Oxidation of Methylsilenes with Molecular Oxygen. A Matrix Isolation Study

Martin Trommer,[†] Wolfram Sander,[*,†] and Andreas Patyk

Contribution from the Institut für Organische Chemie der Technischen Universität, Hagenring 30, D-38106 Braunschweig, Federal Republic of Germany
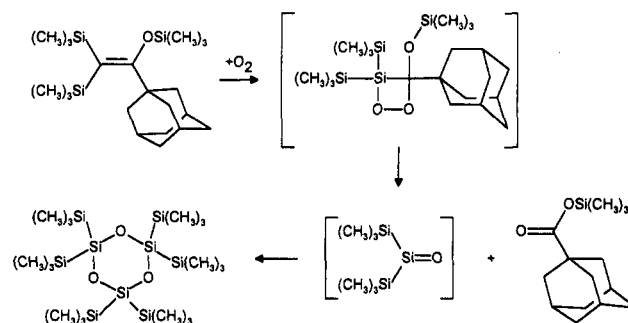
Received June 4, 1993[®]

Abstract: The photochemical and thermal oxidation of 1-methylsilene (2-silapropene) (**1a**), 1,1-dimethylsilene (**1b**), and 1,1,2-trimethylsilene (**1c**) has been investigated in O_2-doped argon matrices. All silenes **1** are easily photooxidized in matrices containing more than 1% O_2, but trimethylsilene (**1c**) is the only silene that exhibits thermal reactivity toward oxygen at temperatures as low as 20–40 K. The photochemical reactivity increases from **1a** to **1c** with increasing number of methyl groups at the double bond and decreasing ionization potential. Key intermediates in both the photochemical and the thermal oxidation of **1** are siladioxetanes **9**. These species are labile even in low-temperature matrices and could not be identified spectroscopically, but evidence comes from the observed oxidation products such as a complex between methylsilanone and formaldehyde **8a** and the formylsilanols **10**. An additional oxidation pathway is observed for **1c** with a methyl group at the C-atom of the silene moiety. Here, the primary adduct of **1c** and ${}^3O_2$, triplet-diradical T-**21c**, can either ring-close to give dioxetane **9c** and the products derived of it or produce dimethylvinylsilyl hydroperoxide (**22**) via H-abstraction from a methyl group.

Introduction

Since Gusel'nikov and Flowers presented experimental evidence for the existence of a silene,[1] compounds with silicon–carbon double bonds have drawn much attention. Matrix isolation was used for the first direct spectroscopic characterization of a silene,[2,3] and meanwhile several stable silenes have been characterized by X-ray crystallography.[4] The chemistry of silenes **1**, in particular cycloaddition reactions, has been thoroughly studied. Despite the interest in the chemistry of **1** and the ease of the oxidation of these compounds, the reaction with molecular oxygen has not yet been studied systematically.[4–6] In their 1985 review Raabe and Michl[6] state, "All known silenes react with molecular oxygen. This reaction is quite violent". Brook et al.[4a] described the oxidation of a stable silene as a "vigorous reaction in air with the formation of white smoke". In the reaction with dilute dry O_2 the corresponding carbonyl compound and the cyclic trimer of the silanone were formed, which indicates the intermediate formation of a siladioxetane (Scheme I). So far, direct spectroscopic evidence for the existence of a siladioxetane has not been presented.

The reaction of an olefin or silene with triplet oxygen (${}^3O_2$) to produce stable singlet products is formally spin-forbidden, and the question arises at which point along the reaction coordinate the intersystem crossing (ISC) occurs. While thermal reactions of olefins with singlet oxygen (${}^1O_2$) have been thoroughly studied, reactions with ${}^3O_2$ are in general slow radical chain reactions leading to allyl hydroperoxides, or combustion reactions at high

Scheme I

temperatures.[7] The oxidation of some electron-rich olefins,[8] such as tetramethylethylene[9] or tetramethylbutatriene,[10] was studied using matrix isolation spectroscopy. However, even in solid oxygen a thermal reaction was not observed and irradiation into charge-transfer absorptions of olefin–oxygen complexes was required to induce oxidation.

1a   **1b**   **1c**
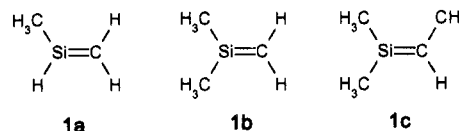
To gain some insight into oxidation mechanisms of unsaturated compounds, we investigated the thermal and photochemical reactions of 1-methylsilene (2-silapropene) (**1a**), 1,1-dimethylsilene (**1b**), and 1,1,2-trimethylsilene (**1c**) in oxygen-doped argon matrices at 10–40 K. Matrix IR spectra of these silenes have already been reported in the literature (for a review, see ref 6). Methylsilene **1a** was subjected to several matrix isolation studies by Michl et al.[11–14] and Maier et al.[15–17] An issue of special interest in these investigations was the thermal and photochemical

(1) Gusel'nikov, L. E.; Flowers, M. C. *Chem. Commun.* **1967**, 864.
(2) Chapman, O. L.; Chang, C. C.; Kolc, J.; Jung, M. E.; Lowe, J. A.; Barton, T. J.; Tumey, M. L. *J. Am. Chem. Soc.* **1976**, *98*, 7844–6.
(3) Chedekel, M. R.; Skoglund, M.; Kreeger, R. L.; Shechter, H. *J. Am. Chem. Soc.* **1976**, *98*, 7846–8.
(4) (a) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667–72. (b) Wiberg, N.; Wagner, G.; Müller, G. *Angew. Chem.* **1985**, *97*, 220–1.
(5) (a) Davidson, I. M. T.; Dean, C. E.; Lawrence, F. T. *J. Chem. Soc., Chem. Commun.* **1981**, 52–3. (b) *Organic Peroxides*; Ando, W., Ed.; Wiley: New York, 1992.
(6) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419–509.
(7) Houben-Weyl, Methoden der organischen Chemie. In *Organische Peroxo-Verbindungen*; Kropf, H., Ed.; Thieme: Stuttgart, 1988, Vol. E 13.

(8) Hashimoto, S.; Akimoto, H. *J. Phys. Chem.* **1987**, *91*, 1347–54.
(9) Hashimoto, S.; Akimoto, H. *J. Phys. Chem.* **1986**, *90*, 529–32.
(10) Sander, W.; Patyk, A. *Angew. Chem.* **1987**, *99*, 495; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 475–7.
(11) Drahnak, T. J.; Michl, J.; West, R. *J. Am. Chem. Soc.* **1979**, *101*, 5427–8.
(12) Drahnak, T. J.; Michl, J.; West, R. *J. Am. Chem. Soc.* **1981**, *103*, 1845–6.

equilibrium between **1a** and dimethylsilylene (**2**). A variety of methods have been reported for the synthesis of silene **1a** or silylene **2** (which rearranges to **1a** on irradiation with visible light), including photolysis of dodecamethylcyclohexasilane,[11,12,14] photolysis of dimethyldiazidosilane,[18,19] flash vacuum pyrolysis (FVP) of silabicyclo[2.2.2]octadienes,[16] and FVP of disilanes.[17] Matrix isolation of dimethylsilene (**1b**) by gas-phase pyrolysis of 1,1-dimethyl-1-silacyclobutane with subsequent trapping of the products in argon at 10 K was described independently by Gusel'nikov et al.[20] and Nefedov et al.[21] Trimethylsilene (**1c**) was the first silene that has been characterized spectroscopically. Chapman et al.[2] and Chedekel et al.[3] reported the synthesis and matrix isolation of **1c** by photolysis of (trimethylsilyl)diazomethane, while Mal'tsev et al.[22] used flash vacuum pyrolysis of the same precursor with subsequent trapping in a low-temperature matrix for the generation of the silene.

With increasing number of methyl groups at the Si=C double bond the electron density at the π-system increases. The vertical ionization potential IP_v of **1b** was determined by photoelectron spectroscopy to 8.0 eV.[23] Using this value to calibrate the semiempirical AM1[24] method, we estimate the ionization potentials of **1a** and **1c** to 8.3 and 7.6 eV, respectively. Thus, the reactivity toward oxygen is expected to increase considerably from **1a** to **1c**.
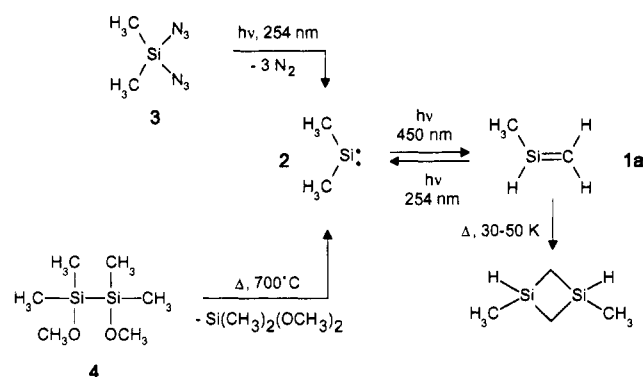
Results

General Procedure for the Oxidation of Silenes. All reactions were followed by IR spectroscopy, and the experiments were performed with both $^{16}O_2$ and $^{18}O_2$ to facilitate the assignment of spectra. Three different types of experiments were used to examine the oxidation of **1** in O_2-doped argon matrices:

(i) The thermal reactivity was probed by warming matrices from 10 up to 40 K. Silenes **1** were generated in matrices at 10 K either photochemically from diazo precursors or by gas-phase pyrolysis with subsequent trapping in argon. At 10 K diffusion of oxygen in solid argon is very slow and no reaction is observed after days, even if the reaction occurs without activation barrier in the gas phase or in solution. At temperatures above 30 K the diffusion of oxygen is rapid and oxidations controlled by diffusion (e.g. reactions of triplet carbenes and $^3O_2$) are complete within several minutes. Above 40 K the vapor pressures of argon and oxygen are too high and matrices evaporate rapidly.

