# α-Trimethylsilyl Boronic Esters. Pinacol Lithio(trimethylsilyl)methaneboronate, Homologation of Boronic Esters with [Chloro(trimethylsilyl)methyl]lithium, and Comparisons with Some Phosphorus and Sulfur Analogues

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Pinacol (trimethylsilyl)methaneboronate has been prepared from (trimethylsilyl)methylmagnesium chloride and has been lithiated with lithium 2,2,6,6-tetramethylpiperidide. Pinacol lithio(trimethylsilyl)-methaneboronate with alkyl halides efficiently yields pinacol 1-(trimethylsilyl)alkane-1-boronates and with aldehydes or ketones eliminates silicon exclusively to form pinacol 1-alkene-1-boronates, with mostly *Z* isomers resulting from the aldehydes. The latter behavior contrasts with a boron-substituted Wittig reagent, [(1,3,2-dioxaborin-2-yl)methylene]phosphorane, which eliminates boron first and phosphorus second, converting benzophenone to tetraphenylallene and benzaldehyde to 1,3-diphenylallene. The lithio(trimethylsilyl)methaneboronate does eliminate boron first in its condensation with carboxylic esters, which yields (trimethylsilyl)methyl ketones. Attempted lithiation of α-trimethylsilyl boronic esters beyond the first member of the series failed. α-Trimethylsilyl boronic esters were also synthesized efficiently by homologation of boronic esters with [chloro(trimethylsilyl)methyl]lithium. Attempted analogous homologations with [halo(phenylthio)methyl]lithium were unsuccessful.

α-Trimethylsilyl boronic esters constitute a new class in the series of α-substituted boronic esters we have been investigating.[1-4] In view of the α lithiations of alkane-1,1-diboronic esters[3] and α-(phenylthio)alkaneboronic esters,[4] as well as the numerous reported α lithiations of silyl compounds,[5,6] we anticipated the lithiation of α-(trimethylsilyl)alkaneboronic esters. This hope has been realized only in the case of pinacol (trimethylsilyl)-methaneboronate (1), the lithio derivative **2** of which has shown useful reactivity toward alkyl halides, aldehydes, ketones, and esters. An alternative to the synthesis of α-(trimethylsilyl)alkaneboronic esters by reaction of **2** with alkyl halides is the homologation of boronic esters with [(trimethylsilyl)chloromethyl]lithium, the first homologation of boronic esters to be successfully developed. This has precedent in the analogous homologations of trialkylboranes.[7] However, equally precedented homologations with PhSCHXLi[8] have proved inapplicable to boronic esters.

Table I. Pinacol α-(Trimethylsilyl)alkaneboronates, $RCH(SiMe_3)BO_2C_2Me_4$ (3), from Alkylation of Pinacol Lithio(trimethylsilyl)methaneboronate (2) with Alkyl Halides (R-X)

| R of R-X and 3 | X | bp of 3, °C (torr) | % yield |
|---|---|---|---|
| $CH_3(CH_2)_3$ | I | 47-50 (0.05) | 74 |
| $CH_3(CH_2)_4$ | Br | 58-62 (0.05) | 85 |
| $CH_3(CH_2)_5$ | Br | 68-71 (0.05) | 79 |
| $C_6H_5CH_2$ | Br | 90-94 (0.15) | 83 |
| $C_6H_5CH_2CH_2$ | I | 96-101 (0.07) | 79 |
| $C_6H_5OCH_2CH_2$ | Br | 106-111 (0.07) | 81 |
| $CH_3C(O_2C_2H_4)(CH_2)_3$ | Cl | 104-108 (0.07) | 53 |

Table II. Pinacol Alkeneboronates, $RR'C{=}CHBO_2C_2Me_4$ (4), from Reaction of Pinacol Lithio(trimethylsilyl)methaneboronate (2) with Carbonyl Compounds (RCOR')

| R | R' | bp of 4, °C (torr) | % yield |
|---|---|---|---|
| $CH_3(CH_2)_5$ | H | 75-79 (0.15) | 73 |
| $CH_3(CH_2)_3$ | $CH_3(CH_2)_3$ | 72-76 (0.1) | 74 |
| $C_6H_5$ | H | 80-84 (0.2) | 84 |
| $C_6H_5$ | $C_6H_5$ | 135-139 (0.2) | 85 |
| $-(CH_2)_5-$ | | 58-62 (0.1) | 87 |

## Results

**Lithiated Pinacol (Trimethylsilyl)methaneboronate (2).** The Grignard reagent from (chloromethyl)trimethylsilane[9] reacted with trimethyl borate followed by aqueous workup to yield crude (trimethylsilyl)methaneboronic acid, which was esterified with pinacol to form pinacol (trimethylsilyl)methaneboronate (1) (systematic name 2-[(trimethylsilyl)methyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane).

(1) Preliminary communications: (a) Matteson, D. S.; Majumdar, D. *J. Chem. Soc., Chem. Commun.* **1980**, 39–40. (b) Matteson, D. S.; Majumdar, D. *J. Organomet. Chem.* **1980**, *184*, C41–C43.

(2) (a) Matteson, D. S.; Mah, R. W. H. *J. Am. Chem. Soc.* **1963**, *85*, 2599–2603. (b) Review: Matteson, D. S. *Acc. Chem. Res.* **1970**, *3*, 186–193. (c) Review: Matteson, D. S. *Synthesis* **1975**, 147–158. (d) Review: "Gmelins Handbuch der Anorganischen Chemie", 8th ed.; New Supplement Series; Niedenzu, K., Buschbeck, K.-C., Eds.; Springer-Verlag: Berlin, 1977; Vol. 48, Part 16, pp 37–72.

(3) (a) Matteson, D. S.; Moody, R. J. *Organometallics* **1982**, *1*, 20–28. (b) *J. Am. Chem. Soc.* **1977**, *99*, 3196–3197.

(4) (a) Matteson, D. S.; Arne, K. H. *Organometallics* **1982**, *1*, 280–288. (b) *J. Am. Chem. Soc.* **1978**, *100*, 1325–1326.

(5) Burford, C.; Cooke, F.; Ehlinger, E.; Magnus, P. *J. Am. Chem. Soc.* **1977**, *99*, 4536–4537.

(6) Some examples: (a) Carey, F. A.; Court, A. S. *J. Org. Chem.* **1972**, *37*, 939–943, 1926–1929. (b) Jones, P. F.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1972**, 526. (c) Seebach, D.; Gröbel, B.-T.; Beek, A. K.; Braun, M.; Geiss, K.-H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 443–444. (d) Seebach, D.; Kolb, M.; Gröbel, B.-T. *Tetrahedron Lett.* **1974**, 3171–3174. (e) Gröbel, B.-T.; Bürstinghaus, R.; Seebach, D. *Synthesis* **1976**, 121–123. (f) Taguchi, H.; Shimoji, K.; Yamamoto, H.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2529–2531. (g) Sachdev, K.; Sachdev, H. S. *Tetrahedron Lett.* **1976**, 4223–4226. (h) Reich, H. J.; Shah, S. K. *J. Org. Chem.* **1977**, *42*, 1773–1776. (i) Ayalon-Chass, D.; Ehlinger, E.; Magnus, P. *J. Chem. Soc., Chem. Commun.* **1977**, 772–773. (j) Cooke, F.; Magnus, P. *Ibid.* **1977**, 513.

