Contribution to the Chemistry of Boron, 235[1]

Reactions of Prolinol with Borane–Tetrahydrofuran: Anomalous Dimerization of a 1,3,2-Oxazaborolidine

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The reaction of (*S*)-prolinol (LH) with $H_3B \cdot THF$ proceeds via $[L_2BH_2]BH_4$, which decomposes with elimination of hydrogen at ca. −40°C to give the BH_3 adduct of spirocyclic **7**. On heating, **7** loses more H_2 to give the "anomalous" dimerization product **11**, which features a tetracoordinated B atom in a "tetrahedral" BN_2O_2 unit and another B atom in an N_2BH_2 environment. It is also shown that the product resulting from the reaction of pseudoephedrin with $H_3B \cdot THF$ undergoes an analogous anomalous dimerization, affording product **8**.

1,3,2-Oxazaborolidines **1**[2] are much less reactive than 1,3,2-dioxaborolanes **2**[3]. This is due to strong B–N π-bonding, which considerably reduces the Lewis acidic character of the boron atom[4]. Nevertheless, the 1,3,2-oxazadiborolidines serve as useful reagents for enantioselective hydroborations, as shown by J. M. Brown et al.[5] for the hydroboration of *p*-methoxystyrene with the (4*S*,5*R*)-pseudoephedrino borane **3**[6]. Without a catalyst 1,3,2-oxazaborolidines carrying BH groups do not exhibit hydroboration reactivities towards C=C bonds, and they proved to be only weak reducing agents[2]. This behavior may result not only from B–N π-bonding but also from steric effects. Considering these effects, one may expect an increased reactivity for the bicyclic 1,3,2-oxazaborolidine **4** derived from (*S*)-prolinol. Due to the bridgehead position of the nitrogen atom, B–N π-bonding should be weakened owing to the expected more pronounced *s* character of its lone electron pair. Moreover, a center of asymmetry next to boron atoms could favor enantioselectivity. For instance, the 5,5′-diphenyl derivative **5**[7] is used for catalytic enantioselective reductions of prochiral ketones (CBS reduction), and ee values of up to 99% were achieved[8]. Compounds **3**–**5** contain a basic nitrogen atom and a Lewis acidic boron atom. The former may coordinate with BH_3 of the oxazaborolidine; the latter may bind to the oxygen atom of the carbonyl group, thus activating this group. It is also known that 1,3,2-oxazaborolidines dimerize. J. M. Brown et al.[5] found that the pseudoephedrin borane derivative (4*R*,5*R*)-3,4-dimethyl-5-phenyl-1,3,2-oxazaborolidine **3** undergoes a temperature-dependent reversible dimerization as described by eq. 1. The dimer was described as a ten-membered heterocycle **6** containing a tetracoordinated borate unit and a bis(amido)borinium moiety[9]. This assignment is based on ^{11}B-NMR data. However, the required allene-type structure for the borinium part of this molecule makes the proposed structure quite asymmetric, and this is not in accordance with its NMR data. In particular, the reported $\delta^{11}B$ value for the borinium atom ($\delta = 8.8$) does not correspond with the suggested structure[9]. It was, therefore, of interest to reliably determine the molecular structure of compound **6** and to synthesize and characterize the 1,3,2-oxazaborolidine derived from (*S*)-prolinol (2-hydroxymethylpyrrolidine).

Reaction of (*S*)-Prolinol with Borane–Tetrahydrofuran

(*S*)-Prolinol is readily available by $LiAlH_4$ reduction of proline[10]. On treatment with $H_3B \cdot THF$ in a THF solution and in a 1:1 molar ratio, a reaction according to eq. 2 was expected. However, only 75% of the calculated amount of hydrogen was liberated at ambient temperature.

Moreover, the ^{11}B-NMR spectrum of the resulting solution shows two signals in an intensity ratio of 1:1 at $\delta = 5.1$ and -16.9. These signals are compatible with the presence of tetracoordinated boron atoms, but not with the formation of compound **7**. The signal at lower field is a singlet whereas the high-field signal is a 1:3:3:1 quartet with $^1J(^{11}B^1H) = 87$ Hz. These data are consistent with the formation of a compound with structure **8a** or **8b**. On sublimation or heating to 120–150 °C this intermediate loses a fourth mol of H_2. However, the recorded ^{11}B-NMR spectrum is inconsistent with the formation of an oxazaborolidine **7** because two signals at $\delta = 8.7$ (singlet) and -1.7 [1:2:1 triplet, $^1J(^{11}B^1H) = 110$ Hz] are observed. These resonances prove the presence of tetracoordinated boron atoms and are compatible with the structure of compound **9**, a so-called anomalous dimer[11]. "Normal" dimerization of **8** should lead to structure **10**. Thus, the reaction of (*S*)-prolinol with borane in THF proceeds according to eq. 3. Anomalous dimers are known from the chemistry of triazadiborolidines[11], and **6** would be another example although of a different type. In this context it is interesting that

