employed for calculation of R_w and in least-squares refinement.

The structure was solved by using MULTAN. The E map contained the positions for 21 of the nonhydrogen atoms. The other nonhydrogen atoms and the hydroxy hydrogen were located from Fourier syntheses. The remaining hydrogen positions were calculated by using the riding option in SHELX-76. A total of 176 parameters was varied and included a scale factor, positional parameters for oxygen and carbon, anisotropic thermal parameters for the oxygens, and isotropic thermal parameters for the remaining atoms. The final R was 0.072, and R_w = 0.072.

Final positional and thermal parameters are given in Tables VI and VII. A list of calculated and observed structure factors is available.[34]

Acknowledgment. This work was supported by a grant from the United States Public Health Service (AI-15027).

Registry No. 4, 50693-03-3; 4 (aldol isomer 1), 71748-73-7; 4 (aldol isomer 2), 71699-76-8; 4 (aldol isomer 3), 76581-91-4; 5, 76498-36-7; 5 (aldol isomer 1), 76514-43-7; 5 (aldol isomer 2), 76514-44-8; 6, 72519-57-4; 7, 76498-37-8; 7 (aldol isomer 1), 76498-38-9; 8, 76498-39-0; 8 (aldol isomer 1), 76498-40-3; 8 (aldol isomer 2), 76498-41-4; 9, 76498-42-5; 9 (aldol isomer 1), 76498-43-6; 9 (aldol isomer 2), 76548-83-9; 9 (aldol isomer 3), 76581-95-8; 10, 76498-44-7; 10 (aldol isomer 1), 76498-45-8; 10 (aldol isomer 2), 76548-84-0; 10 (aldol isomer 3), 76548-85-1; 10 (aldol isomer 4), 76548-86-2; 11, 76498-46-9; 11 (aldol isomer 1), 76498-47-0; 11 (aldol isomer 2), 76581-96-9; 11 (aldol isomer 3), 76548-87-3; 11 (aldol isomer 4), 76548-88-4; 12, 76498-48-1; 12 (aldol isomer 1), 76498-49-2; 12 (aldol isomer 2), 76548-89-5; 12 (aldol isomer 3), 76548-90-8; 12 (aldol isomer 4), 76548-91-9; 13, 76498-50-5; 13 (aldol isomer 1), 76498-51-6; 13 (aldol isomer 2), 76548-92-0; 13 (aldol isomer 3), 76548-93-1; 13 (aldol isomer 4), 76548-94-2; 14, 76498-52-7; 14 (aldol isomer 1), 76498-53-8; 14 (aldol isomer 2), 76548-95-3; 14 (aldol isomer 3), 76548-96-4; 14 (aldol isomer 4), 76548-97-5; 15, 76498-54-9; 15 (aldol isomer 1), 76498-55-0; 15 (aldol isomer 2), 76548-98-6; 15 (aldol isomer 3), 76548-99-7; 15 (aldol isomer 4), 76549-00-3; 16, 582-52-5; 16 (benzyl derivative), 18685-18-2; 17, 51306-24-2; 18, 18467-77-1; 19, 52507-90-1; 20, 20880-92-6; 20 (aldehyde oxidation product), 32786-02-0; 21, 76498-56-1; 22, 50767-73-2; 23, 76498-57-2; 24, 76498-58-3; 25, 76498-59-4; 26, 76498-60-7; 27, 4064-06-6; 28, 14131-84-1; 29, 38088-60-7; 30, 18422-54-3; 34, 72519-59-6; 35, 72581-18-1; 36/37, 76549-01-4; 38, 76498-61-8; 39, 76514-45-9; 40, 76549-02-5; 41, 76549-03-6; 43, 76549-04-7; 44 (isomer 1), 76549-05-8; 44 (isomer 2), 34880-62-1; 46, 15186-48-8; 47, 22323-80-4; 48, 76498-62-9; 49, 76498-63-0; 50, 72581-16-9; 51, 72581-15-8; 52, 72519-58-5; 53, 72581-17-0; 54, 76498-64-1; 55, 76498-65-2; 56, 76498-66-3; 57, 76549-06-9; 58, 76498-67-4; 59, 76549-07-0; 60, 76549-08-1; 61, 76549-09-2; 65, 72507-50-7; benzyl chloride, 100-44-7; aldehyde intermediate (Scheme I), 23558-05-6; potassium 2,3:4,5-di-*O*-isopropylidene-β-D-*arabino*-2-hexulopyranosonate, 54162-42-4; (chloromethyl)trimethylsilane, 2344-80-1; 3-mercaptole acetal 1,2-dideoxy-5,6:7,8-di-*O*-isopropylidene-β-D-*arabino*-3,4,5-nonotriulo-5,9-pyranose, 76498-68-5; bis(trimethylsilyl)acetamide, 10416-58-7; propionyl chloride, 79-03-8; benzaldehyde, 100-52-7.

Supplementary Material Available: Tables of atomic coordinates and thermal parameters (Tables VI and VII), bond lengths (Table VIII), and bond angles (Table IX) (6 pages). Ordering information is given on any current masthead page.

(34) See the paragraph at the end of the paper regarding supplementary material.

Stereoselective Synthesis of Alcohols. 8. Diastereoselective Synthesis of β-Methylhomoallyl Alcohols via Crotylboronates[1,2]

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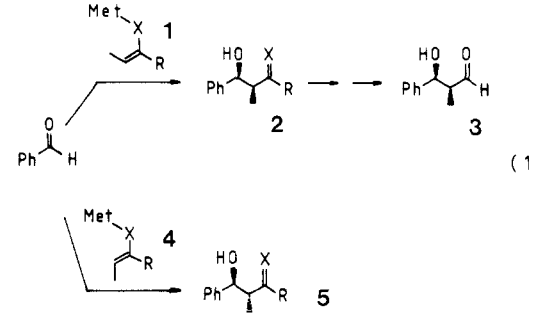
Received August 4, 1980

The (*E*)- and (*Z*)-butenylbis(dimethylamino)boranes **6c** and **8c** were obtained by starting from butenyl Grignard or butenylpotassium compounds. The aminoboranes were converted by pinacol to the crotylboronates **6d** and **8d**. These reagents have been added to various aldehydes, forming the homoallyl alcohols **15** and **16** with a diastereoselectivity of >95%.

