Evidence for a Metastable *trans*-Cycloalkene Intermediate in the Photochemistry of 1,1,4,4-Tetramethyl-1,4-disilacyclohept-2-ene

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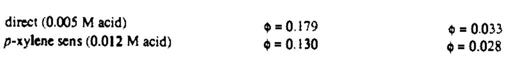
Abstract: Direct, *p*-xylene sensitized, and methyl benzoate sensitized photolyses of 1,1,4,4-tetramethyl-1,4-disilacyclohept-2-ene (**1**) in acidified methanol produced ethenyldimethyl[3-(methoxydimethylsilyl)propyl]silane (**2**) and 2-(methoxymethyl)-1,1,3,3-tetramethyl-1,3-disilacyclohexane (**3**) as the major products. Plots of reciprocal quantum yield of **2** or **3** against reciprocal sulfuric acid ($[H_2SO_4]^{-1}$) gave comparable intercept/slope ratios for direct ($(1.5\text{–}2.1) \times 10^4\ M^{-1}$) and *p*-xylene triplet sensitized ($(1.4\text{–}1.8) \times 10^4\ M^{-1}$) photolyses, suggestive of a common intermediate produced via the singlet and triplet. A reactive intermediate was trappable in the dark. Upon completion of methyl benzoate sensitized photolyses at −75 °C with methylcyclohexane as the solvent, siphoning of the photolysate into acidified methanol gave 11–16% yields of **2** and **3**. The half-life of 0.002 12 M intermediate in methylcyclohexane was 101 min at 20 °C, and the species decayed by strict second-order kinetics, giving a mixture of six dimers from self-dimerization. The intermediate was assigned as the trans isomer of reactant **1** from NMR spectral data of its Diels–Alder cycloadduct, produced in 11% yield upon addition of cyclopentadiene to the cold photolysate in the dark. With 11,12-dimethylene-9,10-dihydro-9,10-ethanoanthracene as the 1,3-diene, a crystalline cycloadduct of *trans*-**1** was obtained in 8% yield, and its structure was determined by X-ray crystallography.

While strained trans isomers of six- and seven-membered ring cycloalkenes have been studied by a variety of methods, including chemical trapping,[1,2] laser flash photolyses,[3] and time-resolved photoacoustic calorimetry,[4] only *trans*-cycloheptene has been characterized by low-temperature NMR spectroscopy.[5] *trans*-Cycloheptene is nonetheless unstable with respect to *E*,*Z* isomerization[1,5b] and highly reactive towards strong acid.[1] When generated photochemically from its cis isomer in acidified methanol, acid-catalyzed addition of solvent rapidly occurs to form the methyl ether as a product.[1,6,7] We have been interested in establishing the intermediacy of silicon analogues of *trans*-cycloalkenes in photoalcoholyses of flexible, medium-ring 1,4-disilacycloalk-2-enes, because excited-state protonation could not be excluded as an alternate mechanism for photoalcoholyses of 1,1,3,3-tetramethyl-1,3-disilacyclopent-4-ene.[8] We now report kinetic and trapping evidence in support of a metastable *trans*-cycloalkene intermediate in photoalcoholyses of 1,1,4,4-tetramethyl-1,4-disilacyclohept-2-ene (**1**).

Results and Discussion

Direct photolyses of 10^{-2} M solutions of disilacycloheptene **1** in deoxygenated methanol containing 0.005 M sulfuric acid at 214 nm with a Philips zinc lamp gave alcohol addition products **2** and **3**, as shown in eq 1. These adducts with methanol were also obtained in 254-nm sensitized photolyses using 0.8 M *p*-xylene or 0.07 M methyl benzoate as triplet[9] and singlet[10] sensitizers, respectively. Chemical yields determined by GC analyses are summarized in Table I. Products **2** and **3** were isolated by preparative GC and identified spectroscopically; in the case of **2** an authentic sample was independently synthesized for comparison.



1 2 3 (1)

direct (0.005 M acid) $\phi = 0.179$ $\phi = 0.033$
p-xylene sens (0.012 M acid) $\phi = 0.130$ $\phi = 0.028$

Quantum yields for 214-nm direct and 254-nm *p*-xylene-sensitized photolyses of **1** in 0.005 M or 0.012 M sulfuric acid in methanol (eq 1) were determined by using uranyl oxalate actinometry at both wavelengths, as described previously.[11] The formation of adducts **2** and **3** required catalytic amounts of strong acid in the medium. Rigorous exclusion of acid by distillation of the methanol from magnesium methoxide[2] led to ≤1% yields of **2** and **3**, and less efficient photoprocesses assumed greater relative importance.

Table I. Yields of Direct, *p*-Xylene, and Methyl Benzoate Photolyses of Disilacycloheptene **1**

run	reactant 1 mmol	additive	*T*, °C	solvent	yield, % 1	2	3
direct	0.565	none	2	MeOH[a]	36	54	11
triplet	1.39	*p*-Xylene	2	MeOH[a]	30	47	13
singlet	1.09	$PhCO_2Me$	2	MeOH[a]	53	44	9
trapping	0.624	$PhCO_2Me$	−75	MC[b]	65	13	4

[a] Runs contained 0.005 M H_2SO_4. [b] Run performed with methylcyclohexane (MC) as the solvent. Aliquot added to 0.005 M H_2SO_4 in MeOH in the dark.

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(1) (a) Inoue, Y.; Ueoka, T.; Kuroda, T.; Hakushi, T. *J. Chem. Soc., Chem. Common.* **1981**, 1031. (b) Inoue, Y.; Ueoka, T.; Kuroda, T.; Hakushi, T. *J. Chem. Soc., Perkin Trans. 2* **1983**, 983.

(2) Dauben, W. G.; van Riel, H. C. H. A.; Robbins, J. D.; Wagner, G. J. *J. Am. Chem. Soc.* **1979**, *101*, 6383.

(3) (a) Bonneau, R.; Joussot-Dubien, J.; Salem, L.; Yarwood, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 4329. (b) Bonneau, R.; Joussot-Dubien, J.; Yarwood, A. J.; Peyeyre, J. *Tetrahedron Lett.* **1977**, 234. (c) Bonneau, R. *J. Photochem.* **1987**, *36*, 311.

(4) Goodman, J. L.; Peters, K. S.; Misawa, H.; Caldwell, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 6803.

(5) (a) Wallraff, G. M.; Michl, J. *J. Org. Chem.* **1986**, *51*, 1794. (b) Bergman, A.; DeFilippis; Squillacote, M. E. *Abstracts of Papers*; 197th American Chemical Society Meeting, Dallas, Texas, April 9–14, 1989; American Chemical Society: Washington, DC, 1989; Abstract No. 245.

(6) Kropp, P. J. *J. Am. Chem. Soc.* **1969**, *91*, 5783.

(7) (a) Kropp, P. J. *Org. Photochem.* **1979**, *5*, 1. (b) Steinmetz, M. G. *Ibid.* **1987**, *8*, 67.

(8) Steinmetz, M. G.; Langston, M. A.; Mayes, R. T.; Udayakumar, B. S. *J. Org. Chem.* **1986**, *51*, 5051.

(9) (a) See also ref 8. (b) Snyder, J. J.; Tise, F. P.; Davis, R. D.; Kropp, P. J. *J. Org. Chem.* **1981**, *46*, 3609.

(10) (a) Inoue, Y.; Takamuku, S.; Kunitomi, T.; Sakurai, H. *J. Chem. Soc., Perkin 2* **1980**, *2*, 1672. (b) Inoue, Y.; Matsumoto, N.; Hakushi, T.; Srinivasan, R. *J. Org. Chem.* **1981**, *46*, 2267.

(11) (a) Steinmetz, M. G.; Udayakumar, B. S.; Gordon, M. S. *Organometallics* **1989**, *8*, 530. (b) Forbes, G. S.; Heidt, L. J. *J. Am. Chem. Soc.* **1934**, *56*, 2363. (c) Leighton, W. G.; Forbes, G. S. *Ibid.* **1930**, *52*, 3139. (d) Pitts, J. N.; Margerum, J. D.; Taylor, R. P.; Brim, W. *Ibid.* **1955**, *77*, 5499.

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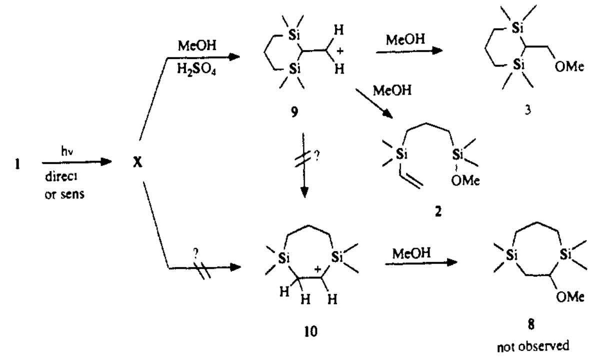
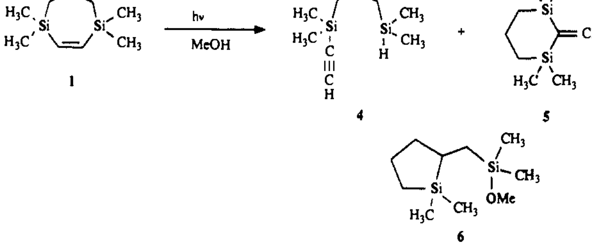
Scheme I

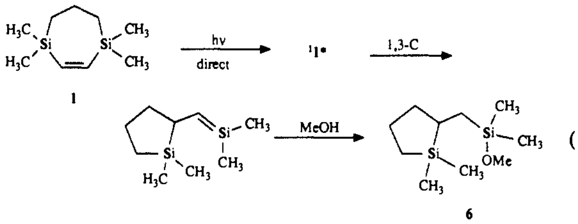


Photolysis of 10^{-2} M disilacycloheptene **1** at 214 nm with "acid-free" methanol (distilled from magnesium methoxide) as the solvent (eq 2) gave 2% of alkyne **4**, 3% of 2-methylenedisilacyclohexane **5**, and 16% of a methanol adduct identified as 2-[(methoxydimethylsilyl)methyl]-1,1-dimethyl-1-silacyclopentane (**6**), in addition to 31% unreacted **1** and 2% of 1,3-bis(methoxydimethylsilyl)propane (**7**).[12] Capillary GC–MS analysis also revealed six dimeric products of reactant **1**. The volatile products were isolated by preparative GC and identified by comparison of spectral data to independently synthesized samples (Experimental Section). Low yields (0.2–1% each) of **4–6** were generally observed in acid-catalyzed direct photolyses, as described in the Experimental Section. Controls showed that **1–5** were stable for at least 22 h and **6** was stable for at least 3 h in the presence of 0.005 M sulfuric acid in methanol (Experimental Section).



