

### 540. *Hydrides of Germanium.*

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Monogermene has been prepared by reduction of aqueous germanate solutions with tetrahydroborate (borohydride), and higher germanes—up to nonagermanes—have been prepared by decomposition of monogermene in an ozonizer-type silent electric discharge. The higher germanes were separated by gas-liquid chromatography and were identified by their vapour pressures, infrared spectra, mass spectra, and proton magnetic resonance spectra.

THE first extensive study of germanium hydrides was by Dennis and his co-workers<sup>1</sup> who prepared mono-, di-, and tri-germane by the acid hydrolysis of magnesium germanide. By a similar method, Amberger<sup>2</sup> has prepared tetra- and penta-germane. Monogermene has been obtained on reduction of germanic acid or germanium chloride solutions by lithium aluminium hydride,<sup>3</sup> by lithium hydrotri-t-butoxyaluminum,<sup>4</sup> and by tetrahydroborate (borohydride) solutions.<sup>5</sup>

Schwarz and Heinrich<sup>6</sup> obtained di- and tri-silane by passing monosilane through an ozonizer-type electric discharge. Diborane<sup>7</sup> was decomposed to higher hydrides, and arsine<sup>8</sup> was decomposed to diarsine by a similar electric-discharge system but the technique had not been tried for monogermene. We have prepared monogermene in good yield by reduction of aqueous alkaline germanate solutions and we have prepared germanes—up to nonagermanes—by the decomposition of monogermene in an electric discharge.

#### EXPERIMENTAL

*Reduction of Aqueous Germanate Solutions.*—Mono-, di-, and tri-germane were prepared by slow addition of an alkaline solution of potassium tetrahydroborate and germanium dioxide to an acidic medium. A current of oxygen-free nitrogen was used to sweep the

<sup>1</sup> Dennis, Corey, and Moore, *J. Amer. Chem. Soc.*, 1924, **46**, 657.

<sup>2</sup> Amberger, *Angew. Chem.*, 1959, **71**, 372.

<sup>3</sup> Finholt, Bond, Wilzbach, and Schlesinger, *J. Amer. Chem. Soc.*, 1947, **69**, 2692.

<sup>4</sup> Sujishi and Keith, *J. Amer. Chem. Soc.*, 1958, **80**, 4138.

<sup>5</sup> Piper and Wilson, *J. Inorg. Nuclear Chem.*, 1957, **4**, 22; Macklen, *J.*, 1959, 1989; Jolly, *J. Amer. Chem. Soc.*, 1961, **83**, 335.

<sup>6</sup> Schwarz and Heinrich, *Z. anorg. Chem.*, 1935, **221**, 277.

<sup>7</sup> Kotlensky and Schaeffer, *J. Amer. Chem. Soc.*, 1958, **80**, 4518.

<sup>8</sup> Shriver and Jolly, U.S. Atomic Energy Commission UCRL 5148 (February, 1958).

hydrides from the reaction vessel as they were formed. The hydrides were condensed in traps surrounded by liquid nitrogen and were separated and purified by distillation *in vacuo*. When sulphuric acid was used a large amount of foaming occurred; this could be reduced by adding about 1% of a polyglycol, but larger amounts of hydroborate were then needed to give comparable yields. A large amount of yellow-orange residue was formed during the reaction. This residue was identified from its decomposition products and from its infrared spectrum (KBr pellets) as a polymeric germane ( $\text{GeH}_x$ ).<sup>9</sup> The yield of monogermane was not improved when the concentration of the sulphuric acid was changed or when hydrochloric acid was used.

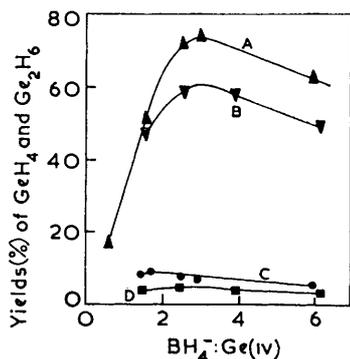


FIG. 1. Yields of monogermane and digermane (based on the concentration of  $\text{GeH}_4$ ). Yield of  $\text{GeH}_4$  when (A) glacial acetic acid and (B) sulphuric acid is used, and of  $\text{Ge}_2\text{H}_6$  when (C) glacial acetic acid and (D) sulphuric acid is used.

