photochlorination of neohexane.[19] Further there is no report of a solvolysis of a pinacolyl halide or arenesulfonate leading to unrearranged products. However, the observation[20] that active pinacolyl hydrogen sulfate in sulfuric acid racemizes faster than it rearranges is intriguing, implying that rotation within the ion pair and collapse to the starting material are faster than rearrangement. There are no reports of earlier efforts to prepare free pinacolyl cations by deamination, deoxideation, or anodic oxidation.

Experimental Section

2,3,3-Trimethylbutanoic Acid. This acid (prepared by students of F. C. Whitmore) was recrystallized from pentane (−78°) yielding white crystals, mp 53–54°, 98% pure; nmr: singlet (9 H) at 1.00 (δ scale), doublet (3 H) centered at 1.16, quartet (1 H) centered at 2.27, and singlet (1 H) at 12.01 ppm (lit.[21] mp 48–50°).

Electrolyses of Potassium 2,3,3-Trimethylbutanoate. The electrolysis technique has been reported.[2] The results are given in Table IV. Because of the small absolute amounts of these products, most of them were identified solely by comparison of vpc retention times to those of known compounds. The major products were also identified by ir.

Acknowledgment. The authors thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Army Research Office, and the Air Force Office of Scientific Research for partial support of this research. P. H. R. gratefully acknowledges fellowships from the National Science Foundation and Esso Research and Engineering Co.

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[19] F. C. Whitmore, H. I. Bernstein, and L. W. Mixon, *J. Am. Chem. Soc.*, **60**, 2539 (1938).

[20] N. C. Deno and M. S. Newman, *ibid.*, **73**, 1920 (1951).

[21] W. S. Ropp, Ph.D. Thesis, The Pennsylvania State College, 1949, p 101.

Silylene Chemistry. I. The Thermolysis of Methoxypolysilanes[1]

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Contribution from the Organometallic Research Laboratory,
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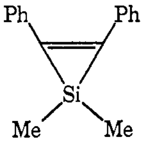
Received December 26, 1967

Abstract: Kinetic, mass spectral, and chemical evidence is presented for the formation of divalent silicon (silylene) species in the thermolysis of methoxypolysilane derivatives. In the absence of alternative "trapping" agents, the silylenes insert into the silicon–oxygen bond of the parent methoxypolysilane. These silylenes could be intercepted by a variety of acetylenes to give 1,4-disilacyclohexadienes. This reaction appears to involve a rather specific dimerization of silacyclopropene intermediates. The silylenes could also be intercepted by butadienes to give silacyclopent-3-enes. The silylenes could not be intercepted by simple olefins such as tetramethylethylene.

In recent years a number of reports concerning the intermediacy of divalent organosilicon (silylene) species have appeared.[2] Two general methods have been used for the generation of these silylenes: (1) the reaction of diorganodichlorosilanes with metals,[3–8] and (2) the thermal decomposition of appropriate substrates.[1,3,8,9]

In 1962, Volpin and coworkers reported[3] that the reaction of dimethyldichlorosilane with sodium and the pyrolysis of $(Me_2Si)_{55}$ gave dimethylsilylene. This claim was based on the isolation of the novel 1,1-dimethyl-2,3-diphenylsilirene (1) when the reactions were carried out in the presence of diphenylacetylene. Since this initial report it has been shown by mass spectral,[10] molecular weight,[11] and X-ray[12] studies that the compound believed to have structure 1 is really the dimer 2. It has geen suggested[9a] that compound 1 might have been an intermediate in the formation of 2.



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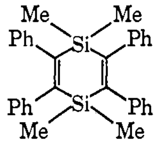

2

Skell and Goldstein[4] reported the formation of dimethylsilylene from the reaction of dimethyldichlorosilane with sodium–potassium vapor at 260–280°. Insertion of dimethylsilylene into the Si–H bond of trimethylsilane to give pentamethyldisilane (3) was observed,[4] and the absence of hexamethyldisilane and

$$\mathrm{Me_2Si\!:} + \mathrm{Me_3SiH} \longrightarrow \underset{\mathbf{3}}{\mathrm{Me_3SiSiMe_2H}}$$

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[1] For a preliminary account of this work, see (a) W. H. Atwell and D. R. Weyenberg, *J. Organometal. Chem.* (Amsterdam), **5**, 594 (1966); (b) *Chem. Eng. News*, 30 (Sept 4, 1967).

[2] (a) The following discussion will be limited to organosilylenes. For an excellent review of inorganic, organometallic, and organic analogs of carbenes, see O. M. Nefedov and M. N. Manakov, *Angew. Chem. Intern. Ed. Engl.*, **5**, 1021 (1966). (b) For a review of silylene chemistry, see W. H. Atwell and D. R. Weyenberg, *ibid.*, in press.

[3] M. E. Volpin, Yu. D. Koreshkov, V. G. Dulova, and D. N. Kursanov, *Tetrahedron*, **18**, 107 (1962).

[4] P. S. Skell and E. J. Goldstein, *J. Am. Chem. Soc.*, **86**, 1442 (1964).

[5] O. M. Nefedov and M. N. Manakov, *Angew. Chem.*, **76**, 270 (1964).

[6] R. A. Braun, *J. Am. Chem. Soc.*, **87**, 5516 (1965).

