ability of CHR to twist within **2** and **3**; both factors could influence the overall rate of the coupling reactions. Electronic factors may be important too, with electronegative substituents stabilizing the M_2-(μ-CHR) bonding. Perhaps a clearer picture of these stereoelectronic effects will emerge when we have completed further studies involving disubstituted alkylidenes.

Acknowledgment. We gratefully acknowledge support of this work by a grant (R.S.D.) from the Australian Research Grants Scheme. S.M.J. thanks the Commonwealth Government for a Postgraduate Research Award. Help with spectroscopic monitoring of reactions was provided by Ian Grayson, Felicity McLure, and Jo Weigold.

Registry No. **1**, 98395-25-6; **2a**, 107870-63-3; **2a′**, 107870-66-6; **2b**, 107799-58-6; **2d**, 107870-65-5; **3a**, 107799-56-4; **3a′**, 107870-64-4; **3b**, 107799-57-5; **3c**, 107799-59-7; **3d**, 107799-60-0; **4**, 107819-48-7; $N_2CH(CO_2Et)$, 623-73-4; $N_2CH(SiMe_3)$, 18107-18-1; $N_2CH(CH{=}CH_2)$, 2032-04-4; $N_2CH(CF_3)$, 371-67-5; Rh, 7440-16-6.

Supplementary Material Available: Tables of thermal parameters, hydrogen atom coordinates, and equations for planes (3 pages); a listing of the structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

1,2-Siloxetanes: Formation, Structure, and Rearrangements

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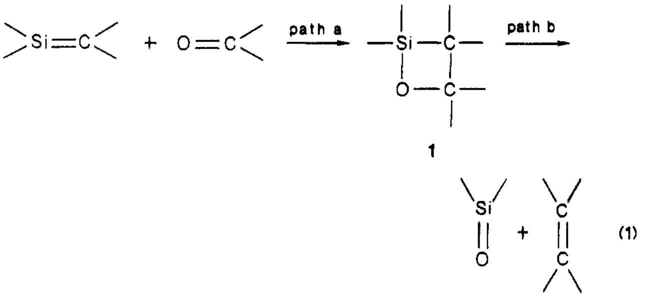
A variety of relatively stable silenes react with representative nonenolizable aldehydes and ketones to yield moderately stable 1,2-siloxetanes, some of which have been isolated as solids. A crystal structure of one siloxetane, 2,2-bis(trimethylsilyl)-4,4-diphenyl-3-adamantyl-3-(trimethylsiloxy)-2-siloxetane, has been obtained [crystal data: $C_{33}H_{52}O_2Si_4$, monoclinic, space group $C2/c$, $a = 38.652$ (13) Å, $b = 10.470$ (2) Å, $c = 17.081$ (8) Å, $\beta = 101.99$ (3)°, $U = 6761$ Å^3, $D_{calcd} = 1.14$ g cm^{-3} for $Z = 8$; $R = 0.062$ for 1605 observed ($I > 3\sigma(I)$) reflections] which shows all bonds of the slightly folded ring to be somewhat elongated, especially the C–C bond (1.67 Å). In some cases, in addition to the [2 + 2] siloxetane adducts, related [2 + 4] bicyclo [4.4.0] isomers were observed from the silene + ketone reactions, where the 4π component was derived either from the silene or from an aromatic ketone. Examples of interconversions between the [2 + 2] and [2 + 4] isomers were noted. Only one of the siloxetanes, **1g**, underwent the "normal" [2 + 2] retroreaction to silanone and alkene on thermolysis [crystal data of the siloxyalkene **16**: $C_{26}H_{28}OSi$, monoclinic, space group $P2_1/n$, $a = 9.335$ (2) Å, $b = 10.868$ (2) Å, $c = 22.211$ (6) Å, $\beta = 98.02$ (2)°, $U = 2231$ Å^3, $D_{calcd} = 1.15$ g cm^{-3} for $Z = 4$; $R = 0.077$ for 801 observed ($I > 3\sigma(I)$) reflections]. All the other siloxetanes underwent an intramolecular rearrangement involving siloxy and aryl group migrations. A two-step dipolar mechanism best explains the cycloaddition reactions while the interconversions between [2 + 2] and [2 + 4] products appear to involve 1,3-sigmatropic processes.

Introduction

Siloxetanes **1** have long been regarded as the product of reaction of a silene with a carbonyl compound[1] (eq 1, path a). However, until recently direct proof that siloxetanes were actually formed has been lacking because of their apparent instability, and evidence for their formation has rested primarily on the detection and/or isolation of the alkene and the silanone (oligomers) expected if the anticipated siloxetanes had broken down in a retro [2 + 2] sense (path b). Some direct evidence for siloxetanes has recently become available. Thus Märkl postulated the formation of several siloxetanes by thermolysis of a silene head-to-head dimer in the presence of a variety of nonenolizable carbonyl compounds.[2] In some cases siloxetanes were apparently isolated, but in other cases different types of product were obtained, believed to arise from complex rearrangements of the initially formed siloxetanes. Wiberg has described the formation of a remarkably stable siloxetane as well as a related [2 + 4] adduct from reaction of a relatively stable silene with benzophenone[3] and Ando recently described the formation of a siloxetene under rather special circumstances.[4]



Discussion

We have examined the reactions of the relatively stable silenes obtained by photolysis of a variety of polysilylacylsilanes with several nonenolizable aldehydes and ketones under two sets of conditions (Scheme I). Cophotolysis of the acylsilane **2** in the presence of the carbonyl compound at λ ⩾ 360 nm gave essentially identical results to those obtained when the carbonyl compound was added in the dark to a solution of the preformed silene **3**. Thus the additions occurring are "dark" reactions of the silene

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† Present address: Department of Chemistry, McMaster University, Hamilton, Canada.

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

(2) Märkl, G.; Horn, M. *Tetrahedron Lett.* **1983**, *24*, 1477.

(3) Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141. Wiberg, N.; Preiner, G.; Scheida, O. *Chem. Ber.* **1981**, *114*, 3518.

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

Scheme I

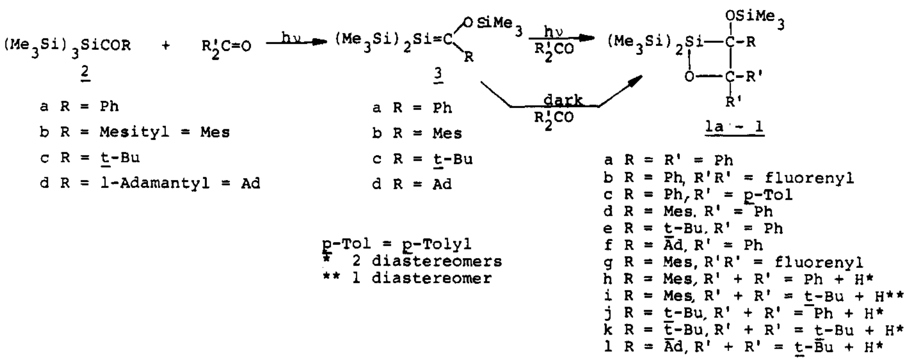

Table I. Crystal Data, Details of Intensity Measurements, and Structure Refinements[a] for Siloxetane 1f

compd	$C_{33}H_{52}O_2Si_4$ (**1f**)
system	monoclinic
a, Å	38.652 (13)
b, Å	10.470 (2)
c, Å	17.081 (8)
β, deg	101.99 (3)
U, Å^3	6761
fw/*F*(000)	581.1/2528
Z/D_{calcd}, g cm^{-3}	8/1.14
space group	*C*2/*c*
μ(Mo K_α), cm^{-1}	2.0
reflns in cell detmn	24
no./*θ* range, deg	6.4 < *θ* < 12.8
scan widths, deg	0.70 + 0.35 tan *θ*
max scan time, s	50
std reflns (no./interval, s)[b]	3/6500
max 2*θ* (deg)/octants	52/*h*,*k*,±*l*[c]
tot. no. colld (inc. Stds)	9655
unique data	5101[d]
structure soln[e]	direct methods, least-squares, Fourier calcn
no. of data *I* > 3*σ*(*I*)	1605
R_1 (R_2)	0.0624 (0.0634)
max Δ/*σ*	0.28
weights, value of *p*	0.0045[f]
max peak final Δ*F* Fourier, e Å^{-3}	0.44 (no. Si(1))

[a] Enraf-Nonius CAD-4 diffractometer; *θ*–2*θ* scans; Mo K_α radiation (λ = 0.71069 Å); graphite monochromator; *T* = 298 K. [b] Ca. 12.5% loss in intensity for standard reflections corrected for after data reduction. Lorentz and polarization corrections applied to all data. [c] Peak profiles somewhat broad so it was decided to collect 2056 additional data with negative *k* indices and 2*θ* ≤ 35° and then average equivalent reflections. [d] A total 2559 systematically absent or zero F_o data rejected and 1679 symmetry-equivalent reflections then averaged ($R_{merge}(F)$ = 0.059) to give number of data indicated. [e] Programs: Enraf-Nonius SDP package on PDP 11/23 or SHELX on Gould 9705 computers. Scattering factors stored in programs were taken from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974. Hydrogen atoms were located in Δ*F* Fourier maps and their positions then optimized. Methyl groups in **1f** were refined as rigid groups with common *U* = 0.118 (10) Å^2; other H atoms with *U* = 0.054 (6) Å^2. [f] Weights $w = (\sigma^2(F) + pF^2)^{-1}$.

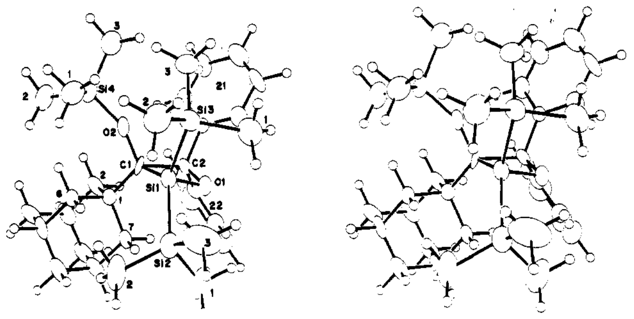

Figure 1.

Table II. Final Positional Parameters for Compound 1f

atom	*x*	*y*	*z*
Si(1)	0.3686 (1)	0.4715 (3)	0.4475 (2)
Si(2)	0.4011 (1)	0.2875 (3)	0.4208 (2)
Si(3)	0.3120 (1)	0.3979 (3)	0.4612 (2)
Si(4)	0.3106 (1)	0.7644 (3)	0.3302 (2)
O(1)	0.3916 (2)	0.5232 (6)	0.5374 (4)
O(2)	0.3455 (2)	0.7294 (6)	0.3989 (4)
C(1)	0.3757 (2)	0.6518 (9)	0.4234 (5)
C(2)	0.3882 (2)	0.6584 (10)	0.5232 (6)
C(11)	0.4031 (3)	0.6835 (9)	0.3717 (6)
C(12)	0.4099 (3)	0.8290 (10)	0.3668 (6)
C(13)	0.4355 (3)	0.8567 (12)	0.3109 (6)
C(14)	0.4193 (3)	0.8070 (12)	0.2265 (7)
C(15)	0.4142 (3)	0.6652 (12)	0.2305 (6)
C(16)	0.3884 (2)	0.6337 (10)	0.2854 (5)
C(17)	0.4389 (3)	0.6178 (10)	0.4003 (6)
C(18)	0.4649 (3)	0.6470 (12)	0.3453 (6)
C(19)	0.4704 (3)	0.7907 (12)	0.3435 (7)
C(110)	0.4494 (3)	0.5988 (12)	0.2608 (6)
C(21)	0.4446 (3)	0.2928 (13)	0.4919 (8)
C(22)	0.4087 (4)	0.2627 (12)	0.3176 (7)
C(23)	0.3794 (4)	0.1411 (11)	0.4461 (12)
C(31)	0.3212 (3)	0.2996 (12)	0.5560 (7)
C(32)	0.2909 (3)	0.2922 (12)	0.3759 (7)
C(33)	0.2779 (3)	0.5181 (13)	0.4736 (8)
C(41)	0.2918 (3)	0.6178 (11)	0.2739 (7)
C(42)	0.3198 (4)	0.8850 (11)	0.2553 (7)
C(43)	0.2786 (3)	0.8431 (13)	0.3826 (8)
C(211)	0.3594 (2)	0.7108 (10)	0.5642 (5)
C(212)	0.3500 (3)	0.6390 (11)	0.6243 (6)
C(213)	0.3255 (3)	0.6850 (13)	0.6676 (7)
C(214)	0.3115 (3)	0.8045 (13)	0.6527 (8)
C(215)	0.3216 (3)	0.8804 (13)	0.5938 (7)
C(216)	0.3449 (3)	0.8329 (10)	0.5488 (6)
C(221)	0.4232 (3)	0.7191 (10)	0.5641 (6)
C(222)	0.4274 (3)	0.8516 (11)	0.5682 (6)
C(223)	0.4593 (3)	0.9059 (12)	0.6075 (7)
C(244)	0.4867 (3)	0.8266 (15)	0.6434 (7)
C(225)	0.4825 (3)	0.6986 (14)	0.6415 (7)
C(226)	0.4508 (3)	0.6472 (12)	0.6019 (6)

with the >C=O group. As pointed out by Michl,[5] if these reactions are initiated by attack of a lone pair of electrons of the carbonyl oxygen on the silicon atom, these nominal [2 + 2] reactions are not pericyclic and hence not thermally disallowed in the Woodward–Hoffmann sense.

