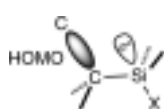


A Silyl Substituent Can Dictate a Concerted Electrocyclic Pathway: Inward Torquoselectivity in the Ring Opening of 3-Silyl-1-cyclobutene

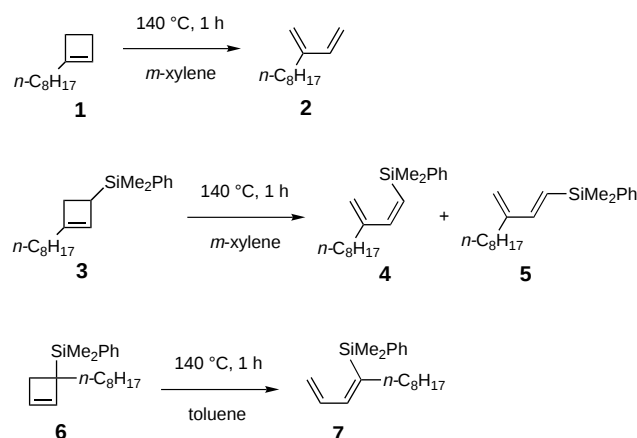
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A thermal conrotatory ring-opening reaction of cyclobutenes to produce 1,3-butadienes has been a source of continuing interest from the viewpoints of both organic and theoretical chemistry. The substituent effects on this reaction have been well studied in terms of torquoselectivity, namely, inward versus outward rotation.^[1] Theoretical studies proved that the stereochemical trend is subject to electronic control rather than steric control. For example, outward rotation is preferred by electron-donating substituents, such as a hydroxy group at the 3-position. In contrast, it was predicted that an electron-accepting substituent at the 3-position would prefer inward rotation.^[2] However, experimentally verified examples of this phenomenon have been limited to the CHO,^[3] COCl,^[3] and CF₃^[4] substituents. Even CO₂Et^[5] and CN^[6] groups favor outward rotation. On the other hand, it is known that, while the silicon atom in a Si–C linkage is depleted of its negative charge, silicon can accommodate electron density from a neighboring p orbital in its low lying σ^* orbital.^[7] The HOMO of the transition state of the ring-opening reaction of 1-cyclobutene is primarily concentrated on the cleaving C3–C4 σ orbital, which is a good electron donor. Thus, we anticipated that a silyl substituent at the 3-position would possibly accept the HOMO electron of the transition state, to result in its stabilization. Here, we report the interesting effects of the silyl substitution on a concerted thermal ring-opening reaction of 1-cyclobutene.

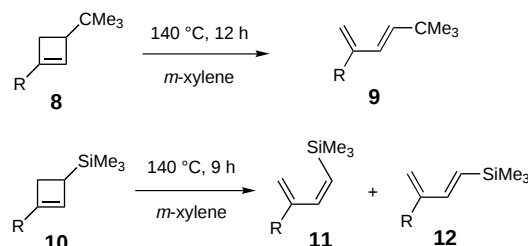


First, the reactions of 1-octyl-1-cyclobutene (**1**) and its silyl-substituted analogues **3** and **6** were examined (Scheme 1). After heating a solution of **1** at 140 °C for 1 h, only 12 % of **1** underwent a ring-opening reaction to produce 1,3-diene **2**. In contrast, when a mixture of **3** and **6** (58:42)^[8] was heated under the same conditions, complete conversion to the corresponding 1,3-dienes (**4**, **5**, and **7**; 96 % overall yield) was observed. An NMR analysis of the product mixture revealed that the ratio (**4** + **5**):**7** was identical with that of **3**:**6**, to confirm that the 1,3-dienes **4** and **5** arose from **3**, and the 1,3-diene **7** from **6**, in a specific manner. The reactions of **3** and **6** are therefore described separately in Scheme 1.

Interestingly, the *cis* isomer **4**, formed by inward rotation, was favored over the *trans* isomer **5**, formed by outward rotation (**4**:**5** = 83:17). The ratio **4**:**5** was constant through the reaction and even after heating for a longer period, which



Scheme 1. Ring-opening reactions of cyclobutenes **1**, **3**, and **6**.



Scheme 2. Ring-opening reactions of cyclobutenes **8** and **10**. R = PhMe₂C.

suggests that the ratio was kinetically determined. The preference for inward rotation was opposed to what might be expected on steric grounds. Moreover, only the *cis* isomer **7** was produced by inward rotation of **6**.^[9] The inward-selective ring opening reaction of **6** also took place at 110 °C in toluene and completed in 1 h.^[10] These results suggested that a silyl substituent at the 3-position of 1-cyclobutene accelerates the ring-opening reaction and prefers inward, rather than outward, rotation.

