279. *The Silicon–Germanium Hydrides.*

By P. L. TIMMS, C. C. SIMPSON, and C. S. G. PHILLIPS.

A new group of inorganic compounds, the silicon–germanium hydrides $Si_xGe_yH_{2x+2y+2}$, have been prepared by hydrolysis of MgGeSi alloys or SiO–GeO mixtures, or by pyrolysis of a germane with a silane. Gas–liquid chromatography in conjunction with chlorinations and pyrolyses has been used to distinguish the compounds, in terms of the total number of atoms, the silicon–germanium ratio, the presence or absence of chain branching, and the order of silicon and germanium atoms in the chain.

THE classical work of Stock[1] and Dennis, Corey, and Moore[2] established that silicon and germanium form volatile hydrides formally analogous to the alkanes. No compounds of greater complexity than hexasilane and trigermane were reported by these workers, and no structural isomers were isolated.

Recent work by Amberger,[3] Borer and Phillips,[4] and Drake and Jolly[5] has indicated that higher germanes and silanes can be prepared either by hydrolysis of magnesium silicide and germanide, or by electrical discharge methods. The last two sets of workers, using gas-chromatographic separation instead of fractional condensation, were able to show the presence of structural isomers of the tetra- and higher hydrides.

A new class of compounds, the silicon–germanium hydrides, analogous to the silanes and germanes, with the general formula $Si_xGe_yH_{2x+2y+2}$, were prepared by acid hydrolysis of alloys made from SiGe alloys and magnesium, by the action of hydrofluoric acid on a mixed SiO–GeO preparation, or by pyrolysis of a germane with a silane. The simplest compound of the series, $SiGeH_6$, has recently been prepared independently by an electrical discharge method by MacDiarmid and Spanier.[6]

Numerous possibilities of isomerism make the series of compounds potentially very complex. Thus, with the hydrides containing five atoms in the skeleton there could be four analogues distinguished by a different silicon–germanium ratio each with (a) n-, iso-, and neo-structural isomers, and (b) a number of position isomers (*i.e.*, with different Si–Ge sequences) of each of the structural isomers, making a total of 48 compounds. In practice the number of compounds appears to be more restricted and it is thought that no neo-isomer or compound containing a linkage of type Si·[Ge]$_n$·Si has yet been prepared.

By means of gas-chromatographic separation, 15 distinct peaks have been identified as silicon–germanium hydrides, distinguished by differences in the total number of atoms, the silicon–germanium ratio and/or the degree of branching. In three of these cases, it has been shown that a single peak is given by a mixture of two position isomers, and in one case the individual position isomers have been synthesised by pyrolysis.

No indication of unsaturated or cyclic silicon–germanium hydrides has been obtained.

EXPERIMENTAL

Starting Materials for Hydride Preparations.—The most useful preparation for the silicon–germanium hydrides has been acid hydrolysis of a MgSiGe alloy, prepared from a SiGe alloy. Different SiGe alloys gave varying amounts of the hydrides, so several alloys in the composition range Si_9Ge–$SiGe_3$ were made, by heating intimate mixtures of −60 mesh silicon and germanium powders (respectively, 99·8 and 99·9% pure) in alumina boats in a hydrogen-filled alumina tube furnace to about 1400° for 1 hr. (With germanium-rich alloys, better mixing

[1] Stock, " Hydrides of Boron and Silicon," Cornell University Press, Ithaca, New York, 1933.
[2] Dennis, Corey, and Moore, *J. Amer. Chem. Soc.*, 1924, **46**, 657.
[3] Amberger, *Angew. Chem.*, 1959, **71**, 372.
[4] Borer and Phillips, *Proc. Chem. Soc.*, 1959, 189.
[5] Drake and Jolly, *Proc. Chem. Soc.*, 1961, 379.
[6] MacDiarmid and Spanier, *Inorg. Chem.*, 1963, **2**, 215.

was achieved by first preparing an alloy of composition SiGe and then melting this with the required extra germanium.)

The alloys were crushed to −60 mesh in an agate mortar, mixed with magnesium powder (a low phosphorus and boron grade) in a roughly $1 : 2.1$ atomic ratio, and heated in alumina boats in hydrogen for 1 hr. Magnesium silicide and silicon-rich mixtures were prepared at 550—600°, and magnesium germanide and germanium-rich mixtures at 700—750°.

The SiO–GeO mixtures were prepared by arranging that SiO and GeO vapours from heated silicon and silica (1400°) and germanium and germania (900°), respectively, were quenched together on to a water-cooled copper cold-finger in the hot zone of the furnace. More than about 25% of GeO in the mixture rendered the solid insoluble in acid and incapable of yielding hydrides.

The Hydride Handling Apparatus.—The glass apparatus contained three main parts: (i) the preparation unit for reaction of alloys with acid and collection of the hydrides, (ii) the separation unit comprised of two g.l.c. columns (12 ft. × 1 cm.) packed, respectively, with 10% Silicone 702 and 10% tritolyl phosphate on Celite, a katharometer (Pretzel cell, Gow-Mac Instrument Co., U.S.A.), and a trapping unit for collecting up to six separate fractions emerging from the columns, (iii) an analysis section where reactions and measurements on the hydrides could be carried out either in flowing hydrogen or nitrogen streams, or under vacuum.

