(*E*)-**3c**, 86766-13-4; (*Z*)-**3d**, 82491-43-8; (*E*)-**3d**, 82491-44-9; (*Z*)-**3e**, 86766-14-5; (*E*)-**3e**, 86766-15-6; (*Z*)-**3f**, 86766-16-7; (*E*)-**3f**, 86766-17-8; (*Z*)-**3g**, 86766-18-9; (*E*)-**3g**, 86766-19-0; **3h**, 78485-09-3; **3i**, 82491-45-0; (*Z*)-**3j**, 82491-47-2; (*E*)-**3j**, 82491-48-3; **3k**, 86766-20-3; **3l**, 82491-46-1; **4a**, 86766-21-4; **4j**, 86766-22-5; **5a**, 86832-53-3; **5j**, 86832-54-4; **6a**, 86832-55-5; **6j**, 86832-56-6; **7a**, 86832-57-7; **7j**, 86832-58-8; **18**, 93-56-1; **19a**, 6397-70-2; *threo*-**20a**, 86766-23-6; *erythro*-**20a**, 86766-24-7; *erythro*-**20b**, 86766-25-8; *threo*-**20b**, 86766-26-9; **21**, 42052-51-7; $TiCl_4$, 7550-45-0; $FeSO_4$, 7720-78-7; LAH, 16853-85-3; LAD, 14128-54-2; 1-phenylethanol-*1,2-d*$_2$, 86766-27-0; 1-phenylpropanol-*1-d*, 32047-42-0; 1-phenylethanol-2-*d*, 84599-50-8; benzyl alcohol-α-*d*, 4546-45-6; methylmagnesium bromide, 75-16-1; 1-octyne, 629-05-0; phenylacetylene, 536-74-3; benzenemethanol, 100-51-6; 1-phenylethanol, 98-85-1; 1-phenylpropanol, 93-54-9; benzaldehyde, 100-52-7; acetophenone, 98-86-2; propiophenone, 93-55-0; butyrophenone, 495-40-9; benzaldehyde-α-*d*, 3592-47-0; acetophenone-α-*d*, 60507-03-1.

Organoboranes. 32. Homologation of Alkylboronic Esters with Methoxy(phenylthio)methyllithium: Regio- and Stereocontrolled Aldehyde Synthesis from Olefins via Hydroboration

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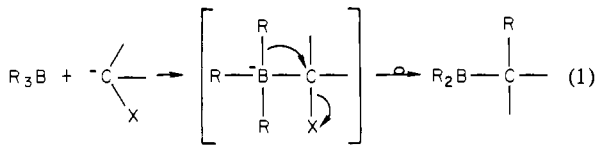
Contribution from the Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907. *Received March 25, 1983*

Abstract: Homologation of 2-alkyl-1,3,2-dioxaborinanes, $RBO_2C_3H_6$ (**1**), to α-methoxyalkyl derivatives, $RCH(OMe)BO_2C_3H_6$ (**2**), was achieved by reaction with LiCH(OMe)SPh, followed by treatment with $HgCl_2$. The intermediates **2** were smoothly oxidized with hydrogen peroxide in a pH 8 phosphate buffer to give the corresponding aldehydes, RCHO (**3**). The alkyl groups of **1** were introduced by the hydroboration method. Thus, heptanal, 3-phenylbutanal, 2-ethylpentanal, cyclohexanecarbaldehyde, *trans*-2-methylcyclopentanecarbaldehyde, and *exo*-norbornanecarbaldehyde were prepared in fair to good yields from 1-hexene, 2-phenylpropene, 3-hexene, cyclohexene, 1-methylcyclopentene, and norbornene, respectively. Furthermore, both *threo*- and *erythro*-2,3-dimethylpentanal were obtained in 96% diastereomeric purity from (*E*)- and (*Z*)-3-methyl-2-pentene, respectively. The migration of the alkyl group from boron to carbon proceeds with retention of configuration. Thus, by taking every advantage of the hydroboration reaction, this sequence provides a new method for introducing the formyl group into olefins in a regio- and stereocontrolled manner.

The carbenoid-induced 1,2-migration of organic groups from boron to carbon (eq 1) is one of the most convenient and promising



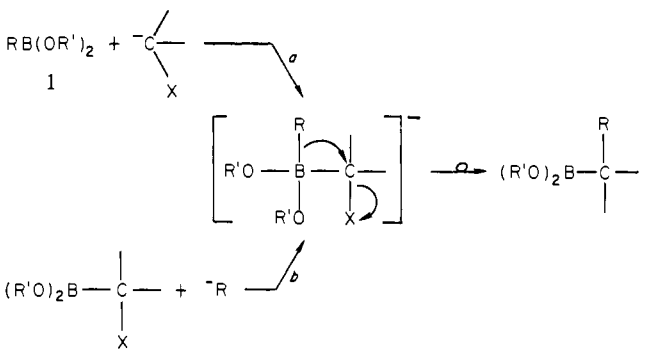
(1)

C–C bond-forming reactions via organoboranes, R_3B.[1] A large number of carbenoid reagents have been successfully applied for such transformations. In many of these reactions, only one of the three R groups are utilized.

In some cases the use of 9-organyl-9-borabicyclo[3.3.1]nonanes circumvents this difficulty.[2] However, in other cases, these derivatives are not effective.[3] Accordingly, there would be major advantages in developing synthetic reactions that could utilize boronic esters **1** with their single organic group as the boron component (approach *a* in Scheme I).

In fact, in the boron-assisted substitution reaction (approach *b*)[4] and some other related reactions,[5] alkoxy has been effectively

Scheme I



used as a nonmigrating "blocking" group. We are particularly interested in approach *a* since in this way those organic groups that are readily formed by the hydroboration reaction can be further incorporated into organic molecules.

Intermediates **1** are now readily available by hydroboration of alkenes with dihaloboranes, followed by alcoholysis.[6] However,

(1) (a) Negishi, E. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1983; Vol. 7, Chapter 45.6–45.11. (b) Pelter, A.; Smith, K. In "Comprehensive Organic Chemistry"; Barton, D. H. R., Ollis, W. D., Jones, D. N., Eds.; Pergamon Press: Oxford, 1979; Vol. 3, Part 14. (c) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975.

