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Reactions of Stable Silenes with Grignard Reagents

A. G. Brook,* Pauline Chiu, John McClenaghnan, and Alan J. Lough

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

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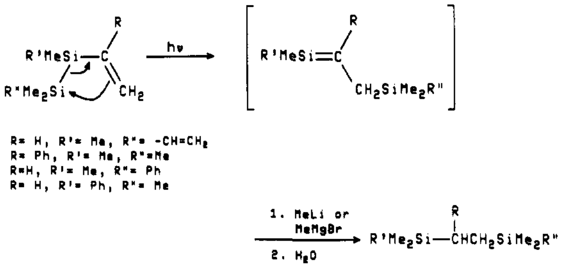
Grignard reagents have been found to add to members of the family of stable silenes $(Me_3Si)RSi{=}C(OSiMe_3)R'$ (R = Me_3Si, Ph; R' = Ad or *t*-Bu). Two types of product were formed, namely a family of compounds where one molecule of Grignard reagent R″MgX was involved, leading to products with the structures **6**, $Me_3SiOSiRR''CHR'(SiMe_3)$, and a family where two molecules of Grignard reagent were involved, leading to products with structures **7**, $RR''_2SiCHR'(SiMe_3)$. The crystal structure of one compound, **6baa** (R = Ph, R' = Ad, R″ = Me), was obtained, confirming the structure assigned to this family of compounds. It is evident that, in the course of forming these products, a trimethylsilyl group originally attached to the sp^2-hybridized silicon atom of the silene apparently underwent a 1,2-migration to the adjacent carbon atom (which had been sp^2-hybridized in the parent silene). The original trimethylsiloxy group either underwent a reverse 1,2-rearrangement from carbon to silicon, forming **6**, or else was eliminated during the reaction, yielding **7**. The proportions of products **6** and **7** were found to be insensitive to the amount of Grignard reagent or the temperature at which the reaction occurred but were sensitive to the polarity of the solvent system, more product of structure **6** being formed in less polar solvents. In a related study it was shown that reaction of *t*-BuLi with a (polysilyl)acylsilane gave rise to a product in which a molecule of *t*-BuLi had added to a silene formed in the course of the reaction. Mechanisms explaining the formations of these products are given.

The availability of relatively stable compounds containing a silicon-carbon double bond[1,2] has allowed the study of the chemistry of the multiple bond under mild conditions familiar to the organic chemist. Several recent studies have described reactions of silenes of the family $(Me_3Si)_2Si{=}C(OSiMe_3)R'$ (**2**) with dienes and alkenes,[3] carbonyl compounds,[4] isonitriles,[5,6] α,β-unsaturated aldehydes and ketones,[7] and α,β-unsaturated esters,[8] as well as the photochemistry of some of the silenes.[9] These studies have shown both great similarities in the chemistries of the Si=C and the C=C bonds and remarkable differences in some cases, many of which involve unusual intramolecular rearrangements. We have now extended these studies of the silicon-carbon double bond to their reactions with Grignard reagents.

There has been little study of the reactions of silenes with organometallic reagents. Kumada et al.[10] reported the photolysis of several alkenyldisilanes in the presence of methyllithium or methylmagnesium bromide. Under the photochemical conditions the disilane was shown to undergo a 1,3-silaallylic rearrangement to give a silene. In the presence of the organometallic reagent, addition across the silicon-carbon double bond occurred with the regiochemistry expected of a polarized $Si^{\delta+}{=}C^{\delta-}$ double bond interacting with a polar organometallic species $Me^{\delta-}{-}MgX^{\delta+}$ to give the products shown in eq 1.



(1)

More recently Auner described work that nominally involved reaction of *tert*-butyllithium with a silene.[11] Again addition of the organometallic across the Si=C appeared to have occurred, and the final product **3**, obtained in up to 30% yield depending on the solvent, was accompanied by other more complex structures **4** and **5**, as shown in Scheme I.

We expected our family of silenes to follow this general behavior of simple addition across the ends of the Si=C bond, but it soon became apparent that more complex processes were involved.

Reaction Conditions and Products

Grignard reagents were allowed to react with stable silenes[1,12] under two sets of conditions. In the first method, the silene was preformed by photolysis of the corresponding acylsilane, and the Grignard reagent was then added to the silene in the dark. This method had some disadvantages because it is slower and because it is very difficult to cleanly convert all the acylsilane to silene, and hence some residual acylsilane (or products derived therefrom) was usually present in the product mixture. The second method involved cophotolysis of a solution of the acylsilane in the presence of the Grignard reagent, which usually was found to react with the silene as rapidly as it was formed. This method had the advantages of generally giving cleaner products and requiring a shorter

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

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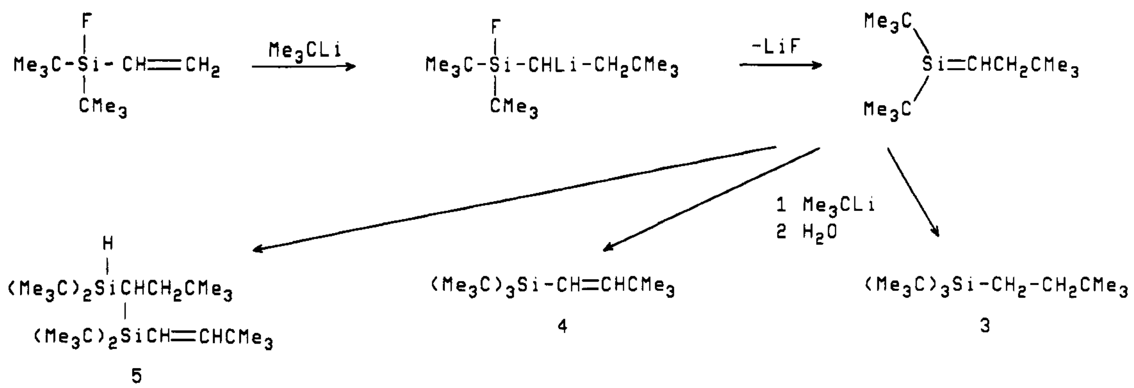
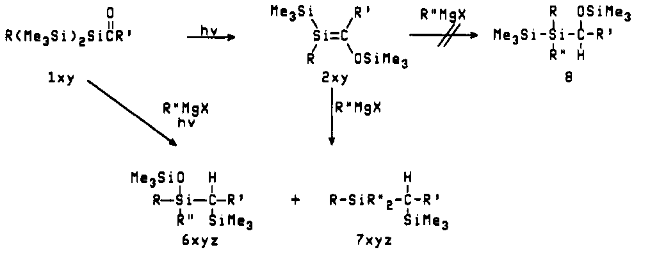
Scheme I



Scheme II



x = a R = Me_3Si
b R = Ph

y = a R' = Ad
b R' = t-Bu
c R' = Ph

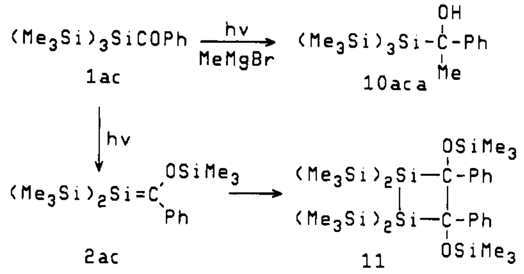
z = a R'' = Me
b R'' = CD_3
c R'' = Et
d R'' = $PhCH_2$
e R'' = Ph
f R'' = Me_3SiO

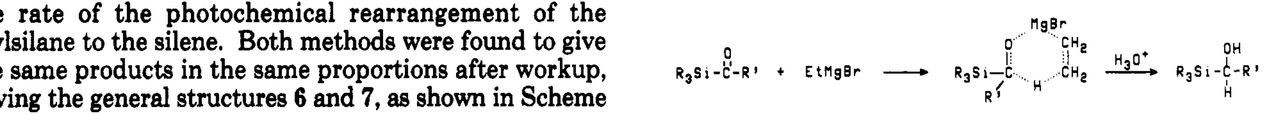
time to carry out. However, the cophotolysis method was limited to Grignard reagents whose rates of addition to the carbonyl group of the acylsilane were slow compared to the rate of the photochemical rearrangement of the acylsilane to the silene. Both methods were found to give the same products in the same proportions after workup, having the general structures **6** and **7**, as shown in Scheme II. It follows that the addition of the Grignard reagent to the silene was a "dark" reaction. No products **8**, corresponding in structure to the simple adduct of the Grignard reagent to the silene, were detected.

As a typical example of the reaction, when MeMgBr was allowed to react with the silene **2aa**[13] in diethyl ether for 15 min, a mixture of compounds was obtained upon workup. The two products **6aaa**[13] and **7aaa**[13] together accounted for over 90% of the total product mixture, with **6aaa** being the major product. By variation of the Grignard reagents and the substituents of the silenes, two families of compounds, **6** and **7**, were generated as shown in Scheme II. The mixtures of **6** and **7** were sometimes separable by chromatography or fractional crystallization. All of the products could be handled in air and were relatively stable toward hydrolysis. Details of the structural assignments are given below.

In two cases cophotolysis reactions of Grignard reagents with acylsilanes did not give the same products as were obtained from the addition of Grignard reagents to the preformed silene because the Grignard reagent reacted rapidly with the acylsilane before it could photoisomerize to the silene. One example of such reactions involved the treatment of acylsilanes with EtMgBr. The combination of these two reagents resulted in an immediate reaction in which a β-hydrogen atom of the ethyl group rapidly reduced the acylsilane to the related carbinol **9** (eq 2).

Scheme III





This type of behavior has been observed previously[14] for even very simple acylsilanes. Hence when EtMgBr was employed, it was only possible to obtain the products **6** and **7** by adding the Grignard reagent to the preformed silenes.

The other reaction that did not give the usual products **6** and **7** involved the cophotolysis of benzoyltris(trimethylsilyl)silane (**1ac**) with MeMgBr, where the carbinol **10aca** was formed (Scheme III). The reaction of the sterically undemanding methyl Grignard reagent with the carbonyl group of the acylsilane was evidently faster than the photoisomerization of the acylsilane **1ac** to the silene **2ac**, since only the carbinol **10aca** was isolated. It is not possible to treat the silene **2ac** (synthesized by prephotolysis of the acylsilane **1ac**) with Grignard reagents because the silene **2ac** rapidly forms the dimer **11**.[16]

While addition of the Grignard reagent to the carbonyl group of the acylsilane was possible in principle for all the cophotolysis experiments, the experimental results indicated that acylsilanes with R' groups bulkier than Ph evidently created too much steric hindrance for the addition reaction to the carbonyl group to proceed at a significant rate. The above experiments also inferred that Grignard reagents probably could not react under either sets of

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[13] In this paper most compounds will be listed by a number followed by two or three letters. For acylsilanes and silenes, such as **1aa** or **2ba**, the first letter defines the R group attached to the silicon atom and the second letter defines the R' group attached to carbon in $(Me_3Si)_2RSi-CO-R'$ (**1**), or $Me_3SiRSi{=}C(OSiMe_3)R'$ (**2**), respectively, where for R **a** = Me_3Si, **b** = Ph and for R' **a** = Ad, etc., as defined in Scheme II. For the products such as **6aaa** or **7aad** the first two letters have the same meanings as above and the third letter defines the R'' group of the R''MgX reagent used in the reaction, e.g., **a** = Me– and **d** = $PhCH_2$–, etc. In almost all cases the R'' group becomes attached to the original sp^2-hybridized Si of the silene involved.

