SUBSTITUTION REACTIONS IN ORGANOCYCLOSILOXANES CONTAINING FUNCTIONAL GROUPS ATTACHED TO THE SILICON ATOM

K. A. Andrianov and A. B. Zachernyuk

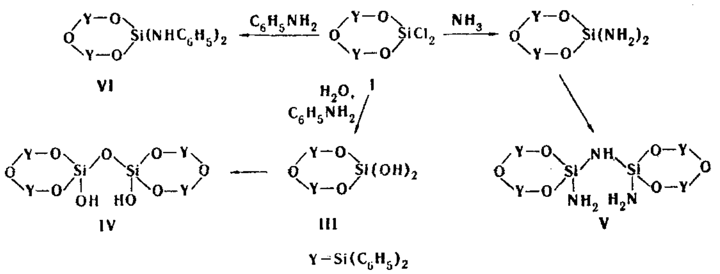
UDC 542.(938+958):547.79'128

New hydroxy and amino derivatives of diphenylcyclosiloxanes were synthesized by the reaction of 1,1-dichlorotetraphenylcyclotrisiloxane and chlorotetraphenylcyclotrisiloxane with nucleophilic reagents. Replacement of the halogen attached to the silicon atom in these reactions is not accompanied by ring opening.

Only three papers [1-3] have been devoted to the study of the chemical transformations of organohalocyclosiloxanes in nucleophilic substitution reactions, whereas it is known that organocyclosiloxanes are extremely active in reactions with nucleophilic and electrophilic reagents. Under the influence of even catalytic amounts of the latter, they may react with ring opening to give polymers.

The activity of organocyclosiloxanes in reactions with nucleophilic reagents increases when the substituents attached to the silicon atom increase its positive polarizability. In this connection, a study of organocyclosiloxanes containing two identical or different functional groups attached to the silicon atom is of great theoretical interest.

In the present research we have studied some nucleophilic substitution reactions in previously synthesized [4,5] six-membered cyclic compounds – 1,1-dichlorotetraphenylcyclotrisiloxane (I) and chlorotetraphenylcyclotrisiloxane (II).



The product of the hydrolysis of I under mild conditions (pH 6.5-7.0) is tetraphenylcyclotrisiloxane-1,1-diol (III), the structure of which is confirmed by the results of functional analysis and the IR spectrum. The signal of the protons of the hydroxyl groups in the PMR spectrum of III lies at 6.34 ppm, and the ratio of the intensities of the $H_{C_6H_5}$ to H_{OH} signals (10.2 : 1) also confirms its structure. Diol III readily condenses even at room temperature, and when it is refluxed in dilute solution in o-xylene it condenses to give a solid, the percentage of hydroxyl groups in which corresponds to the formula of siloxane IV. Further condensation at the hydroxyl groups does not occur under the indicated conditions.

A crystalline substance was isolated from the mixture of the products of ammonolysis of I in liquid ammonia. Two bands at 3395 and 3480 cm^{-1}, characteristic for the stretching vibrations of the amino

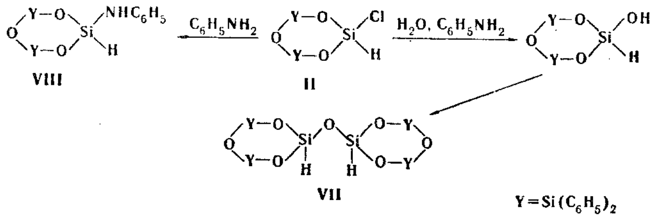
---

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1183-1185, September, 1972. Original article submitted August 5, 1971.

groups, a band at 1552 cm^{-1}, which corresponds to the deformation vibrations of the amino groups, and a maximum at 915 cm^{-1}, characteristic for the asymmetrical stretching vibrations of the Si–N–Si grouping, were observed in the IR spectrum of the mixture. This made it possible to assume that the compound obtained is the product of partial condensation of the initially formed 1,1-diaminotetraphenylcyclotrisiloxane. The ratio of the intensities of the $H_{C_6H_5}$ to H_{NH} signals (8.07:1) in the PMR spectrum, the results of elementary analysis, and the molecular weight found for the compound correspond to formula V. When V is heated to the melting point, it undergoes further condensation with ammonia evolution. In this case, the formation of cyclic structures is likely, since the absorption bands characteristic for primary amino groups are absent in the IR spectra of the condensation products.

The reaction of I with aniline proceeds with the formation of 1,1-dianilinotetraphenylcyclotrisiloxane (VI). Compound VI is stable at room temperature but undergoes partial condensation with the liberation of aniline on vacuum distillation.

A study of the hydrolysis and ammonolysis of chlorotetraphenylcyclotrisiloxane (II) demonstrated that the active halogen atom can be replaced without involvement of the Si–H bond:



Tetraphenylcyclosiloxanol is formed in the hydrolysis of II in the presence of aniline, since intense absorption bands corresponding to hydroxyl groups are present in the IR spectrum of the reaction product. However, it undergoes condensation on vacuum distillation, as a result of which a compound, which, according to the results of elementary analysis and the IR spectrum, corresponds to formula VII, was obtained.

