centage of each complex, and plots of ln (concentration) vs time were made to determine the competitive rates of reaction. From the slopes of these lines during the first 2 half-lives of reaction, $k_H = 5.66\ (0.41) \times 10^{-6}\ s^{-1}$ and $k_D = 5.28\ (0.10) \times 10^{-6}\ s^{-1}$.

Equilibration of $(C_5Me_5)Rh(PPh_3)(C_6H_5)H$ with 1 Equiv of H_2. $(C_5Me_5)Rh(PPh_3)H_2$ (13.5 mg, 0.024 mmol) was dissolved in C_6D_6, and the solution was placed in an NMR tube attached to a ground glass joint. The solution was freeze-pump-thaw-degassed and flame-sealed under vacuum. Irradiation of the sample was carried out (180-W Hg lamp, $\lambda > 300$ nm) with cooling by a jet of compressed air. After irradiation for 30 min, only 1% of the starting material remained, with the only product being $(C_5Me_5)Rh(PPh_3)(C_6D_5)D$. The sample was placed in the dark at 24 °C. After 97 days, the sample exhibited a ratio of 1.25:1.00 for $(C_5Me_5)Rh(PPh_3)H_2$:$(C_5Me_5)Rh(PPh_3)(C_6D_5)D$. ^1H NMR (C_6D_6): $(C_5Me_5)Rh(PPh_3)H_2$ δ −13.009 (dd, J = 38.8, 28.7 Hz, 2 H), 1.876 (d, J = 1.8 Hz, 15 H), 7.017 (m, 9 H), 7.663 (m, 6 H); $(C_5Me_5)Rh(PPh_3)(C_6D_5)D$ δ 1.604 (d, J = 1.8 Hz, 15 H), 6.987 (m, 9 H), 7.445 (dd, J = 9.7, 8.1 Hz, 6 H).

Reaction of $(C_5Me_5)Rh(PPh_3)(C_6H_5)H$ with Excess Added H_2. $(C_5Me_5)Rh(PPh_3)(C_6H_5)H$ (0.0026 mmol) was dissolved in 0.5 mL of C_6D_6, and the solution was placed in an NMR tube attached to a resealable Teflon valve. 1,4-Dioxane (0.01 mL, 10.3 mg, 0.117 mmol) was added to the tube via syringe to serve as an internal standard. The solution was freeze-pump-thaw-degassed three times and cooled to 0 °C with an ice bath. Hydrogen gas was placed above the solution (650 mm, 0.07 mmol, 26 equiv) by filling the vacuum line with hydrogen and opening the Teflon valve. The sample was heated at 68 °C in the dark and the reaction monitored periodically by ^1H NMR spectroscopy to determine the rate of formation of $(C_5Me_5)Rh(PPh_3)H_2$.

Reaction of $(C_5Me_5)Rh(PMe_2Ph)(C_6H_5)H$ with H_2. $(C_5Me_5)Rh(PMe_2Ph)(C_6H_5)H$ (0.015 mmol) was dissolved in 0.5 mL of C_6D_6 and placed into a resealable NMR tube. The solution was subjected to three freeze-pump-thaw degas cycles. Dioxane (3 mm, 0.049 L, 296 K, 0.0080 mmol) was condensed into the NMR tube. The solution was cooled to 0 °C, and H_2 (681 mm) was placed over the solution. The sample was heated to 62 °C and the formation of $(C_5Me_5)Rh(PMe_2Ph)H_2$ monitored by the growth of the C_5Me_5 resonance in the ^1H NMR spectrum at δ 1.945 versus dioxane.

Reaction of $(C_5Me_5)Rh(PMePh_2)(C_6H_5)H$ with H_2. A solution of $(C_5Me_5)Rh(PMePh_2)(C_6H_5)H$ was prepared as above. The sample was cooled to 0 °C, and H_2 (647 mm) was placed over the solution. After 1 day at room temperature, the only change noted was a decrease in the hydride signal due to exchange with C_6D_6. The sample was heated to 68 °C, and the growth of the resonance in the ^1H NMR spectrum at δ 1.898 was monitored with time for the formation of $(C_5Me_5)Rh(PMePh_2)H_2$.

Reaction of $(C_5Me_5)Rh(PMe_3)(C_6H_5)H$ with H_2. A solution of $(C_5Me_5)Rh(PMe_3)(C_6H_5)H$ (0.038 mmol) was prepared as above. Hydrogen (670 mm) was placed above the solution on the high-vacuum line. The ^1H NMR resonances for the C_5Me_5 ligands of starting material $(C_5Me_5)Rh(PMe_3)(C_6H_5)H$ (δ 1.786) and of the product $(C_5Me_5)Rh(PMe_3)H_2$ (δ 2.065) were monitored with time, while the sample was maintained at 24.5 °C. (The reaction was too fast to monitor at 68 °C.)

Acknowledgment. We thank the U.S. Department of Energy (Grant DE-FG02-86ER13569) for their support of this work and the Exxon Education Foundation.

Bromide Ion Catalyzed Dimerization of 3,3-Diphenyl-6-oxa-3-silabicyclo[3.1.0]hexane. Structure Determination and Ring Contraction of 2,2,6,6-Tetraphenyl-4,8-divinyl-1,5-dioxa-2,6-disilacyclooctane and Synthesis of 2,2,4,4-Tetraphenyl-6-vinyl-1,3-dioxa-2,4-disilacyclohexane

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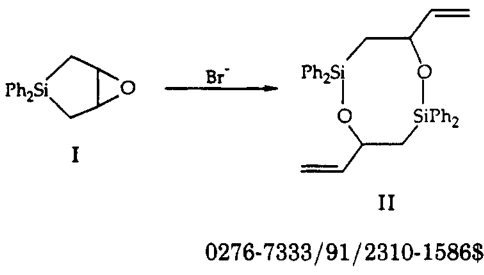
Received October 11, 1990

Bromide ion catalyzed dimerization of 3,3-diphenyl-6-oxa-3-silabicyclo[3.1.0]hexane (I) yields *cis*- and *trans*-2,2,6,6-tetraphenyl-4,8-divinyl-1,5-dioxa-2,6-disilacyclooctane (II). The structure of *trans*-II has been determined by a combination of ^1H, ^{13}C, and ^{29}Si NMR spectroscopy and X-ray crystallography. *trans*-II crystallizes in the monoclinic space group $P2_1/n$, with a = 7.105 (3) Å, b = 12.613 (3) Å, c = 15.455 (5) Å, β = 94.21 (3)°, and V = 1381.2 (8) Å^3 for Z = 2. The structure was refined to a final agreement factor of 0.055 for 1374 reflections. Pyrolysis of II at 150 °C yields 2,2,4,4-tetraphenyl-6-vinyl-1,3-dioxa-2,4-disilacyclohexane (III) and 1,3-butadiene. The kinetics of this first-order ring contraction reaction of *trans*-II have been determined: E_a = 32.2 ± 1.5 kcal/mol, S = 1.3 ± 0.2 eu.

