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# Polygermoxanes Suitable for Biochemical Purposes: II Linear Trigermoxanes (High-viscosity Oils)

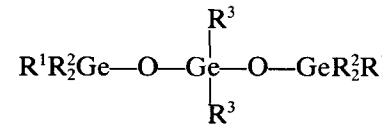
Gilles Duverneuil,* Pierre Mazerolles*† and Elisabeth Perrier‡
* Laboratoire des Organométalliques, URA CNRS 477, Université Paul-Sabatier, 118 route de Narbonne, 31 062 Toulouse Cedex, France, and ‡ Métaleurop-Recherche, 1 avenue Albert Einstein, BP 120, 78 193 Trappes Cedex, France

**Linear trigermoxanes, $R^1R^2_2GeOGe(R^3)_2OGeR^2_2R^1$, a new series of organogermanium compounds, were synthesized by reaction of a lithium organogermanolate with a suitable organogermanium dihalide. With alkyl or phenyl substituents, these trigermoxanes are structurally unstable viscous oils, due to redistribution reactions. When $R^3$ substituents are bulky groups, such as mesityl, trigermoxanes are thermally and structurally stable oils; depending on the $R^1$ and $R^2$ substituents their viscosities lie in the range 240 to more than 1500 cPo (mPa s) at 20 °C. When both terminal germanium atoms are substituted with two mesityl groups, trigermoxanes are stable glassy solids.**

**Keywords: trigermoxanes; lithium organogermanolates; bulky groups; viscosity**

## INTRODUCTION

Digermoxanes $(R^1R^2R^3Ge)_2O$ ($R^1$, $R^2$, $R^3$ = n-alkyl) are thermally stable oils. Depending on the nature of the substituents, their viscosity varies in the range 1 cPo ($R^1 = R^2 = R^3 = CH_3$) to 45 cPo ($R^1 = R^2 = R^3 = n\text{-}C_{12}H_{25}$); the introduction of aryl substituents increases the viscosity (71 cPo at 20 °C for $[2,4,6\text{-}(CH_3)_3C_6H_2](CH_3)_2Ge]_2O$).[1] In order to obtain more viscous oils, to extend the range of products suitable for biomedical applications, we investigated the synthesis of a series of linear trigermoxanes,

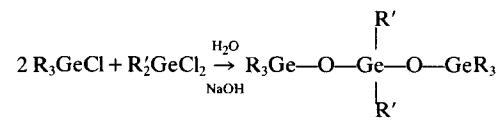


their structural stability and their viscosities at different temperatures.

## RESULTS AND DISCUSSION

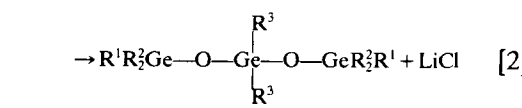
### Synthesis

The more direct route to these trigermoxanes could be the co-hydrolysis of a mixture of 2 mol of a trialkylgermanium monohalide and 1 mol of a dialkylgermanium dihalide [Eqn [1]]



[1]

but in this reaction, side products such as $(R_3Ge)_2O$ and $(R'_2GeO)_n$ (n = 3, 4), difficult to remove from the trigermoxane, are also formed, and contaminate the desired product. For this reason, we investigated a more specific synthesis involving the reaction of two equivalents of a lithium organogermanolate with a dialkylgermanium dihalide (Eqn [2]):



[2]

Lithium organogermanolates are obtained by cleavage of the Ge–O bonds of a cyclogermoxane with an organolithium compound (Eqn [3]):[2,3]

$$n\,R^1Li + (R^2_2GeO)_n \rightarrow n\,R^1R^2_2GeOLi (n = 3 \text{ or } 4) \quad [3]$$

† Author to whom correspondence should be addressed.