[14] Brook, A. G.; Quigley, M. A.; Peddle, G. J. D.; Schwartz, N.; Warner, C. M. *J. Am. Chem. Soc.* **1960**, *82*, 5102.

[15] Wright, A.; West, R. *J. Am. Chem. Soc.* **1974**, *96*, 3214.

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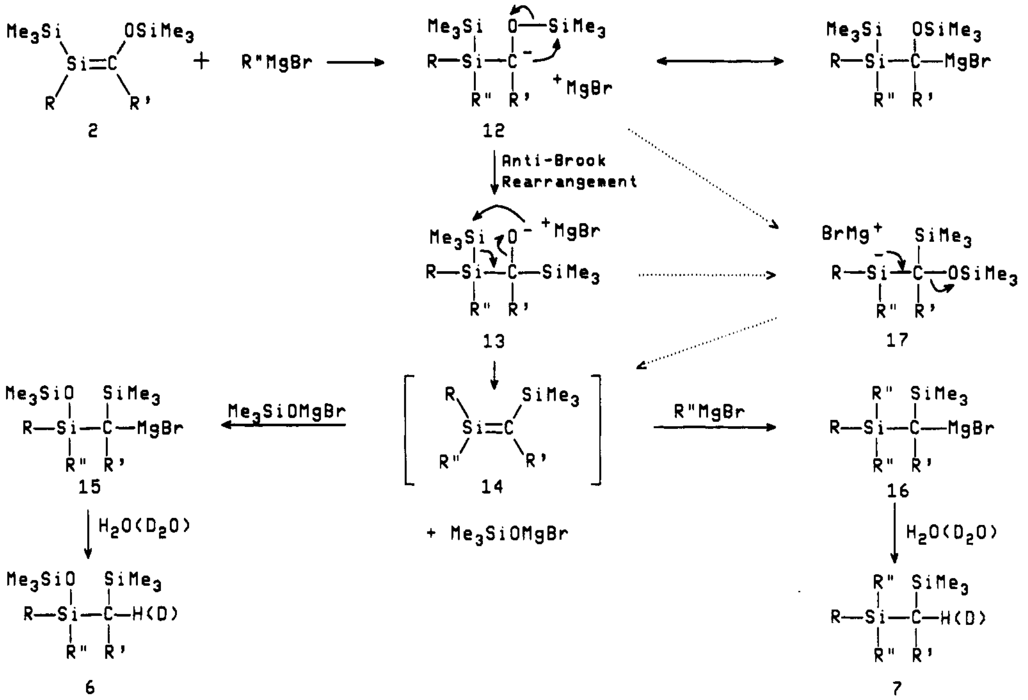
Scheme IV



conditions with silenes whose R′ group was less bulky than phenyl, because under cophotolysis conditions the Grignard reagent would add rapidly to the carbonyl group of the acylsilane before silene was formed, and prephotolysis of the acylsilane would form the stable silene dimers. The combination of acylsilanes and Grignard reagents successfully employed is indicated in Scheme II.

In the course of studying the various combinations of Grignard reagents and silenes under varying conditions, several facts became obvious. The proportions of the products **6** and **7** were insensitive to the temperature of the reaction, the same proportions being obtained from reactions run at room temperature, 0 °C, or −7 °C. Reactions run at colder temperatures, e.g. −23 to −78 °C, almost totally failed to occur, in part because of solubility problems, so that after aqueous acidic workup the major products isolated were the hydration products of the silene (see below).

The proportions of the products **6** and **7** were also insensitive to the amount of Grignard reagent employed, with essentially the same proportions being formed regardless of whether 1, 3 or 6 equiv of Grignard reagent was added.

However, the proportions of the products **6** and **7** formed by either the addition or the cophotolysis methods of reaction were very sensitive to the nature of the solvents used. Some results are given in Table I. Thus, the formation of **6aaa** relative to **7aaa** was strongly favored in pentanes, and in ether most of the product ratios favored **6** relative to **7** by at least 3:1. However, when THF was employed as solvent, the formation of **7** became strongly favored (>10:1), and it was essentially the only product formed in some cases. Mixtures of solvents changed the product ratios in the expected manner. For example, while the ratio of **6aaa** to **7aaa** was 10:1 in pentanes, the inclusion of 10% ether changed the product ratio to 7:1. A possible explanation for this striking sensitivity to the polarity of the solvent will be advanced when a mechanism is proposed below to explain the reactions.

Each of the type **6** compounds contain two stereocenters and might have been expected to appear as a mixture of diastereomers. However, the reactions forming them were evidently highly stereoselective, since only one diastereomer was observed or isolated in each case, although small amounts (<5%) of a second diastereomer could have been present. In one experiment an effort was made to isomerize the immediate precursor of **6aaa** to its diastereomer, and another set of NMR signals was obtained that could have been due to the second diastereomer.

Table I. Dependence of Product Ratios on Solvent Systems

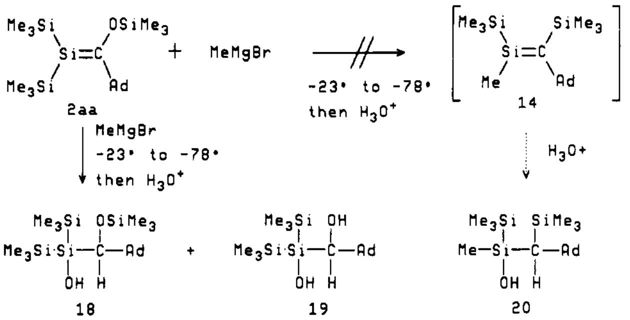
	solvent used		
product ratio	pentanes	diethyl ether	THF
6aaa:7aaa	10:1	3:1	1:20
6aab:7aab		3:1	
6aac:7aac		2.5:1	1:10
6aad:7aad		3:1	
6aaa:7aae	1:1	1:2	
6aba:7aba		4:1	
6baa:7baa		5:1	1:30
6bac:7bac		5:1	

General Mechanism of the Reactions

From the structures of the products of the reactions reported above, several features are immediately obvious. Thus, the formation of type **6** products involves the incorporation of one molecule of Grignard reagent R″MgX, where the R″ group becomes attached to the sp^2-hybridized silicon atom of the silene. In addition, 1,2-rearrangements occurred in which a trimethylsilyl group, originally attached to the sp^2-hybridized silicon atom of the silene, appeared to have migrated to the adjacent carbon atom, and a trimethylsiloxy group, originally attached to the sp^2-hybridized carbon atom of the silene, apparently migrated to the adjacent silicon atom.

In the case of the formation of type **7** products, two molecules of Grignard reagent were involved, their R″ groups becoming attached to the original sp^2-hybridized silicon atom. In addition, a trimethylsilyl group apparently rearranged from silicon to the adjacent carbon atom, and the original trimethylsiloxy group was eliminated (detected by NMR spectroscopy in an unhydrolyzed reaction mixture as $Me_3SiOMgX$ and being converted to volatile trimethylsilanol and hexamethyldisiloxane on workup).

Scheme V



A plausible explanation for the major details of these reactions is given in Scheme IV. The initial reaction between the silene and Grignard reagent logically involves addition of the R″ group to the relatively electropositive sp^2-hybridized silicon atom of the silene to yield a carbanion or carbanion-like species **12**, when then undergoes an anti-Brook type rearrangement[15] to the oxyanion **13**. The oxyanion can then rearrange according to the general sense of the Peterson olefination reaction,[16,17] to yield the silene **14** and trimethylsilanolate. Readdition of the trimethylsilanolate generated in the course of the above elimination with the expected regiochemistry to silene **14** would form the anionic species **15**, which is the immediate precursor of the observed product **6**. Alternatively, silene **14** could add a second molecule of Grignard reagent to yield the anion **16**, the immediate precursor of the observed product **7**.

Some justification for the above sequence of reactions is as follows, starting from the end and working backward. In working up the reactions, if D_2O was employed it was observed that the ^1H NMR signals attributable to the methine hydrogen atom in **6** and **7** were no longer present. This indicated that the immediate precursors to these products were carbanionic in character, as might have been expected. This conclusion was supported by the ^{13}C and ^{29}Si NMR spectra of the reaction mixture obtained from the reaction of MeMgBr with the silene **2aa** taken immediately prior to workup where a 1:1 correspondence between the signals of the reaction mixture, i.e. **15** and **16**, and of a mixture of **6aaa** and **7aaa** was noted. (The only exceptions were the signals in the ^{13}C NMR spectra belonging to the carbon atoms that carried the negative charge or MgX group, which could not be assigned with confidence.) Thus, it was further concluded that no rearrangements occurred during the workup of the reaction mixtures. These observations support the position that **15** and **16** are the immediate precursors to **6** and **7**.

Attempts to demonstrate the formation of the intermediate silene **14** (or any of the other possible intermediates) by running the reactions at lower temperature, in hopes that it might accumulate in the system, failed. Silene **2aa** and MeMgBr were employed as a model system. At −23 °C or lower no reaction occurred between the reagents, and the products formed were **18** and **19**, the expected hydration and hydrolysis products of silene **2aa**, as shown in Scheme V. At −7 °C or higher **6aaa** and **7aaa** were the major products from the reaction, with some water adduct **18** also being formed. There was no evidence for the product **20** expected from the addition of water across the Si=C bond of silene **14** at any temperature. In support of the step **14** → **15** (Scheme IV) it was shown that silenes of this general type could add trimethylsilanolate ion. Thus treatment of silene **2aa** with lithium trimethylsilanolate in ether, under the same general conditions as the reactions with R″MgX, gave rise to a high yield (>90%) of the product **7aaf**, as outlined in Scheme VI. These results can be interpreted as arising from the addition of trimethylsilanolate to silene **2aa**, giving rise to carbanion **21**, which on undergoing the anti-Brook rearrangement would give oxyanion **22**. This on loss of trimethylsilanolate as proposed above in Scheme IV would form the intermediary silene **23**. Readdition of trimethylsilanolate would yield carbanion **24**, which on hydrolysis should yield the product **7aaf**, as observed experimentally. Thus, this reaction with silanolate parallels the mechanism proposed in Scheme IV, but where R″ = Me_3SiO. These results give strong support to the proposal that Me_3SiO^- adds to an intermediary silene (**14**) formed in the course of the reaction sequence leading to the final reaction products **6** and **7**.

If the above reaction scheme is correct, it follows that the proportions of the products **6** and **7** formed in the reaction are the result of a competition of trimethylsilanolate and Grignard reagent for the silene **14**. A dependence on the solvent system of the proportions of products formed was indeed observed, as described above. It follows that the solvation of the various species—silanolate, Grignard reagent, and silene **14**—must be very important in determining the results. If the silanolate eliminated in the proposed previous step by **13** does not escape easily from the solvent cage (such as when the solvent, e.g. pentane, is a poor coordinator), its reaction with **14** to give the adduct **15** should be favored over the situation where, in the presence of a good solvating medium like THF, the silanolate becomes solvated and escapes from the cage. Under these latter circumstances, attack by the Grignard reagent present should be more favored leading to higher proportions of **7** as observed.

The early part of Scheme IV concerns the manner by which a trimethylsilyl group becomes attached to the carbon atom of the original silene **2**, and the oxygen (or trimethylsiloxy group) is lost from carbon, and it has not been possible to distinguish between several closely related possibilities. Given that the first step, addition of the Grignard reagent to the silene, occurs, yielding the anion **12**, there is ample precedent for the carbanion–oxyanion isomerization (anti-Brook rearrangement), which is a thermodynamically favored process.[15] Loss of silanolate from a system such as **15** has close precedent in the Peterson reaction[16,17] and in related studies involving the reaction of an acylsilane with *tert*-butyllithium described below.