We wish to report the bromide ion catalyzed dimerization of 3,3-diphenyl-6-oxa-3-silabicyclo[3.1.0]hexane (I) to yield a mixture of *cis*- and *trans*-2,2,6,6-tetraphenyl-4,8-divinyl-1,5-dioxa-2,6-disilacyclooctane (II). This high-yield (87%) reaction is carried out at 80 °C in a mixed solvent system of acetone and benzene. The ratio of *cis*-II to *trans*-II is found to be highly dependent on the exact solvent composition used. Mixtures of *cis*-II and *trans*-II with compositions from 9/91 to 32/68 were obtained. The nature of this solvent effect is not understood. The molecular weight of II has been determined by mass spectroscopy. The structure of *trans*-II has been elucidated by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy as well as by X-ray crystallography (see Figure 1 for an ORTEP diagram of *trans*-II and Tables I and II for atomic coordinates and bond lengths and angles of *trans*-II) on a 9/91 mixture of



I

II

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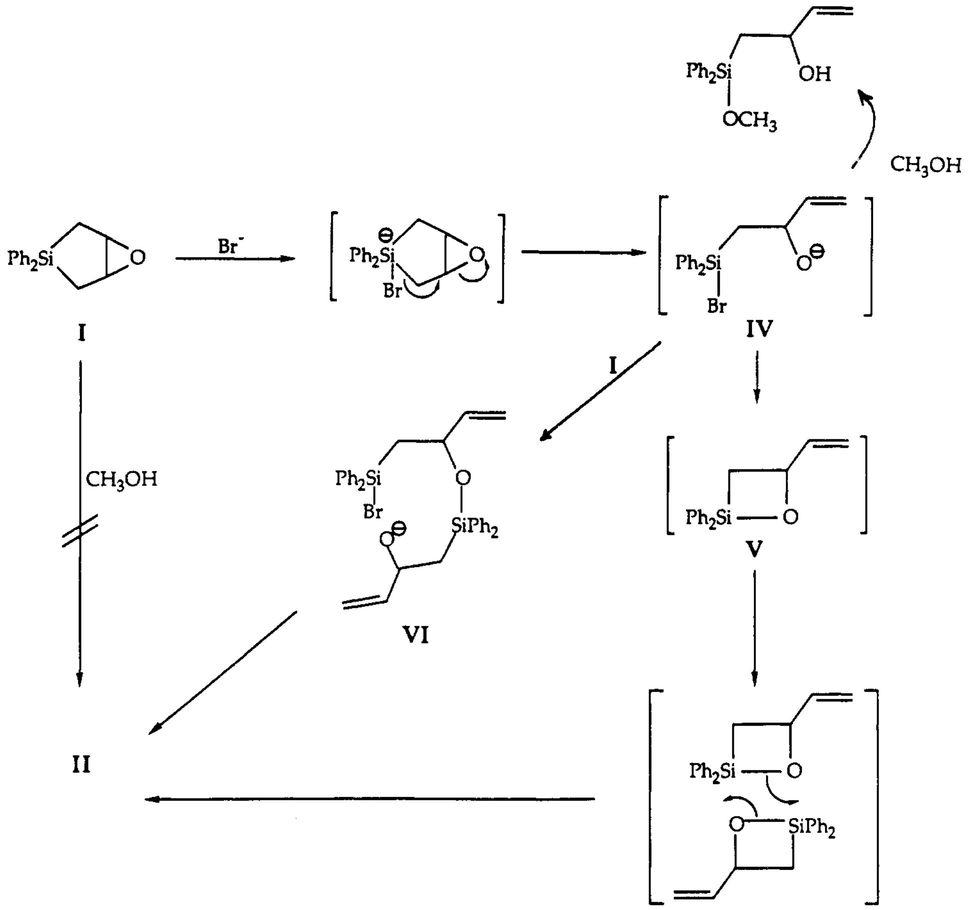
Scheme I



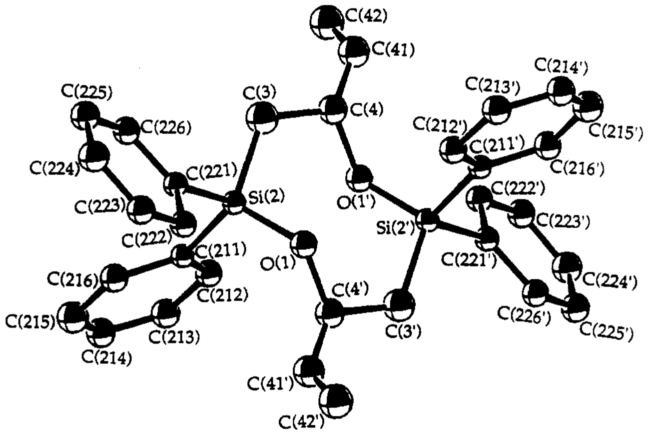


Figure 1. ORTEP diagram of *trans*-II. An inversion center is situated at the center of the molecule.

cis-II and *trans*-II. The structure of *cis*-II has been determined spectroscopically by subtraction of signals due to *trans*-II from spectra determined on a 32/68 mixture of *cis*-II and *trans*-II.

