synthesis of B_2D_6. It should be noted that exposure of the product to air causes reappearance of the B–H IR absorption after several minutes. Evidently hydrogen reexchange with moisture in the air occurs readily. The melting point of $(CH_3)_3N{\cdot}BD_3$ was 93–94 °C (lit.[2] mp 94 °C).

Nöth and Beyer[5] reported a method for the generation of diborane from trimethylamine–borane involving the apparent Lewis acid displacement reaction shown in eq 2. Their report

$$(CH_3)_3N{\cdot}BH_3 + BF_3{\cdot}O(C_2H_5)_2 \xrightarrow{(C_2H_5)_2O} (CH_3)_3N{\cdot}BF_3 + (C_2H_5)_2O + {}^1/_2B_2H_6 \qquad (2)$$

indicates the use of diethyl ether as solvent for the reaction but, in our hands, dichloromethane was preferable. (Our attempted use of ether as a solvent gave only 20–30% isolated yields of diborane.) In a typical reaction 2.10 g (27.4 mmol) of $(CH_3)_3N{\cdot}BD_3$ was placed in a 250-ml flask connected to a vacuum line via a Teflon valve and glass O-ring joint. The bulb was evacuated and 40 ml of dry CH_2Cl_2 along with 24.0 mmol of BF_3 condensed in at −196 °C. (Note: trimethylamine–borane is appreciably volatile at 25 °C and is rapidly pumped away if not cooled during evacuation.) The Teflon valve was then closed and the reaction mixture allowed to warm to room temperature with stirring. After 18 h the contents of the flask were fractionated through traps at −78, −130, and −196 °C until no more B_2D_6 collected in the −196 °C trap. The yield was 11.6 mmol (96.6%, based on BF_3) and the product was identified by its IR spectrum. Careful comparison of the spectra of the product and those of B_2D_5H and B_2D_6[6] showed that little if any of the former was present.

In order to avoid contamination of the product with BF_3 it is essential to use at least a 15 mol % excess of $(CH_3)_3N{\cdot}BD_3$, which may be recovered from the solid residue of the reaction by fractional sublimation. Trifluoroborane is difficult to fractionate from B_2D_6 but can be removed from BF_3/B_2D_6 mixtures by reaction with additional $(CH_3)_3N{\cdot}BD_3$. We have found in earlier studies[7] that about 3 mol % of $(CH_3)_3N{\cdot}BF_2H$ is formed in this reaction but this was considered a negligible loss of yield. Other acids such as BCl_3 and BBr_3 are unsuitable for the displacement because of halogen–hydrogen exchange.

The overall yield in the synthesis of B_2D_6 depended strongly on the extent of deuteration desired. When 90–93% deuterium sufficed, the overall yield was about 68%, but, if nearly quantitative deuteration was desired, the yield decreased to about 58% (assumes recovery of excess $(CH_3)_3N{\cdot}BD_3$ used in the second step).

Scale-up of the reaction appears to be limited only by the capacity of the fractionation train used to isolate the B_2D_6. Thus far the largest single reaction we have carried out produced 25 mmol of B_2D_6. A possible hazard exists during the second step if air is inadvertently admitted to the reaction vessel.

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Registry No. $(CH_3)_3N{\cdot}BH_3$, 75-22-9; $(CH_3)_3N{\cdot}BD_3$, 1538-39-2; B_2D_6, 20396-66-1.

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Gas-Phase Reaction of Ammonia with Thionyl Chloride

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The gas-phase reaction of ammonia with thionyl chloride was reported by Schenk in 1942.[3] The products of the reaction were observed to be thionyl imide, HNSO, and ammonium chloride according to the reaction

$$SOCl_2(g) + 3NH_3(g) \rightarrow HNSO(g) + 2NH_4Cl(s) \qquad (1)$$

Subsequent to this initial preparation of thionyl imide its infrared,[4] microwave,[5] ultraviolet,[6] and photoelectron spectra[7] and the photolysis of matrix-isolated[8] HNSO have been reported. In addition to the stoichiometric products shown in eq 1, SO_2 was also observed in varying amounts depending upon the experimental conditions.[4–6] The most obvious explanation for the production of SO_2 involves the reaction[9]

$$HNSO + H_2O \rightarrow SO_2 + NH_3 \qquad (2)$$

which could result from water contamination of either the reagents or the vacuum line. Kirchoff[5] noted that the relative amount of SO_2 could be decreased by carrying out the reaction at low pressures (12 Torr of NH_3 and 4 Torr of $SOCl_2$) and that the amount of SO_2 remained relatively constant with time whereas the amount of HNSO decreased. This was an indication that SO_2 was formed during the initial reaction only.