(2) (a) Brown, H. C.; Rogić, M. M.; Nambu, H.; Rathke, M. W. *J. Am. Chem. Soc.* **1969**, *91*, 2147. (b) For more information, see ref 1c.

(3) (a) Hooz, J.; Gunn. D. M. *Tetrahedron Lett.* **1969**, 3455. (b) Naruse, M.; Utimoto, K.; Nozaki, H. *Tetrahedron Lett.* **1973**, 1847, 2741; *Tetrahedron* **1974**, *30*, 2159, 3037. (c) This problem has been shortly reviewed in a study on relative migratory aptitude: Slayden, S. W. *J. Org. Chem.* **1981**, *46*, 2311.

(4) (a) Matteson, D. S. *Prog. Boron Chem.* **1970**, *3*, 117. (b) Rathke, M. W.; Chao, E.; Wu, G. *J. Organomet. Chem.* **1976**, *122*, 145. (c) Brown, H. C.; De Lue, N. R.; Yamamoto, Y.; Maruyama, K.; Kasahara, T.; Murahashi, S.; Sonoda, A. *J. Org. Chem.* **1977**, *42*, 4088.

(5) (a) Zweifel, G.; Polston, N. L.; Whitney, C. C. *J. Am. Chem. Soc.* **1968**, *90*, 6243. (b) Evans, D. A.; Thomas, R. C.; Walker, J. A. *Tetrahedron Lett.* **1976**, 1427. Evans, D. A.; Crawford, T. C.; Thomas, R. C.; Walker, J. A. *J. Org. Chem.* **1976**, *41*, 3947. (c) Carlson, B. A.; Brown, H. C. *J. Am. Chem. Soc.* **1973**, *95*, 6876. Cf. Brown, H. C.; Katz, J.-J.; Carlson, B. A. *J. Org. Chem.* **1973**, *38*, 3968.

(6) (a) Brown, H. C.; Ravindran, N.; Kulkarni, S. U. *J. Org. Chem.* **1980**, *45*, 384. (b) Brown, H. C.; Campbell, J. B., Jr. *Ibid.* **1980**, *45*, 389 and references cited therein.

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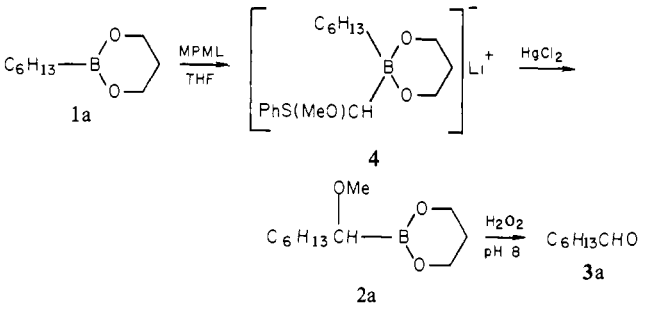
Scheme II



intermediates **1** are much less reactive than R_3B, and most of the carbenoid reagents that work with R_3B fail with **1**. For example, $CHCl_2OMe$ ($CHCl_3$, $CHCl_2F$, or $CHClF_2$)/$LiOCEt_3$, $BrCH_2CO_2Et$ (or $ClCH_2CN$)/KOAr, and N_2CHCO_2Et result in practically no reaction with **1**.[7]

Thus, until the recent discoveries by Matteson and Majumdar,[8] there had been no effective means for homologating **1** (approach *a*). Dichloromethyllithium homologates **1** to $RCHClB(OR')_2$[8a,b] and chloro(trimethylsilyl)methyllithium converts **1** to $RCH(SiMe_3)B(OR')_2$.[8c]

In this paper is described our own effort with a new homologation reagent, methoxy(phenylthio)methyllithium (MPML),[9] which readily achieves transfer of the organic group from boron to carbon with the aid of mercury(II) chloride, converting the intermediate into the α-methoxy derivative **2**. Subsequent oxidation provides the corresponding aldehydes **3** in good yields (eq 2).

$$\underset{\mathbf{1}}{RB(OR')_2} \xrightarrow[(2)\ HgCl_2]{(1)\ MPML} \underset{\mathbf{2}}{RCH(OMe)B(OR')_2} \xrightarrow{[O]} \underset{\mathbf{3}}{RCHO} \qquad (2)$$

Prior to this study, we briefly studied direct oxidation of α-chloroalkylboronic esters obtained by the Matteson's homologation reaction.[8a] Although they were pursuing different objectives with their α-chloro derivatives, the synthesis of chiral alcohols,[8b] oxidation of these intermediates might also provide a desirable route to aldehydes, as mentioned by the authors. Actually, it has been shown by Rathke, et al., that the α-chloro derivatives obtained by a different route (approach *b*) provide the corresponding aldehydes on oxidation in a phosphate-buffered medium.[4b] However, only three aldehydes were prepared, and the yields range widely, from 85% to 70% to 30% in the three cases examined (all were GC yields). our own study of this sequence suggested some problem with the oxidation step, since the yields of aldehyde were in most cases significantly lower (vide infra) than those reported for the homologation reaction itself (80–90%).[8a]

Results and Discussion

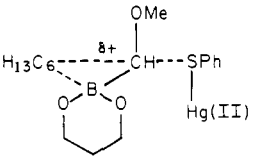
When lithiation of methoxymethyl phenyl sulfide was done by the original procedure (*n*-BuLi/THF, −30 °C/0.5 h)[9a] and the intermediate quenched with D_2O, only 75% of the material was recovered with 90% deuteration (estimated by GC and ^1H NMR, respectively). The lithiation was improved by using *s*-BuLi at lower temperature (ca. −50 °C). Subsequent D_2O quench after 1 h of stirring gave 94% recovery with 97% deuterium incorporation.

