1039

## Reactions of Monosilylarsine with Some Boron Lewis Acids and the **Reaction of Monosilylphosphine with Boron Tribromide**

By J. E. Drake • and J. Simpson, Department of Chemistry, The University, Southampton

The reactions of monosilylarsine with diborane, monobromodiborane, boron trichloride, and boron tribromide are discussed together with the reaction of monosilylphosphine with boron tribromide. Definite adducts are formed in all the reactions except that of diborane in which condensation to trisilyarsine occurs. A mechanism is suggested for this condensation and for the apparently anomalous reactions with boron tribromide.

THE reactions of organoarsines, particularly as donor molecules to transition metals, are well known but there is much less information about unsubstituted arsine or silvlarsines. No direct evidence for the formation of an adduct was found in the reactions of arsine with boron trifluoride <sup>1</sup> and diborane <sup>2</sup> although both the boron compounds form adducts with phosphine 1,3 as do monobromodiborane,<sup>4</sup> boron trichloride, and boron tribromide.<sup>5</sup> Similar adducts are also formed with monosilvlphosphine<sup>6,7</sup> but the reaction with the tribromide has not been studied and we here report on that. There is very little information about monosilylarsine, apart from reports of its <sup>1</sup>H n.m.r. spectrum,<sup>8</sup> mass spectrum,<sup>9</sup> and a preliminary study of its infrared and Raman spectra,10 but the reaction of trimethylsilyldimethylarsine with boron trifluoride to give trimethylsilyl fluoride and dimethylarsinylboron diffuoride has been reported.<sup>7</sup> The reactions of some boron Lewis acids with monosilylarsine are also discussed.

#### EXPERIMENTAL

Apparatus.-The experiments were carried out in a conventional Pyrex glass vacuum system with greaseless stopcocks (G. Springham and Co. Ltd., Harlow, Essex; Viton A diaphragm) where reactants might be susceptible to grease. Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer with a gas cell (5 cm. path length) fitted with KBr windows. <sup>1</sup>H n.m.r. spectra were recorded on a Varian A60 spectrometer.

Materials .- Diborane was prepared by the action of sulphuric acid on potassium borohydride 11 and purified by vacuum-line distillation (Found: M, 27.9. Calc. for  $B_2H_6$ : M, 27.69). Careful distillation was carried out to purify commercial samples of boron trichloride (Found: M, 118.0. Calc. for BCl<sub>3</sub>: M, 117.2) and boron tribromide [vapour pressure at 0°, 19.0 mm. (lit.,<sup>12</sup> 19.0 mm.)]. The reaction of diborane and boron tribromide was the source for monobromodiborane [vapour pressure at  $-45^{\circ}$ , 42 mm. (lit.,<sup>13</sup> 41 mm.)]. Monosilylphosphine was prepared and its purity checked as described.<sup>6</sup> To avoid repetition it may be assumed that, unless otherwise stated, the purity

of all the well-known compounds formed was checked by molecular-weight or vapour-pressure determinations and by infrared spectroscopy.

Preparation and Purification of Monosilylarsine.-Equimolar amounts of monosilane and arsine were subjected to a 12 kv ozoniser-type silent electric discharge.14 The quantities of the hydrides were such that, when they were completely vapourised, the total pressure in the system was between 200 and 250 mm. Hg. The discharge tube was maintained at  $-78^{\circ}$  with a trap adjacent to it at  $-96^{\circ}$ On completion of a discharge run, hydrogen was pumped away through a series of U-traps surrounded by liquid nitrogen and then all the volatile products from the discharge were distilled out. Monosilylarsine was separated from the other volatile materials by a preliminary condensation at  $-126^{\circ}$  followed by repeated condensation at  $-112^{\circ}$  at which disilane was volatile. Further repeated distillations through traps at -96 to  $-196^{\circ}$  gave reasonably pure SiH<sub>3</sub>·AsH<sub>2</sub>. From the <sup>1</sup>H n.m.r. spectrum <sup>15</sup> of the final product it was estimated that some 1-3% of trisilane remained despite these precautions. Further purification by gas-liquid chromatography was not possible because so much of the monosilylarsine was decomposed on the columns.

