Reactions of Stable Silenes with Dienes and Alkenes: [2 + 2], [2 + 4], and Ene Reactions

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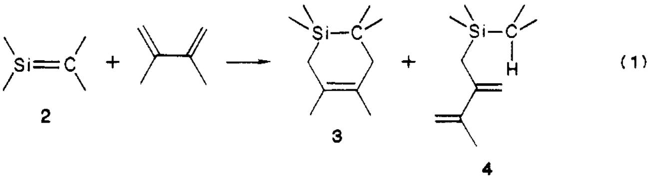
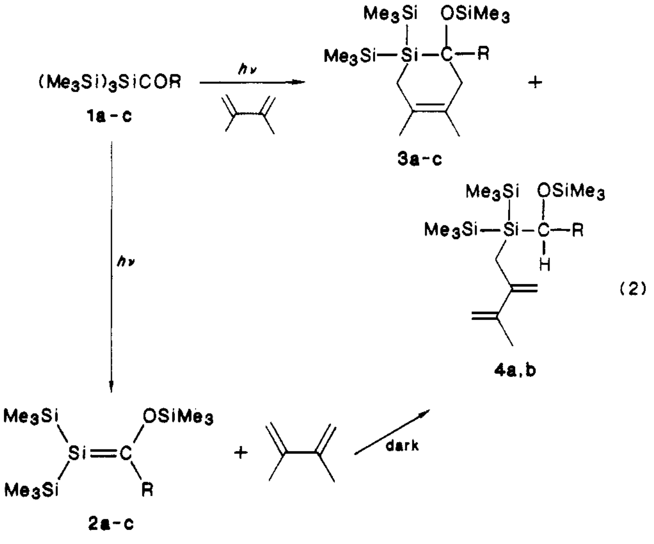
Reactions of a variety of stable silenes, $(Me_3Si)_2Si{=}C(OSiMe_3)R$, with several dienes and alkenes under photochemical or dark conditions have been studied. While [2 + 4] cycloaddition predominated with 2,3-dimethylbutadiene and cyclopentadiene, it was found that [2 + 2] cycloaddition, probably by a concerted process, was the major reaction pathway with 1,3-butadiene and a significant pathway with 1,3-cyclohexadiene. Reactions with alkenes that contained allylic hydrogen (1-octene, α-methylstyrene) gave only "ene" products, but reactions with styrene or vinylnaphthalene gave clean "dark" [2 + 2] cycloadditions. Evidence is presented that these reactions do not involve free radical processes.

Much of our knowledge of the chemistry of silenes has come from studies of highly reactive species generated at relatively high temperatures (for recent reviews see ref 1 and 2). Silenes normally form mixtures of [2 + 4] cycloaddition products and "ene" products from reaction with dienes (occasionally accompanied by [2 + 2] products), and "ene" products are the usual products from reactions with simple alkenes.[1,2] While this knowledge is important, it does not follow that reactions or mechanisms that prevail at high temperature are relevant to reactions carried out at room temperature or below with relatively "stable" silenes. Some studies of silenes with dienes and alkenes at room temperature have been described previously, including studies by ourselves,[3] by Wiberg,[4,5] by Jones,[6] and by Kumada.[7] Variable behavior, strongly dependent on the structures of both the silene and the unsaturated hydrocarbon, has been observed. This paper extends our knowledge of the behavior of representative members of the family of silenes $(Me_3Si)_2Si{=}C(OSiMe_3)R$ (derived by photolysis of acylsilanes) with representative dienes and alkenes. While all possible combinations of silene with unsaturated hydrocarbon have not been studied, it seems probable that the overall results reflect the general behavior to be expected.

Dienes

Previous studies have established that "stable" silenes **2** react with 2,3-dimethyl-1,3-butadiene at or near room temperature to give the anticipated products, the Diels–Alder cycloadduct silacyclohexene **3** as the major product, accompanied in some cases by **4**, the product of the intermolecular "ene" reaction.[3-7] The present results have shown that both **3** and **4** are formed in "dark" reactions of the silenes **2** (obtained by photolysis of related acylsilanes **1**) with the diene. Thus essentially the same mixture of Diels–Alder, **3**, and "ene" products, **4**, was obtained, regardless of whether a mixture of acylsilane and 2,3-dimethylbutadiene was cophotolyzed or whether a sample of preformed silene was treated with the diene in the dark. However, the "dark" reactions of preformed silene with the diene occurred much more rapidly (<0.5 h) than the same reactions carried out involving direct photolysis of the reagents. Evidently under the conditions employed, photochemical rearrangement of the acylsilane to the silene was the rate-controlling step.





a, R = Ad; b, R = *t*-Bu; c, R = Mes

Wiberg[4] has reported that the silene $Me_2Si{=}C(SiMe_3)_2$ normally gave about 20% of the "ene" product with 2,3-dimethylbutadiene while Kumada with the much less hindered $Me_2Si{=}CHCH_2SiMe_2Ph$ observed no "ene" product.[7] In our reactions using silenes **2a–c**, which are believed to be very sterically hindered due to the four relatively bulky groups attached to the ends of the silicon–carbon double bond, the amount of "ene" product is often about 40% of the total products. This suggests that as the steric hindrance by the silene increases, the "ene" pathway becomes relatively more favorable. The mesitylsilene[8] **2c** appears to be an exception, since despite the bulk of the mesityl group, no "ene" product was observed either with the diene or with simple alkenes (see below).

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

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

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

[4] Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141.

[5] Wiberg, N.; Wagner, G. *Chem. Ber.* **1986**, *119*, 1455, 1467.

[6] Jones, P. R.; Lee, M. E.; Lin, L. T. *Organometallics* **1983**, *2*, 1039. Jones, P. R.; Lim, T. F. O.; Pierce, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 4970.

[7] Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1978**, *149*, 37.

[8] For convenience, throughout this paper acylsilanes and their related silenes will be named on the basis of the R group present in **1** or **2**, e.g., adamantylacylsilane for **1a** and mesitylsilene for **2c**.

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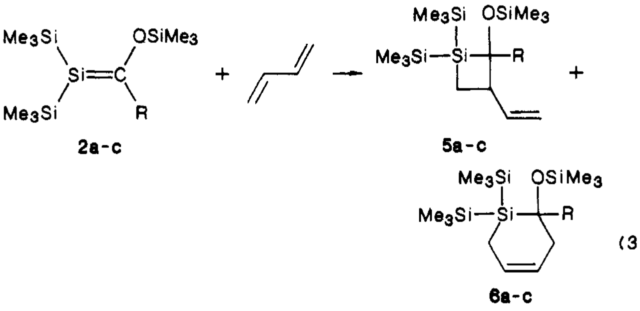
Table I[a]

reactn conditns	products and yields		
	5a (major)	**5a** (minor)	**6a**
10 °C, C_6H_6, light	42	34	24
10 °C, pentane, light	43	36	21
room temp, pentane, dark	44	37	19
10 °C, Et_2O, light	46	36	18
room temp, Et_2O, dark	45	37	18
−78 °C, Et_2O, light	54	34	12
−78 °C, Et_2O, dark	49	36	15

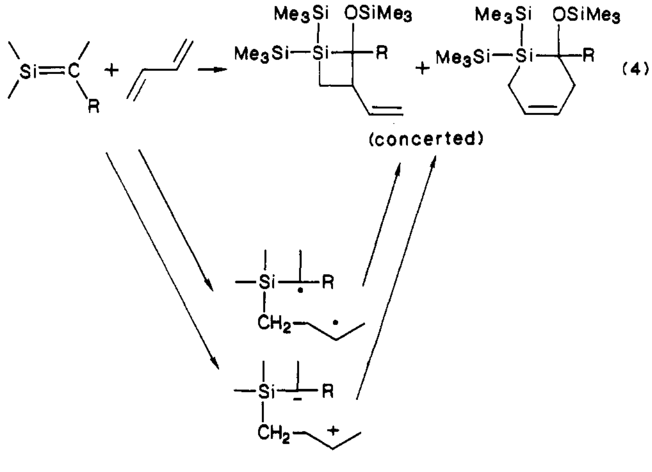
[a] Proportions of the products were determined by NMR spectroscopy.

Having reconfirmed this relatively conventional behavior of the silenes with 2,3-dimethylbutadiene, it was surprising to find that when 1,3-butadiene itself was used (eq 3), significant amounts of both [2 + 2] and [2 + 4] cycloaddition products **5** and **6** were formed. The adamantyl- and *tert*-butylsilenes gave about 80% of the [2 + 2] adducts (as an approximately 1:1 mixture of diastereomers) while the mesitylsilene gave about 25% [2 + 2] adduct (as an approximately 4:1 mixture of diastereomers) and 75% of the [2 + 4] adducts. As before, essentially the same mixture of products was formed, regardless of whether the cycloadditions occurred during photolysis or in the dark. Only one regioisomer from the [2 + 2] pathway was detected. (Jones has reported [2 + 2] cycloaddition as the major pathway from very different silenes reacting with butadiene but stated that both possible regioisomers were formed:[6] however, it is now known that only one regioisomer was formed.[9])



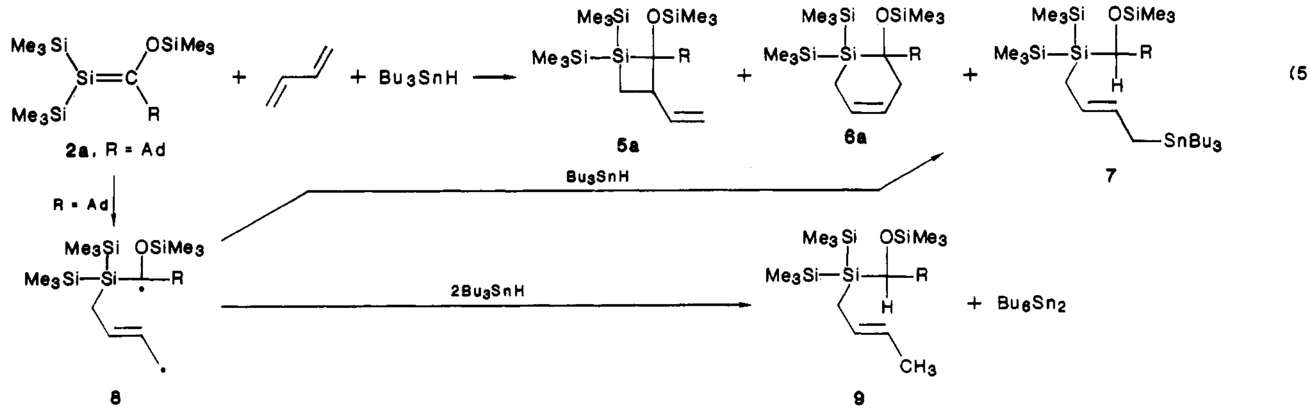
a R = Ad; b, R = *t*-Bu; c, R = Mes

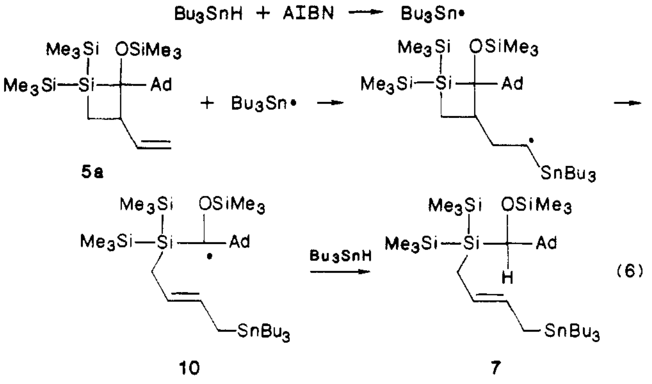
Mechanism of [2 + 2] Cycloadditions. The mechanism of these "dark" [2 + 2] cycloadditions is a matter of some interest. A concerted process is formally disallowed by Woodward–Hoffmann rules but may be possible if d-orbital participation or the dipolar character of the silicon–carbon double bond causes relaxation of the rules. Two-step processes, involving either diradical or dipolar intermediates as depicted below (eq 4), must also be considered, and such intermediates, already stabilized at the allylic end, would also be highly stabilized at the other active site when the R group was aryl in nature, so they cannot be dismissed without careful consideration.



