SYNTHESIS OF TRI- AND TETRACYCLOSILOXANES WITH FUNCTIONAL GROUPS ATTACHED TO THE SILICON ATOMS

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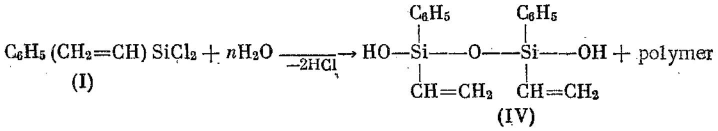
The cyclization reactions of silanes and siloxanes, containing more than two functional groups in the molecule, have received little study. Methods are reported in the literature for the synthesis of tetravinyltetraphenylcyclotetrasiloxane [1] and triphenylcyclotrisiloxane [2] in ~8% yields. The purpose of the present paper was to study the cycloformation reactions in the hydrolytic and heterofunctional condensation of some vinyl(hydro) phenylsilanes and siloxanes. We studied the hydrolytic condensation of phenylvinyldichlorosilane (I), phenyldichlorosilane (II) and 1,3-dichloro-1,3-dihydrodiphenyldisiloxane (III), and the heterofunctional condensation of 1,3-dihydroxy-1,3-divinyldiphenyldisiloxane (IV) with phenylvinyldichlorosilane and 1,3-dichloro-1,3-divinyldiphenyldisiloxane (V).

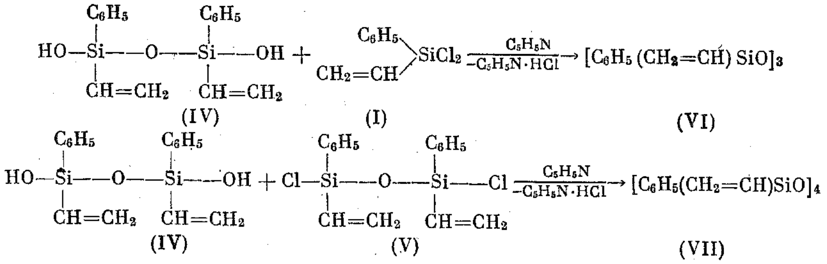
The hydrolytic condensation of (I) in ether at 20-25°C, and at –5 to –15°, proceeds with the formation of 1,3-dihydroxy-1,3-divinyldiphenyldisiloxane (IV) (and not of phenylvinylcyclosiloxanes, as could have been assumed if we start with the data on the hydrolytic condensation of methylphenyldichlorosilane, run under analogous conditions)



$$\underset{(I)}{C_6H_5(CH_2{=}CH)SiCl_2} + nH_2O \xrightarrow[-2HCl]{} \underset{(IV)}{HO-\underset{CH=CH_2}{\overset{C_6H_5}{Si}}-O-\underset{CH=CH_2}{\overset{C_6H_5}{Si}}-OH} + \text{polymer}$$

The yield of (IV) is 52%. Chromatographic analysis of the obtained compound disclosed that it exists as two stereoisomeric forms, analogous to the previously described 1,3-dihydroxy-1,3-dimethyldiphenyldisiloxane [3].

Subsequently, to obtain trivinyltriphenylcyclotrisiloxane (VI) and tetravinyltetraphenylcyclotetrasiloxane (VII) we studied the heterofunctional condensation of (IV) with (I) and (V) in the presence of HCl acceptors



$$\underset{(IV)}{HO-\underset{CH=CH_2}{\overset{C_6H_5}{Si}}-O-\underset{CH=CH_2}{\overset{C_6H_5}{Si}}-OH} + \underset{(I)}{\overset{C_6H_5}{\underset{CH_2=CH}{}}\!>\!SiCl_2} \xrightarrow[-C_5H_5N\cdot HCl]{C_5H_5N} \underset{(VI)}{[C_6H_5(CH_2{=}CH)SiO]_3}$$

$$\underset{(IV)}{HO-\underset{CH=CH_2}{\overset{C_6H_5}{Si}}-O-\underset{CH=CH_2}{\overset{C_6H_5}{Si}}-OH} + \underset{(V)}{Cl-\underset{CH=CH_2}{\overset{C_6H_5}{Si}}-O-\underset{CH=CH_2}{\overset{C_6H_5}{Si}}-Cl} \xrightarrow[-C_5H_5N\cdot HCl]{C_5H_5N} \underset{(VII)}{[C_6H_5(CH_2{=}CH)SiO]_4}$$

Using a 1 : 1 mole ratio, we studied the effect of the reaction conditions for the heterofunctional condensation of (IV) with (I) on the yield of (VI). The obtained data are given in Table 1. As can be seen from the presented data, the optimum result was obtained when the starting reactants were mixed in toluene at 20-25°, with subsequent heating of the reaction mass at 110-120°, and the use of pyridine as the HCl acceptor. The use of excess (I) when running the reaction fails to lead to an increase in the yield of (VI).

