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Evidence for Formation of Silenes Strongly Influenced by Reversed Si═C Bond Polarity

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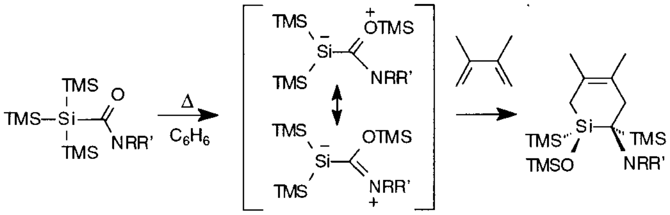
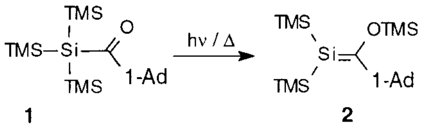
ABSTRACT



Transient silenes that are strongly influenced by reversed Si═C bond polarization are formed upon heating of tris(trimethylsilyl)silylamides. The silenes are trapped with 2,3-dimethyl-1,3-butadiene to quantitatively yield only one of the possible diastereomers of the functionalized cyclic allylsilanes.

Si═C double-bonded compounds, so-called silenes,[1] are highly reactive species. They tend to dimerize in the absence of reaction partners, and it was not until 1981 that Brook and co-workers managed to generate the first silene, 1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-2-(1-adamantyl)-1-silaethene (**2**, Scheme 1), that could be isolated and studied by X-ray crystallography.[2] In reactions between silenes and dienes, many silenes yield not only the expected [4 + 2] adducts but also large quantities of [2 + 2] adducts.[3] When the diene has allylic hydrogens, the two species may react in an ene reaction.[4]

Scheme 1



We now seek silenes that react more selectively, that are easily accessible, less vulnerable to dimerization, and less air- and moisture-sensitive than presently studied silenes. Our belief is that such silenes could be of general interest for organic synthesis. Among Si═C bonded species, it is noteworthy that lithium 2-silenolates (Scheme 2) react quantitatively with dienes to yield [4 + 2] adducts.[5] The

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(1) For recent reviews on silenes, see: (a) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71. (b) Müller, T.; Ziche, W.; Auner, N. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley-Interscience, New York, 1998; Vol. 2, Chapter 16, p 857.

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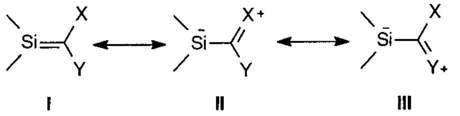
Scheme 2

Lithium 2-silenolate 4-Silatriafulvene

substituted 4-silatriafulvenes of Kira and co-workers show similar reactivity toward 2,3-dimethyl-1,3-butadiene.[6] The question is what property unifies the 2-silenolates and 4-silatriafulvenes?

The partially positive charge at Si in silenes is reduced by electron delocalization from π-donor substituents at C (resonance structures **II** and **III**, Scheme 3). This effect is called reversed polarization and was concluded by Apeloig and Karni to be the most important electronic factor that influences silene reactivity.[7] Primarily, it reduces the electrophilicity of the silene.[8−10] 2-Silenolates, 4-silatriafulvene, and silene **2** are species influenced by reversed SiC bond polarity. In 4-silatriafulvene, the reverse-polarized resonance structure has a negatively charged Si and a cyclopropenyl cation ring.

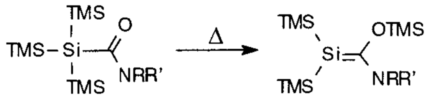
Scheme 3



However, the neutral silenes **2** and 4-silatriafulvenes are not fully described by **II** and **III** since such a silene should be a zwitterion with a Si−C single bond and a Si that resembles the pyramidal Si of a silyl anion. In **2** and 4-silatriafulvene, the SiC bond lengths are 1.764 and 1.743 Å, according to X-ray crystallography and MP2/6-311++G(d,p) ab initio calculations, respectively. Even though these SiC bonds are elongated when compared to that of $H_2Si{=}CH_2$ (1.704 Å according to millimeter wave spectroscopy),[11] they are much shorter than regular Si−C single bonds (~1.87 Å).[12]

The question is if neutral silenes that are more strongly influenced by reversed polarization can be formed, and if so, what are their reactivities? According to DFT calculations, two strongly π-electron-donating groups X and Y in the 2-position ensure that the silene is described by the zwitterionic structures **II** and **III**.[13] This criterion is fulfilled by 1,1-bis(trimethylsilyl)-2-amino-2-(trimethylsiloxy)silenes (**4**, Scheme 4), which could possibly be generated from silylamides **3** through a [1,3]-silyl shift from Si to O (cf. Brook's procedure[2] for formation of **2**). According to B3LYP/6-31G(d) calculations,[14−16] **4a** is strongly influenced by reversed polarization since it has an Si−C single bond and a pyramidal Si (Figure 1). B3LYP/6-31G(d) calculations also show that **4a** is 17.5 kcal/mol less stable than **3a** and that the transition state separating the two species is only 9.1 kcal/mol above **4a**.

