TELOMERIZATION OF ORGANOCYCLOSILOXANES

K. A. ANDRIANOV AND V. V. SEVERNYI

Institute of Elemento-Organic Compounds,
Academy of Sciences, Moscow (U.S.S.R.)

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Telomerization, which is the polymerization of an unsaturated compound in the presence of another substance, which breaks up to form the terminal groups of the new polymer, is widely used for synthesis of various oligomerous organic compounds.

Using telomerization as means of obtaining oligomers with inorganic main chains framed by organic groups would be of great theoretical and practical interest. Such reactions have not been described in the literature, but the use of experience gained by us employing the telomerization reaction for the synthesis of organic oligomers was not possible because of the lack of elemento-organic polymerizable monomers with double bonds E=O or E=E (E=element). In the present case, the authors proceeded from organocyclosiloxanes, and not from compounds with double bonds. Diorganodichlorosilanes were used as the substances which cause polymerization and supply the polymerizing molecules with end groups. When equimolecular amounts of hexamethylcyclotrisiloxane (D_3) and dimethyldichlorosilane were heated together at 250° in a sealed glass ampoule there was an 84.3 % conversion into a telomer homologous mixture according to the following reaction:

$$n[(CH_3)_2SiO]_3 + (CH_3)_2SiCl_2 \longrightarrow ClSi(CH_3)_2[OSi(CH_3)_2]_{3n}Cl\,.$$

Telomers with n = 1, 2 and 3, whose characteristics and physical data are given in Table 1, were isolated.

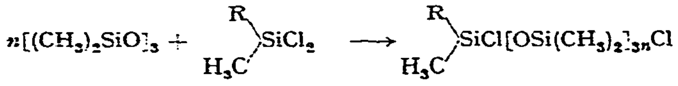
TABLE 1

PHYSICAL PROPERTIES OF THE DIFUNCTIONAL TELOMERS

Formula	*Boiling point* °*C/mm*	d_4^{20}	n_D^{20}	MR_D *Calculated*	MR_D *Found*
$Cl(CH_3)_2Si[OSi(CH_3)_2]_3Cl$	111/2	1.0110	1.47027	—	—
$Cl(CH_3)_2Si[OSi(CH_3)_2]_6Cl$	135/4	0.9996	1.4035	141.67	140.81
$Cl(CH_3)_2Si[OSi(CH_3)_2]_9Cl$	186/4	0.9927	1.4048	197.76	196.92
$Cl(CH_3)HSi[OSi(CH_3)_2]_3Cl$	75/5	1.0242	1.4012	81.22	80.77
$Cl(CH_3)HSi[OSi(CH_3)_2]_6Cl$	137/5	1.0052	1.4031	137.29	136.44
$Cl(CH_3)HSi[OSi(CH_3)_2]_9Cl$	180/5	0.9912	1.4043	193.36	192.81
$Cl(CH_3)(CH_2{=}CH)Si[OSi(CH_3)_2]_3Cl$	59/3	1.0240	1.4138	88.75	88.94
$Cl(CH_3)(CH_2{=}CH)Si[OSi(CH_3)_2]_6Cl$	117/3	1.0083	1.4111	145.37	145.89
$Cl(CH_3)(C_6H_5)Si[OSi(CH_3)_2]_3Cl$	99/5	1.0649	1.4518	105.32	104.86
$Cl(CH_3)(C_6H_5)Si[OSi(CH_3)_2]_6Cl$	152/5	1.0473	1.4462	161.39	162.00

Octamethylcyclotetrasiloxane (D_4) possessed low activity under similar conditions.

The influence of the substituents of the silicon atom on the activity of organochlorosilanes in the telomerization of (D_3) was studied by extending the reaction to other diorganodichlorosilanes, *viz.*, methyldichlorosilane, methylvinyldichlorosilane and methylphenyldichlorosilane. This is represented by the following equation:



$$n[(CH_3)_2SiO]_3 + \overset{R}{\underset{H_3C}{}}{>}SiCl_2 \longrightarrow \overset{R}{\underset{H_3C}{}}{>}SiCl[OSi(CH_3)_2]_{3n}Cl$$

where R = H, $CH_2{=}CH$, C_6H_5.

