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ORGANOPOLYGERMANES

I. α,ω-DIPHENYLPOLYMETHYLPOLYGERMANES. PREPARATION AND PHENYLDIMETHYLGERMYLLITHIUM-CATALYZED DISPROPORTIONATION

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SUMMARY

Nine new organopolygermanes have been prepared, including four lower members of the homologous series of α,ω-diphenylpolymethylpolygermanes of the formula $Ph(Me_2Ge)_nPh$, where $n=2$–5. With the exception of the compound with $n=2$, each of the α,ω-diphenylpolygermanes undergoes disproportionation very readily in the presence of phenyldimethylgermyllithium as catalyst in tetrahydrofuran to produce an equilibrium mixture composed mainly of these four homologs. In no case were detectable amounts formed of the higher members or of permethylated cyclopolygermanes, $(Me_2Ge)_n$.

INTRODUCTION

In our recent work it has been shown that every member of the homologous series of α,α,α,ω,ω,ω-hexaphenylpolymethylpolysilanes of the formula (A) can be converted into two permethylated cyclopolysilanes, *i.e.*, $(Me_2Si)_5$ and $(Me_2Si)_6$ in the molar ratio of approximately 1/9, and hexaphenyldisilane when treated with a catalytic amount of triphenylsilyllithium in tetrahydrofuran (THF) at room temperature[1]. Similarly, every member of the homologous series of α,ω-diphenylpolymethylpolysilanes with the formula (B) readily undergoes disproportionation under the influence of phenyldimethylsilyllithium as catalyst to give an equilibrium mixture that is composed of several lower homologs of the polysilanes (B) along with dodecamethylcyclohexasilane[2].

$$\underset{\substack{n=1\text{–}6\\ \text{(A)}}}{Ph_3Si(Me_2Si)_nSiPh_3} \xrightarrow[\text{THF}]{Ph_3SiLi} Ph_3SiSiPh_3 + \frac{n\cdot x}{5}(Me_2Si)_5 + \frac{n\cdot y}{6}(Me_2Si)_6 \quad (x+y=1)$$

$$\underset{\substack{n=1\text{–}3\\ \text{(B)}}}{PhMe_2Si(Me_2Si)_nSiMe_2Ph} \xrightarrow[\text{THF}]{PhMe_2SiLi} (Me_2Si)_6 + \sum_{x=0}^{x=3} PhMe_2Si(Me_2Si)_xSiMe_2Ph$$

As an extention of this research, we have prepared some lower members of the homologous series of α,ω-diphenylpolymethylpolygermanes of the general formula (I) and examined their behavior toward the action of phenyldimethylgermyllithium in tetrahydrofuran.

$$\mathrm{PhMe_2Ge(Me_2Ge)_nGeMe_2Ph}\quad (\mathrm{I})\qquad n=0\text{–}3$$

SYNTHESIS

The synthesis of those compounds represented by the formula (I) was accomplished by reacting phenyldimethylgermyllithium with appropriate chlorogermanes in tetrahydrofuran. An excess of the germyllithium was avoided in order to prevent possible disproportionation of the polygermanes formed. The required chlorogermanes were prepared most conveniently and in satisfactory yields by hydrochlorodephenylation of suitable phenyl-substituted germanes with dry hydrogen chloride in the presence of catalytic amounts of anhydrous aluminum chloride in chloroform at room temperature. The following equations summarize the reactions employed for preparation.

$$\mathrm{Ph_2GeMe_2+HCl}\xrightarrow{a}\underset{(\mathrm{II})}{\mathrm{PhMe_2GeCl}}\mathrm{+PhH}$$

$$\underset{(\mathrm{I},\,n=0)}{\mathrm{PhMe_2GeGeMe_2Ph}}\ \overset{a}{-}\!\left[\begin{array}{l}\xrightarrow{\mathrm{HCl}}\underset{(\mathrm{III})}{\mathrm{ClMe_2GeGeMe_2Ph}}\mathrm{+PhH}\\[1ex]\xrightarrow{2\,\mathrm{HCl}}\underset{(\mathrm{IV})}{\mathrm{ClMe_2GeGeMe_2Cl}}\mathrm{+2\,PhH}\end{array}\right.$$

