

5.10 (d, $J = 10$ Hz, 1 H, terminal =CH), 5.19 (d, $J = 16$ Hz, 1 H, terminal =CH), 5.45 (q, 1 H, =CHCH₂), 6.05 (t, 1 H, CH₂=CH-CH=), 6.66 (dt, $J = 15, 9$ Hz, 1 H, CH₂=CH); NMR (C₆D₆) δ 1.0-1.8 (m, 18 H), 1.97 (eight line m, 1 H, CHCH₂OH), 2.23 (m, 1 H, =CCH), 2.27 (m, 1 H, C(3a)H), 2.37 (m, 1 H, =CCH), 3.00 (broad s, 1 H, C(1)H), 3.34 (dt, $J = 11, 5$ Hz, 1 H, C(9a)H), 3.68 (dt, $J = 10, 4$ Hz, 1 H, CHOH), 4.00 (td, $J = 10, 3$ Hz, 1 H, CHOH), 5.07 (d, $J = 10$ Hz, 1 H, terminal =CH), 5.17 (d, $J = 16$ Hz, 1 H, terminal =CH), 5.39 (q, $J = 7$ Hz, 1 H, =CHCH₂), 6.10 (t, $J = 9$ Hz, 1 H, CH₂=CHCH=), 6.68 (dt, $J = 15, 9$ Hz, 1 H, CH₂=CH); exact mass calcd for C₁₉H₃₁NO m/e 289.2405, found m/e 289.2414.

Acknowledgment. We thank Richard Weisenberger and Dr. Charles Cottrell for their assistance in obtaining mass and 300-MHz ¹H NMR spectra, respectively, at The Ohio State University Chemical Instrument Center. Financial support from The National Institutes of Health (GM-27647) is gratefully acknowledged. We also thank the NIH for a grant (GM-27431) to Ohio State University in support of the acquisition of a Bruker WM 200-MHz

NMR spectrometer used during the course of this research. We thank Yeun-Min Tsai for performing the free radical chemistry presented herein.

Registry No. (±)-1, 75685-48-2; (±)-2, 84275-40-1; (±)-5, 78341-47-6; (±)-6, 78341-48-7; (±)-7, 78341-49-8; (±)-8, 78308-01-7; (±)-9, 78308-02-8; (±)-10, 78308-03-9; (±)-11 (isomer 1), 84236-36-2; (±)-11 (isomer 2), 84236-39-5; (±)-13, 78308-05-1; (±)-14, 78308-06-2; (±)-16, 78308-08-4; (±)-17 (isomer 1), 84236-37-3; (±)-17 (isomer 2), 84236-38-4; (±)-18, 80664-54-6; (±)-19, 78308-09-5; (±)-20, 78308-10-8; (±)-21, 78308-11-9; (±)-22, 78392-00-4; (±)-23, 78308-12-0; (±)-24, 78341-51-2; (±)-25, 78328-74-2; (±)-26, 78392-01-5; (±)-27, 75685-52-8; (±)-28, 78392-02-6; (±)-29, 84175-95-1; (±)-30, 84175-96-2; (±)-31, 84236-40-8; (±)-32, 84175-97-3; (±)-33, 84175-98-4; (±)-34, 84236-41-9; (±)-35, 84175-99-5; (±)-36, 84176-00-1; (±)-37, 84176-01-2; (±)-38, 84176-02-3; (±)-39, 84176-03-4; (±)-40, 84236-42-0; (±)-41, 84236-43-1; 2-cyclohexen-1-one, 930-68-7; 1,3-butadiene, 106-99-0; succinimide, 123-56-8; ethyl bromoacetate, 105-36-2; *tert*-butylchlorodiphenylsilane, 58479-61-1; pinacol (*E*)-1-(trimethylsilyl)-1-propene-3-boronate, 79309-68-5; 1-(trimethylsilyl)-3-*tert*-butyldimethylsilyl-1-propyne, 78978-51-5.

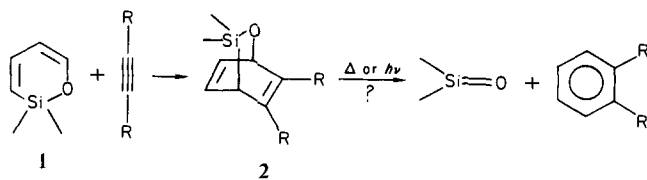
Direct Thermal and Photochemical Generation of Silanones¹

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Abstract: 2-Silapyrans (1,2-oxasilins) are synthesized by the pyrolysis of 1-disilanyl-4-methoxy-1,3-butadienes via initial 1,5-silyl migration to afford an intermediate 1-sila-1,3-butadiene. Diels-Alder reaction of the silapyrans and perfluoro-2-butyne does not lead to isolable adducts but rather leads to apparent extrusion of silanone (R₂Si=O), which is trapped by a variety of reagents. Reaction of the silapyrans and maleic anhydride provides stable adducts that extrude silanones upon either thermolysis or photolysis. No evidence could be found for rearrangement of a silylsilanone to a siloxysilylene.

Silanones,² compounds containing a silicon-oxygen double bond, have been suggested as transient intermediates in a variety of reactions since 1952 when Andrianov and Sokolov proposed their involvement in the thermal redistribution of polydimethylsiloxanes.³ However, the study of these intriguing ketone analogues has been hampered by the lack of a convenient precursor. From the onset the ultimate goal of this project was the synthesis of a convenient thermal and/or photochemical silanone precursor from which the generation of silanone would not be accompanied by the production of products reactive to silanones. Thus, we selected the 7-oxa-8-silabicyclo[2.2.2]octadiene (**2**) ring system as our target. This



choice was predicated by the knowledge that silenes⁴ and disilenes⁵ had been successfully generated by thermally induced retrograde Diels-Alder reactions of the 7-sila- and 7,8-disilabicyclo[2.2.2]octadienes. The obvious route to **2** would be a Diels-Alder reaction between a 1,2-oxasilin (**1**) and an acetylene. However, no good synthetic route to the 1,2-oxasilin ring existed.

(1) A preliminary account of a portion of this work has appeared: Barton, T. J.; Wulff, W. D. *J. Am. Chem. Soc.* **1979**, *101*, 2735.

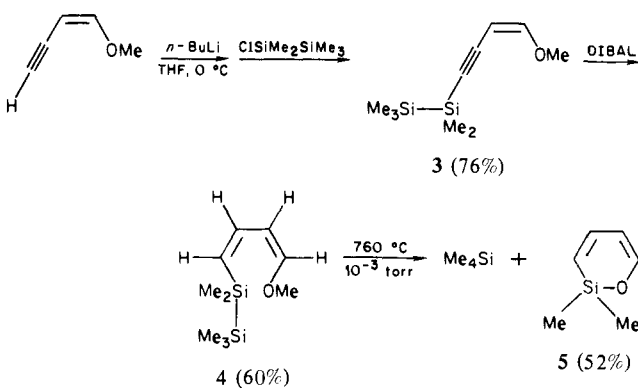
(2) For a general review of π -bonded silicon see: Gusev'nikov, L. E.; Nаметкин, N. S. *Chem. Rev.* **1979**, *79*, 529.

(3) Andrianov, K. A.; Sokolov, N. N. *Dokl. Akad. Nauk SSSR* **1952**, *82*, 909.

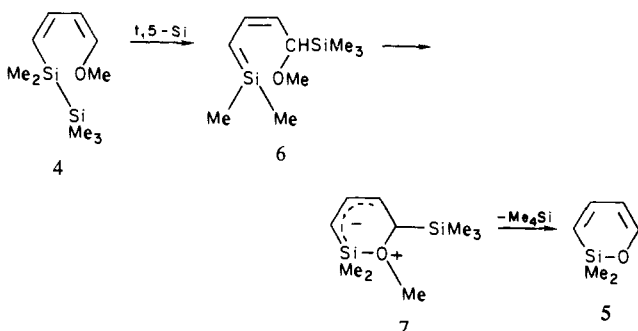
(4) Barton, T. J.; Kline, E. A. *J. Organomet. Chem.* **1972**, *42*, C21.

(5) Roark, D. N.; Peddle, G. J. D. *J. Am. Chem. Soc.* **1972**, *94*, 5837.

