Cycloaddition and Other Reactions of Silenes with α,β-Unsaturated Esters

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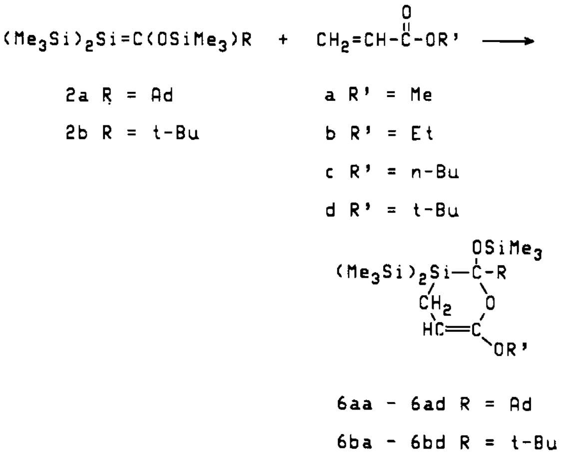
Several silenes of the family $(Me_3Si)_2Si{=}C(OSiMe_3)R$ were found to react in a [2 + 4] manner with a variety of acrylate esters to give 1-sila-3-oxacyclohex-4-enes as products, as confirmed by an X-ray structure. With crotonate esters the same silenes yielded 1-sila-2-oxacyclohex-3-enes when the reaction was carried out in the dark, with minor amounts of γ-silylcrotonate products, the result of nominal addition of the allylic C—H bond across the ends of the Si=C bond, also being formed. On the other hand, cophotolysis of the relevant acylsilane with the crotonate esters led to formation of the γ-silylcrotonates as the major product. The structures of these species were confirmed by a crystal structure. Reactions with methacrylate esters gave acyclic α-(silylmethyl)acrylate products as a result of nominal insertion of the silene into the allylic C—H bond. Maleate and fumarate esters each gave a mixture of the same two diastereomers from [2 + 4] cycloaddition to the C=C—C=O(OR) system, forming 1-sila-3-oxacyclohex-4-enes. Reactions with ethyl cinnamate involved [2 + 4] cycloadditions of the opposite regiochemistry, leading to 1-sila-2-oxycyclohex-3-enes. These latter products readily hydrolyzed to silalactones, as shown by a crystal structure.

An earlier study of the reactions of simple aldehydes and ketones with silenes of the family $(Me_3Si)_2Si{=}C(OSiMe_3)R$ showed that stable siloxetanes were frequently the major products of the reaction, accompanied in some cases by products which were nominally [2 + 4] adducts.[1] These findings led us to investigate the behavior of α,β-unsaturated aldehydes such as propenal, crotonaldehyde, or cinnamaldehyde. As reported in the accompanying paper, these carbonyl compounds gave primarily [2 + 4] cycloadducts having both possible regiochemistries, together with minor amounts of accompanying siloxetanes in some cases.[2] With use of α,β-unsaturated ketones such as methyl vinyl ketone and benzalacetophenone, [2 + 4] cycloadducts were obtained involving addition of the silicon–carbon double bond across the ends of the α,β-unsaturated system with both possible regiochemistries. A summary of the findings, with the structures of the major and minor products (first and second product structures shown), is given in Scheme I.

This behavior appeared to be in accord with the known reactivities of α,β-unsaturated aldehydes and ketones, where 1,2-addition predominates with the aldehydes and 1,4-addition predominates with the ketones, although some of the regiochemistries observed were surprising. These results led us to investigate the reactions of the silenes **2** with simple esters and with α,β-unsaturated esters. Somewhat to our surprise, the silenes showed no reaction at all with simple esters such as ethyl acetate and methyl benzoate, and the exclusive mode of reaction observed with a variety of acrylate esters involved the [2 + 4] cycloaddition of the silene to the α,β-unsaturated system C=C—C=O of the esters, yielding essentially quantitatively a single isomer of a series of 1-sila-3-oxacyclohex-4-enes **6** as shown in eq 1. This was shown to be a "dark" reaction, since the same product was produced from the reaction of preformed silene with the ester in the dark as was obtained when a mixture of the ester and the parent acylsilane (from which the silene is formed on photolysis) was cophotolyzed.



(1)

The structures of these species were determined by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy and by the crystal structure determination of one compound, **6ad**, derived from the adamantylsilene[3] and *tert*-butyl acrylate. These data clearly established the regiochemistry of the additions. The ORTEP diagram of the crystal structure is shown in Figure 1. Details of the NMR spectra and crystal structure are discussed later.

Reactions of the same silenes with ethyl and methyl crotonates were next investigated to see if, as was found when the reactions of the silenes with the α,β-unsaturated aldehydes propenal and crotonaldehyde[2] were studied, the regiochemistry of the major reaction products was reversed when the methyl substituent was added. Instead, it was found that in changing from acrylate esters to crotonate esters, a new reaction mode was operative in which the allylic C-H atoms of the C-methyl group added across the ends of the silicon–carbon double bond, resulting in the silylacrylate **7** being formed. When the reaction with the crotonates was carried out by cophotolysis of the relevant acylsilane with the ester, **7** was the major product formed. However, when the reaction was carried out in the dark between preformed silene and ester, the [2 + 4] cycloadduct **8**, a 1-sila-2-oxacyclohex-3-ene, was the major product, with **7** being formed in minor amounts. This was the only reaction studied where the proportions of the products formed depended in a significant way on the

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

[2] Brook, A. G.; Hu, S. S.; Chatterton, W. J.; Lough, A. J. *Organometallics*, preceding paper in this issue.

[3] Throughout this paper the polysilylacylsilanes and the silenes will be described in terms of the hydrocarbon group attached to the carbonyl group or sp^2-hybridized carbon of the silene, respectively: thus, $(Me_3Si)_3SiCO$-*t*-Bu is the (*tert*-butylacyl)silane and $(Me_3Si)_2Si{=}C(OSiMe_3)Ad$ is called the adamantylsilene.

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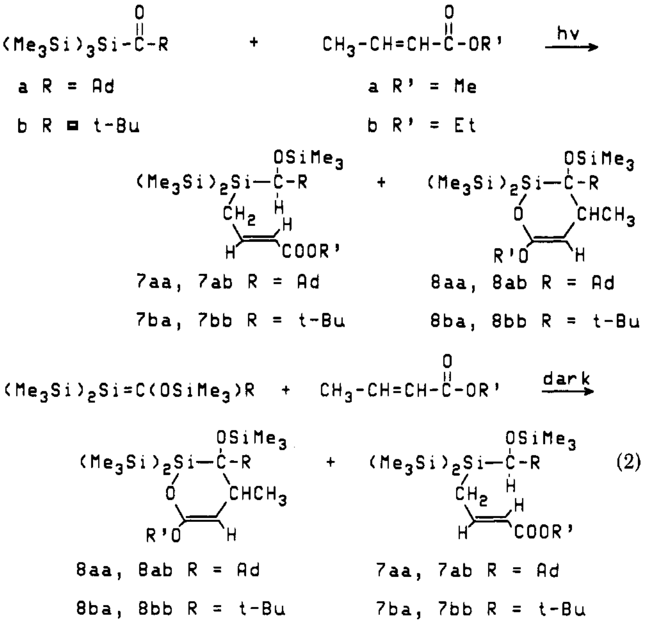
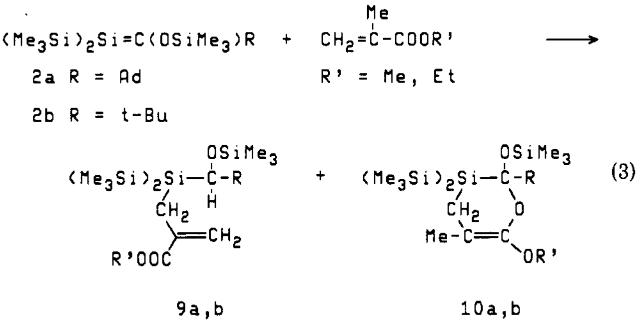


presence or absence of light, and the results may signify the intervention of different reaction intermediates under the different reaction conditions.

The crystal structure of the product **7aa** (R′ = Me) from the adamantylsilene and methyl crotonate was determined with use of X-ray diffraction methods; its ORTEP diagram is given in Figure 2. The NMR data for four products of this family are given in the Experimental Section.

In order to explore further the generality of the above C–H insertion reaction, the reactions between the silenes and methacrylate esters were explored. The major products were found to be the α-(silylmethyl)acrylates **9**, structures that could have resulted from addition of the allylic C–H atoms of the *C*-methyl group to the ends of the silicon–carbon double bond (eq 3), although an "ene" reaction could also explain the structure of the products in this case. Small amounts of minor products, the 1-sila-3-oxacyclohex-4-enes **10** resulting from [2 + 4] addition of the silene across the α,β-unsaturated system, were also observed, as shown in eq 3. The proportions of products were insensitive as to whether the reactions were carried out in the dark or by cophotolysis.



The formation of the α-(silylmethyl)acrylate products **9** from the methacrylate esters could be explained by an "ene" reaction as shown in Scheme II. Such processes have been observed previously involving silenes such as **2**.[4] However, a simple "ene" reaction would not explain the structures of the products formed from the crotonate esters, and it would be necessary to propose that following the "ene" reaction, a 1,3-silaallylic rearrangement occurred.

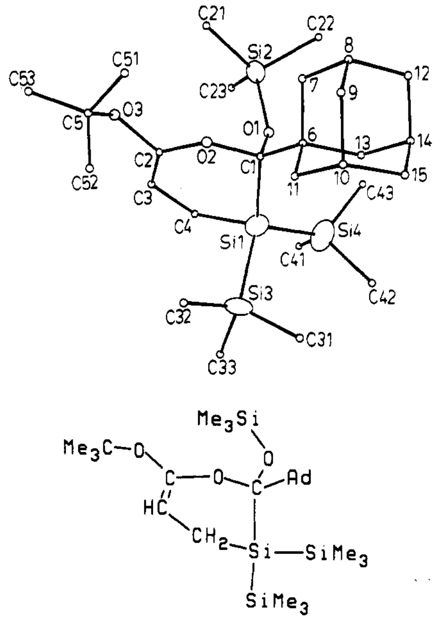


Figure 1. Diagrams of compound **6ad**, from the adamantylsilene and *tert*-butyl acrylate.

