Formation of a 1,3,2,4-Dioxadiborinanide, a Novel Boron-Containing Heterocycle, by Hydrolysis of a Tetracoordinate 1,2-Oxaboretanide and Its Crystal Structure

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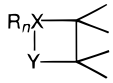
Summary: New reactivity of tetracoordinate 1,2-oxaboretanides was revealed by the formation of a 1,3,2,4-dioxadiborinanide, a novel boron-containing heterocycle. X-ray crystallographic analysis indicated that it has distorted-tetrahedral and trigonal-planar boron atoms and that the six-membered ring is boatlike. Furthermore, an interesting crystal-packing view was observed.

Introduction

In the course of our studies on heteracyclobutanes **1** containing a highly coordinate main-group element at the position adjacent to the heteroatom,[1] we have reported the synthesis of tetracoordinate 1,2-oxaboretanides **2a**, i.e., intermediates of the Boron-Wittig reaction under basic conditions.[2,3] To investigate the substituent effect, we tried to synthesize the 3-unsubstituted derivative **2b**. We now report the formation and crystal structure of a 1,3,2,4-dioxadiborinanide, a novel boron-containing heterocycle, which was obtained instead of **2b**.

Results and Discussion

Deprotonation of β-hydroxyalkylborane **3**, which was prepared from (lithiomethyl)dimesitylborane,[4] with KH in the presence of 18-crown-6 followed by workup in air afforded the 1,3,2,4-dioxadiborinanide **4**, in sharp contrast to the synthesis of **2a** (Scheme 1).[2]



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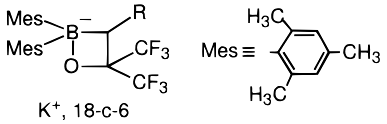
X= Si⁻, Ge⁻, Sn⁻, P, S, Se

Y= O, N



K^+, 18-c-6

2a: R= CH_3

2b: R= H

In the ^1H and ^{13}C NMR spectra of **4** the signals due to the mesityl group disappeared. The ^{19}F NMR spectrum of **4** showed two sets of A_3B_3 signals with centers at δ_F −78.31, −78.57, −78.84, and −80.39 (^4J(F,F) = 10 Hz), indicating the presence of a chiral center. In the ^{11}B NMR spectrum two signals were observed at δ 4.0 and 30.0, which can be assigned to tetracoordinate and tricoordinate boron nuclei, respectively.

The X-ray crystallographic analysis of **4** indicated that it has a 1,3,2,4-dioxadiborinanide structure (Figure 1).[5] This is the first example of a 1,3,2,4-dioxadiborinane ring, although a 1,4,2,5-dioxadiborinane derivative has been reported.[6] The conformation of the six-membered ring was boatlike, and the geometries of B1 and B2 atoms were distorted tetrahedral and trigonal planar, respectively. The bond lengths B1−O1 (1.53(1) Å), B1−O2 (1.51(1) Å), and B1−O3 (1.43(1) Å) containing a tetracoordinate boron atom are significantly longer than those of B2−O2 (1.36(1) Å) and B2−O4 (1.34(1) Å), containing a tricoordinate boron atom, because the

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(1) Kawashima, T.; Okazaki, R. *Synlett* **1996**, 600−608 and references therein. Ohno, F.; Kawashima, T.; Okazaki, R. *J. Am. Chem. Soc.* **1996**, *118*, 697−698. Kawashima, T.; Soda, T.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1096−1098. Kawashima, T.; Ohno, F.; Okazaki, R.; Ikeda, H.; Inagaki, S. *J. Am. Chem. Soc.* **1996**, *118*, 12455−12456. Kawashima, T.; Watanabe, K.; Okazaki, R. *Tetrahedron Lett.* **1997**, *38*, 551−554. Kawashima, T.; Okazaki, R.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2500−2502. Ohno, F.; Kawashima, T.; Okazaki, R. *Chem. Commun.* **1997**, 1671−1672. Kawashima, T.; Naganuma, K.; Okazaki, R. *Organometallics* **1998**, *17*, 367−372.

(2) Kawashima, T.; Yamashita, N.; Okazaki, R. *J. Am. Chem. Soc.* **1995**, *117*, 6142−6143.

(3) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press: London, 1988; pp 338−339. Pelter, A.; Smith, K. In *Comprehensive Organic Synthesis: Selectivity, Strategy, and Efficiency in Modern Synthetic Chemistry*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 1, pp 487−503. Pelter, A. *Pure Appl. Chem.* **1994**, *66*, 223−233.