(7) (a) Rosario, O.; Oliva, A.; Larson, G. L. *J. Organomet. Chem.* **1978**, *146*, C8–C10. (b) Larson, G. L.; Arguelles, R.; Rosario, O.; Sandoval, S. *Ibid.* **1980**, *198*, 15–23.

(8) (a) Yamamoto, S.; Shiono, M.; Mukaiyama, T. *Chem. Lett.* **1973**, 961–962. (b) Hughes, R. J.; Pelter, A.; Smith, K. *J. Chem. Soc., Chem. Commun.* **1974**, 863. (c) Mendoza, A.; Matteson, D. S. *J. Organomet. Chem.* **1978**, *156*, 149–157.

(9) (a) Whitmore, F. C.; Sommer, L. H. *J. Am. Chem. Soc.* **1946**, *68*, 481–484. (b) Peterson, D. *J. Org. Chem.* **1968**, *33*, 780–784.

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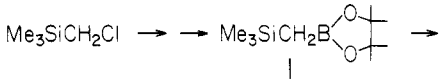
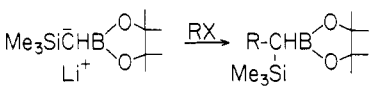
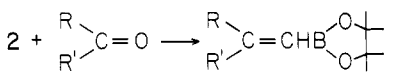
Lithiation of 1 was accomplished under conditions similar to those reported for lithiation of bis(propanediol) methanediborate,[3] with lithium tetramethylpiperidide (LiTMP) as base, tetramethylethylenediamine (TMEDA) as activator, and tetrahydrofuran (THF) as solvent. Treatment of the resulting solution of pinacol lithio(trimethylsilyl)methaneboronate (2) with various alkyl halides gave good yields of the corresponding pinacol 1-(trimethylsilyl)alkane-1-boronates (3), summarized in Table I. In exploratory experiments, the use of lithium diisopropylamide (LDA) in place of LiTMP lowered the yields of 3 by 10–15%. No test of the necessity of the TMEDA was made.

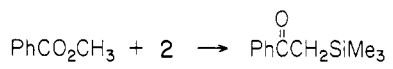




Reaction of pinacol lithio(trimethylsilyl)methaneboronate (2) with aldehydes or ketones yielded pinacol alkeneboronates 4 as summarized in Table II. The distilled products 4 showed no trimethylsilyl peaks near δ 0 in the proton NMR spectra, indicating that silicon is eliminated exclusively, presumably as the volatile bis(trimethylsilyl) ether. From the characteristic vinylic proton patterns in the NMR spectra, which had been well established previously,[10] it was found that the alkeneboronates 4 derived from aldehydes consisted of a mixture of about 70% *Z* and 30% *E* isomers.

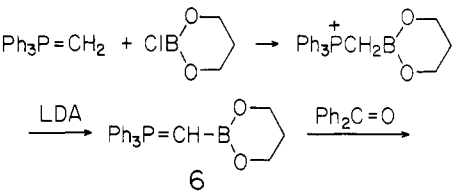


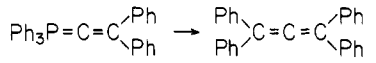
In contrast to the exclusive elimination of silicon in the reactions with aldehydes and ketones, reaction of 2 with methyl benzoate resulted in boron elimination as the major pathway, yielding α-(trimethylsilyl)acetophenone (5). Similar results were obtained with methyl cyclohexanecarboxylate, which yielded mostly (trimethylsilyl)methyl cyclohexyl ketone. However, the presence of bis(pinacol) diborate, $Me_4C_2O_2BOBO_2C_2Me_4$, interfered with the purification of these (trimethylsilyl)methyl ketones by distillation.



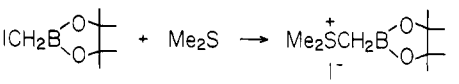
Several attempts were made to deprotonate α-(trimethylsilyl)alkaneboronic esters other than 1, all of them totally unsuccessful. For example, treatment of pinacol 1-(trimethylsilyl)hexane-1-boronate with LiTMP and TMEDA at various temperatures, followed by addition of 1-bromopentane, led only to recovery of unchanged starting boronic ester. Similarly negative results were obtained with 1,3-propanediol cyclohexyl(trimethylsilyl)methaneboronate. 1,3-Propanediol (trimethylsilyl)methaneboronate was prepared and tested as an alternative to 1 but was recovered unchanged when subjected to conditions that led to lithiation and alkylation of 1.

**A Boron-Substituted Wittig Reagent.** The chemistry of the lithio(trimethylsilyl)methaneboronic ester 2 just described has much in common with that of Wittig reagents. We have also prepared a boron-substituted Wittig reagent (6) by treatment of methylenetriphenylphosphorane with 1,3-propanediol–boron chloride followed by LDA. Reaction in situ with benzophenone gave tetraphenylallene, or with benzaldehyde gave 1,3-diphenylallene, in 40–60% yields. Heptanal with 6 failed to yield any allenic product.

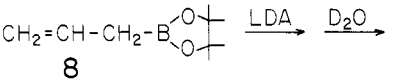


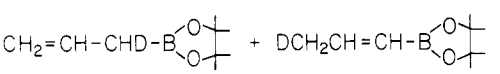


**Other Attempted Lithiations.** A sulfonium-substituted boronic ester, dimethyl[(4,4,5,5-tetramethyl-1,3,2-dioxaborol-2-yl)methyl]sulfonium iodide (7), was prepared. An attempt to lithiate 7 and condense it with benzaldehyde failed to yield any unsaturated product, and it appeared that the acidic and less hindered *S*-methyl groups were attacked preferentially.



Pinacol allylboronate 8 was readily lithiated by LiTMP and TMEDA, as shown by proton NMR analysis of the recovered 8 and its 1-propeneboronate isomer after treatment with $D_2O$, which attacked mainly the α-position. Methyl iodide also appeared to attack lithiated 8 mainly at the α-position, but butyl iodide and trimethylsilyl chloride attacked mainly at the γ-position. Gross mixtures were obtained in all cases, and it did not appear that lithiated 8 could function as a useful synthetic reagent.





