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Polygermoxanes Suitable For Biochemical Purposes. Part I. Digermoxanes (Low-viscosity Oils)

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In order to replace silicones in some of their biomedical applications, e.g. syringe lubrication, implants etc., a series of digermoxanes $(R^1R^2R^3Ge)_2O$ ($R = n-$alkyl, aryl) were synthesized. These compounds are thermally stable oils; their viscosities, depending on the nature of substituents, lie in the range 1–72 cPo (mPa s) at 20 °C.

Keywords: Polygermoxanes, applications, oils, viscosity

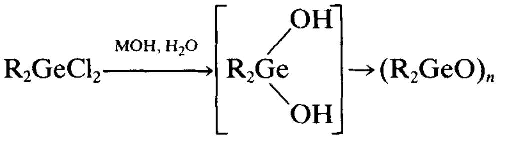
INTRODUCTION

Several types of silicones are widely used in a number of biochemical applications, such as oils for syringe lubrication and gel implants for aesthetic purposes.

During the last few years, however, some people complained of possible side-effects of silicones in the body, mainly due to their nonbiodegradability and possible accumulation; in some cases, silicones are thought to have caused auto-immune diseases.[1] All these problems, which result from the non-biodegradability of silicones lead to an interdiction, in some countries, on the use of silicone prostheses for breast reconstitution.

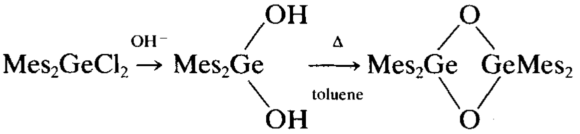
The homologous organogermanium compounds, organogermoxanes, being non-toxic[2–4] and supposedly biodegradable[5] [due to the weaker energy of the germanium–oxygen bond (361.2 kJ mol^{-1} compared with 466.2 kJ mol^{-1} for the silicon–oxygen bond bond)] might replace silicones in some of their biochemical applications. The germanium–carbon bond is also weaker than the silicon–carbon bond.

Several germanium analogues of silicones, $(R_2GeO)_n$, are described in the literature; they were prepared by base hydrolysis of the corresponding organogermanium dihalides, through unstable *gem*-(dihydroxy) intermediates (Scheme 1).



Scheme 1 Preparation of organogermoxanes ($n = 3$ and/or4; $R = CH_3$,[6–10] C_2H_5,[11–13] $n-C_3H_7$,[14,15] $i-C_3H_7$,[16–18] $n-C_4H_9$,[19,20] $t-C_4H_9$,[21,22] C_6H_5[23–26] etc.). $M = Na, K$.

However, when very bulky substituents on germanium are used, such as the mesityl (2,4,6-phenyl) group (Mes), the crystalline, stable, dihydroxydimesitylgermane (**1**) was isolated, leading to the stable dimesitylgermoxane dimer (**2**) by refluxing over molecular sieves for 5 h in toluene (Scheme 2).



1 m.p. 122 °C

2 m.p. 121 °C

Scheme 2

In the case of alkyl or phenyl groups, the germoxane is usually obtained as the trimer, the tetramer or a mixture of these two forms. However, unlike silicones, cyclic dialkylgermoxanes are not structurally stable; their structure changes in time, leading to higher-molecular-weight species. For instance, $[(CH_3)_2GeO]_4$ (m.p. 92 °C) becomes a higher

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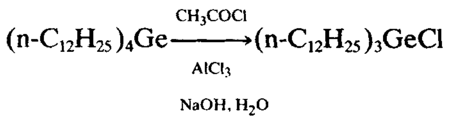


$$(n\text{-}C_{12}H_{25})_4Ge \xrightarrow[AlCl_3]{CH_3COCl} (n\text{-}C_{12}H_{25})_3GeCl \xrightarrow{NaOH,\ H_2O} [(n\text{-}C_{12}H_{25})_3Ge]_2O$$

Scheme 3

polymer $[(CH_3)_2GeO]_n$ (m.p. 133 °C) after several months.[10] Similarly, a pasty mixture of diethylgermoxanes $[(C_2H_5)_2GeO]_n$ ($n = 3, 4$; b.p. 145–155 °C/17 mmHg) solidifies after standing for some hours.[7] Therefore, due to the change of their physical properties, these compounds cannot be used for the envisaged purposes.

We therefore investigated other series of more stable germoxanes.

