respectively. The physical and spectroscopic properties of the products are given in Table I.

General Procedure for Reaction of 7 with MAC. A mixture of 7 (0.001 mol), MAC (0.002 mol), and CH_3CN (30 mL) in a sealed tube was heated at 200 °C for 20 h. The resulting mixture was treated by the same method described in 8. From the benzene–acetone (10:1) fraction, the compounds shown by 8 were obtained (40%).

General Procedure for Reaction of 6 with DMAD. A mixture of 6 (0.0015 mol) and DMAD (0.006 mol) in DMF (30 mL) was heated at 100 °C for 10 h. The reaction mixture was evaporated under a reduced pressure. The residue was recrystallized from $CHCl_3$–MeOH to give 9. The physical and spectroscopic properties of the products are given in Table I.

***N*-Phenyl-3,9a-dihydro-3,9a-ethano-9-(ethoxycarbonyl)-7-(methoxycarbonyl)-2-methyl-1-azacycl[3.3.3]azine-10,11-dicarboximide (10).** A mixture of 6d (0.002 mol) and PMI (0.004 mol) in DMF (30 mL) was heated at 100 °C for 10 h. The reaction mixture was evaporated under a reduced pressure. The residue was submitted to column chromatography on alumina. From the benzene–acetone (2:1) fraction, 10 was obtained in 80% yield (recrystallization solvent, $CHCl_3$–MeOH): mp 193–194 °C; mass spectrum, m/e 312 (M^+ – PMI); IR (KBr) 1720, 1660 cm^{-1}; UV λ_{max} (EtOH) 265 (log ϵ 4.15, sh), 272 (4.20), 306 (4.28), 375 (3.90), 505 (3.89), nm; ^1H NMR δ 1.37 (3 H, t, OCH_2CH_3), 2.40 (3 H, s, CH_3), 3.37 (1 H, dd, J = 3, 10 Hz, $C_{11}H$), 3.68 (3 H, s, OCH_3), 4.19 (1 H, d, J = 3 Hz, $C_{10}H$), 4.20 (2 H, q, OCH_2CH_3), 4.47 (1 H, d, J = 10 Hz, C_3H), 6.25 (1 H, d, J = 7 Hz, C_4H), 6.76–6.88 and 7.20–7.40 (5 H, m, Ph) 7.10 (1 H, dd, J = 7, 10 Hz, C_5H), 8.24 (1 H, s, C_8H), 8.60 (1 H, d, J = 10 Hz, C_6H).

Dimethyl 4-Cyano-1,6-diazacycl[3.3.3]azine-2,3-dicarboxylate (12). A mixture of 11 (0.01 mol) and DMAD (0.02 mol) in DMF (30 mL) was heated at 100 °C for 10 h. The resulting mixture was treated by the same method described in 10. From the benzene–acetone (20:1) fraction, 12 was obtained in 20% yield (recrystallization solvent, $CHCl_3$–MeOH): mp 197–198 °C; mass spectrum, m/e 310 (M^+); IR (KBr) 2200, 1735 cm^{-1}; UV λ_{max} (EtOH) 236, 284, 363, 415, 428 nm; ^1H NMR δ 3.23 (3 H, s, OCH_3), 3.76 (3 H, s, OCH_3), 5.68 (1 H, d, J = 8 Hz, C_7H or C_9H), 5.82 (1 H, d, J = 8 Hz, C_7H or C_9H), 6.76 (1 H, s, C_5H), 6.84 (1 H, t, J = 8 Hz, C_8H).

Tetramethyl 1,6-Diazacycl[3.3.3]azine-2,3,4,5-tetracarboxylate (13). A mixture of 11 (0.01 mol) and DMAD (0.02 mol) in CH_3CN (100 mL) was refluxed for 10 h. The resulting mixture was treated by the same method described in 10. From the benzene–acetone (20:1) fraction, 13 was obtained in 15% yield (recrystallization solvent, CH_3Cl–MeOH): mp 248–249 °C; mass spectrum, m/e 401 (M^+); IR (KBr) 1760, 1730, 1710 cm^{-1}; UV λ_{max} (EtOH) 262 (log ϵ 4.28), 286 (4.28), 364 (4.31), 437 (4.13) nm; ^1H NMR δ 3.59 (6 H, s, 2 OCH_3), 3.80 (6 H, s, 2 OCH_3), 5.95 (2 H, d, J = 8 Hz, C_7H and C_9H), 6.98 (1 H, t, J = 8 Hz, C_8H).

