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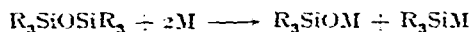
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## SHORT COMMUNICATIONS

### Cleavage reactions of some hexasubstituted disiloxanes by alkali metals

A number of studies concerned with the cleavage reactions of disiloxanes using organometallic compounds have been reported\*. It was shown that the cleavage reaction of symmetrical hexasubstituted disiloxanes by organolithium compounds gave tetrasubstituted silanes and lithium silanolate.<sup>6</sup>

As products of the alkali metal cleavage of a hexasubstituted disiloxane one would expect a trisubstituted silylmetallic compound and a salt of the corresponding silanol



In the present investigation, the lithium cleavage of hexaphenyldisiloxane in tetrahydrofuran gave, after acid hydrolysis, triphenylsilane (67.3%) and triphenylsilanol (76%). The same reaction in 2-methyltetrahydrofuran gave an 84.6% yield of triphenylsilane and an 83.2% yield of triphenylsilanol. When tetrahydropyran was used as the solvent, triphenylsilane and triphenylsilanol were formed in 80.8% and 79.6% yields, respectively. The cleavage reactions started without an appreciable initial time lag.

The ease with which these disiloxane cleavage reactions started prompted us to study the effect of a small amount of added hexaphenyldisiloxane in the lithium cleavage reaction of hexaphenyldisilane<sup>8</sup>. It was observed that the cleavage reaction started in a shorter length of time when a small amount of hexaphenyldisiloxane was present as compared to an identical run which did not contain the disiloxane.

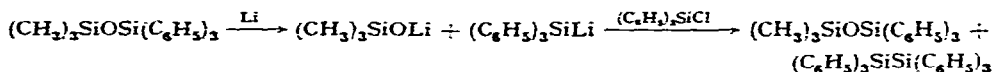
Cleavage reactions using rubidium and cesium in tetrahydrofuran were also carried out. The rubidium cleavage of hexaphenyldisiloxane gave, after reaction with chlorotriphenylsilane, a 69.4% yield of hexaphenyldisilane. Under similar conditions, an 89.7% yield of hexaphenyldisilane was isolated from the cesium cleavage reaction.

Like hexaphenyldisiloxane, hexa-*p*-tolylidisiloxane was readily cleaved by lithium to give, after acid hydrolysis, a 79.3% yield of tri-*p*-tolylsilane and an 81.6% yield of tri-*p*-tolylsilanol.

The lithium cleavage of the unsymmetrical disiloxane, 1,1,1-trimethyl-3,3,3-triphenyldisiloxane gave, after treatment with chlorotriphenylsilane, a 48.9% yield

\* For some general information on cleavage reactions of disiloxanes see refs. 1-7.

of hexaphenyldisilane. 1,1,1-Trimethyl-2,2,2-triphenyldisilane was not isolated. It appears that the alkali metal brought about scission of the bond between oxygen and the silicon atom containing the aryl groups.



Attempts to cleave hexamethyldisiloxane using lithium or cesium in tetrahydrofuran were unsuccessful.

### Experimental

All melting points are uncorrected. The reactions were carried out under an atmosphere of dry, oxygen-free nitrogen. Tetrahydrofuran, boiling at 65–66°, and 2-methyltetrahydrofuran, boiling at 85–86°, were freed from peroxides and moisture before use by refluxing over sodium, followed by distillation from lithium aluminum hydride.

*Hexaphenyldisiloxane and lithium in tetrahydrofuran.* A small amount of tetrahydrofuran (5 ml) was added to a mixture of 5.35 g (0.01 mole) of hexaphenyldisiloxane and 0.69 g (0.1 g-atom) of lithium. About 1 min after the addition of the solvent was started, the mixture became yellow, indicating that the cleavage had started. An additional amount of solvent (45 ml) was added slowly to the mixture, and stirring was continued for 1 h at room temperature. The deep brown solution gave a positive Color Test I<sup>9</sup>. The clear solution was filtered under nitrogen through glass wool and poured into an excess of ice cold, dilute sulfuric acid (4 N). The hydrolyzed solution was extracted with ether, and the ether extract was dried over anhydrous sodium sulfate. Removal of the solvent from the ether solution left a viscous residue, which was chromatographed on alumina. Elution of the column with petroleum ether (b.p. 60–70°) gave 1.75 g (67.3 %) of triphenylsilane, identified by comparison of the infrared spectrum with that of an authentic sample. Elution of the column with methanol gave 2.1 g (76.0 %) of triphenylsilanol, m.p. 154–155° (mixture melting point). The infrared spectrum was identical with that of an authentic sample of triphenylsilanol.

