

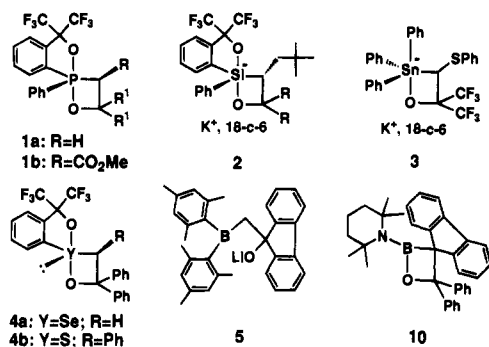
Synthesis, Structure, and Thermolysis of a Tetracoordinate 1,2-Oxaboretanide: An Intermediate of the Boron–Wittig Reaction under Basic Conditions

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In the course of our study on oxetanes bearing highly coordinate main group elements at the neighboring position we achieved the syntheses of pentacoordinate 1,2-oxaphosphitanes **1a,b**,^{1a} 2-oxasiletanides **2**,^{1b} and 1,2-oxastannetanides **3**,^{1c} i.e., intermediates of the Wittig,² Peterson,³ and tin–Peterson⁴ reactions, respectively. On the other hand, we have recently found that oxetanes with group 16 elements, i.e., 1,2-oxaselectanides **4a** and 1,2-oxathietanes **4b**, have structures similar to those of group 14 and 15 element analogues, but yield no olefins on heating.⁵ Successful syntheses of a series of oxetanes bearing group 14, 15, and 16 elements and group-dependent thermal behavior prompted us to investigate the synthesis of a group 13 element analogue, a tetracoordinate 1,2-oxaboretanide, an intermediate of the boron–Wittig reaction under basic conditions.⁶



Although a lithium salt **5** of a β -hydroxy borane was studied, the structural characterization has been carried out only by ¹H NMR and IR spectroscopy.⁷ We now report the synthesis, crystal structure, and thermolysis of a tetracoordinate 1,2-oxaboretanide.

Sequential treatment of (1-lithioethyl)dimesitylborane (**6**)^{7,8} (1.24 mmol) with 1.6 equiv of benzaldehyde (THF, –72 °C,

(1) (a) Kawashima, T.; Kato, K.; Okazaki, R. *J. Am. Chem. Soc.* **1992**, *114*, 4008–4010. Kawashima, T.; Kato, K.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 869–870. Kawashima, T.; Takami, H.; Okazaki, R. *J. Am. Chem. Soc.* **1994**, *116*, 4509–4510. (b) Kawashima, T.; Iwama, N.; Okazaki, R. *Ibid.* **1992**, *114*, 7598–7599. (c) Kawashima, T.; Iwama, N.; Okazaki, R. *Ibid.* **1993**, *115*, 2507–2508.

(2) For reviews, see: Smith, D. J. H. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon: Oxford, 1979; Vol. 2, pp 1316–1329. Gosney, I.; Rowley, A. G. In *Organophosphorus Reagents in Organic Synthesis*; Cadogan, J. I. G., Ed.; Academic Press: New York, 1979; pp 17–153. Maryanoff, B. E.; Reitz, A. B. *Phosphorus Sulfur* **1986**, *27*, 167–189. Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863–927.

(3) For reviews, see: Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981; pp 141–152. Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983; pp 58–73. Ager, D. J. *Synthesis* **1984**, 384–398. Ager, D. J. *Org. React. (N.Y.)* **1990**, *38*, 1–223.

(4) For reviews, see: Kauffmann, T. *Top. Curr. Chem.* **1980**, *92*, 109–147. Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 410–429. Perey, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987; pp 176–177.

(5) Kawashima, T.; Ohno, F.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 10434–10435. Kawashima, T.; Ohno, F.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2094–2095.

1.5 h) and then with aqueous NH₄Cl at –72 °C gave a diastereomeric mixture of β -hydroxy boranes **7a** (53%) and **7b** (9%) after dry column chromatography (SiO₂, hexane–CH₂Cl₂ (1:1)). A similar reaction using 3.3 equiv of hexafluoroacetone (THF, –72 °C, 2 h) gave **7c** (12%) after purification by flash column chromatography (SiO₂, hexane–CH₂Cl₂ (9:1)), HPLC (column: JAIGEL H-1, H-2, Japan Analytical Industry), and recrystallization from acetonitrile–CH₂Cl₂.⁹ While Pelter et al. assigned **7a** as the *erythro* isomer by NMR and chemical derivation,⁷ we have confirmed its stereochemistry by X-ray crystallographic analysis of the trimethylsilyl ether (TMS-**7a**).¹⁰ Thermolysis of **7a** gave quantitatively (*Z*)- β -methylstyrene (**8a**), whereas that of **7b** afforded (*E*)-isomer **8b**, indicating that the boron–Wittig reaction under neutral conditions proceeds stereospecifically via *syn* elimination of a hydroxyborane in sharp contrast to *anti* elimination reported previously for the reaction under acidic conditions.¹¹ This result suggests the possibility that a 1,2-oxaboretanide exists as an intermediate in the reaction under basic conditions. Since **7a** and **7b** were not very stable, **7c** was used to examine such a possibility. Deprotonation of **7c** with KH in the presence of 18-crown-6 (THF, –72 → 25 °C) afforded quantitatively tetracoordinate 1,2-oxaboretanide **9**¹² (Scheme 1).

