Silicon Migration from Oxygen to Carbon and Decarbonylation in Methoxytriphenylsiloxycarbene
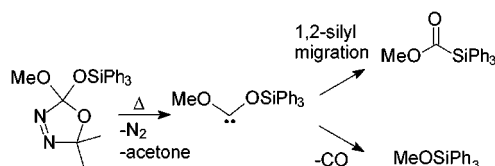
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ABSTRACT

Thermolysis of 2-methoxy-2-triphenylsiloxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline affords methyl triphenylsilylformate and methyl triphenylsilyl ether via methoxytriphenylsiloxycarbene. Kinetics show that the carbene undergoes *reversible* 1,2-triphenylsilyl migration (Brook rearrangement) as well as *irreversible* decarbonylation. Computed transition states and activation energies (B3LYP/6-31+G*) suggest that the migration of the silyl group from oxygen to carbon occurs through an "in plane" transition state with the carbene lone pair forming a new bond to silicon. Decarbonylation involves a four-membered ring, achieved by nucleophilic attack of the oxygen atom of the methoxy group at silicon.

Δ^3-1,3,4-Oxadiazolines (**1**) are now established thermal sources of dialkoxy-, alkoxyamino-, and alkoxythioalkoxy-carbene intermediates[1,2] that can also function as photo-chemical precursors of dialkylcarbenes or cycloalkylidenes for kinetic studies by LFP (Scheme 1).[3] The special properties of silyl moieties in carbene chemistry that have emerged recently[4,5] including the apparent migration of trimethylsilyl to the carbene (or carbenoid) site of a cyclopropylidene, to

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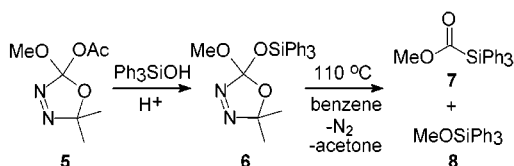
Scheme 1
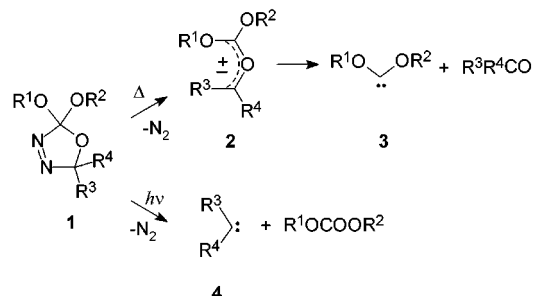
the exclusion of allene formation (eq 1),[6] led us to try to generate (MeO(Ph$_3$SiO)C:) by the oxadiazoline route.

(1)
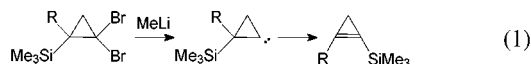
Treatment of acetoxyoxadiazoline **5**[7] with triphenysilanol and catalytic trifluoroacetic acid afforded **6** in ca. 33% yield (Scheme 2). After chromatography on silica, **6** was heated

Scheme 2

in degassed benzene for 24 h at 110 °C, in a sealed tube. Major products were acetone, methyl triphenylsilylformate (**7**), and methyl triphenylsilyl ether (**8**), with **7**:**8** = 1:3 (Scheme 2).

Isolation of **7** and heating it in benzene (150 °C, 24 h, sealed tube) converted it cleanly to **8**, as reported by Brook and co-workers.[8] The rate constant for this process at 110

°C was only 6.5×10^{-6} s^{-1}, too small to account for the formation of **8** from oxadiazoline **6** via **7** (Table 1).

Table 1. Thermolysis Rate Constants Determined by ^{1}H NMR Spectroscopy

precursor	solvent	thermolysis rate constant (110 °C)
6	benzene	$k_{obs} = 8.1 \times 10^{-5}$ s^{-1}
	methanol	$k_{obs} = 6.1 \times 10^{-5}$ s^{-1}
7	benzene	$k_{obs} = 6.5 \times 10^{-6}$ s^{-1}
	methanol	$k_{obs} = 8.2 \times 10^{-4}$ s^{-1}

Thermolysis of **6** in toluene did not afford bibenzyl, and added TEMPO did not lead to any detectable products of radical trapping.[9,10] It is therefore likely that carbene **9** (Scheme 3) is responsible for the formation of both **7** and **8**.

