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Studies on the Thermal Ring-Opening Reactions of *cis*-3,4-Bis(organosilyl)cyclobutenes

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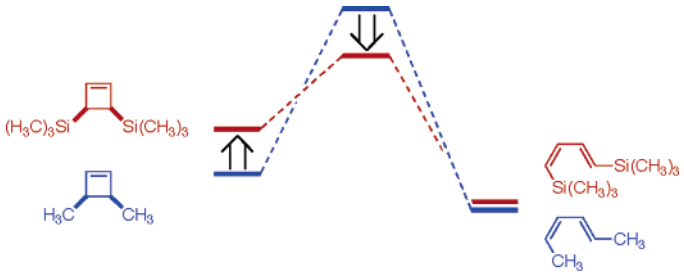
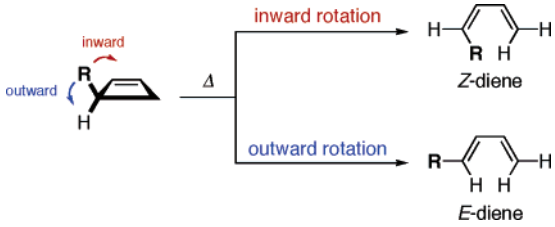


Three *cis*-3,4-bis(organosilyl)cyclobutenes were synthesized, and their thermal ring-opening reactions were studied. The ring-opening reaction of *cis*-3,4-bis(trimethylsilyl)cyclobutene proceeded remarkably faster than that of *cis*-3,4-dimethylcyclobutene. The significant rate acceleration was explained by assuming (i) stabilization of the transition state by electron delocalization from the cyclobutene HOMO to the Si−CH_3 σ^* orbital, (ii) destabilization of the ground state by intramolecular interaction between the C−Si σ orbitals and the π orbital of cyclobutene, and (iii) through-space steric repulsion of the two bulky trimethylsilyl groups in a *cis* arrangement. The ring-opening reaction of unsymmetrical *cis*-3,4-bis(arylsilyl)cyclobutenes having electronically different arylsilyl groups was also examined. The inward preference increased in the order, *p*-$CH_3OC_6H_4$−Si, C_6H_5−Si, *p*-$CF_3C_6H_4$−Si, supporting the interpretation of the origin of the inward preference of silyl substituents on the basis of a stabilizing interaction between the cyclobutene HOMO and the Si−C σ^* orbital at the transition state.

1. Introduction

An electrocyclic ring-opening reaction of cyclobutenes to produce conjugated 1,3-dienes has been a source of continuing interest in terms of the rotational behavior of the substituents. Woodward−Hoffmann rules state that, under thermal conditions, the substituents located at the 3- and 4-positions rotate in a same direction, that is, in a conrotatory fashion.[1] Another stereochemical feature, which is also of fundamental importance, concerns the direction of the rotation relative to the cleaving σ bond; a substituent can move toward the breaking C3−C4 bond (inward rotation) or away from it (outward rotation) during the thermal ring-opening reaction. The selectivity of the rotational direction has been termed "torquoselectivity" by Houk and has been intensively studied theoretically and experimentally since the 1980s (Scheme 1, the 1,3-butadiene-type products are depicted in an s-*cis* conformation for convenience in this paper).[2]

SCHEME 1. Ring-Opening Reaction of 3-Substituted Cyclobutene



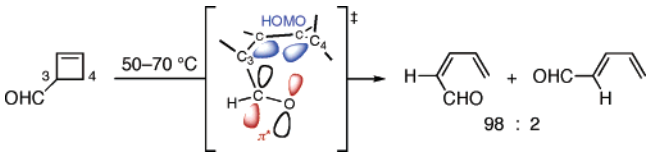
Simple steric arguments would predict that outward rotation is preferred over inward rotation because inward rotation suffers from more steric repulsion than outward rotation. However, there are examples which contradict this expectation. Substituents of

(1) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1970.

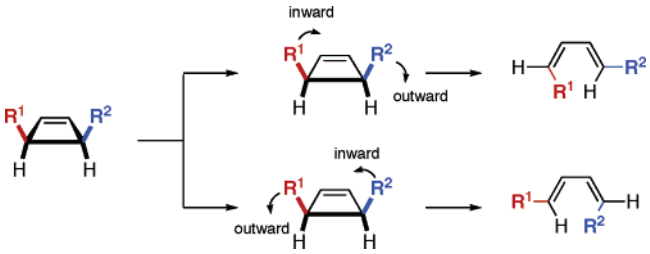
(2) (a) Durst, T.; Breau, L. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon Press: Oxford, 1991; Vol. 5, pp 675−697. (b) Dolbier, W. R., Jr.; Koroniak, H.; Houk, K. N.; Sheu, C. *Acc. Chem. Res.* **1996**, *29*, 471.

