

Allylation Reactions

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

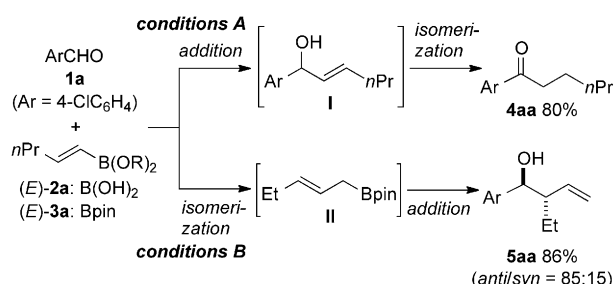
Hiroshi Shimizu, Tomohiro Igarashi, Tomoya Miura, and Masahiro Murakami*

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 allylboron 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/vinyl 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), $[\{\text{Rh}(\text{OH})(\text{cod})\}_2]$ (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), $[\text{Rh}(\text{nbd})(\text{CH}_3\text{CN})_2]\text{SbF}_6$ (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 $[\{\text{Rh}(\text{OH})(\text{cod})\}_2]$ (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

[*] H. Shimizu, T. Igarashi, Dr. T. Miura, Prof. Dr. M. Murakami
Department of Synthetic Chemistry and Biological Chemistry
Kyoto University, Katsura, Kyoto 615-8510 (Japan)
E-mail: murakami@sbchem.kyoto-u.ac.jp
Homepage: <http://www.sbchem.kyoto-u.ac.jp/murakami-lab/>

[**] This work was supported in part by MEXT (Grant-in-Aid for Scientific Research on Innovative Areas Nos. 22105005 and 22106520, Young Scientists (A) No. 23685019) and the Asahi Glass Foundation.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201105148>.

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)(CH₃CN)₂]SbF₆ (5 mol%) and dppe (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 preferential 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 H₂O 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-dioxoisindolin-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)].

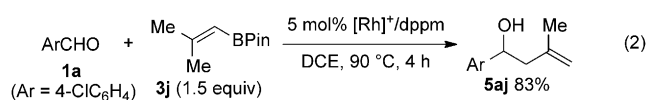
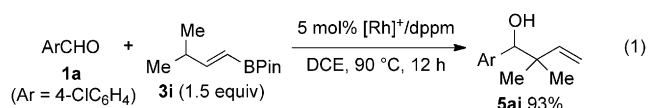


Table 1: Allylation reaction of **1a** with alkenylboronates **3b–h**.^[a]

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

[a] Reaction conditions: **1a** (0.4 mmol), **3** (0.6 mmol), [Rh(nbd)-(CH₃CN)₂]SbF₆ (5 mol%), and dppe (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)-(CH₃CN)₂]SbF₆/dppe. [e] Using **3d** (1.2 mmol) and 7.5 mol% of [Rh(nbd)-(CH₃CN)₂]SbF₆/dppe. 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

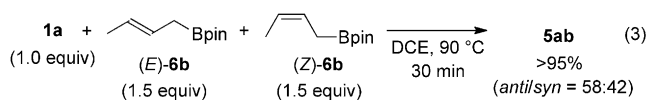
Table 2: Allylation reaction of aldehydes **1b–i** with (*Z*)-**3a**.^[a]

Entry	1	R ¹	5	t [h]	Yield [%] ^[b]	<i>anti/syn</i> ^[c]
1	1b	Ph	5ba	12	90	96:4
2	1c	4-NO ₂ C ₆ H ₄	5ca	3	94	99:1
3	1d	4-MeO ₂ C ₆ H ₄	5da	6	96	98:2
4	1e	4-CH ₃ C(O)C ₆ H ₄	5ea	6	82	97:3
5	1f	3-MeOC ₆ H ₄	5fa	12	94	98:2
6	1g	2-MeC ₆ H ₄	5ga	12	90	95:5
7	1h	PhCH ₂ CH ₂	5ha	12	79 ^[d]	90:10
8	1i	Cy	5ia	24	62 ^[e]	91:9

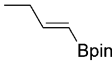
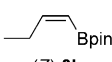
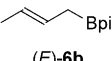
[a] Reaction conditions: **1** (0.4 mmol), (*Z*)-**3a** (0.6 mmol), [Rh(nbd)-(CH₃CN)₂]SbF₆ (5 mol%), and dppe (5 mol%) in DCE (4 mL) for 12 h at 90 °C. [b] Yield of the isolated product. [c] Determined by ¹H NMR spectroscopy. [d] Using (*Z*)-**3a** (1.2 mmol). [e] Using (*Z*)-**3a** (1.2 mmol) and 10 mol% of [Rh(nbd)-(CH₃CN)₂]SbF₆/dppe. 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)].



