

Dimethoxydimethylsilane from Silicon Atoms and Dimethyl Ether: A Combined Matrix-Spectroscopic and Density Functional Theory Study^[‡]

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The reaction between silicon atoms and dimethyl ether (**6**) has been studied in an argon matrix at 10 K and in solid dimethyl ether (**6**) at temperatures up to 80 K. In the initial step, a triplet *n*-adduct **T-5** is formed between a silicon atom and **6**. The next step needs photochemical activation. Depending on the relative dimethyl ether/argon ratio, the photoproduct is either dimethylsilanone (**1**) or singlet methoxymethylsilylene (**S-2**), which, in the presence of an excess of **6**, exists as a dimethyl ether complex **8** of silylene **S-2**. Longer irradiation transforms dimethyl ether addition compounds **S-8-t/S-8-c**

into dimethoxydimethylsilane (**7**). If irradiation is applied directly during cocondensation of silicon atoms with **6**, the only detectable products are **8** and **7**. Upon further irradiation of the pure dimethyl ether matrix, the rest of **8** is also photoisomerized, and dimethoxydimethylsilane (**7**) is observed exclusively. The structural elucidation of all new species is based on comparison of the experimental observations with density functional theory calculations.

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Introduction

During the past six years, we have studied the reactions of thermally generated silicon atoms with a variety of low molecular weight reactants in an argon matrix. The reaction products were identified by IR and UV/Vis spectroscopy, aided by comparison with calculated spectra. The method turned out to be very versatile and successful.^[1] The selected substrates were mainly molecules with isolated, conjugated, or aromatic π bonds, and compounds containing π bonds and free electron pairs at the same time.

Of special interest are molecules possessing *n* electrons only in combination with σ bonds. Reactions between silicon atoms and target molecules of this type are relevant for understanding of the Rochow–Müller synthesis.^[2] In a recent essay, Seyferth describes the enormous importance of this “direct synthesis” of dichlorodimethylsilane by treatment of a silicon/copper alloy with methyl chloride.^[3] At the same time he points out, as has also been commented by Pachaly and Weis,^[4] that even today, more than 60 years after its discovery in 1940, the mechanism of this process is still unknown. It was our hope that investigation into the behavior of Si atoms in a matrix may throw some light upon the fundamental reactions occurring on the surface of the Si/Cu contact mass used in the Rochow–Müller synthesis.

We therefore started a project dealing with the reactions of silicon atoms with substrates such as water, methanol, dimethyl ether (**6**), and methyl halides.^[1n,5]

Dimethyl ether (**6**) is of special interest:^[6] if silane **7** could be produced starting from **6**, one would avoid all the environmental problems of “chlorine chemistry”.^[7] Unfortunately, dimethyl ether (**6**) cannot be transformed into dimethoxydimethylsilane (**7**) under “direct synthesis” conditions.^[8] An early claim in this respect^[9] could not be verified.^[10] However, ether **6** reacts with “activated” silicon (ground to a thickness of 2.8 microns; presence of promoter elements) in a glass ampoule at 260 °C in the presence of methyl bromide as a catalyst.^[11] Even when the closed reaction vessel is replaced by a conventional open fluidized bed reactor and the same components are treated with “activated” silicon (325 °C; 100–200 microns) silane **7** can still be isolated in low yield.^[12] If the alkyl halide is absent, no reaction occurs. In such a case the reactivity of the silicon can be enhanced by removing the surface layer of SiO₂ and by reducing the size of the silicon particles. For instance, this can be achieved by application of an “atomization” of molten silicon (particle sizes in the range 0.1–1 microns).^[13] It fits into this context that it was claimed at a recent meeting that “atomized” silicon alloy can yield silane **7** upon treatment with **6** under standard Rochow–Müller conditions.^[14] The extreme would be the reaction of dimethyl ether (**6**) with atomic silicon. Study of the atomic domain is of interest per se, but should at the same time give important information on the basic reactions between higher Si aggregates and ether **6**.

In this paper, the first in an anticipated series dealing with reactions between silicon atoms and ($\sigma + n$) systems,

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the results with dimethyl ether (**6**) as the substrate molecule are discussed.

Results and Discussion

The reactions under discussion can be understood by consideration of the basic features of atomic silicon. Firstly, it has a triplet ground state. According to the law of spin conservation, the primary reaction product should be a triplet molecule. Secondly, the silicon atom has an empty 3p orbital. As a consequence, strongly electrophilic behavior should be expected. No wonder that all molecules with (π) and ($\pi + n$) electrons are excellent partners.^[1] By analogy, dimethyl ether (**6**) should easily be attacked at the free electron pair with formation of the triplet n-adduct **T-5**.

In this context it is surprising that Khabashesku, Margrave, et al., who investigated the reaction between silicon atoms and **6** independently,^[15] do not consider any triplet species in their theoretical discussion. As is shown in Scheme 1, however, the first step has to be the formation of the triplet n-adduct **T-5**. The reaction of the starting materials to form the corresponding singlet adduct **S-5** is calculated to be endothermic and should not occur. On the other hand, Khabashesku and Margrave did reach their experimental goal in finding a new route to dimethylsilanone (**1**). Our investigations complete their work insofar as we are able to describe not only the generation of dimethylsilanone (**1**) [insertion of silicon into one molecule of dimethyl ether

(**6**), but also of dimethoxydimethylsilane (**7**) (insertion of silicon into two molecules of **6**). Depending on the argon/dimethyl ether ratio, different reaction channels are used. Under technical conditions (that is, in the presence of a high concentration of **6**), the formation of dimethylsilanone (**1**) will not occur. On the contrary, under such conditions dimethoxydimethylsilane (**7**) may be expected as the preferred product.

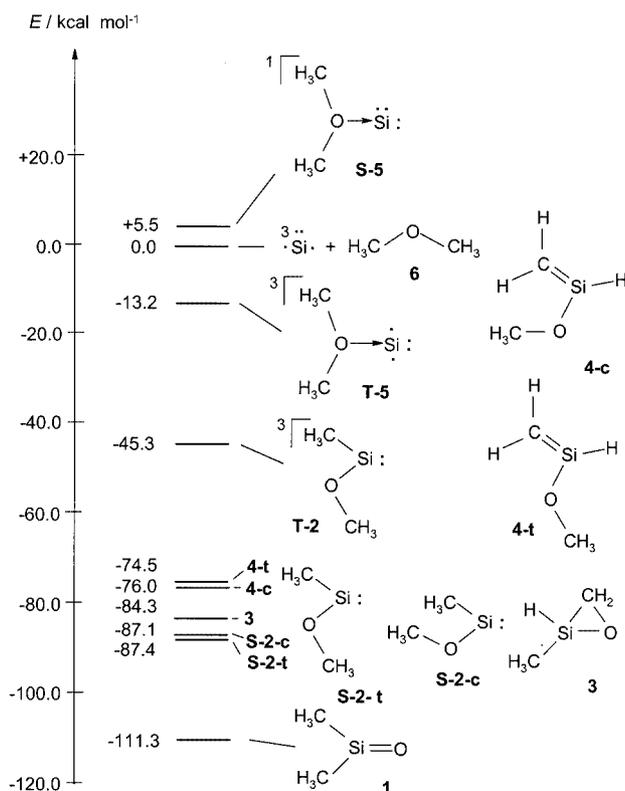
Calculations

For the structural identification of the expected species it was necessary to obtain the calculated vibrational spectra. In addition to the theoretical treatments of Khabashesku and Margrave^[15] we also carried out some calculations on our own, using the Gaussian package of programs.^[16] To obtain an overview of the C_2H_6OSi potential energy surface, several stationary points, together with the corresponding vibrational spectra, were calculated with the 6-311+G** basis set and the B3LYP functional. The results are presented in Table 1, while Scheme 1 shows the calculated relative energies of some minima.

Table 1. Calculated energies of some C_2H_6OSi isomers (B3LYP/6-311+G**)

Species (point group, state)	Energy, ZPE included [Hartrees] ^[a]
S-1 (C_1 , 1A_1)	-444.569365
S-2-t (C_1 , 1A_1)	-444.533119
S-2-c (C_1 , 1A_1)	-444.530694
S-3 (C_1 , 1A_1)	-444.526250
4-c (C_1 , 1A_1)	-444.513113
4-t (C_s , $^1A'$)	-444.510619
T-2 (C_1 , 3A_1)	-444.473841
T-5 (C_1 , 3A_1)	-444.412962
S-5 (C_{2v} , 1A_1)	-444.383145

^[a] 3Si (3P) -289.394168. C_2H_6O **6** (C_1 , 1A_1) -154.997777.



