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Chloro Derivatives of Pentaborane(9)

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The aluminum chloride catalyzed chlorination of pentaborane(9) produces 1-chloropentaborane(9) in high yield. Reversible isomerization of 1-chloro- to 2-chloropentaborane(9) occurs readily in ether solution. The aluminum chloride catalyzed chlorination of 2-chloropentaborane(9) produces the first example of a dihalopentaborane(9), 1,2-dichloropentaborane(9), in good yield. This material isomerizes in the presence of hexamethylenetetramine to produce what appears to be an inseparable mixture of 2,3- and 2,4-dichloropentaborane(9).

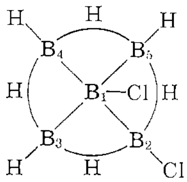
Until recently there had been little interest in the direct chlorination of pentaborane(9), B_5H_9—a lack no doubt partially attributable to the report that attempted chlorinations of B_5H_9 in carbon disulfide solution resulted in explosions.[1]

The successful preparation of 2-chloropentaborane(9), 2-ClB_5H_8, by the high-temperature reaction of 1-bromopentaborane(9) with aluminum chloride[2] established the stability of a boron–chlorine bond in a higher borane system and prompted us to reinvestigate the direct chlorination of B_5H_9.

Subsequently we found that B_5H_9 reacts smoothly with chlorine in boron trichloride solution at low temperatures, when catalyzed by aluminum chloride, to produce 1-chloropentaborane, 1-ClB_5H_8, in high yield.[3] Attempts to chlorinate B_5H_9 in the absence of aluminum chloride result in low yields (10–30%) of 2-ClB_5H_8 and only traces of 1-ClB_5H_8. Similar low yields are obtained when no solvent is employed or when the reaction is carried out in the gas phase.[4]

The isomerization of 1-ClB_5H_8 to 2-ClB_5H_8 occurs cleanly at room temperature in diethyl ether solution. The equilibrium constant for $1\text{-ClB}_5H_8 \rightleftharpoons 2\text{-ClB}_5H_8$ is about 4. The rate of equilibration does not appear to be greatly concentration dependent. In contrast to these observations Burg and Sandhu[5] found that 1-BrB_5H_8 reacts with dimethyl ether at 0° to produce substantial quantities of B_5H_9, CH_3Br, and intractable materials along with a 50% yield of 2-BrB_5H_8. At 24° $B(OCH_3)_3$ is formed along with the 0° reaction products, and at 38° all of the BrB_5H_8 is destroyed but a 30% yield of $1\text{-CH}_3B_5H_8$ is obtained. Investigations in these laboratories indicate that 1-IB_5H_8 also reacts with ethers, but in a manner different from 1-BrB_5H_8. Further detailed studies are clearly required in order to elucidate the course of these reactions.

When 2-ClB_5H_8 is chlorinated in boron trichloride solution in the presence of aluminum chloride, a moderately high yield of 1,2-dichloropentaborane(9), $1,2\text{-Cl}_2B_5H_7$, is obtained. The ^{11}B nmr spectrum (Figure 1) of this compound is readily assigned by comparing it with the spectra obtained for 1- and 2-ClB_5H_8 (Table I). The *trans* effect observed in the ^{11}B nmr spectrum of this and other 2-substituted pentaborane(9) derivatives[2,4,6] is of interest as a source of data that may eventually allow a definitive theoretical treatment of the factors involved in chemical shift trends for nuclei having spins greater than $^1/_2$. The ^1H nmr spectrum of $1,2\text{-Cl}_2B_5H_7$ (Figure 2) contains a quartet arising from the terminal hydrogen atoms coupled to ^{11}B (the coupling of hydrogen with the 20% ^{10}B is not resolved). The terminal hydrogen atoms appear to be magnetically equivalent even though the boron atoms B(3,5) are quite different from B(4).



