

Unusual Cleavage of the $\equiv\text{SiOSi}\equiv$ Group by Organosilicon Hydrides: A New Route to α,ω -Dihydrooligopermethylsiloxanes

Academician M. G. Voronkov, S. V. Basenko, I. A. Gebel', and Yu. A. Chuvashhev

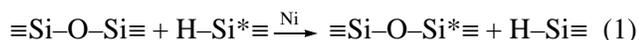
Received June 11, 2003

Until our studies, α,ω -dihydrooligopermethylsiloxanes had been poorly studied [1, 2] and no convenient methods for their synthesis had been reported. At the same time, the compounds are undoubtedly of considerable synthetic and practical interest.

Previously, one of us showed for the first time that, in the presence of colloidal nickel (formed in situ), organosilicon hydrides, namely, trialkylsilanes R_3SiH , are efficient reducing agents. In particular, they readily reduce phenyl halides, $\text{C}_6\text{H}_5\text{X}$ ($\text{X} = \text{Cl}$ [3], Br [4], I [5]), to give benzene (being converted in high yield into the corresponding trialkylhalosilanes, R_3SiX), as well as tin halides and alkylchlorostannanes [6]. 1,1,3,3-Tetramethyldisiloxane undergoes disproportionation on modified aluminosilicates to yield dimethylsilane [7, 8].

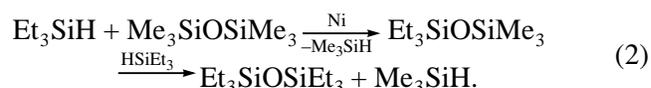
Here, we studied the autocleavage and condensation of 1,1,3,3-tetramethyldisiloxane (**I**) in the presence of colloidal nickel formed in situ. The reaction readily proceeds at ambient temperature and even on cooling to $5\text{--}10^\circ\text{C}$. The reaction yields α,ω -dihydrooligopermethylsiloxanes ($\text{H}(\text{Me}_2\text{SiO})_n\text{SiMe}_2\text{H}$, $n = 3\text{--}11$, mainly $n = 3\text{--}5$) and dimethylsilane.

α,ω -Dihydrooligopermethylsiloxanes result from the previously unknown intermolecular cleavage of $\equiv\text{Si-O-Si}\equiv$ groups by Si-H bonds under the influence of colloidal nickel:

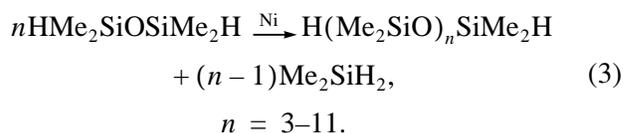


We, in cooperation with Yu.I. Khudobin, established the possibility of this reaction using the simplest example of the reaction of hexamethyldisiloxane with triethylsilane in the presence of colloidal nickel. The reaction takes place on refluxing of a mixture of these reagents (a 1 : 2 molar ratio) for 20 h. The conversion of hexamethyldisiloxane is 70%. The reaction leads to

hexaethyldisiloxane, 1,1,1-trimethyl-3,3,3-triethyldisiloxane, and trimethylsilane:

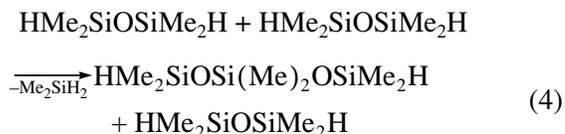


The reaction of autocleavage and condensation of 1,1,3,3-tetramethyldisiloxane (**I**) proceeds according to the following general scheme:



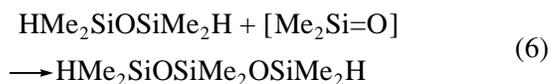
Hydrogen is a byproduct of this reaction, which is likely to result from the disproportionation of dimethylsilane.

