The Pyrolysis of Organodisilanes

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It has previously been reported[1] that hexamethyldisilane undergoes rearrangement at 600°C to give trimethyl(dimethylsilylmethyl)silane. The experiments described below will deal with the analysis of the products of this reaction, together with related investigations.

After hexamethyldisilane was passed slowly through a quartz tube heated at 600°C, the reaction products were collected in a trap immersed in a liquid-nitrogen bath. The careful examination of the reaction mixture by gas chromatography revealed that there were two main products, trimethylsilane (I) and trimethyl(dimethylsilylmethyl)silane (II), along with unchanged hexamethyldisilane. The formation of these compounds is consistent with the reaction scheme we proposed earlier:

$$(CH_3)_3Si\text{-}Si(CH_3)_3 \rightarrow 2(CH_3)_3Si\cdot$$

$$\begin{aligned}(CH_3)_3Si\cdot + (CH_3)_3SiSi(CH_3)_3 &\rightarrow \\ \underset{\text{(I)}}{(CH_3)_3SiH} &+ (CH_3)_3SiSi(CH_3)_2CH_2\cdot\end{aligned} \tag{2}$$

$$(CH_3)_3SiSi(CH_3)_2CH_2\cdot \rightarrow \cdot Si(CH_3)_2CH_2Si(CH_3)_3 \tag{3}$$

$$\begin{aligned}\cdot Si(CH_3)_2CH_2Si(CH_3)_3 + (CH_3)_3SiSi(CH_3)_3 &\rightarrow \\ \underset{\text{(II)}}{(CH_3)_3SiCH_2Si(CH_3)_2H} &\\ + (CH_3)_3SiSi(CH_3)_2CH_2\cdot&\end{aligned} \tag{4}$$

The ratio of the amount of II to that of I was found to be approximately 4 : 1 by gas chromatographic analysis. Accordingly, this value indicates that the average kinetic chain length of the reaction is about 4.

In this connection, a typical free radical reaction initiated by benzoyl peroxide in hexamethyldisilane was investigated at 80°C. The main products of the reaction between hexamethyldisilane and benzoyl peroxide were benzene, benzoic acid, 1, 2-bis(pentamethyldisilanyl)ethane (III), benzylpentamethyldisilane, and a small amount of an unidentified compound. No rearranged product, II, was formed. Therefore, in a solution at a low temperature, the pentamethyldisilanylmethyl radical does not undergo rearrangement as in the pyrolysis. Only dimerization was the main fate of this free radical.

$$2(CH_3)_3SiSi(CH_3)_2CH_2\cdot \rightarrow \underset{\text{(III)}}{(CH_3)_3SiSi(CH_3)_2CH_2CH_2(CH_3)_2SiSi(CH_3)_3}$$

Judging from this fact, the reaction 3 seems to be rate-determining and to require a higher activation energy than the other processes.

Finally, it is interesting to note that 1, 2-diphenyltetramethyldisilane did not undergo rearrangement at 600°C. The recovered material was essentially as pure as the starting material. Apparently, the substitution of phenyl groups increases the dissociation energy of the silicon-silicon bond.

Experimental

Trimethylsilane (I).—This was prepared from trimethylchlorosilane by reduction with lithium aluminum hydride in di-*n*-butyl ether.

Trimethyl(dimethylsilylmethyl)silane (II). — This was prepared from trimethyl(dimethylchlorosilylmethyl)silane by reduction with lithium aluminum hydride in ether. To a stirred suspension of 4.4 g. (0.11 mol.) of lithium aluminum hydride in 200 ml. of dry ether, there was added, drop by drop, 25 g. (0.138 mol.) of trimethyl(dimethylchlorosilylmethyl)silane dissolved in 100 ml. of ether. During the addition, a gentle reflux of the ether was observed to take place. The reaction mixture was heated to reflux for 7 hr. and then submitted to distillation under reduced pressure. After the solvent had been removed, the mixture was fractionally distilled to give 12 g. (59%)

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[1] K. Shiina and M. Kumada, *J. Org. Chem.*, **23**, 139 (1958).

of II boiling at 118°C, n_D^{20} 1.4168. Topchiev et al.[2] prepared II from dichloro(trichlorosilylmethyl)silane, b. p. 119—20°C, n_D^{20} 1.4158.

The Pyrolysis of Hexamethyldisilane.—Hexamethyldisilane (40 g., 0.27 mol.) was passed slowly through a 3.7×50 cm. quartz tube mounted in a thermostatted furnace at 600°C. The reaction products, with unchanged hexamethyldisilane, were collected in a trap which was directly linked with the quartz tube and immersed in a liquid-nitrogen bath. The amount of material recovered was 38 g. The mixture was then analyzed on a gas chromatographic column packed with Apiezon L on Celite 545. The components were eluted on this column in the order of I (4.3 mol.%), a trace of an unidentified component, hexamethyldisilane (78.2 mol.%), II (17.5 mol.%), and a trace of another unidentified component.

The Attempted Pyrolysis of 1, 2-Diphenyltetramethyldisilane.—Diphenyltetramethyldisilane (20 g.; 0.074 mol.) was evaporated at reduced pressure (2 mmHg) and then passed slowly through the quartz tube described above at 600°C. The material thus recovered (17 g.) was analyzed on a gas chromatographic column packed with Apiezon L on Celite 545; this disclosed a single peak of the starting material.

The Decomposition of Benzoyl Peroxide in Hexamethyldisilane.—To a 200 ml. four-necked flask equipped with a mechanical stirrer, a reflux condenser, a thermometer, and a gas inlet tube, there were added 15 g. (0.062 mol.) of benzoyl peroxide and 100 g. (0.683 mol.) of hexamethyldisilane. The mixture was then heated at 100°C, stirred for 6 hr. under a slow stream of nitrogen, and cooled. The reaction mixture was washed with a saturated sodium bicarbonate solution and with water. The organic layer was dried and subjected to distillation. The fraction boiling at temperatures up to 110°C and that boiling at 110—113°C were mainly composed of recovered hexamethyldisilane and a small amount of benzene. The fraction boiling over the range from 100 to 120°C at 18 mmHg was found to consist mainly of 1, 2-bis(pentamethyldisilanylmethyl)ethane,[3] plus a small amount of benzylpentamethyldisilane. Both compounds were separated by gas chromatography (Silicone DC 550 on Celite 545) and identified by comparing their infrared spectra and retention times with those of authentic samples.

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[2] A. V. Topchiev, N. S. Nametkin and L. S. Povarov, *Doklady Akad. Nauk S. S. S. R.*, **97**, 99 (1954).

[3] H. Sakurai, T. Kishida, A. Hosomi and M. Kumada, *J. Organometal. Chem.* in press.