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REACTIONS OF DISULFUR DINITRIDE WITH BORON TRIFLUORIDE  
AND BORON TRICHLORIDE

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Reactions of Disulfur Dinitride with Boron  
Trifluoride and Boron Trichloride

by R. Lyle Patton and William L. Jolly

Abstract

Disulfur dinitride reacts with boron trichloride in dichloromethane to form the following compounds (each of which can be obtained as the principal product by suitable choice of reaction conditions):  $S_4N_4BCl_3$ ,  $S_2N_2(BCl_3)_2$ , and an apparently polymeric material  $(S_2N_2BCl_3)_x$ . At  $0^\circ$ ,  $S_2N_2(BCl_3)_2$  loses  $BCl_3$  to form a simple adduct  $S_2N_2BCl_3$  which can be reconverted to the diadduct by treatment with  $BCl_3$  at  $-78^\circ$ . Whereas  $SbCl_5$  displaces  $BCl_3$  from  $S_2N_2BCl_3$  to form  $S_2N_2(SbCl_5)_2$ , the polymeric material  $(S_2N_2BCl_3)_x$  is inert toward both  $BCl_3$  and  $SbCl_5$ . The properties of  $S_2N_2BCl_3$  and  $S_2N_2(BCl_3)_2$  indicate that the  $S_2N_2$  ring structure remains intact. Reaction of  $S_2N_2$  with  $BF_3$  yields only  $S_4N_4BF_3$ .

In a study of the reactions of  $S_2N_2$  with  $SbCl_5$  we have shown that  $S_2N_2$  forms the adducts  $S_2N_2SbCl_5$  and  $S_2N_2(SbCl_5)_2$ , in which the  $S_2N_2$  ring remains intact.<sup>1</sup> To further explore the reactions of  $S_2N_2$  as a Lewis base and the effects of coordination upon its stability, this study has been extended to include boron trifluoride and boron trichloride.

### Experimental Section

General. The methods for the manipulation and characterization of volatile and moisture-sensitive materials and for the preparation of  $S_2N_2$  have been described.<sup>1</sup> Boron trichloride and boron trifluoride (Matheson) and antimony pentachloride (J. T. Baker Co.) were purified by vacuum-line fractional condensation. The observed 0° vapor pressure of the  $BCl_3$  was 477 mm (literature,<sup>2</sup> 477 mm). The observed -111.6° vapor pressure of  $BF_3$  was 310 mm (literature,<sup>3</sup> 312 mm). Boron trifluoride was measured by pressure-volume methods, and  $BCl_3$ ,  $SbCl_5$ , and  $S_2N_2$  by weight loss of tarred storage bulbs after distillation in vacuo into reaction vessels.

Reactions were normally carried out in a vacuum-line reactor consisting of a small Erlenmeyer flask attached by a 14/20 ground joint (sealed with Kel-F wax) to a Delmar-Urry 0-4 mm O-ring stopcock. The absence of grease prevented absorption of solvents and allowed use of the reactor as a tarred vessel for determining solid product weights. In a typical study,  $S_2N_2$  and  $CH_2Cl_2$  were distilled into the reactor and warmed to 20° to dissolve the  $S_2N_2$ , and then rapidly frozen at -196°. The volatile Lewis acid was then distilled in, and the reactor was warmed to the desired reaction

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temperature. The solvent and volatile products were removed and separated in vacuo, and the remaining non-volatile solids were weighed and then removed in the glove bag. Antimony pentachloride and  $\text{BF}_3$  could be cleanly fractionated from  $\text{CH}_2\text{Cl}_2$  and directly measured, whereas  $\text{BCl}_3$  could not and was determined by hydrolysis and titration of the boric acid with standard NaOH in the presence of mannitol.

