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(*R,R*)-2,3-Butanediol and (*s*)-Pinanediol Allylboronates in Chiral Synthesis of (2*S*,3*S*)-3-Methyl-5-hexen-2-ol

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ABSTRACT

(R,R)-*Butanediol (dichloromethyl)boronate* (**1**) *with 1 equiv. allylmagnesium halide yields* (R,R)-*2,3-butanediol* (*1*S)-(*1-chloro-3-butenyl*)*boronate* (**3**) *together with the diallylated product* (R,R)-*2,3-butanediol (1-allyl-3-butenyl)boronate* (**4**). *The formation of* **4** *is unprecedented in reactions of α-chloroboronic esters with Grignard reagents. With methylmagnesium bromide* **3** yielded (R,R)-*2,3-butanediol* (*1*S)-(*1-methyl-3-butenyl*)*boronate* (**5**), *which failed to hydrolyze with water. Hydrolysis of* **3** *yielded impure α-chloroboronic acid, which was esterified with pinacol and treated with methylmagnesium bromide to form* **6**, *which with (dichloromethyl)lithium followed by methylmagnesium bromide yielded diastereomeric boronic esters* **7** *and* **8**. *Oxidation by hydrogen peroxide yielded* (2S,3S)- *and* (2R,3S)-*3-methyl-5-hexen-2-ol* (**9** *and* **10**, *ees unknown). Treatment of* (s)-*pinanediol allylboronate* (**11**) *with (dichloromethyl)lithium at −100°C followed by zinc chloride at up to 25°C has proceeded in the normal way to form* (s)-*pinanediol* (*1*S)-(*1-chloro-3-butenyl*)-*boronate* (**12**), *which has been elaborated via* **13**, **14**, *and* **15** *to* (2S,3S)-*3-methyl-5-hexen-2-ol* (**9**) *in 95% de.*

INTRODUCTION

Asymmetric synthesis via α-chloroboronic esters can provide efficient routes to a wide variety of structures in high chiral purities [1,2]. In the present investigation, we have examined the reaction of allylmagnesium halides with (*R,R*)-2,3-butanediol (dichloromethyl)boronate [3] (**1**) and of (*s*)-pinanediol allylboronate (**11**) with (dichloromethyl)lithium as routes to esters of (1*S*)-(1-chloro-3-butenyl)boronic acid and (2*S*,3*S*)-3-methyl-5-hexen-2-ol (**9**). Unsaturated chiral alcohol **9** was chosen as a potentially useful intermediate for the synthesis of insect pheromones such as those of the pine sawfly [4]. The carbon–carbon double bond of **9** could be used as a starting point for the further carbon–carbon connections needed.

(*R,R*)-2,3-Butanediol (dichloromethyl)boronate (**1**) has been shown to react with alkylmagnesium halides at −78°C to form borate complexes (**2**) which rearrange in the presence of zinc chloride at 20°C to form (*R,R*)-2,3-butanediol [(alkyl)(chloro)-methyl]boronates in 84–90% de [diastereomeric excess, defined as $100(x_1 - x_2)$, where x_1 and x_2 are the mole fractions of the two diastereomers] [3]. Although this is not as diastereoselective as the reaction of (*s*)-pinanediol alkylboronates with (dichloromethyl)lithium, which usually leads to (*s*)-pinanediol [(alkyl)(chloro)methyl]boronates in ≥97% de [1,2], the butanediol esters have some useful properties. Among these are the ease of hydrolysis of butanediol α-chloroboronic esters to α-chloroboronic acids, which are often crystalline [3].

Another useful property is the C_2 symmetry of the (*R,R*)-2,3-butanediol ester group, which results in the same borate complex **2** regardless of whether it is formed from (*R,R*)-2,3-butanediol (dichloromethyl)boronate (**1**) and an alkylmetal reagent or from (*R,R*)-2,3-butanediol alkylboronate and (dichloromethyl)lithium [3]. Thus, **1** can be made and stored as a convenient reagent for making a variety of chiral α-chloroboronic esters merely by

