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Stable Solid Silaethylenes

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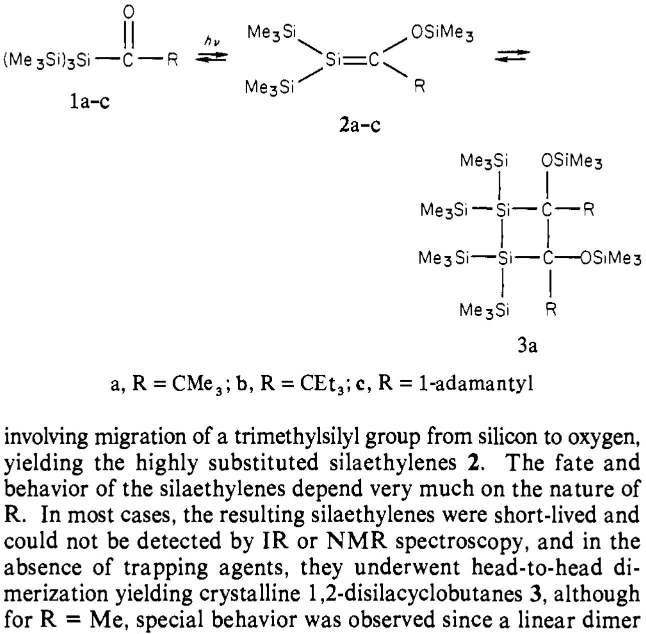
Abstract: A solid silaethylene, 1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-2-(1-adamantyl)-1-silaethene (**2c**), has been isolated from the photolysis of the isomeric acylsilane. The silaethylene was characterized by IR, Raman, UV, ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, and mass spectroscopy and by its ionization potential. The crystal structure shows a slightly twisted molecule with a silicon–carbon double-bond length of 1.764 Å. The molecule smokes vigorously in air, yielding a cyclic trisiloxane and the silyl ester of adamantane-1-carboxylic acid. Other reactions and comparisons with other silaethylenes in solution are described. In addition, 1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-2-(1,1-diethylpropyl)-1-silaethene (**2b**) has been obtained as a solid.

Research on silaethylenes (silenes) has grown dramatically since 1967, when Gusel'nikov and Flowers[1] presented compelling evidence for the first time that these species could exist, if only as transient intermediates. The subsequent intense research activity[2] generated the challenge to see whether a silaethylene could be sufficiently stabilized to exist for some time at room temperature. We have addressed this challenge and now report the isolation and characterization of two solid silaethylenes, indefinitely stable at room temperature under argon.[3]

We have previously reported[4] that several tris(trimethylsilyl)acylsilanes (**1**) cleanly undergo photochemical rearrangement involving migration of a trimethylsilyl group from silicon to oxygen, yielding the highly substituted silaethylenes **2**. The fate and behavior of the silaethylenes depend very much on the nature of R. In most cases, the resulting silaethylenes were short-lived and could not be detected by IR or NMR spectroscopy, and in the absence of trapping agents, they underwent head-to-head dimerization yielding crystalline 1,2-disilacyclobutanes **3**, although for R = Me, special behavior was observed since a linear dimer was obtained.[4] When R = CMe_3, the silaethylene **2a** was relatively stable and could be observed spectroscopically (IR, UV, NMR) in the photolysis solution in equilibrium with its dimer **3a** over a period of about 2 weeks at room temperature, during which time **2a** and **3a** slowly reverted to the parent acylsilane **1a**. It was significant to find from the crystal structure of **3a** that the ring C–C bond was 1.66 Å long,[5] indicative of severe steric crowding in the molecule. In fact, the crowding was so severe as to preclude free rotation of the *tert*-butyl group, which appeared in both the ^{1}H and ^{13}C NMR spectra as three separate resonances, one for each methyl group.



1a-c

2a-c

3a

a, R = CMe_3; b, R = CEt_3; c, R = 1-adamantyl

It appeared probable that steric effects, particularly those caused by the R group, played a very important role in stabilizing this silaethylene, although the silyl groups on silicon and the siloxy group on carbon probably also contribute to the overall stability. Thus, when R = phenyl, the potential conjugation of the silicon–carbon double bond (hereafter Si=C) with the aromatic π system did not appear to be important, since the silaethylene was too reactive to survive long enough to be observed spectroscopically. Also, substitution on phenyl by *o*- or *p*-methoxy groups,[6] by a p-*t*-Bu group, or by 3,5-dimethyl groups failed to stabilize the molecules significantly since no silaethylenes were observed and only dimers were produced. Electron-withdrawing groups such as CF_3 did not appear to stabilize Si=C, since again no silaethylenes could be detected. In order to evaluate the effect of replacing CMe_3 by other bulky or even bulkier groups, other acylsilanes were prepared by using the conventional synthesis shown in eq 1. Distinct improvements in yield were realized by

$$(Me_3Si)_3SiLi + ClC(=O)R \rightarrow (Me_3Si)_3SiC(=O)R \quad (1)$$

using solid $(Me_3Si)_3SiLi{\cdot}3THF$[7] dissolved in inert solvents instead of $(Me_3Si)_3SiLi$ prepared in THF as employed previously.[8]