Reaction of Monosilylarsine and Diborane.--Monosilylarsine (0.88 mmole) and diborane (0.44 mmole) were condensed together at  $-196^{\circ}$  into a reaction vessel (approximately 10 ml. capacity). The mixture was allowed to stand for 1 hr at various temperatures from -112 to  $25^{\circ}$ but in no case was there any sign of solid formation and the unchanged hydrides were recovered quantitatively.

The experiments were then carried out in small-volume reaction vessels. Typically, monosilylarsine (0.44 mmole) and diborane (0.22 mmole) were condensed at  $-196^{\circ}$  into a semimicro n.m.r. tube 16 which was then sealed. On warming to  $-20^{\circ}$  the <sup>1</sup>H n.m.r. spectrum of the liquid showed only unchanged monosilylarsine. However, on warming to  $0^{\circ}$  the spectrum changed and continued to change for 1 hr. (Figure). A small amount of solid, part of which redissolved in the liquid, was also formed during this period. The tube was then recooled to  $-196^{\circ}$  and broken open on the vacuum line and a small amount of non-condensable gas

<sup>8</sup> J. E. Drake and W. L. Jolly, *J. Chem. Phys.*, 1963, **38**, 1033. <sup>9</sup> F. E. Saalfeld and M. V. McDowell, *Inorg. Chem.*, **1967**, **6**,

96. 10 J. E. Drake and J. Simpson, Spectrochim. Acta, to be published.

<sup>11</sup> H. G. Weiss and I. Shapiro, J. Amer. Chem. Soc., 1959, 81, 6167.

 <sup>12</sup> A. Stock and E. Kuss, Ber., 1914, 47, 3113.
 <sup>13</sup> H. I. Schlesinger and A. B. Burg, J. Amer. Chem. Soc., 1931, 53, 4321.

 <sup>14</sup> J. E. Drake and W. L. Jolly, *Chem. and Ind.*, 1962, 1470.
 <sup>15</sup> J. E. Drake and W. L. Jolly, UCRL Report, 10,422, 1962.
 <sup>16</sup> J. Simpson, Ph.D. Thesis, University of Southampton, 1967.

<sup>&</sup>lt;sup>1</sup> D. R. Martin and R. E. Dial, J. Amer. Chem. Soc., 1950,

<sup>72, 852.</sup> <sup>2</sup> F. G. A. Stone and A. B. Burg, J. Amer. Chem. Soc., 1954,

<sup>76, 386.</sup> <sup>3</sup> R. W. Rudolph, R. W. Parry, and C. F. Farran, *Inorg.* 

<sup>.</sup> E. Drake and J. Simpson, Inorg. Nuclear Chem. Letters, 1967, **3**, 87.

<sup>&</sup>lt;sup>5</sup> E. L. Gamble and P. Gilmont, J. Amer. Chem. Soc., 1940, **62**, 717.

<sup>&</sup>lt;sup>6</sup> J. E. Drake and J. Simpson, *Inorg. Chem.*, 1967, 6, 1984. <sup>7</sup> C. R. Russ and A. G. MacDiarmid, *Angew. Chem. Internat.* 

Edn., 1966, 5, 418.

Reaction of monosilylarsine and diborane at  $0^\circ$  in a sealed tube

Reactants (mmole)			Products (mmole)			
Time (hr)	SiH <sub>3</sub> ·AsH <sub>2</sub>	B <sub>2</sub> H <sub>6</sub>	SiH <sub>3</sub> ·AsH <sub>2</sub>	(SiH <sub>3</sub> ) <sub>2</sub> AsH	(SiH <sub>3</sub> ) <sub>3</sub> As	AsH <sub>3</sub> /B <sub>2</sub> H <sub>6</sub>
0.3	0.44	0.22	0.18	0.06	0.04	0.34
1	0.44	0.22		0.06	0.10	0.34
3	0.44	0.22		0.06	0.09	0.30

was pumped away. The condensable products were fractionated to give a mixture of arsine and diborane (0.34 mmole) at  $-196^{\circ}$ , disilylarsine (0.06 mmole identified by its infrared and <sup>1</sup>H n.m.r. spectra <sup>16</sup>) at  $-126^{\circ}$ , and trisilylarsine (0.1 mmole, purity confirmed by its <sup>1</sup>H n.m.r. spectrum <sup>17</sup>) at  $-78^{\circ}$ . A small amount of involatile white solid, which rapidly darkened on exposure to air, remained in the tube.



