were effected by gas chromatography on a silicone-firebrick column at 190° using helium carrier gas. The chromatograph consisted of four completely resolved peaks. Retention times for the first and last peaks were identical with known samples of N-trimethylborazole and hexamethylborazole, respectively; intermediate peaks were assumed to represent the two unsymmetrical species. Relative peak areas were equated to weight %, a method which gave less than 5% error on known mixtures of N-trimethylborazole and hexamethylborazole. The reduction step produced >95% of theory on known mixtures of B-trichloro-N-trimethylborazole and hexamethylborazole. Reaction times were increased until duplicate values were obtained, indicating equilibrium (see Fig. 1 and 2). The results are listed in Tables I–III.

N-Trimethylborazole–Hexamethylborazole Exchange.—N-Trimethylborazole (2.668 g., 21.8 mmoles) and hexamethylborazole (1.429 g., 8.68 mmoles) were mixed in a drybox. Approximately 0.2-ml. samples of this mixture were placed in Pyrex ampoules, flushed with nitrogen, sealed under vacuum, and placed in an oil bath at 175°. The samples were withdrawn periodically, cooled, and opened under nitrogen. The liquid product mixtures were analyzed by gas chromatography as above. The results are listed in Table IV.

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CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY,
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Tris-(ethanolamineborane) Borate and Ethanolamineborane[1]

BY HENRY C. KELLY AND JOHN O. EDWARDS

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Tris-(ethanolamineborane) borate, prepared by the reaction of ethanolamine with diborane in tetrahydrofuran, is a crystalline, hygroscopic solid which decomposes with loss of hydridic hydrogen at room temperature. In the presence of hydroxylic materials, it is converted to ethanolamineborane, a colorless and viscous liquid which has a higher kinetic stability than the parent borate. Identification and structure determination of these products were based on analyses, properties, and B^{11} nuclear magnetic resonance spectra.

Introduction

This investigation of the ethanolamine–diborane system was undertaken as part of a study of the reactions of diborane with difunctional reagents. Results obtained in the ethylenediamine–diborane reaction have been described.[1,2] In connection with the synthesis and characterization of boron–hydrogen compounds, we were interested in the effect of a second functional group on the stability and properties of an amineborane function in the same molecule.

Under the conditions described here, the reaction of diborane with ethanolamine gives tris-(ethanolamineborane) borate. No dialkoxyborane, as obtained in the reaction of diborane with methanol,[3] or heterocyclic compounds were isolated. Recently, comparable results were reported by Miller[4,5] in the synthesis of borane addition compounds of two other aminoalkyl borates. Tris-(ethanolamineborane) borate is easily hydrolyzed to ethanolamineborane. The preparation and properties of this hydroxyalkylamineborane and its parent borate are described herein.

Experimental

Materials.—Ethanolamine (Eastman) was dried by azeotropic distillation with dry benzene and then distilled, b.p. 169–170°. Boron trifluoride ethyl ether complex (Eastman) was distilled *in vacuo*, b.p. 54° (25.5 mm.). Lithium aluminum hydride (95+% purity) was obtained from Metal Hydrides, Inc. Diethyl ether (Mallinckrodt, anhydrous) was used without treatment. Tetrahydrofuran (Matheson Co.) and 1,2-dimethoxyethane (Eastman) were boiled under reflux for several hours with lithium aluminum hydride and distilled using a Widmer column; tetrahydrofuran, b.p. 65.5°; 1,2-dimethoxyethane, b.p. 85°. Other organic compounds were purified by conventional techniques.