(2)

The qualitative dependence of the yields of **2** and **3** on the presence of strong acid suggests a mechanism for methanol addition to **1** resembling that for acid-catalyzed photoalcoholyses of medium-ring carbocyclic alkenes (Scheme I). Although two carbocations, **9** and **10**, can be envisioned as potential intermediates, cation **9** is expected to assume a more important role in the formation of **2** and **3** as a result of additional hyperconjugative stabilization of positive charge afforded by the second β silyl group.[13] Potential mechanisms for the formation of **4** and **5** have been discussed previously with regard to analogous products formed in photolyses of 1,1,3,3-tetramethyl-1,3-disilacyclopentene.[8] A reasonable mechanism for the formation of methanol adduct **6** involves excited state 1,3-C migration followed by nucleophilic addition of methanol to the resultant silene intermediate, as shown in eq 3.[14]



(3)

Kinetic evidence for a ground-state intermediate as species X in Scheme I was provided by plots of reciprocal quantum yield (ϕ^{-1}) of **2** or **3** against reciprocal acid ($[H_2SO_4]^{-1}$) for concentrations of acid ranging from 1×10^{-4} M to 1×10^{-2} M. From these plots the ratio of intercept/slope, $k_H\tau$, was obtained, where τ is the lifetime of the species trapped through protonation and k_H is the rate of protonation.[2] Since the $k_H\tau$ values of products **2** and **3** were comparable for the direct ($k_H\tau = (1.5–2.1) \times 10^4$ M^{-1}) and p-xylene-sensitized ($(1.4–1.8) \times 10^4$ M^{-1}) photolyses, a common ground-state intermediate appeared to be involved in both the singlet and triplet reactions.[15] The trapping studies described below, employing methyl benzoate as a singlet sensitizer, implicate a long-lived ground-state intermediate, which we believe could account for the higher $k_H\tau$ values observed for **1** compared to cycloheptene (770 M^{-1} [1b]).

Inoue and co-workers have reported that a methyl ether is formed in 15–16% yield upon addition of acid to cold methanolic solutions of *trans*-cycloheptene, produced through low temperature photolyses of its cis isomer with methyl benzoate as a singlet sensitizer.[1b] Similar trapping experiments with **1** provided evidence for an analogous *trans*-cycloalkene intermediate as the precursor to adducts **2** and **3**. Solutions of 10^{-1} M **1** and 0.07 M methyl benzoate in 50 mL of methylcyclohexane were irradiated with a 12-W Philips low-pressure mercury lamp (254 nm) at −75 °C under argon.[12] After 2–3 h aliquots were siphoned into cold, deoxygenated 0.005 M acidic methanol. Workup with pentane followed by GC analysis showed 11–16% yields of **2** plus **3** in a ca. 3:1 ratio, no detectable **6**, and only traces of **4** and **5**. The combined yield of products **2** and **3** was only ca. 0.6% in control runs whereby −75 °C photolysates were warmed and then kept at 20 °C for at least 8 h before addition to acidic methanol.

The intermediate giving rise to **2** and **3** in the above trapping experiments did not decay by simple first-order kinetics. The half-life of this species depended on its initial concentration, and successive half-lives became longer as decay progressed. The half-life of 0.00212 M intermediate in methylcyclohexane was 101 min at 20 °C, as determined by GC analyses of **2** and **3** in aliquots treated with acidified methanol, with the assumption that the concentration of adducts was proportional to the concentration of intermediate. The decay followed second-order kinetics (k = 0.078 M^{-1} s^{-1}, R = 0.9983), consistent with dimerization of two molecules of *trans*-**1**. In contrast, *trans*-cycloheptene has been reported to decay via unimolecular E,Z isomerization (half-life 45 s, extrapolated to 25 °C[1b]).

GC–MS analyses showed that as the decay of *trans*-**1** progressed, a mixture of six dimers of m/z 368 formed. In attempts to obtain sufficient amounts of dimeric material for characterization, we performed methyl benzoate photolyses at 2 °C in methylcyclohexane. The dimers were produced in a somewhat different ratio (Experimental Section), but with the same fragmentation patterns as found upon warming of photolysates of the low-temperature photolyses. Only one of the dimeric products was successfully isolated in pure form by preparative GC. ^{13}C

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(12) 1,3-Bis(methoxydimethylsilyl)propane (**7**) is believed to derive from photooxidation of **1** and further reaction of the oxidation products with methanol. In early trapping experiments involving −75 °C photolysis of **1** in pentane as the solvent, two oxidation products of m/z 200 formed. Siphoning of aliquots into methanol led to their disappearance, and **7** was observed instead, whereas addition of aliquots to acidified methanol gave a cyclic siloxane, 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane. Oxidation was minimized by using a solvent of higher viscosity, methylcyclohexane, rather than pentane in subsequent trapping experiments.

(13) (a) Ibrahim, M. R.; Jorgenson, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 819. (b) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *Ibid.* **1985**, *107*, 1496. (c) Li, X.; Stone, J. A. *Ibid.* **1989**, *111*, 5586. (d) Lambert, J. B.; Wang, G.; Finzel, R. B.; Teramura, D. H. *Ibid.* **1987**, *109*, 7838. (e) Lambert, J. B.; Finzel, R. B. *Ibid.* **1982**, *104*, 2020.

(14) (a) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (b) Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1.

(15) This conclusion is subject to two assumptions. Protonation of both the singlet and triplet excited states could also give rise to similar $k_H\tau$ values. Since τ and k_H are expected to differ, depending on multiplicity, this possibility seems unlikely. We could not test direct involvement of the singlet excited state by fluorescence quenching, since **1** exhibited no detectable fluorescence. Alternatively, a triplet pathway common to both the direct and p-xylene-sensitized photolyses could give rise to the similar $k_H\tau$ values, if the quantum yield for intersystem crossing of **1** is near unity. Although this is testable, in principle, through quenching studies, such experiments can be inconclusive, e.g., when the triplet is too short-lived to be quenched. In direct photolyses of **1** no quenching is observed with 0.01 M *trans,trans*-1,4-diphenyl-1,3-butadiene as an additive, after correcting for the reduction in efficiency attributable to competitive absorption of light by quencher. In addition, no quenching is detected when photolysates are saturated with oxygen.

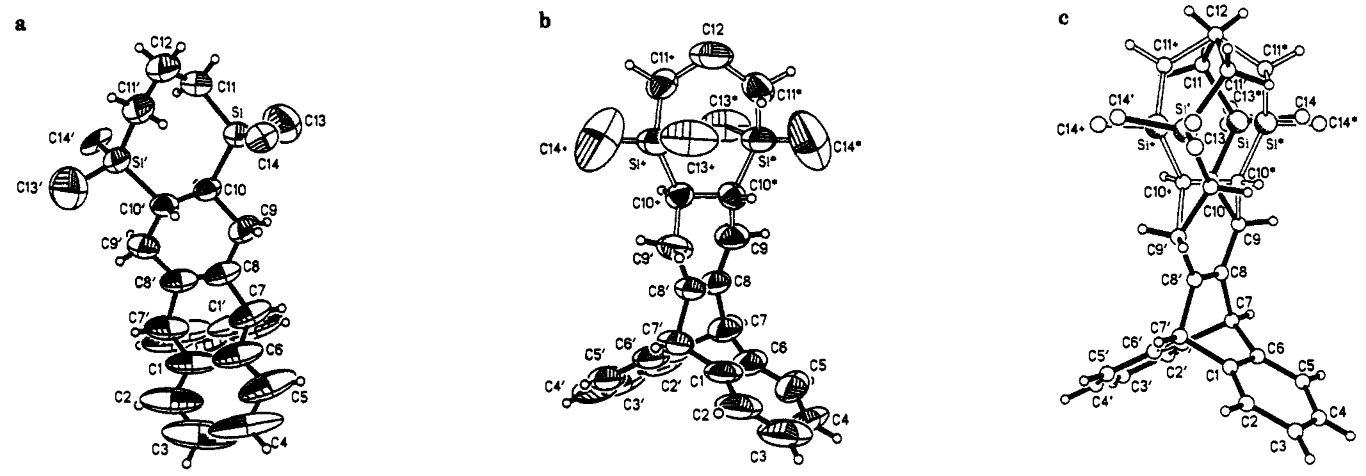
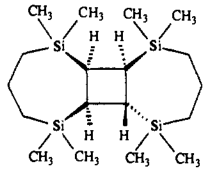


Figure 1. (a) ORTEP view of the major enantiomer of **14**; (b) minor enantiomer; and (c) ball and stick composite of both enantiomers situated about the crystallographic C_2-axis at $^1/_2,y,^1/_4$ in the unit cell. Atoms labeled with a prime (′) are related to those labeled without a prime and those labeled with a plus ($^+$) are related to those with an asterisk (*) by the crystallographic C_2-axis, which passes through carbon atom C_{12} and bisects C_8–$C_{8'}$, C_{10}–$C_{10'}$, and C_{10^*}–C_{10^+} bonds. Hydrogen atoms are omitted for the minor isomer at carbon atoms C_9 and C_{12} as well as for all terminal methyl groups of both enantiomers.

NMR (APT) spectroscopy showed one peak for each carbon in the molecule (Experimental Section), including the four methine carbons, which were nonequivalent. This dimer was thus assigned the unsymmetrical cis,trans-fused cyclobutane structure **11**.[16] ^{1}H and ^{13}C NMR spectroscopy suggested that the major dimeric component was olefinic. However, the presence of an impurity precluded reliable analysis of the spectral data.