A tentative mechanism for the formation of α,ω -dihydrooligopermethylsiloxanes may be represented by two schemes. The siloxanes may result from the intermolecular cleavage of the Si-O-Si group by Si-H bonds:

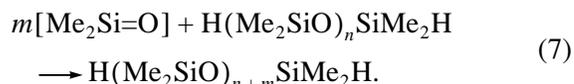


$\xrightarrow[\text{-Me}_2\text{SiH}_2]{} \text{HMe}_2\text{SiOSi}(\text{Me})_2\text{OSiMe}_2\text{OSiMe}_2\text{H}$, and so on.

Another possible mechanism of reaction (3) is the intermediate formation of dimethylsilanone as a result of the geminal decomposition of disiloxane (**I**) followed by its insertion into the Si-O bond [9–11]:



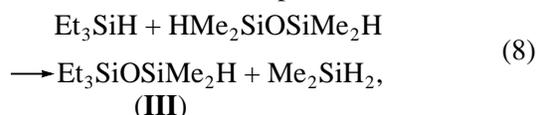
or, in the general form,



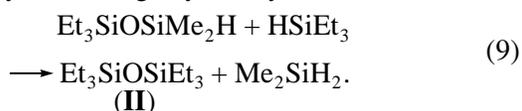
Favorsky Institute of Chemistry, Siberian Division,
Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk,
664033 Russia

To establish the mechanism of reaction (1), we studied the reaction of disiloxane **I** with a twofold excess of triethylsilane in the presence of colloidal nickel. As the products of this reaction, hexaethyltrisiloxane (**II**) and 1,1-dimethyl-3,3,3-triethyltrisiloxane (**III**) were isolated and characterized. In addition, 1,1,3,3-tetramethyl-5,5,5-triethyltrisiloxane (**IV**), 3,3-dimethyl-1,1,1,5,5,5-hexaethyltrisiloxane (**V**), 3,3,5,5-tetramethyl-1,1,1,7,7,7-hexaethyltetrasiloxane (**VI**), dimethylsilane, and hydrogen were identified using spectroscopy and chromatography–mass spectrometry.

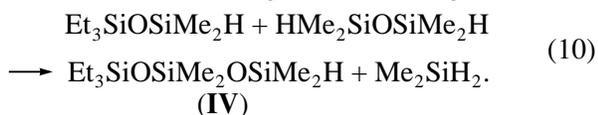
The formation of disiloxane **II** can be explained by a two-step reaction of triethylsilane with disiloxane **I** to give disiloxane **III** at the first step,



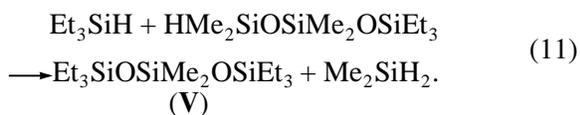
followed by its cleavage by triethylsilane,



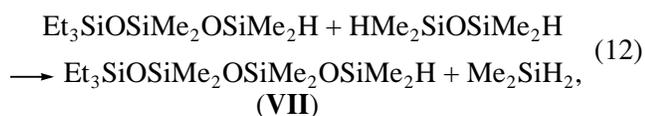
Trisiloxane **IV** results from the reaction of disiloxane **III** with siloxane **I** according to the following scheme:



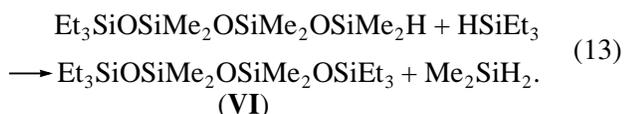
The reaction of triethylsilane with trisiloxane **IV** yields trisiloxane **V**:



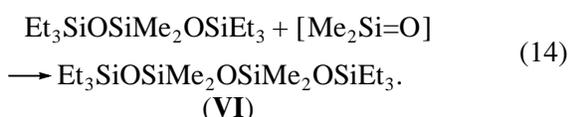
The formation of tetrasiloxane **VI** might be explained by the reaction of trisiloxane **IV** with disiloxane **I**,