1,6-Diazacycl[3.3.3]azine Hydrobromide (14). A solution of 13 (0.5 g) in 48% HBr (20 mL) was refluxed for 3 h. The green solution was evaporated under a reduced pressure. The residue was recrystallized from MeOH to give 14 in quantitative yield: mp >300 °C; mass spectrum, m/e 169 (M^+ – HBr); UV λ_{max} (EtOH) 220 (log ϵ 4.00, sh), 268 (4.21), 273 (4.20, sh), 336 (3.49), 356 (3.56), 392 (3.72), 414 (3.66) nm; ^1H NMR (Me_2SO-d_6) δ 5.25 (2 H, d, J = 6 Hz, C_3H and C_4H), 5.92 (2 H, d, J = 8 Hz, C_7H and C_9H), 6.95 (2 H, d, J = 6 Hz, C_2H and C_5H), 7.20 (1 H, t, J = 8 Hz, C_8H).

1,6-Diazacycl[3.3.3]azine (15). A solution of 14 (0.5 g) in water (50 mL) was made basic to litmus with K_2CO_3 and instantly extracted with $CHCl_3$ (30 mL). The extract was dried (Na_2SO_4) and evaporated under a reduced pressure. The residue was dried in vacuum desiccator (2 mmHg) for 5 min. The NMR spectrum of crude free base 15 was recorded: ^1H NMR δ 3.90 (2 H, d, J = 5 Hz, C_3H and C_4H), 4.78 (2 H, d, J = 8 Hz, C_7H and C_9H), 6.05 (2 H, d, J = 5 Hz, C_2H and C_5H), 6.10 (1 H, t, J = 8 Hz, C_8H) (see Figure 1).

Acknowledgment. We are very grateful to H. Mazume for microanalytical data, to M. Owatari for the measurement of IR and UV spectra, to K. Inada for the measurement of NMR spectra, and to N. Yamaguchi for the measurement of mass spectra, all of this university.

Organoboranes. 41. Reaction of Organoboranes with (Dichloromethyl)lithium. Scope and Limitations. Synthesis of Homologated Primary and Secondary Alcohols

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Homologated primary alcohols were prepared from alkylboronic esters by the reaction with (dichloromethyl)lithium, $LiCHCl_2$, followed by KIPBH treatment and oxidation. Homologated secondary alcohols were prepared from representative dialkylborinic esters and trialkylboranes by the reaction with $LiCHCl_2$, followed by treatment with base and oxidation. The yields are generally good with both boronic and borinic esters. On the other hand, the reactions with trialkylboranes exhibited a sensitivity to large steric requirements in the trialkylborane reactant.

In the last decade, many new reactions and reagents have been developed for converting organoboranes into organic molecules, particularly by C–C bond formation.[2] Now, a variety of synthetically interesting organoboranes are readily available,[2,3] including chiral alkyl derivatives.[4] For further transformations of these valuable intermediates, it is desirable not only to find new reactions or reagents but also to define the scope and limitation of their applicability.

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Carbanionic reagents bearing potential leaving group(s) (generally such heteroatom substituents as halogen, oxygen, or sulfur) at the α-position homologate the organyl-B linkage. The reaction generally proceeds through ate complex formation with subsequent 1,2-migration of organyl group(s) from boron to the original carbanionic center by displacement of the leaving group. This method provides a highly convenient practical way to achieve C–C bond-forming transformations via organoboranes under very mild conditions.[2,5]

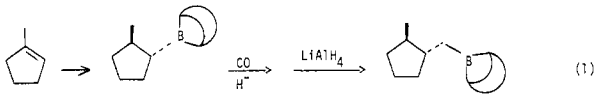
(Dichloromethyl)lithium, $LiCHCl_2$, is one of those reagents. It is stable only at low temperature.[6] Nevertheless, the availability of the starting materials (dichloromethane and *n*-butyllithium) and the simplicity of its preparation makes it an attractive reagent.

