



Boron trifluoride facilitated transesterification of dioxaborolanes



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ABSTRACT

The direct transesterification of dioxaborolanes (alkane-1,2-diol based boronate esters) was explored. Using $\text{BF}_3 \cdot \text{OEt}_2$, alkane-1,2-diol based mono- and bis-boronate esters (i.e., pinacol and ethylene glycol) have been converted quantitatively to either benzene-1,2-diol or alkane-1,3-diol based boronate esters. In the case of pinacol esters, esterification is facilitated by the accompanying pinacol rearrangement, thus shifting the reaction equilibrium.

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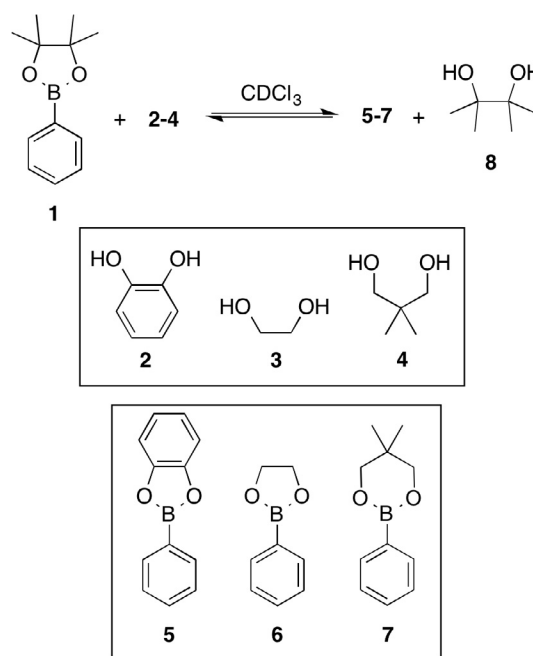
Introduction

Boronic acids have the ability to react with diols to give cyclic boronate esters.¹ This reversible transformation is driven by the removal of water from the medium. The dynamic covalent nature of this reaction has led to its application in a number of areas.^{2–4} It has also enabled the synthesis of large and complex compounds such as boronate ester based linear oligomers/polymers,^{5–7} macrocycles,^{8–14} and covalent organic frameworks.^{15–17} Much of this work has involved the use of commercially available bis-boronic acids as one of the monomer components. For the design and synthesis of new boronic acid based monomers, pinacol boronate esters, have been the ideal choice due to their stability and ease of isolation.¹ Subsequent deprotection/hydrolysis, such as NaIO_4 oxidation,^{18,19} diethanolamine exchange,²⁰ transesterification with polystyrene supported boronic acid,²¹ and via intermediate potassium trifluoroborates^{22–24} has allowed the isolation of the free boronic acid species. Despite these advances, purification of free boronic acids remains challenging¹ and the seemingly superfluous hydrolysis step may be eliminated if appropriate conditions for direct transesterification are available. Therefore, we have initiated experiments to investigate the viability of a direct transesterification method.

Results and discussion

The transesterification of pinacol ester **1** was studied with catechol (**2**, a model for an aromatic 1,2-diol), ethylene glycol (**3**,

as a model of a less sterically encumbering aliphatic 1,2-diol), neopentyl glycol (**4**, as a model of an aliphatic 1,3-diol) (Scheme 1). Equimolar amounts of ester **1** and diols **2–4** were mixed in CDCl_3 and the samples were monitored over time by ^1H NMR spec-



Scheme 1. Transesterification of pinacolyl boronate ester **1**.

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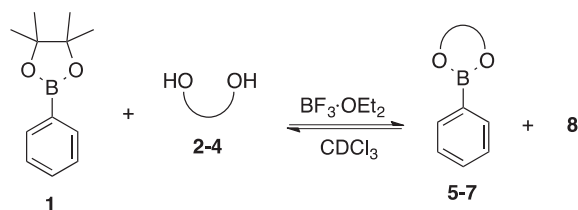
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Table 1
Transesterification of **1** with diols **2–4** in the absence and presence of BF₃·OEt₂.

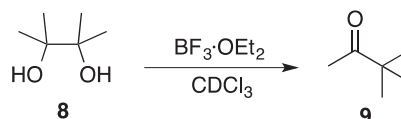
Entry	Diol	BF ₃ ·OEt ₂ (equiv) ^a	Conversion	Time (h)
1	2	0	<5%	>100
2	2	1 ^b	<5%	N/A
3	2	2 ^b	23%	>10
4	2	5 ^b	67%	>40
5	2	1	83%	>40
6	2	2	94%	>40
7	2	5	100%	<24
8	3	0	10%	>100
9	3	5	24%	<17
10	4	0	32%	>100
11	4	5	100%	<6

^a BF₃·OEt₂ equiv was determined by integration of the appropriate ¹H NMR signals.

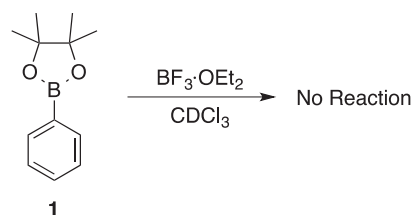
^b BF₃·OEt₂ was freshly distilled from CaH₂.



