ON THE TELOMERIZATION REACTION OF DIMETHYLCYCLOSILOXANES

ARTICLE 2. PREPARATION OF LINEAR α-CHLORO-ω-TRIMETHYLSILOXYDIMETHYLSILOXANES

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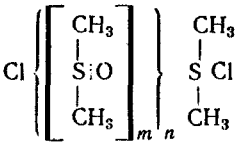
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 9,
pp. 1610-1615, September, 1961
Original article submitted November 28, 1960

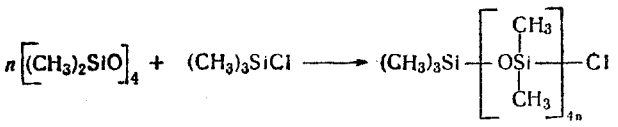
A method for preparing oligomeric dimethylsiloxanes with a functional group at one end of the siloxane chain, is described in the literature [1]. The authors proceed from oligomeric α, ω-dichlorodimethylsiloxanes prepared by the partial hydrolysis of dimethyldichlorosilane. By replacing one of the end chlorine atoms with an organic radical by means of organolithium compounds, linear dimethylsiloxanes, having one to five silicon atoms in the molecule, with a chlorine atom at one end of the siloxane chain, can be obtained in yields up to 40%. In the preceding articles [2,3] we showed that the reaction of dimethyldichlorosilane with dimethylcyclosiloxanes gives a series of α, ω-dichlorodimethylsiloxanes having the following structure:



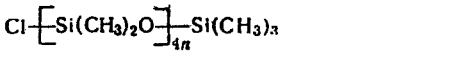
where m is the number of silicon atoms in the original ring, and n= 1,2,3, etc.

It was of interest to carry out the telomerization reaction of dimethylcyclosiloxanes, using not a difunctional compound but a monofunctional one as the chain-terminating substance.

The present article is devoted to a description of the reaction of octamethylcyclotetrasiloxane with trimethylchlorosilane. When the reaction is carried out between equimolar quantities of the indicated substances at a temperature of 250°C for 5 hr, it goes according to the equation:

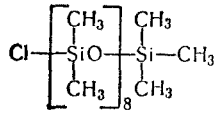
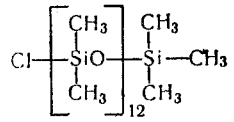
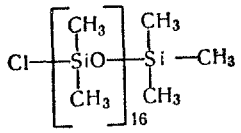


As in the case of the interaction of dimethyldichlorosilane and octamethylcyclotetrasiloxanes, the mechanism of the given reaction apparently consists in coordination of the trimethylchlorosilane silicon atom with an octamethylcyclotetrasiloxane oxygen atom, followed by ring rupture. In this case the chlorine atom combines with the octamethylcyclotetrasiloxane silicon atom, and the trimethylsilyl group goes to the oxygen atom. Further chain growth also takes place through the coordination of the terminal silicon atom, bound to halogen, and the octamethylcyclotetrasiloxane oxygen atom. Subsequent ring cleavage and formation of a new siloxane bond leads to lengthening of the chain by four dimethylsiloxane links. Thus members of a homologous series of the following composition are obtained:



Telomers with n = 2, 3, and 4 were isolated from the reaction mixture. The properties of these products are given in Table 1.

TABLE 1. Physical Properties of α-Chloro-ω-trimethylsiloxydimethylsiloxanes

Formula	Physical Properties				
	b.p., °C (p, mm Hg)	d_4^{20}	n_D^{20}	MR found	MR calc.
	197—199 (20)	0,9535	1,4012	178,84	179,03
	194—196 (3)	0,9592	1,4023	253,52	253,89
	233—235 (3)	0,9655	1,4035	327,52	328,50

The first member of the series (n = 1) was not isolated in pure form owing to the relative proximity of the boiling points of octamethylcyclotetrasiloxane and 1-chlorohendecamethylpentasiloxane, as a result of which the chlorine content in the fraction with b.p. 123-127°C (20 mm), corresponding to this monochloride [1], was invariably diminished appreciably.

