Protodeborylation of Triorganoboranes

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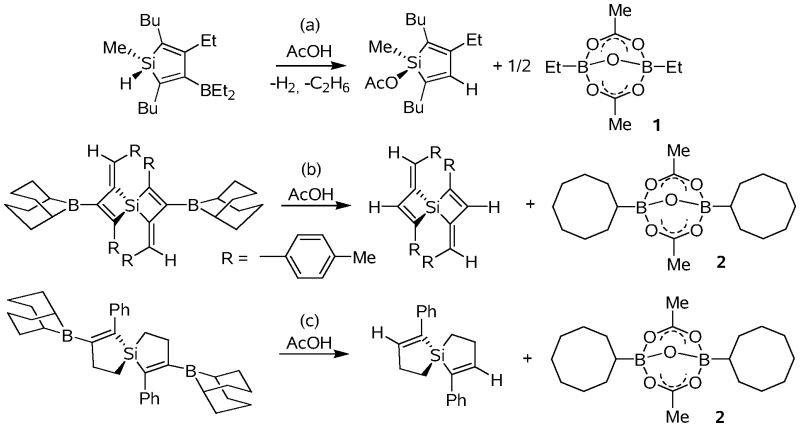
Protodeborylation of triorganoboranes, usually carried out under mild reaction conditions using an excess of acetic acid, affords 1,5-dialkyl-3,7-dimethyl-4,8,9-trioxa-2,6-dioxonia-1,5-diboratabicyclo [3.3.1]nona-2,6-dienes OB(R)OC(Me)OB(R)OC(Me)O [**1** (R = Et), **2** (R = cyclooctyl)]. Acetoxy(dialkyl)boranes and di(acetoxy)alkylboranes were not formed in an appreciable amount. Compounds **1** and **2** were characterized by NMR spectroscopy (^{1}H, ^{11}B, ^{13}C NMR) in solution, the molecular structure of **2** was determined by X-ray analysis. The gas-phase geometry of **1** was optimized by calculations [B3LYP/6-311+G(*d*, *p*) level of theory], and its NMR parameters were also calculated at the same level of theory.

Key words: Acetolysis, Protodeborylation, Diboroxanes, NMR, X-Ray, DFT Calculations

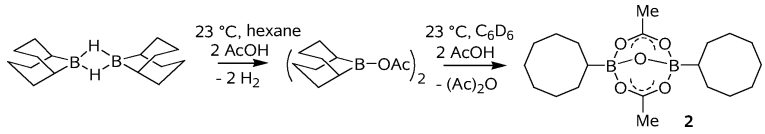
Introduction

Treatment of triorganoboranes with acetic acid is frequently used for protodeborylation [1 – 3]. In general, the major interest is focused on obtaining the organic material, and less attention is given to the boron containing products. The latter are often converted into water-soluble compounds and disposed. A systematic study of the reaction of triethylborane with anhydrous carboxylic acids [4] has shown that cleavage of the first of the three B–C bonds is a fast process, followed by a less rapid second B–C bond cleavage, while cleavage of the third B–C bond requires harsh reaction conditions. There is little doubt about the nature of the first product, in this case acetoxy(diethyl)borane, $AcOBEt_2$, considering several well characterized 9-acyloxy-9-borabicyclo[3.3.1]nonanes [5, 6]. In contrast di(acetoxy)alkylboranes have never been isolated [7, 8]. In the course of 1,1-ethylboration reactions of alkyn-1-ylmetal compounds [9, 10], and also by combining 1,2-hydroboration with 1,1-organoboration [11, 12], numerous alkenyl(diethyl)boranes or 9-alkenyl-9-borabicyclo[3.3.1]nonanes have been obtained. These compounds are attractive for protodeborylation reactions [13, 14], since they give access to heterocycles with a novel pattern of substituents as shown below for three examples of silanes (Scheme 1).

In the present work, we have studied the boron-containing compounds which result from the reactions shown as examples in Scheme 1.



Scheme 1. Examples of acetolysis of triorganoboranes containing the diethylboryl (a) or the 9-borabicyclo [3.3.1]nonyl group (b, c). The synthesis of the triorganoboranes will be reported elsewhere [26].



