((Trityloxy)methyl)boronic Esters

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Sodium trityl oxide with 2-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [pinacol (bromomethyl)boronate (**1**)] in dimethyl sulfoxide efficiently yields 4,4,5,5-tetramethyl-2-[(triphenylmethoxy)methyl]-1,3,2-dioxaborolane (**3**), which can be transesterified with chiral diols to form other [(triphenylmethoxy)methyl]-1,3,2-dioxaborolanes. These can undergo chain extension with (dichloromethyl)lithium in the normal manner and are potentially useful synthetic intermediates. The majority of known boronic esters are liquids, but the trityl group confers crystallinity on several examples. Six structures have been determined: 4,4,5,5-tetramethyl-2-[(triphenylmethoxy)methyl]-1,3,2-dioxaborolane (**3**), [*R*-(4α,5β)]-4,5-dicyclohexyl-2-[(triphenylmethoxy)methyl]-1,3,2-dioxaborolane (**4**), [*S*-(4α,5β)]-4,5-bis(1-methylethyl)-2-[(triphenylmethoxy)methyl]-1,3,2-dioxaborolane (**5**), (*R*)-pinanediol ((trityloxy)methyl)boronate (***ent*-6**), (*S*)-pinanediol (*S*)-(1-chloro-2-(trityloxy)ethyl)boronate (**7a**), and (*S*)-pinanediol (*S*)-(1-bromo-2-(trityloxy)ethyl)boronate (**7b**). The 1,3,2-dioxaborolane ring is very nearly planar, consistent with strong oxygen–boron π-bonding.

Introduction

The boronic ester function is known to facilitate nucleophilic displacement of halide at the adjacent carbon.[1] The nucleophile generally attacks the boron atom first to form a borate complex and then displaces the α-halide in an internal rearrangement, permitting the use of unusual nucleophiles such as Grignard reagents[2] or lithio(hexamethyldisilazane).[3]

Reported nucleophilic displacements by trityl oxide ion at carbon are confined to the reaction of its potassium salt with methyl iodide[4] or sulfate[5] to form trityl methyl ether or with benzyl bromide to form trityl benzyl ether.[5] With ethyl iodide, elimination to ethylene resulted.[4] There is also a report that (trityloxy)(ethyl)-zinc reacts with ethylene oxide at both the Zn–O and the Zn–C bonds.[6]

Though originally chosen for potential synthetic utility, several trityloxy-substituted boronic esters have provided crystals suitable for X-ray crystallography. Most known boronic esters are liquids. Crystal structures of simple boronic acids or esters appear to be confined to phenylboronic acid,[7] its mannitol ester,[8] and some of its six-membered cyclic esters.[9] Alkylboron-dioxy compounds are represented by a hybrid boroxin/borazine $(CH_3B)_3O_2NAr$[10] and a bis(ethylboryl) 2,3-dihydroxyfumarate.[11] In other structures, the boron atom is tetracoordinate, though the fourth bond may be relatively weak, as in the ethylene glycol ester of (1*R*)-1-acetamido-3-(methylthio)propylboronic acid.[12]

Results

In exploratory experiments, lithium trityl oxide was prepared in THF from butyllithium and trityl alcohol and treated with pinacol (chloromethyl)boronate,[13] (bromomethyl)boronate (**1**),[14] or (iodomethyl)boronate. Yields of pinacol ((trityloxy)methyl)boronate (**3**) varied, usually between 30% and 60% but occasionally 0% or 90%, with no perceptible relationship to any controlled experimental variables, including the presence or absence of DMSO (1 equiv), the radical initiator azobis(isobutyronitrile), the photosensitizer benzophenone, the use of DME in place of THF, or reaction temperatures between 0 °C and reflux.

Consistent high yields of pinacol ((trityloxy)methyl)-boronate (**3**) were obtained when sodium trityl oxide in DMSO, easily prepared from trityl alcohol and sodium hydride, was treated with pinacol (bromomethyl)boronate (**1**). The reaction is complete at room temperature overnight. Conventional aqueous workup yielded solid **3** with ~10% of unchanged trityl alcohol as the major

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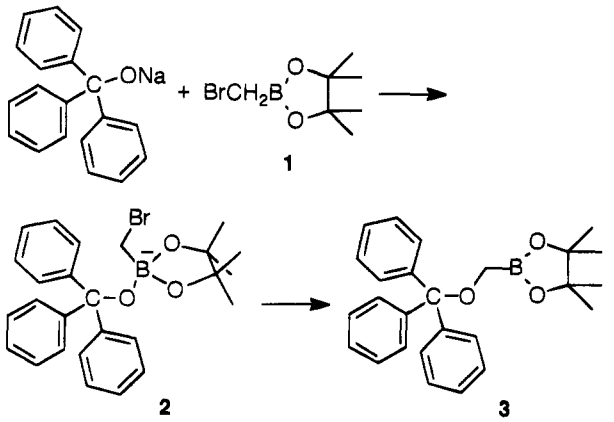
Table 1. Bond Distances in 1,3,2-Dioxaborolane Rings