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A series of trigermoxanes were prepared, viz;

$R^1 = R^2 = CH_3$; $R^3 = C_2H_5$ (**1**), i-$C_3H_7$ (**2**), $C_6H_5$ (**3**)

$R^1 = R^2 = C_6H_5$; $R^3 = CH_3$ (**5**), $C_2H_5$ (**6**)

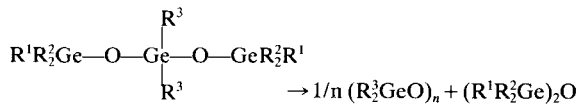
$R^1 = R^3 = CH_3$; $R^2 = C_6H_5$ (**7**)

$R^1 = R^2 = C_6H_5$; $R^2 = CH_3$ (**8**)

$R^1$ = n-$C_4H_9$; $R^2 = C_6H_5$; $R^3 = CH_3$ (**9**)

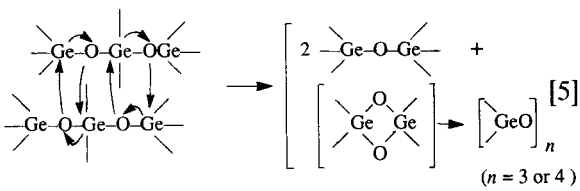
Compound **4** is 1,1-bis(trimethylgermyloxy)-3-methyl-1-germacyclopent-3-ene. Compounds **5** and **6** are crystalline solids and therefore are not suitable for the application being considered. Compounds **7** and **9** could not be purified because they partially decompose by distillation and also by liquid chromatography on silica.

On the other hand, thermally stable compounds **1**, **2**, **3**, **4** and **8** could be purified by distillation under low pressure. Unfortunately, these trigermoxanes are viscous oils and are structurally unstable: slow redistribution reactions take place and lead to the formation of polydialkylgermoxanes and bis(trialkyl)digermoxanes (Eqn [4]):




[4]

These redistribution reactions may be explained by an intermolecular four-centred concerted mechanism (Eqn [5]):




[5]

In order to suppress these undesirable reactions, by restricting the approach of germanium–oxygen bonds by neighbouring molecules, we used bulky groups (2,4,6-trimethylphenyl-, i.e. mesityl) for $R^3$ substituents. These groups have the supplementary advantage of increasing markedly the viscosity of the molecule. The following trigermoxanes of this type were synthesized:

$R^3 = C_6H_2(CH_3)_3$; $R^1 = R^2 = CH_3$ (**10**)

$R^1 = C_2H_5$; $R^2 = CH_3$ (**11**)

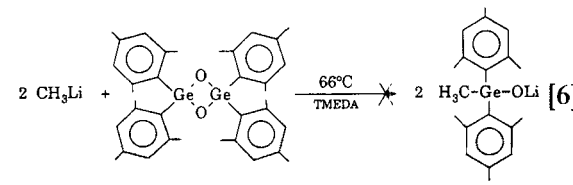
$R^1 = CH_3$; $R^2 = C_2H_5$ (**12**)

$R^1$ = n-$C_4H_9$; $R^2 = CH_3$ (**13**)

$R^1 = R^2 = C_2H_5$ (**14**)

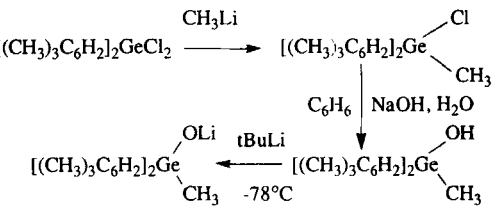
These trigermoxanes are thermally stable (up to 300 °C), distillable, viscous oils. Due to the protection of Ge–O bonds with mesityl groups, the compounds are structurally stable and no change was observed in their NMR spectra after prolonged heating at 100 °C.

In order to obtain a series of compounds having a markedly higher viscosity we synthesized trigermoxanes in which the terminal germanium atoms were substituted with two mesityl groups. Our attempts to prepare methyl(dimesityl)germanolates by reaction of methyl-lithium with the cyclic digermoxane were unsuccessful; no reaction was observed, even in refluxing tetrahydrofuran in the presence of tetramethylethylene diamine (Eqn [6]):




[6]

but the desired lithiumgermanolate was obtained by using the reactions shown in Scheme 1.