Introduction

β-Methylalkanol units of both threo and erythro configuration[3] are a characteristic structural element of numerous macrolide[7] and polyether antibiotics. This caused interest in the development of new synthetic methods which allow the diastereoselective generation of β-methylalkanols.[8] Special attention has been given to those reactions in which new carbon–carbon bonds are formed via aldol addition, e.g., eq 1 (Met = Li, X = O).



In the aldol addition two prochiral components, the aldehyde and the enolate, are allowed to react. Hence, two diastereomeric products, the erythro adduct **2** and the threo adduct **5**[3] may result. This motivated the search for stereoselective synthetic methods which would lead to either the threo or the erythro isomer in high yield.[8] Thus it has been the aim of several investigations[8] to develop pairs of stereoisomeric reagents **1** and **4** which are capable of converting aldehydes stereoselectively to the adducts **2** and **5**, respectively. Useful reagents of this type should

(1) For paper VII, see R. W. Hoffmann and T. Herold, *Chem. Ber.*, **114**, 375 (1981).

(2) Portions of this work have been reported in preliminary form: R. W. Hoffmann and H. J. Zeiβ, *Angew. Chem.*, **91**, 329 (1979); *Angew. Chem., Int. Ed. Engl.*, **18**, 306 (1979).

(3) The terms erythro and threo are used in the sense defined by Heathcock[4] and Maskens.[5] This conforms to usage by most of the groups working on aldol-type additions. It should be made clear that this usage is contrary to the rules defined by *Chemical Abstracts* or *Beilstein*.[6]

(4) C. H. Heathcock, C. T. Buse, W. A. Kleschick, M. C. Pirrung, J. E. Sohn, and J. Lampe, J. Org. Chem., **45**, 1066 (1980).

(5) K. Maskens and N. Polgar, *J. Chem. Soc., Perkin Trans 1*, 109 (1973).

(6) *Beilstein, 4th ed.*, 4/1, XIV (1977); *Chem. Abst.*, **76**, Index Guide, 941 (1972).

(7) S. Masamune, G. S. Bates, and J. W. Corcoran, *Angew. Chem.*, **89**, 602 (1977); *Angew. Chem., Int. Ed. Engl.*, **16**, 585 (1977).

(8) Recently reviewed by P. A. Bartlett, *Tetrahedron*, **36**, 2 (1980).

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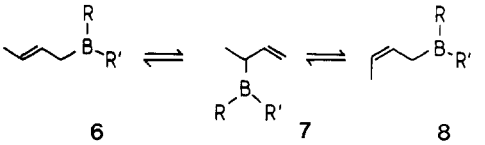
fulfill the following conditions: (i) each of the stereoisomeric synthons 1 and 4 should be conveniently available; (ii) the stereoisomeric synthons 1 and 4 should not equilibrate under the reaction conditions required; (iii) each of the synthons 1 and 4 should add to aldehydes, forming diastereospecifically only one of the adducts 2 or 5; (iv) the addition of 1 and 4 to the aldehydes should be irreversible; (v) the structural elements R and X in 1 and 4 should allow easy transformation of the adducts into an aldol, e.g. 2 → 3; (vi) chiral modification of the reagents 1 and 4 should easily be achieved.

Lithium enolates having special substituents R[4,9] fulfill most of these conditions satisfactorily. They have been used in total syntheses of methymycin[10] and monensin.[11] The reaction of the corresponding ester enolates[12] is also noteworthy. A change from lithium enolates to enol borinates (Met = BR_2, X = O, in eq 1) resulted in improvements with respect to conditions iii and iv.[13] Crotylchromium reagents (4, Met = Cr, X = CH_2, R = H, in eq 1)[14] are highly ranked with regard to condition v. Generally crotyl–metal compounds readily comply with conditions iii and v. However, crotyl–metal compounds pose problems with regard to conditions i and ii, because only tin,[15,16] germanium,[16] and silicon[16,17] derivatives possess sufficient E/Z stability.[18] However, their addition to ketones and aldehydes requires either high reaction temperatures[19] or catalysis by strong Lewis acids.[20] In contrast, the crotylboronates 1 and 4 (Met = $B(OR)_2$, X = CH_2, R = H, in eq 1) are considerably more reactive, the addition to aldehydes occuring at or below ambient temperature.[2] In as much as the crotylboronates fulfill at least the conditions ii–vi, they should be almost ideal reagents for diastereoselective C–C bond formation.

Results and Discussion

Preparation of Stereohomogeneous (*Z*)- and (*E*)-Crotylboronates. (*E*)- and (*Z*)-crotylboron derivatives 6 and 8 equilibrate via borotropic rearrangement involving the 1-methylallyl compound 7 as an intermediate. Di-



6 7 8

a, R = CH_2CH_3; R′ = $N(CH_3)_2$
b, R = OCH_3; R′ = $N(CH_3)_2$
c, R = $N(CH_3)_2$; R′ = $N(CH_3)_2$
d, R,R′ = $OC(CH_3)_2C(CH_3)_2O$
e, R = OCH_3; R′ = OCH_3
f, R = $N(CH_3)CH_2CH_2N(CH_3)$
g, R,R′ = OCH_2CH_2O

alkylcrotylboron compounds[21,22] are fluxional molecules at room temperature, the rate of rearrangement decreasing with increasing π-donor property of the substituents on boron.[23] Whereas one oxygen substituent on boron is not sufficient to suppress the borotropic shift at −20 °C,[24] one amino substituent in **7a** renders this compound stable up to 150 °C.[25] The doubly donor substituted derivatives **7b** and **7c** failed to rearrange to **6** below 170 °C.[26] Hence, the corresponding linear compounds **6b** and **6c** should not equilibrate at ambient temperature with their isomers **8b** and **8c**. Crotylboronates such as **6d** and **8d** are configurationally less stable, but can be handled at room temperature.[2,27] Their tendency to E/Z isomerization[28] increases in the presence of Lewis acids,[20,30] a fact that turned out to be a major handicap in our attempts to synthesize **6d** and **8d**.

