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The Preparation of 2-Chloropentaborane from 1-Bromopentaborane and Aluminum Chloride

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Previously, chloropentaborane could be prepared only in microquantities from the chlorination of pentaborane in the presence of aluminum chloride.[1] Further, the procedure that has generally been used to halogenate pentaboranes has resulted in the formation of 1-halopentaboranes.[1-3] We wish to report a halogen interchange reaction between aluminum chloride and 1-bromopentaborane to give 2-chloropentaborane.

Experimental

1-Bromopentaborane.—As previously described,[1,3] 1-bromopentaborane (m.p. 38.5–39°) was prepared at ambient temperature from bromine and pentaborane (Olin Mathieson) in the presence of aluminum chloride.

2-Chloropentaborane.—Purified 1-bromopentaborane (4.39 mmoles) and aluminum chloride (18.5 mmoles) were sublimed into a 1-l. flask and subsequently heated for 17 hr. at 150°. Fractional condensation through traps at −30, −65, and −190° yielded 0.70 mmole of unreacted 1-brompentaborane; 0.91 mmole of a mixture containing B_5H_9, BCl_3, $HBCl_2$, B_2H_6, and HCl (infrared analysis); and 35 mg. (0.36 mmole, 8.2%) of 2-chloropentaborane; mol. wt. calcd. 97.5, found (gas density) 99 ± 3; vapor pressure 19 mm. at 28°; m.p. −41 to −40°. The mass spectrum of 2-chloropentaborane contains the parent peak at $m/e = 100$ and exhibits a pattern very similar to that of the chloropentaborane previously isolated in microquantities.[1,4] An isotopic analysis of the high-field mass peaks was consistent for a five-boron[5] and single chlorine compound. The infrared spectrum of 2-chloropentaborane (strong bands at 3.82, 6.9–7.6, 9.3–9.8, and 11.1–11.6 μ; medium band at 8.85 μ; weak bands at 5.57, 7.9, 10.1, 10.6, 12.0, 13.1, 14.6, and 14.8 μ) was similar to, but not identical with, that of pentaborane and various other substituted pentaboranes.

Attempted Preparations of 2-Bromopentaborane. (A) 1-Bromopentaborane and Aluminum Bromide.—Aluminum bromide (32 mmoles) and 1-bromopentaborane (4.5 mmoles) were sublimed into a 2-l. flask and subsequently heated for 17 hr. at 150°. The product mixture was subjected to fractional condensation, and each fraction was examined with the B^{11} n.m.r. The only boron-containing material (*ca.* 40 mg.) that volatilized at ambient temperature and was trapped at −50° gave a B^{11} n.m.r. spectrum identical with that of 1-bromopentaborane.

(B) Elevated Temperature.[6]—1 Bromopentaborane (2.0 mmoles) was sealed into a 25-ml. flask equipped with a 5-mm. diameter tube for taking n.m.r. spectra. The lowest temperature at which the disappearance of 1-bromopentaborane occurred at a reasonable rate was 160°. At the end of 2 hr. a considerable quantity of yellow solid had formed on the walls of the flask; however, the H^1 and B^{11} n.m.r. patterns of the volatile fraction (0.45 mmole) were those of 1-bromopentaborane.

Attempted Halogen Exchange between Boron Trichloride and 1-Bromopentaborane.—1-Bromopentaborane (2.3 mmoles) and boron trichloride (8.1 mmoles) were sealed into a 25-ml. flask equipped with a 5-mm. diameter tube for taking n.m.r. spectra. The lowest temperature at which a significant change occurred in the B^{11} n.m.r. spectrum was *ca.* 150°, 18 hr. The intensity of the pattern attributed to 1-bromopentaborane had greatly diminished (*ca.* 20-fold) and there was no indication that any other boron-containing material was present except for the large signal of boron trichloride.

Results and Discussion

The reaction between aluminum chloride and 1-bromopentaborane to yield 2-chloropentaborane is the first observed halogen exchange in a polyborane. The mechanism for the exchange may involve a bridged intermediate or transition state analogous to the structure of the aluminum chloride dimer; however, the low yield of the product near the decomposition temperature (*ca.* 150–160°) of 1-bromopentaborane may suggest a fragmentation–exchange–recombination sequence.

The B^{11} nuclear magnetic resonance spectrum of 2-chloropentaborane, taken both at 12.8 and 32.1 Mc., consisted of a singlet, δ −0.5,[7,8] corresponding to the chlorinated boron (B^2–Cl) and three doublets, δ +12.5, J = 177 c.p.s. ($B^{3,5}$–H); δ +22, J = 178 c.p.s. (B^4–H); δ +51, J = 179 c.p.s. (B^1–H), in an area ratio of 1:2:1:1, respectively. The unique boron diagonally opposite the B–Cl in the base of the tetragonal pyramid (B^4–H) is located at unusually high field for a basal B–H.[7,9] This may be attributed to a long-range effect similar to that found in substituted benzenes.[10]

The H^1 n.m.r. (60 Mc.) agrees with the structural assignment for 2-chloropentaborane with a low-field quartet in the region of basal terminal hydrogens, a high-field quartet in the region assigned to an apical terminal hydrogen, and a broad bridge hydrogen region in the ratio of 3:1:4, respectively. Since a bulk susceptibility correction was not made, the H^1 n.m.r. chemical shifts are given relative to the B^1–H resonance: $B^{3,4,5}$–H = −1.8 p.p.m.; B–H_{bridge}–B = +2.2 p.p.m. Most terminal hydrogen resonances of pentaborane compounds are broad (half-width usually 0.8 p.p.m. at 60 Mc.), which may account for the apparent absence of a shift between the two types of basal terminal hydrogens in 2-chloropentaborane. A similar argument may be advanced for the apparent absence of a shift between the two types of bridge hydrogens.

