943. *The Reaction of Trigermane with Iodine*

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Recent studies [1,2] have shown that digermanyl halides, Ge_2H_5X, may be prepared from digermane. The present study extends these investigations to trigermane, Ge_3H_8, which reacts smoothly with iodine, at −63°, with evolution of hydrogen iodide. Evidence is presented that the product is trigermanyl iodide, which can be converted into monodeuterotrigermane.

Trigermane could react with, for example, iodine in two ways to cleave either a Ge–H bond (equation 1) or a Ge–Ge bond (equation 2).

$$Ge_3H_8 + I_2 = Ge_3H_7I + HI \qquad (1)$$

$$Ge_3H_8 + I_2 = Ge_2H_5I + GeH_3I$$
$$+ I_2 \longrightarrow GeH_3I + GeH_2I_2 \qquad (2)$$

Digermane reacts as in equation (1). Thermochemical data give no guidance to which of these reactions will be preferred, as the average Ge–Ge bond energy in trigermane has been variously determined as 5 kcal./mole less,[3] or as 1 kcal./mole more,[4] than in digermane. The only reaction of trigermane reported in the literature is that with sodium in ammonia.[5] This is analogous to equation (2), with cleavage of all Ge–Ge bonds.

The present work provides indirect evidence that trigermane reacts with iodine, at −63°, mainly according to equation (1). The isolation of trigermanyl iodide is impossible as the product decomposes rapidly at 0°, a temperature at which its vapour pressure is too low to allow it to be distilled from the reaction vessel. (Digermanyl iodide can just be distilled at 0° with about 20% loss by decomposition.)

The evidence for the formation of trigermanyl iodide as the major product of the reaction is, first, the recovery of 70—80% of the hydrogen iodide predicted from equation (1)—see Table 1—and, second, the formation of a deuterated trigermane by the reaction of the iodinated product with lithium tetradeuteroaluminate. A separate experiment showed that there was no isotope exchange between trigermane and the deuteride under similar experimental conditions. The deuterated trigermane was identified as a trigermane species by its distillation behaviour, its vapour pressures, and its molecular weight. The presence of deuterium was shown by a spectral band of medium intensity at 1495 cm.$^{-1}$ due to the Ge–D stretching mode.

A further experiment, aimed at converting the trigermanyl iodide into the more volatile chloride by reaction with silver chloride, yielded only decomposition products.

Some spectroscopic evidence is available to indicate that substitution takes place at the central germanium atom in trigermane. The i.r. spectral absorptions due to bending modes of Ge_3H_8 and Ge_3H_7D may be assigned, by comparison with the spectra of trisilane [6] and of the digermanyl halides,[7] as shown in Table 2. The principal change in the spectrum of deuterotrigermane, compared with trigermane, involves the shift of a band to 733 cm.$^{-1}$ from 700 cm.$^{-1}$. This trigermane band can be assigned as a GeH_2 mode, and its shift indicates that substitution involves the central germanium atom. The proton magnetic resonance spectrum of the deuterotrigermane fits an A_6B system in which the weak B signals are overlapped and largely swamped by the A_6 doublet.

All the evidence is consistent with reaction (1), followed by

$$Ge_3H_7I + LiAlD_4 \xrightarrow[-63^\circ]{Me_2O} Ge_3H_7D$$

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[1] K. M. Mackay and P. J. Roebuck, *J.*, 1964, 1195.
[2] A. G. MacDiarmid, E. J. Spanier, K. M. Mackay, and P. Robinson, unpublished work.
[3] F. E. Saalfeld and H. J. Svec, *Inorg. Chem.*, 1963, **2**, 50.
[4] S. R. Gunn and L. G. Green, *J. Phys. Chem.*, 1964. **68**, 946.
[5] C. A. Kraus and E. S. Carney, *J. Amer. Chem. Soc.*, 1934, **56**, 765.
[6] S. D. Gokhale and W. L. Jolly, *Inorg. Chem.*, 1964, **3**, 946.
[7] K. M. MacKay and P. Robinson, unpublished observations.

as the main reaction. Substitution probably takes place on the central germanium atom.

Analysis of the minor products of the iodination reaction yielded germyl iodide, GeH_3I. These samples were always mixed with other compounds, such as trigermane, from which quantitative separation was impossible. Germyl chloride, GeH_3Cl, and germylene dichloride, GeH_2Cl_2, were observed in the products from the reaction with silver chloride, and a deuterated monogermane species was recovered in the reaction with lithium tetradeuteroaluminate. In addition, digermanyl iodide, Ge_2H_5I, was found among the products when an attempt was made to distil trigermanyl iodide at room temperature. While all these compounds could arise from decomposition and rearrangement of trigermanyl iodide fragments, it seems more likely that they provide evidence that reaction (2) occurs as a side reaction in the iodination. On the basis of the hydrogen iodide recovery, reaction (1) occurs to the extent of 75—90% [depending on whether reaction (2) consumes one mole of iodine or two] with reaction (2) accounting for the rest of the iodine.

The first three germanes are now known to react smoothly with iodine at low temperatures to substitute one hydrogen atom. The best recoveries of hydrogen iodide are 99% with GeH_4, 93% with Ge_2H_6, and 84% with Ge_3H_8. These values show that the reactivity of the Ge–H bond is similar in all three hydrides and that the Ge–Ge bonds in trigermane are only a little more reactive than that in digermane. This behaviour is in accord with recent results that place the electronegativity of germanium nearly equal to that of hydrogen.