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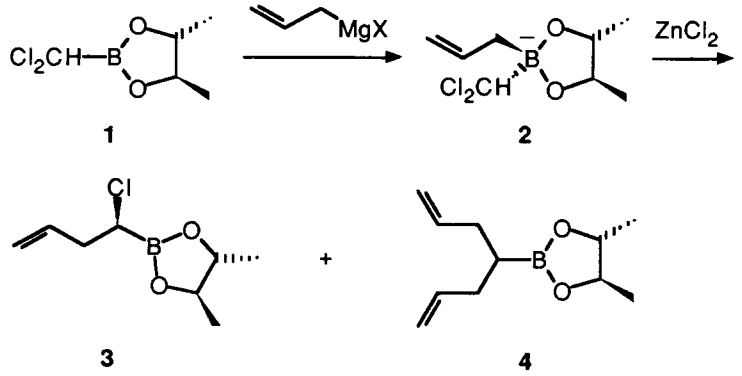
adding the appropriate Grignard or lithium reagent. Treatment of **1** with an allylmagnesium reagent avoids the need to make a labile allylboronic ester intermediate. In contrast, pinanediol esters lack C_2 symmetry, and pinanediol (dichloromethyl)boronate is not useful in asymmetric synthesis because it alkylates on the wrong face of the boron atom with respect to yielding any diastereoselectivity [5].

The study that follows provides new information regarding the problems of working with butanediol boronic esters and allylic boronic esters and reconfirms the reliability of pinanediol boronic esters as general reagents for directed asymmetric synthesis.

RESULTS

(R,R)-2,3-Butanediol Esters

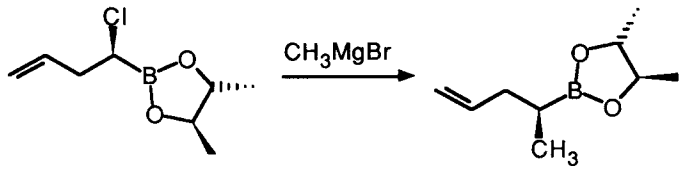
(*R,R*)-2,3-Butanediol (dichloromethyl)boronate [3,6] (**1**) was treated with a stoichiometric amount of allylmagnesium bromide or chloride at −78°C to form the borate complex **2**. Rearrangement of **2** in the presence of zinc chloride led to the expected product, (*R,R*)-2,3-butanediol (1*S*)-1-chloro-3-butenylboronate (**3**), together with an unexpected major byproduct, (*R,R*)-2,3-butanediol (1-allyl-3-butenyl)boronate (**4**). By stoichiometry, there should have been unchanged **1** remaining, but this was evidently lost in the workup and incomplete material balance was seen instead.



1 **2** **3** **4** (1)

Although **3** was never obtained in good purity, further transformation was pursued to see whether the byproduct **4** might be separated from later intermediates. First, treatment of **3** with methylmagnesium halide yielded (*R,R*)-2,3-butanediol (1*S*)-1-methyl-3-butenylboronate (**5**), which was separated from **4** by fractional distillation.

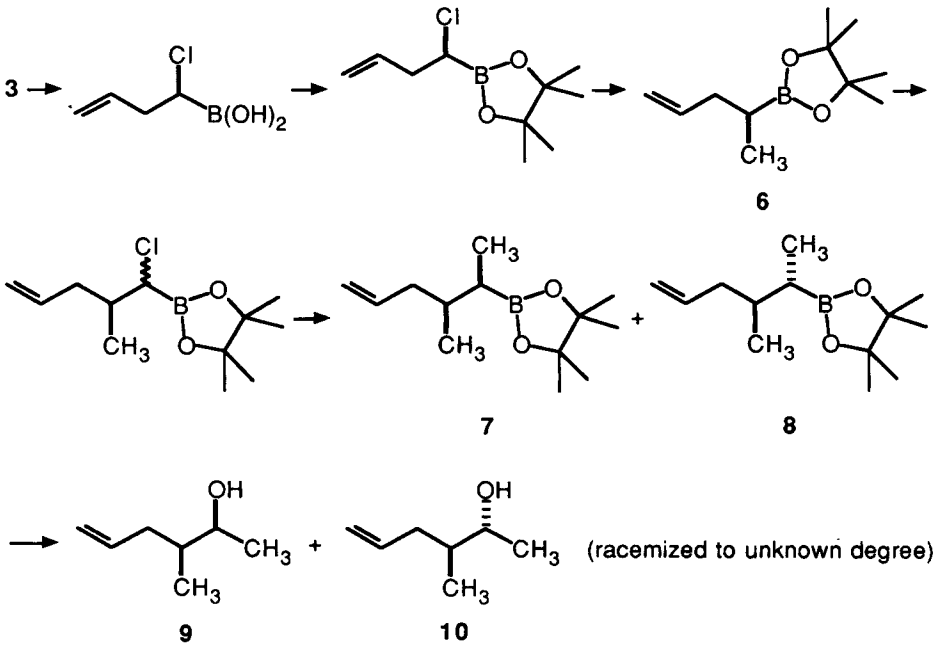
Attempts were then made to hydrolyze **5** to the



3 **5** (2)

corresponding boronic acid, but the ether–water partitioning which led to rapid hydrolysis of 2,3-butanediol α-chloroboronates failed to affect **5**, and attempts to catalyze the reaction with acid failed. An attempt to transesterify **5** with diethanolamine under conditions previously successful with certain pinacol boronic esters [7] also failed.

