HETEROFUNCTIONAL CONDENSATION OF CHLOROSILANES WITH TETRA- AND HEXAPHENYLSILOXANEDIOLS

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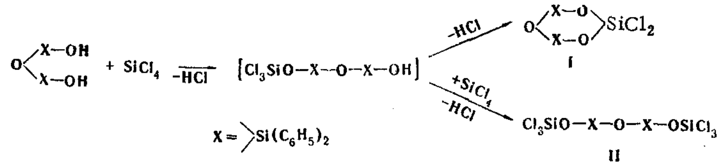
A number of new chloro- and hydrochlorosiloxanes with cyclic and linear structures were synthesized by the condensation of tetraphenyldisiloxane-1,3-diol and hexaphenyltrisiloxane-1,5-diol with silicon tetrachloride and trichlorosilane. The effects of the starting ratio of the reactants and dilution on the reaction rates and yields of cyclosiloxanes were studied.

Branched molecules and polymers are usually formed in the condensation of polyfunctional organic compounds, whereas differences in the specificity of the process because of the high probability of the formation of cyclic molecules [1,2] can be expected in the condensation of polyfunctional organosilicon compounds because of the large size of the silicon atom and the steric effect of the framework groups. Cyclization during condensation will limit the increase in the branched character of the molecule [3].

In the present paper, we examine the condensation of silicon tetrachloride and trichlorosilane with difunctional compounds – tetraphenyldisiloxane-1,3-diol and hexaphenyltrisiloxane-1,5-diol.

Two compounds are formed in the reaction of silicon tetrachloride with tetraphenyldisiloxane-1,3-diol with a chlorosilane (C) to diol (D) ratio of 1 : 1:



Thus, even for an equimolar ratio of the reagents, the reaction gives not only a cyclosiloxane, as indicated in [2], but also a compound of linear structure.

A study of the condensation in concentrated solution demonstrated that, when the C-to-D ratio is 1 : 2, the reaction products are fusible and soluble polymers. The conversion of tetraphenyldisiloxane-1,3-diol with respect to the evolved hydrogen chloride is about 50% (Fig. 1); i.e., silicon tetrachloride reacts as a functional compound, and two of the chlorine atoms do not enter into the reaction. The character of the process does not change as the initial concentration of reagents changes (Fig. 2). The calculated (from experimental data) concentration order (n) of the reaction is 2.83, and rate constant (k) is 0.018 (g-eq/liter)$^{1.83}$ · sec^{-1}. As the percentage of silicon tetrachloride increases, both the rate of hydrogen chloride evolution and conversion of diol increase. Moreover, the reaction proceeds with predominant blocking of the hydroxyl groups of the diol by trichlorosilyl groups to form linear II (Fig. 1). The yield of II increases from 30% (C : D = 2 : 1) to 60% (C : D = 3 : 1). When C : D = 6 : 1, the yield reaches 93%.

At high dilution, this reaction proceeds considerably more slowly with predominant formation of I (C : D = 1 : 2), and the unchanged diol subsequently undergoes condensation to give hexaphenylcyclotrisiloxane. In this case, the yield of II also increases as the C : D ratio increases (Table 1).

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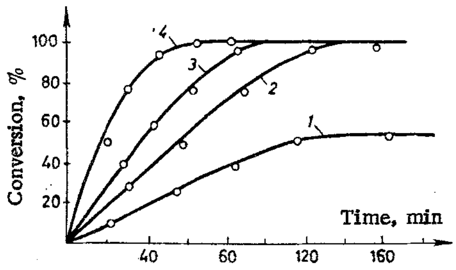


Fig. 1. Dependence of the conversion of tetraphenyldisiloxane-1,3-diol on the starting reagent ratio (C : D): 1) 1 : 2); 2) 1 : 1; 3) 2 : 1; 4) 4 : 1.

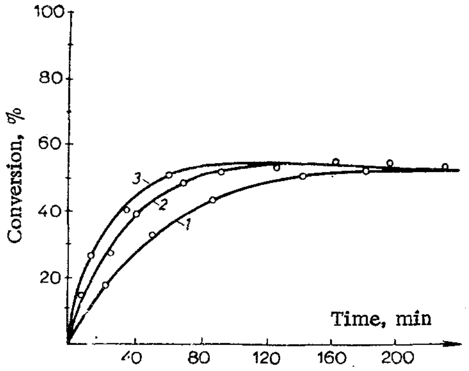


Fig. 2. Dependence of the conversion of tetraphenyldisiloxane-1,3-diol on its initial concentration ($[D]_0$) when C : D = 1 : 2: 1) $[D]_0 = 0.35$ g-eq/liter; 2) $[D]_0 = 1.85$ g-eq/liter; 3) $[D]_0 = 2.83$ g-eq/liter.