Scheme 4



3 **4**

3a / **4a**: R = R' = Me
3b / **4b**: R = R' = Ph
3c / **4c**: R = Me, R' = Ph

Slightly discouraging is that formation of **4a** through photolysis of tris(trimethylsilyl)-*N*,*N*-dimethyl-silylamide (**3a**) was attempted before[17] and found to be unsuccessful since no reaction occurred upon long irradiation. However,

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(13) Silenes $H_2Si{=}C(NH_2)_2$ and $H_2Si{=}C(OH)(NH_2)$ have Si−C bond lengths of 1.930 and 1.904 Å, respectively, at the B3LYP/6-31+G(d,p) level and could be considered as Si−C single bonded.

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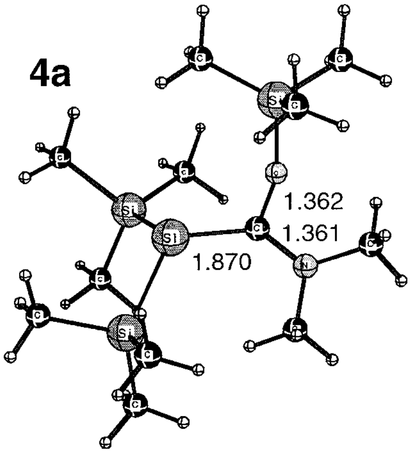


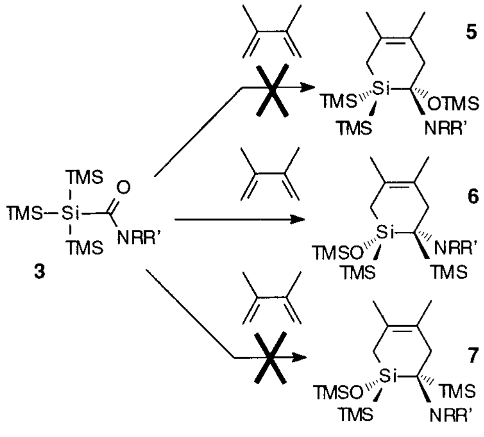
ΣSi = 336.6° N-C-Si-Si = -8.5°
ΣC = 359.8° O-C-Si-Si = 53.0°
ΣN =359.5° C-N-C-Si = 10.2° / -160.9°

Figure 1. Optimal geometry of the lowest energy conformer of **4a** at the B3LYP/6-31G(d) level. Distances are given in Å.

the low barrier that separates **4a** from **3a** will allow a facile backreaction when **4a** is formed.

In this work, we used a thermolytic approach instead of a photolytic approach. Evidence for formation of **4** may be obtained through trapping experiments, and **3** was therefore heated in the presence of 2,3-dimethyl-1,3-butadiene. Initially, the reactions were done in NMR tubes, sealed under a vacuum. Monitoring by NMR reveals that the reactions proceed cleanly to give only one product.

Scheme 5



To our surprise, the [4 + 2] adducts **6**, instead of the anticipated **5**, were identified as the sole products (Scheme 5 and Table 1), as verified by X-ray crystallography (Figure 2).[18] This implies either that the *Z*-isomers of silenes **8** are formed (Scheme 6) or that **4** is formed and trapped by 2,3-dimethyl-1,3-butadiene followed by rearrangement of **5** to **6**. In contrast to reactions of many other silenes with dienes, neither [2 + 2] nor ene adducts result.[1,3,4]

Table 1. Thermolysis Reactions of **3** in the Presence of 2,3-Dimethyl-1,3-butadiene for Formation of **6**

compound	temp (°C)	time	yield (%)	solvent
3a	180	2 days	88	toluene
3b	100	2 h	97	benzene
3b	65	2 days	97	benzene
3c	100	3 h	95	benzene

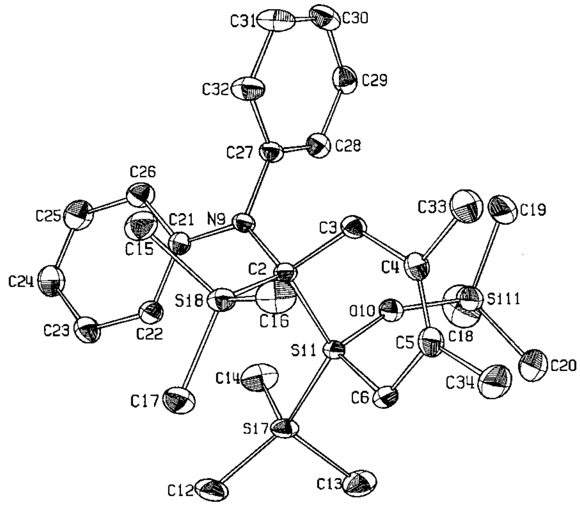
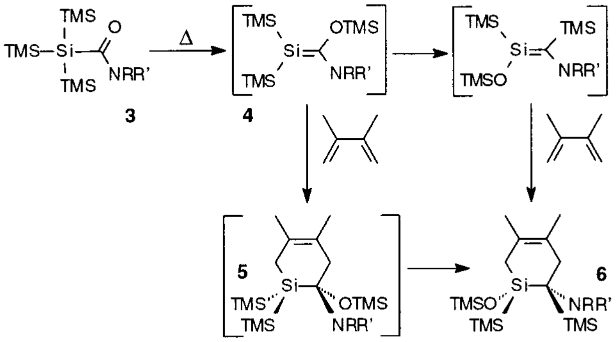


Figure 2. ORTEP drawing of one molecule of the cyclic allyl silane **6b**. The other molecule in the asymmetric unit is similar.

