Anhydrations of 10, 12, and 22-25. A solution of **10** (24.5 mg) in 5 mL of aqueous NaOH (Ph 12) was stirred at room temperature for 50 min, neutralized with aqueous 5% HCl, filtered, and chromatographed on column A. After elution with water (100 mL), gradient elution from aqueous 10% methanol (500 mL) to aqueous 40% methanol (500 mL) gave **17** (16.5 mg, 77.5%). A procedure similar to that described above afforded **18** (13.1 mg, 73.7%) from **12** (18 mg). FABMS: *m/z* **17** 1299 (M + H^+), 1321 (M + Na^+), **18** 1299 (M + H^+). ^{13}C NMR (CD_3OD, characteristic absorptions): δ **17** 22.90, 50.29, 55.11, 61.64, 72.80, 73.68, 74.46, 74.66, 83.04, 103.45, 103.70, 132.74; **18** 22.90, 50.29, 55.16, 61.55, 71.15, 73.00, 73.58, 74.60, 82.69, 103.94, 104.23, 132.69.

A solution of **22** (19.3 mg) in 10 mL of aqueous NaOH (pH 12) was stirred at room temperature for 7 h, neutralized with 1% HCl, filtered, and chromatographed on column A. After elution with water (75 mL), gradient elution from aqueous 10% methanol (500 mL) to aqueous 40% methanol (500 mL) gave **26** (9.3 mg, 59.9%). Similarly, **23** (30.0 mg), **24** (45.0 mg), and **25** (10.0 mg) afforded, respectively, **27** (15.7 mg, 61.2%), **28** (24.5 mg, 73.9%), and **29** (3.8 mg, 46.9%), where the reaction times were 2.1, 1, and 2.3 h for **23-25**, respectively. FABMS: *m/z* **26-29** 831 (M + H^+), 853 (M + Na^+). ^{13}C NMR (D_2O, characteristic absorptions): δ **26** 24.61, 63.12, 72.77, 73.35, 73.89, 74.96, 76.57, 76.81, 77.05, 96.99, 101.18, 134.61; **27** 24.56, 52.30, 55.51, 63.21, 71.16, 71.89, 73.16, 73.94, 76.08, 98.55, 99.18, 134.37. **28** 25.05, 63.16, 71.94, 73.84, 74.47, 75.15, 75.74, 75.98, 76.96, 79.39, 102.54, 134.22; **29** 24.52, 52.30, 55.95, 63.12, 72.03, 73.59, 75.59, 75.74, 99.62, 134.52. ^1H NMR (D_2O): δ **28** 3.97-4.02 ($H_{6''b}$), 4.12 ($H_{4''}$, dd, $J_{3'',4''}$ = 4.3 Hz, $J_{4'',5''}$ = 2.1 Hz), 4.17 ($H_{6''a}$, d, $J_{6''a,6''b}$ = 10.9 Hz), 4.43 ($H_{2''}$, dd, $J_{1'',2''}$ = 2.5 Hz, $J_{2'',3''}$ = 5.8 Hz), 4.54 ($H_{5''}$), 4.62-4.69 ($H_{3''}$), and 5.23 ($H_{1''}$, d, $J_{1'',2''}$ = 2.5 Hz) (see Figure 3).

Anhydrations of 22-25 Followed by Reduction with $NaBH_4$. A solution of **22** (5.0 mg) in 5 mL of aqueous NaOH (pH 12) was stirred at room temperature for 8 h and then neutralized with 5% HCl. Under ice-cooling, $NaBH_4$ (50 mg) was added to the solution. The solution was kept at 2 °C overnight, neutralized with 5% HCl, and chromatographed on column A with elution of water (100 mL) followed by gradient elution from aqueous 10% methanol (500 mL) to aqueous 40% methanol (500 mL) to give **30** (2.5 mg, 61.9%). Similarly, **23** (6.9 mg), **24** (11.9 mg), and **25** (3.4 mg) gave, respectively, **31** (2.1 mg, 37%), **32** (2.4 mg, 21%), and **33** (1.0 mg, 35%), where the times of alkali treatment were 2.5, 3, and 2 h, respectively. FABMS: *m/z* **30** and **31** 833 (M + H^+), 855 (M + Na^+), **32** 855 (M + Na^+), **33** 833 (M + H^+).

Complete Acetylation of 20 and 30-33. The title compound (2.0 mg) was treated conventionally with pyridine (0.5 mL) and acetic anhydride (0.5 mL) at room temperature for 2 d. The crude product was purified by HPLC on the analytical column with gradient elution from aqueous 50% CH_3CN (30 mL) to aqueous 80% CH_3CN (30 mL) to give the completely acetylated oligosaccharide. The retention times (the flow rate; 0.5 mL/min) were 84, 65, 65, 57, and 66 min for **21**, **34**, **35**, **36**, and **37**, respectively. FABMS: *m/z* **21** 1625 (M + H^+), 1647 (M + Na^+), **34** 1337 (M + H^+), 1359 (M + Na^+), **37** 1337 (M + H^+), FDMS: *m/z* **35** and **36** 1359 (M + Na^+). The FABMS fragmentation patterns were shown in Figure 2.

Acknowledgment. We thank Japan Maize Products Co. Ltd. (Nihon Shokuhin Kako) for a generous gift of β-cyclodextrin. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

Supplementary Material Available: ^{13}C NMR spectra of **17**, **18**, and **26-29** (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Selenium-Directed Stereoselective [2 + 2] Cycloaddition Reactions Promoted by Lewis Acids: A Novel Zwitterionic Intermediate

Shoko Yamazaki,* Hiroyuki Fujitsuka, and Shinichi Yamabe

Department of Chemistry, Nara University of Education, Takabatake-cho, Nara 630, Japan

Hatsue Tamura

Institute of Chemistry, College of General Education, Osaka University, Osaka 560, Japan

Received May 19, 1992

The reaction of (trimethylsilyl)vinyl selenide **1** and (trimethylsilyl)allenyl selenide **2** with vinyl ketones **3a-c** in the presence of a Lewis acid gave cyclobutane derivatives stereoselectively. The reaction of **1** and **3a-c** with $SnCl_4$ was quenched either with Et_3N to give cyclobutanes **4a-c** or with H_2O to give acylsilanes **11a-c**. The formation of both products is explained in terms of a zwitterionic intermediate. The cis relationship between the phenylseleno group and the carbonyl group of **4a-c** is rationalized by consideration of a combination of secondary-orbital interactions and steric effects in the early stage of intermediate formation.

Introduction

[2 + 2] Cycloadditions are symmetry forbidden but important reactions in organic synthesis. Cyclobutane skeletons, which are formed in these reactions, are used for many organic transformations[1] and appear in several natural products.[2] The photochemical cycloaddition of olefins,[3] the thermal cycloaddition of electrophilic and nucleophilic olefins,[4] and the cycloaddition of ketenes with olefins[5] have been extensively studied. Recently, several studies on the Lewis acid-promoted [2 + 2] cycloaddition reaction of heteroatom-substituted olefins with olefins activated by an electron-withdrawing group (for example, [2 + 2] cycloadditions of silyl enol ethers,[6] simple enol ethers,[7] and vinyl sulfides[8] with electron-deficient olefins)

(1) (a) Bellus, D.; Ernst, B. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 797. (b) Wong, H. N. C.; Lau, K.-L.; Tam, K.-F. *Top. Curr. Chem.* **1986**, *133*, 83. (c) Trost, B. M. *Ibid.* **1986**, *133*, 3. (d) Oppolzer, W. *Acc. Chem. Res.* **1982**, *15*, 135. (e) Carruthers, W. *Cycloaddition Reactions in Organic Synthesis*; Pergamon Press: New York, 1990; p 332.

(2) (a) Corey, E. J.; Cheng, X. *The Logic of Chemical Synthesis*; John Wiley and Sons: New York, 1989. (b) Thomas, A. F.; Bessiere, Y. The Synthesis of Monoterpenes, 1980-1986. In *The Total Synthesis of Natural Products*; Apsimon, J., Ed.; John Wiley and Sons: New York, 1988; Vol. 7, p 275.

(3) Wender, P. A. In *Photochemistry in Organic Synthesis*; Coyle, J. D., Ed.; Royal Society of Chemistry: London, 1986; p 163.

(4) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 117, 199.

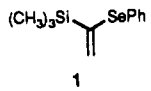
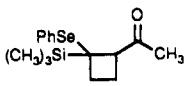
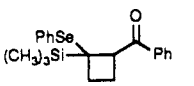
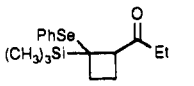
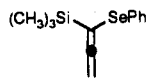
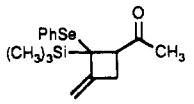
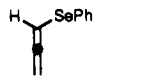
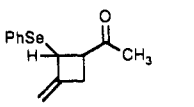
(5) Brady, W. T. In *The Chemistry of Ketenes, Allenes, and Related Compounds*; Patai, S., Ed.; John Wiley and Sons: New York, 1980; p 279.

(6) Clark, R. D.; Untch, K. G. *J. Org. Chem.* **1979**, *44*, 248, 253.

(7) Baar, M. R.; Ballesteros, P.; Roberts, B. W. *Tetrahedron Lett.* **1986**, *27*, 2083.