When the high-field member of the terminal hydrogen quartet is subtracted from the broad bridge hydrogen resonance, two maxima remain which can be reduced to two peaks having identical areas and half-height widths similar (160 ± 5 cps) to the half-height width of bridge hydrogens of 1-chloropentaborane(9). These resonances have been tentatively assigned to the two bridge hydrogen atoms adjacent to B(2) (b) at low field and those adjacent to B(4) (c) at higher field, in accordance with the positions observed for bridge hydrogen resonances in 1-[3] and 2-ClB_5H_8[6] and B_5H_9.[6]

Isomerization of $1,2\text{-Cl}_2B_5H_7$ occurs at room temperature in the presence of hexamethylenetetramine, producing a low yield of what appears to be an inseparable mixture of 2,3- and $2,4\text{-Cl}_2B_5H_7$. The ^{11}B nmr spectrum of the mixture contains a singlet at 1.0 ppm and doublets at 12.4, 23.3, and 49.8 ppm. The resonances may be tentatively assigned to B(2,3 and

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(1) I. Shapiro and H. Landesman, *J. Chem. Phys.*, **33**, 1590 (1960). These authors reported mass spectral evidence for microquantities of a chloropentaborane contaminated with carbon tetrachloride from a small-scale reaction. Pentaborane(9) forms shock-sensitive mixtures with carbon tetrachloride: "Pentaborane," Callery Chemical Co. Technical Bulletin CT-1300, Oct 1, 1961.

(2) T. Onak and G. B. Dunks, *Inorg. Chem.*, **3**, 1060 (1964).

(3) Preliminary report: D. F. Gaines, *J. Am. Chem. Soc.*, **88**, 4528 (1966).

(4) A. B. Burg has developed a low-pressure gas-phase synthesis of 2-chloropentaborane(9) in which there is a 13% conversion of pentaborane of which 72% is 2-chloropentaborane and less than 10% is 1-chloropentaborane: 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967; *J. Am. Chem. Soc.*, **90**, 1407 (1968).

(5) A. B. Burg and J. S. Sandhu, *ibid.*, **87**, 3787 (1965).

(6) T. Onak, G. B. Dunks, I. W. Searcy, and J. Spielman, *Inorg. Chem.*, **6**, 1465 (1967).

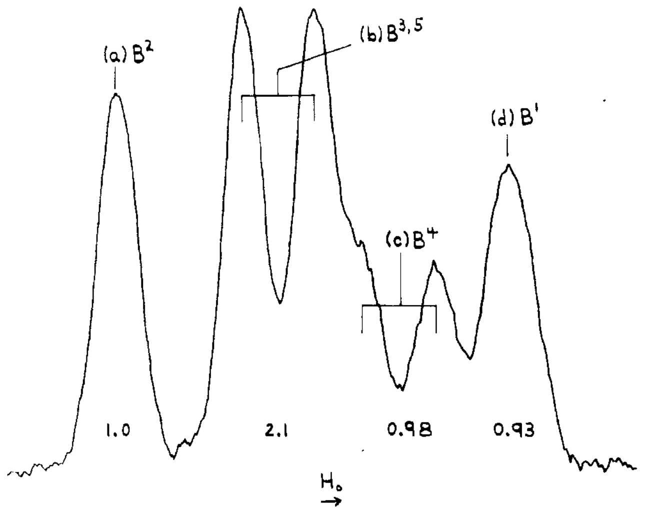

Figure 1.—The 32.1-Mc ^{11}B nmr spectrum of 1,2-$Cl_2B_5H_7$. Approximate integrated areas are indicated beneath the resonances.

TABLE I

THE ^{11}B NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS OF SEVERAL CHLOROPENTABORANES(9) AT 32.1 Mc

	B(2) δ^a	B(3,5)–H δ $(J)^b$	B(4)–H δ (J)	B(1)–Cl δ	B(1)–H δ (J)
1-ClB_5H_8	11.8 (170)			29.3	. . .
2-ClB_5H_8[c]	−0.5	12.5 (177)	22 (178)	. . .	51 (179)
1,2-$Cl_2B_5H_7$	1.0	13.0 (171)	22.1 (167)	30.3	. . .

[a] Chemical shifts in ppm (±0.3) from $BF_3 \cdot O(C_2H_5)_2 = 0.0$. [b] Coupling constants in cps (±5). [c] Data from ref 2.

