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CONDENSATION OF OLIGOORGANOSILSESQUIAZANES WITH DIPHENYLSILANEDIOL

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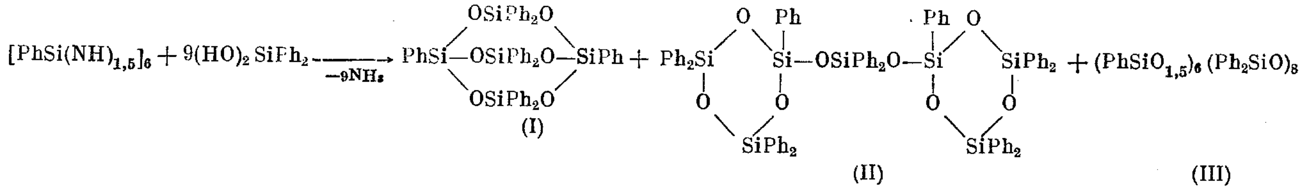
It is known that the condensation of trisodium organotrihydroxysilanes and organotriethoxysilanes with diorganodichlorosilanes [1, 2], and of organotrichlorosilanes with diphenylsilanediol (DPSD) [3, 4] and oligodiorganosiloxanes [5-7] leads to the formation of polycyclic oligoorganosiloxanes. In these reactions catalysts are used, whose residues are difficult to remove and cause contamination of the products. In the present work, we studied the possibility of synthesizing polycyclic oligoorganosiloxanes without using catalysts, by condensation of oligoorganosilsesquiazanes with DPSD.

We found [8] that the reaction of oligoethylsilsesquiazane with DPSD proceeds with a vigorous liberation of NH_3 and leads to the formation of polycyclic oligoorganosiloxanes at 50°C, and oligophenylsilsesquiazane on heating to 80°C. In both cases, the bulk of NH_3 was liberated during the first 3-4 h. An increase in the time of heating and elevation of temperature do not lead to an appreciable increase in the amount of NH_3. Thus, when oligophenylsilsesquiazane was reacted with DPSD at 120°C even for 50 h, the amount of NH_3 did not exceed 80% of the theoretical.

Oligophenylsilsesquiazane is less active in the reaction with DPSD than oligoethylsilsesquiazane. This is probably because the bulky phenyl radicals attached to the Si atom screen the reactive imino groups and thus decrease the probability of their encounter and reaction with the silanol groups of DPSD.

The reaction of oligophenylsilsesquiazane with DPSD proceeds with the formation of bi-, tri-, and polycyclic compounds according to the following scheme:



The crystalline products (I)-(III) (see Table 1) were isolated from the reaction mixture by fractional precipitation with methanol from the benzene solutions, followed by recrystallization of the fractions obtained from benzene. For (I), the elemental composition, the molecular weight, content of phenylsilsesquioxane and diphenylsiloxane units, determined by the method of preparative chromatography, correspond to the data for 1,3,3,5,7,7,10,10-octaphenylbicyclo[3.3.3]pentasiloxane. The absence of signals of the NH and OH group pro-

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TABLE 1. Properties of Polycyclic Compounds Prepared

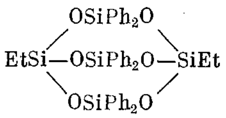
Compound	Yield, %	mp, °C	Found/Calculated, %						Found/Calculated		Empirical formula
			C	H	Cl	Si	$RSiO_{1,5}$	Ph_2SiO	Ph : Et	mol. wt.	
(I)	4	275–277	67,4/67,56	5,01/4,73	–	15,7/16,43	30,08/30,28	69,85/69,27	–	810/853,3	$C_{48}H_{40}O_6Si_5$
(II)	35	127–129	71,45/69,19	5,44/8,84	–	14,03/15,73	27,2/20,67	72,8/79,33	–	1230/1249,9	$C_{72}H_{60}O_8Si_7$
(III)	57	107–112	67,35/67,14	5,08/4,70	–	15,66/16,65	20,7/32,82	67,5/67,16	–	2150/2361,5	$C_{132}H_{110}O_{17}Si_{14}$
(IV)	7	178–180	63,01/63,45	5,0/5,32	–	18,1/18,55	20,8/21,43	78,2/78,57	1 : 2,9/1 : 3	710/757,2	$C_{40}H_{40}O_6Si_5$
(V)	52	150–153	68,1/68,54	3,6/3,78	–	16,5/16,87	12,1/12,18	87,12/87,82	1 : 5,8/1 : 6	1300/1332,0	$C_{76}H_{50}O_9Si_8$
(VI)	62	127–128	64,85/65,14	5,02/4,56	6,65/6,41	15,0/15,23	28,1/28,33	71,83/71,67	–	540/553,2	$C_{30}H_{25}ClO_3Si_3$
(VII)	75	80–82	62,2/61,81	4,92/4,99	7,0/7,02	16,1/16,68	–	–	1 : 3,9/1 : 4	500/505,2	$S_{26}H_{25}ClO_3Si_3$