Transfer of volatile materials from trap to trap was mainly through electrically-heated semi-capillary tubing (2 mm.) in fast streams of hydrogen (200—600 ml./min.). The hydrogen used was purified catalytically and dried through a trap cooled by liquid oxygen. All the traps for collecting the hydrides were U-tubes (5 mm.), containing 1 cm. of Celite coated with Silicone 702 held between layers of glass wool, and they could be cooled in liquid oxygen or solid CO_2–acetone. Apart from the vacuum section, most taps were of 2 mm. bore, spring-loaded, lubricated with Silicone grease, and heated electrically to 100°. The g.l.c. columns were vapour-jacketed, and normally operated at room temperature or 64.5°.

The apparatus was designed for preparing samples of up to 200—300 mg., and for handling pure samples of individual hydrides of 10 μg.—30 mg. Compounds boiling above about 250° were not readily handled. A preparation and separation apparatus working on a fifteenth of this scale was connected to the main apparatus and was used in much of the exploratory work on the compounds and for separating very small samples produced in the larger apparatus.

Preparation of the Hydrides.—In a typical preparation, a total of 2 g. of an alloy of nominal composition $Mg_{20}Si_9Ge$ was tamped into five 1 cm. × 1 cm. thin-walled aluminium-foil cylinders. During 15 min., the cylinders were added one by one to 200 ml. of hydrofluoric acid (10% w/w) in a polythene flask (1 l.), where the foil dissolved quickly, releasing the alloy into the acid. Hydrogen was bubbled at 600 ml./min. into the flask to carry the hydrides through a drying tube, containing phosphorus pentoxide (*ca.* 20 g.), and into a trap cooled by liquid oxygen. The hydrogen was maintained for 40 min. after the addition of the alloy. A blow-off, operating at 12 cm. of mercury, avoided excessive pressures in the reaction flask, and the flushing hydrogen emerged into the atmosphere through a mercury bubbler and was burnt.

The bulk of the monosilane and monogermane in the 150—200 mg. of hydrides formed was normally removed by warming the trap to −80°. The residual higher hydrides were then carried in a stream of hydrogen to one of the traps immediately before the g.l.c. columns.

Isolation of the Individual Compounds.—The hydrides were injected on to the g.l.c. columns by immersing the trap containing them in boiling water and allowing the column flow of hydrogen to be 400—600 ml./min. As peaks emerged from the column, indicated by the detector response fed to a potentiometric recorder, they could be directed into any of six cooled traps. After completion of a run, individual peaks were commonly recycled through the chromatographic system, usually on a different column or at a different temperature, to ascertain that they were pure before analysing them.

Analytical Methods.—(1) *Gold chloride reactor.* The silicon–germanium hydrides reacted with heated gold chloride [7,8] which converted them quantitatively into the corresponding tetrachlorides and hydrogen chloride. Individual compounds were passed slowly in nitrogen over gold chloride (*ca.* 1 g.) at 170° contained in a glass boat fused to a B 10 glass cone. Part of the chloride was reduced to gold, and the volatile material—chlorine (from the heated chloride), hydrogen chloride, and the tetrachlorides—were collected, separated on a column (4 ft. × 3 mm.)

[7] Phillips and Timms, *Analyt. Chem.,* 1963, **35**, 505.
[8] Phillips, Powell, Semlyen, and Timms, *Z. analyt. Chem.,* 1963, **197**, 202.

packed with 10% Silicone 702 on Celite, and detected with a gas-density balance to enable quantitative results to be obtained directly from peak area ratios. When necessary the boat attached to the cone could be readily transferred to a chlorine-filled apparatus at 200° to rechlorinate the gold.

Hydride samples of 5—100 μg. were conveniently handled by this method.

(2) *The pyrolysis and synthesis units.* Hydrides were thermally cracked at 290—350° to give mainly simpler volatile fragments.[7,8] One cracker was a Pyrex tube (5 cm. × 4 mm.) packed with glass wool and heated electrically. Hydrides were passed through the tube in hydrogen or nitrogen streams with a residence time of about 1 sec., and volatile materials were trapped and then separated on a gl.c. column (5 ft. × 3 mm.) packed with 10% Silicone 702 on Celite operated at room temperature. Reproducible g.l.c. " cracking patterns " were obtained with samples larger than about 30 μg.

Silicon–germanium hydrides were formed, by condensing a silane with a germane of similar boiling point in a trap before an 8 cm. × 1 cm. Pyrex tube, which was packed with glass wool and heated to 350—370°. The hydrides were evaporated quickly from the trap to pass through the tube with a residence time of 0·3—0·6 sec. in a hydrogen stream, the products being trapped and separated by g.l.c.

(3) *Molecular-weight determinations.* An approximate method based on the comparison of density-balance and katharometer responses,[7] and a more accurate method, depending on a pressure–volume measurement on a sample of vapour and the density-balance response to the same sample were used.[9]

(4) *Melting points.* Stock's ring method[1] was used with minimum samples of 1 mg., temperatures being measured with a corrected spirit thermometer, or a copper–constantan thermocouple.