*Hexaphenyldisiloxane and lithium in 2-methyltetrahydrofuran.* A mixture of 2.7 g (0.005 mole) of hexaphenyldisiloxane, 0.35 g (0.05 g-atom) of lithium metal, and 4 ml of 2-methyltetrahydrofuran was stirred at room temperature. The cleavage started after about 30 min of stirring, and the mixture slowly turned brown. After 4 h of stirring, the solution was hydrolyzed as described previously. The usual work-up gave 1.1 g (84.6 %) of triphenylsilane and 1.15 g (83.2 %) of triphenylsilanol. The identities of these products were established by a comparison of the infrared spectra and mixture melting point determinations with authentic samples.

*Hexaphenyldisiloxane and lithium in tetrahydropyran.* The cleavage reaction involving 2.7 g (0.005 mole) of hexaphenyldisiloxane and 0.35 g (0.05 g-atom) of lithium was carried out in 40 ml of tetrahydropyran. The mixture became yellow after 15 min, indicating that cleavage had started. The mixture was stirred for 4 h. The work-up after acid hydrolysis gave 1.05 g (80.8 %) of triphenylsilane and 1.1 g (79.6 %) of triphenylsilanol.

*Hexaphenyldisiloxane and rubidium in tetrahydrofuran.* A mixture of 2.7 g (0.005 mole) of hexaphenyldisiloxane, 1.33 g (0.015 g-atom) of rubidium metal and 40 ml of tetrahydrofuran was stirred at room temperature for 1 h. The cleavage reaction started within 5 min as evidenced by the brown color of the mixture. After

1 h of stirring, the mixture was deep black-brown and gave a positive Color Test I. The solution was added slowly to 2.95 g (0.01 mole) of chlorotriphenylsilane dissolved in 25 ml of tetrahydrofuran. The mixture gave a negative Color Test I and was hydrolyzed by the addition of water. An insoluble residue was removed by filtration and dried to give 1.8 g (69.4 %) of hexaphenyldisilane, m.p. 365–367° (mixture melting point).

The aqueous filtrate was extracted with ether. Removal of the solvent left a white residue which was treated with cold methanol. The methanol-insoluble portion was crystallized from benzene to give 2.6 g (97.2 %) of hexaphenyldisiloxane, m.p. 226–228° (mixture melting point). The methanol-soluble portion was 0.6 g (21.7 %) of triphenylsilanol, m.p. 153–154° (mixture melting point), after recrystallization from cyclohexane.

*Hexaphenyldisiloxane and cesium in tetrahydrofuran.* In a similar experiment, 2.7 g (0.005 mole) of hexaphenyldisiloxane, 1.7 g (0.013 g-atom) of cesium metal and 50 ml of tetrahydrofuran was stirred for 1 h. The cleavage started within less than 1 min, and the deep red-brown solution obtained after 1 h of stirring gave a positive Color Test I. Derivatization was carried out with 2.95 g (0.01 mole) of chlorotriphenylsilane. Work-up as in the previous reaction gave 2.0 g (77.1 %) of hexaphenyldisilane, m.p. 365–367°, 2.4 g (89.7 %) of hexaphenyldisiloxane, m.p. 226–228° and 0.4 g (14.5 %) of triphenylsilanol, m.p. 154–155°. The identities of the products were established by mixture melting point determinations with authentic samples.

