IR (neat) 3310 (m), 2960 (w), 2880 (w), 2010 (s), 1930 (s), 1675 (s), 1410 (w), 1355 (w), 1245 (w), 1000 (m), 830 (m), 780 (m), 655 (s) cm^{-1}. Anal. Calcd: C, 41.21; H, 3.03; N, 6.01. Found: C, 41.44; H, 3.28; N, 5.85.

Preparation of (η^5-Cyclopentadienylmethyl acrylate)dicarbonylnitrosylchromium (38). Compound **37** (0.54 g, 2.3 mmol) was dissolved in 50 mL of benzene, and pyridine (0.38 mL, 4.6 mmol) was added. The mixture was cooled to 0 °C, and acryloyl chloride 0.38 mL, 4.6 mmol) was added. The mixture was then stirred for 2.5 h while warming slowly to 25 °C. The reaction mixture was poured into water and the organic layer washed three times with dilute sodium bicarbonate solution. The organic layer was then dried over anhydrous magnesium sulfate and filtered. The solvent was removed under vacuum to give 0.37 g (56%) of **38** as a red liquid. An analytical sample was obtained by molecular distillation: ^1H NMR ($CDCl_3$) δ 4.84 (2 H, s, CH_2), 5.03 (2 H, t, Cp $H_{3,4}$), 5.27 (2 H, t, Cp $H_{2,5}$), 5.76–6.46 (3 H, m, vinyl); IR (neat) 3125 (w), 2025 (s), 1950 (s), 1705 (s), 1630 (w), 1450 (w), 1400 (m), 1285 (w), 1260 (w), 1165 (s), 1055 (w), 1035 (w), 975 (m), 820 (w), 800 (m), 665 (w), 630 (s) cm^{-1}. Anal. Calcd: C, 46.00; H, 3.16; N, 4.88. Found: C, 46.24; H, 3.43; N, 4.75.

Preparation of (η^5-Methylcyclopentadienyl)dicarbonylnitrosylchromium (39). Freshly cracked methylcyclopentadiene (15.20 g, 0.19 mol) was added in four portions to 250 mL of THF containing sodium sand (3.10 g, 0.14 mol). The mixture was then refluxed until all the sodium had reacted. The THF was removed under vacuum (0.01 mmHg) followed by addition of 200 mL of DMF and chromium hexacarbonyl (24.00 g, 0.11 mol). The mixture was refluxed for 15 h and the DMF removed under vacuum (0.01 mmHg). THF (200 mL) was added followed by 98% acetic acid (13.0 mL, 0.22 mol), and the mixture was stirred for 30 min at 25 °C. To this was added slowly *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (30.00 g, 0.14 mol), and stirring was continued for 30 min. The solvent was removed under vacuum and the resulting residue extracted with a total of 1 L of pentane. The solvent was concentrated to 400 mL, washed with water, and then dried over anhydrous magnesium sulfate. The solution was filtered and the solvent removed under vacuum to give 15.2 g (57%) of **39** as a red liquid. An analytical sample was obtained by molecular distillation: ^1H NMR ($CDCl_3$) δ 1.96 (3 H, s, CH_3), 4.93 (4 H, s, Cp H_{2-5}); IR (neat) 2920 (w), 2010 (s), 1940 (s), 1685 (s), 1480 (w), 1450 (w), 1370 (w), 1170 (m), 1025 (w), 815 (m), 695 (w), 660 (m), 620 (s) cm^{-1}. Anal. Calcd: C, 44.25; H, 3.25; N, 6.45. Found: C, 44.51; H, 3.36; N, 6.40.

Reaction of (η^5-Formylcyclopentadienyl)dicarbonylnitrosylchromium (13) with Lithium Aluminum Hydride-/Aluminum Chloride. Aluminum chloride (267 mg, 2.0 mmol) was added to a stirred suspension of lithium aluminum hydride (76 mg, 2.0 mmol) in ether. After the mixture was stirred for 10 min, a solution of **13** (400 mg, 1.7 mmol) in 10 mL of ether was added dropwise. After the addition was complete, the reaction mixture was stirred for 30 min and then hydrolyzed with a solution of dilute hydrochloric acid. The ether layer was washed with water, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed under vacuum on Florisil and the resulting residue added to a column of Florisil (15 × 1.5 cm). Elution of the column with hexane produced a red band that was collected under nitrogen. Removal of the solvent under vacuum gave 90 mg (24%) of **39**. Further elution with hexane/ether removed another red band that was collected under nitrogen. The solvent was removed under vacuum to give 160 mg (34%) of **37**.

Registry No. **10**, 73249-47-5; **11**, 73249-48-6; **12**, 73249-49-7; **13**, 79086-51-4; **14**, 64539-47-5; **19**, 86507-93-9; **22**, 86507-94-0; **23**, 86507-95-1; **24**, 72360-41-9; **25**, 86507-96-2; **26**, 77060-52-7; **27**, 80340-00-7; **28**, 80340-02-9; **29**, 75862-52-1; **30**, 86507-97-3; **32**, 86507-98-4; **33**, 80339-99-7; **35**, 86507-99-5; **37**, 86508-00-1; **38**, 86508-01-2; **39**, 86508-02-3; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; *p*-$CH_3C_6H_4SO_2N(NO)CH_3$, 80-11-5; MeOC(O)OMe, 616-38-6; EtOC(O)OEt, 105-58-8; CH_3CO_2H, 64-19-7; CH_3Li, 917-54-4; cyclopentadiene, 542-92-7; sodium formylcyclopentadienide, 78207-69-9; sodium acetylcyclopentadienide, 78207-70-2; methylcyclopentadiene, 26519-91-5; 6-(dimethylamino)fulvene, 696-68-4; acryloyl chloride, 814-68-6.

Homologation of Boronic Esters to α-Chloro Boronic Esters

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Received May 3, 1983

The homologation of boronic esters, $RBO_2C_2R'_4$ (**7**), with (dichloromethyl)lithium to form α-chloro boronic esters, R–CHCl–$BO_2C_2R'_4$ (**3**), has been found to be a highly efficient process. R may be primary, secondary, or tertiary alkyl, cycloalkyl, alkenyl, allyl, aryl, or benzyl, and functional substituents in R may include α-benzyloxy, β or remote carbalkoxy, or a remote ketal substituent. R′ was H or CH_3. The homologation failed in the presence of an α-phenylthio or an α-boronic ester substituent. The α-chloro boronic esters readily undergo nucleophilic replacement of chloride with a variety of reagents, including thiophenolate, benzyl oxide, an ester enolate, or alkyl groups from Grignard or lithium reagents. Either 100% C-alkylation or a majority of O-alkylation and Cope rearrangement could be obtained when *tert*-butyl lithioacetate reacted with pinacol 3-chloro-1-propene-3-boronate. The β-benzyloxy boronic ester (**11**) obtained by homologation of pinacol 1-(benzyloxy)pentane-1-boronate (**10**) decomposed slowly by β boron–oxygen elimination above 100 °C but was stable enough to permit replacement of the α-chlorine by methylmagnesium bromide to form **12**, which was oxidized with sodium perborate to a mixture of diastereomeric 3-(benzyloxy)-2-heptanols (**13**).

The efficient reaction of α-halo boronic esters with Grignard reagents to form carbon–carbon bonds by boron-assisted S_N2 displacement was discovered by us 20 years ago,[1] and its utility for joining sterically hindered alkyl groups has been demonstrated recently by Brown, Yamamoto, and co-workers.[2] However, the previously known routes to α-halo boronic esters[2-5] have not been

(1) Matteson, D. S.; Mah, R. W. H. *J. Am. Chem. Soc.* **1963**, *85*, 2599–2603.

(2) Brown H. C.; De Lue, N. R.; Yamamoto, Y.; Maruyama, K. *J. Org. Chem.* **1977**, *42*, 3252–3254. Brown, H. C.; De Lue, N. R.; Yamamoto, Y.; Maruyama, K.; Kasahara, T.; Marahashi, S.; Sonoda, A. *Ibid.* **1977**, *42*, 4088–5092.