(ii) Photooxidation was investigated by irradiation (starting at 600 nm and going stepwise to 250 nm) in O_2-doped argon matrices at 10 K. Diffusion of oxygen is negligible at 10 K, and only O_2 molecules which are trapped in the same matrix cage as the silenes can react. The photooxidation stopped after a certain degree of conversion, depending on the O_2 concentration. Generally with 1% O_2 only a small fraction of molecules were oxidized, while with 10% the reaction went to almost completion. Prolonged

(13) Arrington, C. A.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 6176–7.

(14) Arrington, C. A.; Klingensmith, K. A.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1984**, *106*, 525–30.

(15) Reisenauer, H. P.; Mihm, G.; Maier, G. *Angew. Chem.* **1982**, *94*, 864–5.

(16) Maier, G.; Mihm, G.; Reisenauer, H. P. *Chem. Ber.* **1984**, *117*, 2351–68.

(17) Maier, G.; Mihm, G.; Reisenauer, H. P.; Littmann, D. *Chem. Ber.* **1984**, *117*, 2369–81.

(18) Vancik, H.; Raabe, G.; Michalczyk, M. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1985**, *107*, 4097–8.

(19) Raabe, G.; Vancik, H.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 671–7.

(20) Gusel'nikov, L. E.; Volkova, V. V.; Avakyan, V. G.; Nametkin, N. S. *J. Organomet. Chem.* **1980**, *201*, 137–50.

(21) Nefedov, O. M.; Maltsev, A. K.; Khabashesku, V. N.; Korolev, V. A. *J. Organomet. Chem.* **1980**, *201*, 123–36.

(22) Maltsev, A. K.; Korolev, V. A.; Khabashesku, V. N.; Nefedov, O. M. *Dokl. Akad. Nauk SSSR* **1980**, *251*, 1166–8.

(23) Dyke, J. M.; Josland, G. D.; Lewis, R. A.; Morris, A. *J. Phys. Chem.* **1982**, *86*, 2913–6.

(24) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–9.
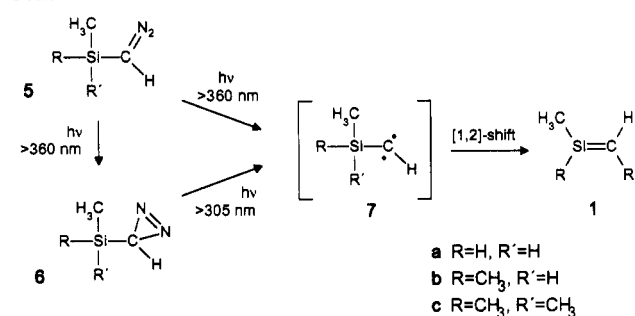
(25) Conlin, R. T.; Kwak, Y. W. *Organometallics* **1984**, *3*, 918–22.

Scheme II

irradiation did not lead to a higher degree of conversion in these bimolecular reactions. Diffusion of O_2 is not required for the oxidation when silenes **1** are generated in matrix cages containing oxygen. The oxygen is distributed statistically in the matrix, and at O_2 concentrations larger than 2% the chance is high that a silene molecule is produced in close proximity to an O_2 molecule. This leads to thermal oxidation products if the silenes **1** react thermally with O_2, or to photooxidation if the wavelength used for precursor photolysis also leads to photooxidation (which was true in most instances). Thus, investigation of the photooxidation of **1** with long-wavelength irradiation was only possible if the silene was produced by FVP with subsequent trapping in the matrix at 10 K.

(iii) A combination of both methods is the photooxidation at 30–35 K. In a first step silene **1** is produced by irradiation of the precursor at 10 K and characterized spectroscopically. The second step is irradiation at a different wavelength at 30–35 K, at which temperature oxygen diffuses rapidly (time scale of minutes), and thus a more complete photooxidation of **1** is achieved.

Matrix Isolation of Methylsilene (1a). The chemistry of **1a** is complicated by the thermal interconversion between **1a** and silylene **2** in the gas phase at high temperatures[16,25,26] and the photochemical interconversion of these species under the conditions of matrix isolation.[13,17] Thus, most precursors produce mixtures of **1a** and **2**, and subsequent visible light irradiation (λ = 450 nm) has to be used to obtain mainly **1a**.[17] The oxidation of **2** has been described elsewhere.[27]

Matrix isolation of silene **1a** in oxygen-doped argon matrices was achieved by three independent routes:

(i) Irradiation (λ > 240 nm, Ar/O_2, 10 K) of dimethyldiazidosilane (**3**) in 0.25–1% O_2-doped argon matrices produced dimethylsilylene (**2**), which was converted to **1a** by irradiation with λ = 450 nm (Scheme II). This route was used to investigate the oxidation of **2**,[27] but is less suitable for the oxidation of **1a**. The major disadvantage is the short-wavelength irradiation required to produce **2**, which leads to local heating of the matrix and rapid diffusion of trapped O_2. As a result, at higher O_2 concentrations than 1%—which are necessary to induce the photooxidation of silene **1a**—the yield of **1a** was already too low for spectroscopic characterization after precursor photolysis and only oxidation products of **1a** and **2** were observed.

(ii) FVP (650–700 °C) of 1,2-dimethoxytetramethyldisilane (**4**) and subsequent trapping in O_2-doped matrices gave mixtures of **1a** and **2** (Scheme II). The disadvantage of this method is that large amounts of dimethyldimethoxysilane, other thermolysis products from **4**, and unreacted **4** are trapped in the matrix. IR absorptions of these fragments overlap with those of **1a** and its oxidation products. FVP of **4** in the presence of oxygen in the hot zone revealed that **2** is efficiently trapped in the gas phase to produce dimethyldioxasilirane, while **1a** is much less reactive

(26) Conlin, R. T.; Kwak, Y. W. *J. Am. Chem. Soc.* **1986**, *108*, 834–5.

(27) Patyk, A.; Sander, W.; Gauss, J.; Cremer, D. *Angew. Chem.* **1989**, *101*, 920–22; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 898–900.

(28) Häser, M.; Ahlrichs, R. *J. Comput. Chem.* **1989**, *10*, 104.

Scheme III

a R=H, R'=H

b R=CH₃, R'=H

c R=CH₃, R'=CH₃

toward O_2.[27] With this method it was possible to trap **1a** in matrices doped with up to 10% O_2.

(iii) Irradiation ($\lambda > 360$ nm, Ar/O_2, 10 K) of (methylsilyl)-diazomethane (**5a**) yielded a mixture of **1a** and (methylsilyl)-diazirine (**6a**), but no **2** (Scheme III). Photolysis ($\lambda > 305$ nm) of diazirine **6a** (or diazomethane **5a**) produced **1a** in a clean reaction. Presumably, this reaction proceeds via carbene **7a**, which is too short-lived to be observed even under the conditions of matrix isolation. In 10% O_2-doped argon matrices irradiation of **5a** gave silene **1a** in amounts still large enough to be easily detected, although large quantities of oxidation products were formed as well. Method iii proved to be most convenient to investigate the thermal and photochemical reactivity of **1a** toward $^3O_2$.

Silene **1a** produced by all three methods was characterized by comparison of matrix IR and UV–vis spectra with that reported in the literature.[11–17]

Oxidation of Methylsilene (1a). Mixtures of **1a** and **2**, generated by the pyrolytic route (ii), were trapped in argon or O_2-doped argon at 10 K. Annealing of these matrices for 12 h at 35 K, 1 h at 42 K, or several seconds at 50 K (at this temperature argon rapidly evaporates) produced only dimethyldioxasilirane,[27] the O_2 adduct of **2**, and 1,3-dimethyl-1,3-disilacyclobutane, the dimer of **1a**. The latter compound was identified by comparison with the data reported by Michl et al.[12] A thermal reaction of **1a** and O_2 was not observed under these conditions, which reveals that silene **1a** is less reactive toward O_2 than silylene **2**.
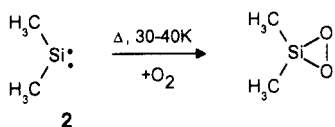
Irradiation of matrices containing **1a** and 10% O_2 with yellow light ($\lambda = 575 \pm 21$ nm, 10 K) gave within 30 min approximately 30% conversion of **1a** to an oxidation product **8a**. Under these conditions neither **1a** nor O_2 absorb light, and thus we assume that excitation occurs via a charge-transfer transition of a silene–oxygen complex. The yield of **8a** did not increase after prolonged irradiation, and in matrices doped with less than 5% O_2 no photooxidation was observed. The oxidation product **8a** exhibited characteristic absorptions at 2125 cm⁻¹, assigned to a Si–H stretching mode, at 1640 cm⁻¹, which was red-shifted by 29 cm⁻¹ on ¹⁸O labeling, assigned to a carbonyl absorption, and at 1159 cm⁻¹, again exhibiting a large isotopic red-shift of 38 cm⁻¹ and assigned to a Si–O stretching mode (Table I, Figure 1). On the basis of these IR data, the subsequent photochemistry observed (vide infra), and AM1[24] and ab initio[28,29] calculations of the vibrational spectrum, **8a** was tentatively assigned the structure of a complex between formaldehyde and methylsilanone. Compared to matrix-isolated formaldehyde ($\nu_{C=O} = 1738, 1742$ cm⁻¹)[30] and methylsilanone ($\nu_{Si=O} = 1209.6$ cm⁻¹),[31] the C=O and Si=O

(29) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *93*, 165–9.

