

Experimental Section

Solvents.—Ethanol was distilled from ethyl phthalate-sodium ethoxide, methanol was distilled from magnesium amalgam.

Salts.—Trimethylsulfonium iodide was precipitated from a mixture of methyl iodide and excess dimethyl sulfide left for over 24 hr in nitromethane at room temperature. It was converted to the hydroxide with moist silver oxide, and then to the appropriate $(\text{CH}_3)_3\text{SX}$ compound by neutralization with HX ($\text{X} = \text{Cl}, \text{Br}, \text{ClO}_4, \text{NO}_3$). These salts and all lithium or sodium salts were recrystallized from acetone-ether mixtures and dried *in vacuo* at 50° for at least 48 hr. They were neutral in aqueous solution. In the cases where AgX is only sparingly soluble, the purity of $(\text{CH}_3)_3\text{SX}$, NaX , and LiX was confirmed by a potentiometric titration against standard silver nitrate. For reactions in the presence of a buffer salt (*cf.* Table I), trimethylsulfonium perchlorate and the sodium or lithium salts of X were mixed in the solvent without isolation of Me_3SX . This was an advantage for $\text{X} = \text{OEt}$, because the salt is difficult to isolate without decomposition. Trimethylsulfonium fluoride was prepared from $(\text{CH}_3)_3\text{SClO}_4$ and potassium fluoride by precipitation of KClO_4 .

Technique of Runs.—Reactions were carried out in sealed tubes at 100.0° in an oil-bath thermostat. Triplicate tubes were removed at each time interval, the contents poured into ice-water, and X^- was estimated potentiometrically with silver nitrate, for $\text{X} = \text{Br}, \text{Cl}, \text{I}, \text{SCN}, \text{N}_3$, and CN . With $\text{X} = \text{F}$, reaction was in sealed silver reaction tubes at 100°. The contents of duplicate tubes were washed into cold methanol and nitrogen was bubbled through each to remove methyl fluoride and dimethyl sulfide. An equal volume of excess sodium methoxide was added to each sample and one sample was analyzed immediately for methoxide by titration with hydrochloric acid to pH 4. The other sample was heated at 100° for 2 hr to decompose $(\text{CH}_3)_3\text{S}^+$ (reaction 1, $\text{X} = \text{OMe}$) and was then analyzed for methoxide as above. The differences between the two titrations gave the concentration of $(\text{CH}_3)_3\text{S}^+$ which had not reacted with fluoride ion in the original sample. Methanolysis accompanied attack by fluoride ion, as shown by formation of acid during reaction. This was allowed for¹⁸ in the calculation of k_2 for reaction 1 ($\text{X} = \text{F}$).

Solvolytic of trimethylsulfonium perchlorate was followed by measuring $d[\text{H}^+]/dt$ by titration with sodium hydroxide. Reaction 1 ($\text{X} = \text{OEt}$) was killed with excess hydrochloric acid and back-titrated with sodium hydroxide.

Reactions were rarely followed to >30% completion because solvolysis of CH_3X and the reverse reaction (1) interfered with the kinetics in some cases ($\text{X} = \text{I}$). The pH of each sample was measured ($\text{X} = \text{Br}, \text{Cl}, \text{I}, \text{SCN}, \text{N}_3, \text{SCN}$). Acid was often detected after 20% reaction ($\text{X} = \text{halogen}$) at high ionic strength; such samples were affected by solvolysis and were not used in the calculation of rate constants.

Calculation of Rate Constants.—Equation 19 was used to calculate rate constants.

$$k_2^\mu = \frac{x}{at_x(a-x)} \quad (19)$$

where x is the decrease of $[\text{X}^-]$ in time t_x between two successive samples, a and $a - x$ are the stoichiometric concentrations of X^- at the first and the second of two successive samples, respectively, and μ is the mean ionic strength between the two successive samples.

Reaction Products.—Dimethyl sulfide was identified as the mercuric chloride complex,¹⁹ and consumption of X^- was followed with silver nitrate. Acid was not produced in samples used for estimation of rate constants except for solvolysis reactions and attack by fluoride ion. Methyl cyanide from (1) ($\text{X} = \text{CN}$) was hydrolyzed and the ammonia was estimated.²⁰ The yield was quantitative, showing that CH_3NC was not formed.

