Stereoselective Reaction of α-Sulfinyl Carbanion Derived from Chiral 2-(Trialkylsilyl)ethyl Sulfoxides: Evidence for a Novel Silicon−Oxygen Interaction

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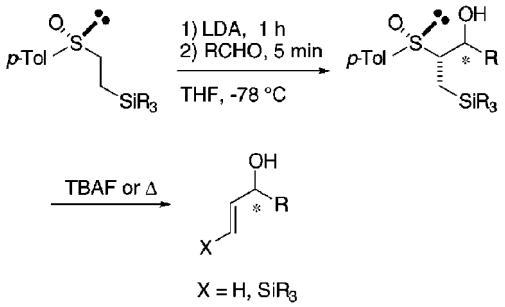
Reactions of α-sulfinyl carbanions, derived from *p*-tolyl sulfoxides bearing various alkyl groups, with various electrophiles were examined. The reaction of α-sulfinyl carbanions, derived from the *β*-silylethyl sulfoxides, with ketones or trimethyl phosphate, gave the syn products with high stereoselectivity. Interaction between the silicon in the trialkylsilyl group and the carbonyl oxygen in nucleophiles was postulated to stabilize the transition state, leading preferably to the syn diastereisomers. This novel silicon−oxygen interaction was supported by an MO calculation study using the MOPAC 93/PM3 and the Gaussian 94 Beche3LYP/3-21+G* methods.

Introduction

Asymmetric carbon−carbon bond formation induced by chiral α-sulfinyl groups has been extensively studied, and it is the subject of several excellent reviews.[1] However, this type of reaction often proceeds with low stereoselectivity;[2] e.g., the reaction of α-sulfinyl carbanions derived from alkyl *p*-tolyl sulfoxides[3] with aldehydes results in the formation of all four possible diastereomeric adducts with poor stereoselectivity.[2g] There are several isolated examples of improved stereoselectivity such as the reaction via lithium metal exchange,[2c,3a,f] and reactions of sulfoxides bearing a sterically bulky group such as the *tert*-butyl[2a,3a] or 1-naphthyl groups.[4] However, no highly stereoselective reactions of α-sulfinyl carbanions, generated from the generally used phenyl or *p*-tolyl sulfoxides, have been reported.

Recently, we reported that the reaction of α-sulfinyl carbanions derived from *β*-(trimethylsilyl)ethyl sulfoxides with aldehydes proceeded with extremely high stereoselectivity on the face of the carbanion α to the sulfinyl group (Scheme 1).[5]

Scheme 1



This reaction provides a convenient method for the preparation of optically pure allylic alcohols via subsequent thermal elimination of the sulfinyl group or concurrent elimination of the sulfinyl and silyl groups. More recently, we communicated highly stereoselective *β*-addition of the *β*-silyl-α-sulfinyl carbanion to α,*β*-unsaturated carbonyl compounds as well as stereoselective intramolecular cyclizations.[5b] We now report, in detail, the reactions of the α-sulfinyl carbanion, derived from *p*-tolyl sulfoxides bearing various alkyl groups such as *β*-(trialkylsilyl)ethyl, *γ*-(trimethylsilyl)propyl, propyl, and 3,3-dimethylbutyl groups, with various electrophiles, and we propose a novel silicon−oxygen interaction in the transition state.

Results and Discussion

Preparation of Sulfoxides 1. The starting sulfoxides **1a**, **1b**, and **1f** were prepared by alkylation of the α-sulfinyl carbanions derived from the corresponding chiral methyl *p*-tolyl sulfoxides with (iodomethyl)trialkylsilane as previously reported.[5a] Chiral propyl *p*-tolyl

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(1) For recent reviews, see: (a) Carreño, M. C. *Chem. Rev.* **1995**, *95*, 1717. (b) Walker, A. J. *Tetrahedron*: *Asymmetry* **1992**, *3*, 961. (c) Solladie, G. *Pure Appl. Chem.* **1988**, *60*, 1699. (d) Solladie, G. *Synthesis* **1981**, 185.

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1a; R = *p*-Tol, R' = $CH_2CH_2SiMe_3$
1b; R = *p*-Tol, R' = $CH_2CH_2SiMePh_2$
1c; R = *p*-Tol, R' = $CH_2CH_2CH_3$
1d; R = *p*-Tol, R' = $CH_2CH_2CH_2SiMe_3$
1e; R = *p*-Tol, R' = $CH_2CH_2{}^tBu$
1f; R = ^{t}Bu, R' = $CH_2CH_2SiMe_3$
1g; R = $CH_2CH_2SiMe_3$, R' = Tip

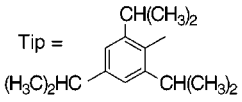
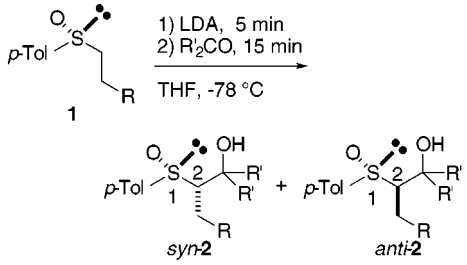


Figure 1.

