Reaction between I and maleic anhydride gave the adduct of bicyclo[4.2.0[octa-2,4-diene. Cope, *et al.*,[9] found that a mixture of the cycloöctatrienes reacted with maleic anhydride to give a *single* Diels–Alder adduct and that this adduct is that expected from the bicycloöctadiene. Furthermore, it was found that 1,3,6-cycloöctatriene is not converted into the 1,3,5-cycloöctatriene–bicycloöctadiene equilibrium mixture unless heated with strong base. These facts thus provide additional evidence that I is not 1,3,6-cycloöctatriene-iron tricarbonyl.

Degradation of I with triphenylphosphine to yield a 1,3,5-cycloöctatriene-bicycloöctadiene mixture, in agreement with pyrolysis experiments described earlier,[4b] also strongly suggests that the 1,3,6-cycloöctatriene group is not present in I, since triphenylphosphine would be too weak a base to isomerize 1,3,6-cycloöctatriene.

Preparation of I in 24% yield and II in 5% yield from 94% pure 1,3,5-cycloöctatriene again indicates that 1,3,6-cycloöctatriene is not involved in the complexes. However, yield data cannot provide conclusive evidence for the structure of I or II because certain hydrocarbons might isomerize in the presence of iron carbonyl. However, if isomerization of an unsaturated hydrocarbon in the presence of iron carbonyls were to occur, the isomer finally present in the iron complex probably would be the one most similar to butadiene, in view of the high stability of butadiene-iron tricarbonyl.[14a] Thus we have found that iron pentacarbonyl reacts with 1,4-pentadiene to give *trans*-1,3-pentadiene-iron tricarbonyl.[14b] Hence any isomerization of the three C_8H_{10} hydrocarbons by iron carbonyls, if it were to occur, should favor formation of bicyclo[4.2.0]octa-2,4-diene-iron tricarbonyl.

[CONTRIBUTION FROM U. S. BORAX RESEARCH CORPORATION, ANAHEIM, CALIF.]

Tetra-(amino)-diborons[1]

BY R. J. BROTHERTON, A. L. MCCLOSKEY, L. L. PETTERSON AND H. STEINBERG

RECEIVED JUNE 10, 1960

Tetra-(dimethylamino)-diboron has been prepared in high yields by the reaction of halo-bis-(dimethylamino)-boranes with highly dispersed molten sodium. This diboron compound is stable at 200° in the presence of dry air. Reactions of tetra-(dimethylamino)-diboron with primary and secondary amines have led to a variety of tetra-(amino)-diborons.

Introduction

Knowledge of the chemistry of boron compounds has accelerated rapidly in recent years, and a variety of new boron compounds have been prepared and studied. However, with the exception of certain boron hydrides, only a few examples of materials containing normal covalent boron-boron bonds have been reported. The over-all objective of the present investigation has been the preparation and characterization of such compounds, and the immediate objective has been the study of diboron compounds.

No system of nomenclature for diboron compounds has been generally accepted, and for this reason Urry, *et al.*,[2] have described diboron compounds by chemical formula only. However, the number and complexity of diboron derivatives which are now becoming available necessitates the use of some type of systematic nomenclature, and diboron compounds (except for the tetrahalo-derivatives) will be referred to as substituted diborons in this and in succeeding papers of this series. A suggested alternate method of nomenclature would refer to diboron compounds as derivatives of diborane-(4). Wartik, *et al.*,[3] originally suggested the name tetrachlorodiborine for B_2Cl_4 but subsequently used diboron tetrachloride, a type of nomenclature which has since become generally accepted for this compound and for other halide derivatives.

