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REACTION OF DIPHENYLDICHLOROSILANE DISPROPORTIONATION

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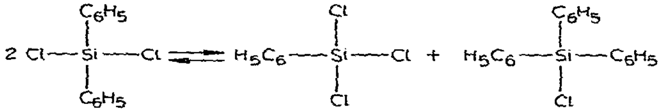
Those silicoorganic polymers in which the main chain contains, in addition to oxygen, phenylene links, exhibit an increased thermal stability[1]. We were, therefore, interested in perfecting a method for obtaining chlorodisilylphenylenes as a basis for the preparation of such polymers.

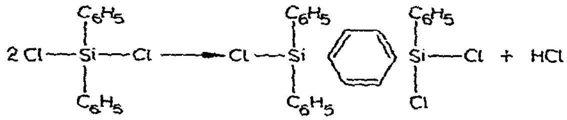
The substance investigated in our research was diphenyldichlorosilane. The reaction of radical redistribution under a thermal effect is very typical of organochlorosilanes. It has been found that the phenomenon of disproportionation can be observed when diphenyldichlorosilane is subjected to high temperatures.



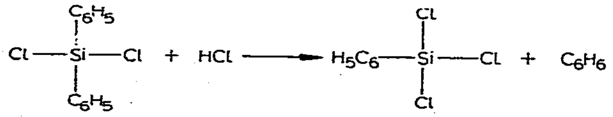
$$2\,Cl-\overset{C_6H_5}{\underset{C_6H_5}{Si}}-Cl \rightleftharpoons H_5C_6-\overset{Cl}{\underset{Cl}{Si}}-Cl + H_5C_6-\overset{C_6H_5}{\underset{Cl}{Si}}-C_6H_5$$

The experiments were performed in an inclined quartz tube filled with alumina-silica (50–65% SiO_2, 45–30% Al_2O_3). Below 460°, diphenyldichlorosilane was quite stable. Its thermal rearrangement, however, takes place at higher temperatures and is a reversible reaction. Diphenyldichlorosilane was also obtained when equivalent amounts of phenyltrichlorosilane and triphenylchlorosilane were heated under the same conditions. The equilibrium state could not be attained, however, because the products of reaction were constantly removed.

Small amounts of diphenyl were separated from the reaction products, which testifies to the radical nature of the disproportionation reaction. Benzene, triphenyltrichlorodisilylphenylene and hydrogen chloride were also formed together with phenyltrichlorosilane, triphenylchlorosilane and diphenyl. We concluded, therefore, that disproportionation is accompanied by dehydrochlorination of diphenyldichlorosilane:



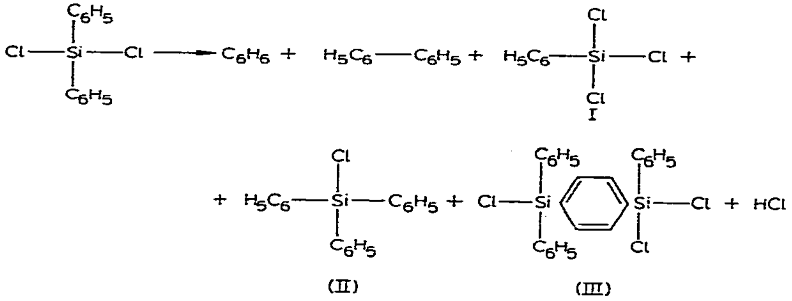
However, only insignificant amounts of hydrogen chloride could be detected in the experiments. This can be attributed to the fact that the hydrogen chloride formed during the experiment reacts with diphenyldichlorosilane to produce phenyltrichlorosilane and benzene:



$$Cl-\overset{C_6H_5}{\underset{C_6H_5}{Si}}-Cl + HCl \longrightarrow H_5C_6-\overset{Cl}{\underset{Cl}{Si}}-Cl + C_6H_6$$

This is also confirmed by the fact that benzene is produced in quantities that are approximately equivalent to the amount of phenyltrichlorosilane, if the phenyltrichlorosilane that forms as a result of disproportionation is disregarded.