Reaction of  $\text{S}_2\text{N}_2$  with  $\text{BF}_3$ .- Disulfur dinitride (0.71 mmole),  $\text{BF}_3$  (3.175 mmoles), and  $\text{CH}_2\text{Cl}_2$  (4 ml) were distilled into a reactor at  $-196^\circ$ . Upon warming to  $-78^\circ$ , a white suspension formed which became yellow at  $-45^\circ$ , brown at  $0^\circ$ , and slowly formed an intense burgundy solution at  $20^\circ$ . The  $\text{CH}_2\text{Cl}_2$  and excess  $\text{BF}_3$  (2.817 mmoles) were pumped off, leaving 84 mg. of a burgundy solid which was identified as  $\text{S}_4\text{N}_4\text{BF}_3$  on the basis of its infrared spectrum,<sup>4</sup> its melting point of  $145^\circ$  (literature,<sup>4</sup>  $145$ - $147^\circ$ ) and its characteristic of slowly losing  $\text{BF}_3$  when pumped on at room temperature. Complete conversion of  $\text{S}_2\text{N}_2$  to  $\text{S}_4\text{N}_4\text{BF}_3$  requires 0.355 mmoles of  $\text{BF}_3$  (observed, 0.358 mmole), forming 83 mg of  $\text{S}_4\text{N}_4\text{BF}_3$ .

$\text{S}_2\text{N}_2$ - $\text{BCl}_3$  Reaction at  $0^\circ$ .- Disulfur dinitride (1.55 mmoles),  $\text{BCl}_3$  (4.97 mmoles), and  $\text{CH}_2\text{Cl}_2$  (10 ml) were frozen together in a reactor at  $-196^\circ$ . The mixture was held at  $-78^\circ$  for 2 hrs. while the  $\text{CH}_2\text{Cl}_2$  melted and the solution above the white solid became slightly yellow. The mixture was then warmed slowly to  $0^\circ$  while stirring. Only slight darkening of the suspension occurred until the temperature reached  $-35^\circ$ , above which the suspension turned, in rapid succession, yellow, grey, grey-green, black, brown, and yellow. Then with brief effervescence, a dark red solution formed. During one half hour at  $0^\circ$  this solution slowly turned light orange, and a slight film of an orange plastic material appeared. The appearance

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of the solution was then unaffected by warming to 20° or cooling to -78°. The reaction mixture was held at -78° while BCl<sub>3</sub> was distilled off in vacuo and then warmed to 0° while removing the remaining CH<sub>2</sub>Cl<sub>2</sub>. A slight amount of N<sub>2</sub> (0.017 mmole) was evolved in the reaction. No precipitation occurred during the solvent removal, but as the last of the CH<sub>2</sub>Cl<sub>2</sub> distilled off, the solution darkened to orange-brown and finally left 0.314 g. of a solid plastic-like layer. (Calculated for 1.55 mmoles (S<sub>2</sub>N<sub>2</sub>BCl<sub>3</sub>)<sub>x</sub>: 0.324 g.) Repeated cooling to -196° and warming to 0° broke up this solid, but no further gases were evolved.

Several similar reactions were run with variations in the time held at -80°, the rate of warming, and the time held at 0°. The visual observations of the reactions and products were the same. All the results are summarized in Table I. Only N<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, BCl<sub>3</sub>, and slight traces of

Table I. Reactions of S<sub>2</sub>N<sub>2</sub> with BCl<sub>3</sub> at 0°

S <sub>2</sub> N <sub>2</sub> (mmoles)	BCl <sub>3</sub> S <sub>2</sub> N <sub>2</sub>	N <sub>2</sub> evolved (mmoles)	Product wt (mg)	Calculated for (S <sub>2</sub> N <sub>2</sub> BCl <sub>3</sub> ) <sub>x</sub> (mg)
0.54	5.1	trace	108	113
0.77	4.8	0.003	161	161
1.16	2.6	0.011	240	242
1.42	3.2	0.015	300	297
1.55	3.2	0.017	314	324
2.90	3.2	trace	607	607

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$S_2Cl_2$  were distilled from the reactions, leaving a product of composition  $(S_2N_2BCl_3)_x$ .

Nujol mulls of these products all absorbed strongly throughout the region  $670-1350\text{ cm}^{-1}$  with prominences on this general broad absorption occurring at  $1300, 1240, 1080, 970,$  and  $730\text{ cm}^{-1}$ . Broad absorptions also occurred at  $640$  and  $510\text{ cm}^{-1}$ . These absorption maxima differed slightly in different samples in position and relative intensity.