Siloxetanes **1** were initially formed in the solution in most cases, either as an essentially pure compound (from the symmetrical ketones benzophenone or fluorenone) or as a pair of diastereomers (from the representative aldehydes pivaldehyde or benzaldehyde). These products were characterized fully by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy and in some cases by isolation and other analytical procedures. However, most of the siloxetanes were not very stable in air, or at temperatures above 25 °C. Thus they were difficult to isolate and purify, although

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

Table III. Selected Bond Distances (Å) and Angles (deg) for Compound 1f

	Bond Distances		
Si(1)–Si(2)	2.394 (5)	O(2)–C(1)	1.413 (11)
Si(1)–Si(3)	2.378 (5)	C(1)–C(2)	1.673 (12)
Si(1)–O(1)	1.696 (6)	C(1)–C(11)	1.549 (15)
Si(1)–C(1)	1.963 (10)	C(2)–C(211)	1.532 (14)
Si(4)–O(2)	1.635 (6)	C(2)–C(221)	1.527 (13)
O(1)–C(2)	1.438 (12)	⟨Si–Me⟩	1.868
	Bond Angles		
Si(2)–Si(1)–Si(3)	106.8 (2)	Si(1)–O(1)–C(2)	98.5 (5)
–O(1)	103.4 (3)	Si(4)–O(2)–C(1)	148.2 (6)
–C(1)	129.2 (3)	Si(1)–C(1)–O(2)	118.2 (6)
Si(3)–Si(1)–O(1)	109.5 (3)	–C(2)	81.4 (5)
–C(1)	120.2 (3)	–C(11)	117.8 (7)
O(1)–Si(1)–C(1)	79.2 (3)	O(2)–C(1)–C(2)	108.9 (7)
Si(1)–Si(2)–C(21)	106.9 (5)	–C(11)	109.1 (7)
–C(22)	118.9 (4)	C(2)–C(1)–C(11)	119.1 (7)
–C(23)	110.0 (6)	O(1)–C(2)–C(1)	97.4 (7)
Si(1)–Si(3)–C(31)	104.3 (4)	–C(211)	109.0 (8)
–C(32)	112.0 (5)	–C(221)	106.8 (7)
–C(33)	118.7 (4)	C(1)–C(2)–C(211)	113.5 (7)
O(2)–Si(4)–C(41)	111.0 (4)	–C(221)	121.6 (8)
–C(42)	113.2 (5)	C(211)–C(2)–C(221)	107.4 (8)
–C(43)	106.6 (5)		

many remained unchanged in solution in the dark for days or weeks.

The crystal structure was obtained of siloxetane **1f**, the product from the adamantylsilene[6] and benzophenone, one of the few siloxetanes that could be successfully crystallized[7] (Tables I–III). The resulting structure (Figure 1) contains a four-membered siloxetane ring which is folded by 20° about the Si(1)–C(2) axis and in which all ring bonds are longer than the usual acyclic value. Details of the crystal structure are given below. This crystal structure, and the close similarity of the NMR properties of **1f** with those of the other species **1a–l**, clearly establishes these as a family of siloxetanes.

Siloxetane NMR Data. Each of the more than a dozen siloxetanes prepared had ^{29}Si resonances for the ring silicon atom in the range 42–65 ppm, with most compounds resonating in the range 50–56 ppm. It is well-known that the chemical shifts of silicon in rings is very dependent on ring size.[8] The chemical shift of the silicon atom of silacyclobutane occurs at +18.9 ppm,[9] and more complex silacyclobutanes (where CH_2 replaces the O in siloxetanes) resonate in the range −31 to −14 ppm.[10] Thus it is obvious that oxygen in the ring strongly deshields the ring silicon atom of siloxetanes. Both ring carbons of the siloxetanes resonated in the ^{13}C range 95–107 ppm. These data can be meaningfully compared with that of a disiloxetane of known crystal structure prepared by Weidenbruch.[11] The disiloxetane ring silicon resonances (determined by us on a sample provided by Professor Weidenbruch) came at 50.8 and 55.2 ppm: the ring carbon of the disiloxetane resonated at 94.2 ppm. Hence there is a striking similarity in the chemical shifts (and crystal structures) between the two types of compound, despite rather different groups being attached to the ring atoms.

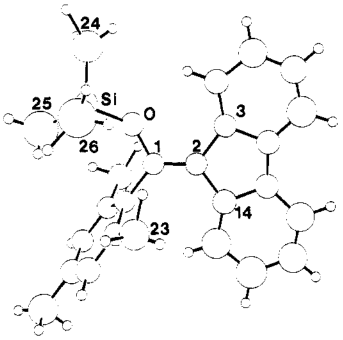
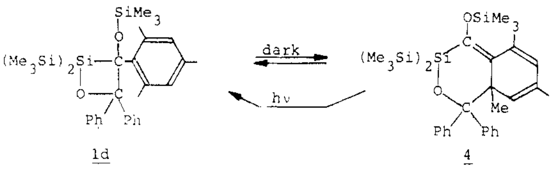
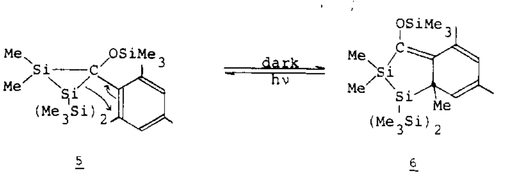


Figure 2. ORTEP view of compound **16**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are drawn with uniform isotropic thermal parameters. Selected bond distances (Å), bond angles (deg), and torsion angles (deg) are as follows: Si(1)–O(1) = 1.660 (7), O(1)–C(1) = 1.390 (9), C(1)–C(2) = 1.341 (11), C(1)–C(15) = 1.484 (12), C(2)–C(3) = 1.489 (12), and C(2)–C(14) = 1.473 (12); Si(1)–O(1)–C(1) = 135.2 (6), O(1)–C(1)–C(2) = 117.9 (9), O(1)–C(1)–C(15) = 113.9 (8), C(2)–C(1)–C(15) = 128.2 (9), C(1)–C(2)–C(3) = 126.5 (9), C(1)–C(2)–C(14) = 126.1 (9), and C(3)–C(2)–C(14) = 107.5 (9); τ(O(1)–C(1)–C(2)–C(3)) = 5 (2), τ(O(1)–C(1)–C(2)–C(14)) = −175 (1), τ(C(15)–C(1)–C(2)–C(3)) = −178 (1), and τ(C(15)–C(1)–C(2)–C(14)) = 2 (2).

Siloxetane Ring Expansions. We have observed several entirely unexpected reactions of the siloxetanes under mild thermal conditions. Thus the siloxetane **1d** derived from the reaction of the mesitylsilene **3b** with benzophenone spontaneously underwent ring expansion at room temperature in the dark to give a 1.8:1 mixture of the [4.4.0] bicyclic compound **4** together with unchanged siloxetane (eq 2). After purification, a solution of **4** slowly isomerized in the dark at room temperature to the same 1.8:1 mixture of **4** and **1d**. This strongly suggests that this reversible isomerization involves 1,3-sigmatropic rearrangements, particularly since the same rearrangements occurred in the presence of an excess of tributyltin hydride (a good radical trap) or in the presence of excess methanol, which would have been expected to intercept a dipolar intermediate. The ring expansion of **1d** is similar to the recently reported rearrangement[12] of the mesityldisilacyclopropane **5** to the bicyclo [4.3.0] ring system **6** (eq 3), and structurally related parts of the two molecules **4** and **6** have virtually identical ^{1}H, ^{13}C, and ^{29}Si NMR spectral properties. Like the [4.3.0] system, the [4.4.0] compound **4** could be reconverted quantitatively to its precursor **1d** by brief photolysis at λ ≥ 360 nm. This indicates there is a second (i.e., photochemical as well as thermal) pathway for the ring contraction process.



(2)



(3)

The scope, mechanism, and possible synthetic application of these rearrangements in which small rings spontaneously expand into aromatic ring systems creating

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[6] Here and throughout the paper silenes (e.g., **3**) and acylsilanes (e.g., **2**) will be identified by the R group present (e.g., mesitylsilene, phenylacylsilane).

[7] Crystals of the fluorenyl compound **1g** were also examined. These were monoclinic, space group (probably) $P2_1/c$, with a = 20.359 (4) Å, b = 16.797 (5) Å, c = 21.525 (4) Å, β = 111.75 (2)°, U = 6837 Å^3, and Z = 8 (two independent molecules). This compound was less stable than **1f**.

[8] Cragg, R. H.; Lane, R. B. *J. Organomet. Chem.* **1985**, *291*, 153.

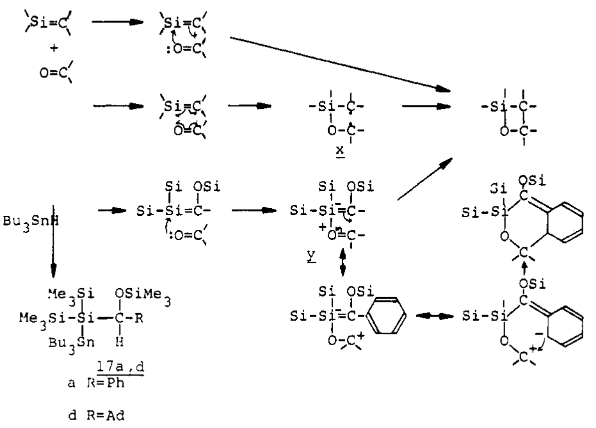
[9] Schraml, J.; Bellama, J. M. *Determ. Org. Struct. Phys. Methods* **1976**, *6*, 203.

[10] Unpublished studies by A. G. Brook, M. Hesse, and K. Vorspohl.

[11] Schäfer, A.; Widenbruch, M.; Pohl, S. *J. Organomet. Chem.* **1985**, *282*, 305.

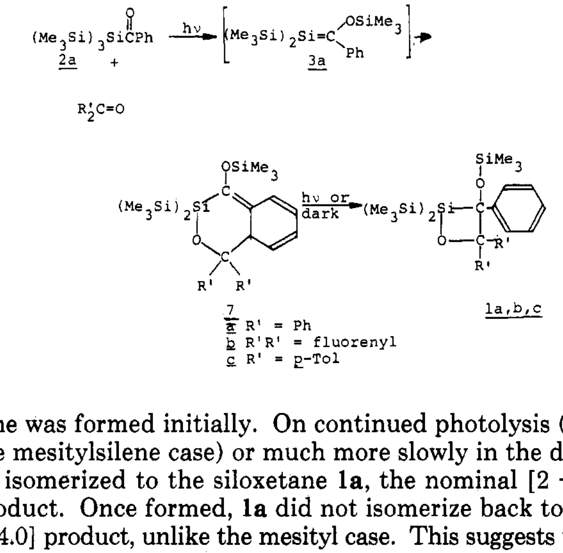
[12] Brook, A. G.; Wessely, H.-J. *Organometallics* **1985**, *4*, 1487.

Scheme II

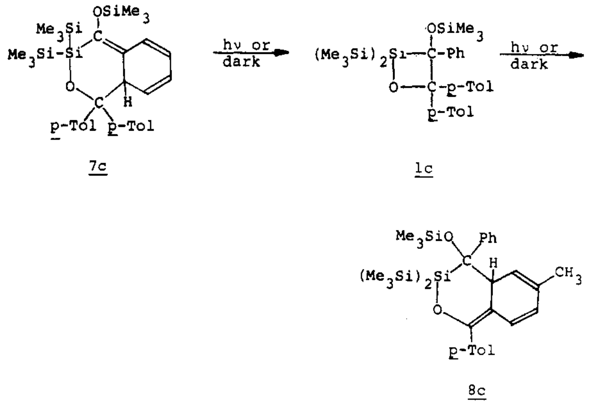


conjugated trienes are currently the subject of further investigation in these laboratories. Thus the *cis*-diene component of **4**, **6**, or **7a–c** should be able to serve as a diene in Diels–Alder reactions with maleic anhydride and other dienophiles, and hence such species may be valuable dienes for the synthesis of a variety of [2.2.0] bicyclooctyl and -octenyl derivatives.