<sup>1</sup>H N.m.r. spectra of the reaction of monosilylarsine and diborane
(a) Initially at -20°. (b) After 20 min. at 0°. (c) After 1 hr. at 0°

The experiment was repeated so that the reactants were kept at  $0^{\circ}$  for varying times before the tubes were opened and the products were analysed as described above (Table).

Reaction of Monosilylarsine and Monobromodiborane (1:1 Addition).-In a typical reaction, monosilylarsine (0.44 mmole) and monobromodiborane (0.44 mmole) were condensed together at  $-196^{\circ}$  in the 10 ml. reaction vessel, warmed to  $-78^\circ$ , and kept at that temperature for 1 hr. A white solid was formed and an infrared examination of the vapour above it indicated the presence of diborane. On warming to  $-63^{\circ}$ , the infrared spectrum showed that monobromosilane was also present and the evolution of the monobromosilane continued until the temperature reached  $-23^{\circ}$ , whereupon a non-volatile white solid was left. Fractionation of all the volatile material gave diborane (0.23 mmole) passing through a trap at  $-126^\circ$ , and monobromosilane (0.41 mmole). The infrared spectrum of the diborane fraction showed peaks corresponding to small amounts of arsine impurity.

Reaction of Monosilylarsine and Monobromodiborane (2:1 Addition).---Monosilylarsine (0.44 mmole) and monobromodiborane (0.22 mmole) were condensed together under conditions identical to those described for the 1:1 addition and kept at  $-78^{\circ}$  for 1 hr. A white solid was formed and diborane, together with small quantities of unchanged monosilylarsine, was detected from an infrared examination of the volatile material. At  $-63^{\circ}$  neither of these was detectable and the only volatile material was monobromosilane. However, between -45 and  $-23^{\circ}$ , arsine, monosilvlarsine, and diborane were also evolved. After 1 hr. at  $-23^{\circ}$  all of the volatile material was distilled from the reaction vessel, leaving a white solid residue which gave no further gaseous products after some hours at room temperature. The volatile materials were fractionated to give a mixture of arsine and diborane (0.13 mmole), a mixture of monosilylarsine (0.08 mmole) and monobromosilane (0.21 mmole) at  $-126^{\circ}$ , and trisilylarsine (0.04 mmole) with a small amount of disilylarsine (<0.01 mmole) at  $-78^{\circ}$ . The separations of SiH<sub>3</sub>·AsH<sub>2</sub> from SiH<sub>3</sub>Br, and of (SiH<sub>3</sub>)<sub>3</sub>As from (SiH<sub>3</sub>)<sub>2</sub>AsH, were achieved by repeated distillations through traps at -112 and  $-78^{\circ}$  respectively.

Reaction of Monosilylarsine and Boron Trichloride.—In a typical experiment, monosilylarsine (0.66 mmole) and boron trichloride (0.66 mmole) were kept at  $-78^{\circ}$  for 1 hr. during which a white solid of negligible vapour pressure was formed. On warming to  $-63^{\circ}$  the pressure above the solid increased owing to the evolution of monochlorosilane. When the temperature was raised to  $-45^{\circ}$ , the solid decomposed with much frothing to leave a colourless wax. There was no further evolution of gas on warming to room temperature and monochlorosilane (0.63 mmole) was the only volatile product. The residual solid decomposed slightly when heated to  $100^{\circ}$  to give off hydrogen, arsine (0.01 mmole), and boron trichloride (0.02 mmole).