In order to prove the presence of 1-chlorohendecamethylpentasiloxane the corresponding fraction was hydrolyzed and then condensed to the dimer—diicosamethyldecasiloxane—which was then identified by the boiling point, specific gravity, refractive index, molar refraction, and data of elementary analysis (Table 2). Investigation of the physical properties of members of the homologous series of Formula 1 with respect to the number of silicon atoms in the molecule revealed no anomalies in the properties of the telomeric homologs. The boiling points, specific gravities, and refractive indices vary regularly as the number of silicon atoms is increased.

When the effect of the molar ratio of octamethylcyclotetrasiloxane to trimethylchlorosilane in the original mixture on the composition of the reaction products was studied, it was found that the telomerization reaction does not lead to the formation of any one individual compound at any of the ratios investigated (1 : 1, 2 : 1, 3 : 1); a mixture of telomers is always formed. In this case the maximum yield is observed for a telomer with a chain length greater by four dimethylsiloxane links than that corresponding to the stoichiometric ratio in the original mixture. Thus when the ratio of octamethylcyclotetrasiloxane to trimethylchlorosilane is 1 : 1, not monochloropentasiloxane but monochlorononasiloxane is obtained in maximum yield, etc.

Curves of distribution according to molecular weight for different ratios of reacting components are shown in Fig. 1. In Fig. 2 the yields of various reaction products are shown with respect to the initial ratio of octamethylcyclotetrasiloxane to trimethylchlorosilane; from these it is evident that an increase in the given ratio leads to a decrease in the yield of lower telomers and a sharp increase in the yield of high-boiling products. It is also evident that a decrease in the content of trimethylchlorosilane, which opens up the octamethylcyclotetrasiloxane, in the original mixture in the region of the ratios studied, does not diminish the degree of conversion of octamethylcyclotetrasiloxane.

EXPERIMENTAL

Reaction of Octamethylcyclotetrasiloxane with Trimethylchlorosilane. Octamethylcyclotetrasiloxane (b.p. 174-176°C, mol. wt. 296.5) and trimethylchlorosilane (b.p. 57-57.5°C, mol. wt. 108.6; Cl 32.8%) were used for the syntheses. Into a dry, stainless steel autoclave of 0.5-liter capacity was put a mixture of the calculated quantities

of octamethylcyclotetrasiloxane and trimethylchlorosilane. The apparatus was kept at 250°C for 5 hr, cooled, and the reaction mixture fractionated. The fractionation was done by means of Favorskii flask with a 25 mm fractionating column. The percentage of chlorine was determined by titration in all fractions collected. Data on the charge in the apparatus, material balance of fractionation, and determination of the percentage of chlorine in the fractions, and also the results of calculation of the content of pure products in the intermediate fractions, are given for studied ratios of octamethylcyclotetrasiloxane to trimethylchlorosilane, equal to 1 : 1, 2 : 1, and 3 : 1 in Tables 3, 4, and 5, respectively. Fractions IV, VI, and VII (Table 3) were distilled twice, the following pure products being isolated: $Cl[(CH_3)_2SiO]_8Si(CH_3)_3$, $Cl[(CH_3)_2SiO]_{12}Si(CH_3)_3$ and $Cl[(CH_3)_2SiO]_{16}Si(CH_3)_3$, analytical data for which are given in Table 6.

