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# Reactions of Monogermylarsine and Monogermylphosphine with Water and Hydrogen Sulphide

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Water assists the condensation of monogermylarsine and monogermylphosphine to form the trigermyl species by way of digermylarsine and digermylphosphine both of which are isolated. On the other hand hydrogen sulphide reacts with the monogermyl species to give digermyl sulphide by way of germanethiol. The reactions have been followed by <sup>1</sup>H n.m.r. spectroscopy, and the spectra of several of the compounds are discussed. Methods of preparation of monogermyl-arsine and -phosphine are compared.

MONOSILYLPHOSPHINE and monosilylarsine both react readily with water to give disiloxane quantitatively 1,2 This ready formation of disiloxane by direct reaction with water is well established for many compounds containing the SiH<sub>3</sub> group, but compounds containing GeH<sub>3</sub> are reasonably stable to hydrolysis, although (GeH<sub>3</sub>)<sub>2</sub>O is formed when GeH<sub>3</sub>NCNGeH<sub>3</sub> is treated with

water.<sup>3</sup> We find that water will not react directly with either monogermylarsine or monogermylphosphine, but it does assist their condensation, eventually to give the trigermyl species. Digermylarsine, which is formed as an intermediate, is conveniently prepared by this method. By contrast, hydrogen sulphide reacts with both monogermyl-arsine and -phosphine to give digermyl

<sup>3</sup> S. Cradock and E. A. V. Ebsworth, J. Chem. Soc. (A), 1968, 1423.

G. Fritz, Z. anorg. Chem., 1955, 280, 332.
 J. Simpson, Ph.D. Thesis, Southampton University, 1967. 6 K

sulphide with germanethiol as intermediate. <sup>1</sup>H n.m.r. spectroscopy has been used to follow the reactions and to characterise digermylarsine, digermylphosphine, and germanethiol.

#### EXPERIMENTAL

Apparatus.—The experiments were carried out in a conventional Pyrex glass vacuum system with greaseless stopcocks (Springham and Co., Harlow, Essex; Viton A diaphragm). The ozoniser-type silent electric discharge has been described in detail elsewhere.<sup>4</sup> The <sup>1</sup>H n.m.r. spectra were recorded in sealed n.m.r. tubes (ca. 2 mm. o.d.) on a Varian-A60 variable-temperature high-resolution spectrometer. Infrared spectra were recorded on a Perkin-Elmer 337 in a gas cell (5 cm. path length) fitted with potassium bromide windows and in a brass cell-holder with potassium bromide plates designed to give liquid films under airtight ' conditions.

Starting Materials.—Germane, phosphine, and silane were obtained commercially in cylinders (Matheson Co.), and were purified by pumping off the non-condensable gases in the usual way. Arsine was prepared by the addition of borohydride to arsenate solution,<sup>5</sup> and monobromogermane by the direct reaction of bromine with germane.<sup>6</sup> Monogermylphosphine was prepared by the action of monobromogermane on monosilylphosphine 7 which had been previously prepared by the action of an ozoniser-type silent electric discharge on an equimolar mixture of silane and phosphine.<sup>8</sup> Some samples of monogermylarsine were prepared by the action of the discharge on equimolar mixtures of germane and arsine. Hydrogen sulphide was prepared by first plunging a length of burning magnesium ribbon into a mixture of aluminium and sulphur powders in a nickel crucible, and then adding water dropwise to the contents of the crucible in the vacuum system.<sup>9</sup> Distillation of the products through a trap at  $-45^{\circ}$  into one at  $-196^{\circ}$ gave hydrogen sulphide sufficiently pure that no signal attributable to water could be seen in its <sup>1</sup>H n.m.r. spectrum.10

Preparation of Monogermylarsine from 'LiAl(AsH<sub>2</sub>)<sub>4</sub>'.---The 'LiAl(AsH<sub>2</sub>)<sub>4</sub>' (ca. 9 mmoles) was prepared by condensing arsine on to lithium aluminium hydride dissolved in diglyme such that the pressure of gas at room temperature was just below atmospheric. The reaction was continued for a total of ca. 100 hr. under the conditions described in detail by other workers for the preparation of the corresponding phosphide.<sup>11</sup> Monobromogermane (ca. 4 mmoles) was then condensed on to the 'LiAl(AsH<sub>2</sub>)<sub>4</sub>' at  $-196^\circ$ , and the contents were allowed to warm to  $-45^\circ$ . A solution which turned to a green-brown colour in  $\frac{1}{2}$  hr. was formed. The temperature was raised to room temperature and the volatile products were removed. Distillation through a trap at  $-78^{\circ}$  into one at  $-196^{\circ}$  gave arsine (ca. 6 mmoles) in that at  $-196^{\circ}$  and monogermylarsine (ca. 2 mmoles; its infrared <sup>8</sup> and <sup>1</sup>H n.m.r. spectra <sup>12</sup> confirming its purity) in the one at  $-78^{\circ}$ .

