Evaluation of β- and γ-Effects of Group 14 Elements Using Intramolecular Competition

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To evaluate β-effects and γ-effects of group 14 elements, we have devised a system in which the intramolecular competition between γ-elimination of tin and β-elimination of silicon, germanium, and tin can be examined. Thus, the reactions of α-acetoxy(arylmethyl)stannanes with allylmetals (metal = Si, Ge, Sn) in the presence of BF_3·OEt_2 were carried out. The reactions seem to proceed by the initial formation of an α-stannyl-substituted carbocation, which adds to an allylmetal to give the carbocation that is β to the metal and γ to tin. The β-elimination of the metal gives the corresponding allylated product, and the γ-elimination of tin gives the cyclopropane derivative. In the case of allylsilane, the cyclopropane derivative was formed as a major product, whereas in the case of allylgermane the allylated product was formed predominantly. In the case of the allystannane the allylated product was formed exclusively. These results indicate that the γ-elimination of tin is faster than the β-elimination of silicon, but slower than the β-elimination of germanium and tin. The theoretical studies using *ab initio* molecular orbital calculations of the carbocation intermediates are consistent with the experimental results. The effect of substituents on silicon was also studied. The introduction of sterically demanding substituents on silicon disfavored the β-elimination of silicon probably because of the retardation of nucleophilic attack on silicon to cleave the carbon−silicon bond.

Introduction

Enormous advances have been made in the study of the electronic effects of group 14 elements such as silicon and tin,[1] and these studies uncovered a rich variety of chemistry of organo group 14 element compounds. The ability of group 14 elements to promote the formation of a positive charge, such as a carbocation, at the β-position is known as β-effect, and numerous synthetic transformations based on this effect have been developed so far.[2,3] Although the ability of group 14 elements to promote the formation of a positive charge at the γ-position (γ-effect) is less popular, it is also utilized in organic synthesis.[4,5] Extensive experimental and theoretical studies have been carried out on the origin of β-effects[6] and γ-effects[4a,7] of group 14 elements. The interaction of the C−M (M = Si, Ge, Sn) σ orbital with a vacant p orbital of the developing carbocation has proved to play a central role, although inductive effects cannot be ignored. In other words, the σ−π conjugation or hyperconjugation is responsible for the β-effect. The percaudal homohyperconjugation is responsible for the γ-effect. These mechanistic insights are consistent with significant geometric requirements of these effects observed experimentally. The ground-

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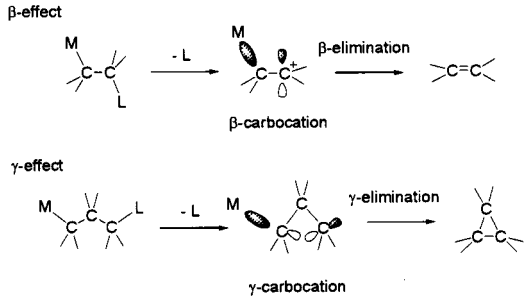
Scheme 1

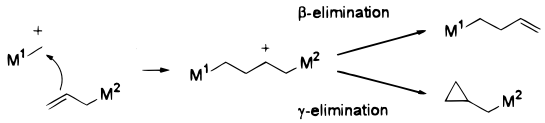


state interaction of the C−M σ orbital with the σ^* orbital of the C−L (L = leaving group) bond to be cleaved has also been suggested.[7l] Studies on the relative magnitude of these effects have been carried out mainly based on solvolysis experiments; such studies indicate that the magnitude of the effects increases in the order Si < Ge < Sn, and that the β-effect is larger than the γ-effect if we employ the same group 14 element.

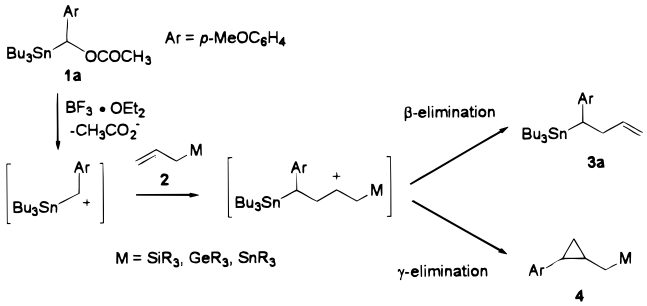
Another important aspect of β-effects and γ-effects of group 14 elements is facile elimination. When a β-carbocation is formed, the cleavage of the C−M bond takes place smoothly to form a carbon−carbon double bond. In the case of a γ-carbocation, the cleavage of the C−M bond leads to the formation of a cyclopropane ring. Therefore, group 14 elements such as silicon and tin have been utilized to control the fate of carbocations in organic synthesis.[8] Control of reaction pathways using β- and γ-effects of silicon and tin opened a number of opportunities of cationic reactions in organic synthesis. Therefore, the evaluation of the elimination process is significantly important from a synthetic point of view, although experimental and theoretical studies reported in the literature have focused on the formation of carbocation intermediates. The evaluation of the β-elimination and the γ-elimination processes is rather difficult because these processes are not usually rate-limiting processes.[6,7]

Thus, to evaluate the relative ease of the elimination, we devised a system in which the intramolecular competition between the β- and the γ-elimination of group 14 elements can be examined (Scheme 2).[9] If we generate a carbocation that is γ to M^1 and β to M^2, there should be the competition between the γ-elimination of M^1 and the β-elimination of M^2. The β-elimination leads to the formation of the homoallyl M^1 compound, and γ-elimination leads to the formation of the cyclopropane derivative.

Scheme 2



Scheme 3



So, we can analyze the relative ease of the β-elimination and the γ-elimination by the product analysis. As a method for the generation of this type of carbocation, we chose the addition of a carbocation α to M^1 onto an allylmetal (allyl-M^2). The addition should take place at the terminal carbon to generate the carbocation γ to M^1 and β to M^2.

In a preliminary study, we were surprised to find that the γ-elimination of tin was faster than the β-elimination of silicon.[9] On the basis of the facile γ-elimination of tin, we have developed a new cyclopropanation reaction of "tin carbenoid" with alkenes.[10] Thus, we have studied the relative ease of γ-elimination and β-elimination of group 14 elements in detail using this intramolecular competition protocol. To get a deeper insight into the competition, we also carried out theoretical studies using ab initio molecular orbital calculations, because the geometric and electronic structures of the carbocation intermediates having group 14 metals at both β- and γ-positions might give us crucial information about the relative magnitude of β- and γ-effects of group 14 elements. Herein we report on the full details of these studies.

Results and Discussion

Intramolecular Competition. To generate a carbocation having both γ-tin and β-M (M = Sn, Ge, Si), we carried out the addition of an α-tin-substituted carbocation to the corresponding allylmetals.[11] 4-Methoxyphenyl(acetoxy)methyltributylstannane (**1a**), which was readily prepared by the addition of stannyllithium to *p*-anisaldehyde followed by acetylation, was used as a precursor of the carbocation.