Table 1. Reaction of Certain *β*-Substituted Ethyl *p*-Tolyl Sulfoxides 1a−e with Acetone and Cyclohexanone



entry	substrate no.	R	R′$_2$CO	product	yield (%)	syn/anti[a]
1	**1a**	$SiMe_3$	Me_2CO	**2a**	88	96:4
2	**1b**	$SiMePh_2$	Me_2CO	**2b**	73	>98:2
3	**1c**	CH_3	Me_2CO	**2c**	89	88:12
4	**1c**	CH_3	cyclohexanone	**2d**	80	88:12
5	**1d**	CH_2SiMe_3	Me_2CO	**2e**	93	73:27
6	**1d**	CH_2SiMe_3	cyclohexanone	**2f**	88	84:16
7	**1e**	^{t}Bu	Me_2CO	**2g**	98	33:67

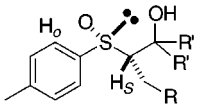
[a] Determined by ^{1}H NMR.

sulfoxide (**1c**), *p*-tolyl 3-(trimethylsilyl)propyl sulfoxide (**1d**), and *p*-tolyl 3,3-dimethylbutyl sulfoxide (**1e**) were prepared on treatment of (−)-menthyl (*S*)-*p*-toluenesulfinate with propylmagnesium bromide, 3-(trimethylsilyl)-propylmagnesium chloride, and 3,3-dimethylbutylmagnesium bromide, respectively. The sulfoxides **1f** and **1g** were prepared by treatment of (*R*)-*tert*-butyl methyl sulfoxide or (*S*)-methyl 2,4,6-triisopropylphenyl sulfoxide[6] with 1.1 equiv of LDA at −78 °C and subsequently with (iodomethyl)trimethylsilane (Figure 1).

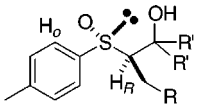
Reaction of Sulfoxides 1 with Ketones. We have already reported that the α-sulfinyl carbanion, having a trialkylsilyl group at the *β*-position, reacts with an electrophile with high stereoselectivity at the α-position.[5] It is noteworthy that the α-sulfinyl carbanion derived from *β*-trialkylsilylethyl sulfoxides shows extremely high stereoselection on the carbanion face. To clarify the mechanism leading to the exceptionally high stereoselective reaction, we first studied the stereoselectivity in the reaction of the α-sulfinyl carbanions bearing various alkyl groups. The results obtained in the reaction of the α-sulfinyl carbanion generated from several chiral sulfoxides with ketones are summarized in Table 1.

(*R*)-*p*-Tolyl sulfoxides carrying various alkyl groups such as 2-(trimethylsilyl)ethyl (**1a**), 2-(methyldiphenyl)-silylethyl (**1b**), propyl (**1c**), 3-(trimethylsilyl)propyl (**1d**), and 3,3-dimethylbutyl groups (**1e**) were treated with 1.2 equiv of LDA in THF at −78 °C for 5 min to generate the lithium carbanion, which was then reacted with acetone or cyclohexanone at the same temperature for 5 min, giving the products *syn*-**2** and *anti*-**2** in high yields. The diastereoselectivity was determined by the ^{1}H NMR spectra of the crude mixture. The reaction of the α-sulfinyl carbanions, derived from 2-(trimethylsilyl)- and 2-(methyldiphenylsilyl)ethyl sulfoxides **1a** and **1b**, with acetone proceeded with high stereoselectivity to give products **2a** and **2b** in syn/anti ratios of 94:6 (Table 1, entry 1) and >98:2 (Table 1, entry 2). On the other hand, the reaction of the propyl sulfoxide **1c** proceeded with lower stereoselectivity, giving the products **2c** and **2d** with both in syn/anti ratios of 88:12 with acetone and with cyclohexanone (Table 1, entries 3 and 4). The remarkable role of the *β*-silyl group on the stereoselection of the α-sulfinyl carbanion was further verified by the reaction of the 3-(trimethylsilyl)propyl sulfoxide **1d** with acetone or cyclohexanone, in which the products **2e** and **2f** were formed with considerably low stereoselectivity (Table 1, entries 5 and 6). Furthermore, the 3,3-dimethylbutyl sulfoxide **1e**, in which the trimethylsilyl group in **1a** was replaced with a *tert*-butyl group, showed reversed stereoselectivity, resulting in the predominant formation of the 1,2-anti compound. This fact suggests that the high stereoselectivity in the reaction of **1a** would not result from the steric demands of the *β*-trimethylsilyl group, but possibly be due to some electronic reasons. All these results show that the *β*-silyl group plays a crucial role in inducing high stereoselectivity on the carbanion face.

Table 2. Significant ^{1}H NMR Chemical Shifts for the Configurational Assignment of the *β*-Hydroxy Sulfoxides



syn-**2**



anti-**2**

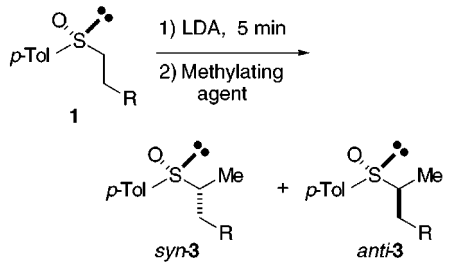
no.	product R	R′	*syn*-**2** H_S	H_O	OH	*anti*-**2** H_R	H_O	OH
2a	$SiMe_3$	Me	2.57	7.41	2.00	3.02	7.71	5.71
2b	$SiMePh_2$	Me	2.66		1.83			
2c	CH_3	Me	2.32	7.47	2.63	2.75	7.70	5.71
2d	CH_3	$-(CH_2)_5-$	2.30	7.45	2.69	2.71	7.69	5.27
2e	CH_2SiMe_3	Me	2.32	7.45	2.80	2.82	7.69	5.55
2f	CH_2SiMe_3	$-(CH_2)_5-$	2.34	7.44	2.87	2.70	7.67	5.21
2g	^{t}Bu	Me	2.68	7.50	2.37	2.95	7.69	5.43