tons in the PMR spectra confirms the cyclic structure of (I). In the IR spectra of (I) there are absorption bands of the Si–Ph (1430 cm^{-1}) and Ph (3060, 1600 cm^{-1}) groups. For the Si–O–Si group, a broad band in the 1125-1020 cm^{-1} region was observed with a maximum at 1070-1060 cm^{-1}. The absorption bands characteristic of the NH and OH groups were not present.

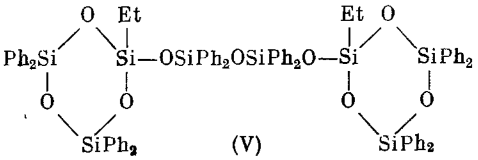
In the IR spectrum of (II) absorption bands are present which are characteristic of the Si–O–Si fragment, with a maximum at 1025-1020 cm^{-1}, which indicates the presence of six-membered organosiloxane rings. The elemental composition, molecular weight, content of phenylsilsesquioxane and diphenylsiloxane units corresponded to the data for 1,1-bis-(pentaphenylcyclotrisiloxano)diphenylsiloxane. For (III), the elemental composition, molecular weight, content of phenylsilsesquioxane and diphenylsiloxane units corresponded to the above given formula. In the IR spectra there were absorption bands characteristic of the Si–Ph (1430 cm^{-1}), Ph (3060, 1600 cm^{-1}), and Si–O–Si (1137-1020 cm^{-1}) groups, and bands at 1090, 1060, 1030, and 1025 cm^{-1}. The presence of several absorption bands in the region characteristic of the Si–O–Si group is explained by the complexity of the structure of the polycyclic organosiloxane, and mutual influence of the groups. The cyclic structure of the product is confirmed by the absence of the NH and OH group signals in the IR and PMR spectra. The structure of the products can be expressed by several formulas.

The reaction of oligoethylsesquiazane with DPSD leads to the formation of tricyclic (IV) and bicyclic (V) (see Table 1).

For (IV), the elemental analysis, molecular weight, content of ethylsilsesquioxane and diphenylsiloxane units, the ratio between the ethyl and phenyl groups, calculated from the PMR spectra, correspond to the structure of 1,5-diethyl-3,3,7,7,10,10-hexaphenylbicyclo-[3.3.3]pentasiloxane. In the IR spectra of (IV) there were absorption bands characteristic of the Si–Et (1260, 1230 cm^{-1}), Si–Ph (1430 cm^{-1}), and Si–O–Si (1125-1020 cm^{-1}) bonds with a maximum at 1070-1060 cm^{-1}. The cyclic structure of (IV) was confirmed by the absence of signals of the NH and OH groups in the IR and PMR spectra. In the IR spectra of (V) there are absorption bands characteristic of the Si–O–Si fragment (1125-1020 cm^{-1}) with a maximum at 1023-1020 cm^{-1}, which indicates the presence of six-membered organosiloxane rings. The elemental composition, molecular weight, content of ethylsilsesquioxane and diphenylsiloxane units, the ratio between the phenyl and ethyl groups, calculated from the PMR spectra, correspond to the data for 1,3-bis(ethyltetraphenylcyclotrisiloxano)tetraphenyldisiloxane (V)

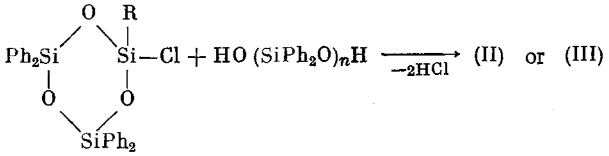


(IV)



(V)

To confirm the structure of compounds (II) and (V), we carried out their alternative synthesis. Compound (II) was obtained by reacting of 1-chloro-1-phenyltetraphenylcyclo-trisiloxane (VI) with DPSD, and (V) by reacting 1-chloro-1-ethyltetraphenylcyclotrisiloxane (VII) with 1,3-diphydroxytetraphenyldisiloxane (VIII). The products were identical in all their properties with the above-described compounds



R=Ph (VI), Et (VII), $n = 1, 2$.

