

and elsewhere<sup>2</sup> to proceed to completion under much milder conditions than did the overall reaction. Neither of the two intermediates in sequence A could therefore reach significant concentrations during reaction and therefore would escape detection.

The experimental data thus were fully consistent with sequence A, in which there was a primary and slow substitution of trimethylamine-borane by 4-methylpyridine-borane. This was followed by a very rapid conversion of the neutral 4-methylpyridine-dibromoborane to the bromohydrobis(4-methylpyridine)boron(1+) ion which in turn yields the final 2+ ion at a relatively fast rate.

**Relative Reactivities.** The facts presented here and in previous work<sup>1-3</sup> allow one to make the following generalizations regarding the reactivities of haloboranes and haloborane cations toward eventual substitution by nitrogen bases.

When diiodoboranes are used in place of bromoboranes, a general increase of reactivity with respect to halide loss results,<sup>1,2</sup> as is the case for halide loss from monohaloboranes.<sup>3</sup> There is a further enhancement of reactivity when one compares trimethylamine adducts with adducts of pyridine bases. Although cations tend to be less reactive than neutral boranes, the latter relationship is maintained also for cationic species, since (4-CH<sub>3</sub>py)<sub>2</sub>BHBr<sup>+</sup> appeared to be more reactive than the dissymmetric [(4-CH<sub>3</sub>py)(CH<sub>3</sub>)<sub>3</sub>N]BHBr<sup>+</sup>.

These facts allow one to formulate strategies for the synthesis of unsymmetrically substituted boron cations via nu-

cleophilic displacements. For example, the racemate of the dissymmetric [(4-CH<sub>3</sub>py)(CH<sub>3</sub>)<sub>3</sub>N]BH<sup>+</sup> ion, though capable of existence,<sup>9</sup> is not obtainable for X = Br by simple displacements, because trimethylamine-dibromoborane is too unreactive toward halide loss and instead loses trimethylamine when exposed to 4-methylpyridine. Optimal reactivity is achieved in 4-methylpyridine-diiodoborane, which allows displacement of iodide even by trimethylamine. Similarly, the enhancement of reactivity by the presence of iodide and a pyridine ring made possible the synthesis of the mixed-tris-(amine) cation (4-CH<sub>3</sub>py)BH<sup>2+</sup> via pyridine-diiodoborane.

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**Registry No.** (4-CH<sub>3</sub>C<sub>5</sub>H<sub>7</sub>N)<sub>2</sub>BH<sub>2</sub>Br, 74081-68-8; (4-CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>BHBr<sub>2</sub>, 74081-69-9; (4-CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>BBR<sub>3</sub>, 74081-70-2; [(4-CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>N)(CH<sub>3</sub>)<sub>3</sub>N]BHI<sub>2</sub>, 74081-71-3; [(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>(4-CH<sub>3</sub>C<sub>5</sub>H<sub>5</sub>N)]BHI<sub>2</sub>, 74081-72-4; (4-CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>BBR<sub>2</sub>(PF<sub>6</sub>), 27882-74-2; [(4-CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>N)(CH<sub>3</sub>)<sub>3</sub>N]BHI(PF<sub>6</sub>), 74081-74-6; [(4-CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>N)]BH(PF<sub>6</sub>)<sub>2</sub>, 74081-76-8; [(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>(4-CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>N)]BH(PF<sub>6</sub>)<sub>2</sub>, 74112-68-8; (4-CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>N)<sub>3</sub>BHBr<sub>2</sub>, 72541-47-0; (4-CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>N)<sub>3</sub>BH(PF<sub>6</sub>)<sub>2</sub>, 25338-40-3; [(4-CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>N)(CH<sub>3</sub>)<sub>3</sub>N]BHBr<sub>2</sub>, 74081-77-9; [(C<sub>5</sub>H<sub>5</sub>N)(4-CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>N)]BH<sub>2</sub>PF<sub>6</sub>, 22638-66-0; [(C<sub>5</sub>H<sub>5</sub>N)(CH<sub>3</sub>)<sub>3</sub>N]BHI<sub>2</sub>, 74081-78-0; (CH<sub>3</sub>)<sub>3</sub>N·BH<sub>2</sub>Br, 5275-42-3; 4-CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>N·BH<sub>3</sub>, 3999-39-1; C<sub>5</sub>H<sub>5</sub>N·BH<sub>3</sub>, 110-51-0.