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Table I. Homologation of Unfunctionzlied Boronic Esters (1) to α-Chloro Boronic Esters (3) with (Dichloromethyl)lithium[a]

R of 1 and 3	ester type[b]	α-chloro boronic ester (3) bp, °C (torr)	yield grams	yield %
$CH_3(CH_2)_3$	a	75-79 (4)	1.42[a]	80
$CH_3(CH_2)_3$	b	50-51 (0.06)	22.0[c c]	86[c]
$CH_3(CH_2)_7$	a	80-85 (0.1)	1.98	85
$CH_3CH_2CH(CH_3)$	a	88-90 (5)	1.35	77
$(CH_3)_3C$	a	61-62 (2)	1.38	78
c-C_5H_9	a	83-85 (1)	1.55	82
c-C_5H_9	c	110-115 (4)	1.67	82
c-C_6H_{11}	a	87-89 (0.25)	1.74	86
c-C_6H_{11}	b	75-79 (0.2)	9.54[d]	73
CH_2=CH	b	67-70 (2)	18.7[e]	90
(*E*/*Z*)-CH_3CH=CH	b	90-94 (4)	1.89	83
CH_2=$CHCH_2$	b	50-52 (0.3)	1.89	87
C_6H_5	a	95-97 (0.25)	1.80	91
C_6H_5	b	85-90 (0.15)	2.26	85
$C_6H_5CH_2$	a	90-94 (0.15)	1.78	84
$C_6H_5CH_2$	d	49-51 (0.04)	12.5[f]	58[f]

[a] All reactions were run with 10 mmol of 1, except as noted. Functionalized boronic esters are listed separately in structure diagrams and the Experimental Section. [b] a, ethylene glycol; b, pinacol; c, propane-1,3-diol; d, methyl. [c] Run on 0.1096 mol of 1b by "method B", Experimental Section. All other data are for "method A". [d] 50-mmol scale. [e] 0.1023-mol scale. [f] 0.100-mol scale. Recovered 20-25% unchanged 1d. Product was treated with a few milliliters of 2,2-dimethoxypropane before distillation as precaution against accidental hydrolysis.

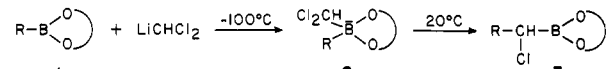
convenient or general enough to encourage use of this process in synthesis.

Since our preliminary communication on the present work,[6] we have further developed the homologation of boronic esters with (dichloromethyl)lithium to form α-chloro boronic esters and have found that it provides a remarkably stereoselective and general directed chiral synthesis that promises to be especially useful for assembling adjacent chiral centers.[7-9] The work with achiral and racemic boronic esters reported here in detail forms the basis for the new chiral synthesis method and also indicates some of its possible scope, part of which has already been realized.[9]

Our first attempt to homologate a boronic ester with (dichloromethyl)lithium was prompted by our success in homologating boronic esters with [chloro(trimethylsilyl)-methyl]lithium.[10] Other reagents successfully used for homologating trialkylboranes had failed with boronic esters,[10b] but the reaction of dichloromethaneboronic esters with alkyllithiums reported by Rathke and co-workers[5] must proceed by way of the same type of borate complex 2 that is an intermediate in our homologation process. Thus, from the outset we were assured of success but not necessarily of novel developments.

Results

(Dichloromethyl)lithium was prepared from butyllithium and dichloromethane in tetrahydrofuran (THF) at −100 °C[5,11] and then treated with the boronic ester 1 to be homologated. The resulting solution was allowed to stand at room temperature overnight in order to rearrange the intermediate borate complex (2) to the α-chloro boronic ester (3), which was isolated simply by filtering the precipitated lithium chloride and distilling the product. Yields were generally high, as summarized in Table I, and most of the products were analytically pure as prepared.



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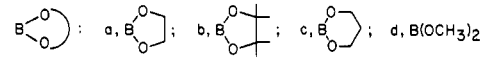
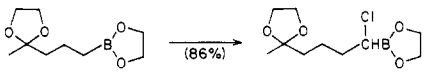


Having found efficient homologation conditions, the question of major interest was the compatibility of this process with the presence of functional groups in R. For synthetic applications, the critical functions are ethers, ketals (or acetals), and carboxylic esters. Each of these three classes of substituents has been tested successfully, though it was found that the oxygen functionality considerably slows the rearrangement of the borate intermediate (2) to the α-chloro boronic ester (3), requiring heating to complete the reaction in some cases. Conventional methods were used to prepare two of the test compounds, ethylene glycol 4-ketopentane-1-boronate ethylene ketal (4) from the Grignard reagent and methyl borate and



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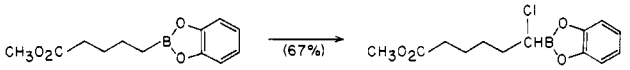

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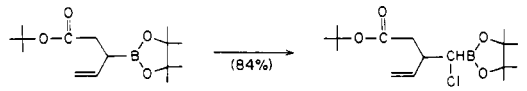


8 9

catechol 4-carbomethoxybutane-1-boronate (6) by hydroboration of methyl pent-5-enoate with catecholborane.[12,13] Synthesis from α-chloro boronic esters (3) provided the other two substrates, *tert*-butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborol-2-yl)pent-4-enoate (8) and pinacol 1-(benzyloxy)pentane-1-boronate (10). The β-benzyloxy boronic ester product (11) was unstable to distillation,

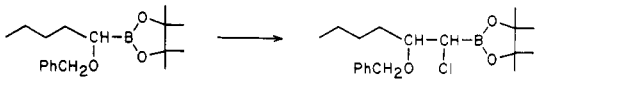
(3) Matteson, D. S.; Liedtke, J. D. *Chem. Ind. (London)* **1963**, 1241. Matteson, D. S.; Schaumberg, G. D. *J. Org. Chem.* **1966**, *31*, 726-731. Matteson, D. S.; Cheng, T. C. *Ibid.* **1968**, *33*, 3055-3060.
(4) Matteson, D. S.; Arne, K. *J. Am. Chem. Soc.* **1978**, *100*, 1325-1326. Matteson, D. S.; Arne, K. H. *Organometallics* **1982**, *1*, 280-288.
(5) Rathke, M. W. Chao, E.; Wu, G. *J. Organomet. Chem.* **1976**, *122*, 145-149.
(6) Matteson, D. S.; Majumdar, D. *J. Am Chem. Soc.* **1980**, *102*, 7588-7590.
(7) Matteson, D. S.; Ray, R. *J. Am. Chem. Soc.* **1980**, *102*, 7590-7591. Matteson, D. S.; Ray, R.; Rocks, R. R. *Organometallics*, following paper in this issue.
(8) Matteson, D. S.; Sadhu, K. M.; Lienhard, G. E. *J. Am. Chem. Soc.* **1981**, *103*, 5241-5242.
(9) Matteson, D. S.; Sadhu, K. M. *J. Am. Chem. Soc.* **1983**, in press.
(10) (a) Matteson, D. S.; Majumdar, D. *J. Organomet. Chem.* **1983**, *184*, C41-C43. (b) Matteson, D. S.; Majumdar, D. *Organometallics* **1983**, *2*, 230-236. (c) Reagent: Burford, C.; Cooke, F.; Ehlinger, E.; Magnus, P. *J. Am. Chem. Soc.* **1977**, *99*, 4536-4537.
(11) Köbrich, G.; Flory, K.; Drischel, W. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 513. Köbrich, G.; Merkle, H. R.; Trapp, H. *Tetrahedron Lett.* **1965**, 969-972.
(12) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1975**, *97*, 5249-5255.
(13) This may be the first hydroboration of an unsaturated ester with catecholborane, which was not tested with functionalized compounds.[12] We found that catecholborane attacked the ketone in preference to the double bond of hex-5-en-2-one (NMR evidence), and attempted hydroboration of diethyl allylmalonate yielded a complex mixture, apparently as a result of reaction of the acidic hydrogen with the borane.

