atoms were refined with anisotropic thermal parameters and H atoms with one common isotropic thermal parameter (U = 0.0158 (16) Å^2). Weights were introduced in the final refinement cycles; convergence was reached at R = 0.025.

Crystal data and numerical details of the structure determination are given in Table VII. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table IX. Neutral atom scattering factors were taken from Cromer and Mann[42] and corrected for anomalous dispersion.[46] All calculations were performed with SHELX76[47] and the EUCLID package[48] (geometrical calculations and illustrations) on a MicroVAX cluster.

Acknowledgment. The Netherlands Foundation for Chemical Research (SON) and The Netherlands Organization for Scientific Research (NWO) are thanked for financial support (A.L.S., W.J.J.S.). Thanks are also due to A. J. M. Duisenberg for the X-ray data collection of (PAN)Pd(CH$_3$)Cl (**5a**) and D. Heidenrijk for the collection of the X-ray data for (PAN)$_2$PdCl$_2$ (**3b**). We thank H. Luyten, P. G. M. Schilder, J. M. Ernsting, and J. H. G. Frijns for their technical assistance. We are grateful to Shell Reseach BV for financial support.

Supplementary Material Available: Tables of H atom coordinates, anisotropic thermal parameters, and bond distances and angles for **3b** and **5a** (12 pages). Ordering information is given on any current masthead page.

OM910656O

(45) Sheldrick, G. M. SHELXS86: Program for Crystal Structure Determination; University of Göttingen: Göttingen, Federal Republic of Germany, 1986.
(46) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.
(47) Sheldrick, G. M. SHELX76: Crystal Structure Analysis Package; University of Cambridge: Cambridge, U.K., 1976.
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Organoboranes. 54. Exploration of the Reactions of (α-Haloallyl)lithium with Organoborane Derivatives. Simple and Convenient Procedure for the Synthesis of Three-Carbon Homologated Boronate Esters and Terminal Alkenes

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The synthetic utility of (α-haloallyl)lithium generated in situ for the facile transfer reaction of various organoborane derivatives, such as R_3B, R_2BOR', and $RB(OR')_2$, has been explored. This has led to the synthesis of α-vinylboronate esters, $RCH(CH{=}CH_2)B(OR')_2$, which are readily isomerized thermally to the corresponding allylboronate esters with the boron atom on the less substituted carbon atom, $RCH{=}CHCH_2B(OR')_2$. Catalytic hydrogenation of these allylboronate esters furnishes saturated boronate esters, $RCH_2CH_2CH_2B(OR')_2$, providing a three-carbon homologation of the original R–B< moiety. Protonolysis in place of hydrogenation affords the corresponding terminal alkenes $RCH_2CH{=}CH_2$.

In view of their synthetic promise, the reactions of organoboranes with carbenoid reagents bearing a potential leaving group, such as $LiCCl_3$, $LiCH_2SMe$, $LiCHCl_2$, $LiCH_2Cl$, and LiCHCl(OMe), have been the focal point of several investigations in the recent past.[2] Such one-carbon homologations of organoboranes have led to the synthesis of pheromones, L-ribose, amino acids, and α-chiral compounds[3] in high enantiomeric purities. The remarkable difficulty encountered in the generation of such unstable carbenoids has been circumvented by the discovery of the practicality of in situ procedures.[4-6] As a part of our ongoing program on the synthetic utility of the homologation of organoboranes, we became interested in developing a protocol for three-carbon homologation. This involves the generation of α-heteroatom-substituted allylic carbanions. A search of the literature revealed very few reports on the formation of α-substituted allylic carbanions and their regioselective reaction with electrophiles.[7] Suzuki et al. had utilized this methodology in the synthesis

(1) (a) Postdoctoral research associate on Grant CHE-8706102 from the National Science Foundation. (b) Postdoctoral research associate (on leave from India) on Grant CHE-8706102 from the National Science Foundation.
(2) (a) Matteson, D. S. *Chem. Rev.* **1989**, *89*, 1535 and references cited therein. (b) Brown, H. C. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1983; Vol. 7, Chapter 45.1.
(3) Rangaishenvi, M. V.; Singaram, B.; Brown, H. C. *J. Org. Chem.* **1991**, *56*, 3286.
(4) (a) Matteson, D. S.; Hurst, G. D. *Organometallics* **1986**, *5*, 1465. (b) Cainelli, G.; Ronchi, A. U.; Bertini, F.; Grasselli, P.; Zubiiana, G. *Tetrahedron* **1971**, *27*, 6109.
(5) Sadhu, K. M.; Matteson, D. S. *Organometallics* **1985**, *4*, 1687.
(6) Brown, H. C.; Singh, S. M.; Rangaishenvi, M. V. *J. Org. Chem.* **1986**, *51*, 3150.
(7) (a) Evans, D. A.; Andrews, G. C.; Buckwalter, B. *J. Am. Chem. Soc.* **1974**, *96*, 5560. (b) Still, W. C.; Macdonald, T. L. *J. Am. Chem. Soc.* **1974**, *96*, 5561. (c) Biellmann, J. F.; Ducep, J. B. *Org. React.* **1982**, *27*, 1. (d) For a recent reference, see: Julia, M.; Verpeaux, J.; Zahneisen, T. *Synlett* **1990**, 769.

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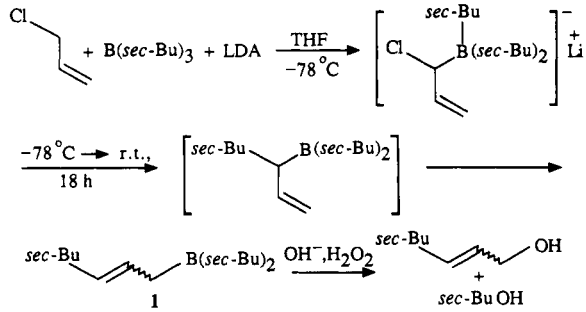
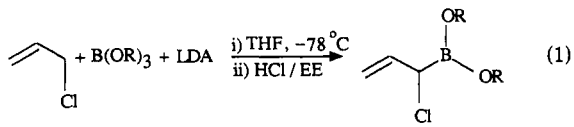
Scheme I



of 1-alkenes and 1,5-alkadienes.[8a] (γ-Chloroallyl)lithium, prepared by the transmetalation reaction between $Ph_3PbCH_2CH{=}CHCl$ and *n*-BuLi, has proven to be a useful intermediate for the synthesis of heterocyclic compounds.[8b] A simple and elegant procedure for the regioselective generation of (α-haloallyl)lithium, $LiCH(X)CH{=}CH_2$, which circumvents the difficulty of "self-consumption", was proposed by Macdonald et al.[9] Very recently, we successfully demonstrated[10] the in situ preparation and utility of $LiCH(X)CH{=}CH_2$ for a simple and convenient synthesis of (α-chloroallyl)boronate esters (eq 1).



(1)

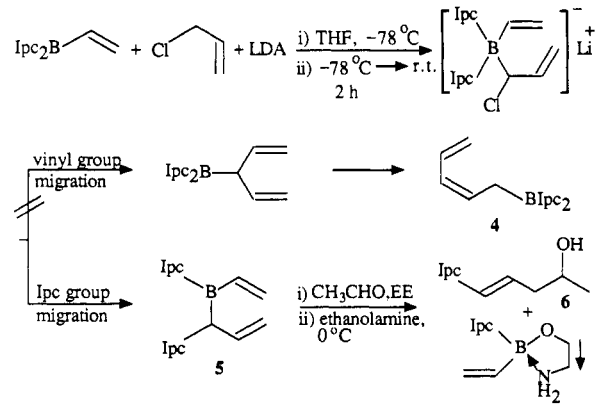
Such α-heteroatom-substituted allylboronates are valuable intermediates for the synthesis of δ-lactones via the allylboration reaction.[11] Herein we report the results realized in our exploration of the reactions of (α-haloallyl)lithium with representative examples of three different organoborane derivatives, R_3B, R_2BOR', and $RB(OR')_2$.

