Allylation Reactions

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Rhodium-Catalyzed Reaction of 1-Alkenylboronates with Aldehydes Leading to Allylation Products**

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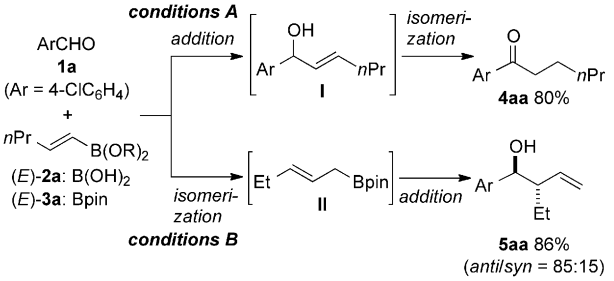
Dedicated to Professor Alfredo Ricci on the occasion of his retirement

The allylation reaction of carbonyl compounds with γ-substituted allylboron reagents is one of the most reliable procedures for the regio- and diastereoselective synthesis of homoallylic alcohols, and hence, is widely used in organic synthesis.[1] As the stereochemistry of the C–C double bond of the substituted allylboron reagent dictates the stereochemistry of the resultant homoallylic alcohols, it is crucial to obtain stereochemically defined γ-substituted allylboron reagents. Conventional preparative methods for allylboron reagents include: 1) the substitution reaction of boron compounds with allylmetal reagents and 2) the substitution reaction of halomethylboron compounds with alkenylmetal reagents. Recently, different approaches[2–7] have been developed to address the issue associated with the lability of allyboron reagents towards hydrolysis, a feature which often hampers chromatographic isolation of the isomers; one approach is to generate a substituted allylboron reagent in situ and immediately treat it with a carbonyl compound. For example, a ruthenium(IV)-catalyzed cross-metathesis reaction of 2-propenylboronate and an alkene generates an (*E*)-γ-substituted allylboronate and the subsequent addition of an aldehyde to the reaction mixture results in an allylation reaction to furnish a homoallylic alcohol with moderate to high *anti* selectivity.[3] A palladium(0)-catalyzed substitution reaction of an allylic alcohol with diboronic acid generates an *E*-γ-substituted allylboronic acid, which reacts with a coexisting aldehyde to give a homoallylic alcohol with high *anti* selectivity.[4] Hydroboration of an allene with Soderquist borane (10-TMS-9-BBD-H) generates a (*Z*)-γ-substituted allylborane and the subsequent addition of an aldehyde produces a homoallylic alcohol with moderate to high *syn* selectivity.[5] We envisaged that an alkene isomerization reaction[8] could be utilized for the generation of γ-substituted allylboronates (2-alkenylboronates) from 1-alkenylboronates, which are readily accessible by the hydroboration of terminal alkynes. Iridium(III) and nickel(0) complexes are known to catalyze such isomerization reactions.[9] However, the substrates have been limited to 3-alkoxy- and 3-siloxy-1-alkenylboronates, and it is believed that the oxygen substituent at the 3-position directs the isomerization, as is the case with allylic ether/vinylic ether isomerization. There has been no report about the use of simple 1-alkenylboron compounds as the substitute of 2-alkenylboron reagents. We describe herein a one-pot allylation reaction of aldehydes with 1-alkenylboronates, a convenient and straightforward method for the synthesis of stereodefined homoallylic alcohols from terminal alkynes and aldehydes.

The reaction of 4-chlorobenzaldehyde (**1a**) with (*E*)-1-pentenylboronic acid (**2a**) was initially examined in the presence of a rhodium(I) catalyst (Scheme 1). As reported by Miyaura and co-workers,[10] 4-chlorophenyl pentyl ketone



Scheme 1. A rhodium-catalyzed reaction of **1a** with (*E*)-**2a** and (*E*)-**3a**. Conditions A: **1a** (0.2 mmol), (*E*)-**2a** (0.3 mmol), [{Rh(OH)(cod)}$_2$] (2.5 mol%), and dppf (5 mol%) in 1,4-dioxane/H_2O (6:1, 2 mL) for 12 h at 100°C. Conditions B: **1a** (0.2 mmol), (*E*)-**3a** (0.3 mmol), [Rh(nbd)(CH$_3$CN)$_2$]SbF$_6$ (5 mol%), and dppm (5 mol%) in DCE (2 mL) for 12 h at 90°C. Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl, cod = cyclooctadiene, dppf = 1,1′-bis(diphenylphosphino)ferrocene, dppm = bis(diphenylphosphino)methane, DCE = 1,2-dichloroethane, nbd = norbornadiene.