Table II. Nucleophilic Displacement Reactions of α-Chloro Boronic Esters (3)

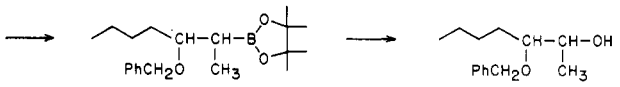
R of 3	ester type[a]	nucleophile	product structure	bp, °C (torr)	yield, %
c-C_5H_9	a	NaSPh	(c-C_5H_9)CH(SPh)$BO_2C_2H_4$	120-124 (0.2)	91
c-C_6H_{11}	b	NaSPh	(c-C_6H_{11})CH(SPh)$BO_2C_2Me_4$	137-143 (0.2)	93
$(CH_3)_3C$	a	NaSPh	t-BuCH(SPh)$BO_2C_2H_4$	105-110 (0.2)	88
$CH_3(CH_2)_3$	b	$LiOCH_2Ph$	BuCH(OCH_2Ph)$BO_2C_2Me_4$	109-111 (0.07)	87
CH_2=CH	b	t-BuO_2CCH_2Li	**8**	67-70 (0.07)	80[b]
(E)-CH_3CH=CH	b	t-BuO_2CCH_2Li	(E)-CH_3CH=CH, t-BuO_2CCH_2 > $CHBO_2C_2Me_4$	77-78 (0.07)	70
c-C_5H_9	a	n-BuLi	(c-C_5H_9)CH(n-Bu)$BO_2C_2H_4$	85-89 (3)	92
c-C_5H_9	a	c-$C_6H_{11}MgCl$	(c-C_5H_9)CH(c-C_6H_{11})$BO_2C_2H_4$	85-88 (0.1)	94
c-C_5H_9	a	PhMgBr	(c-C_5H_9)CH(Ph)$BO_2C_2H_4$	90-93 (0.1)	90

[a] a, ethylene glycol; b, pinacol. [b] Excess *tert*-butyl acetate used in making lithio derivative. When excess LDA was used, products were **16** (40%) and **8** (22%) (estimated by NMR). Distillation accompanied by some decomposition. Yield is of **13** based on **10** when **11** and **12** were not distilled; see text.

undergoing slow β-elimination of pinacol benzyl borate at 100 °C.



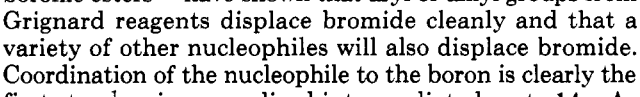
10 **11**



12 **13**

Although compatible with the foregoing most essential substituents for synthetic purposes, limits to the functional group compatibility of the homologation process were found. A free ketone interferes, as shown by the attempted homologation of ethylene glycol 4-ketopentane-1-boronate, which was partially recovered unchanged in a complex mixture of products which distilled with difficulty from the lithium salts obtained. (This substrate was obtained by hydrolyzing the boronic ester ketal **4** to the keto boronic acid and then reesterifying with just enough ethylene glycol to restore the boronic ester.) Another failure was pinacol (phenylthio)methaneboronate, which was recovered partly unchanged and was partly converted to thioanisole and pinacol dichloromethaneboronate. Ethylene glycol (phenylthio)methaneboronate had previously been homologated efficiently by [chloro(trimethylsilyl)methyl]lithium,[10] and this negative result was not entirely anticipated. Propanediol methanediboronate was also tested and was partially recovered unchanged and, apparently, partially converted to volatile products not collected (as if homologation was followed by B–Cl elimination). A final negative result was the attempted reaction of (trichloromethyl)lithium with ethylene glycol cyclopentaneboronate, 90% of which was recovered unchanged.

The second question of interest was the efficiency of replacement of the α-chloride from α-chloro boronic esters (**3**) by various nucleophiles. Previous studies with α-bromo boronic esters[1-3] have shown that aryl or alkyl groups from Grignard reagents displace bromide cleanly and that a variety of other nucleophiles will also displace bromide. Coordination of the nucleophile to the boron is clearly the first step,[1] as in generalized intermediate borate **14**. As

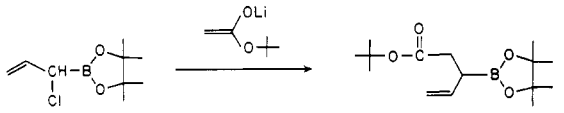


3 **14**

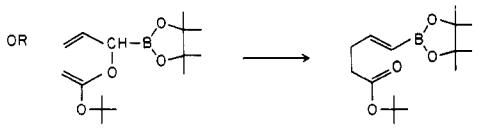
R' = alkyl, aryl, phenylthio, benzyloxy; M = Mg, Li, Na

indicated in Table II, yields are generally very high in the α-chloro boronic ester series, and *sec*-alkaneboronic esters of some complexity and considerable steric hindrance are easily constructed. Potentially useful α-phenylthio boronic esters[4] can be made easily, even when the displacement is on a neopentyl carbon (**3**, R = *t*-Bu). Displacement by benzyl oxide proved routine.

tert-Butyl lithioacetate[14] offers the possibility of either O- or C-alkylation, and on reaction with pinacol 3-chloro-1-propene-3-boronate (**15**) was found to yield exclusively the simple C-alkylation product **8**, provided no excess of lithium diisopropylamide (LDA) over *tert*-butyl acetate was used in the enolate preparation. The homologue pinacol 1-chloro-2-butene-1-boronate behaved similarly. However, when a small excess of LDA was used, 60–70% of the product from **15** and **16**, corresponding to O-alkylation and Cope rearrangement. If this suggested



15 **8**



16

mechanism is correct, the Cope rearrangement is rapid at room temperature, **16** and no O-alkylation intermediate being detected by NMR examination of the undistilled product. Only the *E* isomer of **16** was detectable in the 60-MHz NMR spectrum. The moderate complexing agents for lithium cation, THF and triglyme,[15] did not cause formation of any **16** in the absence of excess LDA, and use of the potassium enolate also yielded exclusively the C-alkylation product **8**. The effect of strong cation complexing agents such as crown ethers, which might be expected to promote O-alkylation, has not been tested.

A third question was whether the reaction might be carried out at the more familiar temperature, −78 °C, by generating the (dichloromethyl)lithium from LDA and dichloromethane in 1,2-dimethoxyethane (DME) in the presence of the boronic ester, as described for other substrates.[16,17] Pinacol boronic esters are sufficiently sterically

(14) Rathke, M. W.; Sullivan, D. F. *J. Am. Chem. Soc.* **1973**, *95*, 3050–3051.
(15) Matteson, D. S.; Erdik, E. *Organometallics* **1983**, *2*, 1083–1088.

hindered that the boron either is not attacked or is perhaps reversibly attacked by LDA in the α-phenylthio boronic ester series,[4] and we therefore tested homologation of pinacol butaneboronate with (dichloromethyl)lithium generated in situ, with excellent results (86%). Subsequently, the more complex boronic esters **8** and **10** were homologated by this procedure. There does appear to be a limitation to the less reactive α-chloro boronic esters for this technique, inasmuch as pinacol (*E*)-1-propene-1-boronate yielded only 50% of the homologation product, pinacol (*E*)-1-chloro-2-butene-1-boronate. Perhaps the allylic chloride is reactive toward the diisopropylamine present under these reaction conditions.

The reactivity of **3c** (R = cyclopentyl) toward LDA and lithium 2,2,6,6-tetramethylpiperidide was examined briefly. Much unchanged **3c** was recovered, but from the 60-MHz NMR spectrum of the higher boiling distillate it appeared that S_N2 substitution was the major reaction (~20%).

