A Spiropentasiladiene and Other Strained Silicon-Containing Rings

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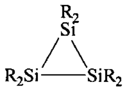
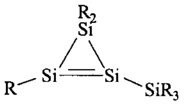
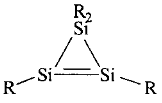
Although the chemistry of unsaturated silicon compounds and small rings containing silicon atoms has experienced a rapid development over the past 25 years, silicon chemistry is still far removed from the broad chemistry of its homologue carbon. Whereas cyclopropanes and cyclopropenes represent well known classes of compounds, the synthesis of the first cyclotrisilane **1a** did not succeed until 1982. Masamune et al. prepared this compound from the reductive elimination of halogen from a diaryldichlorosilane.[1] The reason for the relatively late synthesis of cyclotrisilanes is the greater ring strain compared to that of the carbon analogues. This strain manifests itself in the facile light-induced cleavage of two Si–Si bonds under formation of disilenes $R_2Si{=}SiR_2$ and silylenes R_2Si:; the latter dimerize to afford further disilene. An exception is the highly strained cyclotrisilane **1b**, which under photolytical conditions decomposes into a disilene and a silylene, both of which could be characterized by numerous trapping reactions.[3, 4]



1a R = 2,6-$Me_2C_6H_3$
1b R = *t*Bu



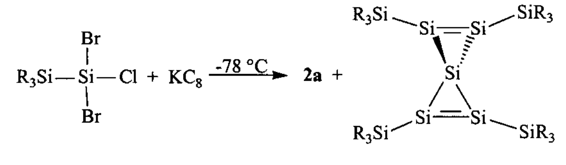
2a R = *t*BuMe$_2$Si



2b R = *t*Bu$_2$MeSi

Very little is known about the chemical behavior of the first cyclotrisilenes **2a** and **b**, which were only recently synthesized by Kira et al. and Sekiguchi et al., **2b** was structurally characterized.[5, 6] A more detailed investigation of the dehalogenation of the oligosilane **3** revealed a surprising result; in addition to the main product **2a**, red crystals of the spiro pentasiladiene **4** could be isolated in 3.5% yield [Eq. (1)].[7]

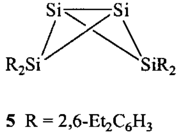
Compound **4** is the first thermally stable spiropentadiene comprising Group 14 elements. Even though the analogous carbon spiro compound C_5H_4, as well as the 1,1′-dichloro derivative could indeed be generated, both molecules decompose in solution within minutes, even at temperatures below $-100\,^{\circ}C$.[8, 9] The most striking feature of the structure of **4** is the twisting of the two halves of the molecule by 78.26°. This arrangement allows through-space interactions between the π orbitals as well as the π* orbitals of both double bonds and leads to the breaking of the degeneracy of these orbitals. The energy values calculated for the interactions between the π as well as the π* orbitals of the parent compound Si_5H_4 with D_2 symmetry are reflected by the electronic spectrum, where the longest wavelength absorptions of **4** at 560 nm and 500 nm are shifted bathochromically compared to the cyclotrisilenes **2a** (482 nm) and **2b** (466 nm).[10]



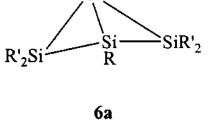
3 R = *t*BuMe$_2$Si **4** (1)

A further achievement of the Kira group is the preliminary solution to another problem of silicon chemistry: the bond-stretch isomerism in tetrasilabicyclo[1.1.0]butanes. A number of theoretical investigations had predicted the existence of two bond-stretch isomers of these compounds, in which the bond lengths between the bridge-head atoms differ. The molecule containing a short "central" bond was considered to be a classical molecule with closed shells, with the length of the bridge bond in the range typical for Si–Si single bonds. On the other hand, this bond was expected to be markedly stretched in the second isomer, where the central bond was predicted to exhibit a noticeable singlet biradical character.[11, 12] The substituents at the bridge-head atoms are expected to have a significant influence over the bond length. In this context, medium sized groups, such as the methyl group, should be suitable candidates for the observation of bond-stretch isomerism in substituted tetrasilabicyclo[1.1.0]butane compounds.[11g]

