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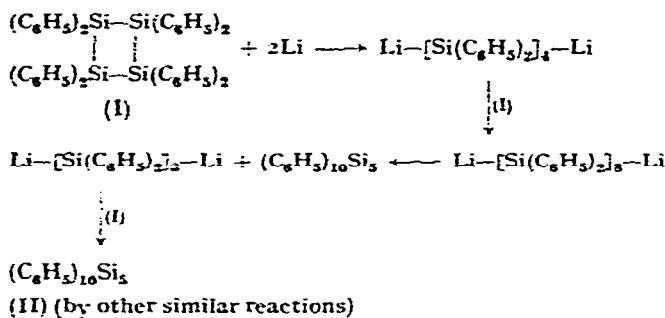
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## The reaction of dichlorodiphenylsilane with magnesium

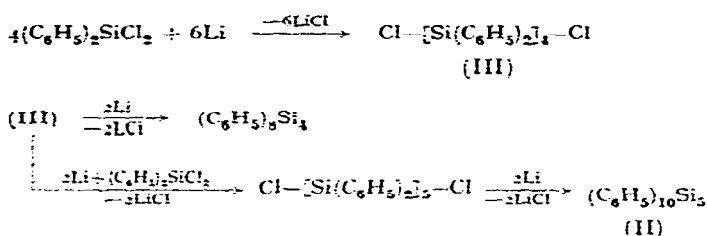
Some investigations by Kipping and co-workers<sup>1</sup> and more recent studies in these laboratories<sup>2</sup> have shown that three crystalline compounds can be obtained from the reaction of dichlorodiphenylsilane with sodium<sup>1,2</sup> in toluene and with lithium in tetrahydrofuran<sup>2</sup>. One of these compounds has been identified as octaphenylcyclotetrasilane<sup>1,2,3</sup> while the structure of the second has recently been shown to be decaphenylcyclopentasilane\*. On the basis of chemical evidence, the third compound is believed to be dodecaphenylcyclohexasilane<sup>3b</sup>.

The yields of these two cyclic polysilanes were originally below 20%<sup>1,2</sup>. However, by a carefully controlled rate of addition of dichlorodiphenylsilane to lithium in tetrahydrofuran, octaphenylcyclotetrasilane has been obtained in yields as high as 75%<sup>4</sup>. Under these conditions only about 10% of the cyclic pentasilane is obtained. Using essentially the same technique with a slight excess of lithium, and a longer reaction time, decaphenylcyclopentasilane has been isolated in nearly quantitative amounts<sup>4</sup>. These results indicate that octaphenylcyclotetrasilane is the primary product of the reaction of dichlorodiphenylsilane with alkali metals, and is the precursor of decaphenylcyclopentasilane, the more thermodynamically favored compound. This is also supported by the fact that the four-membered ring compound has been converted into the next higher homolog by trace amounts of alkali metals<sup>5</sup>. The transformation may be illustrated by the following equations:

\* The structure of this compound had been proposed as dodecaphenylcyclohexasilane<sup>2b</sup>. More recent evidence, however, has shown it to be the cyclic pentasilane<sup>2a</sup>.



The reaction of dichlorodiphenylsilane with lithium may be illustrated by the following sequence of equations:



However, if this route to decaphenylcyclopentasilane is being followed to an appreciable extent, the yields of the two cyclic compounds would be expected to be more nearly comparable than is observed.

It has been shown that magnesium in tetrahydrofuran is able to couple chlorosilanes without detectable silicon-silicon bond cleavage in most cases<sup>6</sup>. However, decaphenylcyclopentasilane has been isolated in small amounts in the cyclization of 1,4-dichlorooctaphenyltetrasilane with Mg/EtI, and in larger yields in attempted cyclizations of 1,6-dichlorododecaphenylhexasilane with Mg/EtI<sup>7</sup>.

