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Corresponding Member of the Academy of Sciences of the USSR K. A. ANDRIANOV, V. V. SEVERNYI

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## Abstract

## Full Text

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# THE TELOMERIZATION REACTION OF ORGANO-CYCLOSILOXANES WITH DIMETHYLDICHLOROSILANE

The telomerization reaction of dimethylcyclosiloxanes with organochlorosilanes, first described for the interaction with dimethyldichlorosilane ([1]), was subsequently studied in a considerable number of examples of the interaction of octamethylcyclotetrasiloxane and hexamethylcyclotrisiloxane with organochlorosilanes of various functionality ([2-4]). We have established that this reaction is of a general nature and is applicable not only to dimethylcyclosiloxanes, but also to other organocyclosiloxanes.

In the present work, reactions between various organocyclosiloxanes of the general formula $(R'R''SiO)_3$, where $R' = R'' = C_2H_5$, $R' = CH_3$ and $R'' = C_6H_5$, and dimethyldichlorosilane have been studied.

The choice of six-membered rings as the object of study is due to the fact that, in studying the reaction with dimethylcyclosiloxanes, it was established that six-membered rings are considerably more active in the telomerization reaction than eight-membered ones.

The telomerization reaction proceeds according to the equation:

$$(R'R''SiO)_3 + (CH_3)_2SiCl_2 \rightarrow ClSi\begin{matrix}CH_3\\|\\CH_3\end{matrix} - \left(\begin{matrix}R'\\|\\OSi\\|\\R''\end{matrix}\right)_{3n} Cl$$

and leads to the formation of telomer homologs with $n = 1, 2, 3, ....$

When carrying out the telomerization reaction of hexaethylcyclotrisiloxane with dimethyldichlorosilane at 250° for 5 h in sealed glass ampoules, the conversion of cyclosiloxane was 65.0%, and that of dimethyldichlorosilane 53.4%. Telomers of the formula

$$\mathrm{Cl-Si(CH_3)_2-\left(OSi(C_2H_5)_2\right)_{3n}-Cl}$$

were isolated with $n = 1$ and 2, in yields (based on the sum of telomers) of 64.8 and 17.6%, respectively. The still residue, apparently consisting of telomers with $n > 2$, amounted to 18.6%. The physical properties of the isolated compounds and their analytical data are given in Table 1.

The reaction of methylphenylcyclosiloxanes with dimethyldichlorosilane in a steel autoclave is accompanied by cleavage of siloxane bonds with formation of oligomers

$$\mathrm{ClSi(CH_3)_2-\left(OSi(C_6H_5)CH_3\right)_n-Cl,}$$

evidently due to the influence of catalytic amounts of ferric chloride formed on the walls of the autoclave. When the reaction of trimethyltriphenylcyclotrisiloxane with dimethyldichlorosilane was carried out in a glass ampoule under the same conditions, it proceeded as a telomerization reaction. In this case, the conversion of dimethyldichlorosilane was 36.5%, and that of cyclosiloxane 88.6%. The isolated telomer homologs

$$\mathrm{ClSi(CH_3)_2-\left(OSi(C_6H_5)CH_3\right)_{3n}-Cl}$$

with $n = 1$ and 2 (see Table 1), were obtained in yields of 32.9 and 4.9%. The still residue was formed in an amount of 63.2%.

**Table 1**

**Physical properties of the telomers**

$$\mathrm{Cl-Si(CH_3)_2-\left(OSiR'R''\right)_{3n}-Cl}$$

| R′ | R″ | $n$ | b.p., °C/mm | $d_4^{20}$ | $n_D^{20}$ | $MR_D$, calc. | $MR_D$, found |
|---|---|---|---|---|---|---|---|
| $C_2H_4$ | $C_2H_5$ | 1 | 150/5 | 1.0102 | 1.4303 | 113.47 | 113.11 |
| $C_2H_4$ | $C_2H_5$ | 2 | 175–178/0.01 | 0.9988 | 1.4364 | 197.46 | 197.32 |
| $CH_3$ | $C_6H_5$ | 1 | 198/4 | 1.1276 | 1.5118 | 144.78 | 144.30 |
| $CH_3$ | $C_6H_5$ | 2 | 201–203/0.01 | 1.1310 | 1.5304 | 260.07 | 259.72 |

