ORGANOSILICON COMPOUNDS WITH CARBON BRIDGES

BETWEEN THE ATOMS OF SILICON

COMMUNICATION 2. THE INTERACTION WITH ALUMINUM HALIDES

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In the preceeding communication [1], we reported on the polycondensation of 1,2-hexamethyldisilylethane which was observed by us, and which is specific for the chemistry of the organosilicon compounds. At the same time, two schemes for the mechanism of this transformation were suggested:

a) an intramolecular process occurring in the complex with $Al_2X_6 CH_3... \downarrow . Si(CH_3)_2CH_2CH_2... \downarrow .Si(CH_3)_...$ Al_2X_6 , as a result of which Si(CH_3)_4 and the biradical [-Si(CH_3)_2CH_2CH_2-] are formed; the latter is transformed into the cyclic polymers [-Si(CH_3)_2CH_2CH_2-]n.

b) an intermolecular process occurring between $(CH_3)_3SiCH_2CH_2$, $Si(CH_3)_2$... \downarrow . (CH_3) and Zl_2X_6 ... $(CH_3)_3Si$... \downarrow . $CH_2CH_2Si(CH_3)_3$, and leading to the formation of a linear dimer $(CH_3)_3SiCH_2CH_2Si(CH_3)_2CH_2CH_2Si(CH_3)_3$ and to products of its further transformation. At that time, we isolated from the mixture of polymers only the cyclic products $[-(CH_3)_2SiCH_2CH_2CH_2CH_2-]n$, where n = 2,3.

In the present work, we have investigated the behavior of 1,3-disilylpropane in an analogous reaction. The transformation proceeds here according to a scheme analogous to (b)

$$(CH_3)_3SiCH_2CH_2CH_2CH_2 \cdot V \cdot Si(CH_3)_3 \cdots Al_2X_6 + CH_3 \cdot V \cdot Si(CH_3)_2CH_2CH_2CH_2CH_2Si(CH_3)_3 \longrightarrow (1)$$

$$\longrightarrow (CH_3)_3SiCH_2CH_2CH_2Si(CH_3)_2CH_2CH_2CH_2Si(CH_3)_3 + Al_2X_6 + Si(CH_3)_4 \longrightarrow (1)$$

The dimer which is formed reacts further in similar fashion, giving principally linear polymers of the type $(CH_3)_3SiCH_2CH_2[CH_2]Si(CH_3)_2CH_2CH_2CH_2]_nSi(CH_3)_3$, where $n \ge 1$. The first two members of the series were isolated (n = 1 and 2); the structures of these were confirmed by their infrared spectra. The structure of the dimer was additionally confirmed by a second synthesis according to the scheme (2):

$$(CH_{2}=CHCH_{2})_{2}Si(CH_{3})_{2} \xrightarrow{HSiCH_{3}CI_{2}} [CI_{2}(CH_{3})SiCH_{2}CH_{2}CH_{2}]_{2}Si(CH_{3})_{2} \rightarrow$$

$$\xrightarrow{CH_{3}MgCl} (CH_{3})_{3}SiCH_{2}CH_{2}CH_{2}Si(CH_{3})_{2}CH_{2}CH_{2}CH_{2}Si(CH_{3})_{3}$$

$$(2)$$

The properties of the substances obtained according to schemes (1) and (2) were identical. The cyclic dimer previously obtained by another reaction [2] was not observed. As a result of the investigation, the activities of the derivatives of 1,3-disilylpropane which contain different ratios of CH_3 - and Cl-groups at the Si atom are established to fall in the following (decreasing activity) series for the polycondensation reaction:

$$\begin{array}{c} ({\rm CH}_3)_3{\rm Si}({\rm CH}_2)_3{\rm Si}({\rm CH}_3)_3 \geqslant ({\rm CH}_3)_3{\rm Si}({\rm CH}_2)_3{\rm Si}({\rm CH}_3){\rm Cl}_2 > \\ ({\rm I}) & ({\rm II}) \\ \\ > ({\rm CH}_3)_3{\rm Si}({\rm CH}_2)_3{\rm Si}{\rm Cl}_3 \gg {\rm Cl}_3{\rm Si}({\rm CH}_2)_3{\rm Si}{\rm Cl}_3 \\ ({\rm III}) & ({\rm IV}) \end{array}$$