In a general form, the thermal rearrangement takes the following course:



Elemental analyses of products I and II correspond to phenyltrichlorosilane and triphenylchlorosilane, respectively, and their constants to the available literary

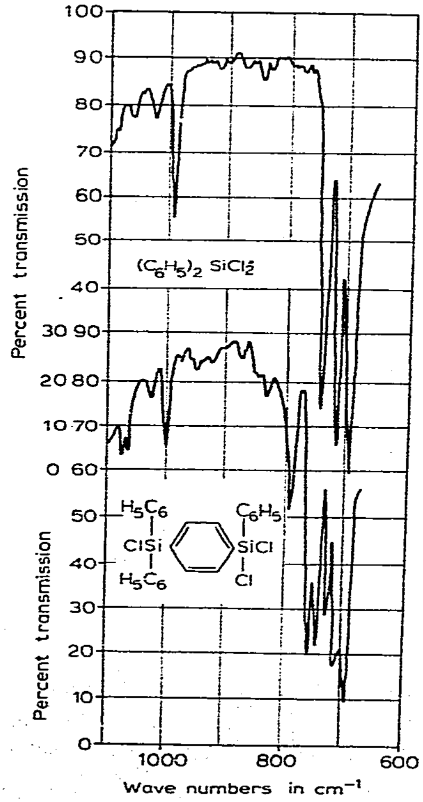
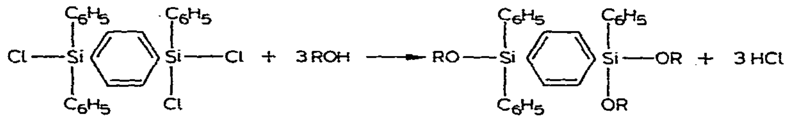


Fig. 1. Infrared spectra of diphenyldichlorosilane and triphenyltrichlorodisilylphenylene.

data. The presence of trace amounts of diphenyl in the reaction products, has been proved chromatographically. The elemental analysis and the molecular weight of product III correspond to triphenyltrichlorodisilylphenylene. The presence of additional absorption bands (compared with diphenyldichlorosilane) in the region of 750–790 cm^{-1} corresponding in the infrared spectra of organic compounds to disubstituted benzenes, see Fig. 1, indicates, apparently, the presence of a phenylene grouping in product III. The position of the groups in triphenyltrichlorodisilylphenylene has not yet been ascertained.

To prove that triphenyltrichlorodisilylphenylene can be obtained from a thermal rearrangement of diphenyldichlorosilane, we have obtained from product III its ethoxy- and phenoxy derivatives by the following scheme:



where $R = C_2H_5$; C_6H_5

Triphenyltriethoxydisilylphenylene and triphenyltriphenoxydisilylphenylene have been identified by analysis, molecular weight determinations and infrared spectra. The properties of all reaction products obtained are given in Table 1.

In order to determine the conditions for obtaining the maximum amount of triphenyltrichlorodisilylphenylene we have studied the thermal rearrangement of

