Volume 3
Number 2
January 27, 1964

Inorganic Chemistry

Contribution No. 915 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Delaware

# Chemistry of Boranes. VII.[1] Octachlorononaborane-9 and Its Salts

By J. A. Forstner, T. E. Haas, and E. L. Muetterties

*Received September 16, 1963*

Octachlorononaborane-9, $B_9Cl_8H$, is a volatile, solid pyrogenic product of $H_2B_{10}Cl_{10}\cdot xH_2O$. In aqueous solution $B_9Cl_8H$ is reduced to the dianion, $B_9Cl_8H^{-2}$.

The decomposition of $B_2Cl_4$ at 0° has been reported to yield nonvolatile BCl polymers, as well as yellow crystalline $B_4Cl_4$[2] and red crystalline $B_8Cl_8$.[3] Both molecules have been shown to be polyhedral cages of boron atoms, each bonded to a chlorine atom.[3,4]

Recently, Urry, *et al.*, have reported that stable free radicals are formed in the spontaneous disproportionation of $B_2Cl_4$.[5] The red solid $B_{12}Cl_{11}$ was characterized as well as dark purple crystals corresponding to $(B_1Cl_{0.9-1.1})_x$.

We have prepared a new polyhedral chloroborane, $B_9Cl_8H$, by degradation of the acid of $B_{10}Cl_{10}^{-2}$.[6] This new borane has moderate thermal stability but is degraded by water to boric acid. In the hydrolysis, one of the intermediates is the dianion $B_9Cl_8H^{-2}$, which has been isolated from the hydrolysis reaction by precipitation with a large cation.

**Synthesis.**—The crystalline acid, $(H_3O)_2B_{10}Cl_{10}\cdot 5H_2O$, undergoes reversible dehydration under vacuum to a dihydrate at 150°.

$$(H_3O)_2B_{10}Cl_{10}\cdot 5H_2O \rightleftharpoons 3H_2O + (H_3O)_2B_{10}Cl_{10}\cdot 2H_2O$$

An irreversible decomposition occurs at 260° and red crystals of $B_9Cl_8H$ sublime from the reaction zone. The other volatile products of decomposition are hydrogen, hydrogen chloride, and traces of water. Most of the boron, however, is found in the nonvolatile residue which has an approximate composition of $B_{2.0}Cl_{1.0}O_{1.1}$.

**Characterization.**—Octachlorononaborane-9 was purified by vacuum sublimation. Elemental analyses were consistent with the proposed formulation, but these were not sufficient in themselves to establish composition rigorously. Additional information obtained from spectroscopic data and hydrolysis studies did provide definitive characterization.

The mass spectrum of $B_9Cl_8H$ was complex with all $B_xCl_y$ fragments represented through $B_{10}Cl_{10}$. However, the peaks above $m/e = 382$ ($B_9Cl_8$) were of very low intensity and may have arisen by recombinations within the spectrometer. The most intense mass number was 298 ($B_8Cl_6^+$ and possibly $B_5Cl_7^+$). The fragmentation pattern established the presence of hydrogen and the absence of oxygen. Solution molecular weight determinations were also consistent with the $B_9Cl_8H$ formulation. Furthermore, direct oxygen analyses by reaction of $B_9Cl_8H$ with $KBrF_4$ gave results comparable to blank determination. Thus the presence of oxygen in the red crystals can be rigorously excluded.

Pure $B_9Cl_8H$ is diamagnetic and therefore must have an odd number of hydrogen atoms. The $B^{11}$ n.m.r. data (*vide infra*) show that one of the nine boron atoms is directly bonded to one hydrogen atom. Quantitative hydrolytic hydrogen determinations also fix the number of hydrogen atoms per $B_9Cl_8$ as one.

**Chemical Properties.**—Exposure of $B_9Cl_8H$ to the atmosphere leads to the formation of boric acid. On addition of this chloroborane to water a vigorous reaction ensues in some cases accompanied by ignition, presumably of the hydrogen gas which is evolved. Exclusion of air from the hydrolysis reaction permits a

---

[1] Paper VI: E. L. Muetterties, *Inorg. Chem.*, **2**, 647 (1963).

[2] G. Urry, T. Wartik, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **74**, 5809 (1952).

[3] R. A. Jackson and W. N. Lipscomb, *ibid.*, **80**, 5571 (1958); *J. Chem. Phys.*, **31**, 605 (1959).

