

gave crude diiodo-*p*-carborane which was recrystallized twice from hexane. The colorless crystalline product (0.78 g, 14%) obtained proved to be pure diiodo compound and, in addition, a single isomer as shown by vpc.

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The Chemistry of μ -Mercaptodiborane

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Treatment of solid $[(C_2H_5)_4N][HS(BH_3)_2]$ with anhydrous hydrogen chloride at -78° produces hydrogen and the new compound μ -mercaptodiborane, μ -HSB₂H₅. The bridge structure of μ -mercaptodiborane is confirmed by the ¹¹B nmr spectrum. Thermal decomposition of μ -mercaptodiborane in the gas phase at low pressure yields diborane, hydrogen sulfide, and involatile products. Liquid-phase decomposition results in the formation of diborane, hydrogen, and an involatile glassy solid. In the gas phase μ -mercaptodiborane undergoes boron isotope exchange with ¹⁰B₂H₆. Treatment of μ -mercaptodiborane with excess liquid deuterium chloride at -78° produces μ -DSB₂H₅. The liquid-phase decomposition of μ -DSB₂H₅ produces mainly HD, while gas-phase decomposition yields hydrogen sulfide containing deuterium and B₂H₆. The rate of decomposition of μ -mercaptodiborane in the gas phase is insensitive to the presence of diborane.

Introduction

In a recent communication¹ we reported the preparation and some of the properties of μ -mercaptodiborane. The only other reported compound of this type is the S-methyl derivative, μ -CH₃SB₂H₅, prepared by Burg and Wagner² by passing diborane over (CH₃SBH₂)_x or (CH₃)₃N·H₂BSCCH₃ at 90° . The μ -methylthiodiborane shows poor thermal stability at room temperature and quickly decomposes back to diborane and methylthio-borane polymer. The sulfur-bridge structure postulated by the authors was later confirmed by ¹¹B nmr spectroscopy.³

The properties of μ -mercaptodiborane show some expected similarities to those of μ -methylthiodiborane, but the presence of a labile hydrogen in place of the methyl group gives rise to significant differences in chemical behavior. In this paper we describe the details of the preparation and characterization of μ -mercaptodiborane and report some of its basic chemical properties.

Experimental Section

General Information.—Conventional high-vacuum techniques were used throughout this investigation. Hydrogen sulfide, CP grade, was purchased from the Matheson Co. and was used without further purification. Tetraethylammonium borohydride was purchased from Alfa Inorganics, Inc., and was recrystallized from 2-propanol before use. The ¹⁰B₂H₆ was prepared by the reduction of ¹⁰BF₃·O(C₂H₅)₂ (96% ¹⁰B; ¹⁰BF₃ obtained as CaF₂·¹⁰BF₃ from Oak Ridge National Laboratories) with lithium aluminum hydride. All other compounds used in this work either

were purchased commercially or were prepared by standard methods.

Nuclear magnetic resonance (nmr) spectra were obtained with a Varian HA-100 spectrometer equipped with standard accessories and a 32.1-MHz probe for ¹¹B studies. Boron-11 and proton chemical shifts are relative to diethyl ether-boron trifluoride and tetramethylsilane, respectively. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6E double-focusing spectrometer. Infrared spectra were obtained with Perkin-Elmer 137 and 337 spectrophotometers.

Preparation of μ -Mercaptodiborane.—Typically, in a 500-ml reaction vessel 0.731 g (5.05 mmol) of tetraethylammonium borohydride was solvolyzed to $[(C_2H_5)_4N][HSBH_3]$ over a 24-hr period in 3 ml of liquid hydrogen sulfide at -78° .⁴ After the hydrogen had been removed, 3.14 mmol of diborane was condensed into the vessel and the mixture was warmed to -78° and allowed to stand for 20 min. The resulting solution of $[(C_2H_5)_4N][HS(BH_3)_2]$ ⁵ was cooled to -196° ; the vessel was opened to the vacuum line and rewarmed to -78° so that the hydrogen sulfide would slowly sublime away over a 24-hr period. The solid residue was then treated with an excess of hydrogen chloride at -78° for 20 min; about 7.2 mmol of hydrogen was produced in this reaction. The μ -mercaptodiborane was isolated by fractionation through -78° into -126° ; further purification was accomplished by distilling the product through -95° into -126° . This experiment produced 1.17 mmol (23% yield) of μ -mercaptodiborane.