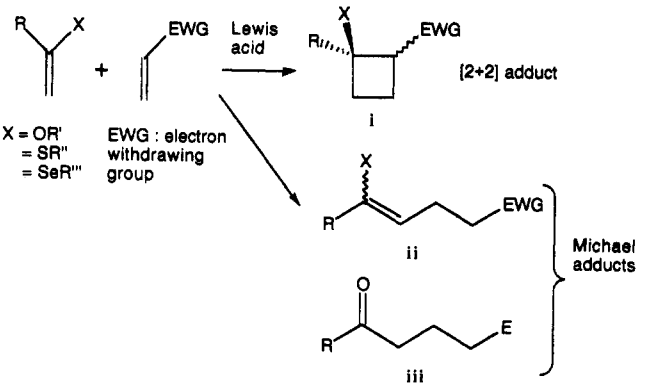
0022-3263/92/1957-5610$03.00/0

Table I. [2 + 2] Cycloadditions of Vinyl and Allenyl Selenides

entry	vinyl/allenyl selenide	vinyl ketone	Lewis acid	product	isolated yield, %
1	 1	 **3a**[a]	$SnCl_4$[c]	 **4a**	66
2		**3a**[b]	$AlCl_3$[d]	**4a**	41
3		**3a**[b]	$EtAlCl_2$[c]	**4a**	54
4		 **3b**[a]	$SnCl_4$[c]	 **4b**	85
5		 **3c**[a]	$SnCl_4$[c]	 **4c**	49
6	 2	**3a**[b]	$AlCl_3$[e]	 **5a**	70
7	 6	**3a**[b]	$AlCl_3$[f]	 7	11

[a] Ca. 1 equiv of **3a–c** was used. [b] 3.7–4.5 equiv of **3a** was used. [c] −78 °C, 3 h. Quenched with Et_3N. [d] −78 °C, 3 h. Quenched with H_2O. [e] −20 °C, 1 h. Quenched with H_2O. [f] −78 °C, 1 h → −20 °C, 2 h. Quenched with H_2O.

have been reported. Although asymmetric [2 + 2] cycloadditions of vinyl sulfides using a chiral titanium reagent have been examined,[8c] the diastereoselectivity in the reactions of silyl enol ethers[6] and some vinyl sulfides[8c,d] was not sufficiently high and was not rationalized. The usefulness of Lewis acids for promoting high regio- and stereoselectivities has been shown in many reactions, including carbonyl additions[9] and Diels–Alder reactions.[10] Wide applicability of Lewis acids in promoting stereoselectivity in [2 + 2] cycloadditions is also expected but has not yet been demonstrated, probably because the mechanism for Lewis acid-mediated [2 + 2] cycloadditions is only poorly understood. In some cases, small changes in the reaction conditions lead to the formation of Michael adducts **ii** or **iii** instead of, or along with, [2 + 2] adduct **i**,[6-8,11] and the structure of the intermediate remains to be clarified. In this work, we describe a highly stereoselective [2 + 2] cycloaddition of olefins and allenes with a new substituent, a phenylseleno group. We also obtained Michael adducts **iii** under the same reaction conditions simply by changing the workup. The same zwitterionic intermediate is proposed for both [2 + 2] adduct **i** and Michael adduct **iii**. The factors that may control the stereochemistry in the Lewis acid-promoted [2 + 2] cycloadditions are simple steric effects, chelation, neighboring-group participation, and secondary orbital interactions in the early stage of the reaction. We examined the exclusive stereoselectivity of the [2 + 2] cycloaddition observed in this work in terms of these factors.



To develop [2 + 2] cycloadditions of olefins with new types of substituents and to examine the effects of the substituents on the selectivity, we attempted a [2 + 2] reaction of silylvinyl selenides in the presence of Lewis acids. Previously, we found that electrophilic reactions of 1-(phenylseleno)-1-(trimethylsilyl)ethene (**1**) with α,β-unsaturated acid chlorides proceed regioselectively.[12] In this work, we report that the reaction of (trimethylsilyl)vinyl selenide **1** and 1-(phenylseleno)-1-(trimethylsilyl)-1,2-propadiene (**2**) with vinyl ketones **3a–c** in the presence of a Lewis acid gave cyclobutane derivatives, i.e., [2 + 2] adducts **i**, stereoselectively. We have also found that when the reaction of **1** and **3a–c** with $SnCl_4$ is quenched with H_2O instead of Et_3N, only acylsilanes **11a–c**, i.e., Michael adducts **iii**, are obtained.

Results

A. [2 + 2] Cycloaddition. Table I summarizes the [2 + 2] cycloaddition reactions. The reaction of **1**[12] and methyl vinyl ketone (**3a**) (ca. 1 equiv) was carried out in

(8) (a) Takeda, T.; Fujii, T.; Morita, K.; Fujiwara, T. *Chem. Lett.* **1986**, 1311. (b) Hayashi, Y.; Narasaka, K. *Chem. Lett.* **1989**, 793. (c) Hayashi, Y.; Narasaka, K. *Chem. Lett.* **1990**, 1295. (d) Hayashi, Y.; Niihata, S.; Narasaka, K. *Chem. Lett.* **1990**, 2091.

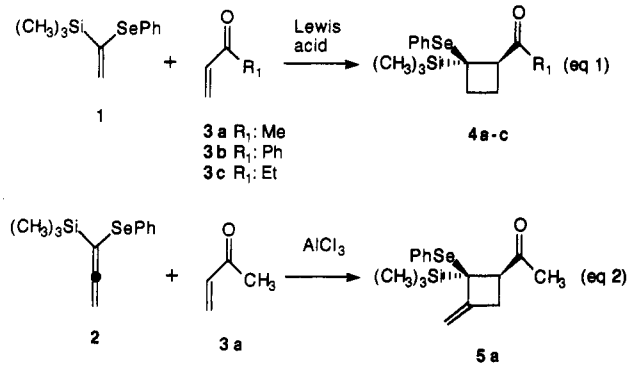
(9) (a) Evans, D. A. *Sciene (Washington)* **1988**, *240*, 420. (b) Reetz, M. T.; Hullmann, M.; Massa, W.; Berger, S.; Rademacher, P.; Heymann, P. *J. Am. Chem. Soc.* **1986**, *108*, 2405.

(10) (a) Oppolzer, W. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 876. (b) Paquette, L. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1974; Vol. 3, Chapter 4. (c) Masamune, S.; Choy, W.; Petersen, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1. (d) Birney, D. M.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 4127.

(11) Narasaka, K.; Soai, K.; Aikawa, Y.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 779.

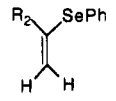
(12) Yamazaki, S.; Mizuno, W., Yamabe, S. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1555.

CH_2Cl_2 in the presence of $SnCl_4$ (1.25 equiv) at −78 °C for 3 h. Quenching with triethylamine (ca. 2 equiv) gave cyclobutyl ketone **4a** in 66% yield (entry 1). $AlCl_3$ and $EtAlCl_2$ also were effective for promoting the [2 + 2] cycloaddition in the reaction between **1** and an excess of **3a** (3.7 equiv) (entries 2, 3). The reaction of **1** and vinyl ketone **3b** or **3c** in the presence of $SnCl_4$ gave **4b** or **4c**, respectively (entries 4, 5). The reaction of **2**[13] and an excess of **3a** (4.5 equiv) with $AlCl_3$ (1.1 equiv) in CH_2Cl_2 at −20 °C for 1 h gave **5a** in 70% yield (entry 6). In the reaction of **2** and **3a**, no Danheiser [3 + 2] cycloadduct[14] was detected.[15] The reaction of allenyl phenyl selenide (**6**)[16] with **3a** (3.9 equiv) in the presence of $AlCl_3$ (−78 °C → −20 °C) gave **7** in only 11% yield (entry 7). In this [2 + 2] cycloaddition, exclusive regioselectivity was found.



When $TiCl_4$ was used as a Lewis acid in the reaction of **1** and **3a**, a complex mixture was obtained. The reaction of **2** and **3a** did not proceed when $SnCl_4$, $TiCl_4$, or $FeCl_3$ was used as a Lewis acid. Neither **1** or **2** reacted with 2-cyclohexen-1-one when $SnCl_4$, $AlCl_3$, or $EtAlCl_2$ was used as a Lewis acid.

The reaction of phenyl vinyl selenide (**8**)[17] and 2-(phenylseleno)propene (**9**),[17] which do not have a Me_3Si group, with **3a** in the presence of $SnCl_4$ gave a complex mixture. These results suggest that the Me_3Si group suppresses side reactions by a steric effect.



8 R_2: H
9 R_2: Me

Cycloadducts **4** and **5a** are single stereoisomers.[18] The stereochemistry of **4a** was determined by 2D NOESY. There was no NOE between H_a (δ 3.50–3.54, m) and H_b (δ 7.55–7.60, m). This observation suggests that H_a and the phenylseleno group are trans, i.e., the carbonyl group and the phenylseleno group are cis. To confirm this assignment, we synthesized the other stereoisomer of **4a**, **14**, for NOE study (vide infra). The acetalization of **4a** with

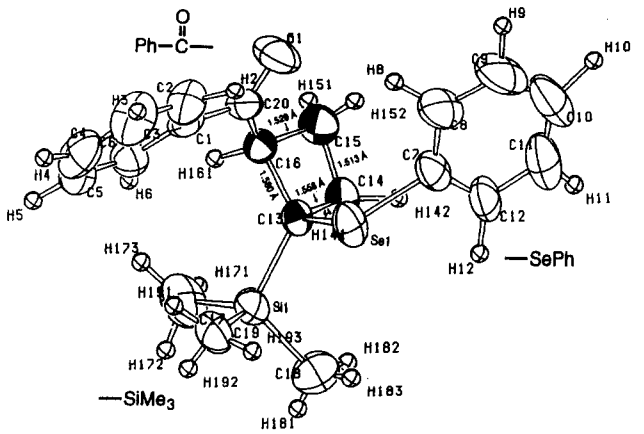
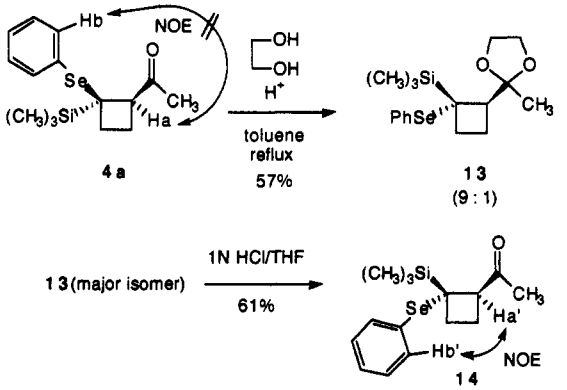


Figure 1. ORTEP[41] drawing of **4b** (50.0% probability ellipsoids). Note that the SePh substituent is cis to the benzoyl group.

ethylene glycol in the presence of *p*-toluenesulfonic acid in refluxing toluene gave **13** (9:1 isomeric mixture) in 57% yield. The deacetalization of the major isomer of **13** with 1 N HCl/THF at room temperature gave **14** in 61% yield. The 2D NOESY spectrum of **14** clearly shows the existence of an NOE between $H_{a'}$ (δ 3.23–3.27, m) and $H_{b'}$ (δ 7.61–7.64, m). Therefore, $H_{a'}$ and $H_{b'}$ are cis. The cis relationship between the carbonyl group and the phenylseleno group in **4c** and **5a** was also suggested by the absence of an NOE between C*H*COR$_1$ (R_1 = Et and Me) and the ortho H of SePh. The stereochemistry of **4b** was confirmed by single-crystal X-ray analysis (Figure 1); the phenylseleno group and the carbonyl group of **4b** are also cis.