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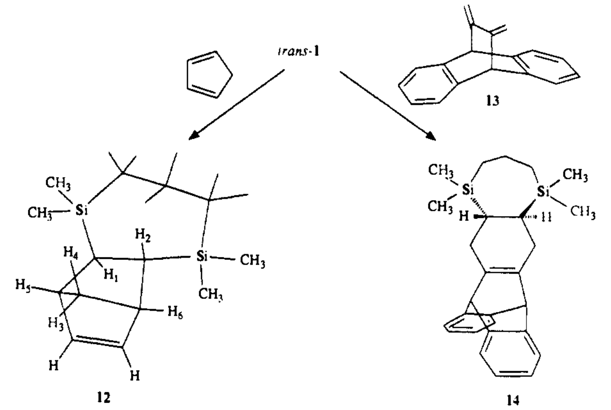
The identity of the metastable intermediate in the low-temperature photolyses was assigned as *trans*-**1** from low-temperature trapping experiments utilizing Diels–Alder cycloaddition with cyclopentadiene and 9,10-dihydro-11,12-dimethylene-9,10-ethanoanthracene **13**[17] (Scheme II) as the 1,3-dienes. Either a methylcyclohexane solution of cyclopentadiene or an ethereal methylcyclohexane suspension of **13** was added to cold photolysates in the dark after conducting the methyl benzoate sensitized photolyses of **1** in methylcyclohexane at −75 °C. The yield of cycloadduct **12** was 11% by GC analysis, whereas **14** was isolated in 8% yield after purification, which involved removal of excess **13** by reaction with maleic anhydride, followed by base hydrolysis of the anhydrides and extractive workup. Before adding 1,3-diene **13**, an aliquot siphoned from the photolysate into acidified methanol showed a 10% total yield of adducts **2** plus **3** by GC analysis.

^{1}H and ^{13}C NMR spectra of **12** indicated an unsymmetrical structure with a trans ring fusion. Distortion of the bicyclic ring led to an increase in the H_1–C–C–H_2 dihedral angle to 153° (Scheme II) according to molecular mechanics calculations.[18] This accounted for the unusually large 8.8 Hz coupling observed for the H_1 and H_2 protons,[19] which appeared as doublets at δ 0.40 and 1.05, respectively. Decoupling experiments showed H_2 to be further coupled to H_6 by 2.7 Hz, while H_1 exhibited a small 1.1 Hz *W* coupling to H_3.[20] The lack of appreciable coupling of H_1 to H_5 was consistent with the 88° H_1–C–C–H_5 dihedral angle of the calculated structure; H_2–C–C–H_6 was 62°.

Scheme II



The structure of cycloadduct **14** was determined by X-ray crystallography. Cocrystallization of two enantiomeric C_2-forms of **14** produced a disordered solid-state structure composed of a predominant (74%) enantiomer (Figure 1a) and a minor (26%) enantiomer (Figure 1b). Nonetheless, both structures could be refined satisfactorily. Each cycloadduct clearly exhibited trans-fused cyclohexene and disilacycloheptane rings. In addition, ^{1}H and ^{13}C NMR spectra were obtained, utilizing a heterocorrelated 2D spectrum to make assignments. The spectra were consistent with a symmetrical structure having chemically equivalent methine protons at carbons C_{10} in Figure 1, and irradiation of the allylic methylene protons of the cyclohexene ring collapsed the methine multiplet at δ 0.68–0.72 to a singlet.

The diminished reactivity of *trans*-**1** with respect to *E,Z* isomerization is possibly attributable to thermodynamic stabilization of *trans*-**1** relative to its cis isomer by relief of steric in-

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(16) The four possible remaining cyclobutane dimers have two-fold symmetry.

(17) (a) The use of 9,10-dihydro-11,12-dimethylene-9,10-ethanoanthracene[17b,c] for Diels–Alder trapping was suggested by a referee. (b) Eaton, P. E.; Maggini, M. *J. Am. Chem. Soc.* **1988**, *110*, 7230. (c) Hart, H.; Bashir-Hashemi, A.; Luo, J.; Meador, M. A. *Tetrahedron* **1986**, *42*, 1641.

(18) The molecular mechanics calculations were performed with the program MMP2(85), which was obtained from QCPE, Department of Chemistry, Indiana University, Bloomington, IN 47005.

(19) Coupling constants were estimated by the Karplus correlation: Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1981; p 210.

(20) (a) As with the H_3 and H_4 protons of cycloadduct **12**, in norbornene the bridging methylene proton that is syn to the double bond appears downfield from the anti methylene proton; this syn proton also experiences a small *W* coupling with the endo protons of the C_2 bridge.[20b–e] (b) Marchand, A. P. *Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems*; Verlag Chemie: Deerfield Beach, FL, 1982; p 30. (c) Marchand, A. P.; Rose, J. E. *J. Am. Chem. Soc.* **1968**, *90*, 3724 and references cited therein. (d) Franzus, B.; Baird, W. C.; Chamberlain, N. F.; Hines, T.; Snyder, E. I. *Ibid.* **1968**, *90*, 3721. (e) Tori, K.; Aono, K.; Hata, Y.; Muneyuki, R.; Tsuji, T.; Tanida, H. *Tetrahedron Lett.* **1966**, 9.

teractions[21] between the dimethylsilyl groups in the unsymmetrical chair conformation. The MNDO[22] calculated difference in $\Delta H_f°$ of 23.6 kcal mol^{-1} for *cis*- and *trans*-**1** (−63.57 kcal mol^{-1} (trans) and −87.16 kcal mol^{-1} (cis)) is comparable to, if not less than, cycloheptene (25.1 kcal mol^{-1} [23,24]). Our MNDO calculations also show 1.5–2.7° increases in the Si—C═C bond angles with 4–5° reductions in the C–Si–C bond angles of *trans*-**1** compared to the carbocyclic analogue. Thus, stabilization could alternatively result from relief of angle strain at the double bond, to the extent that silicon can accommodate bond angles approaching 90° elsewhere in the molecule.[25]

Experimental Section

Spectra were recorded with the following spectrometers: Varian EM 360 L (60 MHz, ^{1}H NMR), GE QE-300 and GN-300 (300 MHz ^{1}H, 75 MHz ^{13}C NMR), JOEL FX 60 Q (15 MHz, ^{13}C NMR), Analect FX-6200 (FTIR), and Perkin-Elmer 320 (UV). A Hewlett Packard 5890 GC and HP-5970 mass selective detector were used for GC–MS analyses, which were performed at 70 eV with a 0.25 mm × 30 m DB-1 capillary column programmed at 35 °C for 4 min and then 250 °C at 10 °C min^{-1}.

Preparative GC separations were performed on a Gow-Mac Series 580 gas chromatograph with He as carrier gas at 30 mL min^{-1} flow rate on the following columns: column A, 9 ft × $^1/_4$ in. 15% didecyl phthalate on 80/100 mesh Chromosorb P, column B, 7 ft × $^1/_4$ in. 10% OV-101 on 60/80 mesh Chromosorb W, column C, 10 ft × $^1/_4$ in. 10% OV-7 on 60/80 mesh Chromosorb PAW.

A Varian 1400 gas chromatograph equipped with a flame-ionization detector and an HP 3390A electronic integrating recorder was used for analytical separations. Nitrogen was the carrier gas at a flow rate of 30 mL min^{-1}. Detector response was calibrated against standard mixtures on the following columns: column D, 12 ft × $^1/_8$ in 10% didecyl phthalate on 100/120 mesh Supelcoport, column E, 22 ft × $^1/_8$ in. 10% OV-101 on 100/120 mesh Supelcoport.

Methanol (CMS, Chempure, distilled from magnesium methoxide) and methylcyclohexane (Aldrich, 99% pure) were used as solvents in photolyses. Ethynyldimethyl[3-(dimethylsilyl)propyl]silane (**4**),[26] 2-methylene-1,1,3,3-tetramethyl-1,3-disilacyclohexane (**5**)[26] and 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane (**15**)[27] were synthesized by literature methods.

1,1,4,4-Tetramethyl-1,4-disilacyclohept-2-ene (7).[28] Acetylene was passed through a 1 m × 2.5 cm column of activated alumina and bubbled into a nitrogen prepurged, refluxing solution of 11.2 g of 80% pure 1,1,2,2-tetramethyl-1,2-disilacyclopentane[27] containing ca. 20% of 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane (**15**), which was a byproduct from the previous synthetic step,[27] and 0.70 g (1.0 mmol) of bis(triphenylphosphine)palladium(II) chloride in 200 mL of dry benzene (distilled from sodium). The reaction required 5 h. Most of the benzene was then removed by short-path distillation at reduced pressure (32 °C, 120 mm). The concentrated mixture was filtered, the Pd(0) precipitate was washed with 20 mL of pentane, which was combined with the filtrate. After distillation of the solvent further distillation of the residue through a 6-in. Vigreaux column gave 6.77 g (66% yield, corrected for 80% pure starting material) of NMR pure 1,1,4,4-tetramethyl-1,4-disilacyclohept-2-ene (**1**),[28] bp 66–67 °C (12 mm). The MS, ^{1}H NMR, and IR data matched previously reported spectra.[28] The UV spectrum was as follows: λ_{max} (pentane) < 200 nm, shoulder 228 nm (ϵ 1110). Prior to photolyses the disilacycloheptene was subjected to preparative GC on column A at 140 °C.

Ethenyldimethyl[3-(methoxydimethylsilyl)propyl]silane (2). To 625 mg (0.0257 g-atom) of magnesium was added a portion of a solution of 3.42 g (21.0 mmol) of (chloropropyl)dimethylvinylsilane (Huls–Petrarch) in 10 mL of tetrahydrofuran. The mixture was heated to initiate the reaction, the remainder of the (chloropropyl)dimethylvinylsilane solution was added dropwise, and the reaction mixture was refluxed 45 min. A solution of 5.4 mL (5.8 g, 44 mmol) of dichlorodimethylsilane in 10 mL tetrahydrofuran was added dropwise. The reaction mixture was refluxed an additional 12 h and then cooled and filtered. After the tetrahydrofuran was removed by distillation through a 30-cm Vigreaux column, benzene was added, followed by suction filtration and distillation of the solvent. Spinning-band distillation of the residue at 84–85 °C (40 mm) gave 803 mg (17% yield) of [3-(chloromethylsilyl)propyl]ethenyldimethylsilane, which was carried on to the next step without further purification.