compd	bond	distance (Å)	bond	distance (Å)	bond	distance (Å)
3	B(1)–C(1)	1.560(4)	B(1)–O(2)	1.316(4)	B(1)–O(3)	1.314(4)
	C(3)–O(2)	1.438(4)	C(2)–O(3)	1.426(4)	C(2)–C(3)	1.543(4)
3[a]	B(2)–C(33)	1.555(4)	B(2)–O(4)	1.318(4)	B(2)–O(5)	1.333(3)
	C(28)–O(4)	1.448(3)	C(27)–O(5)	1.441(4)	C(27)–C(28)	1.545(4)
4	B(1)–C(6)	1.552(9)	B(1)–O(2)	1.339(7)	B(1)–O(5)	1.383(6)
	C(3)–O(2)	1.478(7)	C(4)–O(5)	1.441(7)	C(3)–C(4)	1.539(7)
4[a]	B(51)–C(56)	1.581(10)	B(51)–O(52)	1.331(8)	B(51)–O(55)	1.353(9)
	C(53)–O(52)	1.429(7)	C(54)–O(55)	1.435(7)	C(53)–C(54)	1.553(8)
5	B(1)–C(6)	1.554(13)	B(1)–O(2)	1.356(11)	B(1)–O(5)	1.347(14)
	C(3)–O(2)	1.456(11)	C(4)–O(5)	1.433(9)	C(3)–C(4)	1.560(14)
ent-**6**	B(1)–C(6)	1.605(16)	B(1)–O(2)	1.346(14)	B(1)–O(5)	1.336(15)
	C(3)–O(2)	1.473(12)	C(4)–O(5)	1.444(12)	C(3)–C(4)	1.553(15)
7a	B(1)–C(6)	1.580(8)	B(1)–O(2)	1.362(7)	B(1)–O(5)	1.343(8)
	C(3)–O(2)	1.440(7)	C(4)–O(5)	1.478(6)	C(3)–C(4)	1.531(8)
7b	B(1)–C(6)	1.566(17)	B(1)–O(2)	1.372(15)	B(1)–O(5)	1.361(16)
	C(3)–O(2)	1.444(14)	C(4)–O(5)	1.454(13)	C(3)–C(4)	1.539(16)

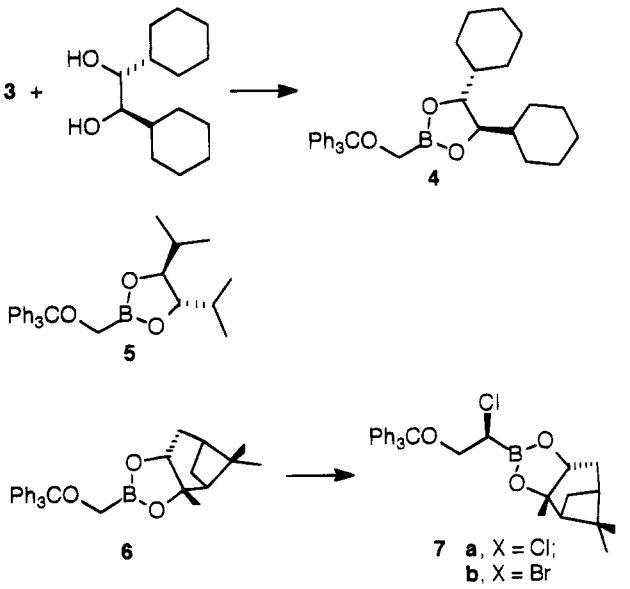
[a] At second site in unit cell.

impurity, and the relative solubilities of the two species were not promising for purification by recrystallization.



Separation of the product **3** from unchanged trityl alcohol could be accomplished by chromatography, but for preparative purposes a more efficient process was required. Basic hydrolysis of **3** was carried out in a two-phase (ether/water) system with the aid of pentaerythritol, which assists in solubilizing the sodium salt of the boronic acid in water[15] and leaves the trityl alcohol and pinacol in the ether. Regeneration of **3** was accomplished by acidification and treatment with pinacol in pentane, from which excess pinacol can be extracted with water.

Transesterification of **3** with the chiral diols (*R*,*R*)-1,2-dicyclohexylethanediol[16] or (*S*,*S*)-2,5-dimethyl-3,4-hexanediol[17] to form the boronic ester **4** or **5**, respectively, occurred readily in pentane at room temperature. The pinanediol ester[18] **6** was similarly prepared from **3** and (*S*)-pinanediol, or its enantiomer ***ent*-6** from (*R*)-pinanediol, and **6** was converted to the (1-chloro-2-(trityloxy)ethyl)boronic ester **7a** or the bromo analogue **7b** by treatment with (chloromethyl)lithium or (bromomethyl)lithium followed by zinc chloride according to previously reported methods.[19,20] The boronic esters **3**, **4**, **5**, **6** (or its enantiomer ***ent*-6**), **7a**, and **7b** all crystallized from pentane and yielded crystals suitable for X-ray analysis.



Boron–carbon and boron–oxygen bond distances in 1,3,2-dioxaborolane rings are summarized in Table 1. The average of the sixteen B–O bond distances found in the six crystal structures is 1.344 (±0.020) Å, and the average of the eight exocyclic B–C distances is 1.569 (±0.018) Å. The other C–O and C–C distances within the five-membered ring are also tabulated.