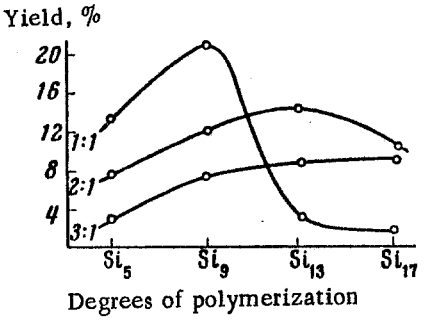


Fig. 1

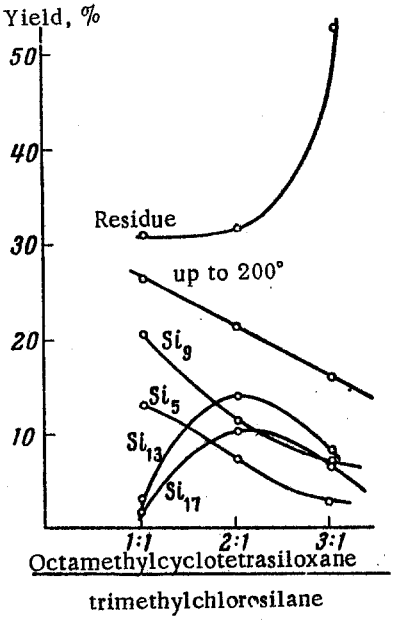


Fig. 2

TABLE 2. Physical Properties of Diicosamethyldecasiloxane

Data	Physical properties				Analytical data, %		
	B.p., °C (p, mm Hg)	d_4^{20}	n_D^{20}	MR	C	H	Si
Experimental	168—170 (2)	0,9254	1,3982	197,08	35,29 35,19	8,61 8,62	37,38 37,25
Literature and calculated	176 (3) 161 (1,1)	0,925	1,3988	198,46	34,98	8,81	37,15

Preparation of Diicosamethyldecasiloxane. A 25.8 g quantity of the product (fraction II, Table 4) with a chlorine content of 4.15; 4.10% was stirred with 30 g of water at 20°. The upper, oil layer was separated and was condensed by refluxing at 120°C for 3 hr. Then it was washed with water to remove HCl, dried, and distilled in vacuo. There was obtained 7.28 g of a fraction boiling at 165-173°C (2 mm) (63%). On distillation of this fraction pure diicosamethyldecasiloxane, $(CH_3)_3SiO[Si(CH_3)_2O]Si(CH_3)_3$ Found: C 35.29; 35.19; H 8.61; 8.62; Si 37.38; 37.25%. Calculated: C 34.98; H 8.81; Si 37.15%. The physical properties of this compound are given in Table 2.

SUMMARY

1. The telomerization reaction of octamethylcyclotetrasiloxane with trimethylchlorosilane leads to the formation of telomeric homologs of linear structure, having the composition: $Cl[(CH_3)_2SiO]_{4n}-Si(CH_3)_3$.

TABLE 3.* Results of the Reaction of Octamethylcyclotetrasiloxane with Trimethylchlorosilane at the Ratio 1:1. [The autoclave was charged with 293 g of a mixture containing 214.5 g (0.724 mole) of octamethylcyclotetrasiloxane and 78.5 g (0.724 mole) of trimethylchlorosilane. After the reaction 288 g was recovered; 280 g was subjected to fractionation.]

Fraction	B.p., °C (p, mm Hg)	Yield, g	Cl content, %	Content in fractions, g			
				Si_5 calculated Cl=8.75%	Si_9 calc. Cl=5.05%	Si_{13} calc. Cl=3.55%	Si_{17} calc. Cl=2.74%
I	up to 200 (760)	67,00	— —	—	—	—	—
II	up to 100 (20)	5,72	6,63; 6,81	4,41	—	—	—
III	100—130 (20)	24,81	6,50; 6,55	18,50	—	—	—
IV	130—185 (20)	29,45	6,10; 6,57	10,15	19,30	—	—
V	185—225 (20)	27,63	5,33; 5,38	2,28	25,35	—	—
VI	195 (3)	16,74	6,04; 5,62	2,62	14,12	—	—
VII	195—220 (3)	8,57	3,67; 3,25	—	—	8,57	—
VIII	220—240 (3)	6,32	2,28; 2,40	—	—	—	5,40
IX	240—280 (3)	17,46	1,57; 1,70	—	—	—	—
X	Residue (3)	70,34	— —	—	—	—	—
	Losses —	5,96	— —	—	—	—	—
Total	g	280	—	37,96	58,77	8,57	5,40
	%	100	—	13,56	20,99	3,06	1,93

* In Tables 3 - 5 the yield of telomers was calculated with allowance for their content in the intermediate stages.

TABLE 4.* Results of the Reaction of Octamethylcyclotetrasiloxane with Trimethylchlorosilane at the Ratio 2:1. [The autoclave was charged with 307.6 g of a mixture containing 260 g (0.876 mole) of octamethylcyclotetrasiloxane and 47.6 g (0.438 mole) of trimethylchlorosilane. After the reaction 303.16 g was recovered; 299 g was subjected to fractionation.]