(**4aa**) was isolated in 80% yield when **1a** (1.0 equiv) was treated with (*E*)-**2a** (1.5 equiv) in the presence of [{Rh(OH)(cod)}$_2$] (2.5 mol%) and dppf (5 mol%) in 1,4-dioxane/H_2O (6:1) at 100°C for 12 hours (conditions A). An alkenylrhodium(I) species is generated in situ by the transmetalation of (*E*)-**2a** by rhodium(I) complex and adds to the aldehyde **1a** to give the allylic alcohol **I**. Alkene isomerization and keto/enol tautomerization follow to afford **4aa**.

We investigated the reaction conditions in detail using (*E*)-1-pentenylboronic acid (**2a**) and its ester (*E*)-**3a** to find reaction conditions under which a different product, that is, homoallylic alcohol **5aa**, was selectively obtained as the C–C

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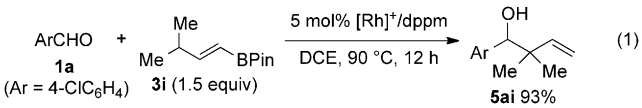
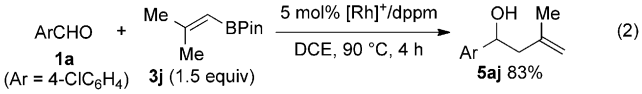
bond forming product. When **1a** (1.0 equiv) was treated with (*E*)-1-pentenylboronic pinacolate (**3a**, 1.5 equiv) in the presence of $[Rh(nbd)(CH_3CN)_2]SbF_6$ (5 mol%) and dppm (5 mol%)[11] in 1,2-dichloroethane at 90°C for 12 hours (conditions B), 1-(4-chlorophenyl)-2-ethylbut-3-en-1-ol (**5aa**) was isolated in 86% yield with reasonable diastereoselectivity (*anti*/*syn* = 85:15).[12] The formation of the homoallylic alcohol **5aa** is accounted for by the following pathway (Scheme 1, bottom). The rhodium(I) catalyst promotes alkene isomerization of (*E*)-**3a** rather than transmetalation (boron to rhodium), thus generating 2-pentenylboronate **II**. Then, addition of **II** to **1a** spontaneously occurs via a six-membered chair-like transition state to produce **5aa**. The *anti* selectivity observed with **5aa** suggests the preferential formation of the *E* isomer of 2-pentenylboronate **II** in the isomerization process or the preferencial carbonyl addition of the *E* isomer over the *Z* isomer of **II** (see below).[13] While the transmetalation/carbonyl addition precede alkene isomerization under conditions A using the hydroxorhodium(I) species in protic media, alkene isomerization precedes the carbonyl addition under conditions B. We assume that, under conditions B in which there is no hydroxide ligand on rhodium and no nucleophilic H_2O in the media, transmetalation is retarded and isomerization is facilitated by the cationic rhodium center.

Thus, it had been proven that simple 1-alkenylboronates could be used as the substitute of 2-alkenylboron reagents. The *E* isomers of other 1-alkenylboronates **3b–e**, which were readily accessible by simple *cis* hydroboration of terminal alkynes with pinacolborane,[14] were subjected to the rhodium(I)-catalyzed allylation reaction with **1a** (Table 1). (*E*)-1-Butenylboronate **3b** and (*E*)-3-cyclopentyl-1-propenylboronate **3c** gave the corresponding homoallylic alcohols **5ab** and **5ac**, respectively, with good diastereoselectivities (Table 1, entries 1 and 2). The reaction of (*E*)-3-isopropyl- and (*E*)-3-phenyl-1-propenylboronates **3d** and **3e**, having a bulkier substituent at the 3-position, showed a higher diastereoselectivity (Table 1, entries 3 and 4).