In the ¹H and ¹³C NMR spectra of **9** two mesityl groups were separately observed, although the signals for one of the mesityl groups were very broad, presumably because of the hindered rotation of the mesityl group due to the change in hybridization from sp² to sp³ by the ring formation. In the ¹⁹F NMR spectrum of **9** were observed two quartets with centers of δ_F –78.22 and –70.41 (⁴J_{FF} = 10.7 Hz), whose difference in the chemical shift ($\Delta\delta$ 7.81) was much larger than that ($\Delta\delta$ 1.42) of the starting **7c**, probably because of the enlargement of their nonequivalency emerging also from the ring formation. An upfield shift (from δ 80.3 for **7c** to δ 9.9 for **9**) observed in the ¹¹B NMR spectrum indicates that compound **9** has a tetracoordinate borate structure.

The X-ray crystallographic analysis of **9** indicated that it has a tetracoordinate 1,2-oxaboretanide structure (Figure 1).¹³ This

(6) 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, 1991; Vol. 1, Chapter 2.2, pp 487–503. Pelter, A. *Pure Appl. Chem.* **1994**, *66*, 223–233.

(7) Pelter, A.; Buss, D.; Pitchford, A. *Tetrahedron Lett.* **1985**, *26*, 5093–5096. Pelter, A.; Buss, D.; Colclough, E.; Singaram, B. *Tetrahedron* **1993**, *49*, 7077–7103.

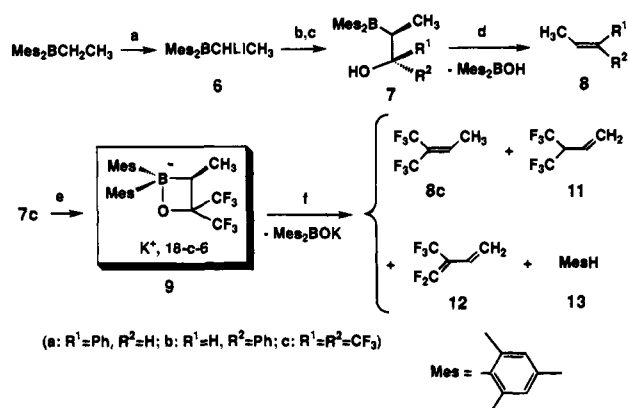
(8) Pelter, A.; Williams, L.; Wilson, J. W. *Tetrahedron Lett.* **1983**, *24*, 627–630. Pelter, A.; Singaram, B.; Williams, L.; Wilson, J. W. *Tetrahedron* **1993**, *49*, 2965–2978.

(9) The reaction gave a complex mixture, from which Mes₂BOH (21%) and Mes₂BCH=CHCMeC(CF₃)₂OH (6%) were obtained as other identified products. Further details are described in the supplementary material.

(10) C₃₀H₄₄BOSi, FW = 456.55, crystal dimensions (mm) 0.50 × 0.20 × 0.05, orthorhombic, space group *Pbca*, *a* = 17.077(8) Å, *b* = 22.09(1) Å, *c* = 15.417(7) Å, *V* = 5816(4) Å³, *Z* = 8, *D*_{calcd} = 1.04 g/cm³, *R* = 0.094 (*R*_w = 0.061). A single crystal for X-ray analysis was grown in CH₂Cl₂. For full details of the crystallographic structure analysis, see the supplementary material.

(11) The typical boron–Wittig reaction has been demonstrated to proceed via *anti* elimination of a hydroxyborane under acidic conditions: see refs 6–8.

