

SYNTHESIS OF TELOMERS HAVING DIFFERENT FUNCTIONALITIES, THE TELOMERIZATION REACTION MECHANISM

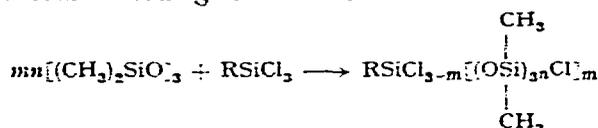
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(Received July 9th, 1963)

In a previous article¹ the authors considered the telomerization reaction of organo-cyclosiloxanes and difunctional alkyl- or -aryl-chlorosilanes, leading to the synthesis of difunctional telomers. The present work is devoted to the extension of this reaction to organochlorosilanes with various functional groups and to a discussion of the reaction mechanism.

The telomerization reaction of hexamethylcyclotrisiloxane (D_3) with organotrichlorosilanes proceeds according to the scheme²:



where, $n = 1, 2, 3 \dots$, $m = 1, 2, 3$ and $R = CH_3, C_2H_5, CH_2=CH, C_6H_5$.

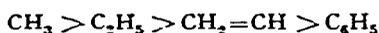
Here, as in the case of the reaction with difunctional organochlorosilanes, (D_3) conversion as well as the yield of telomers involving various degrees of polymerization (mn) depends on the type of organic radical R on the silicon atom. The data in Table I

TABLE I
REACTION RESULTS OF (D_3) WITH $RSiCl_3$

R	Ratio	Conversion %		Yield of telomers with $n =$			
	$RSiCl_3/(D_3)$	$RSiCl_3$	(D_3)	1	2	3	Higher
CH_3	1:1	61.6	92.2	70.0	8.7	2.2	18.0
CH_3	1:2	79.0	89.0	21.0	9.6	5.5	62.3
CH_3	1:2*	33.7	52.5	—	68.7	17.3	13.8
C_2H_5	1:1	76.5	89.4	88.5	7.7	—	3.8
C_2H_5	1:2	93.1	84.7	29.0	12.5	10.5	48.0
$CH_2=CH$	1:1	77.3	86.0	74.6	14.6	6.4	4.4
C_6H_5	1:1	68.2	81.9	73.9	13.8	5.5	5.8

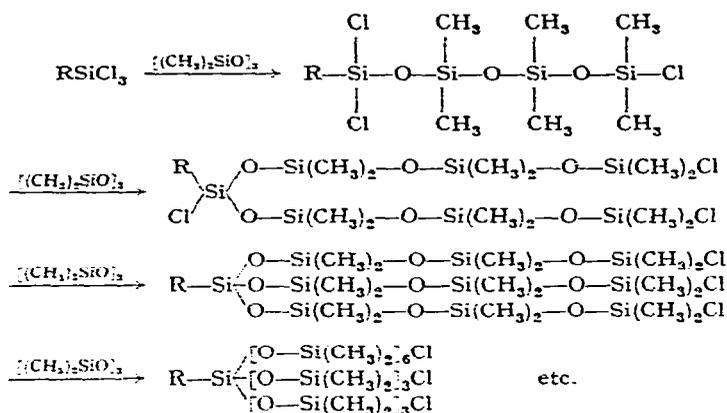
* Equimolecular amounts (D_3) and the telomers with $n = 1$ are actually taken into the reaction.

clearly illustrates this. Table I shows that the activity of organotrichlorosilanes when telomerized with dimethylcyclosiloxanes and estimated according to the conversion of dimethylcyclosiloxane, is in the following order



which is similar to that found earlier for diorganodichlorosilanes. Reactions performed with methyltrichlorosilane and ethyltrichlorosilane with an excess of dimethylcyclo-siloxane resulted in a reduction of the yield of the $n = 1$ telomer, an insignificant increase in the yield of $n = 2$ and 3 telomers, but a considerable increase in the yield of the higher telomers. It is interesting to note that the composition of products of the reaction differs from that produced in a single-stage reaction, if the reaction of one mole of methyltrichlorosilane with two moles of hexamethylcyclotrisiloxane is carried out in two stages with isolation of 1,1,7-trichloroheptamethyltetrasiloxane, formed at the first stage. In the latter case, as well as in the reaction of equimolecular amounts, the product of telomerizing of the first molecule of hexamethylcyclotrisiloxane is formed with a high yield and the higher telomers are formed in insignificant amounts. It is obviously connected with the fact that the activity of organochlorosilane depends greatly upon number of chlorine atoms bonded with one silicon atom.