Scheme 2. Reaction of the 9-borabicyclo[3.3.1]nonane dimer with acetic acid. The 9-acetoxy-9-borabicyclo[3.3.1]nonane is formed first in high yield (see Fig. 1), followed by reaction with more acetic acid to give smoothly compound **2** in essentially quantitative yield.

Results and Discussion

The ethylboron compound **1** was readily identified, since it is known [15] and had been prepared in essentially quantitative yield by a completely different route, *viz.* the reaction of two equivalents of triethylboroxine, $(EtBO)_3$, with three equivalents of acetic acid anhydride, $(Ac)_2O$. The presence of cyclooctyl groups in **2** is clearly evident from the typical pattern in the ^{13}C NMR spectra which is quite different from that for the 9-borabicylo[3.3.1]nonane system (Fig. 1). Suitable crystalline material of **2** could

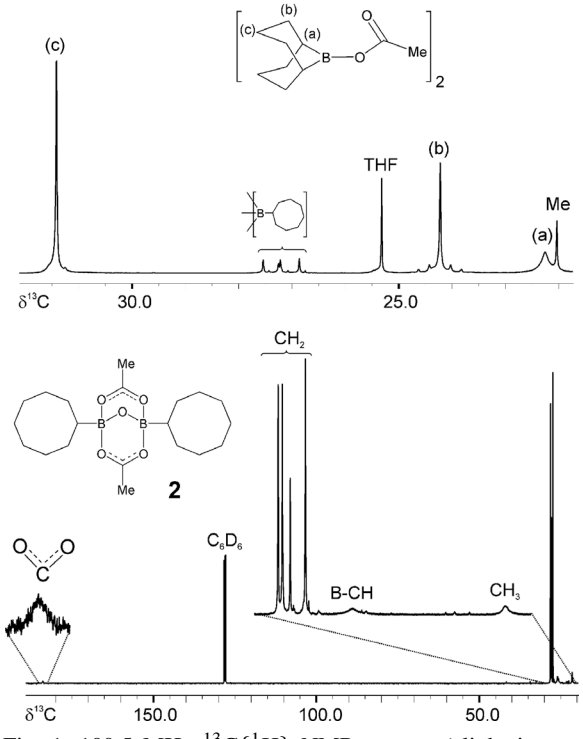
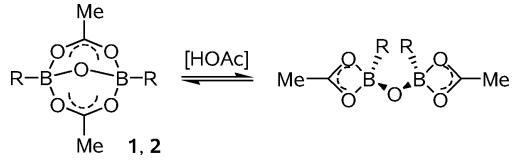


Fig. 1. 100.5 MHz $^{13}C\{^1H\}$ NMR spectra (aliphatic carbon atoms) of non-purified 9-acetoxy-9-borabicyclo[3.3.1] nonane (upper trace) and of the reaction solution containing the cyclooctylboron compound **2** (lower trace). Note the small signals in the upper trace which already represent a cyclooctyl group. Broad signals are typical of the boron-bonded carbon atoms [28] (see text for the broad $^{13}C(C(Me)O_2)$ signals).



Scheme 3.

be isolated for X-ray structural analysis (*vide infra*). The reactions studied here (Scheme 1) require an excess of acetic acid in order to achieve complete protodeborylation, and it can be assumed that $(Ac)_2O$ is generated in the course of the formation of **1** or **2**. Indeed, it has been reported that the attempted synthesis of tri(acetoxy)borane, $B(OAc)_3$, frequently leads, also by elimination of $(Ac)_2O$, to $O[B(OAc)_2]_2$ [16], which possesses a closely structural framework analogous to that of **1** or **2**.