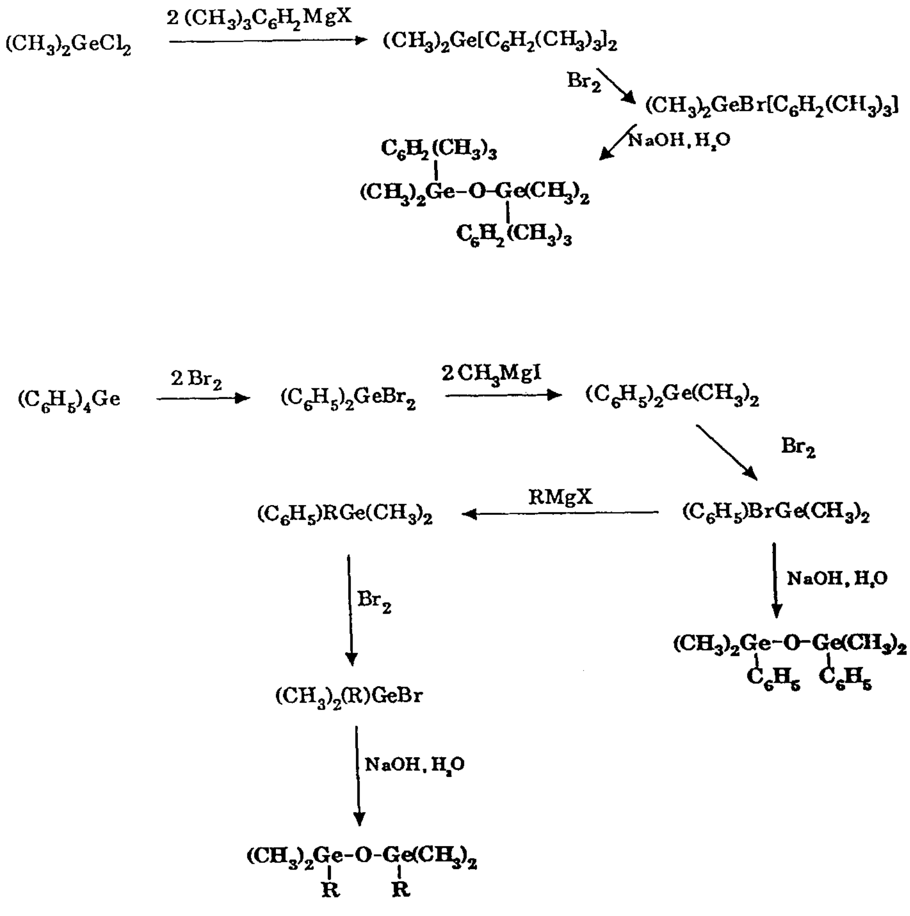
RESULTS AND DISCUSSION

This work describes the synthesis and the physical properties (especially the viscosity) of two families of digermoxanes $(R^1R^2R^3Ge)_2O$.

Synthesis

Symmetrical digermoxanes: $R^1 = R^2 = R^3 = CH_3$ (3),[7,8,27,28] C_2H_5 (4),[14,17,29,30] C_4H_9 (5),[18,30,31] $C_{12}H_{25}$ (29)

Compounds **3**, **4** and **5** were obtained by base hydrolysis of the corresponding alkylgermanium halides. Similarly, **29** was obtained in 86% yield by hydrolysis of tridodecylgermanium chloride



$R = n\text{-}C_3H_7,\ n\text{-}C_4H_9,\ n\text{-}C_5H_{11},\ n\text{-}C_6H_{13},\ n\text{-}C_8H_{17},\ n\text{-}C_{12}H_{25}.$

Scheme 4 Synthesis of mixed digermoxanes $[R(CH_3)_2Ge]_2O$.

Table 1 Densities and viscosities (cPo) of germoxanes $(R_3Ge)_2O$ at 20, 30, 40 and 50 °C

R	CH_3	C_2H_5	n-C_4H_9	n-$C_{12}H_{25}$
M	251.24	335.30	503.42	1175.90
d_4^{20}	1.220_4	1.155_5	1.017_0	0.950_7
d_4^{30}	1.205_4	1.147_6	1.009_5	0.942_0
d_4^{40}	1.190_0	1.136_3	0.999_5	0.935_7
d_4^{50}	1.179_8	1.127_2	0.992_3	0.928_4
η (20 °C)	1.0	2.4	7.5	40.6
η (30 °C)	1.0	2.0	5.5	28.5
η (40 °C)	1.0	1.9	4.5	19.5
η (50 °C)	1.0	1.8	3.7	14.5

resulting from the cleavage of tetradodecylgermane with acetyl chloride in the presence of aluminium chloride[32] (Scheme 3).

Mixed digermoxanes: $R^1 = R^2 = CH_3$; $R^3 =$ n-C_3H_7 (21), n-C_4H_9 (22), n-C_5H_{11} (23), n-C_6H_{13} (24), n-C_8H_{17} (25), n-$C_{12}H_{25}$ (26), C_6H_5 (27), $C_6H_2(CH_3)_3$ (28)

These digermoxanes, in which the germanium atom is bonded to two smaller groups and to a chain of increasing length, were investigated to estimate the influence of the shape of the molecule on its viscosity.

