Some peculiarities of hydrosilylation of α,ω-divinyloligosilanes

T. A. Pryakhina, A. I. Chernyavskii, T. V. Strelkova, and B. G. Zavin*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: 007 (095) 135 5085

The stability of Si—Si bonds in linear and cyclic permethyloligosilanes and in α,ω-divinyloligosilanes under conditions of hydrosilylation in the presence of the Speier's catalyst was studied. Polycarbosilanes containing silylene fragments in their backbone chains were prepared by the reaction of 1,4-bis(dimethylsilyl)benzene with α,ω-divinyloligosilanes. It was found that the structure of these polymers is disturbed due to the side reaction involving the cleavage of the Si—Si bond in vinyloligosilanes under the action of H_2PtCl_6.

Key words: hydrosilylation, α,ω-divinyloligosilanes, polycarbosilanes.

Hydrosilylation, *i.e.*, addition of hydride(organo)-silanes to multiple carbon—carbon bonds, is among the methods used most frequently for the formation of Si—C bonds in the preparation of polycarbosilanes (PCS).[1] However, at present, published data on the synthesis of PCS by hydrosilylation of oligosilanes are quite scarce. Apparently, this is due to the fact that the capability of Si—Si bonds of being cleaved in reactions catalyzed by transition-metal complexes[2] substantially hampers the preparation of polymers by hydrosilylation of compounds containing unsaturated C—C bonds with hydride-oligosilanes. In addition, the hexachloroplatinic acid, which is used as the catalyst in hydrosilylation, is known[3,4] to exhibit high catalytic activity in disproportionation of various organosilicon compounds. Therefore, it is no wonder that attempts to carry out hydrosilylation of alkenes and alkynes with pentamethyldisilane in the presence of H_2PtCl_6 have led only to the products resulting from the cleavage of Si—Si bonds.[5,6] Hydrosilylation of compounds containing multiple C—C bonds with pentamethyldisilane and 1,2-dihydrotetramethyldisilane could be accomplished only in the presence of other transition-metal complexes, for example, using $PtCl_2(C_2H_4)(C_5H_5N)$[7] or $NiCl_2(PEt_3)_2$ as catalysts.[8] However, it has been shown recently[9] that divinyldisilane reacts fairly readily with chlorodimethylsilane in the presence of H_2PtCl_6 without cleavage of the Si—Si bond. Nevertheless, despite the studies cited above, hydrosilylation of oligosilanes has not been adequately investigated.

The purpose of the present work was to study the stability of Si—Si bonds in oligosilanes under the conditions of hydrosilylation in the presence of the Speier's catalyst, as well as to study the possibility of synthesizing PCS of a regular structure by hydrosilylation of α,ω-divinyloligosilanes.

Results and Discussion

Experiments have shown that when linear $Me(SiMe_2)_nMe$ (n = 2 to 4) or cyclic $(Me_2Si)_6$ permethyloligosilanes are kept with catalytic amounts of H_2PtCl_6 for 10 h at 60—70 °C, no substantial changes in their silicon skeleton occur. The addition of vinyl-containing compounds, for example, styrene, to the permethyloligosilanes has no effect on the stability of the Si—Si bonds, which remain unchanged at 70 °C even when the concentration of the catalyst is five times higher than that normally used in this reaction. These results are in agreement with the published data,[10] according to which the Si—Si bonds in oligosilanes are cleaved during the reaction with olefins in the presence of platinum compounds only if the silicon atoms in the initial molecules carry electron-withdrawing substituents (F, Cl, OMe, Ph) or hydrogen atoms.

Upon heating (60—70 °C) in the presence of H_2PtCl_6, α,ω-divinyloligosilanes, unlike permethyloligosilanes, undergo a series of transformations including cleavage not only of the double bond but also of the Si—Si bond. In fact, according to GLC, 2 h after the catalyst has been added, the degree of conversion of 1,2-divinyltetramethyldisilane (**1**) is ~20% at 60 °C. This yields products whose chromatographic retention times are longer than that of disilane **1**. According to GLC, 8h after the introduction of H_2PtCl_6, the initial compound **1**, which is characterized by a single ^{29}Si NMR signal in the region of −24.21 ppm, is totally absent from the reaction mixture. Its ^{29}Si NMR spectrum exhibits signals, which can be assigned to silicon atoms incorporated in the following groups:

$CH_2{=}CH\underline{Si}Me_2SiMe_2CH_2CH_2-$ (−24.43 ppm),
$-CH_2CH_2\underline{Si}Me_2SiMe_2-$ (−14.21 ppm),

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 10, pp. 2547—2549, October, 1996.

