The Preparation of Some Silanol Derivatives of Triphenylsiloxy-substituted Siloxanes

Toshio TAKIGUCHI, Minoru ABE, Kōji URANO and Takeo SAKUMA

Department of Synthetic Chemistry, Kiryu College of Technology, Gunma University, Tenjin-cho, Kiryu

(Received June 17, 1967)

In the course of the preparation of hydroxyl derivatives of some triphenylsiloxy-substituted chlorosilanes, the following silanols were isolated and characterized; hexaphenyltrisiloxane-3, 3-diol, 3, 5-di(triphenylsiloxy)hexaphenyltetrasiloxane-3, 5-diol, and triphenylsiloxysilanetriol, the latter two being new compounds. The 3, 5-diol melting at 179°C was obtained from the reaction of 3, 3-dichlorohexaphenyltrisiloxane with zinc oxide, followed by hydrolysis, while the triol melting 78°C was obtained by the hydrolysis of triphenylsiloxytrichlorosilane in ether, using aniline as a hydrogen-chloride acceptor.

The silanols were all crystalline substances of less chemical stability, especially towards acid and alkali. The tendency to condense to polysiloxane was especially marked in the case of the triol; storing the triol in a sealed soda lime glass ampoule still could not prevent its condensation.

All attempts to obtain tris(triphenylsiloxy)-silanol from the corresponding chlorosilane were unsuccessful.

Experimental

Triphenylsiloxytrichlorosilane. The reaction of sodium triphenylsilanolate (neut equiv 295—297) with silicon tetrachloride in dry toluene gave triphenylsiloxytrichlorosilane, mp 47—48°C, bp 180—183°C/3 mmHg (lit., mp 47—48°C, bp 256—260°C/30 mmHg[1]), the yield being 52% (mean).

Found: Si, 13.6; Cl, 25.4%; mol wt, 370. Calcd for $C_{18}H_{15}OSi_2Cl_3$: Si, 13.7; Cl, 26.0%; mol wt, 410.

3, 3-Dichlorohexaphenyltrisiloxane. The reaction of sodium triphenylsilanolate with an equimolar triphenylsiloxytrichlorosilane in dry benzene gave 3, 3-dichlorohexaphenyltrisiloxane as an acicular crystal in a consistent yield of 50—53%, mp 140—141°C (lit., mp 134—135°C[1]).

Found: Si, 12.8; Cl, 9.9%; mol wt, 622. Calcd for $C_{36}H_{30}O_2Si_3Cl_2$: Si, 13.0; Cl, 10.9%; mol wt, 649.

3-Chloro-3-triphenylsiloxyhexaphenyltrisiloxane. Triphenylsilanol (55.2 g, 0.2 mol) was converted to sodium triphenylsilanolate in dry benzene and then

1) V. S. Chugunov, *Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk,* **1956**, 1059.

added to silicon tetrachloride (6.8 g, 0.04 mol), after which the mixture was allowed to reflux for 5 hr. From the resultant mixture, 3-chloro-3-triphenylsiloxyhexaphenyltrisiloxane, mp 239—240°C (lit., mp 219—220°C) was obtained as fine platelets, the yield being 80% (28 g).

Found: Si, 13.1; Cl, 3.34%; mol wt, 898. Calcd for $C_{54}H_{45}O_3Si_4Cl$: Si, 12.6; Cl, 4.0%; mol wt, 889.

Triphenylsiloxysilanetriol. In a 2-*l* three-necked flask equipped with a stirrer, a condenser, and a dropping funnel, there were placed freshly distilled aniline (14.0 g, 0.015 mol), distilled water (0.27 g, 0.015 mol), 1000 m*l* of dry ether, and enough acetone to render the mixture homogeneous. With vigorous stirring, a cooled solution of triphenylsiloxytrichlorosilane (20.5 g, 0.005 mol) in 300 m*l* of ether was added, drop by drop, over a period of 2 hr to the mixture in the flask, which had been cooled in a dry ice - kerosene bath. After the entire addition, the white precipitates, aniline hydrochloride, was removed by filtration, and the filtrate was concentrated to 100 m*l* *in vacuo*, after which a 200-m*l* portion of hot hexane was added. After the resultant product had stood overnight, the fine needles which had formed were collected and rinsed twice with cold cyclohexane to give 3.1 g (17.9%) of triphenylsiloxysilanetriol melting at 78°C.

Found: C, 58; H, 5.0; Si, 15.7%; OH/mol, 2.92 (Zerewitinoff); mol wt, 359. Calcd for $C_{18}H_{18}O_4Si_2$: C, 61.0; H, 5.1; Si, 15.9%; OH/mol, 3.0; mol wt, 355.

As has been anticipated, the triol was extremely unstable; the addition of a trace amount of acid or alkali to the triol solution rapidly polymerized the triol to insoluble white precipitates.

