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Base-Catalysed Reductive Relay Hydroboration of Allylic Alcohols with Pinacolborane to Form Alkylboronic Esters

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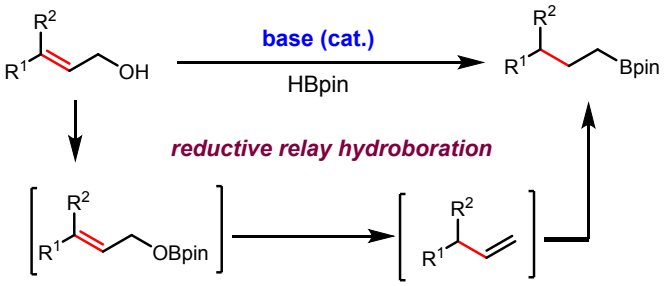
An unprecedented base-catalysed reductive relay hydroboration of allylic alcohols is described. Commercially available ^{n}BuLi was found to be a robust transition-metal-free initiator for this protocol, affording various boronic esters in high yield and selectivity. Mechanistically, this methodology involves a one-pot three-step successive process (dehydrocoupling / allylic hydride substitution/ anti-Markovnikov hydroboration).

Organoboronic esters are an important class of synthetic intermediates, which are commonly used in the field of total synthesis, drug development and materials science.[1] Organoboronic esters are attractive because of their easy availability, appropriate reactivity and stability, and low toxicity. The versatile C-B bonds can be transformed into a wide variety of products, including those bearing C-C, C-N, C-O, and C-X (X = halide) bonds.[2] Accordingly, numerous well-defined transition-metal complexes have been developed to enable highly selective hydroboration reactions of unsaturated hydrocarbons to form alkylboronic esters.[3,4] In addition, main group metals[5], and metal-free catalysis[6,7] have recently been reported to promote hydroboration of unsaturated bonds. However, in contrast, simple base-catalysed hydroboration of alkenes and alkynes[8] has been less investigated,[9] despite that it serves as a sustainable and easy to handle hydroboration method as no need of complicated preparation of ligands and catalysts.

On the other hand, metal-catalysed tandem alkene isomerization/hydroboration reactions[10,11] and cascade borylative reactions[12] have recently been advanced to afford borylated products otherwise synthesized in multi-step reactions. Such cascade reactions are highly desirable, as potentially tedious workup and purification steps can be avoided.[13] However, to our knowledge, a base-catalysed alkene isomerization and hydroboration sequential reaction remains unknown. We became interested in developing base-catalysed reductive relay hydroboration of allylic alcohols as a convenient approach to access alkylboronic esters (Scheme 1). In particular, we envisioned that a suitable base would promote a dehydrocoupling of allylic alcohols and pinacolborane,[14] and further promote a subsequent allylic hydride substitution to form a transient terminal alkene, which would then undergo hydroboration again to afford the alkylboronic ester products. If successful, this approach would be particularly attractive due to not only the abundance of a base catalyst but also the easy accessibility of starting materials[15] relative to the preparation of a specific terminal alkene bearing α-substitutions or toxic alkyl halides for borylation reactions[16]. We noted that, although the metal-catalysed allylic substitution with hydride nucleophiles is known,[17] the proposed base-catalysed allylic hydride substitution is an unprecedented process.[18] Moreover, base-catalysed hydroboration of α-alkene remain unexplored.[8] In addition, the control of regioselectivities in these multi-hydroboration processes is non-trivial.[3] Herein, as a continuation of our works on alkene hydroboration,[19] we report a base-catalysed reductive relay hydroboration of allylic



Scheme 1. Base-catalysed reductive relay hydroboration of allylic alcohols (this work)

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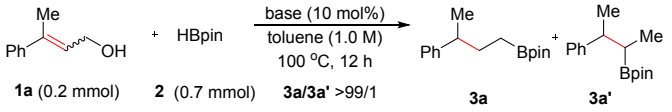
alcohols and derivatives with pinacolborane to prepare a wide variety of alkylboronic esters in one chemical step.