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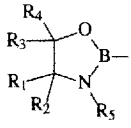

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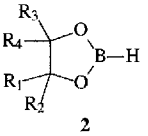

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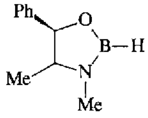

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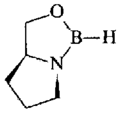

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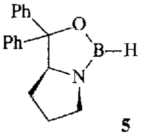

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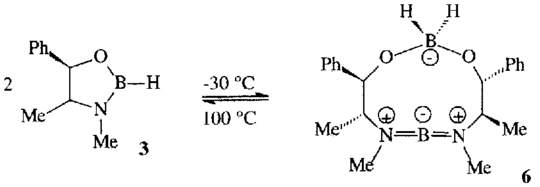

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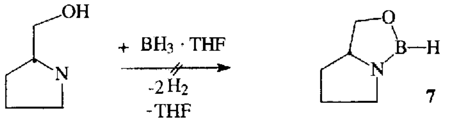

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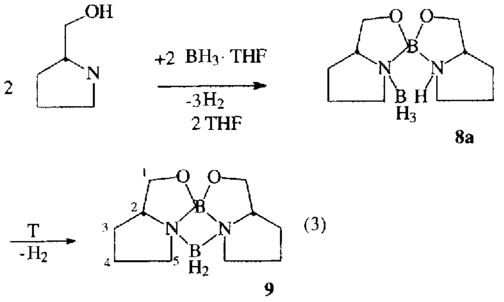

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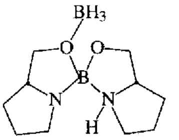
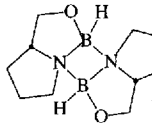


8b



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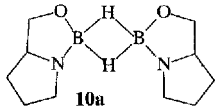
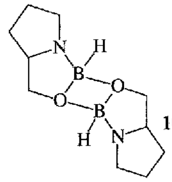


10a



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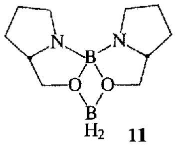
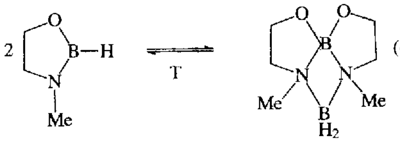


11



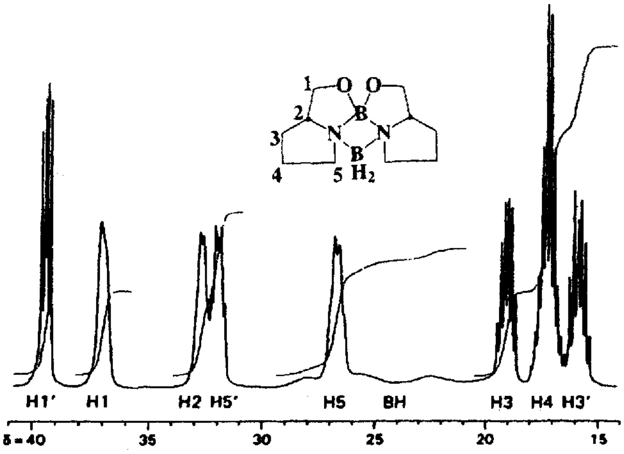
(4)

Meller et al.[12] observed a monomer-dimer equilibrium (4) for 3-methyl-1,3,2-oxazaborolidine where dimerization also proceeds anomalously.

Spectroscopic Studies

An analysis of the ^{1}H- and ^{13}C-NMR spectra of compounds **8a**, **8b** and **9** supports the conclusion drawn from the ^{11}B-NMR spectra. In addition to structure **9**, one has to consider also the alternative structure **11**, which is, however, less likely because nitrogen atoms are usually much more basic than oxygen atoms and the former should therefore prefer the bridge position between the two boron atoms. Nevertheless, both **9** and **11** are expected to display C_2 symmetry. This is in accord with a single set of ^{1}H resonances for the 2-pyrrolidinylmethoxy substituent. Relevant data are presented in the Experimental Section, and the ^{1}H-NMR spectrum of **9**, which is not first order, is displayed in Figure 1.