For analysis the product was hydrolyzed in 1 *N* sulfuric acid to yield hydrogen of hydrolysis, hydrogen sulfide, and boric acid according to eq 1. Hydrogen was measured with a Toep-



ler pump-gas buret assembly, hydrogen sulfide was isolated and determined by high-vacuum techniques, and boric acid was titrated as the D-mannitol complex with standard base.

(1) P. C. Keller, *Chem. Commun.*, 209 (1969).

(2) A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **76**, 3307 (1954).

(3) E. L. Muetterties, N. E. Miller, K. J. Packer, and H. C. Miller, *Inorg. Chem.*, **3**, 870 (1964).

(4) P. C. Keller, *ibid.*, **8**, 1965 (1969).

(5) The $[(C_2H_5)_4N][HS(BH_3)_2]$ can also be prepared from $[(C_2H_5)_4N]SH$ and B₂H₆ in liquid hydrogen sulfide: J. D. Cotton and T. C. Waddington, *J. Chem. Soc., A*, 789 (1966).

Anal. Calcd for HSB_2H_5 (mmol/g): H_2 , 83.80; H_2S , 16.76; $\text{B}(\text{OH})_3$, 33.52; mol wt, 59.7. Found: H_2 , 80.44; H_2S , 16.54; $\text{B}(\text{OH})_3$, 32.13; mol wt (vapor density), 59.4.

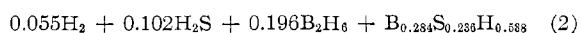
A sample of μ -mercaptodiborane, purified by repeated trap-to-trap fractionation through -95° into 126° , exhibited the following vapor pressures: 9.5 mm (-63.5°), 28 mm (-45°), 100 mm (-22.8°), 152 mm (-12°), and 279 mm (0°). The compound has an extrapolated boiling point of 27° . The gas-phase infrared spectrum exhibits bands at the following frequencies (in cm^{-1}): 2600 (s), 2510 (s), 2280 (w, PR), 1850 (m, PQR), 1755 (s, PR), 1600 (m, PQR), 1135 (w, PR), 1035 (w, PQR), 975 (m, PR), 970 (m, PQR), 860 (w, br). The monoisotopic mass spectrum is presented in Table I.

TABLE I
MASS SPECTRUM OF $^{11}\text{B}_2^1\text{H}_6^{32}\text{S}$

<i>m/e</i>	Intens	Ion	<i>m/e</i>	Intens	Ion
60	0.5	$\text{B}_2\text{H}_6\text{S}^+$	34	43.0	H_2S^+
59	18.0	$\text{B}_2\text{H}_5\text{S}^+$	33	17.5	HS^+
58	40.5	$\text{B}_2\text{H}_4\text{S}^+$	32	13.5	S^+
57	100.0	$\text{B}_2\text{H}_3\text{S}^+$	27	35.0	B_2H_5^+
56	90.0	$\text{B}_2\text{H}_2\text{S}^+$	26	5.0	B_2H_4^+
55	21.5	B_2HS^+	25	2.0	B_2H_3^+
54	2.5	B_2S^+	24	7.0	B_2H_2^+
47	0.8	BH_4S^+	23	0.6	B_2H^+
46	13.5	BH_3S^+	22	0.9	B_2^+
45	27.5	BH_2S^+	13	17.5	BH_2^+
44	13.0	BHS^+	12	2.9	BH^+
43	3.0	BS^+	11	9.0	B^+

The low-temperature ^{11}B and ^1H nmr spectra of pure liquid μ -mercaptodiborane are shown in Figures 1 and 2, respectively. Within a -10 to -75° temperature range there was no indication of collapse or broadening of the ^{11}B spectrum owing to intramolecular hydrogen exchange of the type observed for the structurally related μ -aminodiboranes.^{6,7}

