

TABLE VII  
 POTENTIAL ENERGY DISTRIBUTION (%) FOR  $H_3^{11}B_3^{16}O_3$ 

Symmetry ( $D_{3h}$ )	Calcd freq, $cm^{-1}$	Force constants				
		$f_s$	$f_t$	$f_{\alpha} = f_{\beta}$	$f_{\xi}$	$f_{i\xi}$
$A_1'$	2616	98.6	0.6	0.8	0.0	0.0
$A_1'$	906	1.3	13.2	85.5	0.0	0.0
$A_1'$	811	0.1	86.2	13.7	0.0	0.0
$A_2'$	1448	0.0	100.9	0.0	0.0	-1.0
$A_2'$	1183	0.0	7.5	0.0	108.4	-16.0
$E'$	2613	98.8	0.7	0.5	0.0	0.0
$E'$	1403	0.3	94.4	11.6	11.4	-17.6
$E'$	1200	0.2	22.1	2.7	79.6	-4.6
$E'$	998	0.6	67.4	8.6	16.2	7.2
$E'$	530	0.1	14.9	85.5	1.1	-1.6

for showing which force constants are most instrumental for determining the vibrational frequencies.

Because of the many isotopic species of boroxine

which can be prepared, it would be possible to extend these calculations by including many more interaction constants. Until a more detailed knowledge of the structure is obtained, a detailed calculation would not be any more meaningful than the one presented. Except for the large negative interaction constant the values for the other constants seem to be quite reasonable. The large negative interaction constant may be necessary because of the polarity of the bonds in boroxine and/or because of the use of an incorrect model ( $D_{3h}$  symmetry, bond lengths, etc.). The value for the BH stretching constant is only slightly higher than those reported for borazine. A comparison of the other constants with borazine will have to await a calculation for the borazine molecule based upon the new vibrational assignments being reported in the literature.<sup>16,17</sup>

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## Bis-Amine Derivatives of $BH_2^+$ with Methylpyridines

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Boron cations,  $H_2B(\text{amine})_2^+$ , with a number of different methylpyridines, have been synthesized through three different routes: (1) from sodium borohydride, iodine, and various amines; (2) from trimethylamine borane, iodine, and amines; (3) from trimethylamine monoiodoborane and different amines. The third method, involving heating of trimethylamine monoiodoborane with excess of the appropriate amine, is found to be the most convenient one and it gives high yields. The boronium<sup>1</sup> salts were quite stable and were characterized by analysis of the hexafluorophosphates and by their uv, ir, and nmr spectra.

### Introduction

A number of boronium salts and their properties have been prepared by Muettterties<sup>2,3</sup> and Douglass,<sup>4</sup> and a study of the synthesis and formation kinetics of bis(pyridine)boronium ion has recently been published.<sup>5</sup> We now wish to report three apparently general synthetic methods to prepare bis(amine)boron cations, where two alkylpyridines are coordinated to a  $BH_2^+$  group. The syntheses proceed from (1) borohydride salts, (2) trimethylamine borane, or (3) trimethylamine monoiodoborane, and give excellent yields of boron cations under mild conditions and from readily available starting materials. The third method is the most convenient and gives the highest yields with the least amounts of impurities or by-products. The general usefulness of these syntheses is illustrated by using methylpyridines and dimethylpyridines as examples.

(1) In accord with past usage, the term boronium is used here to designate a boron cation. The Nomenclature Committee of the American Chemical Society recommends the term bis(amine)dihydroboron(H).

(2) N. E. Miller and E. L. Muettterties, *J. Am. Chem. Soc.*, **86**, 1033 (1964).

(3) E. L. Muettterties, *Pure Appl. Chem.*, **10**, 53 (1965).

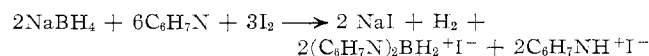
(4) J. E. Douglass, *J. Am. Chem. Soc.*, **86**, 5431 (1964).

(5) G. E. Ryschkewitsch, *ibid.*, **89**, 3145 (1967).

### Experimental Section

**Materials.**—Picolines and lutidines were obtained from Eastman Organic Chemicals and K & K Laboratories, Inc., respectively. The amines were distilled when necessary and dried and stored over Molecular Sieve 3A. Trimethylamine borane was used as obtained from Callery Chemicals Co. Sodium borohydride was supplied in good purity by Metal Hydrides, Inc. All other chemicals were reagent grade and were used without any further purifications, but were dried over Molecular Sieve when appropriate.