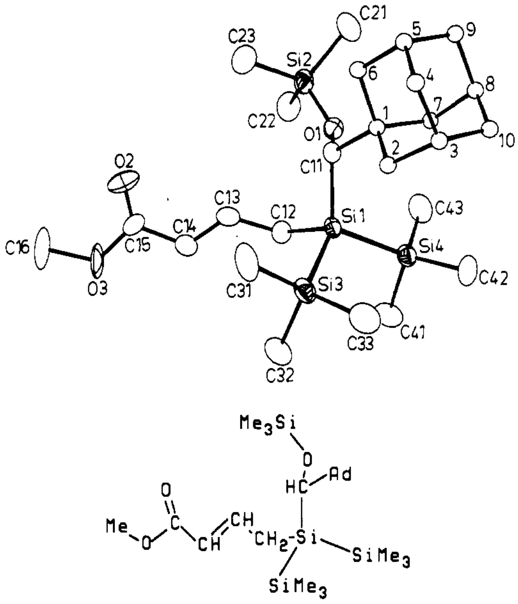


Figure 2. Diagrams of compound **7aa**, from the adamantylsilene and methyl crotonate.

While such silaallylic processes have been observed,[5] they normally require temperatures of 200 °C or higher; hence, they are unlikely to occur rapidly at room temperature, as would be required to explain the present results.

An alternative to an "ene" pathway is the 1,2-C–H insertion pathway shown in Scheme II. To our knowledge, the direct addition of a C–H bond across the ends of a silicon–carbon double bond, as distinct from its participation in an "ene" process, is very uncommon; extended reaction of our silenes with toluene or para-substituted toluenes failed to show any insertion reactions into their benzylic C–H bonds. Thus, direct addition, by a polar or radical or concerted process, appears to be most unusual.

It is significant that the reaction of the silene with the crotonate esters was noticeably slower than with the acrylate esters. When the crotonate reactions were run in the dark with preformed silene, much of the silene rear-

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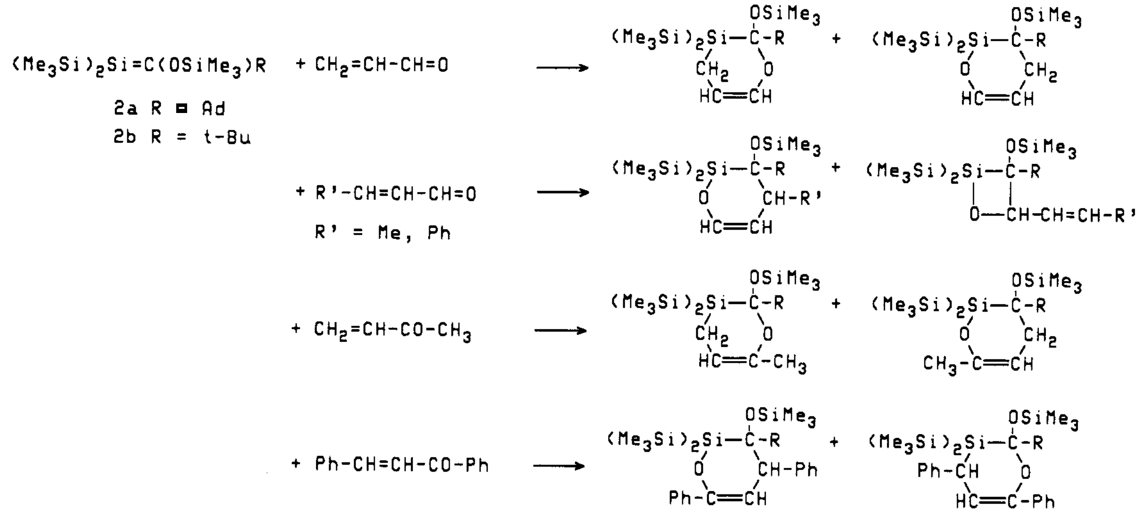
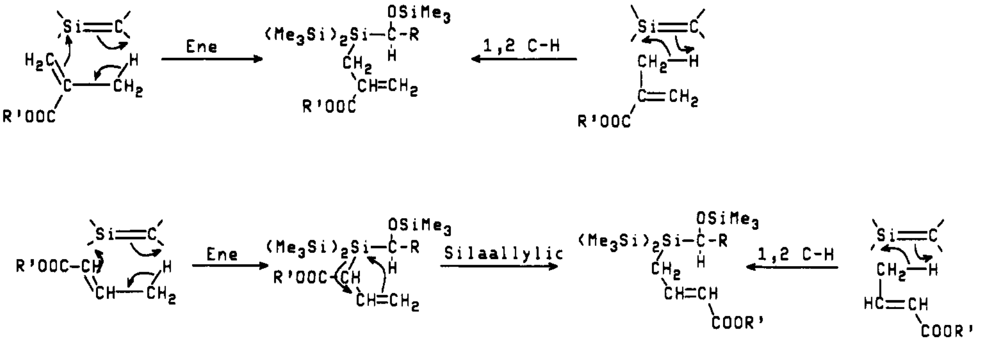
[4] Brook, A. G.; Vorspohl, K.; Ford, R. R.; Hesse, M.; Chatterton, W. J. *Organometallics* **1987**, *6*, 2128.

[5] Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1975**, *95*, 8678.

Scheme I

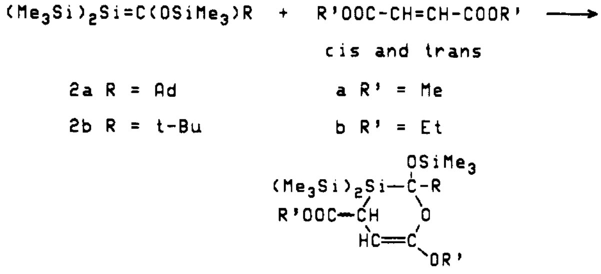


Scheme II



ranged over the 2-day course of the reaction back to the parent acylsilane, a known process,[6] resulting in only low yields of adducts and much recovered crotonate ester and parent acylsilane. In contrast, reactions of preformed silenes with acrylate esters appeared to be complete in a few minutes, and no acylsilane was observed. This result suggests that significant steric inhibition to cyclization may be introduced when the acrylates are replaced by crotonates.

When either diethyl maleate or diethyl fumarate was employed as the α,β-unsaturated ester, the same mixture of the two diastereomers **11ab** and **12ab** was formed, although not in exactly the same proportions (eq 4). As-



(4)

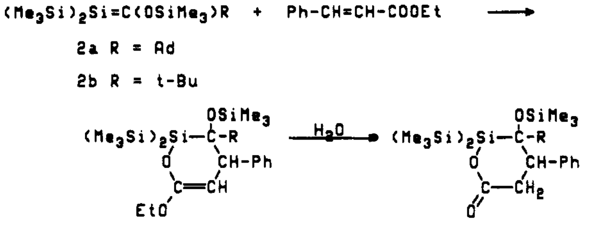
11aa,ab,ba major isomers

12aa,ab,ba minor isomers

suming that the [2 + 4] cycloaddition reaction is concerted, the proportions need not be the same, since the mixtures of products from maleate or fumarate esters would be derived from different transition states. The NMR data for these compounds, given in Table II, clearly indicated, particularly from the ring ^{29}Si resonance at about −40 to −45 ppm, that they, like the acrylate ester adducts, were 1-sila-3-oxyacyclohex-4-enes, with the two isomers observed being the two diastereomers to be expected from a molecule containing two stereocenters.

It was noted that the proportions of the two diastereomers observed related directly to the nominal size of the R group of the silene employed and the size of the alkoxy group of the ester. Thus, the proportions of isomers observed for R = *t*-Bu in the silene and R′O = MeO in the fumarate ester were 1.2:1; with R = Ad and dimethyl fumarate the proportions were approximately 2:1, while with the adamantylsilene and diethyl maleate the proportions were about 4.5:1. This is consistent with steric forces playing a significant role in determining the proportions of the two isomers. The major diastereomer presumably has the carboalkoxy group on the ring syn to the less bulky trimethylsiloxy group.

In contrast to the results with maleate and fumarate esters, when ethyl cinnamate was allowed to react with the adamantyl- and *tert*-butylsilenes, the sole products obtained were the 1-sila-2-oxacyclohex-3-enes **13a** and **13b** (eq 5), as shown by their NMR spectra. When **13a** stood



(5)

13a,b 14a,b

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

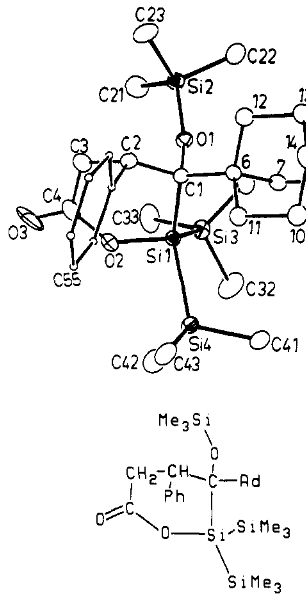


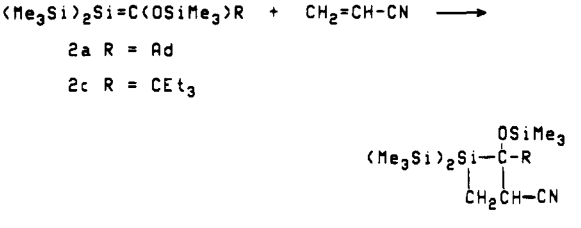
Figure 3. Diagrams of lactone **14a**, from the adamantylsilene and ethyl cinnamate, after hydrolysis.

for 1 month unprotected from air or moisture, it hydrolyzed to the silalactone **14a** as shown by the crystal structure of the material, whose ORTEP diagram is shown in Figure 3. The related *tert*-butyl derivative **13b** behaved similarly.

That **13a**, a ketene acetal, should hydrolyze under very mild conditions is not surprising, and deliberate hydrolysis of **13a** with water showed mixtures of **13a** and **14a** to be present as the hydrolysis proceeded.

The regiochemistries of the [2 + 4] cycloaddition reactions of the silenes with acrylate, maleate, and fumarate esters were the same but were reversed with the crotonate esters and with ethyl cinnamate. It is evident that the regiochemistry of addition of a silicon–carbon double bond to an α,β-unsaturated ester is very sensitive to the nature of substituents on the conjugated system, as was also found with α,β-unsaturated aldehydes and ketones.[2]

Finally, the reactions of the adamantyl- and (triethylmethyl)silenes with acrylonitrile were briefly investigated. In this system [2 + 4] cycloaddition could not be expected and it was of interest to see whether [2 + 2] addition occurred across the carbon–nitrogen triple bond or the carbon–carbon double bond. The products were found to be diastereomeric pairs of [2 + 2] adducts of the silene with the carbon–carbon double bond to give the cyano-substituted silacyclobutanes **15a,c** (eq 6), whose NMR spectra confirmed the structures. No reaction involving the carbon–nitrogen triple bond was observed either with acrylonitrile or with simple nitriles such as aceto- and benzonitrile.