(*Z*)-Crotylboronates. Synthetic access to the (*Z*)-crotylboronate **8e** was made possible by the principal studies of Schlosser,[28,31] who converted (*Z*)-butenylpotassium (**9**)[32] to **8e** by the action of fluorodimethoxyborane (**10**) followed by oxidation to (*Z*)-butenol. He also obtained other allylboronates by reaction of allylpotassium compounds with **10**.[28] In our attempts to prepare **8e** from **9** and **10** we had difficulties in decomposing the initially formed ate complex. Thermal cracking of the ate complex or addition of a Lewis acid such as BF_3OEt_2[29] was sufficient

(9) C. H. Heathcock, C. T. Buse, and J. E. Sohn, "Abstracts of Papers", 175th National Meeting of the Americal Chemical Society, Anaheim, CA, 1978, ORGN 20; C. H. Heathcock, M. C. Pirrung, C. T. Buse, J. P. Hagen, S. D. Young, and J. E. Sohn, *J. Am. Chem. Soc.*, **101**, 7077 (1979); C. H. Heathcock and C. T. White, *ibid.*, **101**, 7076 (1979).

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(19) K. König and W. P. Neumann, *Tetrahedron Lett.*, 495 (1967); C. Servens and M. Pereyre, *J. Organomet. Chem.*, **35**, C20 (1972). Cf., however, V. Peruzzo and G. Tagliavini, *J. Organomet. Chem.*, **162**, 37 (1978).

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(22) Oxidation of disiamylhepten-2-yl-1-boron led also to products derived from the hepten-1-yl-3 isomer: E.-I. Negishi, T. Yoshida, A. Silveira, Jr., and B. L. Chiou, *J. Org. Chem.*, **40**, 814 (1975).

(23) P. Jutzi and A. Seufert, *Chem. Ber.*, **112**, 2481 (1979), and references quoted.

(24) M. M. Midland and S. B. Preston, *J. Org. Chem.*, **45**, 747 (1980).

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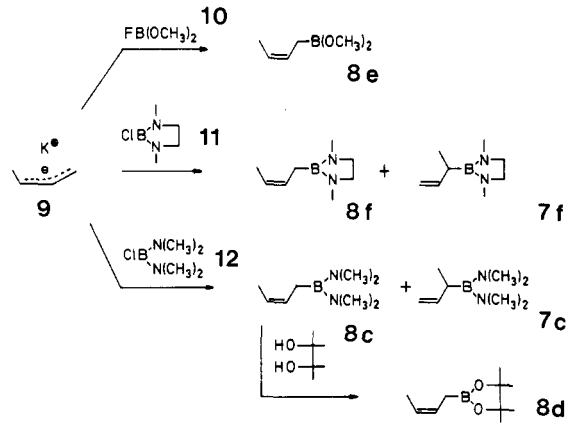
(28) M. Schlosser and G. Rauchschwalbe, *J. Am. Chem. Soc.*, **100**, 3258 (1978).

(29) J. Blais, A. L'Honoré, J. Soulié, and P. Cadiot, *J. Organomet. Chem.*, **78**, 323 (1974).

(30) R. W. Hoffmann, G. Feussner, H.-J. Zeiß, and S. Schulz, *J. Organomet. Chem.*, **187**, 321 (1980).

(31) G. Rauchschwalbe and M. Schlosser, *Helv. Chim. Acta*, **58**, 1094 (1975).

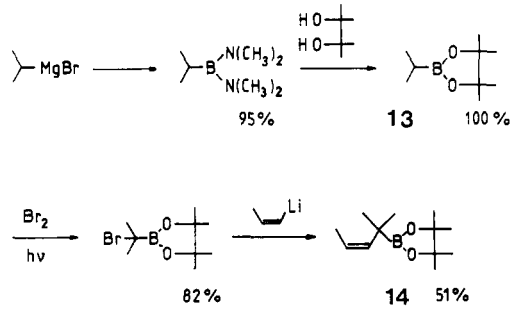
(32) M. Schlosser and M. Stähle, *Angew. Chem.*, **92**, 497 (1980); *Angew. Chem., Int. Ed. Engl.*, **19**, 487 (1980).



to cause the undesired E/Z isomerization of **8e** to **6e** as well as disproportionation, forming methyl dicrotylboronate and tricrotylboron. Reaction of **9** with chlorodimethoxyborane or 2-chloro-1,3,2-dioxaborolane (cf. ref 30) also caused isomerization of **8e**. Hence, reaction with a weaker Lewis acid, such as **11**[33] was necessary. Its reaction with **9** led to 43% of a 10:1 mixture of **8f** and **7f**. Since allyldiaminoboranes possess considerable thermal stability,[26] **8f** could be obtained from this mixture by distillation in >95% purity. Unfortunately, the diamino derivative **8f** did not undergo clean addition to aldehydes (cf. eq 1).[34]

Access to the required crotylboronates was finally gained via the following sequence. Reaction of **9** with bis(dimethylamino)chloroborane[35] (**12**) resulted in 45% of a 10:1 mixture of **8c** and **7c**, from which isomerically pure (>95% Z) **8c** was obtained by distillation over a 1-m spinning-band column. The (dimethylamino)boron derivative **8c** was then quantitatively converted to the more reactive, but also more labile, crotylboronate **8d** simply by addition[36] of 1 equiv of pinacol.

Another route to (Z)-2-alkenyl-1-boronates was recently described by Brown.[27] We followed his procedure in preparing **14** from **13**.

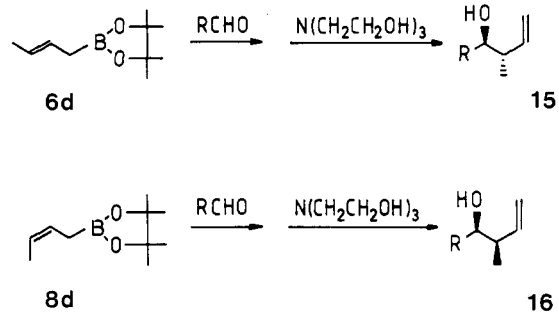


(*E*)-**Crotylboronates.** Our initial attempts to arrive at (E)-crotylboronates by reaction of crotyltin derivatives with 2-chloro-1,3,2-dioxaborolane led to mixtures of **6g**, **7g**, and **8g**,[30] which could not be distilled without causing interconversion of the isomers. Our experience in the Z series suggested the use of the amino compound **6c** as a more stable precursor of (E)-crotylboronates. Unfortunately, we were unable to react bis(dimethylamino)-chloroborane (**12**) with (E)-crotyltrialkyltin compounds. We therefore turned to the reaction of crotylmagnesium chloride with **12**, which had been previously studied by Hancock.[26] We obtained 60–90% of a mixture of **6c**, **7c**, and **8c**, which could be isomerized in 78% yield by heating with $ZnBr_2$ for 75 h at 120 °C to a 7:3 mixture of **6c** and **8c**. **6c** was obtained from this mixture by distillation on a spinning-band column. Purities of >90% were easily realized, but sufficient care must be taken in order to reach >95%.

