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The Preparation and Properties of 1,2-Diethyl-1,2-bis-(dimethylamino)- and 1,2-Bis-(dimethylamino)-1,2-diphenyldiborons[1,2]

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1,2-Diethyl-1,2-bis-(dimethylamino)- and 1,2-bis-(dimethylamino)-1,2 diphenyldiborons have been prepared from the appropriate chloroboranes and sodium and found to be stable to temperatures over 100°. The boron–boron bonds in these derivatives are more susceptible to cleavage by a variety of chemical reagents than are those in the related tetra-(amino)-diborons.

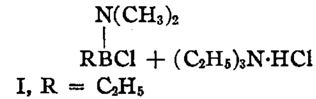
Introduction

Stock[3] prepared the first diboron compound, diboron tetrachloride, B_2Cl_4, in 1925 and found it to be unstable at room temperature and above. Subsequently it has been observed that diboron compounds with substituent groups which can effectively release electrons are significantly more stable. For example, tetra-(dimethylamino)-diboron, $B_2[N(CH_3)_2]_4$, is stable to at least 200°[4] and tetraalkoxydiborons up to 100° and above.[5] Several reported attempts to prepare tetraalkyldiborons have been unsuccessful.[6,7] In some cases the desired tetraalkyldiborons apparently formed but decomposed immediately to trialkylboranes. This instability has been attributed to the inability of alkyl substituents to effectively satisfy the electron-deficient boron atoms; the related boron hydride, B_2H_4, is expected to be unstable for the same reason. Diboron compounds containing both dialkylamino and alkyl or aryl substituents now have been prepared and shown to have thermal stabilities intermediate between tetra-(amino)-diborons and the postulated tetraalkyldiborons. A number of reactions of mixed diboron compounds have been studied, and it appears that the boron–boron bonds in these derivatives are much more susceptible to attack by a variety of chemical reagents than the boron–boron bonds in related tetra-(amino)-diborons.

Results and Discussion

As an initial approach to the preparation of the desired mixed diboron compounds, the reactions of alkyl and aryl-(dimethylamino)-haloboranes with sodium were studied. At the time, the only reported example of an alkyl or aryl-(dimethylamino)-haloborane was chloro-(dimethylamino)-methylborane, $CH_3B(Cl)N(CH_3)_2$, which had been prepared by a sealed tube reaction between dimethyl-(dimethylamino)-borane, $(CH_3)_2BN(CH_3)_2$ and dichloro-(dimethylamino)-borane, $Cl_2BN(CH_3)_2$.[8] When this reaction was repeated, small amounts of chloro-(dimethylamino)-methylborane were obtained, but the method proved to be impractical except on a very small scale. Consequently an improved general procedure for the preparation of alkyl and aryl-(dialkylamino)-haloboranes was developed. By this method chloro-(dimethylamino)-ethylborane (I) and chloro-(dimethylamino-phenylborane (II) have been prepared in good yields. The first step (eq. 1) is the probable formation of an amine adduct of the alkyl or aryldihaloborane. Addition of a tertiary amine leads to the amino hydrochloride and the desired compounds (eq. 2). Preparation of these materials by the same general synthetic scheme has been described

$$RBCl_2 + (CH_3)_2NH \longrightarrow RBCl_2 \cdot HN(CH_3)_2 \qquad (1)$$



$$RBCl_2 \cdot HN(CH_3)_2 + (C_2H_5)_3N \longrightarrow \overset{\displaystyle N(CH_3)_2}{\overset{|}{R B Cl}} + (C_2H_5)_3N \cdot HCl \qquad (2)$$

I, $R = C_2H_5$
II, $R = C_6H_5$

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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 contracts AF 33 (616)-5931 and 7303.

[2] This work was described originally in WADD Technical Report 60-911, "Research on Inorganic Polymer Systems," January, 1961.

[3] A. Stock, A. Brandt, and H. Fischer, *Ber.*, **58**, 643 (1925).

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

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

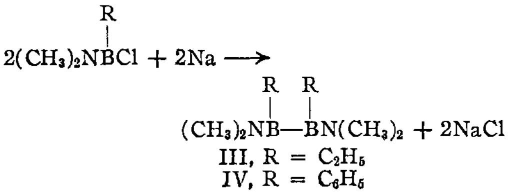
[6] G. Urry, T. Wartik, R. E. Moore, and H. I. Schlesinger, *ibid.*, **76**, 5293 (1954).

