Syntheses and Theoretical Studies of Exocyclic γ-Oxoalkenyltrimethylsilanes. An Approach to the Stereodefined Exocyclic Tetrasubstituted Alkenes

Kazuhiko Nakatani,*[1] Tomoko Izawa, and Sachihiko Isoe

Institute of Organic Chemistry, Faculty of Science, Osaka City University, 3-3-138, Sugimoto, Sumiyoshi, Osaka 558, Japan

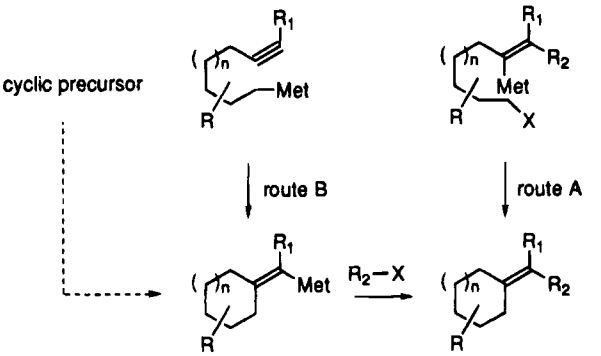
Received July 19, 1994[⊗]

The *Z*-selectivity in the dehydration of α-hydroxy-γ-oxoalkyltrimethylsilanes under acidic conditions was studied from experimental and theoretical points of view. Experimental results showed that (*Z*)-γ-oxoalkenyltrimethylsilanes were thermodynamic products under these conditions. The dehydration studies of the compound involving the *tert*-butyl group instead of the TMS group pointed out that not only steric but also electronic effects of Si could contribute to the distribution of the products as well as their stereochemistries. Theoretical studies using *ab initio* calculation at the 6-31G* level indicated that the (*Z*)-isomer was thermodynamically more stable than the corresponding (*E*)-isomer. Detail examinations of the optimized structures showed that the configuration of Si in the (*Z*)-isomer was slightly distorted from tetrahedral. Interpretation of the geometrical change of Si to rationalization of the thermodynamic preference was discussed from the viewpoint of possible coordination of the carbonyl oxygen to Si. Those (*Z*)-γ-oxoalkenyltrimethylsilanes would have potential to be the novel type of alkenylmetal compounds in organic synthesis as we demonstrated in the construction of stereodefined exocyclic tetrasubstituted alkene.

Introduction

Stereoselective synthesis of carbocycles involving tri- and tetrasubstituted exocyclic alkenes is one of the fundamental subjects attracting much attention in organic chemistry.[2] Among a number of methods, sequences involving an electrophilic trapping of the stereodefined alkenylmetals have been extensively studied.[3-8] These sequences could be roughly classified in two types by whether the alkenylmetals were incorporated in carbocycles (Scheme 1). One sequence consisted in a preparation of the stereodefined acyclic alkenylmetal bearing an electrophile appendage at its geminal position and the subsequent ring closure between the two reactive centers (route A).[3,4] The other uses exocyclic alkenylmetals with defined stereochemistry. From acyclic precursors a quick access to such exocyclic alkenylmetals with high degree of stereocontrol was realized by intramolecular carbometalation to the internal alkynes (route B);[5-10] methodologies using cyclic precursors, however, are not well established yet.[11]

Scheme 1



As a part of program aiming at the synthesis of exocyclic tetrasubstituted alkenes we studied preparations of stereodefined exocyclic alkenylmetals from cyclic precursors. We recently described facile synthesis of either (*E*)- or (*Z*)-γ-oxoalkenyl trimethylsilanes (*e.g.*, **2** and **3**) by dehydrating the novel α-hydroxy-γ-oxoalkyl

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1994.

(1) Present address: Department of Synthetic Chemistry and Biological Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606-01, Japan.

(2) (a) Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841–870. (b) Negishi, E. *Acc. Chem. Res.* **1987**, *20*, 65–72. (c) Negishi, E. in Advances in Metal–Organic Chemistry, Liebeskind, L. S., Ed.; JAI Press: London, 1989; Vol. 1, pp 177–207. (d) Trost, B. M. *Acc. Chem. Res.* **1990**, *23*, 34–42.

(3) Li: Negishi, E.; Zhang, Y.; Bagheri, V. *Tetrahedron Lett.* **1987**, *28*, 5793–5796.

(4) Si: (a) Overman, L. E.; Bell, K. L. *J. Am. Chem. Soc.* **1981**, *103*, 1851–1853. (b) Overman, L. E.; Malone, T. C. *J. Org. Chem.* **1982**, *47*, 5297–5300. (c) Fukuzaki, K.; Nakamura, E.; Kuwajima, I. *Tetrahedron Lett.* **1984**, *25*, 3591–3594. (d) Okuda, Y.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 2483–2486. (e) Overman, L. E.; Bell, K. L.; Ito, F. *J. Am. Chem. Soc.* **1984**, *106*, 4192–4201. (f) Corey, E. J.; Seibel, W. L. *Tetrahedron Lett.* **1986**, *27*, 905–908. (g) Overman, L. E.; Castaneda, A.; Blumenkopf, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 1303–1304.

(5) Mg: (a) Fujikura, S.; Inoue, M.; Utimoto, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 1999–2002. Mg/Cu: (b) Sternberg, E. D.; Volhardt, K. P. C. *J. Org. Chem.* **1984**, *49*, 1574–1583.

(6) Li: (a) Bailey, W. F.; Ovaska, T. V.; Leipert, T. K. *Tetrahedron Lett.* **1989**, *30*, 3901–3904. (b) Wu, G.; Cederbaum, F. E.; Negishi, E. *Tetrahedron Lett.* **1990**, *31*, 493–496. (c) Bailey, W. F.; Ovaska, T. V. *Tetrahedron Lett.* **1990**, *31*, 627–630. (d) Bailey, W. F.; Ovaska, T. V. *J. Am. Chem. Soc.* **1993**, *115*, 3080–3090.

(7) Cu: Rao, S. A.; Knochel, P. *J. Am. Chem. Soc.* **1991**, *113*, 5735–5741.

(8) Zn/Cu: Yeh, M. C. P.; Knochel, P. *Tetrahedron Lett.* **1989**, *30*, 4799–4802. (b) Crandall, J. K.; Ayers, T. A. *Organometallics* **1992**, *11*, 473–477.

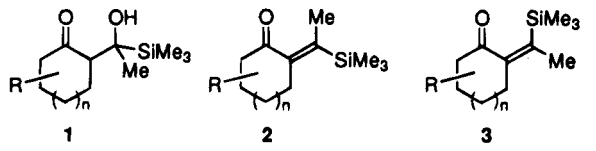
(9) Ti/Al: Harms, A. E.; Stille, J. R. *Tetrahedron Lett.* **1992**, *33*, 6565–6568.

(10) Pd: (a) Trost, B. M.; Lee, D. C. *J. Am. Chem. Soc.* **1988**, *110*, 7255–7258. (b) Zhang, Y.; Negishi, E. *J. Am. Chem. Soc.* **1989**, *111*, 3454–3456. (c) Negishi, E.; Noda, Y.; Lamaty, F.; Vawter, E. J. *Tetrahedron Lett.* **1990**, *31*, 4393–4396. (d) Fournet, G.; Balme, G.; Gore, J. *Tetrahedron* **1991**, *47*, 6293–6304.

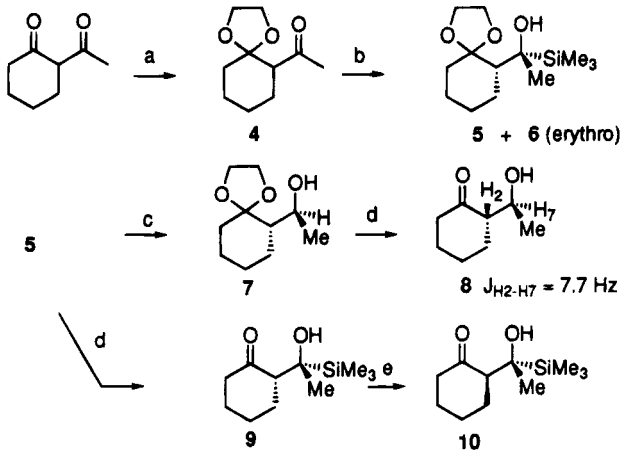
(11) Recent reports for exocyclic alkenes with other synthetic methods, see: (a) Corey, E. J.; Seibel, W. L. *Tetrahedron Lett.* **1986**, *27*, 909–912. (b) Takahashi, A.; Kirio, Y.; Sodeoka, M.; Sasai, H.; Shibasaki, M. *J. Am. Chem. Soc.* **1989**, *111*, 643–647. (c) Miyaura, N.; Ishikawa, M.; Suzuki, A. *Tetrahedron Lett.* **1991**, *32*, 2571–2574. (d) Nagasawa, K.; Zako, Y.; Ishihara, H.; Shimizu, I. *Tetrahedron Lett.* **1991**, *32*, 4937–4940. (e) Yamaguchi, M.; Hayashi, A.; Hirama, M. *J. Am. Chem. Soc.* **1993**, *115*, 3362–3363.

0022-3263/94/1959-5961$04.50/0

Chart 1



Scheme 2[a]



[a] (a) $(CH_2OH)_2$, *p*-TsOH, benzene, reflux; (b) Me_3SiLi, HMPA–THF, −78 °C; (c) TBAF, DMF, rt; (d) PPTS, acetone–H_2O, reflux; (e) DBU, CH_2Cl_2, rt.

trimethylsilanes[12] (*e.g.*, **1**) (Chart 1) and an attempt to transform **2** or **3** into tetrasubstituted exocyclic alkenes.[13]

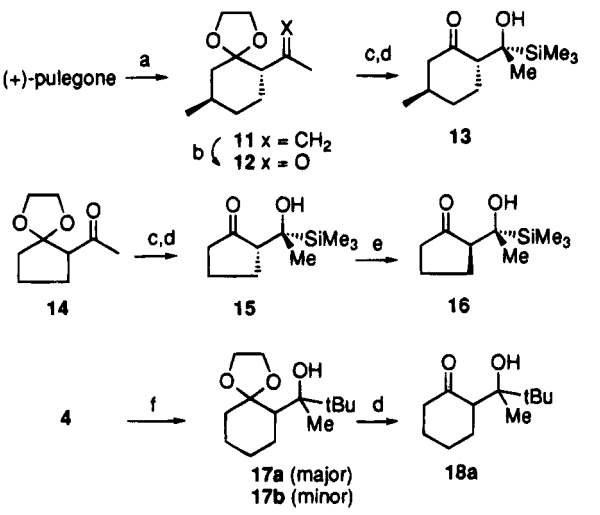
Dehydration of **1** went on not only in a stereospecific manner under the MsCl–Et_3N conditions but also stereoselectively giving **3** in the presence of acid catalysts. To get an insight into the *Z*-selectivity under the acidic conditions, we took *ab initio* studies of equilibrated structures of **2** and **3**. The calculation at the 6-31G* level showed that the configuration of Si in **3** is slightly distorted from tetrahedral. These configurational changes could be due to some interactions between Si and the carbonyl functionality.[14]

Results and Discussion

Preparation of α-Hydroxy-γ-oxoalkyl Trimethylsilanes. Our synthesis of α-hydroxy-γ-oxoalkyl trimethylsilanes employed a nucleophilic addition of the R_3Si anion into the carbonyl functionality in 2-acetylcycloalkanone ethylene acetal followed by acetal hydrolysis (Scheme 2).

