# SYNTHESIS OF BRANCHED OLIGOMERS WITH A CENTRAL SILICON ATOM AND HYDROXYL GROUPS AT THE ENDS OF BRANCHING

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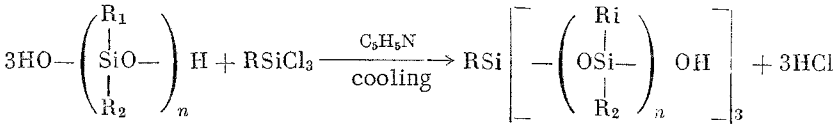
The synthesis of polyfunctional oligomers containing monofunctional groups at the branch ends is of great interest for obtaining three-dimensional polymers of regular structure [1].

Tetrafunctional oligomers with a central titanium or silicon atom are described in the literature [2, 3], and also trifunctional oligomers with a central aluminum atom [4]. There is no information in the literature on the synthesis of trifunctional organosiloxane oligomers. Such oligomers possess interest for obtaining polymers of regular structure with previously assigned properties, suitable for use as lacquers intended for various purposes.

The usual methods for the synthesis of polyorganosiloxanes, containing molecules with branched, cross-linked and three-dimensional chains, are based on the hydrolysis of di- and trifunctional alkyl(aryl)halosilanes, or of the derivatives of orthosilicic acid esters, and subsequent thermal polycondensation or catalytic polymerization of the hydrolysis products. As a rule, these methods do not permit obtaining polymers from the reaction mixture with a functionality less than 2.5. The synthesis of polymers from trifunctional oligomers opens up the possibility of obtaining branched and cross-linked polymers with a low functionality.

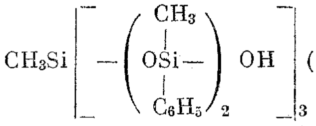
In this paper we studied the reaction for obtaining trifunctional oligomers from alkyl(aryl)trihalosilanes and $\alpha,\omega$-dihydroxypolyorganosiloxanes. The reaction was run in accordance with the scheme



$$3HO-\left(\overset{R_1}{\underset{R_2}{Si}}O-\right)_n H + RSiCl_3 \xrightarrow[\text{cooling}]{C_5H_5N} RSi\left[-\left(O\overset{R_1}{\underset{R_2}{Si}}-\right)_n OH\right]_3 + 3HCl$$

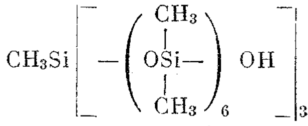
The use of a double excess of the functional groups of one of the components and mild reaction conditions should keep the reaction from going in the direction of polymer formation. For the synthesis we used methyltrichlorosilane and phenyltrichlorosilane as the alkyl(aryl)trihalosilanes, and as the $\alpha,\omega$-dihydroxypolydimethylsiloxanes those compounds containing 6, 9 and 14 silicon atoms in the siloxane chain, and also 1,3-dihydroxy-1,3-dimethyl-1,3-diphenylsiloxane.

As a result, the following new compounds were synthesized.



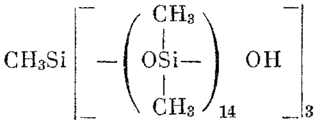
$$CH_3Si\left[-\left(O\overset{CH_3}{\underset{C_6H_5}{Si}}-\right)_2 OH\right]_3$$

(I),



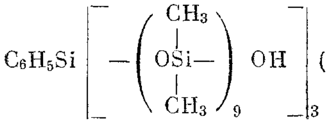
$$CH_3Si\left[-\left(O\overset{CH_3}{\underset{CH_3}{Si}}-\right)_6 OH\right]_3$$

(II),



$$CH_3Si\left[-\left(O\overset{CH_3}{\underset{CH_3}{Si}}-\right)_{14} OH\right]_3$$

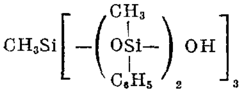
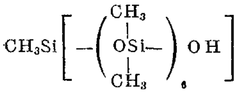
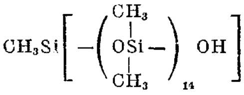
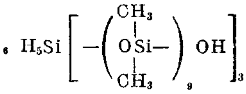
(III),



$$C_6H_5Si\left[-\left(O\overset{CH_3}{\underset{CH_3}{Si}}-\right)_9 OH\right]_3$$

(IV)