The 1,3,2-dioxaborolane rings of all six compounds **3**–**7a** are close to planar, and *syn* pairs of substituents are in an eclipsed conformation. Dihedral angles observed for the C–C–C–C linkages involving *trans* and *cis* 4,5-substituents are summarized in Table 2, which also includes recalculated data for the only previously studied C_2-symmetric 1,3,2-dioxaborolane in mannitol

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Table 2. Dihedral Angles at Positions 4 and 5 of 1,3,2-Dioxaborolane Rings

compd	diol moiety	atom set (~120°)	angle (deg)	atom set (~0°)	angle (deg)
3	pinacol	C(7)–C(3)–C(2)–C(4)	138.6	C(6)–C(3)–C(2)–C(4)	11.7
		C(6)–C(3)–C(2)–C(5)	116.5	C(7)–C(3)–C(2)–C(5)	10.4
				O(2)–C(3)–C(2)–O(3)	10.2
3	pinacol	C(32)–C(27)–C(28)–C(29)	120.0	C(29)–C(28)–C(27)–C(31)	6.8
		C(30)–C(28)–C(27)–C(31)	134.5	C(30)–C(28)–C(27)–C(32)	7.7
				O(4)–C(28)–C(27)–O(5)	6.9
4	DICHED[a]	C(11)–C(3)–C(4)–C(11′)	112.6	O(5)–C(4)–C(3)–O(2)	2.7
4	DICHED[a]	C(61′)–C(54)–C(53)–C(61)	120.1	O(55)–C(54)–C(53)–O(52)	6.5
5	DIPED[b]	C(12)–C(4)–C(3)–C(9)	131.3	O(5)–C(4)–C(3)–O(2)	7.9
***ent*-6**	pinanediol	C(10)–C(4)–C(3)–C(9)	131.3	C(10)–C(4)–C(3)–C(11)	0.9
				O(5)–C(4)–C(3)–O(2)	4.3
7a	pinanediol	C(11)–C(3)–C(4)–C(18)	127.9	C(14)–C(4)–C(3)–C(11)	4.9
				O(2)–C(3)–C(4)–O(5)	2.0
7b	pinanediol	C(11)–C(3)–C(4)–C(18)	127.9	C(14)–C(4)–C(3)–C(11)	2.8
				O(2)–C(3)–C(4)–O(5)	4.0
PhB[c]	mannitol	C(2)–C(3)–C(4)–C(5)	136.3	O(5)–C(3)–C(4)–O(6)	8.3

[a] 1,2-Dicyclohexyl-1,2-ethanediol. [b] 1,2-Diisopropyl-1,2-ethanediol (= 2,5-dimethyl-3,4-hexanediol). [c] Calculated for the central 1,3,2-dioxaborolane ring (C_2-symmetric) of mannitol tris(phenylboronate) from data in ref 8.

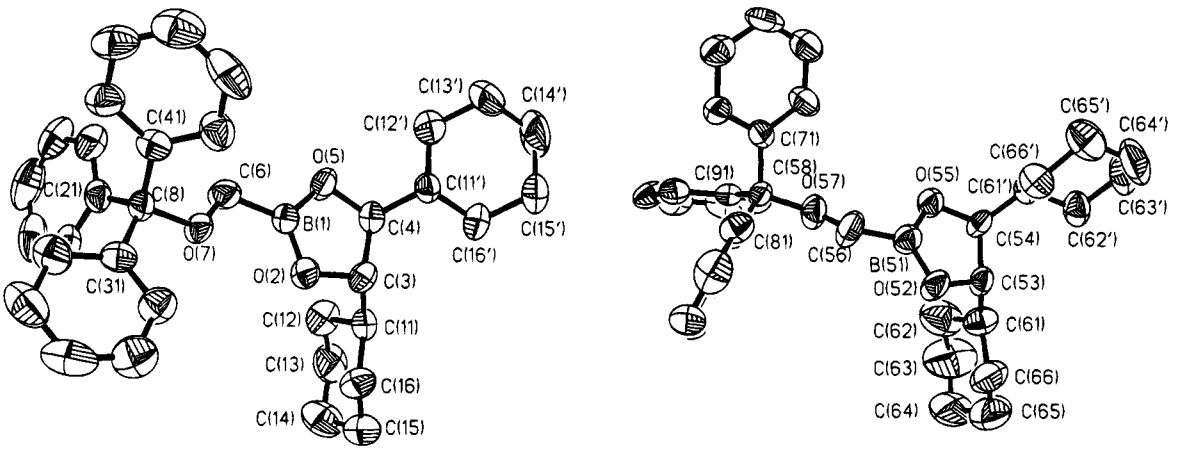

Figure 1. ORTEP drawings of the two crystallographically independent molecules in [*R*-(4α,5β)]-4,5-dicyclohexyl-2-[(triphenylmethoxy)methyl]-1,3,2-dioxaborolane (**4**) (H atoms omitted).