Addition of (trimethylsilyl)lithium (TMSLi)[15] prepared under Hudrlik's conditions[15b] to the ketone **4**, obtained by monoacetalization of 2-acetylcyclohexanone with ethylene glycol, produced the α-hydroxy trimethylsilane **5** accompanied by a small amount of its diastereoisomer **6**. Stereochemistry of **5** was examined through conversion into the aldol **8** by reaction with TBAF in DMF[16] followed by hydrolysis of the acetal functionality in the resulting alcohol **7**. In the ^1H NMR of **8**, the coupling constant between H_2–H_7 (7.7 Hz) obtained by decoupling experiments was in a good agreement with that reported for the *threo*-**8**.[17] Since desilylation of α-hydroxy silanes under the TBAF–DMF conditions went on with retention of the configuration at the carbon bearing silicon functionality,[16] stereochemistry of **5** was, thus, determined as *threo*. Acid hydrolysis of the acetal functionality in **5** afforded the *threo*-α-hydroxy-γ-oxoalkyl trimethylsilane **9**. *Erythro*-isomer **10** was efficiently obtained by base-induced isomerization of **9**. Thus, treating **9** with diazabicyclo[5.4.0]undecene (DBU) resulted in epimerization at the carbon α to the carbonyl group giving a mixture of **9** and **10**, which could be easily separated by flash chromatography. Another *threo*-α-hydroxy silane **13** bearing a methyl substituent at the C_9 position was prepared from pulegone by way of the methyl ketone **12** (Scheme 3). Attempts to introduce a phenyldimethylsilyl ($PhMe_2Si$) group instead of the TMS group using $PhMe_2SiLi$[18] were unsuccessful due to enolization of the methyl ketone functionality. When the reaction of $PhMe_2SiLi$ with **12** was quenched with D_2O, the recovered **12** incorporated a deuterium at the methyl position.

Scheme 3[a]



[a] (a) $(CH_2OH)_2$, *p*-TsOH, benzene, reflux; (b) O_3, MeOH, rt, then Me_2S, rt; (c) Me_3SiLi, HMPA–THF, −78 °C; (d) PPTS, acetone–H_2O, reflux; (e) DBU, CH_2Cl_2, rt; (f) *t*-BuLi, ether, −78 °C.

To assess the effect of the size of the ring on dehydration, we prepared the five-membered analogs **15** and **16** from ethyl 2-oxocyclopentanecarboxylate by way of the methyl ketone **14**. The aldol **18a** having a *tert*-butyl group instead of the TMS group was also synthesized from **4** to examine the effect of Si on dehydration.

Dehydration of α-Hydroxy-γ-oxoalkyl Trimethylsilanes. Dehydration of α-hydroxy-γ-oxoalkyl trimethylsilanes was carried out in methylene chloride and the ratio of the products was determined by gas–liquid chromatography. The dehydration products (Chart 2) were isolated after aqueous work-up followed by silica gel column chromatography. The results of the dehydration are summarized in Table 1.

(12) Nakatani, K.; Izawa, T.; Odagaki, Y.; Isoe, S. *J. Chem. Soc., Chem. Commun.* **1993**, 1365–1367.

(13) To the best of our knowledge, neither preparation of α-hydroxy-γ-oxoalkyl trimethylsilanes incorporated in cyclic structures nor their dehydration reactions to give exocyclic γ-oxoalkenyl trimethylsilanes have been reported. For preparation of acyclic γ-oxoalkenyl trimethylsilanes, see Fleming, I.; Perry, D. A. *Tetrahedron* **1981**, *37*, 4027–4034.

(14) (a) Voronkov, M. G.; Frolov, Yu. L.; D'yakov, V. M.; Chipanina, N. N.; Gubanova, L. I.; Gavlilova, G. A.; Klyba, L. V.; Aksamentova, T. N. *J. Organomet. Chem.* **1980**, *201*, 165–177. (b) Albanov, A. I.; Gubanova, L. I.; Larin, M. F.; Pestunovich, V. A.; Voronkov, M. G. *J. Organomet. Chem.* **1983**, *244*, 5–16.

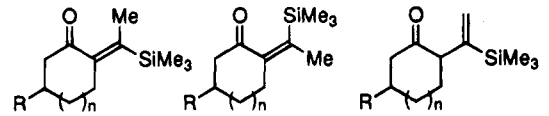
(15) (a) Still, W. C. *J. Org. Chem.* **1976**, *41*, 3063–3064. (b) Hudrlik, P. F.; Waugh, M. A.; Hudrlik, A. M. *J. Organomet. Chem.* **1984**, *271*, 69–76.

(16) (a) Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 6809–6811. (b) Nakada, M.; Urano, Y.; Kobayashi, S.; Ohno, M. *J. Am. Chem. Soc.* **1988**, *110*, 4826–4827.

(17) Curran, D. P. *J. Am. Chem. Soc.* **1983**, *105*, 5826–5833.

(18) Ager, D. J.; Fleming, I.; Patel, S. K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2520–2526.

Chart 2



n =1, R = H	**19**	**20**	**21**
n =1, R = Me	**22**	**23**	**24**
n =0, R = H	**25**	**26**	**27**

Table 1. Dehydrations of α-Hydroxy-γ-oxoalkyl Silanes

		product ratio[b-d]		
sm	conditions[a]	**19**	**20**	**21**
9	A, 0 °C, 27 h	31	10	9
9	B, 0 °C, 3.5 h	66 (71)[e]	6(5)	28
9	C, rt, 45 h	13 (14)	87 (65)	*f*
9	D, 0 °C, 4 h	6 (7)	94 (73)	*f*
9	E, rt, 106 h	5 (6)	95 (73)	*f*
10	B, 0 °C, 1.5 h	3	69	29
10	D, 0 °C, 44 h	9	91	*f*
		22	**23**	**24**
13	B, 0 °C, 1 h	70	3	24
13	D, rt, 9 h	8 (4)	92 (76)	*f*
		25	**26**	**27**
15	B, 0 °C, 1 h	85	4	11
15	E, rt, 406 h	18	82	*f*
16	B, 0 °C, 3.5 h	6	36	18
16	D, rt, 7 days	1	27	*f*

[a] Conditions A: Et_3N (4.2 equiv), MsCl (2 equiv); B: Et_3N (12.6 equiv), MsCl (6 equiv); C: Et_3N (2.2 equiv), MsCl (2 equiv); D: CSA (0.25 equiv); E: PPTS (0.25 equiv). [b] Product ratio was determined by GLC analysis. [c] Figures in parentheses are isolated yields. [d] Remainder, recovery of starting. [e] Combined isolated yield of **19** and **21**. [f] Not detected.

Table 2. Chemical Shifts (δ) of Me Group in ^1H NMR[a]

	19	**20**	**22**	**23**	**25**	**26**
$SiMe_3$	0.07	0.36	0.09	0.36	0.03	0.37
Me	1.99	1.65	2.00	1.67	2.42	1.68

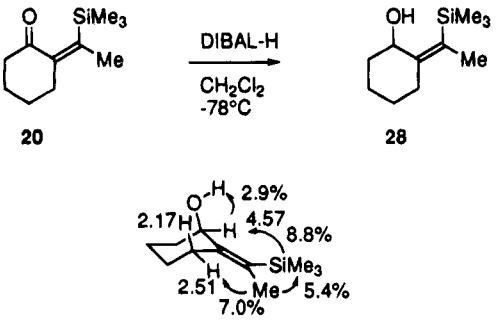
[a] Measured in C_6H_6-d_6.

Under the standard $MeSO_2Cl$ (MsCl)–Et_3N conditions for dehydration of aldols (conditions A), dehydration of **9** proceeds slowly with low selectivity giving the (*E*)-γ-oxoalkenyl trimethylsilane **19** and the (*Z*)-isomer **20** accompanied by the unconjugated enone **21**. Stereochemistries of the conjugated enones were primarily assigned from the chemical shifts of both the alkenyl methyl and the methyl groups on Si in their ^1H NMR spectra (Table 2).

In these compounds, the methyl signal on the same side as the carbonyl functionality is considered to be downfield due to a deshielding effect of carbonyl group.[19,20] Confirmation of these assignments was obtained by measuring NOE differential spectra of the alcohol **28** derived from **20** (Scheme 4).

Increases of the reaction rate by using excess reagents (conditions B) resulted in the predominant formation of **19**. On the other hand, with a lesser amount of Et_3N against MsCl (conditions C) the product ratio dramatically changed to give **20** as the major product. Under these conditions the reaction medium became acidic by

Scheme 4



formation of Et_3N·HCl and/or Et_3N·$MeSO_3H$ as dehydration continued; acid catalysts, thus, seemed to be effective for this dehydration. Treatment of **9** with either *dl*-camphorsulfonic acid (CSA) (conditions D) or pyridinium *p*-toluenesulfonate (PPTS) (conditions E) afforded **20** with high selectivity (94:6–95:5). Under these acidic conditions **21** was not detected at all. In the case of **10** with *erythro*-configuration, **20** was a predominant product under the conditions B. Under the conditions D, dehydration of **10** required a prolonged reaction time but resulted in the selective formation of **20**.

Dehydrations of **13** and **15** both involving *threo*-configurations were similarly dependent on the reaction conditions to give predominantly either the (*E*)-isomers **22** and **25** under the conditions B or the (*Z*)-isomers **23** and **26** on acid treatment, respectively. The *Z*-selectivity in dehydration of **15** involving the cyclopentanone ring under the acidic conditions was slightly lower than that of cyclohexanone analogs. Dehydration of the *erythro*-isomer **16** also indicated similar distribution of products as that of **10**, though its reactivity toward both the acidic and MsCl–Et_3N conditions was substantially low.

