

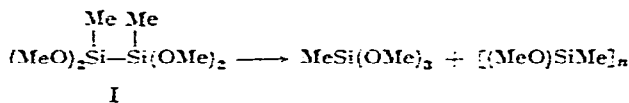
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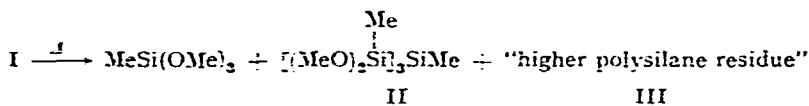
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Thermolysis of methoxy-substituted polysilanes*

In a previous report¹ we have described the base-catalyzed silicon-silicon-silicon-methoxy redistribution with substituted polysilanes. In the case of dimethyltetramethoxydisilane (I), the base-catalyzed redistribution was extremely rapid at 130°, and within five minutes 98% of the theoretical methyltrimethoxysilane was obtained based on the stoichiometry in equation (1).



During the course of this latter investigation we observed that I undergoes thermal redistribution in the absence of added base. Thus, when I was heated at 1 for 40 h, the products were methyltrimethoxysilane, tris(methyldimethoxysilyl)methylsilane (II) and a viscous nonvolatile polysilane residue (III)**.

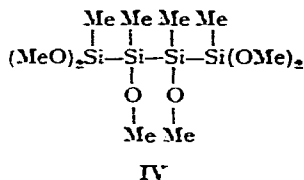


Compound II was isolated from the residue III by distillation; b.p. 110-111°/mm, yield 20-25% (*Anal.* Found: C, 33.5, 33.8; H, 8.53, 8.60; Si, 30.8%, mol. wt. by mass spectroscopy, calcd. for C₁₀H₂₀Si₄O₆: C, 33.5; H, 8.40; Si, 31.3%; mol.

* Redistribution studies with polysilanes. Part II. For Part I see ref. 1. Presented in part at the Division of Organic Chemistry, 150th National Meeting of the American Chemical Society, Atlantic City, New Jersey, Sept. 13-17, 1965. Abstracts, p. 76S.

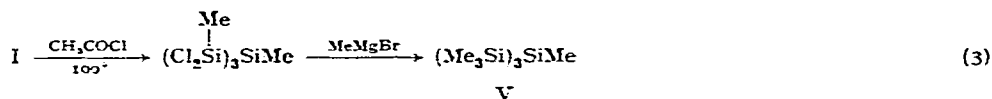
** The reaction proceeds equally well in metal, Vycor® or acid-washed glass tubes.

358.) Assignment of the unusual branched-chain structure II rather than the linear structure IV did not follow straightforwardly from the spectral properties.

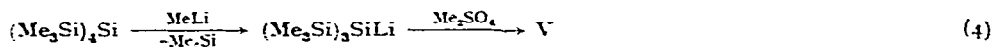


The UV-spectrum showed no λ_{max} above $200 \text{ m}\mu$, consistent with the results previously reported² for other branched-chain derivatives. The absence of an absorption in the $235\text{--}40 \text{ m}\mu$ region^{1,3} argued strongly against the linear structure IV. However, the NMR spectrum* showed singlets at 6.51 and 9.78 τ (ratio 3:2) assigned to the MeOSi and MeSi protons, respectively. The NMR results are consistent with structure II only if a fortuitous equivalence in chemical shift of the two MeSi groups is assumed. The necessity of this assumption prompted us to obtain chemical evidence for the assignment of structure II.

Compound I was converted to the permethylated derivative V in an overall yield of 87% (3). Compound V (b.p. $94\text{--}5^\circ/8 \text{ mm}$) was purified by VPC and isolated as a low-melting waxy solid.



The UV spectrum of V showed no λ_{max} above $200 \text{ m}\mu$, consistent with a branched-chain structure. The NMR spectrum showed the expected singlets at 9.86 and 9.95 τ assigned to the Me_3Si and MeSi protons, respectively (ratio 3:1). Finally, samples of V prepared by two previously reported procedures, (4)⁴ and (5)⁵, were identical in all respects to that prepared according to (3).