**Synthesis of Bis(amine)boron Cations.** (1). **From Sodium Borohydride.**<sup>5</sup>—Sodium borohydride (94% hydride purity), 0.793 g (19.7 mmol), was slurried in 24 ml of 4-picoline. Iodine solution, 7.290 g (29.0 mmol) in 190 ml of benzene, was added very slowly while the picoline-borohydride slurry was stirred. During the addition of iodine, hydrogen gas was evolved, and in the early stages, the reaction was very fast. The solution was heated gradually to 70°, and the addition of iodide was continued. When all the iodine had been added, a permanent iodine color developed, and, on further heating for 1 hr, the color still persisted. The amounts of iodine used corresponded closely to the quantities calculated according to



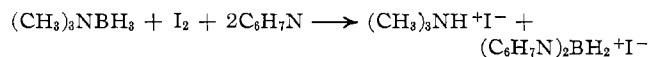
The reaction mixture was evaporated to dryness under vacuum, and the resulting solid mixture was extracted with 100 ml of dry chloroform and filtered. The leftover solid, after washing with

warm chloroform and drying, weighed 3.007 g and was identified by infrared and qualitative analysis as sodium iodide (20 mmol). The filtrate was treated with trimethylamine gas to convert the picolinium salt to the less soluble trimethylammonium iodide. The ammonium salt weighed 2.850 g and had an ir spectrum identical with that of an authentic sample. The remaining solution was evaporated at room temperature, affording 6.075 g of bis(4-picoline)boronium iodide (89.0% yield). Bis(2-picoline)- and bis(3-picoline)boronium salts were prepared by similar procedures, and yields are given in Table I.

TABLE I  
YIELDS OF BIS-AMINE  $\text{BH}_2^+\text{I}^-$  SALTS

Amine	From $\text{NaBH}_4$ , %	From $(\text{CH}_3)_3\text{NBH}_3$ , %	From $(\text{CH}_3)_3\text{NBH}_2\text{I}$ , %
2-Picoline	83	90	90
3-Picoline	88	96	92
4-Picoline	89	86	91
2,3-Lutidine			93
2,4-Lutidine		62	89
2,5-Lutidine			91
2,6-Lutidine			84
3,4-Lutidine		70	97
3,5-Lutidine			98

(2). **From Trimethylamine Borane.**<sup>4,5</sup>—Trimethylamine borane, 2.00 g (27.5 mmol), was dissolved in 25 ml of 2-picoline. Solid iodine, 6.978 g (27.5 mmol), or iodine in benzene solution was added in small portions over a 15-min period. An exothermic reaction started immediately. The reaction mixture was heated gradually to 70° and heating was continued until the iodine color was discharged (about 1 hr). The temperature was then raised to 110° and the mixture was refluxed for 2 hr. After evaporation to dryness, the solid mixture was extracted with 100 ml of chloroform. The less soluble  $(\text{CH}_3)_3\text{NH}^+\text{I}^-$  was filtered off (4.382 g, 23.4 mmol). On saturating the filtrate with trimethylamine, an additional crop of trimethylammonium iodide was obtained (1.172 g, 6.2 mmol). The solution was then evaporated at room temperature affording 8.016 g (90% yield) of bis(2-picoline)-boronium iodide. Thus reaction had occurred according to



By a similar procedure, boronium salts of 3-picoline, 4-picoline, 2,4-lutidine, and 3,4-lutidine were prepared; their yields are given in Table I.

(3). **From Trimethylamine Monoiodoborane.**<sup>6</sup>—Iodoborane was prepared by a modification of the method of Nöth.<sup>7</sup> Trimethylamine borane, 1.902 g (26.1 mmol), was dissolved in 30 ml of dry benzene. Solid iodine, 2.774 g (10.9 mmol), was added in small portions while the solution was stirred, and the flask was loosely stoppered between additions of iodine. The reaction was very vigorous. After all of the iodine had been added, the solution attained a very light violet color and 20 ml of 3-picoline was added. The benzene was then distilled off and the mixture was heated to 110° for 3–4 hr. After cooling, filtering, and washing with benzene and a small amount of ether, the dried product of bis(3-picoline)boronium iodide weighed 6.480 g (92% yield). By this method, boronium salts of all picolines and lutidines were prepared. Their yields are given in Table I.