After removal from the reactor, the product did not redissolve in either  $CH_2Cl_2$  or  $CCl_4$  at  $20^\circ$ , although some darkening of the solvent and  $S_2Cl_2$  evolution occurred. Distillation of  $CH_2Cl_2$  back into the reactor once resulted in slight coloring of the solvent and release of  $S_2Cl_2$  and, in another case, in vigorous  $N_2$  evolution at  $-10^\circ$ .

In a sealed capillary the  $(S_2N_2BCl_3)_x$  remained solid on heating to  $360^\circ$  - becoming brown above  $120^\circ$  and shrinking with evolution of a yellow liquid above  $160^\circ$ . When  $(S_2N_2BCl_3)_x$  was held at  $20^\circ$  for 4 weeks or at  $55^\circ$  for 4 days, considerable decomposition occurred, with formation of  $BCl_3, S_2Cl_2, N_2$  and traces of  $SCl_2$ . Pyrolysis at  $90^\circ$  or higher yielded  $S_2Cl_2, SCl_2, N_2$ , and only traces of  $BCl_3$ . The relative amounts of the volatile products and the empirical composition of the residue did not correspond to any unique stoichiometry.

Liquid boron trichloride (10.70 mmoles) was distilled onto 161 mg. of  $(S_2N_2BCl_3)_x$ , and the mixture was held at  $0^\circ$  for 2 hours, then cooled to  $-78^\circ$  and held for one hour before pumping off the  $BCl_3$  at that temperature. Exactly 10.70 mmoles of  $BCl_3$  was recovered, indicating that no  $BCl_3$  uptake by  $(S_2N_2BCl_3)_x$  occurred at  $-78^\circ$ . Antimony pentachloride (3.11 mmoles) was

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then distilled onto the  $(S_2N_2BCl_3)_x$ , and the mixture was twice held at  $20^\circ$  for 30 min. followed by cooling to  $-78^\circ$  and pumping. No gases were removed. The reactor was then warmed to  $20^\circ$  while pumping to remove all the free  $SbCl_5$ . No  $BCl_3$  or other gases were removed and the product weight remained 161 mg. Antimony pentachloride obviously did not displace  $BCl_3$  from or add to the  $(S_2N_2BCl_3)_x$ .

$S_2N_2-BCl_3$  Reaction at  $-78^\circ$ . - When suspensions of  $S_2N_2$ ,  $CH_2Cl_2$  and excess  $BCl_3$  were held for extended periods at  $-78^\circ$  and then subjected to pumping at that temperature to remove the  $CH_2Cl_2$  and excess  $BCl_3$ , measurement of the unreacted  $BCl_3$  showed that products approaching the composition  $S_2N_2(BCl_3)_2$  were obtained. The reaction times and calculated  $BCl_3/S_2N_2$  ratios for the products for several runs were: 6 hr., 1.67; 15 hr., 1.83; 2.5 days, 1.865; 5 days, 1.96; 6.5 days, 1.83. When the product of the 6.5-day run (containing 0.86 mmole of  $S_2N_2$  and 1.57 mmoles of  $BCl_3$ ) was warmed slowly while pumping, the creamy white solid evolved 0.70 mmole of  $BCl_3$  between  $-35$  and  $0^\circ$ . Further pumping at  $0^\circ$  for 2 hrs. evolved 1 mg of  $S_2Cl_2$  and no  $BCl_3$ . These data correspond to an empirical product composition  $S_2N_2 \cdot 1.01 BCl_3$ ; the product weight (178 mg) was also in good agreement with that calculated for the formation of  $S_2N_2BCl_3$  (179 mg). (In each of the above runs, similar evolution of  $BCl_3$  on warming to  $0^\circ$  left a product composition of  $S_2N_2BCl_3$ .) The remaining solid was treated with a measured excess of  $BCl_3$  in  $CH_2Cl_2$  at  $-78^\circ$  for two hours, and then the reaction mixture was evacuated at that temperature. The product retained 0.625 mmole of the  $BCl_3$ , but all of this  $BCl_3$  was evolved when the product was again warmed to  $0^\circ$  in vacuo. In a repetition of this