We started our investigation by examining hydroboration of 3-phenylbut-2-en-1-ol (**1a,** E/Z: 6/1) with HBpin to form alkylboronic ester **3a** in the presence of 10 mol% of various base catalysts (Table 1). At the outset, the control reaction between **1a** and HBpin was conducted at 100 °C in the absence of base, product **3a** formed in trace amount (entry 1). We reasoned that bases or nucleophiles could easily form adducts with Lewis acidic boranes (HBpin) to activate the B-H bonds with a more hydridic character,[20] which thus facilitate the hydroboration processes. Indeed, the use of base catalysts, including ^{t}BuOK, ^{t}BuONa, and ^{t}BuOLi, all promoted the hydroboration reactions, affording 52-69% yields of **3a** (entries 2-4). Surprisingly, the use of weak bases (KOAc and K_3PO_4) as an initiator for the hydroboration would deliver moderate yields of **3a**, while the reactions using KOH and CsF gave lower yields (entries 5-8). We rationalized that the potential bidentate coordination of acetate and phosphate anion to boron center might accelerate the hydroboration. We were pleased to find that ^{n}BuLi was the best catalyst for this cascade transformation, providing **3a** in 83% yield (entry 9). Finally, increasing the reaction temperature to 130 °C further improved the yield to 96% (entry 10). Importantly, all these reactions proceeded in excellent regioselectivity, delivering linear alkylboronic esters as a single isomer.

Table 1. Reaction optimization



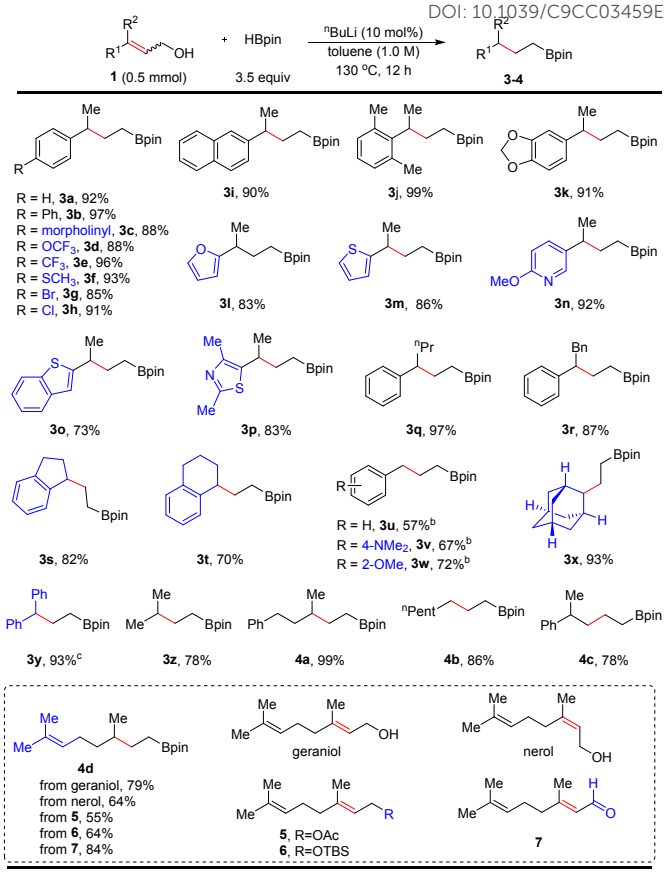
1a (0.2 mmol) **2** (0.7 mmol) **3a/3a'** >99/1 **3a** **3a'**

Entry	Base	Yield (%)[a]	Entry	Base	Yield (%)[a]
1	/	<5	6	K_3PO_4	52
2	^{t}BuOK	57	7	CsF	40
3	^{t}BuONa	52	8	KOH	9
4	^{t}BuOLi	69	9	^{n}BuLi	83
5	KOAc	61	10[b]	^{n}BuLi	96

[a]Yields were determined by NMR analysis using 1,3,5-trimethyl-benzene as an internal standard; the **3a**/**3a'** ratios were determined by GC-MS analysis of the crude reaction mixture. [b]Run at 130 °C.

With the optimized conditions in hand, we next investigated the scope of this novel reductive hydroboration protocol. As shown in Table 2, a diverse array of alkylboronic esters were prepared in high to excellent yields from a series of allylic alcohols substrates, including those bearing 3,3-alkyl, aryl substituents (**3a**-**3t**), 3,3-dialkyl substituents (**3z**, **4a**, **4d**), 3,3-diaryl substituents (**3y**), monoaryl (**3u**-**3w**) and monoalkyl substituents (**4b**, **4c**). In addition to acyclic substrates, the use of cyclic allylic alcohols also gave hydroborylated products in high yields (**3s**, **3t**, **3x**). The steric and electronic effects of aryl substituents were not sensitive to this cascade reaction. Moreover, substrates with many functional groups are compatible in this reaction, including ethers (**3k**, **3n**, **3w**), a thioether (**3f**), a trifluoromethyl group (**3e**), a trifluoromethoxyl