Diboron tetrachloride and its derivatives are the only reported examples of simple compounds containing boron–boron bonds. Diboron tetrachloride has been prepared by the electric discharge[2–5] and microwave[6] reductions of boron trichloride, and a number of its chemical reactions have been studied.[2,3,7–12] Several unsuccessful attempts to isolate compounds containing boron–boron bonds from reactions of haloboranes and active metals have been reported. Wiberg and Ruschmann[13] has observed that a reaction occurred between sodium and chlorodimethylborane, but boron–boron bonded materials could not be isolated. No reactions were reported in the attempted reductions of bromodiphenylborane[14] or trichloroborazole[15] with sodium, but bulk sodium was apparently used in these experiments. It has been observed in this Laboratory in many cases that bulk sodium is not sufficiently active to react with

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[1] The research reported in this document was supported by Wright Air Development Division of the U. S. Air Force under Contract AF 33(616)-5931. It was presented in part at the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960.

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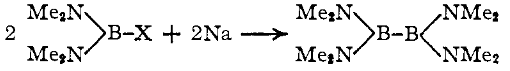
boron halides. Wiberg[16] reported that reduction of chlorodimethoxy- or chlorodiethoxyborane with sodium amalgam gave tetramethoxy- and tetraethoxydiborons. Attempts to repeat Wiberg's preparation of tetraethoxydiboron in this Laboratory have been unsuccessful.[17]

During the present investigation, a simple method has been developed for the preparation of tetra-(dimethylamino)-diboron from halo-bis-(dimethylamino)-boranes and active metals. The ready availability of tetra-(dimethylamino)-diboron has led to the preparation and study of a number of diboron compounds which will be described in this and in subsequent publications. The present paper describes the preparation of tetra-(dimethylamino)-diboron from halo-bis-(dimethylamino)-boranes and the conversion of tetra-(dimethylamino)-diboron to other tetra-(amino)-diborons by transamination reactions.

Results and Discussion

Tetra-(dimethylamino)-diboron (I) is the only reported example of a tetra-(amino)-diboron compound. This material was isolated[2] from the reaction of diboron tetrachloride and dimethylamine, but the only data given for the product obtained were its elemental analyses.

Tetra-(dimethylamino)-diboron now has been prepared conveniently in excellent yields by the reaction of highly-dispersed molten sodium with either chloro- or bromo-bis-(dimethylamino)-borane.



$$2\,(Me_2N)_2B\text{-}X + 2Na \longrightarrow (Me_2N)_2B\text{-}B(NMe_2)_2$$

X = Cl or Br I

The requisite haloboranes were obtained by the reaction of tris-(dimethylamino)-borane with the appropriate boron trihalide, a reaction analogous to that used for the preparation of dichloro-(dimethylamino)-borane.[18] Chloro-bis-(dimethylamino)-borane has been prepared previously[19,20] from dimethylamine and boron trichloride, but yields were not given. Bromo-bis-(dimethylamino)-borane has not been isolated previously in pure form, although Wiberg[21] obtained it and dibromo-(dimethylamino)-borane as components of a mixture. The reaction of highly-dispersed molten sodium with bromo-bis-(dimethylamino)-borane was faster than the comparable reaction with the chloroborane, but 80% yields of tetra-(dimethylamino)-diboron were obtained in either case. Of the other active reducing metals investigated, potassium dispersion and sodium-potassium alloy reacted with bromo-bis-(dimethylamino)-borane at lower temperatures than did sodium, but total conversions were lower, perhaps because of surface deactivation of these more reactive reducing metals by the reaction products. The synthesis of tetra-(dimethylamino)-diboron represents the first preparation and isolation of a pure, stable compound containing boron-boron bonds by the reaction of a haloborane and a reducing metal.

$$2B(NMe_2)_3 + BX_3 \longrightarrow 3(Me_2N)_2BX$$

Tetra-(dimethylamino)-diboron was found to be monomeric in benzene solution and gave one mole of hydrogen per mole of diboron compound when hydrolyzed in 10% sodium hydroxide. This result, which can be represented by the equation

$$B_2(NMe_2)_4 + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 4Me_2NH + H_2$$

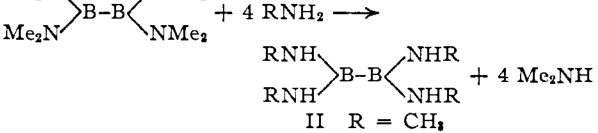
is comparable to that observed when diboron tetrachloride was hydrolyzed in basic solution.[2]