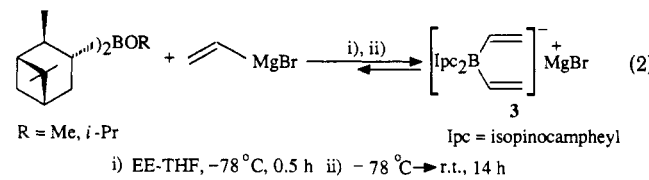
Results and Discussion

For our preliminary study, we chose tri-*sec*-butylborane as a representative example of R_3B. The reaction of this compound with (α-chloroallyl)lithium generated in situ following the reported procedure,[10] followed by the usual transfer reaction, provided the allylborane **1**. In agreement with the structure, the ^{11}B NMR spectrum displayed a peak at δ 81 ppm. The ^1H NMR spectrum was also consistent with the assigned structure. Evidently, the carbenoid anion coordinates with boron to furnish the ate complex. Then, the migration of a *sec*-butyl group leads to the α-vinylborane, which undergoes a facile [1,3]-sigmatropic shift while it is warmed to room temperature (Scheme I). This was further confirmed by the oxidation of **1** with preformed peroxy anion, generated from aqueous NaOH and 30% H_2O_2.

We then decided to test this procedure for a transfer reaction with diisopinocampheylvinylborane, $Ipc_2BCH{=}CH_2$ (**2**). We were particularly interested in this reaction, as it would lead to a chiral allylborane derivative, a useful precursor for our asymmetric allylboration studies. However, the attempted preparation of **2** via the reaction of alkoxydiisopinocampheylborane, Ipc_2BOR, with a vinyl Grignard reagent, analogous to the procedure for the synthesis of $Ipc_2BCH_2CH{=}CH_2$,[12] was not successful. In addition to recovered starting material, there was obtained a product whose ^{11}B NMR spectrum showed a peak at δ 10 ppm, indicative of the ate complex **3** (eq 2).

Scheme II



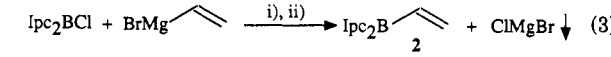


(2)

R = Me, *i*-Pr Ipc = isopinocampheyl

i) EE-THF, −78 °C, 0.5 h ii) − 78 °C→r.t., 14 h

A similar formation of the divinyl ate complex **3** had been observed in our laboratory when 9-methoxy-9-BBN was treated with the vinyl Grignard reagent.[13] However, the desired compound was obtained from (−)-chlorodiisopinocampheylborane and vinyl Grignard reagent. Consistent with structure **2**, the ^{11}B NMR spectrum showed a peak at δ 74 ppm and the ^1H NMR spectrum exhibited the characteristic vinylic pattern (eq 3).



(3)

i) EE-THF, −78 °C, 0.5 h ii) − 78 °C→r.t., 1 h

The structure of the compound was further confirmed by treatment with MeOH (no change in the ^{11}B NMR pattern). $Ipc_2BCH{=}CH_2$ was found to be quite stable, as there was no noticeable redistribution or disproportionation, even upon storage for 1 month at 0 °C. Reaction of compound **2** with (α-chloroallyl)lithium furnished a product whose ^{11}B NMR spectrum showed a peak at δ 82 ppm, indicating the completion of the transfer reaction. Its ^1H NMR spectrum did not exhibit the characteristic pattern for (2,4-pentadienyl)diisopinocampheylborane (**4**) but was in good agreement with the spectrum for the compound **5**. This was further confirmed by allylboration with acetaldehyde to obtain the corresponding homoallylic alcohol derivative **6** (Scheme II).

Evidently the Ipc group had undergone migration in preference to the vinyl group. The chemical purity of the homoallylic alcohol derivative was determined by GC analysis and its structure confirmed by mass spectral data. However, no attempt was made to determine the optical purity.

For study of the transfer reaction of the (α-chloroallyl)lithium species with a borinate ester, 9-methoxy-9-BBN was selected as an appropriate example. In this case

(8) (a) Hara, S.; Imai, S.; Hara, T.; Suzuki, A. *Synth. Commun.* **1982**, *12*, 813. (b) Mauzé, B. *J. Organomet. Chem.* **1979**, *170*, 265; **1980**, *202*, 233. Doucouré, A.; Mauzé, B.; Miginiac, L. *J. Organomet. Chem.* **1982**, *236*, 139. Ongoka, P.; Mauzé, B.; Miginiac, L. *Synthesis* **1985**, 1069.

(9) Macdonald, T. L.; Narayanan, B. A.; O'Dell, D. E. *J. Org. Chem.* **1981**, *46*, 1504.

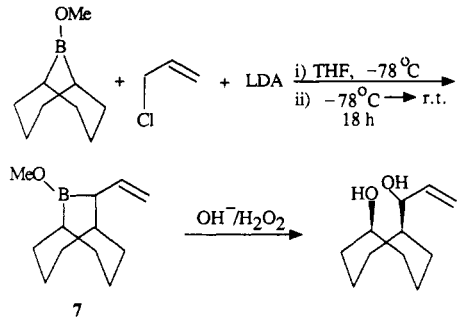
(10) Brown, H. C.; Rangaishenvi, M. V. *Tetrahedron Lett.* **1990**, *49*, 7113, 7115.

(11) For the synthesis of α-heteroatom-substituted allylboronate esters and 2,4-pentadienyl boronate esters, see: Hoffmann, R. W.; Landmann, B. *Chem. Ber.* **1986**, *119*, 1039.

(12) Brown, H. C.; Jadhav, P. K. *J. Am. Chem. Soc.* **1983**, *105*, 2092.

(13) Kramer, G. W.; Brown, H. C. *J. Organomet. Chem.* **1974**, *73*, 1.

Scheme III

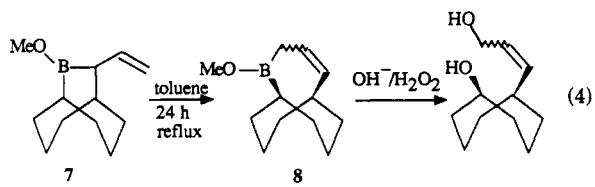


7

the α-vinylborinate **7** was obtained, whose structure was established both by spectral data (^{11}B and ^{1}H NMR) and by oxidation (Scheme III).

To confirm the structure of the allylic borinate ester **7**, we undertook its preparation by an alternate route. Hydroboration of a 100% excess of propargyl chloride with 9-BBN, analogous to the method of Zweifel et al.,[14] furnished the vinylborane intermediate (^{11}B NMR: δ 80 ppm). Addition of THF and stirring at room temperature for 12 h gave a product whose ^{11}B NMR spectrum showed a peak at δ 58 ppm corresponding to the formation of the R_2BOR' species. Evidently THF coordinates with the vinylborane, displacing the chloride to provide an intermediate, which on transesterification with MeOH at 25 °C for 6 h afforded the desired α-vinylborinate ester **7**. Alternatively, treatment of the hydroboration product of propargyl chloride with 1 equiv of anhydrous NaOMe in MeOH furnishes **7** in almost quantitative yield (Scheme IV).

Very recently we have taken advantage of the thermally induced [1,3]-sigmatropic shift in α-substituted allylboronate esters to provide the isomeric allylboronate esters with the boron on the less substituted carbon atom.[10] Refluxing the borinate ester **7** in toluene for 24 h affords the desired borinate ester **8** (eq 4). The structure of compound **8** is confirmed by spectral analysis and its purity by GC analysis of the oxidation product diol as its bis(trimethylsilyl) ether.