Its reaction with organoboranes was first reported by Köbrich and co-workers in 1967.[7] The reaction with triphenylborane with subsequent oxidation gave benzyhydrol in a yield of 62% with a minor amount of benzophenone (10%).

Rathke et al. used this reagent for preparing diisopropyl (dichloromethyl)boronate, $Cl_2CHB(O\text{-}i\text{-}Pr)_2$, and studied the nucleophilic substitution of this intermediate with organolithium or Grignard reagents.[8]

Later, Matteson and Majumdar established that this reagent successfully homologates organylboronic esters, $RB(OR')_2$, to α-chloroalkyl derivatives, $RCHClB(OR')_2$,[5c,d] a valuable development since it had been previously thought that such boronic esters were inert to reagents of this kind.

Even though these α-chloro boronic esters were shown to react with a wide variety of nucleophiles,[9] the reduction of these α-chloro boronic esters has not been previously described. It was apparent that a simple, successful reduction of the α-chloro boronic acids would then provide a valuable entry into the one-carbon homologated boronic esters and to the homologated primary alcohols to which they are readily oxidized. We recently developed a practical method for such homologation via the carbonylation of *B*-alkylborabicyclo[3.3.1]nonane (*B*-alkyl-9-BBN) in the presence of potassium triisopropoxyborohydride (KIPBH), followed by reduction of the intermediate by lithium aluminum hydride[10] (eq 1). Howevever, there is no simple



(1)

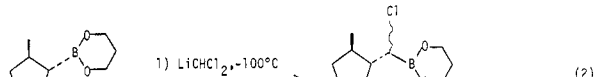
procedure currently available to prepare the corresponding boronic esters from the homologated *B*-alkyl-9-BBN derivatives.

Additionally, to our knowledge, the reaction of $LiCHCl_2$ with dialkylborinic esters, R_2BOR', as well as with trialkylboranes, R_3B, has not been studied systematically. Previously, we reported that a related carbanionic reagent, (dichloromethoxymethyl)lithium, converts R_2BOR' to ketones[11] and R_3B to tertiary alcohols.[12] Analogously, $LiCHCl_2$ should convert both R_2BOR' and R_3B to homologated secondary alcohols.

In this paper we report a systematic study of the reactions of $LiCHCl_2$ with various organoborane intermediates with a view to preparing homologated primary and secondary alcohols.

Results and Discussion

The boronic esters, 2-(*trans*-2-methylcyclopentyl)-1,3,2-dioxaborinane and 2-*exo*-norbornyl-1,3,2-dioxaborinane, selected for this study were prepared by procedures described previously.[5e] A slurry of (dichloromethyl)lithium ($LiCHCl_2$) in tetrahydrofuran (THF) was prepared[5c] at −100 °C and the boronic ester was added dropwise, maintaining the temperature at −100 °C. After the addition, the reaction mixture became clear and it was allowed to warm to 25 °C. Usually the reaction mixture turns dark at −40 °C due to the decomposition of the excess (10%) $LiCHCl_2$. The reaction mixture was stirred at 25 °C for 3 h. The ^{11}B NMR spectrum of the reaction mixture showed clearly one peak in the range of boronic esters (δ +27–28), but shifted to a higher field from the starting boronic esters (δ +30–32) due to the α-chloro substituent. The α-chloro boronic esters were isolated and purified by distillation (eq 2 and 3). It should be pointed out that these α-chloro boronic esters described above are difficult to prepare by any other method currently available.[5c]



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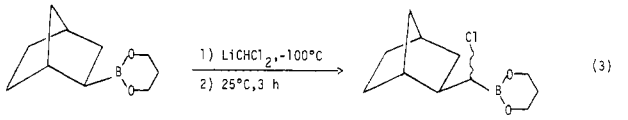
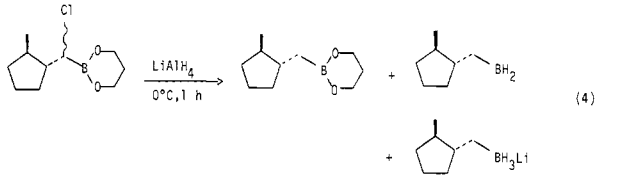


(3)

To reduce the α-chloro boronic esters, we selected two commercially available complex metal hydrides, viz., lithium aluminum hydride ($LiAlH_4$) and potassium triisopropoxyborohydride (KIPBH). Reduction of the α-halo boronic esters with 0.25 equiv and 1.0 equiv of $LiAlH_4$ at 0 °C was complex. The ^{11}B NMR spectrum of the reaction mixture showed the presence of several products (eq 4).



