Mechanistic Study of the Ring-Enlargement Reaction of (3-Oxa-2-silacyclopentyl)methyl Radicals into 4-Oxa-3-silacyclohexyl Radicals. Evidence for a Pentavalent Silicon-Bridging Radical Transition State in 1,2-Rearrangement Reactions of β-Silyl Radicals

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Abstract: A mechanistic study was performed on a novel radical ring-enlargement reaction of (3-oxa-2-silacyclopentyl)methyl radicals into 4-oxa-3-silacyclohexyl radicals. Two pathways, one via a pentavalent silicon-bridging radical transition state (or intermediate), the other via β-elimination to give a ring-opened silyl radical, can be postulated. The radical reactions of **1** and **2**, which are precursors for a (3-oxa-2-silacyclopentyl)-methyl radical **C′** and a 4-oxa-3-silacyclohexyl radical **D′**, respectively, showed that the ring-enlargement rearrangement of **C′** into **D′** is irreversible. ^{1}H NMR analysis of the radical reactions of **8a** and **8b**, which have an asymmetric center at silicon, indicated that the configuration at the silicon atom is retained via a pentavalent silicon-bridging radical transition state (or intermediate) during the ring-enlargement reaction. Furthermore, examination of the radical ring-enlargement reaction with a deuterium-labeled substrate **12D** showed that the ring-enlargement reaction did not involve β-elimination to give a ring-opened silyl radical. Based on these results, we conclude that the ring-enlargement reaction occurs via a pentavalent silicon-bridging radical transition state (or intermediate). This is the first experimental evidence for such a pentavalent silicon radical, which has been previously postulated to understand radical reactions of organic silicon compounds.

Introduction

There has been growing interest in radical reactions of silicon-containing compounds because of their versatility in organic synthesis.[1] Recently, we developed a regio- and stereoselective method for introducing the 1-hydroxyethyl, 2-hydroxyethyl, and vinyl groups at the position β to a hydroxyl group in halohydrins or α-phenylselenoalkanols using an intramolecular radical cyclization reaction with a dimethyl- or diphenylvinylsilyl group as a temporary connecting radical-acceptor tether (Scheme 1).[2,3] Thus, the selective introduction of both 1-hydroxyethyl and 2-hydroxyethyl groups can be achieved, depending on the concentration of Bu_3SnH in the reaction system, via a 5-*exo*-cyclization intermediate **E** or a 6-*endo*-cyclization intermediate **F**, respectively, after oxidative ring-cleavage by treating the cyclization products under Tamao oxidation conditions,[4] as shown in Scheme 1.[2a,b] A vinyl group can also be introduced by photoirradiating the vinylsilyl ether **A** in the presence of $(Bu_3Sn)_2$, and then treating the resulting atom-transfer 5-*exo*-cyclization product **I** with fluoride ion.[3] We also investigated the radical cyclization mechanism by deuterium-labeling experiments with Bu_3SnD.[2a,b] The results suggested that the kinetically favored 5-*exo*-cyclized radical **C**, formed from radical **B**, was trapped when the concentration of Bu_3SnH was high enough to give **E**. At lower concentrations of Bu_3SnH and higher reaction temperatures, radical **C** rearranged into the more stable ring-enlarged 4-oxa-3-silacyclohexyl radical **D**, which was then trapped with Bu_3SnH to give **F**. This radical reaction with a vinylsilyl tether has been successfully applied to the synthesis of biologically important branched nucleosides[2b−d] and *C*-glycosides.[2e]

As far as we know, this is the first such ring-enlarging rearrangement reaction of β-silyl radicals reported in the literature. This rearrangement can also be considered a 1,2-silicon shift from carbon to carbon in β-silyl carbon-centered radicals. There is no precedent for this type of silicon shift,[5,6] although 1,2-silicon shift reactions of nitrogen-,[7] oxygen-,[8] and

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(2) (a) Shuto, S.; Kanazaki, M.; Ichikawa, S.; Matsuda, A. *J. Org. Chem.*, **1997**, *62*, 5676−5677. (b) Shuto, S.; Kanazaki, M.; Ichikawa, S.; Minakawa, N.; Matsuda, A. *J. Org. Chem.*, **1998**, *63*, 746−754. (c) Ueno, Y.; Nagasawa, Y.; Sugimoto, I.; Kojima, N.; Kanazaki, M.; Shuto, S.; Matsuda, A. *J. Org. Chem*. **1998**, *63*, 1660−1667. (d) Sugimoto, I.; Shuto, S.; Mori, S.; Shigeta, S.; Matsuda, A. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 385−388. (e) Yahiro, Y.; Ichikawa, S.; Shuto, S.; Matsuda, A. *Tetrahedron Lett*. **1999**, *40*, 5527−5531.

(3) Sugimoto, I.; Shuto, S.; Matsuda, A. *J. Org. Chem*. **1999**, *64*, 7153−7157.

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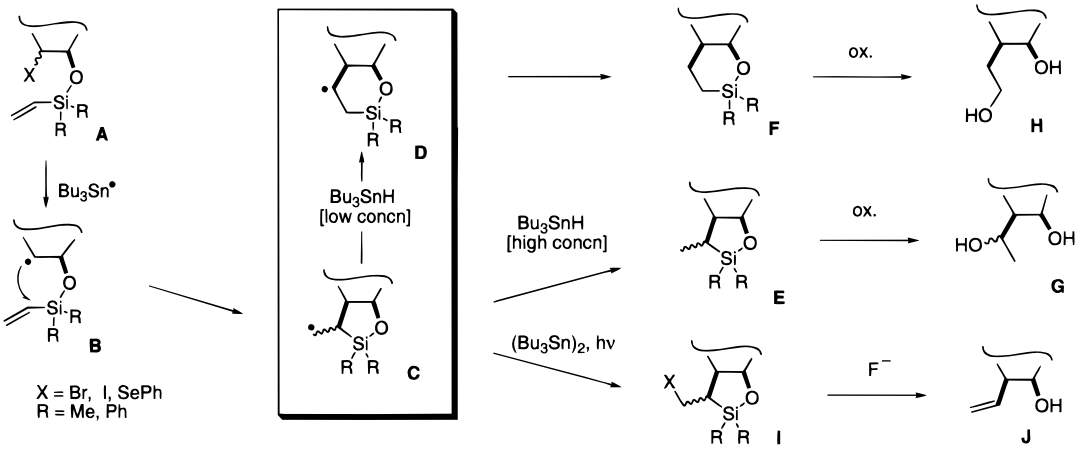
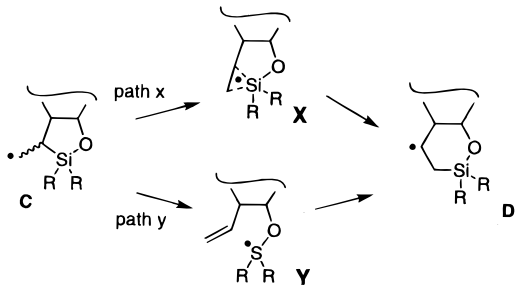
Scheme 1



Scheme 2

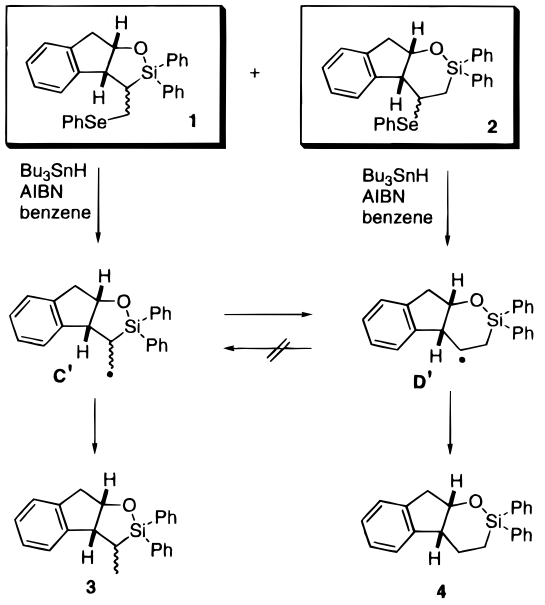


sulfur-centered[9] radicals have been reported. However, the reaction mechanism is still unclear.

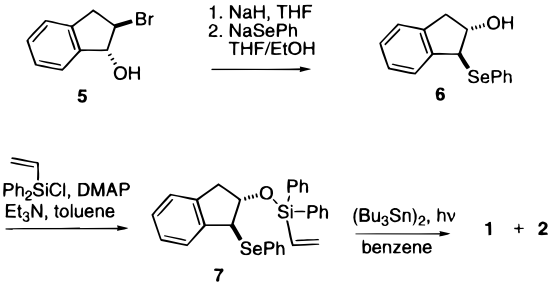
Two possible pathways for the ring-enlargement reaction (Scheme 2) may be postulated: one via a transition state (or intermediate) **X** in which the silicon atom expands its valence shell to five (path x), the other via β-elimination to give the ring-opened silyl radical **Y** (path y), which subsequently undergoes 6-*endo*-cyclization to give **D**. The mechanism of this radical rearrangement reaction, which may be related mechanistically to the above known radical 1,2-silicon shifts, has been of great interest to us. In this report, we describe the results of our mechanistic study demonstrating that the ring-enlargement reaction occurs via a pentavalent silicon-bridging radical transition state (or intermediate) **X**.

Reactions with the Radical Precursors for (3-Oxa-2-silacyclopentyl)methyl and 4-Oxa-3-silacyclohexyl Radicals. First, we investigated the reaction of **1** and **2**, which are precursors for a (3-oxa-2-silacyclopentyl)methyl radical **C′** and a 4-oxa-3-silacyclohexyl radical **D′**, respectively (Scheme 3).[10] Such experiments would clearly confirm that 4-oxa-3-silacyclohexyl radical **D** is produced from (3-oxa-2-silacyclopentyl)methyl radical **C** via a novel ring-enlargement reaction (Scheme 1), as previously suggested by deuterium-labeling experiments,[2a,b] and also would clarify whether the corresponding reverse reaction, i.e., ring-contraction of radical **D** into radical **C**, actually occurs.