In contrast to **5**, **3** was readily hydrolyzed by ether and aqueous sulfuric acid, but attempts to recrystallize the resulting α-chloroboronic acid failed (Scheme 1). The crude boronic acid, probably extensively racemized, was then esterified with pinacol and treated with methylmagnesium bromide to form pinacol 1-methyl-3-butenylboronate (**6**). (Dichloromethyl)lithium converted **6** to a mixture of α-chloroboronic esters, which was treated with methylmagnesium bromide to form pinacol (1*R*,2*S*)- and (1*S*,2*S*)-(1,2-dimethyl-4-pentenyl)-boronate (**7** and **8**). Oxidation of **7** and **8** with hydrogen peroxide yielded a mixture of (2*S*,3*S*)-3-methyl-5-hexen-2-ol (**9**) and (2*R*,3*S*)-3-methyl-5-hexen-2-ol (**10**), racemized to an undetermined degree, which yielded a ^{13}C NMR identical to that previously reported [8].



SCHEME 1

(s)-*Pinanediol Esters*

As a result of the problems encountered with the (*R,R*)-2,3-butanediol esters, the synthesis was redesigned to utilize the well-established (*s*)-pinanediol esters [1,2]. As noted in the introduction, it would not be possible to achieve stereoselection from (*s*)-pinanediol (dichloromethyl)boronate, and therefore (*s*)-pinanediol allylboronate (**11**) was synthesized.

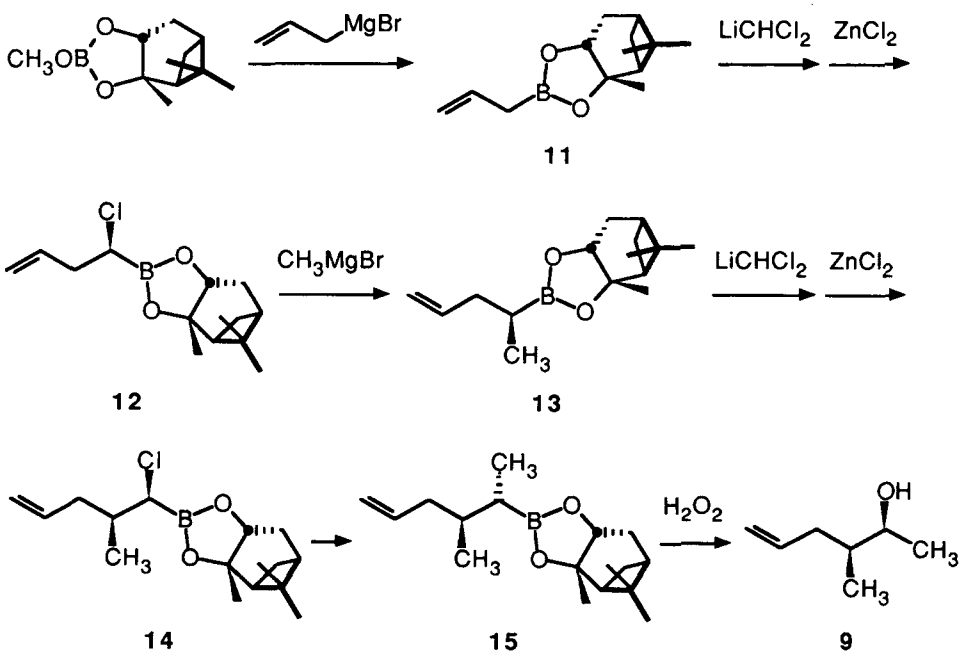
The synthesis of simple allylboronic esters is straightforward [9] but prone to variable yields [10]. We made di-*n*-hexyl allylboronate [11] and transesterified it with pinanediol to produce **11** (Scheme 2). However, rather than work out the exact conditions for a reproducible preparation of dihexyl allylboronate, we undertook the direct treatment of pinanediol methoxyboronate [2] with allylmagnesium bromide and obtained (*s*)-pinanediol allylboronate (**11**) in high yield.