**Scheme 1**

Three new trigermoxanes of this type (**18**, **19** and **20**) were synthesized by reaction of this lithium germanolate with the suitable dialkylgermanium dihalides $R^3_2GeCl_2$:

$R^1 = CH_3$; $R^2 = (CH_3)_3C_6H_2$; $R^3 = CH_3$ (**18**), $C_2H_5$ (**19**), n-$C_4H_9$ (**20**)

These trigermoxanes, purified by liquid chromatography on silica (eluent pentane–THF) are stable, glassy solids at room temperature.

## Viscosity

Viscosities were determined with a falling-ball viscometer, silicon oil (Fluka DC 200, 1070 mPa s) being used as standard; they were calculated from Stokes's equation. The viscosity

**Table 1** Densities and viscosities (cPo) of compounds **11**, **12**, **13** and **14**

| | **11** | **12** | **13** | **14** |
|---|---|---|---|---|
| $M$ | 606.40 | 634.46 | 662.51 | 662.51 |
| $d_4^{20}$ | $1.225_2$ | $1.230_1$ | $1.191_5$ | $1.209_6$ |
| $d_4^{30}$ | $1.215_3$ | $1.221_0$ | $1.183_3$ | $1.202_5$ |
| $d_4^{40}$ | $1.206_3$ | $1.212_3$ | $1.174_6$ | $1.191_5$ |
| $d_4^{50}$ | $1.196_8$ | $1.203_5$ | $1.166_5$ | $1.184_6$ |
| $\eta$(20 °C) | 672 | 770 | 244 | 1515 |
| $\eta$(30 °C) | 332 | 385 | 115 | 555 |
| $\eta$(40 °C) | 152 | 179 | 63 | 313 |
| $\eta$(50 °C) | 79 | 94 | 38 | 157 |

values for compounds **11**, **12**, **13** and **14** are listed in Table 1.

Figure 1 shows the variation of the viscosity of these compounds as a function of the temperature, in agreement with Arrhenius law. The constants $A$ and $B$ (Table 2) were determined from experimental straight lines.

## CONCLUSION

Linear trigermoxanes are obtained by reaction of a lithium germanolate with an organogermanium dihalide; with alkyl or phenyl substituents, the trigermoxanes are structurally unstable due to redistribution reactions. When the central germanium atom is substituted with bulky groups (such as mesityl) the germanium–oxygen bonds are protected and the resulting trigermoxanes are thermally and structurally stable; depending on the nature of other substituents, the viscosity of these oils lies in the range 240 to more than 1500 cPo at 20 °C. On the other hand, when the first and the third germanium atoms are both substituted with two mesityl groups, the resulting trigermoxanes are stable glassy solids.

## EXPERIMENTAL

### Equipment:

$^1$H NMR spectra were recorded on a Brucker AC 80 (80, 131 MHz) instrument. $^{13}$C NMR spectra were recorded on a Brucker AC 250 instrument. Mass spectra were recorded, by electron impact, on a Hewlett–Packard 5989 spectrometer and by chemical ionisation (methane) on a Nermag R10-10 spectrometer.

### Syntheses

**Lithium trimethylgermanolate**

To a solution of 2 g (4 mmol) of octamethylcyclotetragermoxane in 30 ml of anhydrous diethyl