The possibility that a diradical mechanism was involved was investigated by comparing the results of reactions of silene with butadiene in the absence and presence of excess tributyltin hydride, an efficient radical trap. Silene **2a** reacting with butadiene in the dark (eq 5) gave yields in the ratio 46:36:18 for the major:minor isomers of **5a**:**6a**, whereas in the presence of tin hydride the yields were 5:36:20 with a new compound, **7**, also being formed in 39% yield. Hence **7** was formed at the expense of the *major* isomer of **5a** only. These results are inconsistent with a diradical, **8**, being the immediate precursor of **5** and **6**, since removal of **8** by tin hydride to form **7** should effect the yields of both diastereomers of **5** equally and probably should not effect the ratio of **5**:**6**. Further, it would be anticipated that **8** might react with 2 equiv of the tin hydride yielding **9** and hexabutylditin, but neither of these species were formed. Finally, it was shown that if the reaction product mixture of **5** and **6** (formed in the absence of tin hydride) was treated with tin hydride and a trace of AIBN (eq 6), the major isomer of **5a** was destroyed and **7** was formed. Hence **7** must arise by attack of the tin radical on **5a** to form a radical which rearranges with ring opening to **10**, which then reacts with tin hydride yielding the **7** observed. In total, these experiments strongly argue against the intermediacy of a diradical like **8** in the reaction of silene **2** with butadiene.

It is more difficult to probe the possible intermediacy of a dipolar species (written here as if the silene has acted as an electrophile, consistent with previous arguments[4]) since any reagent that might intercept the dipolar species is almost certain to react vigorously with the silene.



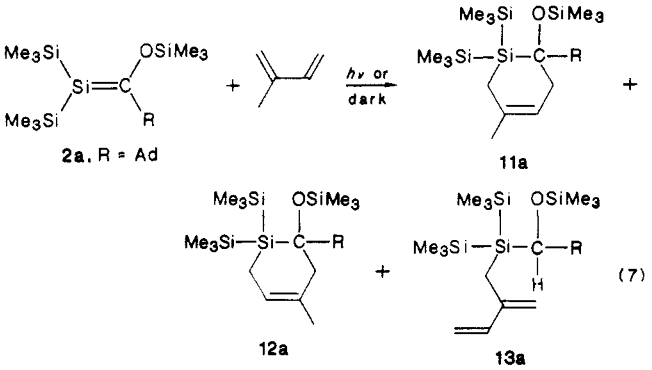


5a 10 7

However the results from a series of cycloadditions run in solvents of variable polarity (Table I) suggest that dipolar species are unimportant. Thus, a dipolar process might be expected to be favored in a more polar solvent and would be revealed through enhancement of the rate of cycloaddition or by alteration of the proportions of products. In fact, no significant change in rates and, as indicated in Table I, no significant changes in product composition were detected within the limited range of solvents that could be used. Consistent with Wiberg's observations,[4] there was some evidence that the proportion of the [2 + 4] adduct increased to a small extent at the expense of [2 + 2] adduct with increasing reaction temperature.

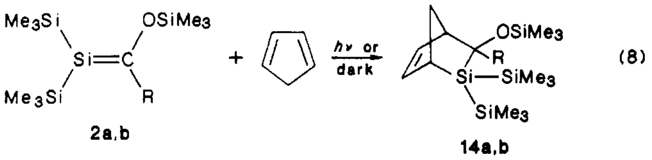
Hence, unlike the case of silene reactions with carbonyl compounds,[10] where significant evidence for a two-step dipolar process was noted, the present case appears not to involve a two-step process but is consistent with a concerted [2 + 2] process.

Other Dienes. When isoprene was used as the diene, a mixture of products was obtained including both possible [2 + 4] regioisomers **11a** and **12a** and the "ene" product **13a** (eq 7). This mixture was not easily separated, but it was possible to establish the structures and proportions of products by using NMR techniques. The two silacyclohexenes **11a** and **12a** were obtained in the ratio of about 1:3 with the "ene" product constituting about 11% of the total product. These results are in contrast to results recently reported by Wiberg[11] using a different silene, where the ratio of products whose structures corresponded to **11a** and **12a** was 66:8. Wiberg attributed the preponderance of the "meta" product to be the result of the significantly polarized Si=C bond of his silene reacting in the anticipated sense with the somewhat polarized isoprene, using the known regiochemistry of Diels–Alder coupling of isoprene with an α,β-unsaturated carbonyl compound as a model. However, whereas in the Wiberg case the regiochemistry corresponds to that of **11a** being strongly favored over **12a**, consistent with the anticipated polarization of the silene and diene, with silene **2a** the opposite regiochemistry is favored, but to a lesser extent: e.g., **11a**:**12a** = 1:3. This preference appears to be consistent both with predictions based on the steric hindrance to be expected in the transition states leading to the two products and with frontier orbital predictions. It is known from calculations on model silenes related to **2a**[12] that the larger coefficient of both the HOMO and LUMO is located on silicon (in contrast to simpler more polar silenes), so that the regiochemistry of [2 + 4] cycloaddition corresponding to **12a** appears to be somewhat favored. In the Wiberg series of relative reactivities of dienes in [2 + 4] cycloaddition reactions with his silene,[4] the order was reported to be 2,3-dimethylbutadiene > isoprene > butadiene: our results, based on yields of the [2 + 4] cycloadducts, were consistent with this order.



2a, R = Ad **11a** **12a** **13a**

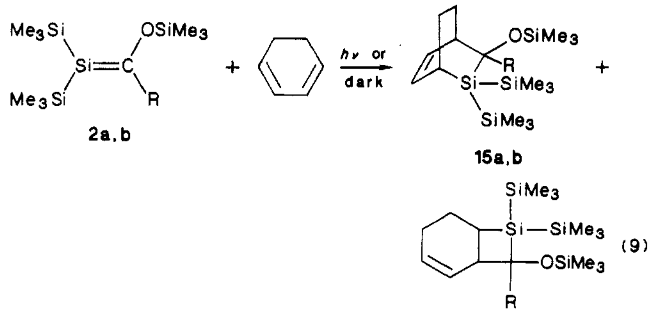
The only other dienes investigated were cyclopentadiene and 1,3-cyclohexadiene. Jones[6] reported, using cyclopentadiene with different silenes prepared under very different conditions than ours, that only [2 + 4] cycloadducts (four isomers) were formed. In our case (eq 8) only a single [2 + 4] adduct, **14**, was formed with cyclopentadiene (>95% yield), either photochemically or in the dark, using either the adamantyl- or *tert*-butylsilenes. The data do not unambiguously define which of the two possible stereoisomers (endo or exo) is formed, but models suggest that the isomer where the siloxy group is adjacent to the methylene bridge is less crowded. The absence of other products suggests that the rigidity of the diene ring system is not favorable to "ene"-type reactions. The structures of the cycloadducts were confirmed by detailed NMR studies using 2-D and special pulse sequence techniques.



2a,b **14a,b**

a, R = Ad; **b**, R = *t*-Bu

The major product of the reaction of 1,3-cyclohexadiene with the adamantyl- or *tert*-butylsilenes (eq 9) was also found to be a [2 + 4] addition product, as confirmed by detailed NMR studies (see below). The complex reaction mixture actually contained four isomers: two [2 + 4] isomers, which constituted about 80% of the mixture and two [2 + 2] isomers, which comprised the remaining 20%, as judged by ^{29}Si NMR spectroscopy (the ring silicon atoms of [2 + 4] isomers usually resonate at significantly higher field than occurs in [2 + 2] isomers). Because the isomers



2a,b **15a,b** **16a,b**

a, R = Ad; **b**, R = *t*-Bu

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(9) Jones, P. R., private communication.

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

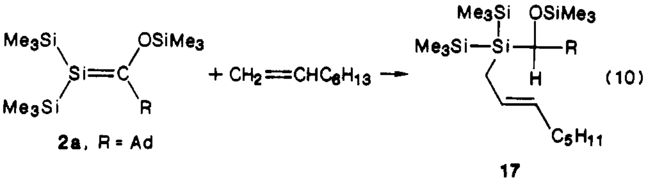
(11) Wiberg, N.; Schurz, K.; Fischer, G. *Chem. Ber.* **1986**, *119*, 3498.

(12) Apeloig, Y.; Karni, M. *J. Am. Chem. Soc.* **1984**, *106*, 6676.

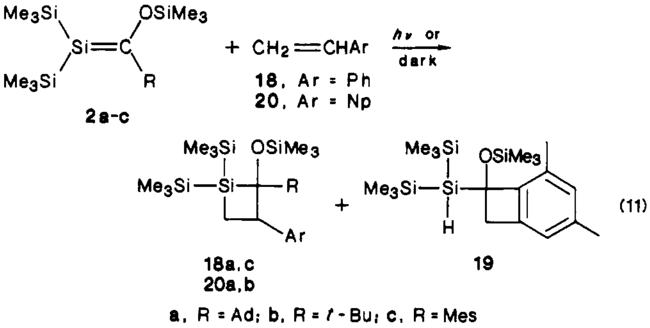
could not be separated due to the similarity of their chemical and physical properties, it was not possible to assign structures to all of them unambiguously.

Reactions with Alkenes. In light of the finding that butadiene underwent [2 + 2] cycloadditions with members of our family of silenes, it was of interest to observe whether alkenes might also show this behavior. In a few cases "simple" silenes have been reported to undergo [2 + 2] additions with alkenes,[2,13] but more commonly "stable silenes" have been found to undergo only "ene" reactions. Wiberg[4] has reported the relative reactivities of various alkenes in the "ene" reaction with the silene $Me_2Si{=}C(SiMe_3)_2$.

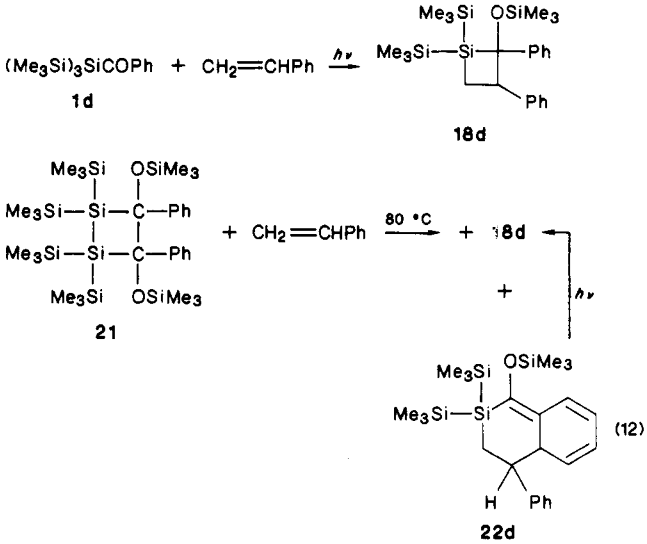
In a brief investigation, the adamantylsilene was found to give only the "ene" product **17** with the representative simple alkene 1-octene (eq 10), but by contrast, the mesitylsilene failed to react with 1-octene or with cyclohexene, regardless of whether the reactions were attempted under photochemical or thermal conditions. This is another example where the mesityl system has been found to exhibit behavior somewhat different from other members of the silene family.



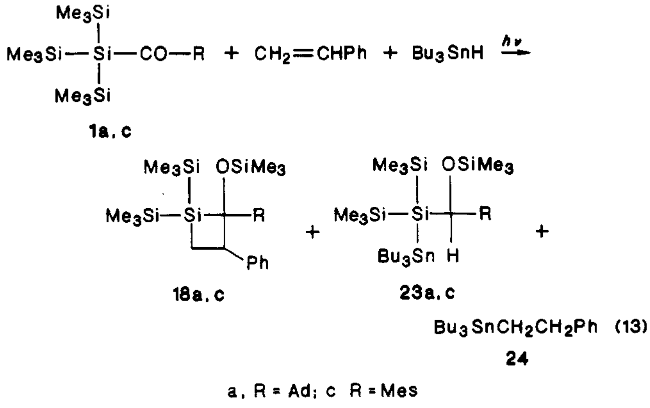
With conjugated alkenes such as styrene or 2-vinylnaphthalene (eq 11), the only reaction observed by using the silenes **2** (R = Ad, *t*-Bu) was [2 + 2] cycloaddition to give in each case a 50:50 diastereomeric mixture of the single regioisomer shown (**18** or **20**) regardless of whether the reaction was conducted photochemically or with preformed silene in the dark. The mesitylsilene **2c** gave only a single [2 + 2] cycloadduct, presumably with the Mes and Ph groups trans to each other. This compound was sufficiently sterically crowded that free rotation of the mesityl group was prevented (three nonequivalent methyl groups in the NMR spectra). When the silene **2c** was preformed photochemically, it was accompanied by an equal amount of the known and previously observed benzocyclobutene **19**.[14] However, when acylsilane **1c** was cophotolyzed with styrene, only the cycloadduct **18c** was obtained. The fact that no benzocyclobutene was found in the photolysis solution demonstrates that the reaction of silene **2c** with styrene is faster than the photochemical conversion of **2c** to **19**.