Conductance of Trimethylsulfonium Bromide.—The conductance of this salt in dry ethanol was measured⁷ at 25 and 72° in a tightly stoppered cell. Measurements were made between 10^{-2} and $10^{-4} M$. Association constants were calculated by the Fuoss method.²¹ A linear extrapolation of $K_{25} = 320$ and $K_{72} = 450$ gave $K_{100} = 550$.

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The Boron-Nitrogen Bond from the Boron-Sulfur Bond

S. JERUMANIS AND J. M. LALANCETTE

Department of Chemistry, University of Sherbrooke, Sherbrooke, Quebec, Canada

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Boron sulfide and alkyl orthothioborates react with primary and secondary amines and with hydrazines to give aminoboron derivatives.

The boron-nitrogen bond can be formed by means of several types of reactions between organic bases and inorganic sources of boron. Boron halides,^{1,2} boron hydrides,^{3,4} and organometallic derivatives with boron halides^{5,6} have been used as sources of compounds containing boron and nitrogen. In the course of a systematic investigation of the reactivity of boron sulfide toward organic molecules, the reaction of B_2S_3 with bases (amines and hydrazines) as a source of nitrogen derivatives of boron has been examined.

Mikhailov and his co-workers have reported the formation of the B-N bond starting from the B-S bond.^{4,7}

In one instance the new nitrogen derivative of boron was obtained by the action of 1,6-hexanediamine on 2,4,6-triisobutylthio-1,3,5-trimethylborazine to give polymeric material. But neither boron sulfide (B_2S_3) nor orthothioboric esters $[(\text{RS})_3\text{B}]$ have been used as starting material for the preparation of aminoboron compounds. In fact, dialkyl alkylthioborate esters have been prepared by the reaction of alkanethiols with trimethylamine alkylboranes.⁸

We have already shown that boron sulfide behaves as a dehydrogenating agent with organic molecules containing labile hydrogens, such as alcohols, mercaptans, and active methylene groups,⁹⁻¹¹ and it was expected that the hydrogen carried by amino groups would be reactive enough to interact with B_2S_3 .

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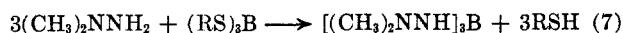
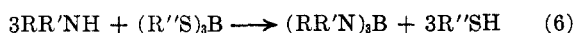
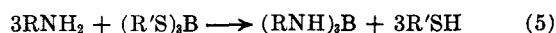
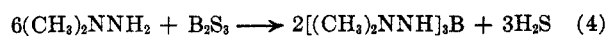
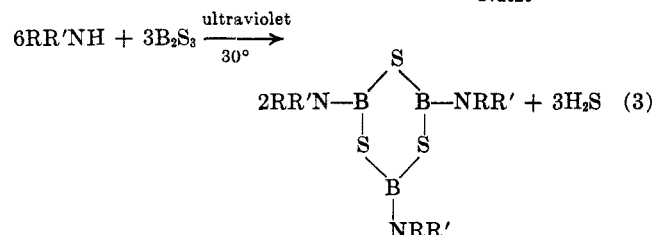
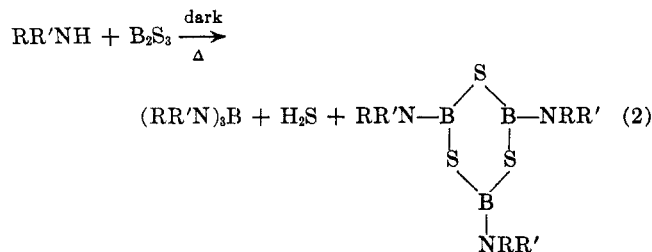
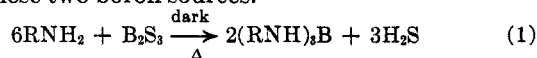
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Results and Discussion

Several nitrogen bases reacted with boron sulfide and orthothioboric esters. The following series of reactions (1-8) sums up the behavior of these bases toward these two boron sources.