Telomers with n = 1, 2 and 3, formed as a result of the reaction of (D_3) with methyldichlorosilanes, were isolated and characterized by their physical properties (see Table 1). Conversion data for the parent substances and yields of individual telomers depending upon the molar relationship of reagents are shown in Table 2.

TABLE 2

YIELDS OF TELOMERS AT THE REACTION OF (D_3) WITH $R(CH_3)SiCl_2$ (in per cent of their sum)

R	*Ratio $R(CH_3)SiCl_2:(D_3)$*	*Conversion*		*Yield of telomers with n =*			
		$R(CH_3)SiCl_2$	*(D_3)*	*1*	*2*	*3*	*Highest*
CH_3	1:1	67.3	93.3	69.4	15.6	4.1	10.9
H	1:1	81.0	97.1	83.1	7.1	3.1	3.9
H	1:2	100	87.5	31.8	42.8	9.5	14.3
$CH_2{=}CH$	1:1	95.3	90.1	71.2	11.8	—	8.7
$CH_2{=}CH$	1:2*	52.8	48.7	—	67.4	—	25.5
C_6H_5	1:1	49.6	86.2	76.2	7.6	—	13.6

* The reaction was carried out in two stages with the isolation of the telomer with n = 1, obtained at the first stage.

There is a high conversion factor for the reaction, and the increasing of the content of (D_3) increases the yield of the higher telomers. However, even in this case lower telomers are still formed with a preferable yield, which may indicate a higher activity of methyldichlorosilane as compared with telomers formed consecutively by this reaction so that the reaction proceeds by successively joining (D_3) molecules to the parent organochlorosilane; this was proved experimentally by the reaction with methylvinyldichlorosilane. 1,7-Dichloro-1-vinylheptamethyltetrasiloxane obtained in the first stage (telomer with n = 1) was again reacted with (D_3) in the result of which a corresponding series of telomers was obtained. The properties of the isolated compounds and analytical data are shown in Table 1, and conversion data of reagents and yields data of telomers are given in Table 2.

Telomers with n = 1 and 2 were separated out after the reaction of (D_3) with methylvinyldichlorosilane. Corresponding data for this reaction are given in Tables 1 and 2. (D_3) conversion data can be used to measure the reactivity of compounds such as $R(CH_3)SiCl_2$, and their dependence on the kind of radical R, all the reactions being carried out under similar conditions. As shown in Table 2 the activity of the organochlorosilanes studied is dependent upon R and can be summarized in the following manner:

$$H > CH_3 > CH_2{=}CH > C_6H_5,$$

which corresponds to the series of increase of the $+I$ effect.

The above reactions were carried out with hexamethylcyclotrisiloxane. Later on this reaction was also studied for various organocyclosiloxanes of the common formula $(R'R''SiO)_3$ (where $R' = R'' = C_2H_5$; $R' = CH_3$ and $R'' = C_2H_3$; $R' = CH_3$ and $R'' = C_6H_5$) and dimethyldichlorosilane.

It was found that in this case interaction also proceeded according to the scheme of a telomerization reaction:

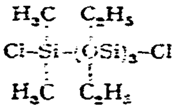
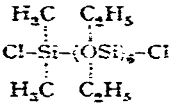
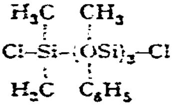
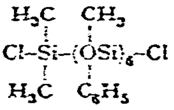
$$n(R'R''SiO)_3 + (CH_3)_2SiCl_2 \longrightarrow ClSi(CH_3)_2(OSiR'R'')_{3n}Cl$$

and led to formation of telomer homologous with n = 1, 2, 3 . . .

The properties of the products isolated in this reaction are shown in Table 3 and their yields and conversion of the parent products in Table 4.