The Monogermylarsine-Water System in Sealed Tubes.-

<sup>4</sup> S. D. Gokhale, J. E. Drake, and W. L. Jolly, J. Inorg. Nuclear Chem., 1965, 27, 1911.
<sup>5</sup> W. L. Jolly and J. E. Drake, Inorg. Synth., 1963, 7, 34.
<sup>6</sup> T. N. Srivastava, M. Onyszchuk, and J. E. Griffiths, Canad.

J. Chem., 1962, 40, 579.

<sup>7</sup> J. É. Drake, N. Goddard, and J. Simpson, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 361.

<sup>8</sup> J. E. Drake and W. L. Jolly, Chem. and Ind., 1962, 1470.

### J. Chem. Soc. (A), 1968

Typically, monogermylarsine (0.5 mmole) and water (0.05 mmole)mmole) were condensed into an n.m.r. tube (ca. 2 mm. o.d.) which was then sealed and allowed to warm to room temperature. The <sup>1</sup>H n.m.r. spectrum was then recorded sequentially during several days. Initially, the spectrum showed only the typical resonances of monogermylarsine, with the 1:2:1 triplet due to GeH<sub>3</sub> at 3.65 p.p.m. to low field of tetramethylsilane,<sup>12</sup> and water. However, the magnitude of the triplet was gradually reduced, with the appearance of a 1:1 doublet at 3.83 p.p.m. due to the  ${\rm GeH}_3$  resonance of digermylarsine and a singlet at  $3{\cdot}98$ p.p.m. due to that of trigermylarsine. The relative amounts of mono-, di-, and tri-germylarsine species were obtained by the integration of each spectrum, and the changes in these relative amounts with time are shown, for a typical set of results, in Table 1. The signal attributable

### TABLE 1

Condensation of monogermylarsine in the presence of water

Time	Monogermylarsine	Digermylarsine	Trigermylarsine
(days)	(%) *	(%)	(%)
0	100	0	0
1	75	<b>20</b>	5
<b>2</b>	62	29	9
3	50	33	17
4	44	38	18
6	40	37	23

\* Moles per cent of germylarsines present.

to water remained throughout the reaction. Similar sets of results were obtained with different amounts of water present in the range 0.05-0.5 mmoles.

Isolation and <sup>1</sup>H N.m.r. Spectrum of Digermylarsine.-The above procedure was carried out to the point where the <sup>1</sup>H n.m.r. spectrum indicated that the reaction had reached the situation where about 80% of the monogermylarsine had condensed. The tube was then re-cooled to  $-196^{\circ}$  and broken open on the vacuum line. There were no noncondensable gases, and the volatile contents of the tube were conveniently separated by trap-to-trap distillations. Arsine (0.15 mmole), which contained trace amounts of germane, passed through a trap at  $-96^\circ$ , monogermylarsine (0.10 mmole) passed through one at  $-45^{\circ}$ , and digermylarsine (ca. 0.1 mmole) [Found: M, 226  $\pm$  5. Calc. for  $(GeH_3)_2AsH: M, 227\cdot1$  through one at  $-22^\circ$ . The digermylarsine fractions from several runs were combined, and the <sup>1</sup>H n.m.r. spectrum (Figure 1) confirmed the assignment. The parameters are in Table 2 along with those for other relevant species.

The initial <sup>1</sup>H n.m.r. spectrum indicated that the sample of digermylarsine was at least 95% pure, but when the spectrum was recorded at subsequent intervals, additional signals were seen, attributable to the formation of monoand tri-germylarsine as well as arsine, so that after ca. 8 days the mole % of the germylarsines was 20% mono-, 35%di-, and 45% tri-.

The Monogermylarsine-Water System at Pressures always less than Atmospheric.—Monogermylarsine (0.40 mmole) and

9 A. Tian and S. Aubanel, Compt. rend. Trav. Faculté Sci.

Marseille, 1942, 1, 97. <sup>10</sup> W. G. Schneider, H. J. Bernstein, and J. A. Pople, J. Chem.