When R = CEt_3, photolysis of the acylsilane **1b** gave a yellow solution having λ_{max} 339 nm and strong IR absorption at 1133 cm^{-1}, values very close to those observed for **2a**, and hence containing the silaethylene. ^{13}C and ^{29}Si NMR signals were observed at 207 and 54 ppm, respectively (relative to Me_4Si), also characteristic of Si=C, but there was no evidence for the presence of the dimer (e.g., **3b**) in the system, logically because the bulkier CEt_3 (relative to CMe_3) now caused such severe steric effects as to totally inhibit formation of **3b**. Silaethylene **2b** was less stable than **2a**, reverting to parent acylsilane **1b** at least twice as fast as **2a** reverted to **1a**, presumably as a consequence of increased steric strain in the silaethylene itself. Since no dimer was present in the photolysis mixture, attempts were made to crystallize the silaethylene. Removal of solvent or a vacuum line gave a viscous yellow semisolid containing **2b** contaminated with much acylsilane **1b**. The proportions of **1b** to **2b** in the liquid changed only slightly over a period of a month, indicating that **2b** was reasonably stable in the absence of solvents. However, after photolysis at −78 °C in ether, removal of the solvent on a vacuum line gave a crystalline material that gave very pale yellow plates on recrystallization, mp 79–83 °C. This material exhibited the same behavior, in-

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[1] Gusel'nikov, L. E.; Flowers, M. C. *Chem. Commun.* **1967**, 864.

[2] For reviews on silaethylenes, see: Gusel'nikov, L. E.; Nametkin, N. S.; Vdovin, V. M. *Acc. Chem. Res.* **1975**, *8*, 18. Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529. Coleman, B.; Jones, M., Jr. *Rev. Chem. Intermed.* **1981**, *4*, 297.

[3] A preliminary communication has appeared: Brook, A. G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. *J. Chem. Soc., Chem. Commun.* **1981**, 191.

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

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

[6] Brook, A. G.; Kallury, R. K.; Poon, Y. C. *Organometallics* **1982**, *1*, 987.

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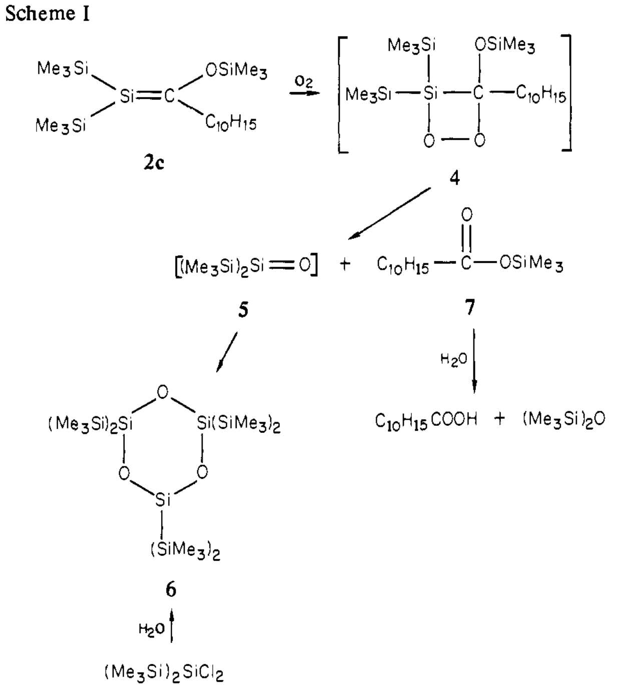
Scheme I



cluding vigorous reaction in air with the formation of white smoke, that the more fully characterized adamantylsilaethylene **2c** displays (see below).

When R = 1-adamantyl (hereafter $C_{10}H_{15}$), photolysis of **1c** gave a yellow solution, again containing much silaethylene but no dimer, as established by NMR spectroscopy. Removal of the ether solvent gave an off-white crystalline solid, which could be recrystallized from dry ether at low temperatures (to remove acylsilane present) to give slightly off-white needles of **2c**, mp 92–95 °C (under argon). This material has been kept sealed in a vial under argon for more than 9 months without change, suggesting it is indefinitely stable under these conditions. However, when exposed to air, the compound immediately and vigorously forms white smoke with melting and evaporation. With dilute dry oxygen under controlled conditions, the major products of the reaction (see Scheme I) are the cyclic trimer **6** of bis(trimethylsilyl)silanone (**5**) and the trimethylsilyl ester of adamantane-1-carboxylic acid (**7**), which presumably arise from breakdown of an intermediate siladioxetane (**4**) not yet isolated. The structures of **6** and **7** have been established spectroscopically and by independent synthesis.

Crystal Structure. The identity of the adamantylsilaethylene **2c** has been established chemically and spectroscopically and from its crystal structure, determined by X-ray diffraction at −50 °C. Figure 1 gives an ORTEP plot of the molecule and some of the bond lengths and bond angles that are of particular relevance.[9] Of greatest interest is the carbon–silicon double bond, found to be 1.764 (3) Å, considerably shorter than the normal length of a silicon–carbon single bond (1.87–1.91 Å)[10] but somewhat longer than the 1.69–1.73-Å bond lengths obtained from various MO calculations for $H_2Si{=}CH_2$ or $Me_2Si{=}CH_2$.[11-13] Other bond lengths are close to the values found previously in other compounds judged to be reasonable models. Thus, the Si–Me bonds ranged in length from 1.854 to 1.877 (4) Å, and the OSi–Me bonds from 1.829 to 1.862 (4) Å. The carbon–carbon bonds can be considered to be in three groups: bonds to C_2 (1.539–1.540 (5) Å); bonds to these three carbons (1.525–1.534 (5) Å); and the remaining C–C bonds (1.517–1.534 (5) Å). Hence, chemically equivalent bonds were found to be remarkably similar in length. Intramolecular hydrogen–hydrogen distances were all longer than 2.25 Å, with the smallest, between different groups in the molecule, being 2.366 Å between a methyl hydrogen on silicon atom Si3 and a facing hydrogen on the adamantyl group. Most bond angles were also close to "normal values" (the C–C–C bond angles within the adamantyl group varied from 108.3 to 111.0° and C–C–H bond angles varied from 105.0 to 114.5°), although the Si–O–C bond angle of 134.0° is somewhat larger than the 124–130° range found in model compounds.[14-16] In addition, there is significant distortion from 120° of the angles about the two sp^2-hybridized atoms of the double bond, almost certainly to reduce steric interactions between bulky groups, especially Me_3Si and adamantyl. These matters will be elaborated on later.

