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Boron Heterocycles. V. Preparation and Characterization of Selected Heteronuclear Diboron Ring Systems[1]

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Several new heteronuclear diboron ring systems have been prepared from reactions of $B_2[N(CH_3)_2]_4$ and B_2Cl_4 with selected diols and ethanedithiol. The compounds prepared are crystalline solids, most of which are monomeric in solution and are soluble in common organic solvents. Chemical observations and boron-11 nmr provide indirect evidence for structures. Properties and reactions are discussed.

Introduction

Among the best known heteronuclear diboron ring compounds are those which have been prepared from diamines, either by transamination of tetrakis(dimethylamino)diboron, $B_2[N(CH_3)_2]_4$, or its derivatives[2-5] or by reductive metal coupling reactions.[2] The few reported examples of oxygen-containing diboron heterocycles were prepared by reductive coupling and were apparently impure.[5-7]

Although the reactions of $B_2[N(CH_3)_2]_4$ and its disubstituted derivatives with various simple alcohols have been studied extensively,[8-10] there has been no apparent effort to study reactions with diols or dithiols to produce heteronuclear diboron ring systems. By the same token, the reactions of diboron tetrachloride, B_2Cl_4, with diols and dithiols have been essentially unstudied. The reaction of B_2Cl_4 with ethylene glycol[11] has been reported, but no product was isolated, while treatment of B_2Cl_4 with ethylenediamine produced a polymeric material.[12,13]

The principal objectives of the present investigation have been to synthesize and study monomeric heteronuclear diboron ring systems which also contain oxygen, sulfur, or nitrogen in the ring, using $B_2[N(CH_3)_2]_4$ and B_2Cl_4 as starting materials.

A number of new compounds have been prepared as a result of this work and indirect evidence for their structures from chemical and boron-11 nmr observations have been obtained.

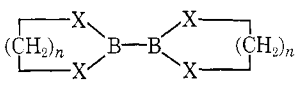
Results and Discussion

Oxygen- and Sulfur-Containing Rings.—From reactions analogous to those used to prepare tetraalkoxydiborons,[9,10] ethylene glycol, ethanedithiol, 1,3-propanediol, and catechol were allowed to react with tetrakis(dimethylamino)diboron in the presence of hydrogen chloride in a 2:1:4 molar ratio. Monomeric species of molecular formulas $B_2(O_2C_2H_4)_2$ (I), $B_2(S_2C_2H_4)_2$ (II), $B_2(O_2C_3H_6)_2$ (III), and $B_2(O_2C_6H_4)_2$ (IV), respectively, were obtained.

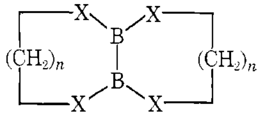
$$B_2[N(CH_3)_2]_4 + 4HCl + 2HX(CH_2)_nXH \longrightarrow B_2[X_2(CH_2)_n]_2 + 4(CH_3)_2H_2NCl$$

I, $X = O, n = 2$
II, $X = S, n = 2$
III, $X = O, n = 3$
IV, $X = O, (CH_2)_n = C_6H_4$

Two structures are possible: (A) bicyclic or (B) fused ring



A



B

The correct structures are not known at the present time; however, chemical data strongly favor the fused-ring structure for I. Boron-11 nmr spectra of these compounds show equivalent boron atoms; their respective chemical shifts and physical properties are given in Table I.

The reactions cited above seem to take place in two distinct steps, with 1,2-dichloro-1,2-bis(dimethylamino)diboron being formed initially at low temperature (−96 to −78°) and then reacting with the diol or dithiol above −78° to produce the heterocyclic system

$$B_2[N(CH_3)_2]_4 + 4HCl \longrightarrow B_2Cl_2[N(CH_3)_2]_2 + 2(CH_3)_2H_2NCl$$

$$B_2Cl_2[N(CH_3)_2]_2 + 2HXCH_2CH_2XH \longrightarrow B_2(X_2C_2H_4)_2 + 2(CH_3)_2H_2NCl$$

To check the feasibility of this scheme as a possible mechanism, an authentic sample of $B_2Cl_2[N(CH_3)_2]_2$[14-16]

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[1] Part IV: G. E. McAchran and S. G. Shore, *Inorg. Chem.*, **5**, 2044 (1966).

[2] M. P. Brown, A. E. Dann, D. W. Hunt, and H. B. Silver, *J. Chem. Soc.*, 4648 (1962).

[3] R. J. Brotherton, U. S. Patent 3,120,501 (1964).

[4] H. Noth, P. Fritz, and W. Meister, *Angew. Chem.*, **73**, 762 (1961).

[5] H. Noth and P. Fritz, *Z. Anorg. Allgem. Chem.*, **324**, 129 (1963).

[6] R. J. Brotherton and W. G. Woods, French Patent 1,297,628 (1962); U. S. Patent 3,009,941 (1961).

[7] R. J. Brotherton, "Progress in Boron Chemistry," Vol. I, H. Steinberg and A. L. McClosky, Ed., The Macmillan Co., New York, N. Y., 1964, Chapter 1.

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

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

[10] A. L. McClosky, R. J. Brotherton, and L. L. Petterson, Belgian Patent 588,487 (1960); British Patent 872,769 (1961); French Patent 1,255,563 (1961); Italian Patent 626,940 (1961); U. S. Patent 3,062,823 (1962).

[11] H. I. Schlesinger, *et al.*, "Hydrides and Borohydrides of Light Elements," Reports to the Office of Naval Research, 1948–1957.

[12] W. B. Fox, Doctoral Dissertation, The Pennsylvania State University, 1961.

[13] A. K. Holliday, J. J. Marsdern, and A. G. Massey, *J. Chem. Soc.*, 3348 (1961).

[14] M. P. Brown and H. B. Silver, *Chem. Ind.* (London), 85 (1963).

