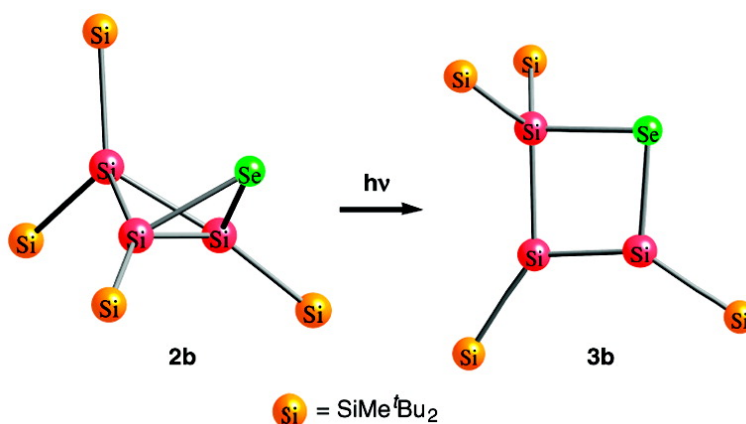


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Isomeric Metamorphosis: Si₃E (E = S, Se, and Te) Bicyclo[1.1.0]butane and Cyclobutene

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Bicyclo[1.1.0]butane, the most highly strained bicyclic compound, is among the most fascinating organic molecules, and it has intrigued chemists for nearly five decades. Its butterfly-type structure, along with a nonclassical bonding mode, makes it a very attractive target for long-standing experimental and theoretical pursuits.¹ It is now well-established that bicyclo[1.1.0]butane and its heavy analogues can exist in two isomeric forms, featuring either short or long bridging bonds.² Another aspect of bicyclo[1.1.0]butane chemistry, particularly interesting from the viewpoint of the conservation of orbital symmetry, involves its interplay with the valence isomers, of which 1,3-butadiene and cyclobutene are particularly important. Examples of the stable bicyclo[1.1.0]butanes comprising heavier group 14 elements are scarce.³ The interconversion of such heavy bicyclo[1.1.0]butanes is also largely unexplored, being represented by the thermal isomerization of tetrasilabicyclo[1.1.0]butane to tetrasilacyclobutene,⁴ and the thermal isomerization of heavy bicyclo[1.1.0]butanes to heavy cyclopropenes.⁵ In this work, we present a new method for the synthesis of heavy bicyclo[1.1.0]butane derivatives, and discuss their unusual structural features and unprecedented photochemical isomerization to heavy cyclobutenes.

The most common method for the synthesis of bicyclo[1.1.0]butane derivatives is the reductive dehalogenation of 1,3-dihalo-cyclobutanes, smoothly forming transannular 1,3-bonds.⁵ We have employed a novel approach for the preparation of bicyclo[1.1.0]butane, namely, [1 + 2] cycloaddition of a chalcogen E (E = S, Se, and Te) to the Si=Si bond of **1**.⁶ Thus, 2-thia-, 2-selena-, and 2-tellura-1,3,4-trisilabicyclo[1.1.0]butanes **2a–c** were prepared in good yields by the reaction of **1** with an excess of propylene sulfide (or one equivalent of elemental S) in benzene, or excess of elemental Se and Te in THF, respectively, and isolated in the form of yellow-orange crystals (Scheme 1).⁷

The bicyclo[1.1.0]butanes **2a–c** exhibit folded structures in solution with the resonances of the skeletal Si atoms being diagnostically high-field shifted: bridging Si atoms (−22.0 ppm for **2a**, −29.8 ppm for **2b**, and −34.4 ppm for **2c**) and bridgehead Si atoms (−119.9 ppm for **2a**, −132.0 ppm for **2b**, and −164.2 ppm for **2c**). The crystal structures of **2a–c** were determined by X-ray crystallography (Figure 1).⁷

The interplanar angles in both **2b** and **2c** are acute: 110.34(6)° and 109.4(2)°, respectively. Of particular importance are the exceedingly short bridging Si–Si bonds in **2b** and **2c** of 2.2616(19) and 2.2771(13) Å, respectively, which are by far shorter than the average value of 2.34 Å, and are close to the upper limit of the Si=Si double bond range of 2.138–2.289 Å.⁸ These values are also greatly shortened compared with those of other known bicyclo[1.1.0]butanes with the bridging Si–Si bonds, 2.373(3)^{3b} and 2.412(1)^{3c} Å, and are very close to a value previously reported by us for trisilabicyclo[1.1.0]butane (2.2664(9) Å).⁵ Such structural features of **2** are highly reminiscent to those in oxa-,^{9a,b} thia-,^{9c} and selena-^{9d} disiliranes, where the Si–Si bonds are also very short

