SYNTHESIS AND POLYMERIZATION OF

2,2,6-TRIMETHYL-6-ALKYL(ARYL)-1-OXA-2,6-DISILACYCLOHEXANES

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The polymerization of 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane was studied previously [1, 2]. In the present paper we studied the effect of the nature of the radical attached to silicon on the polymerization rate of disilacyclohexanes of general formula



in the presence of nucleophilic and electrophilic catalysts. For this were synthesized the ethyl-, amyl-, phenyl-, and chlorophenyl-2,2,6-trimethyl-1-oxa-2,6-disilacyclohexanes according to the reaction



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In studying the reaction products of arylmethylallylethoxysilanes with dimethylhydrochlorosilane, or of dimethylallylethoxysilane with either dimethyl- or methylamylhydrochlorosilane, in the presence of H_2PtCl_6 it was found that, besides the addition reaction, a rearrangement of the chloro and ethoxy groups attached to the silicon is also observed. Thus, gas-chromatographic analysis of the reaction products, distilling in a 1-2° range, disclosed that the isolated fractions are not pure products, but instead contain, together with (IV), also bis(chlorosilyl)propane. Elemental analysis always gave a higher chlorine content than is required by theory.

2,2,6-Trimethyl-6-amyl-1-oxa-2,6-disilacyclohexane was obtained by several routes, which are represented by the scheme



In all cases the yield did not exceed 20-30%. The properties of the obtained compounds are given in Table 1.

The purity of the obtained compounds prior to polymerization was verified by employing the method of the GLC, NMR, and IR spectra. In the IR spectra for all of the rings containing alkyl radicals the value of the ν_{as} of the Si-O-Si bond, independent of the size of the radical attached to silicon, was equal to 990 cm⁻¹. In order to ascertain the effect of the nature of the radical on the vibrations of the Si-O-Si bond a calculation was made of their integral intensities A. In Table 2 are given the obtained values of A for the starting rings. It was shown that the integral intensity increases slightly with increase in the size of the alkyl radical.

For the polymerization were taken disilacyclohexanes containing two types of substituents: electron-acceptor (C_6H_5 , C_6H_4Cl) and electron-donor (ranging from CH_3 to C_5H_{11}). The anionic polymerization was run in the presence of 0.7% KOH at 120°. In Fig. 1 are given the kinetic curves that express the conversion of the polymer as a function of time. As can be seen, replacing the methyl radical by an alkyl radical sharply lowers the polymerization rate (from $k_{CH_3} = 4 \cdot 10^{-3}$ down to $k_{C_2H_5} = 0.2 \cdot 10^{-3} \text{ min}^{-1}$). This is explained by the fact that electron-donor substituents press the electrons on the silicon atom, and a redistribution of the electron density at the active center occurs. The silicon atom exhibits a less electropositive character with increase in the electron-donor properties of the substituent, and the rate of formation of the transition complex slows up. In addition, the steric effect also makes its contribution to a slowing up of the process. The obtained values of k_s for the alkyl radicals are close to each other, and the difference in the values of k_s lies within the limits of experimental error ($k_{C_2H_5} = 0.27 \cdot 10^{-3}$, $k_{C_3H_7} = 0.74 \cdot 10^{-3}$, $k_{C_5H_{11}} = 0.89 \cdot 10^{-3} \text{ min}^{-1}$).

The presence of phenyl and chlorophenyl substituents in the disilacyclohexanes increases the reaction rate somewhat $(k_{CH_3} = 4 \cdot 10^{-3}, k_{C_6H_5} = 4.3 \cdot 10^{-3}, k_{C_6H_4Cl} = 4.5 \cdot 10^{-3} \text{ min}^{-1})$ when compared with methyl, since the formation of the transition complex with the base of the disilacyclohexanes containing electron-acceptor substituents increases with increase in the electronegativity of the substituent: C_6H_4Cl , C_6H_5 . The ability of these substituents to withdraw electrons imparts a more electropositive character to the silicon atom and in this way facilitates a coordination of the anion (OH⁻) with the silicon. In the given case it is probable that the conjugation effect, which is opposite to the -I effect of the substituent, introduces a correction in the total effect of the radical. The rate constants of the disilacyclohexanes during anionic polymerization are given in Table 2.