Experimental.—All compounds were handled in a conventional vacuum system. Vapour pressures were measured in a glass spiral gauge fitted with a greaseless tap. Infrared (i.r.) spectra were recorded with a Perkin-Elmer 521 spectrometer in a 10-cm. cell with potassium bromide windows. The proton magnetic resonance spectrum was measured on an AEI RS2 spectrometer at 60 Mc./s.

The reaction of trigermane and iodine. Trigermane was condensed on to iodine and the dark brown mixture was held at −63° for 1 hr. Products volatile at −63° were then removed and fractionated. The main details of the reactions are given in Table 1. In all the runs traces of hydrogen, monogermane, and digermane were also found. The germanes were identified by their i.r. spectra and estimated to make up not more than 3 mole-% of the trigermane used.

TABLE 1

	Reactants				Product		
	Ge_3H_8		I_2		HI		
Run	(mg.)	(mmole)	(mg.)	(mmole)	(mg.)	(mmole)	% *
1	39·6	0·18	44·4	0·18	17·4	0·135	75
2	108·0	0·48	112·4	0·443	40·8	0·319	74
3	368·0	1·63	353·4	1·39	146·0	1·14	82
4	226·9	1·01	262·2	1·03	48·3 plus a fraction which was lost before weighing		

* Based on the iodine used.

In run 1, the reaction mixture was allowed to warm above −63° and the volatile materials were examined spectroscopically. At −22° and at 0° small samples were recovered which contained trigermane and germyl iodide, GeH_3I, which could not be separated. The fraction volatile at room temperature contained trigermane, germyl iodide, and small amounts of digermane and digermanyl iodide, Ge_2H_5I. No evidence of a volatile trigermane derivative was found.

The reaction with silver chloride. In run 2, after removal of material volatile at −63°, pure, dry silver chloride was added to the reaction mixture. Little reaction occurred below −22°. At 0°, the volatile sample contained trigermane (37·2 mg.) and an inseparable mixture of digermane and germyl chloride, GeH_3Cl (25·8 mg.). A further sample (22·3 mg.), obtained at room temperature, contained germyl chloride, germylene dichloride, monogermane, and a trace of digermane. All these products must arise from reaction with the silver chloride of trigermanyl iodide or germyl iodide, accompanied by decomposition or rearrangement of any trigermanyl species. No evidence for a volatile trigermanyl chloride was obtained.

The reaction with lithium tetradeuteroaluminate. In run 3, the reaction mixture was treated with an excess of lithium tetradeuteroaluminate (44·0 mg., 1·05 mmole; deuterium content >98%) in dimethyl ether for half an hour at −63°. The solvent was removed at −78°, and found to contain a small amount of deuterated monogermane. The pure trigermane fraction (332·5 mg., 1·47 mmole; 90% of original trigermane) contained the 15% excess of trigermane used in the reaction. Its i.r. spectrum showed a band of medium intensity at 1495 cm.$^{-1}$, the position expected for Ge–D stretching.

This preparation was repeated (run 4) except that unchanged trigermane was removed before deuteration: a total fraction of 37·0 mg. was recovered containing trigermane and germyl iodide. After deuteration, no monogermane fraction was found. The ether-free trigermane fraction was recovered in 48% yield (108·8 mg., 0·48 mmole). This product had M 227·3 (H_7DGe_3 requires M = 226·8). The vapour pressures (mm. Hg) were: 11·1 (0°); 15·0 (5·3°); 21·8 (12·0°). Literature values for Ge_3H_8 [8] (mm. Hg) are: 15·5 (2·4°); 21·3 (10·0°).

Table 2 lists the infrared bands of trigermane and of deuterotrigermane, recorded at 7 mm. pressure in the gas phase.

TABLE 2

Infrared bands of the trigermanes

Frequency (cm.$^{-1}$)		
Ge_3H_8	Ge_3H_7D	Assignment
2136sh	2127sh	Ge–H stretch
2078vs	2074vs	
2025sh		
	1495m	Ge–D stretch
929sh	925sh	
876m, br	873m, br	GeH_3 and GeH_2 deformations (overlapping bands)
795vs	796vs	GeH_3 sym. deformation
	733s	GeH or GeHD deformation (*a*)
700m		GeH_2 wagging (*b*)
640d, vs	632vs	GeH_3
634d, vs		
	594mw	GeHD?
568vw		GeH_2?
516vw	515w	
429w	424vw	
	370vw	

(*a*) Compare 906 m. as an Si–H mode in isotetrasilane.[6] (*b*) Compare strong doublets at 720 (GeH_5Cl), 700 (Ge_2H_5Br), 680 (Ge_2H_5I) corresponding to the *a′* mode at 1287 cm.$^{-1}$ in the ethyl chloride spectrum.

The proton magnetic resonance spectrum of the deuterotrigermane, as a 50% solution in tetramethylsilane, showed a close doublet with peaks at τ 6·58 and 6·62. The peaks are of approximately equal intensity but the high-field peak has a half-height width of 3·1 compared with 2·0 c./sec. for the low-field one.

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