

ly prepared neutral solution of selenoxide **3** liberated selenophene **1** very slowly into hexane until 40% NaOH was added, when rapid liberation of **1** occurred. Dehydration of the selenoxide hydrate, via the ylide **7**, would appear to be a likely mechanism for this unprecedented reaction.

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### References and Notes

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- Adduct **2** gave satisfactory elemental analyses; it was also characterized by its NMR spectrum (DMSO-*d*<sub>6</sub>):  $\delta$  6.03 (s, 2 H), 7.18–7.63 (m, 4 H). The analogous adduct of TCNE and isothlanaphthene showed  $\delta$  6.20 (s, 2 H), 7.20–7.70 (m, 4 H).
- By comparison, the values (CDCl<sub>3</sub>) for H<sub>1</sub> and H<sub>3</sub> for isothlanaphthene (previously unreported) and isobenzofuran<sup>1a</sup> are  $\delta$  7.63 and 8.00. The same relative positions ( $\delta$  7.70, 7.19, and 7.40) have been observed for the  $\alpha$ -protons of selenophene, thiophene, and furan, respectively: L. M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2d ed, Pergamon Press, New York, 1969, p 209.

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### Evidence for the Dimerization of Dimethylsilylene to Tetramethyldisilene

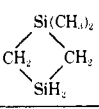
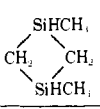
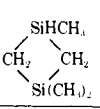
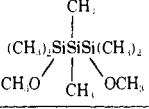
Sir:

In studying the mechanisms of silylene reactions we have uncovered evidence for the gas-phase dimerization of dimethylsilylene to tetramethyldisilene.



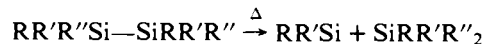
Since these observations point to a new reaction of silylene and to a new route to sila-olefins, they seem worth reporting.

Table I. Product Yields from Pyrolysis of

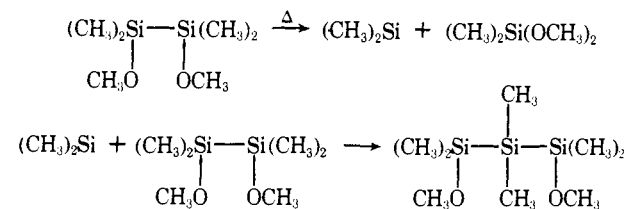
Temp, °C	% dec of disilane	(CH <sub>3</sub> ) <sub>2</sub> SiH	Product yield, % <sup>b</sup>			
						
(A. No added substrate)						
600	40	None detected	12	14	2	14
700	94	4	10	17	8	2
700	92	4	8	13	6	1
(B. Tenfold excess of CH <sub>3</sub> C≡CH <sup>c</sup> )						
620	49	None detected	<1	<1	<1	43
740	100	2	5	9	4	25

<sup>a</sup> All pyrolyses employed a seasoned hot zone consisting of a 10 mm i.d. × 12 cm quartz tube. The temperatures are measured at the outer surface of the tube. Products are condensed at 77 K within 2 cm of the hot zone. The disilane vapor flowed into the hot zone at a rate of ca. 200 mg/h, and a total of 200 or 400 mg was pyrolyzed in each experiment. <sup>b</sup> All yields were determined relative to the (CH<sub>3</sub>)<sub>2</sub>Si(OCH<sub>3</sub>)<sub>2</sub> product. <sup>c</sup> When propyne was present no trisilane product was detected.

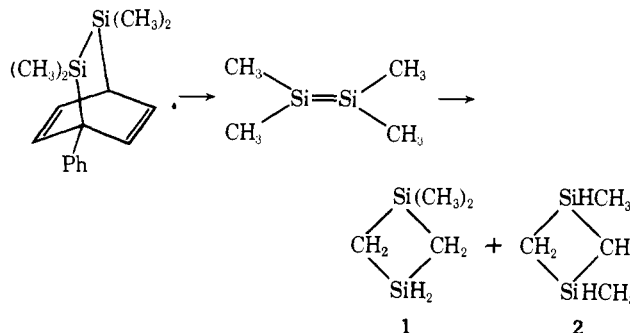
The pyrolysis of disilane and its derivatives is a well-established method for the generation of divalent silicon species, silylenes.<sup>1</sup>