Tetra-(dimethylamino)-diboron was stable in the presence of dry air at 200°. It did not react with pure oxygen at 100° and was recovered essentially unchanged from a distillation at 195-208° under atmospheric conditions (except for the exclusion of water). These observations show that tetra-(dimethylamino)-diboron is significantly more stable than diboron tetrachloride which decomposes slowly at room temperature[2] and reacts rapidly with oxygen at $-78°$.[10]

The increased stability of tetra-(dimethylamino)-diboron compared to diboron tetrachloride can perhaps be related to the fact that the unshared electron-pairs on nitrogen can participate in pi-bonding with the vacant boron orbitals. In a similar case, diboron tetrafluoride was found to be more thermally stable[8] and to have a shorter boron-boron bond[22,23] than diboron tetrachloride, possibly because fluorine can participate in pi-bonding more effectively than chlorine in this type of system.

Tetra-(dimethylamino)-diboron is particularly adaptable to transamination reactions because of the volatility of dimethylamine. A recent investigation in these Laboratories[24] has shown the transamination reaction of simple tris-(amino)-boranes to be quite general with many types of primary and secondary amines, and this appears to be the case for diboron compounds as well. The major limiting factor appears to be the steric nature of the entering amine, and certain transaminations of tetra-(dimethylamino)-diboron with bulky amines have been unsuccessful for this reason.

Tetra-(methylamino)-diboron (II), tetra-(*n*-hexylamino)-diboron (III) and tetra-(anilino)-diboron (IV) have been prepared by the transamination of tetra-(dimethylamino)-diboron with the appropriate primary amine.



$$(Me_2N)_2B\text{-}B(NMe_2)_2 + 4\,RNH_2 \longrightarrow (RNH)_2B\text{-}B(NHR)_2 + 4\,Me_2NH$$

II $R = CH_3$
III $R = CH_2(CH_2)_4CH_3$
IV $R = C_6H_5$

The transmination of tetra-(dimethylamino)-diboron with *t*-butylamine was found to be ex-

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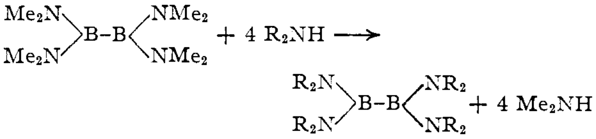
TABLE I

VAPOR PRESSURES OF $B_2(NMe_2)_4$

T, °C.	22.5	45.0	49.5	55.0	69.5	81.5	85.0	96.0	115.5	125.0	135.0
P, mm., obsd.	0.20	0.90	1.40	1.70	3.65	7.65	9.50	15.2	35.5	50.6	74.1
calcd.	0.20	0.97	1.30	1.67	3.82	7.22	8.73	14.5	35.3	51.8	75.7

ceedingly slow, and the comparable reaction of tris-(dimethylamino)-borane with t-butylamine gave a similar result. Construction of Fisher-Taylor-Hirschfelder models of tris-(dimethylamino)-borane and tetra-(dimethylamino)-diboron suggests that the close approach of t-butylamine to a boron atom is severely restricted in both cases.

The transamination of tetra-(dimethylamino)-diboron with di-n-butylamine gave tetra-(di-n-butylamino)-diboron (V). The transamination of tetra-(dimethylamino)-diboron with diphenylamine was very slow, and the transamination product, tetra-(diphenylamino)-diboron (VI), was difficult to purify.



V R = $CH_2(CH_2)_2CH_3$
VI R = C_6H_5

Experimental

Standard vacuum-line apparatus and techniques were used wherever high-vacuum operations were indicated. All experiments which were performed outside of the vacuum line were conducted in an atmosphere of dry, oxygen-free nitrogen. Microanalyses were done by Dr. Adelbert Elek, Los Angeles, California, and by Schwarzkopf Laboratories, Woodside, New York. Boron analyses were performed by a Parr bomb fusion method,[25] since diboron compounds are not easily hydrolyzed to boric acid by normal hydrolysis techniques.