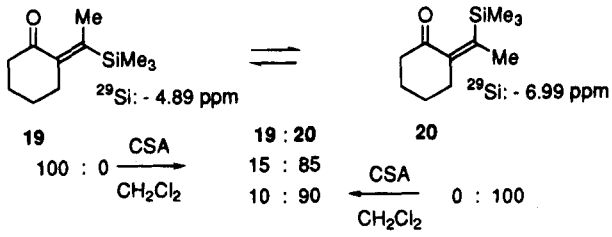
Dehydration of *threo*- and *erythro*-α-hydroxy-γ-oxoalkyl trimethylsilanes under the excess $MeSO_2Cl$–Et_3N conditions proceeds in an *anti*-stereospecific fashion giving (*E*)- and (*Z*)-γ-oxoalkenyl trimethylsilanes, respectively, though the regioselectivity of dehydration was slightly dependent on the size of the ring (conjugated enone:unconjugated enone = 7:3 for cyclohexanone and 9:1 for cyclopentanone derivatives). The reactivities toward acid catalysts, however, were highly dependent on the stereochemistry and structure of α-hydroxy-γ-oxoalkyl trimethylsilanes, decreasing in the order of **9** > **10** ≫ **15** > **16**. In dehydration of **9**, the (*Z*)-enone **20** was the kinetically favorable product. When the reaction of **9** with CSA was determined before completion of dehydration, the product distribution was identical with that at completion. Dehydration of **10** under the CSA conditions also kinetically gave **20**, but simultaneous epimerization of **10** to **9** was detected on TLC analysis. Therefore, the possibility that CSA-catalyzed dehydration of **10** partially proceeded *via* **9** is conceivable. With the less acidic catalyst (PPTS), neither dehydration nor epimerization of **10** was observed. The slow reaction of **15** and **16** toward acids suggested that these dehydrations went on under thermodynamic control.

To investigate the *Z*-selectivity of dehydration under the acidic conditions, we conducted equilibration experiments of (*E*)- and (*Z*)-γ-oxoalkenyl trimethylsilanes. Upon treatment of the pure **19** and **20** with CSA separately at room temperature in methylene chloride, the ratios of **19** and **20** in the mixture obtained were nearly identical (15:85 from **19** and 10:90 from **20**) (Scheme 5). These experiments showed that the energy difference between the two compounds was roughly

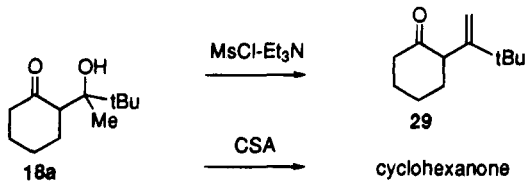
(19) (a) Tori, K.; Horibe, I.; Schigemoto, H. *Tetrahedron Lett.* **1975**, 2199–2202. (b) Dieter, R. K.; Fishpaugh, J. R.; Silks, L. A. *Tetrahedron Lett.* **1982**, *23*, 3751–3754.

(20) The use of $CDCl_3$ in ^1H NMR measurements often caused $E \rightarrow Z$ isomerization, and of more importance the chemical shifts differences of methyl signals between the *E* and *Z* isomers were rather small. These observations also consisted with those of previous work.[19a]

Scheme 5



Scheme 6



estimated as 1 kcal/mol at 25 °C, with **20** being thermodynamically more stable than **19**. Therefore, we could conclude that the observed *Z*-selectivity under the acidic conditions was due to the thermodynamic stability of *Z*-γ-oxoalkenyl trimethylsilanes. The kinetic formation of **20** in the dehydration of **9** might be accounted for by some stabilization at a late transition state.[21]

The role of the TMS group in the stabilization of the *Z*-form was considered from steric and electronic points of view. Bulkiness of the TMS group was often compared with that of the *tert*-butyl (t-Bu) group.[22] Since the C—Si bond is much longer than the C—C bond, the TMS group is spatially large, whereas the t-Bu group has condensed bulkiness. From a viewpoint of A-value, bulkiness of substituents decreased in the order of t-Bu > TMS ≈ Et > Me.[22] To clarify the role of the TMS group in dehydration discussed above, we carried out reactions of **18a** bearing the t-Bu group with excess MsCl–Et_3N and CSA. In contrast to α-hydroxy silanes, dehydration of **18a** under the MsCl–Et_3N conditions afforded the unconjugated enone **29** in low yield, with none of exocyclic alkenes being obtained. Furthermore, acid treatment (CSA) of **18a** did not induce dehydration but gave a retroaldol product, cyclohexanone (Scheme 6).

Selective dehydration toward the methyl group under the MsCl–Et_3N conditions could be accounted for by considering that the t-Bu group would cause much more steric congestion than the TMS group upon formation of exocyclic alkenes, whereas complete suppression of the retroaldol pathway in the acid-catalyzed reaction of α-hydroxy trimethylsilanes seemed to be the consequence of enhanced HOMO level of *p* orbital of the oxygen in the hydroxyl group.[23] Those electronic effects of the TMS group playing a significant role to control a reaction pathway may also contribute to stereochemistries of products. To get an insight into the thermodynamic preference of (*Z*)-γ-oxoalkenyl trimethylsilanes, we conducted theoretical calculation studies of **19** and **20**.

Theoretical Studies. Preliminary semiempirical calculation of heats of formation of both **19** and **20** using the PM3 method indicated that the (*E*)-isomer **19** was more stable than the (*Z*)-isomer **20** by ca. 1 kcal/mol.[24] Since these results were different from those of equilibration experiments, semiempirical models were not suitable for discussing structures of **19** and **20**. Therefore, we took *ab initio* studies using various basis sets to optimize their structures. The geometries of **19** and **20** were optimized using indicated basis sets after determination of their conformational isomers at the PM3 level. For assessment of their total energies (Table 3), it is reasonable to use the optimized structures of **19** and **20** at the 6-31G* level (**19**/6-31G* and **20**/6-31G*, respectively) for the following discussions.

In the optimized structure of **19** (**19**/6-31G*) (Figure 1) the cyclohexanone moiety takes a chairlike conformation and the dihedral angle for $\angle O-C_1-C_2-C_7$ is 49.9°, showing that the ketone carbonyl and vinylsilane functionalities are not on the same plane. On the other hand, the conformation of the cyclic moiety in the optimized structure of **20** (**20**/6-31G*) looks like a half-chair giving a rather flat structure for the ketone–vinylsilane moiety ($\angle O-C_1-C_2-C_7$ is 29.9°).

Comparison of the two structures in detail showed that the configuration of Si in the **20**/6-31G* is slightly distorted from tetrahedral. Thus, two bond angles ($\angle C_7-Si-C_9$ and $\angle C_9-Si-C_{10}$) in the **20**/6-31G* were smaller than those of the **19**/6-31G*, whereas the other two angles ($\angle C_7-Si-C_{10}$ and $\angle C_{10}-Si-C_{11}$) became larger (Table 4). Of particular interest were the bond lengths of $Si-C_7$ and $Si-C_9$ in the **20**/6-31G*, substantially longer than those of the **19**/6-31G* (Table 5). To make a geometrical change of Si clear we employed the distance between Si and the plane defined by three of four carbons on Si as an index. As shown in Table 6 the distance between Si and the $C_7-C_{10}-C_{11}$ plane in the **20**/6-31G* was the shortest among others, whereas those of Si to $C_7-C_9-C_{10}$ and $C_7-C_9-C_{11}$ became long in 0.026 and 0.035 Å, respectively. Those results indicated a slight geometrical change of Si in the **20**/6-31G*, with C_9 occupying the pseudoapical position in a trigonal bipyramid. It seemed that the other apical position could be the carbonyl oxygen.

Since such configurational distortion was not observed in the **19**/6-31G* as well as in the optimized structure of the vinyltrimethylsilane **30** at 3-21G(*) (Chart 3, supplementary material), it would be due to some interactions of the carbonyl functionality to Si. With these experimental and theoretical results in hand, we hypothesized that the thermodynamic stability of (*Z*)-isomer could be rationalized by a weak coordination of the carbonyl oxygen to the silicon atom in the Me_3Si group. Calculation of the bond order between oxygen and silicon in the **20**/6-31G* indicated a very weak coordination.[25] However, as shown in Figure 2, 3-21G(*) calculation of the hypothetical compound **31** involving the SiF_3 group clearly showed that coordination of carbonyl oxygen to Si in the (*Z*)-γ-oxoalkenyl silanes became apparent when Si was substituted with much more electronically negative substituents than the methyl group. Since it is known that the essential factor for such intramolecular coordination (O→Si) was that silicon should have at least one electronically negative substituent,[14] it might be assumed that the α,β-unsaturated-γ-carbonyl moiety in **20** was consistent with this requirement. Pentacoordinate Si atoms involved in intramolecular coordination were often differentiated from that in the noncoordinated structure by the chemical shifts in ^{29}Si NMR.[14] A small

(21) Similar observations of *Z*-selectivity using tributylstannane instead of trimethylsilane have been reported. Takeda, T.; Sugi, S.; Nakayama, A.; Suzuki, Y.; Fujiwara, T. *Chem. Lett.* **1992**, 819–822.

(22) Hwu, J. R.; Wang, N. *Chem. Rev.* **1989**, *89*, 1599–1615 and references cited therein.

(23) Yoshida, J.; Maekawa, T.; Murata, T.; Matshunaga, S.; Isoe, S. *J. Am. Chem. Soc.* **1990**, *112*, 1962–1970.

(24) Semiempirical and *ab initio* calculations were performed using SPARTAN molecular modeling software (version 3.0).

(25) Calculated bond orders for **20** and **31** were 0.044 and 0.346, respectively.

Table 3. Total Energy (in hartree) of 19 and 20

	PM3	RHF/STO−3G	RHF/3-21G	RHF/3-21G(*)	RHF/6-31G*	MP2/6-31G*[a]
19	−86.89[b]	−782.6379	−787.71063	−787.80133	−791.99524	−793.67834
20	−85.89[b]	−782.64015	−787.71876	−787.80960	−791.99846	−793.68270
$\Delta E^{b,c}$	−1.00	0.23	5.10	5.18	2.02	2.74

[a] Single point energy calculation with the optimized structure at the RHF/6-31G* level. [b] Reported in kcal/mol. [c] $E_{19} - E_{20}$.

