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Stereoselective Dehalogenation of (*Z*)-1-Halo-1-alkenyldialkylborane with Tributyltin Hydride: The Behavior of Tributyltin Hydride as a Hydride Donor

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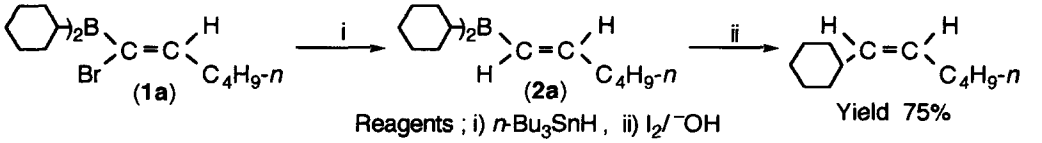
Abstract: The reaction of (*Z*)-1-halo-1-alkenyldialkylborane (**1**) with tributyltin hydride (*n*-Bu_3SnH) at 0 °C or room temperature results in reductive removal of the halogen atom to afford (*E*)- or (*Z*)-1-alkenyldialkylborane whose stereochemistry depends on the dialkylboryl group and the alkenyl group of **1**.

Alkenylboranes have been shown to be potential intermediates in organic synthesis.[1] In our study of the chemistry of substituted alkenylborane having one or more functionalities in the neighborhood of the carbon–carbon double bond,[2] our interest focused on the reaction of (*Z*)-1-halo-1-alkenyldialkylborane (**1**) with tributyltin hydride (*n*-Bu_3SnH) which is widely used for radical chain reactions.[3] We envisioned that the use of *n*-Bu_3SnH would produce a new type of reaction of alkenylborane whose radical process in organic synthesis had not yet been explored. In this communication, we describe that the reaction of **1** with *n*-Bu_3SnH results in stereocontrolled formation of (*E*)-1-alkenyldialkylborane (**2**) by a radical process or (*Z*)-1-alkenyldialkylborane (**3**) by an ionic process where *n*-Bu_3SnH acts either as a radical source or as a hydride donor.

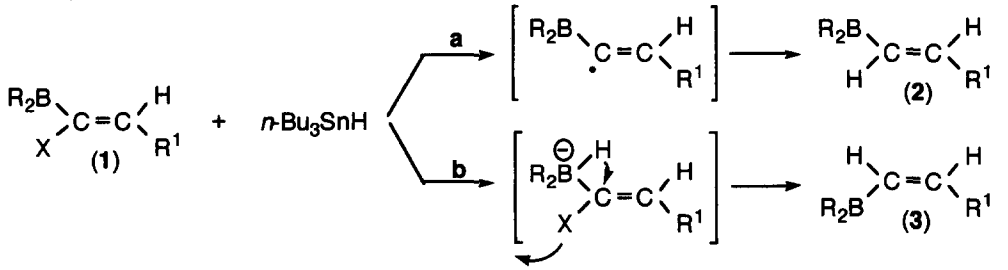
We examined the reaction of (*Z*)-1-bromo-1-hexenyldicyclohexylborane (**1a**), obtained by hydroboration of 1-bromo-1-hexyne with dicyclohexylborane, with *n*-Bu_3SnH in tetrahydrofuran (THF) at 0 °C for 1 h. In the ^1H NMR spectrum of the reaction mixture, a triplet at 6.05 ppm arising from the alkenyl proton of **1a** disappeared completely while a couple of double triplets appeared at 6.20 and at 6.73 ppm (J = 17.6 Hz, *trans* alkenyl protons) indicating that (*E*)-1-hexenyldicyclohexylborane (**2a**) was formed in a stereoselective manner. This result suggests that the displacement of the bromine atom of **1a** by the hydrogen atom of *n*-Bu_3SnH occurs with retention of configuration. The formation of **2a** was further confirmed by a rearrangement reaction where an alkyl group from the boron atom of (*E*)-1-alkenyldialkylborane migrates to the α-alkenyl carbon atom with inversion of configuration at the migration terminus to provide (*Z*)-alkene.[4] Thus, (*Z*)-1-cyclohexyl-1-hexene was obtained in 75% yield with high stereoselectivity (99%) by *in situ* treatment of the above reaction mixture with aq. NaOH and iodine (Scheme 1).



Scheme 1

To clarify the radical process, we carried out the above reaction in the presence of galvinoxyl (2 mol%), a radical scavenger, followed by treatment with aq. NaOH and iodine. In this case, the yield of (*Z*)-1-cyclohexyl-1-hexene decreased to only 10%. The inhibition by galvinoxyl suggests that the reaction occurs in a radical process (path **a** in Scheme 2).