$$\underset{(\mathrm{I},\,n=1)}{\mathrm{PhMe_2Ge(Me_2Ge)GeMe_2Ph}}\mathrm{+2\,HCl}\xrightarrow{a}\underset{(\mathrm{V})}{\mathrm{ClMe_2Ge(Me_2Ge)GeMe_2Cl}}\mathrm{+2\,PhH}$$

$$\mathrm{PhMe_2GeCl+2\,Li}\xrightarrow{b}\mathrm{PhMe_2GeLi+LiCl}$$

$$(\mathrm{II})+\mathrm{PhMe_2GeLi}\xrightarrow{b}\underset{(\mathrm{I},\,n=0)}{\mathrm{PhMe_2GeGeMe_2Ph}}\mathrm{+LiCl}$$

$$\mathrm{Me_2GeCl_2+2\,PhMe_2GeLi}\xrightarrow{b}\underset{(\mathrm{I},\,n=1)}{\mathrm{PhMe_2Ge(Me_2Ge)GeMe_2Ph}}\mathrm{+2\,LiCl}$$

$$(\mathrm{III})+\mathrm{PhMe_2GeLi}\xrightarrow{b}(\mathrm{I},\,n=1)+\mathrm{LiCl}$$

$$(\mathrm{IV})+2\,\mathrm{PhMe_2GeLi}\xrightarrow{b}\underset{(\mathrm{I},\,n=2)}{\mathrm{PhMe_2Ge(Me_2Ge)_2GeMe_2Ph}}\mathrm{+2\,LiCl}$$

$$(\mathrm{V})+2\,\mathrm{PhMe_2GeLi}\xrightarrow{b}\underset{(\mathrm{I},\,n=3)}{\mathrm{PhMe_2Ge(Me_2Ge)_3GeMe_2Ph}}\mathrm{+2\,LiCl}$$

[a] With $AlCl_3$ in $CHCl_3$. [b] In THF.

The organopolygermanes prepared here are all new compounds. Some physical constants, proton NMR data, and results of elemental analyses for them, together with those for hitherto known diphenyldimethylgermane, are listed in Table 1.

TABLE 1

PHYSICAL CONSTANTS, PROTON NMR AND ANALITICAL DATA FOR ORGANOPOLYGERMANES

Compound	B.p. (°C/mm) and m.p. (°C)	Analyses, found (calcd.) (%)			Chemical shifts (τ)	
		C	H	Cl	Me	Ph
$Ph(Me_2Ge)Ph$[a]	125–126/3	65.56 (65.45)	6.34 (6.28)		9.37 (1-Ge)	2.40– 2.95
$Ph(Me_2Ge)_2Ph$	162/8 25.5–26.5	53.61 (53.45)	6.43 (6.17)		9.50 (1-Ge)	2.56– 2.90
$Ph(Me_2Ge)_3Pb$[b]	170/3.5 6–7.5	46.91 (46.77)	6.25 (6.10)		9.57 (1-Ge) 9.68 (2-Ge)	2.60– 2.95
$Ph(Me_2Ge)_4Ph$[c]	202–203/1.5 16–17	42.46 (42.52)	6.15 (6.08)		9.50 (1-Ge) 9.70 (2-Ge)	2.77– 3.04
$Ph(Me_2Ge)_5Ph$[d]	161–162/0.1	38.92 (39.58)	5.95 (6.04)		9.48 (1-Ge) 9.67 (2-Ge) 9.76 (3-Ge)	2.60– 2.87
$Cl(Me_2Ge)Ph$[e]	110–112/24	44.50 (44.65)	4.92 (5.15)	16.7 (16.5)	9.11 (1-Ge)	2.33– 2.83
$Cl(Me_2Ge)_2Ph$[f]	149/24	38.02 (37.78)	5.45 (5.39)	10.9 (11.1)	9.27[g] (1-Ge) 9.34 (2-Ge)	2.61– 2.94
$Cl(Me_2Ge)_2Cl$	95/24 45.5–47.0	17.64 (17.39)	4.66 (4.38)	26.1 (25.7)	9.08 (1-Ge)	
$Cl(Me_2Ge)_3Cl$	78–79/1.0 23–24	18.79 (19.02)	4.71 (4.78)	18.7 (18.7)	9.14 (1-Ge) 9.40 (2-Ge)	
$Ph_3Ge(Me_2Ge)GePh_3$	– 201–202	64.63 (64.24)	5.11 (5.11)		9.42 (1-Ge)	2.75– 3.00