Cophotolysis of the phenylacylsilane **1d** with styrene gave the expected [2 + 2] adducts **18d** with styrene as a 65:35 mixture of diastereomers. However, when the phenylsilane was thermally generated from its dimer **21**[3] in the presence of styrene, the [2 + 2] adducts (85%) were accompanied by 15% of the nominal [2 + 4] adduct **22d** whose structure suggested that the silene had acted as the 4-π component and the styrene the 2-π component of the reaction. While similar behavior of the phenylsilene has been reported previously in its reactions with carbonyl compounds,[10] this is the only example of nominal [2 + 4] cycloaddition to an arylalkene observed to date. Like the product of silene + carbonyl addition,[10] the [2 + 4] adduct **22d** on further photolysis isomerized to the [2 + 2] adduct **18d**. Once formed, **18d** could not be converted back to the [2 + 4] product either thermally or photochemically.



The mechanism of the [2 + 2] cycloadditions of silenes with styrene does not appear to involve radical processes. Thus the acylsilanes **1a,c** irradiated in the presence of a mixture of styrene plus excess tributyltin hydride (eq 13) gave the same mixture of diastereomeric [2 + 2] products as was obtained when styrene alone was added to silene, accompanied by small amounts of the silene–tin hydride adducts **23a,c** and the stryene hydrostannylation product **24**. Thus the tin hydide had no substantial effect on the course of the reaction with silene. (It is known that in the absence of styrene or other alkene, most silenes rapidly and cleanly add tin hydride across the Si=C double bond to give products with the general structure **23**.[10]) The fact that there was no evidence of polystyrene formation during the photolysis of the acylsilanes with styrene (eq 11), despite the presence of a huge excess of styrene, also strongly suggests that radicals were not involved in the reactions.



The types of alkene that will add in a [2 + 2] manner with our family of silenes appears to be very limited. First the alkene must be activated by an adjacent aryl group

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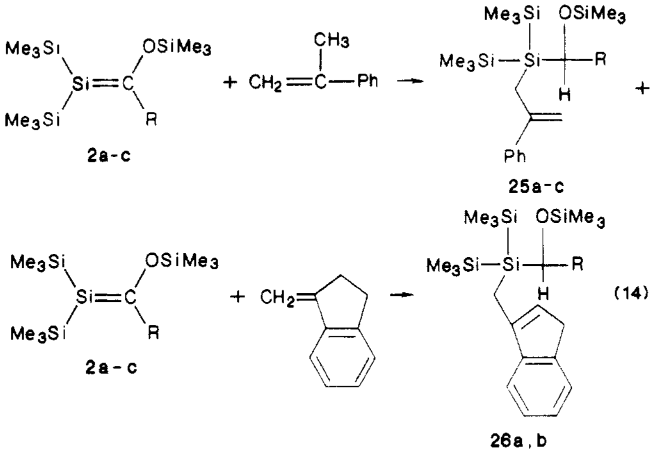
[13] Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529.

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

(styrene or vinylnaphthalene) or by a vinyl group (butadiene). However, even if these conditions are fulfilled, the alkene double bond must not possess α-hydrogen, since both α-methylstyrene and methyleneindan (eq 14) were found to undergo only "ene"-type reactions yielding the products **25** and **26** with no evidence for formation of [2 + 2] adducts. The presence of excess tributyltin hydride during the cophotolysis of acylsilane **1a** with α-methylstyrene did not materially affect the formation of **25a**.



a, R = Ad; **b**, R = *t*-Bu; **c**, R = Mes

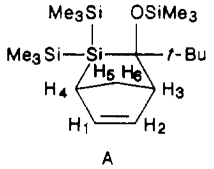
For successful [2 + 2] addition between silenes and alkenes to occur other restraints, steric in origin, must be avoided. 1,1-Diphenylethylene failed to react with the adamantyl-, *tert*-butyl-, or mesitylsilenes and was observed to react only very sluggishly with the less sterically hindered phenylsilene **2d** (eq 14; **2**, R = Ph). However, the products were too unstable to characterize, since even at room temperature they quickly broke down apparently re-forming diphenylethylene and the phenylsilene dimer. Neither *cis*- or *trans*-stilbene reacted with the phenylsilene **2d**, implying that, either for steric or polarity reasons or both, one end of the alkene double bond must be unsubstituted.

It is thus evident that while silenes from the family $(Me_3Si)_2Si{=}C(OSiMe_3)R$ show some of the behavior previously attributed to "simple" silenes in their reactions with alkenes and dienes, some atypical behavior, in particular [2 + 2] cycloaddition, occurs with some combinations of reagents.

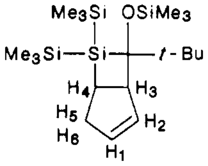
NMR Correlations and Structural Assignments. In the course of the present work a number of new compounds have been prepared whose NMR properties can profitably be compared with earlier data. The chemical shifts of the ring silicon atoms of very simple silacyclobutanes occur at about 18 ppm.[15] For the highly substituted silacyclobutanes reported above, such as **5** (from silenes plus butadiene) or **18** (from styrene) the ring silicon atoms resonate in the range −12 to −31 ppm. This large upfield shift is in accord with the known tendency of trimethylsilyl groups to shield an attached silicon atom.

It is also of interest to compare the highly substituted silacyclobutanes such as **5** or **18** with the similarly substituted siloxetanes recently prepared in this laboratory[10] (from the [2 + 2] reactions of silenes **2** with aldehydes and ketones). Whereas the silacyclobutane ring silicon atoms resonate in the range −12 to −31 ppm, the related siloxetanes resonate in the range 42–65 ppm, with most compounds resonating in the range 50–56 ppm. The large downfield shift observed is consistent with the known influence of oxygen of the chemical shifts of neighboring atoms, including silicon. In contrast, the carbon atoms in the four-membered rings of both the silacyclobutanes and siloxetanes which bear the siloxy group resonate at almost identical positions.

During these studies several new compounds were isolated where the structural assignment relied heavily on detailed NMR studies. The structure assignment of the compound obtained from the *tert*-butylsilene **2b** with cyclopentadiene is a case in point, three possible structures A, B, and C from [2 + 4] or [2 + 2] (two orientations) cycloadditions having to be considered. The structure assignment was complicated by the fact that one of the bridge H_5/H_6 atoms had a chemical shift almost identical with H_4, adjacent to the ring Si. A 2-D correlation experiment ($^1H-^{13}C$) revealed the proton–carbon relationships, since all couplings, except geminal ones, were eliminated. It was evident that H_5/H_6 constituted an AB system. Decoupling experiments were carried out. Irradiation of H_3 collapsed the signal of H_2 to a doublet and also affected both H_5 and H_6. Irradiation of H_4 collapsed H_1 to a doublet and similarly affected the AB system of H_5/H_6. Irradiation at the frequencies of the AB system effected both H_3 and H_4 at the same time. Only structure A is consistent with this data. The structure of the adamantyl analogue **14a**, an even more complex problem since some of the ring protons were buried in the proton signals of the adamantyl group, was assigned similarly.



A



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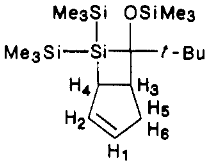
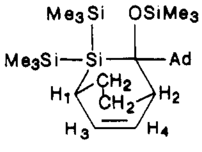
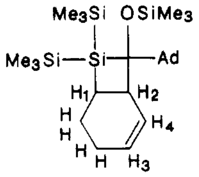


C

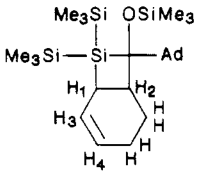
The same assignment problems also occurred with the products obtained from cyclohexadiene, where structure D, E, or F had to be considered. The issue was resolved by using similar 2-D $^1H-^{13}C$ correlations together with decoupling experiments, leading to the assignment of D as the structure of the major isomer isolated.



D



E



F

The other structural problem solved by 2-D NMR concerned which regioisomer, **11a** or **12a**, was the major product of the reaction of silene **2a** with isoprene. A 2-D

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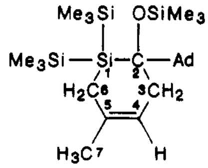
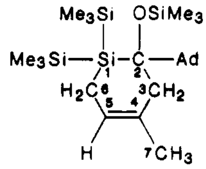
[15] Seyferth, D.; Duncan, D. P.; Schmidbaur, H.; Holl, P. *J. Organomet. Chem.* **1978**, *159*, 137.



11a



12a

NMR direct correlation experiment (^{1}H–^{13}C) gave the proton–carbon relationships. In addition a 2-D NMR long-range coupling experiment (^{1}H–^{13}C) was carried out under conditions which revealed mainly $^3J(^1\mathrm{H}-^{13}\mathrm{C})$ couplings (with residual ^1J couplings). There were two important three-bond couplings to consider. First, carbon C_3 showed a three-bond coupling to the methyl group C_7. Second, there was no ^3J coupling of C_2 to an olefinic CH (which would occur in **11** but not in **12**). These results confirmed the assignment of **12** as the structure of the major product formed from the silene reaction with isoprene.

Experimental Section

Acylsilanes were prepared according to published procedures.[3,14,16] Many reactions were carried out in two modes: (a) by "cophotolysis" of the relevant acylsilane in the presence of the trapping agents (thus photolytically generating the silene in the presence of the trapping reagent) and (b) by prephotolyzing the acylsilane to the silene and then adding the relevant trapping agent to the silene solution in the "dark". All reactions involving silenes were carried out in thoroughly dried glassware under a dry argon atmosphere, utilizing vacuum line techniques. THF and Et_2O were distilled from the sodium ketyl of benzophenone, and benzene or pentane were distilled from $LiAlH_4$.

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 ^{1}H, at 100.570 or 50.309 MHz, respectively for ^{13}C, and 79.489 or 39.746 MHz 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 ^{1}H NMR spectra (residual C_6D_5H), 128.00 ppm for ^{13}C NMR spectra, and 0.00 ppm (external TMS) for ^{29}Si NMR spectra, all relative to TMS. Many reactions were followed by NMR spectroscopy in order to ascertain their completion or the proportion of products. IR spectra were run in various solvents as noted with at least 15 Fourier scans (subtracting background signals).

Where appropriate, APT[17] or DEPT[18] pulse sequences were used for ^{13}C spectra. ^{29}Si spectra were run in either the normal or DEPT mode. 2-D NMR (^{1}H–^{13}C) 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. Abbreviations used: b, broad multiplet; q-C, quarternary carbon; Mes, mesityl (2,4,6-trimethylphenyl); ad, 1-adamantyl.

Due to the inability to separate and purify a number of the silene adducts, their elemental analyses and high resolution mass spectra data were unobtainable. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Reaction of Silene 2a with 2,3-Dimethyl-1,3-butadiene. (a) Cophotolysis. A solution of 1.0 g (2.43 mmol) of the adamantylacylsilane **1a** and 1.0 g (12.14 mmol) of 2,3-dimethyl-1,3-butadiene in 5 mL of benzene was irradiated over 9 h giving an inseparable mixture of a [2 + 4] addition product and an "ene"-type reaction product in a ratio of 1.5:1. The combined yield was >98% (NMR). To isolate the [2 + 4] addition product, the volatile compounds were removed under reduced pressure. The residue was dissolved in 10 mL of toluene, and 0.72 g (7.3 mmol) of maleic anhydride was added. The mixture was heated to 105 °C over 8.5 h. The solvent was removed, and the residue was purified by column chromatography (silica gel 60, *n*-hexane) to yield 720 mg (60% yield) of 2-adamantyl-4,5-dimethyl-1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-1-silacyclohex-4-ene (**3a**) as a colorless solid, which was recrystallized from pentane/acetone (1:1) at −20 °C to yield a solid, mp 200 °C. The Diels–Alder adduct of the "ene" product with maleic anhydride could not be isolated due to decomposition. Spectroscopic data for **3a**: ^{1}H NMR δ 0.14, 0.15, 0.25 (each 9 H, s, Me_3Si), 1.14, 1.90 (2 H, dd, CH_2Si, J = 30.6 Hz), 1.59, 1.77 (each 3 H, s, CH_3), 2.27 (2 H, m, CH_2CO, ^2J < 1 Hz), 1.69–2.01 (15 H, m, ad); ^{13}C NMR δ 0.89, 1.34, 3.40 (Me_3Si), 16.76 (CH_2Si), 21.67, 24.32 (CH_3), 29.55 (CH ad), 37.89, 39.75 (CH_2 ad), 40.23 (q-C ad), 41.73 (CH_2CO), 85.69 (COSiMe$_3$), 125.86, 127.07 (C=C); ^{29}Si NMR δ 5.51 (Me_3SiO), −16.17, −14.86 (Me_3Si), −47.48 (Si ring); MS, *m/e* (relative intensity) 493 (M$^+$, <1), 478 (M$^+$ − Me, 1), 420 (M$^+$ − Me_3Si, 28), 135 (ad$^+$, 100), 73 ([Me_3Si]$^+$, 99). Anal. Calcd for $C_{26}H_{52}OSi_4$: C, 63.34; H, 10.63. Found: C, 63.40; H, 10.44.

