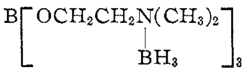
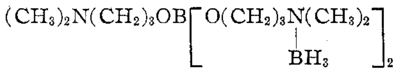
aminoethyl) borate triborane and tris-(3-dimethylaminopropyl) borate bisborane.



$$\mathrm{B}\Big[\mathrm{OCH_2CH_2}\underset{\mathrm{BH_3}}{\underset{|}{\mathrm{N}}}(\mathrm{CH_3})_2\Big]_3$$

I



$$(\mathrm{CH_3})_2\mathrm{N}(\mathrm{CH_2})_3\mathrm{OB}\Big[\mathrm{O}(\mathrm{CH_2})_3\underset{\mathrm{BH_3}}{\underset{|}{\mathrm{N}}}(\mathrm{CH_3})_2\Big]_2$$

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.

Acknowledgments.—The authors wish to thank Mr. Henry Klos of Brown University for the n.m.r. spectra and Dr. S. M. Nagy of M.I.T. for several analyses. The financial support of the U. S. Army Research Office (Durham) is gratefully acknowledged.

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

New Syntheses of Diboron Tetrafluoride

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

Received April 19, 1962

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-

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

---

[1] A. Finch and H. I. Schlesinger, *J. Am. Chem. Soc.*, **80**, 3573 (1958).

[2] P. Ceron, A. Finch, J. Frey, J. Kerrigan, T. Parsons, G. Urry, and H. I. Schlesinger, *ibid.*, **81**, 8368 (1959).

[3] F. Hein and K. Kartte, *Z. anorg. allgem. Chem.*, **307**, 89 (1960).

[4] L. Trefonas and W. N. Lipscomb, *J. Chem. Phys.*, **28**, 54 (1958).

[5] S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 176 (1961).

[6] A. L. McCloskey, J. L. Boone, and R. J. Brotherton, *J. Am. Chem. Soc.*, **83**, 1766, 4750 (1961).

[7] R. J. Brotherton, A. L. McCloskey, L. L. Petterson, and H. Steinberg, *ibid.*, **82**, 6242 (1960).

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

pletely established. The volatile products resulting from reaction at −80° included diboron tetrafluoride and a fraction consisting mainly of thionyl fluoride together with small amounts of silicon tetrafluoride (presumably from the reaction of sulfur tetrafluoride with the glass reaction tube). Warming to −23° or to room temperature resulted in additional diboron tetrafluoride and a mixture containing significant amounts of boron trifluoride and thionyl fluoride. It was very difficult to separate this mixture quantitatively and the precise amounts of each compound were not determined. The total yield of diboron tetrafluoride based on boron monoxide in eq. 1 was 50% of theoretical. Approximately the theoretical amount of thionyl fluoride was recovered. Boron trifluoride may have been produced by B—B bond cleavage during the reaction or possibly may have resulted from small amounts of B_2O_3 present in the boron monoxide used. Lower yields of diboron tetrafluoride (*ca.* 30%) were obtained from similar reactions of sulfur tetrafluoride with tetrahydroxydiboron or tetraethoxydiboron. Postulated reactions in these cases are shown in eq. 2, but these stoichiometries were not

$$B_2(OR)_4 + 4SF_4 \rightarrow B_2F_4 + 4SOF_2 + 4RF \qquad (2)$$
$$R = H, C_2H_5$$

completely verified. The amounts of thionyl fluoride produced in each case approached the theoretical quantity, and significant, but unknown, amounts of ethyl fluoride were isolated from the reaction of sulfur tetrafluoride with tetraethoxydiboron. However, no hydrogen fluoride was isolated from tetrahydroxydiboron, and moderate amounts of molecular hydrogen were evolved. Hydrogen may have resulted from cleavage of the boron–boron bond in diboron tetrafluoride by hydrogen fluoride or by similar cleavage of unreacted tetrahydroxydiboron. Once again quantitative separation of volatile products proved to be difficult. No attempt was made to identify the nonvolatile residues in these reactions.

In each of these reactions lower yields of diboron tetrafluoride were obtained when excess sulfur tetrafluoride was used. This is possibly a result of the apparent formation of a 1:1 adduct of diboron tetrafluoride with sulfur tetrafluoride, as shown in eq. 3. This adduct, which formed at −80°, decomposed slowly at room temperature. Boron trifluoride also

$$SF_4 + B_2F_4 \rightarrow SF_4 \cdot B_2F_4 \qquad (3)$$

forms a 1:1 adduct with sulfur tetrafluoride.[9,10] The boron trifluoride adduct can be sublimed, presumably without decomposition, at 80° and atmospheric pressure.[9] The diboron tetrafluoride adduct apparently decomposes slowly at room temperature, since boron trifluoride was formed. This may be a source of boron trifluoride in the reactions noted above.