$-CH_2CH_2SiMe_2CH_2CH_2-$, and
$CH_2=CHSiMe_2CH_2CH_2-$ (−3.52 to −4.64 ppm).

The formation of these groups confirms the cleavage of the double bond in disilane **1** and also of the Si—Si bond.

We have also studied the effect of the Speier's catalyst on the stability of vinyl-containing oligosilanes that incorporate more extended oligosilane chains than disilane **1**. A mixture of 2,3-divinyloctamethyltetrasilane (**2**) and 2,3,4-trivinylnonamethylpentasilane (**3**) (in a ratio of 5.5 : 1) and the Speier's catalyst was kept for 8 h at 60 °C. Within 3 h after the addition of H_2PtCl_6, an increase in the viscosity of the reaction mixture could be observed by sight; probably, this was due to the formation of higher-molecular-weight compounds and/or of partially cross-linked products. A GLC analysis of the reaction mixture showed that the content of the initial **2** and **3** decreased, and no new low-molecular-weight compounds appeared instead. After 8 h, the ^{29}Si NMR signals corresponding to the initial **2** [−14.51 ppm (Me_3Si) and −47.14 ppm (Me_3Si—Si)] and **3** [−14.35 ppm (Me_3Si), −43.15 ppm (Me_3Si—Si—Si), and −45.08 ppm (Me_3Si—Si)] totally disappear and only two broad signals in the region of 3.0 ppm and 9.0 ppm remain in the spectrum. Subsequently, cross-linked structures are formed, apparently through the $>SiMeCH_2CH_2-$ trifunctional moieties, which result from the cleavage of the Si—Si bonds followed by the addition of the fragments thus formed to the C=C bonds in the initial **2** and **3**.

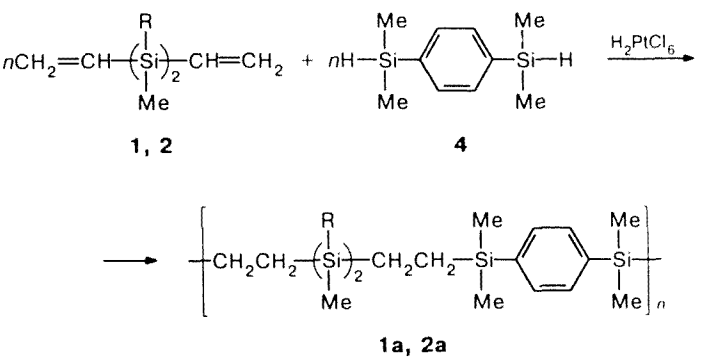
Analysis of the data obtained indicates that in their behavior toward hydrosilylation, vinyloligosilanes differ substantially from the vinylsiloxanes, vinylsilanes, and unsaturated organic compounds we studied previously,[11] which undergo no substantial changes in the presence of catalytic amounts of H_2PtCl_6. However, the destruction and structurization processes, which occur in vinyloligosilanes in the presence of the Speier's catalyst, become noticeable ~2 h after the introduction of the catalyst. Therefore, when vinyloligosilanes are used as the starting unsaturated compounds for hydrosilylation, the reaction route and, hence, the structure of the reaction products are determined by the ratio of the rate of the addition of hydrosilane to the vinyl group at a silicon atom in the oligosilane to the rate of the cleavage of the Si—Si bonds. Therefore, we suggested that by using reactive hydrosilylating reagents, for example, 1,4-bis(dimethylsilyl)benzene (**4**), which rapidly add to sterically non-hindered unsaturated bonds,[12] one would be able to perform hydrosilylation of α,β-divinyloligosilanes under mild conditions without cleavage of the Si—Si bond, because hydrosilylation will proceed at a higher rate than the destructive reactions (Scheme 1).

In fact, disilane **1** smoothly reacts with an equimolar amount of dihydride **4** in the presence of H_2PtCl_6 at 50—55 °C, in conformity with the above scheme, and the polymer **1a** thus formed has a regular structure, according to the ^{29}Si NMR data (see Experimental). The molecular weight of polymer **1a**, found from its characteristic viscosity ($[\eta] = 0.57$) was equal to $1.2 \cdot 10^5$.