Thus, the reaction of **1a** with an allylmetal **2** was carried out in the presence of $BF_3{\cdot}OEt_2$ (Scheme 3). The reaction with allyltributylstannane (**2a**) gave rise to the exclusive formation of the allylated product (**3**) (Table 1, entry 1). The reaction seems to proceed by the following mechanism: The elimination of the acetoxy group with the aid of $BF_3{\cdot}OEt_2$ gives the α-stannyl-substituted carbocation, which adds to **2a** to give the carbocation intermediate having two stannyl groups at both β- and γ-positions. The exclusive formation of **3** indicates that

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(8) For example, Li, T.; Janda, K. D.; Lerner, R. A. *Nature* **1996**, *379*, 326−327 and references therein.

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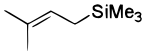
(10) (a) Sugawara, M.; Yoshida, J. *Synlett.* **1998**, 1057−1058. (b) Sugawara, M.; Yoshida, J. *Tetrahedron Lett.* **1999**, 40, 1717−1720.

(11) Reactivities of allylsilanes, allylgermanes, and allylstannanes with carbenium ions has been studied extensively. See ref 6n.

Table 1. Reactions of α-Acetoxybenzylstannane (1a) with Allylmetal (2)[a]

entry	allylmetal		yield(%)[b]	3a/4[c]	*cis/trans* of 4[c]
					
1[d]	M = $SnBu_3$	**2a**	83	100/0	-
2	M = $GeEt_3$	**2b**	84	94/6	88/12
3	M = $SiMe_3$	**2c**	89	7/93	87/13
4	M = Si^tBuMe_2	**2d**	95	0/100	80/20
5	M = Si^iPr_3	**2e**	94	0/100	76/24
6	M = $SiMe_2Ph$	**2f**	88	2/98	82/18
7	M = $SiMePh_2$	**2g**	87	0/100	87/13
8	M = $SiPh_3$	**2h**	91	0/100	90/10
9	M = $Si(OEt)_3$	**2i**	62	0/100	87/13
10	M = $SiMe_2SiMe_3$	**2j**	82	20/80	84/16
11		**2k**	97	0/100	84/16

[a] Reaction condition; 0.40 mmol of **1a**, 1.1 equiv of **2**, 1.1 equiv of BF_3·OEt_2 in toluene at −23 °C for 25−80 min. [b] Isolated yield of a mixture of **3a** and **4**. [c] Determined by ^1H NMR analyses. [d] 1.3 equiv of **2a** was used.

Table 2. Relative Energies and Geometries of A_{Sn} and B_{Sn}

	A_{Sn}	B_{Sn}
relative energy (kcal/mol)[a]	0.00	1.54
Atom Distance (Å)		
Sn(1)−C(1)	2.19	2.19
C(1)−C(2)	1.59	1.58
C(2)−C(3)	1.51	1.52
C(1)−C(3)	2.47	2.58
C(3)−C(4)	1.40	1.40
C(4)−Sn(2)	2.46	2.45
Angle (deg)		
C(1)−C(2)−C(3)	105.7	112.9
C(2)−C(3)−C(4)−Sn(2)	−95.5	92.4
Mulliken Atomic Charge[b]		
Sn(1)	0.45	0.45
C(1)	−0.36	−0.41
C(2)	0.09	0.11
C(3)	0.33	0.39
C(4)	−0.17	−0.20
Sn(2)	0.65	0.65

[a] Including correction for ZPE. [b] The atomic charge densities of hydrogens are summed into the heavy atom.

Table 3. Relative Energies and Geometries of A_{Ge}, B_{Ge}, and C_{Ge}

	A_{Ge}	B_{Ge}	C_{Ge}
relative energy (kcal/mol)[a]	0.0	1.99	7.11
Atom Distance (Å)			
Sn−C(1)	2.20	2.19	2.37
C(1)−C(2)	1.60	1.58	1.66
C(2)−C(3)	1.50	1.51	1.47
C(1)−C(3)	2.43	2.56	1.71
C(3)−C(4)	1.42	1.41	1.53
C(4)−Ge	2.23	2.23	2.02
Angle (deg)			
C(1)−C(2)−C(3)	102.9	111.9	65.7
C(2)−C(3)−C(4)−Ge	−96.0	90.6	144.2
Mulliken Atomic Charge [b]			
Sn	0.47	0.46	0.70
C(1)	−0.36	−0.40	−0.29
C(2)	0.10	0.11	0.20
C(3)	0.42	0.46	0.34
C(4)	−0.19	−0.20	−0.30
Ge	0.56	0.57	0.35

[a] Including correction for ZPE. [b] The atomic charge densities of hydrogens are summed into the heavy atom.

the β-elimination of tin is much faster than the γ-elimination of tin.

The reaction with allyltriethylgermane (**2b**) resulted in the predominant formation of the allylated product **3**, although a small amount of cyclopropane **4b** was obtained as a byproduct (entry 2). This result indicates that the β-elimination of germanium is faster than the γ-elimination of tin, but the difference is smaller than that between β-elimination of tin and γ-elimination of tin.

The reaction of **1a** with allyltrimethylsilane (**2c**), however, mainly afforded cyclopropane **4c** together with a small amount of **3a** (entry 3), indicating that the γ-elimination of tin is faster than the β-elimination of silicon. This result suggests that γ-effect can be stronger than β-effect if we employ different elements.

These results indicate that the β-elimination of tin and the β-elimination of germanium are much faster than the γ-elimination of tin, whereas the γ-elimination of tin is faster than the β-elimination of silicon. To the best of our knowledge, this is the first example of the direct intramolecular competition between the β-elimination and the γ-elimination of group 14 elements.

In the elimination process, nucleophilic attack at group 14 elements plays a crucial role, because the cleavage of the carbon−group 14 element bond is usually assisted

Table 4. Relative Energies and Geometries of A_{Si}, B_{Si}, and C_{Si}

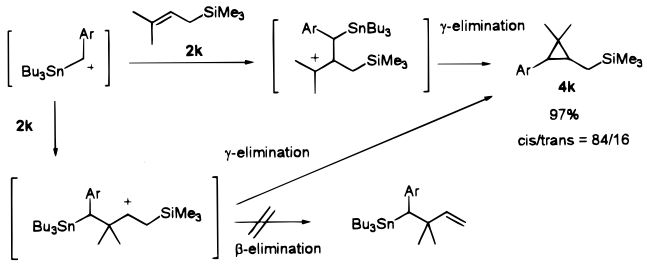
	A_{Si}	B_{Si}	C_{Si}
relative energy (kcal/mol)[a]	0.0	2.92	3.31
Atom Distance (Å)			
Sn−C(1)	2.22	2.20	2.38
C(1)−C(2)	1.63	1.60	1.67
C(2)−C(3)	1.47	1.49	1.47
C(1)−C(3)	2.28	2.50	1.69
C(3)−C(4)	1.44	1.42	1.53
C(4)−Si	2.05	2.09	1.94
Angle (deg)			
C(1)−C(2)−C(3)	94.6	107.9	64.9
C(2)−C(3)−C(4)−Si	−99.9	89.5	146.8
Mulliken Atomic Charge[b]			
Sn	0.51	0.48	0.70
C(1)	−0.36	−0.39	−0.28
C(2)	0.11	0.10	0.19
C(3)	0.51	0.53	0.32
C(4)	−0.31	−0.28	−0.36
Si	0.54	0.56	0.42

[a] Including correction for ZPE. [b] The atomic charge densities of hydrogens are summed into the heavy atom.