Phys., 1958, 28, 601.
 <sup>11</sup> A. E. Finholt, C. Helling, V. Imhof, L. Nielsen, and E. Jacobsen, *Inorg. Chem.*, 1963, 2, 504.
 <sup>12</sup> J. E. Drake and W. L. Jolly, *J. Chem. Phys.*, 1963, 38, 1033.

water (0.20 mmole) were condensed into a vessel (ca. 10 ml. capacity) and held at room temperature. The infrared spectrum of the gas initially was that expected for a mixture containing only monogermylarsine and water, but changes gradually occurred consistent with the condensation of the monogermylarsine. These changes were much less definitive than those observed by <sup>1</sup>H n.m.r. spectroscopy, but it was apparent after ca. 160 hr. that equilibrium had been reached. The reactants were then fractionated, giving arsine (ca. 0.16 mmole; its infrared spectrum indicating the indicated only the presence of water (0.2 mmole). A viscous, fairly involatile liquid was left,  $v_{max}$  (film) 2090, 875, 830, 790, and 745 cm.<sup>-1</sup>. An attempt to record its <sup>1</sup>H n.m.r. spectrum in solution was not successful.

Self-condensation of Monogermylarsine.---Monogermylarsine (typically ca. 1.0 mmole) was sealed in a semimicro n.m.r. tube, and the room-temperature <sup>1</sup>H n.m.r. spectrum run at intervals. Once more the initial spectrum was that of pure monogermylarsine; however, signals attributable to the formation of di- and tri-germylarsine began to appear,

	The H	n.m.r. param	eters for rela	ited hydrides	5		
Compound	δ(GeH) (p.p.m.) *	δ(AsH) (p.p.m.)	δ(PH) (p.p.m.)	δ(SH) (p.p.m.)	J <sub>HH'</sub>   (c./sec.)	<i>J</i> рн  (с./sec.)	$ J_{PH'} $ (c./sec.)
AsH <sub>3</sub>		1.61					
GeH <sub>3</sub> AsH' <sub>2</sub>	3.65	$1 \cdot 10$			4.8		
$(GeH_3)_2AsH'$	3.83	0.41			4.5		
$(GeH_2)_3$ As	3.98						
PH'3			1.72				182
GeH <sub>3</sub> PH' <sub>2</sub>	3.67		1.41		<b>4</b> ·8	15.3	180
$(GeH_3)_2 PH'$	3.88		0.78		4.7	15.7	171
(GeH <sub>3</sub> ) <sub>3</sub> P	4.04					15.9	
H <sub>2</sub> S				0.77			
GeH <sub>3</sub> SH <sup>'</sup>	4.47			-0.29	$4 \cdot 2$		
(GeH <sub>3</sub> ) <sub>2</sub> S	4.64						
GeH <sub>3</sub> SMe	4.48				(0.60)		

TABLE 2 

\* Chemical shifts measured in p.p.m. to low field of internal tetramethylsilane (+).

presence of trace amounts of germane) through a trap at  $-78^{\circ}$ , monogermylarsine (0.08 mmole) through one at  $-45^{\circ}$ , and digermylarsine (ca. 0.1 mmole; its <sup>1</sup>H n.m.r.



FIGURE 1 The <sup>1</sup>H n.m.r. spectrum of digermylarsine (p.p.m. to low field of Me<sub>4</sub>Si)

spectrum confirming its purity, and its infrared spectrum <sup>13</sup> showing strong bands in the GeH<sub>3</sub> stretching and deformation regions at 2055, 816, 784 cm.<sup>-1</sup>) through one at  $-22^{\circ}$ . The infrared spectrum of the remaining volatile fraction J. E. Drake and C. Riddle, to be published. 13

<sup>14</sup> S. Cradock, E. A. V. Ebsworth, G. Davidson, and L. A. Woodward, J. Chem. Soc. (A), 1967, 1229.

but after considerably longer time intervals. The fastest reaction showed 54% mono-, 35% di-, and 9% tri- after 36 days, and the slowest 96% mono-, 4% di-, and < 1% triafter 41 days.

In none of the condensation processes involving the germylarsines was more than 4% of germanium given off as germane.