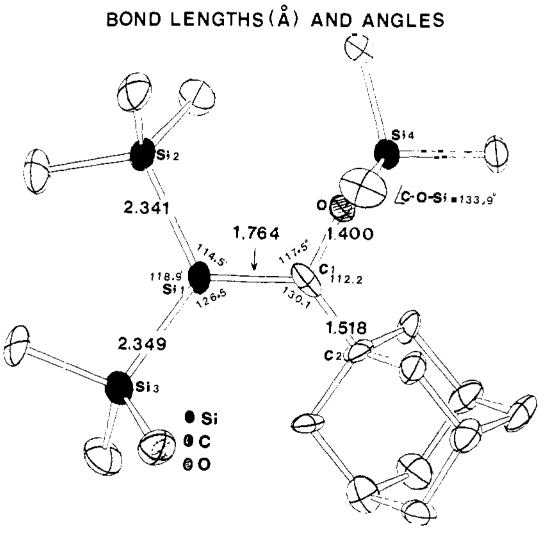
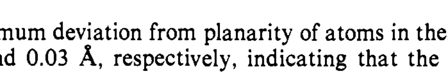


Figure 1. ORTEP diagram of silaethylene **2c** with important bond lengths and angles.

Figure 1 does not show that the molecule is actually twisted, an angle of 14.6° existing between the planes



The maximum deviation from planarity of atoms in these planes is 0.01 and 0.03 Å, respectively, indicating that the formally sp^2-hybridized Si and C atoms are truly planar. Examination of a model of this compound does not reveal any particularly strong steric interactions, and rotation of the halves of the molecule to remove the angle of twist does not appear to create significant additional steric interactions. Hence, it is possible that the molecule is twisted in the crystal lattice as a result of crystal packing forces; in solution it could be planar, but this is far from certain.

Spectroscopic Studies. The infrared spectrum of the silaethylene **2c** run as a Nujol mull (Figure 2) showed only one strong band (at 1135 cm^{-1}) (Table II) not present in the acylsilane precursor (top spectrum) (Table I). This band was also observed for **2a** and **2b** at 1130–1133 cm^{-1} in solution (Table II) and hence is characteristic of these types of silaethylenes. Since the IR spectrum shows no absorptions near 1050 cm^{-1}, expected for the Si–O–C stretch,[17] the 1133-cm^{-1} band may be due to this absorption, displaced because the carbon is sp^2 hybridized, because of steric interactions, or because of both effects. The same band is also seen in the Raman spectrum, run as a solid. Both Nefedov et al.[18] and Gusel'nikov et al.[19] have calculated that the Si=C

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(9) Full details of the crystal structure determination will be published elsewhere by S. C. Nyburg and A. G. Brook.

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Table I. Physical Properties of Acylsilanes, $(Me_3Si)_3SiCOR$

	R = CMe_3	R = CEt_3[a]	R = 1-adamantyl[b]
yield, %	70	79	64
mp, °C	182-184	161-162	65-66
IR, cm^{-1} (CCl_4), >C=O	1620	1613	1620
UV, λ_{max} (ϵ)	348 (100), 366 (127), 380 (97) (C_6H_{12})	368 (289) (Et_2O)	366 (210) (Et_2O)
NMR, ^1H, ppm	(CCl_4) 0.23 (s, 27 H), 1.00 (s, 9 H)	(C_6D_6) 0.40 (s, 27 H), 0.89 (t, J = 6 Hz, 9 H), 1.63 (q, J = 6 Hz, 6 H)	(CCl_4) 0.22 (s, 27 H), 1.5-2.2 (br m, 15 H)
^{13}C (C_6D_6) C=O	244.6	246.7	245.9
Me_3Si	2.1	2.1	2.1
R	49.3, 25.1	59.4, 24.4, 8.5	51.7, 37.2, 37.0, 28.4
^{29}Si (C_6D_6) Si–C(O)	−78.1	−79.4	−78.8
Me_3Si	−11.5	−12.0	−11.5
m/z, (EI) percent	317 $(M - Me)^+$ 6	359 $(M - Me)^+$ 3	410 $(M)^+$ 16
	275 $(M - CMe_3)^+$ 7	345 $(M - Et)^+$ 15	395 $(M - Me)^+$ 10
	259 $(M - Me_3Si)^+$ 22	301 $(M - Me_3Si)^+$ 18	337 $(M - Me_3Si)^+$ 25
	247 $[(Me_3Si)_3Si]^+$ 55	247 $[(Me_3Si)_3Si]^+$ 100	247 $[(Me_3Si)_3Si]^+$ 38

[a] Anal. Calcd for $C_{17}H_{42}OSi_4$: C, 54.47; H, 11.29. Found: C, 53.87; H, 11.25. [b] Anal. Calcd for $C_{20}H_{42}OSi_4$: C, 58.46; H, 10.30. Found: C, 58.49; H, 10.09.