Bromo-bis-(dimethylamino)-borane.—A solution of 188 g. (0.75 mole) of boron tribromide in 100 ml. of pentane was added over a period of 30 minutes to a vigorously-stirred solution of 215 g. (1.5 moles) of tris-(dimethylamino)-borane in 200 ml. of pentane at −50 to −40°. The pentane was removed by rapid distillation at 1.5 mm., and the residue was distilled to give 340.1 g. (84.5% yield) of bromo-bis-(dimethylamino)-borane, b.p. 20–28° (0.5 mm.).

Anal. Calcd. for $C_4H_{12}N_2BBr$: C, 26.82; H, 6.70; N, 15.65; B, 6.05; Br, 44.6. Found: C, 26.11; H, 6.96; N, 16.30; B, 6.19; Br, 43.5.

Chloro-bis-(dimethylamino)-borane.—A solution of 38.74 g. (0.27 mole) of tris-(dimethylamino)-borane in 40 ml. of pentane was added slowly with vigorous stirring to 15.78 g. (0.135 mole) of boron trichloride in 40 ml. of pentane at −70 to −50°. After a total addition time of 45 minutes, the reaction mixture was warmed to 0° and stirred for 1 hr. The pentane was removed by distillation at atmospheric pressure, and the residue was distilled at 25 mm. to give 42.15 g. (77% yield) of chloro-bis-(dimethylamino)-borane,[19,20] b.p. 50–52° (25 mm.), n^{24}D 1.4491.

Tetra-(dimethylamino)-diboron. (a) **From Bromo-bis-(dimethylamino)-borane.**—A solution of 532 g. (2.97 moles) of bromo-bis-(dimethylamino)-borane in 170 ml. of toluene was added slowly during a 45-minute period to highly-dispersed molten sodium (78.0 g., 3.39 moles) in 400 ml. of toluene at 110°. The reaction was continued for an additional 2.5 hr. at 110°, and the resulting solids were filtered. The toluene was removed from the filtrate by vacuum distillation and the residue distilled at 55–57° (2.5 mm.) to give 235.7 g. (80.5% yield) of tetra-(dimethylamino)-diboron, n^{22}D 1.4683. A mixture of unidentified halogen-containing products was also obtained in a higher boiling fraction.

Anal. Calcd. for $C_8H_{24}N_4B_2$: C, 48.55; H, 12.22; N, 28.31; B, 10.93; mol. wt., 197.9. Found: C, 48.40; H, 11.90; N, 28.20; B, 11.14; mol. wt., 194.1 (cryoscopic in benzene).

(b) **From Chloro-bis-(dimethylamino)-borane.**—Chloro-bis-(dimethylamino)-borane (970 g., 7.22 moles) was added slowly to 183 g. (7.94 g. atoms) of highly-dispersed molten sodium over a 2 hr. period at 125–150°. The mixture was stirred for an additional 30 minutes, the sodium chloride and unreacted sodium collected on a filter and the filtrate distilled to give 556 g. (78% yield) of tetra-(dimethylamino)-diboron.

(c) **Vapor Pressures.**—The vapor pressures of tetra-(dimethylamino)-diboron were measured in a high-vacuum line over the range 0–135°. The data may be expressed by the equation

$$\log P_{\text{mm.}} = \frac{-2759.6}{T} + 8.6405$$

The results over the temperature range 22.5–135.0° are given in Table I. These values imply a heat of vaporization of 12.6 kcal./mole over the temperature range 22.5 to 135°, a Trouton constant of 26.3, and an extrapolated boiling point of 206° at 760 mm.

(d) **Basic Hydrolysis.**—Tetra-(dimethylamino)-diboron (0.1970 g., 0.997 mmole) was heated in a sealed ampoule with 5 ml. of 10% sodium hydroxide for 19 hr. at 115° to give 21.0 cc. (0.938 mmole) of hydrogen.