Reactions of the phenylsilene with benzophenone and other ketones (eq 4) showed closely related behavior. Here the first detectable product from the co-photolysis of benzophenone with the phenylacylsilane **2a**[6] (the phenylsilene **3a** is not stable and rapidly dimerizes so it cannot be preformed[13]) was the bicyclo[4.4.0] system **7a**, the nominal [2 + 4] adduct of the silene (4π) with the ketone (2π) (eq 4). No evidence could be found that the siloxetane was formed initially. On continued photolysis (like the mesitylsilene case) or much more slowly in the dark, **7a** isomerized to the siloxetane **1a**, the nominal [2 + 2] product. Once formed, **1a** did not isomerize back to the [4.4.0] product, unlike the mesityl case. This suggests that in this case the [4.4.0] product is the kinetic isomer and the [2 + 2] product is the thermodynamic isomer. Similar behavior was also observed with fluorenone. However an additional isomerization was noted when di-*p*-tolyl ketone was photolyzed with the phenylacylsilane **2a**. After formation of the bicyclo[4.4.0] compound **7c** and its photochemical isomerization to the normal siloxetane **1c** as described above, further photolysis over 24 h (or standing for 3 days in the dark) yielded a different bicyclo[4.4.0] compound shown to have the structure **8c**, nominally derived from the silene (2π) and the aryl ketone (4π). This behavior is similar to that reported by Wiberg,[3] where a [2 + 4] adduct was formed from reaction of the stable silene $Me_2Si{=}C(SiMe_3)SiMe(t\text{-}Bu)_2$ with benzophenone at lower, but not higher temperatures.



(4)



(5)

In contrast to the above example where the isomerization of the [2 + 2] adduct to the [2 + 4] adduct **8c** could be observed and monitored, the reactions of the *tert*-butyl- and adamantylsilenes (**3c** and **3d**) with fluorenone or benzophenone led directly to the [2 + 4] cycloaddition products **8a,b** (fluorenone) or **8e,f** (benzophenone) (eq 6), without any evidence for the prior formation of the siloxetane. The red-colored trienes **8a,b** (from fluorenone) were accompanied in each case by a small amount of the aromatized isomer **9a,b** which would result from a subsequent photochemical 1,3-sigmatropic shift of hydrogen. None of the usual [2 + 2] siloxetane was formed during several days at room temperature. Further conversion of **8a,b** to **9a,b** could be effected by extended photolysis. Attempted thermal rearrangement of **8a** at 80 °C failed to cause its isomerization to **9a** or to the isomeric [2 + 2] siloxetane but did result in its rearrangement to the isomer **10a** by a process not yet investigated. Both **9a** and **9b** were stable for over a week at 70 °C, consistent with their fully aromatic structure.

In contrast to the above, the [2 + 4] adducts formed with benzophenone, **8e,f**, on standing in the dark over 24 h completely rearranged to the expected siloxetanes **1e,f**. The above are the only examples to date of the mode of [2 + 4] addition where the carbonyl species provides the 4π component. All reactions between any of the silenes with the representative aldehydes led only to the formation of the [2 + 2] siloxetane as a mixture of diastereomers: no [2 + 4] adducts were ever observed.

It is clear that in these cycloadditions either the silene or the carbonyl compound may provide the 4π component of a [2 + 4] cycloaddition reaction. However, other combinations of silene and carbonyl compound yield [2 + 2] adducts which do not rearrange further. What determines which process will occur is not yet fully understood.

Siloxetane Thermal Rearrangements. All but one of the highly substituted siloxetanes follow a common rearrangement pathway when heated in solution in the range 75–110 °C. This pathway is exemplified by the behavior of the siloxetane **1b**. When heated in refluxing toluene, clean rearrangement of **1b** to the isomeric silyl ether **11** occurred, which on hydrolysis gave 9-hydroxy-10-phenylphenanthrene **12**. This particular system had been studied earlier by Märkl[2] under different conditions where he heated the dimer of the phenylsilene **3a** to 110 °C with fluorenone. (We had previously shown that under these conditions the 1,2-disilacyclobutane dimer dissociated to the silene monomer.[13]) Märkl failed to observe any siloxetane **1b** but obtained compound **11**, which he suggested arose from **1b** by a thermal rearrangement. Our current results confirm the correctness of Märkl's explanation: however we believe the mechanism he proposed, which lacks any supporting evidence, is unnecessarily

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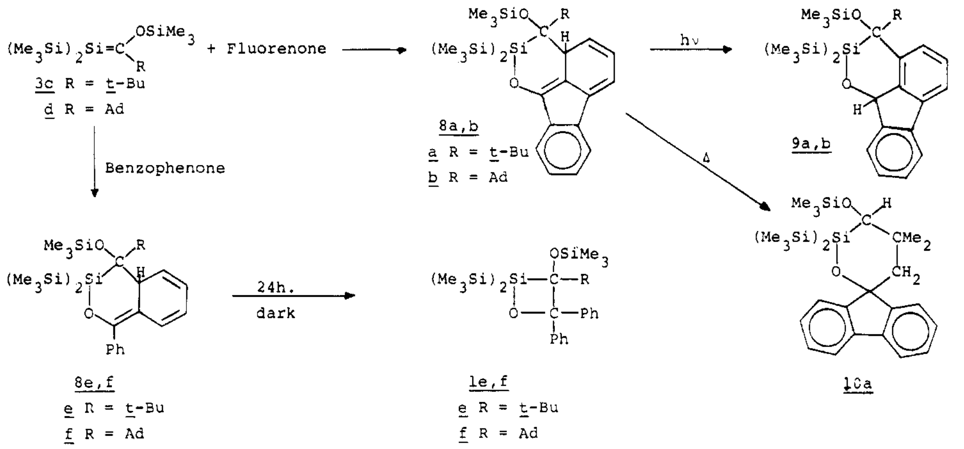
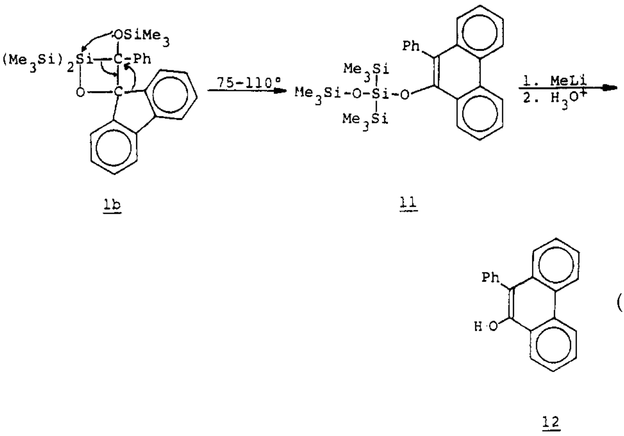
(13) Brook, A. G.; Harris, J. W.; Lennon, J.; El Sheikh, M. *J. Am. Chem. Soc.* **1979**, *101*, 83.



(6)

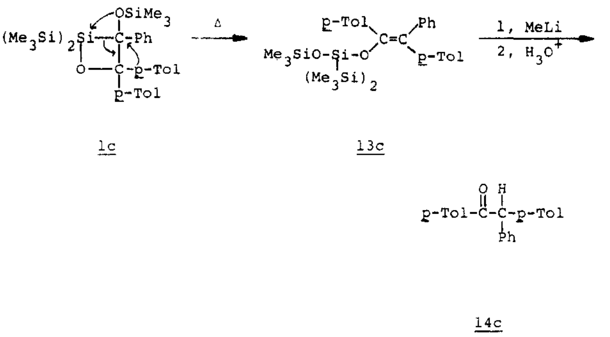
complex. We suggest that the simple process initiated by attack of the siloxy oxygen on the ring silicon with subsequent bond breaking and group migration as shown in eq 7 is a more likely interpretation of what happens.



(7)

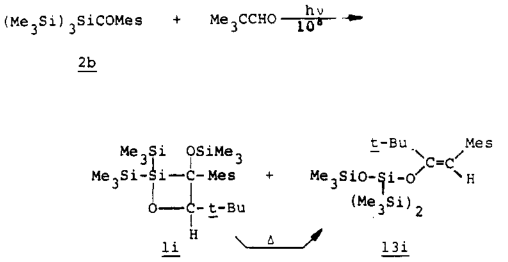
Another important example of this thermal isomerization involves the conversion of the siloxetane **1c** to the silyl enol ether **13c** (a single isomer): this on hydrolysis yielded the known ketone **14c** (two nonequivalent tolyl groups by ^1H or ^{13}C NMR spectroscopy). This latter experiment confirms that a 1,2-aryl migration occurs in the course of the thermal rearrangement of a siloxetane derived from benzophenone, as postulated by Märkl.[2]

Isomerization of a siloxetane to its silyl enol ether isomer was observed to occur at room temperature or lower in one case. Thus photolysis of the mesitylacylsilane **2b** with pivaldehyde for 12 h at 10 °C gave a 1:2 mixture of the expected siloxetane **1i** (as a single diastereomer) and its isomer **13i**: identical results were obtained when preformed silene **3b** was treated with pivaldehyde in the dark.



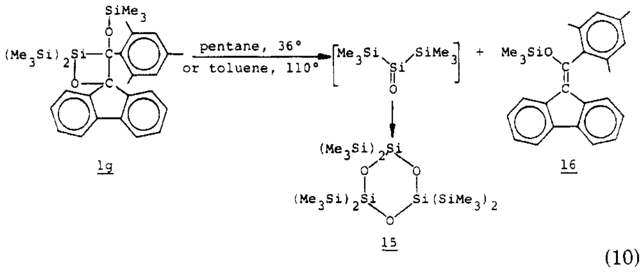
(8)

When the mixture of **1i** and **13i** was heated at 70 °C, the proportions of products slowly changed to 1:4, but this thermolysis did not result in the formation of either a geometric or structural isomer of **13i**. These results suggest that one of the expected diastereomers of **1i** is very thermally unstable, probably because of steric hindrance, and rapidly isomerizes to **13i**. The second diastereomer (the one actually observed), being much less sterically hindered, is more stable. It only rearranges slowly at elevated temperature by hydrogen migration (but not *t*-Bu migration) to the single geometric isomer of **13i** observed (geometry not established). The structure of **13i** was determined in part by ^{13}C APT NMR experiments which showed that the carbon atom at 159.33 ppm (attached to $OSi(SiMe_3)_2OSiMe_3$) carried no hydrogen atom.



(9)

This same intramolecular rearrangement pathway was observed for all the other siloxetanes that were thermally rearranged, with one exception, namely, the siloxetane **1g** formed from the mesitylsilene **3b** with fluorenone. This compound, for undetermined reasons which are probably steric in origin, followed the "normal" retro [2 + 2] cleavage reaction (eq 1, path b). Thus, as the result of heating a solution of the siloxetane in the range 75–110 °C (eq 10), the trimer of bis(trimethylsilyl)silanone **15** and the siloxyalkene **16** were obtained. The crystal structure of this molecule (Figure 2, Tables IV and V) indicates a small twist angle of 5°[14] about the C=C bond, which has a length of 1.34 Å, and bond angle distortion of up to 8° from the normal 120° at the sp^2-hybridized carbon atoms. The



(10)

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[14] This value for the torsion angle is much smaller than that found in several other fluorenyl and other crowded alkenes. See: Lee, J.-S.; Nyburg, S. C. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 560. Sakurai, H.; Nakadaira, Y.; Tobita, H.; Ito, T.; Toriumi, K.; Ito, H. *J. Am. Chem. Soc.* **1982**, *104*, 300. Sakurai, H.; Tobita, H.; Nakadaira, Y.; Kabuto, C. *J. Am. Chem. Soc.* **1982**, *104*, 4288. Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 477.

Table IV. Crystal Data, Details of Intensity Measurements and Structure Refinements[a] for Compound 16

compound	$C_{26}H_{28}OSi$ (**16**)
system	monoclinic
a, Å	9.335 (2)
b, Å	10.868 (2)
c, Å	22.211 (6)
β, deg	98.02 (2)
U, Å^3	2231
fw/F(000)	384.6/824
Z/D_{calcd}, g cm^{-3}	4/1.15
space group	$P2_1/n$
μ(Mo K$\bar{\alpha}$), cm^{-1}	1.1
reflns in cell detmn	25
No./θ range, deg	$4.9 < \theta < 11.4$
scan widths, deg	$0.60 + 0.35 \tan \theta$
max scan time, s	50
std reflns (no./interval, s)	3/6000
max 2θ (deg)/octants	$50/h,k,\pm l$
tot. No. Colld (inc. stds)	4546
unique data	2802[b]
structure soln[c]	direct methods, least squares, and Fourier calcn
no. of data $I > 3\sigma(I)$	801
R_1 (R_2)	0.0773 (0.0955)
max Δ/σ	0.22
weights, value of p	0.10[d]
max peak final ΔF Fourier, e Å^{-3}	0.24

[a] Enraf-Nonius CAD-4 diffractometer; θ–2θ scans; Mo K$\bar{\alpha}$ radiation (λ = 0.71069 Å); graphite monochromator; T = 298 K. [b] A total 1447 systematically absent or zero F_o data rejected and 156 symmetry equivalent reflections then averaged (R_{merge} (F) = 0.066). [c] Programs: Enraf-Nonius SDP package on PDP 11/23 or SHELX on Gould 9705 computers. Scattering factors stored in programs were taken from *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974. Hydrogen atoms were located in ΔF Fourier maps and their positions then optimized. [d] Weights $w = 4F^2\{\sigma^2(I) + (pF^2)^2\}^{-1}$.

mesityl group lies almost perpendicular to the plane of the fluorenyl ring system. The rate of cleavage of this siloxetane was greatly accelerated by traces of moisture (from hours to minutes) or somewhat accelerated if no precautions to exclude air were taken, so that sometimes cleavage occurred during a few-minute reflux in pentane. Under these conditions it seems possible that the much less sterically hindered H_2O can take the role of the second siloxetane molecule in the mechanism proposed by Streitwieser[15] as the pathway for siloxetane decomposition. However, it appears that in general the retrocleavage reaction (path b, eq 1) is *not* the preferred pathway for these highly substituted siloxetanes, quite probably for steric reasons.