Scheme 3
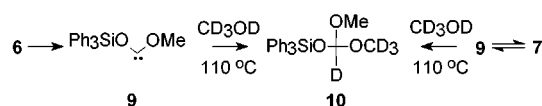
Thermolysis of **6** in methanol-d_4 afforded orthoformate **10**, the ^{2}H NMR spectrum of which showed both the expected OCD$_3$ and the orthoformyl CD signals. However, the yield was low (∼8%) and both ester **7** and ether **8** were coproducts. The majority of the product was ether **8** (unlabeled). The rate constant for conversion of **7** to **8** is much larger in methanol than in benzene (Table 1), suggesting that this process occurs through a polar transition state. Thermolysis of **7** in CD$_3$OD at 110 °C also afforded **10**, again in low yield, Scheme 3. Thus, it appears that rearrangement of the carbene intermediate is fast relative to trapping with methanol, which we assume occurs with a bimolecular rate constant (ignoring an isotope effect) of ca. 1×10^5 M^{-1} s^{-1}, the measured rate constant for trapping dimethoxycarbene.[11]

The most straightforward interpretation of these results involves thermal cycloreversion of **6**, to generate nitrogen gas and a carbonyl ylide[12] that fragments rapidly to acetone and **9**. Carbene **9** rearranges by migration of the triphenylsilyl group from oxygen to carbon by a Brook rearrangement. Several cases of gas-phase migrations of an alkyl group from oxygen to carbon in dialkoxycarbenes are known. From the preferential migration of 2,2,2-trifluoroethyl relative to methyl or ethyl,[13] it appears that negative charge develops in the migrating group. Those dialkoxycarbenes do not rearrange appreciably in solution, however, suggesting that triphenylsilyl is a superior migrating group. This discovery has implications for the thermal generation of other carbenes by rearrangements of silyl analogues. It may be possible to design systems with other double bonds, such as C=N, that will rearrange similarly (i.e., diaminocarbenes, R$_2$NC(=NR)-SiR$_3$ → R$_2$N(NRSiR$_3$)C: and alkoxyaminocarbenes, ROC-(=NR)SiR$_3$ → RO(NRSiR$_3$)C:, or R$_2$NC(=O)SiR$_3$ → R$_2$N-(OSiR$_3$)C:).

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(9) It is well established that other metallo formates containing Sn, Se, or Te can undergo thermal or photochemical M−C bond homolysis to give acyl radical/metal radical pairs. Acyl radicals then can undergo either decarboxylation or decarbonylation. See: Lucas, M. A.; Schiesser, C. H. *J. Org. Chem.* **1996**, *61*, 5754 and references therein.

(10) Some dialkoxycarbenes fragment in solution to radical pairs. See: (a) Venneri, P. C.; Warkentin, J. *J. Am. Chem. Soc.* **1998**, *120*, 11182. (b) Merkley, N.; El-Saidi, M.; Warkentin, J. *Can. J. Chem.* **2000**, *78*, 356. (c) Reid, D. L.; Hernández-Trujillo, J.; Warkentin, J. *J. Phys. Chem. A* **2000**, *104*, 3398.

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To probe for the mechanism of silyl migration, B3LYP/6-31+G* calculations with the Gaussian 98 suite of programs[14] were carried out on the 1,2-silyl migration in a model compound, methoxysiloxycarbene (MeOCOSiH₃).

The transition state structures, **TS$_{AD}$** and **TS$_{BE}$**, for 1,2-silyl migration in the trans−trans conformer (**A**) and the cis−trans conformer (**B**) of methoxysiloxycarbene are shown in Figure 1. Also shown are the corresponding products, anti
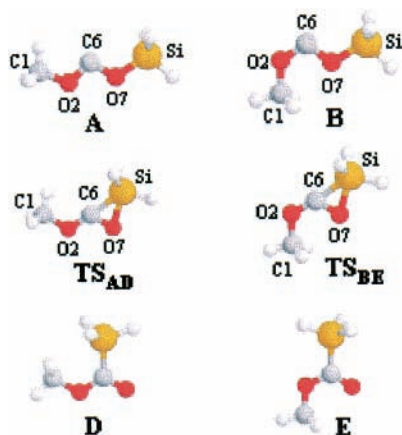

Figure 1.

methyl silylformate (**D**) and syn methyl silylformate (**E**). The computed activation barriers for 1,2-silyl migration in **A** and **B** are 10.3 and 7.62 kcal/mol, respectively. These barriers were calculated as the differences between the zero-point corrected electronic energies of the transition states and that of **A**, the lowest energy ground-state carbene conformer.