[7] E. Wiberg and W. Ruschmann, *Ber.*, **70**, 1583 (1937).

[8] C. E. Erickson and F. C. Gunderloy, Jr., Abstracts of Papers presented at the 136th National Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1959, p. 54-N.

recently independently by Niedenzu and Dawson.[9] Noth and Fritz[10] have prepared these mixed compounds by an alternative route. Both I and II are colorless liquids which do not ignite in air and are monomeric in the vapor state. Reactions of I and II with molten sodium yielded the desired mixed diboron compounds as shown in eq. 3. This reaction is analogous to the method which has been used to prepare tetra-(amino)-diborons from bis-(dialkylamino)-haloboranes.[4,11]

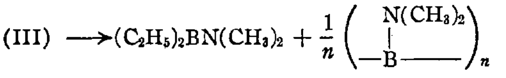
1,2-Diethyl-1,2-bis-(dimethylamino)-diboron (III) is a mobile colorless liquid which is monomeric in the vapor state. 1,2-Bis-(dimethylamino)-1,2-diphenyldiboron (IV) is a white crystalline solid melting at 101–103°. Noth and Fritz[9 10] have described comparable preparative reactions in their recent independent study but reported that III was unstable.



$$2(CH_3)_2NB(R)Cl + 2Na \longrightarrow (CH_3)_2NB(R)\text{—}B(R)N(CH_3)_2 + 2NaCl \quad (3)$$

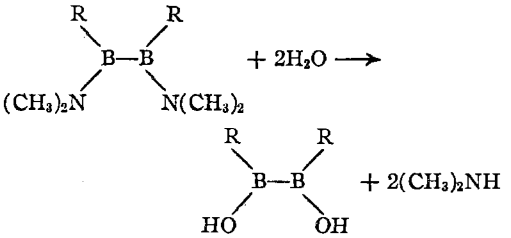
III, $R = C_2H_5$
IV, $R = C_6H_5$

Both III and IV showed good stability; the diethyl derivative (III) was stable to about 140° and yielded about 0.3 molar equivalent of diethyl-(dimethylamino)-borane, $(C_2H_5)_2BN(CH_3)_2$, when heated for 21 hr. at 200°. Heating III for 137 hr. at 300° yielded 0.13 molar equivalent of hydrogen, 0.12 molar equivalent of ethane, and a significant amount of $(C_2H_5)_2BN(CH_3)_2$. It appears that decomposition is very slow at 200° and probably proceeds by disproportionation as shown in eq. 4; the proposed amino boron polymer was not isolated. At 300° decomposition is more complex. The thermal stability of the diphenyl derivative (IV) was not studied in detail, but it appeared to be stable at least up to its melting point (101–103°). The stabilities of these diboron compounds appear to be intermediate between diboron tetrachloride, which is unstable at room temperature[6], and tetra-(dimethylamino)-diboron, which is stable to at least 200°.[4]



$$\text{(III)} \longrightarrow (C_2H_5)_2BN(CH_3)_2 + \frac{1}{n}\left(\overset{N(CH_3)_2}{\overset{|}{\text{—}B\text{—}}}\right)_n \quad (4)$$

Neutral hydrolysis of 1,2-diethyl-1,2-bis-(dimethylamino)-diboron and 1,2-bis-(dimethylamino)-1,2-diphenyldiboron might be expected to occur by displacement of the dimethylamino groups as shown in eq. 5. This is based on the earlier observations that tetra-(dimethylamino)-diboron hydrolyzes without cleavage of the boron–boron bond[12] and that the boron–carbon bond in other alkyl and arylboron derivatives is relatively stable to hydrolysis. However, addition of III to water resulted in the evolution of approximately one molar equivalent of hydrogen and cleavage of the boron–boron bond. The residual products always retained some dimethylamino groups. When the phenyl derivative (IV) was added to water or to aqueous hydrochloric acid, starting material was recovered unchanged. Tetra-(dimethylamino)-diboron is readily hydrolyzed to tetrahydroxydiboron under comparable conditions in aqueous acid.[12] When homogeneous hydrolysis was carried out in tetrahydrofuran–hydrochloric acid, cleavage of the boron–boron bond occurred with the production of benzeneboronic acid as shown in eq. 6.