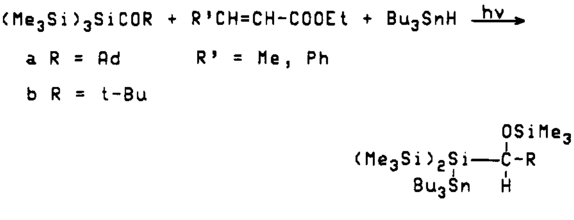


$$(Me_3Si)_2Si{=}C(OSiMe_3)R + CH_2{=}CH{-}CN \longrightarrow (Me_3Si)_2\underset{CH_2}{Si}{-}\overset{OSiMe_3}{\underset{CH{-}CN}{C}}{-}R \qquad (6)$$

2a R = Ad
2c R = CEt$_3$

15a,c

In hopes of obtaining further information about the mechanisms of the above cycloadditions with esters, several cophotolyses of the acylsilanes with esters were carried out in the presence of tributyltin hydride (as shown in eq 7), which might have trapped any radical intermediates. In



$$(Me_3Si)_3SiCOR + R'CH{=}CH{-}COOEt + Bu_3SnH \xrightarrow{h\nu} (Me_3Si)_2\underset{Bu_3Sn}{Si}{-}\overset{OSiMe_3}{\underset{H}{C}}{-}R \qquad (7)$$

a R = Ad R' = Me, Ph
b R = t-Bu

16a,b

every case the major product of the reactions was **16**, the tin hydride adduct to the silene, a known compound.[4] Despite the presence of 1 equiv of methyl crotonate, **16** was the only reaction product. With ethyl cinnamate, **16** constituted 80% of the reaction products and the other 20% was the previously observed cycloadduct **13a**. The regiochemistry of the reaction forming **16** is not consistent with a [2 + 2] process dominated by polar influences but could be the result of a radical chain reaction.

It is evident from the above results that members of our family of silenes readily undergo [2 + 4] cycloaddition reactions with α,β-unsaturated esters, and there was no evidence for [2 + 2] reactions with either the C=O group or with the C=C part of the esters. Studies also showed that there was no reaction at all between the silenes and simple esters such as ethyl acetate and methyl benzoate. Both possible regiochemistries were observed with the α,β-unsaturated esters and depended on the substituents on the α,β-unsaturated system. Evidently the regiochemistry of these additions is often very sensitive to factors other than the anticipated polarities of the silene double bond and of the α,β-unsaturated system, be it an aldehyde, ketone or ester, as was also noted in the accompanying paper.[2] This phenomenon has also been observed previously in [2 + 4] cycloadditions of dienes with acrylic acid,[7] where both possible regiochemistries were observed. These results have been explained in terms of frontier orbital interactions.[8] The reactions of our silenes with simple acrylate esters can be explained in the same manner as was used to explain the regiochemistries of the reactions of the silenes with α,β-unsaturated aldehydes and ketones.[2] Thus, the HOMO of the silene, with its higher coefficient located on silicon, as calculated by Apeloig,[9] will interact with the LUMO of the unsubstituted acrylate esters, where the higher coefficient of the frontier orbital appears to be located on the terminal carbon atom of the unsaturated system, accounting for the formation of the 1-sila-3-oxacyclohex-4-enes. The formation of the 1-sila-2-oxacyclohex-3-ene from the crotonate esters and ethyl cinnamate is in accord with a cyclization reaction dominated by the silaphilic character of oxygen and is consistent with the anticipated polarity of the reagents, as most commonly prevails in [2 + 4] cycloadditions. Steric effects introduced by the β-substituent in the crotonate and cinnamate esters may also be a factor leading to their reaction with the opposite regiochemistry. Finally, with esters that possessed allylic hydrogen, while the expected [2 + 4] cyclizations prevailed in reactions carried out in the dark, nominal insertion of the Si=C bond into the C—H bond was the major reaction observed if carried out under photolysis conditions. The mechanism of these latter reactions is not

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(7) Alder, K.; Schumacher, M.; Wolff, O. *Justus Liebigs Ann. Chem.* **1949**, *564*, 79.

(8) Fleming, I. In *Frontier Orbitals and Organic Chemical Reactions*; Wiley: London, 1976; pp 129, 141–142.

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

fully understood at present.

NMR Studies

^1H, ^{13}C, and ^{29}Si NMR spectra were obtained for all the silene–acrylate adducts **6aa** to **6bd**. The proton spectra were easily analyzed for the ABX patterns of the three ring protons in the sequence Si—CH_AH_B—CH_C═, which appeared as three doublets of doublets at about 1.2, 1.7, and 4.0 ppm, with approximate values of the coupling constants J_{AB} – 16.4 Hz (geminal coupling) and J_{AC} = 8.0 Hz and J_{BC} = 1.8 Hz (vicinal couplings) for the CH_AH_B and CH_C ring protons, respectively, in each of the 1-sila-3-oxacyclohex-4-enes. These values are consistent with the proposed structures. The X-ray structure of **6ad**, whose ORTEP diagram is shown in Figure 1, confirmed the structure assignment.

The other notable feature of the ^1H spectra was the multiplets found for the $-OCH_2-$ protons of the ethyl and *n*-butyl esters. Each of the diastereotopic protons of the $CH_{A'}H_{B'}$ group was observed as partially overlapping doublets of quartets for the ethyl esters and doublets of triplets for the *n*-butyl esters.

Strongly supportive of the regiochemistry of the cycloadditions was the finding that the signal for the ring methylene group (confirmed by use of the APT pulse sequence) occurred at high field, with a chemical shift of about 1.8–2.0 ppm in the ^{13}C spectra, consistent with its attachment to the ring silicon atom. A methylene group attached to a ring carbon atom would absorb at about 31 ppm.[2] The ring ═CH carbon atom was much farther downfield at about 70 ppm, as expected, while the ring quaternary carbon atom to which the trimethylsiloxy group was attached had a chemical shift of about 112 ppm. The sp^2-hybridized carbon bearing two oxygen atoms, ═C(OR′)—O–, resonated in the range 154–159 ppm, slightly upfield of the position where ester carbonyl groups were found to absorb, as in the maleate and fumarate adducts (174–176 ppm) 11 and 12.

Each of the ^{29}Si NMR spectra revealed four signals: both trimethylsilyl groups attached to silicon resonated in the −13 to −16 ppm region, as is normally found,[1-3] the trimethylsiloxy group resonated at about 9.5 ppm in the acrylate adducts, and the ring silicon atoms, strongly shifted upfield both by the two attached trimethylsilyl groups and by being in a six-membered ring, were observed in the range of −53 to −55 ppm, the same range found for the structurally related adducts of the silenes with α,β-unsaturated aldehydes and ketones.[2]

Both the proton-coupled ^{29}Si spectra and the ^1H–^{29}Si 2D NMR spectra obtained for the methyl acrylate adduct **6aa** of the adamantylsilene confirmed the structures proposed for these compounds. It was found that both trimethylsilyl groups attached to the ring silicon atom not only coupled to the protons of their respective methyl groups (J = 6.4 and 6.5 Hz) but each also coupled detectably to only one hydrogen of the ring CH_2 group (J = 1.7 Hz for Me_3Si with ^{29}Si δ of −14.98; J = 2.75 Hz for Me_3Si group with ^{29}Si δ of −15.64), accounting for the doublet of decets observed in the proton-coupled ^{29}Si NMR spectrum.

The NMR spectra of the fumarate and maleate ester adducts **11** and **12** with the silenes showed ^{29}Si signals in positions very similar to those for the acrylate adducts, consistent with these products also being 1-sila-3-oxacyclohex-4-enes, with slightly different substituents. Thus, the ring silicon atom signals occurred in the range −40 to −44 ppm, whereas the ethyl cinnamate adducts, which possessed the 1-sila-2-oxacyclohex-3-ene structures, had their ring ^{29}Si NMR adsorptions in the range 20–22 ppm. The proton spectra were complex in some regions: e.g., in the spectra of the products of diethyl maleate and fumarate with the adamantylsilene, **11ab** and **12ab**, the CH_3 parts of the EtO groups of both diastereomers of the major and minor adducts resonated at about 1.0 ppm, as overlapping triplets, and each of the diastereotopic protons of $-CH_{A'}H_{B'}$—O– of the ketene acetal EtO groups of the products had two overlapping doublets of quartets, while the ester EtO group displayed a quartet, all in the range 3.5–4.2 ppm.

The silacyclobutanes **15a,c** obtained from the [2 + 2] additions of the silenes with acrylonitrile, in common with other silacyclobutanes, had the ring silicon atom absorption occurring in the range −11 to −16 ppm, a range characteristic of a four-membered ring containing silicon bonded to carbon.[4]

X-ray Structural Determinations

It appears that steric features dominate the structural aspects of molecules **7aa** and **14a**. The Si–Si bond lengths in compound **14a** (2.3928 (13) and 2.3861 (13) Å) are longer than those in compound **7aa** (2.358 (4) and 2.350 (4) Å). The elongation of the Si–Si bond in **14a** may be caused by steric impediment of the greater molecular bulk in **14a** than in **7aa**. The average values for a Si–C(sp^3) bond length in **7aa** and **14a** (1.860 (10) and 1.860 (4) Å, respectively) are in accord with those found in other structures containing bonds of this type[10] (mean value 1.857 (18) Å).

In **14a** there is especially pronounced bond angle widening for the angles C(1)–O(1)–Si(2) (145.62 (18)°) and C(1)–Si(1)–Si(4) (126.99 (10)°); the angles at O(2)–Si(1)–Si(4) (99.83 (9)°) and O(1)–C(1)–Si(1) (100.31 (17)°) are smaller than expected. In **7aa** the effect is not so dramatic but bond angles C(11)–O(1)–Si(2) (135.8 (5)°) and C(11)–Si(1)–Si(3) (116.24 (29)°) are wider and the angles O(1)–C(11)–Si(1) (104.6 (5)°) and C(12)–Si(4)–Si(1) (101.58 (29)°) are slightly smaller than expected. These bond angles deviate from the values expected on the basis of hybridization principles, but the deviations are consistent with steric demands.

