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The Infrared and Hydrogen-1 Nuclear Magnetic Resonance Spectra of the Methylstibines

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Received May 3, 1968

In the only paper¹ on the methylstibines CH_3SbH_2 and $(\text{CH}_3)_2\text{SbH}$ to appear so far, their preparation and some physical and chemical properties were described. For the series $(\text{CH}_3)_n\text{SbH}_{3-n}$, $n = 0-3$, the infrared spectrum² and proton chemical shift³ of SbH_3 and the mass spectrum⁴ and infrared^{5a} and Raman spectra^{5b,6} of $(\text{CH}_3)_3\text{Sb}$ have been reported. In order to supplement the data available on this series of compounds, we report the infrared and ^1H nmr spectra of methylstibine and dimethylstibine.

Experimental Section

A conventional vacuum line was used for the preparation and handling of the methylstibines. The infrared spectra were recorded on a Grubb-Parsons Spectromaster, using an 8-cm gas cell, fitted with potassium bromide windows. The instrument was calibrated against the characteristic bands of polystyrene. The infrared spectra of methylstibine and dimethylstibine were recorded at 90 and 35 mm pressure, respectively. Higher pressures were not feasible owing to the tendency of the methylstibines in the liquid state to decompose at temperatures greater than 0° . The nmr spectra were recorded as solutions in benzene, using TMS as internal standard. The chemical shifts were extrapolated to infinite dilution. The spectra were recorded at magnet temperature on a Varian Associates HR 100 spectrometer. Prior to any measurements being made, the individual sample was redistilled and its molecular weight was redetermined. Such a procedure was found to be necessary as both compounds decompose slowly at -78° , the temperature at which they were stored.

Preparation of Dimethyl- and Methylstibine.—A solution of 30 g of bromodimethylstibine (prepared from dibromotrimethylantimony⁷) in approximately 100 ml of dibutyl ether was frozen to -196° under an atmosphere of N_2 . At this temperature, LiAlH_4 (5 g) in 100 ml of dibutyl ether was added under a flow of N_2 . The reduction was carried out under N_2 at a pressure of 300 mm in a 500-ml, three-necked, round-bottomed flask, connected to a series of traps at -196° . The reaction mixture was initially warmed to -78° , at which temperature thorough mixing was possible. After 0.5 hr no reaction was observed to have occurred. On raising the temperature to -45° , immediate reaction occurred; the solution turned from the characteristic gray color associated with the suspension of LiAlH_4 to a green-

yellow. This was followed by a rapid evolution of gas and the solution turned brown and finally black. The vessel was allowed to warm up to room temperature over a period of 2 hr. After this time, the remaining volatile products, together with some ether, were pumped out of the solution and the reaction vessel was then isolated from the trap section. Purification was achieved by a trap to trap distillation. In the initial stages, extensive decomposition occurred, forming black deposits in the vacuum line. Separation was achieved using the following series of distillation temperatures: room temperature, -45° , -65° , -78° , -196° . The trap at -45° contained a small quantity of trimethylstibine, together with dibutyl ether, the traps at -65° and -78° contained dimethylstibine and some methylstibine, and the trap at -196° contained methylstibine. Repeated distillation through the -65° and -78° traps afforded a good separation of the two stibines. These were isolated in a molar ratio of methylstibine to dimethylstibine of approximately 1:3, with an over-all yield of about 45%, based on antimony.

Results and Discussion

The formation of methylstibine from the reduction of bromodimethylstibine was also observed by Burg and Grant.¹ The most likely explanation is the presence of dibromomethylstibine in the starting material, rather than a rearrangement during the reaction. It has been observed⁸ that the cracking of dibromotrimethylantimony at 160° , at pressures greater than 100 mm of N_2 , gives a yellow oil and as volatiles trimethylstibine as well as methyl bromide. On distilling the yellow oil and collecting the fraction coming over at $60-120^\circ$ (20 mm), the presence of trimethyl-, bromodimethyl-, and dibromomethylstibines was observed from the nmr spectrum of the fraction. In addition, butylation of the yellow oil gave the methyl dibutyl- and dimethylbutylstibines. The material used in the reduction with LiAlH_4 was the crystalline solid obtained from allowing the yellow oil to stand at room temperature for approximately 1 week.