Scheme I



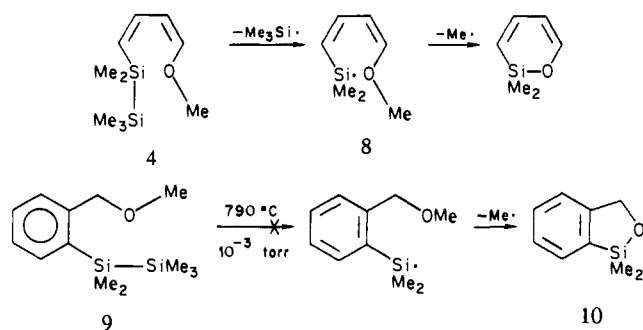
Scheme II



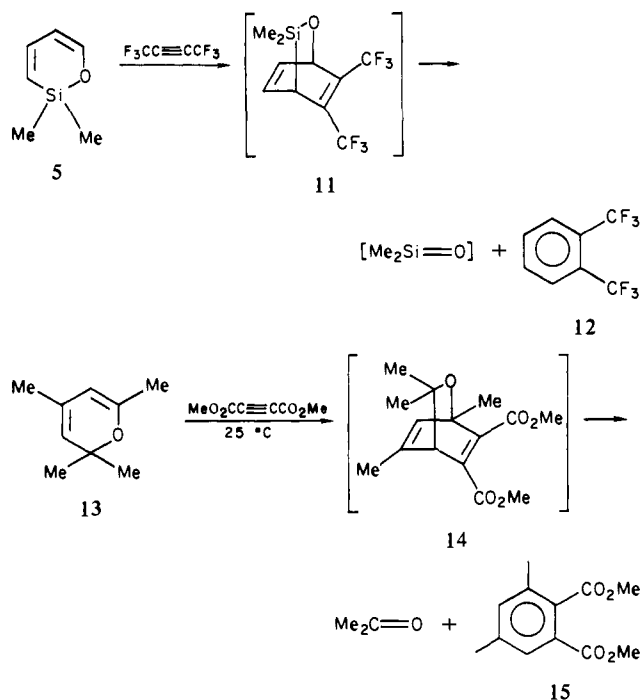
Results and Discussion

This research had as its origin the serendipitous discovery that flash vacuum pyrolysis (FVP) of (*Z,Z*)-1-(pentamethyl-

Scheme III



Scheme IV

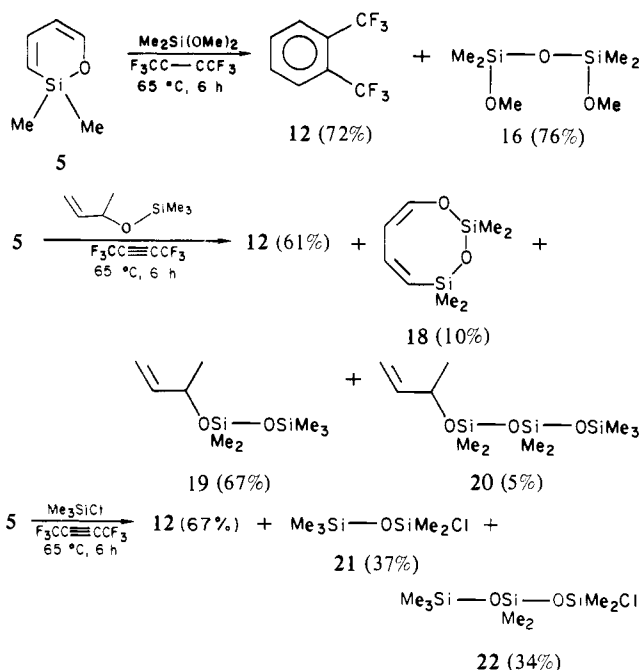


silanyl)-4-methoxy-1,3-butadiene (**4**) (synthesized as shown in Scheme I) at 760 °C (10^{-3} torr) afforded 2,2-dimethyl-1-oxa-2-silacyclohexa-3,5-diene (**5**) in 52% yield.⁶

The formation of **5** is easily rationalized by initial 1,5-sigmatropic migration of trimethylsilyl⁷ to generate 1-sila-1,3-pentadiene **6**, followed by silicon-oxygen bond formation to produce zwitterion **7** and elimination of tetramethylsilane (Scheme II). However, an alternative sequence involving initial homolytic cleavage of the Si-Si bond in **4**, followed by intramolecular homolytic displacement of methyl by attack on the ether oxygen by silyl radical **8**, had to be considered (Scheme III). The pyrolysis of a model system, disilane **9**, was investigated to determine the likelihood of this radical route. If Si-Si homolysis and radical displacement of $\cdot\text{CH}_3$ were occurring for **4**, one would expect **9** to afford the cyclic siloxane **10**. However, FVP of **9** at 620 °C (10^{-3} torr) afforded no decomposition, and even at 790 °C undecomposed **9** comprised >90% of the pyrolysate. GC/MS analysis of the minor components of this pyrolysate revealed no evidence for any isomer of **10**. Thus, it seems reasonably certain that the conversion of **4** to oxasilin **5** does not take place by a radical pathway.

To our surprise, while perfluoro-2-butyne reacts completely with oxasilin **5** in ~1 day at room temperature (6 h at 60 °C), *o*-bis(trifluoromethyl)benzene (**12**) is formed at the same rate (as

Scheme V



observed by NMR). We have never observed the presumed initial adduct **11**, as it apparently undergoes decomposition even at room temperature through extrusion of the silanone bridge (Scheme IV). As the analogous extrusions of silenes⁴ and disilenes⁵ require elevated temperatures, it was not obvious that the extreme thermal lability of **11** was consistent with a retro Diels-Alder reaction. However, we find that the reaction of tetramethylpyran (**13**) and dimethyl acetylenedicarboxylate proceeds smoothly at room temperature to afford only acetone and phthalate **15** (Scheme IV). Thus, the spontaneous decomposition of **11** is in keeping with the behavior of its carbon analogue **14**.

Evidence that dimethylsilanone is formed in the reaction of **5** and perfluoro-2-butyne was obtained by chemical trapping (Scheme V). With the exception of insertion into the strained Si-C bond of silacyclopropanes,⁸ the only proposed reaction of silanones (of which we were aware) prior to this work was the oft-postulated insertion into Si-O bonds.⁹ Indeed, when the cycloaddition reaction of **5** and perfluoro-2-butyne was conducted in the presence of excess dimethyldimethoxysilane, in addition to a 72% yield of **12**, a 76% yield of *sym*-tetramethyldimethoxydisiloxane (**16**), the expected product from insertion of dimethylsilanone into an Si-O bond of the trap was obtained. Likewise, when the Diels-Alder reaction was run with excess 3-butenyl trimethylsilyl ether (**17**), three products were obtained that apparently arose from Si-O insertion by silanone. Cyclic disiloxane **18** formally arises from silanone insertion into starting material **5** while disiloxane **19** is the expected trapping product from **17**. The formation of trisiloxane **20** can be accounted for by the capture of a second molecule of silanone by **19**. The combined yield of **18**, **19**, and **20** is a remarkable 82% based on the yield of **12** and hence the maximum amount of dimethylsilanone formed. What we thought to be¹⁰ the first example of silanone insertion into a Si-Cl bond was obtained when dimethylsilanone was generated in the presence of a large excess

(8) Seyferth, D.; Lim, T. F. O.; Duncan, D. P. *J. Am. Chem. Soc.* **1978**, *100*, 1626.

(9) See, for example: Okinoshima, H.; Weber, W. P. *J. Organomet. Chem.* **1978**, *149*, 279. Goure, W. F.; Barton, T. J. *Ibid.* **1980**, *199*, 33. Barton, T. J.; Hoekman, S. K.; Burns, S. A. *Organometallics* **1982**, *1*, 721 and references therein as well as ref 2.

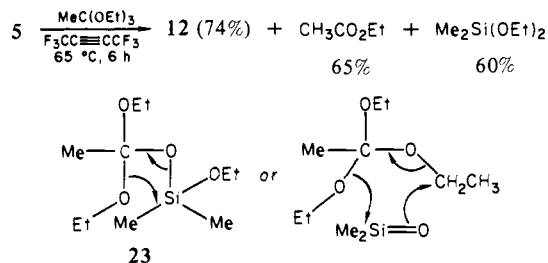
(10) After our preliminary report of this reaction (ref 1) Prof. I. M. T. Davidson kindly informed us that they had anticipated us by several years. Unfortunately we had overlooked this report [Davidson, I. M. T.; Thompson, J. F. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 2260], which states that cothermolysis of Me_2SiCl and D_4 affords **21**.