The steric effect is more pronounced in **14a** because of the presence of the saturated six-membered ring with the phenyl substituent. Atoms Si(1), O(2), C(4), C(3), and C(1) in **14a** form a plane (maximum deviation −0.044 (2) Å for O(2)) with C(2) −0.651 (3) Å from the plane. The angle between this plane and the plane of the phenyl group is 100°. The orientation of the phenyl ring, with respect to rotation about the C(2)–C(51) bond, is consistent with minimizing intramolecular interactions of ortho hydrogen atoms. There may also be a weak attractive interaction between O(3) and H(56) (O–H distance 2.636 (5) Å). The steric demands of the trimethylsilyl groups and the adamantyl group upon the phenyl ring are reflected in the magnitude of the bond angle C(1)–C(2)–C(51), which is 120.19 (26)°.

The ester side chain in molecule **7aa** has an extended conformation with all torsion angles close to 180°, except for the angle Si(1)–C(12)–C(13)–C(14), which is −116.0 (10)°.

Experimental Section

All NMR spectra were run on either a Varian XL 400 or Gemini 200 MHz spectrometers in deuteriobenzene solvent. The APT[11]

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

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

Table I. NMR Data for Silene–Acrylate Ester Adducts 6a (R = Ad) and 6b (R = *t*-Bu)[a]

	6aa, R′ = Me	**6ab**, R′ = Et	**6ac**, R′ = *n*-Bu	**6ad**, R′ = *t*-Bu	**6ba**, R′ = Me	**6bb**, R′ = Et	**6bc**, R′ = *n*-Bu	**6bd**, R′ = *t*-Bu
^{1}H NMR								
Me_3Si	0.23	0.24	0.24	0.22	0.21	0.22	0.22	0.21
	0.25	0.27	0.28	0.28	0.24	0.24	0.24	0.23
	0.31	0.33	0.34	0.38	0.27	0.31	0.31	0.35
H_A	1.22 dd	1.24 dd	1.25 dd	1.24 dd	1.21 dd	1.24 dd	1.24 dd	1.15 dd
H_B	under Ad	1.70 dd	1.76 dd	1.80 dd	1.67 dd	1.70 dd	1.69 dd	1.71 dd
H_C	3.94 dd	4.01 dd	4.04 dd	4.51 dd	3.93 dd	4.01 dd	4.04 dd	4.50 dd
$J(H_A\text{-}H_B)$	16.4	16.5	16.4	17.4	16.4	16.5	16.4	17.4
$J(H_A\text{-}H_C)$	8.1	8.0	8.0	6.9	8.1	8.0	8.0	6.9
$J(H_B\text{-}H_C)$	2.1	2.1	2.1	2.7	2.1	2.1	2.1	2.7
R	1.55–1.99 m				1.08	1.09	1.09	1.08
R′O	3.25	$H_{A'}$ 3.55 dq[b] $H_{B'}$ 3.64 dq Me 1.10 t	$H_{A'}$ 3.64 dt[c] $H_{B'}$ 3.73 dq Me 0.79 t CH_2 1.3–1.58 (4 H, m)	1.31	3.23	$H_{A'}$ 3.54 dq[d] $H_{B'}$ 3.63 dq Me 1.06 t	$H_{A'}$ 3.64 dt[e] $H_{B'}$ 3.72 dt Me 0.79 t CH_2 1.25–1.56 (4 H, m)	1.29
^{13}C NMR								
Me_3Si	−0.04	−0.04	−0.03	0.29	−0.13	−0.13	−0.15	0.19
	0.50	0.51	0.52	0.75	0.38	0.39	0.37	0.54
Me_3SiO	2.16	2.15	2.17	2.35	2.08	2.08	2.05	2.26
r Si-CH_2	1.75	1.86	1.89	2.35	2.08	2.08	2.05	2.26
Ad CH	28.67	28.65	28.66	28.67				
Ad CH_2	37.29	37.26	37.27	37.33				
Ad CH_2	38.36	38.34	38.35	38.42				
C quat	41.65	41.62	41.64	41.48				
Me$_3$C-C					26.43	26.44	26.34	26.47
Me$_3$*C*-C					40.09	40.08	40.08	39.86
MeO	54.28				54.27			
Me$_3$*C*O				77.60				77.67
CH$_3$-(C)-O		14.74	13.54	29.13		14.73	13.53	29.10
-*CH*$_2$-O-		63.00	67.25			62.99	67.22	
-*CH*$_2$- of Bu			19.30, 31.45				19.27, 31.42	
r *CH*$_C$=	69.88	71.02	70.97	85.10	69.93	71.06	71.01	84.93
r *C*-OSi	112.91	112.77	112.77	113.22	112.01	111.90	111.86	112.11
r *C*-OR′	159.34	158.43	158.60	154.92	159.34	158.41	158.57	154.94
^{29}Si NMR								
Me_3SiO	9.45	9.39	9.44	9.79	9.34	9.38	9.36	9.70
Me_3Si	−14.83	−14.75	−14.75	−14.22	−14.92	−14.85	−14.88	−14.37
	−15.45	−15.44	−15.42	−15.97	−15.49	−15.46	−15.49	−16.05
r Si	−55.09	−55.23	−55.23	−56.35	−53.68	−53.72	−53.89	−54.98

[a] Legend: Ad = 1-adamanyl; d = doublet; dd = doublet of doublets; dq = double of quartets; m = multiplet; r = ring. Coupling constants listed above are in Hz, and chemical shifts are in ppm. [b] In **6ab**, **6ac**, **6bb**, and **6bc** the *O*-methylene protons were diastereotopic and the $OCH_{A'}H_{B'}\text{–}CH_n$ system was observed as overlapping doublets of quartets (R′ = Et) or doublets of triplets (R′ = *n*-Bu). $J(H_A{'}\text{–}CH_3) = J(H_{B'}\text{–}CH_3) = 7.0$ Hz. $J(H_{A'}\text{–}H_{B'}) = 9.3$ Hz. [c] $J(H_{A'}\text{–}CH_2) = J(H_{B'}\text{–}CH_2) = 6.3$ Hz, $J(H_{A'}\text{–}H_{B'}) = 9.4$ Hz. [d] $J(H_{A'}\text{–}CH_3) = J(H_{B'}\text{–}CH_3) = 7.0$ Hz, $J(H_{A'}\text{–}H_{B'}) = 9.4$ Hz. [e] $J(H_{A'}\text{–}CH_2) = J(H_{B'}\text{–}CH_2) = 6.3$ Hz, $J(H_{A'}\text{–}H_{B'}) = 9.4$ Hz.

pulse sequence was used to help in the assignment of the peaks in the ^{13}C spectra, and the ^{29}Si spectra were run in the DEPT[12] or NOE-suppressed modes.

Polysilylacylsilanes were prepared according to published procedures.[6] Acrylate and other esters were obtained from Aldrich Chemical Co. and were distilled from P_2O_5 before use. Benzene and deuteriobenzene were dried over lithium aluminum hydride and distilled before use.

The reactions were run in two modes. Method A involved cophotolysis of equimolar amounts of the parent acylsilane and the ester in deuteriobenzene in an NMR tube under argon at room temperature for 1 or 2 days with use of two or three 100-W PAR 38 mercury lamps, which provide radiation mainly at 360 nm and longer. In method B the acylsilane was prephotolyzed in deuteriobenzene for about 24 h at room temperature and then at −20 °C for 12–24 h (to maximize the amount of silene and minimize the amount of residual acylsilane). One equivalent of the acrylate or other ester was then added to the silene solution, and the system was kept in the dark for 24 h, although, judging by the color change and by the ^{1}H NMR spectrum, the reactions with the acrylate esters were usually complete in less than 15 min. In every case (except when crotonate esters were involved—see below) the results from the two methods were identical, and essentially quantitative yields of the 1-sila-3-oxacyclohex-4-enes **6** were obtained when acrylate esters were employed, as shown by their NMR spectra. Typical procedures with acrylate esters are described in detail below, and similar procedures were used with the other esters. In some cases, attempts to isolate the products yielded viscous oils or inseparable mixtures. In cases where pure compounds were not actually isolated, the ^{1}H, ^{13}C, and ^{29}Si NMR spectra of the compound or mixture are supplied as supplementary material. Some of these spectra contain signals due to $(Me_3Si)_4Si$, a known and difficult to remove inert impurity present in some batches of the parent acylsilane. In the ^{29}Si spectra, its signals occur at −9.7 and −135 ppm.

Reaction of the Adamantylsilene 2a with Methyl Acrylate. Formation of 6aa. With use of method A, 103 mg (0.25 mmol) of (adamantylcarbonyl)tris(trimethylsilyl)silane (**1a**) and 23 μL (0.25 mmol) of methyl acrylate were introduced into a 5-mm NMR tube under an argon atmosphere along with about 0.6 mL of deuteriobenzene. The tube was sealed under argon and photolyzed at about 8–10 °C for about 24 h with two 100-W PAR 38 lamps. The NMR spectra indicated the presence of a single species, **6aa**, whose NMR spectral data are given in Table I.

A larger run with 1.0 mmol of each reagent, photolyzed for 2 days, gave, after removal of the solvent and chromatography on a rotary TLC device with hexane–chloroform–acetone (10:1:1) as eluent, a colorless viscous liquid. Anal. Calcd for $C_{24}H_{48}O_3Si_4$:

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[12] White, P. S. The NRCVAX Crystal Structure System (PC Version); University of North Carolina: Chapel Hill, NC, 1990.

C, 57.99; H, 9.74. Found: C, 57.70; H, 9.50.

Reaction of Adamantylsilene 2a with *tert*-Butyl Acrylate in the Dark (Method B). Formation of 6ad. A solution of 103 mg (0.25 mmol) of the (adamantylacyl)silane in 0.6 mL of deuteriobenzene was photolyzed in an NMR tube under an argon atmosphere for 24 h at room temperature, followed by a further 24 h at about −20 °C. To this pale yellow solution of the silene **2a** was added 1 equiv of *tert*-butyl acrylate by microsyringe. The color rapidly disappeared over a few minutes, at which time NMR spectra confirmed that the cycloaddition reaction was complete. Removal of the solvent and recrystallization from ethyl acetate gave 0.11 g of the adduct **6ad**, mp 128–129 °C. Anal. Calcd for $C_{26}H_{54}Si_4O_3$: C, 60.16; H, 10.10. Found: C, 60.62; H, 10.21. MS (*m/e*): calcd for M$^+$ 538.3150, found 538.3100; calcd for (M − isobutene)$^+$ 482.2524, found 482.2519. The NMR data are given in Table I.

The reactions of other silenes and other acrylate esters were carried out in a similar manner. In each case only a single product was formed in essentially quantitative yield. The NMR data for the products of the adamantyl- and *tert*-butylsilenes with acrylate esters are listed in Table I.