(4)

However, the reaction of the α-halo boronic ester with KIPBH in diethyl ether (EE) at 25 °C was facile and was complete within 0.5 h. The exothermic reaction was controlled by the rate of addition and by water-bath cooling (eq 5). The homologated boronic acid on oxidation afforded the corresponding homologated primary alcohols (eq 6). This sequence is particularly attractive for those cases where stereoisomers are possible. Thus, hydro-

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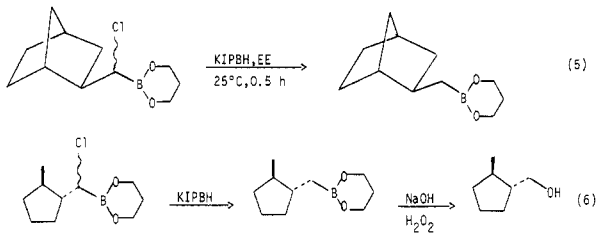
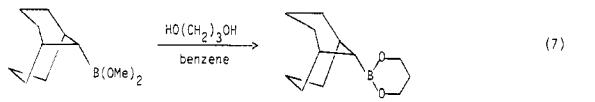


boration of 2-methylenenorbornane would be expected to give the endo derivative predominantly,[10] whereas application of the above procedure provides the exo derivative exclusively. Similarly, hydroboration of 2-(methylmethylene)cyclopentane yields a mixture predominating in the cis isomer, whereas the above procedure produces only the trans isomer.

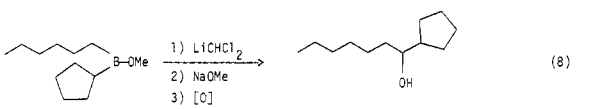
Next, we explored the reaction of various dialkylborinic esters with $LiCHCl_2$. A solution of the dialkylborinic ester was added to a slurry of $LiCHCl_2$ at −100 °C and the temperature was maintained at −100 °C by the rate of addition. The reaction mixture generally became clear and then a large amount of solid appeared. It might be the "ate" complex (Scheme I). When the mixture was allowed to warm to 25 °C, the solid dissolved, followed by the precipitation of LiCl. The reaction mixture was stirred at 25 °C for 1 h and the ^{11}B NMR spectrum showed cleanly one peak in the range of borinic esters (δ +46–49) but shifted to a higher field from the starting borinates (δ +53–56). This might be due to the single alkyl-migrated product. This intermediate was converted into a boronic ester (^{11}B NMR δ +30–32) on treatment with 1 equiv of sodium methoxide. Subsequent oxidation gave the secondary alcohols. In a separate experiment, the dimethyl 9-bicyclo[3.3.1]nonylboronate was converted into 2-(9-bicyclo[3.3.1]nonyl)-1,3,2-dioxaborinane, which was then easily isolated by distillation (eq 7).



Following the general procedure, various borinic esters were converted into the corresponding homologated secondary alcohols (Table I). Methyl esters of the borinic acid, especially in the case of hindered borinic acid, give better yields of the secondary alcohols compared to the corresponding isopropyl esters.

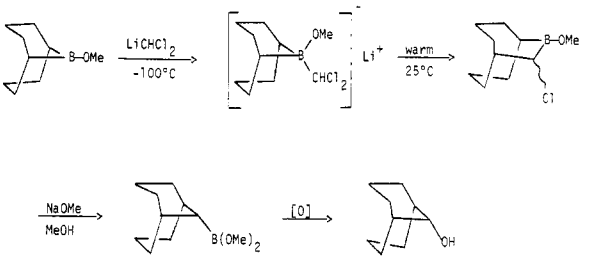
Generation of $LiCHCl_2$ in situ was also effective[5c] and was easier to control, particularly on a larger scale. Thus, slow addition of lithium diisopropylamide (LDA) to a mixture of methyl dicyclohexylborinate and CH_2Cl_2 in THF at −78 °C gave an 81% isolated yield of dicyclohexylmethanol.