Table II. Properties of Silaethylenes $(Me_3Si)_2Si{=}C(OSiMe_3)R$

	R = CMe_3	R = CEt_3	R = $C_{10}H_{15}$
IR, cm^{-1} (C_6D_6)	1130	1133	(Nujol) 1263 (m), 1255 (m), 1247 (m), 1195 (w), 1135 (s), 1101 (w), 1007 (w), 933 (w)
Raman, cm^{-1}			(solid) 1310 (w), 1257 (m), 1194 (m), 1170 (s), 1132 (s), 1097 (w), 1002 (m), 970 (w), 932 (w)
UV, λ_{max} (ϵ)	339 (5200) (hexane)	342 (7060) (Et_2O)	340 (7400) (Et_2O)
NMR, ^1H (C_6D_6) Me_3Si	0.28, 0.34, 0.39	0.40, 0.44, 0.48	0.41, 0.47, 0.51
R	1.25	0.87 (t, J = 6 Hz, 9 H) 1.60 (q, J = 6 Hz, 6 H)	1.8-2.2 (br)
^{13}C (C_6D_6) =C<	212.7	207.3	214.2
Me_3Si	1.7, 2.7, 3.5	1.9, 2.8, 3.5	2.0, 2.7, 3.6
R	43.1, 31.2	52.6, 27.0, 8.5	45.2, 42.7, 37.3, 29.4
^{29}Si(C_6D_6) Me_3Si	−12.1, −12.6	−12.4, −12.9	−12.8, −13.4
Me_3SiO	13.4	12.7	12.9
Si=	41.5	54.3	41.4
IP (PES)			7.7 ev
(EI) m/z			410 $(M)^+$
			395 $(M - Me)^+$
(CI) m/z percent		375 $(M + 1)^+$ 100	411 $(M + 1)^+$ 30
		359 $(M + 1 - CH_4)^+$ 18	410 $(M)^+$ 25
		346 $(M + 1 - C_2H_5)^+$ 15	396 $(M + 1 - Me)^+$ 40
		302 $(M + 1 - Me_3Si)^+$ 25	395 $(M - Me)^+$ 100
			337 $(M - Me_3Si)^+$ 5

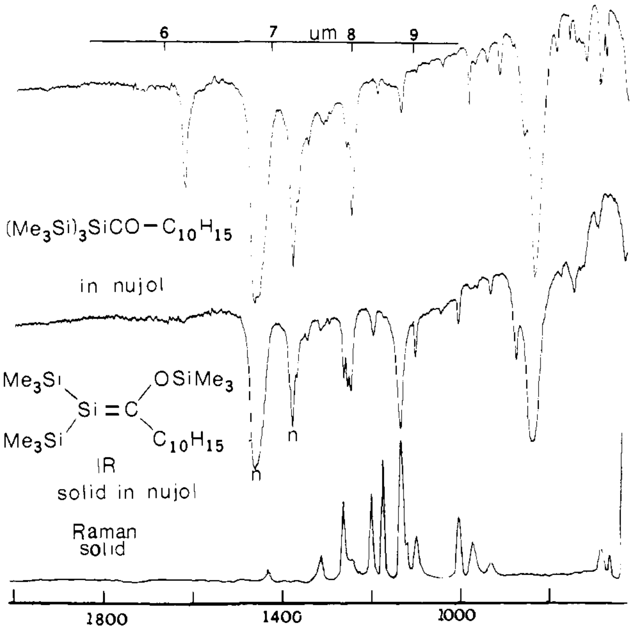

Figure 2. Infrared spectrum of acylsilane **1c** in Nujol (top) and silaethylene **2c** in Nujol (middle) and Raman spectrum of **2c** as a solid (bottom).

stretching absorption of dimethylsilaethylene, $Me_2Si{=}CH_2$, should occur at about 1000 cm^{-1}, and they have observed a band at 1003 cm^{-1} in argon matrix-trapped molecules at 10 K. It is not clear the extent to which bulky, electron-releasing substituents would alter the position of such an absorption, but several bands at 935, 975, and 1005 cm^{-1} are observed in the Raman spectrum of **2c** and weak bands at 1007 and 933 cm^{-1} are observed in the infrared spectrum. One of these may be the Si=C stretching vibration.

As mentioned earlier, solutions of these silaethylenes are yellow, due to a broad band with a λ_{max} at 340 nm, which tails into the visible region. The extinction coefficient is about 7400 for **2c**, based on the absorption of a solution of the acylsilane **1c** in ether that was photolyzed with four 100-W lamps until all the acylsilane had been converted to silaethylene. This value compares closely with the values of 339 nm (ϵ 5200) estimated for **2a** by a different method.[4] The magnitude of the extinction coefficient for these silaethylenes suggests that the double bond has considerable π-bond character, as suggested also by the ionization potential of **2c**, determined by photoelectron spectroscopy to be 7.7 eV. This value is much lower than those of most alkenes, which lie in the range 8.5–10.5 eV,[20] and it is significantly lower than that of $H_2Si{=}CH_2$, found by Bock to be 8.8 eV,[21] and $Me_2Si{=}CH_2$,

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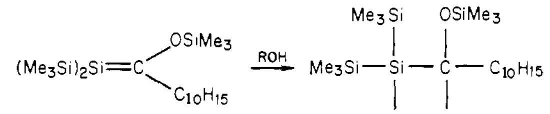
found to be 8.3 eV by Koenig and McKenna.[22] Evidently **2c** is a very electron-rich species that readily loses an electron. In addition, the radical cation of **2c** has been made and its ESR spectrum determined; discussion of the IP and ESR work will be published elsewhere.[23]

