methyl-B,B′-diborazyl Oxide (Va).—Into a nitrogen-filled 15-ml. centrifuge cone fitted with a rubber septum was placed 0.3931 g. (2.12 mmoles) of pentamethyl-B-chloroborazine and 3 ml. of ether. An estimated 0.39–0.44 mmole of distilled water was added by mixing 0.25 ml. of water with 10 ml. of ether and adding 0.77 ml. of this mixture to the agitated borazine solution which deposited a white, milky solid. Addition of 0.2145 g. (2.12 mmoles) of triethylamine resulted in an evolution of heat and precipitation of 0.1826 g. of crude triethylammonium chloride, which was removed by filtration. The ethereal filtrate was evaporated leaving a solid residue which was sublimed at 50° to recover 0.1630 g. (0.881 mmole, 41.5%) of pentamethyl-B-chloroborazine. Further sublimation at 100° yielded 0.0791 g. of solid and left 0.0124 g. of glassy residue. The latter sublimate, recrystallized from isopropylamine and resublimed, had a m.p. 125–129°. However, the infrared spectrum was identical with that of decamethyl-B,B′-diborazyl oxide (m.p. 133–134°) isolated from attempted dehydrohalogenation experiments (*vide supra*). The mixture melting point of these two materials was 126–130°.

(b) **Preparation of Poly(1,3,5,6-tetramethyl-2,4-borazylene Oxide) (VII).**—Into a 100-ml. nitrogen-filled septum bottle equipped with a magnetic stirring bar was placed 2.2805 g. (11.10 mmoles) of tetramethyl-B-dichloroborazine and 50 ml. of ether. A 0.200-ml. (11.11 mmoles) quantity of distilled water was slowly syringed into the stirred borazine solution, producing a voluminous white precipitate. Addition of 2.2774 g. (22.51 mmoles) of triethylamine resulted in considerable evolution of heat. The stirring was continued for 1 hr., after which the solids were filtered, washed with two 10-ml. portions of ether, and vacuum-dried to give 2.6060 g. (18.93 mmoles, 86.7%) of tan, amorphous powder, characterized by infrared and elemental analyses as predominantly triethylammonium chloride. *Anal.* Calcd. for $C_6H_{16}NCl$: N, 10.18; Cl, 25.76. Found: N, 10.58; Cl, 24.37; B, 2.87. Only a trace of material volatilized from the filtrate residue at 150° on attempted vacuum sublimation. The residual light brown glass weighed 1.0790 g. (7.164 mmoles as monomer, 64.7%), melted over the range 180–200°, and showed the characteristic B–O–B infrared absorption (10.52 μ) shown by this class of compounds. *Anal.* Calcd. for $(C_4H_{12}N_3B_3O)_n$: C, 31.89; H, 8.03; mol. wt., $(150.6)_n$. Found: C, 29.17; H, 8.13; mol. wt., 3512 ($n = 23.2$).

(c) **Preparation of Low Molecular Weight 2,4-Borazylene Oxides (VI).**—Co-hydrolysis of a mixture of 1.1146 g. (6.021 mmoles) of pentamethyl-B-chloroborazine and 0.6186 g. (3.010 mmoles) of tetramethyl-B-dichloroborazine with the stoichiometric quantity of aqueous triethylamine yielded on sublimation the following fractions: (1) 0.2102 g. (0.6667 mmole) or 22.1% of the pentamethyl-B-chloroborazine as decamethyl-B,B′-diborazyl oxide (obtained at 100°), identified by m.p. 126–131° and infrared spectrum; (2) 0.2051 g. of a colorless sticky sublimate (obtained at 140°), m.p. 133–155°, mol. wt. 478.6, tentatively characterized as a "dioxide" (VI where $n = 1$, mol. wt. 465.9–469.9); and (3) 0.4460 g. of a brittle yellow glassy residue of molecular weight 734.5 or approximately a "tetraoxide" (VI where $n = 3$, mol. wt. 766.2–771.1).