Reaction of **11** with (dichloromethyl)lithium in the established manner readily yielded (*s*)-pinanediol (1*S*)-(1-chloro-3-butenyl)boronate [12] (**12**), with no sign of any byproduct analogous to **4**. The reaction of **12** with methylmagnesium bromide proceeded normally to yield (*s*)-pinanediol (1*S*)-(1-methyl-3-butenyl)boronate (**13**). Reaction of **13** with (dichloromethyl)lithium yielded (*s*)-pinanediol (1*S*,2*S*)-(1-chloro-2-methyl-4-pentenyl)boronate (**14**) in a ~2 : 1 mixture with unchanged **13**, which evidently resulted from use of a shorter than normal reaction time. No attempt was made to purify **14**, which was readily converted by methylmagnesium bromide to easily purified (*s*)-pinanediol (1*S*,2*S*)-(1,2-dimethyl-4-pentenyl)boronate (**15**). Oxidation of **15** with alkaline hydrogen peroxide furnished the target alcohol (2*S*,3*S*)-3-methyl-5-hexen-2-ol (**9**) in 95% diastereomeric excess as shown by NMR analysis. The enantiomeric purity was not measured directly but should have been as high as that of the pinanediol used as chiral director, ≥99% ee.

DISCUSSION AND CONCLUSIONS

The byproduct (*R,R*)-2,3-butanediol (1-allyl-3-butenyl)boronate (**4**) derived from (dichloromethyl)boronic ester **1** is unprecedented in α-haloboronic ester chemistry. The allylmagnesium halide was titrated and used in stoichiometric amounts, but ratios of **4** to α-chloroboronic ester **3** varied from 1 : 3 to 3 : 1. Since allylmagnesium halide was not present in excess, these results imply that an allyl anion is transferred from anion **2** to **3** during the course of the reaction. The yields of **3** and **4** were significantly less than quantitative, and it appeared that unchanged **1** may have been lost via hydrolysis (to which it is unusually sensitive [3]) during the aqueous workup.

Stronger evidence for this hypothesis might be obtained if reaction of butanediol allylboronate with (dichloromethyl)lithium were found to yield **4**. However, an attempt to prepare butanediol allylboronate by transesterification of dihexyl allylboronate failed. Evidently the allyl group underwent protolytic cleavage during attempted fractional distillation of the alcohol–ester mixture.



SCHEME 2

A second unexpected result was the failure of (*R,R*)-2,3-butanediol (1*S*)-1-methyl-3-butenylboronate (**5**) to hydrolyze. It is not apparent why this compound should differ so sharply from the analogous (1-chloroalkyl)boronates, but we have recently confirmed that other butanediol alkylboronates also fail to hydrolyze [13]. This is a disappointing finding, inasmuch as secondary alkylboronic esters such as **5** are chirally stable, but α-chloroboronic esters such as **3** epimerize very readily [3].

It may be concluded that (*R,R*)-2,3-butanediol is not a generally convenient chiral director for the α-chloroboronic ester synthesis, at least as far as can be ascertained from the chemistry observed to date. There are a few circumstances where hydrolysis of a boronic ester intermediate to a boronic acid could be useful, for example if the chiral director needs to be changed for installation of the next carbon, and it may be possible to develop the butanediol ester chemistry for that purpose. In contrast, pinanediol esters have consistently provided efficient reactions and high chiral selectivities.

EXPERIMENTAL

General

Enantiomerically pure (*s*)-pinanediol (100.0 ± 0.1% measured ee) was made by recrystallization of the potassium borate salt of (*s*)-pinanediol [2]. Reactions involving air-sensitive reagents were run under argon. Tetrahydrofuran (THF) was freshly distilled from benzophenone ketyl. Butyllithium and allylmagnesium bromide (Aldrich Chemical Company) were titrated against 2-propanol with 1,10-phenanthroline as indicator [14]. "Powdered anhydrous zinc chloride" was prepared by stirring granular reagent-grade anhydrous zinc chloride under vacuum at 100°C several hours, resulting in a fine free-flowing powder [2]. Liquids were transferred via glass syringes with stainless steel needles or via cannula through rubber septa. Both 90-MHz ^{1}H and 22-MHz ^{13}C NMR spectra were taken on a JEOL FX90Q Fourier transform instrument, and 200-MHz ^{1}H and 50-MHz ^{13}C NMR spectra were taken on a Nicolet NT-200 instrument. Optical rotations were measured with a Jasco DIP-181 digital polarimeter. Melting points were taken in capillary tubes in a Thomas-Hoover liquid bath melting point apparatus and are uncorrected. Boiling points are uncorrected. Microanalyses were by Galbraith Laboratories, Knoxville, Tennessee.