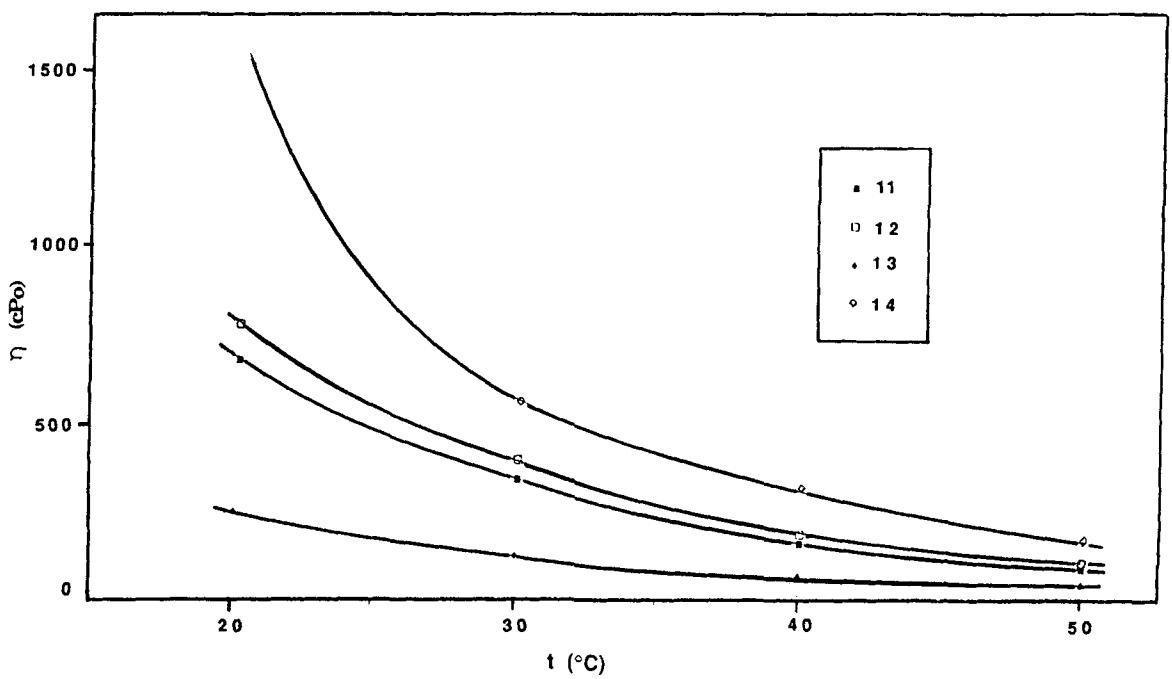



**Figure 1** Variation of viscosity of compound **11**, **12**, **13** and **14** with temperature.

**Table 2** Expression of Arrhenius' function for the compounds **11**, **12**, **13** and **14**

| Compound | Arrhenius' function $\eta = A\,e^{-B/T}$ |
|---|---|
| **11** | $\eta = 6.29 \times 10^{-8}\, e^{6757/T}$ |
| **12** | $\eta = 1.11 \times 10^{-7}\, e^{6650/T}$ |
| **13** | $\eta = 4.92 \times 10^{-7}\, e^{5833/T}$ |
| **14** | $\eta = 1.40 \times 10^{-7}\, e^{6730/T}$ |

ether are added, at 0 °C, under stirring, 10 ml of an ethereal 1.6 M solution of methyl-lithium. The mixture is then refluxed for 45 min.

**3,3-Diethyl-**
**1,1,1,5,5,5-hexamethyltrigermoxane (1)**
A solution of 1.61 g (8 mmol) of diethylgermanium dichloride in 25 ml THF is added dropwise at 20 °C under stirring to the above lithium trimethylgermanolate solution and then refluxed. The development of the reaction is checked by NMR; at the end of the reaction the mixture is cooled, the solvent is removed and the residue distilled under reduced pressure giving 1.91 g (4.8 mmol, 60% yield) of trigermoxane **1**. B.p. 45 °C/1 mm Hg. $n_D^{20} = 1.447_0$. $^1$H NMR (80 MHz, $CDCl_3$, $\delta$ ppm): 0.34 (s, 18H); 0.97 (m, 10H). Analysis: Calcd: C, 30.18; H, 7.04. Found: C, 30.20; H, 7.36%.

**1,1,1,5,5,5-Hexamethyl-**
**3,3-di-isopropyltrigermoxane (2)**
From the reaction of lithium trimethylgermanolate with di-isopropylgermanium dichloride (61% yield). B.p. 72 °C/0.2 mm Hg. $n_D^{20} = 1.452_0$. $^1$H NMR (80 MHz, $CDCl_3$, $\delta$ ppm): 0.33 (s, 18H); 1.11 (m, 14H).