(4)

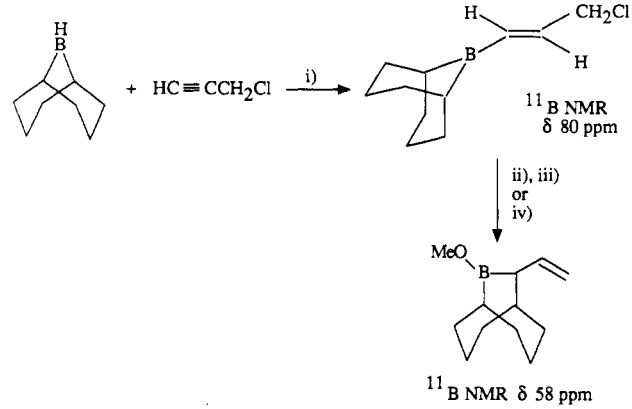
7 8

Next, we explored the utility of (α-haloallyl)lithium for the in situ reaction with boronate esters, followed by the transfer reaction. We have recently reported[10] a simple and convenient approach for the synthesis of (α-chloroallyl)boronate esters and their transformation into α-alkyl- or α-aryl-substituted allylboronate esters by reaction with the appropriate RLi or RMgX reagents (Scheme V).

This reaction is postulated to proceed via the formation of the same ate complex **9**. Therefore, we thought it worthwhile to study such a transfer reaction with boronate esters. Gratifyingly, the reaction of boronate esters in THF with $LiCH(X)CH{=}CH_2$ afforded ate complexes (^{11}B NMR δ 2 ppm), which undergo clean transfer reactions to provide the desired α-organyl-substituted esters (^{11}B NMR δ 31 ppm). This procedure was extended to a series of representative boronate esters, and the results are summarized in Table I.

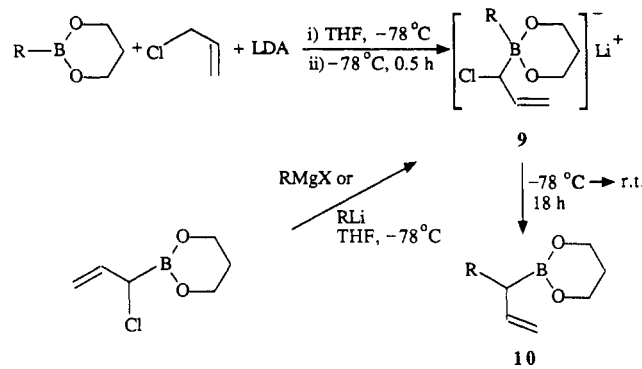
(14) Zweifel, G.; Horng, A.; Snow, J. T. *J. Am. Chem. Soc.* **1970**, *92*, 1427.

Scheme IV[a]



[a] Legend: (i) CCl_4, 25 °C, 4 h; (ii) THF, 25 °C, 12 h; (iii) MeOH; (iv) NaOMe, 25 °C, 12 h.

Scheme V



9 10

Table I. Homologation of Boronate Esters with (α-Chloroallyl)lithium, $LiCH(Cl)CH{=}CH_2$

R in boronate ester $RBO_2(CH_2)_3$	product, $RCH(CH{=}CH_2)BO_2(CH_2)_3$ (**10**) ^{11}B NMR ($CDCl_3$), δ	isolated yield,[a] %	oxidn product[b] $RCH(CH{=}CH_2)OH$
n-hexyl	34	78	1-nonen-3-ol
cyclohexyl	31	80	1-cyclohexyl-2-propen-1-ol
trans-2-methylcyclopentyl	33	82	1-(*trans*-2-methylcyclopentyl)-2-propen-1-ol
exo-bicyclo[2.2.1]heptyl	32	75	1-(*exo*-bicyclo[2.2.1]heptyl)-2-propen-1-ol
tert-butyl	30	70	4,4-dimethyl-1-penten-3-ol
phenyl	29	75	1-phenyl-2-propen-1-ol

[a] Purification by distillation is avoided to prevent a possible [1,3]-sigmatropic shift. [b] Oxidation was performed via inverse addition of allylic boronate ester to the preformed peroxy anion using H_2O_2–NaOH, and the product alcohols were purified by fractional distillation and preparative GC.

The reactions of (α-haloallyl)boronate esters with 1 equiv of RMgX or RLi at −78 °C, followed by warming to room temperature, also furnish the desired α-alkyl- or α-aryl-substituted boronate esters. The assigned structure of these allylboronate esters has been confirmed by spectral and GC analyses of the oxidation product. The results are summarized in Table II.

The [1,3]-sigmatropic shift of boron in α-substituted allylborane produces the thermodynamically more stable isomer with the boron on the less substituted carbon atom. This reaction has been examined for α-substituted allylborane[15] but is apparently unexplored for the α-substituted allylborinate or boronate esters. We decided to undertake

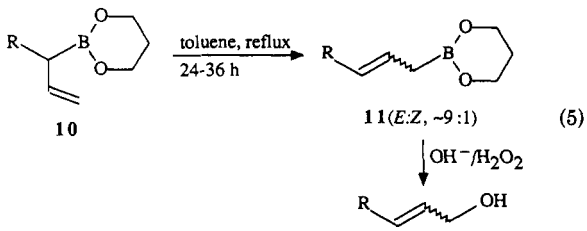
(15) (a) Bubnov, Yu. N. *Pure Appl. Chem.* **1987**, *59*, 895. (b) Mikhailov, B. M.; Bubnov, Yu. N. *Organoboron Compounds in Organic Synthesis*; Harwood: London, New York, 1984.

Table II. Nucleophilic Displacement of the (α-Chloroallyl)boronate Ester by Representative RLi or RMgX Reagents

nucleophile RLi or RMgX	product,[a] $RCH(CH{=}CH_2)$-$BO_2(CH_2)_3$ (10) ^{11}B NMR ($CDCl_3$), δ	isolated yield, %	oxidn product[b] $RCH(CH{=}CH_2)OH$
n-C_4H_9Li	32	78	1-hepten-3-ol
n-$C_6H_{13}MgCl$	32	80	1-nonen-3-ol
sec-C_4H_9Li	31	72	4-methyl-1-hexen-3-ol
ChxMgCl	31	80	1-cyclohexyl-2-propen-1-ol
t-C_4H_9MgCl	30	70	4,4-dimethyl-1-penten-3-ol
C_6H_5Li	29	75	1-phenyl-2-propen-1-ol
$C_6H_5CH_2MgCl$	30	77	1-phenyl-3-buten-2-ol
(allyl)MgCl	31	75	7-phenyl-1,4-heptadien-7-ol[c]

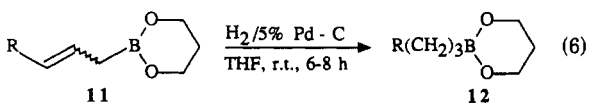
[a] Purification by distillation is avoided to prevent a possible [1,3]-sigmatropic shift. [b] Oxidation was performed via inverse addition of allylic boronate ester to the preformed peroxy anion using H_2O_2-NaOH, and the product alcohols were purified by fractional distillation and preparative GC. [c] Product characterized by allylboration with PhCHO.

a systematic study to test such rearrangement with boronate esters **10**. Refluxing **10** in toluene for 24 h (36 h for R = *t*-Bu) places the boron on the less substituted carbon atom to provide the desired allylboronate ester **11** (eq 5).



The assigned structures of these allylic boronate esters have been confirmed by spectral data and GC analysis of the oxidation products. In most cases, the boronate esters **11** are a mixture of stereoisomers with the *E* isomer predominating (*E*:*Z* ≈ 9:1) (Table III). This observation is in agreement with recent theoretical calculations.[16]

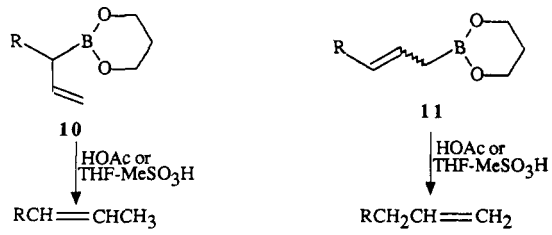
Recently we reported[17] a convenient method for preparing (*Z*)-1-alkenylboronates by hydrogenation of alkynylboronates. A similar hydrogenation of boronate ester **11** in THF using the Brown/Brown automatic gasimeter[18] provides the desired boronate ester **12** (eq 6) (Table IV).