(R,R)-*2,3-Butanediol* (*1*S)-(*1-Chloro-3-butenyl*)*boronate* (**3**)

(*R,R*)-2,3-Butanediol (dichloromethyl)boronate (**1**) was prepared from diisopropyl (dichloromethyl)-boronate [3,6] and (*R,R*)-2,3-butanediol as previously described [3]. A solution of 17.7 g (97 mmol) of **1** in 150 mL of THF was stirred at −78°C during the dropwise addition of 97 mmol of 1.98 *M* allylmagnesium chloride in THF (Aldrich Chemical Company) over a 30-min period. After 3 min, the stopper of the flask was removed for a few seconds

while a flow of argon was maintained and 8.28 g (61-mmol) of powdered anhydrous zinc chloride [2] was added in one portion. The mixture was concentrated under vacuum and treated with petroleum ether and saturated aqueous ammonium chloride. Concentration yielded 14.1 g (77% calculated as **3**) of a crude mixture of ~77% (*R,R*)-2,3-butanediol (1*S*)-(1-chloro-3-butenyl)boronate (**3**) and ~23% (*R,R*)-2,3-butanediol (1-allyl-3-butenyl)boronate (**4**). In several different runs, the ratio of **3** to **4** as indicated by 90-MHz NMR spectra varied from 3 : 1 to 1 : 3, with no interpretable relationship to slight variations in conditions. Attempts to determine the diastereomer ratio quantitatively by conversion of **3** to the pinanediol ester were unsuccessful because of interference by the several species present, but the evidence available suggests that not much epimerization of **3** occurred.

(R,R)-*2,3-Butanediol* (*1*S)-(*1-Methyl-3-butenyl*)*boronate* (**5**) *and* (R,R)-*2,3-Butanediol* (*1-Allyl-3-butenyl*)*boronate* (**4**)

A solution of a mixture estimated to contain 24.3 g (129 mmol) of crude **3** and 13.3 g (68.5 mmol) of **4** according to NMR analysis in 600 mL of THF was stirred at −78°C during the dropwise addition of 66.3 mL (176 mmol) of 2.65 *M* methylmagnesium bromide in ether over a period of ~2 h. The reaction mixture was allowed to warm to 20–25°C overnight. The mixture was concentrated on a rotary evaporator and worked up with petroleum ether and saturated aqueous ammonium chloride. Distillation yielded 6.8 g, bp 60–68°C (20 torr), which was slightly impure **3**; 200-MHz NMR ($CDCl_3$), δ 0.99 (d, J = 6.7 Hz, 3, BCHCH_3), 1.16 (m, 1, C*H*B), 1.28 (m, 6, CH_3CHO), 2.15 (m, 2, C=CHCH_2), 3.98 (m, 2, C*H*OB), 4.9–5.1 (m, 2, H_2C=CH), 5.82 (m, 1, H_2C=C*H*); 22.5-MHz ^{13}C NMR ($CDCl_3$), δ 15.0, 21.0, 37.4, 79.9, 114.8, 138.6, presumably broad *C*B peak not seen. Analysis, calculated for $C_9H_{17}BO_2$; C, 64.33; H, 10.20; B, 6.43; found, C, 63.78; H, 9.57; B, 6.28. After a 3.9-g intermediate fraction, **4** was collected, 2.3 g, bp 90–95°C (20 torr); 200-MHz ^{1}H NMR ($CDCl_3$), δ 0.99 (d, 4% of 3 H's, CH_3 of **3** impurity), 1.27 (m, 7, CH_3CHOB + C*H*B), 2.18 (m, 4, C=CHCH_2), 3.98 (m, 2, C*H*OB), 4.9–5.1 (m, 4, H_2C=CH), 5.82 (m, 2, H_2C=C*H*); 22.5-MHz ^{13}C NMR ($CDCl_3$), δ 21.2, (30.0, weak, impurity or noise), 34.8, 79.9, 115.0, 138.4, presumably broad *C*B peak not seen. Analysis, calculated for $C_{11}H_{19}BO_2$, C, 68.08; H, 9.87; B, 5.57; found, C, 66.79; H, 10.19; B, 5.48.