Table I. Diastereoselective Addition of Crotylboronates to Aldehydes

compd	boronate 6d:8d	aldehyde, R =	homoallyl alcohol 15:16
15a	93:7	C_6H_5	94:6
15b	93:7	CH_3	93:7
15c	93:7	C_2H_5	93:7
15d	93:7	$(CH_3)_2CH$	96:4
16a	<5:>95	C_6H_5	4:96
16b	<5:>95	CH_3	3:97
16c	<5:>95	C_2H_5	3:97
16d	<5:>95	$(CH_3)_2CH$	6:94

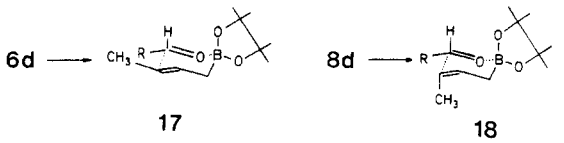
Reaction of Crotylboronates with Aldehydes. The crotylboronates **6d** or **8d** were reacted with an equimolar amount of an aldehyde at −78 °C. After being warmed, the resulting borates were decomposed by addition of triethanolamine according to our earlier procedure.[1] ^1H NMR analysis of the crude products indicated that the homoallyl alcohols **15** and **16** were formed almost quantitatively. In most cases studied here the product alcohol and the pinacol formed had similar boiling points. Pure samples of the alcohols **15** and **16** were therefore obtained by preparative VPC.



The diastereoselectivity in the reaction of the crotylboronates with aldehydes was tested with a sample of **6d** which contained 7% **8d** (by ^{13}C NMR). The sample of **8d** used was isomerically pure (>95% by ^{13}C NMR). The ratio of **15**/**16** was determined by VPC. Since the isomeric purity of the crotylboronates is known only to ±5%, the results in Table I demonstrate that both of the crotylboronates **6d** and **8d** add to aldehydes with high kinetic diastereoselectivity. The assignment of the relative configuration of the products, **15a** (threo) and **16a** (erythro), rests on secure ^1H NMR data.[37] In the case of compounds **15b** and **16b** it has been established by unambiguous NMR data[38] that the threo isomer **15b** shows the shorter retention time on VPC. The assignments of **15c**/**16c** and **15d**/**16d** are based on the relative retention times on VPC.[39]

One can assume that the reaction occurs via cyclic six-membered transition states having chair conformations, such as **17** and **18**. The educt and product stereochemistry

(33) T.-T. Wang, P. J. Busse, and K. Niedenzu, *Inorg. Chem.*, **9**, 2150 (1970).
(34) H.-J. Zeiß, Dissertation, Universität Marburg, 1980.
(35) N. Nöth and P. Fritz, *Z. Anorg. Allg. Chem.*, **322**, 297 (1963).
(36) Cf. J. E. Burch, W. Gerrard, and E. F. Mooney, *J. Chem. Soc.*, 2200 (1962).
(37) J. A. Coxon and G. S. C. Hii, *Aust. J. Chem.*, **30**, 835 (1977).
(38) P. A. Bartlett and K. K. Jernstedt, *J. Am. Chem. Soc.*, **99**, 4829 (1977); P. A. Bartlett, personal communication, 1977.
(39) H. Felkin, Y. Gault, and G. Roussi, *Tetrahedron*, **26**, 3761 (1970).



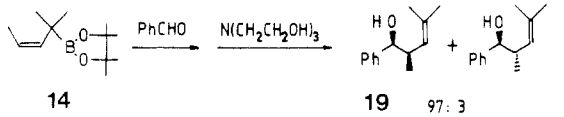
17 18

are properly related if the residue R of the aldehyde occupies exclusively an equatorial position.[13b] This may be caused by 1,3-interaction with the oxygen atoms on boron, of which one is necessarily axially oriented.

The diastereoselectivity observed on reaction of the crotylboronates surpasses that of the allenylboronates.[40] In the *Z* series it corresponds to that obtained with the lithium (*Z*)-enolates[4] and the (*Z*)-enol borinates.[13] The advantage of the crotylboronates becomes apparent in the *E* series. Whereas lithium (*E*)-enolates usually show low diastereoselectivity on addition to aldehydes,[4] the reaction of the (*E*)-crotylboronate **6d** resulted in a remarkably high diastereoselectivity. It also surpasses the threo selectivity of simple (*E*)-enol borinates[13c] and matches that of enol borinates having voluminous residues on boron.[13b,d] In our case, however, the bulk of the pinacol unit on boron is not responsible for the magnitude of the diastereoselectivity, since the methyl crotylboronates **6e** and **8e** added to aldehydes with undiminished high diastereoselectivity.[34] The origin of the high diastereoselectivity observed can probably be traced to the short B–O distances in the compact transition states **17** and **18** as proposed by Evans.[13b]

In both of the transition states **17** and **18** the residue R of the aldehyde is exposed to a gauche interaction with the methyl group of the crotylboronate. Hence, the reactivity of **6d** and **8d** toward aldehydes should not differ substantially. In order to test this, we reacted isobutyraldehyde with 2 equiv of a 1:1 mixture of **6d** and **8d**. This led to the homoallyl alcohols **15d** and **16d** in a 2:1 ratio, showing that **6d** is only slightly more reactive. The small difference in reactivity between the geometric isomers of the crotylboronates is sufficient, however, to increase the proportion of **15d** formed in the reaction of isobutyraldehyde with **6d** and **8d**, respectively, which are not isomerically pure (cf. the data in Table I).