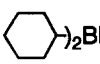
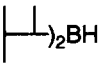
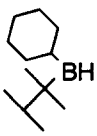
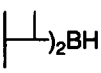
The reactions of several types of **1** with *n*-Bu_3SnH were conducted at 0 °C or at room temperature for 1 h. The results obtained by ^1H NMR analysis are summarized in Table 1. The reaction of (*Z*)-1-bromo-1-hexenyldisiamylborane (**1b**) gave a mixture of (*E*)-1-hexenyldisiamylborane (**2b**) and its *Z*-isomer (**3b**) in a ratio of 46 : 54. In a similar reaction employing (*Z*)-1-bromo-1-hexenylsiamylthexylborane (**1c**), (*E*)-1-hexenylsiamylthexylborane (**2c**) and its *Z*-isomer (**3c**) were formed in the ratio 10 : 90. These results showed that the *Z*-isomer increased with an increase of the bulkiness of the dialkylboryl group of **1**. More remarkable results were demonstrated in the reaction of (*Z*)-1-bromo-3,3-dimethyl-1-butenyldialkylborane whose alkenyl group is very bulky. Thus, the reaction of (*Z*)-1-bromo-3,3-dimethyl-1-butenyldicyclohexylborane (**1d**) having a less bulky diakylboryl group proceeded with retention of configuration to provide (*E*)-3,3-dimethyl-1-butenyldicyclohexylborane (**2d**) in >99% isomeric purity, to the contrary, the reaction of (*Z*)-1-bromo-3,3-dimethyl-1-butenylcyclohexylthexylborane (**1e**) having a bulkier diakylboryl group proceeded with inversion of configuration to provide (*Z*)-3,3-dimethyl-1-butenylcyclohexylthexylborane (**3e**) in >99% isomeric purity. To our knowledge, there is no example where completely opposite stereoselectivity is accomplished merely by changing the bulkiness of the dialkylboryl group. In marked contrast to the case of **1a**, the reaction of **1c** with *n*-Bu_3SnH was not inhibited by the presence of galvinoxyl, indicating that **3c** was formed through an ionic process.[5] It has been known that the reaction of **1** with inversion of configuration proceeds through an ate-complex formation.[2a-d,6] Accordingly, we speculate that, in the case of sterically very hindered **1** where the approach of the tributyltin radical (*n*-$Bu_3Sn\bullet$) to the halogen atom of **1** is rather difficult, the reaction proceeds predominantly through the ate-complex formed by transfer of a hydride from *n*-Bu_3SnH to give **3** (path **b** in Scheme 2).



Scheme 2

Interestingly, the reaction of (*Z*)-1-bromo-2-phenylethenyldisiamylborane (**1f**) with *n*-Bu_3SnH gave (*Z*)-2-phenylethenyldisiamylborane (**3f**) exclusively, demonstrating a marked contrast to the reaction of **1b**. Another interesting result was obtained in the reactions of (*Z*)-1-iodo-2-phenylethenyldicyclohexylborane (**1g**) and (*Z*)-1-iodo-2-phenylethenyldisiamylborane (**1h**). Thus, in the presence of a small amount of air the reaction provided (*Z*)-2-phenylethenyldialkylborane (**3g** and **3h**=**3f**) in 99% isomeric purity, whereas in the absence of air the reaction gave a mixture of (*E*)- and (*Z*)-2-phenylethenyldialkylborane. On the other hand, no change in the ratio of stereoisomers by addition of air was observed in the reaction of (*Z*)-1-bromo-1-alkenyldialkylborane such as **1f**. Although no mechanistic study has been made on the effect of air, oxygen in the added air may

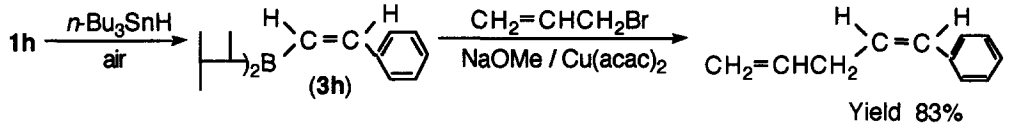
Table 1 The reaction of (*Z*)-1-halo-1-alkenyldialkylboranes with tributyltin hydride [a]