(5)

$$IV + 4H_2O + 2HCl \longrightarrow$$
$$2C_6H_5B(OH)_2 + 2(CH_3)_2NH{\cdot}HCl + H_2 \quad (6)$$

The related reactions of III with methanol also led to cleavage of the boron–boron bond with the formation of hydrogen and dimethoxyethylborane as shown. The addition of methanol to the di-(hydrogen chloride) adduct of III gave comparable results. Hydrogen also was obtained when ethanol was added to III or its hydrogen chloride adduct, but the cleavage reaction was significantly slower than those observed with water or methanol. In this case diethoxyethylborane, $C_2H_5B(OC_2H_5)_2$, was identified as one of the reaction products. No cleavage was observed previously when alcohols were added to tetra-(dimethylamino)-diboron, with or without added hydrogen chloride.[4]

$$III + 4ROH \longrightarrow$$
$$2C_2H_5B(OR)_2 + 2(CH_3)_2NH + H_2 \quad (7)$$
$$R = CH_3,\ C_2H_5$$

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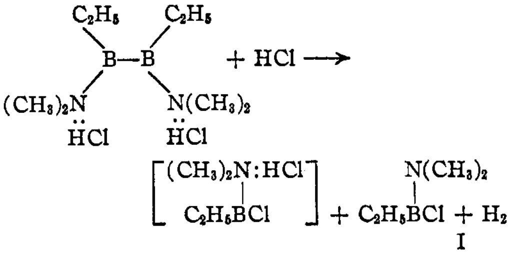
(9) K. Niedenzu and J. W. Dawson, *J. Am. Chem. Soc.*, **82**, 4223 (1960).

(10) H. Noth and P. Fritz, *Angew. Chem.*, **73**, 408 (1961).

(11) H. Noth and W. Meister, *Chem. Ber.*, **94**, 509 (1961).

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

When anhydrous hydrogen chloride was added to III in a 2/1 molar ratio the solid adduct $(C_2H_5)_2B_2[N(CH_3)_2]_2\cdot 2HCl$ formed. This material was stable below room temperature but decomposed at room temperature and above in the presence of one additional molar equivalent of hydrogen chloride. Products included approximately 80% of the theoretical hydrogen which would be obtained by complete cleavage of the boron–boron bond and significant amounts of a material which appears to be chloro-(dimethylamino)-ethylborane (I), as shown in eq. 8. This reaction illustrates once again the reactive nature of the boron–boron bond in this mixed alkylamino system. Boron–boron bond cleavage was not observed previously when excess hydrogen chloride was added to diboron tetrachloride[13] or tetraethoxydiboron.[5]


(8)

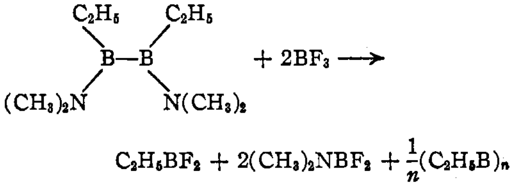
Transamination reactions of tetra-(dimethylamino)-diboron have been used to prepare a variety of aminodiborons.[4] Transamination of III with either di-*n*-propyl or di-*n*-butylamine was extremely slow, and pure products were not obtained in either case.

1,2-Diethyl-1,2-bis-(dimethylamino)-diboron (III) did not react with oxygen at room temperature, but oxygen consumption became apparent at 60° and above. The products of the oxygen reaction were not isolated, but it is probable that it proceeded through the same type of oxygen addition which was postulated previously.[5] The reactivity of diboron compounds with oxygen is illustrated by the following order of increasing reactivity. This order is comparable to that observed for thermal stability of diboron compounds,