Scheme 3



Scheme 4



The precursors **1** and **2** were prepared by the atom-transfer radical cyclization reaction[11] of the vinylsilyl ether **7** as shown in Scheme 4. (±)-1-Phenylseleno-2-indanol (**6**), prepared from (±)-*trans*-2-bromo-1-indanol (**5**) via indanol 1,2-epoxide, was treated with diphenylvinylchlorosilane, DMAP, and Et_3N in

(5) A gas phase 1,2-shift of a trimethylsilyl group from carbon to carbon in an aromatic β-silyl biradical at >450 °C has been reported: Johnson, G. C.; Stofko, J. J., Jr.; Lockhart, T. P.; Brown, D. W.; Bergman, R. G. *J. Org. Chem.* **1979**, *44*, 4215−4218.

(6) A gas-phase 1,2-shift of a trimethylsilyl group from silicon to carbon radical is observed at 600 °C; however, no 1,2-shift occurs when the same radical is generated in solution: Sakurai, H.; Kishida, T.; Hosomi, A.; Kumada, M. *J. Organomet. Chem.* **1967**, *8*, 65−68.

(7) (a) West, R.; Boudjouk, P. *J. Am. Chem. Soc.* **1973**, *95*, 3938−3987. (b) Harris, J. M.; MacInnes, I.; Walton, J. C.; Maillard, B. *J. Organomet. Chem.* **1991**, *403*, C25−28. (c) Harris, J. M.; Walton, J. C.; Maillard, B.; Grelier, S.; Picard, J.-P. *J. Chem. Soc., Perkin Trans. 2* **1993**, 2119−2123. (d) Roberts, B. P.; Vazquez-Persaud, A. R. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1087−1095.

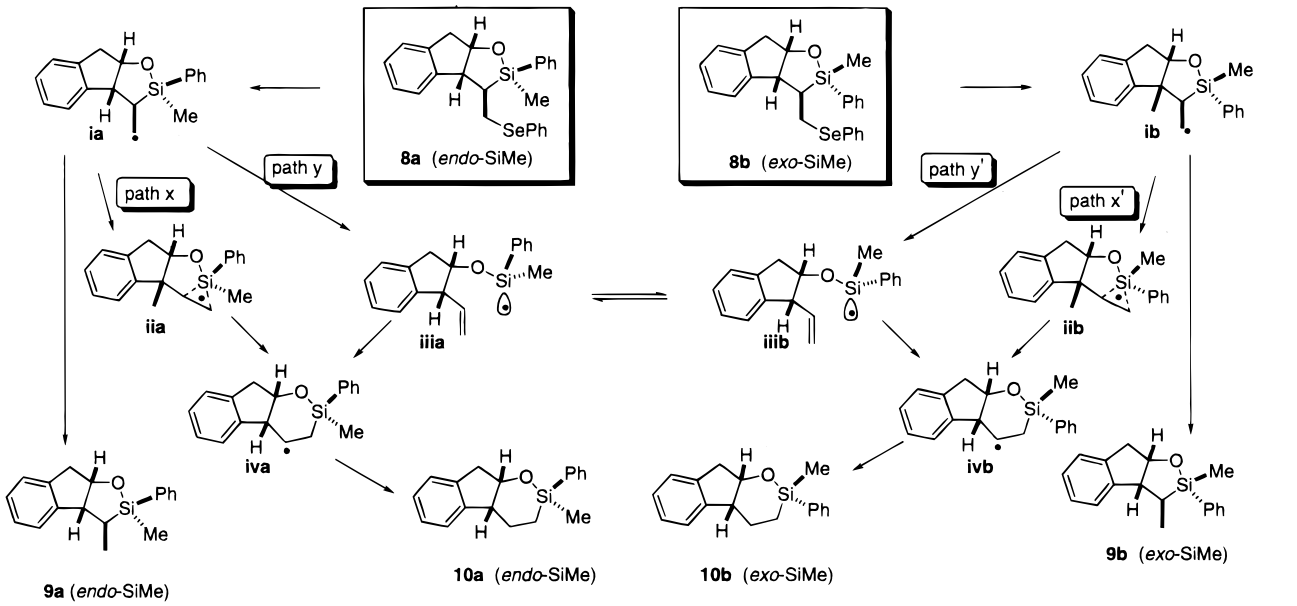
(8) Tsai, Y.-M.; Cherng, C.-D. *Tetrahedron Lett.* **1991**, *32*, 3515−3518.

(9) Pitt, C. G.; Fowler, M. S. *J. Am. Chem. Soc.* **1968**, *90*, 1928−1930.

(10) Radical reactions of **1** and **2** have been described in a communication: Sugimoto, I.; Shuto, S.; Matsuda, A. *Synlett*. **1999**, 1766−1768.

(11) Curran, D. P.; Chang, C. *J. Org. Chem.* **1986**, *54*, 3140−3157.

Scheme 5

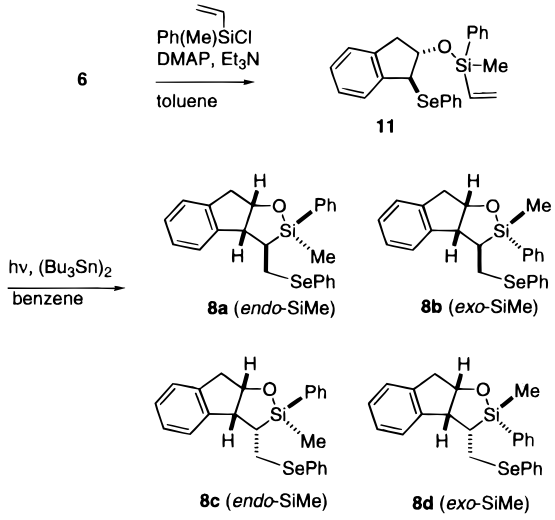


toluene to give vinylsilyl ether **7**. Photoirradiation of a solution of **7** and $(Bu_3Sn)_2$ (0.01 equiv) in benzene with a high-pressure mercury lamp at room temperature under an argon atmosphere gave the expected atom-transfer 5-*exo*-cyclization product **1** in 59% yield. When the photoreaction was carried out at 80 °C, the ring-enlarged atom-transfer product **2** was obtained in 21% yield along with **1** in 36% yield.

A solution of 1.2 equiv of Bu_3SnH and 0.6 equiv of AIBN in benzene was added slowly over 4 h, using a syringe-pump, to a solution of **1** in refluxing benzene. The reaction gave the ring-enlargement product **4** as a major product along with the directly reduced product **3** (yield 70%, **3**:**4** = 9:91, based on its ^{1}H NMR spectrum), after purification by silica gel column chromatography. On the other hand, when **2** was treated under conditions identical with those for **1**, only the direct reduction of radical **D′** occurred affording **4** in 72% yield as the sole product; the corresponding ring-contracted product **3** was not obtained. These results clearly demonstrate that the (3-oxa-2-silacyclopentyl)methyl radical **C′** readily rearranged into the ring-enlarged 4-oxa-3-silacyclohexyl radical **D′** (Scheme 3), which is consistent with the previous results suggested by deuterium-labeling experiments.[2a,b] The results also suggest that the corresponding reverse reaction, i.e., ring-contraction of **D′** into **C′**, did not occur or was very slow.

The Configuration at the Silicon Atom during the Radical Ring-Enlargement Reaction. We next investigated the reaction mechanism of the radical rearrangement by using **8a** and **8b** as substrates. Both have a methyl and a phenyl group on the silicon atom, and are therefore stereoisomers. The configurations at the silicon atom in the ring-enlargement reaction products derived from the radical reactions of **8a** and **8b** should be dominated by the reaction mechanism shown in Scheme 5. Treatment of **8a** (*endo*-SiMe isomer) or **8b** (*exo*-SiMe isomer) with Bu_3SnH/AIBN would produce radical **ia** or **ib**, respectively. Direct reduction of **ia** or **ib** by Bu_3SnH gives **9a** or **9b**, respectively. If the radical ring-enlargement reaction of **ia** or **ib** proceeds via ring-opened silyl radical **iiia** or **iiib** (path y or y′ in Scheme 5), isomerization at the silicon atom of **iiia** or **iiib** should occur, at least to some extent, before re-cyclization to give a mixture of 6-*endo*-cyclized radicals **iva** and **ivb**. Consequently, a mixture of **10a** (*endo*-SiMe product) and **10b** (*exo*-SiMe product), which are stereoisomers at the silicon atom, would be obtained.

Scheme 6



Alternatively, the configuration at the silicon atom of **8a** or **8b** should be retained during the rearrangement process to give the ring enlargement product **10a** or **10b**, respectively, when the radical rearrangement proceeds via the pentavalent silicon-bridging radial transition state (or intermediate) **iia** or **iib** (path x or x′ in Scheme 5).

The substrates **8a** and **8b** were synthesized by a method similar to the one for the preparation of **1** and **2** (Scheme 6). (±)-1-Phenylseleno-2-indanol (**6**) was treated with methylphenylvinylchlorosilane, DMAP, and Et_3N in toluene to give vinylsilyl ether **11**, which was an inseparable mixture of stereoisomers at the silicon atom. Photoreaction of **11** in the presence of $(Bu_3Sn)_2$ in benzene gave atom-transfer 5-*exo*-cyclization products as a mixture of four stereoisomers, **8a**, **8b**, **8c**, and **8d**, in 56% yield (**8a**:**8b**:**8c**:**8d** = 48:35:9:8). These products were successfully separated by HPLC, and their stereochemistries were confirmed by NOE experiments (Figure 1).[12] The major products **8a** and **8b** were used in the subsequent experiments.

(12) When the methyl protons and the methyne proton adjacent to the silicon were irradiated, NOEs as shown in Figure 1 were observed.