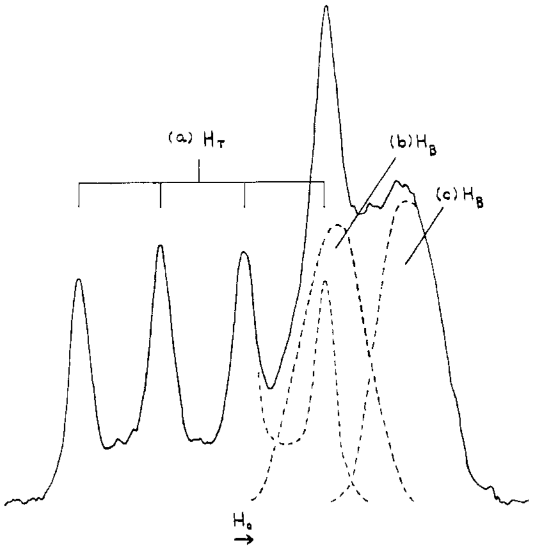

Figure 2.—The 100-Mc ^1H nmr spectrum of 1,2-$Cl_2B_5H_7$. Chemical shift values (and coupling constants) for the indicated hydrogen nuclei are (a) 7.05 (168 ± 5), (b) 9.77, and (c) 11.29. The area ratio of terminal to bridge hydrogens is $H_T:H_B$ = 3.0:4.1.

2,4)–Cl, B(3,5)–H from 2,4-$Cl_2B_5H_7$, B(4,5)–H from 2,3-$Cl_2B_5H_7$, and B(1)–H, respectively, based on the chemical shift trends observed for 2-ClB_5H_8,[2] 1,2-$Cl_2B_5H_7$, 2-$CH_3B_5H_8$,[6] and 2,3-$(CH_3)_2B_5H_7$.[6] In the 2-substituted compounds there is a *trans* effect which causes a pronounced upfield shift of the B(4)–H resonance relative to B(2-5)–H in B_5H_9 whereas the B-(3,5)–H resonance is essentially unchanged. This *trans* effect is observed in the spectrum of 2,3-$(CH_3)_2$-B_5H_7 and is thus expected to occur in 2,3-$Cl_2B_5H_7$. In the anticipated spectrum of 2,4-$Cl_2B_5H_7$ the B-(3,5)–H resonance should occur at about the same position as it does in 2-ClB_5H_8 and 1,2-$Cl_2B_5H_7$. A *trans* effect on B(2,4)–Cl might be expected but has not been observed. Friedman and Lipscomb[7] have recently determined the molecular structure of 2,3-$(CH_3)_2B_5H_7$, the sole product of the base-catalyzed isomerization of 1,2-$(CH_3)_2B_5H_7$.[8] The rationale they presented for the selective isomerization of 1,2-$(CH_3)_2$-B_5H_7 is based primarily on bridge hydrogen crowding in the transition state due to the size of the methyl groups. As this crowding would be considerably reduced when chlorine atoms replace the methyl groups, it is perhaps not surprising that a mixture of isomers may be obtained from the isomerization of 1,2-$Cl_2B_5H_7$.

Experimental Section

The reagents used were all of the highest quality offered by the suppliers and were used as received. Standard vacuum techniques were used throughout this investigation.[9] The chlorination experiments were carried out in a separate part of the vacuum system. All joints and glass stopcocks were lubricated with Kel-F grease. Chlorine was measured as a gas, the pressure being measured with a mercury manometer protected by a 2-cm layer of S.A.E. 30 Fluorolube oil. Reaction flasks were fitted with Delmar O-ring stopcocks (Viton-A O-rings) and contained Teflon-covered stirring bars. All of the chloropentaboranes(9) appeared to be stable at room temperature when pure in the absence of air and moisture. Hydrolysis and oxidation in air were rapid.

1-Chloropentaborane(9).—In a nitrogen-filled glove bag, about 3 g of finely ground $AlCl_3$ was placed in a reaction flask of about 1.1-l. volume. The flask was evacuated and 66 mmoles of B_5H_9, 33.4 mmoles of Cl_2, and about 20 ml of BCl_3 were condensed into it. The flask was then closed, warmed to −78°, and stirred until the B_5H_9 had dissolved, then slowly warmed with stirring to room temperature over a 3-hr period. The yellow Cl_2 color was completely discharged at this time. The flask was cooled to 0° and stirred overnight. The volatile materials were then transferred to a distilling vessel similar to that described by Burg and Kratzer.[10] The condenser was filled with a Dry Ice–alcohol slush and the boiler allowed to warm so that the HCl and BCl_3, along with part of the excess B_5H_9, distilled from the flask to another flask cooled in liquid nitrogen. The material that did not distil past the −78° condenser was subsequently distilled several times into a trap cooled to −30°. The material condensed at −30°, essentially pure 1-ClB_5H_8, amounted to 2.86 g (29.3 mmoles), a yield of 87.8% based on Cl_2.