[4] M. Atoji and W. N. Lipscomb, *Acta Cryst.*, **6**, 547 (1953); *J. Chem. Phys.*, **21**, 172 (1953).

[5] G. Urry, E. P. Schram, and S. I. Weissman, *J. Am. Chem. Soc.*, **84**, 2654 (1962); E. P. Schram and G. Urry, *Inorg. Chem.*, **2**, 405 (1963).

[6] W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, E. L. Muetterties, and J. C. Sauer, *J. Am. Chem. Soc.*, **84**, 1056 (1962); W. H. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia, and E. L. Muetterties, *Inorg. Chem.*, **3**, 159 (1964).

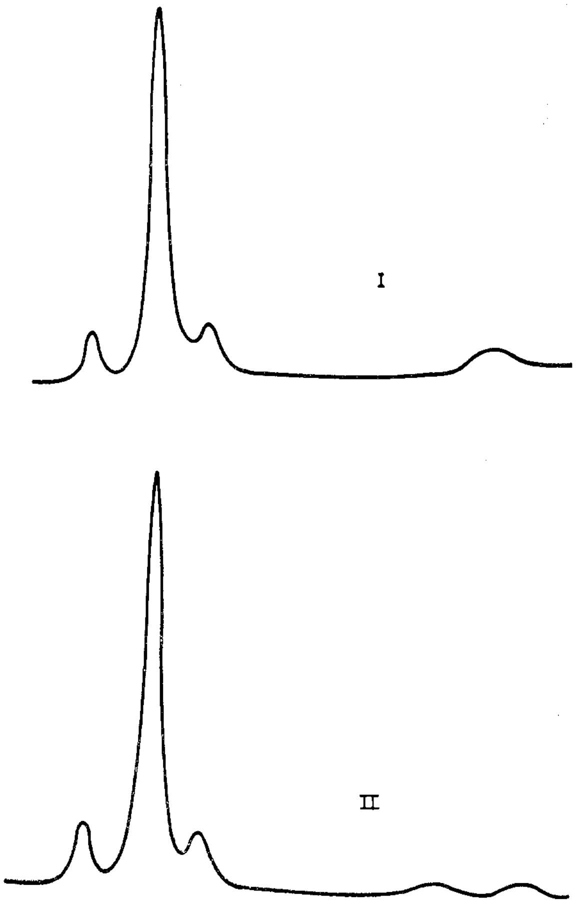


Fig. 1.—$B^{11}$ n.m.r. spectra for $B_9Cl_8H$: I, doubly irradiated at 60 Mc.; II, singly irradiated

smooth reaction which is nearly complete in 24 hr.

$$B_9Cl_8H + 27H_2O \xrightarrow{75°} 9H_3BO_3 + 8HCl + 10H_2 \quad (1)$$

One of the initial hydrolysis products was isolated by immediately adding a solution of an alkylammonium halide to the reaction mixture of $B_9Cl_8H$ and water. Under these conditions precipitates of the alkylammonium salts of $B_9Cl_8H^{-2}$ were formed. These salts on dissolution in hot water hydrolyzed to give boric acid. This anion does not have the stability of the halogen derivatives of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$.[6]

Generation of $B_9Cl_8H^{-2}$ in the hydrolysis reaction is difficult to explain. Mass spectrometric analysis of the volatile hydrolysis products showed only hydrogen to be present; thus, a direct reaction of $B_9Cl_8H$ with water to give $B_9Cl_8H^{-2}$ as in eq. 2 is ruled out. Furthermore,

$$B_9Cl_8H + 3H_2O \longrightarrow 2H_3O^+ + B_9Cl_8H^{-2} + 0.5O_2 \quad (2)$$

oxidation of water to hydrogen peroxide, as in eq. 3,

$$B_9Cl_8H + 4H_2O \longrightarrow 2H_3O^+ + B_9Cl_8H^{-2} + H_2O_2 \quad (3)$$

appears unlikely because no positive diphenylamine spot test for peroxide was detected with the hydrolysate. There is, of course, the possibility that peroxide is rapidly reduced to hydroxide ion in this reaction system. The only other alternative is to ascribe the source of electrons for $B_9Cl_8H^{-2}$ formation to some other hydrolysis intermediate. Since boric acid was also detected in these hydrolysis experiments in which $B_9Cl_8H$ was isolated, it is not possible to state whether $B_9Cl_8H^{-2}$ is or is not a primary hydrolysis product.