The starting organogermanes, alkyldimethylphenylgermanes $(C_6H_5)(CH_3)_2GeR$, were synthesized in four steps, viz.:

(1) cleavage of two phenyl groups of tetraphenylgermane by bromine in ethyl bromide (88% yield);

(2) alkylation by methylmagnesium iodide (91% yield);

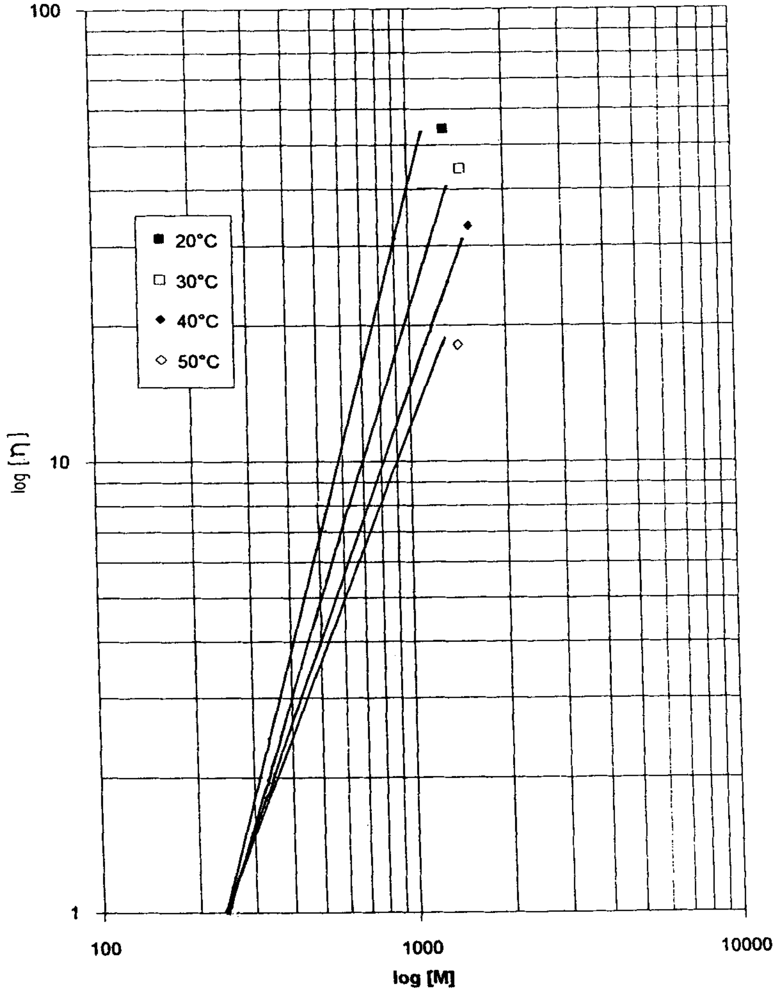


Figure 1 log $\eta = f(\log M)$ at 20, 30, 40 and 50 °C for the compounds $(R_3Ge)_2O$. The lines are drawn from the data listed in Table 1.

Table 2 Expression of the viscosity ($\eta = AM^B$; M = molecular mass; A, B = constants) for germoxanes $(R_3Ge)_2O$ at several temperatures

Temperature (°C)	A	B	η
20	7.58×10^{-6}	2.2	$7.58\times10^{-6}\,M^{2.2}$
30	5.50×10^{-6}	2.2	$5.50\times10^{-6}\,M^{2.2}$
40	6.50×10^{-5}	1.8	$6.50\times10^{-5}\,M^{1.8}$
50	6.44×10^{-5}	1.75	$6.44\times10^{-5}\,M^{1.75}$

(3) cleavage of one phenyl group by bromine[33] (86% yield);

(4) alkylation by an excess of a suitable Grignard reagent (56–78% yield).

Bis(dimethylmesitylgermyl) oxide was prepared similarly in two steps from dimethyldimesitylgermane in 60% overall yield.

These syntheses are illustrated in Scheme 4.

Viscosities

We used a falling-ball viscometer and cyclohexanol ($\eta = 68$ cPo at 20 °C[34]) as standard. The viscosities were calculated from Stokes' equation related to this kind of instrument.

$(R_3Ge)_2O$

Experimental results obtained for different temperatures (20, 30, 40 and 50 °C) (Table 1) show that the viscosities of these digermoxanes as a function of their molecular weight are given by Eqn [1] (Fig. 1):

$$\log \eta = \log A + B \log M \qquad [1]$$

The values of constants A and B, determined from the straight lines in Fig. 1, are given in Table 2.