Discussion

The major significance of the work reported here is that it has led the way to a highly promising general method of directed chiral synthesis.[7-9] The ethylene glycol and pinacol boronic esters reported here are less sterically hindered and more reactive than the pinanediol esters used in the chiral synthesis and consequently more tolerant of variations in structures and reaction conditions, which has been helpful for exploratory purposes. The relative sluggishness of the homologation of the ketal-, ester-, and ether-substituted boronic esters **4**, **6**, and **10**, requiring vacuum pyrolysis to complete the rearrangement of the borate intermediate (**2**) in the conversions of **4** to **5** and of **6** to **7**, forewarned us of impending difficulties with functional substituents in the chiral synthesis,[7] which have been fully overcome by zinc chloride catalysis.[9] The apparent formation of S_N2 displacement products on reaction of **3** with LDA suggested the successful solution to the surprisingly difficult and long unsolved problem of amino boronic acid synthesis.[8]

The stability of β-alkoxy boronic esters such as **11** and **12** is crucial to the applicability of the homologation to the controlled chiral synthesis of 1,2-diols,[9] which constitute a ubiquitous structural feature of natural products. Prior to this work, the extreme lability of β-bromo boronic esters toward bases as mild as water,[18] as well as the instability toward rapid elimination exhibited by β-alkoxy-substituted trialkylboranes,[19] offered scant hope of such stability.

In view of the ready availability of pure (*E*)-alkeneboronic esters[20,21] and (*Z*)-enolates,[22] the O-alkylation/Cope rearrangement process illustrated by the conversion of **15** to **16** may have interesting chiral applications, which remain to be tested.

The racemic α-chloro boronic esters produced in this work are potential aldehyde precursors, as shown by our early peroxide oxidation of an α-chloro boronic ester as a structure proof[23] as well as Rathke's work.[5] The conversion to α-phenylthio boronic esters, which can be oxidized with *N*-chlorosuccinimide to monothioacetals or acetals,[24] constitutes another formal route to aldehydes. α-Chloro boronic esters are much more versatile synthetic intermediates than aldehydes, but the conversion may become useful in the future as a final stage of some natural products syntheses.

Experimental Section

General Data. All reactions involving carbanionic reagents were carried out under argon. Tetrahydrofuran (THF), diethyl ether, and 1,2-dimethoxyethane (DME) were freshly distilled from sodium benzophenone ketyl. Butyllithium in hexane was purchased from Alfa or Aldrich and was titrated against 2-propanol with 1,10-phenanthroline as indicator. Amines were distilled from calcium hydride and stored over 5-Å molecular sieves. Proton NMR spectra were determined on a Varian EM-360 instrument and are referred to internal tetramethylsilane. Elemental analyses were by Galbraith Laboratories, Knoxville, TN.

Unfunctionalized Boronic Esters (1). These were prepared as previously described.[10,25,26] New compounds included ethylene glycol *tert*-butylboronate (**1a**, R = $C(CH_3)_3$): bp 28–30 °C (12 torr); NMR (CCl_4) δ 1.00 (s, 9, CCH_3), 4.26 (s, 4, OCH_2). Anal. Calcd for $C_6H_{13}BO_2$: C, 56.31; H, 10.24; B, 8.45. Found: C, 56.39; H, 10.40; B, 8.23. Also new was pinacol vinylboronate (**1b**, R = $CH{=}CH_2$), made by transesterification of the dibutyl ester with pinacol: bp 34–35 °C (7 torr); NMR (CCl_4) δ 1.30 (s, 12, CCH_3), 6.1–6.2 (m, 3, $CH{=}CH_2$). Anal. Calcd for $C_8H_{15}BO_2$: C, 62.39; H, 9.82; B, 7.02. Found: C, 62.53; H, 9.93; B, 6.88.

α-Chloro Boronic Esters (3). Method A. A solution of 0.7–1.0 mL (11–16 mmol) of dichloromethane in 20 mL of THF was cooled to −100 °C in a 95% ethanol/liquid nitrogen slush bath[17] and stirred magnetically during the dropwise addition of 10.5 mmol of *n*-butyllithium (1.6–2.0 M in hexane) from a syringe over a period of 5 min. The butyllithium must be chilled before contacting the dichloromethane solution, either by bringing the tip of the syringe needle to within about 5 mm of the surface of the cold solution or, more conveniently, by running the butyllithium solution down the cold wall of the reaction flask.[27] After about half of the butyllithium had been added, a white precipitate of (dichloromethyl)lithium formed. The solution should remain colorless or pale yellow. Darkening is a sign of overheating and decomposition. After 5–30 min, a solution of 10 mmol of the boronic ester **1** in 5 mL of diethyl ether was injected in one portion, resulting in dissolution of the precipitate of (dichloromethyl)-lithium. (In some cases, precipitation of the borate complex **2** followed.) The solution was allowed to warm slowly to 20–25 °C and kept overnight. Fifty milliliters of dichloromethane was added to precipitate the lithium chloride (optional), the solution was filtered and concentrated under vacuum, and the product **3** was distilled, discarding a small forerun of unchanged **1**. Samples prepared in this manner were usually analytically pure, though some were redistilled. Yields and boiling points are listed in Table I, NMR data in Table III, and elemental analyses in Table V. Necessary deviations from the general procedure are noted below.

(16) Corey, E. J.; Jautelat, M.; Oppolzer, W. *Tetrahedron Lett.* **1967**, 2325–2328.

(17) (Dichloromethyl)lithium is not stable much above −100 °C, and we are mystified by reports that it could be made at −65 °C.[11] In our experience thermometers often suffer column separation and yield false high readings at these low temperatures, and we have learned to judge temperatures solely by the consistency of the 95% ethanol slush bath, which should have a thick syrupy consistence or be partly frozen during the addition of the butyllithium. The freezing point of THF, −108 °C, sets the lower bound on the temperature.

(18) Matteson, D. S.; Liedtke, J. D. *J. Org. Chem.* **1963**, *28*, 1924–1925. Matteson, D. S.; Liedtke, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 1526–1531.

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(20) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1972**, *94*, 4370–4371.

(21) Matteson, D. S.; Jesthi, P. K. *J. Organomet. Chem.* **1976**, *110*, 25–37.

(22) Masamune, S.; Ellingboe, J. W.; Choy, W. *J. Am. Chem. Soc.* **1982**, *104*, 5526–5527.

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(24) Mendoza, A.; Matteson, D. S. *J. Chem. Soc., Chem. Commun.* **1978**, 357–358. Mendoza, A.; Matteson, D. S. *J. Organomet. Chem.* **1978**, *156*, 149–157.

(25) Dimethyl benzylboronate: Matteson, D. S.; Krämer, E. *J. Am. Chem. Soc.* **1968**, *90*, 7261–7266.

(26) Boronic esters form rapidly on contact of the boronic acid with ethylene glycol or pinacol hydrate. We have found it convenient to dissolve the boronic acid and a few per cent excess of the diol together in ether and then to add petroleum ether to ensure complete separation of the water and any excess diol from the organic phase, which is distilled to yield the pure boronic ester.[4,6] The azeotropic distillation method[4] requires less solvent and is preferred by us for large scale (~1 mol) runs.

(27) We thank K. M. Sadhu for developing the latter technique.

(28) Hall, H. K., Jr.; Schaefer, J. P.; Spanggord, R. J. *J. Org. Chem.* **1972**, *37*, 3069–3075.

Table III. 60-MHz Proton NMR Spectra of Unfunctionalized α-Chloro Boronic Esters (3)

R of 3	ester type[a]	solvent	chemical shifts, δ (splitting, group)[b] R	CHClB	ester
n-C_4H_9	a	CCl_4	0.96 (t, CH_3), 1.3-1.9 (CH_2)	3.43 (t)	4.36
n-C_4H_9	b	$CDCl_3$	0.9-2.0 (C_4H_9)	3.47 (t)	1.31
n-C_8H_{17}	a	CCl_4	0.93 (t, CH_3), 1.3-1.9 (CH_2)	3.43 (t)	4.36
sec-C_4H_9	a	CCl_4	1.0 ($2CH_3$), 1.50 (CH_2), 1.8 (CH)	3.52, 3.60[c]	4.43
$(CH_3)_3C$	a	CCl_4	1.06 (s, CH_3)	3.26 (s)	4.32
c-C_5H_9	a	CCl_4	1.63 (CH_2), 2.4 (CH)	3.50 (d)	4.40
c-C_5H_9	c[d]	CCl_4	1.63 (CH_2) (CH indistinct)	3.06 (d)	2.03, 4.16
c-C_6H_{11}	a	CCl_4	1.50 (CH_2), 2.06 (CH)	3.26 (d)	4.39
c-C_6H_{11}	b[d]	CCl_4	1.50 (CH_2), 2.1 (CH)	3.13 (d)	1.26
CH_2=CH	b	$CDCl_3$	5.28 5.45 (CH_2=), 6.15 (=CH)[e]	4.07 (d)	1.34
(E)-CH_3CH=CH	b	$CDCl_3$	1.77 (d, CH_3), 5.8 (m, CH=CH)	4.01 (d)	1.32
CH_2=$CHCH_2$	b	CCl_4	2.59 (m, CH_2), 5.1-5.8 (CH_2=CH)	3.36 (t)	1.26
C_6H_5	a	CCl_4	7.56 (narrow, C_6H_5)	4.69 (s)	4.36
C_6H_5	b[d]	CCl_4	7.43 (narrow m, C_6H_5)	4.36 (s)	1.23
$C_6H_5CH_2$	a	CCl_4	3.16 (m, CH_2), 7.39 (C_6H_5)	3.50 (m)	4.26
$C_6H_5CH_2$	d	$CDCl_3$	3.20 (m, CH_2), 7.47 (C_6H_5)	3.65 (m)	3.68