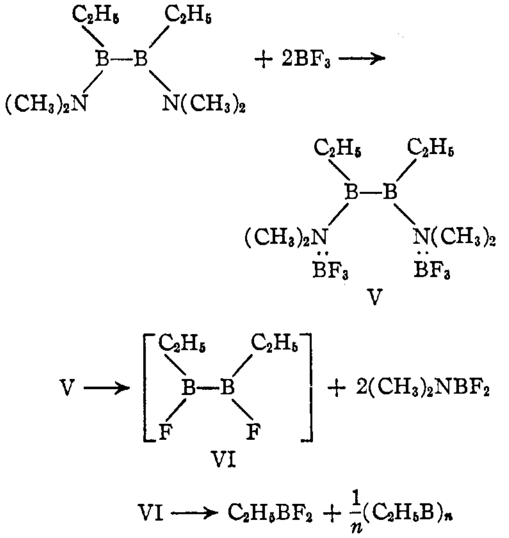
$$B_2[N(CH_3)_2]_4 < B_2R_2[N(CH_3)_2]_2 < B_2(OR)_4 < B_2Cl_4$$

and once again reactivity decreases approximately with the availability of electrons on the boron-bonded atoms of the substituent groups.

Products identified from the reaction of III with an equimolar amount of boron trifluoride included difluoroethylborane, $C_2H_5BF_2$, and possibly ethyl-(dimethylamino)-fluoroborane, $(CH_3)_2NB(F)C_2H_5$. The reaction of a 2/1 molar ratio of BF_3 to III yielded one mole of difluoroethylborane and approximately two moles of difluoro-(dimethylamino)-borane, $(CH_3)_2NBF_2$. The over-all stoichiometry which was followed in this reaction with two moles of boron trifluoride can be represented by eq. 9. The residual material which is represented as a polymer of composition $(C_2H_5B)_n$ on the basis of its empirical formula (calculated by difference) was a yellow viscous liquid which had no appreciable vapor pressure at 126°. The mechanism of the over-all reaction given above has not been determined, but one possible sequence involves formation of a di-(boron fluoride) addition product (V) followed by exchange of fluoro and dimethylamino groups to give 1,2-diethyl-1-2-difluorodiboron (VI), which can disproportionate as shown in eq. 12 to give $(C_2H_5B)_n$ and $C_2H_5BF_2$. There are many known examples of the type of halogen–amine exchange proposed in eq. 11; for example, the preparations of chloro- and bromo-bis-(dimethylamino)-boranes from tris-(dimethylamino)-borane and the boron trihalides.[4] The proposed disproportionation of $(C_2H_5)_2B_2F_2$ is related to the disproportionation reactions observed with the diboron tetrahalides, which give boron trihalides and haloboron polymers $(BX)_n$.[6]



$$C_2H_5BF_2 + 2(CH_3)_2NBF_2 + \frac{1}{n}(C_2H_5B)_n \qquad (9)$$


(10)

(11)

$$VI \longrightarrow C_2H_5BF_2 + \frac{1}{n}(C_2H_5B)_n \qquad (12)$$

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(13) T. Wartik and E. F. Apple, *J. Am. Chem. Soc.*, **80**, 6155 1958).

Experimental

Standard vacuum-line apparatus and techniques were used wherever high-vacuum operations are 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. Boron analyses were performed by a Parr bomb fusion method.[14]

Chloro-(dimethylamino)-ethylborane (I).—Dimethylamine (19.04 g., 0.42 mole) was added slowly with stirring to 46.8 g. (0.42 mole) of ethyldichloroborane in 300 ml. of pentane at −78°. The reaction mixture was warmed to room temperature, 42.7 g. (0.42 mole) of triethylamine added, and the mixture stirred overnight. The resulting amine hydrochloride was collected on a filter, and the solvent was removed by distillation of the filtrate at reduced pressure. Distillation of the residue gave 32.30 g. (64% yield) of chloro-(dimethylamino)-ethylborane, b.p. 20° (1 mm.).

Anal. Calcd. for $C_4H_{11}BClN$: C, 40.3; H, 9.03; N, 11.74; B, 9.08; mol. wt., 119. Found: C, 41.6; H, 9.30; N, 11.50; B, 8.90; mol. wt., 119 (gas density method).

1,2-Diethyl-1,2-bis-(dimethylamino)-diboron (III).—A solution of 30.67 g. (0.26 mole) of chloro-(dimethylamino)-ethylborane in 50 ml. of high-boiling mineral oil was added at room temperature to a dispersion of 8.0 g. (0.35 mole) of sodium in 350 ml. of mineral oil. The mixture was heated with vigorous stirring to 125° and stirred for 5 hr. at this temperature. The solids were removed by filtration and the filtrate distilled to give 10.0 g. (46% yield) of 1,2-diethyl-1,2-bis-(dimethylamino)-diboron, b.p. 70–73° (8 mm.), $n^{24}\mathrm{D}$ 1.4440.

