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A Highly Selective Synthesis of Versatile (E)-1-Phenylthio Vinylstannanes[1]

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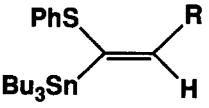
Key Words: Hydrostannation; Palladium(0); Tributyltin Hydride; 1-Phenylthio-1-alkynes; (E)-1-Phenylthio Vinylstannanes

Abstract: *An efficient, palladium-catalyzed hydrostannation of 1-phenylthio-1-alkynes 1 is described. This novel tributyltin hydride addition provides versatile 1-phenylthio vinylstannanes 2 regio- and stereoselectively.*

In connection with several projects currently under investigation in our laboratory, we required a fast and general route to a variety of 1-phenylthio vinylstannanes such as **2a**, **2b**, **2c**, **2d**, and **2e**. The importance of both vinyl sulfides[3] and vinylstannanes[4] as useful synthetic intermediates provided an additional incentive for the stereoselective construction of these previously unknown olefins.

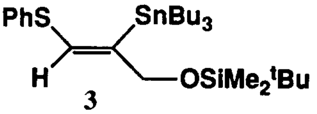
$PhS-C\equiv C-R$

1



2

a, R = $CH_2OSiMe_2{}^tBu$
b, R = CH_2OH
c, R = CH_3
d, R = $CH(OH)CH_2OSiMe_2{}^tBu$
e, R = $CH_2OCH_2CON(OCH_3)CH_3$



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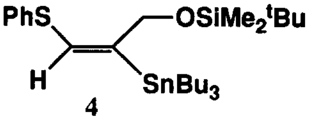


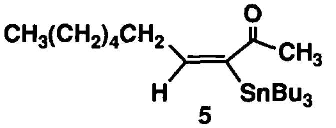
4

Early experimentation focusing on application of various tributylstannyl-radical addition protocols to **1a** resulted either in regioisomer **3** as the major product[5] or in variable composition mixtures of **3** and **4** with **4** predominating.[6] In light of these results we turned our attention to hydrostannation reactions of **1a** that would proceed by a polar mechanism and therefore were likely to provide the desired regioisomer **2a**. Consequently, we have recently described a stannylcuprate addition to **1a** producing **2a** in 65% yield.[11]

Pursuing the development of a more convenient and efficient access to **2**, we set out to examine the palladium-catalyzed hydrostannation[12] of 1-phenylthio-1-alkynes **1**. We now report that this process is highly regio- and stereoselective affording 1-phenylthio vinylstannanes **2** in very good yields (Table I).[13] For most of the entries in Table I only a trace amount of regioisomeric products such as **4** (for entry 1) could be detected (>20:1) by the analytical methods employed.[14] The complete stereoselectivity observed was established to be *syn* by consideration of tin-vinylic hydrogen coupling constants in the ^{1}H NMR spectra of products **2** (average value ~50 Hz, *cis* Sn^{117}/Sn^{119}).[15] Catalysis by Pd(0) seems to be extremely efficient (1 mol% or less) since a control reaction of **1a** and Bu_3SnH (benzene; 23°C, 48h) was found to be very slow giving rise to a mixture of **2a**, **3**, and **4** (~35% overall yield) presumably by both polar and free-radical mechanisms.

In a general procedure, the 1-phenylthio-1-alkyne **1** (5.0 mmol) was weighed into a flame-dried, round-bottomed flask and dissolved in benzene (20 ml, distilled from sodium benzophenone ketyl) under argon (23°C). To the resulting solution was added tetrakis(triphenylphosphine)palladium(0) (0.05 mmol, 58 mg) rapidly, followed by tributyltin hydride (neat, dropwise via syringe; 1.05 equiv, 5.25 mmol, 1.4 ml). After a few minutes complete conversion to a single, less polar product was detected by sg TLC (15% benzene in hexane). Benzene was removed on a rotary evaporator and the oily residue was purified by sg filtration using hexane as the initial eluting solvent (75-90% yields).

