

# DIVALENT SILICON INTERMEDIATES IN THE PYROLYSIS OF ALKOXYPOLYSILANES

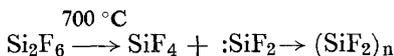
DONALD R. WEYENBERG and WILLIAM H. ATWELL

*Director of Development, Dow Corning Corporation, Midland, Michigan, U.S.A.*

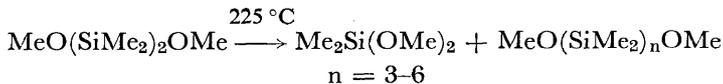
The inorganic divalent silicon species,<sup>1</sup> dihalosilylenes, have been known for many years, and difluorosilylene,<sup>2</sup> in particular, has been studied quite intensively. The structure of this relatively stable species (150 sec half-life at 0.1 mm pressure and 25°C) has been determined and its chemistry is currently under investigation in several laboratories. Renewed interest has also been observed in the chemistry of dichlorosilylene.<sup>3</sup>

The silylenes bearing an organic substituent, although believed to be reactive intermediates in many syntheses, have remained a relatively poorly understood subject. The absence of a general, convenient, and less ambiguous source of silylenes has been a serious handicap in establishing the general chemistry of these intermediates. It is now apparent that the thermolysis of alkoxydisilanes provides such a source of silylenes, and in this paper we shall review the evidence supporting the intermediacy of silylenes in this reaction as well as the general picture of the chemistry of organosilylenes which is emerging from these studies.

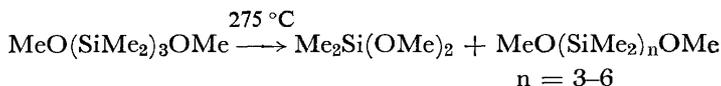
The halodisilanes are known to undergo a redistribution reaction at elevated temperatures to yield silanes and higher polysilanes<sup>1</sup> and this decomposition has been shown in some cases to proceed *via* the formation of dihalosilylenes.<sup>1, 4</sup>



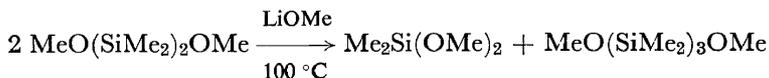
We observed recently<sup>5</sup> that the alkoxydisilanes undergo an analogous redistribution reaction at much lower temperatures to yield again an alkoxy-silane and higher alkoxy-polysilanes.



It is this reaction which has proved to be a most convenient and quite general source of silylenes. The alkoxy-ended polysilanes are stable under the above reaction conditions, but will undergo a similar reaction at more elevated temperatures.

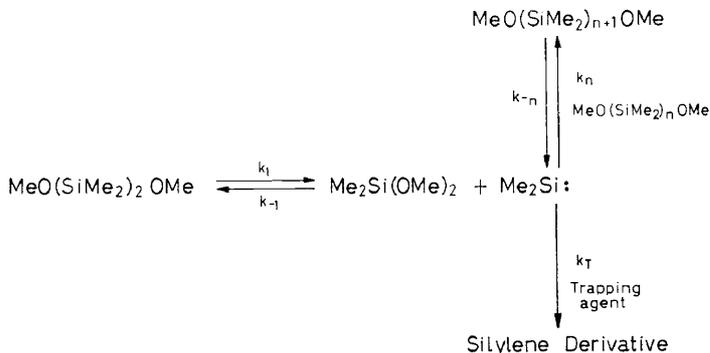


It should be noted that there is *no evidence for silylene intermediates* in the base-catalyzed redistributions of halo- or alkoxydisilanes,<sup>1b, 6</sup>



In fact, reagents which intercept the silylene in the thermal reaction do not alter the course of the latter base-catalyzed reaction.<sup>7</sup>

Three lines of evidence support the intermediacy of silylenes in these thermolyses; the interception (trapping) of these intermediates, the kinetics of the thermolyses and the detection of dimethylsilylene by mass spectral studies.



