

Structure and Reactivity of an Isolable Seven-Membered-Ring *trans*-Alkene**

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Abstract: The isolation and characterization of a *trans*-oxasilacycloheptene is reported. Single-crystal X-ray crystallographic studies indicate a high level of strain and deviation from ideal geometry. Reactions with several electrophiles demonstrated the nucleophilicity of the C=C double bond, affording oxasilacycloheptane and tetrahydrofuran products as single diastereomers.

Seven-membered-ring *trans*-alkenes are uncommon synthetic targets as a consequence of their challenging synthesis and instability under atmospheric conditions.^[1,2] Few examples of these compounds have been synthesized, and trapping experiments^[3–6] or low-temperature spectroscopy^[7] have been used to verify the formation of these compounds. Two examples, however, have been isolated and characterized by X-ray crystallography.^[8,9] These seven-membered-ring *trans*-alkenes incorporated one or more silicon atoms^[8,9] that relieve strain due to longer bonds to these atoms.^[10] In this Communication, we report the isolation of a strained seven-membered-ring *trans*-alkene. Although the ring contains one silicon atom, X-ray crystallographic analysis indicates that the distortion of the ring approaches the distortion calculated for *trans*-cycloheptene.

The seven-membered-ring *trans*-alkene **3** was synthesized in 72% overall yield on a multigram scale (Scheme 1). This

one-flask, two-step synthesis involved the formation of vinylsilacyclopropane **2** by silylene transfer to diene **1** followed by diastereoselective addition to benzaldehyde.^[11] Previously, the structure of alkene **3** was inferred only from spectroscopic data, and all attempts at purification proved unsuccessful. The alkene was highly reactive, undergoing thermal rearrangement with a half-life of twelve hours at 22 °C. Herein, we have developed a procedure for isolating crystalline alkene **3**. The reaction mixture was filtered through Celite with hexanes to remove residual silver salts, and the filtrate was concentrated and crystallized at 0 °C. The purified compound could be stored at low temperatures, enabling preliminary studies of its reactivity. Structural analysis by X-ray crystallography confirmed the structure of **3** and provided insight into the structural consequences of strain on the olefin (Figure 1).^[12]

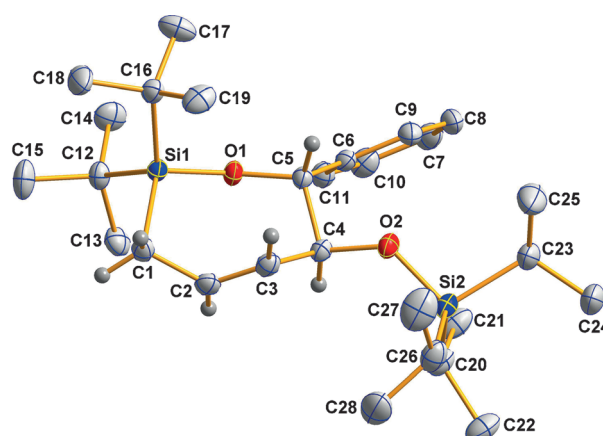
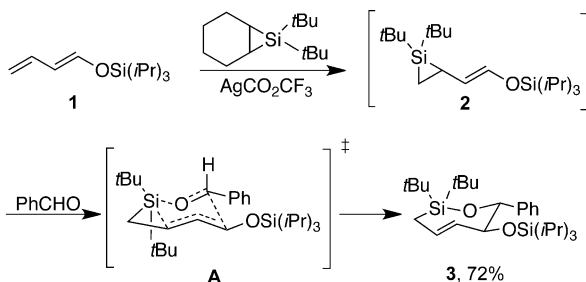


Figure 1. Molecular structure of *trans*-oxasilacycloheptene **3**. Thermal ellipsoids set at 50% probability. Hydrogen atoms, except those on the ring, have been removed for clarity. Selected bond lengths [Å] and angles [°]: C1–C2 1.498(2), C2–C3 1.335(2), C3–C4 1.484(2), C4–C5 1.582(2), C5–O1 1.418(2), O1–Si1 1.663(1), Si1–C1 1.927(2); Si1–C1–C2 96.2(1), C4–C3–C2 116.2(1).



Scheme 1. Synthesis of *trans*-oxasilacycloheptene **3**.

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The amount of strain in alkene **3** can be assessed by examining the deformation of the sp^2 -hybridized centers of the C=C double bond (Figure 2).^[13] This deformation can be quantified by several different parameters. The misalignment of the p orbitals that results from constraining a *trans* double bond in a medium-sized ring is measured by both the torsion angle (θ) and the twisting angle (ϕ ; Figure 2).^[14] The C=C–C–C torsion angle (θ) of **3** is 126.1°, which is a 53.9° distortion away from the ideal torsion angle (180.0°). The average twisting angle (ϕ) is 23.3° away from coplanarity. To regain some of the orbital overlap lost by twisting, the sp^2 -hybridized carbons in alkene **3** undergo rehybridization.^[15]

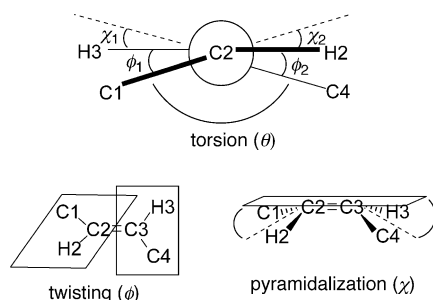


Figure 2. Modes of distortion in strained alkenes. Dashed lines represent the projections of the C1–C2 and C4–C3 axes.

