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Highly (*E*)-Selective $\text{BF}_3 \cdot \text{Et}_2\text{O}$ Promoted Allylboration of Chiral Nonracemic α -Substituted Allylboronates and Analysis of the Origin of Stereocontrol

Ming Chen and William R. Roush

Department of Chemistry, Scripps Florida, Jupiter, Florida 33458

Abstract

γ -Methyl substituted homoallylic alcohols **2** were prepared in 71–88% yield, $E:Z > 30:1$ and 93% to >95% e.e. via $\text{BF}_3 \cdot \text{Et}_2\text{O}$ -promoted allylboration with α -Me-allylboronate **1**. The origin of high *E* selectivity is proposed.

The asymmetric carbonyl allylboration reaction is a valuable method for C–C bond formation. In the vast majority of cases that have been described, the asymmetric induction derives from the use of chiral auxiliaries attached to boron.^{1,2} Although not as widely adopted in the literature, the addition of enantioenriched α -substituted allylboronates to carbonyl compounds is a useful alternative.^{3–5} Pioneered by Hoffmann *et al.*, carbonyl addition reactions of enantioenriched α -substituted allylboronates **3** proceed with near perfect chirality transfer.^{3–4} A mixture of (*Z*)- and (*E*)-homoallylic alcohols **4**, **5** can be generated from two competing transition states **TS-3** and **TS-4** (Figure 1). The ratio of the two homoallylic alcohols depends in part on the electronic property of the group at the α -position. When the α -substituent is a polar group,³ such as an alkoxy group or halogen atom, allylboration proceeds predominately via **TS-3** to give (*Z*)-homoallylic alcohol **4**. Although the exact origin of the high (*Z*)-selectivity remains unclear, several factors, including steric effects, dipolar effects, and stereoelectronic minimization of π - σ^* delocalization in the transition states have been proposed^{3l} and supported by computational studies.^{4s} However, when the α -substitution is a nonpolar alkyl group,^{4,5} a mixture of (*Z*)- and (*E*)-homoallylic alcohols, **4** and **5**, is often obtained. Until recently, synthetically useful selectivity has

roush@scripps.edu .

Supporting Information Available: Experimental procedures and spectroscopic data for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

proven challenging to achieve with enantioenriched α -alkyl substituted allyl- or (*E*)-crotylboronates.⁵¹⁻ⁿ 9

Lewis or Brønsted acid promoted allylboration with allylboronate reagents is an important emerging topic in carbonyl allylation chemistry.⁶⁻⁷ As demonstrated by Hall and coworkers, allylboration in the presence of catalytic amount of a chiral, nonracemic Lewis or Brønsted acid provides homoallylic alcohols in high yields and excellent enantioselectivities.⁸ However, Lewis or Brønsted acid promoted allylboration with enantioenriched, α -substituted allylboronates largely remains underdeveloped.⁹ Recently, Hall reported the enantioselective synthesis and Lewis acid promoted allylboration of α -TMSCH₂ substituted allylboronates that generate (*E*)- δ -TMSCH₂-substituted homoallylic alcohols with excellent selectivities.^{9c}

In connection with an ongoing problem in natural product synthesis, we had occasion to explore Lewis acid promoted allylboration of enantioenriched α -substituted allylboronates. We found and report herein that (*E*)- δ -methyl-homoallylic alcohols **2** are obtained in good yields and excellent enantioselectivities from BF₃·Et₂O promoted allylboration reactions of **1**.¹⁰ In addition, we have found that δ -chloro-substituted homoallylic alcohols **14** can also be obtained in good yield and 3-6:1 (*E*)-selectivity from BF₃·Et₂O promoted allylboration reactions of **13**. The origin of (*E*)-selectivity in these reactions is proposed.

α -Methyl-substituted allylboronate **8** was prepared from methyl boronate **6**,¹¹ by using the Matteson homologation (Scheme 1).¹² Allylboration reactions of hydrocinnamaldehyde with **8** are summarized in Table 1. The non-catalyzed reaction provided a 1:1.4 mixture of *ent*-**2a** and **9** (entry 1). Similar results were obtained when the reaction was performed in the presence of 10% Sc(OTf)₃ (entry 2). When the reaction was carried out in the presence of either 10% or stoichiometric BF₃·Et₂O, a 3:1 mixture of *ent*-**2a** and **9** was obtained (entries 3 and 4). In spite of additional attempts to optimize this reaction, we were unable to achieve synthetically useful selectivity in allylboration reactions of **8**.