Spectroscopic data for "ene"-type reaction product 2-methyl-3-[3-adamantyl-2,2-bis(trimethylsilyl)-3-(trimethylsiloxy)-2-silapropyl]-1,3-butadiene (**4a**): ^{1}H NMR δ 0.19, 0.28, 0.33 (each 9 H, s, Me_3Si), 1.1–2.3 (20 H, m, CH_2Si, CH_3 ad), 3.99 (1 H, s, CHOSiMe$_3$), 5.0, 5.19, 5.23, 5.35 (4 H, m, CH_2 sp^2); ^{13}C NMR δ 1.50, 1.79, 1.90 (each Me_3Si), 15.84 (CH_2Si), 21.46 (CH_3), 29.10 (CH ad), 37.41, 39.75 (CH_2 ad), 41.49 (q-C ad), 81.58 (CHOSiMe$_3$), 113.73, 113.84 (CH_2 sp^2), 145.08, 147.07 (q-C sp^2); ^{29}Si NMR δ 14.50 (Me_3SiO), −13.94, −15.68 (Me_3Si), −42.68 (Me_3Si*Si*).

(b) Dark Reaction. A solution of 100 mg (0.24 mmol) of **1a** in Et_2O was irradiated overnight giving silene **2a**. 2,3-Dimethyl-1,3-butadiene (100 mg) was added, and the sample was stored at room temperature in the dark over 0.5 h. The NMR spectra of the resulting reaction mixture indicated the presence of the same products **3a** and **4a** in the same ratio as observed by using the cophotolysis procedure.

Reaction of 2b with 2,3-Dimethyl-1,3-butadiene. (a) Cophotolysis. A solution of 100 mg (0.3 mmol) of **1b** and 100 mg of 2,3-dimethyl-1,3-butadiene in C_6D_6 was irradiated over 1.5 h giving an inseparable mixture of a [2 + 4] addition product **3b** and an "ene"-type reaction product **4b** in a ratio of 1.5:1. **3b**: ^{1}H NMR δ 0.15, 0.16, 0.28 (each 9 H, s, Me_3Si), 1.03 (9 H, s, *t*-Bu), 1.61, 1.80 (each 3 H, s, CH_3), 1.12–2.3 (4 H, m, CH_2 ring); ^{13}C NMR δ 0.56, 1.07, 3.11 (each Me_3Si), 16.70 (CH_2Si), 21.49, 24.11 (each CH_3), 27.89 (*Me*$_3$C), 38.37 (Me$_3$*C*), 43.04 (CH_2CO), 84.07 (*C*OSiMe$_3$), 125.77, 126.81 (q-C sp^2); ^{29}Si NMR δ 14.52 (Me_3SiO), −15.26, −16.28 (Me_3Si), −46.16 (Si ring). **4b**: ^{1}H NMR δ 0.18, 0.26, 0.31 (each 9 H, s, Me_3Si), 1.03 (9 H, s, *t*-Bu), 1.12–2.3 (2 H, m, CH_2Si), 1.9 (3 H, s, CH_3), 4.06 (1 H, s, CHOSiMe$_3$), 5.0–5.3 (4 H, m, CH_2 sp^2); ^{13}C NMR δ 1.47, 1.78, 1.83 (each Me_3Si), 16.10 (CH_2Si), 21.44 (CH_3), 29.02 (*Me*$_3$C), 36.25 (Me$_3$*C*), 80.35 (*C*HOSiMe$_3$), 113.61, 113.87 (each CH_2 sp^2), 144.89, 147.03 (q-C sp^2); ^{29}Si NMR δ 5.05 (Me_3SiO), −14.18, −15.69 (Me_3Si), −40.64 (*Si*SiMe$_3$).

(b) Dark Reaction. The same procedure as employed with **1a** + 2,3-dimethyl-1,3-butadiene was used yielding **3b** and **4b** as above in the same ratio. The reaction was complete in 0.5 h.

Preparation of 4,5-Dimethyl-2-mesityl-1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-1-silacyclohex-4-ene (3c). (a) Cophotolysis. A solution of 100 mg (0.25 mmol) of acylsilane **1c** and 150 mg (1.8 mmol) of 2,3-dimethyl-1,3-butadiene in approximately 1 mL of C_6H_6 was irradiated to yield the [2 + 4] addition product **3c** as the only detectable product: ^{1}H NMR δ −0.14, 0.03, 0.34 (each 9 H, s, Me_3Si), 1.35, 1.67 (2 H, dd, CH_2Si, ^2J = 14.8 Hz), 1.89 (6 H, s, CH_3), 2.03 (3 H, s, MeMes), 2.57 (6 H, s, MeMes), 2.92, 3.14 (2 H, dd, CH_2CO, ^2J = 13 Hz), 6.80 (2 H, m, CH arom); ^{13}C NMR δ −0.11, 1.85, 3.14 (Me_3Si), 19.75 (CH_2Si), 20.42, 21.44, 21.83 (*p*-MeMes and 2 × CH_3), 26.94 (*o*-MeMes), 49.33 (CH_2CO), 84.52 (COSiMe$_3$), 127.46, 127.62, 129.49, 135.86, 142.53 (q-C sp^2), 132.38 (CH sp^2); ^{29}Si NMR δ 9.84 (Me_3SiO), −11.75, −15.08 (Me_3Si), −26.91 (Si ring); MS, *m/e* (relative intensity) 477 (M$^+$, 9), 462 (M$^+$ − Me, <1), 404 (M$^+$ − Me_3Si, 8), 73 ([Me_3Si]$^+$, 100).

Preparation of 2-Adamantyl-1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-1-silacyclohexen-4-ene (6a) and 2-Adamantyl-1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-3-vinyl-1-silacyclobutane (5a). A solution of 1.0 g (2.4 mmol)

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

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

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

of acylsilane **1a** and excess 1,3-butadiene in C_6H_6 was irradiated over 2.5 h to yield the [2 + 2] addition products **5a** (mixture of diastereoisomers in the ratio 46:36) and the [2 + 4] addition product **6a** in a ratio of 82:18 (**5a**:**6a**). Only the major diastereoisomer of the [2 + 2] addition could be separated from the reaction mixture by several recrystallizations from pentane–acetone at −20 °C. **5a** (major diastereoisomer): ^{1}H NMR δ 0.30, 0.33 (27 H, s, Me_3Si), 1.68–1.99 (15 H, m, ad), 0.94 (1 H, dd, one part of ABX system, ^{2}J = 13.6 Hz, ^{3}J = 5.3 Hz, *H*CHSi), 1.74 (1 H, dd, one part of ABX system, ^{3}J = 9.4 Hz, HC*H*Si), 3.68 (1 H, ddddd, ^{3}J = 8.7 Hz, ^{4}J = 1.2 Hz, ^{4}J = 0.8 Hz, CH ring), 6.37 (1 H, ddd, ^{3}J = 17.0 Hz, ^{3}J = 10.0 Hz, CH vinyl), 5.03, 4.93 (each 1 H, ddd, ^{2}J = 2.0 Hz, CH_2 vinyl); ^{13}C NMR δ 1.41, 1.58, 4.77 (each Me_3Si), 9.14 (CH_2 ring), 29.15 (CH ad), 37.87, 39.76 (CH_2 ad), 40.98 (q-C ad), 58.54 (CH ring), 97.83 (q-C ring), 112.33 (CH_2 sp^2), 141.81 (CH sp^2); ^{29}Si NMR δ 5.81 (Me_3SiO), −15.80, −15.83 (Me_3Si), −17.96 (Si ring); IR 1251 (Si—C), 1629 (C=C), 3070 (HC=C) cm^{-1}; MS, *m/e* (relative intensity) 465 (M^+, 5), 450 (M^+ − Me, <1), 411 (M^+ − C_4H_6, 3), 392 (M^+ − Me_3Si, 5), 73 ($[Me_3Si]^+$, 100). Anal. Calcd for $C_{24}H_{48}OSi_4$: C, 61.99; H, 10.41. Found: C, 61.59; H, 10.22. **5a** (minor diastereoisomer): ^{1}H NMR δ 0.26, 0.30, 0.36 (each 9 H, s, Me_3Si), 0.97, 1.55 (each 1 H, AB part of ABX system, CH_2Si), 3.33 (1 H, X part of ABX system, CH ring), 5.07, 5.16 (2 H, m, CH_2 vinyl), 6.08 (1 H, m, CH vinyl); ^{13}C NMR δ 0.64, 1.38, 5.08 (each Me_3Si), 9.43 (CH_2Si), 29.18 (CH ad), 37.44, 37.61 (CH_2 ad), 41.36 (q-C ad), 48.94 (CH ring), 100.87 (q-C ring), 114.96 (CH_2 sp^2), 142.89 (CH sp^2); ^{29}Si NMR δ 4.42 (Me_3SiO), −15.33, −17.34 (Me_3Si), −27.78 (Si ring). **6a** ([2 + 4] isomer): ^{1}H NMR δ 0.22, 0.23, 0.28 (each 9 H, s, Me_3Si), 1.3 (2 H, m, CH_2Si), 1.65–1.95 (15 H, m, ad), 2.24 (2 H, m, CH_2CO), 5.42, 5.93 (each 1 H, m, CH ring); ^{13}C NMR δ 0.29, 1.14, 3.17 (each Me_3Si), 7.50 (CH_2Si), 29.29 (CH ad), 37.44, 37.61 (CH_2 ad), 39.34 (q-C ad), 33.90 (CH_2CO), 85.08 (q-C ring), 127.66, 128.37 (CH ring); ^{29}Si NMR δ 6.01 (Me_3SiO), −16.48, −14.34 (Me_3Si), −49.18 (Si ring).

Reaction of 2b and 1,3-Butadiene. Preparation of 2-*tert*-Butyl-1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-1-silacyclohex-4-ene (6b) and 2-*tert*-Butyl-1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-3-vinyl-1-silacyclobutane (5b). A solution of 0.5 g (1.5 mmol) of **1b** and excess 1,3-butadiene in 10 mL of Et_2O was irradiated over 6.5 h to yield a [2 + 2] addition product **5b** (as a mixture of diastereoisomers in a ratio of 1.1:1) and a [2 + 4] addition product **6b** in a ratio of 4:1 (**5b**:**6b**). The major diastereoisomer of the [2 + 2] addition could be separated by repeated flash chromatography (silica gel, *n*-hexane). **5b** (major diastereoisomer): ^{1}H NMR δ 0.25, 0.29, 0.33 (each 9 H, s, Me_3Si), 1.01, 1.42 (2 H, AB part of ABX system, CH_2Si, ^{2}J = 13.5 Hz), 1.09 (9 H, s, *t*-Bu), 3.59 (1 H, m, CH ring), 4.98, 5.07 (2 H, m, C*H*$_2$=CH), 6.35 (1 H, m, CH_2=C*H*); ^{13}C NMR δ 1.24, 1.38 (each Me_3Si), 4.15 (Me_3SiO), 8.34 (CH_2Si, ^{1}J(Si–C) = 33 Hz), 28.57 ((*C*H$_3$)$_3$C), 38.89 ((CH_3)$_3$*C*), 58.25 (CH ring), 96.47 (COSi), 112.64 (*C*H$_2$=CH), 141.49 (CH_2=*C*H); ^{29}Si NMR δ 5.12 (Me_3SiO), −15.17, −15.90 (Me_3Si), −18.96 (Si ring). **5b** (minor diastereoisomer): ^{1}H NMR δ 0.26, 0.29, 0.34 (each 9 H, s, Me_3Si), 0.99 (9 H, s, *t*-Bu), 1.00, 1.57 (2 H, second-order ABX system, CH_2Si), 3.30 (1 H, m, CH ring), 5.06, 5.14 (2 H, m, C*H*$_2$=CH), 6.11 (1 H, m, CH_2=C*H*); ^{13}C NMR δ 0.18, 1.33 (each Me_3Si), 4.99 (Me_3SiO), 8.01 (CH_2Si, ^{1}J(Si–C) = 32 Hz), 29.30 ((*C*H$_3$)C), 37.70 ((CH_3)$_3$*C*), 50.15 (CH ring), 99.36 (COSi), 114.99 (*CH*$_2$=CH), 142.35 (CH_2=*C*H); ^{29}Si NMR δ 4.25 (Me_3SiO), −15.22, −17.31 (Me_3Si), −25.79 (Si ring). **6b** ([2 + 4] isomer): ^{1}H NMR δ 0.19, 0.21, 0.26 (each 9 H, s, Me_3Si), 0.98 (9 H, s, *t*-Bu), 1.29, 1.77 (2 H, m, CH_2Si), 2.14–2.31 (2 H, m, *C*H$_2$CO), 5.39, 5.91 (2 H, m, C*H*=C*H*); ^{13}C NMR δ 0.48, 1.08 (each Me_3Si), 3.11 (Me_3SiO), 9.49 (CH_2Si, ^{1}J(Si–C) = 37 Hz), 27.74 ((*C*H$_3$)$_3$C), 38.46 ((CH_3)$_3$*C*), 35.38 (*C*H$_2$CO), 83.68 (*C*OSi), 127.61, 128.44 (*C*H=*C*H); ^{29}Si NMR δ 6.0 (Me_3SiO), −14.52, −16.39 (Me_3Si), −47.47 (Si ring).