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procedure without  $\text{CH}_2\text{Cl}_2$ , 0.615 mmole of  $\text{BCl}_3$  was retained at  $-78^\circ$  and then evolved at  $0^\circ$ . In a second repetition of the procedure, 0.56 mmole of  $\text{BCl}_3$  was retained at  $-78^\circ$  and then evolved at  $0^\circ$ . Then the remaining product was treated with 3.90 mmoles of antimony pentachloride at  $20^\circ$  for 1 hour. After cooling to  $-78^\circ$  for one half hr., the reactor was evacuated at  $-78^\circ$ , and  $\text{BCl}_3$  was removed. The reactor (still containing the  $\text{SbCl}_5$ ) was twice warmed to  $20^\circ$  and returned to  $-78^\circ$  for further  $\text{BCl}_3$  removal, then warmed to  $20^\circ$  to pump off the  $\text{SbCl}_5$ . The total  $\text{BCl}_3$  removed (0.55 mmole) corresponded to the  $\text{BCl}_3$  reversibly absorbed in the previous treatment (0.56 mmole). The weight gain, corrected for the  $\text{BCl}_3$  lost, corresponded to the absorption of 1.08 mmoles of  $\text{SbCl}_5$ .

A similar sequence of experiments, in which  $\text{BCl}_3$  was absorbed at  $-78^\circ$  and removed at  $0^\circ$ , was performed on the product of the 15-hr. run mentioned above containing originally 1.30 mmoles of  $\text{S}_2\text{N}_2$ . The final  $\text{BCl}_3$  treatment, in which 1.03 mmoles of  $\text{BCl}_3$  was evolved at  $0^\circ$ , was again followed by treatment with excess  $\text{SbCl}_5$ . 0.99 mmole of  $\text{BCl}_3$  was evolved while  $\text{SbCl}_5$  (2.05 mmoles) was retained. The infrared spectrum of the products after treatment with  $\text{SbCl}_5$  showed the presence of  $\text{S}_2\text{N}_2(\text{SbCl}_5)_2$ .<sup>1</sup> Extraction of the product with dichloromethane yielded a solution from which pure  $\text{S}_2\text{N}_2(\text{SbCl}_5)_2$  was obtained (identified by its infrared spectrum<sup>1</sup>) and left some residue with the appearance and infrared spectrum of  $(\text{S}_2\text{N}_2\text{BCl}_3)_x$ .

The creamy white products of composition  $\text{S}_2\text{N}_2\text{BCl}_3$  yellowed slightly when warmed at  $0^\circ$  during the course of subsequent  $\text{BCl}_3$  treatments, and slowly darkened to orange with evolution of  $\text{S}_2\text{Cl}_2$  when warmed above  $0^\circ$ . However, at  $-15^\circ$  in sealed tubes the material remained stable indefinitely

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without darkening or change in its infrared absorptions. In a sealed capillary it turned red-orange at 50° before melting at 55° with decomposition.

When dichloromethane was distilled onto  $S_2N_2BCl_3$  at -196° and warmed to -78°, the conversion of  $S_2N_2BCl_3$  to  $(S_2N_2BCl_3)_x$  occurred relatively rapidly, with rapid darkening of the solution. Whenever excess  $BCl_3$  was present, darkening of the solution did not occur until around -35°.

In Nujol mulls, the infrared spectra of fresh samples of  $S_2N_2BCl_3$  showed the following peaks (in  $cm^{-1}$ ): 1115 (ms), 950 (w), 840 (m), 788 (wm), 728 (s-broad), 682 (mw), 610 (ms), and 467 (m). An  $S_2N_2BCl_3$  sample was allowed to stand 24 hours at 20° and a Nujol mull taken; the  $S_2N_2BCl_3$  absorptions were gone and absorptions characteristic of  $(S_2N_2BCl_3)_x$  had appeared.

Addition of  $BCl_3$  to  $S_2N_2$  at 20°.- Slow addition of a  $BCl_3$  (2.20 mmoles) solution to  $S_2N_2$  (1.58 mmoles) in  $CH_2Cl_2$  at 20° in the glove bag resulted in a black, opaque suspension which cleared after several minutes to a dark red solution which finally turned orange-red. Concentration and cooling of this solution yielded pure crystals of  $S_4N_4BCl_3$  as shown by its infrared spectrum<sup>4</sup> and melting point of 136° (literature,<sup>4</sup> 137-138°). Infrared spectrometry indicated that the residue from evaporation of the remaining solvent consisted of  $S_4N_4BCl_3$ , with no  $S_4N_4$  or  $S_2N_2BCl_3$  impurity.