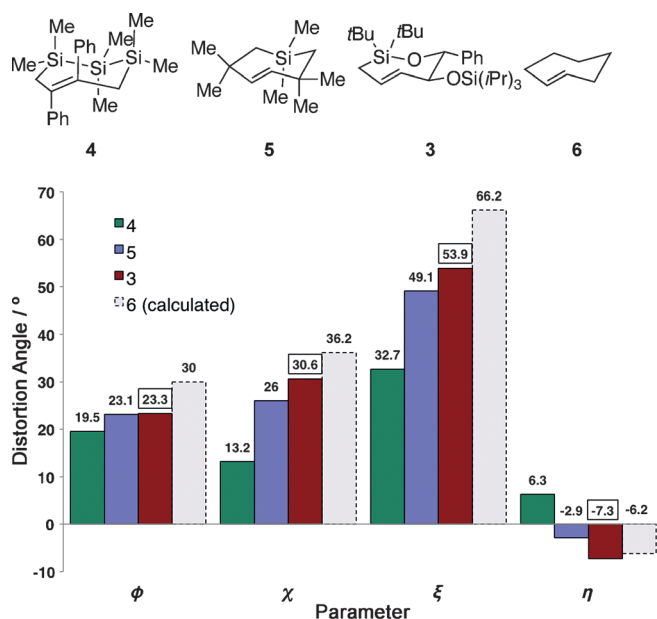


Figure 3. Distortion angles of *trans*-oxasilacycloheptene **3**, previously reported *trans*-silacycloheptenes **4** and **5**, and all-carbon *trans*-cycloheptene **6**.

This rehybridization, measured by average pyramidalization (χ),^[16,17] can be seen by the deviation from planarity at the alkene carbon atoms. Alkene **3** deviates from planarity by 30.6°.

Of the isolated seven-membered-ring *trans*-alkenes, **3** deviates the most from ideal geometry as determined by these parameters. Figure 3 shows an analysis of the strain of *trans*-oxasilacycloheptene **3**, the two other *trans*-silacycloheptenes that have been characterized by X-ray crystallography (**4** and **5**),^[8,9] and the calculated values for all-carbon *trans*-cycloheptene (**6**).^[18] The overall strain of the C=C double bond is measured by ξ , the sum of the twisting and pyramidalization angles (ϕ and χ , respectively). Conversely, η , the difference between ϕ and χ , indicates which of the two plays a larger role in relieving strain.^[13] Similar to *trans*-silacycloheptene **5** and the calculated structure of *trans*-cycloheptene **6**, *trans*-oxasilacycloheptene **3** relieves strain mostly by pyramidalization, but to a larger extent than the others. The enhanced distortion of *trans*-oxasilacycloheptene **3** may be attributed to the short C–O and Si–O bonds (1.42 Å and 1.66 Å, respectively),

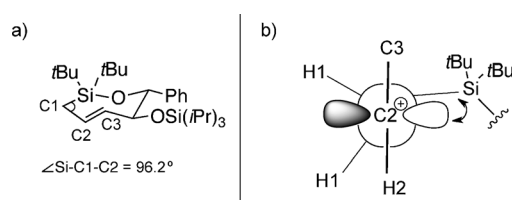
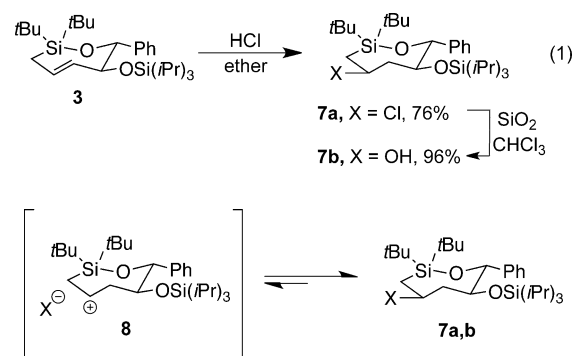


Figure 4. a) Allylic bond angle of **3**. b) Hyperconjugative stabilization of a carbocation generated at C2.

compared to the longer C–Si and Si–Si bonds in silanes **4** and **5** (1.91 Å and 2.39 Å, respectively).^[8,9]