by the nucleophilic attack on the group 14 element.[12] The ease of such nucleophilic attack should be affected by the nature of the substituent on the group 14 elements. To examine this effect, we carried out the reaction of **1** with several allylsilanes having different substituents on silicon (entries 4−10). Cyclopropanes **4** were formed as major products irrespective of the nature of the substituent, but there exist definite substituent effects on the ratio of **3a**/**4**. The introduction of bulky groups such as *tert*-butyl group and phenyl group on silicon caused the exclusive formation of cyclopropane **4**. This is probably because bulky substituents retard the nucleophilic attack on silicon, and therefore, the elimination of the β-silyl group becomes slower. The introduction of electronegative substituents such as ethoxy groups on silicon also favors the formation of the cyclopropane **4**. The introduction of electronegative groups on silicon might cause a slight decrease of the energy level of C−Si σ orbital,[13] which in turn disfavors the interaction with the neighboring empty p orbital of the carbocation, although more data should be accumulated before the elucidation of the detailed mechanism. It should be noted that in the case of the disilanyl group, β-silicon elimination is more favorable in comparison with the trimethylsilyl group. It has been reported that a disilanyl group enhances the β-effect of silicon in electrophilic reactions of vinylsilanes,[14] and the present result is consistent with this report.

The effect on the substituent on carbon was also examined. The reaction with **2k**, which has two methyl groups at the terminal position, gave rise to exclusive formation of cyclopropane derivative (entry 11). This result might be explained by the attack of the tin-substituted carbocation at β carbon to form the tertiary carbocation γ to both tin and silicon (Scheme 4). Then, the γ-elimination of the stannyl group took place to give cyclopropane **4k** because the γ-elimination of the silyl

Scheme 4



group seems to be much less favorable. Another possibility to be considered is as follows. The initial addition takes place at the carbon bearing two methyl groups. Facile γ-eliminatin of tin then takes place to give cyclopropane **4k**. The presence of two methyl groups should facilitate the cyclization to form the cyclopropane ring (*gem*-dimethyl effect).

The effect of the substituent on γ-tin is interesting (Scheme 5). The reaction of **1b**, which has triphenylstannyl group instead of tributyl group, with allyltributylstannane **2a** gave the corresponding allylated product **3b** exclusively. The reaction with allyltriethylgermane **2b** also led to the exclusive formation of **3b**, although the reaction of **1a** with **2b** gave a small amount of the cyclopropane derivative. To our surprise, the reaction of **1b** with allyltrimethylsilane **2c** gave rise to the predominant formation of **3b**. The substitution of the tributylstannyl group by triphenylstannyl group reversed the selectivity. The β-effect of silicon is stronger than the γ-effect of tin in this case. The retardation of the nucleophilic attack on tin by bulky phenyl groups seems to be responsible.

These results indicate that the relative ease of β- and γ-elimination is quite sensitive to the nature of the substituent on group 14 elements.

Ab Initio Molecular Orbital Calculations of Carbocation Intermediate. To get a deeper insight into the factors which govern the reaction pathways, we carried out ab initio molecular orbital calculations of the carbocation intermediates.[15] The cations of $SnH_3CH_2CH_2$-$CHCH_2MH_3$ (M = Sn, Ge, and Si) were chosen as model compounds, and the calculations were carried out at MP2/LANL2DZ level with full geometry optimization.

M = Sn. In the case of M = Sn, two structures ($\mathbf{A_{Sn}}$ and $\mathbf{B_{Sn}}$) were obtained as local minima as shown in Figure 1. In $\mathbf{A_{Sn}}$ two tin atoms are located in the opposite side of the plane of the formal carbon−carbon double bond of the allylstannane, whereas in $\mathbf{B_{Sn}}$ they are in the same side. $\mathbf{A_{Sn}}$ is 1.54 kcal/mol more stable than $\mathbf{B_{Sn}}$. In both structures, the distance between C(3) and C(4) (1.4 A) is very close to the bond length of normal carbon−carbon double bond. The torsion angles of C(2)−C(3)−C(4)−Sn(2) indicate that the C(2)−C(3) bond and the C(4)−Sn(2) bond are perpendicular with each other. These data indicate that the carbocation at C(3) interacts with the neighboring C(4)−Sn(2) σ orbital quite effectively. The longer bond length of C(4)−Sn(2) in comparison with that of C(1)−Sn(1) suggests that the C(4)−Sn(2) bond is weakened by such interaction and ready to be cleaved to form the carbon−carbon double bond. On the other hand, the distance between C(1) and C(3)

(12) For example, Bassindale, A. R.; Taylor, P. G. The chemistry of organic silicon compounds; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; pp 839−892.

(13) Yoshida, J.; Tsujishima, H.; Nakano, K.; Isoe, S. *Inorg. Chim. Acta* **1994**, 220, 129−135.

(14) It has been reported that a disilanyl group is able to enhance the β effect of silicon in the electrophilic reaction of vinylsilane. Dixon, T. A.; Steele, K. P.; Weber, W. P. *J. Organomet. Chem.* **1982**, *231*, 299.

(15) The MO calculations of $H_3MCH_2CH_2^+$ (M = Si, Ge, Sn) were reported in the literature. Nguyen, K. A.; Gordon, M. S.; Wang, G.-T.; Lambert, J. B. *Organometallics* **1991**, *10*, 2798−2803.

