Organometallics 1989, *8*, 693–709

deep purple (the color of Fp_2). We could not detect any other organic products.

Preparation of Enolate Complexes 6c,d and 8c,d. 1,3-Dioxolanes (acetals) of α-halo ketones were prepared by the published method.[32] NaFp or Na/KFp* (10 mmol) in THF (10 mL) was added to a THF solution (20 mL) of appropriate 1,3-dioxolane (12 mmol) at −78 °C. After the mixture was stirred for 3 h at room temperature, the volatiles were removed under reduced pressure. The product was extracted with ether (100 mL) and filtered through silica gel. The acetal linkage was hydrolyzed by stirring with 1/10 N HCl(aq), and then the organic layer was dried over $MgSO_4$. **6** and **8** were isolated by column chromatography followed by recrystallization from Et_2O. **6c**: 50% yield. **6d**: 48% yield; yellow prisms; mp 90 °C. Anal. Calcd for $C_{16}H_{14}O_4Fe$: C, 58.93; H, 4.33. Found: C, 59.27; H, 4.48. IR: 2004, 1961 cm^{-1}. **8c**: 46% yield; yellow prisms; mp 118 °C. Anal. Calcd for $C_{20}H_{22}O_3Fe$: C, 65.59; H, 6.06. Found: C, 65.62; H, 6.09. IR: 1988, 1937 cm^{-1}. **8d**: 45% yield; yellow prisms; mp 105 °C. Anal. Calcd for $C_{21}H_{24}O_4Fe$: C, 63.65; H, 6.10. Found: C, 63.82; H, 6.08. IR: 1995, 1946 cm^{-1}.

Preparation of 8b. **8b** was prepared according to the published method by using Na/KFp* in place of NaFp. **8b**: 41% yield; yellow crystals; mp 110 °C. Anal. Calcd for $C_{14}H_{18}O_3Fe$: C, 57.95; H, 6.25. Found: C, 58.30; H, 6.41. IR: 1990, 1940 cm^{-1}.

Preparation of Diiron Enolate Complexes 7 and 9. **7** and **9** were prepared in a similar manner to **3**. **7a**: 72% yield; deep red crystals; mp 119 °C; FDMS, *m/z* 497 [FpFp*(CH_2CO_2Me)] Anal. Calcd for $C_{22}H_{25}BF_4O_6Fe_2$: C, 46.52; H, 4.44. Found: C, 46.68; H, 4.50. IR: 2018, 2001, 1977, 1959 cm^{-1}. **7b**: 63% yield; deep red crystals; mp 126 °C; FDMS, *m/z* 467 [FpFp*(CH_2CHO)] Anal. Calcd for $C_{21}H_{23}BF_4O_5Fe_2$: C, 45.54; H, 4.18. Found: C, 45.80; H, 4.20. IR: 2032, 1983 cm^{-1}. **7c**: 63% yield; deep red crystals; mp 118 °C; FDMS, *m/z* 543 [FpFp*(CH_2COPh)] Anal. Calcd for $C_{27}H_{27}BF_4O_5Fe_2$: C, 51.47; H, 4.32. Found: C, 51.58; H, 4.25. IR: 2032 (sh), 2024, 1981, 1973 (sh) cm^{-1}. **7d**: 42% yield; deep red oil. Anal. Calcd for $C_{28}H_{29}BF_4O_6Fe_2$: C, 50.95; H, 4.43. Found: C, 51.46; H, 4.58. **9a**: 52% yield; deep red crystals; mp 88 °C; FDMS, *m/z* 467 [FpFp*(CH_2CHO)] Anal. Calcd for $C_{22}H_{25}BF_4O_6Fe_2$: C, 46.52, H, 4.44. Found: C, 46.18; H, 4.21. IR: 2060, 2012, 1996, 1948 cm^{-1}. **9b**: 58% yield; deep red crystals; mp 122 °C. Anal. Calcd for $C_{21}H_{23}BF_4O_6Fe_2$: C, 45.54; H, 4.18. Found: C, 45.62; H, 4.23. IR: 2061, 2011, 2000 (sh), 1956 cm^{-1}.

Preparation of 11. To a CH_2Cl_2 solution (10 mL) of Cp_2ZrMe_2 (454 mg, 1.8 mmol) was added to **10** (816 mg, 1.5 mmol)[7c] dissolved in 5 mL of CH_2Cl_2. After gas evolution had ceased, hexane (20 mL) was added. During the removal of the volatiles **11** precipitated as an orange solid, which was collected. Owing to its sensitivity to moisture, an analytically pure sample of **11** could not be obtained. **11**: 58% yield; orange solid; mp 137 °C.

Reaction of 12 with 2a. **12** (998 mg, 2.75 mmol) and **2** (836 mg, 2.50 mmol) were stirred in CH_2Cl_2 (40 mL). After 1 and 72 h a 10-mL portion of the mixture was separated and evaporated to dryness. After being washed with ether, the solid was dissolved in CH_2Cl_2 and treated with PPh_3 (1.5 equiv) for 15 min. Then, the volatiles were removed in vacuo. The product ratio **12**/**6c** was determined by ^1H NMR after extraction with ether.

Acknowledgment. We are grateful to the Asahi Glass Foundation for Industrial Technology and the Ministry of Education, Science and Culture of the Japanese Government for financial support of this research. We thank Mr. Hideki Omori for FDMS measurements.

Registry No. **1a**, 107040-55-1; **1b**, 107040-56-2; **1c**, 111615-23-7; **1d**, 118377-80-3; **2a**, 63313-71-3; **2b**, 116037-29-7; **2c**, 112617-73-9; **3a**, 116017-02-8; **3b**, 118398-15-5; **3c**, 116037-31-1; **3d**, 116017-04-0; **3e**, 118398-17-7; **3f**, 118398-19-9; **3g**, 118398-21-3; **6a**, 12214-69-6; **6b**, 55337-26-3; **6c**, 12319-47-0; **6d**, 118377-81-4; **7a**, 118377-86-9; **7b**, 118377-88-1; **7c**, 118377-90-5; **7d**, 118377-92-7; **8a**, 118378-01-1; **8b**, 118377-84-7; **8c**, 118377-82-5; **8d**, 118377-83-6; **9a**, 118377-94-9; **9b**, 118377-96-1; **9c**, 118377-98-3; **9d**, 118378-00-0; **10**, 111582-14-0; **11**, 116100-36-8; **12**, 12319-80-1; Cp_2ZrMe_2, 12636-72-5.

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[32] Visweswariah, S.; Prakash, G.; Bhushan, V.; Chandrasekaran, S. *Synthesis* 1982, 309.

Photochemical Rearrangements of Stable Silenes

Kim M. Baines, A. G. Brook,* R. R. Ford, P. D. Lickiss, A. K. Saxena, W. J. Chatterton, J. F. Sawyer, and B. A. Behnam

Lash Miller Chemical Laboratories, University of Toronto, Toronto M5S 1A1, Canada

Received June 15, 1988

Photolysis of acylsilanes $(Me_3Si)_2RSiCOR'$ (R = Me, *t*-Bu, Ph, Me_3Si; R′ = *t*-Bu, Ad, bicyclooctyl, Mes, CEt_3) gave silenes $Me_3SiRSi{=}C(OSiMe_3)R'$, whose subsequent chemistry was dependent on the steric size of the R and R′ groups and on their facile photochemical excitation by UV light. Thus when R = Me or Ph and R′ = Ad or R = Me_3Si and R′ = bicyclooctyl, head-to-head dimerization occurred giving 1,2-disilacyclobutanes, whereas when R = *t*-Bu and R′ = Ad or R = Ph and R′ = CEt_3, stable silenes were formed. Some of these silenes, e.g. when R = *t*-Bu or Ph, subsequently underwent complex photochemical isomerizations yielding new silenes (observable by NMR spectroscopy for R = *t*-Bu and R′ = Ad or R = Ph and R′ = CEt_3). Most of the new isomeric silenes ultimately dimerized to give 1,3-disilacyclobutanes by head-to-tail dimerization as expected from their structures. The crystal structures of four of these dimers (details in the following paper) and one silene–methanol adduct (details herein) were determined by X-ray methods, thus unambiguously establishing the structures of the dimers and of their immediate silene precursors. The data reported have been interpreted on the basis that each acylsilane on photolysis formed only one of the two possible silene geometric isomers, which reacted nonstereospecifically when trapped by added methanol since in each case a diastereomeric mixture of methanol adducts was isolated. A dyotropic-like rearrangement from a twisted silene excited state has been proposed as the simplest mechanism possible to account for the silene-to-silene isomerizations, but this has not been confirmed experimentally.

Introduction

The availability of silenes that are stable at room-temperature has made it possible to study some of the chemistry of these species under "normal" mild conditions, e.g. in solution at room temperature (see recent reviews for an outline of these studies[1,2]). Among the reactions that have been studied recently with our family of stable silenes $(Me_3Si)_2Si{=}C(OSiMe_3)R$ (**2**), derived from photolysis of the related acylsilanes $(Me_3Si)_3SiCOR$ (**1**), are [2 + 2]

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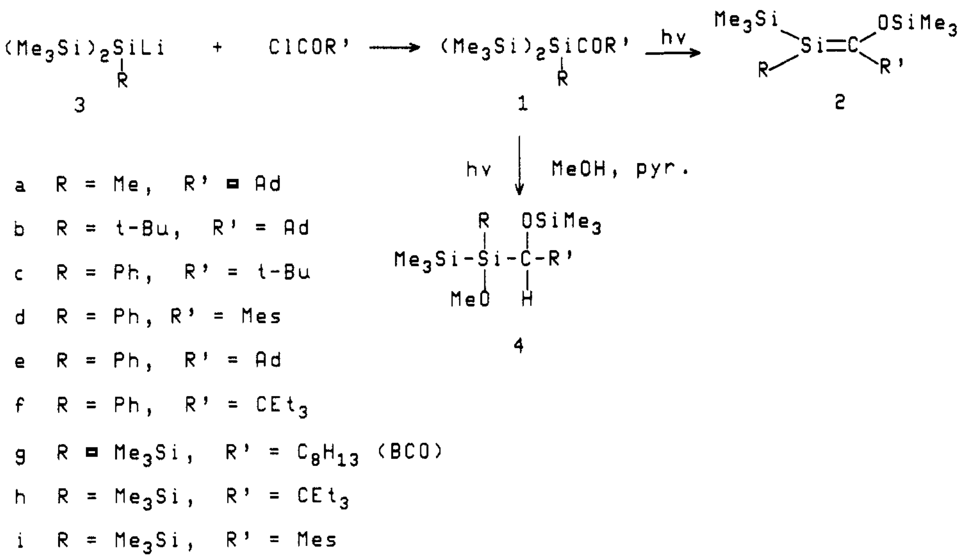
[1] Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* 1986, *25*, 1.

[2] Raabe, G.; Michl, J. *Chem. Rev.* 1985, *85*, 419.

0276-7333/89/2308-0693$01.50/0

Scheme I



cyclizations (with ketones,[3] dienes, and alkenes[4]), and [2 + 4] cyclizations (with ketones[3] and dienes[4]), as well as earlier studies involving dimerization and the addition of methanol.[5,6]

It is evident that the stability (toward dimerization etc.) and reactivity of these silenes are due both to the steric bulk of the substituents on the silicon–carbon double bond, as well as to their electronic influences.[7] This research was initiated to investigate the effects of replacing one of the trimethylsilyl groups on the sp^2-hybridized silicon atom of these silenes by an alkyl or aryl group, e.g. Me, *t*-Bu, or Ph. As will be seen, this substitution caused dramatic changes in the behavior of some of the silenes.

One of the consequences of replacing one of the silyl groups on the silene by an R group is that it introduces the possibility of geometrical isomerism in stable silenes for the first time (all previously reported stable silenes, e.g. $(Me_3Si)_2Si{=}C(OSiMe_3)R$[8,9] and $Me_2Si{=}C(SiMe_3)SiMeR'_2$[10] have identical groups on the sp^2-hybridized silicon atom: some important studies which involve geometric isomers of "unstable" silenes formed at elevated temperatures have been reported.[11] As will be seen, all the results from the present research indicate that only one of two possible geometrical isomers was formed in detectable amounts in each of several cases and that these reacted in a nonstereospecific manner with methanol.

In the course of investigating the chemistry of the silenes, a number of additional simpler systems were studied, which served to delineate better the generality of the behavior and physical properties of families of acylsilanes, silenes, their 1,2-disilacyclobutane dimers, and their methanol adducts. A number of tables of definitive NMR data are presented for these families of compounds.

Discussion

The acylsilanes $(Me_3Si)_2RSiCOR'$ (**1**; R = Me, *t*-Bu, Ph; R' = *t*-Bu; Ad = 1-adamantyl; BCO = [2.2.2]bicyclooctyl; Mes = mesityl, CEt_3) required for photolysis to the silenes were prepared by conventional procedures involving coupling of a silyllithium reagent **3** with the appropriate acid chloride (Scheme I). Photolysis of these acylsilanes gave the silenes **2**. If methanol containing a trace of pyridine (used to avoid methanolysis of the siloxy group in the adducts—see below) was present in the acylsilane solution being photolyzed, the product in each case was a diastereomeric mixture (varying from about 1:1 to 3:1 depending on R and R') of the expected methanol adducts **4**. The significance of the fact that mixtures of diastereomers were formed will be discussed below. It is appropriate to discuss the results of the photolyses in C_6D_6 or MeOH of each category of acylsilane separately. NMR and crystal structure data that support and confirm the structures assigned to various products will be discussed after the chemistry has been described.

The Methylsilene 2a, $(Me_3Si)MeSi{=}C(OSiMe_3)Ad$. The photolysis of the methylacylsilane **1a**[12] in perdeuteriobenzene at about 10 °C led to the immediate generation of the anticipated head-to-head dimer **5a**. No evidence for the presence of silene **2a** in the solution during or at the end of the photolysis was found by using ^1H, ^{13}C, or ^{29}Si NMR spectroscopy, indicating that this relatively sterically unhindered silene was quite short-lived. Only one of several possible stereoisomers of the head-to-head dimer was detected by NMR spectroscopy or observed on isolation, indicating that only a single geometric isomer of the silene was formed and that it dimerized in only one of the possible ways to give the single head-to-head dimer observed. The structure was assumed to be that of the "all-trans" isomer **5a**, consistent with the crystal structure of a previously studied dimer[5] (Scheme II).

The fact that a head-to-head dimer having adamantyl groups on adjacent ring carbon atoms was formed was at first surprising. It had previously been argued,[8] in connection with the related silene $(Me_3Si)_2Si{=}C(OSiMe_3)Ad$, that its total failure to dimerize was due to the steric repulsions of bulky groups on the ring-carbon atoms which

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[3] Brook, A. G.; Chatterton, W. J.; Sawyer, J. F.; Hughes, D. W.; Vorspohl, K. *Organometallics* **1987**, *6*, 1246.

[4] Brook, A. G.; Vorspohl, K.; Ford, R. R.; Hesse, M.; Chatterton, W. J. *Organometallics* **1987**, *6*, 2128.

[5] Brook, A. G.; Nyburg, S. C.; Reynolds, W. F.; Poon, Y. C.; Chang, Y.-M.; Lee, J.-S.; Picard, J.-P. *J. Am. Chem. Soc.* **1979**, *101*, 6750.

[6] Brook, A. G.; Harris, J. W.; Lennon, J.; El Sheikh, M. *J. Am. Chem. Soc.* **1979**, *101*, 83.

[7] Apeloig, Y.; Karni, M. *J. Am. Chem. Soc.* **1984**, *106*, 6676.

[8] Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon. Y. C.; Chang, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667.

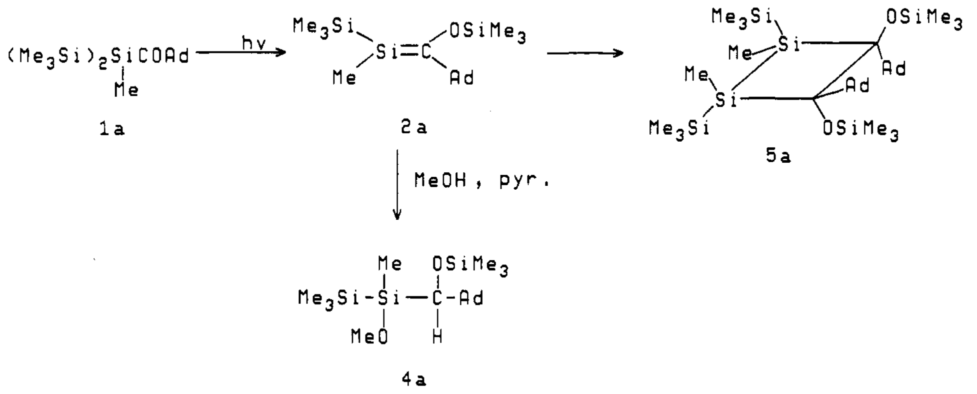
[9] Brook, A. G.; Wessely, H.-J. *Organometallics* **1985**, *4*, 1487.

[10] Wiberg, N.; Wagner, G.; Mueller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 229.

[11] Jones, P. R.; Bates, T. F. *J. Am. Chem. Soc.* **1987**, *109*, 913.

[12] In this paper the acylsilanes and silenes will be named on basis of the group present replacing Me_3Si on silicon: e.g., **1a** = methylacylsilane and **2b** = *tert*-butylsilene.

Scheme II



would be present in a head-to-head dimer. However, in the present case the steric bulk at the ring-silicon atoms in the dimer should be appreciably less, due to the replacement of a trimethylsilyl group by the considerably smaller methyl group. Thus, by small alterations of bond angles to the ring atoms, accommodation of the bulky groups into a moderately stable head-to-head dimer is evidently possible. Consistent with this was the finding that the dimer was somewhat unstable, either in air, or when dissolved in methanol at room temperature where it was rapidly converted to a diastereomeric mixture of the silene methanol adducts **4a**, identical with those formed on photolysis of the acylsilane in methanol, implying facile dissociation of the dimer into the silene monomer.

Formation of the *tert*-Butylsilene 2b, $(Me_3Si)(t\text{-}Bu)Si{=}C(OSiMe_3)Ad$. Photolysis of the *tert*-butylacylsilane **1b** initially yielded the anticipated silene **2b** (see Scheme III), which was "stable" in that it was sufficiently long-lived to be capable of study at room temperature by NMR spectroscopy as described below. The NMR spectra indicated that only one of the two possible geometrical isomers had been formed in detectable amount. However, if methanol was added to the photolysis solution, two diastereomeric methanol adducts **4b**, in 3:1 proportions, having the expected structures were obtained, which were the same species formed when the acylsilane **1b** was photolyzed in the presence of methanol. The stereochemical implications of these results will be discussed below.