A mixture of 803 mg (3.64 mmol) of [3-(chlorodimethylsilyl)propyl]ethenyldimethylsilane, 0.20 mL (4.9 mmol) of methanol, 0.48 mL (4.1 mmol) of quinoline, and 3 mL of pentane was refluxed for 18 h. The cold mixture was then washed three times with 3 mL of water, three times with 2 mL of 5% hydrochloric acid, and once with 3 mL of saturated sodium chloride and dried over anhydrous sodium sulfate. After distillation of the pentane, short-path distillation of the residue at 85–88 °C (10 mm) gave 560 mg (71% yield) of ethenyldimethyl[3-(methoxydimethylsilyl)propyl]silane (**2**). The product was further purified by preparative GC on column A at 115 °C. Spectral data were as follows: ^{1}H NMR (CCl$_4$) δ 0.07 and 0.10 (overlapping singlets, 12 H, methyl), 0.64 (m, 4 H, methylene), 1.37 (m, 2 H, methylene), 3.41 (s, 3 H, methoxy), 5.34–6.47 (m, ABC pattern, 3 H, vinyl); ^{13}C NMR (CDCl$_3$, ppm) −3.3, −2.5, 17.6, 19.7, 20.5, 50.1, 131.2, 139.2; IR (CCl$_4$) 3.28, 3.38, 3.43, 3.53, 7.11, 8.00, 8.40, 8.76, 9.17, 10.52, 11.02, 12.03 μm; GC–MS *m/z* (relative intensity) no parent, 201 (21), 173 (23), 101 (18), 89 (100), 88 (10), 85 (34), 84 (8), 59 (81), 58 (13), 45 (12), 43 (18), 31 (10). Anal. Calcd for $C_{10}H_{24}OSi_2$: C, 55.49; H, 11.17. Found: C, 55.02; H, 10.80.

2-(Methoxydimethylsilyl)methyl-1,1-dimethyl-1-silacyclopentane (6). To a stirred mixture of 821 mg (6.51 mmol) of 1,1-dimethyl-2-methylene-1-silacyclopentane[26] and 26.4 mg (0.051 mmol) of chloroplatinic acid under nitrogen was added, dropwise, over a period of 15 min, 672 mg (7.10 mmol) of neat dimethylchlorosilane. Stirring was continued for an additional 2 h, after which excess dimethylchlorosilane was removed by distillation. The crude product was extracted with 10 mL of pentane. Distillation of the pentane gave 1.14 g of crude 1,1-dimethyl-2-[(chlorodimethylsilyl)methyl]-1-silacyclopentane, which was used without further purification in the next step. The GC–MS spectral data were as follows: retention time 13.4 min, *m/z* (relative intensity) 220 (5), 205 (8), 178 (7), 177 (5), 164 (5), 151 (6), 127 (90), 111 (23), 99 (131), 95 (23), 93 (54.0), 85 (22), 78 (7), 73 (21), 65 (29), 59 (100), 53 (4), 43 (57).

A solution of 1.14 g (5.18 mmol) of 1,1-dimethyl-2-[(chlorodimethylsilyl)methyl]-1-silacyclopentane in 5 mL of pentane was added dropwise to a mixture of 1.00 g (7.78 mmol) of quinoline and 0.250 mL (197 mg, 6.17 mmol) of methanol with stirring under nitrogen. The reaction mixture was refluxed overnight. After cooling the reaction mixture with an ice bath 25 mL of pentane and 25 mL of water were added. The organic fraction was separated and the aqueous phase was extracted with 10 mL of pentane. The combined organic phases were washed five times with 25 mL of water, once with 5% HCl, and once with saturated sodium chloride and dried over anhydrous sodium sulfate. Distillation of the pentane gave 1.01 g of 1,1-dimethyl-2-[(methoxydimethylsilyl)methyl]-1-silacyclopentane (**6**), which was purified by preparative GC on column C at 155 °C. The spectral data were as follows: ^{1}H NMR (60 MHz, CCl$_4$) δ 0.006, 0.040, 0.073 (three overlapping singlets, 12 H, methyl), 0.47 to 2.10 (complex multiplets, 9 H, methylene and methine), 3.34 (s, 3 H, methoxy); ^{13}C NMR (15 MHz, CDCl$_3$) δ −3.48, −1.66 (two overlapping peaks), −1.34, 12.1, 15.4, 19.7, 23.9, 37.2, 48.9; IR (CCl$_4$) 3.38, 3.41, 3.50, 3.53, 6.89, 7.09, 7.99, 8.40, 9.15, 11.9, 12.3, 12.57 μm; GC–MS, retention time 13.0 min, *m/z* (relative intensity) 216 (3), 201 (12), 187 (49), 174 (49), 173 (62), 160 (8), 147 (4), 133 (16), 127 (3), 111 (10), 99 (28), 98 (10), 97 (6), 89 (100), 73 (11), 59 (88), 55 (4), 45 (11), 43 (19). Anal. Calcd for $C_{10}H_{24}OSi_2$: C, 55.49; H, 11.18. Found: C, 55.64; H, 11.01.

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(21) A similar rationale was employed in an attempted by Jendralla to synthesize a kinetically stable *trans*-cycloheptene: Jendralla, H. *Tetrahedron Lett.* **1982**, *23*, 3657.

(22) (a) The calculations used the MNDO Hamiltonian[22b] implemented in AMPAC (QCPE program no. 506). Our version had the revised MNDO parameters for silicon.[22c] (b) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (c) Dewar, M. J. S.; Friedheim, J.; Grady, G.; Healy, E. F.; Stewart, J. J. P. *Organometallics* **1986**, *5*, 375.

(23) Relative to $\Delta H_f° = -1.8$ kcal mol^{-1} of *cis*-cycloheptene: Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377.

(24) Wallraff, G. M.; Boyd, R. H.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 4550.

(25) (a) Grev, R. S.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1987**, *109*, 6569. (b) Cherry, W.; Epiotis, N.; Borden, W. T. *Acc. Chem. Res.* **1977**, *10*, 167. (c) Chandrasekhar, J.; Schleyer, P. v. R. *J. Organomet. Chem.* **1985**, *289*, 51. (d) Gordon, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 7419. (e) In some respects the situation also resembles that of silacyclobutane, for which the longer Si–C bond distances and smaller apical angle to silicon are compensated in part by an increase in the CH_2–CH_2–CH_2 bond angle.[25f] Its strain energy is comparable to cyclobutane.[25g,h] A similar effect appears to be operative in silacyclopropene, which is calculated to be less strained than cyclopropene.[25d] (f) Eckert-Maksic, M.; Kovacevic, K.; Maksic, Z. B. *J. Organomet. Chem.* **1979**, *168*, 295. (g) Gusel'nikov, L. E.; Nametkin, N. S. *Ibid.* **1979**, *169*, 155. (h) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

(26) Steinmetz, M. G.; Udayakumar, B. S. *J. Organomet. Chem.* **1989**, *378*, 1.

(27) Kumada, M.; Tamao, K.; Takubo, T.; Ishikawa, M. *J. Organomet. Chem.* **1967**, *9*, 43.

(28) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1975**, *97*, 931.

(29) Ishikawa, M.; Kumada, M.; Sakurai, H. *J. Organomet. Chem.* **1970**, *23*, 63.

1,3-Bis(Methoxydimethylsilyl)propane (7). To a solution of 1.60 mL (1.26 g, 39.5 mmol) of methanol and 5.10 g (39.5 mmol) of quinoline in 10 mL of pentane was added dropwise 3.00 g (13.2 mmol) of 1,3-bis(chlorodimethylsilyl)propane[29] with stirring under nitrogen. After 2 h of reflux the reaction mixture was cooled in an ice bath and filtered to remove salts. The filtrate was diluted with 15 mL of pentane, washed seven times with 50 mL of cold water and once with saturated sodium chloride solution, and dried over anhydrous sodium sulfate. Distillation of the pentane gave 3.00 g of crude 1,3-bis(methoxydimethylsilyl)propane (**7**) contaminated with quinoline, which was removed by preparative GC on column A at 140 °C. The spectra data were as follows: ^{1}H NMR (60 MHz, CCl_4) δ 0.006 (s, 12 H, methyl), 0.42–0.74 (m, 4 H, methylene), 1.04–1.60 (m, 2 H, methylene), 3.32 (s, 6 H, methoxy); IR (CCl_4), 3.38, 3.43, 3.53, 7.98, 8.40, 8.75, 9.15, 10.12, 11.03, 12.03, 12.49, 12.57, 12.70, 12.87, 13.59 µm; GC–MS (70 eV), retention time 12.4 min, *m/z* (relative intensity), no parent, 205 (18), 188 (22), 177 (11), 173 (10), 163 (4), 159 (3), 147 (2), 131 (2), 115 (2), 105 (26), 101 (2), 99 (4), 91 (4), 89 (100), 88 (16), 75 (8), 73 (7), 72 (5), 59 (75), 55 (2), 43 (12). Anal. Calcd for $C_9H_{24}O_2Si_2$: C, 49.03; H, 10.97. Found: C, 48.84; H, 11.16.

General Procedure for Preparative Direct Photolyses. Direct photolyses at 214 nm were performed with a quartz immersion well apparatus of 55 mL volume, utilizing an air-cooled 16-W Philips zinc lamp as the source of light. Photolyses at 254 nm were performed with an air-cooled 12-W Philips low-pressure mercury lamp. Photolysates were purged with nitrogen or argon 1 h prior to and during photolyses, and the temperature was maintained at 2 °C with a constant temperature bath. For the low-temperature runs the apparatus consisted of a quartz Dewar insert and pyrex outer vessel, and the photolysates were purged for 90 min with argon (delivered through copper tubing via an Alltech Associates Oxy-Trap) prior to and during irradiations. Runs were performed with methanol distilled from magnesium methoxide or with methanol containing 0.005 M sulfuric acid.

