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Stereoselective Synthesis of (*E*)- and (*Z*)-1-Alkenyltributylstannanes From (*E*)- and (*Z*)-1-Alkenyldialkylboranes Using a Cross-Coupling Reaction with Tributyltin Halide

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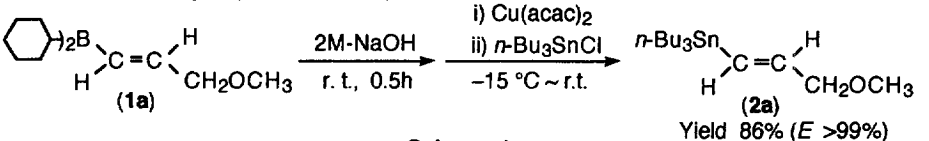
Abstract: The cross-coupling reaction of (*E*)- or (*Z*)-1-alkenyldialkylborane with tributyltin halide using copper (II) acetylacetonate [$Cu(acac)_2$] as catalyst in the presence of NaOH proceeds under extremely mild and aqueous conditions to give (*E*)- or (*Z*)-1-alkenyltributylstannane stereoselectively. © 1997 Elsevier Science Ltd.

Alkenylstannanes are useful building blocks in synthetic organic chemistry[1] and have been directly synthesized by hydrostannation of alkynes using either radical initiators[2] or transition metal catalysts.[3] However, the hydrostannation using radical initiators often exhibits poor stereoselectivity and the reaction using transition metal catalysts usually exhibits poor regioselectivity. Recently, it has been reported that *trans*-hydrostannation of alkynes can be performed regio- and stereoselectively by a Lewis acid such as $ZrCl_4$ or $HfCl_4$.[4] There have been also other methods in which alkenylstannanes are indirectly prepared by metalstannation of alkynes,[5] transmetallation of the alkenyl group[6] or homologation of aldehydes with *n*-$Bu_3SnCHBr_2$.[7] We report here a new and general route to both (*E*)- and (*Z*)-1-alkenyltributylstannanes using a cross-coupling reaction of (*E*)- and (*Z*)-1-alkenyldialkylboranes with tributyltin halide.

The reaction procedure for preparation of (*E*)-1-alkenyltributylstannane (**2**) is very simple. Thus, successive treatment of (*E*)-1-alkenyldialkylborane (**1**), obtained by hydroboration of 1-alkyne with dialkylborane in THF, with 1 equiv of 2M-NaOH at room temperature and 1 equiv of tributyltin chloride (*n*-Bu_3SnCl) in the presence of a catalytic amount of $Cu(acac)_2$[8] (5 mol%) at –15 °C to room temperature provided **2** in excellent yields with high stereoselectivity. For example, as shown in Scheme 1, (*E*)-3-methoxy-1-propenyldicyclohexylborane (**1a**), prepared by the hydroboration of 3-methoxy-1-propyne with dicyclohexylborane, reacted with *n*-Bu_3SnCl to produce **2a**[9] in 86% isolated yield, based on 3-methoxy-1-propyne, with high isomeric purity (> 99%) (entry 1 in Table 1).