Experimental

Standard vacuum line apparatus and techniques were used in all experiments. Technical grade sulfur tetrafluoride was obtained from the Organic Chemicals Department of E. I. du Pont de Nemours and Co., Inc., and used without further purification except that all gases which were not condensable at −196° were removed.

Diboron Tetrafluoride. (a) From Boron Monoxide.—Boron monoxide (3.82 mmoles calculated as B_2O_2) was prepared by the quantitative removal of water from 0.3422 g. (3.82 mmoles) of tetrahydroxydiboron[6,11] during 3.5 hr. at 275° under vacuum. Sulfur tetrafluoride (180 cc., 8.04 mmoles) was added and the mixture was cooled at −80° for 16 hr. before warming to room temperature. Examination of the infrared spectrum of the product mixture indicated that it contained no unreacted sulfur tetrafluoride. The volatile products were fractionally condensed in baths at −80, −119, and −196°. The bath at −119° contained 0.9 mmole of diboron tetrafluoride containing a trace of thionyl fluoride. The more volatile product (6.5 mmoles) from the −196° trap was shown to contain predominantly thionyl fluoride along with a small amount of silicon tetrafluoride. Warming the residual products to room temperature yielded an additional 1.0 mmole of diboron tetrafluoride and 3.3 mmoles of a mixture of thionyl fluoride and boron trifluoride. Diboron tetrafluoride (total yield 1.9 mmoles, 50% of theory) was identified by its vapor pressure of 16 mm. at −78° (lit.,[1] 15 mm. at −80.1°); its molecular weight, found, 100; calculated, 97.6; and its melting point, −60° (lit.[1] −55.4 to −56.4°). In addition, the infrared spectrum was identical with that reported by Barr and Wartik.[12]

(b) **From Tetrahydroxydiboron.**—Sulfur tetrafluoride (11.0 mmoles) was condensed on tetrahydroxydiboron[6] (2.61 mmoles) at −196° in a 50-ml. ampoule and the resulting mixture warmed to −80°. After holding this mixture for 4 days at −80°, the −196° non-condensables were removed; 10.1 mmoles of a mixture of silicon tetrafluoride and thionyl fluoride was obtained by distillation of the resulting volatile products from −78 and −112°. No sulfur tetrafluoride could be detected in these fractions. The white solid residue from the reaction at −80° was warmed to room temperature. Vigorous bubbling was observed during this warming procedure, and the solid began to liquefy. The −196° non-condensables (0.37 mmole) were removed, and the residue was held at 25° for 23 hr. Fractional condensation yielded 0.884 mmole (33.8% yield) of diboron tetrafluoride plus 1.16 mmoles of a mixture of boron trifluoride and thionyl fluoride and 0.31 mmole of hydrogen.

(c) **From Tetraethoxydiboron.**—Sulfur tetrafluoride (3.44 mmoles) was condensed on tetraethoxydiboron[13] (0.843 mmole) in a 70-ml. ampoule at −196° and the mixture warmed to −80°. After 17.5 hr. at −80°, the volatile products (4.28 mmoles) were fractionally condensed and shown by infrared spectral analysis to be a mixture of silicon tetrafluoride, thionyl fluoride, and ethyl fluoride. The residue from treatment at −80° was warmed to room temperature. Fractionation of the resulting volatile components gave 0.254 mmole (30.2% yield) of diboron tetrafluoride. A liquid [possibly $(C_2H_5O)_2BF$] with an apparent vapor pressure of 5 mm. at 25° and non-volatile at −80° also was isolated along with an unidentified liquid which was not volatile at room temperature.

Reaction of Diboron Tetrafluoride and Sulfur Tetrafluoride.—Sulfur tetrafluoride (1.28 mmoles) was condensed at −196° into a bulb containing diboron tetrafluoride (0.610 mmole) and the system held at −80° for approximately 30 min. Distillation from −80° yielded a 0.705–mmole mixture which was shown by infrared analysis to be predominantly unreacted sulfur tetrafluoride, which presumably was formed by reaction with the glass apparatus. This stoichiometry suggests the formation

---

[9] N. Bartlett and P. L. Robinson, *Chem. Ind.* (London), 1351 (1956).

[10] A. L. Oppegard, W. C. Smith, E. L. Muetterties, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 3835 (1960).

[11] T. Wartik and E. F. Apple, *ibid.*, **77**, 6400 (1955).

[12] J. B. Barr, Ph.D. Thesis, Pennsylvania State University, 1960.