With glacial acetic acid practically no foaming occurred, very little residue was formed, and the yields of mono- and di-germane were improved.

In Fig. 1, the percentage yields of monogermane and digermane (based on the moles of germanium in solution) are plotted against the ratio of tetrahydroborate to germanate in the alkaline solution. Plots are shown for the addition of the alkaline solution to glacial acetic acid and to sulphuric acid. The best results were obtained with a ratio of  $\text{BH}_4^-:\text{Ge(IV)}$  of about 3:1, when the yields, based on the amount of germanium dioxide, were monogermane 73% and digermane 9%. Trigermane was more easily recovered from the sulphuric acid system, but the yield was never greater than 2.5%.

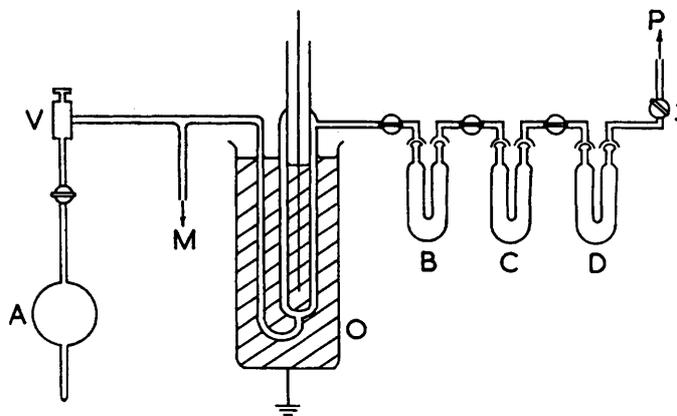


FIG. 2. Apparatus for the low-pressure discharge system.

A, Reservoir; M, manometer; O, ozonizer; P, pump.

*Effect of Electrical Discharge on Monogermane.*—(a) *The low-pressure system.* The apparatus is shown in Fig. 2. The flow of monogermane from reservoir A into the reaction vessel was controlled by the needle valve V, and the pressure was determined by the dibutyl phthalate manometer M. The ozonizer was surrounded by a cold-bath containing acetone, solid

<sup>9</sup> Drake, U.S. Atomic Energy Commission UCRL 9709 (May, 1961).

carbon dioxide, and hydrochloric acid, the bath being earthed. The inner finger, filled with the same cooling mixture, was connected to a high-voltage a.c. supply. Higher germanes were condensed in the ozonizer, and mono- and di-germane were condensed in traps B, C, and D, which were at liquid-nitrogen temperature. Hydrogen was pumped out continuously through stopcock 1. Consecutive runs under the same conditions of voltage, pressure, and flow-rate gave similar results, even when the ozonizer was not cleaned between each run. The conditions were varied to give voltages from 4 to 15 kv, pressures from 0.5 to 5.0 cm. of dibutyl phthalate, and flow-rates from 0.025 to 25.0 mmoles of monogermane per min. Fig. 3 shows the percentage decomposition of monogermane and the percentage yield of digermane (based on the monogermane decomposed) for different flow-rates, at two conditions of constant voltage and pressure. The best conditions (high voltage, high pressure, and medium flow-rates) gave di-

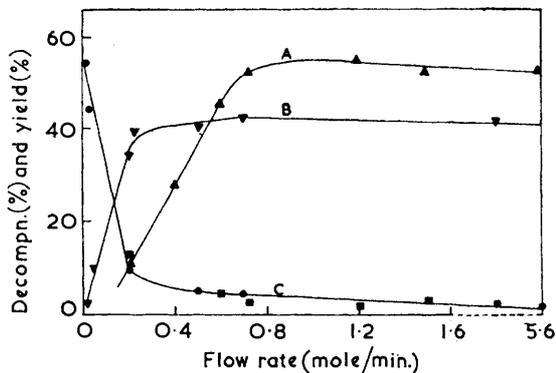


FIG. 3. Decomposition (%) of  $\text{GeH}_4$  and yield (%) of  $\text{Ge}_2\text{H}_6$  (ozonizer at  $-78^\circ$ ). Yield of  $\text{Ge}_2\text{H}_6$  at (A) 15 kv and 4.5 cm. Hg, and (B) 8 kv and 2 cm. Hg; (C) Decomposition of  $\text{GeH}_4$  at 8 kv and 2 cm. Hg (●) and at 15 kv and 4.5 cm. Hg (■).

germane in 55% yield and trigermane in 10% yield. Because the percentage conversion was low, only 1 mmole of digermane and about 0.1 mmole of trigermane were obtained from the passage of 100 mmoles of monogermane.