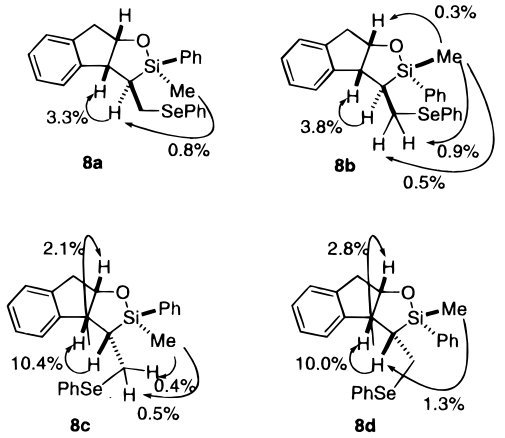


Figure 1.

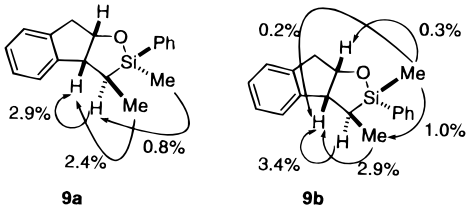


Figure 2.

The radical reaction of **8a** was next carried out. A benzene solution of Bu_3SnH (1.5 equiv) and AIBN (0.6 equiv) was added slowly over 4 h to a refluxing solution of **8a** (0.01 M) in benzene. A mixture of products **9a**, **9b**, **10a**, and **10b** was obtained in 44% yield (**9a**:**9b**:**10a**:**10b** = 22:13:63:2), after purification by silica gel column chromatography. Each of these was isolated in pure form by HPLC, and their stereochemistries were determined by their ^{1}H NMR spectra and NOE experiments (Figure 2).[13] Throughout this experiment, we noticed that isomerization of the radical reaction products at the silicon atom occurred during silica gel column chromatography.[14,15] Therefore, we analyzed the reaction products directly by ^{1}H NMR without purification, after the reactions of **8a** and **8b** were carried out under conditions identical with those described above. The SiMe signals in the ^{1}H NMR spectra (−0.1− 0.5 ppm) of the products derived from the radical reaction of **8a** and **8b** are shown in Figures 3B and 3C, and the SiMe signals of a mixture of **9a**, **9b**, **10a**, and **10b**, which are observed at −0.02, 0.47, 0.18, and 0.43 ppm, respectively, are also shown in Figure 3A as a reference. When **8a**, which has an *endo*-Me group at the silicon, was treated with $BuSn_3H$/AIBN in benzene, the SiMe signals of the products were observed at 0.18 and −0.02 ppm, which were identical with those of the *endo*-Me groups of the ring-enlargement product **10a** and the directly reduced product

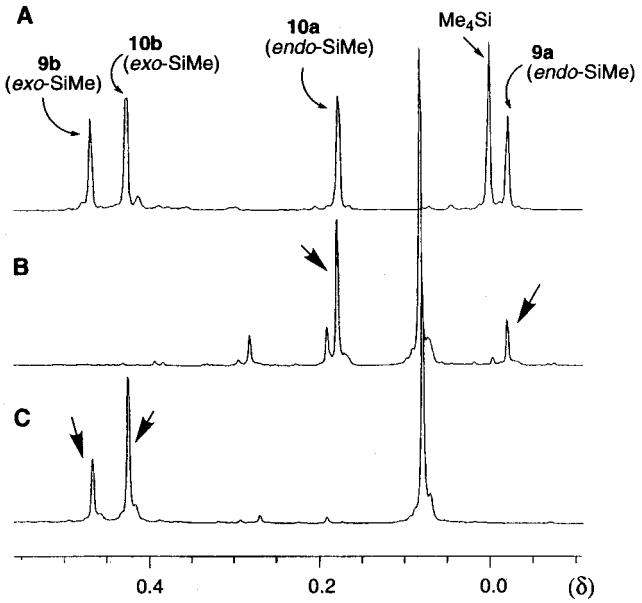


Figure 3. Silyl methyl signals in the ^{1}H NMR spectrum ($CDCl_3$, 500 MHz): a mixture of **9a**, **9b**, **10a**, and **10b** (A); products of the radical reaction of **9a** (B); and products of the radical reaction of **9b** (C).

9a, respectively, while signals corresponding to the *exo*-SiMe products **9b** and **10a** were not detected at all (Figure 3B). Similarly, the radical reaction of *exo*-SiMe substrate **8b** gave the corresponding *exo*-SiMe products **9b** and **10b**, as shown in Figure 3C. These results demonstrate that the configuration at the silicon atom is retained during the ring-enlargement reaction and that a ring-opened silicon radical like **iiia** or **iiib** is not produced. The most likely explanation for the configuration-retaining reaction pathway of the radical ring-enlargement is that it proceeds via pentavalent silicon-bridging radical transition states (or intermediates) **iia** and **iib** (paths x and x′).

Elucidation of the Mechanism with a Deuterium-Labeled Substrate. We designed a deuterium-labeled substrate **12D** to further elucidate the reaction pathway of the ring-enlargement reaction. Our strategy is summarized in Scheme 7. Reaction of **12D** with Bu_3SnH/AIBN would generate the *exo*-cyclized radical **vi** via the allylic radical **v**. If the ring-enlargement reaction of **vi** proceeds via a pentavalent silicon-bridging radical transition state (or intermediate) **vii**, it would produce the ring-enlargement product **13D**, with the deuterium label at the terminal methylene carbon (path x). On the other hand, if β-elimination of **vi** occurs, a mixture of ring-enlargement products **13D** and **14D**, the latter of which is deuterium labeled at the methylene adjacent to the silicon, should be obtained, since the resulting silyl radical **viii** can cyclize to both the labeled and unlabeled terminal methylenes which are regiochemically equivalent.

The synthesis of the deuterium-labeled substrate **12D** as well as unlabeled **12** is shown in Scheme 8. An α,β-unsaturated ethyl ester **16**, prepared from commercially available ethyl fumarate **15**, was reduced with $LiAl(OMe)_3D$[16] or DIBAL to give deuterium-labeled alcohol **17D** or unlabeled **17**, respectively. Successive treatment of **17** with PhSeCN/Bu_3P[17] and TBAF in THF gave **18**, which was further treated with diphenylvinylchlorosilane/DMAP/Et_3N in toluene to afford the substrate **12** for the radical reaction. Similarly, the deuterium-labeled substrate **12D** was prepared from **17D**.

(13) Although the stereochemistries of **9a** and **9b** were confirmed by the NOE data as shown in Figure 2, no NOE was observed when the silyl methyl protons of **10a** or **10b** were irradiated. Therefore, the configurations at the silicon of **10a** and **10b** were confirmed based on chemical shifts of the methyl groups attached to the silicon of the compounds having benzo-[*f*]-2-oxa-3-silabicyclo[3.3.0]octane or benzo[*g*]-2-oxa-3-silabicyclo[4.3.0]-nonane structure synthesized in this study: the signals of the *exo*-SiMe protons in **1b**, **1d**, **9b**, and **10b** (0.43−0.57 ppm) were observed at lower fields compared with those of the *endo*-SiMe protons in **1a**, **1c**, **9a**, and **10a** (−0.02−0.18 ppm) presumably due to deshielding by the benzene ring condensed with the 2-oxa-3-silabicyclo[3.3.0]octane or 2-oxa-3-silabicyclo-[4.3.0]nonane ring (see Figure 2).

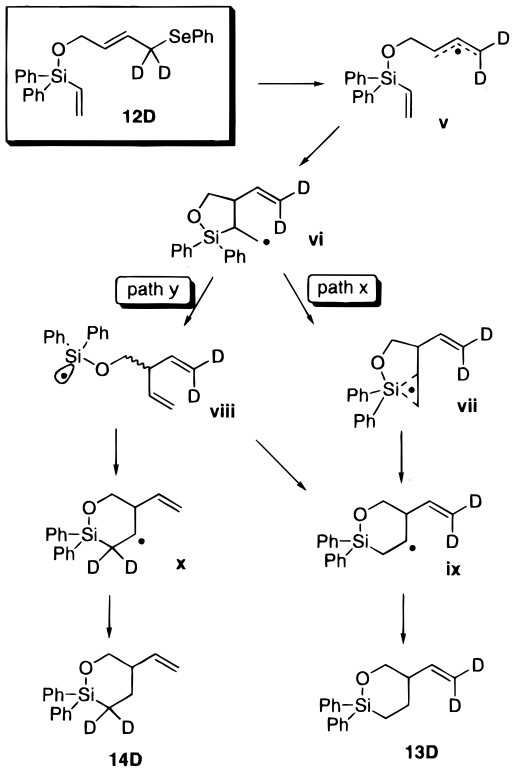
(14) It is known that inversion of configuration at a silicon atom in organo-silicon compounds readily occurs via pseudorotation: Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17−31.

(15) For example, when pure **9a** was passed through a silica gel column with a solvent system of Et_2O−hexane, a mixture of **9a** and **9b** (ratio, ca. 1:1) was obtained.

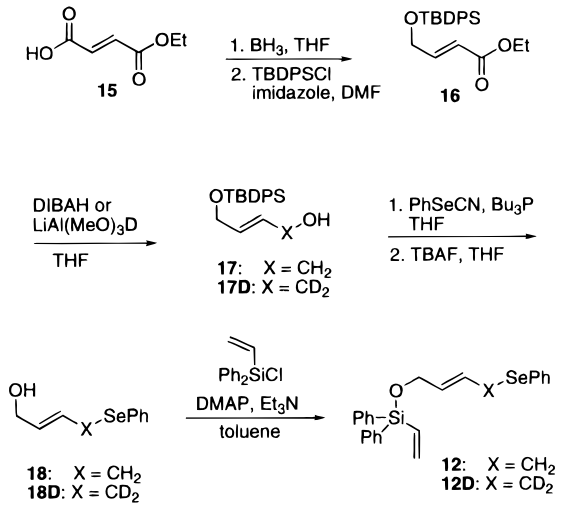
(16) Brown H, C.; Weissman, P. M. *J. Am. Chem. Soc.* **1965**, *87*, 5614−5620.

(17) Grieco, P. A.; Gilman, S.; Nishizawa, M. *J. Org. Chem.* **1976**, *41*, 1485−1486.