$[R(CH_3)_2Ge]_2O$: R = alkyl chain

The values of the viscosities for these compounds are listed in Table 3. The variation of the viscosities as a function of the molecular weight is similar to that observed for $(R_3Ge)_2$. In this case, the values of constants A and B for different temperatures are given in Table 4.

The values of the viscosities for compounds **27** and **28** are listed in Table 5.

These experimental results show that, in a series of similar compounds, viscosity increases with the molecular mass (Fig. 1). However, a comparison between two different aliphatic series (symmetrical and mixed germoxanes) reveals that, for a given molecular mass, the viscosity of a digermoxane having a long aliphatic chain is higher than that of the corresponding symmetrical compound (Fig. 2).

Indeed, a structure of type **a** (linear) allows arrangements by superposition of molecular planes, which enhances the shear stress, while a structure of type **b** (branched), is less favourable to such arrangements (higher disorder). The lack of a series of distinct planes leads to a lower viscosity.

On the other hand, the introduction of aryl groups strongly increases the viscosity. This effect is still more pronounced with branched aryl substituents such as mesityl groups (Table 6).

Variation of η versus temperature

The variation of viscosity as a function of temperature is very marked for the more viscous germoxanes of each series (**5**, **29** and **25**, **26**). For these compounds Arrhenius' law was verified from the general equation (Eqn [2]):

$$\ln \eta = \ln A - B/T \qquad [2]$$

It is possible to draw experimental curves and

Table 3 Densities and viscosities (cPo) of germoxanes $[R(CH_3)_2Ge]_2O$ at 20, 30, 40 and 50 °C

R	CH_3	n-C_3H_7	n-C_4H_9	n-C_5H_{11}	n-C_6H_{13}	n-C_8H_{17}	n-$C_{12}H_{25}$
M	251.24	307.28	335.30	363.32	391.34	447.38	559.46
d_4^{20}	1.220_4	1.144_0	1.124_8	1.086_5	1.055_1	1.043_5	0.992_8
d_4^{30}	1.205_4	1.133_3	1.114_7	1.076_8	1.044_5	1.032_8	0.986_3
d_4^{40}	1.190_0	1.122_1	1.105_7	1.065_8	1.036_0	1.023_8	0.977_4
d_4^{50}	1.179_0	1.111_2	1.094_7	1.055_8	1.026_0	1.013_7	0.968_9
η (20 °C)	1.0	1.7	2.1_5	2.4	3.0	5.2	13.1
η (30 °C)	1.0	1.5	2.0	2.1_5	2.5_5	4.0	9.3
η (40 °C)	1.0	1.4_5	1.8	1.9	2.1_5	3.3	7.2
η (50 °C)	1.0	1.4_5	1.6	1.8	1.9_5	2.5	5.7_5

Table 4 Expression of the viscosity ($\eta = AM^B$; M = molecular mass; A, B = constants) for germoxanes $[R(CH_3)_2Ge]_2O$ at several temperatures

Temperature (°C)	A	B	η
20	6.02×10^{-8}	3.01	$6.02 \times 10\, M^{3.01}$
30	5.76×10^{-7}	2.60	$5.76 \times 10^{-7}\, M^{2.6}$
40	2.07×10^{-6}	2.35	$2.07 \times 10^{-6}\, M^{2.35}$
50	6.72×10^{-6}	2.12	$6.72 \times 10^{-6}\, M^{2.12}$

to determine A and B for each of these compounds (Table 7). It is possible that these compounds have a pseudo-Newtonian behaviour.

CONCLUSION

While cyclic germanium analogues of silicones, dialkylgermoxanes, are structurally unstable, hexa-alkyldigermoxanes are thermally stable oils; their viscosities depend on the nature of the substituents (molecular weight, shape of the molecule, number of aryl groups) and lie in the range 1–72 cPo (or mPa s) at 20 °C. Therefore, due to their probable non-toxicity and their apparent biodegradability, they have potential for use for biomedical purposes.

EXPERIMENTAL

Equipment

The ^{1}H NMR spectra were recorded at 80 MHz on a Brucker AC 80 (80, 131 MHz) instrument. The mass spectra were recorded (by electronic impact) on a Hewlett–Packard 5989 spectrometer (70 eV).

Syntheses

Dihydroxydimesitylgermane (**1**)

A solution of 1.4 g (3.66 mmol) of dichlorodimesitylgermane in benzene was shaken strongly for 15 min with a solution of sodium hydroxide (5 g) in 75 cm^3 of water; the organic layer was separated and dried over calcium chloride. After removal of the solvent, 1.05 g (3.04 mmol) of **1** was obtained. Yield 83%; m.p. 122 °C. Molecular weight (camphor): Found: 344; Calcd: 344.6. Mass spectrum: m/z (rel. intensity): 328 (26) $(M-H_2O)^+$; 312 (6) $(M-2OH)^+$. ^{1}H NMR (δ, $CDCl_3$): 1.84 (s, 2H); 2.28 (s, 6H); 2.45 (s, 12H); 6.83 (s, 4H). IR spectrum: large band between 3100 and 3500 cm^{-1}.

