1-Deuteriopentaborane Rearrangement[1]

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Intramolecular deuterium–protium exchange takes place in 1-deuteriopentaborane when catalyzed by 2,6-dimethylpyridine at room temperature. In contrast, an intermolecular exchange mechanism prevails when 1-deuteriopentaborane undergoes deuterium–protium exchange at 145°.

Recently, a number of 1-substituted pentaboranes have been reported to give rearranged products under a variety of conditions.[3-5] The conversion of 1-alkylpentaboranes to 2-alkylpentaboranes is accomplished either by heating (ca. 200°)[5] or in the presence of 2,6-dimethylpyridine.[3] Heretofore, no substantiating evidence in support of proposed intramolecular[3,4] or intermolecular[3,5] mechanisms has been reported. In an effort to elucidate the nature of the rearrangement we have chosen to investigate 1-deuteriopentaborane under rearrangement conditions.

Experimental

1-Deuteriopentaborane in 2,6-Dimethylpyridine; 15 Min.—2,6-Dimethylpyridine,[6] 5.7 mmoles, and 1.1 mmoles of 1-deuteriopentaborane[7] (see Table I and Fig. 1) were mixed and allowed to stand at 25.0° for 15 min. The mixture was subsequently fractionated through −65° and −190° traps. An infrared spectrum of the product, 1.0 mmole, trapped at −190°, was similar to but not identical with that of the starting compound, 1-deuteriopentaborane. The major difference was a substantial decrease of intensity in the 14.2–14.5 μ region. The major portion of the product was sealed in a 5-mm. tube in order to obtain the H^1 n.m.r. spectrum; a small quantity was reserved for mass spectroscopic analysis (see Table I).

Table I

Partial Monoisotopic (B^{11}) Mass Spectra of the Deuterio-pentaboranes

m/e	1-DB_5H_8 for 2,6-dimethyl-pyridine expt.	After subjecting 1-DB_5H_8 to 2,6-dimethylpyridine 15 min.	After subjecting 1-DB_5H_8 to 2,6-dimethylpyridine 2 hr.	1-DB_5H_8 for thermal expt.	After subjecting 1-DB_5H_8 to thermal treatment 145°[a]	After subjecting 1-DB_5H_8 to thermal treatment 200°[a]
64	7.8	11.7	25.0	6.9	64.2	62.3
65	100.0	100.0	100.0	100.0	80.7	75.0
66	2.3	2.5	10.2	2.7	29.1	25.7
67	0.45	0.54	1.0	0.34	4.9	5.2
68	...	...	Trace	...	0.69	1.0

[a] Based on m/e 60 = 100.

2-Hr.—2,6-Dimethylpyridine,[6] 5.0 mmoles, and 1.0 mmole of 1-deuteriopentaborane[7] (see Table I and Fig. 1) were mixed and allowed to stand at 25.0° for 2.0 hr. The mixture was subsequently fractionated through −65° and −190° traps. An infrared spectrum of the product, 0.7 mmole, was similar to but not identical with that of the starting compound, 1-deuteriopentaborane. As noted above (15-min. run), a decrease of intensity in the 14.2–14.5 μ region was observed. The major portion of the product was sealed in a 5-mm. tube for H^1 n.m.r. analysis after reserving a small quantity for mass spectroscopic analysis.

Thermal Rearrangement of 1-Deuteriopentaborane: Minimum Temperature, 145°.—1-Deuteriopentaborane,[7] 1.0 mmole, was sealed into a 25-ml. vessel equipped with a 5-mm. glass tube at one end for taking n.m.r. spectra. After heating the sample for 20 hr. at 135° the H^1 n.m.r. spectrum indicated a minor change had taken place. The flask and its contents were sub-

(1) This work was supported by a grant (NSF-G19505) from the National Science Foundation.

(2) Participant in National Science Foundation Undergraduate Research Participation Program (G-21893), Summer, 1962.

(3) T. P. Onak, J. Am. Chem. Soc., **83**, 2584 (1961).

(4) R. Grimes and W. N. Lipscomb, Proc. Natl. Acad. Sci. U. S., **48**, 496 (1962).

(5) T. P. Onak and F. J. Gerhart, Inorg. Chem., **1**, 742 (1962).

(6) Purified according to the procedure described by H. C. Brown, S. Johnson and H. Podall, J. Am. Chem. Soc., **76**, 5556 (1954).

