

Table VIII. Nuclear Magnetic Resonance Parameters^a for $\text{PhSO}_2\text{CH}_2=\text{CH}_{\text{II}}\text{CH}_2\text{IIX}$

X	H _I (d) ^b	H _{II} (d of t) ^c	CH ₂ (d) ^d	Aromatic	Other
Cl	6.7	7.0	4.2	7.8	
Br	6.64	7.08	3.98	7.8	
OSO ₂ CH ₃	6.7	7.0	4.88	7.8	3.03 (OSO ₂ CH ₃)
OH ^e	5.3	7.0	4.25	7.8	3.4 (OH)
OCH ₃	6.62	7.0	2.9	7.8	3.3 (OCH ₃)
SO ₂ Ph	6.4	6.77	3.96	7.8	
SCN	6.72	7.08	3.7	7.8	

^a Chemical shifts are reported in δ values measured in parts per million (ppm) relative to TMS. ^b All are doublets, $J_{\text{I,II}} = 15$ Hz. ^c All are doublets of triplets, $J_{\text{I,II}} = 15$ Hz, $J_{\text{II,III}} = 6$ Hz. ^d All are doublets, $J_{\text{II,III}} = 6$ Hz. ^e Measured in DMSO-*d*₆.

Table IX. Microanalyses^a for Compounds Described in the Experimental Section

Compound	Mol formula	Calcd		Found	
		C	H	C	H
6	C ₁₂ H ₁₆ O ₂ S	64.25	7.19	64.14	7.18
3 , X = Br	C ₁₂ H ₁₅ O ₂ BrS	47.52	4.94	47.45	4.94
3 , X = Cl	C ₁₂ H ₁₄ O ₂ ClS	55.70	5.84	55.68	5.89
3 , X = OH	C ₁₂ H ₁₆ O ₃ S	59.97	6.71	59.98	6.64
4 , X = Cl	C ₁₀ H ₁₁ O ₂ ClS	52.06	4.80	51.96	4.89
4 , X = Br	C ₁₀ H ₁₁ O ₂ BrS	43.65	4.03	43.85	4.11
4 , X = OMe	C ₁₁ H ₁₄ O ₃ S	58.38	5.24	58.23	6.30
4a-4b	C ₁₀ H ₁₁ O ₂ ClS	52.06	4.80	51.82	4.79
4 , X = SCN	C ₁₁ H ₁₁ O ₂ NS ₂	52.15	4.38	51.70	4.49
5 , X = OMs	C ₁₀ H ₁₂ O ₃ S ₂	43.46	4.38	43.42	4.29
5 , X = OMe	C ₁₀ H ₁₂ O ₃ S	57.15	4.77	57.20	4.69
5 , X = N ₃	C ₉ H ₉ O ₂ N ₃ S	48.42	4.06	48.50	4.02
5 , X = SO ₂ C ₆ H ₅	C ₁₅ H ₁₄ O ₄ S ₂	55.88	4.38	55.80	4.44
5 , X = SCN	C ₁₀ H ₉ O ₂ NS ₂	50.19	3.80	50.13	3.70
3 , X = OMe	C ₁₃ H ₁₈ O ₃ S	61.39	7.13	61.36	7.04
11	C ₁₂ H ₁₄ O ₂ S	64.83	6.35	64.77	6.47
15 , Y = NC ₃ H ₁₀	C ₁₇ H ₂₃ O ₂ NS ^b	66.94	8.23	66.84	8.20
3 , X = SO ₂ Ph	C ₁₈ H ₂₀ O ₄ S ₂	59.32	5.53	59.50	5.60
15 , X = SO ₂ Ph	C ₁₈ H ₂₀ O ₄ S ₂	59.32	5.53	59.08	5.56
3 , X = SPh	C ₁₃ H ₁₉ O ₂ S ₂	65.02	6.06	64.66	6.08
3 , X = NCS	C ₁₃ H ₁₅ O ₂ NS ₂	55.49	5.37	55.28	5.46
16	C ₈ H ₈ BrN	41.41	4.63	41.23	4.65
18	C ₁₂ H ₁₃ O ₂ NS	61.25	5.57	61.13	5.64

^a By Micro Tech, Skokie, Ill. ^b Calcd: N, 4.67. Found: 4.56.

diphenylsulfonylpropene **5** (X = SO₂C₆H₅): mp 102.5–103°; nmr, Table VIII.

(d) With Potassium Thiocyanate. Reaction of bromide **5** with a tenfold excess of KSCN in acetone at 25° for 30 min gave 1-phenylsulfonyl-3-prop-1-enyl thiocyanate (**5**, X = SCN): mp 103.5–104.5°; nmr, Table VIII. None of the isothiocyanate could be detected.