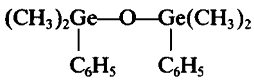
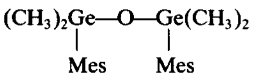
Tetramesityldigermoxane (**2**)

A solution of **1** (3.44 g, 10 mmol) in 8 cm^3 toluene was refluxed for three hours over molecular sieves. After removal of the solvent, 3.1 g (9.5 mmol) was obtained. Yield 95%; m.p. 121 °C. ^{1}H NMR (δ, $CDCl_3$): 2.22 (s, 6H); 2.35 (s, 12H); 6.71 (s, 4H). Mass spectrum: m/z (rel. intensity): 654 (5) $(M)^+$; 535 (12) $(M-\text{Mes})^+$; 328 (7) $(M-\text{Mes}_2\text{GeO})^+$.

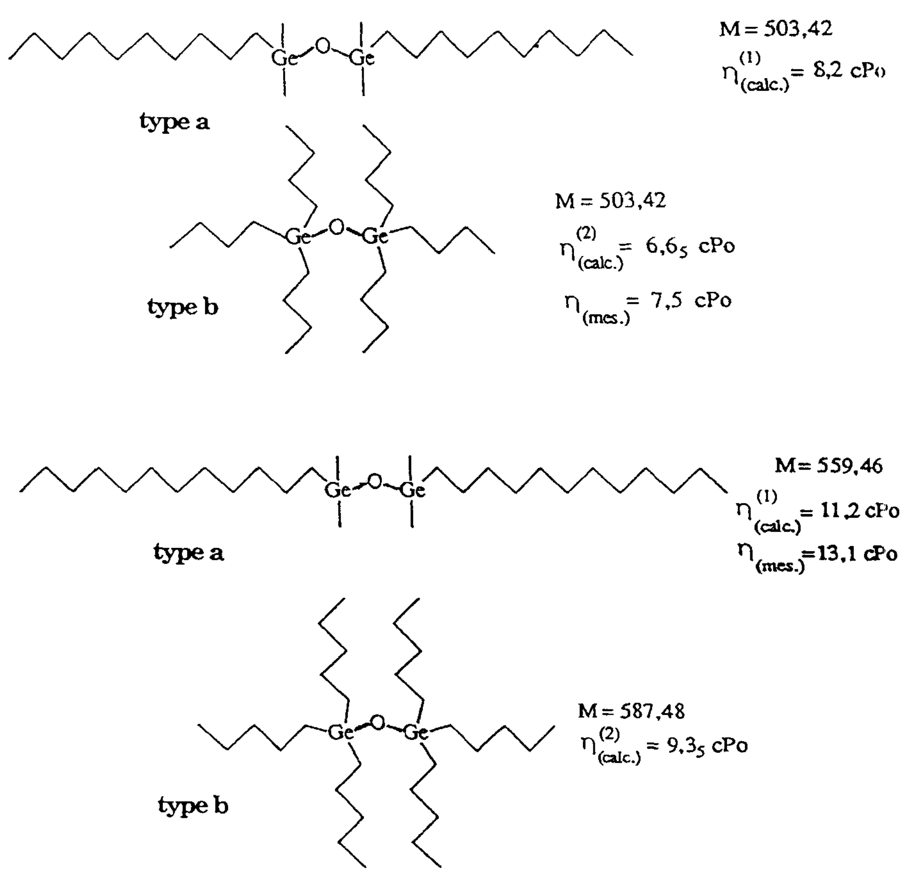
Tridodecylgermanium chloride (**6**)

To a mixture of tetradodecylgermane (7.48 g, 10 mmol) and aluminium chloride (1.33 g, 10 mmol) in a 150 cm^3 flask filled with argon, acetyl chloride (1.17 g, 15 mmol) was added dropwise under stirring at room temperature. The mixture was then heated at 60 °C for one hour

Table 5 Densities and viscosities (cPo) at 20, 30, 40 and 50 °C

	 $(CH_3)_2Ge(C_6H_5)-O-Ge(C_6H_5)(CH_3)_2$	 $(CH_3)_2Ge(\text{Mes})-O-Ge(\text{Mes})(CH_3)_2$
M	375.34	459.4
d_4^{20}	1.289_1	1.300_2[a]
d_4^{30}	1.278_0	1.294_1[a]
d_4^{40}	1.269_8	1.283_2
d_4^{50}	1.259_3	1.274_2
η (20 °C)	7.2_5	71.1[a]
η (30 °C)	5.3_0	39.2[a]
η (40 °C)	4.1_5	23.5
η (50 °C)	3.4	15.6

[a] In superfusion.