It should be noted that of the two crotylboronates the *E* isomer **6d** is the more reactive reagent. This contrasts to the aldol addition of the lithium enolates in which the (*E*)-enolate is less reactive than the (*Z*)-enolate by a factor of 7–8.[4,41] Even the sterically hindered (*Z*)-boronate **14** (isomeric purity >95% by ^{13}C NMR) added to benzaldehyde with high diastereoselectivity. The major isomer formed is tentatively assigned structure **19** based on the relative retention times on VPC.[39]



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The purpose of the present study was to establish the diastereoselectivity of the addition of **6d** and **8d** to aldehydes. For preparative applications the glycol component of the crotylboronate should be chosen such that it can easily be separated by distillation from the desired product alcohol. If this condition is met, isolated yields of homoallyl alcohols of either threo or erythro type were consistently above 85%.[42,43] Hence, crotylboronates such as **6d** and **8d** could be ideal reagents for diastereoselective C–C bond formation.[44] They are configurationally stable under the reaction conditions and add to aldehydes in an irreversible reaction with high kinetic diastereoselectivity. The elaboration of the resulting homoallyl alcohols to aldol-type compounds poses no problem.[42] The crotylboronate reagents can be subjected to chiral modification allowing asymmetric synthesis of homoallyl alcohols[1,42] as well as C–C bond formation under double stereodifferentiation.[43] Finally, the marked chemoselectivity[45] of the crotylboronates in favor of reaction with an aldehyde function is of advantage. These assets are a strong motivation to improve the preparation of stereohomogeneous **6c** and **8c**, which at present is still inconvenient.

Experimental Section

All temperatures quoted are uncorrected. Ether, 1,2-dimethoxyethane, tetrahydrofuran, and dichloromethane were refluxed for 24 h over NaH and subsequently filtered over basic alumina W 200 (activity super I, Woelm, Eschwege). The solvents were stored over 3-Å molecular sieves under dry nitrogen. All reactions involving organometallic compounds were carried out in flame-dried glassware under dry nitrogen. Silica gel 60 (70–230 mesh, ASTM, Merck, Darmstadt) served for chromatography and adsorptive purification. Analytical gas–liquid partition chromatography (GLC) was done with a Perkin-Elmer Gas chromatograph F-900 on a 150-ft capillary column with UCON, 53 psi N_2, at the temperatures indicated. Preparative GLC was done on a Varian Aerograph A 90 P-3 with a 5 ft × 0.25 in. column with 5% Carbowax on Chromosorb G (AW-DMCS, 130 mL of He/min) at the temperatures indicated. ^1H NMR spectra were recorded on Varian T-60, EM-360, HA-100, XL-100, and JEOL FX-100 spectrometers. Chemical shifts are given in δ values downfield from Me_4Si. ^{13}C NMR spectra were recorded on Varian CFT-20, XL-100, and JEOL FX-100 spectrometers. Chemical shifts are given in δ values downfield from Me_4Si. ^{11}B NMR spectra were recorded on Varian HA-100 and XL-100 spectrometers. Chemical shifts are given in δ values downfield from external BF_3–Et_2O. IR spectra were recorded on Perkin-Elmer IR 33 and Beckmann IR 157. Elemental analyses were performed by Mikroanalytisches Laboratorium Beller, Göttingen.

(*Z*)-Crotylpotassium (9).[46] (*Z*)-2-Butene, 6.0 g (0.108 mol) (Baker-Chemicals), was condensed at −78 °C into a silanized flask. Potassium *tert*-butoxide, 11.2 g (0.1 mol) (Merck, Darmstadt, dried for 48 h in vacuo at 80 °C), and 59.2 mL of a 1.69 M solution of *n*-butyllithium in *n*-hexane were added at −78 °C. The mixture was allowed to reach room temperature over 4 h. The resulting orange brown suspension of **9** was stirred for 14 h at room temperature.

Dimethyl (*Z*/*E*)-2-Butenyl-1-boronate (8e/6e). Fluorodimethoxyborane (**10**,[31] 9.18 g, 0.1 mol) was added dropwise to a stirred suspension of 0.1 mol of (*Z*)-crotylpotassium at −78 °C. After 1.5 h at this temperature the mixture was slowly warmed to room temperature. After a further 1.5 h the mixture was cooled again to −78 °C and 14.18 g (0.1 mol) of BF_3–Et_2O was added. After reaching room temperature the precipitate was filtered and the filtrate freed of solvent. The remaining material was fractionated over a 15-cm column: bp 51–52 °C (15 torr) 1.15 g (9%) of a 3:1 mixture of **8e** and **6e**; [lit.[47] bp 42–44 °C (15 torr)]; ^1H NMR as in ref 47; ^{13}C NMR ($CDCl_3$) (**8e**) 12.23, 51.14, 122.83, 125.56; ^{13}C NMR ($CDCl_3$) (**6e**) 17.71, 51.14, 124.58, 126.54.

(40) E. Favre and M. Gaudemar, *J. Organomet. Chem.*, **92**, 17 (1975).
(41) J. E. Dubois and P. Fellmann, *Tetrahedron Lett.*, 1225 (1975).
(42) R. W. Hoffmann and W. Ladner, *Tetrahedron Lett.*, 4653 (1979).
(43) R. W. Hoffmann and H.-J. Zeiß, *Angew. Chem.*, **92**, 218 (1980); *Angew. Chem., Int. Ed. Engl.*, **19**, 218 (1980).
(44) The only difficulties noted so far arose in the reaction of **8d** with sterically hindered aldehydes. In such cases the addition became rather sluggish, so that side reactions dominated or even won out in the addition.[11]
(45) R. W. Hoffmann, G. Feussner, G. Eichler, G. Schnelle, and S. Tabche, unpublished results, 1976–1980.
(46) M. Schlosser, J. Hartmann, and V. David, *Helv. Chim. Acta*, **57**, 1567 (1974).
(47) B. M. Mikhailov and V. F. Pozdnev, *Izv. Akad. Nauk SSSR, Ser. Khim*, 1477 (1967).