The reagent which is always present in the above scheme to intercept the silylene is either the parent disilane or a polysilane thus formed. Three additional classes of trapping agents, which provide high yields of a derivative with a corresponding decrease in the yield of polysilanes, are acetylenes, 1,3-dienes and alcohols (methanol). Each class will be discussed in more detail later in this review. It is important at this point to note that none of these trapping agents accelerates the decomposition of the disilane; in fact, as expected from the above scheme, the presence of these reagents actually reduces the rate of disilane consumption. In the reaction of hexamethoxydisilane and methanol, which will be discussed later, the reaction has been shown to be first-order in disilane and zero-order in the trapping agent, methanol.

The kinetics of the thermolysis of 1,2-dimethoxytetramethyldisilane clearly confirm the implications of the above data—the rate-determining step in this reaction is the unimolecular decomposition of the disilane,  $k_n \gg k_{-1}$ . (As was stated previously,  $k_{-n}$  is negligible under these conditions.) This was most simply shown by observing the extent of decomposition of the disilane after a given interval of time as a function of its initial concentration in an inert diluent, benzene. As shown in *Table 1*, the half-life was indeed constant over a four-fold change in initial concentration as is demanded by a *rate-determining unimolecular decomposition*. A more detailed analysis<sup>8</sup> showed an excellent kinetic correlation of the experimental data with the following more complete kinetic model (see *Figure 1*),

SILYLENES FROM ALKOXPOLYSILANES

Table 1. Effect of concentration on the thermolysis of MeO(SiMe<sub>2</sub>)<sub>2</sub>OMe (at 220 < 2°C)

Time (hr)	Conc. Disilane (wt. % in benzene)	MeO(SiMe <sub>2</sub> ) <sub>n</sub> OMe (glc area %)				
		n =	1	2	3	4
2.0	Neat		9.0	77.8	13.1	—
	75		8.7	78.5	13.0	—
	50		8.4	80.0	12.0	—
	25		7.8	80.0	12.3	—
	av.		8.5 (± 0.7)	79.1 (± 1.3)	12.6 (± 0.5)	—
3.5	Neat		21.9	48.6	24.9	4.5
	75		23.1	45.6	26.4	4.9
	50		22.8	46.3	26.0	4.9
	25		21.2	47.8	25.5	4.7
	av.		22.6 (± 0.9)	47.1 (± 1.5)	25.7 (± 0.7)	4.7 (± 0.2)

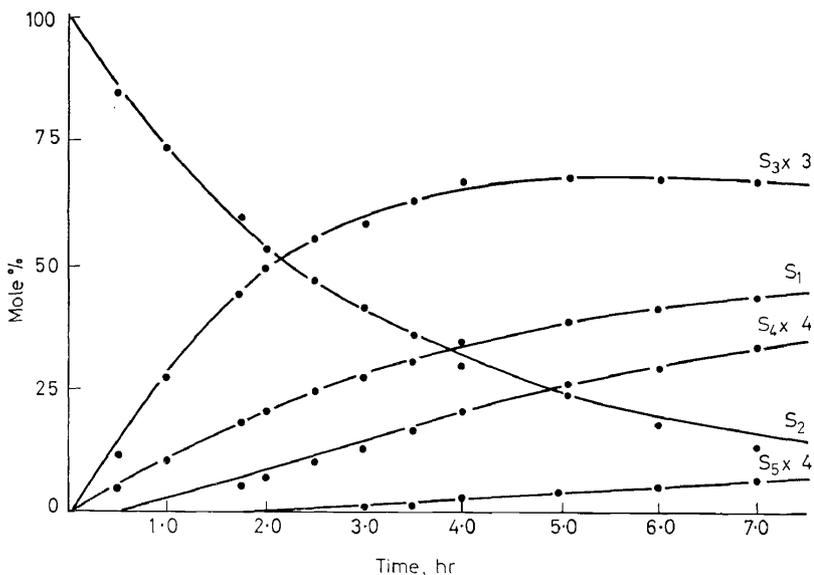
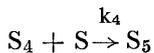
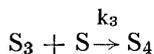
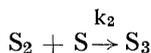
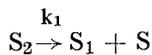
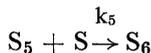


Figure 1. Kinetics of MeO(SiMe<sub>2</sub>)<sub>2</sub>OMe thermolysis (at 220 ± 2°C)



