

## TRIPHENYLSILYLITHIUM-CATALYZED DISPROPORTIONATION OF $\alpha,\alpha,\alpha,\omega,\omega,\omega$ -HEXAPHENYLPOLYMETHYLPOLYSILANES TO PERMETHYLATED CYCLOPOLYSILANES AND HEXAPHENYLDISILANE

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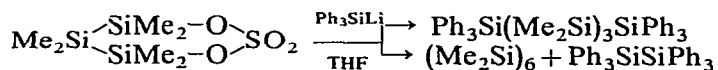
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### SUMMARY

Hexaphenylpolymethylpolysilanes of the formula  $\text{Ph}_3\text{Si}(\text{Me}_2\text{Si})_n\text{SiPh}_3$  (I) have been found to undergo disproportionation with catalytic amounts of triphenylsilyllithium in tetrahydrofuran at room temperature into two permethylated cyclopolysilanes,  $(\text{Me}_2\text{Si})_5$  (II) and  $(\text{Me}_2\text{Si})_6$  (III), and hexaphenyldisilane. The product (II) is always formed in preference to (III) in the early stages of reaction except in the case of (I) having  $n=6$ . After many hours, however, the amount of (III) increases at the expense of (II), and finally an equilibrium mixture of (II) and (III) in the ratio of approximately 1/9 is formed. A possible mechanism is discussed. Chemical shifts for methyl protons of (I) are recorded.

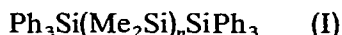
### INTRODUCTION

In a recent article<sup>1</sup> we reported that the action of triphenylsilyllithium on hexamethyltrisilylene sulfate in tetrahydrofuran (THF) led to the formation of 1,1,1,5,5,5-hexaphenylhexamethylpentasilane in 63.5% yield when the silyllithium reagent was used in slight deficiency, while dodecamethylcyclohexasilane was formed in 67% yield, together with hexaphenyldisilane in 83.5% yield, when the lithium reagent was used in some excess and the reaction was continued under reflux over a prolonged period of time:



Formation of the cyclohexasilane was also observed upon treatment of tetramethyl-disilylene sulfate and octamethyltetrasilylene sulfate with an excess of triphenylsilyllithium for many hours. For this reaction, leading to the cyclohexasilane, we tentatively proposed a mechanism involving initial formation of  $\alpha,\alpha,\alpha,\omega,\omega,\omega$ -hexaphenylpolymethylpolysilanes which undergo a sequence of Si-Si/Si-Li redistributions.

In an effort to throw light on the reaction pathway for this cyclization process, we have now prepared six individual members of the homologous series of  $\alpha,\alpha,\alpha,\omega,\omega,\omega$ -hexaphenylpolymethylpolysilanes of the general formula

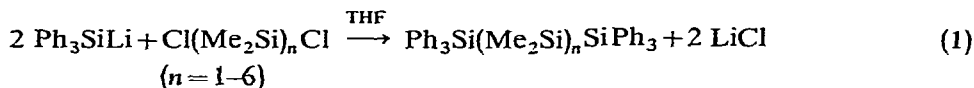


where  $n=1-6$ , and examined the action of a catalytic amount of triphenylsilyl-lithium on each of them. Proton NMR data are also reported for (I).

## RESULTS AND DISCUSSION

### Preparation of (I)

All the  $\alpha,\alpha,\alpha,\omega,\omega,\omega$ -hexaphenylpolymethylpolysilanes (I) were prepared by the reaction of appropriate  $\alpha,\omega$ -dichloropolymethylpolysilanes with triphenylsilyl-lithium<sup>2</sup> in tetrahydrofuran (THF). Here we took care to avoid an excess of the silyl-lithium:



Most of these compounds have been prepared previously by Gilman *et al.* by the same procedure, and were listed with their melting points in a review article<sup>3</sup>, but no experimental details were given. Yields, melting points, and analytical data for our products are shown in Table 1.

