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Journal of Organometallic Chemistry 499 (1995) 1–5

Journal of Organometallic Chemistry

Photolysis of some organosilylene precursors in a molecular beam ☆

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Received 5 January 1995; in revised form 21 February 1995

Abstract

The condensed-phase organosilylene precursors $PhMeSi(SiMe_3)_2$ (**1**), $PhSi(SiMe_3)_3$ (**2**), and $(Me_2Si)_6$ (**3**) were photolyzed in a molecular beam using a pulsed supersonic jet and mass spectrometric detection. Under ~ 10 ns pulsed UV illumination, we have found for the gas-phase trisilane precursors **1** and **2** that one photon results in removal of only one $-SiMe_3$ group. Even at the highest laser power densities used, there is no evidence of removal of a second $-SiMe_3$ to form a silylene. On the other hand, a single photolysis photon was capable of producing the silylene for the cyclohexasilane ring precursor, **3**.

Keywords: Silicon; Mass spectrometry; Molecular beams; Photochemistry

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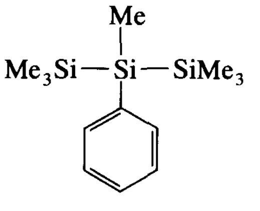
1. Introduction

Organosilylenes are ubiquitous and important reactive intermediates in organosilicon chemistry [1]. A convenient route to the generation of organosilylenes, either in solution [2] or cold inert matrices [3], is the photolysis of cyclopolysilanes (Eq. (1)) or 2-aryltrisilanes (Eq. (2)).

$$(RR'Si)_n \xrightarrow{h\nu} (RR'Si)_{n-1} + RR'Si: \qquad (1)$$

$$ArRSi(SiMe)_2 \xrightarrow{h\nu} Me_3SiSiMe_3 + ArRSi: \qquad (2)$$

If it were possible to generalize these preparations to the gas phase, a number of new studies could take place, among them new reaction kinetics studies or molecular beam based studies of various organosilylenes and their reaction products (conformational studies of stable aryldisilanes in supersonic expansions have been reported [4]). It is not clear, however, that there will always be transferability of the above preparative methods to the gas phase. Photochemically-induced rearrangements and multiple photochemical steps may be possible under steady-state illumination in the matrix which do not occur in pulsed gas-phase photolysis. Consequently, we have studied the molecular beam photochemistry of the potential silylene generators **1**–**3** using pulsed UV irradiation.



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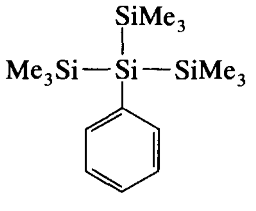

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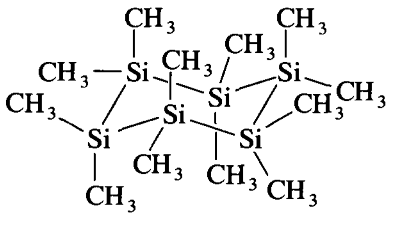

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2. Experimental section

The experiments were carried out using a molecular beam photoionization time-of-flight spectrometer [5]. Helium gas was passed through heated sample containers into which the precursors were placed. A General Valve series 9 pulsed valve was used to produce 10 Hz 150 μs gas pulses which were passed through a 0.5 × 4

☆ Dedicated to Hideki Sakurai on the occasion of his retirement from Tohoku University.

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SSDI 0022-328X(95)00325-8

mm^2 slit skimmer to form a molecular beam. Laser beams at 248 nm (Lambda Physik Lextra excimer) and/or 266 nm (Continuum YG680 Nd:YAG, 4th harmonic) were focused and directed through the photoionization region of the molecular beam.

The trisilanes **1** and **2** were synthesized according to previously reported procedures [6]. Dodecamethylcyclohexasilane (**3**) was purchased from Petrarch, now United Chemical Technology, Inc.