Reaction of 2c and 1,3-Butadiene. Preparation of 2-Mesityl-1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-1-silacyclohex-4-ene (6c) and 2-Mesityl-1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-3-vinyl-1-silacyclobutane (5c). A solution of 0.5 g (1.27 mmol) of the mesitylacylsilane **1c** and excess 1,3-butadiene in C_6H_6 was irradiated over 5 h to yield an inseparable mixture of a [2 + 2] addition product **5c** (as a mixture of diastereoisomers in a ratio of 4.3:1 and a [2 + 4] addition product **6c** in a ratio of 3:1 (**6c**:**5c**). The mixture was purified by preparative TLC (Chromatatron, silica gel, *n*-hexane); yield 550 mg (96%). **5c** (major diastereoisomer): ^{1}H NMR δ −0.12, −0.08, 0.25 (each 9 H, s, Me_3Si), 1.14, 1.44 (2 H, AB part of ABX system, CH_2Si, ^{2}J = 29 Hz), 2.04, 2.41 (9 H, s, CH_3Mes), 3.80 (1 H, m, CH ring), 5.02 (2 H, m, C*H*$_2$=CH), 6.46 (1 H, m, *CH*=CH_2), 6.63 (2 H, m, CH sp^2); ^{13}C NMR δ −0.60, −0.11, 2.64 (each Me_3Si), 11.74 (CH_2Si, ^{1}J(Si–C) = 30 Hz), 20.79, 23.40, 25.08 (each CH_3, Mes), 52.28 (CH ring), 86.88 (*C*HOSi), 112.42 (*C*H$_2$=CH), 143.85 (CH$_2$=*C*H), 132.37 (b, CH sp^2, Mes), 134.06, 139.02, 140.27, 143.50 (q-C sp^2); ^{29}Si NMR δ 11.96 (Me_3SiO), −13.59, −15.97 (Me_3Si), −16.87 (Me_3Si*Si*). **5c** (minor diastereomer) (since this was formed in only small amounts, due to overlapping etc., it was not possible to make unambiguous assignments of all signals and only a few characteristic peaks are given): ^{1}H NMR δ 4.0 (CH ring), 5.99 (*CH*=CH_2); ^{13}C NMR δ 14.52 (CH_2Si), 56.77 (CH ring), 87.45 (COSi), 115.42 (*C*H$_2$=CH), 142.20 (CH_2=*C*H). **6c** ([2 + 4] isomer): ^{1}H NMR δ −0.22, −0.11, 2.54 (each 9 H, s, Me_3Si), 1.50 (2 H, m, CH_2Si), 2.04, 2.49 (×2) (9 H, s, CH_3, Mes), 3.0 (2 H, d, CH_2CO), 5.83, 6.13 (2 H, m, C*H*=C*H*), 6.60, 6.66 (2 H, m, CH sp^2, Mes); ^{13}C NMR δ −0.21, 1.95, 2.49 (each Me_3Si), 12.24 (CH_2Si, ^{1}J(Si–C) = 29 Hz), 20.57, 27.11 (*p*- and 2*o*-CH_3, Mes), 41.18 (*C*H$_2$CO), 84.09 (COSi, ^{1}J(Si–C) = 59 Hz), 129.02, 129.32 (*C*H=*C*H), 130.29, 131.76 (CH sp^2, Mes), 135.29, 136.01, 143.50 (q-C, Mes); ^{29}Si NMR δ 9.99 (Me_3SiO, ^{1}J(Si–C) = 59 Hz), −11.78 (Me_3Si, ^{1}J(Si–Si) = 74 Hz), −15.71 (Me_3Si, ^{1}J(Si–Si) = 66 Hz), −28.01 (Me_3Si*Si*, ^{1}J(Si–Si) = 74 Hz, ^{1}J(Si–Si) = 66 Hz).

Reaction of 2a with 1,3-Butadiene in the Presence of Bu_3SnH. (a) Cophotolysis. A solution of 1.0 g (2.43 mmol) of **1a**, 1.41 g (4.8 mmol) of Bu_3SnH, and excess 1,3-butadiene in Et_2O was irradiated over 6.0 h. The spectroscopic data showed that in addition to the usual [2 + 2] and [2 + 4] isomers a new compound **7** was formed. Yields (NMR): **5a** (major):**5a** (minor):**6a**:**7** = 38%:34%:16%:12%.

(b) Dark Reaction. A solution of 0.1 g (0.24 mmol) of **1a** was irradiated over 16 h to yield **2a**. The silene solution was added to a solution of excess 1,3-butadiene and 0.33 mL (1.22 mmol) of Bu_3SnH in 5 mL of Et_2O and stored overnight. The spectroscopic data showed the presence of **7** besides the normal [2 + 2] and [2 + 4] products. Yields (NMR): **5a** (major):**5a** (minor):**6a**:**7** = 5%:36%:20%:39%.

Reaction of 5a (Major Diastereomer) with Bu_3SnH. Preparation of 1-Adamantyl-6-(tributylstannyl)-2,2-bis(trimethylsilyl)-1-(trimethylsiloxy)-2-silahex-4-ene (7). A solution of 0.13 g (0.28 mmol) of **5a** (major isomer), 0.38 mL (1.4 mmol) of Bu_3SnH, and a catalytic amount of AIBN in 5 mL of toluene was heated to 80 °C over 5.5 h. All volatile compounds were removed under reduced pressure, and the residue was purified by preparative TLC (Chromatatron, silica gel, *n*-hexane). The only compound detectable was **7**: ^{1}H NMR δ 0.35, 0.38, 0.41 (each 9 H, s, Me_3Si), 0.9–2.2 (46 H, b, ad + 3 × Bu + 2 × CH_2), 3.94 (1 H, s, CHOSi), 5.6–5.85 (2 H, b, HC=C); ^{13}C NMR δ 1.49, 1.53, 1.78 (each Me_3Si), 9.52 (α-CH_2Bu, ^{1}J(Sn–C) = 312 Hz), 14.04 (CH_3Bu), 27.86 (γ-CH_2Bu, ^{3}J(Sn–C) = 53 Hz), 29.68 (β-CH_2Bu, ^{2}J(Sn–C) = 19 Hz), 14.64 (C=*C*H$_2$Sn, ^{1}J(Sn–C) = 271 Hz), 16.12 (CH_2Si, ^{1}J(Si–C) = 31 Hz), 29.14 (CH ad), 37.44, 41.53 (CH_2 ad), 37.92 (q-C ad), 80.68 (CHOSi, ^{1}J(Si–C) = 53 Hz), 124.33 (*C*H=*C*H, accidental overlap); ^{29}Si NMR δ 14.07 (Me_3SiO), −14.75, −15.44 (Me_3Si), −43.11 (*Si*SiMe_3).

Standard Procedure for the Reaction of Silene 2a and 1,3-Butadiene in Different Solvents. (a) Cophotolysis. A solution of 1.0 g (2.4 mmol) of acylsilane **1a** in different solvents was prepared in a Schlenk tube. Excess 1,3-butadiene was condensed on top of the solutions at −78 °C. The solution was photolyzed under various conditions. After reaction, the volatile compounds were removed and the ^{1}H NMR spectra were recorded to determine the yields of the different isomers (given in Table I).

(b) Dark Reaction. A solution of 0.5 g (1.2 mmol) of **1a** in 10 mL of Et_2O was irradiated at −78 °C to give a 100% yield of silene **2a**. The ether was then removed under reduced pressure and was replaced by 10 mL of the required solvent. Excess butadiene was condensed on top of the solution, and the mixture was then stored in the dark over 24 h. Workup was done as in the cophotolysis case.

Reaction of the Adamantylsilene 2a with Isoprene. A solution of 0.2 g (0.48 mmol) of **1a** and 0.17 g (2.4 mmol) of isoprene in C_6D_6 was irradiated over 4.5 h giving an inseparable mixture of a [2 + 4] adduct (two isomers: **11a**:**12a** = 1:3) and an "ene"-type product, **13a**, in a ratio of 8:1 (**11** + **12**:**13**) along with several other products in small amounts. The mixture could not be separated by chromatography or crystallization. **11a**: ^{1}H NMR δ 0.21, 0.28, 0.34 (each 9 H, s, Me$_3$Si), 0.85–2.23 (22 H, m, ad + 2 × CH$_2$ + CH$_3$), 5.0–6.0 (1 H, m, *H*C=C); ^{13}C NMR δ 1.80, 1.85, 3.10 (each Me$_3$Si), 13.08 (CH$_2$Si), 25.0–41.3 (ad, CH$_2$CO, CH$_3$), 84.54 (COSiMe$_3$), 122.63 (CH sp^2), 134.21 (q-C sp^2); ^{29}Si NMR δ 5.77 (Me$_3$SiO), −14.45, −16.29 (Me$_3$Si), −48.31 (Si ring). **12a**: ^{1}H NMR δ 0.20, 0.22, 0.30 (each 9 H, s, Me$_3$Si), 0.85–2.23 (22 H, m, ad + 2 × CH$_2$ + CH$_3$), 5.0–6.0 (1 H, m, *H*C=C); ^{13}C NMR δ 0.65, 1.03, 3.24 (each Me$_3$Si), 9.05 (CH$_2$Si), 25.89 (CH$_3$), 39.22 (*C*H$_2$CO), 29.07–41.3 (ad), 85.57 (*C*OSiMe$_3$), 122.44 (CH sp^2), 133.9 (q-C sp^2); ^{29}Si NMR δ 5.29 (Me$_3$SiO), −14.52, −16.44 (Me$_3$Si), −49.22 (Si ring). **13a**: ^{1}H NMR δ 0.18, 0.19, 0.20 (each 9 H, s, Me$_3$Si), 1.6–2.23 (17 H, m, ad + CH$_2$), 4.0 (1 H, s, *CH*OSiMe$_3$), 5.0–6.0 (5 H, m, vinyl H); ^{13}C NMR δ Me$_3$Si (no assignment possible due to overlapping), 14.24 (CH$_2$Si), 29.0–41.3 (ad), 81.61 (*CH*OSiMe$_3$), 113.77, 117.14 (each CH$_2$ sp^2), 141.72 (CH sp^2), 145.88 (q-C sp^2); ^{29}Si NMR δ 14.57 (Me$_3$SiO), −13.88, −15.63 (Me$_3$Si), −42.36 (*Si*SiMe$_3$).

Preparation of 3-Adamantyl-2,2-bis(trimethylsilyl)-3-(trimethylsiloxy)bicyclo[2.2.1]-2-silahept-5-ene (14a). (a) Cophotolysis. A solution of 100 mg (0.24 mmol) of **1a** and 0.17 g (2.5 mmol) of freshly distilled cyclopentadiene in benzene was irradiated over 4 h. The [2 + 4] adduct **14a** was formed in >95% yield (NMR): mp 149 °C; ^{1}H NMR δ 0.24, 0.28, 0.34 (each 9 H, s, Me$_3$Si), 1.49–1.99 (m, ad), 1.95 (1 H, m), 2.29 (2 H, m), 2.96 (1 H, dd, *H*CCOSiMe$_3$), 5.60 (1 H, dd, C=C*H*), 6.67 (1 H, dd, C=C*H*); ^{13}C NMR δ 1.86, 2.46, 5.14 (Me$_3$Si), 31.08 (HCSi), 29.35 (CH ad), 37.59, 41.87 (CH$_2$ ad), 40.55 (q-C ad), 48.28 (CH$_2$), 51.30 (HCCO), 102.40 (COSiMe$_3$), 129.76, 138.94 (C=C); ^{29}Si NMR δ 5.50 (OSiMe$_3$), −14.27, −17.52 (Me$_3$Si), −28.31 (Si ring); MS, M$^+$ 476.2794, C$_{25}$H$_{48}$OSi$_4$ requires 476.2769.