Reaction of Adamantylsilene with Methyl Crotonate. The photolysis of equimolar amounts of the (adamantylacyl)silane and methyl crotonate in deuteriobenzene for 48 h gave as the major product the γ-silylacrylate **7aa**. Small amounts of minor products, including the 1-sila-2-oxacyclohex-3-ene **8aa** as well as a trace of a third unidentified compound, were also detected by some weak NMR signals. Removal of the solvent and recrystallization from hexane gave pure crystalline material, mp 79–80 °C, for which the structure was determined by X-ray methods. Anal. Calcd for $C_{25}H_{50}O_3Si_4$: C, 58.76; H, 9.86. Found: C, 58.54; H, 9.85. MS (*m/e*): calcd for (M − H)$^+$ 509.2759, found 509.2775; calcd for (M − Me)$^+$ 495.2602, found 495.2624. ^{1}H NMR: δ 0.21, 0.22, 0.23 (each 9 H, s, Me$_3$Si), 1.8 (part of H$_A$ of ring Si—CH$_A$H$_B$—CH$_D$=H$_C$—CO$_2$Me system, remaining part under Ad signals), 2.17 (1 H, d × d × d, H$_B$, J_{AB} = 12.2, J_{BC} = 1.4, J_{BD} = 7.8 Hz), 1.43–2.0 (Ad), 3.44 (MeO), 3.77 (1 H, s, Si—C*H*OSiMe$_3$), 6.00 (1 H, d × d, H$_D$, J_{CD} = 15.3 Hz (trans)), 7.47 (1 H, d × d × d, H$_C$, J_{AC} = 9.9 Hz). ^{13}C NMR: δ 0.81 (two Me$_3$Si overlapped), 1.27 (OSiMe$_3$), 17.79 (SiCH$_2$), 28.67 (Ad CH), 36.96, 41.02 (Ad CH$_2$), 37.55 (Ad quat C), 50.63 (MeO), 80.21 (*C*H—OSiMe$_3$), 118.95, 150.05 (-CH=CH-), 166.90 (C=O). ^{29}Si NMR: δ −13.92, −15.30 (Me$_3$Si), 14.89 (OSiMe$_3$), −40.43 (central Si). **8aa (minor product, partial)**: ^{1}H NMR δ 0.26, 0.28, 0.37 (s, Me$_3$Si), 1.21 (d, *Me*CH ring) 2.6 (m, CH$_B$—Me), 3.29 (s, MeO), 3.57 (d, ring =CH$_B$, *J* = 5.9 Hz); ^{13}C NMR δ 0.03, 1.40 (Me$_3$Si), 3.06 (OSiMe$_3$), 29.09 (Ad CH), 37.32, 40.4 (Ad CH$_2$), 53.33 (MeO); ^{29}Si NMR δ −15.12, −15.91 (Me$_3$Si), 5.61 (OSiMe$_3$), 11.68 (ring Si).

Reaction of Adamantylsilene with Methyl Crotonate in the Dark. A solution of 0.25 mmol of the (adamantylacyl)silane **1** in 0.5 mL of deuteriobenzene was photolyzed for 2 days at 10 °C. To this was added 0.25 mmol of methyl crotonate by microsyringe. The reaction was kept in the dark at room temperature for 2 days, at which point the NMR spectra showed the presence of three species, the cyclic [2 + 4] adduct **8aa**, acylsilane **1** (from retrorearrangement of the silene), and the γ-silylacrylate **7aa** in the proportions 60:24:16. **8aa (major product)**: ^{1}H NMR δ 0.26, 0.29, 0.37 (9 H, s, Me$_3$Si), 1.21 (3 H, s, Me of MeCH$_A$—CH$_B$=C system, *J* = 6.9 Hz), 2.63 (1 H, s, H$_A$, J_{AB} = 5.9 Hz), 3.29 (3 H, s, MeO), 3.58 (1 H, d, H$_B$); ^{13}C NMR δ 0.03, 1.41 (Me$_3$Si), 3.06 (OSiMe$_3$), 24.04 (*Me*CH$_A$), 29.10 (Ad CH), 37.32, 40.27 (Ad CH$_2$), 40.55 (Ad quat C), 53.33 (MeO), 37.58 (ring =CH), 89.18 (ring *C*—OSiMe$_3$), 156.18 (ring =C—(OMe)—O–); ^{29}Si NMR δ −15.12, −15.91 (Me$_3$Si), 5.61 (OSiMe$_3$), 11.68 (ring Si). The data for **7aa** and for the (adamantylacyl)silane were identical with those reported above or with those in previous work.[6]

Reaction of Adamantylsilene with Ethyl Crotonate. Cophotolysis of a equimolar solution of (adamantylacyl)silane and ethyl crotonate in deuteriobenzene for 2 days gave rise to a single product, the γ-silylcrotonate **7ab**, which was characterized by NMR spectroscopy. **7ab**: ^{1}H NMR δ 0.23 (18 H, s, two overlapping Me$_3$Si), 0.24 (9 H, s, Me$_3$Si), 1.00 (3 H, t, Me of EtO, *J* = 7.1 Hz), 1.8 (part of 1 H, d × d × d, H$_A$ of Si—CH$_A$H$_B$—CH$_D$=CH$_C$—COOEt), 1.6–2.0 (Ad), 2.18 (1 H, d × d × d, H$_A$ of Si—CH$_A$H$_B$—CH$_D$=CH$_C$—COOEt), 1.6–2.0 (Ad), 2.18 (1 H, d × d × d, H$_B$, J_{AB} = 12.2, J_{BC} = 1.6, J_{BD} = 7.8 Hz), 4.06 (2 H, q, CH$_2$ of EtO), 6.01 (1 H, d × d × d, H$_C$, J_{AC} = 1.3, J_{CD} = 15.3 Hz (trans)), 7.47 (1 H, d × d × d, H$_D$, J_{AD} = 10.0 Hz); ^{13}C NMR δ 0.81 (two Me$_3$Si), 1.28 (OSiMe$_3$), 14.11 (Me of EtO), 17.75 (SiCH$_2$), 28.69 (Ad CH), 36.97, 41.04 (Ad CH$_2$), 37.58 (Ad quat C), 59.62 (CH$_2$ of EtO), 80.22 (*C*H—O—SiMe$_3$), 119.45, 149.68 (-CH=CH-), 166.46 (C=O); ^{29}Si NMR δ −13.94, −15.28 (Me$_3$Si), 14.89 (OSiMe$_3$), −40.51 (central Si).

Reaction of Adamantylsilene with Ethyl Crotonate in the Dark. A solution of about 0.25 mmol of the adamantylsilene was prepared by photolyzing a deuteriobenzene solution of the (adamantylacyl)silane for 2 days at 10 °C. Then 0.25 mmol of ethyl crotonate was added by microsyringe, and the solution was left in the dark for 2 days. NMR analysis indicated the formation of the cyclic 1-sila-2-oxacyclohex-3-ene **8ab** in about 40% yield and the presence of (adamantylacyl)silane **1** and the γ-silylcrotonate **7ab** in 50 and 10% yields, respectively. **8ab**: ^{1}H NMR δ 0.29, 0.32, 0.38 (9 H, s, Me$_3$Si), 1.10 (3 H, t, Me of EtO, *J* = 7.0 Hz), 1.23 (3 H, d, Me of Me—CH$_A$—CH$_B$= system, $J_{H_A\text{-}Me}$ = 6.9 Hz), 2.64 (1 H, d × q, H$_A$, *J* = 7.0 Hz), 4.07 (2 H, q, CH$_2$ of EtO), 3.66 (1 H, d, H$_B$); ^{13}C NMR δ 0.00, 1.47 (Me$_3$Si), 3.08 (OSiMe$_3$), 14.87 (*C*H$_3$CH$_2$), 24.05 (*C*H$_3$CH ring), 29.10 (Ad CH), 37.31, 40.25 (Ad CH$_2$), 40.45 (Ad quat C), 37.17 (Me*C*H ring), 61.81 (CH$_2$ of EtO), 80.87 (ring =CH), 89.18 (ring *C*—OSiMe$_3$), 155.41 (ring =C(OEt)—O–); ^{29}Si NMR δ −15.20, −15.98 (Me$_3$Si), 5.61 (OSiMe$_3$), 11.43 (ring Si).

Reaction of *tert*-Butylsilene with Methyl Crotonate. Cophotolysis of the acylsilane and ester in deuteriobenzene gave a major compound, the silylcrotonate **7ba**, and a small amount of a second product, the 1-sila-2-oxacyclohex-3-ene **8ba**, on the basis of its ^{29}Si NMR absorption attributed to the ring silicon atom at 12.21 ppm and other incomplete data. **7ba**: ^{1}H NMR δ 0.18, 0.19, 0.21 (each 9 H, s, Me$_3$Si), 0.89 (9 H, s, Me$_3$C), 1.83 (1 H, d × d × d, H$_A$ of Si—CH$_A$H$_B$—CH$_D$=CH$_C$—CO$_2$Me system, J_{AB} = 12.2, J_{AC} = 1.1, J_{AD} = 9.75 Hz), 2.14 (1 H, d × d × d, H$_B$, J_{BC} = 1.6, J_{BD} = 7.9 Hz), 5.97 (1 H, d × d × d, J_{CD} = 15.3 Hz (trans)), 3.44 (3 H, MeO), 3.82 (1 H, s, Si—CH—OSiMe$_3$); ^{13}C NMR δ 0.67, 0.75 (Me$_3$Si), 1.14 (OSiMe$_3$), 17.99 (SiCH$_2$), 28.53 (*Me*$_3$C), 35.66 (Me$_3$*C*), 50.58 (MeO), 78.97 (Si—*C*H—OSiMe$_3$), 119.04, 149.88 (-CH=CH-), 166.80 (C=O); ^{29}Si NMR δ −14.12, −15.34 (Me$_3$Si), 14.92 (OSiMe$_3$), −38.97 (central Si). **8ba (minor product)**: ^{29}Si NMR δ −15.13, −16.04 (Me$_3$Si), 5.57 (OSiMe$_3$), 12.21 (ring Si).