The major amount of the material remained in the pot. It consisted of methyl bis(2-butenyl-1)borinate and tricrotylboron which had ^{1}H NMR spectra corresponding to literature data.[47]

2-((*Z*)-2-Butenyl-1)-1,3-dimethyl-1,3,2-diazaborolane (8f). A suspension of **9** (0.05 mol) was diluted at −78 °C with 40 mL of precooled dimethoxyethane. This suspension was transferred to a cooled (−40 °C) funnel and added dropwise to a solution of 6.63 g (50 mmol) of **11**[33] in 20 mL of dimethoxyethane at −78 °C. After being stirred for 2 h the mixture was allowed to reach room temperature and was filtered. The filtrate was freed of solvent and the remainder was fractionated over a 15-cm column: bp 80–82 °C (15 torr): 3.27 g (43%) of a 1:10 mixture of **7f** and **8f**; ^{1}H NMR ($CDCl_3$) (**7f**) 1.05 (d, J = 7 Hz, 3 H), 1.60 (m, br, 1 H), 2.60 (s, 6 H), 3.07 (s, 4 H), 4.62–5.07 (m, 2 H), 5.50–6.32 (m, 1 H); ^{1}H NMR ($CDCl_3$) (**8f**) 1.37–1.80 (m, br, 2 H), 1.60 (d, J = 5 Hz, 3 H), 2.60 (s, 6 H), 3.07 (s, 4 H), 5.08–5.75 (m, 2 H); ^{13}C NMR ($CDCl_3$) (**7f**) 13.97, 33.61, 51.31, 110.25, 142.69; ^{13}C NMR ($CDCl_3$) (**8f**) 12.32, 33.61, 51.31, 121.57, 127.17; no signals of **6f**, which occur at 17.82, 33.61, 51.31, 123.56, 127.98; ^{11}B NMR ($CDCl_3$) (**8f**) 31.78. Anal. Calcd for $C_8H_{17}BN_2$: C, 63.10; H, 11.27; N, 18.42. Found: C, 63.23; H, 11.45; N, 18.25.

Bis(dimethylamino)chloroborane (12).[48] BCl_3 (70.2 g, 0.6 mol) (−20 °C) was added dropwise from a cooled funnel into a well-stirred solution of 121.4 g (1.2 mol) of triethylamine in 1 L of petroleum ether (40–60 °C) at 0 °C. While the resulting suspension was well stirred at room temperature, 54.1 g (1.2 mol) of dimethylamine was added dropwise from a cooled (−20 °C) dropping funnel over 3–4 h. The mixture was refluxed for 1 h and filtered under nitrogen. The voluminous filter cake was washed several times with 100 mL of petroleum ether. The combined filtrates were freed of solvent and distilled: bp 44 °C (15 torr); 58.8 g (73%) of **12** as a colorless liquid; ^{1}H NMR (CCl_4) 2.74.

If noticeable amounts of tris (dimethylamino)borane were present (δ 2.47) the exact amount of BCl_3 was added to comproportionate[49] these materials to **12**. If (dimethylamino)dichloroborane was present (δ 2.9) the appropriate amount of dimethylamine was added and, after filtration, the total material was redistilled.

(*Z*)-(2-Butenyl-1)-bis(dimethylamino)borane (8c). The suspension of 0.05 mol of (*Z*)-crotylpotassium in *n*-hexane at −78 °C was diluted with 30 mL of precooled THF. After 30 min 6.7 g (0.05 mol) of bis(dimethylamino)chloroborane (**12**) was added slowly. After being stirred for 1 h at −78 °C the mixture was allowed to reach room temperature and was freed of solvent. The glassy residue was kept in a 30 °C bath and the volatiles were condensed in vacuo into a cold trap, yielding 5.95 g of a colorless liquid which was subsequently fractionated on a 15-cm column: bp 69.5–72 °C (11 torr); 3.3 g (45%) of a 1:10 mixture of (1-butenyl-3)-bis(dimethylamino)borane (**7c**) and (*Z*)-(2-butenyl-1)-bis(dimethylamino)borane (**8c**). Pure **8c** was obtained on a 1-m spinning-band column: bp 100.8–101.4 °C (100 torr), 1 drop/min, reflux ratio 50:1; ^{1}H NMR ($CDCl_3$) 1.48–1.95 (m, br, 2 H), 1.62 (d, J = 5 Hz, 3 H), 2.68 (s, 12 H), 5.05–5.88 (m, 2 H); ^{13}C NMR ($CDCl_3$) 12.52, 40.15, 121.04, 128.64; ^{11}B NMR ($CDCl_3$) 33.19. Anal. Calcd for $C_8H_{19}BN_2$: C, 62.37; H, 12.43; N, 18.18. Found: C, 62.15; H, 12.49; N, 18.27.

2-((Z)-2-Butenyl-1)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8d). A solution of 4.90 g (32 mmol) of **8c** in 15 mL of THF was added dropwise to a solution of 3.77 g (32 mmol) of pinacol in 20 mL of THF at room temperature. After 14 h the product was freed of solvent and the crude material was purified by trap-to-trap distillation in vacuo: 5.80 g (100%) of **8d**; bp 37 °C (0.1 torr); ^{1}H NMR ($CDCl_3$) 1.25 (s, 12 H), 1.45–1.95 (m, 5 H), 5.12–5.95 (m, 2 H); ^{13}C NMR ($CDCl_3$) 12.30, 24.51, 82.85, 123.37, 124.84; ^{11}B NMR ($CDCl_3$) 32.90. Anal. Calcd for $C_{10}H_{19}BO_2$: C, 65.97; H, 10.52. Found: C, 66.05; H, 10.60.

Isopropylbis(dimethylamino)borane. A Grignard reagent was prepared from 12.3 g (0.1 mol) of 2-bromopropane and 2.60 g (0.1 mol) of magnesium in 40 mL of ether. Titration indicated a Grignard content of 0.08 mol. To this solution was added at room temperature a solution of 10.7 g (0.08 mol) of **12** in 50 mL of *n*-pentane. After being stirred over night the precipitate was filtered and the filtrate freed of solvent. Distillation over a 20-cm column yielded 10.7 g (95%) of product: bp 145.5 °C (760 torr); ^{1}H NMR ($CDCl_3$) 0.88–1.30 (m, br, 7 H), 1.70 (s, 12 H). Anal. Calcd for $C_7H_{19}BN_2$: C, 59.18; H, 13.48; N, 19.72. Found: C, 59.27; H, 13.36; N, 19.63.

2-(Isopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13). Pinacol (8.85 g, 75 mmol) in 50 mL of THF and 10.7 g (75 mmol) of isopropylbis(dimethylamino)borane in 20 mL of THF were reacted as for the preparation of **8d**: 12.8 g (100%); bp 44 °C (15 torr); ^{1}H NMR ($CDCl_3$) 0.98 (s, 7 H), 1.22 (s, 12 H); ^{13}C NMR ($CDCl_3$) 17.77, 24.56, 82.49. Anal. Calcd for $C_9H_{19}BO_2$: C, 63.56; H, 11.26. Found: C, 63.60; H, 11.17.