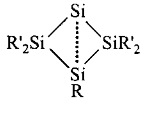
The as yet only structurally confirmed tetrasilabicyclo[1.1.0]butane **5** exhibits a transanular Si–Si separation of merely 237.3 pm, apparently a result of the bulky *tert*-butyl groups at the bridge-head atoms, and is thus classified as an



5 R = 2,6-$Et_2C_6H_3$



6a



6b

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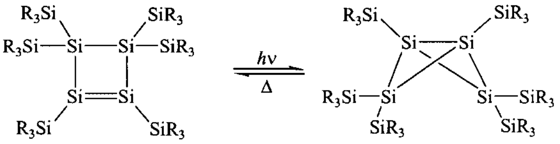
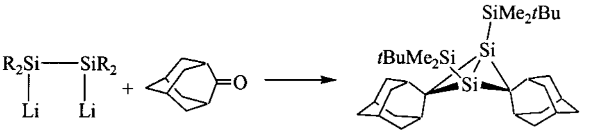
isomer containing a short central bond.[13] According to calculations carried out for the parent compound Si_4H_6, the isomer **6b** with its large transanular Si$\cdots$Si separation of >280 pm and a dihedral angle of 142° for the Si_4 skeleton, is more stable than the classical isomer **6a**, for which no energy minimum was found.[11h] Another molecule, **8** also containing the bicyclo[1.1.0]butane framework, results from the photolysis of the tetrasilene **7** by a 1,2-silyl shift. However, even at ambient temperature **8** rearranges thermally back to compound **7** [Eq. (2)].[14]



7 $R_3Si = tBuMe_2Si$ **8** (2)

A strong indication for the existence of a molecule with a long central Si–Si bond was obtained by Kira et al. for the 1,3-disilabicyclo[1.1.0]butane **10**, which was obtained by an as yet unknown mechanism from the treatment of the dilithiated compound **7** with adamantanone [Eq. (3)].[15]



9 $R = tBuMe_2Si$ **10** (3)

The distance between the two central silicon atoms of 241 pm is rather long for an Si–Si bond. The dihedral angle between the two Si-C-Si planes is markedly opened with a value of 141.1°, whereas the Si-Si-R angle, which, in spite of the bulky substituents, has a value of 118.1°. DFT calculations for the model compounds **A** and **B** (Figure 1), which contain methyl and silyl groups instead of the adamantyl and *tert*-butyl substituents in **10**, reveal noticeable differences between those structures containing a long, and those containing a short central Si–Si bond. The central separation in **A** amounts to 244.8 pm (**B**: 220.1 pm), the dihedral angle is 141.5° (**B**: 126.7°) and the R-Si-Si angle is 106.9° (**B**: 152.1°). In analogy to calculations for the bicyclo[1.1.0]tetrasilane, the bond-stretch isomer with the larger separation is favored energetically. The newly observed structure of **10** corresponds far more to that of **A**, both in the solid state and in solution. Not only the separation as well as both angles, but also the chemical shifts of the ring atoms of the framework in the ^{13}C and ^{29}Si NMR spectra are in very good agreement with the calculated values.

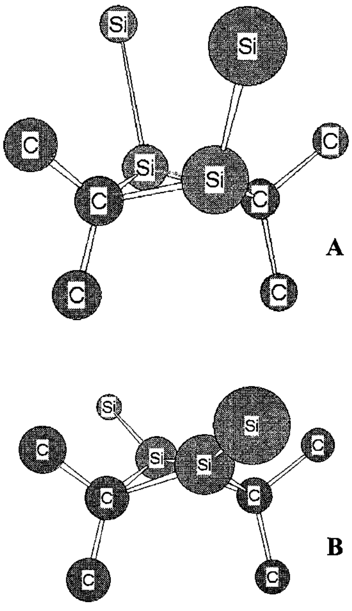
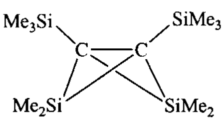


Figure 1. Model compounds **A** (long central Si–Si bond) and **B** (short central Si–Si bond). Hydrogen atoms are omitted.