10.1021/jo070039n CCC: $37.00
Published on Web 04/14/2007

SCHEME 2. Ring-Opening Reaction of 3-Formylcyclobutene



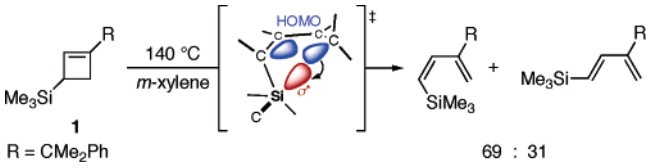
SCHEME 3. Ring-Opening Reaction of Unsymmetrical *cis*-3,4-Disubstituted Cyclobutenes



an electron-accepting nature rotate preferentially inward; that is, they move into a significantly more congested environment.[3] For example, the ring-opening reaction of 3-formylcyclobutene produces (*Z*)-penta-2,4-dienal stereoselectively via inward rotation of the formyl group (Scheme 2).[3a] An orbital interaction theory proposed by Rondan and Houk provides a clear explanation for the contrasteric rotational behavior of electron-accepting substituents.[4] During the thermal ring-opening reaction, the σ orbital connecting the 3- and 4-carbons of cyclobutene breaks up in a conrotatory fashion and the distorted σ orbital becomes the HOMO at the transition state. The electron density of the HOMO is mostly concentrated between the 3- and 4-carbons. Likewise, the σ^* orbital of the C3−C4 linkage, which has a node in the middle, is distorted by conrotation to become the LUMO of the transition state. When a substituent at the 3-position rotates inward, it approaches the distorted C3−C4 linkage of the parent cyclobutene skeleton, and at the transition state, it comes into the vicinity of the HOMO, which is potentially a good electron donor. If the rotating substituent possesses an energetically low-lying vacant orbital, it accepts electron density from the HOMO. Such electron delocalization stabilizes the inward transition state relative to the outward transition state.

It is interesting to examine the substituent effects on the ring-opening reaction of *cis*-3,4-disubstituted cyclobutenes (Scheme 3). Since both substituents rotate in the same direction under thermal conditions according to the Woodward−Hoffmann rules, one substituent has to rotate outward and the other has to rotate inward. If the two different substituents in a *cis* arrangement possess opposite preferences in torquoselectivity, their preferences reinforce the torquoselectivity. On the other hand, if the two substituents possess the same torquoselective preferences, either outward or inward, their preferences for rotational direction have to mismatch and competition arises in determining rotational direction. Thus, the stereochemical outcome of the ring-opening reaction reflects the magnitude of rotational preferences of the two substituents.

SCHEME 4. Ring-Opening Reaction of 3-Silylcyclobutene



We recently discovered the interesting preference of silyl groups for inward rotation (Scheme 4).[5−8] This preference of silyl substituents can be understood on the basis of the Houk's theory by invoking the electron-accepting nature of silyl substituents. Whereas the σ orbital of a Si−C linkage is energetically high-lying enough to donate its electron density to nearby vacant orbitals, the antibonding σ^* orbital of a Si−C linkage is energetically low-lying.[9] In addition, the Si−C σ^* orbital is polarized toward the silicon end due to the difference in electronegativity. Therefore, the Si−C σ^* orbital is potentially a good electron acceptor, accommodating electron density on the silicon end. At the inward transition state, the energetically low-lying σ^* orbital on silicon is in the vicinity of the HOMO of the opening cyclobutene skeleton, that is, the breaking C3−C4 σ orbital which is distorted by conrotation. Thus, overlap can occur between the two orbitals, providing stabilization to the inward transition state through the electron delocalization.

Our communication[5a] was followed by two papers, wherein the preference of inward rotation of silyl substituents was studied from a theoretical point of view. Whereas the theoretical study by Houk's group supports our interpretation based on the HOMO−σ^* interaction,[10] Inagaki and his co-workers offer the explanation of geminal σ-bond participation.[11] If an electronically biased substituent, either electron-withdrawing or electron-donating, is introduced on silicon at the 3-position of a cyclobutene, opposite electronic influences are excepted for the substituent depending on which electronic interaction, HOMO−σ^* interaction or geminal σ-bond participation, dominates at the transition state (vide infra). In order to obtain experimental information about the origin of the contrasteric inward preference of silyl substituents, we synthesized one symmetrical and

(3) (a) Rudolf, K.; Spellmeyer, D. C.; Houk, K. N. *J. Org. Chem.* **1987**, *52*, 3708. (b) Piers, E.; Lu, Y.-F. *J. Org. Chem.* **1989**, *54*, 2267. (c) Dolbier, W. R., Jr.; Gray, T. A.; Keaffaber, J. J.; Celewicz, L.; Koroniak, H. *J. Am. Chem. Soc.* **1990**, *112*, 363. (d) Jefford, C. W.; Bernardinelli, G.; Wang, Y.; Spellmeyer, D. C.; Buda, A.; Houk, K. N. *J. Am. Chem. Soc.* **1992**, *114*, 1157. (e) Niwayama, S.; Houk, K. N. *Tetrahedron Lett.* **1993**, *34*, 1251 and references therein.

(4) (a) Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 2099. (b) Kirmse, W.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 7989.

(5) (a) Murakami, M.; Miyamoto, Y.; Ito, Y. *Angew. Chem., Int. Ed.* **2001**, *40*, 189. (b) Murakami, M.; Miyamoto, Y.; Ito, Y. *J. Am. Chem. Soc.* **2001**, *123*, 6441. (c) Murakami, M.; Hasegawa, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 4874.