Acknowledgment.—We wish to thank Dr. Kendrick R. Eilar for helpful discussions, Mr. Robert G. Adler for molecular weight determinations, Mr. M. E. Persons for microcombustion analyses, Mr. Kent A. Smitheman for vapor phase chromatographic analyses, Mrs. Nancy J. Naumann and Mr. Karl H. Sterner for infrared analyses, and Mr. L. D. Freeman for some of the preliminary experiments.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, LOS ANGELES STATE COLLEGE,
LOS ANGELES, CALIFORNIA, AND THE NATIONAL ENGINEERING SCIENCE COMPANY, PASADENA, CALIFORNIA

B_5H_9–DCl Exchange Catalyzed by $AlCl_3$

BY THOMAS P. ONAK AND ROBERT E. WILLIAMS

Received August 8, 1961

Treatment of pentaborane-9 with deuterium chloride in the presence of aluminum chloride results in the rapid exchange of hydrogen and deuterium in the 1-position. 1-Deuteriopentaborane was identified by the B^{11} and H^1 n.m.r. spectra and confirmed by the stoichiometry of the exchanging species at equilibrium.

Introduction

Perdeuteriopentaborane[1,2] and 1,2,3,4,5-pentadeuteriopentaborane[3] are the only deuterium-substituted pentaborane species (see Table I) reported in the literature. In this work is described a synthesis of 1-deuteriopentaborane by deuterium exchange of pentaborane-9 with deu-

---

(1) H. J. Hrostowski and G. C. Pimentel, *J. Am. Chem. Soc.*, **76**, 998 (1954).

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

(3) (a) W. S. Koski, J. J. Kaufman, and P. C. Lauterbur, *J. Am. Chem. Soc.*, **79**, 2382 (1957); (b) exchange of $B_2{}^{10}H_6$ with B_5H_9 indicates that some bridge deuteration also is taking place as indicated by infrared and mass spectral data; J. F. Ditter, unpublished data.

TABLE I

EXCHANGE DATA AND EXPERIMENTAL METHODS OF SYNTHESIS OF HYDROGEN–DEUTERIUM ISOTOPIC SPECIES OF PENTABORANE-9

Hydrogen–deuterium isotopic species				
Apical 1-	Basal term. 2,3,4,5-	Bridge μ,μ,μ,μ-	% DCl in DCl–HCl mixture after exchange (calcd.)[a]	Summary of experimental methods of synthesis
H	H	H	93	A. Stock[b]
D	H	H	62	From pentaborane, *e.g.*, isotope-species (H,H,H), using method (*c*)
H	D	H	31	From (D,D,H) using method (*d*)
H	H	D	31	From (D,D,D) using method (*f*)
D	D	H	27	From (H,H,H) using method (*e*)
D	H	D	27	From (H,H,D) using method (*c*)
H	D	D	19	From (D,D,D) using method (*d*)
D	D	D	17	H. J. Hrostowski and G. C. Pimentel[g]

[a] Calculated after assuming equilibration of 93% DCl–7% HCl in a 2:1 ratio with pentaborane to obtain each isotopic species. Within each isotopic species there will be a statistical distribution of non-deuterio-, mono-deuterio-, etc., pentaboranes which need not be considered in detail here. [b] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933. [c] Exchange with DCl in the presence of aluminum chloride, this report. [d] Exchange with HCl in the presence of aluminum chloride, this report. [e] Exchange with B_2D_6, ref. 3a. [f] Exchange with B_2H_6, ref. 3a. [g] See ref. 1.

terium chloride in the presence of aluminum chloride.[4] The remaining partially hydrogenated–partially deuterated pentaborane species now may be prepared by various combinations of the previously reported syntheses[1–3] and the following synthesis.

Experimental

Deuterium Chloride.—Twenty-three mmoles of aluminum chloride was sublimed into a 1-l. flask. To this was added 75 mmoles of deuterium oxide (99.5%) and the flask (equipped with break-off-seals) then was sealed and heated at 200° for 18 hr. The deuterium chloride was removed from the reaction flask and purified using fractional condensation techniques. A 45-millimole yield of 93% deuterium chloride (7% hydrogen chloride) was obtained as determined by infrared analysis (Beckman IR-5). All of the following studies were carried out with the 93% deuterium chloride. Also, all infrared analyses of deuterium chloride–hydrogen chloride mixtures are accurate to within ± 2%.

