Short Communication

Some stibine sulfides and stibine selenides

Relatively little is reported on compounds having the general formula R_3SbX, where X is the sulfur or selenium atom. Löwig and Schweizer[1] prepared triethylstibine by the reaction of potassium antimonide with ethyl halides and then studied the reaction of this compound with both selenium and sulfur. They reported a melting point of 100° for triethylstibine sulfide, but none for the corresponding selenide, although reasonably good analytical data were reported for the latter compound.

Triphenylstibine sulfide has been prepared[2] by the action of hydrogen sulfide on triphenylstibine dichloride and since at one time it was an important pharmaceutical[3], "Sulfoform", its further characterization does not seem to be necessary.

The oxidation of triphenylstibine by selenium dioxide has been reported[4] to yield triphenylstibine oxide and triphenylstibine selenide, but no physical properties were reported for the latter compound.

The only other example of a trialkylstibine sulfide or selenide we have been able to locate is that of tripropylstibine sulfide[5].

Because of our interest in the preparation and properties of compounds having the general formula R_3MX, where M is a group V and X is a group VI atom, we have undertaken the preparation of the stibine sulfides and stibine selenides reported herein.

Stibines. All the stibines were prepared by the reaction of antimony trichloride with the appropriate Grignard reagent, except in the case of the *n*-butyl derivative for which commercial *n*-butyllithium was used. The ether solution was hydrolyzed in the usual manner after which the layers were separated, the ether layer dried, and the stibine purified by vacuum distillation.

It is recommended that the stibines be collected in previously weighed containers so that transfer is not necessary in order to determine the sample weight during their subsequent use. The stibines are so exceedingly sensitive to atmospheric oxygen that the importance of *minimizing exposure to the atmosphere cannot be overemphasized.*

Stibine sulfides and selenides. To a weighed quantity of freshly distilled stibine, preferably contained in the flask into which it was originally distilled, or transferred under nitrogen if necessary, was added sodium-dried benzene or absolute alcohol (250 ml of solvent for every 0.025 mole of stibine). Under a nitrogen atmosphere, which was maintained throughout the time of the reaction, was added a ten percent excess of either sulfur or selenium and the mixture refluxed for a period of time as indicated in Table 1. After cooling to room temperature, the solution was filtered through a sintered glass funnel of medium porosity, under nitrogen, to remove the bulk of the unreacted chalcogen.

When the compound was a liquid, it was necessary to remove the major portion of the solvent under reduced pressure (20–25 mm). Last traces of solvent were removed under a pressure of 1.5 mm, or less, after initial warming to 30–35°. The liquid sulfide may contain dissolved sulfur which will crystallize on cooling to 0°. Removal of the last traces of dissolved sulfur by repeated cooling and filtration of the cold stibine sulfide is a tedious, but necessary operation.

TABLE 1

STIBINE SULFIDES AND SELENIDES, R_3SbX

R	*X*	*Solvent and time of reflux, h*	*Melting point*	*Refractive index at 25°*	Analyses[b]									
					C		*H*		*Sb*		*S*		*Se*	
					calcd.	*found*	*calcd.*	*found*	*calcd.*	*found*	*calcd.*	*found*	*calcd.*	*found*
Ethyl	S	Ethanol, 2	118°[a]		20.90	20.59	6.27	6.35			13.30	13.00		
						20.37		6.23				13.04		
n-Propyl	S	Benzene, 4.5	35°		38.21	38.13	7.44	7.29	43.04	43.24	11.31	11.28		
n-Butyl	S	Benzene, 4.5		1.5528	44.33	44.19	8.32	8.14	37.45	37.27				
Cyclohexyl	S	Benzene, 3	144°[a]		53.50[c]	52.95	8.25	8.25	30.12[c]	30.10	7.95	7.81		
						52.96		8.18						
Ethyl	Se	Ethanol, 2	124°[a]		25.00	25.03	5.23	5.26	27.42	27.47				
n-Propyl	Se	Benzene, 3		1.5840					36.91	36.96			23.42	23.40
n-Butyl	Se	Benzene, 9		1.5534	38.73	38.77	7.40	7.55	32.73	32.82			21.22	21.30

[a] Recrystallized from absolute ethanol. [b] All analyses checked by Galbraith Labs., Knoxville, Tennessee. [c] The C, H and Sb, S analyses were run on separate preparations.

When the compound was a solid, the solution was concentrated until crystals formed on cooling. Additional crystals were obtained by further concentrating and cooling of the filtrate. The compounds prepared are given in Table 1.