[a] Spectra of functionally substituted boronic esters entered individually in Experimental Section. [b] Satisfactory integrals were obtained, and multiplicities not indicated were typical of group. [c] Appearance of triplet, interpreted as two doublets consistent with structure because diastereomers expected. [d] This ester not analyzed for elements. [e] J_{trans} = 18 Hz (δ 5.45), J_{cis} = 10 Hz (δ 5.28), and J_{HCH} = 1.5 Hz.

Table IV. 60-MHz Proton NMR Spectra of Compounds $RCHYBO_2C_2R_4'$ Derived from α-Chloro Boronic Esters (3) by Nucleophilic Displacement

R	Y	R′	chemical shift, δ (splitting)[a] R	Y	CHYB	R′ (s)
c-C_5H_9	SPh	H	1.66 (br)	7.39 (m)	2.63 (d)	4.16
c-C_6H_{11}[b]	SPh	CH_3	1.73 (br)	7.39 (m)	2.46 (d)	1.16
$(CH_3)_3C$	SPh	H	1.06 (s)	7.36 (m)	2.53 (s)	4.16
n-C_4H_9	OCH_2Ph	CH_3	0.9-1.7 (m)	4.63 (s), 7.47	3.38 (t)	1.30
c-C_5H_9	n-C_4H_9	H	0.89 (t), 1-2	1.5 (m)		4.19
c-C_5H_9	c-C_5H_{11}	H	1.3 (br m)	1.3 (m)		4.13
c-C_5H_9	Ph	H	1.6 (br m)	7.23 (m)		4.16

[a] Satisfactory integrals were obtained. Solvent CCl_4 except R = C_4H_9 and Y = OCH_2Ph (10), $CDCl_3$. [b] No elemental analysis.

Table V. Elemental Analyses of Unfunctionalized $RCHYBO_2C_3R_4'$[a]

R of 3	Y	R′	anal. calcd (found) C	H	B	Cl [or S]
n-C_4H_9	Cl	H	47.65 (47.89)	8.00 (8.04)	6.13 (5.89)	20.09 (20.25)
n-C_4H_9	Cl	CH_3	56.81 (56.61)	9.54 (9.33)	4.65 (4.41)	15.24 (15.00)
n-C_8H_{17}	Cl	H	56.81 (57.03)	9.54 (9.45)	4.65 (4.38)	15.24 (15.06)
sec-C_4H_9	Cl	H	47.65 (47.55)	8.00 (8.06)	6.13 (5.92)	20.09 (19.81)
$(CH_3)_3C$	Cl	H	47.65 (47.43)	8.00 (7.80)	6.13 (5.91)	20.09 (20.23)
c-C_5H_9	Cl	H	50.98 (50.78)	7.48 (7.39)	5.73 (5.93)	18.81 (19.05)
c-C_6H_{11}	Cl	H	53.39 (53.33)	7.96 (7.91)	5.34 (5.46)	17.51 (17.32)
CH_2=CH	Cl	CH_3	53.39 (53.52)	7.96 (8.04)	5.34 (5.47)	17.51 (17.74)
CH_3CH=CH[b]	Cl	CH_3	55.47 (55.08)	8.38 (8.21)	4.99 (4.83)	16.37 (16.08)
CH_2=$CHCH_2$	Cl	CH_3	55.47 (55.18)	8.38 (8.45)	4.99 (4.88)	16.37 (16.34)
C_6H_5	Cl	H	55.03 (56.41)[c]	5.13 (5.42)	5.50 (5.87)	18.05 (16.92)
$C_6H_5CH_2$	Cl	H	57.34 (57.55)	5.29 (5.32)	5.16 (4.95)	16.92 (16.74)
$C_6H_5CH_2$	Cl	d	56.53 (56.62)	6.64 (6.53)	5.09 (4.91)	16.69 (16.78)
c-C_5H_9	SPh	H	64.14 (64.25)	7.30 (7.22)	4.12 (4.30)	[12.23 (12.46)]
$(CH_3)_3C$	SPh	H	62.42 (63.14)	7.66 (7.60)	4.32 (4.19)	[12.82 (13.17)]
n-C_4H_9	OCH_2Ph	CH_3	71.06 (71.19)	9.61 (9.50)	3.55 (3.44)	
c-C_5H_9	Ph	H	73.07 (72.94)	8.32 (8.40)	4.70 (4.55)	
c-C_5H_9	n-C_4H_9	H	68.59 (68.27)	11.03 (11.22)	5.14 (4.94)	
c-C_5H_9	c-C_6H_{11}	H	71.20 (71.30)	10.67 (10.57)	4.58 (4.50)	

[a] Functionally substituted compounds: see text of Experimental Section. [b] E/Z isomer mixture. [c] Not purified, appeared somewhat unstable. Pinanediol α-chlorobenzylboronate has been purified after considerable difficulty.[15] [d] $PhCH_2CHClB(OCH_3)_2$.

This procedure has also been carried out on a 100-mmol scale without difficulty.

Method B. LDA was prepared by adding 11.5 mmol of butyllithium in hexane to 11.5 mmol of magnetically stirred diisopropylamine cooled in an ice bath. Just before use, the viscous solution was thinned with 1–2 mL of THF. A solution of 10.4 mmol of the pinacol boronic ester (**1b**) in 10 mL of DME was chilled with a dry ice/acetone bath (−78 °C) and stirred magnetically during the dropwise addition of the LDA solution through a double-ended needle with the aid of a slight pressure of argon. The cooling bath was removed, allowing warming to 20 °C in 1 h, and the reaction was completed by stirring at 30–35 °C for 30 min. (The precipitation of lithium chloride suggested that the rearrangement of **2** to **3** is considerably faster in DME than in THF.) The solution was concentrated under vacuum, and the product **3b** was distilled from the residue of lithium chloride. Data

for products are included in Tables I, III, and V.

Ethylene Glycol 4-Ketopentane-1-boronate Ethylene Ketal (4). The Grignard reagent was prepared from 32.8 g of 5-chloro-2-pentanone ethylene ketal and 6.6 g of magnesium in 100 mL of THF, cooled to −78 °C, and treated with 40% excess of trimethyl borate. After a day at 20 °C, the mixture was worked up with aqueous hydrochloric acid and extracted with ether. The extract was treated with excess ethylene glycol and cyclohexane, and the cyclohexane/water azeotrope was distilled. The product **4** was distilled: bp 66 °C (0.05 torr); 15.6 g (39%); NMR ($CDCl_3$) δ 0.87 (m, 2, CH_2B), 1.32 (s, 3, CH_3), 1.65 (m, 4, CH_2CH_2), 4.00 (s, 4, OCH_2), 4.27 (s, 4, OCH_2). Anal. Calcd for $C_9H_{17}BO_4$: C, 54.04; H, 8.57; B, 5.40. Found: C, 53.91; H, 8.62; B, 5.60.