(b) Dark Reaction. A solution of 100 mg (0.24 mmol) of **1a** in Et$_2$O was photolyzed at −78 °C to form only **2a**. The solution was warmed to room temperature and 0.17 g (2.5 mmol) of freshly distilled cyclopentadiene was added. After 3 h the [2 + 4] adduct **14a** was present in essentially quantitative yield.

Preparation of 3-*tert*-Butyl-2,2-bis(trimethylsilyl)-3-(trimethylsiloxy)bicyclo[2.2.1]-2-silahept-5-ene (14b). (a) Cophotolysis. Cophotolysis of the *tert*-butylacylsilane **1b** with excess cyclopentadiene in benzene over 4 h gave a single oily [2 + 4] cycloadduct, **14b**, in >95% yield (NMR): ^{1}H NMR δ 0.20, 0.25, 0.32 (each 9 H, s, Me$_3$Si), 1.01 (9 H, s, CMe$_3$), 1.99 (1 H, ddd, CH$_2$), 2.26 (1 H, m, CH$_2$), 2.30 (1 H, m, HCSi), 2.85 (1 H, dd, HCCO), 5.60 (1 H, dd, C=*CH*CSi), 6.04 (1 H, dd, *HC*=CCSi); ^{13}C NMR δ 2.01, 2.49, 5.03 (Me$_3$Si), 30.82 (*C*H$_3$C), 31.72 (CHSi), 38.76 (CH$_3$*C*), 48.19 (CH$_2$), 52.71 (*C*HCO), 100.67 (*C*OSiMe$_3$), 129.74 (C=*C*CSi), 138.87 (*C*=CCSi); ^{29}Si NMR δ 5.34 (Me$_3$SiO), −14.47, −17.38 (Me$_3$Si), −26.99 (Si ring); MS, M$^+$ 398.2324, C$_{19}$H$_{42}$OSi$_4$ requires 398.2313.

(b) Dark Reaction. With use of the same procedure as described above for **2a** with cyclopentadiene, again only the single adduct **14b** was obtained in >95% yield (NMR).

Preparation of 3-Adamantyl-2,2-bis(trimethylsilyl)-3-(trimethylsiloxy)bicyclo[2.2.1]-2-silaoct-5-ene (15a). (a) Cophotolysis. A solution of 0.1 g (0.24 mmol) of **1a** and 0.17 g (0.21 mmol) of cyclohexadiene in C$_6$H$_6$ was photolyzed over 4 h. The [2 + 4] addition product **15a** was formed as the major product in 67% yield (NMR): mp 202 °C; ^{1}H NMR δ 0.28, 0.32, 0.34 (each 9 H, s, Me$_3$Si), 1.55–1.95 (15 H, m, ad), 1.20, 2.09 (2 H, m, CH$_2$), 1.71, 1.96 (2 H, m, CH$_2$), 2.02 (1 H, m, CHSi), 2.95 (1 H, m, CHCO), 5.85 (1 H, dd, HC=C), 6.13 (1 H, dd, HC=C); ^{13}C NMR δ 2.78, 2.93, 5.04 (Me$_3$Si), 21.70 (CH$_2$), 22.35 (CHSi), 27.39 (CH$_2$), 29.17 (CH ad), 37.39, 40.13 (CH$_2$ ad), 40.67 (q-C ad), 39.18 (CHCO), 97.47 (CO), 133.07, 133.58 (C=C); ^{29}Si NMR δ 5.70 (Me$_3$SiO), −14.33, −18.05 (Me$_3$Si), −28.30 (Si ring); MS, M$^+$ − Me$_3$Si 417.2459, C$_{23}$H$_{41}$OSi$_3$ requires 417.2454.

(b) Dark Reaction. A solution of 0.1 g (0.24 mmol) of acylsilane **1a** in C$_6$D$_6$ was irradiated over 20 h to yield **2a**. Cyclohexadiene (0.17 g, 0.21 mmol) was added under argon, and the mixture was kept in the dark. The reaction is complete after 15 min and yielded the same mixture of isomers as the cophotolysis.

Preparation of 3-*tert*-Butyl-2,2-bis(trimethylsilyl)-3-(trimethylsiloxy)bicyclo[2.2.2]-2-silaoct-5-ene (15b). (a) Cophotolysis. The same procedure was employed as with **1a** above to give **15b** in 65% yield: ^{1}H NMR δ 0.20, 0.27, 0.29 (each 9 H, s, Me$_3$Si), 0.95 (9 H, s, *t*-Bu), 1.55–2.00 (3 H, m, CH$_2$ and CHSi), 2.10 (2 H, m, CH$_2$), 2.69 (1 H, ddd, CHCO), 5.87, 6.12 (2 H, dd, HC=CH); ^{13}C NMR δ 2.77, 2.91, 4.85 (Me$_3$Si), 21.88, 27.36 (CH$_2$), 22.30 (CHSi), 29.33 ((CH$_3$)$_3$C), 39.35 ((CH$_3$)$_3$*C*), 40.98 (CHCO), 95.39 (CO), 133.35 (*C*=*C*); ^{29}Si NMR δ 5.64 (Me$_3$SiO), −14.67, −17.74 (Me$_3$Si), −27.39 (Si ring); MS, *m/e* (relative intensity) 412 (M$^+$, <1), 397 (M$^+$ − Me, <1), 355 (M$^+$ − *t*-Bu, 2), 339 (M$^+$ − Me$_3$Si, 6), 73 ([Me$_3$Si]$^+$, 100).

(b) Dark Reaction. The same procedure as with **2b** (above) was employed, and the dark reaction yielded the same product mixture as obtained from the cophotolysis.

Preparation of 1-Adamantyl-2,2-bis(trimethylsilyl)-1-(trimethylsiloxy)-2-siladec-4-ene (17). A solution of 0.2 g (0.49 mmol) of the adamantylacylsilane **1a** and 0.36 g (3.2 mmol) of 1-octene in C$_6$D$_6$ was irradiated over 19.5 h giving an "ene"-type reaction product in a quantitative yield (NMR) as a single isomer. The product was purified by preparative TLC (chromatatron, silica gel, *n*-hexanes): yield 170 mg (66%); ^{1}H NMR δ 0.23, 0.28, 0.29 (each 9 H, s, Me$_3$Si), 0.8–2.1 (28 H, m, ad + CH$_2$Si + (CH$_2$)$_4$CH$_3$), 3.81 (1 H, s, CHOSi), 5.47, 5.67 (2 H, m, *CH*=*CH*); ^{13}C NMR δ 1.45, 1.49, 1.69 (each Me$_3$Si), 14.36 ((CH$_2$)$_4$*C*H$_3$), 16.23 (CH$_2$Si, ^1J(Si–C) = 36 Hz), 22.99, 29.89, 31.88, 33.39 ((CH$_2$)$_4$CH$_3$), 29.07 (CH ad), 37.39, 41.47 (CH$_2$ ad), 37.86 (q-C ad), 80.54 (*CH*OSi), 128.56, 129.37 (*C*H=*C*H); ^{29}Si NMR δ 14.04 (Me$_3$SiO), −14.73, −15.59 (Me$_3$Si), −43.12 (Me$_3$Si*Si*); IR (neat) 2850–2959 (aliph CH), 1647 (C=C), 1247 (CHSi) cm^{-1}; MS, *m/e* (relative intensity) 507 (M$^+$ − Me, 2), 451 (M$^+$ − C$_5$H$_{11}$, 11), 449 (M$^+$ − Me$_3$Si, 46), 411 (M$^+$ − C$_8$H$_{15}$, 11), 285 (M$^+$ − CH(OSiMe$_3$)ad, 5), 237 (CH$^+$(OSiMe$_3$)ad, 25), 135 (ad$^+$, 22), 73 (Me$_3$Si$^+$, 100).

Photolysis of the Mesitylacylsilane 1c with 1-Octene. A solution of 0.1 g (0.25 mmol) of **1c** and excess 1-octene in benzene was photolyzed for 18 h. NMR spectra indicated that **2c** was formed, along with some benzocyclobutene **19**, but no reaction product with 1-octene was obtained. Heating the mixture over 24 h to 60 °C also failed to give a product with 1-octene.

Photolysis of 1c with Cyclohexene. A solution of 0.1 g (0.25 mmol) of **1c** in excess cyclohexene was photolyzed for 18 h. NMR spectra indicated that silene **2c** was formed together with some benzocyclobutene **19**. No reaction occurred with the olefin. Heating the mixture to 60 °C over 24 h also failed to give a product.

Preparation of 2-Adamantyl-3-phenyl-1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-1-silacyclobutane (18a). (a) Cophotolysis. A solution of 0.5 g (1.22 mmol) of acylsilane **1a** and 0.64 g (6.1 mmol) of styrene in 10 mL of dry benzene was photolyzed over 6 h yielding **18a** as a 1:1 mixture of diastereoisomers. The volatile compounds were removed under reduced pressure. The residue was purified by preparative TLC (Chromatatron, *n*-hexane, silica gel) giving a colorless oil in 76% yield: ^{1}H NMR δ 0.045, 0.322, 0.342, 0.355, 0.358, 0.373 (each 9 H, s, Me$_3$Si), 1.07, 1.65 (2 H, AB part of ABX system, CH$_2$Si, J(AB) = 12.6 Hz, J(AX) = 9.0 Hz, J(BX) = 15.0 Hz, one isomer), 0.94, 2.10 (2 H, A′B′ part of A′B′X′ system, CH$_2$Si, J(A′B′) = 12.0 Hz, J(A′X′) = 6.9 Hz, J(B′X′) = 13.5 Hz, other isomer), 1.5–2.0 (30 H, m, ad), 4.02 (1 H, X′ part of A′B′X′ system, *CH*CH$_2$), 4.37 (1 H, X part of ABX system, *CH*CH$_2$), 7.05–7.61 (10 H, m, Ph); ^{13}C NMR δ 0.48, 1.31, 1.78, 2.27, 3.72, 4.46 (each Me$_3$Si), 7.32, 8.28 (CH$_2$ ring), 29.12, 29.21 (CH ad), 37.20, 37.40, 41.12 (CH$_2$ ad), 39.49, 42.56 (q-C ad), 50.0, 58.70 (CH ring), 97.22, 103.91 (q-C ring), 126.35, 126.62, 127.77, 128.15, 128.94, 130.25 (CHPh), 143.82, 143.85 (q-C ring); ^{29}Si NMR δ 5.19, 5.77 (Me$_3$SiO), −12.63, −14.87, −15.70, −16.85 (Me$_3$Si), −24.31, −31.26 (Si ring); IR (neat) 2850–2980 (CH aliph), 3023–3086 (CH arom), 1251 (CSi) cm^{-1}; MS, *m/e* (relative intensity) 514 (M$^+$, 1.5), 499 (M$^+$ − Me, <1), 441 (M$^+$ − Me$_3$Si, 3.5), 410 (M$^+$ − PhCH=CH$_2$, 4.5), 326 ([PhCH=C(ad)OSiMe$_3$]$^+$, 15), 73 ([Me$_3$Si]$^+$, 100).

(b) Dark Reaction. A solution of 0.05 g (0.12 mmol) of **1a** in C$_6$D$_6$ was photolyzed over 17 h to form silene **2a** in about 80% yield. To this solution was added 0.028 mL of styrene under argon, and the mixture was kept in the dark. The yellow silene solution was immediately decolorized, and addition was complete in less than 15 min. The only product formed was the [2 + 2] addition product **18a** as a 1:1 mixture of diastereoisomers (^{1}H NMR).