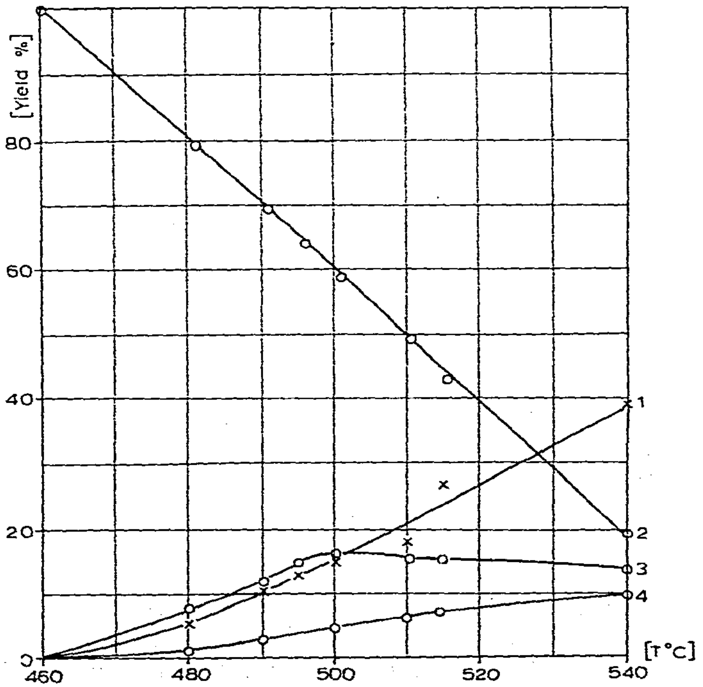
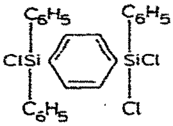
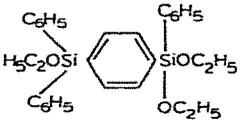
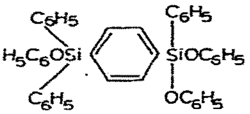


Fig. 2. The yields of phenyltrichlorosilane (1), diphenyldichlorosilane that did not participate in the reaction (2), mixture of high-boiling chlorosilanes (3) and benzene (4) as a function of the reaction temp.

TABLE 1

Formula	*B.p. (°C/mm)*	*M.p. (°C)*	n_D^{20}	d_4^{20}	*Mol. wt.*		*MR*	
					Found	*Calcd.*	*Found*	*Calc*
C_6H_6	80	—	1.5005	0.8778	—	—	—	—
$C_6H_5SiCl_3$*	201–203	—	1.5229	1.3048	—	—	49.51	48.77
$(C_6H_5)_3SiCl$**	—	93–94.5	—	—			—	—
	235–270 (5.5)	—	1.6250	1.2541	484 460	471	132.78	132.3
	237(1)***	—	—	—	463 458	499	—	—
	262–264(1)***	—	1.6162	1.1547	597 606	643	194.57	194.55

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* Ref. 2: b.p. 201°, $d_5^{25} = 1.321$, $n_D^{20} = 1.5240$.

** Ref. 2: m.p. 94–96°.

*** B.p. has been determined according to Sivolobov.

diphenyldichlorosilane in the temperature range 480–540° at a constant feed rate of diphenyldichlorosilane. The results of the experiments have shown that the amount of diphenyldichlorosilane taking part in the reaction increases in proportion to the rise in temperature. As rise in temperature increased (see Fig. 2) the yield of phenyltrichlorosilane and benzene. The yield of the mixture of high-boiling chlorosilanes, consisting of triphenylchlorosilane and triphenyltrichlorodisilylphenylene, reached a maximum at a temperature of 500°. The mixture obtained at this temperature contained triphenylchlorosilane in 3.0% yield and triphenyltrichlorodisilylphenylene in 10.7% yield based on the initial amount of diphenyldichlorosilene, or 7.2% and 30.2%, respectively, of the diphenyldichlorosilane that participated in the reaction.

EXPERIMENTAL

The device used to study the thermal transformation of diphenyldichlorosilane was an inclined oven 0.6-m long with electrical heating. The oven contained a quartz tube, one metre long and 20 mm in diameter two-thirds filled with 5-mm lumps of alumina–silica aluminosilicate. Diphenyldichlorosilane was added from a dropping funnel. To overcome the small pressure in the system, the upper part of the dropping

emental analysis (%)							
und				*Calcd.*			
	H	*Si*	*Cl*	*C*	*H*	*Si*	*Cl*
	—	—	—	—	—	—	—
.40	2.58	12.44	49.06	34.06	2.38	13.26	50.33
.13	2.69	12.55	48.75				
2.84	4.95	10.22	11.76	73.38	3.79	10.50	11.98
2.91	4.89	10.38	11.84				
1.98	4.24	10.65	22.23	61.44	4.06	11.95	22.58
1.95	4.12	10.84	22.45				
2.62	6.88	10.38		72.25	6.87	11.25	
2.89	7.01	10.52					
78.38	5.59	7.47		78.47	5.33	8.73	
78.33	5.30	7.91					

funnel was connected to a reaction tube. Before the experiment the system was blown through with nitrogen. Diphenyldichlorosilane was fed at a rate of 25–30 g/h. The products of reaction were condensed in the unheated section of the tube and drained into a flask. The hydrogen chloride evolved was absorbed in water. The reaction products were fractionated *in vacuo*. The low-boiling reaction products were caught in a trap.

