Notes

Addition Reactions of Bis(pinacolato)diborane(4) to Carbonyl Enones and Synthesis of (pinacolato)$_2$BCH$_2$B and (pinacolato)$_2$BCH$_2$CH$_2$B by Insertion and Coupling

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Summary: The title compound adds to α,β-unsaturated carbonyls to give the products of 1,4-addition after hydrolysis of the intermediate boron enolates, in 68−86% isolated yield (four examples). In addition, we discovered that diazomethane reacts with bis(pinacolato)diborane to insert methylene to give (pinacolato)$_2$BCH$_2$B in 83% yield. An alternative synthesis involved coupling of (pinacolato)BCH$_2$I with various metals.

Boronic acids have a variety of important uses and applications. They are highly valued synthetic intermediates[1] and also possess significant biological activity.[2] Hydroboration,[3] haloboration,[4] reactions with organometallics,[5] and homologation[6] are important protocols for their preparation. A more recent and very convenient method for the preparation of boronic acids involves diborane(4) derivatives.[7] In particular, tetraalkoxydiborane(4) compounds have been shown to add to alkenes,[8] alkynes,[9] 1,3-butadienes,[10] allylic acetates,[11] methylenecyclopropanes,[12] substituted 4-arylbut-3-en-2-ones,[13] and various other substrates.[14] Mechanistic and theoretical studies of diboration have also been reported.[15] The latter reaction reported by Marder and Norman et al. is particularly interesting, in that it opens the way for addition of diborane(4) compounds to other α,β-unsaturated systems. Three-membered[16] and five-membered[17] aminodiborane(4) derivatives undergo insertion reactions with CO and isonitrile to give inter-

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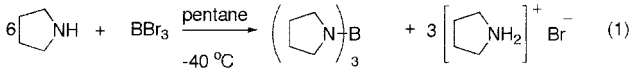
mediates that rearrange to interesting compounds. In the following we report our findings on addition of bis(pinacolato)diborane(4) to cyclic enones, *trans*-cinnamaldehyde, and methyl *trans*-cinnamate and CH_2N_2 insertion into the boron−boron bond.

Results and Discussion

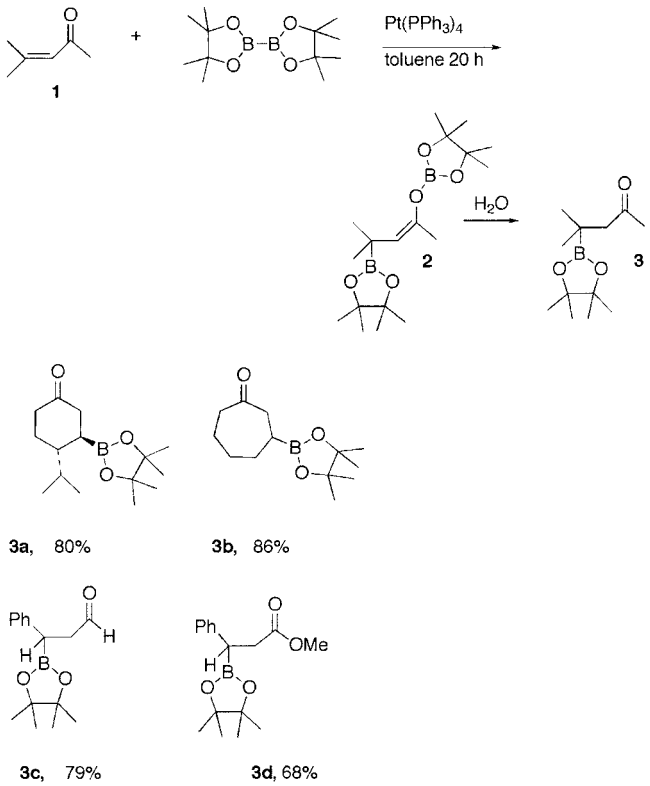
Preparation of Bis(pinacolato)diborane(4). Bis(pinacolato)diborane(4) is usually prepared from bis(dimethylamino)haloborane.[18] We had difficulty in obtaining dimethylamine or its derivatives from commercial sources and sought an alternative amine.[19] Various $(R_2N)_2BX$, i.e., with R = Et, *i*-Pr, etc. and X = Cl, Br, failed to give B−B compounds in the dehalogenation step. However, dipyrrolidinoamine behaved like dimethylamine in that bis(pyrrolidino)bromoborane was debrominated by sodium to give tetrakis(pyrrolidino)diborane(4).[20] The precursor, tris(pyrrolidino)borane, is readily prepared from BBr_3 in pentane at −40 °C and 6 equiv of pyrrolidine (eq 1). After the bromide salt was filtered, distillation afforded tris(pyrrolidino)borane in 81% yield: mp 40 °C, bp 105 °C/1.5 mmHg.