The configurations of the products **2a**−**g** were determined as follows. The relative stereochemistry of the major product **2d** was assigned to be 1,2-syn (see the tentative numbering in Table 1) by the X-ray crystal structure analysis. The absolute configuration of the sulfinyl-substituted carbon of *syn*-**2d** was determined to be *S*. The stereochemistry of the adduct *syn*-**2b** was deduced by the X-ray crystal structure analysis of the absolute configuration of the sulfone, which was prepared by the *m*-CPBA oxidation of **2b**. The stereochemistry of other products **2a**−**c**,**e**−**g** was assigned to be the same as that of *syn*-**2d** by comparison of the difference in the chemical shifts between the major and minor products in the NMR spectra (Table 2).

In the ^{1}H NMR spectra, the major products showed an upfield shift in comparison with the minor adducts in

(6) **1g** was prepared from diacetone D-gulucosyl 2,4,6-triisopropylbenzenesulfinate: Mase, N.; Watanabe, Y.; Ueno, Y.; Toru, T. *J. Org. Chem*. **1997**, *62*, 7794. More recently, we reported an efficient method for the preparation of sulfinates: Watanebe, Y.; Mase, N.; Tateyame, M.; Toru, T. *Tetrahedron*: *Asymmetry* **1999**, *10*, 737.

Table 3. Methylation Reaction of *p*-Tolyl Sulfoxides 1a−e



entry	substrate no.	substrate R	methylating agent	product	yield (%)	*syn*-**3**/*anti*-**3**[a]
1	**1a**	$SiMe_3$	MeI	**3a**	91	50:50
2	**1a**	$SiMe_3$	$(MeO)_3PO$	**3a**	94	96:4
3	**1b**	$SiMePh_2$	MeI	**3b**	92	51:49
4	**1b**	$SiMePh_2$	$(MeO)_3PO$	**3b**	69	94:6
5	**1c**	CH_3	MeI	**3c**	57	54:46[b]
6	**1c**	CH_3	$(MeO)_3PO$	**3c**	64	88:12[b]
7	**1d**	CH_2SiMe_3	MeI	**3d**	83	61:39
8	**1d**	CH_2SiMe_3	$(MeO)_3PO$	**3d**	80	83:17
9	**1e**	^{t}Bu	MeI	**3e**	84	28:72
10	**1e**	^{t}Bu	$(MeO)_3PO$	**3e**	68	19:81

[a] Determined by ^{1}H NMR. [b] Determined by HPLC.

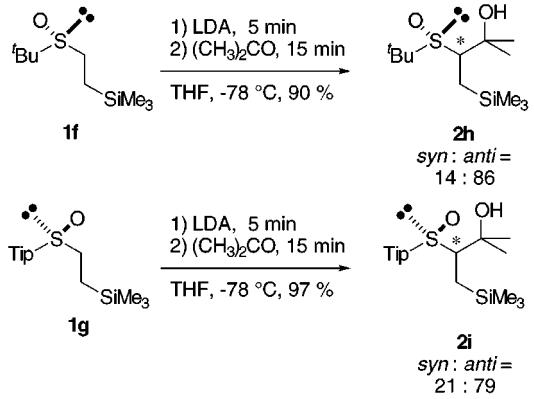
signals due to the ortho protons of the aromatic ring, the methine protons α to the sulfinyl, and the hydroxy protons.

Methylation of Sulfoxides 1. We next studied the methylation reaction of carbanions derived from sulfoxides **1**. The methylation was carried out with methyl iodide or trimethyl phosphate. The reactions with methyl iodide were performed at −78 °C in a manner similar to the reaction with ketones, whereas the α-sulfinyl carbanion was treated with trimethyl phosphate at 0 °C. The results are summarized in Table 3.

The methylation of **1a**−**e** with methyl iodide gave products *syn*-**3** and *anti*-**3** with low stereoselectivity (Table 3, entries 1, 3, 5, and 7). On the other hand, the methylation with trimethyl phosphate proceeded with high stereoselectivity in the reaction of sulfoxides **1a** and **1b** bearing a trimethylsilyl or methyldiphenylsilyl group at the position *β* to the sulfinyl group (Table 3, entries 2 and 4). The reactions starting with other sulfoxides **1c** and **1d** lowered the stereoselectivity (Table 3, entries 6 and 8) as in the reactions with ketones. The selectivity was again reversed in the reaction of 3,3-dimethylbutyl sulfoxide **1e** (Table 3, entries 9 and 10). The configuration of the major methylated products formed in the reaction with trimethyl phosphate was tentatively assigned as 1,2-syn by analogy with the stereochemical outcome obtained above in the reactions with carbonyl compounds, since it is known that the methylation of lithium carbanions with trimethyl phosphate proceeds with chelation to phosphate oxygen.[7]

Proposed Reaction Mechanism through a Novel Si−O Interaction. The results show that the silyl group in *p*-tolyl 2-(trimethylsilyl)ethyl sulfoxide **1a** or *p*-tolyl 2-(methyldiphenylsilyl)ethyl sulfoxide **1b** has a significant effect on the stereoselection of the α-carbanion face, and the silyl group should be placed at the position *β* to the sulfinyl to induce the high stereoselectivity. The reactions of the lithium carbanions of *tert*-butyl and

Scheme 2



triisopropylphenyl sulfoxides bearing a *β*-silylethyl group **1f** and **1g** were examined as the reaction having a bulky group (Scheme 2).

