

Synthesis and Characterization of Cyclic Silenolates



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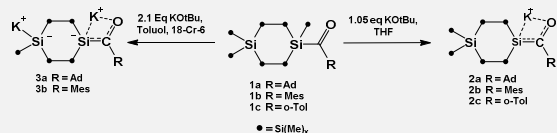


Introduction

Although silenes have been known for more than forty years, the synthesis and characterization of these compounds are still a challenging endeavor. Based on earlier work by Ottosson¹ and Ohshita² the previously unknown cyclic silenolates **2a-c** and **3a-b** have been synthesized by the reaction of acylcyclohexasilanes with one or two equivalents of KOtBu.^{3,4} The nature of the anions (silenide or silenolate) and consequently the outcome of subsequent reaction steps largely depends on the substituent R at the carbonyl function. Detailed X-ray- and NMR-analysis of **2a-c** and **3a-b** corroborate this deduction.

Cyclic Silenolates

Our new cyclic acylsilanes **1a-c** reacted cleanly with 1.05 or 2.1 eq. of KOtBu to give the corresponding cyclic silenolates **2a-c** and the dianionic species **3a,b**, respectively.



Upon heating to 50 °C **2b** undergoes a hitherto unknown 1,4-trimethylsilyl-migration and cleavage of the cyclohexasilane cycle to form the anion **4** which could be trapped with MeI to give an enantiomeric mixture of **5** from which the (S)-enantiomer could be crystallized.

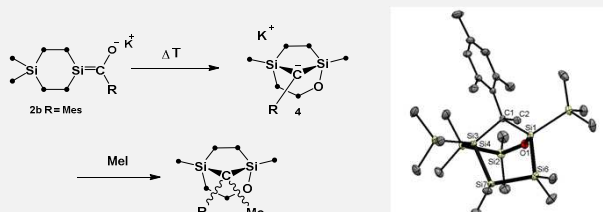
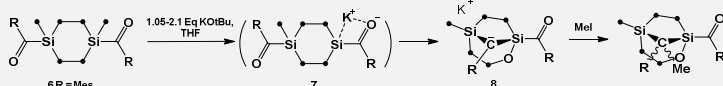


Figure 1: ORTEP diagram for (S)-**5**.

Bis-silenolates could not be obtained because the silenolate intermediate **7** formed in the reaction of 1,4-bis-acylcyclohexasilane **6** with 1.05 to 2.1 eq. of KOtBu as the primary product immediately rearranges to the carbanionic species **8** in a related process:



For **2a-c** and **3a,b** two resonance structures can be drawn: one with the negative charge residing predominately on the silicon atom (I), while in the other one (II) it is located on the oxygen atom.

Table 1: ²⁹Si-NMR Shifts for the Silicon atoms attaching to the carbonyl function

R	acylsilanes (ppm) ^a	silenolates (ppm) ^a	dianionic-species (ppm) ^a
Mes	-71.14	-73.53	-69.38
o-Tol	-66.79	-66.95	
Ad	-72.71	-91.88	-87.73

^a in C₆D₆ at 22 °C

²⁹Si NMR analysis suggests increasing contributions of structure II for the aromatic compounds **2b,c** and **3b** as indicated by a marked low field shift of the Si₁ signal relative to the adamantyl derivatives **2a** and **3a** (Table 1). Similar trends were reported earlier by Ohshita et al.²

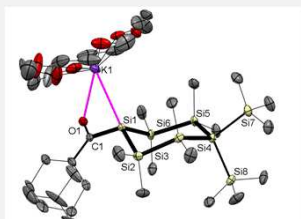


Figure 2: ORTEP diagram for **2a** (1:1 adduct with [18]crown-6).

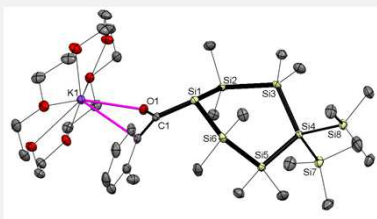


Figure 3: ORTEP diagram for **2c** (1:1 adduct with [18]crown-6).

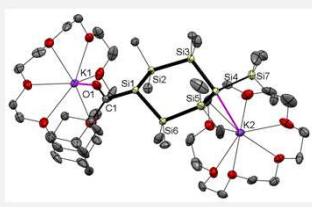


Figure 4: ORTEP diagram for **3a** (1:2 adduct with [18]crown-6).

