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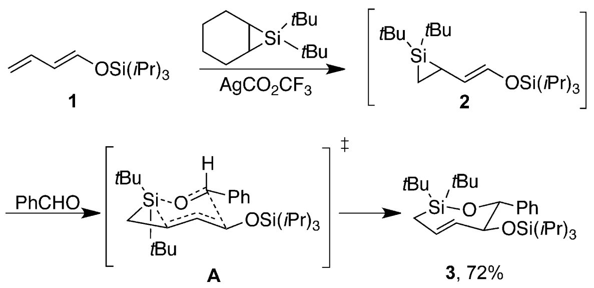
Structure and Reactivity of an Isolable Seven-Membered-Ring *trans*-Alkene**

*Brisa Hurlocker, Chunhua Hu, and K. A. Woerpel**

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]



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

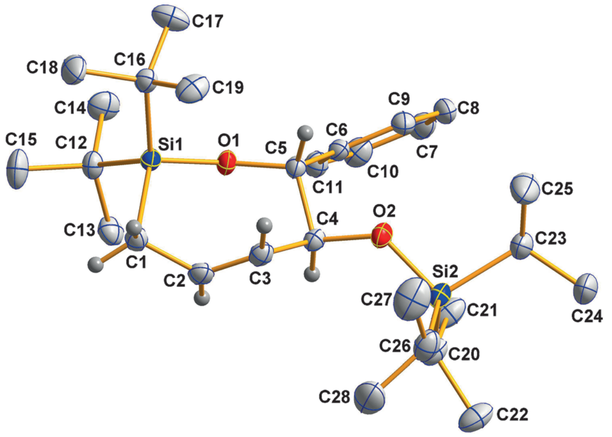


Figure 1. Molecular structure of *trans*-oxasilacycloheptene **3**. Thermal ellipsoids set at 50 % probability. Hydrogen atoms, except those on the ring, have been removed for clarity. Selected bond lengths [Å] and angles [°]: C1-C2 1.498(2), C2-C3 1.335(2), C3-C4 1.484(2), C4-C5 1.582(2), C5-O1 1.418(2),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

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]

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[*] B. Hurlocker, Dr. C. Hu, Prof. K. A. Woerpel
Department of Chemistry, New York University
100 Washington Square East, New York, NY 10003 (USA)
E-mail: kwoerpel@nyu.edu

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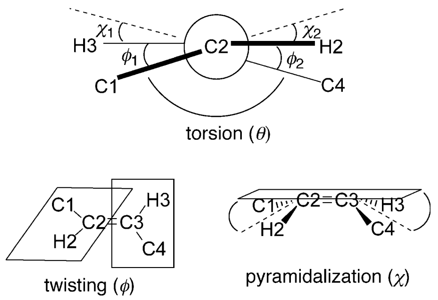


Figure 2. Modes of distortion in strained alkenes. Dashed lines represent the projections of the C1–C2 and C4–C3 axes.

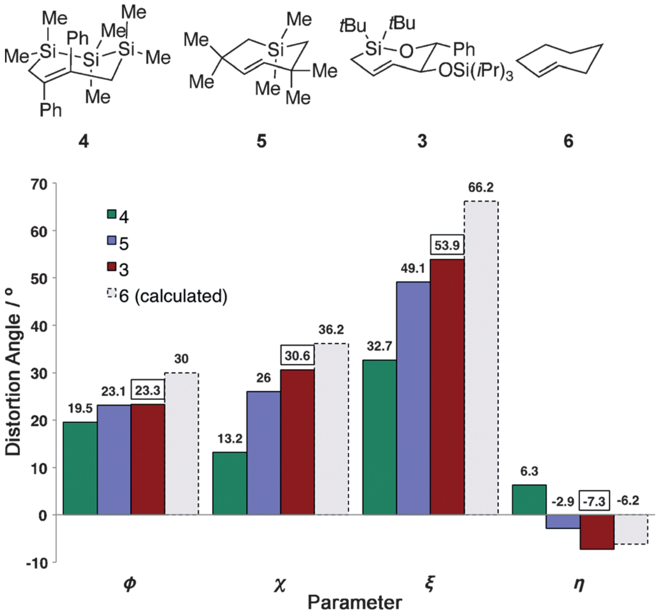


Figure 3. Distortion angles of *trans*-oxasilacycloheptene **3**, previously reported *trans*-silacycloheptenes **4** and **5**, and all-carbon *trans*-cycloheptene **6**.