Reaction of *tert*-Butylsilene with Ethyl Crotonate. This reaction led to a major product, the γ-silylcrotonate **7bb**, together with a smaller amount of a second product that, on the basis of its ^{29}Si NMR spectrum, was probably the 1-sila-2-oxacyclohex-3-ene **8bb**, which would result from [2 + 4] cycloaddition. **7bb (major product)**: ^{1}H NMR δ 0.19 (18 H, s, two Me$_3$Si, accidental overlap), 0.20 (9 H, s, Me$_3$Si), 0.89 (Me$_3$C), 0.99 (3 H, t, Me of EtO, *J* = 7.2 Hz), 1.83 (1 H, d × d × d, H$_A$ of Si—CH$_A$H$_B$—CH$_D$=CH$_C$—CO$_2$Et system, J_{AB} = 12.2, J_{AC} = 1.1, J_{AD} = 9.8 Hz), 2.14 (1 H, d × d × d, H$_B$, J_{BC} = 1.5, J_{BD} = 7.9 Hz), 3.82 (1 H, s, Si—C*H*—OSiMe$_3$), 4.04 (CH$_2$ of EtO), 5.97 (1 H, d × d × d, H$_C$, J_{CD} = 15.3 Hz), 7.43 (1 H, d × d × d, H$_D$); ^{13}C NMR δ 0.68, 0.76 (Me$_3$Si), 1.15 (OSiMe$_3$), 14.09 (Me of EtO), 17.94 (SiCH$_2$), 28.54 (*Me*$_3$C), 35.67 (Me$_3$*C*), 59.57 (CH$_2$ of EtO), 78.98 (Si—*C*H—OSiMe$_3$), 119.52, 149.53 (-CH=CH), 166.36 (C=O); ^{29}Si NMR δ −14.13, −15.33 (Me$_3$Si), 14.91 (OSiMe$_3$), −39.05 (central Si). **8bb (minor product)**: ^{29}Si NMR δ −15.20, −16.11 (Me$_3$Si), 5.57 (OSiMe$_3$), 11.97 (ring Si).

Reaction of Adamantylsilene with Methyl Methacrylate. Cophotolysis of the (adamantylacyl)silane with 1 equiv of methyl methacrylate in deuteriobenzene led to two compounds, the α-(silylmethyl)acrylate **9a** and a small amount of the 1-sila-3-oxacyclohex-4-ene **10a**, in the ratio >4:1. **9a (major product)**: ^{1}H NMR δ 0.25, 0.26, 0.31 (each 9 H, s, Me$_3$Si), 1.6–2.1 (Ad), 2.23 (1 H, d × d, H$_A$ of Si—CH$_A$H$_B$—C(COOMe)=CH$_C$ system, J_{AB} = 14.6, J_{AD} = 1.0 Hz), 2.39 (1 H, d × d × d, H$_B$, J_{BC} = 1.1, J_{BD} = 1.6 Hz), 3.40 (3 H, s, MeO), 4.04 (1 H, s, SiC*H*—OSiMe$_3$), 5.48 (1 H, d × d, H$_C$, J_{CD} = 2.4 Hz), 6.13 (1 H, d × d, H$_D$); ^{13}C NMR δ 1.42, 1.49 (Me$_3$Si), 2.12 (OSiMe$_3$), 15.65 (SiCH$_2$), 28.77 (Ad CH), 37.08, 41.03 (Ad CH$_2$), 38.60 (Ad quat C), 51.22 (MeO), 82.45 (Si*C*H—OSiMe$_3$), 123.19 (=CH$_2$), 141.14 (=C sp^2), 168.11 (C=O); ^{29}Si NMR δ −13.77, −15.69 (Me$_3$Si), 14.52 (OSiMe$_3$), −39.83 (central Si). **10a (partial)**: ^{1}H NMR δ 0.23, 0.24, 0.27 (each 9 H, s, Me$_3$Si), 1.6–2.1 (Ad), 3.44 (MeO); ^{13}C NMR δ 0.03, 0.64 (Me$_3$Si), 2.27

Table II. NMR Data for Silene–Maleate and –Fumarate Ester Adducts[a]

	11ab	12ab	11ab	12ab	11aa	12aa	11ba	12ba
R	Ad	Ad	Ad	Ad	Ad	Ad	*t*-Bu	*t*-Bu
R′	Et	Et	Et	Et	Me	Me	Me	Me
ester	maleate	maleate	fumarate	fumarate	fumarate	fumarate	fumarate	fumarate
product	major	minor	major	minor	major	minor	major	minor
ratio major:minor	4.5:1		3.2:1		2.1:1		1.2:1	
^{1}H NMR								
Me_3Si	0.30 0.35 0.38	0.23 0.24 0.43	0.30 0.35 0.38	0.23 0.24 0.43	0.28 0.32 0.37	0.22 0.35 0.41	0.24 0.35 0.34	0.18 0.27 0.38
H_A	3.58 d	2.78 d	3.58 d	2.78 d	3.60 d	2.73 d	3.56 d	2.73 d
H_B	3.63 d	*b*	3.63 d	*b*	4.40 d	4.11 d	4.43 d	4.09 d
J_{AB}	6.9	6.1	6.9	6.1	2.6	6.1	2.8	6.1
R	1.5–2.0						1.08	1.07
CH_3–C–O–	two overlapping triplets ($\delta \sim 1.0, \sim 1.02,\ J = 7$)							
–CH_2–O–	overlapping quartets[c]							
MeO (1)					3.26	3.27	3.25	3.22
MeO (2)					3.40	3.41	3.39	3.39
^{13}C NMR								
Me_3Si	1.32 1.60	0.81 1.32	1.32 1.61	0.82 1.32	1.23 1.50	0.77 1.17	0.91 1.12	0.68 1.46
Me_3SiO	2.43	3.26	2.43	3.27	2.40	3.22	2.39	2.94
CH_3–C–O (1)	13.88	13.63	13.88	13.98	MeO (1) 51.28	51.34	50.68	51.32
CH_3–C–O (2)	14.49	14.60	14.49	14.60	MeO (2) 54.38	54.14	54.32	54.05
Ad CH	28.61	28.73	28.62	28.73	28.60	28.73	*Me*$_3$C 26.85	27.03
Ad CH_2	37.09	37.01	37.09	37.01	37.09	37.00	Me$_3$*C* 40.83	45.09
Ad CH_2	38.39	38.05	38.39	38.05	38.38	38.03		
C quat	42.43	41.93	42.44	41.93	42.42	41.90		
–O–CH_2– (1)	60.06	60.70	60.06	60.70				
–O–CH_2– (2)	63.28	62.90	63.29	62.89				
r *C*HCOOR	26.43	25.12	26.46	25.125	26.14	24.72	26.20	24.93
r CH=	72.41	70.68	72.42	70.68	71.21	69.63	71.44	69.67
r C–OSi	115.15	112.65	115.16	112.69	115.24	112.77	114.99	111.84
r *C*(OR)–O–	157.77	158.79	157.77	158.80	158.75	159.68	158.94	159.79
C=O	175.78	174.08	175.79	174.08	176.02	174.38	175.70	174.37
^{29}Si NMR								
Me_3SiO	10.83	10.43	10.82	10.43	11.03	10.70	10.95	10.57
Me_3Si	−13.42 −14.39	−13.81 −14.40	−13.43 −14.40	−13.81 −14.40	−13.49 −14.47	−13.81 −14.47	−13.92 −14.53	−13.73 −14.71
r Si	−43.98	−42.79	−44.00	−42.81	−44.05	−42.54	−40.64	−40.93

[a] Legend: Ad = 1-adamantyl; d = doublet; m = multiplet; r = ring. Coupling constants are in Hz, chemical shifts are in ppm. [b] Signal lies in –CH_2–O region. [c] One quartet ($\delta \sim 3.5$, $J = 7.0$) and two d × q (δ 3.8, 4.17 $J = 7.1, 10.9$). 1.5–2.0

($OSiMe_3$), 10.64 ($SiCH_2$), 28.65 (Me), 28.88 (Ad CH), 37.32, 38.18 (Ad CH_2), 41.71 (Ad quat C), 53.90 (MeO), 76.2 (ring Me—C=), 112.55 (ring *C*—$OSiMe_3$), 165.52 (ring =C(OMe)—O–); ^{29}Si NMR δ −14.96, −15.31 (Me_3Si), 9.37 ($OSiMe_3$), −55.06 (ring Si).

Reaction of *tert*-Butylsilene with Methyl Methacrylate. Cophotolysis of the (*tert*-butylacyl)silane with 1 equiv of methyl methacrylate in deuteriobenzene led to two compounds, the α-(silylmethyl)acrylate **9b** and a small amount of the 1-sila-3-oxacyclohex-4-ene **10b**, in the ratio 5.7:1. **9b (major product)**: ^{1}H NMR δ 0.23 (18 H, s, Me_3Si), 0.29 (9 H, s, Me_3Si), 0.99 (9 H, s, *Me*$_3$C), 2.22 (1 H, d × d, H_A of Si—CH_AH_B—C(COOMe)=CH_C system, $J_{AB} = 14.2$, $J_{AD} = 1.0$ Hz), 2.37 (1 H, d × d × d, H_B, $J_{BC} = 1.1$, $J_{BD} = 1.0$ Hz), 3.96 (3 H, s, MeO), 4.10 (1 H, s, SiC*H*—$OSiMe_3$), 5.44 (1 H, d × d, H_C, $J_{CD} = 2.7$ Hz), 6.09 (1 H, d × d, H_D); ^{13}C NMR δ 1.32 (two Me_3Si), 1.40 ($OSiMe_3$), 15.94 ($SiCH_2$), 28.64 (*Me*$_3$C), 35.76 (Me$_3$*C*), 51.21 (MeO), 81.17 (Si*C*H—$OSiMe_3$), 123.05 (=CH_2), 141.08 (=C sp^2), 168.03 (C=O); ^{29}Si NMR δ −13.95, −15.74 (Me_3Si), 14.61 ($OSiMe_3$), −37.89 (central Si). **10b** (partial): ^{1}H NMR δ 0.20, 0.21, 0.24 (each 9 H, s, Me_3Si), 1.06 (9 H, s, Me_3C), 3.42 (MeO); ^{13}C NMR δ −0.06, 0.53 (Me_3Si), 1.83 ($OSiMe_3$), 9.73 ($SiCH_2$), 26.84 (Me), 26.57 (*Me*$_3$C), 40.14 (Me$_3$*C*), 51.05 (MeO), 83.63 (ring Me—*C*=); ^{29}Si NMR δ −15.09, −15.33 (Me_3Si), 9.37 ($OSiMe_3$), −52.57 (ring Si).

Reaction of the Silenes with Maleate and Fumarate Esters. Reactions of the silenes with the maleate and fumarate esters were carried out in a similar manner by photolyzing mixtures of the appropriate acylsilane and ester in deuteriobenzene or by adding ester to preformed solutions of the silenes. In each case the two diastereomers 11 and 12 were obtained in varying proportions; these were not easily separated, but their NMR data were obtained from the mixture and are listed in Table II. In some cases a trace of another unidentified compound could be observed.