(6) For other examples of 1,2-oxasilin synthesis see: Childs, M. E.; Weber, W. P. *J. Org. Chem.* **1976**, *41*, 1799. Chernyshev, E. A.; Komalenkova, N. G.; Bashkirova, S. A. *Zh. Obshch. Khim.* **1971**, *41*, 1175.

(7) Barton, T. J.; Wulff, W. D.; Arnold, E.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 2733.

of trimethylchlorosilane to yield both the mono and bis adducts **21** and **22** in a combined yield of 71% (based on **12**).

Insertion of a silanone into a carbon-oxygen bond has not been reported. When **5** was reacted with perfluoro-2-butyne in the presence of excess triethyl orthoacetate, two products, ethyl acetate (65%) and dimethyldiethoxysilane (60%), were obtained in addition to **12** (74%). These products can be rationalized by in-



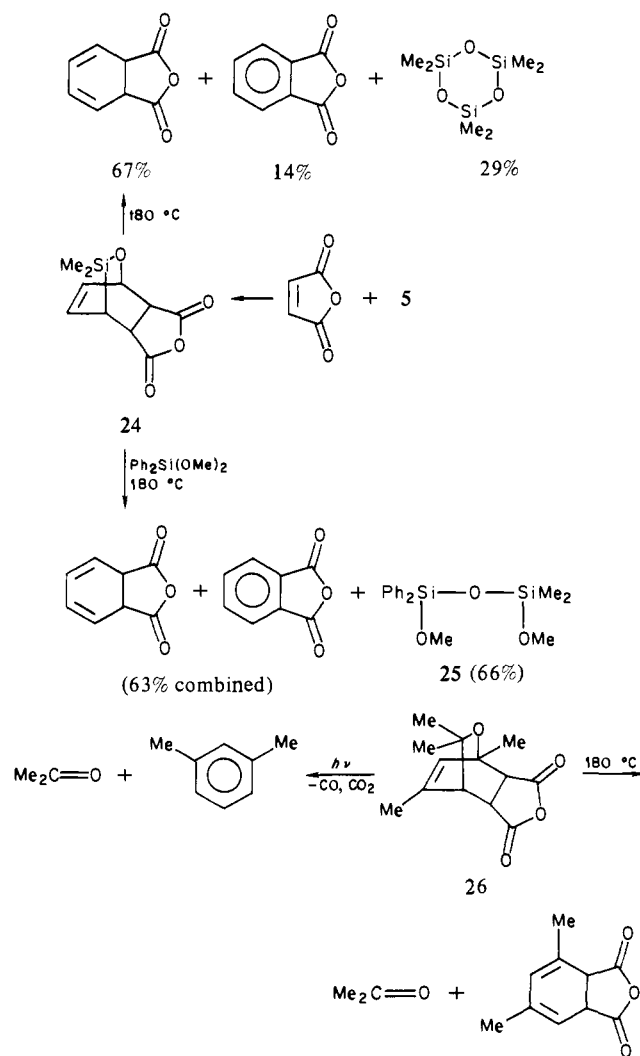
sertion of silanone into a C-O bond to form orthoester **23**, followed by β elimination of the diethoxysilane. However, it is possible to envision a single concerted (6e) reaction of dimethylsilanone and triethyl orthoacetate to afford the same products. Thus, the results do not demand C-O insertion.

In addition to the above, reactions of **5** and perfluoro-2-butyne were carried out in the presence of each of the following potential silanone traps: diethyl ether, ethylene oxide, triethylsilane, tetramethylethylene oxide, 1,1,3,3-tetramethyl-1,3-disilacyclobutane, and *trans*-cinnamyl methyl ether. In each case GC/MS analysis of the reaction mixture revealed no evidence for products that could be construed as having resulted from reaction of the trapping reagent and dimethylsilanone. This was true for the attempted reaction with tetramethylethylene whether or not the reaction was performed in a glass or Teflon vessel.

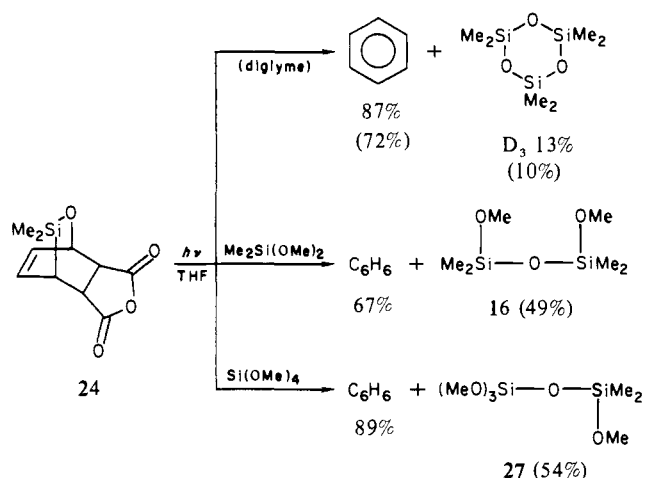
It would appear that the reaction of **5** and the acetylene provides dimethylsilanone, but both the utility and the mechanistic interpretation of this reaction are hampered by our inability to isolate or observe the intermediate adduct **11**. Thus, although it would appear unlikely, it is possible that the above apparent reactions of dimethylsilanone are actually reactions of **11**, which acts as a "silanone-transfer agent" in bimolecular processes with the various traps. However, the reaction of **5** and maleic anhydride did afford the Diels-Alder adduct **24** (80%) as a stable, crystalline solid. Heating a solution of **24** in *o*-dichlorobenzene produced a mixture of 1,2-dihydrophthalic anhydride (67%), phthalic anhydride (14%), and a mixture of permethylcyclosiloxanes, mainly hexamethylcyclotrisiloxane, in 29% yield (Scheme VI). As the formation of these cyclosiloxanes has often been used as evidence for the intermediacy of dimethylsilanone (which then undergoes cyclic oligomerization), this result is clearly consistent with extrusion of the silanone bridge from **24**. Indeed, when **24** is heated in dimethoxydiphenylsilane, the expected product of dimethylsilanone insertion, 1,1-diphenyl-1,2-dimethoxydisiloxane **25**, was obtained in 66% yield. Additional supportive evidence¹¹ for silanone generation from **24** is found in the fact that the analogous carbon system **26** undergoes the same type of decomposition to extrude acetone when heated at the same temperature.

Ultraviolet irradiation of ethereal solutions of **24** through quartz produced clean decomposition to benzene and cyclosiloxanes with observable gas evolution (Scheme VII). Again it was determined that the analogous carbon system **26** underwent similar photochemical decomposition to *m*-xylene and acetone. Thus, by analogy, irradiation of **24** provides the first example of direct photochemical silanone generation. Further evidence for silanone formation in the photolysis of **24** was obtained by performing the decomposition in THF solution containing either dimethyldimethoxysilane or tetramethoxysilane to produce the expected

Scheme VI



Scheme VII



products of silanone, **16** and **27**, respectively, in ca. 50% yields.

The influence of added traps on the rate of photochemical decomposition of **24** was examined by following the formation of benzene in reactions containing different concentrations of trap. Figure 1 shows a typical result for a reaction mixture containing a 7-fold excess of $\text{Me}_2\text{Si}(\text{OMe})_2$ and for the reaction containing no added trap. As can be seen in Figure 1, no change in the rate of benzene formation is effected by the addition of trap. Similar results were obtained by using $(\text{MeO})_4\text{Si}$ as the trap in concentrations ranging from zero to a 16-fold excess.

(11) Attempts to determine the kinetics of the thermal decomposition of **24** and the possible influence of siloxane traps on the rate of trapping were unsuccessful due to experimental difficulties in accurately following the reactions by NMR, GC, or HPLC. However, to the small extent that the results could be trusted, it appeared that at least two mechanisms for trapping were in competition.