Perhaps the most definitive characterization of silaethylene **2c** and its analogues comes from their NMR data. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra each display sharp, different absorptions for each of the three trimethylsilyl groups present. Since the two trimethylsilyl groups attached to silicon are nonequivalent, even up to 60 °C, the highest temperature studied to date (no broadening of the absorptions was observed), it is clear that there is no freedom of rotation about the silicon–carbon double bond. A strongly deshielded ^{13}C signal is observed for the sp^2-hybridized carbon of the silaethylene at 214 ppm, lower than the range of 80–160 ppm usually observed for sp^2-hybridized carbons in simple alkenes. The ^{29}Si spectrum contains, in addition to signals at −12.8 and −13.4 ppm for the two Me_3Si groups on silicon and 12.9 ppm for the Me_3SiO group, an absorption at 41.4 ppm (also 41 ppm for **2a** but 54 ppm for **2b**). This is a remarkable position for silyl-substituted silicon but is reasonable for the hitherto unobserved absorption of sp^2-hybridized silicon, which by analogy with sp^2-hybridized carbon can be expected to absorb 100 or more ppm downfield of the sp^3-hybridized position. The silyl-substituted silicons in **1a–c** absorb at about −78 ppm; that in $(Me_3Si)_2SiMe_2$ absorbs at −48.5 ppm.[24]

Use of high-field FT-NMR spectrometers has allowed observation of the one-bond coupling across the silicon–carbon double bond. The 84-Hz magnitude observed for this coupling constant in this sp^2–sp^2-hybridized situation is significantly larger, as expected, than the 64–70-Hz values observed for one-bond Si–C couplings involving sp^3-hybridized silicon and sp^2-hybridized carbon,[25] as in the parent acylsilanes. In addition, the one-bond coupling between adjacent silicon atoms in the silaethylene, involving sp^3–sp^2 hybridization, was observed to be 72 Hz, substantially larger than the range 52–65 Hz found for coupling between silicons when each is sp^3 hybridized as in the acylsilanes **1a–c**, in $(Me_3Si)_4Si$, or in $(Me_3Si)_3SiCH_3$.[26] Further discussion of both the chemical shift and coupling constant data for a variety of acylsilanes and silaethylenes will be found in a forthcoming paper.[27]

Finally, the mass spectrum of the solid silaethylene has been obtained. Study of a number of 1,2-disilacyclobutanes[28] has shown that under electron-impact conditions, no parent ions M^+ are observed and most of the spectrum derives from dissociation of the dimer back to the monomer ion $(M/2)^+$ and ions derived there-from such as $(M/2 - Me)^+$, $(M/2 - Me_3Si)^+$, etc. However, under methane chemical ionization conditions, the parent $(M + 1)^+$ ion of the dimer is always observed. This is relevant to the mass spectrum of silaethylene **2c**, where the EI spectrum shows the appropriate parent ion $M^+ = 410$ and derived fragment ions such as $(M - Me)^+$, etc., and the CI spectrum shows the appropriate $(M + 1)^+ = 411$ ion. Thus, the mass spectrum leaves no doubt about the monomeric nature of the solid studied.

Chemistry of Stable Silaethylenes. The chemistry of the adamantylsilaethylene **2c** and its analogues has not been extensively elaborated, in large part because the bulky substituents attached to provide stability inhibit attack by many reagents. Methanol and water readily add across the silicon–carbon double bond of **2c** to give the expected products **8**. Unlike **2a**, which reacts cleanly with 1-phenylpropyne, **2b** reacts sluggishly at best, giving mixtures of products and starting materials, and **2c** does not undergo either reaction with phenylpropyne or a Diels–Alder reaction with 2,3-dimethylbutadiene, unlike other silaethylenes in this family.[4] Further studies of the chemistry of these compounds are in progress.



2c

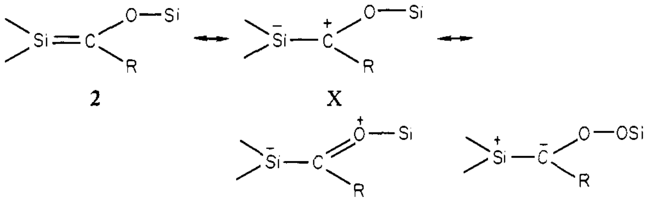
8a, R = Me
b, R = H

Each of the silaethylenes **2a–c** reverts to the parent acylsilane relatively rapidly. As mentioned previously, **2b** reverts to acylsilane much more rapidly than does **2a**. The reversion of **2c** to acylsilane **1c** was followed quantitatively by UV spectroscopy and was found to follow clean first-order kinetics. The half-life in ether at 25 °C was 15.8 h—i.e., $k = 1.22 \times 10^{-5}\ s^{-1}$. The disappearance of the silaethylene, as monitored by UV spectroscopy paralleled the reduction in the silaethylene content of the solution as followed by NMR spectroscopy, strongly supporting the belief that the yellow color of the photolysis solutions is due to the silaethylene present.

Discussion

The preceding data fully characterize compound **2c** and establish its structure as that of a silaethylene, with a multiple bond between carbon and silicon that possesses considerable π character.

Some further comments are warranted about the structure of **2c**, as one member of a general family of silaethylenes, several members of which have been studied spectroscopically. In particular, it seems important to comment on the possible polar character of the silicon–carbon double bond and the extent, if any, to which polarized forms such as X and Y or Z appear to be important in defining the character of the molecule.



2 X

Y Z

It is very unlikely that the ylide-like structure Z contributes importantly to the structure of the silaethylene. Simple silaethylenes, expected to be polarized like Z because of the differences in electronegativity between silicon and carbon, readily undergo head-to-tail dimerization,[2] but **2** fails in all cases to dimerize in this manner, even when nonbulky groups like methyl or trifluoromethyl are attached to carbon. While this could partly be the result of severe steric inhibition toward head-to-tail dimerization, it probably arises primarily from a lack of strong polarization of the double bond, because the electronic effects of the substituents on the bond oppose and largely neutralize the polarization arising from electronegativity differences. If the sp^2-hybridized carbon of the silaethylene had significant carbanionic character, it should be relatively shielded by virtue of the negative charge acquired, as with the ylid $Me_3P^+—CX_2^- \leftrightarrow Me_3P{=}CX_2$ (X = H and/or Me_3Si) where $\delta\ ^{13}C = 125.7–128.7$ for the ylidic carbon.[29] In contrast, the sp^2-hybridized carbon in the silaethylene is strongly deshielded to about 214 ppm (as also observed in transition metal–carbene complexes,[29b] which share other similarities with these silaethylenes), consistent with the acquisition of a positive charge through contributions from