DISCUSSION

Initially a comparison was made, by gas-chromatographic analysis, of the volatile products from acid hydrolysis of a mechanical mixture of magnesium silicide and germanide, with the combined products from the compounds hydrolysed separately. These were found to be identical. However, hydrolysis of an alloy made from magnesium and a silicon–germanium alloy gave all the peaks, previously observed on the chromatograms of the mechanical mixture, plus several new peaks. By using the Silicone 702 and tritolyl phosphate columns at two temperatures, the fifteen new peaks could be distinguished and their components trapped in sufficient amount for analysis. Because of their mode of formation and the similarity of their gas-chromatographic behaviour with that of the silanes and germanes, it was suggested that the compounds were silicon germanium hydrides of general formula, $Si_xGe_yH_{2x+2y+2}$. The preparation using SiO–GeO mixtures was comparatively tedious, but the same compounds were obtained, thus confirming they were mixed silicon–germanium hydrides.

Most of the peaks were established as silicon–germanium hydrides by their reaction with gold chloride. The results gave three types of information; (*a*) chromatography of the volatile products always showed peaks corresponding to silicon tetrachloride, germanium tetrachloride, and hydrogen chloride proving the presence of Si, Ge, and H in the compounds; (*b*) as no other peak was obtained, possible impurities, such as phosphorus, fluorine, and oxygen were absent, since these would all give volatile products; (*c*) measurement of the peak areas enabled the silicon : germanium and, in some cases, the silicon : hydrogen ratio to be obtained.[7,8] The former was always close to integral allowing the empirical formula of the skeleton to be assigned for the first 11 peaks in order of their g.l.c. retention volumes as follows: (SiGe), (Si_2Ge), ($SiGe_2$), (Si_3Ge), (Si_3Ge), (SiGe), (SiGe), ($SiGe_3$), (Si_4Ge), ($SiGe_3$), (Si_4Ge).

As the first peak appeared between Si_2H_6 and Ge_2H_6 on chromatograms it seemed likely to be $SiGeH_6$, so that the other two compounds with a 1 : 1 atom ratio probably contained the skeleton Si_2Ge_2. The presence of pairs of compounds with the same Si : Ge ratio close to each other on chromatograms suggested that these were structural isomers.

[9] Phillips and Timms, *J. Chromatog.*, 1961, **5**, 131.

Much information about the hydrides could be obtained from their g.l.c. behaviour. For example, confirmatory evidence for the silicon : germanium ratio was derived from observations of peak positions and sizes in the following ways.

(i) Germanes are more retarded relative to silanes on tritolyl phosphate columns (polar phase) than on Silicone 702 (non-polar phase). (This presumably arises because of the greater polarisability of germanium.) Similar retardation of germanium-rich hydrides takes place on either column with rise of temperature. (The variation of retention time with temperature is directly related to the heat of solution [10] so that silicon-rich hydrides have higher heats of solution than germanium-rich ones of comparable retention time. As the free energy of solution is directly related to the retention time, then similarly the entropy of solution of the silicon-rich will be more unfavourable than for the germanium-rich ones, thus confirming that the silicon-rich compounds will have more atoms in the chain for a given retention time. Hence, on tritolyl phosphate, n-Ge_4H_{10} emerges some time after n-Si_5H_{12} and just before n-Si_6H_{14}.) These variations of relative retention time are of great practical value in the isolation of individual silicon–germanium hydrides.

(ii) Germanium-rich alloys give larger relative yields of the supposed germanium-rich compounds than silicon-rich alloys and *vice versa.*

Similarly, the presence of structural isomers, suggested by the chlorination results, was proved in three ways:

(i) With alkanes, silanes, and germanes, branched isomers emerged before straight-chain isomers on the columns used. With silanes and germanes at room temperature the ratio of the retention times for the branched to normal compounds falls in the range 0·6—0·7. The ratios of the retention times of the supposed iso-/n-silicon–germanium hydrides all fell within this range.

(ii) The peak areas for the supposed iso-/n-pairs were all fairly constant irrespective of the composition of the alloy hydrolysed. This effect was also observed with the known iso-/n-silanes and germanes (Table 1).

(iii) The second peak of each pair showed a greater tendency to be asymmetric (sloping front, sharp tail) even when the sizes of the peaks were the same. This behaviour is also characteristic of normal silanes and germanes.

(iv) All the supposed straight-chain isomers were strongly adsorbed by a column of 5 Å molecular sieve while the supposed branched-chain compounds were not so retarded. This behaviour is characteristic of straight- and branched-chain alkanes, silanes, and germanes.

When the logarithms of the relative retention times for silanes and germanes were plotted against the number of atoms in the chain, two straight lines were obtained for the normal compounds, which converged at zero atoms in the chain : a so-called " theoretical hydrogen point." By referring the retention times to this point it was possible to express log (relative retention time), *i.e.,* log t_R, for any normal silane or germane by a formula :

$$\log t_R \ (Si_nH_{2n+2}) = nk_{Si}$$
$$\log t_R \ (Ge_nH_{2n+2}) = nk_{Ge} \qquad (1)$$

where n is the number of atoms on the skeleton, and k_{Si} and k_{Ge} are constants for a particular column and temperature. Retentions of branched-chain isomers could be expressed as

$$\log t_R' \ (Si_nH_{2n+2}) = nk_{Si} - k_{Si}'$$
$$\log t_R' \ (Ge_nH_{2n+2}) = nk_{Ge} - k_{Ge}' \qquad (2)$$

where k_{Si}' and k_{Ge}' differ by about 0·03 log units. In practice retention times were measured relative to isopentasilane, so that before comparison with experimental values, calculated values of log t_R were adjusted by a constant K equal to the log t_R value

[10] Littlewood, Phillips, and Price, *J.,* 1955, 1480.

of isopentasilane relative to theoretical hydrogen for a particular column and temperature [isopentasilane may not always be a convenient standard, the retention times of benzene relative to isopentasilane ($t_R = 100$) are **35**, **47**, and **98**, **100**, for Silicone 702 and tritolyl phosphate columns, each at 20 and 64·5°].

