaction mixture was transferred via cannula to a reaction flask containing 2.06 g (10 mmol) of CuBr·SMe$_2$ in 20 mL of THF maintained at −80 °C.[14] After an additional 1 h of stirring at −80 °C, 2.60 mL of allyl bromide (3.63 g, 30 mmol) was introduced.[16] The reaction mixture was then allowed to warm to room temperature. After the oxidative workup with alkaline hydrogen peroxide, the organic layer was then washed with water, dried over MgSO$_4$, and concentrated. The residue was filtered through a short aluminum oxide (acid washed from Merck) column.[17] Distillation on a short-path distilling head afforded 3.43 g (80% yield) of **2a** as a colorless liquid: bp 66 °C (0.01 torr); IR (neat) 1640 (w), 1605 (w), 1455 (m), 1375 (w), 1190 (w), 990 (m), 910 (s), 760 (s), 710 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 5.72 (ddt, 1 H), 5.02 (dm, 1 H), 4.99 (dm, 1 H), 2.79 (dt, 2 H), 2.22 (t, 2 H), 2.12 (q, 2 H), 1.28 (br, 8 H), 0.96 (t, 3 H), 0.89 (t, 3 H), 0.14 (s, 9 H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 148.00, 139.45, 137.75, 115.51, 43.79, 34.24, 31.98, 30.97, 29.47, 23.39, 22.75, 14.10, 13.86, −7.63. Anal. Calcd for C$_{16}$H$_{32}$Sn: C, 56.01; H, 9.40. Found: C, 56.15; H, 9.40.

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Fund, Administered by the American Chemical Society, for the support of this research. The JEOL GX-270 NMR spectrometer (270 MHz in ^{1}H) used in this research was purchased by funds derived in part from an NSF grant (RII 8011453).

Kai-Hsuan Chu, Kung K. Wang*
Department of Chemistry
West Virginia University
Morgantown, West Virginia 26506

Received December 26, 1985

---

[7] Normant, J. F.; Cahiez, G.; Chuit, C. *J. Organomet. Chem.* **1974**, *77*, 269–279.

[8] Goure, W. F.; Wright, M. E.; Davis, P. D.; Labadie, S. S.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 6417–6422.

[9] (a) Ensley, H. E.; Buescher, R. R.; Lee, K. *J. Org. Chem.* **1982**, *47*, 404–408. (b) Hibino, J.-i.; Matsubara, S.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 2151–2154. (c) Matsubara, S.; Hibino, J.-i.; Morizawa, Y.; Oshima, K.; Nozaki, H. *J. Organomet. Chem.* **1985**, *285*, 163–172. (d) Piers, E.; Chong, J. M. *J. Org. Chem.* **1982**, *47*, 1602–1604. (e) Westmijze, H.; Ruitenberg, K.; Meijer, J.; Vermeer, P. *Tetrahedron Lett.* **1982**, *23*, 2797–2798.

[10] Baekelmans, P.; Gielen, M.; Malfroid, P.; Nasielski, J. *Bull. Soc. Chim. Belg.* **1968**, *77*, 85–97.

[11] Corey, E. J.; Beames, D. J. *J. Am. Chem. Soc.* **1972**, *94*, 7210–7211.

[12] Collins, P. W.; Jung, C. J.; Gasiecki, A.; Rappo, R. *Tetrahedron Lett.* **1978**, 3187–3190.

[13] ^{13}C NMR (67.9 MHz, CDCl$_3$, Me$_4$Si). **5**: δ 136.86, 131.52, 130.10, 114.17, 36.35, 34.24, 31.93, 29.54, 28.77, 24.99, 22.71, 18.03, 14.11, 13.52. **6**: δ 136.86, 131.80, 129.83, 114.16, 36.86, 32.15, 31.92, 29.70, 29.12, 27.21, 22.73, 17.48, 14.11, 13.24.

[14] At higher reaction temperatures, vinylstannanes were produced with lower yields and significant amount of 3-decyne was also isolated. This is presumably due to the elimination of (trimethylstannyl)copper to form 3-decyne at higher temperatures as observed previously.[15]

[15] (a) Cox, S. D.; Wudl, F. *Organometallics* **1983**, *2*, 184–185. (b) Piers, E.; Chong, J. M. *J. Chem. Soc., Chem. Commun.* **1983**, 934–935.

[16] (a) In the case of methyl iodide, 2 equiv of HMPA and 3 equiv of triethyl phosphite were also introduced. The reaction mixture was then allowed to warm to room temperature and stirred for 18 h. (b) The corresponding disubstituted vinylstannane was also obtained by simply introducing methanol at −80 °C (76% yield).

[17] Partial hydrolysis of vinylstannanes was observed with silica gel column.