[15] H. Noth and W. Meister, *Z. Naturforsch.*, **17B**, 714 (1962).

[16] S. C. Malhotra, *Inorg. Chem.*, **3**, 862 (1964).

Table I

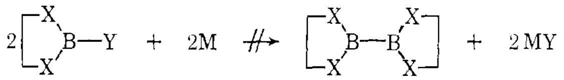
Nmr Chemical Shifts

Compound	Solvent	$B^{11\,a}$	$H^{1\,b}$: CH_2	CH_3	C_6H_4	Mp, °C	Subl pt, °C (10^{-4} mm)
$B_2(O_2C_2H_4)_2$	CH_2Cl_2	−31.5	5.85			168–170	50–55
$B_2(S_2C_2H_4)_2$	CH_2Cl_2	−68.3	6.68			170–175 dec	
$B_2(O_2C_3H_6)_2$	CH_2Cl_2	−28.6	8.12 (center) 6.12 (end)			158–162	45–50
$B_2(O_2C_6H_4)_2$	CH_2Cl_2	−30.7			2.69	195–198	120–130
$B_2Cl_2(O_2C_2H_4)$	$CHCl_3$	−30.8	4.74			175–180 dec	
$B_2Cl_2(S_2C_2H_4)$	Diglyme	−67.8				175–185 dec	
$B_2[N(CH_3)_2]_2(S_2C_2H_4)$	CH_2Cl_2	−43.7	7.12	7.23		63–66	70–80 (sl dec)
$B_2(S_2C_2H_4)_2 \cdot 2NH(CH_3)_2$	CH_2Cl_2	−11.8	7.06	7.35		108–114	
$B_2[(NCH_3)_2C_2H_4]_2$	CH_2Cl_2	−33.7	6.83	7.34		45–47	
$B_2[(NH)_2C_6H_4]_2$	CH_3CN	−27.9				>280	230–235 (slowly)

[a] Ppm with respect to $F_3B \cdot O(C_2H_5)_2$ as external reference. [b] Solvent served as internal reference.

when treated with ethylene glycol and with ethanedithiol yielded I and II, respectively.

Reported attempts to prepare IA by reductive coupling were apparently unsuccessful,[7,11] while attempts to synthesize IIIA and IVA by reductive coupling with dispersed molten sodium in the presence of a small amount of triethylamine resulted in the formation of impure diboron compounds.[7] In experiments not described here, we have also been unable to prepare pure samples of IA and IIA by reductive coupling, with and without the presence of amine bases



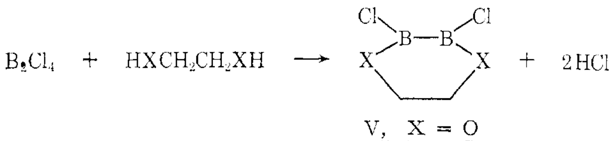
X = O, S
Y = Cl, Br
M = Na, Na–Hg, Li, or Mg

Products identical with I, II, III, and IV, on the basis of X-ray powder diffraction data and melting point data were obtained when B_2Cl_4 reacted with ethylene glycol, ethanedithiol, 1,3-propanediol, and catechol in 1:2 molar ratios

$$B_2Cl_4 + 2HX(CH_2)_nXH \longrightarrow B_2[X_2(CH_2)_n]_2 + 4HCl$$

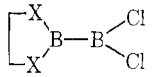
However, the reaction of B_2Cl_4 with 1,3-propanedithiol, *o*-aminophenol, 2-mercaptoethanol, or styrene glycol afforded only polymeric products. The presence of considerable amounts of hydrogen choride evolved had no apparent effect on the diboron products.

Six-membered rings were prepared when diboron tetrachloride was treated with ethylene glycol and with ethanedithiol in 1:1 molar ratios



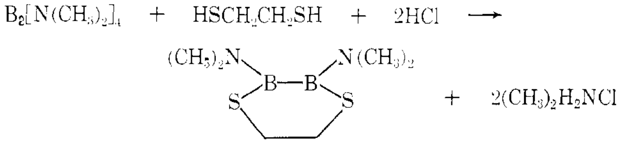
V, X = O
VI, X = S

These compounds are white crystalline solids which react rapidly with moisture. Molecular weight determinations of V in chloroform support a monomeric species. Compound VI was not sufficiently soluble in appropriate solvents for molecular weight determinations. Boron-11 nmr spectra of V and VI showed equivalent boron atoms in each compound, which prompted the assignment of the six-membered ring structure given above as opposed to the five-membered ring isomer shown below.



The reaction of B_2Cl_4 with 1,3-propanediol or catechol in 1:1 molar stoichiometry resulted in the formation of polymeric materials.

The reaction of $B_2[N(CH_3)_2]_4$ with ethanedithiol and hydrogen chloride in a molar ratio of 1:1:2, respectively, yielded $B_2[N(CH_3)_2]_2(S_2C_2H_4)$ (VII)



VII

The boron-11 nmr spectrum of VII indicated equivalent boron atoms; this suggested the six-membered ring structure. The potential usefulness of this compound is characterized by its ease of preparation, high yields, solubility in many common organic solvents, and its readily displaced dimethylamino groups.

An attempt at an analogous reaction involving $B_2[N(CH_3)_2]_4$ with ethylene glycol and hydrogen chloride in a 1:1:2 molar ratio did not yield $B_2[N(CH_3)_2]_2(O_2C_2H_4)$. Dimethylammonium chloride and $B_2(O_2C_2H_4)_2$ were identified as products from the reaction in addition to a polymeric material which contained boron–boron bonds.