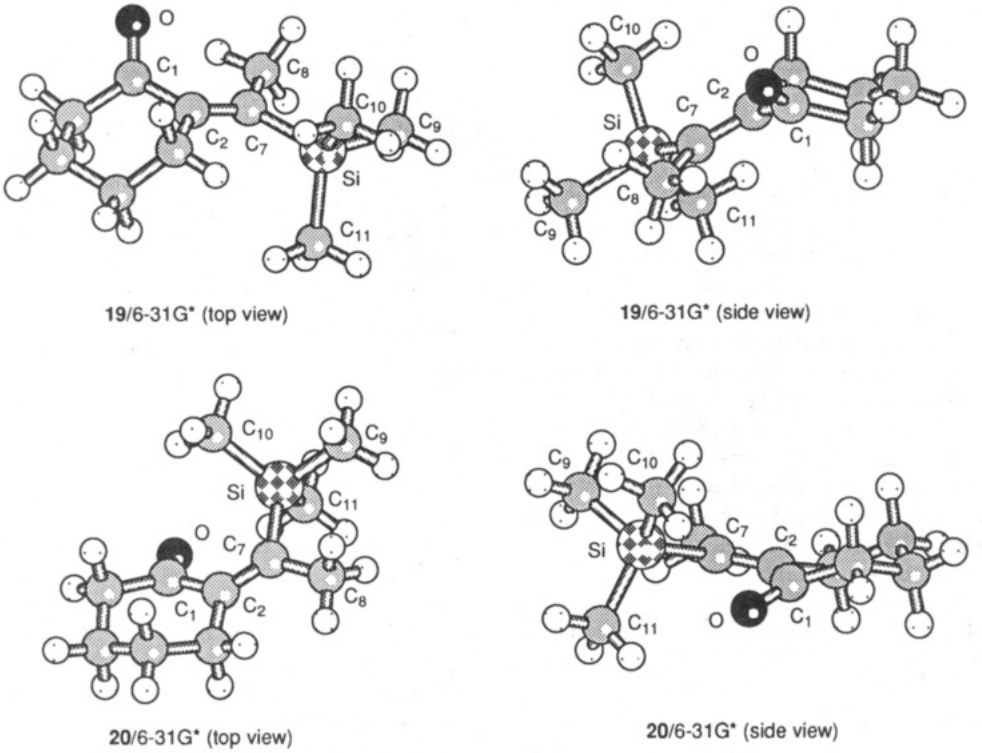


Figure 1. Ball and stick representations of optimized structures of **19** and **20** at the 6-31G* level. Structures were viewed from both top and side.

Table 4. Selected Bond Angles (deg) in 19/6-31G* and 20/6-31G*

	C_7-Si-C_9	C_7-Si-C_{10}	C_7-Si-C_{11}	C_9-Si-C_{10}	C_9-Si-C_{11}	$C_{10}-Si-C_{11}$
19/6-31G*	109.103	111.512	111.523	106.757	106.923	110.787
20/6-31G*	105.816	114.670	111.267	104.304	107.150	112.810

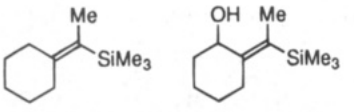
Table 5. Bond Lengths of Si−C (Å) in 19/6-31G* and 20/6-31G*

	$Si-C_7$	$Si-C_9$	$Si-C_{10}$	$Si-C_{11}$
19/6-31G*	1.920	1.894	1.895	1.896
20/6-31G*	1.932	1.904	1.894	1.889

Table 6. Distance from Si to the Plane Defined by Three Carbons on Si (Å)

	distance from Si to the plane			
	7-9-10	7-9-11	7-10-11	9-10-11
19/6-31G*	0.645	0.643	0.576	0.671
20/6-31G*	0.671	0.678	0.517	0.672

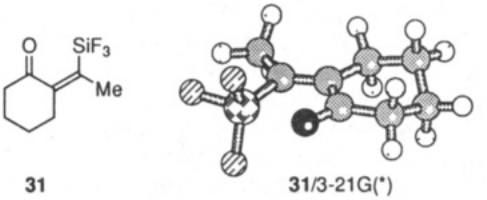
Chart 3



30 **33**

upfield shift of Si in **20** (δ −6.99) compared to that observed in **19** (δ −4.89) may support a weak coordination.

The *Z*-selectivity in dehydration of the α-hydroxy trimethylsilanes was discussed and rationalization of the thermodynamic preference of (*Z*)-γ-oxoalkenyl trimethylsilanes by the possible weak coordination of the carbonyl oxygen to Si was presented. However, we do not exclude any other interpretations such as that an attractive interaction between the carbonyl oxygen and Si may not be important but that the resulting geometrical change of Si could decrease the steric repulsion between two groups. Further theoretical studies using higher basis levels were essential to reach rigorous rationalization of these experimental results.[26]



31

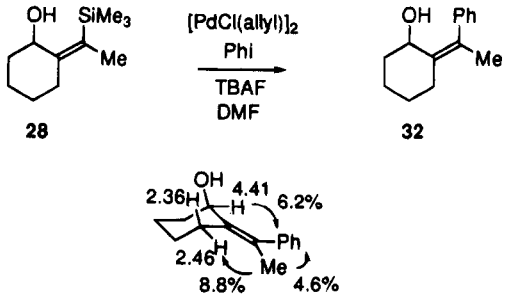
31/3-21G(*)

Figure 2. Ball and stick representation of the optimized structure of **31** at the 3-21G(*) level.

Transformation into Exocyclic Tetrasubstituted Alkenes. With stereodefined exocyclic alkenylsilanes in hand, we have examined their transformation into exocyclic tetrasubstituted alkenes.[27] In **20**, conjugation of the alkenyl moiety to the carbonyl group seemed to

(26) So far 6-31G* is the highest level to carry out calculations in a reasonable time (maximum 2 weeks) on the computational facility available for us.

Scheme 7



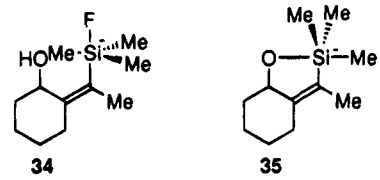
decrease electrophilic reactivities of alkenylsilanes; it was, therefore, reduced with DIBAL to the alcohol **28**. Preliminary examination of electrophilic substitution of **28** as well as its acetate showed that those alkenylsilanes were not stable under Lewis acidic conditions.

We then focused our attention on Pd-catalyzed cross-coupling reactions of alkenylsilanes realizing a C—C bond formation in a neutral medium. Hatanaka and Hiyama have developed the fluoride-induced Pd-catalyzed cross-coupling reaction of alkenylsilanes with aryl and alkenyl halides under mild conditions.[28,29] Accordingly, the (*Z*)-γ-hydroxy vinylsilane **28** was treated with iodobenzene in the presence of TBAF and a catalytic amount of allylpalladium chloride dimer to give the exocyclic tetrasubstituted alkene **32** as a sole product in 60% isolated yield (Scheme 7). Its *Z*-stereochemistry was unambiguously confirmed by NOE difference spectra, with none of the stereoisomers being detected in HPLC and ^{13}C NMR analysis.

It was reported that only ethenyltrimethylsilane could participate in the cross-coupling reaction due to low reactivity of alkenyltrimethylsilanes.[28b] Therefore, in original studies alkenylsilanes with enhanced reactivity by introducing electronically more negative substituents than the methyl group were used for the cross-coupling reaction. In spite of steric congestion as well as lack of electronegative substituents, the alkenyltrimethylsilane **28** showed an extraordinary reactivity under the fluoride-induced cross-coupling conditions. In contrast to **28**, the (*E*)-γ-hydroxy vinylsilane **33** (Chart 3) derived from reduction of **19** was totally inert under the same conditions as those for **28** giving **32**. Furthermore, since neither **19** nor **20** could undergo the cross-coupling reaction, they were recovered unchanged. Taking into account these results we reasoned that the reactivity of **28** is due to some interactions of the hydroxyl group and the silicon atom under these conditions.

In these fluoride-induced cross-coupling reaction it was rationalized that the pentacoordinate fluorosilicate[30] (*e.g.*, **34**) (Chart 4) derived from alkenylsilane and F^- was the key intermediate, which could transfer the alkenyl substituent onto Pd under mild conditions.[28c] Among compounds we examined for cross-coupling studies, only **28** could form the pentacoordinate silicate by an intramolecular coordination of an alkoxide ion. The reaction of **28** with iodobenzene using tetrabutylammonium hydroxide instead of TBAF in the cross-coupling conditions gave **32** in 20% isolated yield.[31] This result supported that the key intermediate in the cross-coupling reaction of **28** could be the silicate **35** involving intramolecular alkoxide coordination.[32] These cross-coupling studies emphasized that intramolecular coordination would be a powerful tool in the cross-coupling reaction of alkenyltrimethylsilanes.[33]

Chart 4



Conclusion

Dehydration studies of α-hydroxy-γ-oxoalkyl trimethylsilanes under acidic conditions indicated that the preferential formation of the (*Z*)-γ-oxoalkenyl trimethylsilanes was due to not only steric but also electronic effects of Si. Equilibration experiments showed that the (*Z*)-isomers were thermodynamically more stable than the corresponding (*E*)-isomers. Theoretical studies using *ab initio* calculation at the 6-31G* level also indicated the thermodynamic preference of the (*Z*)-isomers and of more importance that the configuration of Si is slightly distorted form tetrahedral. Possibilities that a weak coordination of the carbonyl oxygen to Si in the TMS group causing geometrical change of Si was discussed; however, further studies were essential to reach a rigorous conclusion.

Experimental Section

Melting point was determined with a Yamato MP-21 melting point apparatus and was uncorrected. ^1H NMR spectra were measured with JEOL FX-100 (100 MHz) or JEOL JNM GX-400 (400 MHz) spectrometers. Coupling constants (*J* values) are reported in hertz. ^{13}C NMR spectra were measured with a JEOL JNM GX-400 (100 MHz) spectrometer. The chemical shifts are expressed in ppm downfield from tetramethylsilane, using tetramethylsilane (δ = 0) or residual chloroform (δ = 7.25) and benzene (δ = 7.20) as an internal standard. IR spectra were recorded on a JASCO A-102 spectrometer. Mass spectra were recorded on a JMS D-300 or AX-500. Gas liquid chromatography was carried out on a Shimadzu GC-8A using the column (2 m) equipped with OV-

(27) For excellent reviews of reactions of alkenylsilanes, see: (a) Negishi, E. *Organometallics in Organic Synthesis*; Wiley: New York, 1980; pp 394–454. (b) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981. (c) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988. (d) Panek, P. S. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 1, pp 579–627.

(28) (a) Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 918–920. (b) Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1989**, *54*, 268–270. (c) Hatanaka, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1990**, *112*, 7793–7794. (d) Hatanaka, Y.; Hiyama, T. *Synlett.* **1991**, 845–853 and references therein.

(29) For a related approach to the exocyclic alkenes using fluoride-induced Pd-catalyzed coupling reaction, see: (a) Tamao, K.; Kobayashi, K.; Ito, Y. *J. Am. Chem Soc.* **1989**, *111*, 6478–6480. (b) Tamao, K.; Kobayashi, K.; Ito, Y. *Tetrahedron Lett.* **1989**, *30*, 6051–6054.