Obviously, with successive stages of telomerization according to the scheme:

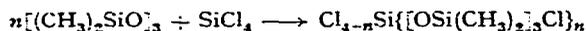


the telomer activity is reduced as a result of each addition of a hexamethylcyclotrisiloxane molecule. In organotrichlorosilane and telomer molecules the trifunctional silicon atom bonded carries at least one chlorine atom with a larger partial positive charge, than when it is connected with chlorosilicon terminal atoms, as a result of which the first additions proceed, probably, via the trifunctional silicon atom, and telomers with $n \geq 2$ represent branched products.

The sharpest change in activity probably occurs when organotrichlorosilane reacts to form the first telomer and it does not change after the fourth, fifth, and subsequent stages of reaction, when there is only elongation of the branches formed as a result of adding the first three hexamethylcyclotrisiloxane molecules.

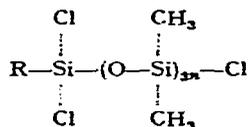
The physical properties of telomers of the homologous series studied are shown in Table 2.

Silicon tetrachloride is the only widely available telogen for receiving tetrafunctional telomers. In the reaction of equimolecular amounts of (D_3) and silicon tetrachloride, (D_3) conversion amounted to 100%. 8.6% of unreacted SiCl_4 was recovered from the reaction mixture, and telomers, formed according to the equation:



were isolated; $n = 1$ and 2 having yields 71.5 and 13.5% respectively.

TABLE 2
PHYSICAL PROPERTIES OF TRI- AND TETRAFUNCTIONAL TELOMERS



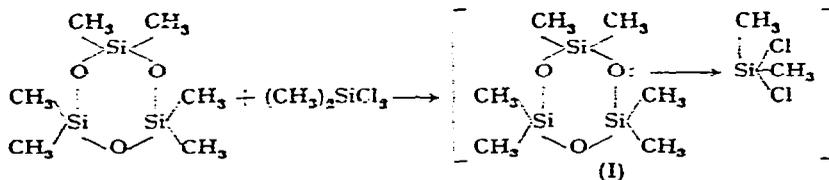
Formula	Boiling point °C/mm	d_4^{20}	n_D^{20}	M _R D	
				Calcd.	Found
CH ₃ SiCl ₂ OSi(CH ₃) ₂₋₃ Cl	72/4	1.0827	1.4094	85.23	85.00
CH ₃ SiCl ₂ OSi(CH ₃) ₂₋₆ Cl	138/4	1.0309	1.4083	141.29	141.01
CH ₃ SiCl ₂ OSi(CH ₃) ₂₋₉ Cl	174/3	1.0173	1.4079	197.36	197.73
C ₆ H ₅ SiCl ₂ OSi(CH ₃) ₂₋₃ Cl	93/4	1.0864	1.4147	88.57	88.99
C ₆ H ₅ SiCl ₂ OSi(CH ₃) ₂₋₆ Cl	148/4	1.0465	1.4119	144.64	144.27
C ₆ H ₅ SiCl ₂ OSi(CH ₃) ₂₋₉ Cl	183/4	1.0232	1.4096	200.17	200.68
CH ₂ =CHSiCl ₂ OSi(CH ₃) ₂₋₃ Cl	76/3	1.0749	1.4160	89.39	89.39
CH ₂ =CHSiCl ₂ OSi(CH ₃) ₂₋₆ Cl	145/3	1.0420	1.4125	145.48	144.85
C ₆ H ₅ SiCl ₂ OSi(CH ₃) ₂₋₃ Cl	102/2	1.1272	1.4575	105.01	104.89
C ₆ H ₅ SiCl ₂ OSi(CH ₃) ₂₋₆ Cl	160-162/2	1.0707	1.4391	161.09	160.37
C ₆ H ₅ SiCl ₂ OSi(CH ₃) ₂₋₉ Cl	192-194/2	1.0439	1.4262	216.18	215.82
Cl ₃ SiOSi(CH ₃) ₂₋₃ Cl	65/4	1.1475	1.4079	84.94	84.36
Cl ₃ SiOSi(CH ₃) ₂₋₃ Cl	132/4	1.0870	1.4108	140.96	140.36

An attempt was also made to carry out the reaction of (D₃) with trimethylchlorosilane, however the reagents were fully recovered in an unchanged condition. Thus, with the decrease of function according to the series:



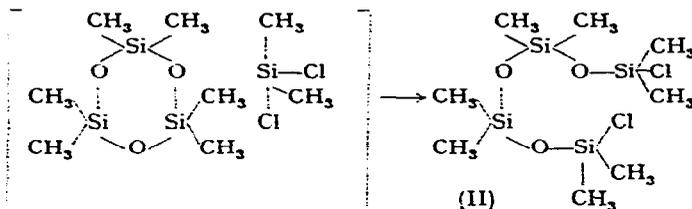
the considerable reduction in the activity of organochlorosilanes during telomerization is probably connected with changing the electron-acceptor properties of the silicon atom when replacing the chlorine atom ($-I$ -effect) with the methyl group ($+I$ -effect).