[7] O. M. Nefedov, M. N. Manakov, and A. D. Petrov, *Dokl. Akad. Nauk SSSR*, **154**, 395 (1964); *Chem. Abstr.*, **60**, 3904 (1964), and references cited therein.

[8] O. M. Nefedov, G. Garzo, T. Szekely, and V. I. Shiryaev, *Proc. Akad. Sci. USSR, Chem. Sect.*, **164**, 945 (1965).

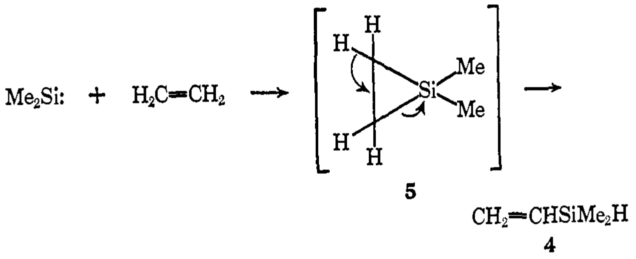
[9] (a) H. Gilman, S. G. Cottis, and W. H. Atwell, *J. Am. Chem. Soc.*, **86**, 1596 (1964); (b) *ibid.*, **86**, 5584 (1964).

[10] F. Johnson, R. S. Gohlke, and W. H. Nasutavicus, *J. Organometal. Chem.* (Amsterdam), **3**, 233 (1965).

[11] R. West and R. E. Bailey, *J. Am. Chem. Soc.*, **85**, 2871 (1963).

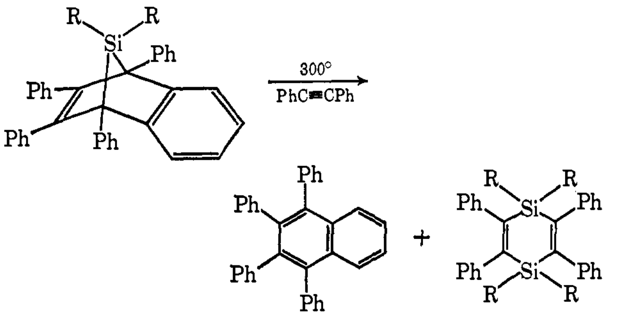
[12] N. G. Bokii and Yu. T. Stuchkow, *J. Struct. Chem.*, **6**, 543 (1965).

sym-tetramethyldisilane suggested a singlet state for this silylene. The reaction of dimethylsilylene with ethylene gave vinyldimethylsilane (**4**), presumably *via* an intermediate silacyclopropane (**5**).[4]



Nefedov and Manakov[5] proposed dimethylsilylene to explain the products obtained from: (a) the reaction of dimethyldichlorosilane with lithium and (b) the pyrolysis of $(Me_2Si)_n$ in the presence of ethylene and related olefins. Although the reaction products of dimethyldichlorosilane with metals in the presence of various conjugated olefins[7] and also hexafluoroacetone[6] have been explained in terms of a dimethylsilylene intermediate, the formation of these products can also quite adequately be explained by alternative mechanisms.[13,14] Furthermore, no evidence was found for the intermediate formation of diphenylsilylene in the reaction of diphenyldichlorosilane with lithium.[15]

Although several studies support the intermediacy of dimethylsilylene in the pyrolysis of $(Me_2Si)_n$,[2,3,5,8] exceedingly low yields of derivatives are obtained. An alternate pyrolytic approach which has given much improved yields of silylene derivatives involves the thermal decomposition of the novel 7-silanorbornadienes.[9] The generation of dimethyl- and diphenylsilylene in the presence of diphenylacetylene *via* this procedure gave the corresponding disilacyclohexadienes **2** and **6**.[9] The thermal decomposition of these 7-silanorbornadienes in the presence of ethylene and other olefins has been reported[2,16] to proceed with the formation of heterocyclic and heterolinear products consistent with a dimethylsilylene intermediate.



2, R = Me (50–67%)
6, R = Ph (63%)

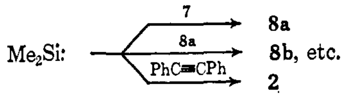
Recently, we have reported[1] that the thermolysis of *sym*-dimethoxytetramethyldisilane (**7**) proceeds readily at 225° to give dimethyldimethoxysilane and the α,ω-dimethoxypermethylpolysilanes (**8**). A mechanism involving an α elimination of **7** to give dimethylsilylene,

$$\underset{7}{MeO(SiMe_2)_2OMe} \longrightarrow Me_2Si(OMe)_2 + MeO(SiMe_2)_nOMe$$

8a, $n = 3$
b, $n = 4$
c, $n = 5$

followed by a series of insertion reactions with **7**, was suggested. Strong support for this proposal was found in the isolation of the disilacyclohexadiene **2**

$$7 \xrightarrow{\Delta} Me_2Si(OMe)_2 + Me_2Si:$$



when the thermolysis of **7** was carried out in the presence of diphenylacetylene. The present paper describes our recent work on the generation of silylenes *via* the thermolysis of **7** and related polysilanes.

Results and Discussion

Strong evidence for the intermediacy of silylenes in the thermolysis of methoxypolysilanes has been derived from kinetic, mass spectral, and chemical "trapping" studies. We will consider each of these studies on *sym*-dimethoxytetramethyldisilane (**7**) which, to date, has been examined in greatest detail. In addition, "trapping" studies will be described with related methoxy-substituted polysilanes.