As is known, cyclotrisiloxanes and cyclotetrasiloxanes, with various substituents attached to the silicon atoms, can correspondingly exist as two and as four spatial isomers [4]. Chromatographic analysis of

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TABLE 1. Yield of Trivinyltriphenylcyclotrisiloxane (VI) as a Function of the Reaction Conditions

Solvent	HCl acceptor	Mixing temp. of reagents, °C	Duration of reflux, h	Yield of cycle, in % of theory
Ether	Triethylamine	—10 — —15	6	23
"	Pyridine	—10 — —15	6	27
"	"	20 — 25	6	32
Benzene	"	20 — 25	6	58
Toluene	"	20 — 25	6	66

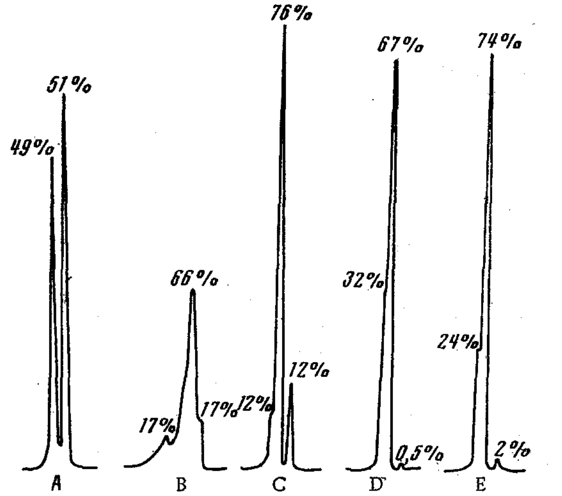


Fig. 1. Chromatograms of phenylcyclosiloxanes: A) trivinyltriphenylcyclotrisiloxane; B) tetravinyltetraphenylcyclotetrasiloxane; C, D, and E starting and crystalline fractions of tetraphenylcyclotetrasiloxane.

the obtained (VI) disclosed that it represents a mixture of two isomers (Fig. 1A) in an ~1 : 1 ratio. A measurement of the ratios of the integral intensities of the phenyl and vinyl protons in the NMR spectrum of (IV) shows a good agreement of the found value (0.596) with the calculated value (0.6). The IR spectroscopy data also corroborate the structure of the synthesized trivinyltriphenylcyclotrisiloxane (VI). The physicochemical constants and the elemental analysis results for (VI) are given in Table 2.

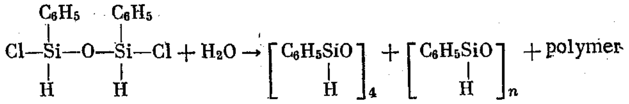
When run under the optimum conditions (see Table 1), the heterofunctional condensation of (IV) with (V) gives tetravinyltetraphenylcyclotetrasiloxane (VII) in 57% yield. Chromatographic analysis of the obtained (VII) disclosed the presence of three of the four possible isomeric forms (see Fig. 1B). Here two of the isomers exit as one peak, with their total amount in the mixture equal to ~66%. The elemental analysis results and the physicochemical constants for the obtained compound are given in Table 2.

To synthesize the cyclic tetraphenylcyclotetrasiloxane (VIII) we studied the hydrolytic condensation of (II) and (III), which was obtained as described in [5]. The hydrolysis of (II) under mild conditions gives a mixture of oligomeric and polymeric products. After distilling off the solvent in a vacuum of ~10-15 mm, the obtained neutral hydrolyzate represents a clear viscous mass, which, after evacuation at 2 mm of Hg for 4 h, is converted to a clear paste, in which connection benzene collects in the trap. On attempted fractional distillation the paste quickly turns yellow, with the formation of an infusible and insoluble product. The formation of benzene in an amount equal to 27-35% of the total amount of phenyl groups, contained in the distilled hydrolyzate, is possible due to the processes that are indicated below (slowly at room temperature and rapidly when heated)

$$\geqslant Si-C_6H_5 + H-Si\leqslant \rightarrow \geqslant Si-Si\leqslant + C_6H_6$$

$$\geqslant Si-C_6H_5 + HO-Si\leqslant \rightarrow \geqslant Si-O-Si\leqslant + C_6H_6$$