In the absence of further photolysis, **2b** reverted back to **1b**, the expected behavior,[5,6] but in the process of photochemically converting all of **1b** to **2b** a new set of NMR signals was observed, attributed to the formation of a new silene A. Continued photolysis eventually converted all of **1b** via **2b** to A. Before discussing the structure of the new silene A, it is instructive to describe its ultimate fate. Silene A, apparently a single geometric isomer of a single species, based on its clean ^1H, ^{13}C, and ^{29}Si NMR spectra, survived in solution for days or weeks before spontaneously dimerizing. Sometimes freezing and thawing of the C_6D_6 solution would induce dimerization, but seeding with either of the ultimate major products failed to accelerate the dimerization process. Once initiated, dimerization led to an insoluble major product, shown by X-ray diffraction studies to have the structure **9b**, a soluble second dimer, shown by X-ray methods to have structure **10b**, both 1,3-disilacyclobutanes, and a third minor species not fully characterized. It is evident that the immediate silene precursors to **9b** and **10b** have the structures **8b** and **6b**, respectively, which, lacking silyl groups attached to the sp^2-hybridized silicon atom or siloxy groups attached to sp^2-hybridized carbon atom, underwent the "normal" head-to-tail dimerization observed for "simple" silenes. However, it was not immediately obvious how either **6b** or **8b** arose from the initial silene **2b** and which, if either, was the structure of silene A.

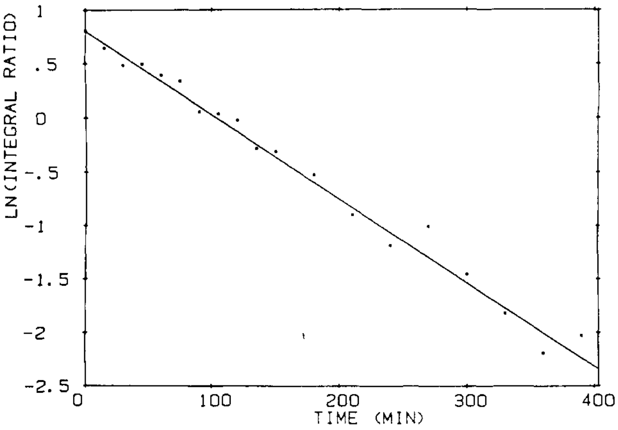


Figure 1. Disappearance of acylsilane **1b** during photolysis: □, observed data: —, calculated line.

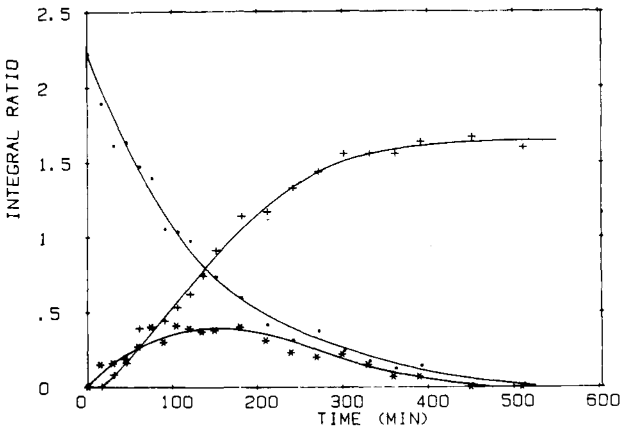
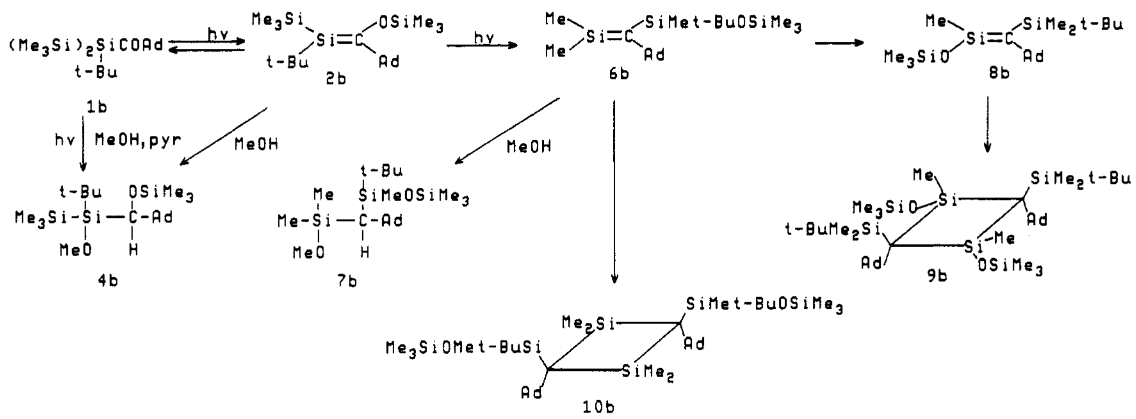


Figure 2. Photolysis of acylsilane **1b**. Monitoring products formed vs time: □, acylsilane **1b**; *, silene **2b**, +, silene **6b**.

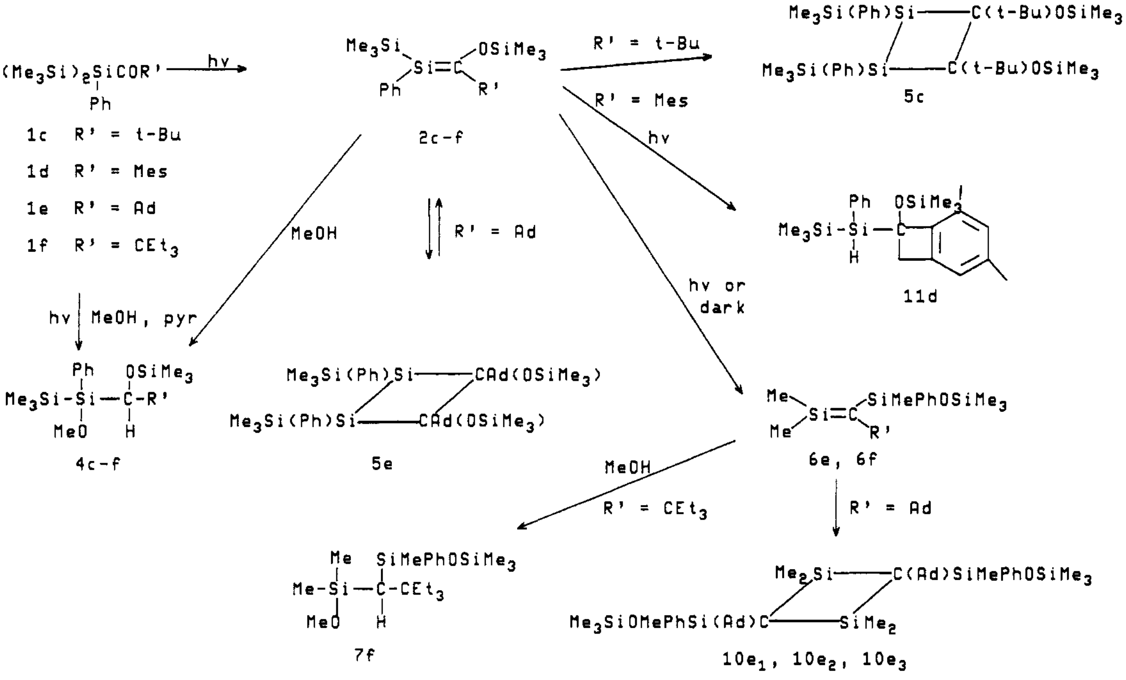
Silene A was characterized by treatment with methanol yielding a pair of diastereomeric methanol adducts which were assigned the structure **7b** on the basis of NMR data. Confirmation that this assignment was correct was shown by the X-ray crystal structure of one of the isomers. Thus it seems very probable that silene A has the structure **6b**: how this remarkable rearrangement of **2b** to **6b** occurs will be discussed below.

The kinetics of the sequence of reactions **1b** → **2b** → **6b** were followed by both ^1H NMR and UV spectroscopy. The disappearance of **1b** followed clean first-order kinetics

Scheme III



Scheme IV



(see Figure 1), and the overall kinetics were consistent with the transformations **1b** → **2b** → **6b** being a consecutive sequence of reactions as illustrated in Figure 2. Silene **2b** absorbed at 340 nm, the expected value,[8] and as its absorbance diminished, a strong absorption attributed to **6b** at 290 nm (with a shoulder at 260 nm) appeared in the solution. Further photolysis led to the disappearance of the shoulder at 260 nm, but the absorption at 290 nm persisted for days.

Photochemical Behavior of the Phenylsilenes 2c–f, $(Me_3Si)PhSi{=}C(OSiMe_3)R'$ (R' = *t*-Bu, Mes, Ad, CEt_3). Photolysis of the family of acylsilanes **1c–f**, bearing a phenyl group attached to silicon in place of a trimethylsilyl group, also resulted in some unusual behavior as summarized in Scheme IV: the compounds where R' = Ad and CEt_3 were found to behave very similarly to the *tert*-butylsilene **6b** described above. It is appropriate to describe these in order of increasing complexity.

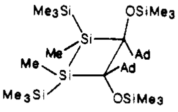
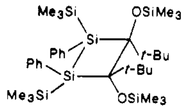
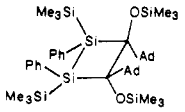
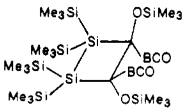
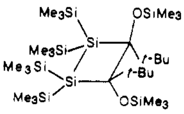
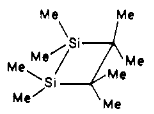
Photolysis of the acylsilane **1c**, R' = *t*-Bu, evidently gave rise to the expected "unstable" silene **2c** (not observable by NMR spectroscopy), as shown by the isolation of the "normal" head-to-head dimer **5c**, characterized by NMR spectroscopy as discussed below. Evidently the silene was not sufficiently sterically hindered for head-to-head dimerization to be inhibited, but the dimer was somewhat unstable: thus, stirring in methanol for 1 h led to 40% conversion to the methanol adducts **4c** of the silene.

Silene **2c** was also characterized by direct trapping with methanol: photolysis of acylsilane **1c** in methanol yielded a diastereomeric mixture of adducts **4c** whose structures were based on their NMR spectral properties, shown to be very similar to those of related methanol adducts (see Table III).

The phenylacylsilane **1d**, $(Me_3Si)_2PhSiCOMes$, also gave an unstable silene, **2d**, on photolysis which could not be observed directly, although it could be trapped by methanol as a pair of diastereomers, **4d**. In the absence of the trapping agent, prolonged photolysis of the silene caused an intramolecular reaction yielding the benzocyclobutene **11d**, behavior observed previously with another silene bearing a mesityl group on carbon.[9] Failure to form a dimer can be attributed to excessive steric strain that would result from adjacent bulky mesityl groups.

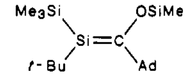
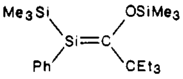
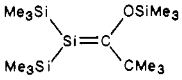
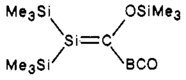
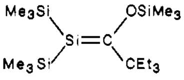
Photolysis of the phenylacylsilane **1e** resulted in the most unusual chemistry of members of this family. Brief photolysis in an inert solvent led to two apparently stereoisomeric intermediates, **5e**, in a 3:1 ratio as measured by NMR spectroscopy. The two isomeric species appeared and disappeared simultaneously during photolysis. When methanol was added to the solution containing these in-

Table I. Selected NMR Resonances for 1,2-Disilacyclobutanes[a]

							
	5a	5c	5e (3:2)		5g	ref 5	ref 13
			A	B			
^{29}Si							
Me_3Si	-11.25	-11.9	-12.3	-15.2	-8.5, -10.5	-9.5, -10.8	
Si ring	-25.6	-18.5	-2.5	-2.8	-46.7	-43.7	11.6
Me_3SiO	2.3	-0.5	2.5	2.1	-0.5	0.01	
^{13}C							
C ring	110.8	109.3	113.7	115.0	113.6	112.7	31.1

[a] BCO = C_8H_{13} = [2.2.2]bicyclooctyl. Geometries presumed to be "trans" by analogy.[5]

Table II. Selected NMR Resonances of Siloxy-Substituted Silenes[a]

					
	2b	2f	ref 15	2g	2h
^{29}Si					
Me_3Si	-13.2	-12.3	-12.1, -12.6	-12.3, -12.8	-12.4, -12.9
Si=	73.7	61.6	41.5	42.4	54.3
Me_3SiO	12.3	13.2	13.4	13.3	12.7
^{13}C					
C=	195.6	191.2	212.7	212.7	207.3
Me_3C	28.3				

[a] BCO = C_8H_{13} = [2.2.2]bicyclooctyl. Spectra run in C_6D_6.

termediates, the same pair of diastereomeric methanol adducts, **4e**, of silene **2e** was formed, as was obtained when acylsilane **1e** was photolyzed in the presence of methanol. This facile dissociation to the silene monomer is typical of sterically crowded 1,2-disilacyclobutane head-to-head dimers[6] and strongly suggests that the compounds **5e** are two stereoisomeric head-to-head dimers derived from and in equilibrium with silene **2e**. The intense yellow color of the photolysis solution suggested that these dimers might be in equilibrium with the silene monomer **2e**. All attempts to detect the monomer by NMR spectroscopy failed, but the UV absorption observed could be attributed to the presence of the silene (see Experimental Section). While the intermediates **5e** appeared during the initial stages of the photolysis, they disappeared during continued photolysis over the 16–24 h required to isomerize the remaining acylsilane **1e**, yielding the final reaction products even before all the acylsilane had been isomerized. Unlike the previous case of the *tert*-butylsilene **2b**, light was not required although it significantly accelerated the conversion of the intermediates **5e** to the final products **10e**$_1$, **10e**$_2$, and **10e**$_3$, shown to be a 10:5:3 mixture of three stereoisomeric head-to-tail dimers derived from silene **6e** (which was not detected at any time). The structures of two of the dimers **10e**$_1$ and **10e**$_2$ were obtained by X-ray diffraction methods: the structure of **10e**$_3$ was deduced by consideration of the NMR data as described below.

The structures of the dimers **10e**$_{1-3}$ indicate that the originally formed silene **2e** has undergone profound structural changes prior to forming the three dimers, each of which appears to be derived from silene **6e**. The structural similarities of dimers **10e**$_{1-3}$ to the dimer **10b** derived from silene **2b** via **6b** suggests that similar chemical processes are involved.

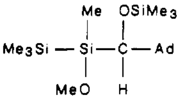
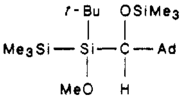
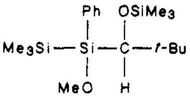
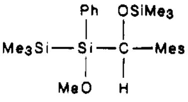
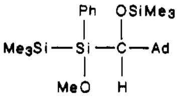
In the hope that the initially formed silene corresponding to **2b** might be stabilized if some other group was attached to the sp^2-hybridized carbon atom, the phenylacylsilane **1f** bearing a triethylmethyl group on the carbonyl carbon atom was photolyzed. In this case, the silene **2f**, although short-lived, could be observed and characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. In addition, the silene was trapped as a pair of methanol adducts whose structures, based on comparisons with other related systems (see Table III), were assigned as **4f**. On further photolysis silene **2f** isomerized to a complex mixture of products, among which the isomeric silene **6f** apparently was present, based on the similarity of the chemical shifts of many ^1H and ^{13}C NMR absorbances to those observed for *tert*-butylsilene **6b**. Furthermore, addition of methanol to this complex mixture yielded, after separation, a pair of methanol adducts **7f** with NMR properties very similar to the methanol adducts **7b** derived from silene **6b**. Thus it appears that the behavior of the phenylsilene **6f** bearing CEt_3 parallels very closely the behavior of the *tert*-butylsilene **6b** bearing Ad. It was not established whether head-to-tail dimers of **6f** were among the several products of photolysis.

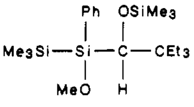
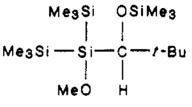
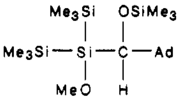
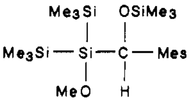
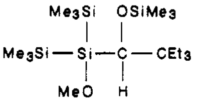
Three other acylsilanes belonging to the family $(Me_3Si)_3SiCOR'$ were also briefly studied, where R' = bicyclooctyl (BCO), triethylmethyl, and mesityl.

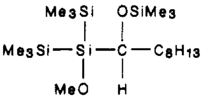
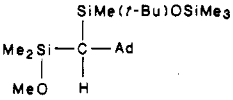
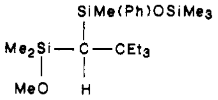
The bicyclooctylsilene **2g** (formed by photolysis of **1g**) could be observed in solution in equilibrium with its head-to-head dimer **5g** (monomer: dimer = 2.7:1). The unstable dimer when isolated was found to react readily with methanol and to decompose in air. The silene was readily trapped with 2,3-dimethylbutadiene as the expected [2 + 4] cycloadduct **12g** accompanied by some "ene" product, and the dimer when heated at 200 °C with anthracene gave the expected silene–anthracene [2 + 4] adduct. This behavior is virtually identical with that reported previously for the silene $(Me_3Si)_2Si{=}C(OSiMe_3)(t\text{-Bu})$ and its dimer,[5,6] including the fact that each of the three ethylene ($-CH_2CH_2-$) branches of the bicyclooctyl ring in the dimer **5g** had separate ^{13}C and ^1H NMR resonances due to hindered rotation, as did the three Me groups of the *tert*-butyl group of the corresponding *tert*-butyl dimer.

The preparations of acylsilanes **1h** and **1i** and their corresponding silenes **2h** and **2i** have been reported previously:[8,9] here the data for their methanol adducts **4h** and **4i** are reported for comparison purposes (see Table III).

