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Academician A. N. NESMEYANOV, R. Kh. FREIDLINA, and E. Ts. CHUKOVSKAYA

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Abstract

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THERMAL TELOMERIZATION OF TRICHLOROSILANE WITH ETHYLENE

Silicon compounds containing an Si–H bond are capable of adding to the double and triple bonds of unsaturated compounds. In a previous paper [1] we gave a brief survey of such reactions [2–12].

Recently the addition of trichlorosilane to the double bond of acrylonitrile, 2-vinylpyridine, and allyl cyanide in the presence of organic bases has been described, and an ionic mechanism for these reactions has been proposed [13,14]:

$$Cl_3SiH + B \rightarrow Cl_3Si^- + BH^+$$

$$\overset{\delta+}{C}H_2 = \overset{\delta-}{C}HR + Cl_3Si^- \rightarrow Cl_3SiCH_2\overline{C}HR$$

$$Cl_3SiCH_2\overline{C}HR + BH^+ \rightarrow B + Cl_3SiCH_2CH_2R,$$

where B is an organic base

$$R = CN,\ CH_2CN,\ N$$

Nozakura found [14,15] that tetrapyridinenickel chloride catalyzes the addition of trichlorosilane to vinyltrichlorosilane, 1-octene, and styrene. Moreover, in all the cases listed the reaction leads to the formation of a mixture of two isomers: $SiCl_3CH_2CH_2R$ and

$$CH_3{-}CH{-}R, \qquad \overset{|}{SiCl_2}$$

where $R = SiCl_3,\ C_6H_{13},\ C_6H_5$.

Our attempt to carry out the telomerization reaction in stainless-steel autoclaves, using methyldichlorosilane, ethyldichlorosilane, and triethylsilane with ethylene and propylene in the presence of benzoyl peroxide or tert-butyl peroxide at 100–140° and a pressure of 100–300 atm, did not give a positive result.

Positive results were obtained by us [1] in the thermal telomerization reaction of methyldichlorosilane with ethylene at 260–275° and a pressure of 560 atm.

Under these conditions a mixture of substances of the structure $CH_3SiCl_2(CH_2CH_2)_{nH}$ is formed, from which compounds for which $n = 1$–6 were isolated in individual form.

In the present paper we report the performance of the thermal telomerization reaction of trichlorosilane with ethylene.

The reaction was carried out in a half-liter autoclave made of EYa-1T steel. Into the autoclave were charged 60 g of trichlorosilane, and after purging with nitrogen, ethylene was introduced. The reaction mixture was heated to 285°, the maximum pressure being 200 atm. The reaction was conducted for 2 hours. During this time the pressure fell to 40 atm. The experiment was repeated 4 times; the reaction products were combined and subjected to fractional distillation. In all, 261 g of trichlorosilane was charged. The weight of the reaction products was 353 g. The product

fractionated on a column with 15 theoretical plates. 10 g of the starting trichlorosilane and 269 g of individual alkyltrichlorosilanes of the structure $Cl_3Si(CH_2CH_2)_{nH}$, where n = 1—5, were distilled off. The residue (42 g) is a mixture of higher alkyltrichlorosilanes. The properties and yields of the alkyltrichlorosilanes obtained are summarized in Table 1.

Table 1

$SiCl_3(CH_2CH_2)_{nH}$

n	Yield, g	Yield, % of total products	n_D^{20}	d_4^{20}	MR found	MR calcd.	b.p., °C/mm found	b.p., °C/mm lit.	Source	Si, % calcd.	Si, % found
1	69	20.1%	–	–	–	–	98	97 – 100	(16)	–	–
2	87	25.3%	1.4352	1.1577	43.19	42.82	146 – 147	147 – 151	(17)	14.65	14.72
3	54	15.4%	1.4440	1.1094	52.51	52.12	87 – 89/30	127/38	(18)	12.78	14.45; 12.83; 12.59
4	45	13.1%	1.4490	1.0744	61.76	61.41	96.5/10	119/28 – 231 – 232/731	(18)	11.33	11.26; 11.67

n	Yield, g	Yield, % of total products	n_D^{20}	d_4^{20}	MR found	MR calcd.	b.p., °C/mm found	b.p., °C/mm lit.	Source	Si, % calcd.	Si, % found
5*	14	4.0%	1.4547	1.0501	71.17	70.71	76/2	183/84	(18)	10.17	10.55; 10.58
$n >$ 5	42	12.2%									

* For $SiCl_3C_{10}H_{21}$. Calculated, %: C 43.56; H 7.67; Cl 38.62.
Found, %: C 43.68; 43.71; H 7.79; 7.71; Cl 38.21; 38.03.

The telomerization reactions studied by us, like the addition reactions described in the literature, proceeded through cleavage of the Si—H bond, as is proved by the absence of this bond in the compounds obtained. The structure of the alkyltrichlorosilanes is confirmed by determination of the molecular refraction, and also by obtaining the corresponding trimethylalkylsilanes from them by the Grignard reaction. The properties of the trimethylalkylsilanes obtained are given in Table 2.

Table 2

$(CH_3)_3Si(CH_3CH_2)_nH$

n	Formula	b.p., °C/mm	n_D^{20}	d_4^{20}	MR calcd.	MR found	C, % calcd.	C, % found	H, % calcd.	H, % found	Si, % calcd.	Si, % found
2	$C_4H_9Si(CH_3)_3$	40/30	1.4203	0.7203	44.14	44.12	64.66	64.44; 64.47	13.85	13.83; 13.87	21.57	21.29; 21.46
3	$C_6H_{13}Si(CH_3)_3$	58/41	1.4160	0.7412	53.35	53.58	68.30	68.48; 68.28	14.01	14.02; 14.02	17.73	17.56; 17.61
4	$C_8H_{17}Si(CH_3)_3$	74/12	1.4242	0.7646	62.58	62.21	70.89	71.03; 71.14	14.07	14.03; 14.18	15.05	14.59; 14.53

* For literature data on the constants of these compounds, see (18).

The yields of trichloroalkylsilanes of different molecular weight show a certain regularity characteristic of the telomerization reaction (noted by us also for the case of telomerization of methyldichlorosilane with

ethylene): the maximum yield was obtained for the compound for which $n = 2$ (25–26%). The yield of the remaining alkyltrichlorosilanes decreases with increasing value of n, amounting to 4% of the sum of all products for $n = 5$.

Conclusion

The reaction of thermal telomerization of trichlorosilane with ethylene was carried out at a temperature of 270–285° and a pressure of 200 atm. From the resulting mixture of products, alkyltrichlorosilanes of the structure $Cl_3Si(CH_2CH_2)_{nH}$, where $n = 1$—5, were isolated individually, and their trimethyl derivatives were obtained by the Grignard reaction.

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