Preparation of the Infrared Cell Containing Aluminum Chloride.—A 10-cm. gas cell equipped with sodium chloride optics was outfitted with a U-tube which in turn was attached to a reagent sidearm. Also attached to the main body of the cell was a stopcock with an adjoining mercury reservoir. During use, the mercury was introduced into the stopcock sidearm in order to keep any chemicals put inside the cell from prolonged contact with the stopcock grease. About 50 mg. of anhydrous aluminum chloride was sublimed from the reagent sidearm into the U-tube and the sidearm subsequently sealed off from the rest of the cell. An infrared spectrum of the cell indicated no absorption from 2 to 16 μ.

Deuterium Exchange of Pentaborane with Deuterium Chloride in the Presence of Aluminum Chloride.—Deuterium chloride (93%) and pentaborane-9 (Olin Mathieson), in a 2:1 mole ratio, respectively, were condensed into the infrared cell containing aluminum chloride. Two separate experiments were carried out with pentaborane at pressures of 20 and 200 mm. Upon warming to room temperature exchange took place rapidly, as indicated by the immediate increased intensities in the infrared spectrum at 5.06 μ (B–D) and 3.41 and 3.56 μ (HCl) accompanied by decreased intensities at 4.69 and 4.91 μ (DCl). Exchange appeared to be nearly complete within a 2-hr period, as evidenced by no further significant infrared changes in the next 21-hr. period. The mixture within the gas cell was fractionally condensed through −100 and −190° baths. Infrared analysis of the material in the −190° bath indicated a mixture of 63% DCl–37% HCl. The −100° bath material consisted of 63% 1-deuteriopentaborane (*vide infra*) and 37% pentaborane. Through a series of exchanges 90% 1-deuteriopentaborane was prepared, the deuterium content of which was determined by infrared analysis of the DCl–HCl mixture after equilibrium had been established in the last exchange. The infrared spectrum of the 90% 1-deuteriopentaborane is quite similar to that of pentaborane except for new bands at 5.06 μ and 14.2–14.6 μ, in addition to some changes in the 6.9–9.3 μ and 10.8–11.6 μ regions. Eight-tenths of a mmole samples of 63% and 90% 1-deuteriopentaborane and pentaborane in 5-mm. (o.d.) glass tubes were sealed for B^{11} and H^1 nuclear magnetic resonance spectra.

Thermal Stability of 1-Deuteriopentaborane.—One mmole of 90% 1-deuteriopentaborane was sealed into a 1-l. flask equipped with break-off seals. After allowing it to stand for 17 hr. at 105°, 1.0 mmole of 1-deuteriopentaborane was recovered unchanged as determined by infrared and B^{11} n.m.r. spectra.

Deuterium Chloride and Pentaborane (without Catalyst).—One-fourth mmole of pentaborane and three-fourths mmole of deuterium chloride were condensed into a 10-cm. infrared gas cell. After allowing the mixture to

---

(4) This method is somewhat analogous to the deuterium exchange of decaborane with deuterium chloride in the presence of aluminum chloride reported by J. A. Dupont and M. F. Hawthorne, Abstracts, 138th National Meeting, American Chemical Society, New York, N. Y., p. 46-N, and erroneously reported in *J. Am. Chem. Soc.*, **81**, 4998 (1959).

come to room temperature a series of infrared spectra were taken over a period of 120 hr. All spectra revealed that no detectable deuteration of pentaborane had taken place. This mixture then was condensed into the infrared cell containing aluminum chloride, whereupon hydrogen-deuterium exchange with pentaborane promptly took place.

Deuterium Chloride and 1-Methylpentaborane in the Presence of Aluminum Chloride.—One-fourth mmole of 1-methylpentaborane[5] and three-fourths mmole of deuterium chloride were condensed into the infrared cell containing aluminum chloride. After allowing the mixture to come to room temperature a series of infrared spectra were taken over a period of two hr. All spectra revealed that no detectable deuteration of 1-methylpentaborane had taken place. Unchanged 1-methylpentaborane (0.24 mmole) was recovered by using fractional condensation techniques.

