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Boron–Sulfur Ring Compounds

By J. A. Forstner and E. L. Muetterties

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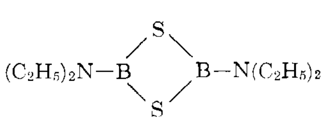
We wish to report a simple, direct synthesis of boron–sulfur ring structures. Hydrogen sulfide attacks trialkylamine boranes at 200° to give hydrogen, alkane, and the cyclic boron sulfides. The type of ring structure obtained is dependent upon the trialkylamine borane employed. With triethylamine borane, the dithiaboretane **1** is formed exclusively, whereas with the methyl analog the six-membered ring **2** (borthiin) is obtained. Compound **2** has been previously described by Wiberg and Sturm.[1] The dithiaboretane structure has been known only with B-sulfhydro[2,3] and B-ethylmercapto substituents.[1] Surprisingly, the highly strained ring of **1** is stable to 200° and does not rearrange to a borthiin structure as does $(HSBS)_2$.[1]



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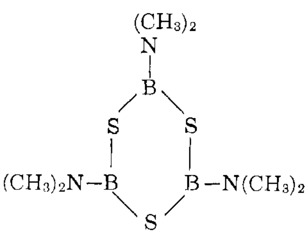

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Experimental Section

Materials.—Hydrogen sulfide (Matheson) was fractionated before use. Triethylamine borane was made in these laboratories and distilled, b.p. 65–68° (2 mm.). Trimethylamine borane (Callery) was used directly.

$(BN(C_2H_5)_2S)_2$.—Triethylamine borane (12.5 g., 0.1 mole) and hydrogen sulfide (6.5 g., 0.2 mole) were heated at 200° for 3 hr. in a 100-ml. stainless steel bomb. The gaseous products were vented and burned in a gas–oxygen flame. The viscous liquid product was heated under vacuum at 100°, yielding a white, solid sublimate. The latter was resublimed and crystallized from pentane to yield 4.2 g. of a white, very hygroscopic solid, soluble in chloroform and carbon tetrachloride, and melting at 70° under vacuum.

Anal. Calcd. for $B_2S_2N_2C_8H_{20}$: C, 41.8; H, 8.78; N, 12.2; B, 9.39; S, 27.9. Found: C, 42.4, 42.1; H, 8.80, 8.98; N (Kjeldahl), 12.0, 12.1; N (Dumas), 12.4, 12.5; B, 9.43, 9.44; S, 28.6, 28.5.

Molecular weight measurements confirm the proposed formulation: calcd. 230; found, cryoscopically in benzene (14 mg./100 g. of benzene), 234; ebullioscopically in carbon tetrachloride (0.11–0.49 mg./100 g. of CCl_4), 232. Mass spectral data, obtained by direct injection into the heated inlet of a spectrometer, confirmed these molecular weight data. The infrared spectrum (as a Nujol mull) included absorptions at 1715 (w), 1695 (w), 1635 (w), 1315 (m), 1265 (s), 1215 (m), 1190 (s), 1130 (s), 1095 (m), 1080 (m), 1065 (m), 995 (m), 980 (m), 945 (m), 885 (m), 830 (m), and 780 (m) cm.$^{-1}$.

The proton n.m.r. spectrum (carbon tetrachloride solution) consists of a distinct methylene quartet and methyl triplet at −3.3 and 1.2 p.p.m., respectively, referenced to external tetramethylsilane. The B^{11} resonance spectrum in the same solvent consists of a singlet at −18.5 p.p.m., referenced to external trimethyl borate.

$(BN(CH_3)_2S)_3$.—Trimethylamine borane (7.3 g., 0.1 mole) and hydrogen sulfide (6.5 g., 0.2 mole) were heated in a 100-ml. stainless steel bomb at 200° for 3 hr. The volatile products were vented and burned. The white, solid product was sublimed twice under vacuum at 200° to yield 4.7 g. of white solid, moderately soluble in acetone and chloroform and melting at 117° (lit.[1] 118°).

Anal. Calcd. for $B_3S_3N_3C_6H_{18}$: C, 27.6; H, 6.91; N, 16.1; B, 12.4; S, 36.9. Found: C, 28.4, 27.6; H, 6.79, 7.12; N, 15.9; B, 12.8; S, 38.6.

The infrared spectrum (as a Nujol mull) consisted of absorptions at 1300 (m), 1230 (w), 1190 (m), 1100 (s), 1080 (m), 1060 (m), 1000 (w), 975 (s), 930 (s), and 715 (w) cm.$^{-1}$.

The molecular weight found ebullioscopically in chloroform (0.20–1.00 mg./100 g. of $CHCl_3$) was 239 (calcd. for trimer, 261). The mass spectrum obtained by direct injection (system held at 70°) demonstrated the molecular weight to be 261. The peak at m/e 260 was 70% as intense as that at m/e 261, as would be predicted for three boron atoms in the molecule.

The H^1 resonance spectrum ($CDCl_3$ solution) consists of a singlet at −2.4 p.p.m. referenced to external tetramethylsilane. The B^{11} spectrum was a singlet at −20.1 p.p.m., referenced to external trimethyl borate.

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[1] E. Wiberg and W. Sturm, *Z. Naturforsch.*, **8b**, 689 (1953); **10b**, 108 (1955); *Angew. Chem.*, **67**, 483 (1955).

[2] E. Wiberg and W. Sturm, *Z. Naturforsch.*, **8b**, 530 (1953).

[3] A. Stock and O. Poppenberg, *Ber.*, **34**, 399 (1901).

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Phosphorus–Fluorine Chemistry. XVII.[1] Nuclear Magnetic Resonance Studies of Pentafluorophosphates

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In a previous communication[2] we have reported the unusual rearrangement of the covalent $C_6H_5PF_3N(CH_3)_2$ into the ionic $[C_6H_5PF[N(CH_3)_2]_2]^+[C_6H_5PF_5]^-$. The rearrangement was found to occur most rapidly for the product obtained by the dimethylaminolysis of $C_6H_5PF_4$ in ether at 0°[3]

$$2C_6H_5PF_4 + 2(CH_3)_2NH \longrightarrow C_6H_5PF_3N(CH_3)_2 + [(CH_3)_2NH_2]^+[C_6H_5PF_5]^-$$

We have now carried out the dimethylaminolysis with CH_3PF_4 and find that the $CH_3PF_3N(CH_3)_2$ formed undergoes the same type of rearrangement. While the F^{19} n.m.r. spectrum of $[CH_3PF_5]^-$ shows a simple first-order pattern, the F^{19} spectrum[2,3] of $[C_6H_5PF_5]^-$ is more complicated because of the closeness of the chemical shifts between the two different fluorine atom en-

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[1] Previous paper in this series: R. Schmutzler, *J. Chem. Soc.*, 5630 (1965).

[2] R. Schmutzler, *J. Am. Chem. Soc.*, **86**, 4500 (1964).

[3] R. Schmutzler and G. S. Reddy, *Inorg. Chem.*, **4**, 191 (1965).