Scheme 1. Calculated relative energies of some C_2H_6OSi isomers (B3LYP/6-311+G**)

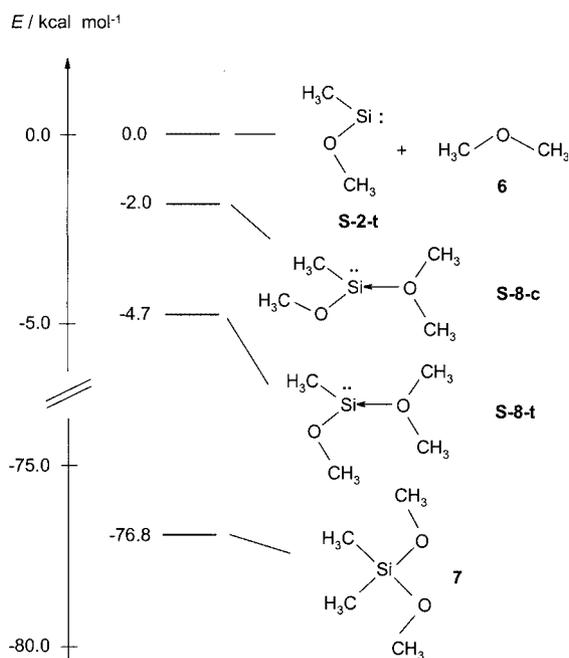
The global minimum is dimethylsilanone (**1**). The two next higher isomers on the energy scale are *s-trans*-methoxymethylsilylene (**S-2-t**) and *s-cis*-methoxymethylsilylene (**S-2-c**). Like all silylenes, they have singlet ground states. For instance, the excited triplet state **T-2-t** lies 42.1 kcal·mol⁻¹ above **S-2-t**. The calculated energy difference between the two rotamers of **2** is negligible (0.3 kcal·mol⁻¹). The next higher candidate is siloxirane **3**, followed by the *s-cis* and *s-trans* forms of methoxysilene **4**. The molecule expected as the primary addition product of a silicon atom to dimethyl ether (**6**), triplet n-adduct **T-5**, is 13.2 kcal·mol⁻¹ lower in energy than the starting materials. In this case the T/S gap is 18.7 kcal·mol⁻¹ in favor of **T-5**. As a result of this, **S-5** is assumed not to be a reaction product from 3Si atoms and **6**. Only excited 1Si atoms (T/S gap amounts to 25.8 kcal·mol⁻¹) would give **S-5** in an exothermic reaction, but these are not available when the atoms are generated by evaporation of bulk silicon.

In order to acquire some information about the fate of silylene **2** in the presence of a second molecule of dimethyl ether (**6**) we checked whether silylene **S-2-t** can experience stabilization by donor/acceptor interaction with **6**. Indeed, the two partners form a weak complex **S-8-t**. This means that, if **S-2-t** is created in a matrix at very low temperature in the presence of an excess of dimethyl ether (**6**), a complex such as **8** should be present. Such solvation might be the prerequisite for the direct synthesis of silane **7**. This compound represents the global minimum on the $C_4H_{12}O_2Si$ energy hypersurface and would be expected to be generated from the two starting material molecules **S-2-t** and **6** in a rather exothermic ($\Delta H_r = 76.8 \text{ kcal}\cdot\text{mol}^{-1}$) process. The results are presented in Table 2 and Scheme 2.

Table 2. Calculated energies of some $C_4H_{12}O_2Si$ isomers (B3LYP/6-311+G**)

Species (point group, state)	Energy, ZPE included [Hartrees] ^[a]
7 ($C_1, {}^1A_1$)	-599.653315
S-8-t ($C_1, {}^1A_1$)	-599.538452
S-8-c ($C_1, {}^1A_1$)	-599.534110

^[a] **S-2-t** ($C_1, {}^1A_1$) -444.533119. C_2H_6O **6** ($C_1, {}^1A_1$) -154.997777.



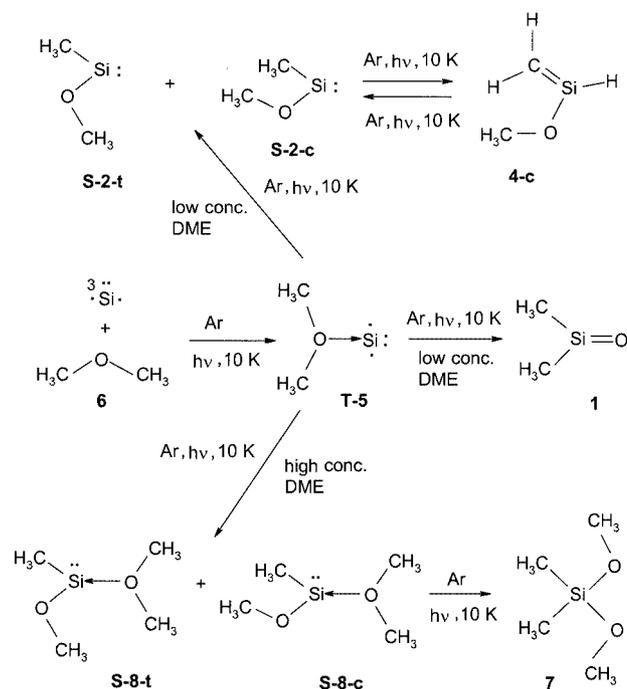
Scheme 2. Calculated relative energies of some $C_4H_{12}O_2Si$ isomers (B3LYP/6-311+G**)

Matrix Experiments

Reactions in Argon Matrices

In the standard experiments, a gaseous mixture of dimethyl ether (**6**) and argon was deposited together with silicon atoms, generated by resistive heating of a silicon rod to

a temperature of ca. 1380 °C, onto a CsI window at 10 K. FT-IR and UV/Vis spectra of the matrices were taken. Subsequent photochemical transformations were initiated by irradiation of the matrices with light of the appropriate wavelength. Many experiments (ca. 75) were necessary in order to reveal all the facets of the Si/dimethyl ether system. Only a few typical runs, revealing some special features, are discussed explicitly.



a) Changes in the IR Spectra of *n*-Adduct T-5 Depending on the Dimethyl Ether/Argon Ratio

It is a contradiction per se to apply matrix isolation for the study of intermolecular reactions. By definition, the basic idea of this technique is to have isolated guest molecules in the surroundings of a huge amount of argon atoms (ratio $\leq 1:1000$) forming the host lattice, in order to avoid any reaction between the entrapped species. If one wants to enforce intermolecular reactions of the guest molecules it is necessary to raise the concentration of the reaction partners. According to our experience this situation is reached if one uses dimethyl ether (**6**) and argon in the ratio of 1:250. Upon simultaneous cocondensation of silicon atoms on a spectroscopic window at 10 K a new species, showing three sharp IR bands at 880, 1040, and 1140 cm^{-1} (Figure 1, a), is detected. These absorptions are identical with those reported by Khabashesku and Margrave.^[15] Comparison between the calculated and experimental bands (Figure 1, a) leaves no doubt that the primarily formed product is triplet *n*-adduct **T-5** (Table 3) and not the singlet isomer **S-5** (Table 2 in Supporting Information).

For our purpose it was important to know whether the IR spectra can help in determining whether **T-5** can experience any change through solvation with an additional molecule of dimethyl ether (**6**). This is indeed so. If the concen-