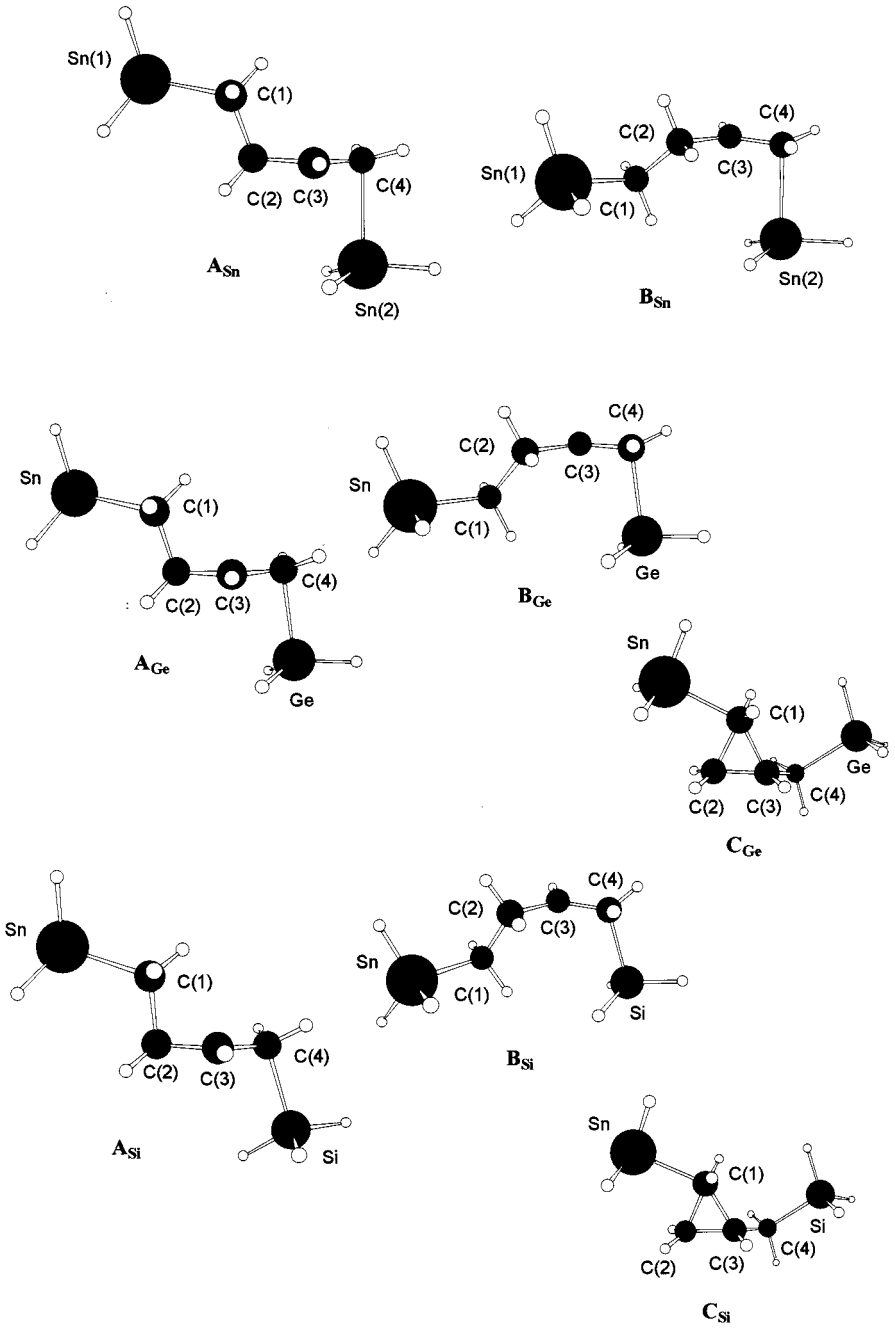
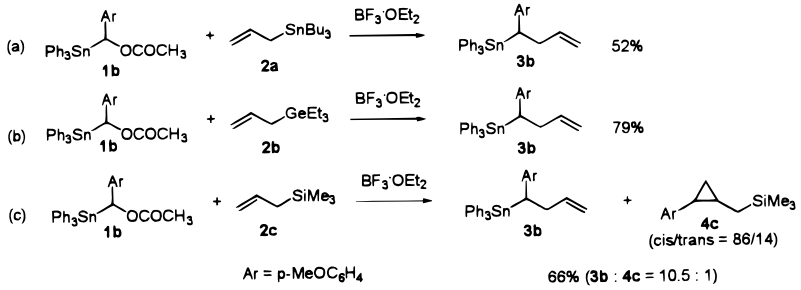


Figure 1. Optimized geometries of cationic intermediates.

Scheme 5



is very long, and this distance indicates that the interaction between the p orbital of the carbocation at C(3) and the back lobe of C(1)−Sn(1) σ orbital is negligible. The large angle of C(1)−C(2)−C(3) also indicates the absence of such percaudal interaction. Therefore, in structures $\mathbf{A_{Sn}}$ and $\mathbf{B_{Sn}}$, the β-tin (Sn(2)) stabilizes the carbocation at C(3) more effectively than γ-tin (Sn(1)). The larger atomic charge at Sn(2) in comparison with that at Sn(1) also indicates the larger effects of β-tin and the predominant cleavage of the Sn(2)−C bond.

M = Ge. In the case of germanium, three structures ($\mathbf{A_{Ge}}$, $\mathbf{B_{Ge}}$, and $\mathbf{C_{Ge}}$) were obtained as local minima (Figure 1). Geometries of $\mathbf{A_{Ge}}$ and $\mathbf{B_{Ge}}$ are similar to those of $\mathbf{A_{Sn}}$ and $\mathbf{B_{Sn}}$, respectively, and these structures seem to be the intermediates for the formation of the allylated product **3** as in the case of the allylstannane. Structure $\mathbf{C_{Ge}}$ is quite different from structures $\mathbf{A_{Ge}}$ and $\mathbf{B_{Ge}}$. In structure $\mathbf{C_{Ge}}$ the cyclopropane ring is almost formed because the distance between C(1) and C(3) (1.71 A) is close to that of a normal carbon−carbon single bond and the angle of C(1)−C(2)−C(3) (65.7°) is close to 60°, indicating the existence of the strong percaudal interaction. The longer bond length of Sn−C(1) of $\mathbf{C_{Ge}}$, in comparison with those in $\mathbf{A_{Ge}}$ and $\mathbf{B_{Ge}}$, is also consistent with the presence of such interaction. The bond length of C(3)−C(4) of $\mathbf{C_{Ge}}$ is much longer than those of $\mathbf{A_{Ge}}$ and $\mathbf{B_{Ge}}$ and the bond length of C(4)−Ge of $\mathbf{C_{Ge}}$ is much shorter than those of $\mathbf{A_{Ge}}$ and $\mathbf{B_{Ge}}$. These results indicate that in $\mathbf{C_{Ge}}$ γ-tin stabilizes the carbocation at C(3) more effectively than β-germanium and that this structure leads to the γ-elimination of tin to form cyclopropane **4**. The larger atomic charge at Sn of $\mathbf{C_{Ge}}$ compared with those in $\mathbf{A_{Ge}}$ and $\mathbf{B_{Ge}}$ also suggest the larger effect of tin in $\mathbf{C_{Ge}}$. The structure of $\mathbf{C_{Ge}}$ seems to be similar to those of protonated cyclopropanes[16] which play important roles in biological and chemical transformations involving carbocations, although the edged hydrogen is replaced by the stannyl group.

As to the energies of these structures, $\mathbf{A_{Ge}}$ is 1.99 kcal/mol more stable than $\mathbf{B_{Ge}}$ and 7.11 kcal/mol more stable than $\mathbf{C_{Ge}}$. These data imply that the β-elimination is more favorable than γ-elimination of tin, which is consistent with the experimental result, i.e., allylated product **3** was obtained preferentially together with a small amount of cyclopropane **4**.

M = Si. In the case of silicon, three structures ($\mathbf{A_{Si}}$, $\mathbf{B_{Si}}$, and $\mathbf{C_{Si}}$) were obtained as local minima as shown in Figure 1. The most stable structure is $\mathbf{A_{Si}}$, which is 2.92 kcal/mol more stable than structure $\mathbf{B_{Si}}$ and 3.31 kcal/mol more stable than $\mathbf{C_{Si}}$. The structure $\mathbf{A_{Si}}$ is, however, somewhat different from $\mathbf{A_{Sn}}$ and $\mathbf{A_{Ge}}$. In $\mathbf{A_{Si}}$, the bond length of C(3)−C(4) is slightly longer than those in $\mathbf{A_{Sn}}$ and $\mathbf{A_{Ge}}$. This indicates that the interaction of the carbocation at C(3) with the neighboring C−Si σ orbital is less effective than similar interactions with C−Sn and C−Ge σ orbitals. On the other hand, the distance between C(1) and C(3) is slightly shorter than those in $\mathbf{A_{Sn}}$ and $\mathbf{A_{Ge}}$, implying the existence of the percaudal interaction between the p orbital of the carbcation at C(3) and the back-lobe of the C−Sn σ orbital. The smaller angle of C(1)−C(2)−C(3) of $\mathbf{A_{Si}}$ (94.6°) in comparison with those of $\mathbf{A_{Sn}}$ (105.7°) and A_{Ge} (102.9°) also suggests the presence of such interaction. Therefore, structure $\mathbf{A_{Si}}$ seems to lead to the formation of both allylated product **3** and cyclopropane **4**.