TABLE 3

PHYSICAL PROPERTIES OF TELOMERS ON THE BASIS OF HEXAETHYLCYCLOTRISILOXANE AND TRIMETHYLTRIPHENYLCYCLOTRISILOXANE

Formula	*Boiling point °C/mm*	d_4^{20}	n_D^{20}	MR_D	
				Calculated	*Found*
 $\mathrm{Cl{-}\underset{H_3C}{\overset{H_3C}{Si}}{-}(\underset{C_2H_5}{\overset{C_2H_5}{OSi}})_3{-}Cl}$	150/5	1.0102	1.4303	113.47	113.11
 $\mathrm{Cl{-}\underset{H_3C}{\overset{H_3C}{Si}}{-}(\underset{C_2H_5}{\overset{C_2H_5}{OSi}})_6{-}Cl}$	175–178/0.01	0.9988	1.4364	197.46	197.32
 $\mathrm{Cl{-}\underset{H_3C}{\overset{H_3C}{Si}}{-}(\underset{C_6H_5}{\overset{CH_3}{OSi}})_3{-}Cl}$	198/4	1.1276	1.5118	144.78	144.30
 $\mathrm{Cl{-}\underset{H_3C}{\overset{H_3C}{Si}}{-}(\underset{C_6H_5}{\overset{CH_3}{OSi}})_6{-}Cl}$	201–203/0.01	1.1310	1.5304	260.07	259.72

The reaction trimethyltrivinylcyclotrisiloxane with dimethyldichlorosilane was carried out at 250° and 200°. In both cases, individual telomers were not isolated because a solid insoluble polymer was formed as a result of the reaction, probably at the expense of the polymerization of the vinyl group. As unreacted dimethyldichlorosilane can be distilled off from the polymer, one can estimate its

TABLE 4

CONVERSION OF REAGENTS AND YIELDS OF TELOMERS AT REACTIONS OF EQUIMOLECULAR AMOUNTS OF $(CH_3)_2SiCl_2$ AND $(R'R''SiO)_3$

Cyclosiloxane $(R'R''SiO)_3$	*Conversion*		*Yield of telomers (% of sum)*		
	$(CH_3)_2SiCl_2$	$(R'R''SiO)_3$	$n = 1$	$n = 2$	$n \geq 3$
$[(CH_3)_2SiO]_3$	67.3	93.3	69.4	15.6	15.0
$[(CH_2{=}CH)(CH_3)SiO]_3$	13.0	—*	—*	—*	—*
$[(C_6H_5)(CH_3)SiO]_3$	36.5	83.6	32.9	4.9	63.2
$[(C_2H_5)_2SiO]_3$	53.4	65.0	64.3	17.6	18.6

* Not determined due to polymerization by double bonds.

conversion, which is only 13% at 250°. Hexaorganocyclotrisiloxanes can be placed in the following series of decreasing activity for the telomerization reaction:

$$[(CH_3)_2SiO]_3 > [(C_2H_5)_2SiO]_3 > [CH_3(C_6H_5)SiO]_3 > [(CH_2{=}CH)(CH_3)SiO]_3$$

when their reactivity, estimated by the conversion of dimethyldichlorosilane (see Table 4) is compared.

EXPERIMENTAL

The telomerization of organocyclotrisiloxanes with diorganodichlorosilanes was carried out in sealed glass ampoules, volume of 150–200 cm^3. The reactants were kept in a salt bath at 250° for 5 hours. The isolation of unreacted initial components and telomers was carried out by distillation on a column of 10tt; first at atmospheric pressure and then at a pressure of 2–5 mm. The high boiling-point telomers were isolated from a Klyzen bulb at a pressure of 10^{-2} mm.

TABLE 5

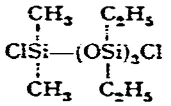
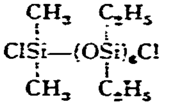
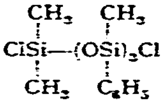
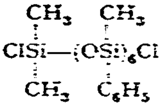
ANALYTICAL DATA OF DIFUNCTIONAL TELOMERS