The Monogermylphosphine-Water System in Sealed Tubes. -Typically, monogermylphosphine (0.4 mmole) and water (0.1 mmole) were condensed at  $-196^{\circ}$  into a semimicro n.m.r. tube which was then sealed. On warming to room temperature, a white solid formed at the interface of the two liquids, and its formation increased on shaking. The <sup>1</sup>H n.m.r. spectrum was recorded, and signals attributable to monogermylphosphine,<sup>12</sup> digermylphosphine (see section on its self-condensation), trigermylphosphine,<sup>14</sup> germane,<sup>15</sup> and phosphine <sup>16</sup> could all be detected before the signals became too broad.

The Monogermylphosphine–Water System at Pressures always less than Atmospheric.—Monogermylphosphine (0.40 mmole) and water (0.20 mmole) were condensed into the 10-ml. reaction vessel and held at room temperature for 1 hr. Separation of the volatile components by trap-to-trap distillation gave phosphine (0.28 mmole; its infrared spectrum indicating the presence of some 20% of germane) in a trap at  $-196^{\circ}$ , and trigermylphosphine (0.12 mmole; its infrared spectrum 14 confirming its purity) in one at  $-78^{\circ}$ . After removal of water (ca. 0.2 mmole), a small amount of white solid was left together with a very viscous liquid,  $v_{max}$  2060s, 840w, 805w, 778s, 730w, 715w, and 645w cm.<sup>-1</sup>.

Self-condensation of Monogermylphosphine.---Monogermylphosphine (typically ca. 1 mmole) was condensed into a semimicro n.m.r. tube which was then sealed and allowed

E. A. V. Ebsworth, S. G. Frankiss, and A. G. Robiette, J. Mol. Spectroscopy, 1964, 12, 299.
 R. M. Lynden-Bell, Trans. Faraday Soc., 1961, 57, 888.

to warm to room temperature. The initial <sup>1</sup>H n.m.r. spectrum showed only resonances attributable to monogermylphosphine, but subsequent recordings of the spectrum

#### TABLE 3

Self-condensation of monogermylphosphine

$GeH_3PH_2$ (%) *	(GeH <sub>3</sub> ) <sub>2</sub> PH (%)	$(\text{GeH}_3)_3\text{P}$	$\mathrm{GeH}_4$ †
100	0	0	1:0
86	14	0	1:0.4
77	22	1	1:0.7
<b>74</b>	<b>23</b>	3	$1 : 1 \cdot 0$
68	<b>27</b>	5	$1 : 1 \cdot 2$
<b>74</b>	19	7	$1:2{\cdot}0$
	GeH <sub>3</sub> PH <sub>2</sub> (%) * 100 86 77 74 68 74	$\begin{array}{ccc} {\rm GeH_3PH_2} & ({\rm GeH_3})_2 {\rm PH} \\ (\%) & & (\%) \\ 100 & 0 \\ 86 & 14 \\ 77 & 22 \\ 74 & 23 \\ 68 & 27 \\ 74 & 19 \\ \end{array}$	$\begin{array}{cccc} {\rm GeH_3PH_2} & ({\rm GeH_3})_2 {\rm PH} & ({\rm GeH_3})_3 {\rm P} \\ (\%) & (\%) & (\%) \\ 100 & 0 & 0 \\ 86 & 14 & 0 \\ 77 & 22 & 1 \\ 74 & 23 & 3 \\ 68 & 27 & 5 \\ 74 & 19 & 7 \end{array}$

\* Moles per cent of germylphosphines present.  $\dagger$  Ratio of GeH\_3PH\_2 to GeH\_4.

showed a diminishing of the intensities of the monogermylphosphine resonances as signals attributable to the presence of phosphine and di- and tri-germylphosphine appeared.



FIGURE 2 The <sup>1</sup>H n.m.r. spectrum of digermylphosphine; broken lines indicate the presence of trigermylphosphine (p.p.m. to low field of Me<sub>4</sub>Si)

Integration of the signals gave an estimate of the extent of reaction at any time (Table 3).