Scheme 2. Transesterification of **1** with diols **2–4** in the presence of BF₃·OEt₂.



Scheme 3. BF₃·OEt₂ facilitated rearrangement of pinacol **8**.



Scheme 4. BF₃·OEt₂ reaction with pinacol ester **1**.

troscopy. Among the model diols studied, neopentyl glycol (**4**) showed the highest transesterification (32%) whereas catechol (**2**) exhibited the lowest transesterification (5%) (Table 1 and Fig. 1, hollow markers). In addition to the low conversion, the transesterification is a slow process that takes >100 h to reach equilibrium.

To increase the rate of the transesterification, alternative conditions were sought. Increasing the temperature to 50 °C had little effect; therefore, the use of a Lewis acid catalyst, specifically BF₃·OEt₂, was investigated. This catalyst has been shown to be effective in COF synthesis with acetonide protected diols.²⁵ Pinacol ester **1** was mixed with neopentyl glycol (**4**, 1 equiv) in CDCl₃ and BF₃·OEt₂ (5 equiv) was added (Scheme 2). Soon after mixing, transesterification began and was essentially complete within 6 h. In the presence of BF₃·OEt₂ there was not only an increase in rate, but surprisingly 100% conversion to ester **7** was observed.

Interestingly, the signals corresponding to free pinacol were not observed in the ¹H NMR spectrum, however two new signals were observed at $\delta = 2.3$ and 1.2 ppm (Fig. S2). In this reaction, the participation of BF₃·OEt₂ is not limited to catalyzing the esterification; it also facilitates the pinacol rearrangement to pinacolone **9** (Scheme 3). This concurrent consumption of pinacol shifts the transesterification equilibrium to the right, which results in the quantitative formation of neopentyl glycol ester **7**. In a separate experiment under identical conditions, pinacol was mixed with BF₃·OEt₂ and complete conversion to pinacolone was observed (Fig. S3).

In the absence of neopentyl glycol (Scheme 4), there was no appreciable change, which means that the process relies in part on the transesterification step. This unforeseen, yet justifiable,

result prompted a more detailed look into the BF₃·OEt₂ promoted transesterification.

The BF₃·OEt₂ promoted transesterification of **1** was then carried out separately with catechol (**2**) and then with ethylene glycol (**3**, discussed below). In both cases, the rate and the percent conversion increased in the presence of BF₃·OEt₂ (Fig. 1). The transesterification with catechol (**2**) reached 100% conversion within 30 h (Fig. 2). This was in stark contrast to the 5% conversion in the absence of BF₃·OEt₂. It should also be noted that the presence of phenylboronic acid or triphenylboroxine could not be detected (protons equivalent to H_a typically appear at 7.7 or 8.2 ppm, respectively), which means that if these are intermediates they are short-lived under these conditions.

To determine the optimal amount of BF₃·OEt₂ needed for the transesterification, BF₃·OEt₂ was freshly distilled from CaH₂; however, this had an adverse effect on the reaction (Table 1 entries 2–4). Therefore, straight from the bottle (“wet” BF₃·OEt₂) was used.²⁶

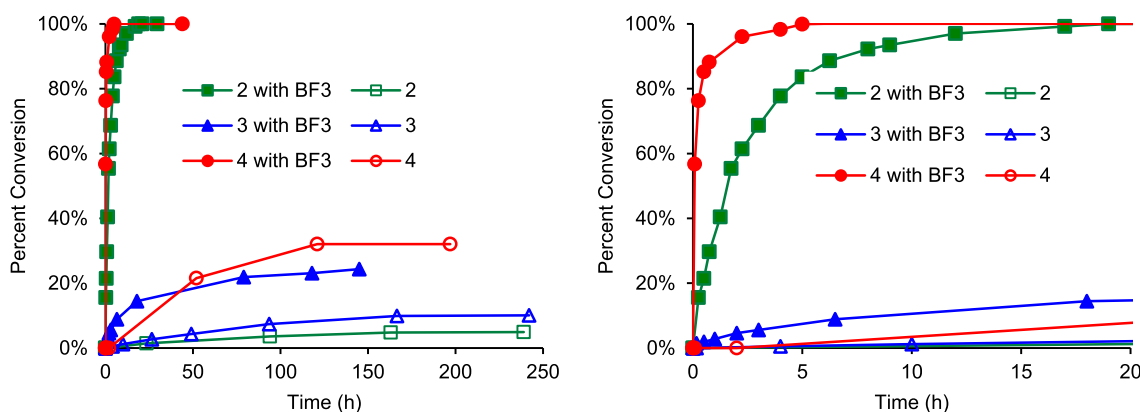


Fig. 1. Reaction progress of **1** and diols **2–4** with BF₃·OEt₂ (solid markers) and without BF₃·OEt₂ (hollow markers) in CDCl₃. Left: 0–250 min. Right: 0–20 min.

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