The reaction of alkyl *tert*-butyl sulfoxides with carbonyl compounds is known to lead to the exclusive formation of the 1,2-anti diastereomers.[3a] The reaction of sulfoxides having a bulky substituted such as the *tert*-butyl group is supposed to proceed through a boatlike transition state. The stereochemical outcome in the reaction of **1f** and **1g** is partly similar to those previously reported; the reaction proceeded with predominant formation of the 1,2-anti diastereomers, but not with complete 1,2-anti selectivity, showing that the *β*-silyl group has some role to divert the stereoselection favorably into 1,2-syn stereoselectivity. The problem is what kind of effects would be expected for the silyl group to induce the 1,2-syn stereoselection. The steric demands of the silyl group would not be so important since 3,3-dimethylbutyl sulfoxide **1e** did not give the product with high stereoselectivity. We have to take into account the stereoelectronic effect of the silyl group. The diastereoselective deprotonation is unlikely, since the carbanion α to the sulfinyl group is reported to be sp^2 or configurationally labile.[8] In fact, we found that the carbanion, derived from **1a** and LDA, gave a diastereomeric mixture of deuterated sulfoxides in a ratio of ca. 7:3 upon treatment with D_2O or MeOD. Provided that deuteration of the α-sulfinyl carbanion proceeded with retention of configuration,[7a,9] deprotonation of **1a** would form a mixture of the two diastereomeric α-sulfinyl carbanions **anions 1** and **2** (Figure 2), giving the corresponding syn and anti diastereomers, respectively, when reacted with electrophiles. Nonetheless, *β*-silylethyl sulfoxides **1a** and **1b** show great preference for the formation of the syn diastereomer. These facts are in good accord with the assumption that the α-sulfinyl carbanion should be configurationally labile. In addition, it was confirmed that no retroaldol reaction occurred in the present system as follows: The α-sulfinyl carbanion prepared from **1a** was treated with hexanal at −78 °C and subsequently with benzaldehyde (Scheme 3).

As a result, the hexanal-reacted aldol product was exclusively formed, indicating that no retroaldol reaction occurred through the course of the reaction. In addition,

(7) (a) Biellmann, J. F.; Vicens, J. J. *Tetrahedron Lett.* **1978**, 467. (b) Chassaing, G.; Lett, P.; Marquet, A. *Tetrahedron Lett.* **1978**, 471.

(8) (a) Chassaing, G.; Marquet, A. *Tetrahedron* **1978**, *34*, 1399. (b) Lett, R.; Chassaing, G. *Tetrahedron* **1978**, *34*, 2705. (c) Marsch, M.; Massa, W.; Harms, K.; Baum, G.; Boche, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1011. (d) Boche, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 277.

(9) (a) Yamamoto, Y.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1980**, 239. (b) Hoppe, D.; Carstens, A.; Krämer, T. *Angew. Chem., Int. Ed. Engl.* **1990**, *24*, 1424.

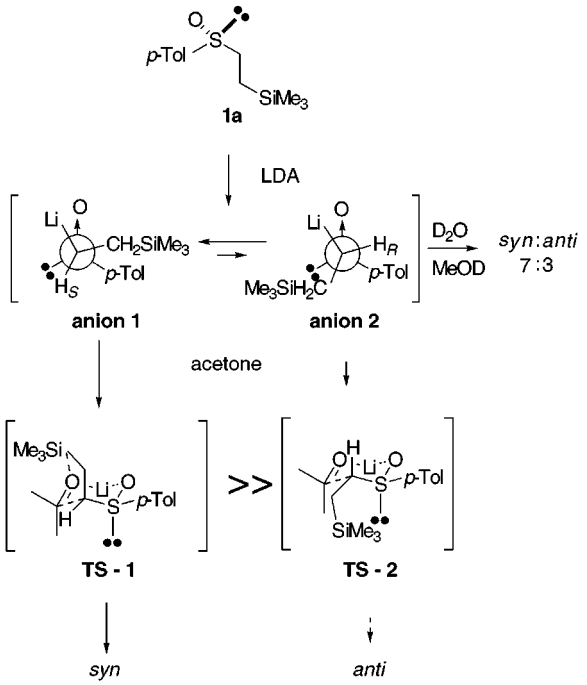
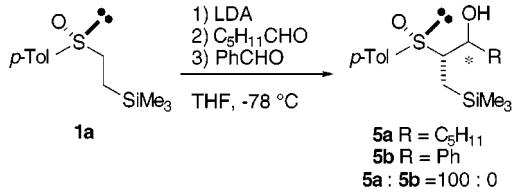


Figure 2. Proposed transition state for **1a** with carbonyl compound.

Scheme 3



treatment of a THF solution of **2a** (syn/anti = 96:4) with 1.5 equiv of LDA at −78 °C resulted in complete recovery of **2a**. The above results suggest that the stereoselective outcome in the reaction of **1a** should be kinetically controlled. Provided that the reaction proceeds via a chairlike transition state that has been postulated in the reaction of α-sulfinyl carbanions,[2d,3a] the syn diastereomer is formed via **TS-1** (Figure 2), where **TS-1** is assumed to be much more stable than **TS-2**. We should propose that the silicon of the trialkylsilyl group interacts with the carbonyl or the sulfinyl oxygen in the transition state, stabilizing **TS-1**.

