# Photochemistry and Photooxidation of Acylsilanes

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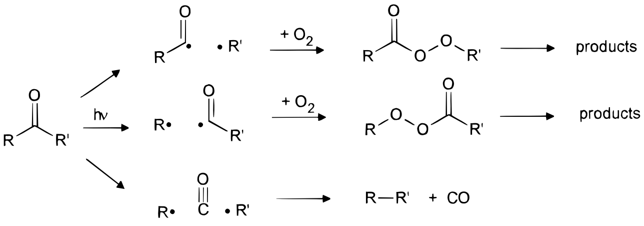
The photochemistry and photooxidation of three acylsilanes—formyltrimethylsilane (**1a**), acetyltrimethylsilane (**1b**), and benzoyltrimethylsilane (**1c**)—has been studied in argon and $O_2$-doped argon matrices. UV irradiation in argon very slowly results in the decarbonylation of **1a** and **1b**, while **1c** is stable under these conditions. The major photoproduct of **1b** is trimethyl(vinyloxy)silane. In $O_2$-doped argon matrices irradiation leads to the insertion of an $O_2$ molecule into the Si−CO bond. Other oxidation products observed are the trimethylsilyl esters of the corresponding carboxylic acids and carbonates. These results can be rationalized if we assume that the primary photoprocesses of **1** are α-cleavage of the Si−CO bond to give radical pairs and [1,2]-silyl shifts to give siloxycarbenes.

## Introduction

The photooxidation of carbonyl compounds frequently leads to complex product mixtures and has been subject to several mechanistic studies.[1−4] Generally the oxidation is initiated by α-cleavage of the carbonyl compound with subsequent trapping of the radical pairs with molecular oxygen.



In addition to the α-cleavage, acylsilanes **1** show a further photochemistry, which is not possible with other carbonyl compounds: the [1,2]-silyl shift to siloxycarbenes **2**.[5−8] These carbenes are extremely labile and rapidly rearrange back to **1**. For methylsiloxycarbene a barrier of only 4.7 kcal/mol has been calculated at the CCSD(T) level of theory.[9] The transient carbenes **2** can be trapped with pyridine[10] or other trapping reagents for singlet carbenes.[11,12]

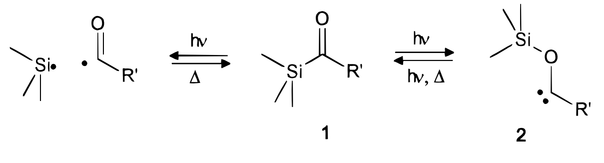
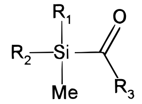


**Table 1. Comparison of C=O Stretching Vibrations of Acylsilane Compounds, Matrix-Isolated in Argon at 10 K**

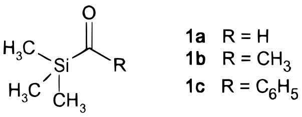


| compound | | |
|---|---|---|
| no. | $R_1$, $R_2$, $R_3$ | $\nu_{C=O}$ (cm$^{-1}$) |
| **1a** | Me, Me, H | 1661 |
| **1b** | Me, Me, Me | 1652 |
| **1c** | Me, Me, Ph | 1628 |
| **1d**[a] | OH, H, H | 1655 |
| **1e**[a] | OH, Me, H | 1655 |
| **1f**[b] | Me, H, H | 1661 |

[a] Reference 14. [b] Reference 9.

There is one report on the direct spectroscopic characterization of **2** in a laser flash photolysis experiment.[13] Recently we were able to synthesize derivatives of **2** by an alternative route via the reaction of silenes and formaldehyde.[9]

In this paper we describe the photochemistry and photooxidation of formyltrimethylsilane (**1a**), acetyltrimethylsilane (**1b**), and benzoyltrimethylsilane (**1c**) in argon and oxygen-doped argon matrices at cryogenic temperatures. Some preliminary aspects of the photooxidation of **1a** have been reported in an earlier paper on the oxidation of silenes.[14]



## Results and Discussion

**Photooxidation of Formyltrimethylsilane (1a).** Short-wavelength UV irradiation ($\lambda$ > 240 nm) of matrix-isolated **1a** (argon, 10 K, Table 1) very slowly leads to the decomposition of the aldehyde and to the

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⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1995.