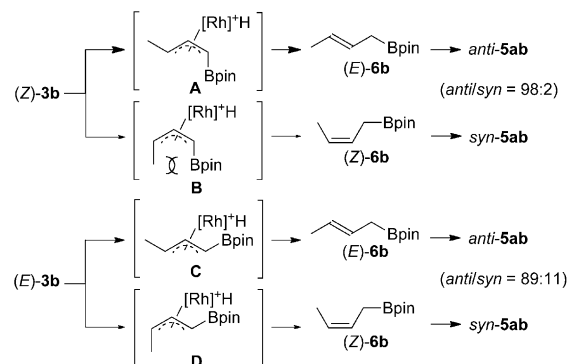
Secondly, (*E*)-1-butenylboronate **3b**, (*Z*)-1-butenylboronate **3b** and (*E*)-crotylboronate **6b** were separately treated with a catalytic amount of the rhodium(I) complex (90 °C, 1,2-dichloroethane) in the absence of the aldehyde **1a**, and their isomerization reactions were monitored by ¹H 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 selec-

 (<i>E</i>)- 3b	5 mol % [Rh] ⁺ /dppm			
	DCE, 90 °C	3b	+	6b
		<i>E/Z</i>	3b/6b	<i>E/Z</i>
	0 min	100:0	100:0	–
 (<i>Z</i>)- 3b	5 mol % [Rh] ⁺ /dppm			
	DCE, 90 °C	3b	+	6b
		<i>E/Z</i>	3b/6b	<i>E/Z</i>
	0 min	0:100	100:0	–
 (<i>E</i>)- 6b	5 mol % [Rh] ⁺ /dppm			
	DCE, 90 °C	3b	+	6b
		<i>E/Z</i>	3b/6b	<i>E/Z</i>
	0 min	–	0:100	100:0
	20 min	43:57	29:71	91:9
	6 h	92:8	70:30	66:34

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

tively, 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**.

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

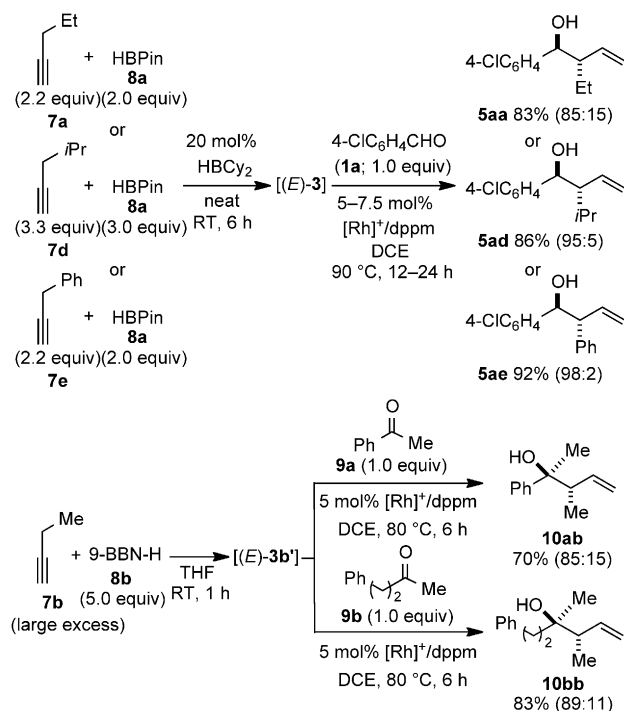


Scheme 3. Proposed isomerization pathways through π -allyl rhodium intermediates.

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**.

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 diastereoselective 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)(CH₃CN)₂]SbF₆ (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-SiO₂ (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).

Received: July 22, 2011

Published online: October 4, 2011

Keywords: aldehydes · allylation · diastereoselectivity · isomerization · rhodium