(30) For general reviews of organofluorosilicate, see: (a) Kumada, M.; Tamao, K.; Yoshida, J. *J. Organomet. Chem.* **1982**, *239*, 115–132. (b) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. P. *Chem. Rev.* **1993**, *93*, 1371–1448.

(31) The reaction conditions using tetrabutylammonium hydroxide were not optimized.

(32) A reaction of γ-hydroxyalkenyl silanes possessing phenyl substituent(s) on silicon atom with TBAF giving a cyclic silyl ether have been reported. Oda, H.; Sato, M.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron* **1985**, *41*, 3257–3268. In these reactions, intramolecular participation of an oxygen lone pair to pentacoordinate fluorosilicate was considered to account for a facile substitution of the phenyl group with fluoride ion. Extension of this rationalization to our results could be ruled out, because the phenyl substituent on the silicon atom was indispensable for these reactions.

(33) For recent reports describing reactions mediated by intramolecular coordination to silicon atom, see: (a) Corriu, R. J. P.; Lanneau, G. F.; Yu, Z. *Tetrahedron* **1993**, *49*, 9019–9030, (b) Yamamoto, Y.; Takeda, Y.; Akiba, K. *Tetrahedron Lett.* **1989**, *30*, 725–728 and references cited therein.

1. Fuji Davison Silica Gel BW-200 was used for silica gel flash chromatography. Precoated TLC plates Merck silica gel 60 F_{254} was used for preparative TLC. HPLC was performed on μPorasil P/N series columns with Waters Liquid Chromatography Model 510 using a differential refractometer R401. Anhydrous reactions were performed under N_2 atmosphere. Ether and tetrahydrofuran (THF) were distilled under N_2 from sodium/benzophenone ketyl prior to use. Dichloromethane (CH_2Cl_2) was distilled from P_2O_5 prior to use. Calculations were performed on SGI INDY (R4000SC personal workstation) with Spartan molecular modeling software (version 3.0).

6-Acetyl-1,4-dioxaspiro[4.5]decane (4). A solution of 2-acetylcyclohexanone (4.00 g, 29 mmol), ethylene glycol (2.66 g, 0.46 mmol), and *p*-TsOH (0.3 g) in benzene (150 mL) was heated at reflux with azeotropic removal of the resulting water overnight. The reaction mixture was diluted with EtOAc and washed with H_2O and saturated $NaHCO_3$. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Flash chromatography of the residue (SiO_2, 11% EtOAc/toluene) afforded **4** (2.55 g, 49%) as a colorless oil: ^1H NMR (C_6D_6) δ 1.01 (m, 1H), 1.32 (ddd, 1H, J = 14.7, 11.0, 4.3 Hz), 1.41–1.66 (4H), 1.75 (dt, 1H, J = 12.8, 4.7 Hz), 1.93 (m, 1H), 2.00 (s, 3H), 2.55 (dd, 1H, J = 10.1, 4.0 Hz), 3.31–3.49 (4H); ^{13}C NMR (C_6D_6) δ 23.7, 23.8, 26.8, 31.4, 35.3, 56.8, 64.1, 64.5, 109.7, 206.9; IR ($CDCl_3$) 2930, 1705, 1360, 1150, 1085, 1030 cm^{-1}; MS (*m/e*) (%) 184 (M^+) (27), 169 (7), 141 (43), 113 (22), 99 (100), 86 (28); HRMS calcd for $C_{10}H_{16}O_3$ (M^+) 184.1099, found 184.1119.

***threo*-6-[1-Hydroxy-1-(trimethylsilyl)ethyl]-1,4-dioxaspiro[4.5]decane (5).** A solution of hexamethyldisilane (1.92 g, 13.1 mmol, 2.7 mL) in hexamethylphosphoric triamide (HMPA) (5.3 mL) was cooled to frozen at −78 °C. To this frozen mixture methyllithium (4.4 mL, 1.5 M in ether, 6.5 mmol) and then THF (9 mL) were added and this mixture was warmed up to 0 °C. After a few minutes the solids melted sufficiently so that stirring was possible. During stirring for 15 min, the color of the solution became bright red to indicate the formation of Me_3SiLi. This mixture was then cooled to −78 °C and a solution of **4** (481 mg, 2.6 mmol) in THF (1.8 mL) was added. The mixture was stirred for 30 min and then quenched with saturated NH_4Cl. The resulting mixture was warmed up to ambient temperature and extracted with EtOAc (3 × 15 mL). The combined extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Flash chromatography of the residue (SiO_2, 10% EtOAc/hexane) afforded **5** (370 mg, 55%) as a colorless oil accompanied by a small amount (less than 2%) of diastereoisomer **6**: ^1H NMR (C_6D_6) δ 0.18 (s, 9H, $SiMe_3$), 0.96–1.08 (2H), 1.26–1.76 (3H), 1.34 (s, 3H, Me), 1.92 (dd, 1H, J = 12.8, 3.7 Hz), 3.22–3.52 (4H), 3.76 (s, 1H, OH); ^{13}C NMR (C_6D_6) δ −1.0, 21.5, 23.9, 26.7, 27.3, 33.6, 35.7, 55.9, 62.4, 68.3, 112.9; IR ($CHCl_3$) 3480, 2960, 2920, 2875, 1450, 1380, 1340, 1245, 1145, 1090, 1030, 930, 870, 840 cm^{-1}; MS (*m/e*) (%) 258 (M^+) (1), 243 [$(M - Me)^+$] (85), 229 (7), 213 (22), 197 (94), 185 (34), 171 (50), 153 (33), 130 (3), 125 (11), 109 (10), 99 (53), 87 (30), 81 (26), 73 (100), 55 (7); HRMS calcd for $C_{12}H_{23}O_3Si$ [$(M - Me)^+$] 243.1417, found 243.1431.

***threo*-6-(1-Hydroxyethyl)-1,4-dioxaspiro[4.5]decane (7).** To a solution of **5** (30.6 mg, 0.12 mmol) in DMF (0.42 mL) was added TBAF (0.21 mL, 1.0 M in THF, 0.72 mmol) and the mixture was stirred at room temperature for 3 days. After dilution with brine the resulting mixture was extracted with EtOAc. The combined extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered, and then concentrated *in vacuo*. Flash chromatography of the residue (SiO_2, 20% EtOAc/hexane) afforded **7** (14.0 mg, 63%, conv 93%) and **5** (9.7 mg, 32% recovery): ^1H NMR ($CDCl_3$) δ 1.10 (d, 3H, J = 6.7 Hz), 1.23–1.52 (8H), 1.70 (m, 1H), 1.81 (m, 1H), 3.99 (m, 1H), 4.18 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 20.5, 23.5, 24.1, 26.7, 33.9, 50.5, 63.7, 64.5, 67.4, 112.1; IR (C_6H_6) 3470, 2925, 1290, 1170, 1135, 1080, 980, 930 cm^{-1}; MS (*m/e*) (%) 186 (M^+) (11), 171 (27), 143 (28), 124 (17), 115 (8), 99 (100), 86 (12), 73 (8), 55 (7).

***threo*-2-(1-Hydroxyethyl)cyclohexanone (8).** To a solution of **7** (10.1 mg, 0.05 mmol) in acetone (0.7 mL) and H_2O (0.3 mL) was added PPTS (3.4 mg, 0.01 mmol) and the mixture was heated at reflux for 5.5 h. After concentration *in vacuo*, the resulting mixture was diluted with H_2O and extracted with EtOAc. The extract was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Flash chromatography of the residue (SiO_2, 20% EtOAc/toluene) afforded **8** (6.7 mg, 87%) as a colorless oil: ^1H NMR ($CDCl_3$) δ 1.15 (d, 3H, J = 6.1 Hz), 1.36 (dq, 1H, J = 3.7, 12.8 Hz), 1.62–2.42 (8H), 3.60 (s, 1H), 3.91 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 19.8, 24.9, 27.7, 30.6, 42.7, 57.6, 67.8, 215.7; IR ($CHCl_3$) 3500, 2940, 1690, 1450, 1400, 1200, 1130, 1080, 915 cm^{-1}; MS (*m/e*) (%) 143 [$(M + H)^+$] (4), 127 [$(M - Me)^+$] (8), 124 (77), 109 (21), 98 (100), 91 (2), 83 (45), 70 (74), 55 (29); HRMS calcd for $C_7H_{11}O_2$ [$(M - Me)^+$] 127.0759, found 127.0748.

***threo*-2-[1-Hydroxy-1-(trimethylsilyl)ethyl]cyclohexanone (9).** A solution of **5** (87.0 mg, 0.34 mmol) in acetone (6 mL) and H_2O (3 mL) was added PPTS (2.9 mg, 0.12 mmol) and the mixture was heated at reflux for 1.5 h. After concentration *in vacuo*, the resulting mixture was diluted with H_2O and extracted with EtOAc. The extract was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Flash chromatography of the residue (SiO_2, 10% EtOAc/hexane) afforded **9** (53.4 mg, 74%) as a colorless oil: ^1H NMR ($CDCl_3$) δ 0.05 (s, 9H, $SiMe_3$), 1.23 (s, 3H, Me), 1.57–2.42 (9H), 3.70 (s, 1H, −OH); ^{13}C NMR (C_6D_6) δ −1.7, 24.4, 25.5, 27.7, 30.6, 43.1, 60.0, 67.5, 214.4; IR ($CHCl_3$) 3520, 2975, 1690, 1255, 1135, 845 cm^{-1}; MS (*m/e*) (%) 214 (M^+) (1), 199 [$(M - Me)^+$] (15), 181 (20), 169 (13), 157 (12), 124 (32), 116 (10), 109 (28), 98 (13), 84 (19), 73 (100), 59 (6), 55 (20); HRMS calcd for $C_{10}H_{19}O_2Si$ [$(M - Me)^+$] 199.1155, found 199.1143.

erythro-2-[1-Hydroxy-1-(trimethylsilyl)ethyl]cyclohexanone (10). To a solution of **7** (47.3 mg, 0.22 mmol) in CH_2Cl_2 (1.5 mL) was added DBU (33 μL, 0.22 mol) and the mixture was stirred for 2 days at room temperature. After dilution with H_2O the resulting mixture was extracted with EtOAc. The combined extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Flash chromatography of the residue (SiO_2, 10% EtOAc/hexane) afforded **10** (23.5 mg, 50%) as a colorless oil accompanied by the recovery of the starting material (16.7 mg, 35%): ^1H NMR ($CDCl_3$) δ 0.04 (s, 9H, $SiMe_3$), 1.25 (s, 3H, Me), 1.40–1.70 (3H), 1.90 (m, 1H), 2.01–2.09 (2H), 2.25–2.39 (2H), 2.59 (dd, 1H, J = 13.1, 5.2 Hz), 3.87 (s, 1H, OH); ^{13}C NMR (C_6D_6) δ −0.9, 20.7, 25.5, 27.0, 29.8, 43.0, 56.8, 66.9, 215.1; IR ($CHCl_3$) 3500, 2925, 1685, 1440, 1335, 1300, 1240, 1070, 825, 745 cm^{-1}; MS (*m/e*) (%) 214 (M^+), 199 [$(M - Me)^+$] (3), 185 (2), 169 (3), 157 (3), 124 (7), 116 (17), 109 (6), 98 (19), 83 (7), 73 (100), 59 (6), 55 (22); HRMS calcd for $C_{10}H_{19}O_2Si$ [$(M - Me)^+$] 199.1155, found 199.1130.