	R_2BH	X	R^1	Alkenyl protons (δ) [b] (2) / (3)	Ratio **2** : **3** [c]
a	 $)_2BH$	Br	*n*-C_4H_9	**2a**-1-H 6.20 (dt, *J*=17.6 and 1.2 Hz) **2a**-2-H 6.73 (dt, *J*=17.6 and 6.5 Hz)	>99 : <1 [d] (99 : 1) [e]
b	 $)_2BH$			**2b**-1-H 6.20 (dt, *J*=17.6 and 1.2 Hz) [f] 6.25 (dt, *J*=17.6 and 1.2 Hz) **2b**-2-H 6.69 (dt, *J*=17.6 and 6.4 Hz) [f] 6.74 (dt, *J*=17.6 and 6.4 Hz) **3b** 5.90—6.00 (m, 2H)	46 : 54 [d] (45 : 55) [e]
c	 BH			**3c** 5.60—5.85 (m, 2H)	10 : 90 [g]
d	 $)_2BH$	Br	*t*-C_4H_9	**2d** 5.44 (s, 2H)	>99 : <1 [g]
e	 BH			**3e** 5.34 (d, *J*=15.6 Hz) 5.68 (d, *J*=15.6 Hz)	<1 : >99 [g]
f	 $)_2BH$	Br		**3f** 6.24 (d, *J*=15.1 Hz) [f] 6.25 (d, *J*=15.1 Hz) 6.94 (d, *J*=15.1 Hz)	1 : 99 [g] (1 : 99) [e,g]
g	 $)_2BH$	I		**3g** 6.17 (d, *J*=15.1 Hz, 1H) [h,i]	31 : 69 [d] (1 : 99) [e]
h	$)_2BH$			**3h** = **3f**	35 : 65 [d] (1 : 99) [e]

a) The reaction of **1** (1mmol) with *n*-Bu_3SnH (1 mmol) was carried out for 1 h. b) ^1H NMR spectra of the reaction mixture, after removal of THF, were obtained in $CDCl_3$ solutions containing TMS. c) Determined by ^1H NMR spectra of the reaction products. d) Carried out at 0 °C. e) In the presence of a small amount of air (1 ml). f) A mixture of two diastereoisomers in the ratio of *ca.* 1 : 1. g) Carried out at room temperature. h) Signal of the other alkenyl proton overlapped that of phenyl protons. i) One of the alkenyl protons of **2g**, prepared by hydroboration of phenylethyne, appeared as a doublet at δ 7.00 (*J*=18.3 Hz).

inhibit the reaction of path **a** in Scheme 2. These results suggest that the ratio of stereoisomers is affected not only by the bulkiness of the dialkylboryl group of **1** but also by both the inductive effect of R^1 in **1** and the bond energy of the carbon–halogen bond.

The stereoselective preparation of **3** is of importance in application of alkenylboranes to the synthesis of stereodefined compounds, because **3** having *Z*-configuration in the alkenyl moiety can not be obtained by the usual hydroboration of 1-alkyne with dialkylborane. Another important characteristic of the present reaction is that the preparation of **3** from **1** is accomplished under neutral conditions in marked contrast to other methods[7] in which strong basic reagents are used. The potential usefulness of the present reaction in organic synthesis is demonstrated in the following cross-coupling reaction[8] as well as in the migration reaction depicted in Scheme 1. For example, the copper(II) acetylacetonate-catalyzed cross-coupling reaction of **3h** with 3-bromopropene afforded (*Z*)-1-phenyl-1,4-pentadiene[9] in 83% overall yield in a one-pot manner from the preparation of disiamylborane (Scheme 3).



Scheme 3

In summary, we have found that *n*-Bu_3SnH acts as a hydride donor as well as a source of *n*-$Bu_3Sn\bullet$ for **1** and the reaction of **1** with *n*-Bu_3SnH provides a practically applicable method for the preparation of **3**, potential intermediates. Studies on the mechanism and the synthetic scope of this reaction are now in progress.

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9. ^1H NMR (200 MHz, $CDCl_3$) δ 3.00—3.15 (m, 2H, CH_2), 5.00—5.25 (m, 2H, CH_2=), 5.70 (dt, *J* = 11.5 and 7.6 Hz, 1H, 2-H), 5.80—6.05 (m, 1H, =CH), 6.52 (br d, *J* = 11.5 Hz, 1H,1-H), 7.10—7.45 (m, 5H, aromatic H); ^{13}C NMR ($CDCl_3$) δ 32.7 (CH_2), 115.3 (CH_2=), 126.7 (CH=), 128.2 (CH= x 2), 128.6 (CH= x 2), 129.4 (CH=), 130.1 (CH=), 136.6 (CH=), 137.3 (C=); IR (film) 1637, 914, 767, 698 cm^{-1}.

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