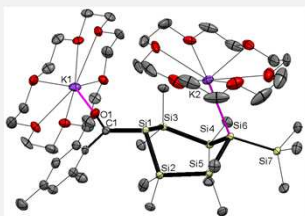


Figure 5: ORTEP diagram for **3b** (1:2 adduct with [18]crown-6).

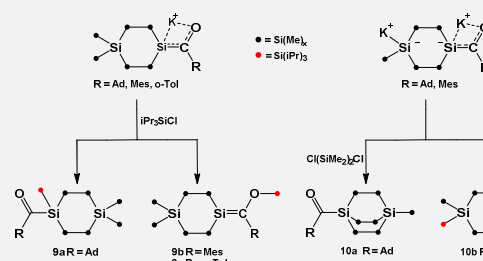
Single crystal X-ray crystallography showed different coordination of the K⁺ counterion to the SiC(R)O moiety in the solid state structure of **2a,c** and **3a,b**. While **2a** and **3a,b** can be described as acyl silyl anions **2c** exhibits increased silenolate character.

Table 1: Selected bond lengths d(Å) and sum of valence angles $\Sigma\text{O}(\text{Si})$ and $\Sigma\text{O}(\text{C})$ for **2a,c** and **3a,b**.

	2a	2c	3a	3b
d Si ₁ –C ₁	1.966	1.874	1.916	1.892
d Si ₁ –K ₁	3.603	4.935	5.215	5.102
d C ₁ –O ₁	4.899	3.257	3.672	3.843
d C ₁ –O ₂	1.244	1.260	1.254	1.254
d K ₁ –O ₁	2.743	2.701	2.579	2.614
$\Sigma\text{O}(\text{Si})$	316.7°	326.8°	314.4°	312.5°
$\Sigma\text{O}(\text{C})$	359.9°	359.7°	359.7°	360°

Cyclic Silenes and Germenes

If the silenolates **2a-c** and **3a,b** were reacted with chlorosilanes either silenes or new acylsilanes were formed depending on the nature of R attached to the carbonyl C: With aromatic R-groups the silenes **9b,c** and **10b** were obtained while aliphatic R-groups gave rise to the formation of the new acyl silanes **9a** and **10a**.



With this powerful synthetic strategy we also achieved the synthesis of the exocyclic germenolates **12a,b** and the first exocyclic germene **13b**:

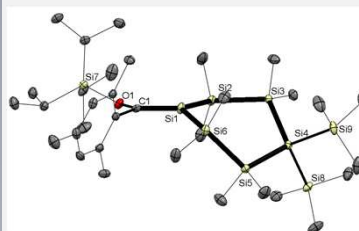
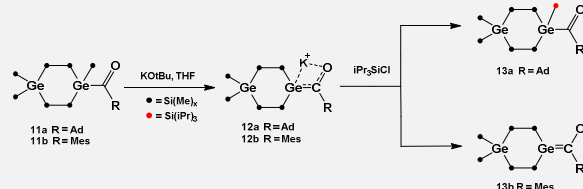


Figure 6: ORTEP diagram for compound **9b**.

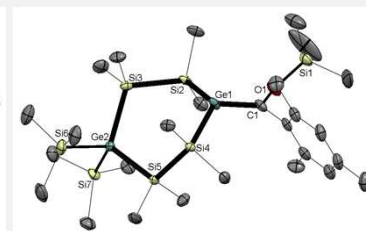


Figure 7: ORTEP diagram for compound **12b**.

Table 2: Pyramidalization angles α and torsion angle γ of silene **9b**, germene **12b** and (Me₂Si)₂Si=C(OSiMe₂)₂ (Brook silene)⁵

	9b	12b	Brook Silene
α Si ₁ /Ge ₁	4.97°	9.68°	1.05°
α C ₁	1.49°	0.74°	1.49°
torsions angle γ	5.68°	14.04°	14.38°

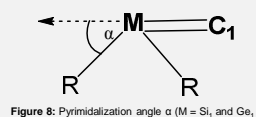


Figure 8: Pyramidalization angle α (M = Si, and Ge,)

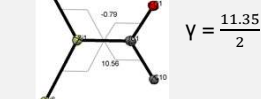


Figure 9: Calculated torsion angle γ of **9b**

Acknowledgement

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References

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