Table III. Selected NMR Resonances of Silene Methanol Adducts

	 $Me_3Si{-}\overset{Me}{\underset{MeO}{Si}}{-}\overset{OSiMe_3}{\underset{H}{C}}{-}Ad$ 4a (2:1)		 $Me_3Si{-}\overset{t\text{-}Bu}{\underset{MeO}{Si}}{-}\overset{OSiMe_3}{\underset{H}{C}}{-}Ad$ 4b (3:1)		 $Me_3Si{-}\overset{Ph}{\underset{MeO}{Si}}{-}\overset{OSiMe_3}{\underset{H}{C}}{-}t\text{-}Bu$ 4c		 $Me_3Si{-}\overset{Ph}{\underset{MeO}{Si}}{-}\overset{OSiMe_3}{\underset{H}{C}}{-}Mes$ 4d (1.3:1)		 $Me_3Si{-}\overset{Ph}{\underset{MeO}{Si}}{-}\overset{OSiMe_3}{\underset{H}{C}}{-}Ad$ 4e (9:5)	
	A	B	A	B	A	B	A	B	A	B
^{29}Si										
Me_3Si	-20.8	-20.8	-21.1	-20.8	-25.9	-26.4	-20.8	-20.3	-21.4	-20.8
SiOMe	11.5	7.8	14.0	11.5	-6.3	-6.6	1.0	2.1	-1.2	-2.3
Me_3SiO	15.3	15.9	14.7	14.6	11.0	10.7	17.9	17.9	16.2	15.0
^{13}C										
CHOSi	81.0	79.8	79.1	79.8	79.2	81.2	67.7	68.4	80.2	82.4
MeO	51.3	51.2	51.3	51.2	51.7	52.6	52.4	52.5	51.9	52.9
Me_3C			22.0	22.8						

	 $Me_3Si{-}\overset{Ph}{\underset{MeO}{Si}}{-}\overset{OSiMe_3}{\underset{H}{C}}{-}CEt_3$ 4f		 $Me_3Si{-}\overset{Me_3Si}{\underset{MeO}{Si}}{-}\overset{OSiMe_3}{\underset{H}{C}}{-}t\text{-}Bu$ ref 6	 $Me_3Si{-}\overset{Me_3Si}{\underset{MeO}{Si}}{-}\overset{OSiMe_3}{\underset{H}{C}}{-}Ad$ ref 8	 $Me_3Si{-}\overset{Me_3Si}{\underset{MeO}{Si}}{-}\overset{OSiMe_3}{\underset{H}{C}}{-}Mes$ 4i	 $Me_3Si{-}\overset{Me_3Si}{\underset{MeO}{Si}}{-}\overset{OSiMe_3}{\underset{H}{C}}{-}CEt_3$ 4h
	A	B				
^{29}Si						
Me_3Si	-21.6	-18.7	-17.7, -19.3	-17.6, -19.4	-18.4, -18.9	-17.1, -18.7
SiOMe	-0.9	-0.8	10.3	10.7	17.2	10.35
Me_3SiO	15.6	17.2	15.0	15.0	16.7	15.0
^{13}C						
CHOSi	78.0	79.6	79.8	81.0	69.0	78.1
MeO	51.9	52.9	53.8	53.8	54.3	53.9

	 $Me_3Si{-}\overset{Me_3Si}{\underset{MeO}{Si}}{-}\overset{OSiMe_3}{\underset{H}{C}}{-}C_8H_{13}$ 4g	 $Me_2\underset{MeO}{Si}{-}\overset{SiMe(t\text{-}Bu)OSiMe_3}{\underset{H}{C}}{-}Ad$ 7b (3:2)		 $Me_2\underset{MeO}{Si}{-}\overset{SiMe(Ph)OSiMe_3}{\underset{H}{C}}{-}CEt_3$ 7f	
		A	B	A	B
^{29}Si					
Me_nSi	-17.4, -19.1	18.3	17.0	18.0	17.7
SiOMe	9.98	10.5	10.7	-3.2	-0.8
Me_3SiO	15.1	5.8	6.0	8.5	7.9
^{13}C					
CH-	79.0	30.1	32.3	31.7	32.0
MeO	53.8	48.3	49.5	49.4	49.1

[a] Solvent C_6D_6. C_8H_{13} = [2.2.2]bicyclooctyl.

Structure Determinations of Products by NMR and X-ray Methods. The structures of many of the compounds involved in this study were determined by NMR methods, particularly ^{13}C and ^{29}Si NMR spectroscopy, and comparisons with many previously studied compounds were most important for the structural assignments. Several tables are given which compare important characteristic resonances for structurally related compounds. Where the data are in complete accord with previous results (e.g. the methanol adducts **1a–i**, silene **2g**, and its dimer **5g**, etc.), specific discussion of the NMR results will not be given.

The chemical shifts of the ^{29}Si NMR resonances of dimer **5a** led to the assignment of its structure. Only three ^{29}Si NMR signals, at 2.31 (Me_3SiO), -11.25 (Me_3Si), and -25.63 (ring Si) ppm, were observed, and a proton-coupled ^{29}Si NMR spectrum in the DEPT mode supported this structural assignment. The chemical shift of the ring-silicon atom in 1,2-disilacyclobutanes is very sensitive to the substituents on the silicon atom: the following ring-silicon atom NMR data are relevant: Me_2Si, 3–8 ppm (this paper), 11.6 ppm;[13] Ph_2Si, +2.4 to -0.6 ppm;[14] $(Me_3Si)_2Si$, -40 to -47 ppm[5] (this paper). Hence the chemical shift observed at -25.6 ppm where the ring-silicon atom bears one methyl and one trimethylsilyl group is roughly midway between the known dimethyl- and bis(trimethylsilyl)-substituted cases, as would be expected.

The ^{13}C NMR spectrum also supported the structural assignment of **5a**. There were three signals in the methyl–silyl region. The least intense, at -3.97 ppm, was assigned to the methyl group on the ring-silicon atom. The other signals were assigned based on the observed one-bond ^{29}Si–^{13}C coupling constants. The signal at 1.51 ppm, with $^1J(^{29}Si–^{13}C)$ of 44.4 Hz, was attributed to the Me_3Si group (previously observed values fall in the range 44–47 Hz[15]), and the signal at 5.87 ppm, with $^1J(^{29}Si–^{13}C)$ of 61.1 Hz, was assigned to the trimethylsiloxy group (previously observed values range from 59 to 61 Hz[15]). The ring-carbon signal occurred at 110.8 ppm (previously observed values range from 108 to 115 ppm for ring carbons bearing a trimethylsiloxy substituent and an R group varying in structure from benzyl through phenyl to *tert*-butyl[15,16]). Some of these values, for both new and previously described 1,2-disilacyclobutanes, are summarized in Table I.

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(13) Marsmann, H. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: New York, 1981; Vol. 17, p 65.

(14) Ishikawa, M.; Fuchikami, T.; Kumada, M.; Higuchi, T.; Miyamoto, S. *J. Am. Chem. Soc.* **1979**, *101*, 1348. Fritz, G.; Matern, E. *Z. Anorg. Allg. Chem.* **1976**, *426*, 28.

(15) Brook, A. G.; Abdesaken, F.; Gutekunst, G.; Plavac, N. *Organometallics* **1982**, *1*, 994.

(16) Baines, K. M.; Brook, A. G. *Organometallics* **1987**, *6*, 692.

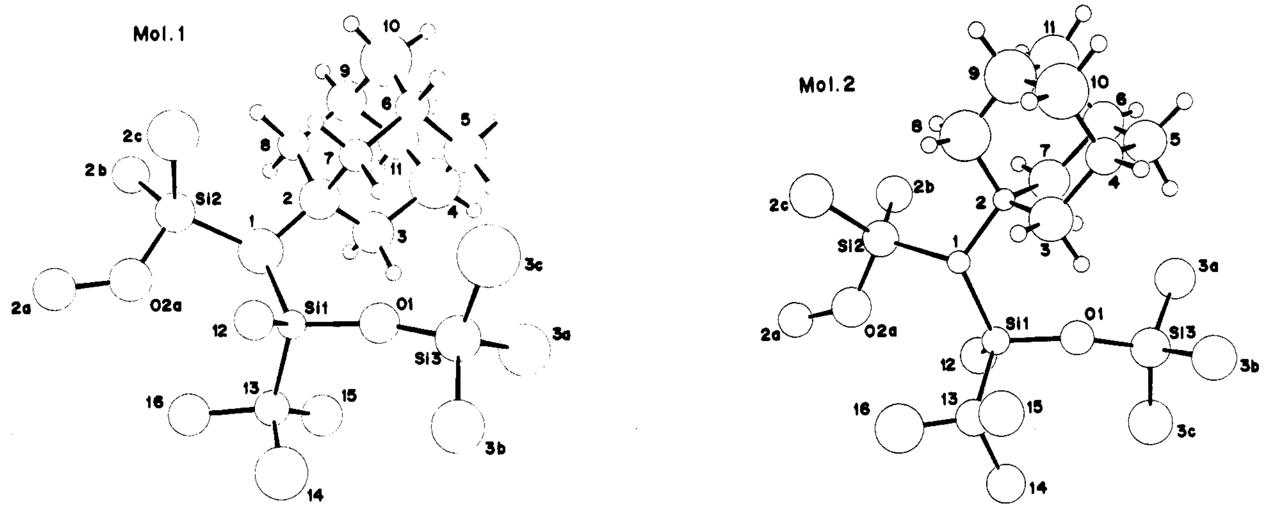


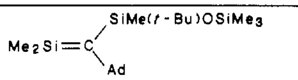
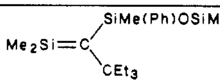
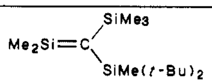
Figure 3. ORTEP view of the two molecules in the methanol adduct **7b** showing the opposite configurations at Si(1). Hydrogen positions in the Ad groups have been drawn with uniform isotropic thermal parameters.

Silene **2b**, $(Me_3Si)(t\text{-}Bu)Si{=}C(OSiMe_3)Ad$, was characterized by its NMR resonances. The position of the sp^2-hybridized carbon atom of the double bond, at 195.6 ppm, is close to the range observed for other siloxy-substituted silenes (197–214 ppm[15]), and, as expected, the absorption of the sp^2-hybridized silicon atom, at 73.7 ppm, was considerably deshielded relative to the shifts previously observed for bis(trimethylsilyl)-substituted silicon atoms (37–54 ppm[15]), but substantially upfield of the chemical shift observed by Wiberg[10] at 144.2 ppm for the stable dialkylated silene $Me_2Si{=}C(SiMe_3)SiMe(t\text{-}Bu)_2$ (see Table II for comparative data on other silenes).

Photolysis of silene **2b**, characterized above, gave an isomeric silene A, trapped as a pair of diastereomeric methanol adducts (**7b**), one of which was purified, free of the second diastereomer. Its ^1H, ^{13}C, and ^{29}Si NMR spectra led to the assignment of structure **7b**: the ^{29}Si NMR spectrum was particularly informative. The fully coupled spectrum showed three signals, at 5.01 (decet, $^2J(^{29}Si-^1H) = 6.6$ Hz, Me_3SiO), 9.79 (multiplet), Me_2Si), and 18.29 (broad multiplet, MeSi) ppm. When the spectrum was run while selectively irradiating at the proton frequency of the *t*-Bu group, neither of the signals at 5.01 or 9.79 ppm showed any significant change (being too remote from the *t*-Bu group for observable coupling) whereas the signal at 18.29 ppm collapsed to a simpler signal analyzed as a quartet (Me–Si) split into doublets (adjacent C–H), consistent with structure **7b** but not with the structure of a methanol adduct which would be derived from silene **8b**, a possible alternative structure as noted earlier (see Scheme III). Table III reports NMR data for a series of methanol adducts from this and previous studies. Crystals of **7b** of borderline size and quality were eventually obtained after several recrystallizations. As mentioned earlier, the structure of **7b** (Figure 3) was solved by X-ray diffraction methods although refinement of the weak data set below $R = 12\%$ was not possible (see Experimental Section). The two independent molecules in the asymmetric unit are mirror images, and a least-squares fit of the non-hydrogen atoms in molecule 1 with the mirror-equivalent atoms in molecule 2 shows maximum deviations of 0.41 Å for the atoms C(*n*2b). The crystal packing consists of layers of molecules parallel to *a* with $z \sim {}^1/_8, {}^3/_8, {}^5/_8, {}^7/_8$. Each layer consists of molecules 1 and 2 of opposite hand. Although the conformations of both molecules are well established, the high *R* factor results in high esd's for individual bond lengths (0.03–0.06 Å) and bond angles (2–4°), and these are available as supplementary material. In the Si–O–Si moieties, the Si–O distances (Å) and Si–O–Si angles are 1.59 (3), 1.64 (3), 159 (2)° and 1.65, 1.65 (3), and 153 (2)° in the two molecules.

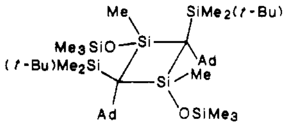
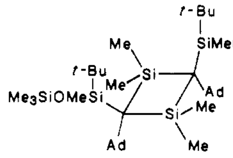
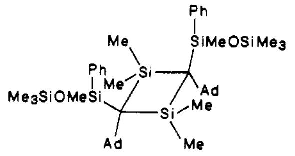
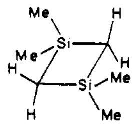
The NMR data and the X-ray structure of the methanol adduct **7b** have been discussed at some length since the structure of **7b** implies a structure for its silene precursor A, namely, **6b**. However, the spectroscopic properties of silene A were not, on initial consideration, entirely consistent with this formulation. In particular, both the ^1H and ^{13}C NMR data of silene A indicated that there were only three types of Me–Si groups in the ratio of 3 (Me_3SiO):2 $(Me_2Si?)$:1 (MeSi) (as expected for structure **8b** but not for **6b**, where the ratio 3:1:1:1 is anticipated, since the two Me groups on the sp^2-hybridized Si atom would be expected to be magnetically nonequivalent. The ^{29}Si NMR spectrum of silene A showed three signals at 6.33 (Me_3SiO), 8.55 (Si sp^3), and 126.5 (Si=C) ppm. This latter value clearly indicates that there cannot be silyl substituents on the sp^2-hybridized silicon atom of **6b**, since resonances at 60–70 ppm are normally found with one attached silyl group and values of 40–55 ppm when two silyl groups are attached (see Table II). A chemical shift of 126 ppm is appropriate for the Me_2Si group in **6b**, being close to the 144 ppm observed for Wiberg's silene $Me_2Si{=}C(SiMe_3)SiMe(t\text{-}Bu)_2$ (see Table IV). However, a chemical shift of 126 ppm is inconsistent with structure **8b** $(Me(Me_3SiO)Si{=}CAd(SiMe_2(t\text{-}Bu))$— see Scheme III), since the Me_3SiO group should deshield the sp^2-hybridized silicon atom to well below 144 ppm. The fully proton-coupled ^{29}Si spectrum showed the signal at 6.33 ppm as a decet as expected and each of the other signals as complex multiplets. The signal at 126.5 ppm observed in the coupled INEPT mode can be interpreted as a distorted septet (consistent with Me_2Si), and is certainly not a quartet as demanded by structure **8b**. The $^1H-^{29}Si$ 2D NMR spectrum of silene **6b** clearly showed that the silicon peak at 126 ppm correlated only to the proton peak at 0.61 ppm whose intensity corresponded to two methyl groups, again indicating that two nominally equivalent methyl groups were attached to the sp^2-hybridized silicon atom of the silene. The absorption of the sp^2-hybridized carbon atom of **6b** at 118.1 ppm was shifted considerably upfield relative to the carbon atom in **2b** (195.6 ppm) as would be expected if a trimethylsiloxy group was replaced by a silyl group. Thus, other than the surprising single signal of the two methyl groups on silicon (which will be discussed

Table IV. Selected NMR Resonances for Dimethylsilenes

	 **6b**	 **6f**	 ref 10
^{29}Si			
Me_2Si=	126.5	*a*	144.2
Si sp^3	8.6	*a*	−4.6 (Me_3Si)
Me_3SiO	6.3	*a*	6.0 (MeSi)
^{13}C			
C=	118.1	110.6	77.2 (C_7D_8)
Me_3C	21.1		21.8

[a] Not observed due to short lifetime.

Table V. Selected NMR Resonances for 1,3-Disilacyclobutanes

	 **9b**	 **10b**	 10e$_1$	10e$_2$	10e$_3$	 ref 14
^{29}Si						
Si ring	4.3	7.1	3.1	−2.6	5.5	−2.7
Si sp^3	3.9	4.2	−3.0	4.6, 2.4	6.0	
Me_3SiO	7.8	2.5	7.14	7.08	8.8	
^{13}C						
C ring	50.7	43.1	43.4	43.1	41.2	−3.0
Me_3C	24.6	25.1				

further below) the data for silene A are in reasonable accord with structure **6b**, and *not* with structure **8b**. Other structures such as Me(*t*-Bu)Si=C(Ad)$SiMe_2OSiMe_3$ cannot be correct, since the ^{13}C NMR spectrum of silene A clearly indicated that the *t*-Bu group was attached to sp^3-hybridized Si (δ(Me_3C) 21 observed—see Table II) and not sp^2-hybridized Si (where a value of δ(Me_3C) 28 would be expected from data known for several model compounds including structure **2b** (Table II)).

The Structures of Dimers 9b and 10b. A brief discussion about the NMR spectra of dimers **9b** and **10b**, which formed from silene **6b**, is in order although the data did not lead to an unambiguous assignment of structures independent of the X-ray diffraction findings (for structures see Scheme III). Dimer **9b** had three different ^{1}H NMR methyl-on-silicon signals with the intensity ratio of 6:4:2. Its ^{29}Si NMR spectrum showed signals for three unique silicon atoms, all at positions inconsistent with the presence of Si–Si bonds, while the ^{13}C NMR spectrum showed that both *tert*-butyl and both adamantyl groups were magnetically equivalent. These data together with the ring-silicon atom signal at 4.26 ppm and the ring-carbon atom signal at 50.74 ppm were entirely consistent with the 1,3-disilacyclobutane structure found by X-ray crystallography (see Table V for a summary of NMR data for several 1,3-disilacyclobutanes).

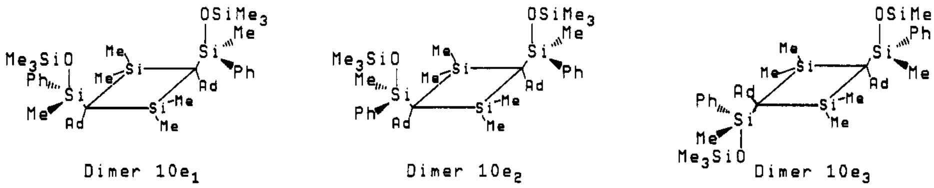
Dimer **10b** had four signals in the Me–Si region of the ^{1}H NMR spectrum with the intensity ratio of 6:2:2:2 (note that a C_2 axis of rotation passes perpendicularly through the center of the ring) due to the trimethylsiloxy and three different Me–Si groups (also seen in the ^{13}C NMR spectrum). The ring-carbon atom absorbed at about 43 ppm and the ^{29}Si NMR spectrum showed three unique silicon absorptions consistent with the crystal structure: the signal of the ring-silicon atom at 7.13 ppm clearly indicated the absence of silicon–silicon bonds. On the basis of the crystal structures of these dimers, it is obvious that the original silene **2b** has undergone some remarkable transformations in rearranging to silenes **6b**, and **8b**, as discussed below.

Photolysis of acylsilane **1c** led to formation of a single dimeric species assigned the 1,2-disilacyclobutane head-to-head dimeric structure **5c** as described above. The ring carbon atom was observed at the normal position, 109 ppm (usual range 100–115 ppm), while the ring-Si atom signal at −18.5 ppm was appropriately downfield of the positions (−40 to −49 ppm) normally found for bis(trimethylsilyl)-substituted ring-silicon atom resonances in 1,2-disilacyclobutanes[15] (see Table I).

Photolysis of acylsilane **1e** initially gave rise, as described above, to a pair of isomeric species assigned the 1,2-disilacyclobutane structures **5e** (see Scheme IV). The ^{13}C NMR data contained resonances attributable to a pair of isomeric head-to-head dimers, particularly those at 113.5 and 115.0 ppm due to the ring-carbon atoms. However, the ring-Si atom resonances occurred at −2.5 and −3.0 ppm, respectively, positions somewhat downfield of expectations based on the behavior of the *t*-Bu analogue **5c** described above. However, all other resonances, and the chemical behavior, were in better accord with these species being head-to-head dimers than head-to-tail dimers (1,3-disilacyclobutanes) for which no precedents for facile dissociation to the silene monomer have been observed. The somewhat unusual chemical shifts of the ring-silicon atoms may be due to electronic effects of the attached phenyl groups in these highly crowded compounds.

Photolysis of acylsilane **1f** gave rise to the short-lived silene **2f** which could be characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. The chemical shifts for the sp^2-hybridized Si and C atoms at 61.6 and 191 ppm, respectively, were in complete accord with previous findings (for $(Me_3Si)_2Si{=}C(OSiMe_3)CEt_3$ the values were 54.3 and 207.3 ppm[15]) (see Table II for other related data).