The mixed dialkylborinate, methyl cyclopentyl-*n*-hexylborinate, prepared by stepwise hydroboration,[13] gave the corresponding homologated secondary alcohol (eq 8).

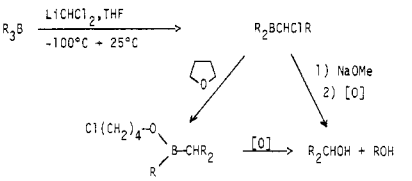


Boracyclic derivatives were also converted to the corresponding cycloalkanols cleanly. Instead of NaOMe, sodium hydroxide can also be used for promoting the second alkyl migration. Thus, after the first alkyl migration, successive addition of 2 equiv of 3 N NaOH and H_2O_2 to the reaction

Scheme I



Scheme II



mixture also gave the secondary alcohol in high yield.

We then turned our attention to the reaction of various trialkylboranes with $LiCHCl_2$. The reaction was carried out by the addition of the trialkylboranes to $LiCHCl_2$, maintaining the temperature at −100 °C. Solid trialkylboranes were added as THF solutions (1.0 M) and the others as neat liquids. The reaction mixture was then allowed to reach 25 °C. The ^{11}B NMR spectrum of the reaction mixture consisted of two peaks at δ +87 and +57. The latter was predominant after 1 h at 25 °C. The peak at δ +87 may be due to the trialkylborane formed by the first alkyl migration and the peak at δ +57 may be due to the borinic ester formed by the second alkyl migration induced by THF (Scheme II).

The yields of the homologated secondary alcohols, R_2CHOH, were high when R = primary alkyl and were moderate when R = cycloalkyl. The yields dropped markedly when R = acyclic secondary alkyl or when one bulky 1,1,2-trimethylpropyl (thexyl) group was introduced (Table II). Evidently, the reaction is very sensitive to the steric requirement of the trialkylboranes. It should be pointed out that the yields of alcohols correspond inversely to the steric requirements of the trialkylboranes, as judged by the stereoselectivity achieved in the reduction of 2-methylcyclohexanone with the corresponding lithium trialkylborohydrides.[14]

The results are rather puzzling to us when compared with the fact that (dichloromethoxymethyl)lithium, the probable intermediate generated from α,α-dichloromethyl methyl ether and lithium triethylcarboxide at 0 °C, smoothly reacts with trialkylboranes of even larger steric hindrance—for example, dicyclopentylthexylborane and *tert*-butyldicyclohexylborane,[12b] although the reaction conditions are very different. Genertaton of $LiCHCl_2$ in situ in the presence of R_3B provided practically no improvement (Table II). At present, the controlling factor still remains unclear.

Conclusion

The α-chloro boronic esters, prepared from $LiCHCl_2$ and boronic esters, undergo facile reduction to the corresponding homologated boronic esters. Oxidation of these boronic esters afford the corresponding homologated alcohols in good yields. This sequence is very attractive for the synthesis of boronic esters and alcohols that are not available by the direct hydroboration route.

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Table I. Preparation of Secondary Alcohols from Dialkylborinic Esters[a]

borinic esters	bp (°C/torr)	secondary alcohols	GC yield[c] (isolated yield), %	bp (°C/torr) or mp °C	lit. (°C/torr) or mp °C	ref
methyl di-*n*-butylborinate	25/0.2[b]	5-nonanol	81 (74)	88–90/18	97/20	23
methyl di-*n*-hexylborinate	80/0.2	7-tridecanol	87 (81)	41		24
methyl di-2-butylborinate	25/0.2[b]	3,5-dimethyl-4-heptanol	73 (63)	80–82/18	185–187/755	25
methyl dicyclopentylborinate	70/0.3	dicyclopentylmethanol	91 (86)	43	45	26
methyl dicyclohexylborinate	76–78/0.05	dicyclohexylmethanol	94 (81)[d]	62–63	66	27
isopropyl dicyclohexylborinate	92/0.5	dicyclohexylmethanol	54			
methyl di-*exo*-norbornylborinate	98/0.2	di-*exo*-norbornylmethanol	78 (76)	80–81	80	28
methyl cyclopentyl-*n*-hexylborinate	70/0.2	1-cyclopentyl-1-heptanol	70 (63)	80–81/0.4	91–92/8	29
B-methoxyborinane	50–52/40	cyclohexanol	92			
B-methoxy-9-borabicyclo[3.3.1]nonane	80–81/13	9-hydroxybicyclo[3.3.1]nonane	96 (88)[e]	206–208	207–208	30