The storage of the triol in a soda-lime glass ampoule was not found free from objection, while the use of an acid-rinsed Pyrex glass ampoule was rather effective in preventing the polymerization, *i. e.*, very little lowering in the melting point was observed after three months' storage.

The triol was well defined by the IR absorption spectra; X-ray powder patterns were also recorded for purposes of rapid identification. They may be shown as follows:

IR Data: 3613(M), 3480(S), 3062(M), 1592(W), 1487(W), 1430(S), 1191(W), 1120(VS), 1080(S), 1028(W), 997(W), 940(S), 675 cm^{-1}(S). X-Ray powder patterns: d, $kX(I/I_0)$, 17.70(0.46), 9.94(0.45), 5.99 (0.28), 5.34(0.45), 4.98(1.00), 4.82(0.80), 4.35(0.54), 3.99(0.36), 3.92(0.23), 3.31(0.33).

Hexaphenyltrisiloxane - 3, 3 - diol. A procedure analogous to the hydrolysis of triphenylsiloxytrichlorosilane was applied to 3, 3-dichlorohexaphenyltrisiloxane. From the direct hydrolysis of 3, 3-dichlorohexaphenyltrisiloxane (13.0 g, 0.02 mol), a white crystalline mass melting at 146—155°C was obtained. The recrystallization of the product from benzene-hexane (1 : 1) afforded 10.6 g (86%) of pure hexaphenyltrisiloxane-3, 3-diol melting at 167—169°C (lit., mp 168—169°C[1]).

Found: Si, 13.5%; mol wt, 623. Calcd for $C_{36}H_{32}O_4Si_3$: Si, 13.7%; mol wt, 613.

3, 5-Di(triphenylsiloxy)hexaphenyltetrasiloxane-3, 5-diol. A solution of tetrahydrofuran containing 3, 3-dichlorohexaphenyltrisiloxane (13.0 g, 0.02 mol) and finely-powdered zinc oxide (2.4 g, 0.03 mol) was refluxed for an additional 2 hr. After the resultant mixture had been evaporated to about half a volume, a white crystalline mass was obtained, from which 5.1 g (34%) of 3, 5-di(triphenylsiloxy)hexaphenyltetrasiloxane-3, 5-diol melting at 179°C was isolated, together was 6.2 g (50.6%) of hexaphenyltrisiloxane-3, 3-diol, the hydrolysis product of the starting material.

By refluxing an alcoholic solution of hexaphenyltrisiloxane-3, 3-diol in the presence of caustic alkali, this 3, 5-diol was also obtained in a yield of less than 8% (mean), the majority of the 3, 3-diol being converted to the cleavage product, including hexaphenyldisiloxane and the high-melting phenylpolysiloxanes.

Found: C, 70; H, 5.1; Si, 14.5%; OH/mol, 1.90; mol wt, 1240 (ebullioscopically in chloroform). Calcd for $C_{72}H_{60}O_7Si_6$: C, 71.7; H, 5.0; Si, 14.0%; OH/mol, 2.0; mol wt, 1206.

IR Data: 3645(M), 3026(M), 1590(M), 1485(M), 1425(VS), 1188(M), 1155(M), 1115(VS), 1068(VS), 1026(S), 995(S), 945(M), 842(M), 742(S), 680 cm^{-1} (VS). X-Ray powder patterns: d, $kX(I/I_0)$, 12.30 (1.00), 9.31(0.24), 6.66(0.25), 6.15(0.35), 4.75(0.47), 4.65(0.77), 4.40(0.32), 4.29(0.72), 4.19(0.28), 3.33 (0.45).

Hydrolysis of Tris(triphenylsiloxy)chlorosilane. The hydrolysis of tris(triphenylsiloxy)chlorosilane was carried out by several methods, however, the corresponding silanol could not be obtained in any appreciable quantities.

From the reaction of the chlorosilane with sodium hydrogen carbonate in ethyl acetate at the refluxing temperature, the starting chlorosilane was recovered entirely unchanged. This procedure[2] has been reported to give the corresponding silanol almost quantitatively when applied to diphenyldichlorosilane as a sample.

Very similar results were obtained when the chlorosilane was hydrolyzed in ether, using aniline as hydrogen-chloride acceptor.

Refluxing the solution of the chlorosilane in benzene-ethanol (1 : 1) in the presence of sodium hydroxide gave hexaphenyldisiloxane as the sole crystalline product; this is in direct contrast to the information given by Chugunov[1] who has reported the formation of tris(triphenylsiloxy)silanol from this sort of reaction.

A variety of runs involving variations in the concentration of alkali, the refluxing temperature, and the time only resulted in minor fluctuations in the yield of hexaphenyldisiloxane, which varied from 70 up to 85%. These conflicting results still remain unsolved; further, more detailed investigations are being undertaken.

The authors' thanks are due to the Shin-etsu Chemical Industrial Co. for the supply of triphenylchlorosilane used in the present work.

2) T. Takiguchi, This Bulletin, **32**, 556 (1959).