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Oxidation of Methyl(phenyl)silylene−Synthesis of a Dioxasilirane

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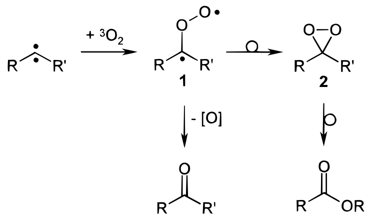
Abstract: The oxidation of methyl(phenyl)silylene, **3f**, with molecular oxygen is investigated using matrix isolation spectroscopy in combination with DFT calculations. The UV irradiation (λ > 305 nm) of phenylsilyldiazomethane, **8**, matrix-isolated in argon at 10 K, produces silylene **3f** in very high yield. In O_2 doped argon matrixes, the thermal reaction of **3f** with O_2 could be directly monitored by IR spectroscopy. The only reaction product is dioxasilirane **5f**, presumably formed via cyclization of silanone *O*-oxide **4f**. DFT calculations reveal that the activation barrier for the **4f** → **5f** cyclization is less than 1 kcal/mol, too small to allow the matrix isolation of **4f**. Dioxasilirane **5f** is photolabile, and irradiation with blue light (λ > 420 nm) results in a [1,2]-phenyl migration to give silaester **7f**. The product of the methyl migration, silaester **13**, is formed as a minor constituent.

Introduction

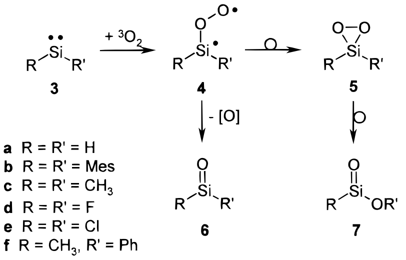
A general route for the matrix isolation and spectroscopic characterization of carbonyl *O*-oxides **1**—the "Criegee intermediates"—is the reaction of carbenes with molecular oxygen.[1−6] Carbonyl oxides are photolabile, and visible light irradiation results in cyclization to the corresponding dioxiranes **2** or in the loss of the terminal oxygen atom and formation of carbonyl compounds (Scheme 1). This reaction sequence can be used for the preparative-scale synthesis of carbonyl oxides or stable dioxiranes.[7−9]

While many examples of carbene oxidations have been reported, only three papers on the reaction of silylenes (silanediyls) **3** with molecular oxygen have been published.[10−12] Ando et al. investigated the oxidation of dimesitylsilylene **3b** in solid oxygen at 16 K. During UV photolysis of the precursor of **3b** (the corresponding trisilane), a new IR absorption at 1084 cm^{-1} was observed, which was claimed to be the O−O stretching vibration of dimesitylsilanone *O*-oxide **4b** (Scheme 2).[10,13] The assignment of the 1084 cm^{-1} vibration was based on comparison with RHF/6-31G(d) calculations for the triplet state of the parent silanone oxide **4a** (no minimum for singlet **4a** was located at this level of theory).[10] The direct thermal reaction of **3b** with $^3O_2$ was not found, and other IR bands of **4b** were not reported. In later communications, a singlet ground state of **4a** and a small activation barrier for the **4a** → **5a** rearrangement was predicted on the basis of MP2 calculations.[11,13]

Scheme 1



Scheme 2



In our laboratory, the oxidation of dimethyl-, difluoro-, and dichlorosilylene **3c−e** was investigated in O_2 doped argon matrixes (Scheme 2).[11,12,14,15] Dimethylsilylene **3c** was found to react thermally in 0.5% O_2 doped argon matrixes at temperatures as low as 40 K.[11] This indicates that the activation barrier for this oxidation must be very small or zero. The only

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product is dimethyldioxasilirane, **5c**, while dimethylsilanone *O*-oxide, **4c**, the proposed precursor of **5c**, is not observed. This is in contrast to carbene oxidations, where carbonyl oxides **1** are the primary thermal products and dioxiranes **2** are formed on secondary photolysis of **1**.[4] Under the assumption that the thermal reaction of silylenes **3** with molecular oxygen leads to silanone oxides **4** as the primary products, it follows that the barrier of the **4** → **5** rearrangement must be considerably smaller than that of the **1** → **2** rearrangement. This is in agreement with MP2 calculations, which predict a barrier of 22.8 kcal/mol for the carbonyl oxide, but only 6.5 kcal/mol for the silanone oxide rearrangement (parent compounds, $R = R' = H$).[11]

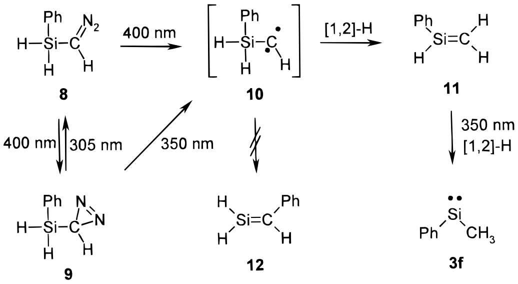
Despite the high affinity of silicon toward oxygen, the halogenated silylenes **3d** and **e** can be matrix-isolated in neat solid oxygen at 10 K, and even annealing of the oxygen matrix at 40 K does not result in any thermal reaction.[12] Irradiation with UV or visible light is required to induce the reaction, and the only products formed are the dioxasiliranes **5d** and **e**, respectively.

The limited number of experimental studies on the oxygenation of silylenes is mainly due to the lack of suitable precursors.[16] The photolysis of matrix-isolated trisilanes[10,17−19] produces silylenes in close proximity to disilenes or other products of the precursor decomposition rather than matrix-isolated silylenes. Gas-phase thermolysis of disilanes and other thermal precursors[20−22] requires very high temperatures, and the photolysis of diazidosilanes[23,24] short-wavelength UV irradiation. In all of these cases, the yields of silylenes are rather poor. Here we describe a route to the matrix isolation of a silylene in high yield which allows study of the oxygenation reaction in detail.