(6) A similar or related effect of silyl substituents was observed in other electrocyclic reactions. A ring-opening reaction of silyloxetene: (a) Shindo, M.; Matsumoto, K.; Mori, S.; Shishido, K. *J. Am. Chem. Soc.* **2002**, *124*, 6840. (b) Mori, S.; Shindo, M. *Org. Lett.* **2004**, *6*, 3945. Nazarov cyclization: (c) Denmark, S. E.; Wallace, M. A.; Walker, C. B., Jr. *J. Org. Chem.* **1990**, *55*, 5543. (d) Smith, D. A.; Ulmer, C. W., II. *J. Org. Chem.* **1993**, *58*, 4118.

(7) For inward preference of tin and boron substituents, see: (a) Murakami, M.; Hasegawa, M.; Igawa, H. *J. Org. Chem.* **2004**, *69*, 587. (b) Murakami, M.; Usui, I.; Hasegawa, M.; Matsuda, T. *J. Am. Chem. Soc.* **2005**, *127*, 1366.

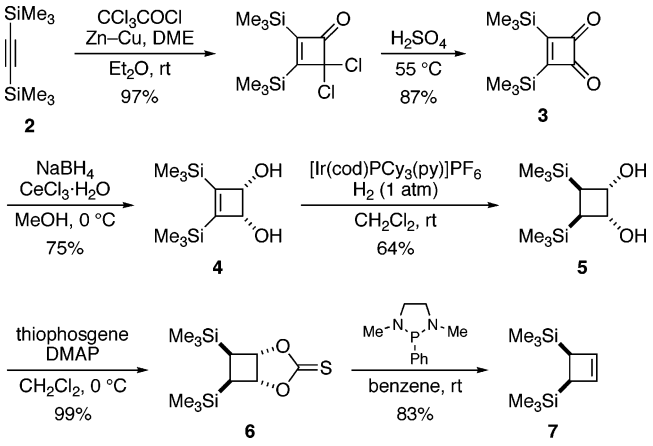
(8) For an accelerating effect of (organosilyl)methyl substituents in the ring opening of benzocyclobutenes, see: Matsuya, Y.; Ohsawa, N.; Nemoto, H. *J. Am. Chem. Soc.* **2006**, *128*, 412.

(9) (a) Bock, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1627. (b) Giordan, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 6544. (c) Giordan, J. C.; Moore, J. H. *J. Am. Chem. Soc.* **1983**, *105*, 6541.

(10) (a) Lee, P. S.; Zhang, X.; Houk, K. N. *J. Am. Chem. Soc.* **2003**, *125*, 5072. (b) Shindo, M.; Sato, Y.; Shishido, K. *J. Org. Chem.* **2000**, *65*, 5443.

(11) (a) Yasui, M.; Naruse, Y.; Inagaki, S. *J. Org. Chem.* **2004**, *69*, 7246. (b) Ikeda, H.; Kato, T.; Inagaki, S. *Chem. Lett.* **2001**, 270.

SCHEME 5. Synthesis of *cis*-3,4-Bis(trimethylsilyl)cyclobutene 7[a]



[a] DME = 1,2-dimethoxyethane; cod = 1,5-cyclooctadiene; PCy_3 = tricyclohexylphosphine; py = pyridine; DMAP = 4-dimethylaminopyridine.

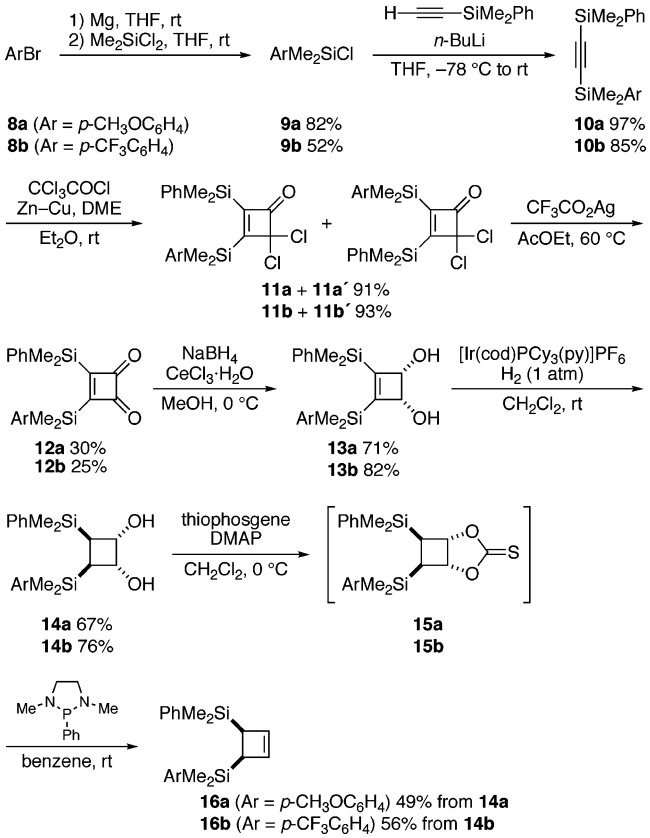
two unsymmetrical *cis*-3,4-bis(organosilyl)cyclobutenes and examined their ring-opening reactions. In this paper, we describe the results of a systematic study of the ring-opening reactions of *cis*-3,4-bis(organosilyl)cyclobutenes.