9-Methyl-6-(1-methylvinyl)-1,4-dioxaspiro[4.5]decane (11). A solution of (+)-pulegone (8.37 g, 55 mmol), ethylene glycol (4.10 g, 3.7 mL, 66 mmol), and *p*-TsOH (120 mg, 0.6 mmol) in benzene (200 mL) was refluxed with azeotropic removal of H_2O for 24 h. After the mixture was cooled and diluted with water, it was extracted with EtOAc. The extract was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Flash chromatography of the residue (SiO_2, 3.2% EtOAc/hexane) afforded **11** (7.07 g, 66%): ^1H NMR ($CDCl_3$) δ 0.87 (d, 3H, J = 6.1 Hz), 0.90 (m, 1H), 1.04–1.28 (2H), 1.52–1.75 (4H), 1.76 (s, 3H), 2.16 (dd, 1H, J = 13.1, 4.0 Hz), 3.60–4.02 (4H), 4.79 (s, 1H), 4.82 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 22.1, 23.4, 29.4, 30.6, 34.4, 45.3, 51.7, 64.7, 64.9, 111.0, 113.3, 145.9; IR (C_6H_6) 2925, 1635, 1445, 1370, 1305, 1260, 1205, 1150, 1105 cm^{-1}; MS (*m/e*) (%) 196 (M^+) (4), 181 (5), 153 (3), 139 (11), 126 (10), 113 (100), 99 (6), 86 (26), 81 (4), 73 (2), 69 (13), 55 (10); HRMS calcd for $C_{12}H_{20}O_2$ (M^+); 196.1464, found 196.1486.

6-Acetyl-9-methyl-1,4-dioxaspiro[4.5]decane (12). To a solution of **11** (6.78 g, 34.6 mmol) in MeOH (300 mL) was bubbled through ozone for 7.5 h at room temperature. Dimethyl sulfide (200 mL) was added and the mixture was stirred overnight. After evaporation of the volatile material the residue was diluted with H_2O and extracted with EtOAc. The extract was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Flash chromatography of the residue (SiO_2, 14% EtOAc/hexane) afforded **12** (5.58 g, 81%): ^1H NMR ($CDCl_3$) δ 0.85 (d, 3H, J = 6.1 Hz), 1.05 (t, 1H, J = 12.5 Hz), 1.58–1.94 (6H), 2.17 (s, 3H), 2.67 (dd, 1H, J = 12.8, 3.7 Hz), 3.74–3.98 (4H); ^{13}C NMR ($CDCl_3$) δ 21.8, 26.1,

30.0, 31.5, 33.1, 44.4, 57.0, 64.2, 64.7, 109.8, 209.6; IR ($CDCl_3$) 2950, 1705, 1360, 1150, 1175, 1155, 1055 cm^{-1}; MS (*m/e*) (%) 198 (M^+) (4), 183 (1), 155 (3), 141 (7), 125 (7), 113 (100), 99 (22), 86 (27), 77 (3), 69 (24), 55 (43); HRMS calcd for $C_{11}H_{18}O_3$ (M^+) 198.1256, found 198.1251.

***threo*-2-[1-Hydroxy-1-(trimethylsilyl)ethyl]-5-methylcyclohexane-1-one (13).** A THF (1 mL) solution of **12** (292 mg, 1.47 mmol) was treated with Me_3SiLi prepared from $Me_3SiSiMe_3$ (1.48 mL, 7.37 mmol) and MeLi (2.46 mmol, 1.5 M in Et_2O, 3.69 mmol) in HMPA (3 mL) and THF (6 mL) to afford hydroxy silane (101 mg, 25%): ^1H NMR (C_6D_6) δ 0.02 (s, 9H), 0.85 (d, 3H, J = 6.7 Hz), 0.93 (m, 1H), 1.20 (s, 3H), 1.47–1.90 (6H), 3.83–3.98 (4H); ^{13}C NMR (C_6D_6) δ −1.0, 21.9, 26.9, 27.4, 30.3, 35.2, 42.1, 55.2, 62.3, 62.4, 68.2, 113.0; IR ($CDCl_3$) 3480, 2960, 1245, 1095, 1045, 835 cm^{-1}; MS (*m/e*) (%) 272 (0.4), 257 [(M − Me)$^+$] (52), 243 (3), 227 (12), 211 (57), 199 (16), 185 (32), 167 (17), 155 (10), 145 (20), 113 (32), 95 (36), 81 (6), 73 (100), 55 (7); HRMS calcd for $C_{13}H_{25}O_3Si$ [(M − Me)$^+$] 257.1574, found 257.1585. The above hydroxy silane (218 mg, 0.80 mmol) and PPTS (60.6 mg, 0.24 mmol) was treated in aqueous acetone as described for **9** to afford **13** (121 mg, 66%): ^1H NMR (C_6D_6) δ 0.14 (s, 9H), 0.60 (d, 3H, J = 6.1 Hz), 0.79 (m, 1H), 1.30 (s, 3H), 1.30–1.53 (4H), 1.81 (m, 1H), 2.03–2.17 (2H), 3.71 (s, 1H); ^{13}C NMR ($CDCl_3$) δ −1.7, 22.3, 24.4, 29.5, 34.2, 51.4, 59.5, 67.7, 67.7, 215.2; IR ($CHCl_3$) 3520, 2960, 1695, 1450, 1250, 1195, 1130, 1100 cm^{-1}; MS (*m/e*) (%) 228 (0.4), 213 [(M − Me)$^+$] (21), 195 (29), 185 (17), 169 (17), 157 (21), 138 (48), 123 (48), 95 (34), 81 (21), 73 (100); HRMS calcd for $C_{11}H_{21}O_2Si$ [(M − Me)$^+$] 213.1311, found 213.1323.

6-Acetyl-1,4-dioxaspiro[4.4]nonane (14). A solution of 6-formyl-1,4-dioxaspiro[4.4]nonane[34] (5.71 g, 36.6 mmol) in Et_2O (107 mL) was treated MeLi (51.8 mL, 1.6 M in Et_2O, 36.6 mmol) at −78 °C for 3 h. The reaction was quenched and the resulting mixture was diluted with H_2O and extracted with EtOAc. The extract was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Flash chromatography of the residue (SiO_2, 11% EtOAc/hexane) afforded alcohol (5.79 g, 92%): ^1H NMR ($CDCl_3$) δ 1.14 (d, 3H, J = 6.1 Hz), 1.37 (dq, 1H, J = 8.7, 4.1 Hz), 1.46–1.85 (5H), 1.92 (dd, 1H, J = 17.7, 8.6 Hz), 3.42 (s, 1H), 3.77–4.03 (5H); ^{13}C NMR (C_6D_6) δ 20.6, 21.5, 26.7, 35.2, 51.8, 63.8, 64.3, 68.3, 118.7; IR ($CDCl_3$) 3550, 2970, 2900, 1410, 1360, 1320, 1280, 1240, 1150, 1120, 1030, 1010, 950 cm^{-1}; MS (*m/e*) (%) 172 (5) (M^+), 157 (6), 143 (6), 129 (5), 110 (75), 90 (100), 84 (14), 73 (8), 55 (21); HRMS calcd for $C_9H_{16}O_3$ (M^+) 172.1100, found 172.1105. To a mixture of PCC (3.42 g, 15.9 mmol), NaOAc (128 mg, 168 mmol), and Celite (3.5 g) in CH_2Cl_2 (35 mL) was added the alcohol (963 mg, 5.6 mmol), and the mixture was stirred overnight at room temperature. The reaction was diluted with Et_2O and the resulting precipitate was filtered through Florisil and Celite and the filtrate was concentrated *in vacuo*. Flash chromatography of the residue (SiO_2, 13% EtOAc/hexane) afforded **14** (717 mg, 75%): ^1H NMR (C_6D_6) δ 1.58 (m, 1H), 1.66–1.81 (4H), 2.16 (m, 1H), 2.12 (s, 3H), 3.05 (t, 1H, J = 8.2 Hz), 3.82–3.99 (4H); ^{13}C NMR (C_6D_6) δ 21.9, 25.6, 30.1, 36.7, 58.4, 64.0, 64.6, 118.5, 204.8; IR ($CDCl_3$) 2960, 2910, 1715, 1360, 1320, 1210, 1170, 1120, 1080 cm^{-1}; MS (*m/e*) (%) 170 (M^+) (4), 155 (2), 141 (5), 112 (11), 99 (100), 55 (15); HRMS calcd for $C_9H_{14}O_3$ (M^+) 170.0943, found 170.0935.

***threo*-2-[1-Hydroxy-1-(trimethylsilyl)ethyl]cyclopentanone (15).** Me_3SiLi prepared from $Me_3SiSiMe_3$ (3.55 mmol, 0.71 mL) and MeLi (1.85 mL, 1.6 M in Et_2O, 2.96 mmol) in HMPA (1.42 mL) and THF (7.8 mL) was added to **14** (201 mg, 1.18 mmol) to give *threo*-hydroxy silane (124 mg, 43%, 67% conversion) and its *erythro*-isomer (10.3 mg, 4%) accompanied by **14** (72 mg, 36% recovery): ^1H NMR ($CDCl_3$) δ 0.03 (s, 9H), 1.31 (s, 3H), 1.42–1.94 (6H), 2.08 (dd, 1H, J = 11.0, 8.5 Hz), 3.33 (s, 1H), 3.80–4.04 (4H); ^{13}C NMR (C_6D_6) δ −2.5, 22.1, 24.4, 27.9, 37.8, 51.2, 62.8, 63.3, 66.9, 121.5; IR ($CDCl_3$) 3500, 2960, 2890, 1350, 1320, 1250, 1205, 1145, 1100, 1045, 1015, 950, 840 cm^{-1}; MS (*m/e*) (%) 229 [(M − Me)$^+$] (48), 199 (27), 183 (51), 171 (24), 157 (33), 139 (24), 127 (12), 99 (47), 87 (18), 73 (100); HRMS calcd for $C_{11}H_{21}O_3Si$ [(M − Me)$^+$] 229.1260, found 229.1249. The above *threo*-hydroxy silane (30.6 mg, 0.13 mmol) was treated with PPTS (10.2 mg, 0.04 mmol) in refluxing acetone (2 mL) and H_2O (1 mL) to give **15** (22.5 mg, 90%): ^1H NMR ($CDCl_3$) δ 0.04 (s, 9H), 1.25 (s, 3H), 1.68–1.79 (2H), 2.01–2.05 (2H), 2.10–2.22 (2H), 2.32–2.38 (m, 1H), 3.79 (s, 1H); ^{13}C NMR ($CDCl_3$) δ −1.9, 20.6, 25.2, 26.8, 39.1, 58.9, 68.1, 222.8; IR ($CHCl_3$) 3460, 2950, 1720, 1250, 840 cm^{-1}; MS (*m/e*) (%) 185 [(M − Me)$^+$] (18), 169 (12), 157 (18), 110 (64), 101 (8), 95 (52), 82 (25), 73 (100), 67 (23); HRMS calcd for $C_9H_{17}O_2Si$ [(M − Me)$^+$] 185.0998, found 185.1006.

