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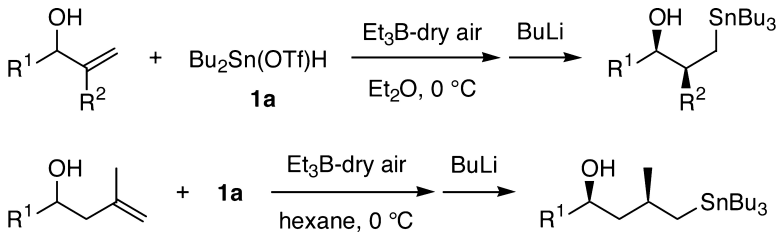

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Highly Diastereoselective Hydrostannylation of Allyl and Homoallyl Alcohols with Dibutyl(trifluoromethanesulfoxy)stannane

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Heteroatom-substituted alkylstannanes are valuable as synthetic equivalents of functionalized alkyl anions.[1] Hydrostannylation of alkenes with hydrostannanes provides convenient routes to alkylstannanes bearing a heteroatom(s) at the β- or a more remote position.[1,2] Particularly, hydrostannylation reactions involving stannyl radicals are quite useful because they are tolerant of various polar functionalities and applicable to both unactivated and activated alkenes.[3] However, there are few examples of diastereoselective synthesis of functionalized alkylstannanes by alkene hydrostannylation.[4] We have previously reported that dibutyl(trifluoromethanesulfoxy)stannane ($Bu_2Sn(OTf)H$, **1a**) realizes highly regio- and stereoselective homolytic hydrostannylation of various alkynols.[5] The high Lewis acidity of **1a** plays a crucial role for the regio- and stereocontrol.[6] We herein report highly diastereoselective hydrostannylation of allyl and homoallyl alcohols with **1a**, which is the first example of acyclic stereocontrol in hydrostannylation of unactivated alkenes.[4]

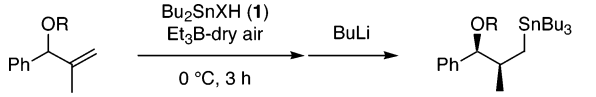
We initially examined the hydrostannylation of allyl alcohol **2a** to optimize the reaction conditions (Table 1). Hydrostannane **1a** reacted spontaneously with **2a** in hexane at 0 °C. Butylation of the reaction mixture with BuLi gave γ-stannylated alcohol **3a** in moderate yield with good *syn* diastereoselectivity (entry 1). Addition of Et_3B−dry air as radical initiator increased not only the reaction rate but also the *syn* selectivity (entry 2).[7] The use of Et_2O as solvent also was effective in improving the diastereoselectivity. Thus the Et_3B-initiated hydrostannylation of **2a** with **1a** in Et_2O achieved high *syn* selectivity (entry 3).[8] Under the same conditions, Bu_2SnClH (**1b**), a less Lewis acidic hydrostannane, added to **2a** efficiently, but the diastereoselectivity was rather low (entry 5). Additionally, methyl ether **2a′** was inferior to **2a** in both reactivity and stereoselectivity (entry 6). These results suggest that a strong Sn−O coordination brings about the successful hydrostannylation of **2a** with **1a**.[9]

The present hydrostannylation using **1a** was applied to other allyl alcohols **2b**−**g** (Table 2). The Et_3B-initiated reactions of **2b**−**d** at 0 °C gave the corresponding γ-stannylated alcohols **3b**−**d**, respectively, with good to high *syn* selectivity (entries 1−3). The stereoselectivity increased with an increase in the bulkiness of the α-substituent R^1. Treatment of **2e**,**f** with **1a** at 0 °C resulted in exclusive formation of deoxygenated alkenes.[10] Lowering the reaction temperature to −78 °C effectively suppressed this undesired reaction to afford **3e**,**f** in good yield (entries 4 and 5). Allyl alcohol **2g**, bearing an electron-withdrawing group at the β-position, also underwent the stereoselective hydrostannylation with **1a** (entry 6). γ-Substituted allyl alcohol **2h** as well as **2e**,**f** was converted into the corresponding deoxygenated alkenes at 0 °C. The reaction at −78 °C gave the desired product **3h** as a single isomer (entry 7).[11]

