Hydrostannation of C–C multiple bonds with Bu_3SnH prepared *in situ* from Bu_3SnCl and Et_3SiH in the presence of Lewis acid catalysts

Vladimir Gevorgyan, Jian-Xiu Liu and Yoshinori Yamamoto*

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-77, Japan

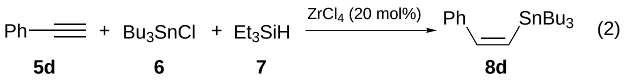
A number of alkynes 5, allene 11 and alkene 13 smoothly underwent hydrostannation with tributyltin hydride 1, prepared *in situ* from tributylchlorostannane 6 and triethylsilane 7 in the presence of catalytic amounts of Lewis acids.

Since the first synthesis of tributyltin hydride **1** by Finholt *et al.* in 1947,[1] this compound has become one of the most frequently used organometallic reagents in organic synthesis.[2] Along with wide applicability as a hydrogen source in various kinds of reductions,[2] Bu_3SnH is the most popular hydrostannation agent for the synthesis of vinyl-[3] and allyl-stannanes.[4] The latter, due to their great versatility as building blocks, are of increasing importance in modern synthetic organic chemistry.[5] Recently we reported regio- and stereo-selective methods for the synthesis of vinyl- and allyl-tributylstannanes *via* Lewis acid-catalyzed *trans*-hydrostannation of acetylenes[6] and allenes.[7] Although Bu_3SnH is commercially available, it gradually decomposes after storage in a refrigerator for a prolonged period of time;[8] consequently, distillation is needed before use. It occurred to us that *in situ* generation of **1** from stable precursors would be synthetically more convenient for the hydrostannation reaction. The generation of Bu_3SnH *in situ* from more stable stannyl precursors and hydride sources could serve this purpose.[9] In general, the preparation of commercially available tributyltin hydride **1** is carried out by the reduction of tributyltin oxide **2** with hydrosiloxane **3** [reaction (1)].[10]

$$\underset{\mathbf{2}}{n\,(Bu_3Sn)_2O} + \underset{\mathbf{3}}{2\,(MeSiHO)_n} \xrightarrow{\text{heat}} \underset{\mathbf{1}}{2n\,Bu_3SnH} + \underset{\mathbf{4}}{2\,(MeSiO_{1.5})_n} \quad (1)$$

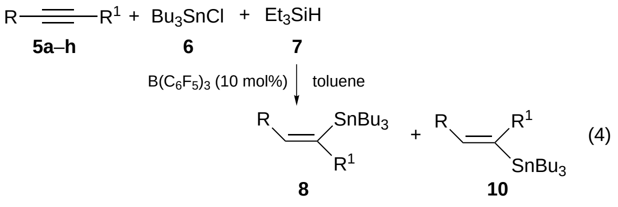
Accordingly, we attempted to employ this method for the *in situ* preparation of **1** under the conditions of the Lewis acid-catalyzed hydrostannation reaction.[6,7] However, no hydrostannation products were detected, instead the starting alkynes were recovered quantitatively. It is probable that, due to the strong affinity of the Lewis acid for the oxygen of either the reactants (**2** and/or **3**) or of the byproduct **4**, it is deactivated and thus not effective as a catalyst in the hydrostannation reaction. Hence, a non-oxygen containing precursor should be employed for the *in situ* preparation of **1**.

Herein we report the first example of the Lewis acid-catalyzed hydrostannation reaction of alkynes with tributyltin hydride **1**, prepared *in situ* from Bu_3SnCl **6** and Et_3SiH **7** [reactions (2) and (4)].