Ethylene Glycol 4-Ketopentane-1-boronate. A 4.0-g (20-mmol) sample of ethylene glycol 4-ketopentane-1-boronate ethylene ketal (**4**) was dissolved in 12 mL of 2 M hydrochloric acid and kept 2.5 h at 20 °C. The product was extracted into ether, washed with water, and concentrated to yield crude 4-ketopentane-1-boronic acid (2.2 g), which was treated with 1 equiv (1.05 g) of ethylene glycol and distilled, yielding product contaminated with 15% **4** (NMR analysis): redistilled, bp 46 °C (0.05 torr); 2.0 g (64%), still contained 3% **4** but yielded satisfactory elemental analysis; NMR ($CDCl_3$) δ 0.85 (t, 2, CH_2B), 1.74 (m, 2, $CH_2CH_2CH_2$), 2.16 (s, 3, CH_3), 2.51 (t, 2, CH_2CO), 4.26 (S, 4, OCH_2). Anal. Calcd for $C_7H_{13}BO_3$: C, 53.90; H, 8.40; B, 6.93. Found: C, 53.54; H, 8.52; B, 6.62.

Ethylene Glycol 1-Chloro-5-ketohexane-1-boronate Ethylene Ketal (5). The usual "method A" for making α-chloro boronic esters was followed, starting from 2.18 g (10.9 mmol) of ethylene glycol 4-ketopentane-1-boronate ethylene ketal (**4**). At the point where the dichloromethane solution was filtered to remove lithium chloride, a voluminous precipitate was collected instead, 2.3 g. Heating the solid under vacuum resulted in melting and apparent decomposition at 70–100 °C, and the product **5** was distilled at 114–120 °C (0.1 torr); 1.32 g. The dichloromethane solution was distilled separately and yielded 1.03 g of **5**: combined yields 86%; redistilled, bp 93 °C (0.03 torr); NMR ($CDCl_3$) δ 1.33 (s, 3, CH_3), 1.68 (m, 6, $(CH_2)_3$), 3.53 (t, 1, CHClB), 4.00 (s, 4, OCH_2), 4.37 (s, 4, OCH_2). Anal. Calcd for $C_{10}H_{18}BClO_4$: C, 48.33; H, 7.30; B, 4.35; Cl, 14.27. Found: C, 48.11; H, 7.58; B, 4.52; Cl, 14.29.

Catechol 4-Carbomethoxybutane-1-boronate (6). The sodium salt of 4-pentenoic acid (from hydrolysis and decarboxylation of diethyl allylmalonate) was reacted with methyl iodide in moist dimethyl sulfoxide to yield methyl 4-pentenoate: bp 70 °C (~100 torr) (lit.[28] bp 122 °C); NMR typical vinyl pattern, δ 5.0–6.3, consistent with structure. A mixture of 40 mmol of methyl 4-pentenoate and 41 mmol of catecholborane was heated 90–110 °C for 2.5 h and the product **6** was distilled: bp 95 °C (0.03 mm); 6.4 g (68%); mp 28–29 °C after further purification by fractional freezing; NMR ($CDCl_3$) δ 1.35 (m, 2, CH_2B), 1.77 (m, 4, CCH_2CH_2C), 2.45 (m, 2, CH_2CO), 3.78 (s, 3, OCH_3), 7.35 (m, 4, Ar*H*). Anal. Calcd for $C_{12}H_{15}BO_4$: C, 61.58; H, 6.46; B, 4.62. Found: C, 61.40; H, 6.50; B, 4.34.

Catechol 1-Chloro-5-carbomethoxypentane-1-boronate (7). The α-chloro boronic ester procedure, "method A", was followed with a 2.4-g (10.3 mmol) sample of **6** up to the point where the reaction mixture had stood overnight and lithium chloride should have precipitated. Instead, a voluminous precipitate was found, which dissolved in dichloromethane. Stirring a solution in 50 mL of dichloromethane and 10 mL of petroleum ether overnight resulted in precipitation of some lithium chloride, but concentration left a residue that remained a gummy solid up to 70 °C. After overnight at 25 °C (0.1 torr), reheating (0.1 torr) melted the solid at 90 °C with some gas (solvent?) evolution and lithium chloride precipitation, and the product was distilled: 2.0 g (67%); bp 119–121 °C (0.03 torr); NMR ($CDCl_3$) δ 1.73 (m, 4, CH_2CH_2), 2.1 (m, 2, CH_2CHClB), 2.40 (m, 2, CH_2CO), 3.73 (s, 3, OCH_3), 3.97 (t, J = 7 Hz, 1, CHClB), 7.33 (m, 4, Ar*H*). Anal. Calcd for $C_{13}H_{16}BClO_4$: C, 55.27; H, 5.71; B, 3.83; Cl, 12.55. Found: C, 55.22; H, 5.83; B, 3.92; Cl, 12.35. Another run was made in which the reaction mixture in THF was heated to reflux (precipitate dissolved) overnight, which led to only 47% **7**, with 20% recovery of **6** and considerable undistillable residue.

Pinacol 4-Carbo-*tert*-butoxy-1-butene-3-boronate (8). A 10.6-mmol portion of *tert*-butyl acetate was added from a syringe to 10.4 mmol of LDA (from diisopropylamine and 1.6 M butyllithium in hexane) in 20 mL of THF stirred at −78 °C. A 10.0-mmol portion of pinacol 3-chloro-1-propene-3-boronate (**3b**, R = vinyl) was then added to the cold, stirred mixture from a syringe, and the solution was kept at 20 °C overnight. Distillation yielded **8**: bp 68–71 °C (0.07 torr); 2.26 g (80%); NMR ($CDCl_3$) δ 1.26 (s, 12, $C(CH_3)_2$), 1.46 (s, 9, $C(CH_3)_3$), 2.3 (m, 1, CHB), 2.51 + 2.53 (m, 2, CH_2CO_2), 5.1 (m, 2, $=CH_2$), 6.0 (m, 1, =CH). The use of the shift reagent Eu(fod) revealed that the diastereotopic CH_2CO_2 protons appear as an overlapping pair of doublets, J = 6 and 8 Hz (coupled to CHB). For the vinyl group, J_{trans} = 18 Hz, J_{cis} = 10 Hz, and J for C=CHCHB is 6 Hz. Anal. Calcd for $C_{15}H_{27}BO_4$: C, 63.85; H, 9.64; B, 3.83. Found: C, 63.62; H, 9.55; B, 4.09. The only product was **8** in runs in which the *tert*-butyl lithioacetate was prepared as a slurry in petroleum ether,[14] which on addition of **3b** led to a gelatinous mass finally dissolved by added ether and THF (80%); or when the reaction was carried out in 10 mL of DME and 2 g of triglyme; or when *tert*-butyl potassioacetate was prepared from potassiohexamethyldisilazane in THF at −78 °C (48%). In all of these runs a slight excess of *tert*-butyl acetate over metal amide was used.

Pinacol (*E*)-5-Carbo-*tert*-butoxy-2-pentene-4-boronate. A 15-mmol sample of pinacol (*E*)-1-chloro-2-butene-1-boronate (**3b**, R = (*E*)-CH_3CH=CH, from homologation of the pinacol ester of (*E*)-1-propene-1-boronic acid[21]) was added from syringe to *tert*-butyl lithioacetate which had been prepared from 15.7 mmol of *tert*-butyl acetate and 15.0 mmol of LDA in 10 mL of THF and was stirred at −78 °C. After being warmed to 20 °C, the mixture was concentrated, the residue was treated with 30 mL of ether, the lithium chloride was filtered, and the product was distilled: bp 78–79 °C (0.07 torr); 3.13 g (70%); NMR ($CDCl_3$) δ 1.27 (s, 12, $C(CH_3)_2$), 1.47 (s, 9, $C(CH_3)_3$), 1.67 (d, J = 4.5 Hz, 3, $=CHCH_3$), 2.2 (m, 1, CHB), 2.45 + 2.48 (m, 2, CH_2CO_2), 5.5–5.6 (m, 2, $CH=CH$). The diastereotopic CH_2CO_2 protons were examined in the presence of Eu(fod) shift reagent and found to show a pattern of two overlapping doublets, J = 6 and 9 Hz (coupled to CHB). Anal. Calcd for $C_{16}H_{29}BO_4$: C, 64.88; H, 9.87; B, 3.65. Found: C, 65.09; H, 9.88; B, 3.61.