TABLE 1

YIELDS, MELTING POINTS, AND ANALYTICAL DATA FOR  $\alpha,\alpha,\alpha,\omega,\omega,\omega$ -HEXAPHENYLPOLYMETHYLPOLYSILANES,  $\text{Ph}_3\text{Si}(\text{Me}_2\text{Si})_n\text{SiPh}_3$  (I)

$n$ in (I)	Formula	Yield (%)	M.P. (°C)	C (%) found (calcd.)	H (%) found (calcd.)
1	$\text{Ph}_3\text{Si}(\text{Me}_2\text{Si})\text{SiPh}_3$	58	232-233 <sup>a</sup>	79.07 (79.11)	6.43 (6.29)
2	$\text{Ph}_3\text{Si}(\text{Me}_2\text{Si})_2\text{SiPh}_3$	55	216-217 <sup>b</sup>	75.63 (75.64)	6.68 (6.67)
3	$\text{Ph}_3\text{Si}(\text{Me}_2\text{Si})_3\text{SiPh}_3$	64	191-192 <sup>c</sup>	72.36 (72.76)	6.61 (6.98)
4	$\text{Ph}_3\text{Si}(\text{Me}_2\text{Si})_4\text{SiPh}_3$	50	188-189 <sup>d</sup>	70.38 (70.33)	7.28 (7.24)
5	$\text{Ph}_3\text{Si}(\text{Me}_2\text{Si})_5\text{SiPh}_3^e$	33	151-152	68.43 (68.24)	7.36 (7.47)
6	$\text{Ph}_3\text{Si}(\text{Me}_2\text{Si})_6\text{SiPh}_3$	34	157.5-158.5 <sup>f</sup>	66.61 (66.44)	7.49 (7.67)

<sup>a</sup> Reported<sup>4</sup>: 223-227°. <sup>b</sup> Reported<sup>3</sup>: 209-210°. <sup>c</sup> Reported<sup>3</sup>: 185-186.5°. <sup>d</sup> Reported<sup>3</sup>: 180-182°. <sup>e</sup> New compound. <sup>f</sup> Reported<sup>3</sup>: 154-156°.

### Chemical shifts for methyl protons in (I)

Table 2 lists the chemical shifts of methyl protons in the hexaphenylpolymethylpolysilanes (I). A most striking feature that can be seen is that the chemical shift of the protons of methyl groups on a silicon atom located at the  $\beta$  position with respect to a nearer triphenylsilyl end group appears at the highest field of all. Doubtless, this is because there is good chance for these protons, as revealed by examination of molecular models, to occupy positions near the six-fold axes of the benzene rings so that they experience shielding effects caused by the ring current. In the case of



curve for  $n=3$  were obtained. It will be seen from Fig. 1 that, in the cases of  $n$  being 1 through 4, the formation of the cyclopentasilane (II) occurs somewhat in preference to that of the cyclohexasilane (III) in the early stages of reaction and passes through a maximum value after about 17 h and then decreases gradually to reach an apparent equilibrium value of approximately 10%, whereas the formation of the cyclohexasilane (III) continues to increase up to about 90%. In the case of  $n=5$ , a considerable amount of the cyclopentasilane is produced in the early stages of reaction, reaching a maximum value of approximately 70% after about 20 h, but the amount again decreases with increasing reaction time and finally reaches essentially the same equilibrium value as that obtained from compounds with  $n=1-4$ . On the other hand, the profile for  $n=6$  is considerably different from that for each of the lower homologs in that the formation of the cyclohexasilane (III) constitutes the main reaction from the outset.