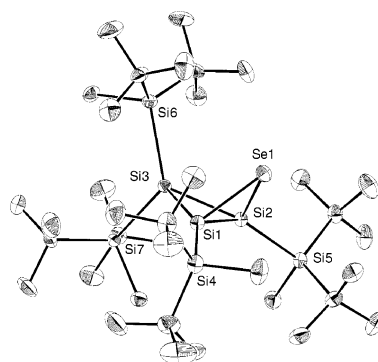
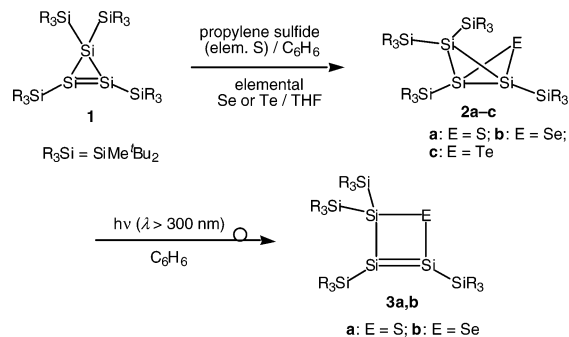


Figure 1. ORTEP drawing of **2b**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1–Si2 = 2.2616(19), Si1–Se1 = 2.3570(15), Si2–Se1 = 2.3419(13), Si1–Si3 = 2.3821(18), Si2–Si3 = 2.3782(19), Si1–Si4 = 2.389(2), Si2–Si5 = 2.3823(19), Si3–Si6 = 2.4325(19), Si3–Si7 = 2.4093(18). Selected bond angles (deg): Se1–Si1–Si2 = 60.89(5), Si1–Si2–Se1 = 61.56(5), Si2–Se1–Si1 = 57.54(5), Si1–Si2–Si3 = 67.72(6), Si2–Si3–Si1 = 56.73(6), Si3–Si1–Si2 = 61.55(6). Torsion angle (deg): Si3–Si1–Si2–Se1 = 110.34(6).

Scheme 1



(2.227–2.303 Å): a phenomenon realized in the framework of significant π -complex nature of such three-membered rings, which have electronegative chalcogens.^{9a,d} Similarly, the particular bonding situation around the bridgehead Si in **2** can be viewed from the standpoint of the important contribution of the chalcogen–trisilirene π -complex character to the overall structure of these compounds. Indeed, the bridgehead Si–Si bonds in **2** are steadily stretched on going from **2a** to **2c** in accord with the decrease in electronegativity of the chalcogen atom. Moreover, a partial rehybridization of the bridgehead Si atoms and some double bond character of the Si1–Si2 bridge were manifested in the appreciable alignment of the bridgehead substituents along the Si₃-ring plane. Thus, the sum of the bond angles around the bridgehead Si1 and Si2 atoms (ignoring the chalcogen atoms) were 356.4° and 350.9°, respectively, for **2b**, and 355.9° and 350.3°, respectively, for **2c**.

Interestingly, bicyclo[1.1.0]butanes **2a** and **2b** were transformed into their valence isomers, the heavy cyclobutenes **3a** and **3b**, upon

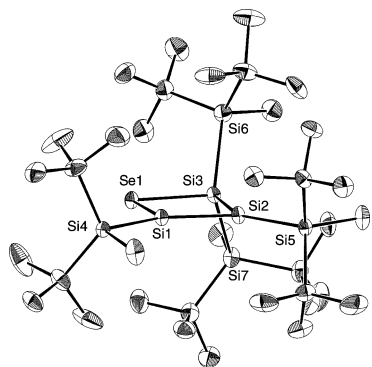


Figure 2. ORTEP drawing of **3b**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1–Si2 = 2.1706(12), Si2–Si3 = 2.3806(12), Si1–Se1 = 2.2791(9), Si3–Se1 = 2.3569(9), Si1–Si4 = 2.3629(12), Si2–Si5 = 2.3656(12), Si3–Si6 = 2.4209(14), Si3–Si7 = 2.4281(14). Selected bond angles (deg): Se1–Si1–Si2 = 98.62(4), Si1–Si2–Si3 = 86.17(4), Si2–Si3–Se1 = 90.85(4), Si3–Se1–Si1 = 84.34(3). Torsion angle (deg): Si4–Si1–Si2–Si5 = 0.08(7).