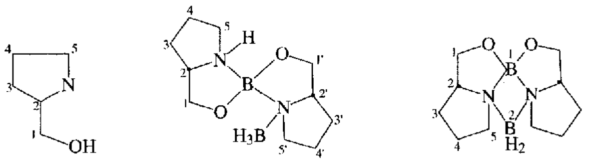
Figure 1. 400 Hz ^{1}H-NMR spectrum of compound **8** at 30 °C in $CDCl_3$ solution. Only three out of the four H_2B resonances can be observed as broad signals



The assignment of the proton resonances is based on H,H- and C,H-COSY experiments. As expected for a prolinolate unit the protons of the CH_2 groups are not chemically equivalent. This results in fairly complex coupling patterns for the protons at C-3 and C-4. The resonances for the hydrogen atoms at C-1 and C-5 are fairly broad and remain unchanged at 100 °C (in [D$_8$]toluene). This broadening may be due to coupling with the B nuclei. This is a situation usually not observed because the quadrupole relaxation of the boron nuclei is rapid, and coupling is normally only observed for atoms directly bound to boron[13] (see the broad quartet for the H atoms bound to boron in Figure 1). But if the boron atoms reside in a tetrahedral environment, the effect of quadrupolar relaxation is less significant than in a trigonal-planar environment.

The signal for the second H atom in position 1 (1-H) is a doublet of doublets. Therefore, it interacts with the H atom at C-2. According to Karplus[14] the value of the vicinal coupling is at a minimum for a dihedral angle of 90°[15]. For 1-H, the coupling constant ^2J(H,H) is 9.77 Hz, and for ^3J(H,H) we find 5.86 Hz. The C_2 point-group symmetry of compound **9** is also revealed by its ^{13}C-NMR spectrum. Compared to prolinol all resonances are shifted to lower field (see Table 1).

Table 1. ^{11}B- and ^{13}C-NMR data (chemical shift δ) of (*S*)-prolinol, intermediate **8** and compound **9**



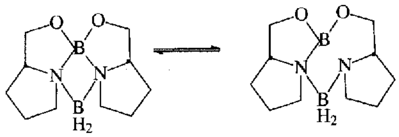
δ^{11}B			5.1 (s, B^1)	−16.9 (q, B^2)[a]	8.7 (s, B^1) −1.7 (B^2)[b]
δ^{13}C	C1	63.6	59.0	67.0	67.1 (t)
	C2	59.5	61.3 (b)	65.1 (b)	67.0 (d)
	C3	26.9	27.0	28.2	31.7 (t)
	C4	24.9	23.9	25.9	25.7 (t)
	C5	45.6	46.0	54.4	52.3 (t)

[a] t, ^1J(BH) 110 Hz. – [b] ^1J(BH) = 87 Hz. ^{1}H NMR (CDCl$_3$): 1.57 (m, 2H, H-3′), 1.70 (m, 2H, H-4.4′), 1.90 (m, 2H, H-3), 2.37 (b, q, 2H, BH$_2$, ^1J(BH) = 88 Hz, 2.64 (dt, 2H, H-5), 3.67 (b, 2H, H-1), 9.92 (dd, 2H, H-1′), ^2J(HH) = 9.77 Hz, ^3J(HH) = 5.86 Hz.

The intermediate **8a**, on the other hand, shows two sets of ^{13}C-NMR signals for the prolinol moiety. One set of signals is close to that of compound **9**, whereas the second is closer to prolinol itself except for the unique CH group of the pyrrolidine ring. This suggests that structure **8a** is the more likely isomer.

The mass spectrum of compound **9** exhibits an ion $M^{\bullet +}$ with the correct isotopic pattern for two boron atoms in the molecule. This ion is also the peak of largest abundance. It is fragmented to an ion of half its mass, *m/z* = 110, with one boron atom. Obviously, it results from the cation of the oxazaborolidine **8**, and this ion is observed with 70% relative abundance. Therefore, there should be a good chance of observing also this species at higher temperatures in solution. However, at 100 °C in [D$_8$]toluene no doublet is found in the proton-coupled ^{11}B-NMR spectrum. This excludes the formation of **7** at higher temperatures in solution. The only new signal that appears besides the signals for compound **9** is a singlet at δ = 20.4, which grows in at the expense of the singlet for the BO$_2$N$_2$ group of compound **9**. On cooling the solution, the original spectrum of **9** is restored.