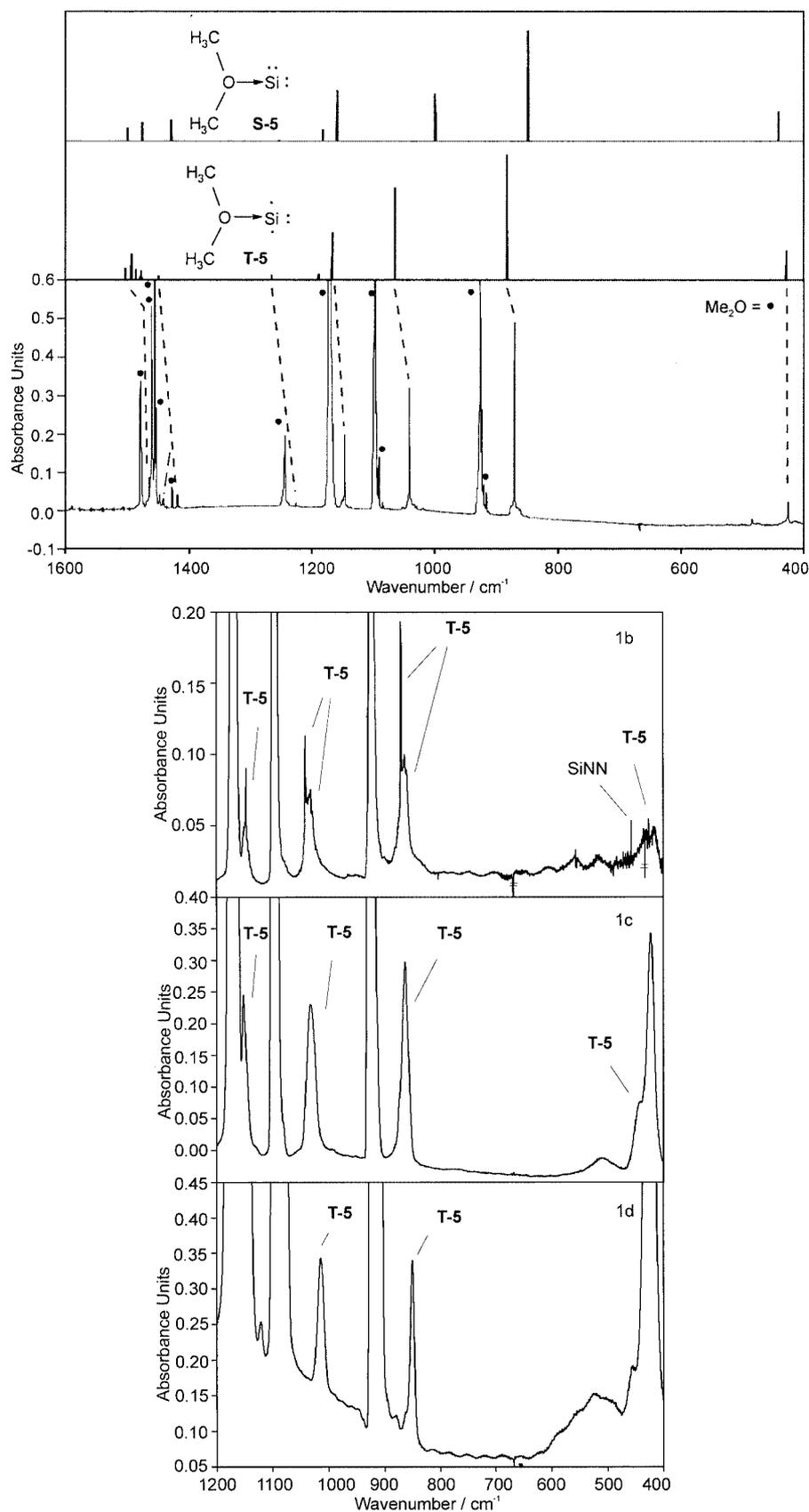


Figure 1. a) Top: calculated (B3LYP/6-311+G**) IR spectrum of singlet n-adduct S-5; center: calculated (B3LYP/6-311+G**) IR spectrum of triplet n-adduct T-5; bottom: FT-IR spectrum of the reaction product of Si atoms with dimethyl ether (**6**) in an argon matrix at 10 K (ratio **6**/Ar = 1:250); b)–d) dependence of the IR spectra of n-adduct T-5 on the concentration of dimethyl ether (**6**); 1b) ratio **6**/Ar = 1:100; 1c) ratio **6**/Ar = 1:10; 1d) pure dimethyl ether (**6**)

Table 3. Calculated (B3LYP/6-311+G**) and experimentally measured IR spectra of C₂H₆OSi isomer T-5

Sym.	Approx. description	Calculation	Experiment			
			6/Ar 1:250	6/Ar 1:100	6/Ar 1:10	6 pure/40K
a ₁	torsion	125.1(1.7)	—	—	—	—
a ₁	torsion	180.0(0.0)	—	—	—	—
a ₁	SiOC a-def.	198.8(0.4)	—	—	—	—
a ₁	SiO str.	224.4(15.8)	—	—	—	—
a ₁	SiOC s-def.	248.2(20.0)	—	—	—	—
a ₁	COC s-def.	428.0(23.5)	425.3 (m)	425.5 (m)	444.8 (m)	—
a ₁	CO s-str.	882.6(107.0)	870.3 (s)	870.3 (s)	—	—
a ₁	CO a-str.	1065.5(73.2)	—	863.5 (m) ^[a]	863.0 (s)	850.0 (s, br)
a ₁	CH ₃ rock	1153.2(0.9)	—	1041.5 (s)	—	—
a ₁	CH ₃ rock	1167.5(38.0)	—	1040.7 (s)	—	—
a ₁	CH ₃ rock	1189.5(4.8)	—	1031.5 (m) ^[a]	1032.1 (s)	1013.0 (s, br)
a ₁	CH ₃ rock	1265.7(4.2)	—	—	—	—
a ₁	CH ₃ s-def.	1450.0(3.7)	1247.8 (w)	1247.4 (w)	—	—
a ₁	CH ₃ s-def.	1477.0(2.4)	1418.8 (w)	1418.7 (w)	1420.8 (w)	—
a ₁	CH ₃ d-def.	1478.6(7.6)	1441.7 (w)	1441.8 (w)	—	—
a ₁	CH ₃ d-def.	1486.7(8.6)	1444.2 (w)	1444.2 (w)	—	—
a ₁	CH ₃ d-def.	1493.7(21.2)	1486.7(8.6)	1447.7 (w)	—	—
a ₁	CH ₃ d-def.	1503.1(9.8)	1493.7(21.2)	1455.7 (m)	1455.5 (m)	—
a ₁	CH ₃ s-str.	3018.6(28.1)	1503.1(9.8)	1464.4 (w)	1464.3 (w)	—
a ₁	CH ₃ s-str.	3024.9(61.5)	3018.6(28.1)	2856.4 (w)	2856.8 (w)	—
a ₁	CH ₃ d str.	3092.1(50.2)	3024.9(61.5)	2863.3 (w)	2863.7 (w)	—
a ₁	CH ₃ d-str.	3093.7(0.3)	3092.1(50.2)	— ^[b]	— ^[b]	—
a ₁	CH ₃ d-str.	3151.6(1.5)	3093.7(0.3)	2946.0 (w)	2946.0 (w)	—
a ₁	CH ₃ d-str.	3153.0(8.19)	—	—	—	—
a ₁	CH ₃ d-str.	3153.0(8.19)	3019.8 (w)	3020.0 (w)	—	—

[a] Additional broad, shifted signal close to the baseline. [b] Signal at 2940.0 cm⁻¹ (6/Ar = 1:250) and 2939.7 cm⁻¹ (6/Ar = 1:100), probably due to CH₃ rocking vibration overtones.

tration of **6** is increased to an even higher level (ratio 6/Ar = 1:100), the three sharp bands are accompanied by broad absorptions showing a small shift to lower wavenumbers (Figure 1, b and Table 3). The narrow lines disappear completely when the concentration of **6** is ten times as high (ratio 6/Ar = 1:10; Figure 1, c) or if pure dimethyl ether (**6**) is cocondensed with silicon atoms (Figure 1, d and Table 3).

The UV spectra of n-adduct T-5 are influenced in a similar manner (Figure 2). For instance, as long as T-5 is matrix-isolated in argon (ratio 6/Ar = 1:100; curve a), three

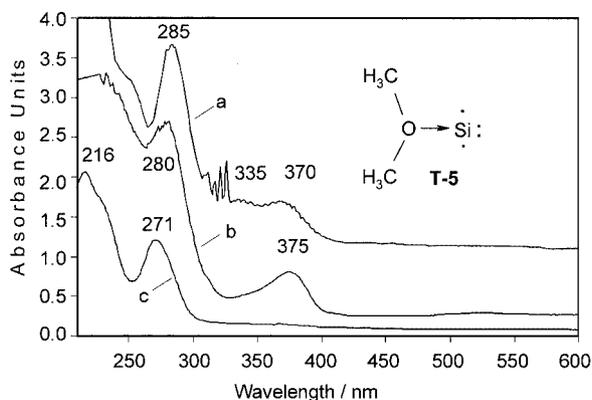


Figure 2. Dependence of the UV/Vis spectrum of n-adduct T-5 on the concentration of dimethyl ether (**6**); curve a: ratio 6/Ar = 1:100; curve b: ratio 6/Ar = 1:10; curve c: pure dimethyl ether (**6**)

distinct absorptions at 285, 335, and 375 are observed. If the scale is expanded, an additional broad band of T-5 in the 500–650 nm range can be detected. A higher concentration of **6** (ratio 6/Ar = 1:10; curve b) causes a change insofar as two absorptions at 280 and 375 nm are now measured. In solid dimethyl ether (**6**, curve c) these two bands are further hypsochromically shifted to 216 and 271 nm. Under these conditions the absorptions at longer wavelengths are too low in intensity for direct observation.

