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Abstract

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HIGH-TEMPERATURE CHLORINATION OF PHENYLTRICHLOROSILANE

At present, the chlorination of organosilicon compounds with chlorine in the liquid or vapor phase at temperatures of 20–200° in the presence of catalysts or reaction initiators has been studied in sufficient detail (see [1–4]). Vapor-phase chlorination of alkyl- and arylsilane chlorides with chlorine is usually carried out at the boiling temperatures of the starting compounds ([1]). Only alkylsilyl halides ([5]) and vinyltrichlorosilane ([6]) have been subjected to high-temperature (250–600°) chlorination with chlorine in the gas phase. Thus, it may be considered that the reaction of high-temperature chlorination of organosilicon compounds is, in essence, only beginning to be studied.

It seemed of interest to apply the high-temperature chlorination reaction to phenyltrichlorosilane. First of all, it was necessary to determine the possibility of carrying out a continuous process of chlorination of phenyltrichlorosilane at elevated temperatures (200–500°). On the other hand, it was necessary to obtain an answer to the question of what the ratio of ortho-, meta-, and para-isomers would be.

Table 1

Ratio of isomers formed during high-temperature chlorination of $C_6H_5SiCl_3$ (in percent)*

Isomer	Chlorination with quartz packing	Chlorination with quartz packing	Chlorination with quartz packing	Chlorination with packing of activated carbon	Chlorination with packing of activated carbon	Chlorination with packing of activated carbon
	350°	400°	450°	350°	400°	450°
Ortho-	22	26	36	14	26	32
Meta-	39	37	35	37	33	36
Para-	39	37	29	49	41	32

* The ratio of isomers in the mixture was determined by means of NMR spectra, according to the previously described method (7), with an accuracy of up to ±2-4%.

Already the first experiments on chlorination of phenyltrichlorosilane in a tube packed with quartz at 350° justified our expectations. The yield of monochloro derivatives was 19% based on the amount passed through and 58% based on the phenyltrichlorosilane that entered into reaction. The most unexpected result was the ratio of the ortho-, meta-, and para-isomers, namely $o : m : n = 22 : 39 : 39$. Thus, in this case the meta-directing ability of the $SiCl_3$ group (7) is no longer manifested. The amount of meta-isomer in the mixture, as the data in Table 1 show, changes almost not at all with increasing temperature up to 450°, although the ratio between the ortho- and para-isomers shifts toward ortho-chlorophenyltrichlorosilane.

The initial ratio of ortho-, meta-, and para-isomers formed in the first stage of chlorination, owing to their further chlorination to polychlorides, may differ somewhat from that given in Table 1. However, this deviation, taking into account the small amounts of polychlorides and the equal probability of their formation under our conditions from any of the isomers, is evidently very small. This is indicated, in particular, by the results of experiment No. 1 (see Table 2), where the formation of polychlorides did not occur.

Table 2

Conditions and results of experiments on high-temperature chlorination of $C_6H_5SiCl_3$ and $(CH_3)_2SiCl_2$

Exp. No.	Initial silane chloride	Amount, g	Feed rate: silane, g	Feed rate: chlorine, l/h	Reaction temp., °C	Tube packing	Amount of condensate, g	Yield: monochlorides, g	Yield: polychlorides, g	Yield of monochlorides, %: based on silane chloride taken	Yield of monochlorides, %: based on silane chloride that entered into reaction
1	$C_6H_5SiCl_3$	152.0	34.2	3.65	350	Quartz	150.2	32.8	–	19	58
2	$C_6H_5SiCl_3$	155.3	34.2	3.65	400	Quartz	163.4	63.0	7.3	35	69

Exp. No.	Initial silane chloride	Amount, g	Feed rate: silane, g	Feed rate: chlorine, l/h	Reaction temp., °C	Tube packing	Amount of condensate, g	Yield: monochlorides, g	Yield: polychlorides, g	Yield of monochlorides, %: based on silane chloride taken	Yield of monochlorides, %: based on silane chloride that entered into reaction
3	$C_6H_5SiCl_3$	147.6	34.2	3.65	450	Quartz	155.0	40.2	12.5	24	57
4	$C_6H_5SiCl_3$	—	34.2	4.75	350	Activated carbon	146.9	45.7	11.4	—	—
5	$C_6H_5SiCl_3$	143	34.2	3.65	400	Same	145.2	31.3	7.1	19	48
6	$C_6H_5SiCl_3$	162.9	34.2	3.65	450	Same	159.8	20.8	4.6	11	39
7	$(CH_3)_2SiCl_2$	—	27.5	3.3	250	Same	240.1	13.2	19.4	—	—
8	$(CH_3)_2SiCl_2$ in a solution of $SiCl_4$ (50:50)	307 (mixture)	13.8	2.39	300	Quartz	273.2	*	*	—	—

* From the reaction products, CCl_4 (6.9 g) was isolated. B.p. 76.1-77.5° at 748 mm; chloromethylsilyl chlorides were formed in a very small amount (~10 g).

was observed. If activated carbon is used instead of quartz packing, the ratio of isomers at the same temperatures remains almost unchanged, although the reaction itself usually begins at lower temperatures and is accompanied by slight destruction of phenyltrichlorosilane at the Si—C bond.

We have also shown that dimethyldichlorosilane, both on activated carbon and on quartz packing, in a mixture with $SiCl_4$, is readily chlorinated at 250-400°. In all cases, however, significant cleavage of the Si—C bond was observed, as well as formation of di- and trichlorides. We believe that high-temperature chlorination is a homolytic reaction.

The change in the isomer ratio, as in the high-temperature halogenation of chloro- and bromobenzenes ([8]), is evidently associated with a change in the activation energy for chlorination of different positions of the benzene nucleus as the temperature rises.

Experimental Part

1. Chlorination procedure. High-temperature chlorination of phenyltrichlorosilane was carried out in a glass tube 25 mm in diameter and 500 mm long, heated by means of a furnace to the reaction temperature (250–500°). The tube was filled with birch activated carbon (BAU, GOST 6217-52) or with pieces of quartz. The rate of chlorine flow was measured with a rheometer. The chlorine was first dried with concentrated H_2SO_4 in a Tishchenko bottle and, before entering the furnace, was mixed with dry nitrogen. $C_6H_5SiCl_3$ and $(CH_3)_2SiCl_2$ were metered by means of a sensor. Before the start of the experiment the furnace was heated to the reaction temperature and purged with dry nitrogen. The reaction products were condensed in a cooler and collected in a receiver. The temperature in the furnace was measured with a thermocouple in the immediate vicinity of the end of the tube, through

through which chlorine was fed. The conditions and results of the experiments on chlorination of $C_6H_5SiCl_3$ are presented in Tables 1 and 2.

2. Determination of the composition of the reaction products. The reaction products were first distilled under vacuum and then on a rectification column with 35–40 theoretical plates. During the fractionation of the chlorination products of phenyltrichlorosilane, the following were collected for spectral analysis: 1) unreacted $C_6H_5SiCl_3$; 2) the fraction 228–236° (mainly 230–233°)—a mixture of meta- and parachlorophenyltrichlorosilanes; 3) the fraction 236–250° (mainly 240–242°)—orthochlorophenyltrichlorosilane with an admixture of other products. The residue, consisting of a small amount of dichlorides, was distilled under vacuum.

The composition of fractions 2 and 3 was determined by means of Raman spectra, according to the procedure described in work (7). Known pure samples of ortho-, meta-, and parachlorophenyltrichlorosilanes, obtained by us earlier (7), were used as standards.

The results of the analysis are presented in Table 1.

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