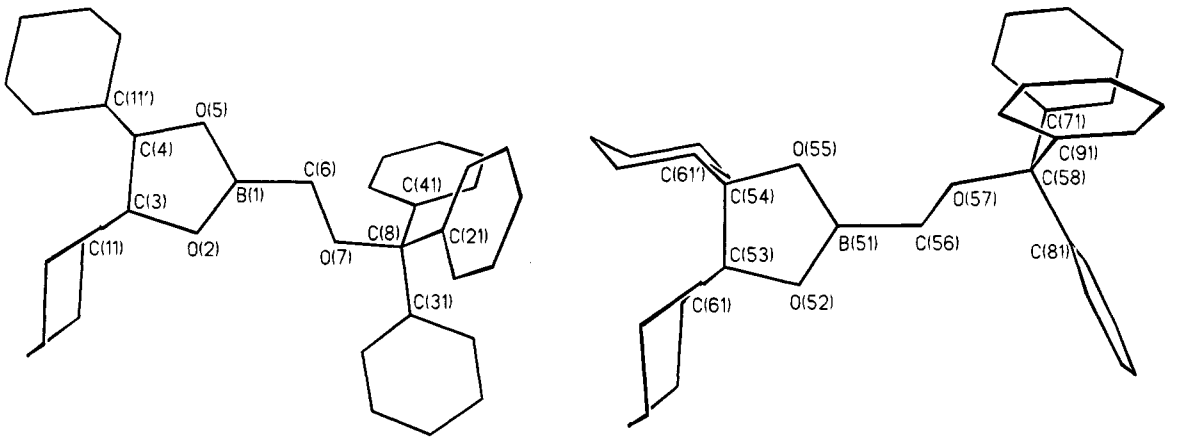

Figure 2. Line drawings of the two crystallographically independent molecules in [*R*-(4α,5β)]-4,5-dicyclohexyl-2-[(triphenylmethoxy)methyl]-1,3,2-dioxaborolane (**4**) (H atoms omitted).

tris(phenylboronate).[8] ORTEP drawings of **4** at the two different crystal lattice sites are shown in Figure 1, line drawings in Figure 2. The planarity of the rings is shown by the dihedral angles of the C–C–O–B and O–B–O–C linkages within the rings in Table 3.

The sums of the bond angles around the boron atoms of the 1,3,2-dioxaborolane rings are all very close to 360°, indicating that the boron atoms are strictly planar. Mannitol tris(phenylboronate) also has planar boron atoms.[8] Bond angles involving the dioxaborolane rings are summarized in Table 4.

Discussion

The trityl oxide anion is extremely sterically hindered and would not ordinarily be useful as a nucleophile in S_N2 reactions, as the scanty literature indicates.[4–6] Neighboring group assistance by the boronic ester function is presumably a major factor in the displacement of bromide from **1** by trityl oxide, and the formation of intermediates analogous to the postulated borate **2** has been supported strongly by previous evidence.[1,2] The critical step is rearrangement of **2** with loss of

Table 3. Dihedral Angles (B–O–C–C and O–B–O–C) in 1,3,2-Dioxaborolanes

compd	diol moiety	atom set	angle (deg)	atom set	angle (deg)
3	pinacol	C(2)–C(3)–O(2)–B(1)	7.8	O(2)–B(1)–O(3)–C(2)	5.5
		B(1)–O(3)–C(2)–C(3)	9.9	O(3)–B(1)–O(2)–C(3)	2.0
3	pinacol	C(27)–C(28)–O(4)–B(2)	7.0	O(5)–B(2)–O(4)–C(28)	4.3
		B(2)–O(5)–C(27)–C(28)	4.9	C(27)–O(5)–B(2)–O(4)	0.6
4	DICHED[a]	B(1)–O(2)–C(3)–C(4)	1.5	O(5)–B(1)–O(2)–C(3)	0.2
		C(3)–C(4)–O(5)–B(1)	2.9	O(2)–B(1)–O(5)–C(4)	2.1
4	DICHED[a]	B(51)–O(52)–C(53)–C(54)	4.7	C(53)–O(52)–B(51)–O(55)	1.1
		C(53)–C(54)–O(55)–B(51)	6.0	O(52)–B(51)–O(55)–C(54)	3.4
5	DIPED[a]	C(4)–C(3)–O(2)–B(1)	7.1	O(5)–B(1)–O(2)–C(3)	3.6
		B(1)–O(5)–C(4)–C(3)	6.3	C(4)–O(5)–B(1)–O(2)	2.0
***ent*-6**	pinanediol	C(3)–C(4)–O(5)–B(1)	4.9	O(5)–B(1)–O(2)–C(3)	0.9
		B(1)–O(2)–C(3)–C(4)	2.2	O(2)–B(1)–O(5)–C(4)	3.9
7a	pinanediol	C(3)–C(4)–O(5)–B(1)	0.6	O(5)–B(1)–O(2)–C(3)	4.6
		C(4)–C(3)–O(2)–B(1)	3.8	O(2)–B(1)–O(5)–C(4)	3.3
7b	pinanediol	B(1)–O(5)–C(4)–C(3)	0.2	O(5)–B(1)–O(2)–C(3)	6.9
		C(4)–C(3)–O(2)–B(1)	6.4	O(2)–B(1)–O(5)–C(4)	4.1
Mannitol tris(BPh)[b]		B(3)–O(6)–C(4)–C(3)	4.7	O(6)–B(3)–O(5)–C(3)	6.5
		C(4)–C(3)–O(5)–B(3)	8.9	O(5)–B(3)–O(6)–C(4)	0.8

[a] Defined in Table 2. [b] Calculated for central 1,3,2-dioxaborolane ring (C_2-symmetric) from data in ref 8.

