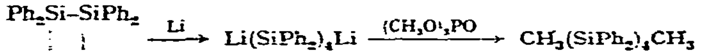
Lithium cleavage of octaphenylcyclotetrasilane

With the elucidation of the structure of octaphenylcyclotetrasilane[1–3], interest has turned to the potential use of this reactive cyclosilane for the preparation of other polysilanes. The demonstrated high reactivity of this compound toward reagents such as iodine[1,4], oxidizing agents[4], and tetrachloroethane[4] make it an attractive candidate for other cleavage reactions.

The cleavage of octaphenylcyclotetrasilane, (I), with lithium, followed by treatment of the reaction mixture with trimethyl phosphate has been reported to give 1,4-dimethyl-1,1,2,2,3,3,4,4-octaphenyltetrasilane in 27 % yield[2]. Similarly, the lithium



$$\begin{array}{c}Ph_2Si{-}SiPh_2\\ |\qquad\quad |\\ Ph_2Si{-}SiPh_2\end{array} \xrightarrow{Li} Li(SiPh_2)_4Li \xrightarrow{(CH_3O)_3PO} CH_3(SiPh_2)_4CH_3$$

cleavage products of (I) were treated with diphenylmethylchlorosilane in an attempt to prepare 1,6-dimethyl-1,1,2,2,3,3,4,4,5,5,6,6-dodecaphenylhexasilane. From this reaction, two incompletely characterized products were described[6].

The examination of the products from this latter reaction has been extended and it has been found that 1,6-dimethyl-1,1,2,2,3,3,4,4,5,5,6,6-dodecaphenylhexasilane is formed to the extent of 25 %. The proof of structure of the compound was obtained by an examination of its proton magnetic resonance spectrum which revealed a ratio of aromatic to methyl protons of 10.1 to 1 (required 10 to 1). The hexasilane was also prepared by the sodium coupling of 1-methyl-3-chloro-1,1,2,2,3,3-hexaphenyltrisilane.

$$2CH_3(SiPh_2)_3Cl \xrightarrow{Na} CH_3(SiPh_2)_6CH_3$$

When the dilithio compound as prepared above was allowed to react with diphenylchlorosilane, the yield of 1,1,2,2,3,3,4,4,5,5,6,6-dodecaphenylhexasilane was only 18–20 %. However, when a modified reaction vessel, in which the lithium cleavage products were allowed to be in contact with the reaction mixture for a short period of time, was used, the yield of the hexasilane increased to 35–40 %. Treatment of the 1,1,2,2,3,3,4,4,5,5,6,6-dodecaphenylhexasilane with phosphorus pentachloride leads to high yields of 1,6-dichloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecaphenylhexasilane, which is in turn converted to the 1,6-dimethyl derivative by means of methylmagnesium iodide.

$$Li(SiPh_2)_4Li + 2ClSiPh_2H \longrightarrow H(SiPh_2)_6H$$

The low yield of products derived from 1,4-dilithiooctaphenyltetrasilane as a result of the lithium cleavage of octaphenylcyclotetrasilane, as opposed to that of 1,5-dilithiodecaphenylpentasilane obtained from the cleavage of decaphenylcyclopentasilane[7,8], might be explained by the ease with which the cyclotetrasilane undergoes reaction with silyllithium compounds[9], which are present in the reaction mixture. The resulting products could then also be cleaved by lithium to give a variety of products, the formation of which of course reduces the yield of specific products from 1,4-dilithio-1,1,2,2,3,3,4,4-octaphenyltetrasilane.

Experimental

All reactions were carried out under an atmosphere of dry oxygen-free nitrogen. Melting points are uncorrected.

Preparation of 1,6-dimethyl-1,1,2,2,3,3,4,4,5,5,6,6-dodecaphenylhexasilane. A. A mixture of 3.39 g (0.00567 mole) of 1-methyl-3-chloro-1,1,2,2,3,3-hexaphenyltrisilane[10] and 0.2 g of sodium in 35 ml of xylene was refluxed for 6 h. A purple color developed as the reaction proceeded. The mixture was hydrolyzed in an alcoholic acid solution. The organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated before adding petroleum ether (b.p. 60–70°). The cooled mixture gave 1.4 g (22 %) of a solid, m.p. 175–188°. Two recrystallizations from benzene and petroleum ether raised the melting point of the solid to 205–207°. Its infrared spectrum was very similar to the spectra of 1,4-dimethyl-1,1,2,2,3,3,4,4-octaphenyltetrasilane and 1,5-dimethyl-1,1,2,2,3,3,4,4,5,5-decaphenylpentasilane. The NMR integration gave the value of 10.1 to 1 for the ratio of aromatic hydrogen to aliphatic hydrogen. 1,6-Dimethyldodecaphenylhexasilane requires ten aromatic hydrogens to one aliphatic hydrogen. (Found: C, 79.19, 79.36; H, 5.88, 5.96; Si, 14.60, 14.68. $C_{74}H_{66}Si_6$ calcd.: C, 79.09; H, 5.92; Si, 14.79 %.)