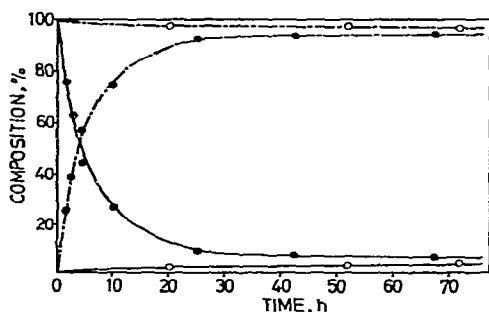


Fig. 2. Equilibration of polymethylcyclopolysilanes with  $\text{Ph}_3\text{SiLi}$ . —,  $(\text{Me}_2\text{Si})_5$ ; - - -,  $(\text{Me}_2\text{Si})_6$ ; ●, from  $(\text{Me}_2\text{Si})_5$ ; ○, from  $(\text{Me}_2\text{Si})_6$ .

These results suggested that the cyclopolysilanes (II) and (III) would be interconvertible under these conditions, and we confirmed that this is indeed the case. Fig. 2 illustrates the profiles for this interconversion *vs.* time.



The observed final molar ratio of cyclopentasilane (II) to cyclohexasilane (III), together with the molar ratio of the starting substance to the catalyst employed and the extent of conversion, is summarized in Table 3.

### Reaction mechanism

A considerable amount of work has been done mainly by Gilman and his coworkers on the cleavage by silylmetallic compounds of the silicon-silicon bond<sup>4,6-11</sup> and there has been some evidence for the formation of somewhat stabilized permethylated polysilylmetallic compounds<sup>10,12,13</sup>. In view of these facts and, in the light of the reaction pathway proposed by Gilman and Tomasi<sup>4</sup> for the formation of dodecamethylcyclohexasilane from lithium coupling of dimethyldichlorosilane in the presence of triphenylsilyllithium as catalyst in tetrahydrofuran, a mechanism can be suggested for the triphenylsilyllithium-catalyzed disproportionation of (I) to the cyclopolysilanes (II) and (III) and hexaphenyldisilane. This involves relatively fast initial formation of a pseudo-equilibrium mixture among several lower members of

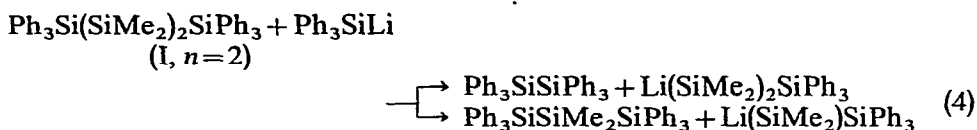
TABLE 3

CONVERSION OF  $\text{Ph}_3\text{Si}(\text{Me}_2\text{Si})_n\text{SiPh}_3$  (I) INTO  $(\text{Me}_2\text{Si})_5$  (II) AND  $(\text{Me}_2\text{Si})_6$  (III) WITH  $\text{Ph}_3\text{SiLi}$  AS CATALYST

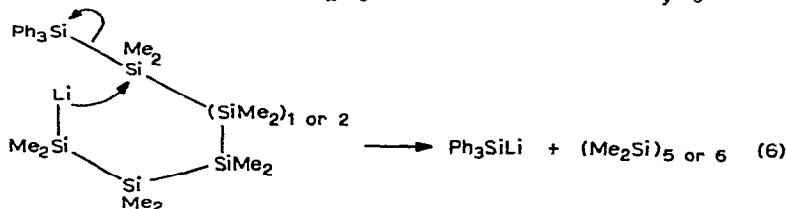
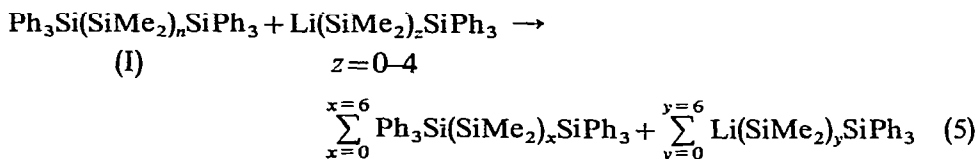
Starting substance	Molar ratio of start. subst. to catalyst	Conversion (%)	Final molar ratio of (II) to (III)
(I, $n=1$ )	14/1	62	10/90
(I, $n=2$ )	13/1	90	12/88
(I, $n=3$ )	6/1	76	12/88
(I, $n=4$ )	7/1	84	7/93
(I, $n=4$ )	7/1	86	8/92
(I, $n=6$ )	8/1	85	5/95
(II)	26/1	<i>a</i>	7/93
(III)	5/1	<i>b</i>	4/96