***erythro*-2-[1-Hydroxy-1-(trimethylsilyl)ethyl]cyclopentanone (16).** Treatment of **16** (21.1 mg, 0.11 mmol) with DBU (16.1 mg, 15.8 μL, 0.11 mmol) in CH_2Cl_2 (1 mL) gave **16** (12.0 mg, 57%, 67% conversion) and **15** (3.1 mg, 15% recovery): ^1H NMR ($CDCl_3$) δ 0.03 (s, 9H), 1.16 (s, 3H), 1.53 (m, 1H), 1.73 (m, 1H), 1.95–2.17 (3H), 2.23–2.47 (2H), 4.22 (s, 1H); ^{13}C NMR ($CDCl_3$) δ −3.7, 20.0, 21.0, 27.4, 40.0, 55.2, 67.7, 225.7; IR ($CDCl_3$) 3460, 2940, 1715, 1345, 1250, 1155, 840 cm^{-1}; MS (*m/e*) (%) 185 [(M − Me)$^+$] (8), 169 (6), 157 (11), 110 (56), 95 (43), 82 (22), 73 (100), 67 (24), 55 (11); HRMS calcd for $C_9H_{17}O_2Si$ [(M − Me)$^+$] 185.0998, found 185.1004.

6-(1-*tert*-Butyl-1-hydroxyethyl)-1,4-dioxaspiro[4.5]decane (17a and 17b). To a solution of **4** (307 mg, 1.67 mmol) in Et_2O (15 mL) was added t-BuLi (4.94 mL, 1.7 M in pentane, 8.4 mmol) at −78 °C and the mixture was stirred for 3 h. The reaction was quenched with saturated NH_4Cl and the resulting mixture was extracted with EtOAc. The extract was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Flash chromatography of the residue (SiO_2, 5% EtOAc/hexane) afforded major adduct **17a** (131 mg, 32%) and minor adduct **17b** (53.9 mg, 13%) accompanied by **4** (61.4 mg, 20% recovery). **17a**: ^1H NMR ($CDCl_3$) δ 0.91 (s, 9H), 1.14 (s, 3H), 1.23 (m, 1H), 1.33 (m, 1H), 1.45 (m, 1H), 1.57–1.72 (4H), 1.79 (m, 2H), 2.07 (m, 1H), 3.95–4.16 (m, 4H), 4.85 (s, 1H); ^{13}C NMR (C_6D_6) δ 20.6, 24.0, 26.1, 26.2, 29.8, 36.8, 40.5, 46.4, 63.1, 63.7, 78.3, 113.9; IR (neat) 3470, 2950, 1370, 1165, 1150, 1110, 1090, 1070, 1040, 975, 950, 925 cm^{-1}; MS (*m/e*) (%) 242 (1) (M^+), 224 (4), 185 [(M − ^{t}Bu)$^+$] (81), 142 (14), 129 (7), 113 (5), 99 (99), 87 (10), 81 (10), 57 (11); HRMS calcd for $C_{14}H_{26}O_3$ (M^+) 242.1883, found 242.1893. **17b**: ^1H NMR (C_6D_6) δ 1.09 (s, 9H), 1.11–1.36 (2H), 1.37 (s, 3H), 1.40–1.55 (2H), 1.57–1.68 (2H), 1.74 (dt, 1H, J = 12.8, 3.1 Hz), 1.93 (s, 1H), 2.04 (m, 1H), 2.13 (dd, 1H, J = 12.2, 3.1 Hz), 3.30–3.50 (4H); ^{13}C NMR (C_6D_6) δ 23.7, 24.2, 26.1, 26.3, 26.9, 29.0, 35.6, 40.1, 62.5, 62.5, 77.8, 112.5; IR (C_6H_6) 3600, 3500, 2930, 1445, 1370, 1145, 1090, 945, 935 cm^{-1}; MS (*m/e*) (%) 242 (0.1), 224 (1), 185 [(M − ^{t}Bu)$^+$] (57), 142 (14), 129 (7), 99 (100), 87 (58).

2-(1-*tert*-Butyl-1-hydroxyethyl)cyclohexanone (18a). **17a** (130 mg, 0.54 mmol) was hydrolyzed as described for **5** to afford **18a** (86.9 mg, 82%): ^1H NMR ($CDCl_3$) δ 0.92 (s, 9H), 1.13 (s, 3H), 1.48–1.78 (3H), 1.88 (m, 1H), 2.09 (m, 1H), 2.20–2.47 (3H), 2.78 (dd, 1H, J = 11.9, 4.6 Hz), 5.01 (s, 1H); ^{13}C NMR (C_6D_6) δ 20.4, 25.6, 26.8, 28.6, 32.5, 39.3, 44.0, 55.0, 76.9, 217.1; IR ($CHCl_3$) 3440, 2950, 2870, 1690, 1450, 1395, 1375, 1310, 1130, 1100, 1005, 910 cm^{-1}; MS (*m/e*) (%) 183 [(M − Me)$^+$] (2), 165 (2), 141 [(M − ^{t}Bu)$^+$] (100), 99 (57), 83 (18), 70 (23), 57 (48); HRMS calcd for $C_{11}H_{19}O_2$ [(M − Me)$^+$] 183.1386, found 183.1381.

(*E*)-2-[1-(trimethylsilyl)ethylidene]cyclohexanone (19). General Procedure for Dehydration under Et_3N–MsCl Conditions. To a solution of **10** (77.6 mg, 0.36 mmol) in CH_2Cl_2 (3.1 mL) was added Et_3N (0.46 g, 4.6 mmol, 0.64 mL) and MsCl (0.25 g, 2.2 mmol, 0.17 mL) at 0 °C and the mixture was stirred for 1 h. After dilution with H_2O, the resulting mixture was extracted with EtOAc. The combined extracts were washed with saturated $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Flash chromatography of the residue (SiO_2, 16% EtOAc/hexane) afforded a mixture of **19** and **21** (50.7 mg, 71%) and **20** (3.6 mg, 5%). GLC analysis of the crude products showed that the ratio of the three products was 66:6:28 (**19**:**20**:**21**). Due to difficulty of separation of **19** from **21**, pure sample of **19** for spectral analysis was obtained from equilibration reaction of **20**. **19**: VPC t_R 7.4 min (100–240 °C, 10 °C/min); ^1H NMR (C_6D_6) δ 0.07 (s, 9H, $SiMe_3$), 1.32–1.47 (4H), 1.99 (s, 3H, Me), 2.21 (t, 2H, J = 6.4 Hz), 2.28 (m, 2H); ^{13}C NMR (C_6D_6) δ −0.1, 19.6, 26.1, 26.5, 35.7, 44.3, 138.0, 148.9, 203.9; ^{29}Si NMR (C_6D_6) δ −4.89; IR (C_6H_6) 2930, 2860, 1690, 1445, 1420, 1270, 1250,

(34) Nakatani, K.; Arai, K.; Hirayama, N.; Matsuda, F.; Terashima, S. *Tetrahedron* **1992**, *48*, 633–650.

1165, 1115, 1065, 920, 890, 835, 755 cm^{-1}; MS (*m/e*) (%) 196 (M^+) (13), 180 (98), 165 (28), 152 (65), 137 (13), 125 (4), 105 (7), 97 (8), 93 (14), 73 (100); HRMS calcd for $C_{11}H_{20}OSi$ (M^+) 196.1284, found 196.1292.

(*Z*)-2-[1-(Trimethylsilyl)ethylidene]cyclohexanone (20). General Procedure for Dehydration with Acid Catalysts. To a solution of **9** (45.8 mg, 0.21 mmol) in CH_2Cl_2 (5.5 mL) was added CSA (12.4 mg, 0.05 mmol) and the mixture was stirred at 0 °C for 4 h. The reaction mixture was quenched with addition of saturated $NaHCO_3$ and extracted with EtOAc. The combined extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Flash chromatography of the residue (SiO_2, 16% EtOAc/hexane) afforded **20** (30.9 mg, 74%), **19** (3.1 mg, 7%), and **10**, diastereoisomer of **9**, (2.1 mg, 5%) all as colorless oils. GLC analysis of the crude products showed that the ratio of the two was 6:94 (**19**:**20**). **20**: VPC t_R 6.5 min (100–240 °C, 10 °C/min); ^1H NMR (C_6D_6) δ 0.36 (s, 9H, $SiMe_3$), 1.28–1.43 (4H), 1.65 (s, 3H, Me), 2.17–2.23 (4H); ^{13}C NMR (C_6D_6) δ 0.6, 19.0, 23.6, 24.0, 29.6, 40.7, 145.5, 151.8, 200.4; ^{29}Si NMR (C_6D_6) δ −6.99; IR (C_6H_6) 2950, 2860, 1675, 1555, 1320, 1280, 1240, 1150, 1070, 905, 840, 755 cm^{-1}; MS (*m/e*) (%) 196 (M^+) (1), 181 [$(M - Me)^+$] (100), 167 (6), 153 (3), 139 (3), 105 (3), 97 (2), 79 (3), 75 (45), 59 (4); HRMS calcd for $C_{11}H_{20}OSi$ (M^+) 196.1284, found 196.1262.