The above results clearly reveal two important modes of reaction of these siloxetanes, whose behavior is much more complex than has been recognized previously. First, it appears that thermal rearrangement involving attack by the siloxy oxygen on the adjacent ring silicon is the preferred mode of decomposition. Secondly, siloxetanes having aryl groups attached to either of the ring carbons are very susceptible to ring expansions, which result in bicyclo [4.4.0] systems. Evidently, in the cases in which significant amounts of both isomers exist in equilibrium due to reversible sigmatropic processes, there is a close balance between the strain energy in the four-membered siloxetane ring and the loss of aromatic resonance energy resulting from the formation of the triene system.

Mechanism of Siloxetane Formation. The siloxetanes (whose identity as a family rests securely on the crystal structure of compound **1f**, together with the very close similarity of the ^1H, ^{13}C, and ^{29}Si NMR chemical shifts of all the other siloxetanes with those of **1f**) could arise from the reaction of the carbonyl compounds with the silenes by any of several processes. These include a concerted one-step addition or two-step processes that could involve either a diradical intermediate **x** or a dipolar intermediate **y**. These possibilities are outlined in Scheme II. It is difficult to completely eliminate any of these pathways, but for various reasons, indicated below, we favor a two-step dipolar process. It is a fact that there are long-lived ESR signals observable both in solutions of the silenes and in silene solutions containing added ketone. However experiments showed that siloxetane formation still occurred as a major pathway when several equivalents of the powerful radical trap tributyltin hydride were added to the silene–ketone solutions, although some silene was diverted from siloxetane formation due to its reaction with tin hydride in a radical-type orientation giving compounds **17a,d** (Scheme II). However the fact that the large excess of tin hydride failed to inhibit siloxetane formation seriously or to trap any of the intermediate diradical **x** appears to be strong evidence against a radical mechanism.

It is not possible to test for the presence of a dipolar intermediate **y** in the same way since any conceivable trap for a dipolar species, e.g., alcohols, would be expected to react vigorously with the silene. Intuitively, pathways involving the dipolar intermediates appear very reasonable. It is known that silenes can coordinate strongly with oxygen—e.g., the Wiberg silene–THF complex.[16] Also, the intermediate **y** (Scheme II) can be stabilized by delocalization of the negative charge on silicon into the attached trimethylsilyl groups (but probably not onto the adjacent carbon because of the attached electronegative oxygen). Furthermore, when aryl groups are attached either to the silene carbon or to the carbonyl group of the ketone, charge delocalization into the aromatic ring can account for the formation of the various [2 + 4] cycloaddition products observed. We are actively attempting to find definitive

Table V. Final Positional Parameters for Compound 16

atom	x	y	z
Si(1)	0.1313 (5)	0.1199 (4)	0.8266 (2)
O(1)	0.0175 (8)	0.0042 (7)	0.8307 (3)
C(1)	−0.106 (1)	−0.014 (1)	0.8576 (5)
C(2)	−0.128 (1)	−0.126 (1)	0.8803 (5)
C(3)	−0.027 (1)	−0.233 (1)	0.8833 (5)
C(4)	0.106 (1)	−0.247 (1)	0.8666 (6)
C(5)	0.175 (1)	−0.361 (1)	0.8774 (6)
C(6)	0.110 (1)	−0.451 (1)	0.9064 (6)
C(7)	−0.020 (2)	−0.440 (1)	0.9224 (7)
C(8)	−0.094 (1)	−0.327 (1)	0.9139 (5)
C(9)	−0.230 (1)	−0.289 (1)	0.9252 (6)
C(10)	−0.337 (1)	−0.349 (1)	0.9544 (6)
C(11)	−0.458 (2)	−0.294 (1)	0.9619 (7)
C(12)	−0.489 (2)	−0.175 (1)	0.9420 (7)
C(13)	−0.385 (1)	−0.109 (1)	0.9130 (7)
C(14)	−0.258 (1)	−0.165 (1)	0.9059 (5)
C(15)	−0.201 (1)	0.094 (1)	0.8551 (5)
C(16)	−0.294 (1)	0.127 (1)	0.8003 (5)
C(17)	−0.381 (1)	0.227 (1)	0.7982 (5)
C(18)	−0.388 (1)	0.297 (1)	0.8478 (6)
C(19)	−0.305 (1)	0.266 (1)	0.9023 (6)
C(20)	−0.214 (1)	0.165 (1)	0.9063 (5)
C(21)	−0.288 (1)	0.048 (1)	0.7448 (7)
C(22)	−0.490 (2)	0.407 (1)	0.8455 (7)
C(23)	−0.130 (1)	0.135 (1)	0.9685 (6)
C(24)	0.206 (2)	0.170 (2)	0.9023 (8)
C(25)	0.273 (2)	0.051 (1)	0.7889 (7)
C(26)	0.049 (2)	0.246 (2)	0.7844 (9)

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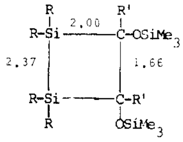
(15) Bachrach, S. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 1186.

(16) Wiberg, N.; Wagner, G.; Muller, G.; Riede, J. *J. Organomet. Chem.* **1984**, *271*, 381.

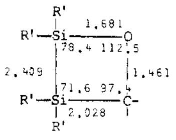
evidence about these reactions and until this is complete will defer further discussion of the mechanistic aspects of these reactions. However, it is now quite clear that relatively stable siloxetanes can be formed and isolated and that they display a remarkable variety of molecular rearrangements.

Siloxetane Crystal Structure. The crystal structure of the siloxetane **1f** showed the four-membered ring to be nonplanar with abnormally long bonds. Thus the observed bond lengths (in Å) in the ring (with standard bond lengths to four-coordinate Si in parentheses) were Si–O = 1.696 (6) [1.610 (4)[17]], Si–C(1) = 1.963 (10) [1.872 (1)[17]], C(1)–C(2) = 1.673 (12) [1.54], and O–C(2) = 1.438 (12) [1.41]. Bond lengths in related disilacyclobutane and disiloxetane structures are also often longer than standard values although it is notable that the present C(1)–C(2) bond is one of the longest C–C bonds ever observed, being longer than that found in the disilacyclobutane A[18,19] (see below). However the present Si–C bond length is slightly shorter than the bond in A (2.00 Å) or in the disiloxetane B[8] mentioned above (2.028 (4) Å), while the present Si–O and C–O bond lengths are comparable to those observed for B.

These siloxetane bond lengths are very long compared to the calculated values of Streitwieser.[15] This clearly reflects the presence of significant strain in the molecule due to steric crowding, consistent with the tendency of the siloxetanes to rearrange under mild conditions as described above. Some of this crowding has been reduced by folding the ring by 20.1° about the Si(1)–C(2) axis. This fold angle is comparable to the fold angle (17.9°) in the 1,3-disilacyclobutane C.[20] In **1f** this has the effect of forcing the trimethylsilyl group $Me_3Si(2)$ and phenyl ring (22) toward "equatorial" positions on the ring and away from the adamantyl group while forcing the groups $Me_3Si(3)$ and the phenyl ring (21) together on the opposite side of the siloxetane ring. This results in large differences between the Si(3,4)–Si(1)–O(1),C(1) bond angles (up to 25.8°) and differences up to 14.8° between the C(211,221)–C(2)–O(1),C(1) angles (Table III), with the smaller angles involving the oxygen. [The differences at C(1) are somewhat smaller.] Furthermore, steric interactions involving the $OSiMe_3$ group are somewhat reduced as the Si(4)–O(2)–C(1) angle [148.2 (6)°] is significantly enlarged over comparable COSi angles in the less sterically crowded compound **16** above [135.2 (6)°] and in an adamantylsilene [134.2°].[21] Notably the Si(4)–O(2) distance [1.635 (6) Å] is slightly shorter than that in **16** [1.660 (7) Å], and this is consistent with the trend of decreasing Si–O bond lengths with increasing Si–O–Si bond angles observed in several disiloxanes.[22]

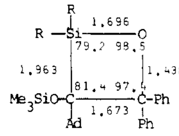


A

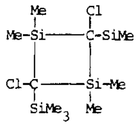


B

R = Me_3Si R' = t-Bu



1f

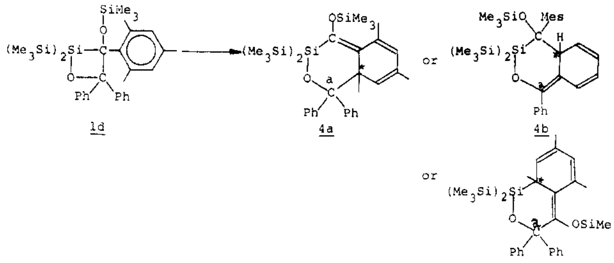


C

In the remaining Me_3Si and Ad groups evidence of the steric strain in the molecule can be seen in the substantial differences in the Si–Si–Me and C(1)–C(11)–C(Ad) angles, although the Si–$SiMe_3$ (and C(1)–Ad) distances appear normal and are somewhat shorter than those observed in A [2.43 Å]. Thus, the difference between largest and smallest angles is 12.0° (Si(2)), 14.4° (Si(3)), 6.6° (Si(4)), and 5.6° (C(11)), with the largest angles at Si(2) and Si(3) [119°] such that the interactions C(22)–Ad and C(33)–Ph(21) are reduced (Figure 1).

Structure Proofs Using NMR Spectroscopy. In the course of these studies a number of novel compounds were obtained, and many of the structure determinations depended heavily on detailed NMR studies: some of the important details are set forth below.

It is evident that the siloxetane **1d** is the immediate precursor of the rearrangement product assigned the [4.4.0] bicyclic structure **4**. Three structures had to be seriously considered for this product, depending on (a) whether it was the mesityl or a phenyl group that was involved in a 1,3-sigmatropic ring expansion process yielding **4a** or **4b** or (b) whether the siloxetane cleaved instead at the silicon–carbon bond and expanded into the mesityl group to yield **4c**. Structure **4b** could be immediately eliminated since the actual compound showed three nonequivalent CH_3 groups (one at 33.75 ppm attached to a quaternary sp^3-hybridized carbon atom) and only two vinylic CH groups together with six aromatic CH groups (APT):[23] **4b** would have shown only two CH_3 signals (2:1 ratio) at 20–26 ppm and four vinylic CH groups. In addition the sp^3-hybridized carbon marked with an asterisk at 46.65 ppm was shown by a ^{13}C APT experiment to be quaternary, again eliminating structure **4b**.



Structure **4c** was eliminated by a coupled ^{13}C experiment. The carbon atom labeled a (86.39 ppm) showed strong (three-bond) coupling to the protons (^1H, 2.31 ppm) of the CH_3 group (^{13}C, 33.75 ppm) (related by a 2-D ^1H–^{13}C experiment) attached to C* (46.65 ppm): this coupling could be removed by irradiating at the proton frequency during the ^{13}C spectrum, causing the complex multiplet of C_a to collapse considerably. Hence C_a must be three bonds removed from the methyl protons, consistent with structure **4a** but not **4c**.

The structure of the [2 + 4] cycloaddition product of silene **3a** with benzophenone was more difficult to assign.

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(17) Klebe, G. *J. Organomet. Chem.* **1985**, *293*, 147.

(18) 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.

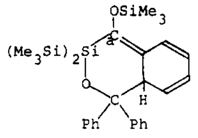
(19) Acyclic bond lengths up to 1.671 Å [for $(p\text{-}FC_6H_4)(CF_3)_2CC(CF_3)_2(p\text{-}FC_6H_4)$] have been observed. See: Kanagasabapathy, V. M.; Sawyer, J. F.; Tidwell, T. T. *J. Org. Chem.* **1985**, *50*, 503.

(20) Fritz, G.; Thomas, J.; Peters, K.; Peters, E.-M.; v. Schauring, H. G. *Z. Anorg. Allg. Chemie* **1984**, *514*, 61.

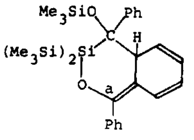
(21) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *J. Amer. Chem. Soc.* **1982**, *104*, 5667. Nyburg, S. C.; Brook, A. G.; Abdesaken, F.; Gutekunst, G.; Wong-Ng, W. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 1632.