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), 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]

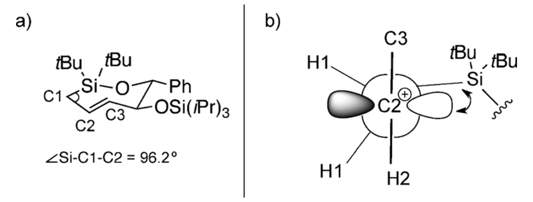
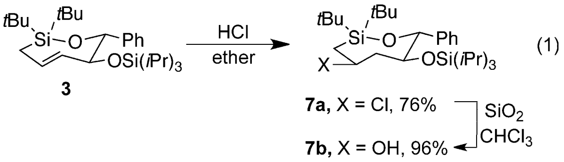


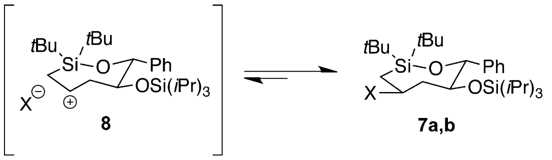
Figure 4. a) Allylic bond angle of **3**. b) Hyperconjugative stabilization of a carbocation generated at C2.

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 σ_{Si1-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 σ_{Si1-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 SiO_2 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]

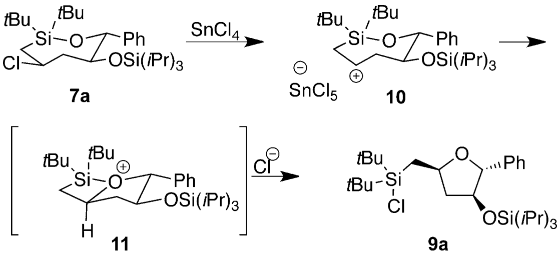


(1)



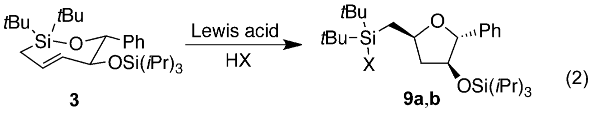
Scheme 2. Stereoselective addition to the β-silyl carbocation.

As anticipated, transannular reactions with the oxygen atom were observed. When oxasilacycloheptane **7a** was treated with $SnCl_4$, rearrangement product **9a** was formed.



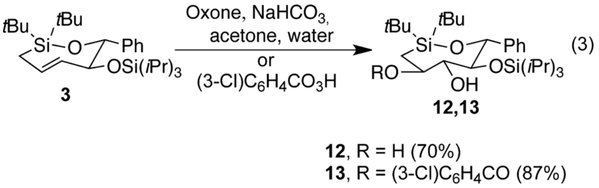
Scheme 3. Mechanism of formation of tetrahydrofuran **9a**.

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]

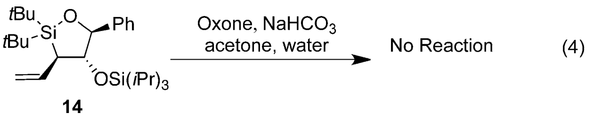


a. X = Cl, Lewis acid = $TiCl_4$ (66%), $SnCl_4$ (73%)
b. X = F, Lewis acid = $BF_3 \cdot OEt_2$ (63%)

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)].



12, R = H (70%)
13, R = (3-Cl)C_6H_4CO (87%)



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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[12] X-ray data of **3**: $C_{28}H_{50}O_2Si_2$; $M_r = 474.86$; $0.54 \times 0.48 \times 0.04\,mm^3$; monoclinic; $P2_1/c$ (no. 14); $a = 14.7647(15)$ Å, $b = 14.2306(14)$ Å, $c = 14.5781(15)$ Å, $\beta = 107.620(2)°$, $V = 2919.3(5)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.080\,g\,cm^{-3}$; $\mu = 0.142\,mm^{-1}$; $T = 100$ K; $2\theta_{max} = 56.68°$; $\lambda(Mo\,K\alpha) = 0.71073$ Å; 52963 measured reflections and 7281 independent reflections; $R_{int} = 0.0444$; R_1 $(I > 2\sigma(I)) = 0.0413$, wR_2 (all data) = 0.1175; $S = 1.055$; residual electron density: 0.461 and $-0.308\,e^-$ Å^{-3}. CCDC-103244 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[33] Control reactions in which addition of (iPr)$_2$NEt preceded the addition of the Lewis acid gave no product, indicating that the hydrogen halide was necessary for reactivity.

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