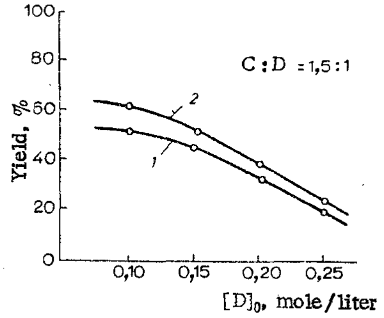
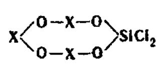


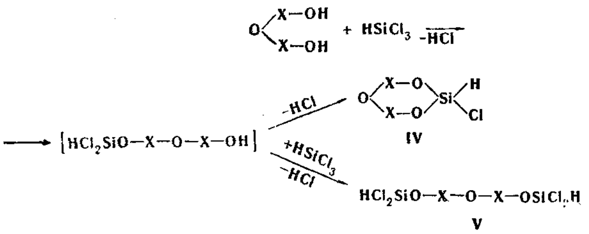
Fig. 3. Dependence of the yield of cyclosiloxanes on the initial tetraphenyldisiloxane-1,3-diol concentration: 1) yield of I (in the reaction with silicon tetrachloride); 2) yield of IV (in the reaction with trichlorosilane).

Cyclosiloxane III was similarly obtained in 48% yield in the reaction of silicon tetrachloride with hexaphenyltrisiloxane-1,5-diol.



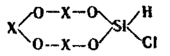
III

It was found that the condensation of tetraphenyldisiloxane-1,3-diol with trichlorosilane also proceeds with the formation of cyclic (IV) and linear (V) hydrochlorosiloxanes:



Additional confirmation of the structures was obtained by means of the PMR spectra, and the purity of these compounds was established. The ratio of the integral intensities of the signals of the aromatic protons and the protons bonded to the silicon atom corresponds (within the limits of the permissible error in the measurements) to the formulas presented for them.

The condensation of trichlorosilane with hexaphenyltrisiloxane-1,5-diol proceeds similarly. The cyclic reaction product (VI) was isolated in 67% yield.



VI

The high yields of eight-membered ring compounds III and VI as compared with six-membered ring compounds I and IV may be explained by the nature of the conformations of the hexaphenyltrisiloxane-1,5-diol molecules in solution, which is due to intramolecular hydrogen bonds [4].

The yield of cyclic products increases on dilution because of a decrease in the probability of intermolecular interaction (Fig. 3).

The IR spectra of the synthesized compounds contain absorption bands characteristic for the $Si-C_6H_5$ bond (1429 cm^{-1}) and the Si−O−Si bond (1025-1040 cm^{-1} for six-membered rings, 1090 cm^{-1} for eight-membered rings, and 1060 cm^{-1} for linear compounds). An intense absorption maximum at 2220 cm^{-1} was observed in the IR spectra of the hydrochloro compounds.

TABLE 1. Dependence of the Composition of the Products of the Condensation of Silicon Tetrachloride (C) and Tetraphenyldisiloxane-1,3-diol (D) on the Reagent Ratio

C : D	Conc.		Overall yield, %	
	I	II	I	II
1,25 : 1	77,6	22,4	48,8	14,1
2,0 : 1	69,2	30,8	42,9	19,1
3,0 : 1	31,3	68,7	21,8	48,2
4,0 : 1	4,0	96,0	3,8	91,2

EXPERIMENTAL

The chromatographic analysis was carried out with a Tswett-4 chromatograph with a column 2 m long and 3 mm in diameter packed with Cellite-545 (50-60 mesh) with an SKT-FT-50 liquid phase applied to it (20%). The column temperature was 300°, the carrier gas (helium) flow rate was 50 ml/min, and the detector was a katharometer.

The PMR spectra of carbon tetrachloride solutions of the hydrochlorosiloxanes were recorded with a Hitachi-Perkin-Elmer R-20 spectrometer with tetramethylsilane as the internal standard.

The reagents used were silicon tetrachloride with bp 57.6° and trichlorosilane with bp 31.5°. Tetraphenyldisiloxane-1,3-diol and hexaphenyltrisiloxane-1,5-diol were synthesized by known methods [5,6] and had mp 110 and 116.5° (from heptane), respectively.