(22) Karle, I. L.; Karle, J. M.; Nielsen, C. J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 64.

Two possibilities had to be considered, depending on whether the 4π component came from the silene, giving **7a**, or the ketone, giving **18**. A 2-D ^1H–^{13}C experiment using shift correlations allowed assignment of specific protons being bonded to specific carbon atoms, as well as the assignment of which protons were three-bond-coupled to specific neighboring carbon atoms. Thus the entire carbon skeleton could be assembled and was found to be that of structure **7a**. This assignment was confirmed by observing changes in the ^1H-coupled ^{13}C spectrum. Carbon C_a resonated at 155.36 ppm (sp^2): irradiation at the frequency of the protons of the Me_3SiO group should affect C_a (by four-bond coupling) in structure **7a** but should not affect C_a in structure **18**. In the experiment the multiplet of C_a collapsed when irradiated at the proton frequency, consistent with structure **7a**.



7a



18

The structure **8a** was confirmed by ^1H and ^{13}C experiments. The proton spectrum of this red conjugated aryl triene showed three vinyl hydrogens and one sp^3-type CH at 4.32 ppm (in addition to four aromatic sp^2-type CH groups). The ^{13}C spectrum (APT) indicated seven sp^2-type CH groups and five sp^2-quaternary carbon atoms. 2-D NMR spectra showed that the aliphatic proton was attached to an sp^3-type carbon atom at 45.04 ppm, consistent with the assigned structure. The structure of **10a** was also assigned on the basis of NMR experiments; in particular a 2-D ^1H–^{13}C experiment was necessary to unambiguously assign the locations of the chemical shifts of the CH_2 AB system. It is planned to present full details of these complex NMR experiments in a separate publication.

Experimental Section

All NMR were run either on a Varian XL400 spectrometer or a Varian XL200 spectrometer operating at 399.941 or 200.057 MHz, respectively, for ^1H, at 100.570 or 50.309 MHz, respectively, for ^{13}C, and 79.459 MHz or 39.746 MHz, respectively, for ^{29}Si. FTIR spectra were run on a Nicolet analytical instrument 5DX.

All NMR spectra were run in C_6D_6 unless otherwise noted, locked on deuterium, and referenced at 7.15 ppm for ^1H NMR spectra (residual C_6D_5H), 128.00 ppm for ^{13}C NMR spectra, and 0.00 ppm (external Me_4Si) for ^{29}Si NMR spectra, all relative to Me_4Si. Many reactions were followed by NMR spectroscopy in order to ascertain their completion or the proportion of products. IR spectra were run in Nujol with at least 15 Fourier scans (subtracting background signals).

Where appropriate, APT[23] or DEPT[24] pulse sequences were used for ^{13}C spectra. All ^{29}Si spectra were run in the DEPT[24] mode or, in special cases, coupled INEPT.[25] 2-D NMR (^{13}C–^1H) experiments were run by using conditions to provide chemical shift correlations via either direct or long-range C–H couplings, to allow unambiguous assignment of all important signals (some aromatic sp^2 quaternary or CH signals could not be assigned unambiguously).

Abbreviations used: b = broad multiplet; q-C = quaternary carbon; Mes = mesityl (2,4,6-trimethylphenyl); Ad = 1-adamantyl; Fl = fluorenyl nucleus; p = para position (assigned by comparing intensities of aromatic carbons).

Due to the instability of the siloxetanes and many of the bicyclo [4.4.0] compounds, elemental analyses or high-resolution mass spectra data were unobtainable. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Siloxetane Formations and Thermolyses. Formations. Method A. In a typical procedure, into a clean, dry 5-mm NMR tube, fitted with a screw cap, were placed equimolar amounts of the acylsilane and the ketone (typically approximately 100 mg of acylsilane and 50 mg of ketone). The system was then evacuated in a Schlenk tube and flushed with argon. Approximately 0.3 mL of C_6D_6 (dried over $LiAlH_4$ and distilled) was added to the NMR tube, and the screw cap was sealed under the argon atmosphere.

The solution in the NMR tube was photolyzed inside a water-cooled Dewar flask maintained at 10 °C, using three external 100-W PAR38 mercury spot lamps (BLAK RAY long wavelength ultraviolet lamps, Ultraviolet Products Inc.).

Method B. The apparatuses and procedures were the same as those for method A, except that only the acylsilane in C_6D_6 was photolyzed to yield the corresponding silene, to which was added a C_6D_6 solution of the relevant ketone under argon. The system was kept in the dark at ambient temperatures until the reaction was complete.

Thermolyses. Method C. The siloxetane was placed in a Schlenk tube with 5 mL of toluene and refluxed under argon for 2 h. The toluene was then removed under vacuum to leave quantitative yields of the thermolysis products.

Method D. The siloxetane prepared by method A or B was heated in its sealed NMR tube to 75 °C for the required length of time. The NMR tube (Wilmad 507-PP) survived the internal pressure of C_6D_6 at this temperature for days and even weeks.

Preparation of 1a. Benzoyltris(trimethylsilyl)silane (**2a**) and benzophenone were photolyzed for 24 h (method A) to give >95% **1a**. Since the silene dimerized rapidly, it was impossible to form **1a** by using method B: ^1H NMR δ −0.23, 0.18, 0.38 (each 9 H, s, Me_3Si), 6.79–8.07 (15 H, b); ^{13}C NMR δ −0.16, 0.08, 1.54 (each Me_3Si), 97.43, 99.77 (q-C sp^3 ring C), 126.50 (p), 127.01, 127.10 (p), 127.17, 127.42, 127.48 (p), 128.53, 129.73, 132.72 (C–H sp^2), 142.94, 143.57, 146.78 (q-C sp^2); ^{29}Si NMR δ −17.35, −17.02 (each Me_3Si), 12.29 (Me_3SiO), 55.32 (ring Si).

Photolysis of the above mixture for only 3 h gave **7a** (see below).

Preparation of 1b. The acylsilane **2a** and an equimolar amount of 9-fluorenone were photolyzed for 24 h under method A reaction conditions to yield >95% **1b**: ^1H NMR δ −0.44, 0.34, 0.53 (each 9 H, s, Me_3Si), 6.8–8.3 (13 H, b); ^{13}C NMR δ 0.19, 0.23, 1.66 (each Me_3Si), 96.34, 103.34 (q-C sp^3 ring C), 119.72, 119.94, 126.47, 126.92, 127.08, 127.68, 127.76, 127.82, 128.53, 129.20, 129.82 (C–H sp^2), 139.11, 139.87, 141.64, 147.89, 149.72 (q-C sp^2); ^{29}Si NMR δ −19.19, −16.53 (each Me_3Si), 13.24 (Me_3SiO), 65.98 (ring Si).

Photolysis of the above mixture for only 3 h gave **7b** (see below).

Preparation of 1c. Equimolar amounts of **2a** and 4,4′-dimethylbenzophenone were co-photolyzed for 24 h (method A) and gave >90% **1c** with a trace of **8c**: ^1H NMR δ 0.04, 0.21, 0.35 (each 9 H, s, Me_3Si), 1.99, 2.16 (each 3 H, s, Me-Ph), 6.8–8.1 (13 H, b); ^{13}C NMR δ −0.15, 1.20, 1.80 (each Me_3Si), 21.04, 21.55 (each Me-Ph), 97.35, 99.90 (q-C sp^3 ring C), 127.41, 127.84, 127.88, 128.09, 128.44, 128.69, 129.37 (C–H sp^2), 139.42, 139.46, 139.96, 143.09, 144.23 (q-C sp^2); ^{29}Si NMR δ −17.05, −16.30 (each Me_3Si), 11.94 (Me_3SiO), 54.68 (ring Si).

Photolysis of the above mixture for only 3 h gave **7c** (see below), while extended photolysis of **1c** for 24 h gave **8c** (see below).

4,4-Diphenyl-2,2-bis(trimethylsilyl)-3-mesityl-3-(trimethylsiloxy)-2-siloxetane (1d). A solution of 110 mg (0.28 mmol) of mesitoyltris(trimethylsilyl)silane (**2b**) and 51 mg (0.28 mmol) of benzophenone were allowed to react (method A) for 4 h to yield **1d** (>98%). The siloxetane **1d** was also formed by using method B (200 mg (0.51 mmol) of the acylsilane and 95 mg (0.52 mmol) of benzophenone): ^1H NMR δ −0.27, −0.06, 0.46 (each 9 H, s, Me_3Si), 2.03, 2.09, 2.32 (each 3 H, s, CH_3-Mes) 6.6–8.0 (12 H, b); ^{13}C NMR δ 0.33, 0.71, 2.72 (each Me_3Si), 20.76, 21.80, 26.14 (each CH_3-Mes), 98.31, 100.43 (q-C sp^3, ring C), 126.09, 127.09, 127.32, 127.35, 129.97, 130.37, 131.04, 132.84 (C–H sp^2), 137.83, 137.95, 138.13, 139.36, 145.61, 146.37 (q-C sp^2); ^{29}Si NMR δ −16.63, −15.82 (each Me_3Si), 9.41 (Me_3SiO), 42.30 (ring Si).

Isomerization of 1d to 4. The siloxetane **1d**, left in the dark at ambient temperatures in C_6D_6 solution in the sealed NMR tube for 12–24 h, rearranged to a 1.8:1 mixture of **4** and **1d**, after which

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

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

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

no further change occurred. The mixture of **4** and **1d** was completely reconverted to **1d** by photolysis for 3 h (method A). **4**: ^{1}H NMR δ -0.11, 0.20, 0.50 (each 9 H, s, Me$_3$Si), 1.39, 1.60, 2.33 (each 3 H, s, CH$_3$-Mes), 5.4–5.6 (2 H, b, sp^2 C–H Mes), 7.0–8.1 (10 H, b, Ph); ^{13}C NMR δ -0.58, 0.87, 1.40 (each Me$_3$Si), 21.73, 24.77, 33.75 (each CH$_3$-Mes), 46.65 (q-C sp^3-CH$_3$), 86.39 (q-C sp^3 *C*Ph$_2$), 126.75, 126.84, 127.39, 127.55, 127.99, 129.78, 130.07, 130.27 (C–H sp^2), 127.02, 133.51, 142.38, 146.44, 149.07, 158.22 (q-C sp^2); ^{29}Si NMR δ -16.98, -16.03 (each Me$_3$Si), -5.25 (ring Si), 18.14 (Me$_3$SiO).

Compound **4** was separated from **1d** on a 2-mm silica gel plate with a 80:20 dichloromethane/hexane solvent system. The solvent was then removed, and C$_6$D$_6$ was added to the system. The sample was then allowed to sit at ambient temperatures for 12 h after which the identical 1.8:1 mixture of **4**/**1d** was found to be present.

Preparation of 1e. A solution of pivaloyltris(trimethylsilyl)silane (**2c**) was photolyzed for 24 h (method B), and then an equimolar amount of benzophenone was allowed to react with the silene for 72 h to yield >90% **1e**: ^{1}H NMR δ 0.02, 0.23, 0.36 (each 9 H, s, Me$_3$Si), 0.96–1.14 (9 H, b, *tert*-butyl, restricted rotation), 6.8–8.2 (10 H, b); ^{13}C NMR δ 0.75, 1.60, 3.48 (each Me$_3$Si), 39.66 (Me$_3$*C*), 24.94, 29.85, 46.64 (each (*C*H$_3$)$_3$C), 96.96, 103.83 (q-C sp^3 ring C), 126.02, 126.69, 127.51, 128.31, 128.56, 130.17 (C–H sp^2), 148.07, 148.77 (q-C sp^2); ^{29}Si NMR δ -17.55, -17.22 (each Me$_3$Si), 6.65 (Me$_3$SiO), 50.22 (ring Si).

Preparation of 1f. A solution of 110 mg (0.27 mmol) of **2d** was photolyzed for 28 h (method B) and then allowed to react with 47 mg (0.26 mmol) of benzophenone for 72 h to yield >90% **1f**: mp 137–139 °C; ^{1}H NMR δ 0.07, 0.26, 0.44 (each 9 H, s, Me$_3$Si), 1.5–2.2 (15 H, b, Ad), 6.8–8.2 (10 H, b); ^{13}C NMR δ 0.93, 1.99, 4.31 (each Me$_3$Si), 28.41, 29.04, 29.51, 29.97, 37.02, 37.07, 37.21, 41.19, 42.15, 43.34, 46.28 (Ad), 97.61, 107.61 (q-C sp^3 ring C), 126.10, 126.61, 127.58, 128.44, 129.34, 130.17 (C–H sp^2), 147.76, 148.75 (q-C sp^2); ^{29}Si NMR δ -16.63, -15.55 (each Me$_3$Si), 6.76 (Me$_3$SiO), 51.25 (ring Si); IR 1105.3 (Si–O), 1244.1, 839.8, 711.5 cm^{-1} (Me$_3$Si). Anal. Calcd for C$_{33}$H$_{52}$O$_2$Si$_4$: C, 66.83; H, 8.84. Found: C, 67.19; H, 8.86.