The Structures of Dimers 10e$_{1-3}$ by NMR Studies. The structures of the three dimers **10e$_1$**, **10e$_2$**, and **10e$_3$** obtained from silene **6e** as a result of the isomerization of silene **2e** were not unambiguously defined by their NMR data. All ring-silicon atom absorptions lay in the range 3–6 ppm, indicating the absence of bonds to other silicon



Dimer $10e_1$ cis-RR:SS

Dimer $10e_2$ cis-RS:SR

Dimer $10e_3$ trans-RR:SS

Figure 4. 1,3-Disilacyclobutanes $10e_1$ (cis-*RR*:*SS*), $10e_2$ (cis-*RS*:*SR*), and $10e_3$ (trans-*RR*:*SS*).

atoms, and the quaternary ring-carbon atoms, while difficult to distinguish from the adamantyl quaternary carbon atoms, resonated in the range 41–43 ppm, values consistent with head-to-tail (but not head-to-head) dimers. The crystal structure of the major dimer $10e_1$ showed it to be the cis-*RR*:*SS* dimer of silene **6e**, which possesses a 2-fold rotation axis perpendicular to the ring. (cis implies that the adamantyl groups are on the same side of the plane of the four-membered ring—see Figure 4). Thus there were four absorptions in the methyl–silyl region of the ^1H NMR spectrum with the intensity ratio of 18:6:6:6, corresponding to the trimethylsiloxy groups and three equivalent pairs of methyl groups (two on the ring-silicon atoms and one on the silyl side chain). Dimer $10e_2$, isolated in intermediate amount, was shown by X-ray analysis to be the cis-*RS*:*SR* isomer, with a mirror plane perpendicular to the ring and coinciding with the ring diagonal through the two ring-silicon atoms. Consistent with this was the finding of six different Me–Si absorptions in the ^1H NMR spectrum, with the intensity ratio of 18:6:3:3:3:3. These absorptions are due to two equivalent trimethylsiloxy groups, two equivalent side-chain methyl groups, and four nonequivalent methyl groups, since each methyl group on both ring-silicon atoms is in a different magnetic environment.

The structure of the minor isomer $10e_3$ was assigned on the basis of its NMR spectral data. The methyl–silyl signals in the ^1H NMR spectrum occurred with an intensity ratio of 18:6:6:6 consistent with either the trans-*RR*:*SS* or trans-*RS*:*SR* dimers of silene **6e** (trans implies that the adamantyl groups are on opposite sides of the plane of the ring). The trans-*RR*:*SS* isomer possesses a twofold rotation axis which lies through the two ring-silicon atoms, leading to four nonequivalent silicon atoms ($10e_3$ had four different silyl signals in the ^{29}Si NMR spectrum). In contrast the trans-*RS*:*SR* isomer, with a center of inversion in the ring, would have only three uniquely different silicon atoms. Since all the other data for $10e_3$ were similar to that of $10e_1$ and $10e_2$, it is clear that dimer $10e_3$ has the structure of the trans-*RR*:*SS* compound. Thus all of the dimers observed are derived from a single silene with the structure **6e**.

The fourth possible dimer from silene **6e**, namely, the trans-*RS*:*SR* head-to-tail dimer, was not detected but could well have been present in small amounts in the mother liquor from which $10e_{1-3}$ were crystallized.

As mentioned above, the structures of the silenes obtained from the unusual rearrangements of the initially formed *tert*-butyl and phenylsilenes **2b** and **2e** were unambiguously established by determination of the crystal structures of the dimers derived therefrom. Full crystallographic details are provided in the following paper.[36]

All four dimers with established crystal structures, i.e. **9b** and **10b** (from **8b** and **6b**, respectively) and $10e_1$ and $10e_2$ (both "cis" isomers from **6e**) and dimer $10e_3$, whose "trans" structure was determined from its NMR data, are head-to-tail dimers. This is to be expected since each of the silene monomers which underwent dimerization is a "simple" silene (i.e. they lack silyl groups attached to an sp^2-hybridized silicon atom or a siloxy group attached to an sp^2-hybridized carbon atom, features which usually characterize silenes which undergo head-to-head dimerization[5,6,8]). "Simple" silenes are well-known to dimerize in a head-to-tail manner, driven by the polarization of the silicon–carbon double bond. By virtue of the symmetry of each molecule, regardless of how the ring of any of the dimers is bisected back to monomer, only a single silene species was produced in each case.

Mechanism of the Silene-to-Silene Rearrangements. The data given above clearly demonstrate that some of the silenes **2** formed initially in the usual manner involving a photochemical 1,3-sigmatropic rearrangement of a silyl group from silicon to oxygen of an acylsilane **1**, subsequently undergo further photochemical rearrangements (see Scheme V). These involve in each case rearrangement of a trimethylsilyl group of **2** from silicon to carbon, migration of the trimethylsiloxy group of **2** from carbon to silicon, and a 1,3-methyl migration from silicon to silicon, resulting in silenes assigned the structure D, based on the crystal structures of several head-to-tail dimers and one methanol adduct.

Since the silene isomerizations have been shown to be photochemical processes, it seems reasonable to invoke an excited state B of silene **2** as an intermediate in this process. Since the π bond of a silene is much weaker than that of an alkene and these silenes absorb in the same region as the output of the UV lamps employed (340–360 nm, see Experimental Section), this excitation is readily achieved and the excited twisted state of such a heavily substituted molecule may be reasonably stable and long-lived.[6,8,17] The twisted geometry of the excited state (either as a singlet or a triplet[18]), and its orbitals, appear appropriate to facilitate the required siloxy and silyl shifts (by a dyotropic rearrangement?—see below) as depicted in Scheme V, ultimately giving the rearranged silene C, presumably in its ground state. Since there is no experimental observation for the formation of C (no dimers or derivatives), this infers that the 1,3-methyl migration required to give rise to the observed silene product D must occur very rapidly, as has been observed previously in some cases.[10,19,20] The precise mechanism by which such 1,3-silyl migrations occur has not been established to date. However, unless some dramatic rearrangement occurs in the process of dimerization or reaction with methanol, D is the species that dimerizes, reacts with methanol, and which is observed spectroscopically.

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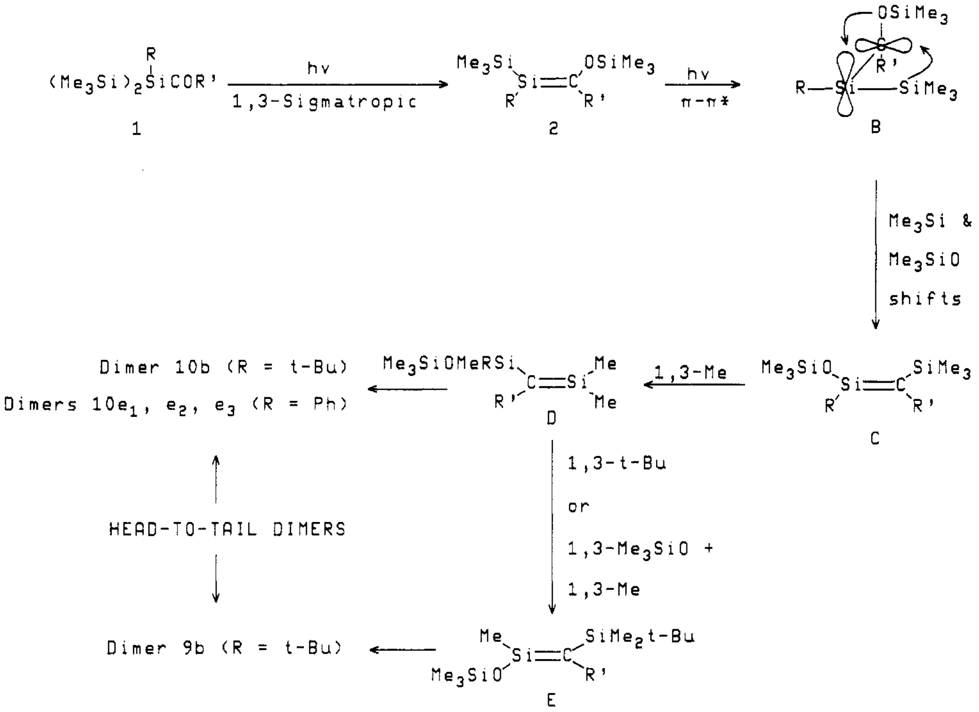
(17) For calculations on the excited states of silenes see: Schmidt, M. W.; Gordon, M.; Dupuis, M. *J. Am. Chem. Soc.* **1985**, *107*, 2585. Yoshioka, Y.; Goddard, J. D.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1981**, *103*, 2452. Hanamura, M.; Nagase, S.; Morokuma, K. *Tetrahedron Lett.* **1981**, *22*, 1813 and references contained therein.

(18) We are unable to establish the multiplicity of this species since any possible quenchers (dienes, amine oxides, etc.) or sensitizers (ketones) are known to react readily with the silene.

(19) Wiberg, N.; Wagner, G. *Chem. Ber.* **1986**, *119*, 1467. We are grateful to Professor Wiberg for providing us with additional details of the NMR spectra of his stable silenes.

(20) Eaborn, C.; Happer, D. A. R.; Hitchcock, P. B.; Hopper, S. P.; Safa, K. D.; Washburne, S. S.; Walton, D. M. *J. Organomet. Chem.* **1980**, *186*, 309.

Scheme V



Using Scheme V, the formation of E, the necessary precursor of the dimer **9b** found as a photochemical product, can be explained either by a 1,3-*tert*-butyl migration from D (which seems somewhat unlikely because of the bulk of the group) or by successive 1,3-trimethylsiloxy and 1,3-methyl migrations. Ando has reported a 1,3-shift of an ethoxy group in a silene.[21]

Several experimental details deserve comment. In interpreting the above results, it was a matter of concern that both the proton and ^{13}C NMR spectra of two silenes, **6b** and **6f**, assigned the general structure D, showed only three Me-on-silicon signals in the ratio of 3:2:1, instead of four signals in the ratio 3:1:1:1 as a result of the anticipated nonequivalence of the two methyl groups attached to the sp^2-hybridized silicon atom. Unless the two methyl groups are accidentally equivalent, there must be some process that allows these two methyl groups to become magnetically equivalent (possibly by rotation about the nominal Si=C bond in D) under very mild conditions. A twisted conformation or free rotation would lead to the observed 3:2:1 ratio of intensities of signals. In this connection it is significant to note that the ^1H and ^{13}C NMR spectra of the Wiberg silene $Me_2Si{=}C(SiMe_3)SiMe(t\text{-}Bu)_2$ also do not show separate resonances for the two methyl groups attached to the sp^2-hybridized silicon atom at room temperature. However, in the Wiberg case the ^1H resonance attributable to the $Me_2Si{=}$ group begins to show signs of separating into two different Me–Si signals at −70 °C, while the ^{13}C spectrum clearly shows two separate resonances in an approximate 1:1 ratio for the $Me_2Si{=}$ group at this temperature (−70 °C).[19] Low-temperature (−50 to −85 °C) ^1H NMR spectra of both silenes **6b** and **6f** show some indications of broadening and possible splitting of the proton signal attributed to the $Me_2Si{=}$ group. Thus, in both the present case and the Wiberg case, at least at room temperature, the structural formulations for the dimethylsilenes, as determined chemically, are not in complete accord with the spectroscopic behavior of these species. The NMR and ESR data (see below) may be an indication of a phenomenon, possibly associated at least in part with the rapid 1,3-methyl shift, not presently fully recognized or understood.

The rearrangements of the two groups Me_3Si and Me_3SiO between silicon and carbon, if simultaneous, essentially constitute a dyotropic rearrangement[22] across a double bond. No confirmed precedents for dyotropic rearrangements across double bonds have been reported, although West has proposed this process as a possible explanation of some observed disilene isomerizations.[23] Dyotropic rearrangements of silyl groups across single bonds are well precedented.[22]

A variety of multistep pathways involving possible intermediary silylenes, carbenes, or disilacyclopropanes can be written and have been considered as alternative interpretations of the silene isomerizations. However, all attempts using trapping agents to intercept possible intermediates, such as those proposed in a preliminary communication,[24] have failed to date. Thus attempts to intercept possible silylene intermediates with silanes or carbene intermediates with methanol failed. Some disilacyclopropanes with structures closely related to possible reaction intermediates have been synthesized and isolated[25] but, unlike the case where a mesityl group was attached to the original sp^2-hybridized carbon atom of the silene,[9] when the attached group was Ad or *t*-Bu the disilacyclopropanes did not rearrange under mild conditions, and hence they seem unlikely candidates as reaction intermediates.

Finally, the interpretation outlined in Scheme V helps to explain the differences in behavior of silene **2** where R = Me or Me_3Si, which do not undergo subsequent photochemical isomerization, with the behavior where R = *t*-Bu or Ph, where subsequent photoisomerization is observed.

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(21) Ando, W.; Sekiguchi, A.; Sato, T. *J. Am. Chem. Soc.* **1981**, *103*, 5573.

(22) Reetz, M. T. *Adv. Organomet. Chem.* **1977**, *16*, 33.

(23) Yokelson, H. B.; Maxka, J.; Siegel, D. A.; West, R. *J. Am. Chem. Soc.* **1986**, *108*, 4239.

(24) Brook, A. G.; Safa, K. D.; Lickiss, P. D.; Baines, K. M. *J. Am. Chem. Soc.* **1985**, *105*, 4338.

(25) Unpublished studies from these laboratories by W. J. Chatterton.

Silene **2a** (R = Me) rapidly dimerizes to its head-to-head dimer **5a**, and this process must be more rapid than photoisomerization (dimerization would not be inhibited by the small size of the Me group, compared to the situation where Ph or *t*-Bu groups are attached to the silicon atom). No member of the family of silenes **2** where R = Me_3Si has been observed to photoisomerize in the manner described above, despite attempts to effect isomerization.[25] When the R′ group on carbon is relatively small (R′ = *t*-Bu, Ph, BCO), head-to-head dimerization occurs readily (more rapidly than photoisomerization), and when R′ is larger (Ad, CEt_3), the silenes remain as stable monomers. In contrast, when the R group on silicon is relatively bulky (*t*-Bu, Ph), there appears to be considerably greater steric congestion in the silene **2**, inhibiting planarity and presumably reducing the energy barrier to the twisted species B (Me_3Si is also bulky, but the long Si–C single bond should reduce the effective steric hindrance markedly). Species such as B or D may be relatively stable in a twisted conformation and hence might show radical character. Consistent with this was the finding that a perdeuteriotoluene solution of **6b** (D, R = *t*-Bu, R′ = Ad) even after standing for 2 weeks at about −20 °C showed a relatively intense, broad, characterless ESR signal, consistent with the presence in solution of a long-lived radical species bearing an attached silicon atom. It may be that the achievement of twisted geometries such as that of B are relatively facile processes in these rather sterically hindered molecules.

We are continuing to investigate details of these rearrangement pathways, and the roles that size of substituent and electronic effects play on the ease of these silene rearrangements.

Stereochemistry of the Reactions. It is worthwhile considering some of the stereochemical features of these reactions. The methylsilene **2a**, which could exist as two geometrical isomers, led to only a single dimer **5a** although it reacted with methanol to give a diastereomeric mixture of methanol adducts. There is no evidence suggesting that one geometric isomer of a possible pair of silenes was isomerized to the other isomer under the experimental conditions employed. Hence the results are best interpreted as due to the formation of a single silene geoisomer (whose geometry might alter from case to case depending on the relative sizes of the substituents) which reacted nonstereospecifically with methanol, most probably by a two-step process involving initial attack by the methanol oxygen atom on the sp^2-hybridized silicon atom of the silene.

This interpretation applies equally well with silenes **2b**, **2e**, and **2f**, for which there is further supporting evidence. When the *tert*-butylacylsilane **1b** was photolyzed, only a single geometric isomer of silene **2b** could be observed by NMR techniques, yet a 3:1 ratio of diastereomeric methanol adducts was obtained. While silene **2e** derived from the phenylacylsilane **1e** could not be observed by NMR methods because of its rapid but reversible dimerization (the spectra of the dimers can be explained on the basis of a single silene geometric isomer), it also formed a diastereomeric mixture of methanol adducts. Finally silene **2f**, observed as a single geometric isomer, gave a mixture of methanol adducts. Tests confirmed that a pure diastereomer, when dissolved in methanol, did not isomerize to the observed mixture of diastereomers over prolonged periods of time, either in the dark or when photolyzed. Jones has recently provided compelling evidence[11,26] that certain silene adducts from which a silene is liberated at high temperature in the presence of traps such as methanol or trimethylmethoxysilane react in a stereospecific manner. However, both the silenes involved and the reaction conditions employed were very different, and hence it may not be appropriate to compare Jones' and our results. In the present case all the evidence supports the position that on photolysis of the acylsilanes only a single silene geometrical isomer is formed and that this reacts in a nonstereospecific manner with methanol.

Finally, it is interesting to note that during the course of these studies there was no evidence that dimers derived from the combination of two different silenes were ever formed in detectable amounts, despite the fact that in some cases two different silenes must have existed in solution at the same time. It is evident that some remarkable and selective chemistry has occurred during the course of these reactions, which are currently under further investigation in our laboratories.

Experimental Section

All reactions were carried out in oven-dried glassware under an atmosphere of dry argon. Solutions were transferred with syringes or cannulae. THF and Et_2O were distilled from the sodium ketyl of benzophenone, pentanes or benzene were distilled from $LiAlH_4$, and MeOH was distilled from magnesium methoxide prior to use. MeLi was obtained from the Aldrich Chemical Co. The acid chlorides were prepared by reaction of the corresponding carboxylic acids with thionyl chloride and were distilled prior to use. 1-Adamantanecarboxylic acid chloride was used as received from Aldrich Chemical Co. Chromatography was carried out on silica gel columns or on "Chromatotron" silica plates.

NMR spectra were recorded on a Varian CFT-20, XL-200, or XL-400 or Bruker WP-80 spectrometer using deuteriated benzene as solvent unless otherwise noted. The standards used were as follows: residual C_6D_5H, δ 7.15 for ^1H NMR spectra; C_6D_6 central transition, δ 128.00 for ^{13}C NMR spectra, Me_4Si as an external standard, δ 0.00 for ^{29}Si NMR spectra. The ^{29}Si NMR spectra were usually recorded by using the INEPT[27] or DEPT[28] pulse sequence, and ^{13}C NMR signal assignments were made by using the DEPT[28] or APT[29] pulse sequences or by recording the proton-coupled spectra. IR spectra were recorded on a Nicolet 5DX FT instrument, and mass spectra were recorded by using a Du Pont 21-490 mass spectrometer (reported in mass-to-charge units, *m*/*z*, with intensities of peaks relative to the base peak and ion identity in parentheses). Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

Photolyses were carried out by using two to four 100-W Par 38 mercury spot lamps (Blak-Ray, Ultraviolet Products Inc., $\lambda \geqslant 360$ nm). Solutions were photolyzed under an atmosphere of argon in Pyrex Schlenk or NMR tubes immersed in a cold water bath (10–15 °C).