From the changes in the IR and UV spectra depending on the concentration of **6**, one has to conclude that it is possible to differentiate between a purely isolated n-adduct T-5 and a dimethyl ether solvated complex of T-5, which will probably behave differently upon irradiation.

b) Wavelength-Dependent Photoreactions of n-Adduct T-5 in Argon Matrices Containing Dimethyl Ether in Low Concentrations

Irradiation of n-adduct T-5 in a diluted argon matrix (ratio 6/Ar = 1:500) with 578-nm light (Figure 3, a) results in a small amount of dimethylsilanone (**1**) (Table 4), together with a mixture of *s-trans*-methoxymethylsilylene (S-2-t) (Table 5) and *s-cis*-methoxymethylsilylene (S-2-c) (Table 6). We already knew the IR bands of **2** from our earlier studies, when the same compound had been generated by pyrolysis of dimethyltetramethoxydisilane.^[17] At that time it was not possible to differentiate the *s-cis* from the *s-trans* conformer of **2**. Knowing now the theoretical spectra of S-2-c and S-

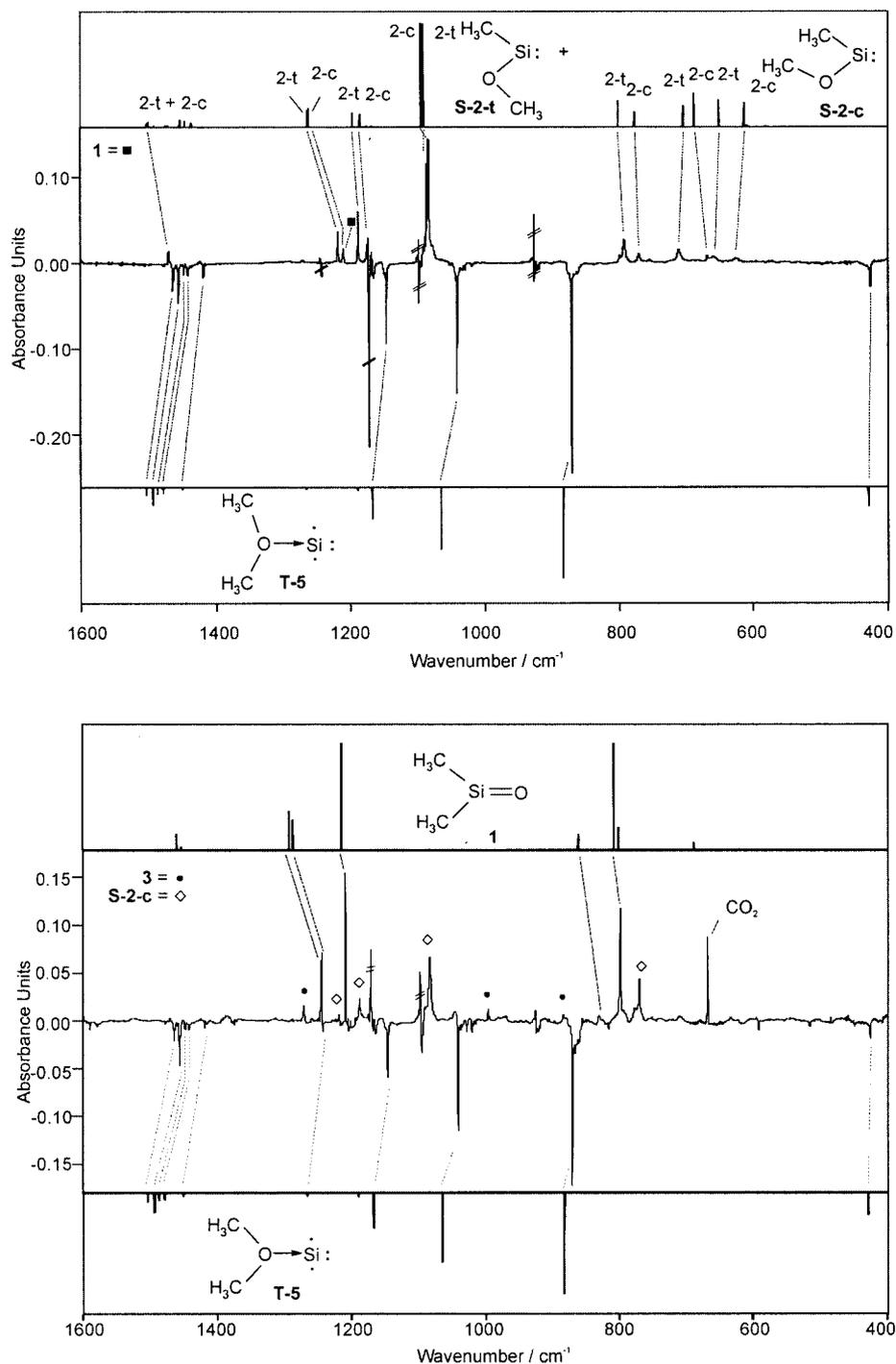


Figure 3. a) Irradiation of n-adduct **5-T** in a diluted matrix (ratio $6/\text{Ar} = 1:500$); top: calculated (B3LYP/6-311+G**) IR spectrum of a mixture of silylenes **S-2-t** and **S-2-c**; center: difference FT-IR spectrum for the photoreaction $\text{T-5} \rightarrow \text{S-2-t} + \text{S-2-c}$ (obtained by subtraction of the spectra before and after irradiation with 578 nm for 40 h); bottom: calculated (B3LYP/6-311+G**) IR spectrum of triplet n-adduct **T-5**; b) irradiation of n-adduct **5-T** in a diluted matrix (ratio $6/\text{Ar} = 1:500$); top: calculated (B3LYP/6-311+G**) IR spectrum of silanone **1**; center: difference FT-IR spectrum for the photoreaction $\text{T-5} \rightarrow \text{1} + \text{S-2-c}$ (obtained by subtraction of the spectra before and after irradiation with 290 nm for 1 h); bottom: calculated (B3LYP/6-311+G**) IR spectrum of triplet n-adduct **T-5**

2-t, it is obvious that both conformers are formed upon long-wavelength irradiation of n-adduct **T-5**.

One may ask how the silicon atom inserts into the O–CH₃ bond of **T-5** upon photoexcitation. In the transition to silylene **S-2-c/S-2-t**, spin inversion has to occur. Two possible pathways can be derived from calculations.

One alternative is that n-adduct **T-5** splits into H₃C and H₃C–O–Si radicals in an exothermic ($\Delta E = -15.7 \text{ kcal}\cdot\text{mol}^{-1}$) reaction. The activation energy of this process amounts to $\Delta E = 18.7 \text{ kcal}\cdot\text{mol}^{-1}$. The thus formed radicals may then recombine, with formation of silylene **S-2-c/S-2-t**. The second possibility, the concerted rearrangement

Table 4. Calculated (B3LYP/6-311+G**) and experimentally measured IR spectrum of C₂H₆OSi isomer **S-1**

Sym.	Approx. description	Calculation	Experiment		
			6/Ar 1:250	6/Ar 1:100	6/Ar 1:10
a ₁	torsion	7.6(0.0)	—	—	—
a ₁	torsion	71.7(0.7)	—	—	—
a ₁	CSiC bend	216.3(0.1)	—	—	—
a ₁	CH ₃ twist	257.0(17.3)	—	—	—
a ₁	CSiO bend	288.4(37.9)	—	—	—
a ₁	SiC s-str.	619.2(2.4)	—	—	—
a ₁	SiC a-str.	687.9(10.3)	—	—	—
a ₁	CH ₃ rock	690.3(0.0)	—	—	—
a ₁	CH ₃ rock	801.2(27.9)	776.2 (w)	777.0 (w)	—
a ₁	CH ₃ rock	808.1(126.3)	798.7 (s)	798.7 (s)	—
a ₁	CH ₃ rock	861.5(20.0)	830.2 (w)	830.5 (w)	—
a ₁	SiO str.	1215.5(126.7)	1209.8 (vs)	1209.9 (vs)	1211.8 (w)
a ₁	CH ₃ s-def.	1287.8(36.5)	1244.2 (m)	1244.5 (w)	—
a ₁	CH ₃ s-def.	1293.3(47.0)	1245.8 (m)	1245.9 (w)	—
a ₁	CH ₃ d-def.	1443.7(1.8)	—	—	—
a ₁	CH ₃ d-def.	1445.3(0.0)	—	—	—
a ₁	CH ₃ d-def.	1454.6(4.9)	—	—	—
a ₁	CH ₃ d-def.	1460.4(20.1)	1411.0 (w)	—	—
a ₁	CH ₃ s-str.	3022.5(0.3)	—	—	—
a ₁	CH ₃ s-str.	3206.0(2.1)	—	—	—
a ₁	CH ₃ d-str.	3084.3(0.0)	—	—	—
a ₁	CH ₃ d-str.	3087.1(7.4)	—	—	—
a ₁	CH ₃ d-str.	3129.2(1.6)	—	—	—
a ₁	CH ₃ d-str.	3129.3(1.8)	—	—	—

Table 5. Calculated (B3LYP/6-311+G**) and experimentally measured IR spectra of C₂H₆OSi isomer **S-2-t**