(1) Calculated from equation in table 2
(2) Calculated from equation in table 4

Figure 2 Other viscosities compared (at 20 °C): $\eta^{(1)}$ were calculated from the equation and constants in Table 2, and $\eta^{(2)}$ similarly from Table 4.

Table 6 Viscosities at 20 °C of compounds **5**, **27** and **28**

Compound	M	η (cPo)
$[(n\text{-}C_4H_9)_3Ge]_2O$	503.42	7.5
$[(CH_3)_2(C_6H_5)Ge]_2O$	375.34	7.2_5
$[(CH_3)_2(2,3,6\text{-}(CH_3)_3C_6H_2)Ge]_2O$	459.40	71.1

Table 7 $\eta = f(T)$ for compounds **5**, **29**, **25** and **26**

	η(cPo)
$[(n\text{-}C_4H_9)_3Ge]_2O$	$5.97 \times 10^{-3} \exp(-2075/T)$
$[(n\text{-}C_{12}H_{25})_3Ge]_2O$	$3.26 \times 10^{-3} \exp(-2747/T)$
$[n\text{-}C_8H_{17}(CH_3)_2Ge]_2O$	$1.49 \times 10^{-3} \exp(-2400/T)$
$[n\text{-}C_{12}H_{25}(CH_3)_2Ge]_2O$	$2.49 \times 10^{-3} \exp(-2500/T)$

and, after cooling, the organic layer was extracted with pentane. After removal of the solvent, distillation of the residue gave 5.10 g (8.3 mmol) of **6**. Yield 83%. $n_D^{20} = 1470_1$. Analysis: Found: Cl 5.96; Calcd: Cl 5.77%.

Dimethylphenylgermanium bromide (**7**)

A solution of bromine (13.58 g, 85 mmol) in 100 cm^3 of ethyl bromide was added dropwise, at 0 °C, to a solution of dimethyldiphenylgermane (21.83 g, 85 mmol) in 50 cm^3 of the same solvent. At the end of the reaction (24 h) the distillation of the mixture gave **7**. Yield 74%; b.p. 121 °C/ 23 mmHg. $n_D^{20} = 1.559_3$. ^{1}H NMR (δ, $CDCl_3$): 1.08 (s, 6H); 7.46 (m, 5H). Analysis: Found: C 36.96, H 4.19; Calcd: C 37.00, H 4.27%.

Bromodimethylmesitylgermane (**8**)
In a similar way, **8** was prepared by addition of bromine (7.04 g, 44 mmol) to 15 g (44 mmol) of dimethyldimesitylgermane. Yield 61%; b.p. 111 °C/0.2 mmHg. ^{1}H NMR (δ, $CDCl_3$): 1.21 (s, 6H); 2.24 (s, 3H); 2.51 (s, 6H); 6.86 (s, 2H).

Alkyldimethylphenylgermanes
n-Hexyldimethylphenylgermane (**12**)
Alkylation of **7** (11.05 g, 42.5 mmol) with an excess (0.1 mol) of n-hexylmagnesium bromide in diethyl ether gave, after the usual treatment, 8.11 g (30.6 mmol) of **12**. Yield 72%; b.p. 90 °C/0.5 mmHg. $n_D^{20} = 1.499_5$. ^{1}H NMR (δ, $CDCl_3$): 0.38 (s, 6H); 1.1 (m, 13H); 7.38 (m, 5H). Mass spectrum: m/z (rel. intensity); 251 (9) $(M - CH_3)^+$; 181 (100) $(M - C_6H_{13})^+$. Analysis: Found: C 63.80, H 9.53; Calcd: C 63.47, H 9.13%.

Similarly, the following were also obtained.

Dimethylphenyl-n-propylgermane (**9**)
Yield 78%; b.p. 104 °C/18 mmHg (lit.[35] 71 °C/5.5 mmHg). $n_D^{20} = 1.506_9$ (lit. [35]1.508_0). ^{1}H NMR (δ, $CDCl_3$): 0.523 (s, 6H); 1.25 (m, 7H); 7.53 (m, 5H). Mass spectrum: m/z (rel. intensity); 209 (5) $(M - CH_3)^+$; 181 (100) $(M - C_3H_7)^+$. Analysis: Found: C 59.44, H 8.41; Calcd: C 59.29, H 8.14%.

n-Butyldimethylphenylgermane (**10**)
Yield 75%; b.p. 114 °C/17 mmHg (lit.[35] 71 °C/1 mmHg). $n_D^{20} = 1.504_7$ (lit.[35] 1.504_3). ^{1}H NMR (δ, $CDCl_3$); 0.4 (s, 6H); 1.13 (m, 9H); 7.38 (m, 5H). Mass spectrum: m/z (rel. intensity); 223 (8) $(M - CH_3)^+$; 181 (100) $(M - C_4H_9)^+$. Analysis: Found: C 60.90, H 8.81; Calcd: C 60.84, H 8.51%.