Pinacol (*1*R,*2*S)- *and* (*1*S,*2*S)-(*1,2-Dimethyl-4-pentenyl*)*boronate* (**7** *and* **8**) *and Enantiomers*

A solution of 9.15 g (54.5 mmol) of (*R,R*)-2,3-butanediol (1*S*)-(1-methyl-3-butenyl)boronate (**5**) in THF was added to 57 mmol of (dichloromethyl)-lithium in 60 mL of THF stirred at −100°C in the usual manner. The mixture was treated with 6.9 g (50 mmol) of anhydrous zinc chloride and then allowed to warm to 20–25°C overnight. Concentration under vacuum was followed by workup with 200 mL of ether and 100 mL of 1 *M* sulfuric acid. After washing with two additional portions of sulfuric acid, the boronic acid still contained butanediol ester as indicated by NMR analysis, and the diol was removed by washing with 500 mL of ice water. Concentration of the ether phase yielded 3.9 g of crude 1-chloro-2-methyl-3-butenylboronic acid. Several attempts to crystallize this material over a period of 7 d yielded very little solid, and the entire lot was finally treated with excess pinacol, dried, and concentrated to 6.9 g of pinacol 1-chloro-2-methyl-3-butenylboronate. This pinacol boronic ester in 60 mL of THF at −78°C was treated with 28 mmol of methylmagnesium bromide, then allowed to warm to 20–25°C overnight. The usual workup with ether and water was followed by chromatography on silica with 1% ether in petroleum ether, R_f of **7** and **8** ~0.6; 2.3 g. The analytical sample was further purified by kugelrohr distillation; 200-MHz ^{1}H NMR ($CDCl_3$), δ 0.90 (d, 3, CH_3), 0.96 (s, 3, centered in d, 1, BC*H*CH_3), 1.23 (s, 12, CCH_3), 1.62 (m, 1, C*H*CH_3), 1.90 (m, 1, half of C=CHCH_2), 2.17 (m, 1, half of C=CHCH_2), 4.9–5.05 (m, 2, H_2C=CH), 5.78 (m, 1, H_2C=C*H*). Analysis, calculated for $C_{13}H_{25}BO_2$, C, 69.66; H, 11.24; B, 4.82; found, C, 69.50; H, 11.22; B, 4.78.

(2S,3S)- *and* (2R,3S)-(*3-Methyl-5-hexen-2-ol* (**9** *and* **10**) *and Enantiomers*

Oxidation of a mixture of **6** and **7** with hydrogen peroxide and sodium hydroxide in aqueous THF [2] followed by workup with water and ether and distillation yielded an approximately equimolar mixture of **9** and **10**. The 22.5-MHz ^{13}C NMR spectrum agreed with the 100-MHz spectrum reported [8], average deviation of peak positions ±0.20 δ, largest deviation −0.51 δ. By difference between the ^{1}H NMR spectrum of this mixture and that of 97% **9** prepared from **15** (see below) the spectrum of **10** follows: 200-MHz ^{1}H NMR ($CDCl_3$), δ 0.88 (d, J = 6.8 Hz, 3, CHCH_3), 1.15 (d, J = 6.4 Hz, 3, HOCHCH_3), 1.6 (m, 1, C*H*CH_3), 1.8 (br s, O*H*), 1.95 (m, 1, CH_2=CHC*H*H), 2.2 (m, 1, CH_2=CHCH*H*), 3.65 (m, 1, C*H*OH), 5.0–5.1 (m, 2, CH=CH_2), 5.81 (m, 1, C*H*=CH_2).

(s)-*Pinanediol Allylboronate* (**11**)

Potassium (*s*)-pinanediol borate was converted to (*s*)-pinanediol methoxyboronate as previously described [2] bp 60–62°C (0.15 torr). A 10.45-g (.0587-mol) sample of freshly distilled (*s*)-pinanediol methoxyboronate in 25 mL of THF was stirred at −78°C during the dropwise addition of 36 mL (0.54

mol) of 1.5 *M* allylmagnesium bromide in diethyl ether over a 30-min period. The cold (initially −78°C) reaction mixture was treated with 10 mL of water, then 20 mL of 6 *M* hydrochloric acid. The phases were separated and the aqueous phase was extracted with three 30-mL portions of ether. The combined organic phase was washed with 50 mL of 10% sodium chloride and a small amount of solid sodium bicarbonate, just enough to raise the pH to 5. The organic phase was dried over magnesium sulfate, filtered, and concentrated on a rotary evaporator. The residue was chromatographed with 5% diethyl ether in petroleum ether on a column that contained 500 mL of silica gel. The product was collected in the fractions between 250 and 800 mL of eluant. Distillation yielded 9.0 g (82%) of (*s*)-pinanediol allylboronate (**11**), bp 52–53°C (0.15 torr); 200-MHz ^{1}H NMR ($CDCl_3$), δ 0.84 (s, 3, pinyl CCH_3), 1.11 (d, J = 10.8 Hz, 1, pinyl CH), 1.29 (s, 3, pinyl CCH_3), 1.39 (s, 3, pinyl CCH_3), 1.75–2.45 (m, 7, CH_2B + pinyl CH), 4.28 (dd, 1, $CHOB$), 4.9–5.1 (m, 2, $CH{=}CH_2$), 5.89 (m, 1, $CH{=}CH_2$). When the procedure was scaled up to 0.17 mol of (*s*)-pinanediol methoxyboronate and allylmagnesium chloride was used in place of the bromide, the yield of **1** was 34.7 g (91%), bp 60–63°C (0.1 torr). Analysis, calculated for $C_{13}H_{21}BO_2$, C, 70.94; H, 9.62; B 4.91, found, C, 70.89; H, 9.56; B, 5.19.