2-(2-Bromopropyl-2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. To a solution of 12.8 g (75 mmol) of **13** in 100 mL of *n*-pentane was added 12.06 g (75 mmol) of bromine and the mixture was irradiated with a 275-W light bulb. The bromine was decolorized under spontaneous reflux. Fractionation yielded 13.6 g (82%) of product: bp 46–48 °C (3 torr); ^{1}H NMR ($CDCl_3$) 1.28 (s, 12 H), 1.77 (s, 6 H); ^{11}B NMR ($CDCl_3$) 31.4. Anal. Calcd for $C_9H_{18}BBrO_2$: C, 43.42; H, 7.29; Br, 32.10. Found: C, 43.56; H, 7.30; Br, 31.96.

2-(1,1-Dimethyl-2-butenyl-1)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14). A 1.7 M solution of *tert*-butyllithium (20 mmol) in *n*-pentane was added dropwise at −120 °C to a solution of 1.2 g (10 mmol) of (*Z*)-1-bromopropene in 40 mL of THF/pentane (3:1).[50] After 1 h the mixture was brought to −90 °C and 2.5 g (10 mmol) of 2-(2-bromopropyl-2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added. The temperature rose over 1 h to −78 °C. Finally after room temperature was reached the volatile components were trap to trap distilled in vacuo. The condensate was freed of solvent, leaving 1.1 g (51%) which was used as prepared: ^{1}H NMR ($CDCl_3$) 1.18 (s, 6 H), 1.32 (s, 12 H), 1.70 (d, J = 6 Hz, 3 H), 5.28–5.52 (m, 2 H); ^{13}C NMR ($CDCl_3$) 14.82, 24.58, 25.89, 82.97, 123.34, 139.61.

(*E*)-(2-Butenyl-1)-bis(dimethylamino)borane (6c). A Grignard solution was prepared by adding a solution of 13.5 g (0.15 mol) of crotyl chloride in 20 mL of THF at 0 °C over 1 h to a suspension of 10.5 g (0.44 mol) of magnesium in 150 mL of THF. To the filtered Grignard solution was added at −15 °C a solution of 20.2 g (0.15 mol) of **12** in 40 mL of THF. After 1 h at room temperature the mixture was freed of solvent and triturated with 200 mL of petroleum ether. The magnesium chloride was filtered and the filtrate was freed of solvent to give 21.1 g (91%) of colorless liquid consisting of **6c**, **7c**, and **8c**. This material was heated for 75 h to 120 °C with 3.45 g (15 mmol) of $ZnBr_2$. The products were distilled in vacuo into a cold trap, giving 16.5 g (78%) of a 3:7 mixture of **8c** and **6c**, bp 70 °C (13 torr). Pure **6c** was obtained by distillation over a 1-m spinning-band column: bp 98.6 °C (100 torr), 1 drop/2 min, reflux ratio 100:1; ^{1}H NMR ($CDCl_3$) 1.5–2.0 (m, 2 H), 1.68 (d, J = 5 Hz, 3 H), 2.71 (s, 12 H), 4.95–5.90 (m, 2 H); ^{13}C NMR ($CDCl_3$) 18.06, 40.12, 122.90, 129.34. Anal. Calcd for $C_8H_{19}BN_2$: C, 62.37; H, 12.43; N, 18.18. Found: C, 62.44; H, 12.39; N, 18.12.

2-((*E*)-2-Butenyl-1)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6d). Was prepared as for **8d**: ^{1}H NMR ($CDCl_3$) 1.03 (s, 12 H), 1.50–2.00 (m, 2 H), 1.68 (d, J = 5 Hz, 3 H), 5.28–5.62 (m, 2 H); ^{13}C NMR ($CDCl_3$) 17.84, 24.60, 82.91, 125.00, 125.74. Anal. Calcd for $C_{10}H_{19}BO_2$: C, 65.67; H, 10.52; B, 5.94. Found: C, 66.14; H, 10.45; B, 5.81.

Reaction of Crotylboronates with Aldehydes. General Procedure. Variant A. Crotylboronate **6d** or **8d** (30 mmol) in 20 mL of ether was cooled to −78 °C. The aldehyde (30 mmol) was added and the mixture was allowed to reach room temperature. The next day 30 mmol of triethanolamine was added and the resulting suspension was stirred for 2 h. After filtration the filtrate was freed of solvent. ^{1}H NMR of the crude product indicated that ≥90% homoallyl alcohol was formed. The diastereomer ratio was checked at this stage by analytical GLC. Distillation over a 15-cm column or trap-to-trap distillation resulted in partial separation of the crude alcohol from pinacol and residual triethanolamine. Final purification was achieved by

(48) Following a general outline of H. Steinberg and R. J. Brotherton, "Organoboron Chemistry II", John Wiley & Sons, New York, 1966, p 90.

(49) R. J. Brotherton, A.-L. McCloskey, L. L. Petterson, and H. Steinberg, *J. Am. Chem. Soc.*, **82**, 6242 (1960).

(50) H. Neumann and D. Seebach, *Chem. Ber.*, 111, 2785 (1978).

preparative GLC.

Variant B. Crotylboronate **6d** or **8d** (10 mmol) in 10 mL of petroleum ether was cooled to −78 °C. The aldehyde (10 mmol) was added and the mixture was allowed to reach room temperature over 5 h. The next day 10 mmol of triethanolamine in 3 mL of CH_2Cl_2 was added and the resulting suspension was stirred for 2 h. The mixture was filtered over 30 g of silica gel, from which the product was eluted with CH_2Cl_2. The filtrate was freed of solvent and the diastereomer ratio was determined by analytical GLC. The alcohols were purified by preparative GLC.

(3*S,4*S**)-4-Hydroxy-3-methyl-4-phenylbutene (15a):** variant B; GLC temperature 130 °C (analytical), 165 °C (preparative); yield 80%; ^1H NMR ($CDCl_3$) 0.86 (d, J = 7 Hz, 3 H), 2.10 (s, 1 H), 2.50 (m, 1 H), 4.34 (d, J = 7 Hz, 1 H), 5.08–5.27 (m, 2 H), 5.64–6.08 (m, 1 H), 7.31 (s, 5 H) (cf. ref 37). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.51; H, 8.79.