The last member of the series did not react in the presence of $AlBr_3$ taken in quantities up to 40 mole percent, even at a temperature of 200°. For the series members (II) and (III), judging from the low-boiling products of the reaction, the conversion proceeded according to schemes (3) and (4), which are similar to (b)

$$Cl_{2}RSiCH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}Si(CH_{3})_{3}\cdots \downarrow \cdot Al_{2}X_{6}+Cl\cdots \downarrow \cdot Si(Cl)(R)CH_{2}CH_{2}CH_{2}Si(CH_{8})_{3}\cdots \cdots \rightarrow Cl_{2}RSiCH_{2}CH_{2}CH_{2}Si(Cl)(R)CH_{2}CH_{2}CH_{2}Si(CH_{3})_{3}+(CH_{3})_{3}SiCl+Al_{2}X_{6}$$

$$(3)$$

etc.,

$$CI_{2}RSiCH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}Si(CH_{3})_{3} \cdot \downarrow \cdot AI_{2}X_{6} + CH_{3} \cdot \downarrow \cdot Si(CH_{3})_{2}CH_{2}CH_{2}CH_{2}SiCI_{2}R \longrightarrow$$

$$CI_{2}RSiCH_{2}CH_{2}CH_{2}Si(CH_{3})_{2}CH_{2}CH_{2}CH_{2}CH_{2}SiCI_{2}R + (CH_{3})_{4}Si + AI_{2}X_{6} \qquad (4)$$

The formation of Si(CH₃)₄ from the trichloride (III) indicates that the reaction proceeds via an intermolecular mechanism. In these experiments, there was formed in addition to the low boiling product a polymeric residue which contained hydrolyzable chlorine. When reaction (1) was carried out at a temperature below 90-100°, up to 0.95 M of Si(CH₃)₄ was isolated per mole of (CH₃)₃SiCH₂CH₂CH₂Si(CH₃)₃, and there was formed a rubbery polymer of composition close to $[-Si(CH_3)_2CH_2CH_2CH_2-]$ (SiC₅H₁₀). However, on further heating, especially in the presence of considerable quantities of the catalyst, the evolution of Si(CH₃)₄ begin anew. We have suggested that the linear disilylpropane polymers which are formed undergo a structuration according to a scheme similar to (1) with a scission of the \equiv Si... \downarrow . CH₂CH₂CH₂Si \equiv bond. This reaction is accompanied by the formation of Si(CH₃)₄ and of a 3-dimensional polymer of the type:

$$= SiCH_2CH_2CH_2CH_2Si = CH_2CH_2CH_2Si = CH_2CH_2CH_2Si = CH_2CH_2Si = CH_2CH_2$$

In order to demonstrate the validity of our proposal we obtained a polymer of known linear structure by the method of [3]

 $(CH_3)_2HSiCH_2CH=CH_2 \xrightarrow{Pt/C} -[-(CH_3)_2SiCH_2CH_2CH_2-]_n -$

and subjected it to heating with AlCl₃. Si (CH₃)₄ was indeed evolved from the reaction mixture, and an insoluble three-dimensional polymer was formed.

Just as in the case of the derivatives of 1,2-disilylethane, so, too, for the 1,3-disilylpropane derivatives, an increase of the mole percent of AlX_3 led to a decrease of the temperature at the beginning of the reaction. $AlBr_3$ was a more active catalyst than $AlCl_3$.

The scissioning of the Si-C bond of the disilylpropane group apparently takes place then when the compounds contain \equiv SiGH₂CH₂CH₂Si \equiv and \equiv Si-O-Si \equiv groups. Thus, in an attempt to split [Cl(CH₃)₂SiCH₂CH₂CH₂SiCH₃(C₂H₅)]₂O at the Si-O-Si bond [4] by the action of AlX₃, we did not succeed in isolating the α, ω -dichloride Cl(CH₃)₂SiCH₂CH₂CH₂CH₂Si(CH₃) (C₂H₅)Cl; a complex mixture of methyl- and ethyl-chlorosilanes with a b. p. less than 130° was formed in the reaction instead.

EXPERIMENTAL

The starting material, the disilylpropane compounds, were obtained according to known methods [5]; their properties were identical with those cited in the literature [5, 6]. The polymer $-[Si(CH_3)_2CH_2CH_2CH_2-]n -$ was obtained according to the methods of [3] in the form of a viscous, colorless oil with b. p. greater than 300°.