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## Boron Subhalide Chemistry. Formation of Octabromomethylnonaborane, CH<sub>3</sub>B<sub>9</sub>Br<sub>8</sub>, and Other Alkylated Nonaboranes from Triethylammonium Decabromodecaborate

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The thermal decomposition of [(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NH]<sub>2</sub>B<sub>10</sub>Br<sub>10</sub> has been investigated to determine if the oxidative-decomposition reaction of perhalogenated borane anion salts other than (H<sub>3</sub>O)<sub>2</sub>B<sub>10</sub>Cl<sub>10</sub> might prove to be a viable synthetic route for the preparation of substituted boron subhalides. At temperatures near 430 °C the trialkylammonium salt is found to decompose to yield predominantly the new compound CH<sub>3</sub>B<sub>9</sub>Br<sub>8</sub>. The decomposition appears to be radical in nature. By varying the reaction conditions we can also isolate other previously unknown alkylated boron subbromides, C<sub>2</sub>H<sub>5</sub>B<sub>9</sub>Br<sub>8</sub>, (CH<sub>3</sub>)<sub>2</sub>B<sub>9</sub>Br<sub>7</sub>, and CH<sub>3</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>B<sub>9</sub>Br<sub>7</sub>, along with B<sub>9</sub>Br<sub>9</sub>, but in smaller amounts. The boron chemical shifts of B<sub>9</sub>Br<sub>9</sub> (-60.4 ppm) and CH<sub>3</sub>B<sub>9</sub>Br<sub>8</sub> (-62.2 ppm) are shown to be very deshielded relative to the chemical shifts of similar nine-atom frameworks that contain 2n + 2 framework electrons.

### Introduction

Little is known about the boron subhalides, e.g., B<sub>4</sub>Cl<sub>4</sub>, B<sub>8</sub>Cl<sub>8</sub>, or B<sub>9</sub>Cl<sub>9</sub>, and less about their derivatives. These compounds are of interest because they have two fewer framework electrons than are usually required by the well-known framework electron-structural correlation.<sup>1</sup> In part, the subhalides have been little studied because there are few convenient syntheses available.

The earliest preparation of these compounds involved the formation, in discharge reactions, of B<sub>2</sub>Cl<sub>4</sub> which was then thermally decomposed to yield the very unusual radical species B<sub>12</sub>Cl<sub>11</sub> along with a number of polyhedral boron subchlorides, B<sub>n</sub>Cl<sub>n</sub> (n = 4, 7-12).<sup>2</sup> Diboron tetrabromide is similarly reported, primarily on the basis of mass spectral results, to yield a number of polyhedral boron subbromides, B<sub>n</sub>Br<sub>n</sub> (n = 7-10), when heated.<sup>3</sup> The yields of the boron subhalides obtainable

from these decompositions are not known.

Two other preparations each of which yields only one polyhedral product have been reported. The first is the oxidation of the borane anion B<sub>9</sub>H<sub>9</sub><sup>2-</sup> which, when reacted with 20 equiv of SO<sub>2</sub>Cl<sub>2</sub>, forms B<sub>9</sub>Cl<sub>9</sub> in 30% yield.<sup>4</sup> The second is the thermal decomposition of the hydronium salt of the perchlorinated borane anion (H<sub>3</sub>O)<sub>2</sub>B<sub>10</sub>Cl<sub>10</sub>. From the latter reaction one of the very few known derivatives of the boron subhalides, B<sub>9</sub>Cl<sub>8</sub>H, has been isolated.<sup>5</sup> Aside from its synthetic aspects the second reaction is of particular interest because several events must occur contemporaneously: oxidation of the anion to the subhalide; substitution of one of the ligands; and reduction in cage size. Since the original publication, however, there have been no further studies to indicate

(1) K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976).