Determination of Photochemical Product Yields of Photolyses Conducted with Methanol or Acidified Methanol as the Solvent. Solutions of 0.010–0.045 M of 1,1,4,4-tetramethyl-1,4-disilacyclohept-2-ene (**1**) and nonane or tridecane as internal standard with either methanol or methanol containing 0.005 M sulfuric acid were irradiated following the general procedure for photolyses. Aliquots taken at time intervals were diluted with 0.5 mL of pentane and washed five times with 1 mL of water prior to GC analyses. GC analyses were performed on column D (95 °C) to quantify unreacted disilacycloheptene **1** (retention time 29.5 min), ethenyldimethyl[3-(methoxydimethylsilyl)propyl]silane (**2**) (retention time 44.4 min), 2-(methoxymethyl)-1,1,3,3-tetramethyl-1,3-disilacyclohexane (**3**) (retention time 71.0 min), ethynyldimethyl[3-(dimethylsilyl)propyl]silane (**4**)[26] (retention time 17.8 min), 2-methylene-1,1,3,3-tetramethyl-1,3-disilacyclohexane (**5**)[26] (retention time 23.3 min), 1,1-dimethyl-2-[(methoxydimethylsilyl)methyl]-1-silacyclopentane (**6**) (retention time 61.8 min), 1,3-bis(methoxydimethylsilyl)propane (**7** (retention time 51.0 min), and 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane (**15**)[27] (retention time 6.80 min). Detector response was calibrated with standard solutions of authentic samples, except for methanol adduct **3**, for which the detector response of **2** was used. Identities of peaks were checked by coinjection of authentic samples of **1**, **2**, and **4–7** and **15** for each analytical column used.

Direct Photolysis (214 nm) of 1,1,4,4-Tetramethyl-1,4-disilacyclohept-2-ene (1) in Acidified Methanol. The general procedures for photolysis and product analysis were used (vide supra). A solution of 104 mg (0.565 mmol) of disilacycloheptene **1** and 12 mg of nonane in 55 mL of methanol containing 0.005 M sulfuric acid and was irradiated for 2 h. Absolute yields of product formation are given in Table I. In addition to unreacted **1** (36% yield), ethenyldimethyl[3-(methoxydimethylsilyl)-propyl]silane (**2**) (54% yield) and 1,1,3,3-tetramethyl-2-(methoxymethyl)-1,3-disilacyclohexane (**3**) (11% yield) were found by GC analysis. Minor products were ethynyldimethyl[3-(dimethylsilyl)propyl]silane (**4**) (0.5% yield), 1,1,3,3-tetramethyl-2-methylene-1,3-disilacyclohexane (**5**) (1% yield), and 1,1-dimethyl-2-[(methoxydimethylsilyl)methyl]-1-silacyclopentane (**6**) (0.2%). No other products were observed by GC or GC–MS. The photolysate was diluted with 50 mL of pentane, washed seven times with 50 mL of cold water and once with saturated sodium chloride solution, and dried over anhydrous sodium sulfate. After distilling the bulk of the solvent, unreacted disilacycloheptene **1** and products **2** and **3** were isolated by preparative GC on column B at 110 °C. Product **2** was identified by comparison of spectral data (^{1}H NMR, IR, GC–MS) to an authentic sample, whereas **3** was only identified spectroscopically (vide infra). An additional run was performed, as above, to obtain sufficient quantities of product **3**. The spectral data for **3** were as follows: ^{1}H NMR (300 MHz, CCl_4) δ –0.01, 0.01 (overlapping singlets, 12 H, methyl), 0.28–2.25 (complex multiplets, 7 H, methylene and methine), 3.23 (s, 3 H, methoxy), 3.50 (d, J = 8 Hz, 2 H, methylene); ^{13}C NMR (75 MHz, $CDCl_3$) δ –4.36, 0.0, 16.0, 17.2, 18.2, 57.6, 71.6; IR (CCl_4) 3.38, 3.46, 3.50, 3.55, 7.25, 7.99, 9.06, 9.71, 10.57, 11.06, 11.99, 12.33, 12.41, 12.74, 12.87, 12.95, 13.13, 13.22 µm; GC–MS retention time 13.4 min, *m/z* (relative intensity) no parent, 201 (13), 187 (14), 174 (20), 173 (38), 160 (9), 133 (8), 111 (5), 101 (17), 99 (6), 89 (100), 85 (18), 72 (45), 71 (7), 59 (68), 58 (8), 45 (14), 43 (17). Anal. Calcd for $C_{10}H_{24}OSi_2$: C, 55.48; H, 11.17. Found: C, 55.30; H, 11.30.

Direct Photolysis (214 mm) of 1,1,4,4-Tetramethyl-1,4-disilacyclohept-2-ene (1) in "Acid-Free" Methanol. A solution of 103 mg (0.559 mmol) of **1** and 10 mg of nonane internal standard in 55 mL of methanol (distilled from magnesium methoxide) was irradiated for 4 h following the general procedure for direct photolyses. After photolysis GC analysis of an aliquot by the general procedure (vide supra) showed unreacted starting material **1** (31% yield), alkyne (**4**) (2% yield), methylenedisilacyclohexane **5** (3% yield), 1,3-bis(methoxydimethylsilyl)propane (**7**) (2% yield), 1,1-dimethyl-2-[(methoxydimethylsilyl)methyl]-1-silacyclopentane (**6**) (16% yield), and methanol adduct **2** (1% yield). Methanol adduct **3** could not be quantified due to its low yield. In addition to products **2–7** GC–MS analyses showed six dimers of **1** at long retention times which exhibited parent ions of *m/z* 368. Two additional photolyses were performed following the above procedure, and the volatile photoproducts were isolated from the combined runs by preparative GC on column B (110 °C). Since products **2** and **7** were obtained as a mixture on column B, final preparative separation was effected with column C (110 °C). Products **2** and **4–7** were identified by comparison of spectral data to authentic samples.

***p*-Xylene-Sensitized Photolysis (254 nm) of 1,1,4,4-Tetramethyl-1,4-disilacycloheptene (1) in Acidified Methanol.** A solution of 256 mg (1.39 mmol) of **1**, 1.99 g (18.7 mmol) of *p*-xylene sensitizer, and 14.0 mg of tridecane as internal standard in 50 mL of methanol containing 0.005 M sulfuric acid was irradiated at 2 °C for 3 h following the general procedure. GC analysis of an aliquot on column E at 95 °C showed unreacted starting material **1** (30% yield), methanol adduct **2** (47% yield), and methanol adduct **3** (13% yield). In addition two minor *p*-xylene addition products with disilacycloheptane **1** (M^+ *m/z* 290) appeared at longer retention times. The photolysate was diluted with 30 mL of pentane, washed five times with 50 mL of cold water and once with saturated sodium chloride solution, and dried over anhydrous sodium sulfate. After distilling the pentane methanol adducts **2**, **3**, and the unreacted disilacycloheptene **1** were isolated by preparative GC on column B at 115 °C and identified by ^{1}H NMR spectroscopy and GC–MS analysis.

Methyl Benzoate Sensitized Photolysis (254 nm) of 1,1,4,4-Tetramethyl-1,4-disilacyclohept-2-ene (1) in Acidified Methanol. A solution of 201 mg (1.09 mmol) of **1**, 548 mg (4.03 mmol) of methyl benzoate, and 19.3 mg of tridecane as internal standard in 50 mL of methanol containing 0.005 M sulfuric acid was irradiated at 2 °C, following the general procedure for photolyses (vide supra). After 10 min of irradiation GC analysis (see standard procedure, vide supra) showed unreacted starting material **1** (78% yield), methanol adduct **2** (18% yield), and methanol adduct **3** (4% yield). No other products, including methanol adduct **6**, which was checked on column E to avoid overlap with methyl benzoate, were detected by GC or GC–MS analyses. The photolysis was performed for a total of 3 h.

The above procedure was performed a second time. After 34 min 53% of unreacted starting material and methanol adducts **2** and **3** (44% and 9% yields, respectively) were found by GC analysis. GC and GC–MS showed no other products including **4–7**, **15**, or dimers of disilacycloheptene **1**. The photolysis was continued for a total of 2.5 h, the photolysate was combined with the previous run, and unreacted **1** and products **2** and **3** were isolated by preparative GC on column B (110 °C) and characterized by ^{1}H NMR, IR, and GC–MS.

Methyl Benzoate Sensitized Photolysis (254 nm) of 1,1,4,4-Tetramethyl-1,4-disilacyclohept-2-ene (1) in Methylcyclohexane. A solution of 201 mg (1.09 mmol) of **1**, 483 mg (3.55 mmol) of methyl benzoate, and 20.5 mg of tridecane as internal standard in 50 mL of methylcyclohexane (Aldrich, 99% pure) was irradiated following the general procedure (vide supra), while maintaining the photolysate at –75 °C with a dry ice–methanol slush bath. After 3.75 h of photolysis, an aliquot was siphoned into methanol containing 0.005 M sulfuric acid (prepurged with argon). The acidified methanol and methylcyclohexane mixture was washed five times with 1 mL of cold water. GC–MS and GC analysis (general procedure for product analysis) showed unreacted disilacycloheptene **1** (66% yield), methanol adduct **2** (8% yield), methanol adduct **3** (3% yield), alkyne **4** (0.4% yield), methylenedisilacyclohexane **5** (0.2% yield), and three products of addition of methylcyclohexane to **1**.

The photolysis apparatus containing the cold photolysate was placed in a constant temperature bath maintained at 20 °C in the dark. Once the photolysate reached constant temperature, aliquots were siphoned into acidified methanol at time intervals, worked up, and analyzed by GC–MS and GC as described above. Over an 8-h period methanol adducts **2** and **3** decreased to 0.6% yield, while six dimeric products of **1** exhibiting *m/z* 368 (M^+, parent) were observed to buildup in the photolysate.

A plot of the reciprocal of the concentration of methanol adducts **2** plus **3** against time gave a straight line (r = 0.9983) with a slope of 0.078 L mol^{-1} sec^{-1} (Figure 2, supplementary material). From the initial concentrations of **2** plus **3** observed at 20 °C (0.00212 M) the second order half-life for the intermediate giving rise to the methanol adducts was calculated to be 101 min.