We examined the calculations of energies of the intermediates as well as the transition states to prove the stereochemical course of the reactions with ketones. The α-sulfinyl carbanion, generated from *β*-silylethyl sulfoxides with LDA, would exist as an equilibrating mixture of **anion 1** and **anion 2** which have four-centered chelating structures.[8a,10] Indeed, calculations for the carbanions of the simplified methyl *β*-silylethyl sulfoxide by both the Gaussian 94 Beche3LYP/3-21+G*[11] and MOPAC93/PM3 methods[12] showed only small energy differences between the anions corresponding to **anion**

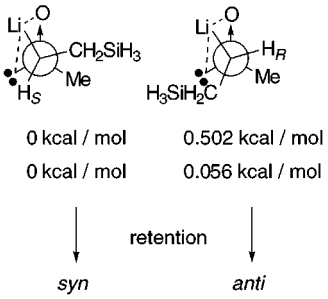


Figure 3. Calculation for anions **1** and **2** by PM3 and Beche3LYP/3-21+G*.

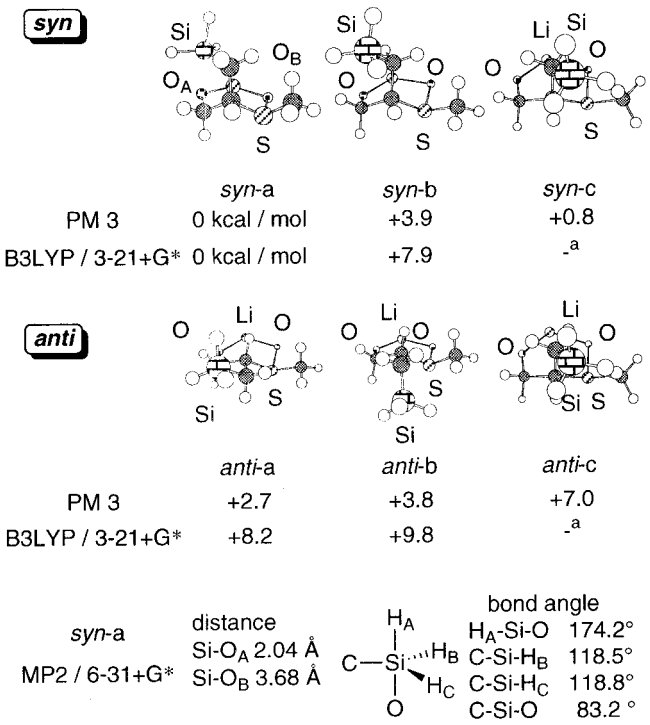


Figure 4. Geometry optimization of the product. [a]The structures *syn*-c and *anti*-c were less stable and moved to *syn*-b and *anti*-b, respectively, on optimization.

1 and **anion 2**, 0.056 and 0.502 kcal/mol, respectively, as shown in Figure 3.

To gain more quantitative insight, the stabilities of the lithiated products were estimated by the MO calculation. The calculation with PM3 was carried out using the reaction product of the simplified *β*-silylethyl sulfoxide such as $CH_3SOCH_2CH_2SiH_3$ and CH_2O. Calculations were performed starting from two sets of three gauche conformers from the syn and anti cyclic structures in which the silylethyl groups are placed at the axial and equatorial positions. The relative energies of the opti-

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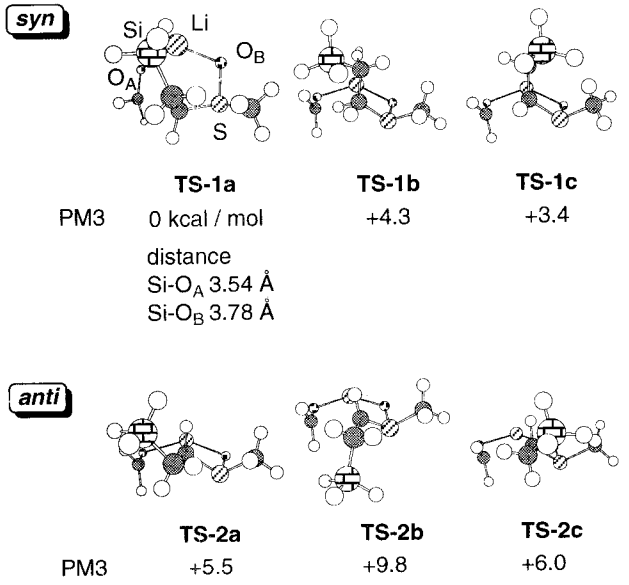

Figure 5. Transition-state calculation for the reaction of *β*-silylsulfoxide.

mized structure obtained by calculations are depicted in Figure 4. The calculation starting from the gauche conformer in which the SiH_3 group is directed toward the lithium resulted in the most stable conformer *syn*-a, in which the silicon possesses a trigonal bipyramidal structure.[13] Calculations with Beche3LYP/3-21+G* gave similar results.