(2) E. P. Schram and G. Urry, *Inorg. Chem.*, **2**, 405 (1963); G. F. Lanthier, J. Kane, and A. G. Massey, *J. Inorg. Nucl. Chem.*, **33**, 1569 (1971).

(3) M. S. Reason and A. G. Massey, *J. Inorg. Nucl. Chem.*, **37**, 1593 (1975).

(4) R. M. Kabani and E. H. Wong, *J. Chem. Soc., Chem. Commun.*, 462 (1978).

(5) J. A. Forstner, T. E. Haas, and E. L. Muetterties, *Inorg. Chem.*, **3**, 155 (1964).

whether this decomposition is specific to hydronium salts and perchlorinated borane anions or if this type of decomposition reaction might possibly prove to be a general preparative route to derivatives of the boron subhalides.

The present preliminary study was designed to reveal more details of the thermal decomposition-oxidation reaction of the halogenated borane anions. The triethylammonium salt of the decabromodecaborate(2-) ion,  $(\text{Et}_3\text{NH})_2\text{B}_{10}\text{Br}_{10}$ , was selected as a substrate since the results obtained from this compound might answer several questions about the nature of the decomposition simultaneously. For example, it was of interest to find whether oxonium cations,  $\text{R}_3\text{O}^+$ , were required to provide the cage ligand, or if ammonium cations might also serve. Additionally, this salt would test whether brominated cage compounds could be formed by this procedure and if they would then have the requisite stability for their subsequent isolation. Further, it was important to learn if ligands other than hydride could be incorporated into any subhalide that might be isolated. Finally, since cage size reduction from ten membered to nine membered, as in the case of  $\text{B}_{10}\text{Cl}_{10}^{2-}$ , is still relatively rare, it was of interest to determine if a similar reduction in cage size was indicated in the thermal decomposition of  $(\text{Et}_3\text{NH})_2\text{B}_{10}\text{Br}_{10}$ .

### Experimental Section

During the thermal decomposition experiments conventional vacuum lines and gloveboxes were used throughout. Boron NMR spectra at 28.8 MHz were obtained from a Bruker HFX-90 spectrometer while proton NMR spectra at 60 or 80 MHz were provided by Varian T-60 and Bruker WP-80 instruments, respectively. Chemical shifts are referenced to external  $\text{BF}_3\cdot\text{OEt}_2$  or tetramethylsilane; less positive chemical shifts are deshielded. Infrared data were from a PE 1257 spectrophotometer; mass spectra were recorded by an AEI MS-30 double-focusing spectrometer operating at 70 eV and ambient temperature. Decaborane, 90% recovery, was sublimed at 74 °C prior to use. Triethylamine, bp 89 °C, was distilled from KOH after treatment with phenyl isocyanate.

The reaction of  $\text{B}_{10}\text{H}_{14}$  with triethylamine formed  $(\text{Et}_3\text{NH})_2\text{B}_{10}\text{H}_{10}$  which, after recrystallization from water/ethanol, was isolated in 85% yield and identified by comparison with the reported spectroscopic properties of the compound.<sup>6</sup> Bromination of the anion was effected by the slow addition of bromine to a 50/50 aqueous ethanol solution containing the hydride. After recrystallization from water, IR and NMR indicated only  $(\text{Et}_3\text{NH})_2\text{B}_{10}\text{Br}_{10}$ <sup>7</sup> in 68% yield; absorptions indicative of boron hydrides were absent. The group 1 (Na, K, Cs) containing salts were prepared by standard cationic exchange-precipitation reactions,<sup>6</sup> which were monitored by atomic absorption. Alternatively, the metal borohydride, e.g.,  $\text{Na}_2\text{B}_{10}\text{H}_{10}$ , could be isolated and then brominated, as above.