On the basis of the above mentioned experimental data the following mechanism for telomerization of organocyclosiloxanes with alkyl- or aryl-chlorosilanes seems to be likely. The reaction begins by coordinating one of the oxygen atoms of organocyclosiloxane and a silicon atom of organochlorosilane, for example, dimethyldichlorosilane, with the formation of an intermediate complex with a pentacovalent silicon atom according to the following scheme:



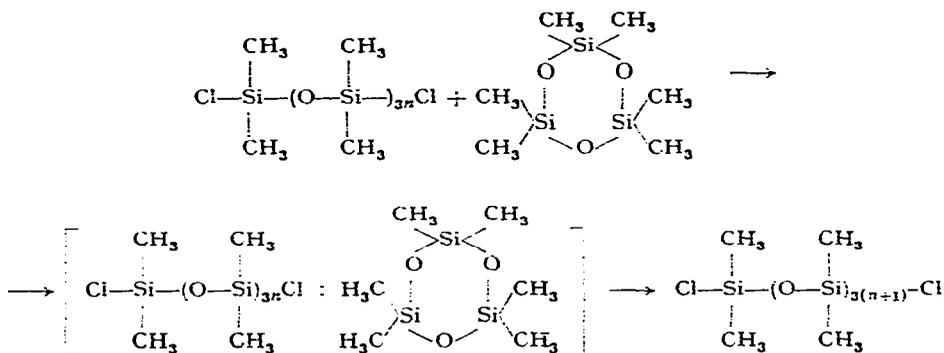
As a result of redistributing the bonds in complex (I) a break of the stressed ring takes place with chlorine addition to the silicon atom and the dimethylchlorosilyl

group to the oxygen atom with the formation of the first member of the homologous series (II):



As it is clear from all known reactions of reversible catalytic splitting of the bonds Si-O-Si, the nonreversible character of the above reaction is explained by the reaction proceeding at the expense of the tension energy of six-membered organocyclosiloxanes. It also explains the high activity of (D₃) the tension of which is estimated at ≈ 9 kcal/mole (ref. 4), the insignificant activity of (D₄) (ref. 5) with small tension and the complete inactivity of the linear organosiloxanes.

In its turn the product (I) formed by the reaction, is able to coordinate with another molecule of the cyclic organosiloxane with the formation and decay of the complex according to the scheme:



The increase of the number of dimethylsiloxane groups in the molecule resulting from each interaction corresponds to the number of silicon atoms in the parent cyclic compound.

To confirm the complex formation in the system of organochlorosilane-dimethylcyclosiloxane, two more actively interacting components, (D₃ and SiCl₄) were investigated. The investigation for complexes in this system was carried out by two methods: dielectrometric and cryoscopic titration.

Dielectrometric titration⁶ overestimated the dipole moment by 0.8 D, when compared with additive values. This result is considered to be due to the formation of an intermolecular bond of the donor-acceptor type.

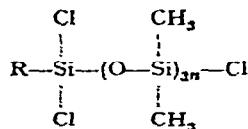
In the cryoscopic titration⁷ of (D₃) solution by silicon tetrachloride in benzene, a molecular weight of 312 was found, compared with a theoretical value of 170.

This probably occurs as a result of some SiCl₄ molecules forming addition compounds with (D₃) molecules and decreasing the number of kinetically independent particles in the solution. Thus, these dielectrometric and cryoscopic titration data

confirm that the telomerization reaction proceeds via an intermediate complex as was suggested above.

The silicon atom in the intermediate complex (I), which arose as a result of a nucleophilic attack, is more electronegative than in the parent position as it actually gets an additional pair of electrons. From the point of view of the supply of