1-Cyano-3-bromo-3-methyl-1-butene (16). Reaction of 9 g (60 mmol) of 1-bromo-3-methyl-2-butene with 2.4 g (70 mmol) of powdered NaCN in 350 ml of dry DMF for 2.5 hr at 40° gave 4.5 g (79%) of 4-methyl-3-pentenitrile: bp 107–109° (75 mm). Bromine addition followed by dehydrobromination (as in the preparation of bromide **3**) gave as a first fraction 14% of 1-cyano-4-methyl-1,4-pentadiene (**17**): bp 35–38° (1.5 mm); nmr δ 1.87 (m, 3 H), 5.39 (br s, 2 H), 5.39 (d, $J = 16$ Hz, 1 H), 7.1 (d, $J = 16$ Hz, 1 H). The second fraction was 3.9 g (47%) of **16**: bp 38–40° (0.3 mm); ir (μ) 3.25 (w), 3.34 (w), 4.5 (m), 6.12 (w), 6.87 (m), 7.2 (m), 7.28 (m), 9.06 (s), 10.05 (m), 10.33 (m); nmr δ 1.86 (s, 6 H), 5.52 (d, $J = 16$ Hz, 1 H), 6.90 (d, $J = 16$ Hz, 1 H).

Reactions of 16. (a) With Sodium Benzenesulfonate. Reaction of **16** with 2 mol of PhSO₂Na in DMF at 50° for 2 hr gave 1-cyano-3-phenylsulfonyl-3-methyl-1-butene (**18**): mp 108–109°; nmr δ 1.5 (s, 6 H), 5.32 (d, $J = 17$ Hz, 1 H), 6.73 (d, $J = 17$ Hz, 1 H), 7.65 (m, 5 H).

(b) With Lithium Azide. Reaction of **16** with LiN₃ in MeOH at reflux for 45 min gave over 98% of the corresponding tertiary azide: nmr δ 1.38 (s, 6 H), 5.63 (d, $J = 17$ Hz, 1 H), 6.72 (d, $J = 17$ Hz, 1 H). Reduction with H₂/Pd gave an amine: nmr δ 1.2 (s, 6 H), 1.8 (m, 2 H), 2.4 (m, 2 H), 2.78 (s, br, 2 H). The benzamide was an oil: nmr δ 1.4 (s, 6 H), 2.26 (s, 4 H), 6.16 (s, br, 1 H), 7.6 (m, 5 H). Treatment of the amide with 0.2 M NaOMe in MeOH for 2 days at 25° caused the δ 2.26 nmr resonance to disappear.

(c) With Methanol. Methanolysis of **16** at reflux for 14 hr gave 30% of diene **17** and 70% of tertiary methyl ether, 4-methoxy-4-methyl-2-pentenitrile (nmr analysis).

Reactions of 7,8-Disilabicyclo[2.2.2]octa-2,5-dienes. Evidence for the Transient Existence of a Disilene¹

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Abstract: Three 7,8-disilabicyclo[2.2.2]octa-2,5-dienes (**1**, **2**, and **3**) were prepared and found to thermally decompose to give an intermediate containing a silicon-silicon double bond. The intermediate was trapped by dienes and found to rearrange in the absence of a trap. A mass spectral study of **1**, **2**, and **3** supported the postulated pathway of decomposition.

Evidence has recently been found for the existence of highly reactive species containing multiple

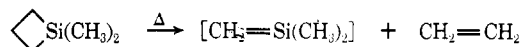
($p-\pi$) bonds to silicon.^{2,3} Gusel'nikov and Flowers² have shown that 1,1-dimethyl-1-silacyclobutane, when

(1) (a) Taken in part from the Ph.D. Thesis of D. N. R., University of Alberta, 1970. (b) For a preliminary account of this work, see G. J. D. Peddle, D. N. Roark, A. M. Good, and S. G. McGeachin, *J. Amer. Chem. Soc.*, **91**, 2807 (1969).

(2) (a) L. E. Gusel'nikov and M. C. Flowers, *Chem. Commun.*, 864 (1967); (b) M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, 419 (1969).

(3) M. Kumada, K. Jamao, M. Ishikawa, and M. Matsuno, *Chem. Commun.*, 614 (1968).

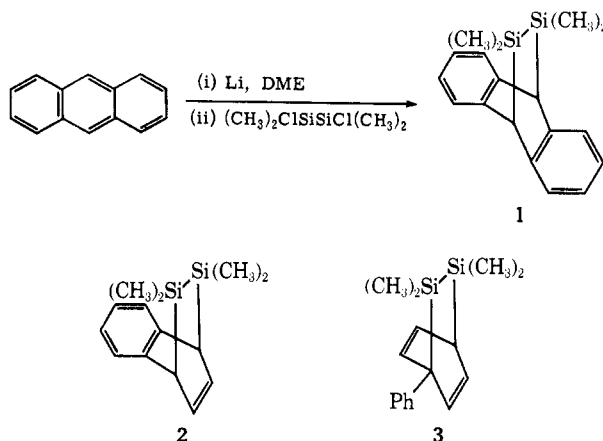
pyrolyzed at low pressures, undergoes a unimolecular decomposition to give ethylene and a reactive intermediate. This intermediate was postulated to contain a silicon-carbon double bond based on the results of several trapping and kinetics experiments.



We felt that it might be possible to generate an intermediate containing an alkyl-substituted silicon-silicon double bond *via* the retrodiene reaction⁴ of a 7,8-disila-bicyclo[2.2.2]octa-2,5-diene, and in this paper we wish to report the results of such a study.