The reaction of trimethyltrivinylcyclotrisiloxane with dimethyldichlorosilane was carried out in sealed glass ampoules at 250–200°. In both cases it was not possible to isolate individual telomers, since the reaction yields a solid insoluble polymer, apparently through polymerization at the vinyl groups. In view of the high functionality of the monomer (trimethyltrivinylcyclotrisiloxane), equal to 6, crosslinked polymers can form even at a low degree of polymerization. Since unreacted dimethyldichlorosilane can be distilled off from the polymer, this makes it possible to estimate its conversion, which at 250° is only 13%.

When comparing the reactivity toward dimethyldichlorosilane, estimated from its conversion, hexaorganotricyclotrisiloxanes can be arranged in the following order of decreasing activity in the telomerization reaction:

$$[(CH_3)_2SiO]_3 > [(C_2H_5)_2SiO]_3 > [CH_3(C_6H_5)SiO]_3 > [(CH_2{=}CH)CH_3SiO]_3.$$

## Experimental Part

The following were used for the syntheses: hexaethylcyclotrisiloxane (b.p. 108°/5 mm, $n_D^{20}$ 1.4308), trimethyltriphenylcyclotrisiloxane (b.p. 180–190°/4 mm), trimethyltrivinylcyclotrisiloxane (b.p. 58°/5 mm; $n_D^{20}$ 1.4221), and dimethyldichlorosilane (Cl 55.3%).

**Reaction with hexaethylcyclotrisiloxane.** A mixture of 34.3 g (0.106 mol) of hexaethylcyclotrisiloxane and 14.5 g (0.106 mol) of dimethyldichlorosilane was kept for 5 h in a sealed glass ampoule at 250°. Rectification of the mixture on a 10 theoretical-plate column at 760 mm gave 6.7 g of dimethyldichlorosilane, and at 5 mm 11.0 g of hexamethylcyclotrisiloxane (108–109°/5 mm) and 19.6 g of telomer with $n = 1$ (150–153°/5 mm).

Found, %: C 38.80; 39.01; H 8.62; 8.62; Si 26.75; 26.64; Cl 16.15; 16.30
$C_{14}H_{36}Si_4O_3Cl_2$. Calculated, %: C 38.83; H 8.28; Si 26.70; Cl 16.30

The still residue was distilled at $1 \cdot 10^{-2}$ mm. Obtained: 5.4 g of telomer with $n = 2$ (175–178°/0.01 mm).

Found, %: C 42.15; 42.08; H 8.98; 8.82; Si 26.25; 26.08; Cl 9.41; 9.26
$C_{30}H_{76}Si_7O_6Cl_2$. Calculated, %: C 42.03; H 8.90; Si 26.41; Cl 9.57

Still residue: 5.7 g.

The reaction of 3.6 g (0.028 mole) of dimethyldichlorosilane with 11.5 g (0.028 mole) of trimethyltriphenylcyclotrisiloxane was carried out under the same conditions. On distillation at 760 mm, 2.0 g of dimethyldichlorosilane was obtained, and at 5 mm, 1.3 g of trimethyltriphenylcyclotrisiloxane (190–195°/5 mm) and 3.9 g of telomer with $n = 1$ (205–209°/5 mm. Cl found 12.94; 13.06%; Cl calculated 13.22%). On distillation at $1 \cdot 10^{-2}$ mm, 0.6 g of telomer with $n = 2$ was obtained (196–201°/0.01 mm. Cl found 7.42; 7.32%; Cl calculated 7.51%) and 7.2 g of still residue with Cl 3.85%. The physical properties of the telomers coincided with those found earlier.

The reaction of 10 g (0.077 mole) of dimethyldichlorosilane with 20 g (0.077 mole) of trimethyltrivinylcyclotrisiloxane was carried out analogously. A solid polymer formed, from which, on heating to 200°, 8.7 g of dimethyldichlorosilane was distilled off. When the reaction was carried out at 200° after 2 hr of heating, a liquid reaction mixture was obtained, from which 9.1 g of dimethyldichlorosilane was recovered. On heating to 200° in vacuum for the purpose of isolating the telomers, the still residue was converted into a hard brittle polymer.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

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