Structure $\mathbf{B_{Si}}$ seems to lead to the formation of allylated product **3**. The structural analyses of $\mathbf{C_{Si}}$ indicate that this structure leads to the formation of cyclopropane **4** as in the cases of germanium. It is noteworthy that the energy of $\mathbf{C_{Si}}$ is comparable to that of $\mathbf{B_{Si}}$. Therefore, the results of calculations suggest that both the β-elimination of silicon and the γ-elimination of tin take place with similar possibilities. This seems to be consistent with the experimental results: The γ-elimination of Bu_3-Sn is faster than the β-elimination of Me_3Si, whereas the γ-elimination of Ph_3Sn is slower than the β-elimination of Me_3Si.

All of the calculations described above were carried out for carbocations in a vacuum without a counterion. Under this condition the formation of the carbocation **A**, **B**, and **C** from the α-tin-substituted carbocation and the allylmetal is quite exothermic. The real reactions, however, take place in the solution phase and the solvent molecules should play crucial roles for both the formation of these cations and the elimination of the metal. The counteranion should also play a significant role in these processes. Although these factors are omitted in the present calculations, the information obtained here still helps us to elucidate the mechanistic insight into the nature of group 14 elements in the γ- and β-effects. Future theoretical studies involving the solvent molecules and counteranions will hopefully delineate detailed mechanistic insights of the present problem.

Conclusion

The intramolecular competition revealed that the γ-elimination of Bu_3Sn is faster than the β-elimination of Me_3Si but slower than the β-elimination of Et_3Ge and Bu_3Sn. The introduction of sterically demanding substitutents on silicon disfavors the β-elimination of silicon. The introduction of phenyl groups on tin reversed the selectivity (β-Me_3Si > γ-Ph_3Sn). Therefore, relative ease of γ-elimination and β-elimination is quite sensitive to the substituents. The *ab initio* molecular orbital calculations of the carbocation intermediate are, in principle, consistent with the experimental results. The results of these studies will provide a significant insight into the β- and γ-effects of group 14 elements and a valuable guide to the control of the reactions involving carbocation intermediates.

Experimental Section

(Acetoxy)(tributylstannyl)(*p*-methoxyphenyl)methane (1a). To a solution of lithium diisopropyl amide (LDA) (15.5 mmol) in THF (30 mL) was added Bu_3SnH (4.80 mL, 18.0 mmol) at −72 °C. After being stirred at 0 °C for 35 min, a solution of *p*-anisaldehyde (1.85 mL, 15.1 mmol) in THF (2.0 mL) was added at −72 °C, and the reaction mixture was stirred at the same temperature for 40 min. After the reaction mixture was warmed to 0 °C, sat. aq NH_4Cl (ca. 10 mL) was added, and the organic phase was separated. The aqueous phase was extracted with ether (×3), and the combined organic phase was washed with sat. aq NaCl, and dried over $MgSO_4$. After removal of the solvent, the corresponding α-hydroxystannane was obtained which was used for the acetylation without purification.

To a solution of the α-hydroxystannane thus obtained in 1,2-dichloroethane (30 mL) was added pyridine (2.40 mL, 21.2 mmol) and Ac_2O (2.0 mL, 29.6 mmol) at 0 °C. The reaction mixture was stirred at room-temperature overnight. After removal of the solvent, water and ether was added, and the organic phase was separated. The aqueous phase was extracted with ether (×3), and the combined organic phase was washed with 1 N HCl aq and sat. aq $NaHCO_3$, and dried over $MgSO_4$. After removal of the solvent, the residue was purified via flash chromatography to obtain 5.81 g (83%) of the title compound. TLC R_f 0.20 (hexane/AcOEt 50/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.7−0.95 (m, 15 H), 1.10−1.35 (m, 6 H), 1.35−

(16) For example, (a) Sieber, S.; Buzek, P.; Schleyer, P. v. R.; Koch, W.; Carneiro, J. W. de M. *J. Am. Chem. Soc.* **1993**, *115*, 259−270. (b) Saunders, M.; Vogel, P.; Hagen, E. L.; Rosenfeld, J. *Acc. Chem. Res.* **1973**, *6*, 53−59. (c) Collins, C. J. *Chem. Rev.* **1969**, *69*, 534−550.

1.45 (m, 6 H), 2.11 (s, 3 H), 3.79 (s, 3 H), 5.83 (t, J_{Sn-H} = 9.0 Hz, 1 H), 6.83 (d, J = 8.7 Hz, 2 H), 7.05 (d, J = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.84, 13.53, 20.98, 27.25, 28.72, 55.26, 73.19, 113.98, 125.58, 134.95, 157.58, 171.08; IR (neat) 1720 (C = O) cm^{-1}; MS (EI) *m/e* (%) 413 ($M^+ - C_4H_9$, 32); HRMS calcd for $C_{22}H_{38}O_4Sn - C_4H_9$ 413.1138, found 413.1123. Anal. Calcd for $C_{22}H_{38}O_3Sn$: C, 56.31; H, 8.16. Found: C, 56.18, H, 8.34.

(Acetoxy)(triphenylstannyl)(*p*-methoxyphenyl)methane (1b). To a solution of lithium diisopropylamide (LDA) (2.80 mmol) in THF (5 mL) was added Ph_3SnH (934 mg, 2.66 mmol) at −78 °C. After being stirred at −20 °C for 25 min, *p*-anisaldehyde (0.30 mL, 2.45 mmol) was added at −72 °C, and the reaction mixture was stirred at the same temperature for 10 min. To the obtained solution of the α-hydroxystannane was added pyridine (0.33 mL, 4.10 mmol) and Ac_2O (0.33 mL, 3.49 mmol) at −78 °C. The reaction mixture was stirred at room-temperature overnight. Water and CH_2Cl_2 was added, and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (×2), and the combined organic phase was washed with 1*N* HCl aq, sat. aq $NaHCO_3$, and dried over $MgSO_4$. After removal of the solvent, the residue was purified via flash chromatography to obtain 564.7 mg (44%) of the title compound. TLC R_f 0.22 (hexane/AcOEt 5/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.91 (s, 3 H), 3.77 (s, 3 H), 6.18 (t, J_{Sn-H} = 11.1 Hz, 1 H), 6.78 (d, J = 8.7 Hz, 2 H), 7.05−7.20 (m, 2 H), 7.30−7.45 (m, 15 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.71, 55.29, 74.45, 114.09, 127.11, 128.47, 129.03, 132.76, 137.35, 138.35, 158.34, 171.55; IR (neat) 1711 (C = O) cm^{-1}; MS (EI) *m/e* (%) 530 (18), 528 (13); HRMS calcd for $C_{28}H_{26}O_3Sn$ 528.0904, found 530.0900.

Allylsilanes. Allylsilanes (**2c**−**k**) were prepared by the reaction of allylmagnesium bromide with the corresponding chlorosilanes in good yields.