Reaction of Monosilylarsine with Boron Tribromide.— Typically, monosilylarsine (0.44 mmole) and boron tri-

<sup>17</sup> E. A. V. Ebsworth and G. M. Sheldrick, *Trans. Faraday Soc.*, 1966, **62**, 3282.

bromide (0.44 mmole) were kept together for 1 hr. at  $-78^{\circ}$ . A white solid of negligible vapour pressure was formed. When the temperature was raised to  $-63^{\circ}$  mono- and dibromosilane were obtained. The evolution of SiH<sub>2</sub>Br<sub>2</sub> continued as the temperature was raised in stages to  $-23^{\circ}$ , and at  $0^{\circ}$  small amounts of tribromosilane could also be detected. After 2 hr. at room temperature there was no more evolution of gas but the white solid had changed to a wax. All the volatile products were fractionated giving monobromosilane (0.01 mmole) at  $-196^{\circ}$ , dibromosilane (0.39 mmole) at  $-112^{\circ}$ , and tribromosilane (0.03 mmole)at  $-78^{\circ}$ . The infrared spectrum of the wax, obtained as a smear between KBr discs, showed broad bands at 2490, 2430, and 2080 cm.<sup>-1</sup>. In other experiments, the reactants were rapidly warmed to room temperature from  $-78^{\circ}$  and then traces of monobromodiborane were detected in addition to the brominated silanes.

Reaction of Monosilylphosphine and Boron Tribromide.---In a typical experiment, monosilylphosphine (0.66 mmole) and boron tribromide (0.66 mmole) were kept at  $-78^{\circ}$ for 1 hr. The small quantity of volatile material at this temperature was unchanged monosilylphosphine. At  $-63^{\circ}$ , the pressure became negligible and a white solid was formed. At  $-45^{\circ}$  monobromosilane was the only volatile material but at  $-23^{\circ}$  both mono- and di-bromosilane were evolved and continued to be evolved at room temperature. The volatile materials were then distilled off leaving a white solid which continued to decompose slowly with the evolution of di- and tri-bromosilane. Gentle heating was required to release all of the gaseous products leaving a wax. As described above, the volatile material was separated and identified to give monobromosilane (0.14 mmole), dibromosilane (0.44 mmole), and tribromosilane (0.04 mmole). The infrared spectrum of the wax (KBr discs) showed bands principally at 2465, 2405, 2380, 1060, 825, and 790 cm.<sup>-1</sup>.

#### DISCUSSION

Monosilylarsine does not react with diborane under experimental conditions that give diborane in the gaseous phase, which is to be expected because neither does monosilylphosphine.<sup>6</sup> However, under pressure in a sealed tube, monosilylphosphine forms the adduct SiH<sub>3</sub>·PH<sub>2</sub>,BH<sub>3</sub>,<sup>18</sup> but with monosilylarsine amounts of arsine, disilylarsine, and trisilylarsine are formed in proportions dependant on the duration of the reaction (Table). The course of this reaction can be followed by observing the changes that occur in the <sup>1</sup>H n.m.r. spectrum over a period. The spectrum (Figure, a) which was run immediately after a mixture of monosilylarsine and diborane had been warmed to  $-20^{\circ}$ , shows the triplet-quartet pattern expected for unchanged  $SiH_3 \cdot AsH_2$ <sup>15</sup> [ $\delta SiH = 3.68$  p.p.m. (lit., 3.67 p.p.m. to low field of internal TMS)]. The resonance due to  $B_2H_6$ would not be observed at this spectrum amplitude. The Figure, b shows the spectrum after 20 min. at 0° in which peaks at 3.71 and 3.79 p.p.m. are growing at the expense of the SiH<sub>3</sub> resonance triplet of monosilylarsine. This is consistent with the appearance of a doublet centred at 3.74 p.p.m. due to the formation of disilylarsine,<sup>16</sup> the high-field SiH<sub>3</sub> branch of which adds a shoulder to the central branch of the SiH<sub>3</sub>·AsH<sub>2</sub> triplet. The lowfield components of the two hydrides are then more or

less coincident at 3.79 p.p.m. The integration of this spectrum indicates that some contribution is added from the SiH<sub>3</sub> resonance of trisilylarsine (lit.,<sup>17</sup> 3.85 p.p.m.). The broad AsH resonance is slightly distorted by the AsH resonance of disilylarsine. The additional resonance at 1.51 p.p.m. is readily assigned to arsine (lit.,<sup>19</sup> 1.51 p.p.m.). The spectrum after 1 hr. (Figure, c) shows clearly the SiH<sub>3</sub> resonances of di- and tri-silylarsine but that due to monosilylarsine is no longer visible. The peaks centred at 3.36 p.p.m. are due to the trisilane impurity.