Isolation and <sup>1</sup>H N.m.r. Spectrum of Digermylphosphine.--The above procedure was repeated, and the condensations allowed to continue for ca. 60 hr., at which time the tubes were re-cooled to  $-196^{\circ}$  and broken open on the vacuum line. Unreacted monogermylphosphine, germane, and phosphine passed through a trap at  $-63^{\circ}$ . Digermylphosphine, which was then separated from trigermylphosphine by passage through a trap at  $-45^{\circ}$ , was condensed on to tetramethylsilane in an n.m.r. tube which was then sealed. The <sup>1</sup>H n.m.r. spectrum (Figure 2) was recorded immediately, and the parameters are in Table 2. It was not possible to obtain a spectrum of pure digermylphosphine, since further condensation was so rapid that the doublet of singlets centred at 4.04 p.p.m. due to the GeH<sub>3</sub> resonance in trigermylphosphine were seen in the initial run and rapidly increased in intensity. They are shown in

<sup>17</sup> T. D. Goldfarb and S. Sujishi, J. Amer. Chem. Soc., 1964, 86, 1679.

the spectrum as broken lines. The condensations involving germylphosphines led to some 30% of the germanium appearing as germane.

The Monogermylphosphine-Hydrogen Sulphide System.— Typically, monogermylphosphine (0.30 mmole) and hydrogen sulphide (0.15 mmole) were condensed at  $-196^{\circ}$  into a semimicro n.m.r. tube which was then sealed and allowed to warm to room temperature. The <sup>1</sup>H n.m.r. spectrum, which was run immediately, showed only signals attributable to monogermylphosphine <sup>12</sup> and hydrogen sulphide.<sup>10</sup> After *ca.* 1 hr. additional peaks were recorded corresponding to a singlet at 4.64 p.p.m., subsequently proved to be due to the presence of (GeH<sub>3</sub>)<sub>2</sub>S, and also a doublet at 4.47 p.p.m. with

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(a) Reaction of monogermylphosphine and hydrogen sulphide

	Sulph	licio	
Time	GeH <sub>3</sub> PH <sub>2</sub>	$GeH_3SH$	(GeH <sub>3</sub> ) <sub>2</sub> S
(days)	(%) * -	(%)	(%)
0	100	0	0
1	63	8	29
2	30	10	60
3	0	6	94

(b) Reaction of monogermylarsine and hydrogen sulphide

Time (days)	GeH <sub>3</sub> AsH <sub>2</sub> plus condensed species (%) *	GeH <sub>3</sub> SH	$(GeH_3)_2S$
0	100	0	0
$\check{2}$	81	12	7
3	76	13	11
6	71	17	12
8	72	17	11
9	71	15	14
* I	Percentage of germy	yl groups pre	sent.

a related quartet at -0.29 associated with the presence of GeH<sub>3</sub>SH. Also, there were resonances due to phosphine. The monogermylphosphine and the hydrogen sulphide resonances decreased in intensity as those of phosphine and the germyl sulphides increased [Table 4(a)] until, after *ca.* 35 hr., there were no further changes. The tube was then re-cooled to  $-196^{\circ}$  and broken open on the vacuum line. Fractionation of the volatile products gave phosphine (*ca.* 0.29 mmole; its infrared spectrum indicating trace amounts of germane) in a trap at  $-196^{\circ}$ , and digermyl sulphide (0.14 mmole; its purity confirmed by its infrared spectrum <sup>17</sup>) in one at  $-78^{\circ}$ . The <sup>1</sup>H n.m.r. spectrum of this fraction confirmed that the singlet at 4.64 p.p.m. was due to (GeH<sub>3)2</sub>S. No non-consensable gases or other volatile compounds were detected.

Reaction of Digermyl Sulphide with Hydrogen Sulphide. Digermyl sulphide (0·2 mmole) and hydrogen sulphide (1·0 mmole) were condensed into a semimicro n.m.r. tube which was then sealed and allowed to warm to room temperature. The <sup>1</sup>H n.m.r. spectrum showed the resonance to be expected for digermyl sulphide and hydrogen sulphide. There was also the doublet-quartet pattern readily assignable to germanethiol, which grew in intensity to reach equilibrium in ca.  $\frac{1}{2}$  hr., by which time ca. 60% conversion into GeH<sub>3</sub>SH had occurred (Figure 3 shows the regions of the spectrum assigned to GeH<sub>3</sub>SH). The n.m.r. parameters for the germyl sulphides are in Table 2. The tube was then recooled to  $-196^{\circ}$ , and broken open on the vacuum line, but fractionation of the products gave only (GeH<sub>3</sub>)<sub>2</sub>S and H<sub>2</sub>S. The Monogermylarsine-Hydrogen Sulphide System. Typically, monogermylarsine (0·43 mmole) and hydrogen sulphide (0·36 mmole) were condensed into a semimicro n.m.r. tube which was then sealed and allowed to warm to room temperature. The <sup>1</sup>H n.m.r. spectrum was recorded at intervals, and signals indicating various amounts of mono-, di-, and tri-germylarsine as well as germyl sulphide and germanethiol were seen as indicated in Table 4(b). After the reaction had proceeded for 200 hr. the n.m.r. tube was re-cooled to  $-196^{\circ}$  and broken open on the vacuum line. Trap-to-trap distillations of the volatile components gave arsine (0·25 mmole; its infrared spectrum indicating the presence of *ca*. 15% germane) in a trap at  $-196^{\circ}$ , monogermylarsine (0·16 mmole;  $v_{max}$ . 2100, 845, and 550 cm.<sup>-1</sup> in addition to bands expected for the pure hydride <sup>15</sup>) in one at