2. Results and Discussion

2.1. Synthesis of *cis*-3,4-Bis(organosilyl)cyclobutenes. The synthesis of *cis*-3,4-bis(trimethylsilyl)cyclobutene **7** is shown in Scheme 5. This represents a general method for the synthesis of cyclobutenes having two organosilyl groups at the 3- and 4-positions in a *cis* arrangement. Cyclobutenedione **3** was prepared from 1,2-bis(trimethylsilyl)ethyne **2** according to a literature procedure.[12] The dione **3** was then reduced to the *cis*-diol **4** with $NaBH_4/CeCl_3 \cdot H_2O$.[13] The olefinic diol **4** was subjected to hydrogenation using a cationic iridium catalyst under homogeneous conditions.[14] The two hydroxyl groups coordinate to iridium to cause *syn* hydrogenation from the same face, thus providing the two trimethylsilyl groups in a *cis* relationship. Next, the *cis*-1,2-diol unit of **5** was converted into a carbon−carbon double bond by the Corey−Hopkins method.[15] A reaction of **5** with thiophosgene afforded the cyclic thiocarbonate **6**. Reductive deoxygenation at room temperature using 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine produced the desired *cis*-3,4-bis(trimethylsilyl)cyclobutene **7**.

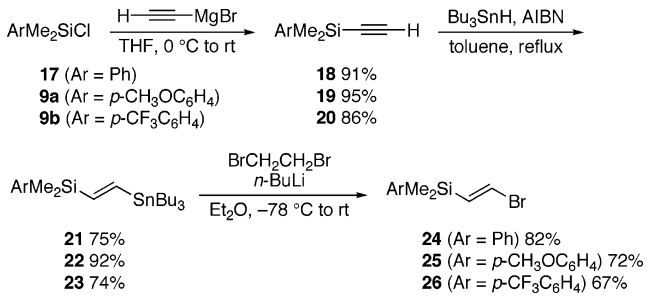
Unsymmetrical *cis*-3,4-bis(organosilyl)cyclobutenes **16a** and **16b** were synthesized according to an analogous procedure starting from unsymmetrically substituted 1,2-bis(organosilyl)-ethynes **10a** and **10b**, respectively (Scheme 6). The unsymmetrical 1,2-bis(organosilyl)ethynes **10a** and **10b** were prepared from the corresponding substituted phenyl Grignard reagents and ethynyldimethyl(phenyl)silane. Unlike the synthesis of **7**, H_2SO_4 was not used for hydrolysis of these α-dichlorocyclobutenones **11** since concomitant cleavage of the Si−aryl linkages was noted. Instead, a silver salt ($AgOCOCF_3$) could be employed in the conversion of **11a** and **11b** to the corresponding α-diketones **12a** and **12b**,[16] although the yield was marginally acceptable.

SCHEME 6. Synthesis of Unsymmetrical *cis*-3,4-Bis(organosilyl)cyclobutenes 16[a]



[a] See Scheme 5 for abbreviations.

SCHEME 7. Synthesis of (*E*)-1-Bromo-2-silylethenes (24−26)

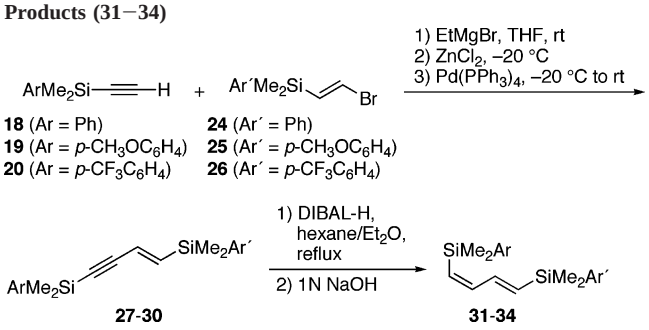


2.2. Synthesis of Authentic Samples of the Ring-Opening Products. It is not straightforward to identify the stereochemistries of compounds which result from the conrotatory ring-opening reaction of unsymmetrical cyclobutenes **16a** and **16b**. Therefore, stereochemically authentic samples of the products **31**, **32**, **33**, and **34** were independently prepared by cross-coupling reactions, as shown in Scheme 7 and Table 1.[17] The stereochemistries of the ring-opening products were determined by comparison of the ^1H NMR spectra with those of the authentic samples.

2.3. Thermal Ring-Opening Reactions of *cis*-3,4-Bis(organosilyl)cyclobutenes. *cis*-3,4-Bis(trimethylsilyl)cyclobutene

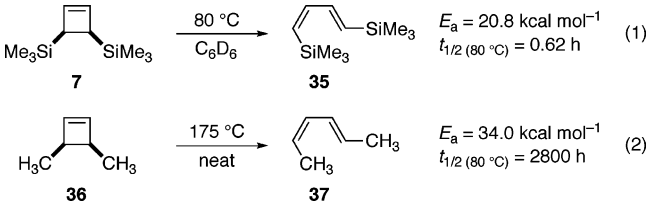
(12) Zhao, D. C.; Allen, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1993**, *115*, 10097.
(13) Luche, J.-L. *J. Am. Chem. Soc*. **1978**, *100*, 2226.
(14) (a) Crabtree, R. H.; Davis, M. W. *Organometallics* **1983**, *2*, 681. (b) Crabtree, R. H.; Davis, M. W. *J. Org. Chem.* **1986**, *51*, 2655.
(15) Corey, E. J.; Hopkins, P. B. *Tetrahedron Lett.* **1982**, *23*, 1979.
(16) Liu, R.; Marra, R. M.; Tidwell, T. T. *J. Org. Chem.* **1996**, *61*, 6227.
(17) Andreini, B. P.; Carpita, A.; Rossi, R.; Scamuzzi, B. *Tetrahedron* **1989**, *45*, 5621.