Reactions using boron sulfide as starting material (eq 1-4) proceeded even at room temperature without dilution but were generally performed in the presence of benzene or toluene at reflux temperature in order to accelerate the reaction. Generally, primary and secondary amines (aniline, diethylamine) led mainly to the corresponding trisaminoboron derivative. In the case of diethylamine the trisamino derivative was accompanied by lesser amounts of borosulfide. However, the course of the reaction of diethylamine with B_2S_3 can be oriented toward the production of diethylaminoborosulfide exclusively, according to eq 3, if the reaction mixture is irradiated with ultraviolet light.

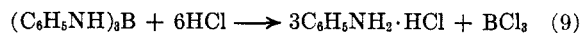
With hydrazines, only *N,N*-dimethylhydrazine has given a stable boron derivative (eq 4 and 7). Unsubstituted hydrazine or phenylhydrazine gave very unstable compounds either with boron sulfide or alkyl orthothioborates. In one instance such a compound, obtained from anhydrous hydrazine and ethyl orthothioborate, has decomposed spontaneously and explosively.

The nature of the tris(1,1-dimethylhydrazo)boron given by reactions 4 and 7 has been ascertained by molecular weight determination, analysis for boron, and infrared spectroscopy. Although the molecular weight and the boron analysis (titrimetric determination, in presence of mannitol¹²) are in excellent agreement with the calculated values, it has been impossible to obtain good results for C, H, and N through the standard microanalytical techniques because of incomplete combustion.

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The infrared spectrum of *N,N*-dimethylhydrazoboron is also in accordance with the proposed formula. It has been reported¹³ that in compounds such as borazoles, the B-N stretching frequency is to be found between 1373 and 1472 cm^{-1} . The boron derivative of 1,1-dimethylhydrazine gives a band of medium intensity at 1336 cm^{-1} that could be attributed to the B-N stretching in this molecule. If this interpretation is accepted, one should conclude that the B-N band shows considerable double bond character. This conclusion is supported by the abnormally high N-H stretching frequency found at 3440 cm^{-1} . The highest NH frequency found in 1,1-dimethylhydrazine is at 3340 cm^{-1} . Such a high NH frequency (3420 cm^{-1}) is reported for tris(diethylamino)boron.¹⁴ Double bond character has also been indicated by Werner and O'Brien¹⁵ for the B-O bond in orthoboric esters, from spectroscopic evidence.

It has been reported² that tris(phenylamino)boron gives trichlorotriphenylborazole and aniline hydrochloride when treated with hydrochloric acid. Under anhydrous conditions, in benzene, and with an excess of acid, we have found that HCl reacts to give boron trichloride rather than trichlorotriphenylborazole. A quantitative yield of aniline hydrochloride and boric acid (after hydrolysis of BCl_3 by water) was obtained from this reaction, according to eq 9.



The stability of boron nitride toward hydrolysis has been shown to be determined to a large extent by the method used for the preparation of the sample. If the compound is prepared at high temperature (1600°), it is almost inert toward water¹⁶ and is then well crystallized. However, a low temperature of formation gives an amorphous molecule much more sensitive to water.¹⁷ Our results are in agreement with these earlier reports; the material that we obtained by ammonolysis of butyl orthothioborate at room temperature gave no definite pattern on X-ray diffraction analysis and was slowly decomposed by atmospheric moisture. The Kjeldahl determination brought about a quantitative decomposition of the material, as indicated by the result of this analysis.

Of the amines examined, only *p*-nitrosoaniline and diphenylamine failed to react.

Experimental Section¹⁸

The Reaction of Amines with Ethyl Orthothioborate. A. Aniline.—To a solution of 3.48 g (0.018 mole) of ethyl orthothioborate in 20 ml of dry toluene, a solution of 5.00 g (0.054 mole) of aniline in the same amount of toluene was added slowly, at room temperature with stirring. The reaction mixture was then refluxed for 6 hr under a nitrogen atmosphere. This reflux was accompanied by an evolution of ethanethiol (infrared spectrum). On allowing the mixture to cool after the reflux, a white solid crystallized out which was tris(phenylamino)boron, mp 170–171° (lit.⁶ mp 170°), yield 83%.