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(SN)<sub>x</sub> - BCl<sub>3</sub> Reaction. - A sample of (SN)<sub>x</sub> was obtained as a by-product from several S<sub>2</sub>N<sub>2</sub> preparations. It was separated from S<sub>4</sub>N<sub>4</sub> and sulfur impurities by repeated extraction with carbon disulfide until no further yellowing of the carbon disulfide occurred. This (SN)<sub>x</sub> was then weighed into a tarred reactor consisting of an O-ring stopcock attached to a 50 ml Erlenmeyer flask by a joint waxed with Kel-F wax. In one experiment, 1.185 g. of BCl<sub>3</sub> and 3 ml of CH<sub>2</sub>Cl<sub>2</sub> were distilled onto 172 mg of (SN)<sub>x</sub> in a reactor and held for 2 hours at 0°. No evidence of reaction was observed. The suspension was then warmed to 20° and held 4 days to yield an orange-yellow solid and orange solution together with approximately 10% of the original black particles of (SN)<sub>x</sub>. The yellow solid was filtered off and the orange filtrate was subjected to pumping at 0° for 1 day to remove the solvent, after which only an orange plastic film remained. Both this orange plastic film and the yellow solid exhibited infrared absorptions very similar to those of (S<sub>2</sub>N<sub>2</sub>BCl<sub>3</sub>)<sub>x</sub>. Upon heating in a sealed capillary the yellow solid behaved like (S<sub>2</sub>N<sub>2</sub>BCl<sub>3</sub>)<sub>x</sub>. It did not melt on heating to 360°, but darkened above 100° and shrank with evolution of a yellow liquid above 160°.

In a second experiment, 70 mg of (SN)<sub>x</sub> and 1.0445 g of BCl<sub>3</sub> were placed in a tarred reactor and held at 0° for 2 days with no reaction. Dichloromethane (5 ml) was distilled into the reactor, and the suspension was held with occasional stirring for 7 days, during which only slight yellowing of the solution occurred. The suspension was then stirred at 20° for 2 days, after which it appeared that all of the black (SN)<sub>x</sub> particles had been consumed, leaving an orange solution above a yellow solid. The solvent and excess BCl<sub>3</sub> were removed by pumping, first at -80° and then while warming to 0°, until all volatiles had been removed.

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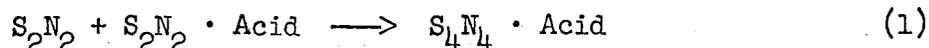
Nitrogen (0.080 mmole) was collected in the Toepler pump buret, and 124 mg of an orange-yellow solid remained. If we assume that the small amount of evolved nitrogen corresponded to the decomposition of some  $(SN)_x$  to the elements and that the principal product was  $(S_2N_2BCl_3)_x$ , we calculate that the residue should have weighed 147 mg. The infrared spectrum of the solid was the same as that of the product of the first reaction.

### Results and Discussion

Reaction with Boron Trifluoride.- When disulfur dinitride is added to excess boron trifluoride in dichloromethane, only  $S_4N_4BF_3$  is formed,

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whereas the analogous reaction with  $\text{SbCl}_5$  yields an adduct of  $\text{S}_2\text{N}_2$ . We believe the difference may be explained by the relative weakness of  $\text{BF}_3$  as a Lewis acid compared with  $\text{SbCl}_5$  and by the assumption that the  $\text{S}_4\text{N}_4$  acid adduct is formed by a second-order reaction:



In the case of  $\text{S}_2\text{N}_2\text{SbCl}_5$ , the equilibrium concentration of  $\text{S}_2\text{N}_2$  is too low for this reaction to proceed at an appreciable rate unless an excess of  $\text{S}_2\text{N}_2$  is added to the system. In the case of  $\text{S}_2\text{N}_2\text{BF}_3$ , the equilibrium concentration of  $\text{S}_2\text{N}_2$  is high enough for the reaction to proceed and to prevent the isolation of  $\text{S}_2\text{N}_2\text{BF}_3$ .