To the thus generated MPML solution, 1 equiv of 2-hexyl-1,3,2-dioxaborinane (**1a**) was added and the mixture was allowed to come to room temperature. ^{11}B NMR showed that **1a** (δ 30.5) was completely converted to the ate complex (**4**, δ 8) (Scheme II). The intermediate **4** was stable (no change after standing overnight at room temperature); it did not rearrange spontaneously. However, the alkyl migration was readily induced by adding mercury(II) chloride to give the α-methoxy derivative **2a** (δ 30.5). Oxidation of **2a** with hydrogen peroxide proceeded smoothly in a pH 8 phosphate buffer medium, being completed in 3 h at room temperature. GC analysis with tetradecane internal standard showed formation of heptanal in 92% yield with only a trace amount of hexanol (1–2%). In an independent run, **2a** was isolated by distillation and characterized by ^1H NMR. The methoxy proton was observed at δ 3.3 as a sharp singlet, and the methine proton at δ 2.95 as a triplet (J = 5.5 Hz) broadened by coupling with boron.

Application of other thiophilic reagents, such as CuI, MeI, Me_2SO_4, and $Me_3O^+BF_4^-$, resulted in lower yields of the migration product (13–59%, estimated as heptanal). An attempt to activate the methoxy group instead of the phenylthio group with $BF_3{\cdot}OEt_2$ gave only 35% of heptanal.

It should be noted that unsuccessful attempts to homologate boronic esters have been recorded by Matteson with some sulfur-stabilized methyllithium reagents, LiCHXSPh (**5**, X = SR, SR_2^+, NMe_3^+, or Cl).[8c] Since PhSCH=CHSPh was the isolated product in these reactions, it was concluded that in all cases the ate complex, if formed, dissociated to the carbene, PhSCH. Our ^{11}B NMR study of an equimolar mixture of **5** (X = SPh) and **1a** showed that the ate complex formation was disfavored in the equilibrium,[10] in contrast to MPML (**5**, X = OMe) (vide supra).

This striking difference might be simply due to the more basic nature of MPML compared with the reagents examined by Matteson.[8c] However, tight ate complex formation is not the only factor for the success with MPML, since we also observed that $LiCH_2SPh$ (**5**, X = H) formed stable ate complex with **1a**, but the complex, on treatment with the same series of electrophiles, largely dissociated to starting **1a** and probably an ylide. Thus, the methoxy group must be playing an important role in the migration step. These observations suggest S_Ni character in or prior to the transition state of migration (**6**).



6

Some other esters of hexylboronic acid (**1b–f**) were then explored under the same reaction conditions. Except for **1d** and **1f**, heptanal was obtained in good yields (Table I). When the Matteson–Rathke sequence was applied to the same series of hexylboronic esters, only moderate yields (51–66%) of heptanal were obtained, except for **1c** (82%). Thus, for this particular purpose, i.e., aldehyde synthesis, the combination of MPML and aliphatic cyclic boronates appears to be the best choice. Furthermore, the higher reaction temperature possible with MPML (−50 °C), compared to the much lower temperature required for dichloromethyllithium (−100 °C), makes it easier to perform and control the reaction.

The trimethylene ester functionality was chosen for all subsequent reactions because of its wider accessibility.[11] In contrast to the highly bulky tertiary alkyl derivative (**1n**), primary and secondary alkyl derivatives were all converted to one-carbon-extended aldehydes in good yields (Table I). The failure with **1n**, as well as the poor result with **1f**, suggests that the ate complex formation with MPML may be disfavored with these relatively hindered boronic esters. However, it should be mentioned that Matteson successfully homologated a *tert*-butylboronic ester with dichloromethyllithium.[8a]

(7) Unpublished results by T. Imai and H. C. Brown.

(8) (a) Matteson, D. S.; Majumdar, D. *J. Am. Chem. Soc.* **1980**, *102*, 7588. (b) Matteson, D. S.; Ray, R. *Ibid.* **1980**, *102*, 7590. An improved procedure appeared after this article had been accepted, see: Matteson, D. S.; Sadhu, K. M. *Ibid.* **1983**, *105*, 2077. (c) Matteson, D. S.; Majumdar, D. *J. Organomet. Chem.* **1980**, *184*, C41; *Organometallics* **1983**, *2*, 230.

(9) (a) Trost, B. M.; Miller, C. H. *J. Am. Chem. Soc.* **1975**, *97*, 7182. (b) de Groot, Ae.; Jansen, B. J. M. *Tetrahedron Lett.* **1981**, *22*, 887.

(10) This spectral observation also supports Matteson's conclusion on an attempted substitution reaction of bis(phenylthio)methylboronic esters with butyllithium (Mendoza, A.; Matteson, D. S. *J. Org. Chem.* **1979**, *44*, 1352).

(11) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1970**, *92*, 6983.

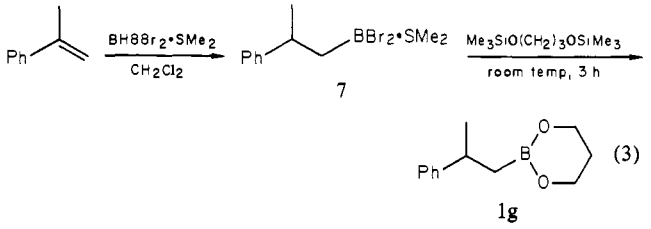
Table I. Preparation of Aldehydes from Alkylboronic Esters by Reaction with LiCH(OMe)SPh Followed by $HgCl_2$ Treatment and Hydrogen Peroxide Oxidation in pH 8 Phosphate Buffer[a]