(30) Harvey, K. B.; Ogilvie, J. F. *Can. J. Chem.* **1962**, *40*, 85–91.

(31) Withnall, R.; Andrews, L. *J. Am. Chem. Soc.* **1986**, *108*, 8118–9.

(32) Sander, W. *Angew. Chem.* **1990**, *102*, 362–72; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 344–54.

stretching modes in **8a** are considerably red-shifted by approximately 100 and 49 cm⁻¹, respectively.

These observations are in good agreement with semiempirical and ab initio calculations. According to AM1 and ab initio calculations (RHF 6-31G(d,p) basis set), complex **8a** is stabilized relative to noncomplexed formaldehyde and methylsilanone by 9.8 and 25.8 kcal/mol, respectively. The results of the ab initio calculations can be summarized as follows (only the 6-31G(d,p) results are given; the AM1 geometry is similar): The structure of **8a** is described best as a $H_2C=O$ molecule sitting on top of the plane defined by the heavy atoms of $(CH_3)HSi=O$ (Figure 2). The carbonyl oxygen atom is coordinated to the silicon atom (200-pm distance), and one of the hydrogen atoms of the aldehyde is coordinated to the silanone oxygen atom (215.4-pm distance). Compared to the noncomplexed molecules, the C=O bond of the aldehyde is lengthened from 121.1 to 123.3 pm, and the Si=O bond of the silanone from 157.5 to 160.2 pm. This results in red-shifts of $\nu_{C=O}$ and $\nu_{Si=O}$ by 100 and 68 cm⁻¹ (wavenumbers scaled by 0.9), respectively, quite close to the experimental values (100 and 49 cm⁻¹) (Table I).

The formation of **8a** is rationalized by cleavage of 3-methyl-3-sila-1,2-dioxetane (**9a**), which is the primary adduct of **1a** and O_2, but not observed under the reaction conditions (Scheme IV). **8a** is photolabile and readily converted to formylmethylsilanol (**10a**) on irradiation with green light ($\lambda = 480 \pm 22$ nm) (Figure 1). In the IR spectrum the characteristic stretching modes expected for **10a** are easily identified: O–H at 3656, C–H (aldehyde) at 2664, Si–H at 2133, and C=O at 1657 cm⁻¹ (Table II). Trimethylformylsilane (**16**) was matrix-isolated as a reference and exhibited C–H (aldehyde) and C=O stretching modes at 2624 and 1662 cm⁻¹, respectively.

Silanol **10a** was also obtained when diazo compound **5a** was irradiated in O_2-doped matrices (route iii, Figure 3). Because irradiation at $\lambda = 360$ or 305 nm was required to cleave **5a**, the primary product **8a** was not observed under these conditions. The relative yields of **10a** and **1a** depended on the O_2 concentration: with 5% O_2 **10a** was the major product, while with 1% O_2 mainly **1a** was obtained.

At high O_2 concentrations (>5%) two further products, methylsilyl formate (**13a**) (Scheme V) and hydroxymethylsilyl peroxyformate (**14a**) (Scheme VI), were formed. Formate **13a** was characterized by comparison with an authentic matrix-isolated sample, while the assignment of **14a** is tentative and based on the IR spectra and its subsequent photochemistry. Compounds **13a** and **14a** were not directly produced by the oxidation of silene **1a**. Formate **13a** was produced in >5% O_2-doped matrices during irradiation ($\lambda > 305$ nm) of diazomethane **5a** or diazirine **6a**, while the other precursors (**3** and **4**) did not yield **13a**. At O_2 concentrations of less than 10% the yield dropped drastically. Thus, **13a** is most likely a trapping product of carbene **7a** (Scheme V). The carbene is too short-lived to be observed spectroscopically, but can be trapped in the presence of high O_2 concentrations. Carbonyl O-oxide **11a** and dioxirane **12a**, which we propose as intermediates in the transformation of **7a** to **13a**, are both expected to be photolabile[32] and thus not observed under the reaction conditions.

Peroxide **14a** is the product of the photooxidation ($\lambda > 335$ nm) of **10a** (Figure 3). Irradiation of **10a** produces pairs of formyl and hydroxymethylsilyl radicals (Norrish Type I cleavage[33]) in a matrix cage, which rapidly recombine to **10a** in the absence of a trapping agent (Scheme VI). In the presence of O_2 in the matrix cage the radical pair is trapped to give peroxide **14a**. This requires a high O_2 content of the matrix (>5%). At lower O_2 concentrations photooxidation of **10a** was only observed if the matrix was annealed at 30–35 K during photolysis to allow diffusion of O_2. Peroxide **14a** is stable toward 335-nm irradiation, but short-wavelength UV irradiation ($\lambda > 280$ nm) produced

(33) Brook, A. G.; Dillon, P. J.; Pearce, R. *Can. J. Chem.* **1971**, *49*, 133–5.

(34) Durig, J. R.; Sullivan, J. F.; Qtaitat, M. A. *J. Mol. Struct.* **1991**, *243*, 239–73.

Table I. IR Spectroscopic Data of Complex **8a**, Matrix-Isolated in Argon at 10 K

8a, argon, 10 K			$(CH_3)HSi=O^a$		$H_2C=O^b$		$6\text{-}31G(d,p)^c$			
ν, cm⁻¹	I, %ᵈ	ν_i/ν^e	ν, cm⁻¹	ν_i/ν^e	ν, cm⁻¹	I, %ᵈ	N^f	ν, cm⁻¹	I, %ᵈ	assignmentᵍ
					2862	s	30	2869.1	11	
					2796	vs	29	2836	7	
2125.2	42.9	1.0					28	2005.6	100	Si–H str
1640.2	42.9	0.982			1742	vs	27	1586.5	97	C=O str
1433.8	57.1	0.994					24	1411.9	43	
1252.1	100	1.0					23	1271.7	17	
1159.0	42.9	0.967	1207.6	0.964			20	1010.2	96.2	Si=O str
923.8	28.6						19	864	13	
898.2	42.9						18	810.3	53	
748.7	35.7	0.997					17	732.2	59	
							16	680.6	25	

ᵃ Methylsilanone; only selected absorptions are listed; ref 32. ᵇ Formaldehyde; only selected absorptions are listed. ᶜ Ab initio calculations on the RHF level using a 6-31G(d,p) basis set. Frequencies are scaled by 0.9. ᵈ Relative intensity. ᵉ Ratio of $^{18}O/^{16}O$ isotopic frequencies. ᶠ Number of calculated vibration. The assignment is based on band positions and relative intensities and is only tentative. ᵍ Approximate description.
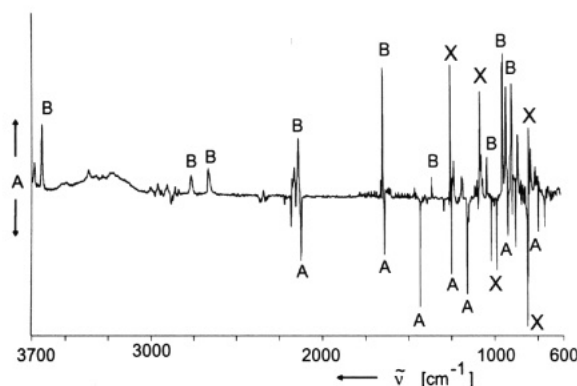

Figure 1. IR difference spectrum showing changes on irradiation ($\lambda = 480$ nm, argon, 10 K) of matrix-isolated complex **8a**: bottom part, bands disappearing; top part, bands appearing on irradiation; A, bands assigned to **8a**; B, bands assigned to **10a**; ×, artifact due to incomplete subtraction of strong bands.

CO_2 and a further product with O–H stretching modes at 3706, 3699, and 3694 cm⁻¹ (all three bands are red-shifted by 11 cm⁻¹ on ^{18}O-labeling), which was tentatively assigned to methylsilanediol (**15a**). The carbonyl absorption of **14a** was found at 1776 cm⁻¹ and exhibits a red-shift of 39 cm⁻¹ on ^{18}O-labeling. When a 1:1 mixture of $^{18}O_2$ and $^{16}O_2$ was used for the photooxidation, the three isotopomers $C^{18}O_2$, $C^{18}O^{16}O$, and $C^{16}O_2$ were produced in a ratio of 1:2:1. This indicates that two molecules of oxygen are involved in the production of carbon dioxide, in accordance with the proposed mechanism (Scheme VI).

Further confirmation for the Norrish Type I cleavage in formylsilanes stems from the investigation of the analogous photooxidation of trimethylformylsilane (**16**). Irradiation ($\lambda = 345$ nm) of **16** in 5% O_2-doped argon matrices produced trimethylsilyl peroxyformate (**17**) (Scheme VI), which decomposed to CO_2 and trimethylsilanol on shorter-wavelength irradiation ($\lambda > 280$ nm). In the absence of oxygen trimethylformylsilane proved to be photostable. If $^{18}O_2$ was used for the oxidation of **16**, $C^{18}O^{16}O$ was formed exclusively, which proves that one of the oxygen atoms in CO_2 comes from the aldehyde oxygen atom. Irradiation ($\lambda > 335$ nm) of **16** in a 5% HCl-doped argon matrix produced trimethylchlorosilane and formaldehyde.