Anal. Calcd. for $C_8H_{22}B_2N_2$: B, 12.9; C, 57.2; H, 13.1; N, 16.7; mol. wt., 168. Found: B, 12.7; C, 56.7; H, 13.3; N, 16.7; mol. wt., 167 (gas density method).

Chloro-(dimethylamino)-phenylborane (II).—Dimethylamine (9.99 g., 0.22 mole) was added slowly to a solution of 35.30 g. (0.22 mole) of phenyldichloroborane in 250 ml. of pentane at 0°. The resulting mixture was warmed to room temperature, and 22.26 g. (0.22 mole) of triethylamine in 100 ml. of pentane was added rapidly. The reaction mixture was stirred overnight, the solid amine hydrochloride collected on a filter, and the pentane removed from the filtrate by distillation at reduced pressure. The residue was distilled to give 26.88 g. (71.6% yield) of chloro-(dimethylamino)-phenylborane, b.p. 51–52° (0.2 mm.), $n^{24}\mathrm{D}$ 1.5320.

Anal. Calcd. for $C_8H_{11}BClN$: B, 6.54; N, 8.36. Found: B, 6.49; N, 8.11.

1,2-Bis-(dimethylamino)-1,2-diphenyldiboron (IV).—A solution of chloro-(dimethylamino)-phenylborane (33.5 g., 0.20 mole) in 50 ml. of xylene was added with vigorous stirring to 6.0 g. (0.26 mole) of sodium in 350 ml. of xylene at 130–140°. The reaction mixture was refluxed for 2 hr., sodium chloride and unreacted sodium were removed by filtration, and xylene was removed from the filtrate by distillation at reduced pressure. The residual crude solid product was recrystallized from toluene to give 12.0 g. (46% yield) of 1,2-bis-(dimethylamino)-1,2-diphenyldiboron, m.p. 101–103°.

Anal. Calcd. for $C_{16}H_{22}B_2N_4$: B, 8.19; C, 72.8; H, 8.3; mol. wt., 264. Found: B, 8.14; C, 72.4; H, 8.53; mol. wt., 255 (cryoscopic in benzene).

Thermal Decomposition of 1,2-Diethyl-1,2-bis-(dimethylamino)-diboron (III). (a) **At 200°**.—Heating 43.2 cc. (1.93 mmoles) of 1,2-diethyl-1,2-bis-(dimethylamino)-diboron for 41 hr. at 200° yielded a pale yellow non-volatile liquid, a trace of −196° non-condensables, *ca.* 0.5 cc. (0.022 mmole) of dimethylamine, and 13.5 cc. (0.6 mmole) of a liquid which was condensable at −80° with an apparent vapor pressure of 11 mm. at 25° and a molecular weight of 95.5. A slight B–H absorption at 4.05 μ in its gas-phase infrared spectrum decreased in intensity on standing at room temperature, and repeated attempts to purify the liquid by low-temperature fractionations were unsuccessful. The elemental analyses below suggest that this liquid is impure diethyl-(dimethylamino)-borane.

Anal. Distillate, calcd. for $C_2H_5BN(CH_3)_2$, ($C_6H_{16}NB$): C, 63.77; H, 14.26; N, 12.40; mol. wt., 102.8. Found: C, 63.28; H, 14.07; N, 10.55; mol. wt., 95.5. Residue, found: C, 52.00; H, 11.05; N, 19.85.

(b) **At 300°**.—Heating 49.7 cc. (2.22 mmoles) of 1,2-diethyl-1,2-bis-(dimethylamino)-diboron for 137 hr. at 300° produced 6.4 cc. (0.29 mmole) of hydrogen, 5.8 cc. (0.26 mmole) of ethane, a trace of dimethylamine, and a −80° condensate with an apparent vapor pressure of 10–12 mm. at 22°. Weak B–H absorption was observed in the infrared spectrum of this condensate at about 4 μ. This material appeared to be identical with that obtained from the 200° decomposition studies above. A non-volatile brown liquid residue (89 mg.) remained. This residue, when heated for 18 hr. at 450°, yielded residual black flaky solid, 11.4 cc. (0.51 mmole) of hydrogen, 3 cc. (0.13 mmole) of ethane, and a small amount of a volatile liquid similar to the −80° condensate above.