The thermolysis of **7** was reported previously[1] to proceed at temperatures of 225–250°. The most convincing evidence for the above reaction scheme where the α elimination is the rate-determining step comes from a preliminary examination of the kinetics of this reaction. Since the disilane **7** would be disappearing by both the α elimination and by reaction with dimethylsilylene, the simplest test for the unimolecular nature of this reaction would be the effect of solvent on the extent of decomposition; *only with a unimolecular rate-determining step would the extent of decomposition be independent of dilution.* The data in Table I show that this is indeed the case when the thermolysis of **7** is carried out in benzene over a fourfold concentration range. In addition, these data show that the ratio of the other telomers is insensitive to this concentration

Table I. Effect of Concentration on the Thermolysis of $MeO(SiMe_2)_2OMe$ (**7**) at 220 ± 2°

Time, hr	Concn of 7[a]	$MeO(SiMe_2)_nOMe$ (glpc area %) 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	79.1	12.6	
		(±0.7)	(±1.3)	(±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	47.1	25.7	4.7
		(±0.9)	(±1.5)	(±0.7)	(±0.2)

[a] Weight per cent in benzene.

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(13) (a) D. R. Weyenberg, L. H. Toporcer, and A. E. Bey, *J. Org. Chem.*, **30**, 4096 (1965); (b) D. R. Weyenberg, L. H. Toporcer, and M. J. Napoli, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., 1961, p 31Q.

(14) C. L. Frye, R. M. Salinger, and T. J. Patin, *J. Am. Chem. Soc.*, **88**, 2343 (1966).

(15) H. Gilman and D. J. Peterson, *ibid.*, **87**, 2389 (1965).

(16) O. M. Nefedov, T. Szekely, *et al.*, *Intern. Sym. Organosilicon Chem., Prague*, 65 (1965).

change. Furthermore, the rate of disappearance of **7** is *not accelerated* by the presence of "trapping" agents such as acetylenes. A more complete analysis of the kinetics of this reaction will be the subject of a separate publication.

Evidence for the formation of silylenes was also obtained by mass spectral studies. Dimethylsilylene molecular ion (*m/e* 58) is detected as a short-lived intermediate when the thermolysis of **7** is carried out in the inlet system of a mass spectrometer.[17]

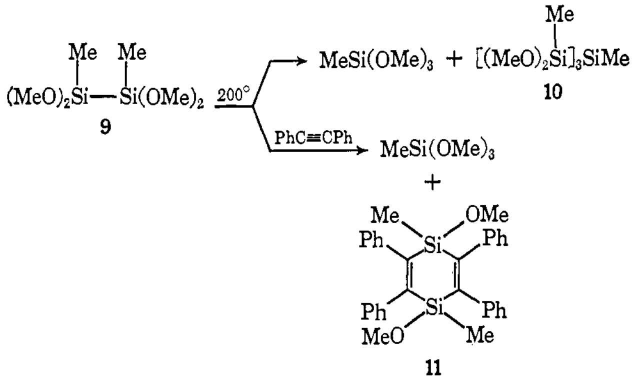
The thermolytic generation of silylenes appears to be a general reaction for methoxy-substituted polysilanes. We reported previously[1] the thermolysis of 1,3-dimethoxyhexamethyltrisilane (a) at temperatures of 250–275° to give dimethyldimethoxysilane and the polysilane series $\mathrm{MeO(SiMe_2)}_n\mathrm{OMe}$ (n = 4, 5, etc.). When **8a** was heated in the presence of diphenylacetylene, the disilacyclohexadiene **2** was obtained in good yield.

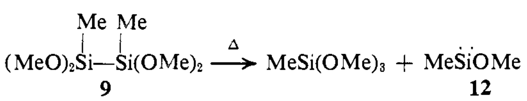
$$\underset{\mathbf{8a}}{\mathrm{MeO(SiMe_2)_3OMe}} \xrightarrow[\mathrm{PhC{\equiv}CPh}]{\text{excess}} \mathrm{Me_2Si(OMe)_2} + \mathbf{2}$$

(30% based on the above equation)

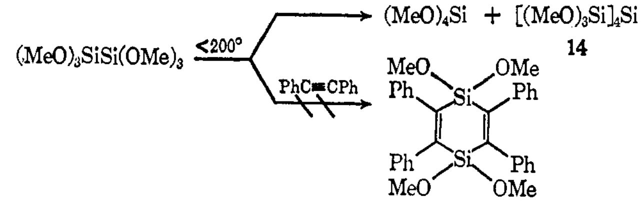
However, a comparison of the temperature needed for thermolysis of **7** and **8a** indicates the substantially *greater thermal stability of MeOŠiŠiŠiOMe relative to the MeOŠiŠiOMe unit.*

We have previously noted[1] that *sym*-dimethyltetramethoxydisilane (**9**) is less stable thermally than **7**. Thus, heating **9** at 200° gave methyltrimethoxysilane, tris(methyldimethoxysilyl)methylsilane (**10**), and a "nonvolatile polysilane residue." When **9** is heated in the presence of diphenylacetylene the major volatile products are then methyltrimethoxysilane and 1,4-dimethoxy-1,4-dimethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexadiene (**11**). These results are consistent with the formation of methylmethoxysilylene (**12**) in the thermal decomposition of **9**.