Matrix Isolation and Oxidation of Dimethylsilene (1b). Silene **1b** was produced—in analogy to **1a** (route iii)—by irradiation ($\lambda > 345$ nm, 10 K) of (dimethylsilyl)diazomethane (**5b**) (Scheme III). Both loss of nitrogen with subsequent (1,2)-H shift to give silene **1b** and rearrangement to diazirine **6b** was observed with $\lambda > 345$ nm irradiation. With $\lambda > 305$ nm irradiation **1b** was formed in a very clean reaction. The IR spectrum of **1b** obtained by this method was in good agreement with those generated by thermolysis of silacyclobutanes.[20,21]

In O_2-doped argon matrices the chemistry of **1b** was similar to that of **1a** (Schemes IV–VI). The major difference was that
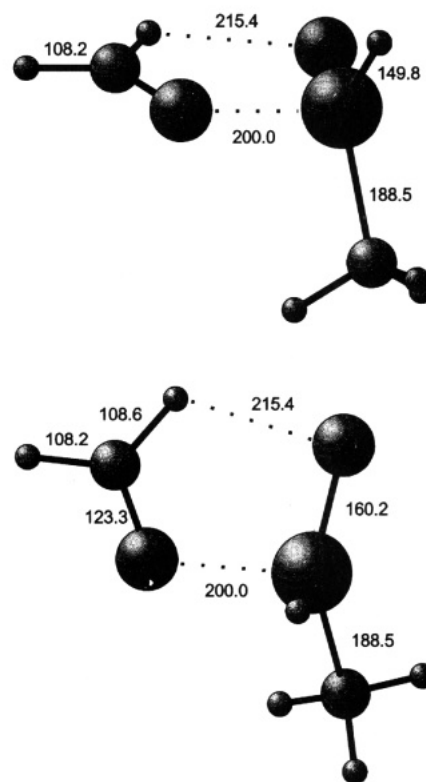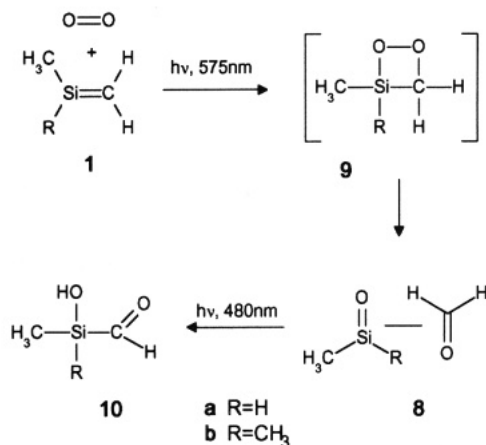

Figure 2. Ab initio optimized structure of the formaldehyde–methylsilanone complex **8a** using the RHF/6-31g(d,p) basis set. Selected bond lengths in picometers.

Scheme IV

photooxidation of **1b** occurred at lower O_2 concentrations and more rapidly compared to that of **1a**. Thus, in contrast to **1a**, silene **1b** was completely oxidized in 10% O_2-doped matrices after

Table II. IR Spectroscopic Data of Methylformylsilanol (**10a**), Matrix-Isolated in Argon at 10 K

10a, argon, 10 K			$(CH_3)_3SiCHO^a$		10a, 6-31G(d,p)^b			
ν, cm⁻¹	I, %^{c}	ν_i/ν^d	ν, cm⁻¹	I, %^{d}	N^e	ν, cm⁻¹	I, %^{d}	assignment^f
3656.4	34.8	0.997			33	3649.7	62	
3645.7	15.2	0.997						O–H str
2768.4	4.5	0.996	2751.5	12	30	2838.0	10	
2760.7	3.0							
2664.1	9.1	0.998	2622	39	29	2776.7	52	aldehyde
2654.3	4.5							C–H str
2133.4	47.0	1.0			28	2018.5	80	Si–H str
1656.9	40.9	0.977	1661.2	88	27	1618.2	59	C=O str
1655.1	28.8							
1258.2	50.0	0.997	1252.1	87	23	1280.1	15	
940.3	50.0				22	898.7	79	
909.4	100	0.990	880.3	69	21	877	19	
867.8	66.7	1.0	864.8	100	20	858.9	100	
748.2	33.3	1.0	765.4	15	18	739.1	93	
			711.7	29	17	719.5	18	

^{a} Trimethylformylsilane; only selected absorptions are listed. ^{b} Ab initio calculations on the RHF level using a 6-31G(d,p) basis set. Frequencies are scaled by 0.9. ^{c} Relative intensity. ^{d} Ratio of $^{18}O/^{16}O$ isotopic frequencies. ^{e} Number of calculated vibration. The assignment is based on band positions and relative intensities and is only tentative. ^{f} Approximate description.
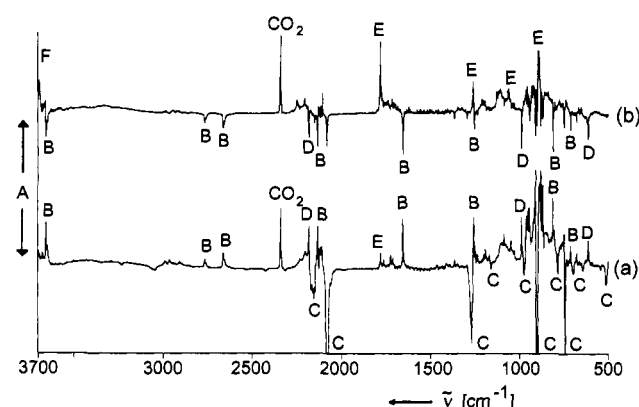

Figure 3. IR difference spectra showing the oxidation of **5a** and subsequent photochemistry: (a) bottom part, bands disappearing, and top part, bands appearing on irradiation of **5a** ($\lambda \geq 320$ nm) in a 5% O₂-doped argon matrix at 10 K; (b) bottom part, bands disappearing, and top part, bands appearing on irradiation ($\lambda \geq 335$ nm) in a 5% O₂-doped argon matrix at 35 K; C, bands assigned to **5a**; B, bands assigned to **10a**; D, bands assigned to **1a**; E, bands assigned to **14a**; F, band assigned to methylsilanediol (**15a**).

irradiation of the precursor. At lower O₂ concentrations formylsilanol **10b** was the major product (Scheme IV, Table III, Figure 4), while at higher O₂ concentrations in addition formate **13b** (Scheme V) and silyl peroxyformate **14b** (Scheme VI) were produced. When the temperature in 5% O₂-doped matrices was kept at 30–35 K during photolysis to allow diffusion, the photooxidation of **1b** could be directly observed. A complex of dimethylsilanol and formaldehyde (**8b**) was not observed, which is in accordance with the expected lability of **8b** under the irradiation conditions required for photolysis of the precursor **5b**.

Matrix Isolation and Oxidation of Trimethylsilene (1c). For the synthesis of silene **1c** the method described by Chapman et al.[2] and Chedekel et al.[3] was used. Irradiation ($\lambda > 360$ nm, 10 K) of (trimethylsilyl)diazomethane (**5c**) yielded diazirine **6c** and silene **1c** (Scheme III). Short-wavelength irradiation ($\lambda > 300$ nm) resulted in complete photolysis of **5c** and **6c** and the formation of **1c** in high yields. Under these conditions the (1,2)-shift of the methyl group was rapid, and attempts to trap carbene **7c** by annealing matrices doped with 1% CO or O₂ failed. At high O₂ concentrations (>5%) formate **13c** was formed during photolysis of **5c**, again indicating that carbenes **7** are at least long-lived enough to be trapped by oxygen molecules in close proximity to the carbene center.

Warming of argon matrices containing **1c** from 10 to 25 K produced peculiar irreversible shifts of several IR absorptions assigned to **1c**, which has not been described previously. These

shifts of up to 20 cm⁻¹ (e.g. the absorption at 1116 cm⁻¹ is shifted to 1099 cm⁻¹) were reproducible in several experiments. A similar phenomenon was observed in nitrogen, but not in xenon matrices. A reasonable explanation is the formation of a geometrically distorted silene **1c** after the methyl shift at 10 K in solid argon or nitrogen. Annealing at higher temperatures leads to the "relaxed" silene, while in xenon, with larger matrix cavities, annealing is not required.
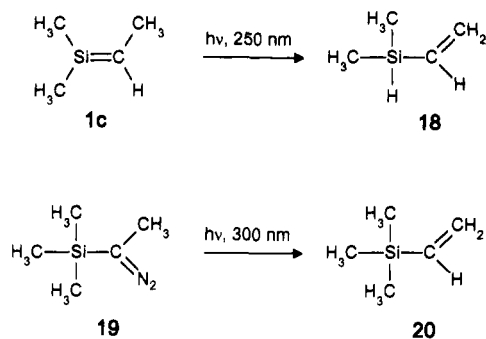

Silene **1c** was stable at $\lambda > 300$ nm irradiation, but rearranged slowly to dimethylvinylsilane (**18**) at $\lambda > 250$ nm irradiation (mercury high-pressure arc lamp and quartz optics). **18** exhibits a strong Si–H stretching vibration, split to several components, at 2132, 2125, and 2116 cm⁻¹. Comparison with IR data of methylvinylsilane[34] and trimethylvinylsilane (**20**) (synthesized in an argon matrix by irradiation of (trimethylsilyl)diazoethane (**19**)) revealed the similarity of the vinylsilanes.

Silene **1c** could also be produced in 0.1–5% O₂-doped argon matrices. The best results were obtained with 0.5–1% O₂. At higher O₂ concentrations mainly products of the photooxidation of **5c** were formed, while at lower O₂ concentrations dimerization of **1c** to produce 1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutane[2,22] was more efficient than the thermal reaction with O₂. Warming of these matrices from 10 to 25 K resulted in a slow oxidation, at 40 K in a rapid oxidation, of **1c** and the formation of two major products (Figure 5). In a typical experiment (0.8% O₂) 35% of silene **1c** was oxidized after 40 min. The oxidation products were identified as dimethylvinylsilyl hydroperoxide (**22**) and dimethyl-(vinyloxy)silanol (**23**) (Scheme VII). The relative yields of **22** and **23** were dependent on the matrix temperature at which the oxidation was carried out. Below 30 K **23** was the major product, while above 30 K mainly **22** was formed.