The results with silanes and germanes suggested that the retention times of straight-chain silicon–germanium hydrides might be expressed by a formula of type

$$\log t_R\ (\mathrm{Si}_x\mathrm{Ge}_y\mathrm{H}_{2x+2y+2}) = xk_{\mathrm{Si}} + yk_{\mathrm{Ge}} \qquad (3)$$

and the branched-chain compounds by

$$\log t_R'\ (\mathrm{Si}_x\mathrm{Ge}_y\mathrm{H}_{2x+2y+2}) = xk_{\mathrm{Si}} + yk_{\mathrm{Ge}} - \mathrm{c} \qquad (4)$$

where c is given empirically as $k_{\mathrm{Si}}' + [k_{\mathrm{Ge}}' - k_{\mathrm{Si}}'][y/(x + y)]$.

The agreement between calculated and observed $\log t_R$ values has already been shown graphically elsewhere.[8]

The mixed hydrides decomposed smoothly at 290—350° to give mainly simpler volatile fragments, with germanium, hydrogen, and a little silicon. Under these conditions silanes were scarcely cracked at all, so that the formation of a particular silane during cracking of a mixed hydride was an immediate indication of the silicon-chain length in the molecule. Three other types of evidence of structure were also obtained:

(i) The size of the skeleton was demonstrated by the complexity of the cracking products. Thus iso- and n-$\mathrm{Si}_2\mathrm{Ge}_2\mathrm{H}_{10}$, giving $\mathrm{Si}_2\mathrm{H}_6$ and $\mathrm{Si}_2\mathrm{GeH}_8$, clearly contained an Si·Si(Ge)$_2$ skeleton.

(ii) The presence of position isomers was revealed. Thus iso-$\mathrm{Si}_4\mathrm{GeH}_{12}$ gave a mixture of iso- and n-tetrasilane in a 1:3 ratio indicating the presence of the two skeletons Si·Si(Si)·Si·Ge and Si·Si(Ge)·Si·Si. The method of predicting g.l.c. retention times for the mixed hydrides indicates that position isomers will have identical retention times.

(iii) With large samples of hydrides, structural isomers and higher homologues of a compound were formed in addition to the simpler compounds, so that the parent could be characterised as a member of a particular homologous series.

The mechanism of the thermal decomposition of the hydrides would appear to involve direct formation of GeH_2 radicals [11] thus

$$\cdot\mathrm{SiH}_2\cdot\mathrm{SiH}_2\cdot\mathrm{GeH}_3 \longrightarrow \cdot\mathrm{SiH}_2\cdot\mathrm{SiH}_3 + \mathop{:}\mathrm{GeH}_2$$

or

$$\cdot\mathrm{SiH}_2\cdot\mathrm{GeH}_2\cdot\mathrm{GeH}_3 \longrightarrow \cdot\mathrm{SiH}_2\cdot\mathrm{GeH}_3 + \mathop{:}\mathrm{GeH}_2$$

The $\mathop{:}\mathrm{GeH}_2$ radicals seem to be able to add directly to silanes, germanes, or silicon–germanium hydrides, thus explaining the formation of higher homologues during pyrolysis. The absence of Si–Si bond cleavage may rule out the alternative mechanism, $\cdot\mathrm{SiH}_2\cdot\mathrm{SiH}_2\cdot\mathrm{GeH}_3 \longrightarrow \cdot\mathrm{SiH}_2\cdot\mathrm{SiH}_2\cdot + \mathrm{GeH}_3\cdot$, as the formation of silyl radicals should cause changes in the silicon-chain length.

With the exception of SiGeH_6 and iso- and n-$\mathrm{Si}_5\mathrm{GeH}_{14}$, all the silicon–germanium hydrides isolated have been synthesised from a germane and a silane. The products have in all cases been consistent with the given mechanism. When trigermane was cracked with n-tetrasilane, iso- and n-$\mathrm{Si}_4\mathrm{GeH}_{12}$ were formed. The iso-compound was clearly [Si·Si(Ge)·Si·Si]H_{12}. By cracking trigermane with isotetrasilane only one $\mathrm{Si}_4\mathrm{GeH}_{12}$ was obtained, and this was clearly [Si·Si(Si)·Si·Ge]H_{12}, the other possibility [Si·Si·(Si)$_2$·Ge]H_{12} apparently not being formed in measurable amount. Both from a direct comparison of the retention times of the individual compounds, and from measurements of the peak width of the mixture compared with the individuals, it was found that [Si·Si(Ge)·Si·Si]H_{12} was retarded 1—1·5% more than [Si·Si(Si)·Si·Ge]H_{12} on a tritolyl phosphate column.

