SYNTHESIS OF ORGANOSILICON COMPOUNDS CONTAINING PHENYLENESILOXANE MOLECULAR CHAINS

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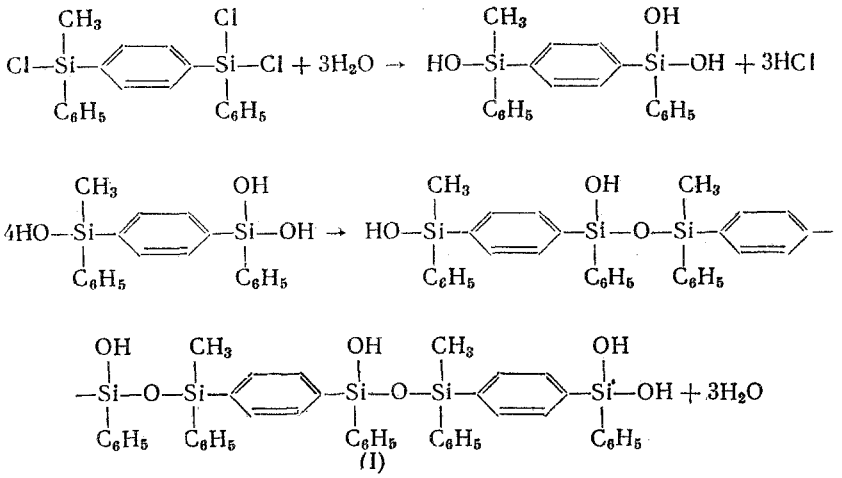
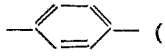
In previous communications [1-3] we described some organosilicon compounds containing silicon atoms in the para positions in benzene. In the further development of these investigations we examined the hydrolysis of 1-(chloromethylphenylsilyl)-4-(dichlorophenylsilyl)benzene and of p-bis(dichlorophenylsilyl)benzene in an aqueous-ethereal medium. The experiments showed that, unlike trifunctional compounds such as alkyl(or aryl)halosilanes and alkyl(or aryl)alkoxysilanes, the above compounds, despite their high functionality, do not form high polymers on hydrolysis.

On hydrolysis of 1-(chloromethylphenylsilyl)-4-(dichlorophenylsilyl)benzene in an acid medium, reaction proceeds with formation in 99.1% yield of a crystalline compound in accordance with the scheme:



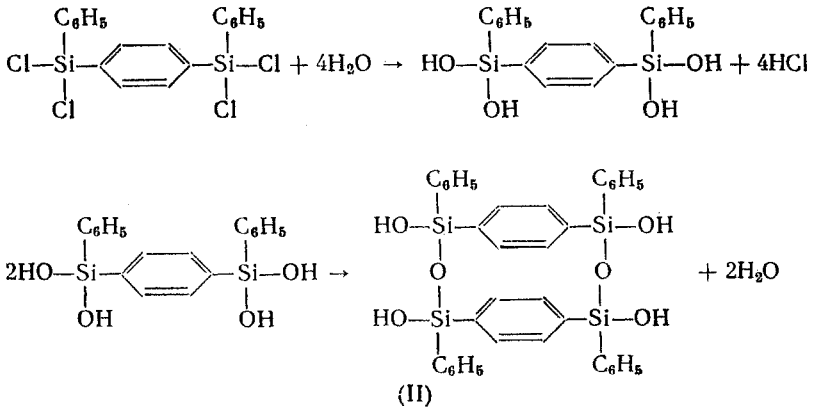
(I)

Investigation of this compound showed that it contained 7.5% of hydroxy groups; its molecular weight was 1329. The elementary composition corresponded to the compound (I).