In contrast to the above described reaction, the hydrolytic condensation of (III) proceeds with the formation of a liquid mixture of oligomeric products, from which a mixture of the stereoisomers of 1,3,5,7-tetraphenylcyclotetrasiloxane (VIII) was isolated in up to 37% yield



$$\underset{(III)}{Cl-\underset{H}{\overset{C_6H_5}{Si}}-O-\underset{H}{\overset{C_6H_5}{Si}}-Cl} + H_2O \rightarrow \underset{(VIII)}{\left[\begin{array}{c}C_6H_5SiO\\ |\\ H\end{array}\right]_4} + \underset{n>4}{\left[\begin{array}{c}C_6H_5SiO\\ |\\ H\end{array}\right]_n} + \text{polymer}$$

Besides the eight-membered cyclic siloxane, some high-boiling siloxanes could be distilled from the reaction mixture at a pressure of 1 mm (bp up to 300°), which represent ~30% of the weight of the distilled products. The solid product remaining in the still pot is readily soluble in aromatic solvents.

Tetraphenylcyclotetrasiloxane (VIII) is a colorless oily liquid that crystallizes partially on standing. Three of the four possible isomers were recorded when the obtained (VIII) was subjected to chromatographic analysis (see Fig. 1C). Two of the isomers exit as one peak, and their total amount in the mixture is ~76%. Both of the crystalline fractions (Table 3) are mainly a mixture of three isomers, slightly contaminated (0.5-2%) with the fourth isomer (see Fig. 1D and E). The elemental composition and amount of

TABLE 2. Elemental Analysis Results and Physicochemical Constants for Cyclosiloxanes of General Formula $[C_6H_5(R)SiO]_n$

Compound	n	R	Bp, °C (p, mm of Hg)	n_D^{20}	d_4^{20}	MR		Mol. wt.		Found, %			Empirical formula	Calculated, %		
						Found	Calculated	Found†	Calculated, %	C	H	Si		C	H	Si
(VI)	3	$CH_2=CH$	160—165(1)	1,5545	1,1149 1,1124	128,07	128,34	448	444,7	64,91	5,55	19,14	$C_{24}H_{24}O_3Si_3$	64,82	5,44	18,95
(VII)	4	$CH_2=CH$	238—240 (1) Mp 142—143	1,5587	—	—	—	598	592,9	65,08	5,52	19,08	$C_{32}H_{32}O_4Si_4$	64,82	5,44	18,95
(VIII)*	4	H	230—234(1,5)	1,5632	1,1549 1,1572	137,36	136,88	540	488,8	59,08	5,08	23,20	$C_{24}H_{24}O_4Si_4$	58,97	4,95	22,98

* Labile hydrogen, see Table 3.

† The molecular weight was determined ebullioscopically in benzene.

Si–H groups in the crystalline fractions and the residual mother liquor are in good agreement with the data obtained for the starting (VIII).

From the NMR spectra it could be established that the compound remaining in the mother liquor and the starting fraction are a mixture of four isomers. Differences are not observed in the IR spectra of all of the isolated fractions. A study of the IR spectra confirms the structure of the synthesized tetraphenylcyclotetrasiloxane (VIII). The elemental analysis results and the physicochemical constants for the obtained compound are given in Table 2.

EXPERIMENTAL METHOD

The GLC was run on a Tswett-4 chromatograph equipped with a 2 m × 3 mm column, which was packed with 5% SCTPT-50 deposited on Celite 545. Helium was used as the carrier gas at a flow rate of 50 ml/min, while the detection was based on the heat conductivity.

In the study we used chromatographically pure phenylvinyldichlorosilane (I) and phenyldichlorosilane (II), which were obtained by the fractional distillation of the technical products through a column (length 60 cm), which was packed with glass Raschig rings, and using a total condensation head.