[1] Tso, T.-L.; Lee, E. K. C. *J. Phys. Chem.* **1984**, *88*, 5475−82.

[2] Tso, T.-L.; Lee, E. K. C. *J. Phys. Chem.* **1984**, *88*, 5465−74.

[3] Diem, M.; Lee, E. K. C. *J. Phys. Chem.* **1982**, *86*, 4507−12.

[4] Sodeau, J. R.; Beeby, A.; Whyte, L. J. *Spectrochim. Acta, Part A* **1990**, *46*, 887−901.

[5] Alberti, A.; Degl-Innocenti, A.; Pedulli, G. F.; Ricci, A. *J. Am. Chem. Soc.* **1985**, *107*, 2316−9.

[6] Porter, N. A.; Iloff, P. M. *J. Am. Chem. Soc.* **1974**, *96*, 6200−2.

[7] Brook, A. G.; Duff, J. M. *Can. J. Chem.* **1973**, *51*, 352−60.

[8] Brook, A. G.; Dillon, P. J.; Pearce, R. *Can. J. Chem.* **1971**, *49*, 133−5.

[9] Trommer, M.; Sander, W.; Ottosson, C-H.; Cremer, D. *Angew. Chem.* **1995**, *107*, 999−1001.

[10] Perrin, H. M.; White, W. R.; Platz, M. S. *Tetrahedron Lett.* **1991**, *32*, 4443−6.

[11] Bourque, R. A.; Davis, P. D.; Dalton, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 697−9.

[12] Duff, J. M.; Brook, A. G. *Can. J. Chem.* **1973**, *51*, 2869−83.

[13] (a) Kirmse, W.; Steenken, S.; Guth, M. Unpublished results. (b) Guth, M. Dissertation, Bochum, 1993.

[14] Trommer, M.; Sander, W.; Patyk, A. *J. Am. Chem. Soc.* **1993**, *115*, 11775−83.

0276-7333/96/2315-0189$12.00/0

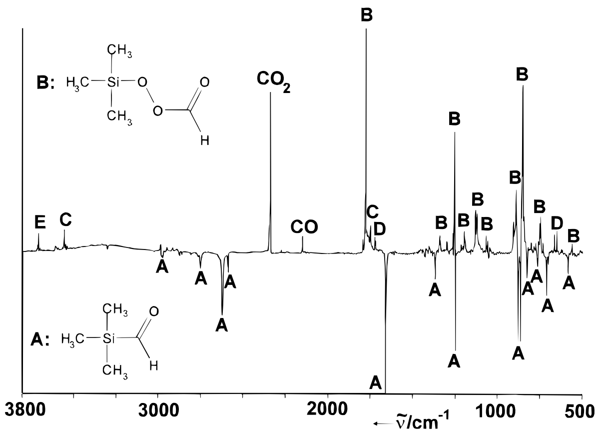
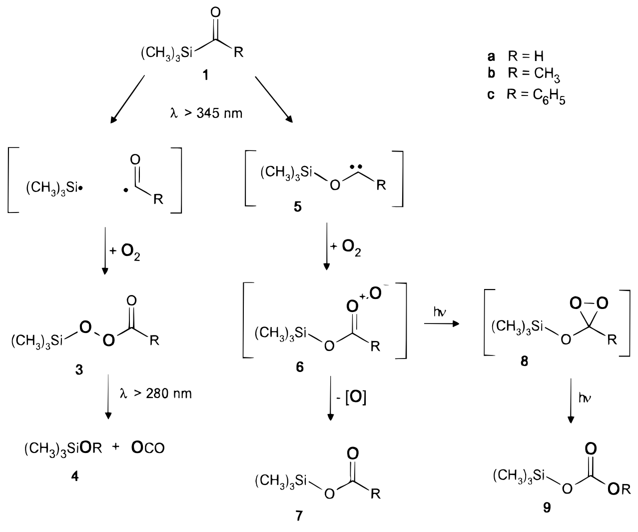


**Figure 1.** IR difference spectrum showing the photooxidation ($\lambda > 345$ nm) of formyltrimethylsilane (**1a**) in 5% $O_2$-doped argon matrices at 36 K: bottom part, bands disappearing; top part, bands appearing on irradiation of **1a**. Assignment of bands: A, bands assigned to **1a**; B, bands assigned to **3a**; C, bands assigned to **9a**; D, bands assigned to **7a**; E, band assigned to **4a**.