	$RB(OR')_2$ (1) R	OR'	RCHO (3)	yield, % isolated (GC)	physical properties	lit.
a	hexyl	P[b]	heptanal	(92)	mp (2,4-DNP) 105-108 °C	*c*
b	hexyl	E[d]	heptanal	(87)		
c	hexyl	Pi[e]	heptanal	(94)		
d	hexyl	C[f]	heptanal	(43)		
e	hexyl	OMe	heptanal	(83)		
f	hexyl	O-*i* Pr	heptanal	(38)		
g	2-phenylpropyl	P	3-phenylbutanal	70[g]	bp 62-65 °C (0.15 torr), n^{20}_D 1.5169, mp (2,4-DNP) 124-125 °C	*h*
h	1-ethylbutyl	P	2-ethylpentanal	69 (86)	bp 77-79 °C (110 torr), n^{20}_D 1.4070 mp (2,4-DNP) 123-124 °C	*i*
i	1,2-dimethylbutyl[j]	P	*threo*-2,3-dimethylpentanal	60[g]	bp 78-81 °C (110 torr), n^{20}_D 1.4116, mp (2,4-DNP) 88-90 °C	*k*
j	1,2-dimethylbutyl[l]	P	*erythro*-2,3-dimethylpentanal	64[g]	bp 79-82 °C (110 torr), n^{20}_D 1.4113, mp (2,4-DNP) 88-90 °C	*k*
k	cyclohexyl	P	cyclohexanecarbaldehyde	(86)	mp (2,4-DNP) 172-173 °C	*m*
l	*trans*-2-methylcyclopentyl	P	*trans*-2-methylcyclopentanecarbaldehyde	64	bp 85-86 °C (110 torr), n^{20}_D 1.4363	*n*
m	*exo*-norbornyl	P	*exo*-norbornanecarbaldehyde	78	bp (bath temp) 80-85 °C (14 torr), n^{20}_D 1.4729	*o*
n	1,1,2-trimethylpropyl	P	(2,2,3-trimethylbutanal)	(≤2)		

[a] The reactions were done by the standard procedure (See Experimental Section for details) in 5-mmol scale for GC analysis or 10-mmol scale for isolation of aldehyde, except 1g, 1i and 1j. These were done in 25-mmol scale by directly starting from appropriate olefins. [b] P = $[O(CH_2)_3O]_{1/2}$, 1,3-propanediol ester. [c] mp (2,4-DNP) 108 °C: Schriner, R. L.; Fuson, R. C.; Curtin, D. Y. "The Systematic Identification of Organic Compounds", 5th ed.; Wiley: New York, 1964; p 108. [d] E = $[O(CH_2)_2O]_{1/2}$, 1,2-ethanediol ester. [e] Pi = $[O(CMe_2)_2O]_{1/2}$, pinacol ester. [f] C = $[o\text{-}OC_6H_4O]_{1/2}$, catechol ester. [g] Overall yield on the basis of the starting olefin. [h] bp 92-93 °C (14 torr), mp (2,4-DNP) 123-123.5 °C: Adams, R.; Garber, J. D. *J. Am. Chem. Soc.* **1949**, *71*, 522. [i] bp 63-64 °C (50 torr), mp (2,4-DNP) 123 °C: Sutter, H.; Wijkman, N. *Justus Liebigs Ann. Chem.* **1933**, *505*, 248. [j] Derived from (*E*)-3-methyl-2-pentene. [k] bp 141-142 °C, mp (2,4-DNP) 88-89 °C: Ferrari, G.; Casagrande, C. *Farmaco, Ed. Sci.* **1963**, *18*, 780. [l] Derived from (*Z*)-3-methyl-2-pentene. [m] mp (2,4-DNP) 172 °C: Heilbren, I.; Jones, E. R. H.; Richardson, R. W. R.; Sondheimer, F. *J. Chem. Soc.* **1949**, 733. [n] bp 148-150 °C, n^{20}_D 1.4386: Nenitzescu, C. D.; Vantu, G. G. *Bull. Soc. Chim. Fr.* **1935**, *2*, 2209. [o] bp 66-68 °C (12 torr): Alder, K.; Stein, G. *Justus Liebigs Ann. Chem.* **1934**, *514*, 197.

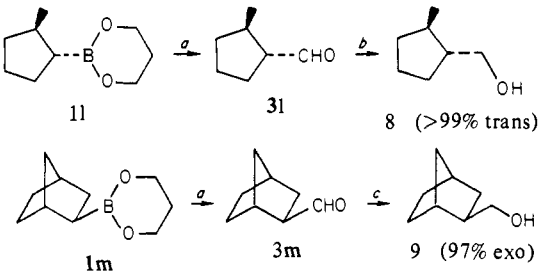
Isolation of aldehydes was done on a 10- or 25-mmol scale, using 5% excess MPML. The oxidation product was first steam-distilled, then extracted into ether, and purified by distillation. Although the crude products were fairly clean on GC analysis, direct distillation resulted in some contamination by decomposition products.

One of the methods of converting $RBBr_2{\cdot}SMe_2$ to (2*R*)-1,3,2-dioxaborinane may be emphasized here, since this provides the boronic esters pure enough to be used directly to the next step. For example, hydroboration of 2-phenylpropene with $BHBr_2{\cdot}SMe_2$ gave regioselectively **7** (^{11}B NMR δ 3.2, s). Then **7** was treated with 1 equiv of 1,3-bis(trimethylsiloxy)propane to cleanly give **1g** (^{11}B NMR δ 30.1, s) (eq 3).[12]



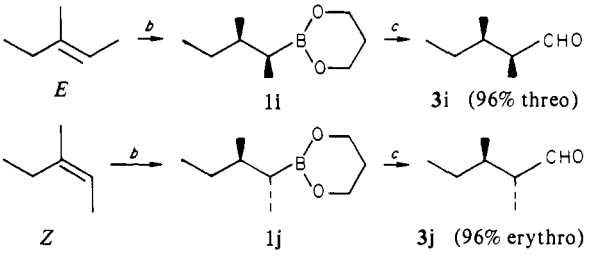
The migration proceeds with retention of configuration at the migrating carbon atom as observed in other related 1,2-migration reactions of organoboranes.[1a] Thus, the trans geometry of **1l**, obtained by hydroboration of 1-methylcyclopentene, was retained in the product (**3l**) (Scheme III). Similarly, the *exo*-norbornyl derivative (**1m**) gave the exo aldehyde **3m**. The aldehydes **3l** and **3m** were reduced to the well-characterized alcohols **8** and **9**, respectively, to confirm their configurations. Melting point of the 3,5-dinitrobenzoate of **8** agreed with that reported for the trans isomer.[13] The isomeric purity of **8** was more than 99%, on the basis of its ^{13}C NMR spectrum. The ^{13}C NMR spectrum of **9** agreed with that reported for the exo isomer,[14] and its isomeric purity was estimated to be 97%.