Sym.	Approx. description	Calculation	Experiment		
			6/Ar 1:250	6/Ar 1:100	6/Ar 1:10
a ₁	torsion (MeSi)	36.5(0.2)	—	—	—
a ₁	torsion (MeO)	127.8(0.0)	—	—	—
a ₁	COSi op-def.	166.3(4.9)	—	—	—
a ₁	COSi op-def.	187.1(2.2)	—	—	—
a ₁	COSi ip-def.	316.2(10.4)	—	—	—
a ₁	CH ₃ rock (MeSi)	607.8(3.1)	—	—	—
a ₁	SiC str.	649.9(62.4)	658.7 (w)	658.2 (w)	634.5 (w)
a ₁	SiO str. + CH ₃ rock	702.7(49.2)	709.3 (m)	709.0 (m)	—
a ₁	CH ₃ rock (MeSi)	801.0(60.3)	791.8 (m)	792.0 (m)	781.6 (s)
a ₁	CO a-str.	1091.3(239.7)	1086.8 (s)	1086.6 (s)	—
a ₁	CH ₃ rock (MeO)	1175.8(0.8)	—	—	—
a ₁	CH ₃ rock (MeO)	1197.4(34.6)	1189.0 (m)	1188.9 (m)	—
a ₁	CH ₃ s-def. (MeSi)	1263.5(38.6)	1219.2 (m)	1219.0 (m)	1218.2 (w)
a ₁	CH ₃ d-def. (MeSi)	1436.0(9.3)	—	—	—
a ₁	CH ₃ d-def. (MeSi)	1446.7(14.0)	—	—	—
a ₁	CH ₃ s-def. (MeO)	1473.9(3.0)	—	—	—
a ₁	CH ₃ d-def. (MeO)	1491.7(2.9)	—	—	—
a ₁	CH ₃ d-def. (MeO)	1502.1(9.4)	1470.4 (w)	1470.2 (w)	—
a ₁	CH ₃ s-str. (MeO)	3000.1(75.6)	2842.5 (w)	2841.9 (w)	—
a ₁	CH ₃ s-str. (MeSi)	3001.6(2.8)	—	—	—
a ₁	CH ₃ d str. (MeSi)	3068.8(9.8)	—	—	—
a ₁	CH ₃ d-str. (MeO)	3073.8(33.6)	—	—	—
a ₁	CH ₃ d-str. (MeO)	3093.6(27.4)	—	—	—
a ₁	CH ₃ d-str. (MeSi)	3095.2(13.2)	—	—	—

of **T-5** into **T-2** (followed by intersystem crossing **T-2** → **S-2**), is less likely since this pathway demands an activation energy of 28.3 kcal·mol⁻¹.

Additional structural evidence for **2** is its reversible photoisomerization into methoxysilene **4**. Silylene **2** has its UV

maximum at $\lambda_{\text{max.}} = 357$ nm, silene **4** at $\lambda_{\text{max.}} = 245$ nm.^[17] We repeated this interconversion with the mixture of **S-2-c** and **S-2-t** generated from **T-5** by irradiating the matrix with light of wavelength 366 nm. Under these conditions, silanone **1** remained untouched, but the two rotamers of **2**

Table 6. Calculated (B3LYP/6-311+G**) and experimentally measured IR spectrum of C₂H₆OSi isomer **S-2-c**

Sym.	Approx. description	Calculation	Experiment	
			6/Ar 1:250	6/Ar 1:100
a ₁	torsion (MeO)	57.5(0.3)	–	–
a ₁	torsion (MeSi)	112.0(0.1)	–	–
a ₁	COSiC twist	195.8(9.3)	–	–
a ₁	COSiC s-def.	198.1(2.9)	–	–
a ₁	COSiC a-def.	339.4(9.9)	–	–
a ₁	CH ₃ rock (MeSi)	579.8(2.4)	–	–
a ₁	SiC str.	612.6(56.3)	622.4 (w)	–
a ₁	CO bend + CH ₃ rock (MeSi)	686.6(78.9)	679.3 (w)	697.0 (w)
a ₁	CH ₃ rock (MeSi)	776.4(34.2)	770.4 (m)	770.4 (m)
a ₁	CO str.	1094.7(242.1)	1084.5 (s)	1084.2 (s)
a ₁	CH ₃ rock (MeO)	1168.4(3.1)	–	–
a ₁	CH ₃ rock (MeO)	1186.1(30.1)	–	–
a ₁	CH ₃ s-def. (MeSi)	1262.5(43.0)	1211.7 (w)	1211.7 (w)
a ₁	CH ₃ d-def. (MeSi)	1436.9(9.6)	–	–
a ₁	CH ₃ d-def. (MeSi)	1453.6(16.6)	–	–
a ₁	CH ₃ s-def. (MeO)	1471.7(2.6)	–	–
a ₁	CH ₃ d-def. (MeO)	1498.1(1.4)	–	–
a ₁	CH ₃ d-def. (MeO)	1500.1(11.7)	–	–
a ₁	CH ₃ s-str. (MeSi)	2991.2(5.5)	–	–
a ₁	CH ₃ s-str. (MeO)	3019.4(59.5)	–	–
a ₁	CH ₃ d-str. (MeSi)	3055.6(14.4)	–	–
a ₁	CH ₃ d-str. (MeSi)	3083.8(22.1)	–	–
a ₁	CH ₃ d-str. (MeO)	3089.4(22.5)	–	–
a ₁	CH ₃ d-str. (MeO)	3092.0(27.5)	–	–

Table 7. Calculated (B3LYP/6-311+G**) and experimentally measured IR spectrum of C₂H₆OSi isomer **4-c**

Sym.	Approx. description	Calculation	Experiment 6/Ar 1:250
a ₁	torsion	71.6(0.0)	–
a ₁	torsion	141.3(8.6)	–
a ₁	COSiC def.	149.7(10.4)	–
a ₁	COSiC def.	332.5(11.2)	–
a ₁	HSiCH ₂ wagg.	365.1(26.1)	–
a ₁	HSiCH ₂ wagg.	587.0(9.5)	561.9 (w)
a ₁	SiH bend + CH ₂ op-rock	676.1(25.2)	652.9 (w)
a ₁	HSiCH ₂ wagg.	707.5(50.3)	671.4 (m)
a ₁	SiO str.	733.5(14.5)	752.1 (w)
a ₁	SiH bend + CH ₂ ip-rock	879.2(113.3)	862.7 (s)
a ₁	SiC str.	1015.8(56.8)	1002.2 (m)
a ₁	CO str.	1124.2(280.2)	1100.2 (s)
a ₁	CH ₃ rock	1173.7(0.9)	–
a ₁	CH ₃ rock	1201.3(68.4)	1184.1 (w)
a ₁	CH ₂ scissor	1382.0(28.3)	1318.2 (w)
a ₁	CH ₃ s-def.	1482.4(1.5)	–
a ₁	CH ₃ d-def.	1498.4(10.9)	1462.5 (w)
a ₁	CH ₃ d-def.	1498.5(9.2)	1464.3 (w)
a ₁	SiH str.	2319.0(56.6)	2241.8 (m)
a ₁	CH ₃ s-str.	3014.2(52.8)	2854.7 (vw)
a ₁	CH ₃ d-str.	3075.2(34.9)	–
a ₁	CH ₃ d-str.	3116.8(22.9)	–
a ₁	CH ₂ s-str.	3144.2(6.1)	–
a ₁	CH ₂ a-str.	3233.0(0.1)	–

Table 8. Calculated (B3LYP/6-311+G**) and experimentally measured IR spectrum of C₂H₆OSi isomer **4-t**

Sym.	Approx. description	Calculation	Experiment 6/Ar 1:250
a''	torsion	9.8(2.9)	–
a''	torsion	70.4(0.0)	–
a'	COSiC def.	166.9(0.6)	–
a'	COSiC def.	297.0(14.1)	–
a''	HSiCH wagg.	366.0(25.0)	–
a''	HSiCH wagg.	571.8(15.1)	541.2 (w)
a'	SiH bend + CH ₂ op-rock	654.7(5.9)	–
a''	HSiCH ₂ wagg.	703.4(50.3)	– ^[a]
a'	SiO str.	752.6(62.5)	766.0 (m)
a'	SiH bend + CH ₂ ip-rock	886.8(93.2)	867.4 (m)
a'	SiC str.	1024.2(11.5)	–
a'	CO str.	1132.0(337.2)	1118.8 (s)
a''	CH ₃ rock	1176.5(0.9)	–
a'	CH ₃ rock	1211.0(139.4)	1187.9 (m)
a'	CH ₂ scissor	1376.4(29.2)	–
a''	CH ₃ s-def.	1484.4(1.4)	–
a''	CH ₃ d-def.	1493.7(4.3)	–
a'	CH ₃ d-def.	1506.0(9.0)	1473.1 (w)
a'	SiH str.	2260.7(66.7)	2192.5 (m)
a'	CH ₃ s-str.	3009.1(68.5)	2850.7 (w)
a'	CH ₃ d-str.	3080.2(38.9)	–
a''	CH ₃ d-str.	3099.4(26.8)	–
a'	CH ₂ s-str.	3149.1(6.1)	–
a'	CH ₂ a-str.	3243.8(6.9)	–

^[a] Overlapped by **4-c**.

were isomerized. The main product was the *s-cis* species **4-c** (Table 7), accompanied by some **4-t** (Table 8). This effect is probably not reflecting the higher thermodynamic stability of **4-c** with regard to **4-t**, but just indicating the posi-

tion of the photoequilibrium between the two conformers. The back reaction to **2** could easily be initiated by irradiation with 254-nm light.