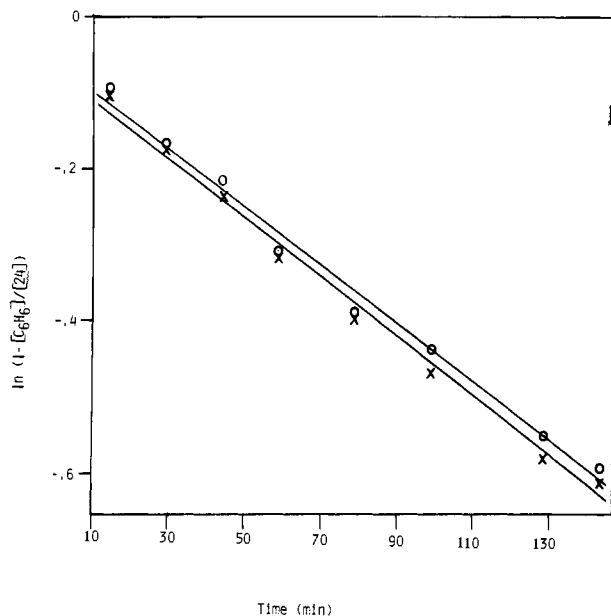
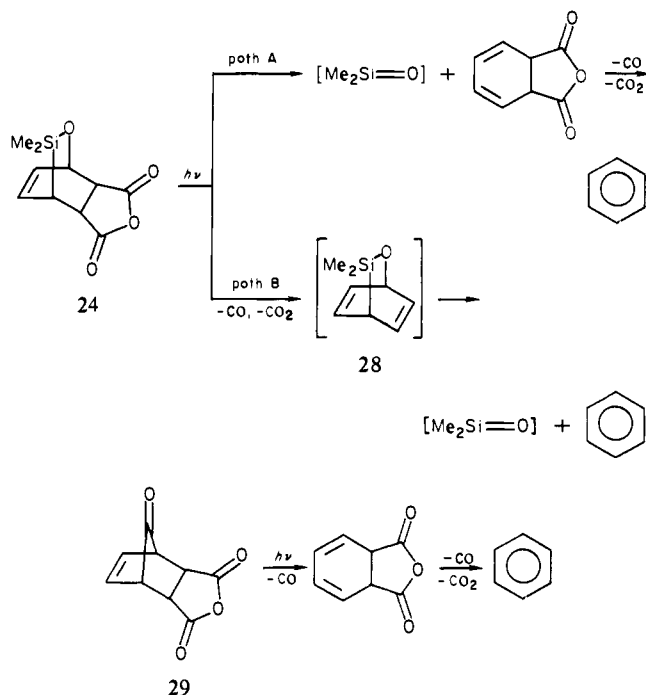


Figure 1. Photochemical decomposition of **24** in THF with (X) a 7-fold excess of $\text{Me}_2\text{Si}(\text{OMe})_2$ and without (O) added trap.

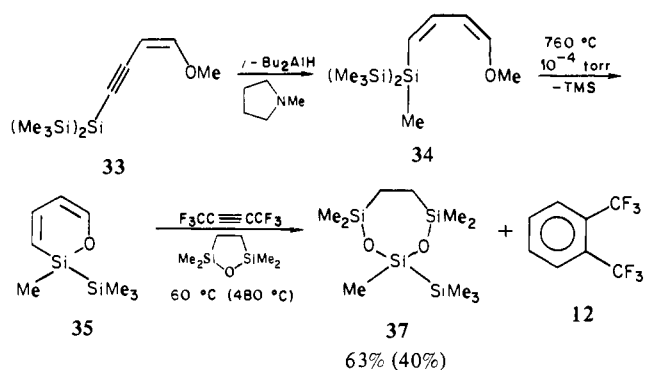
Scheme VIII



The fact that the photochemical decomposition of **24** is independent of added traps is consistent with two different initial pathways (Scheme VIII). Path A initially extrudes silanone to form 1,2-dihydrophthalic anhydride. This anhydride was not observed, nor was observation expected as it was independently demonstrated to rapidly decompose to benzene under these reaction conditions. Path A is also consistent with the reported initial photoextrusion of CO^{12} from **29**. Path B involves initial loss of CO and CO_2 followed by aromatization by silanone extrusion. We favor path B because preliminary results from the laboratory of Professor O. L. Chapman (UCLA) reveal that in the low-temperature photolysis of matrix-isolated **24** the infrared spectrum shows formation of CO and CO_2 but not benzene. Thus, the possibility of traps reacting with intermediate bicyclo[2.2.2]octadiene **28** cannot be discounted. The final word on this subject

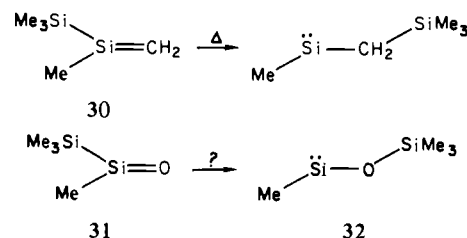
(12) Fuchs, B.; Scharf, G. *J. Org. Chem.* **1981**, *46*, 5395.

Scheme IX



will not come until direct observation of the silanone is achieved.

Recently¹³ we have discovered that silenes will thermally rearrange to silylenes if the silene is substituted on silicon by trimethylsilyl as for **30**. Thus, we thought it not unlikely that if



silylsilanone **31** could be generated under appropriate conditions it would undergo 1,2-silyl migration from silicon to oxygen to form siloxysilylene **32**. A major driving force in this rearrangement would be the formation of an additional strong Si-O σ bond.

In order to probe the possibility of the silanone-silylene rearrangement 1-methyl-1-(trimethylsilyl)sila- α -pyran (**35**) was synthesized by flash vacuum pyrolysis of 4-methoxy-1-(heptamethyl-2-trisilyl)-1,3-butadiene (**34**) in 46% yield (GC) (Scheme IX). Reaction of **35** and perfluoro-2-butyne at 60 °C in the presence of excess triethylsilane did not produce any adducts as would be expected from insertion of **32** into the Si-H bond of the trap. In contrast, when cyclic disiloxane **36** was added to the reaction mixture a 63% yield of cyclic trisiloxane **37**¹⁴ was obtained. Thus, if indeed silanone **30** is formed under these conditions; it does not rearrange. Indeed, when a mixture of **35** and **36** was copolymerized at 480 °C in a vertical flow with perfluoro-2-butyne as the carrier gas, silanone adduct **37** was still formed in 40% yield.

Reaction of silapyran **35** with maleic anhydride afforded the Diels-Alder adduct **38** in 33% yield after recrystallization as a mixture of trans and cis isomers. Thermolysis of **38** in dimethyldimethoxysilane at 150 °C for 8 h produced three major products: 1,2-dihydrophthalic anhydride (53%), phthalic anhydride (16%), and disiloxane **39** (39%). Likewise, photochemical decomposition of **38** in $\text{Me}_2\text{Si}(\text{OMe})_2$ afforded disiloxane **39** in 29% yield. Thus, there is no evidence that silanone **31** undergoes rearrangement to silylene **32**.

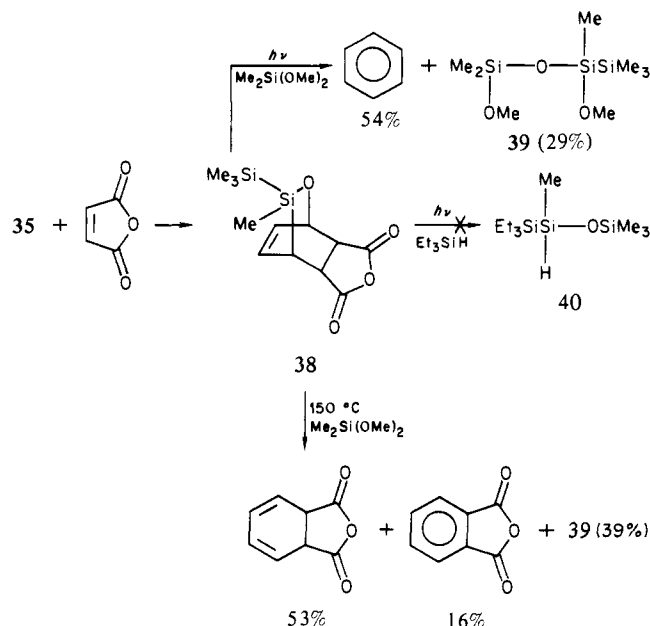
Experimental Section

General Information. Routine proton NMR spectra were recorded on a Varian EM-360, A-60, or JOEL FX90Q spectrophotometers. All chemical shifts are reported as parts per million (δ scale) from Me_4Si . GC/MS spectra were obtained by using a Finnigan Model 4000 mass spectrometer. Exact masses were recorded on a AEI-MS-902. IR spectra were recorded on a Beckman IR 4250 spectrophotometer and UV spectra were obtained by using a Perkin-Elmer 320 spectrophotometer.