Results and Discussion

Photochemistry of Phenylsilyldiazomethane, 8. The photolysis of matrix-isolated silyldiazomethanes is a convenient way for the synthesis of silenes.[25−29] Silenes and their isomeric silylenes are of similar energy[30] and, in several cases, can be interconverted photochemically. Thus, visible irradiation of dimethylsilylene results in a [1,2]-H shift to 2-silapropene, which on UV irradiation rearranges back to the silylene.[20,23,31]

Scheme 3



Visible-light irradiation ($\lambda > 400$ nm) of phenylsilyldiazomethane, **8**, matrix-isolated in argon at 10 K, results in the complete disappearance of all IR absorptions assigned to **8**. Newly formed bands in the range 2192−2147 cm^{-1} indicate Si−H bonds (SiH stretching vibrations), and a weak absorption at 1640 is typical of a diazirine (NN stretching vibration). Several minutes of UV irradiation ($\lambda > 305$ nm) of the product mixture results in the partial recovery of **8**, which strongly indicates that phenylsilyldiazirine, **9**, is one of the products of the 400-nm photolysis of **8** (Scheme 3). This type of photochemical interconversion of diazo compounds with diazirines has been frequently observed with silyldiazomethanes.[25−28]

A second constituent of the 400-nm irradiation of **8** is 1-phenylsilene, **11**. This silene was independently synthesized by Maier et al. via a thermal retro Diels−Alder reaction in the gas phase with subsequent trapping of the products in solid argon.[33] Comparison of our IR data with that reported by Maier et al.[33b] allows attribution of absorptions at 2192, 1433, 1122, 965, 961, 852, and 738 cm^{-1} to silene **11**. The assignment of IR absorptions to diazirine **9** and silene **11** is in qualitative agreement with calculations at the B3LYP/6-311++G(d,p) level of theory.

The photolysis of **8** was also followed by UV spectroscopy, which shows the disappearance of the 220- and 228-nm absorptions of diazo precursor **8** and simultaneously the formation of a broad absorption with $\lambda_{\max} = 308$ nm assigned to the mixture of **9** and **11** (Figure 1). For silene **11**, an absorption maximum at 300 nm was reported,[33a] again in agreement with our finding.

Prolonged UV irradiation leads to the complete decomposition of **8**, **9**, and **11** and formation of a compound with strong IR absorptions at 1429, 1092, 735, and 695 cm^{-1}. In the UV−vis spectrum, an intense absorption with a maximum at 260 nm and a broad absorption with a maximum at 482 nm are growing in. The visible absorption results in an orange−red coloring of the matrix. Such broad absorptions in the visible range are characteristic of silylenes, while alkyl- and monoaryl-substituted silenes absorb around 250 and 300 nm, respectively.[31−34] DFT calculations of the IR spectrum of methyl(phenyl)silylene, **3f**,

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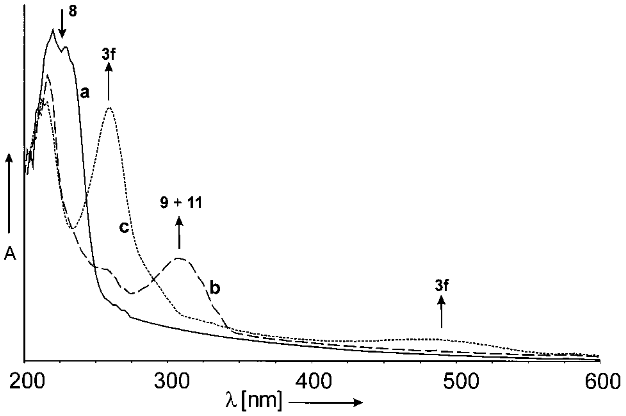

Figure 1. UV−vis spectra showing the photochemistry of phenylsilyldiazomethane **8**. (a) Spectrum of **8**, matrix-isolated in argon at 10 K. (b) Same spectrum after 400-nm irradiation. The main products are now diazirine **9** and silene **11**. (c) Same spectrum after 305-nm irradiation. The major constituent is now silylene **3f**.

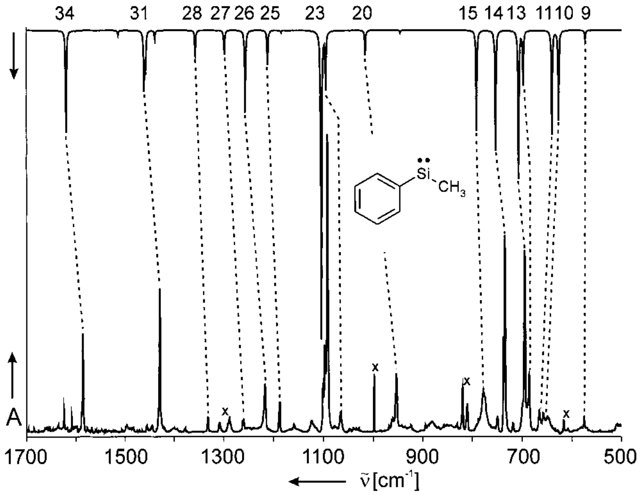

Figure 2. Bottom: IR spectrum (in absorbance) of methyl(phenyl)silylene **3f**, matrix-isolated in argon at 10 K. The silylene was generated by 305-nm irradiation of **8**. Top: IR spectrum of **3f**, calculated at the B3LYP/6-311++G(2d,p) level of theory.

demonstrate that this silylene is the major photoproduct (Figure 2, Table 1). West reported a UV−vis maximum of **3f** in a hydrocarbon glass at 490 nm,[32] close to the 482-nm absorption in argon.