Both transition state structures are in keeping with nucleophilic attack by the carbene lone pair at silicon. The dissociating O7−Si bond lengthens from 1.71 Å in **A** to 1.92 Å in **TS$_{AD}$**, while the C6−O7−Si angle shrinks from 115.4° to 73.4°. Likewise, the O7−Si bond lengthens from 1.72 Å in **B** to 1.91 Å in **TS$_{BE}$**, while the C6−O7−Si angle shrinks from 114.8° to 73.7°. The O2−C6−O7−Si dihedral angles, 175.6° in **TS$_{AD}$** and 180.0° in **TS$_{BE}$**, indicate essentially planar transition state structures (Figure 1). This means that in these structures, the breaking O7−Si bond eclipses the carbene σ nonbonding orbital. The charge development in the two transition states, obtained from natural population
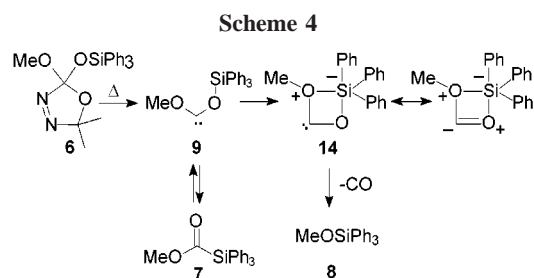
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analysis (NPA),[15] is consistent with nucleophilic attack by the carbene lone pair at silicon. There is a buildup of 0.197e and 0.178e on the silyl group, along with 0.003e and 0.025e on C6, and a loss of 0.164e and 0.157e from O7 in **TS$_{AD}$** and **TS$_{BE}$**, respectively. The electron buildup on C6 is likely due to the developing C6−O7 double bond.

Frontier molecular orbital coefficients obtained for methoxysiloxycarbene also support the notion of nucleophilic attack by the carbene lone pair at silicon. The magnitudes of these coefficients suggest that the HOMO is primarily made up of nonbonding σ orbitals on O2, O7, and C6 while the LUMO is in essence the O7−Si σ* orbital. Thus, since the geometries of **A** and **B** allow maximum interaction between the C6 σ nonbonding orbital (HOMO) and the O7−Si σ* orbital (LUMO), they favor nucleophilic attack by the carbene σ lone pair at silicon. This mechanism resembles one postulated for acyl migrations in acyloxycarbenes that involves nucleophilic attack of the carbene carbon onto the carbonyl carbon during acyl migration.[16]

The mechanism by which the carbene and the ester are decarbonylated is more complex. The overall result in the case of **9** is also reminiscent of the rearrangement of alkoxyhalocarbenes, which do so by fragmentation to carbon monoxide, carbocation, and halide ion (eq 2). The latter then

$$X\!\!\diagdown\!\!OR \longrightarrow \left[X^- \; \overset{O}{\underset{}{C}} \; {}^+R \right] \longrightarrow RX \; + \; CO \qquad (2)$$
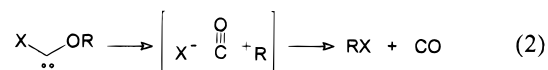
combine, in the absence of carbocation scavengers, to afford alkyl halide in high yield.[17,18] An analogous process in the case of **9** would involve the triphenylsilyl cation/methoxide anion pair. However, methoxide is sufficiently more basic than halide ions to make such an ion pair mechanism unlikely in benzene. We propose that the ester is decarbonylated via the carbene which cyclizes to afford the four-membered intermediate **14** by attack of the silophilic methoxy oxygen at silicon (Scheme 4).

Scheme 4

This mechanism is supported by the fact that the conversion of ester **7** to ether **8** is more than 10-fold slower than thermolysis of **6** in benzene, but **6** gives rise to **7** and **8** in

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1:3 ratio. Moreover, both **6** and **7** afforded the same product of apparent trapping of **9** with methanol.