(*E*)-2-[1-(Trimethylsilyl)ethylidene]-5-methylcyclohexanone (22): ^1H NMR (C_6D_6) δ 0.09 (s, 9H), 0.67 (d, 3H, J = 6.1 Hz), 1.07 (m, 1H), 1.47 (m, 1H), 1.59 (m, 1H), 1.79 (dd, 1H, J = 13.7, 11.3 Hz), 2.00 (d, 3H, J = 2.4 Hz), 2.42 (ddd, 1H, J = 14.0, 4.3, 1.8 Hz), 2.57 (dt, 1H, J = 14.0, 4.3 Hz); ^{13}C NMR (C_6D_6) δ −0.1, 19.6, 21.7, 29.3, 33.1, 34.6, 52.3, 138.0, 148.3, 203.5; IR (C_6H_6) 2910, 1685, 1520, 1470, 1390, 1250, 1170 cm^{-1}; MS (*m/e*) (%) 210 (M^+) (10), 195 (37), 194 (44), 179 (12), 152 (37), 137 (7), 119 (5), 107 (7), 97 (6), 73 (100), 59 (18); HRMS calcd for $C_{12}H_{22}OSi$ (M^+) 210.1441, found 210.1423.

(*Z*)-2-[1-(Trimethylsilyl)ethylidene]-5-methylcyclohexanone (23): ^1H NMR (C_6D_6) δ 0.36 (s, 9H), 0.66 (d, 1H, J = 6.1 Hz), 0.92 (ddt, 1H, J = 13.8, 11.3, 5.1 Hz), 1.40–1.54 (2H), 1.67 (s, 3H), 1.75 (dd, 3H, J = 16.5, 11.6 Hz), 1.92 (m, 1H), 2.38 (ddd, 1H, J = 17.1, 4.9, 2.4 Hz), 2.43 (dt, 1H, J = 17.1, 4.3 Hz); ^{13}C NMR (C_6D_6) δ 0.6, 19.1, 21.5, 28.5, 30.4, 32.1, 49.0, 127.9, 144.9, 200.3; IR (C_6H_6) 2950, 2860, 1670, 1545, 1470, 1390, 1280, 1245, 1070, 840, 760 cm^{-1}; MS (*m/e*) (%) 210 (M^+) (1), 195 [$(M - Me)^+$] (100), 181 (2), 165 (6), 153 (4), 139 (2), 121 (2), 105 (2), 91 (4), 75 (48), 69 (2), 59 (9); HRMS calcd for $C_{11}H_{19}OSi$ [$(M - Me)^+$] 195.1205, found 195.1192.

(*E*)-2-[1-(Trimethylsilyl)ethylidene]cyclopentanone (25): ^1H NMR (C_6D_6) δ 0.03 (s, 9H), 1.33 (quint, 2H, J = 7.5 Hz), 1.97 (t, 2H, J = 7.9 Hz), 2.23–2.28 (2H), 2.42 (t, 3H, J = 2.1 Hz); IR ($CHCl_3$) 2900, 1690, 1585, 1250, 1130, 840 cm^{-1}; MS (*m/e*) (%) 182 (M^+) (9), 166 (100), 151 (20), 139 (12), 123 (6), 111 (11), 97 (7), 73 (85), 59 (14); HRMS calcd for $C_{10}H_{18}OSi$ (M^+) 182.1127, found 182.1141.

(*Z*)-2-[1-(Trimethylsilyl)ethylidene]cyclopentanone (26): ^1H NMR (C_6D_6) δ 0.37 (s, 9H), 1.37 (quint, 2H, J = 7.6 Hz), 1.68 (t, 3H, J = 1.5 Hz), 1.95 (t, 2H, J = 7.9 Hz), 2.14 (dt, 2H, J = 7.3, 1.2 Hz); ^{13}C NMR (C_6D_6) δ −0.66, 19.7, 21.6, 29.6, 39.2, 146.0, 152.4, 206.7; IR ($CHCl_3$) 2930, 1700, 1585, 1240, 840 cm^{-1}; MS (*m/e*) (%) 181 [$(M - H)^+$] (1), 167 (100), 151 (5), 139 (3), 111 (2), 91 (3), 75 (32), 59 (4); HRMS calcd for $C_{10}H_{17}OSi$ [$(M - H)^+$] 181.1049, found 181.1028.

(*Z*)-2-[1-(Trimethylsilyl)ethylidene]cyclohexan-1-ol (28). To a solution of **20** (15.2 mg, 0.08 mmol) in CH_2Cl_2 (2 mL) was added DIBAL (83 μL, 1.5M in hexane, 0.08 mmol) at −78 °C and the mixture was stirred for 1 h. After quenching the reaction with addition of H_2O (3 drops) and ether (ca. 1 mL), the resulting mixture was warmed up to room temperature and diluted with EtOAc. A white precipitate that formed was filtered off and the filtrate was concentrated *in vacuo*. Flash chromatography of the residue (SiO_2, 10% EtOAc/hexane) afforded **28** (15.1 mg, 98%) as colorless prisms: mp 63.8–64.0 °C (recryst from hexane); ^1H NMR ($CDCl_3$) δ 0.14 (s, 9H, $SiMe_3$), 1.04 (s, 1H, OH) 1.18 (tq, 1H, J = 13.0, 3.6 Hz), 1.37–1.47 (2H), 1.62 (d, 3H, J = 1.2 Hz), 1.70 (m, 1H), 1.87–2.01 (2H), 2.18 (m, 1H), 2.51 (m, 1H), 4.58 (m, 1H); ^{13}C NMR (C_6D_6) δ 1.0, 17.1, 20.7, 25.7, 27.9, 34.7, 71.3, 128.2, 151.9; IR (C_6H_6) 3400, 2925, 1245, 1085, 970, 850 cm^{-1}; MS (*m/e*) (%) 198 (M^+) (8), 183 [$(M - Me)^+$] (23), 169 (17), 141 (7), 125 (7), 108 (12), 93 (58), 79 (20), 75 (100), 59 (12), 55 (11); HRMS calcd for $C_{11}H_{22}OSi$ (M^+) 198.1441, found 198.1444. Anal. Calcd for $C_{11}H_{22}OSi$ C, 66.60; H, 11.18%. Found: C, 66.39; H, 11.28%.

(*E*)-2-[1-(Trimethylsilyl)ethylidene]cyclohexan-1-ol (33): ^1H NMR (C_6D_6) δ 0.16 (s, 9H), 1.12–1.45 (4H), 1.63 (m, 1H), 1.59 (s, 3H), 1.71 (m, 1H), 1.81–2.01 (2H), 2.31 (m, 1H), 2.47 (m, 1H), 4.74 (m, 1H); IR (C_6H_6) 3600, 3460, 2940, 1450, 1250, 975, 850, 840 cm^{-1}; MS (*m/e*) (%) 198 (M^+) (15), 183 (45), 169 (27), 165 (8), 155 (4), 141 (6), 125 (8), 108 (19), 93 (75), 73 (100), 59 (9); HRMS calcd for $C_{11}H_{22}OSi$ (M^+) 198.1441, found 198.1419.

2-(1-*tert*-Butylvinyl)cyclohexanone (29). To a solution of **18a** (14.5 mg, 0.07 mmol) and Et_3N (16.3 mg, 22.5 μL, 0.16 mmol) in CH_2Cl_2 (2 mL) was added MsCl (16.7 mg, 11.3 μL, 0.15 mmol) and the reaction was continued overnight. Aqueous workup and flash chromatography afforded **29** (4.1 mg, 12%) and recovery of starting material: ^1H NMR (C_6D_6) δ 1.02 (s, 9H), 1.12–1.65 (5H), 1.79 (ddt, 1H, J = 3.1, 4.9, 13.4 Hz), 1.89 (ddt, 1H, J = 1.2, 6.1, 12.8 Hz), 2.27 (ddt, 1H, J = 1.8, 3.7, 13.4 Hz), 2.88 (dd, 1H, J = 5.5, 12.8 Hz), 4.82 (s, 1H), 5.28 (s, 1H); IR (C_6H_6) 2930, 1720, 1450, 1365, 1100 cm^{-1}; MS (*m/e*) (%) 180 (M^+) (20), 165 (2), 151 (52), 123 (22), 109 (5), 95 (29), 81 (11), 67 (100); HRMS calcd for $C_{12}H_{20}O$ (M^+) 180.1515, found 180.1494.

(*Z*)-2-(1-Phenylethylidene)cyclohexan-1-ol (32). To a degassed solution of **28** (33.2 mg, 0.17 mmol) and allylpalladium chloride dimer (1.2 mg, 3 μmol) in DMF (1 mL) was added TBAF (0.17 mL, 1 M in THF, 0.17 mmol) at 0 °C under argon atmosphere. Iodobenzene (68.4 mg, 0.34 mmol, 38 μL) was then added and the mixture was stirred for 3.5 h at 50 °C. After cooling the reaction mixture was diluted with H_2O and extracted with EtOAc. The organic extract was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Flash chromatography of the residue (SiO_2, 10% EtOAc/toluene) afforded **32** (20.2 mg, 60%) as a colorless oil: ^1H NMR (C_6D_6) δ 0.74 (br, 1H), 1.15–1.43 (3H), 1.65 (m, 1H), 1.76 (m, 1H), 1.86 (d, 3H, J = 1.2 Hz), 1.90 (tq, 1H, J = 13.4, 4.0 Hz), 2.36 (m, 1H), 2.46 (m, 1H), 4.40 (br s, 1H), 7.04–7.20 (5H); ^{13}C NMR (C_6D_6) δ 20.2, 20.6, 25.2, 27.4, 34.2, 67.9, 126.3, 128.0, 128.2, 128.3, 136.0, 144.1; IR ($CHCl_3$) 3620, 3450, 2950, 2875, 1495, 1445, 1380, 1135, 1080, 980, 910 cm^{-1}; MS (*m/e*) (%) 202 (M^+) (33), 187 [$(M - Me)^+$] (22), 169 (12), 159 (16), 145 (20), 129 (18), 105 (98), 98 (100), 83 (13), 73 (17), 57 (22); HRMS calcd for $C_{14}H_{18}O$ (M^+) 202.1358, found 202.1378.

Theoretical Calculation of 19 and 20. Geometries of **19** and **20** were at first optimized by the semiempirical PM3 method, with conformational isomers being examined by means of a conformation search module incorporated in Spartan. Geometry optimization at *ab initio* level was then carried out using the PM3 optimized structures as the initial geometry.

Acknowledgment. The authors thank Professor Y. Ito, Professor K. Tamao, and Mr. A. Kawachi (Kyoto University) for ^{29}Si NMR measurements, Dr. Y. Hatanaka (Sagami Chemical Research Center), and Professor W. J. Hehre (University of California, Irvine) for valuable discussions and suggestions. We also thank Mr. Odagaki for X-ray analysis and Asahi Kasei Joho Systems Co., Ltd. for MP2 calculations. Financial support by Grant-in-Aid for scientific research from Ministry of Education, Science and Culture of Japan is acknowledged.

Supplementary Material Available: Calculated coordinates and copies of NMR spectra (39 pages). This material is contained in 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.