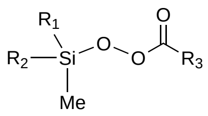
**Scheme 1**



formation of small amounts of CO and trimethylsilane. This photodecomposition is incomplete even after 10 h of irradiation. If the matrix is doped with 5% HCl, 320 nm irradiation produces chlorotrimethylsilane and formaldehyde, which have been identified by comparison with authentic matrix-isolated material. The conversion of **1a** is incomplete at 10 K, where the diffusion of HCl is inhibited, but goes to completion if the matrix is irradiated at 36 K, where diffusion of small molecules is feasible. This clearly reveals that the photochemical α-cleavage takes place even at 320 nm irradiation. However, in the absence of a trapping reagent, recombination to **1a** is much more efficient compared to decarbonylation. There is no hint for a [1,2]-silyl shift from these experiments.

In 5% $O_2$-doped argon matrices irradiation with $\lambda >$ 345 nm results in the formation of a compound as the main product which has been tentatively assigned the structure of trimethylsilyl peroxyformate (**3a**) (Scheme 1; Figure 1). Again, irradiation at 10 K results in only partial conversion, while at 30−35 K **1a** is completely oxidized within several hours. **3a** exhibits strong IR vibrations at 1779 ($\nu_{C=O}$), 1131 ($\nu_{C-O}$), 1124 ($\nu_{C-O}$), 1070 ($\nu_{Si-O}$), 1060 ($\nu_{Si-O}$), and 898 cm$^{-1}$ ($\nu_{O-O}$). The C=O stretching mode (Table 2) is close to that of methyl peroxyformate (1785 cm$^{-1}$).[4] If $^{18}O_2$ is used in the photooxidation, the C−O and Si−O stretching vibrations are characteristically red-shifted, while the C=O stretching vibration, as expected, is not effected.

**Table 2. Comparison of C=O Stretching Vibrations of Silyl Peroxy Esters, Matrix-Isolated in Argon at 10 K**



| compound no. | R1, R2, R3 | $\nu_{C=O}$ (cm$^{-1}$) |
|---|---|---|
| **3a** | Me, Me, H | 1779 |
| **3b** | Me, Me, Me | 1788 |
| **3c** | Me, Me, Ph | 1776 |
| **3e**[a] | OH, H, H | 1781 |
| **3f**[a] | OH, Me, H | 1777 |

[a] Reference 14.

On short wavelength irradiation peroxide **3a** decomposes to trimethylsilanol (**4a**) and $CO_2$. If $^{18}O_2$ is used, $C^{16}O^{18}O$ is formed as the only isotopomer, which demonstrates that only one oxygen atom in the $CO_2$ molecule stems from $O_2$ and confirms the proposed reaction mechanism. These experiments clearly show that in $O_2$-doped matrices the initially formed radical pair is trapped by molecular oxygen (Scheme 1).

Trimethylsilyl formate (**7a**) as well as another carbonyl compound, which has been tentatively assigned the structure of trimethylsilyl carbonate (**9a**), are byproducts of the photooxidation of **1a**. Formate **7a** was identified by comparison with authentic matrix-isolated material. The use of $^{18}O_2$ results in the formation of **7a**, labeled at the carbonyl oxygen but not at the ether oxygen atom. Carbonate **9a** exhibits a strong C=O stretching vibration at 1750 cm$^{-1}$ and the O−H stretching vibration at 3555 cm$^{-1}$, which both are strongly red-shifted on $^{18}$O-labeling. Again, the silyl ether oxygen atom is not isotopically labeled.