Formula	*C*		*H*		*Si*		*Cl*	
	Calcd.	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*
$Cl(CH_3)_2Si[OSi(CH_3)_2]_6Cl$	29.29	29.50 29.49	7.37	7.44 7.76	34.21	34.20 33.93	12.37	12.19 11.89
$Cl(CH_3)_2Si[OSi(CH_3)_2]_9Cl$	30.15	30.28 30.25	7.59	7.37 7.58	35.23	35.26 35.92	8.91	8.40 8.97
$Cl(CH_3)HSi[OSi(CH_3)_2]_3Cl$	24.94	25.07 24.72	6.53	6.69 6.29	33.24	33.27 33.45	21.09	20.80 20.47
$Cl(CH_3)HSi[OSi(CH_3)_2]_6Cl$	27.90	28.08 28.15	7.17	7.29 7.32	35.07	35.35 35.17	12.69	12.38 12.66
$Cl(CH_3)HSi[OSi(CH_3)_2]_9Cl$	29.21	28.56 28.73	7.42	7.41 7.32	35.18	36.25 36.11	9.07	9.36 9.65
$Cl(CH_3)(CH_2{=}CH)Si[OSi(CH_3)_2]_3Cl$	29.97	29.77 29.63	6.65	6.65 6.53	31.09	30.99 30.71	19.51	19.21 19.14
$Cl(CH_3)(CH_2{=}CH)Si[OSi(CH_3)_2]_6Cl$	30.70	30.52 30.45	7.23	7.17 7.23	33.45	33.15 33.11	12.12	12.39 12.63
$Cl(CH_3)(C_6H_5)Si[OSi(CH_3)_2]_3Cl$	39.42	39.62 39.83	6.35	6.47 6.51	27.21	27.11 27.02	17.18	17.43 17.35
$Cl(CH_3)(C_6H_5)Si[OSi(CH_3)_2]_6Cl$	35.98	36.17 36.25	6.95	7.03 7.05	31.01	31.19 31.32	11.85	12.14 12.19

The properties of individual telomers are shown in Tables 1 and 3, and their yields in Tables 2 and 4. The analytical data for the telomers, on the basis of (D_3), are shown in Table 5, and on the basis of hexaethylcyclotrisiloxane and trimethyltriphenylcyclotrisiloxane in Table 6.

TABLE 6

ANALYTICAL DATA OF TELOMERS ON THE BASIS OF HEXAETHYLCYCLOTRISILOXANE AND TRIMETHYLTRIPHENYLCYCLOTRISILOXANE

Formula	C		H		Si		Cl	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
 $\mathrm{Cl}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\text{—}(\mathrm{O}\underset{\mathrm{C_2H_5}}{\overset{\mathrm{C_2H_5}}{\mathrm{Si}}})_3\mathrm{Cl}$	38.83	38.80 39.01	8.28	8.62 8.62	26.70	26.75 26.64	16.30	16.15 16.30
 $\mathrm{Cl}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\text{—}(\mathrm{O}\underset{\mathrm{C_2H_5}}{\overset{\mathrm{C_2H_5}}{\mathrm{Si}}})_6\mathrm{Cl}$	42.03	42.15 42.08	8.90	8.98 8.82	26.41	26.25 26.08	9.57	9.41 9.26
 $\mathrm{Cl}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\text{—}(\mathrm{O}\underset{\mathrm{C_6H_5}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}})_3\mathrm{Cl}$	51.31	50.68 50.47	5.58	5.84 6.04	20.82	21.15 21.46	13.22	13.62 13.32
 $\mathrm{Cl}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\text{—}(\mathrm{O}\underset{\mathrm{C_6H_5}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}})_6\mathrm{Cl}$	55.72	55.25 55.24	5.71	5.73 5.47	20.75	21.14 20.94	7.51	7.12 7.21

SUMMARY

A new reaction of organocyclosiloxanes with diorganodichlorosilanes was discovered. This telomerization reaction proceeds without any catalysts according to the following equation:

$$r'r''SiCl_2 + n(R'R''SiO)_3 \rightarrow r'r''SiCl(R'R''SiO)_{3n}Cl.$$

Reactions of the hexamethylcyclotrisiloxane ($R' = R'' = CH_3$) with different diorganodichlorosilanes ($r' = CH_3$; $r'' = H$, CH_3, $CH_2{=}CH$, C_6H_5) and dimethyldichlorosilanes ($r' = r'' = CH_3$) with different hexaorganocyclotrisiloxanes ($R' = CH_3$; $R'' = CH_3$, $CH_2{=}CH$, C_6H_5; $R' = R'' = C_2H_5$) have been studied. A step-wise reaction mechanism was confirmed.

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