A closely related alternative process, namely that the carbanion **12** isomerizes to the silanion **17** as a result of a 1,2-migration of a trimethylsilyl group in the course of the reaction, may be possible. Such a process was proposed by Wustrack and Oehme for the addition of (tris(trimethylsilyl)silyl)lithium to simple ketones,[18] although, in their reaction, loss of trimethylsilanolate did not occur from the silanion. In our studies, when reactions were run and quenched at low temperature in the hope of accumulating and trapping one of the intermediates in the sequence of reactions, no evidence for the formation of the expected silane (Si–H) linkage from protonation of **17** was found. Obviously the silanion could have a very short lifetime, immediately eliminating trimethylsilanolate to form silene **14**. However, the structures of silanion **17** and that proposed by Oehme are very similar, and it is not

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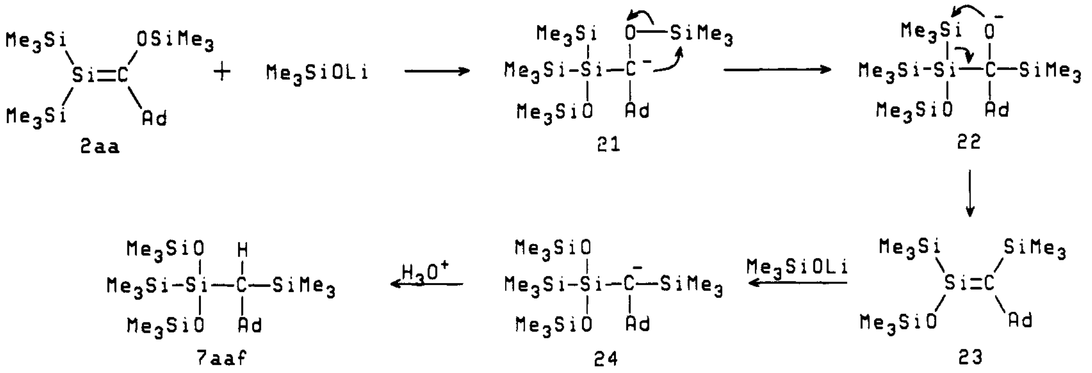
(17) Ager, D. J. *Synthesis* **1984**, *5*, 384.

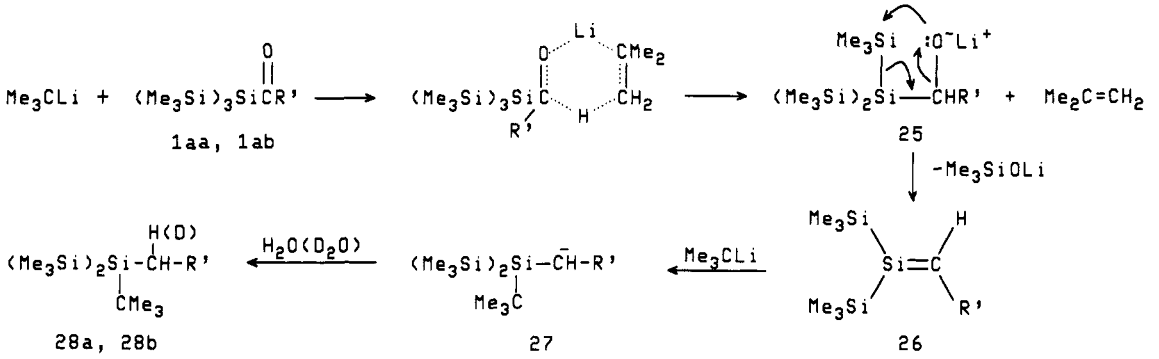
(18) Wustrack, R.; Oehme, H. *J. Organomet. Chem.* **1988**, *352*, 95.

(19) Pegg, D. T.; Doddrell, D. M.; Bendell, M. R. *J. Chem. Phys.* **1982**, *77*, 2745.

Scheme VI



Scheme VII



obvious why one but not the other would eliminate trimethylsilanolate. Hence, we do not favor a pathway involving discrete formation of silanion **17**.

Another experiment that supports the proposals of the mechanism given in Scheme IV involved the treatment of the acylsilanes **1aa** and **1ab** with *tert*-butyllithium. A rapid reaction occurred, during which a gas, shown to be isobutene, was evolved, and the end products having the structures $(Me_3Si)_2$-*t*-$BuSiCH_2R'$ (R′ = Ad (**28a**), *t*-Bu (**28b**)) (Scheme VII) were isolated in good yield if 2 equiv of *tert*-butyllithium was employed but in less than 50% yield if only 1 equiv was used. A CHD group was shown to be adjacent to the R′ group if the reaction mixture was worked up in D_2O. The structures of the products isolated from these reactions clearly indicate that reduction of the carbonyl group and a loss of trimethylsilanolate have occurred and that a *tert*-butyl group has become attached to silicon. The reaction is believed to occur as shown in Scheme VII. There was no evidence that trimethylsilanolate added to silene **26**. Thus, reaction of the acylsilane with the sterically demanding *tert*-butyllithium led to reduction of the acylsilane by the β-hydrogens of the organometallic reagent and formation of isobutene and the oxyanion **25**, which then lost trimethylsilanolate to give an intermediary silene **26**. In an excess of *tert*-butyllithium, addition then occurred to the silicon atom of the double bond yielding the carbanion **27**, which on hydrolysis (deuterolysis) gave the products isolated, **28a**,**b**. These results support the proposal that silanolate can spontaneously eliminate from ions such as **13** or **17** (Scheme IV) and that organometallic reagents can add to the silicon end of a silicon–carbon double bond. Whether the loss of trimethylsilanolate from ions such as **13** or **25** is a concerted or a stepwise process cannot be established from these results.

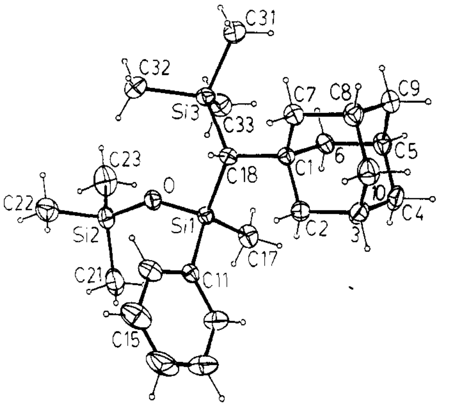


Figure 1. View of the molecule, showing the atomic labeling scheme. Thermal ellipsoids are at the 25% probability level. Hydrogen atoms have been assigned as spheres of arbitrary radius.

Proofs of Structure for the Disiloxanes 6

The crystal structure of compound **6baa**, derived from the reaction of the silene **2ba** with MeMgBr, was obtained, and its ORTEP diagram is shown in Figure 1. It shows a trimethylsiloxy group bonded to the silicon atom, which had been sp^2-hybridized in the silene, and a trimethylsilyl group attached to what had originally been the sp^2-hybridized carbon atom of the silene and establishes unambiguously the structures of the type **6** compounds. A summary of the crystal data and details of the intensity collection and least-squares parameters are given in Table II. The data reveal some lengthening of bonds to both Si1 and C18, as well as bond angle distortion from the tetrahedral value at both Si1 (from 106 to 114°) and C18 (from 110 to 118°), indicative of steric crowding at these atoms.

The ^1H, ^{13}C and ^{29}Si spectra of compound **6baa** established typical chemical shifts for the atoms in the various environments of this compound, thus facilitating the assignment of signals and structures to the products obtained from other combinations of silene and Grignard reagent. All of the type **6** products had NMR properties similar to those of **6baa**. Both compounds **6aad** (from the adamantylsilene and $PhCH_2MgBr$) and **6baa** (from the phe-

Table II. Summary of Crystal Data, Details of Intensity Collection, and Least-Squares Refinement Parameters

empirical formula	$C_{24}H_{42}OSi_3$
M_r	430.9
cryst size, mm	0.30 × 0.15 × 0.15
cryst class	monoclinic
space group	$P2_1/c$
a, Å	16.142 (4)
b, Å	6.801 (1)
c, Å	23.983 (6)
β, deg	95.28 (1)
V, Å^3	2621.5 (10)
Z	4
D_{calc}, g cm^{-3}	1.09
μ(Mo Kα), cm^{-1}	1.9
$F(000)$	944
ω-scan width, deg	0.7 + 0.35 tan θ
range θ collcd, deg	1–22.5 ($\pm h,k,l$)
tot. no. of reflcns	3860
no. of unique reflcns	3417
R_{int}	0.035
no. of obsd data [$I > 3\sigma(I)$]	1882
weighting g	0.000 45
R	0.043
R_w	0.043
goodness of fit	1.49
largest Δ/σ	0.003
no. of params refined	254
max density in ΔF map, e/Å^3	0.24

nyladamantylsilene and MeMgBr) contain the essential structural features of the type **6** products, and a few features will be discussed as representative of this family of disiloxanes.

One feature of the type **6** compounds was the single proton on the methine carbon. This proton resonated at 0.64 and 0.73 ppm in **6aad** and **6baa**, respectively, a high-field position due to the shielding effect of two α-silicon atoms. Such upfield chemical shifts were inconsistent with structures such as **8** (Scheme II), the product of the 1,2-addition of the Grignard reagent to the silene, where model compounds suggest the adjacent Me_3SiO group would deshield the proton to about 3 ppm.[9]

The ^{13}C chemical shifts of the methine carbon atoms in the compounds **6** ranged from 31.9 to 35.4 ppm, too upfield to be consistent with the structure of **8** (Scheme II), where the methine carbon bears a trimethylsiloxy group and where the carbon atom of model compounds have chemical shifts near 80 ppm.[9] Chemical shifts in the range 30–35 ppm are characteristic of a methine carbon bonded to a trimethylsilyl group as models show.[9]

The R′ groups of the type **6** compounds resonated at characteristic frequencies, the adamantyl group of **6aad** resonating at 29.44, 36.69, 45.69, and 36.13 ppm. In **6baa** the adamantyl signals were at 29.72, 36.93, 45.58, and 36.19 ppm. These correspond to the adamantyl CH, CH_2 (two signals), and quaternary C atoms, respectively. The more downfield of the two adamantyl CH_2 signals belonged to the methylene carbon atoms adjacent to the quaternary center. The chemical shifts of these CH_2 groups are diagnostic of the nature of the substituent on the β-carbon atom. When an electron-withdrawing substituent (e.g. $-OSiMe_3$, $-OH$) is attached, the CH_2 signal is found in the range 37–41 ppm. When the substituent is an electron-donating group (e.g. $-SiMe_2R$, $-SiMe_2X$, $-H$), the CH_2 group resonates in the range 45–46 ppm. This correlation has not been previously recognized. All of the disiloxanes bearing adamantyl groups (**6aaa**, **6aae**, **6baa**, **6bab**)) showed CH_2 signals in the latter range. This observation is in agreement with the trimethylsilyl, not the trimethylsiloxy group, being bonded to the carbon atom to which the adamantyl group is attached.