The formation of **7a** and **9a** and the observed isotopic labeling can be rationalized if carbene **5a** is postulated as an intermediate. The carbene is trapped by $O_2$ to produce carbonyl O-oxide **6a**, which is photochemically labile[15] and splits off an oxygen atom to give **7a** or rearranges to dioxirane **8a**. Dioxiranes are generally also labile toward irradiation with blue light (ca. 400 nm),[15] and thus isolation of a dioxirane is not expected under the conditions required for the photooxidation of **1a**. Carbonate **9a** is the expected product of the rearrangement of **8a**.

**Photochemistry and Photooxidation of Acetyltrimethylsilane (1b).** Irradiation ($\lambda > 280$ nm) of matrix (argon) isolated silane **1b** produces (vinyloxy)silane **10** as the major product (Figure 2). According to IR studies by Marchand et al.,[16,17] two conformers of

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

(16) Dedier, J.; Marchand, A.; Forel, M. T. and Frainnet, E. *J. Organomet. Chem.* **1974**, *81*, 161−75.

(17) Dédier, J.; Marchand, A. *Spectrochim. Acta, Part A* **1982**, *38*, 339−49.

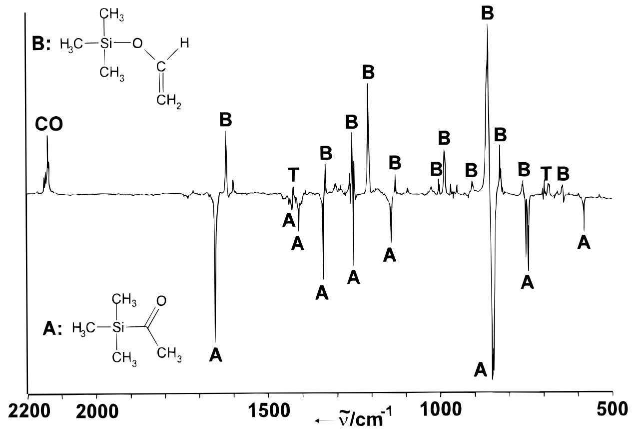
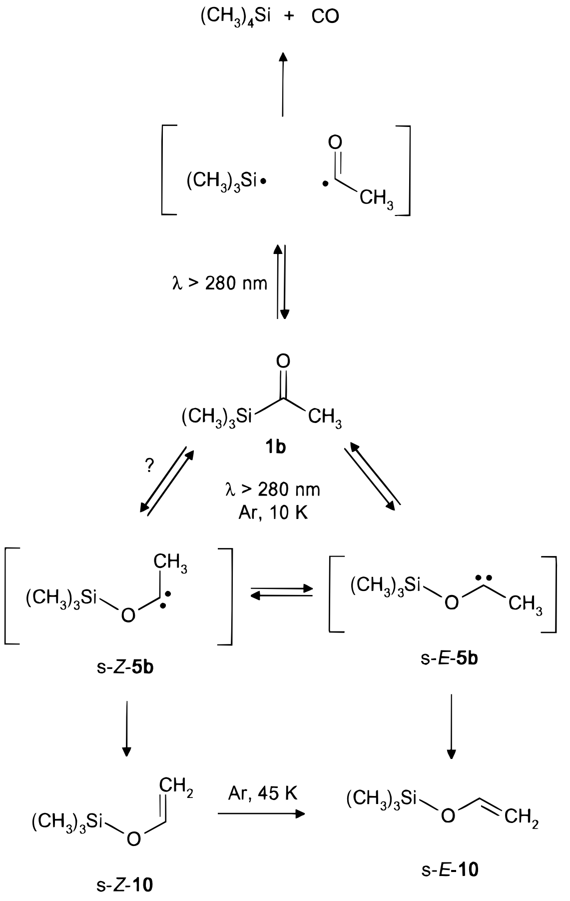


**Figure 2.** IR difference spectrum showing the photoreaction ($\lambda$ > 280 nm) of acetyltrimethylsilane (**1b**) in argon matrices at 10 K: bottom part, bands disappearing; top part, bands appearing on irradiation of **1b**. Assignment of bands: A, bands assigned to **1b**; B, bands assigned to s-*Z*-**10**; T, bands assigned to tetramethylsilane.