(4) Pelter, A.; Singaram, B.; Williams, L.; Wilson, J. W. *Tetrahedron Lett.* **1983**, *24*, 623−626. Pelter, A.; Singaram, B.; Williams, L.; Wilson, J. W. *Tetrahedron* **1993**, *49*, 2965−2978.

(5) Crystal data: $C_{20}H_{31}B_2F_{12}KO_{11}$, FW = 736.16, crystal dimensions (mm) 0.60 × 0.35 × 0.05, triclinic, space group $P\bar{1}$ (No. 2), a = 10.578(2) Å, b = 16.819(3) Å, c = 10.064(2) Å, α = 97.79(2)°, β = 115.52(1)°, γ = 98.21(2)°, V = 1559.6(7) Å^3, Z = 2, ρ_{calcd} = 1.567 g cm^{-3}, μ = 2.93 cm^{-1}, F(000)= 752.00. The intensity data ($2\theta < 55.1°$) were collected at 296 K on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.716 09 Å), and the structure was solved by direct methods (SIR97). The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1932 observed reflections ($I > 3.00\sigma(I)$) and 418 variable parameters with R (R_w)= 0.070 (0.040).

(6) Hillman, M. E. D. *J. Am. Chem. Soc.* **1962**, *84*, 4715−4720. Hillman, M. E. D. *J. Am. Chem. Soc.* **1963**, *85*, 1626−1628. Patzold, P.; Redenz-Stormanns, B.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 900−902.

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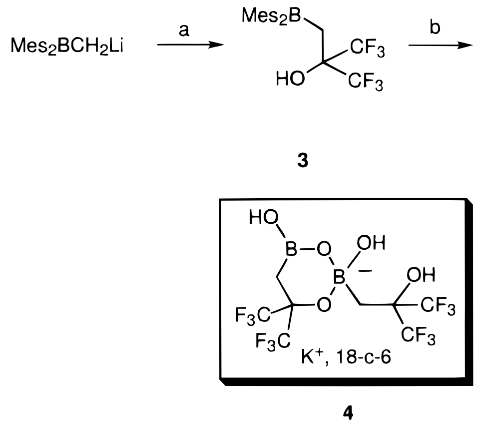
Scheme 1[a]



[a] Legend: (a) excess $(CF_3)_2C{=}O$, THF, −78 °C, 2.5 h; aqueous NH_4Cl, −78 °C; (b) KH, 18-c-6, THF, −78 °C, 30 min; −78 to +25 °C; THF, 25 °C, 1 h.

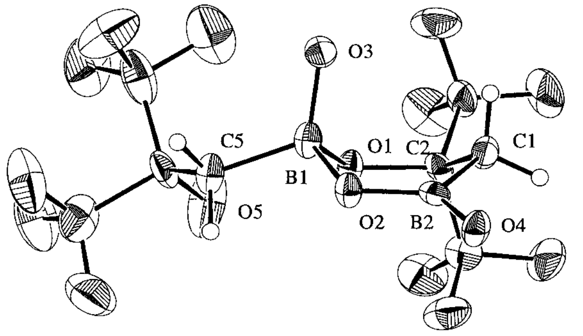
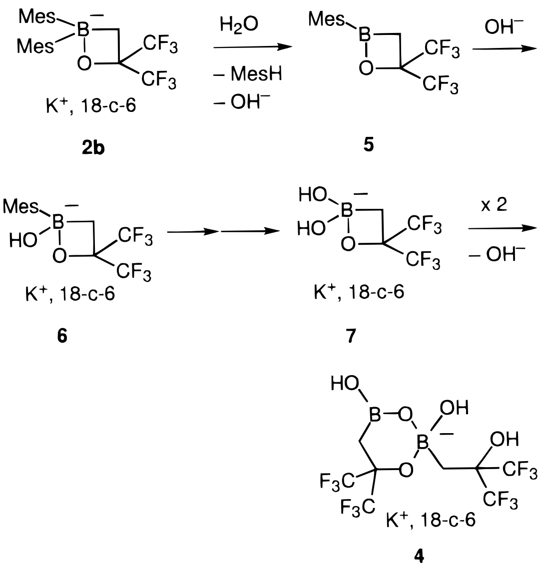