Scheme III



[a] (i) MPML/THF; (ii) $HgCl_2$; (iii) H_2O_2/pH 8 buffer. [b] $NaBH_4$/EtOH. [c] LAH/ether.

Scheme IV[a]



[a] Only one enantiomer is shown for each compound. [b] (i) $BHBr_2{\cdot}SMe_2/CH_2Cl_2$; (ii) $Me_3SiO(CH_2)_3OSiMe_3$. [c] (i) MPML/THF; (ii) $HgCl_2$; (iii) H_2O_2/pH 8 buffer.

The most important feature of this aldehyde synthesis might be this clear stereochemical outcome, achieved by taking advantage of the stereochemistry of the hydroboration stage and the retention

(12) There is a precedent for such an exchange reaction between boron halides and silyl ethers, in which Si–O bond cleavage is emphasized (Wiberg, E.; Kruerke, U. *Z. Naturforsch., B* **1953**, *8B*, 608, 609, 610).

(13) Owen, L. N.; Peto, A. G. *J. Chem. Soc.* **1955**, 2383.

(14) Brouwer, H.; Stothers, J. B.; Tan, C. T. *Org. Magn. Reson.* **1977**, *9*, 361.

of the homologation stage. This advantage is nicely illustrated by the stereospecific synthesis of *threo*- and *erythro*-2,3-dimethylpentanal from (*E*)- and (*Z*)-3-methyl-2-pentene, respectively (Scheme IV). In both cases, ca. 4% of contamination of the product by the diastereomeric isomer was detected by ^{13}C NMR. Since the starting olefins were at least 99% isomerically pure, these contaminations may be due to partial epimerization during the oxidation. The configurations were confirmed by converting them to the corresponding carboxylic methyl esters by a reported procedure.[15a] ^1H NMR spectral patterns for those samples enriched in either isomer have been reported.[15b] Although the Ag_2O oxidation suffered from a considerable degree of epimerization, **3i** gave threo-rich and **3j** gave erythro-rich ester.

In conclusions, this aldehyde synthesis from alkylboronic esters, when combined with the hydroboration reaction, provides a new method of introducing aldehyde functionality into olefins in a regio- and stereocontrolled manner.

Experimental Section

GC was performed with a Hewlett-Packard 5750 instrument. ^1H NMR spectra were obtained in most cases with a Perkin-Elmer R32 (90 MHz) and for special purposes a Varian T-60 (60 MHz) or Varian XL-200 (200 MHz) spectrometer; ^{11}B NMR and wide-band ^1H-decoupled ^{13}C NMR spectra were obtained with a Varian FT80A spectrometer. Chemical shift values, all in $CDCl_3$, are given in ppm relative to internal Me_4Si in ^1H and ^{13}C NMR and relative to $BF_3{\cdot}OEt_2$ in ^{11}B NMR. IR spectra were recorded with a Perkin-Elmer 137 spectrophotometer. Elemental analysis were done in the Purdue University Microanalytical Laboratory. Melting and boiling points are uncorrected.

THF was freshly distilled from benzophenone ketyl prior to use. Methoxymethyl phenyl sulfide was prepared by adding chloromethyl methyl ether to a solution of lithium thiophenolate in THF,[9] 82% yield, bp 112–113 °C (18 torr) [lit.[16] bp 108 °C (12 torr)]. Mercury(II) chloride (Aldrich) was used without further purification. A cyclohexane solution of *s*-BuLi (Alfa) was estimated to be 1.43 M by Watson–Eastham's method with 2,2′-biquinoline as the indicator.[17] Hydrogen peroxide (Mallinckrodt) was estimated to be 9.9 M. A phosphate buffer solution was prepared by alternate addition of Na_2HPO_4 and KH_2PO_4 into distilled water to adjust the solution to pH 8 by a pH meter and ca. 2.5 M in total phosphate conmcentration. (*E*)- and (*Z*)-3-methyl-2-pentene (Albany) were both isomerically pure (≥99% by ^{13}C NMR) and used without further purification.

All reactions were done in a dry round-bottom flask equipped with a septum-capped side arm, stopcock-controlled connecting tube, and a magnetic stirring bar. A nitrogen atmosphere was maintained throughout the reaction. Reagents were introduced by a syringe or by a double-ended needle through the side arm.

Alkylboronic Esters (1). Alkylboronic esters were prepared by known methods, with minor modifications if necessary, isolated by distillation, except **1g**, **1i**, and **1j**, and characterized by physical and spectral properties. All of the boronic esters had a singlet ^{11}B NMR peak at δ 30–36. Some new compounds are described at the end of this paragraph. For known compounds, method of preparation, isolated yield (%), bp (°C (torr)), and $n^{20}{}_D$ were as follows: **1e**,[6a] hydroboration of 1-hexene with $BHBr_2{\cdot}SMe_2$ in dichloromethane[6a] followed by methanolysis in pentane at 0 °C (method A), 86, 86–87 (25), 1.4066; **1b**,[18] transesterification of **1e** with 1,2-ethanediol by azeotropic removal of methanol with benzene or cyclohexane (method B), 94, 89–92 (35), 1.4231; **1d**,[18] hydroboration of 1-hexene with catecholborane,[19] 76, 87–88 (0.5), 1.4855; **1k**,[20] hydroboration of cyclohexene with $BHCl_2{\cdot}SMe_2$ in the presence of BCl_3 in pentane[6a] followed by filtration of $BCl_3{\cdot}SMe_2$ and treatment with 1,3-propanediol (method C), 76, 104–108 (14–15), 1.4608; **1m**,[20] redistribution method[20] with $BH_3{\cdot}SMe_2$[21] instead of $BH_3{\cdot}THF$ and with no solvent, 93, 68–72 (0.05), 1.4790.