To illustrate the synthetic utility of these new, highly substituted cyclobutanes, we carried out a formal synthesis of (±)-junionone (**21**),[19] a cyclobutane monoterpenoid, from **4a** by the following chemical transformations. Oxidation of **4a** with $NaIO_4$/THF–H_2O or MCPBA/CH_2Cl_2 gave sila-Pummerer products **15** ($NaIO_4$ 27%, MCPBA 36%) and **16** ($NaIO_4$ 7%, MCPBA 10%) as major products.[20]

(13) Compound **2** was prepared in 53% yield by treatment of α-lithioallenyl phenyl selenide[16] with chlorotrimethylsilane. Compound **2** was about 90% pure. (A small amount of unchanged allenyl phenyl selenide (**6**) and another unidentified impurity were present.)

(14) Danheiser, R. L.; Carini, D. J.; Basak, A. *J. Am. Chem. Soc.* **1980**, *102*, 6311. Danheiser, R. L.; Carini, D. J.; Fink, D. M.; Basak, A. *Tetrahedron* **1983**, *39*, 935.

(15) It has been reported that 1-(trimethylsilyl)-1-(methylthio)-1,2-propadiene and electron-deficient olefins give not [3 + 2] cycloadducts but [2 + 2] cycloadducts in the presence of $EtAlCl_2$.[8d]

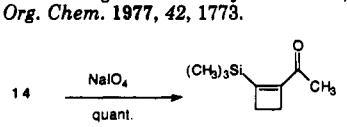
(16) Reich, H. J.; Shah, S. K.; Gold, P. M.; Olson, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 3112.

(17) Reich, H. J.; Willis, W. W.; Clark, P. D. *J. Org. Chem.* **1981**, *46*, 2775.

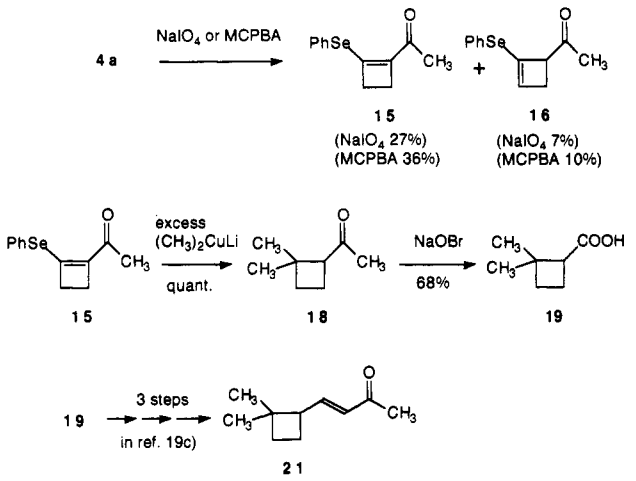
(18) The stereochemistry of **7** (entry 7, Table I) was not determined.

(19) (a) Thomas, A. F.; Ozainne, M. *J. Chem. Soc., Chem. Commun.* **1973**, 746. (b) Gaoni, Y. *Tetrahedron Lett.* **1982**, *23*, 5219. (c) Ghosh, A.; Banerjee, U. K.; Venkateswaran, R. V. *Tetrahedron* **1990**, *46*, 3077.

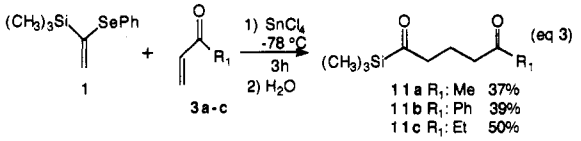
(20) The cis relationship between the phenylseleno and the carbonyl group in **4a** is also supported by these oxidation reactions. Oxidation of **4a** with $NaIO_4$ or MCPBA gave none of the selenoxide syn elimination product **17** while oxidation of **14** with $NaIO_4$/MeOH gave **17** quantitatively, probably because of the existence of an acidic proton cis to the phenylseleno group in **14**. For a discussion of selenoxide syn elimination versus sila-Pummerer rearrangement of α-silyl selenoxide, see: Reich, H. J.; Shah, S. K. *J. Org. Chem.* **1977**, *42*, 1773.



Treatment of **15** with a large excess of lithium dimethylcuprate at 0 °C gave **18** quantitatively.[21] Oxidation of **18** with sodium hypobromite gave **19** in 68% yield. The spectra of **19** and its methyl ester (**20**) are in accord with the reported data. Transformation of **19** to (±)-junionone (**21**) has already been reported.[19c]



B. Acylsilane Formation. When the reaction of $SnCl_4$, **1**, and vinyl ketones **3a–c** in CH_2Cl_2 at −78 °C was quenched with H_2O, acylsilanes **11a–c**, respectively, were obtained in 37–50% yield, and no cyclobutyl ketones were produced (eq 3). In these experiments, **1**, functioning as



an acyl silane enolate anion equivalent $^-CH_2COSi(CH_3)_3$,[22] attacks vinyl ketones **3a–c** to give formal Michael adducts **11a–c**. Nucleophilic attack of H_2O on intermediate **12**, which is described in the Discussion, and subsequent hydrolysis may give these acylsilanes.

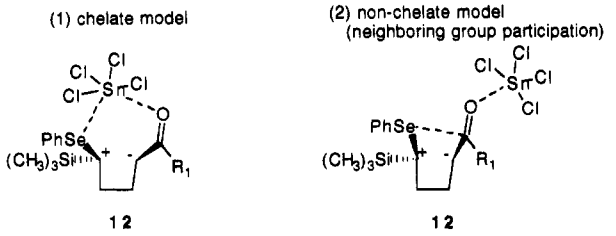
Acylsilanes **11a–c** can also be obtained from cyclobutanes **4a–c**. Treatment of cyclobutane **4a** with $SnCl_4$ at −78 °C and then with H_2O gave **11a** in 65% yield. This result shows that the cyclobutane ring is cleaved readily and suggests that **12** is also produced when the cyclobutane is treated with $SnCl_4$. The large C_{13}–C_{16} distance (1.580 Å) in **4b**, as shown in Figure 1, may account for the ease of the ring cleavage.

Discussion

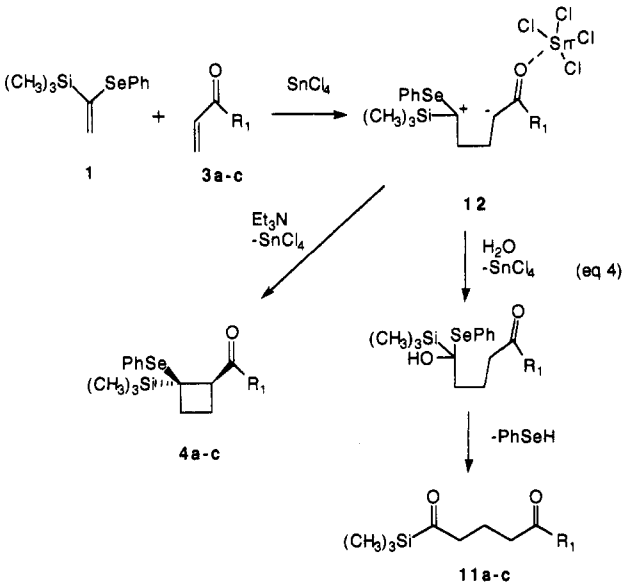
In our [2 + 2] cycloaddition reactions, there are two topics, A and B, that we must address.

(A) Formation of the [2 + 2] Product vs the Michael Product. In the reaction of a silyl enol ether and an unsaturated ester in the presence of $TiCl_4$, two kinds of products, [2 + 2] cycloadducts[6] and Michael adducts,[11] have been reported. The reaction of simple enol ethers and di-*tert*-butyl methylenemalonate in the presence of zinc bromide also gave either [2 + 2] cycloadducts or Michael adducts, depending on the reaction temperature and workup conditions.[7] In the case of the vinyl sulfide,

Chart I



the cycloadduct was the major product and the Michael product was a byproduct.[8b] We believe that our [2 + 2] cycloaddition proceeds in a polar stepwise fashion (eq 4).



In the first step, nucleophilic vinyl selenide **1** attacks electrophilic olefins **3a–c**, which are activated by a Lewis acid, to give carbonium ion **12**, which is stabilized by the PhSe group. (The Me_3Si group seems to have no electronic effect in this step.[23]) Attack of water on the cationic carbon of **12** and subsequent elimination of PhSeH afford Michael adducts **11a–c**. Workup with Et_3N, which removes the Lewis acid, $SnCl_4$, from the carbonyl group, affords cyclobutanes **4a–c**. The regioselectivity is the same as that in the $TiCl_4$-mediated reaction of **1** and α,β-unsaturated acid chlorides.[12]

(B) The Origin of the Diastereoselectivity. Since the phenylseleno group and the carbonyl group of **4a–c** are in a cis orientation, a chelated intermediate is possible. That is, in the cyclobutane ring-forming step, the metal of the Lewis acid may be coordinated to both the selenium and carbonyl oxygen atoms to generate the cis stereochemistry of the phenylseleno and the carbonyl group (Chart I (1)). A nonchelated model of intermediate carbonium ion **12** involves neighboring-group participation[24] by electron donation from selenium to the carbonyl carbon (Chart I (2)). The stabilizing effect of the electron dona-

(21) Smith, A. B., III; Levenberg, P. A.; Jerris, P. J.; Scarborough, R. M., Jr.; Wovkulich, P. M. *J. Am. Chem. Soc.* **1981**, *103*, 1501 and reference 45 cited therein.

(22) Acyl silane silyl enol ethers, RCH=C(SiMe$_3$)(OSiMe$_3$), are reported to work as acyl silane enolate anion equivalents toward acetals in the presence of BF_3·OEt_2. Sato, T.; Arai, M.; Kuwajima, I. *J. Am. Chem. Soc.* **1977**, *99*, 5828.

(23) For a discussion of β-silicon stabilization of a carbonium ion, see: (a) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworth: London, 1983. (b) Fleming, I.; Dunogues, J.; Smithers, R. *Org. React.* **1989**, *37*, 57. Fleming, I. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon: Oxford, 1979; Vol. 3, p 539. (c) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983. (d) Magnus, P. D.; Sarker, T.; Djuric, S. In *Comprehensive Organometallic Chemistry*; Wilkinson, G. W., Stone, F. G. A., Abel, F. W., Eds.; Pergamon: Oxford, 1982; Vol. 7, p 515.

(24) Molander, G. A.; Haar, J. P., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 3608 and references cited therein.