Examination of entry 6 (Table I) reveals that the parent 1-phenylthio vinylstannane **2f** can be efficiently synthesized without recourse to α-lithiation of phenyl vinyl sulfide.[16] Comparison of products **2g**[17] and **2h** (entries 7 and 8) with vinylstannanes **5** and **6** produced by Pd(0)-catalyzed hydrostannation of 3-decyne-2-one[12c,d] and 1-phenyl-1-propyne[12b,c] respectively, points out the strong regiochemical control exerted by sulfur induced polarization in alkynyl sulfides **1**. More direct evidence for this electronic effect was obtained by hydrostannation of the sulfoxide corresponding to **1a** which gave rise to both regioisomers **7** and **8** in a 2:1 ratio (80% yield).[18] Preliminary results suggest that similar levels of regio- and stereoselectivity can be expected from the Pd(0)-catalyzed hydrostannation of 1-phenylseleno-1-alkynes **9**. Specifically, alkynyl selenides **9a** and **9b** were found to yield (E)-1-phenylseleno vinylstannanes **10a** and **10b** almost exclusively (75% isolated yield).



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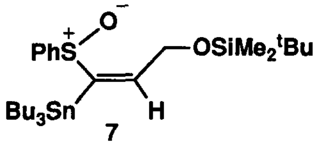

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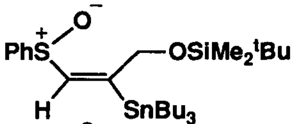

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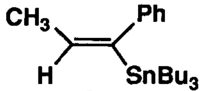
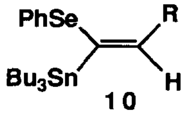


6

$PhSe{-}C{\equiv}C{-}R$

9 a , R = $CH_2OSiMe_2{}^tBu$
b , R = CH_2OH



10

In conclusion, the procedure reported herein by virtue of its wide scope and combination with the facile transmetallation of vinylstannanes, constitutes a very attractive alternative to the sometimes inconvenient and inconsistent α-lithiation[15,19] as the means toward the synthesis of functionalized vinyl sulfides. Work is in progress on the application of stannanes **2** and **10** to the synthesis of trisubstituted olefins as well as other interesting target molecules.

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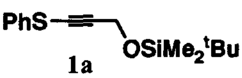
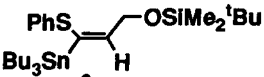
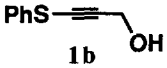
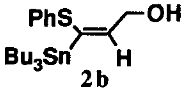
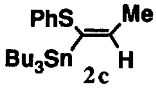
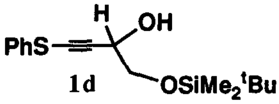
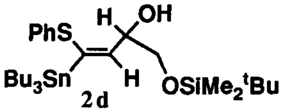
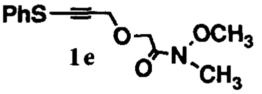
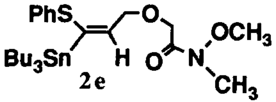
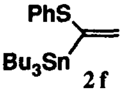
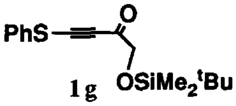
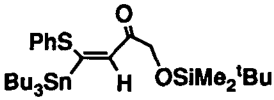
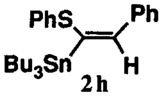
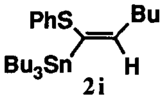
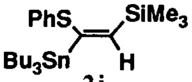
Table I

Entry	Phenylthioalkyne[a]	Vinylstannane[b]	%Yield[c]
1.	 1a	 2a	90
2.	 1b	 2b	84
3.	PhS—≡—Me 1c	 2c	79[d]
4.	 1d	 2d	80
5.	 1e	 2e	90
6.	PhS—≡ 1f	 2f	87
7.	 1g	 2g	88
8.	PhS—≡—Ph 1h	 2h	75[d]
9.	PhS—≡—Bu 1i	 2i	82[d]
10.	PhS—≡—SiMe$_3$ 1j	 2j	85