This new signal demonstrates the formation of a new species **12** with a tricoordinated boron atom, and because the sum of the intensities of this signal and that at δ = 5.1 remains equal to the intensity of the signal for the BH$_2$ group we conclude that a B–N bond is cleaved as described in eq. 5.



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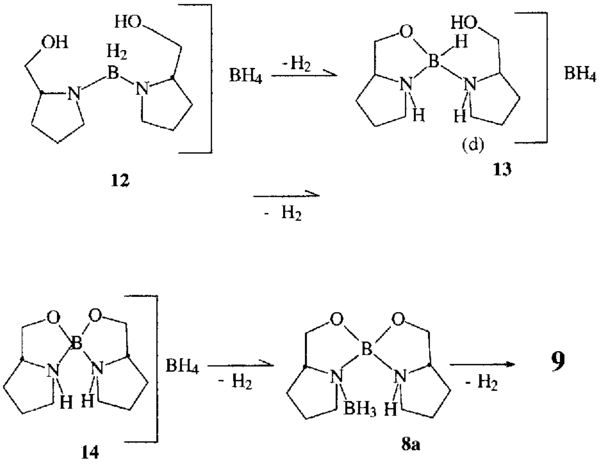


Molecular Structures

In order to confirm the conclusions drawn from the NMR data, the molecular structures of compound **9** and of the pseudoephedrin derivative **6** were determined by single-crystal X-ray methods. The result for compound **9** is shown in Figure 2a. This figure not only reveals the presence of a planar four-membered B$_2$N$_2$ ring and excludes the isomer **11**, but also demonstrates an almost uncrowded situation for the BH$_2$ group (see Figure 2b).

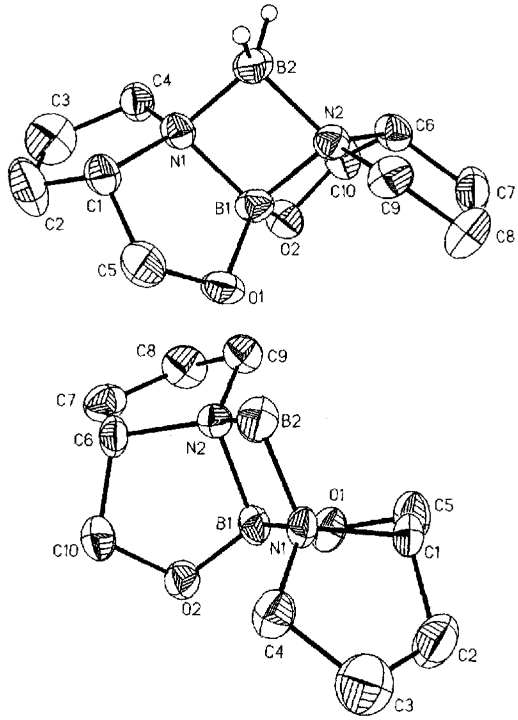
In addition, the C_2 symmetry of the molecule becomes apparent on the basis of the solution NMR data; however, a closer look at bond lengths and bond angles demonstrates that the corresponding parameters are not equal within the limits of standard deviations. Therefore, the molecule in the solid state has no C_2 axis. Typically, the four B–N bond lengths are 1.594(5), 1.599(5), 1.58(1), and 1.597(9) Å. These distances represent B–N single bonds between tetracoordinated nitrogen and boron atoms[16]. Even more pronounced than the difference of 0.02 Å between the shortest and longest B–N bonds is the difference in bond length between the two B–O bonds (0.076 Å).

Inspection of Figure 2b shows that the pyrrolidine rings are present in an envelope conformation with C5 and C4 deviating most from the mean plane, and both are bent towards the oxygen atoms. The strain of the five-membered BNC$_2$O rings is apparent from the angle of 80.6° between the BO$_2$ and B$_2$N$_2$ planes, with a deviation of 9.4° from the ideal value of 90°.

In contrast to compound **9** it was difficult to grow single crystals of suitable quality of compound **6** although various methods and solvents were tested. Nevertheless, one crystal gave a satisfactory diffraction pattern, and Figure 3 represents the molecular structure of the "pseudoephedrine borane".

