$2\theta < 50.7$ degrees and $I > 3.0\,\sigma(I)$.[27] Further refinement employed anisotropic thermal parameters for the 15 non-hydrogen atoms, and unit-weighting converging at $R_1 = 0.073$ and $R_w = 0.079$. Hydrogen atoms were generated by using idealized geometry and a 0.95-Å C–H bond distance and were included and refined isotropically. Final cycles of full-matrix least-squares refinement included a least-squares refineable isotropic extinction correction and a non-Poisson weight scheme, converging at $R_1 = 0.0354$ and $R_1 = 0.0407$, with an estimated error in the observation of unit weight of 1.519. The largest shift/error for a non-hydrogen atom in the final cycle was 0.06, and the average shift/error was 0.01. The largest peak present in the difference Fourier calculated from the fully refined model had a density of 0.30 e/Å^3 and together with the remaining less intense peaks could not be attributed to molecular disorder or lattice solvation.

Supplementary Material Available: Tables of atomic fractional coordinates, anisotropic thermal parameters for non-hydrogen atoms, bond lengths, bond angles, and 400-MHz ABX spectra of **4a**/**4b** and **8a**/**8b** (6 pages); tables of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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[27] The R values are defined as $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_\omega = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, where w is the weight given each reflection. The function which is minimized is $\Sigma w(|F_o| - K|F_c|)^2$, where K is the scale factor.

Notes

Synthesis through the Interconversion of Methoxyboranes and Boron Hydrides: 9-BBN Systems

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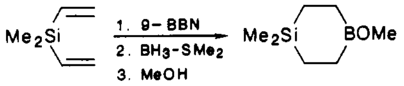
As a dialkylborane, 9-borabicyclo[3.3.1]nonane (9-BBN)[2] is unrivaled in both stability and selectivity.[3] Derivatives of 9-BBN are also both easily prepared from 9-BBN and have a variety of important synthetic applications.[4] Included in these applications is the preparation of isomerically pure boracycles, which are not available from the direct cyclic hydroboration process. This approach is outlined below for our recent synthesis of the silaborinane system.[5]



Thus, 9-BBN functions as a catalyst, first forming a diboryl adduct from α,ω-dienes, exchanging with BMS (borane–methyl sulfide) to equilibrate to the cyclic dialkylborane, and finally being converted to *B*-MeO-9-BBN with methanol. While several methods for effecting the separation of these organoborane products have been attempted by us and others, the best case found for the above example gives ca. 65% recovered 9-BBN. The remaining 9-BBN must be converted to its methoxy derivative and separated from the desired methoxyboracycle by fractional distillation. Thus, in a general sense, the difference in boiling points between cyclic borinate esters and *B*-MeO-9-BBN provides the basis of their isolation in pure form. Clearly, an efficient method for converting this byproduct back to 9-BBN would be desirable so that the true catalytic role of 9-BBN in the formation of boracycles could be realized.

Studies by Brown and Kulkarni[6] have revealed that exchange between BMS and *B*-MeO-9-BBN could be effected to give 9-BBN and $B(OMe)_3$ as the reaction products. We confirmed this finding by ^{11}B NMR, observing only **3** and **4**, together with minor (<10%) amounts of **1** and **2**, in the reaction mixture.

$$\underset{\mathbf{1}}{3[B\text{-MeO-9-BBN}]} + \underset{\mathbf{2}}{BH_3\text{–}SMe_2} \rightarrow \underset{\mathbf{3}}{{}^3/_2[\text{9-BBN}]_2} + \underset{\mathbf{4}}{B(MeO)_3}$$