**1,1,1,5,5,5-Hexamethyl-**
**3,3-diphenyltrigermoxane (3)**
From the reaction of lithium trimethylgermanolate with diphenylgermanium dichloride (52% yield). B.p. 108 °C/0.7 mm Hg. $n_D^{20} = 1.528_g$. $^1$H NMR (80 MHz, $CDCl_3$, $\delta$ ppm): 0.36 (s, 18H); 7.55 (m, 10H). Analysis: Calcd: C, 43.74; H, 5.71 Found: C, 43.81; H 5.72%.

**1,1-Bis(trimethylgermyloxy)-3-methyl-**
**1-germacyclopent-3-ene (4)**
From the reaction of lithium trimethylgermanolate with 1,1-di-iodo-1-germa-3-methylcyclopent-3-ene (53% yield). B.p. 82–84 °C/2.2 mm Hg. $n_D^{20} = 1.471_0$. $^1$H NMR (80 MHz, $CDCl_3$, $\delta$ ppm): 0.36 (s, 18H); 1.55 (m, 7H); 5.65 (m, 1H). Analysis: Calcd: C, 32.37; H, 6.42; Found: C, 32.39; H, 6.48%.

**3,3-Dimethyl-**
**1,1,1,5,5,5,-hexaphenyltrigermoxane (5)**
From the reaction of lithium triphenylgermanolate with dimethylgermanium dichloride (73% yield). M.p. 137 °C. $^1$H NMR (80 MHz, $CDCl_3$, $\delta$ ppm): 0.11 (s, 6H); 7.40 (m, 30H).

**3,3-Diethyl-**
**1,1,1,5,5,5-hexaphenyltrigermoxane (6)**
From the reaction of lithium triphenylgermanolate with diethylgermanium dichloride (68% yield). M.p. 92–94 °C. $^1$H NMR (80 MHz, $CDCl_3$, $\delta$ ppm): 0.88 (m, 10H); 7.45 (m, 30H).

**1,3,3,5-Tetramethyl-**
**1,1,5,5-tetraphenyltrigermoxane (7)**
From the reaction of lithium methyldiphenylgermanolate with dimethylgermanium dichloride (80% yield). $^1$H NMR (80 MHz, $CDCl_3$, $\delta$ ppm): 0.25 (s, 6H); 0.81 (s, 6H); 7.45 (m, 20H).

**1,1,5,5-Tetramethyl-**
**1,3,3,5-tetraphenyldigermoxane (8)**
From the reaction of lithium dimethylphenylgermanolate with diphenylgermanium dichloride (41% yield). B.p.: 87–90 °C/0.1 mm Hg. $n_D^{20} = 1.573_0$. $^1$H NMR (80 MHz, $CDCl_3$, $\delta$ ppm): 0.77 (s, 12H); 7.48 (m, 20H).

**1,5-Di-n-butyl-3,3-dimethyl-**
**1,1,5,5-tetraphenyltrigermoxane (9)**
From the reaction of lithium n-butyldiphenylgermanolate with dimethylgermanium dichloride (70% yield). $^1$H NMR (80 MHz, $CDCl_3$ $\delta$ ppm): 0.61 (s, 6H); 1.28 (m, 18H); 7.51 (m, 20H).

**1,1,1,5,5,5-Hexamethyl-**
**3,3-dimesityltrigermoxane (10)**
From the reaction of lithium trimethylgermanolate with dimesitylgermanium dichloride (62.5% yield). B.p. 135 °C/0.1 mm Hg; m.p. 84–86 °C. $^1$H NMR (80 MHz, $CDCl_3$, $\delta$ ppm): 0.22 (s, 18H); 2.23 (s, 6H); 2.45 (s, 12H); 6.45 (s, 4H). Mass spectrum (70 eV), (*m/z* relat. int.): 578 (2) $(M^+)$; 53 (3) $(M-CH_3)^+$; 444 (25) $(M-CH_3, C_6H_2CH_3)_3)^+$.