The structures and relative energies of phenylsilylcarbene **10** and several of its rearranged products were calculated with the B3LYP method and a large triple-ζ basis set (6-311++G(d,p), all relative energies include the zero-point energy ZPE) (Figure 4). At this level of theory, the singlet−triplet splitting ΔE_{ST} of methylene is reproduced within 3 kcal/mol,[35] and for the singlet closed-shell molecules involved in this study the error should be even smaller. As expected, for carbene **10** a triplet ground state is calculated. The singlet close shell structure S-**10** could not be located; instead, a transition-state TS-**10** (20.2 kcal/mol above T-**10**), connecting silenes **11** and **12,** was found (Scheme 4). This transition state is 68.3 and 65.4 kcal/mol higher in energy than **11** and **12**, respectively. Thus, the photolysis of **8** on the singlet potential energy surface produces a structure close to TS-**10**. At this point, neither the intersystem crossing to triplet carbene T-**10** nor the [1,2]-Ph migration to **12** can compete with the [1,2]-H migration to silene **11**, which is the precursor of silylene **3f**.

Table 1. IR Spectroscopic Data of Methyl(phenyl)silylene, **3f**

	argon, 10 K		B3LYP/6-311++G(2d,p)			
no	ν, cm^{-1}	I^a	ν, cm^{-1}	I^a	sym	assignment^b
42	3085.7	2	3184	26	A′	C−H str
41	3075.1	15	3174	34	A′	C−H str
37	3055.3	4	3095	17	A′	CH_3 str
36	3023.6	6	3054	11	A″	CH_3 str
35	2964.9	6	2995	6	A′	CH_3 str
34	1585.5	33	1620	32	A′	ring str
32	1496.2	3	1515	1	A′	skel. ring, in pl. C−H
31	1429.5	48	1462	19	A′	skel. ring, in pl. C−H
29	1378.4	1	1439	2	A′	HCH bend
28	1332.0	5	1357	8	A′	skel. ring, in pl. C−H
27	1260.5	4	1299	7	A′	skel. ring, in pl. C−H
26	1217.7	16	1257	26	A′	HCH bend
25	1187.8	10	1212	11	A′	skel. ring, in pl. C−H
24	1159.3	2	1185	1	A′	skel. ring, in pl. C−H
23	1091.7	100	1105	100	A′	skel. ring, in pl. C−H
22	1065.1	6	1095	18	A′	skel. ring, in pl. C−H
20	953.6	19	1016	8	A′	ring breathing
15	777.7	13	792	32	A′	CH_3 rock
14	735.2	66	754	38	A″	C−H wag
13	695.5	61	709	47	A″	C−H wag
12	686.8	11	700	17	A′	
11	666.1	7	641	33	A′	Si−CH_3 str
10	657.9	3	629	28	A′	Si−CH_3 str
	649.7	3				
9	575.4	5	575	3	A″	C−H wag

[a] Relative intensity based on the strongest peak. [b] The assignment of experimental and calculated IR absorption is based on peak positions and peak intensities and for the weak absorptions is only tentative.

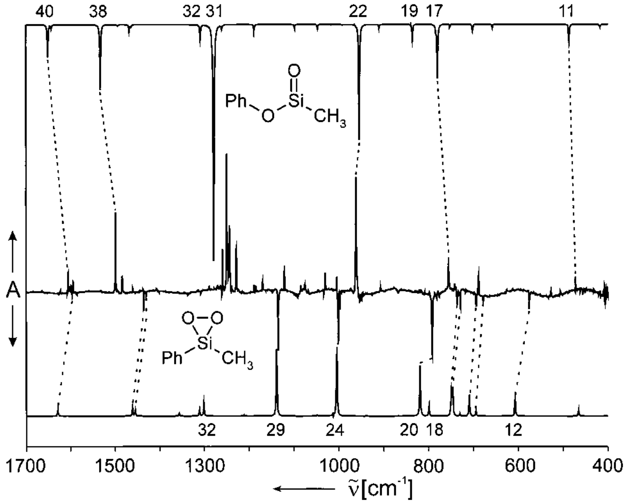

Figure 3. Center: Difference IR spectrum showing the photochemistry (420-nm irradiation) of methyl(phenyl)dioxirane **5f**. Bands pointing downward are disappearing during the irradiation and assigned to **5f**; bands pointing upward are appearing and mainly assigned to silaester **7f**. Bottom: IR spectrum of **5f**, calculated at the B3LYP/6-311++G(d,p) level of theory. Top: IR spectrum of **7f**, calculated at the B3LYP/6-311++G(d,p) level of theory.

The barrier for the [1,2]-H migration of **11** to give **3f** is 37.9 kcal/mol, and the reaction energy is almost zero. Although **11** is formed with a huge excess energy of 68.3 kcal/mol, the activation barrier should be large enough to efficiently prevent the **11** → **3f** rearrangement. Most likely this rearrangement is a photochemical secondary reaction during the UV photolysis of **8**/**9**.