Table I. Final Atomic Coordinates for *trans*-2,2,6,6-Tetraphenyl-4,8-divinyl-1,5-dioxa-2,6-disilacyclooctane

atom	*x*	*y*	*z*
O1	−0.0160 (6)	0.1165 (3)	1.0182 (2)
Si2	0.0634 (2)	0.1119 (1)	0.9218 (1)
C211	−0.1259 (6)	0.0969 (4)	0.8312 (3)
C212	−0.2351 (7)	0.0061 (4)	0.8184 (3)
C213	−0.3709 (8)	−0.0016 (5)	0.7490 (4)
C214	−0.3981 (9)	0.0803 (5)	0.6916 (4)
C215	−0.2925 (9)	0.1699 (5)	0.7026 (4)
C216	−0.1582 (8)	0.1783 (4)	0.7715 (4)
C221	0.1898 (7)	0.2401 (4)	0.9076 (3)
C222	0.3297 (8)	0.2504 (5)	0.8508 (4)
C223	0.4233 (9)	0.3452 (6)	0.8422 (5)
C224	0.3824 (9)	0.4310 (5)	0.8895 (5)
C225	0.2461 (9)	0.4238 (4)	0.9462 (4)
C226	0.1489 (8)	0.3295 (4)	0.9554 (3)
C3	−0.2365 (9)	−0.0020 (6)	1.0788 (5)
C4	−0.1949 (12)	0.1027 (5)	1.0505 (6)
C41	−0.3158 (12)	0.1874 (8)	1.0396 (6)
C42	−0.3674 (11)	0.2616 (6)	1.0840 (6)

The reaction of bromide ion with I (Scheme I) probably proceeds by nucleophilic attack at the silyl center to form a pentacoordinate silicate intermediate, which rearranges to yield the alkoxy intermediate (2-oxido-but-3-en-1-yl)diphenylbromosilane (IV). We have, in fact, been able to trap IV by carrying out the reaction with a small amount of added methanol. In this case, (2-hydroxy-but-3-en-1-yl)diphenylmethoxysilane is isolated in high yield. Control experiments carried out demonstrate that both I and II are stable to methanol in the absence of bromide ion. The observation that 3,3-dimesityl-6-oxa-3-silabicyclo[3.1.0]hexane only undergoes 5% reaction under similar conditions, bromide ion in acetone and benzene at 80 °C, is consistent with the suggestion that nucleophilic attack at the silyl center is essential for this reaction to occur. Apparently the bulky mesityl groups provide sufficient steric hindrance to make this difficult. The thermodynamic driving force for this reaction undoubtedly results, at least partially, from the relief of ring strain provided by opening of the epoxide.[1] Such an alkoxide (IV) could undergo intramolecular nucleophilic attack on the silyl center with loss of bromide to form the strained ring 2,2-

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[1] The strain energy of ethylene oxide has been estimated to be 28 kcal/mol: Cox, J. D. *Tetrahedron* **1972**, *19*, 1175.

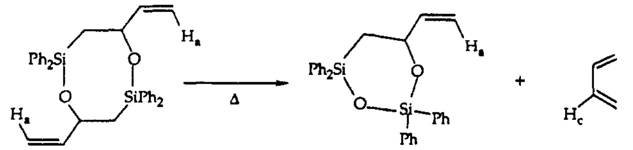
Table II. Important Bond Distances (Å) and Angles (deg) for *trans*-2,2,6,6-Tetraphenyl-4,8-divinyl-1,5-dioxa-2,6-disilacyclooctane

O1–C4	1.411 (7)	C216–C215	1.381 (7)
Si2–O1	1.632 (3)	C221–C222	1.380 (7)
Si2–C3′	1.853 (5)	C221–C226	1.390 (7)
Si2–C211	1.879 (5)	C222–C223	1.379 (8)
Si2–C221	1.871 (5)	C223–C224	1.349 (8)
C211–C212	1.389 (6)	C225–C224	1.356 (8)
C211–C216	1.387 (6)	C226–C225	1.389 (7)
C212–C213	1.392 (7)	C3–C4	1.429 (9)
C213–C214	1.367 (8)	C41–C4	1.374 (10)
C215–C214	1.361 (8)	C41–C42	1.232 (10)
O1–Si2–C211	114.1 (2)	C212–C211–C216	116.9 (4)
O1–Si2–C221	106.1 (2)	C212–C213–C214	120.3 (5)
C211–Si2–C221	108.9 (2)	C215–C214–C213	119.7 (5)
O1–C4–C3	115.7 (5)	C216–C215–C214	120.2 (6)
O1–C4–C41	115.6 (5)	C221–C222–C223	121.2 (5)
Si2–O1–C4	134.4 (5)	C221–C226–C225	121.0 (5)
Si2–C211–C212	123.4 (4)	C222–C221–C226	116.8 (5)
Si2–C211–C216	119.7 (4)	C222–C223–C224	121.2 (6)
Si2–C221–C222	122.1 (4)	C225–C224–C223	119.3 (6)
Si2–C221–C226	121.2 (4)	C226–C225–C224	120.5 (6)
C211–C212–C213	121.0 (5)	C3–C4–C41	128.0 (7)
C211–C216–C215	121.8 (5)	C42–C41–C4	137.0 (10)

diphenyl-2-silaoxetane (V). Attempts to spectroscopically observe V by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy during this reaction were unsuccessful. In particular, no ^{29}Si NMR signal in the region of 50–60 ppm, which has been reported to be characteristic of silaoxetanes, is observed.[2] Head-to-tail dimerization of two molecules of V could lead to II. This pathway, however, seems unlikely. While 1,2-silaoxetanes have been proposed as transient intermediates in a number of reactions,[3-5] only extremely sterically congested examples have been isolated.[2,6,7] A 1,2-silaoxetane such as V would be expected to decompose rapidly via a retro [2 + 2] cycloaddition reaction pathway to yield a reactive diphenylsilanone and 1,3-butadiene. The possibility that a high-yield reaction could proceed by the dimerization of two unstable short-lived intermediates such as V seems most unlikely.