Neither mass spectroscopy or proton resonance spectroscopy was helpful in structural investigations of the silicon–germanium hydrides, the former because of the complexity introduced by five germanium and three silicon isotopes, and the latter because of the

[11] Fensham, Tamaru, Bondart, and Taylor, *J. Phys. Chem.*, 1955, **59**, 806.

small and very similar chemical shifts of silyl and germyl groups. The general structure of molecules could be affirmed, but no information on the possible presence of small amounts of isomers such as $(Si \cdot Ge \cdot Si)H_8$ could be obtained.

RESULTS

Individual Compounds.—The evidence for the identity of each of the fifteen silicon-germanium hydride peaks is summarised below in the following form:

Probable formula; Si : Ge ratio determined from the gold chloride reaction (a) observed log t_R, silicone 702, 20° (calc. value), (b) observed log t_R, silicone 702, 64·5° (calc. value), (c) observed log t_R, tritolyl phosphate, 20° (calc. value), (d) observed log t_R, tritolyl phosphate, 64·5° (calc. value) [N.B., all t_R values refer to isopentasilane as 100], (e) effect of 5Å molecular sieve, *i.e.*, adsorbed or not adsorbed, (f) pyrolysis products, (g) synthesis route, (h) other evidence where available.

1. $SiGeH_6$; 0·99 : 1 (a) 0·23 (0·20), (b) — (0·65), (c) 0·41 (0·42), (d) — (0·77); (e) adsorbed; (f) SiH_4 plus $SiGe_2H_8$ and iso- and n-$SiGe_3H_{10}$; (g) not directly synthesised but is major product of pyrolysis of $SiGe_2H_8$.

2. Si_2GeH_8; 1·96 : 1 (a) 0·96 (0·96), (b) 1·20 (1·22), (c) 1·10 (1·11), (d) 1·32 (1·31); (e) adsorbed; (f) Si_2H_6 (major), iso- and n-$Si_2Ge_2H_{10}$ (minor); no $SiGeH_6$ indicating absence of the isomer $SiGeSiH_8$; (g) Ge_2H_6 plus Si_2H_6, 350°, 0·5 sec.; products Si_2GeH_8 (major), iso- and n-$Si_2Ge_2H_{10}$ and $Si_2Ge_3H_{12}$ (minor). The Si_2GeH_8, with the known skeleton Si–Si–Ge is indistinguishable by n.m.r. spectra, mass spectra, and pyrolysis products from the product of acid hydrolysis which is probably thus mainly Si–Si–Ge and not Si–Ge–Si; (h) *M*, 138·2, (Calc. 136·8), mass spectra: major bands at mass numbers 56—64, 98—111, 127—139, corresponding to Si_2, SiGe, and Si_2Ge species with and without hydrogen. The molecular-ion region 134—139 was rather weak. n.m.r. spectra; complex, main bands but not fine structure coincident with trigermane and trisilane spectra; difficult to distinguish SiSiGe and SiGeSi sequence in the molecule.

3. $SiGe_2H_8$; 0·49 : 1 (a) 1·27 (1·28), (b) 1·50 (1·47), (c) 1·41 (1·43), (d) 1·55 (1·57); (e) adsorbed; (f) SiH_4 and $SiGeH_6$ (major), iso- and n-$SiGe_3H_{10}$ (minor); (g) no direct synthesis from SiH_4. $SiGeH_6$ plus Ge_2H_6 340°, 0·5 sec., gives $SiGe_2H_8$ and higher homologues; (h) the m. p. provides useful confirmation of structure (Table 2).

4, 5. iso-, n-Si_3GeH_{10}; 2·90 : 1, 2·92 : 1 iso- (a) 1·54 (1·55), (b) 1·66 (1·66), (c) 1·62 (1·64), (d) 1·71 (1·71); n- (a) 1·72 (1·73), (b) 1·79 (1·80), (c) 1·80 (1·81), (d) 1·85 (1·86); (e) n- adsorbed, iso- not adsorbed; (f) iso-Si_3GeH_{10} to Si_3H_8 plus traces of n-Si_3GeH_{10}, n-Si_3GeH_{10} to Si_3H_8 plus some iso-Si_3GeH_{10}; (g) both from Si_3H_8 plus Ge_2H_6 or Ge_3H_8 at 350°, 0·5 sec.; (h) *M* iso (approx.) 171, n (approx.) 170, more accurate method 165 (Calc. 166·8); nearly constant peak area ratio (Table 1).

6, 7. iso- and n-$Si_2Ge_2H_{10}$; 0·98 : 1 and 0·97 : 1, iso- (a) 1·85 (1·86), (b) 1·90 (1·90), (c) 1·93 (1·94), (d) 1·96 (1·97); n- (a) 2·03 (2·04), (b) 2·04 (2·04), (c) 2·12 (2·13), (d) 2·10 (2·11); (e) n- adsorbed, iso- not adsorbed; (f) iso-$Si_2Ge_2H_{10}$ to Si_2H_6, Si_2GeH_8, and trace n-$Si_2Ge_2H_{10}$, n-$Si_2Ge_2H_{10}$ to Si_2H_6, Si_2GeH_8, and trace iso-$Si_2Ge_2H_{10}$; (g) both peaks from Si_2H_6 or Si_2GeH_8 plus digermane, 350°, 0·4 sec.; (h) nearly constant peak area ratio (Table 1).