TABLE 3
ANALYTICAL DATA OF TRI- AND TETRAFUNCTIONAL TELOMERS



Formula	C %		H %		Si %		Cl %	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$\text{CH}_3\text{SiCl}_2\text{OSi}(\text{CH}_3)_{2,3}\text{Cl}$	22.55	22.51 22.48	5.67	5.58 5.81	30.20	30.54 30.70	28.69	28.63 28.85
$\text{CH}_3\text{SiCl}_2\text{OSi}(\text{CH}_3)_{2,6}\text{Cl}$	26.35	26.27 26.42	6.57	6.48 6.55	33.11	32.78 33.02	18.01	18.33 18.48
$\text{CH}_3\text{SiCl}_2\text{OSi}(\text{CH}_3)_{2,9}\text{Cl}$	28.04	28.27 28.40	7.00	6.93 6.93	34.38	34.43 34.52	13.14	12.81 12.98
$\text{C}_2\text{H}_5\text{SiCl}_2\text{OSi}(\text{CH}_3)_{2,3}\text{Cl}$	24.96	24.81 24.85	5.93	6.27 6.07	29.12	29.16 29.41	27.65	27.71 27.85
$\text{C}_2\text{H}_5\text{SiCl}_2\text{OSi}(\text{CH}_3)_{2,6}\text{Cl}$	27.68	27.42 27.39	6.74	6.74 6.73	32.35	32.14 31.91	17.53	18.25 18.31
$\text{C}_2\text{H}_5\text{SiCl}_2\text{OSi}(\text{CH}_3)_{2,9}\text{Cl}$	28.61	28.87 29.07	7.12	7.21 7.21	33.75	34.08 33.78	12.85	12.77 12.71
$\text{CH}_2=\text{CHSiCl}_2\text{OSi}(\text{CH}_3)_{2,3}\text{Cl}$	25.03	25.53 25.50	5.48	5.72 5.67	29.41	30.03 30.00	27.81	26.93 27.09
$\text{CH}_2=\text{CHSiCl}_2\text{OSi}(\text{CH}_3)_{2,6}\text{Cl}$	27.80	27.80 28.01	6.44	6.35 6.35	32.51	32.59 32.74	17.60	17.54 17.29
$\text{C}_6\text{H}_5\text{SiCl}_2\text{OSi}(\text{CH}_3)_{2,3}\text{Cl}$	33.31	33.59 33.63	5.31	5.36 5.28	26.00	25.53 25.89	24.62	24.91 24.33
$\text{C}_6\text{H}_5\text{SiCl}_2\text{OSi}(\text{CH}_3)_{2,6}\text{Cl}$	32.80	32.54 32.59	6.24	6.66 6.42	29.92	30.51 30.23	16.51	16.96 16.64
$\text{C}_6\text{H}_5\text{SiCl}_2\text{OSi}(\text{CH}_3)_{2,9}\text{Cl}$	32.78	32.70 32.65	6.72	6.59 6.62	32.01	32.21 32.41	12.15	12.52 12.15
$\text{Cl}_3\text{SiOSi}(\text{CH}_3)_{2,3}\text{Cl}$	18.35	18.73 18.79	4.61	4.62 4.62	28.57	28.80 28.71	36.26	35.66 35.60
$\text{Cl}_3\text{SiOSi}(\text{CH}_3)_{2,6}\text{Cl}$	23.47	23.85 23.81	5.97	5.68 5.67	32.00	31.67 31.74	23.11	23.63 23.74

electrons, substituents having positive induction effects should slow down the reaction of telomerization while the substituents with the negative *I*-effect should accelerate it. The experimental data are in accordance with these conclusions, for the biggest decrease in the activity of the organochlorosilanes occurs on the substitution of the chlorine atom ($-I$ -effect) by the methyl group ($\div I$ -effect) in the series:



The activity of organochlorosilanes is influenced not only by the change of sign of the *I*-effect, but also by the changes of its value within that sign. In the field of $-I$ -effects, this is illustrated by the decrease of activity when chlorine is replaced with

group $-\text{[OSi(CH}_3)_2]_3\text{Cl}$ so that the telomer reacts less actively than the initial organochlorosilane. The series found by the authors:



which is in accordance with the relative electron-donor properties of the substituents, is an example of influence on the activity of organochlorosilane with the value of the I -effect of the substituents in the field of positive values. It is known that the $+I$ -effect increases from CH_3 to C_2H_5 and the vinyl and phenyl groups appear to be more powerful donors at the expense of the conjugation of π -electrons with the 3d-orbitals of the silicon atom. Thus, the suggested mechanism of the reaction corresponds completely to the experimental data obtained by the authors.

EXPERIMENTAL

The reactions of (D_3) with organotrichlorosilanes and silicon tetrachloride were carried out in sealed glass ampoules, volume 150–200 cm^3 . They were kept in salt bath at 250° for 5 hours.

Unreacted parent components and telomers were isolated by distillation of the mixture on the column of rott; first at atmospheric pressure and then at 2–5 mm. The properties of isolated telomers and their yields are shown in Tables 2 and 1, and the data of the analysis in Table 3.

SUMMARY

The telomerization reaction is applied to organochlorosilanes having different Cl numbers. The applicability of this reaction to the synthesis of telomers of different functionality is shown. A mechanism is proposed for the formation of the intermediate complex, and for the decomposition, with release of tensile energy, of its six-membered siloxane rings.

The formation of intermediate complexes is supported. The influence of the induction effects of substituents on Si atoms in organochlorosilanes upon their activity in the telomerization reaction with organocyclosiloxanes is discussed.

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