A Mechanistic Study of Thermal and Photochemical Isomerization between Hexasilyltetrasilabicyclo[1.1.0]butane and Hexasilyltetrasilacyclobutene

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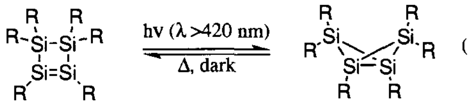
Thermal isomerization of hexakis(*t*-butyldimethylsilyl)-tetrasilabicylo[1.1.0]butane (**2**) to the corresponding tetrasilacyclobutene (**1**) as well as photochemical isomerization of **1** to **2** was confirmed using substituent-labeling experiments to proceed via 1,2-silyl-migration instead of skeletal isomerization.

We have recently reported isolation and characterization of the first stable cyclic disilene, hexakis(*t*-butyldimethylsilyl)-tetrasilacyclobutene (**1**, R = *t*-BuMe$_2$Si), together with the facile photochemical conversion of **1** to the corresponding tetrasilabicyclo[1.1.0]butane (**2**) and its thermal reversion to **1** (Eq. 1).[1] The interconversion between **1** and **2** is mechanistically quite interesting because no precedent of such isomerization has been reported. Whereas the first tetrasilabicyclo[1.1.0]butane was isolated by Masamune et al.,[2] the corresponding interconversion has not been reported.[3] It is well known that the thermal decomposition of a bicyclo[1.1.0]butane gives the corresponding 1,3-butadiene probably via the Woodward-Hoffmann allowed concerted pathway,[4] while photolysis of cyclobutene provides also 1,3-butadiene as a major product.[5]



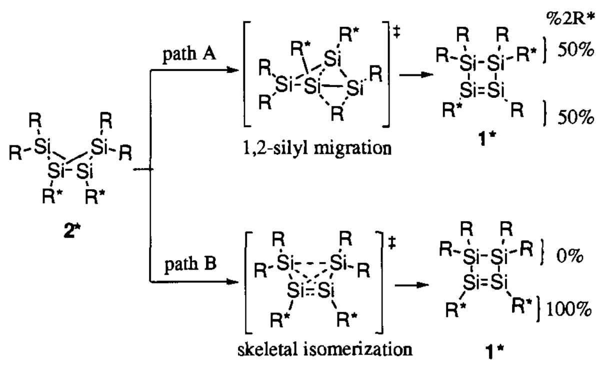
(1)

1 **2**

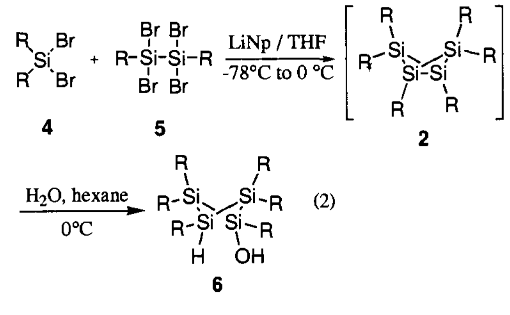
(R = *t*-BuMe$_2$Si)

As shown in the previous report,[1] the activation parameters for the thermal isomerization of **2** to **1** are $\Delta H^\ddagger$ = 16.5 kcal·mol^{-1} and $\Delta S^\ddagger$ = -20.8 cal·mol^{-1}·K^{-1}, which were determined by monitoring the time course of the absorption band of **1**. The large negative $\Delta S^\ddagger$ value suggests that the transition-state structure of the thermal isomerization would be significantly restricted, and therefore, any multi-step mechanisms involving bond-cleavage at the rate-determining step may be eliminated from the possible mechanisms. There are two plausible pathways for the isomerization of **2** to **1** as shown in Scheme 1: a concerted or a step-wise isomerization involving 1,2-silyl migration accompanied by cleavage of the central Si-Si bond of **2** (path A)[6] and a concerted skeletal isomerization (path B).[7] By labeling the two R groups on bridgehead silicons of **2** by two R* groups, the two pathways A and B will be discriminated. Thus, if the isomerization occurs via path A, one of the two R* groups will be found on the unsaturated silicon atoms (USi) of **1**, while the other at the saturated ring silicon atoms (SSi); the distribution of two R* groups over four-membered ring (%2R*) should be 50% at USi and 50% at SSi. On the other hand, in case of skeletal isomerization (path B), the %2R* should be 100% at USi.

