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Preliminary communication

Cyclic heteroatom permethylpolysilanes
I. Dodecamethylgermacyclohexasilane and dodecamethyl-1,4-digermacyclohexasilane

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The family of permethylated cyclic silicon compounds, $(Me_2Si)_n$ where $n = 5, 6, 7$, and 8 has recently been synthesized[1, 2] and shown to have spectral properties of great interest[3]. From these studies it became apparent that cyclic polysilanes containing one or more heteroatoms in the ring would likewise be both interesting and important for purposes of spectral comparisons.

A few examples of these heteroatom permethylated cyclopolysilanes have been reported, principally by Wannagat and Kumada. A review of these compounds has appeared recently[4]. Hengge and Brychey recently reported the preparation of a series of heteroatom perphenylated cyclopentasilanes[5], but the presence of the phenyl groups makes these compounds less desirable for further spectroscopic study.

We now report the synthesis and characterization of two new permethylated species, dodecamethylgermacyclohexasilane and dodecamethyl-1,4-digermacyclohexasilane★. In addition, we report strong evidence for the complete series of compounds $Me_{10}Si_xGe_{5-x}$ where $x = 0–5$, $Me_{12}Si_yGe_{6-y}$ where $y = 0–6$, and $Me_{14}Si_zGe_{7-z}$ where $z = 0–7$. Of these compounds only those where $x = 5$, $y = 0$ and 6, and $z = 7$ have previously been reported[1, 2, 6].

The compounds are prepared from the reaction of mixtures of dimethyldichlorosilane and dimethyldichlorogermane with lithium dispersion in tetrahydrofuran at room temperature. After workup by hydrolysis, gas chromatographic analysis of the crystalline products shows the presence of all the above mentioned compounds. (See Fig.1). In a typical reaction, workup after 24 hours yielded 16–20% crystalline material containing about 20% $Me_{12}Si_5Ge$ and 10% $Me_{12}Si_4Ge_2$. No polymeric materials were detected.

The distribution of these products is similar to that observed in the preparation of the $(Me_2Si)_n$ series in that the six-membered ring products are produced in greatest amount. Small amounts of eight-membered ring compounds are also detected in most samples.

It is expected that for many of the compounds represented in Fig.1, more than one isomer would be possible. Indeed, in the digermacyclohexasilane sample this was

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★A dodecamethyldigermacyclohexasilane isomer may have been synthesized earlier, but the sample was not obtained in pure form[9].