On the other hand, attack by the alkoxide oxygen of IV on the silyl center of a second molecule of I with concomitant ring opening could lead to VI. Intramolecular attack by the alkoxy oxygen of VI at the remote diphenylbromosilyl center would result in formation of a Si–O bond and the unstrained eight-membered-ring species II. While we do not have definitive evidence that would permit us to distinguish between these alternative pathways, we favor the latter.

Pyrolysis of a 9/91 mixture of *cis*-II and *trans*-II either as the neat compounds or in DMSO solvent at about 150 °C leads to loss of 1,3-butadiene and formation of 2,2,4,4-tetraphenyl-6-vinyl-1,3-dioxa-2,4-disilacyclohexane (III) in quantitative yield. Related ring contraction reactions have been reported.[8,9] For example, a substituted 1,5-dioxa-2,6-disilacycloocta-3,7-diene has been recently reported to undergo contraction to yield a 1,3-dioxa-2,4-disila-5-cyclohexene and an acetylene.[10]



II III

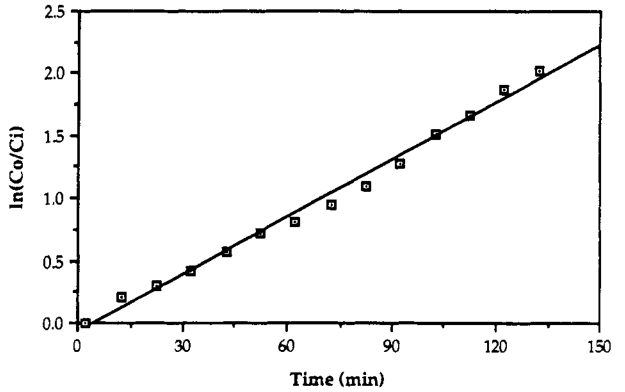


Figure 2. Kinetic plot of the disappearance of *trans*-II at 413 K.

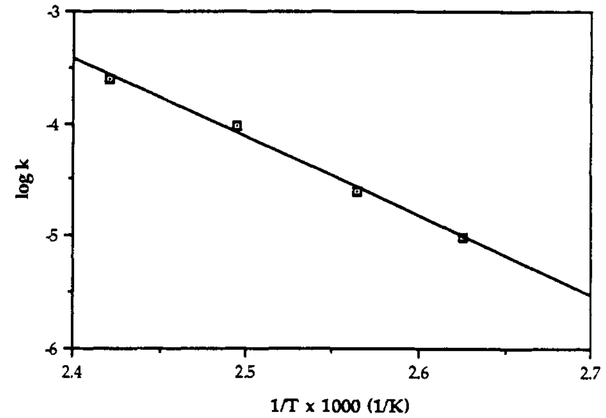


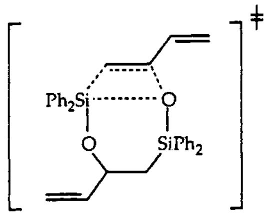
Figure 3. Arrhenius plot.

Table III. Rate of Disappearance of *trans*-II at Various Temperatures[a]

temp, K	rate, s^{-1}	temp, K	rate, s^{-1}
381.0	9.86×10^{-6}	401.0	9.45×10^{-5}
390.0	2.50×10^{-5}	413.0	2.54×10^{-4}

[a] The rate of appearance of III at 413 K was 2.76×10^{-4} s^{-1}. The rate of appearance of 1,3-butadiene at 413 K was 2.79×10^{-4} s^{-1}.

This transannular reaction probably involves formation of a strong Si–O bond simultaneous with loss of 1,3-butadiene:



The nonbonded Si2–O1′ and Si2′–O1 distances (Figure 1) observed by X-ray crystallography (3.05 Å) are shorter than the sum of the van der Waals radii (3.60 Å).[9] This

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(2) Brook, A. G.; Chatterton, W. J.; Sawyer, J. F.; Hughes, D. W.; Vorspohl, K. *Organometallics* **1987**, *6*, 1246.

(3) Roark, D. N.; Sommer, L. H. *J. Chem. Soc., Chem. Commun.* **1973**, 167.

(4) Barton, T. J.; Kilgour, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 2278.

(5) For a recent review see: Raab, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

(6) Saso, H.; Yoshida, H.; Ando, W. *Tetrahedron Lett.* **1988**, 4747.

(7) Sekiguchi, A.; Ando, W. *J. Am. Chem. Soc.* **1984**, *106*, 1486.

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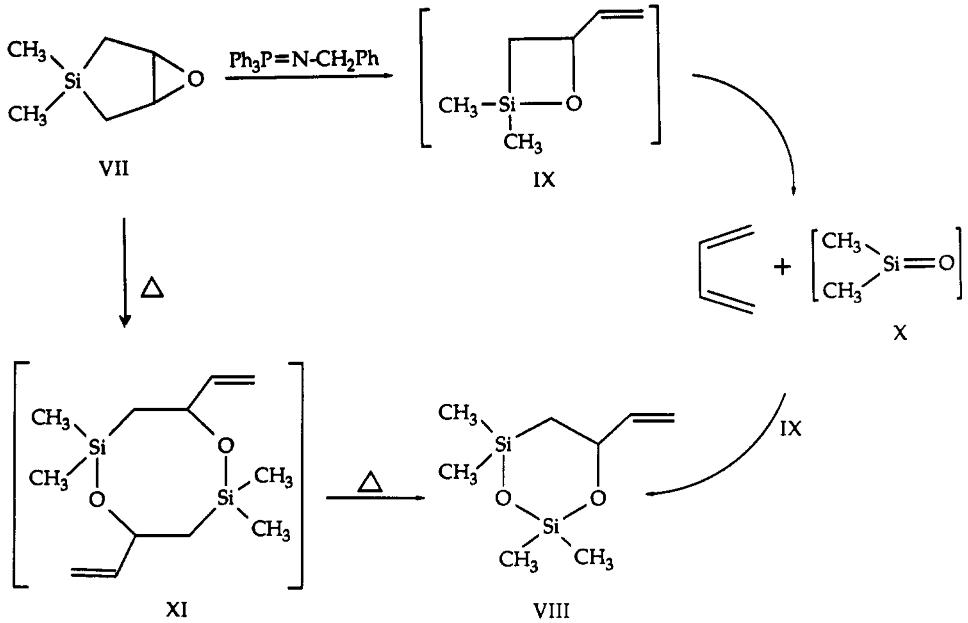
(9) Maas, G.; Schneider, K.; Ando, W. *J. Chem. Soc., Chem. Commun.* **1988**, 72.