(s)-*Pinanediol* (*1*S)-(*1-Chloro-3-butenyl*)*boronate* (**12**)

(Dichloromethyl)lithium was generated by addition of 42 mmol of 1.49 M butyllithium in hexane dropwise down the side of the flask to 3.9 g (46 mmol) of dichloromethane in 50 mL of THF stirred at −100°C over a period of 5 min [2]. A solution of 8.67 g (39.4) mmol) of pinanediol allylboronate (**1**) in 30 mL of THF was cooled in a −78°C bath [15] and transferred via cannula to the stirred suspension of (dichloromethyl)lithium over a period of 15 min. After 5 min, the stopper of the flask was removed for a few seconds while a flow of argon was maintained and 3.67 g of anhydrous zinc chloride was added in one portion. The mixture was allowed to warm to 20–25°C and stirred overnight. The mixture was concentrated, first on a rotary evaporator, then pumped down to 0.1 torr and stirred 20 min. The residue was treated with 100 mL of petroleum ether followed by a mixture of 75 mL of saturated aqueous ammonium chloride and 4 mL of ammonium hydroxide. The phases were separated and the aqueous layer was extracted with three 30-mL portions of petroleum ether. The combined organic phase was dried over anhydrous magnesium sulfate and filtered through a small bed of Celite. The solution was concentrated (0.7 torr); 10.9 g (theory 10.6 g) containing ~12% THF and ~15% unconverted **11**; 200-MHz ^{1}H NMR ($CDCl_3$), δ 0.84 (s, 3, CCH_3), 1.185 (d, J = 11.0 Hz, 1, pinyl CH) [epimer at estimated 1.175, not resolvable], 1.29 (s, 3, CCH_3), 1.42 (s, 3, CCH_3), 1.8–2.4 (m, 5, pinyl CH), 2.60 (m, 2, $CH_2{=}CHCH_2$), 3.51 (t, J = 7.4 Hz, 1, $CHCl$) [epimer, 3.49 (t, J = 7.5 Hz, 2% based on peak at 690 Hz)], 4.37 (dd, 1, $CHOB$), 5.05–5.2 (m, 2, $CH{=}CH_2$), 5.87 (m, 1, $CH{=}CH_2$).

(s)-*Pinanediol* (*1*S)-(*1-Methyl-3-butenyl*)*boronate* (**13**)

A solution of 9.64 g (<36 mmol) of crude **1** in 100 mL of THF was stirred at −78°C during the dropwise addition of 14 mL of 2.51 *M* methylmagnesium bromide in ether over a period of 10 min. The cooling bath was removed, and after 2 h the mixture had warmed to room temperature. The solution was concentrated under vacuum until the pressure reached 0.1 torr. The residue was treated with 100 mL of petroleum ether and stirred for 2 h. The solution was filtered through a pad of magnesium sulfate with the aid of argon pressure. Concentration of the filtrate under vacuum to 0.1 torr yielded 6.36 g (71%) of **3** suitable for use in the next step. An additional 1.17 g (13%) of **13** was obtained by treatment of the residual salts with water, extraction with petroleum ether, and concentration, total 84%; 200-MHz ^{1}H NMR ($CDCl_3$), δ 0.84 (s, 3, pinyl CCH_3), 1.00 (d, 3, $BCHCH_3$), 1.12 (d, J = 10.8 Hz, 1, pinyl CH), ~1.15 (partially obscured m, 1, CHB) 1.28 (s, 3, pinyl CCH_3), 1.36 (s, 3, pinyl CCH_3), 1.39 (s, 5% impurity, pinyl CCH_3), 1.8–2.4 (m, 7, $C{=}CHCH_2$ + pinyl CH), 4.26 (dd, 1, $CHOB$), 4.9–5.1 (m, 2, $CH{=}CH_2$), 5.83 (m, 1, $CH{=}CH_2$). An analytical sample was chromatographed but yielded an inexplicably high boron analysis. Analysis, calculated for $C_{15}H_{25}BO_2$, C, 72.60; H, 10.15; B 4.36, found, C, 72.02; H, 9.90; B, 5.34.