An attempt to effect the conversion of 1-bromopentaborane to a chloropentaborane using boron trichloride was unsuccessful, as also were attempts to convert 1-bromopentaborane to 2-bromopentaborane using either aluminum tribromide or thermal rearrangement conditions.[6]

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Effect of Carrier Gas on the Transpiration of Zinc Chloride[1]

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There are reports in the older literature[2] that $Zn(NH_3)Cl_2$ is stable enough to be distilled. That is, presumably the zinc ammonia complex is stable in the gas phase. A calculation of the upper limit for the energy of addition of an NH_3 to a gaseous $ZnCl_2$ molecule can be made using the approach and the parameters given by Basolo and Pearson[3] for the solvation of gaseous ions. Their treatment was modified to the present case by taking into account the negative ions, assumed to form a linear, symmetrical $ZnCl_2$ molecule. The upper limit to the energy of association, obtained when the NH_3 molecule was placed as close as ionic radii would allow to the Zn, was about 35 kcal. Thus it seemed reasonable to look for the gaseous complex molecule.

Such a gaseous complex would manifest itself as an apparent increase in the vapor pressure of zinc chloride in a transpiration experiment with ammonia as the carrier gas. Accordingly, transpiration experiments were made with several different carrier gases, some inert (N_2, He, SF_6) and some possibly reactive (NH_3, HCl). In all these experiments, the apparent vapor pressure of the zinc chloride was essentially the same. Thus we found no evidence for gaseous complexes with HCl and NH_3 and no effect with inert carrier gases having molecular weights that differ as much as those of He and SF_6.

The experimental arrangement was the same as that described earlier,[4] except that when HCl or NH_3 was used as a carrier gas, the amount of gas passed was determined by absorbing it in known amounts of base or acid solutions and back-titrating. The containers were fused quartz. The agreement of the pressures measured at different flow rates (fourfold change for N_2 and twofold for He—see Table I) indicates that the gas stream was saturated and diffusion was negligible in these experiments.

TABLE I
VAPOR PRESSURE OF $ZnCl_2$ IN VARIOUS GASEOUS ATMOSPHERES

Gas (1 atm. total press.)	Flow rate, cc./min.	Temp., °C.	P ($ZnCl_2$), mm.	P ($ZnCl_2$), mm., cor. to 393.3°	
N_2	5	389.4	0.378	0.432	(av.) 0.438
	12	388.1	0.368	0.447	
	21	387.1	0.351	0.439	
	21	387.7	0.361	0.435	
He	22	387.7	0.352	0.427	0.428
	12	387.3	0.348	0.429	
	12	386.2	0.336	0.426	
	22	384.1	0.308	0.422	
	22	394.8	0.456	0.437	
HCl	14	394.1	0.489	0.474	0.464
	19	393.1	0.460	0.467	
	18	394.1	0.465	0.451	
He	21	394.2	0.459	0.447	0.433
	9	393.3	0.418	0.418	
SF_6	22	395.6	0.488	0.453	0.444
	12	396.1	0.486	0.435	
$N_2 + NH_3$	17	397.3	0.459	0.367	0.368
(15:1)	17	397.3	0.421	0.369	
NH_3	16	397.3	0.455	0.398	0.421
	15	397.3	0.507	0.444	
N_2	27	396.9	0.490	0.435	0.423
	27	397.3	0.468	0.410	

The results obtained, in chronological order, are given in Table I. The last column gives the pressure of zinc chloride corrected to a standard temperature. With N_2, He, and SF_6 the results were the same, within experimental error. No measurements by other investigators are available in this temperature range; however, the present data for those gases are within 10% of the value (0.48 mm.) extrapolated from the transpiration data of ref. 4. The results for HCl seemed to be higher than those for the inert gases, which may indicate a small percentage of gaseous $ZnCl_2$–HCl complex; however, it may have been the result of a small, systematic error in handling the HCl relative to the other gases, or an impurity in the HCl.

When the first experiments with NH_3 were analyzed, the weight of material transported was about twice that expected for an inert gas. This apparent evidence in favor of a gaseous complex molecule was found to be due to the transport of NH_4Cl (formed by ammonolysis of $ZnCl_2$) together with the $ZnCl_2$. Two distinct bands of condensate were found in the sample collector. Analysis of four samples of the one that condensed at lower temperatures gave chloride contents ranging from 65.5 to 66.5%. This was concluded to be NH_4Cl (theoretical Cl 66.3%). Chloride analysis of the other band was used to determine the amount of $ZnCl_2$ present. (The amount of Cl in this band was about 92% of that expected for $ZnCl_2$. It is believed that some NH_3 crystallized with the $ZnCl_2$.) When the partial pressures of $ZnCl_2$ in the NH_3-containing gases were calculated from the amounts of $ZnCl_2$ in the condensate, the results shown in Table

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[2] For reference see, for example, P. Pascal, "Nouveau Traité de Chimie Minérale," Vol. V, Masson, Paris, 1962, p. 151.

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