We next examined the hydrostannylation of homoallylic alcohols **4** with **1a**. The Et_3B-initiated reaction of **4a** in Et_2O at 0 °C gave δ-stannylated alcohol **5a** in high yield with *syn* selectivity (96%, *syn*:*anti* = 83:17). The stereoselectivity could be improved by using hexane as solvent (Scheme 1). Under these conditions, **4b**−**d** also underwent highly efficient and highly stereoselective hydrostannylation. The extent of diastereoselectivity was not so sensitive to the bulkiness of the α-substituent R^1 as that in the reaction of allyl alcohols **2**. The hydrostannylation of **4e** followed by butylation formed stannylated lactone **6** with high *cis* selectivity.

The hydrostannylation reactions of **2a** and **4a** with **1a** were suppressed by galvinoxyl, a radical scavenger, and accelerated by Et_3B−dry air. Accordingly, the present hydrostannylation proceeds probably via the radical chain mechanism involving a β-stannylalkyl

Table 1. Hydrostannylation of Allyl Alcohol **2a** with **1**[a]

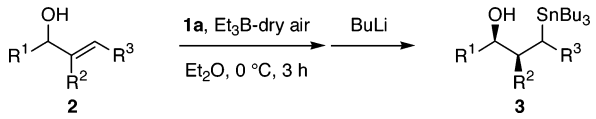


2a, R = H; **2a'**, R = Me — **3a**, R = H; **3a'**, R = Me

entry	X (Bu_2SnXH)	substrate	solvent	yield (%)[b]	*syn*:*anti*[c]
1[d]	OTf (**1a**)	**2a**	hexane	66	89:11
2	OTf	**2a**	hexane	74	92:8
3	OTf	**2a**	Et_2O	75	97:3
4	OTf	**2a**	THF	75	95:5
5	Cl (**1b**)	**2a**	Et_2O	72	79:21
6[e]	OTf	**2a′**	Et_2O	8	83:17

[a] Unless otherwise noted, the initial hydrostannylation step was carried out with **1** (1.10 mmol), **2a** (1.00 mmol), Et_3B (1.0 M in hexane, 0.050 mmol), and dry air (5 mL) in solvent (2 mL) at 0 °C. The resultant mixture was diluted with Et_2O (2 mL) and treated with BuLi (1.6 M in hexane, 2.5 mmol) at 0 °C for 20 min. [b] Isolated yield. [c] Determined by ^1H NMR analysis of the isolated product. [d] The hydrostannylation was performed without Et_3B−dry air for 6 h. [e] The butylation was performed with BuLi (1.2 mmol) at −78 °C for 30 min.

Table 2. Hydrostannylation of Allyl Alcohols **2** with **1a**[a]



2 — **3**

	Substrate					
entry	R^1	R^2	R^3		yield (%)[b]	*syn*:*anti*[c]
1	Me	Me	H	**2b**	88	84:16
2	*i*-Pr	Me	H	**2c**	75	95:5
3	*t*-Bu	Me	H	**2d**	71	97:3
4[d,e,f]	4-MeO−Ph	Me	H	**2e**	68	92:8
5[d,e,g]	1-naphthyl	Me	H	**2f**	83	93:7
6[e,h]	Ph	CO_2Me	H	**2g**	64	92:8
7[d,e]	Ph	$(CH_2)_4$		**2h**	83	*i*

[a−c] See footnotes *a*−*c* in Table 1. [d] The hydrostannylation was performed at −78 °C for 6 h. [e] The butylation was performed at −78 °C for 30 min. [f] With Et_3B (0.2 mmol) and dry air (20 mL). [g] With Et_3B (0.1 mmol). [h] With BuLi (2.2 mmol). [i] Single isomer. For the relative configuration, see the Supporting Information.