(Allyl)(tributylstannyl)(*p*-methoxyphenyl)methane (3a). A Typical Procedure of Intramolecular Competition Reaction. To a solution of (acetoxy)(tributylstannyl)(*p*-methoxyphenyl)methane **1a** (189.4 mg, 0.40 mmol) and allyltributylstannane (160 μL, 0.52 mmol) in toluene (1.0 mL) was added BF_3·OEt_2 (56.0 μL, 0.44 mmol) at −23 °C. The reaction mixture was stirred at the same temperature for 1 h until most of **1a** was consumed (by TLC). The reaction was quenched by the addition of Et_3N (100 μL). The mixture was passed through a silica gel short column to remove insoluble materials (Et_2O eluted). After removal of the solvent, the residue was purified via flash chromatography to obtain 149.0 mg (83%) of the title compounds. TLC R_f 0.39 (hexane/AcOEt 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.73−0.79 (m, 6 H), 0.85 (t, J = 7.5 Hz, 9 H), 1.18−1.50 (m, 12 H), 2.56−2.80 (m, 4 H), 3.77 (s, 3 H), 4.92 (ddt, J = 10.2, 1.2, 1.2 Hz, 1 H), 5.01 (ddt, J = 17.1, 1.8, 1.5 Hz, 1 H), 5.76 (ddt, J = 17.1, 10.2, 6.6 Hz, 1 H), 6.78 (d, J = 7.5 Hz, 2 H), 6.93 (t, J = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.00, 13.54, 27.37, 28.97, 32.64, 37.00, 55.21, 113.79, 114.91, 127.25, 138.62, 139.11, 156.26; MS (EI) *m/e* (%) 452 (M^+, 8); HRMS calcd for $C_{23}H_{40}OSn$ 452.2101, found 452.2081.

The reactions of **1a** and **1b** with allylmetals were carried out in a similar fashion. The products were isolated via flash chromatography as a mixture of isomers. Each isomers were isolated by GPC. Stereochemistry of the cyclopropane derivatives was determined by ^{1}H NMR analyses based on the vicinal coupling constant (for cis J = 8.7−8.0 Hz, for trans J = 5.4−4.8 Hz).

(Allyl)(triphenylstannyl)(*p*-methoxyphenyl)methane (3b). TLC R_f 0.39 (hexane/AcOEt 5/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.80−3.00 (m, 2 H), 3.33 (t, J = 7.2 Hz, 1 H), 3.79 (s, 3 H), 4.92 (d, J = 10.2 Hz, 1 H), 4.99 (d, J = 17.1 Hz, 1 H), 5.72−5.85 (m, 1 H), 6.75−6.78 (m, 2 H), 7.00−7.04 (m, 2 H), 7.30−7.50 (m, 15 H),; ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.16, 37.19, 55.21, 113.95, 115.87, 128.42, 128.47, 128.92, 135.92, 137.41, 138.11, 138.59, 157.07; MS (EI) *m/e* (%) 512 (8), 510 (6); HRMS calcd for $C_{29}H_{28}OSn$ 512.1162, found 512.1185.

1-(*p*-Methoxyphenyl)-2-[(triethylgermyl)methyl]cyclopropane (4b) (a mixture of isomers, *cis*/*trans* = 88/12). TLC R_f 0.45 (hexane/AcOEt 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ For *cis*-**4b**, 0.11 (dd, J = 13.8, 10.2 Hz, 1 H), 0.45 (dd, J = 6.0, 5.4 Hz, 1 H), 0.70 (q, J = 8.1 Hz, 6 H), 0.75−1.10 (m, 3 H), 0.97 (t, J = 8.1 Hz, 9 H), 2.00 (td, J = 8.4, 6.0 Hz, 1 H), 3.79 (s, 3 H), 6.82 (d, J = 8.7 Hz, 2 H), 7.09 (d, J = 8.4 Hz, 2 H), For *trans*-**4b**, the characteristic signal, 3.77 (s, 3 H, OMe); ^{13}C NMR (75 MHz, $CDCl_3$) δ 3.90, 8.84, 10.35, 11.70, 15.21, 21.18, 55.18, 113.33, 130.17, 131.70, 157.72.; MS (EI) *m/e* (%) 322 (M^+, 20); HRMS calcd for $C_{17}H_{28}OGe$ 322.1352, found 322.1362.

***cis*-1-(*p*-Methoxyphenyl)-2-[(trimethylsilyl)methyl]cyclopropane (*cis*-4c).** TLC R_f 0.41 (hexane/AcOEt 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.13 (dd, J = 10.5, 9.9 Hz, 1 H), −0.03 (s, 9 H), 0.40−0.54 (m, 2 H), 0.95−1.10 (m, 2 H), 1.98 (td, J = 8.7, 6.0 Hz, 1 H), 3.79 (s, 3 H), 6.82 (d, J = 8.7 Hz, 2 H), 7.10 (d, J = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.55, 11.25, 14.15, 15.18, 20.21, 55.15, 113.28, 130.26, 131.87, 157.71; MS (EI) *m/e* (%) 234 (M^+, 90); HRMS calcd for $C_{14}H_{22}OSi$ 234.1440, found 234.1436. Anal. Calcd for $C_{14}H_{22}OSi$: C, 71.73; H, 9.46. Found: C, 71.47, H, 9.64.

***trans*-1-(*p*-Methoxyphenyl)-2-[(trimethylsilyl)methyl]cyclopropane (*trans*-4c).** TLC R_f 0.41 (hexane/AcOEt 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.03 (s, 9 H), 0.54−0.74 (m, 3 H), 0.80−0.92 (m, 2 H), 1.49 (dt, J = 8.4, 4.8 Hz, 1 H), 3.77 (s, 3 H), 6.80 (d, J = 8.7 Hz, 2 H), 6.93 (d, J = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.52, 17.55, 18.99, 22.13, 24.06, 55.25, 113.77, 126.49, 136.21, 157.48; MS (EI) *m/e* (%) 234 (M^+, 90), 219 (100); HRMS calcd for $C_{14}H_{22}OSi$ 234.1440, found 234.1433.

***cis*-1-(*p*-Methoxyphenyl)-2-[(*tert*-butyldimethylsilyl)methyl]cyclopropane (*cis*-4d).** TLC R_f 0.39 (hexane/AcOEt 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.09 (s, 3 H), −0.04 (s, 3 H), −0.09−0.0 (m, 1 H), 0.42−0.60 (m, 2 H), 0.81 (s, 9 H), 0.95−1.10 (m, 2 H), 2.00 (td, J = 8.4, 6.0 Hz, 1 H), 3.80 (s, 3 H), 6.83 (d, J = 8.7 Hz, 2 H), 7.08 (d, J = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −6.15, −5.89, 10.98, 11.80, 14.59, 16.41, 20.75, 26.43, 55.17, 113.30, 130.14, 131.73, 157.71; MS (EI) *m/e* (%) 276 (M^+, 30); HRMS calcd for $C_{17}H_{28}OSi$ 276.1910, found 276.1918. Anal. Calcd for $C_{17}H_{28}OSi$: C, 73.85; H, 10.21. Found: C, 73.57, H, 10.49.