Small samples, 0.5–1.0 g, of each of the perbrominated compounds were individually placed in 10 × 400 mm Pyrex or quartz tubes which were attached to a vacuum line and evacuated. A series of traps maintained at -196 °C were utilized to retain any condensable gases which might be evolved as the samples were heated by a tube furnace that surrounded the bottom 15 cm of the reactors. Noncondensable gas formation was indicated by a thermocouple vacuum gauge.

When the metal-containing salts  $\text{Na}_2\text{B}_{10}\text{Br}_{10}$ ,  $\text{K}_2\text{B}_{10}\text{Br}_{10}$ , or  $\text{Cs}_2\text{B}_{10}\text{Br}_{10}$  were heated to temperatures as high as 1000 °C, no decomposition to yield molecular subhalides was evident. Triethylammonium decabromodecaborate, however, smoothly decomposed at temperatures that varied slightly but were most often near 430 °C. The onset of the reaction was indicated by a pressure rise which was followed by the evolution of gaseous material, part of which passed through the traps and part of which did not. Simultaneously, a bright red ring which slowly increased in volume formed slightly above the mouth of the furnace.

After termination of the reaction the contents of the traps were fractionated and examined by IR and mass spectrometry which in-

Table I.  $[(\text{C}_2\text{H}_5)_3\text{NH}]_2\text{B}_{10}\text{Br}_{10}$  Decomposition Products

compd	<i>m/e</i>	rel amt <sup>8</sup>
$\text{B}_9\text{Br}_9$	817	55
$\text{C}_2\text{H}_5\text{B}_9\text{Br}_8$	766	5
$\text{CH}_3\text{B}_9\text{Br}_8$	752	100
$\text{C}_2\text{H}_5(\text{CH}_3)\text{B}_9\text{Br}_7$	701	3
$(\text{CH}_3)_2\text{B}_9\text{Br}_7$	687	10

dicated that  $\text{HBr}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{C}_2\text{H}_5\text{Br}$ ,  $\text{C}_3\text{H}_7\text{Br}$ , and  $\text{C}_4\text{H}_9\text{Br}$ , along with  $\text{BBr}_3$  and  $(\text{C}_2\text{H}_5)_3\text{N}$ , had formed. The Pyrex reactor was sealed with a torch and removed to a glovebox where the sublimate, in 15% yield, was dissolved in  $\text{CCl}_4$  to form a red solution. Although the sublimate did survive brief exposure to the atmosphere, typically air was excluded insofar as practical. The boron and proton NMR of the solution each contained a broad singlet at -62.2 ppm and  $\tau$  10.06, respectively. Infrared data indicated the presence of methyl groups and brominated, caged boranes by absorptions near 2950 and 960  $\text{cm}^{-1}$ .<sup>3</sup> Mass spectra proved to be most informative, containing the ions [*m/e*, ion (intensity)]: 752,  $\text{CH}_3\text{B}_9\text{Br}_8$  (100%); 566,  $\text{B}_8\text{Br}_6$  (44%); 501,  $\text{CH}_3\text{B}_8\text{Br}_5$  (28%), corresponding to the molecular ion for  $\text{CH}_3\text{B}_9\text{Br}_8$  and the loss of  $\text{CH}_3\text{BBr}_2$  and  $\text{BBr}_3$  from that ion.<sup>8</sup> Each of the ions was contained in an envelope of the distributions and intensities expected from the required isotopic composition.