Cophotolyses of acylsilanes with methanol were always carried out in the presence of a trace of pyridine, experience having demonstrated, as had been observed previously,[37] that, unless a trace of base was present during the photolysis, methanolysis of the Me_3SiOC– group in the resulting methanol adducts to Me_3SiOMe and –COH occurred. Addition of methanol to the preformed silene or to dimers in the dark did not employ pyridine: this difference in the experimental conditions may explain cases where the ratio of diastereomeric methanol adducts obtained from two different pathways differed somewhat.

Methyltris(trimethylsilyl)silane. $(Me_3Si)_3SiLi\cdot3THF$[30] (4.89 g, 0.1 mol) dissolved in pentanes (200 mL) and THF (25 mL) was added dropwise over 0.5 h to an ice-cooled solution of methyl iodide (10 mL, 0.16 mol) in pentanes (250 mL). A fine white

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[27] Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760.

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[29] Patt, S. L.; Shoolery, J. N. *J. Magn. Reson.* **1982**, *46*, 535.

[30] Gutekunst, G.; Brook, A. G. *J. Organomet. Chem.* **1982**, *225*, 1.

precipitate appeared immediately in the pale yellow reaction mixture. After being stirred overnight at room temperature, the reaction mixture was filtered and then worked up under aqueous conditions. Distillation yielded 24.5 g (54%) of a colorless semisolid with properties identical with those reported.[31]

***tert*-Butyltris(trimethylsilyl)silane.** A solution of *tert*-butyltrichlorosilane (63.9 g, 0.33 mol) in THF (100 mL) was added dropwise to a heterogeneous mixture of trimethylchlorosilane (182 mL, 1.44 mol) and small, flattened (by hammering) pieces of lithium metal (13.9 g, 2 g-atom) in THF (250 mL). The reaction was stirred with a mechanical stirrer for 18 days, the required time for completion of the reaction as determined by ^{1}H NMR spectroscopy. After filtration and then aqueous workup, the product was purified by sublimation (80 °C at approximately 2 mmHg) to yield 80.4 g (79%) of a white solid: mp (sealed tube) >295 °C (sublimed before melting). ^{1}H NMR δ 0.26 (s, SiMe$_3$, ^2J(Si–H) = 6.4 Hz), 1.16 (s, *t*-Bu); ^{13}C NMR δ 2.44 (SiMe$_3$, ^1J(Si–C) = 44.0 Hz), 21.29 (*C*Me$_3$), 32.86 (C*Me*$_3$); ^{29}Si NMR δ −13.60 (SiMe$_3$), −62.12 (*Si*Si$_3$); MS, *m/z* 304 (15, M$^+$), 247 (27, M$^+$ − *t*-Bu), 173 (30), 131 (21), 73 (100, [SiMe$_3$]$^+$).

Phenyltris(trimethylsilyl)silane. A solution of phenylmagnesium bromide, made from bromobenzene (16 mL, 0.15 mol) in THF (200 mL) and magnesium turnings (4 g) in THF (10 mL), was added dropwise over 1.5 h to a solution of tris(trimethylsilyl)silyl bromide[32] (38.7 g, 0.12 mol) in THF (50 mL). After the solution was stirred at room temperature for 21 h, the precipitated salts were removed by filtration and washed with pentanes. After aqueous workup, distillation under reduced pressure yielded 36.8 g (95%) of a colorless semisolid: ^{1}H NMR (CDCl$_3$) δ 0.26 (s, SiMe$_3$, ^2J(Si–H) = 6.4 Hz), 7.21–7.60 (m, Ph); ^{13}C NMR (CDCl$_3$) δ 1.39 (SiMe$_3$, ^1J(Si–C) = 44.9 Hz), 127.48 (*p*-C), 127.83 (*m*-C), 135.36 (ipso-C), 136.59 (*o*-C) (Ph); ^{29}Si NMR δ −12.69 (SiMe$_3$), −76.45 (*Si*Si$_3$); MS, *m/z* 324 (30, M$^+$), 309 (11, M$^+$ − Me), 251 (19, M$^+$ − SiMe$_3$), 174 (100, [Si(SiMe$_3$)$_2$]$^+$).

(1-Adamantylcarbonyl)methylbis(trimethylsilyl)silane (1a). MeLi (36 mL, 50 mmol) in Et$_2$O was added to a solution of methyltris(trimethylsilyl)silane (13.1 g, 50 mmol) in THF (250 mL). After the solution was stirred at room temperature for 24 h, most of the solvent (240 mL) was removed under reduced pressure and the residue was dissolved in pentanes (150 mL). The golden orange silyllithium reagent was then added via a double-ended needle to an ice-cooled solution of 1-adamantanecarboxylic acid chloride (10.9 g, 60 mmol) in pentanes (100 mL). The reaction mixture, protected from light, was then warmed to room temperature and stirred for 3 h. The precipitated salts were removed by filtration and washed with Et$_2$O. After workup under acidic conditions, the desired product was isolated by preparative liquid chromatography (80:20 hexanes–dichloromethane) and purified by Kugelrohr distillation (pot temperature 150 °C, 0.05 mmHg) to yield 9.0 g (51%) of a waxy white solid: mp 32–34 °C; ^{1}H NMR δ 0.20 (s, 18 H, SiMe$_3$), 0.43 (s, 3 H, Me), 1.46–2.02 (m, 15 H, Ad); ^{13}C NMR δ −0.38 (SiMe$_3$), −5.70 (Me), 28.44 (CH, Ad), 37.10, 37.19 (2 CH$_2$, Ad), 52.03 (quat C, Ad), 247.25 (C=O); ^{29}Si NMR δ −13.72 (SiMe$_3$), −50.38 (*Si*Si$_2$); IR (KBr disk) 1613 (s, C=O) cm^{-1}; MS, *m/z* 352 (10, M$^+$), 337 (7, M$^+$ − Me), 189 (100, [(MeSi(SiMe$_3$)$_2$]$^+$): M$^+$ requires 352.2074, found 352.2062.

(1-Adamantylcarbonyl)*tert*-butylbis(trimethylsilyl)silane (1b). MeLi (37 mL, 52 mmol) in Et$_2$O and TMEDA (8 mL) were added to a solution of *tert*-butyltris(trimethylsilyl)silane (15.2 g, 50 mmol) in THF (150 mL). The reaction mixture was heated to 50 °C for 31 h at which time a ^{1}H NMR spectrum of the reaction mixture revealed that approximately 50% of the starting material (at 0.24 ppm) remained, but no MeLi was left (due to its decomposition in THF at elevated temperatures[33]), and thus, more MeLi (32 mL, 40 mmol) and TMEDA (6.4 mL) were added. The reaction mixture was stirred at 50 °C for an additional 24 h, at which time, a ^{1}H NMR spectrum revealed that although some of the silane remained, decomposition of the silyllithium reagent had begun and thus the reaction was stopped to prevent further formation of the decomposition product ((Me$_3$Si)$_2$(*t*-Bu)SiLi, 0.07 ppm; decomposition product, 0.17 ppm). The brown silyllithium reagent solution was cooled to room temperature and added dropwise, via a double-ended needle, to an ice-cooled solution of 1-adamantanecarboxylic acid chloride (9.98 g, 50 mmol) in pentanes (150 mL). The orange reaction mixture was then warmed to room temperature and stirred for 4 h before being worked up under acidic conditions. The residue was purified by using preparative liquid chromatography (85:15 hexanes–dichloromethane) and afforded 20% of recovered starting material, 10% of (Me$_3$Si)$_2$(*t*-Bu)Si(CH$_2$)$_4$OCOAd, and 6.91 g (38%) of the desired acylsilane as pale yellow platelets: mp 87–88 °C; ^{1}H NMR δ 0.30 (s, 18 H, SiMe$_3$), 1.19 (s, 9 H, CMe$_3$), 1.5–2.1 (m, 15 H, Ad); ^{13}C NMR δ 2.13 (SiMe$_3$), 22.13 (quat C, *C*Me$_3$), 31.72 (C*Me*$_3$), 28.42 (CH, Ad), 37.04, 37.08 (2 CH$_2$, Ad), 51.46 (quat C, Ad), 246.53 (C=O); ^{29}Si NMR δ −15.48 (SiMe$_3$), −32.24 (*Si*Si$_2$); IR (KBr disk) 1622 (s, C=O) cm^{-1}; MS, *m/z* 394 (2, M$^+$), 379 (5, M$^+$ − Me), 337 (14, M$^+$ − CMe$_3$), 73 (100, [SiMe$_3$]$^+$), UV (hexane) λ_{max} (ϵ) 220 (9000), 260 (1300, shoulder), 380 nm (200). Anal. Calcd for C$_{21}$H$_{42}$Si$_3$O: C, 63.88; H, 10.72. Found: C, 63.48; H, 10.35.

Pivaloylbis(trimethylsilyl)phenylsilane (1c). Phenyltris(trimethylsilyl)silane (14.5 g, 44.6 mmol) in THF (100 mL) was stirred at room temperature with MeLi (1.4 M in Et$_2$O, 32 mL) for 48 h. The solvents were removed under reduced pressure, and the resulting solid was recrystallized from pentanes at −20 °C to yield 17.1 g (81%) of pale yellow solid silyllithium reagent. This material (which appeared to have the formula (Me$_3$Si)$_2$PhSiLi·3THF based on the integration of its ^{1}H NMR spectrum) was dissolved in pentanes (150 mL) and then added slowly over 1.5 h to a solution of pivaloyl chloride (36 mmol) in pentanes (50 mL) at 0 °C. After the solution was warmed to room temperature and stirred for an additional 0.5 h, workup yielded a yellow solid which on recrystallization from pentanes at −78 °C gave 9.8 g (81%) of a colorless product: mp 30–33 °C; ^{1}H NMR δ 0.21 (s, 18 H, Me$_3$Si), 0.90 (s, 9 H, *t*-Bu), 7.2–7.6 (Ph); ^{13}C NMR δ 0.53 (Me$_3$Si), 25.27 (*Me*$_3$C), 50.30 (Me$_3$*C*), 247.16 (C=O), 128.48, 129.13, 135.92, 137.07 (Ph); ^{29}Si NMR δ −13.38 (Me$_3$Si), −44.59 (Me$_3$Si*Si*).

Mesitoylbis(trimethylsilyl)phenylsilane (1d). This compound was prepared in the usual manner by coupling (bis(trimethylsilyl)phenylsilyl)lithium–tris(tetrahydrofuran) with the acid chloride of mesitoic acid in pentanes. After isolation and purification by flash chromatography (80:20 hexanes–dichloromethane) a 54% yield of a yellow solid, mp 46–47 °C, was obtained: ^{1}H NMR δ 0.27 (18 H, s, SiMe$_3$), 2.06 (6 H, s, *o*-Me), 2.02 (3 H, s, *p*-Me), 6.53 (2 H, s, Ar), 7.05–7.57 (5 H, m, Ph); ^{13}C NMR δ 0.13 (Me$_3$Si), 19.69 (*o*-Me), 21.00 (*p*-Me), 127.72, 127.96, 132.32, 134.26, 135.53, 138.07, 145.42 (Ar), 247.80 (C=O); ^{29}Si NMR δ −13.91 (SiMe$_3$), −46.59 (*Si*Si$_2$); IR (neat) 1609 (s, C=O) cm^{-1}; M$^+$ requires 398.1917, found 398.1928.

(1-Adamantylcarbonyl)phenylbis(trimethylsilyl)silane (1e). This compound was prepared in a similar manner to **1c** above but using 1-adamantanecarboxylic acid chloride. The crude pale yellow product was recrystallized from methanol to give 9.47 g (57%) of a crystalline solid: mp 93–94 °C; ^{1}H NMR δ 0.29 (s, 18 H, SiMe$_3$), 1.31–1.86 (m, 15 H, Ad), 7.02–7.71 (m, Ph); ^{13}C NMR δ 0.50 (SiMe$_3$, ^1J(C–Si) = 45.7 Hz), 28.31 (CH, Ad), 36.87, 37.42 (2 CH$_2$, Ad), 53.04 (quat C, Ad), 128.40, 129.06, 136.12, 137.11 (Ph), 247.12 (C=O); ^{29}Si NMR δ −13.45 (SiMe$_3$), −44.75 (*Si*Si$_2$); IR (KBr disk) 1609 (s, C=O) cm^{-1}; MS, *m/z* 414 (17, M$^+$), 399 (8, M$^+$ − Me), 251 (78, [SiPh(SiMe$_3$)$_2$]$^+$), 135 (100, [Ad]$^+$); C$_{23}$H$_{38}$Si$_3$O requires 414.2231, found 414.2224; UV (hexane) λ_{max} (ϵ) 220 (9600), 245 (9500), 260 (6100, shoulder), 380 nm (200). Anal. Calcd for C$_{23}$H$_{38}$Si$_3$O: C, 66.60; H, 9.23. Found: C, 66.67; H, 9.28.

(Triethylacetyl)bis(trimethylsilyl)phenylsilane (1f). This acylsilane was prepared in the standard manner and was isolated by flash chromatography (90:10 hexanes–dichloromethane) and was purified by chromatography (98:2 hexanes–dichloromethane) to yield a colorless oil: ^{1}H NMR δ 0.32 (18 H, s, Me$_3$Si), 0.64 (9 H, t, CH$_3$), 1.48 (6 H, q, CH$_2$), 7.11–7.73 (5 H, m, Ph); ^{13}C NMR δ 0.83 (Me$_3$Si), 8.42 (CH$_3$), 24.36 (CH$_2$), 60.58 (Et$_3$*C*), 128.43 (*m*-C, Ph), 129.15 (*p*-C, Ph), 136.02 (*o*-C, Ph), 136.88 (ipso-C, Ph), 247.97 (C=O); ^{29}Si NMR δ −13.85 (Me$_3$Si), −45.52 (*Si*–Si$_2$): IR (neat) 1614 (s, C=O), cm^{-1}; MS, *m/z* 349 (2, M$^+$ − Et), 305 (10, M$^+$ − Me$_3$Si), 251 (100, (Me$_3$Si)$_2$PhSi$^+$).

([2.2.2]Bicyclooctylcarbonyl)tris(trimethylsilyl)silane (1g). Coupling of the acid chloride[34] of [2.2.2]bicyclooctane-

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carboxylic acid with 1 equiv of (tris(trimethylsilyl)silyl)lithium-tris(tetrahydrofuran)[30] in pentane at −78 °C gave after workup and recrystallization from methanol an 85% yield of the acylsilane: mp 52–53 °C; ^{1}H NMR δ 0.42 (27 H, s, Me_3Si), 1.3–1.7 (br, bicyclooctyl = BCO); ^{13}C NMR δ 2.29 (Me_3Si), 25.48 (CH, BCO), 26.05, 26.82 (CH_2, BCO), 50.40 (quat BCO), 245.6 (C=O); ^{29}Si NMR δ −11.5 (Me_3Si, ^1J(Si–Si) = 55.9, ^1J(Si–C) = 45.6 Hz), −78.7 (*Si*Si_3, ^1J(Si—C=O) = 64.1 Hz); IR (CCl_4) 1632 (s, C=O) cm^{-1}. Anal. Calcd for $C_{18}H_{40}Si_4O$: C, 56.16; H, 10.49. Found: C, 56.38; H, 10.44.

Photolysis of Acylsilane 1a. Preparation of Dimer 5a. A solution of acylsilane **1a** (1.25 g) in C_6H_6 (5 mL) was photolyzed for 19 h. The solution remained colorless throughout the photolysis, and a colorless crystalline solid precipitated. The solvent was removed under vacuum to give >95% yield of the head-to-head dimer **5a**, as determined by ^{1}H NMR spectroscopy. Upon exposure to the ambient atmosphere, the solid decomposed to give an uncharacterized gummy residue. Properties of **5a**: ^{1}H NMR δ 0.32, 0.42 (2s, each 9 H, $SiMe_3$), 0.54 (s, 3 H, SiMe), 1.66–2.17 (m, 15 H, Ad); ^{13}C NMR δ −3.97 (SiMe), 1.51 ($SiMe_3$, ^1J(Si–C) = 44.4 Hz), 5.87 ($OSiMe_3$, ^1J(Si–C) = 61.1 Hz), 29.47 (b s, CH, Ad), 37.65 (b s, two CH_2, Ad), 42.45 (quat C, Ad), 110.75 (ring C); ^{29}Si NMR δ 2.31 ($OSiMe_3$), −11.25 ($SiMe_3$), −25.63 (ring Si).

Photolysis of Acylsilane 1a in Methanol. Formation of the Methanol Adduct 4a. Method A. A solution of acylsilane **1a** (100 mg) in C_6D_6 (0.7 mL) containing a few drops of methanol and a drop of pyridine was photolyzed for 2.5 h. A 1:1 ratio of diastereomers of the methanol adducts **4a** were obtained in a yield of >95% as determined by ^{1}H NMR spectroscopy. **Method B.** Dimer **5a** (170 mg), obtained from the photolysis of acylsilane **1a** in benzene, was dissolved in C_6H_6 (15 mL) containing methanol (5 mL). After the solution was stirred at room temperature for 24 h, the solvents were removed under reduced pressure and the residue was shown by ^{1}H NMR spectroscopy to contain only the diastereomers of the methanol adducts of **4a** in a 2:1 ratio. Since conditions for the separation of the two diastereomers could not be found, the methanol adducts **4a** were isolated and analyzed as a mixture. The colorless oil was found to decompose upon prolonged exposure to the atmosphere. **Diastereomer A**: ^{1}H NMR δ 0.24, 0.26 (2s, 18 H total, $SiMe_3$), 0.34 (s, 3 H, SiMe), 3.22 (s, 1 H, CH), 3.35 (s, 3 H, OMe), 1.65–2.00 (m, Ad); ^{13}C NMR δ −1.10 (SiMe), −0.64, 1.18 (2 $SiMe_3$), 29.08 (CH, Ad), 37.51, 40.81 (2 CH_2, Ad), 37.64 or 37.76 (quat C, Ad), 51.29 (OMe), 81.02 (CH); ^{29}Si NMR δ 15.35 ($OSiMe_3$), 11.48 (SiOMe), −20.85 ($SiMe_3$). **Diastereomer B**: ^{1}H NMR δ 0.19, 0.28 (2s, each 9 H, $SiMe_3$), 0.35 (s, 3 H, SiMe), 3.28 (s, 3 H, SiOMe), 3.33 (s, 1 H, CH), 1.65–2.00 (m, Ad); ^{13}C NMR δ −2.53 (SiMe), −0.42, 1.28 (2 $SiMe_3$), 29.08 (CH, Ad), 37.53, 40.68 (2 CH_2, Ad), 37.64 or 37.76 (quat C, Ad), 51.20 (OMe), 79.83 (CH); ^{29}Si NMR δ 15.89 ($OSiMe_3$), 7.79 (SiOMe), −20.85 ($SiMe_3$, accidental overlap). MS data of diastereomeric mixture: MS, *m/z* 384 (2, M$^+$), 369 (10, M$^+$ − Me), 280 (9, M$^+$ − $MeOSiMe_3$), 73 (100, $[SiMe_3]^+$).