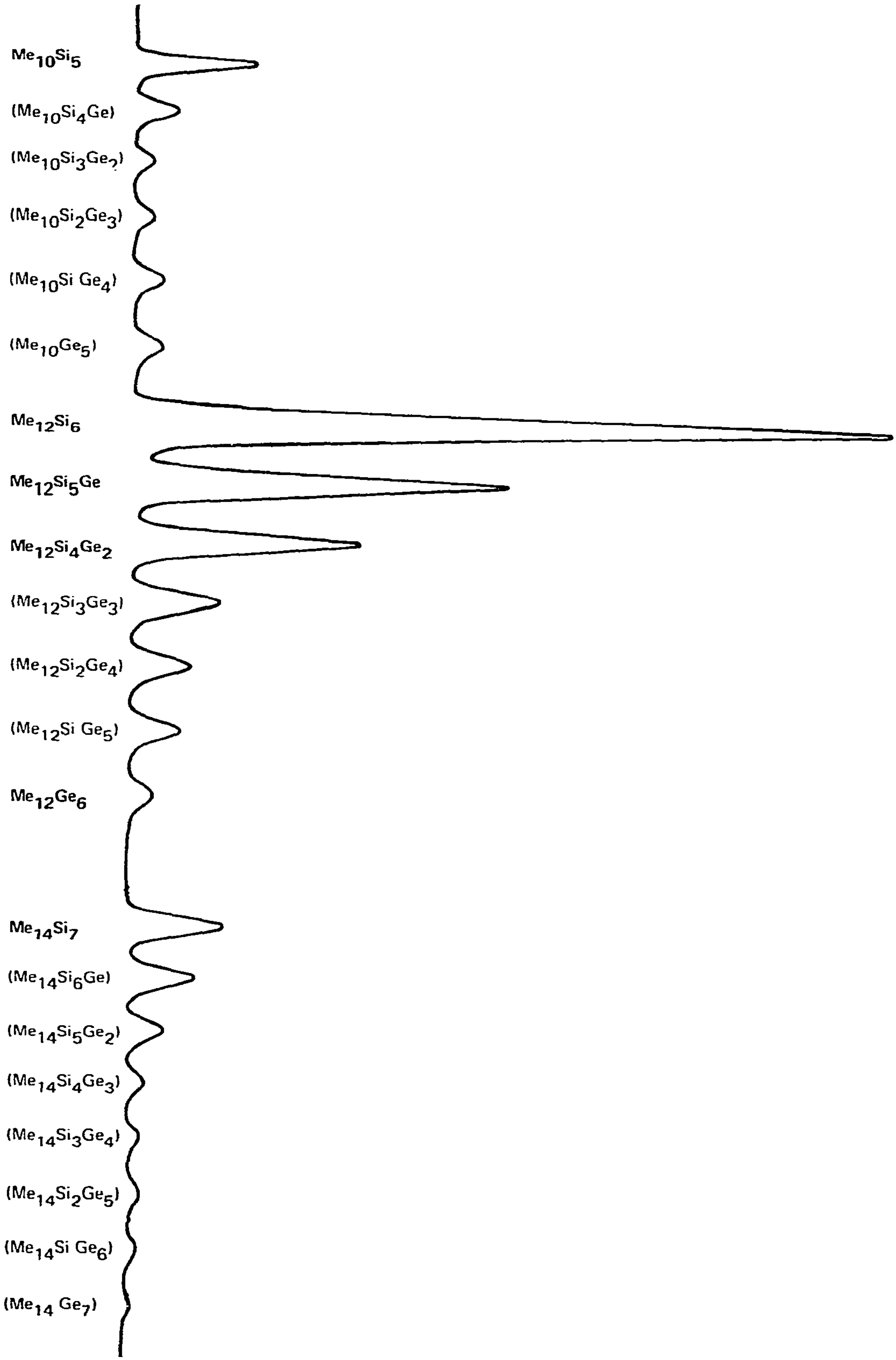
$Me_{10}Si_5$
$(Me_{10}Si_4Ge)$
$(Me_{10}Si_3Ge_2)$
$(Me_{10}Si_2Ge_3)$
$(Me_{10}Si\ Ge_4)$
$(Me_{10}Ge_5)$
$Me_{12}Si_6$
$Me_{12}Si_5Ge$
$Me_{12}Si_4Ge_2$
$(Me_{12}Si_3Ge_3)$
$(Me_{12}Si_2Ge_4)$
$(Me_{12}Si\ Ge_5)$
$Me_{12}Ge_6$
$Me_{14}Si_7$
$(Me_{14}Si_6Ge)$
$(Me_{14}Si_5Ge_2)$
$(Me_{14}Si_4Ge_3)$
$(Me_{14}Si_3Ge_4)$
$(Me_{14}Si_2Ge_5)$
$(Me_{14}Si\ Ge_6)$
$(Me_{14}\ Ge_7)$

TABLE 1

PROPERTIES OF THE GERMACYCLOPOLYSILANES

Compound	m.p. (°C)	Analysis found (caicd.) (%)[a]			mol. wt. found (caled.)
		C	H	Si	
$Me_{12}Si_5Ge$	216-220	36.56 (36.63)	9.02 (9.22)	35.80 (35.69)	394[b] (393.4)
1,4-$Me_{12}Si_4Ge_2$	249-251	32.69 (32.91)	7.99 (8.28)	25.91 (25.65)	438[b] (437.9)

[a] It has been reported[7] that routine carbon-hydrogen analyses of germanium-containing organic compounds may be low.