(b) *The high-pressure system.* The apparatus was altered to a closed system in which the monogermane was at a pressure of about 30 cm. of mercury. A Toepler pump was used to circulate the monogermane, and the amount of the monogermane to be decomposed could be varied by changing the size of a reservoir. The ozonizer was still kept at  $-78^\circ$  and the discharge was run for various lengths of time. The amount of monogermane was measured both before and after each run. Hydrogen was not pumped out until the end of a run and so the change in the pressure gave an indication of the extent of the decomposition of the monogermane according to the reaction  $\text{GeH}_4 \rightarrow \text{GeH}_x + \frac{1}{2}(4-x)\text{H}_2$ . (In most runs  $x$  was 2.0–2.5.)

Table 1 shows the percentage decomposition of monogermane and the percentage yields of

TABLE 1.

Results from the high-pressure discharge system, with the ozonizer at  $-78^\circ$ .

Voltage (kv)	Pressure (cm. Hg)	Time (hr.)	Decompn. (%) of $\text{GeH}_4$	Yield (%)		
				$\text{Ge}_2\text{H}_6$	$\text{Ge}_3\text{H}_8$	$\text{Ge}_4\text{H}_{10}$
10	10	2.0	94.5	8.0	30.0	—
10	20	1.0	19.3	38.6	26.0	9.5
10*	20	1.0	8.0	25.9	19.2	10.9
10†	20	1.0	52.7	14.6	9.8	9.9
10	20	2.0	84.0	25.4	26.9	8.9
10	20	3.0	86.9	28.6	26.1	8.6
10*	20	3.0	67.5	5.1	6.3	8.9
10	20	3.5	91.1	11.5	—	—
10	20	5.5	95.2	12.0	30.0	—
10	30	2.0	75.2	34.8	26.8	—
10	30	5.5	95.0	26.7	29.7	—
15	20	2.0	93.8	26.5	28.1	—
15	30	2.0	94.8	26.6	26.6	—
15	40	5.5	88.4	39.0	31.8	12.0

\* Ozonizer at  $0^\circ$ . † Ozonizer at  $25^\circ$ , with another cold trap at  $-78^\circ$  in the system.

di-, tri-, and tetra-germane for different conditions of voltage, pressure, and time. Under the best conditions 8 mmoles of both di- and tri-germane were obtained from 100 mmoles of monogermane in about an hour.

TABLE 2.  
Retention times (min.) at various temperatures.

Species	Flow: 60 c.c./min.				Flow: 88 c.c./min.				
	95°	125°	150°	190°	110°	145°	160°	170°	190°
Ge <sub>2</sub> H <sub>6</sub> .....	1.0	0.55	—	—	0.55	~0.35	—	—	—
iso-Ge <sub>4</sub> H <sub>10</sub> ...	2.9	1.5	1.0	0.5	1.5	0.8	0.8	0.6	~0.45
n-Ge <sub>4</sub> H <sub>10</sub> ...	3.5				1.7	0.9			
neo-Ge <sub>4</sub> H <sub>12</sub> ...	6.4	2.5	1.3	—	3.2	1.5	1.3	—	—
iso-Ge <sub>5</sub> H <sub>12</sub> ...	9.4	3.4	2.0	1.1	4.5	2.0	1.7	1.2	0.95
n-Ge <sub>5</sub> H <sub>12</sub> ...	13.5	4.0	2.2		5.5	2.4	1.9	1.4	
Ge <sub>6</sub> H <sub>14</sub> A ...	—	—	3.6	1.6	9.0	3.8	2.6	2.0	1.5
B ...	—	—	3.9		11.3	4.8	3.4	2.5	1.9
C ...	—	9.0	4.4		13.5	5.2	3.7	2.7	2.2
D ...	—	12.0	5.2	2.2	17.5	6.6	4.5	3.4	2.2
Ge <sub>7</sub> H <sub>16</sub> E ...	—	—	—	—	—	—	—	4.0	2.6
F ...	—	—	6.5	—	—	10.0	6.7	4.8	3.1
G ...	—	—				10.2			
H ...	—	—				7.9	2.9	—	12.0
I ...	—	—	8.8	3.4	—	15.0	8.8	6.3	4.0
J ...	—	—	11.0	4.0	—	18.0	10.5	7.8	4.8
K ...	—	—	15.0	4.7	—	18.6	10.8	8.0	—
Ge <sub>8</sub> H <sub>18</sub> .....	—	—	—	7.0—11.0	—	—	—	—	6.5—10.0
L ...	—	—	—	—	—	—	—	—	7.5
M ...	—	—	—	—	—	—	—	—	8.5
Ge <sub>9</sub> H <sub>20</sub> .....	—	—	—	14—20	—	—	—	—	13.5—20