[a] Known compound[3,4]. [b] n_D^{20} 1.5861, d_4^{20} 1.3086. [c] n_D^{20} 1.5960, d_4^{20} 1.3539, [d] n_D^{20} 1.6055, d_4^{20} 1.4304. [e] n_D^{20} 1.5419, d_4^{20} 1.2800. [f] n_D^{20}1.5544. [g] The value for protons in the $ClMe_2Ge$ group.

ACTION OF $PhMe_2GeLi$ ON (I)

The disproportionation of all the members of the homologous series of the polygermanes (I) in the presence of $PhMe_2GeLi$ as catalyst proceeded at room temperature much more readily than that of their silicon counterparts, with the exception of 1,2-diphenyltetramethyldigermane (I, $n=0$), which did not undergo any change. The reaction mixtures remained homogeneous throughout the course of reaction. Monitoring by VPC of the progress of reaction revealed that several lower homologs of the polygermanes (I, $n=0$ to 3) were produced within approximately 30 min as an apparent equilibrium mixture, and that its composition was primarily dependent upon the value of n in the starting polygermane (I). The concentration of a component of the mixture fairly rapidly decreased with increasing germanium chain length. Table 2 illustrates the data obtained.

TABLE 2

EQUILIBRATION OF $PhMe_2Ge(Me_2Ge)_nGeMe_2Ph$(I) WITH $PhMe_2GeLi$ IN THF

Starting substance	Composition of equilibrium mixture (%)			
	(I, $n=0$)	(I, $n=1$)	(I, $n=2$)	(I, $n=3$)
(I, $n=1$)	54	30	12	4
(I, $n=2$)	43	31	18	8
(I, $n=3$)	40	28	22	10

In no case were appreciable amounts of the higher homologs of (I) formed; and no trace of cyclogermanes such as $(Me_2Ge)_6$ was detected, in marked contrast to the PhR_2SiLi-catalyzed disproportionation of $PhR_2Si(Me_2Si)_nSiR_2Ph$, where R is Ph or Me[1,2]. No formation of cyclogermanes was also observed when Ph_3Ge-$(Me_2Ge)GePh_3$ was treated with Ph_3GeLi; hexaphenyldigermane was the only identifiable product. These results suggest that the polygermane compounds with sufficiently long germanium–germanium chains, such as $PhR_2Ge(Me_2Ge)_nGeR_2Ph$ where R = Ph or Me and $n=5$ or 6, are too labile under the reaction conditions to survive until they undergo cyclization.

EXPERIMENTAL

Diphenyldimethylgermane

This compound was prepared in 81% yield by the action of phenylmagnesium chloride[5] in THF on dichlorodimethylgermane (obtained by the "direct synthesis" as described by Rochow[6]).

Hydrochlorodephenylation of $Ph(Me_2Ge)_nPh$

The four chlorogermanes, (II)–(V), were prepared in essentially the same manner. The following description of the synthesis of 1-chloro-2-phenyltetramethyldigermane (III) is typical.

In a 300-ml three-necked flask, provided with an air-tight stirrer, a gas-inlet tube the stem of which extended into the liquid nearly the bottom of the flask, and a reflux condenser was placed, a mixture of 29 g (0.081 mole) of 1,2-diphenyltetramethyldigermane (I, $n=0$), 0.5 g of anhydrous aluminum chloride and 100 ml of chloroform. Into the stirred mixture was passed dry hydrogen chloride at room temperature, and the extent of reaction was monitored by VPC analysis of small samples extracted periodically from the reaction mixture. After about 3 h, the starting substance disappeared with the formation of the chloride (III) being at its maximum. At that time the introduction of hydrogen chloride was discontinued and 10 ml of acetone was added to the mixture for the purpose of deactivating the catalyst. Removal by distillation of the solvent and benzene produced during reaction, followed by fractional distillation of the residue under reduced pressure gave 10.5 g (41% yield) of (III).

