Copper(I)-Catalyzed Transfer of 1-(Trimethylsilyl)-1-alkenyl Group from Boron to Tin: Regio- and Stereoselective Synthesis of *(E)*-1-(Tributylstannyl)-1-(trimethylsilyl)-1-alkenes

Masayuki Hoshi,* Kazuya Shirakawa, Kiyoshige Takeda

Department of Applied and Environmental Chemistry, Kitami Institute of Technology, 165 Koen-cho, Kitami, Hokkaido 090-8507, Japan
Fax +81(157)24 7719; E-mail: hoshi@lilac.hokkai.net

Received 11 December 2000

Abstract: Stereoselective transfer of 1-(trimethylsilyl)-1-alkenyl group from boron to tin has been realized by a catalytic amount of copper(I) iodide in the presence of aqueous NaOH under extremely mild reaction conditions to provide (*E*)-1-(tributylstannyl)-1-(trimethylsilyl)-1-alkenes (**2**) exclusively in good to high yields.

Key words: transfer, copper(I) iodide, boron, tin, 1,1-dimetalloalkene

Dimetalloalkenes have been increasingly useful in synthetic organic chemistry because in many cases, each metal moiety can be substituted separately with different electrophiles to furnish polysubstituted alkenes in a regio- and stereoselective manner.[1] The synthetic utility of 1-silyl-2-stannylalkene[1b,2] and 1-boryl-2-silylalkene,[1b,3] both of which exhibit the different reactivities of these metal moieties in electrophilic substitution, have been demonstrated. On the other hand, 1,1-dimetalloalkenes have also been useful synthons in a variety of carbon-carbon bond forming reactions.[1c] Although 1-boryl-1-silylalkene is readily available via hydroboration of 1-silyl-1-alkyne,[4] 1-silyl-1-stannylalkene cannot be obtained regioselectively by hydrostannation of 1-silyl-1-alkyne.[5] In this paper, we report a regio- and stereoselective route to (*E*)-1-(tributylstannyl)-1-(trimethylsilyl)-1-alkenes (**2**) using copper(I) iodide-catalyzed reaction of (*Z*)-1-(trimethylsilyl)-1-alkenyldialkylboranes (**1**) with tributyltin chloride in the presence of aq. NaOH.

We examined the reaction of (*Z*)-1-(trimethylsilyl)-1-hexenyldicyclohexylborane (**1a**), prepared by hydroboration of 1-(trimethylsilyl)-1-hexyne with dicyclohexylborane, with tributyltin chloride and thus found that copper(I) salt and aq. NaOH were required to perform the desired reaction, transfer of 1-(trimethylsilyl)-1-hexenyl group from boron to tin. The results carried out under several conditions are shown in Table 1. When 10 mol% of copper(I) iodide was used, the desired reaction proceeded at 0 °C to room temperature to form (*E*)-1-(tributylstannyl)-1-(trimethylsilyl)-1-hexene (**2a**)[6] in 91% yield in a stereoselective manner (entry 2). Copper (I) bromide and chloride also catalyzed the reaction in a similar manner to give **2a** in moderate yields (entries 4 and 5), respectively, while copper(II) acetylacetonate-catalyzed reaction gave a mixture of stereoisomers (entry 6). Consequently, copper(I) iodide was identified as the optimal catalyst for further exploration.

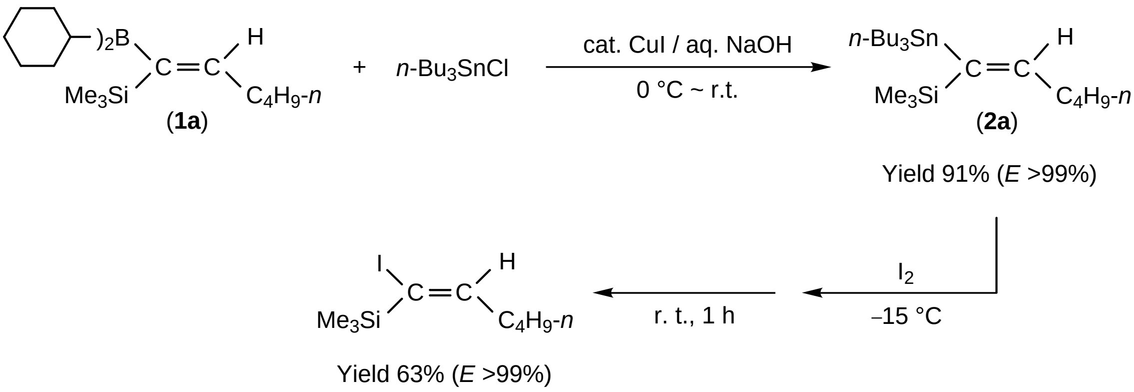
Table 1 Effects of copper compound and its amount[a]