*Effect of Heat on Monogermane.*—In these experiments the ozonizer was replaced by a heated tube. In the low-pressure system the yields were about half as great as those from the corresponding ozonizer system. In the high-pressure system it was impossible to get yields of di- and tri-germane greater than 3%.

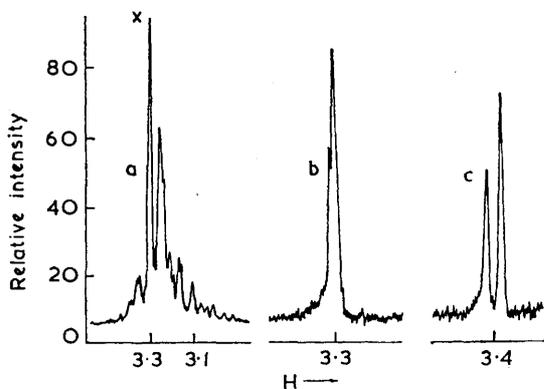


FIG. 4. Proton magnetic resonance spectra of (a) trigermane, (b) n-tetragermane, and (c) isotetragermane (in p.p.m. referred to an external sample of tetramethylsilane).

*Separation and Identification of the Germanes.*—(a) *Separation.* The b. p. of mono-, di-, and tri-germane are sufficiently far apart to allow their separation by fractional condensation in the usual vacuum-line apparatus. Distillation through traps cooled to  $-33^\circ$ ,  $-63^\circ$ , and  $-112^\circ$  removed tetra-, tri-, and di-germane, respectively.

The other hydrides were separated by gas-liquid chromatography on columns containing 10% of silicone fluid on Celite.<sup>10</sup> By varying the flow rate of the helium carrier gas and the temperature of the column, many peaks could be resolved.

A list of the retention times for various conditions is given in Table 2. The two isomers

<sup>10</sup> Drake and Jolly, *Proc. Chem. Soc.*, 1961, 379.

of tetragermane and the pentagermanes were collected from the column by a technique similar to that described by Simmons and Kelley.<sup>11</sup>

(b) *Identification.* Mono- and di-germane were characterized by their vapour pressures and infrared spectra; the spectra were recorded on a Perkin-Elmer Infracord spectrophotometer, model 137. The infrared spectra and the mass spectra of tri-, n-tetra-, and isotetra-germane, and of a mixture of the pentagermanes, were obtained. The proton magnetic resonance spectra of three of the germanes are shown in Fig. 4. The spectrum of digermane gave the chemical shift for  $\text{GeH}_3$  as 3.4 p.p.m. to lower field of tetramethylsilane as external standard; all these spectra were recorded on a Varian, model A-60, spectrometer.

#### DISCUSSION

*Preparation.*—The preparation of monogermane that we have described is an extremely useful one because the germane can be obtained pure in a short time and high yields are obtained with small excesses of tetrahydroborate (see Fig. 1). We found that the yield of monogermane is gradually lowered as the excess of the reducing agent is increased beyond three-fold. Sujishi and Keith<sup>4</sup> reported a similar result with lithium hydrotri-t-butoxyaluminate as the reducing agent. Although the yield of monogermane is lower, the amount of germanium(IV) that is reduced continues to rise, because large quantities of the polymeric hydride  $(\text{GeH})_x$  are now formed.