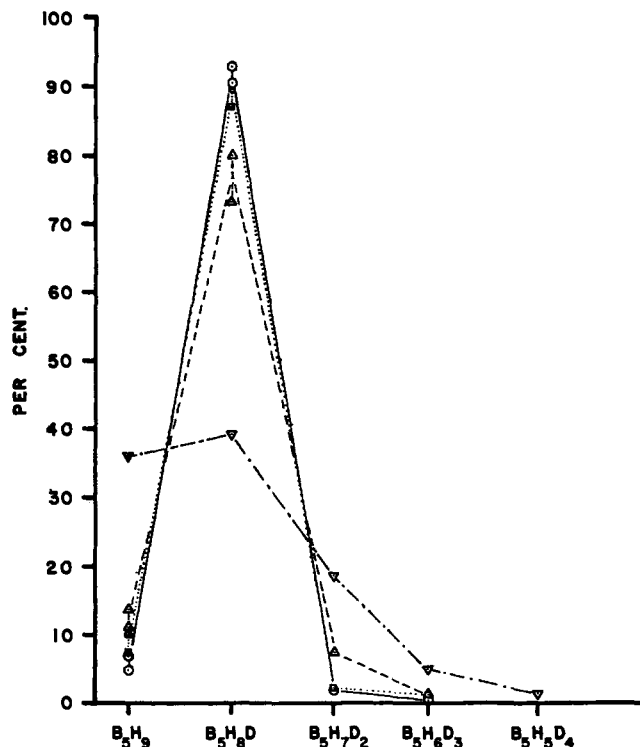(7) Prepared using the procedure described by T. Onak and R. E. Williams, Inorg. Chem., **1**, 106 (1962).

sequently heated at 145° for 20 hr. after which the H^1 n.m.r. spectrum revealed that a major change had occurred. Very little decomposition occurred at this temperature with nearly quantitative recovery of material having about the same volatility characteristics as pentaborane. The infrared spectrum of the product was similar to but not identical with that of the starting compound, 1-deuteriopentaborane. Again, an intensity decrease in the 14.2–14.5 μ region was noted. **200°:** 1-Deuteriopentaborane,[7] 1 mmole, was sealed in a flask equipped with a break-off seal and heated at 200° for 20 hr. About 0.8 mmole of material having nearly the same volatility characteristics as pentaborane was isolated. The remainder of the starting material appeared to have decomposed to hydrogen and yellow solids. The infrared spectrum of the major product was similar to but not identical with that of 1-deuteriopentaborane. Again, as with the 145° run, the major infrared change was a decrease in intensity in the region 14.2–14.5 μ.

B^{11} n.m.r. of 1-Deuteriopentaborane in 2,6-Dimethylpyridine.—One millimole of 1-deuteriopentaborane[7] and 5 mmoles of 2,6-dimethylpyridine[6] were sealed in 5-mm. tubing. The ensuing reaction was followed by means of B^{11} n.m.r. spectrum for a 2-hr. period. Within the first 15 min. the high field singlet[7] of 1-deuteriopentaborane was replaced by an apparently poorly resolved doublet due to the superposition of a B–H doublet and the residual B–D singlet[8]; simultaneously, a partial collapse of the low field doublet occurred. The shape of the peaks suggested that deuterium–protium exchange at the apical and basal positions was roughly 90% of the equilibrium value. After 45 min. no further change in the shape of the pentaborane peaks was observed.

Amount of Pentaborane Decomposition by 2,6-Dimethylpyridine; 2 Hr.—Pentaborane, 2.88 mmoles, and 2,6-dimethylpyridine,[6] 14.4 mmoles, were mixed and allowed to stand at 25.0° for 2.0 hr. The volatile contents were fractionated within a 10-min. period through −50° and −190° traps. The −190° trap contained 2.07 mmoles of pentaborane which represents 71.9% of the original quantity. The remainder had reacted to form 2,6-dimethylpyridineborane and polymeric materials,[9] both of which remained in the reaction flask.

Mass Spectra.—All mass spectra were taken on a CEC 21-620 instrument.

N.m.r.—The proton nuclear magnetic resonance spectra were taken on a Varian A-60 n.m.r. spectrometer. The B^{11} n.m.r. spectra were taken with a Varian V-4300 high resolution n.m.r. spectrometer operating at 12.83 Mc.

