TELOMERIZATION OF DIMETHYLCYCLOSILOXANES

COMMUNICATION 3. TELOMERIZATION REACTIONS WITH DICHLOROMETHYLVINYLSILANE AND DICHLOROMETHYLPHENYLSILANE

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In previous communications it was reported that dimethylcyclosiloxanes react with dichlorodimethylsilane [1-3] and with chlorotrimethylsilane with formation of oligomers of general formula

$$A-\left(\begin{array}{c}M\\|\\OSi\\|\\M\end{array}\right)_{4n}-X \quad \text{where} \quad X = Cl;\ A = ClSiM_2- \text{and} M_3Si-;\ M = CH_3-$$

In the present communication we describe the telomerization of octamethylcyclotetrasiloxane with dichloromethylvinylsilane and with dichloromethylphenylsilane. In carrying out these reactions it was of interest to study the effect of varous substituents on the course of the telomerization.

The experiments showed that the reaction of equimolecular amounts of octamethylcyclotetrasiloxane and dichloromethylvinylsilane proceeded in accordance with the equation

$$(M_2SiO)_4 + \begin{array}{c}CH_2{=}CH\\|\\SiCl_2\\|\\M\end{array} \rightarrow Cl-\begin{array}{c}CH_2{=}CH\\|\\Si\\|\\M\end{array}-(OSiM_2)_{4n}-Cl$$

A mixture of telomer-homologs was then formed; of these we isolated α-chloro-α-methyl-α-vinyl ω-chloro-ω,ω-dimethyl polysiloxanes for which $\underline{n} = 1, 2$, and 3 and characterized them by their boiling points, refractive indices, specific gravities, molecular refractions, elementary analyses, and bromine values. The properties of the compounds isolated are given in Table 1, and the elementary analyses and bromine values are given in Table 4.

TABLE 1

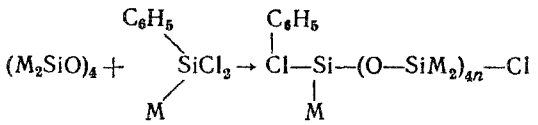
Formula	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	*MR*	
				Calc.	Found
$CH{=}CH_2$ CH_3 $Cl-Si-(OSi)_4-Cl$ CH_3 CH_3	107 (3)	1,0115	1,4153	108,44	108,24
$CH_2{=}CH$ CH_3 $Cl-Si-(OSi)_5-Cl$ CH_3 CH_3	197—199 (3)	0,9966	1,4121	183,02	183,29
$CH_2{=}CH$ CH_3 $Cl-Si-(OS)_{12}-Cl$ CH_3 CH_3	255—257 (3)	0,9849	1,4086	259,01	258,31

TABLE 2.

Formula	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	MR	
				Calc.	Found
	147—149 (3)	1,05232	1,4524	124,01	123,92
	239—241 (3)	1,0483	1,4458	198,59	198,54

After several repeat experiments it was found that the average conversion of dichloromethylvinylsilane was 32.8% and that of octamethylcyclotetrasiloxane was 54.0%. The yield of telomers was 45.1% on the weight of the original mixture, and the contents of the individual telomer-homologs with $\underline{n} = 1$, 2, and 3 were 18.5%, 30.8%, and 14.6%, respectively. Higher telomers with a degree of polymerization of $\underline{n} > 3$ were formed to the extent of 36.1%. Thus compounds of the α-chloro-α-methyl-α-vinyl ω-chloro-ω, ω-dimethyl polysiloxane series with given numbers of silicon atoms have been prepared by the telomerization reaction; this is as yet the only reaction by means of which the synthesis of such compounds has been effected.

The reaction between octamethylcyclotetrasiloxane and dichloromethylphenylsilane was carried out with the object of preparing telomer-homologs of the α-cholro-α-methyl-α-phenyl ω-chloro-ω, ω-dimethyl polysiloxane series. The first experiments showed that under standard conditions (250°, three hours) the conversion was very low (the total amount of telomers was less than 10% on the weight of the reactants taken). Further experiments were carried out at 300° for five hours with 2 moles of dichloromethylphenylsilane to each mole of octamethylcyclotetrasiloxane. However, even under these conditions the conversion was only 18.4%; the conversion of dichloromethylphenylsilane was 9.1% and that of octamethylcyclotetrasiloxane was 19.0%. From the reaction products



we isolated telomer-homologs with $\underline{n} = 1$ and 2, and 49.0% of the total amount of telomers boiled above 350° (3 mm). The properties of 1, 9-dichlorononamethyl-9-phenylpentasiloxane and 1, 17-dichloroheptadecamethyl-17-phenylnonasiloxane are given in Table 2.

Hence, in the reaction of octamethylcyclotetrasiloxane with dichloromethylphenylsilane telomer-homologs of the α-chloro-α-methyl-α-phenyl ω-chloro-ω, ω-dimethyl polysiloxane series are formed.