Where S = (Me<sub>2</sub>Si:) and

S<sub>n</sub> = MeO(SiMe<sub>2</sub>)<sub>n</sub>OMe



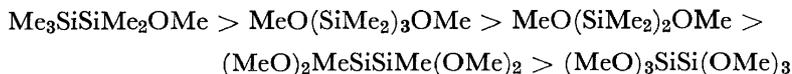
and allowed evaluation of  $k_1$  and the relative values of  $k_2$  through  $k_5$  (at  $220 = 2^\circ\text{C}$ ).

$$\left. \begin{array}{l} k_1 = 4.7 \times 10^{-5} \text{ sec}^{-1} \\ k_2 = 1.00 \\ k_3 = 0.87 = 0.10 \\ k_4 = 0.60 = 0.10 \\ k_5 = 0.50 = 0.10 \end{array} \right\} \text{Relative Rates}$$

Further evidence that the intermediate, which is formed in the unimolecular decomposition and subsequently captured by the various trapping agents, is indeed a silylene comes from a preliminary mass spectral study.<sup>9</sup> 1,2-Dimethoxytetramethyldisilane was introduced continuously into an MS-12 mass spectrometer, maintained at a constant ionizing potential and source temperature, by means of a variable temperature glass "leak" line. When the temperature of the line was greater than  $325^\circ\text{C}$ , a parent ion  $m/e$  58 was observed with an appearance potential of *Ca* 12-13 ev. This temperature corresponds to the conditions where decomposition of this disilane is first observed in a flow system (*Ca* 8-10 sec contact times). This new species which is being transported from the reaction zone to the instrument is most certainly dimethylsilylene.

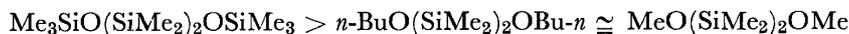
This thermolysis reaction is quite general for polysilanes with an oxy-ligand, however, the rate of decomposition varies widely with the substitution at the silicon. Thus, the stability of the disilane decreases as shown with hexamethoxydisilane being the most labile.

#### Thermal Stability:



The nature of the oxy-ligand is also important with the siloxy-derivatives exhibiting a stability considerably greater than that of the alkoxy-derivatives.

#### Thermal Stability:



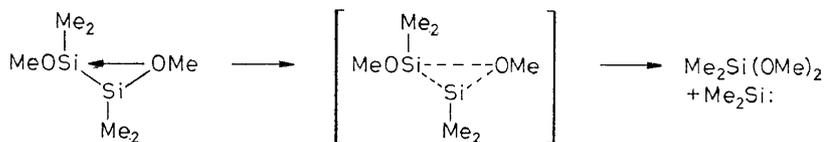
The more general nature of the thermolysis and the effect of substituent on the stability of the disilane is demonstrated by the following relative reactivity scheme.

#### Thermal Stability:



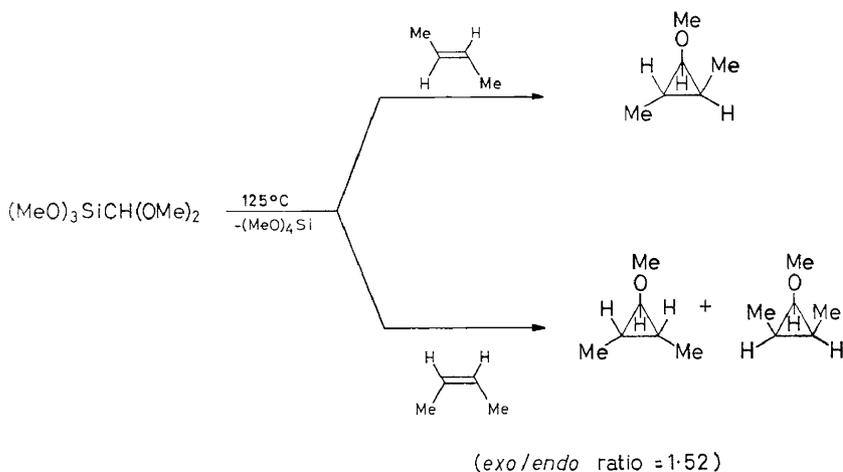
The thermolysis of alkoxy-polysilanes appears to be another example of an  $\alpha$  elimination with an "organometallic reagent": a reaction which is

characteristic of many compounds having an element bearing a pair of electrons and a metal (or metalloid) bonded to a common carbon atom.<sup>10</sup> In this case the common atom is silicon and the reaction involves migration of methoxy from one silicon to an adjacent silicon as shown below for 1,2-dimethoxytetramethyldisilane.