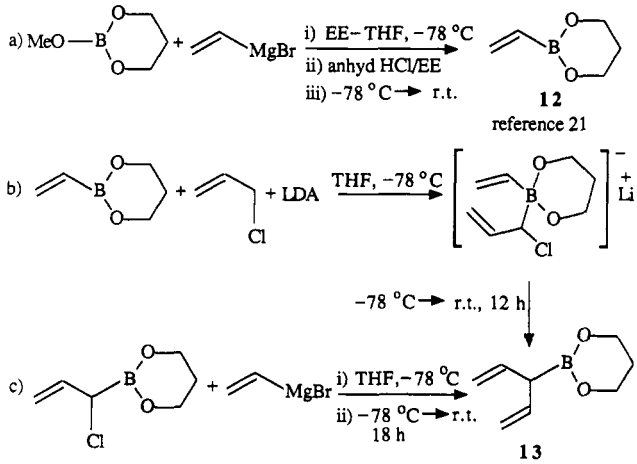
Evidently, by this reaction sequence, we have achieved the three-carbon homologation of representative 2-alkyl- and 2-aryl-1,3,2-dioxaborinanes. This protocol nicely supplements the previously established procedures for the sequential one-carbon homologation of boronate esters.

Protonolysis of the allylborane intermediates proceeds with allylic rearrangement. We have demonstrated[19] such protonolysis for allylboronate esters prepared by the one-carbon homologation of alkenylboronate esters. We extended this protonolysis procedure to allylboronate esters **10** and also to the thermally isomerized allylboronate esters **11**, utilizing either refluxing acetic acid or methanesulfonic acid. As expected, protonolysis proceeds with boratropic rearrangement to provide an internal alkene or a terminal alkene (Scheme VI), depending on the nature of the allylboronate. The results are summarized in Table V.

Scheme VI



Scheme VII



In connection with a study on allylboration of dienylboronates, we required the boronate ester **13**.[11] These boronates are difficult to prepare via metalation of 1,4-pentadiene,[20] as the major product realized is the boronate ester with the boron atom situated on the terminal carbon atom of the diene moiety. The synthesis of the desired boronate **13** was accomplished in two ways using the $LiCH(Cl)CH{=}CH_2$ species (Scheme VII).

Conclusion

We have successfully demonstrated the synthetic utility of the labile (α-haloallyl)lithium species for the transfer reaction of all three types of organoboranes R_3B, R_2BOR', and $RB(OR')_2$. The major significance of the work reported here is the accessibility of α-vinylboronate esters which can be conveniently isomerized to the thermodynamically more stable allylboron derivatives. A simple catalytic hydrogenation of these allylboronates provides a saturated boronate ester, while protonolysis leads to the terminal alkene $RCH_2CH{=}CH_2$. We are extending this methodology for a facile synthesis of medium-ring boracyclanes which are currently accessible only by the more tedious sequential one-carbon homologation.[22]

The synthetic importance of allylboronate esters in organic synthesis is well documented, especially for the allylboration of aldehydes. The allylboron intermediates reported in this study should have wide synthetic applications in allylboration.

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(17) Srebnik, M.; Bhat, N. G.; Brown, H. C. *Tetrahedron Lett.* **1988**, *29*, 2635.
(18) Brown, H. C. *Organic Synthesis via Boranes*; Wiley-Interscience: New York, 1975; pp 218–222.
(19) Brown, H. C.; Phadke, A. S.; Bhat, N. G. Manuscript in preparation.
(20) Brown, H. C.; Bhat, K. S.; Randad, R. S. Unpublished results.
(21) Brown, H. C.; Bhat, N. G.; Srebnik, M. *Tetrahedron Lett.* **1988**, *29*, 2631.
(22) (a) Brown, H. C.; Phadke, A. S.; Rangaishenvi, M. V. *J. Am. Chem. Soc.* **1988**, *110*, 6263. (b) *Heteroat. Chem.* **1990**, *1*, 83.

Table III. Thermal [1,3]-Sigmatropic Rearrangement[a] of the Allylboronate Esters 10

R in boronate ester 10	isomerizn product RCH=CH~$CH_2BO_2(CH_2)_3$ (11) ^{11}B NMR ($CDCl_3$), δ	bp, °C (mm)	isolated yield, %	oxidn product[c] RCH=$CHCH_2OH$
n-butyl	32	112–114 (17)	88	2-hepten-1-ol[d]
n-hexyl	32	80–82 (0.1)	90	2-nonen-1-ol
cyclohexyl	31	75–78 (0.1)	90	3-cyclohexyl-2-propen-1-ol
trans-2-methylcyclopentyl	32	84–85 (0.1)	86	3-(*trans*-2-methylcyclopentyl)-2-propen-1-ol
exo-bicyclo[2.2.1]heptyl	33	91–93 (0.3)	82	3-(*exo*-bicyclo[2.2.1]heptyl)-2-propen-1-ol
tert-butyl	30	84–85 (10)	84[b]	4,4-dimethyl-2-penten-1-ol
phenyl	29	110–113 (20)	91	3-phenyl-2-propen-1-ol[d]
benzyl	31	103–105 (8)	90	4-phenyl-2-buten-1-ol

[a] Performed in refluxing toluene for 24 h. [b] Required 36 h for the completion of isomerization. [c] Oxidation was performed via inverse addition of allylic boronate ester to the performed peroxy anion, and the product alcohols were purified by fractional distillation and preparative GC. [d] GC analysis reveals a 9:1 *E*–*Z* mixture.

Table IV. Catalytic Hydrogenation[a] of the Allylboronate Ester 11 in THF at 25 °C

R in boronate ester 11	hydrogenation product $R(CH_2)_3BO_2(CH_2)_3$ (12) ^{11}B NMR ($CDCl_3$), δ	isolated yield, %	oxidn product[b] $R(CH_2)_3OH$
n-butyl	32	84	1-heptanol
n-hexyl	32	86	1-nonanol
cyclohexyl	31	88	3-cyclohexyl-1-propanol
tert-butyl	30	82	4,4-dimethyl-1-pentanol
phenyl	29	90	3-phenyl-1-propanol
benzyl	31	88	4-phenyl-1-butanol

[a] Carried out in a Brown/Brown automatic gasimeter using 5% Pd–C catalyst over a period of 6–8 h at 25 °C. [b] Oxidized using alkaline H_2O_2 at 25 °C; the oxidation product alcohol was purified by distillation and preparative GC.

Experimental Section

All operations were carried out under a nitrogen atmosphere with oven-dried glassware.[18] The ^{11}B NMR spectra were recorded on a Varian FT-80A and Varian Gemini-300 spectrometer, and the chemical shifts are in δ (ppm) relative to BF_3·OEt_2 with chemical shifts downfield from BF_3·OEt_2 as positive. The ^{1}H NMR spectra were scanned on a Varian T-60 or Varian Gemini-300 spectrometer. The chemical shifts are in δ ppm relative to TMS. Gas chromatographic analyses were carried out in a Hewlett-Packard 5890-A gas chromatograph with an FID detector using either (a) a $^1/_8$ in. × 12 ft 5% SP-2100 on Chromosorb W or (b) a 10% Carbowax 20M on Chromosorb W column. IR and mass spectra were recorded on Perkin-Elmer 137 and Finnegan spectrometers, respectively.

Materials. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl prior to use. Anhydrous diethyl ether (EE) was purchased from Mallinckrodt Inc. and was used directly. Allyl chloride and allyl bromide were purchased from the Aldrich Chemical Co. and distilled prior to use. Diisopropylamine was distilled over CaH_2. *n*-Butyllithium in hexane was estimated to be 2.2 M. Alkyllithiums and Grignard reagents used in this study were purchased from Aldrich Chemical Co. and estimated prior to use.