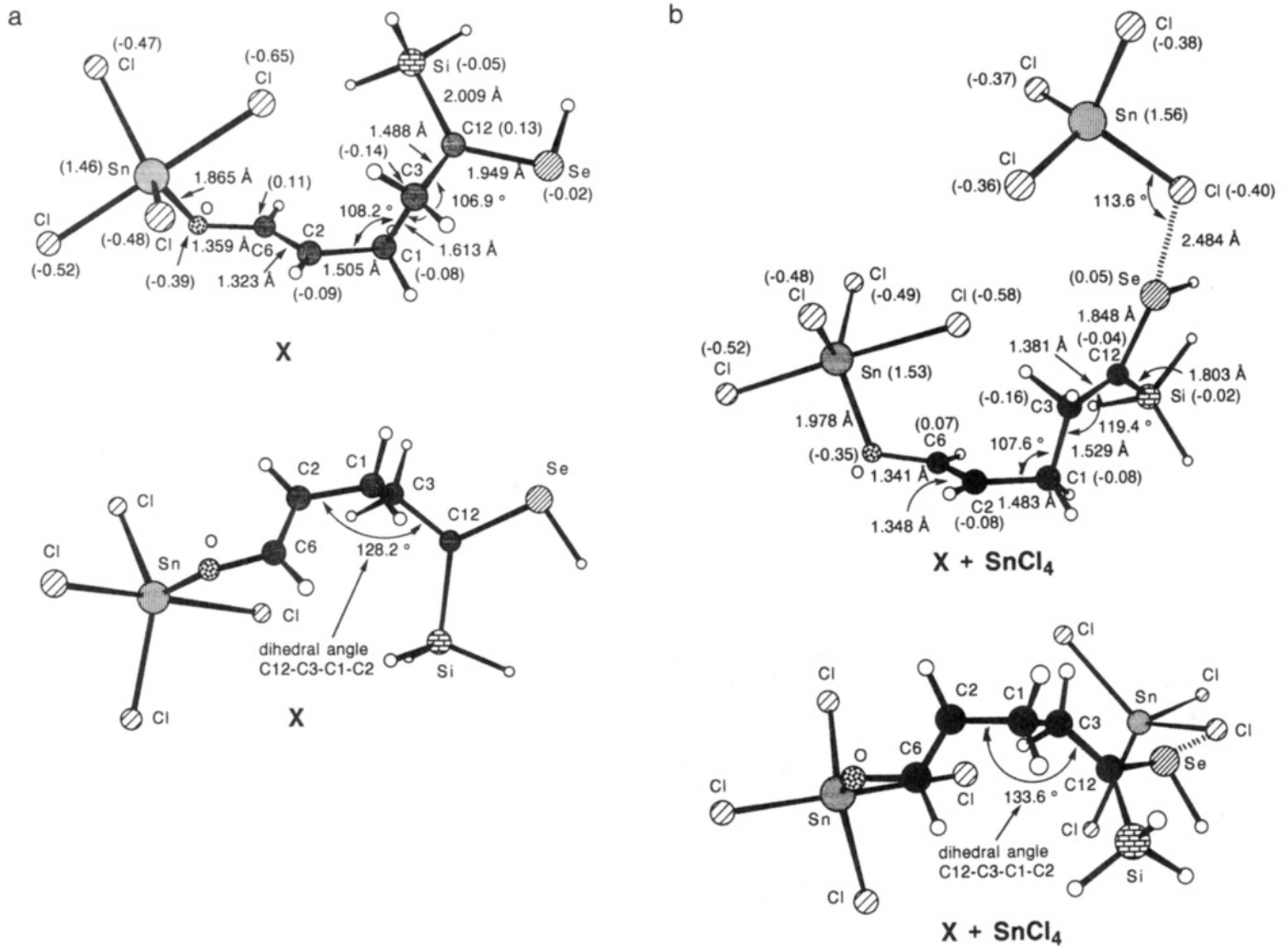


Figure 2. (a) Two views of the ab initio RHF/LANL1MB-optimized[25,26] geometry of a model zwitterion intermediate **X**. Numbers in parentheses denote net atomic charges (positive, cationic). The atom numbering is different from that in Figure 1. Selected atomic distances are as follows: C_3–C_6 = 3.483 Å, C_2–C_{12} = 3.595 Å, Se–Sn = 7.989 Å, and Se–C_6 = 5.855 Å. (b) Two views of the PM3-optimized[29] geometry of **X** + $SnCl_4$. Numbers in parentheses denote net atomic charges (positive, cationic) of RHF/LANL1MB (LANL1MB//PM3). Selected atomic distances are as follows: C_3–C_6 = 3.160 Å, C_2–C_{12} = 3.583 Å, Se–Sn = 6.541 Å, and Se–C_6 = 5.582 Å.

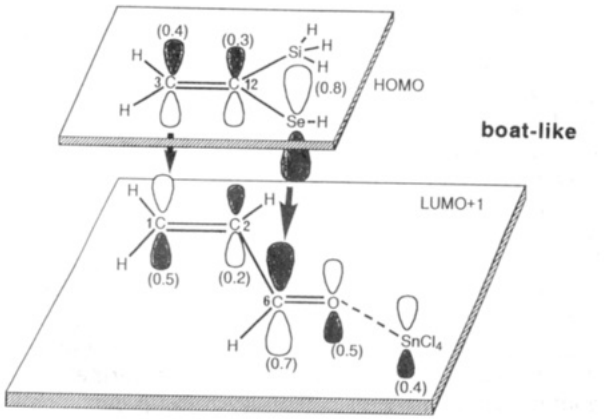
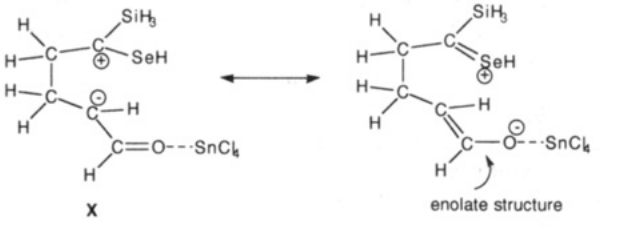


Figure 3. Frontier-orbital interaction scheme for the cis orientation of fragment molecules 1-hydroseleno-1-silylethene and acrolein coordinated by $SnCl_4$ of model intermediate **X**. Numbers in parentheses show absolute values of frontier-orbital coefficients. The LUMO of the $SnCl_4$-coordinated acrolein is σ^* localized at $SnCl_4$. The atom numbering is the same as that in Figure 2.

tion forces a cis orientation of the phenylseleno group and the carbonyl group.

(C) Theoretical Investigation. In order to determine whether **12** was an intermediate in the reaction of **1** and **3a–c**, an ab initio geometry optimization (OPT) and a vibrational analysis (FREQ) were carried out for model compound **X**. A basis set for the restricted Hartree–Fock (RHF) calculations was adopted. The basis set was the so-called LANL1MB implemented in the GAUSSIAN 90 program package.[25] LANL1MB includes the effective core potential (ECP)[26] for the inner-shell electrons and the STO-3G minimal basis set for the valence electrons. The vibrational analysis with RHF/LANL1MB was performed using the numerical second derivatives of the total energy to check whether the calculated structure of **X** was at the energy minimum or at the saddle point. The results are shown in Figure 2a.[27,28]



(25) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzalez, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. GAUSSIAN *90, Revision F*; Gaussian, Inc.: Pittsburgh, PA, 1990.

(26) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

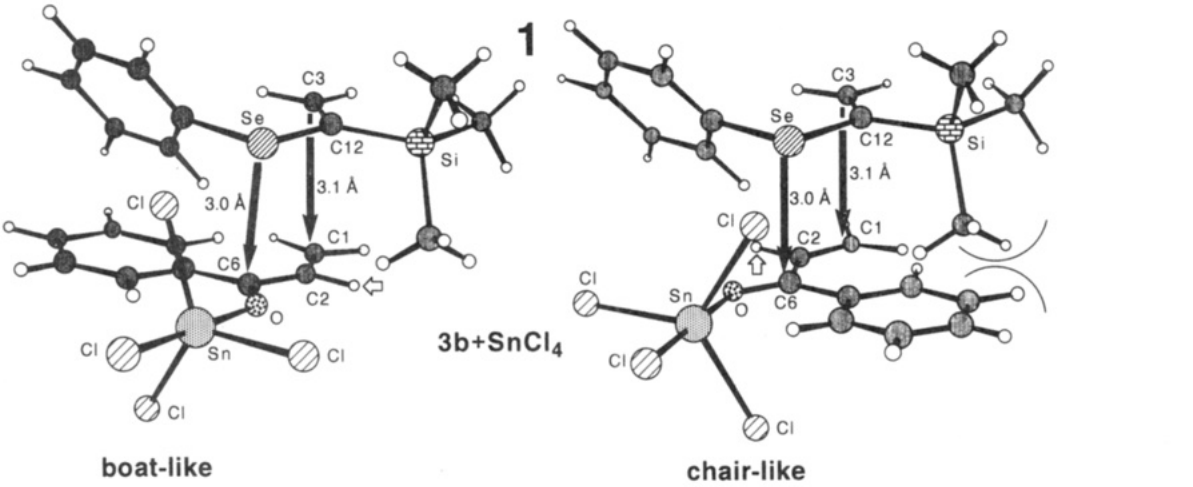
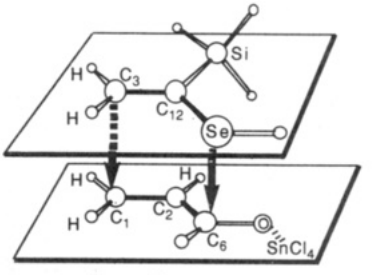
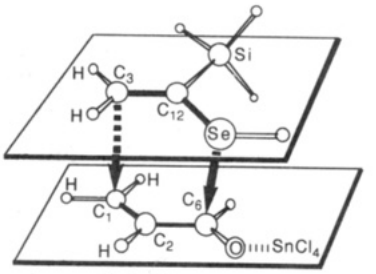


Figure 4. Two possible pathways for the [3 + 3] cycloaddition of **1** and **3b** to form product **4b**. The scheme depicted in Figure 3 is the parent system of the boat-like path. The phenyl group attached to Se is nonplanar relative to the vinyl plane because of the steric repulsion between the ortho and vinyl protons. Clearly, the chair-like path is unfavorable owing to the TMS–Ph repulsion. If the vinyl proton indicated by the white arrows was replaced with a bulky group such as *tert*-butyl or TMS, large steric repulsion with the TMS group attached to C_{12} would prohibit the boat-like [3 + 3] path.