Results and Discussion

Rearrangement in 2,6-Dimethylpyridine.—1-Deuteriopentaborane rapidly rearranges in 2,6-dimethylpyridine as indicated by B^{11} and H^1 n.m.r. spectra. This rearrangement involves a rapid equilibration of the deuterium atom with all the hydrogen positions in the pentaborane framework. Within a 15-min. period a partial collapse of the low field doublet (basal B–H) of pentaborane[10] occurred in the B^{11} n.m.r. Simultaneously, the high field singlet (apical B–D) developed into a poorly resolved doublet. The recovered pentaborane fraction of the reaction mixture exhibited nearly the same H^1 n.m.r. spectrum as non-deuterated pentaborane which indicated bridge-hydrogen participation in the exchange. The deuterium–protium exchange in 1-deuteriopentaborane may occur by either an intramolecular[3,4] or intermolecular[5,11] mechanism. The intramolecular mechanism would be expected to give rise to only the three space isomers of B_5H_8D (1-, 2- and

(8) B^{11}–D spin–spin coupling is not resolved in these B^{11} n.m.r. spectra.

(9) T. P. Onak, R. E. Williams and H. G. Weiss, J. Am. Chem. Soc., **84**, 2830 (1962).

(10) J. N. Shoolery, Discussions Faraday Soc., **19**, 215 (1955).

(11) I. Shapiro and B. Keilin, J. Am. Chem. Soc., **77**, 2663 (1955).

Fig. 1.—Concentration of deuteriopentaboranes before and after treatment with 2,6-dimethylpyridine: 1, O, ——, 1-DB$_5$H$_9$ (starting material); 2, □, ..., after 15 min. with 2,6-dimethylpyridine; 3, Δ, – – – –, after 2 hr. with 2,6-dimethylpyridine; 4, ∇, – · – · – ·, calculated for intermolecular (bridge and terminal) hydrogen exchange.[11a]

Fig. 2.—Concentration of deuteriopentaboranes before and after heating: 1, O, ——, 1-DB$_5$H$_9$ (starting material); 2, □, ..., after 145° treatment; 3, Δ, – – – –, after 200° treatment; 4, ∇, – · – · – ·, calculated for intermolecular (bridge and terminal) hydrogen exchange.[8]

μ); however, an intermolecular mechanism would be expected to give a nearly statistical distribution of non-deuterated, monodeuterated, dideuterated, the other polydeuterated pentaboranes and all of their space isomers. H^1 and B^{11} n.m.r. spectra may not distinguish between intra- and intermolecular exchange products; however, the mass spectra of the various products necessarily differ. From mass spectroscopic data (Table I) the product of the 15-min. reaction of 1-deuteriopentaborane in 2,6-dimethylpyridine contains only one deuterium (Fig. 1); therefore, the rearrangement under these conditions is intramolecular. Since the mass spectra of the reactant and product in this case are almost identical, interpretation of the data is not complex; however, it was desirable to determine the relative concentration of the various deuterated pentaboranes for comparison with the reactant and products under the differing rearrangement conditions. In order to obtain the relative concentrations the raw mass spectral data were treated as follows: 1. Partial monoisotopic mass spectra (with respect to boron) were prepared from the observed spectra (Table I).[12] 2. It was assumed that the fragmentation pattern of pentaborane is nearly independent of the B^{10}, B^{11}, H^1 and D isotopes. From the general monoisotopic patterns exhibited by pentaborane, pentaborane-d_9 and pentaborane-d_8,[12] an average relative intensity pattern for B$_5$H$_{9-n}$D$_n$ is approximately: B$_5$H$_{9-n}$D$_n$ = 75; B$_5$H$_{8-n}$D$_n$ = 0; B$_5$H$_{7-n}$D$_n$ = 75; B$_5$H$_{6-n}$D = 0; B$_5$H$_{5-n}$

(11a) Curves 1, 2 and 3 were determined from the mass spectroscopic data (Table I) using the assumptions stated in the text of the report. Maximum and minimum concentrations are depicted by vertical lines. The lines between adjacent deuterated pentaboranes are drawn from midpoints of maximum and minimum concentrations. This is done for convenience only and is not to be regarded with any special physical significance. Assuming equivalence of B–H and B–D bonds, a theoretical composition representing equilibrium intermolecular exchange (curve 4) was calculated from the composition given by curve 1.