3. Results

3.1. 266 nm and 248 nm photolysis of 2-phenylheptamethyltrisilane (1)

In this case the parent ion mass is 266 amu. Each $SiMe_3$ group corresponds to 73 amu. Fig. 1 shows mass spectra as the relative 266 nm laser fluence is increased. (Benzene, $m/e = 78$, indole, $m/e = 117$, and naphthylamine, $m/e = 143$, were used as mass calibrators. The peaks with labelled masses from 78 to 143 are not due to the reaction monitored.) As the relative 266 nm laser fluence increases, the gradual growth of an ion peak at $m/e = 193$ is evident. This species must arise from photoionization of the $SiPhMe(SiMe_3)$ radical. However, regardless of the incident pulse energy and the extent to which the laser beam was focused, it was not possible to observe the appearance of a mass at 120 amu, corresponding to removal of a second $SiMe_3$ group.

Fig. 2 shows a plot of the 193 amu peak signal, $I(m/e = 193)$ as a function of relative laser pulse energy, I_{266}. The best integer power-dependence fit, I_{266}^n, is $n = 3$. On the other hand, the best fit of the power dependence for the peak due to the precursor mass at $m/e = 266$ was second power. For each of the three precursor compounds considered, the parent precursor ion peak was scaled as laser intensity squared (one such fit is shown in Fig. 5). These second power fits are consistent with the fact that the energy of two photons is sufficient to photoionize any of the species present. The $n = 3$ power dependence of the 193 amu peak is consistent with one photon breaking the $Si-SiMe_3$ bond followed by two-photon ionization (i.e. a 1 + 2 photon process). Alternatively, two-photon ionization of the precursor could be followed by photolysis due to a third photon (a 2 + 1 process). Similar results were observed using 248 nm laser pulses, although the relative yield of $m/e = 193$ was lower. This was the case even though considerably more pulse energy was available at 248 nm. The simplest explanation would be that the gas-phase precursor absorbance at 266 nm is better than at 248 nm. When both 248 nm and 266 nm pulses are used with $I_{248} \gg I_{266}$, under conditions such that no $m/e = 193$ amu signal was observed by operating either laser alone, power-dependence fitting shows that $I(m/e = 193) \propto I_{248}^2$ and $I(m/e = 193) \propto I_{266}$. All of the preceding data can be understood in terms of the absorption of one photon at 266 nm, resulting in breaking of one $Si-SiMe_3$ bond, followed by two-photon ionization of the 193 amu radical. Using either 248 nm pulses, 266 nm pulses, or a combination, it was not possible under any circumstances (increased laser fluence, tighter beam focus) to observe the appearance of a mass peak at $m/e = 120$, which would correspond to removal of a second $SiMe_3$ to form the silylene.

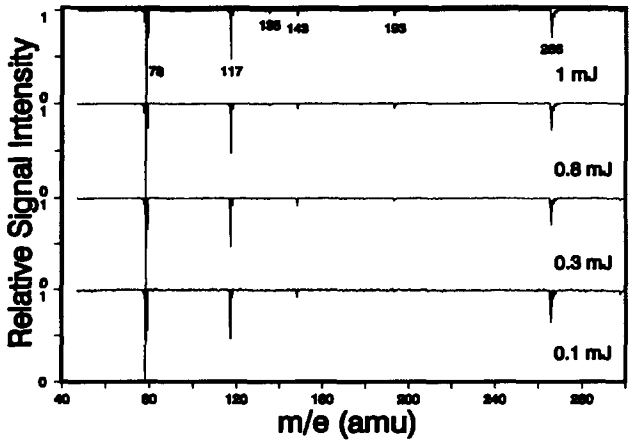


Fig. 1. 266 nm photolysis of 2-phenylheptamethyltrisilane (**1**) with mass 266 amu. Mass spectra are taken with increasing laser fluence. The pulse energies indicated are correct relatively but not absolutely.

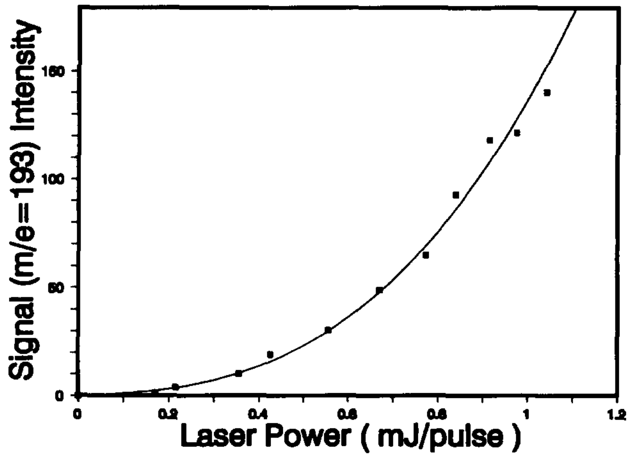


Fig. 2. Photolysis of **1**. Laser-power dependence (relative power) of the $m/e = 193$ mass peak. The solid line represents a third power fit for which $R = 0.992$.