The interaction of the 1,3-disilylpropane compounds with the aluminum halides was carried out in a flask with a downward inclined condenser and a trap for the low-boiling products (temperature 0 to -10°). The disilylpropanes were

used in 25-40 g quantities. A mixture of the disilylpropanes and AIX_3 was slowly heated on an oil bath. The temperature interval from the beginning of boiling to the appearance in the condenser of the vapors of the low boiling substance was taken to be the temperature of the beginning of the reaction. The low boiling substances which were formed were distilled out with isooctane into a column of 20 theoretical plates and were identified by boiling point, $n^{20}D$, and the infrared spectra. The polymeric residue was dissolved in benzene or ether. In the case of the polymer obtained from the $(CH_3)_3SiCH_2CH_2CH_2Si(CH_3)_3$, the benzene solutions were treated with water for the decomposition of the catalyst; they were washed with a solution of soda, with water, and were dried over calcium chloride. After the removal of the solvent, the polymeric residue was analyzed. When the polycondensation reaction of 1.3-hexamethyldisilylpropane was carried out with the separation of greater than 0.95 M of Si(CH₃)₄ per mole of disilylpropane, the high molecular weight rubbery polymer which was formed was only partially soluble in benzene. Preparations of AIX_3 labeled chemically pure were used in the experiments. The use of sublimed $AICl_3$ and the performance of the polycondensation of $(CH_3)_3SiCH_2CH_2CH_2Si(CH_3)_3$ in an atmosphere of nitrogen led to an increase of the temperature of the beginning of the reaction. The results of the experiments are presented in the table.

1,3-Disilylpropane	AlX ₃ , mole %	Temperature of the beginn ing of the reaction,* °C	Temp. at the end of the re- action, °C	The product of the reaction in mole η of the initial material
	AICI Aunto 5)			The starting material
$(CH_3)_3$ SICH ₂ CH ₂ CH ₂ SI(CH ₃) ₃ The same	$AlCl_3(40)$	80-90	95	Si(CH ₃) ₄ (93),
» »	AlBr ₃ (5)	8090	90	Polymer Si(CH ₃) ₄ (91),
(CHa)aSiCHaCHaCHaSi(CHa)Cla	$A1Br_{2}(5)$	145-180	**	**
The same	AlBr ₃ (10)	8090	180	$Si(CH_3)_4$ (7,5), $Si(CH_3)_3C1$ (72),
		445 440	**	Polymer **
(CH ₃) ₃ SiCH ₂ CH ₂ CH ₂ SiCl ₃	$AlBr_3(10)$	120-130	220	Si(CH ₃) ₄ (22), Si(CH ₃) ₃ Cl (27), Polymer
Cl ₃ SiCH ₂ CH ₂ CH ₂ SiCl ₃	AlBr ₃ (up to			The starting material

* The temperature of the reaction mixture: when the reaction did not occur, the mixture was boiled 3-5 min, and the starting material was distilled out.

* * Was not determined.

The interaction of 1,3-hexamethyldisilylpropane with aluminum bromide. A mixture of 37.0 g (0.198 M) of the disilylpropane and 2.6 g (0.01 M) of AlBr₃ was heated on an oil bath in a flask with a good water condenser which communicated with the atmosphere through a trap cooled to -70° . At a temperature of 67-72° a low boiling substance began to be formed. After 8 hr of boiling the temperature in the flask was lowered to 55°. On the following day the reflux condenser was replaced by an inclined condenser, and the low boiling substances which had been formed were distilled off on an oil bath heated to 70-85° until 9.5 g of condensate had been collected; it consisted of Si(CH₃)₄. After the usual work-up of the heavy residue, the solvent was distilled away and the residue was distilled in vacuo. The following fractions were obtained: Fraction I,65-67° (18 mm), 7.0 g; Fraction II, 67° (18 mm) -120° (5 mm) mostly at 118-120° (5 mm), 1 g; Fraction III, 122-124° (5 mm), 5.0 g; Fraction IV, 123-180° (2 mm) 3.8.

The undistilled residue was a viscous, light yellow oil weighing 7.0 g, $n^{20}D = 1.4642$. The molecular weight of the residue (here and below, this was determined by the cryoscopic method in benzene) was 563. Found: C 60.08, 59.78; H 12.30, 12.12; Si 28.87%, 28.50. Si(CH₃)₂CH₂CH₂CH₂. Calculated: C 59.91; H 12.02; Si 28.02%.