The amounts of hydrides recovered at the conclusion of these runs is also consistent with the overall condensation reactions in the presence of diborane being (1) and (2). The yield of disilylarsine relative to that of tri-

$$2\mathrm{SiH}_3 \cdot \mathrm{AsH}_2 \longrightarrow (\mathrm{SiH}_3)_2 \mathrm{AsH} + \mathrm{AsH}_3 \qquad (1)$$

$$3\mathrm{SiH}_3 \cdot \mathrm{AsH}_2 \longrightarrow (\mathrm{SiH}_3)_3 \mathrm{As} + 2\mathrm{AsH}_3$$
 (2)

silylarsine is increased when the reaction is stopped after 20 min. as is to be expected if  $(SiH_3)_2AsH$  is an intermediate. However, their relative yields remain the same when the reaction time is increased from 1 to 3 hr. indicating that the reaction stops when all the monosilylarsine is consumed. The formation of a white solid which redissolves during the reaction could indicate the formation of  $SiH_3 \cdot AsH_2, BH_3$  as the essential intermediate. The corresponding borane adduct is readily formed with monosilylphosphine under these conditions and the reactions with monoboromodiborane also support the idea of the 'BH<sub>3</sub>' catalytic effect. The mechanism in the Scheme would account for these observations.

$$\begin{array}{c} \operatorname{SiH}_{3} \cdot \operatorname{AsH}_{2} + \frac{1}{2}\operatorname{B}_{2}\operatorname{H}_{6} \longrightarrow \operatorname{SiH}_{3} \cdot \operatorname{AsH}_{2}, \operatorname{BH}_{3} \\ \operatorname{SiH}_{3} \cdot \operatorname{AsH}_{2} + & \longrightarrow \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & &$$

(

The high pressure reaction of arsine and diborane<sup>2</sup> gives the polymer  $(AsH_2 \cdot BH_2)_n$  and hydrogen possibly through the transient formation of  $AsH_3, BH_3$ . This would account for the small quantities of hydrogen and of solid residue found in our experiments and for the fact that the amounts of diborane and arsine recovered are slightly less than quantitative.

The overall reaction between equimolar amounts of monosilylarsine and monobromodiborane is (3). By  $SiH_3 \cdot AsH_2 + B_2H_5Br \longrightarrow$ 

$$\operatorname{SiH}_{3}\mathrm{Br} + \frac{1}{2}\mathrm{B}_{2}\mathrm{H}_{6} + \frac{1}{n}(\mathrm{AsH}_{2}\cdot\mathrm{BH}_{2})_{n} \quad (3)$$

<sup>18</sup> J. E. Drake and J. Simpson, Chem. Comm., 1967, 249.

<sup>19</sup> E. A. V. Ebsworth and G. M. Sheldrick, *Trans. Faraday* Soc., 1967, **63**, 1070.

analogy with the monosilylphosphine system <sup>6</sup> the reaction may proceed by the monobromodiborane adduct. In this case it would have only a transitory existence, liberating diborane at  $-78^{\circ}$  and giving the monobromoborane adduct (reaction 4). Monosilylarsine-monobromoborane is a white solid which begains to decompose able to  $PH_3$ ,  $BCl_3$  nor  $AsH_3$ ,  $BCl_3$  so any difference in stabilities cannot be related to changes in donor properties resulting from silyl substitution.