FIGURE 3 The <sup>1</sup>H n.m.r. spectrum of germanethiol [p.p.m. (+) to low field of Me<sub>4</sub>Si]

 $-112^{\circ}$ , and digermyl sulphide (0.08 mmole; additional  $\nu_{max.}$  784, 677, and 635 cm.<sup>-1</sup> assignable to small amounts of digermylarsine) in one at  $-63^{\circ}$ . The presence of *ca*. 10 moles % of digermylarsine in the digermyl sulphide fraction was confirmed by the <sup>1</sup>H n.m.r. spectrum, as was the presence of traces of GeH<sub>3</sub>SH in the monogermylarsine fraction.

### DISCUSSION

The samples of monogermylarsine used in these studies are prepared either by the action of an ozoniser-type silent electric discharge on an equimolar mixture of germane and arsine,<sup>8</sup> or by the reaction of monobromogermane on 'LiAl(AsH<sub>2</sub>)<sub>4</sub>'. Both methods give mixtures of products that are readily separated by trap-to-trap distillation on the vacuum line to give pure monogermylarsine. In the latter case the yields are not as good as other workers have found for the corresponding preparation of monogermylphosphine from lithium aluminium phosphide.<sup>18</sup> Nevertheless, a useful alternative synthetic route is provided even though the preliminary preparations are time-consuming. The samples of monogermylphosphine are prepared by the reaction of monobromogermane on monosilylphosphine<sup>7</sup> which has been prepared by the action of the discharge on a silane-phosphine mixture.<sup>8</sup> In this way the formation of digermane, which is comparatively difficult to separate from monogermylphosphine, and which is usually formed along with it in other methods, is avoided.

We noted earlier that, whereas the Si-As and Si-P bonds in monosilyl-arsine and -phosphine are quantitatively cleaved by water within minutes, the Ge-As bond in monogermylarsine is stable to attack under the same conditions even after 1 hour.<sup>19</sup> This can be attributed to the relative ease of formation of  $(SiH_3)_2O$  compared with  $(GeH_3)_2O$ . However, when monogermylarsine and water are held together for periods greatly in excess of 1 hour, the monogermylarsine condenses partly to di- and tri-germylarsine. Two reactions, (1a) and (1b), which are apparently set up, are conveniently followed by <sup>1</sup>H n.m.r. spectroscopy. The rate of loss of monogermyl-

$$\begin{array}{c} \operatorname{GeH_3AsH_2} + \operatorname{GeH_3AsH_2} \rightleftharpoons & (\operatorname{GeH_3})_2\operatorname{AsH} + \operatorname{AsH_3} & (\operatorname{1a}) \\ \operatorname{GeH_3AsH_2} + (\operatorname{GeH_3})_2\operatorname{AsH} \rightleftharpoons & (\operatorname{GeH_3})_3\operatorname{As} + \operatorname{AsH_3} & (\operatorname{1b}) \end{array}$$

arsine in the early stages of reaction obeys second-order kinetics, but effectively an equilibrium situation is reached with not much change in the composition of the mixture after 4 days when the ratio of mono-, di-, and tri-germylarsines is 2:2:1. Separation of the products indicates that, apart from trace amounts of germane and solid deposit, the amounts of product are those indicated by the integration of the spectra. Although the presence of water has a consistent effect on the condensation, its mode of participation is not clear. The self-condensation process occurs when spectroscopically pure monogermylarsine is sealed up by itself, but the time taken to reach equilibrium is markedly longer and also not reproducible. These variations are presumably dependent on the presence of trace impurities in the hydride or the glass, so the water may just be providing a consistent 'impurity'. The action of diborane, which has been shown to bring about the irreversible condensation of monogermylarsine very rapidly,<sup>19</sup> is presumably quite different, and possibly involves weak adduct-formation.

