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PHENYLDIMETHYLSILYLLITHIUM-CATALYZED DISPROPORTIONATION OF α,ω-DIPHENYLPOLYMETHYLPOLYSILANES

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SUMMARY

Each member of the homologous series of α,ω-diphenylpolymethylpolysilanes of the formula $PhMe_2Si(Me_2Si)_nSiMe_2Ph$ (I), where $n = 1$–3, has been found to undergo disproportionation very readily in the presence of phenyldimethylsilyllithium as catalyst in tetrahydrofuran at room temperature to produce an equilibrium mixture consisting mainly of four lower homologs of (I), with $n = 1$–3, along with dodecamethylcyclohexasilane (II). The composition of the mixture depends primarily upon the chain length of the starting material. Under the same conditions, mixtures of (II) and (I, $n = 0$) in the molar ratio of 1/6, 1/3, and 1/2 gave the same equilibrium mixtures as those obtained from the disproportionation of (I, $n = 1$), (I, $n = 2$), and (I, $n = 3$), respectively.

INTRODUCTION

In a previous paper[1] it was shown that every member of the homologous series of α,α,α,ω,ω,ω-hexaphenylpolymethylpolysilanes of the formula $Ph_3Si(Me_2Si)_n$-$SiPh_3$, with $n = 1$–6 undergoes disproportionation to hexaphenyldisilane and permethylcyclopentasilane and -hexasilane when treated with a catalytic amount of triphenylsilyllithium in tetrahydrofuran (THF) at room temperature. As part of a continuing program to investigate redistribution reactions involving organometalloidal catenation compounds, we have examined the behavior of some lower members of homologous series of α,ω-diphenylpolymethylpolysilanes of the formula (I) in phenyldimethylsilyllithium-catalyzed disproportionation reactions. It was hoped that more information about the cyclization mechanism would be obtained by using such systems because it would be possible to estimate by vapour phase chromatography (VPC) the quantities not only of the formed cyclopolysilane(s) but also of all the linear polysilanes (I) produced, and hence to follow the progress of reaction more fully than in the previous investigation.

$PhMe_2Si(Me_2Si)_nSiMe_2Ph$ (I) $n = 0$–3

RESULTS AND DISCUSSION

The disproportionation of all the members of the homologous series of polysilanes (I) in the presence of a catalytic amount of phenyldimethylsilyllithium[2] proceeded smoothly at room temperature, except for 1,2-diphenyltetramethyldisilane (I, $n=0$). The reaction mixture remained homogeneous throughout the course of reaction, in marked contrast to the triphenylsilyllithium-catalyzed disproportionation of $Ph_3Si(Me_2Si)_nSiPh_3$ which involved precipitation of hexaphenyldisilane[1]. Monitoring by VPC of the progress of reaction revealed that all the lower homologs of the polysilane (I) with $n=0$–3 were formed along with dodecamethylcyclohexasilane (II)[3]; an equilibrium mixture was obtained irrespective of which homolog of (I) was employed as a starting material (eqn. 1). The composition of the equilibrium mixture

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

was primarily dependent upon the value of n in the starting polysilane (I). The concentration of a component of the mixture generally decreased with increasing silicon chain length. Fig. 1 illustrates an observed product distribution *vs.* time for the

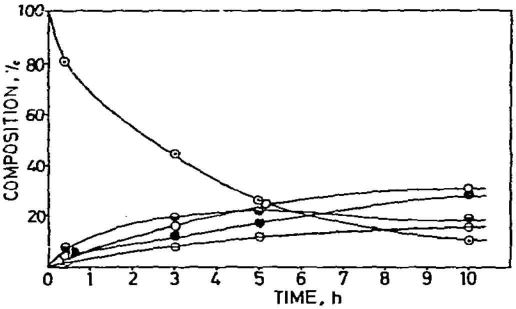

Fig. 1. Observed product distribution *vs.* time for the $PhMe_2SiLi$-catalyzed disproportionation of $PhMe_2Si$-$(Me_2Si)_3SiMe_2Ph$ (I, $n=3$). ●, (I, $n=0$); ○(I, $n=1$); ◒, (I, $n=2$); ⊙, (I, $n=3$); ⊖, $(Me_2Si)_6$.

TABLE 1

EQUILIBRATION AMONG $PhMe_2Si(Me_2Si)_nSiMe_2Ph$ (I) AND $(Me_2Si)_6$ (II) with $PhMe_2SiLi$ AS CATALYST

Starting substance(s)	Composition of equilibrium mixture (%)				
	(II)	(I, $n=0$)	(I, $n=1$)	(I, $n=2$)	(I, $n=3$)
(I, $n=1$)	2	42	33	15	8
(I, $n=2$)	9	37	30	15	9
(I, $n=3$)	16	28	29	17	11
(II)+6 equiv. (I, $n=0$)	2	45	33	14	6
(II)+3 equiv. (I, $n=0$)	9	34	32	17	8
(II)+2 equiv. (I, $n=0$)	18	24	28	19	10

disproportionation of (I, $n = 3$). In every case only negligible amounts of decamethylcyclopentasilane were formed. This is understandable if one remembers the result from the Ph_3SiLi-catalyzed disproportionation of $Ph_3Si(Me_2Si)_nSiPh_3$[1], which indicates that the ratio of $(Me_2Si)_5$ to $(Me_2Si)_6$ at equilibrium only amounts to less than 1/10. The data obtained are listed in Table 1.