The solid product of the replacement of chlorine by a phenylamino group – anilinotetraphenylcyclotrisiloxane (VIII) – was obtained by the action of aniline on II.

The investigations demonstrated that substitution reactions in I and II proceed without ring opening. The absorption maximum at 1025-1040 cm^{-1}, which is characteristic for the vibrations of the siloxane bond in the starting rings, serves as an additional confirmation of the cyclic structures of all of the synthesized compounds.

EXPERIMENTAL

Tetraphenylcyclotrisiloxane-1,1-diol (III). A solution of 12.6 g (25.6 mmole) of I in 40 ml of dry diethyl ether was added with stirring to 0.89 g (49 mmole) of water and 4.57 g (49 mmole) of aniline in 75 ml of diethyl ether and 15 ml of acetone at 0° in the course of 1.5 h while maintaining the pH of the medium at 6.5-7.0. The salt of aniline was removed by filtration, and 80% of the solvent was evaporated to precipitate crystals with mp 54-58°. Recrystallization from diethyl ether gave 7.8 g of III as plates with mp 61°. Found: C 60.9; H 4.5; Si 17.8; OH 7.2%. $C_{24}H_{22}O_5Si_3$. Calculated: C 60.7; H 4.6; Si 17.7; OH 7.2%.

A solution of 2.4 g of III in 48 ml of o-xylene was refluxed for 10 h. Removal of the xylene gave a vitreous product (probably siloxane IV) with mp 80-84°. Found: OH 3.9%. $C_{48}H_{42}O_9Si_6$. Calculated: OH 3.7%.

Ammonolysis of I. A total of 30 ml of dry diethyl ether and 10 ml of dry ammonia were placed in a three-necked flask cooled with a mixture of acetone and dry ice. The mixture was stirred while 5.12 g (0.01 mole) of I in 15 ml of diethyl ether was added in the course of 30 min. The precipitated ammonium chloride was then removed rapidly by filtration under argon. The solvent was evaporated, and the residue was recrystallized from petroleum ether to give 2.1 g of crystalline V with mp 128-130° (dec.). Found: C 62.0; H 4.7; Si 18.1; N 2.3%; mol. wt. 914. $C_{48}H_{45}N_3O_6Si_6$. Calculated: C 62.1; H 4.8; Si 18.0; N 4.5%; mol. wt. 927.

1,1-Dianilinotetraphenylcyclotrisiloxane (VI). A solution of 6.8 g (13 mmole) of I in 25 ml of benzene was added in the course of 1.5 h to a solution of 6.2 g (65 mmole) of aniline in 30 ml of benzene with vigorous stirring at room temperature. The mixture was refluxed for another 3 h, after which the precipitate was removed by filtration, and the filtrate was evaporated. The residue was recrystallized from benzene–petroleum ether to give 4.6 g of VI with mp 167-168°. Found: C 69.5; H 5.3; N 4.4; Si 13.1%. $C_{36}H_{32}N_2O_3Si_3$. Calculated: C 69.2; H 5.1; N 4.5; Si 13.4%.

Hydrolysis of II. A 4.6-g (97 mmole) sample of II was hydrolyzed in the presence of 0.9 g (97 mmole) of aniline, as in the case of I. Removal of the solvent gave a viscous uncrystallizable liquid. Fractionation gave 0.98 g of VII with bp 340-350° (0.02 mm) Found: C 62.5; H 4.9; Si 18.8%. $C_{48}H_{42}O_7Si_6$. Calculated: C 64.1; H 4.7; Si 18.7%.

1-Anilinotetraphenylcyclotrisiloxane (VIII). This compound (3.3 g), with mp 143.5-145° (from n-heptane), was obtained by the method used to obtain VI from 6.6 g (14 mmole) of II and 3.0 g (32 mmole) of aniline. Found: C 66.7; H 5.2; N 2.4; Si 15.3%. $C_{30}H_{27}NO_3Si_3$. Calculated: C 67.5; H 5.1; N 2.6; Si 15.8%.

The PMR spectra of III and V in acetone were recorded with a Hitachi-Perkin Elmer R-20 spectrometer. Tetramethylsilane was used as the internal standard. The IR spectra were recorded with a UR-10 spectrophotometer.

LITERATURE CITED

1. N. N. Sokolov and S. M. Akimova, Zh. Obshch. Khim., 26, 2276 (1956).
2. K. A. Andrianov, L. M. Volkova, and L. M. Tartakovskaya, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 264 (1963).
3. K. A. Andrianov and L. M. Volkova, Izv. Akad. Nauk SSSR, Otd.Khim. Nauk, 264 (1962).
4. T. C. Wu and C. A. Hirt, J. Organomet. Chem., 11, 17 (1968).
5. K. A. Andrianov, A. B. Zachernyuk, and S. A. Danilov, Khim. Geterotsikl. Soedin., 893 (1972).