The greater stability of the siloxy-derivatives and of the more highly methylated derivatives would be quite consistent with this model.

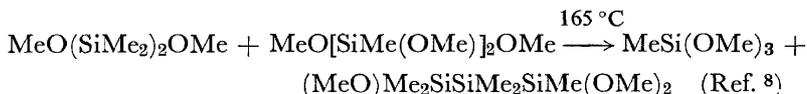
These considerations suggested that alkoxy-derivatives might be more reactive in other  $\alpha$  elimination reactions; and, indeed, this appears to be the case with silicon derivatives. We have recently observed that (dimethoxy-methyl)trimethoxysilane is an excellent source of methoxycarbene at relatively low temperatures and neutral conditions as illustrated by the following reaction with *cis*- and *trans*-but-2-ene.<sup>11</sup>



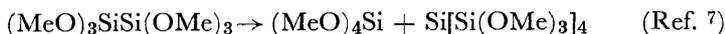
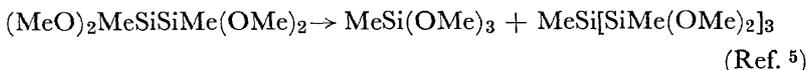
Thermolysis of this silane occurs at temperatures significantly lower than those reported for trichloromethyltrichlorosilane<sup>10</sup> and is first-order in silane.

Having established the intermediacy of silylenes in these reactions, we can now turn our attention to some basic reactions of these species. The first intriguing question concerns the reaction of silylenes with alkoxy polysilanes. The formation of the series  $\text{MeO}(\text{SiMe}_2)_n\text{OMe}$  in the thermolysis of the disilane ( $n = 2$ ) could be explained by insertion of dimethylsilylene into either silicon-silicon or silicon-oxygen bonds. In addition to the mechanistic

and kinetic results discussed previously, direct chemical evidence has been obtained which demonstrates silicon-oxygen insertion.



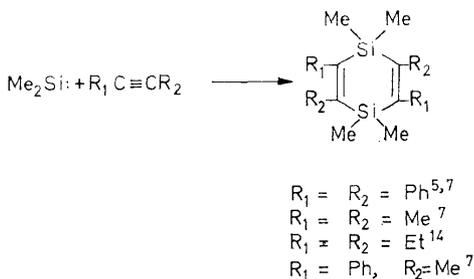
Under conditions where only the dimethyltetramethoxydisilane will undergo thermolysis, the dimethoxytetramethyldisilane captures the methylmethoxysilylene. This silicon-oxygen insertion reaction is consistent with another interesting phenomenon—only the most highly “branched” polysilanes are isolated from thermolysis of tetra- and hexamethoxy-disilanes.



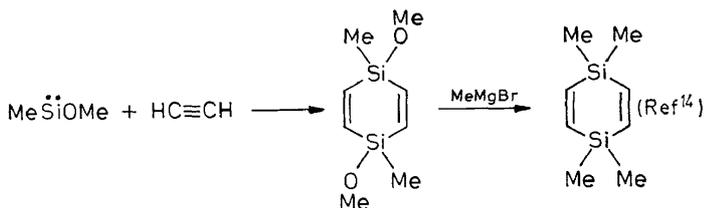
The insertion of silylene into the silicon-oxygen bond of either trimethylmethoxysilane or dimethyldimethoxysilane is not competitive with related insertions into methoxypolysilane. This indicates an unusual order of relative reactivities for the various alkoxydisilanes toward dimethylsilylene.<sup>12</sup>