In a similar reaction involving about 2 g of $AlCl_3$, about 40 ml of BCl_3, 49.6 mmoles of Cl_2, and 55 mmoles of B_5H_9, the yield was reduced to 74.4%.

The characterization of 1-ClB_5H_8 was as reported in a previous communication.[3]

Gas-phase chlorinations, even at low pressures and when diluted with inert gases, tended to inflame. These reactions were considered to be potentially very hazardous and will not be described here.[4]

Reactions between Cl_2 and B_5H_9 in the liquid phase and in BCl_3 solution at low temperatures produced mostly 2-ClB_5H_8. The yields have never exceeded 30% and were generally less than 20%.

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(7) L. B. Friedman and W. N. Lipscomb, *Inorg Chem.*, **5**, 1752 (1966).

(8) T. P. Onak, L. B. Friedman, J. H. Hartsuck, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 3439 (1966).

(9) R. T. Sanderson, "High Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(10) A. B. Burg and R. Kratzer, *Inorg. Chem.*, **1**, 725 (1962).

2-Chloropentaborane(9).—The isomerization of $1\text{-}ClB_5H_8$ to $2\text{-}ClB_5H_8$ occurs cleanly in diethyl ether solution at room temperature. A number of isomerization experiments were carried out in nmr tubes in an attempt to obtain kinetic data. Owing to the nature of the ^{11}B nmr spectra, however, reliable data could not be obtained. It was found however that the equilibrium mixture in diethyl ether at room temperature contained about 80% $2\text{-}ClB_5H_8$ and that 1–5 *M* solutions appeared to be near equilibrium after 1 day. The isolation of $1\text{-}ClB_5H_8$ and $2\text{-}ClB_5H_8$ was readily accomplished by repeated fractional condensations at -30 and $-63°$, respectively.

The $2\text{-}ClB_5H_8$ was identified by comparison of its ^{11}B nmr, infrared, and mass spectra with those previously reported.[2]

1,2-Dichloropentaborane(9).—In a preparation similar to that used for $1\text{-}ClB_5H_8$, 8.0 mmoles of $2\text{-}ClB_5H_8$ was condensed into a 125-ml reaction flask that had previously been charged with about 0.5 g of $AlCl_3$. About 10 ml of BCl_3 and 9.3 mmoles of Cl_2 were then condensed into the flask. The flask was warmed, with stirring, from -75 to $-25°$ over a 9-hr period, and then stored at 0° for 12 hr. The product was separated from the yellow reaction solution and purified using procedures similar to those described for $1\text{-}ClB_5H_8$. The $1,2\text{-}Cl_2B_5H_7$ was condensed at $-30°$, melted over the range 18.2–19.5°, and exhibited a vapor pressure of considerably less than 1 mm at room temperature. The yield of $1,2\text{-}Cl_2B_5H_7$ was 0.688 g (5.2 mmoles), or 65%. There was 1.9 mmoles of $2\text{-}ClB_5H_8$ recovered from the reaction.

In similar reactions that were allowed to warm more rapidly the yields were 45 ± 5%.

The composition and structure of $1,2\text{-}Cl_2B_5H_7$ were determined by nmr, infrared, and mass spectral studies. The mass spectrum cuts off at *m/e* 136, which corresponds to $^{11}B_5H_7{}^{37}Cl_2{}^+$. The most intense peaks in the parent group at *m/e* 131 and 132 correspond to the most probable combination of boron and chlorine isotopes in the parent skeleton. The ^{11}B nmr spectrum (Figure 1) of $1,2\text{-}Cl_2B_5H_7$, obtained at 32.1 Mc, is tabulated in Table I. The ^1H nmr spectrum of $1,2\text{-}Cl_2B_5H_7$, obtained at 100 Mc, is shown in Figure 1 along with tentative assignments of the resonances. The infrared spectrum of $1,2\text{-}Cl_2B_5H_7$ was obtained in carbon disulfide solution and in the gas phase. Owing to the low volatility of the compound, the gas-phase spectrum contains only the most intense absorptions. The major bands (cm^{-1}) were found at 2620 (s), 1800 (w, br), 1530 (s, br), 1385 (s, br), 1190 (sh), 1165 (s), 1075 (w), 1050 (m), 1028 (s), 980 (sh), 970 (s), 875 (s), 825 (w), 775 (w), 660 (m), 630 (m).