At ambient temperature, $B_2[N(CH_3)_2]_4$ and ethanedithiol in slightly less than 1:2 molar ratio reacted directly to produce the dimethylamine adduct $B_2(S_2C_2H_4)_2[NH(CH_3)_2]_2$

$$B_2[N(CH_3)_2]_4 + 2HSCH_2CH_2SH \longrightarrow B_2(S_2C_2H_4)_2[NH(CH_3)_2]_2 + 2NH(CH_3)_2$$

This compound is identical with the product which is obtained from the direct addition of dimethylamine to $B_2(S_2C_2H_4)_2$. The large upfield shift from the parent compound in the boron-11 nmr spectrum confirms the fact that boron is quaternary in the adduct rather than an isomeric compound with trigonal borons, such as

$B_2(SC_2H_4SH)_2[N(CH_3)_2]_2$. Replacement of all of the dimethylamino groups by a reaction similar to the one indicated above could not be achieved, even when the reactants in appropriate molar ratio were refluxed vigorously.

Nitrogen-Containing Rings.—The reaction of B_2Cl_4 with *sym*-dimethylethylenediamine in a 1:4 molar ratio

$$B_2Cl_4 + 4C_2H_4[NH(CH_3)]_2 \longrightarrow \underset{\text{VIII}}{B_2[(NCH_3)_2C_2H_4]_2} + 2C_2H_4[NH_2(CH_3)Cl]_2$$

yielded a product which was shown to be identical by comparison of physical properties and X-ray powder diffraction pattern data with the species obtained from the transamination of $B_2[N(CH_3)_2]_4$.[2] On the other hand, the reaction of B_2Cl_4 with *o*-phenylenediamine in a 1:4 molar ratio produced an amorphous material which was unlike that produced from the transamination of $B_2[N(CH_3)_2]_4$.[7,17] Reaction in a 1:6 molar ratio did, however, produce a crystalline material containing $B_2[(NH)_2C_6H_4]_2$, as shown by X-ray powder diffraction data

$$B_2Cl_4 + 6(NH_2)_2C_6H_4 \longrightarrow \underset{\text{IX}}{B_2[(NH)_2C_2H_4]_2} + 4C_6H_4NH_2NH_3Cl$$

but it could not be successfully purified.

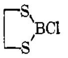
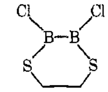
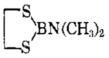
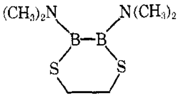
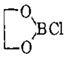
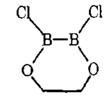
Brown[2] has shown that the products obtained from the transamination of $B_2[N(CH_3)_2]_4$ with several diamines were identical with those produced by reductive coupling. Therefore, if rearrangement does not take place in the coupling reaction, the products from the diboron tetrachloride reaction and the transamination reaction probably assume bicyclic structures analogous to IA.

Nmr Spectra.—Acid-base studies have shown that sulfur-containing borolanes are stronger Lewis acids than the analogous oxygen-containing derivatives.[1,18] Similar results were obtained in the present study in that sulfur-containing derivatives were shown to react more completely with methylamine, dimethylamine, and trimethylamine than the oxygen-containing diboron compounds. Boron-11 chemical shifts for the oxygen-containing borolanes are at considerably higher fields than for the sulfur-containing borolanes, which implies greater electron density around boron in the oxygen-containing compounds than in the sulfur ones.[18,19] We have obtained similar results from heteronuclear diboron ring compounds. The oxygen-substituted heterocycles have chemical shifts which are some 30 ppm upfield from those of the analogous sulfur-substituted heterocycles. Data are presented in Table I.

An interesting feature of the boron-11 chemical shift data is brought out in Table II. Insertion of a monosubstituted boron substituent into the five-membered ring borolane structure to produce a six-membered ring containing a boron–boron bond results in only relatively small changes of the chemical shifts. While this could imply that the electron density around boron is essentially unchanged, such a conclusion should be drawn only with considerable reservation. Proton nmr chemical shift data cast no additional light to aid in explaining this observation.

TABLE II

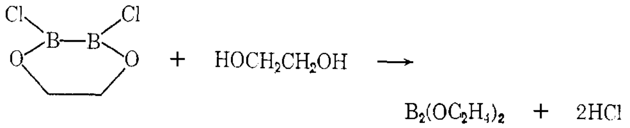
COMPARISON OF BORON-11 CHEMICAL SHIFT DATA

Compound	δ^a	Compound	δ
	−62.7		−67.8
	−45.3[b]		−43.7
	−31.4		−30.8

[a] All chemical shifts are referred to $BF_3 \cdot O(C_2H_5)_2$. [b] J. Crist, The Ohio State University, unpublished results.

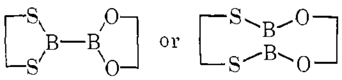
The chemical shifts of the heterocyclic diboron compounds prepared in this investigation are, in general, similar to those reported for acyclic, tetrasubstituted diboron compounds.

Reactions.—The reaction of V with ethylene glycol produced I

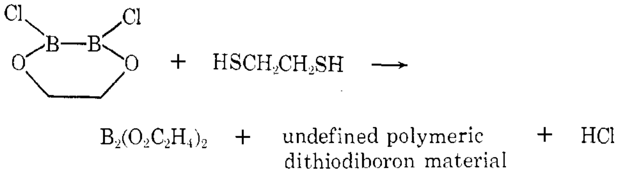


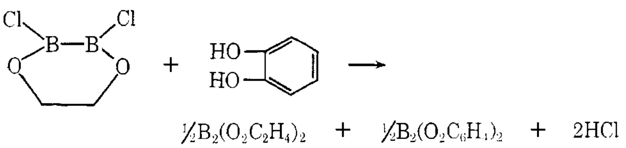
While this result supports, indirectly, the fused ring structure IB, possible rearrangement in solution cannot be precluded. The reaction of VI with ethanedithiol produced small amounts of II.