Because a large number of very volatile products, e.g., the alkyl bromides, were produced in the reaction but only one subhalide had been isolated (above), a short survey of the possibility of influencing the number and type of boron-containing products was undertaken. When small amounts of trialkylammonium halides were added and the furnace was very slowly heated to the minimum decomposition temperature, near 400 °C, the observed boron-containing products, present in only about 5% yield, were  $\text{CH}_3(\text{C}_2\text{H}_5)_2\text{B}_9\text{Br}_7$  and  $(\text{CH}_3)_2\text{B}_9\text{Br}_7$  isolated in a 1:1 ratio as determined by mass spectrometry. Mass spectrum of  $\text{CH}_3(\text{C}_2\text{H}_5)_2\text{B}_9\text{Br}_7$  [*m/e*, ion (intensity)]: 701,  $\text{CH}_3(\text{C}_2\text{H}_5)_2\text{B}_9\text{Br}_7$  (100%); 621,  $\text{CH}_3(\text{C}_2\text{H}_5)_2\text{B}_9\text{Br}_6$  (20%).  $(\text{CH}_3)_2\text{B}_9\text{Br}_7$ : 687,  $(\text{CH}_3)_2\text{B}_9\text{Br}_7$  (100%); 607,  $(\text{CH}_3)_2\text{B}_9\text{Br}_6$  (15%); 501,  $\text{CH}_3\text{B}_8\text{Br}_5$  (10%). Boron NMR chemical shift: -62.4 ppm, with very slightly deshielded shoulder. <sup>1</sup>H NMR chemical shifts were  $\tau$  10.06, methylnonaborane resonances, and  $\tau$  10.10 ( $\text{CH}_3$ ) and 10.16 ( $\text{CH}_2$ ), ethylnonaborane resonances.

When the furnace was elevated, to increase the length of the flight path of the substrate through the high-temperature region, only  $\text{CH}_3\text{B}_9\text{Br}_8$  and  $\text{B}_9\text{Br}_9$  were isolated in a 2:1 ratio from the red substrate. For  $\text{B}_9\text{Br}_9$ : <sup>11</sup>B NMR -60.4 ppm; mass spectrum [*m/e* (ion intensity)], 817 ( $\text{B}_9\text{Br}_9$ , 95%), 737 ( $\text{B}_8\text{Br}_6$ , 5%), 566 ( $\text{B}_8\text{Br}_6$ , 100%); major IR absorptions<sup>3</sup> 950, 650, 450  $\text{cm}^{-1}$ .

For determination of the range of products that could be produced from a single decomposition reaction, the temperature of the furnace was increased from ambient as rapidly as possible. The sublimate obtained, in about 20% yield, was variegated in hue, bright red away from the furnace and a much deeper, ruby red nearest the orifice of the furnace. The boron NMR spectrum of the sublimate contained a very broad (90 Hz) resonance centered at -61.9 ppm while the proton NMR contained methyl and ethyl resonances similar to those noted above. Mass spectrometry of the sublimate indicated that  $\text{B}_9\text{Br}_9$  and the alkyl- and dialkylnonaboranes  $\text{RB}_9\text{Br}_8$  and  $\text{R}_2\text{B}_9\text{Br}_7$  ( $\text{R} = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ) were all present as shown in Table I.

The individual properties of these compounds will be commented upon subsequently, but, collectively, all of the mono- and dialkylnonaboranes are highly colored; however, the intensity of the coloration decreases upon increasing alkyl substitution. All react slowly with the atmosphere, but each is stable enough to survive brief exposure to temperatures of 400 °C and to the air for periods of about 30 min. All are soluble in and stable toward nonpolar solvents like  $\text{CCl}_4$  and hexane and also soluble in but, as might be expected of very electron-deficient compounds, more reactive toward Lewis bases such as ethereal solvents. Each of the compounds can be sublimed at tem-

(6) M. F. Hawthorne and R. L. Pilling, *Inorg. Synth.*, **9**, 16 (1967); E. L. Muettterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *Inorg. Chem.*, **3**, 444 (1964).  
 (7) W. H. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia, and E. L. Muettterties, *Inorg. Chem.*, **3**, 159 (1964).