Hydroperoxide **22** exhibits the O–H stretching mode at 3570–3585 cm⁻¹ (split into four absorptions by matrix site effects or by the presence of several conformers), which is red-shifted by

(35) Blaschette, A.; Bressel, B. *Inorg. Nucl. Chem. Lett.* **1968**, *4*, 175–8.
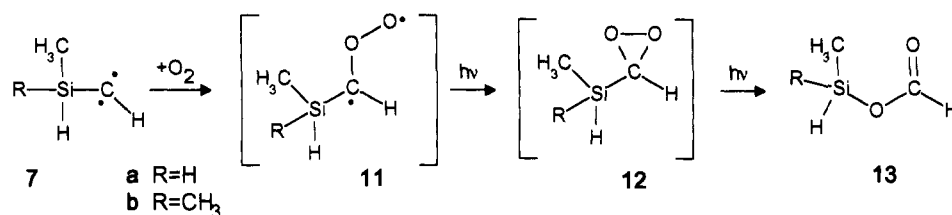
Scheme V

Scheme VI
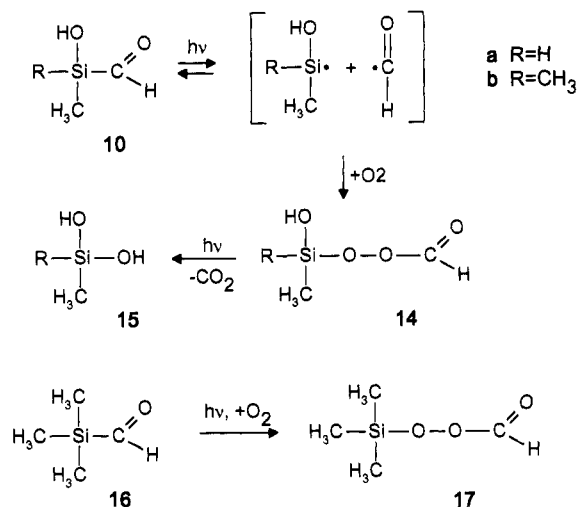
11 cm^{-1} on ^{18}O-labeling (Table IV). Matrix-isolated dimethylvinylsilanol (24) and neat trimethylsilyl hydroperoxide (25)[35] were used as reference compounds for the characterization of 22. The O–H stretching vibration of 22 was found at significantly lower frequency than that of silanol 24 (3703–3709 cm^{-1}, argon, 10 K), but is close to the O–H stretching vibration of unassociated hydroperoxide 25 (3565 cm^{-1}).[35] A strong absorption at 900 cm^{-1} with an ^{18}O isotopic shift of 30 cm^{-1} was assigned to the O–O stetching vibration, which is in excellent agreement with that reported for 25 (900 cm^{-1}).[35,36]
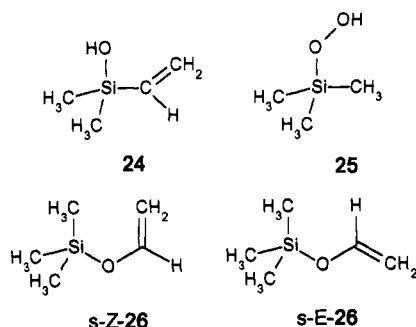
The O–H stretching vibration of silanol 23 was found at 3700 cm^{-1} (at considerably higher frequency than 22, Table V). The most intense absorption at 1203 cm^{-1} exhibited a large red-shift on ^{18}O-labeling and was assigned to the C–O stretching vibration. The characterization of 23 was confirmed by comparison with (s-Z)- and (s-E)-trimethyl(vinyloxy)silane ((s-Z-26 and (s-E)-26),[37,38] which reveals that 23 is formed in the s-Z conformation as shown in Scheme VII.

Discussion

Silenes 1a–c are well suited for the investigation of the oxidation of electron-rich olefins. Silenes 1 are produced in very clean

(36) Bressel, B. Diplomarbeit, Technische Universität Braunschweig, 1967.
(37) Dedier, J.; Marchand, A.; Forel, M. T.; Frainnet, E. *J. Organomet. Chem.* **1974**, *81*, 161–75.
(38) Dédier, J.; Marchand, A. *Spectrochim. Acta, Part A*, **1982**, *38*, 339–49.
(39) Dewar, M. J. S. *QCPE* **1990**, *506*.

reactions from carbenes 7 via hydrogen (1a and 1b) and methyl shifts (1c), respectively (Scheme III). These rearrangements are rapid under the conditions necessary for the photolysis of 5, and thus carbenes 7 could not be observed directly. Indirect evidence for 7a and 7b stems from oxygen trapping at high O$_2$ concentrations (>5%), leading to 13a and 13b (Scheme V).

As expected from the estimated ionization potentials, the reactivity of 1 toward oxygen increases with increasing number of methyl groups at the double bond. Silenes 1a and 1b are thermally stable in O$_2$-doped matrices, while 1c is easily oxidized under the same conditions. The thermal reaction of 1c and ^{3}O$_2$ at temperatures as low as 25–40 K is expected to produce triplet-diradical T-21c as the primary adduct. In the photooxidation of 1a and 1b ISC could also occur in the excited states of 1 to produce T-1 followed by the spin-allowed formation of singlet oxidation products in the reaction with ^{3}O$_2$. The singlet–triplet splitting in 21 is estimated (and also calculated by AM1) to be small, and thus ISC can easily occur in this species. Ring-closure of S-21 eventually leads to siladioxetane 9. Although we were not able to directly observe diradicals 21 or dioxetanes 9 by spectroscopic methods, the formation of oxidation products such as 8, 10, 22, or 23 strongly suggests the intermediacy of these labile species. Indirect evidence for the formation of 21 is the production of 22 in the oxidation of 1c (Scheme VII). If ISC in T-21 is slow enough, H-abstraction on the triplet surface can efficiently compete with ring-closure to 9c (via S-21).

Dioxetanes 9a and 9b are unstable under the photolytic conditions required to induce photooxidation of 1a and 1b, respectively. 1c is oxidized thermally, and thus 9c must be thermally labile, as well. Whether the excess energy produced in the exothermic formation of 9c leads to the fragmentation (hot reaction in the matrix) or 9c (and other siladioxetanes 9) is intrinsically unstable cannot be decided by our experiments. Fragmentation of 9 leads to the formation of a silanone and an aldehyde in the same matrix cage, which produce after reorientation complex 8. The formation of 8 is highly exothermic, despite the formation of a silanone. This complex could—for experimental reasons—only be observed in the case of 8a. Semiempirical AM1 as well as ab initio calculations reveal a substantial stabilization of this complex compared to the non-complexed components. According to these calculations, the complex has an interesting structure with a nearly planar five-membered ring consisting of the Si–O bond of the silanone and the H–C–O atoms of formaldehyde (Figure 2). The calculated "nonbonding" Si–O distance between the Si-atom and the formaldehyde O-atom is only 2 Å and thus only 15% larger than a covalent Si–O bond. This strong stabilizing interaction is reflected in the observed large IR shifts of the C=O and Si=O stretching modes. The formation of 8a from dioxetane 9a requires the reorientation of either the silanone or the formaldehyde molecule, which is driven by the strong dipole–dipole interaction between these two molecules after their formation in the "wrong" orientation.

The photochemical rearrangement of complex 8 to silyl aldehyde 10 requires transfer of a hydrogen atom from the aldehyde to the silanone oxygen, followed by bond formation between the two radical centers at the silicon and carbon atoms.

(40) Martin, M. *Synth. Commun.* **1983**, *13*, 809–11.

Table III. IR Spectroscopic Data of Dimethylformylsilanol (**10b**), Matrix-Isolated in Argon at 10 K

10b, argon, 10 K			(CH₃)₃SiCHOᵃ		10b, 6-31G(d,p)ᵇ			
ν, cm⁻¹	I, %ᶜ	ν_i/ν^d	ν, cm⁻¹	I, %ᶜ	Nᵉ	ν, cm⁻¹	I, %ᶜ	assignmentᶠ
3660.2	52	0.997			42	3648.3	63	O–H str
3651.2	26	0.997						O–H str
3645.9	24	0.997						O–H str
2764.2	10	0.995	2751.5	12	37	2834.3	11	
					36	2833.1	13	
2658.9	11	0.997	2622	39	35	2762.3	56	aldehyde
2653.7	22							C–H str
1655.0	47	0.978	1662	88	34	1617.8	59	C=O str
			1287.9	6	28	1279	11	
1258.8	100	1.0	1252.1	87	27	1275	25	
1051.3	62	0.983			26	891.3	26	
952.2	84	0.976	880.3	69	25	879.3	37	
941.6	96							
868.8	67		864.7	100	24	861.5	81	
805.7	66	1.0	826.9	26	23	829.3	14	
			711.7	29	21	729.5	100	
			702.7	11	19	677.3	18	
547.8	10	0.984	585.7	14	17	569.9	12	

ᵃ Trimethylformylsilane; only selected absorptions are listed. ᵇ Ab initio calculations on the RHF level using a 6-31G(d,p) basis set. Frequencies are scaled by 0.9. ᶜ Relative intensity. ᵈ Ratio of ¹⁸O/¹⁶O isotopic frequencies. ᵉ Number of calculated vibration. The assignment is based on band positions and relative intensities and is only tentative. ᶠ Approximate description.
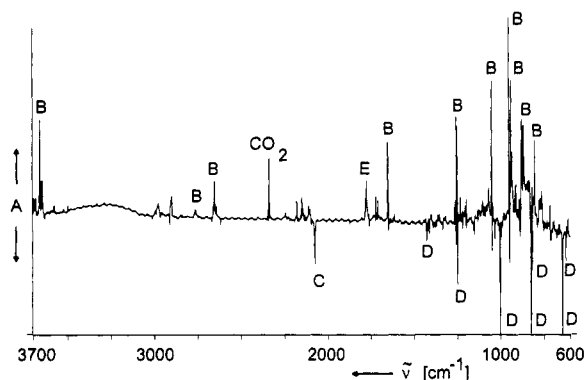