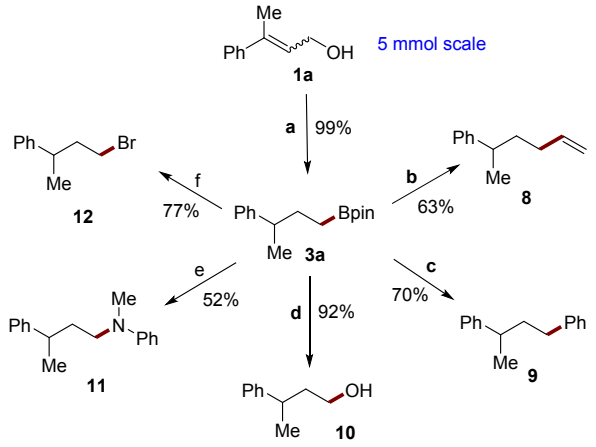
Table 2. Substrate scope[a]



[a]Isolated yields are given; Unless otherwise indicated, single regioisomer (>99/1) of hydroborated products were obtained. [b]24 h. [c]Linear/branched ratio is 94:6.

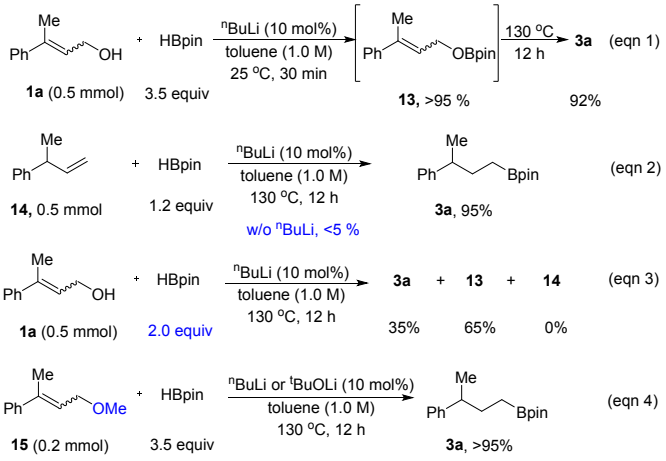
group (**3d**), amines (**3c**, **3v**) and trisubstituted alkenes (**4d**). Most remarkably, substrates possessing aryl bromide (**3g**), aryl chloride (**3h**), furan (**3l**), thiophene (**3m**), benzothiophene (**3o**), pyridine and thiazole (**3n**, **3p**), functional groups which are reactive to ^{n}BuLi through lithium-halogen exchange or deprotonation even at low temperature, participated in this reaction smoothly affording high yields of products. These results indicated that the reaction conditions be considerably mild as ^{n}BuLi was quenched through the formation of borane adducts with HBpin. To further examine the functional group compatibility of this protocol, an additive-based robustness screen was conducted.[21,22] The screen suggested the tolerance of the reaction to benzylic alcohols, acetals, secondary amines, morpholine, indoles, pyrroles, carbazoles, and benzothiadiazole. Ester, amide, and nitrile functional groups were likely reduced to alcohol and amines respectively under the reaction conditions although the product **3a** was obtained in high yields. The use of geraniol and nerol both gave good yields of alkylboronic ester product **4d**. Substrates with acetate (**5**) and silyl ether (**6**) leaving group also provided products in synthetically useful yields. Interestingly, the use of an enal **7** underwent a selective 1,2-reduction followed by the reductive relay hydroboration process to form **4d** in high yield. It is noteworthy that in all these cases trisubstituted alkene moieties were kept intact under these conditions.

Next, a gram-scale reaction (5 mmol scale) using **1a** was successfully performed to deliver alkylboronic ester **3a** in near quantitative yield, highlighting the practicality of the hydroboration method (Scheme 2). To further demonstrate the synthetic utility of our hydroboration method, we converted C-B bonds in **3a** into various important classes of carbon-carbon and carbon-heteroatom bonds.[23] For example, **3a** smoothly underwent vinylation and arylation to produce **8**[23a] and **9**[4d] in good efficiency, respectively. In addition, the subjection of **3a** to a typical oxidation condition and oxidative amination condition readily afforded an alcohol **10** and an amine **11**,[23b] respectively. Finally, simple bromination condition furnished alkyl bromide **12** in 77% yield.[23c] Given the easy availability of substrates and rich chemistry of organoboron compounds, the current reductive hydroboration protocol would provide a convenient and powerful mean of the transformation of allylic alcohols.