[a] All analytical runs were done on a 5-mmol scale and all preparative runs on a 25-mmol scale. [b] The material was collected int a flask cooled by a dry ice–acetone bath. Distillation at a higher temperature resulted in disproportionation. [c] Tetradecane or hexadecane was used as the internal standard. [d] $LiCHCl_2$ was generated in situ. See Experimental Section. [e] Treatment of NaOMe was replaced by 2 equiv of NaOH (3 M), followed by addition of H_2O_2.

Table II. Preparation of Secondary Alcohols from Trialkylboranes by Reaction with (Dichloromethyl)lithium[a]

trialkylborane	secondary alcohol[b]	GC yield, %
tributylborane	5-nonanol	90
trihexylborane	7-tridecanol	92
tris(2-methylpropyl)-borane	2,6-dimethyl-4-heptanol	85
tri-*exo*-norbornylborane	di-*exo*-norbornylmethanol	72
tricyclopentylborane	dicyclopentylmethanol	68
dihexylthexylborane	7-tridecanol	48
dicyclopentylthexylborane	dicyclopentylmethanol	12
tris(2-butyl)borane	3,5-dimethyl-4-heptanol	4[c]

[a] All reactions were done on a 5-mmol scale. [b] Each alcohol was identified by GC coinjection with an authentic sample. [c] The yield was only slightly increased when excess $LiCHCl_2$ was used: 8% yield with 20% excess; 14% yield with 100% excess $LiCHCl_2$. In situ generation of $LiCHCl_2$ resulted in 7% yield of the alcohol (78% yield based on the conversion estimated from the amount of 2-butanol).

Secondary alcohols can be prepared from dialkylborinic esters, generally in good yield, by reacting with $LiCHCl_2$, followed by oxidation. The use of trialkylboranes in this transformation is limited to relatively unhindered derivatives. The secondary alcohol synthesis described here is an attractive alternative to carbonylation of trialkylboranes.[15]

Experimental Section

General Methods. GC analysis was performed with a Varian 1400 or a Hewlett-Packard 5750 instrument with a Hewlett-Packard 3380A integrator by using a 10% CW20M (6 ft × 0.25 in.) or a 15% DEGS (8 ft × 0.25 in.) column and an appropriate hydrocarbon internal standard. ^1H NMR spectra were obtained with a Perkin-Elmer R32 spectrometer. ^{11}B and ^{13}C NMR spectra were obtained with a Varian FT80A spectrometer. The chemical shift values (all in $CDCl_3$) are given in ppm relative to Me_4Si for ^1H and ^{13}C and relative to $BF_3{\cdot}OEt_2$ for ^{11}B resonance peaks. IR spectra were recorded with a Perkin-Elmer 137 spectrophotometer. Elemental analyses were done at the Purdue University Microanalytical Laboratory. Melting and boiling points are all uncorrected.

The handling of air-sensitive trialkylboranes and dialkylborinic esters was done according to the standard procedure described previously.[16]

Materials. The solvent THF was freshly distilled from a benzophenone ketyl solution prior to use. Dichloromethane (Aldrich Gold Label or Baker Photrex) was dried over 4-Å molecular sieves. A hexane solution of *n*-BuLi (Alfa) was estimated to be 2.1 M by the method of Watson and Eastham.[17] Diisopropylamine was refluxed and distilled over KOH. Methanol solution of sodium methoxide was titrated to be 4.2 M. Potassium triisopropoxyborohydride (KIPBH, 1.0 M) in THF was purchased from Aldrich Chemical Company.

The boronic esters,[5e] borinic esters,[13,18–21] and the trialkylboranes[22] were prepared by procedures described previously.