2,2-Dichlorotetraphenylcyclotrisiloxane (I). A flask equipped with a stirrer, thermometer, reflux condenser, and a bubbler for passage of argon was charged with 18 g (0.1 mole) of silicon tetrachloride and 41.4 g (0.1 mole) of tetraphenyldisiloxane-1,3-diol in 660 ml of dry benzene. The mixture was stirred at room temperature for 24 h while passing a slight stream of argon to remove hydrogen chloride, from the evolution of which the diol conversion was determined. The solvent was removed, and the resulting viscous residue was vacuum-distilled to give a fraction (60%) with bp 232-233.5° (1 mm) containing 70% I and 30% II. Compound I was isolated by recrystallization from carbon tetrachloride and redistilled to give 23.1 g of I with mp 82.5-83°. Found: C 56.0; 55.9; H 3.6, 3.7; Cl 13.9, 13.7; Si 16.5, 16.4%; mol. wt. 510. $C_{24}H_{20}Cl_2O_3Si_3$. Calculated: C 55.2; H 3.8; Cl 13.9; Si 16.3%; mol. wt. 512.

1,1,1,7,7,7-Hexachlorotetraphenyltetrasiloxane (II). A solution of 4.16 g (0.01 mole) of tetraphenyldisiloxane-1,3-diol in 20 ml of ether was added slowly to a solution of 6.8 g (0.04 mole) of silicon tetrachloride in 15 ml of dry ether, and the mixture was refluxed for 2 h. The excess silicon tetrachloride and solvent were removed by distillation, and II was isolated by vacuum distillation to give 80% of a product with bp 233° (1 mm), n_D^{20} 1.5512 and d_4^{20} 1.3274. Found: C 42.4, 42.5; H 2.9, 3.0; Cl 31.4, 31.5; Si 16.1, 16.3%; MR_D 163.4. $C_{24}H_{20}Cl_6O_3Si_4$. Calculated: C 42.3; H 2.9; Cl 31.3; Si 16.5%; MR_D 163.3.

2,2-Dichlorohexaphenylcyclotetrasiloxane (III). This compound was synthesized in the same way as I from 61.4 g (0.1 mole) of hexaphenyltrisiloxane-1,5-diol and 17 g (0.1 mole) of silicon tetrachloride. The fraction (51%) with bp 250° (0.02 mm) was isolated and purified to give a product with mp 104°. Found: C 60.7; H 4.1, 4.3; Cl 9.3; Si 16.2, 16.1%; mol. wt. 700. $C_{36}H_{30}Cl_2O_4Si_4$. Calculated: C 60.9; H 4.3; Cl 9.9; Si 15.8%; mol. wt. 709.

2-Chloro-4,4,6,6-tetraphenylcyclotrisiloxane (IV). This compound was synthesized in 60% yield in the same way as I from 13.5 g (0.1 mole) of trichlorosilane and 41.6 g (0.1 mole) of tetraphenyldisiloxane-1,3-diol and had bp 217° (1 mm) and mp 100.5-101°. Found: C 60.5, 60.4; H 4.2, 4.2; Cl 6.8, 7.1; Si 17.6, 17.6%; mol. wt. 475. $C_{24}H_{21}ClO_3Si_3$. Calculated: C 60.4; H 4.4; Cl 7.4; Si 17.7%; mol. wt. 477.

1,1,7,7-Tetrachloro-3,3,5,5-tetraphenyltetrasiloxane (V). This compound (93%) was obtained from 13.5 g (0.1 mole) of trichlorosilane and 10.4 g (0.025 mole) of tetraphenyldisiloxane-1,3-diol, as in the preparation of II, and had bp 218.5° (1 mm), n_D^{20} 1.5559 and d_4^{20} 1.2462. Found: C 47.9, 47.5; H 3.5, 3.5; Cl 23.0, 22.9; Si 18.4, 18.4%; MR_D 158.5. $C_{24}H_{22}Cl_4O_3Si_4$. Calculated: C 47.0; H 3.6; Cl 23.2; Si 18.3%; MR_D 158.7.

2-Chloro-4,4,6,6,8,8-hexaphenylcyclotetrasiloxane (VI). This compound (67%) was synthesized by the method used to obtain I from 13.5 g (0.1 mole) of trichlorosilane and 61.4 g (0.1 mole) of hexaphenyltrisiloxane-1,5-diol and had bp 282° (1 mm) and mp 84-85°. Found: C 63.6; H 4.28; Cl 5.8; Si 16.8%; mol.wt. 670. $C_{36}H_{31}ClO_4Si_4$. Calculated: C 64.0; H 4.6; Cl 5.3; Si 16.6%; mol. wt. 675.

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