Reaction of trimethylstibine with selenium. Trimethylstibine was refluxed with excess selenium in benzene as previously described. After treatment in the usual manner, *i.e.*, filtration followed by concentration, there deposited on cooling a pale yellow crystalline material. Immediately upon exposure, even to traces of air, the crystals rapidly decomposed to give elemental selenium. The material appeared to be stable indefinitely if stored under benzene.

Analysis of this product gave the following results: C, 11.86, 12.05; H, 2.98, 3.15; Sb, 38.87, 38.50; Se, 46.50, 46.83. This corresponds reasonably well to a stoichiometry of the formula $(CH_3)_3SbSe_2$. The latter requires C, 10.97; H, 2.79; Sb, 37.49; Se, 48.62%.

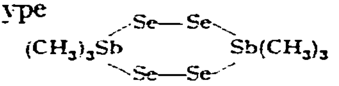
It is apparent that there is a large difference in the melting point observed by us for triethylstibine sulfide (117°) and that reported by Löwig and Schweizer[1] (100°). An even greater discrepancy exists between the melting point we observed for tripropylstibine sulfide (35°) and that reported by Dyke and Jones[5] (88°). The disagreement in the case of the triethyl compound may be due simply to a difference in purity. The disagreement with Davies and Jones may possibly be due to the formation of a hydrate by their compound since their preparation involved the reaction of hydrogen sulfide with triethylstibine oxide which would lead to the concurrent formation of mole of water. We have noted that this compound is extremely hygroscopic. No mention of drying or recrystallization was made in their paper. The elemental analysis we report is complete, however, whereas only antimony was determined in the previous claim for the preparation of this compound and this deviated by 1% from the theoretical value.

When the compounds were solids, purification by recrystallization was not too difficult and all could be obtained as colorless crystals. The liquids, however, were not sufficiently stable to permit purification by vacuum distillation. At pressures as low as 0.01 mm, all the liquids decomposed at temperatures approaching 100°. When heating was carried beyond this point, thermal decomposition took place. Some stibine was reformed along with precipitates of antimony sulfides which remained in the distilling flask. Concurrent formation of dialkyl sulfides and dialkyl selenides is possible, but these compounds were never absolutely identified.

It was noted also, especially in the case of the sulfides, that when the reflux time during the synthesis was carried on for extended periods, *e.g.*, about 12 h, large amounts of antimony sulfide were formed. This is undoubtedly due to the thermal instability of the trialkylstibine sulfide. Because of the instability of these compounds, the reflux time is quite critical. The conversion of the trialkylstibine to the sulfide or selenide by direct combination with the elements is apparently quantitative, but the reaction must be terminated and the product isolated before any significant thermal decomposition takes place. It will be noted that neither of the amyl compounds is reported. We have carried out the reaction of triamylstibine with both elemental selenium and sulfur a number of times, but in no case have we been able to obtain a pure compound. This will undoubtedly be true in other cases and purification techniques, perhaps chromatographic separation, will be needed for the isolation of some of these compounds in pure form. This also points out the extreme importance of using stibines of high purity when this preparative method is utilized. Our failure in the case of the amyl compounds may well be due to the impurity of our stibine sample.

In all cases, these compounds slowly undergo auto-decomposition on standing. Visible formation of orange precipitates, presumably antimonious sulfide or selenide, occurs after two to three weeks, even when the samples are contained in sealed tubes. The orange to amber color of the liquid compounds which was characteristic in every case may be due to the presence of a fine suspension of colloidal sulfide or selenide, even in the freshly prepared compounds.

In the case of the apparent formation of trimethylstibine diselenide, this may be a cyclic structure of the type



which decomposes to give selenium and the normal selenide. The solubility characteristics of this compound along with its extreme instability complicates its study, but its physicochemical properties will be further investigated in an effort to learn more about its structure.

We have been interested in locating the fundamental M–X vibration[6,7,8] where M is a group V element and X a group VI element. For a "pure" Sb=S double bond we calculate from Gordy's rule and the fundamental equation for a harmonic oscillator[6], a force constant of 3.48×10^5 dynes cm^{-1} and $\tilde{\nu}_{Sb=S} = 131$ cm^{-1}. This sets an upper limit with respect to the frequency at which this vibration is located, since either a lower bond order, or a larger value for the reduced mass, which will be the case for the Sb–Se bond, will result in a lowering of the frequency. There will be obvious difficulties in locating these vibrations both with respect to instrumentation and sampling because of the low frequencies involved. We have begun this investigation with the use of a Perkin-Elmer model 301 double grating spectrometer and hope to report the results in the near future.

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