

951. *The Chromatography of Gases and Vapours. Part VIII.¹
Some Alkyl Derivatives of Silicon and Germanium.*

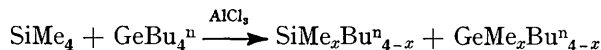
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The synthesis and interconversion of a number of mixed alkyls of silicon and germanium and some of their hydrogen, chlorine, and bromine derivatives have been studied by gas-liquid chromatography.

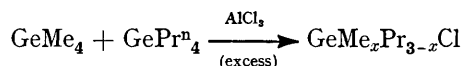
SEVERAL reactions that may be used to prepare mixed alkyl silanes and mixed alkyl germanes and their derivatives, in which one of the alkyl groups has been replaced by hydrogen or chlorine, have been investigated. Mixed methyl, ethyl, n-propyl, and n-butyl tetra-alkyl silanes and germanes, in approximately statistical distributions, are obtained by the action of mixed organo-metallic reagents on tetrachlorosilane and tetrachloro-germane, *e.g.*,



or by redistribution reactions of the symmetrical tetra-alkyls, *e.g.*,



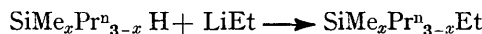
With excess of aluminium chloride in the redistribution reactions, cleavage of single alkyl groups gives the mixed trialkyl chloro-derivatives, *e.g.*,



Reduction with lithium aluminium hydride converts these to the corresponding hydrides, which may be reconverted to the monochloro-compounds with thionyl chloride, thus:



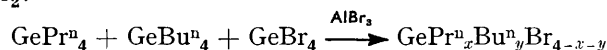
Substitution of chlorine or hydrogen in trialkyl silanes and of chlorine in trialkylgermanes with organo-metallic reagents gives tetra-alkyl derivatives, *e.g.*,



In the redistribution and cleavage reactions of germanes involving tetra-n-butylgermane, di- as well as tri-chloro-germanes are formed:



Further, two tetra-alkyl germanes redistribute with tetrabromogermane, in the presence of aluminium bromide, to give mono-, di-, and tri-bromogermanes, and the mixture contains $\text{RR}'\text{GeBr}_2$:



¹ Part VII, *J.*, 1963, 1202.

The investigations have been considerably facilitated by analysing the products by gas chromatography, which has not only enabled them to be clearly separated but has helped in the identification. With a 2-cm. diameter gas-chromatographic column a number of individual compounds have been prepared on the 100-mg. scale.

EXPERIMENTAL

Preparation of Tetra-alkyl Silanes and Germanes.—Tetraethylsilane, tetra-*n*-propylsilane, tetra-*n*-butylsilane, trimethyl-*n*-propylsilane, dimethyl-di-*n*-propylsilane, and methyl-tri-*n*-propylsilane were prepared by the action of alkyl-lithiums on 5 ml. of the chlorosilanes in diethyl ether.² Tetraethylgermane, tetra-*n*-propylgermane, and tetra-*n*-butylgermane were prepared from 5 ml. of tetrachlorogermane and the corresponding Grignard reagents in diethyl ether;³ for tetramethylgermane di-*n*-butyl ether was used as solvent.⁴ The boiling-points and infrared spectra of the compounds were in agreement with the literature.⁵ Their purity was confirmed by gas chromatography.

Tetra-alkyl silanes. Two alkyl-lithiums (2½ moles of each) were mixed and added dropwise to about 5 ml. tetrachlorosilane (1 mole) in diethyl ether with stirring in an atmosphere of dry nitrogen. After the addition was complete, the solution was refluxed for 1½ hr. Distilled water was then run into the flask, which was cooled in an ice-bath. The ether fraction was isolated and dried (Na₂SO₄). Distillation gave a mixture of tetra-alkyl silanes. Tetramethylsilane, when present, distilled over in the ether fraction and was not recovered. Yields were in the range 80–90%.

Tetra-alkyl germanes. Two Grignard reagents (3 moles of each) were mixed and added dropwise to 5 ml. tetrachlorogermane (1 mole) in diethyl ether under dry nitrogen with constant stirring. The solution was refluxed for 1 hr. The ether was then distilled off and the mixture remaining heated on a water-bath for 4 hr. After cooling in ice, ether was added and dilute HCl run in. The ether layer was separated and dried. A mixture of tetra-alkyls, except tetramethylgermane, was obtained by distillation. Yields were in the range 60–70%.