The ^{29}Si NMR spectra of all the **6** family of compounds had two strong upfield signals: the trimethylsilyl groups, attached to carbon and hence analogous to TMS, resonated in the range −2 to 0 ppm. The trimethylsiloxy groups, attached to silicon and hence relatively shielded, resonated in the range 5–9 ppm. (By contrast, trimethylsiloxy groups attached to carbon normally resonate in the range 13–15 ppm.) These positions are normal.[9]

The chemical shift of the "central" silicon atoms of the type **6** compounds depended on the attached substituents. Compounds like **6aaa–6aad**, which had both a trimethylsiloxy group and a trimethylsilyl group attached in addition to an alkyl R″ group, absorbed in the range 6–7 ppm. When a phenyl group was attached to the central silicon atom, as in **6aae** or **6baa**, the silicon absorption was shifted upfield to the 0 to −3 ppm range.

Mass spectra were obtained for compounds **6aaa**, **6aad**, **6aae**, **6aba**, and **6baa**. All of them showed typical fragments such as [M^+], [$M^+ - CH_3$], and [Me_3Si^+]. The [$M^+ - Me_3Si$] fragment was observed only for compounds in which there was a trimethylsilyl group bonded to silicon. This clearly identified the compounds that possessed a Me_3Si–Si linkage. Another fragment that was helpful in structure elucidation was [M^+ − 221], i.e. [$(Me_3SiO)RR'Si^+$], which resulted from the cleavage of the central silicon–carbon bond. The mass spectrum of **6aad** showed this fragment with a relative abundance of 11; in the spectrum of **6baa**, [M − 221^+] was the most abundant fragment.

Structural Proof for Disubstituted Silanes 7

The NMR spectra of the minor products from the reactions of the silenes **2** with various Grignard reagents in ether indicated that they constituted a family of compounds having the structures **7**. Compounds **7aaa** (from the adamantylsilene and MeMgBr) and **7aae** (from the adamantylsilene and PhMgBr) will be used as examples to discuss some of the NMR properties and the correlations with the structural features of this family.

The chemical shift of the proton on the methine carbon was influenced strongly by the nature of the R and R″ groups attached to the central silicon atom. When R″ was an alkyl group, as in **7aaa**, the proton peak occurred at 0.20 ppm. When the reaction mixture yielding **7aaa** was worked up by using D_2O, this signal was absent. If R or R″ was an aryl group, this proton signal was shifted downfield. For example, in **7aae** where the two R″ groups were phenyl, the proton resonated at 1.00 ppm.

In each of the type **7** compounds, the R″ groups on the central silicon atom were diastereotopic, because the adjacent carbon atom was a stereocenter. Thus, the nonequivalent methyl groups of **7aaa** produced two three-proton singlets at 0.24 and 0.32 ppm and ^{13}C signals at 0.08 and 2.09 ppm.

In the ^{13}C NMR spectra the methine carbon atom of type **7** compounds occurred at chemical shifts as low as 29.9 ppm and as high as 32.1 ppm, depending on the environment. In each case, the methine carbon in the type **7** compound was more shielded than in the analogous type **6** compound, due to the absence of the electron-withdrawing (deshielding) trimethylsiloxy group. Examples include **6aaa** and **7aaa**, whose methine carbon atoms resonated at 35.41 and 30.71 ppm, respectively, and **6aae** and **7aae**, where they resonated at 31.91 and 31.85 ppm, respectively.

Each type **7** compound showed at least two signals in the ^{29}Si NMR spectra. One, due to the trimethylsilyl group, resonated at approximately 0 ppm, indicating an attachment to a carbon atom. The chemical shift of the other silyl peak, due to the "central" silicon atom, was dependent on the nature of the substituents. In **7aaa** the central silicon atom has three alkyl groups and one silyl group attached; hence, its chemical shift is expected to be upfield from TMS and was found to occur at −15.95 ppm. The central silicon in **7aae** resonated at −19.36 ppm, more shielded than in **7aaa** because two of the alkyl substituents were replaced by phenyl groups.

Mass spectrometry provided further support for these structures of the type **7** compounds, where a typical fragmentation pattern was observed. These fragments included [M$^+$], [M$^+$ − Me], and [Me$_3$Si$^+$]. The [M$^+$ − Me$_3$Si] fragment was also found in 100% relative abundance for both of the representative compounds **7aaa** and **7aae** and confirmed that these compounds possessed a trimethylsilyl group attached to a silicon atom. Most informative of all was finding the fragment that resulted from the cleavage of the central silicon–carbon bond, i.e. the [RR″$_2$Si$^+$] ion. These fragments, where R = Me$_3$Si, confirmed the presence of the disilyl moieties in the molecule.

Experimental Section

Experiments were performed with oven-dried glassware under argon by using standard inert-atmosphere and vacuum-line techniques. Reaction solvents were dried and double-distilled before use: diethyl ether and tetrahydrofuran were dried over sodium and benzophenone: pentanes and toluene were dried over lithium aluminum hydride. Photolysis experiments were carried out by using two to three 100-W PAR 38 mercury spot lamps irradiating at 360 nm and longer.

All NMR spectra were obtained on either a Varian XL400 spectrometer or a Gemini 200 spectrometer and were run in C$_6$D$_6$ unless otherwise specified. Where necessary, APT[20] and DEPT[19] pulse sequences were used in obtaining ^{13}C NMR spectra, and all ^{29}Si NMR spectra were obtained by using the DEPT sequence. In the determination of the proportions of products formed, the ^{1}H NMR signals sometimes overlapped seriously: in such cases proportions were obtained by using the intensities of ^{13}C NMR signals for groups in similar environments.

IR spectra were obtained on a Nicolet 5DX FT-IR instrument.

Low-resolution and high-resolution mass spectra were obtained on a VG70-250S mass spectrometer. The peaks were reported in mass-to-charge units (*m*/*z*), followed by their intensities relative to the base peak in parentheses.

Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

General Procedures. Preparations of the acylpolysilanes from which the stable silenes were obtained have been reported elsewhere.[4,5,6] The additions of Grignard reagents to silenes were performed by using the following two general methods.

Method I. Addition of the Grignard Reagent to Preformed Silene. In a typical procedure, an approximately 0.25 M solution of acylsilane (300–400 mg) in a Schlenk tube was photolyzed by using three UV lamps for approximately 15 h inside a water-cooled Dewar flask maintained at 10 °C. Conversion of the acylsilane to silene was completed by continued photolysis for an additional 15 h inside a Dewar flask maintained at −78 °C by a dry ice–acetone bath. To this silene solution was added with vigorous stirring (bar magnet) 1.1 equiv of Grignard reagent. After being stirred for 2 h at room temperature, the reaction mixture was worked up by pouring into an excess of 5% HCl. Pentanes were added, and the organic layer after washing, drying, and removal of the solvents under reduced pressure gave the product mixture.

Method II. Cophotolysis of the Acylsilane with Grignard Reagent. The acylsilane solution was prepared under argon in a Schlenk tube as in method I. The Grignard reagent (1.1 equiv) was added to the solution by syringe. After thorough stirring, the Schlenk tube was sealed and was subjected to photolysis for 24 h inside a water-cooled Dewar flask using three lamps. The resultant product was worked up in the usual manner.

Reaction of Silene 2aa and MeMgBr in Ether. Isolation of 6aaa and 7aaa. MeMgBr (1.8 mL, 3 M, 1.1 equiv) in ether was added to a solution of the silene prepared by the photolysis of 2.04 g (0.005 mol) of (1-adamantylcarbonyl)tris(trimethylsilyl)silane (**1aa**) in ether (method I). After workup, purification by radial chromatography with hexanes afforded a major fraction, which was >90% of the total product. NMR spectroscopy indicated the presence of a 3:1 mixture of **6aaa** and **7aaa**, but attempts to obtain pure **6aaa** by chromatography failed, although some enrichment of **6aaa** was achieved and pure **7aaa** was isolated. **6aaa** (containing some **7aaa**): ^{1}H NMR δ 0.16 (9 H, s, Me$_3$SiSi), 0.21 (9 H, s, Me$_3$SiC), 0.27 (9 H, s, OSiMe$_3$), 0.45 (1 H, s, SiCH), 0.51 (3 H, s, MeSi), 1.64, 1.81, 1.93 (15 H, m, Ad); ^{13}C NMR δ −0.52 (Me$_3$SiSi), 2.51 (*Me*$_3$SiC), 4.63 (OSiMe$_3$), 6.03 (MeSiO), 29.52 (CH Ad), 35.16 (SiCH), 36.52 (q C of Ad), 36.81, 45.39 (CH$_2$ of Ad); ^{29}Si NMR δ −20.77 (Me$_3$*Si*Si), −0.69 (Me$_3$SiC), 6.29 (OSiMe$_3$), 6.37 (MeSiO); MS *m*/*z* 426 (1, M$^+$), 411 (17, M$^+$ − Me), 353 (100, M$^+$ − Me$_3$Si), 205 (27, Me$_3$Si(OSiMe$_3$)MeSi$^+$), 147 (53), 73 (100, Me$_3$Si$^+$). **7aaa**: mp 53–54 °C. Anal. Calc for C$_{19}$H$_{40}$Si$_3$O: C, 64.69; H, 11.43. Found: C, 64.57; H, 11.49. ^{1}H NMR: δ 0.18 (9 H, s, Me$_3$SiSi), 0.20 (1 H, s, SiCH), 0.22 (9 H, s, Me$_3$SiC), 0.24 (3 H, s, MeSi), 0.32 (3 H, s, MeSi), 1.63 (6 H, br t, CH$_2$ of Ad), 1.74 (6 H, br d, CH$_2$ of Ad), 1.92 (3 H, m, CH of Ad); ^{13}C NMR: δ −0.50 (Me$_3$SiSi), 0.80, 2.09 (MeSi), 5.08 (*Me*$_3$SiC), 29.78 (CH of Ad), 30.71 (SiCH), 36.65 (q C of Ad), 36.98, 45.63 (CH$_2$ of Ad); ^{29}Si NMR: δ −19.90 (Me$_3$*Si*Si), −15.95 (Me$_2$Si), −0.58 (Me$_3$SiC); MS *m*/*z* 352 (2, M$^+$), 337 (18, M$^+$ − Me), 279 (95, M$^+$ − SiMe$_3$), 205 (81), 131 (35, Me$_3$SiMe$_2$Si$^+$), 73 (100, Me$_3$Si$^+$). Calc for M$^+$ C$_{19}$H$_{40}$Si$_3$: *m*/*z* 352.2437. Found: *m*/*z* 352.2454.

Reaction of Silene 2aa and MeMgBr in THF. A solution of acylsilane **1aa** (2.04 g, 0.005 mol) in 10 mL of THF was photolyzed to the silene **2aa**. To it was added 2 mL (3 M, 0.006 mol) of MeMgBr in ether (method I). The orange color of the silene solution faded to a dark yellow upon the addition of MeMgBr. After 2 h, the reaction mixture was worked up and purified by chromatography with hexanes to yield a colorless oil. Its ^{13}C NMR spectrum showed that it was a 1:20 mixture of **6aaa** and **7aaa**. When this oil was dissolved in approximately 5:1 hexanes and ethyl acetate, large colorless crystals of **7aaa** formed in the cold.

Cophotolysis of (1-Adamantylcarbonyl)tris(trimethylsilyl)silane (1aa) and MeMgBr in Ether. A solution of acylsilane **1aa** (0.42 g, 0.001 mol) and 0.35 mL (3 M, 1.1 equiv) of MeMgBr were cophotolyzed in 4 mL of Et$_2$O (method II). After overnight photolysis and workup, the product was purified by chromatography with hexanes. On the basis of NMR spectroscopy, the major fraction was found to be a 3:1 mixture of **6aaa** and **7aaa**.