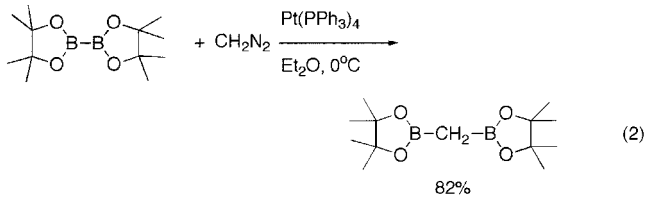
Addition Reactions of Bis(pinacolato)diborane(4). On the basis of the reported 1,4-addition of catecholborane to α,β-unsaturated carbonyl compounds,[21] Marder and Norman et al. showed that bis(pinacolato)diborane(4) adds to 4-arylbut-3-en-2-ones to give hydrolysis sensitive boron enolates that readily rearrange to β-boryl ketones.[13] Here we report that bis(pinacolato)diborane(4) also adds to 4-isopropylcyclohexenone, cycloheptenone, *trans*-cinnamaldehyde, and methyl *trans*-cinnamate in a 1,4-manner to give β-boryl carbonyl compounds (**3a**−**d**) after hydrolysis (Scheme 1).

The intermediate enol borates, **2**, are moisture-sensitive and were not isolated. Compounds **3a**−**d** are stable, and their structures were determined by ^1H, ^{13}C, and ^{11}B NMR, GCMS, and elemental analyses. The methylene protons in compounds **3a**,**c**,**d** are diastereotopic and gave two signals in the ^1H NMR. The assignments were confirmed by 2D C−H HETCOR and APT experiments. The $^3J_{H-H}$ coupling constants (for **3c**,**d**) are consistent with the assignments. In the ^1H and ^{13}C NMR spectra of compounds **3c**,**d** the diastereotopic methyl groups in pinacol gave different signals. This was not observed in compounds **3a,b**. However, the diastereotopic isopropyl methyl groups in **3a** showed different signals. This may partially be due to hindered rotation of the isopropyl group next to the bulky dioxaborolane group. The peaks of the isopropyl methyl groups are located at 0.82 and 0.97 ppm, showing shifts of 0.1 ppm upfield and 0.4 ppm downfield, respectively, compared to the starting material. The trans relative stereochemistry of **3a** was determined by *J*-resolved homonuclear coupling.

Scheme 1. 1,4-Addition of Bis(pinacolato)diborane to α,β-Unsaturated Carbonyls



Insertion of CH_2N_2 and Preparation of $(pinacolato)_2BCH_2B$ and $(pinacolato)_2BCH_2CH_2B$. BCB compounds are usually prepared by double hydroboration of terminal alkynes with dialkylboranes.[22] They are interesting precursors to *gem*-bimetallics such as BCLi[23] and BCMgX.[24] We report here that the parent compound, $(pinacolato)_2BCH_2B$, can be prepared in high yield by reaction with diazomethane (eq 2). This reaction has not been described before.



The reaction of diazomethane with bis(pinacolato)diborane(4) gave good results. Insertions into $(R_2N)_2B-B(NR_2)_2$, where R = Me, Et, Pr, were not successful. Two mechanisms for the insertion are possible: (1) addition/1,2-migration to and from boron as in the Hooz reac-

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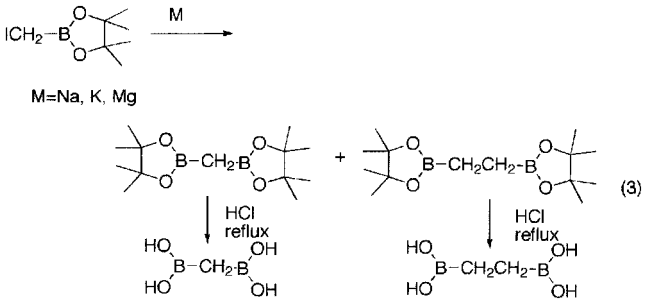
Table 1. Coupling of ICH_2BX_2 with Different Metals[a]

entry	metal/excess, %	solvent	BCCB:BCB[b]	% yield[c]
1	Na/15	benzene	34:66	94
2	Na/35	benzene	96:4	94
3	Na/15	toluene	84:16	90
4	Na/15	THF	68:32	85
5	K/15	benzene	67:33	88
6	Mg/60	ether	50:50	85

[a] X_2 = pinacolato. Conditions: overnight reflux. [b] Determined by GCMS. [c] Isolated yield for both BCCB and BCB before purification by column chromatography.

tion[25] or (2) oxidative addition of B−B to a Pt(0) complex, insertion of CH_2 into the Pt−B bond, migration, and reductive elimination.[11] No insertion was observed without Pt(0); therefore, the latter mechanism is probably operating. However, reaction of ethyl diazoacetate with bis(pinacolato)diborane(4) with or without a transition metal did not give any products.