**Structure of $B_9Cl_8H$.**—The infrared spectrum exhibited by $B_9Cl_8H$ includes the weak B–H absorption at 2590 cm.$^{-1}$, as well as boron–chlorine cage absorptions at 1030 (vs) and 835 (m) cm.$^{-1}$. The similarity of the structure of $B_9Cl_8H$ to that of $B_{10}Cl_{10}^{-2}$ [6] is suggested by these infrared data, since $B_{10}Cl_{10}^{-2}$ absorbs strongly at 1000 cm.$^{-1}$ and moderately at 847 cm.$^{-1}$. However, the intensity of the band near 850 cm.$^{-1}$ relative to that near 1000 cm.$^{-1}$ is less in $B_9Cl_8H$ than in $B_{10}Cl_{10}^{-2}$. The simplicity of the infrared spectrum of $B_9Cl_8H$ suggests a cage structure.

$B^{11}$ magnetic resonance data (Fig. 1) indicate a configuration with one boron bonded to hydrogen and eight to chlorine, in relative intensities 1:6:1:1, the last digit representing the high-field doublet in Fig. 1 (II). The hydrogen-substituted boron gives rise to the doublet seen in Fig. 1 (II); double irradiation at 60 Mc. causes the doublet to coalesce to a singlet as in Fig. 1 (I). Thus, the eight chlorine-bonded borons are of three types spectrally, in relative abundance 6:1:1.

A cage structure is proposed for $B_9Cl_8H$, rather than an open one such as that of nonaborane[7] ($B_9H_{15}$), since insufficient substituent nuclei are present in $B_9Cl_8H$ to accommodate an open structure. The simplicity of the infrared spectrum indicates a noncomplex structure as might be expected for a cage. A minimum of four unique boron atom environments is required from the n.m.r. data. *Idealized* structures (Fig. 2) considered for nonaborane cages are the square antiprism or the dodecahedral [$Mo(CN)_8$] model with a terminal $BCl_2$ group (II), or with a BCl group bridging two (III), three (IV), or four (V and VI) boron atom positions. Another cage model considered but dropped because no isomer met the n.m.r. requirements is VII. It should be noted that the differences among these various idealized geometries is very small indeed; therefore, the solid-state geometry of $B_9Cl_8H$, when established, may not necessarily coincide with spectroscopic data for $B_9Cl_8H$ in solution or the gaseous state.

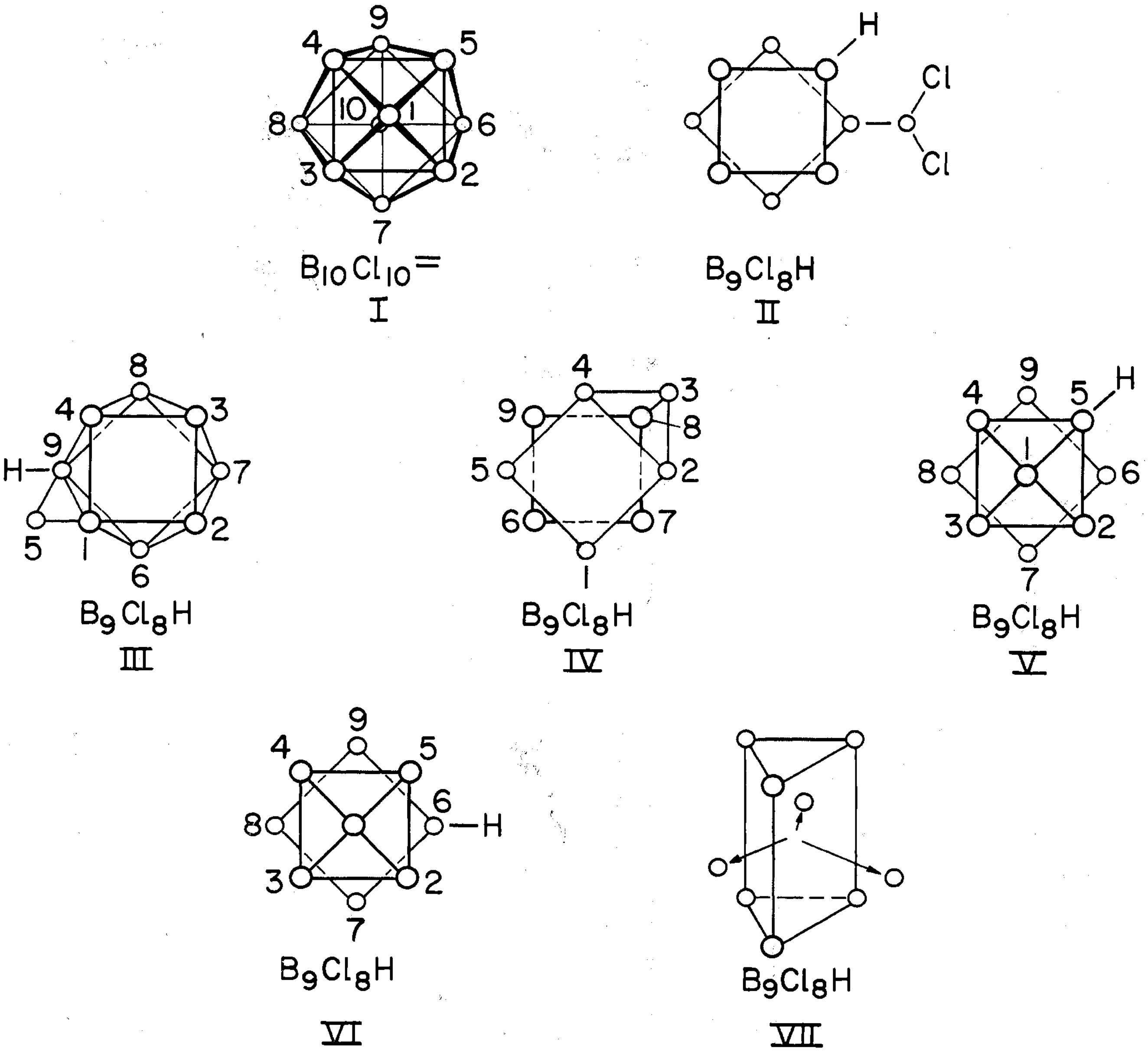
Structure II does not appear to be a favorable possibility because $B_9Cl_8H$ is transparent in the infrared region where sharp absorption is ascribed to the $BCl_2$ group in $B_2Cl_4$[8] and $B_{12}Cl_{11}$.[5] Moreover, II should on hydrolysis rapidly yield a $B(OH)_2$ function and this was not observed.