Entry	Cu compound	(mol%)	Yield of **2a** (%)$^{b)}$
1	CuI	5	81
2		10	91
3		30	86
4	CuBr	10	71
5	CuCl	10	66
6	Cu(acac)$_2$	5	53$^{c)}$

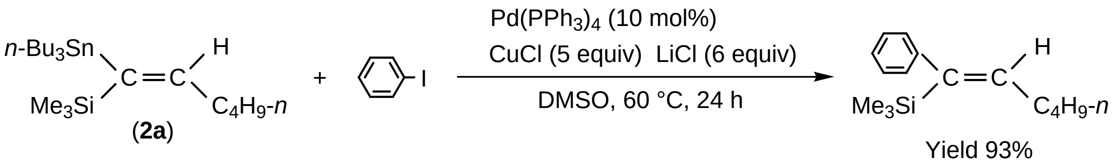
[a] Stoichiometric reaction of **1a** with n-Bu$_3$SnCl was carried out in the presence of 1 equiv of 2M-NaOH. [b] GLC yields based on 1-(trimethylsilyl)-1-hexyne employed. [c] At the same time, Z-isomer was formed in 21% yield.

To elucidate the stereochemistry of **2a**, we made use of iodinolysis of alkenyltin compounds where the conversion of carbon-tin bond to carbon-iodine bond proceeds with retention of configuration.[7] Thus, the reaction of **1a** with tributyltin chloride followed by iodinolysis, which proceeded acceptably even under aqueous conditions, gave (*E*)-1-iodo-1-(trimethylsilyl)-1-hexene[8] in 63% overall yield in a one-pot manner from the preparation of dicyclohexylborane (Scheme 1). The ^{1}H NMR spectrum of the product revealed that in the alkenyl region there is only one triplet at 7.17 ppm, which is consistent with that reported in the literature.[9] This result demonstrates that the geometry of **2a** is *E*, and thus stereoselective transfer of 1-(trimethylsilyl)-1-hexenyl group from boron to tin has been accomplished by the present reaction.

The reactions of several types of **1**,[1b] which bear structurally and electronically diverse R^2, with tributyltin chloride were carried out under the conditions using additive and varying the type of R^1 and the amount of aq. NaOH, and the results are summarized in Table 2. The addition of NaI (an equivalent amount to tributyltin chloride) to the reaction mixture resulted in a moderate improvement of the reaction yield (entries 2 and 6); however, there is no clear indication for the role that NaI plays in the reaction. The reaction starting from 3-methoxy- or 3-(methoxymethoxy)-1-(trimethylsilyl)-1-propyne gave a mixture of regioisomeric products, respectively. This is due to a lack of regioselectivity in the hydroboration. The regioselective formation of desired products was thus



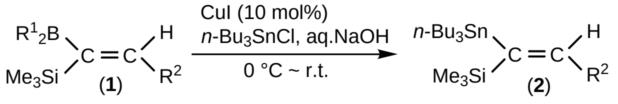
Scheme 1

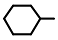
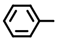
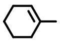


Scheme 2

achieved by employing dihexylborane which was prepared by successive reaction of 1-hexene with $BH_2Br{\bullet}SMe_2$ [10] and $LiAlH_4$.[11] Moreover, increasing the amount of aq. NaOH, the products, **2f** and **2g**, were obtained in good yields (entries 7 and 8). In all cases listed in Table 2, (*E*)-1-(tributylstannyl)-1-(trimethylsilyl)-1-alkenes (**2**) were obtained regio- and stereoselectively, indicating that a wide range of **2** can be formed using this strategy. Although we have no clear evidence for the reaction mechanism at present, it is likely copper(III) species might participate in the present reaction, as previously reported by Liebeskind et al[12a,b] and Evans et al.[12c]