3.2. 266 nm photolysis of 2-phenyl,2-trimethylsilylhexamethyltrisilane (2)

The results obtained were very similar to those obtained for compound **1**. A peak at $m/e = 338$, corresponding to the precursor molecule **2** appears. A peak at

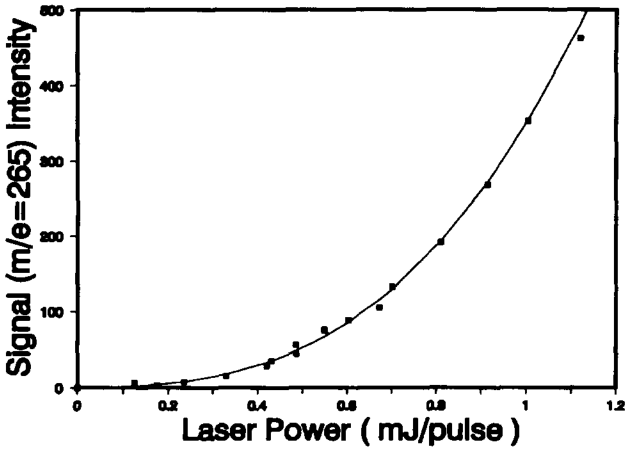


Fig. 3. 266 nm photolysis of 2-phenyl,2-trimethylsilyl-hexamethyltrisilane (2) with mass 338 amu. Laser-power dependence (relative energy units) of the $m/e = 265$ peak. The solid line represents a fit to an $n = 3$ power for which $R = 0.984$.

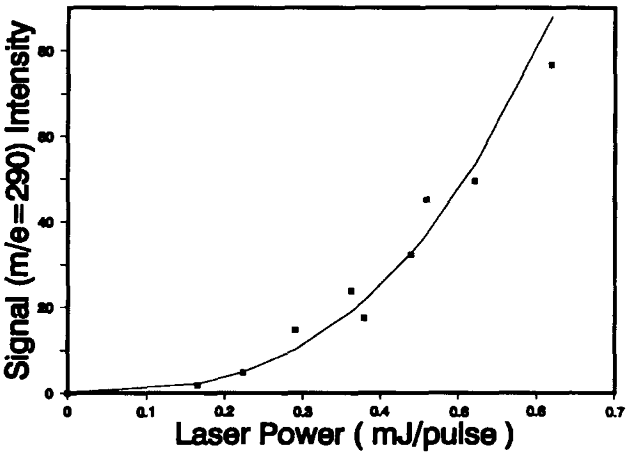


Fig. 4. 266 nm photolysis of $(Me_2Si)_6$ (3) with mass 348 amu. Laser-power dependence (relative energy units) of the $m/e = 290$ peak. The solid line represents an $n = 3$ power fit for which $R = 0.977$.

265 amu (i.e. 338 amu less 73 amu, the mass of $SiMe_3$) also appears with increasing intensity as the laser pulse energy is increased. Under no conditions (tightness of focus, pulse energy), however, is a signal observed at 192 amu, corresponding to removal of a second $SiMe_3$ group. When $I(m/e = 265)$ is plotted against I_{266} (Fig. 3) a good $I(m/e = 265) \alpha I_{266}^3$ dependence is obtained.

