Heteroatom Chemistry
Volume 1, Number 2, 1990

(1-Methoxyvinyl)boronic and (1-Chlorovinyl)boronic Esters

Donald S. Matteson* and Ellen C. Beedle

Department of Chemistry, Washington State University, Pullman, Washington 99164-4630, U.S.A.

Received 10 April 1989.

ABSTRACT

(s)-Pinanediol (1-methoxyvinyl)boronate (**1**) *was prepared from (1-methoxyvinyl)-lithium and triisopropyl borate followed by* (s)-*pinanediol. Attempted reaction with (dichloromethyl)lithium failed, and reaction with butylmagnesium chloride followed by acetic acid yielded a mixture of diastereomers of* (s)-*pinanediol (1-methoxy-1-methyl-pentyl)boronate* (**2**). (s)-*Pinanediol (1-chlorovinyl)boronate* (**4**) *has been prepared by dehydrochlorination of* (s)-*pinanediol 1,1-dichloroethylboronate* (**3**) *with lithium chloride in dimethylformamide. Reaction of* **4** *with (dichloromethyl)lithium yielded* (s)-*pinanediol (1*S)-*(1,2-dichloroallyl)boronate* (**5**) *in 92% diastereomeric excess. Reaction of* **5** *with RMgX resulted in a 3 : 1 ratio of displacement of the 1-Cl from carbon by R to displacement of the entire 1,2-dichloroallyl group from boron by R. With lithium benzyl oxide, displacement of the 1-Cl from* **5** *failed entirely. Reaction of* **4** *with (dibromomethyl)lithium was inefficient and yielded a gross mixture of diastereomers.*

INTRODUCTION

(1-Methoxyvinyl)boronic esters represent a new class of boronic esters of unknown reactivity patterns. The closest model compounds would be the (1-methoxyvinyl)borates postulated as intermediates in reactions of (1-methoxyvinyl)lithium with trialkylboranes [1].

Our interest in (1-methoxyvinyl)boronic esters was prompted by their possible utility as acetyl synthons in the highly selective asymmetric synthesis with boronic esters [2, 3]. A brief investigation of the chemistry of (*s*)-pinanediol (1-methoxyvinyl)boronate (**1**) convinced us that **1** was not going to be useful for this purpose, and we turned to investigation of (*s*)-pinanediol (1-chlorovinyl) boronate (**4**). Previous examples of (1-haloalkenyl) boronic esters have been made by hydroboration of 1-haloacetylenes [4], not an applicable route to the parent member of the series. The synthesis of **4** required a new approach based on dehydrochlorination of (*s*)-pinanediol (1,1-dichloroethyl)boronate (**3**), which has recently become available via a simple route [5, 6]. The reactions of **4** observed have turned out to be more complex than anticipated, and the synthetic utility of this compound is limited.

RESULTS

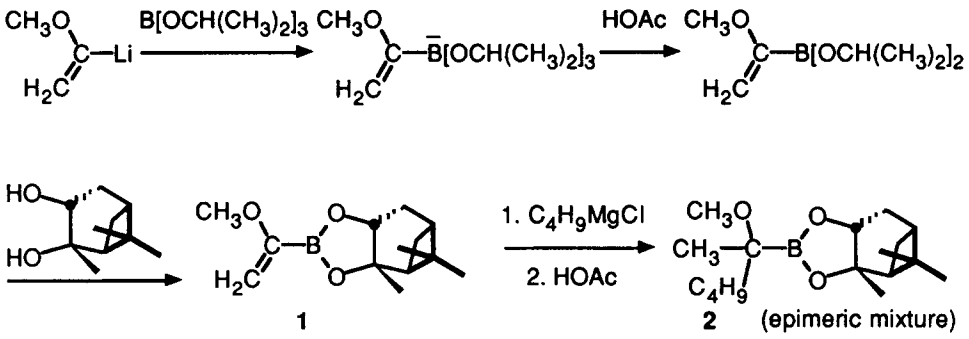
(s)-*Pinanediol (1-Methoxyvinyl)boronate* (**1**)

(1-Methoxyvinyl)lithium was prepared in the usual manner [7] and added to triisopropyl borate. Instead of the hydrogen chloride used in the Brown-Cole workup procedure [8], acetic acid was used, and excess acid was neutralized before proceeding. The labile diisopropyl (1-methoxyvinyl)boronate was distilled and then transesterified with (*s*)-pinanediol to form (*s*)-pinanediol (1-methoxyvinyl) boronate (**1**).