Analytical Gas-chromatographic Apparatus.—Samples were analysed in 3, 6, 10, and 13% squalane and 10% Silicone 702 columns at 100°. Embacel (May and Baker; 60–100 mesh; acid-washed) was used as the solid support, and treated with hexamethyldisilazane, as described by Bohemen *et al.*⁶ Flame-ionisation equipment and katharometers were used as detectors, and hydrogen as carrier gas. Injections were made through a serum-cap from a Hamilton microlitre syringe. Retention times were calculated relative to mesitylene.

The flame-ionisation detector was calibrated by means of a Gow-Mac gas-density detector as described previously.⁷ The compounds studied were found to give responses on the detector approximately in proportion to the number of carbon atoms they contain.

Preparative Gas-chromatographic Apparatus.—A column of 13.5% squalane on treated Embacel, of 2 m. length and 18 mm. internal diameter, was used for preparative separations. The column was built in two sections, which were joined by a glass capillary U-tube of 3 mm. internal diameter and was enclosed in a vapour jacket at 100°. A detachable sample trap was used, and samples transferred from it to the injection U-trap by a stream of hydrogen. The total effluent was passed into a katharometer detector on a low-sensitivity range and the collection traps switched in by a magnetically controlled two-way outlet. The column efficiency exceeded 1000 theoretical plates and the column was used for compounds boiling between 60 and 200°. The purity of the compounds, which were prepared on a 100-mg. scale, was established by gas chromatography.

RESULTS AND DISCUSSION

Tetra-alkyl Silanes and Germanes.—Preparation. Mixed alkyls of the type MR₁R₂R₃R₄ (M = Si, Ge; R₁, R₂, R₃, R₄ = Me, Et, Prⁿ, Buⁿ) were prepared from tetrachlorosilane and tetrachlorogermane with mixed organo-metallic reagents, and by redistribution reactions

² Gilman and Clark, *J. Amer. Chem. Soc.*, 1946, **68**, 1675.

³ Kraus and Flood, *J. Amer. Chem. Soc.*, 1932, **54**, 1635.

⁴ Gladstein, Rodé, and Soborovskii, *Zhur. Obskchei. Khim.*, 1959, **29**, 2155 (Eng. Trans., 2120).

⁵ Kaufman, "Handbook of Organometallic Compounds," Van Nostrand, New York, 1961.

⁶ Bohemen, Langer, Perrett, and Purnell, *J.*, 1960, **2444**.

⁷ Powell, Semlyen, Blofeld, and Phillips, *J.*, 1964, **280**.

of tetra-alkyl silanes and germanes. Both methods gave approximately statistical distributions of products. The relative amounts of tetra-alkyls formed in four reactions are shown in Table I.

TABLE I.
Mole-% of products from mixed tetra-alkyl reactions.

Reaction	Et ₄ M	Et ₃ Pr ⁿ M	Et ₂ Pr ⁿ ₂ M	EtPr ⁿ ₃ M	Pr ⁿ ₄ M
SiCl ₄ + EtLi + Pr ⁿ Li.....	6	26	38	24	6
GeCl ₄ + EtMgBr + Pr ⁿ MgBr.....	11	30	35	20	5
SiEt ₄ + SiPr ⁿ ₄	8	28	37	22	5
GeEt ₄ + GePr ⁿ ₄	8	27	35	23	7
Statistical distribution.....	6.25	25	37.5	25	6.25

Mixed tetra-alkyl silanes were prepared by a modification of Gilman and Clark's method,² mixed organo-lithium reagents being added to tetrachlorosilane in diethyl ether. When tetrachlorosilane was added to the mixed alkyl-lithiums, mixed products with much higher proportions of the lower-boiling silanes were formed. Grignard reactions gave mixed products but in lower yields.

The corresponding tetra-alkyl germanes were prepared by the addition of mixed Grignard reagents to tetrachlorogermane as described for the symmetrical compounds by Kraus and Flood.³ Organo-lithium reagents gave lower yields of the tetra-alkyl compounds, less