The polyaddition of dihydride **4** to tetrasilane **2** occurs more slowly under the same conditions, which is probably due to steric factors, *viz.*, to the fact that the vinyl group at the silicon atom is shielded by the trimethylsilyl group. In addition to the signals due to silicon atoms, referring to the corresponding structural groups in polymer **2a** (−1.26, −15.27, and −37.42 ppm), the ^{29}Si NMR spectrum exhibits a signal at −2.04 ppm. The latter appears probably due to the fact that, since the reaction under consideration occurs more slowly than the reaction of disilane **1**, tetrasilane **2** has time to interact with the Speier's catalyst to give defective structures containing phenylene fragments, the latter being incorporated into the polymeric chain.

Thus, by hydrosilylation of α,ω-divinyloligosilanes, we have prepared PCS containing silylene fragments in the backbone chain. It was also found that, under the conditions of hydrosilylation, H_2PtCl_6 can cause catalytic activation of not only C=C bonds but also the Si—Si bonds in vinyloligosilanes. Depending on the contributions of these processes, the structure of the

Scheme 1



1, 2 **4**

1a, 2a

1, 1a: R = Me
2, 2a: R = $SiMe_3$

macromolecules formed may be disturbed and, consequently, PCS of irregular structure can form.

Experimental

GLC analysis was carried out on an LKhM-8MD chromatograph (equipped with a 0.3×100 cm stainless-steel column, 5% SE-30 on Chromaton N-AW-DMCS, and a heat-conductivity detector. Temperature was programmed from 30 to 300 °C at a rate of 12 deg min^{-1}; helium was used as the carrier gas).

^{29}Si NMR spectra were recorded on a Bruker WP-200SY spectrometer (39.76 MHz) using tetramethylsilane as the internal standard.

The linear and cyclic permethyloligosilanes were obtained by the co-condensation of dichlorodimethylsilane and chrorotrimethylsilane with sodium according to a known procedure;[13] disilane **1** was prepared by a known method[14] involving the reaction of chlorodimethylvinylsilane with magnesium. Tetrasilane **2** and pentasilane **3** were synthesized by a previously described procedure[15] consisting of co-condensation of dichloromethylvinylsilane and chlorotrimethylsilane with sodium.

The [η] value for polymer **1a** was determined in toluene at 25 °C on a Ubellode viscosimeter with a hanging level.

Hydrosilylation of disilane 1. A portion (1 mL) of the mixture prepared from dihydride **4** (2.73 g, 14 mmol) and disilane **1** (2.38 g, 14 mmol) was heated to 50 °C, and 0.0014 mL of a 0.01 *M* solution of $H_2PtCl_6 \cdot 6H_2O$ in THF was added with stirring (the proportion of the Speier's catalyst was $2 \cdot 10^{-5}$ mol of H_2PtCl_6 per mole of dihydride **4**). After the beginning of the reaction, which was accompanied by an increase in the viscosity of the reaction mixture, the rest of the mixture of compounds **4** and **1** was slowly added dropwise in such a way as to maintain the temperature of the reaction mixture below 55 °C. The ^{29}Si NMR spectrum recorded 2 h after the beginning of the addition of H_2PtCl_6 showed that compounds **4** and **1** were entirely converted. The resulting polymer **1a** was dissolved in toluene and reprecipitated with methanol. Yield 95%. Found (%): C, 59.75; H, 9.63; Si, 30.62. $C_{18}H_{36}Si_4$. Calculated (%): C, 59.26; H, 9.95; Si, 30.79. ^{29}Si NMR (CCl_4), δ: −1.25 (s, CH_2—Si—C_6H_4); −14.94 (s, CH_2Si—$SiCH_2$).

Polymer **2a** was prepared in 87% yield in a similar way under the same conditions from tetrasilane **2** (2.12 g, 7 mmol) and dihydride **4** (1.36 g, 7 mmol). Found (%): C, 55.41; H, 10.27; Si, 34.32. $C_{22}H_{48}Si_6$. Calculated (%): C, 54.92; H, 10.06; Si, 35.02. ^{29}Si NMR (CCl_4), δ: −1.26 (s, CH_2—Si—C_6H_4); −15.27 (s, Me_3Si); −37.42 (s, CH_2Si—$SiCH_2$).

The authors wish to thank N. V. Pertsova (Institute of Organoelement Compounds of the RAS) for determining the characteristic viscosity and molecular weight of polymer **1a**.

The work was carried out with the financial support of the Russian Foundation for Basic Research (Project No. 94-03-09637).

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Received June 17, 1996