Reactions with Boron Trichloride at  $0^\circ$ .— The results of the reactions in which  $\text{S}_2\text{N}_2$  and  $\text{BCl}_3$  were warmed to  $0^\circ$  in dichloromethane show that a product of composition  $(\text{S}_2\text{N}_2\text{BCl}_3)_x$  was formed. However, the broad, diffuse, varying infrared spectra of these products showed no correspondence to known  $\text{S}_2\text{N}_2$ ,  $\text{S}_4\text{N}_4$ , or  $\text{BCl}_3$  adducts. Also, it was not possible to displace  $\text{BCl}_3$  from  $(\text{S}_2\text{N}_2\text{BCl}_3)_x$  with  $\text{SbCl}_5$  as might have been expected for a simple adduct inasmuch as  $\text{SbCl}_5$  is a stronger Lewis acid than  $\text{BCl}_3$  and does effect this displacement on  $\text{S}_4\text{N}_4\text{BCl}_3$ .<sup>2</sup> Thus it appears that  $(\text{S}_2\text{N}_2\text{BCl}_3)_x$  is not an adduct involving intact  $\text{S}_2\text{N}_2$  and  $\text{BCl}_3$  units, but rather that some degree of chlorination of the sulfur atoms and some polymerization has occurred. The inability of the product to dissolve after removal of the dichloromethane suggests that the degree of polymerization increased in the solid or highly concentrated state.

The reaction of polymeric sulfur nitride,  $(\text{SN})_x$ , with boron trichloride gives a material having the same properties and approximately the same composition as the  $(\text{S}_2\text{N}_2\text{BCl}_3)_x$  prepared from  $\text{S}_2\text{N}_2$  and  $\text{BCl}_3$  at  $0^\circ$ . However

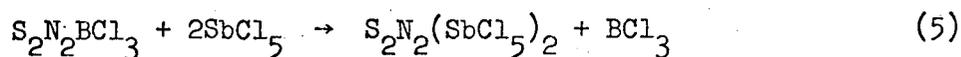
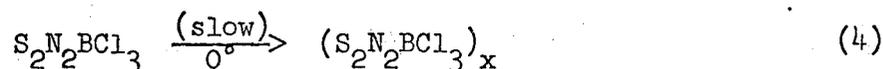
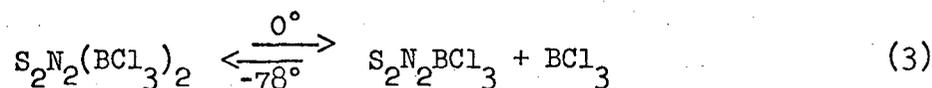
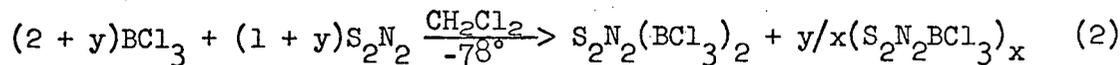
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the  $(\text{SN})_x\text{-BCl}_3$  reaction must be carried out at temperatures around  $20^\circ$ , and at these temperatures side reactions take place, precluding the isolation of a pure product.