By substantially the same techniques, the following chlorogermanes were obtained from the corresponding diphenylgermanes in yields indicated in parentheses: phenyldimethylchlorogermane (II) (86%), 1,2-dichlorotetramethyldigermane (IV) (84%), and 1,3-dichlorohexamethyltrigermane (V) (69%).

Preparation of α,ω-diphenylpolymethylpolygermanes (I)

Since the four α,ω-diphenylpolygermanes, (I, $n=0$) to (I, $n=3$), were prepared in essentially the same manner, only the synthesis of 1,2-diphenyltetramethyldigermane (I, $n=0$) is described.

Phenyldimethylgermyllithium was prepared from 4.8 g (0.7 g-atom) of lithium and 50 g (0.23 mole) of phenyldimethylchlorogermane in 300 ml of THF, in accordance with the techniques used by Gilman *et al.* for the preparation of triphenylgermyllithium[7,8]. Unchanged lithium was removed by filtration under dry nitrogen pressure and the greenish black solution was added dropwise to 50 g (0.23 mole) of phenyldimethylchlorogermane diluted with 50 ml of THF with stirring. After the addition was completed, the mixture was stirred for an additional 10 min and then hydrolyzed with dilute hydrochloric acid. The organic layer was worked up in the usual way and finally fractionally distilled to give 78 g (93% yield) of (I, $n=0$).

The following polygermanes were prepared in the same way from appropriate chlorogermanes: 1,3-diphenylhexamethyltrigermane (I, $n=1$), 80% from 1-phenyl-2-chlorotetramethyldigermane, 43% from dimethyldichlorogermane; 1,4-diphenyloctamethyltetragermane (I, $n=2$), 31% from 1,2-dichlorotetramethyldigermane; and 1,5-diphenyldecamethylpentagermane (I, $n=3$), 41% from 1,3-dichlorohexamethyltrigermane. In the cases of the tetra- and pentagermanes, formation of some amounts of disproportionation products was also observed.

1,1,1,3,3,3-*Hexaphenyldimethyltrigermane*

This compound was prepared, in 45% yield, in essentially the same manner by reaction of triphenylgermyllithium[7,8] with dimethyldichlorogermane.

Action of $PhMe_2GeLi$ on (I)

The following is typical of the techniques employed.

In a 50 ml Erlenmeyer flask, previously flushed with pure nitrogen and sealed with a serum cap, was placed a solution of 4.0 g (7 mmole) of (I, $n=2$) in 15 ml of THF. The solution was stirred magnetically at room temperature, and 2 ml of a THF solution containing 2.5 mmole of phenyldimethylgermyllithium was added through the serum cap with a hypodermic syringe. At suitable intervals small aliquots of the solution were extracted through the serum cap by means of a syringe and analyzed by VPC. Several minutes after the start, four peaks corresponding to the disproportionation products as well as to the starting substance appeared in the VPC and an apparent equilibrium was established within 30 min. No appreciable peaks other than the four appeared.

Action of Ph_3GeLi on $Ph_3Ge(Me_2Ge)GePh_3$

In a 100-ml three necked flask, previously flushed with nitrogen, was placed a solution of 1.1 g (1.5 mmoles) of $Ph_3Ge(Me_2Ge)GePh_3$ in 20 ml of THF. To the stirred solution was added 1.2 ml of a THF solution of triphenylgermyllithium (0.4 mmole). Periodically, small aliquots of the solution were extracted and analyzed by VPC. However, no formation of volatile products was observed even after 3 days although the color of the reaction mixture due to the germyllithium remained unchanged. At this point, the reaction mixture was hydrolyzed and worked up in the usual way. Concentration of the organic layer afforded crystals. Recrystallization of them from a benzene/ethanol mixture gave hexaphenyldigermane, characterized by analysis (Found: C, 71.40; H, 4.86. $C_{36}H_{30}Ge_2$ calcd.: C, 71.14; H, 4.97%.) and by comparison of its IR spectrum with that of an authentic sample.

Attempted action of $PhMe_2GeLi$ on Ph_2GeMe_2 and on (I, $n=0$)

Neither of these germanes was found to undergo any change even when treated with one equivalent of phenyldimethylgermyllithium in THF under reflux for several hours.

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