Scheme 7



Scheme 8



First, the radical reaction of **12** was performed under thermodynamic conditions; Bu_3SnH/AIBN was added slowly over 4 h to a refluxing solution of **12** in benzene. The reaction mixture was subsequently treated under Tamao oxidation conditions, and the resulting 3-hydroxymethyl-4-pentenol was isolated as the corresponding dibenzoate **20** by treating it with BzCl/pyridine (Scheme 9). A similar reaction of **12** with Bu_3SnD instead of Bu_3SnH gave the corresponding deuterium-labeled product **21**, in which a deuterium was incorporated exclusively at the 2-position based on the ^1H NMR spectrum. These results confirmed that the radical ring-enlargement reaction occurred in this system as expected. Therefore, we next investigated the radical reaction of deuterium-labeled substrate **12D**. Thus, **12D** was subjected to the above-mentioned radical reaction with Bu_3SnH/AIBN and the subsequent successive two-step treatments. The product, after purification by HPLC, was analyzed by ^1H NMR, and the spectrum is shown with that of unlabeled

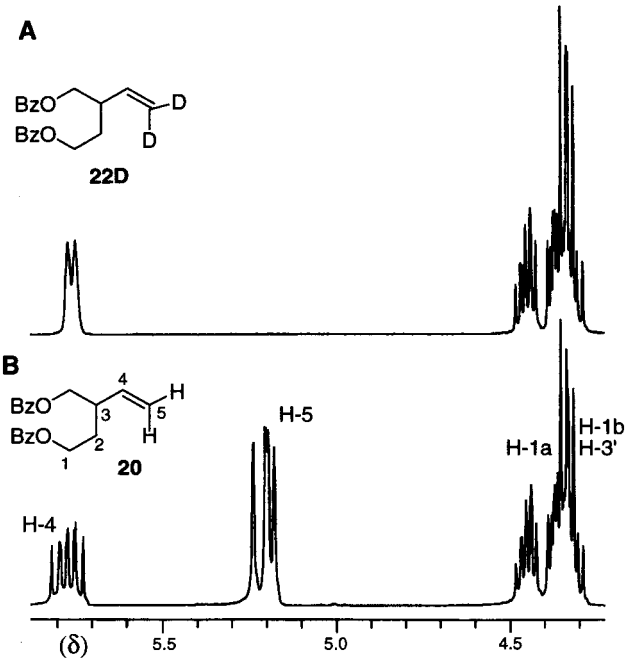
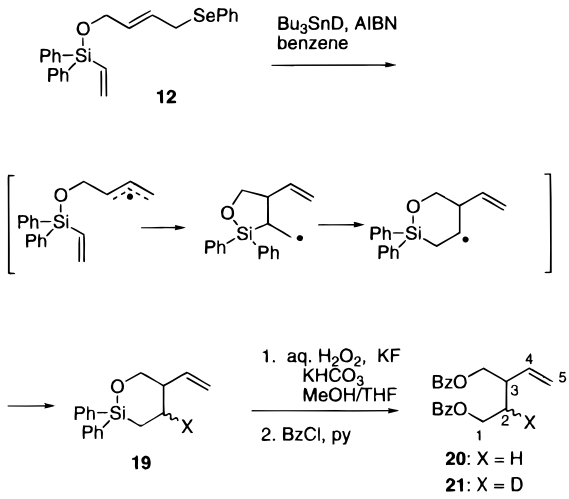


Figure 4. ^1H NMR spectra of **22D** (A) and **20** (B) ($CDCl_3$, 500 MHz).

Scheme 9



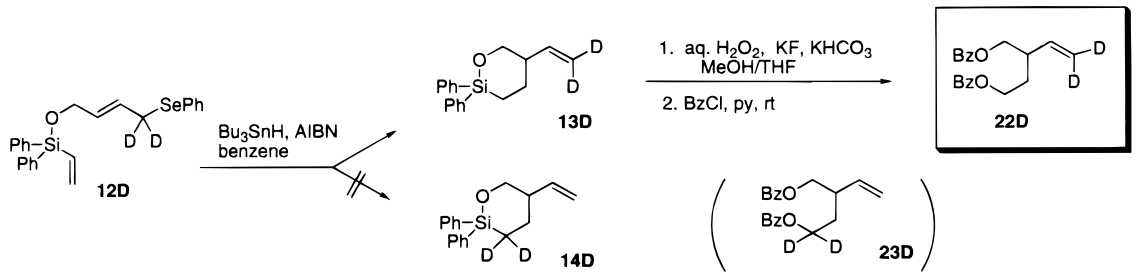
20 as a reference in Figure 4. The spectrum clearly shows that the protons at the terminal methylene in product **22D** were exclusively replaced by deuteriums and that the regioisomerically labeled **23D** was not detected at all (Scheme 10). Accordingly, these results suggest that the ring-enlargement reaction of radical **vi** is not likely to occur via a ring-opened silicon radical **viii** but rather via the pentavalent silicon-bridging radical transition state (or intermediate) **vii** in Scheme 7.[18]

Discussion

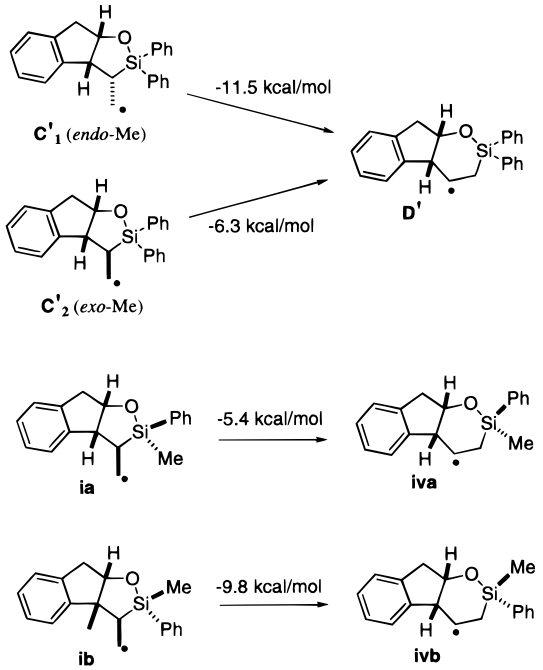
We have shown that (3-oxa-2-silacyclopentyl)methyl radicals rearrange into ring-enlarged 4-oxa-3-silacyclohexyl radicals with various substrates, i.e., indanols,[2a] nucleosides,[2b,c] hexopyranoses,[2e] and a 2-butenol derivative used in this study. These results suggest that this rearrangement reaction is general in (3-oxa-2-silacyclopentyl)methyl radicals.

(18) The secondary deuterium effect in the cyclization of radical **viii** should be considered. It is known that addition of alkyl radicals to an alkene is slightly facilitated when the terminal CH_2═ of the alkene is replaced by CD_2═: Feld, A.; Stefani, A. P.; Szwarc, M. *J. Am. Chem. Soc.* **1962**, *84*, 4451−4453.

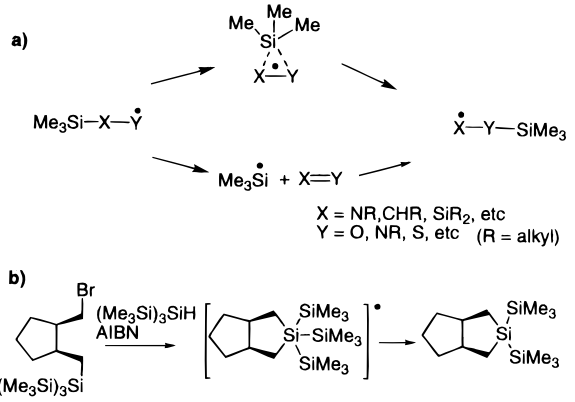
Scheme 10



Scheme 11



Scheme 12



The rearrangement reaction appears to be irreversible based on the study with **2**, which is a precursor for a 4-oxa-3-silacyclohexyl radical. We undertook a theoretical investigation of the (3-oxa-2-silacyclopentyl)methyl radical **C′** and the ring-enlarged 4-oxa-3-silacyclohexyl radical **D′** by computational methods to compare their stabilities. Geometry optimizations and single-point energy calculations were performed using PM3 and ab initio calculations at the UHF/STO-3G level, respectively. Two stereoisomers, i.e., *endo*-Me radical **C′$_1$** and *exo*-Me radical **C′$_2$**, should be considered for (3-oxa-2-silacyclopentyl)-methyl radical **C′**. The ring-enlarged radical **D′** is 11.5 and 6.3 kcal/mol more stable than **C′$_1$** and **C′$_2$**, respectively, based on the heat of formation (Scheme 11).[19] Similar results were obtained from the calculations on radicals **ia**, **ib**, **iva**, and **ivb** with an asymmetric silicon center (Scheme 11). These computational results clearly support the experimental data indicating that the ring-enlargement rearrangement is irreversible.

The reactions with substrates **8a** and **8b**, which have an asymmetric center at the silicon atom, showed that the configuration at the silicon atom is retained during the rearrangement reaction. This suggests that the radical ring-enlargement proceeds via pentavalent silicon-bridging radical transition states (or intermediates) **iia** and **iib** (paths x and x′), without producing a ring-opened silicon radical like **iiia** or **iiib**. The rates of inversion at the silicon center of asymmetric silyl radicals should be considered, since asymmetric silyl radicals have been reported to be configurationally stable compared with asymmetric carbon radicals.[20] The rates of inversion at the silicon center of asymmetric silyl radicals were determined by Ingold and co-workers to be $(3-12) \times 10^9$ s^{-1} at temperatures from 0 to 80 °C.[20e] On the other hand, 6-*endo*-cyclizations of pent-4-enylsilyl radicals have been studied.[21] Ingold and co-workers observed that the rate constant for 6-*endo*-cyclization of 3-dimethylpent-4-enylsilyl radical was $<10^9$ s^{-1} at −100 °C and $>10^7$ s^{-1} at room temperature.[21a] Considering these results, isomerization at the silicon atom should occur, at least to some extent, if the ring-opened silicon radical **iiia** or **iiib** is involved in the reaction process, since 6-*endo*-cyclization of pent-4-enylsilyl radicals has been shown to be slower than isomerization at silicon.