Results and Discussion

The reaction between 1,1,2,2-tetramethyl-1,2-dichlorosilane and 2 equiv of the radical anion of anthracene in 1,2-dimethoxyethane gave a 27% yield of 2:3,5:6-dibenzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (**1**).⁵ Similarly the radical anions of naphthalene and biphenyl gave 2,3-benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (**2**) and 1-phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (**3**) in 42 and 13% yields, respectively.⁵



When heated in sealed tubes **1**, **2**, and **3** were found to thermally decompose at 500, 360, and 260°, respectively. The products obtained were a quantitative yield of the respective aromatic hydrocarbons, a trace of trimethylsilane, and an involatile viscous white oil which was highly soluble in organic solvents. The nmr spectrum of the white oil gave only peaks in the silicon methyl region (τ 9.5–10.5) while the infrared spectrum showed a broad weak silicon-hydride absorption (2100 cm^{-1}). The properties of this material were not analogous with those reported for polydimethylsilanes; the low molecular weight cyclic forms are volatile⁶ whereas the higher molecular weight forms are insoluble in most organic solvents.⁶

Based on evidence to be discussed later, we felt that this white oil was probably a polymer resulting from the polymerization of rearranged tetramethyldisilene.⁷

The relative stabilities of **1**, **2**, and **3** offered some insight into the mechanism of their decomposition.

(4) H. Kwart and K. King, *Chem. Rev.*, **68**, 415 (1968).

(5) Spectral data are given in the Experimental Section.

(6) E. Carberry and R. West, *J. Amer. Chem. Soc.*, **91**, 5440 (1969).

(7) Tetramethyldisilene is the name that we have chosen to give to the structure $(\text{CH}_3)_2\text{Si}=\text{Si}(\text{CH}_3)_2$, since the hydrogenated form, $(\text{CH}_3)_2\text{SiHSiH}(\text{CH}_3)_2$, is generally referred to as tetramethyldisilane.⁸

(8) J. V. Vrenovitch and R. West, *J. Organometal. Chem.*, **3**, 138 (1965).

When a dienophile reacts with an aromatic diene, a decrease in resonance energy results, with the amount of decrease depending on the particular aromatic diene.⁹ The larger the decrease in resonance energy, the greater is the energy barrier to reaction. This has been used to explain why maleic anhydride reacts smoothly with anthracene, only slightly with naphthalene, and not at all with benzene.⁹ Reversing this argument, a biphenyl adduct should undergo the retrodiene reaction more easily than a naphthalene adduct, and a naphthalene adduct should disproportionate more easily than an anthracene adduct. The observed relative thermal stabilities of **1**, **2**, and **3** were therefore consistent with decomposition *via* a retrodiene reaction.

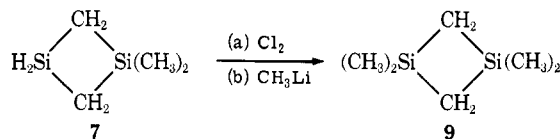
A low-pressure pyrolysis was performed on **2** and on **3**. The technique used was to slowly sublime the compound through an oven at low pressure and catch any products in a liquid nitrogen cold trap. After all of the material had been sublimed through the oven, the trap was allowed to warm and the volatile material was condensed into a second trap containing cyclopentane and held at -196° .

The cyclopentane solutions from the pyrolysis of both **2** and **3** contained, in addition to the respective aromatic hydrocarbons, five products which are shown in Table I along with their per cent yield. Compounds

Table I. Volatile Pyrolysis Products of **2** and **3**

Name	% yield from 2
Trimethylsilane (4)	3
3,3-Dimethyl-1,3-disilabutane (5)	0.5
2-Methyl-2,4-disilapentane (6)	2
1,1-Dimethyl-1,3-disilacyclobutane (7)	30
1,3-Dimethyl-1,3-disilacyclobutane (8)	10

4, **5**, **6**, and **8** were identified by comparison of their glc retention times and mass spectral fragmentation patterns with those of authentic compounds. A small amount of **7** was isolated by preparative glc. When **7** was treated with chlorine followed by methylolithium, 1,1,3,3-tetramethyl-1,3-disilacyclobutane (**9**) was pro-



duced as the only product. All of the spectral data were also consistent with the structure assigned to **7**.⁵

A reasonable, although unproven, pathway for the formation of the two major products, **7** and **8**, is shown in Scheme I.

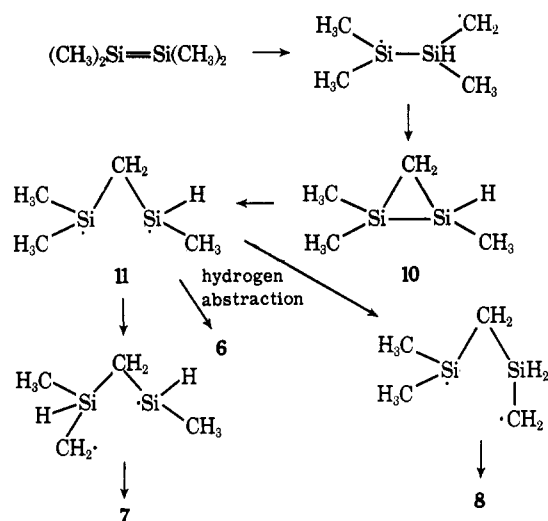
The proposed first step, the rearrangement of tetramethyldisilene to form the disilacyclopropane, **10**, is very similar to the reverse of the 1,1-dimethyl-1-silacyclopropane-dimethylvinylsilane rearrangement previously observed by Skell and Goldstein.¹⁰

The proposed second step in the overall reaction is the rearrangement of **10** to **7** and **8**. In this step the strain in the three-membered ring, **10**, causes the silicon-

(9) G. W. Wheland, "Resonance in Organic Chemistry," Wiley, New York, N. Y., 1955, pp 377–381.