The optimized geometry together with all the positive frequencies clearly demonstrates that a zwitterionic intermediate does exist in our [2 + 2] cycloaddition and that the chelated structure in Chart I (1) is unlikely because of the large Se···Sn separation. The neighboring-group participation in Chart I (2) is also ruled out owing to the large Se···C=O separation. It is noteworthy that the C_2–C_6 bond distance (1.323 Å) and the C_6–O bond distance (1.359 Å) of **X** are consistent with an enolate structure with a formal negative charge on oxygen. Additionally, to determine whether another $SnCl_4$ molecule interacts with zwitterionic intermediate **X**, the geometry optimization using the semiempirical PM3 method[29] in MOPAC (version 6)[30] was applied to **X** and $SnCl_4$. The second $SnCl_4$ molecule would be coordinated with the cationic site of species **X**, while the first $SnCl_4$ molecule in **X** is coordinated with the enolate oxygen atom. The results of the geometry optimization are shown in Figure 2b. A chlorine atom of the second $SnCl_4$ molecule seems to interact with selenium (calculated Se–Cl bond distance 2.484 Å; standard Se–Cl bond distance 2.16 Å), and the interaction may stabilize the zwitterionic intermediate **X**. Geometric parameters of **X** calculated using the PM3 method are similar to those calculated using RHF/LANL1MB. In the **X** + $SnCl_4$, both chelation (1) and neighboring-group participation (2) are also ruled out.

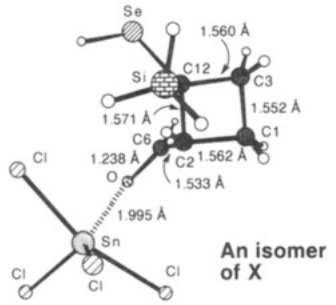
Whereas neighboring-group participation in the intermediate is unlikely, a secondary-orbital interaction may be a driving force in the early stage of the reaction. To check the Alder rule, the optimized geometries of fragment molecules of model intermediate **X** were used to investigated the frontier orbital interactions (Figure 3). The HOMO is largely localized at Se and the LUMO+1 is largest at the carbonyl carbon; these facts lead to a significant secondary-orbital interaction and, accordingly, to the cis orientation. In other words, the frontier-orbital interaction is regarded as symmetry allowed [3 + 3] rather than as [2 + 2]. In Figure 3, a boat-like [3 + 3] cycloaddition path is presented. However, a chair-like path, which avoids the C_{12}···C_2 orbital-phase cancellation and gives rise to the trans product, appears to be more favorable than the boat-like path.





To determine which of these paths was more favorable, we constructed two possible geometries for the combina-

(27) A cyclobutane–$SnCl_4$ complex was also calculated by the ab initio method. Determination of the geometry of this complex was quite difficult technically. In this form, the O···Sn distance (1.995 Å) is larger than that of **X** (1.865 Å) in Figure 2a. The bond elongation indicates that the $SnCl_4$ coordination is more effective in **X** and that cyclobutane formation is most likely completed after $SnCl_4$ is removed by a base.



(28) In **X**, two ion-center carbons are apparently trivalent, and it is conceivable that **X** has a biradical nature. To check whether **X** was biradical, a symmetry-broken "spin-wave" UHF MO calculation was performed by taking (HOMO + LUMO) and (HOMO–LUMO) as initial α- and β-spin orbitals, respectively. The UHF electronic structure was 5.63 kcal/mol less stable than the RHF one, which suggests that **X** is not biradical but zwitterionic.

(29) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209, 221.

(30) Stewart, J. J. P. MOPAC, version 6, QCPE, program no. 455, Indiana University, Oct 1990.

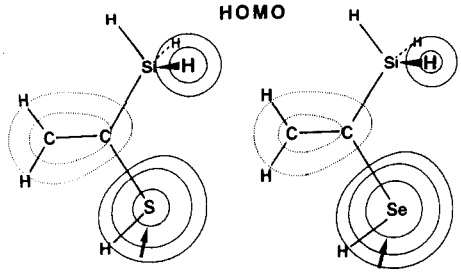


Figure 5. Comparison of contour map of HOMO's drawn at 1.5 Å above the molecular plane. The p_π component on Se is shown to be larger than that on S.

tions of **1** and **3b**···$SnCl_4$ (Figure 4). At an early stage of the [3 + 3] cycloaddition, with the Se···C_6 distance set to 3.0 Å, a C_3···C_1 distance of 3.1 Å is obtained by the use of appropriate O–C_6–Se–C_{12} dihedral angles (130° for boat and 160° for chair, respectively). This molecular-model orientation figure demonstrates that the chair-like path suffers from a large steric repulsion between the TMS group of **1** and the phenyl group of **3b**. Thus, the chair-like path, which appears to be favorable, is ruled out by the large steric repulsion.[31] A combination of the secondary-orbital interaction and steric effect leads to a boat-like transition state and thus to cis products **4a–c**.

As the reaction proceeds, the steric repulsion between $SnCl_4$ and SeH (i.e., SePh) weakens the Se···C_6 interaction, resulting in the intermediate **X**. The cis relationship between SePh and COR_1 in **12**, originating from the HOMO–(LUMO+1) interaction, is maintained in the cyclobutane product. These MO calculations, which include the metal and all the ligands of the Lewis acid, provide new insight into the effect of Lewis acids on stereoselective processes and should help in the design and improvement of Lewis acid-mediated reactions.

Heteroatoms such as oxygen, sulfur, and nitrogen have been extensively used as effective directing ligands in selective organic synthesis, and the selenium-directed [2 + 2] cycloadditions and acylsilane formations described here show that selenium can also be a versatile directing atom. A large orbital extension on the Se atom in the HOMO works efficiently to enhance the diastereoselectivity. Figure 5 shows the difference in orbital extension on sulfur and selenium. The larger size of the orbital on Se compared to that on S is clearly shown by the black arrows. The $SnCl_4$-coordinated carbonyl carbon of the vinyl ketone can approach the Se atom more readily leading to a [3 + 3] path and, accordingly, cis selectivity. Wide synthetic application of these highly substituted products can be expected.

In summary, we have shown new synthetic uses for vinyl selenides in [2 + 2] cycloaddition and acylsilane synthesis. Selenium works as a nucleophilic center in the early stage of the addition, but in the zwitterionic intermediate that is generated, selenium is an electrophilic acceptor toward the chloride ion of the second $SnCl_4$ as shown in Figure 2b. The ambiphilic character of selenium may be used effectively in the [2 + 2] cycloaddition reactions.[32] Further studies on the selectivity of selenium effects are in progress.

Experimental Section

General Methods. Melting points are uncorrected. IR spectra were recorded on a JASCO FT-IR 5000 spectrophotometer. NMR spectra were recorded in $CDCl_3$ on a JEOL FX-200 or JEOL JNM-GSX400 spectrometer. For the ^1H and ^{13}C spectra, Me_4Si was used as an internal reference. Mass spectra were determined on a JMS-SX102 spectrometer. Gas chromatography (GC) was performed on a Yanaco G180 chromatograph fitted with a thermal conductivity detector and a packed column (silicone GE SE30 2%, Chromosorb W 60/80 mesh, AW-DMCS, 2 m). All reactions were carried out under a nitrogen atmosphere.

1-(Phenylseleno)-1-(trimethylsilyl)ethene (1). Compound **1** was prepared by reaction of [1-(trimethylsilyl)vinyl]magnesium bromide and PhSeBr.[9] Purification by column chromatography (silica gel containing 10% H_2O, hexane containing 1% triethylamine) at low temperature (−40 °C) gave **1** in reproducible yield (51–60%).

***c*-1-Acetyl-*r*-2-(phenylseleno)-2-(trimethylsilyl)cyclobutane (4a) (Table I, Entry 1).** To a solution of $SnCl_4$ (1.95 g, 7.5 mmol) in dry dichloromethane (3.0 mL) cooled to −78 °C was added **1** (1.53 g, 6.0 mmol) in dichloromethane (6.0 mL). Methyl vinyl ketone (**3a**) (386 mg, 5.51 mmol) was then added. The mixture was stirred at −78 °C for 3 h. The reaction mixture was quenched with triethylamine (1.14 g, 11.3 mmol), and then saturated aqueous $NaHCO_3$ was added to the mixture. The mixture was extracted with dichloromethane. The organic phase was dried (Na_2SO_4) and evaporated in vacuo. The residue was purified by column chromatography over silica gel eluting with hexane–ether (4:1) to give **4a** (1.19 g, 66%, R_f = 0.4). **4a**: pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.213 (s, 9 H, $Si(CH_3)_3$), 1.71–1.85 (m, 2 H), 2.02–2.13 (m, 1 H), 2.19 (s, 3 H, $COCH_3$), 2.32–2.42 (m, 1 H), 3.50–3.54 (m, 1 H, $CHCOCH_3$), 7.24–7.36 (m, 3 H, meta, para H of SePh), 7.56–7.59 (m, 2 H, ortho H of SePh); NOE's were observed between δ 1.71–1.85 and δ 2.02–2.13, δ 1.71–1.85 and δ 2.32–2.42, δ 1.71–1.85 and δ 3.50–3.54, δ 1.71–1.85 and δ 7.56–7.59, and δ 2.19 and δ 3.50–3.54 by 2D NOESY; ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) −3.369, 19.67, 26.15, 30.03, 38.85, 52.75, 127.0, 128.6, 128.7, 138.5, 207.3; IR (neat) 2956, 1711, 1354, 1174, 1249, 839, 741, 692 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 43 (41), 73 (100), 95 (100), 143 (100), 169 (100), 326 (61); exact mass M^+ 326.0615 (calcd for $C_{15}H_{22}OSeSi$ 326.0606).

Reaction of 1 and 3a with $AlCl_3$ (Table I, Entry 2). To a mixture of $AlCl_3$ (166 mg, 1.25 mmol) and dichloromethane (0.5 mL) cooled to −78 °C was added **1** (255 mg, 1.0 mmol) in dichloromethane (1.0 mL). Compound **3a** (258 mg, 3.68 mmol) was then added. The mixture was stirred at −78 °C for 3 h. Water was added to the reaction mixture. The mixture was extracted with dichloromethane, and the organic phase was washed with saturated aqueous $NaHCO_3$, dried (Na_2SO_4), and evaporated in vacuo. The residue was purified by column chromatography over silica gel eluting with hexane–ether (4:1) to give **4a** (134 mg, 41%).

Reaction of 1 and 3a with $EtAlCl_2$ (Table I, Entry 3). To a mixture of a 0.95 M *n*-hexane solution of $EtAlCl_2$ (1.32 mL, 1.25 mmol) and dichloromethane (0.5 mL) cooled to −78 °C was added **1** (255 mg, 1.0 mmol) in dichloromethane (1.0 mL). Compound **3a** (64 mg, 0.92 mmol) was then added. After 2 h, **3a** (193 mg, 2.75 mmol) was added to the mixture. The resulting mixture was stirred for an additional hour. To the reaction mixture was added triethylamine (190 mg, 1.88 mmol) and then water. The mixture was extracted with dichloromethane, and the organic phase was washed with saturated aqueous $NaHCO_3$, dried (Na_2SO_4), and evaporated in vacuo. The residue was purified by column chromatography over silica gel eluting with hexane–ether (4:1) to give **4a** (175 mg, 54%).