Apparatus.—Many manipulations were carried out using a "Stock type" vacuum apparatus.[6,7]

Preparation and Properties of Tris-(ethanolamineborane) Borate.—A total of 14.3 g. of 95% lithium aluminum hydride (13.6 g., 0.36 mole of pure $LiAlH_4$) was suspended in 500 ml. of diethyl ether and stirred under streaming nitrogen. To this suspension was added, dropwise, a solution of 115 g. (0.81 mole) of boron trifluoride etherate in 100 ml. of diethyl ether. The evolved diborane was passed through a condenser (−80°) and into a second vessel, cooled in ice water and containing 125 ml. of freshly distilled tetrahydrofuran. Exit gases were passed through a second condenser (−80°) and through moist acetone to destroy excess diborane. To the tetrahydrofuran–borane solution was added, dropwise, a solution consisting of 6.1 g. (0.10 mole) of ethanolamine diluted to 37 ml. with tetrahydrofuran concurrent with addition of the last two-thirds of the boron trifluoride etherate to the diborane generator. After completion of the addition of ethanolamine, the system was purged with dry nitrogen and maintained at 0° for 4.5 hr. During this time, some of the diethyl ether from the diborane generator was passed by entrainment in the stream of nitrogen into the tetrahydrofuran solution.

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Solvent and excess diborane were removed from a 25-ml. sample of solution by vacuum evaporation to give 0.25 g. of a white crystalline solid. *Anal.* Calcd. for $B(OCH_2CH_2NH_2BH_3)_3$: H (active), 3.90; B, 18.61; N, 18.07. Found: H (active), 3.89, 3.87; B, 18.68, 18.45; N, 17.55, 17.82; p*K* ethanolamine hydrochloride, 9.62, 9.60 (lit.[8] 9.44). An additional 7.0 g. of product was recovered from the remainder of the solution; total of yield, 7.25 g. (94% of theory based one thanolamine, assuming the stoichiometry of eq. 1).

$$3HOCH_2CH_2NH_2 + 2B_2H_6 \xrightarrow{THF} B(OCH_2CH_2NH_2BH_3)_3 + 3H_2 \quad (1)$$

The product decomposed with loss of hydridic hydrogen on standing at room temperature *in vacuo* or in tetrahydrofuran solution, but could be stored for several days at 0° *in vacuo* without significant decomposition.

When treated with water, tris-(ethanolamineborane) borate undergoes partial hydrolysis with evolution of hydrogen. Quantitative evolution of hydridic hydrogen occurs when the original borate, or the aqueous solution of partially hydrolyzed product, is treated with mineral acid, *e.g.*

$$B(OCH_2CH_2NH_2BH_3)_3 + 12H_2O + 3H^+ \longrightarrow 4B(OH)_3 + 3HOCH_2CH_2NH_3^+ + 9H_2 \quad (2)$$

After neutralization, the hydrolysate is titrated (using a Beckman Model GS pH meter) in the presence of mannitol to determine the boron content, and then to the ethanolammonium ion end point to determine amino nitrogen.

Preparation and Properties of Ethanolamineborane.—This compound has been prepared by hydrolysis of tris-(ethanolamineborane) borate in aqueous sodium hydroxide, in aqueous potassium hydroxide, in mixtures of water and triethylamine, and by solvolysis in methanol. Most favorable yields were obtained as described below.

A total of 3.65 g. of tris-(ethanolamineborane) borate [H (hydridic), 3.74; corresponding to 3.50 g. (1.50 mmoles) of pure borate] was added slowly at about 0° to a solution consisting of 2.05 g. (36.6 mmoles) of KOH pellets in 5 ml. of water. The mixture was agitated to dissolve solid matter. The clear solution evolved gas slowly on standing at 0°, evolution becoming more rapid as the system was warmed to 25°. A total of 5 ml. of tetrahydrofuran was added with stirring, resulting in the formation of two layers. The aqueous layer was washed five times with 5-ml. portions of fresh tetrahydrofuran, and the washings were combined with the original tetrahydrofuran layer. This solution then was dried over magnesium sulfate. After solids were removed by filtration, tetrahydrofuran was removed *in vacuo* to give 2.50 g. of a nearly colorless, slightly opaque oil. *Anal.* Calcd. for $HOCH_2CH_2NH_2BH_3$ (74.93): H (hydridic), 4.04; B, 14.44; N, 18.69. Found: H (hydridic), 4.00, 4.02; B, 14.15, 14.08; N, 18.32, 18.30; pK_a ethanolamine hydrochloride, 9.63, 9.63 (lit.[8] 9.44). The yield was 74% of theory based on 3.50 g. of tris-(ethanolamineborane) borate and assuming the stoichiometry

$$B(OCH_2CH_2NH_2BH_3)_3 + 3H_2O + OH^- \xrightarrow{H_2O} 3HOCH_2CH_2NH_2BH_3 + B(OH)_4^- \quad (3)$$

Hydridic hydrogen, boron, and nitrogen were determined by hydrolysis and subsequent titration of the hydrolysate as described for ethane 1,2-diamineborane[2] and tris-(ethanolamineborane) borate.