(10) P. S. Skell and E. J. Goldstein, *J. Amer. Chem. Soc.*, **86**, 1442 (1964).

Scheme I

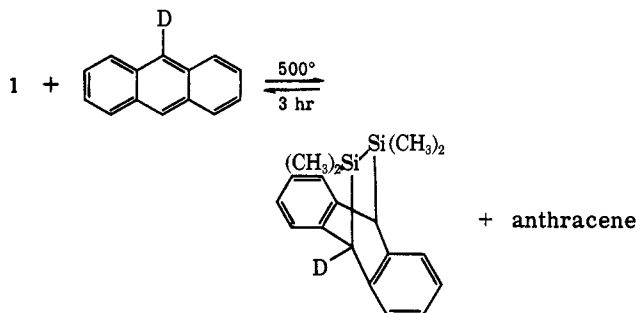


silicon bond to rupture giving the diradical 11. If 11 abstracts two hydrogens the minor product 6 will be formed. Since the secondary radical on 11 should be inductively less stable than the tertiary radical, it would be expected to rearrange faster. This would explain the observation that more 7 is formed than 8.

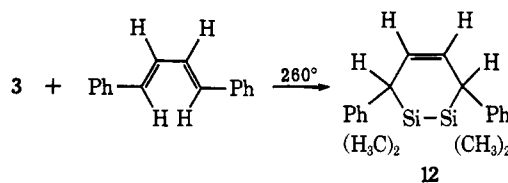
The comparatively low yields of volatile products encountered in the neat pyrolysis of 1, 2, and 3 are not surprising since all of the postulated intermediates should be very prone to polymerization.

In order to obtain more direct evidence for the initial formation of tetramethyldisilene from the pyrolysis of 1, 2, and 3, we felt that it would be best to trap the tetramethyldisilene in a chemical reaction. Since the Diels-Alder reaction is reversible, if tetramethyldisilene is formed *via* a retro-Diels-Alder process, the disilene should be trapped *via* a Diels-Alder reaction. To be a suitable diene two criteria had to be met. First the diene must obviously be stable at the temperatures required for the decomposition of 1, 2, or 3, and second, the product formed after reaction with the diene must also be thermally stable at these same temperatures.

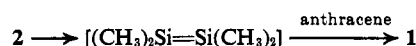
When 1 was pyrolyzed at 500° for 3 hr in the presence of 7 equiv of 9-deuterioanthracene, exchange of the tetramethyldisilene bridge occurred to give a statistical mixture of monodeuterated and undeuterated 1. Both 2 and 3 at their respective decomposition temperatures reacted with anthracene, to give virtually quantitative yields of 1.



Compound 3 was also found to react with naphthalene to give a virtually quantitative yield of 2 and with *trans*,*trans*-1,4-diphenyl-1,3-butadiene to give a 29% yield of a compound tentatively identified as 3,6-diphenyl-4,4,5,5-tetramethyl-4,5-disila-1-cyclohexene (12).



In order to determine whether this was a bimolecular reaction between the adduct and the diene or whether it was a unimolecular decomposition of the adduct to form "free" tetramethyldisilene, followed by the reaction of the tetramethyldisilene with the diene, several experiments were performed in which 1 equiv of 2 was heated to 335° for 15 min in the presence of from 1 to 10 equiv of anthracene. It was found in all cases that a 15% decomposition of 2 had resulted, thus indicating that the decomposition was indeed unimolecular.



The reactions of 1, 2, and 3 with various dienes provided strong evidence for the existence of tetramethyldisilene as a reactive intermediate. In order to obtain further evidence a detailed mass spectral study was undertaken.

In the last decade there has been a great deal of interest in the analogy between electron-impact fragmentation and the fragmentation induced by pyrolysis.¹¹ Numerous examples pointing to the analogy between electron-impact and thermally induced retrodiene reactions have been reported.¹²⁻¹⁵ Daugherty¹⁶ has shown that theoretically one should expect an analogy between electron-impact and thermally induced retrodiene reactions if a significant metastable peak accompanies the electron-impact reaction and if it is a high probability reaction.

The mass spectra of 1, 2, and 3 were quite simple, the major fragment in each case occurring at m/e 116. An exact mass on the m/e 116 peak showed it to have a molecular formula consistent with tetramethyldisilene.¹⁷ All three compounds gave significant metastable peaks for the $(\text{parent})^+ \rightarrow 116^+$ transition. To show that this was a high probability transition, mass spectra were taken at 10, 15, and 20 eV as well as at 70 eV. These results are shown in Tables II-IV.