Mixed heteronuclear diboron ring compounds such as



have not been reported. The following reactions represent attempts in this laboratory to prepare such mixed-ring systems. These attempts always failed, producing only the more symmetrical species which have been prepared by more direct synthetic routes





Analogous reactions starting with $B_2Cl_2(S_2C_2H_4)$ and

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(17) R. J. Brotherton and L. L. Petterson, Belgian Patent 588,759 (1960); British Patent 875,051 (1961); French Patent 1,251,598 (1960); Italian Patent 626,522 (1961); U. S. Patent 3,048,632 (1962).

(18) D. E. Young, G. E. McAchran, and S. G. Shore, *J. Am. Chem. Soc.*, **88**, 4390 (1966).

(19) M. F. Hawthorne, *ibid.*, **83**, 1345 (1961).

treating it with either ethylene glycol or catechol in a 1:1 molar ratio always yielded $B_2(O_2C_2H_4)_2$ or $B_2(O_2C_6H_4)_2$ as the only identifiable diboron product. Unreacted $B_2Cl_2(S_2C_2H_4)$ and polymeric species were always present. No evidence was obtained for the existence of a mixed diboron heterocycle at ambient temperatures in any of the above reactions.

An attempt to produce a mixed-ring system through the transamination of $B_2[N(CH_3)_2]_2(S_2C_2H_4)$ by treating it with *o*-phenylenediamine in benzene produced a very slow reaction at room temperature to form $B_2[(NH)_2C_6H_4]_2$ as the only identifiable diboron product. Ethanedithiol and dimethylamine were liberated in the reaction. A possible intermediate in this reaction is the formation of a dimethylamine adduct which could, in principle, rearrange to produce the products cited above.

When dimethylamine is allowed to react with VI in a 4:1 molar ratio, VII is isolated as the reaction product

$$B_2Cl_2(S_2C_2H_4) + 4NH(CH_3)_2 \longrightarrow B_2[N(CH_3)_2]_2(S_2C_2H_4) + 2(CH_3)_2H_2NCl$$

The analogous reaction of $B_2Cl_2(O_2C_2H_4)$ with dimethylamine afforded a diboron material which was polymeric. As aforementioned, $B_2[N(CH_3)_2]_2(O_2C_2H_4)$ could not be prepared by the interaction of $B_2[N(CH_3)_2]_4$ with ethylene glycol and hydrogen chloride in a 1:1:2 molar ratio, respectively.

Because B_2Cl_4 is not easily prepared, attempts to prepare $B_2Cl_2(S_2C_2H_4)$ and $B_2Cl_2(O_2C_2H_4)$ by procedures which do not require this reagent were undertaken. The reaction of $B_2[N(CH_3)_2]_2(S_2C_2H_4)$ with hydrogen chloride in a 1:2 molar ratio did not yield $B_2Cl_2(S_2C_2H_4)$ or $B_2Cl_2(S_2C_2H_4)[NH(CH_3)_2]_2$ but formed dimethylammonium chloride and an amorphous solid containing boron–boron bonds. When a 1:4 molar ratio was used, the following reaction was observed

$$B_2[N(CH_3)_2]_2(S_2C_2H_4) + 4HCl \longrightarrow B_2Cl_4[NH(CH_3)_2]_2 + HSCH_2CH_2SH$$

The product $B_2Cl_4[NH(CH_3)_2]_2$ proved to be identical by melting point and X-ray powder diffraction pattern data with that synthesized from the interaction of $B_2[N(CH_3)_2]_4$ with hydrogen chloride in a 1:6 molar ratio.[16]

The reaction of $B_2[N(CH_3)_2]_2(S_2C_2H_4)$ with BCl_3 in a 1:2 molar ratio resulted in the formation of $B_2Cl_2(S_2C_2H_4)$, $Cl_2BN(CH_3)_2$, and an unidentified polymeric solid which contained boron–boron bonds. An analogous reaction with BF_3 gave no evidence for the formation of $B_2F_2(S_2C_2H_4)$.

Boron trichloride, at 400–500 mm, was passed over $B_2(S_2C_4H_4)_2$ and over $B_2(O_2C_2H_4)_2$ in separate reactions at 50–60°. Products from the $B_2(S_2C_2H_4)_2$ included $\underline{SC_2H_4SB}Cl$, $B_2Cl_2(S_2C_2H_4)$, an amorphous solid which contained sulfur and boron–boron bonds, and unreacted $B_2(S_2C_2H_4)_2$. The reaction of BCl_3 with $B_2(O_2C_2H_4)_2$ produced $\underline{OC_2H_4OB}Cl$, small amounts of $B_2Cl_2(O_2C_2H_4)$, an amorphous solid containing boron–boron bonds, and unreacted $B_2(O_2C_2H_4)_2$. In these reactions more $B_2Cl_2(S_2C_2H_4)$ was formed than $B_2Cl_2(O_2C_2H_4)$; however, yields in both cases were small.

Experimental Section

Reagents.—B_2Cl_4 was prepared and purified by previously described procedures.[20,21] $B_2[N(CH_3)_2]_4$, obtained as a complimentary sample from the U. S. Borax Co., was heated vigorously over Na and distilled under vacuum. BCl_3 was purified by distillation through traps maintained at −78 and −97° into one at −196°. $HOCH_2CH_2OH$, $HOCH_2CH_2CH_2OH$, and $HSCH_2CH_2SH$ were dried by heating them to near their boiling points over a mixture of BaO and CaH_2 and then recovered by fractional vacuum distillation. *sym*-Dimethylethylenediamine was dried by warming over Na and fractionally distilled under vacuum. Cathechol and *o*-phenylenediamine were used directly. Reagent grade NH_2CH_3, $NH(CH_3)_2$, and $N(CH_3)_3$ were dried over Na and recovered by vacuum distillation. HCl was obtained from a commercial cylinder and was used directly. Benzene, CH_2Cl_2, and pentane were refluxed vigorously over a mixture of $CaCl_2$ and CaH_2 and distilled into storage bulbs.