| TABI | LE 1 | | | | | | | | | | | | | | | | |
|--|--|--|--|---|--------------------------------------|------------------|---|---|----------------|-----------------------------|--|------------|--|---------|---------------|--|--------------------------|
| | Compon | pu | | (| | | | (M | æ | | Found | η, | | | Calco | ., <i>d</i> o | |
| No. | for | nula | | هم. (p, mm] | Hg) | $^{n}_{D}$ | d_4^{20} | found | calcd. | ς Ω | ——— Н | | ប៊ | U | Ξ | si | 5 |
| Ι | (CH3)2Si (CH1)3Si (CF | I ₃)C ₂ H ₆ | | 48-49 | (10) | 1,4324 | 0,8796 | 55,55 | 56,12 | 52,57 | 10,95 | 1,22 | | 10,16 | 10,63 | 29,92 | |
| Ш | (CH3)*Si (CH_J)*Si (CF | 1 ₈)C ₆ H ₁₁ | | 116-115 |) (25) | 1,4385 | 0,8726 | 69,25 | 69,97 | 57,79 | 11,59 | 4,16 | 1 | 57,30 | 11,31 | 24,37 | .1 |
| 111 | (CH ₂) ₂ Si (CH ₂) ₅ Si (CE | I3,C ₆ H ₄ Cl | | 115-11 | 16 (3) | 1,5100 | 1,0612 | 76,26 | 76,48 | 53,95 | 7,22 | 20,50 1 | 11,48 | 53,25 | 7,02 | 20,71 | 13,14 |
| IV | $(CH_3)_2 Si (CH_2)_3 Si (CI_2)_4 Si (CI_2)_5 Si (CI_$ | Ha)CsH11 | | 160 (2. | 2) | 1,4445 | 0,9154 | 85,57 | 86,57 | 51,53 51,54 | 10,30 | 9,21 4 | 14,14 | 52,98 | 10,51 | 19,02 | 12,04 |
| Δ | UC2H5 CU CH3(C6H5)SICH2CH= | =CH2 | | 118-12 | 1 (17) | 1,4942 | 0,9393 | 63,87 | 64,57 | 69,04 | 8,57 | 4,40 | 1 | 39,81 | 8,74 | 13,60 | 1 |
| | OC2Ha CH3SI (C6H1)HCl CIC6H4SI (CH3) (OC3 | Hs)2 | | 146: 979i | 148 9 (3) | 1,4218 1,4837 | 0,8878 1,0601 | 43,07 65,95 | 43,97 66,06 | 47,36 53,81 | 10,44 6,95 | 1,50 | 14,50 | 47,87 | 10,01 6,94 | 18,61 11,45 | 23,59 14,50 |
| TABI | - H | | | _ | - | | - | - | | - | - | - | - | - | - | - | |
| | | | k-10-3 | , min | | kR/kCH | | lg | kR/kCH3 | | | | | | | | [|
| | Radical | * v | 0. <i>7%</i> KOH | Q 70% PDSSA | КOF | Id I | DSSA | КОН | PDS | SA | Conve % | rsion, | ηsp | н | °, | A - 10 ⁴ , M ^{- 1} - ci | liter n ⁻² |
| CH CGH CGH CGH CGH CGH CGH CH CH CH CH CH CH CH CH CH CH CH CH CH | l Эндснаснаст Сенал-Сснал- | $\begin{array}{c} & 0.0 \\ & 0.10 \\ & 0.115 \\ & -0.113 \\ & -0.13 \\ & +0.60 \\ & +0.87 \end{array}$ | $\begin{array}{c} 4,0\\ 0,27\\ 0,74\\ 0,74\\ 4,3\\ 4,51\\ 4,51\end{array}$ | $\begin{array}{c} 11.9\\ 0.74\\ 7.70\\ 9.80\\ 7.70\\ 11.69\\ 11.3\end{array}$ | 0,06 1,07 1,12 1,12 1,12 | 555 | $\begin{array}{c}1\\0,062\\0,485\\0,646\\0,644\\0,644\end{array}$ | $\begin{array}{c} 0 \\ -1,7328 \\ -0.7328 \\ 0.6498 \\ 0.032 \\ 0.0492 \\ 0.0492 \\ 0.0492 \\ -1 \end{array}$ | | 2076 729 0841 1911 | 80,5 55,66 64,16 80,5 80,5 80,5 80,5 80,5 80,5 80,5 80,5 | []) []) | $\begin{array}{c} 0,105\\ 0,105\\ 0,117\\ 0,117\\ 0,103\\ \end{array}$ | · []] · | | , 1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 | |