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structures X and Y. Moreover, ylide-like molecules can be expected to show relatively facile freedom of rotation about the "double" bond, resulting in magnetic equivalence of groups attached. This was found for the aforementioned ylide, where the methyl groups on phosphorus were magnetically equivalent, even when $CX_2 = CHSiMe_3$. However, in the silaethylene, the trimethylsilyl groups attached to silicon were nonequivalent and their NMR spectra showed no signs of broadening up to 60 °C, the maximum temperature at which they could be studied. Thus, there is no evidence of rotation about the double bond, and no evidence of ylide-like behavior by the silaethylene.

It is a matter of considerable interest whether the observed silicon–carbon double-bond length of 1.764 Å is "normal" for a silaethylene or whether it is "stretched" as a result of steric or other effects. Several molecular orbital calculations for simple silaethylenes such as $H_2Si{=}CH_2$ or $Me_2Si{=}CH_2$[11-13] have yielded bond lengths between 1.69 and 1.73 Å, rather shorter than the measured value, whereas a recent electron-diffraction study reported a bond length of 1.83 Å.[30] West has recently reported that the silicon–silicon double-bond length for the solid disilene, $(mesityl)_2Si{=}Si(mesityl)_2$, is 2.156 Å (preliminary value).[31] If half this value represents the atomic radius of sp^2-hybridized silicon and this is added to 0.67 (half the value of a typical carbon–carbon length of 1.34 Å), the sum, 1.75 Å, is remarkably close to the length found in the crystal structure determination, which thus appears reasonable for a tetrasubstituted double bond. Thus, there is no reason to invoke significant stretching due to steric or other effects, particularly since it is known for highly hindered alkenes that severe steric interactions result in very little stretching of a carbon–carbon double bond (usually less than 0.01 Å) and that the strain is primarily relieved by twisting of the molecule about the double bond and by bond-angle distortions at the sp^2-hybridized atoms.[32] Both of these latter effects are observed in the crystal structure of the silaethylene and presumably reflect the relief of any steric strain present.

Contributions from structures X and Y to the overall structure explain several observations and could account for some lengthening of the silicon–carbon double bond relative to an unsubstituted silaethylene such as $H_2Si{=}CH_2$. Polarization due to electron release, particularly by the siloxy group, would oppose that due to electronegativity differences, resulting in a relatively unpolarized double bond. At the same time, loss of electron density from carbon explains the observed deshielding of the sp^2-hybridized carbon and infers that the sp^2-hybridized silicon, observed at the remarkably low field position of $\delta\ ^{29}Si = 41.4$, should be relatively shielded. This appears to be the case since West's symmetrical disilene has $\delta\ ^{29}Si = 63.6$, although part of the difference in chemical shifts is undoubtedly due to differences in the nature of the attached substituents (Me_3Si vs. Ar).

In summary, the data are consistent with some contributions from X and Y to the overall structure of the silaethylenes, resulting in a relatively unpolarized double bond that, lacking a driving force for head-to-tail dimerization, undergoes head-to-tail dimerization (probably by a radical pathway) when sterically possible. However, further data on other silaethylenes are necessary before a better understanding of the character of the silicon–carbon double bond in these systems can be reached. The present results, however, convincingly demonstrate that it is possible to stabilize a silicon–carbon double bond so that it may be studied as a solid at room temperature.

Experimental Section

NMR spectra were generally run in C_6D_6 unless otherwise noted, referenced for ^1H NMR at 7.27 ppm and for ^{13}C NMR at 128.00 ppm relative to Me_4Si. Spectra were obtained on Varian T-60 and HA-100 instruments, on a Bruker WP80 instrument, and on the Bruker 400-MHz instrument of the S. W. Ontario Regional NMR Centre, located at the Department of Chemistry, University of Guelph.

Chemical manipulations were carried out on vacuum lines under an atmosphere of 99.999% pure argon. All solvents were carefully dried and distilled over sodium and/or lithium aluminum hydride.

Photochemical investigations employed one to four 100-W PAR 38 mercury spot lamps (BLAK RAY long-wavelength ultraviolet lamps, Ultraviolet Products Inc.). Samples were kept either at ambient temperatures or in cold-water jackets at about 6 °C.

Ultraviolet spectra were obtained on a Cary 118 UV-VS spectrometer, and infrared spectra were recorded on a Unicam SP1025 infrared instrument. The mass spectra were obtained on a Du Pont 21-490 mass spectrometer equipped with a high-pressure chemical ionization source, with source temperature 60 °C and methane gas at 0.3 torr.

Crystal Structure. Because of their high reactivity, crystals of silaethylene **2c** were handled on a vacuum line under argon. X-ray data were collected initially at room temperature on an automated Picker four-circle diffractomer. The structure of the crystal, which belongs to the triclinic system, was solved by using MULTAN,[33] which showed the space group to be $P\bar{1}$. The molecular structure agreed with that assigned on chemical and spectroscopic grounds.

While sealed in capillaries, some crystals exposed to the X-rays appeared to acquire an oily coating. Perhaps because of this, the crystal used for the X-ray analysis slipped in the capillary and had to be realigned six times during data collection. The reflection data thus left much to be desired.

Accordingly, a second data set was collected with a new crystal at −50 °C (at which temperature the crystal remained rigidly in place) on a Syntex $P\bar{1}$ diffractometer.[34] A total of 5868 reflections were collected with graphite-monochromatized Mo Kα radiation, of which 3067 were considered significant on the criterion $I > 3\sigma(I)$ (for details of the data collection and treatment, see ref. 35).