(10) Schneider, K.; Daucher, B.; Fronda, A.; Maas, G. *Chem. Ber.* **1990**, *123*, 589.

Scheme II



suggests that transannular Si–O interactions are important in II.

Consistent with the proposed mechanism, the kinetics of this pyrolysis process are found to be first order in II (Figure 2 and Table III). The energy of activation has been calculated by an Arrhenius plot (Figure 3). The energy of activation is found to be 32.2 ± 1.5 kcal/mol, while the entropy of activation is 1.3 ± 0.2 eu. This latter value is probably the result of a delicate balance of two factors. The proposed reaction pathway involves a highly ordered transition state in which a Si—O bond and a C=C double bond are formed simultaneously with scission of a Si—C and a C—O single bond. Such a transition state is expected to have a large negative entropy of activation. On the other hand, one molecule of II is converted into a molecule of III and a molecule of 1,3-butadiene in the reaction. The entropy of activation of such a fragmentation reaction is expected to be positive. Apparently, the two effects cancel each other in this case.

It should be noted that we have previously reported that 3,3-dimethyl-6-oxa-3-silabicyclo[3.1.0]hexane (VII) is converted to 2,2,4,4-tetramethyl-6-vinyl-1,3-dioxa-2,4-disilacyclohexane (VIII) and 1,3-butadiene on treatment with a catalytic amount of *N*-benzyltriphenylphosphoranimine at 130 °C (Scheme II). A similar reaction with I yields III and 1,3-butadiene directly. This reaction of VII was proposed to involve formation of 2,2-dimethyl-4-vinyl-2-silaoxetane (IX) as a key intermediate. Decomposition of IX by a retro [2 + 2] cycloaddition reaction was proposed to lead to 1,3-butadiene and the reactive dimethylsilanone ($(CH_3)_2Si{=}O$ (X)), which inserted into the strained Si—O single bond of IX to form VIII.[11] An analogous mechanism has been proposed to account for the formation of 2,2,4,4-tetramethyl-1,3-dioxa-2,4-disilacyclohexane on treatment of (2-hydroxyethyl)dimethylbromosilane with pyridine.[12] Nevertheless, from what we now know about the thermal stability of II, it seems more likely that the conversion of VII to VIII proceeds by initial conversion of VII into 2,2,6,6-tetramethyl-4,8-divinyl-1,5-dioxa-2,6-disilacyclooctane (XI), which is unstable under the reaction conditions (130 °C) and undergoes transannular ring contraction to yield VIII as above. Preliminary experiments with bromide ion catalysis at 80 °C support this conclusion.

Experimental Section

NMR Analysis. ^1H, ^{13}C, ^{29}Si NMR spectra were recorded on an IBM Bruker 270-SY or Bruker AM-360 spectrometer operating in the Fourier transform mode. ^{13}C NMR spectra were run with broad-band proton decoupling. A DEPT pulse sequence was used to obtain ^{29}Si NMR spectra. This was effective since all the silicon atoms have at least one methylene group bonded to them.[13] Identical ^{29}Si NMR spectra could be obtained by use of a heteronuclear gated decoupling pulse sequence (NONOE) with a pulse delay of 30 s.[14] Ten to fifteen percent (w/v) solutions in chloroform-*d* were used to obtain ^{13}C and ^{29}Si NMR spectra. Five percent (w/v) solutions were used to obtain ^1H NMR spectra. Chloroform was utilized as an internal standard for ^1H and ^{13}C NMR spectra. ^{29}Si NMR spectra were externally referenced to TMS.

IR spectra were recorded on a Perkin-Elmer PE-281 spectrometer. Spectra of oils were taken as neat films on NaCl plates. IR spectra of solids were taken on KBr pellets.

Mass Spectral Analysis. Low-resolution mass spectra were obtained on a Finnigan Mat Incos 50 GCMS instrument at an ionizing voltage of 70 eV. A 0.25 mm × 30 m fused silica DB-5 capillary column was used in the gas chromatographic inlet of the mass spectrometer. High-resolution mass spectra were obtained at the University of California Riverside Mass Spectrometry Facility on a VG-7070 EHF mass spectrometer at an ionizing voltage of 20 eV. Exact masses were determined by peak matching against known masses of perfluorokerosene.

X-ray Structure Analysis. Crystals suitable for X-ray diffraction were grown by vapor diffusion of a $CHCl_3$ solution against hexane at 0 °C. A crystal of dimensions $0.44 \times 0.43 \times 0.30$ mm^3 was mounted on a glass fiber in air and placed in a Siemens/Nicolet/Syntex $P2_1$ diffractometer for diffraction analysis. The angular settings of 15 well-centered reflections revealed a monoclinic unit cell whose dimensions are given in Table S1 of the supplementary material. Three monitor reflections showed no significant decrease in intensity during data collection, which was carried out with Mo Kα radiation up to a 2θ maximum of 45°. Other details of the data collection and data processing are given in Table S1.

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[11] Baceiredo, A.; Juengst, C. D.; Manuel, G.; Weber, W. P. *Chem. Lett.* **1987**, 237.

[12] Barton, T. J. *Pure Appl. Chem.* **1980**, *52*, 615.

[13] Pegg, D. T.; Doddrell, D. M.; Bendall, M. R. *J. Chem. Phys.* **1982**, *77*, 2745.

[14] Freeman, F.; Hill, H. D. W.; Kaptein, R. *J. Magn. Reson.* **1972**, *7*, 327.