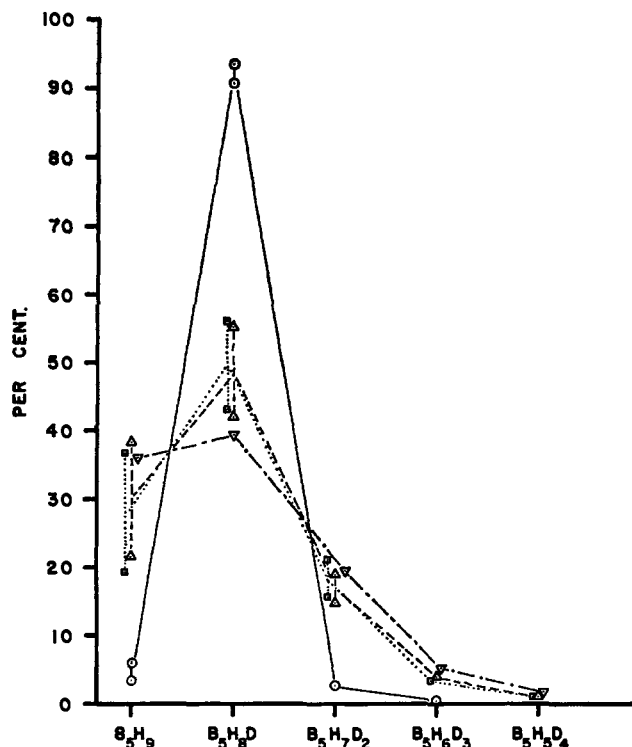(12) I. Shapiro and J. F. Ditter, *J. Chem. Phys.*, **26**, 798 (1957).

D$_n$D = 100. 3. It is realized that the mass spectra of pentaborane species which have the same number of deuterium atoms will be different; however, these differences are assumed to be minor for our present purpose, e.g., see similarities between 1-deuteriopentaborane and the scrambled monodeuteriopentaborane spectra from the 15-min. 2,6-dimethylpyridine run (Table I).

From the above assumptions and resulting calculations the amounts of deuterated species are shown in Fig. 1. It is evident that very little intermolecular exchange has taken place in pentaborane at the end of the 15-min. period in 2,6-dimethylpyridine. However, at the end of a 2-hr. period a slight change may be detected and a comparison of the amounts of poly-deuterated pentaboranes with an amount calculated from statistical intermolecular exchange reveals that a minor amount of intermolecular exchange has taken place. One explanation for the slow intermolecular exchange may be that at the end of 2 hr. enough 2,6-dimethylpyridineborane has been formed from penta-borane decomposition (ca. 28%) to give rise to an appreciable exchange of borane groups with pentaborane. Another possibility includes borane exchange between pentaborane and "unstable" 2,6-dimethylpyridine–B$_4$H$_6$ adduct.

Thermal Rearrangement.—The above results along with the observation that both 2,6-dimethylpyridine and heat promote the rearrangement of pentaborane compounds[3,5] led to an investigation of 1-deuteriopenta-borane rearrangement at elevated temperatures. Although it is known that pentaborane is dominated by intermolecular hydrogen exchange at 200°,[11] the possibility remained that intramolecular exchange could take place at a lower temperature.

The lowest temperature at which the rearrangement of 1-deuteriopentaborane occurred at a satisfactory rate was ca. 145°. This was determined by following

the H^1 n.m.r. while increasing temperature. After the 145° treatment the H^1 n.m.r. spectrum changed from the original 1-deuteriopentaborane pattern[7] to nearly that of pentaborane.[10] Another aliquot of 1-deuteriopentaborane subjected to 200° for 20 hr. gave a H^1 spectrum indistinguishable from pentaborane; therefore, this product was regarded as completely-scrambled (bridge and terminal) deuteriopentaborane(s). An area measurement of the low field peak of the high field quartet, prior to heating and after heating at 145° and 200°, indicated that the material which had been subjected to 145° for 20 hr. was roughly 80% rearranged. Mass spectral analysis of the 145° and 200° products gave the polydeuterated pentaborane distribution expected of nearly total intermolecular re-arrangement (Fig. 2). From these data, coupled with the H^1 n.m.r. results, there appears to be little evidence that intramolecular rearrangement takes place at a lower temperature than intermolecular exchange. It is obvious that a pressure–temperature interdependence must be considered in future studies along these lines.[13]