Apparatus.—Standard high-vacuum techniques were used for handling volatile material. Transfer of nonvolatile materials took place in an inert-atmosphere box. Cryoscopic molecular weight determinations were performed in benzene using a Beckmann thermometer. When $CHCl_3$ served as the solvent, molecular weight data were obtained using a Mechrolab vapor pressure osmometer, Model 301A. Infrared spectra were obtained using a Perkin-Elmer 337 recording grating spectrometer. Solid samples were examined as KBr disks. The spectra were frequency calibrated with the aid of polystyrene. X-Ray powder diffraction patterns of crystalline solids were obtained using a camera of 11.46-cm effective diameter and Cu Kα radiation. All B^{11} nmr spectra were taken at 19.25 Mc on a Varian HR-60 spectrometer using saturated solutions in 15 mm sample tubes. $BF_3 \cdot O(C_2H_5)_2$ served as an external reference. Proton nmr spectra were obtained with a Varian A-60 spectrometer and the solvent served as the internal reference.

Elemental Analyses.—Carbon and hydrogen analyses were commercially obtained. Boron analyses were performed by the Parr bomb fusion method. Chlorine analyses were obtained by potentiometric titration with $AgNO_3$. Nitrogen determinations were performed using the micro Kjeldahl method. Quantitative cleavage of the boron–boron bond and the subsequent evolution of hydrogen was accomplished by heating the diboron compound in 10 *N* NaOH solution at 110° in a closed system. Liberated H_2 was measured in a calibrated section of the vacuum system.

Melting Points and Sublimation Points.—Melting points were determined in open capillaries and are uncorrected. Sublimation points were determind at 10^{-3}–10^{-4} mm.

General Reaction Conditions.—Reactions mixtures were initially stirred at −97 or −78° for 2–3 hr, then allowed to warm to room temperature over a 3–4-hr period where stirring was continued for the duration of the experiment.

Syntheses and Properties. 1. $\mathbf{B_2(O_2C_2H_4)_2}$.—(a) In a typical experiment, HCl (32.2 mmoles) was allowed to expand into a reaction vessel containing a mixture of $B_2[N(CH_3)_2]_4$ (7.4 mmoles), $HOCH_2CH_2OH$ (15.4 mmoles), and 35 ml of CH_2Cl_2 which was stirred at −96°. Reaction was allowed to take place over a temperature range of −96 to 25° for 16 hr. CH_2Cl_2 was distilled away under vacuum leaving behind a copious white residue. This residue was reduced in particle size to a coarse powder, agitated in 85–90 ml of benzene, and filtered with a vacuum-filtering apparatus. Dimethylammonium chloride was collected on the frit. Evaporation of the benzene from the filtrate produced a white solid in yields estimated at 65–75%. The product was also separated from $(CH_3)_2H_2NCl$ by sublimation at 40–45°.

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(b) In a typical reaction, B_2Cl_4 (3.95 mmoles) and 30 ml of CH_2Cl_2 were distilled into a reaction vessel containing 8.03 mmoles of $HOCH_2CH_2OH$ which was maintained at −196°. Reaction was allowed to occur over a temperature range of −78 to 25° for 15 hr; a clear solution with no insoluble material resulted. Slightly less than 16 mmoles of HCl was liberated in the reaction. CH_2Cl_2 and HCl were distilled slowly from the reaction vessel under vacuum which resulted in the formation of a white crystalline solid. Purification was achieved by sublimation at 40–45°. An X-ray powder diffraction pattern of this solid was identical with that obtained from the product in part (a).

$B_2(O_2C_2H_4)_2$ is soluble in CH_2Cl_2, benzene, ethers, and other organic solvents. No change occurred in the X-ray powder pattern when the compound was recovered from refluxing benzene.

Anal. Calcd for $C_4H_8B_2O_4$: C, 33.89; H, 5.69; B, 15.27; O, 45.15; mol wt, 141.74. Found: C, 33.74; H, 5.82; B, 15.31; mol wt, 146.2 (0.085 *m*) in benzene. Base hydrolysis gave 0.99 mole of hydrogen per mole of $B_2(O_2C_2H_4)_2$.

X-Ray powder diffraction pattern data, *d* (relative intensity): 6.30 (s), 4.28 (vs), 4.03 (m), 3.75 (w), 3.60 (vs), 3.48 (vs), 3.20 (w), 3.12 (w), 2.858 (w), 2.710 (vw), 2.629 (w), 2.581 (w), 2.344 (m), 2.262 (m), 2.136 (m), 1.965 (vw), 1.935 (vw), 1.836 (vw), 1.796 (vw), 1.742 (m), 1.647 (w), 1.572 (vw), 1.546 (vw).

Infrared spectrum (KBr, cm^{-1}): 3012 (m), 2985 (m), 2915 (m), 1916 (w), 1866 (vw), 1488 (m), 1475 (s), 1426 (w), 1404 (m), 1387 (s), 1351 (m), 1196 (s), 1145 (s), 985 (m), 978 (m), 964 (sh), 922 (s), 759 (m), 755 (m), 676 (w), 668 (w), 484 (m).

2. **$B_2(S_2C_2H_4)_2$**.—Procedures were essentialy the same as those described in sections 1(a) and 1(b). However, it was found that a slight excess of $HSCH_2CH_2SH$ was required to enhance the formation of $B_2(S_2C_2H_4)_2$ and reduce the formation of polymeric materials. In order to prevent side reactions in this preparation, the condensation of HSC_2H_4SH onto $B_2[N(CH_3)_2]_4$ at −196° was necessary. Yields from this reaction were estimated at 85–90% of theory. $B_2(S_2C_2H_4)_2$ is soluble in most organic solvents and decomposes readily when exposed to atmospheric conditions.