Oxygenation of Methyl(phenyl)silylene, 3f. Irradiation ($\lambda > 305$ nm) of diazo compound **8** in a 0.5% O_2 doped argon matrix at 10 K produces mainly silylene **3f** and small amounts of oxidation products. As long as the matrix is kept at 10 K, no

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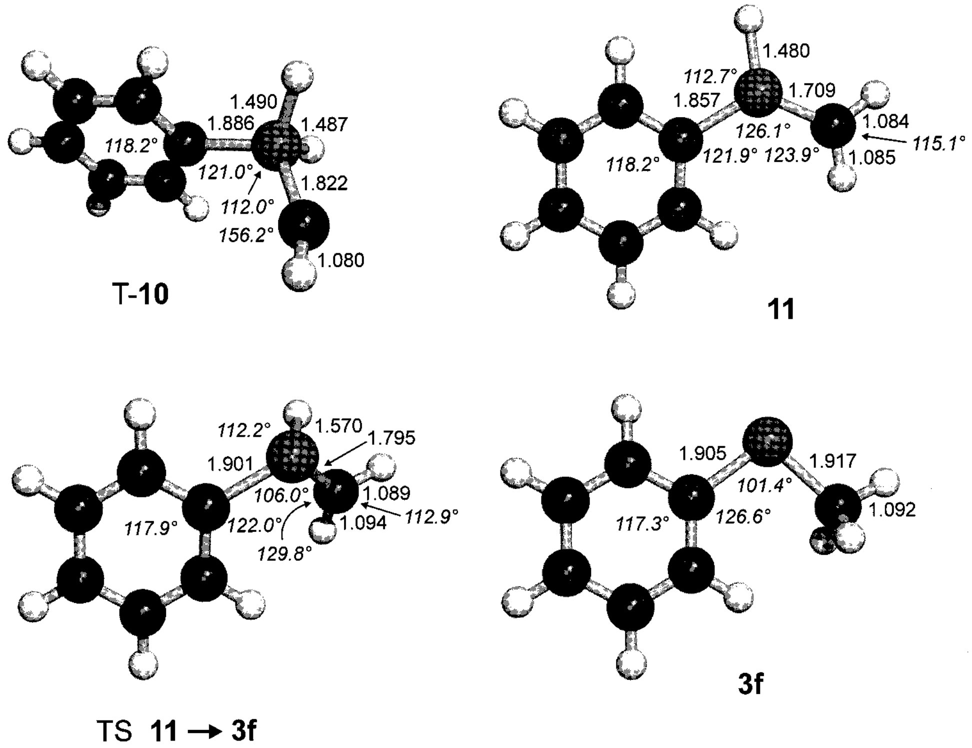
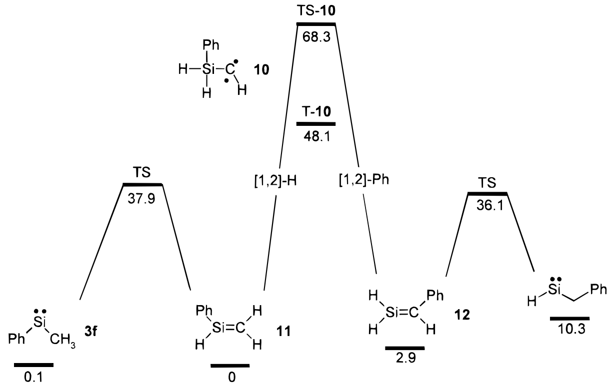
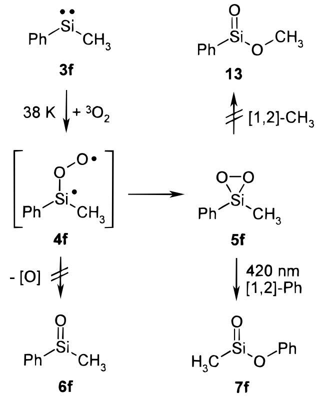


Figure 4. Geometries and some structural data of **3f** and several of its isomers calculated at the B3LYP/6-311++G(d,p) level of theory.

Scheme 4



Scheme 5



further reaction is observed; however, annealing the matrix at 38 K for 1 h results in the almost complete reaction of **8** and formation of a new compound, A, with strong IR absorptions at 1136, 1002, and 793 cm^{-1} (Figure 3). Compound A is photolabile, and on irradiation with $\lambda > 420$ nm readily rearranges to a compound B. This reaction sequence, thermal reaction with molecular oxygen on annealing in an O_2 doped argon matrix and photochemical rearrangement of the primary thermal product, was also observed with dimethylsilylene **3c**.[11] It is thus tempting to assign A to methyl(phenyl)dioxasilirane, **5f**, and B to either methyl(phenoxy)silanone, **7f**, or methoxy(phenyl)silanone, **13** (Scheme 5). Again, the comparison of the experimental and DFT-calculated IR data allows identification of the species formed in the matrix and confirmation of this assignment (Tables 2 and 3).

The three-membered ring in **5f** shows two characteristic vibrations: the strong Si−O stretching mode at 1002 cm^{-1} (calculated, 1005 cm^{-1}) and the weak O−O stretching mode at 577 cm^{-1} (calculated, 608 cm^{-1}). In **5c**, these two absorptions are found at 1013 cm^{-1} (strongest peak in the spectrum) and 554 cm^{-1} (weak),[11] which is an additional confirmation of the assignment of A to **5f**. On $^{18}O_2$ labeling, the Si−O stretching vibration is red-shifted by 25.3 cm^{-1} (calculated, 28 cm^{-1}) and the O−O stretching vibration by 23.5 cm^{-1} (calculated, 21 cm^{-1}). Other products, and in particular the silanone oxide **4f**, are not found as thermal products of the oxygenation of silylene **3f**.