**Homologation of Boronic Esters.** Reactions of alkyl halides with boron-substituted carbanions work well only if the alkyl group is primary. In order to make α-substituted boronic esters that were inaccessible by the alkylation route, we undertook a search for homologations of boronic esters analogous to the well-known homologations of trialkylboranes. For example, trialkylboranes, $R_3B$, are homologated by [bis(phenylthio)methyl]lithium, $(PhS)_2CHLi$, to form α-phenylthio boranes $R_2BCH(SPh)R$.[8] However, numerous attempts to homologate boronic esters, $RB(OR')_2$, with PhSCHXLi, where X was SPh, $SMe_2^+$, $NMe_3^+$, or Cl, all failed. 1,2-Bis(phenylthio)ethene, PhSCH=CHSPh, was the characteristic byproduct, in addition to unchanged $RB(OR')_2$. Two typical examples of the many attempts are described in the Experimental Section. Mediocre successes have been reported elsewhere when the postulated tetracoordinate borate intermediate was assembled in reverse order, starting with $PhSCHXB(OR')_2$ and RMgX or RLi.[4a,11] In the best of these, X was Br and R was Ph, but the reaction

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

(11) Mendoza, A.; Matteson, D. S. *J. Org. Chem.* **1979**, *44*, 1352–1354.

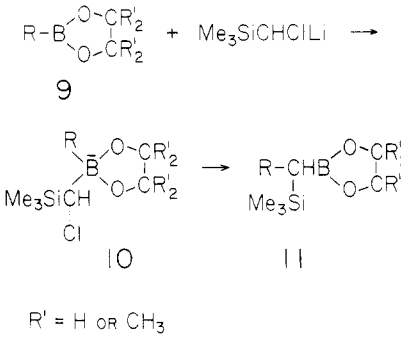
Table III. Homologation of Cyclic Boronic Esters, $RBO_2(CR'_2)_2$ (9), with [Chloro(trimethylsilyl)methyl]lithium, $Me_3SiCHClLi$, To Form α-Trimethylsilyl Boronic Esters, $RCH(SiMe_3)BO_2(CR'_2)_2$ (11)

| R | R' | bp of 11, °C (torr) | % yield |
|---|---|---|---|
| 1-butyl | H | 80-84 (4) | 86 |
| 1-butyl | $CH_3$ | 48-51 (0.07) | 80 |
| 2-butyl | H | 86-90 (5) | 85 |
| 1-octyl | H | 80-85 (0.15) | 83 |
| allyl | $CH_3$ | 90-94 (4) | 78 |
| 1-propenyl[a] | $CH_3$ | 86-90 (3.5) | 74 |
| cyclopentyl | H | 96-99 (4) | 80 |
| cyclohexyl | H | 72-75 (1) | 81 |
| phenyl | H, $CH_3$[b] | 85-89 (0.1) | 76 |
| benzyl | H | 80-85 (0.1) | 77 |
| $C_6H_5SCH_2$ | H | 108-110 (0.05) | 80 |

[a] *Z,E* mixture. [b] The ethylene glycol ester was homologated, and the product was transesterified with pinacol to yield 11, R = Ph, R' = $CH_3$.

failed when R was *n*-butyl,[4a] even though simpler α-halo boronic esters have long been known to undergo replacement of halide by alkyl on treatment with Grignard reagents.[2a]

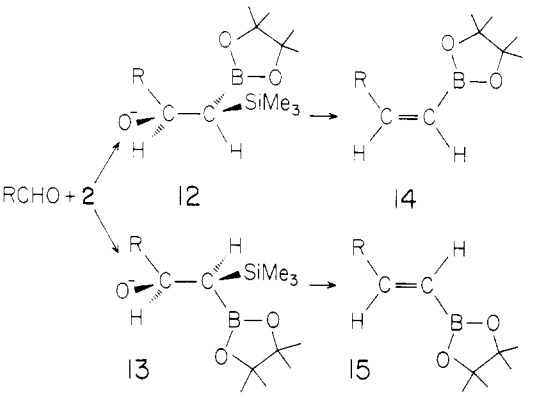
In sharp contrast to all of the difficulties with the sulfur-substituted series, [chloro(trimethylsilyl)methyl]lithium[5,12] was found to homologate cyclic boronic esters **9** very efficiently to the corresponding α-trimethylsilyl boronic esters **11**, presumably by way of the usual type of tetracoordinate borate intermediate **10**. Results are summarized in Table III.



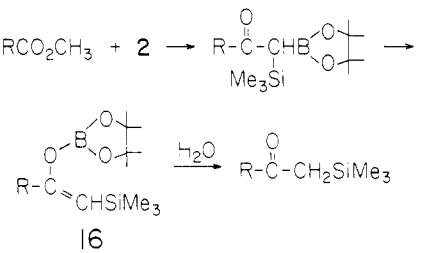

## Discussion

**Silicon Elimination.** We had not expected the elimination of silicon in preference to boron in the reactions of pinacol lithio(trimethylsilyl)methaneboronate (**2**) with aldehydes and ketones. Usually, boron–carbon bonds are more easily cleaved than silicon–carbon bonds, perhaps because boron coordinates more easily with bases that typically catalyze such cleavages. Our experience with Wittig-like boronic ester reagents indicated them to be much more efficient in condensations with ketones than the corresponding trimethylsilyl reagents,[11] though the efficiency of the boron reagents may lie in lesser steric hindrance to the initial carbon–carbon bond formation or in lower basicity toward enolizable ketones and may have nothing to do with the subsequent elimination step.

The predominance of the *Z* isomer **14** in the mixture of 1-alkene-1-boronic esters formed from **2** and aldehydes was also unanticipated and may be contrasted with the high predominance of the *E* isomer **15** from reactions of aldehydes with lithiomethanediboronic esters.[3,10] However, in the latter case, the choice between the two boron atoms is not made until the elimination step itself, and the result is reasonable on steric grounds. In contrast, the initial attack of the silyl reagent **2** on the aldehyde to form the postulated intermediates **12** and **13** probably fixes the ultimate geometry of the products **14** and **15**. Since deprotonation of β-hydroxy silanes normally results in stereospecific syn elimination,[13] that pathway is illustrated. However, the preference for formation of intermediate **12** over **13** is not readily explained.




The preferential elimination of boron in the reaction of **2** with carboxylic esters was what we expected and is postulated to proceed by way of boron enolate **16**. α-Silyl ketones isomerize readily to silyl enolates only on heating above 100 °C,[14] and in view of our previous failure to observe any evidence for stability of postulated α-boryl ketone intermediates,[3] it appears likely that the 1,3 shift of boron from the α-carbon to the carbonyl oxygen is many orders of magnitude faster than the analogous shift of silicon. The vacant and acidic p orbital of the boron atom makes this 1,3 shift Woodward–Hoffmann allowed, but the much less acidic d orbital of the silicon leaves the 1,3 shift with partially forbidden character, though it is intramolecular, as shown by the retention of configuration at silicon.[14]




**Boron Elimination in Preference to Phosphorus.** The formation of tetraphenylallene or 1,3-diphenylallene from the boron substituted Wittig reagent **6** and benzophenone or benzaldehyde, respectively, provides clear evidence that boron is eliminated in preference to phosphorus. If the phosphorus were eliminated first, the product would be an alkeneboronic ester. An attempt to deprotonate an alkeneboronic ester has failed,[3a] and even the deboronation of alkene-1,1-diboronic esters, which should be easier than deprotonation, appears not to occur.[15]

(12) We thank Professor George Rubottom of the University of Idaho for a timely reminder of the availability of this reagent.