The coupling of halosilanes with magnesium may possibly proceed through the formation of an intermediate silyl Grignard reagent, with silicon directly bonded to magnesium. While no such reagent has been isolated, its intermediate formation has been proposed by several workers<sup>8-11</sup>. Selin and West reported substantial evidence for the triphenylsilyl Grignard reagent<sup>8</sup>. Chlorotriphenylsilane was coupled by cyclohexylmagnesium bromide, phenyl and 2-methylcyclohexyl Grignard reagents to give good yields of hexaphenyldisilane. Hexamethyldisilane could not be isolated from attempts to couple chlorotrimethylsilane in the same manner. However, when a mixture of chlorotriphenylsilane and chlorotrimethylsilane was used 1,1,1-trimethyl-2,2,2-triphenyldisilane could be isolated. It has been reported that magnesium coupling, in tetrahydrofuran, of organochlorosilanes that do not contain an aromatic group bonded to silicon affords significant amounts of products resulting from solvent cleavage<sup>6c, 12-14</sup>.

The reaction of dichlorodiphenylsilane with magnesium was carried out in an effort to further substantiate the method of formation of decaphenylcyclopentasilane in the reactions of dichlorodiphenylsilane with alkali metals. It was shown that

octaphenylcyclotetrasilane does not react with magnesium or with a mixture of magnesium and magnesium iodide in tetrahydrofuran. Thus the route to the five-membered ring compound shown in the first reaction scheme should be prevented.

Under varied conditions, the yield of octaphenylcyclotetrasilane ranged from 8–59 %, while the yield of the higher, cyclic homolog was less than 3 %. This is compatible with the proposed routes to these two compounds, in that octaphenylcyclotetrasilane, once formed, is not converted into decaphenylcyclopentasilane by magnesium. The small amounts of the five-membered ring compound can be accounted for by the cyclization of the 1,5-dichloride, a reaction which was shown to occur in good yield in a separate experiment under similar conditions.

The higher yields of octaphenylcyclotetrasilane were obtained when a mixture of cyclohexene and tetrahydrofuran was used as the solvent\*. The role of the hydrocarbon is not known at this time. The effect is evidently not due to a simple dilution, as the amount of the four-membered ring compound obtained upon the addition of an equal volume of cyclohexane was considerably lower. The use of cyclohexene did not affect the yield of decaphenylcyclopentasilane.

### *Experimental*

All reactions were carried out in oven-dried glassware under atmospheres of dry, oxygen-free nitrogen. Solvents other than tetrahydrofuran (THF) were dried by storage over sodium wire. The THF was dried and purified by refluxing over sodium wire, and distilled into lithium aluminum hydride. The solvent was then distilled from the hydride immediately before use.

In the reactions of dichlorodiphenylsilane with magnesium, the reagents were combined in two different manners. In some cases, solutions of dichlorodiphenylsilane and the solvent were added to magnesium at reflux temperature over a period of about 2 h. Other runs were carried out by adding the solvent to a mixture of magnesium and dichlorodiphenylsilane heated to 65°. In comparable runs, the yield of octaphenylcyclotetrasilane was not appreciably affected by the mode of mixing.

*Dichlorodiphenylsilane and magnesium.* The reactions were carried out under various conditions as described in Table 1. In general, 4.8 g (0.2 g-atom) of magnesium turnings, which had been treated with a few drops of ethyl iodide, was refluxed in 100 ml of THF (or a mixture of THF and other solvents) with 25.3 g (0.1 mole) of dichlorodiphenylsilane for the reported length of time. The reaction mixtures were decanted from the remaining magnesium and hydrolyzed in dilute acid. Octaphenylcyclotetrasilane was filtered off and washed with hot benzene. If this product did not melt between 315–320°, it was purified by extraction with benzene in a heated Soxhlet apparatus. The filtrate and benzene wash solution were combined, dried over sodium sulfate and the solvents removed. Acetone was added to the oily residue and a small amount of insoluble product slowly precipitated, which melted over a wide range at temperatures above 380°. From the runs using 0.1 mole of dichlorodiphenylsilane, this material was not obtained in sufficient amounts to be purified, but was tentatively identified as decaphenylcyclopentasilane. This was confirmed by carrying out reactions starting with 0.5 mole of dichlorodiphenylsilane and isolating 2–3 % yields of pure

\* Cyclohexene was used as a possible trapping agent for "diphenylsilylene". The results of this study will be presented in a subsequent publication<sup>15</sup>.