8, 9. iso-, n-$SiGe_3H_{10}$; 0·32 : 1, 0·33 : 1, iso- (a) 2·14 (2·17), (b) 2·14 (2·14), (c) 2·25 (2·24), (d) 2·21 (2·22); n- (a) 2·32 (2·36), (b) 2·30 (2·29), (c) 2·44 (2·45), (d) 2·37 (2·38); (e) n- adsorbed, iso- not adsorbed; (f) both to $SiGeH_6$ and $SiGe_2H_8$; (g) $SiGeH_6$ or $SiGe_2H_8$ plus di- or tri-germane 340°, 0·5 sec., to iso- and n-$SiGe_3H_{10}$; (h) nearly constant peak area ratio (Table 1).

10, 11. iso-, n-Si_4GeH_{12}; 4·09 : 1, 3·93 : 1, iso- (a) 2·29 (2·30), (b) 2·24 (2·23), (c) 2·44 (2·45), (d) 2·37 (2·38); n- (a) 2·48 (2·48), (b) 2·39 (2·37), (c) 2·50 (2·51), (d) 2·40 (2·40); (e) n- adsorbed, iso- not adsorbed; (f) iso-Si_4GeH_{12} to iso- plus n-Si_4H_{10} (1 : 3 ratio) suggesting that, when prepared by hydrolysis, it is a mixture of $[Si \cdot Si(Ge) \cdot Si \cdot Si]H_{12}$ and $[Si \cdot Si(Si) \cdot Si \cdot Ge]H_{12}$. n-$Si_4GeH_{12}$ gives only n-Si_4H_{10}; (g) $[Si \cdot Si(Ge) \cdot Si \cdot Si]H_{12}$ and $[Si \cdot Si(Si) \cdot Si \cdot Ge]H_{12}$ made, respectively, from n-Si_4H_{10} and iso-Si_4H_{10} and Ge_3H_8, 360°, 0·4 sec. n-Si_4GeH_{12} from n-Si_4H_{10} and Ge_3H_8, same conditions; (h) nearly constant peak area ratio (Table 1).

12, 13. iso-, n-$Si_3Ge_2H_{12}$; no gold chloride analysis, iso- (a) — (2·61), (b) 2·48 (2·45), (c) 2·61 (2·64), (d) 2·52 (2·51); n- (a) — (2·80), (b) 2·62 (2·62), (c) 2·83 (2·83), (d) 2·65 (2·66); (e) n- adsorbed, iso- not adsorbed; (f) iso-$Si_3Ge_2H_{12}$ to Si_3H_8 and n-, iso-Si_3GeH_{10} (1 : 1 ratio), n-$Si_3Ge_2H_{12}$ to Si_3H_8 and n-Si_3GeH_{10} plus 10% iso-Si_3GeH_{10}; (g) both from Si_3H_8 plus Ge_2H_6 or

Si_3GeH_{10} plus Ge_3H_8, 350°, 0·4 sec. Pyrolysis of the iso-$Si_3Ge_2H_{12}$ formed gives iso-, n-Si_3GeH_{10} in 1·2 : 1 ratio indicating a different distribution of position isomers than in the hydrolytic product; (h) nearly constant peak area ratio (Table 1).

14, 15. iso-, n-Si_5GeH_{14}; no gold chloride analysis, iso- (a) — (3·07), (b) 2·82 (2·81), (c) — (3·02), (d) 2·78 (2·80); n- (a) — (3·24), (b) 2·97 (2·97), (c) — (3·20), (d) 2·96 (2·94); (e) n-adsorbed, iso- not adsorbed; (f) iso-Si_5GeH_{14} to iso- and n-Si_6H_{12} in a 2 : 3 ratio indicating that it is a mixture of position isomers. n-Si_5GeH_{14} to n-Si_5H_{12}; (g) synthesis has not been attempted, but both 2- and 3-branched isomers could be formed and these may have different t_R values; (h) nearly constant peak area ratio (Table 1).

Two additional compounds have been made from Si_2GeH_8 and digermane; from their mode of formation and their g.l.c. retention data, the compounds are thought to be iso- and n-$Si_2Ge_3H_{12}$, iso- (b) 2·69 (2·68), (d) 2·73 (2·76), n- (b) 2·86 (2·86), (d) 2·91 (2·92).

Preparative Yields of the Compounds.—1. *Alloy hydrolysis.* All yields are quoted as per cent of germanium appearing in the hydride.

The silicon-rich hydrides were mostly prepared in optimum yield from an alloy of nominal composition $Mg_{20}Si_9Ge$; approximate values are:

Si_2GeH_8 (3%); n-Si_3GeH_{10} (1·5%); n-Si_4GeH_{12} (0·3%); n-Si_5GeH_{14} (0·07%).

Many of the germanium-rich hydrides and those containing equal amounts of silicon and germanium were best made from an alloy, Mg_4SiGe, with the approximate yields:

$SiGeH_6$ (0·6%); $SiGe_2H_8$ (0·4%); n-$SiGe_3H_{10}$ (0·03%); n-$Si_2Ge_2H_{10}$ (0·2%); n-$Si_3Ge_2H_{12}$ (0·02%).

TABLE 1.