If one changes from 578- to 290-nm light, n-adduct **T-5** yields mainly silanone (**1**), a small amount of methoxymethylsilylene (**S-2**) (Figure 3, b and Table 4), and a trace of 2-methylsiloxirane (**3**) (Figure 3, b and Table 9). This spectrum is in good accordance with the one reported by Khabashesku, Margrave, et al.^[15] Remarkably, mainly **S-2-c** and almost no **S-2-t** is present under these conditions. One can argue that the *s-trans* conformer **S-2-t** would undergo the [1,2] methyl shift to provide **1** more easily than **S-2-c**. It also makes sense that shorter wavelengths generate more silanone **1**. The higher energy helps to enforce a twofold methyl migration (formation of **1**), whereas with light of lower energy the reaction stops after migration of one methyl group (yielding **2**). This argument is substantiated by separate runs, which showed that **2** is only very slowly (even with 254 nm) transformed into **1**.

c) Wavelength-Dependent Photoreactions of n-Adduct T-5 in Argon Matrices Containing Dimethyl Ether in High Concentration

If one wants to enable the enclosed silylene **2** to react with a second molecule of **6** instead of isomerizing to silanone **1**, one has to start with a matrix in which **2** is not really isolated but is already complexed, as indicated in formula **S-8-c** or **S-8-t**. Such a species can be expected if one irradiates not an isolated n-adduct **T-5** but a dimethyl ether addition compound of **T-5** (weak complex with **6**). If this kind of interaction is stabilizing, such a solvate should be formed upon annealing a matrix containing both partner

molecules, or one may choose from the very beginning a concentration of dimethyl ether (**6**) that guarantees for statistic reasons that each n-adduct **T-5** has a molecule of **6** in its direct vicinity.

Such a situation applies if one irradiates a matrix prepared by cocondensation of Si atoms together with dimethyl ether (**6**) and argon in the ratio $6/\text{Ar} = 1:10$ at 10 K. Light of 290 nm wavelength isomerizes the solvated (broad IR signals, Figure 4, a) n-adduct **T-5** to a mixture of the silylene/dimethyl ether complexes **S-8-c** and **S-8-t** within 4 h, the latter complex being the main component (Figure 4, b and Table 10). In comparison with the “naked” silylenes **2-c** and **2-t**, the dimethyl ether addition compounds show an additional IR band at 1048 cm^{-1} (arising from the attached dimethyl ether molecule), which at the beginning of the irradiation is hidden by one of the strong absorptions of the n-adduct **T-5**. In addition, the bands of silane **7**, identified by comparison with authentic material, can be detected (Figure 4, b). Only a small amount of silanone **1** is formed under these conditions. If the wavelength is now changed to 254 nm for 2.5 h, the silylene component of complex **8** inserts into the O–C bond of the adjacent dimethyl ether (**6**) molecule and silane **7** is generated (Figure 4, c). That means that the “intermolecular” insertion is preferred over the intramolecular methyl shift from the oxygen to the divalent silicon atom.

The sequence **T-5** → **S-8** → **7** can also be monitored by UV spectroscopy (Figure 5). Upon irradiation with long-wavelength light ($\lambda > 534\text{ nm}$) the bands of **T-5** (280, 375,

Table 9. Calculated (B3LYP/6-311+G**) and experimentally measured IR spectrum of C₂H₆OSi isomer **3**

Sym.	Approx. description	Calculation	Experiment 6/Ar 1:250
a ₁	torsion	126.4(0.3)	–
a ₁	CSiC def.	213.4(1.4)	–
a ₁	CSiO def.	230.6(10.2)	–
a ₁	HSiO def.	564.3(0.8)	–
a ₁	HSiC def. + CH ₂ rock + CH ₃ rock	627.6(17.4)	634.3 (w)
a ₁	HSiC def. + CH ₂ rock + CH ₃ rock	706.1(42.4)	678.4 (w)
a ₁	SiC str. + CH ₃ rock	717.0(26.4)	–
a ₁	HSiO def. + CH ₃ rock	725.4(15.6)	733.3 (w)
a ₁	CH ₂ rock	822.1(75.1)	809.8 (w)
a ₁	CH ₂ rock + CH ₃ rock	832.9(56.9)	825.7 (w) ^[a]
a ₁	SiH bend + CH ₃ rock	900.2(70.5)	884.2 (w)
a ₁	SiH bend	1012.7(98.6)	996.6 (m)
a ₁	CH ₂ twist	1103.6(3.5)	–
a ₁	CH ₂ wagg	1131.0(3.3)	–
a ₁	CH ₃ s-def.	1300.5(24.5)	1271.9 (s)
a ₁	CH ₃ d-def.	1453.8(5.7)	–
a ₁	CH ₃ d-def.	1456.8(5.7)	–
a ₁	CH ₂ scissor	1471.4(2.0)	–
a ₁	SiH str.	2247.0(119.6)	2175.2 (m) 2176.9 (m)
a ₁	CH ₃ s-str.	3027.9(2.6)	–
a ₁	CH ₂ s-str.	3070.5(25.9)	–
a ₁	CH ₃ d-str.	3094.7(5.6)	–
a ₁	CH ₃ d-str.	3115.9(3.8)	–
a ₁	CH ₂ d-str.	3146.3(14.3)	–

^[a] Sh, overlap with a peak of isomer **1** at 830.2 cm^{-1} .

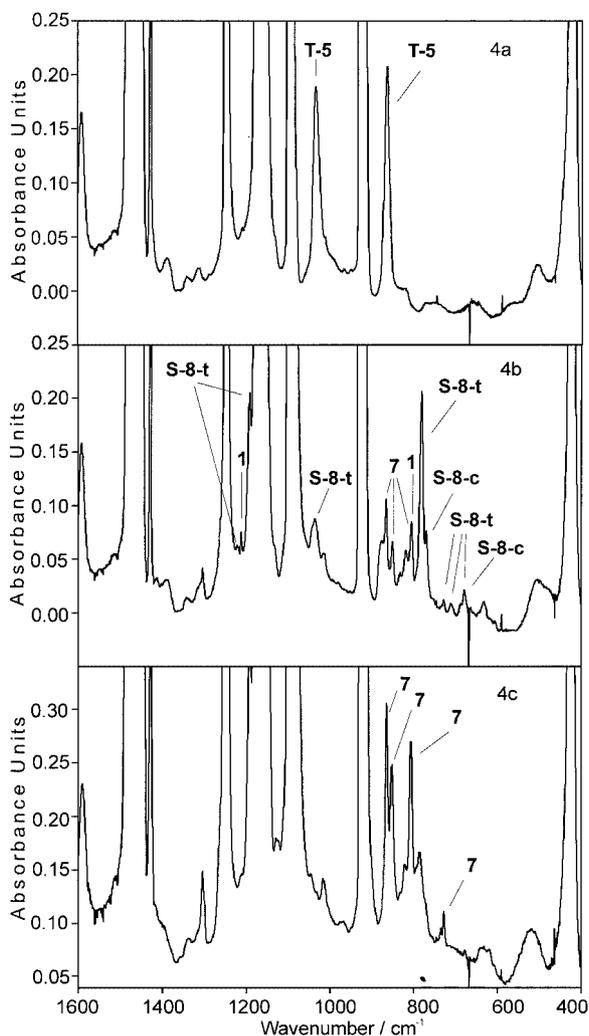


Figure 4. a)–c) Irradiation of n-adduct **5-T** in a higher concentrated matrix (ratio **6**/Ar = 1:10); a) IR spectrum of n-adduct **T-5** (solvated by excess of **6**) before irradiation; b) IR spectrum for the photoreaction $\text{T-5} \rightarrow \text{S-8-t} + \text{S-8-c} + 7$ on application of 290-nm light for 4 h; c) IR spectrum of the final product dimethoxydimethylsilane (**7**) after subsequent irradiation at 254 nm for 2.5 h

and 524 nm; curve a) disappear, while at the same time the absorption of **S-8** (272 nm; curve b) increases. During longer irradiation at 254 nm all UV maxima vanish (formation of silane **7**).

These results were confirmed in a series of experiments with silicon atoms in which the dimethyl ether/argon ratio was continuously changed from 1:1000 to pure ether **6** (see below). Detectable amounts of silanone **1** diminished in parallel with the higher concentration of **6** and in a pure dimethyl ether matrix no silanone **1** was observed but practically only silane **7**.

d) Warm-up Experiments

For a preparative application of the synthesis of silane **7** from Si atoms and dimethyl ether (**6**) it is necessary that the n-adduct **T-5** is stable enough to be irradiated at least

77 K (liquid nitrogen temperature). Unfortunately, it turned out that both, n-adduct **T-5** and silylene **2**, are completely stable in an argon matrix at 35 K, but both compounds are decomposed unspecifically as soon as the argon is evaporated and the residue (**T-5** or **2** in solid **6**) is warmed to a temperature higher than 60 K.

e) Irradiation During Cocondensation

Being aware of the thermal instability of the intermediates **T-5** and **S-2**, it was tempting to test whether there would be a better chance of obtaining silane **7** if the Si atoms and dimethyl ether (**6**) were trapped on the spectroscopic window and the condensate simultaneously irradiated. If the concentration of dimethyl ether (**6**) were high enough, each newly formed n-adduct molecule should immediately be transformed into silane **7**.