Pinanediol is a useful chiral director for the Matteson homologation.¹³ We hoped that allylboronate **1** would provide access to the desired (*E*)-homoallylic alcohols with excellent selectivity based on Hall's work.^{9c} Accordingly, allylboronate **1** was prepared with high diastereoselectivity from **10** (Scheme 2).¹⁴

Results of allylboration of hydrocinnamaldehyde with reagent **1** are presented in Table 2. The reaction in the absence of Lewis acid gave a 1.5:1 mixture of alcohols **2a** and *ent*-**9** (entry 1). With the addition of 10% Sc(OTf)₃, a 3:1 mixture of **2a** and *ent*-**9** was obtained (entry 2). Gratifyingly, when the reaction was carried out in the presence of 10% BF₃·Et₂O, (*E*)-homoallylic alcohol **2a** was obtained as the only product (*E*:*Z* > 30:1) in 94% e.e. and 79% yield (entry 3).

As summarized in Table 3, BF₃-mediated allylboration of a variety of aldehydes using **1** proceeded with near perfect chirality transfer. (*E*)- δ -Methyl-substituted homoallylic alcohols **2a-2f** were obtained in 93% to >95% e.e. and 71-88% yield. The corresponding (*Z*)-isomers were not detected in any of these experiments.

We suspect the high (*E*)-selectivity in these reactions originates from minimization of 1,3-*syn*-pentane interactions in the competing transition states.¹⁶ As shown in Figure 2, it is conceivable that BF₃ will coordinate to the lower lone pair of electrons (in blue) of the oxygen atom distal to the angular methyl group to minimize steric interactions.¹⁷ If so, **TS-1** is disfavored due to a 1,3-*syn*-pentane interaction between the pseudo-axial methyl group and the BF₃ ligand; this interaction is absent in **TS-2**. Accordingly, product formation

proceeds via **TS-2** and homoallylic alcohols with (*E*)-olefin geometry are obtained with excellent selectivity.

We were intrigued by the possibility that $\text{BF}_3 \cdot \text{Et}_2\text{O}$ promoted aldehyde allylboration could be used to induce (*E*)-selectivity with reagents that have much higher intrinsic preference for positioning of the α -substituent in a pseudo-axial position in the allylboration transition state. α -Chloro-substituted allylboronates, such as **13**, are known to give (*Z*)- δ -chloro-substituted homoallylic alcohols, e.g., **15**, with high (*Z*)-selectivity in allylboration reactions.³

The sensitive α -chloro-substituted allylboronates **13a** and **13b** were synthesized and their allylboration reactions were explored (Table 4). The reaction of hydrocinnamaldehyde with **13a** in the absence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ provided (*Z*)- δ -chloro-homoallylic alcohol **15a** in 72% yield.¹⁸ Similarly, crotylboration with **13b** gave alcohol **15b** in 70% yield.¹⁸ In both cases, high (*Z*)-selectivity ($\geq 10:1$) was observed, consistent with Hoffmann's report.³ However, when these reactions were performed in the presence of 10% $\text{BF}_3 \cdot \text{Et}_2\text{O}$, reagent **13a** provided a 6:1 mixture of δ -chloro-homoallylic alcohols **14a** and **15a**.¹⁸ and reagent **13b** provided a 3:1 mixture of alcohols **14b** and **15b**.¹⁸

These data indicate that the strong preference of reagents **13** to react with aldehydes via a transition state analogous to **TS-5** (but lacking the BF_3 ligand) can be overridden in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$. As shown in Figure 3, **TS-5** is disfavored owing to the 1,3-*syn*-pentane interaction. In the competing (and now favored) transition state **TS-6**, the α -Cl substitution is positioned in a pseudo-equatorial arrangement to minimize interactions with the chlorine substituent. Ultimately, these reactions lead to the formation of (*E*)-homoallylic alcohols **14** with 3-6:1 (*E*)-selectivity.