Table 4. Bond Angles in 1,3,2-Dioxaborolane Rings

compd	atom set	angle (deg)	atom set	angle (deg)	atom set	angle (deg)
3	O(3)–B(1)–O(2)	111.9(3)	O(4)–B(2)–O(5)	113.0(2)	O(3)–C(2)–C(3)	103.5(2)
	O(3)–B(1)–C(1)	127.7(2)	O(4)–B(2)–C(33)	126.5(2)	C(2)–C(3)–O(2)	101.6(2)
	C(1)–B(1)–O(2)	120.4(3)	C(33)–B(2)–O(5)	120.5(3)	O(4)–C(28)–C(27)	103.5(2)
	B(1)–O(3)–C(2)	110.5(2)	B(2)–O(4)–C(28)	109.8(2)	C(28)–C(27)–O(5)	102.9(2)
	B(1)–O(2)–C(3)	111.3(3)	B(2)–O(5)–C(27)	110.2(2)		
4	O(5)–B(1)–O(2)	113.4(5)	O(52)–B(51)–O(55)	114.5(6)	O(2)–C(3)–C(4)	103.6(4)
	O(5)–B(1)–C(6)	119.7(5)	O(52)–B(51)–C(56)	123.4(6)	O(5)–C(4)–C(3)	105.6(4)
	O(2)–B(1)–C(6)	126.8(5)	O(55)–B(51)–C(56)	122.1(5)	O(52)–C(53)–C(54)	103.4(4)
	B(1)–O(2)–C(3)	109.0(4)	B(51)–O(52)–C(53)	109.4(5)	O(55)–C(54)–C(53)	104.8(5)
	B(1)–O(5)–C(4)	108.3(4)	B(51)–O(55)–C(54)	107.5(4)		
5	O(2)–B(1)–O(5)	113.1(8)	O(2)–B(1)–C(6)	123.1(10)	O(5)–B(1)–C(6)	123.8(8)
	B(1)–O(2)–C(3)	108.8(8)	B(1)–O(5)–C(4)	110.0(7)		
	O(2)–C(3)–C(4)	103.6(6)	O(5)–C(4)–C(3)	103.9(7)		
ent-6	O(2)–B(1)–O(5)	116.6(10)	O(2)–B(1)–C(6)	119.2(10)	O(5)–B(1)–C(6)	124.2(9)
	B(1)–O(2)–C(3)	106.8(8)	B(1)–O(5)–C(4)	107.6(8)		
	O(2)–C(3)–C(4)	103.7(8)	C(3)–C(4)–O(5)	105.1(8)		
7a	O(2)–B(1)–O(5)	114.5(5)	O(2)–B(1)–C(6)	122.0(6)	O(5)–B(1)–C(6)	123.5(5)
	B(1)–O(2)–C(3)	107.7(4)	B(1)–O(5)–C(4)	108.1(4)		
	O(5)–C(4)–C(3)	103.5(4)	O(2)–C(3)–C(4)	106.0(4)		
7b	O(2)–B(1)–O(5)	113.4(10)	O(2)–B(1)–C(6)	122.2(11)	O(5)–B(1)–C(6)	124.4(10)
	B(1)–O(2)–C(3)	108.4(9)	B(1)–O(5)–C(4)	107.9(8)		
	O(2)–C(3)–C(4)	104.5(8)	O(5)–C(4)–C(3)	105.2(8)		

bromide ion. Dipolar aprotic solvents in general[21] and DMSO in particular[22] often accelerate S_N2 reactions, though the effects depend strongly on relative polarities and solvations of starting materials and transition states and are not necessarily predictable in systems that lack clear precedents.

In the light of subsequent findings, it is conceivable that the irreproducible reactions observed during the exploratory phase of the work actually occurred during aqueous workup, which was always done before NMR spectra were taken.

Although previous literature has provided B–C and B–O bond distances for a scattered group of boronic esters and related compounds,[7–12] the present results are the first to correlate a series of simple boronic esters of the 1,3,2-dioxaborolane type. Compounds of this class have proved particularly useful in asymmetric synthesis,[1,13,16,23] and insight into their steric properties is therefore useful.

The near planarity of the 1,3,2-dioxaborolane ring places considerable eclipsing strain on the carbon atoms in the ring. MMX calculations with the PC Model program[24] using parameters that neglect oxygen–boron π-bonding suggest that the 4,5-carbon atoms would twist to a semistaggered conformation, and thus are an unsatisfactory model. Parameters that make the O–B–O group as rigid as an allyl anion yield approximately the right degree of flatness in the ring. All of the transition states of interest for asymmetric synthesis involve some degree of coordination of a Lewis base with the boron atom. When the boron atom is made tetracoordinate, even though the fourth ligand is weakly bound, the groups around the 4,5-carbon–carbon bond in the five-membered ring become semistaggered in a known structure,[12] and the modeling program is in reasonable agreement. Both the modeling program and organic chemist's experience agree in predicting that large *trans* substituents on the ring will adopt the pseudoequatorial conformation, but structure data to test this prediction are not yet available.