Neutral Hydrolysis of 1,2-Diethyl-1,2-bis-(dimethylamino)-diboron (III).—1,2-Diethyl-1,2-bis-(dimethylamino)-diboron (186 mg., 1.1 mmoles) and water (49 mg., 2.7 mmoles) appeared to be immiscible initially, but after 16.5 hr. at room temperature, 21.5 cc. (0.96 mmole) of hydrogen and 24.1 cc. (1.07 mmoles) of dimethylamine were evolved. An additional 20 mg. (1.1 moles) of water appeared to have no effect on the remaining white solid, but it dissolved completely in an approximately 30-fold excess of water. Fractionation of the solution yielded a white solid sublimate, m.p. 118–120°.

Basic Hydrolysis of 1,2-Diethyl-1,2-bis-(dimethylamino)-diboron (III).—A mixture of 26.9 mg. (1.6 mmoles) of 1,2-diethyl-1,2-bis-(dimethylamino)-diboron and *ca.* 5 ml. of 10% sodium hydroxide yielded 32.2 cc. (1.4 mmoles) of hydrogen (88% of theory) during 51 hr. in an ampoule at 125°. Ethane (10.3 cc., 0.46 mmole), some dimethylamine, and a slightly volatile white solid also were observed among the volatile products.

Hydrolysis of 1,2-Bis-(dimethylamino)-1,2-diphenyldiboron (IV).—1,2-Bis-(dimethylamino)-1,2-diphenyldiboron (0.61 g.) was shaken for 10–15 min. with 6 ml. of 0.1078 *N* hydrochloric acid at room temperature. The resulting white solid (m.p. 97–98°) was filtered, and its infrared spectrum was shown to be identical with that of the starting material.

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[14] D. L. Hunter, L. L. Petterson, and H. Steinberg, *Anal. Chim. Acta*, **21**, 523 (1959).

The sample recovered from above was dissolved in a solution consisting of 20 ml. of tetrahydrofuran, 3 ml. of water, and 0.61 ml. of 6.19 *N* hydrochloric acid. The solution was shaken for 30 min. at room temperature, and all volatile components were removed at reduced pressure. The white residual solid was treated with 25 ml. of water, and the insoluble portion collected on a filter. This material melted at 200–210°, did not reduce silver nitrate except after warming, and had an infrared spectrum which was identical to that of benzeneboronic acid. Dehydration of this white solid by distilling the benzene–water azeotrope or by sublimation at 200° (0.1 mm.) gave a white solid, m.p. 210–213°. A mixed melting point with an equal amount by weight of benzeneboronic anhydride was 209–215°, and the infrared spectra of the two materials were identical.

Reaction of 1,2-Diethyl-1,2-bis-(dimethylamino)-diboron (III) with Methanol (a).—A mixture of 48.7 mg. (0.29 mmole) of 1,2-diethyl-1,2-bis-(dimethylamino)-diboron and 9.0 mg. (0.28 mmole) of methanol produced 1.1 cc. (0.05 mmole) each of hydrogen and dimethylamine during 15.5 hr. at room temperature. The addition of excess methanol (26.9 mg., 0.84 mmole) to the residue yielded 3.8 cc. (0.17 mmole) of hydrogen, 1.4 cc. (0.06 mmole) of dimethylamine, and 19.2 cc. (0.86 mmole) of a mixture composed of methanol, dimethylamine, and a material which was presumably ethyldimethoxyborane, $C_2H_5B(OCH_3)_2$. This mixture consumed 9.1 cc. (0.4 mmole) of added excess hydrogen chloride, presumably by the formation of dimethylamine hydrochloride, $(CH_3)_2NH \cdot HCl$. The residual material, which had vapor pressures of 22 mm. at 0° and 64 mm. at 25°, appeared to be impure ethyldimethoxyborane (mol. wt. obsd. 90; calcd. 101.8). The low molecular weight impurity was probably methanol, which has a similar vapor pressure (30 mm. at 0°).