Cophotolysis of Acylsilane 1aa and MeMgBr in Pentanes. The solvent in MeMgBr (0.6 mL, 3 M in ether, 0.002 mol) was removed by pumping on the vacuum line. To the residue was added a solution of 0.68 g of the acylsilane **1aa** in 5 mL of pentanes (method II). This resulted in an inhomogeneous mixture because the MeMgBr was not totally soluble in the pentanes. After photolysis for 2 days with continuous vigorous stirring, workup gave an oil shown by NMR spectroscopy to be a 10:1 mixture of **6aaa** and **7aaa**. Chromatography on silica gel using hexanes failed to separate the mixture.

Cophotolysis of 1aa and MeMgBr in THF. A solution of acylsilane **1aa** (0.44 g, 0.001 mol) in 4 mL of THF and 0.8 mL of MeMgBr in ether (3 M, 0.0024 mol) were cophotolyzed overnight (method II), during which time a quantity of white solid, shown to be **7aaa**, settled to the bottom of the Schlenk tube. The reaction mixture was worked up as usual and was shown to be >95% **7aaa** by NMR spectroscopy.

Reaction of Silene 2aa and CD$_3$MgI in Ether. Preparation of 6aab and 7aab. The Grignard reagent CD$_3$MgI was prepared from 0.33 g of Mg and 0.5 mL CD$_3$I in 10 mL of diethyl ether. CD$_3$MgI (2.6 mL, 0.8 M, 1 equiv) was added to the silene solution made from the photolysis of 0.89 g (0.002 mol) of acylsilane **1aa** in 5 mL of ether. After reaction overnight, workup, including a radial chromatography using hexanes, gave as the major fraction a colorless oil shown by NMR spectroscopy to be a 3:1 mixture of **6aab** and **7aab**, which could not be separated. **6aab**: ^{1}H NMR δ 0.15 (9 H, s, Me$_3$SiSi), 0.20 (9 H, s, Me$_3$SiC), 0.26 (9 H, s, Me$_3$SiO), 0.44 (1 H, s, SiCH), 1.64 (6 H, br t, CH$_2$ of Ad), 1.80 (6 H, br d, CH$_2$ of Ad), 1.92 (3 H, br m, CH of Ad); ^{13}C NMR δ

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−0.13 (Me$_3$SiSi), 3.20 (*Me*$_3$SiC), 5.00 (Me$_3$SiO), ≈6.37 (m, CD$_3$SiO), 29.88 (CH of Ad), 35.41 (SiCH), 36.80 (q C of Ad), 37.10, 45.63 (CH$_2$ of Ad); ^{29}Si NMR: δ −21.06 (Me$_3$*Si*Si), −1.89 (Me$_3$SiC), 6.10 (Me$_3$SiO), 6.10 (CD$_3$SiO). **7aab**: ^{1}H NMR δ 0.17 (9 H, s, Me$_3$SiSi), 0.19 (1 H, s, SiCH), 0.21 (9 H, s, Me$_3$SiC), 1.6–2.1 (≈15 H, br, Ad); ^{13}C NMR δ −0.43 (Me$_3$SiSi), 0.85, 2.24 (CD$_3$Si), 5.11 (*Me*$_3$SiC), 29.83 (CH of Ad), 30.59 (SiCH), 36.7 (q C of Ad), 37.05, 45.63 (CH$_2$ of Ad); ^{29}Si NMR: δ −20.70 (Me$_3$*Si*Si), −16.37 ((CD$_3$)$_2$Si), −0.97 (Me$_3$SiC).

Reaction of Silene 2aa and EtMgBr in Ether. Preparation of 6aac and 7aac. A solution of **1aa** (1.16 g, 0.003 mol) in 5 mL of Et$_2$O was photolyzed to the isomeric silene **2aa**. EtMgBr (2.8 mL, 1.22 M), made from 0.63 g of Mg and 1.5 mL of EtBr in 15 mL of Et$_2$O, was added to the preformed silene (method I). After 1 h, the reaction was worked up. The product was purified by chromatography using 10% CH$_2$Cl$_2$ in hexanes. The product mixture was found to be **6aac** and **7aac** in a 2.5:1 ratio. Attempts to separate the two components by chromatography failed. **6aac**: ^{1}H NMR (CDCl$_3$) δ 0.12 (9 H, s, Me$_3$SiSi), 0.14 (9 H, s, Me$_3$SiC), 0.16 (9 H, s, Me$_3$SiO), 0.72–1.10 (≈5 H, m, CH$_2$CH$_3$), 1.6–2.0 (≈15 H, br, Ad); ^{13}C NMR δ 0.68 (Me$_3$SiSi), 3.20 (*Me*$_3$SiC), 5.20 (Me$_3$SiO), 8.68 (CH$_3$ of Et), 13.33 (CH$_2$ of Et), 29.88 (CH of Ad), 33.86 (SiCH), 36.59 (q C of Ad), 37.17, 45.84 (CH$_2$ of Ad); ^{29}Si NMR: δ −21.22 (Me$_3$*Si*Si), −2.33 (Me$_3$SiC), 5.43 (Me$_3$SiO), 8.89 (EtSi). **7aac**: ^{1}H NMR δ 0.25 (9 H, s, Me$_3$SiSi), 0.28 (9 H, s, Me$_3$SiC), 0.80–0.88 (≈4 H, m, CH$_2$ of Et), 1.00–1.14 (≈6 H, m, CH$_3$ of Et), 0.21 (1 H, s, SiCH), 1.6–2.0 (≈15 H, br, Ad); ^{13}C NMR δ 1.18 (Me$_3$SiSi), 5.13 (*Me*$_3$SiC), 6.17, 7.77 (CH$_2$ of Et), 9.17, 9.57 (CH$_3$ of Et), 29.56 (CH of Ad), 28.55 (SiCH), 36.83 (q C of Ad), 36.69, 45.78 (CH$_2$ of Ad); ^{29}Si NMR δ −15.96 (Me$_3$*Si*Si), −15.81 (Et$_2$Si), −0.49 (Me$_3$SiC).

Reaction of Silene 2aa and EtMgBr in THF. Silene **2aa** was made by photolyzing 0.4 g (0.001 mol) of the acylsilane **1aa** in THF. When photolysis was complete, 0.8 mL (1.2 M, 2 equiv) of EtMgBr in Et$_2$O was added (method I). The overnight reaction was quenched by working up with dilute acid. The product mixture, according to its NMR spectra, was **6aac** and **7aac** in a ratio of 1:10.

Reaction of Silene 2aa and PhCH$_2$MgBr in Ether. Preparation of 6aad and 7aad. A 1.1 M PhCH$_2$MgBr solution was made from 0.50 g of Mg and 2 mL of PhCH$_2$Br in 15 mL of ether. To a silene solution made from the photolysis of 1.12 g of acylsilane **1aa** was added 2.6 mL of the Grignard reagent (method I). The overnight reaction was quenched by dilute acid. The product mixture, an oil, was found to contain **6aad** and **7aad** in a 3:1 ratio. These components were best separated by chromatography using hexanes, where the first fraction was **6aad** and the second fraction was **7aad**. These were further purified by recrystallization from acetone. **6aad**: mp 77–78 °C. Anal. Calc for C$_{27}$H$_{50}$Si$_4$O: C, 64.47; H, 10.02. Found: C, 64.32; H, 10.08. ^{1}H NMR: δ 0.11 (9 H, s, Me$_3$SiSi, J_{CH} = 6.6 Hz), 0.17 (9 H, s, Me$_3$SiC, J_{CH} = 6.4 Hz), 0.33 (9 H, s, Me$_3$SiO), 0.64 (1 H, s, SiCH), 1.64 (6 H, br t, CH$_2$ of Ad), 1.81 (6 H, br d, CH$_2$ of Ad), 1.92 (3 H, br m, CH of Ad), 2.46 (1 H, d, CH$_2$ of benzyl, J_{HH} = 14 Hz), 2.63 (1 H, d, CH$_2$ of benzyl, J_{HH} = 14 Hz), 7.02–7.24 (5 H, m, Ph); ^{13}C NMR δ 0.24 (Me$_3$SiSi), 2.75 (*Me*$_3$SiC), 4.93 (Me$_3$SiO), 29.44 (CH of Ad), 30.95 (CH$_2$ of benzyl), 34.18 (SiCH), 36.13 (q C of Ad), 36.69, 45.69 (CH$_2$ of Ad), 124.88 (*p*-CH of Ph), 128.61, 129.48 (*m*-, *o*-CH of Ph), 140.44 (ipso C of Ph); ^{29}Si NMR δ −20.43 (Me$_3$*Si*Si), −1.61 (Me$_3$SiC), 5.36 (Me$_3$SiO), 6.50 (PhCH$_2$SiO); MS *m/z* 502 (0.3, M$^+$), 487 (15, M$^+$ − Me), 429 (100, M$^+$ − Me$_3$Si), 411 (49, M$^+$ − PhCH$_2$), 281 (11, Me$_3$SiO(Me$_3$Si)PhCH$_2$Si$^+$), 73 (53, Me$_3$Si$^+$). Calc for C$_{26}$H$_{47}$Si$_4$O, (M − Me)$^+$: *m/z* 487.2704. Found: *m/z* 487.2710. **7aad** (viscous oil): ^{1}H NMR δ 0.01 (9 H, s, Me$_3$SiSi), 0.39 (9 H, s, Me$_3$SiC), 0.72 (1 H, s, SiCH), 1.6–1.9 (≈15 H, br, Ad), 2.44 (1 H, d, CH$_2$ of benzyl, J_{HH} = 14.6 Hz), 2.49 (1 H, d, CH$_2$ of benzyl, J_{HH} = 13.8 Hz), 2.73 (1 H, d, CH$_2$ of benzyl, J_{HH} = 14.6 Hz), 2.75 (1 H, d, CH$_2$ of benzyl, J_{HH} = 13.8 Hz), 7.01–7.15 (≈5 H, m, Ph); ^{13}C NMR δ 1.63 (Me$_3$SiSi), 5.86 (*Me*$_3$SiC), 23.12, 26.82 (CH$_2$ of benzyl), 29.40 (CH of Ad), 29.97 (SiCH), 36.42 (q C of Ad), 36.50, 45.88 (CH$_2$ of Ad), 124.88, 124.92 (*p*-CH of Ph), 128.60, 128.60 (overlap), 129.40, 129.88 (*o*-, *m*-CH of Ph), 140.87, 140.99 (ipso C of Ph); ^{29}Si NMR: δ −15.02 (Me$_3$*Si*Si), −13.21 ((PhCH$_2$)$_2$Si), −0.44 (Me$_3$SiC).

Cophotolysis of the Acylsilane 1aa with PhCH$_2$MgBr in Ether. To 0.99 g (0.002 mol) of (1-adamantylcarbonyl)tris(trimethylsilyl)silane (**1aa**) in 5 mL of ether was added 1.6 mL of a 1.7 M PhCH$_2$MgBr solution (method II). The mixture was photolyzed at room temperature for 2 days and then worked up as usual. The oil was found to contain **6aad** and **7aad** in a 3:1 ratio.