Table 2 Transfer of 1-(trimethylsilyl)-1-alkenyl group from boron to tin catalyzed by copper(I) iodide[a]



Entry	R^1	R^2	Product	Yield (%)[b)]
1		n-C_4H_9	**2a**	91
2			**2a**	97[c)]
3		t-C_4H_9	**2b**	88
4			**2c**	91
5			**2d**	86
6		$ClCH_2(CH_2)_2$	**2e**	94[c)]
7	n-C_6H_{13}	CH_3OCH_2	**2f**	82[d)]
8		$CH_3OCH_2OCH_2$	**2g**	74[e)]

Unless otherwise stated, stoichiometric reaction of **1** with n-Bu_3SnCl as carried out in the presence of **1** equiv of 2M-NaOH. [b] GLC yield ased on 1-(trimethylsilyl)-1-alkyne employed. [c] 1 equiv of NaI was dded. [d] 2 equiv of 2M-NaOH was used. [e] 2.5 equiv of 2M-NaOH was sed.

The synthetic utility of **2** thus prepared has been demonstrated by the palladium catalyzed cross-coupling reaction with aromatic halide (Stille reaction) (Scheme 2). The reaction of **2a** with iodobenzene in the presence of a catalytic amount of $Pd_2(dba)_3$ scarcely proceeded under the conditions described in the literature.[13] The system containing $Pd(PPh_3)_4$ reported by Corey et al,[14] however, successfully catalyzed the reaction to provide the corresponding coupling product[15] as the sole isomer in 93% yield.

In summary, we have found that copper(I) iodide-catalyzed transfer of 1-(trimethylsilyl)-1-alkenyl group from boron to tin has enabled the development of the first regio- and stereoselective synthesis of (*E*)-1-(tributylstannyl)-1-(trimethylsilyl)-1-alkenes (**2**). Products **2** would make trisubstituted alkenes readily accessible with high stereospecificity. Studies on the mechanism and the synthetic scope of this reaction are now in progress.

References and Notes

(1) For reviews, see: (a) Ishiyama, T.; Miyaura, N. *J. Synth. Org. Chem. Jpn*. **1999**, *57*, 503. (b) Suginome, M.; Ito, Y. *Chem. Rev*. **2000**, *100*, 3221. (c) Marek, I. *Chem. Rev*. **2000**, *100*, 2887.
(2) Mitchell, T. N.; Killing, H.; Dicke, R.; Wickenkamp, R. *J. Chem. Soc., Chem. Commun*. **1985**, 354. Chenard, B. L.; Laganis, E. D.; Davidson, F.; RajanBabu, T. V. *J. Org. Chem*. **1985**, *50*, 3666. Chenard, B. L.; Van Zyl, C. M. *J. Org. Chem*. **1986**, *51*, 3561. Mitchell, T. N.; Wickenkamp, R.; Amamria, A.; Dicke, R.; Schneider, U. *J. Org. Chem*. **1987**, *52*, 4868.
(3) Suginome, M.; Nakamura, H.; Ito, Y. *Chem. Commun*. **1996**, 2777. Suginome, M.; Matsuda, T.; Ito, Y. *Tetrahedron* **1999**, *55*, 8787.

(4) Zweifel, G.; Backlund, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 3184. Hassner, A.; Soderquist, J. A. *J. Organomet. Chem.* **1977**, *131*, C1. Miller, J. A.; Zweifel, G. *Synthesis* **1981**, 288.

(5) Zhang, H. X.; Guibé, F.; Balavoine, G. *J. Org. Chem.* **1990**, *55*, 1857.

(6) **2a**: ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 9H), 0.8–1.0 (m, 18H), 1.1–1.7 (m, 16H), 2.1–2.35 (m, 2H), 6.48 (t, *J* = 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.54 (Me × 3), 10.54 (CH_2 × 3), 13.63 (Me × 3), 14.04, 22.43, 27.36 (CH_2 × 3), 29.23 (CH_2 × 3), 31.92, 36.56, 141.29 (>C=), 159.05 (=CH-); IR (neat) 2956, 2925, 2854, 1566, 1461, 1377, 1247, 858, 835, 750, 684 cm^{-1}; MS (EI) m/z 389 ($M^{+\bullet}$ 57, 100%), 387 ($M^{+\bullet}$ 57, 75), 385 ($M^{+\bullet}$ 57, 43), 235 (31), 233 (26), 231 (16), 193 (31), 191 (22), 189 (13), 179 (40), 177 (36), 175 (24), 139 (12), 135 (11), 121 (12), 73 (36), 59 (12).