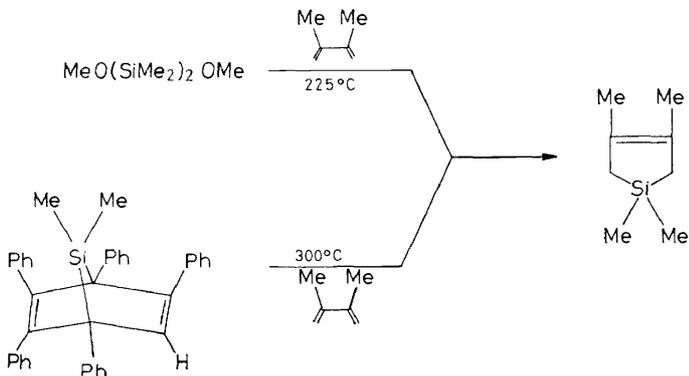
Unsaturated organic compounds, because of their wide use in the capture of carbenes and because they provide a potential route to the unknown silacyclopropanes and silacyclopropenes, are of particular interest as trapping agents. The diarylacetylenes, first used by Volpin<sup>13</sup> for intercepting silylenes, have proven to be very efficient trapping agents; high yields of disilacyclohexadiene derivatives are obtained. We have extended the scope of this reaction to a variety of acetylenes.



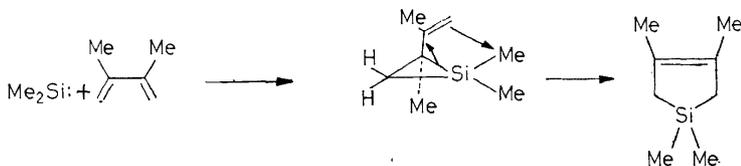
These reactions presumably involve the dimerization of intermediate silacyclopropenes.<sup>7</sup> The corresponding disilacyclohexadienes have been obtained using methylmethoxysilylene<sup>7</sup> and the parent disilacyclohexadiene has been isolated in reactions with acetylene. Repeated attempts, however, to extend this reaction to the dimethoxysilylene from hexamethoxydisilane have not yielded disilacyclohexadienes.



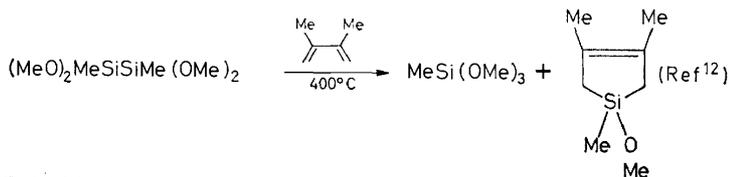
Conjugated olefins have been found to be excellent trapping agents for silylene intermediates. Silacyclopentenes are obtained from 2,3-dimethylbutadiene and dimethylsilylene which is generated either from the methoxydisilane or from an appropriate 7-silanorbornadiene. <sup>7</sup>

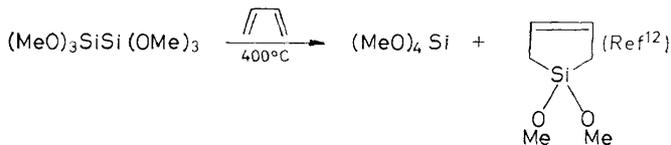


Although this reaction is formally a 1-4 addition of a silylene across the unsaturated system, it could also involve a vinyl-substituted silacyclopropane intermediate.

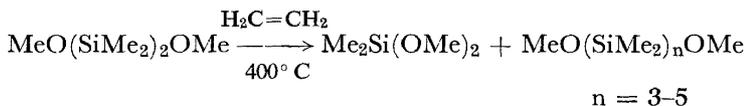


These reactions are quite conveniently carried out in the vapour phase where side reactions involving dimerization of the diene are minimized and yields of the silacyclopentene are high (over 60 per cent). The utility and versatility of the butadienes as trapping agents are indicated by the following examples.





Although reactions of ethylene with dimethylsilylene have been observed by Skell<sup>15</sup> and by Nefedov,<sup>16</sup> neither ethylene nor tetramethylethylene compete successfully with the parent disilane for the silylene.

