

The pyrolysis mechanism was studied by following the reaction parameters (loss of  $B_2H_6$ , formation of new species) as a function of temperature at successively increasing pressures of diborane in the furnace.

With a pressure of diborane of  $5 \times 10^{-8}$  to  $2 \times 10^{-7}$  atm. in the furnace, the  $B_2H_6$  was 50% decomposed at 750°K. and the presence of a new monoborane species was detected.<sup>15</sup> No hydrides heavier than  $B_2H_6$  were present. Increasing the  $B_2H_6$  pressure to  $5 \times 10^{-6}$  atm. caused 50%  $B_2H_6$  decomposition at only 525°K.; ions containing three, but *not* four, five, or more boron atoms were detectable.

At  $\approx 10^{-4.5}$  atm.  $B_2H_6$  pressure and 425°K. triborane ion peaks were clearly observed at masses 34 through 39. Simultaneously, the presence of "shutterable" peak intensities between masses 46 and 52 (in the ratios 0.5:1.0:1.0:0.5:0.2:( $<0.07$ ):( $<0.03$ ), respectively) and the absence of peaks corresponding to ions with five or more borons showed that a tetraborane was present, but  $B_5$  and higher hydrides were not. In contrast with the known mass spectrum of tetraborane-10,<sup>3,16</sup> the peaks at masses 36-38 were 50% larger than any tetraborane peak between masses 46 and 50.

With the same pressure, an increase in temperature was accompanied by a slight decrease in the  $B_3$  intensities, an increase in the  $B_4$ , and a very rapid increase in the  $B_5$  intensities.

Interpretation of the mass spectra and temperature dependence of the  $B_3$ - $B_4$ -, and  $B_5$ -boron containing ions indicate the presence of triborane and a new tetraborane. First, the mass spectrum at peaks 46-52 given above is different from the well-characterized  $B_4H_{10}$  spectrum,<sup>3,16</sup> where the ratios of peak intensities are 0.6:0.9:1.0:1.0:1.0:0.2:0.1, respectively. Since this mass spectrometer has systematically reproduced the mass spectra of other known compounds, this is good evidence for a new tetraborane with fewer hydrogens than  $B_4H_{10}$ .

This offers the possibility that the  $B_3H_x$  ions are produced by fragmentation of this new tetraborane species, which is possibly  $B_4H_8$ . However, on electron impact, all the known boron hydrides produce ions of greatest intensity which contain the same number of boron atoms as the parent molecule. Since at times the  $B_3$ -containing ions were at least 50% larger than any  $B_4$ -containing ion, and the  $B_3$ ,  $B_4$ , and  $B_5$  ions had different temperature dependence, the conclusion that a neutral triborane species is formed is reasonably justified. The formation of a tetraborane prior to pentaborane is in accord with the arguments of Schaeffer,<sup>9</sup> Lipscomb,<sup>17</sup> and others,<sup>18</sup> as well as the tentative observation in ref. 3, footnote 7. However, we are at present unable to prove conclusively whether the observed tetraborane is  $B_4H_8$  or a mixture of  $B_4H_8 + B_4H_{10}$ , and whether it is produced *via* reaction 4 or 4'.

Although to date no other direct observation of  $B_4H_8$  has been made, evidence exists that it may play an important role in the formation of  $B_5H_{11}$ . Independent kinetic studies<sup>19,20</sup> of the  $B_4H_{10} + B_2H_6$  reaction indi-

cate that  $B_4H_8$  is almost certainly the first reaction product of  $B_4H_{10}$  prior to its conversion to  $B_5H_{11}$ . More recently, Brennan and Schaeffer<sup>21</sup> observed the thermal decomposition of  $B_4H_{10}$  in the presence of carbon monoxide. They isolated  $B_4H_8CO$  as the major reaction product. The close agreement between the kinetics of the  $B_4H_{10}$ -CO and  $B_4H_{10}$ - $B_2H_6$  reactions also indicates that the same intermediate,  $B_4H_8$ , is common to both systems.

**Acknowledgment.**—This work was supported by the United States Atomic Energy Commission and by the Northwestern University Materials Research Center of the Advanced Research Projects Agency.

(20) R. K. Pearson and L. J. Edwards, Abstracts, 132nd National Meeting of the American Chemical Society, New York, N. Y., 1957, p. 15N.

(21) G. L. Brennan and R. Schaeffer, *J. Inorg. Nucl. Chem.*, **20**, 205 (1961).