(13) Hudrlik, P. F.; Peterson, D. *J. Am. Chem. Soc.* **1975**, *97*, 1464–1468.

(14) Brook, A. G.; MacRae, D. M.; Limburg, W. W. *J. Am. Chem. Soc.* **1967**, *89*, 5493–5495.

(15) Moody, R. J.; Matteson, D. S. *J. Organomet. Chem.* **1978**, *152*, 265–270. When first observed, the replacement of a boronic ester group by alkyl was thought to involve a boron-substituted vinylic carbanion, but subsequent investigation conclusively ruled out such a mechanism. Negative evidence lost in the refereeing process included the fact that the supposed anion could not be trapped by butyl iodide: Moody, R. J., Ph.D. Thesis, WSU, 1977.

Initial boron elimination, on the other hand, would yield a phosphonium salt which could be deprotonated to a vinylidenephosphorane that would lead to the allene.

In view of the apparent limitation of this synthesis to symmetrical arylallenes, no further work has been undertaken.

**Homologation of Boronic Esters.** The failure of attempted homologations of boronic esters with PhSCHXLi and the formation of 1,2-bis(phenylthio)ethene instead suggests that the boron of boronic esters, in sharp contrast to that of trialkylboranes, is not acidic enough to bind the stabilized anions of the class $PhSCHX^-$ irreversibly. Loss of $X^-$ leaves the relatively stable carbene PhSCH, which could dimerize if it accumulated in high enough concentration, but which can probably faster attack the more abundant $PhSCHX^-$ or even its boronic ester complex directly to form the "carbene dimer".

In contrast to the sulfur-substituted carbanions, [chloro(trimethylsilyl)methyl]lithium is a very strong base and probably cannot dissociate from the boronic ester once it is bound. Silylcarbenes are generated only with difficulty[16] and would be unlikely to form directly or indirectly. Thus, the only reaction pathway available to the postulated [chloro(trimethylsilyl)methyl]borate intermediate **10** is the observed rearrangement to α-trimethylsilyl boronic ester **11**, a reaction type which has ample precedent.[2]

We have reported the efficient analogous homologation of boronic esters with (dichloromethyl)lithium elsewhere.[17,18]

**Synthetic Potential.** Pinacol (trimethylsilyl)methaneboronate (**1**) is easier to make than diboronic esters[3] or triboronic esters,[2c,d] alternative reagents suitable for conversion of carbonyl compounds to the homologous alkene-1-boronic esters. One rather prosaic use of alkene-1-boronic esters is as precursors to aldehydes,[19] though the pinacol esters produced in the present work require longer oxidation times than the ethylene glycol esters described previously, and the direct use of [chloro(trimethylsilyl)methyl]lithium to accomplish the same net homologation[5] would normally be chosen, with a few possible exceptions.[19] The alkeneboronic esters are ultimately of more interest for their potential utility as starting materials for chiral synthesis.[18] The predominantly *Z* geometry of the alkene-1-boronic esters derived from **2** and aldehydes is of particular interest in that regard. The possibility of increasing the *Z*/*E* ratio by varying the relative bulk of the silyl and boronic ester groups remains to be explored.

α-Silylated boranes produced by homologation of trialkylboranes are readily oxidized to α-hydroxy silanes by hydrogen peroxide,[7] and α-trimethylsilyl boronic esters are expected to behave similarly, as has been demonstrated for one example.[20]

Our failure to deprotonate α-(trimethylsilyl)alkaneboronic esters other than the silylmethaneboronic ester **1** is a considerable limitation on the synthetic utility of these compounds. The much greater flexibility of α-chloro boronic esters as synthetic intermediates has turned our major efforts in that direction. However, some additional useful properties of trimethylsilyl boronic esters are explored in the following paper.[20]

Our brief investigation of the synthesis of (trimethylsilyl)methyl ketones is insufficient to define how useful this route might become. Published routes to the two examples we made lack convenience or efficiency,[21,22] and with the assumption that the purification problems we encountered could be overcome with modest effort (careful redistillation or chromatography), our route offers considerable advantage.

## Experimental Section

**General Data.** Reactions involving carbanions were carried out under argon. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl. Amines were distilled from calcium hydride and stored over molecular sieves. Butyllithium was titrated against 2-propanol to the 1,10-phenanthroline endpoint. (Chloromethyl)trimethylsilane was purchased from Petrarch, Inc. Proton NMR spectra were taken at 60 MHz with a Varian EM-360 intrument and are referred to the trimethylsilyl group of trimethylsilyl compounds or to internal tetramethylsilane for other compounds. (The trimethylsilyl peak was verified to be at δ 0.0 compared to internal tetramethylsilane in three cases: pinacol α-(trimethylsilyl)benzylboronate, ethylene glycol cyclohexyl(trimethylsilyl)methaneboronate, and ethylene glycol cyclopentyl(trimethylsilyl)methaneboronate.) Elemental analyses were by Galbraith Laboratories, Knoxville, TN.

**Pinacol (Trimethylsilyl)methaneboronate (1).** The Grignard reagent was prepared from (chloromethyl)trimethylsilane in ether on a 0.1-mol scale as described in the literature.[9] The Grignard solution was transferred under argon to an addition funnel, and 13 mL of trimethyl borate in 25 mL of ether was placed in a separate addition funnel, both attached to a flask equipped with a mechanical Teflon paddle stirrer and containing 50 mL of ether. The flask was cooled in a −78 °C bath, and the contents were stirred vigorously during the simultaneous dropwise addition of the Grignard and trimethyl borate solutions.[23] The mixture was stirred 2–3 h at −78 °C and allowed to warm to 25 °C overnight and then treated with 100 mL of ice-cold 2 M hydrochloric acid. The product was extracted with 3 × 100 mL of 5:1 ether/dichloromethane, the solution was concentrated, and the solid residue was recrystallized from water to yield 65–75% (trimethylsilyl)methaneboronic acid, which was not characterized but treated with an equivalent amount of pinacol hydrate in hexane overnight. Separation and distillation yielded the pinacol ester **1**: bp 70–72 °C (12 torr); 60-MHz NMR ($CCl_4$) δ 0.0 (s, 11, $CH_2SiCH_3$), 1.25 (s, 12, $CCH_3$). Anal. Calcd for $C_{10}H_{23}BO_2Si$: C, 56.08; H, 10.82; B, 5.05; Si, 13.11. Found: C, 55.83; H, 10.87; B, 4.91; Si, 13.30.

**Pinacol Lithio(trimethylsilyl)methaneboronate (2) Solutions.** Lithium tetramethylpiperidide was made from 10 mmol of 2,2,6,6-tetramethylpiperidine in 15 mL of THF by addition of 10 mmol of 2 M butyllithium in hexane with stirring at 0 °C. A solution of 10 mmol (2.14 g) of pinacol (trimethylsilyl)methaneboronate (**1**) in 10 mL of THF was added by syringe, followed by addition of 10 mmol of 1,2-bis(dimethylamino)ethane (TMEDA). The solution was stirred 2–3 h at 0 °C before use.