Several attempts were made to react **1** with (dichloromethyl)lithium, but it appeared that the product decomposed. Attempted acid hydrolysis of **1** failed to yield any evidence for the corresponding

* To whom correspondence should be addressed.

1042-7163/90/$3.50 + .25



acetylboronic ester, which is evidently very labile. In view of the known rearrangement reactions of (1-methoxyvinyl)borates derived from trialkylboranes [1], we undertook the reaction of **1** with a Grignard reagent followed by acetic acid. The rearrangement proceeded smoothly to form (*s*)-pinanediol (1-methoxy-1-methylpenyl)boronate (**2**) as the major product, but the apparent diastereomer ratio based on nuclear magnetic resonance (NMR) analysis was only ~2 : 1. Addition of zinc chloride before the acetic acid improved the yield, but the diastereomer ratio was shifted to ~1 : 1.

(s)-*Pinanediol (1-Chlorovinyl)boronate* (4)

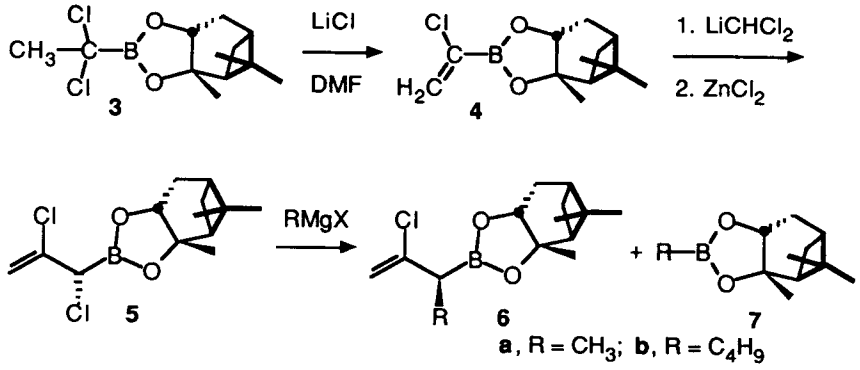
(1-Chlorovinyl)lithium is not an accessible reagent, and therefore an indirect approach was undertaken to the synthesis of (*s*)-pinanediol (1-chlorovinyl) boronate (**4**). Dimethyl (1,1-dichloroethyl)boronate is easily prepared from 1,1-dichloroethane, lithium diisopropylamide (LDA), and trimethyl borate [5] and transesterification with (*s*)-pinanediol has yielded pinanediol (1,1-dichloroethyl)boronate (**3**) [6]. The dehydrobromination of an α-bromo boronic ester, $Cl_3CCH_2CHBrB(OC_4H_9)_2$, has been reported previously [9].

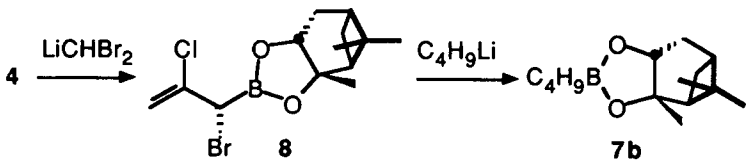
Rather than using the previously reported dehydrohalogenating agent, *tert*-butylamine [9], we decided to try lithium chloride in dimethylformamide (DMF), reasoning that the only likely side reaction would be the inconsequential displacement of chloride by chloride. As expected, heating **3** with lithium chloride in DMF readily yielded **4.**

Reaction of **4** with (dichloromethyl)lithium in the usual manner proceeded normally to provide (*s*)-pinanediol (1*S*)-(1,2-dichloroallyl)boronate (**5**). Epimerization of **5** with lithium chloride in tetrahydrofuran (THF) [10] revealed the positions of the ^1H NMR absorptions of the (1*R*)-isomer, and the original sample of **5** was found to have a 96 : 4 ratio of **5** to its epimer.

Attempts to react **5** with lithium benzyl oxide according to well-established procedures [2, 11] led only to deboronation to pinanediol benzyloxyboronate. We then turned to alkylation with Grignard reagents. Methylmagnesium bromide with **5** yielded a separable 3 : 1 mixture of (*s*)-pinanediol (1*S*)-(1-methyl-2-chloroallyl)boronate (**6a**) and (*s*)-pinanediol methylboronate (**7a**). Butylmagnesium chloride with **5** yielded a mixture of (*s*)-pinanediol (1*S*)-(1-butyl-2-chloroallyl)boronate (**6b**) and (*s*)-pinanediol butylboronate (**7b**).