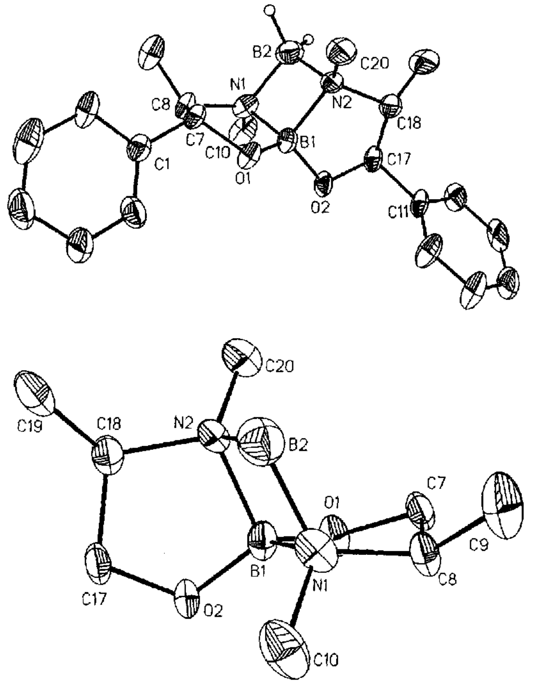
The framework of this compound is the same as for compound **9**. Thus, the X-ray result disproves the structure **6**

Figure 2. (a) ORTEP plot of the molecular structure of compound **9** in the crystal; (b) conformation of one of the $BNOC_2$ rings; thermal ellipsoids are shown for 25% probability[a]



[a] Selected bond lengths [Å] and angles [°]: B1–O2 1.382(5), B1–O1 1.446(4), B1–N1 1.594(5), B1–N2 1.599(5), B2–N2 1.597(9), B2–N1 1.58(1), N1–C1 1.476(8), N2–C6 1.500(8), O1–C5 1.43(1), O2–C10 1.419(9); O2–B1–O1 116.2(3), O2–B1–N1 120.8(3), O1–B1–N1 104.0(2), O2–B1–N2 105.8(3), O1–B1–N2 115.6(3), N1–B1–N2 92.4(3), N2–B2–N1 93.2(5), C1–N1–B2 120.0(6), C4–N1–B1 118.1(6), C6–N2–B2 118.7(6), C9–N2–B1 120.5(5), B1–N2–B2 86.7(4), C6–N2–C9 106.8(6); O1–B1–N1–C1 −1.2, O1–C5–C1–N1 −22.4, N2–B1–O2–C10 −22.0, O2–C10–C6–N2 −31.4, C4–N1–C1–C2 14.1, C6–N2–C9–C8 −29.8, O2–B1–N2–C6 2.1.

Figure 3. (a) ORTEP plot of the molecular structure of dimeric **3** in the crystal; thermal ellipsoids are plotted to represent a 25% probability; (b) skeletal atoms of **3** demonstrate the difference in configuration compared to compound **9** (see Figure 2c); hydrogen atoms are excluded for clarity except those of the BH_2 group[a].



[a] Selected bond lengths [Å] and angles [°]: B1–O2 1.40(1), B1–O1 1.41(1), B1–N1 1.63(2), B1–N2 1.64(2), B2–N2 1.59(2), B2–N1 1.61(2), N1–C10 1.51(2), N2–C20 1.46(2), O1–C7 1.42(1), O2–C17 1.43(1); O2–B1–O1 119(1), O2–B1–N1 118(1), O1–B1–N1 105.3(9), O2–B1–N2 104.0(9), O1B1–N2 116(1), N1–B1–N2 91.8(8), N2–B2–N1 95(1), C8–N1–B2 122(1), C8–N1–B1 103.7(8), C20–N2–B2 118(1), C20–N2–B1 118(1), C18–N2–B1 103.8(8), C18–N2–B2 119(1); O1–B1–N1–C8 −2.2, O1–C7–C8–N1 −31.6, N2–B1–O2–C17 −19.6, C18–N2–B1–O2 −1.3, O2–C17–C18–N2 −32.2; deviation from the mean plane O1 B1 N1 C8 [Å]: O1 0.009, B1 0.012, N1 0.123, C8 0.008, C7 0.46; deviation from the mean plane O2 B1 N2 C18 [Å]: O2 −0.005, B2 0.008, N2 −0.007, C18 0.005, C17 −0.78; interplanar angle [°]: O1–B2–O2/B_2N_2 99.5.