The positions of the silicon atom and the four atoms attached to it were obtained by direct methods with the crystallographic package SHELX-86.[15] The rest of the non-hydrogen atoms were subsequently located from a series of structure factor/difference Fourier calculations. The cyclic molecule was found to be situated on a crystallographic center of inversion, which related one half of the eight-membered ring to the other half. During the structural analysis, it was found that the α-carbon of the vinyl group was partially disordered, a phenomenon probably related to the fact that the sample crystal was grown from a 91/9 ratio of trans/cis isomers. After collection of X-ray data, the crystal was dissolved in chloroform-*d*. ^{1}H NMR spectrum of this material was identical with that of the starting 91/9 mixture of *trans*-II/*cis*-II.

The X-ray analysis was completed with several cycles of full-matrix least-squares refinement,[16] with anisotropic thermal parameters assigned to all atoms except the α-vinyl carbon atoms. The final agreement factor was 5.47% for 1374 nonzero reflections. A final difference Fourier map showed the absence of any residual electron density. A molecular plot, shown in Figure 1, confirms that the dominant configuration of molecule II is trans. The atomic coordinates are listed in Table I. Important bond lengths and angles are given in Table II. Other results of the structural analysis have been deposited as supplementary material.[17]

Kinetic Measurements of the Rate of Conversion of II to III. The kinetic measurements were carried out on an IBM-Bruker AM-360 spectrometer equipped with a variable-temperature probe. The temperature of the probe was controlled by balancing a flow of cold nitrogen gas with a heater. The temperature was measured with a thermocouple. The temperature in the probe was calibrated by measuring the chemical shift difference between the CH_2 and OH groups of ethylene glycol. Temperatures were reproducible to 0.5 °C, and the accuracy was ±1 °C. A sample of II (7.1 mg, 1.4×10^{-2} mmol) in DMSO-d_6 (0.5 mL) was thermostated in the NMR probe at the desired temperature for 3 min. The time for temperature equilibration of the sample in the NMR probe was determined to be 3 min. The NMR probe was always stabilized at the reaction temperature for at least 5 min before an experiment was begun. The reactions were monitored by disappearance of the H_a signal of *trans*-II. FID's were collected every 10 min at 390, 401, and 413 K and every 20 min at 381 K. Fourier transform of these FID's permits integration of the concentration of the starting material *trans*-II. The rate constants reported were obtained by a first-order kinetic analysis (Table III). The rate of appearance of H_a of III as well as the appearance of H_c of 1,3-butadiene was also measured at 413 K. These rates were in agreement with one another within 1%. They are both 10% greater than the rate obtained from the disappearance of *trans*-II. This is probably due to the fact that both III and 1,3-butadiene are formed not only from the pyrolysis of *trans*-II but also from the pyrolysis of *cis*-II apparently at comparable rates. These rate constants are accurate to ±6% or less. An Arrhenius plot (Figure 3) permits the determination of the activation parameters.

Diphenyldichlorosilane and dimesityldichlorosilane were purchased from Petrarch. The former was purified by fractional distillation prior to use. Magnesium powder was obtained from Aldrich.

All solvents were dried and purified by accepted methods.[18] All glassware was dried overnight in an oven at 120 °C, assembled, and flame-dried under an atmosphere of purified argon. Similarly, all reactions and transfers were conducted under an inert atmosphere.

Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

We have included complete spectral data for known compounds, if this information has not been previously reported.

1,1-Diphenyl-1-silacyclopent-3-ene was prepared by the reaction of diphenyldichlorosilane, 1,3-butadiene, and magnesium in THF. A fraction with bp 148–150 °C (0.2 mm) in 64% yield was isolated (lit.[19] bp 132 °C (0.02 mm)). ^{1}H NMR: δ 1.97 (d, 4 H, *J* = 0.94 Hz), 6.15 (t, 2 H, *J* = 0.94 Hz), 7.44–7.53 (m, 6 H), 7.67–7.71 (m, 4 H). ^{13}C NMR: δ 16.84, 127.90, 129.45, 131.00, 134.67, 135.71. ^{29}Si NMR: δ 8.51. IR: ν 3050, 3030, 3000, 2900, 2870, 1600, 1460, 1440, 1390, 1190, 1110, 935, 805, 790, 725, 710, 625 cm^{-1}.

3,3-Diphenyl-6-oxa-3-silabicyclo[3.1.0]hexane (I) was prepared by the reaction of 1,1-diphenyl-1-silacyclopent-3-ene with *m*-chloroperbenzoic acid. A white crystalline solid with mp 81 °C in 90% yield was obtained (lit.[20] mp 81 °C). ^{1}H NMR: δ 1.56 (d, 2 H, *J* = 16.1 Hz), 1.87 (d, 2 H, *J* = 16.1 Hz), 3.70 (s, 2 H), 7.42–7.52 (m, 6 H), 7.63–7.70 (m, 4 H). ^{13}C NMR: δ 15.02, 57.73, 127.65, 127.91, 129.28, 129.44, 134.65, 135.09, 135.18. ^{29}Si NMR: δ 7.69.

1,1-Dimesityl-1-silacyclopent-3-ene. In a 500-mL round-bottom three-neck flask equipped with a efficient reflux condenser, a cold finger condenser, a rubber septum, and a Teflon-covered magnetic stirring bar was placed magnesium powder (0.7 g, 29 mmol), THF (80 mL), and dimesityldichlorosilane (8.9 g, 26 mmol). The reflux condenser was connected to a refrigerated cooling unit. A mixture of ethylene glycol and water cooled to −20 °C was circulated through the reflux condenser. The cold finger condenser was filled with dry ice/acetone. It was connected to a tank of 1,3-butadiene. 1,3-Butadiene (50 mL) was condensed into a volumetric flask and was then transferred to the reaction flask via a cannula. The reaction mixture was stirred for 150 h. During this time it turned dark green. The reaction was quenched by addition of a saturated aqueous ammonium chloride solution. The excess 1,3-butadiene was permitted to evaporate. The organic layer was separated, washed with water (3 × 100 mL), dried over anhydrous magnesium sulfate, and filtered, and the volatile solvents were removed by evaporation under reduced pressure. The residue was purified by fraction distillation through a 15-cm vacuum-jacketed Vigreux column. A central fraction with bp 210–215 °C (0.9 mm) in 4.5-g (53%) yield was obtained. ^{1}H NMR: δ 2.02 (d, 4 H, *J* = 1 Hz), 2.21 (s, 6 H), 2.32 (s, 12 H), 6.02 (t, 2 H, *J* = 1 Hz), 6.76 (s, 4 H). ^{13}C NMR: δ 20.93, 22.72, 24.02, 129.06, 131.28, 133.83, 138.43, 143.74. ^{29}Si NMR: δ 3.26. IR: ν 3020, 2960, 2900, 2720, 1600, 1550, 1450, 1400, 1370, 1095, 1070, 1025, 950, 840, 805, 795, 650 cm^{-1}. Anal. Calcd for $C_{22}H_{28}Si$: C, 82.4; H, 8.80. Found: C, 82.16; H, 8.74.