2-[(*trans*-2-Methylcyclopentyl)chloromethyl]-1,3,2-dioxaborinane. A solution of dichloromethane (2 mL) in 30 mL of freshly distilled THF was cooled to −105 °C to 100 °C in a 1:1 diethyl ether-*n*-pentane/liquid nitrogen bath and stirred magnetically during the dropwise addition of 22 mmol of *n*-butyllithium (2.1 M in hexane) from a syringe. The butyllithium was chilled before contacting the dichloromethane solution by bringing the tip of the syringe needle very close to the surface of the cold solution. After the addition, the reaction mixture was stirred at −100 °C for 15 min. The reaction mixture should remain colorless or pale yellow. Darkening is a sign of decomposition. A solution of 2-(*trans*-2-methylcyclopentyl)-1,3,2-dioxaborinane (20 mmol) in 10 mL of THF was then added dropwise, maintaining the temperature below −100 °C. The reaction mixture was allowed to worm slowly to 25 °C. The reaction mixture usually turns dark at −40 °C. The stirring was continued for 3 h at 25 °C. The reaction mixture was transferred by using a double-ended needle into another flask containing 200 mL of *n*-pentane with stirring. The clear supernatant was decanted and the LiCl was washed with *n*-pentane (2 × 10 mL). The washings were combined with the supernatant solution and concentrated under reduced pressure (12 torr), and the product was purified by distillation, 85%: bp 74–76 °C (0.01 torr); ^1H NMR ($CDCl_3$) δ 0.8–1.1 (m, 3 H), 1.2–2.2 (m, 10 H), 3.27 (br d, J = 7 Hz, 1 H), 4.1 (t, J = 7 Hz, 4 H); ^{11}B NMR δ +27.7 (s).

2-(*exo*-Norbornylchloromethyl)-1,3,2-dioxaborinane was prepared as described above from 20 mmol of 2-*exo*-norbornyl-1,3,2-dioxaborinane, 80%: bp 102–104 °C (0.01 torr); ^1H NMR

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($CDCl_3$) δ 0.9–2.6 (m, 13 H), 2.87 (d, J = 12 Hz, 1 H), 4.03 (t, J = 7 Hz, 4 H); ^{11}B NMR δ +27.9 (s).

Reduction of 2-[(*trans*-2-Methylcyclopentyl)chloromethyl]-1,3,2-dioxaborinane Using KIPBH. The α-chloro boronic ester (20 mmol) was dissolved in diethyl ether (EE) so as to give a 1.0 M solution, and 20 mmol of KIPBH was added with stirring at 25 °C. The exothermic reaction was controlled by the rate of addition of KIPBH and by water-bath cooling to maintain the temperature below 30 °C. Reaction was complete within 0.5 h, as indicated by the ^{11}B NMR analysis. The EE was evaporated under reduced pressure (12 torr) and the residue was stirred with 40 mL of 1:1 MeOH–H_2O at 25 °C for 12 h to hydrolyze $(i\text{-PrO})_3B$ and the product. The reaction mixture was extracted with EE (2 × 20 mL), washed with water (2 × 10 mL), and dried over anhydrous $MgSO_4$. Evaporation (25 °C, 12 torr) of the solvent gave the crude homologated boronic acid.

Oxidation of the boronic acid with alkaline hydrogen peroxide afforded (*trans*-2-methylcyclopentyl)methanol which was purified by distillation, 79%, bp 110–112 °C (80 torr); ^1H NMR (200 MHz, $CDCl_3$) δ 1.04 (d, J = 7 Hz, 3 H), 1.2–1.9 (m, 8 H), 3.4–3.8 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 20.0, 24.0, 29.5, 35.0, 37.0, 49.7, 66.8.

***exo*-Norbornylmethanol.** 2-(*exo*-Norbornylchloromethyl)-1,3,2-dioxaborinane (20 mmol) was reduced as described above using KIPBH. Oxidation of the homologated boronic acid with alkaline hydrogen peroxide afforded *exo*-norbornylmethanol, which was purified by distillation, 83%: bp 96–96 °C (15 torr); ^1H NMR ($CDCl_3$) δ 0.8–1.8 (m, 9 H), 2.16 (s, 2 H), 3.26 (d, J = 8 Hz, 2 H), 4.1 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 29.1, 30.0, 34.2, 35.2, 36.3, 38.2, 44.7, 66.3.