TABLE I  
REACTION OF DICHLORODIPHENYLSILANE WITH MAGNESIUM

Solvent(s)	Hours reflux	% (C <sub>6</sub> H <sub>5</sub> ) <sub>5</sub> Si <sub>4</sub> <sup>a</sup> Crude	Pure
THF	12	11.0	8.3
THF	24	17.1	13.2
THF	48	19.2	16.5
THF	72 <sup>b</sup>	20.4	17.6
THF/cyclohexene <sup>c</sup>	72 <sup>b</sup>	57.0	50.5
THF/cyclohexane <sup>c</sup>	72	21.4	12.6

<sup>a</sup> The results from the reactions using 0.1 mole of dichlorodiphenylsilane. The crude yield of octaphenylcyclotetrasilane is based on the amount of benzene-insoluble material obtained, which usually melted in the range 300–320°; this product was considered to be of satisfactory purity when it melted 315–320° (mixed m.p.). <sup>b</sup> From reactions starting with 0.5 mole of dichlorodiphenylsilane, similar yields of octaphenylcyclotetrasilane were obtained. However, there was also isolated between 2.4–2.7% yields of pure decaphenylcyclopentasilane. <sup>c</sup> The ratio by volume of THF/hydrocarbon solvent was 3/1.

decaphenylcyclopentasilane, m.p. 455–459° (mixed m.p.). Attempts to isolate other products were unsuccessful.

*Octaphenylcyclotetrasilane and magnesium (attempted).* The magnesium was cleaned with dilute hydrochloric acid and dried at 130° for 3 h before use. Similarly treated magnesium was found to be effective in the preparation of benzylmagnesium chloride in good yield. A mixture of 5.0 g (0.007 mole) of octaphenylcyclotetrasilane and 2.4 g (0.1 g-atom) of powdered magnesium was refluxed in 100 ml of THF for 5 days. The mixture was poured upon a solution of ammonium chloride and, after hydrogen evolution ceased, the remaining solids were filtered, washed with water, ethanol and hot benzene. Upon drying, there was obtained 4.8 g (96%) of recovered starting material, m.p. 317–320° (mixed m.p.).

*Octaphenylcyclotetrasilane and magnesium/magnesium iodide (attempted).* A mixture of magnesium and magnesium iodide was prepared in ether by the reaction of 6.4 g (0.05 g-atom) of iodine and 1.2 g (0.05 g-atom) of magnesium turnings. Subsequent to the removal of the ether by distillation from THF, 7.3 g (0.01 mole) of octaphenylcyclotetrasilane was added and the suspension refluxed for 30 h. The solids were filtered and the magnesium separated mechanically. The remaining solids were washed with water, ethanol, and benzene to give 6.6 g (90.5%) of recovered starting material, m.p. 317–320° (mixed m.p.). The organic filtrate and the benzene wash solution were combined, hydrolyzed in dilute acid, worked up in the usual manner, and dried. Evaporation of the solvents left only a trace of impure octaphenylcyclotetrasilane, m.p. 300–350°, the infrared spectrum of which showed the presence of material containing the siloxane group.

The same quantities of starting materials were used in a second experiment, with ether as solvent instead of THF. Subsequent to refluxing for 24 h, 7.0 g (96%) of starting material was recovered, m.p. 317–319° (mixed m.p.).

*Cyclization of 1,5-dichlorodecaphenylpentasilane with magnesium.* A mixture of 4.9 g (0.005 mole) of the dichloride, 2.4 g (0.1 g-atom) of magnesium and 8–10 drops of ethyl iodide, was refluxed in 20 ml of THF for 6 h. The reaction mixture was de-

canted away from the excess magnesium and hydrolyzed in excess dilute acid. The solid product present was filtered, washed with water, dried, and recrystallized from a mixture of benzene and petroleum ether to give 2.9 g (63.7 %) of decaphenylcyclopentasilane, m.p. 454–463° (mixed m.p.).

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