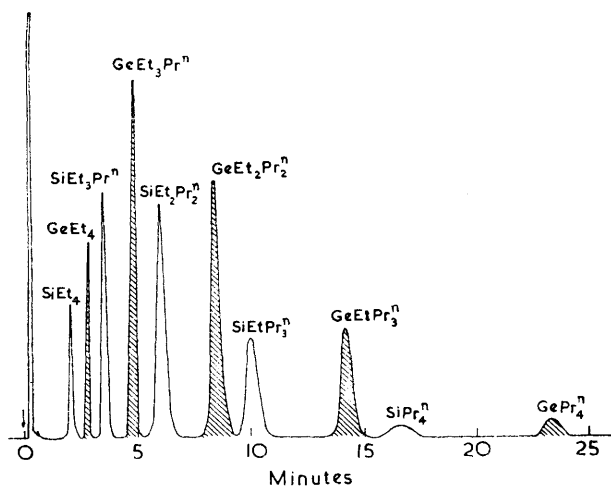


FIG. 1. Redistribution of tetraethylsilane and tetra-n-propylgermane. Chromatogram with 13% squalane column at 100° and flame-ionisation detector.

than 40% compared with more than 60% for the Grignard reactions, and polymeric side-products were formed, as has been noted in the simple reactions.⁸ High-boiling solvents, which are recommended for the organo-lithium reactions,⁹ were avoided because, in general, the products boiled over a wide temperature range.

Redistribution reactions of tetra-alkyl silanes, stannanes and plumbanes were studied by Calingaert *et al.*¹⁰ Simple tetra-alkyl silanes and germanes (0.2 g. of each) redistributed on refluxing with catalytic amounts of aluminium chloride to give five ($MR_4 + MR'_4$ or $MR_xR'_{4-x}$), ten ($MR_4 + M'R'_4$) or fifteen ($MR_4 + MR'_4 + MR''_4$) products. These reactions have been studied by Pollard and his group at Bristol working independently; their investigation, also by gas chromatography, included redistribution reactions involving alkyl stannanes. Fig. 1 shows a chromatogram obtained by redistribution of tetraethylsilane and tetra-n-propylgermane. Analysis at intervals showed that the time to reach equilibrium depends on several factors, but in all cases was less than 90 minutes.

⁸ Gilman, Hughes, and Gerow, *J. Org. Chem.*, 1959, **24**, 352.

⁹ Johnson and Nebergall, *J. Amer. Chem. Soc.*, 1949, **71**, 1720.

¹⁰ Calingaert *et al.*, *J. Amer. Chem. Soc.*, 1940, **62**, 1099.

TABLE 2.
Log t_R in squalane at 100°.

	Silanes		Germanes			Silanes		Germanes	
	obs.	calc.	obs.	calc.		obs.	calc.	obs.	calc.
Me ₃ Bu ⁿ	1.29	(1.35)	1.42	(1.49)	MePr ⁿ ₂ Bu ⁿ	2.47	(2.44)	2.61	(2.58)
MeEt ₃	1.43	(1.49)	1.57	(1.63)	MeEtBu ⁿ ₂	2.49	(2.45)	2.64	(2.59)
Me ₂ Pr ⁿ ₂	1.60	(1.65)	1.77	(1.79)	EtPr ⁿ ₃	2.52	(2.51)	2.66	(2.66)
Me ₂ EtBu ⁿ	1.61	(1.66)	1.77	(1.80)	Pr ⁿ ₄	2.74	(2.74)	2.89	(2.88)
MeEt ₂ Pr ⁿ	1.70	(1.73)	1.84	(1.87)	EtPr ⁿ ₂ Bu ⁿ	2.77	(2.75)	2.91	(2.89)
Et ₄	1.80	(1.80)	1.94	(1.94)	Et ₂ Bu ⁿ ₂	2.82	(2.76)	2.95	(2.90)
Me ₂ Pr ⁿ Bu ⁿ	1.90	(1.90)	2.04	(2.04)	MeBu ⁿ ₃	2.99	(2.93)	3.14	(3.07)
MeEtPr ⁿ ₂	1.95	(1.96)	2.09	(2.10)	Pr ₃ Bu ⁿ	2.99	(2.99)	3.13	(3.13)
Et ₂ Pr ⁿ	2.05	(2.04)	2.18	(2.18)	EtPr ⁿ Bu ⁿ ₂	3.03	(3.00)	3.16	(3.14)
Me ₂ Bu ⁿ ₂	2.15	(2.14)	2.31	(2.28)	Pr ⁿ ₂ Bu ⁿ ₂	3.24	(3.23)	3.38	(3.37)
MePr ₃	2.20	(2.20)	2.35	(2.34)	EtBu ⁿ ₃	3.30	(3.24)	3.40	(3.38)
Et ₂ Pr ⁿ ₂	2.29	(2.27)	2.42	(2.41)	Pr ⁿ Bu ⁿ ₃	3.49	(3.48)	3.61	(3.62)
Et ₂ Bu ⁿ	2.32	(2.28)	2.45	(2.42)	Bu ⁿ ₄	3.72	(3.72)	3.85	(3.86)