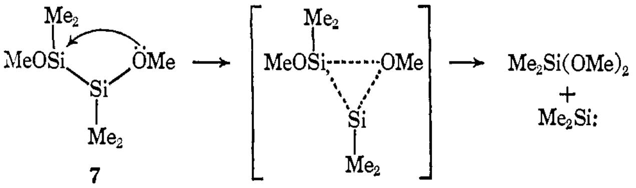
$$\underset{\mathbf{9}}{\mathrm{(MeO)_2\overset{Me}{Si}{-}\overset{Me}{Si}(OMe)_2}} \xrightarrow{\Delta} \mathrm{MeSi(OMe)_3} + \underset{\mathbf{12}}{\mathrm{Me\ddot{S}iOMe}}$$



$$\underset{\mathbf{13}}{\mathrm{(MeO)_3SiSi(OMe)_3}} \xrightarrow{\Delta} \mathrm{(MeO)_4Si} + \underset{\mathbf{16}}{\mathrm{(MeO)_2Si:}}$$

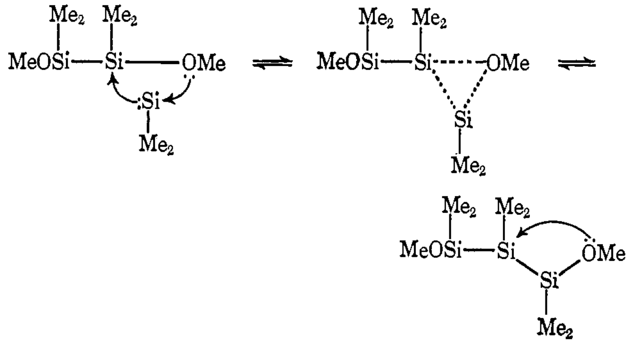
Similar studies with hexamethoxydisilane (**13**) show it to be even less thermally stable than **7** and **9**, decomposing to tetramethoxysilane, tetrakis(trimethoxysilyl)silane (**14**), and a viscous "nonvolatile polysilane residue." However, when the decomposition of **13** was carried out in the presence of diphenylacetylene, no products were isolated which would have arisen from the reaction of dimethoxysilylene (**16**) with diphenylacetylene. Thus, while the formation of dimethoxysilylene (**16**) is expected by analogy with the previous thermolysis reactions, the reactivity of **16** with acetylenes appears to be markedly different than **12**. This behavior parallels the drastic change in reactivity between methoxycarbene and dimethoxycarbene.[18] Thus, although monoalkoxycarbenes are intercepted by simple olefins, the combined electron-donating ability of two oxygens appears to substantially decrease the conventional reactivity of the carbene.

This thermolysis of alkoxypolysilanes appears to be another example of an α elimination: 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. In this case the common atom is a silicon atom and the reaction involves migration of methoxy from one silicon to an adjacent silicon as shown below for **7**.



From electronic and statistical considerations this scheme is consistent with the following observed order of increasing thermal stability: $\mathrm{(MeO)_3SiSi(OMe)_3} < \mathrm{(MeO)_2MeSiSiMe(OMe)_2} < \mathrm{MeO(SiMe_2)_2OMe} < \mathrm{MeO(SiMe_2)_3OMe} < \mathrm{Me_3SiSiMe_2OMe}$.

The formation of the $\mathrm{MeO(SiMe_2)}_n\mathrm{OMe}$ series **8** in the thermolysis of **7** could be explained by insertion of $\mathrm{Me_2Si}$: into either SiSi or Si–O bonds. While direct evidence on this point is lacking,[19] we favor insertion



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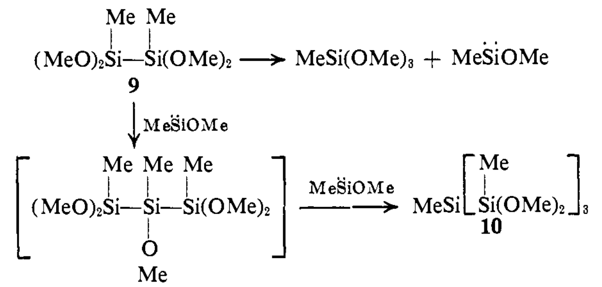
[17] Detailed results of this study, carried out with R. S. Gohlke, to be submitted for publication.

[18] (a) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964; (b) D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *J. Am. Chem. Soc.*, 88, 582 (1966).

[19] A detailed kinetic study of the thermolysis of $\mathrm{MeO(SiMe_2)_2OMe}$ is in progress and will hopefully elucidate this question.

into the SiO bond for the following reasons. (1) The reasonable assumption that the thermolysis of $MeO(SiMe_2)_3OMe$ (**8a**) is also an α elimination forces us to the conclusion that the reverse of this process is insertion of the silylene into the silicon–oxygen bond. (2) The formation of the branched-polysilane derivatives **10** and **14** from the thermolysis of **9** and **13** is readily understood in terms of SiO insertion and the previously noted increased thermal stability of the $MeO\ddot{Si}\ddot{Si}\ddot{Si}OMe$ unit, *i.e.*



$$(MeO)_2\overset{Me}{\overset{|}{Si}}{-}\overset{Me}{\overset{|}{Si}}(OMe)_2 \longrightarrow MeSi(OMe)_3 + Me\ddot{Si}OMe$$