We also examined the use of the corresponding *Z* isomers of **3a–e**, which were accessible by the rhodium(I)-catalyzed *trans*-hydroboration reaction of terminal alkynes developed by Miyaura and co-workers.[15] The *Z* isomers underwent an allylation reaction with **1a** to give the homoallylic alcohols **5aa–ae** in comparable or better yields than the *E* isomers (Table 1, entries 5–9). It was noteworthy that all *Z* isomers of **3a–e** showed much higher diastereoselectivities (*anti*/*syn* = 94:6 ≈ > 99:1) than the corresponding *E* isomers. Thus, (*Z*)-1-alkenylboronates proved better substitutes for (*E*)-2-alkenylboronates in terms of reactivity as well as stereoselectivity. In addition, functionalized (*Z*)-1-alkenylboronates **3f–h**, having siloxy, benzoyloxy, and 1,3-dioxoisoindolin-2-yl groups in the alkyl chain also afforded *anti*-homoallylic alcohols **5af–ah** stereoselectively in high yields (Table 1, entries 10–12). Furthermore, the reactions with 3-methyl-1-butenylboronate **3i** and 2-methyl-1-propenylboronate **3j** proceeded in an analogous manner to give the homoallylic alcohols **5ai** and **5aj**, respectively, in high yields [Eqs. (1) and (2)].

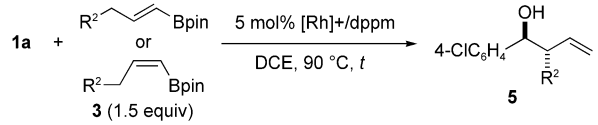


(1)



(2)

Table 1: Allylation reaction of **1a** with alkenylboronates **3b–h**.[a]

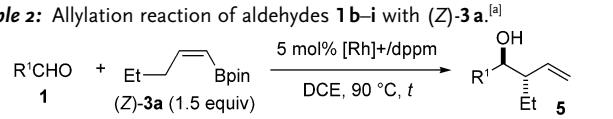


Entry	**3**	R^2	**5**	*t* [h]	Yield [%][b]	*anti*/*syn*[c]
1	(*E*)-**3b**	Me	**5ab**	12	71	89:11
2	(*E*)-**3c**	*c*-pent	**5ac**	24	89[d]	88:12
3	(*E*)-**3d**	*i*Pr	**5ad**	24	86[e]	96:4
4	(*E*)-**3e**	Ph	**5ae**	12	91	96:4
5	(*Z*)-**3a**	Et	**5aa**	12	86	96:4
6	(*Z*)-**3b**	Me	**5ab**	12	91	98:2
7	(*Z*)-**3c**	*c*-pent	**5ac**	24	89[d]	94:6
8	(*Z*)-**3d**	*i*Pr	**5ad**	12	91[e]	> 99:1
9	(*Z*)-**3e**	Ph	**5ae**	12	95	> 99:1
10	(*Z*)-**3f**	$(CH_2)_3OTBS$	**5af**	12	91	97:3
11	(*Z*)-**3g**	$(CH_2)_3OBz$	**5ag**	12	97	99:1
12	(*Z*)-**3h**	$(CH_2)_3N(Phth)$	**5ah**	12	93	96:4

[a] Reaction conditions: **1a** (0.4 mmol), **3** (0.6 mmol), $[Rh(nbd)(CH_3CN)_2]SbF_6$ (5 mol%), and dppm (5 mol%) in DCE (4 mL) for 12 h at 90°C. [b] Yield of the isolated product. [c] Determined by ^1H NMR spectroscopy. [d] Using **3c** (1.2 mmol) and 10 mol% of $[Rh(nbd)(CH_3CN)_2]SbF_6$/dppm. [e] Using **3d** (1.2 mmol) and 7.5 mol% of $[Rh(nbd)(CH_3CN)_2]SbF_6$/dppm. Bz = benzoyl, Phth = phthaloyl ,TBS = *tert*-butyldimethylsilyl.