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B. Diethylamine.—With diethylamine a similar technique gave tris(diethylamino)boron, bp 104–106° (9 mm) (lit.⁶ bp 200°), with a yield of 80%.

Reaction of Butyl Orthothioborate with Ammonia.—A solution of 10.0 g (0.036 mole) of butyl orthothioborate in 150 ml of dry carbon tetrachloride was stirred at room temperature for 3 hr in the presence of an excess of gaseous anhydrous ammonia. A white solid gradually precipitated and was filtered off. This material, containing boron and nitrogen but no sulfur, was boron nitride, 0.75 g (0.030 mole). A 0.1040-g sample gave 0.0705 g of NH₃ by the Kjeldahl method, corresponding to 56% N in the compound (calcd for BN, 56.5% N). The X-ray diffraction showed no definite pattern with this material, indicating that the product was amorphous.

The Reaction of Hydrazines with Orthothioboric Esters. A. Anhydrous Hydrazine.—A solution of 9.6 g (0.30 mole) of anhydrous hydrazine¹⁹ in 50 ml of chloroform was added slowly with stirring to a solution of 38.8 g (0.20 mole) of ethyl orthothioborate in 200 ml of the same solvent, under nitrogen atmosphere. The addition was slightly exothermic and was accompanied by precipitation of a white solid. This solid material contained sulfur, nitrogen, and boron, melted over 350°, and exhibited very poor stability. In one particular instance, it decomposed spontaneously and explosively while being kept in a desiccator under vacuum. Because of this instability, it has been found impossible to obtain much reliable information of the structure of this molecule. Determination of hydrazine by the potassium iodate method and boron (as boric acid on fresh sample) gave 37.6% NH₂-NH₂ and 8.0% boron. The molecule is very sensitive to water, giving ethanethiol, boric acid, and hydrazine on hydrolysis.

Similar behavior was observed with phenylhydrazine, the only difference being that the compound obtained was more unstable than the derivative of unsubstituted hydrazine. Atmospheric oxygen seems to have a particularly adverse effect of this compound since it turns red very rapidly when exposed to air.

B. 1,1-Dimethylhydrazine.—To a solution of 6.5 g (0.11 mole) of 1,1-dimethylhydrazine in 200 ml of toluene, a solution of 10.0 g (0.036 mole) of butyl orthothioborate in 200 ml of toluene was added with stirring. The reaction mixture was then refluxed for 3 hr and allowed to cool. A white solid crystallized out which contained boron and nitrogen but no sulfur. This material was stable, but very hygroscopic, giving 1,1-dimethylhydrazine and boric acid when treated with water. It melted at 99–101° with some decomposition. *Anal.* Calcd for C₈H₂₁BN₃: B, 5.75; mol wt, 188.087. Found: B, 5.70; mol wt (cryoscopy in benzene), 193, 199, 177, 187, 190 (av 189). The substance shows no absorption maximum between 200 and 400 m μ . In the infrared spectrum (CCl₄), it had bands at 3340 (m), 3380 (m), 3336 (m), and 1330 cm⁻¹ (m). For authentic 1,1-dimethylhydrazine, bands (CCl₄) were at 3340 (w), 3290 (vw), 3193 (m), and 3133 cm⁻¹ (m). No bands appear between 1431 and 12.97 cm⁻¹.

Reaction of Amino Groups with Boron Sulfide. A. Aniline.—To a well-stirred suspension of 6.25 g (0.053 mole) of boron sulfide in 50 ml of dry benzene was added slowly, at room temperature, a solution 47.4 g (0.51 mole) of freshly redistilled aniline in benzene. The addition was followed by a 24-hr reflux. All these operations were done under a dry nitrogen atmosphere and in darkness. The hot reaction mixture was filtered over an asbestos pad and gave white needles on cooling; a yield of 70% (based on aniline) of tris(phenylamino)boron, mp 169°, was obtained after recrystallization in benzene (lit.⁶ mp 170°). *Anal.*

Calcd for C₁₈H₁₈BN₃: C, 75.28; H, 6.31; N, 14.63. Found: C, 75.01; H, 6.31; N, 14.63.