Pinacol (*E*)-4-Carbo-*tert*-butoxy-1-butene-1-boronate (16). *tert*-Butyl lithioacetate was prepared in 10 mL of THF from 11.3 mmol of LDA and 9.7 mmol of *tert*-butyl acetate and was cooled at −78 °C and stirred during the addition of 9.7 mmol of pinacol 3-chloro-1-propene-3-boronate (**3b**, R = CH_2=CH) from a syringe. After overnight at 20 °C, petroleum ether was added, the lithium chloride was filtered, and the solution was concentrated under vacuum at 30 °C. The NMR spectrum indicated that **8** and **16** were the only products. Distillation yielded 1.70 g (62%) of the mixture, 60% **16**, and 40% **8**. Slow redistillation separated the material into fractions, the last of which was pure **16**: bp 82–83 °C (0.05 mm); NMR ($CDCl_3$) δ 1.30 (s, 12, $C(CH_3)_2$), 1.48 (s, 9, $C(CH_3)_3$), 2.41 (slightly br s, 4, CH_2CH_2), 5.59 (d, J = 19 Hz, 1, $CH=CHB$), 6.68 (m, 1, $CH_2CH=CHB$). With Eu(fod) shift reagent, the CH_2CH_2 signal was resolved to a downfield triplet, J = 8 Hz, and an upfield multiplet. The $CH_2CH=CH$ showed J = 3.5 Hz (t) and 19 Hz (d). Anal. Calcd for $C_{15}H_{27}BO_4$: C, 63.85; H, 9.64; B, 3.83. Found: C, 63.83; H, 9.77; B, 3.74.

Pinacol 4-Chloro-3-(carbo-*tert*-butoxymethyl)-1-butene-4-boronate (9). Pinacol 4-carbo-*tert*-butoxy-1-butene-3-boronate (**8**, 2.115 g, 7.5 mmol) was homologated with (dichloromethyl)-lithium according to "method B". A voluminous precipitate of the intermediate borate complex (**2**) was formed, which required about 0.5 h at room temperature to dissolve and react in DME, with precipitation of lithium chloride. Distillation yielded **9**: bp 99–101 °C (0.05 torr); 2.10 g (84%); NMR ($CDCl_3$) δ 1.30 (s, 12, $C(CH_3)_2$, 1.47 (s, 9, $C(CH_3)_3$), 2.1–3.8 (complex series of multiplets, 4, O_2CCH_2CHCHC1B, two diastereomers), 5.1–5.5 (m, 2, $=CH_2$, two diasteromers), 5.6–6.4 (m, 1, =CH, two diastereomers). Anal. Calcd for $C_{16}H_{28}BClO_4$: C, 58.12; H, 8.54; B, 3.27. Found: C, 58.21; H, 8.69; B, 3.15.

Pinacol 1-(Benzyloxy)pentane-1-boronate (10). Anhydrous benzyl alcohol (2.7 g, 25 mmol) in DME (25 mL) was titrated with 1.6 M butyllithium in hexane to the 1,10-phenanthroline endpoint at −78 °C. Pinacol 1-chloropentane-1-boronate (**3b**, R = n-C_4H_9, 5.81 g, 25 mmol) was added from a syringe to the cold, stirred solution. When the mixture was warmed to 20 °C, some precipitate formed. To ensure completion, the mixture was refluxed 2 h. Filtration and distillation yielded 7.10 g (93%) **10**: bp 102–106

°C (0.05 torr); NMR and analytical data, Tables IV and V.

Pinacol 1-Chloro-2-(benzyloxy)hexane-1-boronate (11). Pinacol 1-(benzyloxy)pentane-1-boronate (**10**, 3.04 g, 10 mmol) was homologated by "method B". From the voluminous precipitate remaining after the solution was warmed to 20 °C, which dried to a white powder on pumping off the solvent, the reaction was judged incomplete. The solid dissolved in 10 mL of THF and was kept overnight at 20 °C. Addition of ether and petroleum ether precipitated lithium chloride, which was filtered. The product **11** distilled with some decomposition at 125–130 °C (0.05 torr, maintained by cooling receiver in dry ice); 3.01 g (85%) crude, containing ~15% pinacol benzyl borate ($PhCH_2OBO_2C_2Me_4$), estimated from the NMR singlet at β 5.03. Slow molecular distillation at 50–65 °C (0.01 torr) removed most of the impurity. The undistilled residue of **11** was analyzed: NMR ($CDCl_3$) δ 0.8–1.7 (m, *n*-C_4H_9), 1.32 (s, $C(CH_3)_2$), 3.75 (m, 2, OC*HCH*Cl1B), 4.75 (m, 2, OCH_2Ph), 7.51 (s, 5, C_6H_5), complexity of multiplets consistent with two diastereomers. Anal. Calcd for $C_{19}H_{30}BClO_3$: C, 64.70; H, 8.57; B, 3.07; Cl, 10.05. Found: C, 64.81; H, 8.70; B, 2.91; Cl, 9.21.

2-(Benzyloxy)hexanal 2,4-Dinitrophenylhydrazone. A crude sample of pinacol 1-chloro-2-(benzyloxy)hexane-1-boronate (**11**) was treated with 2,4-dinitrophenylhydrazine and excess sodium perborate in sulfuric acid/water/ethanol. The precipitate was chromatographed on silica with ether/petroleum ether and recrystallized from 95% ethanol: mp 84–86.5 °C; NMR ($CDCl_3$) δ 0.8–1.8 (m, 9, C_4H_9), 4.17 (m, 1, OCH), 4.64 (s, 2, OCH_2Ph), 7.50 (s, 5, C_6H_5), ~7.56 (half-concealed d, 1, N=CH), 8.10 (d, J = 10 Hz, 1, $(O_2N)_2C_6H$), 8.50 (dd, J = 2.5 and 10 Hz, 1, $(O_2N)_2C_6H'$), 9.32 (d, J = 2.5 Hz, 1, $(O_2N)_2C_6H''$), 11.32 (s, 5 Hz wide at half-height, 1, NH). Anal. Calcd for $C_{19}H_{22}N_4O_5$: C, 59.06; H, 5.74, N, 14.50. Found: C, 58.95; H, 5.71; N, 14.56.

Pinacol 3-(Benzyloxy)heptane-2-boronate (12). Pinacol 1-(benzyloxy)pentane-1-boronate (**10**, (3.01 g, 9.9 mmol) was homologated by "method A", and after 24 h at 20 °C the THF solution of **11** was cooled to −78 °C and treated with an equivalent amount of methylmagnesium bromide. Aqueous workup and distillation, 100–140 °C (0.2 torr), resulted in extensive decomposition and recovery of ~40% **12** together with an eqimolar amount of pinacol benzyl borate: total 1.8 g; NMR ($CDCl_3$) δ 0.8–1.7 (m, C_4H_9 + $CHCH_3$), 1.23, 1.29 (s, s, $C(CH_3)_2$), 3.73 (m, OCH), 4.6–4.8 (m, $COCH_2Ph$), 5.03 + 5.10 (s, s, $BOCH_2Ph$), 7.51, (s, C_6H_5).

3-(Benzyloxy)-2-heptanol (13). Pinacol 1-(benzyloxy)pentane-1-boronate (**10**) (3.07 g, 10.1 mmol) was homologated by "Method A" and after overnight at 20 °C was refluxed 10 min. The solution of **11** was cooled to −78 °C, and 11 mmol of methylmagnesium bromide (2.9 M in ether) was added. After overnight at 20 °C, the mixture was heated to 55 °C (water bath) for 5 min, then cooled, and worked up with ether and dilute aqueous phosphoric acid. The ether extract was concentrated to 50 mL and cooled in an ice bath. A slurry of 3.1 g of sodium perborate in water followed by 1 g of sodium hydroxide in water (total 75 mL) was added, and the mixture was stirred 3 days at 20–25 °C. Extraction with ether and distillation yielded 1.59 g (71%) of **13**: bp 91 °C (0.1 torr); NMR ($CDCl_3$) δ 0.8–1.7 (m, C_4H_9), 1.06 (d, $CH3_CH$), 3.2–4.0 (m, 3, $CHCHOH$), 4.52 (s, 2, CH_2), 7.30 (s, 5, C_6H_5). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.49; H, 10.10.