suggested by J. M. Brown et al.[5]. The bonding parameters are similar to those of compound **9**, but because the esd values are about twice as large as those for compound **9** a detailed discussion is not justified. Nevertheless, the envelope conformation of the pyrrolidine ring is much more pronounced than for compound **9**, as shown by C7 and C17 lying 0.46 and 0.78 Å above the mean plane of the NC4 units. A comparison of the "core" structure of compound **9** with the "pseudoephedrinoborane" reveals that the differences in the $BONC_2$ units are due to the different arrangements of the substituents. Thus, in the latter case the Me and Ph groups are *trans* to one another whereas in **9** the substituents are in *syn* positions. The latter causes a larger C–C–C angle, resulting in a flatter five-membered $BONC_2$ ring. It should be noted, however, that the hydrogen atoms of the BH_2 group are better sterically protected by the methyl groups than in compound **9**.

Formation of the Polycyclic Compound 9

Eq. 2 describes a two-step process for the formation of compound **9**. The ^{11}B-NMR data do not furnish any evidence that 1,3,2-oxazaborolidine **4** is an intermediate. Actually, the intermediate **8a** detected by ^{11}B-NMR spectroscopy already contains a preformed structure for the formation of **9**. It was therefore of interest to see if additional information could be gained from low-temperature reactions of $H_3B \cdot THF$ with (*S*)-prolinol, by following the reaction using ^{11}B-NMR spectroscopy.

Figure 4 depicts a series of ^{11}B-NMR spectra recorded at various temperatures. Relevant data and their assignment are summarized in Table 2.

Immediately after mixing the components at −60 °C the ^{11}B-NMR spectrum shows two prominent signals: a broad signal at $\delta = -17.6$ and a quintuplet at −40.6. In addition, there is a minor signal at $\delta = 2.1$, which increases in intensity when the solution is allowed to warm up. At −40 °C a new signal at $\delta = 6$ appears, the intensity of which rapidly increases on warming to −20 °C. By this stage the quintuplet has almost vanished, as has the signal at $\delta = 2.1$. When the solution reaches 20 °C another signal at $\delta = 9.8$ appears, and finally only four signals remain: a sharp resonance at $\delta = 9.8$, an intense singlet at $\delta = 6$, a triplet at $\delta =$

Figure 4. ^{11}B-NMR spectra of the reaction of S-prolinol with BH_3 in THF (^1H-undecoupled) recorded at different temperatures

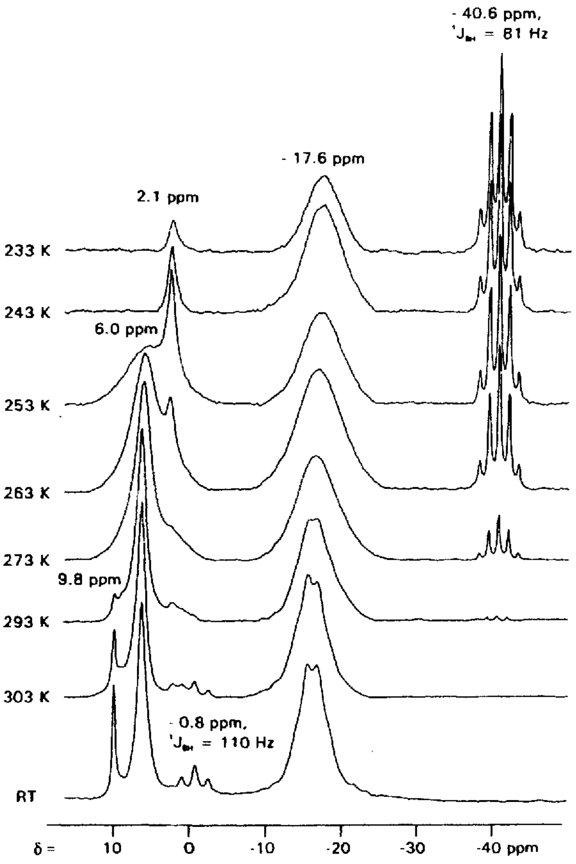


Table 2. Assignment of the signals of the ^{11}B-NMR spectra recorded during warming of a 1:1 mixture of S-prolinol and $H_3B \cdot THF$