Compound **11aa**, the major isomer from the reaction of the adamantylsilene with dimethyl fumarate, was obtained pure as a colorless viscous oil after TLC separation of the reaction mixture with CCl_4–hexane–ethyl acetate (8:4:1) as eluent. Anal. Calcd for $C_{26}H_{50}O_5Si_4$: C, 56.27, H, 9.08. Found: C, 56.50; H, 9.20.

Reaction of the Adamantylsilene 2a with Ethyl Cinnamate. Equimolar quantities of the (adamantylacyl)silane **1a** and ethyl cinnamate were photolyzed together in deuteriobenzene over 2 days. A single product, the 1-sila-2-oxacyclohex-3-ene **13a**, mp 175–176 °C, was formed, as identified by its NMR spectra. **13a**: ^{1}H NMR δ 0.33, 0.40, 0.42 (each 9 H, s, Me_3Si), 1.03 (3 H, t, Me of CH_3—$CH_{A'}H_{B'}$—O system, $J_{H_{A'}\text{-}Me} = J_{H_{B'}\text{-}Me} = 7.1$ Hz), 1.6–2.0 (Ad), 3.52 (1 H, d × q, $H_{A'}$, $J_{A'B'} = 9.5$ Hz), 3.64 (1 H, d × q, $H_{B'}$), 3.94, 3.98 (2 H, each d, H_A and H_B of ring CH_APh—CH_B=C—O system, $J_{AB} = 7.4$ Hz), 6.95–7.15 (3 H, m, Ar), 7.35–7.45 (2 H, m, Ar); ^{13}C NMR δ 1.47, 1.64 (Me_3Si), 4.18 ($OSiMe_3$), 14.63 (Me of EtO), 62.24 (CH_2 of EtO), 28.97 (Ad CH), 37.05, 39.70 (Ad CH_2), 41.71 (Ad quat C), 49.83 (*C*HPh), 80.50 (ring CH=), 93.60 (ring *C*—$OSiMe_3$ sp^3), 126.54, 128.49, 131.04 (Ar CH), 146.14 (Ar ipso), 156.22 (ring =*C*(OEt)—O—); ^{29}Si NMR δ −13.92, −16.60 (Me_3Si), 5.99 ($OSiMe_3$), 22.07 (ring Si); MS (CI); *m/e*) 587 $(M + 1)^+$, 571 $(M - Me)^+$, 513 $(M - Me_3Si)^+$.

If the sample containing **13a** was not carefully sealed from air or moisture, it slowly hydrolyzed to the silalactone **14a**. Deliberate exposure to moisture yielded pure crystalline **14a**, mp 284–285 °C, for which a crystal structure was obtained. Anal. Calcd for $C_{29}H_{50}O_3Si_4$: C, 62.31; H, 9.01. Found: C, 62.25; H, 9.18. MS (*m/e*): calcd for $(MH)^+$ 559.2915, found 559.2913. ^{1}H NMR: δ 0.27 (9 H, s, Me_3Si), 0.35 (18 H, s, two Me_3Si, accidental overlap),

Table III. Crystal Data and Least-Squares Parameters

	6ad	7aa	14a
empirical formula	$C_{27}H_{54}O_3Si_4$	$C_{25}H_{50}O_3Si_4$	$C_{29}H_{50}O_3Si_4$
M_r	529.1	511.0	559.1
cryst class	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a, Å	17.785 (4)	9.016 (2)	10.233 (2)
b, Å	10.137 (3)	11.159 (2)	15.535 (8)
c, Å	18.507 (4)	17.334 (4)	20.179 (4)
α, deg		91.55 (2)	
β, deg	90.25 (2)	102.16 (2)	97.22 (2)
γ, deg		110.84 (2)	
V, Å^3	3336.5	1583.3	3182.4
Z	4	2	4
D_{calc}, g cm^{-3}	1.07	1.07	1.17
μ(Mo Kα), cm^{-1}	1.96	2.03	2.07
$F(000)$	1184	560	1216
ω scan width, deg	$0.8 + 0.35 \tan\theta$	$0.6 + 0.35 \tan\theta$	$0.6 + 0.35 \tan\theta$
range θ collected, deg	1–20	1–25	1–25
total no. of rflns	3866	2176	5932
no. of unique rflns	3105	2176	4681
R_{int}	0.091		0.057
no. of obsd data [$I > 3\sigma(I)$]	1877	1391	3311
weighting g	0.005 00	0.000 83	0.001 16
R	0.170	0.046	0.041
R_w	0.190	0.045	0.046
goodness of fit	3.00	1.21	1.35
largest Δ/σ	0.02	0.06	0.01
no. of params refined	173	290	326
max density in ΔF map, e/Å^3	1.36[a]	0.25	0.28

[a] Largest residual electron density peaks were less than 1.6 Å from Si atoms and were not chemically significant.

2.58 (1 H, d × d, H_A of ring C(=O)—CH_AH_B—CH_CPh– system, J_{AB} = 16.5, J_{AC} = 2.9 Hz), 3.28 (1 H, d × d, H_B, J_{BC} = 5.2 Hz), 3.52 (1 H, d × d, H_C), 6.95–7.2 (Ar); ^{13}C NMR δ 0.89, 1.02 (Me_3Si), 4.40 ($OSiMe_3$), 39.63 (ring CH_ACH_B), 28.66 (Ad CH), 36.56, 39.14 (Ad CH_2), 41.87 (Ad quat C), 50.16 (ring CH_CPh–), 93.42 (ring C—$OSiMe_3$), 127.51, 128.29, 129.50 (Ar CH), 142.29 (ipso), 168.27 (C=O); ^{29}Si NMR δ −13.86, −15.14 (Me_3Si), 8.00 ($OSiMe_3$), 30.70 (ring Si).

Reaction of *tert*-Butylsilene with Ethyl Cinnamate. Equimolar quantities of the (*tert*-butylacyl)silane **1b** and ethyl cinnamate were photolyzed together in deuteriobenzene over 2 days. A single product, the 1-sila-2-oxacyclohex-3-ene **13b**, was formed, as identified by its NMR spectra. **13b**: ^{1}H NMR δ 0.25, 0.38, 0.39 (each 9 H, s, Me_3Si), 0.90 (9 H, s, *t*-Bu), 1.03 (3 H, t, Me of CH_3—$CH_{A'}H_{B'}$—O system, $J_{H_{A'}\text{-}Me} = J_{H_{B'}\text{-}Me}$ = 7.1 Hz), 3.51 (1 H, d × q, $H_{A'}$, $J_{A'B'}$ = 9.5 Hz), 3.63 (1 H, d × q, $H_{B'}$), 3.93, 3.97 (each 1 H, d, H_A and H_B of ring CH_APh—CH_B=C—O system, J = 6.96 Hz), 6.95–7.15 (3 H, m, Ar), 7.35–7.45 (2 H, m, Ar); ^{13}C NMR δ 1.37, 2.48 (Me_3Si), 3.99 ($OSiMe_3$), 14.58 (Me of EtO), 28.72 (*Me*$_3$C), 39.19 (Me_3*C*), 51.12 (*C*HPh), 62.24 (CH_2 of EtO), 80.19 (ring CH=), 92.46 (ring *C*—$OSiMe_3$ sp^3), 126.51, 128.47, 130.95 (Ar CH), 145.99 (Ar ipso), 156.29 (ring =*C*(OEt)—O–); ^{29}Si NMR δ −13.98, −16.82 (Me_3Si), 5.85 ($OSiMe_3$), 21.94 (ring Si).

Hydrolysis of **13b** gave the silalactone **14b**. ^{1}H NMR: δ 0.25, 0.29, 0.33 (each 9 H, s, Me_3Si), 0.81 (9 H, s, Me_3C), 2.58 (1 H, d × d, H_A of ring C(=O)—CH_AH_B—CH_CPh– system, J_{AB} = 16.5, J_{AC} = 2.9 Hz), 3.28 (1 H, d × d, H_B, J_{BC} = 5.2 Hz), 3.52 (1 H, d × d, H_C), 6.95–7.2 (Ar); ^{13}C NMR δ 0.89, 1.02 (Me_3Si), 4.40 ($OSiMe_3$), 39.63 (ring CH_AH_B), 28.66 (Ad CH), 36.56, 39.14 (Ad CH_2), 41.87 (Ad quat C), 50.16 (ring *C*H_CPh–), 93.42 (ring C—$OSiMe_3$), 127.51, 128.29, 129.50 (Ar CH), 142.29 (ipso), 168.27 (C=O); ^{29}Si NMR δ −13.89, −15.40 (Me_3Si), 7.89 ($OSiMe_3$), 31.13 (ring Si).

Reaction of Adamantylsilene with Acrylonitrile. The (adamantylacyl)silane (200 mg) was cophotolyzed with 1 equiv of acrylonitrile in 0.5 mL of deuteriobenzene at 10 °C for 17 h, at which time a colorless solution was present. NMR spectroscopy revealed a 1.3:1 mixture of two diastereomers, **15a$_1$** and **15a$_2$**. **15a$_1$ (major isomer)**: ^{1}H NMR δ 0.09, 0.19, 0.55 (each 9 H, s, Me_3Si), 1.08 (1 H, d × d, H_A of ring Si—CH_AH_B—CH_C—CN system, J_{AB} = 12.4, J_{AC} = 7.8 Hz), 1.4–2.0 (m, Ad and H_B), 3.22 (1 H, d × d, H_C, J_{BC} = 12.5 Hz); ^{13}C NMR δ −0.50, 0.55 (Me_3Si), 4.87 ($OSiMe_3$), 8.74 (ring $SiCH_2$), 31.55 (ring CH), 28.49 (Ad CH), 36.82, 39.89 (Ad CH_2), 38.54 (Ad quat C), 98.29 (ring C—$OSiMe_3$), 121.50 (CN); ^{29}Si NMR δ −15.08, −16.78 (Me_3Si), 9.12 ($OSiMe_3$), −16.05 (ring Si) (identity of the Si signals was confirmed by a ^{1}H–^{29}Si-coupled NMR spectrum in which the $OSiMe_3$ signal showed a clean decet, the Me_3Si signals showed complex multiplets with a recognizable decet, and the ring Si signal was a broad unsplit signal). **15a$_2$ (minor isomer)**: ^{1}H NMR δ 0.19 (18 H, s, overlapping Me_3Si), 0.22 (9 H, s, Me_3Si), 1.16 (1 H, d × d, H_A, J_{AB} = 13.8, J_{AC} = 8.2 Hz), 1.4–2.0 (Ad plus H_B), 3.36 (1 H, d × d, H_C, J_{BC} = 10.1 Hz); ^{13}C NMR δ 0.50, 0.61 (Me_3Si), 3.64 ($OSiMe_3$), 9.00 (ring $SiCH_2$), 37.38 (ring CH), 28.62 (Ad CH), 36.82, 37.89 (Ad CH_2), 39.72 (Ad quat C), 95.47 (ring C—$OSiMe_3$), 121.74 (CN); ^{29}Si NMR δ −14.90, −15.39 (Me_3Si), 8.70 ($OSiMe_3$), −11.08 (ring Si).