The 2,6-dimethylpyridine promoted rearrangement of alkylpentaboranes[3,5] probably proceeds by a mechanism similar to that observed for 1-deuteriopentaborane. Subjecting a 1-alkylpentaborane to 2,6-dimethylpyridine probably results in a slow intramolecular rearrangement (ca. 4 hr. at ambient temperature) to the more thermodynamically stable 2-alkylpentaboranes. Since 1-deuteriopentaborane and 1-alkyl-pentaboranes are stable at room temperature in the absence of 2,6-dimethylpyridine, it is probable that a pentaborane–2,6-dimethylpyridine adduct is the rearranging species. If in forming the Lewis base adduct the apical boron becomes equivalent to any other boron, the dissociation of the adduct will allow that boron to become a basal boron atom. When R = alkyl, the more thermodynamically stable 2-alkyl derivative will result.[5] Such an unstable intermediate might have the structure I which is similar to the known 2,4-dimethylenetetraborane. It is probable that the Lewis base would attack one of the base borons (most electropositive). In any case the alkylated borons would be less susceptible to Lewis base attack by virtue of steric and possibly by inductive factors. In such a fashion the alkyl substituted boron would become structurally equivalent to one of the other borons (see I). Since it is known that wholesale tautomerism of hydrogens[14] and accompany-

(13) The presence of trace quantities of boron hydride impurities (e.g., B_2H_6) cannot be ruled out and may account for the intermolecular exchange; see W. S. Koski, J. J. Kaufman and P. C. Lauterbur, J. Am. Chem. Soc., 79, 2382 (1957).
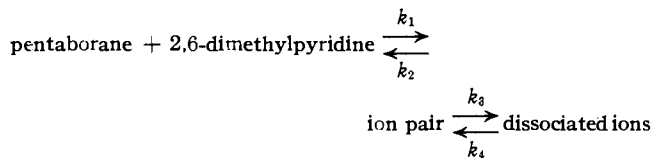

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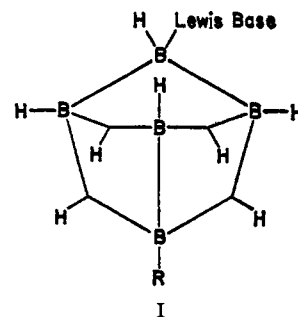
ing skeletal rearrangement is endemic in boron hydride Lewis base adducts, only a slight amount of rearrangement is necessary to accomplish such an intermediate. Speculation as to the specific sequence of the many possible atomic movements appears presumptive with the data available.

No detectable amounts of dialkyl or other poly-alkylated pentaboranes are formed during the thermal rearrangement of 1-alkylpentaboranes[5]; therefore, the alkyl migration probably proceeds by an intramolecular mechanism and the possibility that a boron–carbon bond is broken is remote.[4] Although it is almost certain that intramolecular hydrogen tautomerism accompanies the alkyl migration, it is not known whether intermolecular hydrogen exchange is taking place simultaneously. Experiments are now in progress to determine the minimum temperature necessary for intra- and/or intermolecular deuterium–protium exchange in the 1-alkylmonodeuteriopentaboranes.[15]

(14) (a) R. E. Williams, J. Inorg. Nucl. Chem., 20, 198 (1961); (b) R. E. Williams, 140th Natl. Meeting Am. Chem. Soc., Chicago, Ill., Sept., 1961.

(15) Note Added in Proof.—In a recent publication (J. Am. Chem. Soc., 85, 831 (1963)) Hough, Edwards and Stang have reported the isolation of trimethylammonium monoethylpentaborate as an intermediate in the re-arrangement of 1-ethylpentaborane with trimethylamine. A salt of a similar nature, existing as an intimate ion pair in solution, could be an intermediate in the base-catalyzed intramolecular rearrangement of 1-deuteriopentaborane with 2,6-dimethylpyridine.

$$\text{pentaborane} + 2,6\text{-dimethylpyridine} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} $$

$$\text{ion pair} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \text{dissociated ions}$$

From the B^{11} n.m.r. and hydrogen exchange data $k_2 \gg k_1$ and $k_2 \gg k_3$.