9

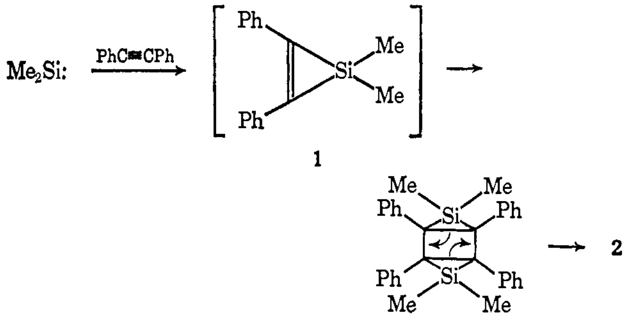
$$\downarrow Me\ddot{Si}OMe$$

$$\left[(MeO)_2\overset{Me}{\overset{|}{Si}}{-}\underset{\underset{Me}{\overset{|}{O}}}{\overset{Me}{\overset{|}{Si}}}{-}\overset{Me}{\overset{|}{Si}}(OMe)_2\right] \xrightarrow{Me\ddot{Si}OMe} MeSi\left[\overset{Me}{\overset{|}{Si}}(OMe)_2\right]_3$$

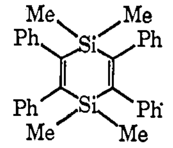
10

From the above discussion it is apparent that the mechanism involved in the thermolysis of the methoxy-substituted polysilanes is distinctly different from our previously reported[20] lithium methoxide catalyzed redistribution of these compounds. Furthermore, when *sym*-dimethoxytetramethyldisilane (**7**) was heated (100°) in the presence of diphenylacetylene and a catalytic amount of lithium methoxide, no disilacyclohexadiene (**2**) was formed. The only products formed were dimethyldimethoxysilane and the polysilanes **8a** and **8b**, in agreement with our previously reported results.[20]

Although diphenylacetylene has been used successfully for the capture of silylene intermediates to give the corresponding disilacyclohexadienes,[1–3,9,11] little is known concerning the mechanism of these "trapping" reactions. A reaction path involving the intermediate formation of the silacyclopropane **1** followed by dimerization through the π system has been suggested[9a] to explain the formation of the disilacyclohexadiene **2**.



However, the thermolysis of the disilane **7** in the presence of a mixture of diphenylacetylene and dimethylacetylene gave only the disilacyclohexadienes **2**, **17**, and **18**. No evidence was found for the formation of the disilacyclohexadiene **19**, which would be expected from dimerization of the silacyclopropenes **1** and **20** if the π-dimerization mechanism was operative. Furthermore, heating the disilane **7** with phenylmethylacetylene gave the disilacyclohexadienes **19** and **21**. No evidence was found for the formation of **17** which would be predicted (along with **21**) if the reaction path involved π dimerization of the silacyclopropene **22**. Thus, while the above results do not in any way exclude the intermediacy of silacyclopropenes, they do eliminate from further consideration the π-dimerization mechanism for disilacyclohexadiene formation.



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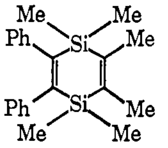

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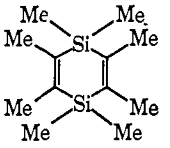

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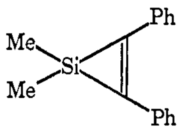

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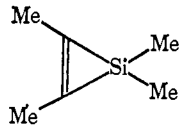

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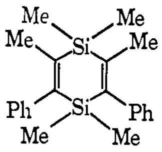

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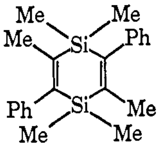

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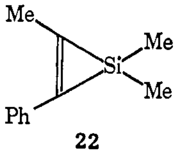

22

The formation of the disilacyclohexadienes could also be explained by a dimerization of the diradical **23**. While the direct formation of **23** is inconsistent with the previously demonstrated[4] singlet nature of dimethylsilylene, its indirect formation from the silacyclopropene **1** would be possible. Regardless of its mode of formation, it seems reasonable to expect that **23** would react with the excess diphenylacetylene present to give 1,1-dimethyltetraphenyl-1-silacyclopentadiene (**24**).[9a] We have not detected **24** in these reactions and we have shown that it is not converted to the disilacyclohexadiene **2** when present during the reaction.

In the absence of an unusually stable and selective biradical of the type **23**, we feel that the formation of the disilacyclohexadienes proceeds by a rather specific dimerization of silacyclopropene intermediates with rupture of the carbon–silicon ring bonds. The assigned selectivity of these silacyclopropene intermediates would suggest they may have sufficient stability to allow detection in the vapor phase, and experiments designed to answer these questions are currently in progress.

Dimethylbutadiene was found to react with dimethylsilylene generated from either the pyrolysis of the disilane **7** or the 7-silanorbornadiene **27**. The silacyclopentene **26**[13b] was obtained in moderate yield from both reactions. While the silacyclopentene **26** is formally a product of 1,4 addition of the silylene, presently we favor the reaction path involving prior formation of the vinyl-substituted silacyclopropane **25**.