In work with [(benzyloxy)alkyl]boronic esters, we had found that the use of (diboromomethyl)lithium to make α-bromo boronic esters instead of α-chloro boronic esters led to improved yields and stereoselectivities [11]. We therefore tested the reaction of (chlorovinyl)boronic ester **4** with (dibro-





momethyl)lithium and obtained bromo ester **8**. However, the ^1H NMR spectrum indicated that the **8** contained ~30% of the (1*R*)-epimer, as well as ~25% unchanged **4**. Reaction of **8** with butyllithium yielded only butylboronic ester **7b**.

DISCUSSION

The methoxyvinyl group of (*s*)-pinanediol (1-methoxyvinyl)boronate (**1**) is apparently too acid labile to allow **1** to react as a typical boronic ester with (dichloromethyl)lithium. Perhaps acid-catalyzed migration of the dichloromethyl group to the methoxyvinyl group is faster than migration of methoxyvinyl to dichloromethyl. Nothing in our results would encourage further experimentation.

In contrast, the reaction of **1** with butylmagnesium chloride followed by acid to form (*s*)-pinanediol (1-methoxy-1-methylpentyl)boronate (**2**) is highly efficient and might be useful in a different synthetic context. The (methoxyvinyl)borate complex that leads to **2** could be made by reaction of the butylboronic ester **7b** with (1-methoxyvinyl) lithium, and oxidation of **2** produced by this route should produce a ketone, with the net result being a conversion of $RB(OR')_2$ to $RCOCH_3$.

The lack of stereoselection in the conversion of **1** to **2** is disappointing. However, pinanediol boronic esters have two diastereomers with respect to the chiral boron atom, and the diastereomer involved in the reaction we examined is the wrong one to produce any appreciable diastereoselection [6, 12]. The question whether this reaction can produce useful diastereoselection remains unanswered until (1-methoxyvinyl)-lithium is added to a pinanediol boronic ester or a chiral director having C_2 symmetry [13] is tested.

The chlorovinyl group of (*s*)-pinanediol (1-chlorovinyl)boronate (**4**) behaves normally in the reactions with (dihalomethyl)lithium reagents. Although nucleophiles can displace halide from (1-haloalkenyl)boronic esters [4], this is clearly not the major mode of reaction of **4** with (dihalomethyl)lithiums. We attribute the poor diastereoselection in the formation of the α-bromo boronic ester **8** to the high reactivity of the allylic system toward halide exchange [10].

The failure of (*s*)-pinanediol (1,2-dichloroallyl) boronate (**5**) to undergo simple chloride displacement with lithium benzyloxide has precedent in the behavior of simple (1-chloroallyl)boronic esters toward alkoxides [14]. What happens to the allylic group is not understood, though some sort of allyl anion transfer from one boron to another or to an electrophile encountered in workup seems likely. A (1-methoxyallyl)boronic ester has been made previously and was found to decompose easily [14]. On the other hand, lithio(hexamethyl)disilazane reacts perfectly normally with (*s*)-pinanediol (1*S*)-(1-chloroallyl)boronate [15].

The reaction of **5** with butylmagnesium chloride to form (*s*)-pinanediol (1*S*)-(1-butyl-2-chloroallyl)boronate (**6b**) has close precedent in the behavior of (*s*)-pinanediol (1*S*)-(1-chloroallyl)boronate toward butylmagnesium bromide [16]. However, the cleavage of a substantial fraction of the borate intermediate from **5** to (*s*)-pinanediol butylboronate (**7b**) was unexpected, and underscores the lability of the carbon—boron bond of allylic α-halo boronic esters.

The degree of inefficiency in the preparation of (*s*)-pinanediol (1-bromo-2-chloroallyl)boronate (**8**) is anomalous, but the epimerization is not surprising. The first α-bromo boronic esters prepared had β-alkoxy substituents, which made them all relatively inert to epimerization [11]. α-Bromo boronic esters have been found generally superior to the chloro analogues for amino acid synthesis, except that pinanediol (1-bromo-2-phenylethyl)boronate epimerized to an appreciable extent and the chloro analogue did not [17]. From the present results, it appears that allylic α-bromo boronic esters epimerize so readily that they will be difficult to use in synthesis.