**Reaction of Pinacol Lithio(trimethylsilyl)methaneboronate (2) Solutions with Alkyl Halides.** A 10-mmol sample of the alkyl halide was added by syringe to the solution of **2** described in the preceding paragraph, and the mixture was allowed to warm to 25 °C overnight. A 50-mL sample of 5:1 ether/dichloromethane was added, and the solution was washed with saturated sodium chloride and dried over magnesium sulfate. Distillation yielded the corresponding pinacol α-trimethylsilyl boronates **3**. Yields and boiling points are summarized in Table I and proton NMR and analytical data in Table IV.

**Reaction of Pinacol Lithio(trimethylsilyl)methaneboronate (2) Solutions with Aldehydes and Ketones.** The solution of **2** prepared as described above was cooled to −78 °C, and the aldehyde or ketone (10 mmol) was added by syringe. The

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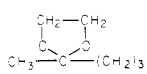
Table IV. 60-MHz Proton NMR Spectra ($CCl_4$) and Elemental Analyses for Pinacol α-Trimethylsilyl Boronates, $RCH(SiMe_3)BO_2C_2Me_4$ (3)

| R | NMR,[a] δ | | calcd (found) | | | |
|---|---|---|---|---|---|---|
| | SiCHB | R | C | H | B | Si |
| $CH_3(CH_2)_3$ [b,c] | 0.33 | 0.9-1.3 | 62.21 (61.33[d]) | 11.56 (11.74) | 4.00 (3.81) | 10.39 (10.48) |
| $CH_3(CH_2)_4$ [b] | 0.33 | 0.9-1.3 | 63.37 (63.20) | 11.70 (11.59) | 3.80 (3.62) | 9.88 ((10.04) |
| $CH_3(CH_2)_5$ [b] | 0.33 | 0.9-1.3 | 64.41 (64.21) | 11.82 (11.66) | 3.62 (3.61) | 9.41 (9.42) |
| $C_6H_5$ [e] | 1.90 | 7.2 | 66.20 (65.96) | 9.38 (9.51) | 3.72 (3.72) | 9.68 (9.88) |
| $C_6H_5CH_2$ [b] | 0.73 | 2.69 (d), 7.23 | 67.10 (66.71) | 9.61 (9.74) | 3.55 (3.39) | 9.23 (9.21) |
| $C_6H_5CH_2CH_2$ [b] | 0.33 | 1.66, 2.59, 7.23 | 67.91 (68.10) | 9.82 (9.83) | 3.40 (3.19) | 8.82 (8.99) |
| $C_6H_5OCH_2CH_2$ [b] | 0.33 | 1.83, 3.83, 6.8-7.2 | 64.66 (64.47) | 9.35 (9.48) | 3.23 (3.06) | 8.40 (8.65) |
|  [b] | 0.33 | 1.5, 3.89 (s) | 59.64 (59.55) | 10.30 (10.12) | 3.16 (3.01) | 8.20 (8.50) |
| $CH_2=CHCH_2$ [c] | 0.33 | 2.16, 5.03-5.82 | 61.41 (61.23) | 10.70 (10.89) | 4.25 (4.05) | 11.05 (11.30) |
| $CH_3CH=CH$ [c] | 1.50 | 1.66, 5.43 | 61.41 (61.22) | 10.70 (10.65) | 4.25 (4.02) | 11.05 (11.24) |

[a] All spectra showed a singlet assigned the value δ 0.00 [$(CH_3)_3Si$] and a singlet near δ 1.2 (range of 1.13-1.23) [$(CH_3)_2C$]. The SiCHB peak was characteristically broad, with fine structure partially resolved. Appropriate splittings and satisfactory integrals were observed. [b] Compound prepared by alkylation of **2**. [c] Prepared by homologation of $RBO_2C_2Me_4$ (**9**). [d] Through oversight, no attempt was made to correct this single errant analysis. [e] Prepared by homologation of $PhBO_2C_2H_4$ and transesterification with pinacol.

Table V. 60-MHz Proton NMR Spectra ($CCl_4$) and Elemental Analyses for Pinacol Alkene-1-boronates, $RR'C=CHBO_2C_2Me_4$ (4)

| R | R′ | NMR ($CCl_4$),[a] δ | | | calcd (found) | | |
|---|---|---|---|---|---|---|---|
| | | R | R′ | =CHB | C | H | B |
| $CH_3(CH_2)_5$ | H [b] | 0.9-1.4, 2.3 | 6.53 | 5.35[c] | 70.60 (70.76) | 11.43 (11.67) | 4.54 (4.38) |
| $CH_3(CH_2)_3$ | $CH_3(CH_2)_3$ | 0.9-1.4, 2.3 | | 5.10 | 72.18 (72.20) | 11.74 (11.80) | 4.06 (3.92) |
| $C_6H_5$ | H [b] | 7.2-7.7 | (7.5) | 5.56[d] | 73.07 (72.91) | 8.32 (8.51) | 4.70 (4.46) |
| $C_6H_5$ | $C_6H_5$ | 7.4 | 7.4 | 6.03 | 78.45 (78.30) | 7.57 (7.64) | 3.53 (3.29) |
| $-(CH_2)_5-$ | | 1.63, 2.4 | | 5.03 | 71.81 (72.01) | 9.90 (9.75) | 4.62 (4.48) |

[a] Pinacol $CCH_3$ characteristically at δ 1.23, range of 1.13-1.26. Multiplicities and integrals of all peaks are consistent with assigned structures. [b] About two-thirds *Z* isomer. [c] For *Z* isomer, $J$ = 13 Hz. *E* isomer, δ 5.40 ($J$ = 20 Hz). [d] *Z* isomer, $J$ = 14 Hz. *E* isomer, δ 6.13 ($J$ = 18 Hz). The *E* isomer has been characterized previously.[3,8]

mixture was stirred 2–3 h at −78 °C and allowed to warm to 25 °C overnight. Treatment with 50 mL of cold 2 M hydrochloric acid, extraction with 5:1 ether/dichloromethane, washing with saturated sodium chloride, drying over magnesium sulfate, and distillation yielded the alkeneboronic esters **4**. Yields and boiling points are summarized in Table II and 60-MHz proton NMR spectra and analytical data in Table V.

**α-(Trimethylsilyl)acetophenone (5).** A solution of **2** (10 mmol) at −78 °C was treated with 10 mmol of methyl benzoate, stirred 3 h at −78 °C, and allowed to warm to 25 ° overnight. A 50-mL sample of 10% potassium dihydrogen phosphate solution was added to 0 °C. After extraction with 5:1 ether/dichloromethane, washing with saturated sodium chloride, and drying over magnesium sulfate, the product **5** was distilled: bp 52–58 °C (0.25 torr) [lit.[21] bp 104 °C (3 torr)]; 1.1 g, 49% corrected for the presence of 14% bis(pinacol) diborate as indicated by the NMR peak at δ 1.2; NMR ($CCl_4$) δ 0.0 (s, 9, $SiCH_3$), 2.82 (s, 2, $SiCH_2CO$), 7.6–8.0 (m, 5, $C_6H_5$).