$\delta^{11}B$		9.8 (s)	6.0 (s)	2.1 (s)	−0.8 (t)	17.6 (br.)	−40.6 (quint)
$^1J_{BH}$ [Hz]		–	–	–	110	–	81
T [K]	223	0	0	3	0	60	37
	233	0	0	4	0	55	41
	243	0	0	5	0	54	41
	253	0	29	0	0	48	23
	263	0	31	0	0	52	17
	273	0	48	0	0	45	6
	283	0	46	0	0	51	1
	293	0	40	0	0	56	1
	303	3	46	0	5	46	0
	r.t.	6	42	0	–	45	0

−0.8 [^1J(BH) = 110 Hz] and a quadruplet at δ = −17.6 [^1J(BH) = 120 Hz]. The signals at δ = 9.8 and −0.8 arise from compound **9** whereas the dominating signals at δ = 6 and −17.6 (s, q) stem from compound **8a**.

Discussion

The reaction of (*S*)-prolinol with $BH_3 \cdot THF$ proceeds stepwise. In the first step a tetrahydroborate **12** is formed. This, on warming, releases hydrogen, and the BH_3 adduct **8a** results from this decomposition via intermediates such as **13** and **14**. Heating of **8a** affords the final product **9**, which features a pentacyclic structure. As indicated, **9** can be considered as an "anomalous" dimerization product of the oxazaborolidine **4**, which was the expected product of this reaction[17]. An analogous reaction occurs between pseudoephedrin and $BH_3 \cdot THF$. The dimer of **3** does not have the structure **6** as suggested, but possesses the same skeletal structural features as compound **9**. In contrast to the dimeric "pseudoephedrinoborane", heating of which leads to a monomeric 1,3,2-oxazaborolidine[5], only opening of one bond at the BO_2N_2 unit is observed for **9** at higher temperatures. From bond strength arguments we conclude that a B−N rather than a B−O bond is cleaved.

There is no doubt that the formation of a tetrahydroborate at low temperature in THF solution is unusual. Indeed, $BH_3 \cdot THF$ in THF solution is the reagent of choice for the preparation of $BH_3 \cdot L$ adducts by THF displacement reactions[17]. However, solutions of $BH_3 \cdot THF$ show a fairly high electrical conductivity and at low temperature a quintuplet is observed in the ^{11}B-NMR spectrum, albeit of low intensity and normal resolution[18]. No ^{11}B-NMR signal for a cationic species $H_2B(THF)_2^+$ is observable, however. This may be due to rapid exchange reactions with $BH_3 \cdot THF$. Therefore, the formation of species **12** and **13** is not unlikely[19], and this would account for the fact that, even at a very early stage of the reaction, no 1,3,2-oxazaborolidine is generated but instead the pentacyclic compound **8** is observed. If one takes into account the formation of **9** and $(\mathbf{3})_2$, a more systematic study seems to be appropriate in order to understand the influence of electronic and steric factors on the formation of monomeric and anomalously dimerized 1,3,2-oxazaborolidines.

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Experimental Section

All experiments were conducted under anhydrous conditions under argon or dinitrogen or in vacuo. Diborane was prepared from $NaBH_4$ and BF_3 in diglyme and passed into THF to obtain a solution of $BH_3 \cdot THF$ in THF. The pseudoephedrinoborane **6** was prepared as described in ref.[5]. – NMR: Bruker AC P200 (^{11}B), Jeol GSX 270 (^{11}B) and Jeol EX 400 (^1H, ^{13}C); Standard: internal TMS (^1H, ^{13}C), external $BF_3 \cdot OEt_2$ (^{11}B), external $NaNO_3$: (^{14}N). – MS: Varian CH7. – X-ray: Siemens P4, SHELXTL and SHELX93 programs[20].

9: (*S*)-Hydroxymethylpyrrolidine (1.23 g, 12.2 mmol) was dissolved in 10 ml of THF. Dropwise addition of $BH_3 \cdot THF$ (7.0 ml of a 2 M $BH_3 \cdot THF$ solution) to the obtained solution at ambient temperature led to evolution of H_2, which ceased after about 1 h (20.3 mmol of H_2 collected). At this time the ^{11}B-NMR spectrum showed two signals of about equal intensity at δ = 5.2 (s) and −16.9 (q). Removal of volatile material in vacuo proceeded smoothly but at the end of this work-up process the residue started foaming with gas evolution. Heating of the remaining material to 110−120°C/5μ bar resulted in a crystalline "sublimate". This material was purified by a second sublimation. Recrystallization from a hexane/THF solution yielded clear crystals. Yield: 0.42 g of