A similar result was also obtained by further optimization of *syn*-a performed by MP2/6-31+G*. In the optimized structure, the distance of Si−O_A is 2.04 Å, which is shorter than the sum (3.62 Å) of the van der Waals radii of silicon and oxygen.[14] The bond angles shown at the bottom in Figure 4 indicate that the silicon has a trigonal bipyramidal structure. These results strongly suggest that the reaction proceeds via the transition state including a silicon−carbonyl oxygen interaction. To confirm the mechanistic hypothesis, the transition state optimization was carried out by PM3 for the reaction of *β*-silylethyl sulfoxide. The transition structure was fully optimized without any constraint and was characterized by vibrational frequency calculations, leading to a transition state with a negative frequency. The results of the calculations are shown in Figure 5 as energy differences relative to the most stable transition state **TS-1a**.

The calculations showed that the six-membered transition structures bearing the silylmethyl group at the axial position were more stable than the equatorial transition structures. In the most stable transition state **TS-1a**, the silicon atom comes closer to the carbonyl oxygen and is situated at a distance of 3.54 Å from the carbonyl oxygen atom.[15] Although this distance is longer than that of typical hypercoordinated silicon compounds, it shows a certain but weak attracting interaction between the silicon and the carbonyl oxygen. This is the first example of the interaction in the transition state verified by MO calculations, although there are reports in which Si−O and Si−N interactions have seen assumed in the transition state.[16] In general, the pentacoordinated silicons have at least an electron-withdrawing atom or group such as F, Cl, Br, OR, SiR_3, or CF_3.[13c,17] A similar bicyclic transition state involving Si−O interaction would also be the one for the methylation of *β*-silyl-α-sulfinyl carbanion with trimethyl phosphate to give the 1,2-syn products with high stereoselectivity (Table 3). The methylation with iodomethane, on the other hand, showed low stereoselectivity, because it does not proceed through the cyclic transition state involving a silicon interaction.

We showed that an extremely high stereoselectivity in the reaction of α-carbanions, derived from *β*-silylethyl *p*-tolyl sulfoxides, with electrophiles is due to a novel silicon−carbonyl oxygen interaction in the transition state on the basis of the stereochemical results from the reactions of several sulfoxide derivatives as well as the MO calculations. Furthermore, readily accessible *β*-silylethyl *p*-tolyl sulfoxides are synthetically useful as a chiral vinyl anion equivalent. Extending the methodology to other substrates and understanding further the mechanism of the reaction will be the focus of future work.

Experimental Section

General Procedure for the Preparation of Sulfoxide. (*R*)-Propyl *p*-Tolyl Sulfoxide (1c). A solution of propylmagnesium bromide, prepared from propyl iodide (0.925 mL, 10.2 mmol), magnesium (210.5 mg, 8.66 mg atom), and ether (8.5 mL), was slowly added to a solution of (−)-menthyl (*S*)-*p*-toluenesulfinate (1.00 g, 3.39 mmol) in a mixture of anhydrous ether (15 mL) and THF (7 mL) at temperature ranging from 0 to 10 °C. The mixture was stirred at room temperature for 25 min and then hydrolyzed with saturated aqueous NH_4Cl solution. The aqueous solution was extracted with CH_2Cl_2. The combined organic extracts were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure to leave a residue that was purified by column chromatography (silica gel, hexane/ethyl acetate = 70:30) to give **1c** (592 mg, 96%) as a colorless solid: $[\alpha]^{20}_D$ +201.0° (*c* 0.90, EtOH) (lit.[18] $[\alpha]^{21}_D$ +202.0° (*c* 0.90, EtOH)).

(*R*)-*p*-Tolyl 3-(Trimethylsilyl)propyl Sulfoxide (1d). The reaction was carried out as described above using (−)-menthyl (*S*)-*p*-toluenesulfinate (1.00 g, 3.40 mmol) and 3-(trimethylsilyl)propylmagnesium chloride, prepared from 1-chloro-3-(trimethylsilyl)propane (1.75 mL, 10.2 mmol) and magnesium (228 mg, 9.38 mg atom). Purification by column chromatography (silica gel, hexane/ethyl acetate = 80/20) afforded **1d** (858 mg, 99%): $[\alpha]^{24}_D$ +174.8 (*c* 0.32, acetone); ^{1}H NMR *δ* 0.01 (s, 9H), 0.45−0.76 (m, 2H), 1.51−1.90 (m, 2H), 2.42 (s, 3H), 2.50−2.95 (m, 2H), 7.33 (d, 1H, *J* = 8.3 Hz), 7.51 (d, 2H, *J* = 8.3 Hz); IR (KBr) 3045, 1300, 1245, 1080 cm^{-1}; SIMS *m*/*z* (rel intensity) 254 (M^+, 20), 91 (100). Anal. Calcd for $C_{13}H_{22}OSSi$: C, 61.36; H, 8.71. Found: C,61.10; H, 8.97.

(*R*)-3,3-Dimethylbutyl *p*-Tolyl Sulfoxide (1e). The reaction was carried out as described above except using (−)-

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menthyl (*S*)-*p*-toluenesulfinate (1.00 g, 3.40 mmol) and 3,3-dimethylbutylmagnesium bromide, prepared from 1-bromo-3,3-dimethylbutane (1.68 g, 10.2 mmol) and magnesium (220.0 mg, 9.05 mg atom). Purification by column chromatography (silica gel, hexane/ethyl acetate = 80/20) afforded **1e** (687 mg, 90%): $[\alpha]^{21}_D$ +181.8 (*c* 0.33, acetone); ^{1}H NMR δ 0.88 (s, 9H), 1.45−1.60 (m, 2H), 2.43 (s, 3H), 2.65−2.85 (m, 2H), 7.94 (d, 1H, *J* = 7.4 Hz), 8.24 (d, 2H, *J* = 7.4 Hz); IR(KBr) 3040, 1040 cm^{-1}; SIMS *m*/*z* (rel intensity) 224 (M^+,35), 209 (50), 91 (100). Anal. Calcd for $C_{13}H_{20}OS$: C, 69.53; H, 8.99. Found: C, 69.32; H, 9.25.