Figure 1. ORTEP drawing of **4** with thermal ellipsoid plots (30% probability). K^+ and 18-c-6 are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): B1−O1 = 1.53(1); B1−O2 = 1.51(1); B1−O3 = 1.43(1); B1−C3 = 1.65(1); B2−O2 = 1.36(1); B2−O4 = 1.34(1); B2−C1 = 1.60(1); C1−C2 = 1.53(1); C2−O1 = 1.409(9); O1−B1−O2 = 107.7(8); O1−B1−O3 = 113.8(8); O1−B1−C3 = 103.7(7); O2−B1−O3 = 107.4(8); O2−B1−C3 = 106.1(8); O3−B1−C3 = 117.6(8); O2−B2−O4 = 122.1(9); O2−B2−C1 = 116.9(8); O4−B2−C1 = 121.0(9).

bonds of the latter have some degree of double-bond character and hence become unusually short.[7] These long and short bond lengths are in ranges of 1.43−1.55 and 1.28−1.43 Å for the B−O bond lengths of tetra- and tricoordinate boron atoms, respectively.[8] The bonds B1−C3 (1.65(1) Å) and B2−C1 (1.60(1) Å) are reasonable compared with those (1.62−1.69 Å) of the previously known tetracoordinate borates.[9] The smallest and largest bond angles around the B1 atom are 103.7(7)° (O2−B1−C3) and 117.6(8)° (O3−B1−C3), respectively, which considerably deviate from a tetrahedral angle, showing that B1 is in a distorted-tetrahedral environment. The sum of bond angles around the B2 atom was 360.0°, indicating that the B2 atom has a trigonal-planar geometry.

As shown in Figure 2, two oxygen atoms of the 4-hydroxy groups of two dioxadiborinanide anions coordinate to the same K1 cation, while two oxygen atoms of their alcoholic hydroxy groups coordinate to different K2 cations, respectively, making a linear column, where K1 and K2 cations are located at centrosymmetrical positions. Intermolecular hydrogen bondings between the 2-OH group of the molecule in a column and the O1 atom of the neighboring molecule in the next column make a two-dimensional supramolecular sheet structure. The interatomic distances (2.909(6) Å) between O and K1 atoms are shorter than those (3.714(7) Å) between O and K2, probably because the former hydroxy groups are directly attached to the borate anion and are attracted to the cation center by electrostatic attraction more than the latter.

Scheme 2. Plausible Mechanism



Thermolysis (60 °C, 30 h, in $CDCl_3$) of **2b** in a sealed NMR tube gave the corresponding alkene (60%), in sharp contrast to that of **2a**, which gave the complex mixture in solution.[2]

The peak due to mesitylene was observed at *m*/*z* 120, but that due to mesitol was not found in the GC-MS spectra of the reaction mixture, indicating that the mesityl−boron bond of **2b** was cleaved by the hydrolysis. Although three intermediates were observed when the formation reaction of **4** was monitored by ^{19}F and ^{11}B NMR spectroscopy,[10] and they were tentatively assigned to tricoordinate 1,2-oxaboretane **5** (δ_B 49 (br s), δ_F −79.99 (s)), 2-hydroxy-1,2-oxaboretanide **6** (δ_B 3.6 (br s), δ_F −77.88 (q, ^4J(F,F) = 9.8 Hz), −80.38 (q, ^4J(F,F) = 9.8 Hz)), and 2,2-dihydroxy-1,2-oxaboretanide **7** (δ_B 3.6 (br s), δ_F −78.37 (s)) (Scheme 2),[11] the detailed mechanism still remains unclear at present.

Experimental Section

All melting points were uncorrected. All solvents used in the reactions were purified by the reported methods. THF was purified by distillation from benzophenone ketyl before use. All reactions were carried out under an argon atmosphere unless otherwise noted. Dry column chromatography was

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(7) Coulson, C. A.; Dingle, T. W. *Acta Crystallogr.* **1968**, *B24*, 153−155. Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 7029−7036.

(8) Odom, J. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 1, pp 253−310.

(9) Farmer, J. B. *Adv. Inorg. Chem. Radiochem.* **1982**, *25*, 187−237.

(10) The ^{19}F and ^{11}B NMR spectroscopy can provide useful information on the nonequivalence between two geminal trifluoromethyl groups and on the coordination number of the central boron, respectively.

(11) A similar formation of a six-membered ring from **7** is well-known to have taken place in metal-hydrated borates: Edwards, J. O.; Ross, V. *J. Inorg Nucl. Chem.* **1960**, *15*, 329−337. See also ref 7.