Dimethyl-n-pentylphenylgermane (**11**)
Yield 71%; b.p. 130 °C/17 mmHg (lit.[35] 91.5 °C/5 mmHg). $n_D^{20} = 1.502_0$ (lit.[35] 1.501_5). ^{1}H NMR (δ, $CDCl_3$): 0.38 (s, 6H); 1.11 (m, 11H); 7.34 (m, 5H). Mass spectrum: m/z (rel. intensity); 237 (8) $(M - CH_3)^+$; 181 (100) $(M - C_5H_{11})^+$. Analysis: Found: C 62.20, H 8.92; Calcd: C 62.23, H 8.84%.

Dimethyl-n-octylphenylgermane (**13**)
Yield 68%; b.p. 123 °C/0.5 mmHg. $n_D^{20} = 1.496_0$. ^{1}H NMR (δ, $CDCl_3$): 0.38 (s, 6H); 1.10 (m, 17H); 7.36 (m, 5H). Mass spectrum: m/z (rel. intensity); 279 (5) $(M - CH_3)^+$; 181 (100) $(M - C_8H_{17})^+$.

n-Dodecyldimethylphenylgermane (**14**)
Yield 56%; b.p. 141 °C/0.1 mmHg. $n_D^{20} = 1.491_2$. ^{1}H NMR (δ, $CDCl_3$): 0.37 (s, 6H); 0.9 (m); 1.27 (m); 7.36 (m, 5H). Mass spectrum: m/z (rel. intensity); 335 $(M - CH_3)^+$; 181 $(M - C_{12}H_{25})^+$.

n-Alkyldimethylgermanium bromides
n-Hexyldimethylgermanium bromide (**18**)
Dropwise addition of bromine (4.82 g, 30.2 mmol) to 8.0 g (30.2 mmol) of **12** in ethyl bromide at 0 °C gave, after the usual treatment, 5.49 g (20.5 mmol) of **18**. Yield 68%, b.p. 58 °C/0.3 mmHg. $n_D^{20} = 1.472_5$. ^{1}H NMR (δ, $CDCl_3$): 0.87 (s, 6H); 1.31 (m, 13H). Analysis: Found: C 35.91, H 7.44; Calcd: C 35.77, H 7.44%.

Compounds **15–17**, **19** and **20** were prepared in a similar way. In the case of **15–17**, which have short chains (C_2 to C_5), separation by distillation of the bromide and the bromobenzene resulting from the cleavage is more difficult; it is easier to treat the mixture with an excess of sodium hydroxide, which converts the bromide into a high-boiling-point oxide, easily separable from unchanged bromobenzene. The germoxane can then be transformed into the corresponding bromide by treatment with a large excess of hot hydrobromic acid. Yields of **15–17** are therefore not reported.

Dimethyl-n-propylgermanium bromide (**15**)
Yield not determined; b.p. 62 °C/59 mmHg. $n_D^{20} = 1.473_7$. ^{1}H NMR (δ, $CDCl_3$): 0.78 (s, 6H); 1.12 (m, 7H). Analysis: Found: C 26.61, H 6.04; Calcd: C 26.01, H 5.08%.

n-butyldimethylgermanium bromide (**16**)
Yield not determined; b.p. 61 °C/17 mmHg. $n_D^{20} = 1.474_2$. ^{1}H NMR (δ, $CDCl_3$): 0.79 (s, 6H); 1.15 (m, 9H). Analysis: Found: C 30.24, H 6.49; Calcd: C 30.06, H 6.30%.

Dimethyl-n-pentylgermanium bromide (**17**)
Yield not determined; b.p. 88 °C/17 mmHg. $n_D^{20} = 1.475_2$. ^{1}H NMR (δ, $CDCl_3$): 0.79 (s, 6H); 1.15 (m, 11H). Analysis: Found: C 33.71, H 6.95; Calcd: C 33.13, H 6.75%.

Dimethyl-n-octylgermanium bromide (**19**)
Yield 62%; b.p. 151 °C/0.5 mmHg. $n_D^{20} = 1.470_9$. ^{1}H NMR (δ, $CDCl_3$): 0.78 (s, 6H); 1.11 (m, 17H). Analysis: Found: C 41.88, H 8.06; Calcd: C 40.61, H 7.84%.

n-Dodecyldimethylgermanium bromide (**20**)
This compound was not isolated and was directly converted into the corresponding oxide.