Figure 4. IR difference spectrum showing the photooxidation ($\lambda \geq 335$ nm) of silene **1b** in a 1.0% O₂-doped argon matrix at 35 K: bottom part, bands disappearing; top part, bands appearing on irradiation of **1b**; D, bands assigned to **1b**; B, bands assigned to **10b**; C, band assigned to **5b**; E, band assigned to **14b** (photooxidation product of **10b**).
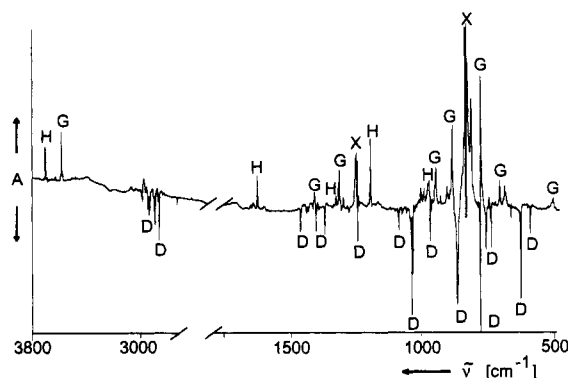

Figure 5. IR difference spectrum showing the oxidation of silene **1c** in a 1.0% O₂-doped argon matrix at 35 K: bottom part, bands disappearing; top part, bands appearing during annealing the matrix within 1 h; D, bands assigned to **1c**; G, bands assigned to **22**; H, bands assigned to **23**; X, artifact of bands which do not completely subtract, mainly assigned to a contamination of hexamethyldisiloxane.

In the case of **8c** the H-atom is abstracted from the methyl group of acetaldehyde. This leads to an oxallyl radical, which produces the very stable silanol **23** by the formation of a new bond between oxygen and silicon. We therefore conclude that siladioxetanes **9** as well as silanone–aldehyde complexes **8** play a key role in the oxidation of silenes **1**.

Experimental Section

Calculations. The ab initio calculations were carried out using TURBOMOLE[28,29] and standard basis sets. MOPAC (version 6)[39] was used for the semiempirical AM1[24] calculations.

Materials and General Methods. ¹H- and ¹³C-NMR spectra were taken at 400.1 and 100.6 MHz, respectively (Bruker AM 400), in CDCl₃ as solvent, except where noted, with (CH₃)₄Si as internal standard. Mass spectra (EI, 70 eV) were taken on a Varian MAT CH7 or MAT 8222. All reactions involving moisture-sensitive silicon reactants were performed under an atmosphere of dry nitrogen or argon. Prior to matrix isolation volatile compounds— including all silyldiazomethanes—were purified by preparative scale GLC using a Shimadzu GC-8a gas chromatograph with a 6-m SE54 column.

Methylsilyl Trifluoromethanesulfonate (Methylsilyl Triflate). The triflate was prepared in analogy to a procedure by Bassindale and Stout[41] for the synthesis of dimethylsilyl triflate. Trifluoromethanesulfonic acid (1 equiv) was added dropwise to neat phenylmethylsilane at room temperature. The crude mixture was used for the synthesis of (methylsilyl)diazomethane (**5a**) and methylsilyl formate (**13a**) without purification. ¹H-NMR (CDCl₃, 400 MHz): δ = 0.67 (t, 3H, J = 3.45 Hz), 4.92 (q, 2H, J = 3.44 Hz).

(Methylsilyl)diazomethane (5a). **5a** was synthesized in analogy to a procedure by Martin[40] for the synthesis of (trimethylsilyl)diazomethane. Freshly prepared methylsilyl triflate (17.02 mmol, 3.31 g) diluted in 10 mL of dry ether was added dropwise to equimolar quantities of diazomethane (17.02 mmol, 0.72 g in 70 mL of diethyl ether) and ethyldiisopropylamine (17.6 mmol, 3 mL) at –78 °C. After complete addition the mixture was allowed to warm to room temperature within 1 h. After filtration the yellow solution was carefully concentrated by distillation (bath temperature below 60 °C). The remaining mixture was purified by preparative GLC (45 °C, det./inj. 100 °C). **5a** was obtained in 23% yield (GC) as a yellow oil. ¹H-NMR (CDCl₃, 400 MHz): δ = 0.28 (t, 3H, J = 4.04 Hz), 2.65 (t, 1H, J = 2.20 Hz), 4.19 (dq, 2H, J = 4.02, 2.27 Hz). ¹³C-NMR (CDCl₃, 100 MHz): δ = –7.73, 20.47. MS m/e (rel int): 86 (M⁺, 74), 71 (18). IR (Ar, 10 K): 3229.3 (1), 3042.1 (1), 2422.2 (3), 2174.7 (6), 2163.6 (6), 2150.9 (21), 2148.3 (17), 2141.6 (6), 2127.6 (15), 2080.1 (100), 1278.6 (5), 1270.1 (17), 1256.5 (7), 965.2 (4), 953.4 (11), 936.8 (5), 927.5 (6), 897.4 (100), 864.5 (6), 783.0 (4), 743.0 (14), 728.5 (4), 697.9 (3), 644.6 (2), 516.4 (3), 513.0 (4), 506.7 (4), 487.7 (1), 467.2 (1) cm⁻¹ (rel int). HRMS calcd for C₂H₆N₂Si, 80.030 027; found 80.0300 ± 2 ppm.

Methylsilyl Formate (13a). A mixture of dry pyridine (17.1 mmol, 1.38 mL), formic acid (17.0 mmol, 0.64 mL), and 35 mL of dry toluene was cooled to –70 °C. After dropwise addition of methylsilyl triflate (17.0 mmol, 3.31 g) in 10 mL of toluene the mixture was allowed to warm up. The pyridinium salt was removed by filtration and washed with dry

(41) Bassindale, A. R.; Stout, T. *J. Organomet. Chem.* **1984**, *271*, C1-C3.
(42) Linderman, R. J.; Suhr, Y. *J. Org. Chem.* **1988**, *53*, 1569–72.
(43) (a) Harris, G. I. *J. Chem. Soc.* **1963**, 5978–82. (b) Harris, G. I. *J. Chem. Soc. B* **1970**, 492–6.
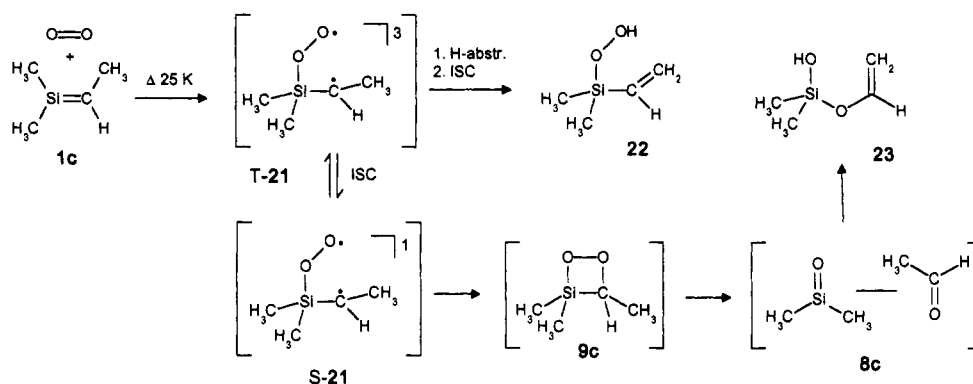
Scheme VII

Table IV. IR Spectroscopoic Data of Dimethylvinylsilyl Hydroperoxide (22), Matrix-Isolated in Argon at 10 K

22, argon, 10 K			24, argon, 10 K[a]		25, neat[b]		
ν, cm^{-1}	I, %[c]	ν_i/ν^d	ν, cm^{-1}	I, %[c]	ν, cm^{-1}	I, %[c]	assignment[e]
3584.7	19	0.997	3708.9	20	3565	vs	O–H str
3581.6	28	0.997	3702.6	19			O–H str
3577.4	17	0.997					O–H str
3570.3	12	0.997					O–H str
3072.5	11	1.0	3059.1	11			=C–H str
2619.2	8	0.995					
1602.6	9	1.0	1600.2	16			C=C str
1400.5	15	1.0	1410.5	25	1386	m	
1320.9	22	0.995			1307	w	
1290	9	0.996	1255.9	56			
1259.7	62	1.0	1253.5	56	1257	s	
965.8	19	1.0	959.6	33			
960.6	24	1.0	956	28			
900.2	52	0.967			900	s	O–O str
793.1	100	0.996	799.7	100	767	m	
722.7	16	0.990	712.3	20	717	m	
703.9	19	0.989	704.3	22			
523.4	9	0.999	526.3	21			

[a] Silanol 24; only selected absorptions are listed. [b] Hydroperoxide 25, neat at room temperature; only selected absorptions are listed; refs 36, 37. [c] Relative intensity. [d] Ratio of ^{18}O/^{16}O isotopic frequencies. [e] Approximate description.