EXPERIMENTAL

The IR spectra of the synthesized compounds were recorded on the UR-10 apparatus in KBr, NaCl, and LiF tablets in the region of 400-4000 cm^{-1} region, and the PMR spectra on the Hitachi—Perkin—Elmer R-20 apparatus (60 MHz). The molecular weights were determined by the ebulioscopic method in acetone. The properties of the compounds obtained are listed in Table 1.

Condensation of Oligophenylsilsesquiazane with Diphenylsilanediol. A 125.4 g portion (0.58 mole) of diphenylsilanediol (DPSD) in 350 ml of toluene was added with stirring to 50 g (0.064 mole) of freshly prepared oligophenylsilsesquiazane in 250 ml of toluene. The mixture was stirred for one more hour, and then toluene was distilled and the residue was left to stand for 5 h at 120°C. Thus, 149.2 g (90.5%) of a condensate was obtained, which was subjected to fractional precipitation with methanol from a benzene solution, with subsequent recrystallization of the fractions obtained from benzene. Yield, 5.97 g of (I), 52.2 g of (II), and 85 g of (III).

Condensation of Oligoethylsilsesquiazane with Diphenylsilanediol. By using the above procedure, from 25 g (0.052 mole) of freshly prepared oligoethylsilsesquiazane and 101.8 g (0.47 mole) of DPSD, 110.5 g (93%) of a condensate was obtained, from which 7.2 g of (IV) and 57.5 g of (V) were isolated.

1,1-Bis(pentaphenylcyclotrisiloxano)diphenylsiloxane (II). A 0.977 g portion (4.52 mmoles) of DPSD in 50 ml of absolute benzene and 5 g (9.04 mmoles) of (VI) in 50 ml of absolute benzene were added simultaneously and at equal rate to 0.716 g (9.04 mmoles) of pyridine in 25 ml of absolute benzene. Pyridine hydrochloride formed was filtered, benzene distilled, and the residue recrystallized from benzene. Yield, 3.3 g (80%) of (II).

1,3-Bis(ethyltetraphenylcyclotrisiloxano)tetraphenyldisiloxane (V). By a similar procedure, from 2.24 g (5.4 mmoles) of (VIII) and 5.45 g (5.4 mmoles) of (VII) in the presence of 0.854 g (10.8 mmoles) of pyridine, 5.25 g (73%) of (V) were obtained.

1-Chloro-1-phenyltetraphenylcyclotrisiloxane (VI). A 3.06 g portion (14.5 mmoles) of phenyltrichlorosilane in 50 ml of absolute benzene and 6 g (14.5 mmoles) of (VIII) in 50 ml of absolute benzene were added simultaneously and at equal rate to 2.29 g (0.029 mole) of pyridine in 25 ml of absolute benzene. Pyridine hydrochloride formed was filtered, benzene distilled, and the residue recrystallized from benzene. Yield, 5 g of (VI).

1-Chloro-1-ethyltetraphenylcyclotrisiloxane (VII). Similarly to the preparation of (VI), from 2.37 g (1.45 mmole) of $EtSiCl_3$ and 6 g (1.45 mmole) of (VIII) in the presence of 2.29 g (29 mmoles) of pyridine, 5.45 g of (VII) were obtained.

CONCLUSIONS

Condensation of oligophenyl- and oligoethylsilsesquiazanes with diphenylsilanediol proceeds with the liberation of NH_3 and leads to the formation of 1,3,3,5,7,7,10,10-octaphenylbicyclo[3.3.3]pentasiloxane, 1,5-diethyl-3,3,7,7,10,10-hexaphenylbicyclo[3.3.3]-pentasiloxane, 1,1-bis(pentaphenylcyclotrisiloxano)diphenylsiloxane, and 1,3-bis(ethyltetraphenylcyclotrisiloxano)tetraphenyldisiloxane. The last two siloxanes were also obtained by the reaction between 1-chloro-1-phenyltetraphenylcyclotrisiloxane with diphenylsilanediol, and between 1-chloro-1-ethyltetraphenylcyclotrisiloxane with 1,3-dihydroxytetraphenyldisiloxane, respectively.

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