To get further experimental verification of this effect, cyclobutenes **8** and **10** were prepared and their reactivities compared. Cyclobutenes **8** and **10** have an identical structure except the tertiary element, that is, a carbon atom of a tertiary butyl group versus a silicon atom of a trimethylsilyl group. When heated at 140 °C, **8** underwent ring opening with outward rotation to give exclusively the *trans* isomer **9** (92 %),^[9] which is in agreement with the result of 3-methyl-1-cyclobutene.^[11] On the other hand, **10** furnished a mixture of *cis* isomer **11** and *trans* isomer **12**, with the former predominating (**11**:**12** = 69:31; 95 % overall yield). The reaction of **10** ($k = 0.53 \text{ h}^{-1}$ at 140 °C) was faster than that of **8** ($k = 0.32 \text{ h}^{-1}$ at 140 °C). The proportion of *cis* and *trans* isomers **11**:**12** was again opposite to what would be predicted as a result of simple steric argument. The contrasting results of **8** and **10** confirm that a silyl substituent prefers inward rotation.

For density functional theory calculations, 3-silyl-1-cyclobutene (**13**) was taken as a model and the transition states for outward and inward rotations were computationally located.^[12] The potential-energy diagram is shown in Figure 1. The activation energy for inward rotation to *cis* product **15** is 1.67 kcal mol⁻¹ lower than that of outward rotation to *trans*

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product **14**. In the case of 3-methyl-1-cyclobutene, the carbon counterpart of **13**, the calculated preference is just the opposite, that is, the outward rotation is favored by 5.3 kcal mol⁻¹.^[13]

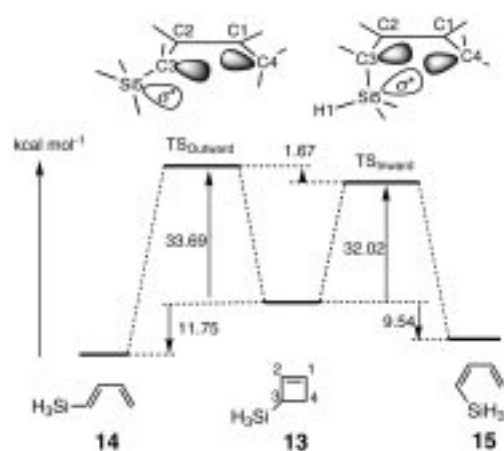


Figure 1. Potential-energy diagram of ring opening reactions of 3-silyl-1-cyclobutene **13**.

For the inward transition state of **13**, the angle C4-C3-Si5 is 92° and the dihedral angle C4-C3-Si5-H1 is 170°. These structural features indicate that the Si5-H1 σ^* orbital eclipses well with the breaking C3-C4 σ orbital, where the HOMO electron is primarily concentrated, and thus accommodates some of the HOMO electron density. For the outward transition structure, in which the angle C4-C3-Si5 is as much as 132°, an analogous stabilizing interaction of the silicon σ^* orbital with the HOMO is smaller. Thus, the observed inward preference and accelerating effect of a silyl substituent can be explained by assuming electron-accepting interactions of the rather low lying σ^* orbital of the silicon atom with the HOMO orbital of the inward transition state.^[14]

The substitution effects of silicon are now widely utilized in a variety of organic reactions.^[15] The stabilization of β -cations in electrophilic reactions of organosilicon compounds is one of the most exploited. The present study discloses an interesting influence of silyl substituents on a concerted electrocyclic reaction. Further investigations of the effects of silyl substituents on other concerted electrocyclic reactions are underway.

Experimental Section

11 and **12**: A solution **10** (30.0 mg, 0.10 mmol) in *m*-xylene (2 mL) was heated at 140 °C for 9 h under an argon atmosphere. The cooled reaction mixture was filtered through a pad of florisil and the filtrate was purified by preparative thin-layer chromatography (silica gel, *n*-hexane) to afford **11** and **12** (69:31, 28.6 mg, 95 %) as a colorless oil. **11**: ¹H NMR (200 MHz, CDCl₃): δ = 0.12 (s, 9H), 1.42 (s, 6H), 5.09 (d, *J* = 1.4 Hz, 1H), 5.15 (d, *J* = 1.4 Hz, 1H), 5.43 (d, *J* = 14.8 Hz, 1H), 6.36 (d, *J* = 14.8 Hz, 1H), 7.18–7.38 (m, 5H); ¹³C NMR (75 MHz, CDCl₃): δ = 0.3, 28.4, 42.8, 111.3, 125.9, 126.3, 128.1, 131.3, 147.2, 148.0, 156.2; elemental analysis: calcd for C₁₆H₂₄Si: C 78.62, H 9.90; found: C 78.86, H 10.14. **12**: ¹H NMR (300 MHz, CDCl₃): δ = 0.07 (s, 9H), 1.44 (s, 6H), 5.09 (s, 1H), 5.35 (s, 1H), 5.90 (d, *J* = 18.6 Hz, 1H), 6.09 (d, *J* = 18.6 Hz, 1H), 7.11–7.30 (m, 5H); ¹³C NMR (75 MHz, CDCl₃): δ = -1.5, 28.9, 42.9, 109.8, 125.7, 126.3, 128.1, 130.9, 144.1, 148.3, 156.0; elemental analysis: calcd for C₁₆H₂₄Si: C 78.62, H 9.90; found: C 79.01, H 10.22.

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- [10] No appreciable reaction of **1** occurred at 110 °C. The reaction of **3** at 110 °C was slower than that of **6** and took 3 days to reach completion. The ratio of **4**:**5** formed at 110 °C was 89:11.
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