The nitrogen carrying off the H₂S from the reaction gave 30.0 g of lead sulfide (98.6% of the expected amount) after washing with 10% lead acetate solution.

B. N,N-Dimethylhydrazine.—Using a similar technique with N,N-dimethylhydrazine, a yield of 69% of tris(N,N-dimethylhydrazo)boron, mp 99–101°, was obtained. The infrared spectrum of this substance was identical with that of the same molecule prepared from *n*-butyl orthothioborate.

C. α -Naphthylamine.—With α -naphthylamine, tris(α -naphthylamino)boron, mp 214–220°, was obtained (85% yield). This substance, being insoluble in benzene, was filtered with the excess of B₂S₃ and then extracted with CS₂. *Anal.* Calcd for C₃₀H₂₄BN₃: C, 82.32; H, 5.53; N, 9.61. Found: C, 82.41; H, 5.77; N, 9.25.

D. 4-Nitrosoaniline.—In the case of 4-nitrosoaniline, 55 g (0.45 mole) in benzene was refluxed for 24 hr in the presence of 8.0 g (0.67 mole) of boron sulfide. No evolution of H₂S was noted, and 52 g of 4-nitrosoaniline was recovered unchanged. The boron sulfide remained unaffected by the treatment.

E. Diphenylamine.—A solution of 67 g (0.40 mole) of diphenylamine, mp 53°, was refluxed for 42 hr in presence of 8.0 g (9.068 mole) of boron sulfide. The sulfide was recovered unaltered, and 65 g of diphenylamine, mp 51°, was obtained by evaporation of the benzene.

F. Diethylamine.—Using a similar technique except that the reaction was allowed to proceed in darkness, diethylamine (57 g, 0.78 mole) gave two products upon reaction with boron sulfide (total yield, 65–70%). The first fraction (60–65% of the total yield) was tris(diethylamino)boron, bp 59° (0.20 mm). *Anal.* Calcd for C₁₂H₃₀BN₃: C, 63.30; H, 13.31; N, 18.45. Found: C, 62.90; H, 13.31; N, 18.40. The second fraction, a yellow viscous oil (35–40% of the total yield), boiled at 114° (0.05 mm) and was tris(diethylamino)borosulfide. *Anal.* Calcd for C₁₂H₃₀B₃N₃S₃: B, 9.4; N, 12.10; mol wt, 344.9. Found: B, 9.05; N, 11.92; mol wt (cryoscopy in benzene), 342, 328, 374 (av 348). Hydrolysis by water of this material followed by titration allowed the recovery of 95% of the diethylamine as its hydrochloride. The infrared spectrum of the second fraction (CCl₄) had bands at 1260 (s), 1212 (w), 1187 (m), 1130 (m), 988 (w), and 970 cm⁻¹ (m). Infrared spectra of alkyl orthothioborates show bands in the region of 940 cm⁻¹.²⁰

When the same amounts of boron sulfide (suspension in benzene) and diethylamine were stirred at room temperature for 20 hr, under irradiation with ultraviolet light (a Hanovia Utility 140-w ultraviolet quartz lamp) through Pyrex, only tris(diethylamino)borosulfide was obtained.

Decomposition of Triphenylaminoboron by Anhydrous HCl.—A solution of 12.83 g (0.045 mole) of tris(phenylamino)boron in dry benzene was saturated with dry HCl gas at room temperature. A white precipitate appeared and was filtered off. This substance was aniline hydrochloride, mp 197–198°, 17.30 g (calculated according to eq 9, 17.37 g). The perfectly clear filtrate containing BCl₃ was shaken with distilled water for 2 hr, the benzene was decanted, and the acid solution was titrated to a phenolphthalein end point with 0.1 N NaOH. An excess of mannitol was then added and boric acid was determined by titration: found, 2.4 g of H₃BO₃; calcd, 2.76 g.

Acknowledgment.—The authors thank Professor A. Cabana for his comments on infrared spectra and the National Research Council of Canada and Defence Research Board of Canada for financial assistance.

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