The cleavage of **8** by butyllithium to form pinanediol butylboronate (**7b**) and not the product **6b** from displacement of bromide was unexpected. There is reason to suspect that the use of butyllithium in place of butylmagnesium halide, rather than the change from the chlorine of **5** to the bromine of **8**, was the controlling factor. In earlier work, (*s*)-pinanediol (1*S*)-(1-chloroallyl)boronate with butylmagnesium bromide yielded fairly clean (*s*)-pinanediol (1*S*)-(1-vinylpentyl)boronate, which was oxidized to (3*S*)-1-hepten-3-ol of high enantiomeric purity [16]. NMR evidence indicated that small amounts of butanol (7–8 mol%) and 2-hepten-1-ol (2%–3%) were formed as byproducts [18]. However, when butyllithium was used in place of the magnesium reagent, the alcohol product had a very low rotation ("10% ee"), and boiling point evidence suggested that a large proportion of butanol may have been present [18]. Ordinarily our experience has indicated that magnesium and lithium re-

agents can be used interchangeably for reactions with α-halo boronic esters [2, 3], but it appears that with (α-haloallyl)boronic esters the magnesium reagents give much better results.

CONCLUSIONS

We have synthesized a (1-methoxyvinyl)boronic ester (**1**) and shown that its reaction with a Grignard reagent followed by acid efficiently yields the corresponding [(methyl)(methoxy)(alkyl)methyl]boronic ester (**2**). However, the usual type of reaction of (dichloromethyl)lithium with boronic esters does not take place with **1**, and no identifiable product was obtained.

We have shown that a (1,1-dichloroalkyl)boronic ester (**3**) can be dehydrochlorinated to a (1-chlorovinyl)boronic ester (**4**), and that **4** undergoes normal reaction with (dichloromethyl)lithium to produce the (1,2-dichloroallyl)boronic ester **5** in synthetically useful yield. The major reaction of **5** with alkylmagnesium halides produces the expected [(1-chlorovinyl)(alkyl)methyl]boronic esters (**6**), accompanied by significant amounts of anomalous cleavage to alkylboronic esters (**7**).

EXPERIMENTAL SECTION

General Data

Reactions involving carbanions were run under an atmosphere of argon. Tetrahydrofuran was freshly distilled from benzophenone ketyl. Other reagent-grade chemicals were used as purchased. (*s*)-Pinanediol was prepared from (+)-α-pinene of 99% ee purchased from Aldrich Chemical Company. NMR spectra were run on a Nicolet NT-200 or JEOL FX-90 instrument, mass spectra on a VG Instruments 7070 EHF mass spectrometer. Chromatography was carried out with Merck 230- to 400-mesh silica gel. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

(s)-*Pinanediol (1-Methoxyvinyl)boronate* (**1**)

Methyl vinyl ether was bubbled into 3 mL of THF at −78°C until the volume had increased by approximately 3 mL (40 mmol). After addition of 15 mL more THF and cooling, 27 mmol of 1.7M *tert*-butyllithium in cyclohexane was added dropwise, the mixture was warmed to 0°C (and became clear and colorless) and cooled again to −78°C, then transferred by cannula to a solution of 4.7 g (25 mmol) of triisopropyl borate in 50 mL of THF at −78°C. The solution was warmed to 25°C over a period of 1 h and stirred 1 additional h. Acetic acid (1.4 mL) and phenolphthalein indicator were added, and solid sodium bicarbonate was added in small portions until the endpoint was reached. The mixture was filtered and the solid was washed with ether. The solution was concentrated under vacuum (>5 torr) and the diisopropyl (1-methoxyvinyl)boronate was distilled at 52–62°C (5 torr), 2.26 g, air sensitive; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.18 (d, J = 6 Hz, 12, $CH(CH_3)_2$), 3.51 (s, 3, OCH_3), 3.2–3.8 (m, 4, $OCH(CH_3)_2$ + $=CH_2$). This isopropyl ester was treated with 2.07 g of pinanediol in 20 mL of diethyl ether overnight to form **1**, then concentrated and distilled, bp 75–84°C (0.05 torr), solidified in freezer; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.85 (s, 3), 1.17 (s, *tert*-Bu impurity ?, 0.5), 1.19 (d, J = 11 Hz, 1), 1.29 (s, 3), 1.39 (s, 3), 1.75–2.55 (m, 5), 3.57 (s, 3, OCH_3), 4.36 (dd, 1, *CH*OB), 4.74 (broad s, 1, $=CHH$), 4.88 (d, J = 1.7 Hz, 1, $=CHH$); MS (10 eV) *m/e* calcd ($C_{13}H_{21}BO_3$) 236.1584, obs 236.1575.