**Cyclohexyl (Trimethylsilyl)methyl Ketone.** The procedure described for the preparation of **5** in the preceding paragraph was followed, substituting methyl cyclohexanecarboxylate for methyl benzoate. Cyclohexyl (trimethylsilyl)methyl ketone, bp 59–63 °C (0.25 torr), containing 10% bis(pinacol) diborate by NMR analysis was obtained in 67% contained yield: NMR ($CCl_4$) δ 0.0 (s, 9, $SiCH_3$), 1.50 (m, 10, $CH_2$), 2.00 (m, 1, CHCO), 2.06 (s, 2, $SiCH_2CO$) (Lit.[22] δ 2.02 ($SiCH_2CO$)).

**1,3-Propanediol (Trimethylsilyl)methaneboronate.** (Trimethylsilyl)methaneboronic acid and 1,3-propanediol in hexane were refluxed with a Dean–Stark trap to remove the water, and the product was distilled: bp 63–65 °C (45 torr); NMR ($CCl_4$) δ 0.0 (s, 11, $CH_2SiCH_3$), 1.93 (m, 2, $CH_2$), 4.03 (t, 4, $CH_2O$).

**Attempted Deprotonation of Other α-Trimethylsilyl Boronic Esters.** The deprotonation procedure successfully used to convert **1** to **2** was tested with 1,3-propanediol (trimethylsilyl)methaneboronate, 1,3-propanediol (trimethylsilyl)cyclohexylmethaneboronate, and pinacol 1-(trimethylsilyl)hexane-1-boronate, followed by addition of 1-iodobutane or 1-bromopentane. In all three cases, 80–85% of the unchanged starting boronic ester was recovered. The attempted deprotonations were all repeated at 25 °C, again with no evidence of reaction. Lithium diethylamide or diisopropylamide failed to deprotonate pinacol 1-(trimethylsilyl)hexane-1-boronate, and *sec*-butyllithium or *tert*-butyllithium led to 50% loss of the boronic ester but no evidence of alkylation.

**Boronic Esters 9.** Boronic acids were prepared by a variant of the standard procedure,[23] as described in some detail for **1**. Esterification with pinacol was carried out as in the preparation of **1**. Esterification with ethylene glycol was accomplished by distilling the water azeotrope from a hexane solution and collecting the water in a Dean–Stark trap. Residual ethylene glycol was removed by treatment with anhydrous calcium chloride. The products **9** were distilled under reduced pressure. Several have been reported previously: **ethylene glycol 1-butaneboronate**, bp 60–62 °C (5 torr) (lit.[24] bp 122–122.5 °C); **pinacol 1-butaneboronate**;[11] **ethylene glycol phenylboronate**, bp 85–89 °C (5 torr) (lit.[24] bp 218–220 °C); **ethylene glycol benzylboronate**, bp 55 °C (0.1 torr) [lit.[25] bp 60 °C (0.1 torr)]; **ethylene glycol (phenylthio)methaneboronate**;[4] **1,3-propanediol cyclohexaneboronate**, bp 85–90 °C (5 torr) [lit.[26] bp 93–94 °C (6 torr)]; **ethylene glycol cyclohexaneboronate**, bp 73–76 °C (5 torr) (lit.[27] lacks experimental details). Anal. Calcd for $C_8H_{15}BO_2$: C, 62.39; H, 9.82; B, 7.02. Found: C, 62.44; H, 9.75; B, 7.24. The others were not found in the literature. **Pinacol allylboronate** was distilled from a little galvinoxyl to prevent polymerization encountered otherwise: bp 50–53 °C (5 torr); NMR ($CCl_4$) δ 1.26

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Table VI. 60 MHz Proton NMR Spectra ($CCl_4$) and Elemental Analyses for Ethylene Glycol α-Trimethylsilyl Boronates, $RCH(SiMe_3)BO_2C_2H_4$ (11, R = H)

| R | NMR,[a] δ | | calcd (found) | | | |
|---|---|---|---|---|---|---|
| | SiCHB | R | C | H | B | Si |
| 1-butyl | 0.35 | 1.06, 1.33 | 56.08 (56.32) | 10.82 (10.97) | 5.05 (4.93) | 13.11 (13.27) |
| 2-butyl | 0.4 | 1.0, 1.33 | 56.08 (55.85) | 10.82 (10.52) | 5.05 (4.90) | 13.11 (13.00) |
| 1-octyl | 0.35 | 1.06, 1.33 | 62.21 (62.39) | 11.56 (11.65) | 4.00 (3.74) | 10.39 (10.11) |
| cyclopentyl | 0.5 | 1.66 | 58.41 (58.18) | 10.25 (10.16) | 4.78 (4.50) | 12.42 (12.49) |
| cyclohexyl | 0.3 | 1.5 | 60.00 (59.70) | 10.49 (10.32) | 4.50 (4.32) | 11.69 (11.90) |
| benzyl | 0.73 | 2.69, 7.23 | 62.91 (63.04) | 8.53 (8.73) | 4.36 (4.12) | 11.32 (11.04) |
| $C_6H_5SCH_2$- | 0.83 | 2.82, 7.30 | 55.71 (55.54) | 7.55 (7.54) | 3.86 (3.65) | 10.02 (9.81) |

[a] All spectra showed a singlet assigned the value δ 0.00 [$(CH_3)_3Si$] and a singlet near δ 4.2 (range of 4.06–4.26). The SiCHB peaks were broad. Appropriate splittings and satisfactory integrals were observed.

(s, 12, $CCH_3$), 1.73 (d, 2, $CH_2B$), 5.06–5.93 (m, 3, $CH{=}CH_2$). Anal. Calcd for $C_9H_{17}BO_2$: C, 64.33; H, 10.20; B, 6.43. Found: C, 64.09; H, 10.45; B, 6.22. **Pinacol 1-propene-1-boronate** was made by transesterification of the known butyl ester[28] with pinacol: bp 46–47 °C (4 torr); NMR ($CDCl_3$) shows splittings similar to those previously described for the *E* and *Z* boronic acids and ethylene glycol esters,[10] *E*/*Z* ratio about 2, δ 1.28 ($CCH_3$), 1.85 (*E* $CHCH_3$), 1.97 (*Z* $CHCH_3$), 5.4 (*Z* BCH=), 5.5 (*E* BCH=), 6.6 (=$CHCH_3$). Anal. Calcd: see preceding isomer. Found: C, 64.51; H, 9.91; B, 6.57. **Ethylene glycol 2-butaneboronate**: bp 38 °C (10–12 torr); NMR ($CCl_4$) δ 1.03 (m, 6, $CH_3$), 1.50 (m, 3, $CHCH_2$), 4.29 (s, 4, $OCH_2$). Anal. Calcd for $C_6H_{13}BO_2$: C, 56.31; H, 10.24; B, 8.45. Found: C, 56.15; H, 10.21; B, 8.47. **Ethylene glycol cyclopentaneboronate**: bp 57–58 °C (5 torr); NMR ($CCl_4$) δ 1.93 (m, 11, $CH(CH_2)_4$), 4.26 (s, 4, $OCH_2$). Anal. Calcd for $C_7H_{13}BO_2$: C, 60.06; H, 9.36; B, 7.72. Found: C, 60.28; H, 9.57; B, 7.68. **Ethylene glycol 1-octaneboronate**: bp 68–72 °C (0.8 torr); NMR ($CCl_4$) δ 0.89 (t, 3, $CH_3$), 1.29 (m, 14, $CH_2$), 4.23 (s, 4, $OCH_2$). Anal. Calcd for $C_{10}H_{21}BO_2$: C, 65.25; H, 11.50; B, 5.87. Found: C, 65.58; H, 11.61; B, 5.90.