### Scheme 2



**10** have to be considered: the s-*E* conformer s-*E*-**10** and the s-*Z* conformer s-*Z*-**10** (Scheme 2). Comparison of the published spectra with those obtained from our matrix experiments clearly reveals that s-*Z*-**10** is obtained almost exclusively on irradiation of **1b** (Table 3). When the matrix is annealed at 45 K, s-*Z*-**10** slowly isomerizes to s-*E*-**10**. This demonstrates that s-*E*-**10** is thermodynamically more stable than s-*Z*-**10**, and that the barrier of isomerization must be very small. *Ab-initio* calculations at the RHF/6-31G(d,p) level predict the s-*E* rotamer to be more stable than the s-*Z* rotamer by 0.2 kcal/mol. s-*E*-**10** is photochemically stable and particularly does not yield s-*Z*-**10**.

**Table 3. Selected Vibrational Frequencies of (Vinyloxy)silanes s-*Z*-10 and s-*E*-10**

| $\nu$ (cm$^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|
| argon, 10 K | | ref 17 | | RHF/6-31G(d,p)[b] | | |
| s-cis | Δ (trans)[a] | s-cis | Δ (trans)[a] | s-cis | Δ (trans)[a] | assgnt[c] |
| 1621 | +25 | 1621 | +13 | 1669 | +20 | C=C str |
| 1332 | −13 | 1330 | −24 | 1334 | −11 | =CH bend |
| 1207 | −22 | 1203 | −22 | 1208 | −32 | C–O str |
| 987 | +38 | 987 | +21 | 985 | +33 | =$CH_2$ bend |

[a] Difference of the vibrational frequencies of the two conformers (s-*E*-**10** - s-*Z*-**10**). [b] *Ab-initio* calculated vibrational frequencies scaled by 0.9. [c] Assignment according to ref 17.

The most likely precursor of s-*Z*-**10** is the corresponding s-*Z* conformer of carbene **5b**. There is no plausible reason why the [1,2]-H shift in s-*Z*-**5b** should be preferred compared to the rearrangement of s-*E*-**5b**. This means that the s-*E* carbene is not formed at all during the photolysis of **1b** or a different reaction channel with a lower activation barrier exists for this carbene rotamer. Since it is reasonable to assume that the migration of the silicon atom proceeds along the C=O bond opposite to the methyl substituent, s-*E*-**5b** should be the preferred primary photoproduct. Obviously in s-*E*-**5b** the barrier for the [1,2]-silyl migration, leading back to **1b**, is lower than the barrier for the [1,2]-H shift, leading to s-*E*-**10**. The photochemical interconversion of s-*E*-**5b**, which is present in the matrix in a photostationary concentration, and s-*Z*-**5b** produces the s-*Z* rotamer which preferentially rearranges to s-*Z*-**10**.

A similar conformational control in carbene rearrangements has been demonstrated by Strausz et al. in the case of keto carbenes.[18] The s-*E* conformer of the keto carbene (generated from the s-*Z* conformer of the diazo precursor) preferentially undergoes Wolff rearrangement to the ketene, whereas the s-*Z* carbene forms an $\alpha,\beta$-unsaturated ketone via [1,2]-H shift.

More evidence for the formation of carbene **5b** stems from the investigation of the photooxidation of **1b**, which is analogous to that of **1a**. Irradiation ($\lambda$ > 345 nm) of silane **1b** in 5% $O_2$-doped argon matrix at 36 K leads to quantitative oxidation within 12 h and formation of trimethylsilyl peroxyacetate (**3b**) as the main product (Scheme 1). Peroxide **3b** is photolabile and decarboxylates on 280 nm irradiation (10 K) to give trimethylmethoxysilane (**4b**), which was identified by comparison with authentic matrix-isolated material.

The carbene trapping products trimethylsilyl acetate (**7b**) (also identified by comparison with an authentic sample) and methyl trimethylsilyl carbonate (**9b**) are minor byproducts of the photooxidation (Figure 3). Carbonyl *O*-oxide **6b** and dioxirane **8b** are postulated as intermediates but are not expected to be observable under the reaction conditions (UV photolysis).