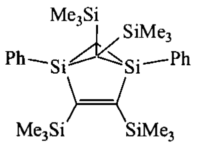
A characteristic feature of all the compounds with long bonds is, according to theoretical investigations, the singlet biradical character of this bond, which was confirmed by multiconfiguration self-consistent field (MCSCF) calculations.[11a] Moreover, low-lying antibonding Si–Si σ* orbitals allow for an efficient interaction with the HOMOs.

Towards the heavier Group 14 elements an increasing tendency to avoid strained three-membered rings in favor of four-membered rings is observed. The s orbitals contract relative to the p orbitals. Consequently only sp hybrid orbitals, which favor orthogonal arrangements, are formed (compare the R-Si-Si angles).[12]

Although bond-stretch isomerism has been considered for the corresponding carbon compounds, it still needs to be demonstrated experimentally.[16] A value of 175 pm was calculated for the isomer with the longer central C–C bond.[11a] This value is in good agreement with the very long C–C bond of 178.1 pm in the 2,4-disilabicyclo[1.1.0]butane derivative **11**.[17] A noticeably elongated C–C bond of 168.0 pm has been observed in the disilabenzvalene **12** which also contains this structural element.[18]

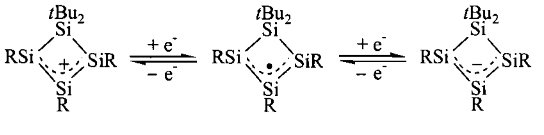


11



12

It can be anticipated from the recent work of Sekiguchi et al. that the chemistry of small silicon rings will have further surprises to offer. In addition to the synthesis of the cyclotetrasilylenium ion **13**,[19] they succeeded for the first time in the isolation and complete characterization of the silyl radical **14**.[20] Further one-electron reduction finally resulted in the cyclotetrasilenide ion **15** [Eq. (4)],[21] of which only an analogous germanium compound had been known to exist.[22]



13 **14** **15** (4)

$R = tBu_2MeSi$

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Microwave-Assisted Reactions in Organic Synthesis—Are There Any Nonthermal Microwave Effects?

Nikolai Kuhnert*

Introduction

The development of resource- and environmentally friendly processes in terms of sustainable chemistry has become a focal point in chemical research in recent years. Of particular importance is a reduction in the amounts of solvents and hazardous substances required, and the more efficient use of energy.[1, 2] Synthetic chemists have neglected alternative sources of heat for chemical reactions, and still rely on isomantles, oil, sand and water baths, or heatguns as heating devices.

The use of microwave (MW) irradiation as a source of heat in synthetic chemistry offers a promising alternative. Microwaves differ from conventional heat sources, in that the solvents or reactants are directly heated without heating the reaction vessel. By conventional methods, the vessel is heated and this then transfers the heat by convection. Microwave heating is more efficient in terms of the energy used, produces a higher temperature homogeneity, and is considerably more rapid than conventional heat sources. The first application of microwave irradiation in chemical synthesis was published in 1986.[3] It is worth noting that the first commercial household microwave oven was introduced to the market in 1954, and that the transfer of microwave technology into the chemistry laboratory has taken the unusually long time of over three decades. In typical microwave ovens, the magnetrons (microwave generators) produce a microwave wavelength of 12.25 cm, which corresponds to a frequency of 2.45 GHz. The basic theory underlying the interaction of microwaves with macroscopic matter was formulated by von Hippel[4] and, for the basic equations, the reader is referred to this work and to an excellent overview by Mingos.[5]

Over the last decade, microwave-assisted chemistry has matured into a highly useful technique and provides an interesting alternative for heating chemical reactions. The large number of publications clearly indicates the development of this area of chemistry.[6–11]

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