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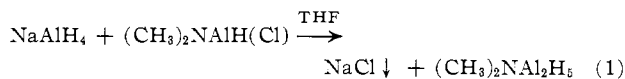
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### The Chemistry of Alane. IV.<sup>1</sup> Dimethylaminodialane, $(CH_3)_2NAl_2H_5$ <sup>2</sup>

Sir:

We wish to report the synthesis of the first known derivative of dialane,  $Al_2H_6$ , the aluminum analog of diborane, by the reaction of sodium aluminum hydride with dimethylaminochloroalane<sup>3</sup> in tetrahydrofuran (THF) according to eq. 1. The precipitation of so-



dium chloride was quantitative and evaporation of the solvent yielded a white, chloride-free solid corresponding to  $(CH_3)_2NAl_2H_5 \cdot THF$ . *Anal.* Calcd.: Al, 30.80; active H, 2.88; H/Al, 2.50. Found: Al, 31.00; active H, 2.88; H/Al, 2.49. Almost all of the associated THF could be removed by precipitating the product from its THF solution with pentane. Dimethylaminodialane was a white solid which decomposed without melting at 130°. Its molecular weight, determined cryoscopically in benzene, was found to be 100 as compared to the calculated value of 103 for the monomer.

The direct reaction of alane and dimethylaminoalane in diethyl ether was found to be a second method for the preparation of dimethylaminodialane. It is well-known that ether solutions of alane are unstable and precipitate polymerized diethyl ether alane.<sup>4,5</sup> When an equimolar solution of dimethylaminoalane was added to freshly prepared diethyl ether alane in ether, no precipitation occurred during 1 week of stand-

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(3) The dimethylaminochloroalane was prepared from dimethylaminoalane and mercuric chloride by the method of J. K. Ruff, *J. Am. Chem. Soc.*, **83**, 1798 (1961), and its composition was confirmed by quantitative hydrolysis of its THF solution.

(4) Cf. A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).

(5) R. Ehrlich, A. R. Young, II, B. M. Lichstein, and D. D. Perry, *Inorg. Chem.*, **2**, 650 (1963).

(15) E. J. Sinke, G. A. Pressley, Jr., A. B. Baylis, and F. E. Stafford, *J. Chem Phys.*, **41**, 2207 (1964).

(16) I. Shapiro, C. O. Wilson, J. F. Ditter, and W. J. Lehmann, *Advances in Chemistry Series No. 32*, American Chemical Society, Washington, D. C., 1961, p. 127.

(17) W. N. Lipscomb, *Advan. Inorg. Radiochem.*, **1**, 149 (1959).

(18) R. P. Clarke and R. N. Pease, *J. Am. Chem. Soc.*, **73**, 2132 (1951).

(19) J. A. Dupont and R. Schaeffer, *J. Inorg. Nucl. Chem.*, **15**, 310 (1960).

TABLE I  
MAJOR X-RAY DIFFRACTION LINES OF  $\text{Me}_2\text{NAl}_2\text{H}_5$   
AND  $\text{Me}_2\text{NAlH}_2$

$\text{Me}_2\text{NAl}_2\text{H}_5$		$\text{Me}_2\text{NAlH}_2$	
d(Å.)	I/I <sub>0</sub>	d(Å.)	I/I <sub>0</sub>
4.47	20	7.31	100
		6.41	5
3.85	100	5.94	5
		5.68	100
3.64	20	5.30	60
		3.75	90
3.30	70	3.64	5
		3.50	5
3.23	70	3.40	20
		3.12	10
2.99	30	3.04	10
		2.79	10
2.91	30	2.57	10
		2.48	10
2.66	20	2.29	10
		2.16	10
2.44	20	2.11	10
		2.05	5
2.32	20	1.94	5
		1.74	5
2.23	20		
2.14	20		

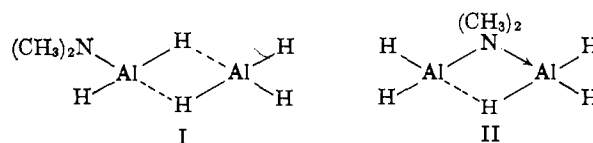
ing at room temperature, indicating that reaction had taken place. Removal of the ether *in vacuo* produced the diethyl ether complex of dimethylaminodialane. *Anal.* Calcd. for  $(\text{CH}_3)_2\text{NAl}_2\text{H}_5 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ : Al, 30.45; active H, 2.84; N, 7.90; H/Al, 2.50. Found: Al, 30.20; active H, 2.70; N, 8.20; H/Al, 2.39. An ebullioscopic molecular weight determination in diethyl ether gave a molecular weight of  $127 \pm 13$  as compared to the calculated value for  $(\text{CH}_3)_2\text{NAl}_2\text{H}_5$  of 103 or a value of 51 calculated for an equimolar mixture of alane and dimethylaminoalane. Attempts to remove the associated ether either at room temperature or at  $66^\circ$  in a vacuum were unsuccessful.