The subject of this note is that thiazyl chloride, NSCl, has been detected as one of the products in the gas-phase reaction of $SOCl_2$ with NH_3. This fact points to a side reaction that is consistent with the production of SO_2 in the initial reaction even when stringent experimental conditions have excluded moisture from the reagents and the vacuum line.

Experimental Section

A standard Pyrex vacuum line utilizing a mercury diffusion pump was employed. A liquid air trap was used to protect the vacuum line from mercury vapor and to protect the mechanical pump and the diffusion pump from ammonia and thionyl chloride vapors. Greaseless "O-ring" seal joints and "O-ring" taps were employed throughout. These joints and taps are capable of 10^{-6} Torr and were purchased from J. Young Ltd., Acton, London. The segment of the vacuum line used for preparing thionyl imide had three greaseless O-ring taps and a vacuum gauge purchased from Gallenkamp (GJ 330), London. This gauge can measure pressures 0–760 Torr with an accuracy of about 10 Torr. One of the O-ring taps had socket joints to connect the 10-cm infrared cell or the 10-cm optical cell for visible and ultraviolet spectra. The other two O-ring taps had socket joints to which the reaction vessel and the ammonia cylinder (Matheson lecture bottle) could be joined.

The reaction vessel was a 1-l. bulb fitted with two greaseless O-ring taps. The upper tap had a greaseless O-ring ball joint to fit the socket on the vacuum line and the lower tap had an O-ring seal joint to connect the tube containing thionyl chloride, $SOCl_2$ (Fluka AG). This tube was fitted with an O-ring seal joint and a few milliliters of $SOCl_2$ was introduced in the dry box. Prior to carrying out any reaction the NH_3 and $SOCl_2$ were degassed of noncondensable vapors by carrying out several freeze–thaw cycles with liquid air. In addition, the ammonia was passed over KOH pellets in a U-tube and subsequently condensed over small pieces of sodium metal to ensure dryness. Ultraviolet and visible spectra were recorded on a Perkin-Elmer 450 instrument and infrared spectra were recorded on a Perkin-Elmer 137 instrument.

Two methods were employed in the preparation of thionyl imide. In the "higher" pressure runs the $SOCl_2$ was first admitted to the 1-l. reaction bulb at a pressure of 70 Torr. Ammonia gas was then admitted in three aliquots which previous calibration experiments showed would give a final NH_3 pressure of 210 Torr. Upon release of the NH_3 gas into the 1-l. reaction bulb containing $SOCl_2$ vapor, reaction was observed by the formation of a white cloud of NH_4Cl and of yellowish and sometimes brownish polymers.[3] The infrared spectrum of the gaseous reaction product always showed the formation of considerable amounts of SO_2 together with HNSO as evidenced by monitoring the intense infrared bands at 1362 and 1261 cm^{-1}, respectively. The visible spectrum exhibited vibronic structure in the region 500–400 nm on transmittance sensitivity mode $5T$ (transmittance scale expanded 5 times). This structure[10] was indicative of the presence of small amounts of thiazyl chloride, NSCl, which was not detectable in the infrared spectrum.

In the second method, involving "lower" pressures, NH_3 was first added to the 1-l. reaction bulb at a pressure of about 30 Torr. Thionyl chloride vapor was then added slowly to the reaction bulb through the vacuum line to achieve the required stoichiometric amount of about 10 Torr. By use of this method, no brown polymer was formed and only a small amount of the yellow polymer was observed. The infrared spectrum showed that a very small amount of SO_2 was present and that the yield of HNSO was comparable to the yield of HNSO produced by the "higher" pressure method. The visible spectrum did not exhibit any absorption bands due to NSCl even by doubling the sensitivity mode of the instrument from $5T$ to $10T$.

Results and Discussion

Our results for the ultraviolet and infrared spectra of thionyl imide are in agreement with the published data.[4,6] A study of the visible spectrum exhibited no absorption bands when the experiment was carried out at "lower" pressures. Under these conditions the relative amount of SO_2 is minimized and that of HNSO is maximized.