Isomerization of $1,2\text{-}Cl_2B_5H_7$.—In a flask similar to that used previously, 138 mg (1.1 mmoles) of $(CH_2)_6N_4$ and 624 mg (4.72 mmoles) of $1,2\text{-}Cl_2B_5H_7$ were brought into contact for 6.5 hr at room temperature. Separation of the products was effected using a low-temperature fractional distillation column.[11] The material of slightly greater volatility than the $1,2\text{-}Cl_2B_5H_7$ froze as a glass even after repeated fractionations. The mass spectrum was similar to that of $1,2\text{-}Cl_2B_5H_7$ with a cutoff at *m/e* 136. The ^{11}B nmr spectrum was consistent with that expected for an approximately equimolar mixture of 2,3- and $2,4\text{-}Cl_2B_5H_7$, though no appreciable separation of these isomers was ever obtained. The yield of the mixed isomers was 193 mg (1.46 mmoles), or 31%.

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(11) J. E. Dobson and R. Schaeffer, design to be published.

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Investigations of the Photochemistry of $H_2B_2O_3$[1]

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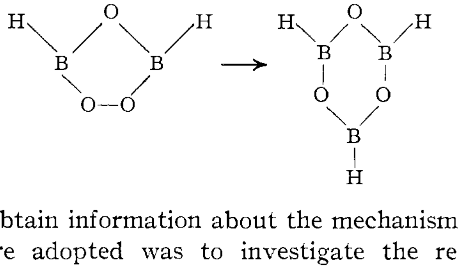
The ultraviolet spectrum of gaseous $H_2B_2O_3$ shows continuous absorption starting at about 2500 Å and extending to shorter wavelengths. The compound photochemically decomposes to yield $B_2O_3(s)$ and $H_2(g)$ and reacts with B_2H_6 to yield boroxine ($H_3B_3O_3$). Rates of the photochemical reactions are much higher than those observed for the thermal reactions and are accelerated by mercury photosensitization. Information on the mechanism of the B_2H_6–$H_2B_2O_3$ reaction was derived from studies with selectively prepared isotopic species of $H_2B_2O_3$.

Introduction

Gaseous $H_2B_2O_3$ was first observed as an intermediate in the slow oxidation of B_5H_9.[2] Later work has shown that $H_2B_2O_3$ is formed in the oxidation of BH_3CO, B_4H_{10} and $H_3B_3O_3$,[3,4] and by electrical discharge or photolysis of low-pressure mixtures of B_2H_6 and O_2.[5,6] One of the more interesting aspects of $H_2B_2O_3$ is its chemical behavior to regenerate $H_3B_3O_3$ by reaction with B_2H_6 under nonthermal conditions.[5] Microwave studies have shown that $H_2B_2O_3$ is a planar molecule with C_{2v} symmetry.[7] It was of interest, therefore, to examine the experimental conditions necessary for the conversion



and to obtain information about the mechanism. The procedure adopted was to investigate the reactions

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(1) Work supported by the Army Research Office, Durham, N. C., and the Advanced Research Projects Agency, Cornell University, Ithaca, N. Y.

(2) J. F. Ditter and I. Shapiro, *J. Am. Chem. Soc.*, **81**, 1022 (1959).

(3) L. Barton, C. Perrin, and R. F. Porter, *Inorg. Chem.*, **5**, 1446 (1966).

(4) G. H. Lee, II, and R. F. Porter, *ibid.*, **6**, 1329 (1966).

(5) L. Barton, S. K. Wason, and R. F. Porter, *J. Phys. Chem.*, **69**, 3160 (1965).

(6) R. F. Porter and F. A. Grimm in "Mass Spectrometry in Inorganic Chemistry," Advances in Chemistry Series, American Chemical Society, Washington, D. C., in press.

(7) W. V. Brooks, C. C. Costain, and R. F. Porter, *J. Chem. Phys.*, **47**, 4186 (1967).