Anal. Calcd for $C_4H_8B_2S_4$: C, 23.32; H, 3.91; B, 10.50; S, 62.27; mol wt, 206.02. Found: C, 21.41; H, 3.77; B, 10.05; mol wt, 209.0 (0.047 *m*) in benzene. Base hydrolysis gave 0.97 mole of hydrogen per mole of $B_2(S_2C_2H_4)_2$.

X-Ray powder diffraction pattern data, *d* (relative intensity): 6.61 (vs), 5.01 (vs), 4.37 (w), 4.08 (vs), 3.83 (vs), 3.49 (m), 3.36 (m), 2.998 (vw), 2.730 (m), 2.644 (w), 2.571 (w), 2.508 (m), 2.163 (m), 1.416 (vw).

Infrared spectrum (KBr, cm^{-1}): 2915 (w), 1464 (w), 1418 (m), 1372 (w), 1299 (w), 1271 (s), 1138 (s), 1010 (vw), 897 (m), 864 (s), 829 (m), 765 (w), 753 (m), 738 (s), 655 (m), 485 (m).

3. **$B_2(O_2C_3H_6)_2$**.—Procedures and techniques used for the preparation and isolation of this compound were essentially identical with those in sections 1(a) and 1(b). $B_2(O_2C_3H_6)_2$ is soluble in benzene, CH_2Cl_2, ethers, and other polar and nonpolar solvents.

Anal. Calcd for $C_6H_{12}B_2O_4$: C, 42.44; H, 7.13; B, 12.75; O, 37.69; mol wt, 169.80. Found: C, 42.13; H, 7.09; B, 12.60; mol wt, 165.1 (0.098 *m*) in benzene.

X-Ray powder diffraction pattern data, *d* (relative intensity): 5.61 (vs), 4.77 (m), 4.36 (vs), 3.94 (vs), 3.45 (s), 3.38 (w), 3.26 (m), 2.912 (vw), 2.801 (vw), 2.629 (m), 2.485 (vw), 2.344 (m), 2.238 (m), 2.062 (w), 1.910 (w), 1.786 (vw).

Infrared spectrum (KBr, cm^{-1}): 2958 (m), 2898 (m), 1492 (sh), 1484 (m), 1420 (m), 1406 (s), 1385 (w), 1279 (sh), 1263 (s), 1200 (s), 1167 (s), 1124 (s), 1048 (w), 1001 (w), 926 (vw), 916 (m), 824 (s), 697 (s), 517 (vw), 450 (m).

4. **$B_2(O_2C_6H_4)_2$**.—Catechol reacted with $B_2[N(CH_3)_2]_4$ or B_2Cl_4 in procedures essentially identical with 1(a) and 1(b) to produce $B_2(O_2C_6H_4)_2$. The product obtained from the reaction with $B_2[N(CH_3)_2]_4$ was impure, but could be purified by sublimation at 120–125°. This compound is sparingly soluble in common organic solvents.

Anal. Calcd for $C_{12}H_8B_2O_4$: C, 60.60; H, 3.39; B, 9.10; O, 26.91; mol wt, 237.82. Found: C, 60.35; H, 3.61; B, 9.09; mol wt, 241.0 (0.043 *m*) in benzene. Base hydrolysis gave 0.96 mole of hydrogen per mole of B–B compound.

X-Ray powder diffraction pattern data, *d* (relative intensity): 8.27 (s), 6.44 (m), 5.37 (vs), 4.56 (w), 4.10 (m), 3.77 (m), 3.59 (vs), 3.35 (s), 3.11 (vs), 2.683 (m), 2.588 (m), 2.449 (vw), 2.330 (vw), 2.230 (w), 2.166 (w), 1.797 (w), 1.671 (w).

Infrared spectrum (KBr, cm^{-1}): 3058 (vw), 1610 (vw), 1597 (w), 1481 (s), 1464 (s), 1422 (m), 1400 (s), 1368 (s), 1346 (m), 1337 (m), 1285 (w), 1271 (m), 1263 (w), 1232 (s), 1214 (sh), 1157 (m), 1148 (s), 1140 (s), 1132 (s), 1117 (s), 1083 (m), 1037 (w), 1000 (w), 940 (w), 930 (m), 901 (w), 892 (m), 861 (m), 851 (w), 811 (s), 766 (m), 754 (s), 740 (s), 732 (s), 554 (s), 475 (w), 457 (w), 419 (s).

5. **$B_2Cl_2(O_2C_2H_4)$**.—B_2Cl_4 (5.89 mmoles) was condensed into a reaction vessel which contained 5.86 mmoles of $HOCH_2CH_2OH$ and 35 ml of CH_2Cl_2 maintained at −196°. Reaction was allowed to occur over a temprature range of −78 to 25° for 16 hr. A white crystalline solid separated from the solution; it was collected on a sintered-glass filter in estimated yields of 85–90%. The filtrate contained $B_2(O_2C_2H_4)_2$ and other materials. Impurities were removed by double extraction with CH_2Cl_2 or by subliming them away at 45–55°. $B_2Cl_2(O_2C_2H_4)$ is only slightly soluble in common organic solvents. It is very sensitive to moisture.

Anal. Calcd for $C_2H_4B_2Cl_2O_2$: C, 15.74; H, 2.64; B, 14.18; Cl, 46.47; O, 20.97; mol wt, 152.61. Found: C, 15.98; H, 2.79; B, 13.85; Cl, 45.30; mol wt, 149.5 (0.027 *m*) in $CHCl_3$. Base hydrolysis gave 0.99 mole of hydrogen per mole of $B_2Cl_2(O_2C_2H_4)$.