Gas chromatographic analyses and separations were performed on a Varian model 3700 or model 920 instrument. GC yields were calculated by using internal standards after determination of the appropriate response factors.

(13) Barton, T. J.; Burns, S. A.; Burns, G. T. *Organometallics* **1982**, *1*, 210.

(14) Okinoshima, H.; Weber, W. P. *J. Organomet. Chem.* **1978**, *155*, 165.



Photochemical reactions were performed by using a 450-W Hanovia high-pressure mercury-arc lamp with a water-cooled quartz jacket. Unless otherwise noted all irradiations were performed in quartz NMR tubes.

All solvents were commercially supplied and distilled from CaH_2 or LiAlH_4 prior to use. Diphenyldimethoxysilane, dimethyldimethoxysilane, tetramethoxysilane, and octamethylcyclotetrasiloxane were obtained from Petrarch Systems, Inc. and were distilled from CaH_2 prior to use. 1,1,4,4-Tetramethyl-1,4-disila-5-oxacyclopentane was obtained from Silar Laboratories and was also distilled from CaH_2 prior to use.

Synthesis of *cis*-1-(Pentamethyldisilanyl)-4-methoxybut-1-en-3-ene (3). *cis*-4-Methoxybut-1-en-3-ene, commercially available from Aldrich Chemical Co. in the form of a 50% aqueous methanol solution, was purified by extraction of the methanol solution with water and ether, drying of the ether layer with sodium sulfate, and then distillation (bp 122–125 °C). A solution of 49.3 g (0.601 mol) in 1.5 L of THF was cooled to 0 °C. To this solution was added 0.601 mol of *n*-butyllithium in hexane over a period of 20 min. This was followed by rapid addition (10 min) of 100.0 g (0.601 mol) of pentamethylchlorosilane. The organic solution was stirred for 1 h, quenched with saturated ammonium chloride, washed with water and saturated sodium chloride, and dried with sodium sulfate. After removal of solvent, distillation gave 97.0 g (76%) of 3: bp 85–87 °C (4 mm); NMR (CCl_4) δ 0.07 (s, 9 H), 0.18 (s, 6 H), 3.81 (s, 3 H), 4.46 (d, 1 H, $J = 7$ Hz), 6.23 (d, 1 H, $J = 7$ Hz); IR (neat) 2970, 2905, 2105, 1635, 1390, 1275, 1250, 1115, 955, 835, 800, 765, 730, 695, 665, and 620 cm^{-1} ; mass spectrum (70 eV), m/e (% relative intensity) 212 (9), 211 (3), 198 (11), 197 (74), 171 (70), 169 (10), 167 (59), 143 (12), 141 (50), 139 (52), 109 (31), 89 (53), 83 (11), 73 (100), 59 (22), calcd for $\text{C}_{10}\text{H}_{19}\text{OSi}_2$ m/e 211.09745, measured m/e 211.097689.

Synthesis of *cis,cis*-1-(Pentamethyldisilanyl)-4-methoxy-1,3-butadiene (4). (A) **Borane Reduction.** The *cis* reduction of 3 was carried out with disiamylborane according to the general method for the *cis* reduction of conjugated acetylenes that has been reported by Zweifel and Polston.¹⁵ Disiamylborane (0.260 mol) was prepared by adding 0.260 mol of $\text{BH}_3 \cdot \text{THF}$ complex to a solution of 36.4 g (0.52 mol) of 2-methyl-2-butene in 125 mL of THF at 0 °C, followed by stirring for 2 h at 0 °C. The solution of disiamylborane was added to a solution of 50 g (0.236 mol) of 3 in 250 mL of THF at 0 °C, and the resultant solution was stirred for 3 h at 0 °C. After addition of 63 mL of glacial acetic acid, the reaction mixture was heated at 55 °C for 5 h. The solution was cooled to room temperature and 220 mL of 20% aqueous sodium hydroxide and 65 mL of 30% H_2O_2 were added slowly and concurrently. After addition, stirring was continued for 30 min and then the aqueous layer was drained off and washed with hexane. The combined organic phase was washed twice with saturated sodium chloride and dried with magnesium sulfate. After removal of solvent, distillation gave 18.7 g of slightly impure 4 (37%, bp 80–89 °C (3 mm)). An analytically pure sample was obtained by preparative GC on a 12 \times 0.25 in. 20% SE-30 on Chromosorb W column at 100 °C for the purpose of obtaining the following spectra: NMR (CCl_4) δ 0.03 (s, 9 H), 0.15 (s, 6 H), 3.63 (s,

3 H), 5.05 (d of d of d, H_C , $J_{BC} = 12$ Hz, $J_{CD} = 6.5$ Hz, $J_{AC} = 1.0$ Hz), 5.32 (d of t, H_A , $J_{AB} = 14$ Hz, $J_{AD} = 1.0$ Hz), 5.84 (d of t, H_D , $J_{BD} = 0.5$ Hz), 7.01 (d of d of d, H_B); mass spectrum (70 eV), m/e (% relative intensity) 199 (11), 111 (54), 89 (21), 73 (100), calcd for $\text{C}_9\text{H}_{19}\text{OSi}_2$ m/e 199.0975, measured m/e 199.0971. Attempted *cis* reduction of the triple bond with hydrogen and Lindlar's catalyst afforded only mixtures of randomly reduced 3.

(B) **DIBAL Reduction.** Alternatively, 3 was reduced to 4 by the procedure of Eisch.¹⁶ *N*-Methylpyrrolidine (15.0 g, 0.18 mol) was added to 180 mL of diisobutylaluminum hydride (1 M in heptane). After stirring at 25 °C for 10 min, 3 (31.8 g, 0.15 mol) was added and stirring was continued at 60 °C for 14 h. The solution was cooled to 25 °C and slowly poured into 200 mL of a H_2O /ice slurry. The organic layer was separated, dried over Na_2SO_4 , and distilled (80–85 °C (3 mm)) to afford 19.3 g of 4 (60%).

Pyrolysis of *cis,cis*-1-(Pentamethyldisilanyl)-4-methoxy-1,3-butadiene (4). Compound 4 (6.30 g) was pyrolyzed by evaporating (100 °C, 10^{-3} torr) through a horizontal quartz tube that was packed with quartz chips and was heated to 760 °C. The pyrolysate was collected in a liquid nitrogen trap and represented an 84% mass recovery. The two major products of the pyrolysis were identified. One of these was identified as tetramethylsilane (30% GC yield) by comparison of its GC retention time and its GC mass spectrum with those of an authentic sample. Distillation of the pyrolysate yields a fraction (80–95 °C, 3.14 g) that is about 60% by weight the major product. The major product was purified for spectral analysis and for all chemical reactions by preparative GC on a 12 ft \times 0.25 in. 15% SE-30 Chromosorb W column at 80 °C. The major product was assigned the structure of 2,2-dimethyl-1-oxa-2-silacyclohexa-3,5-diene (5) (52% GC yield) on the basis of its spectra: NMR (CCl_4) δ 0.29 (s, 6 H), 5.07 (apparent t of d, 1 H, $J = 6$ Hz, and 1 Hz), 5.54 (apparent d of t, 1 H, $J = 14$ Hz, 1 Hz, and 1 Hz), 6.54 (overlapped C_6 H with C_4 H), 6.71 (d of d of d, 1 H, $J = 14$ Hz, 6 Hz, and 1 Hz); mass spectrum (70 eV), m/e (% relative intensity) 126 (20), 111 (100), 8 (14), calcd for $\text{C}_6\text{H}_{10}\text{OSi}$ m/e 126.0501, measured m/e 126.0498; IR (neat) 3065, 3015, 2975, 1620, 1535, 1360, 1270, 1090, 1025, 940, 900, 855, 810, 785, 740, and 705 cm^{-1} . If the pyrolysis of 4 is carried out by dropping through a vertical quartz tube with a nitrogen sweep, the yield of 5 decreases, and the number of minor products increases dramatically.