Compounds	Alloy hydrolysis n/iso ratio	Pyrolytic synthesis n/iso ratio	Compounds	Alloy hydrolysis n/iso ratio	Pyrolytic synthesis n/iso ratio
Si_3GeH_{10}	7·5	1·1	Compare		
$Si_2Ge_2H_{10}$	3·5	3·5	Si_4H_{10}	14·0	
$SiGe_3H_{10}$	1·0	3·5	Si_5H_{12}	2·8	
Si_4GeH_{12}	1·5	0·7	Ge_4H_{10}	4·0	3·5
Si_5GeH_{14}	1·0	0·7	Ge_5H_{12}	1·0	1·2

n-$SiGe_3H_{10}$ was obtained more conveniently from Mg_8SiGe_3 as then only traces of silanes and silicon-rich hydrides were also formed, so that separation was easy. The n/iso ratios are shown in Table 1.

2. *Pyrolytic synthesis.* Si_2GeH_8 was prepared from equimolar quantities of disilane and digermane in about 10% yield based on the Si_2H_6 at 340° for 0·5 sec.; about 50% of the digermane was recovered as volatile material. n-Si_3GeH_{10} and n-$Si_3Ge_2H_{12}$ were prepared in 3 and 0·5% yields, respectively, based on the trisilane from a mixture of one mole proportion of trisilane to two of digermane. Yields of other hydrides have been variable, but are all less than 5% per pass through the pyrolysis unit.

Table 1 shows the ratios of amounts of n- : iso- compounds obtained by hydrolysis and synthesis, the ratios in each case being largely independent of experimental conditions.

TABLE 2.

Melting points and vapour pressures of the hydrides.

Compound	Si_2GeH_8	$SiGe_2H_8$	n-Si_3GeH_{10}	n-Si_4GeH_{12}	Ge_3H_8
M. p.	−113·4°	−108·5°	−87·1°	−71·5°	−105·6 [2]
V. p. (at 0°; mm. Hg) ...	39·6	19·3	4·7		13·9 [2]

Compound	Si_3H_8	n-Si_4H_{10}	iso-Si_5H_{12}	n-Si_5H_{12}	
M. p.	−177·4° [1]	−88·2°	−138°	−74·5°	
V. p. (at 0°; mm. Hg) ...	93·0 [1]				

Some Properties of the Silicon–Germanium Hydrides.—The compounds all have a disagreeable persistent smell, more closely resembling germanes than silanes, and they are unstable in air, either catching fire or oxidising rapidly without ignition. For example, a 5-mg. liquid sample of n-Si_4GeH_{12} became involatile after two minutes exposure to air although it did not immediately change in appearance; subsequently silica and germania were deposited.

Si_2GeH_8 reacted rapidly with aqueous alkali evolving hydrogen but no monogermane.

At 64°, 2—7% of samples of silicon–germanium hydrides were destroyed per pass through the chromatographic columns, traces of germanes and silanes being formed.

Melting points and vapour pressures at 0° of some of the hydrides are shown in Table 2. The melting points within the series $SiGeH_6$, Si_2GeH_8, n-Si_3GeH_{10}, and n-Si_4GeH_{12} show the same " odd–even " variation with chain length as the alkanes, although to a smaller extent. In the series Ge_3H_8, $SiGe_2H_8$, Si_2GeH_8, and Si_3H_8 melting points decrease almost uniformly with the number of germanium atoms. MacDiarmid and Spanier [6] have reported a similar effect in the series Ge_2H_6, $SiGeH_6$, and Si_2H_6.

Further Studies on Silanes.—From the work of Borer and Phillips,[4] it was known that the acid hydrolysis of magnesium silicide gave a mixture of volatile material which appeared to contain many of the possible isomers of the silanes up to n-octasilane. The identity of most of the peaks up to n-pentasilane was established by physical analysis; later peaks were tentatively assigned on the basis of their behaviour with a 5Å sieve and their g.l.c. retention times.

The problem has been re-investigated using the apparatus built for the silicon–germanium hydrides. On the basis of their behaviour on the columns with two different stationary phases, two peaks from the hydrolysis of magnesium silicide were assigned as tetrasilanes, two as pentasilanes, three as hexasilanes, and three as heptasilanes (octasilanes were too high boiling to be handled in the apparatus). The retention times of these peaks could be calculated by

TABLE 3.

Comparison of calculated and observed log t_R values for the silanes.

	Silicone 702				Tritolyl phosphate			
	20°		64·5°		20°		64·5°	
Compound	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
Si_3H_8	0·66	0·65	0·98	0·98	0·79	0·78	1·08	1·06
iso-Si_4H_{10}	1·25	1·24	1·41	1·42	1·32	1·31	1·47	1·47
n-Si_4H_{10}	1·41	1·40	1·54	1·55	1·48	1·48	1·59	1·60
iso-Si_5H_{12}	2·00	2·00	2·00	2·00	2·00	2·01	2·00	2·01
n-Si_5H_{12}	2·17	2·16	2·13	2·13	2·18	2·18	2·13	2·14
" iso-iso-Si_6H_{14} * "	2·57	2·59	2·44	2·44	—	2·53	2·38	2·42
iso-Si_6H_{14}			2·58	2·57	2·68	2·70	2·54	2·55
n-Si_6H_{14}			2·72	2·70	2·87	2·87	2·69	2·68
" iso-iso-Si_7H_{16} * "			3·00	3·00			2·93	2·97
iso-Si_7H_{16}			3·14	3·13			3·07	3·10
n-Si_7H_{16}			3·28	3·26			3·22	3·23

* Calculated from $nk_{Si} - 2k'_{Si}$.

eqns. (1) and (2). The results are shown in Table 3. Satisfactory agreement with experimental values was obtained except for some iso-compounds on tritolyl phosphate at 64·5°. The identity of some of the peaks up to n-hexasilane was confirmed by thermal cracking at 400° The results are summarised in Table 4. Only small yields (1—5%) of the silanes were

TABLE 4.

