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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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 contained some $(CH_3)_2SbH$. Thus it seems that the original analysis of "$(CH_3)_2SbBH_2$" was based upon a $(CH_3)_3Sb$–$(CH_3)_2SbH$–B_5H_9 mixture, closely simulating the reported formula.

Dr. Grant agreed that this succession of low-probability coincidences, and the low availability of infrared and NMR instruments at the time of the original work (1955), would fully account for the erroneous conclusion. We have here an example of the failure of classical standard procedures—analysis and molecular weight of samples having volatility behavior suggesting purity—to develop a correct result.

It is noted that the $NaBH_4$–$(CH_3)_2SbBr$ reaction leaves most of the methyl–antimony and boron hydride material in the diglyme residue, implying the possibility that these components can form a B–Sb–B–Sb··· bonded polymer. In view of the chemical sensitivity of Sb–CH_3 compounds, it now seems that terminal Sb–BH_2 bonding could be even more delicate; then a genuine $(CH_3)_2SbBH_2$ monomer might be very unstable and difficult to make.

Registry No. $(CH_3)_2SbBH_2$, 60646-39-1; $NaBH_4$, 16940-66-2; $(CH_3)_2SbBr$, 53234-94-9; $(CH_3)_3Sb$, 594-10-5; $(CH_3)_2SbH$, 23362-10-9; B_5H_9, 19624-22-7.

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