(*R*)-*tert*-Butyl 2-(Trimethylsilyl) Sulfoxide (1f). To a solution of diisopropylamine (0.090 mmol, 0.640 mmol) in THF (2.0 mL) was added *n*-butyllithium (1.53 mol L^{-1} in hexane, 0.39 mL, 0.598 mmol) at 0 °C, and the mixture was stirred for 30 min. The mixture was then cooled to −78 °C, and a solution of (*R*)-*tert*-butyl methyl sulfoxide (800 mg, 10.1 mmol) in THF (4.0 mL) was added. After the mixture was stirred for 1 h at the same temperature, (iodemethyl)trimethylsilane (2.16 g, 10.1 mmol) was added, and the temperature was allowed to rise to ambient temperature over a period of 2 h. Saturated aqueous NH_4Cl was added under vigorous stirring, and the aqueous solution was extracted with CH_2Cl_2. The combined organic extracts were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure to leave a residue that was purified by column chromatography (silica gel, hexane/ethyl acetate = 60:40) to give **1f** (1.17 g, 85%): $[\alpha]^{19}_D$ −123.0 (*c* 0.66, acetone); ^{1}H NMR δ 0.06 (s, 3H), 0.78 (ddd, 1H, *J* = 6.0, 12.6, 14.2 Hz), 1.21 (ddd, 1H, *J* = 5.6, 12.6, 14.2 Hz), 1.25 (s, 9H), 2.37 (ddd, 1H, *J* = 5.6, 12.6, 12.6 Hz), 2.47 (ddd, 1H, *J* = 6.0, 12.6, 12.6 Hz); IR (neat) 1030 cm^{-1}; MS (EI) *m*/*z* (rel intensity) 206 (M^+, 77), 101 (59). Anal. Calcd for $C_9H_{22}OSSi$: C, 52.37; H, 10.74. Found: C, 52.39; H, 10.54.

(*S*)-2,4,6-Triisopropylphenyl 2-(Trimethylsilyl)ethyl Sulfoxide (1g). To a solution of diisopropylamine (0.090 mmol, 0.640 mmol) in THF (0.60 mL) was added *n*-butyllithium (1.53 mol L^{-1} in hexane, 0.39 mL, 0.598 mmol) at 0 °C, and the mixture was stirred for 30 min. The mixture was then cooled to −78 °C, and a solution of (*S*)-methyl 2,4,6-triisopropylphenyl sulfoxide (106.5 mg, 0.400 mmol) in THF (0.40 mL) was added. After the mixture was stirred for 1 h at the same temperature, (iodemethyl)trimethylsilane (115 mg, 0.539 mmol) was added, and the temperature was allowed to rise to ambient temperature over a period of 2 h. Saturated aqueous NH_4Cl was added under vigorous stirring, and the aqueous solution was extracted with CH_2Cl_2. The combined organic extracts were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure to leave a residue that was purified by column chromatography (silica gel, hexane/ethyl acetate = 85:15) to give **1g** (99 mg, 70%) as a colorless solid: $[\alpha]^{21}_D$ −104.1 (*c* 0.36, acetone); ^{1}H NMR δ 0.04 (s, 9H), 0.71 (ddd, 2H, *J* = 4.5, 14.1, 14.1 Hz), 1.21 (ddd, 2H, *J* = 3.9, 14.1, 14.5 Hz), 1.20−1.35 (m, 18H), 2.75−3.00 (m, 2H), 3.28 (ddd, 1H, *J* = 3.9, 12.9, 14.1 Hz), 3.75−4.15 (m, 2H), 7.08 (s, 2H); IR (neat) 2970, 1370, 1250, 1050 cm^{-1}; SIMS *m*/*z* (rel intensity) 352.2 (M^+,10), 102.1 (100). Anal. Calcd for $C_{20}H_{36}OSSi$: C, 68.12; H, 10.29. Found: C, 68.15; H, 10.30.

