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PREPARATION OF Z-VINYLSTANNANES *VIA* HYDROZIRCONATION OF STANNYLACETYLENES

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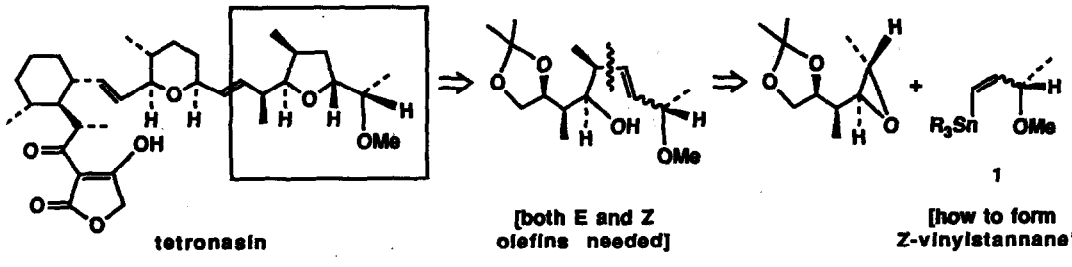
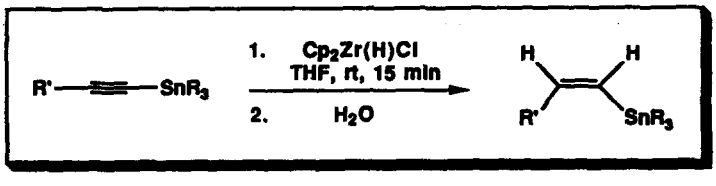
Abstract: *Treatment of tin acetylenes with $Cp_2Zr(H)Cl$ followed by a proton quench affords the corresponding Z-vinylstannanes in high yields.*

In the course of our preparation of the terahydrofuran segment of the antibiotic tetronasin,[1] we required the Z-vinylstannane **1** as a precursor to a higher order cyanocuprate for eventual coupling with an appropriate epoxide.[2] We were quite surprised to find, notwithstanding the explosive growth of organotin chemistry of



late,[3] that these particular tin derivatives are not that readily accessible.[4] Even very recent work on this topic (*i.e.*, vinylstannane chemistry) supports this observation.[5] We now report a simple, efficient procedure for generating vinylstannanes of the Z configuration from readily available acetylenic precursors.[6]



The standard procedure developed involves a hydrozirconation process utilizing THF as solvent rather than the original Schwartz conditions which call for benzene as the reaction medium.[7] These reactions are virtually stereospecific, high yielding, and due to the greater solubility of $Cp_2Zr(H)Cl$ in THF, rapid. A survey of representative examples is given in Table 1. From this sampling the most obvious limitation of the method is related to the propensity of this hydride source to reduce aldehydes and ketones competitively with hydrozirconation.[7,8] Otherwise, the mildness of these conditions tolerate an assortment of desirable functionality.[9]

A typical procedure is given beginning with acetylenic stannane 2 (see Table 1, entry 3). A dry 10 mL round bottom flask purged with and maintained under a blanket of argon, was charged with 40 mg (0.15mmol) of $Cp_2Zr(H)Cl$.[10] To this was added 3 mL of dry THF and 58 mg (0.13 mmol) of 1-tributylstannylbutyn-3-ol benzyl ether. The suspension was stirred for 15 min during which the mixture became a clear yellow solution. It was then diluted with 5mL of pentane and after 10 min of additional stirring, the supernatant was filtered through a short plug of silica gel and concentrated *in vacuo* to afford 53 mg (90%) of Z-tributylstannylbuten-3-ol benzyl ether; IR (neat) cm^{-1} 2900, 1600, 1450, 1360, 910; 1H NMR (300 MHz, $CDCl_3$) δ7.33-7.25(m,5H), 6.55-6.47(dt, J=11,7,1H), 5.92-5.89(d, J=11,1H), 4.50(s, 2H), 3.51-3.46(t, J=7,2H), 2.36-2.33(m,2H), 1.55-0.86(m,27H); MS (m/z, rel int) 395(42), 393(34), 177(29), 175(24), 91(100); HREIMS calcd for $C_{19}H_{31}{}^{120}SnO$ 395.1396; found 395.1433.