Photolysis of Acylsilane 1b. Characterization of Silenes 2b and 6b and Dimers 9b and 10b. A solution of acylsilane **1b** (1.0 g) in C_6H_6 (3 mL) was photolyzed for 19 h. The bright yellow solution was then cooled to −20 °C for several hours. At this temperature the solid benzene matrix was orange in color. Upon warming to room temperature, the orange color faded to yellow, and with shaking, a white solid precipitated from solution. The reaction mixture was left at room temperature for several days to allow completion of the dimerization process, during which time the bright yellow color of the solution faded considerably. The reaction mixture was then decanted, and the precipitate was washed with small aliquots of benzene and dried under vacuum (220 mg). The solid was identified as dimer **9b** and traces of an unidentified product. Dimer **9b** was purified by successive recrystallizations from acetone–CCl_4 or CCl_4 alone, to give colorless rectangular crystals. The pale yellow foam (580 mg) resulting from removal of the solvents from the mother liquor was recrystallized from hot acetone giving dimers **9b** and **10b** in a ratio of 3.5:1. Dimer **10b** was separated from dimer **9b** by fractional crystallization from acetone–chloroform. In the first crop dimer **10b** was obtained pure (30 mg); however, all subsequent crops were contaminated with dimer **9b**. Traces of minor uncharacterized products were also formed during the photolysis.

The above photolysis was repeated several times on different scales in order to follow the sequence of events by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy so that all relevant data pertaining to silenes **2b** and **6b** could be obtained. **Silene 2b**: ^{1}H NMR δ 0.33, 0.39 (2s, each 9 H, $SiMe_3$), 1.33 (s, CMe_3), ca. 1.5–2.2 (m, Ad, overlapped); ^{13}C NMR δ 2.13 ($SiMe_3$, accidental overlap with starting material), 4.47 ($SiMe_3$), 28.34 (*C*Me_3), 31.54 (C*Me*$_3$), 29.35 (CH, Ad), 37.33, 42.34 (2 CH_2, Ad), 43.46 (quat C, Ad), 195.59 (Si=*C*); ^{29}Si NMR δ −13.17 ($SiMe_3$), 12.25 ($OSiMe_3$), 73.69 (*Si*=C). **Silene 6b**: ^{1}H NMR δ 0.19 (s, 9 H, $OSiMe_3$), 0.42 (s, 3 H, SiMe), 0.61 (s, 6 H, $SiMe_2$), 1.08 (CMe_3), 1.6–2.2 (m, Ad); ^{13}C NMR δ 2.75 ($OSiMe_3$), 4.77 (SiMe, ^1J(Si–C) = 54.2 Hz), 6.99 ($SiMe_2$, ^1J(Si–C) = 47.6 Hz), 21.13 (*C*Me_3), 28.45 (C*Me*$_3$), 30.47 (CH, Ad), 37.19, 49.03 (2 CH_2, Ad), 39.65 (quat C, Ad), 118.07 (Si=*C*); ^{29}Si NMR δ 6.33 ($OSiMe_3$, decet), 8.55 (SiMe, m), 126.53 (*Si*=C, probable septet). **Dimer 9b**: mp 220–222 °C; ^{1}H NMR ($CDCl_3$) δ 0.34 (s, 9 H, $OSiMe_3$), 0.50 (s, 6 H, $SiMe_2$), 0.79 (s, 3 H, SiMe), 1.22 (s, 9 H, CMe_3), 1.57–2.51 (m, 15 H, Ad); ^{13}C NMR ($CDCl_3$) δ 2.96 ($SiMe_3$), 8.13 (SiMe), 12.57 ($SiMe_2$), 24.57 (*C*Me_3), 30.79 (C*Me*$_3$), 30.19 (CH, Ad), 36.55, 44.49 (2 CH_2, Ad), 45.57 (quat C, Ad), 50.74 (ring C); ^{29}Si NMR ($CDCl_3$) δ 3.87 ($SiMe_2$), 4.26 (SiMe), 7.82 ($OSiMe_3$); MS, *m/z* 788 (<1, M$^+$), 619 (49), 412 (36), 337 (25, M$^+$/2 − *t*-Bu), 147 (57, $[SiMe_2OSiMe_3]^+$), 133 (63, $[HSiMeOSiMe_3]^+$), 73 (100, $[SiMe_3]^+$). **Dimer 10b**: mp 212–214 °C; ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 18 H, $SiMe_3$), 0.51, 0.58, 0.95 (3s, each 6 H, SiMe), 1.06 (s, 18 H, CMe_3), 1.43–2.34 (m, Ad); ^{13}C NMR ($CDCl_3$) δ 2.91 ($OSiMe_3$), 10.40, 13.07, 13.38 (3 SiMe), 25.09 (*C*Me_3), 30.66 (C*Me*$_3$), 30.14 (CH, Ad), 36.42, 44.63 (2 CH_2, Ad), 43.09, 43.97 (quat C, Ad and ring C); ^{29}Si NMR ($CDCl_3$) δ 2.49 ($OSiMe_3$), 4.15 (SiMe), 7.13 ($SiMe_2$); MS, *m/z* 791 (2, M$^+$), 733 (3, M$^+$ − *t*-Bu), 598 (7, M$^+$ − SiMe(*t*-Bu)$OSiMe_3$), 147 (100, $[SiMe_2OSiMe_3]^+$). **NMR data of an Unidentified Product** (as a mixture with dimer **9b**): ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9 H), 0.59, 0.68, 0.83 (3s, each 3 H), 1.08 (s, 9 H), Ad?—overlap with dimer **9b**?; ^{13}C NMR ($CDCl_3$) δ 3.13, 9.74, 12.99, 14.23, 25.19, 31.36, 29.89, 36.45, 42.40; ^{29}Si NMR ($CDCl_3$) δ 2.64, 3.60 (other signals may be obscured by the signals of dimer **9b**).

Solutions of silene **6b** in C_7D_8 which had been kept in the refrigerator for over 2 weeks gave a single intense ESR signal with g = 2.0026 and a width of 2.8 G, which showed no hyperfine couplings but which had satellites with about 3.8% the intensity of the main signal, consistent with coupling to an adjacent ^{29}Si atom (a = 16 G).

Photolysis of Acylsilane 1b with Methanol and Preparation of the Methanol Adduct 4b. A solution of acylsilane **1b** (500 mg) in C_6D_6 (2 mL) containing methanol (0.5 mL) and pyridine (3 drops) was photolyzed for 2.75 h, and after removal of the solvents under reduced pressure the diastereomeric methanol adducts, formed in a ratio of 3:1 (A to B) as determined by ^{1}H-NMR spectroscopy, were separated by preparative thin-layer chromatography (9:1 hexanes–dichloromethane, silica gel). Diastereomer A (eluted first) was recrystallized from methanol to give colorless needles. Diastereomer B could not be obtained absolutely pure: traces of the carbinol, (Me_3Si)(*t*-Bu)(MeO)Si-CH(OH)(1-Ad), contaminated the sample. **Diastereomer A**: mp 89–90 °C; ^{1}H NMR δ 0.22, 0.35 (2s, each 9 H, $SiMe_3$), 1.13 (s, 9 H, CMe_3), 1.47–2.18 (m, 15 H, Ad), 3.43 (s, 3 H, OMe), 3.50 (s, 1 H, CH); ^{13}C NMR δ 2.31, 2.36 (2 $SiMe_3$), 21.98 (*C*Me_3), 27.71 (C*Me*$_3$), 29.09 (CH, Ad), 37.54, 40.28 (2 CH_2, Ad), 38.25 (quat C, Ad), 53.42 (OMe), 79.08 (CHO); ^{29}Si NMR δ 14.65 ($OSiMe_3$), 14.02 (SiOMe), −21.10 ($SiMe_3$); MS, *m/z* 411 (5, M$^+$ − Me), 369 (7, M$^+$ − *t*-Bu), 237 (29, $[CH(OSiMe_3)Ad]^+$), 73 (100, $[SiMe_3]^+$). Anal. Calcd for $C_{22}H_{46}Si_3O_2$: C, 61.90; H, 10.86. Found: C, 61.94; H, 10.98. **Diastereomer B**: ^{1}H NMR δ 0.25, 0.34 (2s, each 9 H, $SiMe_3$), 1.16 (s, 9 H, CMe_3), 1.52–2.15 (m, Ad), 3.46 (s, 3 H, OMe), 3.57 (s, 1 H, CH); ^{13}C NMR δ 1.72, 2.16 (2 $SiMe_3$), 22.85 (*C*Me_3), 28.61 (C*Me*$_3$), 29.10 (CH, Ad), 37.44, 40.72 (2 CH_2, Ad), 37.85 (quat C, Ad), 53.34 (OMe), 79.79 (CHO); ^{29}Si NMR δ 14.61 ($OSiMe_3$), 11.50 (SiOMe), −20.85 ($SiMe_3$).

Addition of Methanol to Silene 6b. Preparation of 7b. A solution of acylsilane **1b** (500 mg) in C_6D_6 (2 mL) was photolyzed for 17 h. Completion of the photolysis was ensured by following the reaction by ^{13}C NMR spectroscopy. Methanol (0.5 mL) was

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then added to the bright yellow solution, which immediately decolorized and became warm. The volatiles were then removed under vacuum, and the two diastereomers of **7b**, A and B, formed in a ratio of 3:2 as determined by ^{1}H NMR spectroscopy, were separated by chromatography using the Chromatotron (80:20 hexanes–dichloromethane). Diastereomer A, on recrystallization from methanol, gave a colorless crystalline solid. Diastereomer B was isolated as a colorless oil. **Diastereomer A**: mp 78–79 °C; ^{1}H NMR δ 0.25 (s, 9 H, SiMe$_3$), 0.21, 0.29, 0.43 (3s, each 3 H, SiMe), 0.60 (s, 1 H, CH), 1.10 (s, CMe$_3$), 1.62–2.07 (m, Ad), 3.08 (s, OMe); ^{13}C NMR δ 2.92 (SiMe$_3$), 1.60, 1.79, 3.43 (3 SiMe), 20.13 (*C*Me$_3$), 28.13 (C*Me*$_3$), 29.88 (CH, Ad), 30.12 (CH), 37.17, 45.17 (2 CH$_2$, Ad), 35.76 (quat C, Ad), 48.36 (OMe); ^{29}Si NMR δ 18.29 (*Si*Me(*t*-Bu)OSiMe$_3$), 10.52 (Me$_2$*Si*OMe), 5.76 (Me$_3$SiO); MS, *m/z* 426 (<1, M$^+$), 411 (6, M$^+$ – Me), 369 (100, M$^+$ – *t*-Bu). Anal. Calcd for $C_{22}H_{46}Si_3O_2$: C, 61.85; H, 10.86. Found: C, 62.00; H, 10.86. **Diastereomer B**: ^{1}H NMR δ 0.19 (s, 9 H, SiMe$_3$), 0.37 (b s, 6 H, 2 SiMe), 0.45 (s, 3 H, SiMe), 0.60 (s, 1 H, CH), 1.03 (s, 9 H, CMe$_3$), 1.61–2.07 (m, Ad), 3.25 (s, 3 H, OMe); ^{13}C NMR δ 3.12 (SiMe$_3$), 3.37, 3.93, 4.01 (3 SiMe), 20.70 (*C*Me$_3$), 28.55 (C*Me*$_3$), 30.18 (CH, Ad), 32.35 (CH), 36.41 (quat C, Ad), 37.32, 45.77 (2 CH$_2$, Ad), 49.50 (OMe); ^{29}Si NMR δ 16.99 (*Si*Me(*t*-Bu)OSiMe$_3$), 10.71 (Me$_2$SiOMe), 6.05 (Me$_3$SiO); MS, *m/z* 426 (<1, M$^+$), 411 (13, M$^+$ – Me), 369 (100, M$^+$ – *t*-Bu).

Addition of Methanol during the Photolysis of Acylsilane 1b. A solution of acylsilane **1b** (200 mg) in C_6D_6 (2 mL) was photolyzed for 2.5 h. The progress of the photolysis was followed by ^{13}C NMR spectroscopy. When both silene **2b** and silene **6b** were observed in solution, along with unchanged starting material, methanol was added to the photolysis solution. The reaction mixture was then examined by ^{1}H and ^{13}C NMR spectroscopy. The products were identified as the methanol adducts **7b** of silene **6b** in the same proportions observed previously (i.e. 3:2), recovered starting material, and diastereomer A of the methanol adduct **4b**. Only traces of diastereomer **B** were detected.

Kinetic Investigation of the Photolysis of Silene 1b. Acylsilane **1b** (300 mg) was dissolved in C_6D_6 (0.5 mL) and one drop of C_6H_6 (as an internal standard). The solution was then photolyzed for 8.5 h. A ^{1}H NMR spectrum was taken every 15 min during the first 2.5 h of photolysis, then every 0.5 h during the next 4 h of the photolysis, and every hour for the final 2 h. The appearance/disappearance of the starting material **1b** and the intermediate silenes **2b** and **6b** were monitored by integration of the appropriate *tert*-butyl signal after each photolysis period. The signal due to the internal standard was also integrated at each interval. The relevant NMR parameters are given below. The data for the disappearance of the acylsilane (where a plot of ln acylsilane vs time gives a straight line shown in Figure 1) and for the appearance and disappearance of silene **2b** and the appearance of silene **6b** are assembled in Table VI and the integral ratios (ratio of *t*-Bu signal of each species normalized against the standard) for each species are plotted against time in Figure 2.

NMR Parameters for the Kinetic Study: spectral frequency, 80.00 MHz; size, 8K; sweep width, 1000 Hz; transmitter offset, 5750 Hz; pulse width, 0.8 s; acquisition time, 4.0960 s; Hz/point, 0.244, number of scans, 8. Data are given in Table VI.

Monitoring the Photolysis of Silene 1b by Ultraviolet Spectroscopy. An aliquot of a solution of acylsilane **1b** (22.0 mg) dissolved in spectrograde hexane (freshly distilled from $LiAlH_4$) (50.0 mL, 1.12 × 10^{-3} M) was transferred under an inert atmosphere to an ultraviolet cell fitted with a ground glass joint. After the cell was stoppered, the solution was photolyzed at –78 °C for 1 min. In addition to the absorptions attributable to the starting material (220, 260, 380 nm), a new absorption at 340 nm was detected. Photolysis, under the same conditions, for a second minute interval gave rise to a strong absorption in the UV spectrum at 290 nm with shoulders at 260 and 340 nm. Continued photolysis under the same conditions for 25 min led to the disappearance of the two shoulders: only the strong absorption at 290 nm and an absorption at 214 nm remained. The photolysis solution was then left in the dark at room temperature over a period of 3 days during which time the absorption at 290 nm disappeared.

Cophotolysis of Acylsilane 1b and Diethylsilane. A solution of acylsilane **1b** (40 mg), dissolved in C_6D_6 (approximately 1 mL) and freshly distilled Et_2SiH_2 (bp 40–48 °C (lit.[35] bp 56 °C (760 mm Hg)); 25 drops, approximately 100 × molar excess), was photolyzed for 3 h. The volatiles were removed under reduced pressure to give a yellow oil identified as silene **6b** by ^{1}H NMR data. No evidence of any silylene trapping type products was observed.

Table VI. Kinetic Data for Isomerizations 1b → 2b → 6b[a]

time, min	*A*	*B*	*C*
0	2.21	0.00	0.00
15	1.88	0.15	0.00
30	1.60	0.16	0.08
45	1.62	0.19	0.16
60	1.46	0.27	0.39
75	1.38	0.40	0.40
90	1.04	0.30	0.44
105	1.02	0.41	0.53
120	0.96	0.39	0.62
135	0.74	0.37	0.74
150	0.72	0.38	0.91
180	0.58	0.40	1.14
210	0.40	0.31	1.17
240	0.30	0.23	1.33
270	0.36	0.20	1.44
300	0.23	0.22	1.56
330	0.16	0.15	1.56
360	0.11	0.07	1.56
390	0.13	0.07	1.64
450	0.00	0.00	1.67
510	0.00	0.00	1.60

[a] *A* = the integral of the *t*-Bu signal of acylsilane **1b** divided by the integral of the standard (benzene); *B* = the integral of the *t*-Bu signal of silene **2b** divided by the integral of the standard (benzene); *C* = the integral of the *t*-Bu signal of silene **6b** divided by the integral of the standard (benzene).

Cophotolysis of Acylsilane 1b and Triethylsilane. A solution of acylsilane **1b** (50 mg), dissolved in C_6D_6 (approximately 1 mL) and freshly distilled Et_3SiH (bp 104–105 °C (lit.[35] bp 108.8 °C (760 mm Hg)); 25 drops, approximately 60 × molar excess), was photolyzed for 3 h. The volatiles were removed under reduced pressure to give a yellow oil that was redissolved in C_6D_6 and identified as silene **6b** using ^{1}H NMR data. No evidence of any silylene trapping type products was detected.

Photolysis of Pivaloylbis(trimethylsilyl)phenylsilane (1c). Photolysis of acylsilane **1c** (525 mg) in C_6D_6 (2 mL) in an NMR tube for 4 h at room temperature led to the formation of dimer **5c** as a precipitate in essentially quantitative yield: ^{1}H NMR δ 0.27 (Me$_3$Si), 0.42 (Me$_3$SiO), 1.0–1.2 (br m, Me$_3$C), 7.2–7.6 (Ph); ^{13}C NMR δ 0.95 (Me$_3$Si, ^{1}J(Si–C) = 46.2 Hz), 6.22 (Me$_3$SiO, ^{1}J(Si–C) = 61.4 Hz), 27.84, 30.86, 36.63 (each *Me*-C of *t*-Bu), 39.25 Me$_3$*C*, 127.36, 128.44, 137.38, 137.93 (Ph); ^{29}Si NMR δ –18.55 (Me$_3$Si*Si*), –11.94 (Me$_3$Si), –0.31 (Me$_3$SiO).

Formation of the Methanol Adducts 4c from Acylsilane 1c. A solution of acylsilane **1c** (125 mg) in C_6D_6 (0.5 mL) containing a few drops of methanol and a drop of pyridine was photolyzed for 12 h. A 1.5:1 ratio of diastereomeric adducts **4c** was obtained which were studied as a mixture in C_7D_8 solvent. **Diastereomer A**: ^{1}H NMR δ 0.01, 0.45 (each 9 H, s, Me$_3$Si), 1.22 (9 H, s, CMe$_3$), 3.36 (3 H, s, OMe), 3.70 (1 H, s, CH), 7.26–7.85 (5 H, m, Ph); ^{13}C NMR δ 0.72, 0.96 (Me$_3$Si), 28.64 (*Me*$_3$C), 35.78 (Me$_3$*C*), 51.73 (MeO), 79.21 (CH), 127.91 (*m*-C, Ph), 129.62 (*p*-C, Ph), 135.36 (*o*-C, Ph), 137.89 (ipso-C, Ph); ^{29}Si NMR δ 11.08 (Me$_3$SiO), –6.30 (SiOMe), –26.44 (Me$_3$Si). **Diastereomer B**: ^{1}H NMR δ 0.11, 0.31 (each 9 H, s, Me$_3$Si), 1.13 (9 H, s, CMe$_3$), 3.65 (3 H, s, OMe), 3.69 (1 H, s, CH), 7.26–7.85 (5 H, m, Ph); ^{13}C NMR δ –0.41, 0.80 (Me$_3$Si), 28.53 (*Me*$_3$C), 35.92 (Me$_3$*C*), 52.62 (OMe), 81.19 (CH), 128.12 (*m*-C, Ph), 129.26 (*p*-C, Ph), 134.15 (*o*-C, Ph), 139.02 (ipso-C, Ph); ^{29}Si NMR δ 10.70 (Me$_3$SiO), –6.61 (SiOMe), –25.95 (Me$_3$Si).