Infrared Spectra.—The spectra of the two compounds are reproduced in Figure 1, in the range $4000-400\text{ cm}^{-1}$. The results, with assignments, are given in Table I. The analysis of the spectrum of methylstibine must be rather tentative, although the clearly defined band contours which were obtained allowed reasonably unambiguous assignments to be made for many of the more important bands. By analogy with the vibrational spectra of methylamine,⁹ methylphosphine,¹⁰ and silylphosphine,¹⁰ methylstibine behaves as a near-prolate symmetric-top molecule. The approximate rotation constant, B , was calculated to be 0.31 cm^{-1} , using the relationship $\Delta\nu = 2.385(TB)^{1/2}$, where $\Delta\nu$ is the separation between the maxima of the P-R branches of an unambiguous parallel band (the Sb-C stretch at 509 cm^{-1}) and T is the absolute temperature of the measurement (307°K). The corresponding values for methylphosphine¹⁰ and silyl-

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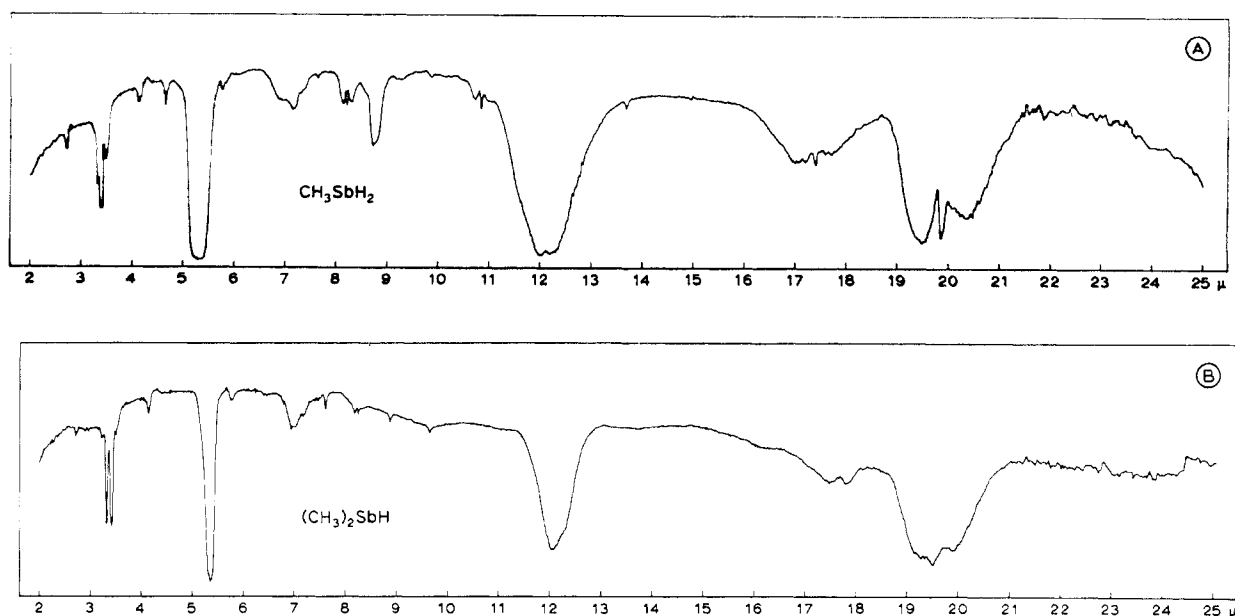


Figure 1.—Infrared spectra of the methylstibines.

TABLE I
INFRARED SPECTRA OF CH_3SbH_2 AND $(\text{CH}_3)_2\text{SbH}$,
IN THE RANGE $4000\text{--}400\text{ CM}^{-1}$

CH_3SbH_2		$(\text{CH}_3)_2\text{SbH}$	
Obsd freq, cm^{-1}	Assignment ^a	Obsd freq, cm^{-1}	Assignment
3704 w	C-H str	3657 w	C-H str
2991 mw		3077 w	
2956 m		2998 s	
2929 m		2929 s	
2869 mw		2857 w	
2409 vw		2409 w	
2162 vw			
2150 vw	$\nu_a(\text{Sb-H})$ str, ν_{11}	1861 vs	Sb-H str
1874 vs		1724 w	
1863 vs		1441 m	
1734 vw		1429 m	
1438 mw, b	$\delta(\text{CH}_3)$ def, ν_4 , ν_{12}	1389 mw	CH ₃ def
1391 mw, b		1311 mw	
1370 mw, sh	$\delta_s(\text{CH}_3)$ sym def, ν_5	1221 w	CH ₃ def
1228 mw		1210 w	
1219 mw		1127 vw	
1205 mw		1074 vw	
1143 m	$\sigma(\text{H}_3\text{C})$ rock, ν_8	1037 vw	H ₃ C rock
933R mw			
922Q mw		827 vs	
909P mw		816 sh	
834 vs	$\sigma(\text{H}_2\text{Sb})$ wag, ν_8	570 m	SbH bend
821 vs		562 m	
585R m		517 sh	
575Q m		512 vs	
567P m	$\nu(\text{Sb-C})$ str, ν_9	502 vs	Sb-C str
513R s			
503Q s			
490P s			