Undoubtedly the best method for preparing higher germanes is by the decomposition of monogermane in a high-pressure discharge system. In experiments at  $-78^\circ$  (see Table I), the percentage yields of tri- and tetra-germane remained constant with time but the percentage yield of digermane was lowered. The vapour pressure of digermane is high enough at  $-78^\circ$  for some of it to be decomposed, but the higher germanes are frozen out as they are formed. Similarly trigermane is not frozen out completely at  $0^\circ$  and so some of it was decomposed and the yields were smaller. The importance of rapid condensation explains to some extent the poor yields in the pyrolysis. If the ozonizer was kept at room temperature and the cold trap was placed some distance beyond the ozonizer to delay condensation of the higher germanes, much better yields were obtained than from the pyrolysis experiments, although the yields were much lower than those when the ozonizer was at  $-78^\circ$ . Thus it seems that the excitation of monogermane by an electrical discharge is intrinsically a better method for bringing about polymerization.

*Separation and Identification.*—Trigermane was identified by its vapour pressure and its mass spectrum. The proton magnetic resonance spectrum (see Fig. 4a) for pure trigermane is very similar to that of trisilane<sup>12</sup> and both spectra are almost mirror images of that of propane.<sup>13</sup> The three spectra are characterized by a small ratio of chemical shift to spin-spin coupling constant for the protons in  $\text{MH}_2$  and  $\text{MH}_3$  ( $M = \text{C}, \text{Si}, \text{or Ge}$ ). By comparison with the spectrum of trisilane, the positions of the centre of the  $\text{GeH}_3$  triplet and the  $\text{GeH}_2$  septet can be assigned to the peaks  $x$  and  $y$ , respectively. The resonance field for  $\text{GeH}_3$  in trigermane is 3.3 p.p.m. lower than that of tetramethylsilane (as an external standard). (The corresponding shift for  $\text{SiH}_3$  in silanes is 3.3–3.6 p.p.m. and for  $\text{CH}_3$  in propane is 1.1 p.p.m., both towards lower field from tetramethylsilane.)

The internal chemical shift from  $\text{GeH}_3$  to  $\text{GeH}_2$  is 0.193 p.p.m. to higher field. The corresponding shift in trisilane is 0.167 p.p.m., also to higher field, and in propane it is 0.438 p.p.m. to lower field. A simple, but by no means complete, explanation of the differences in the spectra can be given on the basis of the relative electronegativities of carbon, germanium, hydrogen, and silicon. The order of the electronegativities is  $\text{C} > \text{H} > \text{Si} \approx \text{Ge}$ . When a hydrogen atom of a methyl group is replaced by a carbon

<sup>11</sup> Simmons and Kelley, "Gas Chromatography," ed. Noebels, Wall, and Brenner, Academic Press, New York, 1959, p. 225.

<sup>12</sup> Turner, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Thesis, Cambridge, October, 1960.

<sup>13</sup> Pople, Schneider, and Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, p. 235.

atom, the electron density around each of the remaining protons is lowered and the proton resonance occurs at a lower field. On the other hand, when a hydrogen atom of either a silyl or a germyl group is replaced by a silicon or germanium atom, respectively, the electron density around the remaining protons is increased and the resonance occurs at a higher field.

The infrared spectra (see Table 3) of tri-, n-tetra-, and isotetra-germane are so similar that they only identify them as being germanium hydrides. On the basis of expected

TABLE 3.

Principal peaks ( $\text{cm.}^{-1}$ ) in infrared spectra of tri-, tetra-, and penta-germanes.