In summary, we demonstrated the highly (*E*)-selective allylboration of aldehydes with reagent **1** in the presence of catalytic amount of $\text{BF}_3 \cdot \text{Et}_2\text{O}$. (*E*)- δ -Methyl substituted homoallylic alcohols **2** were prepared in 71-88% yield and excellent enantioselectivities. (*E*)- δ -Chloro substituted homoallylic alcohols **14** were also obtained in good yields and 3-6:1 (*E*)-selectivity from reagents **13a, b**. We postulate that minimization of 1,3-*syn*-pentane interactions in the transition states is responsible for the (*E*)-selectivity of these reactions.

Supplementary Material

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Figure 1.
Competing transition states for carbonyl addition reaction of α -substituted allylboronates **3**

Scheme 1.
Synthesis of Allylboronate **8**

Scheme 2.
Synthesis of Allylboronate **1**

Figure 2.
Competing transition states for BF_3 -catalyzed aldehyde allylboration with α -methyl allylboronate **1**

Figure 3.
Competing transition states for BF_3 -catalyzed aldehyde allylboration with α -chloro allylboronates **13**

Table 1

Optimization for Allylboration Reactions with **8**

entry	conditions	<i>ent</i> -2a:9 ^a	yield ^b
1	No catalyst, −78 °C - rt, 8 h	1:1.4	67%
2	10% Sc(OTf) ₃ , −78 °C - rt, 8 h	1:1.5	63%
3	10% BF ₃ ·Et ₂ O, −78 °C, 2 h	3:1	78%
4	100% BF ₃ ·Et ₂ O, −78 °C, 2 h	3:1	71%

^aBased on ¹H NMR analysis of the crude reaction mixture.

^bYield of isolated mixture of products.

Table 2Optimization for Allylboration Reactions with **1**

entry	conditions	2a:ent-9 ^a	yield ^b
1	No catalyst, -78 °C - rt, 8 h	1.5:1	71%
2	10% Sc(OTf) ₃ , -78 °C - rt, 8 h	3:1	64%
3	10% BF ₃ ·Et ₂ O, -78 °C, 2 h	> 30:1	79%
4	100% BF ₃ ·Et ₂ O, -78 °C, 2 h	> 30:1	68%

^aBased on ¹H NMR analysis of the crude reaction mixture.^bYield of isolated product(s).

Table 3Preparation of (*E*)- δ -Me-Homoallylic Alcohols **2a-2f**

entry	RCHO	product	yield ^a	% e.e. ^b
1	Ph(CH ₂) ₂ CHO	2a	79%	> 95
2	PhCH ₂ CHO	2b	88%	> 95
3	PhCHO	2c	75%	94
4	CyCHO	2d	71%	> 95
5	BnO(CH ₂) ₂ CHO	2e	84%	93
6	BnOCH ₂ CHO	2f	73%	95

^aYield of isolated (*E*)-homoallylic alcohols.^bEnantiomeric purity and absolute stereochemistry of **2a-2f** were determined by using the Mosher ester analysis.¹⁵

Table 4

Allylboration with α -Cl-Allylboronates **13**

<p> 12a, R = H 12b, R = Me </p> <p> i. CH_2Cl_2, BuLi, $-100\text{ }^\circ\text{C}$ ii. ZnCl_2, $-78\text{ }^\circ\text{C}$, 3 h </p> <p> $\text{13a, R = H, 84\%}$ $\text{13b, R = Me, 72\%}$ </p> <p> conditions $\text{Ph}(\text{CH}_2)_2\text{CHO}$ CH_2Cl_2, 4 Å MS </p> <p> 14a, R = H 14b, R = Me </p> <p> 15a, R = H 15b, R = Me </p>			
entry	conditions	14:15 ^a	yield ^b
1	13a , No catalyst, $-78\text{ }^\circ\text{C}$ - rt, 24 h	1:12	72%
2	13b , No catalyst, $-78\text{ }^\circ\text{C}$ - rt, 24 h	1:10	70%
3	13a , 10% $\text{BF}_3\cdot\text{Et}_2\text{O}$, $-78\text{ }^\circ\text{C}$, 24 h	6:1	63%
4	13b , 10% $\text{BF}_3\cdot\text{Et}_2\text{O}$, $-78\text{ }^\circ\text{C}$, 24 h	3:1	52%

^aBased on ^1H NMR analysis of the crude reaction mixture.^bYield of isolated product(s).