(8) The mass spectra of all of the known boron subhalides and their derivatives contain very large molecular ions. Typically, the intensity of the ions corresponding to the molecular ions less  $\text{BX}_3$ ,  $\text{X} = \text{Cl}, \text{Br}, \text{or } \text{CH}_3$  (above), is not the most intense polyboron envelope in the spectrum, is the second largest. Because of the large number of boron and bromine isotopes present in these ions, the identification is very straightforward. See also: ref 3; M. S. Reason and A. G. Massey, *J. Inorg. Nucl. Chem.*, **38**, 1789 (1976); A. G. Massey, D. S. Urch, and A. K. Holliday, *ibid.*, **28**, 365 (1966); J. Kane and A. G. Massey, *ibid.*, **33**, 1195 (1971).

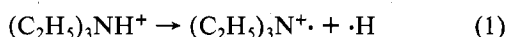
peratures near or below 100 °C, but the thermal stability appears to decrease with increasing alkyl substitution. Thus the most stable borane formed is B<sub>9</sub>Br<sub>9</sub>, which is also the least volatile. The nonaborane usually produced in highest yield, and often the only nonaborane isolated, is CH<sub>3</sub>B<sub>9</sub>Br<sub>8</sub>, the alkylated analogue of HB<sub>9</sub>Cl<sub>8</sub>. If caged species with other than nine boron atoms are produced in this reaction, the amounts formed are small.

### Results and Discussion

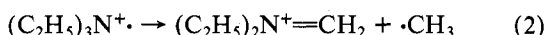
The immediate goal of this study was to determine if any of the boron subborides or their derivatives could be isolated from the thermal decomposition of (Et<sub>3</sub>NH)<sub>2</sub>B<sub>10</sub>Br<sub>10</sub>. If the synthesis were successful, it might result in the first preparation of alkylated derivatives of the boron subborides and it could be an indication that the decomposition-oxidation reaction of perhalogenated borane anions may have considerable utility as a synthetic route in the preparation of boranes containing only 2*n* framework electrons.

In practice, the compound is found to decompose smoothly with the liberation of noncondensable gases, a number of alkyl bromides, and, depending upon the conditions, any of at least five nonaboranes. The yields of the alkylated subborides obtained, 5–15%, while not outstanding, are acceptable. Further, although at least small amounts of several nonaboranes are most likely formed initially, judicious control of the conditions employed can result in a fair degree of selectivity in the number and type of products actually isolated. Lower temperatures appear to favor the formation of the dialkyl derivatives of the B<sub>9</sub> cage, but at higher temperatures the monoalkyl derivative CH<sub>3</sub>B<sub>9</sub>Br<sub>8</sub>, which was the only subhalide usually isolated, predominates and the yield of the dialkyl derivatives is suppressed; B<sub>9</sub>Br<sub>9</sub> is also observed, but always in smaller amounts than CH<sub>3</sub>B<sub>9</sub>Br<sub>8</sub>.

Overall, the reaction appears to be radical in character as evidenced by the number of alkyl bromides formed and the variety of nonaboranes isolated. The formation of the methylated boranes CH<sub>3</sub>B<sub>9</sub>Br<sub>8</sub>, CH<sub>3</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>B<sub>9</sub>Br<sub>7</sub>, and (CH<sub>3</sub>)<sub>2</sub>B<sub>9</sub>Br<sub>7</sub> from the triethylammonium salt appears unusual, but if the reaction does proceed via a radical mechanism, formation of these compounds can be rationalized by invoking the intermediacy of a radical cation formed from the ammonium cation, possibly by the reaction shown in eq 1. Significant



interaction between the nascent hydrogen and the borane anion, which is also present, might be expected. Mass spectrometric studies have shown that the dominant decomposition mode of an alkylammonium radical cation is β cleavage as shown in eq 2, which leads directly to the formation of methyl radicals by a reaction channel which is relatively low in energy.<sup>9</sup>



Three further observations on the products formed in this reaction deserve comment. The first is that all of the products thus far obtained from the oxidative decomposition of both B<sub>10</sub>Br<sub>10</sub><sup>2-</sup> and B<sub>10</sub>Cl<sub>10</sub><sup>2-</sup> are boranes in which cage size reduction from ten to nine membered has occurred. Whether this is a

result of the mechanism by which the oxidative process occurs or is a reflection of the relative stability of nine-membered clusters vs., e.g., eight-membered clusters, is, as yet, unknown. While the results obtained here indicate that it is entirely possible that under some conditions the compound HB<sub>9</sub>Cl<sub>8</sub> could be the only volatile product isolated from the decomposition of (H<sub>3</sub>O)<sub>2</sub>B<sub>10</sub>Cl<sub>10</sub>, it appears likely that other boron-containing products might be expected in differing circumstances.