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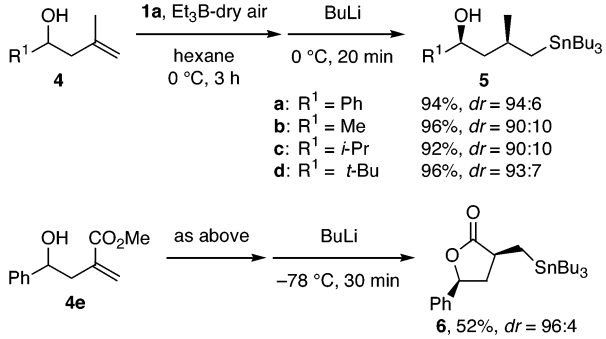
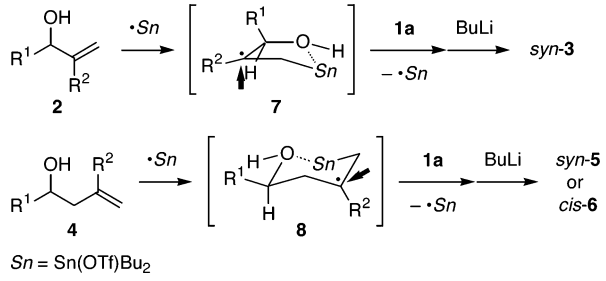
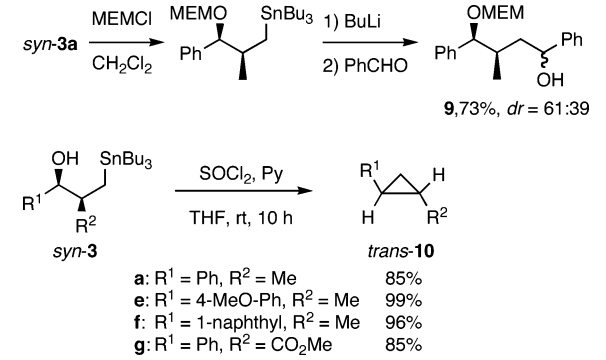
Scheme 1. Hydrostannylation of Homoallyl Alcohols **4** with **1a**



Scheme 2. Origin of Stereochemical Outcomes



Scheme 3. Synthetic Use of Stannylated Alcohols **3**



radical intermediate. Judging from the importance of a strong Sn−O coordination in the stereocontrol, the origin of the stereochemical outcomes can be reasonably explained by chelation models of the radical intermediates (**7** and **8** in Scheme 2).[12] In the hydrostannylation of **2**, H-abstraction of **7** from **1a** occurs from the opposite side to R^1 to avoid its steric hindrance, affording *syn*-**3** predominantly. The radical **8** arising from **4** has a six-membered chelate ring, which takes a chairlike form bearing R^1 at the equatorial position. Since equatorial attack of **1a** to the radical center is sterically favored over axial attack, H-abstraction of **8** followed by butylation provides *syn*-**5** or *cis*-**6**.

To enhance the synthetic utility of the present stereoselective hydrostannylation, γ-stannylated alcohols *syn*-**3** were utilized for C−C bond formation (Scheme 3). Transmetalation of the MEM ether of *syn*-**3a** with BuLi and subsequent reaction with benzaldehyde gave 1,4-diol monoether **9** as a diastereomeric mixture with no erosion of the 1,2-*syn* relative configuration.[13] Upon treatment with pyridine and thionyl chloride, *syn*-**3** could be converted into *trans*-1,2-disubstituted cyclopropanes **10**.[14]

In conclusion, we have demonstrated that the Lewis acidic hydrostannane **1a** is valuable for highly stereoselective homolytic hydrostannylation of allyl and homoallyl alcohols. The formation of the Sn−O coordinate bond in the β-stannylalkyl radical intermediate would be the key factor of the present diastereocontrol. This work provides a novel example of acyclic stereocontrol of radical reactions.

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Supporting Information Available: Experimental details and characterization data (^{1}H NMR, ^{13}C NMR, IR, elemental analysis). This material is available free of charge via the Internet at http://pubs.acs.org.

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