**Homologation of Boronic Esters 9 to α-Trimethylsilyl Boronic Esters 11.** A solution of 2.25 g (18.4 mmol) of (chloromethyl)trimethylsilane in 24 mL of THF was stirred at −78 °C during the dropwise addition of 20.3 mmol of *sec*-butyllithium by syringe. A 20-mmol sample of 1,2-bis(dimethylamino)ethane (TMEDA) was added, and the mixture was stirred 45 min at −78 °C and then allowed to warm to −55 °C.[5] A solution of 14 mmol of the boronic ester **9** in 5 mL of tetrahydrofuran was added by syringe, and the mixture was stirred 10 min at −55 °C (except that when ethylene glycol (phenylthio)methaneboronate was used, better results were obtained when the mixture was cooled to −78 °C immediately after addition of the boronic ester). The mixture was cooled to −78 °C immediately after addition of the boronic ester. The mixture was cooled to −78 °C, and the cooling bath was allowed to warm slowly to 25 °C overnight. A 50-mL sample of ice-cold 2 M hydrochloric acid was added, and the product was extracted with 3 × 60 mL of 5:1 ether/dichloromethane. The organic phase was concentrated under reduced pressure. Ethylene glycol esters were treated with 14 mmol of ethylene glycol and 200 mL of hexane or benzene and refluxed with a Dean–Stark trap to remove water. (Partial hydrolysis of these esters during aqueous workup was observed. Pinacol esters proved stable to water and needed no analogous treatment). Excess ethylene glycol was removed by drying over calcium chloride. The solution was concentrated, and the product (**11**) was distilled under vacuum. Yields and boiling points are summarized in Table III and 60-MHz proton NMR spectra and elemental analyses in Table IV for pinacol esters and in Table VI for ethylene glycol esters. In addition to the tabulated compounds, **1,3-propanediol (trimethylsilyl)cyclohexylmethaneboronate** was similarly prepared, bp 80–85 °C (0.25 torr); 82%; NMR consistent with assigned structure, analysis not obtained.

**[(1,3,2-Dioxaborin-2-yl)methylene]phosphorane 6 in the Synthesis of Arylallenes.** A suspension of 1.57 g (5 mmol) of methyltriphenylphosphonium bromide in 25 mL of THF was treated with 5 mmol of butyllithium at 25 °C, stirred 30 min, and cooled to −78 °C. A solution of 2-chloro-1,3,2-dioxaborinane[29] in 5 mL of THF was added in one portion, yielding an immediate precipitate. After being stirred 10 min at −78 °C and warmed to 0 °C, the mixture was treated with 5 mmol of lithium diisopropylamide in 10 mL of THF and stirred 1 h at 0 °C to form **6**. Either 10 mmol of benzophenone or benzaldehyde in 5 mL of THF was added, and the mixture was stirred 30 min at 0 °C and then refluxed 4–5 h. A 50-mL of cold 10 M phosphoric acid was added, and the product was extracted with 2 × 50 mL of 5:1 ether/dichloromethane. The solution was concentrated, and the product was isolated by chromatography on a silica gel plate with hexane. Tetraphenylallene was recrystallized from ethanol: 0.82 g (47%); mp 162–164 °C (lit.[30] mp 164–165 °C). 1,3-Diphenylallene was obtained in 48% yield: mp 48–50 °C (lit.[31] mp 49–51 °C and 53.5–55.5 °C); NMR ($CDCl_3$) δ 6.53 (s, 1, CH=), 7.5 (m, 5, $C_6H_5$).

**Deprotonation of Pinacol Allylboronate.** Pinacol allylboronate (5 mmol) was added to lithium tetramethylpiperidide (5 mmol) stirred in 10 mL of THF at −78 °C. TMEDA (5 mmol) was added and the mixture was stirred 2 h at −78° C, warmed to −45 °C and stirred 10 min, and then cooled to −78 °C. Excess deuterium oxide was added, and the solution was allowed to warm to room temperature and worked up with aqueous acid in the usual manner. The product recovered had essentially the same 60-MHz proton NMR spectrum as pinacol allylboronate, except that the integral of the doublet at δ 1.73 (CDHB) was diminished to 1 H, and small impurity bands attributed to the isomeric 1-propene-1-boronic ester were present. Mixtures resulted from treatment with chlorotrimethylsilane, 1-iodobutane, or iodomethane in place of deuterium oxide. From the NMR spectra, it appeared that γ attack predominated with the first two of these electrophiles and α attack with the third.

**[(4,4,5,5-Tetramethyl-1,3,2-dioxaborol-2-yl)methyl]dimethylsulfonium Iodide (7).** A solution of 1.34 g (5 mmol) of pinacol iodomethaneboronate in 8 mL of dichloromethane was added to 0.37 mL (5 mmol) of dimethyl sulfide in 5 mL of dichloromethane at 0 °C and kept 2 h at 0 °C. Addition of 50 mL of cold ether precipitated the product (**7**), which was collected and washed with ether and dried under vacuum: 1.65 g (94%); mp 180–183 °C; NMR ($CDCl_3$) δ 1.33 (s, 12, $CCH_3$), 2.17 (s, 2, $SCH_2B$), 3.50 (s, 6, $S(CH_3)_2$). Anal. Calcd for $C_9H_{20}BIO_2S$: C, 32.75; H, 6.11; B, 3.28; I, 38.45; S, 9.72. Found: C, 32.58; H, 5.98; B, 3.19; I,38.66; S, 9.52. Treatment of **7** with an equivalent amount of lithium diisopropylamide in ether at 0 °C followed by benzaldehyde overnight at 25 °C, then dissolving the product in water, and precipitating with sodium hexafluorophosphate yielded a solid. This material showed no evidence of vinylic protons near δ 6 in the NMR.

**Attempted Homologation of Dibutyl 1-Butaneboronate with [Bis(phenylthio)methyl]lithium.** Bis(phenylthio)methane was lithiated with butyllithium in THF at 0 °C, cooled to −78 °C, and treated with an equivalent amount of dibutyl 1-butaneboronate. After warming to room temperature and the usual aqueous workup, distillation yielded unchanged dibutyl butaneboronate and bis(phenylthio)methane. Repetition with

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addition of mercuric chloride, lead(II) chloride, cuprous iodide, or methyl fluorosulfonate after the boronic ester yielded the same result.