No structure based on a BH group bridging three boron atoms in an idealized square antiprism model meets the n.m.r. requirements for boron atom environments. For a bridging BCl group, the isomer represented in IV fits the data if accidental n.m.r. coincidence occurs for boron atoms 1, 2, 5, 6, 7, and 8. For

---

(7) R. E. Dickerson, P. J. Wheatley, P. A. Howell, and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 200 (1957); P. G. Simpson and W. N. Lipscomb, *ibid.*, **35**, 1340 (1961).

(8) M. J. Linevsky, E. R. Shull, D. E. Mann, and T. Wartik, *J. Am. Chem. Soc.*, **75**, 3287 (1953).



$B_{10}Cl_{10}^{=}$ I

$B_9Cl_8H$ II

$B_9Cl_8H$ III

$B_9Cl_8H$ IV

$B_9Cl_8H$ V

$B_9Cl_8H$ VI

$B_9Cl_8H$ VII

Fig. 2.—Idealized structures for $B_9Cl_8H$.

the dodecahedral model with a BH or BCl group bridging three boron atom positions, no isomer would appear to fit very well with the n.m.r. data.

For the square antiprism model with a BCl group bridging two boron atom positions, the isomer depicted in III fits the n.m.r. data nicely in that boron atom positions 1, 5, and 9 are unique and 2, 3, 4, 6, 7, and 8 are identical on a short range environmental basis. A closely related model can be generated from a dodecahedral arrangement of eight boron atoms and a BCl group bridging two positions.

As a final possibility it was presumed that the basic $B_{10}Cl_{10}^{-2}$ structure is not grossly altered and that an apical boron atom was removed in the pyrolysis. Of the three possible isomers, the one with a BH group at the apical position cannot possibly be reconciled with the n.m.r. data. The other two isomers are represented in V and VI. In V, the three pairs of equivalent boron atoms 2–4, 6–9, and 7–8 could be accidentally equivalent in the $B^{11}$ n.m.r. experiment and in VI, pairs 2–5, 3–4, and 7–9 could be accidentally equivalent.

Our spectral data fail to exclude as possible structures III, IV, V, and VI. VI appears more favorable than V because the boron atom bearing a hydrogen atom is adjacent to the position where an apical boron atom was lost. III appears unfavorable due to topological considerations.[9]

## Experimental

**Materials.**—$(CH_3)_4NCl$ and $(C_2H_5)_4NOH$ (Eastman) and $(CH_3)_4NOH$ (Eastman White Label) were used directly in aqueous solutions. The ion-exchange resin employed was Rexyn RG50 (H).