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

of a 1:1 $B_2F_4 \cdot SF_4$ adduct at −80°. The vapor pressure of this adduct increased from approximately 90 mm. at 25° to 101 mm. at 25° after it was stored at room temperature for 1 hr. and 25 min. Analysis of the infrared spectrum of the products volatile at −80° showed the presence of boron trifluoride, diboron tetrafluoride, thionyl fluoride, and sulfur tetrafluoride. The residue was held at room temperature for an additional 64 hr. and then found to be completely volatile at −80°. Based on infrared data, compounds present in this mixture included boron trifluoride, thionyl fluoride, and silicon tetrafluoride. No thionyl fluoride or diboron tetrafluoride was evident in the gaseous products.

CONTRIBUTION NO. 793 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION,
E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE

Chemistry of Silane. I. Preparation of Silane

BY H. L. JACKSON, F. D. MARSH, AND E. L. MUETTERTIES

Received June 18, 1962

Silane has been synthesized directly in conversions up to 80% from silica and silicates by treatment with superatmospheric pressure hydrogen in the presence of aluminum and aluminum chloride. Evidence is presented for an aluminum chlorohydride intermediate

$$\mathrm{Al} + \mathrm{AlCl_3} \overset{H_2}{\rightleftarrows} \mathrm{AlH}_x\mathrm{Cl}_{3-x} \xrightarrow{SiO_2} \mathrm{SiH_4}$$

High yield synthesis of pure silane from silicon halides also has been achieved in similar reactions although aluminum chloride is not a critical reactant.

Synthesis from Silicon Oxides.—The low reactivity of silica toward hydrogen, at least below 1000°, is generally recognized since silica is a common catalyst support in hydrogenation of organic compounds. We have found, however, that silica and silicates are readily hydrogenated to silane in the presence of aluminum and aluminum halides. Conversions of 80% are obtained at 175° and 400 atm. pressure, and the purity of the silane is greater than 99%. Thus, this new reaction system constitutes an important new synthesis of silane.

Aluminum and hydrogen alone are not sufficient for the hydrogenation of silica at temperatures below 800°; an aluminum halide must be present for the over-all reaction

$$3\mathrm{SiO_2} + 4\mathrm{Al} + 2\mathrm{AlX_3} + 6\mathrm{H_2} \longrightarrow \frac{6}{n}[\mathrm{AlOX}]_n + 3\mathrm{SiH_4}$$

At atmospheric pressure, reaction rate is insignificant below 800°, and above 800° isolation of silane requires short contact times because of its thermal instability. Superatmospheric hydrogen pressure drastically reduces the temperature requirement. Thus, at 200°, silane conversion goes from 0% at 1 atm. to 10% at 100 atm. to 76% at 900 atm. Since the reaction is primarily heterogeneous, highest conversions are obtained with high-surface-area silicas, *e.g.*, silica gel and diatomaceous earth, and with vigorous agitation of the reaction medium.

The silane produced by this novel method is consistently of very high purity, >99%. Best results were obtained with aluminum chloride in the form of the aluminum chloride–sodium chloride eutectic (m.p. 120°). Mass spectrometric analysis of typical products showed the possible presence of hydrogen chloride and traces of SiH_3Cl (∼0.05%) and SiH_2Cl_2 (∼0.05%) as principal impurities in the silane. The origin of the chlorosilanes was not established; however, since $SiCl_4$ is not a reaction intermediate, *vide infra*, it is probable that the chlorosilanes were formed by the previously reported aluminum chloride-catalyzed chlorination of silane by hydrogen chloride.[1] At synthesis temperatures above 200°, trace amounts of disilane were detected in the product; the disilane probably was formed by thermal coupling of silane.[2]

Mechanism.—The reaction mechanism for this new silane synthesis has not been definitively characterized. However, the data point very strongly to a volatile aluminum chlorohydride intermediate. The following major points support this thesis:

(1) Silicon tetrachloride is not formed in the reaction of silica with aluminum and aluminum chloride, at, or even significantly above, the temperatures at which high silane conversions are obtained when hydrogen is added to this mixture. Even small equilibrium $SiCl_4$ concentrations are contraindicated since conditions under which the volatile $SiCl_4$ would be removed from the reaction zone did not yield detectable amounts.

(2) Silicon does not appear to be an intermediate since all attempts to hydrogenate silicon under conditions effective for silica were unsuccessful.

(3) A volatile hydride of aluminum is formed in small amounts in the high pressure reaction of Al, AlX_3, and H_2. This species was shown to convert silica to silane and to decompose thermally at 200° in an inert atmosphere to aluminum metal. The final, essentially conclusive proof for the alane intermediate was the formation of silane in a system in which silica was suspended above an aluminum–aluminum chloride–sodium

---

[1] A Stock and C. Sonieski, *Ber.*, **52**, 695 (1919).

[2] K. Stokland, *Kgl. Norske Videnskab. Selskab. Skrifter*, **3**, 1 (1948).