The results with the asymmetric silicon substrates **8a** and **8b** were further confirmed by the study with deuterium-labeled substrate **12D**. Therefore, we conclude that the ring-enlargement reaction is an irreversible process that occurs via a transition state (or intermediate) **X** in which the silicon atom expands its valence shell to five (path x in Scheme 1).

1,2-Silicon shifts of nitrogen-,[7] oxygen-,[8] and sulfer-centered[9] radicals have been reported. It has been postulated that these rearrangements can occur by a dissociative mechanism or by an intramolecular process via a pentavalent silicon-bridging radical transition state (or an intermediate), similar to the one in this study, as shown in Scheme 12a. Harris et al.[7b,c] and Roberts et al.[7d] investigated the reaction mechanism of 1,2-

(19) Heat of formation: **C′$_1$**, −1232.0042536 hartrees; **C′$_2$**, −1232.0125841 hartrees; **D′**, −1232.0226381 hartrees; **ia**, −1043.848567 hartrees; **iva**, −1043.857157 hartrees; **ib**, −1043.842205 hartrees; **ivb**, −1043.857857 hartrees (1 hartree = 627.51 kcal/mol).

(20) (a) Sakurai, H.; Murakami, M.; Kumada, M. *J. Am. Chem. Soc.* **1969**, *91*, 519−520. (b) Brook, A. G.; Duff. J. M. *J. Am. Chem. Soc.* **1969**, *91*, 2118−2119. (c) Sommer, L. H.; Ulland, L. A. *J. Org. Chem.* **1972**, *37*, 3878−3881. (d) Sakurai, H.; Murakami, M.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3384−3387. (e) Chatgilialoglu, C.; Ingold, K. U.; Scainao, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5123−5127.

(21) (a) Chatgilialoglu, C.; Woynar, H.; Ingold, K. U.; Davies, A. G. *J. Chem. Soc., Perkin Trans. 2* **1983**, 555−561. (b) Barton, T. J.; Revis, *J. Am. Chem. Soc.* **1984**, *106*, 3802−3805. (c) A. Sarasa, J. P.; Igual, J.; Poblet, A. M. *J. Chem. Soc., Parkin Trans. 2* **1986**, 861−865. (d) Cai, Y.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 1* **1998**, 467−475.

silicon shifts of silylmethylaminyl radicals by EPR spectroscopy. Both groups independently suggested that the silicon shifts may occur via a pentavalent silicon transition state, since free TMS radicals, which should be produced in the dissociative pathway, were not detected during the silicon shift reactions by EPR.

On the other hand, novel radical substitution reactions at a silicon atom have been reported.[22] Giese and co-workers proposed a pentavalent silicon-bridging transition state (or intermediate) to interpret this kind of radical substitution reaction (Scheme 12b).[22a]

While the structure of the pentavalent silicon radicals is yet unclear, Schiesser and Styles recently reported *ab initio* molecular orbital calculations of pentavalent silicon radical transition states in 1,2-silicon-shift reactions of carbon-, nitrogen-, and oxygen-centered radicals.[23] The calculations suggested that the transition state adopted tetrahedral geometry at the silicon and that the structure appeared to resemble coordinated alkenes, which is consistent with a front-side mechanism for the silicon shifts. Due to the transition state predicted, configuration at the silicon should be retained during the shift when the silicon is an asymmetric center. This may be in agreement with our present experimental results with **8a** and **8b** indicating that the configuration was retained during the rearrangement.

As described above, the reaction mechanisms of these radical rearrangements of organic silicon compounds can be interpreted by postulating a pentavalent silicon radical transition state (or intermediate). This study should be very important, since it presents the first experimental evidence for the pentavalent silicon transition state (or intermediate) in radical reactions of organic silicon compounds.

Experimental Section

Melting points are uncorrected. NMR spectra were recorded at 270, 400, or 500 MHz (^{1}H) and at 100 or 125 MHz (^{13}C), and are reported in ppm downfield from TMS. Mass spectra were obtained by electron ionization (EI) or the fast atom bombardment (FAB) method. Thin-layer chromatography was performed on Merck coated plate $60F_{254}$. Silica gel chromatography was performed with Merck silica gel 5715. Reactions were carried our under an argon atmosphere. HPLC was performed with YMC-Pack SIL-06-s-5 (analytical, 4.6 × 250 mm; preparative, 20 × 250 mm).

(±)-*trans*-1-Phenylseleno-2-indanol (6). A mixture of (±)-*trans*-2-bromoindanol (**5**, 1.07 g, 5.02 mmol) and NaH (0.24 g, 6.0 mmol) in THF (25 mL) was stirred at room temperature for 2 h. A solution of NaSePh, prepared from $(PhSe)_2$ (3.12 g, 10.0 mmol), $NaBH_4$ (1.14 g, 30.1 mmol), and EtOH (25 mL),[24] was added, and the resulting mixture was stirred at room temperature for 10 min. Et_2O and saturated aqueous NH_4Cl were added, and the resulting mixture was partitioned. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated. The residue was purified by silica gel column chromatography (AcOEt/hexane, 1:4) to give **6** (1.42 g, 98%) as an oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53−7.21 (m, 9 H), 4.66 (d, 1 H, J = 1.7 Hz), 4.61−4.59 (m, 1 H), 3.30 (dd, 1 H, J = 16.6, 5.6 Hz), 2.82 (dd, 1 H, J = 16.6, 2.1 Hz), 1.85 (d, 1 H, J = 5.9 Hz);^{13}C NMR (125 MHz, $CDCl_3$) δ 140.7, 140.6, 134.2, 129.4, 129.1, 128.0, 127.7, 127.1, 125.7, 125.3, 79.0, 53.9, 40.0; EI HRMS calcd for $C_{15}H_{14}OSe$ 290.0209, found 290.0195 (M^+). Anal. Calcd for $C_{15}H_{14}OSe$: C, 62.29; H, 4.88. Found: C, 62.18; H, 4.92.

(±)-*trans*-2-*O*-Diphenylvinylsilyl-1-phenylseleno-2-indanol (7). A solution of **6** (1.30 g, 4.49 mmol), Et_3N (0.95 mL, 6.8 mmol), DMAP (55 mg, 0.45 mmol), and diphenylvinylchlorosilane (1.3 mL, 7.1 mmol) in toluene (20 mL) was stirred at room temperature for 5 min. Et_2O and water were added, and the resulting mixture was partitioned. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated. The residue was purified by silica gel column chromatography (Et_2O/hexane, 1:50) to give **7** (2.20 g, 98%) as an oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49−7.14 (m, 19 H), 6.31 (dd, 1 H, J = 20.1, 14.9 Hz), 6.18 (dd, 1 H, J = 15.0, 3.8 Hz), 5.76 (dd, 1 H, J = 20.3, 3.9 Hz), 4.79 (m, 1 H), 4.76 (s, 1 H), 3.13 (dd, 1 H, J = 16.3, 5.3 Hz), 2.87 (dd, 1 H, J = 16.3, 1.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.3, 141.2, 137.3, 135.0, 134.7, 134.3, 134.2, 133.6, 130.0, 129.5, 128.9, 127.8, 127.7, 127.6, 126.8, 125.6, 125.0, 80.3, 54.6, 40.7; EI HRMS calcd for $C_{29}H_{26}OSeSi$ 498.0916, found 498.0912 (M^+). Anal. Calcd for $C_{29}H_{26}OSeSi$: C, 70.00; H, 5.27. Found: C, 70.03; H, 5.38.

Synthesis of Radical Precursor 1. A stirred solution of **7** (9.60 g, 19.3 mmol) and $(Bu_3Sn)_2$ (0.98 mL, 1.9 mmol) in benzene (100 mL) was irradiated with a high-pressure mercury lamp (300 W) at room temperature for 25 h. The solvent was evaporated, and the residue was purified by silica gel column chromatography (Et_2O/hexane, 1:20) to give **1** (5.66 g, 59%) as an oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69−7.00 (m, 19 H), 5.24 (dt, 0.84 H, J = 5.6, 2.4 Hz), 4.96 (n, 0.16 H), 3.99 (dd, 0.16 H, J = 7.7, 4.6 Hz), 3.87 (dd, 0.84 H, J = 4.6, 4.2 Hz), 3.54 (dd, 0.16 H, J = 11.7, 9.0 Hz), 3.31−2.97 (m, 3.84 H), 2.57 (q, 0.16 H, J = 8.7 Hz), 2.19 (ddd, 0.84 H, J = 10.5, 6.6, 2.6 Hz); EI HRMS calcd for $C_{29}H_{26}OSeSi$ 498.0916, found 498.0910 (M^+). Anal. Calcd for $C_{29}H_{26}OSeSi$: C, 70.00; H, 5.27. Found: C, 70.18; H, 5.43.

Synthesis of Radical Precursor 2. A stirred solution of **7** (1.00 g, 2.01 mmol) and $(Bu_3Sn)_2$ (100 μL, 0.20 mmol) in benzene (20 mL) was irradiated with a high-pressure mercury lamp (300 W) at 80 °C for 25 h. The solvent was evaporated, and the residue was purified by silica gel column chromatography (Et_2O/hexane, 1:20) to give **2** (208 mg, 21%; along with **1**, 360 mg, 36%) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14−6.87 (m, 19 H), 5.11 (q, 0.4 H, J = 5.0), 4.86 (m, 0.6 H), 4.23 (dt, 0.6 H, J = 14.4, 2.9 Hz), 4.14 (ddd, 0.4 H, J = 9.0, 4.9, 4.2 Hz), 3.56 (br s, 0.6 H), 3.44 (dd, 0.4 H, J = 7.8, 5.4 Hz), 3.11−2.96 (m, 2 H), 1.79 (m, 1 H, J = 14.4 Hz), 1.51 (dd, 0.4 H, J = 15.1, 9.5 Hz), 1.59 (dd, 0.6 H, J = 14.4, 3.4 Hz); EI HRMS calcd for $C_{29}H_{26}OSeSi$ 498.0916, found 498.0898 (M^+).