Further examination of the reactivity of dimethylsilylene has shown that tetramethylethylene *will not* intercept this species in the thermolysis of **7**. The olefin could not compete with the disilane for the silylene since only the polysilane series **8** was identified. Although this limits the synthetic utility of this method of generating silylenes, it provides a convenient way of determining the relative reactivities of dimethylsilylene toward various reagents. These data suggest that dimethylsilylene is considerably more reactive toward

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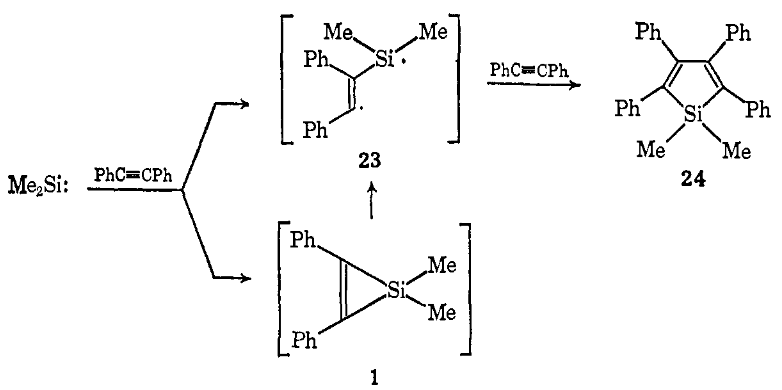
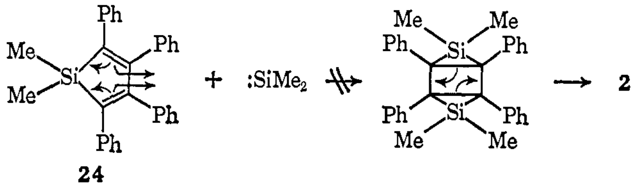
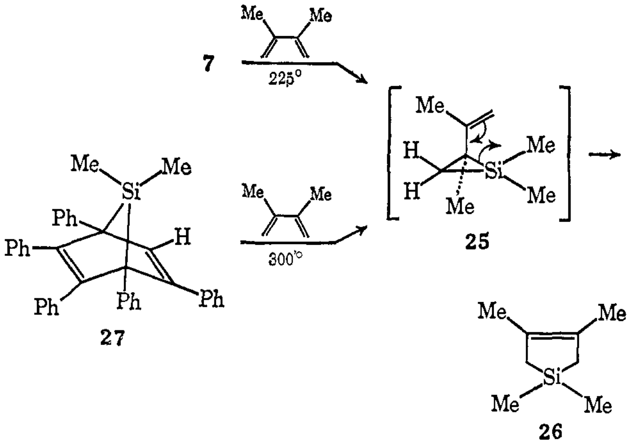
(20) W. H. Atwell and D. R. Weyenberg, *J. Organometal. Chem.* (Amsterdam), 7, 71 (1967).







both acetylenes and conjugated olefins than toward simple olefins.

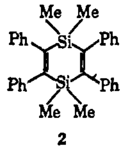
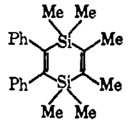
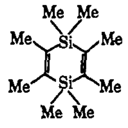
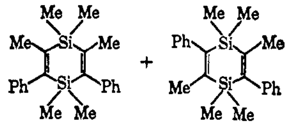
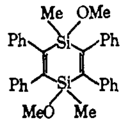
In summary, we have found the thermolysis of methoxypolysilanes to proceed by α elimination to give silylenes detectable by mass spectroscopy as short-lived intermediates. These silylenes have been shown to react with a variety of acetylenes to give the disilacyclohexadiene ring system by what appears to be a rather specific dimerization of silacyclopropene intermediates. In addition, the reaction of dimethylsilylene with 2,3-dimethylbutadiene gave the silacyclopent-3-ene ring system. Finally, the same "trapped" products are obtained when dimethylsilylene is generated from either the disilane **7** or the 7-silanorbornadiene **27**.

We are continuing our studies on the thermolysis of various substituted polysilanes with the expectation that this will be a general method for the formation of silylenes.

Experimental Section

All nmr spectra were obtained with a Varian A-60 spectrometer using tetramethylsilane as internal standard and carbon tetrachloride solvent. Nmr data for the disilacyclohexadiene derivatives is given in Table II. The infrared spectra were obtained with a Perkin-Elmer Model 521 spectrophotometer. Molecular weights were determined with a 90° sector, single-focusing mass spectrometer of 12-in. radius (AEI Model MS-12). Vapor phase chromatography was done with a F & M Model 720 unit, and helium was the carrier gas. The column used was 6 ft × 0.25 in. stainless steel packed with a mixture of Dow Corning silphenylene (25%) and Dow Corning KP-5365 fluid (75%) on 80–100 mesh Chromosorb W (10% by weight of silphenylene). Because of the ease of thermal decomposition of the methoxy-substituted polysilanes, injection port temperatures of ≤225° were employed. Melting points were taken on a Mel-Temp apparatus and are uncorrected, as are the boiling points.

Table II. Nmr Properties of 1,4-Disilacyclohexadienes[a]

Compound[b]	SiMe	CMe	SiOMe
 2	9.92	...	...
 17	9.91	8.17	...
 18	9.92	8.22	...
 19 + 21	9.92	8.40	...
 11	10.04 9.89	... ...	6.52 6.61

[a] Spectra were determined using CCl_4 as solvent and Me_4Si as internal standard ($\tau \pm 0.05$). [b] All compounds gave the correct proton area ratios.