Retention data. Analysis on columns of 2–13% squalane on Embacel at 100° gave essentially similar results. Retention data were expressed as logarithms of retention times relative to mesitylene = 100, and agreement to within ± 0.01 was obtained between chromatograms. Alkyls below C₇ were analysed in the columns at room temperature. It was found possible to make useful estimates for the retention values of mixed alkyl silanes and germanes from those found for the symmetrical MR₄ compounds. Dividing the log t_R values of the latter by four gave constants representing the effect of single alkyl groups on the retention times of mixed alkyls. These are: methyl, 0.14; ethyl, 0.45; n-propyl, 0.69; n-butyl, 0.93; a constant, 0.14, is added to calculate values in the germane series. Table 2 shows the observed values (calculated values in parentheses). The average difference between observed and calculated values is < 0.03 in both series. In general, for lower members (C₇–C₉) the calculated values are higher than observed values, and conversely with higher members (C₁₀–C₁₆). Similar relationships were found with four CR₄ compounds (CMe₃Buⁿ, CMeEt₃, CEt₄, CEt₃Prⁿ). The difference between log t_R values in the carbon and silicon alkyl series is 0.09.

Trialkyl Mono-chlorine and -hydrogen Silanes and Germanes.—When the redistribution reactions were carried out at 220° for 2 hr. with excess of AlCl₃, cleavage of single alkyl groups took place, giving a mixture of trialkylchlorosilanes or germanes as the only volatile products. Four trialkylchloro-compounds were formed from R₄M + R'₄M and ten from R₄M + R'₄M + R''₄M. These compounds were retarded relative to the tetra-alkyl derivatives in Silicone 702, a more polar material than squalane. They were hydrolysed by boiling alkali.

Reduction of the trialkylchloro-silane and -germane mixtures was effected by lithium aluminium hydride in ether, as described for the simple compounds.¹¹ The molar ratios of trialkylhydrides, estimated by gas chromatography, were similar to those of the trialkylchloro-compounds from which they were derived. Thionyl chloride readily reconverted the trialkylgermanes to trialkylchlorogermanes on dropwise addition at room temperature. The corresponding trialkylsilane reaction takes place less readily and is incomplete under similar conditions.

Conversion of the trialkylchlorine and trialkyl hydrogen compounds to tetra-alkyls was carried out with organo-metallic reagents. Mixtures of trialkylchlorosilanes reacted readily with alkyl-lithiums, while the chlorogermanes gave high yields of the tetra-alkyls with Grignard reagents. Trialkylsilanes reacted with alkyl-lithiums on refluxing in diethyl ether, forming the tetra-alkyl silanes. With the corresponding germanes, gas chromatography showed no trace of tetra-alkyl formation, a lack of reaction well known in germanium chemistry.¹²

¹¹ Finholt, Bond, Wilzbach, and Schlesinger, *J. Amer. Chem. Soc.*, 1947, **69**, 2693.

¹² Stone, "Hydrogen Compounds of the Group IV Elements," Prentice-Hall, 1962, p. 87.

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Addition of an alkyl halide gave a vigorous reaction and tetra-alkyl germane formation. The tetra-alkyls formed were identified from their retention times in squalane and Silicone 702, and the relative quantities of each corresponded to the molar ratios of the parent compounds (an example is shown in Table 3).

TABLE 3.
Mole-% of mixed trialkyl germanes in the reactions,
 $R_3GeCl \longrightarrow R_3GeH \longrightarrow R_3GeMe.$

	X = Cl	X = H	X = Me		X = Cl	X = H	X = Me
Et ₃ GeX	28	25	26	EtPr ⁿ ₂ GeX	20	24	25
Et ₂ Pr ⁿ GeX	49	49	44	Pr ⁿ ₃ GeX	3	3	5

TABLE 4.
Log t_R in squalane at 100°.