**Apparatus.**—Infrared spectra were obtained as Nujol mulls on a Perkin-Elmer Model 21 spectrophotometer. Visible and ultraviolet absorption data were secured with a Cary Model 14 spectrometer. Double irradiation was accomplished with an NMR Specialties Model SD 60 spin decoupler ($B^{11}$ saturation by 19.2-

---

[9] W. N. Lipscomb, *Advan. Inorg. Chem. Radiochem.*, **1**, 138 (1959).

Mc. irradiation while observing $H^1$ at 60 Mc., and $H^1$ saturation by 60-Mc. irradiation while examining $B^{11}$ at 19.2 Mc.).

**Preparation of $H_2B_{10}Cl_{10} \cdot xH_2O$.**—The preparation of $Cs_2B_{10}Cl_{10}$ will be described in detail in another paper in this series.[6] The corresponding hydrated acid, $H_2B_{10}Cl_{10} \cdot xH_2O$, was prepared by ion exchange of $Cs_2B_{10}Cl_{10}$ on a strongly acid column at 60°, utilizing one-third of the calculated capacity of the column. The effluent was concentrated by vaccum evaporation of the solvent (pot temperature 50°) for about 5 hr. with the formation of a white solid. The hydration of this material is about seven (neut. equiv. calcd. for $H_2B_{10}Cl_{10} \cdot 7H_2O$, 295; found, 297).

**Pyrolysis to $H_2B_{10}Cl_{10} \cdot 4H_2O$.**—$H_2B_{10}Cl_{10} \cdot 7H_2O$ was heated by means of a tube furnace at 150° for 7 hr. in a closed, previously evacuated system containing a vertical 25-mm. tube and a liquid nitrogen trap. The only volatile product was demonstrated by infrared and mass spectral analyses to be water. A hygroscopic residue[10] remained in the hot zone.

*Anal.* Calcd. for $H_2B_{10}Cl_{10} \cdot 4H_2O$: B, 20.2; Cl, 66.1. Found: B, 20.8; Cl, 67.3.

Neutral equivalents found by titration with 0.1 *N* sodium hydroxide for the product of three preparations were consistent with the tetrahydrate formulation; neut. equiv. calcd., 268; found, 270, 266, 263. Furthermore, infrared analysis was consistent with the formation of the hydrate, no absorption being found in the B–O–B region. The anion was quantitatively recovered from the pyrolysis product by dissolution in water, followed by precipitation as the tetramethylammonium salt.

The tetrahydrate is soluble in tetrahydrofuran and acetonitrile and insoluble in benzene and carbon tetrachloride.

Continued heating at 150° for over a day caused the evolution of only trace amounts of water.

**Preparation of $B_9Cl_8H$.**—A 10.42-g. (19.4 mmoles) sample of $H_2B_{10}Cl_{10} \cdot 4H_2O$ was heated to 260°, then held there for 5 hr., in a closed, previously evacuated system which included a liquid nitrogen trap. Gaseous hydrogen and hydrogen chloride, a yellow residue, and a red sublimate were produced.

The gaseous products consisted of 4.13 mmoles of hydrogen and 8.71 mmoles of hydrogen chloride.

The yellow residue which remained in the hot zone was nonstoichiometric. *Anal.* Found: B, 27.3; Cl, 44.5; O, 22.6. These data indicate the chlorine-poor formulation, $B_{2.0}Cl_{1.0}O_{1.1}$. The residue is soluble in both glyme and water. When the residue was dissolved in water and evaporated to dryness, boric acid remained.

The red sublimate was identified as octachlorononaborane-9. It was purified by resublimation near 35° under vacuum. The product, after a single resublimation, amounted to 0.369 g. (0.966 mmole), a 5% yield.

*Anal.* Calcd. for $B_9Cl_8H$: H, 0.26; B, 25.5; Cl, 74.2. Found: H, 0.46, 0.42, 0.70; B, 25.8, 25.4, 25.2; Cl, 74.5, 73.7, 73.2.

**Properties of $B_9Cl_8H$.**—$B_9Cl_8H$ melts without decomposition at 224–225°. A yellow residue remained on resublimation. The intensity of coloration of $B_9Cl_8H$ is inversely related to purity, since the deeper the red coloration, the greater its tendency toward tackiness. Resublimation was found effective in reducing the tackiness of $B_9Cl_8H$. Very slow sublimation at 35° ($< 1\ \mu$) produced large, clear crystalline aggregates.