Next, the scope of aldehydes was examined using (*Z*)-**3a** (Table 2). An electronically and sterically diverse array of aromatic aldehydes **1b–g** reacted to give the homoallylic alcohols **5ba–ga** in yields ranging from 82% to 96% with high

Table 2: Allylation reaction of aldehydes **1b–i** with (*Z*)-**3a**.[a]

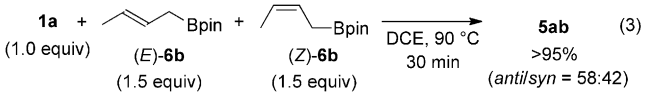


Entry	**1**	R^1	**5**	*t* [h]	Yield [%][b]	*anti*/*syn*[c]
1	**1b**	Ph	**5ba**	12	90	96:4
2	**1c**	$4\text{-}NO_2C_6H_4$	**5ca**	3	94	99:1
3	**1d**	$4\text{-}MeO_2CC_6H_4$	**5da**	6	96	98:2
4	**1e**	$4\text{-}CH_3C(O)C_6H_4$	**5ea**	6	82	97:3
5	**1f**	$3\text{-}MeOC_6H_4$	**5fa**	12	94	98:2
6	**1g**	$2\text{-}MeC_6H_4$	**5ga**	12	90	95:5
7	**1h**	$PhCH_2CH_2$	**5ha**	12	79[d]	90:10
8	**1i**	Cy	**5ia**	24	62[e]	91:9

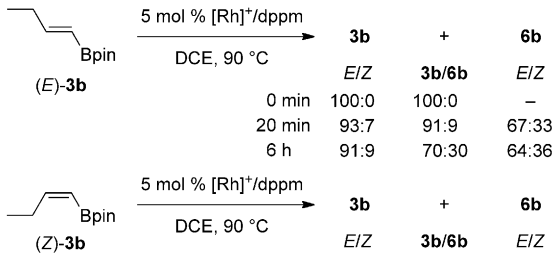
[a] Reaction conditions: **1** (0.4 mmol), (*Z*)-**3a** (0.6 mmol), $[Rh(nbd)(CH_3CN)_2]SbF_6$ (5 mol%), and dppm (5 mol%) in DCE (4 mL) for 12 h at 90°C. [b] Yield of the isolated product. [c] Determined by ^1H NMR spectroscopy. [d] Using (*Z*)-**3a** (1.2 mmol). [e] Using (*Z*)-**3a** (1.2 mmol) and 10 mol% of $[Rh(nbd)(CH_3CN)_2]SbF_6$/dppm. Cy = cyclohexyl.

diastereoselectivities (Table 2, entries 1–6). In addition, aliphatic aldehydes such as 3-phenylpropanal (**1h**) and cyclohexanecarbaldehyde (**1i**) also participated in the reaction. Slightly lower diastereoselectivities were observed with aliphatic aldehydes probably because they were less reactive than aromatic aldehydes and required a longer reaction time, during which the *E*/*Z* ratio of the intermediate 2-pentenylboronate could decrease (Table 2, entries 7 and 8). In contrast to the aldehydes, ketones such as acetophenone and methyl phenethyl ketone failed to undergo the allylation reaction with (*Z*)-**3a**.

The following experiments were carried out to obtain mechanistic insights into the isomerization/addition process. First, a 1:1 mixture of the *E* isomer (1.5 equiv) and *Z* isomer (1.5 equiv) of crotylboronate **6b** was reacted with **1a** (1.0 equiv) to compare their reactivities. The *anti*/*syn* ratio of the resulting homoallylic alcohol **5ab** (>95% yield) was 58:42, suggesting that *E* and *Z* isomers added to the aldehyde **1a** at comparable rates [Eq. (3)].