Investigation of the infrared spectrum showed the presence of vibration frequencies corresponding to the bonds CH_3-Si (800 and 1260 cm^{-1}); C_6H_5-Si (483, 743, 1124 and 1421 cm^{-1});  (545 and 1140 cm^{-1}); HO—Si (850-900, ~3400 and 3680 cm^{-1}). Moreover, vibration frequencies of Si—O—Si bonds lying in the 1075 cm^{-1} region correspond to a linear compound. This is confirmed also by analytical data on hydroxyl content.

The resulting compound was readily soluble in acetone, benzene, chlorobenzene, toluene, carbon tetrachloride, ether, dioxane, s-tetrachloroethane, chloroform, cyclohexanone, aniline, and cresol. Its melting point was 84-85°. When heated, it readily lost water and was converted into a more complex compound.

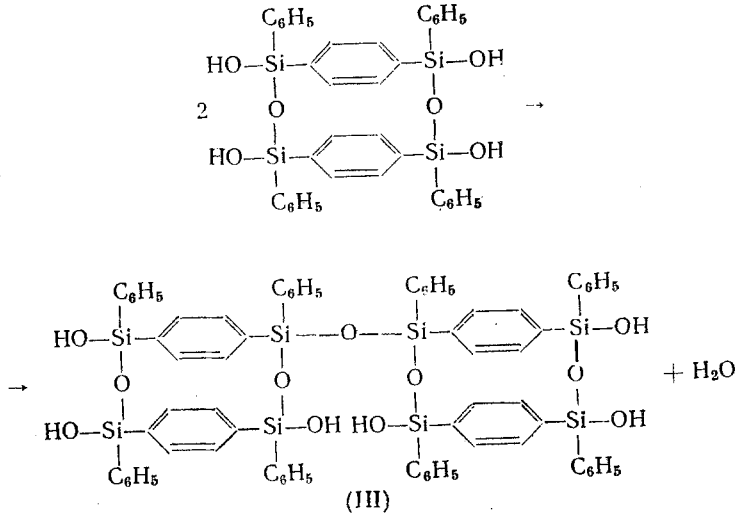
On hydrolysis in an acid medium, p-bis(dichlorophenylsilyl)benzene gives a cyclic compound of low molecular weight in 83.5% yield; this is cyclic phenylenebis(hydroxyphenylsilyl)dioxide, formed in accordance with the scheme:



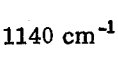
(II)

Investigation of the infrared spectrum of this compound showed the presence of vibration frequencies corresponding to the bonds C_6H_5–Si (483, 473, 1124 and 1421 cm^{-1});  (545 and 1140 cm^{-1}); HO–Si (850-900, ~3400 and 3680 cm^{-1}). The vibration frequencies of Si–O–Si bonds lay in the region 1015-1080 cm^{-1}. The elementary composition and molecular weight corresponded to the compound (II).

Cyclic phenylenebis(hydroxyphenylsilyl) dioxide was soluble in the cold in dioxane, acetone, s-tetrachloroethane, ether, aniline, cyclohexanone, chloroform, methanol, and ethanol; it was soluble hot in benzene, toluene, chlorobenzene, and cresol; it was insoluble in carbon tetrachloride, petroleum ether, 1,2-dibromoethane, cyclohexane, octamethylcyclotetrasiloxane, and water. It melted at 93-104°, i.e., when the compound was heated, polycondensation set in. In boiling benzene condensation resulted in the formation of a polymer of molecular weight 3770. We observed that, on being left for a long time as a 50% solution in ether-toluene mixture, cyclic phenylenebis(hydroxyphenylsilyl) dioxide condenses and becomes insoluble. According to the results of elementary analysis and of infrared-spectrum determinations the condensation of this compound leads to the formation of a bisheterocycle in accordance with the equation:

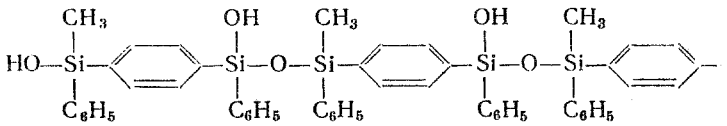


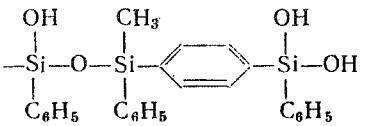
(III)