Fraction I was the starting material itself, 1,3-hexamethyldisilyl propane $n^{20}D$ 1.4220, d^{20}_4 0.7579. Fractions II and III were the linear dimer <u>-</u> (CH₃)₃SiCH₂CH₂[Si(CH₃)₃CH₂CH₂CH₂]Si(CH₃)₃; this substance redistilled completely at 88-91° (3 mm); $n^{20}D$ 1.4420, d^{20}_4 0.7970; found MR 95.79; calculated MR 95.84; found mol wt. 295; calculated 288.

From Fraction IV by redistillation there was isolated what was probably the linear trimer $(CH_3)_3SiCH_2CH_2CH_2$. •[Si(CH₃)₂CH₂CH₂CH₂]₂Si(CH₃)₃ with b. p. 150-160° (2 mm); n²⁰D 1.4521, d²⁰₄ 0.8169; the molecular weight found was 372; calculated 389; found MR 128.4; calculated MR 128.6. Found: C 58.93, 58.76; H 12.09, 12.40; Si 29.10, 28.96%. C₁₉H₄₂Si₄. Calculated: C 58.67; H 12.44; Si 28.88%. The infrared spectrum confirmed the suggested structure of the substance.

The interaction of $-[Si(CH_3)_2CH_2CH_2CH_2]_n$ with AlCl₃. A mixture of 7 g of the polymer $[Si(CH_3)_2CH_2CH_2CH_2]_n$ and 1.5 g of AlCl₃ was heated at 120-200° in a boiling flask. The product of the reaction was 2.0 g of a low boiling substance, which from the data $n^{20}D$ 1.3610, d^{20}_4 0.6498 and the infrared spectrum was identified as Si(CH₃)₄. A dark solid substance remained in the flask.

The synthesis of $(CH_3)_3SiCH_2CH_2CH_2[Si(CH_3)_2CH_2CH_2]Si(CH_3)_3$. An attempt was made to prepare diallyldimethylsilane from 1 M diallyldichlorosilane [7] by methylation with CH_3MgCl . The attempts were successful; the yield of diallyldimethylsilane was 52%. An attempt to methylate the dichloride with Ch_3MgI was unsuccessful. Although in the latter case the reaction was carried out with the same ratios of the reagents and by analogous methods, at the decomposition stage of the reaction mixture with water in contrast to the successful experiment there was a vigorous evolution of propylene (identified as 1,2-dibromopropane); no diallyldimethylsilane at all was isolated; instead [$(CH_3)_2SiO]_3$ was obtained with b. p. 130-133° (atm); m. p. 62-63°, and [$(CH_2 = CH-CH_2)Si(CH_3)_2]_2O$ with b. p. 170-175°; $n^{20}D$ 1.4260, d^{20}_4 0.8250, as well as a considerable quantity of a polymeric substance.*

To 23 g of diallyldimethylsilane heated to 110° was added 2 drops of a 0.1 N solution of H_2PtCl_6 in isopropyl alcohol, followed by the drop-wise addition of 38 g of HSi(CH₃)Cl₂. When the temperature in the flask had reached 180° the mixture was cooled, and an additional 10 g of HSi(CH₃)Cl₂ was added; the contents of the flask were boiled for 2 hr. By distillation of the reaction mixture there was obtained 39 g of [Cl₂(CH₃)SiCH₂CH₂CH₂]₂Si(CH₃)₂ with b. p. 137-138° (2 mm); $n^{20}D$ 1.4720, d^{20}_{4} 1.0976. Found: Cl 38.3, 38.2%. C₁₀H₂₄Cl₄Si₃. Calculated: Cl 38.3%.

The tetrachloride obtained was methylated in the usual manner by the action of Ch₃MgCl taken in a quantity double that calculated. $(CH_3)_3SiCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2Si(CH_3)_3$ was obtained in 68% yield; $n^{20}D$ 1.4420; d^{20}_4 0.7972. The infrared spectrum of this substance and of that obtained in Fractions II and III of the preceeding experiment were identical.

The synthesis of $\alpha_{,}\omega$ -dichlorosilanes. Allyldimethylchlorosilane with b. p. 110° (756 mm); $n^{20}D$ 1.4295, d^{20}_{4} 0.9009 was obtained in 30% yield from 363 g of allyl bromide and 69 g of dimethyldichlorosilane by adding the mixture to 146 g of magnesium in 3 liters of ether. The symmetrical tetraalkyldihydrodisiloxanes were obtained according to the usual methods [8].