***c*-1-Benzoyl-*r*-2-(phenylseleno)-2-(trimethylsilyl)cyclobutane (4b) (Table I, Entry 4).** To a solution of $SnCl_4$ (3.60 g, 13.8 mmol) in dichloromethane (17.3 mL) cooled to −78 °C was added **1** (2.30 g, 9.0 mmol) in dichloromethane (4.1 mL). Phenyl vinyl ketone (**3b**)[33] (1.52 g, 11.5 mmol) was then added. The mixture was stirred at −78 °C for 3 h. The reaction mixture was quenched with triethylamine (2.09 g, 20.7 mmol), and then saturated aqueous $NaHCO_3$ was added to the mixture. The mixture was extracted with dichloromethane. The organic phase was dried (Na_2SO_4) and evaporated in vacuo. The residue was purified by column chromatography over silica gel, eluting with hexane–ether

(31) In eq 1, the case where R_1 = H, which was not examined here, the repulsion-free chair-like path would likely give the trans product.

(32) For reviews of electrophilic and nucleophilic selenium reactions, see: *Organoselenium Chemistry*; Liotta, D., Ed.; John Wiley and Sons: New York, 1987; Chapters 1 and 4.

(33) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.

(4:1) to give **4b** (2.96 g, 85%, R_f = 0.6). **4b**: colorless crystals; mp 63–64 °C (methanol); ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.193 (s, 9 H, $Si(CH_3)_3$), 1.94–2.11 (m, 3 H), 2.55–2.66 (m, 1 H), 4.34–4.41 (m, 1 H, C*H*COPh), 7.20–7.33 (m, 3 H), 7.44–7.57 (m, 5 H), 7.89–7.94 (m, 2 H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) −2.902, 20.54, 27.20, 39.29, 47.84, 127.4, 128.4, 132.6, 137.9, 138.4, 199.8; IR (neat) 3408, 1678, 1249, 837, 739, 692 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 35 (52), 47 (100), 73 (55), 87 (100), 118 (33), 231 (97), 388 (8); exact mass M^+ 388.0748 (calcd for $C_{20}H_{24}OSeSi$ 388.0762). Anal. Calcd for $C_{20}H_{24}OSeSi$: C, 62.00; H, 6.24. Found: C, 61.99; H, 6.33.

***r*-1-(Phenylseleno)-*c*-2-propionyl-1-(trimethylsilyl)cyclobutane (4c) (Table I, Entry 5).** To a solution of $SnCl_4$ (326 mg, 1.25 mmol) in dichloromethane (0.5 mL) cooled to −78 °C was added **1** (255 mg, 1.0 mmol) in dichloromethane (1.0 mL). Ethyl vinyl ketone (**3c**) (77 mg, 0.92 mmol) was then added. The mixture was stirred at −78 °C for 3 h. The reaction mixture was quenched with triethylamine (190 mg, 1.88 mmol), and then saturated aqueous $NaHCO_3$ was added to the mixture. The mixture was extracted with dichloromethane. The organic phase was dried (Na_2SO_4) and evaporated in vacuo. The residue was purified by column chromatography over silica gel, eluting with hexane–ether (1:1) to give **4c** (152 mg, 49%, R_f = 0.75). **4c**: colorless crystals; mp 63 °C (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.209 (s, 9 H, $Si(CH_3)_3$), 1.16 (t, J = 7.2 Hz, 3 H, CH_2CH_3), 1.74–1.86 (m, 2 H), 1.98–2.06 (m, 1 H), 2.24–2.34 (m, 1 H, C*H*HCH_3), 2.36–2.45 (m, 1 H), 2.54–2.64 (m, 1 H, CH*H*CH_3), 3.49–3.53 (m, 1 H, C*H*COEt), 7.25–7.36 (m, 3 H, meta, para H of SePh), 7.54–7.57 (m, 2 H, ortho H of SePh); NOE's were observed between δ 1.16 and δ 2.24–2.34, δ 1.16 and δ 2.54–2.64, δ 1.74–1.86 and δ 1.98–2.06, δ 1.74–1.86 and δ 2.36–2.45, δ 1.74–1.86 and δ 3.49–3.53, δ 1.74–1.86 and δ 7.54–7.57, δ 2.24–2.34 and δ 2.54–2.64, and δ 2.24–2.34 and δ 3.49–3.53 by 2D NOESY; ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) −3.369, 7.317, 19.55, 26.38, 35.67, 39.06, 51.55, 127.1, 128.6, 138.4, 209.8; IR (neat) 2954, 1711, 1437, 839 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 73 (100), 109 (25), 183 (94), 340 (15); exact mass M^+ 340.0748 (calcd for $C_{16}H_{24}OSeSi$ 340.0761). Anal. Calcd for $C_{16}H_{24}OSeSi$: C, 56.62; H, 7.13. Found: C, 56.59; H, 7.15.

1-(Phenylseleno)-1-(trimethylsilyl)-1,2-propadiene (2). An LDA solution in THF–hexane (prepared by the addition of a 1.55 M solution of *n*-butyllithium in hexane (7.41 mL, 11.5 mmol) to a solution of diisopropylamine (1.16 g, 11.5 mmol) in THF (2.5 mL) at −78 °C) was added to a cooled (−78 °C) solution of allenyl phenyl selenide (**6**)[16] g, 11.2 mmol) in THF (15.9 mL). After 1 h, chlorotrimethylsilane (1.22 g, 11.3 mmol) was added. After an additional hour at −78 °C, the mixture was allowed to warm to room temperature and then stirred overnight. Water was added to the reaction mixture. The mixture was extracted with hexane. The organic phases were dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by column chromatography over silica gel eluting with hexane to give **2** (90% pure by GC, 1.77 g, 53%, R_f = 0.6). (A small amount of unreacted **6** and another unidentified impurity were present.) **2**: pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.135 (s, 9 H, $Si(CH_3)_3$), 4.37 (s, 2 H, $=CH_2$), 7.20–7.32 (m, 3 H), 7.47–7.53 (m, 2 H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) −1.267, 70.56, 84.81, 127.2, 128.8, 130.6, 133.3, 208.7; IR (neat) 1922, 1249, 843 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 73 (94), 115 (100), 268 (36); exact mass M^+ 268.0200 (calcd for $C_{12}H_{16}SeSi$ 268.0186).

***c*-1-Acetyl-*r*-2-(phenylseleno)-2-(trimethylsilyl)-3-methylenecyclobutane (5a) (Table I, Entry 6).** To a solution of **2** (86% pure by GC, 197 mg, 0.634 mmol) and methyl vinyl ketone (**3a**) (200 mg, 2.85 mmol) in dichloromethane (0.9 mL) at −20 °C was added $AlCl_3$ (91.1 mg, 0.683 mmol) by portions. The mixture was stirred at −20 °C for 1 h. Water was added to the reaction mixture. The mixture was extracted with dichloromethane, and the organic phase was washed with saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and evaporated in vacuo. The residue was purified by column chromatography over silica gel eluting with hexane–ether (4:1) to give **5a** (149 mg, 70%, R_f = 0.5). Compound **5a** is relatively unstable and decomposes gradually. **5a**: pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.266 (s, 9 H, $Si(CH_3)_3$), 2.27 (s, 3 H, $COCH_3$), 2.45 (dddd, J = 2.5, 2.5, 8.2, 16.3 Hz, 1 H, C*H*H), 3.12 (dddd, J = 2.5, 2.5, 6.7, 16.3 Hz, 1 H, CH*H*), 3.46 (dd, J = 6.7, 8.2 Hz, 1 H, C*H*COCH$_3$), 4.44 (ddd, J = 0.8, 2.5, 2.5 Hz, 1 H, =C*H*H), 4.74 (ddd, J = 0.8, 2.5, 2.5 Hz, 1 H, =CH*H*), 7.23–7.30 (m, 3 H, meta, para H of SePh), 7.51–7.56 (m, 2 H, ortho H of SePh); NOE's were observed between δ 2.45 and δ 3.12, δ 2.45 and δ 3.46, δ 4.44 and δ 4.74, and δ 4.44 and δ 7.51–7.56 by 2D NOESY; ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) −3.077 (CH_3), 30.50 (CH_2), 30.67 (CH_3), 47.96 (C), 49.48 (CH), 108.9 (CH_2), 127.4 (C), 128.4 (CH), 128.4 (CH), 137.5 (CH), 147.7 (C), 206.6 (C) (^{13}C multiplicities were determined from the proton-coupled spectrum.); IR (neat) 2960, 1711, 1659, 1249, 845 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 43 (100), 73 (100), 181 (57), 323 (46), 338 (25); exact mass M^+ 338.0612 (calcd for $C_{16}H_{22}OSeSi$ 338.0606).

1-Acetyl-2-(phenylseleno)-3-methylenecyclobutane (7) (Table I, Entry 7). To a solution of **6** (221 mg, 1.13 mmol) and methyl vinyl ketone (**3a**) (306 mg, 4.38 mmol) in dichloromethane (1.3 mL) at −78 °C was added $AlCl_3$ (151.1 mg, 1.13 mmol) by portions. After 1 h at −78 °C, the mixture was allowed to warm to −20 °C and then stirred for 2 h. Water was added to the reaction mixture. The mixture was extracted with dichloromethane, and the organic phase was washed with saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and evaporated in vacuo. The residue was purified by column chromatography over silica gel eluting with hexane–ether (4:1) to give **7** (32 mg, 11%). **7**: pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 2.06 (s, 3 H, CH_3), 2.66–2.94 (m, 2 H, CH_2), 3.31 (ddd, J = 7.3, 7.4, 9.7 Hz, 1 H, C*H*COCH$_3$), 4.64 (dddd, J = 2.4, 2.5, 2.5, 7.3 Hz, C*H*SePh), 5.02 (ddd, J = 2.3, 2.4, 2.4 Hz, 1 H, =C*H*H), 5.15 (ddd, J = 2.4, 2.5, 2.5 Hz, 1 H, =CH*H*), 7.24–7.36 (m, 3 H, Ph), 7.56–7.64 (m, 2 H, Ph); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) 28.31 (CH_3), 32.05 (CH_2), 44.25 (*C*HSePh), 50.38 (*C*HCOCH$_3$), 109.4, 127.9, 128.7, 129.2, 134.7, 145.5, 206.9 ppm (^{13}C assignments were determined by INEPT and ^{13}C-^{1}H selective decoupling.); IR (neat) 1711, 1578, 1479, 1437, 1359, 1181, 739, 692 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 43 (100), 81 (100), 109 (100), 157 (79), 266 (77); exact mass M^+ 266.0203 (calcd for $C_{13}H_{14}OSe$ 266.0210).