(s)-*Pinanediol (1-Methoxy-1-methylpentyl)boronate* (**2**)

A solution of 743 mg (3.15 mmol) of **1** in 3 mL of THF was stirred at −78°C during the dropwise addition of 3.15 mmol of 2.4 M butylmagnesium chloride in ether. After 10 min the mixture was treated with 0.180 mL (3 mmol) of acetic acid. The solution was concentrated and the residue was dissolved in diethyl ether and washed with water. The product was concentrated and chromatographed on silica with 3:1 light petroleum ether/diethyl ether to yield 548 mg (59%) of a 2:1 mixture of diastereomers of (*s*)-pinanediol (1-methoxy-1-methylpentyl)boronate (**2**); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.85 (s, 3), 0.90 (t, J = 6.8 Hz, 3), 1.16 (d, J = 10.8 Hz, 1), [epimer 1.15 (d, J = 10.8 Hz)], 1.234 (s, 3, BC(OMe)CH_3) [epimer 1.226], 1.29 (s, 3), 1.408 (s, 3) [epimer 1.403], 1.2–2.4 (m, CH_2 + pinyl *CH*), 3.238 (s, 3, OCH_3) [epimer 3.245], 4.33 (dd, 1, *CH*OB) [epimer 4.34]. When the same procedure was repeated except that 0.7 equivalent of zinc chloride was added before the acetic acid, the yield of **2** was 89% and the diastereomer ratio was 53:47.

(s)-*Pinanediol (1-Chlorovinyl)boronate* (**4**)

A solution of 3.10 g (11.2 mmol) of (*s*)-pinanediol 1,1-dichloroethylboronate [5, 6] (**3**) and 1.42 g (33.6 mmol) of lithium chloride in 15 mL of dimethylformamide was heated in an oil bath at 105°C for 2.5 h, at which time the reaction appeared complete by thin-layer chromatography (TLC) analysis. The solution was cooled and concentrated under vacuum. Chromatography of the residue on silica with 3:1 light petroleum ether/diethyl ether yielded 1.97 g (73%) of **4**, mp 50–52°C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.85 (s, 3), 1.15 (d, J = 10.8 Hz, 1), 1.30 (s, 3), 1.45 (s, 3), 1.56 (s, ~0.5, impurity), 1.87–2.46 (m, 5, pinyl *CH*), 4.42 (dd, 1), 6.07 (s, width 2.0 Hz at half-height, 1, $=CHH$), 6.15 (d, J = 0.4 Hz, 1, $=CHH$);

MS (70 eV) *m/e* calcd ($C_{12}H_{18}BClO_2$) 240.1088, obs 240.1138 (30), 225 (50), 171 (70), 145 (75), 96 (100).

(s)-*Pinanediol* (*1S*)-(*1,2-Dichloroallyl*)*boronate* (**5**)

(Dichloromethyl)lithium was prepared in the usual manner [2] by adding 4.1 mmol of butyllithium to 0.4 mL of dichloromethane in 8 mL of THF at −100°C. A solution of 945 mg (3.93 mmol) of (*s*)-pinanediol (1-chlorovinyl)boronate (**4**) in 3 mL of THF was added and the solution was stirred for 10 min at −100°C. A 375-mg (2.75-mmol) portion of powdered anhydrous zinc chloride [2] was added. The cooling bath was allowed to warm slowly to room temperature and stirring of the mixture was continued overnight. The mixture was concentrated under vacuum to half volume and treated with 50 mL of light petroleum ether and a few grams of anhydrous magnesium sulfate [6, 13a]. Filtration through a 2-cm plug of magnesium sulfate and concentration yielded 1.08 g of crude product, whch was chromatographed on silica with 3 : 1 petroleum ether/diethyl ether, 860 mg (76%) of **5**; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.85 (s, 3), 1.24 (d, *J* = 10.9 Hz, 1), 1.30 (s, 3), 1.45 (s, 3), 1.87–2.46 (m, 5, pinyl C*H*), 4.17 (m, 1, C*H*Cl), 4.43 (dd, 1), 5.42 (m, 1, =C*H*H), 5.66 (dd, *J* = 1.2 and 1.8 Hz) [epimer, 5.67, 4%]; MS (70 eV) *m/e* molecular ion not observed, M − 35 calcd ($C_{13}H_{19}BClO_2$) 253.1167, obs 253.1135 (10), 58 (80), 43 (100). An epimeric mixture was prepared by treatment of **5** with lithium chloride in THF [10] and revealed that the ^{1}H NMR spectra of the two isomers differed at the point indicated.