Reaction of Silene 2aa and PhMgBr in Ether. Formation of 6aae and 7aae. PhMgBr was made from 0.63 g of Mg and 2.2 mL of PhBr in 15 mL of ether. The Grignard reagent (1.8 mL, ≈1.4 M, 1.2 equiv) was added to 0.82 g (0.002 mol) of preformed adamantylsilene from the photolysis of the corresponding acylsilane in ether (method I). After reaction overnight, the NMR spectrum of the oily product showed that it was a 1:2 mixture of **6aae** and **7aae**. **6aae**: mp 73–74 °C; ^{1}H NMR δ 0.18 (9 H, s, Me$_3$SiSi), 0.22 (9 H, s, Me$_3$SiC), 0.24 (9 H, s, Me$_3$SiO), 0.69 (1 H, s, SiCH), 1.69–2.04 (15 H, br, Ad), 7.16–7.25, 7.72–7.76 (5 H, m, Ph); ^{13}C NMR δ 0.09 (Me$_3$SiSi), 2.91 (Me$_3$SiC), 4.77 (Me$_3$SiO), 29.81 (CH of Ad), 31.91 (SiCH), 36.75 (q C of Ad), 36.93, 46.44 (CH$_2$ of Ad), 127.70, 134.08 (*o*-, *m*-CH of Ph), 128.78 (*p*-CH of Ph), 142.92 (ipso C of Ph); ^{29}Si NMR δ −20.26 (Me$_3$*Si*Si), −2.28 (PhSiO), −1.18 (Me$_3$SiC), 7.17 (Me$_3$SiO); MS *m/z* 488 (2, M$^+$), 487 (4, M$^+$ − H), 473 (16, M$^+$ − Me), 415 (100, M$^+$ − Me$_3$Si), 267 (53, Me$_3$SiOMe$_3$SiPhSi$^+$), 209 (42), 193 (40), 147 (45), 135 (75, Ad$^+$). **7aae**: mp 133 °C. Anal. Calc for C$_{29}$H$_{44}$Si$_3$: C, 73.08, H. 9.24. Found: C, 72.37; H, 9.17. ^{1}H NMR: δ 0.06 (9 H, s, Me$_3$SiSi), 0.20 (9 H, s, Me$_3$SiC), 1.00 (SiCH), 1.64, 1.94 (15 H, br, Ad), 7.14–7.28, 7.577–7.62, 7.94–7.99 (≈10 H, m, Ph); ^{13}C NMR δ 0.24 (Me$_3$SiSi), 5.28 (*Me*$_3$SiC), 29.51 (CH of Ad), 31.85 (SiCH), 36.552, 46.51 (CH$_2$ of Ad), 36.82 (q C of Ad), 127.84, 128.36, 135.39, 137.02 (*o*-, *m*-CH of Ph), 128.29, 129.05 (*p*-CH of Ph), 137.90, 140.16 (ipso C of Ph); ^{29}Si NMR δ −19.36 (Ph$_2$Si), −15.59 (Me$_3$*Si*Si), 0.74 (Me$_3$SiC); MS *m/z* 476 (2, M$^+$), 461 (10, M$^+$ − Me), 403 (100, M$^+$ − Me$_3$Si), 326 (24, M$^+$ − Me$_3$Si − Ph), 267 (15), 255 (15, Me$_3$SiPh$_2$Si$^+$), 197 (26), 135 (33, Ad$^+$), 73 (22, Me$_3$Si$^+$). Calc for C$_{29}$H$_{44}$Si$_3$: *m/z* 476.2751. Found: *m/z* 476.2754.

Cophotolysis of (1-Adamantylcarbonyl)tris(trimethylsilyl)silane (1aa) and PhMgBr in Ether. A solution of the acylsilane (0.62 g, 0.0015 mol) in 4 mL of Et$_2$O was cophotolyzed overnight with 1.2 mL of PhMgBr in Et$_2$O (≈1.4 M, 1.1 equiv) following method II. After workup, the product mixture was found to be **6aae** and **7aae** in a 1:2 ratio. The mixture was separated by preparative thin-layer chromatography using hexanes. The first fraction, after removal of solvent, afforded a white solid, found to be **6aae** by NMR spectroscopy. The second fraction yielded large white crystals, shown to be **7aae**. When the initial product mixture was dissolved in hexanes, a white solid came out of solution; this solid was also found to be crystals of **7aae**.

Cophotolysis of Acylsilane 1aa and PhMgBr in Pentanes. PhMgBr in ether (2 mL, 1.7 M, 0.0034 mol), together with 0.42 g of (1-adamantylcarbonyl)tris(trimethylsilyl)silane, was pumped on the vacuum line to remove most of the solvent. To the residue was added 4 mL of pentanes, and the inhomogeneous mixture was photolyzed for 3$^1/_2$ days with periodic stirring (method II). The ^{13}C NMR spectrum of the product mixture showed that it consisted of **6aae** and **7aae** in a 1:1 ratio.

Cophotolysis of Pivaloyltris(trimethylsilyl)silane (1ab) and MeMgBr in Ether. Pivaloyltris(trimethylsilyl)silane (**1ab**) (0.30 g, 0.0009 mol) in 3 mL of Et$_2$O was cophotolyzed with 0.4 mL (1.3 equiv) of 3 M MeMgBr (method II). After overnight photolysis, workup gave an oil, which was purified by radial chromatography with hexanes. The ^{13}C NMR spectrum of the oil showed that it was a 4:1 mixture of **6aba** and **7aba**. **6aba**: ^{1}H NMR δ 0.15 (9 H, s, Me$_3$SiSi), 0.20 (9 H, s, Me$_3$SiC), 0.25 (9 H, s, Me$_3$SiO), 0.47 (3 H, s, MeSiO), 0.54 (1 H, s, SiCH), 1.14 (9 H, s, Me$_3$C); ^{13}C NMR δ −0.21 (Me$_3$SiSi), 2.92 (Me$_3$SiC), 4.54 (Me$_3$SiO), 5.96 (MeSiO), 33.48 (SiCH), 34.14 (CMe$_3$), 34.24 (C*Me*$_3$); ^{29}Si NMR −20.97 (Me$_3$*Si*Si), −0.79 (Me$_3$SiC), 6.53 (Me$_3$SiO), 6.60 (MeSiO). **7aba**: ^{1}H NMR δ 0.18 (Me$_3$SiSi), 0.19 (SiCH), 0.21 (Me$_3$SiC), 0.23, 0.29 (MeSi), 1.10 (CMe$_3$); ^{13}C NMR δ −0.55 (Me$_3$SiSi), 0.34, 1.80 (MeSi), 4.66 (Me$_3$SiC), 30.26 (SiCH), ≈34.2 (Me$_3$*C*), 34.16 (*Me*$_3$C); ^{29}Si NMR δ −18.46 (Me$_3$*Si*Si), −16.36 (Me$_2$Si), 0.04 (Me$_3$SiC).

Cophotolysis of Acylsilane 1ba with MeMgBr in Ether. Formation of 6baa, 7baa, and Carbinol 10baa. A solution of (1-adamantylcarbonyl)phenylbis(trimethylsilyl)silane (**1ba**) (0.33 g, 0.0008 mol) in 2 mL of Et$_2$O was cophotolyzed with 0.3 mL of 3 M MeMgBr (1.1 equiv) overnight (method II). After workup, NMR spectroscopy showed the product mixture to be **6baa**, **7baa**, and **10baa**, the carbinol formed by direct addition of the Grignard reagent to the carbonyl group of the acylsilane, in a 3:1:1 ratio. The mixture was separated by preparative thin-layer chromatography using hexanes. The first and major fraction yielded a solid product, **6baa**, further purified by crystallization from a mixture of hexanes and ethyl acetate, in the form of large colorless needles. **6baa**: mp 97 °C. Anal. Calc for $C_{24}H_{42}Si_3O$: C, 66.92; H, 9.84. Found: C, 66.76; H, 9.74. ^{1}H NMR δ 0.04 (9 H, s, Me$_3$SiC), 0.32 (9 H, s, Me$_3$SiO), 0.67 (3 H, s, MeSiO), 0.72 (1 H, s, SiCH), 1.54, 1.76 (6 H, br, CH$_2$ of Ad), 1.82 (3 H, br, CH of Ad), 7.15–7.22, 7.58–7.63 (m, Ph); ^{13}C NMR δ 2.24 (*Me*$_3$SiC), 4.39 (MeSiO), 4.65 (Me$_3$SiO), 29.72 (CH of Ad), 32.10 (SiCH), 36.19 (q C of Ad), 36.93, 45.58 (CH$_2$ of Ad), 127.93, 133.35 (*o*-, *m*-CH of Ph), 129.04 (*p*-CH of Ph), 143.89 (ipso C of Ph); ^{29}Si NMR δ −0.88 (MeSiO), −0.57 (Me$_3$SiC), 8.71 (Me$_3$SiO, $J_{Si-C} = 59.4$ Hz); MS *m/z* 430 (3, M$^+$), 415 (28, M$^+$ − Me), 268 (13, M$^+$ − Me$_3$SiOSiMe$_3$), 209 (100, Me$_3$SiOPhMeSi$^+$), 206 (61, Ad-CHSiMe$_2$$^+$), 135 (23, Ad$^+$), 73 (33, Me$_3Si^+$). Calc for $C_{24}H_{42}Si_3O$: *m/z* 430.2543. Found: *m/z* 430.2544. **7baa**: mp 80 °C. Anal. Calc for $C_{22}H_{36}Si_2$: C, 74.14; H, 10.11. Found: C, 73.05; H, 10.13. ^{1}H NMR δ 0.12 (9 H, s, Me$_3$SiC), 0.41, 0.48 (3 H, s, MeSi), 0.52 (1 H, s, SiCH), 1.57, 1.78, 1.85 (together 15 H, br, Ad), 7.15–7.53 (5 H, m, Ph); ^{13}C NMR δ 2.42, 4.54 (MeSi), 4.87 (*Me*$_3$SiC), 29.82 (CH of Ad), 29.82(SiCH), 36.97, 45.62 (CH$_2$ of Ad), 37.22 (q C of Ad), 127.96, 133.69 (*o*-, *m*-CH of Ph), 128.45 (*p*-CH of Ph), 143.92 (ipso C of Ph); ^{29}Si NMR δ −5.00 (PhSi), −0.81 (Me$_3$Si); MS *m/z* 355 (6, M$^+$), 341 (29, M$^+$ − Me), 205 (38), 135 (100, PhMe$_2$Si$^+$), 121 (25). Calc for $C_{22}H_{36}Si_2$: *m/z* 356.2355. Found: *m/z* 356.2395. **10baa**: ^{1}H NMR δ 0.32 (9 H, s, Me$_3$Si), 0.39 (9 H, s, Me$_3$Si), 0.98 (1 H, s, OH, exchanged with D$_2$O), 1.16 (3 H, s, MeC), 1.58–1.89 (≈15 H, br, Ad), 7.14–7.19, 7.82–7.87 (5 H, m, Ph); ^{13}C NMR δ 1.46, 1.83 (Me$_3$SiSi), 23.28 (*Me*C), 28.81 (CH of Ad), 37.14, 38.23 (CH$_2$ of Ad), 40.59 (q C of Ad), 79.45 (COH), 127.99, 137.46 (*o*-, m-CH of Ph), 128.40 (*p*-CH of Ph), 138.90 (ipso C of Ph); ^{29}Si NMR δ −33.03 (Me$_3$Si*Si*), −15.91, −15.18 (Me$_3$*Si*Si).