EXPERIMENTAL

Reaction of Octamethylcyclotetrasiloxane with Dichloromethylvinylsilane. For the syntheses we used octamethylcyclotetrasiloxane of b.p. 174-176°, (mole. wt. 296.6) and dichloromethylvinylsilane of b.p. 93° (Cl 50.6%). An autoclave was charged with 148.0 g (0.5 mole) of octamethylcyclotetrasiloxane and 70.5 g (0.5 mole) of dichloromethylvinylsilane. The reaction procedure was similar to that for dichlorodimethylsilane [2]. The reaction products (215 g) were fractionated first through a column of 10-plate efficiency and then from a flask having a column. Data on the separation of the products are given in Table 3.

From fraction IV, after passage through the fractionation column, we isolated pure

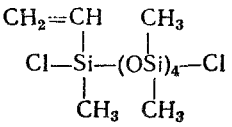


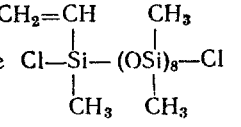
TABLE 3.

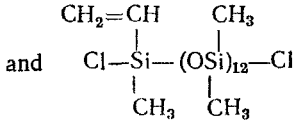
Fraction	B.p. of fraction in °C (p in mm)	Yield, g	Cl content, %	Content of products (g)					
				$CH_2=CH-SiCl_2-CH_3$	$[(CH_3)_2SiO]_4$	Si_5 Cl_{calc} = =16.2	Si_9 Cl_{calc} = = 9.64	Si_{13} Cl_{calc} = = 6.88	Residue
I	up to 100	40,2	50,62	40,2					
II	100—185	74,3	4,29	7,2	67,1				
III	До 90 (3)	2,8	7,8		1,3	1,5			
IV	90—120 (3)	11,1	15,7			11,1			
V	120—185 (3)	20,5	11,5			5,7	14,8		
VI	185—205 (3)	8,4	9,62				8,4		
VII	205—245 (3)	14,6	8,15				7,0	7,6	
VIII	245—265 (3)	6,8	7,14					6,8	
IX	Residue	35,0	6,31						35,0
Total		213,7		47,2	68,4	18,3	30,2	14,4	35,0

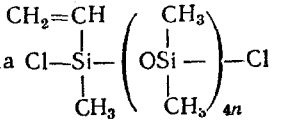
*Average value from two determinations.

TABLE 4.

n	B.p. in °C (p in mm)	C, %		H, %		Si, %		Cl, %		Bromine value	
		calc.	found	calc.	found	calc.	found	calc.	found	calc.	found
1	107,3	30,19	29,95 30,01	6,9	6,75 6,59	32,06	32,65 32,41	16,2	16,1 15,85	36,6	35,2 34,9
2	197—199 (3)	31,04	30,62 30,82	7,54	7,31 7,40	34,33	33,76 33,80	9,64	9,51 9,09	21,6	19,5 20,3
3	255—257 (3)	31,47	31,18 31,10	7,63	7,25 7,40	35,37	35,43 35,30	6,88	6,43 6,80	15,0	11,5 12,0

and from Fractions VI, and VIII, by two distillations from a flask with a column, we obtained pure 

and 

The elementary analyses and bromine values of the compounds isolated of general formula 

are given in Table 4.

Reaction of Octamethylcyclotetrasiloxane with Dichloromethylphenylsilane. The reaction of octamethylcyclotetrasiloxane with dichloromethylphenylsilane was carried out in an outocalve at 300° for five hours. We took 221.5 g (0.72 mole) of octamethylcyclotetrasiloxane and 266.5 g (1.44 moles) of dichloromethylphenylsilane, b.p. 200-202° (Cl 37.0%). From the autoclave we discharged 475 g of product, from which distillation up to 100° (10 mm) gave 390.6 g (Cl 24.8%) of unchanged reactants. From 83.94 g of still residue the first fractionation gave 43.4 g of volatile oligomers which came over up to 350° (3 mm), and the nondistilling residue amounted to 40.5 g. By repeated refraction-

ation of the fraction of b.p. up to 350° (3 mm) we obtained 6.6 g of pure $Cl-Si(C_6H_5)(CH_3)-[OSi(CH_3)_2]_4$. Found: C 37.48; 37.62; H 6.33; 6.35; Si 28.11; 28.33; Cl 15.00; 14.97%. $C_{15}H_{32}O_4Si_5Cl_2$. Calculated: C 36.91; H 6.60; Si 28.75; Cl 14.54% and 2 g of pure $Cl-Si(C_6H_5)(CH_3)-[OSi(CH_3)_2]_8-Cl$. Found: C 36.01; 35.81; H 6.98; 7.11; Si 31.97; 31.62; Cl 9.23; 9.14%; $C_{23}H_{56}O_8Si_9Cl_2$. Calculated: C 35.3; H 7.16; Si 32.2; Cl 9.66%.

SUMMARY

1. The reactions of octamethylcyclotetrasiloxane with dichloromethylvinylsilane and with dichloromethylphenylsilane proceed as teleomerization reactions.

2. Five telomer-homologs of two homologous series were isolated.

3. The telomerization of octamethylcylcotetrasiloxane with dichloromethylvinylsilane and with dichloromethylphenylsilane may serve as a method for the preparation of oligomers for the synthesis of polymers of regular structure.

LITERATURE CITED

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