Although we have reported the isolation of **1** through the reductive coupling of 2,2-dibromo-1,3-di(*t*-butyl)-1,1,3,3-tetramethyltrisilane (**4**, 2 equiv) with 2,2,3,3-tetrabromo-1,4-di(*t*-butyl)-1,1,4,4-tetramethyltetrasilane (**5**, 1 equiv), the facile thermal isomerization of **2** to **1** has suggested that the initial product of the reductive coupling is not **1** but **2**, which isomerizes to **1** during work-up at room temperature. Actually, neither **1** nor the hydrolysis products of **1** were formed in significant yields, when the reductive coupling was carried out at –78 °C; replacement of the solvent with hexane in vacuo at 0 °C, filtration, and then hydrolysis of the filtrate at 0 °C gave the hydrolysis product of **2**, 1-hydroxyhexasilylcyclotetrasilane **6**, in 12% yield (Eq. 2).[9]



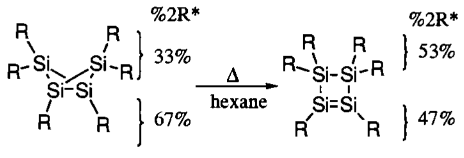
Scheme 1.



(2)

The above result has encouraged us to investigate the mechanism for the thermal isomerization by using a bridgehead-labeled tetrasilabicyclo[1.1.0]butane **2**-d_{12} (R* = *t*-Bu(CD$_3$)$_2$Si), which should be prepared by the reductive coupling of **4** with 2,2,3,3-tetrabromo-1,4-di(*t*-butyl)-1,1,4,4-tetrakis(trideuteriomethyl)tetrasilane (**5**-d_{12})[10] at low temperature. The reductive coupling of **4** with **5**-d_{12} at –78 °C followed by replacement of the solvent with hexane at 0 °C, filtration, and then hydrolysis of a portion of the filtrate at 0 °C in the dark gave 1-hydroxyhexasilylcyclotetrasilane **6**-d_{12}. Warming to room temperature and then work-up of the other portion of the filtrate afforded tetrasilacyclobutene **1**-d_{12}. The sum of %2R* values at SiH and SiOH silicons in **6**-d_{12}, which in turn corresponds to the value at the bridgehead silicons of **2**-d_{12}, was determined by

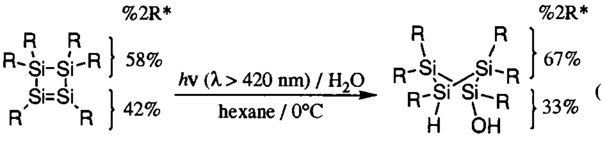
^{1}H NMR to be 67%.[11] Similarly, the %2R* values in **1**-d_{12} were determined as 47% at USi and 53% at SSi. The results imply that the thermal isomerization of **2**-d_{12} with the %2R* value of 67% at the bridgehead silicons gives **1**-d_{12} with that of 47% at USi (Eq. 3). The observed %2R* distribution in **1**-d_{12} is quite similar to that expected for path A, which is 42% at USi and 58% at SSi.[12] The present results exclude all the skeletal isomerization mechanisms involving pathways B and C.[7]



(3)

2-d_{12} **1**-d_{12}

Photolysis of **1**-d_{12} with a similar %2R* distribution as stated above in the presence of excess water in hexane at 0 °C gave **6**-d_{12} quantitatively with the %2R* values of 33% at SiH/SiOH silicons and 67% at the other silicons, which means random distribution of R* in **6**-d_{12}, and therefore, in **2**-d_{12} (Eq. 4). The photochemical isomerization of **1** to **2** should also occur via 1,2-silyl migration.



(4)

1-d_{12} **6**-d_{12}, quantitative

In conclusion, using deuterium-labeled **1** and **2**, we have confirmed that both the thermal isomerization from **2** to **1** and the photochemical isomerization from **1** to **2** proceed via 1,2-silyl migration. The thermal isomerization may occur through a concerted dyotropic-type rearrangement[13] or via the intermediary formation of a tetrasilacyclobutane-1,3-diyl diradical followed by the 1,2-silyl migration to the radical center.[14] In order to gain a further insight into the mechanism of the photochemical isomerization, the detailed knowledge of the excited state nature of **1** will be required. Remarkable difference in the reaction modes between the silicon and carbon analogs of bicyclo[1.1.0]-butane/cyclobutene system would be in part the consequence of the fact that the formation of a silicon analog of a conjugated diene is highly undesirable.[7,8]

Further work to elucidate the detailed mechanisms for reductive coupling to form tetrasilabicyclo[1.1.0]butane is in progress.