Table II. Effect of Varying the Ionization Potential of the Mass Spectrum on 1

Ionization potential, eV	Per cent of total ion current			
	p ⁺	Anthracene ⁺	$[(\text{CH}_3)_2\text{Si}=\text{Si}(\text{CH}_3)_2]^+$	Other
10	89.4	0.5	10.1	
15	39.5	4.7	53.5	2.3
20	31.0	4.4	57.5	7.1
70	13.6	4.2	51.2	31.0

(11) A. Maccoll in "Modern Aspects of Mass Spectrometry," R. I. Reed, Ed., Plenum Press, New York, N. Y., 1968, pp 143-168.

(12) S. Meyerson, J. D. McCollum, and P. N. Rylander, *J. Amer. Chem. Soc.*, **83**, 1401 (1961).

(13) H. Audier, M. Getizon, and W. Vetter, *Bull. Soc. Chim. Fr.*, 1971 (1963).

(14) H. Budzikiewicz, J. I. Brouman, and C. Djerassi, *Tetrahedron*, **21**, 1855 (1965).

(15) J. Strating, B. Zwanenburg, A. Wagenaar, and A. C. Udding, *Tetrahedron Lett.*, 125 (1969).

(16) R. C. Daugherty, *J. Amer. Chem. Soc.*, **90**, 5780 (1968).

(17) Found for $\text{C}_4\text{H}_{12}\text{Si}_2$, 116.0478 (calcd, 116.0478).

Table III. Effect of Varying the Ionization Potential on the Mass Spectrum on 2

Ionization potential, eV	Per cent of the total ion current—			
	p ⁺	Naphthalene ⁺	[(CH ₃) ₂ Si=Si(CH ₃) ₂] ⁺	Other
10	38.8	0.8	60.4	
15	21.7	1.4	74.2	2.7
20	17.7	2.8	59.6	19.9
70	8.0	3.6	43.8	44.6

Table IV. Effect of Varying the Ionization Potential on the Mass Spectrum on 3

Ionization potential, eV	Per cent of the total ion current—			
	p ⁺	Biphenyl ⁺	[(CH ₃) ₂ Si=Si(CH ₃) ₂] ⁺	Other
10	23.6		76.4	
15	8.0	3.5	80.5	8.0
20	4.1	3.7	68.1	24.1
70	2.5	2.0	32.3	63.2

Beside showing that this reaction is a high probability transition, these results also indicate that the ease of reaction increases as one goes from 1 to 2 to 3. As was discussed earlier this is consistent with a retrodiene reaction.

We have shown that a high probability, electrocyclic decomposition of 7,8-disilabicyclo[2.2.2]octa-2,5-dienes occurs on electron impact. This is good evidence that the same mode of decomposition occurs thermally, since this analogy has often been observed experimentally and has a sound theoretical basis.¹⁶

Regardless of the exact fate of tetramethyldisilene, it must be initially formed in a singlet state by a concerted thermally initiated retrodiene reaction. Once formed it may be regarded as having a silicon-silicon pπ-pπ double bond unless steric repulsion of the vicinal methyl groups is greater than the π-bond energy. Such intermediates could conceivably be used *in situ* to prepare compounds which would be difficult to prepare by other means. We also hope that the existence of such intermediates will inspire further theoretical work on their nature.

Experimental Section

General. All reactions were carried out under an atmosphere of dry nitrogen unless otherwise specified. Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were freshly distilled from calcium hydride and shaken with Linde 4A molecular sieves before use. All nmr spectra were taken on a Varian Associates A-60 or HA-100 spectrometer. Chemical shifts were measured from external TMS. Infrared spectra were taken on a Perkin-Elmer 421 spectrometer. Mass spectra were taken on a double-focusing GEC/AEI MS-9 spectrometer or on a GEC/AEI MS-12 spectrometer coupled to a gas chromatograph. An ionization potential of 70 eV was used unless otherwise specified.

2,3:5,6-Dibenzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (1). Anthracene (35.6 g, 0.20 mol) was added to 5.9 g (0.24 g-atom) of 28% lithium dispersion in 250 ml of DME and the mixture was stirred for 3 hr at room temperature and then cooled to -78°. Then 18.7 g (0.10 mol) of 1,1,2,2-tetramethyl-1,2-dichlorodisilane¹⁸ was added over a 1.5 hr period. The mixture was poured onto ice-hydrochloric acid. Diethyl ether was added and the organic layer was separated, washed with water, and dried over anhydrous sodium sulfate. After the volatile material had been removed on a rotary evaporator, the residue was added to carbon

tetrachloride and the excess anthracene was filtered off. Cooling gave 8.0 g (27% yield) of 1, which was further purified by recrystallization (ethanol-chloroform) followed by sublimation (155° (0.01 Torr)) to give white crystals: mp 162–164°; ir (CCl₄) 3083, 3025, 3012, 2955, 2920, 2900, 2850, 1478, 1466, 1450, 1402, 1283, 1246, 1240, 1202, 1060, 1029, 935, 895, 879, and 858 cm⁻¹; nmr (CCl₄) τ 3.0 (s, 8), 6.3 (s, 2), and 10.3 (s, 12); mass spectrum *m/e* 294, 178, 116, 103, and 73. Compound 1 can be stored indefinitely at ambient temperature in a stoppered vial in the dark.