B. To a mixture of 22.0 g (0.0302 mole) of pulverized octaphenylcyclotetrasilane and 1.26 g (0.18 g-atom) of finely cut lithium wire was added 10 ml of tetrahydrofuran (THF). The reaction mixture was stirred until it had become red-brown in color (15–20 min). Then 100 ml of THF was added dropwise, after which the mixture was stirred for 1.5–2.5 h. The solution became dark reddish brown and most of the octaphenylcyclotetrasilane had dissolved. The mixture was filtered through a sintered glass disk and the resulting silyllithium solution was added dropwise to a stirred solution of 21.0 g (0.090 mole) of methyldiphenylchlorosilane in 50 ml of THF.

Color test I[11] was negative after the addition and the mixture was hydrolyzed with 200 ml of 10 % HCl solution. After ether extraction (200 ml), the volatile solvents were removed on a rotary evaporator under reduced pressure. Most of the resinous residue was dissolved in 200 ml of boiling petroleum ether (b.p. 60–70°). After allowing the mixture to cool, 12.1 g of a white solid, m.p. 160–175°, was collected. This solid was reboiled in about 800 ml of petroleum ether and filtered. After washing the residue with 200 ml of boiling petroleum ether, 5.97 g of white solid melting at 194–200° was obtained as the residue. Upon concentration of the combined filtrate and washings to 80 ml, 5.06 g of solid, m.p. 180–182° was collected. By boiling the latter solid in 200 ml of petroleum ether followed by filtration, 2.53 g of solid, m.p. 193–200°, was obtained as the residue and 1.6 g of material, m.p. 170–175°, was isolated from the filtrate. The two combined higher melting solids (8.50 g) were recrystallized from ethyl acetate to give 8.07 g (25 %) of product, melting at 209–211°. A mixed m.p. with a sample of the 1,6-dimethyl-1,1,2,2,3,3,4,4,5,5,6,6-dodecaphenylhexasilane prepared above showed no depression.

The use of lithium dispersion under similar conditions afforded only 17.8 % of the product.

C. A diethyl ether solution of methylmagnesium iodide (0.007 mole) was added to 2.0 g (0.0024 mole) of 1,6-dichloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecaphenylhexasilane dissolved in 50 ml of THF. After refluxing for 12 h the reaction mixture was hydrolyzed by addition to 10 % hydrochloric acid. The crude product was recrystallized from ethyl acetate to give 1.2 g (62.7 %) of 1,6-dimethyl-1,1,2,2,3,3,4,4,5,5,6,6-dodecaphenylhexasilane, m.p. 209–211°. A mixed melting point with the products prepared above was not depressed.

1,1,2,2,3,3,4,4,5,5,6,6-Dodecaphenylhexasilane. The silyllithium solution obtained from octaphenylcyclotetrasilane as described above was added to 21.8 g (0.10 mole) of diphenylchlorosilane. Upon completion of the addition the color test[11] was negative and the reaction mixture was hydrolyzed with 10 % hydrochloric acid. The crude reaction product was treated with hot ethyl acetate containing 5 % ethanol. There crystallized 7.31 g of product, m.p. 164–180°. This solid was recrystallized twice from the same solvent to give 7.1 g (20.0 %) of pure 1,1,2,2,3,3,4,4,5,5,6,6-dodecaphenylhexasilane, m.p. 185–187°. (Found: Si, 15.28, 15.22. $C_{72}H_{62}Si_6$ calcd.: Si, 15.39 %.)

Several other runs under similar conditions gave yields of 18–20 % of the product. When a modified apparatus, which consisted of a flask with a sintered glass bottom through which the tetrahydrofuran-soluble silyllithium compound could be removed continuously from the insoluble reactants, was used, the yield of the hexasilane increased to 35–40 %.

1,6-Dichloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecaphenylhexasilane. A solution of 8.75 g (0.008 mole) of 1,1,2,2,3,3,4,4,5,5,6,6-dodecaphenylhexasilane in 100 ml of carbon tetrachloride was treated with 3.5 g (0.017 mole) of phosphorus pentachloride. The mixture was refluxed for 6 h and was finally stirred at ice-bath temperature to cause precipitation of the product. Filtration and recrystallization from ethyl acetate provided 6.01 g (64.7 %) of pure product, m.p. 239–241°. Several other preparations gave yields of 60 to 70 %.

Acknowledgement

This research was supported in part by the United States Air Force under Contract 33(616)-6463 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Division, Wright-Patterson AFB, Ohio.

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Received July 7th, 1964