When the reaction was carried out at "higher" pressures, a rich vibronic absorption pattern was observed in the region 500–400 nm. On the basis of relative intensities and absolute position of these bands we immediately recognized this pattern as being due to thiazyl chloride, NSCl, which we had been studying independently[10] by subliming trithiazyl trichloride: $N_3S_3Cl_3(s) \rightarrow 3NSCl(g)$. Further experiments showed that NSCl could only be observed in these "higher" pressure experiments that also resulted in considerable amounts of SO_2. In some experiments the intensity of the 1362-cm^{-1} infrared band of SO_2 was comparable to the 1261-cm^{-1} band of HNSO. We also noticed, in agreement with Kirchoff,[5] that the amount of SO_2 remained relatively constant with time after the initial reaction. This fact and the extreme experimental care that we took argue against SO_2 being produced solely from water contamination of the reagents or the vacuum line.

The most likely reaction that is responsible for the concomitant production of SO_2 and NSCl is

$$HNSO + SOCl_2 \rightarrow NSCl + SO_2 + HCl \qquad (3)$$

We favor eq 3 for two reasons. First, SO_2 was observed as a product in the "higher" pressure experiments wherein NH_3 was added to an initial excess of $SOCl_2$. Consequently, there is sufficient $SOCl_2$ present to react with HNSO during the course of the reaction, as required by eq 3. Second, Becke-Goehring et al.[11] observed that a red isomer of thionyl imide (possibly HONS) reacted with an excess of $SOCl_2$ in carbon tetrachloride solution to form $N_3S_3Cl_3$ as the final product. They deduced that a reaction analogous to eq 3 must have occurred with subsequent trimerization of NSCl.

In summary, the detection of NSCl as a by-product in the reaction of NH_3 with $SOCl_2$ explains the fact that the formation of SO_2 occurs mainly as an initial product. We also notice that although the first reported[12] preparation of NSCl (1961) was nearly 20 years after that of HNSO (1942), NSCl was evidently formed concomitantly with HNSO in 1942.

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Registry No. NSCl, 17178-58-4; $SOCl_2$, 7719-09-7; NH_3, 7664-41-7; SO_2, 7446-09-5.

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Correspondence

Restudy of "Dimethylstibinoborine"

AIC60644P

Sir:

Letters dated Jan 28, May 16, and Aug 18, 1976, from Dr. Erwin Mayer (Universitat Innsbruck, Innsbruck, Austria) told of repeated unsuccessful attempts by his student Franz Sklenar to duplicate the synthesis of $(CH_3)_2SbBH_2$. I now have repeated the original reaction,[1] of $NaBH_4$ with $(CH_3)_2SbBr$ in diglyme, at −78 °C with subsequent warming, thereby obtaining diborane and a mixture separable by a high-vacuum microcolumn (−78 °C reflux) into $(CH_3)_3Sb$ (volatility 31 mm at 0 °C) and a fraction which, despite repeated fractionations, persistently showed volatility 42 mm at 0 °C. Although this fraction seemed to agree with the original report of $(CH_3)_2SbBH_2$,[1] its infrared spectrum (Beckman IR-20A instrument) showed no B–H bands; apart from the regions covered by the evident spectrum of $(CH_3)_3Sb$,[2] there appeared only a strong PQR pattern with the Q peak at 1865 cm^{-1} and a weak doublet at 565 cm^{-1}, assignable to Sb–H stretching and bending, respectively. The proton NMR spectrum (Varian T-60 instrument) showed a doublet at 0.83 ppm downfield of TMS ($J = 6.0$ Hz) and a septet at 2.19 ppm ($J = 5.95$ Hz) in the intensity ratio expected for $(CH_3)_2SbH$. Also present was a sharp singlet at 0.73 ppm, representing almost twice as much $(CH_3)_3Sb$. Thus it appears that the original "$(CH_3)_2SbBH_2$" actually was a mixture (probably azeotropic) of $(CH_3)_3Sb$ and $(CH_3)_2SbH$.

Another sample having volatility 42 mm at 0 °C was obtained by the reported alternate method: heating an equimolar mixture of $Sb_2(CH_3)_4$ and B_2H_6 for 2 h at 100 °C,[1] this time with a trace of dimethyl ether as a possible catalyst. This sample seemed to contain a trace of unstable material (probably B_5H_{11}) which soon disappeared, leaving a product having volatility 41 mm at 0 °C. The infrared spectrum of this again showed $(CH_3)_3Sb$, along with peaks assignable to B_5H_9. Dr. Mayer informed me that their similar product