[a]**1a** (5.0 mmol, 1.3 g), ^{n}BuLi (10 mol %), HBpin (3.5 equiv), toluene (5.0 mL), 130 °C, 12 h. [b]1) **1c** (0.2 mmol), vinylmagnesium bromide (4.0 equiv), THF (3.0 mL), -78 °C, 30 min. 2) I_2 (4.0 equiv) in MeOH, r.t., 30 min.[c]**1c** (0.2 mmol), bromobenzene (1.5 equiv), $Pd(OAc)_2$ (10 mol %), rac-BINAP (0.12 equiv), NaOH (15.0 equiv), THF: H_2O (5:1, 1.2 mL), 100 °C, 16 h. [d]**1c** (0.2 mmol), $NaBO_3{}^{\bullet}H_2O$ (3.0 equiv), THF: H_2O (1:1, 2. mL), r.t., 6 h. [e]**1c** (0.2 mmol), N-methylaniline (1.5 equiv), ^{t}BuOO^{t}Bu (2 equiv), $Cu(OAc)_2$ (5 mol%), toluene (2.0 mL), 80 °C, 24 h. [f]1) **1c** (0.2 mmol), phenyllithium (2.0 equiv), THF (1.0 mL), r.t., 30 min. 2) NBS (2.0 equiv), THF (1.0 mL), r.t., 1 h.

Scheme 2. Gram-scale reaction and transformation of **3a**.



Scheme 3. Mechanistic experiments

To further understand the mechanism of this reaction, we performed some additional experiments (Scheme 3). Firstly, the reaction of **1a** with HBpin at the room temperature in the presence of 10 mol% ^{n}BuLi gave a nearly quantitative yield of dehydrocoupling product (**13**) as determined by ^{1}H and ^{11}B NMR analysis (eqn 1). Increasing the temperature to 130 °C converted **13** to product **3a** in high yield (eqn 1). Besides, the formation of $(pinB)_2O$ was observed by ^{11}B NMR analysis. Then, we found that alkene **14** undergo the hydroboration in similarly high efficiency under the standard reaction conditions, indicating **14** could be the real hydroboration precursor to form product **3a** (eqn 2). As expected, no hydroboration reaction of **14** occurred in the absence of ^{n}BuLi. Additionally, when the model reaction was run using 2.0 equiv HBpin under the standard conditions, we observed the formation of **13** and product **3a**, but without the detection of alkene **14**, which suggests the hydroboration of transient terminal alkene might be fast and not the rate-limiting step. Finally, the use of methyl ether of **1a** (**15**) also gave **3a** in a nearly quantitative yield (eqn 4). On the basis of these results, we proposed a plausible catalytic cycle for this reaction. As shown in Figure 1, a dehydrocoupling of allylic alcohol and HBpin give **13**.[14] Further base-promoted regioselective hydroboration of **13** and subsequent β-oxygen elimination (path a) or an S_N2' allylic hydride substitution (path b) produces alkene **14**, which undergoes exclusive anti-Markovnikov hydroboration furnishing the linear alkylboronic ester product **3a**.

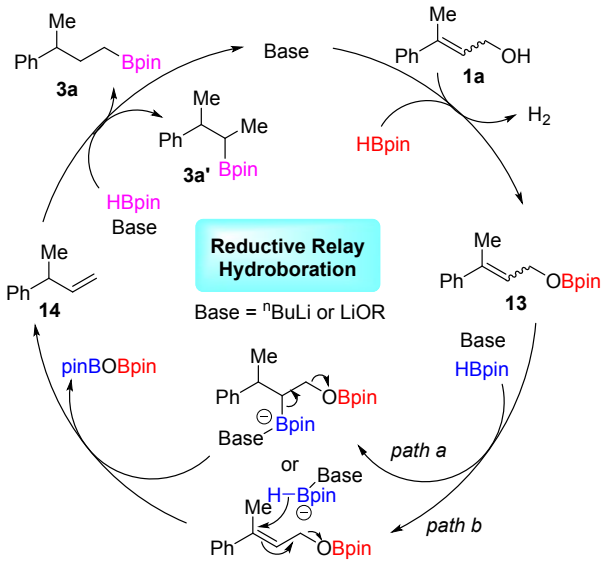


Figure 1. Proposed catalytic cycle.

In summary, we have developed an efficient and unprecedented base-catalysed reductive relay hydroboration of allylic alcohols with pinacolborane. Inexpensive ^{n}BuLi was used as a simple transition-metal-free initiator for this cascade process, converting a diverse variety of allylic alcohols and derivatives bearing various heterocycles and functional groups to alkylboronic esters in a single operation. A mechanism involving a one-pot three-step sequential process was proposed. Efforts to further development of efficient hydroboration reactions are ongoing in our laboratory.

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