TABLE 1. Synthesis of Authentic Samples of the Ring-Opening Products (31−34)



	enyne (yield)	diene (yield)
Ar = Ph, Ar′ = *p*-$CH_3OC_6H_4$ (from **18** and **25**)	**27** (72%)	**31** (78%)
Ar = *p*-$CH_3OC_6H_4$, Ar' = Ph (from **19** and **24**)	**28** (79%)	**32** (70%)
Ar = *p*-$CF_3C_6H_4$, Ar' = Ph (from **20** and **24**)	**29** (52%)	**33** (73%)
Ar = Ph, Ar' = *p*-$CF_3C_6H_4$ (from **18** and **26**)	**30** (65%)	**34** (77%)

SCHEME 8. Ring-Opening Reaction of *cis*-3,4-Bis(trimethylsilyl)cyclobutene 7 and *cis*-3,4-Dimethylcyclobutene 36



7 was heated in C_6D_6 at 80 °C (Scheme 8, eq 1). It underwent a ring-opening reaction in a conrotatory fashion to afford (1*Z*,3*E*)-1,4-bis(trimethylsilyl)butadiene **35**.[17] Remarkably, the half-life at 80 °C was 37 min. The kinetics of the ring-opening reaction were investigated at varying temperatures, and activation parameters $k = 10^{9.5}\exp(-20.8/RT)\ s^{-1}$ were obtained from the Arrhenius plot.[18] The activation parameters of the ring opening of *cis*-3,4-dimethylcyclobutene **36** are reported as $k = 10^{13.9}\exp(-34.0/RT)\ s^{-1}$ (Scheme 8, eq 2).[19] The activation energy of **7** is smaller than that of **36** by more than 13 kcal/mol. The half-life for **36** at 80 °C was 4500 times longer than that for **7**.

Thus, it has a huge effect on the ring-opening reactivity to place the two trimethylsilyl groups at the 3- and 4-positions. The ring-opening reaction of **7** ($k = 78.1\ h^{-1}$ at 140 °C) was significantly fast even if compared with those of 1-(1-methyl-1-phenylethyl)-3-(trimethylsilyl)cyclobutene **1** ($k = 0.530\ h^{-1}$ at 140 °C)[5a] and *trans*-3,4-bis(trimethylsilyl)cyclobutene ($k = 5.04\ h^{-1}$ at 140 °C).[5c]

We assume that the following three factors are responsible for the significant acceleration. The first one is the electronic participation of the trimethylsilyl group which *stabilizes* the transition state (Figure 1a). One of the two trimethylsilyl groups rotates inward to approach the HOMO of the opening cyclobutene skeleton. The energetically low-lying σ^* orbital of the Si−CH_3 linkage accepts electron density from the HOMO at the transition state. The transition state is stabilized by this electron delocalization.

The second factor is the electronic participation of the trimethylsilyl groups which *destabilizes* the ground state of **7**

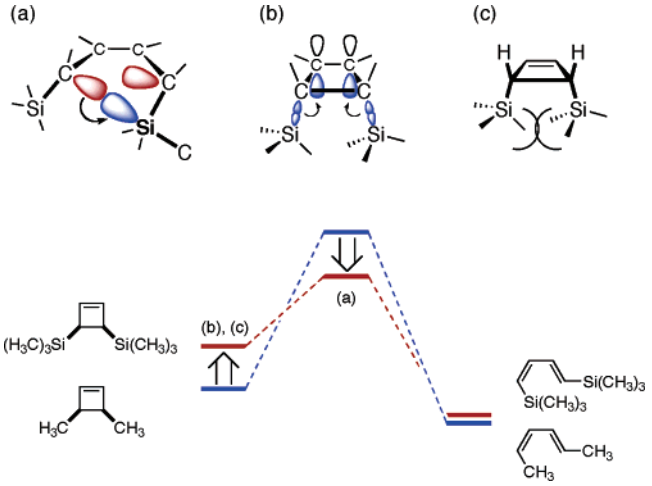


FIGURE 1. Three factors accelerating the ring-opening reaction of *cis*-3,4-bis(trimethylsilyl)cyclobutene **7**.

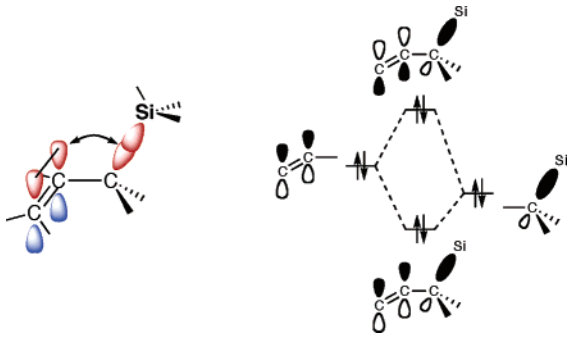


FIGURE 2. σ-Bond interaction between a Si−C bond and an allylic π bond.