By analogy with these reactions with boron trichloride, both monosilylarsine and monosilylphosphine might be expected to react with boron tribromide to give, even-

$$\operatorname{SiH}_{3} \cdot \operatorname{AsH}_{2} + \operatorname{B}_{2}\operatorname{H}_{5}\operatorname{Br} \xrightarrow{-78^{\circ}} \operatorname{SiH}_{3} \cdot \operatorname{AsH}_{2}, \operatorname{BH}_{2}\operatorname{Br} + \frac{1}{2}\operatorname{B}_{2}\operatorname{H}_{6}$$
(4)  
(SiH\_{3} \cdot \operatorname{AsH}\_{2}, \operatorname{B}\_{2}\operatorname{H}\_{5}\operatorname{Br})

at  $-63^{\circ}$  and which by  $-23^{\circ}$  has given the quantitative amount of monobromosilane required by the equation (5). The corresponding adducts of monosilylphosphine

$$\operatorname{SiH}_3$$
·AsH<sub>2</sub>, BH<sub>2</sub>Br  $\longrightarrow$  SiH<sub>3</sub>Br  $+ \frac{1}{n} (\operatorname{AsH}_2 \cdot \operatorname{BH}_2)_n$  (5)

are much more thermally stable. SiH<sub>3</sub>·PH<sub>2</sub>,B<sub>2</sub>H<sub>5</sub>Br is a white solid stable to -63° and SiH<sub>3</sub>·PH<sub>2</sub>,BH<sub>2</sub>Br is stable to  $-45^{\circ}$ . The decomposition of the former adduct in the presence of excess of monosilylphosphine could be explained in terms of the formation of the active 'BH<sub>3</sub>' species. The decomposition products resulting from the reaction of monosilylarsine with monobromodiborane in a 2:1 ratio may be explained similarly. In addition to the quantitative amount of monobromosilane required by equation (3), arsine and di- and trisilyl-arsine are formed. This suggests that the diborane is taken up by the excess of monosilylarsine in the transient formation of SiH<sub>3</sub>AsH<sub>2</sub>BH<sub>3</sub> which then decomposes to give the arsine products and diborane as in the Scheme. The possibility of a condensation catalysed by monobromosilane is discounted because SiH<sub>3</sub>·AsH<sub>2</sub> and SiH<sub>3</sub>Br do not react under these experimental conditions.16

Monosilylarsine reacts with boron trichloride at  $-78^{\circ}$  to give a 1:1 adduct. This white solid decomposes in the temperature range  $-63^{\circ}$  to  $-45^{\circ}$  with the evolution of the amount of monochlorosilane required by the equations (6) and (7). Although the form of this

$$\operatorname{SiH}_3 \cdot \operatorname{AsH}_2 + \operatorname{BCl}_3 \longrightarrow \operatorname{SiH}_3 \cdot \operatorname{AsH}_2, \operatorname{BCl}_3$$
 (6)

$$\operatorname{SiH}_{3}\operatorname{AsH}_{2},\operatorname{BCl}_{3}\longrightarrow \operatorname{SiH}_{3}\operatorname{Cl} + \frac{1}{n}(\operatorname{AsH}_{2}\operatorname{BCl}_{2})_{n}$$
 (7)

reaction is similar to that observed for the monosilylphosphine-boron trichloride system, the temperature at which decomposition of SiH<sub>3</sub>·AsH<sub>2</sub>,BCl<sub>3</sub> occurs again indicates the lower thermal stability of the arsine adduct.



The decompositions of the 'mixed hydride adducts' could result through the formation of a transition state of the form (I). This decomposition route is not avail-

tually, monobromosilane according to the equations (8) and (9),

$$\operatorname{SiH}_3 \cdot \operatorname{MH}_2 + \operatorname{BBr}_3 \longrightarrow \operatorname{SiH}_3 \cdot \operatorname{MH}_2, \operatorname{BBr}_3$$
 (8)

$$\operatorname{SiH}_{3} \cdot \operatorname{MH}_{2}, \operatorname{BBr}_{3} \longrightarrow \operatorname{SiH}_{3} \operatorname{Br} + \frac{1}{n} (\operatorname{MH}_{2} \cdot \operatorname{BBr}_{2})_{n}$$
(9)

where M = As or P. In fact the major volatile product in both systems is the dibrominated species which account for 87% of the available silicon in the monosilylarsine system and 67% in that of monosilylphosphine. Monobromosilane (2 and 20%) and tribromosilane (8 and 7%) are also found in both systems, the yields from the arsine system being given first.