We developed an alternative synthesis of diborylmethane and 1,2-diborylethane from (pinacolato)BCH_2I[26] by coupling with metals (eq 3). The quantity and the



metal determine the ratio of BCB/BCCB (Table 1). The best results for BCCB were obtained by using a 35% excess of Na, whereas for BCB a 15% excess of Na was superior. Both (pinacolato)$_2BCH_2B$ and (pinacolato)$_2$-BCH_2CH_2B could be hydrolyzed to the free bis boronic acids by refluxing for 3 h in aqueous HCl (eq 3). Both BCCB and the BCB esters and acids are stable to moisture and heat. The esters are extremely soluble in hydrocarbon and polar solvents, but the acids are soluble only in water and DMSO. The methylene protons in the BCCB ester (0.85 ppm) are shifted upfield relative to the protons in the BCB compound (1.25 ppm). Both the BCB and BCCB esters showed M^+−Me in their MS spectra. A prominent $M^+ - 141$ peak at *m/e* 141 was observed for the BCCB ester. However, a prominent $M^+ - 184$ peak at *m/e* 84 was observed for the BCB ester.

Experimental Section

General Comments. All reactions were carried out under a nitrogen atmosphere using vacuum line and glovebox techniques. Solvents were purified by distillation from appropriate drying agents under a nitrogen atmosphere. Starting materials were purchased from commercial suppliers and used without further purification.

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution with a Varian Unity spectrometer (300 or 75 MHz) using Me_4-Si as an internal standard. ^{11}B NMR spectra were recorded with a Bruker MSL-400 spectrometer (128 MHz) using $BF_3{\cdot}OEt_2$ as an external standard. GCMS analyses were performed on an HP GCMS instrument (Model GCD PLUS), with an EI detector and 30 m methyl silicone column.

Diboron Reagent. Bis(pinacolato)diborane(4) was prepared from tetrakis(pyrrolidino)diborane(4) by Wurtz coupling of bis(pyrrolidino)bromoborane and then obtained by solvolysis of tetrakis(pyrrolidino)diborane(4) with 2 equiv of pinacol in benzene solution at room temperature.[20]

General Procedure for Hydroboration of Various Unsaturated Carbonyl Compounds. A dry nitrogen-flushed 50 mL flask equipped with a magnetic stirring bar and a reflux condenser attached to a mercury bubbler through a septum inlet was charged with $Pt(PPh_3)_4$ (56 mg, 0.045 mmol) and bis-(pinacolato)diborane(4) (381 mg, 1.5 mmol). The carbonyl compound (1.4 mmol) dissolved in 20 mL of toluene was then added. After the mixture was stirred overnight at 110 °C, the toluene was removed under vacuum. The mixture was washed with a small amount of cold water and extracted with pentane. The extracts were dried over anhydrous magnesium sulfate. The pentane was removed under vacuum, and the product was purified by silica gel column chromatography, with 10% ether/petroleum ether as eluent.

3a: 80% (0.3 g) yield. ^1H NMR ($CDCl_3$): δ 0.82 (d, 3H, CH_3, $^3J_{H-H}$ = 6.6 Hz), 0.97 (d, 3H, CH_3, $^3J_{H-H}$ = 6.6 Hz), 1.23 (s, 12H, CH_3), 1.46 (m, 1H, CHB), 1.53 (m, 1H, CH_2), 1.78 (m, 1H, CH), 1.81 (m, 1H, CH), 1.98 (m, 1H, CH_2), 2.3 (m, 2H, CH_2(C=O)), 2.37 (m, 2H, CH_2(C=O)). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.67 (CH_3), 21.75 (CH_3), 24.65 (CH_3), 27.20 (CH_2), 30.75 (CH), 41.72 (CH_2), 41.70 (CH_2), 42.64 (CH), 83.37 (*C*CH_3), 212.54 (C=O) (*C*HB cannot be detected). ^{11}B NMR ($CDCl_3$): δ 33.46. Anal. Calcd for $C_{15}H_{27}O_3B$: C, 67.73; H, 10.35. Found: C, 67.35; H, 10.56. MS (EI): *m/z* (%) 266 (M^+, 5.74), 251 (2.06), 209 (12.87), 165 (29.64), 141 (9.35), 123 (47.74), 83 (100), 69 (25.47), 41 (78.36), 28 (19.75).