2-Hexyl-1,3,2-dioxaborinane (1a) was prepared from **1e** by method B with 1,3-propanediol, 85%: bp 96–97 °C (14 torr); $n^{20}{}_D$ 1.4322; IR (neat liquid) 2910, 1490, 1430, 1360, 1345, 1330, 1280, 1230, 1190, 1100, 940, and 870 cm^{-1}; ^1H NMR δ 0.45–0.75 (broad t, J = 7.5 Hz, 2 H, BCH_2), 0.75–1.0 (m, 3 H, CH_3), 1.05–1.5 (m, 8 H, 4 × CH_2), 1.9 (p, J = 5.5 Hz, 2 H, borinane CH_2), and 3.95 (t, J = 5.5 Hz, 4 H, 2 × OCH_2). Anal. Calcd for $C_9H_{19}BO_2$: C, 63.56; H, 11.26; B, 6.36. Found: C, 63.79; H, 11.47; B, 6.24.

2-Hexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1c) was prepared from **1e** by method B with pinacol, 95%: bp 98–100 °C (12 torr); $n^{20}{}_D$ 1.4226; IR (neat liquid) 2950, 2910, 2860, 1380, 1325, 1160, 980, 890, and 855 cm^{-1}; ^1H NMR δ 0.4–1.0 (m, 5 H, CH_3 and BCH_2) and 1.0–1.5 (m, containing sharp s at 1.2 ppm, 20 H, 4 × CH_2 and 4 × borolane CH_3). Anal. Calcd for $C_{12}H_{25}BO_2$: C, 67.94; H, 11.88; B, 5.10. Found: C, 67.92; H, 12.14% B, 4.99.

Diisopropyl hexylboronate (1f) was prepared from 1-hexene by method A with isopropyl alcohol, 86%: bp 90–92 °C (14 torr), $n^{20}{}_D$ 1.4042; IR (neat liquid) 2950, 2900, 2860, 1380, 1330, 1140, and 950 cm^{-1}; ^1H NMR δ 0.5–1.0 (m, 5 H, CH_3 and BCH_2), 1.1 (d, J = 6 Hz, 12 H, 4 × CH_3), 1.2–1.4 (m, 8 H, 4 × CH_2), 4.35 (hept, J = 6 Hz, 2 H, 2 × CH). Anal. Calcd for $C_{12}H_{27}BO_2$: C, 67.30% H, 12.71% B, 5.05. Found: C, 67.20; H, 12.49; B, 5.20.

2-(1-Ethylbutyl)-1,3,2-dioxaborinane (1h) was prepared from 3-hexene by method C, 86%: bp 82–85 °C (13 torr); $n^{20}{}_D$ 1.4310; IR (neat liquid) 2930, 1500, 1430, 1375, 1280, 1255, 1240, 1200, 950, and 740 cm^{-1}; ^1H NMR δ 0.4–1.0 (m, 7 H, 2 × CH_3 and BCH), 1.0–1.6 (m, 6 H, 3 × CH_2), 1.9 (p, J = 5.5 Hz, 2 H, borinane CH_2), and 3.95 (t, J = 5.5 Hz, 4 H, 2 × OCH_2). Anal. Calcd for $C_9H_{19}BO_2$: C, 63.56; H, 11.26; B, 6.36. Found: C, 63.37; H, 11.55% B, 6.53.

***trans*-2-(2-Methylcyclopentyl)-1,3,2-dioxaborinane (1l)** was prepared from 1-methylcyclopentene by method C, 82%: bp 107–110 °C (33 torr); $n^{20}{}_D$ 1.4512; IR (neat liquid) 2930, 1500, 1430, 1360, 1320, 1285, 1230, 1215, 1105, 950, and 850 cm^{-1}; ^1H NMR δ 0.4–0.8 (m, 1 H, BCH), 0.95 (d, J = 6.5 Hz, 3 H, CH_3), 1.0–1.3 (m partially overlapping with the d, 1 H, CH), 1.3–2.1 (m containing p at 1.9 ppm (J = 5.5 Hz), 8 H, 4 × CH_2), and 3.95 (t, J = 5.5 Hz, 4 H, 2 × OCH_2). Anal. Calcd for $C_9H_{17}BO_2$: C, 64.32; H, 10.20% B, 6.55. Found: C, 64.18; H, 10.11; B, 6.58.

2-(1,1,2-Trimethylpropyl)-1,3,2-dioxaborinane (1n)[4c] was prepared by hydroboration of 2,3-dimethyl-2-butene with $BH_3{\cdot}SMe_2$ and subsequent treatment of the resulting monoalkylborane[21] with 1,3-propanediol, 84%: bp 77–79 °C (15 torr); $n^{20}{}_D$ 1.4371; Ir (neat liquid) 2930, 2890, 1490, 1425, 1340, 1310, 1280, 1180, 1140, 940, 860, and 780 cm^{-1}; ^1H NMR δ 0.77 (s, 6 H, 2 × CH_3), 0.80 (d, J = 6.8 Hz, 6 H, 2 × CH_3), 1.5 (hept, J = 6.8 Hz, 1 H, CH), 1.9 (p, J = 5.5 Hz, 2 H, CH_2), and 3.95 (t, J = 5.5 Hz, 4 H, 2 × OCH_2).

2-(2-Phenylpropyl)-1,3,2-dioxaborinane (1g). Freshly distilled 2-phenylpropene (25 mmol) was added dropwise to a 3 M solution of $BHBr_2{\cdot}SMe_2$ (25 mmol) in dichloromethane with water bath (ca. 15 °C) cooling, and the mixture was left overnight at room temperature to ensure the hydroboration. Then 1,3-bis(trimethylsiloxy)propane was added (slightly exothermic). After 3 h of stirring, ^{11}B NMR showed clean and complete conversion to **1h** (δ 30, s). In ^1H NMR spectrum, the methyl group appeared exclusively as a doublet (J = 7 Hz) at δ 1.3. The solvent and volatile byproducts (Me_2S and Me_3SiBr) were removed by aspirator vacuum, and the residual boronic ester was used without further purification.