The major constituent of the photolysis products of dioxasilirane **5f** was identified as silaester **7f**. The intense absorption at 963 cm^{-1} (calculated: 953 cm^{-1}) shows an isotopic shift of −24.6 cm^{-1} (calculated: −25 cm^{-1}) in $^{18}O_2$-**7f** and is assigned to the Si−O(Ph) stretching vibration. Two other strong absorptions at 1250 and 1244 cm^{-1} with pronounced ^{18}O-isotopic shifts of −26.2 and −44.2 cm^{-1} are assigned to the C−O and the Si=O stretching vibration of **7f**, respectively (Table 3). Again, band positions, intensities, and isotopic shifts are in excellent agreement with the results of the DFT calculations. In dimethylsilanone, the Si=O stretching vibration is found at 1210 cm^{-1},[36,37] and in dichlorosilanone at 1240 cm^{-1},[38] close to that of **7f**.

In addition to the absorptions of **7f**, several other medium-intensity bands (1484, 1229, 1121, 689, and 528 cm^{-1}) are found in the IR spectrum of the photolysis products of **5f**, which

Table 2. IR Spectroscopic Data for Methyl(phenyl)dioxasilirane, **5f**

	argon, 10 K			B3LYP/6-311++G(d,p)				
no	ν, cm^{-1}	I^a	ν_i/ν^b	ν, cm^{-1}	I^a	ν_i/ν^b	sym	assignment^c
48	3086.3	2	1.000	3191	11	1.000	A′	C−H str
47	3075.2	1		3183	13	1.000	A′	C−H str
46	3071.6	3	1.000	3175	5	1.000	A′	C−H str
44	3058.7	2	1.000	3156	3	1.000	A′	C−H str
43	3024.7	1		3122	1	1.000	A′	CH$_3$ str
42	3015.1	3	1.000	3099	2	1.000	A″	CH$_3$ str
40	1596.8	17	1.000	1629	10	1.000	A′	ring str
37	1435.0	30	1.000	1461	13	1.000	A′	skel. ring, in pl. C−H
36	1432.5	2	1.000	1456	3	1.000	A′	HCH bend
35	1429.5	7	1.000	1455	6	1.000	A″	HCH bend
34	1336.9	3	1.000	1357	4	1.000	A′	skel. ring, in pl. C−H
33	1307.5	5	1.000	1311	10	1.000	A′	HCH bend, ring str
32	1260.3	10	0.998	1301	20	1.000	A′	HCH bend
31	1218.0	4		1211	2	1.000	A′	in pl. C−H bend
29	1135.6	92	0.999	1139	97	0.999	A′	skel. ring, in pl. C−H
27	1033.7	4	0.999	1049	1	0.999	A′	skel. ring, in pl. C−H
25	1013.1	1		1013	3	1.000	A′	ring breathing
24	1002.1	81	0.975	1005	100	0.972	A′	SiO str
	998.2	28						
20	792.7	100	0.999	820	72	0.998	A′	CH$_3$ rock
19	783.4	4	0.994	800	15	0.998	A″	CH$_2$ twist
	777.0	4						
18	737.5	29	0.999	750	40	1.000	A″	C−H wag
17	729.9	17	1.004	747	38	0.996	A′	SiC str, CH$_3$ def
16	717.6	3	0.952	731	3	0.956	A″	SiO def, CH$_3$ def
15	694.5	39	1.000	710	31	1.000	A″	C−H wag
14	678.8	8	0.991	695	8	0.986	A′	
12	576.7	28	0.959	608	25	0.965	A′	O$_2$ str, CH$_3$ def
11	456.3	11	0.999	466	9	1.000	A″	C−H wag

[a] Relative intensity based on the strongest peak. [b] Ratio of the frequencies of the ^{18}O vs ^{16}O isotopomers. [c] The assignment of experimental and calculated IR absorption is based on peak positions and peak intensities and for the weak absorptions is only tentative.

Table 3. IR Spectroscopic Data for Methyl(phenoxy)Silanone, **7f**

	argon, 10 K			B3LYP/6-311++G(d,p)			
no	ν, cm^{-1}	I^a	ν_i/ν^b	ν, cm^{-1}	I^a	ν_i/ν^b	assignment^c
47	3061.8	2	1.000	3190	1	1.000	C−H str
46	3038.0	1	1.000	3183	2	1.000	C−H str
40	1606.3	13	0.998	1634	9	1.000	ring str
39	1598.3	3	1.000	1628	1	1.000	ring str
38	1498.6	51	0.999	1520	17	0.999	skel. ring, in pl. C−H
36				1454	1	1.000	HCH bend
32	1259.1	24	0.998	1299	4	0.999	HCH bend
31	1250.0	89	0.979	1263	100	0.982	C−O str, Si=O str
30	1243.7	30	0.964	1246	1	0.974	C−O str, Si=O str
29	1170.1	7	0.999	1187	2	0.999	in pl. C−H bend
27	1075.8	6	1.000	1095	1	1.000	skel. ring, in pl. C−H
26	1031.2	14	0.999	1044	1	0.999	skel. ring, in pl. C−H
22	962.8	100	0.975	953	29	0.974	Si−O str, ring breath.
21	907.5	2	1.000	911	1	0.998	C−H wag
19	817.6	2	1.000	834	3	0.998	CH$_3$ rock
18				782	2	0.999	CH$_3$ def
17	756.4	30	0.999	768	16	0.997	C−H wag
16	739.9	1	1.001	746	1	0.996	C−O def, C−H wag
15				688	2	1.000	C−H wag
11	473.0	14	0.978	480	5	0.983	
9				414	1	0.976	

[a] Relative intensity based on the strongest peak. [b] Ratio of the frequencies of the ^{18}O vs ^{16}O isotopomers. [c] The assignment of experimental and calculated IR absorption is based on peak positions and peak intensities and for the weak absorptions is only tentative.

indicates the formation of a second, minor photoproduct. Since only the strongest peaks of this minor product are observed, the identification is difficult. On the basis of the comparison with calculated IR spectra, this minor product is tentatively assigned to methoxy(phenyl)silanone, **13**, while several other possible products (e. g., methyl(phenyl)silanone) were ruled out.