(Figure 1b). The two trimethylsilyl groups of **7** are located at the allylic positions of the carbon−carbon double bond and aligned to interact well with the π orbital of the carbon−carbon double bond. The σ orbitals of the C3−Si and C4−Si linkages are energetically higher and, therefore, energetically closer to the π orbital than the corresponding C−CH_3 σ orbitals of **36** (Figure 2). The intramolecular interaction between the C−Si σ orbitals and the π orbital, which are both occupied, results in destabilization of the ground state.[9c,20]

The third factor is through-space steric repulsion between the two sterically bulky trimethylsilyl groups, which also destabilizes the ground state of **7** (Figure 1c). The two trimethylsilyl groups are aligned on the cyclobutene ring such that they eclipse each other. A through-space repulsive interaction arises among them to destabilize the ground state.

We assume these three factors, one stabilizing the transitions state of the ring-opening reaction and the other two destabilizing the ground state of the starting material **7**, provide an explanation for the significant decrease of the activation energy observed in the reaction of **7**.

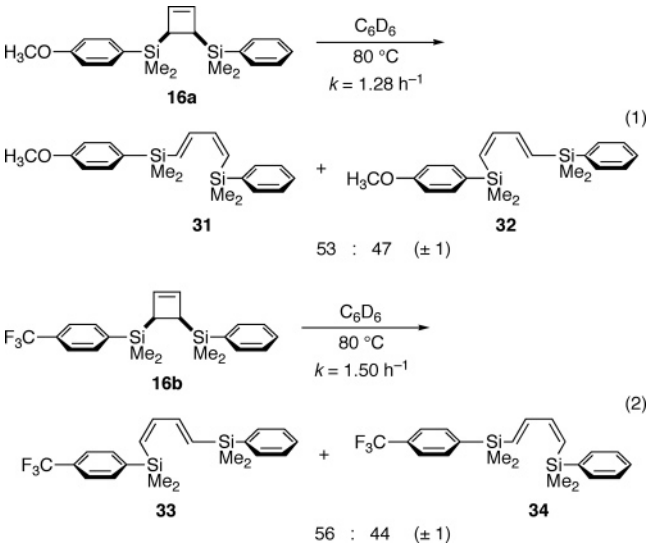
Next, we examined the thermal ring-opening reaction of unsymmetrical cyclobutenes **16a** and **16b** having different

(18) The log *A* values of the ring-opening reaction of cyclobutenes are normally in the range of 11.7−14.0 s^{-1}.[4b] The observed log *A* value of **7** was considerably smaller, although the reason was unclear.

(19) (a) Srinivasan, R. *J. Am. Chem. Soc.* **1969**, *91*, 7557. (b) Winter, R. E. K. *Tetrahedron Lett.* **1965**, *6*, 1207.

(20) Yoshida, J.; Nishiwaki, J. *J. Chem. Soc., Dalton Trans.* **1998**, 2589.

SCHEME 9. Ring-Opening Reaction of Unsymmetrical *cis*-3,4-Bis(organosilyl)cyclobutenes 16a and 16b



organosilyl substituents at the 3- and 4-positions in a *cis* arrangement. The unsymmetrical cyclobutene **16a** is equipped with dimethylphenylsilyl and dimethyl(*p*-methoxyphenyl)silyl substituents. Another unsymmetrical cyclobutene **16b** is substituted by dimethylphenylsilyl and dimethyl(*p*-trifluoromethylphenyl)silyl groups. These organosilyl groups would all prefer inward rotation rather than outward rotation. The key feature in these substrates is that although the different aryl groups on silicon are approximately the same size they are different enough in electronic nature to extend their electronic influence to the σ and σ^* orbitals of the C−Si linkage of the organosilyl substituents. The σ^* energy levels of the aryl−Si linkages decrease in the order, *p*-$CH_3OC_6H_4$−Si, C_6H_5−Si, *p*-$CF_3C_6H_4$−Si.[21] Likewise, the polarization of the aryl−Si σ^* orbital toward the silicon end increases across the series, *p*-$CH_3OC_6H_4$−Si, C_6H_5−Si, *p*-$CF_3C_6H_4$−Si. The stabilizing interaction of the cyclobutene HOMO occurs more efficiently with an energetically closer and more polarized σ^* orbital, both of which should be strongest with the *p*-$CF_3C_6H_4$−Si σ^* orbital among the series. Therefore, if the origin of the inward preference of silyl substituents is related to transition state interactions of HOMO−σ^*, the magnitude of the preference for inward rotation should increase in the order, *p*-$CH_3OC_6H_4$−Si, C_6H_5−Si, *p*-$CF_3C_6H_4$−Si. On the contrary, the electron-donating capability of the σ orbital connecting the C3 carbon and the silicon would decrease in the order, *p*-$CH_3OC_6H_4$Si−C3, C_6H_5Si−C3, *p*-$CF_3C_6H_4$Si−C3, Therefore, the interpretation based on the geminal σ-bond participation would predict that the magnitude of inward preference increases in the reverse order.