[b] Most intense parent peak from mass spectrum assigned to $Me_{12}{}^{28}Si_5{}^{74}Ge$ and $Me_{12}{}^{28}Si_4{}^{146}(Ge_2)$ respectively. Since several isomers exist in appreciable amounts for both silicon and germanium, complex groups of peaks are observed in the parent regions of the mass spectra. A computer program was designed and used to calculate the theoretical intensities of these peaks from a binominal combination of the basic isotopic abundances of carbon, silicon and germanium[10]. Results were found to be in excellent agreement with observed intensities.

substantiated by both proton nuclear magnetic resonance and infrared analysis. Attempts to separate isomers via gas chromatography were unsuccessful.

Preparation of the pure 1,4-digermacyclohexasilane isomer was effected by the reaction of 1,2-dichlorotetramethyldisilane and dimethyldichlorogermane with lithium dispersion under similar conditions. Workup after 30 minutes yielded 2–3% dodecamethyl-1,4-digermacyclohexasilane as the only cyclopolysilane. After extended reaction, however, all the compounds noted in Fig.1 as well as other digerma isomers were detected. This phenomenon is similar to the radical anion redistribution reported for the permethylated cyclopolysilanes[2].

Some properties of the new compounds are summerized in Table 1. The proton NMR (Table 2) and infrared spectra of these compounds have been examined and are consistent with the assigned structures.

In both cases final separation of the pure components from the reaction mixtures was accomplished by preparative gas chromatography of cyclohexane solutions of the cyclic compounds★. Likewise the compounds $Me_{10}Si_5$, $Me_{12}Ge_6$, and $Me_{14}Si_7$ were isolated in this way and characterized from spectroscopic and physical data.

★Good separations were obtained using a 3/8" x 20' column packed with 20% SE-30 silicone on chromosorb W and a helium flow rate of 150 cc/min.

Fig.1. Temperature programmed gas chromatographic trace showing typical distribution of reaction products. (The components which were isolated and identified are indicated by bold lettering; those which have not been fully characterized are tentatively assigned and indicated in parentheses. This gas chromatographic trace was obtained using a 1/8" x 6' column packed with 10% SE-30 silicone on chromosorb W, temperature programmed over the range 160–260°C at a rate of 4°/min using a helium flow rate of 30 cc/min).

TABLE 2

PROTON NMR DATA

Compound	ppm(δ)[a]	Relative intensity	Assignment
$Me_{12}Si_5Ge$	−0.214	1	Ge–CH_3
	−0.186	2	α(Si–CH_3)
	−0.137	2	β(Si–CH_3)
	−0.132	1	γ(Si–CH_3)
1,4-$Me_{12}Si_4Ge_2$	−0.220	1	Ge–CH_3
	−0.199	2	α(Si–CH_3)

[a] It became necessary to use a Varian HA-100 spectrometer to obtain the spectrum for $Me_{12}Si_5Ge$. All values are downfield from tetramethylsilane.

Evidence confirming our tentative structure assignments of the other new compounds in Fig.1 includes both infrared and gas chromatographic data. It was found that the compounds of each ring size are eluted in a regular sequence, at isothermal conditions, as expected for a homologous series, such that log t_R *vs.* molecular weight results in a straight line of characteristic slope for each series, where t_R is the retention time relative to that of the corresponding permethylcyclopolysilane. Also, the retention time of any of the compounds in Fig. 1 was found to be simply related★ to the number of silicon and germanium atoms according to the equation★★.

$$\ln t'_R\ (\mathrm{Me}_{2x+2y}\mathrm{Si}_x\mathrm{Ge}_y) = x - z + \frac{0.84y}{x+y}$$

where t'_R is the retention time of the compound relative to any of the permethylcyclopolysilanes, $Me_{2z}Si_z$.

Preliminary experiments indicate that analogous reactions involving dimethyldichlorostannane produce products having gas chromatographic traces showing a similar distribution of cyclic products.

Further characterization of the other compounds noted in these reactions is presently underway. A comprehensive spectroscopic study of these compounds and their anion radicals will be reported separately.

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★At isothermal conditions with oven temperature in the region of 200°C.

★★A somewhat similar equation has been used by Andrews and Phillips for the identification of linear silicon–germanium hydrides[8].

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