(s)-*Pinanediol* (*1S*)-(*1-Methyl-2-chloroallyl*)*boronate* (**6a**)

A solution of 363 mg (1.26 mmol) of (*s*)-pinanediol (1*S*)-(1,2-dichloroallyl)boronate (**5**) in 2 mL of THF at −78°C was stirred during the addition of 1.38 mmol of 3 M methylmagnesium bromide in diethyl ether. The mixture was allowed to warm to 25°C and stirred overnight. Addition of 20 mL of light petroleum ether and a few grams of magnesium sulfate followed by filtration through a plug of magnesium sulfate and concentration yielded 280 mg of a mixture of 75% (*s*)-pinanediol (1*S*)-(1-methyl-2-chloroallyl)boronate (**6a**) (yield 67%) and 25% (*s*)-pinanediol methylboronate [2] (yield 22%). The analytical sample of **6a** was prepared by distilling the pinanediol methylboronate from the mixture at 60°C bath temperature (0.2 torr) for 30 min, followed by chromatography with 9 : 1 light petroleum ether/diethyl ether on silica; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.84 (s, 3, pinyl CH_3), 1.19 (d, *J* = 11.0 Hz, 1, cyclobutyl C*H*H [2]) 1.24 (d, *J* = 7.3 Hz, 1, CHCH_3), 1.29 (s, 3, pinyl CH_3) 1.40 (s, 3, pinyl CH_3), 1.80–2.42 (m, 6, pinyl C*H* + BC*H*CH_3) 4.32 (dd, *J* = 2.1 and 8.8 Hz, 1, C*H*OB), 5.13–5.16 (m, 2, =CH_2); MS (2.7 eV) *m/e* calcd ($C_{14}H_{22}BClO_2$) 268.1401, obs 268.1533 (2), 253 (5), 145 (35), 40 (100). Anal. Calcd for $C_{14}H_{22}BClO_2$: C, 62.61; H, 8.26. Found: C, 62.62; H, 8.14.

(s)-*Pinanediol* (*1S*)-*1-Butyl-2-chloroallylboronate* (**6b**) *and* (s)-*Pinanediol Butylboronate* (**7b**)

These compounds were obtained in an inseparable 2.5 : 1 mixture by the same procedure used to prepare **6a** but with butylmagnesium chloride instead of methylmagnesium bromide. From 118 mg of **5** the yield of a chromatographed mixture was 116 mg, 70% of **6b** and 28% of **7b** by NMR analysis; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.84 (s, 3, both), 0.90 (t, CH_3 of **7b**), 1.12 (d, *J* = 10.7 Hz, **7b**), 1.21 (d, *J* = 10.9 Hz, **6b**), 1.29 (s, both), 1.2–1.5 (m, (CH_2)$_3$ of **7b**) 1.38 (s, **6b**), 1.40 (s, **7b**), 1.6–2.45 (m, **6b**), 4.25 (dd, *J* = 2.0 and 8.7 Hz, C*H*OB, **6b**, 72%), 4.32 (dd, *J* = 2.0 and 8.7 Hz, C*H*OB, **7b**, 28%), 5.14 (dd, *J* = 0.6 and 1.2 Hz, =C*H*H of **6b**), 5.16 (d, *J* = 1.2 Hz, =CH*H* of **6b**); MS (70 eV) *m/e* 236 (**7b**, $C_{14}H_{25}BO_2$), **6b** not detected.