Properties of Synthesized Oligomers

| Formula of compound | $n_D^{20}$ | $d_4^{20}$ | Found |  |  |  |  | Calculated |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | C, % | H, % | Si, % | OH, % | mol. wt. | C, % | H, % | Si, % | OH % | mol. wt. |
|  $CH_3Si\left[-\left(\overset{CH_3}{\underset{C_6H_5}{OSi}}-\right)_2 OH\right]_3$ (I) | 1,5410 | 1,2356 | 56,48 | 5,95 | 21,22 | 5,84 | 1043 | 56,70 | 5,93 | 21,54 | 5,60 | 910 |
|  $CH_3Si\left[-\left(\overset{CH_3}{\underset{CH_3}{OSi}}-\right)_6 OH\right]_3$ (II) | 1,4125 | 1,0995 | 31,60 | 7,81 | 36,15 | 3,64 | 1401 | 31,13 | 7,99 | 37,31 | 3,57 | 1426 |
|  $CH_3Si\left[-\left(\overset{CH_3}{\underset{CH_3}{OSi}}-\right)_{14} OH\right]_3$ (III) | 1,4100 | 1,1012 | 31,61 | 8,06 | 37,11 | 1,82 | 2802 | 31,85 | 8,06 | 37,60 | 1,59 | 3202 |
|  $_6H_5Si\left[-\left(\overset{CH_3}{\underset{CH_3}{OSi}}-\right)_9 OH\right]_3$ (IV) | 1,4175 | 1,0892 | 33,86 | 7,72 | 36,53 | 2,29 | 2227 | 35,09 | 7,91 | 36,40 | 2,37 | 2154 |

The analysis results for these compounds and some of their properties are given in the table.

The obtained compounds represented fairly mobile clear liquids, soluble in acetone, dioxane, carbon tetrachloride, toluene, benzene, cyclohexanone, heptane and chloroform, and insoluble in methyl alcohol.

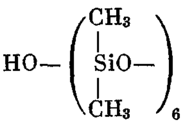
The composition and structure of the new oligomers were confirmed by the elemental analysis, and determination of the functional groups and the molecular weight.

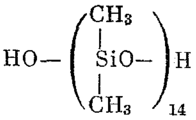
The synthesized oligomers readily undergo condensation at 200° in an inert gas medium with the formation of polymers, possessing a very high thermal elasticity.

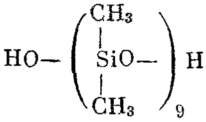
## EXPERIMENTAL

The α,ω-dihydroxypolyorganosiloxanes were obtained in known manner [2] by the hydrolysis of α,ω-dichloropolyorganosiloxanes in alkaline medium at low temperature (–5°). In turn, the α,ω-dichloropolymethylphenylsiloxanes were obtained by the partial hydrolysis of methylphenyldichlorosilane [5], while the α,ω-dichloropolydimethylsiloxanes were obtained by the telomerization reaction of octamethylcyclotetrasiloxane with dimethyldichlorosilane [6].

Preparation of (I). Into a three-necked flask, fitted with a stirrer, a reflux condenser capped with a calcium chloride tube, and a device for cooling, was charged a solution of 41.4 g of 1,3-dihydroxy-1,3-dimethyl-1,3-diphenyldisiloxane (amount of hydroxyl groups 11.6%) in 62 ml of diethyl ether and 11.15 g of pyridine. The flask was cooled and to the oligomer solution at 8° was quickly added a solution of 7.0 g of methyltrichlorosilane (amount of chlorine 71.52%) in 31 ml of diethyl ether. At the end of addition the reaction mixture was stirred for an hour. The obtained precipitate was separated by decantation, while the organic layer was washed until neutral. Then the product was filtered and vacuum-dried to constant weight at 20° and a residual pressure of 2 mm of Hg. We obtained 36.8 g of product (I); yield was 85.14% of theoretical.

Preparation of (II). In a similar manner, from 25.3 g of the diol  $HO-\left(\overset{CH_3}{\underset{CH_3}{SiO}}-\right)_6 H$ (amount of hydroxyl groups 7.35%), 2.7 g of methyltrichlorosilane (amount of chlorine 71.52%) and 4.3 g of pyridine we obtained 15.7 g of product (II); yield was 56.15% of theoretical.

Preparation of (III). In a similar manner, from 56.6 g of the diol  $HO{-}\left(Si(CH_3)_2O{-}\right)_{14}H$ (amount of hydroxyl groups 3.2%), 2.65 g of methyltrichlorosilane (amount of chlorine 71.52%) and 4.2 g of pyridine we obtained 43.2 g of product (III); yield was 74.99% of theoretical.

Preparation of (IV). In a similar manner, from 165.0 g of the diol  $HO{-}\left(Si(CH_3)_2O{-}\right)_{9}H$ (amount of hydroxyl groups 4.76%), 16.5 g of phenyltrichlorosilane (amount of chlorine 49.8%) and 18.2 g of pyridine we obtained 136.2 g of product (IV); yield was 48.70% of theoretical.

## SUMMARY

1. $\alpha,\omega$-Dihydroxydimethyldiphenyldisiloxane and some $\alpha,\omega$-dihydroxypolydimethylsiloxanes were reacted with methyltrichlorosilane and phenyltrichlorosilane to give the previously unknown trifunctional oligomers (I), (II), (III) and (IV) (see table), containing hydroxyl groups at the branch ends.

2. Some of the properties of these compounds were studied.

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