Thermolysis of Pentamethyldisilane and 1*H*-Heptamethyltrisilane

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PREVIOUSLY, we have described[1] that hexamethyldisilane undergoes almost quantitative rearrangement to trimethyl(dimethylsilylmethyl)silane by thermolysis at 400—450° in a sealed tube; this thermolysis differs considerably from the pyrolysis of hexamethyldisilane at low pressure.[2]

Here we report the thermal reactions of polysilane carried out in a sealed tube. When pentamethyldisilane (I) was thermolysed at 300—325° for 15 hr. in a sealed tube, a mixture of trimethylsilane (II), unchanged pentamethyldisilane (I), 1*H*-heptamethyltrisilane (III), 1*H*-nonamethyltetrasilane (IV), 1*H*-undecamethylpentasilane (V), and a small amount of high boiling products (presumably higher members of the homologous series) was obtained. Products other than $Me(SiMe_2)_nH$ were not formed, at least not in detectable amounts, the yield of $Me(SiMe_2)_nH$ (n = 1—5) being higher than 90%.

$$Me_3Si{\cdot}SiMe_2H \rightarrow \Sigma\, Me(SiMe_2)_nH \quad (n = 1, 2, \ldots 5)$$

These compounds were separated from the mixture by preparative g.l.c., and the structures were unequivocally determined by i.r., n.m.r., and u.v. spectroscopy. Since (I),[3] (II), (III),[3] and (IV)[4] are known compounds, their retention times on g.l.c. were also compared with those of authentic samples. U.v. spectra were especially useful to determine the chain-length;[5] λ_{max} (ϵ) in hexane (III) 218 (8090); (IV) 236 (12,600); and (V) 250·5 mμ (18,900).

Thermolysis of (III) gave a similar mixture of products as obtained on pyrolysis but in slightly differing amounts (Table).

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Compound	Temp.	Time (hr.)	$Me(SiMe_2)_nH$ (g.l.c. area %)* n = 1	2	3	4	5
(I)	325°	20	20·1	21·8	25·9	20·5	11·7
	300	15	25·3	28·7	29·2	12·9	3·9
(III)	300	15	9·4	17·2	32·5	27·2	13·7

* Two higher boiling products, presumably compounds of n = 6 and 7, were detected by g.l.c.

These results may be best interpreted in terms of an intermediate, dimethylsilylene. Its initial formation from (I) must be the reverse of the reaction postulated by Skell and Goldstein[6] for insertion of dimethylsilylene into a Si–H bond. Multiple insertion and elimination of dimethylsilylene resulted in redistribution of methylpolysilicon hydrides.

$$Me_3Si{\cdot}SiMe_2H \rightleftharpoons Me_3SiH + Me_2Si{:}$$
$$Me_2Si{:} + Me(SiMe_2)_nH \rightleftharpoons Me(SiMe_2)_{n+1}H$$

Accordingly, the present reaction may be correlated with thermal redistribution of methoxy-substituted disilanes;[7] we have observed that substituted disilanes ($Me_3Si{\cdot}SiMe_2X$, where X = Cl, OPh, and Ph) also undergo similar α-eliminations. However, it is interesting that the presence of the simplest ligand, H, on a silicon–silicon bond gave rise to such an extensive redistribution *via* the silylene intermediate, since a common characteristic of α-eliminations appears to require the presence of an eliminating unit (carbene or silylene), which bonds to both an element bearing a pair of non-bonding electrons, and a metal or metalloid. In the present case, if α-eliminations are operative, bonding electron(s) of Si–H should be involved in the mechanism.

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