**1,5-Diethyl-1,1,5,5-tetramethyl-**
**3,3-dimesityltrigermoxane (11)**
From the reaction of lithium ethyldimethylgerma-

nolate with dimesitylgermanium dichloride (53% yield). B.p. 160–165 °C/0.1 mm Hg. $n_D^{20} = 1.537_8$. $^1$H NMR (80 MHz, $CDCl_3$, $\delta$ ppm): 0.17 (s, 12H); 0.98 (m, 10H); 2.24 (s, 6H); 2.44 (s, 12H); 6.74 (s, 4H). Mass spectrum (70 eV) (*m/z* relat int.): 606 (1) $(M^+)$; 591 (2) $(M-CH_3)^+$; 577 (8) $(M-C_2H_5)^+$; 458 (36) $(M-C_2H_5, C_6H_2(CH_3)_3)^+$. Analysis: Calcd: C, 51.49; H, 7.31. Found: C, 52.91; H, 7.43%.

**1,1,5,5-Tetraethyl-1,5-dimethyl-3,3-dimesityltrigermoxane (12)**

Froom the reaction of lithium diethylmethylgermanolate with dimesitylgermanium dichloride (62%). B.p. 180–183 °C/0.1 mm Hg. $n_D^{20} = 1.539_0$. $^1$H NMR (80 MHz, $CDCl_3$, $\delta$ ppm): 0.09 (s, 6H) 0.88 (m, 20H); 2.21 (s, 6H); 2.42 (s, 12H); 6.72 (s, 4H). $^{13}$C NMR (JMOD, 50 MHz, $CDCl_3$, $\delta$ ppm): −2.04 ($CH_3Ge$); 8.03 ($\underline{C}H_3CH_2$); 10.51 ($CH_2$); 21.13 ($p$-$CH_3$); 23.03 ($o$-$CH_3$); 129.01 (=CH); 136.75 ($C_{1q}$); 138.50 ($C_{4q}$); 143.15 ($C_{2q}$). Mass spectrum (70 eV (*m/z* relat.int.): 634 (4) $(M^+)$; 619 (8) $(M-CH_3)^+$; 605 (100) $(M-C_2H_5)^+$. Analysis: Calcd: C, 53.00; H, 7.62. Found: C, 52.99; H 7.34%.

**1,5-Di-n-butyl-1,1,5,5-tetramethyl-3,3-dimesityltrigermoxane (13)**

From the reaction of lithium n-butyldimethylgermanolate with dimesitylgermanium dichloride (58% yield). B.p. 188–192 °C/0.1 mm Hg. $n_D^{20} = 1.528_8$. $^1$H NMR (80 MHz, $CDCl_3$, $\delta$ ppm): 0.18 (s, 12H); 1.08 (m, 18H); 2.24 (s, 6H); 2.44 (s, 12H); 6.74 (s, 4H). Mass spectrum (70 eV) *m/z* relat. int.): 662 (1) $(M^+$; 647 (2) $(M-CH_3)^+$; 605 (7) $(M-n\text{-}C_4H_9)^+$; 486 (10) $(M-n\text{-}C_4H_9, C_6H_2(CH_3)_3)^+$. Analysis: Calcd: C, 54.39; H, 7.91. Found: C, 54.97; H 7.89%.

**1,1,1,5,5,5-Hexaethyl-3-3-dimesityltrigermoxane (14)**

From the reaction of lithium triethylgermanolate with dimethylgermanium dichloride (54% yield). B.p. 185–189 °C/0.05 mm Hg. $n_D^{20} = 1.542_3$. $^1$H NMR (80 MHz, $CDCl_3$, $\delta$ ppm): 1.02 (m, 30H); 2.09 (s, 6H); 2.66 (s, 12H); 6.75 (s, 4H). Analysis; Calcd: C, 54.39; H, 7.91. Found: C, 55.03; H, 7.85%.