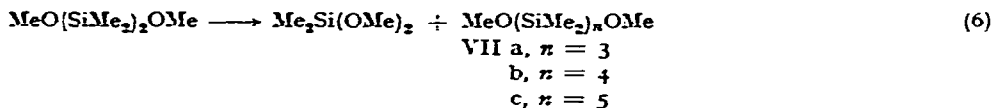


It is interesting to compare the thermal reactivity of I with that previously reported for other organodisilanes. The isomerization of hexamethyldisilane has been reported⁶ to occur at 600° and, in general, pentamethyldisilanyl compounds and methylpolysilanes have been observed⁷ to have good thermal stability. Pentamethyldisilanyl cyanide, a notable exception, has been reported⁷ to undergo a redistribution reaction at 175° .

We observed that other methoxy-substituted polysilanes also undergo this thermal redistribution. When 1,2-dimethoxytetramethyldisilane (VI) was heated at

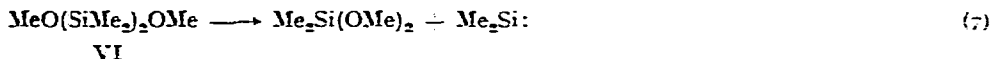
* All NMR spectra were determined at 50 cps with a Varian A60 Spectrometer as ca. 10% solutions in carbon tetrachloride using tetramethylsilane as internal standard.

225° ($t_{1/2} \cong 2$ h) the products were dimethyldimethoxysilane and the homologous series of α,ω -dimethoxypermethylated polysilanes (VII). At a somewhat higher temperature (275°), the trisilane VIIa gave dimethyldimethoxysilane and higher members of the

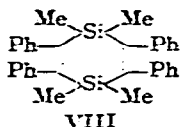


polysilane series VII. While these limited relative reactivities parallel those observed¹ in the base-catalyzed reactions, the distribution of products is quite different. Whereas base-catalysis gave mainly the trisilane VIIa from VI and the pentasilane VIIc from VIIa, the thermolysis gives a more random distribution of the series VII.

Although the nature of these reactions is uncertain, an α -elimination to give a divalent silicon (silene) intermediate (7), followed by a series of insertion reactions starting with the disilane (8) seems quite probable. A similar pathway is envisioned for the thermolysis of I. When the disilane VI was heated at 225° in the presence of



excess diphenylacetylene, 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexadiene (VIII) was isolated in a 49% yield, m.p. 323–5° (lit.⁸ 324–6°, mixed m.p.)*. Compound VIII has been isolated in previously reported reactions believed to involve dimethylsilylene.** Experiments designed to answer these interesting questions will



be part of our continuing study of the thermal reactions of these and related polysilanes.

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* We wish to thank Professor H. Gilman for providing us with a known sample of VIII. Our sample of VIII was also shown to be identical with a sample prepared (see ref. 9) by the method of Volpin, *et al.*¹⁰

** See ref. 8 and pertinent references cited therein.

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ANNOUNCEMENT

Will be published shortly in *Organometallic Chemistry Reviews*:

- R. D. CHAMBERS AND T. CHIVERS, Pentafluorophenyl-metal compounds.
K. NIEDENZU, Synthesis of organohaloboranes.
K. A. ANDRIANOV AND L. M. KHANANASHVILI, Cycle silicon compounds.
K.-H. THIELE, Elektronen-Donator-Acceptor-Komplexe von Alkylverbindungen der Elemente Zink, Cadmium, Quecksilber und Beryllium.
R. MUELLER, Über Silikone. CIX. Über Organo-fluorosilikate und ihre Verwendung zur Darstellung metallorganischer Verbindungen.
F. BONATI, Organometallic derivatives of β -diketones.
M. GIELEN AND N. SPRECHER, Coordination au niveau des atomes de métal du groupe IVB.
G. G. EBERHARDT, Recent developments in the catalytic applications of the organoalkali metal compounds.