Radical Reaction of 1. To a solution of **1** (100 mg, 0.20 mmol) in benzene (20 mL) at 80 °C was added a solution of Bu_3SnH (65 μL, 0.24 mmol) and AIBN (20 mg, 0.03 mmol) in benzene (5 mL) slowly over a 4 h period. The solvent was evaporated, and the residue was purified by silica gel column chromatography (Et_2O/hexane, 1:50) to give a mixture of **3** and **4** (49 mg, 70%, **3**:**4** = 9:91 based on its ^{1}H NMR) as an oil. From the mixture, **3** (33 mg, 47%) and **4** (3 mg, 4%) were obtained as oils in a pure form, respectively, by preparative HPLC separation (AcOEt/hexane, 1:30). **3**: ^{1}H NMR (400 MHz, CDCl) δ 7.64−7.11 (m, 14H), 5.26 (dt, 1 H, J = 6.1, 3.4 Hz), 3.38 (t, 1 H, J = 5.5 Hz), 3.27 (dd, 1 H, J = 16.6, 6.1 Hz), 3.17 (dd, 1 H, J = 16.6, 3.4 Hz), 1.96−1.89 (m, 1 H), 1.21 (d, 3 H, J = 7.8 Hz);^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 140.8, 134.7, 134.4, 134.1, 133.1, 129.9, 129.8, 127.8, 127.5, 127.1, 126.5, 125.1, 124.5, 82.6, 57.5, 41.3, 23.7, 15.8; EI HRMS calcd for $C_{23}H_{22}OSi$ 342.1440, found 342.1428 (M^+). Anal. Calcd for $C_{23}H_{22}OSi$: C, 80.65; H, 6.47. Found: C, 80.46; H, 6.60. **4**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.16 (m, 14 H), 5.00 (ddd, 1 H, J = 5.6, 4.2 Hz), 3.25−3.21 (m, 1 H), 3.17 (dd, 1 H, J = 15.9, 5.6 Hz), 3.08 (dd, 1 H, J = 16.1, 3.9 Hz), 2.36−2.18 (m, 2 H), 1.25 (ddd, 1 H, J = 14.9, 9.3, 4.6 Hz), 1.14 (ddd, 1 H, J = 14.9, 8.6, 4.4 Hz);^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 141.6, 135.8, 135.7, 134.2, 134.0, 129.8, 129.7, 127.9, 127.6, 126.6, 126.4, 125.0, 123.9, 77.6, 47.3, 41.6, 22.0, 6.9; EI HRMS calcd for $C_{23}H_{22}OSi$ 342.1440, found 342.1419 (M^+). Anal. Calcd for $C_{23}H_{22}OSi$: C, 80.65; H, 6.47. Found: C, 80.64; H, 6.59.

Radical Reaction of 2. Radical precursor **2** (100 mg, 0.20 mmol) was treated as described above for the reaction of **1** to give **4** (49 mg, 72%), after silica gel column chromatography (Et_2O/hexane, 1:50).

(±)-*trans*-2-*O*-(Methylphenylvinylsily)-1-phenylseleno-2-indanol (11). Compound **11** (1.84 g, 89%) was obtained as an oil from **6** (1.37 g, 4.74 mmol) as described above for the synthesis of **7**, with methylphenylvinylchlorosilane (1.3 mL, 7.1 mmol) instead of diphenylvinylchlorosilane: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48−7.15 (m,

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(23) Schiesser, C. H.; Styles M. L. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2335−2340.

(24) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 2697−2699.

14 H), 6.15, 6.13 (each dd, each 0.5 H, J = 19.8, 14.8 Hz), 6.06, 6.05 (each dd, each 0.5 H, J = 14.8, 4.2 Hz), 5.77, 5.76 (each dd, each 0.5 H, J = 19.8, 4.2 Hz), 4.69−4.66 (m, 2 H), 3.21−3.16 (m, 1 H), 2.81 (d, 1 H, J = 16.5 Hz), 0.32, 0.31 (each s, each 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 140.9, 136.0, 135.4, 135.0, 134.61,134.56, 133.9, 129.7, 129.54, 129.52, 128.9, 127.71, 127.65, 127.59, 127.56, 126.7, 125.5, 124.9, 79.8, 54.7, 54.6, 40.69, 40.67, −3.06, −3.09; EI HRMS calcd for $C_{24}H_{24}OSeSi$ 436.0760, found 436.0756 (M^+).

Radical Reaction of 11 for the Preparation of 8a and 8b. A stirred solution of **11** (2.18 g, 5.01 mmol) and $(Bu_3Sn)_2$ (250 μL, 500 μmol) in benzene (25 mL) was irradiated with a high-pressure mercury lamp (300 W) at room temperature for 25 h. The solvent was evaporated, and the residue was purified by silica gel column chromatography (Et_2O/hexane, 1:20) to give a mixture of **8a**, **8b**, **8c**, and **8d** (1.23 g, 56%, **8a**:**8b**:**8c**:**8d** = 48:35:9:8, based on its ^{1}H NMR) as an oil. From a part of the oil (100 mg), **8a** (38 mg, 22%), **8b** (29 mg, 16%), **8c** (5 mg, 3%), and **8d** (4 mg, 2%) were obtained in a pure form, respectively, by preparative HPLC separation (AcOEt/hexane, 1:30).

[2*R,3*R**,4*R**,5*S**]-Indano[1,2-*d*]-2-methyl-2-phenyl-3-(phenylselenomethyl)-1,2-oxasilolane (8a)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58−7.00 (m, 14 H), 5.13 (ddd, 1 H, J = 5.3, 1.8 Hz), 3.85 (dd, 1 H, J = 4.4, 3.4 Hz), 3.22 (dd, 1 H, J = 16.6, 5.3 Hz), 3.14 (dd, 1 H, J = 16.6 Hz), 2.92 (dd, 1 H, J = 12.2, 6.8 Hz), 2.89 (dd, 1 H, 12.2, 10.7 Hz), 1.82 (ddd, 1 H, J = 10.3, 6.8, 3.0 Hz), 0.00 (s, 3 H); NOE ($CDCl_3$, 400 MHz) irradiated Si−Me, observed H-3 (0.8%); irradiated H-3, observed H-4 (3.3%); the assignments were in agreement with the H−H COSY spectrum; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 141.2, 134.4, 133.9, 133.1, 130.1, 130.0, 129.0, 128.0, 127.1, 126.9, 126.6, 125.1, 124.3, 82.1, 55.0, 41.5, 31.1, 30.4, −1.1; EI HRMS calcd for $C_{24}H_{24}$-OSeSi 436.0760, found 436.0766 (M^+). Anal. Calcd for $C_{24}H_{24}OSeSi$: C, 66.19; H, 5.55. Ffound: C, 66.02; H, 5.64.

[2*S,3*R**,4*R**,5*S**]-Indano[1,2-*d*]-2-methyl-2-phenyl-3-(phenylselenomethyl)-1,2-oxasilolane (8b)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (m, 14 H), 5.05 (ddd, 1 H, J = 5.0, 1.7 Hz), 3.83 (m 1 H), 3.38 (dd, 1 H, J = 11.8, 6.2 Hz), 3.22 (dd, 1 H, J = 11.7, 4.9 Hz), 3.20−3.15 (m, 2 H), 1.92 (ddd, 1 H, J = 11.4, 6.2, 2.4 Hz), 0.57 (s, 3 H); NOE ($CDCl_3$, 400 MHz) irradiated SiMe, observed 3-CH_2Se (0.9%, 0.5%), H-5 (0.3%); irradiated H-3, observed H-4 (3.8%); the assignments were in agreement with the H−H COSY spectrum; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 141.2, 135.3, 133.4, 133.2, 129.8, 129.5, 129.1, 127.4, 127.1, 127.0, 126.6, 125.0, 124.7, 81.7, 55.5, 41.3, 31.0, 30.5, −4.1; EI HRMS calcd for $C_{24}H_{24}OSeSi$ 436.0760, found 436.0753 (M^+). Anal. Calcd for $C_{24}H_{24}OSeSi$: C, 66.19; H, 5.55. Found: C, 66.18; H, 5.70.

[2*R,3*S**,4*R**,5*S**]-Indano[1,2-*d*]-2-methyl-2-phenyl-3-(phenylselenomethyl)-1,2-oxasilolane (8c)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58−7.20 (m, 14 H), 4.95 (ddd, 1 H, J = 4.9, 2.0 Hz), 3.91 (dd, 1 H, J = 7.8, 5.0 Hz), 3.62 (dd, 1 H, J = 11.4, 9.0 Hz), 3.33 (dd, 1 H, J = 11.4, 9.0 Hz), 3.15 (dd, 1 H, J = 16.7, 4.9 Hz), 3.13 (dd, 1 H, 16.6, 1.1 Hz), 2.19 (ddd, 1 H, J = 9.1 Hz), 0.04 (s, 3 H); NOE ($CDCl_3$, 400 MHz) irradiated SiMe, observed 3-CH_2Se (0.4%, 0.5%); irradiated H-3, observed H-4 (10.4%), H-6 (2.1%); the assignments were in agreement with the H−H COSY spectrum; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 141.3, 136.0, 133.7, 132.7, 130.1, 130.0, 129.0, 127.8, 127.2, 126.9, 126.4, 126.2, 125.5, 82.6, 52.2, 41.7, 31.2, 26.4, −3.9.