**Dimesitylmethylgermanium dichloride (15)**

A portion of 3.8 ml of 1.6 M etheral solution of methyl-lithium is slowly added to a solution of 2.46 g (6.46 mmol) of dimethylgermanium dichloride in 100 ml anhydrous diethyl ether. The mixture is stirred for 1 h at 20 °C and then centrifuged. After removal of the solvent, 2.01 g (5.56 mmol) of the chloride **15** are obtained (86% yield). $^1$H NMR (80 MHz, $CDCl_3$, $\delta$ ppm): 1.31 (s, 3H); 2.25 (s, 6H); 2.37 (s, 12H); 6.82 (s, 4H).

**Hydroxymethyldimesitylgermane (16)**

A concentrated benzene solution of 1.65 g (4.6 mmol) of **15** is shaken with a solution of 7 g of sodium hydroxide in 80 ml water. The organic phase is decanted and dried over sodium sulphate. After removal of the solvent, 1.4 g (4.08 mmol) of **16** are obtained (89.2% yield). $^1$H NMR (80 MHz, $CDCl_3$, $\delta$ ppm): 1.01 (s, 3H); 2.26 (s, 6H); 2.37 (s, 12H); 6.82 (s, 4H).

**Lithium methyldimesitylgermanolate (17)**

Under an argon atmosphere, 1.74 ml of 1.7 M hexane solution of tert-butyl-lithium are slowly added to a solution of 1 g (2.9 mmol) of **16** in 50 ml of toluene cooled at −78 °C; the temperature is then increased to −50 °C giving a yellow solution of lithium germanolate.

**1,3,3,5-Tetramethyl-1,1,5,5-tetramesityltrigermoxane (18)**

To the above solution of lithium methyldimesitylgermanolate, a solution of 0.24 g (1.4 mmol) of dimethylgermanium dichloride in 3 ml anhydrous diethyl ether is added at −50 °C, and the mixture is then refluxed to completion (NMR). After removal of the solvent, the residue is chromatographed on silica gel (eluent: THF/pentane, 20:80, v/v), and 0.64 g (0.81 mmol) of pure trigermoxane **18** are isolated (57% yield). $^1$H NMR (80 MHz, $CDCl_3$, $\delta$ ppm): 0.04 (s, 6H); 0.94 (s, 6H); 2.24 (s, 12H); 2.34 (s, 24H); 6.75 (s, 8H). Mass spectrum (chemical ionization, methane): 785 $(M-1)^+$; 771 $(M+1-CH_4]^+$. Analysis: Calcd. C, 61.07; H, 7.17. Found: C, 61.28; H, 7.43%.

**3,3-Diethyl-1,5-dimethyl-1,1,5,5-tetramesityltrigermoxane (19)**

From the reaction of **17** with diethylgermanium dichloride (48% yield). $^1$H NMR (80 MHz, $C_6D_6$, $\delta$ ppm): 0.91 (m, 10H); 1.06 (s, 6H); 2.10 (s, 12H); 2.50 ;(s, 24H); 6.73 (s, 8H). Mass spectrum (chemical ionization, methane): 813 $(M-1)^+$.

799 $(M+1-CH_4)^+$; 785 $(M+1-C_2H_6)^+$. Analysis: Calcd: C, 61.91; H, 7.42%. Found: C, 61.88; H, 7.32%.

**3,3-Di-n-butyl-1,5-dimethyl-1,1,5,5-tetramesityltrigermoxane (20)**

From the reaction of **17** with di-n-butylgermanium dichloride (39% yield). $^1$H NMR (80 MHz, $C_6D_6$, $\delta$ ppm): 0.95 (m, 18H); 1.09 (s, 6H); 2.11 (s, 12H); 2.52 (s, 24H); 6.73 (s, 8H). Analysis: Calcd: C, 63.44; H, 7.87. Found: C, 63.22; H, 8.07%.

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