(s)-*Pinanediol* (*1S*)- *and* (*1R*)-*1-Bromo-2-chloroallylboronate* (**8**)

Treatment of 457 mg (1.9 mmol) of (*s*)-pinanediol (1-chlorovinyl)boronate (**4**) and 6 mmol of dibromomethane in 4 mL of THF at −78°C with 2.3 mmol of lithium diisopropylamide [11] was followed by addition of 3.9 mmol of 1M zinc chloride in ether (Aldrich Chemical Company) and stirring at 25°C overnight. Workup with light petroleum ether and magnesium sulfate as described for **5** and concentration yielded 0.33 g of a mixture of ~3 parts of **8** (*S*/*R* isomer ratio ~2 or 3 : 1) and 1 part of unconverted **4**; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.85 (s, 3), 1.25 (d, *J* = 11 Hz, 1), 1.30 (s, 3), 1.44 (s, 3), 1.59 (s, ~0.4, impurity), 1.86–2.47 (m, 5), 4.11 (d, *J* = 0.8 Hz, 0.25, (*R*)-BC*H*Br), 4.13 (d, *J* = 0.8 Hz, 0.75, (*S*)-BC*H*Br), 4.42 (dd, (*R*)-**8** + **4** C*H*OB) 4.43 (dd, (*S*)-**8**-C*H*OB), 5.45 (d, *J* = 2 Hz, =C*H*H), 5.76 (m, (*S*)-**8**-=CH*H*), 5.77 (m, (*R*)-**8**-=CH*H*), plus peaks characteristic of **4**. Treatment of this sample of **8** with butyllithium followed by workup with light petroleum ether and magnesium sulfate yielded (*s*)-pinanediol butylboronate (**7b**) as the only detectable product by NMR analysis.

Acknowledgment

We thank the National Institutes of Health for Grant No. GM33801 and the Boeing Corporation for partial support of the departmental purchase of the 200-MHz NMR instrument.

References

[1] [a] A. B. Levy, S. J. Schwartz, *Tetrahedron Lett.*, 1976, 2201–2204. [b] A. B. Levy, S. J. Schwartz, N. Wilson, B. Christie, *J. Organomet. Chem., 156,* 1978, 123.

[2] D. S. Matteson, K. M. Sadhu, M. L. Peterson, *J. Am. Chem. Soc., 108,* 1986, 810.

[3] D. S. Matteson, *Acc. Chem. Res., 21,* 1988, 294.

[4] [a] H. C. Brown, N. G. Bhat, V. Somayaji, *Organometallics, 2,* 1983, 1311. [b] H. C. Brown, T. Imai, *Organometallics, 3,* 1984, 1392. [c] H. C. Brown, T. Imai, N. G. Bhat, *J. Org. Chem., 51,* 1986, 5277.

[5] [a] D. S. Matteson, G. D. Hurst, *Organometallics, 5,* 1986, 1465. [b] D. S. Matteson, G. D. Hurst, U.S. Patent 4,701,545, 20 Oct. 1987, 6; *Chem. Abstr., 109,* 1988, 93315.

[6] D. S. Matteson, G. D. Hurst, *Heteroatom Chem., 1,* 1990, 65.

[7] J. E. Baldwin, G. A. Hofle, O. W. Lever Jr., *J. Am. Chem. Soc., 96,* 1974, 7125.

[8] H. C. Brown, T. E. Cole, *Organometallics, 2,* 1983, 1316.

[9] D. S. Matteson, R. W. H. Mah, *J. Org. Chem., 28,* 1963, 2174.

[10] D. S. Matteson, E. Erdik, *Organometallics, 2,* 1983, 1083.

[11] D. S. Matteson, M. L. Peterson, *J. Org. Chem., 52,* 1987, 5116.

[12] D. J. S. Tsai, P. K. Jesthi, D. S. Matteson, *Organometallics, 2,* 1983, 1543.

[13] [a] K. M. Sadhu, D. S. Matteson, G. D. Hurst, J. M. Kurosky, *Organometallics, 3,* 1984, 804. [b] D. S. Matteson, A. A. Kandil, *Tetrahedron Lett., 27,* 1986, 3831.

[14] R. W. Hoffmann, B. Landmann, *Chem. Ber., 119,* 1986, 1039.

[15] D. S. Matteson, T. J. Michnick, R. D. Willett, C. D. Patterson, *Organometallics, 8,* 1989, 726.

[16] D. S. Matteson, R. Ray, R. R. Rocks, D. J. S. Tsai, *Organometallics, 2,* 1983, 1536.

[17] D. S. Matteson, E. C. Beedle, *Tetrahedron Lett., 28,* 1987, 4499.

[18] D. S. Matteson, unpublished observations, 1983.