**Hexafluorophosphate Salts.**—Some of the boronium iodides prepared from the iodoborane were converted to hexafluorophosphates by adding excess of ammonium hexafluorophosphate. Boronium iodide, 0.500 g, was dissolved in 12 ml of distilled water, and 0.525 g (3.22 mmol) of ammonium hexafluorophosphate was added to precipitate the boronium hexafluorophosphates. The precipitate was washed with 8 ml of water and 20

ml of ether, dried, and weighed. Yields are given in Table II and analytical data are given in Table III.

TABLE II  
YIELDS OF BIS-AMINE  $\text{BH}_2^+\text{PF}_6^-$  SALTS<sup>a</sup>

Amine	Based on $\text{I}^-$ salts, <sup>b</sup> %	Over-all, based on $(\text{CH}_3)_3\text{NBH}_3$ , %
3-Picoline	96	88
4-Picoline	93	84
2,3-Lutidine <sup>c</sup>	77	72
2,5-Lutidine	89	81
2,4-Lutidine	91	88

<sup>a</sup> The salts were readily recrystallized from hot water. <sup>b</sup> Prepared from  $(\text{CH}_3)_3\text{NBH}_2\text{I}$ . <sup>c</sup> Only 0.250 g of  $\text{B}^+$  salt was used.

**Infrared Spectra.**—All of the boronium salts have similar infrared spectra except for the expected differences caused by the known absorptions of the anions. The stretching vibrations for  $\text{BH}_2$  grouping are doublets found in the region 2400–2500  $\text{cm}^{-1}$  and the deformation of the HBH angle is found as an intense band near 1160  $\text{cm}^{-1}$ .<sup>3,4</sup> The absorptions of the free pyridines appearing in the region 1500–1600  $\text{cm}^{-1}$  are shifted to higher wave numbers by 40–50  $\text{cm}^{-1}$ , when the amine is coordinated in the boron cation. The shifts are larger than those observed when the amine is coordinated to  $\text{BH}_3$ .

**Ultraviolet Spectra.**—The uv spectra of the hexafluorophosphates were measured in 95% ethyl alcohol with a Cary 14 spectrophotometer. In all of the salts, three bands with similar molar absorptivities were observed as shown in Table IV. Absorptivities were calculated from two different concentrations and are estimated to be accurate to better than 0.5%.

**Nuclear Magnetic Resonance Spectra.**—The <sup>11</sup>B nuclear resonance spectra were obtained at 19.3 Mc in  $\text{CH}_2\text{Cl}_2$  with trimethyl borate as external reference. In general, the spectra are triplets, as expected. The proton spectra of the  $\text{PF}_6^-$  salts were obtained in  $\text{CH}_2\text{Cl}_2$  and referred to external tetramethylsilane. Owing to excessive line broadening, hydrogens attached to the boron could not be detected. The integrated intensities of the proton spectra agreed well with the expected values. Resonances belonging to the ring protons were assigned on the basis of their relative intensities, their multiplicity, and their relative chemical shifts. Changes in the anion may cause small shifts from the values reported in Table V. The uncertainty in the B–H coupling constants was 10–20 cycles. Because of line broadening, this value could not be measured in some instances.

## Discussion

The boronium iodides prepared in this study are hygroscopic salts which are readily soluble in water, acetone, methylene chloride, and chloroform but insoluble in carbon tetrachloride, benzene, and diethyl ether. Derivatives, such as salts of  $\text{B}(\text{C}_6\text{H}_5)_4^-$ ,  $\text{SbF}_6^-$ , or  $\text{PF}_6^-$ , can be readily prepared by precipitation in cold water. The latter two anions are especially suitable for separation of boronium ions from ammonium salts which tend to be the principal impurities in the iodides prepared by either of the above methods. The high yields of hexafluorophosphates (Table II) show, however, that the iodides are substantially pure; in fact, the losses can be accounted for nearly quantitatively by the solubility of the boronium hexafluorophosphates in water, which is of the order of 0.01 *M* at room temperature but substantially larger near the boiling point.

Water solutions of the iodides are transparent in the visible region, but solutions in methylene chloride generally show broad absorptions in the blue region of

(6) G. E. Ryschkewitsch and J. M. Garrett, *J. Am. Chem. Soc.*, **89**, 4240 (1967).