Preparation of 2-Mesityl-3-phenyl-1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-1-silacyclobutane (18c). (a) Co-

photolysis. A solution of 0.1 g (0.25 mmol) of acylsilane **1c** and excess styrene in 1.0 mL of C_6D_6 was photolyzed for 9 h yielding **18c** as a single diastereoisomer in 96% yield (NMR). The volatile compounds were then removed under reduced pressure. The residue was purified by preparative TLC (Chromatatron, CH_2Cl_2/n-hexane (2:8), silica gel): ^{1}H NMR δ −0.22 (9 H, s, $OSiMe_3$), −0.03, 0.38 (each 9 H, s, Me_3Si), 1.57, 1.73 (2 H, CH_2 ring, AB part of ABX system, ^3J = 11.1 Hz, ^3J = 9.6 Hz, ^2J = −14.0 Hz), 2.03, 2.45, 2.53 (each 3 H, s, CH_3Mes), 4.31 (1 H, CH ring, X part of ABX system), 6.63, 6.70 (each 1 H, m, sp^2 Mes), 7.11, 7.27, 7.71 (5 H, m, sp^2 Ph); ^{13}C NMR δ −0.80, −0.06 (each Me_3Si), 2.25 (Me_3SiO), 17.74 (CH_2 ring), 20.56, 23.66, 26.29 (each CH_3Mes), 53.82 (CH ring), 88.13 (q-C ring), 126.06, 127.93, 130.99 (CH sp^2 Ph), 133.85 (q-C sp^2 Ph), 130.38, 131.43 (CH sp^2 Mes), 136.31, 139.62, 140.87, 147.79 (q-C sp^2 Mes); ^{29}Si NMR δ 12.38 (Me_3SiO), −12.84, −15.88 (Me_3Si), −13.84 (Si ring); IR 2957, 1611, 1448, 1248, 1048, 838 cm^{-1}. MS, *m/e* (relative intensity) 482 (M^+ − Me, 1), 425 (M^+ − Me_3Si, 11), 394 (M^+ − $PhCH{=}CH_2$, 71), 73 ($[Me_3Si]^+$, 100).

(b) Dark Reaction. A solution of 0.21 g (0.53 mmol) of **1c** in C_6D_6 was photolyzed over 7 h yielding a mixture of silene **2c** and benzocyclobutene **19** in an approximately 1:1 ratio. After 0.06 g (0.53 mmol) of styrene was added under argon, the mixture was stored at room temperature in the dark. After 30 min the [2 + 2] reaction of **2c** and styrene was complete, forming **18c** quantitatively as a single diastereoisomer.

Preparation of 3-Naphthyl-2-adamantyl-1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-1-silacyclobutane (20a). (a) Cophotolysis. A solution of 100 mg (0.24 mmol) of acylsilane **1a** and 50 mg (0.32 mmol) of 2-vinylnaphthalene in C_6H_6 was photolyzed over 3.5 h to form **20a** as a mixture of diastereoisomers in a 1.2:1 ratio. The mixture of isomers was purified by preparative TLC (Chromatatron): ^{1}H NMR δ −0.10, 0.34, 0.359, 0.362, 0.37, 0.39 (each 9 H, s, Me_3Si), 0.7–1.3 (2 H, m, *H*CH ring), 1.38–2.00 (31 H, m, 2 × ad and HC*H* ring), 2.23 (1 H, dd, *H*CH ring), 4.09 (1 H, dd, CH ring), 4.47 (1 H, dd, CH ring), 6.88–7.50 (14 H, m, arom H); ^{13}C NMR (of the isomer mixture) δ 0.53, 1.40, 1.84, 2.33 (Me_3Si), 3.37, 4.49 (Me_3SiO), 7.60, 8.52 (CH_2 ring), 29.05, 29.24 (CH ad), 37.14, 37.43, 38.59, 41.27 (CH_2 ad), 39.48, 42.68 (q-C ad), 50.26, 58.93 (CH ring), 97.39, 104.26 (q-C ring), 125.0–129.0 (arom CH), 127.87, 128.50, 132.86, 133.89, 141.17, 142.08 (q-C arom); ^{29}Si NMR (major isomer (based on relative intensities) δ 5.82 (Me_3SiO), −12.77, −15.73 (Me_3Si), −31.18 (Si ring); ^{29}Si NMR (minor isomer) δ 5.13 (Me_3SiO), −14.99, −16.93 (Me_3Si), −24.52 (Si ring); MS *m/e* (relative intensity) 565 (M^+, <1), 550 (M^+ − Me, <1), 492 (M^+ − Me_3Si, 9), 411 (M^+ − $NpCH{=}CH_2$, 20), 376 ($[Me_3SiO(ad)C{=}CHNp]^+$, 52), 263 ($[(Me_3Si)_3SiO]^+$?, 100), 135 (ad^+, 80), 73 ($[Me_3Si]^+$, 100).

(b) Dark Reaction. A solution of 100 mg (0.24 mmol) of **1a** in Et_2O was photolyzed overnight. After 50 mg (0.32 mmol) of 2-vinylnaphthalene was added and the mixture stored at room temperature in the dark, **20a** was formed as a 1.2:1 mixture of diastereomers.

Preparation of 3-Naphthyl-2-*tert*-butyl-1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-1-silacyclobutane (20b). (a) Cophotolysis. The procedure above was followed by using acylsilane **1b**, and after 3.5-h photolysis in the presence of 2-vinylnaphthalene a mixture of diastereomers **20b** in the ratio 1.2:1 was obtained: ^{1}H NMR δ −0.9, 0.32, 0.33, 0.34, 0.38, 0.40 (each 9 H, s, Me_3Si), 0.91, 1.11 (*t*-Bu), 1.74, 2.24 (each 1 H, dd, CH_2Si), 4.12, 4.45 (1 H, dd, CH ring), 6.8–7.5 (7 H, m, arom prot); ^{13}C NMR δ 0.31, 1.29, 1.52, 1.89 (Me_3Si), 3.35, 4.32 (Me_3SiO), 7.76, 8.23 (CH_2 ring), 28.71, 29.54 ($(CH_3)_3C$), 37.78, 40.03 ($(CH_3)_3C$), 51.39, 58.89 (CH ring), 95.19, 102.18 (q-C ring), 125.0–129.3 (CH arom), 127.51, 128.50, 132.50, 133.99, 140.76, 141.60 (q-C arom); ^{29}Si NMR δ (major isomer) (based on relative intensities) 5.73 (Me_3SiO), −13.0, −15.92 (Me_3Si), −23.69 (Si ring); ^{29}Si NMR (minor isomer) δ 4.94 (Me_3SiO), −15.18, −17.03 (Me_3Si), −29.24 (Si ring); HRMS, M^+ − Me_3Si, $C_{23}H_{37}OSi_3$ requires 413.2142, found 413.2161; MS, *m/e* (relative intensity) 487 (M^+, <1), 472 (M^+ − Me, <1), 414 (M^+ − Me_3Si, <1), 298 ($[Me_3SiO(t\text{-}Bu)C{=}CHNaph]^+$, 21), 73 ($[Me_3Si]^+$, 100).

Preparation of 2,3-Diphenyl-1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-1-silacyclobutane (18d) and 5-Phenyl-3,3-bis(trimethylsilyl)-2-(trimethylsiloxy)bicyclo[4.4.0]-3-siladeca-1,7,9-triene (22d). (a) Cophotolysis. A solution of 1.0 g (2.83 mmol) of the phenylacylsilane **1d** and 1.47 g (14.2 mmol) of styrene in 10 mL of dry benzene was photolyzed over 6 h. A clean [2 + 2] reaction occurred forming **18d** as a mixture of two diastereoisomers (NMR: 65:35). The volatile compounds were removed under reduced pressure. The diastereoisomers were then separated by flash chromatography (octane, silica gel) as oils (total 62% yield). Major isomer: ^{1}H NMR δ 0.02, 0.12, 0.43 (each 9 H, Me_3Si), 1.46–1.49 (2 H, AB part of second-order ABX system, CH_2 ring), 4.50 (1 H, X part of second-order ABX system, CH ring), 6.85–7.3 (10 H, m, Ph); ^{13}C NMR δ 0.07, 0.66, 2.62 (Me_3Si), 7.34 (CH_2 ring), 57.05 (CH ring), 85.85 (q-C ring), 125.90, 126.08, 127.66, 127.91, 128.13 (CH sp^2 Ph), 143.47, 144.59 (q-C sp^2 Ph); ^{29}Si NMR δ 13.32 (Me_3SiO), −15.71, −16.84 (Me_3Si), −17.45 (Si ring); MS, *m/e* (relative intensity) 456 (M^+, 2), 441 (M^+ − Me, <1), 383 (M^+ − Me_3Si, 15), 352 (M^+ − $PhCH{=}CH_2$, 4), 268 ($[Me_3SiO(Ph)C{=}CHPh]^+$, 4), 73 ($[Me_3Si]^+$, 100). Minor isomer: ^{1}H NMR δ −0.29, 0.00, 0.45 (each 9 H, Me_3Si), 1.44, 2.13 (2 H, AB part of ABX system, ^3J = 12.6 Hz, ^3J = 8.5 Hz, ^2J = 12.9 Hz, CH_2 ring), 4.37 (1 H, X part of ABX system, CH ring), 6.91–7.62 (10 H, m, Ph); ^{13}C NMR δ −0.73, 0.24, 2.65 (each Me_3Si), 11.73 (CH_2 ring), 53.60 (CH ring), 86.60 (q-C ring), 126.73, 126.95, 128.03, 128.22, 129.05, 130.27 (CH sp^2 Ph), 143.82, 147.09 (q-C sp^2 Ph); ^{29}Si NMR δ 10.50 (Me_3SiO), −14.40, −15.76 (Me_3Si), −17.73 (Si ring); MS *m/e* (relative intensity) 456 (M^+, 6), 441 (M^+ − Me, <1), 383 (M^+ − Me_3Si, 19), 352 (M^+ − $PhCH{=}CH_2$, 6), 268 ($[PhCH{=}CPh(OSiMe_3)]^+$, 16), 73 ($[Me_3Si]^+$, 100).

(b) Dark Reaction. A solution of 30 mg (0.04 mmol) of phenylsilene dimer **21** and 13.3 mg (0.13 mmol) of styrene in dry toluene-d_8 was heated over 11 h at 80 °C. The [2 + 2] product **18d** was formed in about 85% yield (^{1}H NMR) as a 1:1 mixture of diastereoisomers accompanied by the [2 + 4] cycloadduct **22d** in about 15% yield as a pair of isomers, one stable and the other unstable. [2 + 4] Isomer **22d** (stable): ^{1}H NMR δ 0.22, 0.24, 0.25 (each 9 H, s, Me_3Si), 1.1–1.5 (2 H, m, CH_2Si), 2.93, 3.60 (each 1 H, m, $SiCH_2CH$ + CH allyl), 5.3–7.8 (9 H, m, vinyl + Ph); ^{13}C NMR δ −0.41, 1.73 (each Me_3Si), 17.90 (CH_2Si), 45.17, 47.44 ($SiCH_2CH$ + CH allyl), 121.51, 123.58, 123.73, 127.59, 127.76, 129.09, 131.04, 148.29 (Ph, vinyl), 152.34 ($COSiMe_3$); ^{29}Si NMR δ 16.53 (Me_3SiO), −14.61, −16.18 (Me_3Si), −52.71 (Si ring). [2 + 4] Isomer **22d** (unstable): ^{1}H NMR δ 0.07, 0.21, 0.23 (each 9 H, s, Me_3Si), 1.1–1.5 (2 H, m, CH_2Si), 3.35, 3.6 (each 1 H, m, $SiCH_2CH$ + CH allyl), 5.3–7.8 (9 H, m, vinyl + Ph); ^{13}C NMR δ −0.02, 0.13, 1.73 (each Me_3Si), 13.47 (CH_2Si), 44.14, 44.36 ($SiCH_2CH$, CH allyl), 120.82, 123.03, 123.24, 127.95, 129.68, 132.30, 133.15, 133.19, 144.60 (Ph, vinyl), 154.09 ($COSiMe_3$); ^{29}Si NMR δ 16.53 (Me_3SiO), −13.90, −15.25 (Me_3Si), −40.20 (Si ring).