The product is easily supercooled to a viscous fluid but crystallization is promoted by stirring at low temperatures. A melting point of 19–20° was obtained from arrests in time *vs.* temperature curves. Evolution of hydrogen is observed on heating and rapid decomposition occurs above 60°. Ethanolamineborane is soluble in tetrahydrofuran, bis-(2-methoxyethyl) ether, 1,2-dimethoxyethane, and various hydroxylic solvents, *e.g.*, water, ethanol, methanol. No solubility was observed in diethyl ether, benzene, carbon tetrachloride, or 30–60° petroleum ether.

A 6.4-mmole sample of acetone reacted with 0.45 g. (6.1 mmoles) of ethanolamineborane *in vacuo* at 0–25°. Hydrolysis of the mixture gave a volatile product which was dried over magnesium sulfate and distilled *in vacuo* to give 4.6 mmoles (71% yield) of 2-propanol, identified by vapor tension.[9]

No reduction products were observed on treatment of ethanolamineborane with ethyl acetate, acetonitrile, 1-nitropropane, acetic anhydride, or acetamide.

B^{11} N.m.r. Spectra.—Samples of the amineboranes in 1,2-dimethoxyethane solution were contained in 5-mm. o.d. thin walled Pyrex tubes. Spectra were obtained on a Varian HR-60 n.m.r. spectrometer, Model V-4300B, at 19.25 Mc.

For tris-(ethanolamineborane) borate, two peaks in an intensity ratio of 3:1 were observed. The more intense peak, presumably corresponding to the $-BH_3$ boron signal, was found to be on the high field side of the less intense peak, which is attributed to boron in the borate linkage. Both peaks were broad, and the more intense peak could not be resolved into the 1:3:3:1 quadruplet expected for resolution of the $-BH_3$ boron signal.

For ethanolamineborane, a simple boron resonance line split into a quadruplet having peaks of relative intensity 1:3:3:1 was obtained.

Discussion

The evolution of small amounts of hydrogen from samples of tris-(ethanolamineborane) borate in water presumably arises from the initial rapid cleavage of the ester linkage[10,11] to give an acidic (boric acid) solution, a condition favorable for hydrolysis of the amineborane linkage (eq. 4–7).

$$B(OCH_2CH_2NH_2BH_3)_3 + 3H_2O \longrightarrow B(OH)_3 + 3HOCH_2CH_2NH_2BH_3 \quad (4)$$

$$B(OH)_3 + 2H_2O \rightleftharpoons H_3O^+ + B(OH)_4^- \quad (5)$$

$$HOCH_2CH_2NH_2BH_3 + 3H_2O \xrightarrow{H_3O^+} HOCH_2CH_2NH_2 + B(OH)_3 + 3H_2 \quad (6)$$

$$HOCH_2CH_2NH_2 + H_2O \rightleftharpoons HOCH_2CH_2NH_3^+ + OH^- \quad (7)$$

This scheme is supported by the production of ethanolamineborane on alkaline hydrolysis of tris-(ethanol amineborane) borate.

