CONTRIBUTION FROM U. S. BORAX RESEARCH CORPORATION,
ANAHEIM, CALIFORNIA

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

BY L. L. PETTERSON AND R. J. BROTHERTON

Received September 21, 1962

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

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

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.

---

[1] The research reported in this document was supported by the Directorate of Materials & Processes (Materials Central), Aeronautical Systems Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, under Contracts AF 33(616)-5931 and AF 33(616)-7303.

[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).

CONTRIBUTION FROM U. S. BORAX RESEARCH CORPORATION,
ANAHEIM, CALIFORNIA

Transesterification of Tetraalkoxydiborons

BY H. C. NEWSOM AND R. J. BROTHERTON

Received September 22, 1962

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.

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

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

---

[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).

If the reactions of alcohols with tetraalkoxydiborons are similar to those of tetra-(amino)-diborons with hydroxylic reagents, transesterification should occur according to eq. 3.

$$(RO)_2B\text{–}B(OR)_2 + 4R'OH \longrightarrow (R'O)_2B\text{–}B(OR')_2 + 4ROH \quad (3)$$

However, the stability of boron–boron bonds under alcoholysis conditions has not been investigated thoroughly, and B–B cleavage to give trialkoxyboranes might be expected also. Hydrolysis data[4] on tetraalkoxydiborons do not give a clear basis for prediction of B–B bond stability in transesterification reactions: tetraethoxydiboron and tetraisopropoxydiboron reacted with water to give quantitative yields of tetrahydroxydiboron; tetramethoxydiboron underwent extensive B–B cleavage under similar conditions. In boron hydrides containing B–B bonds, reaction of tetraborane or pentaborane-9 with alcohol was reported[5] to give rapid cleavage of the B–B bonds in these molecules. Tetraalkoxydiboron intermediates were postulated in these reactions. Thus, some evidence exists which suggested that B–B cleavage and trialkoxyborane formation might occur in the reaction of tetraalkoxydiborons with alcohols (eq. 4 and 5).

It now has been shown that transesterifications of the type shown in eq. 3 can be carried out without apparent B–B cleavage.

Experimental

Conversion of Tetramethoxydiboron to Tetraisopropoxydiboron.—Tetramethoxydiboron (4.0 g., 0.0275 mole) was dissolved in 25 ml. of petroleum ether (b.p. 60–65°). Isopropyl alcohol (7.20 g., 0.120 mole) was added and the solution refluxed for 65 hr. Solvent and volatile materials then were removed by distillation at 30° (0.3 mm.), leaving 3.02 g. (42.7% yield) of residual tetraisopropoxydiboron, $n^{26}\text{D}$ 1.3971 [lit.[6] for $B_2(O\text{-}i\text{-}C_3H_7)_4$, $n^{25}\text{D}$ 1.3970]. The infrared spectrum was identical with an authentic sample prepared by published[6] procedures.

Anal. Calcd. for $B_2(O\text{-}i\text{-}C_3H_7)_4$, $C_{12}H_{28}B_2O_4$: B, 8.39. Found: B, 8.41.

Conversion of Tetramethoxydiboron to Tetraethoxydiboron (a).—Tetramethoxydiboron (4.0 g., 0.0275 mole) was dissolved in ethanol (10.12 g., 0.22 mole). The solution was distilled through a 3-in. Vigreux column, gradually reducing the pressure so that the last distillate was removed at 30° (2 mm.). The total distillation time was 1 hr.; the pot temperature varied from 35 to 45°. Tetraethoxydiboron, 3.50 g. (63% yield), remained as residue in the distillation flask, $n^{26}\text{D}$ 1.3953 [lit.[6] for $B_2(OC_2H_5)_4$, $n^{25}\text{D}$ 1.3960]. The infrared spectrum was identical with an authentic sample prepared by published[6] procedures.

Anal. Calcd. for $B_2(OC_2H_5)_4$, $C_8H_{20}B_2O_4$: B, 10.74. Found: B, 10.83.