(e) **Distillation at Atmospheric Pressure.**—Tetra-(dimethylamino)-diboron (12.67 g.) was distilled at 195–208° (pot temperature = 225°) under atmospheric conditions except that moisture was excluded from the apparatus. Volatile products were passed through a −80° trap and into a solution of standard hydrochloric acid. When the distillation was complete, the −80° trap was warmed to room temperature and the volatile components also passed through the standard acid. Titration of the standard acid with sodium hydroxide showed that no volatile amines were produced during the distillation. The total recovery of 11.68 g. of distillate remaining in the −80° trap and 0.98 g. of residue in the distillation flask represents 99.8 wt. % of the starting material. The following analytical results show that this distillate was essentially pure starting material, while the refractive index and the nitrogen and boron contents of the residue were slightly low.

	$B_2(NMe_2)_4$	Dist.	Residue
n^{24}D	1.4679	1.4678	1.4662
Boron, wt. %	11.1	11.0	10.5
Nitrogen, wt. %	28.2	27.9	25.8

The infrared spectrum of the distillate corresponded exactly to that of pure tetra-(dimethylamino)-diboron, but the spectrum of the residue was significantly different at wave lengths greater than 11 μ.

The Attempted Reaction of Tetra-(dimethylamino)-diboron with Oxygen.—An excess of dry oxygen was added to one ml. of tetra-(dimethylamino)-diboron in a high-vacuum line at a total oxygen pressure of 67 mm. After the mixture was heated at 100° for 1 hr., it was cooled to room temperature, and the oxygen was removed. There was no net change in the vapor pressure of the starting material. The same result was observed with tetra-(dimethylamino)-diboron in the presence of 186 mm. of oxygen.

Tetra-(methylamino)-diboron.—Methylamine (39.0 g., 1256 mmoles) was distilled from lithium into tetra-(dimethylamino)-diboron (16.0 g., 80.8 mmoles) contained in a heavy-walled glass bomb at −80°. The bomb was sealed and heated for 140 hr. at 75 ± 5°. Excess methylamine and dimethylamine were removed rapidly by distillation at reduced pressure and the residue distilled at 25° (0.5 mm.) to give 9.27 g. (80.8% yield) of colorless tetra-(methylamino)-diboron.

Anal. Calcd. for $C_4H_{16}N_4B_2$: C, 33.80; H, 11.36; N, 39.5; B, 15.3; mol. wt., 142. Found: C, 35.02; H, 11.24; N, 38.6; B, 15.4; mol. wt., 135 (cryoscopic in benzene).

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Tetra-(*n*-hexylamino)-diboron.—Tetra-(dimethylamino)-diboron (4.00 g., 20.21 mmoles) and *n*-hexylamine (8.17 g., 80.8 mmoles) which had been distilled from calcium hydride were heated from 24 to 115° for 3.2 hr. The displaced dimethylamine (101.8% of theor.) was entrained in a stream of dry nitrogen and trapped in aqueous hydrochloric acid. The residual material was dried under vacuum to give 7.78 g. (91% yield) of tetra-(*n*-hexylamino)-diboron as a colorless, non-volatile liquid, $n^{25}\text{D}$ 1.4606.

Anal. Calcd. for $C_{24}H_{56}N_4B_2$: C, 68.30; H, 13.38; N; 13.23; B, 5.11. Found: C, 67.44; H, 14.00; N, 13.15, B, 5.28.

Tetra-(di-*n*-butylamino)-diboron.—A solution of 5.0 g. (0.025 mole) of tetra-(dimethylamino)-diboron and 13.04 g. (0.101 mole) of di-*n*-butylamine (previously distilled from calcium hydride) in 25 ml. of hexane was heated from 76 to 174° for 21.6 hr. The resulting dimethylamine (96% yield) was swept into standard hydrochloric acid in a stream of dry nitrogen. Solvent and unreacted starting material were removed by distillation at 0.1–0.5 mm., and the residue was distilled to give 12.6 g. (93.4% yield) of tetra-(di-*n*-butylamino)-diboron, b.p. 170–183° (0.55 mm.), $n^{25}\text{D}$ 1.4667.