^a Numbering of fundamentals as in ref 10, for CH_3PH_2 .

phosphine¹⁰ have been calculated to be 0.411 and 0.191 cm^{-1} , respectively. A value for the rotation constant A was calculated to be 2.24 cm^{-1} , by assuming methylstibine to be a prolate symmetric top, from the separa-

tion of the subbands in the Q branch of the B-type band at 827 cm^{-1} (the separation was measured to be 3.86 cm^{-1} , with an error of approximately 5%). The corresponding values for methylphosphine¹⁰ and silylphosphine¹⁰ have been calculated to be 2.45 and 1.715 cm^{-1} , respectively. The rotation constants are consistent with the following structural parameters for the molecule: $\angle \text{H-C-H} = \angle \text{H-C-Sb} = 109^\circ 28'$, $\angle \text{H-Sb-H} = \angle \text{H-Sb-C} = 116^\circ 41'$, $r_0(\text{H-C}) = 1.05 \text{ \AA}$, $r_0(\text{Sb-C}) = 2.20 \text{ \AA}$, $r_0(\text{Sb-H}) = 1.70 \text{ \AA}$. The value for $\angle \text{H-Sb-H}$, computed from assumed bond lengths and angles for the $\text{H}_3\text{C-Sb}$ fragment, is $116^\circ 41'$; taking into account the error in estimating A ($\pm 5\%$), which corresponds to an uncertainty of $\pm 4^\circ$, it can be concluded that this angle is significantly larger than the value of $91^\circ 20'$ calculated for SbH_3 .² This result would be consistent¹¹ with the rather low value, when compared with related vibrations in comparable molecules,¹² for the SbH_2 wagging mode, ν_8 , at 575 cm^{-1} , because there must be a considerable increase in the s character of the Sb-H bond in going from a skeletal angle of $91^\circ 20'$ to $116^\circ 41'$.

The spectrum of dimethylstibine could not be analyzed in great detail owing to the low pressure used for the measurement. It is interesting, however, that the Sb-H bending modes are also at low frequencies, suggesting that dimethylstibine possesses a more planar skeleton than stibine.

¹H Nmr Spectra.—The results are given in Table II, together with the chemical shifts of SbH_3 ³ and $(\text{CH}_3)_3\text{Sb}$. Although it is not strictly correct to compare the

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(12) See ref 2 and 10 for infrared spectra of SbH_3 and CH_3PH_2 , respectively. See the following references for the compounds given: (a) SnH_4 , L. May and C. R. Dillard, *J. Chem. Phys.*, **34**, 694 (1961); (b) CH_3SnH_3 , S. F. A. Kettle, Thesis, Cambridge University, 1958; (c) PH_3 , B. Lee and C. K. Wu, *Trans. Faraday Soc.*, **35**, 1366 (1939); (d) $(\text{CH}_3)_2\text{PH}$, H. C. Beachell and B. Katlafsky, *J. Chem. Phys.*, **27**, 182 (1951); (e) SiH_4 , J. H. Meul and M. K. Wilson, *ibid.*, **24**, 385 (1956); (f) CH_3SiH_3 , M. Randic, *Spectrochim. Acta*, **18**, 115 (1962); (g) $(\text{CH}_3)_2\text{SiH}_2$, E. A. V. Ebsworth, M. Onyszchuk, and N. Sheppard, *J. Chem. Soc.*, 1455 (1959).

chemical shift of SbH_3 in CCl_4 at -23° with the chemical shifts of the methylstibines in C_6H_6 at $+27^\circ$, it is interesting that the variation in chemical shift of $\text{HSb}<$, as methyl groups replace protons, parallels the variations observed for other series of compounds, such as $(\text{CH}_3)_n\text{GeH}_{4-n}$.^{13,14} At present, this variation is little understood. In the case of antimony, which possesses a lone pair of electrons and low-lying empty d and f orbitals, the paramagnetic anisotropy of the antimony may play a significant role in determining the actual magnitude of the shielding of the proton directly bonded to the antimony. On the other hand, the amount of s character in the Sb-H bond may have increased in going from SbH_3 to CH_3SbH_2 . In this case, not only will the paramagnetic anisotropy be different, but also, owing to the greater penetration of the s orbital into the core, the protons in methylstibine will be more affected by the electron-withdrawing power of the antimony, and so the chemical shift of CH_3SbH_2 may reasonably be expected to be at lower field than the SbH_3 signal.

