## A Solid Silaethene: Isolation and Characterization

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Summary The first reported solid silaethene, m.p. 95 °C, stable at room temperature under argon, but highly reactive in air has been isolated and characterized by i.r., n.m.r. and mass spectrometry.

The synthesis, characterization, and isolation of a pure silaethene has challenged chemists for many years. We have recently addressed the first of these problems<sup>1-3</sup> and now report the isolation of a solid silaethene, which is stable at room temperature in the absence of air or other reagents. The compound, 2-adamantyl-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-silaethene (2), m.p. 92—95 °C, is produced by photolysis of a solution of the isomeric acylsilane (1), m.p. 64—65 °C.<sup>1,2</sup> Removal of the ether solvent yields a

solid mass, which on recrystallization to remove some accompanying (1) leads to needles of (2), as proved below. The solid (2) on exposure to air immediately reacts exothermically producing white smoke, melts, and some evaporates.

Pure (1), and the mixture of (1) and (2) formed in solution by photolysis, have been characterized by their <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si n.m.r., and i.r. spectra; the data are in the Table. Identical n.m.r. data were obtained from several different freshly prepared solutions of (2). We assign the <sup>13</sup>C absorption at 214·2 p.p.m.† to the sp² hybridized carbon of (2), and the <sup>29</sup>Si absorption at 41·8 p.p.m. to its sp² hybridized silicon.

$$(Me_3Si)_3 \stackrel{b}{SiC} (=0) \stackrel{d}{C_{10}H_{15}} \qquad (Me_3Si)_2 \stackrel{b}{Si} = \stackrel{c}{C} \stackrel{d}{C_{10}H_{15}}$$
(1)

TABLE. <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si n.m.r.<sup>a</sup> and i.r.<sup>b</sup> data for (1) and (2).

 $^{\rm a}$  P.p.m. from Me\_4Si in C\_6D\_6.  $^{\rm b}$  In mineral oil.

None of the n.m.r. spectra shows any evidence for dimeric species, the absorptions of which have been observed and assigned in two other cases with t-butyl or phenyl instead of adamantyl. 1,2, We have observed that in solution (2) reverts to (1) moderately rapidly over several days, or faster if heated.

<sup>†</sup> This value is in close accord with that observed for  $(Me_3Si)_2Si=C(OSiMe_3)Bu^t$ , where the =C resonance was observed at 212·7 p.p.m.; the =C resonance was erroneously assigned in refs. 1 and 2 as the absorption at 112·7 p.p.m., but this signal is due to the ring carbon atoms of the dimer. Three other dimers also have ring carbon absorptions in the range 88—112 p.p.m.

<sup>‡</sup> In the  $^{13}$ C n.m.r. spectra of a few (but not all) samples we have observed weak signals at  $\delta$  98.2, 62.5, and 26.8 p.p.m. These may be due to traces of oxidation or other reaction products, but not all are at positions where dimer signals would be expected.

The <sup>1</sup>H n.m.r. spectrum of a solution of (2) recorded as soon as possible after preparation showed that ca. 94% of silaethene and 6% of acylsilane were present, as determined from the relative intensities of the Me<sub>3</sub>Si signals of (2) at  $\delta$  0.51 or 0.47 compared with the signal of the mixture of (1) and (2) at  $\delta$  0.41 (accidental overlap). With time the amount of (1) increased at the expense of (2).

Using high resolution <sup>13</sup>C n.m.r. spectroscopy it was possible to observe the  ${}^{1}J({}^{29}Si-{}^{13}C)$  coupling constants for the acylsilane (34.0 Hz) and the silaethene (84.3 Hz), the latter larger value being consistent with previous general observations that an increase in coupling constant occurs with a change from sp<sup>3</sup> to sp<sup>2</sup> hybridization.

A suspension of compound (2) in mineral oil gave the strong i.r. absorption at 1135 cm-1 characteristic of a silaethene.2§ No carbonyl absorption at 1620 cm<sup>-1</sup> was observed, except after several hours when a weak band developed. Hence the crystals of (2) do not contain the acylsilane (1) initially.

The mass spectrum of (1) with the spectrometer source at 60 °C and the sample insertion probe at 40 °C gave a typical acylsilane fragmentation pattern:  $M^+$  m/z 410 (100%),  $(M - Me)^+ 395 (75\%)$ ,  $(M - Me_3Si)^+ 337 (90\%)$ ,  $(M - \text{adamantyl})^+$  275 (25%), and smaller fragments. In contrast, under the same conditions the needles of (2) showed an entirely different fragmentation pattern:  $M^+$ m/z 410 (1%),  $(M - C_5H_{15}Si_2)^+$  279 (20%),  $(M - C_5H_{14}^-)$  $Si_3$ )+ 252 (30%),  $(M - C_6H_{17}Si_3)$ +  $\equiv$  (adamantyl-CH-

OSiMe<sub>3</sub>)+ 237 (100%), and smaller ions: none of these ions is observed in the spectrum of (1). However, when the source temperature was raised to ca. 110 °C the observed spectrum was a composite of spectra of (1) and (2), presumably owing to the partial isomerization of (2) back to (1). Under chemical ionization (C.I.) conditions with CH<sub>4</sub>, the needles of (2) gave the ion  $(MH)^+$  at m/z 411 (100%), the molecular weight confirming that the compound was monomeric. These spectra are not those of a head-tohead dimer since, in several examples studied, a strong signal for  $(Me_{12}Si_6)^+$  at m/z 348 is always observed, and under C.I. conditions the (MH)+ peak of the dimer is a major peak.

It is clear from the above data that the solid studied is neither the acylsilane (1) nor a dimer of the silaethene (2). The strong i.r. absorption at 1135 cm<sup>-1</sup> confirms that the material described has the structure attributed to the silaethene (2), and hence it is evident that reasonably stable silaethenes can be isolated and studied. A crystal structure determination is being undertaken.

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<sup>§</sup> This absorption is the only strong absorption characteristic of silaethenes in general, having been observed by us in two other examples. It may be the Si=C stretch, calculated by others as occurring near 1145 cm-1 for H<sub>2</sub>Si=CH<sub>2</sub>: H. B. Schlegel, S. Wolfe, and K. Mislow, J. Chem. Soc., Chem. Commun., 1975, 246. It instantly disappears when oxygen or protic solvents are introduced into the system.

A. G. Brook, S. C. Nyburg, W. F. Reynolds, Y. C. Poon, Y.-M. Chang, J. S. Lee, and J.-P. Picard, J. Am. Chem. Soc., 1979, 101 6750.
A. G. Brook, J. W. Harris, J. Lennon, and M. El Sheikh, J. Am. Chem. Soc., 1979, 101, 83.
A. G. Brook and J. W. Harris, J. Am. Chem. Soc., 1976, 98, 3381.