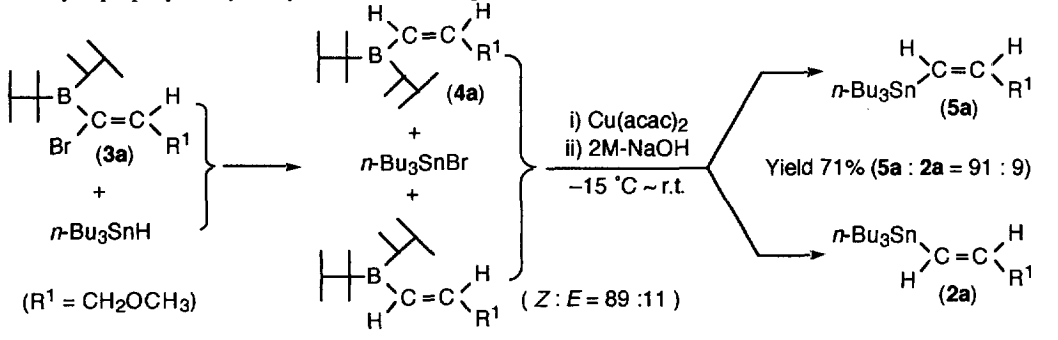


Scheme 1

Similarly, (*E*)-1-hexenyldicyclohexylborane (**1b**), (*E*)-3,3-dimethyl-1-butenyldicyclohexylborane (**1c**) and

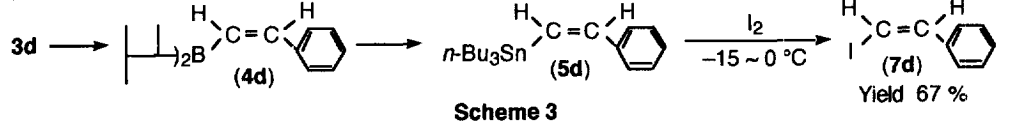
(*E*)-2-phenylethenyldisiamylborane (**1d**) were transformed into the corresponding **2** in excellent yields with > 99% isomeric purity (entries 3, 5 and 7), demonstrating that this reaction is a synthetically useful method for **2**.

Previously, we have reported that the reaction of (*Z*)-1-halo-1-alkenyldialkylborane (**3**), prepared by hydroboration of 1-halo-1-alkyne with the more hindered dialkylborane than dicyclohexylborane, with tributyltin hydride (*n*-Bu_3SnH) underwent dehalogenation with inversion of configuration of the boron moiety to give (*Z*)-1-alkenyldialkylborane (**4**) in a stereoselective manner.[10] Treatment of the above reaction mixture containing **4** and *n*-Bu_3SnX, generated *in situ* by dehalogenation, with a base in the presence of $Cu(acac)_2$ was expected to produce (*Z*)-1-alkenyltributylstannane (**5**) under similar reaction conditions to those depicted in Scheme 1. As expected, (*Z*)-3-methoxy-1-propenyltributylstannane (**5a**)[11] (91% *Z*) was produced in 71% isolated yield (entry 2), based on 1-bromo-3-methoxy-1-propyne, by successive treatment of (*Z*)-1-bromo-3-methoxy-1-propenylsiamylthexylborane (**3a**) as depicted in Scheme 2.



Scheme 2

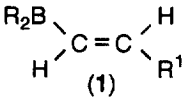
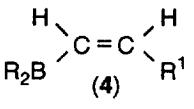
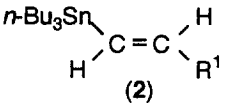
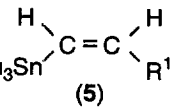
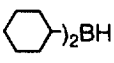
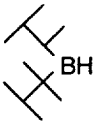
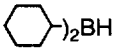
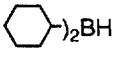
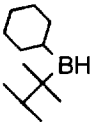
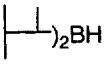
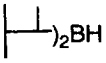
(*Z*)-1-Hexenylsiamylthexylborane (**4b**) and (*Z*)-3,3-dimethyl-1-butenylcyclohexylthexylborane (**4c**), obtained by the reaction of the corresponding **3** with *n*-Bu_3SnH, were also transformed into (*Z*)-1-hexenyltributylstannane (**5b**) (92% *Z*) and (*Z*)-3,3-dimethyl-1-butenyltributylstannane (**5c**) (93% *Z*) in 85 and 71 % isolated yields, respectively (entries 4 and 6). In the case of (*Z*)-2-phenylethenyldisiamylborane (**4d**), (*Z*)-2-phenylethenyltributylstannane (**5d**) was formed similarly, but the product could not be isolated by column chromatography due to isomerization to the *E*-isomer. The formation of **5d**, however, was confirmed by its conversion into the corresponding iododestannylation[12] product. In fact, treatment of the reaction mixture containing **5d** with iodine proceeded acceptably even under aqeous conditions to produce (*Z*)-1-iodo-2-phenylethene (**7d**) (92% *Z*) in 67% isolated yield.