In a similar run a solution of 115 mg (0.624 mmol) of **1**, 501 mg (3.68 mmol) of methylbenzoate and 19.9 mg of tridecane as internal standard in 55 mL of methylcyclohexane was irradiated at −78 °C, as described above. After 2 h irradiation GC analysis of an aliquot showed unreacted starting material **1** (65% yield), methanol adduct **2** (13% yield), methanol adduct **3** (4% yield), 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane (**15**) (0.4% yield), 1,1,3,3-tetramethyl-2-methylene-1,3-disilacyclohexane (**5**) (0.2% yield), and ethynyldimethyl[3-(dimethylsilyl)propyl]silane (**4**) (0.3% yield), in addition to three methylcyclohexane adducts of **1**. The total yield of **2** and **3** decreased to 0.6% after 14 h at 20 °C with accompanying formation of six dimers of reactant **1** by GC–MS analysis.

Trapping of *trans*-1,1,4,4-Tetramethyl-1,4-disilacyclohept-2-ene with Cyclopentadiene. A solution of 306 mg (1.66 mmol) of **1**, 491 mg (3.60 mmol) of methyl benzoate and 21.3 mg of tridecane as internal standard in 50 mL of methylcyclohexane at −75 °C was irradiated at 254 nm for 4 h following the general procedure described above. Upon completion of the photolysis 6 mL of a precooled, argon-saturated solution of freshly distilled cyclopentadiene in methylcyclohexane (1:1, v/v) was siphoned into the cold photolysate in the dark. After 45 min the cold photolysate was allowed to warm to room temperature. GC–MS analysis showed an adduct of disilacycloheptene and cyclopentadiene at 17.3 min with M^+ (parent ion) *m/z* 250 in addition to unreacted disilacycloheptene **1**, dicyclopentadiene, and small amounts of a methylcyclohexane adduct of **1** as well as six dimers of **1**.

The above procedure was repeated three additional times. Quantitative GC–MS analyses, calibrating the detector with a standard mixture, gave yields of cyclopentadiene adduct ranging from 8% to 11%. The photolysates of the four photolyses were combined and the bulk of the methylcyclohexane and disilacycloheptene were distilled in vacuo. The product mixture was further concentrated by short path distillation of mainly methyl benzoate at 33 °C (ca. 1 mm). The cyclopentadiene adduct was isolated by preparative GC on column B at 148 °C, and a molecular distillation was performed to obtain an analytically pure sample. The spectral data for the cyclopentadiene adduct were as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.24 (s, 3 H, methyl), −0.025 (s, 3 H, methyl), 0.051 (s, 3 H, methyl), 0.075 (s, 3 H, methyl), 0.40 (dd, J = 8.8, 1.1 Hz, 1 H, H_1), 0.53–0.57 (m, 2 H), 0.57 (ddd, J = ca. 15, 9.7, 2.0 Hz, 1 H, partially obscured by upfield multiplet), 0.72 (ddd, J = 15.0, 10.4, 2.3 Hz, 1 H), 1.05 (dd, J = 8.8, 2.7 Hz, 1 H, H_2), 1.09 (br d, J = 7.8 Hz, 1 H, H_4), 1.26 (d of multiplets, J = 7.8 Hz, 1 H, H_3), 1.51–1.80 (br m, 2 H), 2.73 (br s, 1 H, H_5), 3.04 (br s, 1 H, H_6), 5.79–5.82 (m, 1 H), 6.12–6.15 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm −4.60 (CH_3), −4.35 (CH_3), −2.33 (two CH_3), 17.07 (CH_2), 18.70 (CH_2), 19.55 (CH_2), 26.17 (CH), 26.91 (CH), 42.84 (CH), 45.46 (CH), 50.18 (CH_2), 131.34 ($C{=}CH$), 138.20 ($C{=}CH$); IR (CCl_4), 3.38, 3.48, 7.07, 7.50, 8.01, 8.65, 8.90, 9.64, 10.60, 10.93, 11.77, 12.14, 12.95, 13.17, 13.30, 13.40, 13.54, 14.76 μm; MS (70 eV) *m/z* (relative intensity) 250 (41), 235 (3.6), 207 (6.0), 150 (32), 143 (5.0), 141 (9), 135 (57), 123 (11), 109 (17), 99 (15), 95 (10), 91 (15), 83 (19), 79 (95), 72 (100), 59 (87), 43 (49). High-resolution MS-EI calcd for $C_{14}H_{26}Si_2$ (M^+) 250.1574, found, 250.1583. Anal. Calcd: C, 67.12; H, 10.46. Found: C, 67.15; H, 10.61.

Trapping of *trans*-1,1,4,4-Tetramethyl-1,4-disilacycloheptene (1) with 9,10-Dihydro-11,12-dimethylene-9,10-ethanoanthracene. A solution of 407 mg (2.21 mmol) of **1**, 501 mg (3.68 mmol) of methyl benzoate, and 14.9 mg of tridecane as internal standard in 50 mL of methylcyclohexane at −75 °C was irradiated at 254 nm for 6 h following the general procedure (vide supra). GC analysis (see general procedure) of an aliquot siphoned into acidified methanol immediately after the photolysis showed 7% of **2** and 2% of **3**. A precooled argon-purged slurry of 750 mg (3.26 mmol) of 9,10-dihydro-11,12-dimethylene-9,10-ethanoanthracene (**13**)[20c] in 5 mL of diethyl ether and methylcyclohexane (1:1 v/v) was then siphoned into the cold photolysate in the dark. After 45 min the cold photolysate was allowed to warm to room temperature. In addition to unreacted disilacycloheptane and the dihydrodimethylene-9,10-ethanoanthracene, quantitative GC–MS analysis of an aliquot showed that a new peak at 27 min with *m/z* 414 (M^+) corresponding to an adduct of disilacycloheptene with 1,3-diene **13** had formed. Small amounts of a methylcyclohexane adduct of **1** and six dimers of **1** were also present in the photolysate. The photolysate was concentrated in vacuo and the remaining volatiles were removed by distillation at 33 °C (ca. 1 mm) to give a crystalline solid. The mixture of dihydrodimethylene-9,10-ethanoanthracene (**13**) and disilacycloheptene cycloadduct **14** was refluxed overnight with excess maleic anhydride in 25 mL of ethyl acetate to remove unreacted **13**, which could not be separated from **14** by silica gel chromatography. After the reaction mixture was cooled, the ethyl acetate was removed in vacuo, and the resulting mixture of cycloadduct **14**, maleic anhydride Diels–Alder adduct of 1,3-diene **13**, and unreacted maleic anhydride was refluxed for 0.5 h with 40 mL of 10% sodium bicarbonate to hydrolyze the anhydrides. The mixture was cooled, diluted with 30 mL of ether, and washed five times with 30 mL of 5% sodium bicarbonate and once with saturated sodium chloride. The ether layer was then separated and dried over anhydrous sodium sulfate. Removal of the ether in vacuo gave 76.8 mg (8% yield) of pure cycloadduct **14** as a colorless crystalline solid, mp 203–204 °C. The product was recrystallized from ethanol in ethyl acetate, and crystals suitable for X-ray crystallography were grown by diffusion of absolute ethanol into hot ethyl acetate. The ^{1}H and ^{13}C NMR assignments were made on the basis of a ^{1}H-^{13}C heterocorrelated 2D spectrum. The spectral data for cycloadduct **14** were as follows (for numbering, see Figure 1a): ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.02 (s, 12 H, Si and Si′ methyls), 0.68–0.72 (m, 2 H, C_{10} and $C_{10'}$ methines), 0.78 (t, J = 7.15 Hz, 4 H, C_{11} and $C_{11'}$ methylenes), 1.68–1.78 (quintet, J = ca. 7.1 Hz, 2 H, C_{12} methylene), 2.08–2.30 (m, 4 H, C_9 and $C_{9'}$ methylenes), 4.74 (s, 2 H, C_7 and $C_{7'}$ methines), 6.95–7.00 (m, 4 H, $C_{2,2',5,5'}$ or $C_{3,3',4,4'}$ benzo), 7.27–7.31 (m, 4 H, $C_{3,3',4,4'}$ or $C_{2,2',5,5'}$ benzo); ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.58 (CH_3), −1.46 (CH_3), 17.19 (CH_2), 17.22 (CH_2), 23.34 ($C_{10,10'}$ CH), 29.77 ($C_{9,9'}$ CH_2), 55.46 ($C_{7,7'}$ CH), 122.23 (benzo CH), 122.35 (benzo CH), 124.15 (benzo CH), 141.98 (C), 146.40 (C), 146.43 (C); GC–MS, retention time 27.0 min, *m/z* (relative intensity), 414 (70), 314 (8), 255 (17), 254 (9), 253 (17), 252 (14), 239 (7), 236 (9), 217 (17), 216 (92), 215 (27), 202 (10), 179 (20), 178 (100), 159 (19), 158 (13), 136 (14), 135 (19), 121 (13), 115 (110), 99 (25), 85 (16), 83 (10), 73 (57), 72 (7), 59 (71), 43 (22). Anal. Calc for $C_{27}H_{34}Si_2$: C, 78.19; H, 8.26. Found: C, 77.92; H, 8.05.