Reactions with Boron Trichloride at  $-78^\circ$ .- The data for reactions performed at  $-78^\circ$ , in which the solvent and excess  $\text{BCl}_3$  were removed at that temperature, indicate the formation of a simple labile diadduct  $\text{S}_2\text{N}_2(\text{BCl}_3)_2$  and a small amount of  $(\text{S}_2\text{N}_2\text{BCl}_3)_x$ . The  $\text{S}_2\text{N}_2(\text{BCl}_3)_2$  dissociates reversibly on warming to  $0^\circ$  to  $\text{BCl}_3$  and a monoadduct  $\text{S}_2\text{N}_2\text{BCl}_3$ . The ability of  $\text{S}_2\text{N}_2\text{BCl}_3$  to add  $\text{BCl}_3$  at low temperatures distinguishes it from  $(\text{S}_2\text{N}_2\text{BCl}_3)_x$ , which is inert to addition of a second mole of  $\text{BCl}_3$ . The slight decrease in the  $\text{BCl}_3$  reversibly absorbed after each successive  $\text{BCl}_3$  replacement was probably caused by a slight amount of the irreversible rearrangement (polymerization)  $\text{S}_2\text{N}_2\text{BCl}_3 \rightarrow (\text{S}_2\text{N}_2\text{BCl}_3)_x$  occurring at temperatures near  $0^\circ$ . This latter reaction occurs readily in dichloromethane solution whenever excess boron trichloride is absent, even at low temperatures. Apparently the polymerization is blocked when both nitrogens of  $\text{S}_2\text{N}_2$  are coordinated to  $\text{BCl}_3$ . The amount of  $\text{BCl}_3$  reversibly absorbed is a measure of the monoadduct  $\text{S}_2\text{N}_2\text{BCl}_3$  present in a mixture of  $\text{S}_2\text{N}_2\text{BCl}_3$  and  $(\text{S}_2\text{N}_2\text{BCl}_3)_x$ , as evidenced by the displacement, on treatment with  $\text{SbCl}_5$ , of  $\text{BCl}_3$  in only the amount equal to that reversibly absorbed in the previous  $\text{BCl}_3$  treatment. This displacement of  $\text{BCl}_3$  to form the known<sup>1</sup> disulfur dinitride adduct  $\text{S}_2\text{N}_2(\text{SbCl}_5)_2$  is in agreement with the relative Lewis acid strengths of  $\text{SbCl}_5$  and  $\text{BCl}_3$  and supports the formulation of  $\text{S}_2\text{N}_2\text{BCl}_3$ , and  $\text{S}_2\text{N}_2(\text{BCl}_3)_2$  as adducts of  $\text{S}_2\text{N}_2$ . The residue of  $(\text{S}_2\text{N}_2\text{BCl}_3)_x$  left after washing out the  $\text{S}_2\text{N}_2(\text{SbCl}_5)_2$  further confirms its presence as the inert material. The data presented correspond quantitatively

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to the reactions:

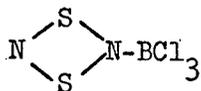


Formation of  $S_4N_4BCl_3$ .-- The formation of  $S_4N_4BCl_3$  by the addition of  $BCl_3$  to an  $S_2N_2$  solution is analogous to the formation of  $S_4N_4SbCl_5$ <sup>1</sup> and  $S_4N_4BF_3$  from  $S_2N_2$ . In each of these reactions, the mechanism is probably the initial formation of an adduct of the type  $S_2N_2 \cdot \text{Acid}$ , followed by reaction 1.

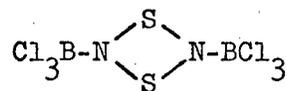
In adducts in which the boron atom of  $BCl_3$  is bonded directly to the central atom of a Lewis base molecule, a broad infrared absorption envelope characteristic of the  $BCl_3$  portion of the adduct is found with maxima in the 700-800  $cm^{-1}$  region.<sup>5</sup> Also, sulfur-nitrogen compounds usually have strong absorptions in and near this region. For example,  $S_2N_2$ ,<sup>6</sup>  $S_2N_2SbCl_5$ ,<sup>1</sup> and  $S_2N_2(SbCl_5)_2$ <sup>1</sup> have absorptions at 795 and 663  $cm^{-1}$ , 800 and 723  $cm^{-1}$ , and 818  $cm^{-1}$ , respectively. It seems likely that all of the infrared absorptions of  $S_2N_2BCl_3$  near this region (at 840 (m), 788 (wm), 728 (s-broad) and 682 (mw)  $cm^{-1}$ ) may result from combinations

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of S-N and  $\text{BCl}_3$  modes. The remaining  $\text{S}_2\text{N}_2\text{BCl}_3$  absorptions (at 1115, 950, 610, and  $467\text{ cm}^{-1}$ ) correspond closely in position and shape to absorptions in  $\text{S}_2\text{N}_2\text{SbCl}_5$ . Thus the infrared and chemical evidence support formulation of  $\text{S}_2\text{N}_2\text{BCl}_3$  and  $\text{S}_2\text{N}_2(\text{BCl}_3)_2$  as adducts of the same type as those of  $\text{S}_2\text{N}_2$  with  $\text{SbCl}_5$  with the structures:



and



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## References

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