*Hexaphenyldisilane and lithium in tetrahydrofuran, with a small quantity of hexaphenyldisiloxane.* Tetrahydrofuran (60 ml) was added slowly to a mixture of 5.2 g (0.01 mole) of hexaphenyldisilane, 0.69 g (0.1 g-atom) of lithium metal and a small quantity (0.1 g) of hexaphenyldisiloxane. The cleavage started within 10 min, and the solution became yellow. After 6 h of stirring at room temperature, the clear, dark brown solution was filtered through glass wool. Acid titration of an aliquot indicated a yield of 92.9 % of silyllithium compound in the solution. Derivatization with 5.9 g (0.02 mole) of chlorotriphenylsilane gave 9.5 g (81.9 %) of hexaphenyldisilane, m.p. 365–367° (mixture melting point).

In an identical run using the same amounts of hexaphenyldisilane, lithium and tetrahydrofuran, but without hexaphenyldisiloxane, it was observed that 25 min were required before initiation of the cleavage reaction.

*Hexa-*p*-tolylidisiloxane and lithium in tetrahydrofuran.* A mixture of 3.1 g (0.005 mole) of hexa-*p*-tolylidisiloxane, 0.4 g (0.05 g-atom) of lithium and 40 ml of tetrahydrofuran was stirred at room temperature for 4 h. The solution became pale brown after 5 min. After 4 h, the solution was deep brown and gave a positive Color Test I. The reaction mixture was hydrolyzed by pouring into an excess of ice-cold sulfuric acid (4 N). Extraction with ether and removal of the solvent from the ether solution gave a viscous liquid which was chromatographed on alumina.

Elution of the column with petroleum ether (b.p. 60–70°) gave 1.2 g (79.3 %) of tri-*p*-tolylsilane, identified by comparison of the infrared spectrum with that of an authentic sample. The infrared spectrum showed the Si–H absorption band at 2105  $\text{cm}^{-1}$ . Elution of the column with methanol gave 1.3 g (81.6 %) of tri-*p*-tolylsilanol, which melted at 97–98° after crystallization from petroleum ether (b.p. 60–70°). The melting point was not depressed when admixed with an authentic sample. The infrared spectrum, which was identical with that of an authentic sample, showed the Si–OH absorption band at 3795  $\text{cm}^{-1}$ .

*1,1,1-Trimethyl-3,3,3-triphenyldisiloxane and lithium in tetrahydrofuran.* Tetrahydrofuran (50 ml) was added slowly to a mixture of 3.5 g (0.01 mole) of 1,1,1-trimethyl-3,3,3-triphenyldisiloxane and 0.69 g (0.1 g-atom) of lithium metal. The cleavage started within 2 min, and the solution slowly turned deep brown. Color Test I was positive. The clear solution was filtered through glass wool and treated with 5.9 g (0.02 mole) of chlorotriphenylsilane dissolved in 30 ml of tetrahydrofuran. Subsequent to aqueous hydrolysis and the usual work-up, there was obtained 2.8 g (54.0%) of hexaphenyldisilane, m.p. 365–367°, 2.7 g (48.9%) of triphenylsilanol, m.p. 153–154° and 1.2 g (34.4%) of 1,1,1-trimethyl-3,3,3-triphenyldisiloxane, m.p. 48–49°. The identities of the products were established by mixture melting point determinations with authentic samples.

*Hexamethyldisiloxane and lithium in tetrahydrofuran.* A mixture of 4.1 g (0.025 mole) of hexamethyldisiloxane, 1.7 g (0.25 g-atom) of lithium metal and 25 ml of tetrahydrofuran was stirred at room temperature. After 144 h, the solution was slightly turbid due to a suspension of finely divided lithium metal. However, Color Test I remained negative throughout the period of stirring, indicating the absence of a cleavage product.

In a second run using the same amounts of reactants and solvent, a small amount of hexaphenyldisiloxane was added. Even after 72 h of stirring, cleavage could not be detected.

*Hexamethyldisiloxane and cesium in tetrahydrofuran.* A mixture of 2.05 g (0.0125 mole) of hexamethyldisiloxane, 3.32 g (0.025 g-atom) of cesium metal and 25 ml of tetrahydrofuran was stirred at room temperature for 72 h. There was no observable reaction and Color Test I remained negative throughout.

In a second run, a small quantity of hexaphenyldisiloxane was added. The solution turned pale black, due to cleavage of hexaphenyldisiloxane, but cleavage of the hexamethyldisiloxane did not take place. Almost all of the hexamethyldisiloxane was recovered.

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