(b).—Tetramethoxydiboron (0.7987 g., 5.49 mmoles) was condensed into a trap in a high vacuum system, and ethanol (9.97 g., 219.6 mmoles) condensed into the same trap at −196°. The trap was isolated from the system, warmed to 55–60° for 1 hr., then again cooled to −196°. No observable pressure of non-condensable gas was registered on the manometer. The temperature of the liquid then was raised to 0° and volatiles were removed. The residual liquid, 0.5695 g., showed no observable vapor pressure at 25° (pressure of tetramethoxydiboron at 25° = 7.2 mm.). Its infrared spectrum matched tetraethoxydiboron (51% yield), $n^{25}\text{D}$ 1.3950 [lit.[6] for $B_2(OC_2H_5)_4$, $n^{24}\text{D}$ 1.3960; for $B_2(OCH_3)_4$, $n^{26}\text{D}$ 1.3888].

Reaction of Tetramethoxydiboron with *t*-Butyl Alcohol.—Tetramethoxydiboron (3.802 g., 0.0261 mole) was added to *t*-butyl alcohol (16.14 g., 0.218 mole) which had been freshly distilled from calcium oxide. Low boiling constituents were removed by distillation through a short Vigreux column at 140 mm. The residue, 3.64 g., was distilled through a 20-cm. spiral wire column to give the following fractions: (A) 1.08 g. of clear liquid, b.p. 47–49° (4 mm.); (B) 0.90 g. of clear liquid, b.p. 47° (2 mm.); (C) white solid residue. Infrared spectra of the products showed no absorption in the 4–5 μ region. All fractions reduced silver nitrate solution.

Anal. Calcd. for $B_2(OCH_3)_4$, $C_4H_{12}B_2O_4$: B, 14.84; for $B_2(O\text{-}t\text{-}C_4H_9)_4$, $C_{16}H_{36}B_2O_4$: B, 6.89. Found: (A) B, 9.88; (B) B, 8.43; (C) B, 22.4.

Results and Discussion

Tetramethoxydiboron was converted to tetraethoxydiboron and to tetraisopropoxydiboron by transesterification with the appropriate alcohol, as shown in eq. 3. If some concomitant B–B cleavage occurred, an intermediate B–H compound would be formed, which might be expected to yield hydrogen under the reaction conditions[7] (1 hr. at 60°), according to eq. 4 and 5. The reaction of tetramethoxydiboron with ethanol therefore

$$(CH_3O)_2B\text{–}B(OCH_3)_2 + C_2H_5OH \longrightarrow (CH_3O)_2BOC_2H_5 + H\text{–}B(OCH_3)_2 \quad (4)$$

$$H\text{–}B(OC_2H_5)_2 + C_2H_5OH \longrightarrow (C_2H_5O)_3B + H_2 \quad (5)$$

was carried out under conditions which would allow detection of small quantities of hydrogen, but no trace could be found.

The absence of hydrogen formation during ethanolysis indicates complete retention of the B–B structure, even for the by-products, which presumably are mixed alkoxydiboron compounds. This is in contrast to the interpretations presented for tetraborane and pentaborane ethanolysis, and suggests that the B–B cleavage observed in those cases occurred somewhere along the reaction coördinate prior to complete substitution of the B–B units, and that tetraalkoxydiborons were not intermediates in the reaction.

Steric limitations in the transesterification reaction were demonstrated in the reaction of *t*-butyl alcohol with tetramethoxydiboron: no $B_2(O\text{-}t\text{-}C_4H_9)_4$ was obtained, although the products did retain B–B bonds. Presumably, mixed methoxy-*t*-butoxydiborons were produced.

---

[4] A. L. McCloskey, R. J. Brotherton, and J. L. Boone, *J. Am. Chem. Soc.*, **83**, 4750 (1961).

[5] I. Shapiro and H. G. Weiss, *J. Phys. Chem.*, **63**, 1319 (1959).

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

[7] Shapiro and Weiss (ref. 5) report the rate of formation of $B(OC_2H_5)_3$ from $HB(OC_2H_5)_2$ to be slow at room temperature.

CONTRIBUTION FROM U. S. BORAX RESEARCH CORPORATION,
ANAHEIM, CALIFORNIA

The Preparation of Some Unsymmetrical Tri-(amino)-boranes

BY R. J. BROTHERTON AND TRENT BUCKMAN

Received October 17, 1962

A variety of tri-(amino)-boranes derived from both