Gas-Phase Decomposition of μ -Mercaptodiborane.—A 0.836-mmol gaseous sample of purified μ -mercaptodiborane was allowed to decompose in a 70-ml Pyrex vessel for 155 min. By the end of this period the inner walls of the bulb had become uniformly opaque owing to the formation of a white solid and minute droplets of a colorless liquid. When the decomposition was quenched by cooling the bulb with liquid nitrogen, the deposited solid and liquid in the upper parts of the vessel did not evaporate and condense in the cold portion of the apparatus. When the reaction vessel was opened to the vacuum line, a small amount of hydrogen was discovered and this was collected and measured with the Toepler pump and gas buret. The volatile products were separated by fractionation through -95° and -126° into -196° . Nothing was retained in the -95° trap. The material stopping at -126° was undecomposed μ -mercaptodiborane; the quantity recovered indicated 41% decomposition in this experiment. The material passing the -126° trap was a mixture of diborane and hydrogen sulfide. This mixture and the involatile residue in the reaction vessel were hydrolyzed in 1 *N* sulfuric acid and hydrogen of hydrolysis, hydrogen sulfide, and boric acid were determined as described above. The stoichiometry of this decomposition is summarized in eq 2. In gas-phase decomposition experiments using lower pressure and longer reaction time, generally much less hydrogen was produced for the same amount of decomposition. Specifically, in an experiment in which 0.340 mmol of μ -mercaptodiborane suffered 42% decomposition in a 120-ml bulb over a 5-hr period only 0.005 mmol of hydrogen appeared.



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(6) W. D. Phillips, H. C. Miller, and E. L. Muettterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

(7) D. F. Gaines and R. Schaeffer, *ibid.*, **86**, 1505 (1964).

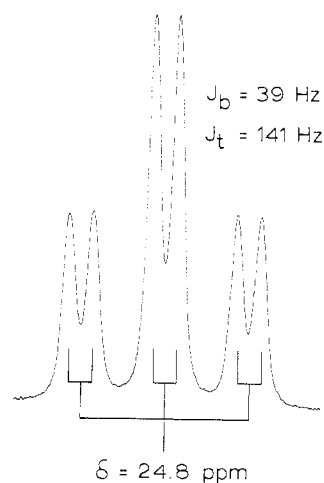


Figure 1.—The ^{11}B nmr spectrum of μ - HSB_2H_5 at -40° .

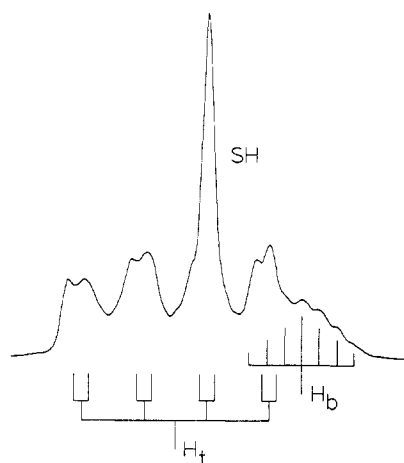
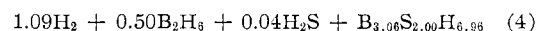
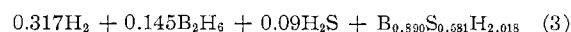


Figure 2.—The ^1H nmr spectrum of μ - HSB_2H_5 at -55° .

Liquid-Phase Decomposition of μ -Mercaptodiborane.—A 0.600-mmol liquid sample of purified μ -mercaptodiborane was allowed to decompose at room temperature for 54 min in a tube of about 1.5-ml internal volume constructed from a heavy-wall 2.3-mm i.d. Pyrex capillary. During this period the liquid in the tube frothed and gradually formed a colorless glassy foam. Volatile product separation and determination and residue analysis were accomplished as described above. The recovered μ -mercaptodiborane indicated that 98.3% decomposition had occurred in the experiment. Equation 3 summarizes the stoichiometry of the reaction; eq 4 presents these data with more nearly integral coefficients.