photochemical irradiation ($\lambda > 300$ nm) in benzene solution (Scheme 1). Both **3a** and **3b** were isolated as orange-red crystals in a yield of 57% and 50%, respectively.⁷ The most essential spectral feature of **3a** and **3b** is a diagnostic low-field shift of resonances of the skeletal doubly bonded Si atoms, of which the Si atom bonded to either S or Se is by far more deshielded: 95.1 ppm (Si–Si=Si) and 195.0 ppm (Si=Si–S) for **3a**, 100.8 ppm (Si–Si=Si) and 192.1 ppm (Si=Si–Se) for **3b**. The skeletal sp^3 -Si atoms were observed at -60.2 ppm in **3a** and at -0.5 ppm in **3b**.¹⁰ The longest wavelength absorption in the UV–vis spectra of both **3a** and **3b**, corresponding to π – π^* electronic transitions, was observed at 454 and 463 nm, which is in the region typical for cyclic disilenes.¹¹ The crystal structures of both **3a** and **3b** were determined by X-ray diffraction, and the structural peculiarities of **3b**, as a representative example (**3a** is isostructural with **3b**), will be discussed below (Figure 2).⁷ The four-membered ring in **3b** is perfectly flat (the sum of the interior bond angles is 359.98°), and the geometry of the Si=Si bond is also ideally planar, with the sum of the bond angles around both Si1 and Si2 atoms being 360.0° , which corresponds to a negligible twisting of the Si=Si bond of 0.08° . The Si=Si bond length of 2.1706(12) Å is typical for cyclic disilenes,¹¹ and all other skeletal bonds also lie in normal regions. These structural and spectral data give evidence for the absence of a notable interaction between the S or Se lone pair and the Si=Si bond. In contrast, in a recently reported four-membered cyclic silene, the doubly bonded Si atom exhibits a markedly pyramidal geometry (342.2°).¹²

Regarding the mechanism of the photochemical isomerization of **2** to **3**, there are three feasible pathways. The first pathway A is represented by a stepwise process involving a concerted disrotatory ring opening of the bicyclo[1.1.0]butane **2a** to form *trans*-1-thia-2,3,4-trisila-1,3-butadiene, *trans*-**4a**, followed by its conformational change to *cis*-1-thia-2,3,4-trisila-1,3-butadiene, *cis*-**4a**, (or a direct transformation of **2a** into *cis*-**4a**), which is completed by the final disrotatory electrocyclic ring closure to form cyclobutene **3a**. The second pathway B is the direct disrotatory transformation of bicyclo[1.1.0]butane **2a** to cyclobutene **3a**, passing by the step of the intermediate formation of 1,3-butadiene **4a**. The final possibility C is represented by a process (stepwise or simultaneous) involving the stretching and breaking of the bridging bond of **2a** through a biradical mechanism, and 1,2-migration of the substituent to form **3a**. To discriminate among these three pathways, we performed photolysis of a deuterium-labeled compound, **2a-d₆**, having the two $^t\text{Bu}_2(\text{CD}_3)\text{Si}$ (*R-d₃*) groups at the bridging Si3 atom, which clearly demonstrated that the migration of the *R-d₃* groups did not take

place during the isomerization of **2a** to **3a**. From this observation, the biradical path C was ruled out, since it implies, a priori, a shift of one of the labeled substituents from bridge to bridgehead position. The concerted stepwise path A, commonly accepted in organic chemistry,^{13,14} also seems improbable, because it requires the intermediate formation of the rather unfavorable *trans*-**4a**, which is highly destabilized compared with **3a** by 20 kcal/mol.^{10b} Therefore, the most likely mechanistic scenario for the isomerization of **2a** to **3a** seems to be pathway B. It is worth mentioning that such a concerted photochemical transformation of bicyclo[1.1.0]butanes to cyclobutenes, which is to be classified as a process obeying the Woodward–Hoffmann orbital symmetry rules,¹⁴ is a novel motif of R_6E_4 valence isomers interplay,^{4,5} still unprecedented in the chemistry of the heavy group 14 elements.¹⁵

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Supporting Information Available: Experimental procedures and spectral data for **2a–c** and **3a,b**, scheme for the mechanism of photochemical isomerization of **2a** to **3a**, tables of crystallographic data including atomic positional and thermal parameters for **2b,c** and **3b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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