Scheme 3

Although the mechanism for the $Cu(acac)_2$-catalyzed cross-coupling reaction has not been elucidated to date, we have observed that the reaction mixture is colored (blue or green) during the cross-coupling reaction with *n*-Bu_3SnX in the presence of $Cu(acac)_2$ and no homo-coupling product was formed without an electrophile such as n-Bu_3SnX. These observations indicate that the intermediate of the present reaction might be a certain alkenyl copper with a ligand rather than simple alkenyl copper.

Table 1 Reaction of (*E*)- or (*Z*)-1-alkenyldialkylborane with tributyltin halide in the presence of a catalytic amount of $Cu(acac)_2$ and aq. NaOH[a]

	 (1)		 (4)	 (2)	 (5)
Entry	R_2BH	R^1		Yield (%) [b]	*E*- : *Z*-Isomer [c]
1		CH_2OCH_3	(**1a**)	90 (86)	**2a** : **5a** = >99 : <1
2			(**4a**)	(71)	**2a** : **5a** = 9 : 91
3		*n*-C_4H_9	(**1b**)	85 (80)	**2b** : **5b** = >99 : <1
4			(**4b**)	90 (85)	**2b** : **5b** = 8 : 92 [d]
5		*t*-C_4H_9	(**1c**)	90 (86)	**2c** : **5c** = >99 : <1
6			(**4c**)	(71)	**2c** : **5c** = 7 : 93
7			(**1d**)	(86)	**2d** : **5d** = >99 : <1
8			(**4d**)	(67) [e]	**6d** [f] : **7d** [g] = 8 : 92

a) Reactions of **4** with *n*-Bu_3SnBr were carried out by successive treatment of **3** with 1 equiv of *n*-Bu_3SnH at room temperature for 1 h and 1 equiv of 2M-NaOH in the presence of 5 mol % of $Cu(acac)_2$ at –15 °C to room temperature. b) Determined by GLC analysis and based on 1-alkyne or 1-bromo-1-alkyne used. Unless otherwise stated, isolated yields after column chromatography on silanized silica gel are given in parentheses. c) Determined by GLC analysis. d) Determined by ^1H NMR analysis. e) Iododestannylation was carried out with 1.1 equiv of I_2 in THF at –15 to 0 °C. Silica gel was used for column chromatography. f) **6d** : (*E*)-1-iodo-2-phenylethene. g) **7d** : (*Z*)-1-iodo-2-phenylethene.

In summary, we have found that (*E*)- and (*Z*)-1-alkenyldialkylboranes can be stereoselectively converted into the corresponding 1-alkenyltributylstannanes by using a $Cu(acac)_2$-catalyzed cross-coupling reaction. This procedure provides a new and interesting approach for regio- and stereoselective preparation of both (*E*)- and (*Z*)-1-alkenyltributylstannanes *via* alkenylborane from 1-alkynes and 1-bromo-1-alkynes in a one-pot manner. Further studies on the mechanism and the scope of this reaction are currently underway.