Germoxanes

Bis(n-hexyldimethylgermyl) oxide (**24**)
5.49 g (20.5 mmol) of **18** was shaken strongly for 15 min with a concentrated solution of sodium hydroxide (8 g in 50 cm^3 water). The resulting oxide was extracted with pentane and the solution dried on sodium sulphate. Distillation gave 3.32 g (17 mmol) of the expected germoxane. Yield 83%; b.p. 115 °C/0.3 mmHg. $n_D^{20} = 1.454_5$. ^{1}H NMR (δ, $CDCl_3$): 0.28 (s, 12H); 1.1 (m, 26H). Mass spectrum: m/z (rel. intensity); 392 (2) $(M)^+$; 377 (6) $(M-CH_3)^+$; 307 (43) $(M-C_6H_{13})^+$. Analysis: Found: C 49.07, H 9.82; Calcd: C 49.06, H 9.78%.

The following compounds were prepared in a similar way.

Bis(dimethyl-n-propylgermyl) oxide (**21**)
Yield 81%; b.p. 55 °C/0.7 mmHg. $n_D^{20} = 1.446_6$. ^{1}H NMR (δ, $CDCl_3$): 0.30 (s, 12H); 1.15 (m, 14H). Mass spectrum: m/z (rel. intensity): 293 (5) $(M-CH_3)^+$; 265 (47) $(M-C_3H_7)^+$. Analysis: Found: C 39.25, H 8.50; Calcd: C 39.89, H 8.24%.

Bis(n-butyldimethylgermyl) oxide (**22**)
Yield 76% b.p. 110 °C/25 mmHg. $n_D^{20} = 1.499_5$. ^{1}H NMR (δ, $CDCl_3$): 0.28 (s, 12H); 1.10 (m, 18H). Mass spectrum: m/z (rel. intensity); 336 (2) $(M)^+$; 321 (5) $(M-CH_3)^+$; 279 (45) $(M-C_4H_9)^+$. Analysis: Found: C 42.57, H 9.29; Calcd: C 42.95, H 9.01%.

Bis(dimethyl-n-pentylgermyl) oxide (**23**)
Yield 77%; b.p. 99 °C/0.3 mmHg. $n_D^{20} = 1.451_5$. ^{1}H NMR (δ, $CDCl_3$): 0.28 (s, 12H); 1.07 (m, 22H). Mass spectrum: m/z (rel. intensity): 364 (1) $(M)^+$; 349 (6) $(M-CH_3)^+$; 293 (48) $(M-C_5H_{11})^+$. Analysis: Found: C 46.15, H 9.80; Calcd: C 46.24, H 9.42%.

Bis(dimethyl-n-octylgermyl) oxide (**25**)
Yield 69%; b.p. 133 °C/0.1 mmHg. $n_D^{20} = 1.459_5$. ^{1}H NMR (δ, $CDCl_3$): 0.29 (s, 12H); 1.05 (m, 34H). Mass spectrum: m/z (rel. intensity): 448 (2) $(M)^+$; 433 (8) $(M-CH_3)^+$; 335 (52) $(M-C_8H_{17})^+$. Analysis: Found: C 56.21, H 10.47; Calcd: C 57.77, H 11.15%.

Bis(n-dodecyldimethylgermyl) oxide (**26**)
Yield 58%; b.p. 205 °C/0.2 mmHg. $n_D^{20} = 1.465_0$. ^{1}H NMR (δ, $CDCl_3$): 0.29 (s, 12H); 1.05 (m, 50H). Mass spectrum: m/z (rel. intensity): 545 (8) $(M-CH_3)^+$; 391 (49) $(M-C_{12}H_{25})^+$.

Bis(dimethylphenylgermyl) oxide (**27**)
Yield 62%; b.p. 136 °C/0.7 mmHg. $n_D^{20} = 1.547_8$. ^{1}H NMR (δ, $CDCl_3$): 0.53 (s, 12H); 7.39 (m, 10H).

Bis(dimethylmesitylgermyl) oxide (**28**)
Yield 53%; b.p. 170 °C/0.2 mmHg; m.p. 31 °C. $n_D^{20} = 1.559_8$. ^{1}H NMR (δ, $CDCl_3$): 0.6 (s, 12H); 2.26 (s, 6H); 2.40 (s, 12H); 6.80 (s, 4H).

Bis(tridodecylgermyl) oxide (**29**)
Yield 86%; not distilled. $n_D^{20} = 1.471_2$. ^{1}H NMR (δ, $CDCl_3$): 0.87 (m); 1.26 (large s). Analysis: Found: C 74.01, H 12.17; Calcd: 73.46, 12.84%.

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