Reaction of (Triethylmethyl)silene with Acrylonitrile. A 100-mg sample of the ((triethylmethyl)acyl)silane **1c** was cophotolyzed with 1 equiv of acrylonitrile at 10 °C for 17 h. NMR spectroscopy showed the presence of the pair of diastereomeric silacyclobutanes **15c** in the ratio 1.4:1. **15c$_1$ (major isomer)**: ^{1}H NMR δ 0.07, 0.17, 0.52 (each 9 H, s, Me_3Si), 0.77 (9 H, t, CH_3 of Et's, J = 7.4 Hz), 1.33 (6 H, CH_2 of Et's), 1.15 (1 H, d × d, H_A of ring Si—CH_AH_B—CH_C—CN system, J_{AB} = 13.0, J_{AC} = 8.0 Hz), 1.73 (1 H, d × d, H_B, J_{BC} = 12.4 Hz), 3.16 (1 H, d × d, H_C); ^{13}C NMR δ −0.40, 0.43 (Me_3Si), 4.69 ($OSiMe_3$), 9.18 (Me of Et), 11.28 (ring $SiCH_2$), 27.31 (CH_2 of Et), 33.94 (ring CH_C—CN), 43.77 (quat C of Et_3C), 97.42 (ring *C*—$OSiMe_3$), 121.78 (CN); ^{29}Si NMR δ −14.24, −15.49 (Me_3Si), 8.86 ($OSiMe_3$), −12.54 (ring Si). **15c$_2$ (minor isomer)**: ^{1}H NMR δ 0.14, 0.20, 0.33 (Me_3Si), 0.82 (t, Me of Et's), 1.42 (q, CH_2 of Et's), 1.22 (m, H_A of ring Si—CH_AH_B—CH_C—CN system), 1.85 (m, H_B, J_{AB} = 18 Hz), 3.47 (d × d, J_{AC} = 2.4, J_{BC} = 10.6 Hz); ^{13}C NMR δ 0.23, 0.59 (Me_3Si), 3.34 ($OSiMe_3$), 9.49 (Me of Et's), 11.98 (ring Si–CH_2), 26.73 (CH_2 of Et's), 38.65 (ring *C*H—CN), 44.73 (quat C of CEt_3), 94.97 (ring C—$OSiMe_3$, 122.30 (CN); ^{29}Si NMR δ −15.40, −15.80 (Me_3Si), 7.77 ($OSiMe_3$), −4.19 (ring Si).

Attempted Reactions of Adamantylsilene with Ethyl Acetate or Methyl Benzoate. A solution of the (adamantylacyl)silane and 1 equiv of ethyl acetate in deuteriobenzene was photolyzed for up to 1 week. NMR spectroscopy indicated no reaction (other than conversion of the acylsilane to the silene) had occurred. Similar lack of any reaction was found when 1 equiv of methyl benzoate was employed.

Attempted Reactions of Adamantylsilene with Acetonitrile or Benzonitrile. Solutions of the (adamantylacyl)silane and either acetonitrile or benzonitrile (>1 equiv) were photolyzed for several days. NMR spectra showed that no reactions had

Table IV. Important Bond Distances (Å) and Angles (deg)

	6ad	**7aa**	**14a**
	Bond Distances		
Si(1)–Si(3)	2.393 (10)	2.358 (4)	2.3928 (13)
Si(1)–Si(4)	2.396 (10)	2.350 (4)	2.3861 (13)
Si(2)–O(1)	1.765 (19)	1.637 (6)	1.6393 (22)
O(1)–C^a	1.430 (28)	1.427 (10)	1.464 (4)
Si(1)–C^a	1.910 (23)	1.933 (7)	1.953 (3)
av Si–C^b	1.78 (3)	1.860 (10)	1.860 (4)
	Bond Angles		
Si(4)–Si(1)–Si(3)	115.3 (3)	112.66 (13)	107.38 (5)
C^a–Si(1)–Si(3)	116.9 (8)	116.24 (29)	113.33 (10)
C^a–Si(1)–Si(4)	113.4 (7)	115.39 (26)	126.99 (10)
O(1)–C^a–Si(1)	90.8 (14)	104.6 (5)	100.31 (7)
C^a–O(1)–Si(2)	138.2 (15)	135.8 (5)	145.62 (18)

[a] Labeled C(1) in **6ad** and **14a** and C(11) in **7aa**. [b] Si–C(H_3) bond length.

occurred other than the conversion of the acylsilane to the adamantylsilene.

Reactions of Silenes with Esters in the Presence of Bu_3SnH. Cophotolysis of a solution of the relevant acylsilane with 1 equiv of ester and 1 equiv of tributyltin hydride in deuteriobenzene for 2–3 days led to the formation of the tin hydride adducts **16a** and **16b**.[4] In the reaction of either the adamantyl- or *tert*-butylsilenes with methyl crotonate, no other adduct was present, and the ester was recovered. With ethyl cinnamate the tin hydride adduct **16a** comprised 80% of the products. The adduct of the adamantylsilene with ethyl cinnamate, **13a**, was formed in 20% yield, and residual ester was recovered. **16a**: ^1H NMR δ 0.25, 0.37, 0.39 (each 9 H, s, Me_3Si), 0.97 (9 H, t, Me of Bu, J = 7.1 Hz), 1.43 (6 H, q, Sn—CH_2), 1.5–2.5 (m, CH_2 of Bu), 4.09 (1 H, s, SiCH); ^{13}C NMR δ 2.45, 2.80 (Me_3Si), 3.01 ($OSiMe_3$), 11.49, 30.42, 27.95, 13.58 (Sn—CH_2—CH_2—CH_2—CH_3, respectively), 28.92 (Ad CH), 36.95, 41.06 (Ad CH_2), 38.52 (Ad quat C), 82.42 (SiCH); ^{29}Si NMR δ −10.26, −10.45 (Me_3Si), 13.20 ($OSiMe_3$, $J(^{29}Si–^{13}C)$ = 5.3 Hz), −76.21 (central Si, $J(^{29}Si–^{119}Sn)$ = 265.8, $J(^{29}Si–^{117}Sn)$ = 254.1 Hz). **16b**: ^1H NMR δ 0.24, 0.34, 0.35 (9 H, s, Me_3Si), 1.00 (9 H, s, *t*-Bu), 0.96 (9 H, t, Me of Bu, overlaps *t*-Bu), 1.1–1.7 (m, CH_2 of Bu), 4.13 (1 H, s, SiCH); ^{13}C NMR δ 2.06, 2.73 (Me_3Si), 2.93 ($OSiMe_3$), 11.32, 30.31, 27.91, 13.54 (Sn—CH_2—CH_2—CH_2—CH_3, respectively), 28.81 (*Me_3*C), 36.57 (Me_3*C*), 80.80 (SiCH); ^{29}Si NMR δ −10.59, −10.62 (Me_3Si), 13.73 ($OSiMe_3$), −72.34 (central Si, $J(^{29}Si–^{119}Sn)$ = 267.6, $J(^{29}Si–^{117}Sn)$ = 255.7 Hz).

X-ray Data and Methods. Each of the compounds studied, **6ad**, **7aa**, and **14a**, proved to be stable to air exposure. All crystals had dimensions in the range 0.25–0.45 mm. Intensity data for all compounds were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature, with use of graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The ω–2θ scan technique was applied with variable scan speeds. Intensities of three standard reflections measured every 2 h showed no variation for compounds **7aa** and **14a**. After 12 h of data collection time, the three standard reflections for a crystal of **6ad** had decayed to 50% of their original intensity. Three different crystals of **6ad** (all of which suffered from serious decay) had to be used to collect a complete data set ($1 < \theta < 20°$). The reflection data from each crystal of compound **6ad** were corrected for linear intensity decay,[13] and batch scale factors (1.0187, 1.0572, and 0.9285) were calculated. No corrections were made for absorption in **6ad**, **7aa**, or **14a**.

For each structure C, O, and Si atoms were refined anisotropically (except for compound **6ad**, in which C atoms were refined with isotropic thermal parameters) 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 overall hydrogen atom thermal parameters for **6ad**, **7aa**, and **14a** refined to 0.133 (10), 0.126 (6), and 0.079 (2) Å^2. Crystal data, data collection, and least-squares parameters are listed in Table III. All calculations were performed with use of SDP,[14] SHELX76,[15] and SHELXS86[16] on a PDP11/23 and an Apollo computer. Some important bond angles and distances are given in Table IV. Atomic coordinates and other data concerning the crystal structures are given in the supplementary material. Although data for the X-ray analysis of **6ad** were collected from three heavily decaying crystals, the direct-methods solution (which refined to R = 0.170) confirmed the structure postulated by the ^1H, ^{13}C, and ^{29}Si NMR data. The results of the X-ray structure determination have been presented only to confirm the atomic connections in cycloadduct **6ad**.

Note about the ORTEP Figures. The ORTEP figures for **6ad**, **7aa**, and **14a**, shown in the text, give the atomic labeling schemes and thermal ellipsoids at the 25% probability level. For the sake of clarity hydrogen atoms have been omitted, and some carbon atoms have been assigned as spheres of arbitrary radius.

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Supplementary Material Available: Tables of atomic coordinates, complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates, and least-squares planes for **6ad**, **7aa**, and **14a** and ^1H, ^{13}C, and ^{29}Si NMR spectra for all compounds or mixtures that were not isolated and purified, which include **6aa**, **6ab**, **6ac**, **6ba**, **6bb**, **6bc**, **6bd**, **7aa** and **8aa**, **7ab** and **8ab**, **7ba** and **8ba**, **7bb** and **8bb**, **9a** and **10a**, **9b** and **10b**, **11aa** and **12aa**, **11ab** and **12ab**, **11ba** and **12ba**, **13a** and **14a**, **13b** and **14b**, **15a**$_1$ and **15a**$_2$, and **15c**$_1$ and **15c**$_2$ (94 pages); listings of observed and calculated structure factors for **6ad**, **7aa**, and **14a** (23 pages). Ordering information is given on any masthead page.

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