Cophotolysis of Acylsilane 1ba and MeMgBr in THF. A solution of the acylsilane **1ba** (0.28 g, 0.0007 mol) in 3 mL of THF was cophotolyzed overnight with 0.5 mL (3 M, 2.2 equiv) of MeMgBr in ether (method II). After workup TLC showed two major products. The mixture was separated by radial chromatography using hexanes to obtain a nonpolar fraction, identified as **7baa** by its NMR spectra. The second, more polar fraction was eluted with 15% CH$_2$Cl$_2$ and was found to be **10baa**.

Reaction of Silene 2ba and EtMgBr in Ether. A solution of (1-adamantylcarbonyl)phenylbis(trimethylsilyl)silane (0.32 g, 0.0008 mol) in 3 mL of ether was photolyzed at −78 °C for 2^1/$_2$ days to convert the acylsilane **1ba** to the silene **2ba** without causing further photoisomerizations to other silene species.[9] To this silene solution was added 0.5 mL (2.68 M, 1.7 equiv) of EtMgBr in ether at −78 °C (method I), and after the solution was left to react at −78 °C overnight, and workup, the ^{13}C NMR spectrum of the oily product mixture indicated the presence of **6bac** and **7bac** in a 5:1 ratio. **6bac**: ^{1}H NMR δ 0.29 (9 H, s, Me$_3$SiC), 0.38 (9 H, s, Me$_3$SiO), 0.80 (1 H, s, SiCH), 1.25 (5 H, br, Et), 1.78, 2.02–2.07 (together 15 H, br, Ad), 7.32–7.39, 7.75–7.80 (5 H, m, Ph); ^{13}C NMR δ 2.18 (Me$_3$SiC), 4.52 (Me$_3$SiO), 7.90 (CH$_3$ of Et), 11.63 (CH$_2$ of Et), 29.61 (CH of Ad), 32.08 (SiCH), 36.31 (q C of Ad), 36.83, 45.58 (CH$_2$ of Ad), 127.80, 133.98 (*o*-, *m*-CH of Ph), 128.95 (*p*-CH of Ph), 142.16 (ipso C of Ph); ^{29}Si NMR (CDCl$_3$) δ −1.37 (Me$_3$SiC), −1.11 (PhSi), 7.47 (Me$_3$SiO). **7bac**: ^{1}H NMR δ 0.35 (≈9 H, s, Me$_3$Si), 0.73 (≈1 H, s, SiCH), 1.1–1.3 (≈10 H, m, Et), 1.6–2.2 (≈15 H, br, Ad), 7.3–7.8 (≈5 H, m, Ph); ^{13}C NMR δ 4.89 (Me$_3$Si), 6.93, 8.24 (CH$_2$ of Et), 8.16, 8.56 (CH$_3$ of Et), 29.61 (CH of Ad), 29.92 (SiCH), 36.83 (q C of Ad), 36.74, 45.78 (CH$_2$ of Ad), 127.80, 134.92 (*o*-, *m*-CH of Ph), 128.49 (*p*-CH of Ph), 140.87 (ipso C of Ph); ^{29}Si NMR δ −2.07 (PhSi), −1.04 (Me$_3$Si).

Reaction of Acylsilane 1ba with EtMgBr. Synthesis of Carbinol 9ba. To 0.30 g (0.0007 mol) of (1-adamantylcarbonyl)phenylbis(trimethylsilyl)silane in 3 mL of Et$_2$O was added 0.3 mL of EtMgBr (≈2.7 M, 1.1 equiv). An immediate reaction occurred, and when the reaction mixture was worked up, the oil isolated was found to be mainly the carbinol **9ba** formed from the reduction of the acylsilane. **9ba**: ^{1}H NMR δ 0.46 (9 H, s, Me$_3$Si), 0.56 (9 H, s, Me$_3$Si), 1.23 (1 H, s, OH), 1.6–2.1 (≈15 H, br, Ad), 3.92 (1 H, s, C*H*OH), 7.2–7.4, 7.7–7.9 (≈5 H, m, Ph); ^{13}C NMR δ 0.82, 1.71 (Me$_3$SiSi), 29.23 (CH of Ad), 37.40 (q C of Ad), 37.69, 41.10 (CH$_2$ of Ad), 78.40 (CHOH), 128.79, 136.73 (*o*-, *m*-CH of Ph), 129.00 (*p*-CH of Ph), 138.48 (ipso C of Ph).

Reaction of Benzoyltris(trimethylsilyl)silane (1ac) with MeMgBr. Synthesis of 10aca. Benzoyltris(trimethylsilyl)silane (0.99 g, 0.003 mol) in 5 mL of Et$_2$O was combined with 1 mL (≈1.1 equiv) of MeMgBr. After reaction for 2 days at room temperature, workup in dilute acid, followed by separation and solvent removal, yielded a yellow solid. This compound was recrystallized from hexanes in the cold to afford white crystals of **10aca**: ^{1}H NMR δ 0.22 (27 H, s, Me$_3$Si), 0.98 (1 H, br, OH), 1.60 (3 H, s, CMe), 6.96–7.38 (≈5 H, m, Ph); ^{13}C NMR δ 2.33 (Me$_3$Si), 33.51 (C*Me*), 73.75 (C–OH), 124.57, 128.19 (*o*-, *m*-C of Ph), 125.74 (*p*-C of Ph), 151.89 (ipso C of Ph); ^{29}Si NMR δ −54.85 (Me$_3$Si*Si*), −13.09 (Me$_3$*Si*Si); MS *m/z* 367 (46, M$^+$ − H), 351 (60), 247 (76, (Me$_3$Si)$_3$Si$^+$), 173 (98), 147 (73), 121 (100).

Reaction of Silene 2aa and Me$_3$SiOLi in Ether. To 2.4 mL (0.011 mol) of Me$_3$SiOSiMe$_3$ in 2 mL of ether was added 6.6 mL of MeLi (1.5 M, 0.009 mol). The ether was pumped off and replaced with 15 mL of THF. A Gilman test[21] of the mixture was positive at this point. The solution was allowed to reflux overnight under argon. After cooling, the reaction mixture was a golden yellow color and gave a negative Gilman test. This Me$_3$SiOLi solution was about 0.67 M. To 0.50 g (0.0012 mol) of preformed silene **2aa** in ether was added 4 mL (2.2 equiv) of the Me$_3$SiOLi reagent. After reaction overnight, the mixture was worked up and purified by radial chromatography using hexanes. The NMR spectra indicated that **7aaf** constituted over 90% of the product. **7aaf**: ^{1}H NMR δ 0.26, 0.27, 0.28, 0.36 (each 9 H, s, Me$_3$Si), 0.38 (1 H, s, SiCH), 1.6–2.0 (≈15 H, br, Ad); ^{13}C NMR δ −0.30 (Me$_3$Si–Si), 2.63 (Me$_3$Si–C), 2.89, 4.69 (Me$_3$SiO), 29.50 (CH of Ad), 36.85, 45.37 (CH$_2$ of Ad), 37.04 (SiCH), 40.33 (q C of Ad); ^{29}Si NMR δ −23.71 (*Si*(OSiMe$_3$)$_2$), −20.15 (Me$_3$*Si*Si), −1.60 (Me$_3$SiC), 5.10, 5.87, (Me$_3$SiO); MS *m/z* 500 (13, M$^+$), 485 (18, M$^+$ − Me), 427 (100, M$^+$ − Me$_3$Si), 279 (19, (Me$_3$SiO)$_2$Me$_3$SiSi$^+$), 135 (58, Ad$^+$), 73 (78, Me$_3$Si$^+$).

Reaction of *tert*-Butyllithium with Acylsilane 1aa. Formation of Bis(trimethylsilyl)-*tert*-butyl(1-adamantylmethyl)silane (28a). A solution of 4.11 g (0.01 mol) of acylsilane **1aa** in 10 mL of THF at −20 °C was treated with 23 mL of 2.6 M (3 equiv) of *tert*-butyllithium in pentane. The exothermic reaction evolved a gas, trapped in bromine in CCl$_4$ and shown to be isobutene by the dibromide isolated. After the mixture was stirred overnight, workup gave a viscous oil, which after chromatography on silica gel and recrystallization from hexane and ethyl acetate gave a colorless solid **28a** in 92% yield. **28a**: mp 100–101 °C. Anal. Calc for $C_{20}H_{44}Si_3$: C, 65.18; H, 11.95. Found: C, 65.34; H, 11.70. ^{1}H NMR: δ 0.31 (s, 18 H, Me$_3$Si), 1.02 (s, 2 H, CH$_2$Ad), 1.13 (s, 9 H, CMe$_3$), 1.60, 1.65, 1.94 (m, 15 H, Ad); ^{13}C NMR δ 2.30 (Me$_3$Si), 20.66 (CH$_2$Ad), 29.54 (Me$_3$*C*), 30.17 (*Me*$_3$C), 31.31 (CH Ad), 32.73 (q C Ad), 36.96, 46.27 (CH$_2$ Ad); ^{29}Si NMR δ −15.92 (Me$_3$Si), −33.37 (Me$_3$Si*Si*).

Reaction of *tert*-Butyllithium with Acylsilane 1ab. Formation of 28b. Following the above procedure, the pivaloylsilane **1ab** (3.32 g, 0.01 mol) in 10 mL of ether was treated with 23 mL (3 equiv) of *tert*-butyllithium in pentane. A gas (isobutene) was evolved immediately. After the mixture was stirred overnight, workup gave a waxy solid, **24**, purified by sublimation. **28b**: mp 108–110 °C. Anal. Calc for $C_{15}H_{38}Si_3$: C, 59.51; H, 12.65. Found: C, 59.56; H, 12.59. ^{1}H NMR: δ 0.30 (s, 9 H, Me$_3$Si), 0.90 (s, 2 H, C*H*$_2$CMe$_3$), 1.07 (s, 9 H, *Me*$_3$CSi), 1.23 (s, 9 H, *Me*$_3$CC); ^{13}C NMR δ 2.21 (Me$_3$Si), 20.69 (*C*H$_2$CMe$_3$), 29.01 (Me$_3$*C*Si), 29.18 (Me$_3$*C*C), 31.14 (*Me*$_3$CSi), 33.60 (*Me*$_3$CC); ^{29}Si NMR δ −16.10 (Me$_3$Si), −32.18 (Me$_3$Si*Si*); MS *m/z* 302 (M$^+$, 4), 245 (M − CMe$_3$$^+$, 30), 73 (Me$_3Si^+$, 100), 57 (Me$_3C^+$, 70). Workup of the reaction with D$_2$O gave the monodeutero analogue of **28b**, *m/z* 303, where the ^{1}H NMR signal at 0.90 ppm corresponded in intensity to only one proton and a ^{13}C NMR signal at 20.69 ppm had diminished intensity.

Experiments To Elucidate the Mechanism of the Reaction. Reactions of Silene 2aa with Excess MeMgBr. A solution of the (adamantylacyl)silane **1aa** (0.43 g, 0.001 mol) in 4 mL of Et$_2$O was cophotolyzed overnight at room temperature with 1.1

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[21] Gilman, H.; Schulze, F. *J. Am. Chem. Soc.* **1925**, *47*, 2002.

mL of MeMgBr (3 M, 3 equiv). After workup NMR spectroscopy indicated the formation of a 3:1 mixture of **6aaa** and **7aaa**. When preformed adamantylsilene **2aa** was added dropwise to a 6-fold excess of Grignard reagent, which was allowed to react at -4 °C overnight, the same 3:1 ratio of products was obtained.