	Ge-H stretching	Ge-H bending	
$\text{Ge}_3\text{H}_8^*$ .....	2080ms	796s	880w
n- $\text{Ge}_4\text{H}_{10}$ .....	2045ms	792s	860w
iso- $\text{Ge}_4\text{H}_{10}$ .....	2060ms	784s	—
$\text{Ge}_5\text{H}_{12}$ .....	2080ms	795s	860w
$(\text{GeH})_2^*$ .....	2060ms	775s	832s

\* These spectra are recorded in an earlier report. Emel us and Mackay (*J.*, 1961, 2676) later reported the positions of the principal peaks of trigermane, which agree with our figures.

relative volatilities, we assumed that n-tetragermane was held longer on the chromatographic column than isotetragermane. A comparison of the mass spectra of the two fractions with the mass spectra of n-butane and isobutane agreed with this assumption. The mass spectrum of the isomer, presumed to be n-tetragermane, had a fragmentation pattern similar to that of n-butane, in that the relative amounts of the fragments were in the order,  $M_3^+ > M_2^+ > M_4^+ > M_1^+$  ( $M = \text{Ge}$  or  $\text{C}$ ). The other isomer, presumed to be isotetragermane, had a fragmentation pattern similar to that of isobutane, the order being  $M_3^+ > M_2^+ > M_1^+ > M_4^+$ . The proton magnetic resonance spectrum of the n-tetragermane (see Fig. 4b) is similar to that of n-butane in that no easily explained pattern is seen. The spectrum of isobutane consists of a series of equally spaced lines, that are presumed to be part of a series of 10, and a strong symmetrical doublet with the same spacing. The spectrum of isotetragermane (see Fig. 4c) was taken in a very dilute solution of n-hexane and consisted of a symmetrical doublet. The series of ten lines caused by the splitting of the (=GeH-) hydrogen was presumably too weak to be seen in these circumstances. From the spacing of the doublet the spin-spin coupling constant  $J_{\text{GeH}, \text{GeH}_2}$  is 4 cycles/sec. ( $J_{\text{CH}, \text{CH}_2}$  is 5 cycles/sec.). The chemical shift of  $\text{GeH}_3$  in isotetragermane is 3.4 p.p.m. to lower field referred to tetramethylsilane. The yield of n-tetragermane was from 4–10 times that of the iso-compound. In making this estimation of yields we assumed that the two species were equally sensitive to detection by our thermal conductivity cell, and so we may be underestimating the yields of the branched species; in the alkanes the sensitivities decrease in the order straight-chain alkanes > dimethylalkanes > trimethylalkanes > monomethylalkanes > tetramethylalkanes, and also all alkanes of a given degree of branching have the same sensitivity irrespective of carbon number. Nevertheless, the relative yields were those that might be expected if, in the discharge tube, tetragermane is built up from  $\text{Ge}_1$  units plus  $\text{Ge}_2$  units and, possibly, pairs of  $\text{Ge}_2$  units.

The pentagermanes were collected as a group from the chromatographic column. The infrared spectrum confirmed that these were germanium hydrides and the mass spectrum confirmed that they were pentagermanes. The peaks were assigned on the basis of the expected relative retention times of the three isomers on the chromatographic column, comparisons were made with tables of the retention times of hydrocarbons on silicone columns, and we assumed that the isomers would emerge in the order neo-, iso-, n-pentagermane. The relative yields of these isomers, based on the area under the peaks, are remarkably close to those predicted on the basis of statistical build-up.

By similar arguments the four peaks of the hexagermanes may be tentatively assigned

as follows: A = 2,2-digermyltetragermane; B = 2,3-digermyltetragermane; C = a mixture of 2-germylpentagermane and 3-germylpentagermane; D = n-hexagermane.

This type of assignment (already hazardous with the hexagermanes) is impossible with the heptagermanes; but it is probable that K is the normal species. For the normal series of hydrocarbons, a plot of the logarithm of the retention time against the number of carbon atoms per molecule gives a straight line.<sup>14</sup> This is also true for the silanes<sup>15</sup> and the germanes.<sup>10</sup>

The relative yields of the isomers varied for each preparation, but for hexa- and heptagermanes, and sometimes for pentagermanes, the normal species was never the most abundant, a result to be expected from statistical considerations. Typical yields of the isomers, calculated from the peak areas and based on the amount of germanium in monogermane that was converted, were as follows: pentagermanes 0.8%, hexagermanes 0.3%, heptagermanes 0.3%, octagermanes 0.05%, and nonagermanes <0.01%.

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<sup>14</sup> Desty and Whyman, *Analyt. Chem.*, 1957, **29**, 320.

<sup>15</sup> Borer and Phillips, *Proc. Chem. Soc.*, 1959, 189.

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