[2*S,3*S**,4*R**,5*S**]-Indano[1,2-*d*]-2-methyl-2-phenyl-3-(phenylselenomethyl)-1,2-oxasilolane (8d)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48−6.87 (m, 14 H), 4.89 (ddd, 1 H, J = 4.7, 4.3 Hz), 3.86 (dd, 1 H, J = 7.9, 4.5 Hz), 3.53 (dd, 1 H, J = 11.2, 6.5 Hz), 3.22 (d, 1 H, J = 16.6 Hz), 3.17 (dd, 1 H, J = 16.6, 4.7 Hz), 3.10 (dd, 1 H, J = 10.8 Hz), 2.18 (ddd, 1 H, J = 9.6, 7.8 Hz), 0.57 (s, 3 H); NOE ($CDCl_3$, 400 MHz) irradiated Si−Me, observed H-3 (1.3%); irradiated H-3, observed H-4 (10.0%), H-5 (2.8%); the assignments were in agreement with the H−H COSY spectrum; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 141.5, 134.1, 133.8, 132.7, 130.0, 129.5, 129.1, 127.3, 127.2, 126.9, 126.5, 126.3, 125.4, 82.5, 52.9, 41.4, 32.8, 26.7, −1.0.

Radical Reactions of 8a and Purification of the Products 9a, 9b, 10a, and 10b. To a solution of **8a** (220 mg, 0.51 mmol) in benzene (50 mL) at 80 °C was added a solution of Bu_3SnH (200 μL, 0.74 mmol) and AIBN (50 mg, 0.30 mmol) in benzene (10 mL) slowly over a 4 h period. The solvent was evaporated, and the residue was purified by silica gel column chromatography (Et_2O/hexane, 1:50) to give a mixture of **9a**, **9b**, **10a**, and **10b** (63 mg, 44%, **9a**:**9b**:**10a**:**10b** = 22:13:63:2, based on ^{1}H NMR) as an oil. From the mixture, **9a** (10 mg, 7%), **9b** (4 mg, 3%), **10a** (28 mg, 20%), and **10b** (1 mg, 0.7%) were obtained in a pure form, respectively, by preparative HPLC separation (AcOEt/hexane, 1:100).

[2*R,3*R**,4*R**,5*S**]-Indano[1,2-*d*]-2,3-dimethyl-2-phenyl-1,2-oxasilolane (9a)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56−7.19 (m, 9 H), 5.13 (dt, 1 H, J = 5.3, 2.2 Hz), 3.34 (t, 1 H, J = 4.4 Hz), 3.21 (dd, 1 H, J = 16.6, 2.2 Hz), 3.14 (dd, 1 H, J = 16.6, 2.0 Hz), 1.65 (dq, 1 H, J = 7.8, 3.5 Hz), 1.04 (d, 3 H, J = 7.8 Hz), −0.02 (s, 3 H); NOE ($CDCl_3$, 400 MHz) irradiated Si−Me, observed H-3 (0.8%); irradiated H-3, observed H-4 (2.9%); irradiated 3-Me, observed H-4 (2.4%); the assignments were in agreement with the H−H COSY spectrum;^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 141.3, 135.4, 133.8, 129.7, 127.7, 127.0, 126.5, 125.2, 124.4, 82.2, 57.6, 41.5, 23.8, 15.9, −1.4; EI HRMS calcd for $C_{18}H_{20}OSi$ 280.1283, found 280.1293 (M^+). Anal. Calcd for $C_{18}H_{20}OSi$: C, 77.09; H, 7.19. Found: C, 77.00; H, 7.26.

[2*S,3*R**,4*R**,5*S**]-Indano[1,2-*d*]-2,3-dimethyl-2-phenyl-1,2-oxasilolane (9b)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25−6.96 (m, 9 H), 5.07 (dt, 1 H, J = 5.4, 2.4 Hz), 3.34 (t, 1 H, J = 4.5), 3.21 (dd, 1 H, J = 16.6, 5.4 Hz), 3.15 (dd, 1 H, J = 16.6, 2.1 Hz), 1.69 (dq, 1 H, J = 7.8, 3.5 Hz), 1.33 (d, 3 H, J = 7.9 Hz), 0.46 (s, 3 H); NOE ($CDCl_3$, 400 MHz) irradiated Si−Me, observed 3-Me (1.0%), H-4 (0.2%), H-5 (0.3%); irradiated H-3, observed H-4 (3.4%); irradiated 3-Me, observed H-4 (2.9%); the assignments were in agreement with the H−H COSY spectrum;^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 141.2, 136.2, 133.3, 129.3, 127.3, 127.0, 126.5, 125.0, 124.7, 81.9, 57.8, 41.2, 23.6, 15.7, −4.4; EI HRMS calcd for $C_{18}H_{20}OSi$ 280.1283, found 280.1303 (M^+).

[2*R,5*R**,6*S**]-Indano[1,2-*e*]-2-methyl-2-phenyl-1,2-oxasilinane (10a)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63−7.17 (m, 9 H), 4.88 (ddd, 1 H, J = 5.8, 3.7 Hz), 3.19−3.14 (m, 2 H), 3.03 (dd, 1 H, J = 16.1, 3.6 Hz), 2.26−2.15 (m, 2 H), 1.00−0.89 (m, 2 H), 0.18 (s, 3 H);^{13}C NMR (125 MHz, $CDCl_3$) δ 143.9, 141.6, 138.1, 133.3, 129.6, 127.9, 126.7, 126.4, 125.0, 123.9, 77.1, 47.3, 41.8, 21.9, 7.7, −1.0; EI HRMS calcd for $C_{18}H_{20}OSi$ 280.1283, found 280.1296 (M^+). Anal. Calcd for $C_{18}H_{20}OSi$: C, 77.09; H, 7.19. Found: C, 77.28; H, 7.28.

[2*S,5*R**,6*S**]-Indano[1,2-*e*]-2-methyl-2-phenyl-1,2-oxasilinane (10b)**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35−7.16 (m, 9 H), 4.93 (ddd, 1 H, J = 6.0, 4.5 Hz), 3.21 (dd, 1 H, J = 12.3, 6.0 Hz), 3.14 (dd, 1 H, J = 16.0, 6.0 Hz), 2.98 (dd, 1 H, J = 16.0, 4.3 Hz), 2.22−2.18 (m, 2 H), 1.04 (ddd, 1 H, J = 14.3, 8.3, 6.0 Hz), 0.77 (ddd, 1 H, J = 14.6, 8.1, 5.6 Hz), 0.43 (s, 3 H);^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 141.5, 133.3, 129.5, 127.7, 126.7, 126.5, 125.0, 124.0, 77.2, 47.2, 41.4, 22.2, 8.3, −1.7; EI HRMS calcd for $C_{18}H_{20}OSi$ 280.1283, found 280.1270 (M^+). Anal. Calcd for $C_{18}H_{20}OSi$: C, 77.09; H, 7.19. Found: C, 77.08; H, 7.34

Radical Reactions of 8a and 8b and ^{1}H NMR Analysis of the Products. To a solution of **8a** or **8b** (22 mg, 0.051 mmol) in benzene (5 mL) at 80 °C was added a solution of Bu_3SnH (60 μL, 0.22 mmol) and AIBN (5 mg, 0.03 mmol) in benzene (5 mL) slowly over a 4 h period. The solvent was evaporated, and the residue was dissolved in $CDCl_3$ and its ^{1}H NMR spectrum (500 MHz) was measured.

(±)-Ethyl *trans*-4-(*tert*-Butyldiphenylsilyloxy)-2-butenoate (16). A mixture of **15** (10.0 g, 69.4 mmol) and BH_3 (1 M in THF, 70 mL, 70 mmol) in THF (30 mL) was stirred at room temperature for 12 h. After aqueous AcOH (50%, 2 mL) was added, the solvent was evaporated, and the residue was partitioned between AcOEt and aqueous $NaHCO_3$ (saturated). The organic layer was washed with brine, dried (Na_2SO_4), and evaporated to give an oil. A mixture of the resulting oil, imidazole (6.81 g, 100 mmol), and TBDPSCl (13.0 mL, 50.0 mmol) in DMF (100 mL) was stirred at room temperature for 3 h. Et_2O and water were added, and the resulting mixture was partitioned. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated. The residue was purified by silica gel column chromatography (Et_2O/hexane, 1:50) to give **16** (7.73 g, 30%) as an oil: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.73−7.35 (m, 10 H), 6.98 (ddd, 1 H, J = 15.8, 3.3, 3.3 Hz), 6.26 (ddd, 1 H, J = 15.8, 2.6, 2.0 Hz), 4.34 (dd, 2 H, J = 3.3, 2.0 Hz), 4.22 (q, 2 H, J = 7.3), 1.31 (t, 3 H, J = 7.3 Hz), 1.08 (s, 9 H).

(±)-*trans*-4-(*tert*-Butyldiphenylsilyloxy)-2-butenol (17). To a solution of **16** (2.06 g, 5.59 mmol) in THF (20 mL) was added slowly

DIBAH (0.95 M in hexane, 14.1 mL, 13.4 mmol) at −78 °C, and the resulting mixture was stirred at the same temperature for 10 min. Et_2O and water were added, and the resulting mixture was partitioned. The organic layer was washed with 1 N HCl and brine, dried (Na_2SO_4), and evaporated. The residue was purified by silica gel column chromatography (AcOEt/ hexane = 1:5) to give **17** (1.80 g, 99%) as an oil: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.69−7.34 (m, 10 H), 5.91 (ddd, 1 H, J = 15.2, 5.3, 1.3 Hz), 5.79 (dt, 1 H, J = 15.2, 4.6 Hz), 4.23−4.21 (m 2 H), 4.14 (m, 2 H), 1.26 (t, 1 H, J = 6.0 Hz), 1.06 (s, 9 H); FAB HRMS (NaI) calcd for $C_{20}H_{26}NaO_2Si$ 349.1600, found 349.1603 (MNa^+).