Diastereomeric 2-(1,2-dimethylbutyl)-1,3,2-dioxaborinanes (1i and 1j) were prepared in the same manner as above from (*E*)- and (*Z*)-3-methyl-2-pentene, respectively, and directly used for the reaction with MPML.

***trans*-2-Methylcyclopentanecarbaldehyde (3l). General Procedure.** In a 100-mL, round-bottom flask, MPML was prepared by adding at −55 to −50 °C 10.5 mmol of *s*-BuLi to a stirred solution of 10.5 mmol of methoxymethyl phenyl sulfide in 20 mL of THF. After 1 h of stirring at −50 °C, 10 mmol of **1l** was added dropwise, but rapidly. The cold bath was allowed to reach −10 to −5 °C in ca. 2 h. Then, under a stream of nitrogen, the top of the flash was opened and 10.5 mmol of well-powdered $HgCl_2$ was added all at once with vigorous stirring. The flash was recapped and flashed with nitrogen. The mixture was stirred for 0.5 h, while the bath temperature reached 0–5 °C. The bath was removed and the stirring was continued for an additional 2 h. If necessary, at this stage, the reaction mixture can be left at room temperature overnight without affecting the yield of the aldehyde. Oxidation was done by successive addition of 5 mL of pH 8 phosphate buffer and 30 mmol of hydrogen peroxide. The initial exothermic reaction was controlled by the rate of addition and by water-bath cooling to maintain the temperature below 40 °C. Stirring was continued for 3 h at room temperature to ensure completion of the oxidation. The flask was then attached to an ordinary steam distillation setup. Steam was introduced slowly until most of the solvent had been distilled out and then vigorously while the flask was heated by an oil bath (100–120 °C). The distillation was continued until the distillate was no longer turbid (usually 200–250 mL collected).

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The aqueous phase of the distillate was saturated with salt and extracted with ether 3 times (25 mL each). The ether extract was dried over $MgSO_4$ and filtered. Most of the solvent was removed by fractionation under nitrogen at atmospheric pressure. The residue was transferred into a semimicro distillation apparatus equipped with a 10-cm Vigreux column, and the remaining small amount of the solvent was distilled off again at atmospheric pressure. Then the product was distilled under reduced pressure: bp 85–86 °C (110 torr); 0.713 g (64%); IR (neat liquid) 1730 cm^{-1} (CO). About 2% of 2-methylcyclopentanol was detected by GC. ^1H NMR δ 0.8–1.35 (m, 3 H, CH_3), 1.35–2.5 (m, 8 H, 3 × CH_2 and 2 × CH), and 9.6 (unresolved d, $J \simeq 2$ Hz, 1 H, CHO); ^{13}C NMR δ 19.6 (CH_3), 24.9 (C-4), 26.5 (C-3), 35.1 (C-5), 36.3 (C-2), 59.8 (C-1), and 203.3 (CHO). Since the ^{13}C NMR sample was contaminated by ca. 5% of trimer (δ 104, OCHRO), an aliquot was reduced with $NaBH_4$ in ethanol to *trans*-2-methylcyclopentylmethanol, 78%: bp 110–111 °C (81 torr); n^{20}_D 1.4491 [lit.[13] bp 110–111 °C (81 torr); n^{20}_D 1.4531]. Melting point of its 3,5-dinitrobenzoyl derivative (54–56 °C) agreed with that reported for the trans isomer [lit.[13] mp 56 °C]. ^{13}C NMR δ 20.0 (CH_3), 23.9 (C-4), 29.5 (C-3), 35.0 (C-5), 36.9 (C-2), 49.7 (C-1), and 65.8 (CH_2OH). In the spectrum, detectable small peaks, which may be due to the cis isomer or some other impurity, did not exceed 1% (by peak height ratios).

***exo*-Norbornanecarbaldehyde (3m).** In the same manner as above, the aldehyde was prepared from **1m** and isolated in 78% yield. Although the material was essentially pure on GC analysis (contamination by *exo*-norbornanol <1%), ^{13}C NMR showed ca. 4% of a set of small peaks, which may be attributable to the endo isomer: major peaks δ 29.2, 29.4, 30.3, 36.17 (C-4), 36.24 (C-7), 38.2 (C-1), 54.7 (C-2), and 203.1 (CHO). In an independent run, the steam-distilled and ether-extracted aldehyde was reduced with $LiAlH_4$ to *exo*-norbornylmethanol, 87% on the basis of **1m**: bp 96–98 °C (15 torr); n^{20}_D 1.4912 [lit.[22] bp 99–100 °C (15–16 torr); $n^{26.5}_D$ 1.4858]. ^{13}C NMR spectrum agreed with that reported[14] for the exo isomer, and contamination by the endo isomer was estimated to 3% as the average of peak-height ratios.

***threo*-2,3-Dimethylpentanal (3i)** was prepared in the same manner as above, but using crude **1i** obtained from 25 mmol of (*E*)-3-methyl-2-pentene, 1.71 g (60% on the basis of the starting olefin): bp 78–81 °C (110 torr); IR (neat liquid) 1735 cm^{-1} (CO). Contamination by 2% of 3-methyl-2-pentanol was detected by GC. The pure sample was obtained by GC isolation in such a condition that the diastereomers could not be separated. ^1H NMR (200 MHz) δ 0.84 (d, J = 6.9 Hz, 3 H, 3-CH_3), 0.93 (t, J = 7.3 Hz, 3 H, 5-CH_3), 1.00 (d, J = 7.0 Hz, 3 H, 2-CH_3), 1.15–1.5 (m, 2H, CH_2), 1.8–2.0 (m, 1 H, 3-CH), 2.25–2.4 (m, 1 H, 2-CH), and 9.67 (d, J = 1.5 Hz, 1 H, CHO). ^{13}C NMR showed 4% contamination by the erythro isomer: major peaks δ 8.3 (C-5 or 3-CH_3), 11.8 (3-CH_3 or C-5), 15.2 (2-CH_3), 27.5 (C-4), 34.6 (C-3), 50.4 (C-2), and 205.6 (CHO). The aldehyde (**3i**) was oxidized with Ag_2O and methylated with diazomethane to give the corresponding carboxylic methyl ester.[15] ^1H NMR (60 MHz) pattern in the 0.5–1.5 ppm region agreed with that reported for threo-enriched (64:36) material.[15b] ^{13}C NMR revealed our sample to be a mixture of threo and erythro esters in 85:15 ratio: major peaks δ 11.4 (C-5 or 3-CH_3), 12.1 (3-CH_3 or C-5), 15.1 (2-CH_3), 27.3 (C-4), 37.0 (C-3), 43.8 (OCH_3), 50.9 (C-2), and 176.6 (CO_2).