$B_9Cl_8H$ absorbs in the infrared at 2590 (w), 1030 (vs), 835 (m), and 673 (m) cm.$^{-1}$. The ultraviolet and visible spectra (in cyclohexane) consisted of absorptions at 384 m$\mu$ ($\epsilon$ 7910), 300 m$\mu$ ($\epsilon$ 17,200), and 263 m$\mu$ ($\epsilon$ 12,100).

$B^{11}$ resonance spectra of $B_9Cl_8H$ in cyclohexane are shown in Fig. 1. The lower pattern (II) depicts the 19.2-Mc. $B^{11}$ spectrum, that above (I), the 19.2-Mc. $B^{11}$ spectrum doubly irradiated at 60 Mc. (referred to trimethyl borate at high field). The high field doublet of low intensity (II) coalesces into a singlet when doubly irradiated (I). Proceeding from low to high field the positions of the peaks are 50.2, 45.3, and 40.5 p.p.m. for the trio and 15.7 and 7.4 p.p.m. for the doublet. Intensities determined by cutting out and weighing the peaks are 1:6:1:0.5:0.5.

Singly sublimed $B_9Cl_8H$ gave a fairly strong e.p.r. signal at $g = 2$ in cyclohexane. Triply sublimed $B_9Cl_8H$ gave a barely discernible e.p.r. signal, indicating that the signal was due to minor impurities. The absence of large chemical shifts and line broadening in the n.m.r. spectra confirms the diamagnetism of $B_9Cl_8H$.

Two series of ebullioscopic molecular weight determinations in benzene (made by successive additions to a solution) on samples from two separate preparations yielded 410, 389, 375, 388, 377, and 376 (calcd. for $B_9Cl_8H$, 382).

$B_9Cl_8H$ (0.150 g., 0.393 mmole) was allowed to stand for 1 week in the presence of 7.74 mmoles of oxygen which had been dried over phosphoric anhydride. The appearance and weight of the solid were unchanged at the end of this period, and the oxygen was recovered quantitatively. $B_9Cl_8H$ (38.0 mg., 0.0995 mmole) and 2.75 mmoles of dried oxygen were sealed in a Carius tube. The tube was heated at 100° for 5 hr. with no apparent reaction. The tube was then heated at 200° for an additional 5 hr. with the formation of a tannish white solid.

**Hydrolysis of $B_9Cl_8H$.**—Quantitative hydrolysis of $B_9Cl_8H$ was investigated by introducing 0.6808 g. (2.17 mmoles) of $B_9Cl_8H$ into a Kjeldahl flask in an inert atmosphere. The flask was evacuated and 50 ml. of degassed water was condensed onto the $B_9Cl_8H$ at −196°. The mixture was allowed to warm to room temperature and stirred for 4 days. After heating at 50° for 3 days, then at 75° for 4 days, hydrogen evolution ceased. The product was cooled to −196° and the noncondensable gas was allowed to pass through a −196° trap into a known volume with a Töpler pump. The noncondensable gas, shown to be hydrogen by mass spectral analysis, corresponded to 9.92 moles of hydrogen evolved per mole of $B_9Cl_8H$, in close agreement with the calculated value of 10 moles.

Subsequent determinations on 0.1328 and 0.1426 g. of $B_9Cl_8H$ yielded 9.98 and 9.99 moles of hydrogen per mole of $B_9Cl_8H$, respectively.

**$[(CH_3)_4N]_2B_9Cl_8H$.**—$B_9Cl_8H$ (0.5 g.) was dissolved in 300 ml. of deoxygenated water. Rapid addition of 1 ml. of a 50% aqueous solution of $(CH_3)_4NCl$ caused the precipitation of the tetramethylammonium salt of the octachlorononaborate dianion, $[(CH_3)_4N]_2B_9Cl_8H$. The precipitate was filtered, and the absence of peroxides in the filtrate was demonstrated by the diphenylamine spot test.[11] The pH of the precipitation medium had no effect upon the nature of the precipitate, since the product obtained from the above strongly acidic solution was identical by infrared and elemental analyses with that obtained from a solution of $B_9Cl_8H$ in water first neutralized with $(CH_3)_4NOH$ and with that from a solution first made strongly basic with $(CH_3)_4NOH$, both prior to addition of $(CH_3)_4NCl$ to complete the precipitation.