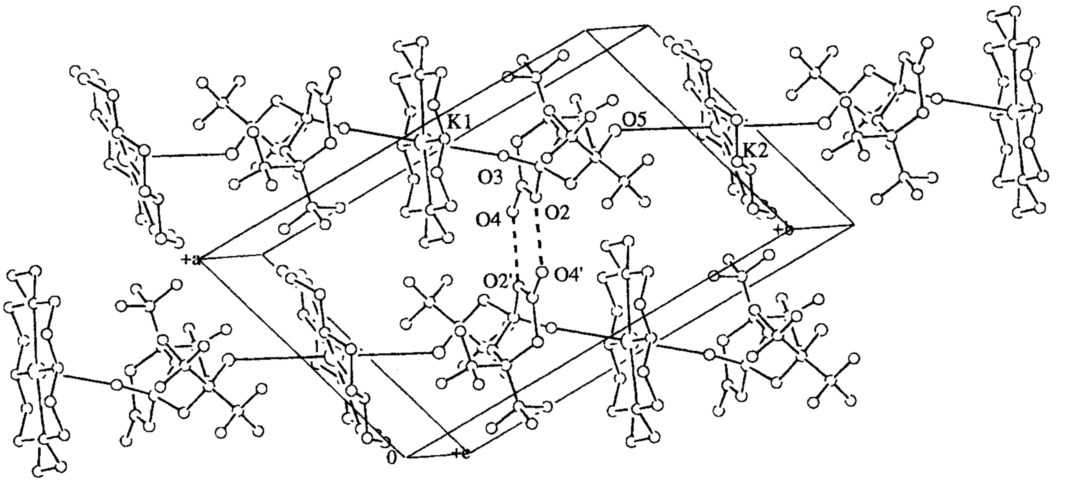

Figure 2. Crystal-packing view of **4**. Selected interatomic distances (Å): O3···K1 = 2.909(6); O5···K2 = 3.714(7); O2···O4′ = 2.794(7), O2′···O4 = 2.794(7).

performed with ISN silica DCC 60A. ^{1}H NMR spectra were recorded on a JEOL JNM-EX270, a JEOL JNM-A500, or a Bruker AM-500 spectrometer, operated at 270, 500, and 500 MHz, respectively. ^{13}C NMR spectra were recorded on a Bruker AM-500 or a JEOL JNM-A500 spectrometer at 126 MHz. ^{19}F (254 MHz) and ^{11}B (86 MHz) NMR spectra were recorded on a JEOL JNM-EX270 spectrometer, whose chemical shifts were relative to $CFCl_3$ and $Et_2O{\cdot}BF_3$, respectively. High-resolution mass spectra were obtained with a JEOL JMS-SX102L spectrometer. GC-MS spectra were recorded with a Shimadzu QP-5000 spectrometer. Melting points were determined on a Yanaco micro melting point apparatus. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, The University of Tokyo.

Preparation of Dimesityl[3,3,3-trifluoro-2-hydroxy-2-(trifluoromethyl)propyl]borane (3). (Lithiomethyl)dimesitylborane was prepared from dimesitylmethylborane (1.14 g, 4.32 mmol) in THF (10 mL) and mesityllithium (4.53 mmol) in THF (20 mL) by the method reported previously.[4] To the solution was added excess hexafluoroacetone (HFA), which was generated by dehydration of hexafluoroacetone trihydrate (11 mmol) in sulfuric acid at 150 °C, by bubbling under dry nitrogen at −78 °C. The reaction mixture was stirred for 2.5 h, treated with aqueous NH_4Cl, and extracted with dichloromethane. The extracts were dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure the residue was subjected to dry column chromatography (SiO_2, hexane−CH_2Cl_2 (10:1)) to afford **3** (517 mg, 1.20 mmol) in 28% yield after recrystallization from acetonitrile.

3: colorless prisms; mp 101.3−103.0 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C, TMS) δ 2.25 (s, 12H; *o*-CH_3 of Mes), 2.27 (s, 6H; *p*-CH_3 of Mes), 2.65 (2, 2H; CH_2), 4.04 (s, 1H: O*H*), 6.84 (s, 4H; *m-H* of Mes); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 27 °C, TMS) δ 21.0 (s, *o*-CH_3 of Mes), 22.9 (s, *p*-CH_3 of Mes), 31.8 (s, *C*H_2), 77.2 (septet, ^2J(C,F) = 30 Hz, *C*$(CF_3)_2$), 123.2 (q, ^1J(C,F) = 285 Hz, *C*F_3), 129.5 (s, *m-C* of Mes), 139.3 (br s, *ipso-C* of Mes), 140.1 (s), 140.4 (s); ^{19}F NMR (254 MHz, $CDCl_3$, 27 °C, Freon) δ −78.87 (s); ^{11}B NMR (86 MHz, $CDCl_3$, 27 °C, $F_3B{\cdot}OEt_2$) δ 79.1 (br s). Anal. Calcd for $C_{22}H_{25}BF_6O$: C, 61.42; H, 5.86. Found: C, 61.28; H, 5.83.