(s)-*Pinanediol* (*1*S,*2*S)-(*1-Chloro-2-methyl-4-pentenyl*)*boronate* (**14**)

The procedure was essentially the same as for the conversion of **11** to **12**, with **13** used in place of **11**, on a 25.6-mmol scale. However, the reaction time after mixing the reagents, adding the zinc chloride, and warming to 20–25°C was only 1 h. After the reaction mixture was concentrated, the residue was treated with petroleum ether and saturated ammonium chloride. Following the usual extraction, drying, filtration, and concentration, **14** was obtained in a ~2 : 1 mixture with unchanged **13**, which evidently resulted from too short a reaction time.

(s)-*Pinanediol* (*1*S,*2*S)-(*1,2-Dimethyl-4-pentenyl*)*boronate* (**15**)

The crude **14** (6.9 g) was used directly. Treatment with methylmagnesium bromide was carried out as described for the conversion of **12** to **13**. The product **15** was worked up with aqueous ammonium chloride in the usual manner and then dis-

tilled. The portion of bp 71–84°C (0.03 torr), 2.87 g, was chromatographed on silica gel with 1% ethyl acetate in hexane; 2.8 g; 200-MHz ^{1}H NMR ($CDCl_3$), δ 0.84 (s, 3, pinyl CCH_3), 0.92 (d, J = 6.6 Hz, 3, CCHCH_3), 0.98 (d, J = 6–7 Hz, 3, BCHCH_3), 1.06 (m, 1, BCHCH$_3$), 1.140 (d, J = 10.6 Hz, 1, pinyl CH), 1.29 (s, 3, pinyl CCH_3), 1.37 (s, 3, pinyl CCH_3), 1.63 (m, 1, CCHCH$_3$), 1.8–2.4 (m, 7, C=CHCH_2 + pinyl CH), 4.25 (dd, 1, CHOB), 4.9–5.1 (m, 2, CH=CH_2), 5.78 (m, 1, CH=CH$_2$). Analysis calculated for $C_{17}H_{29}BO_2$, C, 73.92; H, 10.58; 3.91; found, C, 73.95; H, 10.49; B, 3.91.

(2S,3S)-*3-Methyl-5-hexen-2-ol* (**9**)

Oxidation of **15** with hydrogen peroxide and sodium hydroxide in aqueous THF [2] followed by workup with water and ether and distillation yielded **9** containing 2.5% (±0.5%) **10**; 200-MHz ^{1}H NMR ($CDCl_3$), δ 0.90 (d, J = 6.8 Hz, 3, CHCH_3), 1.17 (d, J = 6.4 Hz, 3, HOCHCH_3), 1.5 (br s, OH), 1.6 (m, 1, CHCH$_3$), 1.95 (m, 1, CH$_2$=CHCHH), 2.2 (m, 1, CH$_2$=CHCHH), 3.75 (m, 1, CHOH), 5.0–5.1 (m, 2, CH=CH_2), 5.81 (m, 1, CH=CH$_2$). A doublet at 1.18 (J = 6.4 Hz) indicated the presence of 8% of an HOCHCH_3 impurity, presumably 4-penten-2-ol.

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[10] Allylboronic esters appear to be unusually sensitive to protodeboronation by water or alcohols. The essential requirements for consistent yields are not fully understood but probably relate to prompt workup and avoidance of too long exposure to acidic or alkaline hydroxylic media.
[11] The preparation was from methyl borate and allylmagnesium bromide in the usual manner [9] followed by aqueous workup and extraction with ether and 1-hexanol; bp 73–75°C (0.1 torr), 200-MHz ^{1}H NMR in agreement with assigned structure, not otherwise characterized.
[12] Chemical Abstracts name: {3*aS*-[2(*R**),3*aα*,4*β*,6*β*,7*aα*]}-2-(1-chloro-3-butenyl)hexahydro-3*a*,5,5-trimethyl-4,6-methano-1,3,2-benzodioxaborole. The 3*aS* designates the absolute configuration of the entire molecule by reference to carbon 3*a*. The 2(*R**) indicates that this is the diastereomer in which the side chain at position 2 would have the *R* configuration if position 3*a* were *R*, but since position 3*a* is *S*, the side chain is *S*.
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[15] Cooling in this manner has not normally been used in analogous reactions and is of doubtful significance.