Preparation of 1g. Photolysis of **2b** and 9-fluorenone for 5 h (method A) yielded >99% **1g**, after recrystallization from cold pentanes: mp 164.5 °C; ^{1}H NMR δ 0.15, 0.35, 0.58 (each 9 H, s, Me$_3$Si), 1.25, 1.95, 2.35 (each 3 H, s, CH$_3$-Mes), 6.4–8.0 (10 H, b); ^{13}C NMR δ 0.43, 0.76, 2.71 (each Me$_3$Si), 20.66, 21.43, 21.71 (each CH$_3$-Mes), 95.44, 101.57 (q-C sp^3 ring C), 119.31, 119.73, 125.75, 126.58, 127.43, 128.96, 129.07, 129.18, 130.17, 130.62 (C–H sp^2), 136.60, 137.32, 137.64, 139.52, 140.71, 141.05, 147.70, 149.07 (q-C sp^2); ^{29}Si NMR δ -16.08, -15.98 (each Me$_3$Si), 10.48 (Me$_3$SiO), 52.93 (ring Si); MS, M$^+$ 574 (1%), (M – [(Me$_3$Si)$_2$Si=O])$^+$ 384 (12%); IR 1063.7 (Si–O), 1247.8, 839.30, 742.33 cm^{-1} (Me$_3$Si). Anal. Calcd for C$_{32}$H$_{46}$O$_2$Si$_4$: C, 66.84; H, 8.06. Found: C, 66.59; H, 7.82.

Preparation of 1h. Equimolar amounts of **2b** and benzaldehyde were photolyzed (method A) for 4 h to yield >99% **1h** (two isomers, 1:1 mixture): ^{1}H NMR δ 0.07, 0.45, 0.49, 0.64, 0.92, 0.94 (each 9 H, s, Me$_3$Si), 2.04, 2.45, 2.51, 2.71, 2.77, 2.87 (each 3 H, s, CH$_3$-Mes), 6.16, 6.45 (each 1 H, s, C–H sp^3), 7.1–8.3 (10 H, b); ^{13}C NMR δ -1.22, -0.24, -0.03, 0.41, 1.66, 2.89 (each Me$_3$Si), 20.73, 20.85, 21.14, 21.80, 23.64, 25.10 (each CH$_3$-Mes), 91.04, 100.54 (C–H sp^3 ring C), 91.474 (2C acc. overlap, q-C sp^3), 127.26, 127.55, 127.75, 127.88, 128.52, 129.00, 129.91, 130.63, 131.26, 131.35 (C–H sp^2), 133.90, 136.18, 136.87, 137.25, 137.51, 138.39, 138.98, 139.23, 141.91, 143.83 (q-C sp^2); ^{29}Si NMR δ -17.84, -16.76, -16.21 (2 Si acc. overlap) (each Me$_3$Si), 12.81, 9.62 (each Me$_3$SiO), 54.36, 54.31 (each ring Si).

Preparation of 1i. An equimolar amount of **2b** and pivaldehyde were co-photolyzed for 24 h (method A) to yield a 2:1 mixture of **13i**/**1i**. Thermolysis of this mixture at 70 °C (method D) for 24 h yielded a 4:1 mixture of **13i**/**1i**. **1i**: ^{1}H NMR δ -0.10, -0.05, 0.37 (each 9 H, s, Me$_3$Si), 1.39 (9 H, s, (C*H*$_3$)$_3$C), 2.04, 2.23, 2.38 (each 3 H, s, CH$_3$-Mes), 5.41 (1 H, s, C–H ring), 6.75 (2 H, b); ^{13}C NMR δ -1.44, -0.31, 3.08 (each Me$_3$Si), 20.69, 21.78, 24.44 (each CH$_3$-Mes), 28.42 ((*C*H$_3$)$_3$C), 46.04 ((CH$_3$)$_3$*C*), 90.35 (q-C sp^3 ring C), 94.72 (sp^3 ring C–H), 130.44, 131.78 (C–H sp^2), 135.45, 136.78, 137.31, 140.34 (q-C sp^2); ^{29}Si NMR δ -17.90, -16.86 (each Me$_3$Si), 10.38 (Me$_3$SiO), 51.93 (ring Si). **13i**: ^{1}H NMR δ 0.17 (9 H, s, Me$_3$SiO), 0.24 (18 H, s, Me$_3$Si), 1.03 (9 H, s, (C*H*$_3$)$_3$C), 2.14 (3 H, s, *p*-CH$_3$-Mes), 2.32 (6 H, s, *o*-CH$_3$-Mes), 5.59 (1 H, b), 6.79 (2 H, b, Mes); ^{13}C NMR δ -1.20 (Me$_3$Si), 2.34 (Me$_3$SiO), 21.14 (*p*-CH$_3$-Mes), 21.90 (*o*-CH$_3$-Mes), 28.85 ((*C*H$_3$)$_3$C), 38.29 ((CH$_3$)$_3$*C*), 102.66 (C–H sp^2), 128.20 (C–H sp^2-Mes), 134.23, 135.59, 136.77 (q-C sp^2), 159.09 (=COSi); ^{29}Si NMR δ -22.16 (Me$_3$Si), -7.23 (central Si), 8.39 (Me$_3$SiO).

Preparation of 1j. Equimolar amounts of **2c** and benzaldehyde were photolyzed (method A) for 24 h to yield >95% **1j** (two isomers, 85:15 ratio, not separable). **1j** (major isomer): ^{1}H NMR δ 0.27 (18 H, s, acc. overlap Me$_3$Si), 0.35 (9 H, s, Me$_3$SiO), 0.91 (9 H, s, Me$_3$C), 6.14 (1 H, s, ring C–H), 6.95–7.7 (5 H, b); ^{13}C NMR δ 0.81, 0.90, 3.50 (each Me$_3$Si), 28.59 ((*C*H$_3$)$_3$C), 38.05 ((CH$_3$)$_3$*C*), 94.40 (C–H sp^3 ring), 101.58 (q-C sp^3 ring), 127.16, 127.64 (2) (C–H sp^2), 142.23 (q-C sp^2); ^{29}Si NMR δ -17.15, -16.30 (each Me$_3$Si), 8.12 (Me$_3$SiO), 53.60 (ring Si). **1j** (minor isomer): ^{1}H NMR δ -0.27, -0.11, 0.20 (each 9 H, s, Me$_3$Si), 1.08 (9 H, s, Me$_3$C), 5.85 (1 H, s, C–H ring), 6.95–7.70 (5 H, b); ^{13}C NMR δ 0.33, 0.56, 3.63 (each Me$_3$Si), 28.66 ((*C*H$_3$)$_3$C), 37.25 ((CH$_3$)$_3$*C*), 88.75 (C–H sp^3 ring C), 101.47 (q-C sp^3 ring C), 127.28, 127.81 (2) (C–H sp^2), 142.25 (q-C sp^2); ^{29}Si NMR δ -17.44, -17.15 (each Me$_3$Si), 6.59 (Me$_3$SiO), 58.17 (ring Si).

Preparation of 1k. The acylsilane **2c** and pivaldehyde were photolyzed (method A) for 24 h to yield >95% **1k** (two isomers, 2.3:1 mixture not separated). **1k** (major isomer): ^{1}H NMR δ 0.22, 0.23, 0.37 (each 9 H, s, Me$_3$Si), 1.17, 1.22 (each 9 H, s, (*C*H$_3$)$_3$C), 4.59 (1 H, s); ^{13}C NMR δ 1.38, 1.80, 3.54 (each Me$_3$Si), 27.80, 28.93 (each (*C*H$_3$)$_3$C), 37.42, 37.75 (each (CH$_3$)$_3$*C*), 101.46 (C–H sp^3 ring), 104.25 (q-C sp^3 ring); ^{29}Si NMR δ -17.42, -16.39 (each Me$_3$Si), 5.97 (Me$_3$SiO), 44.22 (ring Si). **1k** (minor isomer): ^{1}H NMR δ 0.18, 0.21, 0.23 (each 9 H, s, Me$_3$Si), 1.18, 1.24 (each 9 H, s, (C*H*$_3$)$_3$C), 4.85 (1 H, s); ^{13}C NMR δ 1.57, 1.87, 4.01 (each Me$_3$Si), 23.73, 28.93 (each (*C*H$_3$)$_3$C), 37.17, 38.27 (each (CH$_3$)$_3$*C*), 96.78 (C–H sp^3 ring), 100.24 (q-C sp^3 ring); ^{29}Si NMR δ -18.11, -17.50 (each Me$_3$Si), 6.18 (Me$_3$SiO), 56.98 (ring Si).

Preparation of 1l. Photolysis (method A) of **2d** and pivaldehyde gave >99% **1l** (two isomers, 3:1 mixture). **1l** (major isomer): ^{1}H NMR δ 0.265, 0.273, 0.35 (each 9 H, s, Me$_3$Si), 1.18 (9 H, s, (C*H*$_3$)$_3$C), 1.66–2.00 (15 H, b, Ad), 4.61 (1 H, s, ring CH); ^{13}C NMR δ 1.25, 1.64, 3.83 (each Me$_3$Si), 29.02 (CH Ad), 29.44 ((*C*H$_3$)$_3$C), 37.12 (CH$_2$ Ad), 39.81 (q-C Ad), 39.93 ((CH$_3$)$_3$*C*), 104.92 (ring C–H), 107.65 (ring q-C); ^{29}Si NMR δ -17.93, -17.19 (each Me$_3$Si), 5.59 (Me$_3$SiO), 47.13 (ring Si). **1l** (minor isomer): ^{1}H NMR δ 0.22, 0.29, 0.34 (each 9 H, s, Me$_3$Si), 1.16 (9 H, s, (C*H*$_3$)$_3$C), 1.66–2.00 (15 H, b, Ad), 4.54 (1 H, s, ring CH); ^{13}C NMR δ 1.22, 1.87, 4.39 (each Me$_3$Si), 23.46 (CH Ad), 27.64 ((*C*H$_3$)$_3$C), 37.92 (CH$_2$ Ad), 40.71 (q-C Ad), 42.37 ((CH$_3$)$_3$*C*), 94.73 (ring C–H), 102.22 (ring q-C); ^{29}Si NMR δ -18.35, -16.69 (each Me$_3$Si), 6.64 (Me$_3$SiO), 56.80 (ring Si).

Compound 7a. Benzoyltris(trimethylsilyl)silane (**2a**) (100 mg, 0.28 mmol) and 52 mg (0.28 mmol) of benzophenone (method A) were photolyzed for 2–3 h to yield **7a** containing a trace of **1a**. Further photolysis for 24 h or if left in the dark at ambient temperatures for 8 days gave >95% **1a**. **7a**: mp 93–95 °C; ^{1}H NMR δ 0.01, 0.17, 0.39 (each 9 H, s, Me$_3$Si), 4.25–5.99 (5 H, b), 6.8–8.1 (10 H, b); ^{13}C NMR δ -0.80, -0.28, 1.50 (each Me$_3$Si), 51.12 (C–H sp^3), 83.68 (q-C sp^3), 119.76, 122.65, 123.24, 127.07, 127.36, 128.30, 129.65, 130.11, 130.45, 132.02 (C–H sp^2), 133.93, 145.53, 148.17, 155.65 (q-C sp^2); ^{29}Si NMR δ -17.62, -17.10 (each Me$_3$Si), -6.32 (ring Si), 17.97 (Me$_3$SiO); IR 1076.6 (Si–O), 1252.5, 844.53, 756.83 cm^{-1} (Me$_3$Si).

Compound 7b. Equimolar amounts of **2a** and 9-fluorenone were photolyzed (method A) for 3 h to yield **7b** with a trace of **1b**: ^{1}H NMR δ 0.21, 0.26, 0.36 (each 9 H, s, Me$_3$Si), 4.24 (1 H, b, C–H sp^3), 4.9–6.8 (4 H, b, vinyl H's), 7.0–7.9 (8 H, b); ^{13}C NMR δ -0.41, -0.23, 1.31 (each Me$_3$Si), 48.19 (C–H sp^3), 85.77 (q-C sp^3), 119.69, 120.13, 120.28, 121.67, 123.07, 124.94, 125.97, 126.55, 127.56, 128.06, 128.56, 128.90 (C–H sp^2), 133.58, 140.27, 140.93, 148.15, 149.21, 157.49 (q-C sp^2); ^{29}Si NMR δ -18.34, -16.59 (each Me$_3$Si), -4.49 (ring Si), 18.89 (Me$_3$SiO).