(7) H. Nöth and H. Beyer, *Chem. Ber.*, **93**, 2251 (1960).

TABLE III  
ANALYSES

		% C	% H	% N	% B	% P	% F	Mp, °C	
C <sub>12</sub> H <sub>16</sub> N <sub>2</sub> BPF <sub>6</sub>	Calcd	41.89	4.65	8.15	3.15	9.02	33.16		
	(2-pic) <sub>2</sub> BH <sub>2</sub> <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	Found	42.04	4.74	8.31	3.24	8.95	32.96	155-155.5
	(3-pic) <sub>2</sub> BH <sub>2</sub> <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	Found	41.96	4.77	8.20	3.03	8.93	33.05	94.5-95
	(4-pic) <sub>2</sub> BH <sub>2</sub> <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	Found	41.80	4.80	8.01	3.20	9.20	32.93	132.5-133
C <sub>12</sub> H <sub>16</sub> N <sub>2</sub> BAF <sub>6</sub>	Calcd	37.15	4.12	7.22	2.79	19.32 <sup>a</sup>	29.42		
	(4-pic) <sub>2</sub> BH <sub>2</sub> <sup>+</sup> AsF <sub>6</sub> <sup>-</sup>	Found	37.30	4.21	6.98	2.96	19.05 <sup>a</sup>	29.16	140-141
C <sub>14</sub> H <sub>20</sub> N <sub>2</sub> BPF <sub>6</sub>	Calcd	45.19	5.38	7.53	2.91	8.34	30.66		
	(2,3-lut) <sub>2</sub> BH <sub>2</sub> <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	Found	45.37	5.49	7.36	2.89	8.56	30.24	148.5-149.5
	(2,4-lut) <sub>2</sub> BH <sub>2</sub> <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	Found	45.16	5.52	7.62	2.75	8.48	30.39	113-114
	(2,5-lut) <sub>2</sub> BH <sub>2</sub> <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	Found	45.16	5.46	7.36	2.87	8.40	30.41	147.5-148.5
	(2,6-lut) <sub>2</sub> BH <sub>2</sub> <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	Found	45.49	5.47	7.38	2.81	8.28	30.91	133.5-134.5
	(3,4-lut) <sub>2</sub> BH <sub>2</sub> <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	Found	45.14	5.53	7.42	3.06	8.46	30.39	133.5-134
	(3,5-lut) <sub>2</sub> BH <sub>2</sub> <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	Found	45.12	5.49	7.31	2.76	8.60	30.70	203.5-204

<sup>a</sup> % As.TABLE IV  
ULTRAVIOLET SPECTRA OF BIS-AMINE BH<sub>2</sub><sup>+</sup>PF<sub>6</sub><sup>-</sup> SALTS

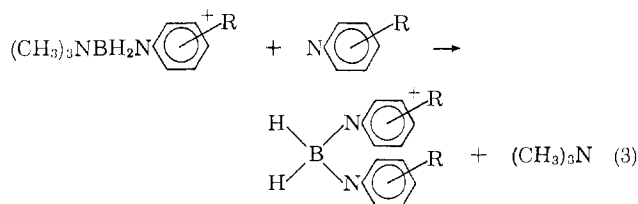
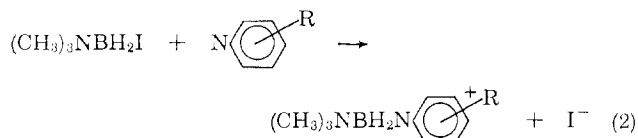
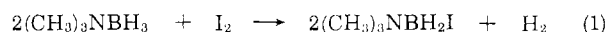
Amine	Molar absorptivity × 10 <sup>-3</sup>	Wavelength, Å
2-Picoline	9.44	2625
	10.85	2680
	8.68	2725
3-Picoline	8.77	2660
	9.42	2670
	6.58	2750
4-Picoline	6.15	2509 <sup>a</sup>
	7.43	2562
	5.22	2637
2,3-Lutidine	10.38	2692
	11.52	2726
	9.09	2795
2,4-Lutidine	9.13	2630
	9.53	2640
	8.53	2700
2,5-Lutidine	10.54	2723 <sup>b</sup>
	11.15	2750
	8.71	2809
2,6-Lutidine	10.54	2683
	9.73	2735 <sup>c</sup>
	7.43	2608 <sup>b</sup>
3,4-Lutidine	7.62	2626
	5.95	2683
	8.08	2667 <sup>b</sup>
3,5-Lutidine	9.20	2715
	6.83	2781