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(24) Available from Serena Software, Bloomington, IN. We thank Professor Mark Midland, University of California, Riverside, CA, for assistance in translating our X-ray data into suitable parameters for boron for this program.

Table 5. Crystal Structure Data

compd	3	4	5	6	7a	7b
empirical formula	$C_{26}H_{29}BO_3$	$C_{34}H_{41}BO_3$	$C_{28}H_{33}BO_3$	$C_{30}H_{33}BO_3$	$C_{31}H_{34}BClO_3$	$C_{31}H_{34}BBrO_3$
mol wt	400.3	509.0	428.4	452.4	500.8	543.3
cryst class	triclinic	monoclinic	trigonal	orthorhombic	orthorhombic	orthorhombic
space group	$P\bar{1}$	$P2_1$	$P3_2$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	10.173(2)	14.827(3)	9.450(2)	12.592(3)	10.074(2)	10.096(2)
b (Å)	10.518(2)	9.225(2)		13.912(3)	15.457(3)	15.473(3)
c (Å)	21.905(4)	22.465(4)	24.719(5)	14.843(3)	17.825(4)	17.961(4)
α (deg)	96.40(3)					
β (deg)	95.47(3)	107.74(3)				
γ (deg)	97.61(3)					
V (Å^3)	2294.2(8)	2926.6(10)	1911.7(7)	2600.2(10)	2775.6(10)	2805.8 (7)
Z	4	4	3	4	4	4
R^a	0.062	0.060	0.066	0.075	0.050	0.071
wR^b	0.127	0.080	0.070	0.047	0.056	0.085

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$.

Experimental Section

X-ray Data Analysis. X-ray data were collected on a Syntex $P2_1$ diffractometer upgraded to Siemens P4 specifications (**6**) or a Nicolet P3 diffractometer upgraded to Siemens P4 specifications (**3**–**5**,**7a**,**b**). Each diffractometer was equipped with a graphite monochromator for Mo Kα radiation (**6**) or Cu Kα radiation (**3**–**5**,**7a**,**b**). Data collections were based on the Siemens XSCANS software.[25] Structure solutions were obtained via the subroutine SOLV in the SHELXTL PLUS program package,[26] and all subsequent calculations were carried out with the routines in this package. Pertinent crystallographic data are given in Table 5, and full listings of collection and refinement parameters, as well as bond distances and angles, are available as supplementary material. Solution and refinement generally was straightforward. Absolute configurations were determined only for **7a** and **7b**. For the other chiral structures (**4**–**6**), the unit cells were chosen so as to give the chemically correct chirality.

In the case of **3** (space group $P\bar{1}$) and **4** (space group $P2_1$), the structures contained two crystallographically independent molecules. In **3**, the conformations of the two independent molecules are essentially identical. The only difference is a slight rotation of the triphenylmethoxy moiety. In **4**, on the other hand, the two independent molecules have distinctly different conformations, as seen in Figure 1. The cyclohexyl groups all assume a chair conformation, but the orientations of the cyclohexane rings with respect to the dioxaborolane rings are different. Similarly, the orientations of the three phenyl groups are nearly the same in each triphenylmethoxy group, but their orientation relative to the dioxaborolane rings are different. In fact, the orientations of the three phenyl groups are nearly identical in all of the compounds. For compounds **3**–**6**, the conformation of the triphenylmethoxy groups relative to the dioxaborolane rings are also essentially identical, except for the molecule containing B(51) in **4**.

4,4,5,5-Tetramethyl-2-[(triphenylmethoxy)methyl]-1,3,2-dioxaborolane (3). A solution of 0.40 mol of sodium trityl oxide was prepared by addition of sodium hydride (17.6 g, 0.44 mol) (60% dispersion in mineral oil) to trityl alcohol (*Chemical Abstracts* name: α,α-diphenylbenzenemethanol) (104.1 g, 0.40 mol) in dimethyl sulfoxide (800 mL) at room temperature overnight. To this mixture was added pinacol (bromomethyl)-boronate (**1**) (88.4 g, 0.40 mol) at 0 °C via cannula. The solution warmed to room temperature and was stirred for 18 h. The mixture was worked up by addition of saturated aqueous ammonium chloride (800 mL) and extracted with diethyl ether (2 × 500 mL). The ether layer was concentrated in a rotary evaporator until only a small amount of ether remained. Pentane was added (100 mL), and on evaporation of the pentane the mixture solidified. The solid was washed several times with distilled water to remove DMSO residue. The crude mixture contained ~10% unchanged trityl alcohol together with the major product, 4,4,5,5-tetramethyl-2-[(triphenylmethoxy)methyl]-1,3,2-dioxaborolane (155 g), which was redissolved in diethyl ether (1 L). The ether solution was treated with aqueous sodium hydroxide (1 M, 1.2 L) and pentaerythritol (136 g, 1 mol). After stirring at room temperature for 18 h, the organic layer was separated from the solution, and the aqueous phase was neutralized by hydrochloric acid (pH ~6) in an ice bath. After 10 min, the cloudy mixture was filtered and the solid was collected. A solution of the solid and pinacol (47.2 g, 400 mmol) in pentane (1 L) was stirred at room temperature for 2 h. The pentane solution was washed with water (3 × 1 L) and dried over magnesium sulfate. Concentration in a rotary evaporator gave pure 4,4,5,5-tetramethyl-2-[(triphenylmethoxy)methyl]-1,3,2-dioxaborolane (**3**) (136 g, 85%): mp 107–109 °C, 300-MHz ^{1}H-NMR ($CDCl_3$) δ 0.88–1.26 (s, 12H, CH_3), 2.86 (s, 2H, CH_2B), 7.18–7.48 (m, 15H, C_6H_5); 75-MHz ^{13}C-NMR ($CDCl_3$) δ 24.80, 83.61, 87.68, 126.71, 127.65, 128.85, 144.13; HRMS calcd for $C_{26}H_{29}BO_3$ (M+) 400.2210, found 400.2207.