Anal. Calcd for C₁₈H₂₂Si₂: C, 73.40; H, 7.53. Found: C, 73.04; H, 7.53.

2,3-Benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (2). Naphthalene (30.0 g, 0.244 mol) was added to 7.0 g (0.357 g-atom) of 28% lithium dispersion in 300 ml of DME and the mixture was stirred for 3 hr at room temperature. After cooling to -78°, 20.0 g (0.108 mol) of 1,1,2,2-tetramethyl-1,2-dichlorodisilane¹⁸ in 100 ml of DME was slowly added. The resulting mixture was poured onto ice-concentrated hydrochloric acid. Diethyl ether was added and the organic layer was separated, washed with water, and dried over anhydrous sodium sulfate. Removal of volatile material (rotary evaporator) left 49.3 g of a yellow oil. This oil was poured into a sublimator and heated to 60–70° (0.1 Torr). In this manner 19.6 g of crystalline material (a mixture of naphthalene and 2,2,3,3,5,5,6,6-octamethyl-1,4-dioxocyclohexasilane by glc) was obtained. On raising the temperature of the sublimator to 80–90°, 11.0 g (42% yield) of 2 was collected, which was further purified by recrystallization (CCl₄) to give white crystals: mp 64–66°; ir (CCl₄) 3055, 3030, 3000, 2945, 2910, 2895, 1462, 1445, 1243, 1238, 1208, 1175, 1128, 1052, 995, 978, and 895 cm⁻¹; nmr (CDCl₃) τ 2.9 (s, 4), 3.9 (d of d, 2, *J* = 5.0, 3.0 Hz), 6.6 (d of d, 2, *J* = 5.0, 3.0 Hz), 9.8 (s, 6) and 10.0 (s, 6); mass spectrum *m/e* 244, 128, 116, 101, 73, 59, 45, and 43.

Anal. Calcd for C₁₄H₂₀Si₂: C, 68.78; H, 8.24. Found: C, 68.97; H, 8.29.

After 2 had been stored for 2 weeks in a stoppered vial in the dark, a mass spectrum showed a large new peak at *m/e* 260. An exact mass measurement on this peak gave 260.1055 (calcd for C₁₄H₂₀Si₂O, 260.1052).

1-Phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (3). A mixture of 25.2 g (0.164 mol) of biphenyl and 1.5 g (0.214 g-atom) of freshly cut and cleaned lithium wire was stirred overnight in 150 ml of anhydrous diethyl ether and 75 ml of THF. Then 15.0 g (0.0805 mol) of 1,1,2,2-tetramethyl-1,2-dichlorodisilane¹⁸ in 75 ml of THF was added at -78°. The reaction mixture was poured onto ice-concentrated hydrochloric acid. The organic layer was separated, washed with water, and dried over anhydrous sodium sulfate. The volatile material was removed on a rotary evaporator leaving a yellow solid, which was placed in a sublimator; 10.6 g of crude biphenyl was sublimed from the mixture at 50–80° (0.1 Torr). The residue was dissolved in carbon tetrachloride and cooled to give white crystals which were washed with cold heptane to obtain 2.73 g (13% yield) of 3 as white crystals: mp 118–121°; ir (CCl₄) 3085, 3055, 3018, 2959, 2925, 2865, 2850, 1792, 1580, 1545, 1479, 1472, 1463, 1425, 1383, 1256, 1240, 1230, 1225, 1206, 1165, 1052, 1015, 945, 908, 903, 879, 868, 835, and 812 cm⁻¹; nmr (CDCl₃) τ 2.5–2.8 (m, 5), 3.7–4.1 (m, 4), 6.8–7.2 (m, 1), 9.7 (s, 6), and 10.0 (s, 6); mass spectrum *m/e* 270, 211, 116, 101, 73, 59, 45, and 43.

Anal. Calcd for C₁₆H₂₂Si₂: C, 71.04; H, 8.20; mol wt, 270.1260. Found: C, 70.72; H, 7.88; mol wt 270.1258.

2,2,4-Trichloro-4-methyl-2,4-disilapentane. After 5.0 g (0.208 g-atom) of magnesium turnings was covered with THF, several drops of dimethyl(chloromethyl)chlorosilane were added. After reaction had begun, 80 g (0.540 mol) of methyltrichlorosilane was added. Then 20 g (0.141 mol) of dimethyl(chloromethyl)chlorosilane in 100 ml of THF was slowly added over 1 hr with vigorous stirring. After addition was complete, the mixture was heated to 70° for 4 hr. After cooling, 100 ml of pentane was added and the resulting precipitate filtered off. Fractional distillation of the filtrate gave 16.0 g (52% yield) of 2,2,4-trichloro-4-methyl-2,4-disilapentane.