(7) For example, see: Ensley, H. E.; Buescher, R. R.; Lee, K. *J. Org. Chem.* **1982**, *47*, 404. Tolstikov, G. A.; Miftakhov, M. S.; Danilova, N. A.; Vel'der, Ya. L. *Synthesis* **1986**, 496.

(8) *(E)*-1-Iodo-1-(trimethylsilyl)-1-hexene: ^{1}H NMR ($CDCl_3$) δ 0.27 (s, 9H), 0.90 (t, *J* = 6 Hz, 3H), 1.15–1.55 (m, 4H), 1.95–2.25 (m, 2H), 7.17 (t, *J* = 7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.21 (Me × 3), 13.84, 22.19, 31.35, 34.89, 106.44 (>C=), 156.69 (=CH-); IR (neat) 2956, 2925, 2856, 1587, 1461, 1249, 840, 758, 626 cm^{-1}; MS (EI) m/z 282 (M^+, 21%), 185 (38), 139 (44), 73 (100).

(9) Zweifel, G.; Murray, R. E.; On, H. P. *J. Org. Chem.* **1981**, *46*, 1292.

(10) Brown, H. C.; Ravindran, N.; Kulkarni, S. U. *J. Org. Chem.* **1979**, *44*, 2417.

(11) Brown, H. C.; Kulkarni, S. U. *J. Organomet. Chem.* **1981**, *218*, 299.

(12) (a) Allred, G. D.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1996**, *118*, 2748. (b) Zhang, S.; Zhang, D.; Liebeskind, L. S, *J. Org. Chem.* **1997**, *62*, 2312. (c) Evans, D. A.; Katz, J. L.; West, T. R. *Tetrahedron Lett.* **1998**, *39*, 2937.

(13) Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585. Farina, V.; Kapadia, S.; Krishnan, B.; Wang, C.; Liebeskind, L. S. *J. Org. Chem.* **1994**, *59*, 5905.

(14) Han, X.; Stoltz, B. M.; Corey, E. J. *J. Am. Chem. Soc.* **1999**, *121*, 7600.

(15) (*Z*)-1-Phenyl-1-(trimethylsilyl)-1-hexene: ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 9H), 0.98 (t, *J* = 6.4 Hz, 3H), 1.3–1.7 (m, 4H), 2.2–2.5 (m, 2H), 6.13 (t, *J* = 7.5 Hz, 1H), 6.95–7.45 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 0.77 (Me × 3), 14.04, 22.47, 32.04, 32.16, 125.21 (=CH-), 127.53 (=CH- × 2), 127.69 (=CH- × 2), 142.96 (>C=), 146.83 (=CH-), 147.40 (>C=); IR (neat) 2956, 2925, 2871, 2858, 1600, 1488, 1465, 1458, 1440, 1249, 887, 837, 765, 700, 619 cm^{-1}; HRMS (EI), $C_{15}H_{24}Si$ requires 232.1647, found 232.1671.

(16) **Typical experimental procedure:** To a stirred solution of **1a** (3 mmol) in THF (12 mL) at 0 °C, copper(I) iodide (0.057 g, 0.3 mmol) and sodium iodide (0.45 g, 3 mmol) were added under an argon flow. Tributyltin chloride (0.813 mL, 3 mmol) and 2M NaOH (1.5 mL, 3 mmol) were then added dropwise to the suspended solution, and the resulting mixture was allowed to warm gradually to room temperature overnight. The reaction mixture was treated with 3M NaOH (3 mL) and 30% H_2O_2 (1.5 mL) at 0 °C and stirred for 1 h at the same temperature to decompose the residual organoboron compound. After removal of THF under reduced pressure, the resultant mixture was extracted with hexane. The extract was washed with water to remove cyclohexanol formed by the above decomposition and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silicagel 60 silanized (Merck), with CH_2Cl_2 as eluent, to give product **2a** (1.123 g, 84%).

Article Identifier:
1437-2096,E;2001,0,03,0403,0405,ftx,en;Y21200ST.pdf