In our initial experiments we found that simple mixing of **6** and **7** in toluene at room temperature did not produce any detectable amount of tin hydride **1**. In contrast, a redistribution took place by the addition of 20 mol% $ZrCl_4$[11] to the same reaction mixture and noticeable amounts of **1** were detected by ^1H NMR analysis of the reaction mixture after one hour [reaction (3)]. Although the mixture contained a large amount of silyl hydride **7** [reaction (3)], it was presumed that, due to the fact that $ZrCl_4$ is not a strong enough Lewis acid to the catalyze hydrosilylation alkynes,[12] this reaction would not compete with the desired hydrostannation process. Motivated by that we applied this method for the *in situ* preparation of **1** and subsequent $ZrCl_4$-catalyzed hydrostannation of phenylacetylene **5d**;[11] as a result the *trans*-addition product (*Z*)-β-(tributylstannyl)styrene **8d** was formed in 52% yield (by ^1H NMR analysis). A brief search for a more efficient Lewis acid catalyst pointed to $B(C_6F_5)_3$. We found that 10 mol% of $B(C_6F_5)_3$ effectively catalyzed the hydrostannation of various alkynes **5** with tributylstannane **1**, generated *in situ* from **6** and **7**, producing the hydrostannation products **8** and **10** in excellent chemical yields [reaction (4), Table 1]. The hydrostannation of all the monosubstituted alkynes tested (**5a–f**) proceeded in a regiospecific manner affording the β-hydrostannation products (**8a–f**, **10**) exclusively (entries 1–6, Table 1). Except for the reactions with **5b** and **5g** in which small amounts of the *cis*-addition products were formed (entries 2,7), the reaction was also *trans*-stereoselective (entries 1,3–6,8, Table 1) as was reported for the conventional method for the Lewis acid-catalyzed hydrostannation of alkynes.[6] The preparation of **8a** from **5a** is representative. Tributylstannyl chloride **6** (1.5 mmol), triethylsilane **7** (1.0 mmol) and **5a** (1 mmol) were consecutively added at 0 °C to a solution of $B(C_6F_5)_3$ (0.1 mmol) in dry toluene (0.25 ml) under an argon atmosphere. After being stirred for 40 min at 0 °C the reaction temperature was allowed to warm to 25 °C and the mixture was stirred for another 3 h. The reaction was quenched by adding Et_3N (0.5 mmol) at ambient temperature. Hexane was added and the resulting mixture was filtered through Celite and concentrated under reduced pressure. Purification by column chromatography (aluminium oxide, 90 mesh, *n*-hexane as eluent) gave 220 mg (78%) of **8a**.

$$\underset{\mathbf{6}}{Bu_3SnCl} + \underset{\substack{\mathbf{7}\\ 89\%}}{Et_3SiH} \xrightleftharpoons{ZrCl_4} \underset{\substack{\mathbf{1}\\ 11\%}}{Bu_3SnH} + \underset{\mathbf{9}}{Et_3SiCl} \quad (3)$$

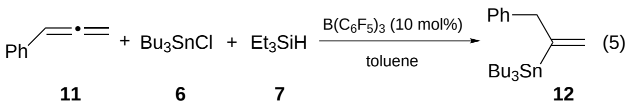


Finally, we disclose our initial experiments on the application of this method for the hydrostannation of an allene and alkene. We reported recently that tributyltin hydride **1** in the presence of Lewis acids reacted with a number of allenes affording the corresponding vinylstannanes in good chemical yields.[7] We found that **1**, prepared *in situ* from **6** and **7** in the presence of 10 mol% of $B(C_6F_5)_3$, smoothly reacted with phenylallene **11**

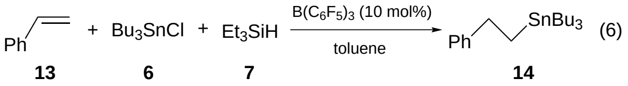
Table 1 $B(C_6F_5)_3$-catalyzed hydrostannation of alkynes with Bu_3SnH generated *in situ* from Bu_3SnCl and Et_3SiH

Entry	R	R^1		Conditions	Yield of **8** + **10**[a] (%)	Ratio **8** : **10**[b]
1	C_6H_{13}	H	**5a**	40 min/0 °C		
				3 h/rt[c]	78	> 95 : 5
2	Cyclohexenyl	H	**5b**	2 h/0 °C	85	86 : 14
3	$PhCH_2$	H	**5c**	4 h/0 °C	85	> 95 : 5
4	Ph	H	**5d**	2.5 h/0 °C	77	> 95 : 5
5	*p*-MeC_6H_4	H	**5e**	2.5 h/0 °C	89	> 95 : 5
6	*p*-$MeOC_6H_4$	H	**5f**	1.5 h/−35 °C	70	> 95 : 5
7	Pentyl	Pentyl	**5g**	40 min/0 °C		
				3 h/rt	90	80 : 20
8	Ph	Ph	**5h**	40 min/0 °C		
				3 h/rt	71	> 95 : 5

[a] Isolated yield. [b] Determined by ^1H NMR analysis of crude reaction mixtures. [c] rt = room temp.



affording the vinylstannane **12** in 51% yield [reaction (5)]. In addition, the same method could be employed for the hydrostannation of alkenes: styrene **13** was converted into the corresponding alkylstannane **14** in 70% isolated yield [reaction (6)]. To the best of our knowledge, reaction (6) is the first



example of the Lewis acid-catalyzed hydrostannation of alkenes.