3,3-Dimesityl-6-oxa-3-silabicyclo[3.1.0]hexane. In a two-neck 250-mL round-bottom flask equipped with a pressure-equalizing addition funnel, a reflux condenser, and a Teflon-covered magnetic stirring bar was placed *m*-chloroperbenzoic acid (1.05 g, 6.1 mmol) and 40 mL of ether. 1,1-Dimesityl-1-silacyclopent-3-ene (1.5 g, 4.7 mmol) and 40 mL of ether were placed in the addition funnel. This solution was added dropwise over 1 h. The reaction mixture was refluxed for 48 h. The organic layer was extracted with dilute sodium hydroxide, washed with water, dried over anhydrous magnesium sulfate, and filtered, and the volatile organic solvents were removed by evaporation under reduced pressure. The white crystalline solid was purified by recrystallization from ether/pentane (4/1); mp 116–118 °C. In this way, 1.23 g of product in 78% yield was obtained. ^{1}H NMR: δ 1.67 (d, 2 H, *J* = 16 Hz), 2.05 (d, 2 H, *J* = 16 Hz), 2.23 (s, 3 H), 2.24 (s, 3 H), 2.33 (s, 6 H), 2.38 (s, 6 H), 3.60 (s, 2 H), 6.75 (s, 2 H), 6.78 (s, 2 H). ^{13}C NMR: δ 20.40, 20.84, 20.91, 23.90, 24.52, 57.22, 129.12, 129.27, 132.95, 133.49, 138.59, 138.64, 143.32. ^{29}Si NMR: δ 0.32. IR: ν 3000, 2950, 2900, 2860, 2720, 1600, 1490, 1410, 1390, 1380, 1240, 1180, 1055, 1020, 920, 845, 815, 775, 695, 650 cm^{-1}. Anal. Calcd for $C_{22}H_{28}OSi$: C, 78.5; H, 8.39. Found: C, 77.87; H, 8.45.

Synthesis of 91/9 *trans-/cis*-2,2,6,6-Tetraphenyl-4,8-divinyl-1,5-dioxa-2,6-disilacyclooctane. In a 50-mL round-bottom flask equipped with a reflux condenser and a Teflon-covered magnetic stirring bar was placed 3,3-diphenyl-6-oxa-3-silabicyclo[3.1.0]hexane (2.52 g, 10 mmol), acetone (7 mL), benzene (3

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mL), and tetra-*n*-butylammonium bromide (0.32 g, 1 mmol). The mixture was refluxed. Aliquots were withdrawn regularly, one every 24 h, from the reaction flask and placed in a 5-mm NMR tube sealed with a rubber septum. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were taken of these samples in an attempt to observe the presence of V. After 160 h, the volatile solvents were removed by evaporation under reduced pressure. The tetra-*n*-butylammonium bromide catalyst was separated from the product by trituration of the residue with pentane (4 × 15 mL). The combined organic layers were dried over anhydrous magnesium sulfate and filtered and the volatile solvents removed by evaporation under reduced pressure. The product was purified by recrystallization from a mixture of pentane/ether (4/1). In this way, a white crystalline solid with mp 113–115 °C in 2.20-g (87%) yield was obtained.

Spectral Data for *trans*-II. ^{1}H NMR: δ 1.56 (dd, 2 H, J = 15.4 and 3.2 Hz), 1.64 (dd, 2 H, J = 15.4 and 10.2 Hz), 4.90–4.97 (br m, 2 H), 4.94 (ddd, 2 H, J = 10.3, 1.4, and 1.2 Hz), 5.14 (ddd, 2 H, J = 17.0, 1.4, and 1.35 Hz), 5.94 (ddd, 2 H, J = 17.0, 10.3, and 5.6 Hz), 7.24–7.36 (m, 12 H), 7.54–7.60 (m, 8 H). ^{13}C NMR: δ 24.95, 72.31, 112.47, 127.63, 127.70, 127.88, 129.57, 129.81, 134.76, 134.79, 135.48, 135.74, 137.13, 143.58. ^{29}Si NMR: δ −8.68. IR: ν 3050, 3030, 3000, 2980, 2960, 2900, 2880, 1580, 1470, 1420, 1390, 1200, 1175, 1100 (s), 1080 (s), 1070 (s), 995, 985, 980, 920, 905, 845, 745, 730, 690 cm^{-1}. MS *m/e* (relative intensity): 452 (2.0), 451 (8.0), 450 (19.0) (M − 54)$^{\bullet+}$ 429 (2.0), 428 (5.0), 427 (13.0) (M − 77)$^+$, 375 (9.0), 374 (2.3), 373 (59.0), 372 (6.0), 322 (4.0), 321 (12.0), 320 (29.0), 319 (100.0). Exact masses were determined for the ions of *m/e* 450 and 427: calcd for $C_{28}H_{28}O_2Si_2$ 450.1491, found 450.1472; calcd for $C_{26}H_{27}O_2Si_2$ 427.1549, found 427.1539.

Spectral Data for *cis*-II. ^{1}H NMR: δ 1.37 (dd, 2 H, J = 15.2 and 2.1 Hz), 1.99 (dd, 2 H, J = 15.3 and 11.4 Hz), 4.60–4.65 (m, 2 H), 4.89 (ddd, 2 H, J = 10.4, 2.7, and 1.3 Hz), 5.01 (ddd, 2 H, J = 17.4, 2.8, and 1.4 Hz), 5.92 (ddd, 2 H, J = 17.0, 10.4, and 5.4 Hz), 7.20–7.45 (m, 12 H), 7.52–7.72 (m, 8 H). ^{13}C NMR: δ 23.47, 70.86, 112.20, 127.60, 127.66, 127.77, 127.95, 129.48, 129.94, 134.23, 134.33, 134.71, 135.34, 136.40, 143.14. ^{29}Si NMR: δ −6.33.