(b) **In the Presence of Hydrogen Chloride.**—In another experiment, the diboron compound (89 mg., 0.53 mmole) was combined with 23.5 cc. (1.05 mmoles) of hydrogen chloride at −196° and warmed to 26°. A non-volatile white solid formed immediately. The only distillate product isolated was 0.6 cc. of material with the same volatility as hydrogen chloride. The addition of 23.5 cc. (1.05 mmoles) of methanol to this white solid caused considerable bubbling with the formation of an additional solid phase; 3.7 cc. (0.17 mmole) of hydrogen and 11.8 cc. (0.526 mole) of ethyldimethoxyborane (obsd. mol. wt. 98) were obtained after 15 hr. at room temperature. Reaction of additional methanol (23.5 cc., 1.05 mmoles) with the non-volatiles produced 4.2 cc. (0.29 mmole) of hydrogen and a 11.3-cc. (0.5 mmole) mixture, which appeared to consist of methanol and ethyldimethoxyborane.

Reaction of 1,2-Diethyl-1,2-bis-(dimethylamino)-diboron (III) with Ethanol (a).—A mixture of equimolar amounts of 1,2-diethyl-1,2-bis-(dimethylamino)-diboron and ethanol (0.48 mole of each) yielded 6.3 cc. (0.28 mmole) of dimethylamine and only a trace of non-condensables during 63 hr. at room temperature. The addition of 10.9 cc. (0.49 mmole) of ethanol to the residue led to some hydrogen formation; after 2 hr. at 50°, and 1.5 hr. at 75°, a total of 2.6 cc. of hydrogen and 4.5 cc. of dimethylamine was obtained. Fractionation of the other volatile products yielded some unreacted starting material and about 7 cc. (0.31 mmole) of ethyldiethoxyborane, $C_2H_5B(OC_2H_5)_2$ (mol. wt. obsd. 126.5, calcd. 129.8). Its vapor pressures (13.4 mm. at 21°; 5.3 mm. at 0°) suggest a boiling point of 120–130° at 760 mm. The reported boiling point is 125° at 760 mm.[15]

(b) **In the Presence of Hydrogen Chloride.**—Hydrogen chloride (210.4 cc., 9.4 mmoles) was added to a mixture of 210.2 cc. (9.4 mmoles) of ethanol and 105.5 cc. (4.7 mmoles) of 1,2-diethyl-1,2-bis-(dimethylamino)-diboron at −78.5°. The mixture was warmed to room temperature and the resulting white solid treated with an additional 49.6 cc. (2.2 mmoles) of ethanol. Volatile products included 3.7 cc. (0.16 mole) of unreacted hydrogen chloride, 50.2 cc. (2.2 mmoles) of hydrogen, and *ca.* 134 cc. (6.0 mmoles) of ethyldiethoxyborane (v.p. at 0°, 4 mm.).

Reaction of 1,2-Diethyl-1,2-bis-(dimethylamino)-diboron (III) with Excess Hydrogen Chloride.—Hydrogen chloride (30.4 cc., 1.35 mmoles) was added to 9.9 cc. (0.44 mmole) of 1,2-diethyl-1,2-bis-(dimethylamino)-diboron and the mixture held at room temperature for 16 hr. Hydrogen (1.8 cc.) and 0.6 cc. of presumably unreacted hydrogen chloride were obtained from the resulting solid residue, along with a small amount of liquid material. Heating the residual solid for 1 hr. at 110° and 0.5 hr. at 120° yielded 6.1 cc. (0.27 mole of hydrogen and 3.0 cc. of a material identified by its infrared spectrum as chloro-(dimethylamino)-ethylborane, $C_2H_5[(CH_3)_2N]BCl$. The white solid remaining was only slightly volatile at room temperature and melted near 92°.

Reaction of 1,2-Diethyl-1,2-bis-(dimethylamino)-diboron (III) with Dry Oxygen.—The vapor pressure of a mixture of 1,2-diethyl-1,2-bis-(dimethylamino)-diboron (15 cc., 0.67 mmole) and oxygen (21 cc., 0.9 mmole) did not change when it was held for 30 min. at 25° and at a total pressure of 177 mm. When the mixture was heated to 60°, the pressure dropped to 160 mm. after 0.5 hr., to 143 mm. after 2.5 hr. at 60–100°, and finally to 95 mm. after 3 hr. at 100°. A total of 10.7 cc. (0.5 mmole) of oxygen was consumed, assuming that no −196° non-condensables were formed during the oxidation steps. Small amounts of dimethylamine (1.0 cc.) and ethane (0.5 cc.) were identified in the −196° condensate. The residual yellow liquid was not investigated further.