Characterization of Intermediates 15 and 16 from Silene 2aa and MeMgBr in Ether. The overnight cophotolysis of 0.25 g (0.0006 mol) of (1-adamantylcarbonyl)tris(trimethylsilyl)silane (**1aa**) with 0.2 mL of MeMgBr (3 M, 1 equiv) in 3 mL of $\mathrm{Et_2O}$ produced the desired intermediates. Most of the ether was removed by pumping on the vacuum line. The residue was dissolved in 0.5 mL of toluene-d_8. Part of this sample was worked up in dilute acid and verified by NMR spectroscopy to be the expected 3:1 mixture of **6aaa** and **7aaa**. The rest of the sample was transferred to an NMR tube and was characterized by NMR spectroscopy. Three species were observed in the NMR spectra, which were attributed to the structures **15**, **16**, and $\mathrm{Me_3SiOMgBr}$, which was an expected byproduct. **15**: ^{13}C NMR ($\mathrm{C_6D_5CD_3}$ + residual $\mathrm{Et_2O}$) δ 1.02 ($\mathrm{Me_3SiSi}$), 3.26 ($\mathit{Me}_3\mathrm{SiC}$), 7.46 (MeSiO), 8.74 ($\mathrm{Me_3SiO}$), 30.59 (CH of Ad), 36.92 ($\mathrm{CH_2}$ of Ad), 38.54 (q C of Ad), 50.34 ($\mathrm{CH_2}$ of Ad); ^{29}Si NMR δ −18.69 ($\mathrm{Me_3}\mathit{Si}\mathrm{Si}$), −17.24 (MeSiO), −8.99, −6.89 ($\mathit{Me}_3\mathrm{SiC/Me_3SiO}$). **16**: ^{13}C NMR δ 1.68 ($\mathrm{Me_3SiSi}$), 2.81, 4.51 (MeSi), 8.69 ($\mathit{Me}_3\mathrm{SiC}$), 30.72 (CH of Ad), 37.12 ($\mathrm{CH_2}$ of Ad), 39.53 (q C of Ad), 48.33 ($\mathrm{CH_2}$ of Ad); ^{29}Si NMR δ −25.85 ($\mathrm{Me_3}\mathit{Si}\mathrm{Si}$), −20.04 ($\mathrm{Me_2Si}$), −7.59 ($\mathrm{Me_3Si{-}C}$). $\mathrm{Me_3SiOMgBr}$: ^{13}C NMR δ 7.60; ^{29}Si NMR δ $\mathrm{Me_3SiOMgBr}$ δ −9.76.

Intermediate 16 from Reaction in THF. The precursor of **7aaa** was generated by the overnight cophotolysis of 0.30 g (0.0007 mol) of (1-adamantylcarbonyl)tris(trimethylsilyl)silane (**1aa**) with 0.5 mL of MeMgBr (3 M, 2 equiv) in 4 mL of THF. After removal of the solvent the residue of **16** and $\mathrm{Me_3SiOMgBr}$ was dissolved in toluene-d_8 and characterized by NMR spectroscopy. Part of the sample was worked up in dilute acid, and the NMR spectrum showed the presence of the expected compound **7aaa** with no trace of **6aaa** present. **16**: ^{1}H NMR ($\mathrm{C_6D_5CD_3}$ + residual THF) δ 0.14 (9 H, s, $\mathrm{Me_3SiSi}$), 0.29 (9 H, s, $\mathrm{Me_3SiC}$), 0.37 (3 H, s, MeSi), 0.45 (3 H, s, MeSi), 1.5–2.1 (br, Ad, overlap with THF); ^{13}C NMR δ 1.72 ($\mathrm{Me_3SiSi}$), 3.17 (SiMe, has fine structure), 4.20 (MeSi), 8.67 ($\mathit{Me}_3\mathrm{SiC}$), 30.63 (CH of Ad), 37.16 ($\mathrm{CH_2}$ of Ad), 39.05 (q C of Ad), 48.07 ($\mathrm{CH_2}$ of Ad); ^{29}Si NMR δ −26.11 ($\mathrm{Me_3}\mathit{Si}\mathrm{Si}$), −20.10 ($\mathrm{Me_2Si}$), −8.09 ($\mathrm{Me_3SiC}$). $\mathrm{Me_3SiOMgBr}$: ^{13}C NMR δ 7.76; ^{29}Si NMR δ −9.80.

Attempted Isomerization of 15 to Its Diastereomer. A sample of (1-adamantylcarbonyl)tris(trimethylsilyl)silane (**1aa**) (0.22 g, 0.0005 mol) was cophotolyzed with 0.25 mL of MeMgBr (3 M, 1.5 equiv) in 3 mL of ether. After overnight photolysis, the ether was removed by pumping, and the residue was redissolved in THF. A sample worked up immediately showed that it was a 3:1 mixture of **6aaa** and **7aaa** as expected. The remaining unhydrolyzed material was allowed to stand in THF overnight. The Gilman test[21] of the material was negative, indicating that the excess Grignard reagent had been consumed. After workup, the NMR spectrum of the product had signals due to **6aaa** and **7aaa**, and in addition there was also another set of signals belonging to a new compound, **6′aaa**, in the overall ratio 1:1:1, believed to be a diastereomer of **6aaa**. **6′aaa**: ^{1}H NMR δ 0.16 (9 H, s, $\mathrm{Me_3SiSi}$), 0.20 ($\mathrm{Me_3SiC}$), 0.27 (9 H, s, $\mathrm{Me_3SiO}$), 0.38 (1 H, s, SiCH), 0.40 (3 H, s, MeSi), 1.6–2.0 (≈15 H, br, Ad); ^{13}C NMR δ −0.78 ($\mathrm{Me_3SiSi}$), 2.25 ($\mathit{Me}_3\mathrm{SiC}$), 4.63 ($\mathrm{OSiMe_3}$), 5.93 (MeSiO), 29.64 (CH of Ad), 33.77 (SiCH), 36.35 (q C of Ad), 36.92, 45.41 ($\mathrm{CH_2}$ of Ad); ^{29}Si NMR δ −20.02 ($\mathrm{Me_3}\mathit{Si}\mathrm{Si}$), −1.51 ($\mathrm{Me_3SiC}$), 3.85 ($\mathrm{Me_3SiO}$), 6.97 (MeSiO).

Low-Temperature Quenching Experiments. General Procedures. All of the low-temperature quenching experiments were performed by using MeMgBr and (1-adamantylcarbonyl)-tris(trimethylsilyl)silane (**1aa**) as starting materials. A typical procedure involved photolysis of a solution of the acylsilane (300–400 mg) in dried $\mathrm{Et_2O}$ in a Schlenk tube at room temperature overnight and then in a −78 °C bath for about 15 h. The adamantylsilene **2aa** thus obtained was kept for 15–30 min in a cold bath at the desired temperature in order to reach the temperature of the bath. To the silene solution was added by syringe 1.1 equiv of MeMgBr with vigorous stirring. When the reaction time was up, the reaction mixture was quenched either by adding 5% HCl or by adding $\mathrm{H_2O}$ in THF followed by the addition of dilute acid to neutralize the aqueous layer. Separation of the layers was facilitated by the addition of NaCl and hexanes to the workup mixture. After removal of solvent on the rotoevaporator, the product mixtures obtained were analyzed by NMR spectroscopy. Most of the ratios of products were estimated by the signal intensities in the ^{13}C NMR spectra, due to serious overlapping of the ^{1}H signals.

Reaction at −78 °C for 15 min. The reaction mixture was stirred vigorously, but the silene and MeMgBr were not completely soluble in the ether. After 15 min, the reaction was quenched by the addition of dilute acid. The product mixture was found to consist mostly of the adamantylsilene–water adduct, **18**. **18**: ^{1}H NMR δ 0.20 (9 H, s, $\mathrm{Me_3SiSi}$), 0.27 (9 H, s, $\mathrm{Me_3SiSi}$), 0.30 (9 H, s, $\mathrm{Me_3SiO}$), 1.37 (1 H, s, OH), 1.67, 1.96 (≈15 H, br, Ad), 3.69 (1 H, s, $\mathrm{C}\mathit{H}\mathrm{OSiMe_3}$); ^{13}C NMR δ −1.01, −0.49 ($\mathrm{Me_3SiSi}$), 0.78 ($\mathrm{Me_3SiO}$), 28.77 (CH of Ad), 37.19 ($\mathrm{CH_2}$ of Ad), 37.38 (q C of Ad), 41.16 ($\mathrm{CH_2}$ of Ad), 82.20 ($\mathit{C}\mathrm{HOSiMe_3}$); ^{29}Si NMR δ −18.36, −17.99 ($\mathrm{Me_3}\mathit{Si}\mathrm{Si}$), 5.65 (SiOH), 16.14 ($\mathrm{OSiMe_3}$).

Reaction at −30 °C for 15 or 45 min. The product mixture obtained consisted mainly of **18**. Similar results were obtained when the reaction time was extended to 45 min.

Reaction at −23 °C for 2 min. After stirring of the reaction mixture for 2 min, acidic workup gave mainly **19** (due to acid hydrolysis of **18**), together with **6aaa**, in a 6:1 ratio. **19**: ^{1}H NMR δ 0.28 (≈18 H, s, $\mathrm{Me_3Si}$ overlap), 1.48 (1 H, br, OH), 1.65–1.69, 1.96 (≈16 H, br m, Ad and OH), 3.32 (1 H, s, $\mathrm{C}\mathit{H}\mathrm{OH}$); ^{13}C NMR δ −1.06, −0.79 ($\mathrm{Me_3Si}$), 28.66 (CH of Ad), 37.19 ($\mathrm{CH_2}$ of Ad), 37.53 (q C of Ad), 40.08 ($\mathrm{CH_2}$ of Ad), 78.04 (CHOH); ^{29}Si NMR δ −18.43 (two $\mathrm{Me_3}\mathit{Si}\mathrm{Si}$), 5.07 (SiOH). When the time was extended to 4 min, the major product was **19** along with **6aaa** in an approximately 5:1 ratio. When the reaction time was extended to 10 min, NMR spectroscopy showed a complex reaction mixture consisting of **6aaa** + **7aaa** and **18** + **19** in a 1:2.7 ratio.

Reaction at −7 °C for 2–3 min. The reaction mixture was stirred vigorously for 2–3 min, after which a solution of $\mathrm{H_2O}$ and THF was added to quench the reaction. The oil obtained on workup was shown by NMR spectroscopy to be a mixture of the silene–water adduct 18 and **6aaa** and **7aaa** in a ratio of 6:3:1. When the time was extended to 15 min, over 95% of the product mixture thus obtained was shown by ^{13}C NMR spectroscopy to be **6aaa** and **7aaa**.

X-ray Structural Determination. The compound proved to be stable to air exposure. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The ω–2θ scan technique was applied with variable scan speeds. The intensities of three standard reflections measured every 2 h showed no decay. Data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods. C, O, and Si atoms were refined anisotropically by full-matrix least squares to minimize $\sum w(F_o - F_c)^2$, where $w^{-1} = \sigma^2(F) + gF^2$. Hydrogen atoms were positioned on geometric grounds (C–H = 0.95 Å) and an overall hydrogen atom thermal parameter refined to a value of 0.087 (2) Å^2. Crystal data, data collection, and least-squares parameters are listed in Table II. All calculations were performed by using SHELX76[22] and SHELXS86[23] on a PDP11/23 and an Apollo computer. An ORTEP[24] diagram of the structure is presented in Figure 1.

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Supplementary Material Available: Tables of atomic coordinates, complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates, and torsion angles (4 pages); a listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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