3b: 86% (0.29 g) yield. ^1H NMR ($CDCl_3$): δ 1.21 (s, 12H, CH_3), 1.44 (m, 2H, CH_2), 1.59 (m, 2H, CHB), 1.84 (m, 2H, CH_2), 1.92 (m, 2H, CH_2), 2.50 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.85 (CH_2), 30.60 (CH_2), 31.39 (CH_2), 43.29 (CH_2), 44.37 (CH_2), 82.98 (*C*CH_3), 215.06 (C=O), 20.11 (*C*HB, broad). ^{11}B NMR ($CDCl_3$): δ 33.78. Anal. Calcd for $C_{13}H_{23}O_3B$: C, 65.60; H, 9.76. Found: C, 65.38; H, 9.72. MS (EI): *m/z* (%) 238 (M^+, 6.47), 223 (3.60), 210 (1.28), 180 (100), 165 (14.85), 152 (33.29), 129 (23.47), 110 (25.60), 95 (34.39), 83 (57.08), 69 (31.28), 55 (62.41), 41 (73.63), 28 (8.31).

3c: 74% (0.27 g) yield. ^1H NMR ($CDCl_3$): δ 1.66 (s, 6H, CH_3), 1.24 (s, 6H, CH_3), 2.81 (m, 2H, CH_2, $^3J_{H-H}$ = 5.15, $^2J_{H-H}$ = 11.21, $^3J_{H-H}$ = 18.4 Hz), 3.04 (dd, 1H, CH, $^3J_{H-H}$ = 5.15, $^3J_{H-H}$ = 18.4 Hz), 7.25 (m, 5H, Ph), 9.80 (s, 1H, C=O(H)). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.46 (CH_3), 24.53 (CH_3), 47.54 (CH_2), 83.64 (*C*CH_3), 125.72 (para CH), 128.42 (ortho or meta CH), 128.57 (ortho or meta CH), 141.18 (ipso), 201.86 (C=O) (*C*HB cannot be detected). ^{11}B NMR ($CDCl_3$): δ 32.88. Anal. Calcd for $C_{15}H_{21}O_3B$: C, 69.29; H, 8.16. Found: C, 69.83; H, 7.98. MS (EI): *m/z* (%) M^+ 260, 245 ($M^+ - 15$, 1.43), 202 (4.96), 177 (6.25), 160 (12.75), 145 (30.89), 132, (56.48), 117 (100), 105 (27.11), 77 (31.50), 84 (49.64) 59 (29.06), 43 (91.38).

3d: 68% (0.28 g) yield. ^1H NMR ($CDCl_3$): δ 1.17 (s, 6H, CH_3), 1.22 (s, 6H, CH_3), 2.67 (dd, 1H, CH_2, $^3J_{H-H}$ = 5.2, $^2J_{H-H}$ = 11.4 Hz), 2.74 (dd, 1H, CH_2, $^2J_{H-H}$ = 11.4, $^3J_{H-H}$ = 18.35 Hz), 2.89 (dd, 1H, CH, $^3J_{H-H}$ = 5.2, $^3J_{H-H}$ = 18.35 Hz), 3.65 (s, 3H, OCH_3), 7.25 (m, 5H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.45 (CH_3), 24.56 (CH_3), 37.10 (OCH_3), 51.57 (CH_2), 83.56 (*C*CH_3), 125.67 (para CH), 128.16 (ortho or meta CH), 128.38 (ortho or meta CH), 141.27 (ipso), 173.82 (C=O) (*C*HB cannot be detected). ^{11}B NMR ($CDCl_3$): δ 32.98. Anal. Calcd for $C_{16}H_{23}O_4B$: C, 66.26; H, 8.01. Found: C, 66.63; H, 7.95. MS (EI): *m/z* (%) 290 (M^+, 16.40), 259 (4.59), 232 (13.97), 201

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(1.44), 190 (20.94), 159 (3.70), 146 (21.98), 131 (54.35), 105 (28.44), 104 (100), 83 (54.65), 77 (11.91), 59 (23.15), 43 (26.51).