Benzocyclobutene 11d from Photolysis of Acylsilane 1d. Photolysis of a solution of acylsilane 1d (300 mg) in benzene (2.5

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mL) for 27 h gave a 2.3:1 ratio of diastereomeric benzocyclobutenes **11d** (NMR). The mixture was chromatographed five times, using 95:5 pentanes–dichloromethane and hexanes–dichloromethane, resulting in purification but not separation of the mixture (35% yield). **Diastereomer A**: ^{1}H NMR δ 0.05, 0.19 (each 9 H, s, SiMe$_3$), 1.80, 2.12 (each 3 H, s, Me), 3.29, 3.54 (2 H, AB system, J_{AB} = 14.2 Hz), 4.78 (1 H, s, SiH), 6.62, 6.68 (each 1 H, s, Ar), 7.03–7.79 (5 H, Ph); ^{13}C NMR δ –0.79, 1.96 (Me$_3$Si), 17.09, 22.06 (Me), 44.49 (CH$_2$), 76.32 (COSi), 121.56, 128.05, 129.44, 129.99, 136.50 (CH Ar), 132.87, 135.27, 138.54, 139.66, 147.53 (quat C); ^{29}Si NMR δ 13.87 (Me$_3$SiO), –18.50 (Me$_3$Si), –24.86 (SiH, ^{1}J(Si–H) = 180.6 Hz). **Diastereomer B**: ^{1}H NMR δ 0.08, 0.29 (each 9 H, s, Me$_3$Si), 2.05, 2.27 (each 3 H, s, Me), 3.24, 3.47 (2 H, AB system, J_{AB} = 14.3 Hz), 4.79 (1 H, s, SiH), 6.47, 6.65 (each 1 H, s, Ar) 7.03–7.79 (5 H, Ph); ^{13}C NMR δ –0.33, 2.09 (Me$_3$Si), 17.13, 22.03 (Me), 44.05 (CH$_2$), 75.31 (COSi), 121.41, 127.99, 129.20, 129.66, 136.22 (CH Ar), 132.51, 134.16, 138.54, 139.81, 146.77 (quat C, Ar); ^{29}Si NMR δ 13.79 (Me$_3$SiO), –18.16 (Me$_3$Si), –28.31 (SiH, ^{1}J(Si–H) = 176.7 Hz).

Photolysis of Acylsilane 1d in Methanol. Formation of Methanol Adduct 4d. A solution of acylsilane **1d** (300 mg) in 1 mL of benzene containing a few drops of methanol and a drop of pyridine was photolyzed for 10 h. A 1.1:1 ratio of diastereomers was formed (NMR), which were purified (but could not be separated) by chromatography (90:10 hexanes–dichloromethane) in a combined yield of 53%. **Diastereomer A**: ^{1}H NMR δ 0.06, 0.35 (each 9 H, s, SiMe$_3$), 2.02 (3 H, s, *p*-Me), 2.13 (6 H, s, *o*-Me), 3.19 (3 H, s, OMe), 5.47 (1 H, s, CH), 6.63, 6.73 (each 1 H, s, Ar), 7.16–7.71 (5 H, m, Ph); ^{13}C NMR (CDCl$_3$) δ –1.07, –0.89, 0.06 (2 SiMe$_3$, one in two conformations?), 20.76, 20.79, 22.17 (Me, restricted rotation), 52.51 (OMe), 67.68 (CH), aromatic C of both diastereomers A + B (not distinguishable), 127.44, 127.73, 128.41, 128.42, 129.04, 130.29, 130.40 (each CH), 133.43, 133.50, 133.71, 134.14, 134.98, 135.00, 135.95, 136.14, 136.55, 137.58, 137.75, 137.89 (each quat C); ^{29}Si NMR (CDCl$_3$) δ –20.87 (SiMe$_3$), 1.05 (SiOMe), 17.96 (OSiMe$_3$). **Diastereomer B**: ^{1}H NMR δ 0.04, 0.26 (each 9 H, s, SiMe$_3$), 2.33, 2.44, 2.78 (each 3 H, s, Me, restricted rotation), 3.53 (3 H, s, OMe), 5.59 (1 H, s, CH), 6.74, 6.86 (each 1 H, s, Ar), 7.16–7.71 (5 H, m, Ph); ^{13}C NMR (CDCl$_3$) δ –1.23, –0.80, –0.12 (2 SiMe$_3$, one in 2 conformations?), 20.89, 21.12, 21.53 (Me), 52.38 (OMe), 68.45 (CH); ^{29}Si NMR (CDCl$_3$) δ –20.34 (SiMe$_3$), 2.16 (SiOMe), 17.96 (Me$_3$SiO).

Photolysis of Acylsilane 1e. Characterization of Two Stereoisomers of Dimer 5e and Three Stereoisomeric Dimers, 10e$_1$, 10e$_2$, and 10e$_3$, Derived from Silene 6e. A solution of acylsilane **1e** (1.5 g) dissolved in C$_6$D$_6$ (2.5 mL) was photolyzed for 19 h. The solution developed an orange color during the early stages of the photolysis, and an NMR spectrum taken at this time had new NMR resonances attributed to two isomers of dimer **5e**. The color faded to yellow as the photolysis progressed (i.e. after 16 h). The solvent was removed under reduced pressure, and the residue was dissolved in pentanes. Dimer **10e$_2$** precipitated from the pentanes solution and was purified by successive recrystallization from acetone–chloroform to afford colorless rectangular crystals. The solvent was then removed from the pentanes-soluble fraction, and the residue was dissolved in acetone causing dimers **10e$_1$** and **10e$_3$** to precipitate. The two dimers were separated by fractional crystallization from acetone: dimer **10e$_1$** precipitated upon cooling a hot acetone solution of the dimers to room temperature, whereas dimer **10e$_3$** precipitated in the cold (–20 °C). Further recrystallization of dimer **10e$_1$** gave colorless rectangular crystals. **Data of the Intermediate Dimers 5e. Major isomer**: ^{1}H NMR (C$_6$D$_5$CD$_3$) δ 0.29, 0.10 (2s, SiMe$_3$), 1.39–2.53 (m, Ad—overlapped with minor isomer), 6.90–8.10 (m, Ph—overlapped with minor isomer); ^{13}C NMR (C$_6$D$_5$CD$_3$) δ 3.19 (SiMe$_3$, ^{1}J(Si–C) = 45.2 Hz), 7.00 (OSiMe$_3$, ^{1}J(Si–C) = 61.6 Hz), 29.50 (CH, Ad), 37.12, 41.30 (2 CH$_2$, Ad), 42.27 (quat C, Ad), 113.65 (ring C), phenyl carbon atoms were not assigned; ^{29}Si NMR δ 2.48 (OSiMe$_3$), –2.50 (ring Si), –12.27 (SiMe$_3$). **Minor isomer**: ^{1}H NMR (C$_6$H$_5$CD$_3$) δ 0.25, –0.03 (2s, SiMe$_3$), 1.39–2.53 (m, Ad—overlapped with major isomer), 6.90–8.10 (m, Ph—overlapped with major isomer); ^{13}C NMR (C$_6$D$_5$CD$_3$) δ 1.93 (SiMe$_3$, ^{1}J(Si–C) = 43.9 Hz), 6.41 (OSiMe$_3$, ^{1}J(Si–C) = 60.5 Hz), 29.20 (CH, Ad), 37.51, 40.97 (2 CH$_2$, Ad), 42.61 (quat C, Ad), 115.03 (ring C), phenyl carbon atoms were not assigned; ^{29}Si NMR δ 2.16 (OSiMe$_3$), –2.79 (ring Si), –15.17 (SiMe$_3$).

Dimers 10e$_1$, 10e$_2$, and 10e$_3$. Dimer 10e$_1$: mp 236–238 °C; ^{1}H NMR: δ 0.19 (s, 9 H, SiMe$_3$), 0.99, 1.07, 1.20 (3s, each 3 H, SiMe), 1.41–2.41 (m, 15 H, Ad), 7.17–7.92 (m, 5 H, Ph); ^{13}C NMR (CDCl$_3$) δ 2.68 (OSiMe$_3$, ^{1}J(Si–C) = 59.9 Hz), 11.72, 11.96, 12.57 (3 SiMe), 30.06 (CH, Ad), 36.41, 44.70 (2 CH$_2$, Ad), 36.41, 43.45 (quat C, Ad and ring C), 127.49, 134.19 (*o*- and *m*-C), 128.01 (*p*-C), 147.28 (ipso-C) (Ph); ^{29}Si NMR (CDCl$_3$) δ 7.14 (OSiMe$_3$), 3.12 (SiMe$_2$), –2.98 (*Si*MePhOSiMe$_3$); MS, *m/z* 831 (38, M$^+$), 471 (25, [SiMe$_2$C(Ad)(SiMePhOSiMe$_3$)SiMe$_2$]$^+$), 414 (22, M$^+$/2), 209 (47, [SiMePhOSiMe$_3$]$^+$), 135 (100, [Ad]$^+$). Anal. Calcd for C$_{46}$H$_{76}$Si$_6$O$_2$: C, 66.60; H, 9.23. Found: C, 66.67; H, 9.40. **Dimer 10e$_2$**: mp 287–290 °C; ^{1}H NMR δ 0.20 (b s, OSiMe$_3$), 0.95, 0.98, 1.07, 1.14, 1.33 (5s, SiMe), 1.45–2.24 (m, Ad), 7.00–7.96 (m, Ph); ^{13}C NMR (CDCl$_3$) δ 2.73 (OSiMe$_3$), 11.06 (b s, 2 SiMe), 12.16, 12.64, 12.77, 12.82 (4 SiMe), 29.99 (CH, Ad), 36.32, 44.19 (2 CH$_2$, Ad), 36.32, 43.13 (2 quat C), 127.44, 134.53 (*o*- and *m*-C), 128.05 (*p*-C), 146.77 (ipso-C) (Ph); ^{29}Si NMR (CDCl$_3$) δ 7.08, 4.58, 2.36, –2.59; MS, *m/z* 831 (49, M$^+$), 471 (36, [SiMe$_2$C(Ad)(SiMePhOSiMe$_3$)SiMe$_2$]$^+$), 414 (27, M$^+$/2), 209 (48, [SiMePhOSiMe$_3$]$^+$), 135 (100, [Ad]$^+$). **Dimer 10e$_3$**: mp 295–296 °C; ^{1}H NMR δ 0.01 (s, 9 H, SiMe$_3$), 0.84, 1.27 (2s, each 3 H, SiMe), 1.02 (b s, 3 H, SiMe), 1.48–2.24 (m, 15 H, Ad), 7.20–7.99 (m, Ph); ^{13}C NMR (CDCl$_3$) δ 2.01 (OSiMe$_3$), 10.47, 12.82, 13.34 (3 SiMe), 29.83 (br, CH, Ad), 36.26 (br, CH$_2$, Ad), 34.79, 41.23 (2 quat C), 127.52, 134.70 (*o*- and *m*-C), 128.20 (*p*-C), 146.46 (ipso-C) (Ph); ^{29}Si NMR (CDCl$_3$) δ 8.82 (OSiMe$_3$), 6.03, 5.49 (2 SiMe$_2$), –0.38 (SiPh); MS, *m/z* 831 (53, M$^+$), 471 (29, [SiMe$_2$C(Ad)(SiMePhOSiMe$_3$)SiMe$_2$]$^+$), 415 (39), 209 (44, [SiMePhOSiMe$_3$]$^+$), 135 (100, [Ad]$^+$).

Preparation of the Methanol Adduct 4e of Silene 2e. Method A. A solution of acylsilane **1e** (1.0 g) dissolved in C$_6$D$_6$ (2 mL) containing methanol (12 drops) and pyridine (12 drops) was photolyzed for 4.5 h. The solvents were removed under reduced pressure and the methanol adducts **4e** (diastereomers A and B), formed in a ratio of 9:5 and in a >95% yield as determined by ^{1}H NMR spectroscopy, were separated by chromatography using the Chromatotron (75:25 hexanes–dichloromethane) (isolated yield 32%).

Method B. The photolysis of acylsilane **1e** (1.0 g) dissolved in C$_6$D$_6$ (2 mL) was followed by ^{13}C NMR spectroscopy in order to determine when a substantial amount of the intermediates **5e** had formed. Thus, after 6 h of photolysis, methanol (1 mL) was added to the orange solution which immediately decolorized. After removal of the solvents, and components of the reaction mixture were separated by chromatography using the Chromatotron to give recovered starting material, the product dimer mixture, diastereomer A (275 mg), which was recrystallized from methanol to give cubic crystals, and diastereomer B (93 mg) as a colorless oil. **Diastereomer A**: mp 61–62 °C; ^{1}H NMR δ –0.04, 0.40 (2s, each 9 H, SiMe$_3$), 1.59–2.08 (m, Ad), 3.28 (s, 3 H, OMe), 3.57 (s, 1 H, CH), 7.17–7.81 (m, 5 H, Ph); ^{13}C NMR δ 0.86, 1.12 (2 SiMe$_3$), 29.19 (CH, Ad), 37.61, 40.99 (2 CH$_2$, Ad) 37.91 (quat C, Ad), 51.91 (OMe), 80.20 (CHO), 128.00, 135.52 (*o*- and *m*-C), 129.68 (*p*-C), 138.18 (ipso-C) (Ph); ^{29}Si NMR δ –21.40 (SiMe$_3$), –1.20 (*Si*SiMe$_3$), 16.23 (OSiMe$_3$); MS *m/z* 431 (9, M$^+$ – Me), 237 (22, [CH(Ad)(OSiMe$_3$)]$^+$), 225 (84, [SiOMePh(OSiMe$_3$)]$^+$), 209 (33, [SiOMePh(SiMe$_3$)]$^+$), 73 (100, [SiMe$_3$]$^+$). Anal. Calcd for C$_{24}$H$_{42}$Si$_3$O$_2$: C, 64.51; H, 9.47. Found: C, 64.50; H, 9.21. **Diastereomer B**: ^{1}H NMR δ 0.04, 0.26 (2s, each 9 H, SiMe$_3$), 1.64–2.02 (m, 15 H, Ad), 3.54 (s, 1 H, CH), 3.61 (s, 3 H, OMe), 7.17–7.68 (m, 5 H, Ph); ^{13}C NMR δ –0.39, 0.94 (2 SiMe$_3$), 29.10 (CH, Ad), 37.50, 40.97 (2 CH$_2$, Ad), 38.07 (quat C), 52.89 (OMe), 82.38 (CHO), 128.21, 134.20 (*o*- and *m*-C), 129.26 (*p*-C), 139.37 (ipso-C) (Ph); ^{29}Si NMR δ –20.84 (SiMe$_3$), –2.30 (*Si*SiMe$_3$), 15.90 (OSiMe$_3$); MS, *m/z* 431 (17, M$^+$ – Me), 237 (25, [CH(Ad)(OSiMe$_3$)]$^+$), 225 (92, [SiOMePh(OSiMe$_3$)]$^+$), 209 (36, [SiOMePh(OSiMe$_3$)]$^+$), 73 (100, [SiMe$_3$]$^+$).

Monitoring the Photolysis of Acylsilane 1e by Ultraviolet Spectroscopy. An aliquot of a solution of acylsilane **1e** (18.8 mg) in spectrograde hexane (freshly distilled from LiAlH$_4$) (50.0 mL, 0.91 × 10^{-3} M) was transferred under an inert atmosphere to an ultraviolet cell fitted with a ground glass joint. After the cell was stoppered the solution was photolyzed at –78 °C for 2 min. In addition to the absorptions characteristic of the starting material at 220, 245, 260, and 380 nm, a new absorption at 332 nm was detected. Further photolysis, under the same conditions, gave no new distinct absorptions and eventually (after 15 min) led to the total disappearance of the absorption at 332 nm. At the end of the photolysis only a broad intense absorption centered at 230 nm remained.

Cophotolysis of Acylsilane 1e and Diethylsilane. A solution of acylsilane **1e** (60 mg), dissolved in C_6D_6 (approximately 1 mL) and freshly distilled Et_2SiH_2 (25 drops, approximately 60 × molar excess), was photolyzed for 6 h. Removal of the volatiles gave a white foam which was redissolved in C_6D_6 and shown to be the same product mixture as obtained when acylsilane **1e** was photolyzed in C_6D_6 in the absence of Et_2SiH_2. No evidence for any silylene trapping type products was detected.

Characterizations of Silenes 2f and 6f from Acylsilane 1f. A solution of acylsilane **1f** (100 mg) in C_7D_8 (0.5 mL) was photolyzed at −78 °C in a dry ice–acetone bath. A bright orange color developed rapidly which disappeared over the duration of the photolyses (many runs at different temperatures and times were used to acquire all data about the two silenes using C_7D_8 as the NMR solvent). **Silene 2f**: ^{1}H NMR δ −0.09, 0.25 (each 9 H, s, Me_3Si), 0.92 (9 H, t, CH_3), 1.47 (q, CH_2, overlapped), 6.92–7.72 (Ph); ^{13}C NMR δ 0.59, 2.19 (Me_3Si), 8.01 (CH_3), 26.20 (CH_2), 50.38 ($\mathit{C}Et_3$), 191.17 (C=Si); ^{29}Si NMR δ 13.21 (Me_3SiO), −12.31 (Me_3Si), 61.60 (Si=C). **Silene 6f**: ^{1}H NMR δ −0.06 (9 H, s, Me_3Si), 0.38 (6 H, s, $SiMe_2$), 0.69 (3 H, s, SiMe); ^{13}C NMR δ 1.73 (Me_3SiO), 5.59 (MeSi), 7.05 (Me_2Si), 110.6 (C= weak); ^{29}Si NMR data could not be obtained because of the short lifetime of the silene.

Formation of the Methanol Adduct 4f from Acylsilane 1f. A solution of acylsilane **1f** (100 mg) in C_6D_6 (0.5 mL) containing a few drops of methanol and a drop of pyridine was photolyzed for 24 h. The ^{1}H NMR spectrum showed formation of two diastereomers of **4f** in a 2:1 ratio. After purification by chromatography (85:15 hexanes–dichloromethane) they were separated by chromatography, diastereomer A being eluted first with 98:2 hexanes–dichloromethane and diastereomer B being eluted with 95:5 hexanes–dichloromethane in a combined yield of 45%. **Diastereomer A**: ^{1}H NMR δ −0.01, 0.37 (each 9 H, Me_3Si), 0.91 (9 H, t, CH_3), 1.58 (6 H, q, CH_2), 3.27 (3 H, s, OMe), 3.98 (1 H, s, CH), 7.16–7.76 (5 H, m, Ph); ^{13}C NMR δ 0.74, 0.97 (Me_3Si), 9.09 (CH_3), 28.13 (CH_2), 42.57 ($\mathit{C}Et_3$), 51.89 (OMe), 78.04 (CH), 127.94 (*m*-C), 129.68 (*p*-C), 135.47 (*o*-C), 138.09 (ipso-C, Ph); ^{29}Si NMR δ 15.69 (Me_3SiO), −0.89 (SiOMe), −21.64 (Me_3Si); MS, *m/e* 395 (0.7, $M^+ - Me$), 277 (61), 225 ([100, SiOMePh(Me_3SiO)]$^+$), 209 (68), 73 (90, Me_3Si); calcd for $C_{21}H_{42}O_2Si_3 - Me^+$ 395.2254, found 395.2254. **Diastereomer B.** ^{1}H NMR δ 0.03, 0.22 (each 9 H, s, Me_3Si), 0.91 (9 H, t, CH_3), 1.47 (6 H, q, CH_2), 3.60 (3 H, s, MeO), 3.97 (1 H, s, CH), 7.14–7.60 (5 H, m, Ph); ^{13}C NMR δ −0.39, 0.87 (Me_3Si), 8.97 (CH_3), 28.27 (CH_2), 42.79 ($\mathit{C}Et_3$), 52.92 (MeO), 79.56 (CH), 128.12 (*m*-C, Ph), 129.28 (*p*-C, Ph), 134.22 (*o*-C, Ph), 139.35 (ipso-C, Ph); ^{29}Si NMR δ 17.19 (Me_3SiO), −0.81 (SiOMe), −18.79 (Me_3Si).