1,3-Dihydroxy-1,3-divinyldiphenyldisiloxane (IV). With stirring, a solution of 134.3 g of (I) in 140 ml of absolute ether was added at –5 to 0° to a mixture of 331 g of ice and 140 ml of ether. After adding all of the chloride the ether layer was separated, while the aqueous layer was extracted twice with ether, and the combined extracts were washed with water until neutral and then dried over anhydrous Na_2SO_4. The reaction mass crystallized while distilling off the solvent in vacuo. The crystals were separated, washed with a 6 : 1 pentane–CCl_4 mixture, and recrystallized from a 10 : 1 hexane–benzene mixture. After removing the solvent the mother liquor was vacuum-distilled, and the distilled (IV) was recrystallized as described above. We obtained 54 g (52%) of (IV) as white crystals with mp 105.5-106° [6]. Found: C 61.33; H 5.77; Si 17.83; OH 10.90%. $C_{16}H_{18}Si_2O_3$. Calculated: C 16.11; H 5.77; Si 17.86; OH 10.80%.

1,3-Dichloro-1,3-divinyldiphenyldisiloxane (V). To a solution of 116.27 g of (I) in 250 ml of absolute toluene was added a mixture of 5.16 g of H_2O and 50 ml of absolute dioxane in 20 h [7]. We obtained 51.1 g (50.8%) of (V) as a colorless oily liquid; bp 140-143° (1 mm); n_D^{20} 1.5446. Found: C 55.02; H 4.55; Si 15.92; Cl 20.02%. $C_{16}H_{16}Si_2OCl_2$. Calculated: C 54.69; H 4.59; Si 15.99; Cl 20.18%.

1,3-Dichloro-1,3-dihydrodiphenyldisiloxane (III). The compound was obtained by vapor-phase hydrolysis as described in [5].

Trivinyltriphenylcyclotrisiloxane (VI). With stirring, to a mixture of 5.61 g of (IV), 250 ml of absolute toluene

TABLE 3. Elemental and Functional Analysis Results for Various Fractions of Tetraphenylcyclotetrasiloxane

Characteristics of fractions	Found, %			H_{labile}, % (Si–H)
	C	H	Si	
Starting fraction	59,18	5,08	23,15	0,85
Crystalline fraction with mp 99° (from heptane) and mp 79.5-80.5° (from isooctane)	58,88	5,02	22,89	0,87
Crystalline fraction with mp 76-80.5°	59,01	4,89	22,97	0,82
Residual mother liquid	59,21	5,16	22,92	0,83
Calculated for $[C_6H_5(H)SiO]_4$	58,97	4,95	22,98	0,83

and 2.82 g of absolute pyridine was added in drops a solution of 3.62 g of (I) in 50 ml of absolute toluene in 30 min. The reaction mixture was refluxed for 6 h. Then it was cooled, the obtained crystals of pyridine hydrochloride were filtered (99.5% yield), and the toluene was distilled from the filtrate using a water-jet pump. The residue was vacuum-distilled. We obtained 5.23 g (66%) of (VI) as a colorless oily liquid with bp 160-165° (1.5 mm).

Tetravinyltetraphenylcyclotetrasiloxane (VII). Employing the above described method, from 4.28 g of (IV), 4.79 g of (V) and 2.15 g of absolute pyridine we obtained 4.6 g (57%) of (VII) as a colorless oily liquid that crystallized on standing.

Tetraphenylcyclotetrasiloxane (VIII). With stirring, a 50% ether solution of 39.5 g of (III) was added to 130 ml of a 1 : 1 water–ether mixture. The ether layer was separated, washed with water until neutral, dried over anhydrous Na_2SO_4, the solvent was distilled off rapidly using a water-jet pump, and the residue was vacuum-distilled twice using an oil pump. We obtained 11.9 g (37%) of (VIII) as a colorless oily liquid that partially crystallized on standing.

CONCLUSIONS

1. The hydrolytic condensation of phenylvinyldichlorosilane fails to yield phenylvinylcyclosiloxanes, and instead 1,3-dihydroxy-1,3-diphenyldivinyldisiloxane is formed.

2. A study was made of the heterofunctional condensation of 1,3-dihydroxy-1,3-diphenyldivinyldisiloxane with phenylvinyldichlorosilane and 1,3-dichloro-1,3-diphenyldivinyldisiloxane, and it was shown that trivinyltriphenylcyclotrisiloxane and tetravinyltetraphenylcyclotetrasiloxane can be synthesized by the given method.

3. The side process of benzene cleavage occurs during the hydrolytic condensation of phenyldichlorosilane. Tetraphenylcyclotetrasiloxane can be obtained by the hydrolytic condensation of 1,3-dichloro-1,3-diphenyldisiloxane.

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