Methyl Benzoate Sensitized Photolysis (254 nm) of 1,1,4,4-Tetramethyl-1,4-disilacycloheptene (1) in Methylcyclohexane in the Absence of Trapping Agents. A solution of 265 mg (1.44 mmol) of 1,1,4,4-tetramethyl-1,4-disilacycloheptene (**1**) 520 mg (3.83 mmol) of methyl benzoate, and 15.6 mg of tridecane as internal standard in 50 mL of methylcyclohexane at 2 °C was irradiated following the general procedure. After 12 h GC–MS analysis of an aliquot showed six disilacycloheptene dimers of *m/z* 368 (M^+, dimers A–F in order of retention time) in addition to unreacted starting material and significant amounts of three products corresponding to the addition of methylcyclohexane to the disilacycloheptene reactant. Dimer C was the predominant dimeric product formed, whereas the major dimer observed in the low-temperature photolyses (vided supra) upon warming was dimer E. The photolysate was concentrated in vacuo and the remaining volatiles were removed by distillation at 33 °C (ca. 1 mm). Only dimer F was obtained in pure form by preparative GC on a 10 ft × 1/4 in. column of 10% OV-101 on 60/80 mesh Chrom PAW at 210 °C, but insufficient material was obtained for elemental analysis. Although the major dimeric component C appeared to be pure by capillary GC–MS, ^{1}H NMR analysis revealed the presence of an impurity, which complicated the interpretation of the spectrum. Otherwise, olefinic absorptions appeared at δ 4.98–5.09 in the ^{1}H NMR spectrum and at δ 123.54 in the ^{13}C NMR spectrum. Dimer F was assigned as cyclobutane dimer **11** from the following spectral data: ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.09 (s, 3 H, methyl), −0.08 (s, 3 H, methyl), −0.064 (s, 3 H, methyl), −0.057 (s, 3 H, methyl), 0.0 (s, 3 H, methyl), 0.05 (s, 3 H, methyl), 0.14 (s, 3 H, methyl), 0.23 (s, 3 H, methyl), 0.43–0.86 (m, ca. 8 H, methylene), 1.48–1.86 (m, 5 H, methylene and methine), 2.11–2.23 (m, 1 H, methine), 2.34–2.45 (m, 2 H, methine); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.98 (CH_3), −3.43 (CH_3), −2.1 (CH_3), −1.58 (CH_3), −1.49 (CH_3), −1.35 (CH_3), −0.28 (CH_3), −0.05 (CH_3), 17.06 (CH_2), 18.27 (CH_2), 18.47 (CH_2), 18.62 (CH_2), 20.31 (CH_2), 20.48 (CH_2), 27.38 (CH), 30.13 (CH), 30.46 (CH), 31.51 (CH); GC–MS, retention time 24.3 min, *m/z* (relative intensity) 368 (27), 253 (10), 225 (5), 195 (6), 194 (9), 180 (30), 168 (14), 154 (12), 141 (8), 139 (11), 115 (7), 99 (28), 95 (6), 85 (9), 83 (10), 73 (100), 59 (47), 45 (9), 43 (11). High-resolution MS-EI calcd for $C_{18}H_{40}Si_4$ (M^+) 368.2208, found 368.2204.

Quantum Yield Determination for Direct Photolysis of Disilacycloheptene 1 in Acidified Methanol. A jacketed aluminum cell holder and lamp enclosure were used as described previously.[11a] Light from a Philips zinc lamp was passed through a 25-mm diameter Acton 214-1B interference filter (42.5% transmittance at 214 nm, 410 Å bandwidth). The lamp enclosure, including filter and sample cell, was flushed at a constant, metered flow of air during photolysis to maintain constant light intensity from run to run. A 10-mm path, quartz cylindrical cell of 3.0-mL volume or a square cell of 4.0-mL volume contained the photolysate, and the sample temperature was maintained at 25 °C by circulating methanol–water through the apparatus from a constant temperature bath.

Procedure **B** of Pitts, Margerum, Taylor, and Brim[11d] was used for uranyl oxalate actinometry. The only modification was a dilution prior to UV analysis of the final actinometer solution. Quantum yields for actinometry at 210–214 nm have been reported by Forbes and Heidt.[11b,c] Actinometry was performed before and after each photolysis of disilacycloheptene **1**, and the average deviation of light output during the quantum yield runs was 1.8%.

A solution of 0.0050 M sulfuric acid in methanol was used to prepare a 25.0-mL stock solution of 0.00836 M (38.5 mg, 0.209 mmol) disilacycloheptene **1** containing 13.7 mg nonane as internal standard. Samples of 4.0-mL volume were irradiated for 16 min and then added to pentane. After the samples were washed with water and dried over anhydrous sodium sulfate, GC analyses were performed on column D at 115 °C. The quantum yields for formation of methanol adducts **2** and **3** were the mean of three determinations (6% average deviation) at 9–11% conversion of reactant **1**.

Plot of $1/\phi$ vs Reciprocal Acid for Direct Photolysis of Disilacycloheptene 1 in Acidified Methanol. The apparatus described above for quantum yield determinations was used. Methanol was purified by distillation from magnesium methoxide and stock solutions of sulfuric acid in methanol were made with concentrations varying from 0.010–0.00027 M. A 50.00-mL stock solution of 183 mg (0.994 mmol) disilacycloheptene **1** and 54.8 mg (0.428 mmol) nonane, used as an internal standard, was also prepared. Photolysates were prepared by mixing equal volumes of reactant and acidified methanol stock solutions. After 12–13-min irradiation of 3.0-mL samples varying in concentration of acid, an equal volume of pentane was added, followed by washing six times with water and drying over anhydrous sodium sulfate. Samples were then analyzed by GC as above to obtain relative quantum yields of formation of products, which were converted to absolute quantum yields by using the values for **2** and **3** determined at 0.005 M sulfuric acid in methanol. The equation of the line obtained for product **2** was $y = (2.76 \times 10^{-4})x + 5.72$ ($r = 0.988$); intercept/slope = 20 700. The data for adduct **3** were as follows: $y = (1.91 \times 10^{-3})x + 28.1$ ($r = 0.758$); intercept/slope = 14 700.

Quantum Yield Determination for *p*-Xylene-Sensitized Photolysis of Disilacycloheptene 1 in Acidified Methanol. A Rayonet reactor containing eight RPR 2537 A lamps was used. In the center was mounted a quartz water jacket containing a Vycor filter into which a Vycor tube containing 5.0 mL of photolysate could be inserted. Methanol solutions of 0.0108 M disilacycloheptene **1** that were 0.789 M in *p*-xylene and 0.012 M in sulfuric acid, with nonane as an internal standard, were purged with nitrogen for 30 min and then irradiated for 5–10 min. After irradiation an equal volume of pentane was added, and the photolysate was washed six times with water and dried over sodium sulfate. Samples were analyzed by GC with use of the same conditions as the direct photolyses. The 254-nm light output was determined by uranyl oxalate actinometry. The quantum yields for formation of methanol adducts **2** and **3** in eq 1 are the average of three determinations (14% average deviation) at 17–19% conversion of reactant **1**.

Plot of $1/\phi$ vs Reciprocal Acid for *p*-Xylene-Sensitized Photolysis of Disilacycloheptene 1 in Acidified Methanol. The Rayonet apparatus with eight lamps was used as described above. Methanol was distilled from magnesium methoxide to remove residual acid. Stock solutions of acidified methanol, varying in the concentration of sulfuric acid (0.020–0.00024 M) were prepared, as well as a solution of 0.0207 M disilacycloheptene, 0.0127 M nonane, and 1.58 M *p*-xylene. Equal volumes of acidified methanol and reactant **1** stock solutions were mixed. Each sample was purged with nitrogen for 30 min and then irradiated for 10–12 min. After irradiation, an equal portion of pentane was added. Each sample was washed six times with water, dried over sodium sulfate, and analyzed by GC with use of the same conditions as described for the direct photolyses. Relative quantum yields of formation of products were converted to absolute quantum yields using the values for **2** and **3** determined at 0.012 M sulfuric acid in methanol (vide supra). The equation for the line obtained for product **2** was $y = (3.98 \times 10^{-4})x + 6.82$ ($r = 0.920$) giving an intercept/slope = 17 000. The data for product **3** were as follows: $y = (2.16 \times 10^{-3})x + 30.6$ ($r = 0.932$); intercept/slope = 14 200.

Controls. A solution of 59.7 mg (0.324 mmol) of alkyne **4** in 25 mL of 0.005 M sulfuric acid in methanol at 25 °C gave 0.3% of a product with m/z 214 (M^+) and 98% of unreacted starting material after 3 h according to GC (column D at 95 °C and GC–MS analyses. After 24 h 93% of the alkyne was present along with 5% of m/z 214 product. This unknown product was not detected in any of the photolyses of **1** in acidified methanol.

A solution of 42.7 mg (0.198 mmol) of 2-(methoxydimethylsilyl)methyl-1,1-dimethyl-1-silacyclopentane (**6**) in 25 mL of methanol containing 0.005 M sulfuric acid at 25 °C showed the presence of 98% of **6** and no other products after 3 h according to GC (column D at 130 °C) and GC–MS analyses.

A solution of 47.8 mg (0.259 mmol) of 1,1,3,3-tetramethyl-2-methylene-1,3-disilacyclohexane (**5**) in 25 mL of methanol containing 0.005 M sulfuric acid showed only unreacted starting material (100% yield) after 22.5 h according to GC (column D at 95 °C) and GC–MS analyses.

GC (column D at 95 °C) and GC–MS analyses of a solution of 46.9 mg (0.217 mmol) of methanol adduct **2** in 25 mL of 0.005 M sulfuric acid in 25 mL of methanol at 25 °C showed only unreacted starting material (97% yield) after 24 h.

A solution of 36.0 mg (0.166 mmol) of **3** in 0.005 M sulfuric acid in 50 mL of methanol at 2 °C showed only 99% yield of unreacted starting material after 24 h as determined by GC (column D at 95 °C) and GC–MS analyses.

GC (column D at 95 °C) and GC–MS analyses of a solution of 48.0 mg (0.260 mmol) of disilacycloheptene **1** in 25 mL of 0.005 M sulfuric acid in methanol at 25 °C after 4 weeks showed the presence of 99% of unreacted starting material.

A 2-mL aliquot of a 0.033 M solution of **1** in methylcyclohexane was treated with 1 mL of freshly distilled cyclopentadiene in methylcyclohexane (1:1 v/v) at −75 °C under argon. After 45 min the reaction mixture was warmed to room temperature. GC–MS analysis showed only disilacycloheptene starting material and dicyclopentadiene (cyclopentadiene dimer). In a similar experiment no adduct of the starting material disilacycloheptene **1** with 9,10-dihydro-11,12-dimethylene-9,10-ethanoanthracene (**13**) was detected by GC–MS analysis.