X-Ray powder diffraction pattern data, *d* (relative intensity): 7.86 (s), 4.92 (s), 4.32 (w), 3.92 (vs), 2.974 (m), 2.814 (s), 2.755 (w), 2.671 (m), 2.449 (m), 2.076 (vvw), 2.029 (vvw), 1.631 (vvw), 1.594 (vvw), 1.535 (vvw).

Infrared spectrum (KBr, cm^{-1}): 2967 (w), 2907 (w), 1484 (vw), 1475 (m), 1404 (w), 1381 (s), 1328 (sh), 1316 (s), 1311 (s), 1267 (w), 1227 (vw), 1192 (s), 1153 (sh), 1139 (s), 1052 (m), 984 (w), 976 (w), 924 (s), 755 (m), 576 (m), 485 (m).

6. **$B_2Cl_2(S_2C_2H_4)$**.—B_2Cl_4 (7.66 mmoles) and 35 ml of CH_2Cl_2 were condensed into a reaction vessel containing 7.64 mmoles of $HSCH_2CH_2SH$ which was maintained at −196°. Reaction was allowed to occur over a temperature range of −78 to 25° for 16 hr; a white solid separated from the reaction mixture and was collected on a sintered-glass filter in an estimated yield of 70–75%. Solids recovered by evaporation of the filtrate were amorphous as shown by X-ray powder diffraction. $B_2Cl_2(S_2C_2H_4)$ is a crystalline solid which is only slightly soluble in most common solvents. For this reason molecular weight determinations could not be obtained. The compound is very sensitive to moisture.

Anal. Calcd for $C_2H_4B_2Cl_2S_2$: C, 13.00; H, 2.18; B, 11.71; Cl, 38.39; S, 34.72; mol wt, 184.75. Found: C, 13.18; H, 2.40; B, 11.99; Cl, 37.90.

X-Ray powder diffraction pattern data, *d* (relative intensity): 10.28 (m), 8.27 (s), 7.02 (vs), 6.26 (s), 5.28 (w), 5.01 (w), 3.83 (s), 3.37 (m), 3.13 (m), 2.629 (m), 2.556 (m), 2.301 (vw), 2.232 (vw), 2.151 (vw), 2.023 (vw), 1.951 (vw).

Infrared spectrum (KBr, cm^{-1}): 3003 (w), 2950 (w), 1424 (m), 1410 (s), 1383 (vw), 1236 (sh), 1149 (s), 964 (w), 929 (w), 847 (m), 836 (m), 816 (m), 718 (w), 690 (s), 664 (m), 630 (s), 602 (s), 574 (s), 539 (m).

7. **$B_2[N(CH_3)_2]_2(S_2C_2H_4)$**.—$HSCH_2CH_2SH$ (9.78 mmoles) and 35 ml of CH_2Cl_2 were condensed into a reaction vessel containing 9.90 mmoles of $B_2[N(CH_3)_2]_4$ at −196°. HCl (19.57 mmoles) was allowed to expand into the reaction mixture while stirring at −96°. The reaction mixture was allowed to stir over a temperature range of −96 to 25° for 15 hr. An insoluble white solid appeared in the reaction mixture. After distilling away the CH_2Cl_2 under vacuum, benzene extraction followed by crystallization from a benzene–pentane solvent system afforded the product as a white crystalline solid in yields estimated to be

90–95%. $B_2[N(CH_3)_2]_2(S_2C_2H_4)$ is soluble in most organic solvents.

Anal. Calcd for $C_6H_{16}N_2B_2S_2$: C, 35.68; H, 7.99; N, 13.87; B, 10.71; S, 31.75; mol wt, 201.98. Found: C, 35.34; H, 7.98; N, 13.74; B, 10.50; mol wt, 219 (0.040 *m*) and 236 (0.064 *m*) in benzene. Base hydrolysis gave 0.98 mole of hydrogen per mole of $B_2[N(CH_3)_2]_2(S_2C_2H_4)$.

X-Ray powder diffraction pattern data, *d* (relative intensity): 7.69 (m), 6.68 (vs), 6.05 (m), 5.56 (vs), 5.01 (m), 4.18 (s), 4.00 (m), 3.83 (s), 3.58 (vs), 3.36 (vs), 3.17 (m), 2.468 (vw), 2.404 (vw), 2.292 (vw), 2.161 (vw), 2.113 (vw), 1.965 (vw), 1.920 (vw), 1.823 (w).

Infrared spectrum (KBr, cm^{-1}): 3106 (w), 2907 (s), 2786 (m), 1508 (sh), 1495 (m), 1450 (m), 1449 (m), 1404 (m), 1381 (s), 1284 (s), 1266 (s), 1198 (m), 1136 (m), 1110 (s), 1055 (vw), 1012 (m), 993 (m), 897 (s), 801 (vw), 767 (vw), 676 (m), 571 (vw).

8. **$B_2(S_2C_2H_4)_2[NH(CH_3)_2]_2$.**—$B_2[N(CH_3)_2]_4$ (4.3 mmoles) and $HSCH_2CH_2SH$ (9.2 mmoles) were mixed together in a closed system without solvent. The mixture was agitated and allowed to equilibrate at room temperature. Crystals slowly began to form at the interface of the liquid mixture and the glass walls of the reaction vessel. The reaction mixture was allowed to stand overnight, yielding a pinkish solid plus excess $HSCH_2CH_2SH$. Recrystallization of this solid from a benzene–pentane solution afforded a white crystalline product. It is soluble in common organic solvents and appears to be stable with respect to evolution of $NH(CH_3)_2$.

Anal. Calcd for $C_8H_{22}N_2B_2S_4$: C, 32.44; H, 7.49; N, 9.46; B, 7.31; S, 43.31; mol wt, 296.22. Found: C, 32.26; H, 7.33; B, 7.13; mol wt, 285 (0.012 *m*) in benzene. Base hydrolysis gave 0.86 mole of hydrogen per mole of $B_2(S_2C_2H_4)_2 \cdot 2NH(CH_3)_2$.