Earlier work has shown that boron tribromide is an effective brominating agent for systems containing Si-H bonds.<sup>20</sup> Thus, the initial stage of the reaction leading to the formation of dibromosilane could involve the bromination of an Si-H bond in SiH<sub>3</sub>·MH<sub>2</sub> followed by co-ordination to the dibromoborane species. The same mechanism would then rationalise the formation of dibromosilane from this adduct as shown in the following equations (10) and (11). A similar sequence could lead

$$SiH_3 \cdot MH_2 + BBr_3 \longrightarrow SiH_2 \cdot BrMH_2, BHBr_2$$
 (10)

SiH<sub>2</sub>Br·MH<sub>2</sub>,BHBr<sub>2</sub> 
$$\longrightarrow$$
  
SiH<sub>2</sub>Br<sub>2</sub> +  $\frac{1}{n}$ (MH<sub>2</sub>·BHBr)<sub>n</sub> (11)

to the formation of a disubstituted adduct which decomposes (12) to give tribromosilane. An obvious

SiHBr<sub>2</sub>·MH<sub>2</sub>,BH<sub>2</sub>Br 
$$\longrightarrow$$
 SiHBr<sub>3</sub> +  $\frac{1}{n}$ (MH<sub>2</sub>BH<sub>2</sub>)<sub>n</sub> (12)

alternative route to di- and tri-bromosilane could involve the further bromination of monobromosilane. However, this is unlikely because under identical conditions of time, pressure, and temperature, the reaction of boron tribromide with SiH<sub>3</sub>Br gives only 15% conversion into SiH<sub>2</sub>Br<sub>2</sub>.<sup>16</sup>

Further evidence for the suggested reaction scheme comes from the infrared spectra of the wax-like solid residues which remain after all the volatile materials are removed. The bands observed at 2465, 2405, and 2380 cm.<sup>-1</sup> agree well with the frequencies reported in

<sup>20</sup> J. E. Drake and J. Simpson, Inorg. Nuclear Chem. Letters, 1966, 2, 219.

# Inorg. Phys. Theor.

the literature for B-H and P-H stretching vibrations in analogous systems.<sup>21</sup> The bands at 825 and 790 cm.<sup>-1</sup> are consistent with the presence of B-Br bonds in the mixture of polymers. Also monobromodiborane is detected in the monosilylarsine-boron tribromide system if the reaction products are warmed rapidly from  $-78^{\circ}$ . It is known <sup>22</sup> that monobromodiborane is a decomposition product of BHBr<sub>2</sub> which is one of the postulated intermediates. More forcing conditions are required to ensure complete evolution of all the silicon-containing volatile products of these reactions than in the other systems investigated. This could be the result of steric hindrance to the transfer of the bromine atom from boron to a silicon atom which already carries a bromine substituent.

Thus monosilylarsine forms adducts with the boron Lewis acids which are for the most part similar to those

<sup>21</sup> A. P. Lane and A. B. Burg, J. Amer. Chem. Soc., 1967, 89,

1040. <sup>22</sup> L. Lynds, T. Wolfram, and C. D. Bass, J. Chem. Phys., 1965, **43**, 3774.

### 1043

formed by monosilylphosphine. An exceptional case is the failure to observe the formation of SiH<sub>3</sub>·AsH<sub>2</sub>,BH<sub>3</sub> as a definite species although the reactions in the monosilylarsine-diborane system are best rationalised on the basis of the adduct's being formed as an intermediate. The self-condensation process may indicate the formation of a weak donor-acceptor bond because in the reaction of monosilylphosphine with boron trifluoride some trisilylphosphine was formed.<sup>7</sup> It has been suggested that BF<sub>3</sub> is a weak acceptor towards second-row elements.<sup>23</sup> In general, the adducts of monosilylarsine were less thermally stable than their phosphorus analogues which is in accord with the stability trend in the reactions of other phosphine and arsine donors.<sup>2,24</sup>

We thank the Chemical Society for a grant to purchase chemicals and the S.R.C. for a maintenance grant (to F. S.).

[7/1457 Received, November 9th, 1967]

<sup>23</sup> D. E. Young, G. E. MacAchran, and S. G. Shore, J. Amer. Chem. Soc., 1966, 88, 4390.
 <sup>24</sup> F. G. A. Stone, Chem. Rev., 1958, 58, 101.