Synthesis and Thermolysis of Disilane 9. To a stirred solution of *o*-bromobenzyl methyl ether¹⁷ (4.4 g, 0.022 mol) in 150 mL Et_2O at 0 °C was added 8.8 mL of 2.5 M *n*-butyllithium in hexane. After 1 h, 4.0 g (0.024 mol) of chloropentamethyldisilane was added and stirring was continued overnight. The mixture was filtered and concentrated by rotary evaporation. Disilane 9 was obtained pure by preparative GC (10 ft, 15% SE-30 on Chromosorb W): NMR (CCl_4) δ 0.01 (s, 9 H), 0.31 (s, 6 H), 3.28 (s, 3 H), 4.32 (s, 2 H), 7.18 (m, 4 H); mass spectrum m/e (% relative intensity) 237 (0.9), 179 (40), 149 (100), 73 (38); calcd for $\text{C}_{12}\text{H}_{21}\text{OSi}_2$ ($\text{M}^+ - \text{CH}_3$) m/e 237.11310, measured m/e 237.11303. Pyrolysis of 9 was conducted by slowly dropping 0.196 g through a vertical quartz tube, packed with quartz chips, swept with N_2 at 30 mL/min, and heated at 790 °C. The pyrolysate (0.165 g) was analyzed by GC/MS and was composed of >90% 9 with no Me_2Si or isomers of 10 detectable.

Reaction of Oxasilin 5 with Perfluoro-2-butyne. A CCl_4 solution of 0.10 g of 5 and a large excess of perfluoro-2-butyne (~ 0.4 mL) was degassed and sealed in a NMR tube. After 20 min at room temperature, no change had occurred. After 10 h at room temperature, the presence of the very characteristic absorption for 1,2-bis(trifluoromethyl)benzene was observed at δ 7.60. No absorptions were observed that could be attributed to the Diels–Alder adduct of 5 and perfluoro-2-butyne. According to GC retention times, if D_3 or D_4 are formed it could only be in small amounts. When the reaction solution was heated at 55 °C for 5 h, all of the oxasilin was consumed. It was found that bis(trimethylsilyl)acetylene did not react with 5 when heated at 65 °C for 7 h.

Reaction of Oxasilin 5 with Perfluoro-2-butyne in the Presence of Dimethyldimethoxysilane. A solution of 0.108 g (0.857 mmol) of 5 and a large excess (~ 0.4 mL) of perfluoro-2-butyne in 1.0 mL of dimethyldimethoxysilane was degassed and sealed in a tube under vacuum. The tube was heated at 65 °C for 6 h. The tube was cooled, opened, and then allowed to warm to remove the excess acetylene. All of 5 had reacted as determined by GC/MS. The two major products were isolated by preparative GC on a 12 ft \times 0.25 in. 15% SE-30 column on Chromosorb W at 82 °C. The more volatile compound was identified as 1,2-bis(trifluoromethyl)benzene (12) (72% GC yield) on the basis of its spectra: NMR (CCl_4) δ 7.86 (m); mass spectrum (70 eV), m/e (% relative intensity) 214 (73), 195 (69), 164 (28), 163 (11), 145 (100), 125

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(19), 114 (9), 95 (18), 75 (23), 69 (26), 50 (11). These spectra match those of an authentic sample. The other major product was identified as *sym*-tetramethyldimethoxydisiloxane (**16**) (76% GC yield) on the basis of its spectra: NMR (CCl₄) δ 0.08 (s, 6 H), 3.74 (s, 3 H); mass spectrum (70 eV), *m/e* (% relative intensity) 180 (12), 179 (81), 149 (100), 133 (16), 119 (28), 82 (13), 75 (10), 59 (21), 43 (13). These spectra match those of an authentic sample of **16**. The yield of **16** is based on the amount of **12** formed. No cyclosiloxanes were observed by GC/MS.

Reaction of Oxasilin 5 with Perfluoro-2-butyne in the Presence of Trimethylsilyl 3-Butenyl Ether (17). A solution of 0.147 g (1.17 mmol) of **5** and a large excess (~0.3 mL) of perfluoro-2-butyne in 1.0 mL of trimethylsilyl 3-butenyl ether was degassed and sealed under vacuum in a tube that was heated at 64 °C for 6.5 h. The tube was cooled and opened, and the excess butyne was allowed to escape. 1,2-Bis(trifluoromethyl)benzene (**12**) (61% GC yield) was identified by comparison of its GC mass spectrum with that of an authentic sample. The other two major products were isolated by preparative GC on a 12 ft 0.25 in. 15% SE-30 on Chromosorb W column at 100 °C. The more volatile of these was identified as (3-butenyloxy)pentamethyldisiloxane (**19**) (67% GC yield) on the basis of its spectra: NMR (CCl₄) δ 0.04 (s, 6 H), 0.15 (s, 9 H), 1.26 (d, 3 H, *J* = 3 Hz), 4.46 (m, 1 H), 5.19 (m, 2 H), 5.98 (m, 1 H); mass spectrum (70 eV), *m/e* (% relative intensity) 218 (10), 203 (24), 149 (100), 147 (41), 73 (10), 55 (44), calcd for C₉H₂₂O₂Si₂ *m/e* 218.1158, measured 218.1158; IR (neat) 3080, 2960, 1640, 1255, 1045, 960, 920, 860, 840, 810, 790, 750, and 680 cm⁻¹. The other major product is tentatively assigned the structure of 2,2,4,4-tetramethyl-1,3-dioxo-2,4-disilacycloocta-5,7-diene (**18**) (10% GC yield) on the basis of its spectra: NMR (CCl₄) δ 0.46 (s, 12 H), 5.61 (d of d, 1 H, *J* = 7 Hz, *J* = 4 Hz, collapses to a doublet, *J* = 7 Hz, upon *h*_ν at δ 6.84), 6.00 (d, 1 H, *J* = 15 Hz), 6.53 (d, 1 H, *J* = 7 Hz, collapses to singlet upon *h*_ν at δ 5.61), 6.84 (d of d, 1 H, *J* = 15 Hz, *J* = 4 Hz, collapses to a doublet, *J* = 15 Hz upon *h*_ν at δ 5.61); mass spectrum (70 eV) *m/e* (% relative intensity) 200 (11), 186 (12), 185 (71), 159 (27), 135 (14), 134 (16), 133 (100), 119 (11), 85 (11), 73 (12). A minor product was tentatively identified as 1-(3-butenyloxy)heptamethyltrisiloxane (**20**) (5.4% GC yield) on the basis of its mass spectrum: *m/e* (% relative intensity) 292 (0.1), 277 (1.6), 233 (32), 221 (40), 206 (49), 191 (11), 103 (14), 73 (23), 55 (100). The yields of **18**, **19**, and **20** are based upon the amount of **12** formed. The yield of **20** takes into account the fact that 2 mole of dimethylsilanone are incorporated. The yields of **18** and **20** were calculated assuming response factors identical with that of **19**.

Reaction of Oxasilin 5 with Perfluoro-2-butyne in the Presence of Triethyl Orthoacetate. A solution of 0.120 g of **5** and a large excess of perfluoro-2-butyne (~0.5 mL) in 1.0 mL of triethyl orthoacetate was degassed and sealed under vacuum in a tube that was heated at 62 °C for 7 h. The tube was cooled and opened and the excess butyne allowed to escape. 1,2-Bis(trifluoromethyl)benzene (**12**) (74% GC yield) was identified by comparison of its GC mass spectrum with that of an authentic sample. Along with **12**, the major products of this reaction were determined to be ethyl acetate (65% GC yield) and dimethyldiethoxy-silane (60% GC yield). These compounds were identified by isolation via preparative GC on a 12 ft \times 0.25 in. 20% SE-30 on Chromosorb W column at 80 °C and comparison of their NMR and mass spectra with those of authentic samples. The yields are based on the amount of **12** formed.