The fact that rapid evolution of all hydridic hydrogen occurs only on addition of aqueous acid indicates that the rate of hydrolysis of the amineborane linkage is pH dependent and decreases as the aqueous solution becomes alkaline. A pH dependence of hydrolysis rate is characteristic of most compounds containing boron–hydrogen bonds.[12–16]

Recently, Miller[4,5] has synthesized tris-(2-dimethyl-

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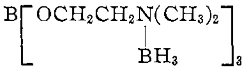
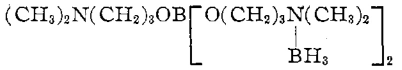
aminoethyl) borate triborane and tris-(3-dimethylaminopropyl) borate bisborane.



$$\mathrm{B}\left[\mathrm{OCH_2CH_2}\underset{\mathrm{BH_3}}{\overset{}{\mathrm{N}}}\mathrm{(CH_3)_2}\right]_3$$

I



$$\mathrm{(CH_3)_2N(CH_2)_3OB}\left[\mathrm{O(CH_2)_3}\underset{\mathrm{BH_3}}{\overset{}{\mathrm{N}}}\mathrm{(CH_3)_2}\right]_2$$

II

Aqueous solutions of I and II are fairly stable and evolve hydrogen only slowly on acidification. The greater hydrolytic stability of these compounds, relative to that of tris-(ethanolamineborane) borate, is presumed to be due to the nature of the products obtained on cleavage of the respective borate linkages. The hydrolytic stability of the tertiary amineboranes as compared to primary amineboranes is indicated.

Ethanolamineborane is similar to other amine boranes in its selectivity as a reducing agent. Below 40°, it is quite stable with respect to dehydrogenation, and, in addition, it is miscible with water. These properties enhance the potential use of the compound as a synthetic reagent. It is interesting that the amine-borane linkage is stable in the presence of the terminal hydroxy group. Thus, ethanolamineborane is a difunctional compound containing both "hydridic" ($-BH_3$), and, in a sense, "protonic" ($-OH$) hydrogen in the same molecule. Its stability suggests that the $\equiv N-BH_3$ linkage can be incorporated into a number of substrates containing various functional groups.

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CONTRIBUTION FROM U. S. BORAX RESEARCH CORPORATION,
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New Syntheses of Diboron Tetrafluoride

BY R. J. BROTHERTON, A. L. McCLOSKEY, AND H. M. MANASEVIT

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Diboron tetrafluoride has been prepared by the reactions of sulfur tetrafluoride with boron monoxide, tetrahydroxydiboron, or tetraethoxydiboron.

Introduction

Diboron tetrafluoride, B_2F_4, has previously been prepared in good yields by the fluorination of diboron tetrachloride with antimony trifluoride[1] and also with allyl fluoride.[2] It also has been postulated as a product from the reaction of boron trifluoride with bis-(diphenyl)-chromium.[3] The structure of the diboron tetrafluoride molecule in the solid state has been demonstrated by Trefonas and Lipscomb[4] using X-ray diffraction techniques, and several of its reactions have been investigated.[1,2,5] Diboron tetrafluoride is significantly more stable to thermal disproportionation than the analogous tetrachloride,[1] and consequently is more convenient to handle and purify. Diboron tetrafluoride has now been prepared by several new routes which do not involve diboron tetrachloride as a starting material.

Discussion

As noted above, diboron tetrafluoride can be prepared by the reaction of diboron tetrachloride and antimony trifluoride. However, the synthesis of large quantities of diboron tetrachloride by presently available methods is tedious, and this starting material is difficult to handle and store conveniently without decomposition. Consequently, a more direct method which does not involve diboron tetrachloride is desirable. Since diboron tetrachloride can be prepared by the reaction of boron trichloride with boron monoxide,[6] the analogous reaction of boron monoxide with boron trifluoride was investigated. However, none of the desired compound could be isolated when the reaction was attempted at 150–200°. The reactions of tetrakis-(dimethylamino)-diboron, $B_2[N(CH_3)_2]_4$,[7,8] with either boron trifluoride or sulfur tetrafluoride also did not lead to diboron tetrafluoride. However, diboron tetrafluoride can be prepared by the fluorination of boron monoxide, tetrahydroxydiboron, or tetraethoxydiboron with sulfur tetrafluoride.

Equation 1 represents the stoichiometry suggested by the reaction with boron monoxide, but the ratios of reactants and products shown have not been com-

$$2(BO)_n + 2nSF_4 \rightarrow nB_2F_4 + 2nSOF_2 \qquad (1)$$

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