These 'water catalysed' condensations provide a convenient route to digermylarsine, since the products can be separated on the vacuum line by trap-to-trap distillations. The <sup>1</sup>H n.m.r. spectrum of the isolated (GeH<sub>3</sub>)<sub>2</sub>AsH' (Figure 1) confirms the assignment. The GeH<sub>3</sub> resonance is the 1:1 doublet at 3.83 p.p.m. to low field of internal tetramethylsilane (all chemical shifts in this paper are given as positive when to low field of Me<sub>4</sub>Si as standard). The doublet arises from spin-spin coupling of the protons on germanium with the one on

<sup>19</sup> J. E. Drake and C. Riddle, J. Chem. Soc. (A), 1968, 2452.

<sup>&</sup>lt;sup>18</sup> D. C. Wingleth and A. D. Norman, *Chem. Comm.*, 1967, 1218.

arsenic  $(J_{\rm HH}^{5} 4.5 \text{ c./sec.})$ . The AsH' resonance centred at 0.41 p.p.m. is a septet arising from the coupling of the arsenic proton with the six equivalent protons on germanium  $(J_{\rm HH'}$  confirmed as 4.5 c./sec.). The observed intensity ratios of the seven lines is 2:6.5:14.7:20:16:9:2, which is in good agreement with the predicted ratio of 1:6:15:20:15:6:1 considering the broadening as a result of the nuclear quadrupole moment of arsenic. Integration also confirms that the ratio of the intensity of the GeH<sub>3</sub> resonance to that of AsH' is 6:1.

The first spectrum run after the digermylarsine is isolated indicates a purity of ca.95%, but it is not stable under these conditions. Subsequent recordings of the spectrum indicate the formation of mono- and trigermylarsine. The GeH<sub>3</sub> resonance of trigermylarsine is seen as a singlet at 3.98 p.p.m., and that of monogermylarsine as a triplet centred at 3.65 p.p.m. The mixture of arsines slowly approaches a constitution not very different from that found with the monogermylarsine condensations.

The condensations in the germylphosphine systems differ from those of the arsines in one important respect. Whereas only trace amounts of germane were found in the products from the latter systems, fairly large amounts are found with the phosphines in addition to solid-polymer formation which is so marked in the water-assisted condensations in the n.m.r. tube that all signals are lost within minutes. It is reasonable to assume therefore that, as well as the two equilibrium processes paralleling those of reactions (1a) and (1b) giving di- and tri-germylphosphine, a non-reversible dissociation to germane and solid polymer also takes place. One result of this is that all the monogermylphosphine is rapidly used up in the water-catalysed reactions, so separation of the products on the vacuum line after 1 hour gives only phosphine, germane, and trigermylphosphine as the volatile products.

However, the condensation can still be used as a route to digermylphosphine. When spectroscopically pure germylphosphine is sealed in an n.m.r. tube, the formation of di- and tri-germylphosphine is evident after only 24 hours. The ratio of mono-, di-, and tri-germylphosphines after *ca*. 3 days is 7.5:2:1, and remains more or less constant for a further 3-4 days. However, this does not represent a true equilibrium situation, because during that time germane is formed such that the amount relative to monogermylphosphine is doubled. This indicates the continual formation of polymeric species with a steady-state relative concentration of the mixture of germylphosphines. When the tube is broken open on the vacuum line, digermylphosphine can be isolated from this mixture. Its <sup>1</sup>H n.m.r. spectrum (Figure 2), which was recorded in an excess of tetramethylsilane in an attempt to slow its decomposition. shows similar fine-structure to that of digermylarsine with the additional coupling due to phosphorus. Thus,

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the GeH<sub>3</sub> resonance in (GeH<sub>3</sub>)<sub>2</sub>PH' is a doublet of doublets as a result of the protons on germanium coupling with the phosphorus atom  $(J_{\rm PH} 15.7 \text{ c./sec.})$  in addition to coupling with the proton attached to it  $(J_{HH'} 4.7 \text{ c./sec.})$ . The spin-spin coupling of phosphorus with its own proton is seen in the widely separated doublet of the PH' resonance  $(J_{PH'} 171 \text{ c./sec.})$  centred at 0.78 p.p.m. The value of this coupling constant is fairly close to that of the corresponding constants in phosphine and monogermylphosphine. There is a fair amount of evidence that this coupling constant is sensitive to changes in hybridisation on the phosphorus atom.<sup>20</sup> The change in the value is only of the order of 5%, so there is apparently no significant alteration in the hybridisation of phosphorus in digermylphosphine compared with phosphine or monogermylphosphine. Only five lines of the expected septet in the PH' resonance resulting from coupling of the germanium protons with the phosphorus proton can be seen clearly. This is, in part at least, due to the rapidly changing spectrum resulting from the decomposition of digermylphosphine.