[*R*-(4α,5β)]-4,5-Dicyclohexyl-2-[(triphenylmethoxy)methyl]-1,3,2-dioxaborolane (4). To a solution of pinacol [(triphenylmethoxy)methyl]boronate (**3**) (100 g, 250 mmol) in pentane (500 mL) was added (*R*,*R*)-1,2-dicyclohexyl-1,2-ethanediol (56.5 g, 250 mmol), and the mixture was stirred for 4 h at room temperature. The solution was washed with water (3 × 500 mL) to remove pinacol. Concentration in a rotary evaporator gave [*R*-(4α,5β)]-4,5-dicyclohexyl-2-[(triphenylmethoxy)methyl]-1,3,2-dioxaborolane (**4**) (121 g, 98%): mp 95–98 °C, 300-MHz ^{1}H-NMR ($CDCl_3$) δ 0.88–1.39 and 1.60–1.83 (m, 22, C_6H_{11}), 2.84 (AB, J = 15.7 Hz, 1, CH_2B), 2.94 (AB, J = 15.7 Hz, 1, CH_2B), 3.91–3.95 (m, 2, BOC*H*), 7.20–7.49 (m, 15, C_6H_5); 75-MHz ^{13}C-NMR ($CDCl_3$) δ 25.87, 26.01, 27.37, 28.37, 42.93, 83.75, 87.67, 126.74, 127.68, 128.85, 144.18; HRMS calcd for $C_{34}H_{41}O_3B$ (M+) 508.3149, found 508.3158. Anal. Calcd for $C_{34}H_{41}BO_3$: C, 80.31; H, 8.13; B, 2.13. Found: C, 80.48; H, 8.27; B, 2.09.

[*S*-(4α,5β)]-4,5-Bis(1-methylethyl)-2-[(triphenylmethoxy)methyl]-1,3,2-dioxaborolane (5). To a solution of 4,4,5,5-tetramethyl-2-[(triphenylmethoxy)methyl]-1,3,2-dioxaborolane (**3**) (40 g, 100 mmol) in pentanes (300 mL) was added (*S*,*S*)-2,5-dimethyl-3,4-hexanediol (14.6 g, 0.10 mol), and the mixture was stirred for 1 h (until the solid dissolved) at room temperature. The solution was washed with water (3 × 300 mL) to remove pinacol. Concentration in a rotary evaporator gave **5** (41.5 g, 97%): mp 48–50 °C, 200-MHz ^{1}H-NMR ($CDCl_3$) δ 0.95 (d, 12, CH_3), 1.7 (m, 1, CH_2B), 2.91 (AB, 2, CH_2B), 3.92 (m, 2, BOC*H*), 7.20–7.51 (m, 15, C_6H_5); HRMS calcd for $C_{28}H_{33}O_3B$ (M+) 428.2523, found 428.2481. Anal. Calcd for $C_{28}H_{33}O_3B$: C, 78.46; H, 7.77; B, 2.57. Found: C, 78.09; H, 7.62; B, 2.18.

(25) *Nicolet Crystallographic Systems Users Guide*, Release 81.3; Nicolet X-ray Instruments: Madison, WI, 1985.
(26) *SHELXTL PLUS*, Release 4.0; Siemens Analytical Instruments, Inc.: Madison, WI, 1990.

(*S*)-Pinanediol ((Trityloxymethyl)boronate (6).[27] A mixture of 4,4,5,5-tetramethyl-2-[(triphenylmethoxy)methyl]-1,3,2-dioxaborolane (**3**) (5.14 g, 12.85 mmol) and (*S*)-pinanediol (2.18 g, 12.85 mmol) in pentane (120 mL) was stirred at room temperature overnight. The solution was washed with water (3 × 100 mL) to remove pinacol. Concentration in a rotary evaporator gave **6** (5.37 g, 92.5%): mp 85–87 °C, 300-MHz ^{1}H-NMR ($CDCl_3$) δ 0.853 (s, 3, CH_3), 1.168 (d, 1, J = 10.8 Hz, pinyl CH), 1.294 (s, 3, CH_3), 1.399 (s, 3, CH_3), 1.50–2.45 (m, 5, pinyl CH), 2.9124 (s, 2, OCH_2B), 4.355 (dd, 1, J = 1.86 and 8.7 Hz, CHOB), 7.15–7.55 (m, 15 C_6H_5); 75-MHz ^{13}C-NMR ($CDCl_3$) δ 23.993, 26.438, 27.052, 28.541, 35.391, 38.107, 39.477, 51.218, 78.076, 86.111, 87.719, 126.75, 127.69, 128.86, 144.12. Anal. Calcd for $C_{30}H_{33}BO_3$: C, 79.65; H, 7.35; B, 2.39. Found: C, 79.24, 79.35; H, 7.17, 7.26; B, 2.30.