The formation of the silaesters **7f** and **13** requires the cleavage of the O−O bond in **5f** and migration of the phenyl or methyl group, respectively. This rearrangement might proceed via a dioxydiradical as an intermediate or, if the diradical is not a minimum on the singlet potential energy surface, be a concerted reaction. The preference of the phenyl migration compared with the methyl migration reflects different migratory aptitudes of phenyl and methyl; however, our experiments do not reveal details of the mechanism of the rearrangement.

The relative stability of the products of the oxygenation of **3f** was calculated using DFT methods (B3LYP/6-311++G(d,p) + ZPE) (Scheme 6). At this level of theory, the experimental IR[39,40] and NMR[41] spectra of carbonyl oxides are nicely reproduced; we therefore used B3LYP theory for the calculation of ground-state properties of **4f** and its isomers.

The reaction of silylene **3f** with $^3O_2$ to give the syn silanone oxide **4f** in its singlet ground state is calculated to be exothermic by 27.8 kcal/mol. The syn conformer of **4f** is clearly a minimum on the potential energy surface, although the activation barrier for the cyclization to **5f** is less than 1 kcal/mol. The anti isomer is even less stable, and the very shallow minimum could only be located with the large triple-ζ, but not with a double-ζ basis set. The singlet−triplet splitting of syn **4f** is calculated to 8.2 kcal/mol, and thus, the spin-allowed reaction of singlet silylene **3f** with $^3O_2$ to give triplet silanone oxide T-**4f** is still exothermic

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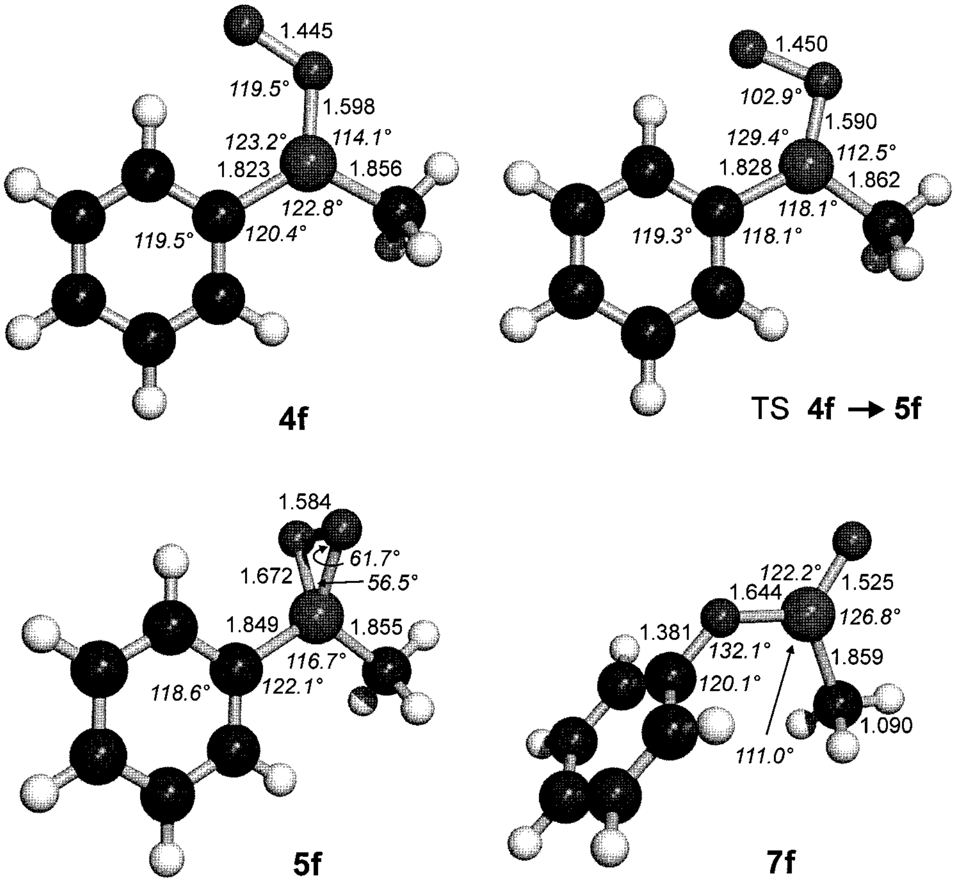
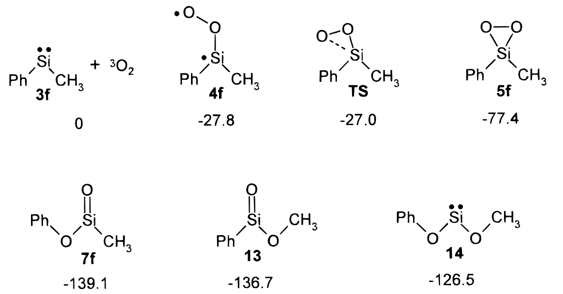


Figure 5. Geometries and some structural data of **5f** and several of its isomers calculated at the B3LYP/6-311++G(d,p) level of theory.

Scheme 6



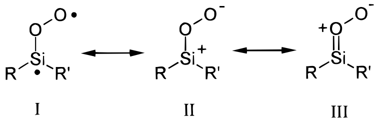
by 19.6 kcal/mol. The cyclization of S-**4f** to dioxasilirane **5f** is strongly exothermic by another 49.6 kcal/mol.