Like Brown, we observed essentially pure methyl borate in the vaccum-removed volatiles. The solid 9-BBN residue contains ca. 10% of *B*-MeO-9-BBN and recrystallization as described from hexanes gives 9-BBN in 66% yield (mp 144–146 °C). The fact that 1,2-dimethoxyethane (MG) is now known to be a superior solvent for the recrystallization of 9-BBN[2] prompted us to repeat this procedure employing this solvent throughout. This change results in an increase in the yield of 9-BBN to 77% (mp 148–152 °C). Concerned as to the more quantitative aspects of the equilibration process, we examined the MG solution by ^{11}B NMR prior to the removal of the volatile components with the finding that **1**:**2**:**3**:**4** were observed in a ca. 23:5:53:19 ratio. While these ratios cannot be measured precisely due to some peak overlap, particularly between **3** and **4**, it is clear that the exchange does not go to completion. Distillation at atmospheric pressure (N_2) of the volatiles up to the boiling temperature of MG (85 °C) revealed that the major volatile boron components were **4** (53%), **2** (9%), and $(MeO)_2BH$ (38%). This result was surprising in light of the fact that only **4** was observed when the solvents were removed in vacuo! Clearly, this implied that the reaction mixture could further equilibrate to give the more volatile $(MeO)_2BH$ (bp 26 °C). 9-BBN (mp 150–152 °C) was isolated from MG in 46% yield with the supernatant containing only **1**. We interpret these results to mean that

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[1] Graduate research student supported by the NIH-MBRS program (RR-08102).

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[6] Brown, H. C.; Kulkarni, S. U. *J. Organomet. Chem.* **1979**, *168*, 281.

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with the removal of Me_2S (bp 38 °C), the heated mixture equilibrates to form both diborane and dimethoxyborane, which distill from the mixture at lower temperatures than does $B(OMe)_3$ (bp 68 °C). The first complexes with the Me_2S in the distillate to reform BMS (**2**).

This finding led us to investigate the reaction of **1** with **2** in a 2:1 stoichiometry employing MG as the reaction solvent. After 2 h at reflux temperature, distillation provides **5** (43%), **2** (22%), and **4** (35%). Recrystallization of the residue gives 9-BBN in 93% yield (mp 154–156 °C).

$$2[\underset{\mathbf{1}}{B\text{-MeO-9-BBN}}] + \underset{\mathbf{2}}{BH_3\text{-}SMe_2} \rightarrow \underset{\mathbf{3}}{[9\text{-BBN}]_2} + \underset{\mathbf{5}}{(MeO)_2BH} + \mathbf{4}$$

Only a trace amount of **1** is observable in the supernatant by ^{11}B NMR with extended pulsing. Thus, the efficient conversion of **1** to **3** has now been accomplished.

It has been reported that 9-BBN failed to react with $B(OMe)_3$ under prolonged reflux in pentane solution.[6] For our proposed equilibration process to be a satisfactory explanation for the formation of **5** in the distillation process, the reaction of **3** with **4** required experimental demonstration.

$$\mathbf{3} + \mathbf{4} \rightarrow \mathbf{1} + \mathbf{5}$$

Unlike the result in pentane, the reaction proceeds to give partial conversion in refluxing MG. However, the slow fractional distillation of the neat 1:1 reagent mixture, first at atmospheric pressure (N_2) and finally at 3 Torr, gives dimethoxyborane and *B*-MeO-9-BBN in 79% and 87% distilled, isolated yields, respectively. For the first time, this process demonstrates the reversibility of the BOMe/BH exchange and provides not only an efficient route to **5**[7] from methyl borate but also illustrates a new efficient method to convert boron hydrides to alkoxyboranes under nonprotic conditions.

Experimental Section

General Methods. All experiments were carried out in predried (4 h at 110 °C) glassware under a nitrogen atmosphere. Standard handling techniques for air-sensitive compounds were employed throughout this study.[3a] 1,2-Dimethoxyethane was distilled from sodium/benzophenone prior to use. Other reagents were either prepared as reported[2–4] or obtained from commercial sources. ^{11}B NMR data were recorded on a JEOL FX-90Q spectrometer. Analyses of boron esters were performed on a Perkin-Elmer Model Sigma 1B gas chromatographic system equipped with either a 6 ft × $^1/_8$ in. 20% SE-30 on DCDMS-treated Chrom W or a 30 m × 0.23 mm i.d. 20% SE-30 vitreous silica open tubular column. Columns were silylated (MSTFA, Pierce) prior to analytical runs for organoboranes and used with a low injection port temperature (120 °C). IR data were obtained on a Perkin-Elmer Model 337 spectrophotometer.