The enantiomer ***ent*-6** was similarly prepared from (*R*)-pinanediol and was used for the X-ray crystal structure determination.

(*S*)-Pinanediol (*S*)-(1-Chloro-2-(trityloxy)ethyl)boronate (7a).[27] To a solution of dichloromethane (2.28 mL, 35.37 mmol) in THF (15 mL) was added 1-butyllithium (10.57 mL, 1.45 M, 15.33 mmol) at −100 °C via cannula. The butyllithium solution was allowed to run down the cold wall of the reaction flask to be chilled before contacting the dichloromethane solution. After 5 min, a solution of (*S*)-pinanediol ((trityloxy)-methyl)boronate (**6**) (5.33 g, 11.7 mmol) was added to the solution via cannula. After 10 min, zinc chloride (2.89 g, 21.2 mmol), which was fused before use, was added to the solution. The solution warmed to room temperature and was kept for 18 h, and then it was worked up by treatment with aqueous ammonium chloride and pentane. The pentane solution was filtered through a column of anhydrous magnesium sulfate (10–15 g) and then concentrated to yield solid **7a** containing 0.9% unchanged **6**, recrystallized from 3:1 pentane/diethyl ether, 4.81 g (81%): mp 165–167 °C, 300-MHz ^{1}H-NMR ($CDCl_3$) δ 0.824 (s, 3, CH_3), 1.211 (d, 1, J = 10.8 Hz, pinyl CH), 1.270 (s, 1, CH_3), 1.382 (s, 3, CH_3), 1.8–2.4 (m, 5, pinyl CH), 3.470 (m, 2, OCH_2CHCl), 3.5823 (dd, 1, J = 4.92 and 6.39 Hz, OCH_2CHCl), 4.3599 (dd, 1, J = 1.95 and 8.79 Hz, CHOB), 7.15–7.55 (m, 15, C_6H_5); 75-MHz ^{13}C-NMR ($CDCl_3$) δ 23.942, 26.341, 26.989, 28.431, 35.104, 38.151, 39.275, 51.051, 65.559, 78.683, 86.584, 87.025, 126.97, 127.73, 128.73, 143.79. Anal. Calcd for $C_{31}H_{34}O_3BCl$: C, 74.34; H, 6.84. Found: C, 74.49; H, 6.73.

(*S*)-Pinanediol (*S*)-(1-Bromo-2-(trityloxy)ethyl)boronate (7b). A solution of (*S*)-pinanediol ((trityloxy)methyl)-boronate (**6**) (4.16 g, 9.20 mmol) and 1.94 mL (27.6 mmol) of dibromomethane in 25 mL of THF was stirred at −78 °C during the dropwise addition of LDA (6.0 mL, 2 M, 12.0 mmol). After 10 min, zinc chloride (3.88 g, 28.5 mmol), which was fused before use, was added to the solution. The solution warmed to room temperature and was kept for 18 h, then was worked up by treatment with saturated aqueous ammonium chloride and pentane. The pentane solution was filtered through a column of anhydrous magnesium sulfate (10–15 g), then concentrated to yield solid (*S*)-pinanediol (*S*)-(1-chloro-2-(trityloxy)ethyl)boronate (**7b**) containing 3% unchanged **6**, recrystallized from 3:1 pentane/diethyl ether, 3.51 g (70%): mp 176–177 °C, 300-MHz ^{1}H-NMR ($CDCl_3$) δ 0.829 (s, 3, CH_3), 1.25–1.28 (m, 4), 1.39 (s, 3, CH_3), 1.8–2.4 (m, 5, pinyl CH), 3.40 (dd, 1, OCH_2CHBr), 3.47–3.52, (m, 2, OCH_2CHBr), 4.35 (dd, 1, J = 1.95 and 8.79 Hz, CHOB), 7.2–7.5 (m, 15, C_6H_5); 75-MHz ^{13}C-NMR ($CDCl_3$) δ 23.95, 26.26, 26.99, 28.38, 35.15, 38.23, 39.27, 51.16, 64.96, 78.55, 86.73, 126.99, 127.75, 128.73, 143.83; HRMS calcd for $C_{31}H_{34}O_3BBr$ (M+) 544.1784, found 544.1771.

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Supplementary Material Available: Tables of data collection parameters, atomic coordinates and equivalent isotropic displacement coefficients, bond lengths, bond angles, anisotropic thermal parameters, and illustrations for compounds **3**–**6** and **7a**,**b** (85 pages). Ordering information is given on any current masthead page.

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(27) Systematic names: **6** is {3a*S*-[3aα,4β,6β,7aα]}-2-[(triphenylmethoxy)methyl]hexahydro-3a,5,5-trimethyl-4,6-methano-1,3,2-benzodioxaborole; **7a** is {3a*S*-[2(*R**),3aα,4β,6β,7aα]}-2-[1-chloro-2-(triphenylmethoxy)ethyl]hexahydro-3a,5,5-trimethyl-4,6-methano-1,3,2-benzodioxaborole.