Two pathways for the decarbonylation of methoxysiloxy-carbene were computed by means of B3LYP/6-31+G*. The first was for nucleophilic attack by O7 on C1 of **B**, while the second was for nucleophilic attack by O2 on the silicon atom of **C**. The ground-state structures, **B** and **C**, as well as the corresponding transition state structures, **TS$_{BF}$** and **TS$_{CF}$**, are shown in Figure 2. The decarbonylation product, methyl
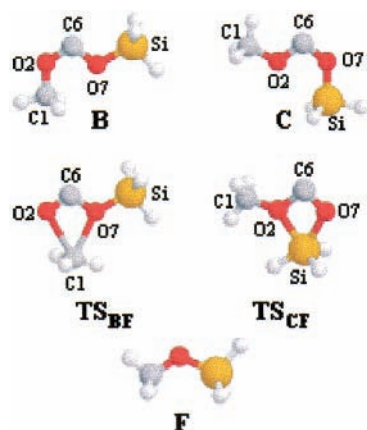

Figure 2.

silyl ether (**F**), is also shown in Figure 2.

In the first pathway, the dissociating C1–O2 and C6–O7 bonds lengthen from 1.463 and 1.345 Å in **B** to 2.454 and 1.370 Å in **TS$_{BF}$** while the developing O2–C6 bond shortens from 1.312 to 1.207 Å. The C1–O2–C6 angle shrinks from 122.5° in **B** to 93.4° in **TS$_{BF}$**, while the O2–C6–O7 angle increases slightly from 110.4° to 113.2°. Moreover, the C1O2C6O7 dihedral angle in **TS$_{BF}$** is 0.0°, meaning that the breaking C1–O2 bond is aligned with the O7 σ nonbonding orbital. These features are consistent with nucleophilic attack by O7 on C1 in concert with the formation of carbon monoxide, C6–O2. NPA analysis

indicates that there is a buildup of 0.130e on C1 and a depletion of 0.048e at O7 as well as a buildup of 0.017e on O2 and a loss of 0.119e from C6. These trends are in accord with nucleophilic attack by O7 at C1.

For the second pathway, the breaking O7–Si and O2–C6 bonds become elongated from 1.337 and 1.729 Å in **C** to 1.471 and 1.968 Å in **TS$_{CF}$**, respectively. The Si–O7–C6 and O2–C6–O7 angles decrease from 107.5° and 128.0° in **C** to 98.4° and 104.0° in **TS$_{CF}$**. The O2–C6–O7–Si dihedral angle in **TS$_{CF}$** is 1.9°, indicating that the breaking O7–Si bond is aligned with the O2 σ nonbonding orbital. Moreover, there is a buildup of 0.116e on O2 and 0.060e on the silicon atom along with a loss of 0.021e from C6 and 0.124e from O7. These features are in accord with nucleophilic attack by the methoxy oxygen on the silicon atom with concomitant formation of carbon monoxide. Intrinsic coordinate (IRC) calculations confirmed that **TS$_{CF}$** is the transition state for decarbonylation of **C** and suggested that the mechanism may be concerted.

The calculated activation barrier for decarbonylation via the cis–trans conformer (**B**) is 39.8 kcal/mol, and that for decarbonylation via the trans–cis conformer (**C**) is 16.9 kcal/mol. On the basis of these activation barriers, decarbonylation should occur exclusively by nucleophilic attack of the methoxy oxygen σ lone pair at the silyl moiety of the trans–cis conformer (**C**). This conclusion is also consistent with the frontier molecular orbital coefficients. As described earlier, the HOMO is made up primarily of nonbonding σ orbitals on O2, O7, and C6, while the LUMO consists primarily of the O7–Si σ* orbital. Thus, the geometry of the trans–cis conformer (**C**) is set up for maximum interaction between the O2 σ orbital (HOMO) and the O7–Si σ* orbital (LUMO). For the alternative pathway (i.e., decarbonylation via **B**), although the HOMO has a sizable coefficient on O7, the coefficient of the LUMO on C1 is negligible, making nucleophilic attack by O7 at C1 an unlikely process.