The infrared spectrum contained frequencies corresponding to the bonds C_6H_5–Si (483, 473, 1124 and 1421 cm^{-1});  (545 and 1140 cm^{-1}); HO–Si (850-900, ~3400 and 3680 cm^{-1}); the vibration frequencies of the Si–O–Si bonds lay in the region 1015-1080 cm^{-1}. The Si–O–Si absorption band at 1080 cm^{-1} in the spectrum of (II) had one maximum, whereas in the spectrum of (III) the most intense Si–O–Si band lay in the range 1015-1080 cm^{-1}. The proportion of hydroxy groups in (III) was less than in (II).

EXPERIMENTAL

Preparation of the Linear Compound. A hydrolysis apparatus was charged with 256.4 g (0.7 mole) of 1-(chloromethylphenylsilyl)-4-(dichlorophenylsilyl)benzene and 700 ml of ether, and hydrolysis was carried out with water at 18-25°. The duration of the hydrolysis was three hours. The ethereal solution was washed with water until neutral and filtered. Removal of ether left gleaming white crystals. We obtained 235.2 g (99.1%) of a substance, m.p. 84-85°, corresponding to the formula:





The substance was purified by two reprecipitations from carbon tetrachloride solution with petroleum ether (2.5 g of the substance was dissolved in 4 ml of carbon tetrachloride, and 10 ml of petroleum ether was added).

We did not establish the positions of the groups in this compound. Found: C 67.34, 67.41; H 5.38, 5.35; Si 16.37, 16.20; OH 7.52, 7.60%; mol. wt. 1305, 1353. $C_{76}H_{74}Si_8O_9$. Calculated: C 67.31; H 5.50; Si 16.57; OH 7.52%; mol. wt. 1356.

Preparation of Cyclic Phenylenebis(hydroxyphenylsilyl) Dioxide. The hydrolysis apparatus was charged with 428.3 g (1 mole) of p-bis(dichlorophenylsilyl)benzene and 1300 ml of ether. The hydrolysis and subsequent treatment were carried out under the conditions indicated for the preparation of the linear compound. We obtained 281 g (83.5%) of a substance corresponding to a cyclic phenylenebis(hydroxyphenylsilyl) dioxide. Found: C 64.20, 64.28; H 4.74, 4.86; Si 16.87, 16.80%; mol. wt. (in dioxane) 681, 682. $C_{36}H_{32}Si_4O_6$. Calculated: C 64.25; H 4.79; Si 16.70%; mol. wt. 673.

Preparation of the Bisheterocycle from Cyclic Phenylenebis(hydroxyphenylsilyl) Dioxide. Toluene-ether solutions of 50% strength, or solutions of greater strength in ether only, were prepared of the cyclic phenylenebis-(hydroxyphenylsilyl) dioxide and kept for 4-6 months, after which condensation to the bisheterocycle had occurred. Found: C 65.37, 65.60; H 4.74, 4.87; Si 16.51, 16.44%. $C_{72}H_{62}Si_8O_{11}$. Calculated: C 61.12; H 4.70; Si 16.93%.

SUMMARY

1. A linear organosilicon compound with a phenylenesiloxane chain and a cyclic phenylenebis(hydroxyphenylsilyl) dioxide was synthesized.

2. A bisheterocyclic compound was isolated.

LITERATURE CITED

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2. K. A. Andrianov, V. E. Nikitenkov and N. N. Sokolov, Izv. AN SSSR, Otd. khim. n. 1960, 1224.
3. K. A. Andrianov, V. E. Nikitenkov and N. N. Sokolov, Vysokomolekulyarnye soedineniya 2, 158 (1960).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
