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 Ottosson and Onshita, the previously unknown cyclic silenolates 2a-c and 3a-b have been synthesized by the reaction of acyclic silacene-silanes with one or two equivalents of KOtBu. The nature of the anions (silene or silolate) and consequently the outcome of reaction step largely depends on the substituent R at the carbonyl function. Detaled 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-trimethylsililyl-migration and cleavage of the cyclocarysilene 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.

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.

Cyclic Silenes and Germenes

If the silenes 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 acylsilanes 9a and 10a.

With this powerful synthetic strategy we also achieved the synthesis of the exocyclic germenes 12a,b and the first exocyclic gemmene 13b.

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References