We were surprised by the formation of **2**, since the 9-borabicyclo[3.3.1]nonane moiety often survives various transformations involving the boron atom, although we have recently observed slow cleavage *via* oxidation/hydrolysis of all B–C bonds of an 9-alkenyl-9-borabicyclo[3.3.1]nonane [17]. However, in previous reports on the treatment of 9-borabicyclo[3.3.1] nonane derivatives with carboxylic acids, no protolysis of one of the endocyclic B–C bonds was mentioned [5, 6, 18, 19]. Therefore, we have studied the reaction of the 9-borabicyclo[3.3.1]nonane dimer with acetic acid. The results are summarized in Scheme 2. The stoichiometric 1 : 1 reaction affords the 9-acetoxy-9-borabicyclo[3.3.1]nonane dimer in high yield. However, the ^{13}C NMR spectra of the reaction solution show that the mixture contains already a small amount of a cyclooctylboron compound (Fig. 1, upper trace). In the presence of an excess of acetic acid, the protolysis of one of the endocyclic B–C bonds starts immediately and is complete after 30 min at r. t.

In the cases of both **1** and **2**, the $^{13}C(CH_3CO_2)$ NMR signals are exchange-broadened. It is conceivable that the equilibrium shown in Scheme 3 is responsible, and the exchange may be catalyzed by unavoidable traces of acetic acid.

Bond/angle	**2**	**1** [15]	**1** (calcd.)	$[(AcO)_2B]_2$ [16]	$[F(AcO)B]_2$ [20]
B1 O1	1.400(2)	1.409	1.403	1.384 (4)	1.392
B2 O1	1.406(2)	1.406	1.403	1.384 (4)	
B2 O2	1.580(2)	1.579	1.602	1.551 (4)	1.532
B1 O3	1.576(2)	1.581	1.593	1.561 (4)	
C1 B1	1.586(2)	n. r.[a]	1.582	–	–
C9 O2	1.267(2)	1.272	1.271	1.269 (4)	1.271
C9 O3	1.268(2)	1.268	1.272	1.267 (4)	
C9 C10	1.490(2)	n. r.[a]	1.497	1.480 (5)	1.512
B1 O1 B2	113.29(14)	112.4	114.7	109.9	108.6
O1 B2 O2	108.57(14)	109.3	108.0	110.2	110.75
C9 O2 B2	119.92(13)	120.4	119.8	119.3	118.8
O2 C9 O3	124.13(15)	123.4	124.0	123.7	122.9
C9 O3 B1	119.39(13)	119.5	119.8	117.7	
O5 B1 O3	101.18(12)	n. r.[a]	100.8	101.6	104.45

Table 1. Selected bond lengths (Å) and angles (deg) for the cyclooctylboron compound **2**, the analogous ethylboron compound **1** (experimental [15] and calcd.) and two other related derivatives for comparison [16, 20].

[a] n. r. = not reported.

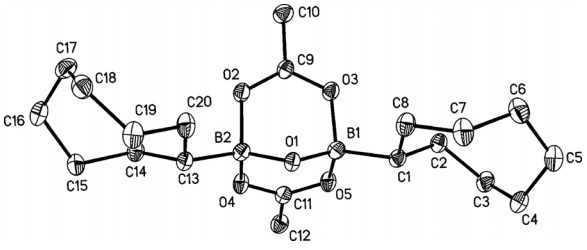


Fig. 2. Molecular structure of the cyclooctylboron compound **2** (ORTEP, 50 % probability ellipsoids; hydrogen atoms are omitted for clarity). See Table 1 for selected bond lengths and angles.

X-Ray structural study of the cyclooctylboron compound ***2***

The molecular structure of **2** is shown in Fig. 2, and selected structural parameters are given in Table 1, together with corresponding data for compounds with comparable structures [15, 16, 20]. The surroundings of the boron atoms are distorted tetrahedral. All bond lengths and angles are in the expected range, and there are only slight variations depending on the groups attached to the boron atoms. Expectedly, the cyclooctyl group in **2** does not affect the structure significantly, when compared with that of **1** [15].

DFT calculations

The gas phase molecular structure of **1** was optimized (B3LYP/6-311+G(d, p) level of theory [21 – 23]), and the structural parameters compare well with the experimental data [15]. The NMR data were calculated [24, 25] at the same level of theory, and again the agreement with experimental data is reasonable. Deviations may be traced to contributions from the equilibrium in Scheme 3 which may affect the experimental solution-state NMR parameters.