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2. For example, see: (a) Nakamura, E.; Imanishi, Y.; Machii, D. *J. Org. Chem.*, **1994**, *59*, 8178–8186; (b) Nozaki, K.; Oshima, K.; Utimoto, K. *Tetrahedron*, **1989**, *45*, 923–933 and references therein.
3. For example, see: (a) Ma, Y.; Huang, X. *Synth. Commun.*, **1997**, *27*, 225–229; (b) Boden, C. D. J.; Pattenden, G.; Ye, T. *J. Chem. Soc., PerkinTrans. 1*, **1996**, 2417–2419; (c) Alami, M.; Ferri, F. *Synlett*, **1996**, 755–756 and references therein.
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5. For example, see: (a) Boden, C. D. J.; Pattenden, G.; Ye, T. *J. Chem. Soc., Perkin Trans. 1*, **1996**, 2417–2419; (b) Barbero, A.; Cuadrado, P.; Fleming, I.; Gonzalez, A. M.; Pulido, F. J.; Rubio, R. *J. Chem. Soc., Perkin Trans. 1*, **1993**, 1657–1662; (c) Sharma, S.; Oehlschlager, A. C. *J. Org. Chem.*, **1989**, *54*, 5064–5073 and references therein.
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8. We have already reported cross-coupling reactions of alkenyldialkylboranes with allyl or 1-alkynyl bromide using $Cu(acac)_2$ as catalyst, see: (a) Hoshi, M.; Masuda, Y.; Arase, A. *Bull. Chem. Soc. Jpn.*, **1983**, *56*, 2855–2856; (b) Hoshi, M.; Masuda, Y.; Nunokawa, Y.; Arase, A. *Chem. Lett.*, **1984**, 1029–1032.
9. ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 0.8—1.0 [m, 15H, $Sn(CH_2CH_2CH_2Me)_3$, incl. at 0.88 (t, J = 7.1 Hz, 9H)], 1.1—1.7 [m, 12H, $Sn(CH_2CH_2CH_2Me)_3$], 3.34 (s, 3H, OMe), 3.95 (dd, J = 4.9 and 1.0 Hz, 2H, CH_2O), 6.06 (dt, J = 19.2 and 4.9 Hz, 1H, =CH), 6.21 (dt, J = 19.2 and 1.0 Hz, 1H, SnCH=); ^{13}C NMR (200 MHz, $CDCl_3$, TMS) δ 9.4 (CH_2 x 3), 13.7 (Me x 3), 27.3 (CH_2 x 3), 29.1 (CH_2 x 3), 57.9 (CH_2O), 76.3 (MeO), 131.3 (CH=), 144.4 (CH=); IR (film) 2956, 2925, 2871, 2852, 2817, 1461, 1116, 1099, 995, 688, 596 cm^{-1}.
10. Hoshi, M.; Takahata, K.; Arase, A. *Tetrahedron Lett.*, **1997**, *38*, 453–456.
11. ^{1}H NMR ($CDCl_3$, TMS) δ 0.8—1.0 [m, 15H, $Sn(CH_2CH_2CH_2Me)_3$, incl. at 0.89 (t, J = 7.1 Hz, 9H)], 1.1—1.7 [m, 12H, $Sn(CH_2CH_2CH_2Me)_3$], 3.33 (s, 3H, OMe), 3.90 (dd, J = 5.4 and 1.5 Hz, 2H, CH_2O), 6.09 (dt, J = 13.2 and 1.5 Hz, 1H, SnCH=), 6.62 (dt, J = 13.2 and 5.4 Hz, 1H, =CH); ^{13}C NMR ($CDCl_3$, TMS) δ 10.7 (CH_2 x 3), 13.7 (Me x 3), 27.3 (CH_2 x 3), 29.2 (CH_2 x 3), 58.0 (CH_2O), 75.2 (MeO), 131.8 (CH=), 143.9 (CH=); IR (film) 2956, 2922, 2852, 1458, 1114, 999, 642, 594, 501 cm^{-1}.
12. Iododestannylation of alkenylstannanes proceeds with retention of configuration. For example, see: (a) Ensley, H. E.; Buescher, R. R.; Lee, K. *J. Org. Chem.*, **1982**, *47*, 404–408; (b) Tolstikov, G. A.; Miftakhov, M. S.; Danilova, N. A.; Vel'der, Ya. L. *Synthesis*, **1986**, 496–499; (c) Zhang, H. X.; Guibe, F.; Balavvoine, G. *J. Org. Chem.*, **1990**, *55*, 1857–1867.

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