Preparation of Boronic Acids and Boronate Esters. The boronic acids and boronate esters were prepared either via the hydroboration of suitable alkene with $HBBr_2$ following the reported procedure[23] or via the organometallic route[24] by reacting alkyl- and/or aryllithium or a Grignard reagent with a borate ester, followed by treatment with anhydrous HCl/EE.

General Procedure for the Homologation of an Organoborane (R_3B, $R_2B(OR')$, and $RB(OR')_2$). The following procedure for the homologation of 2-cyclohexyl-1,3,2-dioxaborinane to 2-(1-cyclohexyl-2-propenyl)-1,3,2-dioxaborinane is representative. A solution of cyclohexylboronate ester (3.36 g, 20 mmol) in THF (20 mL) was cooled to −78 °C using a dry ice–acetone bath. To this was added allyl chloride (1.96 mL, 24 mmol), followed by the dropwise addition of a preformed solution of lithium diisopropylamide (LDA; 24 mmol) in THF (24 mL) (LDA was prepared via the deprotonation of diisopropylamine (3.4 mL, 24 mmol) with *n*-BuLi (10.9 mL, 24 mmol) in THF at −78 °C) by means of a cannula at −78 °C. The reaction mixture was stirred at −78 °C for an additional 0.25 h. The ^{11}B NMR spectrum of an aliquot showed a peak at δ 3 ppm. The reaction mixture was warmed to room temperature and then stirred at 25 °C for 18 h. The ^{11}B NMR spectrum of the reaction mixture showed a peak at δ 31 ppm, indicating the completion of the transfer reaction. THF and volatiles were pumped off in vacuo (20 mm), and the residue was extracted with anhydrous *n*-pentane (2 × 30 mL). The supernatant pentane layer was transferred into another precooled flask by means of a cannula under nitrogen. The residue was triturated with pentane and the pentane extract transferred to the organic portion. Removal of pentane in vacuo afforded the desired 2-(1-cyclohexyl-2-propenyl)-1,3,2-dioxaborinane, in a yield of 80%. Its purification by distillation under reduced pressure was avoided to prevent the possible [1,3]-sigmatropic shift: ^{11}B NMR ($CDCl_3$) δ 31; ^{1}H NMR ($CDCl_3$) δ 0.79–2.43 (m, 14 H), 3.97 (t, 4 H, $BOCH_2$), 4.76–6.2 (m, 3 H, CH=CH_2). The assigned structure was further ascertained via oxidation with preformed peroxy anion generated by reacting aqueous NaOH with 30% H_2O_2. The allylic boronate ester was added to the peroxy anion at 0 °C by means of a cannula and then warmed to 25 °C. Oxidation was complete at 25 °C in 8 h. The product allylic alcohol, i.e., 1-cyclohexyl-2-propen-1-ol, was purified by fractional distillation: bp 90–91 °C/22 mm (lit.[25d] bp 60 °C/0.35 mm); IR (neat; ν_{max}, cm^{-1}) 3359, 990, 920; ^{1}H NMR ($CDCl_3$) δ 0.9–2.0 (m, 12 H), 4.16 (m, 2 H, CHOH), 5.0–6.16 (m, 3 H, CH=CH_2). Its chemical purity was found to be ≥98% by GC analysis.

Generation of (α-bromoallyl)lithium by a similar procedure and reaction with cyclohexylboronate furnished the allylic boronate in 78% yield.

Di-*sec*-butyl(4-methyl-2-hexenyl)borane (1): prepared by the reaction of tri-*sec*-butylborane with (α-chloroallyl)lithium; yield 80%; ^{11}B NMR ($CDCl_3$) δ 86 (s); ^{1}H NMR ($CDCl_3$) δ 0.66–1.59 (m, 25 H), 1.89–2.23 (m, 2 H, BCH), 2.53–2.79 (m, 2 H, BCH_2), 5.26–5.46 (m, 2 H, CH=CH). The purity (95%) of compound 1 was ascertained by GC analysis of the oxidation product allylic alcohol, i.e., 4-methyl-2-hexen-1-ol: Kugelrohr distillation bp 110–112 °C/20 mm (lit.[26d] bp 90 °C/14 mm for *E* isomer); ^{1}H NMR ($CDCl_3$) δ 0.83–1.66 (m, 9 H), 3.53–3.96 (br m, 1 H, OH), 3.92–4.23 (m, 2 H, $-CH_2OH$), 5.43–5.66 (m, 2 H, CH=CH).

Methoxydiisopinocampheylborane, Ipc_2BOMe: prepared by the methanolysis of Ipc_2BH; ^{11}B NMR ($CDCl_3$) δ 55 (s); ^{1}H NMR ($CDCl_3$) δ 0.63–2.50 (m, 34 H), 3.73 (s, 3 H).

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Table V. Protonolysis[a] of the Allylboronate Ester 11

R in boronate ester 11	protonolysis product	isolated yield,[b] %	bp, °C (mm)	^{1}H NMR ($CDCl_3$), δ
n-butyl	1-heptene	70	90–91 (752)	4.8–5.1 (m, 2 H) 5.5–6.1 (m, 1 H)
n-hexyl	1-nonene	72	140–142 (750)	4.8–5.1 (m, 2 H) 5.5–6.1 (m, 1 H)
cyclohexyl	3-cyclohexyl-1-propene	80	80–81 (60)	4.9–5.2 (m, 2 H) 5.6–6.2 (m, 1 H)
tert-butyl	4,4-dimethyl-1-pentene	74	90–91 (752)	4.9–5.1 (m, 2 H) 5.1–6.4 (m, 1 H)
phenyl	3-phenyl-1-propene	81	80–82 (60)	5.0–5.2 (m, 2 H) 5.7–6.3 (m, 1 H)
benzyl	4-phenyl-1-butene	84	78–79 (15)	4.9–5.2 (m, 2 H) 5.7–6.1 (m, 1 H)

[a] Performed on a 10-mmol scale in refluxing acetic acid. [b] Purified by distillation.

Vinyldiisopinocampheylborane (2). To a cooled solution of (−)-Ipc_2BCl (13.32 g, 41.52 mmol) in EE (60 mL) at −78 °C was added a solution of vinylmagnesium bromide (43.7 mL, 0.95 M, 41.52 mmol) in THF through a double-ended needle. The reaction mixture was stirred at −78 °C for 0.5 h and then gradually warmed to 25 °C over a period of 1 h. The ^{11}B NMR spectrum of an aliquot showed a single peak at δ 74 ppm. THF and volatiles were pumped off in vacuo (20 mm), and the residue was extracted with pentane (2 × 50 mL). Removal of pentane afforded the desired *B*-vinyl compound **2** (12.44 g, yield 88%): ^{11}B NMR ($CDCl_3$) δ 74 (s); ^{1}H NMR ($CDCl_3$) δ 0.69–1.30 (m, 24 h), 1.36–2.53 (m, 10 H), 5.69–7.09 (m, 3 H, $CH{=}CH_2$).

Homologation of Compound 2 with $LiCH(Cl)CH{=}CH_2$. Homologation as before afforded a product in 72% yield: ^{11}B NMR ($CDCl_3$) δ 82 (s); ^{1}H NMR ($CDCl_3$) δ 0.9–1.2 (m, 18 H), 1.96–2.73 (m, 17 H), 5.13–6.33 (m, 6 H, $CH{=}CH_2$). Its structure (**5**) was further confirmed by analysis of the allylboration product with acetaldehyde in EE at 25 °C to obtain 5-isopinocampheyl-4-penten-2-ol: IR (neat; ν_{max}, cm^{-1}) 3359 (OH); ^{1}H NMR ($CDCl_3$) δ 0.85 (s, 3 H), 1.10 (s, 3 H), 1.23 (br d, distorted, 6 H), 1.66–2.30 (m, 10 H), 3.83 (m, 1 H), 5.33 (m, 2 H); MS *m/e* 222 (M^+), 204 ($M^+ - H_2O$).

