ORGANIC LETTERS

2008
Vol. 10, No. 17
3861−3863

Two-Step Regio- and Stereoselective Synthesis of *cis*-Vinylstannanes

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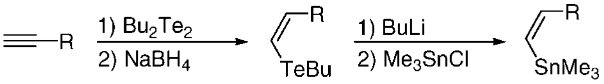
Received June 3, 2008

ABSTRACT



Herein we describe a novel stereoselective synthesis of *cis*-vinylstannanes employing the widely established Li/Te exchange pathway. In contrast to previously reported methods of *cis*-selective hydrostannation (i.e., $ZrCl_4$), this method demonstrates compatibility toward oxygenated substrates.

The Stille coupling[1] of vinyltin reagents with vinyl[2] and aryl halides[2] and triflates[2] is a synthetically useful means for obtaining conjugated double bonds with defined geometry.[1] Unfortunately, methods to access *cis*-vinylstannanes are somewhat limited and often exhibit poor stereoselectivity. To date, *cis*-vinylstannanes have been most commonly synthesized by radical,[3] Lewis acid,[4] and transition metal[5] mediated hydrostannation of alkynes, hydrozirconation[6] of stannyl alkynes, and the transmetalation of vinyl metallic substrates.[7] The use of $ZrCl_4$ as a Lewis acid catalyst in the hydrostannation of alkynes has proven especially valuable,[4b] mainly because the reaction proceeds in an entirely *cis*-selective manner. However, the reaction is not compatible with oxygen-containing functionality, possibly due to coordination to the Lewis acid, as it requires bulky substituents (e.g., TBDMS) on oxygen to facilitate reaction.[4b] The use of bulky substituents on oxygen, however, has not proven to be a general method in order to circumvent this problem.[8,9] Furthermore, in the case of di- and tristannylation the high control over stereochemistry is lost.[4c]

The hydrometalation of alkynes tends to occur in a *syn* fashion to give trans-organometallics. However, isomerization often leads to mixtures of cis and trans isomers. An exception is found in the hydrotelluration of alkynes, which occurs in a highly selective *anti* fashion to give *cis*-vinyltellurides, which are not susceptible to isomerization.[10] Vinyl tellurides are also known to undergo transmetalation to give, for example, vinyl lithium, copper, zinc, magnesium, aluminum, calcium, and sodium reagents with retention of configuration.[11]

With a view to finding a method to selectively synthesize *cis*-vinylstannanes that could also accommodate oxygen functionality, a two-step hydrotelluration lithium−tin exchange protocol was investigated, the results of which are presented herein.

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[1] Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.

[2] Mee, S. P. H.; Lee, V.; Baldwin, S. E. *Chem. Eur. J.* **2005**, *11*, 3294.

[3] Smith, N. D.; Mancuso, J.; Lautens, M. *Chem. Rev.* **2000**, *100*, 3257.

[4] (a) Gevorgyan, V.; Liu, J. X.; Yamamoto, Y. *Chem. Commun.* **1998**, *1*, 37. (b) Asao, N.; Liu, J. X.; Sudoh, T.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 4568. (c) Rim, C.; Son, D. Y. *Org. Lett.* **2003**, *5*, 3443.

[5] Kikukawa, K.; Umekawa, H.; Wada, F.; Matsuda, T. *Chem. Lett.* **1988**, 881.

[6] (a) Bickley, J. F.; Roberts, S. M.; Santoro, M. G.; Snape, T. J. *Tetrahedron* **2004**, *60*, 2569. (b) Bialy, L.; Waldmann, H. *Chem. Eur. J.* **2004**, *10*, 2759. (c) Lipshutz, B.; Keil, R.; Barton, J. *Tetrahedron Lett.* **1992**, *33*, 5861.

[7] Cochran, J. C.; Philips, H. K.; Tom, S.; Hurd, A. R.; Bronk, B. S. *Organometallics* **1994**, *13*, 947.

[8] L'opez, S.; Montenegro, J.; Sa'a, C. *J. Org. Chem.* **2007**, *72*, 9572.

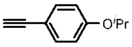
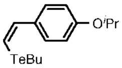
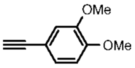
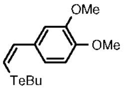
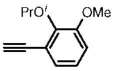
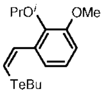
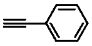
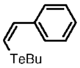
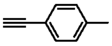
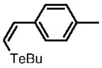
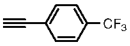
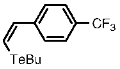
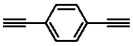
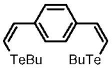
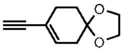
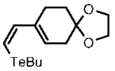
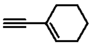
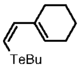
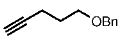
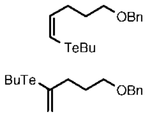
[9] To the best of our knowledge, only one isolated example of *trans*-hydrostannylation employing $B(C_6F_5)_3$ as a Lewis acid catalyst compatible with oxygen functionality has been reported. See ref 4a.

[10] Barross, S. M.; Dabdoub, M. J.; Dabdoub, V. M. B.; Comasseto, J. V. *Organometallics* **1989**, *8*, 1661.

[11] (a) Huang, X.; Liang, C.; Qing, X.; He, Q. *J. Org. Chem.* **2001**, *66*, 74, and references therein. (b) Zeni, G.; Lüdtke, D. S.; Panatieri, R. B.; Braga, A. L. *Chem. Rev.* **2006**, *106*, 1032. (c) Petragnani, N.; Stefani, H. A. *Tellurium In Organic Chemistry*, 2nd, Updated and Enlarged Edition; Academic Press: Amsterdam, The Netherlands, 2007.