The ring-opening reaction of the unsymmetrically disubstituted cyclobutene **16a** and **16b** was carried out at 80 °C in C_6D_6. The reaction of **16a** proceeded with $k = 1.28$ h^{-1} to afford a mixture of 1,3-butadienes **31** and **32** (Scheme 9, eq 1). The 1,3-butadiene **31** which resulted from inward rotation of the dimethylphenylsilyl substituent predominated over the 1,3-butadiene **32** which resulted from inward rotation of the dimethyl(*p*-methoxyphenyl)silyl substituent with a ratio **31**/**32** = 53:47 (±1) (see Experimental Section for determination of the ratio).

The reaction of **16b** proceeded faster ($k = 1.50$ h^{-1}) than that of **16a** to produce a mixture of 1,3-butadienes **33** and **34** (Scheme 9, eq 2). The 1,3-butadiene **33** which resulted from inward rotation of the dimethyl(*p*-trifluoromethylphenyl)silyl substituent predominated over the 1,3-butadiene **34** which resulted from inward rotation of the dimethylphenylsilyl substituent with a ratio of **33**/**34** = 56:44 (±1) (see Experimental Section for determination of the ratio).

The stereochemical deviations observed with the products of the ring-opening reactions of **16a** and **16b** are consistent with expectations based on the stabilizing HOMO−σ^* interaction; the magnitude of inward preference increased in the order, *p*-$CH_3OC_6H_4$−Si, C_6H_5−Si, *p*-$CF_3C_6H_4$−Si. Although differences in activation energies are relatively small (0.084 kcal/mol for **31** vs **32**; 0.17 kcal/mol for **33** vs **34**), these small differences are the consequence of the small structural variation that is given to the pair of competitive substituents in order to minimize influences of other factors. These experimental results supported the interpretation that the origin of the inward preference of silyl substituents is attributed to the electron delocalization from the HOMO to the Si−C σ^* orbital.

3. Conclusion

cis-3,4-Disubstituted cyclobutenes are useful substrates to compare the torquoselectivity of the two different substituents in conrotatory ring-opening reactions. We synthesized the *cis*-3,4-bis(organosilyl)cyclobutenes and examined their ring-opening reactions. The degrees of inward preferences of the *p*-$CF_3C_6H_4Me_2Si$, $C_6H_5Me_2Si$, and *p*-$CH_3OC_6H_4Me_2Si$ groups were compared in the ring-opening reaction of unsymmetrical *cis*-3,4-bis(aryldimethylsilyl)cyclobutenes. The magnitude of inward preference increases in the order, *p*-$CH_3OC_6H_4$−Si, C_6H_5−Si, *p*-$CF_3C_6H_4$−Si. This electronic trend provides important experimental support for explanation of the origin of inward preferences by silyl groups based on the HOMO−σ^* interaction.

4. Experimental Section

(1*R,2*S**)-3,4-Bis(trimethylsilyl)cyclobut-1-ene-1,2-diol (4).** To a solution of **3** (5.00 g, 22.1 mmol) and $CeCl_3 \cdot H_2O$[22] (11.7 g, 44.2 mmol) in MeOH (470 mL) was added $NaBH_4$ (2.20 g, 58.2 mmol) in several portions at 0 °C. The reaction mixture was stirred at 0 °C for 2 h and then quenched with saturated NH_4Cl aqueous solution. The mixture was extracted with AcOEt (100 mL) 10 times. The combined organic extracts were washed with brine, dried over Na_2SO_4, and evaporated. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 3:1) to provide **4** (3.82 g, 16.6 mmol, 75%): ^{1}H NMR (300 MHz) δ 0.17 (s, 18H), 2.25 (d, $J = 6.4$ Hz, 2H), 4.76 (d, $J = 6.4$ Hz, 2H); ^{13}C NMR δ −0.9, 76.0, 172.9; HRMS (EI) calcd for $C_{10}H_{22}O_2Si_2$ (M^+) 230.1158, found 230.1153.

(1*R,2*S**,3*R**,4*S**)-3,4-Bis(trimethylsilyl)cyclobutane-1,2-diol (5).** A mixture of **4** (947 mg, 4.11 mmol) and [Ir(cod)PCy_3(py)]-PF_6[23] (98.8 mg, 0.12 mmol, 3 mol %) in CH_2Cl_2 (8 mL) was stirred under a hydrogen atmosphere at room temperature. After being stirred for 12 h, the reaction mixture was concentrated and passed through a short column of Florisil eluting with Et_2O. The residue

(21) Computational studies [B3LYP/6-31G(d)] were carried out on *p*-$CF_3C_6H_4SiH_3$, $C_6H_5SiH_3$, and *p*-$CH_3OC_6H_4SiH_3$. The natural bond orbital (NBO) analysis showed that the energy levels of the C−Si σ^* orbitals increase in this order, *p*-$CF_3C_6H_4$−Si (131.2 kcal/mol), C_6H_5−Si (139.9 kcal/mol), and *p*-$CH_3OC_6H_4$−Si (144.3 kcal/mol).

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(23) Brown, J. M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 190.

was purified by column chromatography on silica gel (hexane/AcOEt = 2:1) to afford **5** (615 mg, 2.65 mmol, 64%): ^{1}H NMR (300 MHz) δ 0.06 (s, 18H), 1.82 (d, J = 4.8 Hz, 2H), 2.78 (br, 2H), 4.14 (d, J = 4.2 Hz, 2H); ^{13}C NMR δ −1.1, 33.0, 71.8; HRMS (FAB) calcd for $C_{10}H_{23}OSi_2$ (M^+ − OH) 215.1287, found 215.1287.