Reaction of 9-Methoxy-9-borabicyclo[3.3.1]nonane with $LiCH(Cl)CH{=}CH_2$. The reaction of 9-methoxy-9-BBN with (α-chloroallyl)lithium furnished the α-vinyl compound **7** in 76% yield: ^{11}B NMR ($CDCl_3$) δ 58 (s); ^{1}H NMR ($CDCl_3$) δ 0.86–2.53 (m, 15 H), 3.66–3.92 (m, 3 H, OCH_3), 4.67–5.20 (m, 2 H, $=CH_2$), 5.30–6.33 (m, 1 H, =CH). Oxidation with alkaline H_2O_2 gave 5-(1-hydroxy-2-propenyl)cyclooctanol, which was analyzed by GC as its disilyl ether: ^{1}H NMR ($CDCl_3$) for the diol δ 0.92–2.17 (m, 13 H), 2.56 (br s, 2 H, OH, exchanges with D_2O), 3.56–4.26 (br m, 2 H, C*H*OH), 4.76–5.43 (m, 2 H, $=CH_2$), 5.53–6.23 (m, 1 H, C*H*$=CH_2$).

2-(1-Hexyl-2-propenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: yield 78%; ^{11}B NMR ($CDCl_3$) δ 34 (s); ^{1}H NMR ($CDCl_3$) δ 0.93 (br t, 3 H, CH_3), 1.36–1.66 (m, 22 H), 4.7–5.2 (m, 2 H, $=CH_2$), 5.30–6.3 (m, 1 H, =CH). Oxidation provided 1-nonen-3-ol: bp 60–62 °C/3 mm (lit.[25a] bp 100–110 °C/25 mm); IR (neat; ν_{max}, cm^{-1}) 3345, 920; ^{1}H NMR ($CDCl_3$) δ 0.93 (br t, 3 H, CH_3), 1.33 (m, 10 H), 1.90 (br s, 1 H, OH exchanges with D_2O), 4.1 (m, 1 H), 5.0–6.23 (m, 3 H, $CH{=}CH_2$).

2-[1-(*trans*-2-Methylcyclopentyl)-2-propenyl]-1,3,2-dioxaborinane: yield 82%; ^{11}B NMR ($CDCl_3$) δ 33 (s); ^{1}H NMR ($CDCl_3$) δ 1.03 (d, 3 H, CH_3), 1.20–2.30 (m, 11 H), 4.0 (t, 4 H, $BOCH_2$), 4.83–6.17 (m, 3 H, $CH{=}CH_2$).

2-[1-(*exo*-Bicyclo[2.2.1]heptyl)-2-propenyl]-1,3,2-dioxaborinane: yield 75%; ^{11}B NMR ($CDCl_3$) δ 32 (s); ^{1}H NMR ($CDCl_3$) δ 1.02–2.96 (m, 14 H), 3.96 (t, 4 H, $BOCH_2$), 4.79–6.13 (m, 3 H, $CH{=}CH_2$). Oxidation gave 1-(*exo*-bicyclo[2.2.1]-heptyl)-2-propen-1-ol. IR (neat; ν_{max}, cm^{-1}) 3352, 900, 920; ^{1}H NMR ($CDCl_3$) δ 0.87–2.66 (m, 11 H), 3.83 (br m, 2 H, CHOH), 4.96–5.33 (m, 2 H, $CH{=}CH_2$), 5.50–6.20 (m, 1 H, =CH).

2-(1-*tert*-Butyl-2-propenyl)-1,3,2-dioxaborinane: yield 85%; ^{11}B NMR ($CDCl_3$) δ 31 (s); ^{1}H NMR ($CDCl_3$) δ 0.89 (s, 9 H, CH_3), 1.73–2.09 (m, 2 H), 2.73 (d, 1 H), 3.96 (t, 4 H, $BOCH_2$), 4.66–6.20 (m, 3 H, $CH{=}CH_2$). Oxidation furnished 4,4-dimethyl-1-penten-3-ol: bp 126–128 °C/752 mm (lit.[25b] bp 131 °C/760 mm); IR (neat; ν_{max}, cm^{-1}) 3345, 920; ^{1}H NMR ($CDCl_3$) δ 0.89 (s, 9 H, CH_3), 2.26 (br s, 1 H, OH), 3.59–3.79 (m, 1 H, CHOH), 4.92–6.17 (m, 3 H, $CH{=}CH_2$).

2-(1-Phenyl-2-propenyl)-1,3,2-dioxaborinane: yield 75%; ^{11}B NMR ($CDCl_3$) δ 29 (s); ^{1}H NMR ($CDCl_3$) δ 1.66–2.17 (m, 2 H, CH_2), 2.53 (d, 1 H, CH), 4.07 (t, 4 H, $BOCH_2$), 4.73–5.20 (m, 2 H, $CH{=}CH_2$), 5.43–6.20 (m, 1 H, =CH), 7.13–7.46 (m, 5 H, C_6H_5). Oxidation gave 1-phenyl-2-propen-1-ol: bp 94–95 °C/4 mm (lit.[25c] bp 107 °C/17 mm); ^{1}H NMR ($CDCl_3$) δ 4.13 (d, 1 H, CH), 4.73–5.17 (m, 3 H, $=CH_2$ and OH), 5.36–6.23 (m, 1 H, =CH), 7.17 (s, 5 H, C_6H_5).

General Procedure for the Synthesis of 2-(1-Alkyl- or 1-Aryl-2-propenyl)-1,3,2-dioxaborinanes via the Reaction of (α-Chloroallyl)boronate Ester with RLi or RMgBr. The procedure for the preparation of 2-(1-*n*-butyl-2-propenyl)-1,3,2-dioxaborinane is representative. To a cooled solution of (α-chloroallyl)boronate ester (1.51 g, 9.38 mmol) in THF (10 mL) at −78 °C was added a solution of *n*-BuLi in hexane (5.13 mL, 1.95 M, 10 mmol) dropwise by means of a syringe. Stirring was continued at −78 °C for 0.5 h. The ^{11}B NMR spectrum indicated the formation of an ate complex. The reaction mixture was warmed to 25 °C over a period of 18 h, whereupon the transfer reaction was complete, as is evident from the ^{11}B NMR spectrum (δ 32). THF and volatiles were removed in vacuo, and the residue was extracted with pentane (2 × 10 mL). Removal of pentane afforded the desired product (1.3 g, 78% yield): ^{11}B NMR ($CDCl_3$) δ 32 (s); ^{1}H NMR ($CDCl_3$) δ 0.60–2.53 (m, 12 H), 3.96 (t, 4 H, $BOCH_2$), 4.66–6.13 (m, 3 H, $CH{=}CH_2$). Oxidation furnished 1-hepten-3-ol: bp 108–110 °C/100 mm (lit.[25e] bp 83 °C/35 mm); ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 3 H, CH_3), 1.17–1.83 (m, 6 H), 2.07–2.26 (br s, 1 H, OH), 3.83–4.23 (m, 1 H, CHOH), 4.89–5.33 (m, 2 H, $CH{=}CH_2$), 5.53–6.17 (m, 1 H, =CH).

2-(1-*sec*-Butyl-2-propenyl)-1,3,2-dioxaborinane: yield 72%; ^{11}B NMR ($CDCl_3$) δ 31 (s); ^{1}H NMR ($CDCl_3$) δ 0.73–2.59 (m, 12 H), 3.96 (t, 4 H, $-BOCH_2$), 4.63–6.10 (m, 3 H, $CH{=}CH_2$). Oxidation gave 4-methyl-1-hexen-3-ol.