(3*S,4*R**)-4-Hydroxy-3-methylpentene (15b):** variant B; GLC temperature 75 °C (analytical) 60 °C (preparative); yield 40%; ^1H NMR ($CDCl_3$) 1.05 (d, J = 7 Hz, 3 H), 1.20 (d, J = 7 Hz, 3 H), 1.70 (s, 1 H), 2.15 (sextet, J. = 7 Hz, 1 H), 3.4 (p, J = 7 Hz, 1 H), 4.95–5.30 (m, 2 H), 5.55–6.00 (m, 1 H). Anal. Calcd for $C_6H_{12}O$: C, 71.95; H, 12.08. Found: C, 72.04; H, 12.10.

(3*S,4*R**)-4-Hydroxy-3-methylhexene (15c):** variant B; GLC temperature 85 °C (analytical), 70 °C (preparative); yield 62%; ^1H NMR ($CDCl_3$) 1.00 (t, J = 7 Hz, 3 H), 1.08 (d, J = 7 Hz, 3 H), 1.13–1.77 (m, 3 H), 2.22 (sextet, J = 7 Hz, 1 H), 3.18–3.50 (m, 1 H), 4.95–5.30 (m, 2 H), 5.55–6.00 (m, 1 H). Anal. Calcd for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.80; H, 12.40.

(3*S,4*R**)-4-Hydroxy-3,5-dimethylhexene (15d):** variant B; GLC temperature 90 °C (analytical), 70 °C (preparative); yield 59%; ^1H NMR ($CDCl_3$) 0.90 (d, J = 7 Hz, 3 H), 0.95 (d, J = 7 Hz, 3 H), 1.00 (d, J = 6 Hz, 3 H), 1.45–2.00 (m, 2 H), 2.32 (sextet, J = 6 Hz, 1 H), 3.00–3.33 (m, 1 H), 4.95–5.30 (m, 2 H), 5.55–6.00 (m, 1 H). Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.82; H, 12.57.

(3*R,4*S**)-4-Hydroxy-3-methyl-4-phenylbutene (16a):** variant A; GLC temperature 130 °C (analytical), 170 °C (preparative); yield 22%; ^1H NMR ($CDCl_3$) 0.98 (d, J = 7 Hz, 3 H), 2.30–2.73 (m, 1 H), 2.52 (s, 1 H), 4.49 (d, J = 6 Hz, 1 H), 4.85–5.14 (m, 2 H), 5.50–5.93 (m, 1 H), 7.23 (s, 5 H) (cf. ref 37). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.63; H, 8.88.

(3*R,4*R**)-4-Hydroxy-3-methylpentene (16b):** variant A; GLC temperature 75 °C (analytical), 60 °C (preparative); yield 20%; ^1H NMR ($CDCl_3$) 1.04 (d, J = 7 Hz, 3 H), 1.16 (d, J = 6 Hz, 3 H), 2.07 (s, br, 1 H), 2.25 (sextet, J = 7 Hz, 1 H), 3.70 (p, J = 6 Hz, 1 H), 4.91–5.21 (m, 2 H), 5.58–6.00 (m, 1 H). Anal. Calcd for $C_6H_{12}O$: C, 71.95; H, 12.08. Found: C, 71.94; H, 11.92.

(3*R,4*R**)-4-Hydroxy-3-methylhexene (16c):** variant A; GLC temperature 85 °C (analytical), 70 °C (preparative); yield 26%; ^1H NMR ($CDCl_3$) 0.96 (t, J = 7 Hz, 3 H), 1.04 (d, J = 7 Hz, 3 H), 1.17–1.68 (m, 2 H), 1.76 (s, br, 1 H), 2.28 (sextet, J = 7 Hz, 1 H), 3.30–3.52 (m, 1 H), 4.90–5.22 (m, 2 H), 5.58–6.04 (m, 1 H). Anal. Calcd for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.59; H, 12.41.

(3*R,4*R**)-4-Hydroxy-3,5-dimethylhexene (16d):** variant A; GLC temperature 90 °C (analytical), 70 °C (preparative); yield 51%; ^1H NMR ($CDCl_3$) 0.92 (d, J = 7 Hz, 3 H), 0.93 (d, J = 7 Hz, 3 H), 1.03 (d, J = 7 Hz, 3 H), 1.60 (br s, 1 H), 1.71 (octet, J = 7 Hz, 1 H), 2.37 (sextet, J = 7 Hz, 1 H), 3.17 (t, J = 7 Hz, 1 H), 4.88–5.21 (m, 2 H), 5.58–6.02 (m, 1 H). Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.99; H, 12.49.

(4*R,5*S**)-5-Hydroxy-2,4-dimethyl-5-phenylpentene (19):** variant A; GLC temperature 150 °C (analytical), 170 °C (preparative); yield 42%; ^1H NMR ($CDCl_3$) 0.98 (d, J = 6.5 Hz, 3 H), 1.50 (d, J = 2 Hz, 3 H), 1.60 (d, J = 2 Hz, 3 H), 2.08 (br s, 1 H), 2.30–3.08 (m, 1 H), 4.41 (d, J = 6.5 Hz, 1 H), 4.70–5.02 (m, 1 H), 7.15 (s, 5 H). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.95; H, 9.53.

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Registry No. 6c, 69611-00-3; **6d**, 69611-02-5; **6c**, 76347-09-6; **7c**, 51783-26-7; **7f**, 76347-10-9; **8c**, 69610-99-7; **8d**, 69611-01-4; **8e**, 76347-11-0; **8f**, 76347-12-1; **9**, 59304-72-2; **10**, 367-46-4; **11**, 17739-11-6; **12**, 6562-41-0; **13**, 76347-13-2; **14**, 76347-14-3; **15a**, 52922-10-8; **15b**, 1538-22-3; **15c**, 1589-07-7; **15d**, 1502-90-5; **16a**, 52922-19-7; **16b**, 1538-23-4; **16c**, 1538-21-2; **16d**, 1502-91-6; **19**, 76347-15-4; (*Z*)-2-butene, 590-18-1; boron trichloride, 10294-34-5; dimethylamine, 124-40-3; pinacol, 76-09-5; isopropylbis(dimethylamino)borane, 65478-40-2; 2-bromopropane, 75-26-3; 2-(2-bromoprop-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 76347-16-5; (*Z*)-1-bromopropene, 590-13-6; (*E*)-crotyl chloride, 4894-61-5; benzaldehyde, 100-52-7; acetaldehyde, 75-07-0; propionaldehyde, 123-38-6; isobutyraldehyde, 78-84-2.