If a **6**/Ar ratio of 1:100 and 290-nm light were used in such an experiment, roughly equal amounts of n-adduct **S-8-t**, silanone **1**, and silylene **S-2-t** were detected, but no silane **7** (Figure 6, a). Upon subsequent irradiation at 254 nm, the signals of **S-2-t** diminished and those of silane **7** appeared (Figure 6, b). The conclusion was: firstly, one has to use a higher concentration of **6** in order to have ether-solvated n-adducts, and secondly, short-wavelength light has to be applied. Indeed, when a gas stream of silicon atoms, dimethyl ether (**6**), and argon (**6**/Ar = 1:10) was condensed at 10 K and the deposit was irradiated with 254-nm light, the only new product was dimethoxydimethylsilane (**7**).

f) Summary

From the experimental and theoretical findings, the reactions between Si atoms and dimethyl ether (**6**) in an argon matrix can be summarized as follows. The first reaction product is triplet n-adduct **T-5**. Subsequent transformations need photoactivation.^[18] Depending on the applied wavelength and the concentration of **6** in the argon matrix, different pathways are followed. In a diluted matrix the main product is either silylene **S-2-c** (long-wavelength irradiating light) or silanone **1** (short-wavelength irradiation). If the concentration of **6** is increased, the “solvated” n-adduct **T-5** upon photoexcitation affords either complexed silylene **S-8** (long wavelength) or dimethoxydimethylsilane (**7**) (short wavelength).

Reactions in Solid Dimethyl Ether

In view of the results found in an argon matrix, it was a logical consequence to carry out the same kind of experiments in the absence of any argon. A matrix of pure solid dimethyl ether (**6**) provides two advantages: on the one hand, the n-adduct is only surrounded by dimethyl ether molecules (perfect solvation), an ideal prerequisite for intermolecular reactions, and on the other hand, the dimethyl ether matrix softens at a much higher temperature than solid argon, and therefore allows studies over a wider temperature range.

Our expectations were fulfilled. When Si atoms and dimethyl ether (**6**) were slowly deposited at 60 K on a spectro-

Table 10. Calculated (B3LYP/6-311+G**) and experimentally measured IR spectrum of C₄H₁₂O₂Si isomer **S-8-t**

Sym.	Approx. description	Calculation	Experiment	
			6/Ar 1:10	6 pure
a ₁	SiOC torsion (Me ₂ O)	51.9(1.2)	—	—
a ₁	SiOC def. (Me ₂ O)	70.5(2.2)	—	—
a ₁	torsion (MeO) + SiO str. (Me ₂ O)	95.6(1.0)	—	—
a ₁	torsion (MeO)	110.1(0.4)	—	—
a ₁	SiO str. (Me ₂ O)	137.3(12.4)	—	—
a ₁	torsion (MeSi)	146.5(0.2)	—	—
a ₁	SiOC def. (Me ₂ O)	160.8(2.2)	—	—
a ₁	CSiOC def. + torsion (Me ₂ O)	178.1(0.4)	—	—
a ₁	CSiOC def. + torsion (Me ₂ O)	194.3(6.8)	—	—
a ₁	torsion (Me ₂ O)	210.3(0.6)	—	—
a ₁	CSiOC def. + torsion (Me ₂ O)	258.5(3.0)	—	—
a ₁	CSiOC def. + torsion (Me ₂ O)	263.8(24.1)	—	—
a ₁	CSiOC def.	327.9(8.9)	—	—
a ₁	COC s-def.	420.6(21.2)	—	—
a ₁	SiC str.	620.9(34.6)	628.1 (w)	—
a ₁	CH ₃ rock (MeSi) + CO str. (MeO)	675.6(67.5)	678.4 (m)	—
a ₁	CH ₃ rock (MeSi)	718.2(18.5)	709.4 (w)	—
a ₁	CH ₃ rock (MeSi)	787.6(55.3)	768.1 (m) ^[a]	783.0 (m, br)
a ₁	CO s-str. (Me ₂ O)	894.7(103.2)	867.4 (s) ^[a]	861.0 (s, br)
a ₁	CO str. (MeO + Me ₂ O)	1088.8(249.4)	1048.2 (m)	1016.0 (m, br)
a ₁	CO a-str. (Me ₂ O) + CO str. (MeO)	1093.8(57.2)	1071.2 (s)	— ^[b]
a ₁	CH ₃ rock (Me ₂ O)	1158.7(0.5)	—	—
a ₁	CH ₃ rock (Me ₂ O)	1177.6(1.4)	—	—
a ₁	CH ₃ rock (Me ₂ O) + CH ₃ rock (MeO)	1178.2(49.4)	— ^[b]	— ^[b]
a ₁	CH ₃ rock (Me ₂ O)	1189.6(5.4)	—	—
a ₁	CH ₃ rock (Me ₂ O)	1196.5(30.2)	— ^[b]	— ^[b]
a ₁	CH ₃ s-def. (MeSi)	1266.0(36.1)	1221.6 (w)	—
a ₁	CH ₃ rock (Me ₂ O) + s-def. (MeSi)	1271.1(2.0)	—	—
a ₁	CH ₃ d-def. (MeSi)	1449.5(12.5)	— ^[b]	— ^[b]
a ₁	CH ₃ s-def. (Me ₂ O) + d-def. (MeSi)	1451.5(1.2)	—	—
a ₁	CH ₃ d-def. (MeSi) + s-def. (Me ₂ O)	1456.8(8.0)	—	—
a ₁	CH ₃ s-def. (MeO + Me ₂ O)	1474.5(1.3)	—	—
a ₁	CH ₃ s-def. (Me ₂ O + MeO)	1477.0(0.4)	—	—
a ₁	CH ₃ d-def. (Me ₂ O)	1487.5(6.4)	—	—
a ₁	CH ₃ d-def. (Me ₂ O)	1493.2(12.4)	—	—
a ₁	CH ₃ d-def. (MeO + Me ₂ O)	1494.7(3.3)	—	—
a ₁	CH ₃ d-def. (Me ₂ O + MeO)	1501.9(8.6)	—	—
a ₁	CH ₃ d-def. (Me ₂ O + MeO)	1504.3(10.3)	—	—
a ₁	CH ₃ d-def. (Me ₂ O)	1510.8(3.2)	—	—
a ₁	CH ₃ s-str. (MeO)	2984.2(99.4)	—	—
a ₁	CH ₃ s-str. (MeSi)	2999.2(13.2)	—	—
a ₁	CH ₃ d-str. (Me ₂ O)	3006.3(34.1)	—	—
a ₁	CH ₃ s-str. (Me ₂ O)	3013.2(67.6)	—	—
a ₁	CH ₃ d-str. (MeO)	3041.1(44.3)	—	—
a ₁	CH ₃ d-str. (MeSi + MeO)	3062.9(21.4)	—	—
a ₁	CH ₃ d-str. (MeO)	3067.0(40.5)	—	—
a ₁	CH ₃ d-str. (Me ₂ O)	3070.3(61.8)	—	—
a ₁	CH ₃ d-str. (Me ₂ O)	3074.6(8.4)	—	—
a ₁	CH ₃ d-str. (MeSi)	3087.1(21.0)	—	—
a ₁	CH ₃ d-str. (Me ₂ O)	3131.2(6.0)	—	—
a ₁	CH ₃ d-str. (Me ₂ O)	3143.9(2.4)	—	—

^[a] Add. bands for **S-8-c** at 874 (m, sh), 762.0 (m, sh) and 689.1 (m) cm⁻¹; calcd: 900.0(94), 772.5(41) and 689.7(20) cm⁻¹. ^[b] Overlap with strong absorptions of **6**.

scopic window and the solid matrix was at the same time irradiated with 254-nm light, then, according to the IR spectra (Figure 7, a), the intended formation of silane **7** did indeed take place. In addition, the bands of silylene/dimethyl ether complex **S-8-t**, the intermediate on the pathway to **7**, could be detected. The same result is documented in the corresponding UV spectra (Figure 8). Continued ir-

radiation completed the transformation of **S-8-t** into **7** (Figure 7, b), which at the end was the only reaction product. In summary of these results it can be said that the reaction between silicon atoms in solid dimethyl ether (**6**) in combination with irradiation during and after cocondensation is a very effective approach for the “direct” generation of dimethoxydimethylsilane (**7**).