2-(1-Benzyl-2-propenyl)-1,3,2-dioxaborinane: yield 77%; ^{11}B NMR ($CDCl_3$) δ 30 (s); ^{1}H NMR ($CDCl_3$) δ 1.7–2.33 (m, 3 H), 2.86 (d, 2 H, CH_2Ph), 3.96 (t, 4 H, $BOCH_2$), 4.83–6.16 (m, 3 H, $CH{=}CH_2$), 7.23 (m, 5 H, C_6H_5). Oxidation afforded 1-phenyl-3-buten-2-ol:[25a] ^{1}H NMR ($CDCl_3$) δ 2.83 (d, 2 H, CH_2Ph), 4.36 (m, 1 H), 4.66 (s, 1 H, OH exchanges with D_2O), 5.06–6.2 (m, 3 H, $CH{=}CH_2$), 7.13 (m, 5 H, C_6H_5).

2-(1-Vinyl-3-butenyl)-1,3,2-dioxaborinane: yield 75%; ^{11}B NMR ($CDCl_3$) δ 31 (s); ^{1}H NMR ($CDCl_3$) δ 1.43–2.26 (br m, 5 H), 3.96 (t, 4 H, $BOCH_2$), 4.86–5.06 (m, 4 H, $CH{=}CH_2$), 5.46–6.13 (m, 2 H, =CH). Allylboration with PhCHO in EE at 25 °C, followed by treatment with water, gave 7-phenyl-1,4-heptadien-7-ol: IR (neat; ν_{max}, cm^{-1}) 3348, 1602, 880, 920; ^{1}H NMR ($CDCl_3$) δ 2.46–2.83 (m, 5 H), 4.60 (t, 1 H, C*H*OH), 4.8–6.0 (m, 5 H, $CH{=}CH_2$), 7.23 (br s, 5 H, C_6H_5); MS *m/e* 189 ($M^+ + H$).

2-(1-Vinyl-2-propenyl)-1,3,2-dioxaborinane (13): yield 80%; ^{11}B NMR ($CDCl_3$) δ 28 (s); ^{1}H NMR ($CDCl_3$) δ 2.33–2.93 (m, 3 H), 3.98 (t, 4 H, $BOCH_2$), 5.13–6.26 (m, 6 H, $CH{=}CH_2$). The assigned structure for **13** was further ascertained by spectral and GC analysis of the allylboration product with cyclohexanecarboxaldehyde.

General Procedure for the Preparation of 2-(3-Alkyl- or 3-Aryl-2-propenyl)-1,3,2-dioxaborinanes by Thermal Rearrangement. The procedure for thermal isomerization of 2-(1-cyclohexyl-2-propenyl)-1,3,2-dioxaborinane to 2-(3-cyclohexyl-2-propenyl)-1,3,2-dioxaborinane is representative. The allylic boronate was dissolved in toluene and the solution refluxed in an oil bath for 24–36 h. Toluene was removed in vacuo, and the product boronate was purified by distillation under reduced pressure: bp 75–78 °C/0.1 mm; yield 90%; ^{11}B NMR ($CDCl_3$) δ 31 (s); ^{1}H NMR ($CDCl_3$) δ 0.79–2.43 (m, 15 H), 3.97 (t, 4 H, $BOCH_2$), 5.36–5.76 (m, 2 H, CH=CH). Oxidation afforded 3-cyclohexyl-2-propen-1-ol: bp 92–94 °C/20 mm; IR (neat; ν_{max}, cm^{-1}) 3339, 1444, 967; ^{1}H NMR ($CDCl_3$) δ 1.16–1.9 (m, 13 H), 2.1 (br s, 1 H, OH), 4.0–4.26 (m, 2 H, OCH_2), 5.43–5.73 (m, 2 H, CH=CH). GC analysis showed that it is a mixture of *E* and *Z* (9:1) isomers.

2-(2-Heptenyl)-1,3,2-dioxaborinane: bp 112–114 °C/17 mm; ^{11}B NMR ($CDCl_3$) δ 31 (s); ^{1}H NMR ($CDCl_3$) δ 0.86 (t, 3 H, CH_3), 1.03–1.66 (m, 6 H), 1.69–2.17 (m, 4 H), 3.97 (t, 4 H, $BOCH_2$), 5.23–5.53 (m, 2 H, CH=CH). Oxidation furnished 2-hepten-1-ol: bp 80–82 °C/20 mm (lit.[26a] bp 82–84 °C/20 mm for *E* isomer); ^{1}H NMR ($CDCl_3$) δ 0.86 (t, 3 H, CH_3), 1.10–1.73 (m, 4 H), 1.83–2.4 (m, 3 H, CH_2 and OH), 3.92–4.26 (m, 2 H, CH_2OH), 5.50–5.80 (m, 2 H, CH=CH).

2-(2-Nonenyl)-1,3,2-dioxaborinane: bp 80–82 °C/0.1 mm; ^{11}B NMR ($CDCl_3$) δ 32 (s); ^{1}H NMR ($CDCl_3$) δ 0.86 (t, 3 H, CH_3), 1.2–2.17 (m, 14 H), 3.97 (t, 4 H, $BOCH_2$), 5.2–5.6 (m, 2 H, CH=CH). Oxidation gave 2-nonen-1-ol: bp 60–62 °C/3 mm (lit.[26b] 68–73 °C/0.6 mm for *E* isomer); ^{1}H NMR ($CDCl_3$) δ 0.92 (t, 3 H, CH_3), 1.33 (br s, 10 H), 1.66 (br s, 1 H, OH), 4.0–4.26 (m, 2 H, OCH_2), 5.43–5.76 (m, 2 H, CH=CH).

2-(4,4-Dimethyl-2-pentenyl)-1,3,2-dioxaborinane: bp 84–85 °C/10 mm; ^{11}B NMR ($CDCl_3$) δ 30 (s); ^{1}H NMR ($CDCl_3$) δ 0.96 (s, 9 H, Me), 1.85 (d, 2 H, CH_2), 1.94–2.26 (m, 2 H), 3.97 (t, 4 H, $BOCH_2$), 5.62–5.89 (m, 2 H, CH=CH). Oxidation afforded 4,4-dimethyl-2-penten-1-ol: bp 75–76 °C/35 mm (lit.[25b] bp 156–157 °C/760 mm for *E* isomer); ^{1}H NMR ($CDCl_3$) δ 1.0 (s, 9 H, CH_3), 1.36 (br s, 1 H, OH), 4.03–4.4 (m, 2 H, CH_2), 5.33–5.69 (m, 2 H, CH=CH).

2-[3-(*exo*-Bicyclo[2.2.1]heptyl)-2-propenyl]-1,3,2-dioxaborinane: bp 91–93 °C/0.1 mm; ^{11}B NMR ($CDCl_3$) δ 33 (s); ^{1}H NMR ($CDCl_3$) δ 0.89–2.56 (m, 15 H), 3.96 (t, 4 H, $BOCH_2$), 5.2–5.63 (m, 2 H, CH=CH). Oxidation gave 3-(*exo*-bicyclo[2.2.1]-heptyl)-2-propen-1-ol: ^{1}H NMR ($CDCl_3$) δ 0.89–2.50 (m, 12 H), 4.0–4.28 (m, 2 H, CH_2O), 5.26–5.69 (m, 2 H, CH=CH).

2-(3-Phenyl-2-propenyl)-1,3,2-dioxaborinane: bp 110–113 °C/20 mm; ^{11}B NMR ($CDCl_3$) δ 29 (s); ^{1}H NMR ($CDCl_3$) δ 1.2 (d, 2 H, BCH_2), 1.56–2.07 (m, 2 H), 3.96 (t, 4 H, $BOCH_2$), 6.92–7.83 (m, 7 H, C_6H_5CH=CH). Oxidation furnished 3-phenyl-2-propen-1-ol.