Crystal data: triclinic, $P\bar{1}$, $a = 6.541$ (9) Å, $b = 10.057$ (2) Å, $c = 20.391$ (3) Å, $\alpha = 101.69$ (1)°, $\beta = 90.86$ (1)°, $\gamma = 105.77$ (1)°, $Z = 2$ molecules per cell.

The structure was refined by block-diagonal least squares. Non-hydrogen atoms were refined anisotropically by using scattering factors from International Tables.[36] Hydrogen atom positions and isotropic temperature factors were refined by using scattering factors from Stewart, Davidson, and Simpson.[37] The final R was 0.049 and R_w was 0.039. Full details of the atomic parameters, etc., will be published elsewhere.

Typical Synthesis of Acylsilanes: Adamantoyltris(trimethylsilyl)silane (1c). A solution of 15.5 g (32.95 mmol) of $(Me_3Si)_3SiLi{\cdot}3THF$[7] in 250 mL of cyclopentane was added dropwise over 2 h to a solution of 6.6 g (33.2 mmol) of 1-adamantanecarboxylic acid chloride (Aldrich) in 50 mL of cyclopentane at −60 °C in the dark. After warming to 20 °C over 1 h, filtration under argon gave a clear colorless filtrate. Removal of the solvent and recrystallization from MeOH gave 8.1 g (64%) of colorless plates, mp 65–66 °C.

Photolysis of (Triethylacetyl)tris(trimethylsilyl)silane (1b) in Methanol. A solution of 376 mg (1 mmol) of **1b** in 1 mL of benzene and 64 mg (2 mmol) of methanol in an NMR tube was photolyzed at 10 °C over 16 h. Removal of the solvent and recrystallization from acetone gave about 50% of methanol adduct: mp 115–116 °C; ^1H NMR (C_6H_6) δ 4.07 (1 H), 3.33 (3 H, MeO), 1.40 (6 H, q, $J = 6.5$ Hz, CH_2CH_3), 0.88 (9 H, t, $J = 6.5$ Hz, CH_2CH_3), 0.33, 0.27, 0.23 (each 9 H, s, Me_3Si). Anal. Calcd for $C_{18}H_{46}O_2Si_4$: C, 53.1; H, 11.3. Found: C, 53.0; H, 11.3.

Photolysis of (Triethylacetyl)tris(trimethylsilyl)silane with Phenylpropyne. A solution of 84 mg (0.23 mmol) of **1b** in 1.5 mL of benzene and 116 mg (1.0 mmol) of phenylpropyne in an NMR tube was thrice frozen and degassed and then sealed. Photolysis for 15 h at 15 °C resulted in the formation of a yellow solution with NMR signals consistent with the formation of the expected silacyclobutene; ^1H NMR (C_6H_6) δ 1.78 (3 H, s, Me—C=), 1.63 (6 H, q, $J = 7.0$ Hz, CH_2CH_3), 0.90 (9 H, t, $J = 7.0$ Hz, CH_2CH_3), 0.40 (9 H, 3, Me_3SiO), 0.37 (18 H, s, $2Me_3Si$).

Photolysis of (Triethylacetyl)tris(trimethylsilyl)silane (1b). A solution of **1b** in 5 mL of dry ether was photolyzed with two 100-W lamps at 6

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°C under argon for 5 h, at which time no further change in the proportions of silaethylene:acylsilane ($\simeq$65:35) occurred. Removal of the solvent on a vacuum line gave a viscous semisolid material, shown by spectroscopy to contain both silaethylene and acylsilane. The proportions ($\simeq$60:40) in the viscous liquid changed by less than 5% over 30 days. Attempted crystallization from ether at −20 to −30 °C failed to yield a crystalline solid.

When a solution of 1.5 g of **1b** in 10 mL of dry ether was photolyzed at −78 °C with 4 lamps in an unsilvered Dewar flask containing acetone–dry ice, the solution rapidly became strongly yellow colored. After 16 h of photolysis removal of the solvent on a vacuum line gave a solid crystalline mass, samples of which smoked vigorously in air. Recrystallization from ether at −30 °C gave very pale yellow crystals, mp 79–83 °C.

Comparison of Rates of Reversion of Silaethylenes 2a and 2b to Acylsilanes. Separate 0.2 M solutions of the pivaloylsilane **1a** and the (triethylacetyl)silane **1b** in benzene in sealed degassed NMR tubes containing a drop of anisole as an internal standard were photolyzed with one 100-W lamp for 18 h, at which time the ^{1}H NMR data indicated that **1a** was 95% converted to silaethylene **2a** and dimer **3a**, while **1b** was only 75% converted to **2b**.

When the yellow solutions were cooled to −17 °C for 24 h, the solution of **1a** + **2a** + **3a** became colorless and the NMR spectrum indicated **2a** had disappeared, forming **3a**, while the yellow solution of **1b** + **2b** remained unchanged.

When the solutions were reexamined by ^{1}H NMR after 6 days at room temperature, integration indicated that reversion to **1a** was 38% complete, while reversion to **1b** was 73% complete.

Photolysis of Adamantoyltris(trimethylsilyl)silane (1c) and Isolation of Solid Silaethylene 2c. A solution of 4.1 g (10 mmol) of adamantoylsilane **1c** in 7 mL of ether (dried over sodium and then distilled from $LiAlH_4$) under argon was photolyzed with two 100-W lamps at 6 °C (running water jacket) for 12 h. A yellow color rapidly developed in the solution. After 12 h, the ether was removed on a vacuum line, giving a yellow solid, which was dissolved in 5 mL of dry ether and cooled slowly to −20 °C as slightly yellowish needles were formed.

