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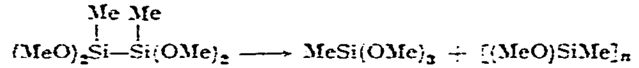
Thermolysis of methoxy-substituted polysilanes*

In a previous report[1] we have described the base-catalyzed sillicon–silicon silicon-methoxy redistribution with substituted polysilanes. In the case of dimethyltetramethoxydisilane (I), the base-catalyzed redistribution was extrer rapid at 130°, and within five minutes 98% of the theoretical methyltrimeth silane was obtained based on the stoichiometry in equation (1).



$$(MeO)_2\overset{Me}{\overset{|}{Si}}-\overset{Me}{\overset{|}{Si}}(OMe)_2 \longrightarrow MeSi(OMe)_3 + [(MeO)SiMe]_n$$

I

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

$$I \xrightarrow{\Delta} MeSi(OMe)_2 + [(MeO)_2\overset{Me}{\overset{|}{Si}}]_3SiMe + \text{"higher polysilane residue"}$$

II 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 $C_{10}H_{30}Si_4O_6$: C, 33.5; H, 8.40; Si, 31.3 %; mol.

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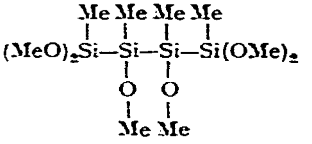
* Redistribution studies with polysilanes. Part II. For Part I see ref. 1. Presented in at the Division of Organic Chemistry, 150th National Meeting of the American Chemical Soci Atlantic City, New Jersey, Sept. 13–17, 1965. Abstracts, p. 76S.

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

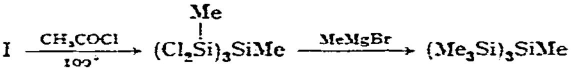
358.) Assignment of the unusual branched-chain structure II rather than the linear structure IV did not follow straightforwardly from the spectral properties.



IV

The UV-spectrum showed no λ_{max} above 200 mμ, consistent with the results previously reported[2] for other branched-chain derivatives. The absence of an absorption in the 235–40 mμ 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. 94–5°/8 mm) was purified by VPC and isolated as a low-melting waxy solid.



$$\mathrm{I} \xrightarrow[100^{\circ}]{CH_3COCl} (Cl_2Si)_3\overset{Me}{Si}Me \xrightarrow{MeMgBr} (Me_3Si)_3SiMe \qquad (3)$$

V

The UV spectrum of V showed no λ_{max} above 200 mμ, 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).

$$(Me_3Si)_4Si \xrightarrow[-Me_4Si]{MeLi} (Me_3Si)_3SiLi \xrightarrow{Me_2SO_4} \mathrm{V} \qquad (4)$$

$$MeSiCl_3 + 3\ Me_3SiCl \xrightarrow[THF]{Li} \mathrm{V} \qquad (5)$$

It is interesting to compare the thermal reactivity of I with that previously reported for other organodisilanes. The isomerization of hexamethyldisilane has been reported[6] to occur at 600° and, in general, pentamethyldisilanyl compounds and methylpolysilanes have been observed[7] to have good thermal stability. Pentamethyldisilanyl cyanide, a notable exception, has been reported[7] 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

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* 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.

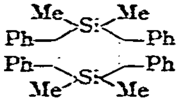
225° ($t_{1/2} \cong 2$ h) the products were dimethyldimethoxysilane and the homologous series of α,ω-dimethoxypermethylated polysilanes (VII). At a somewhat higher temperature (275°), the trisilane VIIa gave dimethyldimethoxysilane and higher members of the polysilane series VII. While these limited relative reactivities parallel those observed[1] 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.

$$\mathrm{MeO(SiMe_2)_2OMe} \longrightarrow \mathrm{Me_2Si(OMe)_2} + \underset{\substack{\text{VII a, } n = 3 \\ \text{b, } n = 4 \\ \text{c, } n = 5}}{\mathrm{MeO(SiMe_2)_nOMe}} \qquad (6)$$

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.

$$\underset{\text{VI}}{\mathrm{MeO(SiMe_2)_2OMe}} \longrightarrow \mathrm{Me_2Si(OMe)_2} + \mathrm{Me_2Si\!:} \qquad (7)$$

$$\mathrm{Me_2Si\!:} + \mathrm{VI} \longrightarrow \underset{\text{VII}}{\mathrm{MeO(SiMe_2)_nOMe}} \qquad (8)$$


VIII

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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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