Compound 7c. Acylsilane **2a** and 4,4′-dimethylbenzophenone were photolyzed for 3 h (method A) and gave >98% **7c**: ^{1}H NMR δ 0.01, 0.18, 0.48 (each 9 H, s, Me$_3$Si), 2.03, 2.08 (each 3 H, s, CH$_3$-Ph), 4.2 (1 H, b, sp^3), 4.9–6.7 (4 H, b, vinyl H), 6.8–8.1 (8 H, b); ^{13}C NMR δ -0.76, -0.23, 1.56 (each Me$_3$Si), 21.03, 21.46 (each CH$_3$-Ph), 51.27 (C–H sp^3), 83.49 (q-C sp^3), 119.82, 122.66, 123.12, 128.32, 128.39, 128.70, 129.04, 130.40 (C–H sp^2), 134.09, 135.89, 136.29, 136.55, 145.54, 155.47 (q-C sp^2); ^{29}Si NMR δ -17.61, -17.06 (each Me$_3$Si), -6.92 (ring Si), 17.73 (Me$_3$SiO).

Preparation of 8a. A solution of 207 mg (0.62 mmol) of pivaloyltris(trimethylsilyl)silane (**2c**) and 116 mg (0.64 mmol) of 9-fluorenone were photolyzed for 24 h (method A) to yield >95% **8a**. Compound **8a** was then photolyzed for 8 days to produce **9a** in a 1.8:1 mixture of **8a** to **9a**. **8a**: ^{1}H NMR δ −0.01, 0.15, 0.37 (each 9 H, s, Me$_3$Si), 1.14 (9 H, s, $(CH_3)_3C$), 4.32 (1 H, b, C–H sp^3), 6.1–7.8 (7 H, b); ^{13}C NMR δ −0.38, 0.39, 3.48 (each Me$_3$Si), 29.52 ($(CH_3)_3C$), 38.71 ($(CH_3)_3C$), 45.04 (C–H sp^3), 82.95 (q-C sp^3), 114.78, 116.98, 120.27, 124.94, 126.47, 127.94, 130.70 (C–H sp^2), 111.33, 133.85, 137.74, 137.91, 154.45 (q-C sp^2); ^{29}Si NMR δ −18.53, −13.44 (each Me$_3$Si), 6.62 (ring Si), 17.78 (Me$_3$SiO). **9a**: ^{1}H NMR δ −0.35, 0.30, 0.42 (each 9 H, s, Me$_3$Si), 1.18 (9 H, s, $(CH_3)_3C$), 5.69 (1 H, b, C–H sp^3), 6.1–7.7 (7 H, b); ^{13}C NMR δ −0.42, 0.60, 4.84 (each Me$_3$Si), 27.83 ($(CH_3)_3C$), 40.88 ($(CH_3)_3C$), 78.51 (C–H sp^3), 84.23 (q-C sp^3), 118.39, 120.49, 124.09, 124.37, 125.81, 127.47, 129.11 (C–H sp^2), 139.16, 139.19, 142.70, 143.66, 147.72 (q-C sp^2); ^{29}Si NMR δ −16.86, −15.63 (each Me$_3$Si), 3.49 (ring Si), 3.67 (Me$_3$SiO).

Thermolysis of 8a. Thermolysis for 24 h (method D) yielded >95% **10a**: ^{1}H NMR δ −0.19, 0.05, 0.27 (each 9 H, s, Me$_3$Si), 0.83, 1.64 (each 3 H, s, $(CH_3)_2C$), 0.43, 1.21 (2 H, AB system CH$_2$, J = 8 Hz), 5.69 (1 H, s, C–H sp^3), 6.9–8.4 (8 H, b); ^{13}C NMR δ −1.65, −1.24, 2.41 (each Me$_3$Si), 15.81 (CH$_2$ sp^3), 18.12 (q-C sp^3), 20.74, 27.81 ($(CH_3)_2C$), 36.67 (C–H sp^3), 84.28 (q-C sp^3), 120.09, 120.23, 124.85, 126.19, 127.96, 128.86, 134.25 (C–H sp^2), 138.80, 140.25, 150.59, 152.35 (q-C sp^2); ^{29}Si NMR δ −22.55, −22.30 (each Me$_3$Si), −6.58 (ring Si), 5.94 (Me$_3$SiO).

Preparation of 8b. After 24 h (method A) a solution of 292 mg (0.71 mmol) of adamantoyltris(trimethylsilyl)silane (**2d**) and 131 mg (0.73 mmol) of 9-fluorenone gave >90% **8b** with a trace of **9b** present. Compound **8b** was then photolyzed for 8 days to yield a 2:1 mixture of **8b** with **9b**. **8b**: ^{1}H NMR δ 0.03, 0.20, 0.39 (each 9 H, s, Me$_3$Si), 1.65–2.05 (15 H, b, Ad), 4.37 (1 H, b, C–H sp^3), 6.05–7.65 (7 H, b); ^{13}C NMR δ −0.05, 0.44, 3.56 (each Me$_3$Si), 29.45, 37.29, 40.96 (Ad), 44.65 (C–H sp^3), 84.44 (q-C sp^3), 114.62, 116.97, 120.20, 124.91, 126.31, 127.93, 131.57 (C–H sp^2), 111.35, 133.97, 137.75, 138.05, 154.58 (q-C sp^2); ^{29}Si NMR δ −18.31, −13.09 (each Me$_3$Si), 6.81 (ring Si), 16.52 (Me$_3$SiO). **9b**: ^{1}H NMR δ −0.33, 0.34, 0.47 (each 9 H, s, Me$_3$Si), 1.65–2.05 (15 H, b, Ad), 5.76 (1 H, b, C–H sp^3), 6.05–7.70 (7 H, b); ^{13}C NMR δ −0.25, 1.00, 5.22 (each Me$_3$Si), 28.43, 37.00, 41.12 (Ad), 78.86 (C–H sp^3), 85.61 (q-C sp^3), 118.39, 120.26, 124.11, 124.34, 127.47, 128.36, 129.11 (C–H sp^2), 139.15, 139.26, 142.88, 144.56, 147.74 (q-C sp^2); ^{29}Si NMR δ −16.36, −15.16 (each Me$_3$Si), 2.18 (ring Si), 3.67 (Me$_3$SiO).

Preparation of 8c. The siloxetane **1c** was photolyzed (method A) for 24 h or was left in the dark at 25 °C for 3 days and yielded >95% **8c** (two isomers, 3.7:1). **8c** (major isomer): ^{1}H NMR δ 0.02, 0.08, 0.26 (each 9 H, s, Me$_3$Si), 2.08 (6 H, s, acc. overlap Me-Ph), 4.8–5.5 (4 H, b), 6.8–8.0 (9 H, b); ^{13}C NMR δ −0.76, −0.57, 0.38 (each Me$_3$Si), 21.07, 21.48 (each Me-Ph), 63.34 (C–H sp^3), 84.83 (q-C sp^3), 124.80, 127.67, 127.94, 128.55, 128.83, 128.89, 130.34, 131.70 (C–H sp^2), 140.93, 142.47, 143.29, 144.81, 145.66 (q-C sp^2), 167.89 (q-C sp^2 =COSi); ^{29}Si NMR δ −19.44, −17.98 (each Me$_3$Si), −1.44 (ring Si), 19.21 (Me$_3$SiO). **8c** (minor isomer): ^{1}H NMR δ 0.03, 0.21, 0.23 (each 9 H, s, Me$_3$Si), 2.12 (6 H, s, acc. overlap Me-Ph), 4.8–5.5 (4 H, b), 6.8–8.0 (9 H, b); ^{13}C NMR δ −0.27, −0.24, 1.04 (each Me$_3$Si), 21.12, 21.13 (Me-Ph), 70.01 (C–H sp^3), 84.83 (q-C sp^3, acc. overlap with major isomer), 122.99, 125.73, 126.37, 128.39, 128.57, 128.78, 128.87, 130.86 (C–H sp^2), 135.40, 135.82, 135.92, 136.32, 137.02, 147.92 (q-C sp^2); ^{29}Si NMR δ −16.32, −15.75 (Me$_3$Si), 5.18 (ring Si), 20.23 (Me$_3$SiO).

Compound 8e. A solution of 290 mg (0.87 mmol) of **2c** was photolyzed for 24 h to generate the silene **3c**. To this silene was added 160 mg (0.88 mmol) of benzophenone, and after 1 h >94% of **8e** was found to be present (two isomers, 2.1:1 ratio not separated) with a trace of **1e**. **8e** (major isomer): ^{1}H NMR δ 0.30, 0.38, 0.40 (each 9 H, s, Me$_3$Si), 1.21 (9 H, s, $(CH_3)_3C$), 4.48 (C–H sp^3), 5.58–6.54 (4 H, b), 7.1–7.8 (5 H, b); ^{13}C NMR δ 0.08, 2.92, 4.36 (each Me$_3$Si), 29.85 ($(CH_3)_3C$), 38.65 ($(CH_3)_3C$), 46.59 (C–H sp^3), 84.21 (q-C sp^3), 118.32, 125.43, 127.00, 128.04, 128.99, 129.30, 129.99 (C–H sp^2), 112.08, 138.49, 152.66 (q-C sp^2); ^{29}Si NMR δ −18.95, −15.14 (Me$_3$Si), 6.46 (ring Si), 10.99 (Me$_3$SiO). **8e** (minor isomer): ^{1}H NMR δ 0.35, 0.41, 0.45 (each 9 H, s, Me$_3$Si), 1.29 (9 H, s $(CH_3)_3C$), 4.35 (1 H, b), 5.37–6.7 (4 H, b), 7.08–8.05 (5 H, b); ^{13}C NMR δ 0.41, 1.64, 4.29 (each Me$_3$Si), 29.64 ($(CH_3)_3C$), 39.55 ($(CH_3)_3C$), 48.80 (C–H sp^3), 86.72 (q-C sp^3), 120.14, 123.93, 126.03, 126.71, 127.50, 128.12, 128.59 (C–H sp^2), 113.32, 138.18, 152.46 (q-C sp^2); ^{29}Si NMR δ −16.66, −16.23 (Me$_3$Si), 4.69 (ring Si), 13.38 (Me$_3$SiO).

Compound 8f. A solution of 110 mg (0.27 mmol) of **2d** was photolyzed for 24 h (method A) and then allowed to react with 47 mg (0.26 mmol) of benzophenone for 1 h to yield >95% **8f** with a trace of **1f** present. **8f**: ^{1}H NMR δ 0.31, 0.36, 0.37 (each 9 H, s, Me$_3$Si), 1.61–2.05 (15 H, b, Ad), 4.2 (C–H sp^3), 7.08–7.71 (9 H, b); ^{13}C NMR δ 0.49, 0.59, 4.46 (each Me$_3$Si), 29.46, 37.30, 41.14, 51.76 (Ad), 46.21 (C–H sp^3), 85.59 (q-C sp^3), 118.52, 125.21, 128.34, 130.13, 130.16, 132.16, 132.19 (C–H sp^2), 112.05, 138.08, 152.63 (q-C sp^2); ^{29}Si NMR δ −18.59, −14.81 (Me$_3$Si), 6.45 (ring Si), 9.31 (Me$_3$SiO).

Extended photolysis (method A) of this compound or sitting in the dark for 3 days yielded siloxetane **1f**.

Thermolysis of 1a. The siloxetane **1a** was thermolyzed following method C or by method D in 24 h to produce the Märkl compound **13a**.[2] This was then converted to **14a** with MeLi/THF followed by H$_3$O$^+$ workup. **13a**: mp 90 °C (lit.[2] mp 92–93 °C); ^{1}H NMR δ −0.07 (18 H, s, Me$_3$Si), 0.05 (9 H, s, Me$_3$SiO), 6.92–7.92 (15 H, b); ^{13}C NMR δ −1.53 (Me$_3$Si), 2.37 (Me$_3$SiO), 127.98, 128.07, 128.32, 128.39, 130.17, 130.64, 131.02, 131.63, 132.05 (C–H sp^2), 124.30, 139.13, 141.81, 142.32, 149.08 (q-C sp^2); ^{29}Si NMR δ −21.79 (Me$_3$Si), −3.88 (central Si), 7.53 (Me$_3$SiO). **14a**: mp 134–135 °C (lit.[26] mp 135–136 °C); ^{1}H NMR δ 5.86 (1 H, s, C–H sp^3), 6.94–8.00 (15 H, b); ^{13}C NMR δ 59.88 (C–H sp^3), 127.49, 128.91, 129.10, 129.37, 129.83, 132.96 (C–H sp^2), 137.48, 140.08 (q-C sp^2), 197.49 (C=O).