Reaction of α-Chloro Boronic Esters (3) with Sodium Thiophenolate. A solution of 10 mmol of the α-chloro ester (**3**) in 10 mL of THF was added to a suspension of 10 mmol of sodium thiophenolate in 20 mL of THF stirred at −78 °C. Absolute ethanol was added dropwise until the precipitate dissolved. Stirring at −78 °C was continued 2–3 h, and the mixture was allowed to warm to 20 °C overnight. Petroleum ether or dichloromethane (50–100 mL) was added to complete the precipitation of sodium chloride, the solution was filtered, and the product was distilled. Yields and boiling points are summarized in Table II, NMR data in Table IV, and elemental analyses in Table V.

Reaction of α-Chloro Boronic Esters (3) with Grignard or Lithium Reagents. A solution of 10.5 mmol of the Grignard reagent in ether (or butyllithium in hexane) was added from a syringe to a solution of 10 mmol of the α-chloro brononic ester (**3**) in 20 mL of THF stirred at −78 °C. The mixture was stirred 2–3 h at −78 °C and allowed to warm to 20 °C overnight. Dichloromethane or petroleum ether (50 mL) was added to precipitate the magnesium or lithium halide, the mixture was filtered, and the product was distilled. Yields are summarized in Table II, NMR data in Table IV, and elemental analyses in Table V.

Attempted Reaction of an α-Chloro Boronic Ester (3c, R = c-C_5H_9) with LiTMP. A solution of 10 mmol of 1,3-propanediol cyclopentylchloromethaneboronate (**3c**, R = c-C_5H_9) in 5 mL of THF was added to 10.5 mmol of lithium tetramethylpiperidine (LiTMP) in 10 mL of THF at −78 °C, after which 5 mmol of tetramethylethylenediamine was added. The mixture was stirred 2 h at −78 °C and then treated with 5 mmol of 1-iodobutane. On distillation, 60% of the **3c** was recovered and 20% of a fraction was obtained which had an NMR spectrum which indicated the presence of tetramethylpiperidyl, cyclopentyl, and 1,3-propanediol boronic ester groups, bp 115–119 °C (0.1 torr).

Attempted Homologation of a Boronic Ester (1a, R = c-C_5H_9) with (Trichloromethyl)lithium. A suspension of (trichloromethyl)lithium was prepared by adding 20 mmol of butyllithium to 20 mmol of chloroform in 32 mL of THF, 8 mL of ether, and 8 mL of petroleum ether cooled to −110 °C with an ether slush bath. Addition of 10 mmol of **1a** (R = c-C_5H_9) in 10 mL of THF followed by overnight at 20 °C and distillation led to recovery of 90% of the unchanged **1a**, confirmed by NMR.

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Registry No. **1a** (R = $CH_3(CH_2)_3$), 10173-39-4; **1a** (R = $CH_3(CH_2)_7$), 83947-60-8; **1a** (R = $CH_3CH_2CH(CH_3)$), 72824-01-2; **1a** (R = $(CH_3)_3C$), 75927-48-9; **1a** (R = c-C_5H_9), 72824-02-3; **1a** (R = c-C_6H_{11}), 66217-60-5; **1a** (R = C_6H_5), 4406-72-8; **1a** (R = $C_6H_5CH_2$), 35895-82-0; **1b** (R = $CH_3(CH_2)_3$, 69190-62-1; **1b** (R = c-C_6H_{11}), 87100-15-0; **1b** (R = CH_2=CH), 75927-49-0; **1b** (R = (*E*)-CH_3CH=CH), 83947-58-4; **1b** (R = (*Z*)-CH_3CH=CH), 83947-59-5; **1b** (R = CH_2=$CHCH_2$), 72824-04-5; **1b** (R = C_6H_5), 24388-23-6; **1c** (R = *c*-C_5H_9), 30169-74-5; **1d** (R = $C_6H_5CH_2$), 25292-03-9; **2a** (R = 1-(*tert*-butoxycarbonylmethyl)-2-propenyl), 87100-26-3; **3a** (R = *n*-C_4H_9, Y = Cl), 75927-52-5; **3a** (R = *n*-C_8H_{17}, Y = Cl), 87100-16-1; **3a** (R = *sec*-C_{4-9}, Y = Cl), 75927-54-7; **3a** (R = $(CH_3)_3C$, Y = Cl), 75927-55-8; **3a** (R = c-C_5H_9, Y = Cl), 75927-56-9; **3a** (R = c-C_6H_{11}, Y = Cl), 75927-57-0; **3a** (R = C_6H_5, Y = Cl), 87100-18-3; **3a** (R = $C_6H_5CH_{21}$ Y = Cl), 75927-60-5; **3a** (R = c-C_5H_9, Y = Sp), 75935-40-9; **3a** (R = $(CH_3)_3C$, Y = SPh), 75927-40-1; **3a** (R = c-C_5H_9, Y = Ph), 75927-41-2; **3a** (R = c-C_5H_9, Y = *n*-C_4H_9), 75927-42-3; **3a** (R = c-C_5H_9, Y = *c*-C_6H_{11}), 75927-43-4; **3b** (R = *n*-C_4H_9, Y = Cl), 75927-53-6; **3b** (R = CH_2=CH, Y = Cl), 75927-58-1; **3b** (R = (*E*)-CH_3CH=CH, Y = Cl), 87100-17-2; **3b** (R = (*Z*)-CH_3CH=CH, Y = Cl), 87100-29-6; **3b** (R = CH_2=$CHCH_2$, Y = Cl), 75927-59-2; **3b** (R = *n*-C_4H_9, Y = OCH_2Ph), 75927-44-5; **3b** (R = *c*-C_6H_{11}, Y = SPh), 87100-20-7; **3b** (R = (*E*)-CH_3CH=CH, Y = *t*-BuO_2CCH_2), 87100-23-0; **3b** (R = c-C_6H_{11}, Y = Cl), 87100-31-0; **3b** (R = C_6H_5, Y = Cl), 87100-32-1; **3c** (R = *c*-C_5H_9, Y = Cl), 87100-32-1; **3d** (R = $C_6H_5CH_2$, Y = Cl), 87100-19-4; **4**, 75927-50-3; **5**, 75927-61-6; **6**, 75927-51-4; **7**, 75927-62-7; **8**, 75927-45-6; **9** (isomer 1), 87100-21-8; **9** (isomer 2), 87100-33-2; **10**, 75927-44-5; **11** (isomer 1), 87100-22-9; **11** (isomer 2), 87100-34-3; **12**, 75927-64-9; **13**, 75927-47-8; **15**, 75927-58-1; **16**, 75927-46-7; $LiCHCl_2$, 2146-67-0; *t*-BuO_2CCH_2Li, 41850-36-6; PhBr, 108-86-1; NaSPh, 930-69-8; $LiOCH_2Ph$, 15082-42-5; *n*-BuLi, 109-72-8; c-$C_6H_{11}Cl$, 542-18-7; LiTMP, 38227-87-1; pinacol, 76-09-5; 5-chloro-2-pentanone ethylene ketal, 5978-08-5; trimethyl borate, 121-43-7; ethylene glycol 4-ketopentane-1-boronate, 87100-24-1; 4-ketopentane-1-boronic acid, 87100-25-2; 4-pentenoic acid sodium salt, 25350-31-6; methyl 4-pentenoate, 818-57-5; catecholborane, 274-07-7; 2-(benzyloxy)hexanal 2,4-dinitrophenylhydrazone, 87100-27-4; 2,4-dinitrophenylhydrazine, 119-26-6; methyl bromide, 74-83-9; pinacol benzylborate, 87100-28-5; 1-iodobutane, 542-69-8; (trichloromethyl)lithium, 2146-66-9; ethylene glycol, 107-21-1; dibutyl vinylboronate, 6336-45-4.