In a flask with a reflux condenser and a dropping funnel were placed 17.5 g of allyldimethylchlorosilane and 1 drop of a 0.1 N solution of H₂PtCl₆ in isopropyl alcohol, and the mixture was heated to boiling. Thereafter during 2 hr there was added dropwise [H(CH₃)(C₂H₅)Si]₂O (in all 10.5 g), after which the mixture was boiled for another 2 hr until the boiling point was 200°. After two successive distillations, 24 g of [ClSi(CH₃)₂CH₂CH₂CH₂CH₂(CH₃). (C₂H₅)Si]₂O, 86% (based on the dichloride taken), was isolated with b. p. 146-147° (2 mm); $n^{20}D$ 1.4550, d^{20}_4 0.9560; found MR 122.4; calculated MR 122.7. Found: Cl 16.3, 17.0%; calculated: Cl 16.4%. In an analogous manner, from 2 molecules of allyldimethylchlorosilane and H(CH₃)₂SiOSi(CH₃)₂H was obtained [ClSi(CH₃)₂CH₂CH₂CH₂Si(CH₃)₂]₂O in 79% yield; b. p. 161-162° (8 mm); $n^{20}D$ 1.4482, d^{20}_4 0.9527; found MR 113.4; calculated MR 113.7. Found: Cl 17.6, 17.6%. Calculated: Cl 17.6%.

The α, ω -dichloride so obtained could be used for the synthesis of polymers with alternating α, ω -disilylpropane and siloxane fragments in the chain [9].

SUMMARY

1. Derivatives of 1,3-disilylpropane, in a manner similar to that of the 1,2-disilylethane compounds, undergo polycondensation with the separation of derivatives of monosilane and the formation of polymers with alternating atoms of Si and trimethylene fragments. The reaction occurs under the action of aluminum chloride and aluminum bromide.

* This curious splitting off of the $-CH_2CH = CH_2$ radical was observed also in the attempt to methylate $CH_2 = CHCH_2SiCl_3$ with CH_3MgI , although in this case $(CH_3)_3SiOSi(CH_3)_3$ was isolated in greater than 90% yield, and propylene was also violently evolved.

2. The application of this reaction to 1,3-hexamethyldisilylpropane yielded a mixture of polymeric homologs from which the linear dimer was isolated: $(CH_3)_3SiCH_2CH_2CH_2Si(CH_3)_2CH_2CH_2Si(CH_3)_3$, the formation of which obviously occurred by intermolecular condensation between $(CH_3)_3SiCH_2CH_2CH_2Si(CH_3)_3$... Al_2X_6 and $(CH_3)_3SiCH_2$. • $CH_2CH_2Si(CH_3)_3$.

3. In the interaction of the polymer $-Si(GH_3)_2 - CH_2CH_2CH_2]_n$ with AlCl₃ the possibility of a structural rearrangement of the linear polymers which contain α, ω -disilylalkane linkages into three-dimensional polymers was shown; this reaction also proceeds with the evolution of Si(CH₃)₄.

LITERATURE CITED

- 1. V. M. Vdovin, K. S. Pushchevaya, and A. D. Petrov, Izv. AN SSSR, Otd. khim. n. 1961, 281.
- 2. J. W. Curru, et al., J. Organ. Chem. 23, No. 8, 1219 (1958).
- 3. V. V. Korshak, A. M. Polyakova, et al., Izv. AN SSSR, Otd. khim. n. 1959, 1116.
- 4. M. G. Voronkov, B. N. Dolgov, and N. A. Dmitrieva, Dokl. AN SSSR 84, 959 (1952).
- 5. V. M. Vdovin and A. D. Petrov, Zh. obshch. khim. 30, 838 (1960).
- 6. A. V. Topchiev, N. S. Nametkin, and S. G. Durgar'yan, Zh. obshch. khim. 30, 927 (1960).
- 7. D. Hurd, J. Amer. Chem. Soc. 67, 1813 (1945).
- 8. V. V. Korshak, A. M. Polyakova, V. M. Vdovin, V. F. Mironov, and A. D. Petrov, Dokl. AN SSSR 129, 960 (1959).
- 9. A. D. Petrov and V. M. Vdovin, Izv. AN SSSR, Otd. khim. n. 1959, 1139.

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