TABLE II
 ^1H NMR SPECTRA OF $(\text{CH}_3)_n\text{SbH}_{3-n}$, $n = 0-3$

Compound	Chem shift, τ		$J(\text{H-H})$, Hz	Ref
	$\text{H}_3\text{C-Sb}$	H-Sb		
SbH_3	...	8.622	...	<i>a</i>
CH_3SbH_2	9.52 (triplet)	8.31 (quartet)	6.32	<i>b</i>
$(\text{CH}_3)_2\text{SbH}$	9.38 (doublet)	7.86 (septet)	5.98	<i>b</i>
$(\text{CH}_3)_3\text{Sb}$	9.33	...	...	<i>b</i>

^a Cf. ref 2; at -23° in CCl_4 , extrapolated to infinite dilution.

^b This work; at $+27^\circ$ in C_6H_6 , extrapolated to infinite dilution.

Acknowledgments.—Financial support under NATO Research Grant No. B-237 (joint program with Professor H. C. Clark, London, Ont.) (to N. A. D. C.) and by N. V. Billiton Maatschappij, the Hague (to H. A. M.), is gratefully acknowledged. The authors wish to thank Professor G. J. M. van der Kerk for his stimulating interest and encouragement.

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The Disproportionation of Digermene in Liquid Ammonia

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Received June 3, 1968

While attempting to measure the acid dissociation constant of digermene in liquid ammonia, we have observed that digermene decomposes in liquid ammonia solution to give germane and a solid germanium hy-

dride of variable composition. Similar base-catalyzed decompositions of digermene have been observed by Bornhorst and Ring,¹ but these workers did not investigate the nature of the solid hydride formed. In view of Glarum and Kraus's earlier report² of the formation of GeH_2 by the reaction of bromobenzene with sodium germal in ammonia, we decided to determine if the same substance can be prepared by the ammonia-catalyzed disproportionation of digermene.

Experimental Section

Standard greaseless vacuum-line techniques were employed. Digermene was prepared according to the method of Jolly and Drake.³ The digermene was shown to be pure by its vapor pressure (235 mm at 0° , invariant with vapor volume, compared with the literature⁴ value of 243 mm), its infrared spectrum (which only showed bands due to digermene⁵), and its mass spectrum (which showed only trace contamination by air). Too little germane was formed in the reactions to permit identification by vapor pressure determination, but its purity was shown by its infrared spectrum⁶ and mass spectrum, neither of which showed even trace contamination by NH_3 or Ge_2H_6 . The spectra were obtained with a Perkin-Elmer Model 137 Infracord spectrometer and a Consolidated Engineering Corp. mass spectrometer, Model 21-620. Ammonia was dried over sodium before its use.

Reactions were carried out in a vessel equipped with two break-seals. A measured amount of digermene and approximately 0.5 ml of liquid ammonia were distilled into the vessel at liquid nitrogen temperature. The vessel was then sealed and placed in a bath of appropriate temperature. When a low-temperature bath was used, care was taken to keep the entire vessel below the level of the bath.

After reaction had proceeded, the vessel was attached to the vacuum line, and one of the seals was opened, keeping the vessel in the low-temperature bath. The volatile contents were then Toepler-pumped through a liquid nitrogen trap until all volatiles had distilled over. A trace of hydrogen could usually be measured in the buret of the Toepler pump. The vessel was then sealed off again and temporarily set aside. The volatiles were then separated. In runs in which all of the digermene had decomposed, it was possible to separate germane and ammonia by means of a -160° trap. However, when digermene was present, the ammonia could not be separated by trap-to-trap distillation; it was removed by distilling the ternary mixture very slowly through a trap of anhydrous magnesium perchlorate at 0° . The germane and digermene were then separated by fractional condensation in traps at -112 and -196° ; the amount of each was determined by pressure-volume techniques.

The solid residue in the reaction vessel was then pyrolyzed at 400° for 2 hr. The hydrogen (identified by mass spectrometry) was then Toepler-pumped through the second break-seal and through a -196° trap to remove any ammonia that might have adhered to the solid. The hydrogen was measured and the germanium mirror was either discarded or dissolved in basic hydrogen peroxide and titrated with a pH meter according to the method of Tchakirian.⁷

Results

The results are presented in Table I. The adequacy of the quantitative measurements is attested by the

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