Methanol Adducts 7f from Silene 6f. A solution of acylsilane **1f** in C_7D_8 (0.5 mL) was photolyzed at −78 °C for 14 h, at which time one of the major components in the solution was silene **6f**. Methanol (0.1 mL) was added to the bright yellow solution which immediately decolorized and became warm. A 1.1:1 ratio of diastereomers of the methanol adducts **7f** were present among other products and were separated in about 10% yield by chromatography (80:20 hexanes–dichloromethane). **Diastereomer A**: ^{1}H NMR δ 0.06 (9 H, s, Me_3SiO), 0.05, 0.23, 0.24, 0.32, 0.33, 0.36 (each 3 H, s, Me–Si, for diastereomers A + B—not individually assignable), 0.66 (1 H, s, CH), 3.22 (3 H, s, OMe); ^{13}C NMR δ 2.10 (Me_3SiO), 2.38, 2.49, 4.47 (MeSi), 9.76 (CH_3), 27.53 (CH_2), 31.76 (CH), 42.42 ($\mathit{C}Et_3$), 49.47 (MeO) (Ph–C could not be assigned); ^{29}Si NMR δ 18.02 (SiOMe), 8.57 (Me_2Si), −3.20 (Me_3SiO). **Diastereomer B.** ^{1}H NMR δ 0.07 (9 H, s, Me_3SiO), (Me–Si, see values for diastereomer A above, each 3 H, s), 0.70 (1 H, s, CH), 3.00 (3 H, MeO); ^{13}C NMR δ 2.18 (Me_3SiO), 2.59, 2.98, 5.51 (Me–Si), 9.76 (CH_3), 27.82 (CH_2), 32.01 (CH), 42.72 ($\mathit{C}Et_3$), 49.17 (MeO); ^{29}Si NMR δ 17.74 (SiOMe), 7.90 (Me_2Si), −0.82 (Me_3SiO).

Silene 2g and Dimer 5g from Photolysis of Bicyclooctylacylsilane 1g. Photolysis of acylsilane **1g** (0.8 g) in C_6D_6 (1.5 mL) under argon in a sealed 10 mm. NMR tube gave rise in the first hour to ^{29}Si NMR signals assigned to silene **2g**. On further photolysis to complete the isomerization a new set of signals appeared, attributed to the dimer **5g**, which slowly precipitated from the solution. In dilute solution the ratio of silene:dimer was about 2.7:1 at ambient temperature. If heated to 70 °C, the system reverted almost totally to acylsilane, but rephotolysis restored the equilibrium mixture of silene and dimer, as shown by the NMR spectra. Dimer **5g** could be isolated as a rather unstable colorless solid which rapidly decomposed in air and which reacted readily with methanol to give the same adduct as was obtained by direct photolysis of the acylsilane in methanol (see below). **Silene 2g**: ^{1}H NMR δ 0.29, 0.36, 0.40, (each 9 H, s, Me_3Si), 1.34–1.94 (br m, C_8H_{13}); ^{13}C NMR δ 1.7, 2.6, 3.3 (Me_3Si), 24.7 (CH, BCO), 26.6, 31.9 (CH_2, BCO), 43.5 (quat C, BCO), 212.7 (C=Si); ^{29}Si NMR δ −12.3, −12.8 (Me_3Si), 13.3 (Me_3SiO), 42.4 (Si=). **Dimer 5g**: ^{1}H NMR δ 0.35, 0.47, 0.51 (each 18 H, s, Me_3Si), 1.34–1.94 (br m, C_8H_{13}); ^{13}C NMR δ 5.5, 6.2, 6.3 (Me_3Si), 25.00 (CH, BCO), 24.24, 25.80, 26.89, 27.60, 27.82, 33.14 (each CH_2, BCO, restricted rotation), 42.8 (quat C, BCO), 113.6 (C ring); ^{29}Si NMR δ −8.5, −10.5 (Me_3Si), −0.5 (Me_3SiO), −46.7 (Si ring).

Methanol Adduct of Silene 2g. Photolysis of acylsilane **1g** in methanol–benzene containing a trace of pyridine over 12 h gave, after workup, 92% of a viscous oil shown to be the adduct **4g**. The same product was obtained by treatment of dimer **5g** with methanol after brief warming to 50 °C: ^{1}H NMR δ 0.20, 0.27, 0.31 (each 9 H, s, Me_3Si), 1.51 (13 H, br, C_8H_{13}), 3.37 (3 H, s, MeO), 3.71 (1 H, s, CH); ^{13}C NMR δ 0.77, 0.92, 1.29 (each Me_3Si), 24.71 (CH, BCO), 26.47, 29.87 (CH_2, BCO), 35.59 (quat C, BCO), 53.83 (MeO), 79.04 (CH); ^{29}Si NMR δ −17.35, −19.11 (Me_3Si), 9.98 (SiOMe), 15.07 (Me_3SiO).

[2 + 4] Cycloaddition of Silene 2g with Dimethylbutadiene. A solution of acylsilane **1g** (0.4 g, 1.0 mmol) and 2,3-dimethylbutadiene (4.4 mmol) in benzene (2 mL) was irradiated for 5.5 h. Removal of the solvent gave 0.37 g of a sticky solid, mp 123–159 °C, which after chromatography on silica gel with pentane gave 0.28 g (59%) of adduct **12g**: mp 192–193 °C. ^{1}H NMR (partial) δ 0.28 0.30, 0.41 (Me_3Si); ^{13}C NMR (partial) δ 0.52, 1.01, 3.11 (Me_3Si), 83.86 (C–O); ^{29}Si NMR δ −14.91, −16.98 (Me_3Si), 5.05 (Me_3SiO), −46.65 (Si ring); MS (EI), *m/z* 467 (0.3, M^+), 452 (1, $M^+ - Me$). Anal. Calcd for $C_{24}H_{50}Si_4O$: C, 61.73; H, 10.79. Found: C, 61.81; H, 10.88. Additional NMR absorbances in the crude material were consistent with the presence of an "ene" product ([2 + 4]:ene = 2:1) as observed in other cases.[4] When dimer **5g** was heated in benzene with 2,3-dimethylbutadiene for 15 min at 75 °C, the NMR spectra indicated that the same adducts had formed in near quantitative yield.

Cycloaddition of Silene 2g with Anthracene. Dimer **5g** (250 mg) and anthracene (232 mg) were heated under vacuum for 75 min at 190–200 °C in a Schlenk tube. The unreacted anthracene was then removed by sublimation, and the crude reaction product was chromatographed on silica gel with pentane to give 105 mg of cycloadduct **12g**: mp 250–251 °C; ^{1}H NMR δ 0.12, 0.17, 0.24 (each 9 H, s, Me_3Si), 1.3–1.7 (br, BCO), 3.96, 4.70 (each 1 H, br s, CH-bridgehead), 6.7–8.1 (8 H, m, Ar); ^{13}C NMR δ 2.36, 2.46, 5.93 (each Me_3Si), 24.73 (CH, BCO), 26.60, 29.82 (CH_2, BCO), 39.03 (quat C, BCO), 41.38, 56.75 (bridgehead C's), 95.37 (C–O), 124–130 (CH, Ar), 141–146 (quat C, Ar); ^{29}Si NMR δ −12.19, −14.57 (Me_3Si), 4.47 (Me_3SiO), −27.97 (Si–Si_2).

Formation of the Methanol Adduct 4i from Acylsilane 1i. A solution of acylsilane **1i** ($(Me_3Si)_3SiCOMes$) (120 mg) in C_6D_6 (0.8 mL) containing a few drops of methanol and a drop of pyridine was photolyzed for 8 h. Removal of the solvent gave an oil that was purified by chromatography (90:10 hexanes–dichloromethane) to yield 54% of shiny colorless crystals: mp 41–42°; ^{1}H NMR δ 0.01, 0.15, 0.24 (each 9 H, s, Me_3Si), 2.09, 2.29, 2.58 (each 3 H, s, Me, restricted rotation), 3.46 (3 H, s, OMe), 5.42 (1 H, s, CH), 6.68, 6.76 (each 1 H, s, CH Ar); ^{13}C NMR δ −0.14, 0.11, 0.21 (Me_3Si), 20.87, 21.26, 22.69 (Me), 54.34 (MeO), 69.02 (CH), 129.19, 130.85 (CH Ar), 132.93, 135.51, 137.73, 138.34 (quat C Ar); ^{29}Si NMR δ 17.16 (Me_3SiO), 16.66 (SiOMe), −18.37, −18.87 (Me_3Si); calcd for $C_{20}H_{42}O_2Si_4 - Me^+$ 411.2027, found 411.2046.

Crystal Data for $Me_2(MeO)Si$-CHAdSiMe(t-Bu)$OSiMe_3$ (7b). Crystal data: $C_{22}H_{46}O_2Si_3$, fw 426.9, monoclinic, space group $P2_1/n$, $a = 17.634$ (8) Å, $b = 10.246$ (7) Å, $c = 30.036$ (11) Å, $\beta = 102.10$ (3)°, $V = 5306$ Å^3, $D_{calcd} = 1.069$ g cm^{-3} for $Z = 8$ (2 independent molecules), $F(000) = 1840$, λ(Mo K$\bar{\alpha}$) = 0.710 69 Å, $\mu = 1.9$ cm^{-1}, $T = 298$ K; unit cell dimensions based on 25 reflections ($3.2 < \theta < 11.3°$). Intensity data collection: Enraf-Nonius CAD4 diffractometer, Mo K$\bar{\alpha}$ radiation (graphite monochromator), ω–2θ scans over scan ranges $(0.65 + 0.35 \tan \theta)°$, maximum scan time 65 s, quadrants h, k, $\pm l$ with $2\theta \leqslant 45°$ and 3 standard

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reflections monitored every 7000 s; 7866 reflections (including standards) measured. Data corrected for Lorentz, polarization, and crystal decay (based on values of standards; 11% decay; maximum rescale factor on F_o = 1.222). After 2502 systematically absent or zero F_o data were rejected and 144 symmetry equivalent reflections (R_{merge} = 0.045) were averaged, a data set of 4968 reflections was obtained.

After several recrystallizations from methanol some small colorless plate shaped crystals were obtained (by W.J.C.). The largest available crystal of dimensions only 0.045 × 0.095 × 0.175 mm was used to collect the above weak data set [after excluding standards, only 1687 (22%) of the above 7614 data were considered observed using the criteria $I \geq 2\sigma(I)$]. Weaknesses in the data led to both $P2_1/c$ and $P2_1/n$ as possible space groups. The latter was shown to be correct. The crystal packing which consists of layers of molecules 1 and 2 parallel to the *ab* face in which the *x* and *z* (but not *y*) coordinates of the two molecules are related by $x_2 \approx {}^1/_2 + x_1$ and $z_2 \approx z_1$ leads to the pseudoabsence $h0l$, $l = 2n$, and helps explain some of the weakness of other sections of the data set.

The structure was solved by the use of direct methods (after several attempts and only after renormalization of several parity groups) to locate two fragments and some spurious peaks. In the early stages of refinement only heavily damped least squares gave meaningful results. All missing atoms were then located, and H atoms in the Ad groups were placed in calculated positions with fixed temperature factors. Hydrogen atoms in the CH_3 groups and the C(*n1*)–H atoms (representing 12% of the electron density) were not included. Refinement of anisotropic temperature factors was not possible (too few reflections available) and least-squares refinements minimizing $\sum w\Delta F^2$ then converged (maximum Δ/σ = 0.12) to the residuals R = 0.1212 (wR = 0.1207) for 1103 reflections with $F > 3\sigma(F)$. Weights in the final cycles were given by $w = [\sigma^2(F) + 0.001\,66F^2]^{-1}$ and a final ΔF map contained no peaks > 0.46 e Å^{-3}. Final positional parameters, bond lengths/bond angles, and structure factors have been deposited as supplementary material.

Acknowledgment. The authors are grateful to the Natural Science and Engineering Research Council of Canada for financial support of this research and for a scholarship for K.M.B.

Registry No. **1a**, 117959-04-3; **1b**, 96760-14-4; **1c**, 117959-09-8; **1d**, 117959-10-1; **1e**, 117959-11-2; **1f**, 117959-12-3; **1g**, 81671-43-4; **1i**, 97551-01-4; **2b**, 117959-16-7; **2f**, 117959-31-6; **2g**, 117959-31-6; **2g** (2,3-dimethylbutadiene cycloadduct), 117959-39-4; **2g** (anthracene cycloadduct), 117959-40-7; **2h**, 81671-50-3; **3a**, 117959-05-4; **3b**, 117959-06-5; **3c**, 109242-61-7; **3g**, 4110-02-5; **4a** (isomer 1), 117959-14-5; **4a** (isomer 2), 117982-86-2; **4b** (isomer 1), 117959-18-9; **4b** (isomer 2), 117959-19-0; **4c** (isomer 1), 117959-23-6; **4c** (isomer 2), 117959-24-7; **4d** (isomer 1), 117959-25-8; **4d** (isomer 2), 117959-26-9; **4e** (isomer 1), 117959-29-2; **4e** (isomer 2), 117959-30-5; **4f** (isomer 1), 117959-33-8; **4f** (isomer 2), 117959-34-9; **4g**, 117959-38-3; **4i**, 117959-41-8; **5a**, 117959-13-4; **5c**, 117959-22-5; **5e** (isomer 1), 118099-30-2; **5e** (isomer 2), 117959-27-0; **5g**, 117982-89-5; **6b**, 117959-17-8; **6f**, 117959-32-7; **7b** (isomer 1), 117959-20-3; **7b** (isomer 2), 117959-21-4; **7f** (isomer 1), 117959-35-0; **7f** (isomer 2), 117959-36-1; **7g**, 117959-38-3; **7h**, 117959-42-9; **7i**, 117959-41-8; **9b**, 96760-17-7; **10b**, 117959-15-6; **10e$_1$**, 118015-90-0; **10e$_2$**, 117959-28-1; **10e$_3$**, 118015-89-7; **11d** (isomer 1), 117982-87-3; **11d** (isomer 2), 117982-88-4; ClCOAd, 2094-72-6; $(Me_3Si)_2$(*t*-Bu)Si$(CH_2)_4$OCOAd, 117959-07-6; ClCO(*t*-Bu), 3282-30-2; ClCOMeS, 938-18-1; ClCOCEt$_3$, 35354-15-5; ClCO(BCO), 21891-38-3; methyltris(trimethylsilyl)silane, 2003-86-3; *tert*-butyltris(trimethylsilyl)silane, 104475-59-4; *tert*-butyltrichlorosilane, 18171-74-9; phenyltris(trimethylsilyl)silane, 4235-65-8; tris(trimethylsilyl)silyl bromide, 5089-31-6; 2,3-dimethylbutadiene, 513-81-5; anthracene, 120-12-7.

Supplementary Material Available: Tables of fractional coordinates and bond distances and angles for **7b** (5 pages); a listing of structure factors (4 pages). Ordering information is given on any current masthead page.

Crystal Structures of Four Sterically Crowded 1,3-Disilacyclobutanes

Kim M. Baines, A. G. Brook,* Paul D. Lickiss, and Jeffery F. Sawyer

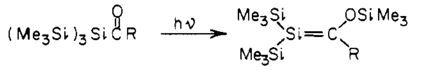
Lash Miller Chemical Laboratories, University of Toronto, Toronto, Canada M5S 1A1

Received June 15, 1988

The crystal structures of the four 1,3-disilacyclobutanes $(R_1R_2SiCR_3R_4)_2$ [**1**, R_1 = Me, R_2 = OSiMe$_3$, R_3 = 1-Ad, R_4 = SiMe$_2$*t*-Bu; **2**, R_1 = R_2 = Me, R_3 = 1-Ad, R_4 = SiMe(*t*-Bu)(OSiMe$_3$) (*R*,*R*:*S*,*S*); **3**, R_1 = R_2 = Me, R_3 = 1-Ad, R_4 = SiMePh(OSiMe$_3$) (*R*,*R*:*S*,*S*); **4**, R_1 = R_2 = Me, R_3 = 1-Ad, R_4 = SiMePh(OSiMe$_3$) (*R*,*S*:*S*,*R*)] whose syntheses by the photolyses of the appropriate (1-adamantylcarbonyl)phenyl- or (1-adamantylcarbonyl)*tert*-butylbis(trimethylsilyl)silane are reported in the previous paper are herein described and discussed. All four compounds contain sterically crowded but essentially planar (fold angles ≤ 5.9°) 1,3-disilacyclobutane rings. Despite the differences in the nature of the R_2 and R_4 substituents, the individual bond lengths and bond angles in the two independent molecules of **1** and in **2**–**4** do not deviate significantly from average values obtained from the dimensions of all the molecules, although the ⟨Si–C⟩ distance [1.962 Å] is significantly longer than a standard Si–C single bond length and is ca. 0.04 Å longer than values observed in other disilacyclobutanes. Additional evidence of steric crowding in these molecules can be seen in the lengthening of the C(ring)–Ad bond lengths to 1.624 Å (average). The significant increases in the already elongated C(ring)–R_4 bond lengths seem to be consistent with approximate cone angles calculated for the R_4 silicon substituents. Similarly, angle deformations result in differences in the maximum and minimum bond angles at each ring atom and in the *tert*-butyl groups of up to 13°. Finally, in the disiloxane moieties the Si–O–Si bond angles vary from 137° to 166° and there is an obvious correlation between the Si–O bond length and the included Si–O–Si angle.

Introduction

The photolysis of tris(trimethylsilyl)acylsilanes is a well-established route to highly substituted silenes.[1]



This mild route has been used to prepare stable silenes (R = 1-adamantyl, CEt$_3$, mesityl, 1-methylcyclohexyl)[2] and has enabled us to investigate the physical properties and

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[1] (a) Brook, A. G.; Harris, J. W.; Lennon, J.; El Sheikh, M. *J. Am. Chem. Soc.* **1979**, *101*, 83. (b) Brook, A. G.; Kallury, R. K. M. R.; Poon, Y. C. *Organometallics* **1982**, *1*, 987.

0276-7333/89/2308-0709$01.50/0