X-Ray powder diffraction pattern data, *d* (relative intensity): 8.93 (m), 7.53 (s), 6.84 (vs), 5.74 (vs), 5.37 (w), 4.98 (m), 4.28 (s), 3.98 (w), 3.65 (m), 3.39 (vw), 3.18 (w), 3.02 (w), 2.931 (m), 2.849 (w), 2.780 (vw), 2.698 (vw), 2.629 (vw), 2.417 (vw), 2.312 (w).

Infrared spectrum (KBr, cm^{-1}): 2994(m), 2915 (s), 2762 (m), 2421 (w), 1464 (s), 1418 (w), 1266 (s), 1222 (sh), 1132 (s), 1106 (m), 1026 (s), 948 (s), 895 (m), 799 (w), 766 (vw), 693 (w), 684 (w).

9. **$B_2[(NCH_3)_2C_2H_4]_2$.**—B_2Cl_4 (5.38 mmoles) and 25 ml of CH_2Cl_2 were distilled into a reaction vessel containing *sym*-dimethylethylenediamine (21.6 mmoles) at −196°. Reaction was allowed to take place over a temperature range of −78 to 25° for 17 hr, resulting in the formation of a white precipitate. After distilling away the CH_2Cl_2, extraction of the residue with benzene followed by pumping away the benzene afforded a white crystalline solid (mp 45–47°). An identical product (shown by X-ray powder diffraction data) was prepared by the transamination of $B_2[N(CH_3)_2]_4$ with *sym*-dimethylethylenediamine; lit. mp 43–44°, bp 85° (5 mm).[2] This compound is soluble in the common organic solvents.

Anal. Calcd for $C_8H_{20}N_4B_2$: C, 49.55; H, 10.40; N, 28.89; B, 11.16; mol wt, 193.92. Found: C, 49.31; H, 10.22; B, 11.02.

X-Ray powder diffraction pattern data, *d* (relative intensity): 8.46 (vs), 7.25 (s), 6.44 (vs), 4.86 (s), 4.37 (s), 4.22 (s), 4.02 (s), 3.83 (m), 3.75 (m), 3.61 (vs), 3.51 (s), 3.38 (m), 3.21 (vw), 2.641 (vw), 2.468 (w), 2.386 (vw), 2.049 (vw), 1.796 (vw).

Infrared spectrum (KBr, cm^{-1}): 2950 (m), 2849 (s), 2809 (s), 2762 (m), 1486 (m), 1470 (w), 1435 (m), 1426 (m), 1397 (sh), 1387 (s), 1264 (s), 1199 (s), 1059 (s), 971 (w), 648 (w), 638 (m), 624 (w), 543 (w), 526 (w), 519 (w).

10. **$B_2[(NH)_2C_6H_4]_2$.**—This compound was prepared by a procedure reported elsewhere through the transamination of $B_2[N(CH_3)_2]_4$ with phenylenediamine in a 1:2 molar ratio.[7,17] This compound showed good thermal and hydrolytic stability. Its low solubility in common organic solvents precluded molecular weight determinations. Attempts to prepare this compound through the reaction of B_2Cl_4 with *o*-phenylenediamine yielded impure material which could not be successfully purified.

Anal. Calcd for $C_{12}H_{12}N_4B_2$: C, 61.63; H, 5.17; N, 23.95; B, 9.25; mol wt, 233.86. Found: C, 61.39; H, 4.96; B, 9.31.

X-Ray powder diffraction pattern data, *d* (relative intensity): 12.03 (vs), 6.61 (m), 6.05 (m), 4.44 (vs), 3.93 (m), 3.78 (w), 3.63 (s), 3.32 (m), 3.17 (m), 3.07 (s), 3.02 (s), 2.826 (w), 2.637 (w), 1.821 (w), 1.726 (vw).

Infrared spectrum (KBr, cm^{-1}): 3425 (w), 3344 (m), 1608 (w), 1592 (m), 1510 (m), 1495 (sh), 1477 (s), 1399 (w), 1319 (s), 1255 (m), 1200 (vw), 1155 (m), 1044 (vw), 922 (w), 909 (w), 758 (m), 746 (s), 738 (m), 661 (m), 631 (m), 575 (w), 479 (m), 469 (vw), 426 (w).

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The Chemistry and Structure of Dioxygenyl Fluoroborate. Fluorine-18 Tracer Studies and Decomposition Kinetics

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O_2BF_4 has been prepared from the reaction of BF_3 with O_2F_2 or O_4F_2 at low temperatures. Isotopic tracer studies of the reaction indicate that the compound is dioxygenyl fluoroborate, $O_2{}^+BF_4{}^-$, rather than a coordination compound, $FO_2 \rightarrow BF_3$. It is suggested that O_2F is the intermediate in both the preparation and decomposition of O_2BF_4. The kinetic data for the thermal decomposition are consistent with the rate law $dP/dt = k_1K_{eq}{}^2/P_{BF_3}{}^2$. The data are explained in terms of the equilibrium $O_2BF_4(s) = O_2F(g) + BF_3(g)$ and a bimolecular process for decomposition of O_2F. Values for the product $k_1K_{eq}{}^2$ are presented for the range 0–32°, from which the sum $2\Delta H_s + E_a$ is found to be 40 kcal/mole.

Introduction

The existence of the dioxygenyl ion ($O_2{}^+$) in dioxygenyl hexafluoroplatinate[1] and in the salts of the group V fluorides[2] seems well established. The product of the reaction[3] of O_2F_2 with boron trifluoride (BF_3) is dioxygenyl fluoroborate (O_2BF_4).

$$O_2F_2 + BF_3 \longrightarrow O_2BF_4 + {}^1\!/_2F_2 \qquad (1)$$

There is no evidence to date, however, that O_2BF_4

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