- [1] For reviews, see: a) W. R. Roush, *Comprehensive Organic Synthesis*, Vol. 2 (Eds.: B. M. Trost, I. Fleming, C. H. Heathcock), Pergamon, Oxford, UK, **1991**, pp. 1–53; b) S. R. Chemler, W. R. Roush, *Modern Carbonyl Chemistry* (Ed.: J. Otera), Wiley-VCH, Weinheim, **2000**, chap. 10; c) J. W. J. Kennedy, D. G. Hall, *Angew. Chem.* **2003**, *115*, 4880; *Angew. Chem. Int. Ed.* **2003**, *42*, 4732; d) S. E. Denmark, J. P. Fu, *Chem. Rev.* **2003**, *103*, 2763; e) H. Lachance, D. G. Hall, *Organic Reactions*, Vol. 73 (Ed.: S. E. Denmark), Wiley, New York, **2008**, and references therein.
- [2] J. W. J. Kennedy, D. G. Hall, *Boronic Acids* (Ed.: D. G. Hall), Wiley-VCH, Weinheim, **2005**, chap. 6, pp. 241–277.
- [3] S. D. Goldberg, R. H. Grubbs, *Angew. Chem.* **2002**, *114*, 835; *Angew. Chem. Int. Ed.* **2002**, *41*, 807.
- [4] a) N. Selander, S. Sebelius, C. Estay, K. J. Szabó, *Eur. J. Org. Chem.* **2006**, 4085; b) N. Selander, A. Kipke, S. Sebelius, K. J. Szabó, *J. Am. Chem. Soc.* **2007**, *129*, 13723; for a similar example, see: c) M. Kimura, T. Tomizawa, Y. Horino, S. Tanaka, Y. Tamaru, *Tetrahedron Lett.* **2000**, *41*, 3627.
- [5] J. Kister, A. C. DeBaillie, R. Lira, W. R. Roush, *J. Am. Chem. Soc.* **2009**, *131*, 14174.
- [6] For recent examples of preparation of α -substituted allylboron reagents, see: a) F. Peng, D. G. Hall, *J. Am. Chem. Soc.* **2007**, *129*, 3070; b) F. Possémé, M. Deligny, F. Carreaux, B. Carboni, *J. Org. Chem.* **2007**, *72*, 984; c) F. Berrée, N. Gernigon, A. Hercouet, C. H. Lin, B. Carboni, *Eur. J. Org. Chem.* **2009**, 329; d) M. Althaus, A. Mahmood, J. R. Suárez, S. P. Thomas, V. K. Aggarwal, *J. Am. Chem. Soc.* **2010**, *132*, 4025; e) M. Chen, W. R. Roush, *J. Am. Chem. Soc.* **2011**, *133*, 5744.
- [7] For examples of diastereoselective synthesis of homoallylic alcohols from aldehydes and nucleophilic precursors like 1,3-dienes, see: a) H. Y. Cho, J. P. Morken, *J. Am. Chem. Soc.* **2008**, *130*, 16140; b) H. Y. Cho, J. P. Morken, *J. Am. Chem. Soc.* **2010**, *132*, 7576; c) J. R. Zbieg, J. Moran, M. J. Krische, *J. Am. Chem. Soc.* **2011**, *133*, 10582.
- [8] For a recent review on transition-metal-catalyzed alkene isomerization, see: K. Tanaka, *Comprehensive Organometallic Chemistry III*, Vol. 10 (Eds.: R. H. Crabtree, D. M. P. Mingos, I. Ojima), Elsevier, Oxford, UK, **2007**, p. 71.
- [9] a) T. Moriya, A. Suzuki, N. Miyaara, *Tetrahedron Lett.* **1995**, 36, 1887; b) Y. Yamamoto, T. Miyairi, T. Ohmura, N. Miyaara, *J. Org. Chem.* **1999**, *64*, 296; c) Y. Yamamoto, K. Kurihara, A. Yamada, M. Takahashi, Y. Takahashi, N. Miyaara, *Tetrahedron* **2003**, *59*, 537; d) M. Murata, S. Watanabe, Y. Masuda, *J. Chem. Res. Synop.* **2002**, 142.
- [10] A. Takezawa, K. Yamaguchi, T. Ohmura, Y. Yamamoto, N. Miyaara, *Synlett* **2002**, 1733.
- [11] The following phosphine ligands gave inferior results (yield of **5aa**, as determined by ¹H NMR spectroscopy; *anti/syn*): PPh₃ (12 %, 50:50), P(2-furyl)₃ (76 %, 78:22), dppe (91 %, 82:18), and dppf (21 %, 81:19).

- [12] The reaction using chiral 1-alkenylboronic ester derived from tartaric acid diisopropyl ester (see: W. R. Roush, A. E. Walts, L. K. Hoong, *J. Am. Chem. Soc.* **1985**, *107*, 8186) gave low enantioselectivity, probably owing to the high reaction temperature.
- [13] When isolated (*E*)-crotylboronate **6b** (1.5 equiv) was reacted with **1a** (1.0 equiv) in 1,2-dichloroethane at 90 °C for 30 minutes, homoallylic alcohol **5ab** was formed in > 95 % yield with high *anti* selectivity (*anti/syn* => 95:5).
- [14] K. Shirakawa, A. Arase, M. Hoshi, *Synthesis* **2004**, 1814, and references therein.
- [15] T. Ohmura, Y. Yamamoto, N. Miyaura, *J. Am. Chem. Soc.* **2000**, *122*, 4990.
- [16] a) S. H. Bergens, B. Bosnich, *J. Am. Chem. Soc.* **1991**, *113*, 958; b) K. Hiroya, Y. Kurihara, K. Ogasawara, *Angew. Chem.* **1995**, *107*, 2445; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2287.
- [17] E. Canales, K. G. Prasad, J. A. Soderquist, *J. Am. Chem. Soc.* **2005**, *127*, 11572.
-