Synthesis of 32/68 *cis*-/*trans*-II. The reaction was carried out as above, except that the ratio of acetone to benzene was 8/2.

Reaction of I with Methanol. In a 20-mL round-bottom flask equipped with a reflux condenser and a Teflon-covered magnetic stirring bar was placed I (1.26 g, 4.99 mmol), benzene (3 mL), acetone (7 mL), and methanol (5 mL). The mixture was heated reflux for 140 h. After this time, the organic solvents were removed by evaporation under reduced pressure. ^{1}H, ^{13}C, and ^{29}Si NMR spectra of the residue indicated that it was recovered I.

Reaction of II with Methanol. In a 20-mL round-bottom flask equipped as above was placed II (20 mg, 4 × 10^{-2} mmol), benzene (2 mL), and methanol (2 mL). The mixture was refluxed for 5 h. The organic solvents were removed by evaporation under reduced pressure. The residue was shown to be recovered II by ^{1}H and ^{13}C NMR spectroscopic analysis.

Reaction of IV with Methanol. In a 50-mL round-bottom flask equipped with a reflux condenser and a Teflon-covered magnetic stirring bar was placed I (500 mg, 2.0 mmol), acetone (7 mL), benzene (3 mL), methanol (10 mL), and tetra-*n*-butylammonium bromide (65 mg, 0.2 mmol). The reaction mixture was heated to reflux for 150 h. The volatile solvents were removed by evaporation under reduced pressure. The residue was triturated with *n*-pentane (4 × 10 mL). The organic layer was separated, dried over anhydrous magnesium sulfate, and filtered and the volatile solvent removed by evaporation under reduced pressure. The product was purified by flash chromatography on silica gel. A mixture of ether and pentane (1/4) was utilized as the eluting solvent. In this way, a 16-mg (29%) yield of **(2-hydroxybut-3-en-1-yl)methoxydiphenylsilane** was obtained. ^{1}H NMR: δ 1.45 (dd, 1 H, J = 15.0 and 4.9 Hz), 1.62 (dd, 1 H, J = 15.0 and 9.0 Hz), 2.57 (d, 1 H, J = 2.7 Hz), 3.55 (s, 3 H), 4.41 (m, 1 H), 4.98 (ddd, 1 H, J = 10.3, 0.9, and 0.9 Hz), 5.15 (dt, 1 H, J = 17.1, 0.95, and 0.92 Hz), 5.92 (ddd, 1 H, J = 17.1, 10.3, and 5.7 Hz), 7.40–7.45 (m, 6 H), 7.60–7.65 (m, 4 H). ^{13}C NMR: δ 24.01, 51.56, 69.77, 112.86, 127.96, 130.05, 134.47, 134.81, 143.16. ^{29}Si NMR: δ −2.29. IR: ν 3600–3300 br, 3080, 3060, 3005, 2980, 2940, 2920, 2840, 1590, 1430, 1190, 1115, 1085, 990, 925, 890, 775, 740, 700 cm^{-1}. Anal. Calcd for $C_{17}H_{20}O_2Si$: C, 71.79; H, 7.09. Found: C, 71.93; H, 7.22.

Pyrolysis of II. II (30 mg, 6 × 10^{-2} mmol) was placed in a 50-mL Schlenk flask. No solvent was added. The flask and its contents were immersed in an oil bath at 150 °C for 2.5 h. A 100% yield of III (26 mg) was obtained. Similar reactions were carried out in DMSO-d_6 solutions in 5-mm NMR tubes that were sealed with rubber septa. 1,3-Butadiene was observed in the ^{1}H NMR spectra of these reaction mixtures. For the spectral properties of III see below.

2,2,4,4-Tetraphenyl-6-vinyl-1,3-dioxa-2,4-disilacyclohexane (III). Mp: 51–53 °C. ^{1}H NMR: δ 1.53 (dd, 1 H, J = 15.1 and 2.2 Hz), 1.68 (dd, 1 H, J = 15.1 and 12.1 Hz), 4.80–4.89 (br m, 1 H), 5.03 (ddd, 1 H, J = 10.4, 1.5, and 1.4 Hz), 5.28 (ddd, 1 H, J = 17.0, 1.5, and 1.5 Hz), 5.99 (ddd, 1 H, J = 17.0, 10.4, and 5.1 Hz), 7.25–7.41 (m, 12 H), 7.45–7.78 (m, 8 H). ^{13}C NMR: δ 23.97, 71.59, 112.66, 127.78, 127.88, 127.94, 127.99, 130.12, 130.34, 130.40, 134.12, 134.52, 134.62, 135.34, 136.00, 142.68. ^{29}Si NMR: δ −9.11, −29.88. IR: ν 3050, 3030, 3005, 2990, 2980, 1580, 1420, 1180, 1110, 1080, 1030, 1010, 960, 905, 845, 730, 710, 690 cm^{-1}. MS: *m/e* (relative intensity) 453 (4.0), 452 (17.0), 451 (46.0), 450 (100.0) M$^{\bullet+}$, 398 (4.0), 397 (10.0), 396 (14.0) (M − C_4H_8)$^{\bullet+}$, 395 (4.0), 375 (3.0), 374 (14.0), 373 (32.0), 372 (62.0) (M − C_6H_6)$^{\bullet+}$, 360 (4.0), 359 (10.0), 322 (4.0), 321 (11.0), 320 (27.0), 319 (87.0), 155 (7.0), 154 (60.0). High-resolution MS: calcd for $C_{28}H_{26}O_2Si_2$ 450.1471, found 450.1464.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Grant No. 89-0007) and the Office of Naval Research. G.M. and W.P.W. thank NATO for a travel grant.

Supplementary Material Available: Tables giving a summary of crystal data and refinement results and temperature factors (2 pages); a listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.