Preparation of *sym*-Dimethoxytetramethyldisilane (7). The compound was prepared by a previously reported[20] procedure with the exception that acetic acid (rather than allyl bromide) was used to deactivate the lithium methoxide catalyst.

Thermolysis of 7. 1. In the Presence of Diphenylacetylene. A mixture of 2.0 g (11.2 mmol) of **7** and 4.0 g (22.4 mmol) of diphenylacetylene was sealed in an ampoule and heated at 225° for 18 hr. The green reaction mixture was dissolved in the minimum amount of hot benzene, cooled, and filtered to give 1.3 g (49%) of the disilacyclohexadiene **2**, mp 323–325° (lit.[9a] mmp 324–326°). The properties of this compound were shown to be identical in all respects with those of a sample of **2** prepared (see ref 11) by the method of Volpin, *et al.*[3]

Anal. Calcd for $C_{32}H_{32}Si_2$: mol wt, 472. Found: mol wt, 472.

2. In the Presence of Dimethylacetylene. A mixture of 3.18 g (17.8 mmol) of **7** and 1.45 g (26.8 mmol) of dimethylacetylene was sealed in an ampoule and heated at 225° for 18 hr. The dimethyldimethoxysilane and excess acetylene were removed with a rotary evaporator. The residue was dissolved in ethanol, cooled, and filtered to give 1.0 g (50%) of the disilacyclohexadiene **18**, mp 71–72°.

Anal. Calcd for $C_{12}H_{24}Si_2$: C, 64.3; H, 10.7; Si, 25.1; mol wt, 224. Found: C, 63.7; 63.0; H, 10.8, 10.8; Si, 26.0, 26.0; mol wt, 224.

3. In the Presence of a Mixture of Diphenyl- and Dimethylacetylene. A mixture of 6.36 g (35.7 mmol) of **7**, 9.52 g (53.4 mmol) of diphenylacetylene, and 2.90 g (53.6 mmol) of dimethylacetylene was sealed in an ampoule and heated at 225° for 18 hr. The green reaction mixture was filtered and the precipitate washed with ethanol to give 0.75 g of **2**, mp and mmp 319–322°. The ethanol filtrate was cooled and filtered. Glpc analysis of the filtrate confirmed the presence of the disilacyclohexadiene **18**; however, no attempt was made to isolate this compound. The solid obtained (1.1 g, mp 145–155°) was recrystallized from a benzene–hexane mixture to give 0.7 g of the disilacyclohexadiene **17**, mp 154–155°.

Anal. Calcd for $C_{22}H_{28}Si_2$: C, 75.8; H, 8.0; mol wt, 348. Found: C, 75.7, 75.8; H, 8.4, 8.4; mol wt, 348.

The nmr spectrum of **17** (see Table II) showed that the chemical shift of the C–Me protons was nearly the same as that found for **18**. In addition, the mass spectrum of **17** showed an intense diphenylacetylene molecular ion, consistent with the proposed structure.[10,21]

The infrared spectrum of **17** contained bands at 524 and 875 cm^{-1} which were not present in the spectrum of the mixture of isomers **19** and **21**. A quantitative analysis of the spectrum of **17** showed that it could contain a maximum of <3% of the isomers **19** and **21**, if any.

4. In the Presence of Methylphenylacetylene. A mixture of 8.90 g (50 mmol) of **7** and 5.81 g (50 mmol) of methylphenylacetylene was sealed in an ampoule and heated at 225° for 18 hr. Addition of methanol, cooling, and filtration gave 2.80 g (32%) of solid, mp 162–175°. The melting point range was not narrowed by further recrystallizations and the presence of the isomers **19** and **21** was indicated.

Anal. Calcd for $C_{22}H_{28}Si_2$: C, 75.8; H, 8.00; mol wt, 348. Found: C, 75.7; 75.7; H, 8.20, 8.30; mol wt, 348.

The nmr spectrum of **19** and **21** (see Table II) showed an increased shielding of the C–Me protons consistent with the presence of the α-substituted phenyl group which because of steric crowding cannot lie in the C═C—Me plane. The mass spectrum of this mixture showed a methylphenylacetylene molecular ion consistent with the proposed structure.[21]

The infrared spectrum of the mixture showed bands at 658 and 930 cm^{-1} which were not present in the spectrum of **17**. Thus, quantitative analysis of the spectrum of **19** and **21** showed that the maximum contamination with **17** could be 1–2%.

5. In the Presence of 2,3-Dimethylbutadiene. A mixture of 6.0 g (33.6 mmol) of **7** and 5.52 g (37.2 mmol) of 2,3-dimethylbutadiene were sealed in an ampoule and heated at 225° for 18 hr. Quantitative glpc analysis using benzene as internal standard indicated that the yield of 1,1,3,4-tetramethyl-1-silacyclopent-3-ene (**26**) was 14.7%. The major silicon-containing products were the $MeO(SiMe_2)_nOMe$ series **8**. A sample of **26** was isolated by a combination of distillation (bp 72° (68 mm)) and preparative glpc and its infrared and nmr spectra were identical in all respects with those of a known sample.[18b]

6. In the Presence of 1,1-Dimethyltetraphenylsilacyclopentadiene (24). A mixture of 2.0 g (10 mmol) of **7** and 0.5 g (10 mmol) of **25**[9a] was heated at 225° for 24 hr. The reaction mixture liquid layer was analyzed by glpc and a normal distribution of the polysilane series **8** was observed. Filtration of the reaction mixture gave 0.42 g (84%) of recovered **24**, mp and mmp 178–180°. No evidence was observed for the formation of the disilacyclohexadiene **2**.