Table V. IR Spectroscopic Data of Dimethyl(vinyloxy)silanol 23, Matrix-Isolated in Argon at 10 K

23, argon, 10 K			(s-z)-26, neat[a]		
ν, cm^{-1}	I, %[b]	ν_i/ν^c	ν, cm^{-1}	I, %[b]	assignment[d]
3706.9	28	0.997			O–H str
3701.4	53	0.997			O–H str
3699.1	45	0.997			O–H str
3060.9	23	1.0	3041	s	=C–H str
1625.8	60	0.999	1621		C=C str
1392.7	25	1.0	1393	s	CH$_2$ def
1332.8	30	0.996	1330		=CH$_2$ def
1203.4	100	0.984	1203		C–O
985.9	75	0.983	987	m	
963.1	55	1.0	960	s	

[a] s-Z Conformer of (vinyloxy)silane 26, neat at room temperature; only selected absorptions are listed; ref 38, 39. [b] Relative intensity. [c] Ratio of ^{18}O/^{16}O isotopic frequencies. [d] Approximate description.

toluene. The filtrate was distilled and the fraction between 70 and 105 °C collected. Purification by preparative GLC (50 °C, det./inj. 110 °C) yielded 0.46 g (5.1 mmol) of **13a** (30%) as a colorless liquid. ^{1}H-NMR (CDCl$_3$, 400 MHz): δ = 0.39 (t, 3H, J = 3.45 Hz), 4.63 (q, 2H, J = 3.45 Hz), 7.99 (s, 1H). ^{13}C-NMR (CDCl$_3$, 100 MHz): δ = -5.33, 161.11. MS m/e (rel int): 89 ((M – H)$^+$, 32), 75 (46), 61 (100). IR (Ar, 10 K): 2970.7 (7), 2946.2 (12), 2914.4 (5), 2210.5 (28), 2186.4 (32), 2182.8 (32), 2154.5 (57), 2150.2 (66), 2140.6 (44), 2136.6 (29), 1774.6 (12), 1768.4 (44), 1764 (15), 1731.3 (17), 1726.5 (74), 1263.9 (12), 1257.8 (31), 1192.4 (98), 1160.9 (27), 986.4 (11), 961.8 (46), 955.3 (28), 946.4 (34), 941.2 (42), 935 (51), 926.6 (72), 922.3 (82), 912.6 (100), 888.3 (12), 867.6 (47), 854.6 (40), 805.7 (12), 757.1 (28), 638.4 (79), 721.3 (12), 680.8 (7), 651.8 (6) cm^{-1} (rel int).

Dimethylsilyl Trifluoromethanesulfonate (Dimethylsilyl Triflate). The triflate was prepared according to a literature procedure of Bassindale

and Stout.[41] The ^{1}H-NMR was identical with that reported in the literature. ^{13}C-NMR (CDCl$_3$, 100 MHz): δ = -1.59, 118.9 (q, J (C,F) = 317.7 Hz).

(Dimethylsilyl)diazomethane (5b). 5b was synthesized as described for (methylsilyl)diazomethane (5a). The only difference was that dimethylsilyl triflate was used instead of methylsilyl triflate. 5b was purified by preparative GLC (45 °C, det./inj. 100 °C). 5b was obtained in 36% yield (GC) as a yellow oil. ^{1}H-NMR (CDCl$_3$, 400 MHz): δ = 0.16 (d, 6H, J = 3.48 Hz), 2.59 (d, 1H, J = 1.52 Hz), 4.28 (d of septet, 1H, J = 3.49, 1.53 Hz). ^{13}C-NMR (CDCl$_3$, 100 MHz): δ = -3.72, 18.22. MS m/e (rel int): 100 (M$^+$, 100), 85 (44), 59 (34). IR (Ar, 10 K): 3224.0 (3), 2972.7 (5), 2181.1 (10), 2137.7 (7), 2131.8 (14), 2126.7 (11), 2074.8 (100), 1270.0 (17), 1265.3 (28), 1262.1 (21), 1257.4 (17), 1253.5 (19), 904.1 (27), 898.7 (26), 895.5 (40), 890.7 (100), 884.9 (49), 880.9 (40), 842.6 (20), 840.2 (18), 776.6 (5), 765.6 (11), 756.9 (5), 748.5 (6), 720.6 (4), 690.5 (5), 626.8 (4), 615.8 (3), 503.8 (7), 501.4 (6), 498.3 (5), 489.0 (2) cm^{-1} (rel int). HRMS calcd for C$_3$H$_8$N$_2$Si, 100.045 68; found 100.0456 ± 2 ppm.

Dimethylsilyl Formate (13b). Chlorodimethylsilane (13.8 mmol, 1.53 mL) was added dropwise to a refluxing mixture of ethyldiisopropylamine (13.8 mmol, 2.35 mL) and formic acid (13.8 mmol, 0.52 mL) in 40 mL of dry ether. After stirring for 2 h at boiling point, the precipitated ammonium salt was filtered off and washed with dry ether. The filtrate was concentrated by distillation (bath temperature was hold below 65 °C). The remaining mixture was purified by preparative GLC (55 °C, det./inj. 120 °C). 13b was obtained in 56% yield (GC) as a colorless liquid. ^{1}H-NMR (CDCl$_3$, 400 MHz): δ = 0.36 (d, 6H, J = 3.0 Hz), 4.82 (septet, 1H, J = 3.0 Hz), 8.04 (s, 1H). ^{13}C-NMR (CDCl$_3$, 100 MHz): δ = -2.23, 161.20. MS m/e (rel int): 103 (M$^+$ – H, 22), 89 (100), 75 (58), 59 (22). IR (Ar, 10 K): 2937.5 (12), 2187.6 (20), 1765.5 (33), 1761.2 (25), 1723.5 (46), 1715.1 (27), 1265.4 (21), 1257.7 (54), 1199.7 (57), 1193.7 (34), 1162.5 (29), 1074.7 (22), 1041.3 (31), 915.7 (74), 908.8 (73), 895.6 (49), 883.2 (100), 831.7 (24), 802.7 (15), 781 (33), 717 (17) cm^{-1} (rel int).

Trimethylformylsilane (16). The formylsilane was prepared by Swern oxidation of (trimethylsilyl)methanol following a literature in-situ procedure.[42] To a mixture of 15 mL of anhydrous ether and oxalyl chloride (5.04 mmol, 0.44 mL) at −78 °C was added dropwise under a N₂ atmosphere dimethyl sulfoxide (5.21 mmol, 0.37 mL). After warming up to −35 °C, the mixture was maintained at that temperature for 30 min and then recooled to −78 °C again. (Trimethylsilyl)methanol was added dropwise. The mixture was warmed up to −40 °C, maintained at this temperature for 1 h, and recooled again to −78 °C. After triethylamine (23.68 mmol, 3.3 mL) was added dropwise, the mixture was stirred for 1 h at this temperature. The reaction mixture was warmed up to 0 °C for 2 h and concentrated by evaporating the ether in vacuum. The remaining mixture was purified by trap to trap distillation in vacuum and finally by preparative GLC (40 °C, det./inj. 70 °C). Trimethylformylsilane (16) was obtained in 12% yield (GC) as a colorless liquid. IR (Ar, 10 K): 2978.9 (17), 2751.5 (12), 2622 (39), 2588.5 (13), 1661.2 (88), 1428 (7), 1384.7 (8), 1369.7 (20), 1287.9 (6), 1252.1 (87), 880.3 (69), 864.8 (100), 826.9 (26), 765.4 (15), 711.7 (29), 702.7 (11), 585.7 (14) cm⁻¹ (rel int).

(Trimethylsilyl)diazomethane (5c). Diazomethane 5c was prepared according to a procedure by Martin[40] and isolated by preparative GLC (50 °C, det./inj. 100 °C). 5c was obtained in 64% yield (GC) as a yellow oil. ¹H-NMR (CDCl₃, 400 MHz): δ = 0.14 (s, 9H), 2.58 (s, 1H). ¹³C-NMR (CDCl₃, 100 MHz): δ = −1.0, 20.58. MS *m/e* (rel int): 114 (M⁺, 42), 99 (22), 73 (30). IR (Ar, 10 K): 3216 (4), 3038 (5), 2972 (25), 2409 (5), 2404.8 (5), 2074 (100), 1596 (5), 1325 (5), 1271 (11),1263 (26),1259 (51),1154 (6), 1032 (9), 847 (100), 750 (18), 710 (11), 689 (6), 684 (8), 616 (5), 492 (9) cm⁻¹ (rel int).

Dimethylvinylsilanol (24). The silanol was synthesized by hydrolysis of chlorodimethylvinylsilane following a general hydrolysis procedure for dichlorosilanes.[43a] In order to avoid condensation of silanol 24, all glassware had to be treated with hexamethyldisilazane. Chlorodimethylvinylsilane (95.31 mmol, 11.5 g) was added dropwise at 0 °C to an intensively stirred aqueous solution of ammonium carbonate (120 mL of water, 12.66 g of NH₄CO₃). The mixture was saturated with sodium chloride and extracted three times with 40 mL of ether. The combined ethereal solutions were dried over magnesium sulfate and concentrated by evaporating the ether in vacuum. The remaining mixture was distilled under reduced pressure (30 °C, 50 Torr). Dimethylvinylsilanol[43b] 8.3 g, 92%) was obtained as a colorless oil. ¹H-NMR (CDCl₃, 400 MHz): δ = 0.16 (s, 6H), 3.34 (s, 1H). ¹³C-NMR (CDCl₃, 100 MHz): δ = −0.38, 132.42, 138.75. IR (Ar, 10 K): 3708.9 (20), 3702.6 (19), 3059.1 (11), 2970.2 (19), 1600.2 (16), 1410.5 (25), 1255.9 (56), 1253.5 (56), 959.6 (33), 956 (28), 894 (22), 843.4 (81), 820.6 (25), 799.7 (100), 782.9 (33), 759 (17), 751 (17), 712.3 (20), 704.3 (22), 530.9 (19.8), 526.3 (21) cm⁻¹ (rel int).