When 1,2-dimethoxy-1,1,2,2-tetramethyldisilane is subjected to gas-phase pyrolysis at low pressure (<100  $\mu$ ) in a flow system at 600 °C, dissociation to dimethylsilylene is indicated by a quantitative yield of dimethoxydimethylsilylene and a 14% yield of the product of attack of dimethylsilylene on its parent disilane,<sup>2</sup> 1,3-dimethoxy-1,1,2,2,3,3-hexamethyltrisilane.



In addition, however, three disilacyclobutanes are obtained in combined yield of 28%, the two formed in greatest yield having previously been characterized as the major stable products resulting from the rearrangement of tetramethyldisilene.<sup>3</sup>



The formation of the same major products from pyrolysis of dimethoxytetramethyldisilane and from tetramethyldisilabicyclooctadienes suggests that tetramethyldisilene may be a common intermediate in the two systems and is formed by dimerization of dimethylsilylene in the former case.

In this communication we wish to summarize briefly our evidence for the formation of disilacyclobutane products, present data consistent with the formation of these products

Table II. Spectroscopic Data for Reaction Products

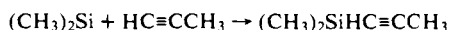
<p>Ir(gas) <math>\text{cm}^{-1}</math> 2965 (m), 2910 (w), 2145 (s), 1358 (w), 1260 (m), 960 (s), 890 (s), 847 (m), 840 (m), 822 (s)</p> <p>Mass spectrum <math>m/e</math> 116 (parent), 115, 101 (base), 73, 59, 43</p> <p>NMR(neat) <math>\delta</math> 4.4 (Si-H, m, 2 H), 0.3 (<math>\text{CH}_3</math>, s, 6 H), 0.2 (<math>\text{CH}_2</math>, m, 4 H)</p>	<p>Ir (gas) <math>\text{cm}^{-1}</math> 2970 (m), 2920 (w), 2140 (s), 1355 (w), 1260 (m), 955 (s), 892 (s), 875 (s), 815 (m), 715 (m)</p> <p>Mass spectrum <math>m/e</math> 116 (parent), 115, 101 (base), 73, 59, 43</p> <p>NMR(neat) <math>\delta</math> 4.7 (Si-H, m, 2 H), 0.3 (<math>\text{CH}_3</math>, d <math>J = 4</math> Hz, ca. 6 H), ca. 0.2 (<math>\text{CH}_2</math>, unresolved m, ca. 4 H)</p>
	<p>(<math>\text{CH}_3</math>)<sub>2</sub>SiHC≡CCH<sub>3</sub> 4</p>
<p>Ir(gas) <math>\text{cm}^{-1}</math> 2965 (m), 2910 (w), 2130 (s), 1360 (w), 1260 (m), 950 (s), 890 (s), 830 (s), 710 (m)</p> <p>Mass spectrum <math>m/e</math> 130 (parent), 129, 115 (base), 73, 59, 43</p> <p>NMR (neat) <math>\delta</math> 4.7 (Si-H, m, 1 H), 0.3 and 0.2 (<math>\text{CH}_3</math> and <math>\text{CH}_2</math>, unresolved multiplets, ca. 13 H)</p>	<p>Ir(gas) <math>\text{cm}^{-1}</math> 2975 (s), 2935 (m), 2200 (s), 2150 (s), 1425 (w), 1375 (w), 1265 (s), 1035 (s), 960 (m), 885 (vs), 845 (s), 780 (s), 770 (s), 745 (s)</p> <p>Mass spectrum <math>m/e</math> 98 (parent), 97, 83 (base), 67, 58, 43</p> <p>NMR(neat) <math>\delta</math> 3.9 (Si-H, m, 1 H), 1.7 (C-<math>\text{CH}_3</math>, d, <math>J = 1.5</math> Hz, 3 H), 0.2 (Si-<math>\text{CH}_3</math>, d, <math>J = 4</math> Hz, 6 H)</p>