The Ge-P bond in monogermylphosphine is cleaved by hydrogen sulphide. The reaction has been followed by <sup>1</sup>H n.m.r. spectroscopy [Table 4(a)], which shows that germanethiol is an intermediate as indicated in (2).

$$2\text{GeH}_{3}\text{PH}_{2} + \text{H}_{2}\text{S} = (\text{GeH}_{3})_{2}\text{S} + 2\text{PH}_{3}$$

$$(2)$$

$$[\text{GeH}_{3}\text{SH}]$$

Digermyl sulphide is identified in the <sup>1</sup>H n.m.r. spectrum by the resonance due to  $GeH_3$ , which is a singlet at 4.64 p.p.m. The spectrum of  $GeH_3SH'$  (Figure 3) has the expected doublet-quartet pattern. Attempts to isolate the thiol failed, since only phosphine, digermyl sulphide, and a trace of germane could be isolated by fractionation. The thiol is also clearly formed in an equilibrium (3) that is set up when digermyl sulphide is sealed with an excess of hydrogen sulphide. Again, on attempting to

$$GeH_3)_2S + H_2S \Longrightarrow 2GeH_3SH$$
 (3)

separate the three components, only digermyl sulphide and hydrogen sulphide could be isolated, although in the corresponding equilibrium reaction involving disilyl sulphide, quantities of silanethiol could be isolated.<sup>21</sup>

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The displacements of the chemical shifts in these germyl compounds show some interesting and consistent trends. Increasing germyl substitution of the protons attached to As, P, or S shows a successive increase in the shielding of the remaining proton(s), with shifts to high field as the less electronegative group is introduced (Table 2). Thus, the chemical shift of  $AsH_3$  is 1.61 p.p.m. to low field of tetramethylsilane, that of  $AsH_2$ in monogermylarsine is at 1.10 p.p.m., and that of  $AsH_1$  in digermylarsine is at 0.41 p.p.m., and the identical trend is found with germyl substitution of phosphine and

<sup>21</sup> H. J. Emeleus, A. G. MacDiarmid, and A. G. Maddock, J. Inorg. Nuclear Chem., 1955, **1**, 194.

<sup>&</sup>lt;sup>20</sup> J. Mavel, Progr. N.m.r. Spectroscopy, 1964, **1**, 251; G. M. Sheldrick, Trans. Faraday Soc., 1967, **63**, 1077.

# Inorg. Phys. Theor.

hydrogen sulphide. Correspondingly, there is a deshielding effect on the protons attached to germanium as the latter is attached to more electronegative entities, so the GeH<sub>3</sub> resonances in monogermylarsine, monogermylphosphine, and germanethiol are successively to lower field, at 3.65, 3.83, and 4.47 p.p.m. respectively. Since further germyl substitution shows a trend in the same direction, it implies that a GeH<sub>3</sub>M entity is more electronegative than an HM entity (M = As, P, or S). Thus, for GeH<sub>3</sub>SH, the GeH<sub>3</sub> resonance is at 4.47, but that of GeH<sub>3</sub>SGeH<sub>3</sub> is at 4.64 p.p.m. If this correlation is reasonable, then the resonance of GeH<sub>3</sub>SCH<sub>3</sub> should be shifted back to high field, as indeed it is, being centred at 4.48 p.p.m.<sup>22</sup>

The Ge-As bond in monogermylarsine further exhibits

its apparent stability relative to the Ge-P bond in monogermylphosphine, in that it is not quantitatively cleaved by hydrogen sulphide as was the phosphine under identical conditions [Table 4(b)]. Instead, an equilibrium situation is reached, in which some cleavage of the bond, as well as some condensation, occurs, so monogermylarsine (66 moles %), digermylarsine (6 moles %), trigermylarsine (2 moles %), digermyl sulphide (7 moles %), and germanethiol (19 moles %) are all present.

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