(12) **9**: colorless prisms; mp 146.0–151.0 °C dec; ¹H NMR (*d*₆-acetone, 500.1 MHz) δ 0.88 (d, ³J = 7.6 Hz, 3H), 2.01 (brs, 3H), 2.06 (s, 3H), 2.07 (s, 3H), 2.22 (brs, 3H), 2.59 (brs, 3H), 2.74 (q, ³J = 7.6 Hz, 1H), 2.80 (brs, 3H), 3.62 (s, 24H), 6.33 (s, 1H), 6.37 (brs, 1H), 6.49 (brs, 1H), 6.54 (s, 1H); ¹³C{¹H} NMR (*d*₆-acetone, 125 MHz) δ 11.4 (s, CH₃), 20.7 (2 × s, *p*-CH₃ of Mes), 22.8 (brs, *o*-CH₃ of Mes), 23.9 (brs, *o*-CH₃ of Mes'), 24.0 (s, *o*-CH₃ of Mes), 24.7 (brs, CH), 25.5 (brs, *o*-CH₃ of Mes'), 70.7 (s, OCH₂CH₂O), 82.8 (septet, ²J_{CF} = 28 Hz, C(CF₃)₂), 126.2 (q, ¹J_{CF} = 291 Hz, C(CF₃)(CF₃')), 126.9 (q, ¹J_{CF} = 286 Hz, C(CF₃)(CF₃')), 127.8 (s, *m*-CH), 128.9 (2 × s, *m*-CH), 129.9 (s, *m*-CH), 131.0 (s, *p*-C), 131.5 (s, *p*-C), 140.5 (brs, *o*-C), 141.0 (s, *o*-C), 143.4 (brs, *o*-C), 144.0 (s, *o*-C), 150.3 (brs, *ipso*-C), 151.1 (brs, *ipso*-C); ¹⁹F NMR (CDCl₃, 253.8 MHz) δ –78.22 (q, ⁴J_{FF} = 10.7 Hz), –70.41 (q, ⁴J_{FF} = 10.7 Hz); ¹¹B NMR (CDCl₃, 86.4 MHz) δ 9.9 (brs). Anal. Calcd for C₃₅H₅₀B₂F₆KO₂: C, 56.30; H, 6.75. Found: C, 56.44; H, 7.00.

Scheme 1^a

^a (a) 1.4 equiv of MesLi, THF, 25 °C, 1 h; (b) 1.6 equiv of PhCHO, THF, -72 °C, 1.5 h; -72 → -55 °C or 3.3 equiv of (CF₃)₂C=O, THF, -72 °C, 2 h; (c) aqueous NH₄Cl; (d) C₆D₆, 90 °C, 2.5 h for 7a, 70 °C, 2 h for 7b; (e) KH, 18-crown-6, THF, -72 → 25 °C; (f) in the solid state, 200 °C, 0.07 Torr, 45 s.

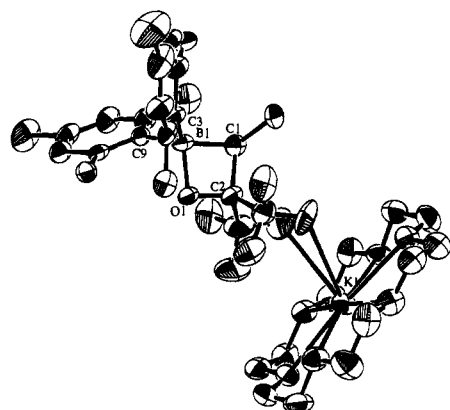


Figure 1. ORTEP drawing of **9** (CH₂Cl₂ is omitted for clarity). Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): B1–O1, 1.59(1); B1–C1, 1.66(2); B1–C3, 1.64(2); B1–C9, 1.68(1); C1–C2, 1.53(1); C2–O1, 1.36(1); C1–B1–C3, 116.1(9); C1–B1–C9, 119.4(9); C3–B1–C9, 113.7(9); C1–B1–O1, 84.6(7); C1–C2–O1, 98.5(8); B1–O1–C2, 92.7(7); O1–C2–C1–B1, 3.3(8).

is the first example of a tetracoordinate 1,2-oxaboretane. The bond B1–O1 (1.59(1) Å) is significantly longer than the B–O bonds of tricoordinate boretane **10** (1.398(5) Å)¹⁴ and trimethyl borate (1.38 Å),¹⁵ because the bonds of the latter have some degree of double bond character and hence become unusually short.^{16,17} Therefore, the absence of such a character makes the B–O bond length of **9** close to the sum of the covalent radii of boron and oxygen (1.54 Å).¹⁸ The bond B1–C1 (1.66(2) Å) is reasonable compared with those (1.62–1.69 Å) of the hitherto known tetracoordinate borates.¹⁹ The bond angles B1–

(13) C₃₃H₅₀BF₆KO₇·CH₂Cl₂, FW = 831.61, crystal dimensions (mm) 0.70 × 0.30 × 0.20, monoclinic, space group P2₁/n, a = 8.997(3) Å, b = 23.093(8) Å, c = 20.67(1) Å, β = 93.50(3)°, V = 4287(2) Å³, Z = 4, D_{calc} = 1.288 g/cm³, R = 0.084 (R_w = 0.113). A single crystal for X-ray analysis was grown in CH₂Cl₂–pentane. For full details of the crystallographic structure analysis, see the supplementary material.