Representative Procedure for the Reaction of Sulfoxides with Carbonyl Compounds. (3*R*)- and (3*S*)-2-Methyl-3-[(*R*)-*p*-tolylsulfinyl]-4-(trimethylsilyl)-2-butanol (*syn*-2a and *anti*-2a). To a solution of diisopropylamine (0.035 mL, 0.249 mmol) in THF (0.23 mL) was added *n*-butyllithium (1.53 mol L^{-1} in hexane, 0.145 mL, 0.222 mmol) at 0 °C, and the mixture was stirred for 10 min. The reaction mixture was cooled to −78 °C, and then a solution of **1a** (44.7 mg, 0.186 mmol) in THF (0.19 mL) was added dropwise over a period of 20 min. The mixture was stirred for an additional 20 min. Acetone (0.020 mL, 0.272 mmol) was then added, and the mixture was stirred for 5 min, the solution was quenched rapidly with saturated aqueous NH_4Cl (3 mL) under vigorous stirring, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2, and the combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product, which was purified by column chromatography (silica gel, dichloromethane/diethyl ether = 90:10) to give *syn*-**2a** (45.5 mg, 82%) and *anti*-**2a** (3.7 mg, 6%). The *syn*-**2a**/*anti*-**2a** ratio was determined to be 96:4 by the ^{1}H NMR analysis of the crude product. *syn*-**2a**: ^{1}H NMR δ −0.33 (s, 9H), 0.63 (dd, 1H, *J* = 7.2, 16.6 Hz), 1.14 (dd, 1H, *J* = 3.4, 16.6 Hz), 1.44 (s, 3H), 1.51 (s, 3H), 1.8−2.2 (br, 1H), 2.41 (s, 3H), 2.57 (dd, 1H, *J* = 3.4, 7.2 Hz), 7.32 (d, 2H, *J* = 8.5 Hz), 7.41 (d, 2H, *J* = 8.5 Hz); ^{13}C NMR δ −1.2, 5.4, 21.3, 28.1, 28.8, 73.0, 73.4, 124.3, 129.8, 137.8, 140.8; IR (KBr) 3375, 1295, 1040 cm^{-1}; SIMS *m*/*z* (rel intensity) 298 (M^+, 12), 69 (100). Anal. Calcd for $C_{15}H_{26}O_2SSi$: C, 60.35; H, 8.78. Found: C, 60.18; H, 8.73. *anti*-**2a**: ^{1}H NMR δ −0.35 (s, 9H), 0.30 (dd, 1H, *J* = 3.0, 16.3 Hz), 0.55 (dd, 1H, *J* = 7.6, 16.3 Hz), 1.22 (s, 3H), 1.60 (s, 3H), 2.44 (s, 3H), 3.02 (dd, 1H, *J* = 3.0, 7.6 Hz), 5.71 (d, 1H, *J* = 0.8 Hz), 7.34 (d, 2H, *J* = 8.1 Hz), 7.71 (d, 2H, *J* = 8.1 Hz); IR (neat) 3380, 1250, 1010 cm^{-1}; SIMS *m*/*z* (rel intensity) 298 (M^+, 11), 69 (100). Anal. Calcd for $C_{15}H_{26}O_2SSi$: C, 60.35; H, 8.78. Found: C, 60.16; H, 8.97.

Representative Procedure for the Reaction of Sulfoxides with Methyl Iodide. (2*R*)- and (2*S*)-2-[(*R*)-*p*-Tolylsulfinyl]-1-(trimethylsilyl)propane (*syn*-3a and *anti*-3a). The α-sulfinyl carbanion was prepared as described above using **1a** (38.7 mg, 0.161 mmol), diisopropylamine (0.030 mL, 0.213 mmol), *n*-butyllithium (1.44 mol L^{-1} in hexane, 0.135 mL, 0.194 mmol). To the resulting solution was added methyl iodide (0.015 mL, 0.241 mmol) at −78 °C, and the mixture was stirred for 15 min. Usual workup gave the crude product, which was purified by column chromatography (silica gel, hexane/ethyl acetate = 80:20) to afford a mixture of *syn*-**3** and *anti*-**3** (37.1 mg, 91%). The *syn*-**3a**/*anti*-**3a** ratio was determined to be 50:50 by the ^{1}H NMR analysis of the crude product.

Representative Procedure for the Reaction of Sulfoxides with Trimethyl Phosphate. The α-sulfinyl carbanion was prepared as described above using **1a** (38.7 mg, 0.161 mmol), diisopropylamine (0.035 mL, 0.249 mmol), *n*-butyllithium (1.44 mol L^{-1} in hexane, 0.17 mL, 0.245 mmol). To the resulting solution was added trimethyl phosphate (0.030 mL, 0.256 mmol). After 15 min, usual workup gave the crude product, which was purified by column chromatography (hexane/ethyl acetate = 70/30) to afford a mixture of *syn*-**3a** and *anti*-**3a** (48.5 mg, 94%). The diastereomeric ratio of the products *syn*-**3a** and *anti*-**3a** was determined to be 96:4 by ^{1}H NMR of the crude product. *syn*-**3a**: ^{1}H NMR δ 0.01 (s, 9H), 0.50 (dd, 1H, *J* = 12.1, 13.6 Hz), 1.07 (dd, 1H, *J* = 2.5, 12.1 Hz), 1.14 (d, 3H, *J* = 6.8 Hz), 2.42 (s, 3H), 2.79 (ddq, 1H, *J* = 2.5, 6.8, 13.6 Hz), 7.30 (d, 2H, *J* = 8.2 Hz), 7.48 (d, 2H, *J* = 8.2 Hz). *anti*-**3a**: ^{1}H NMR δ 0.01 (s, 9H), 0.49 (dd, 1H, *J* = 11.9, 14.3 Hz), 1.08 (dd, 1H, *J* = 2.6, 11.9 Hz), 1.11 (d, 3H, *J* = 6.4 Hz), 2.42 (s, 3H), 2.70−2.90 (m, 1H), 7.31 (d, 2H, *J* = 8.2 Hz), 7.47 (d, 2H, *J* = 8.2 Hz). Mixture of *syn*-**3a** and *anti*-**3a**: IR (KBr) 3040, 1300, 1250, 1050 cm^{-1}; SIMS *m*/*z* (rel intensity) 254.1 (M^+,100), 239.1 (30), 114.2 (100). Anal. Calcd for $C_{13}H_{22}OSSi$: C, 61.36; H, 8.71. Found: C, 61.29; H, 8.83.

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Supporting Information Available: Spectroscopic characterization for the products **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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