Reaction of Oxasilin 5 with Perfluoro-2-butyne in the Presence of Trimethylchlorosilane. A solution of 0.0934 g of **5** and a large excess of perfluoro-2-butyne (~0.5 mL) in 1.0 mL of Me₃SiCl that had been purged with argon was degassed and sealed under vacuum in a tube that was heated for 8 h at 65 °C. The tube was cooled and opened and the excess butyne allowed to escape. The solution was decanted from a light green precipitate and was found to contain three reaction products. 1,2-Bis(trifluoromethyl)benzene (**12**) (36% GC yield) was identified by comparison of its GC mass spectrum with that of an authentic sample. The major product was identified as pentamethylchlorosiloxane (**21**) (37% GC yield) on the basis of its spectra: NMR (CCl₄) δ 0.15 (s, 9 H), 0.42 (s, 6 H); mass spectrum, *m/e* (% relative intensity) 169 (43), 167 (100), 147 (10), 76 (13), 73 (14). The third major product of this reaction was identified as 1-chloroheptamethyltrisiloxane (**22**) (34% GC yield) on the basis of its spectra: NMR δ 0.10 (s, 15 H), 0.42 (s, 6 H); mass spectrum, *m/e* (% relative intensity) 243 (29), 241 (68), 221 (4), 133 (11), 113 (11), 73 (100). The yields of **21** and **22** are based on the amount of **12** formed. The yield of **22** was calculated assuming the response factor of **21** and taking into account that 2 mol of dimethylsilanone are incorporated.

Diels-Alder Reaction of Pyran 13 and Dimethyl Acetylenedicarboxylate. To 0.25 g (0.0018 mol) of freshly prepared 2,2,4,6-tetramethyl pyran (**13**) was added 0.25 g (0.0017 mol) of dimethyl acetylenedicarboxylate in CCl₄. The progress of the reaction was monitored by ¹H NMR. After several hours at 25 °C acetone and dimethyl 3,5-

dimethylphthalate (**15**) were observed in considerable, but undetermined, amounts, along with previously observed products from decomposition of **13**. Compound **15** was identified by comparison of its NMR and mass spectra to those previously reported.¹⁸

Reaction of Oxasilin 5 and Maleic Anhydride. To a benzene solution containing 2.1 g (0.017 mol) of **5** was added 1.5 g (0.015 mol) of freshly sublimed maleic anhydride. The solution was stirred at 60 °C for 20 h. Adduct **24** was isolated and purified by repeated recrystallization from benzene/pentane: 2.7 g (80%); mp 124–125 °C; NMR (DCCl₃) δ 6.40 (m, 2 H), 4.90 (m, 1 H), 3.67 (d of d, 1 H, *J*_{AB} = 9 Hz) 3.18 (d of d, 1 H), 2.63 (m, 1 H), 0.19 (s, 3 H), 0.01 (s, 3 H); UV (THF) λ_{\max} 222 nm (1787); IR (KBr) 2980, 1880, 1790 cm⁻¹; mass spectrum, *m/e* (% relative intensity) 209 (0.4), 152 (61), 137 (88), 78 (90), 75 (100); calcd for C₉H₉O₄Si (M⁺ - 15) *m/e* 209.02701, measured *m/e* 209.02770.

Reaction of Maleic Anhydride and 2,2,4,6-Tetramethylpyran (13). To a THF solution of freshly prepared **13**¹⁹ (0.77 g, 0.0056 mol) was added 0.51 g (0.0052 mol) of maleic anhydride. After stirring for 10 h at room temperature, the reaction mixture was percolated through a Florisil column with hexane/ether eluent. Adduct **26** was purified by recrystallization from ether: 0.43 g (35%); mp 91–92 °C; NMR (DCCl₃) δ 1.00 (s, 3 H), 1.21 (s, 3 H), 1.59 (s, 3 H), 1.81 (d, 3 H, *J* = 1 Hz), 2.80 (d of d, 1 H, *J* = 2 and 4 Hz), 3.10 (d, 1 H, *J* = 9 Hz), 3.65 (d of d, 1 H, *J* = 9 and 4 Hz), 5.76 (m, 1 H); UV (THF) λ_{\max} 223 nm (487); IR (KBr) 2900, 1850, 1780 cm⁻¹; mass spectrum, *m/e* (% relative intensity) 236 (0.3), 138 (30), 123 (100); calcd for C₁₃H₁₆O₄ *m/e* 236.10490, measured *m/e* 236.10505. Thermolysis of **26** was conducted by freeze-thaw degassing a solution of ca. 50 mg of **26** in 3 mL of *o*-dichlorobenzene, sealing the tube under vacuum, and heating at 180 °C for 2 h. All of **26** was decomposed. Acetone was identified by NMR and GC/MS comparison with an authentic sample, while 3,5-dimethyl-1,2-dihydrophthalic anhydride was tentatively identified by its GC/MS [*m/e* (% relative intensity) 178 (M⁺, 20), 150 (M⁺ - CO, 4), 106 (M⁺ - CO + CO₂), 67, 91 (100)].

Thermolysis of 24 with and without Dimethoxydiphenylsilane. A degassed, evacuated tube containing ca. 50 mg of **24** in 2–3 mL of *o*-dichlorobenzene was heated at 180 °C for 2 h. GC analysis revealed three major products: 1,2-dihydrophthalic anhydride (67%),²⁰ phthalic anhydride (14%), and hexamethylcyclotrisiloxane (29%), which were identified by spectral comparison with literature data. When the same thermolysis was conducted with dimethoxydiphenylsilane as the solvent the two anhydrides were obtained in a combined yield of 63% along with a 66% yield of 1,1-dimethyl-1,2-dimethoxy-1,1-diphenyldisiloxane (**25**): NMR (DCCl₃) δ 0.20 (s, 6 H), 3.42 (s, 3 H), 3.59 (s, 3 H), 7.20 (m, 10 H); IR (neat) 3060, 2955, 1590, 1260, 1110 cm⁻¹; mass spectrum, *m/e* (% relative intensity) 303 (M⁺ - CH₃, 16), 241 (M⁺ - Ph, 61), 91 (100); calcd for C₁₅H₁₉Si₂O₃ *m/e* 303.08728, measured *m/e* 303.08692. Gas chromatography of **24** (12 ft, 15% SE-30 on Chromosorb W, 160 °C) allowed isolation of pure 1,2-dihydrophthalic anhydride.

Photolyses of Anhydrides 24 and 26. The general procedure for the photolyses was to place ca. 30 mg of **24** (or **26**) in a quartz NMR tube containing the desired solvent and including an excess of a silanone trapping reagent. After degassing with an argon stream, the tube was septum sealed and subjected to irradiation for 2 h by positioning the tube adjacent to the quartz water jacket surrounding a Hanovia 450-W mercury arc lamp. The progress of the reaction was monitored by NMR. Photolysis of adduct **26** in octamethylcyclotetrasiloxane solution rapidly produced acetone and *m*-xylene, which were identified by NMR and GC/MS comparison with authentic samples. With no added trap, photolysis of **24** in THF (or diglyme) resulted in complete disappearance of **24** and formation of benzene in 87% (72%) yield and hexamethylcyclotrisiloxane, D₃, in 13% (10%) yield. GC/MS analysis revealed small amounts of the higher cyclosiloxanes: D₄ and D₅. Irradiation of **24** in THF with excess dimethyldimethoxy-silane produced benzene (67%) and disiloxane **16** (49%). With tetramethoxy-silane in THF, benzene was formed in 89% along with a 54% yield of 1,1-dimethyltetramethoxydisiloxane (**27**): NMR (DCCl₃) δ 0.01 (s, 6 H), 3.40 (s, 12 H); IR (neat) 2950, 1265, 1080 cm⁻¹; mass spectrum, *m/e* (% relative intensity) 226 (0.02), 211 (99), 181 (100), 151 (89); calcd for C₅H₁₅O₅Si₂ (M⁺ - CH₃) *m/e* 211.04581, measured *m/e* 211.04614.

Photochemical Reactive Rate Analysis. In a typical reaction, equal volumes of a solution of ca. 0.1 g **24** in ca. 1.4 g diglyme (with ca. 0.02 g *tert*-butyl methyl ether as an NMR standard) were added to a series of quartz NMR tubes. The volumes in each tube were equalized by addition of diglyme or trapping reagent [(MeO)₄Si or Me₂Si(OMe)₂]. The molar excess of the trap varied from 0 to 16 in four separate runs. After degassing with argon the tubes were placed equidistant from the

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light source, and the progress of the reaction was followed by NMR. In no case did the presence of trap influence the rate of benzene formation. Photolysis of 1,2-dihydrophthalic anhydride (10 mg in 100 μ L of THF) was conducted in the same fashion and found to produce benzene considerably faster than the decomposition of **24**. The addition of O₂ to the photolysis reactions of **24** produced little or no effect, while the use of benzene as the solvent considerably inhibited the rate of decomposition. Irradiation of **24** in an ESR cavity afforded no radical signal.