[a] Phenylthioacetylene (**1f**) was synthesized from phenyl vinyl sulfide by a two-pot, three-step procedure involving bromination-dehydrobromination and NaNH$_2$/NH$_3$ elimination (Magriotis, P. A.; Brown, J. T., submitted for checking to *Org. Synth.*). Phenylthioalkynes **1d** and **1h** were prepared by Luche reduction of **1g** and reaction of TMS phenylacetylene with phenyl disulfide (CuOTf, CaCO$_3$, THF-dioxane; 80°C, 2h)[20] respectively. [b] All vinylstannane products exhibited spectral properties (^{1}H NMR, IR, and GC/MS) in accord with the assigned structures. The regiochemical outcome of entry 8 was confirmed by inspection of the methyl group signal (^{1}H NMR; doublet, J = 1.8 Hz) of a **2h** derivative obtained by the following sequence: (1) transmetallation (n-BuLi, THF; -30°C, 0.5h) and reaction with hexanal; (2) protection (MOM-Cl, CH$_2$Cl$_2$, diisopropylethylamine; 23°C, 5h); and (3) Ni(0)-catalyzed coupling of the vinyl sulfide with MeMgBr (toluene, 110°C).[3d] Regiochemical assignment of entry 9 was made by analogy and literature data on the hydrostannation of 1-trimethylsilyl-1-alkynes.[12a,c] [c] Isolated yield after preparative TLC or sg flash chromatography. [d] Regioselectivity: **2c** ~19:1 (GC/MS); **2h** ~15:1 (^{1}H NMR); **2i** ~18:1 (GC/MS).

References and Notes

1. Presented at the 32nd National Organic Chemistry Symposium of the American Chemical Society, Minneapolis, Minnesota, June 16-20, 1991.
2. Recipient of the ACS Division of Organic Chemistry Travel Award Program for Outstanding Undergraduate Students (Atlanta National Meeting, April 1991) sponsored by Johnson & Johnson.
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5. This was accomplished by triethylborane[7]- or diisobutylaluminum hydride[8]-catalyzed hydrostannation of **1a** (23°C). The application of these reactions to other 1-phenylthioalkynes will be reported in due course.
6. The most synthetically useful ratio of **3**:**4** was 1:5 and obtained under the conditions reported by Corey[9a] and Jung[9b] (1.3 equiv Bu_3SnH, 95°C, cat. AIBN). These results are consistent with a free radical mechanism,[10] involving *anti* addition of Bu_3SnH followed by isomerization of **3** to the apparently more stable **4**.
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13. The requisite 1-phenylthio-1-alkynes **1** were prepared by reaction of lithium phenylthioacetylide with the appropriate electrophile. Experimental details of these syntheses will be published elsewhere. It is noted that iododestannylation of vinylstannanes **2** proceeded smoothly (90-95% yields of vinyl iodides).
14. GC (HP 5890 Series II)-MS (HP 5970 Mass Selective Detector) equipped with an HP-1 column (50m, 0.2mm ID) and ^1H NMR (Jeol GX 270 MHz). Similar regioselectivity was observed in the hydroboration of **1i**, see: Hoshi, M.; Masuda, Y.; Arase, A. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 447.
15. For comparison, the average *trans* coupling constant of Sn^{117}/Sn^{119}-vinylic hydrogen in **3** is ~190 Hz.
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17. $NaBH_4$ reduction (Luche, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 2227) of **2g** yielded **2d** (85%).
18. Interestingly, hydrostannation of the sulfone gave rise to approximately a 1:1 mixture of regioisomers. Under palladium catalysis, 1-chloro-1-octyne has been reported to consume 1 equiv of tributyltin hydride furnishing (E)-1-chloro-1-tributylstannyl-1-octene exclusively.[12c]
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