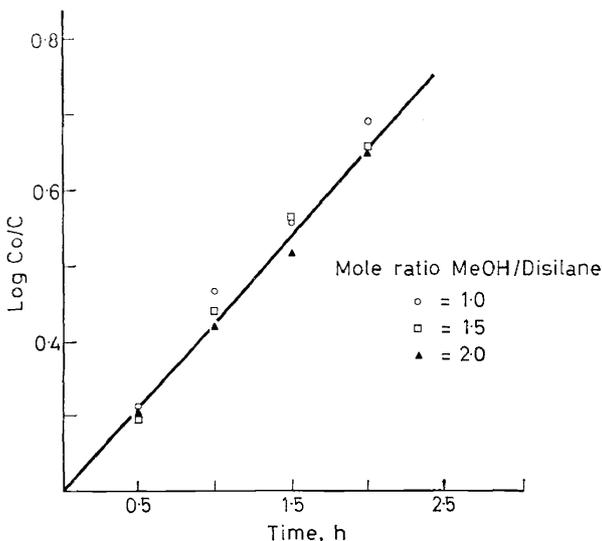


Simple alkanes and benzene are also inert diluents for the thermolysis of 1,2-dimethoxytetramethyldisilane.

A second general method of trapping divalent species, the insertion into single bonds, has also been employed. In addition to the insertion into the silicon-oxygen bonds, which was discussed earlier, these silylenes can also be intercepted by insertion into the oxygen-hydrogen bond of methanol. For example, dimethoxysilylene reacts with methanol to give trimethoxysilane.



The results of a brief kinetic study, which show this reaction to be first-order in disilane and independent of the concentration of methanol, are shown in *Figure 2*. These reactions are complicated by the subsequent but slower reaction of the silicon hydride with the methanol.



*Figure 2.* Kinetic plot for the thermolysis of  $(\text{MeO})_6\text{Si}_2$  in the presence of methanol

It is apparent from these studies that silylenes have a rich and varied chemistry with broad synthetic applications, and that a greater understanding of their preparation, structure and properties will contribute greatly to the field of silicon chemistry.

## References

- <sup>1</sup> For recent reviews of this field, see—(a) O. M. Nefedov and M. N. Manakov, *Angew. Chem Intern. Ed. Engl.* **5**, 1021 (1966); (b) W. H. Atwell and D. R. Weyenberg, *ibid.*, in press.
- <sup>2</sup> J. C. Thompson and J. L. Margrave, *Science*, **155**, 669 (1967).
- <sup>3</sup> P. Timms, *Chem. Eng. News*, **45**, 57 (1967); (b) *Inorg. Chem.*, **7**, 387 (1968).
- <sup>4</sup> M. Schmeisser and K. P. Ehlers, *Angew. Chem.*, **76**, 781 (1962).
- <sup>5</sup> W. H. Atwell and D. R. Weyenberg, *J. Organometal. Chem.*, **5**, 594 (1966).
- <sup>6</sup> W. H. Atwell and D. R. Weyenberg, *J. Organometal. Chem.*, **7**, 71 (1967).
- <sup>7</sup> W. H. Atwell and D. R. Weyenberg, *J. Am. Chem. Soc.*, **90**, 3438 (1968).
- <sup>8</sup> W. H. Atwell, L. G. Mahone, S. F. Hayes and J. G. Uhlmann, *J. Organometal Chem.*, in press.
- <sup>9</sup> R. S. Gohlke and W. H. Atwell, unpublished studies.
- <sup>10</sup> For a discussion of reactions of this type, see—D. Seyferth, J. Y-P. Mui and J. M. Burlitch, *J. Am. Chem. Soc.*, **89**, 4953 (1967).
- <sup>11</sup> W. H. Atwell, D. R. Weyenberg and J. G. Uhlmann, *J. Am. Chem. Soc.* **91**, 2025 (1969).
- <sup>12</sup> W. H. Atwell and J. G. Uhlmann, unpublished studies.
- <sup>13</sup> M. E. Volpin, Yu. D. Koreshkov, V. G. Dulova and D. M. Kursanov, *Tetrahedron*, **18**, 107 (1962).
- <sup>14</sup> E. G. Janzen, J. B. Pickett and W. H. Atwell, *J. Am. Chem. Soc.*, **90**, 2719 (1968).
- <sup>15</sup> P. S. Skell and E. J. Goldstein, *J. Am. Chem. Soc.*, **86**, 1442 (1964).
- <sup>16</sup> O. M. Nefedov and M. N. Manakov, *Angew. Chem.*, **76**, 270 (1964).