Thermolysis of 1b. Thermolysis of **1b** (method C or method D (24 h)) yielded **11**,[2] which was then treated with MeLi/THF, followed by H$_3$O$^+$, to produce **12**.[2] **11**: mp 90 °C (lit.[2] mp 90–91 °C); ^{1}H NMR δ −0.27 (18 H, s, Me$_3$Si), 0.28 (9 H, s, Me$_3$SiO), 6.5–8.0 (13 H, b); ^{13}C NMR δ 1.40 (Me$_3$Si), 2.73 (Me$_3$SiO), 123.02, 123.30, 125.02, 125.46, 126.65, 126.96, 127.14, 127.22, 127.56, 128.96, 132.35 (C–H sp^2), 131.90, 133.68, 137.86, 148.33, 149.61, 150.12, 154.35 (q-C sp^2); ^{29}Si NMR δ −21.73 (Me$_3$Si), 0.16 (central Si), 8.15 (Me$_3$SiO); IR 1052.9 (Si–O), 1252.9, 840, 750 cm^{-1} (Me$_3$Si). **12**: mp 138 °C (lit.[27] mp 142–143 °C); ^{1}H NMR δ 5.33 (1 H, b, OH), 7.1–8.7 (13 H, b); ^{13}C NMR δ 122.91, 123.06, 123.64, 124.88, 125.74, 126.89, 127.12, 127.49, 128.49, 129.84, 131.60 (C–H sp^2), 117.66, 125.66 (2 C), 127.00, 133.05, 134.99, 146.60 (q-C sp^2).

Thermolysis of 1c. Thermolysis (method C) of **1c** gave **13c**, which was then converted to **14c** with MeLi/THF, followed by H$_3$O$^+$ workup. Compound **13c** was also prepared by using the dimer of **3a** and 4,4′-dimethylbenzophenone (method C), the conditions used by Märkl.[2] **13c**: ^{1}H NMR δ 0.09 (18 H, s, Me$_3$Si), 0.14 (9 H, s, Me$_3$SiO), 2.01, 2.06 (each 3 H, s, CH$_3$-Ph), 6.7–7.8 (13 H, b); ^{13}C NMR δ −1.51 (Me$_3$Si), 2.34 (Me$_3$SiO), 21.08, 21.14 (each CH$_3$-Ph), 128.10, 128.74, 129.10, 130.44 (p), 130.68, 131.05, 131.70 (C–H sp^2), 125.95, 135.65, 136.40, 137.56, 139.15, 142.82, 148.99 (q-C sp^2); ^{29}Si NMR δ −21.87 (Me$_3$Si), −4.20 (central Si), 7.36 (Me$_3$SiO). **14c**: mp 67 °C (lit.[28] mp 67.5–68.5 °C); ^{1}H NMR δ 1.91, 2.03 (each 3 H, s, CH$_3$-Ph), 5.92 (1 H, s, C–H sp^3), 6.80–7.95 (13 H, b); ^{13}C NMR δ 20.92, 21.25 (each CH$_3$-Ph), 59.26 (C–H sp^3), 127.05, 128.77, 129.35, 129.41, 129.54, 129.61, 129.68 (C–H sp^2), 135.13, 136.56, 137.04, 140.33, 143.37 (q-C sp^2), 197.25 (C=O).

Thermolysis of 1d and 4. A 1:1.8 mixture of **1d** and **4** was thermolyzed (method D) for 48 h to yield >95% **13d**: ^{1}H NMR δ 0.09 (9 H, s, Me$_3$SiO), 0.12 (18 H, s, Me$_3$Si), 2.06 (3 H, s, *p*-CH$_3$-Mes), 2.21 (6 H, s, *o*-CH$_3$-Mes), 6.6–7.8 (12 H, b); ^{13}C NMR δ −1.40 (Me$_3$Si), 2.37 (Me$_3$SiO), 20.79 (*o*-CH$_3$-Mes), 21.11 (*p*-CH$_3$-Mes), 127.59, 127.86, 128.12, 128.31, 128.78, 129.22, 129.86 (C–H sp^2) 120.65, 136.28, 137.54, 137.68, 139.64, 139.87, 148.30 (q-C sp^2); ^{29}Si NMR δ −21.99 (Me$_3$Si), −3.84 (central Si), 7.58 (Me$_3$SiO).

Thermolysis of 1f. Siloxetane **1f** was thermolyzed (method D) for 24 h to yield >95% **13f** (two isomers, 1:1 mixture not separable); ^{1}H NMR δ −0.01 (18 H), −0.04 (18 H), 0.07 (9 H), 0.11 (9 H) (each Me$_3$Si), 1.3–2.0 (30 H, b, Ad), 7.0–7.7 (20 H, b); ^{13}C NMR δ −1.36, −1.33 (Me$_3$Si), 2.45, 2.32 (Me$_3$SiO), 29.36, 29.64 (C–H Ad), 36.83, 37.25 (CH$_2$ Ad), 43.32, 44.36 (q-C Ad), 121.75, 125.96, 126.11, 126.20, 127.87, 127.91, 128.03, 129.73, 130.17, 130.73, 131.00,

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131.17 (C–H sp^2), 118.36, 131.87, 139.67, 140.91, 141.90, 144.17, 147.09, 147.12 (q-C sp^2); ^{29}Si NMR δ –22.31, –22.12 (each Me$_3$Si), –7.52, –4.57 (each central Si), 6.36, 6.58 (each Me$_3$SiO).

Thermolysis of 1g. Siloxetane **1g** was heated (method C) and then recrystallized in pentanes to yield crystalline **16**, with **15** dissolved in the pentane solution. Alternatively, **1g** was thermolyzed (method D) for 8 days to yield **15** and **16**. **15**: colorless oil; ^{1}H NMR δ 0.28 (Me$_3$Si); ^{13}C NMR δ –0.98 (Me$_3$Si); ^{29}Si NMR δ –22.71 (Me$_3$Si), 7.06 (ring Si). **16**: mp 173–175 °C; ^{1}H NMR δ 0.03 (9 H, s, Me$_3$SiO), 2.11 (3 H, s, *p*-CH$_3$-Mes), 2.15 (6 H, s, *o*-CH$_3$-Mes), 6.77 (2 H, s, sp^2-Mes), 6.3–8.3 (8 H, 8 multiplets, sp^2-Fl); ^{13}C NMR δ 1.04 (Me$_3$SiO), 19.82 (*o*-CH$_3$-Mes), 21.26 (*p*-CH$_3$-Mes), 129.18 (C–H sp^2-Mes), 119.73, 119.92, 121.79, 125.59, 126.06, 126.70, 126.88, 127.19 (C–H sp^2-Fl), 134.71, 136.92 (2 C), 138.37, 138.42, 139.02, 139.27, 139.44, 153.11 (q-C sp^2); ^{29}Si NMR δ 18.99 (Me$_3$SiO); IR 1063.6 (Si—O), 1623.9 (C=C), 1265.3, 846.79 cm^{-1} (Me$_3$SiO). Anal. Calcd for C$_{26}$H$_{28}$OSi: C, 81.20; H, 7.34. Found: C, 81.13; H, 7.39.

Attempts at Trapping Dipolar Intermediates with Methanol. Siloxetane **1d** was prepared (method A) in C$_6$D$_6$, and then 15 equiv of methanol was added to the NMR tube. The sample was left in the dark at ambient temperatures for 24 h, during which time isomerization to **4** occurred as expected to a 1.8:1 mixture of **4**/**1d**. No trapping products were observed, and hence the isomerization probably does not proceed via a dipolar mechanism.

Photolysis of this 1.8:1 mixture in C$_6$D$_6$/MeOH (method A) yielded pure **1d** as before with no trapped dipolar compounds. Attempts at trapping intermediates with methanol between compounds **7a–c** and **1a–c** respectively, also met with failure.

Attempts at Trapping Diradical Intermediates with *n*-Bu$_3$SnH. To a solution of siloxetane **1d** in C$_6$D$_6$ was added excess *n*-Bu$_3$SnH. The sample was left in the dark at ambient temperatures for 24 h, at which time a 1.8:1 mixture of **4**/**1d** was present, and hence *n*-Bu$_3$SnH failed to influence the rearrangement of **1d** to **4**. Photolysis of the mixture in the presence of *n*-Bu$_3$SnH afforded siloxetane **1d** exclusively, and thus the photochemical pathway must also not proceed via any radical intermediates.

Photolysis of **7a–c** to **1a–c** respectively, in C$_6$D$_6$ with excess *n*-Bu$_3$SnH present, produced the siloxetanes exclusively. Cophotolysis of equimolar amounts of an acylsilane (**2a,d**) and benzophenone (method A) with a 2:1 excess of *n*-Bu$_3$SnH present led to siloxetane formation as the major product with about 10% of the silene reacting with the *n*-Bu$_3$SnH to give the adducts **17a,d**. The properties of **17a,d** were very similar. **17a**: ^{1}H NMR δ –0.03, 0.16, 0.25 (each 9 H, s, Me$_3$Si), 0.9–1.6 (27 H, b, Bu), 5.11 (1 H, CH-OSi, $^3J(^{119}$Sn–^{1}H) = 26.6 Hz), 6.9–7.3 (5 H, b, Ph); ^{13}C NMR δ 0.87, 1.90, 2.15 (each Me$_3$Si), 10.36 (CH$_2$-Bu, $^1J(^{119}$Sn–^{13}C) = 255.7 Hz), 30.73 (CH$_2$-Bu, $^2J(^{119}$Sn–^{13}C) = 18.6 Hz), 28.27 (CH$_2$-Bu, $^3J(^{119}$Sn–^{13}C) = 58.0 Hz), 14.03 (CH$_3$-Bu), 70.53 (CH-OSi), 126.34, 126.54 (p), 128.58 (C–H sp^2), 147.04 (q-C sp^2); ^{29}Si NMR δ –58.61 ((Me$_3$Si)$_2$*Si*, $^1J(^{119}$Sn–^{29}Si) = 285 Hz), –11.36, –10.96 (each Me$_3$Si, $^2J(^{119}$Sn–^{29}Si) = 24 Hz), 18.54 (Me$_3$SiO). **17d**: ^{1}H NMR δ 0.21, 0.31, 0.32 (each 9 H, s, Me$_3$Si), 0.8–1.7 (27 H, b, Bu), 1.65–2.0 (15 H, b, Ad), 4.03 (H-C-OSi, $^3J(^{119}$Sn–^{1}H) = 15.6 Hz); ^{13}C NMR δ 2.92, 3.24, 3.45 (each Me$_3$Si), 11.79 (CH$_2$-Bu, $^1J(^{119}$Sn–^{13}C) = 246.3 Hz), 30.71 (CH$_2$-Bu, $^2J(^{119}$Sn–^{13}C) = 19.5 Hz), 28.32 (CH$_2$-Bu, $^3J(^{119}$Sn–^{13}C) = 58.1 Hz), 14.02 (CH$_3$-Bu), 29.26 (CH Ad), 37.32, 41.34 (CH$_2$ Ad), 38.79 (q-C Ad), 82.53 (*C*H-OSi); ^{29}Si NMR δ –76.45 ((Me$_3$Si)$_2$*Si*, $^1J(^{119}$Sn–^{29}Si) = 267 Hz), –10.52, –10.33 (each Me$_3$Si, $^2J(^{119}$Sn–^{29}Si) = 25 Hz), 13.07 (Me$_3$SiO).

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Registry No. **1a**, 107768-27-4; **1b**, 107768-28-5; **1c**, 107768-29-6; **1d**, 107768-30-9; **1e**, 107768-31-0; **1f**, 107768-32-1; **1g**, 107768-33-2; **1h** (isomer 1), 107768-34-3; **1h** (isomer 2), 107768-40-1; **1i**, 107768-35-4; **1j** (isomer 1), 107768-36-5; **1j** (isomer 2), 107768-42-3; **1k** (isomer 1), 107768-37-6; **1k** (isomer 2), 107768-43-4; **1l** (isomer 1), 107768-38-7; **1l** (isomer 2e, 107768-47-8; **2a**, 60154-95-2; **2b**, 97551-01-4; **2c**, 69397-47-3; **2d**, 72189-53-8; **3a**, 60155-00-2; **4**, 107768-39-8; **7a**, 107768-44-5; **7b**, 107768-45-6; **7c**, 107768-46-7; **8a**, 107798-11-8; **8b**, 107798-13-0; **8c** (isomer 1), 107768-50-3; **8c** (isomer 2), 107798-14-1; **8e** (isomer 1), 107768-51-4; **8e** (isomer 2), 107798-15-2; **8f**, 107768-52-5; **9a**, 107768-48-9; **9b**, 107768-49-0; **10a**, 107798-12-9; **11**, 86786-34-7; **12**, 106916-40-9; **13a**, 86786-35-8; **13c**, 107768-53-6; **13d**, 107768-54-7; (*Z*)-**13f**, 107768-55-8; (*E*)-**13f**, 107768-56-9; **13i**, 107768-41-2; **14a**, 1733-63-7; **14c**, 102599-14-4; **15**, 81740-84-3; **16**, 107768-57-0; **17a**, 107768-58-1; **17d**, 107768-59-2; *n*-Bu$_3$SnH, 688-73-3; benzophenone, 119-61-9; 9-fluorenone, 486-25-9; 4,4′-dimethylbenzophenone, 611-97-2; benzaldehyde, 100-52-7; pivaldehyde, 630-19-3.

Supplementary Material Available: Tables of anisotropic thermal parameters for compound **1f** and supplementary bond lengths and angles for compounds **1f** and **16** (5 pages); listings of final structure amplitudes for compounds **1f** and **16** (22 pages). Ordering information is given on any current masthead page.