**Photooxidation of Benzoyltrimethylsilane (1c).** Short wavelength UV irradiation of matrix-isolated silane **1c** (argon, 10 K, $\lambda$ > 240 nm) does not lead to any changes in the IR spectrum after several hours. Irradiation ($\lambda$ > 345 nm) in a 5% $O_2$-doped argon matrix

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[18] Torres, M.; Ribo, J.; Clement, A.; Strausz, O. P. *Can. J. Chem.* **1983**, *61*, 996–8.

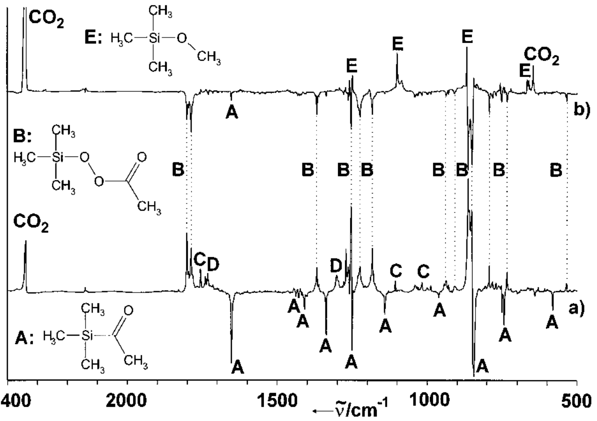

**Figure 3.** IR difference spectra showing the photooxidation ($\lambda$ > 345 nm) of acetyltrimethylsilane (**1b**) in 5% $O_2$-doped argon matrices at 36 K (a) and subsequent photodecarboxylation of trimethylsilyl peroxyacetate on short wavelength irradiation ($\lambda$ > 280 nm) at 10 K (b): (a) bottom part, bands disappearing; top part, bands appearing on irradiation of **1b**; (b) bottom part, bands disappearing; top part, bands appearing on irradiation of **3b**. Assignment of bands: A, bands assigned to **1b**; B, bands assigned to **3b**; C, bands assigned to **9b**; D, bands assigned to **7b**; E, bands assigned to **4b**.

at 37 K results in partial oxidation to a complex product mixture. Presumably several conformers of the oxidation products are present in the matrix which do not rearrange to the thermodynamically most stable conformers even on annealing at 37 K. Trimethylsilyl benzoate (**7c**) has been identified by comparison with authentic matrix-isolated material. Trimethylsilyl perbenzoate (**3c**), which is the main product, decarboxylates to **4c** on 280 nm irradiation. Phenyl trimethylsilyl carbonate (**9c**) was tentatively identified by comparison of its IR spectrum with other carbonic acid ester derivatives.

## Conclusion

The photolysis of matrix-isolated acylsilanes results in the α-cleavage to produce radical pairs and in [1,2]-silyl shifts to produce siloxycarbenes **5** as the major processes. In the absence of trapping reagents and intramolecular reaction channels, the acylsilanes are formed back with high efficiency. Although the radical pairs and carbenes **5** could not be observed by direct spectroscopic methods, compelling evidence for these intermediates comes from the following results:

(i) Photolysis of **1** in $O_2$-doped matrices yields peroxides **3** as the major products. Thus, the radical pairs are efficiently trapped by molecular oxygen. In the case of **1a** the intermediate radical pair was also trapped by HCl. These results demonstrate that the Si–CO bond is cleaved preferentially.

(ii) Short wavelength UV irradiation of **1a**,**b** slowly leads to decarbonylation and formation of silanes as the products of radical recombination. These conditions are required to cleave both bonds α to the carbonyl group.

(iii) The siloxycarbenes are also trapped by molecular oxygen, although the yield of products derived from this process is quite low. This is not unexpected, since the reaction of the singlet carbenes with $^3O_2$ is formally spin-forbidden and thus slow.[19,20]

(iv) Acetyltrimethylsilane (**1b**) yields (vinyloxy)silane **10** via a [1,2]-H shift in the siloxycarbene **5b**. Only one of two possible conformers of **10** is formed, which allows one to obtain information on the conformation of the carbene precursor.