9 (31%). − M.p. 127−129°C. − ^{1}H NMR: δ^{14}N(CDCl$_3$): −327. − MS; *m/z*, (intensity): 221 (100) [M$^+$ − 1], 193 (10) [M$^+$ − C_2H_4], 110 (70) [monomer M′], 82 (64) [M′$^+$ − C_2H_4]. − IR; (cm^{-1}; only CH and BH stretching frequencies are reported): ν(CH$_n$): 2972 (st), 2965 (st), 2897 (m), 2877 (m), 2859 (m); ν(BH$_n$): = 2406 (st), 2345 (st), 2206 m. − $C_{10}H_{20}B_2N_2O_4$ (221.9): calcd. C 54.13, H 9.08, N 12.62; found C 53.66, H 9.36, N 12.41.

Temperature-Dependent NMR Observations: To a solution of (*S*)-prolinol (0.67 g, 6.6 mmol) in 20 ml of THF, a $BH_3 \cdot$ THF solution (1.8 ml, 6.6 mmol of BH_3) was added at −78°C with stirring. 3 ml of the reaction mixture was transferred immediately to a 10-mm NMR tube, and ^{11}B-NMR spectra (^{1}H-coupled and decoupled) were recorded at various temperatures. The results are summarized in Table 2.

X-ray Structure Determinations: **9**: $C_{10}H_{10}B_2N_2O_4$, mol. mass 221.9, crystal size = 0.7 × 0.26 × 0.2 mm, colorless prism, orthorhombic, a = 6.795(4), b = 7.439(6), c = 22.68(1) Å; V = 1173(1) Å^3, Z = 4, space group = $P2_12_12$, μ = 0.078 cm^{-1}, $F(000)$ = 480. Data collection: 2Θ range = 4−45° in ±*h*, ±*k*, ±*l*, 3217 measured reflections, 1581 independent reflections, 1168 observed reflections [$F_o > 4\sigma(F)$]. The structure was solved by direct methods with H atoms in calculated positions except those at the boron atom, which was observed in the Fourier synthesis; non-hydrogen atoms were refined anisotropically, H atoms isotropically. R_w = 0.805, 457 parameters, data-to-parameters ratio 8:1, largest residual electron density 0.96 e/Å^3.

6: $C_{20}H_{28}B_2N_2O_2$, mol. mass 350.06, crystal size: 0.5 × 0.3 × 0.2 mm, colorless fragment, orthorhombic, a = 6.434(3), b = 6.435(2), c = 50.62(1) Å, V = 2096(1) Å, Z = 4, space group = $P2_12_12_1$, d = 1.110 g/cm^3, μ = 0.070 cm^{-1}, $F(000)$ = 752. T = 232 K. − Data collection: 2Θ = 3.2−47° in $-7 \leqslant h \leqslant 7$, $-7 \leqslant k \leqslant 7$, $-56 \leqslant l \leqslant 56$; data collected: 4566 reflections, 3067 independent reflections (R_{int} = 0.0842), 1805 observed reflections [$F > 4\sigma(F)$], ω-scans, scan speed = 4−60°/min, scan range = 1.2°. The structure was solved by direct methods; non-hydrogen atoms were refined with anisotropic thermal parameters; H atoms were included in calculated positions and the parameters refined by the riding model. − Data-to-parameter ratio 7.3:1 [$4\sigma(F)$ level]; R_1 = 0.112, wR_2 = 0.298; GOOF (F^2) = 1.074, largest residual peak/hole = 0.275/−0.381 e/Å^3. H atoms of the BH_2 group were freely refined with isotropic U_i for the H atoms.

Further information on the structure determinations is deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, 76344 Eggenstein-Leopoldshafen, and may be obtained by quoting the depository numbers CSD-405642 and -405644, the name of the authors and the journal citation.

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[19] It should be noted that the reaction of $H_3B \cdot$ THF with amines in THF solution normally affords borane adduct $R_{3-n}H_nN \cdot BH_3$ and not the $[L_2BH_2]BH_4$ salts. S. G. Shore, R. W. Parry, *J. Am. Chem. Soc.* **1955**, *77*, 1−12. − S. G. Shore, D. Cowley, *ibid.* **1965**, *87*, 2755−2756.

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