Fraction	B.p., °C (p, mm Hg)	Yield, g	Cl Content found, %	Content in fractions, g			
				Si_5 calc. Cl=8.75%	Si_9 calc. Cl=5.05%	Si_{13} calc. Cl=3.55%	Si_{17} calc. Cl=2.74%
I	up to 195 (760)	47,70	— —	—	—	—	—
II	up to 130 (20)	25,84	4,15; 4,10	12,16	—	—	—
III	135—150 (20)	11,25	5,72; 5,47	7,20	—	—	—
IV	150—200 (20)	27,60	5,35; 5,67	3,40	24,20	—	—
V	200—230 (20)	21,66	4,56; 4,15	—	11,55	10,11	—
VI	190—210 (3)	19,09	3,49; 3,59	—	—	19,09	—
VII	210—230 (3)	21,81	3,24; 3,26	—	—	13,74	8,07
VIII	230—250 (3)	24,02	2,75; 2,56	—	—	—	24,02
IX	250—280 (3)	29,50	1,09; 0,98	—	—	—	—
X	Residue (3)	66,23	— —	—	—	—	—
	Losses	4,30	— —	—	—	—	—
Total	g	299	— —	22,76	35,75	42,94	32,09
	%	100	— —	7,61	11,96	14,36	10,73

* See footnote - Table 3.

2. New compounds—telomeric homologs containing one chlorine and nine, thirteen, and seventeen silicon atoms in the molecule—were identified and their physical properties studied.

3. The maximum yield of telomers does not correspond to the stoichiometric ratio (n) of the reacting components, but is shifted by one order (n+1) toward the formation of telomers of higher molecular weight.

TABLE 5.* Results of the Reaction of Octamethylcyclotetrasiloxane with Trimethylchlorosilane at the Ratio 3:1. [The autoclave was charged with 203.8 g of a mixture containing 181.7 g (0.612 mole) of octamethylcyclotetrasiloxane and 22.1 g (0.204 mole) of trimethylchlorosilane. After the reaction 199.50 g was recovered; 186.8 g was subjected to fractionation.]

Fraction	B.p., °C (p, mm Hg)	Yield, g	Cl content found, %	Content in fractions, g			
				Si_5 calc. Cl=8.75%	Si_9 calc. Cl=5.05%	Si_{13} calc. Cl=3.59%	Si_{17} calc. Cl=2.74%
I	up to 195 (760)	20,68	— —	—	—	—	—
II	up to 130 (20)	11,88	3,02; 2,80	3,96	—	—	—
III	130-150 (20)	3,80	4,05; 4,12	1,78	—	—	—
IV	150—200 (20)	8,35	4,75; 4,69	—	6,51	1,84	—
V	200—230 (20)	9,0	4,23; 4,13	—	3,78	5,22	—
VI	To 190 (3)	8,10	3,93; 4,11	—	2,54	5,56	—
VII	190—225 (3)	10,27	2,99; 3,00	—	—	3,29	6,98
VIII	225—250 (3)	10,17	2,41; 2,46	—	—	—	10,17
IX	250—280 (3)	8,86	0,62; 1,10	—	—	—	—
X	Residue (3)	91,6	— —	—	—	—	—
	Losses	4,09	— —	—	—	—	—
Total	g	186,8	— —	5,74	12,83	15,91	17,15
	%	100	— —	3,07	7,40	8,52	9,18

* See footnote - Table 3.

TABLE 6. $Cl[(CH_3)_3SiO]_{4n}Si(CH_3)_3$

n	Formula	B.p. (p, mm Hg)	Cl, %		S, %		C, %		H, %	
			calc	found	calc	found	calc	found	calc	found
2	$Cl[(CH_3)_2SiO]_8Si(CH_3)_3$	197—199 (20)	5,0[illegible]	4,95 5,0[illegible]	36,0[illegible]	35,9[illegible] 35,9[illegible]	32,53	32,82 32,70	3,19	8,22 8,17
3	$Cl[(CH_3)_2SiO]_{12}Si(CH_3)_3$	194—196 (3)	3,55	3,0[illegible] 3,47	36,55	36,33 36,53	32,49	32,58 32,62	3,18	8,11 8,12
4	$Cl[(CH_3)_2SiO]_{16}Si(CH_3)_3$	233—235 (3)	2,74	2,50 2,27	36,85	36,36 36,13	32,47	32,95 32,78	8,17	8,11 8,18

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