Preparation of α-[3-(1-Adamantyl)-2,2-bis(trimethylsilyl)-3-(trimethylsiloxy)-2-silapropyl]styrene (25a). A solution of 0.2 g (0.49 mmol) of **1a** and 0.45 g (3.8 mmol) of α-methylstyrene in C_6D_6 was irradiated over 3 h giving an "ene"-type reaction product **25a** in a quantitative yield (NMR). The product was purified by preparative TLC (Chromatatron, *n*-hexane/CH_2Cl_2 (8/2)): yield 230 mg (89%) of a colorless oil; ^{1}H NMR δ 0.23, 0.27, 0.35 (each 9 H, s, Me_3Si), 1.70, 2.02 (15 H, m, ad), 2.21, 2.54 (2 H, AB system, CH_2Si, ^2J = 15.9 Hz), 4.05 (1 H, s, CHOSi), 5.31, 5.40 (2 H, m, $C{=}CH_2$), 7.10–7.55 (5 H, m, Ph); ^{13}C NMR δ 1.76, 1.87, 1.90 (each Me_3Si), 18.39 (CH_2Si, ^1J(Si–C) = 36 Hz), 29.15 (CH ad), 37.46, 41.40 (CH_2 ad), 38.16 (q-C ad), 81.40 (*C*HOSi, ^1J(Si–C) = 52 Hz), 113.64 ($CH_2{=}C$), 126.67, 127.69, 128.59 (CH sp^2), 144.54, 148.47 (q-C sp^2); ^{29}Si NMR δ 14.33 (Me_3SiO, ^1J(Si–C) = 59 Hz), −14.09 (Me_3Si), −15.77 (Me_3Si), −41.55 (Me_3SiSi); IR (neat) 3023–3086 (arom CH), 2847–2960 (aliph CH), 1623 (C=C), 1251 (C-Si) cm^{-1}; MS, *m/e* (relative intensity) 528 (M^+, 21), 513 (M^+ − Me, 2), 455 (M^+ − Me_3Si, 45), 411 (M^+ − $CH_2CPh{=}CH_2$, 5), 291 $(Me_3Si)_2Si^+$ − $CH_2CPh{=}CH_2$, 9), 237 ($CH^+(OSiMe_3)ad$, 56), 135 (ad^+, 18), 73 (Me_3Si, 100).

Preparation of α-[3-*tert*-Butyl-2,2-bis(trimethylsilyl)-3-(trimethylsiloxy)-2-silapropyl]styrene (25b). A solution of 500 mg (1.5 mmol) of **1b** and 0.9 g (7.7 mmol) of α-methylstyrene in C_6H_6 was irradiated over 12 h, yielding an "ene"-type reaction product, **25b**: ^{1}H NMR δ 0.12, 0.13, 0.22 (each 9 H, s, Me_3Si), 0.96 (9 H, s, *t*-Bu), 2.10, 2.40 (2 H, dd, CH_2Si, ^2J = 15.8 Hz), 3.99 (1 H, s, CHO), 5.16, 5.26 (2 H, m, $C{=}CH_2$, ^2J < 1 Hz), 7.0–7.4 (5 H, m, CH arom); ^{13}C NMR δ 1.62–1.82 (Me_3Si), 18.63 (CH_2Si), 29.01 ($(CH_3)_3C$), 36.23 ($(CH_3)_3C$), 80.06 (CHO), 113.49 (CH_2 sp^2), 126.63, 127.63, 128.50 (CH arom), 144.29, 148.32 (q-C sp^2); ^{29}Si

NMR δ 14.36 (Me_3SiO), −14.32, −15.80 (Me_3Si), −39.62 (*Si*$SiMe_3$).

Preparation of α-[3-Mesityl-2,2-bis(trimethylsilyl)-3-(trimethylsiloxy)-2-silapropyl]styrene (25c). A solution of 0.2 g (0.51 mmol) of acylsilane **1c** and 0.45 g (3.8 mmol) α-methylstyrene in 1.0 mL of C_6D_6 was irradiated over 4.5 h giving an "ene"-type reaction product **25c** in quantitative yield (NMR). The product was purified by preparative TLC (Chromatatron, silica gel, *n*-hexane): yield 200 mg (77%); ^{1}H NMR δ 0.02 (×2), 0.22 (27 H, s, 3 × Me_3Si), 2.09, 2.23, 2.55 (each 3 H, s, CH_3Mes), 2.39, 2.53 (2 H, AB system, CH_2Si, ^2J = 13.7 Hz), 5.14, 5.30 (2 H, m, CH_2=C), 5.57 (1 H, s, CHOSi), 6.67, 6.75 (2 H, m, CHMes), 7.07–7.46 (5 H, m, CHPh); ^{13}C NMR δ 0.44, 0.61, 1.16 (each Me_3Si), 20.20 (CH_2Si, ^1J(Si–C) = 33 Hz), 20.89, 21.71, 23.24 (each CH_3, Mes), 65.42 (CHOSi, ^1J(Si–C) = 49 Hz), 112.25 (C=CH_2), 126.81, 127.84, 128.52, 129.28, 130.82 (CH sp^2), 133.03, 135.60, 137.56, 138.71, 142.34, 147.25 (q-C sp^2); ^{29}Si NMR δ 17.15 (Me_3SiO), −13.91, −15.14 (Me_3Si), −32.27 (Me_3Si*Si*); IR (neat) 3058–3086 (arom CH), 2952–2896 (aliph CH), 1609 (C=C), 1251 (CSi) cm^{-1}; MS, *m/e* (relative intensity) 497 (M^+ − Me, <1), 439 (M^+ − Me_3Si, <1), 395 (M^+ − $CH_2CPh{=}CH_2$, 1), 291 ($(Me_3Si)_2Si^+$ − $CH_2CPh{=}CH_2$, 38), 221 ($CH(OSiMe_3)Mes^+$, 100), 119 (Mes^+, 2), 117 (CH_2^+ − $CPh{=}CH_2$, 4), 73 (Me_3Si^+, 82).

Reaction of Acylsilane 1a and α-Methylstyrene in the Presence of Bu_3SnH. A solution of 100 mg (0.24 mmol) of acylsilane **1a**, 58 mg (0.49 mmol) of α-methylstyrene, and 350 mg (1.2 mmol) of Bu_3SnH in 0.5 mL of C_6D_6 was irradiated for 6 h. The NMR spectra of the reaction mixture indicated the formation of the "ene" compound **25a** as the major product, identical with the product formed in the absence of Bu_3SnH (see above). In addition approximately 10% of **23a**, the adduct of the silene **2a** with Bu_3SnH was observed (NMR).[10]

Preparation of 1-[3-(1-Adamantyl)-2,2-bis(trimethylsilyl)-3-(trimethylsiloxy)-2-silapropyl]indene (26a). A solution of 0.5 g (1.2 mmol) of acylsilane **1a** in Et_2O was irradiated overnight. Then 1.0 g of 1-methyleneindan was added, and the mixture was stored at room temperature yielding **26a**, purified by chromatography: ^{1}H NMR δ 0.11, 0.17, 0.37 (each 9 H, s, Me_3Si), 1.7–2.1 (15 H, m, ad), 2.15, 2.41 (2 H, dd, ^2J = 16 Hz), 3.18 (2 H, m, CH_2 ring), 4.13 (1 H, s, CHO), 6.30 (1 H, m, CH olef), 6.95–7.50 (4 H, m, CH arom); ^{13}C NMR δ 1.44, 1.67 (3 × $SiMe_3$), 8.86 (CH_2Si), 29.09 (CH ad), 37.38, 41.40 (CH_2 ad), 38.10 (q-C ad), 81.70 (CHO), 119.65 (HC=), 123.93, 125.08, 126.46, 128.22 (CH arom), 143.71, 143.97, 147.30 (q-C sp^2); ^{29}Si NMR δ 14.70 (Me_3SiO), −14.07, −15.78 (Me_3Si), −41.54 (*Si*$SiMe_3$); MS, *m/e* (relative intensity) 541 (M^+, <1), 526 (M^+ − Me, 1), 468 (M^+ − Me_3Si, 33), 135 (ad$^+$, 28), 73 ($[Me_3Si]^+$, 100).

Preparation of 1-[3-*tert*-Butyl-2,2-bis(trimethylsilyl)-3-(trimethylsiloxy)-2-silapropyl]indene (26b). A solution of 100 mg (0.3 mmol) of the *tert*-butylacylsilane **1b** and 200 mg (1.5 mmol) of 1-methyleneindan in C_6D_6 was photolyzed for 16 h yielding **26b** as the major product: ^{1}H NMR δ 0.09, 0.11, 0.31 (each 9 H, s, Me_3Si), 1.03 (9 H, s, *t*-Bu), 2.12, 2.37 (2 H, dd, CH_2Si, ^2J = 16.2 Hz), 3.16 (2 H, m, CH_2 ring), 4.16 (1 H, s, CHO), 6.24 (1 H, m, CH=), 6.95–7.50 (CH arom); ^{13}C NMR δ 1.38, 1.53, 1.61 (Me_3Si), 9.07 (CH_2Si), 28.97 ($(CH_3)_3C$), 36.19 ($(CH_3)_3C$), 37.87 (CH_2 ring), 80.45 (CHO), 119.59 (HC=), 123.89, 125.04, 126.38, 128.00 (CH arom), 143.62, 143.94, 147.15 (q-C sp^2); ^{29}Si NMR δ 14.70 (Me_3SiO), −14.30, −15.78 (Me_3Si), −39.64 (*Si*$SiMe_3$); MS, *m/e* (relative intensity) 448 (M^+ − Me, <1), 389 (M^+ − Me_3Si, 1), 73 ($[Me_3Si]^+$, 100).

Reaction of Silenes 2a–c with 1,1-Diphenylethylene. Solutions of 0.1 g of acylsilanes **1a–c** and excess 1,1-diphenylethylene in benzene were photolyzed over 24 h. NMR data showed that the silenes were formed but that no reaction with diphenylethylene had occurred. Heating to 65 °C did not lead to any product.

Reaction of Phenylacylsilane 1d with 1,1-Diphenylethylene. Cophotolysis of **1d** and excess 1,1-diphenylethylene in C_6D_6 led to some addition products, which were unstable at room temperature (NMR). Storing the sample at room temperature led to the formation of the phenylsilene dimer **21**. Photolysis of the acylsilane **1d** plus diphenylethylene at 0 °C over 3 h led to the formation of several products as indicated by the NMR spectra (^{1}H, ^{13}C, ^{29}Si): ^{1}H NMR several signals at δ −0.3 to +0.55 (Me_3Si), several small signals at δ 0.9–2.3 (CH_2 AB systems, CH_2 ring attached to Si), δ 4.0–6.0 (several small peaks); ^{13}C NMR −2 to +5 (several Me_3Si), 18.76, 19.51, 19.76 (CH_2Si), 47.59, 49.93, 51.66 (CPh_2), 70.01, 72.39, 83.69 ppm ($COSiMe_3$).

Reaction of Silenes with *cis*- and *trans*-Stilbene. Cophotolysis of the acylsilanes **1a–c** with an excess of either *cis*-stilbene or *trans*-stilbene in C_6D_6 did not lead to the formation of addition products although the silenes **2a**, **2b**, and **2c** were observed (NMR). Heating the solutions of silene and stilbene to 65 °C did not result in formation of an addition product. However, *cis*-stilbene isomerized to its trans form in some cases (**2a,c**).

Registry No. **1a**, 72189-53-8; **1b**, 69397-47-3; **1c**, 97551-01-4; **1d**, 60154-95-2; **2a**, 72189-54-9; **2b**, 81671-49-0; **2c**, 97551-02-5; **3a**, 109908-01-2; **3b**, 109908-03-4; **3c**, 109908-05-6; **4a**, 109908-02-3; **4b**, 109908-04-5; **5** (isomer 1), 109908-06-7; **5a** (isomer 2), 109908-07-8; **5b** (isomer 1), 109927-26-6; **5b** (isomer 2), 109908-09-0; **5c** (isomer 1), 109908-11-4; **5c** (isomer 2), 109908-12-5; **63a**, 109908-08-9; **66**, 109908-10-3; **6c**, 109908-13-6; **7**, 109908-14-7; **11a**, 109908-15-8; **12a**, 109908-16-9; **13a**, 109908-17-0; **14a**, 109908-18-1; **14b**, 109908-19-2; **15a**, 109908-20-5; **15b**, 109927-27-7; **17**, 109908-21-6; **18a** (isomer 1), 109908-22-7; **18a** (isomer 2), 109908-23-8; **18c**, 109908-24-9; **18d** (isomer 1), 109908-29-4; **18d** (isomer 2), 109908-30-7; **19**, 97551-03-6; **20a** (isomer 1), 109908-25-0; **20a** (isomer 2), 109908-26-1; **20b** (isomer 1), 109908-27-2; **20b** (isomer 2), 109908-28-3; 21, 60154-99-6; **22d** (isomer 1e, 109908-31-8; **22d** (isomer 2), 109908-32-9; **23a**, 107768-59-2; **25a**, 109908-33-0; **2kb**, 109908-34-1; **25c**, 109908-35-2; **26a**, 109908-36-3; **26b**, 109908-37-4; Bu_3SnH, 688-73-3; 2,3-dimethyl-1,3-butadiene, 513-81-5; 1,3-butadiene, 106-99-0; isoprene, 78-79-5; cyclopentadiene, 542-92-7; cyclohexadiene, 592-57-4; 1-octene, 111-66-0; cyclohexene, 110-83-8; styrene, 100-42-5; 2-vinylnaphthalene, 827-54-3; 2-methylstyrene, 98-83-9; 1-methyleneindan, 1194-56-5; 1,1-diphenylethylene, 530-48-3.