1-Acetyl-2-(phenylseleno)-2-(trimethylsilyl)cyclobutane Ethylene Ketal (13). A solution of **4a** (978 mg, 3 mmol), ethylene glycol (481 mg, 7.75 mmol), toluene (33.1 mL), and *p*-toluenesulfonic acid (3 mg) was refluxed for 5.5 h in a round-bottomed flask equipped with a Dean–Stark trap and a condenser. The solution was cooled to room temperature, washed with saturated aqueous $NaHCO_3$, and dried over sodium sulfate. The solvent was removed, and the residue was chromatographed on silica gel eluting with hexane–ether (4:1) to give a 9:1 isomeric mixture of **13** (630 mg, 57%, R_f = 0.6). Column chromatography (silica gel) eluting with hexane–chloroform (1:2) of the isomeric mixture gave the pure major isomer of **13** (404 mg, R_f = 0.7). The minor isomer of **13** was not isolated. **13** (major isomer): colorless crystals; mp 63–64 °C (hexane); ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.265 (s, 9 H), 1.37 (s, 3 H), 1.46–1.66 (m, 2 H), 1.79–1.95 (m, 2 H), 3.76–4.00 (m, 4 H), 2.60 (t-like, J = 10 Hz, 1 H), 7.32–7.40 (m, 3 H), 7.56–7.61 (m, 2 H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) −0.449, 20.66, 23.20, 28.02, 40.37, 52.69, 64.25, 65.27, 109.6, 126.7, 128.6, 128.8, 139.2; IR (neat) 2982, 2954, 2882, 1375, 1245, 1087, 1050, 845, 741, 694 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 43 (24), 73 (89), 87 (100), 117 (18), 256 (35), 283 (12), 370 (32); exact mass M^+ 370.0894 (calcd for $C_{17}H_{26}O_2SeSi$ 370.0867). Anal. Calcd for $C_{17}H_{26}O_2SeSi$: C, 55.27; H, 7.09. Found: C, 55.44; H, 7.16.

***t*-1-Acetyl-*r*-2-(phenylseleno)-2-(trimethylsilyl)cyclobutane (14).** To the major isomer of **13** (148 mg, 0.4 mmol) in THF (2.5 mL) at rt was added 1 N hydrochloric acid (2.6 mL). The mixture was stirred for 24 h. The reaction mixture was extracted with ether, and the extracts were washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by column chromatography over silica gel eluting with hexane–ether (2:1) to give **14** (80 mg, 61%, R_f = 0.6). **14**: pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.206 (s, 9 H, $Si(CH_3)_3$), 1.55–1.62 (m, 1 H), 1.99–2.07 (m, 3 H), 2.13 (s, 3 H, $CHCOCH_3$), 3.23–3.27 (m, 1 H, C*H*COCH$_3$), 7.36–7.46 (m, 3 H, meta, para H of SePh), 7.61–7.64 (m, 2 H, ortho H of SePh); NOE's were observed between δ 1.55–1.62 and δ 1.99–2.07, δ 1.55–1.62 and δ 3.23–3.27, δ 1.99–2.07 and δ 3.23–3.27, δ 1.99–2.07 and δ 7.61–7.64, and δ 3.23–3.27 and δ 7.61–7.64 by 2D NOESY; ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) −1.500, 20.11, 27.49, 29.45, 40.63, 55.32, 126.6, 129.0, 129.1, 138.9, 207.9; IR (neat) 2956, 1711, 1361, 1251, 1183, 843, 743, 694, 648 cm^{-1}; MS (70 eV) *m/z* (relative

intensity) 43 (8), 73 (65), 169 (100), 241 (6), 324 (1), 326 (1); exact mass M^+ 326.0569 (calcd for $C_{15}H_{22}OSeSi$ 326.0606).

Oxidation of 4a by MCPBA. *m*-Chloroperbenzoic acid (948 mg, 5.49 mmol) in dichloromethane (20 mL) was added to a cooled (0 °C) solution of **4a** (1.49 g, 4.58 mmol) in dichloromethane (28 mL). The ice bath was removed. After the reaction mixture was stirred at room temperature for 0.5 h, diisoproplyamine (1.37 mL, 9.78 mmol) was added. After 0.5 h, 5% NaOH solution was added to the reaction mixture. The mixture was extracted with dichloromethane, and the organic phase was washed with water, dried (Na_2SO_4), and evaporated in vacuo. The residue was purified by column chromatography over silica gel, eluting with hexane–ether (2:1) to give unchanged **4a** (255 mg, 17%, R_f = 0.7), **16** (116 mg, 10%, R_f = 0.5), and **15** (409 mg, 36%, R_f = 0.4). **15**: yellow oil; ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 2.22 (s, 3 H), 2.36–2.40 (m, 2 H), 2.67–2.71 (m, 2 H), 7.27–7.38 (m, 3 H), 7.59–7.64 (m, 2 H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) 27.11, 27.17, 31.35, 125.9, 129.0, 129.4, 135.7, 141.0, 151.4, 193.4; IR (neat) 2926, 1655, 1557, 1218, 741, 692 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 43 (84), 77 (28), 95 (20), 128 (60), 158 (26), 171 (23), 209 (25), 250 (50), 252 (100); exact mass M^+ 252.0052 (calcd for $C_{12}H_{12}O^{80}Se$ 252.0054), 250.0039 (calcd for $C_{12}H_{12}O^{78}Se$ 250.0061). **16**: yellow oil; ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 2.08 (s, 3 H), 2.72 (ddd, J = 1.1, 2.0, 11.7 Hz, 1 H), 2.80 (ddd, J = 1.1, 4.3, 11.7 Hz, 1 H), 3.76 (dd, J = 2.0, 4.3 Hz, 1 H), 6.30 (bs, 1 H), 7.28–7.35 (m, 3 H), 7.53–7.58 (m, 2 H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) 27.05, 32.89, 57.25, 127.1, 128.1, 129.3, 134.2, 139.0, 207.2; IR (neat) 2922, 1711, 1578, 1479, 1439, 1357, 741, 690 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 43 (100), 77 (41), 95 (41), 128 (58), 157 (28), 250 (40), 252 (68); exact mass M^+ 252.0073 (calcd for $C_{12}H_{12}OSe$ 252.0053).

1-Acetyl-2,2-dimethylcyclobutane (18). Cuprous(I) iodide (538 mg, 282 mmol) was suspended in ether (11 mL), and methyllithium (5.09 mL, 5.6 mmol, 1.1 M in ether) was added dropwise at 0 °C. After the mixture was stirred at 0 °C for 10 min, **15** (225 mg, 0.899 mmol) in ether (7.2 mL) was added dropwise, and the reaction mixture was stirred for 40 min at 0 °C. The mixture was quenched with water. The solution was extracted with ether, dried ($MgSO_4$), and concentrated in vacuo (with ice cooling) to give **18** (113 mg, 100%). The crude **18** was pure enough to use in the next reaction. A pure sample was obtained by column chromatography (silica gel, 2:1 pentane–ether, R_f = 0.5). **18**: colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.990 (s, 3 H), 1.31 (s, 3 H), 1.46–1.83 (m, 3 H), 2.04 (s, 3 H), 2.21–2.37 (m, 1 H), 2.93–3.01 (m, 1 H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) 15.84, 23.17, 29.97, 30.73, 32.13, 40.75, 55.79, 208.6; IR (neat) 2956, 2868, 1707, 1464, 1361, 1180 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 28 (100), 41 (17), 43 (34), 55 (15), 56 (27), 71 (55), 83 (30), 111 (22), 126 (18); exact mass M^+ 126.1014 (calcd for $C_8H_{14}O$ 126.1045).

2,2-Dimethylbutane-1-carboxylic Acid (19). A solution of NaOH (474 mg, 11.9 mmol) in water (4.1 mL) was cooled to −5 °C. Bromine (485 mg, 3.04 mmol) was added dropwise. The cold solution was diluted with dioxane (2.7 mL) that was previously cooled to 13–14 °C. The hypobromite solution was kept at 0 °C. A solution of **18** (0.114 g, 0.903 mmol) in dioxane (12 mL) and water (3.6 mL) was cooled in ice. To the solution was added the cold hypobromite solution dropwise. The mixture was stirred for additional 3 h, and then a solution of Na_2SO_3 (113 mg) in water (1.1 mL) was added. The mixture was acidified by the addition of concentrated hydrochloric acid (0.56 mL) and then extracted twice with ether. The ether solution was extracted with 5% NaOH solution. The water layer was separated, acidified by the addition of concentrated hydrochloric acid, and extracted twice with ether. The ether solution was dried ($MgSO_4$) and evaporated in vacuo to give **19** (70 mg, 68%). **19**:[19c] colorless oil; bp 100 °C (5 mmHg); ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 1.12 (s, 3 H), 1.23 (s, 3 H), 1.62–2.01 (m, 3 H), 2.14–2.34 (m, 1 H), 2.87 (t, J = 8.3 Hz, 1 H), 11.4 (bs, 1 H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) 17.10 (CH_2), 23.58 (CH_3), 30.41 (CH_3), 32.37 (CH_2), 40.34 (C), 47.76 (CH), 180.0 (C) (^{13}C multiplicities were determined by INEPT); IR (neat) 2962, 2870, 1702, 1464, 1423, 1371, 1286, 1249, 1214, 1149, 932 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 128 (10), 100 (100).

Treatment of **19** with diazomethane in ether gave its methyl ester (**20**) quantitatively. **20**:[19c] colorless oil; bp 60 °C (bath temp) (120 mmHg); ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 1.03 (s, 3 H), 1.21 (s, 3 H), 1.65–1.99 (m, 3 H), 2.17–2.36 (m, 1 H), 2.82 (t, J = 8.4 Hz, 1 H), 3.67 (s, 3 H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) 17.16 (CH_2), 23.58 (CH_3), 30.30 (CH_3), 32.25 (CH_2), 39.93 (C), 47.67 (CH), 51.05 (CH_3), 174.0 (C) (^{13}C multiplicities were determined by INEPT); IR (neat) 2958, 2868, 1736, 1437, 1352, 1238, 1195, 1180, 1048 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 87 (100), 114 (35), 142 (3); exact mass M^+ 142.0986 (calcd for $C_8H_{14}O_2$ 142.0994).