Fig. 2. Yield of polymers as a function of the polymerization time $(0.7\% \text{ PDSSA}, t = 55^\circ)$ when R equals: 1) CH₃; 2) C₆H₅; 3) C₅H₁₁; 4) C₆H₄Cl; 5) C₄H₉; 6) C₃H₇.

Fig. 3. Logarithm of the concentration as a function of the polymerization time (0.7% KOH, t = 120°) when R equals: 1) C₆H₄Cl; 2) C₆H₅; 3) CH₃; 4) C₅H₁₁; 5) C₃H₇; 6) C₂H₅.

The cationic polymerization of the disilacyclohexanes was run at 55° in the presence of 0.7% of polydimethylsiloxysulfonic acid (PDSSA), when based on the sulfonic group. The kinetic curves of the cationic polymerization are given in Fig. 2. From Fig. 2 it can be seen that replacing the methyl radical by alkyl and aryl radicals lowers the rate of the polymerization reaction. In the case of proton attack on oxygen the aryl substituents should retard the reaction rate, which is found to be in agreement with the experimental data ($k_{CH_3} = 11.9 \cdot 10^{-3}$, $k_{C_6H_5} = 9.8 \cdot 10^{-3}$, $k_{C_6H_4Cl} = 7.7 \cdot 10^{-3} \text{ min}^{-1}$). In contrast, the insertion of electron-donor substituents should increase the reaction rate. However, the experimental data show that apparently the steric effect is superimposed on the induction effect and masks it.

Formally, the anionic and cationic polymerization reaction at low degrees of conversion (up to 15-20%) is first order (Figs. 3 and 4) and proceeds by a stepwise mechanism. At high degrees of conversion the order of the reaction becomes fractional. The reaction constants ρ^* were calculated on the basis of the experimental data for the polymerization of the disilacyclohexanes containing aryl radicals. The reaction constant ρ^* enters into the Hammett-Taft equation and characterizes the sensitivity of the reaction transformation to structural changes in the reactants. The Taft induction constants were taken from the table given in [3]. The results of the calculations are summarized in Table 2.

Tetramethyl-1-oxa-2,6-disilacyclohexane was taken as a standard. The small values of the ρ^* constant for the cationic polymerization (-0.20) and for the anionic polymerization (+0.06) testify to the low polarity of the transition state and to the small contribution made by the substituent induction effect.

In Fig. 5 is plotted the linear function: $\log k_{\rm R}/k_{\rm CH_3}$ vs σ^* , which suggests the existence of a correlation between the polymerization rate of the disilacyclohexanes containing aryl radicals and the Taft induction constants. The obtained polymers represented low-molecular oligomers with $\eta_{\rm Sp} = 0.07-0.12$ (see Table 2). The thermomechanical curves were recorded for some of them. The insertion of more bulky substituents leads to a weakening of the intermolecular reaction, which is manifested in a shift of the glass-transition temperature in the region of low temperatures. Bis(trimethyl-1-oxa-2,6-disilacyclohexyl) oxide (BDSCHO), having the following structure



was also subjected to polymerization. BDSCHO is easily polymerized, both in the presence of KOH and in the presence of PDSSA, with the formation of insoluble polymers. The polymerization in the presence of KOH proceeds so rapidly that the rate of the process could not be recorded. Thus, within a minute the







Fig. 5. Logarithm of the ratio of the rate constants as a function of the substituent induction effect: 1) cationic polymerization ($\rho^* = -0.20$); 2) anionic polymerization (ρ^* = +0.06).

yield of the polymer was 46% and the formation of a gel was observed. During cationic polymerization the yield of the polymer after 8 h reached 36%, and then gelation was observed. The high activity toward polymerization when the ring is treated with a nucleophilic agent like KOH can be explained by the fact that the silicon atom is attached to two oxygen atoms:



This increases the electropositive character of the silicon and makes it more reactive toward nucleophilic attack by OH. When the ring is treated with PDSSA all of the oxygen atoms in the BDSCHO are equivalent and the polymerization rate is determined only by the steric factor.