Anal. Calcd. for $C_{32}H_{72}N_4B_2$: C, 71.77; H, 13.57; N, 10.48; B, 4.05; mol. wt., 535. Found: C, 71.14; H, 13.10; N, 10.35; B, 4.37; mol. wt., 557 (cryoscopic in benzene).

Tetra-(anilino)-diboron.—A solution of 18.8 g. (202 mmoles) of aniline which previously had been distilled from calcium hydride and 10.0 g. (50.5 mmoles) of tetra-(dimethylamino)-diboron in 300 ml. of benzene was heated for 130 hr. at 81–82°. The theoretical amount of dimethylamine was removed continuously in a stream of dry nitrogen and trapped in standard hydrochloric acid. The reaction mixture was filtered and the solid product dried under vacuum to give 15.0 g. (76.0% yield) of tetra-(anilino)-diboron.

Anal. Calcd. for $C_{24}H_{24}N_4B_2$: C, 73.89; H, 6.20; N, 14.36; B, 5.57. Found: C, 73.84; H, 6.30; N, 14.50; B, 5.51.

Tetra-(anilino)-diboron melted over the range 181–200° with apparent decomposition. It was soluble in aniline, acetonitrile, dioxane and dimethylformamide and insoluble in benzene and diethyl ether.

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

The Preparation and Properties of Some Tetraalkoxydiborons[1]

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

RECEIVED JULY 12, 1960

Several tetraalkoxydiborons and tetraphenoxydiboron have been prepared by the reactions of tetra-(dimethylamino)-diboron with alcohols or phenol in the presence of hydrogen chloride. Tetramethoxy and tetraethoxydiboron were found to be significantly more stable than reported previously.

Introduction

Two examples of tetraalkoxydiboron compounds have been described previously. Wiberg and Ruschmann[2] reportedly prepared tetramethoxy- and tetraethoxydiborons by the reactions of the corresponding chlorodialkoxyboranes with sodium amalgam. Schlesinger, *et al.*,[3] prepared the same diboron compounds by the reactions of diboron tetrachloride with methanol and ethanol. However, Wiberg and Schlesinger fail to agree on the physical properties and stabilities of tetramethoxy- and tetraethoxydiborons. In addition, Wiberg claimed that these materials decomposed to give elemental boron at low temperatures, an observation which was not confirmed by Schlesinger. In a related reaction chlorodi-(isoamyloxy)-borane was added to sodium,[4] but tri-(isoamyloxy)-borane was the only product isolated.

Several tetraalkoxydiborons have now been prepared from tetra-(dimethylamino)-diboron[5] and found to be significantly more stable than anticipated from the results of previous workers, and no elemental boron was isolated among the decomposition products as suggested by Wiberg.[2]

Discussion of Results

Tetraethoxydiboron could not be isolated from the reactions of chlorodiethoxyborane either with sodium amalgam in petroleum ether or with highly dispersed sodium in various solvents. The chloroborane appeared to react with sodium in some cases, but tetraethoxydiboron was not isolated, perhaps because of its instability under conditions necessary for reaction. There is no apparent explanation for the failure to obtain tetraethoxydiboron from chlorodiethoxyborane and sodium amalgam, a result which is in direct contrast with Wiberg's[2] preparations of materials reported to be tetramethoxy- and tetraethoxydiboron by this reaction using chlorodimethoxy- and chlorodiethoxyboranes with sodium amalgam. No reaction was observed between chlorodiethoxyborane and highly dispersed sodium in refluxing diethyl ether, but chlorodiethoxyborane reacted with tetrahydrofuran when it was used as a solvent for the sodium reaction.

This reaction, which is analogous to that of boron trichloride with tetrahydrofuran,[6] is surprising, since Brown and Tierney[7] found that chlorodimethoxyborane did not react with diglyme under similar conditions. The results of this cleavage reaction are summarized in Table I.

Since the related tetra-(amino)-diboron compounds recently have become readily available,[5] their conversion to tetraalkoxydiborons was investigated. The displacement of dimethylamine

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[1] A portion of the research reported in this document was supported by Wright Air Development Division of the U. S. Air Force under Contract AF 33(616)-5931. It was presented in part at the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960.

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