## Experimental Section

**Calculations.** The *ab-initio* calculations were carried out using Gaussian 92[21] and standard basis sets. Geometry optimization and frequency calculations were performed at the RHF/6-31G(d) level of theory.

**Materials and General Methods.** $^1$H- and $^{13}$C-NMR spectra were taken at 400.1 and 100.6 MHz, respectively (Bruker AM 400), in $CDCl_3$ as solvent, except where noted, with $(CH_3)_4Si$ as the 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. All matrix-isolated compounds were purified by preparative scale GLC using a Shimadzu GC-8a or a Siemens RGC 202 gas chromatograph with a 6 m SE54 or 3 m SE30 column, respectively.

**Formyltrimethylsilane (1a).** The formylsilane was prepared by Swern oxidation of (trimethylsilyl)methanol following a literature in-situ procedure.[22] To a mixture or 15 mL of anhydrous ether and oxalyl chloride (5.04 mmol, 0.44 ml) at -78°C was added dropwise under $N_2$ atmosphere dimethyl sulfoxide (5.21 mmol, 0.37 mL). After the mixture was warmed to −35 °C, it was maintained at that temperature for 30 min and then recooled to −78 °C again. (Trimethylsilyl)methanol was added dropwise. The mixture was warmed 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 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 (**1a**) was obtained in 12% yield (GC) as a colorless liquid. EI−MS [*m*/*e* (%)]: 102 (18) [$M^+$], 87 (3) [$M^+$-$CH_3$], 73 (30) [$SiMe_3$]. 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 intensity). HRMS: calcd for $C_4H_{10}SiO$, 102.050 094; found 102.0500 ± 2 ppm.

**Acetyltrimethylsilane (1b).** The acylsilane **1b** was prepared according to a literature procedure by Corey and Seebach[23] and isolated by preparative GLC (SE 30 3 m, 80 °C, det./inj. 150 °C). **1b** was obtained in 26% yield (GC) as a volatile liquid. $^1$H-NMR (400 MHz, [D$_1$]chloroform): $\delta = 2.21$ (s, 3 H, $CH_3$), 0.15 (s, 9 H, $SiMe_3$). $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta = 205.23$ (s), 35.50 (q), −3.42 (q). EI−MS [*m*/*e* (%)]: 116 (16) [$M^+$], 101 (12) [$M^+ - CH_3$], 73 (100) [$SiMe_3$]. IR (Ar, 10 K): 2970 (3), 2949.1 (0.5), 1653.7 (14), 1652.2 (10), 1438.4 (0.5), 1429.7 (1), 1409.9 (3), 1338.4 (8), 1260.3 (2), 1251.6 (15), 1142.6 (3), 849.3 (100), 751.4 (6), 744.4 (6), 641.2 (0.5), 582 (3) cm$^{-1}$ (rel intensity).

**Benzoyltrimethylsilane (1c).** The benzoylsilane **1c** was prepared according to a literature procedure by Corey and

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[19] Ganzer, G. A.; Sheridan, R. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1986**, *108*, 1517−20.

[20] Sander, W. W. *Spectrochim. Acta, Part A* **1987**, *43*, 637−46.

[21] Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92, Revision C*; Gaussian Inc.: Pittsburgh, PA, 1992.

[22] Linderman, R. J.; Suhr, Y. *J. Org. Chem.* **1988**, *53*, 1569−72.

[23] Corey, E. J.; Seebach, D.; Freedman, R. *J. Am. Chem. Soc.* **1967**, *89*, 434−6.