(14) Glaser, B.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 416–417.

(15) Bauer, S. H.; Beach, J. V. *J. Am. Chem. Soc.* **1941**, *63*, 1394–1403.

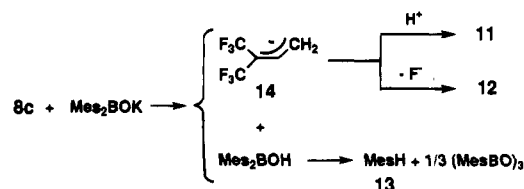
(16) Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 7029–7036.

(17) Coulson, C. A.; Dingle, T. W. *Acta Crystallogr.* **1968**, *B24*, 153–155.

(18) Unfortunately, X-ray crystallographic data for borates to be compared, R₃B–OR', have never been reported. The most recent electron diffraction study of BF₃·OMe₂ showed the B–O bond length (1.75 Å) and bond angle F–B–F (117°); see: Iijima, K.; Yamada, T.; Shibata, S. *J. Mol. Struct.* **1981**, *77*, 271–276. The B–O bond length of **9** is much shorter than that of BF₃·OMe₂, indicating that this bond is stronger than those of boron etherates.

C1–C2 (84.1(8)°) and C1–C2–O1 (98.5(8)°) deviate ca. 25° and 11°, respectively, from the tetrahedral angle in order to construct the four-membered ring. The torsion angle O1–C2–C1–B1 (3.3(8)°) indicates that the four-membered ring is almost planar, which is a common structural feature of oxetanes previously reported.^{1,5} The potassium cation interacts with one fluorine atom in each trifluoromethyl group besides six oxygen atoms of the crown ether. Very interestingly, the bond angles C1–B1–C3, C3–B1–C9, and C1–B1–C9 are 116.1(9)°, 113.7(9)°, and 119.4(9)°, respectively, which are significantly different from the tetrahedral angle,²⁰ showing that it has a distorted tetrahedral structure. It can be reasonably interpreted to be due to the strain resulting from the formation of a four-membered ring through the coordination of the oxido anion toward a vacant *p*-orbital on the boron.

Thermolysis of **9** in the solid (bath temperature: 200 °C, under 0.07 Torr, 45 s) gave the corresponding olefin **8c** (48%) and secondary products of **8c**, olefin **11** (3%) and diene **12** (11%), and mesitylene (**13**) (83%) as volatile materials, while thermolysis of **9** in solution (toluene-*d*₈, 170 °C, 15 min) afforded a complex mixture including a trace amount of **8c** in sharp contrast to the oxetanes containing group 14 and 15 elements previously reported.¹ The formation of **11** and **12** is interpreted in terms of deprotonation of **8c** with Mes₂BOK leading to allyl anion **14**, followed by protonation and elimination of F⁻, respectively. Mesitylene (**13**) is considered to be formed along with (MesBO)₃ by decomposition of intermediary Mes₂BOH.²¹



In conclusion, the first tetracoordinate 1,2-oxaboretanide was synthesized by taking advantage of electronic stabilization at the 4-position and found to be an intermediate of the boron–Wittig reaction under basic conditions with an interesting structure different from those of usual tetracoordinate borates.

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Supplementary Material Available: An experimental procedure for the synthesis of **7a–c** and **9**, physical and spectral data of **7a–c**, and X-ray crystallographic data with tables of thermal and positional parameters, bond lengths, and bond angles for TMS-**7a** and **9** (35 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(19) Odom, J. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 1, Chapter 5.1, pp 253–310.

(20) The sum (Σ) of three angles is calculated to be 349° for **9**. A similar structural distortion has been observed in BF₃·OMe₂ and the following borates bearing a boron–nitrogen bond. For BF₃·OMe₂ (Σ 351°), see ref 18. For MeCN–BF₃ (Σ 342°), see: Hoard, J. L.; Owen, T. B.; Buzzell, A.; Salmon, O. N. *Acta Crystallogr.* **1950**, *3*, 130–137. For 1-oxa-3-azonia-2-boracyclopentane (Σ 343.1°), see: Ebering, E.; Kliegel, W.; Rettig, S. J.; Trotter, J. *Can. J. Chem.* **1989**, *67*, 933–940.

(21) A similar decomposition was reported for Ph₂BOH; see: Abel, E. W.; Gerrard, W.; Lappert, M. F. *J. Chem. Soc.* **1958**, 1451. This mechanism was supported by the fact that treatment of the residue with water gave MesB(OH)₂ as the hydrolysis product of (MesBO)₃.