(1*R,2*S**,6*R**,7*S**)-6,7-Bis(trimethylsilyl)-2,4-dioxabicyclo-[3.2.0]heptane-3-thione (6).** To a mixture of **5** (360 mg, 1.54 mmol) and DMAP (455 mg, 3.78 mmol) in CH_2Cl_2 (10 mL) was added thiophosgene (0.14 mL, 1.84 mmol) slowly. After stirring at 0 °C for 2 h, silica gel was added. The mixture was passed through a short column of Florisil eluting with Et_2O. The filtrate was evaporated to afford **6** (418 mg, 1.52 mmol, 99%): ^{1}H NMR (300 MHz) δ 0.13 (s, 18H), 2.43−2.44 (m, 2H), 5.06−5.07 (m, 2H); ^{13}C NMR δ −1.6, 33.0, 83.8, 193.7; HRMS (FAB) calcd for $C_{11}H_{23}O_2SSi_2$ (M^+ + H) 275.0957, found 275.0957.

(3*R,4*S**)-3,4-Bis(trimethylsilyl)cyclobutene (7).** To a solution of **6** (678 mg, 2.47 mmol) in benzene (1.2 mL) was added 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine (1.4 mL, 7.41 mmol) at room temperature. The reaction mixture was stirred at room temperature for 12 h and then directly subjected to chromatography on silica gel (hexane) to afford **7** (409 mg, 2.06 mmol, 83%): ^{1}H NMR (300 MHz) δ 0.04 (s, 18H), 2.62 (s, 2H), 6.10 (s, 2H); ^{13}C NMR δ −1.0, 39.4, 136.3; HRMS (EI) calcd for $C_{10}H_{22}Si_2$ (M^+) 198.1260, found 198.1259.

General Procedure for Thermal Ring-Opening Reaction. A solution of cyclobutene (0.10 mmol/portion) in degassed C_6D_6 (0.25 mL/portion) was put into a Schlenk flask and then heated at the described temperature in the dark. A portion of the mixture was taken out of the flask by a syringe at intervals. The reaction was monitored by ^{1}H NMR.

Determination of the Ratios 31/32 and 33/34. The authentic sample of **31** (7.25 mg) and the authentic sample of **32** (6.77 mg), both prepared by the cross-coupling reaction, were mixed. The mixture had a weight ratio **31**/**32** = 51.7:48.3. GC analysis of the mixture showed the ratio **31**/**32** = 51.4:48.6. The mixture was analyzed also by ^{1}H NMR. The integral values of the Me_2ArSi singlet signals showed the ratio **31**/**32** = 52.0:48.0. Thus, the ratios estimated by GC analysis and by ^{1}H NMR analysis were in good accord with the weight ratio.

The ring-opening reaction of **16a** was carried out at 80 °C twice. The ratio of the first-run ring-opening reaction was estimated to be **31**/**32** = 52.7:47.3 based upon ^{1}H NMR analysis. The ratio of the second-run ring-opening reaction was estimated to be **31**/**32** = 53.4:46.6 by GC analysis and **31**/**32** = 52.4:47.6 by ^{1}H NMR analysis. Thus, the ratio was determined to be **31**/**32** = 53:47 (±1).

The authentic sample of **33** (7.46 mg) and the authentic sample of **34** (7.46 mg), both prepared by the cross-coupling reaction, were mixed. The mixture had a weight ratio **33**/**34** = 50.0:50.0. The mixture was analyzed by ^{1}H NMR. The integral values of the Me_2ArSi singlet signals showed the ratio **33**/**34** = 49.3:50.7. The integral values of the Si−C*H*═C*H*−C*H*═*CH*−Si signals showed the ratio **33**/**34** = 49.6:50.4. Thus, the two ratios estimated by ^{1}H NMR analysis were in good accord with the weight ratio.

The ring-opening reaction of **16b** was carried out at 80 °C twice. The ratio of the first-run ring-opening reaction was estimated to be **33**/**34** = 55.1:44.9 based upon the integral values of the Me_2ArSi singlet signals and **33**/**34** = 55.2:44.8 based upon the integral values of the Si−C*H*═C*H*-C*H*═*CH*−Si signals. The ratio of the second-run ring-opening reaction was estimated to be **33**/**34** = 56.2:43.8 based upon the integral values of the Me_2ArSi singlet signals and **33**/**34** = 55.8:44.2 based upon the integral values of the Si−C*H*═C*H*−C*H*═*CH*−Si signals. Thus, the ratio was determined to be **33**/**34** = 56:44 (±1).

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Supporting Information Available: Additional experimental procedures and characterization data for compounds **4**−**7**, **10**, **12**−**14**, **16**, and **18**−**34**. Copies of ^{1}H and ^{13}C NMR spectra for compounds **10**, **12**−**14**, **16**, and **18**−**34**. Tables of atom coordinates and total energies of *p*-$CF_3C_6H_4SiH_3$, $C_6H_5SiH_3$, and *p*-$CH_3OC_6H_4SiH_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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