**Attempted Homologation of Ethylene Glycol Benzeneboronate with (Dimethylsulfonium)(phenylthio)methylide.** Addition of 5 mmol of butyllithium to a suspension of [(phenylthio)methyl]dimethylsulfonium bromide in 40 mL of ether at −40 °C and stirring 2 h at −40 °C yielded a clear solution, to which 5 mmol of ethylene glycol phenylboronate was added. A white precipitate resulted immediately. After another hour at −40 °C and overnight at up to 25 °C, the solution was concentrated and distilled. The proton NMR spectrum indicated that the product was a mixture of ethylene glycol benzeneboronate (characteristic phenyl multiplet, clearly not a phenyl-C compound) and 1,2-bis(phenylthio)ethene.

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**Registry No.** **1**, 74213-42-6; **2**, 83947-62-0; **3** (R = $CH_3(CH_2)_3$), 83947-46-0; **3** (R = $CH_3(CH_2)_4$), 74213-44-8; **3** (R = $CH_3(CH_2)_5$), 83947-47-1; **3** (R = $C_6H_5CH_2$), 74213-45-9; **3** (R = $C_6H_5CH_2CH_2$), 74213-46-0; **3** (R = $C_6H_5OCH_2CH_2$), 83947-48-2; **3** (R = $CH_3C(O_2C_2H_4)(CH_2)_3$), 83947-49-3; **3** (R = $CH_2{=}CHCH_2$), 72823-99-5; (*E*)-**3** (R = $CH_3CH{=}CH$), 83947-51-7; (*Z*)-**3** (R = $CH_3CH{=}CH$), 83947-53-9; **3** (R = $C_6H_5$), 83947-57-3; (*Z*)-**4** (R = $CH_3(CH_2)_5$, R′ = H), 74213-47-1; (*E*)-**4** (R = $CH_3(CH_2)_5$, R′ = H), 83947-55-1; **4** (R = R′ = $CH_3(CH_2)_3$), 74213-50-6; (*Z*)-**4** (R = $C_6H_5$, R′ = H), 74213-48-2; (*E*)-**4** (R = $C_6H_5$, R′ = H), 83947-56-2; **4** (R = R′ = $C_6H_5$), 83947-50-6; **4** (R = R′ = $(CH_2)_5$), 74213-49-3; **5**, 13735-78-9; **6**, 83947-64-2; **7**, 83947-65-3; **9** (R = 1-butyl, R′ = H), 10173-39-4; **9** (R = 1-butyl, R′ = $CH_3$), 69190-62-1; **9** (R = 2-butyl, R′ = H), 72824-01-2; **9** (R = 1-octyl, R′ = H), 83947-60-8; **9** (R = allyl, R′ = $CH_3$), 72824-04-5; (*E*)-**9** (R = 1-propenyl, R′ = $CH_3$), 83947-58-4; (*Z*)-**9** (R = 1-propenyl, R′ = $CH_3$), 83947-59-5; **9** (R = cyclopentyl, R′ = H), 72824-02-3; **9** (R = cyclohexyl, R′ = H), 66217-60-5; **9** (R = phenyl, R′ = H), 4406-72-8; **9** (R = benzyl, R′ = H), 35895-82-0; **9** (R = $C_6H_5SCH_2$, R′ = H), 72824-03-4; **11** (R = 1-butyl, R′ = H), 72823-93-9; **11** (R = 2-butyl, R′ = H), 72823-94-0; **11** (R = 1-octyl, R′ = H), 83947-52-8; **11** (R = cyclopentyl, R′ = H), 72823-95-1; **11** (R = cyclohexyl, R′ = H), 72823-96-2; **11** (R = phenyl, R′ = H), 83947-54-0; **11** (R = benzyl, R′ = H), 72823-97-3; **11** (R = $C_6H_5SCH_2$, R′ = H), 72823-98-4; cyclohexyl (trimethylsilyl)methyl ketone, 55629-29-3; 1,3-propanediol (trimethylsilyl)methaneboronate, 83947-63-1; 1,3-propanediol cyclohexaneboranate, 30169-75-6; 1,3-propanediol (trimethylsilyl)cyclohexylmethaneboronate, 83947-61-9; tetraphenylallene, 1674-18-6; 1,3-diphenylallene, 19753-98-1; pinacol iodomethaneboronate, 70557-99-2.

# Pinanediol [α-(Trimethylsilyl)allyl]boronate and Related Boronic Esters

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Homologation of (+)-pinanediol phenylboronate with [chloro(trimethylsilyl)methyl]lithium yielded (α*S*)- and (α*R*)-[α-(trimethylsilyl)benzyl]boronic esters in a 73:27 ratio, as shown by peroxidic deboronation to the known α-(trimethylsilyl)benzyl alcohol. Similar homologations of pinanediol vinyl, (*Z*)-1-propenyl, and isobutyl boronates were carried out, but the diastereoisomeric ratios were not determined. Reaction of the allylic α-trimethylsilyl boronic esters with aldehydes was studied. Pinanediol or pinacol 3-(trimethylsilyl)-1-propene-3-boronates yielded mainly (*Z*)-1-(trimethylsilyl)-1-alken-4-ols with aldehydes. Pinanediol (*Z*)-1-(trimethylsilyl)-2-butene-1-boronate with benzaldehyde yielded (*E*)-1-(trimethylsilyl)-3-methyl-4-phenylbut-1-en-4-ol with only 4% *Z* isomer. The stereochemical implications and utility of these reactions in synthesis are discussed. A brief investigation indicated that pinanediol α-trimethylsilyl boronic esters can be desilylated to boronic esters by tetrabutylammonium fluoride in moist THF.

The homologation of boronic esters with [chloro(trimethylsilyl)methyl]lithium,[1] the directed chiral synthesis by way of homologation of pinanediol boronic esters with (dichloromethyl)lithium,[2] and the utility of allylic boronic esters[3,4] and boranes[5] in stereocontrolled synthesis suggested the possible synthetic utility of pinanediol α-trimethylsilyl boronic esters. We report here a highly stereoselective assembly of four adjacent carbon atoms (two chiral, two olefinic) in the reaction of pinanediol (*Z*)-[α-(trimethylsilyl)crotyl]boronate with benzaldehyde. The synthetic applicability of this reaction is deferred by the low diastereoselectivity (73:27) observed in the homologation of a pinanediol bromide ester with [chloro(trimethylsilyl)methyl]lithium. An apparently general and potentially useful reaction of α-trimethylsilyl boronic esters is the mild and efficient protodesilylation in the presence of fluoride ion, which provides the final step in the first efficient route from boronic esters, $RB(OR')_2$, to their simple homologues, $RCH_2B(OR')_2$.

## Results

**Homologations.** The reaction with [chloro(trimethylsilyl)methyl]lithium[1] has proved readily applicable to the conversion of (+)-pinanediol boronic esters **1** to the homologous diastereoisomeric (+)-pinanediol boronic esters **2** and **3**. One unsatisfactory result was encountered.

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