	Si-Cl	Ge-Cl	Si-H	Ge-H		Si-Cl	Ge-Cl	Si-H	Ge-H
Me ₂ Bu ⁿ	1.53	1.90	1.08	1.29	EtPr ⁿ Bu ⁿ ...	2.48	2.79	2.06	—
Et ₃	1.69	2.01	1.25	1.41	Pr ⁿ ₃	2.46	2.79	2.04	2.21
MePr ⁿ ₂	1.87	—	1.40	—	EtBu ⁿ ₂	2.79	3.08	2.36	2.51
Et ₂ Pr ⁿ	1.95	2.28	1.51	1.67	Pr ⁿ ₂ Bu ⁿ	2.79	—	2.32	—
EtPr ⁿ ₂	2.21	2.53	1.79	1.95	Pr ⁿ Bu ⁿ ₂	3.04	3.33	2.61	—
Et ₂ Bu ⁿ	2.25	2.55	1.79	1.97	Bu ⁿ ₃	3.29	—	2.89	3.04
MeBu ⁿ ₂	2.44	2.80	2.04	2.23					

The retention data for the monochlorides and monohydrides formed in the reactions (C₆ and above) are shown in Table 4. Simple calculations of retention times, as for the tetra-alkyl derivatives, do not show good agreement with those observed. Attempts to provide a simple approximate constant for chlorine and hydrogen, in log t_R values, was much less successful. Very rough estimates may, however, be made within ± 0.10 taking chlorine (on Si), 0.41; chlorine (on Ge), 0.58; hydrogen (on Si or Ge), 0.00. There is a difference of about 0.33 between log t_R for corresponding R₃SiCl and R₃GeCl compounds and about 0.16 between R₃SiH and R₃GeH.

Di- and Tri-chloro- and Bromo-germanes.—In the redistribution and cleavage reactions involving tetra-n-butylgermane, appreciable amounts of R₂GeCl₂, RBuⁿGeCl₂, and Buⁿ₃GeCl₂ were formed in addition to the trialkylchloro-compounds. Grignard reactions on the mixtures gave readily identifiable tetra-alkyl derivatives of dichlorogermanes. Van der Kerk *et al.* have recently studied the redistribution of tetra-n-butylgermane and tetra-chlorogermane;¹³ we repeated their work on a 0.2-ml. scale, showing that the groups exchange under our conditions. Thus exchange of n-butyl and chlorine may account for the formation of the dichloro-compounds.

Simple trialkylbromogermanes are readily formed by cleavage of the tetra-alkyls with bromine in the presence of aluminium bromide.¹⁴ With GeR₄ and GeR'₄, mixed trialkylbromogermanes were formed and undergo similar reactions to the chloro-compounds. Aluminium bromide was found to be much less efficient as a catalyst than aluminium chloride in the germane redistribution reactions. Larger amounts were required, and cleavage of single alkyl groups without statistical distribution was readily effected. Mono-, di-, and tri-bromo-compounds were formed in the redistribution of GeBr₄ and GeR₄ in the presence of aluminium bromide, a reaction described by Mazorrolles.¹⁴ A mixture of two tetra-alkyls was used, and RR'GeBr₂ was shown to be present in the products by formation of tetra-alkyl derivatives with Grignard reagents (an example is shown in Table 5).

Confirmation of the Nature of the Compounds Prepared.—30 of the mixed compounds prepared by the methods outlined were isolated pure from a preparative column. Their infrared spectra, recorded on a Perkin-Elmer 221 infrared spectrophotometer, agreed with

¹³ Van der Kerk, Rijkens, and Janssen, *Rec. Trav. chim.*, 1962, **81**, 764.

¹⁴ Mazerolles, *Bull. Soc. chim. France*, 1961, 1911.

TABLE 5.

Redistribution of $\text{GeBr}_4 + \text{GePr}^n_4 + \text{GeBu}^n_4$ and formation of the ethyl derivatives.

Derivative	Mole %	Derivative	Mole %	Derivative	Mole %
Pr^nGeEt_3	3	$\text{Pr}^n\text{Bu}^n\text{GeEt}_2$	14	$\text{Pr}^n_2\text{Bu}^n\text{GeEt}$	18
Bu^nGeEt_3	8	$\text{Bu}^n_2\text{GeEt}_2$	11	$\text{Pr}^n\text{Bu}^n_2\text{GeEt}$	21
$\text{Pr}^n_2\text{GeEt}_2$	5	Pr^n_3GeEt	12	Bu^n_3GeEt	8

the literature in the 12 cases where these have been published, or else had the expected spectra. Examples of all the types except alkylbromogermanes were studied. In the hydrides, Si-H and Ge-H stretching frequencies depend on the alkyl groups attached, as has been reported for silanes¹⁵ and germanes.¹⁶ The mixed trialkyl hydrides studied had stretching frequencies between those of the simple compounds.

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¹⁵ Smith and Angelotti, *Spectrochim. Acta*, 1959, **15**, 412.

¹⁶ Mathis-Noël, Mathis, and Satgé, *Bull. Soc. chim. France*, 1961, 676.