Seebach[23] and isolated after distillation (44 °C/0.02 mbar) by preparative GLC (SE 30 3 m, 140 °C, det./inj. 200 °C). **1c** was obtained in 53% yield (GC) as a yellow oil. $^1$H-NMR (400 MHz, [D$_1$]Chloroform): $\delta = 7.83-7.81$ (m, 2H, aromat), 7.53−7.43 (m, 3 H, aromat), 0.31 (s, 9 H, SiMe). $^{13}$C-NMR (100 MHz, [D$_1$]Chloroform): $\delta = 217.1$ (s), 141.2 (s), 132.6 (d), 128,6 (d), 127.4 (d), −1.5 (q). EI−MS [*m*/*e* (%)]: 178 (31) [M$^+$], 163 (42) [M$^+$ − CH$_3$], 135 (46), 105 (100) [M$^+$ − SiMe$_3$], 73 (100) [SiMe$_3$]. IR (Ar, 10 K): 3078 (2), 3070 (2), 3055 (3), 1628 (6), 1622 (10), 1618 (8), 1596 (10), 1581 (12), 1449 (7), 1422 (3), 1312 (4), 1253 (17), 1250 (12), 1211 (23), 1173 (8), 923 (2), 848 (35), 843 (100), 838 (100), 779 (12), 757 (11), 697 (5), 692 (9), 689 (11), 623 (10), 617 (5), 599 (5) cm$^{-1}$ (rel intensity).

**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$^{-1}$. 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 cut-off filters were used (50% transmission at the wavelength specified); for narrow-band irradiation, interference filters in combination with dichroic mirrors ("cold mirrors") and cut-off filters were used.

**Trimethylsilyl Peroxyformate (3a).** Photooxidation ($\lambda > 345$ nm, Ar/5%O$_2$, 36 K) of matrix-isolated formyltrimethylsilane (**1a**) produced peroxyformate **3a** as the main product. 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 intensity, ratio of $^{18}$O/$^{16}$O isotopic frequencies $\nu_i/\nu$).

**Trimethylsilyl Peroxyacetate (3b).** Photooxidation ($\lambda >$ 345 nm, Ar/5%O$_2$, 36 K) of matrix-isolated acetyltrimethylsilane (**1b**) produced peroxyacetate **3a** as the main product. IR (Ar, 10 K): 3007.1 (6), 1801.6 (42), 1795.9 (15), 1789.8 (24), 1787.3 (31), 1432.4 (8), 1368.8 (18), 1362.2 (8), 1279.9 (10), 1265 (18), 1255.1 (60), 1184.5 (29), 1181 (15), 1042.4 (5), 1034.2 (3), 989.5 (4), 938.1 (8), 865.4 (79), 860.2 (61), 851.4 (100), 794.1 (16), 785.9 (5), 772.2 (6), 735.2 (13), 631.1 (2), 538.6 (3), 535.8 (7) cm$^{-1}$ (rel intensity).

**Trimethylsilyl Perbenzoate (3c).** Photooxidation ($\lambda >$ 345 nm, Ar/5%O$_2$, 37 K) of matrix-isolated benzoyltrimethylsilane (**1c**) produced peroxybenzoate **3c** as the main product. IR (Ar, 10 K): 1782.6 (15), 1776.1 (10), 1453.7 (6), 1255.5 (100), 1234.3 (17), 1179.7 (4), 1078.7 (4), 1059.6 (7), 1051.5 (5), 1027.9 (7), 904.4 (9), 850.7 (100), 726.8 (2), 701.7 (14) cm$^{-1}$ (rel intensity).

**(s-*Z*)-Trimethyl(vinyloxy)silane (s-*Z*-10)**. Photolysis ($\lambda > 280$ nm, Ar, 10 K) of matrix-isolated acetyltrimethylsilane (**1b**) generated (vinyloxy)silane **10** in s-*Z* conformation as main product (s-*Z*-**10**). IR (Ar, 10 K): 3058.1 (8), 2971 (46), 2940.9 (19), 1645.8 (30), 1333.9 (19), 1303.6 (14), 1255.9 (68), 1179.9 (22), 1167.9 (19), 1093.4 (7), 1025.1 (23), 1018.8 (16), 983.5 (22), 978.2 (19), 958.6 (12), 947.4 (12), 927.5 (9), 903 (29), 891.2 (17), 852.7 (100), 755 (20), 745.3 (12), 680.8 (9), 643.7 (7) cm$^{-1}$ (rel intensity).

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