***trans*-1-(*p*-Methoxyphenyl)-2-[(*tert*-butyldimethylsilyl)methyl]cyclopropane. (*trans*-4d).** TLC R_f 0.39 (hexane/AcOEt 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.02 (s, 3 H), 0.0 (s, 3 H), 0.54−0.70 (m, 2 H), 0.71−0.82 (m, 2 H), 0.84−0.90 (m, 1 H), 0.87 (s, 9 H), 1.50 (dt, J = 8.4, 4.8 Hz, 1 H), 3.78 (s, 3 H), 6.80 (d, J = 8.7 Hz, 2 H), 6.95 (d, J = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −6.03, 16.30, 17.99 (2 carbons), 19.23, 24.52, 26.43, 55.25, 113.79, 126.43, 136.16, 157.49; MS (EI) *m/e* (%) 276 (M^+, 40); HRMS calcd for $C_{17}H_{28}OSi$ 276.1910, found 276.1900.

***cis*-1-(*p*-Methoxyphenyl)-2-[(triisopropylsilyl)methyl]cyclopropane (*cis*-4e).** TLC R_f 0.40 (hexane/AcOEt 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.04 (dd, J = 15.0, 9.9 Hz, 1 H), 0.53 (q, J = 4.5 Hz, 1 H), 0.59 (dd, J = 15.0, 3.3 Hz, 1 H), 0.88−1.15 (m, 23 H), 2.01 (td, J = 8.4, 5.7 Hz, 1 H), 3.80 (s, 3 H), 6.84 (d, J = 8.7 Hz, 2 H), 7.09 (d, J = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.65, 10.87, 12.71, 14.26, 18.64, 18.67, 21.54, 55.15, 113.31, 130.06, 131.59, 157.66; MS (EI) *m/e* (%) 318 (M^+, 35); HRMS calcd for $C_{20}H_{34}OSi$ 318.2379, found 318.2386. Anal. Calcd for $C_{20}H_{34}OSi$: C, 75.40; H, 10.76. Found: C, 75.67, H, 11.01.

***trans*-1-(*p*-Methoxyphenyl)-2-[(triisopropylsilyl)methyl]cyclopropane (*trans*-4e).** TLC R_f 0.40 (hexane/AcOEt 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.55−0.68 (m, 1 H), 0.70−0.75 (m, 1 H), 0.80−1.00 (m, 3 H), 1.05−1.15 (m, 21 H), 1.55 (dt, J = 8.1, 4.5 Hz, 1 H), 3.78 (s, 3 H), 6.79 (d, J = 8.7 Hz, 2 H), 6.94 (d, J = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.82, 14.77, 18.69, 19.13, 25.52, 55.23, 113.74, 126.36, 136.19, 157.43; MS (EI) *m/e* (%) 318 (M^+, 40); HRMS calcd for $C_{20}H_{34}OSi$ 318.2379, found 318.2368.

***cis*-1-(*p*-Methoxyphenyl)-2-[(phenyldimethylsilyl)methyl]cyclopropane (*cis*-4f).** TLC R_f 0.39 (hexane/AcOEt 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.12 (dd, J = 15.0, 10.2 Hz, 1 H), 0.25 (s, 3 H), 0.27 (s, 3 H), 0.44 (q, J = 5.7 Hz, 1 H), 0.75 (dd, J = 15.0, 4.2 Hz, 1 H), 0.90−1.10 (m, 2 H), 1.97 (td, J = 8.4, 6.0 Hz, 1 H), 3.80 (s, 3 H), 6.82 (d, J = 8.7 Hz, 2 H), 7.06 (d, J = 8.7 Hz, 2 H), 7.34−7.36 (m, 3 H), 7.46−7.50 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −3.08, −2.89, 11.37, 14.04, 14.39, 20.37, 55.15, 113.35, 127.72, 128.83, 130.21, 131.62, 133.67,

139.65, 157.75; MS (EI) *m/e* (%) 296 (M^+, 65); HRMS calcd for $C_{19}H_{24}OSi$ 296.1596, found 296.1602. Anal. Calcd for $C_{19}H_{24}OSi$: C, 76.97; H, 8.16. Found: C, 77.26, H, 8.45.

***trans*-1-(*p*-Methoxyphenyl)-2-[(phenyldimethylsilyl)methyl]cyclopropane (*trans*-4f).** TLC R_f 0.39 (hexane/AcOEt 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.31 (s, 3 H), 0.32 (s, 3 H), 0.62−0.70 (m, 1 H), 0.80−1.00 (m, 4 H), 1.49 (dt, J = 8.4, 4.5 Hz, 1 H), 3.78 (s, 3 H), 6.78 (d, J = 8.7 Hz, 2 H), 6.90 (d, J = 8.7 Hz, 2 H), 7.33−7.36 (m, 3 H), 7.40−7.53 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −3.01, −2.89, 17.60, 18.75, 21.28, 24.18, 55.25, 113.72, 126.51, 127.80, 128.92, 133.67, 135.97, 139.44, 157.49; MS (EI) *m/e* (%) 296 (M^+, 95); HRMS calcd for $C_{19}H_{24}OSi$ 296.1596, found 296.1599.

***cis*-1-(*p*-Methoxyphenyl)-2-[(diphenylmethylsilyl)methyl]cyclopropane (*cis*-4g).** TLC R_f 0.36 (hexane/AcOEt 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.43−0.51 (m, 2 H), 0.57 (s, 3 H), 0.96 (td, J = 8.4, 5.1 Hz, 1 H), 1.02−1.20 (m, 1 H), 1.09 (dd, J = 12.0, 3.9 Hz, 1 H), 2.00 (td, J = 8.4, 6.0 Hz, 1 H), 3.81 (s, 3 H), 6.84 (d, J = 8.4 Hz, 2 H), 7.07 (d, J = 8.4 Hz, 2 H), 7.30−7.40 (m, 6 H), 7.50−7.60 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.33, 11.61, 12.87, 13.94, 20.65, 55.17, 113.39, 127.80, 129.15, 130.20, 131.43, 134.57, 137.36, 157.78; MS (EI) *m/e* (%) 358 (M^+, 11); HRMS calcd for $C_{24}H_{26}OSi$ 358.1753, found 358.1755. Anal. Calcd for $C_{24}H_{26}OSi$: C, 80.40; H, 7.31. Found: C, 80.37, H, 7.34.

***trans*-1-(*p*-Methoxyphenyl)-2-[(diphenylmethylsilyl)methyl]cyclopropane. (*trans*-4g).** TLC R_f 0.36 (hexane/AcOEt 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.60 (s, 3 H), 0.68 (dt, J = 8.4, 5.1 Hz, 1 H), 0.84 (dt, J = 8.4, 5.1 Hz, 1 H), 0.90−1.00 (m, 1 H), 1.20 (dd, J = 15.0, 6.6 Hz, 1 H), 1.29 (dd, J = 15.0, 6.6 Hz, 1 H), 1.52 (dt, J = 8.4, 4.8 Hz, 1 H), 3.77 (s, 3 H), 6.76 (d, J = 9.0 Hz, 2 H), 6.82 (d, J = 9.0 Hz, 2 H), 7.30−7.42 (m, 6 H), 7.50−7.59 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.30, 17.72, 18.54, 19.84, 24.41, 55.23, 113.68, 126.55, 127.87, 129.23, 130.20, 134.60, 135.77, 137.26, 157.51; MS (EI) *m/e* (%) 358 (M^+, 20); HRMS calcd for $C_{24}H_{26}OSi$ 358.1753, found 358.1764.