In conclusion, a synthetically useful and convenient method for the Lewis acid-catalyzed hydrostannation of carbon–carbon multiple bonds with tributyltin hydride **1**, prepared *in situ* from easily handled and cheap chlorostannane **6** and hydrosilane **7**, has been developed. The first example of the Lewis acid-catalyzed hydrostannation of an alkene has been demonstrated.

Footnote and References

* E-mail: yoshi@yamamoto1.chem.tohoku.ac.jp

1 A. E. Finholt, A. C. Bond, K. E. Wilzbach and H. I. Schlesinger, *J. Am. Chem. Soc.*, 1947, **69**, 2693.

2 For a leading review, see W. P. Neumann, *Synthesis*, 1987, 665.

3 H. X. Zhang, F. Guibé and G. Balavoine, *J. Org. Chem.*, 1990, **55**, 1857; Y. Ichinose, H. Oda, K. Oshima and K. Utimoto, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 3468; K. Kikuhawa, F. Umekawa, G. Wada and T. Matsuda, *Chem. Lett.*, 1988, 881; H. Miyake and K. Yamamura, *Chem. Lett.*, 1989, 981.

4 H. G. Kuivila, W. Rahman and R. H. Fish, *J. Am. Chem. Soc.*, 1965, **87**, 2835; M. Koreeda and Y. Tanaka, *Tetrahedron Lett.*, 1987, **28**, 143; Y. Ichinose, K. Oshima and K. Utimoto, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2693; T. N. Mitchell and U. Schneider, *J. Organomet. Chem.*, 1991, **405**, 195; K. Koerber, J. Gore and J.-M. Vatele, *Tetrahedron Lett.*, 1991, **32**, 1187.

5 (*a*) M. Pereyre, J.-P. Quintard and A. Rahm, *Tin in Organic Synthesis*, Butterworths, London, 1987; (*b*) A. J. Leusink, H. A. Budding and W. Drenth, *J. Organomet. Chem.*, 1967, **9**, 285; 1967, **9**, 295; (*c*) Y. Yamamoto and N. Asao, *Chem. Rev.*, 1993, **93**, 2207; (*d*) J. K. Stille, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 508; (*e*) R. F. Heck, *Palladium Reagents in Organic Synthesis*, Academic Press, New York, 1985.

6 N. Asao, J.-X. Liu, T. Sudoh and Y. Yamamoto, *J. Org. Chem.*, 1996, **61**, 4568; N. Asao, J.-X. Liu, T. Sudoh and Y. Yamamoto, *J. Chem. Soc., Chem. Commun.*, 1995, 2405.

7 V. Gevorgyan, J.-X. Liu and Y. Yamamoto, *J. Org. Chem.*, 1997, **62**, 2963.

8 G. Bähr and S. Pawlenko, in *Methoden der Organischen Chemie*, ed. E. Müller and O. Bayer, Thieme Verlag, Stuttgart, 1978, vol. 13/6, p. 181; A. G. Davies and P. J. Smith, in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, Pergamon Press, Oxford, 1982, vol. 2, Tin, see also refs. 2, 5(*a*).

9 The reduction of various organic halides with **1** prepared *in situ* from tributyltin chloride and $LiAlH_4$ or $NaBH_4$ has been reported: E. J. Corey and J. W. Suggs, *J. Org. Chem.*, 1975, **40**, 2554; H. G. Kuivila and L. W. Menapace, *J. Org. Chem.*, 1963, **28**, 2165. However, due to the presence of reactive metal hydrides in the reaction mixture, this method could not be applied to the Lewis acid-catalyzed hydrostannation reaction.

10 K. Hayashi, J. Iyoda and I. Shiihara, *J. Organomet. Chem.*, 1967, **10**, 81.

11 Since $ZrCl_4$ was reported to be the best Lewis acid catalyst for *trans*-hydrostannation of alkynes with Bu_3SnH[6] it was chosen for our initial experiments for the *in situ* hydrostannation of alkynes.

12 N. Asao, T. Sudoh and Y. Yamamoto, *J. Org. Chem.*, 1996, **61**, 7654.

Received in Cambridge, UK, 26th August 1997; 7/06187K