<sup>a</sup> Probably 100% <sup>b</sup> Not determined.

the homologous series of (I) as a result of occurrence of a sequence of Si-Si/Si-Li redistributions. Thus if one starts, for example, with (I,  $n=2$ ), the initial redistribution can be depicted by eqn. (4). The polysilyllithium intermediates thus generated,



$\text{LiSiMe}_2\text{SiPh}_3$  and  $\text{Li}(\text{SiMe}_2)_2\text{SiPh}_3$ , may react in an analogous way with the polysilanes  $\text{Ph}_3\text{Si}(\text{SiMe}_2)_n\text{SiPh}_3$  present in the reaction system. Therefore, in general, the Si-Si/Si-Li redistribution of (I) with the silyllithium compounds may be represented by eqn. (5). The polysilyllithium compounds  $\text{Li}(\text{SiMe}_2)_z\text{SiPh}_3$  having the value of



$y=5$  or  $6$  are then capable of undergoing cyclization (eqn. 6). The very low solubility of hexaphenyldisilane, which precipitates almost completely as it forms during reaction, serves to make the overall reaction (2) proceed irreversibly.

It was not possible to estimate relative concentrations of all the lower members of the homologous series  $\text{Ph}_3\text{Si}(\text{Me}_2\text{Si})_n\text{SiPh}_3$  present in a pseudo-equilibrium mixture, because their extremely low volatility prevented VPC analysis. However, in view of the results obtained from analogous reactions of  $\alpha,\omega$ -diphenylpolymethyl-

polysilanes,  $\text{PhMe}_2\text{Si}(\text{Me}_2\text{Si})_n\text{SiMe}_2\text{Ph}$ , with  $\text{PhMe}_2\text{SiLi}^{14}$  and also of  $\alpha,\omega$ -diphenylpolymethylpolygermanes,  $\text{PhMe}_2\text{Ge}(\text{Me}_2\text{Ge})_n\text{GeMe}_2\text{Ph}$ , with  $\text{PhMe}_2\text{GeLi}^{15}$ , it is not unreasonable to assume that the relative amounts of  $\text{Ph}_3\text{Si}(\text{Me}_2\text{Si})_n\text{SiPh}_3$  in the reaction mixture decrease fairly rapidly with increasing silicon chain length. This possible difference in concentration between  $\text{Ph}_3\text{Si}(\text{Me}_2\text{Si})_5\text{SiPh}_3$  and  $\text{Ph}_3\text{Si}(\text{Me}_2\text{Si})_6\text{SiPh}_3$ , and hence between  $\text{Ph}_3\text{Si}(\text{Me}_2\text{Si})_5\text{Li}$  and  $\text{Ph}_3\text{Si}(\text{Me}_2\text{Si})_6\text{Li}$ , in the early stages of reaction seems to be the reason why the cyclopentasilane (II) is always formed initially in preference to the cyclohexasilane (III), except when  $n=6$  in compound (I).

#### EXPERIMENTAL

Reactions were carried out in an atmosphere of dry, oxygen-free nitrogen. Boiling and melting points are uncorrected. The VPC analysis was performed at  $270^\circ$ , a helium flow rate of 30 ml/min, with a 2.5 m (6 mm o.d.) column packed with 20% Apiezon-L. Tetrahydrofuran used as solvent was dried over lithium aluminum hydride and distilled just before use from phenylmagnesium chloride.