<sup>a</sup> The spectral values for 1 agree with those reported in ref 3. <sup>b</sup> The ir values for 2 agree with those reported by W. A. Kriner, *J. Org. Chem.*, 29, 1601 (1964). The close agreement suggests a similar ratio of cis and trans isomers, but no assignment of stereochemistry was given. <sup>c</sup> In addition to the general similarity of the ir spectrum of 3 to those of the dimethyldisilacyclobutanes 1 and 2, the 930 to 970  $\text{cm}^{-1}$  bands are considered characteristic of 1,3-disilacyclobutane derivatives; see R. Damrauer, *Organomet. Chem. Rev. A.*, 8, 110 (1972).

in a second-order reaction of silylenes, and comment on the minor products.

Reaction conditions and product yields are given in Table I both for the pyrolysis of pure dimethoxytetramethyldisilane and for the copyrolysis of the disilane and a tenfold excess of propyne, the latter compound acting as a substrate for dimethylsilylene addition.<sup>4</sup> Spectroscopic data for the disilacyclobutanes and for the propyne adduct of dimethylsilylene are given in Table II. The formation of the minor products trimethylsilane and 1,1,3-trimethyl-1,3-disilacyclobutane (3) is discussed below.

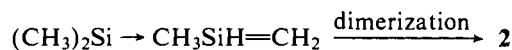
That the disilacyclobutanes are derived from dimethylsilylene intermediates seems assured by the formation of dimethoxydimethylsilane and of dimethoxyhexamethyltrisilane in the neat pyrolysis. When the starting disilane is pyrolyzed in a tenfold excess of propyne (which is stable under the reaction conditions) another product suggestive of silylene intermediates is formed.<sup>5</sup> No dimethylsilylene adduct of the starting disilane is formed in the presence of excess propyne, and the disilacyclobutanes are formed only in reduced yields.



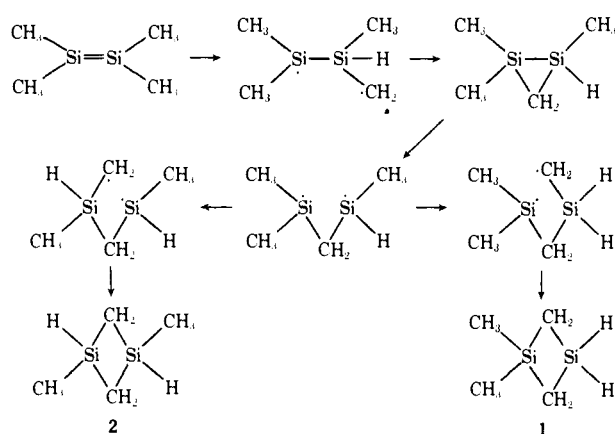
As the pyrolysis temperature is increased from 600 to 700 °C, the ratio of disilacyclobutanes to silylene monoadducts increases both in the presence and absence of propyne. This is consistent with the increasing importance of bimolecular reactions of silylene due to rising silylene concentrations at higher temperatures.

In our experiments the yield of 1,3-dimethyl-1,3-disilacyclobutane (2) always exceeds that of its 1,1-isomer 1. In the work of Roark and Peddle the 1,1-isomer predominates.<sup>3</sup> This difference in product ratios may reflect an internal energy difference, the tetramethyldisilene formed by dimerization of dimethylsilylene being higher in energy than tetramethyldisilene formed by a retrodiene extrusion. Other differences in reaction conditions may also alter the product ratios. In principle, a competing rearrangement of dimeth-

ylsilylene could precede dimerization, and would explain an enhanced yield of the 1,3-dimethyl-1,3-disilacyclobutane.