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References and Notes

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3 For reviews of interconversion among 1,3-butadiene, cyclobutene, and bicyclo[1.1.0]butane, see: (a) W. Leigh, *Chem. Rev.*, **93**, 487 (1993). b) W. R. Dolbier, Jr., H. Koroniak, K. N. Houk, and C. Sheu, *Acc. Chem. Res.*, **29**, 471 (1996).

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5 W. Adam, T. Oppenländer, and G. Zang, *J. Am. Chem. Soc.*, **107**, 3921 (1985).

6 Concertedness of 1,2-silyl migration as shown in Path A (Scheme 1) may not be guaranteed. Since the facile ring puckering is known to occur in the tetrasilabicyclo[1.1.0]butane reported by Masamune et al.[2] and in **2**,[1] rate-determining 1,2-silyl migration in the two-step reaction via intermediary formation of the corresponding tetrasilacyclobutane-1,3-diyl diradical would also be compatible with the observed $\Delta S^{\ddagger}$.

7 A two-step mechanism via thermal isomerization of **2** to the corresponding tetrasila-1,3-butadiene (**3**) followed by the ring-closure to **1** (path C) is possible but highly unlikely on the basis of the large negative $\Delta S^{\ddagger}$ value; for the isomerization of bicyclobutane to cyclobutene, $\Delta S^{\ddagger}$ is reported to be 2.8 cal·mol^{-1}·K^{-1} with $\Delta H^{\ddagger}$ = 39.7 kcal·mol^{-1}.[4b] Whereas the high instability of **3** is theoretically predicted,[8] a stable hexaaryltetrasila-1,3-butadiene was synthesized very recently: M. Weidenbruch, S. Willms, W. Saak, and G. Henkel, *Angew. Chem., Int. Ed. Engl.*, **36**, 2503 (1997).

8 An ab initio MO study has shown that tetrasila-1,3-butadiene is far more unstable than the most stable isomer, tetrasilabicyclo[1.1.0]-butane; the energy difference is 17.9 kcal/mol at the MP2/6-31G* level: M. Zhao and B. M. Gimarc, *Inorg. Chem.*, **35**, 5378 (1996), and references cited therein.

9 Only a small amount of tetrasilacyclobutene **1** (< 1 %) was detected in the hydrolysis products by NMR spectroscopy. It is noted that the reaction of pure **1** with water is quite slow even at room temperature probably due to the steric reason, while **2** is hydrolyzed readily at 0°C to afford 1,3-adduct **6** in a high yield.[1,2] The spectral data of **6** are given in ref. 1.

10 Deuterium content of **5**-d_{12} is determined by ^{1}H NMR spectroscopy to be more than 99%.

11 The results indicate that the scrambling of silyl substituents occurs during the reductive coupling, while the mechanism remains open. Intermolecular scrambling of R* groups does not take place during the reductive coupling nor in the hydrolysis step as confirmed by the MS spectral pattern of **1**-d_{12} and **6**-d_{12}.

12 Since the %R* values are reproducible within ±1%, the small difference between the observed and the expected %2R* distribution may be attributed to the minor contribution from a small amount of **1**-d_{12} formed directly during reductive coupling.[9] An attempted determination of the %2R* distribution in **1**-d_{12} in the hydrolysis products by ^{1}H NMR spectroscopy have failed.

13 M. T. Reetz, *Adv. Organomet. Chem.*, **16**, 33 (1977).

14 For examples of 1,2-silyl shifts, see: a) C. G. Pitt and M. S. Fowler, *J. Am. Chem. Soc.*, **90**, 1928 (1968). b) M. Ballestri, C. Chatgilialoglu, and G. Seconi, *J. Organomet. Chem.*, **408**, C1 (1991). c) M. Ballestri, C. Chatgilialoglu, M. Lucarini, and G. F. Pedulli, *J. Org. Chem.*, **57**, 948 (1992). d) C. Chatgilialoglu, A. Guarini, A. Guerrini, and G. Seconi, *J. Org. Chem.*, **57**, 2208 (1992).