Discussion

A rather rapid hydrogen-deuterium exchange takes place between pentaborane-9 and deuterium chloride in the presence of aluminum chloride. With the concentrations used exchange was nearly complete within two hr. as evidenced by no further change in the infrared spectrum. Infrared examination of the hydrogen chloride-deuterium chloride mixture after a two hr. exchange time between a 2:1 deuterium chloride (93%)-pentaborane mixture indicated a 37:63 HCl:DCl ratio. Comparison of this ratio to column four, Table I, leads to the conclusion that only the apical hydrogen of pentaborane-9 participated in the exchange. A B^{11} n.m.r. spectrum of the deuterated pentaborane, when compared to pentaborane,[6] indicated a collapse of the high field doublet, $\delta = +51.8$, whereas the low field doublet, $\delta = +12.5$, remained unchanged. The extent of the high field doublet collapse was consistent with the assumption that the only exchangeable hydrogen was that in the apical position. The H^1 n.m.r. spectra of pentaborane and the deuterated pentaborane are given in Fig. 1. It can be seen graphically that very little, if any, of the bridge positions[7] have participated in the exchange. A comparison of the various areas[3] indicates that the deuterium content in the bridge positions is less than 5%. However, the additional observation that there is no further change in the infrared spectrum following the initial two hr. of exchange indicates that there must be less than 1% bridge deuteration.

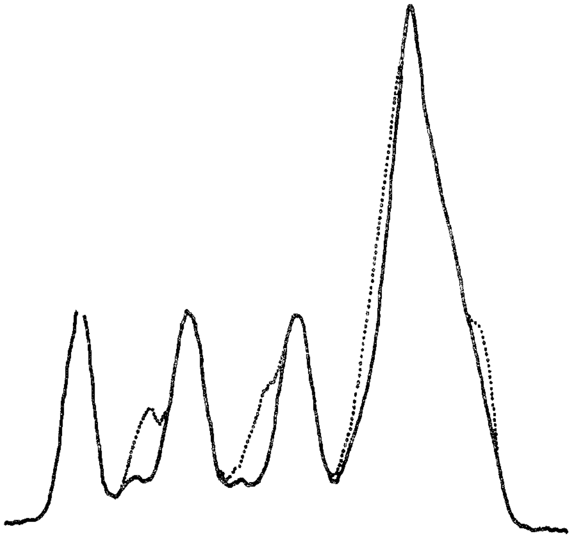

Fig. 1. H^1 n.m.r. spectrum of 90% 1-deuteriopentaborane (———); H^1 n.m.r. spectrum of pentaborane (. . .). Both spectra were taken at 60 Mc. and overlap except where lines are separated.

Attempted deuteration of 1-methylpentaborane with deuterium chloride in the presence of aluminum chloride was unsuccessful as noted by a nearly quantitative recovery of unchanged reactants at the end of a two-hr. period. This result is to be expected with the absence of an exchangeable hydrogen. Also, this substantiates the absence of exchange in the basal and bridge hydrogen positions of pentaborane-9.

No exchange occurs between pentaborane-9 and deuterium chloride over a period of 120 hr. in the absence of an electrophilic catalyst. Therefore, the above hydrogen-deuterium exchange studies are in agreement with the fact that the apical position of pentaborane-9 is the most susceptible to electrophilic attack.[5]

Subjecting the 1-deuteriopentaborane to 105° for 17 hr. did not cause any detectable change in the infrared or B^{11} n.m.r. spectra.

Of the eight hydrogen-deuterium "isotopic species" of pentaborane-9 (Table I), four types, (H,H,H), (H,H,D) (D,D,H), and (D,D,D) have been or can be synthesized using previously described techniques. This report describes a method to synthesize isotopic species (D,H,H); the use of this method (with previous methods) allows the synthesis of all eight hydrogen-deuterium "isotopic species" (last column, Table I).

Acknowledgment.—The authors are indebted to Leroy F. Johnson of Varian Associates for the H^1 n.m.r. spectra. This work was supported in part by the Office of Naval Research.

---

(5) B. N. Figgis and R. L. Williams, *Spectrochim. Acta*, **15**, 331 (1959).

(6) T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Am. Chem. Soc.*, **63**, 1533 (1959).

(7) J. N. Schoolery, *Discussions Faraday Soc.*, **19**, 215 (1955).