The supernatant liquid was removed from the needles, which were washed with 2 × 5 mL of ether at −30 °C to give 2.9 g (70%) of almost colorless silaethylene **2c**, mp 92–95 °C. Since the needles reacted exothermically in air, causing white smoke and melting, no CH analysis was attempted. Spectroscopic data are listed in Table II. The infrared spectrum of the solid, run immediately as a Nujol mull between salt plates sealed from the air, showed no C=O stretch at 1620 cm^{-1}, characteristic of the acylsilane, although over a few hours this band slowly developed. The NMR spectra invariably showed absorption for some acylsilane also present, because of the rapid reversion of silaethylenes to acylsilanes in solution. In particular, the ^{1}H NMR spectrum showed the Me_3Si absorption at 0.41 ppm more intense than required (three Me_3Si signals each of equal intensity) because of accidental overlap with the Me_3Si signal of the acylsilane that also occurs at 0.41 ppm.

Reaction of Adamantylsilaethylene 2c with Methanol. To 260 mg (0.63 mmol) of solid **2c** under argon at −10 °C was added 5 mL of dry methanol containing 5 drops of pyridine. Removal of the solvent gave a white solid, which, after recrystallization from benzene, gave 157 mg (56%) of methanol adduct **8a**: mp 153–155 °C; ^{1}H NMR (C_6D_6) δ 3.80 (1 H, s, CH), 3.47 (3 H, s, OMe), 2.42–1.67 (15 H, m, adamantyl), 0.44, 0.42, 0.36 (9 H each, s, Me_3Si).

Photolysis of the parent acylsilane **1c** in methanol at 10 °C gave the same product in nearly quantitative yield. Anal. Calcd for $C_{21}H_{46}O_2Si_4$: C, 56.9; H, 10.5. Found: C, 56.7; H, 10.4.

Reactions of Adamantylsilaethylene 2c with Water. To 314 mg (0.76 mmol) of solid **2c** under argon at −10 °C was added a solution of 1 mL of water in 4 mL of THF. Removal of the solvents after 2 h gave a viscous liquid with spectroscopic properties expected for the water adduct **8b** (all attempts to crystallize the compound failed): ^{1}H NMR (C_6D_6) δ 3.80 (1 H, s, CH), 2.30–1.69 (15 H, m, adamantyl) 0.42, 0.38, 0.33 (9 H each, s, Me_3Si); IR (neat) 3500 (OH), 1250 (Si–Me), 1050 (Si–O–C) cm^{-1}; MS, *m/z* 428 (M)$^+$, 427 (M − H)$^+$, 413 (M − Me)$^+$.

An identical product was obtained from photolysis of acylsilane **1c** in an H_2O–THF solution for 20 min.

Reaction of Silaethylene 2c with Oxygen. A solution of 0.82 g (2 mmol) of **2c** in 10 mL of dry pentane was irradiated under argon for 16 h and then was allowed to stir at −20 °C in the presence of a 10% mixture of oxygen in argon for 5 h, during which time most of the yellow color disappeared. Removal of the solvent gave a viscous pale yellow liquid that showed IR absorptions at 1625 (recovered starting material ~50%) and 1710 cm^{-1} (due to trimethylsilyl adamantanecarboxylate, *m/z* (CI) 251 (M + 1)$^+$, and siloxane absorption at 1050 cm^{-1} (due to the cyclic trimer of $(Me_3Si)_2Si{=}O$, *m/z* (CI) 571 (M + 1)$^+$). Chromatography of half of the reaction mixture on silica gel (pentane) gave **6** (26%) as a viscous liquid: bp (Kugelrohr) 195 °C (1 mm); ^{1}H NMR (C_6D_6) δ 0.4 (br); IR (Nujol) 2980–2920, 1260, 1050, 845, 800, 705, 695 cm^{-1}; MS (CI) *m/z* 571 ((M + 1)$^+$, 5%) 498 ((M + 1 − Me_3Si)$^+$, 16%), 483 (65%), 468 (100%).

Material with identical properties was obtained by the hydrolysis of $Me_3SiSiCl_2SiMe_3$ with H_2O in THF over 12 h at 22 °C.

The other half of the viscous liquid was treated with dilute $NaHCO_3$ and after acidification gave 44 mg (23%) of adamantane-1-carboxylic acid, mp 173–175 °C (lit. mp 174–175 °C), identical in all respects with an authentic sample.

Attempted Reactions of Adamantylsilaethylene with Phenylpropyne or 2,3-Dimethylbutadiene. A sealed freeze–degassed NMR tube containing 90 mg of adamantoyltris(trimethylsilyl)silane (**1c**) and 25 mg of phenylpropyne in C_6D_6 was irradiated at 6 °C for 12 h. The NMR spectrum was recorded every 60 min and showed the formation of silaethylene **2c**, but no disappearance of phenylpropyne or formation of other products. Prolonged irradiation over several days led to some reaction and a complex mixture of unidentified products. Similar behavior was observed when 2,3-dimethylbutadiene was employed in place of phenylpropyne.

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Registry No. 1a, 69397-47-3; **1b**, 72214-49-4; **1c**, 72189-53-8; **2a**, 81671-49-0; **2b**, 81671-50-3; **2c**, 72189-54-9; **3a**, 69397-56-4; **6**, 81740-84-3; **8a**, 82294-12-0; **8b**, 82294-13-1; 1-adamantanecarboxylic acid chloride, 2094-72-6; methanol, 67-56-1; phenylpropyne, 673-32-5; adamantane-1-carboxylic acid, 828-51-3; 2,3-dimethylbutadiene, 513-81-5; $Me_3SiSiCl_2SiMe_3$, 5181-42-0.