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The Conversion of Tetrakis-(dimethylamino)-diboron to Bis-(dimethylamino)-borane and Tris-(dimethylamino)-borane by Thermal Decomposition[1]

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The recent ready availability of covalent boron–boron bonded compounds[2–4] has provided a convenient approach to a variety of diboron derivatives, and the present work was carried out as part of a study of the thermal stability of these materials. It now has been shown that thermal degradation of tetrakis-(dimethylamino)-diboron at 300° results in significant yields of bis-(dimethylamino)-borane, $[(CH_3)_2N]_2BH$, and tris-(dimethylamino)-borane, $B[N(CH_3)_2]_3$.

Tetrakis-(dimethylamino)-diboron is more thermally stable than most related diboron compounds. For example, diboron tetrachloride,[5] tetramethoxydiboron,[6] and tetraethoxydiboron[6] decompose at 0, 110, and 90°, respectively. Tetrakis-(dimethylamino)-diboron has been recovered in 98% yield after heating for 24 hr. at 200°. Heating in a hydrocarbon solvent for 90 hr. at 260° yielded only a trace of tris-(dimethylamino)-borane and no bis-(dimethylamino)-borane. Thermal treatment for 48 hr. at 285° in an evacuated glass container yielded significant quantities of both tris-(dimethylamino)-borane and bis-(dimethylamino)-borane.

Experimental

Thermal Treatment of Tetrakis-(dimethylamino)-diboron (a) at 300°.—Heating 7.994 g. (40.4 mmoles) of tetrakis-(dimethylamino)-diboron for 48 hr. in an evacuated glass tube at 300° yielded a mixture of 3.14 g. (31.4 mmoles) of bis-(dimethylamino)-borane, 2.36 g. (16.5 mmoles) of tris-(dimethylamino)-borane, 0.114 g. (7.14 mmoles) of methane, and 2.07 g. of a yellow-orange liquid residue. The volatile products were separated and identified using standard vacuum-line techniques. Bis-(dimethylamino)-borane was separated from tris-(dimethylamino)-borane by fractional condensation at −20° or in larger quantities by fractional distillation (b.p. 102–104°) in an atmosphere of dry nitrogen. The presence of methane, bis-(dimethylamino)-borane, and tris-(dimethylamino)-borane was confirmed by infrared absorption spectra, vapor pressures, molecular weights, as well as refractive index and boron analyses where applicable. The liquid yellow-orange residue which was recovered from the original ignition tube contained 13.9% boron and showed absorption at 4.03 μ in the infrared spectrum. The molecular weight of the residue was 268 as determined cryoscopically in benzene.

(b) **At 285°.**—Tetrakis-(dimethylamino)-diboron (7.92 g., 40.0 mmoles) was heated 48 hr. in an evacuated glass tube. Recovered products include 1.96 g. (19.6 mmoles) of bis-(dimethylamino)-borane and 1.73 g. (12.1 mmoles) of tris-(dimethylamino)-borane.

(c) **At 260°.**—A solution containing 42.5 g. of tetrakis-(dimethylamino)-diboron was heated 90 hr. at 260 to 300° in 500 ml. of Benol (white mineral oil). Fractional distillation at 40 mm. yielded a trace of tris-(dimethylamino)-borane; no bis-(dimethylamino)-borane was detected.

(d) **At 200°.**—Tetrakis-(dimethylamino)-diboron (7.023 g.) was heated 24 hr. at 150° and 24 hr. at 200° in an atmosphere of dry nitrogen. The recovered material (6.8674 g., 98%) was shown to be tetra-(dimethylamino)-diboron by its infrared spectrum, which was identical with that of a sample of pure compound.

Thermal Treatment of Tris-(dimethylamino)-borane at 285°.—A 94% recovery of tris-(dimethylamino)-borane was obtained after 7.88 g. was heated 48 hr. The residue (2% of the charge) contained 11.0% boron and 21.2% nitrogen and did not reduce silver nitrate, which indicated the absence of boron–hydrogen or boron–boron bonds.

Discussion

When one molar equivalent of tetrakis-(dimethylamino)-diboron was heated in an evacuated glass tube at 300° for 48 hr. these products were obtained

$$B_2[N(CH_3)_2]_4 \xrightarrow{300^\circ} 0.78[(CH_3)_2N]_2BH + 0.41B[N(CH_3)_2]_3 + 0.18CH_4$$

The composition of the observed volatile reaction products coupled with the analyses of the residue cannot be explained easily on the basis of a simple reaction mechanism. However, it has been shown that tris-(dimethylamino)-borane is thermally stable under conditions (285°) which result in extensive decomposition of tetrakis-(dimethylamino)-diboron and probably cannot be an intermediate in the reactions which lead to methane and bis-(dimethylamino)-borane.

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[2] R. J. Brotherton, A. L. McCloskey, L. L. Petterson, and H. Steinberg, *J. Am. Chem. Soc.*, **82**, 6242 (1960).

[3] H. Noth and W. Meister, *Chem. Ber.*, **94**, 509 (1961).

[4] H. Noth, P. Fritz, and W. Meister, *Angew. Chem.*, **73**, 762 (1961).

[5] G. Urry, T. Wartik, R. E. Moore, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **76**, 5293 (1954).

[6] R. J. Brotherton, A. L. McCloskey, J. L. Boone, and H. M. Manasevit, *ibid.*, **82**, 6245 (1960).

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Transesterification of Tetraalkoxydiborons

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Transesterification is a well known reaction of trialkoxyboranes,[1,2] but the behavior of related tetraalkoxydiborons with alcohols has not been described. Tetra-(amino)-diborons have been reported[3] to react with both water and alcohols to eliminate amine and produce tetrahydroxydiboron and tetraalkoxydiborons, respectively, as shown in eq. 1 and 2.

$$(R_2N)_2B\text{–}B(NR_2)_2 + 4H_2O \longrightarrow (HO)_2B\text{–}B(OH)_2 + 4R_2NH \quad (1)$$

$$(R_2N)_2B\text{–}B(NR_2)_2 + 4R'OH \longrightarrow (R'O)_2B\text{–}B(OR')_2 + 4R_2NH \quad (2)$$

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[1] H. Schiff, *Ann. Suppl.*, **5**, 154 (1867).

[2] M. H. Wuyts and A. Duquense, *Bull. soc. chim. Belges*, **48**, 77 (1939).

[3] H. Noth and W. Meister, *Chem. Ber.*, **94**, 509 (1961).