Formation of Potassium 18-Crown-6 2,4-Dihydroxy-6,6,α,α-tetrakis(trifluoromethyl)-1,3-dioxa-4-bora-2-boratacyclohexane-2-ethanol (4). To a solution of **3** (94.6 mg, 0.220 mmol) and 18-crown-6 (64.7 mg, 0.245 mmol) in THF (10 mL) was added a suspension of KH (19 mg, 0.47 mmol) in THF (1 mL) at −78 °C for 30 min, and then the mixture was warmed to 25 °C and stirring was continued for 1 h. In the air excess KH was filtered off and the filtrate was evaporated to give the crude mixture (186 mg), which was recrystallized from CH_2Cl_2−hexane to give 1,3,2,4-dioxadiborinanide **4** (46.7 mg, 58%). A single crystal for X-ray analysis was grown in CH_2Cl_2−hexane.

4: colorless prisms; mp 110.2−113.5 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C, TMS) δ 0.80 (d, ^2J(H,H) = 15 Hz, 1H; C*H*H′), 0.96 (d, ^2J(H,H) = 15 Hz, 1H; CH*H′*), 1.17 (s, 2H; CH_2), 1.57 (s, 1H; O*H*), 3.62 (s, 24H; (−OCH_2CH_2O−)$_6$), 5.45 (s, 1H; O*H*), 8.21 (s, 1H; O*H*); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 27 °C, TMS) δ 11.4 (br s, *C*H_2), 20.8 (s, *C*H_2), 70.1 (s, O*C*H_2*C*H_2O), 76.5 (septet × 2, ^2J(C,F) = 29 Hz, *C*$(CF_3)_2$), 124.1 (q, ^1J(C,F) = 288 Hz, *C*F_3), 124.4 (q, ^1J(C,F)= 287 Hz, *C*F_3), 124.7 (q, ^1J(C,F) = 284 Hz, *C*F_3), 124.8 (q, ^1J(C,F) = 289 Hz, *C*F_3); ^{19}F NMR (254 MHz, $CDCl_3$, 27 °C, Freon) δ −78.31 (q, ^4J(F,F) = 10 Hz, 3F), −78.57 (q, ^4J(F,F) = 10 Hz, 3F), −78.84 (q, ^4J(F,F) = 10 Hz, 3F), −80.39 (q, ^4J(F,F) = 10 Hz, 3F); ^{11}B NMR (86 MHz, $CDCl_3$, 27 °C, $F_3B{\cdot}OEt_2$) δ 4.0 (br s, 1B), 30.0 (br s, 1B). Anal. Calcd for $C_{20}H_{31}B_2F_{12}KO_{11}{\cdot}H_2O$: C, 31.85; H, 4.41. Found: C, 31.94; H, 4.10.

Synthesis of Potassium, 18-Crown-6 2,2-Dimesityl-4,4-bis(trifluoromethyl)-1,2-oxaboretanide (2b). To a solution of **3** (93.7 mg, 0.218 mmol) and 18-crown-6 (63.4 mg, 0.240 mmol) in THF (10 mL) was added a suspension of KH (20.3 mg, 0.508 mmol) in THF (1 mL) at −78 °C for 30 min, and then the mixture was warmed to 25 °C and stirring was continued for 1 h. Excess KH was removed using a glass filter under argon; the filtrate was concentrated to give the residue, which was recrystallized from THF−hexane to afford **2b** (76%) after quick filtration. In sharp contrast to **2a**, **2b** is very moisture sensitive, giving **4** during treatment in air.

2b: moisture-sensitive colorless crystals; ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C, TMS) δ 1.84 (s, 2H; BCH_2), 2.12 (s, 6H; *p*-CH_3 of Mes), 2.43 (s, 12H; *o*-CH_3 of Mes), 3.50 (s, 24H; OCH_2CH_2O), 6.53 (s, 4H; *m-H* of Mes); ^{19}F NMR (254 MHz, $CDCl_3$, 27 °C, Freon) δ −77.96 (s); ^{11}B NMR (86 MHz, $CDCl_3$, 27 °C, $F_3B{\cdot}OEt_2$) δ = 7.7.

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Supporting Information Available: Crystallographic data with complete tables of bond lengths, angles, and thermal and positional parameters for **4**. This matrial is available free of charge via the Internet at http://pubs.acs.org.

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