Crystallographic Structure Determination of Diels–Alder Adduct 14. Single crystals of $C_{27}H_{34}Si_2$, grown as described above, were at 20 ± 1 °C orthorhombic, space group $PbcnD_{2h}$[14] (No. 60) with $a = 9.307$ (2) Å, $b = 26.549$ (6) Å, $c = 9.985$ (1) Å, $V = 2467$ (1) Å, and $Z = 4$ ($d_{\text{calc}} = 1.117$ g cm^{-3}; μ_a(Mo K_α^-) = 0.15 mm^{-1}). A total of 1703 independent reflections having 2θ(Mo K_α^-) < 45.8° (the equivalent of 0.6 limiting Cu K_α^- spheres) were collected on a computer-controlled Nicolet autodiffractometer using full (1.10°-wide) ω scans and graphite-monochromated Mo K_α^- radiation. The structure was solved using "direct methods" techniques with the Nicolet SHELXTL software package as modified at Crystalytics Company. The resulting structural parameters were refined to convergence (R_1 (unweighted, based on F) = 0.049 for 970 independent reflections having 2θ(Mo K_α^-) < 45.8° and $I > 3\sigma(I)$) by using the counter-weighted full-matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all included hydrogen atoms.

Nonstatistical cocrystallization of two enantiomeric C_2-forms of $C_{27}H_{34}Si_2$ about the C_2-axis produced a disordered solid-state structure in which Si, C_1–C_{14} and Si′, and $C_{1'}$–$C_{14'}$ represent the predominant (74%) enantiomer (Figure 1a) of the asymmetric unit and Si*, C_1-$C_{9'}$, C_{12}, C_{10^*}, C_{11^*}, C_{13^*}, and C_{14^*} and Si$^+$, $C_{1'}$–$C_{9'}$, C_{12}, C_{10^+}, C_{11^+}, C_{13^+}, and C_{14^+} represent the minor (26%) enantiomer (Figure 1b) of the asymmetric unit. The normalized occupany factors for these two enantiomeric forms for the asymmetric unit of $C_{27}H_{34}Si_2$ were least-squares refined by using the most complete structural model. Hydrogen atoms were fixed at idealized positions (assuming sp^2- or sp^3-hybridization of the carbon atoms and a C–H bond length of 0.96 Å) "riding" on their respective carbon atoms for C_2, C_3, C_4, C_5, C_7, and C_9 (and their symmetry related atoms). Hydrogen atoms on C_{10}, C_{11}, C_{12} (major isomer only), C_{10^*}, and C_{11^*} as well as their symmetry-related carbons were included in the structural model as independent isotropic atoms with appropriate partial occupancy factors. Note that H_{11a} is a common position for C_{11} and C_{11^+} and was therefore included in the model with an occupancy factor of 1.0. Hydrogen atoms were omitted for the minor isomer at carbon atoms C_9 and C_{12} as well as for all terminal methyl groups of both enantiomers.

Acknowledgment. Support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We also thank the National Science Foundation (Grant No. CHE-8905465) for financial support for the purchase of a 300-MHz NMR. X-ray crystallographic studies were performed by Crystalytics Co., Lincoln, NE. High-resolution MS performed by the Midwest Center of Mass Spectrometry, an NSF Regional Instrumentation Facility. Professors Sheldon E. Cremer and William A. Donaldson and Mr. Andrew Peterson of Marquette University contributed technical expertise and suggestions for obtaining and interpreting the NMR data.

Supplementary Material Available: Crystallographic data including tables containing anisotropic thermal parameters, and final positional parameters, plot of the second order decay kinetics of *trans*-**1**, MNDO calculated stucture of *trans*-**1**, and the MM2(85) calculated structure of its Diels–Alder cycloadduct with cyclopentadiene, ^{1}H and ^{13}C NMR spectra of cyclopentadiene adduct **12**, table of MNDO calculated bond angles and bond lengths of *trans*-**1** and *trans*-cycloheptene, and the final calculated MNDO Z-matrices of *trans*-**1** and *trans*-1,4-disilacyclohept-2-ene (37 pages); observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

Design and Synthesis of New Fluorinated Ferroelectric Liquid Crystalline Polymers

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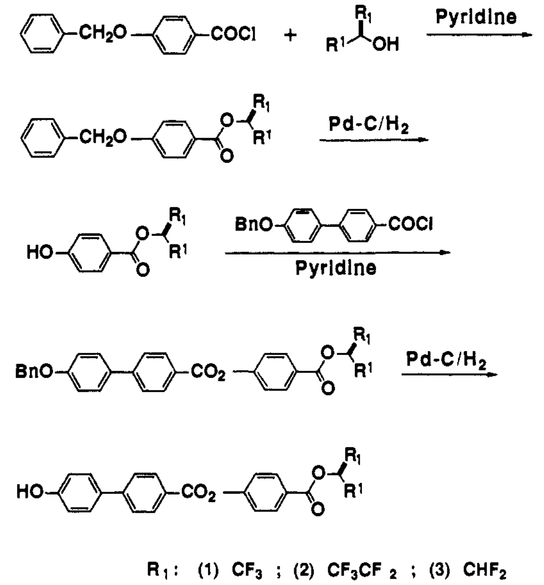
Abstract: The synthesis and specific properties of a new family of fluorinated ferroelectric liquid crystalline polymers of the general structure 1, are described. These materials exhibit quick response time (<10 ms) and large spontaneous polarization (40–70 nC/cm^2) (90 °C). A discussion of the response time–structure relationships is given. The response time becomes faster as the achiral chain connecting the mesogen to the polymer backbone and the chiral chain length becomes shorter. Especially, it is found that a trifluoromethyl group on the stereogenic center enhanced the response time.

Molecular recognition in ferroelectric liquid crystalline polymers is of fundamental importance to the understanding of differences in physical properties between racemic[2-6] and enantiomerically pure materials.[7] Recently, new ferroelectric liquid crystalline polymers with fast response times (3 ms) and large spontaneous polarizations (60 nC/cm^2) (85 °C) have been reported by Walba and Keller.[8] However, with the exception of the above report, studies on the molecular design of ferroelectric liquid crystalline polymers to give quick response times for switching and/or a large spontaneous polarizations have not been undertaken.[9-11] In fact, for ferroelectric liquid crystalline polymers, the minimum reported the response time is 100 ms, and the maximum reported spontaneous polarization P_s observed for liquid crystalline polymers is 6–8 nC/cm^2. In the case of these materials, naturally occurring 2-methylbutanol and 2-methylpentanol were used as the chiral tail groups.[9-14] Therefore, the challenge of preparing new ferroelectric liquid crystalline polymers with rapid response times, large spontaneous polarizations, and low viscosities remains.

We recently reported the possibility of tristable switching in a surface-stabilized ferroelectric liquid crystal display devices (SSFLCDs) of the Clark–Lagerwall type,[15] which had a fluoroalkyl group at the chiral center.[16,17] In this paper we describe work aimed at deriving a basic understanding of the relation between response time and molecular structure which could be applied to be new ferroelectric liquid crystalline polymers with specific properties. The syntheses and some properties of a new family of ferroelectric liquid crystalline polymers possessing a fluoroalkylated chiral tail unit as a mesogenic pendant group are reported in the following.

Scheme I



Molecular Design Considerations

A fundamental objective of conductive polymer design is to select polymers with a quick response time, a large spontaneous polarization density, and a low orientation viscosity. It is possible to correlate specific properties of known ferroelectric liquid crystalline polymers with their structure and physical properties: (1) the response time (rise time) is temperature dependent, (2) the rise time is dependent upon viscosity (it increases with increasing molecular weights), and (3) the response time is dependent upon steric effects. The response time was, with introduction of an α-methyl groups, as in a methacrylic polymers, relative to an acrylic polymers.[18-23] In addition, we have observed

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(2) Ringsdorf, H.; Zentel, R. *Makromol. Chem.* **1982**, *183*, 1245.

(3) Pranoto, H.; Haase, W. *Mol. Cryst. Liq. Cryst.* **1983**, *98*, 299.

(4) Coles, H. J.; Simon, R. *Mol. Cryst. Liq. Cryst. Lett.* **1985**, *1*, 75.

(5) Coles, H. J.; Simon, R. *Mol. Cryst. Liq. Cryst. Lett.* **1986**, *3*, 37.

(6) Finkelmann, H.; Ringsdorf, H. *Makromol. Chem.* **1978**, *179*, 273.

(7) *Ferroelectric Polymers*; Miyata, S., Furukawa, T., Eds.; Kyoritsu: Tokyo, 1988.

(8) Walba, D. M.; Keller, P.; Parmar, D. S.; Clark, N. A.; Wand, M. D. *J. Am. Chem. Soc.* **1989**, *111*, 8273 and references cited therein.

(9) Shibaev, V. P. *Polym. Bull.* **1984**, *12*, 299.

(10) Decobert, G. *Polym. Bull.* **1985**, *14*, 179.

(11) Meredith, G. R. *Macromolecules* **1982**, *15*, 1385.

(12) Shibaev, V. P. *Polym. Commun.* **1983**, *24*, 364.

(13) Coles, H. J. *Mol. Cryst. Liq. Cryst. Lett.* **1984**, *102*, 433.

(14) Coles, H. J. *Polymer* **1985**, *26*, 1801.

(15) Clark, N. A.; Lagerwall, S. T. *Appl. Phys. Lett.* **1980**, *36*, 899.

(16) Suzuki, Y.; Hagiwara, T.; Kawamura, I.; Okamura, N.; Kitazume, T.; Kakimoto, M.; Imai, Y.; Ouchi, Y.; Takezoe, H.; Fukuda, A. *Liquid Cryst.* **1989**, *6*, 167 and references cited therein.

(17) Johno, M.; Itoh, K.; Lee, J.; Ouchi, Y.; Takezoe, H.; Fukuda, A.; Kitazume, T. *Jpn. J. Appl. Phys.* **1990**, *29*, L107.

(18) Talroze, R. V. *Polym. Prepr.* **1983**, *24*, 309.

(19) Finkelmann, H. *J. Chim. Phys. Phys.-Chim. Biol.* **1983**, *80*, 163.

(20) Goozner, R. E. *Makromol. Chem.* **1985**, *185*, 2407.

(21) Koide, K. *Mol. Cryst. Liq. Cryst.* **1986**, *139*, 47.

(22) Ringsdorf, H. *Makromol. Chem.* **1987**, *188*, 1355.

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