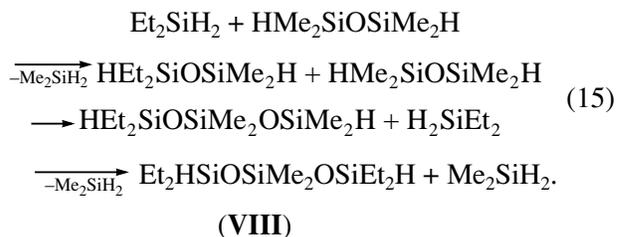
followed by the reaction of nascent tetrasiloxane **VII** with triethylsilane,



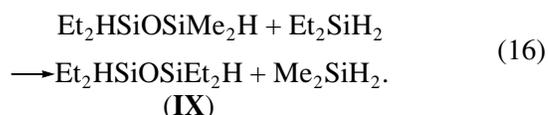
However, the absence of even traces of tetrasiloxane **VII** in the products of reaction of disiloxane **I** with triethylsilane indicates another mechanism of formation of tetrasiloxane **VI**, which is based on the insertion of dimethylsilanone into a molecule of trisiloxane **V**:



The possibility for dimethylsilane formed to cleave the $\equiv\text{Si-O-Si}\equiv$ group was confirmed by the model reaction of equimolar amounts of disiloxane **I** with diethylsilane in the presence of colloidal nickel. Along with α,ω -dihydro-oligopermethylsiloxanes ($\text{H}(\text{Me}_2\text{SiO})_n\text{SiMe}_2\text{H}$ ($n = 2-9$), we identified 3,3-dimethyl-1,1,5,5-tetraethyltrisiloxane (**VIII**), formed in about 5% yield according to the scheme



The formation of trisiloxane **VIII** could also be explained by the insertion of dimethylsilanone into intermediate 1,1,3,3-tetraethyltrisiloxane (**IX**) according to the scheme



However, we failed to identify the latter in the reaction mixture.

In the reaction of disiloxane **I** with an equimolar mixture of di- and triethylsilane (a 1 : 1 : 1 molar ratio) in the presence of colloidal nickel, we identified pentaethyltrisiloxane (**X**), 3,3-dimethyl-1,1,5,5,5-pentaethyltrisilane (**XI**), and 3,3,5,5-tetramethyl-1,1,7,7,7-pentaethyltetrasiloxane (**XII**), along with α,ω -dihydrooligopermethylsiloxanes ($\text{H}(\text{Me}_2\text{SiO})_n\text{SiMe}_2\text{H}$ ($n = 2-4$) and siloxanes (**II-VI**, **VIII**). The formation of siloxanes **II-VI**, **VIII**, and **X-XII** and the absence of higher oligomers with terminal Et_2Si groups indicates that these groups prevent further elongation of the siloxane chain.

EXPERIMENTAL

Reaction of 1,1,3,3-tetramethyldisiloxane with colloidal nickel. 1,1,3,3-Tetramethyldisiloxane (13.4 g, 0.1 mol) and colloidal nickel (0.6 g, 0.01 mol) were placed into a three-necked flat-bottom flask purged with argon and equipped with a reflux condenser and a thermometer and connected to a trap cooled with liquid nitrogen. The reaction mixture was magnetically stirred at ambient temperature for 7 h. Colloidal nickel was filtered off, and the filtrate was distilled at atmospheric pressure and in vacuum (3 mmHg) to give 9.1 g of a product whose composition determined by chromatography–mass spectrometry corresponded to previously described α,ω -dihydrooligopermethylsiloxanes [2]. Dimethylsilane condensed in the cold trap was purged with a dry argon flow and bubbled through a solution of bromine in xylene. The reaction mixture after bromination was distilled over copper metal to give 7.3 g dimeth-

Mass spectra (m/z (I_{rel} , %)) of siloxanes $\text{Et}_3\text{Si}(\text{OSiMe}_2)_n\text{H}$, $n = 1$ (**III**), 2 (**IV**); $\text{Et}_3\text{Si}(\text{OSiMe}_2)_m\text{OSiEt}_3$, $m = 1$ (**V**), 2 (**VI**); $\text{Et}_2\text{HSiOSiMe}_2\text{OSiEt}_2\text{H}$ (**VIII**); and $\text{Et}_3\text{Si}(\text{OSiMe}_2)_p\text{OSiEt}_2\text{H}$, $p = 0$ (**X**), 1 (**XI**)