Exchange of μ -Mercaptodiborane with $^{10}\text{B}_2\text{H}_6$.—To determine whether μ -mercaptodiborane would undergo boron isotope exchange with diborane, 0.335 mmol of purified μ -mercaptodiborane and 1.54 mmol of $^{10}\text{B}_2\text{H}_6$ were allowed to interact in the gas phase for 60 min in a 125-ml bulb. The boron isotope content of the recovered μ -mercaptodiborane was determined mass spectrometrically by examining the *m/e* 10 and 11 peaks under high resolution so that the latter peak was resolved into its $^{10}\text{B}^+\text{H}^+$ (11.020 amu) and $^{11}\text{B}^+$ (11.009 amu) components. The boron isotopic composition was found to be 39% ^{10}B and 61% ^{11}B .

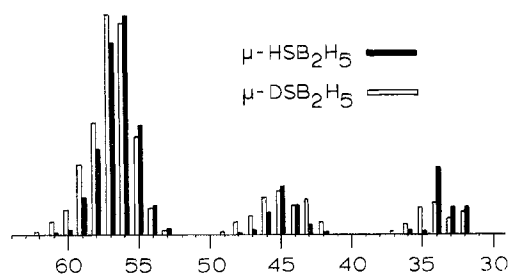


Figure 3.—Comparison of polyisotopic mass spectra of μ -HSB₂H₅ and μ -DSB₂H₅.

Gas-Phase Decomposition of μ -Mercaptodiborane in the Presence of Diborane.—In a typical experiment a 0.296-mmol sample of purified μ -mercaptodiborane was allowed to decompose in the gas phase for 60 min in a 125-ml bulb equipped with a Fisher-Porter Teflon stopcock. The μ -mercaptodiborane recovered from this reaction was 0.255 mmol, implying 14% decomposition. The reaction bulb was then carefully cleaned and dried and the decomposition was repeated in this vessel with 0.292 mmol of fresh μ -mercaptodiborane and 3.50 mmol of diborane. After 60 min at room temperature the reaction was again stopped. Separation of the products resulted in the recovery of 0.255 mmol of μ -mercaptodiborane, implying the same extent of decomposition, within experimental error, in the presence of a 12-fold excess of diborane.

Exchange of μ -Mercaptodiborane with Liquid Deuterium Chloride.—A 21.4-mmol sample of deuterium chloride and 0.827 mmol of purified μ -mercaptodiborane were condensed into a 10-ml reaction tube equipped with a Fisher-Porter Teflon stopcock. The tube was sealed and immersed in a -78° bath for 25 min. No noncondensable gas was present when the vessel was opened to the vacuum manifold. A gas-phase infrared spectrum of a sample of the recovered product was identical with that of pure μ -mercaptodiborane with the sole exception of a slight alteration in the shape of the B-H stretching band at 2600 cm^{-1} . A mass spectrum of another sample of the product revealed that the pattern of peaks arising from sulfur-containing ions generally extended one mass unit higher than found for μ -HSB₂H₅, thus establishing the formation of μ -DSB₂H₅. Figure 3 presents a comparison of the polyisotopic mass spectra of μ -HSB₂H₅ and the μ -DSB₂H₅ prepared in this experiment.

Gas-Phase Decomposition of μ -DSB₂H₅.—A 0.363-mmol sample of μ -DSB₂H₅ was allowed to decompose in the gas phase for 125 min in a 25-ml reaction tube. The polyisotopic mass spectrum of the mixture of hydrogen sulfide and diborane recovered from the decomposition is presented in Figure 4. Assuming a statistical distribution of protium and deuterium in the hydrogen sulfide, we estimate the deuterium content to be 47% based on relative peak intensities. It is well known, however, that compounds with labile deuterium readily lose this isotope by exchange with the walls of the inlet system of the mass spectrometer,⁸ so the estimated deuterium content of the hydrogen sulfide should be regarded as a minimum value.