***cis*-1-(*p*-Methoxyphenyl)-2-[(triphenylsilyl)methyl]cyclopropane (*cis*-4h).** TLC R_f 0.36 (hexane/AcOEt 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.45 (q, J = 5.7 Hz, 1 H), 0.77 (dd, J = 15.3, 9.9 Hz, 1 H), 0.89 (td, J = 8.1, 4.8 Hz, 1 H), 1.14−1.28 (m, 1 H), 1.35 (dd, J = 15.3, 3.9 Hz, 1 H), 1.98 (td, J = 8.4, 6.3 Hz, 1 H), 3.78 (s, 3 H), 6.80 (d, J = 8.7 Hz, 2 H), 7.00 (d, J = 8.7 Hz, 2 H), 7.30−7.42 (m, 9 H), 7.45−7.55 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.01, 12.07, 13.94, 21.10, 55.17, 113.42, 127.81, 129.41, 130.20, 131.23, 135.31, 135.84, 157.78; MS (EI) *m/e* (%) 420 (M^+, 12); HRMS calcd for $C_{29}H_{28}OSi$ 420.1909, found 420.1921. Anal. Calcd for $C_{29}H_{28}OSi$: C, 82.81; H, 6.71. Found: C, 82.31, H, 6.56.

***trans*-1-(*p*-Methoxyphenyl)-2-[(triphenylsilyl)methyl]cyclopropane (*trans*-4h).** TLC R_f 0.36 (hexane/AcOEt 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.65 (dt, J = 8.7, 5.1 Hz, 1 H), 0.80 (dt, J = 8.4, 4.8 Hz, 1 H), 1.00−1.10 (m, 1 H), 1.45−1.63 (m, 3 H), 3.75 (s, 3 H), 6.71 (s, 4 H), 7.25−7.40 (m, 9 H), 7.45−7.50 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.11, 18.57, 19.11, 24.87, 55.25, 113.60, 126.58, 127.90, 129.48, 135.12, 135.87, 135.68, 157.49; MS (EI) *m/e* (%) 420 (M^+, 15); HRMS calcd for $C_{29}H_{28}OSi$ 420.1909, found 420.1926.

1-(*p*-Methoxyphenyl)-2-[(triethoxysilyl)methyl]cyclopropane (4i) (a mixture of isomers, *cis*/*trans* = 87/13). TLC R_f 0.22 (hexane/AcOEt 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ For ***cis*-4i** 0.01 (dd, J = 15.6, 9.9 Hz, 1 H), 0.55 (q, J = 5.4 Hz, 1 H), 0.62 (dd, J = 15.6, 3.9 Hz, 1 H), 1.02 (td, J = 8.7, 5.7 Hz, 1 H), 1.18−1.25 (m, 1 H), 1.21 (t, J = 6.9 Hz, 9 H), 2.03 (td, J = 8.7, 6.3 Hz, 1 H), 3.70−3.90 (m, 10 H), 6.81 (d, J = 8.7 Hz, 2 H), 7.09 (d, J = 8.7 Hz, 2 H), For ***trans*-4i**, the characteristic signal, 6.98−7.02 (m, 2 H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.34, 11.31, 12.43, 18.17, 20.66, 55.20, 58.27, 113.39, 130.32, 131.30, 157.83; MS (EI) *m/e* (%) 324 (M^+, 25); HRMS calcd for $C_{17}H_{28}O_4Si$ 324.1757, found 324.1759.

***cis*-1-(*p*-Methoxyphenyl)-2-[(pentamethyldisilyl)methyl]cyclopropane (*cis*-4j).** TLC R_f 0.42 (hexane/benzene 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.04 (dd, J = 15.0, 10.5 Hz, 1 H), 0.00 (s, 3 H), 0.01 (s, 3 H), 0.03 (s, 9 H), 0.45 (dt, J = 5.7, 4.5 Hz, 1 H), 0.59 (dd, J = 14.4, 3.6 Hz, 1 H), 0.95−1.10 (m, 2 H), 1.98 (td, J = 8.7, 5.7 Hz, 1 H), 3.79 (s, 3 H), 6.83 (d, J = 8.7 Hz, 2 H), 7.07 (d, J = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.12, −4.09, −2.22, 11.70, 13.57, 14.76, 20.68, 55.17, 113.33, 130.20, 131.73, 157.74; MS (EI) *m/e* (%) 292 (M^+, 20); HRMS calcd for $C_{16}H_{28}OSi_2$ 292.1679, found 292.1676. Anal. Calcd for $C_{16}H_{28}OSi_2$: C, 65.69; H, 9.65. Found: C, 65.39, H, 9.42.

***trans*-1-(*p*-Methoxyphenyl)-2-[(pentamethyldisilyl)methyl]cyclopropane (*trans*-4j).** TLC R_f 0.42 (hexane/benzene 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04 (s, 9 H), 0.07 (s, 3 H), 0.60−0.70 (m, 2 H), 0.80−0.92 (m, 3 H), 1.50 (dt, J = 8.4, 4.8 Hz, 1 H), 3.77 (s, 3 H), 6.80 (d, J = 8.7 Hz, 2 H), 6.95 (d, J = 8.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.22, −4.12, −2.29, 17.96, 19.45, 20.37, 24.40, 55.25, 113.79, 126.43, 136.15, 157.49; MS (EI) *m/e* (%) 292 (M^+, 90); HRMS calcd for $C_{16}H_{28}OSi_2$ 292.1679, found 292.1676.

***(1S*,2R*)*-1-(*p*-Methoxyphenyl)-2-[(trimethylsilyl)methyl]-3,3-dimethylcyclopropane (4k)** (a mixture of isomers, 84/16). TLC R_f 0.41 (hexane/AcOEt 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ For (1*S**,2*R**)-**4k** 0.22 (s, 9 H), 0.10 (dd, J = 14.7, 11.1 Hz, 1 H), 0.73 (dd, J = 15.0, 3.6 Hz, 1 H), 0.80−0.90 (m, 1 H), 0.88 (s, 3 H), 1.21 (s, 3 H), 1.67 (d, J = 8.7 Hz, 1 H), 3.79 (s, 3 H), 6.82 (d, J = 8.7 Hz, 2 H), 7.11 (d, J = 8.7 Hz, 2 H), For (1*S**,2*S**)-**4k**, the characteristic signal, 1.34 (d, J = 5.7 Hz, 1 H, ArCH); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.44, 12.57, 17.34, 19.48, 24.32, 29.33, 30.06, 55.11, 113.39, 131.02, 132.16, 157.63; MS (EI) *m/e* (%) 262 (M^+, 100); HRMS calcd for $C_{16}H_{26}OSi$ 262.1753, found 262.1755. Anal. Calcd for $C_{16}H_{26}OSi$: C, 73.22; H, 9.98. Found: C, 73.13, H, 10.14.

Molecular Orbital Calculations. The ab initio calculations were carried out using the GAUSSIAN 98 program[17] at the MP2/LANL2DZ level. All geometries were fully optimized, and all the optimized structures were local minima according to the vibration frequency analysis. Relative energies were corrected for ZPE (zero point energy) calculated at MP2/LANL2DZ.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **1a**, **1b**, **3a**, **3b**, **4b**, **4c**, **4d**, **4e**, **4e**, **4f**, **4g**, **4h**, **4j**, and **4k**. This material is available free of charge via the Internet at http://pubs.acs.org.

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