Preparation of Secondary Alcohols from Dialkylborinic Esters. The following procedure for the preparation of dicyclopentylmethanol from methyl dicyclopentylborinate is typical. A slurry of (dichloromethyl)lithium (28 mmol) in 50 mL of THF was prepared in a 250-mL flask as described previously. A THF solution of methyl dicyclopentylborinate (25 mmol, 2.0 M) was added slowly with stirring. After 15 min of stirring, the cold bath was removed and the mixture was allowed to reach 25 °C and sitrred at 25 °C for 1 h. Then a solution of NaOMe in methanol (25 mmol, 4.2 M) was added, and the exothermic reaction was controlled by the rate of addition and water-bath cooling. After 1 h of stirring, the product was oxidized by successive addition of 3 N NaOH (25 mmol) and hydrogen peroxide (50 mmol, 10.0 M). The hydrogen peroxide was added dropwise so as to control the exothermic reaction. The organic phase was separated and the aqueous phase was extracted with diethyl ether (2 × 25 mL). The organic phase and the ether extracts were combined and dried over anhydrous $MgSO_4$. The solvent was evaporated (25 °C, 12 torr), and the residue on distillation gave 3.6 g (86% yield) of dicyclopentylmethanol, bp 76 °C (0.2 torr), which solidified on standing and further purified by recrystallization.

Preparation of Dicyclohexylmethanol. In Situ Generation of (Dichloromethyl)lithium. Lithium diisopropylamide (LDA) was prepared by adding *n*-butyllithium (27 mmol) to a stirred solution of diisopropylamine (27 mmol) in THF (20 mL) at −10 °C. The LDA solution was then added to a cold (−78 °C) solution of methyl dicyclohexylborinate (25 mmol) and CH_2Cl_2 (28 mmol) in 30 mL of THF. The LDA solution was chilled before contacting the reaction mixture by running the solution down the cold wall of the reaction flask. After 0.5 h of stirring, the cold bath was removed and the mixture was allowed to reach 25 °C. The NaOMe treatment and oxidation were done as described for the preparation of dicyclopentylmethanol. The product, dicyclohexylmethanol, was distilled, bp 150–153 °C (13 torr). The distillate crystallized at 25 °C, and it was further purified by washing with cold pentane, 4.0 g (81% yield), mp 62–63 °C.

Isolation of 2-(9-Bicyclo[3.3.1]nonyl)-1,3,2-dioxaborinane. Following the general procedure, *B*-methoxy-9-borobicyclo[3.3.1]nonane was reacted with $LiCHCl_2$. After the addition of 1 equiv of NaOMe in methanol, all of the volatiles were evaporated under reduced pressure (12 torr) and the residue was dissolved in benzene (100 mL) to precipitate the metal salts. To the clear benzene solution was added 1,3-propanediol (25 mmol), and methanol was removed by azeotropic distillation. The solvent benzene was evaporated under reduced pressure and the product, 2-(9-bicyclo[3.3.1]nonyl)-1,3,2-dioxaborinane, was purified by distillation, 4.1 g (79%): bp 100–102 °C (0.1 torr); ^{11}B NMR δ +31 (s); ^1H NMR δ 0.95 (br s, 2 H), 1.3–2.1 (m, 15 H), 3.95 (t, J = 6 Hz, 4 H); ^{13}C NMR δ 22.4, 22.7, 27.7, 28.8, 29.7, 33.6, 61.5. Anal. Calcd for $C_{12}H_{21}BO_2$: C, 69.25; H, 10.17; B, 5.19. Found: C, 69.16; H, 10.05; B, 5.02.

Reaction of Trialkylboranes with (Dichloromethyl)lithium. All reactions of R_3B with $LiCHCl_2$ were done on 5-mmol scale following the general procedure as described for the reaction of borinic esters. The product alcohols, R_2CHOH and ROH, obtained following oxidation, were analyzed by GC using either tetradecane or hexadecane as the internal standard.

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