Table 2. ^{11}B and ^{13}C NMR data[a] of compounds **1** and **2**, and comparison with calculated data for **1**.

Compound	**1**[b]	**1** (calcd.)[c]	**2**
$\delta^{11}B$	7.4	6.4	8.5
$\delta^{17}O$	37 (B–O–B)	32.4 (B–O–B)	Not measured
	252 (B–O–C)	267.5 (B–O–C)	
$\delta^{13}C$(BR)	9.8 (br), 7.3	14.2, 9.9	26.0 (br), 28.2, 28.0, 27.8, 27.4
$\delta^{13}C(-CO_2)$	183.1	189.9	183.9[d]
$\delta^{13}C$(Me)	22.3	24.3	21.6[d]

[a] Measured in C_6D_6 at 23 °C; (br) indicates the ^{13}C NMR signal broadened by partially relaxed $^{13}C-^{11}B$ spin-spin coupling [28]; [b] taken from ref. [15]; the $\delta^{11}B$ and $\delta^{13}C$ data are in agreement with own measurements; [c] this work; see Experimental Section; [d] ^{13}C NMR signals are broadened by dynamic exchange processes.

Conclusions

Protodeborylation reactions at two B–C bonds starting from triorganoboranes using acetic acid may be quite fast and lead to monoalkylboron compounds containing a bicyclic framework with a B–O–B unit and two chelating acetate groups.

Experimental Section

General

The preparative work and the handling of samples were carried out observing necessary precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. The synthesis of the silole [26] and of the spirosilanes [26] shown in Scheme 1 will be reported elsewhere. Glacial acetic acid (Merck) and the 9-borabicyclo[3.3.1]nonane dimer (Aldrich) were used as commercial samples without further purification. NMR measurements (5 mm o. d. tubes, 23 °C; *ca.* 5 – 10 % in C_6D_6): Varian INOVA 400: ^1H, ^{11}B, and ^{13}C NMR; chemical shifts are given with respect to Me_4Si [δ^1H (C_6D_6) = 7.15; $\delta^{13}C$ (C_6D_6) = 128.0]; $\delta^{11}B$ = 0 for BF_3-OEt_2 with $\Xi(^{11}B)$ =

32.083971 MHz. The melting point (uncorrected) was determined using a Büchi 510 melting point apparatus.

Calculations on **1** were carried out using the GAUSSIAN 03 program package [21]. The B3LYP functional was used [22] together with the 6-311+G(*d*,*p*) basis set [23], and the optimized structure was found to be a minimum on the respective potential energy surface by the absence of imaginary frequencies. NMR parameters (chemical shifts [24] and coupling constants [25]) were calculated using the optimized geometry of **1**. Calculated $\sigma(^{11}B)$ were converted to $\delta^{11}B$ by $\delta^{11}B = \sigma(^{11}B)\,[B_2H_6] - \sigma(^{11}B) + 18$, with $\sigma(^{11}B)\,[B_2H_6] = 84.1$, $\delta^{11}B\,[B_2H_6] = 18.0$ and $\delta^{11}B\,[BF_3\text{-}OEt_2] = 0$, $\sigma(^{13}C)$ data are converted to $\delta^{13}C$ data by $\delta^{13}C = \sigma(^{13}C)\,[SiMe_4] - \sigma(^{13}C)$, with $\sigma(^{13}C)\,[SiMe_4] = 184.0$, $\delta^{13}C\,[SiMe_4] = 0$, and $\sigma(^{17}O)$ data into $\delta(^{17}O)$ by $\delta^{17}O = \sigma(^{17}O)\,[CO] - \sigma(^{17}O) + 350.1$, with $\sigma(^{17}O)\,[CO] = -72.3$, $\delta^{17}O[CO] = 350.1$ and $\delta^{17}O\,[H_2O\ (liquid)] = 0$ [27].