Ion	Compound						
	III	IV	V	VI*	VIII	X	XI
(M) ⁺	190(–)	264(–)	320(1)	394(1)	264(–)	218(–)	292(–)
(M–H) ⁺	189(100)	263(100)	–	–	263(100)	217(100)	291(100)
(M–C ₂ H ₅) ⁺	161(63)	235(14)	291(100)	365(28)	235(18)	189(74)	263(11)
(M–C ₂ H ₅ –C ₂ H ₄) ⁺	133(60)	207(10)	263(11)	–	207(8)	161(47)	235(6)
(M–C ₂ H ₅ –2C ₂ H ₄) ⁺	105(29)	179(6)	235(8)	–	–	133(23)	207(3)
(C ₂ H ₅) ₃ SiO ⁺	131(15)	131(2)	131(2)	–	131(3)	131(10)	131(1)
(C ₂ H ₅) ₂ HSiO ⁺	103(20)	103(12)	103(8)	–	103(5)	103(18)	103(5)
(C ₂ H ₅) ₂ HSi ⁺	87(5)	87(5)	87(7)	87(65)	87(4)	87(7)	87(5)
(CH ₃) ₂ HSiO ⁺	75(7)	75(3)	75(2)	–	75(3)	75(3)	75(1)
C ₂ H ₅ H ₂ Si ⁺	59(8)	59(8)	59(5)	59(43)	59(5)	59(8)	59(3)
Me ₂ HSi ⁺	59(8)	59(8)	–	–	59(5)	59(8)	59(3)

* 277(27), 249(100), 221(67), 193(58), 165(40).

ylidibromosilane, bp 111–112°C, n_D^{20} 1.4720 (lit.: bp 111.5–112.5°C, n_D^{20} 1.4696 [12]).

The reactions in the presence of triethyl- and diethylsilanes were carried out similarly. The mass spectra of the resulting siloxanes are summarized in the table.

REFERENCES

1. Greber, G. and Metzinger, L., *Angew. Chem*, 1960, vol. 72, pp. 189–218.
2. Voronkov, M.G., Basenko, S.V., Nozdrya, S.M., et al., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, no. 7, pp. 1658–1660.
3. Khudobin, Yu.I., Andreeva, N.A., Kharitonov, N.P., et al., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, no. 4, pp. 856–859.
4. Khudobin, Yu.I., Voronkov, M.G., and Kharitonov, N.P., *Izv. Akad. Nauk Latv. SSR, Ser. Khim. Nauk.*, 1967, no. 5, pp. 595–600.
5. Khudobin, Yu.I. and Voronkov, M.G., *Metallorg. Khim.*, 1990, vol. 3, no. 4, pp. 898–901.
6. Khudobin, Yu.I. and Voronkov, M.G., *Metallorg. Khim.*, 1989, vol. 2, no. 6, pp. 1305–1307.
7. Khudobin, Yu.I. and Voronkov, M.G., *VIII soveshchanie po khimii i prakticheskomu primeneniyu kremniorganicheskikh soedinenii* (VIII Conf. on the Chemistry and Practical Use of Organosilicon Compounds) Petersburg, 1992, p. 29.
8. Lewis, L.N., Johnson, D.S., and Rich, J.D., *J. Organomet. Chem.*, 1993, vol. 448, no. 1, pp. 15–18.
9. Voronkov, M.G., *J. Organomet. Chem.*, 1998, vol. 557, no. 1, pp. 143–155.
10. Voronkov, M.G., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 6, pp. 950–956.
11. Voronkov, M.G., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1998, no. 5, pp. 824–834.
12. Bazant, V., Chvalovsky, V., and Rathousky, J., *Organosilicon Compounds*, Prague: Czechoslovak Akad. Sci., 1965, vol. 2(1), p. 51.