9-Borabicyclo[3.3.1]nonane (3). To a stirred solution of **1** (68 g, 0.44 mol) in MG (400 mL) contained in a distillation assembly with a cold finger condensor and fully variable take-off valve was added BMS (24.8 mL, 8.90 M, 0.22 mol) dropwise. The mixture was heated at reflux temperature for 1.5 h, and the distillate was collected until the distillation temperature reached 85 °C. The residual solution was allowed to cool slowly to room temperature to give crystalline **3**. The distillation assembly was removed under a positive pressure of N_2, the flask was septum-sealed, and the contents were further cooled to −20 °C. Decantation of the supernatant under positive N_2 pressure employing a double-ended needle gives **3** to which was added fresh, dry 1,2-dimethoxyethane (250 mL). Dissolution of **3** with heating, followed by slow cooling as above, gives, after drying at 0.1 Torr for 12 h, 50.1 g (93%) of pure **3**; mp 154–156 °C (lit.[2] mp 153–155 °C).

***B*-Methoxy-9-borabicyclo[3.3.1]nonane (1) and Dimethoxyborane (5).** To **3** (24.4 g, 0.200 mol) contained in a distillation assembly as described above with the condensor held at −10 °C employing an external low temperature circulating pump was added methyl borate (**4**) (20.8 g, 0.200 mol). The stirred mixture was heated to reflux temperature and 11.7 g (79%) of pure **5** was collected at 26 °C (lit.[7] bp 25.9 °C at 760 Torr). The residue was distilled at reduced pressure to give 26.6 g (87%), bp 55–56 °C at 3 Torr (lit.[5] bp 81–83 °C at 11 Torr).

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Registry No. 1, 38050-71-4; 2, 13292-87-0; 3, 280-64-8; 4, 121-43-7; 5, 4542-61-4.

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[7] We observed this compound to undergo slow decomposition to diborane and **4** (cf. Burg, A.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1933**, *55*, 4020).

Action of Dinitrogen Tetraoxide on the 5-Hydroxy-3,5-dimethyl-4-oximido-2-isoxazoline System

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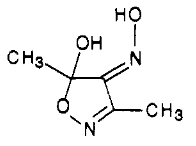
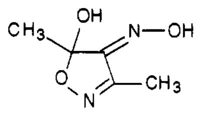
In earlier work[1] we have shown that the product obtained by the action of an equimolar amount of hydroxylamine on isonitrosoacetylacetone is a mixture of the two 5-hydroxy-3,5-dimethyl-4-oximido-2-isoxazoline stereoisomers **1a** and **1b** and not "acetylmethylglyoxime" as had been assumed previously.[2]



1a



1b

We now report on the reactions of these two isomers **1a**, **1b** with dinitrogen tetraoxide (molar ratio 1/1.25) in ether solution. When **1a** or **1b** is suspended in dry ether and treated under stirring and ice-water cooling with dinitrogen tetraoxide a brown solution is immediately formed. After 30 min addition of petroleum ether caused precipitation of white crystals (mp 88–89 °C dec) having a molecular formula $C_5H_7N_3O_6$.

Since it is known that dinitrogen tetraoxide reacts with ketoximes to form *gem*-dinitro compounds (Ponzio reaction),[3] an obvious hypothesis is to assign to this compound the structure **2**. The presence of nitro group vibrations (KBr) (ν_{asym} d 1590, 1570 cm^{-1}; ν_{sym} 1380 sh, 1370 cm^{-1})[4] were consistent, but the strong C═O absorption at 1795 cm^{-1} and the ^{13}C NMR spectrum ruled out this hypothesis.

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[4] Splitting of the NO_2 asymmetrical and symmetrical stretching bands due to vibrational interactions can occur in polynitro compounds; see, e.g.: Brown, J. F. *J. Am. Chem. Soc.* **1955**, *77*, 6341–6351.

0022-3263/87/1952-3442$01.50/0