Solvent-free dimethylaminodialane was obtained from a benzene-ether solution containing 20% diethyl ether by volume. Diethyl ether alane was found to form stable solutions in such a mixture for extended periods and the reaction with an equimolar quantity of dimethylaminoalane produced a quantitative yield of the dialane derivative on freeze drying of the solution. The solid was dried *in vacuo* at room temperature for 20 hr. *Anal.* Calcd. for  $(\text{CH}_3)_2\text{NAl}_2\text{H}_5$ : Al, 52.35; active H, 4.89; H/Al, 2.50. Found: Al, 52.88; active H, 5.18; H/Al, 2.62.

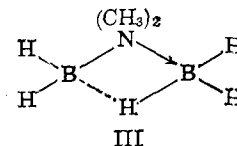
That the product isolated in these reactions is indeed a novel material was shown in several ways. In addition to the failure of diethyl ether alane to precipitate from diethyl ether in the presence of dimethylaminoalane, it was impossible to sublime any dimethylaminoalane from the solid up to  $80^\circ$ , while dimethylaminoalane was sublimed readily from a mixture of the two solids below  $40^\circ$ . The infrared spectrum of the dialane compound shows only one Al-H absorption at  $1725 \text{ cm.}^{-1}$  in THF while a THF solution of dimethylaminoalane absorbs at  $1802 \text{ cm.}^{-1}$ . However, the Al-H absorption of dimethylaminodialane dissolved in benzene appears at  $1802 \text{ cm.}^{-1}$ . Molecular weight determinations in diethyl ether and in benzene showed that dimethylaminodialane was monomeric in both solvents, while dimethylaminoalane is trimeric in

benzene.<sup>6</sup> Finally, the X-ray diffraction pattern of dimethylaminodialane was different from that of dimethylaminoalane (Table I).

Two possible structures can be written for dimethylaminodialane (I and II) depending on whether the nitrogen atom is bridging or not. Both structures show only tetracoordinated aluminum atoms and since the dialane was monomeric in benzene its Al-H absorption in benzene occurred at the frequency characteristic of tetracoordinated aluminum.<sup>5,7</sup> In THF, however,



the Al-H absorption had shifted to the frequency characteristic of pentacoordinated aluminum. Construction of Fisher-Taylor-Hirschfelder models showed that structure I could coordinate with only one THF molecule while II could coordinate with two without steric strain. The Al-H absorption of I, therefore, should split into two bands in THF, one for a tetracoordinated and the other for a pentacoordinated aluminum, while II should show only the pentacoordinated frequency in THF. We favor structure II for dimethylaminodialane since only one Al-H absorption appeared in its infrared spectrum in THF. This structure is also analogous to the structure of dimethylaminodiborane, III.<sup>8</sup>



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(6) J. K. Ruff, *J. Am. Chem. Soc.*, **83**, 2835 (1961).

(7) R. Dautel and W. Zeil, *Z. Elektrochem.*, **64**, 1234 (1960).

(8) H. Hedberg and A. J. Stosick, *J. Am. Chem. Soc.*, **74**, 954 (1952).

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### The Synthesis of the S-Methylthiophenium Ion

Sir:

The sulfur atom of thiophene has an unshared electron pair other than that utilized in the formation of the aromatic sextet, and should therefore be capable of forming S-alkyl derivatives. We report the first synthesis of such a compound. Methylthiophenium hexafluorophosphate (I) was prepared by two procedures. Thiophene was added to a cold suspension of trimethyloxonium fluoroborate<sup>1</sup> in methylene chloride, the mixture was extracted with ice-water, and a saturated solution of sodium hexafluorophosphate was added to the extract to give a white precipitate,

(1) H. Meerwein, G. Hinz, P. Hofmann, E. Kronig, and E. Pfeil, *J. prakt. Chem.*, **147**, 257 (1937).