#### $\alpha,\omega$ -Dichloropolymethylpolysilanes, $\text{Cl}(\text{Me}_2\text{Si})_n\text{Cl}$

All the dichloropolysilanes used here are known; they were prepared by known methods with the exception of the compound with  $n=5$ , which was prepared by the method described below, although an alternative synthesis has been briefly reported by Gilman and Chapman<sup>20</sup>. In the following list, the references given after the values of  $n$  in the general formula  $\text{Cl}(\text{Me}_2\text{Si})_n\text{Cl}$  are to the source or method of preparation:  $n=2^{16,17}$ ;  $n=3^{17,18}$ ;  $n=4^{19}$ ;  $n=6^{21}$ .

1,5-Dichlorodecamethylpentasilane was prepared in 62% yield by aluminum chloride-catalyzed hydrochlorodephenylation with dry hydrogen chloride in chloroform of 1,5-diphenyldecamethylpentasilane<sup>14</sup>, in essentially the same manner as that used in preparation of  $\text{Cl}(\text{Me}_2\text{Si})_4\text{Cl}$  from  $\text{Ph}(\text{Me}_2\text{Si})_4\text{Ph}^{19}$ . It had b.p.  $120\text{--}122^\circ/3$  mm,  $n_D^{20}$  1.5209 and  $d_4^{20}$  0.9688 (reported<sup>20</sup>: b.p.  $87\text{--}89^\circ/0.1$  mm,  $n_D^{20}$  1.5220). (Found: Cl, 19.28.  $\text{C}_{10}\text{H}_{30}\text{Cl}_2\text{Si}_5$  calcd.: Cl, 19.61%.)

#### $\alpha,\alpha,\alpha,\omega,\omega,\omega$ -Hexaphenylpolymethylpolysilanes (I)

The six polysilanes (I) were prepared in essentially the same manner. The following detailed description of the synthesis of 1,1,1,6,6,6-hexaphenyl-octamethyl-tetrasilane (I,  $n=4$ ) is typical.

Triphenylsilyllithium<sup>2</sup> was prepared from 61 g (0.2 mole) of triphenylchlorosilane and 5 g (0.72 g-atom) of lithium in 500 ml of absolute tetrahydrofuran. Unchanged lithium was removed by filtration in dry nitrogen atmosphere. The solution of reagent thus obtained was gradually added with cooling to a stirred solution of 26 g (0.086 mole) of 1,4-dichlorooctamethyltetrasilane diluted with 50 ml of tetrahydrofuran. The instant the reagent dropped its greenish black color vanished. But the rate of decoloration much decreased when about 71% of the reagent had been introduced. At this point the reaction mixture was hydrolyzed with dilute hydrochloric acid. The organic layer containing a considerable amount of crystalline substance was separated from the water layer, and the latter was extracted with several portions of ether. The organic layer and ether extracts were combined and washed

with dilute sodium hydrogen carbonate solution, and then dried over calcium chloride. Evaporation of the solvents gave 41 g of white crystals. Recrystallization of them from an ethanol/benzene mixture afforded 32 g of a pure sample of (I,  $n=4$ ).

*Action of  $Ph_3SiLi$  on the polysilanes (I), (II) and (III).*

The following is a typical procedure. In a 50-ml Erlenmeyer flask, previously flushed with pure nitrogen and sealed with a serum cap, was placed a solution of 1.620 g ( $2.15 \times 10^{-3}$  mole) of (I,  $n=4$ ) and 0.303 g of n-cetane (as internal standard) in 15 ml of tetrahydrofuran. The solution was stirred magnetically at room temperature and 0.2 ml of THF solution containing 0.3 mmole of triphenylsilyllithium 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. The results are illustrated in Fig. 1 and in Table 3.

In a run carried out in a larger scale, we used preparative VPC to isolate a sample of decamethylcyclopentasilane (II), which proved to be identical with that prepared by Carberry and West<sup>5</sup>. (Found: C, 41.50, 41.35; H, 10.32, 10.40; mol. wt. by mass spectroscopy, 290.  $C_{10}H_{30}Si_5$  calcd.: C, 41.30; H, 10.40%; mol. wt., 290.)

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