The attainment of equilibrium in each case could be confirmed by performing the reaction between the cyclohexasilane and 1,2-diphenyltetramethyldisilane (I, $n=0$) employed in the molar ratio of 1/6, 1/3, and 1/2, respectively, in the presence of the silyllithium (eqn. 2), which gave essentially the same equilibrium mixtures as those obtained from the disproportionation of the polysilanes (I, $n=1$), (I, $n=2$), and (I, $n=3$), respectively (see Table 1). It is noteworthy that this type of disproportionation reaction formally bears a close resemblance to the well-known acid- and base-catalyzed "equilibration" of methylpolysiloxanes (eqn. 3) (for pertinent references see *e.g.* ref. 4):

$$(Me_2Si)_6 + n\ PhMe_2SiSiMe_2Ph \underset{n=6,\,3,\,2}{} \xrightleftharpoons[THF]{PhMe_2SiLi} \sum_{x=0}^{x=3} PhMe_2Si(Me_2Si)_xSiMe_2Ph \quad (2)$$

$$(Me_2SiO)_4 + Me_3SiOSiMe_3 \xrightleftharpoons{catalyst} \sum_x Me_3SiO(Me_2SiO)_xSiMe_3 \quad (3)$$

EXPERIMENTAL

All reactions were carried out in an atmosphere of dry, oxygen-free nitrogen. The VPC analysis was performed at 270°, a helium flow rate of 30 ml/min, with a 2.5 m (6 mm o.d.) column packed with 20% Apiezone-L on celite.

Materials

All of the α,ω-diphenylpolymethylpolysilanes, $PhMe_2Si(Me_2Si)_nSiMe_2Ph$ (I), used here are known; they were prepared by known methods with the exception of (I, $n=3$), which was prepared by the method described below. In the following list, the references given after the values of n in the general formula (I) are to the source or method of preparation: $n=0$[2,5]; $n=1$[6,7]; $n=2$[6,8,9].

1,5-Diphenyldecamethylpentasilane (I, $n=3$) was prepared by two methods.

(*a*). An alloy was prepared from 29.8 g (0.76 g-atom) of potassium and 3.1 g (0.14 g-atom) of sodium in 70 ml of n-heptane. To the stirred mixture was added dropwise a solution of 111 g (0.65 mole) of phenyldimethylchlorosilane and 29 g (0.082 mole) of 1,3-dichlorohexamethyltrisilane[10] in 300 ml of benzene at room temperature over a 3-h period. After the addition was completed, the mixture was kept at about 60° with continuous stirring for an additional 24 h. At this point, it was decomposed by adding successively 100 ml of a 1/1 ethanol/acetic acid mixture, 150 ml of 70% aqueous ethanol and water. The organic layer was then separated, worked up in the usual way, and finally distilled to give 52 g (73% yield) of 1,2-diphenyltetramethyldisilane (I, $n=0$), b.p. 139°/2 mm, m.p. 37° (reported: b.p. 128–130°/1.8 mm, m.p.

34–35°) and 13 g (36% yield) of 1,5-diphenyldecamethylpentasilane (I, $n=3$), b.p. 208–211°/2 mm, m.p. 66° (recrystallized from ethanol). (Found: C, 59.45; H, 9.03. $C_{22}H_{40}Si_5$ calcd.: C, 59.38; H, 9.06%.)

(*b*) By using Gilman's techniques[2], phenyldimethylsilyllithium was prepared from 18.1 g (0.106 mole) of phenyldimethylchlorosilane and 2.2 g (0.32 g-atom) of lithium in 120 ml of tetrahydrofuran. Excess lithium was removed by filtration under nitrogen pressure, and the filtrate was added gradually to a stirred solution of 10 g (0.041 mole) of 1,3-dichlorohexamethyltrisilane[10] in 50 ml of tetrahydrofuran with cooling, over a 10-h period. After an additional 4-h stirring at room temperature, the reaction mixture was hydrolyzed with dilute hydrochloric acid. The organic layer was worked up in the usual way and finally distilled in a fractionating column to give 6.5 g (36% yield) of (I, $n=3$).

Dodecamethylcyclohexasilane (II) was prepared by the method reported by Gilman and Tomasi[3].

Action of $PhMe_2SiLi$ on the polysilanes (I) or a mixture of (I, $n=0$) and (II)

Reactions were performed in essentially the manner described for the Ph_3SiLi-catalyzed disproportionation of $Ph_3Si(Me_2Si)_nSiPh_3$[1].

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