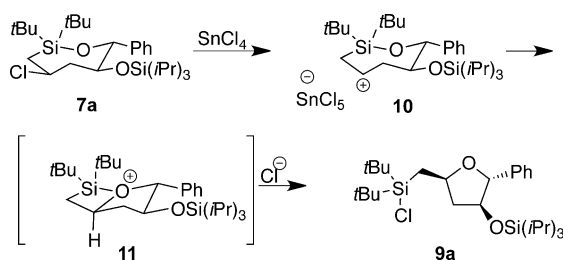
The crystal structure of **3** suggests how the strained alkene might react. Alkene **3** has a bond angle of 96.2° at C1 (Figure 4a). This value is smaller than any bond angle measured in the other seven-membered-ring *trans*-alkenes, and is likely due to hyperconjugative interactions between the $\sigma_{\text{Si-C1}}$ bond and the π -system.^[19] The hyperconjugation and distortion indicate that the C=C double bond should be particularly nucleophilic,^[20] even though the silyl group has an electron-withdrawing oxygen atom.^[21] The donating ability of the $\sigma_{\text{Si-C1}}$ bond would also stabilize a carbocation at the β position (C2) significantly (Figure 4b).^[22,23] This donation would form a structurally constrained intermediate^[24] and increase the lability of a substituent at C2.^[25] If that carbocation were to form, transannular reactions could occur^[26] with the oxygen atom, which resides within 2.7 Å of the double bond. That distance is less than the sum of the van der Waals radii for the two elements.^[27]

As suggested by the structure, the C=C double bond was nucleophilic, and the β -silyl carbocation intermediate was configurationally stable. Treatment of **3** with ethereal hydrogen chloride resulted in stereoselective addition across the C=C double bond to form oxasilacycloheptane **7a** [Eq. (1)]. Exposure of **7a** to SiO₂ resulted in hydrolysis with retention of configuration to form **7b** [Eq. (1)]. The regioselectivity of HCl addition and the stereochemical course of both the addition and hydrolysis reactions are consistent with formation of β -silyl carbocation **8** and trapping without bond rotation (Scheme 2).^[24]



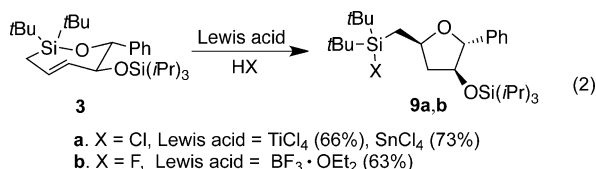
Scheme 2. Stereoselective addition to the β -silyl carbocation.

As anticipated, transannular reactions with the oxygen atom were observed. When oxasilacycloheptane **7a** was treated with SnCl₄, rearrangement product **9a** was formed.

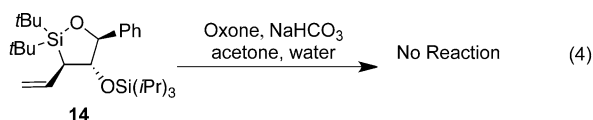
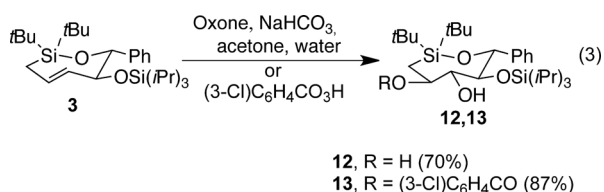


Scheme 3. Mechanism of formation of tetrahydrofuran **9a**.

The Lewis acid could abstract the labile halide,^[28,29] allowing for nucleophilic attack by the intramolecular oxygen atom, forming oxonium ion **11** (Scheme 3).^[30] Addition of a chloride ion to the silicon atom followed by ring opening^[31] resulted in formation of **9a** as a single diastereomer.^[32] The conversion of **3** into tetrahydrofuran products could also be achieved directly by the addition of a Lewis acid [Eq. (2)]. These reactions were likely initiated by hydrogen halides present in the Lewis acid reagents.^[33]



The ease of formation of the β -silyl carbocation intermediate precluded the ability to isolate the epoxide of the alkene. Treatment with dimethyldioxirane (DMDO) generated in situ resulted in stereoselective dihydroxylation [Eq. (3)]. This result could be understood by postulating that epoxidation followed by ring opening of the epoxide would form a β -silyl carbocation intermediate, which would be trapped without bond rotation to give the *syn* addition product **12** [Eq. (3)].^[32] Strain appears to be necessary to see any reaction with DMDO, because the isomeric allylic silane **14** was unreactive [Eq. (4)]. Similarly, epoxidation of *trans*-alkene **3** with *meta*-chloroperoxybenzoic acid (*m*CPBA) provided ester **13** as a single regio- and diastereoisomer [Eq. (3)].



In conclusion, we have isolated a crystalline seven-membered-ring *trans*-alkene. The X-ray crystal structure revealed that it is the most distorted seven-membered-ring

trans-alkene isolated to date. Hyperconjugative effects allow for formation of a stabilized β -silyl carbocation that dictates reactivity to give products as single diastereomers.

Keywords: alkenes · cycloheptenes · medium-ring compounds · silicon · strained molecules

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