<sup>a</sup> Small shoulder. <sup>b</sup> Broad shoulder. <sup>c</sup> Long tail at higher wavelength.

the spectrum. Since the hexafluorophosphates do not absorb in the visible region in either solvent, one may attribute the color of the iodides to charge transfer between I<sup>-</sup> and the pyridine substituent on boron, analogous to the behavior of alkylpyridinium iodides.<sup>8,9</sup> The ultraviolet spectra are similar to the spectra of the free amines: a short-wavelength band and a central more intense band with a shoulder on either side (Table IV). In the boronium salts the absorptions are shifted to larger wavelengths generally by about 50 Å.

The three methods of synthesis presented here appear to be based on a common scheme of reactions: iodination of an amine borane, followed by displacement of

halide by excess amine, and, finally, displacement by coordinated amine to produce a cation with C<sub>2v</sub> symmetry



If readily available NaBH<sub>4</sub> is used as the starting material (method 1): the first step is the formation of BH<sub>3</sub>,<sup>10</sup> which is then trapped by the amine. In fact, pyridine borane<sup>5</sup> and 2-picoline borane were isolated as intermediates in the over-all reaction and were demonstrated to yield the boron cation in subsequent steps (eq 1 and 2). This method, of course, will lead directly to a symmetrical cation without the necessity of further amine displacement (eq 3). The other two methods involve an unsymmetrical intermediate cation which can be isolated under appropriate conditions.<sup>6,11</sup> This type of intermediate has been shown to undergo amine exchange relatively rapidly,<sup>12</sup> according to eq 3.

The high yields obtained in all of the synthetic methods indicate the virtual absence of side reactions involving a boron compound. Nevertheless, the synthesis proceeding from the iodoborane adduct would seem the method of choice if an iodide salt is desired, since here the compound can be obtained without the necessity of separating it from other nonvolatile reaction products. The fact that the yields are virtually independent of the nature of the amine implies that, under the reaction conditions employed here, neither electronic differences nor steric factors in the amines produce

(10) E. M. Kosower, *J. Am. Chem. Soc.*, **77**, 3883 (1955).(9) E. M. Kosower and P. E. Khinedinst, Jr., *ibid.*, **78**, 3493 (1956).(10) G. F. Fuegard and L. H. Long, *Chem. Ind. (London)*, 47 (1965).(11) H. Nöth, H. Beyer, and H. Vetter, *Chem. Ber.*, **97**, 110 (1964).

(12) T. E. Sullivan, M.S. Thesis, University of Florida, 1967.