*1,5-Dicyclooctyl-3,7-dimethyl-4,8,9-trioxa-2,6-dioxonia-1,5-diboratabicyclo[3.3.1]nonane (**2**)*

Procedure 1

To the solution of the respective spirosilane (Scheme 1) (1.7 mmol) in 5 mL of hexane, acetic acid (0.5 mL, in 5 fold excess) was added slowly at r. t. After 30 – 40 min all the volatiles were removed in a vacuum. The oily mixture containing the protodeborylated spirosilane and 1,5-dicyclooctyl-3,7-dimethyl-4,8,9-trioxa-2,6-dioxonia-1,5-diboratabicyclo[3.3.1]nonane (**2**), was taken up in pentane and kept at −25 °C for 24 h. Solid materials settled down, were separated from the liquid fraction, dissolved in pentane, and kept at r. t. for crystallization. After a few days, crystals of **2** suitable for X-ray structural analysis were obtained. The same synthetic procedure was adopted for the reaction of the silole (Scheme 1) and gave the protodeborylated silole with an Si-OAc function and the known ethylboron compound **1** under the same conditions.

Procedure 2

A Schlenk tube was charged with the 9-borabicyclo[3.3.1] nonane dimer (1.14 g, 4.55 mmol) and hexane (10 mL). Acetic acid (0.52 mL, 9 mmol) was added slowly at r. t., and the reaction mixture was stirred for 12 h. All volatile materials were removed in a vacuum, and the solid residue was identified as 9-acetoxy-9-borabicyclo[3.3.1]nonane, which was soluble in THF and much less soluble in pentane, hexane and benzene. The 9-acetoxy-9-borabicyclo[3.3.1]nonane was taken up in benzene to give a suspension, and acetic acid was added in excess. The mixture was stirred for 40 min at r. t., and then volatile materials were removed in a vacuum. The solid residue was dissolved in C_6D_6 and identified as pure **2** by its NMR data (yield after recrystallization: 78 %; m. p. = 72 – 73 °C). 9-Acetoxy-9-borabicyclo[3.3.1]nonane: ^{1}H NMR (400 MHz, [D]$_8$-THF): δ = 0.7 – 1.6 (m, s, BBN, CH_3). – ^{13}C NMR (100.5 MHz, [D]$_8$-THF): δ = 23.2 (CH_3), 174.9 (CO_2), 32.6, 25.4, 23.4 (br) (BBN). – ^{11}B NMR (128.4 MHz, [D]$_8$-THF): δ = 16.6. **2**: ^{1}H NMR (400 MHz, C_6D_6): δ = 1.3 (s, 3H, CH_3), 1.0, 1.6, 1.8, 2.0 (m, m, m, m, 15H, cyclooctyl).

*X-Ray structural analysis of **2***

The X-ray crystal structure analysis of **2** was carried out for a single crystal (selected in perfluorinated oil [29] at r. t.) at 133(2) K using a Stoe IPDS II system equipped with an Oxford Cryostream low-temperature unit. Crystal size = 0.96 × 0.81 × 0.58 mm^3, formula weight = 360.15, triclinic crystal system, space group $P\bar{1}$, unit cell dimensions: a = 8.8325(8), b = 11.2603(10), c = 11.3627(10) Å, α = 112.147(7)°, β = 97.648(7)°, γ = 95.100(7)°, V = 1025.43(16) Å^3, Z = 2. Wavelength λ = 0.71069 Å, absorption coefficient μ = 0.084 mm^{-1}, $F(000)$ = 390 e, θ range for data collection: 1.97 – 25.64°, index ranges *hkl*: ±10, ±13, ±13, completeness to θ = 25.65°: 99.4 %; collected reflections: 13734, independent reflections: 3861, R_{int} = 0.082.

Data/restraints/parameters: 3861/0/244, goodness-of-fit on F^2 = 0.953, final R indices [$I > 2\sigma(I)$]: $R1$ = 0. 0.072, $wR2$ = 0.204, R indices (all data): $R1$ = 0.080, $wR2$ = 0.212. Largest difference peak and hole in final difference map: 1.299 and −1.218 e Å^{-3}. Structure solution and refinement were accomplished using SIR 97 [30], SHELX-97 [31], and WINGX [32].

CCDC 666799 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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