*Anal.* Calcd. for $C_8H_{25}B_9Cl_8N_2$: C, 18.1; H, 4.76; B, 18.4; Cl, 53.5; N, 5.28. Found (neutral soln.): C, 18.4; H, 4.70; B, 17.7; N, 5.40, 5.38. Found (acidic soln.): C, 18.2; H, 4.71; B, 17.9; Cl, 52.1; N, 5.33, 5.33. Found (basic soln.): C, 18.5; H, 4.88; B, 17.5; Cl, 52.2; N, 5.42, 5.37.

The infrared spectrum of $[(CH_3)_4N]_2B_9Cl_8H$ consists of absorptions at 2505 (w), 1280 (m), 1110 (s), 1040 (s, broad), 962 (s), 944 (s), and 820 (w) cm.$^{-1}$.

$[(CH_3)_4N]_2B_9Cl_8H$ neither melts nor changes in appearance when heated to 360° in a sealed, evacuated capillary. It reduces silver nitrate in aqueous solution. The salt is soluble in hot water with quantitative hydrolysis to boric acid. A 0.1-g. sample of $[(CH_3)_4N]_2B_9Cl_8H$ in 60 ml. of water was quantitatively hydrolyzed in 1 month at 25°.

$[(CH_3)_4N]_2B_9Cl_8H$ is soluble in hot alcohol and in acetonitrile but insoluble in tetrahydrofuran, dioxane, dichloromethane, methyl iodide, concentrated phosphoric acid, and chloroform.

---

[10] The tetrahydrate in each case was dark purple. This color disappeared on dissolution in water, and on standing in acetonitrile for a few days. No. e.p.r. signal was observed in acetonitrile. Ultraviolet peaks were observed in acetonitrile at 270 m$\mu$ ($\epsilon$ 142) and 223 m$\mu$ ($\epsilon$ 11,800), both characteristic of $B_{10}Cl_{10}^{-2}$. Two weak absorptions occur in the visible region, at 568 m$\mu$ ($\epsilon$ 15.6) and 417 m$\mu$ ($\epsilon$ 7.5), not found in $B_{10}Cl_{10}^{-2}$. It is suggested that the color of the tetrahydrate is due to minor impurities.

[11] F. Feigl, "Spot Tests I, Inorganic Applications," Elsevier, New York, N. Y., 1954, p. 300.

The salt may be purified by recrystallization from hot anhydrous acetonitrile. Ebullioscopic molecular weight determinations in acetonitrile yielded values of 205 and 214 (calcd. 530). Partial, but not complete (theory 177), ionization in acetonitrile is indicated.[12] No e.p.r. signal was observed with a solution of $[(CH_3)_4N]_2B_9Cl_8H$ in acetonitrile.

The n.m.r. proton spectrum of $[(CH_3)_4N]_2B_9Cl_8H$ consisted of a sharp singlet of moderate intensity at −3.0 p.p.m. (tetramethylsilane reference) due to the N-methyl protons. The components of the quartet expected for a proton attached to boron were not observed because of the low solubility of the salt. Each component of this quartet would necessarily be of an intensity about one hundredth of that of the N-methyl proton resonance.

**$[(C_2H_5)_4N]_2B_9Cl_8H$.**—$B_9Cl_8H$ (0.5 g.) was dissolved in 300 ml. of degassed water. Immediately after dissolution 3 ml. of a 10% aqueous solution of $(C_2H_5)_4NOH$ was added, precipitating $[(C_2H_5)_4N]_2B_9Cl_8H$.

*Anal.* Calcd. for $C_{16}H_{40}B_9Cl_8N_2$: C, 29.9; H, 6.43; B, 15.1; Cl, 44.1; N, 4.35. Found: C, 30.5; H, 6.44; B, 14.5; Cl, 44.2; N, 4.47, 4.44.

Infrared absorptions, as a Nujol mull, include the following: 2505 (w), 1300 (w), 1180 (m), 1165 (m), 1105 (m), 1060 (m), 1045 (m), 1030 (m), 997 (m), 962 (m), 817 (w), and 785 (m) cm.$^{-1}$. Ebullioscopic molecular weight determinations in acetonitrile yielded values of 270 and 258 (calcd. 642), indicating partial ionization.