This product was a colorless liquid: bp 182–185° (lit.¹⁹ bp 186°); nmr (neat) τ 9.1 (s, 2), 9.2 (s, 3), and 9.5 (s, 6); mass spectrum *m/e* 204.9229 (calcd for C₅H₄Si₂Cl₃, 204.9231), 185, 93, 65, 55, 43, and 41. A parent ion at *m/e* 220 was not observed.

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2-Methyl-2,4-disilapentane (6). 2,2,4-Trichloro-4-methyl-2,4-disilapentane (14.0 g, 0.0637 mol) was slowly added to 3.6 g (0.0973 mol) of lithium aluminum hydride in 100 ml of anhydrous diethyl ether and the reaction mixture was refluxed for 5 hr. After cooling, the reaction mixture was poured onto an ice-concentrated hydrochloric acid mixture. The organic layer was separated, washed with water, and dried over anhydrous sodium sulfate. Fractional distillation gave 3.0 g (40% yield) of **6**, a colorless liquid: bp 86–87° (lit.²⁰ bp 88.5°); ir (gas) 2970, 2915, 2163, 2135, 1052, 962, 885, 841, 800, and 769 cm⁻¹; nmr (CDCl₃) τ 5.9–6.4 (m, 3), 9.8–10.0 (m, 9), and 10.1–10.4 (m, 2); the mass spectrum was identical with that reported in the literature.²¹

Anal. Calcd for C₄H₁₄Si₂: C, 40.60; H, 11.92. Found: C, 40.50; H, 12.00.

3,3-Dimethyl-1,3-disilabutane (5). Trimethyl(chloromethyl)silane (15 g, 0.123 mol) was slowly added to 4.0 g (0.165 g-atom) of magnesium turnings in 100 ml of anhydrous diethyl ether and the mixture was refluxed for 0.5 hr. After cooling, the Grignard solution was slowly added to 100 g (0.595 mol) of tetrachlorosilane in 200 ml of anhydrous diethyl ether. After addition was complete, 100 ml of pentane was added and the mixture was filtered. The pentane, ether, and excess tetrachlorosilane were distilled off. Then the residue was diluted with 50 ml of anhydrous diethyl ether and slowly added to 7.0 g (0.184 mol) of lithium aluminum hydride in 100 ml of anhydrous diethyl ether. This mixture was refluxed overnight and then poured onto an ice-concentrated hydrochloric acid mixture. The organic layer was separated, washed with water, and dried over anhydrous sodium sulfate. Fractional distillation gave 2.6 g (18% yield) of **5**, a colorless liquid: bp 75.5°; ir (gas) 2960, 2900, 2150, 1420, 1256, 1140, 1051, 946, 848, 783, 762, and 758 cm⁻¹; nmr (CCl₄) τ 6.5 (t, 3, *J* = 5.0 Hz), 10.0 (s, 9), and 10.3 (q, 2, *J* = 5.0 Hz); the mass spectrum was identical with that reported in the literature.²¹

9-Deuterioanthracene. A mixture of 5.0 g (0.0194 mol) of 9-bromoanthracene, 1.0 g (0.0417 g-atom) of magnesium turnings, and 100 ml of THF was refluxed for 4 hr. The Grignard solution thus formed was added to 50 ml of deuterium oxide, followed by addition of 100 ml of diethyl ether. The organic layer was separated, washed with water, and dried over anhydrous sodium sulfate. The volatile material was removed on a rotary evaporator and the residue was dissolved in ethanol. Cooling yielded 1.0 g (28% yield) of 9-deuterioanthracene, mp 205–218°, which was further purified by sublimation: mp 217–218° (lit.²² mp 218–219°). A mass spectrum showed it to be 62.6% monodeuterated.

Neat Tube Pyrolysis of 2. In a typical run 520 mg of **2** was sealed in an evacuated Pyrex tube (6 cm × 2 mm) and heated to 350° for 24 hr. The tube was cooled in a liquid nitrogen bath; on opening the tube, the contents were dissolved in toluene. A glc trace indicated that 70% decomposition had occurred. It also showed two products, trimethylsilane (trace) and naphthalene (98%). After removal of the volatile material on a rotary evaporator, the naphthalene and starting material were sublimed off, 80° (0.01 Torr), leaving an involatile white oil. A nmr spectrum of this oil in carbon tetrachloride showed a complex absorption at τ 9.4–10.4. Its infrared spectrum in carbon tetrachloride showed a weak, broad absorption at 2100 cm⁻¹.

Neat Tube Pyrolysis of 1. Complete decomposition of **1** occurred when it was heated to 500° for 12 hr. Trimethylsilane (trace), anthracene (100%), and a white oil (similar to that formed by **2**) were the only products.

Neat Tube Pyrolysis of 3. A 67% decomposition of **3** occurred when it was heated to 235° for 23 hr. Trimethylsilane (trace), biphenyl (100%), and a white oil (similar to that formed by **2**) were the only products.