Oxidation of 14.[20] To a solution of **14** (190 mg, 0.58 mmol) in methanol (9.7 mL) at rt was added a solution of $NaIO_4$ (284 mg, 1.3 mmol) in water (1.6 mL). After stirring for 2.5 h, the reaction mixture was extracted with ether. The organic phase was washed with NaCl solution, dried ($MgSO_4$), and evaporated in vacuo to give **17** (100 mg, 100%). **17**: pale yellow oil; bp 60–64 °C (70 mmHg); ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.155 (s, 9 H), 2.17 (s, 3 H), 2.40–2.41 (m, 2 H), 2.76–2.79 (m, 2 H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) −1.968, 26.94, 28.81, 29.62, 154.1, 167.0, 195.2; IR (neat) 2958, 2918, 1680, 1576, 1249, 1209, 841 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 28 (25), 73 (26), 153 (100), 168 (6); exact mass M^+ 168.0968 (calcd for $C_9H_{16}OSi$ 168.0970).

1-(Trimethylsilyl)-1,5-hexanedione (11a). To a solution of $SnCl_4$ (652 mg, 2.5 mmol) in dichloromethane (1.0 mL) cooled to −78 °C was added **1** (408 mg, 1.60 mmol) in dichloromethane (2.0 mL). Methyl vinyl ketone (**3a**) (112 mg, 1.84 mmol) was then added. The mixture was stirred at −78 °C for 3 h. Water was then added to the reaction mixture. The mixture was extracted with dichloromethane, and the organic phase was washed with saturated aqueous $NaHCO_3$, dried (Na_2SO_4), and evaporated in vacuo. The residue was purified by column chromatography over silica gel, eluting with hexane–ether (1:1) to give **11a** (108 mg, 37%, R_f = 0.4). **11a**: pale yellow oil; bp 70 °C (30 mmHg); ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.195 (s, 9 H), 1.75–1.83 (m, 2 H), 2.12 (s, 3 H), 2.43 (t, J = 7.08 Hz, 2 H), 2.64 (t, J = 6.96 Hz, 2 H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) −3.123, 16.36, 29.95, 42.83, 47.23, 208.6, 247.8; IR (neat) 2960, 1717, 1642, 1251, 845 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 43 (59), 73 (100), 115 (67), 130 (63), 158 (13), 186 (8); exact mass M^+ 186.1084 (calcd for $C_9H_{18}O_2Si$ 186.1077). Anal. Calcd for $C_9H_{18}O_2Si$: C, 58.02; H, 9.74. Found: C, 58.28; H, 9.81.

1-Phenyl-5-(trimethylsilyl)-1,5-pentanedione (11b). To a solution of $SnCl_4$ (325 mg, 1.25 mmol) in dichloromethane (0.5 mL) cooled to −78 °C was added **1** (255 mg, 1.0 mmol) in dichloromethane (1.0 mL). Phenyl vinyl ketone (**3b**) (121 mg, 0.92 mmol) was then added. The mixture was stirred at −78 °C for 3 h. Water was added to the reaction mixture. The mixture was extracted with dichloromethane, and the organic phase was washed with saturated aqueous $NaHCO_3$, dried (Na_2SO_4), and evaporated in vacuo. The residue was purified by column chromatography over silica gel eluting with hexane–ether (1:1) to give **11b** (88 mg, 39%, R_f = 0.6). **11b**: pale yellow oil; bp 90 °C (4 mmHg); ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.205 (s, 9 H), 1.94–2.01 (m, 2 H), 2.75 (t, J = 6.84 Hz, 2 H), 2.98 (t, J = 7.08, 2 H), 7.42–7.56 (m, 3 H), 7.94–7.98 (m, 2 H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) −3.191, 16.84, 37.65, 47.36, 128.1, 128.6, 133.0, 136.8, 199.9, 247.9; IR (neat) 2962, 1686, 1642, 1450, 1251, 1226, 847 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 73 (100), 177 (63), 191 (91), 220 (39), 233 (4.6), 248 (2.6); exact mass M^+ 248.1243 (calcd for $C_{14}H_{20}O_2Si$ 248.1233). Anal. Calcd for $C_{14}H_{20}O_2Si$: C, 67.70; H, 8.12. Found: C, 67.57; H, 8.08.

1-(Trimethylsilyl)-1,5-heptanedione (11c). To a solution of $SnCl_4$ (325 mg, 1.25 mmol) in dichloromethane (0.5 mL) cooled to −78 °C was added **1** (255 mg, 1.0 mmol) in dichloromethane (1.0 mL). Ethyl vinyl ketone (**3c**) (77 mg, 0.92 mmol) was then added. The mixture was stirred at −78 °C for 3 h. Water was added to the reaction mixture. The mixture was extracted with dichloromethane, and the organic phase was washed with saturated aqueous $NaHCO_3$, dried (Na_2SO_4), and evaporated in vacuo. The residue was purified by column chromatography over silica gel eluting with hexane–ether (1:1) to give **11c** (92 mg, 50%, R_f = 0.5). **11c**: pale yellow oil; bp 75 °C (30 mmHg); ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.196 (s, 9 H), 1.04 (t, J = 7.33 Hz, 3 H), 1.76–1.83 (m, 2 H), 2.37–2.42 (m, 4 H), 2.64 (t, J = 7.08 Hz, 2 H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) −3.226, 7.811, 16.36, 35.85, 41.33, 47.29, 211.2, 247.8; IR (neat) 2962, 1715, 1642, 1251, 845 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 73 (100), 129 (45), 144 (31), 185 (16), 200 (9); exact mass M^+ 200.1283 (calcd for C_{10}-

$H_{20}O_2Si$ 200.1233). Anal. Calcd for $C_{10}H_{20}O_2Si$: C, 59.95; H, 10.06. Found: C, 59.83; H, 10.00.

Conversion of 4a to 11a. To a solution of **4a** (65 mg, 1.2 mmol) in dichloromethane (1.0 mL) was added $SnCl_4$ (65 mg, 0.25 mmol) in dichloromethane (0.5 mL). The mixture was stirred at −78 °C for 1 h. Water was added to the reaction mixture. The mixture was extracted with dichloromethane, and the organic phase was washed with saturated aqueous $NaHCO_3$, dried (Na_2SO_4), and evaporated in vacuo. The residue was purified by column chromatography over silica gel eluting with hexane–ether (1:1) to give **11a** (24 mg, 65%).

Crystal Structure Determination of 4b. Single crystals of **4b** were obtained from a methanol solution. A crystal of **4b** having dimensions of 0.7 × 0.4 × 0.5 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Mo Kα radiation. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25° carefully centered to a triclinic cell with the following dimensions: a = 10.654 (4) Å, b = 10.677 (4) Å, c = 9.549 (4) Å, α = 107.10 (3)°, β = 110.92 (3)°, γ = 80.86 (3)°, V = 968.0 (7) Å^3. For Z = 2 and FW = 387.45, the calculated density is 1.329 g/cm^3. Based on packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$ (2). The data collected at 23 ± 1 °C using the $\omega - 2\theta$ scan technique to a maximum 2θ value of 60.1°. Scans of (1.73 + 0.35 tan θ)° were made at a speed of 8.0 deg/min (in ω). The ratio of peak counting time to background counting time was 2:1. Of the 5937 reflections that were collected, 5656 were unique (R_{int} = 0.016). The intensities of three representative reflections, which were measured after every 100 reflections, declined by −1.40%. A linear correction factor was applied to the data to account for this phenomenon. The linear absorption coefficient for Mo Kα is 19.8 cm^{-1}. An emperical absorption correction, based on azimuthal scans of several reflections, was applied. The application of the correction resulted in transmission factors ranging from 0.92 to 1.00. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods.[34] The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement[35] was based on 2605 observed reflections ($I > 3.00\sigma(I)$) and 350 variable parameters and converged (largest parameter shift was 3.28 times its esd) with the following unweighted and weighted agreement factors: $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.038$, $R_w = [(\sum\omega(|F_o| - |F_c|)^2/\sum\omega F_o^2)]^{1/2} = 0.037$. The standard deviation of an observation of unit weight[36] was 1.37. The weighting scheme was based on counting statistics and included a factor (ρ = 0.03) to downweight the intense reflections. Plots of $\sum\omega(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin\theta/1$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.42 and −0.33 e$^-$/Å^3, respectively. Neutral atom scattering factors were taken from Cromer and Waber.[37] Anomalous dispersion effects were included in F_{calc};[38] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[39] All calculations were performed using the TEXSAN[40] crystallographic software package of Molecular Structure Corporation.

MO Calculations. An ab initio geometry optimization and a vibrational analysis of model compound **X** (in Figure 2a and ref 27) and of $H_2C{=}C(SiH_3)(SeH)$ and acrolein coordinated by $SnCl_4$ (in Figure 3) were carried out with the GAUSSIAN 90 program package.[25] The basis set for the RHF optimization was LANL1MB,[26] which includes the effective core potential for the inner-shell electrons and the minimal basis set for the valence electrons. The PM3 calculation[29] was made on the structure of **X** + $SnCl_4$ (in Figure 2b), using version 6 of the MOPAC program.[30] All the MO calculations were performed on the CONVEX C-220 computer at the Information Processing Center of Nara University of Education.

Acknowledgment. We are grateful to Prof. I. Murata and Dr. K. Yamamoto (Osaka University) for measurement of NMR (400 MHz), X-ray analysis, mass spectra, and elemental analysis. We also thank Hayashi Memorial Foundation for Female Natural Scientists for generous financial support.

Supplementary Material Available: Tables of positional and thermal parameters, general temperature factor expressions, U's, bond distances, and bond angles for **4b** (in Figure 1); Z matrices of a model zwitterionic intermediate **X** (in Figure 2a) and **X** + $SnCl_4$ (in Figure 2b); and ^{1}H and ^{13}C NMR spectra of **2**, **4a**, **5**, **7**, and **14–20** (45 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(34) Beurskens, P. T.; DIRDIF; Direct Methods for Difference Structures–an automatic procedure for phase extension and refinement of difference structure factors. Technical Report 1984/1, Crystallography Laboratory, Toernooiveld, 6526 Ed. Nijmegen, Netherlands.

(35) Least-Squares: Function minimized: $\sum\omega(|F_o| - |F_c|)^2$, where $\omega = 4F_o/\sum(F_o^2)$, $\sum^2(F_o^2) = [S^2(C + R^2B) + (\rho F_o^2)^2]/L_p^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, L_p = Lorentz-polarization factor, ρ = ρ factor.

(36) $[\sum\omega(|F_o| - |F_c|^2/(N_o - N_v)]^{1/2}$, where N_o = number of observations, N_v = number of variables.

(37) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2 A.

(38) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(39) Cromer, D. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(40) TEXAN-TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985.

(41) Johnson, C. K.; ORTEP II. Report ORNL-5138. Oak Ridge National Laboratory: Oak Ridge, TN, 1976.