These results indicate that silanone oxide **4f** is a very labile species lying in a shallow minimum. Even at low temperature the rapid rearrangement to dioxasilirane **5f** is expected, in particular if the excess energy released on the primary reaction of **3f** with $^3O_2$ is considered.

Although the photochemical rearrangement of **5f** produces silaester **7f** with an unfavorable Si═O bond, this rearrangement is calculated to be exothermic by 61.7 kcal/mol. The energy required to form a Si═O bond is more than compensated for by the loss of the strain energy in the three-membered ring, substitution of a Si−C bond by a Si−O bond, and formation of an additional C−O bond. The migration of a methyl group and formation of silaester **13** is only slightly less exothermic (−59.4 kcal/mol), and even the migration of both the methyl and the phenyl substituent in **5f**, producing silylene **14**, is strongly exothermic (Scheme 6).

Electronic Structure of Silanone Oxide 4f and Dioxasilirane 5f. At the B3LYP/cc-pVTZ level of theory, the C−O distance in formaldehyde oxide **1** (R = R′ = H) is calculated to 1.257 Å, the O−O distance to 1.352 Å, and the C−O−O bond angle to 119.1°. At 1.407 Å, the O−O bond distance in the parent silanone oxide **4a** is considerably longer, and the Si−O−O bond angle of 115.9° is smaller than the C−O−O bond angle in formaldehyde oxide. The substituents in syn-**4f** result in a further lengthening of the O−O bond distance to 1.445 Å (Figure 5). The Si−O distance in **4f** is calculated to be 1.598 Å. While the parent silanone oxide **4a**, like many silyl radicals, is pyramidalized at the silicon atom, the coordination at the silicon atom of **4f** is trigonal planar and the molecule shows C_s symmetry. Obviously, the energy required for the planarization is more than compensated for by the formation of a delocalized π system between the phenyl group and the Si−O−O moiety.

Similar to the carbonyl oxides **1**, diradicaloid (I) and ionic (II and III) resonance structures of silanone oxides **4** can be formulated. Resonance structure II seems to be most appealing since the charges are located at the electropositive silicon and electronegative terminal oxygen atom, respectively. The NPA atomic charges of **4f**, calculated at the B3LYP/6−31 g(d,p) level of theory, reveal a different picture. With −0.61 au, the central oxygen atom in **4f** is more negatively charged than the terminal oxygen atom (−0.47)—in contradiction to resonance structures II and III—and the negative charges at the carbon atoms attached to silicon are even higher (phenyl ipso carbon, −0.62; methyl, −1.25).



In dioxasilirane **5f,** the oxygen atoms are charged by −0.61 and the silicon atom by +2.1 au. The charges at the carbon atoms attached to silicon are very similar to that in **4f**. From that we conclude that the charge distribution in **4f** reflects the differences in the electronegativities of the atoms rather than a special weight of resonance structure II or III. The small singlet−triplet splitting, on the other hand, indicates a large diradicaloid character of silanone *O*-oxides **4**.

The transition state for the **4f** → **5f** rearrangement is only 0.8 kcal/mol above **4f**, and its structure is very close to that of **4f**. The C(Ph)−Si−O−O dihedral angle in the TS is now 12.6° (0° in **4f**), and the Si−O−O bond angle reduced from 119.5° in **4f** to 102.9° (Figure 5). The O−O bond is slightly longer and the Si−O bond slightly shorter than in **4f**. The out-of-plane twisting of the Si−O−O group results in a less efficient conjugation with the phenyl π system and buildup of charge at the terminal oxygen atom.

At 1.59 Å, the calculated O−O bond distance in dioxasilirane **5f** is significantly longer than the O−O distances in the parent dioxirane **2** (R = R′ = H, R(O−O) = 1.516 Å)[42] and dimesityldioxirane (R = R′ = mesityl, R(O−O) = 1.503 Å).[9] The Si−O bond lengths of 1.85−1.86 Å are within the normal range of Si−O single bonds. As expected, the O−Si−O bond angle of 56.8° is smaller than the O−C−O angles of dioxiranes (66° in the parent system and 60° in the dimesityl derivative).

Conclusion

Silylene **3f** is easily accessible in high yields by matrix photolysis of phenylsilyldiazomethane **8**. The combination of matrix IR spectroscopy and DFT calculations allows the detailed investigation of reactions of **3f** with small molecules trapped in the matrix. The reaction of silylene **3f** with $^3O_2$ (Scheme 2) parallels that of the well-established oxidation of carbenes (Scheme 1).[4] The major difference is the larger exothermicity and smaller activation barrier of the **4** → **5** compared with the **1** → **2** rearrangement. Although the calculated barrier depends on the method used for the calculation (MP2 predicts a barrier of about 6 kcal/mol,[11,13] B3LYP ∼1 kcal/mol), it is safe to argue that the activation barrier can be overcome by the thermal excess energy of the oxygenation of silylene **3**. The only reactions where the oxygenation of a silylene could be directly monitored in low-temperature matrixes are that of dimethyl-[11] and methyl(phenyl)silylene, **3c** and **f**, respectively. In both cases, the dioxasiliranes **5** are the only detectable products, although the reaction temperature of 30−45 K should allow isolation of very labile intermediates. We thus conclude that silanone oxides **4** are too labile to be isolated as intermediates in silylene oxidations.

Experimental Part

Calculations. The ab initio and density functional theory calculations were carried out using the Gaussian 98 suite of programs[43] and standard basis sets on an IBM RS/6000 workstation. Geometry optimization and frequency calculations of the singlet species were performed at the B3LYP level of theory with 6-31G(d,p) and 6-311++G(d,p) basis sets. For the triplet species, UB3LYP was used with the same basis set.