3.3. *266 nm photolysis of $(Me_2Si)_6$ (3)*

In addition to a 348 amu mass corresponding to the precursor, a mass peak at 290 amu appears, with $I(m/e = 290)$ growing as the laser intensity increases. The mass at 290 amu corresponds to the loss of one Me_2Si unit from the precursor. There is a corresponding increase in the 58 amu mass channel, but it cannot be followed quantitatively due to the detection of chamber contaminant mass peaks. A plot of $I(m/e = 290)$ versus I_{266} is shown in Fig. 4. Best integral power fits to three such independently generated plots yielded I_{266}^3 dependences. In contrast, a plot of $I(m/e = 348)$ vs. I_{266} plot (Fig. 5) yielded I_{266}^2 dependence. Once again, two photons are needed to ionize each species detected. The additional photon required for appearance of the 290 amu product must result in removal of one Me_2Si unit (i.e. a net of more than one bond broken in the original ring structure), through either a 1 + 2 or 2 + 1 process. In either case, the final outcome of the gas-phase cyclopolysilane photolysis is thus dramatically different from the trisilane cases. As can be seen in Fig. 6, the relative size of the 290 amu peak, reflecting also the concomitant 58 amu peak growth, can be very significant.

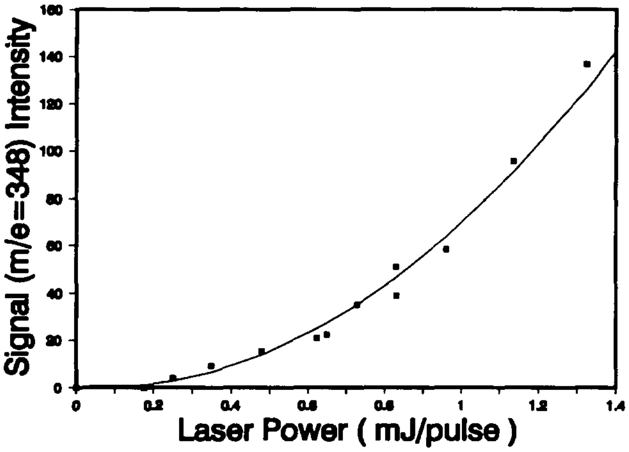


Fig. 5. Photolysis of 3. Laser-power dependence (relative energy units) of the $m/e = 348$ peak. The line represents an $n = 2$ power fit for which $R = 0.984$.

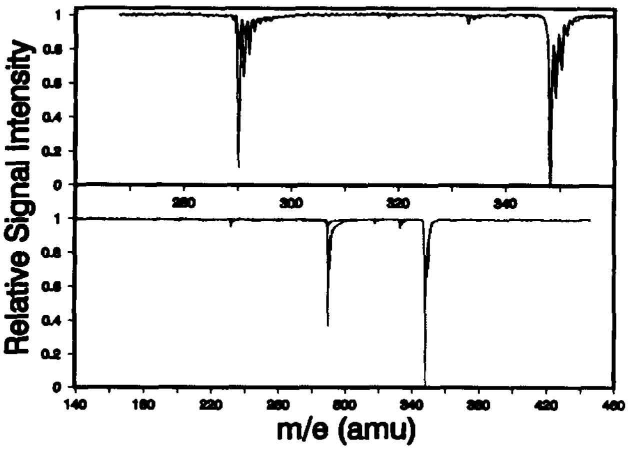


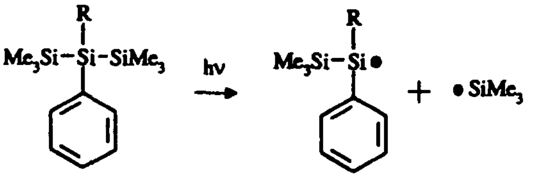
Fig. 6. Photolysis of 3. Each mass spectrum contains two scans, with the 348 amu peaks scaled to be the same size. The 290 amu peak is significantly larger for the higher of the two laser powers.