(±)-*trans*-4-*tert*-Butyldiphenylsilyloxy[1,1-$^2H_2$]-2-butenol (17D). A solution of $LiAl(OMe)_3D$ was prepared by adding MeOH (1.34 mL, 33.1 mmol) to a solution of $LiAlD_4$ (1.0 M in THF, 11.0 mL, 11.0 mmol) at 0 °C. To a solution of **17** (1.69 g, 4.59 mmol) in THF (20 mL) was added slowly the prepared $LiAl(OMe)_3D$ solution at −78 °C, and the resulting mixture was stirred at 0 °C for 10 min. Et_2O and water were added, and the resulting mixture was partitioned. The organic layer was washed with 1 N HCl and brine, dried (Na_2SO_4), and evaporated. The residue was purified by silica gel column chromatography (AcOEt/hexane = 1:5) to give **17D** (1.10 g, 3.35 mmol, 73%) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69−7.35 (m, 10H), 5.90 (d, 1 H, J = 15.6 Hz), 5.78 (dt, 1 H, J = 15.4, 4.4 Hz), 4.22 (dd, 2 H, J = 4.4, 1.7 Hz), 1.73 (br s, 1 H), 1.06 (s, 9 H);^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 133.5, 130.7, 129.6, 128.6, 127.6, 63.7, 62.5 (m), 26.9, 19.3; FAB HRMS (NaI) calcd for $C_{20}H_{24}D_2NaO_2Si$ 351.1723, found 351.1727 (MNa^+).

(±)-*trans*-4-Phenylseleno-2-butenol (18). To a solution of PhSeCl (0.58 g, 3.0 mmol) in THF (5 mL) was added slowly a solution of TMSCN (0.48 mL, 3.6 mmol) in THF (5 mL) at room temperature, and the resulting mixture was evaporated to give PhSeCN as a residue.[25] To a solution of **17** (356 mg, 1.09 mmol) and the prepared PhSeCN in THF (6 mL) was added Bu_3P (0.75 mL, 3.0 mmol) slowly. The resulting mixture was evaporated, and the residue was purified by silica gel column chromatography (Et_2O/hexane = 1:50) to give TBDPS ether of *trans*-4-phenylseleno-2-butenol as an oil. A mixture of the obtained oil and TBAF (1 M in THF, 1.0 mL, 1.0 mmol) in THF (3 mL) was stirred at room temperature for 2 h. The solvent was evaporated, and the residue was purified by silica gel column chromatography (AcOEt/hexane, 1:4) to give **18** (129 mg, 52%) as an oil:.^{1}H NMR (270 MHz, $CDCl_3$) δ 7.56−7.20 (m, 5 H), 5.88−5.77 (m, 1 H, J = 15.2, 4.9, 1.3 Hz), 5.53 (dt, 1 H, J = 15.2, 5.9 Hz), 4.03 (t, 2 H, J = 5.9 Hz), 3.52 (d, 2 H, J = 7.9), 1.12 (t, 1 H, J = 5.9 Hz);^{13}C NMR (67.8 MHz, $CDCl_3$) δ 133.7, 131.6, 128.9, 128.2, 127.3, 62.9, 29.3; EI HRMS calcd for $C_{10}H_{12}OSe$ 228.0063, found 228.0031 (M^+). Anal. Calcd for $C_{10}H_{12}OSe$: C, 52.87; H, 5.32. Found: C, 52.81; H, 5.37.

(±)-*trans*-4-Phenylseleno[4,4-$^2H_2$]-2-butenol (18D). Compound **18D** (131 mg, 26%) was obtained as an oil from **17D** (712 mg, 2.17 mmol) as described above for the synthesis of **18**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.51−7.25 (m, 5 H), 5.82 (d, 1 H, J = 15.2 Hz), 5.53 (dt, 1 H, J = 15.2, 5.9 Hz), 4.05−4.01 (m, 2 H), 1.15 (t, 1 H, J = 5.9 Hz);^{13}C NMR (100 MHz, $CDCl_3$) δ 133.6, 131.5, 128.8, 127.9, 127.2, 62.9; EI HRMS calcd for $C_{10}H_{10}D_2OSe$ 230.0177, found 230.0185 (M^+)

(±)-*trans*-1-Diphenylvinylsilyloxy-4-phenylseleno-2-butene (12). Compound **12** (287 mg, 94%) was obtained as an oil from **18** (159 mg, 0.700 mmol) as described above for the synthesis of **7**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.22 (m, 15 H), 6.44 (dd, 1 H, J = 20.3, 14.9 Hz), 6.26 (dd, 1 H, J = 14.9, 3.9 Hz), 5.87 (dd, 1 H, J = 20.3, 3.9 Hz), 5.87−5.80 (m 1 H), 5.52 (dt, 1 H, J = 15.1, 5.2 Hz), 4.20 (dd, 2 H, J = 5.1, 0.7 Hz), 3.51 (d, 2 H, J = 7.8 Hz);^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 134.9, 133.9, 133.4, 133.2, 131.2, 130.0, 128.8, 127.8, 127.0, 126.9, 63.7, 29.5; EI HRMS calcd for $C_{24}H_{24}OSeSi$ 436.0761, found 436.0743 (M^+). Anal. Calcd for $C_{24}H_{24}OSeSi$: C, 66.19; H, 5.55. Found: C, 66.26; H, 5.73.

(±)-*trans*-1-Diphenylvinylsilyloxy-4-phenylseleno[4,4-$^2H_2$]-2-butene (12D). Compound **12D** (95 mg, 67%) was obtained as an oil from **18D** (75 mg, 0.33 mmol) as described above for the synthesis of **7**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.21 (m, 15 H), 6.44 (dd, 1 H, J = 20.3, 14.9 Hz), 6.26 (dd, 1 H, J = 14.9, 3.9 Hz), 5.87 (dd, 1 H, J = 20.3, 3.7 Hz), 5.81 (d, 1 H), 5.52 (dt, 1 H, J = 15.1, 5.4 Hz), 4.21 (dd, 2 H, J = 5.4, 1.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 134.9, 133.9, 133.4, 133.4, 133.2, 131.2, 129.9, 128.8, 127.8, 127.0, 126.8, 63.7; EI HRMS calcd for $C_{24}H_{22}D_2OSeSi$ 438.0885, found 438.0897 (M^+).

(±)-5-Benzoyloxy-3-(benzoyloxymethyl)-1-pentene (20). To a refluxing solution of **12** (118 mg, 0.27 mmol) in benzene (30 mL) was added a solution of Bu_3SnH (110 μL, 0.41 mmol) and AIBN (23 mg, 0.14 mmol) in benzene (5 mL) slowly over 4 h. The solvent was evaporated to give an oil. A mixture of the obtained oil (430 mg, 0.50 mmol), aqueous H_2O_2 (30%, 570 μL, 5.0 mmol), KF (291 mg, 5.0 mmol), and $KHCO_3$ (125 mg, 1.3 mmol) in MeOH/THF (1:1, 2 mL) was stirred at room temperature for 26 h. After aqueous $Na_2S_2O_3$ (1 M, 5 mL) was added, the resulting insoluble materials were filtered off, and the filtrate was evaporated. A mixture of the residue and BzCl (600 μL, 5.2 mmol) in pyridine (5 mL) was stirred at room temperature for 1 h. Et_2O and water were added, and the resulting mixture was partitioned. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated. The residue was purified by silica gel column chromatography (AcOEt/hexane, 1:19) to give crude **20** (68 mg), which was further purified by HPLC (AcOEt/hexane, 1:19) to give pure **20** (27 mg, 17%) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05−7.42 (m, 10 H), 5.77 (ddd, 1 H, J = 17.6, 10.7, 8.8 Hz), 5.22 (d, 1 H, J = 16.6 Hz), 5.19 (dd, 1 H, J = 10.7, 2.0 Hz), 4.45 (ddd, 1 H, J = 11.6, 5.9 Hz), 4.39−4.29 (m, 3 H), 2.82−2.74 (m, 1 H), 2.14−2.06 (m, 1 H), 1.91−1.83 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 166.3, 137.4, 132.9, 132.8, 130.14, 130.07, 129.48, 129.47, 128.30, 128.29, 117.7, 67.4, 62.7, 40.5, 30.2; EI HRMS calcd for $C_{20}H_{20}O_4$ 324.1361, found 324.1346 (M^+).

(±)-5-Benzoyloxy-3-(benzoyloxymethyl)-[4-^{2}H]pentene (21). Compound **21** (11 mg, 17%) was obtained as an oil from **12** (97 mg, 0.20 mmol) as described above for the synthesis of **20**, with Bu_3SnD instead of Bu_3SnH:^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05−7.42 (m, 10 H), 5.77 (ddd, 1 H, J = 17.1, 10.3, 8.5 Hz), 5.22 (ddd, 1 H, J = 17.1, 1.5, 1.0 Hz), 5.19 (dd, 1 H, J = 10.3, 1.5 Hz), 4.44 (dd, 1 H, J = 11.2, 6.8 Hz), 4.38−4.29 (m, 3 H), 2.81−2.74 (m, 1 H), 2.27−2.05 (m, 1 H), 1.91−1.82 (m, 0.28H); EI HRMS calcd for $C_{20}H_{19}DO_4$ 325.1423, found 325.1450 (M^+).

(±)-5-Benzoyl-3-(benzoyloxymethyl)-[1,1-$^2H_2$]-pentene (22D). Compound **22D** (13 mg, 19%) was obtained as an oil from **12D** (93 mg, 0.21 mmol) as described above for the synthesis of **20**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (m, 10 H), 5.76 (d, 1 H, J = 8.5 Hz), 4.44 (ddd, 1 H, J = 11.0, 6.6, 5.6 Hz), 4.39−4.29 (m, 3 H), 2.82−2.74 (m, 1 H), 2.14−2.06 (m 1H), 1.90−1−81 (m, 1 H);^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 166.2, 137.0, 132.83, 132.77, 130.0, 129.9, 129.39, 129.37, 128.21, 128.20, 117.1 (m), 67.3, 62.6, 40.3, 30; EI HRMS calcd for $C_{20}H_{18}D_2O_4$ 326.1485, found 326.1502 (M^+).

Computations. Initial starting guess geometries were generated using MM2* in MacroModel version 5.0 software. Geometry optimizations and single-point energy calculations were performed using PM3 and UHF/STO-3G in Spartan version 4.0 software.

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Supporting Information Available: ^{1}H NMR spectra of **2**, **11**, **8c**, **8d**, **9b**, **12D**, **16**, **17**, **17D**, **18D**, **21**, and **22D** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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