(Trimethylsilyl)diazoethane. Butyllithium (1.2 mmol in 0.75 mL of hexane) was added to a solution of (trimethylsilyl)diazomethane (1.4 mmol in 3 mL of ether and 3 mL of THF) at −78 °C. After the mixture was stirred for 20 min, methyl iodide (1.2 mmol, 0.08 mL) was added. The mixture was stirred at −78 °C for 30 min and then at 0 °C for 1 h. (Trimethylsilyl)diazoethane was isolated by preparative GLC (column: 3 m SE30; 50 °C, det./inj. 100 °C). The diazoethane was obtained in 30% yield (GC) as a yellow oil. MS *m/e* (rel int): 128 (M⁺, 16), 100 (10), 85 (86), 73 (100), 58 (24). IR (Ar, 10 K): 2928.9 (6), 2893.2 (5), 2866.0 (5), 2048.2 (100), 1460.1 (7), 1378.0 (6), 1311.9 (4), 1291.5 (9), 1261.7 (12), 1252.5 (38), 1047.6 (5), 973.4 (4), 955.6 (11), 750.1 (15), 622.1 (7), 535.2 (3), 486.9 (7) cm⁻¹ (rel int).

Matrix Spectroscopy. Matrix isolation experiments were performed by standard techniques with an APD CSW-202 Displex closed-cycle helium cryostat. Matrices were produced by deposition of argon (Linde, 99.9999%) or mixtures of argon and oxygen (Messer Griesheim, 99.998%) on top of a CsI (IR) or sapphire (UV–vis) window with a rate of approximately 0.15 mmol/min. Infrared spectra were recorded by using a Bruker IFS66 FTIR spectrometer with a standard resolution of 1 cm⁻¹ in the range 400–4000 cm⁻¹. UV–vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer with a resolution of 2 nm. Irradiations were carried out with use of Osram HBO 500 W/2 mercury high-pressure arc lamps in Oriel housings equipped with quartz optics. IR irradiation from the lamps was absorbed by a 10-cm path of water. For broad-band irradiation Schott cutoff filters were used (50% transmission at the wavelength specified), and for narrow-band irradiation, interference filters in combination with dichroic mirrors ("cold mirrors") and cutoff filters were used.

(Methylsilyl)diazirine (6a). Irradiation (λ > 360 nm, Ar, 10 K) of matrix-isolated (methylsilyl)diazomethane (5a) yielded a mixture of (methylsilyl)diazirine (6a) and 2-silapropene (1a). 6a: IR (Ar, 10 K)

2165.2 (11), 2162.9 (11), 2151.2 (16), 1634.4 (4), 1258.2 (8), 969.5 (8), 950.2 (12), 948.1 (14), 943.6 (6), 940.1 (9), 899.4 (100), 869.1 (8), 866.3 (7), 771.2 (4), 766.6 (5), 745.8 (4), 722.5 (4), 682.0 (3), 630.3 (1), 505.7 (3), 496.6 (2) cm⁻¹ (rel int).

2-Silapropene (1a). Photolysis (λ > 305 nm, Ar, 10 K) of matrix-isolated (methylsilyl)diazomethane (5a) or (methylsilyl)diazirine (6a) generated 2-silapropene (1a). 1a: IR (Ar, 10 K) 2195.6 (16), 2189.7 (40), 2186.1 (39), 2181.1 (49), 1426.0 (10), 1411.7 (9), 1393.6 (10), 1297.4 (15), 1254.2 (31), 989.1 (50), 985.9 (50), 880.8 (66), 878.4 (78), 810.3 (100), 713.7 (36), 677.9 (20), 636.9 (5), 615.9 (33), 613.5 (28), 588.9 (4) cm⁻¹ (rel int).

Hydroxymethylsilyl Peroxyformate (14a). Photooxidation (λ > 335 nm, Ar/10% O₂, 35 K) of matrix-isolated methylformylsilanol (10a) produced peroxyformate 14a. IR (Ar, 10 K): 3670.7 (8, −), 3661.9 (12, 0.997), 2207.6 (15, 1.0), 1780.7 (55, 0.979), 1776.6 (17, 0.980), 1262.8 (37, 1.0), 1129.4 (37, 0.975), 1066.8 (25, 0.974), 1060.2 (25, 0.975), 895.4 (100, 0.992) cm⁻¹ (rel int, ratio of ¹⁸O/¹⁶O isotopic frequencies ν₁/ν).

(Dimethylsilyl)diazirine (6b). Irradiation (λ > 360, Ar, 10 K) of matrix-isolated (dimethylsilyl)diazomethane (5b) yielded a mixture of (dimethylsilyl)diazirine (6b) and 1,1-dimethylsilene (1b). 6b: IR (Ar, 10 K) 2976.9 (5), 2141.6 (15), 2129.9 (11), 1594.9 (5), 1432.4 (4), 1296.0 (4), 1257.8 (11), 1254.5 (21), 972.4 (6), 968.6 (8), 959.2 (4), 900.2 (25), 889.7 (100), 886.1 (27), 841.1 (14), 775.2 (7), 768.4 (7), 753.5 (4), 742.4 (5), 723.9 (4), 718.8 (4), 622.3 (4), 611.8 (3) cm⁻¹ (rel int).

1,1-Dimethylsilene (1b). Photolysis (λ > 305 nm, Ar, 10 K) of (dimethylsilyl)diazomethane (5b) or (dimethylsilyl)diazirine (6b) generated 1,1-dimethylsilene (1b). IR (Ar, 10 K): 2991.6 (12), 2968.7 (15), 2896.5 (11), 2862.0 (10), 1423.3 (17), 1413.6 (16), 1265.2 (14), 1261.6 (25), 1003.8 (62), 1002.5 (53), 992.0 (14), 826.2 (100), 818.2 (46), 711.6 (13), 647.1 (43), 643.9 (48), 625.1 (20) cm⁻¹ (rel int).

Hydroxydimethylsilyl Peroxyformate (14b). Photooxidation (λ > 335 nm, Ar/5% O₂, 35 K) of matrix-isolated dimethylformylsilanol (10b) produced peroxyformate 14b. IR (Ar, 10 K): 3667.1 (67, 0.997), 1776.7 (100, 0.978), 1261.4 (sh, 1.0), 1128.5 (50, 0.978), 1069.8 (79, −), 946.3 (79, −) cm⁻¹ (rel int, ratio of ¹⁸O/¹⁶O isotopic frequencies ν₁/ν).

Trimethylsilyl Peroxyformate (17). Photooxidation (λ > 345 nm, Ar/5% O₂, 35 K) of matrix-isolated trimethylformylsilane (16) produced peroxyformate 17. IR (Ar, 10 K): 1785.2 (29, 0.978), 1778.9 (100, 0.999), 1266.1 (14, 0.999), 1266.4 (66, 1.0), 1216.7 (8, −), 1130.9 (33, 0.977), 1123.8 (50, 0.975), 1069.5 (12, 0.976), 1059.9 (11, 0.975), 893 (34, 0.973), 863.6 (80, −), 854.6 (98, 0.994), 787.4 (7, −), 753.1 (18, 1.0), 750 (15, 0.983), 624.9 (4, 0.997), 563.8 (7, 0.975) cm⁻¹ (rel int, ratio of ¹⁸O/¹⁶O isotopic frequencies ν₁/ν).

(Trimethylsilyl)diazirine (6c). Irradiation (λ > 360, Ar, 10 K) of matrix-isolated (trimethylsilyl)diazomethane (5c) yielded a mixture of (dimethylsilyl)diazirine (6c) and 1,1,2-trimethylsilene (1c), as previously described by Chapman et al.[2] 6c: IR (Ar, 10 K): 3008 (10), 1639 (6), 1613 (7), 1418 (4), 1404 (5), 1301 (6), 1296 (5), 1266 (8), 1253 (100), 974 (7), 969 (15), 964 (9), 959 (17), 858 (100), 764 (17), 720 (7), 700 (5), 596 (2) cm⁻¹ (rel int).

1,1,2-Trimethylsilene (1c). Matrix-isolated 1,1,2-trimethylsilene was prepared by irradiation of (trimethylsilyl)diazomethane (5c) (λ > 305 nm, Ar, 10 K) according to a procedure of Chapman et al.[2] IR (Ar, 10 K): 3015.3 (9), 2933.1 (14), 2901.8 (13), 2897.5 (19), 2869.0 (17), 2734.1 (6), 1465.2 (13), 1407.8 (17), 1378.8 (12), 1314.9 (8), 1260.2 (37), 1116.1 (10), 984.9 (26), 882.7 (51), 794.5 (100), 771.9 (16), 645.7 (17), 644.1 (15), 607.7 (9) cm⁻¹ (rel int).

Trimethylvinylsilane. Irradiation (λ > 335, Ar, 10 K) of matrix-isolated (trimethylsilyl)diazoethane produced trimethylvinylsilane. IR (Ar, 10 K): 3062.3 (23), 1597.2 (12), 1413.6 (18), 1409.9 (18), 1407.2 (27), 1404.7 (24), 1402.4 (23), 1249.9 (100), 1006.8 (21), 953.1 (49), 759.2 (67), 697.1 (20), 690.3 (28), 672.1 (34), 512.9 (20) cm⁻¹ (rel int).

Supplementary Material Available: A listing of calculated cartesian coordinates, SCF-energies, and vibrational frequencies and intensities of methylsilanone, formaldehyde, complex 8a, methylformylsilanol (10a), and dimethylformylsilanol (10b) (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.