Lastly, it should be appreciated that there is a regiochemical issue associated with the addition of $Cp_2Zr(H)Cl$ across unsymmetrical acetylenic stannanes. The long carbon-tin bond (*ca.* 2.2Å),[3a] the sensitivity of the hydrozirconation reaction to steric effects,[7] and the polarizability of the carbon-tin bond suggested the Cp_2ZrCl moiety would occupy the position bearing the trialkyltin group. This was readily confirmed by quenching studies (with D_2O, I_2,[11] etc.). While for this study the second-stage protonolysis makes such a question of no consequence, it is well worth recognizing the 1,1-dimetallo nature of the intermediates (4) involved.[12] In light of the significant differences in reactivity between vinylstannanes and vinylzirconates, *e.g.*, toward cuprate transmetallations,[13] species such as 4 can be viewed as stereodefined 1,1-vinyl dianions, where the sequential introduction of two distinct electrophiles (E_1 and E_2) is controlled by the chemistry of each metal. For example, acetylenic stannane 3 can be parlayed into iodide 5 by virtue of the selective halogenation of intermediate 4. Various manipulations of these compounds (*e.g.*, using Pd°, Cu(I), etc.) are currently being examined and will be reported in due course.

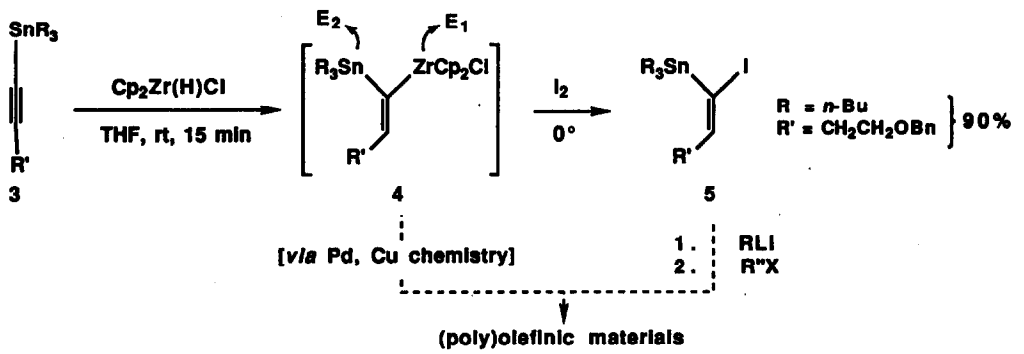
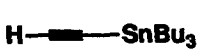
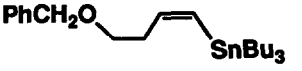
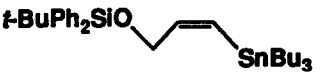
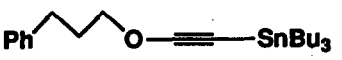
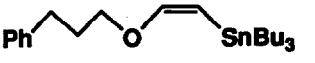
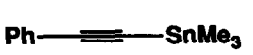
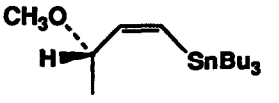
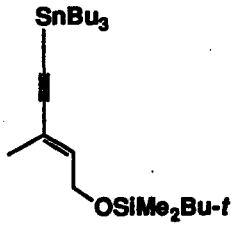
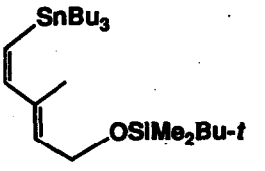


Table 1. Conversion of stannylacetylenes to Z-vinylstannanes *via* hydrozirconation

Entry	Stannane[a]	Product[a]	Yield (%)[b]
1			84
2			92
3			90
4			95
5			94
6			85
7			99
8			97

[a]Characterized by IR, NMR, MS and HRMS data. [b]Isolated, chromatographically pure materials.

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6. Prepared *via* lithiation of the acetylene with MeLi (1 eq) in THF at 0° for 30 min, followed by introduction of R_3SnCl and stirring overnight at rt; see, Bottaro, J.C., Hanson, R.N., Seitz, D.E., *J. Org. Chem.*, **1981**, 46, 5221. See also, Jones, K., Lappert, M.F., *J. Organomet. Chem.*, **1965**, 3, 295; Neuman, W.D., Kleiner, F.G., *Tetrahedron Lett.*, **1964**, 3779.
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10. Obtained from Boulder Scientific Co., Mead, CO., and from the Aldrich Chemical Co. Both gave similar results. Alternatively, we have also used our *in situ* method for generating this reagent; roughly comparable results were obtained on stannylacetylene **2**; *cf.* Lipshutz, B.H., Keil, R., Ellsworth, E.L., *Tetrahedron Lett.*, **1990**, 31, 7257.
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12. See, for example, Tucker, C.E., Knochel, P., *J. Am. Chem. Soc.*, **1991**, 113, 9888, and references therein. Hydrozirconation of an acetylenic ruthenium (II) complex has also been recently reported; Bullock, R.M., Lemke, F.R., Szalda, D.J., *ibid.*, **1990**, 112, 3244.
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