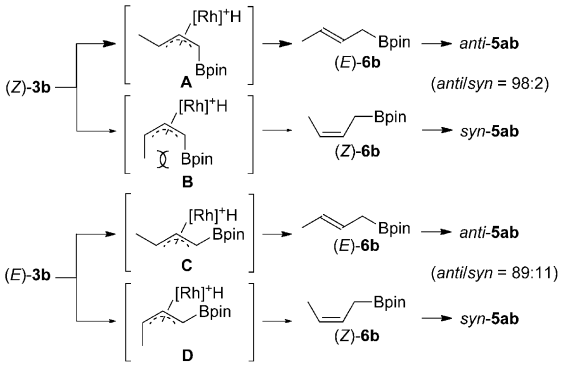


Secondly, (*E*)-1-butenylboronate **3b**, (*Z*)-1-butenylboronate **3b** and (*E*)-crotylboronate **6b** were separately treated with a catalytic amount of the rhodium(I) complex (90 °C, 1,2-dichloroethane) in the absence of the aldehyde **1a**, and their isomerization reactions were monitored by ^{1}H NMR spectroscopy after 20 minutes and 6 hours (Scheme 2). They all underwent isomerization in terms of both the stereochemistry and the position of the carbon–carbon double bond to give a mixture of (*E*)-**3b**, (*Z*)-**3b**, (*E*)-**6b**, and (*Z*)-**6b**. After 6 hours, mixtures of almost identical compositions [(*E*)-**3b**/(*Z*)-**3b**/(*E*)-**6b**/(*Z*)-**6b** = 64:6:19:11] resulted from (*E*)-**3b**, (*Z*)-**3b**, and (*E*)-**6b**. Thus, an equilibrium was reached after 6 h, and the ratio reflects the thermodynamic stabilities of the isomers. Initially, however, (*Z*)-**3b** isomerized faster and more selectively, in favor for (*E*)-**6b**, than (*E*)-**3b**. When starting from (*E*)-**3b**, after 20 minutes the ratio of (*E*)-**3b**/(*Z*)-**3b**/(*E*)-**6b**/(*Z*)-**6b** was 85:6:6:3, which meant that only 15% of (*E*)-**3b** had isomerized and that the *E*/*Z* ratio of the resulting **6b** was 67:33. In contrast, when starting from (*Z*)-**3b**, after 20 minutes the ratio of (*E*)-**3b**/(*Z*)-**3b**/(*E*)-**6b**/(*Z*)-**6b** was 28:20:49:3, which meant that 80% of (*Z*)-**3b** had isomerized and that the *E*/*Z* ratio of the resulting **6b** was >95:5. Thus, the most likely scenario to explain the highly stereoselective production of *anti*-homoallylic alcohol **5ab** from (*Z*)-**3b** is as follows; the double-bond isomerization of (*Z*)-**3b** occurs at the cationic rhodium center in a stereoselective manner to produce (*E*)-**6b**, which immediately reacts with **1a** via a six-membered transition state to afford the *anti*-configured **5ab**.



Scheme 2. A control experiment in the absence of aldehydes.

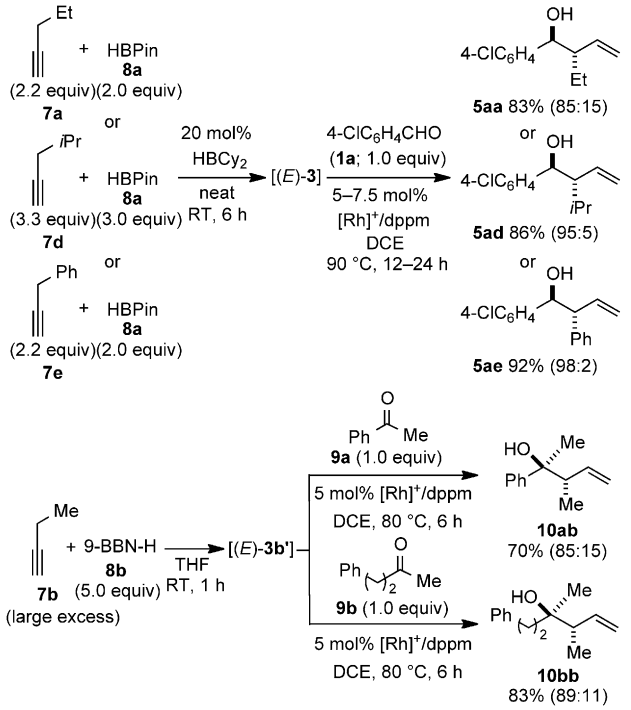
It is presumed that the isomerization of **3b** proceeds through π-allyl rhodium intermediates **A**–**D**[16] and is reversible (Scheme 3). When starting from (*Z*)-**3b**, the intermediate **A** would be significantly more stable than the intermediate **B** for steric reasons and the formation of (*E*)-**6b** is kinetically favored. The resultant (*E*)-**6b** immediately reacts with the aldehyde **1a** in a stereospecific way giving *anti*-**5ab**. Although (*E*)-**6b** is also more stable than (*Z*)-**6b**, the energy difference would be less than that between the intermediates **A** and **B**. Therefore, when the addition reaction to a carbonyl compound is slow, the initial kinetic preference for (*E*)-**6b** over (*Z*)-**6b** gradually decreases. This can account for the lower *anti*/*syn* selectivity observed with the products of the reactions with aliphatic aldehydes (Table 2, entries 7 and 8). When starting from (*E*)-**3b**, the intermediate **C** is more stable than the intermediate **D**, but the energy difference is less than that between the intermediates **A** and **B**. Therefore, the *E*/*Z* selectivity of **6b** under kinetic conditions is not as high as when starting from (*Z*)-**3b**. As shown in Table 1 (entries 3 and 4), (*E*)-**3d** and (*E*)-**3e** having isopropyl and phenyl groups at the 3-position exhibited higher *anti*-selectivity than (*E*)-**3b** having a methyl group at the 3-position. This can be also explained by an increase in the energy difference between intermediates corresponding to **C** and **D**.