7. In the Presence of Tetramethylethylene. A mixture of 0.2 g (1.2 mmol) of **7** and 0.2 g (2.4 mmol) of tetramethylethylene was heated at 225° for 16 hr. Glpc analysis showed the presence of unreacted tetramethylethylene and the polysilane series **8**. No evidence was obtained for the formation of volatile silacyclopentane or disilacyclohexane structures.

Thermolysis of 27 in the Presence of 2,3-Dimethylbutadiene. A mixture of 0.26 g (0.5 mmol) of **27**,[9a] 0.16 g (2.0 mmol) of 2,3-dimethylbutadiene, and 0.22 g of benzene (glpc internal standard) was heated in an ampoule at 300° for 3 hr. Quantitative glpc analysis showed the formation of the silacyclopentene **26** in 38% yield.

Thermolysis of 1,3-Dimethoxyhexamethyltrisilane (8a) in the Presence of Diphenylacetylene. A mixture of 2.0 g (8.5 mmol) of **8a**[20] and 3.1 g (17.0 mmol) of diphenylacetylene was heated at 275° for 28 hr (little reaction at 225°). The green mixture was dissolved in benzene, cooled, and filtered to give 1.2 g of **2**, mp and mmp 321–323° (30% yield based on the formation of 2 equiv of Me_2Si:).

Thermolysis of *sym*-Dimethyltetramethoxysilane[22] (9) in the Presence of Diphenylacetylene. A mixture of 8.4 g (40 mmol) of **9** and 14.4 g (40 mmol) of diphenylacetylene in a 50-ml flask connected to a spinning-band column was heated at 185–190° for 48 hr. During this time 4.5 g (90%) of methyltrimethoxysilane was obtained. The residue was dissolved in benzene and filtered while hot. The filtrate was cooled thoroughly and filtered to give 5.0 g of **11**, mp 211–214° (50%).

Anal. Calcd for $C_{32}H_{32}O_2Si_2$: C, 76.2; H, 6.30; Si, 11.1; mol wt, 504. Found: C, 75.6; 75.2; H, 6.30, 6.28; Si, 10.0, 11.0; mol wt, 504.

The nmr properties (see Table II) are consistent with a 3:1 *cis-trans* mixture of **11**; however, no isomer assignment was possible.

Thermolysis of Hexamethoxydisilane (13). 1. In the Absence of Added Trapping Agents. The disilane **13**[23] (48.4 g, 0.2 mol) was heated at 200° for 5 hr in a 100-ml flask attached to a spinning-band column. At this time 25 g of tetramethoxysilane had distilled over. The residue was fractionally distilled to give 4.2 g of recovered **13**, bp 107° (25 mm). The distillation residue was crystallized from hot hexane to give 3.5 g (22.8%) of tetrakis(trimethoxysilyl)silane (**14**), mp 199–200° dec. The above yields are based on the following stoichiometry.

$$4(MeO)_6Si_2 \longrightarrow 3(MeO)_4Si + \mathbf{14}$$

Anal. Calcd for $C_{12}H_{36}O_{12}Si_5$: C, 28.2; H, 7.1; Si, 28.1. Found: C, 28.5, 28.7; H, 7.3, 7.2; Si, 27.8, 27.9.

The infrared and mass spectra of **14** agreed well with the proposed structure. Although the mass spectrum did not exhibit a parent ion peak, this is consistent with other methoxy-substituted polysilanes (for example, compounds **9**, **10**, and **13**). The nmr of **14** shows SiOMe at τ 6.48 while that of $(MeO)_6Si_2$ shows an SiOMe singlet at τ 6.49.

2. In the Presence of Diphenylacetylene. A mixture of 10.8 g (0.045 mol) of **13** and 16.0 g (0.09 mol) of diphenylacetylene was heated on a spinning-band apparatus at 200° for 6 hr with continual removal of tetramethoxysilane. Excess acetylene was removed by distillation. The residue was crystallized from hexane to give 0.5 g (16.3%) of **14**, mp 198–200°. Repeated attempts to isolate the 1,4-disilacyclohexadiene **15** from these residues were unsuccessful.

Acknowledgments. The authors are grateful to Mrs. Barbara Taub and S. F. Hayes for technical assistance. In addition, we are indebted to our analytical department for their assistance and cooperation throughout this work.

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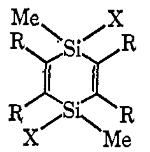
[21] We have studied in detail the mass spectra of numerous disilacyclohexadienes of the type



where X = Me, OR, OH, Cl, H; R = Ph, Me, Et, and H or various combinations of these groups, and will report our results shortly.

[22] J. W. Ryan, *J. Am. Chem. Soc.*, **84**, 4730 (1962).

[23] R. Okawara and T. Tonaka, *Bull. Chem. Soc. Japan*, **27**, 119 (1954).