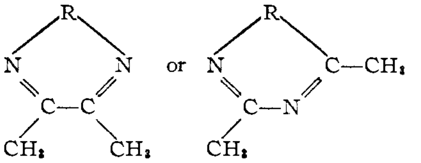
white precipitate consisting of well-formed, needle-shaped crystals deposits from the solution and may be washed free of the slightly colored, supernatant liquid with a small amount of the nitrile. The amount of hydrogen evolved corresponds closely to one mole per mole of $B_{10}H_{14}$ used, and the analysis of the material confirms the fact that two hydrogens have been replaced by two acetonitrile groups. (Calculated for $B_{10}H_{12}\cdot 2CH_3CN$: B, 53.5; C, 23.7; H, 8.9; N, 13.8. Observed: B, 53.2; C, 22.9, 22.6; H, 8.6, 8.4; N, 13.2. Empirical formula: $B_{10.4}H_{17.9}N_{2.0}C_{4.0}$.)

The new compound is non-volatile, apparently indefinitely stable in air, melts over 200° with decomposition, and is insoluble in most organic solvents except acetonitrile. The material is diamagnetic.

The structure of the new compound has not been determined, but several limitations can be imposed on likely structures. Thus, the infrared spectrum shows no evidence of N—H or C=N groups, nor of the original C≡N group. Prolonged reflux with methanol does not completely degrade the compound, but produces a new material showing a strong C=N absorption. The B^{11} nuclear magnetic resonance spectrum is complex but does show that attack has not occurred at the 2,2′ positions. The diamagnetism seems to necessitate a cyclic structure involving linkage of the two nitrile groups. It then seems most probable that the structure involves a carbon-nitrogen "bridge" linking two equivalent borons through utilization of B-N bonds. Two possible structures might be



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where the R group represents the decaborane cage. Alcoholysis of such a compound could easily produce residues showing free C=N, whereas the electron withdrawing decaborane group would probably cause substantial shifts in the original material making the characteristic frequency difficult to identify. The structure is currently being sought by X-ray diffraction studies in Professor Lipscomb's laboratory.

Preliminary studies show that pentaborane-9 behaves in a similar fashion and that other nitriles may be substituted for acetonitrile, although in no case is the reaction as clean as that reported above. Complete studies will be reported at a later date.

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RECEIVED JANUARY 2, 1957

THE DIAMMONIATE OF TETRABORANE

Sir:

Stock, Wiberg, Martini, and Nicklas[1] reported that ammonia in excess added to tetraborane (B_4H_{10}) at −75° in a 4 to 1 ratio to give a product which decomposed when warmed to room temperature. A variety of products including H_2 and NH_3 was recovered from the decomposition process.

Recent work in this laboratory has failed to confirm the existence of a tetraammoniate under a wide variety of conditions; however, a *stable crystalline* diammoniate ($B_4H_{10}\cdot 2NH_3$) has been isolated. The slow addition of ammonia to a cold (−78°) ether solution of B_4H_{10} gave complete ammonia absorption. An excess of B_4H_{10} was always used. After ammonia addition the system was aged for four days at −78° and for twelve hours at −45°. The solution was filtered on a vacuum line filter at −45° to remove a slight turbidity; then the ether was removed at −45° from the clear filtrate. The white solid which was left after removal of the ether was washed with cold dry benzene and transferred to a filter disc. It was then washed through the filter disc with dry ether. Removal of the solvent left a white, dry microcrystalline solid which was characterized as follows. *Anal.* N, 32.3; B, 49.4; H_2 124.3 mmoles/g. Theory for $B_4H_{10}\cdot 2NH_3$: N, 32.1; B, 49.5; H_2, 125.8 mmoles/g. based on the hydrolysis equation

$$B_4H_{10}\cdot 2NH_3 + 8H_2O + 2H^+ \longrightarrow 4HBO_2 + 2NH_4^+ + 11H_2$$

The molecular weight as determined by vapor pressure depression in liquid ammonia was 81. Theoretical for $B_4H_{10}\cdot 2NH_3$ is 87. Yields ran as high as 86% based on the NH_3 used or 78% based on the B_4H_{10} (slight excess used.)

The compound is stable in air and dissolves in cold water with only very slow hydrogen evolution. Acid or platinized platinum accelerates gas liberation. It is soluble in and can be recovered unchanged from perfectly dry ether but, if the compound has been exposed to moist air before solution, a precipitate slowly forms. It can be dissolved in and recovered unchanged from liquid ammonia.

A liquid ammonia solution of the compound reacts at −78° with sodium dissolved in liquid ammonia to give one half mole of H_2 per mole of $B_4H_{10}\cdot 2NH_3$ in less than 20 minutes. A significant yield of the recently described[2] compound NaB_3H_8 was recovered from the residue by leaching with diethyl ether. Identification was by X-ray powder pattern.

The diammoniate of tetraborane gives a definite X-ray powder pattern. Attempts to index it are being made in this laboratory. Additional chemical data on structure will be presented in a subsequent publication.

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(1) A. Stock, E. Wiberg and H. Martini, *Ber.*, **63**, 2927 (1930); A. Stock, E. Wiberg, H. Martini and A. Nicklas, *ibid.*, **65B**, 1711 (1932).

(2) W. Hough, S. J. Edwards and A. D. McElroy, THIS JOURNAL, **78**, 689 (1956).