Scheme 3. Proposed isomerization pathways through π-allyl rhodium intermediates.

Finally, a one-pot diastereoselective synthesis of homoallylic alcohols starting from terminal alkynes was carried out to demonstrate the practical convenience of the present

method (Scheme 4). Treatment of terminal alkynes **7** (2.2–3.3 equiv) with pinacolborane **8a** (2.0–3.0 equiv) in the presence of dicyclohexylborane (20 mol%) generated (*E*)-1-alkenylboronates **3**.[13] Then, 4-chlorobenzaldehyde **1a**



Scheme 4. A one-pot sequence via hydroboration/isomerization/allylation reaction.

(1.0 equiv) and a cationic rhodium(I)/dppm catalyst (5–7.5 mol%) were added to the reaction mixture to cause an isomerization/allylation reaction. After the mixture was stirred at 90°C for 12–24 hours, the corresponding homoallylic alcohols **5aa**, **5ad**, and **5ae** were isolated in high yields with good to high diastereoselectivities. Interestingly, even the ketones **9a** and **9b** successfully participated in the one-pot reaction when 9-borabicyclo[3.3.1]nonane (**8b**, 9-BBN-H) was used for the initial hydroboration reaction because the resulting allylborane intermediate was more reactive than the allylboronic esters.[17]

In summary, we have demonstrated that 1-alkenylboronates, which are readily synthesized by hydroboration of terminal alkynes,[14,15] act as the synthetic equivalent to γ-substituted allylboronates in the presence of a cationic rhodium(I) catalyst. The present reaction provides a unique method for the diastereoseletive synthesis of functionalized homoallylic alcohols.

Experimental Section

Typical procedure for the allylation reaction of aldehydes with (*Z*)-1-alkenylboronates (Table 1, entry 5): $[Rh(nbd)(CH_3CN)_2]SbF_6$ (10.3 mg, 0.02 mmol) and dppm (7.7 mg, 0.02 mmol) were added to an oven-dried side-arm tube. The tube was evacuated and refilled with argon. Then, 1,2-dichloroethane (1 mL) was added via syringe. A solution of **1a** (56.2 mg, 0.40 mmol) and (*Z*)-**3a** (117.7 mg, 0.60 mmol) in 1,2-dichloroethane (3 mL) was added to the resulting orange solution. After heating at 90°C for 12 h, the reaction mixture was cooled to room temperature. The mixture was passed through a pad of florisil (1.5 × 5 cm) and eluted with ethyl acetate (50 mL). The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on diol–SiO_2 (hexane/ethyl acetate = 97:3 ≈ 90:10) to give the product **5aa** as a colorless oil (72.7 mg, 0.345 mmol, 86% yield, *anti*/*syn* = 96:4).

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Keywords: aldehydes · allylation · diastereoselectivity · isomerization · rhodium

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