Preparation of (pinacolato)$_2$BCH$_2$B by Diazomethane Insertion. A dry nitrogen-flushed 50 mL flask equipped with a magnetic stirring bar was charged with Pt(PPh$_3$)$_4$ (74.7 mg, 0.06 mmol) and bis(pinacolato)diborane(4) (508 mg, 2 mmol); 20 mL of diethyl ether was then added to the mixture. Diazomethane[27] (0.0168 mg/mL in ether, 5 mL, 0.084 mg) was slowly added to the mixture at 0 °C. After an additional 2 h the solution was warmed to room temperature and stirred overnight. The solvent was removed under vacuum, and the residue was extracted with pentane, which was then removed under vacuum, and the product was purified by silica gel column chromatography with 10% ether/petroleum ether as eluent to give the product as a colorless oil in 83% (0.44 g) yield. ^{1}H NMR ($CDCl_3$): δ 1.23 (s, 24H, CH_3), 1.25 (s, 2H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 25.11 (CH_3), 83.25 (CCH_3), (*C*HB cannot be detected). ^{11}B NMR ($CDCl_3$): δ 34.12. Anal. Calcd for $C_{13}H_{26}O_4B_2$: C, 58.26; H, 9.7. Found: C, 58.63; H, 9.65. MS (EI): *m*/*z* (%) 268 (M^+, 1.01), 253 (40.65), 238 (2.59), 210 (1.99), 195 (1.29), 168 (9.97), 153 (8.27), 126 (11.45), 127 (8.45), 113 (3.89), 84 (100), 69 (16.17), 55 (10.92), 41 (16.39).

General Procedure for the Coupling Reaction of (pinacolato)BCH$_2$I. A solution of (pinacolato)boratamethylene iodide, (pinacolato)BCH$_2$I[26] (5.36 g, 0.02 mol), in 10 mL of the indicated solvent was added slowly to a mixture of the metal (0.02 mol + excess) and 15 mL of solvent and heated at reflux overnight. The resulting solid was filtered, and the solvent was then removed under vacuum. See Table 1 for detailed reaction conditions. The two products were purified by silica gel column chromatography with 10% ether/petroleum ether as eluent to give pure colorless oily compounds.

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(pinacolato)$_2$BCH$_2$CH$_2$B. ^{1}H NMR ($CDCl_3$): δ 0.85 (s, 4H, CH_2), 1.24 (s, 24H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 4.45 (s, broad, CH_2B), 24.72 (CH_3), 82.70 (CCH_3). ^{11}B NMR ($CDCl_3$): δ 32.98. Anal. Calcd for $C_{14}H_{28}O_4B_2$: C, 59.62; H, 10.00. Found: C, 59.91; H,10.07. MS (EI): *m*/*z* (%) 282 (M^+), 267 (M^+ − 15, 1.40), 253 (0.03), 224 (17.06), 209 (0.06), 185 (1.69), 167 (5.74), 141 (100), 101 (10.09), 84 (31.38), 69 (8.5), 55 (10.33), 41 (12.53).

(HO)$_2$BCH$_2$CH$_2$B(OH)$_2$. Four milliliters of 6 M HCl was added with stirring to (pinacolato)$_2$BCH$_2$CH$_2$B (0.7 g, 2.6 mmol) dissolved in 5 mL of water. The mixture was heated at reflux for 3 h. The water was then removed under vacuum and the residue washed twice with ether and dried under vacuum to give the product as a pure solid in 90% (0.28 g) yield, mp 262 °C. Anal. Calcd for $C_2H_8O_4B_2$: C, 20.41; H, 6.85. Found: C, 20.19; H, 6.76. ^{1}H NMR (DMSO): δ 0.55 (s, 4H, CH_2), 7.28 (s, broad, 4H, OH). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 9.13 (s, broad, CH_2B). ^{11}B NMR (DMSO-d_6): δ 33.78.

(HO)$_2$BCH$_2$B(OH)$_2$. Three milliliters of 6 M HCl was added with stirring to (pinacolato)$_2$BCH$_2$B (0.35 g, 1.31 mmol) dissolved in 5 mL of water. The mixture was heated at reflux for 3 h. The water was then removed under vacuum and the residue washed twice with ether and dried under vacuum to give the product as a pure solid in 93% (0.12 g) yield; mp 245 °C. Anal. Calcd for $CH_6O_4B_2$: C, 11.58; H, 5.85. Found: C, 11.42; H, 5.91. ^{1}H NMR (DMSO): δ 1.18 (s, 2H, CH_2), 7.31 (s, broad, 4H, OH). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 10.21 (s, broad, CH_2B). ^{11}B NMR (DMSO-d_6): δ 34.93.

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