Synthesis of 1-Methyl-1-(trimethylsilyl)sila- α -pyran (35). (A) (*Z*)-1-(2-Heptamethyltrisilanyl)-4-methoxybut-1-yn-3-ene (**33**). Compound **33** was prepared in an identical fashion as for **3** except that (2-chloro)-heptamethyltrisilane was employed in the coupling: 67%; bp 89 °C (0.3 mm); NMR (DCCl₃) δ 0.06 (s, 18 H), 0.12 (s, 3 H), 3.65 (s, 3 H), 4.34 (d, 1 H, *J* = 8 Hz), 6.05 (d, 1 H, *J* = 8 Hz); IR (neat) 2975, 2130, 1630, 1245 cm⁻¹; mass spectrum, *m/e* (% relative intensity) 270 (9), 255 (15), 167 (17), 141 (24), 73 (100); calcd for C₁₂H₂₆Si₃O *m/e* 270.12916, measured *m/e* 270.12928.

(B) (*Z,Z*)-4-Methoxy-1-(2-heptamethyltrisilanyl)-1,3-butadiene (**34**). Diene **34** was prepared by DIBAL reduction of **33** in an identical manner with that employed in the synthesis of **4**: 48%, bp 73 °C (0.1 mm); NMR (DCCl₃) δ 0.13 (s, 9 H), 0.22 (s, 3 H), 3.61 (s, 3 H), 5.01 (d of d of d, 1 H, *J* = 12, 6, and <1 Hz), 5.26 (d of t, *J* = 13 and 1 Hz), 5.79 (d of t, 1 H, *J* = 6, 1, and <1 Hz), 7.01 (d of d of d, 1 H); IR (neat) 2800, 1640, 1250, 1115 cm⁻¹; mass spectrum, *m/e* (% relative intensity) 272 (0.9), 257 (2), 169 (16), 131 (25), 89 (30), 73 (100); calcd for C₁₂H₂₈O₂Si₃ *m/e* 272.14481, measured *m/e* 272.14570.

(C) 1-Methyl-1-(trimethylsilyl)sila- α -pyran (**35**). The procedure used was identical with that described for the pyrolysis of **4**. Thus, pyrolysis of **34** afforded two major products, tetramethylsilane (GC/MS identification only) and **35**, which was isolated by preparative GC (12 ft, 15% OV101 on Chromosorb W): 46%; NMR (CCl₄) δ 0.09 (s, 9 H), 0.30 (s, 3 H), 4.89 (d of t, 1 H, *J* = 7, 7, and 1 Hz), 5.32 (d of t, 1 H, *J* = 15, 1, and 1 Hz), 6.50 (m, 2 H); IR (neat), 3050, 2960, 1610, 1255 cm⁻¹; mass spectrum, *m/e* (% relative intensity) 184 (15), 169 (58), 143 (71), 111 (89), 73 (100); calcd for C₈H₁₆Si₂O *m/e* 184.07698, measured *m/e* 184.07363.

Reaction of 35 and Perfluoro-2-butyne in the Presence of Triethylsilane or 2,2,5,5-Tetramethyl-2,5-disila-1-oxacyclopentane (36). A solution of **35** (60 mg, GC prep) and Me₃SiH (1 mL) in an NMR tube was degassed (freeze-thaw) and a large excess of perfluoro-2-butyne was distilled into the tube. After sealing under vacuum, the tube was heated at 60–70 °C for 10 h. Analysis by GC/MS revealed only **12** as a major product and no evidence for 1,1,1-triethyl-2-methyl-2-trimethylsiloxydisilane, the product expected from insertion of **32** into the Si–H bond of Et₃SiH. When the reaction was run identically, but with **36** replacing Et₃SiH, a clean reaction mixture containing **12** (87%) and cyclic trisiloxane **37** (63%), which was identified by NMR and MS spectral comparison with literature data, was obtained. When each of the above reactions was performed by dropping mixtures of **35** and Et₃SiH or **36** through a

vertical, quartz chip packed tube heated at 440–480 °C with perfluoro-2-butyne as the carrier gas (40 mL/min), virtually identical results were obtained although the yield of **37** dropped to 40% and with Et₃SiH an isomer corresponding to trapping of silanone **31** by starting **35** was detected by GC/MS.

Reaction of 35 and Maleic Anhydride. A solution of **35** (0.61 g, 0.0033 mol) and freshly sublimed maleic anhydride (0.30 g, 0.0030 mol) in 15 mL of benzene was stirred at 70 °C for 12 h. After removal of the benzene, adduct **38** was isolated and purified by recrystallization from hexane/Et₂O to afford 0.31 g (33%) as a mixture of syn and anti isomers: NMR (D₆C₆) δ [–0.05 (s, SiMe), 0.01 (s, SiMe₃), 0.09 (s, SiMe), 0.10 (s, SiMe₃), total 12 H], 2.65 (m, 3 H), 4.82 (m, 1 H), 5.90 (m, 2 H); IR (KBr) 3040, 2960, 1860, 1780, 1250 cm⁻¹; mass spectrum, *m/e* (% relative intensity) 209 (2), 133 (31), 117 (31), 78 (41), 73 (100); calcd for C₁₂H₁₈O₄Si₂ *m/e* 282.07431, measured *m/e* 282.07412.

Photolysis of 38 in the Presence of Et₃SiH or Me₂Si(OMe)₂. Adduct **38** (15 mg) was dissolved in ca. 200 μ L of Et₃SiH or dimethyldimethoxydisilane in a quartz NMR tube, degassed with argon, septum sealed, and irradiated for 2 h. GC/MS and NMR analysis indicated no evidence for disilane **40**, the expected trapping product from silylene **32**. In Me₂Si(OMe)₂ solution the photolysis of **38** afforded benzene (54%) and disiloxane **39** (29%): NMR (DCCl₃) δ 3.61 (s, 2 OCH₃), 0.22 (overlapped SiMe's, 18 H); IR (neat) 2960, 1255, 1060, 1010 cm⁻¹; mass spectrum, *m/e* (% relative intensity) 237 (19), 179 (100), 149 (82), 133 (65), 73 (72); calcd for C₇H₂₁O₃Si₃ (M⁺ – CH₃) *m/e* 237.07986, measured *m/e* 237.08000.

Thermolysis of 38 in Me₂Si(OMe)₂. A solution of **38** (55 mg) in 1.0 mL Me₂Si(OMe)₂ in an NMR tube was degassed (freeze-thaw) and sealed under vacuum. After heating for 8 h at 150 °C the tube was opened and the contents analyzed. The three major products were identified by NMR and GC/MS comparison with authentic samples: 1,2-dihydrophthalic anhydride (54%), phthalic anhydride (16%), and **39** (39%).

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Variations in Mechanism for Photoinduced Valence Isomerization of an Electron-Donor Nonconjugated Diene

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Abstract: Photoisomerization of 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*endo,endo*-dimethanonaphthalene (**3**) has been studied in detail. Rearrangement to the cage photoisomer **4** occurs on direct irradiation or with triplet sensitizers with quantum efficiency as high as 1.0. Irradiation in the presence of electron acceptors whose fluorescence is quenched by **3** also results in cage formation. Quantum yields approach 1.0 for donor–acceptor sensitization in a nonpolar solvent. For this reaction, a mechanism is proposed that involves excitation transfer within an exciplex of sensitizer and **3** and partitioning of locally excited **3** at a biradicaloid geometry. Quantum efficiencies exceed unity for rearrangement sensitized by electron acceptors in polar media. A chain mechanism is proposed that involves radical-cation intermediates obtained through electron transfer from **3**. Irradiation of ground-state (charge-transfer) complexes of **3** and fumaronitrile or diethyl 1,2-dicyanofumarate also results in valence isomerization with quantum yields that are dependent on solvent polarity and excitation wavelength. The options available for photosensitization of **3** and a related diene, norbornadiene, are discussed.

Photochemically induced internal cycloaddition (valence isomerization) of nonconjugated dienes has been the focus of consid-

erable attention for some years.¹ The utility of preparing novel polycyclic compounds possessing significant cumulative ring strain