4. Discussion

In the gas phase, one UV photon resulted in the sole removal of one $SiMe_3$ group for the two trisilane precursors **1** and **2**. It was not possible at any laser fluence to produce a silylene via removal of a second $SiMe_3$ group. In contrast to condensed phase studies, this result is consistent with the homolytic cleavage of just one Si–Si bond to produce a pair of silyl radicals (homolytic cleavage of silicon–silicon bonds has been observed in the photochemistry of polysilane high polymers and strained silicon rings; however, this reactivity is generally not observed for linear aryltrisilanes [7]). The apparent discrepancy between gas-phase (radical pair production) and condensed-phase (silylene production) photolyses, however, may be reconciled by the assumption of a second thermal step for the production of the silylene in the condensed phase. As in the gas phase, the initial photochemical event in condensed phases may be the generation of a trimethylsilyl and an aryldisilanyl radical (Eq. (3)). Within the solvent cage or matrix, a facile secondary reaction involving displacement of a terminal trimethylsilyl group of the aryldisilanyl radical by the trimethylsilyl radical may occur to give the silylene (Eq. (4)). In the absence of a cage effect, such as in the collisionless region of a molecular beam, the likelihood of a subsequent bimolecular event would be exceedingly small and the production of a silylene probably not observed.

The generation of radical pairs in the primary photochemical event in solution may also explain the formation of silene intermediates which sometimes occur as side-products in aryltrisilane photolysis [8]. In this case, a competing attack of the trimethysilyl radical on the ortho carbon of the phenyl ring gives rise to the silene product (Eq. (5)).

In contrast to the trisilane photolyses, one-photon gas-phase photolysis of dodecamethylcyclohexasilanesilane (**3**) efficiently produces dimethylsilylene. Although it is possible that silylene extrusion may occur via a concerted mechanism (a concerted extrusion of silylene from a σ^* excited state would be symmetry allowed [9]) for this precursor, it is also possible that a single-photon photolysis of the ring compound causes only one bond to be broken, producing a 1,6-biradical (Eq. (6)). Intramolecular scission of a terminal Si–Si bond would then yield the silylene and the five-membered ring (Eq. (7)). (A simple α cleavage pathway for the generation of dimethylsilylene from the 1,6 diradical was considered unlikely since it would be anticipated that the trisilanes would also yield silylenes via the same mechanism. In addition, a cleavage pathway has been found not to yield silylenes in the photolysis of polysilane polymers [10]).



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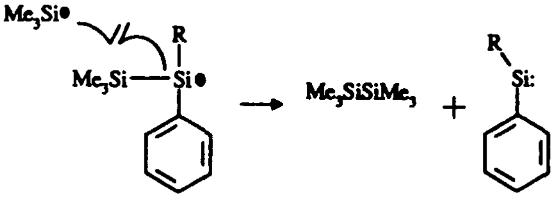

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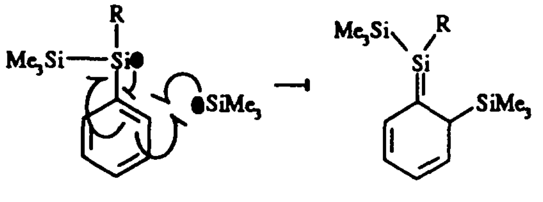

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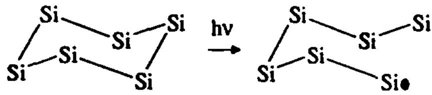

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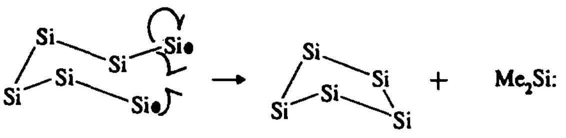

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5. Summary

The photochemistry of 2-aryltrisilanes in a molecular beam significantly differs from that in the condensed phase. Homolytic cleavage of only one silicon–silicon bond occurs in the gas phase, suggesting that the production of silylenes in solution or matrix may involve a further radical-pair reaction in a solvent or matrix cage. Further investigations of 2-aryltrisilanes are in progress, including especially the study of possible biradical reactions. A simple initial approach would involve laser photolysis very early in the gas expansion. At this point biradical collisional encounters are more likely, and subsequent product analysis might reveal the production of silylenes.

The gas-phase photolysis of dodecamethylcyclohexasilane, on the other hand, is similar to condensed-phase results in that dimethylsilylene is efficiently produced. If these results are generalized, photolysis of cyclopolysilane precursors should be a reliable method for producing a number of organosilylenes in the gas phase; either for intrinsic study or to carry out silylene reaction studies. Consequently, investigations are continuing for the gas-phase photolysis of other cyclopolysilanes.

Acknowledgement

The support of the Tulane University Chemistry department is gratefully acknowledged.

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