Formation of **8** from **4** implies exchange of TMSO(C) and TMS(Si) groups. Similar, though photochemically initiated,

Scheme 6



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(18) Crystal data for **6b**: colorless crystals, space group $P\bar{1}$, $a = 11.1473(9)$ Å, $b = 12.954(1)$ Å, $c = 22.317(2)$ Å, $\alpha = 97.649(1)°$, $\beta = 99.830(2)°$, $\gamma = 95.559(2)°$, $V = 3123.3(4)$ Å^3, $Z = 4$, $d_{calc} = 1.119$ g/cm^3, $\mu = 0.210$ mm^{-1}, $R_F = 0.057$. The two molecules in the asymmetric unit are similar.

rearrangements have previously been observed[19] and suggested to proceed either dyotropically or stepwise over a carbene intermediate. However, the absence of [2 + 1] diene-carbene cycloadducts indicates that the stepwise mechanism is not operative for the present rearrangement. Preliminary quantum chemical calculations also disfavor this mechanism, but a conclusion is at present premature and must await additional calculations and experiments. Such an investigation will further reveal if rearrangement from **5** to **6** is a feasible pathway.

The N-substituents strongly influence the required temperature for the cycloaddition reaction (Table 1). Whereas **3a** requires 2 days at 180 °C for complete transformation, only 2 h at 100 °C are needed for **3b**. Interestingly, when the thermolytic formation of **8b** from **3b** is performed in a sealed tube containing ambient atmosphere, the yield is not changed. This reaction can even be carried out by reflux in benzene when fully open to the ambient atmosphere. Even though the yield for formation of **6b** in this case is reduced to 53%, it should indicate that the silene formed (**4b** or **8b**) is less reactive to oxygen and moisture than other silenes.

So if **8** is formed and trapped, is it strongly influenced by reversed polarization? B3LYP/6-31G(d) calculations on **8a** reveal that this is the case (Figure 3). The SiC bond is closer to an Si−C single bond than to an Si═C double bond, and the silene Si is pyramidalized. The energy difference between the *Z*- and *E*-isomers of **8a** is 0.6 kcal/mol at the B3LYP/6-31G(d) level favoring the *Z*-isomer. However, if *Z*-**8** is involved, the selective formation of **6** implies that no *Z*/*E*-isomerization of this silene occurs. Since **8** is almost Si−C single bonded, *Z*/*E*-isomerization should be facile, and the absence of adduct **7** may instead indicate that the pathway **3**→**4**→**5**→**6** is followed.

To conclude, thermolyses of tris(trimethylsilyl)silylamides yield novel transient silenes (**4** and possibly also **8**) that are strongly influenced by reversed Si═C bond polarization and therefore Si−C single bonded. These silenes react quantitatively with 2,3-dimethyl-1,3-butadiene to give cyclic functionalized allyl silanes **6** as single diastereomers. Formation of [2 + 2] or ene adducts was not observed, and our studies give support that silenes influenced by reversed polarity react selectively in a [4 + 2] manner. The silylamides are easily accessed, and the transient silenes generated in the thermolyses are not overly sensitive to air and moisture.

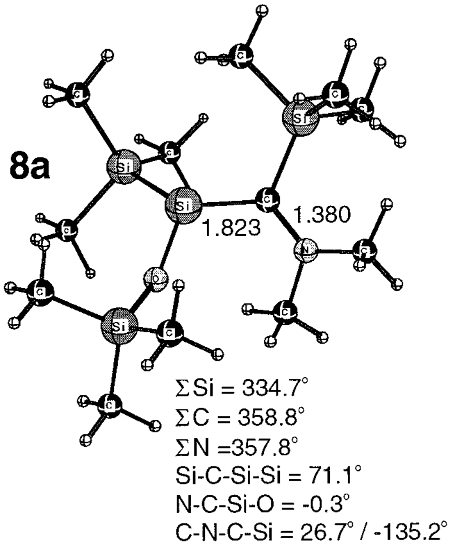

Figure 3. Optimal geometry of the lowest energy conformer of **8a** at the B3LYP/6-31G(d) level. Distances are given in Å.

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Supporting Information Available: Listing of absolute energies and Cartesian coordinates of compounds calculated with B3LYP/6-31G(d) and experimental procedures and characterization data for new compounds prepared as well as crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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