10.1021/ol801251m CCC: $40.75

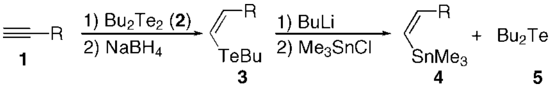
Table 1. Hydrotelluration of Alkynes **1** Affording *cis*-Vinyltellurides **3**

entry	substrate	vinyltelluride	time (h)	yield (%)[a]
1			20	67%
2			18	71%
3			22	79%
4			2.5	61%
5			5	78%
6			3	90%
7			7	78%
8			2.5	75%
9			15	48%
10[b]			21	42%

[a] Isolated yields. [b] Inseparable mixture (ratio 2:1).

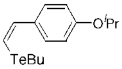
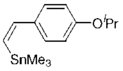
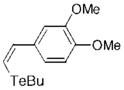
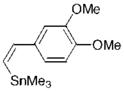
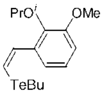
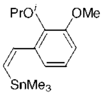
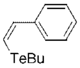
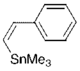
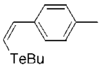
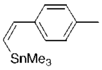
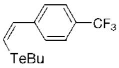
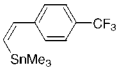
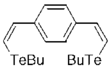
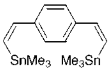
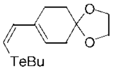
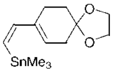
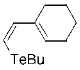
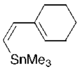
Alkynes (i.e., **1**) (Table 1, entries 1−10) were treated with dibutyl ditelluride **2** and sodium borohydride under standard conditions[11] to give *cis*-vinyltellurides (i.e., **3**) in 48−90% yield (Table 1) (Scheme 1). In all conjugated alkyne cases, regio- and stereoselectivity were maintained. Isolated alkynes (Table 1, entry 10), however, posed regioselectivity problems yielding mixtures of 1,2- and 2,2-disubstituted vinylic tellurides, in favor of the 1,2-disubstituted vinylic tellurides, as previously documented.[12,13]

Scheme 1. Synthesis of *cis*-Vinyl Tellurides **3** and *cis*-Vinylstannanes **4**



The *cis*-vinyl tellurides were uneventfully transmetalated with *n*-butyllithium to the corresponding vinyl lithium, which were subsequently quenched with trimethyltin chloride affording the *cis*-vinylstannanes in 40−68% yield without any detectable *trans*-vinylstannane (Table 2, entries 1−9) (Scheme 1).

Table 2. Transmetalation of *cis*-Vinyl Telluride **3** Affording *cis*-Vinylstannanes **4**

entry	vinyltellurid	vinylstannane	yield (%)[a]
1			46%
2			68%
3			60%
4			50%
5			68%
6			61%
7			40%
8			64%
9			50%

[a] Isolated yields.

Vinylstannanes **4** were accompanied by small amounts of the corresponding protonated alkenes, which were readily removed under vacuum. The removal of dibutyltelluride **5**, however, proved very difficult by distillation or by column chromatography of the nonpolar and/or low molecular weight compounds (i.e., Table 2, entries 4−7, 9[14]). Hence, an efficient method for separation of nonpolar *cis*-vinylstannanes **4** from dibutyl telluride **5** was required. Capitalizing on the fact that dibutyl telluride **5** reacts with methyl iodide to give methyl di-*n*-butyltelluronium iodide **6** under catalyzed ($AgNO_3$, $AgBF_4$)[15] and noncatalyzed conditions,[16] excess methyl iodide (6 equiv) was added to the reaction mixture after

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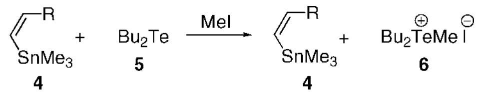
(12) Stefani, H. A.; Costa, I. M.; Zeni, G. *Tetrahedron Lett.* **1999**, *40*, 9215.

(13) Vieira, M. L.; Zinn, F. K.; Comasseto, J. V. *J. Braz. Chem. Soc.* **2001**, *12*, 586.

(14) Purification by silica column chromatography was achieved; however, the general procedure should be followed for ease.

trimethyltin chloride. This workup additive reacted selectively with the dibutyl telluride **5** affording telluronium salt **6**, which could be readily separated from the *cis*-vinylstannane **4** by trituration followed by column chromatography (Scheme 2).

Scheme 2. Removal of Dibutyl Telluride From **4**



In conclusion, developing new methods that access *cis* double bonds selectively for application to the construction of conjugated *cis* double bond systems is of considerable importance, for example, construction of *cis*-configured 1,3,5-trienes for 6π-electrocyclization.[17,18] This body of work demonstrates that access to *cis*-vinylstannanes containing oxygen functionality is now readily achievable allowing further utilization of the Stille reaction to incorporate *cis* double-bond conjugation.

Acknowledgment. We thank the University of Queensland for financial support.

Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra for all compounds, including experimental conditions and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Lenardão, E. J.; Mendes, S. R.; Ferreira, P. C.; Perin, G.; Silveira, C. C.; Jacob, R. G. *Tetrahedron Lett.* **2006**, *47*, 7439.

(16) Balfe, M. P.; Chaplin, C. A.; Phillips, H. *J. Chem. Soc.* **1938**, 341.

(17) Brandänge, S.; Leijonmarck, H. *J. Chem. Soc., Chem. Commun.* **2004**, 292.

(18) Pouwer, R. H.; Schill, H.; Williams, C. M. *Eur. J. Org. Chem.* **2007**, 4699.