The diphenyldichlorosilane used for studying the thermal rearrangement had $d_4^{20} = 1.2234$ and $n_D^{20} = 1.5775$.

TABLE 2

Temp. of expt. (°C)	*Amount of $(C_6H_5)_2SiCl_2$ passed (g)*	*Fractions with b.p. at °C and at 5.5 mm Hg (g)*			*C_6H_6 caught in trap (g)*
		57–70	*135–163*	*above 200*	
460	25.30	—	24.68	—	—
480	28.20	1.48	21.77	2.15	0.51
490	28.89	2.97	20.10	3.18	0.91
490–500	20.20	2.50	12.80	3.04	
500	85.00	11.98	49.64	14.13	3.97
510	25.61	4.45	12.17	3.91	1.58
510–520	21.20	5.70	8.84	3.06	1.48
540	19.03	7.41	3.66	2.51	1.60

Table 2 illustrates the fractional composition of the reaction products.
The fractions boiling 57–70° (at 5.5 mm) were technical phenyltrichlorosilane. When these fractions were distilled at atmospheric pressure, an insignificant amount of crystalline diphenyl was formed at 256–260°. Fractions boiling at 135–163° (at 5.5 mm) represented diphenyldichlorosilane that had not entered into the reaction. The composition of the fractions boiling above 200° (at 5.5 mm) was determined by redistilling and taking fractions over narrower temperature ranges. From the 14.13-g fraction boiling above 200° (at 5.5 mm) obtained at the reaction temperature of 500°, 2.57 g of crystalline triphenylchlorosilane and 9.09 g of triphenyltrichlorodisilylphenylene (a yellow viscous substance readily soluble in benzene, diethyl ether, chloroform, chlorobenzene and other organic solvents) was obtained.

When a mixture containing 12.64 g (0.06 mole) of phenyltrichlorosilane and 17.31 g (0.06 mole) of triphenylchlorosilane was passed through the tube at a reaction temperature of 510°, 0.52 g of benzene, 11.05 g of phenyltrichlorosilane, 4.59 g of diphenyldichlorosilane and 12.00 g of a mixture of chloride boiling above 200° (at 5.5 mm) was obtained.

Preparation of triphenyltriethoxydisilylphenylene (IV)

Into a four-necked flask provided with a stirrer, reflux condenser, thermometer and dropping funnel was placed a 20% solution of product III, 2.47 g (0.005 mole), in benzene. Twice the theoretical amount of ethyl alcohol, 1.00 g (0.03 mole), was added to the solution dropwise with stirring, at 20°. The reaction temperature was raised to 80° and the solution heated until hydrogen chloride ceased to evolve. Distillation produced 1.54 g (59%) of product IV.

Preparation of triphenyltriphenoxydisilylphenylene (V)

Into a four-necked flask was placed 2.41 g (0.004 mole) of chloride III. A 100% excess of phenol in amounts of 2.20 g (0.024 mole) was added to the chloride and the mixture heated to 70°. The contents of the flask were then raised to 150° and stirred until hydrogen chloride ceased to evolve. After the products of reaction had been distilled and refined with petroleum ether 1.74 g (47%) of product V was obtained.

SUMMARY

1. The thermal rearrangement of diphenyldichlorosilane below 540° has been studied.

2. It was found that at 480–540° disproportionation is accompanied by dihydrochlorination with formation of triphenyltrichlorodisilylphenylene,

3. The maximum yield of triphenyltrichlorodisilylphenylene was obtained at a reaction temperature of 500°.

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