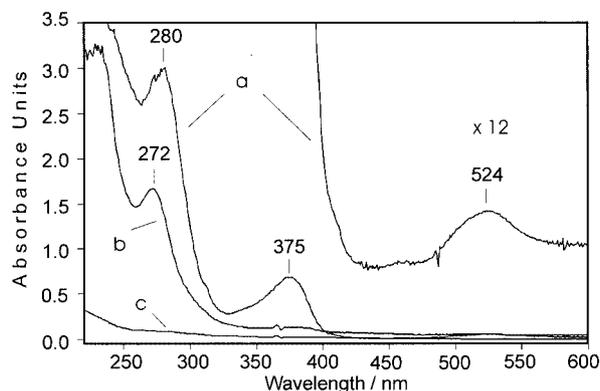


Figure 5. Irradiation of n-adduct **5-T** in a more concentrated matrix (ratio **6**/Ar = 1:10); curve a: UV spectrum of n-adduct **T-5** (solvated with excess **6**) before irradiation; curve b: IR spectrum for the photoreaction **T-5** → **S-8-t** + **S-8-c** with wavelengths > 534 nm for 20 h; curve c: IR spectrum of the final product dimethoxydimethylsilane (**7**) after subsequent irradiation at 254 nm for 2.5 h

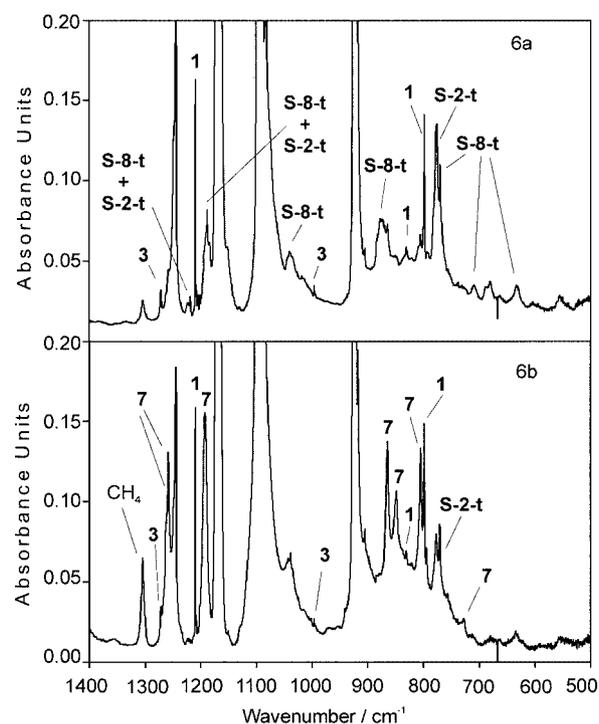


Figure 6. Irradiation of n-adduct **5-T** (ratio **6**/Ar = 1:10) during cocondensation; a) FT-IR spectrum for the photoreaction **T-5** → **S-8-t** + **S-2-t**, achieved by irradiation with 290-nm light during cocondensation (3 h); b) FT-IR spectrum for the photoreaction **S-8-t** → **7** after subsequent irradiation at 254 nm for 2 h

A minor side product in these reactions was methane. An independent study, however, showed that its formation has nothing to do with the involved silicon-containing species but that it originated from a photochemical splitting of the dimethyl ether (**6**) used as matrix material.

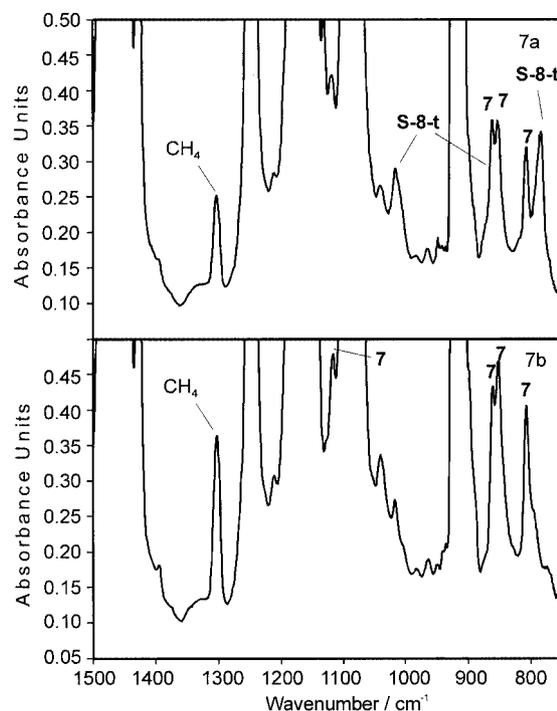
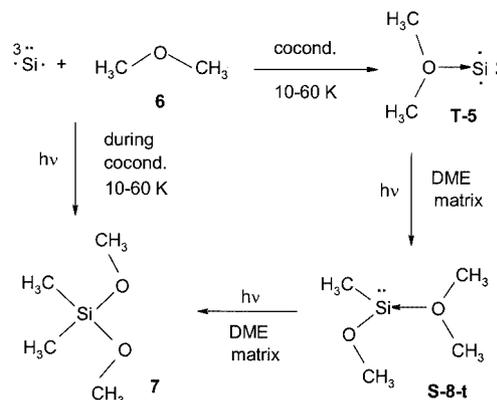


Figure 7. Irradiation of n-adduct **5-T** [in pure dimethyl ether (**6**)] during cocondensation; a) FT-IR spectrum for the photoreaction **T-5** → **S-8-t** + **7**, achieved by irradiation with 290-nm light during cocondensation (60 K; 3 h); b) FT-IR spectrum for the photoreaction **S-8-t** → **7** after subsequent irradiation at 60 K at 254 nm for 2 h

Conclusion

A direct synthesis of dimethoxydimethylsilane (**7**) can be achieved through the reaction between silicon atoms and solid dimethyl ether (**6**) at 60 K with concomitant irradiation with UV light (254 nm). Studies in an argon matrix uncovered all the details of this process, and the basic steps are now well understood. Hopefully, similar studies with methyl halides will contribute to learning more about the intermediates that may play a decisive role in the Rochow–Müller synthesis.

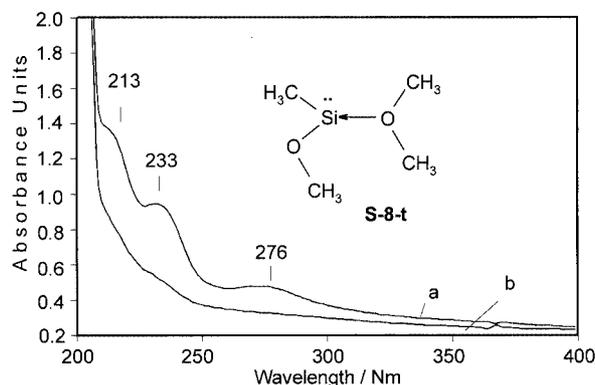


Figure 8. Irradiation of n-adduct **5-T** [in pure dimethyl ether (**6**)] during cocondensation; curve a: UV spectrum for the photoreaction **T-5** \rightarrow **S-8-t** + **7**, achieved by irradiation with 290-nm light during cocondensation (60 K; 3 h); since **7** does not absorb, the maxima have to be attributed to **S-8-t**; curve b: UV spectrum for the photoreaction **S-8-t** \rightarrow **7** after subsequent irradiation at 60 K at 254 nm for 2h

Experimental Section

The cryostat for matrix isolation was a helium closed-cycle refrigeration system (RW2 compressor unit with coldhead 210 base unit and ROK extension module) from Leybold. The matrix IR spectra were measured with an FT-IR instrument (IFS 85 or IFS 55) from Bruker, and the UV/Vis spectra were taken with a Hewlett Packard HP 8453 diode-array spectrophotometer. The light sources used were a mercury high-pressure lamp (HBO, 200 from Osram) with a monochromator (Bausch and Lomb) and a mercury low-pressure spiral lamp with a Vycor filter (Grüntzel). For the production of silicon atoms, a rod of size $0.7 \times 2 \times 22$ mm was cut out from a highly doped silicon wafer and heated resistively by use of a current of 10 A at 10 V. Under these conditions the surface temperature amounted to 1350–1380 °C. The matrix spectrum of **7** in the presence of an excess of dimethyl ether (**6**) was compared with the spectrum of an authentic sample of **7** (Lancaster; 97%), which was degassed by several freeze-pump-thaw cycles and mixed with argon (Messer Griesheim; 9.4) and dimethyl ether (**6**) (Gerling Holz & Co.; 99.9%).

Supporting Information (see also footnote on the first page of this article): Calculated energies, zero point energies, s^2 -values [B3LYP/6-311+G(d,p)], calculated vibrational spectra [B3LYP/6-311+G(d,p)], calculated UV/Vis spectra [TD//B3LYP/6-311+G(d,p)], calculated geometries [B3LYP/6-311+G(d,p)] for the stationary points shown in Scheme 1 and Scheme 2.

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