EXPERIMENTAL METHOD

<u>Methylamylchlorohydrosilane (VI)</u>. The Grignard reagent, obtained from 12 g of Mg and 53.3 g of $C_5H_{11}Cl$ in 50 ml of anhydrous ether, was slowly added to 57.5 g of CH_3SiHCl_2 in 150 ml of anhydrous benzene. The mixture was stirred at 60° for 1 h. The precipitate was filtered. From the filtrate, after distilling off the solvent, was isolated 15.27 g (20.3%) of (VI), bp 146-148°.

<u>Methylchlorophenyldiethoxysilane (VII)</u>. To 171.2 g of methylchlorophenyldichlorosilane, heated to 55° , was slowly added 70 g of absolute ethanol. The mixture was heated for 7 h. The product was distilled twice. We isolated 122.8 g (66.2%) of (VII), bp 115-118° (3 mm).

<u>Methylphenylethoxyallylsilane (V)</u>. To a mixture of 12 g of Mg, 105.04 g of methylphenyldiethoxysilane, 5 ml of anhydrous ether and 0.5 g of Cu_2Cl_2 , heated to 85°, was added 1 ml of CH_3I , and then 38.25 g of allyl chloride was added in drops. The reaction mass was heated at 120° for 3 h. The precipitate was filtered. After distilling off the solvent the residue was fractionally distilled to give 47.0 g (45.5%) of (V), bp 118-121° (17 mm).

<u>1-Dimethylethoxysilyl-3-methylamylchlorosilylpropane (IV)</u>. To a mixture of 13.4 g of dimethylallylethoxysilane, 0.4 ml of a 0.1 N solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropanol, and 3 g of methylamylchlorosilane, heated to 65°, was slowly added 11 g of methylamylchlorosilane. The stirred mixture was heated at 136° for 3 h. Fractional distillation gave 8.5 g (38.2%) of (IV), bp 160-161° (25 mm).

2,2,6-Trimethyl-6-chlorophenyl-1-oxa-2,6-disilacyclohexane (III) was obtained in a similar manner. The disilacyclohexanes where $R = CH_3$, C_3H_7 , C_4H_9 , or C_6H_5 were obtained previously [4].

2,2,6-Trimethyl-6-ethyl-1-oxa-2,6-disilacyclohexane (I). To the C₂H₅MgBr, obtained from 6.54 g of C₂H₅Br and 1.5 g of active Mg, was added 12.5 g of 2,2,6-trimethyl-6-chloro-1-oxa-2,6-disilacyclo-hexane in 20 ml of benzene. The stirred mixture was heated for 5 h and then treated with ice water. Fractional distillation gave 4.61 g (38.2%) of (I), bp 48-49° (10 mm).

<u>Polymerization of Disilacyclohexanes</u>. The anionic polymerization was run as described in [1]. The cationic polymerization of the disilacyclohexanes was run as described in [2]. The IR spectra were taken by N. A. Chumaevskii, who also calculated the integral intensities, for which the authors express their gratitude.

CONCLUSIONS

1. Some new 2,2,6-trimethyl-6-(ethyl, amyl, chlorophenyl)-1-oxa-2,6-disilacyclohexanes were synthesized.

2. The disilacyclohexanes, containing either alkyl or aryl substituents attached to one of the silicon atoms ($R = CH_3 - C_5H_{11}$, C_6H_5 , C_6H_4Cl), were subjected to both anionic and cationic polymerization.

3. The polymerization of the disilacyclohexanes proceeds by a stepwise mechanism, as a first order reaction, independent of the nature of the radical.

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