Materials and General Methods. ^{1}H and ^{13}C NMR spectra were taken at 200.1 and 50.3 MHz, respectively (Bruker AM 400), in $CDCl_3$ as the solvent. Mass spectra (EI, 70 eV) were taken on a Varian MAT CH7 instrument. All reactions involving moisture-sensitive silicon reactants were performed under an atmosphere of dry argon. Precursors for matrix experiments were purified by preparative-scale GLC using a Siemens RGC 202 gas chromatograph.

Phenylsilyl Trifluoromethanesulfonate. The triflate was prepared in a way analogous to a procedure by Bassindale and Stout[44] for the synthesis of dimethylsilyl triflate. Trifluoromethanesulfonic acid (36 mmol, 3.2 mL) was added dropwise to neat diphenylsilane (36 mmol, 6.6 g) at room temperature. After complete addition, benzene (formed as coproduct) was slowly removed under vacuum. The yield of phenylsilyl triflate was quantitatively obtained. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.32−7.67 (m, 5 H, Ph), 5.25 (s, 2 H, SiH_2). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 135.79, 133.32, 129.21, 128.74, 126.52, 121.90, ^1J(C,F) 314 Hz.

Phenylsilyldiazomethane (8). 8 was synthesized in a way analogous to a procedure by Martin[45] for the synthesis of (trimethylsilyl)diazomethane. Freshly prepared phenylsilyl trifluoromethanesulfonate (36 mmol, 9.3 g) was added dropwise to equimolar quantities of diazomethane (36 mmol, 1.5 g in 100 mL of diethyl ether) and ethyldiisopropylamine (40 mmol, 5.2 g) at −65 °C. After complete addition, the mixture was slowly warmed to 0 °C and the white precipitate was removed by rapid filtration through a frit. The yellow solution was concentrated in a first step at −50 °C in vacuo in order to remove excess diazomethane. In a second step, **8** (0.8 g, 15%) was obtained after distillation of the residue under reduced pressure (∼30 °C/0.2 Torr). The yellow distillate was finally purified by preparative GLC (OV 101, 0.5 m, 60 °C, detector/injector 80 °C). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.60−7.65 (m, 2 H, Ph), 7.40−7.42 (m, 3 H, Ph), 4.77 (d, 2 H, SiH_2), 2.87 (t, 1 H, CHN_2).^{13}C NMR ($CDCl_3$, 50 MHz): δ 135.11, 130.40, 128.26, 15.47. EI−MS (m/e (%)): 148 (26) [M^+], 120 (18) [$M^+ - N_2$], 119 (38) [$M^+ - (N_2 + H)$], 105 (100), 93 (28), 91 (19). HRMS calcd for $C_7H_8N_2Si$ 148.0457, obsd 148.0456. IR (argon, 10 K): 3063.1 (1), 2195.3 (2), 2180.0 (2), 2154.6 (3), 2134.0 (7), 2093.0 (14), 2088.2 (100), 2082.9 (51), 1433.0 (5), 1274.0 (2), 1265.8 (8), 1158.0 (2), 1119.3 (11), 951.5 (2), 940.4 (9), 862.2 (100), 860.3 (5), 856.8 (87), 853.7 (9), 851.1 (11), 847.7 (1), 779.1 (3), 746.4 (2), 709.8 (6), 699.0 (2), 587.0 (4), 507.0 (1), 495.6 (3), 451.9 (1) cm^{-1} (relative intensity). UV (argon, 15 K): λ_{max} = 220, 228 nm.

Matrix Spectroscopy. Matrix isolation experiments were performed by standard techniques with an APD CSW-202 Displex closed cycle helium cryostat. Matrixes were produced by deposition of argon (Messer Griesheim, 99.9999%) or mixtures of argon and oxygen (Messer Griesheim, 99.998%) on top of a CsI (IR) or sapphire (UV−vis) window at a rate of approximately 0.15 mmol/min at 30 K. Infrared spectra were recorded by using either a Bruker IFS66 FTIR or an Equinox 55 FTIR spectrometer with a standard resolution of 0.5 cm^{-1} in the range 400−4000 cm^{-1}. UV−vis spectra were recorded

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on a Hewlett-Packard 8452A diode array spectrophotometer with a resolution of 2 nm. Irradiations were carried out using 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 wavelength selection, dichronic mirrors ("cold mirrors") in combination with Schott cutoff filters (50% transmission at the wavelength specified) were used.

Phenylsilyldiazirine (9). Irradiation of matrix-isolated phenylsilyldiazomethane, **8**, with light of the wavelength $\lambda > 400$ nm produced phenylsilyldiazirine, **9**. IR (argon, 10 K): 2174.8 (13), 2171.7 (7), 2162.0 (5), 2151.7 (31), 2149.9 (6), 2147.1 (7), 1638.7 (4), 1433.4 (18), 1294.9 (5), 1191.3 (1), 1121.4 (20), 948.7 (4), 936.8 (35), 858.6 (100), 855.7 (3), 848.1 (4), 844.3 (5), 840.5 (3), 838.9 (9), 701.0 (28), 590.2 (3), 582.1 (10), 470.4 (9) cm^{-1} (relative intensity).

1-Phenylsilene (11). Irradiation of matrix-isolated phenylsilyldiazomethane, **8**, with light of the wavelength $\lambda > 400$ nm produced also 1-phenylsilene, **11**. IR (argon, 10 K): 2192.3 (13), 1433.4 (56), 1317.9 (3), 1282.5 (3), 1191.3 (3), 1122.4 (100), 964.5 (28), 960.9 (19), 917.7 (7), 851.7 (38), 737.6 (42), 656.7 (10), 646.2 (6), 450.7 (9) cm^{-1} (relative intensity).

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