The presence of small amounts of 1,1,3-trimethyl-1,3-disilacyclobutane (3) deserves comment, since this product was *not* found by Roark and Peddle among the rearrangement products of tetramethyldisilene.<sup>3</sup> These workers proposed a mechanism for the formation of the 1,1- and 1,3-dimethyl-1,3-disilacyclobutanes which includes rearrangements to 1,3- and 1,4-diradicals:



Fragmentation of the 1,4-diradicals could generate silaolefins ( $(\text{CH}_3)_2\text{Si}=\text{CH}_2$ ,  $\text{CH}_3\text{SiH}=\text{CH}_2$ , and  $\text{H}_2\text{Si}=\text{CH}_2$ ) which on reaction with dimethylsilylene, present in excess, would give rise to mono-, di-, and trimethyldisilacyclobutanes via mechanisms similar to that proposed by Roark and Peddle.<sup>3</sup> Since the yields of the minor products trimethyldisilacyclobutane and trimethylsilane both rise with temperature, their formation may be related. Mechanisms for the formation of various methylated 1,3-disilacyclobutanes

from trimethylsilyl radicals have been proposed for the pyrolysis of trimethylsilane<sup>6</sup> and tetramethylsilane.<sup>7</sup> Roark and Peddle did detect a 3% yield of trimethylsilane in their low temperature extrusion reactions, and a similar quantity is found in our experiments at 700 °C.

However, we detect no trimethylsilane at 600 °C, and the yields of dimethyldisilacyclobutanes are much higher at both temperatures than that of the trimethyl compound. Therefore whatever secondary reaction is the source of the small amount of trimethyldisilacyclobutane, it seems certain that the dimethyldisilacyclobutanes, formed in competition with silylene addition reactions, are the result of reactions second order in silylene. We favor the dimerization of silylene followed by rearrangements as the operative reaction mechanism.

While the possibility of silylene dimerization has entered previous mechanistic discussions,<sup>8</sup> the facile dimerization even in the presence of a tenfold excess of propyne found in this work suggests that dimerization may compete successfully with other silylene reactions under a variety of reaction conditions.

**Acknowledgments.** The influence of Professor Maitland Jones is very strong on this work, and we thank him for his insight and encouragement. This work was supported by the United States Energy Research and Development Administration. This is technical report COO-1713-61.

## References and Notes

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- D. N. Roark and G. J. D. Peddle, *J. Am. Chem. Soc.*, **94**, 5837 (1972).
- The formation of monomeric products from addition of a silylene to an acetylene has only recently been observed by Ring and co-workers. See C. H. Haas and M. A. Ring, *Inorg. Chem.*, **14**, 2253 (1975). Normally only dimeric products, 1,4-disila-2,5-cyclohexadienes are obtained from addition of silylenes to acetylenes. See ref 1 and T. J. Barton and J. A. Kilgour, *J. Am. Chem. Soc.*, **96**, 7150 (1974).
- Ring (see ref 4) has obtained  $\text{SiH}_3\text{C}\equiv\text{CH}$  from  $\text{SiH}_2 + \text{HC}\equiv\text{CH}$ . The mechanism of this reaction is under active investigation. We believe that ethynylsilane derivatives result from rearrangement of silacyclopropene initial adducts as suggested by Ring.
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- See the discussion by Barton and Kilgour, ref 4.

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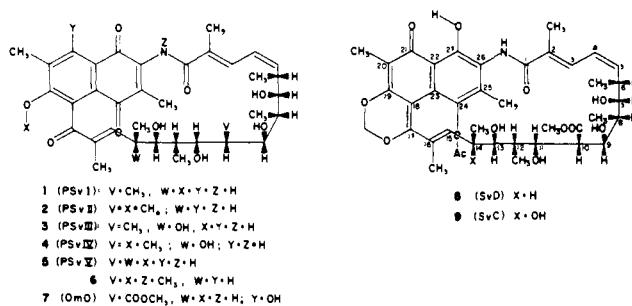
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## Protostreptovaricins I-V<sup>1</sup>

Sir:

Biosynthetic studies of the ansamycins,<sup>2</sup> antibiotics of interest both for their remarkable structures and their biological properties, have recently demonstrated that the rifamycins,<sup>3</sup> the streptovaricins,<sup>4</sup> and geldanamycin<sup>5</sup> arise from propionate (methylmalonate), acetate (malonate), methionine, and a C<sub>7</sub> unit apparently derived from shikimate or a related compound. In our continuing investigation of the accompanying minor components of the streptovaricin complex,<sup>1b,6,7</sup> we describe here the isolation and properties of protostreptovaricins I-V, apparent precursors of streptovaricins containing the complete carbon skeleton of the antibiotics but lacking much of their oxygenation, and assign them structures 1-5, respectively. The protostreptovaricins,

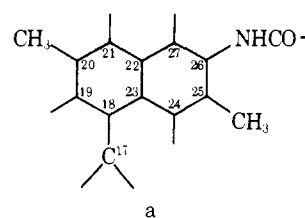
which are active inhibitors of reverse transcriptase, appear to be still earlier precursors of the naphthoquinone ansamycin antibiotics than damavaricin D(DmD, **7**)<sup>1b</sup> or the very recently reported rifamycin W.<sup>8-10</sup>



Protostreptovaricins I-V were isolated in small amounts by repeated chromatography of fractions from the streptovaricin complex.<sup>11</sup> The most abundant, protostreptovaricin I (PSvI), mp 270-271 °C, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +703° (c 0.202, CHCl<sub>3</sub>), has a molecular formula, C<sub>36</sub>H<sub>47</sub>NO<sub>9</sub>,<sup>12</sup> which lacks four carbons and four oxygens of streptovaricin D (SvD, **8**, C<sub>40</sub>H<sub>51</sub>NO<sub>13</sub>).<sup>11</sup> The infrared spectrum of PSvI contains carbonyl absorption at 1665 and 1640 cm<sup>-1</sup> but lacks the enol acetate and carbomethoxyl absorption of SvD. In agreement with this conclusion, the <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of PSvI lacks methoxyl protons (near 3.8 ppm) and one deshielded methyl singlet (acetate, near 2.2 ppm), as well as the methylenedioxy protons (AB quartet near 5.7 ppm) of SvD. However, one more methyl doublet is observed in the <sup>1</sup>H NMR spectrum of PSvI than in that of SvD. Since the carboxyl carbon of SvD is known to be derived from the methyl carbon (C-3) of propionate,<sup>4</sup> the extra methyl can be located at C-10 of PSvI, which is in any event the only available position; this is confirmed in the <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>) discussed below. These changes (-OH for -OAc, -OH HO- for -OCH<sub>2</sub>O-, -CH<sub>3</sub> for -COOCH<sub>3</sub>) account for the four carbons of SvD lacking in PSvI, as well as for three of the four missing oxygens.

The remainder of the ansa bridge protons are found at nearly identical positions for PSvI and SvD:<sup>13</sup> 2-methylidenamide group (8.37 ppm, broad, NH; 7.69 ppm, d, J = 12 Hz, H-3; 6.50, t, J = 12 Hz, H-4; 5.70, t, J = 12 Hz, H-5); a total of five -CHCH<sub>3</sub> methyl doublets at 0.69, 0.76, 0.94, 1.00, and 1.23 ppm; four -CHOH methine protons at 3.47, 3.52, 3.65, and 4.08 ppm; an olefinic doublet at 5.66 ppm, d, J = 10 Hz; four =C-CH<sub>3</sub> singlets at 1.97, 2.02, 2.21, and 2.36 ppm. Confirming these conclusions are the <sup>13</sup>C NMR absorptions (Figure 1) for the aliphatic region, which are generally very close to those for streptovaricin D.<sup>14</sup> Thus, the ansa bridge is like that in SvD except for the substitution of a methyl for a carbomethoxyl group. The structural similarity of the ansa chain of PSvI to that of SvD can be extended to C-16 by the observation of an olefinic doublet at 5.66 ppm (t, J = 10 Hz, H-15) and the olefinic methyl group cited above.

The remainder of the structure (a) of PSvI (C<sub>13</sub>H<sub>8</sub>O<sub>4</sub>)



includes C-17 through C-27 of SvD, with C-26 attached to the amide nitrogen and C-20 and C-25 to methyl groups. The remaining two hydrogens are found at 7.89 (aromatic)