Secondly, the boron NMR chemical shifts of the 2*n* framework electron boranes prepared here, while more shielded than found for B<sub>4</sub>Cl<sub>4</sub>, -85 ppm,<sup>10</sup> are significantly deshielded in comparison to their 2*n* + 2 electron analogues, most likely because of the increased electron density about the boron atoms in the latter compounds. For example, the chemical shift of B<sub>9</sub>Br<sub>9</sub> is -60.4 ppm and that of CH<sub>3</sub>B<sub>9</sub>Br<sub>8</sub> is -62.2 ppm. Each of these resonances is thus about 60–70 ppm less shielded than the resonances observed for B<sub>9</sub>H<sub>9</sub>Br<sub>8</sub><sup>2-</sup> which are located at -1.4 and +9.9 ppm.<sup>11</sup> Alkyl for bromine substitution in the boron subhalides results in further deshielding, ca. 2 ppm, which is slightly smaller in magnitude than the effect when similar substitutions occur in the boron trihalides,<sup>12</sup> in bromocarboranes in general,<sup>13</sup> and in Br-4,5-C<sub>2</sub>B<sub>7</sub>H<sub>9</sub>.<sup>14</sup>

Finally at 28.8 MHz and ambient temperature the boron NMR spectrum of B<sub>9</sub>Br<sub>9</sub> is a singlet whereas the spectra of other nine-membered borane clusters typically contain resonances indicative of well-localized structures. The spectrum of B<sub>9</sub>H<sub>9</sub><sup>2-</sup>, for example, is found to have the absorptions expected for a tricapped trigonal-prismatic species,<sup>11</sup> and the spectrum of the carborane 4,5-C<sub>2</sub>B<sub>7</sub>H<sub>9</sub> similarly reflects a static structure.<sup>14</sup> Whether the spectrum of B<sub>9</sub>Br<sub>9</sub> is an indication of fluctuonality in the molecule or of unresolved differences in chemical shifts is, as yet, not known. Similarly, if the spectrum of CH<sub>3</sub>B<sub>9</sub>Br<sub>8</sub> contains more than one boron resonance, the difference in chemical shifts is not large.

In conclusion oxidative-decomposition reactions of the perhalogenated borane anions appear to offer considerable potential as a synthetic route for the preparation of what may be a large class of compounds, the derivatives of the boron subhalides. These species while lacking the "magic number" of electrons required for "superaromaticity" are stable enough to survive temperatures on the order of 400 °C during their preparation; no decomposition at ambient temperatures has been observed. The boron subhalides represent end members of the closo 2*n* framework electron metalloborane series found by Grimes,<sup>15</sup> among others, and because they are homoatomic cluster compounds, the boron subhalides and their derivatives may prove to be particularly effective probes in the study of cluster systems that violate Wade's seventh rule.<sup>1</sup>

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**Registry No.** [(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NH]<sub>2</sub>B<sub>10</sub>Br<sub>10</sub>, 74081-80-4; C<sub>2</sub>H<sub>5</sub>B<sub>9</sub>Br<sub>8</sub>, 74081-81-5; CH<sub>3</sub>B<sub>9</sub>Br<sub>8</sub>, 74081-82-6; C<sub>2</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>2</sub>B<sub>9</sub>Br<sub>7</sub>, 74185-22-1; (CH<sub>3</sub>)<sub>2</sub>B<sub>9</sub>Br<sub>7</sub>, 74185-21-0; B<sub>9</sub>Br<sub>9</sub>, 74081-83-7.

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