Liquid-Phase Decomposition of μ -DSB₂H₅.—A 0.344-mmol sample of μ -DSB₂H₅ was allowed to decompose for 15 min at room temperature in a 1.5-ml capillary reaction tube similar to that described above. The mass spectrum of the hydrogen produced in this experiment is presented in Table II. If the

TABLE II

<i>m/e</i>	Intensity	Ion
4	6.5	D ₂ ⁺
3	100.0	HD ⁺
2	42.0	H ₂ ⁺ , D ⁺
1	5.5	H ⁺

(8) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 218.

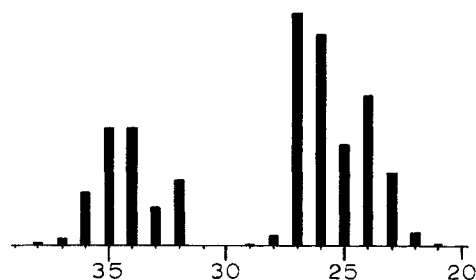
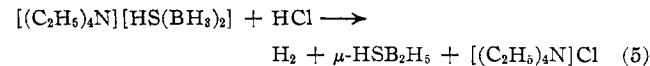


Figure 4.—Polyisotopic mass spectrum of a diborane-hydrogen sulfide mixture from decomposition of gaseous μ -DSB₂H₅.

contribution of D⁺ relative to HD⁺ is assumed to be 2%, the composition of the hydrogen sample is estimated to be D₂ (4.3%), HD (68.4%), and H₂ (27.3%). It is tempting to suggest that the H₂ in the products arises from exchange of HD with diborane; however, examination of the kinetic data of Maybury and Koski⁹ for the exchange of diborane with D₂ shows that only a small fraction of the H₂ could appear by this process under the conditions of the experiment. The observed H₂ may arise from a secondary reaction or from incomplete deuteration of the sample.

Results and Discussion

Preparation of μ -Mercaptodiborane.—The formation of [(C₂H₅)₄N][HS(BH₃)₂] by the addition of diborane to a liquid hydrogen sulfide solution of [(C₂H₅)₄N]SH or [(C₂H₅)₄N][HSB₃] is always accompanied by a side reaction producing hydrogen and an unidentified by-product.^{4,5} Evaporation of the solvent from this mixture at -78° and treatment of the solid residue with an excess of hydrogen chloride produces μ -mercaptodiborane in 20–25% yield. The reaction may be represented by eq 5, but the low yield



and lack of definite stoichiometry suggest the alternative that μ -mercaptodiborane may form by the protonation of the by-product mentioned above. In theory it should be possible to differentiate between these two reactions by treating the [(C₂H₅)₄N][HS(BH₃)₂] residue with deuterium chloride and examining the resulting product for the presence of deuterium. However, in practice the SH proton of μ -mercaptodiborane is labile with respect to exchange with deuterium chloride and the product would always contain deuterium. At this point it is not known for certain which of the two materials in question is the actual precursor to μ -mercaptodiborane.

The spectral properties of μ -mercaptodiborane are fully consistent with the assigned structure. The ¹¹B nmr spectrum establishes the SH bridge geometry, showing a characteristic triplet of doublets. The coupling constants are in good agreement with the values of $J_{\text{terminal}} = 135\text{ Hz}$ and $J_{\text{bridge}} = 35\text{ Hz}$ observed for the S-methyl derivative;³ the chemical shift of μ -methylthiodiborane was not reported. Although not well resolved, the ¹H nmr spectrum clearly exhibits signals from the three proton environments in the

(9) P. C. Maybury and W. S. Koski, *J. Chem. Phys.*, **21**, 742 (1953).

molecule. The SH proton resonance appears as a single peak at -0.46 ppm. The signal arising from the ^{11}B H terminal protons is a characteristic 1:1:1:1 quartet centered at -1.29 ppm which shows some doublet fine structure owing to coupling with the bridge proton. The apparent asymmetry of this doublet splitting is probably due to terminal protons coupled to ^{10}B ($I = 3$, 20% abundance). The bridge proton resonance consists of a broad 1:2:3:4:3:2:1 septet at $+0.86$ ppm arising from equal coupling with two ^{11}B nuclei. Further splitting of this multiplet due to coupling with the four terminal protons is not resolved. The infrared band due to S-H stretching, which usually occurs with low intensity between 2550 and 2600 cm^{-1} , is obscured by the strong B-H stretching absorption at 2600 cm^{-1} .