Reaction of 1,2-Diethyl-1,2-bis-(dimethylamino)-diboron (III) with Boron Trifluoride (a).—A mixture of 1,2-diethyl-1,2-bis-(dimethylamino)-diboron (13.7 cc., 0.61 mmole) and boron trifluoride (27.4 cc., 1.22 mmoles) was held for 15.5 hr. at room temperature and then heated to 139°. During this time, the boron trifluoride was completely consumed. The volatile products included 13.0 cc. (0.58 mmole) of ethyldifluoroborane and 81 mg. (0.87 mmole) of difluoro-(dimethylamino)-borane. Both materials were identified by their infrared spectra; the difluoro-(dimethylamino)-borane melted at 165–166° (lit.[16] 167–169°) and its vapor pressure at 76° was 20 mm. (lit.[17] 20.4 mm.). A non-volatile, yellow, viscous liquid remaining had no appreciable vapor pressure at 126°.

(b).—A comparable reaction with equimolar amounts of 1,2-diethyl-1,2-bis-(dimethylamino)-diboron and boron trifluoride (19.4 cc., 0.87 mmole) led to a mixture of volatile

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products which were distilled from 0° and condensed as follows: A mixture of unreacted starting material and a white solid at −23°, an unidentified liquid which condensed at −80°, and a −80° distillate which consisted of 7.6 cc. (0.34 mmole) of difluoroethylborane. The −80° condensate had an infrared spectrum similar to chloro(dimethylamino)-ethylborane and may have been ethyl(dimethylamino)-fluoroborane, $C_2H_5[(CH_3)_2N]BF$.

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Formation of Pentafluorosulfur Fluorosulfonate and Bispentafluorosulfur Oxide from the Direct Reaction of the Elements[1]

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In addition to SF_6 and S_2F_{10}, the direct reaction of sulfur with fluorine has been found to produce small quantities of pentafluorosulfur fluorosulfonate, SF_5OSO_2F, and bispentafluorosulfur oxide, $(SF_5)_2O$. The compounds S_2F_{10}, SF_5OSO_2F, and $(SF_5)_2O$ have been obtained in a high state of purity by gas chromatographic separations and a number of their physical properties have been examined.

It has been reported that the only products in addition to SF_6 resulting from the reaction of sulfur with fluorine are S_2F_{10}, SF_5OOSF_5, SF_4, S_2F_2, and SO_2.[3,4] Traces of oxygen or oxygen fluorides in the fluorine presumably account for the oxygenated compounds. In view of the presence of bispentafluorosulfur peroxide, SF_5OOSF_5, among the products it appeared possible that other species containing the interesting $-SF_5$ group also might be present. This investigation was performed in order to see if this were the case.

The higher boiling (approximately 30°) fraction remaining after the removal of SF_6 from the products of the reaction of fluorine with sulfur was separated into more than a dozen components by means of gas–liquid chromatographic columns. The three most abundant materials found were S_2F_{10} ($\sim$40%), SF_5OSO_2F ($\sim$30%), and $(SF_5)_2O$ ($\sim$10%).

Since the physical properties reported for S_2F_{10} vary widely (melting points ranging from −92 to −53° have been given[5-8]) the melting point, vapor pressure data, and infrared spectrum of the compound were re-examined.

During the course of the present investigation it was reported that the new compound SF_5OSO_2F was obtained during the irradiation of a mixture of S_2F_{10} and SO_2 by ultraviolet light.[9] It therefore is not surprising to find that SF_5OSO_2F is formed during the reaction of fluorine with sulfur since both S_2F_{10} and SO_2 also are present among the reaction products.[4]

It has been reported previously that SF_5OOSF_5 was a minor product of the reaction of fluorine with sulfur.[3] Although it may be present in the material investigated in this research, it certainly does not appear to be present in as large quantities. Slight variations in reaction conditions would undoubtedly lead to variations in the relative amounts of products obtained, especially since it appears likely that SF_5OOSF_5 is converted to $(SF_5)_2O$ in the presence of SF_5 radicals[10] which might be expected to be present in the reaction system.

The mass spectra of S_2F_{10}, SF_5OSO_2F, and $(SF_5)_2O$ are analogous to that of SF_6[11] in that no

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