CHEMISTRY

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1957

SovietRxiv

Abstract

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CHEMISTRY

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PHOTOCHLORINATION OF ETHYLTRICHLOROSILANE IN THE LIQUID STATE

(Presented by Academician B. A. Kazanskii, 8 VII 1957)

The chlorination of ethyltrichlorosilane by heating with sulfuryl chloride in the presence of benzoyl peroxide (1) and photochlorination in the vapor state with chlorine in the Kursanov apparatus (2) have been described in the literature.

We have carried out the photochlorination of ethyltrichlorosilane in the liquid state with gaseous chlorine under the previously described conditions (3), with illumination by a 150 W incandescent lamp. The starting substance, free from contamination with iron compounds,* had d_4^{20}1.2393 and n_D^{20}1.4259. The duration of the induction period at a temperature of 20—30° was 10 min. After completion of the induction period, gaseous chlorine was fed at a rate of 0.25—0.3 g-mol/hour per 1 g-mol of ethyltrichlorosilane until the specified weight gain was reached. Cooling of the flask with running water ensured a temperature of the liquid being chlorinated equal to 15—20°; under these conditions the chlorine reacted immediately, without coloring the liquid.

After chlorination, the mixtures were separated on a rectification column with porcelain packing having an efficiency of 20 theoretical plates. The composition of the intermediate fractions was calculated from the densities.

The results of the chlorination are given in Table 1.

Table 1

Dependence of the density, refractive index, composition (mole fractions in %) of the mixtures, and ratio of the amounts of α- and β-chloroethyltrichlorosilanes on the degree of chlorination of ethyltrichlorosilane

	Degree of chlorination, g-mol Cl_2 per 1 g-mol $C_2H_5SiCl_3$	Degree of chlorination, g-mol Cl_2 per 1 g-mol $C_2H_5SiCl_3$	Degree of chlorination, g-mol Cl_2 per 1 g-mol $C_2H_5SiCl_3$	Degree of chlorination, g-mol Cl_2 per 1 g-mol $C_2H_5SiCl_3$	Degree of chlorination, g-mol Cl_2 per 1 g-mol $C_2H_5SiCl_3$
	0.75	1	1.25	1.5	2

	Degree of chlorination, g-mol Cl_2 per 1 g-mol $C_2H_5SiCl_3$	Degree of chlorination, g-mol Cl_2 per 1 g-mol $C_2H_5SiCl_3$	Degree of chlorination, g-mol Cl_2 per 1 g-mol $C_2H_5SiCl_3$	Degree of chlorination, g-mol Cl_2 per 1 g-mol $C_2H_5SiCl_3$	Degree of chlorination, g-mol Cl_2 per 1 g-mol $C_2H_5SiCl_3$
d_4^{20}	1.3674	1.4015	1.4375	1.4752	1.5180
n_D^{20}	1.4529	1.4603	1.4671	1.4748	1.4810
$C_2H_5SiCl_3$, %	30	14	4	0	0
$CH_3ClCHSiCl_3$, %	17	18.5	16		
$ClCH_2CH_2SiCl_3$, %	48	54.5	55.5	55	18
Di- and polychloro-substituted products and losses, %	5	13	24.5	45	82
Ratio of the amounts of α- and β-isomers $ClC_2H_4SiCl_3$, %	1 : 2.8	1 : 2.95	1 : 3.45	–	

The composition of the mixtures indicates an unusually high yield of monochloro-substituted products in the photochlorination of ethyltrichlorosilane in the liquid state.

* Noticeable contamination of alkylchlorosilanes with iron leads to a sharp increase in the duration of the induction period and a decrease in the rate of the photochlorination reaction in the liquid phase. When contaminated with iron, a decrease in the yield of monochloro-substituted products is also observed, simultaneously with an increase in the yield of di- and polychloro-substituted products.

At degrees of chlorination of 0.75 and 1 g-mol of Cl_2 per 1 g-mol of $C_2H_5SiCl_3$, the yields based on chlorosilane that has entered into the reaction reach, respectively, 93 and 85%, whereas the corresponding values for diethyldichlorosilane are 78 and 72% ([3]); and in the case of photochlorination in the liquid state of the closest homolog of ethyltrichlorosilane—methyltrichlorosilane—the formation of di- and trichloro-substituted products predominates overwhelmingly ([4]).

At degrees of chlorination of 1.5 and 2 g-mol of Cl_2 per 1 g-mol of $C_2H_5SiCl_3$, among the three possible dichloro-substituted products in the mixtures the β,β-

isomer predominates; a considerably smaller amount of the α, β-isomer is formed, and still less of the α, α-isomer (b.p. about 156°; crystals at room temperature). Among the three possible trichloro-substituted products in the aforementioned mixtures, the isomer with b.p. about 200°, liquid at room temperature, predominates. Calculation of the boiling points of the two liquid trichloro-substituted products gives grounds to suppose that the latter is the α, β, β-isomer.

The closeness of the boiling points of the β-chloro-substituted and α, α-dichloro-substituted compounds, on the one hand, and of the α, β- and β, β-dichloro-substituted compounds, on the other, makes it difficult to separate highly chlorinated mixtures on a column with an efficiency of 20 t.t. For this reason the composition of the mixtures given in the last two columns of Table 1 is approximate, and the estimate of the ratios of the di- and trichloro-substituted isomers is to a considerable extent qualitative.

Upon the action of 0.1 N aqueous sodium hydroxide on α, β- and β, β-chloroethyltrichlorosilanes, 4 atoms of hydrolyzable chlorine are found; when titrating in an alcohol-water medium with mercuric nitrate, 3 atoms of hydrolyzable chlorine are found.*

Table 2

Substance	B.p., °C	d_4^{20}	n_D^{20}	MR_D, found	MR_D, calc.
$CH_2ClCHSiCl_3$	137	1.3934	1.4559	38.61	38.39
$ClCH_2CH_2SiCl_3$	152	1.4190	1.4640	38.50	38.39
$ClCH_2ClCHSiCl_3$	182	1.5352	1.4853	43.41	43.23
$Cl_2CHCH_2SiCl_3$	177.2	1.5243	1.4808	43.38	43.23
$Cl_3C_2H_2SiCl_3$	~ 200	1.6149	1.4990	48.52	48.07

Table 2 gives the physical constants of chlorinated derivatives of ethyltrichlorosilane isolated by rectification on a column with an efficiency of 20 t.t.

A comprehensive comparison of the results presented in this communication with the literature data ([1,2]) makes it possible to regard photochlorination in the liquid state as the most rational method for chlorinating ethyltrichlorosilane.

Received
27 VI 1957

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* Determinations of hydrolyzable chlorine were performed by A. M. Neishumova and L. A. Kondrateva.

Note: Figure translations are in progress. See original paper for figures.