***erythro*-2,3-Dimethylpentanal (3j)** was prepared in the same manner as above in 64% yield, on the basis of the starting (*Z*)-3-methyl-2-pentene; bp 79–82 °C (110 torr); IR (neat liquid) 1735 cm^{-1} (CO). GC analysis showed contamination by 3% of 3-methyl-2-pentanol. The pure sample was obtained by GC isolation and used for the following spectral measurements: ^1H NMR (200 MHz) δ 0.90 (t, J = 7.3 Hz, 3 H, 5-CH_3), 0.98 (d, J = 6.9 Hz, 3 H, 3-CH_3), 1.05 (d, J = 7.0 Hz, 3 H, 2-CH_3), 1.1–1.5 (m, 2 H, CH_2), 1.7–1.9 (m, 1 H, 3-CH), 2.2–2.4 (m, 1 H, 2-CH), and 9.70 (d, J = 1.9 Hz, 1 H, CHO). ^{13}C NMR showed 3–4% contamination by the threo isomer: major peaks δ 10.0 (C-5 or 3-CH_3), 11.7 (3-CH_3 or C-5), 17.0 (2-CH_3), 26.0 (C-4), 35.7 (C-3), 51.4 (C-2), and 205.6 (CHO). The aldehyde was converted to the corresponding carboxylic methyl ester[15] by the Ag_2O–diazomethane sequence. The complex pattern in the 0.5–1.5 ppm region of its ^1H NMR spectrum agreed with that reported for erythro-enriched (62:38) material.[15b] ^{13}C NMR showed our sample to be a mixture of erythro and threo esters in 56:44 ratio: major peaks δ 10.9 (C-5 or 3-CH_3), 13.7 (3-CH_3 or C-5), 16.3 (2-CH_3), 25.8 (C-4), 37.5 (C-3), 44.1 (OCH_3), 50.7 (C-2), and 176.2 (CO_2).

2-(1-Methoxyheptyl)-1,3,2-dioxaborinane (2a). By the general procedure, **1a** (5 mmol) was homologated to **2a**. The reaction mixture was filtered through a short Florisil column. Solvent evaporation and successive distillation gave 0.53 g (50%) of **2a**: bp 67–68 °C (0.03 torr); n^{20}_D 1.4443; IR (neat liquid) 2920, 1520, 1445, 1360, 1285, 1240, 1220, 1200, 1120, and 945 cm^{-1}; ^{11}B NMR δ 29.7 (s); ^1H NMR δ 0.75–1.05 (m, 3 H, CH_3), 1.05–1.45 (m, 8 H, 4 × CH_2), 1.45–1.75 (m, 2 H, 2-CH_2), 1.95 (p, J = 5.5 Hz, 2 H, borinane CH_2), 2.95 (t, J = 5.5 Hz, 1 H, BCHO), 3.3 (s, 3 H, OCH_3), and 4.05 (t, J = 5.5 Hz, 4 H, 2 × OCH_2). Anal. Calcd for $C_{11}H_{23}BO_3$: C, 61.70; H, 10.83; B, 5.05. Found: C, 61.48; H, 10.90; B, 5.22.

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Registry No. 1a, 86290-24-6; **1b**, 86290-25-7; **1c**, 86308-26-1; **1d**, 56554-22-4; **1e**, 2344-23-2; **1f**, 86290-26-8; **1g**, 86290-27-9; **1h**, 86290-28-0; **1i**, 86290-29-1; **1j**, 86290-30-4; **1k**, 30169-75-6; **1l**, 86290-31-5; **1m**, 30154-25-7; **1n**, 63689-74-7; **2a**, 86290-32-6; **3a**, 111-71-7; **3a** (2,4-DNP derivative), 2074-05-7; **3g**, 5445-77-2; **3g** (2,4-DNP derivative), 2269-20-7; **3h**, 22092-54-2; **3h** (2,4-DNP derivative), 23546-52-3; **3i**, 86290-33-7; **3i** (2,4-DNP derivative), 86290-34-8; **3i** (carboxylic methyl ester), 50599-91-2; **3j**, 86290-35-9; **3j** (2,4-DNP derivative), 86290-36-0; **3j** (carboxylic methyl ester), 50599-90-1; **3k**, 2043-61-0; **3k** (2,4-DNP derivative), 3335-68-0; **3l**, 20106-44-9; **3m**, 3574-55-8; **3n**, 86290-37-1; $BHBr_2{\cdot}SMe_2$, 55671-55-8; $BHCl_2{\cdot}SMe_2$, 63462-42-0; $BH_3{\cdot}SMe_2$, 13292-87-0; $HgCl_2$, 7487-94-7; *s*-BuLi, 598-30-1; MPML, 57788-49-5; 1-hexene, 592-41-6; 1,2-ethanediol, 107-21-1; 1,3-propanediol, 504-63-2; pinacol, 76-09-5; 1-methylcyclopentene, 693-89-0; 2,3-dimethyl-2-butene, 563-79-1; 2-phenylpropene, 98-83-9; 1,3-bis(trimethylsiloxy)propane, 17887-80-8; (*E*)-3-methyl-2-pentene, 616-12-6; (*Z*)-3-methyl-2-pentene, 922-62-3; methoxymethyl phenyl sulfide, 13865-50-4; *trans*-1-(3,5-dinitrobenzoyl(oxy)methyl)-2-methylcyclopentane, 86290-38-2; *exo*-norbornylmethanol, 13118-79-1.

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