Pyrolysis of silanes.

Compound	Temp.	Residence time (sec.)	Products				Yield (%) of volatile materials
			iso-Si_4	n-Si_4	iso-Si_5	n-Si_5	
iso-Si_5H_{12}	380°	0·4	✓	✓			1½
n-Si_5H_{12}	400	0·4	(trace)	✓			3
" iso-iso-Si_6H_{14} "	360	0·5		✓	✓		—
iso-Si_6H_{14}	370	0·5	✓	✓	✓		4
n-Si_6H_{14}	370	0·4		✓		✓	5

(i) The n-iso-Si_4H_{10} ratio was 1·1 : 1 from iso-Si_5H_{12} and 1·3 : 1 from iso-Si_6H_{14}; (ii) " iso-iso-Si_6H_{14} " was cracked in nitrogen, the others in hydrogen; (iii) Mono-, di-, and tri-silane appeared on all cracking patterns.

recoverable as cracking fragments, necessitating samples of at least 200 μg. to permit reproducible cracking patterns with the apparatus used.

In addition to those peaks whose positions could be calculated, three other well-defined peaks were obtained. One of these [(b) 2·65 and (d) 2·82] was treated with gold chloride.

The main products were hydrogen chloride and silicon tetrachloride, but a small amount of perchlorosilyl ether was also formed suggesting the presence of an Si·O·Si link in the original compounds.   However, the calculated O : Si ratio (1 : 30) was too low to fit any reasonable formula.

The other two peaks [(b) 3·06 and 3·06, (d) 3·21 and 3·16] in the region of n- and iso-heptasilane may be branched heptasilanes as, by analogy with the alkanes, the relative behaviour of some isomers on different stationary phases is complex and unpredictable.[12]

Further Studies with Germanes.—Borer and Phillips [4] obtained g.l.c. evidence for hydrides up to iso- and n-tetragermane by hydrolysis of magnesium germanide, and Drake and Jolly [5] gave similar evidence for peaks up to n-octagermane prepared by an electrical discharge method.

In this work, compounds up to what is thought to be n-pentagermane were made both by the hydrolysis of magnesium germanide and by the pyrolysis of digermane.   The supposed tetragermane peaks were shown to give tri- and di-germane as major cracking fragments. The supposed pentagermanes have not been pyrolysed, but it was shown that the n- but not the iso- compound was adsorbed by molecular sieve and that the position of the peaks could be accurately described by eqns. 1 and 2.   The calculated and observed values of log t_R for the germanes are shown in Table 5.

A 100-mg. sample of digermane when passed through the 8-cm. cracker tube at 370° yielded 4 mg. of trigermane, 2·6 mg. of tetragermanes, and 1·7 mg. of pentagermanes in a single pass. About 50% of the germanium was recovered as volatiles.

A Preliminary Search for Other Hydride Systems.—No mixed hydride of silicon and tin, germanium and tin, or silicon and boron was obtained by acid hydrolysis of alloys of the type MgSiSn, MgGeSn, or MgBSi.   The only volatile products were, respectively, silanes, germanes, and silanes plus boranes.

TABLE 5.

Comparison of calculated and observed log t_R values for the germanes.

	Silicone 702				Tritolyl phosphate			
	20°		64·5°		20°		64·5°	
Compound	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
Ge_2H_6	0·53	0·52	0·90	0·88	0·75	0·74	1·04	1·05
Ge_3H_8	1·61	1·60	1·72	1·70	1·77	1·77	1·86	1·85
iso-Ge_4H_{10}	2·47	2·48	2·41	2·38	2·58	2·58	2·48	2·48
n-Ge_4H_{10}	2·67	2·68	2·56	2·53	2·78	2·79	2·65	2·66
iso-Ge_5H_{12}			3·18	3·19			3·25	3·28
n-Ge_5H_{12}			3·35	3·34			3·44	3·46

Cracking a germane with a borane did not form B–Ge bonds.   Instead all the germane was decomposed to germanium and hydrogen.   At 270° complete decomposition of germanes, silicon–germanium hydrides, and silanes could be accomplished in 0·5 sec. in the presence of pentaborane, B_5H_9, with almost negligible loss of the borane.

Mixtures of hydrofluoric with dilute sulphuric, hydrochloric, and phosphoric acids reacted with magnesium silicide to form small amounts of, at least, four compounds in addition to the known silanes.   These are thought to contain silicon, hydrogen, and fluorine as they gave silicon tetrachloride and tetrafluoride and hydrogen chloride with gold chloride; however no formula has been elucidated.   The compounds were not formed from 10% hydrofluoric acid and magnesium silicide.

INORGANIC CHEMISTRY LABORATORY, OXFORD.

[Present address (P. L. T.): DEPARTMENT OF CHEMISTRY,
         RICE UNIVERSITY, HOUSTON, TEXAS, U.S.A.]   [*Received, August 22nd, 1963.*]

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