The formation of $\mu\text{-DSB}_2\text{H}_5$ by exchange of μ -mercaptodiborane with liquid deuterium chloride is established by the mass and infrared spectra of the recovered compound. The one mass unit increase in molecular weight is demonstrated by the mass spectrum, while the infrared spectrum shows the absence of deuterium attached to boron. A weak infrared band due to S-D stretching would be obscured by the bridge hydrogen stretch at 1850 cm^{-1} .

Decomposition of μ -Mercaptodiborane.—Like μ -methylthiodiborane, the thermal stability of μ -mercaptodiborane is very poor. One striking difference between the two compounds is the dependence of the product distribution from thermal decomposition of μ -mercaptodiborane upon whether the reaction occurs in the liquid phase or in the gas phase. Liquid-phase decomposition produces hydrogen, diborane, and involatile solid, while gas-phase decomposition at low pressure yields diborane, hydrogen sulfide, and involatile products. Burg and Wagner observed only one mode of decomposition for μ -methylthiodiborane leading to the formation of diborane and methylthio-borane polymer.²

The stoichiometry of the liquid-phase decomposition (eq 4) agrees very well with the equation



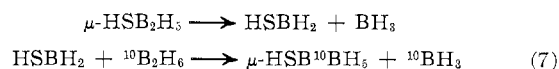
The fact that hydrogen or methane is not produced in the decomposition of μ -methylthiodiborane suggests that the labile SH proton plays an active role in the decomposition of μ -mercaptodiborane. This hypothesis is confirmed by the high percentage of HD found in the hydrogen collected from the decomposition of liquid $\mu\text{-DSB}_2\text{H}_5$.

The problem of the decomposition of μ -mercaptodiborane in the gas phase is more complex. No balanced equation with realistically small integral coefficients

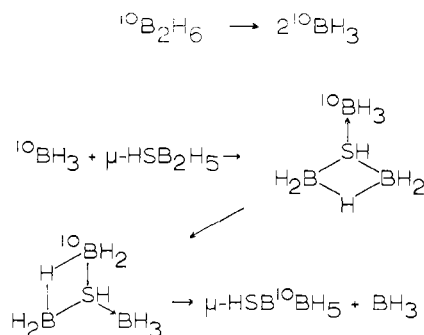
satisfies the observed stoichiometry, which suggests that several reactions may contribute to the over-all process. The mass spectrum of the volatile decomposition products of $\mu\text{-DSB}_2\text{H}_5$ demonstrates that deuterium remains bonded to sulfur throughout the course of the reaction.

These facts suggest that reaction in the liquid phase may occur by attack of one μ -mercaptodiborane molecule upon another, while decomposition in the gas phase may possibly proceed by a dissociation to HSBH_2 and BH_3 followed by attack of either of these intermediates upon an undissociated molecule of μ -mercaptodiborane. The dissociation process should be most important in the gas phase, which is consistent with the observation that almost no hydrogen is produced in reactions at low pressure. The bimolecular reaction should fully predominate in the liquid phase, which is supported by the appearance of only trace quantities of hydrogen sulfide in the decomposition of liquid μ -mercaptodiborane.

Boron Isotope Exchange.—Two reasonable mechanisms can be written to explain the boron isotope exchange between μ -mercaptodiborane and $^{10}\text{B}_2\text{H}_6$. The first involves dissociation of μ -mercaptodiborane



The second proceeds by attack of $^{10}\text{BH}_3$ on μ -mercaptodiborane



Equation 7 suggests that diborane should inhibit the decomposition of μ -mercaptodiborane. Since diborane does not measurably retard the decomposition, the second pathway is preferred over the first. This does not eliminate the possibility that gas-phase decomposition proceeds by dissociation of μ -mercaptodiborane but simply implies that any process like eq 7 is kinetically slow compared to other reactions which lead to decomposition products.

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