$[(C_2H_5)_4N]_2B_9Cl_8H$ is very soluble in acetonitrile with no appreciable temperature coefficient in the 0–82° range. It may be recrystallized from methanol–acetonitrile, but is insoluble in chloroform and dichloromethane. $[(C_2H_5)_4N]_2B_9Cl_8H$ neither melts nor changes appearance when heated in a sealed capillary to 360°. When a solution of this salt (0.2 g.) in 200 ml. of water was heated to 100° for 3 hr., quantitative hydrolysis to boric acid occurred.

The $B^{11}$ resonance spectrum of $[(C_2H_5)_4N]_2B_9Cl_8H$ in acetonitrile consisted simply of a broad signal with a low-field spike.

**Acknowledgment.**—The mass spectral data were obtained by Mr. R. J. Berndt.

---

[12] Similar behavior was observed in the case of $[(C_2H_5)_3NH]_2B_{10}Cl_{10}$. Ebullioscopic molecular weight measurements in acetonitrile yielded 309 and 324 (calcd. for complete ionization, 229).

---

CONTRIBUTION NO. 873 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION,
E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE

# Chemistry of Boranes. IX.[1] Halogenation of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$

BY W. H. KNOTH, H. C. MILLER, J. C. SAUER, J. H. BALTHIS, Y. T. CHIA, AND E. L. MUETTERTIES

*Received September 26, 1963*

Halogenated derivatives of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ have been prepared by reaction of these anions with chlorine, bromine, or iodine and by reaction of $B_{12}H_{12}^{-2}$ with hydrogen fluoride, hydrogen chloride, or fluorine. These derivatives are exceedingly resistant toward thermal degradation and chemical attack.

This is the second of a series of papers which will describe in detail the chemistry of $B_{10}H_{10}^{-2}$ [2a] and $B_{12}H_{12}^{-2}$ [2b] outlined in a recent communication.[3] In the preceding paper,[1] it was shown that salts of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ are thermally stable and resistant toward degradation by acids, bases, and mild oxidizing agents to a degree unique in boron hydride chemistry or inorganic hydride chemistry generally. In addition, these anions react readily with a variety of reagents to give substitution derivatives,[3] some of which rival or exceed the parent anions in chemical and thermal stability. In this context, the halogenated derivatives are outstanding.

The dianions $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ react smoothly in aqueous or alcoholic solutions with chlorine, bromine, iodine, N-iodosuccinimide, and similar reagents to give derivatives in which from one to all of the hydrogens have been replaced by halogen. Conversion of $B_{12}H_{12}^{-2}$ to halogenated derivatives can also be effected with hydrogen halides and with elemental fluorine, although in the latter case some degradation of the cage occurs. Halogenated derivatives of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ which contain other substituents (*e.g.*, $B_{12}Br_{11}OH^{-2}$, $B_{10}Cl_9COC_6H_5^{-2}$, $B_{10}H_2Cl_6[S(CH_3)_2]_2$) will be described in later papers.

**Halogenation.**—The initial reactions of both $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ with chlorine, bromine, and iodine are extremely rapid. The rates decrease as halogenation is continued, $B_{12}H_{12}^{-2}$ being significantly more resistant to electrophilic poly- or perhalogenation than $B_{10}H_{10}^{-2}$. As would be expected, the order of reactivity of the halogens is Cl > Br > I. The initial rapid rates lead to difficulties in isolating some species, particularly those with a low degree of halo substitution. For example, kinetic studies[4] have shown that the first three iodine atoms to enter $B_{10}H_{10}^{-2}$ are kinetically indistinguishable even at −40°, although the rate of iodination of $B_{12}H_{12}^{-2}$ is measurable at 25° and is 70-fold greater than the rate of iodination of $B_{12}H_{11}I^{-2}$. Thus, pure $B_{10}H_9I^{-2}$ cannot be made by simply using one equivalent of iodine, although this procedure is satisfactory for the preparation of $B_{12}H_{11}I^{-2}$. Salts of $B_{10}H_9I^{-2}$ and $B_{10}H_8I_2^{-2}$ have been separated, however, by repeated fractional crystallizations. Kinetic studies have not as yet been completed for the other halogenations, but it is apparent that initial kinetic lack of discrimination between successively entering halogens is even more prevalent with bromine and

---

[1] Paper VIII: *Inorg. Chem.*, in press.

[2] (a) M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **81**, 5519 (1959); (b) *ibid.*, **82**, 3228 (1960).

[3] W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, J. C. Sauer, and E. L. Muetterties, *ibid.*, **84**, 1056 (1962).

[4] Details of these kinetic studies and of related stereochemical work will be published in a later paper.