TABLE V  
 NMR DATA FOR BIS-AMINE  $\text{BH}_2^+\text{PF}_6^-$  SALTS

Amine	$\text{CH}_3$ $\delta$ , ppm	Aromatic protons $\delta$ , ppm ( $J$ , cps)	$M^a$	$^{11}\text{B}$ resonance
$(2\text{-pic})_2\text{BH}_2^+\text{PF}_6^-$	2.68	$\text{H}_{3,6}$ , 7.77	m	$22.3 \pm 1.1$ , $J = 90$ cps
$(3\text{-pic})_2\text{BH}_2^+\text{PF}_6^-$	2.55	$\text{H}_{4,6}$ , 8.27	m	
		$\text{H}_5$ , 7.80	Q	$23.1 \pm 0.8$ b
		$\text{H}_4$ , 8.18 (8)	D	
		$\text{H}_{2,6}$ , 8.57	bD	
$(4\text{-pic})_2\text{BH}_2^+\text{PF}_6^-$	2.58	$\text{H}_{2,6}$ , 8.53 (6)	D	$19.2 \pm 1.1$ b
		$\text{H}_{3,5}$ , 7.67 (6)	D	
$(2,3\text{-lut})_2\text{BH}_2^+\text{PF}_6^-$	2- $\text{CH}_3$ , 2.63	$\text{H}_6$ , 7.60 (6)	T	$20.0 \pm 0.5$
	3- $\text{CH}_3$ , 2.53	$\text{H}_{4,6}$ , 8.20 (6)	D	
$(2,4\text{-lut})_2\text{BH}_2^+\text{PF}_6^-$	2- $\text{CH}_3$ , 2.62	$\text{H}_{3,5}$ , 7.50 (6)	D	$22.0 \pm 0.8$ , $J = 90$ cps
	4- $\text{CH}_3$ , 2.57	$\text{H}_6$ , 8.10 (6)	D	
$(2,5\text{-lut})_2\text{BH}_2^+\text{PF}_6^-$	2- $\text{CH}_3$ , 2.62	$\text{H}_3$ , 7.63 (8)	D	$22.0 \pm 0.8$ , $J = 90$ cps
	5- $\text{CH}_3$ , 2.45	$\text{H}_{4,6}$ , 8.00	b	
$(2,6\text{-lut})_2\text{BH}_2^+\text{PF}_6^-$ <sup>b</sup>	2,6- $\text{CH}_3$ , 1.88	$\text{H}_{3,5}$ , 6.93 (8)	D	$26.6 \pm 1$ , $J = 110$ cps
		$\text{H}_4$ , 7.46	m	
$(3,4\text{-lut})_2\text{BH}_2^+\text{PF}_6^-$	3- $\text{CH}_3$ , 2.43	$\text{H}_6$ , 7.62 (6)	D	$18.9 \pm 0.8$ b
	4- $\text{CH}_3$ , 2.50	$\text{H}_{2,6}$ , 8.4	b	
$(3,5\text{-lut})_2\text{BH}_2^+\text{PF}_6^-$	3,5- $\text{CH}_3$ , 2.50	$\text{H}_4$ , 7.97	bS	$20 \pm 2$
		$\text{H}_{2,6}$ , 7.37	bS	

<sup>a</sup> Symbols: M, multiplicity; S, singlet; D, doublet; T, triplet; Q, quartet; m, complex multiplet; b, broad. <sup>b</sup> In nitromethane.

marked differences, if any, in the reaction rates. Indeed, one should consider the possibility that replacement of iodide by the amines proceeds through ionization of the halogen in the rate-determining step. Although such a mechanism would seem rather unlikely in a medium of low polarity, it would explain the apparent uniformity in reaction rates. On the other hand, rate-determining nucleophilic displacement of iodide by amine can be reconciled with the synthetic results, if one considers the fact that alkyl substitution on pyridine produces only a relatively narrow range of basicities, perhaps not sufficiently large to produce differentiation in yields in the reaction times employed

here. It is more noteworthy that even 2,6-lutidine reacts essentially completely to give a bis(lutidine)-boron cation, in spite of the likelihood that in this compound the substantial crowding around the boron atom should hinder the formation of the product. It appears, therefore, that steric inhibition in any of the reaction steps (eq 1-3), which is probable when the amine is 2,6-lutidine, is not large enough to interfere with a successful synthesis of the bis-amine cation.

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## The Preparation of Germyl Methyl Sulfide and the Proton Nuclear Magnetic Resonance Spectra of Some Sulfur Derivatives of Silane and Germane<sup>1</sup>

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Germyl methyl sulfide has been prepared by the reaction of  $\text{CH}_3\text{SNa}$  with either  $\text{GeH}_3\text{I}$  or  $\text{GeH}_3\text{Cl}$ . Some of its physical and chemical properties have been determined. The compound is thermally stable at room temperature but decomposes in the presence of  $\text{B}_2\text{H}_6$  or  $\text{BF}_3$  to form  $\text{GeH}_4$  and an unidentified solid material. The high-resolution proton nuclear magnetic resonance spectra of various sulfur derivatives of silane and germane have been obtained and are discussed.

Relatively few investigations on the synthesis and properties of sulfur derivatives of monogermane have ever been reported in the literature. The paucity of information on these systems is largely related to prob-

lems associated with their synthesis, low volatility, and questionable thermal stability. Until recently, the only known derivative of this type was digermyl sulfide,  $(\text{GeH}_3)_2\text{S}$ .<sup>2,3</sup> Although a detailed Raman-infrared

(1) Presented, in part, at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

(2) S. Sujishi, Abstracts of the XVIIth International Congress of Pure and Applied Chemistry, Munich, 1959, p 53.

(3) T. D. Goldfarb and S. Sujishi, *J. Am. Chem. Soc.*, **86**, 1679 (1964).