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CHEMISTRY

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1962

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Abstract

Full Text

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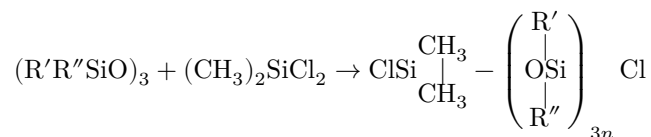
THE TELOMERIZATION REACTION OF ORGANO-CYCLOSILOXANES WITH DIMETHYLDICHLOROSI- LANE

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.

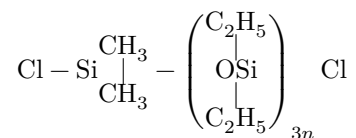
The choice of six-membered rings as the object of study is due to the fact that, in studying the reaction with dimethylcyclosiloxanes, it was established that six-membered rings are considerably more active in the telomerization reaction than eight-membered ones.

The telomerization reaction proceeds according to the equation:



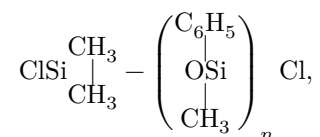
and leads to the formation of telomer homologs with $n = 1, 2, 3, \dots$

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

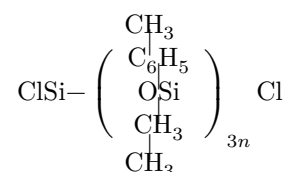


were isolated with $n = 1$ and 2 , in yields (based on the sum of telomers) of 64.8 and 17.6%, respectively. The still residue, apparently consisting of telomers with $n > 2$, amounted to 18.6%. The physical properties of the isolated compounds and their analytical data are given in Table 1.

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



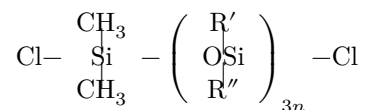
evidently due to the influence of catalytic amounts of ferric chloride formed on the walls of the autoclave. When the reaction of trimethyltriphenylcyclotrisiloxane with dimethyldichlorosilane was carried out in a glass ampoule under the same conditions, it proceeded as a telomerization reaction. In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



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

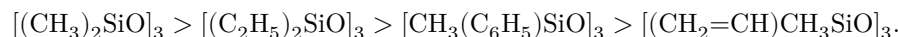
Physical properties of the telomers



R'	R''	<i>n</i>	b.p., °C/mm	d_4^{20}	n_D^{20}	MR_D , calc.	MR_D , found
C ₂ H ₄	C ₂ H ₅	1	150/5	1.0102	1.4303	113.47	113.11
C ₂ H ₄	C ₂ H ₅	2	175– 178/0.01	0.9988	1.4364	197.46	197.32
CH ₃	C ₆ H ₅	1	198/4	1.1276	1.5118	144.78	144.30
CH ₃	C ₆ H 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:



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
C₁₄H₃₆Si₄O₃Cl₂. 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
C₃₀H₇₆Si₇O₆Cl₂. 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.

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Received
4 VI 1962

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

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