2-(4-Phenyl-2-butenyl)-1,3,2-dioxaborinane: bp 103–105 °C/8 mm; ^{11}B NMR ($CDCl_3$) δ 31 (s); ^{1}H NMR ($CDCl_3$) δ 1.66–2.0 (m, 4 H), 2.83 (m, 2 H, CH_2Ph), 3.97 (t, 4 H, $BOCH_2$), 5.6–6.0 (m, 2 H, CH=CH), 7.2 (br s, 5 H, C_6H_5). Oxidation gave 4-phenyl-2-buten-1-ol: bp 98–100 °C/3 mm (lit.[26c] bp 86–87 °C/0.5 mm for *E* isomer); ^{1}H NMR ($CDCl_3$) δ 2.9 (m, 2 H, CH_2Ph), 3.46 (m, 2 H, OCH_2), 4.7 (s, 1 H, OH), 5.26–5.8 (m, 2 H, CH=CH), 7.13 (br s, 5 H, C_6H_5).

Catalytic Hydrogenation of Allylboronate. To a solution of isomerized allylboronate 11 in THF was added a catalytic amount (10% by weight) of 5% Pd on carbon, and this mixture was hydrogenated at 25 °C and 1 atm of pressure over a period of 6–8 h. The reaction mixture was then filtered through a sintered funnel under nitrogen. Removal of THF afforded the desired saturated boronate ester.

2-(3-Cyclohexylpropyl)-1,3,2-dioxaborinane: ^{11}B NMR ($CDCl_3$) δ 31 (s); ^{1}H NMR ($CDCl_3$) δ 0.9–2.36 (m, 19 H), 3.96 (t, 4 H, $BOCH_2$). Oxidation gave 3-cyclohexyl-1-propanol.

2-(4,4-Dimethylpentyl)-1,3,2-dioxaborinane: bp 88–90 °C/10 mm; ^{11}B NMR ($CDCl_3$) δ 30 (s); ^{1}H NMR ($CDCl_3$) δ 0.9 (s, 9 H, CH_3), 1.23–1.93 (m, 8 H), 3.97 (t, 4 H, $BOCH_2$). Oxidation furnished 4,4-dimethyl-1-pentanol.

2-(3-Phenylpropyl)-1,3,2-dioxaborinane: ^{11}B NMR ($CDCl_3$) δ 29 (s); ^{1}H NMR ($CDCl_3$) δ 1.36–2.46 (m, 6 H), 2.5 (t, 2 H, CH_2Ph), 4.1 (t, 4 H, $BOCH_2$), 7.13–7.63 (m, 5 H, C_6H_5).

Protonolysis of Isomerized Allylboronates. (i) Using Acetic Acid. The procedure for the protonolysis of 2-(4-phenyl-2-butenyl)-1,3,2-dioxaborinane is representative. A solution of boronate ester (10 mmol) in acetic acid (10 mL) was refluxed in an oil bath for 4 h. The reaction mixture was poured into ice water and extracted with EE (2 × 20 mL). The combined extracts were washed with water, aqueous $NaHCO_3$ solution, and finally with water. Drying, followed by solvent removal at atmospheric pressure, furnished the desired 4-phenyl-1-butene, which was purified by fractional distillation.

(ii) Using Methanesulfonic Acid. To a solution of 2-(4,4-dimethyl-2-pentenyl)-1,3,2-dioxaborinane (10 mmol) in THF (10 mL) was added $MeSO_3H$ (1 mL). The reaction mixture was refluxed for 2 h, and workup as above afforded 4,4-dimethyl-1-pentene.

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Registry No. **1**, 140411-63-8; **2**, 140411-64-9; **5**, 140411-65-0; **6**, 140411-66-1; **7**, 140438-01-3; **10** (R = c-C_6H_{11}), 132380-31-5; **10** (R = 2-methylcyclopentyl), 140411-67-2; **10** (R = bicyclo[2.2.1]-heptyl), 140411-68-3; **10** (R = Bu-t), 132350-05-1; **10** (R = Ph), 132350-06-2; **10** (R = Bu), 132350-02-8; **10** (R = Bu-s), 132350-04-0; **10** (R = CH_2Ph), 132350-07-3; **10** (R = CH_2CH=CH_2), 132350-08-4; (*E*)-**11** (R = c-C_6H_{11}), 132350-15-3; (*Z*)-**11** (R = c-C_6H_{11}), 132350-16-4; (*E*)-**11** (R = Bu), 132350-09-5; (*Z*)-**11** (R = Bu), 132350-10-8; (*E*)-**11** (R = $(CH_2)_5CH_3$), 132350-11-9; (*E*)-**11** (R = Bu-t), 132350-17-5; (*E*)-**11** (R = *exo*-bicyclo[2.2.1]heptyl), 140411-69-4; (*E*)-**11** (R = Ph), 132350-19-7; (*Z*)-**11** (R = Ph), 132350-20-0; (*E*)-**11** (R = CH_2Ph), 132350-21-1; **12** (R = c-C_6H_{11}), 132350-27-7; **12** (R = Bu-t), 132350-28-8; **12** (R = Ph), 132350-29-9; **13**, 140411-74-1; $CH_3CH_2CH(CH_3)CH$=$CHCH_2OH$, 132350-23-3; $CH_3(CH_2)_5CH(OH)CH$=CH_2, 21964-44-3; $C(CH_3)_3CH(OH)C$-H=CH_2, 24580-44-7; CH_2=$CHCH(Ph)OH$, 4393-06-0; $CH_3(C$-$H_2)_3CH(OH)CH$=CH_2, 4938-52-7; $CH_3CH_2CH(CH_3)CH(OH)C$-H=CH_2, 52093-36-4; CH_2=$CHCH(OH)CH_2Ph$, 6052-66-0; $OHCH(Ph)CH_2CH$=$CHCH_2CH$=CH_2, 140411-75-2; (*E*)-CH_3-$(CH_2)_3CH$=$CHCH_2OH$, 33467-76-4; (*Z*)-$CH_3(CH_2)_3CH$= $CHCH_2OH$, 55454-22-3; (*E*)-$CH_3(CH_2)_5CH$=$CHCH_2OH$, 31502-14-4; (*E*)-$C(CH_3)_3CH$=$CHCH_2OH$, 64081-43-2; (*E*)-PhCH= $CHCH_2OH$, 4407-36-7; (*E*)-$PhCH_2CH$=$CHCH_2OH$, 49676-93-9; $CH_3(CH_2)_6OH$, 111-70-6; $CH_3(CH_2)_8OH$, 143-08-8; CH_2=CHCH-(c-C_6H_{11})OH, 4352-44-7; (*E*)-c-$C_6H_{11}CH$=$CHCH_2OH$, 114096-03-6; (*E*)-c-$C_6H_{11}CH$=$CHCH_2OH$, 42134-55-4; c-$C_6H_{11}(CH_2)_3OH$, 1124-63-6; $C(CH_3)_3(CH_2)_3OH$, 3121-79-7; $Ph(CH_2)_3OH$, 122-97-4; $Ph(CH_2)_4OH$, 3360-41-6; $Ph(CH_2)_2CH$=CH_2, 768-56-9; C(C-$H_3)_3CH_2CH$=CH_2, 762-62-9; $CH_3(CH_2)_4CH$=CH_2, 592-76-7; $CH_3(CH_2)_6CH$=CH_2, 124-11-8; c-$C_6H_{11}CH_2CH$=CH_2, 2114-42-3; $PhCH_2CH$=CH_2, 300-57-2; (*Z*)-PhCH=$CHCH_2OH$, 4510-34-3; $(s\text{-}Bu)_3B$, 1113-78-6; (-)-Ipc_2BCl, 140411-71-8; 2-(1-hexyl-2-propenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 134660-43-8; 5-(1-hydroxy-2-propenyl)cyclooctanol, 140411-72-9; 1-(bicyclo-[2.2.1]heptyl)-2-propen-1-ol, 140411-73-0; (*E*)-3-(*exo*-bicyclo-[2.2.1]heptyl)-2-propen-1-ol, 140411-70-7; 3-(2-methylcyclopentyl)-2-propen-1-ol, 140411-76-3; 2-cyclohexyl-1,3,2-dioxaborinane, 30169-75-6; 9-methoxy-9-borabicyclo[3.3.1]nonane, 38050-71-4; 2-(1-chloro-2-propenyl)-1,3,2-dioxaborinane, 132350-01-7.

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