Low-Pressure Pyrolysis of 2. In a typical run 227.0 mg of **2** was sublimed over a 4-hr period into a quartz tube (32 cm × 15 mm) filled with quartz chips and heated to 490–510° (0.01 Torr). The products were collected in a liquid nitrogen trap 1 cm from the exit port of the furnace. After the sublimation was complete, the liquid nitrogen trap was allowed to warm to room temperature and the material within it which was volatile at 0.01 Torr was distilled into a

flask containing 414.1 mg of cyclopentane cooled in a liquid nitrogen bath. A glc trace of the cyclopentane solution showed six products. Five of these were identified by comparison of glc retention time and mass spectral fragmentation patterns with those of authentic compounds. These products were **4** (3%), **5** (0.5%), **6** (2%), **8** (10%), and naphthalene (7%).²³

By preparative glc, 7.7 mg of the sixth product, **7**, was collected. It is a colorless liquid: ir (gas) 2960, 2905, 2142, 1359, 1260, 963, 958, 888, 844, 837, and 820 cm⁻¹; nmr (CH₂Cl₂) τ 5.6 (quintet, 2, *J* = 4.5 Hz), 9.7 (s, 6), and 9.8 (t, 4, *J* = 4.5 Hz); mass spectrum *m/e* 101, 73, 59, and 43.

When chlorine gas was passed over a cyclopentane solution of **7**, an exothermic reaction occurred with the evolution of gas. Adding methylolithium to this mixture caused a white precipitate to form. A glc trace showed that a product had been formed whose glc retention time and mass spectral fragmentation were identical with those of an authentic sample of 1,1,3,3-tetramethyl-1,3-disilacyclobutane.

Compound **3** was pyrolyzed at 450° in exactly the same manner as **2**. A glc trace showed the same silicon containing products in the same relative amounts as were obtained from **2**.

Pyrolysis of 1 in the Presence of 9-Deuterioanthracene. A mixture of 30 mg (0.103 mmol) of **1** and 200 mg (1.12 mmol) of 9-deuterioanthracene (62.6% monodeuterated) was sealed in an evacuated Pyrex tube (6 cm × 6 mm) and heated to 450–480° for 3 hr. A mass spectrum of the mixture showed that **1** had 14.3% excess *d*₁.

The tube was resealed and heated to 480–510° for 2 hr. Another mass spectrum indicated that **1** had 48.8% excess *d*₁. Complete equilibrium would give 57.3% excess *d*₁. There was no evidence in the mass spectrum of dideuteration.

Pyrolysis of 2 in the Presence of Anthracene. A mixture of 50 mg (0.205 mmol) of **2** and 36.9 mg (0.205 mmol) of anthracene was sealed in an evacuated Pyrex tube and heated to 380° for 1.5 hr. After the tube was opened, a nmr spectrum was taken. The spectrum showed only peaks due to a 1:1 mixture of naphthalene and **1**. This mixture was placed in a sublimator and the naphthalene was sublimed off at 60° (0.1 Torr). The temperature was then raised to 160° and 53.3 mg (90% yield) of a solid, mp 161–164°, was collected. This solid gave a nmr spectrum and mass spectrum which were identical with those of an authentic sample of **1**.

Four tubes each containing 50 mg (0.205 mmol) of **2** as well as 36.5 (0.205 mmol), 73.0 (0.410 mmol), 182.5 (1.025 mmol), and 365.0 mg (2.05 mmol) respectively of anthracene were heated to 335° for 15 min. Nmr spectra of each of these samples showed that the ratio of **2** to **1** was 6.5:1 or 15% decomposition of **2**.

Pyrolysis of 3 in the Presence of Anthracene. A mixture of 100 mg (0.370 mmol) of **3** and 200 mg (1.12 mmol) of anthracene was sealed in an evacuated Pyrex tube and heated to 260–270° for 24 hr. The nmr and mass spectra of the resulting mixture were identical with those of a mixture of anthracene, biphenyl, and **1**. No silicon containing products other than **1** were present.

Pyrolysis of 3 in the Presence of Naphthalene. A mixture of 100 mg (0.370 mmol) of **3** and 200 mg (1.56 mmol) of naphthalene was sealed in an evacuated Pyrex tube and heated to 260–270° for 24 hr. A glc trace showed two product peaks which were identified as biphenyl (97%) and **2** (96%) by comparison of their glc retention times and mass spectral fragmentation patterns with those of authentic samples.

Pyrolysis of 3 in the Presence of 1,4-Diphenyl-1,3-butadiene. A mixture of 440 mg (1.63 mmol) of **3** and 400 mg (1.94 mmol) of *trans,trans*-1,4-diphenyl-1,3-butadiene was sealed in an evacuated Pyrex tube and heated to 260–270° for 24 hr. The tube was then opened and its contents dissolved in carbon tetrachloride. Cooling yielded 150 mg (29% yield) of **12** as white crystals: mp 154.5–156.0°; nmr (CDCl₃) τ 2.5–3.0 (m, 10), 4.0 (d, 2, *J* = 3.0 Hz), 6.9 (d, 2, *J* = 3.0 Hz), 9.9 (s, 6), and 10.1 (s, 6); mass spectrum *m/e* 322, 218, 149, 116, 101, 91, 73, and 59.

Anal. Calcd for C₂₀H₁₆Si₂: C, 74.46; H, 8.12; mol wt, 322.1573. Found: C, 74.49; H, 8.04; mol wt, 322.1570.

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(23) The naphthalene was not quantitatively distilled into the cyclopentane, as crystals of it were found throughout the vacuum line.

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